SPECTROSCOPY AND KINETICS
OF HIGHLY EXCITED
FORMALDEHYDE

by

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Spectroscopy and Kinetics of Highly Excited Formaldehyde

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Abstract

The properties of highly excited polyatomic molecules have long been a subject of considerable concern and speculation within the chemical physics community. Aside from the manifest importance that these transitory species have in various aeronomic and combustion-related problems, the unique characteristics of the high energy regimes in which they exist offer the possibility of reassessing conventional notions regarding molecular structure and dynamics, while simultaneously indicating new directions for future research. This thesis presents several distinct spectroscopic and kinetic studies performed upon molecular formaldehyde in regions of extreme excitation.

The first section of this thesis is concerned with the measurement of electric dipole moments in the first excited singlet electronic state (viz. $\tilde{A}^1A_2$) of formaldehyde. By utilizing the high resolution technique of Stark quantum beat spectroscopy, dipole moments for individual rovibronic levels in the $\nu_4$ out-of-plane bending manifold were determined with a precision approaching 1 part in $10^5$. The results of this study are discussed in terms of their dependence upon rotational, vibrational, and electronic degrees of freedom, as well as upon isotopic substitution. The relationship between electronic structure, as evinced by molecular dipole moments, and the pyramidal equilibrium configuration of the $\tilde{A}$ state is also examined.

The second portion of the thesis deals with collisional self-relaxation phenomena in the $\tilde{A}^1A_2$ state of formaldehyde. The use of time-resolved double resonance techniques permitted determination of collision-induced depopulation rates and state-to-state cross sections for individual rotational eigenstates in the $\nu_4 = 1$ vibrational level. The dominant collisional relaxation channel is shown to be pure rotational energy transfer which appears to follow dipole-dipole scaling and
propensity rules. Polarization-sensitive measurements indicate that elastic reorientation processes (i.e. $M$-changing collisions) are completely negligible in the case of the strongly dipolar long-range interactions which characterize the formaldehyde-formaldehyde collision system. A pronounced tendency for magnetic sublevel distributions to be preserved during inelastic rotation-changing collisions is also observed.

The final section of this thesis presents a study of collision-induced depopulation processes for highly excited regions in the ground electronic state (viz. $\tilde{X}^1A_1$) of formaldehyde. By utilizing a novel time-resolved triple resonance scheme, total removal cross sections were determined for individual molecular eigenstates with $> 11,000\text{cm}^{-1}$ of excitation distributed among their vibrational and rotational degrees of freedom. Although the principal self-relaxation channel entails pure rotational energy transfer, the results of these experiments indicate that both the magnitude and type of excitation (i.e. vibrational as well as rotational) deposited into the molecular framework can influence the collisional properties of highly excited formaldehyde.
This doctoral thesis has been examined by a Committee of the Department of Chemistry as follows:

Professor John S. Waugh__________________________  Chairman

Professor Robert W. Field__________________________  Thesis Co-Supervisor

Professor James L. Kinsey__________________________  Thesis Co-Supervisor

Professor Jeffrey I. Steinfeld________________________
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Dedication

This thesis is dedicated to the members of my family without whose steadfast support and encouragement this work would surely never have reached completion.
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Chapter 1

Dipole Moments in $\tilde{\text{A}}^{1}\text{A}_2$ Formaldehyde

1.1 Introduction

For many years it has been recognized that most molecular processes can be rationalized in terms of forces which are essentially electrical in nature [1, 2]. As a result, electric dipole moments, the first measure of the nonuniform charge distribution within a molecule, have long been utilized in the elucidation of molecular structure and bonding. This electric moment, which characterizes the first-order response of a molecular system subjected to an external electric field, is of primary importance for many of the active research areas in present-day molecular physics, ranging from pure spectroscopy (where transition probabilities are often formulated in terms of dipole operators) to basic studies of collision phenomena (where the interactions between polar molecules are usually dominated by their individual dipole moments). In chemistry, numerous empirical rules based upon hypothetical charge separations (i.e. dipole moments) within neutral molecules have provided considerable insight into the origins of chemical reactivity. Molecular theorists have also become increasingly interested in the electric dipole moment since its dependence on the charge distribution over an entire molecule provides a particularly stringent test for the accuracy of ab initio wavefunctions.

The earliest technique for the determination of molecular electric dipole moments was from dielectric constant measurements of bulk matter [2]. In addition to severe limitations imposed upon the attainable precision by trace impurities within the sample, this method had the serious disadvantage of averaging over all
thermally populated rotation-vibration states as well as all naturally occurring isotopic species. With the advent of microwave spectroscopy in the late 1940s, the accurate measurement of molecular dipole moments for specific rotational levels (associated with a single vibrational state for a particular isotope) became possible through analysis of the spectral modifications induced by an external electric field (i.e. the Stark effect). Various experimental refinements, including the use of molecular beam sources, extremely uniform electric fields, and ultra-sensitive detection schemes, have enabled present-day molecular physicists to determine electric dipole moments for molecules, in their ground electronic states, with a precision approaching one part in $10^6$ [3, 4].

The dependence of electronic structure upon vibrational and rotational degrees of freedom has long been a subject of interest in molecular physics. As a result, substantial effort has been directed towards the measurement of electric dipole moments as a function of rotational and vibrational quantum numbers. Studies of vibrationally excited systems with conventional microwave detection schemes, however, are limited to levels which are thermally populated at room temperature. In the case of formaldehyde, the molecule of principal concern in this thesis, the ultrasensitive technique of molecular beam electric resonance has permitted high precision dipole moments to be obtained for several fundamental vibrational modes [3]. The development of microwave-infrared double resonance [5, 4, 6] and laser Stark spectroscopy [7, 8, 9, 10] has extended dipole measurements to include overtone vibrations in formaldehyde and several other polyatomic species. Recently, work performed in our laboratories has demonstrated the use of a novel folded-variant of optical-optical double resonance [11] as a spectroscopic probe for dipole moments in highly excited vibrational levels of $\tilde{X}^1\Lambda_1$ formaldehyde-$h^\nu$. This technique provides a viable method for the systematic
investigation of ground electronic state dipole moment functions over a wide range of vibrational and rotational excitation.

In contrast to the wide scope of measurements performed on ground electronic states, very little dipole moment information exists for electronically excited polyatomic systems. This sparsity of experimental data stems principally from the stringent demands which dipole moment measurements impose upon the resolution and sensitivity available from traditional techniques of optical spectroscopy. For a moderately-sized molecule such as formaldehyde, where the lowest energy electronic transition occurs at \( \sim 30,000\text{cm}^{-1} \), the spectral shifts produced by reasonable electric field strengths (e.g. 10KV/cm) are only on the order of a few tenths of a wavenumber. The accuracy with which these relatively small Stark splittings can be determined is further compromised, in the case of gas phase samples, by the inhomogenous Doppler broadening associated with the optical transition frequency (i.e. \( > 0.1\text{cm}^{-1} \)). Despite these difficulties, several research groups, most notably that of Klemperer and his coworkers [12, 13], have been able to obtain electric dipole moments for several electronically excited polyatomic species, including formaldehyde. The precision of these measurements, however, is insufficient to ascertain the influence of vibrational and rotational motion upon the electronic structure of the molecule.

The principal goal of the work presented in this Chapter was to perform a systematic investigation of electric dipole moments in the first excited singlet state (viz. the \( \tilde{A}^1A_2 \) state) of formaldehyde. The data obtained in these experiments were of sufficiently high precision to examine the influence of the \( \nu_4 \) out-of-plane bending motion upon the electronic structure of the \( \tilde{A}^1A_2 \) state. The results of these measurements, which involved both formaldehyde and its deuterated analog, are expected to be of considerable utility in assessing the quality of \textit{ab initio}
electronic wavefunctions. Such means for gauging the accuracy of molecular computations is especially important for electronically excited polyatomic systems which are usually more difficult to calculate than the corresponding ground state potential surfaces.

Additional motivation for the dipole moment measurements was provided by several features intrinsic to the electronic potential surfaces of formaldehyde. In particular, our attention was directed towards two questions which are intimately related to the molecular charge distribution of the $\tilde{A}^1A_2$ state:

1. What is the origin of the nonplanar equilibrium configuration that exists in the $\tilde{A}^1A_2$ electronic state of formaldehyde?

From analysis of both the vibrational and rotational structure associated with the $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ electronic transition [14], it has been thoroughly established that the first excited singlet state of formaldehyde possesses a nonplanar equilibrium geometry corresponding to a double minimum potential surface along the $\nu_4$ out-of-plane bending coordinate. The origin of this nonplanarity has been a subject of considerable speculation for many years. In addition to numerous ab initio calculations [15, 16], efforts to understand the electronic nature of this distorted configuration have ranged from the semiempirical molecular orbital correlation diagrams developed by A. D. Walsh in the early 1950s [17] to recent vibronic coupling models proposed by Innes [18].

Since the electronic dipole moment is a sensitive probe of the charge distribution over the entire molecular framework, our high precision measurements could provide some insight into the electronic origin for the nonplanarity of $\tilde{A}^1A_2$ formaldehyde. In particular, the vibronic coupling model of Innes predicts an unusually large isotope effect and a staggering of the dipole moments observed for the lowest vibrational levels in the $\nu_4$ coordinate.

The nonplanar geometry of $\tilde{A}^1A_2$ formaldehyde also suggests that the molecular dipole moment, instead of being oriented only along the C\=O bond (as is the case for the planar $\tilde{X}^1A_1$ ground state), will now possess
a component in the out-of-plane direction. Although vibrational interconversion between the two equilibrium configurations of the double minimum potential surface would tend to average this additional dipole moment component to zero, its presence might be detected, under appropriate experimental conditions, by utilizing a high resolution spectroscopic probe.

2. What is the nature of the couplings which exist between the $\tilde{X}^1A_1$ and $\tilde{A}^1A_2$ electronic states of formaldehyde?

It has been conclusively demonstrated that the characteristic photophysical processes occurring in the $\tilde{A}^1A_2 (S_I)$ electronic state of formaldehyde are dominated by interactions with predissociating, highly excited rotation-vibration levels of the $\tilde{X}^1A_1 (S_0)$ ground electronic state potential surface [19].

*Ab initio* calculations have shown that the $S_I \sim S_0$ coupling parameters, which constitute a breakdown of the Born-Oppenheimer approximation, should be extremely small in magnitude [20]. Since the predissociative widths of the highly excited $S_0$ states are thought to be much smaller than their relative energy spacings [21, 22, 23], any observed effects of the $S_I \sim S_0$ interaction will be strongly dependent upon the proximity (in energy) of an $\tilde{A}^1A_2$ rovibronic level and its perturbing counterpart in the $\tilde{X}^1A_1$ state. This fact was exploited in a series of ingenious experiments, performed by Weisshaar and Moore [24, 22, 25], which utilized the relative Stark tunings of the $S_I$ and $S_0$ states in an external electric field to shift levels into coincidence with one another. The interactions which occur between $\tilde{A}^1A_2$ rovibronic levels and highly excited rotation-vibration levels of the ground potential surface will be accompanied by a partial mixing of the corresponding molecular wavefunctions. This leads to several observable consequences, most notable of which is a decrease in the fluorescence lifetimes of individual rovibronic levels in the electronically excited state due to the competitive relaxation channel of predissociation which $S_I \sim S_0$ coupling introduces.

In analogy to the Weisshaar and Moore experiments, the dipole moment measurements described in this Chapter depend upon the energy level
shifts induced by an external electric field. Although our interests were
directed mainly towards characterization of the \( \tilde{A}^1A_2 \) state, relative
tuning of the \( S_1 \) and \( S_0 \) manifolds was an unavoidable consequence of
the experimental technique. The mixing of wavefunctions which
accompanies \( S_1 \sim S_0 \) interactions can produce a substantial alteration in
the molecular charge distribution. As a result, plots of the Stark
splittings observed for a specific rovibronic level in \( \tilde{A}^1A_2 \) formaldehyde
as a function of the applied electric field might contain sudden
deviations from the expected monotonically increasing behavior. These
*glitches*, which correspond to a local alteration in the effective dipole
moment, would occur at field strengths which tune an \( S_0 \) state into
coincidence with the rovibronic level under investigation. Our
experiments could therefore serve as a probe of highly excited rotation-
vibration levels in the ground electronic potential surface of
formaldehyde.

The successful outcome of the dipole moment studies depended upon being
able to achieve an extraordinarily high degree of precision in the measurement of
spectral modifications induced by an applied electric field. This necessitated that
our experiments be capable of attaining sub-Doppler resolution of relatively small
Stark splittings within individual rovibronic levels of \( \tilde{A}^1A_2 \) formaldehyde. The
past decade has witnessed the development of numerous spectroscopic probes, based
upon the unique properties of laser radiation, which permit resolution beyond the
limits imposed by inhomogenous broadening mechanisms. The more common of
these techniques (e.g. optical-optical double resonance), however, derive their sub-
Doppler resolution from the exceptionally monochromatic emission that can be
produced by tunable continuouswave dye lasers. Unfortunately, such laser sources
are not yet readily available in the ultraviolet region of the spectrum where the
lowest energy electronic transitions of most polyatomic molecules, including
formaldehyde, are located. The weak oscillator strengths encountered in most
polyatomic systems present an additional impediment for those sub-Doppler
techniques (e.g. saturation spectroscopy) which rely upon optical pumping and
saturation.

To circumvent the numerous problems associated with other high resolution spectroscopic probes, our dipole moment studies in $\tilde{A}^1A_2$ formaldehyde have utilized the sub-Doppler technique of quantum beat spectroscopy [26, 27, 28]. This method, which depends more upon the coherence properties of laser radiation rather than its monochromaticity, provides a sensitive and precise means for measuring extremely small energy splittings within excited electronic states. Previous applications of quantum beats have involved investigations of hyperfine [29], Stark [30, 31, 32], and Zeeman [33, 34] interactions mostly in atomic and diatomic systems. The work presented in this thesis, however, represents the first attempt to exploit the exceptional resolution afforded by quantum beat spectroscopy in order to systematically examine the dipole moment function of an electronically excited polyatomic molecule. The results of these experiments have an intrinsic precision (viz. dipole moments determined to $\sim 1$ part in $10^4$) which rivals that achieved by conventional microwave measurements in ground electronic potential surfaces.

The sections which follow will first review the Stark effect and quantum beat spectroscopy with particular emphasis upon application to the formaldehyde system. After a discussion of experimental details, the results of our high-precision dipole studies will be presented. Finally, an interpretation of these measurements, in terms of the electronic structure for the $\tilde{A}^1A_2$ state, will be offered.

1.2 The Stark Effect

1.2.1 Introduction

The effect of an electric field on optical spectra was first described by Johannes Stark during his 1913 studies of discharge-excited hydrogen and helium atoms [35].
Significant advances in the theoretical interpretation of what came to be known as the Stark effect followed when quantum mechanics was developed. In fact, the first application of quantum mechanical perturbation theory was to the Stark effect in hydrogen [36, 37]. The widespread use of electric fields as a tool for spectroscopic research did not occur until the revolution in microwave-related technology brought about by the second World War. This delay of nearly 40 years can be attributed to many factors including the fact that atomic systems, which were of principal concern to early physicists, rarely possess large, first order Stark shifts. As a result, the rather small spectral changes induced by attainable electric field strengths were usually near the resolution limits imposed by measurement techniques available prior to the 1940s. This situation is to be contrasted with that for the magnetic field interactions discovered by Pieter Zeeman in 1896 [38]. Since most atomic spectra do exhibit substantial first order shifts in a magnetic field, the Zeeman effect played a key role for many of the pioneering experiments in spectroscopy. In particular, the Hanle effect and other level crossing phenomena were initially observed in the presence of a magnetic perturbation.

The post WWII application of radar technology to scientific research initiated the field of high-resolution rotational spectroscopy in polyatomic molecules. The larger Stark splittings afforded by molecular systems, in conjunction with the enhanced sensitivity and resolution made possible by the new microwave techniques, permitted increasingly sophisticated studies of electric field effects to be performed. At present, the advent of lasers, as well as the development of numerous optical analogues of magnetic resonance detection schemes, has transformed the Stark effect into an important spectroscopic probe for characterizing the properties of both atoms and molecules. The information derived from these electric field investigations has provided considerable insight into various topics of concern to
present-day molecular physics and chemistry ranging from the basic electronic structure of matter to the nature of inductive effects in chemical reactivity.

In the sections which follow, we will first examine the classical interactions of a molecular system with a static electric field. This will lead, in a natural way, to the form of the Stark Hamiltonian appropriate for the quantum mechanical description of a molecule in an external field. Finally, a discussion of parity and its implications with regards to permanent molecular moments will be presented.

1.2.2 Classical Molecular Interactions with a Static Electric Field

The term "Stark effect" basically refers to any changes induced in the spectrum of a molecular (or atomic) system when it is subjected to a static external electric field. Since molecules can be described, classically, as a collection of charged particles (nuclei and electrons), interactions will occur between the molecular electric multipole moments [2] and the distribution of external charges responsible for the applied field. In this context, the observed spectral modifications can be interpreted as being the consequence of various torques and forces which the electric field exerts upon the molecule.

According to classical electrostatic theory [39], the interaction energy, \( V \), between a molecule and a surrounding static distribution of charge (e.g. an electric field) can be expressed in the following form:

\[
V = \sum_n \sum_m \frac{q_m q_n}{|r_n - r_m|}
\]  

(1.1)

where

\( q_m \) represents the charge on the \( m^{th} \) particle in the molecule,

\( r_m \) denotes the position vector of the \( m^{th} \) particle in the molecule.
relative to the origin of a space-fixed coordinate system,

$q_n$ represents the charge on the $n^{th}$ particle in the external charge distribution,

$r_n$ denotes the position vector of the $n^{th}$ particle in the surrounding charge distribution relative to the origin of a space-fixed coordinate system.

The particles described in expression (1.1) have been divided into two distinct groups depending upon whether they belong to the molecule (subscript $m$) or the surrounding charge distribution (subscript $n$). By assuming that the molecular system is located at the origin of the space-fixed coordinates and the perturbing external charges are widely separated from the molecule (viz. $|r_n| \gg |r_m|$), the denominator of equation (1.1) can be expanded in a series of Legendre Polynomials, $P_k(\cos \Theta_{n,m})$:

\[
\frac{1}{|r_n - r_m|} = \sum_k \frac{(r_n)^k}{(r_n)^{k+1}} P_k(\cos \Theta_{n,m})
\]

(1.2)

where $r_n = |r_n|$, $r_m = |r_m|$, and $\Theta_{n,m}$ is the angle formed between $r_n$ and $r_m$.

The spherical harmonic addition theorem [40] permits the Legendre Polynomials of equation (1.2) to be expressed as a sum of spherical harmonics, $Y_p^k(\theta_m, \phi_m)$:

\[
P_k(\cos \Theta_{n,m}) = \frac{4\pi}{2k+1} \sum_{p=-k}^k Y_p^k(\theta_m, \phi_m)^* Y_p^k(\theta_n, \phi_n)
\]

(1.3)

where

$\theta_m$ and $\theta_m$ are the angular coordinates of $r_m$ with respect to the space-fixed axis system,
\[ \theta_n \text{ and } \phi_n \] are the angular coordinates of \( r_n \) with respect to the space-fixed axis system.

By combining expressions (1.2) and (1.3) and substituting the result back into equation (1.1), the static interaction energy can be reformulated in terms of the electric multipole moments describing the charge distributions present both inside and outside of the molecular system:

\[
V = \sum_k \sum_p \left( \left( \frac{4\pi}{2k+1} \right)^{1/2} \sum_m q_m(r_m)^k Y_p^k(\theta_m,\phi_m) \right) \\
	imes \left( \left( \frac{4\pi}{2k+1} \right)^{1/2} \sum_n \frac{q_n}{(r_n)^{k+1}} Y_p^k(\theta_n,\phi_n) \right)
\]

\[
= \sum_k \sum_p T_p^k(M)^* T_p^k(F)
\]

\[
= \sum_k (T^k(M) \cdot T^k(F))
\]

\[
= \sum_k V^{(k)} \tag{1.4}
\]

where

\( T_p^k(M) \) signifies the \( p^{th} \) component of a rank \( k \) spherical tensor \([41]\) which describes the \( k^{th} \) multipole moment of the molecular charge distribution,

\( T_p^k(F) \) signifies the \( p^{th} \) component of a rank \( k \) spherical tensor which describes the \( k^{th} \) multipole moment of the surrounding charge distribution (viz. external to the molecule),
\( V^{(k)} \) represents the contribution to the energy from interactions between the \( k^{th} \) electric multipole moments.

The successive terms of equation (1.4) denote the interaction of higher and higher electric multipole moments of the molecule with those of the surrounding distribution of charges. In particular, the scalar products corresponding to \( k = 0, 1, \) and \( 2 \) give rise to the three interactions most often encountered in molecular physics:

1. \( k = 0: \)
\[
V^{(0)} = (T^0(Q) \cdot T^0(\Phi))
\]
This represents the interaction of the electric monopole moment or total charge, \( Q \), of the molecule with the electric potential, \( \Phi \), produced by the surrounding charge distribution.

2. \( k = 1: \)
\[
V^{(1)} = (T^1(\mu) \cdot T^1(\nabla \Phi)) = -(T^1(\mu) \cdot T^1(E))
\]
This represents the interaction of the molecular electric dipole moment, \( \mu \), with the gradient of the electric potential or electric field, \( E = -\nabla \Phi \), due to the external charge distribution.

3. \( k = 2: \)
\[
V^{(2)} = (T^2(\Theta) \cdot T^2(\nabla \nabla \Phi)) = -(T^2(\Theta) \cdot T^2(\nabla E))
\]
This represents the interaction of the molecular electric quadrupole moment, \( \Theta \), with the gradient of the electric field, \( \nabla E = -\nabla \nabla \Phi \), caused by the surrounding distribution of charge.

For most spectroscopic studies which utilize the Stark effect, a great deal of effort is made to ensure that the electric field applied to the molecular sample is extremely uniform and homogenous. Consequently, in the absence of a net charge on the molecule under investigation (i.e. \( Q = 0 \)), the expansion presented in equation (1.4) will collapse to a single term describing the interaction between the molecular electric dipole moment, \( \mu \), and the external electric field, \( E \):

\[
V = V^{(1)} = -T^1(\mu) \cdot T^1(E)
\]  \( (1.5) \)
This expression, which represents the scalar product of two vectorial quantities, will become the perturbation Hamiltonian for the quantum mechanical discussion of the Stark effect which follows. Due to the nature of the interaction described by equation (1.5), the measurement of the spectral shifts produced by a homogenous electric field (viz. the Stark effect) has become the most specific and sensitive technique available for the determination of electric dipole moments in molecules.

1.2.3 Quantum Mechanical Description of the Stark Effect

The quantum mechanical operator describing the interaction of a molecular electric dipole moment and an external electric field, $H_{Stark}$, can be formulated, by reference to the classical expression in equation (1.5), as a scalar product between two rank one irreducible spherical tensor operators:

$$H_{Stark} = -\mathbf{T}^1(\mu) \cdot \mathbf{T}^1(\mathbf{E}) = -\sum_p (-1)^p T^1_p(\mu) T^1_{-p}(\mathbf{E})$$

where

$T^1(\mu)$ represents the quantum mechanical operator for the molecular electric dipole moment vector,

$T^1(\mathbf{E})$ represents the quantum mechanical operator for the electric vector of the applied field.

The subscript $p$ which appears in this expression denotes components of the irreducible spherical tensors referred to the space-fixed coordinate system in which the applied electric field is defined. Higher order polarizability and hyperpolarizability terms [42], which describe the interactions associated with field-induced molecular moments, have not been considered in equation (1.6) due to their negligible magnitude at moderate (viz. $< 10000 \text{V/cm}$) electric field strengths [43].
Fabricant, et. al. [3] have suggested that a typical polarization anisotropy of $1 \text{A}^3$ could, at most, contribute $\sim 2 \times 10^{-4} \text{D}$ to the dipole moment measured in the formaldehyde system. The magnitude of this effect is slightly below the limits placed upon the precision of the present Stark measurements.

Appendix A demonstrates how the matrix elements of the Stark Hamiltonian can be evaluated in a basis of symmetric rotor eigenfunctions which are characterized by the quantum numbers $J$, $K$, $M$, and $\gamma$ (cf. below for description of quantum numbers). If the applied electric field is directed only along the space-fixed $z$-axis (viz. $T^1_0(E) = \mathcal{E}$ and $T^1_{\pm 1}(E) = 0$), the appropriate form for the general matrix element of $H_{\text{Stark}}$ is found to be:

$$
\langle \gamma| J K M \rangle | H_{\text{Stark}} | \gamma J K M \rangle = \frac{1}{(-1)^{M-K}} \sqrt{(2J+1)(2J+1)} \mathcal{E}
$$

$$
\times \left( \begin{array}{cc} J' & 1 \\ -M' & 0 \\ M & \end{array} \right) \sum_q \left( \begin{array}{cc} J' & 1 \\ -K' & q \\ K & \end{array} \right) \langle \gamma| T^1_q(\mu) | \gamma \rangle
$$

(1.7)

where $K$ and $M$ signify the projections of the total angular momentum, $J$, along the molecule-fixed and space-fixed $z$-axes respectively and $\gamma$ represents all other quantum numbers (e.g. quantum numbers associated with vibrational and electronic degrees of freedom) required to describe the molecular system.

The subscript "$q$", which is appended to the spherical tensor operator representing the molecular dipole moment, denotes components referred to the molecule-fixed coordinate system. It should be apparent that the derivation of equation (1.7) has assumed an explicit separability of rotational motion from other degrees of freedom. Consequently, $\langle \gamma| T^1_q(\mu) | \gamma \rangle$, which signifies the expectation value for the $q^{th}$ spherical component of the dipole moment in vibronic state $| \gamma \rangle$, has no dependence on rotational quantum numbers. As we shall see later, this is not strictly
the case for a nonrigid molecule [44]. Although hyperfine effects could readily be incorporated into expression (1.7) [43, 45], the rather small magnitude of the predominantly nuclear quadrupole interactions occurring in both formaldehyde-$h_2$ and formaldehyde-$d_2$ [46, 3] indicated that this was not necessary. A notable exception to this statement is to be found in the Stark measurements performed upon the $v_4 = 1$ level of $\tilde{A}^1A_2$ formaldehyde-$d_2$. The manifestation of hyperfine structure in these experiments will be discussed at a later point in this Chapter.

By utilizing the symmetry properties of the Wigner 3-j symbols appearing in equation (1.7), the rotational selection rules for the matrix elements of the Stark Hamiltonian can be easily obtained:

$$\Delta J = 0, \pm 1 \quad \Delta K = 0, \pm 1 \quad \Delta M = 0.$$

These selection rules imply that the total angular momentum, $J$, is no longer a good quantum number in the presence of an electric field. This is due to the fact that the external field, by disrupting the isotropy of space, has invalidated the symmetry labels (viz. $J$) associated with the spatial three-dimensional pure rotation group, $K({\text{spatial}})$ [47, 48]. If the electric field is applied along a specific direction in space (which can be defined as the axis of quantization or the laboratory-fixed $z$-axis), however, the operations of $C_\infty({\text{spatial}})$ will commute with the effective molecular Hamiltonian [49]. As indicated above, the magnetic quantum number, $M$, which denotes the various representations in $C_\infty({\text{spatial}})$, will therefore remain a valid symmetry label for the eigenstates. Since time reversal symmetry is not destroyed by an electric field, the separably degenerate representations of $C_\infty({\text{spatial}})$ will remain intact. This requires that a systematic degeneracy will exist between levels specified by $+M$ and $-M$. 
The effective Hamiltonian for our electric field studies, $H_{\text{eff}}$, can thus be expressed as a sum of two terms:

$$H_{\text{eff}}(\mathcal{E}) = H_0 + H_{\text{Stark}}(\mathcal{E}) \quad (1.8)$$

where $H_0$ represents the effective zero-field Hamiltonian for an asymmetric rotor in a particular vibronic state. The matrix elements associated with this term are described in appendix B. The explicit dependence of $H_{\text{Stark}}$ and therefore $H_{\text{eff}}$ on the applied electric field strength, $\mathcal{E}$, is indicated in equation (1.8).

By evaluating the matrix elements of $H_{\text{eff}}(\mathcal{E})$ in a basis of symmetric top eigenfunctions and subsequently diagonalizing the resulting matrix as a function of $\mathcal{E}$, the effect of a static electric field on the observed pattern of energy levels in an asymmetric rotor can be ascertained. The results of this procedure are illustrated in figure 1-1 for the lowest rotational levels in the vibrationless $\tilde{X}^1A_1$ state of formaldehyde-$h\mathcal{E}$. The most obvious feature presented in this diagram is the fact that application of an external field partially removes the $(2J+1)$-fold spatial degeneracy associated with a state of total angular momentum $J$. As a result, each state of a particular $J$ is partitioned into $J+1$ sublevels designated by the absolute value of their magnetic quantum number $M$.

As indicated by equation (1.7), an asymmetric rotor can generally have components of the molecular dipole moment along all three of the body-fixed axes (viz. $q = 0$, $+1$, and $-1$ in spherical notation). Symmetry restrictions associated with the structure of a particular molecule will often eliminate one or more of these components [2]. Although formaldehyde is rigorously an asymmetric rotor, the inertial constants which characterize the molecular framework closely approximate those of a prolate symmetric top (i.e. $\kappa = -0.96 [50]$). Therefore, in analogy with
Figure 1-1: Stark Effect in Vibrationless $\tilde{X}^1A_1$ Formaldehyde-$h_\gamma$

The Stark shifts associated with the lowest rotational eigenstates in the vibrationless level of $\tilde{X}^1A_1$ formaldehyde-$h_\gamma$ are illustrated as a function of the applied electric field. The rotational quantum numbers corresponding to the individual levels are as follows:

<table>
<thead>
<tr>
<th>Rotational Eigenstate</th>
<th>Zero Field Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0_{0,0}</td>
<td>0.0</td>
</tr>
<tr>
<td>1_{0,1}</td>
<td>2.430</td>
</tr>
<tr>
<td>2_{0,2}</td>
<td>7.286</td>
</tr>
<tr>
<td>1_{1,1}</td>
<td>10.539</td>
</tr>
<tr>
<td>1_{1,0}</td>
<td>10.700</td>
</tr>
<tr>
<td>3_{0,3}</td>
<td>14.566</td>
</tr>
<tr>
<td>2_{1,2}</td>
<td>15.238</td>
</tr>
<tr>
<td>2_{1,1}</td>
<td>15.719</td>
</tr>
</tbody>
</table>

where the tabulated energies are in wavenumbers. The calculated Stark splittings are based upon the rotational constants reported in reference [50] and a dipole moment of $\mu_a = 2.33168$D as determined by Fabricant, et. al. [3].
Stark Effect in $\tilde{X}^1A_1$, Formaldehyde–$h_2$
the symmetry constraints imposed upon a prolate rotor [2], it will prove useful to consider the case in which only one nonzero component of the dipole moment is present. Since the dipole moment will now be directed only along the molecular symmetry axis (viz. the body-fixed z-axis such that $\langle \gamma | T^1_0(\mu) | \gamma \rangle = \mu_0$ and $\langle \gamma | T^1_{\pm 1}(\mu) | \gamma \rangle = 0$), the matrix elements for the Stark Hamiltonian become:

$$
\langle \gamma J K M | H_{Stark} | \gamma J K M \rangle = (-1)^{M-K} \sqrt{(2J+1)(2J'+1)}
\times \left( \begin{array}{cc} J & 1 \\ 0 & M \end{array} \right) \left( \begin{array}{cc} J' & 1 \\ 0 & K \end{array} \right) \mu_0 \mathcal{E}
$$

(1.9)

The symmetry properties of the second 3-j symbol in equation (1.9) indicate that, in this prolate top limit, the Stark Hamiltonian is also diagonal in the quantum number $K$ (i.e. the selection rule $\Delta K = 0$ is obtained). The applicability of this expression to the $\tilde{A}^1A_2$ state of formaldehyde, which, due to its pyramidally distorted equilibrium configuration, is capable of supporting an additional component of the molecular dipole moment in the out-of-plane direction, will be discussed later.

Some insight into the electric field dependence of the Stark splittings illustrated in figure 1-1 can be obtained by considering the effective Hamiltonian of equation (1.8) with the form of $H_{Stark}$ being defined by expression (1.9). First order perturbation theory [51] suggests that the energy for a particular eigenstate will be given by:

$$
E_{\gamma J K M} = E^0_{\gamma J K M} + \langle \gamma J K M | H_{Stark} | \gamma J K M \rangle
$$

$$
= E^0_{\gamma J K M} + \frac{\mu K}{J(J+1)} \mu_0 \mathcal{E}
$$

(1.10)
where

\[ E_{\gamma JK}^0 = E_{\gamma JK}^0 \]

represents the zero-field energy corresponding to a particular molecular energy level designated by the quantum numbers \( \gamma, J, K \), and \( M \). The magnetic quantum number subscript can be dropped since, in the absence of an external electric field, all of the \( M \) levels associated with a given angular momentum, \( J \), are degenerate.

\[ E_{\gamma JK M}(\mathcal{E}) \]

represents the energy of the molecular system, for a rovibronic state specified by the quantum numbers \( \gamma, J, K \), and \( M \), in an electric field of magnitude \( \mathcal{E} \).

The first order or linear Stark effect described by equation (1.10) is rigorously correct only in the case of a true symmetric top, where states having \( +\mathcal{K} \) and \( -\mathcal{K} \) projections of the total angular momentum on the body-fixed \( z \)-axis are exactly degenerate [52]. Further clarification of this point will be provided in the following section which deals with parity and molecular dipole moments. Expression (1.10) is approximately valid, however, when the Stark interactions induced by the electric field are comparable in magnitude to the intrinsic asymmetry splitting of an asymmetric rotor.

In order to apply equation (1.10) to the formaldehyde energy levels in figure 1-1, the quantum number \( K \) can be approximated by the near prolate value of \( K_a \) associated with an asymmetric top. Expression (1.10) thus indicates that the Stark shifts should increase with increasing \( K_a \) and decrease with increasing \( J \) with the largest splittings corresponding to \( |M| = J \). These trends are even more evident in the low field Stark tuning patterns depicted in figure 1-2 for specific rotational eigenstates in the vibrationless level of \( \tilde{X}^1A_1 \) formaldehyde-\( h_2 \). The \( J = 2 \) eigenstates illustrated in this diagram are of particular concern for the quantum beat studies discussed in the present Chapter.

The plots presented in figure 1-2 indicate that if the value of the applied
Figure 1-2: Stark Effect for Rotational Levels in $\tilde{X} \, ^1A_1$ Formaldehyde-$h_\gamma$.

The low field Stark effect for $J = 2$ rotational eigenstates in the vibrationless level of $\tilde{X} \, ^1A_1$ formaldehyde-$h_\gamma$ is illustrated. Each level of a given total (rotational) angular momentum $J$ splits into $J+1$ sublevels, designated by the absolute value of the magnetic quantum number $M$, under the influence of the Stark perturbation.
Stark Splitting (GigaHertz)

Applied Field (KiloVolts/cm)
electric field is known and the levels involved in a spectroscopic transition have been positively identified, then the molecular dipole moment can be determined from the magnitude of the energy level shifts produced by the Stark effect. Depending upon the details of the experimental technique employed, these measurements can be performed for states described by a wide range of rotational, vibrational, and electronic quantum numbers. Since the dipole moment is a global property which is influenced by the charge distribution over the entire molecule, the changes induced in the electronic wavefunction by variations in the rotational and vibrational degrees of freedom can be systematically explored. Perhaps of even greater significance are the possibilities which exist for examining the subtle effects that accompany isotopic substitution [53, 54] and the breakdown of conventional notions regarding molecular structure (i.e. the Born-Oppenheimer approximation) [55, 47].

1.2.4 Parity and Molecular Dipole Moments

The nature and manifestation of permanent electric dipole moments requires a careful consideration of the inversion or parity operator [48], \(E^*\), which has the effect of inverting the spatial coordinates of all particles (both nuclei and electrons) in a molecule through the origin of the space-fixed axis system (normally taken to be the molecular center of mass). In the absence of an externally applied field, the molecular Hamiltonian, \(H_0\), will commute with \(E^*\):

\[
[H_0, E^*] = 0
\]

As a result, the eigenfunctions of the zero-field Hamiltonian, \(\{\psi_n^0; n = 0, 1, \cdots \}\), can be labeled by their behavior under the inversion operator:
\[ E^* |\psi^0_n \rangle = \pm |\psi^0_n \rangle \]

The eigenstates are described as having either even or odd (i.e. + or −) total parity depending on whether the eigenvalue associated with the inversion operator is +1 or −1 respectively.

From the definition presented in equation (1.4), it can be readily demonstrated that the electric dipole moment is an operator of odd parity, namely \( E^* T^1(\mu) = -T^1(\mu) \). As a result, symmetry arguments dictate that the quantum mechanical expectation value of \( T^1_p(\mu) \) in a molecular eigenstate of definite parity will be zero:

\[ \langle T^1_p(\mu) \rangle_n = \langle \psi^0_n |T^1_p(\mu)|\psi^0_n \rangle = 0 \]

Therefore, no single eigenstate of definite parity can give nonzero expectation values for any space-fixed component of the electric dipole moment. This prediction appears to be contradicted by the nonzero dipole moments reported as experimentally measured quantities in numerous molecular systems for which parity constitutes a valid symmetry label. This discrepancy arises because most molecules possess a permanent electric dipole moment only when referred to the body-fixed system of coordinates. Since the Heisenberg Uncertainty Principle prohibits a freely-rotating molecule from being oriented along a preferential direction in space [51], the laboratory-fixed components of the dipole moment will necessarily average to zero. A close inspection of Appendix A demonstrates that an essential step in the evaluation of the Stark Hamiltonian matrix elements (i.e. equation (1.7)) entails a transformation into the molecule-fixed axis system.
For the special situation in which two states of opposite parity (viz. \( |\psi_0^0\rangle \) and \( |\psi_0^-\rangle \)) are exactly degenerate, the predicted behavior can be quite different. As a result of the degeneracy, a new set of eigenstates of mixed parity can be defined:

\[
|\psi_a^0\rangle = \frac{1}{\sqrt{2}} \left( |\psi_+^0\rangle + |\psi_-^0\rangle \right)
\]

\[
|\psi_b^0\rangle = \frac{1}{\sqrt{2}} \left( |\psi_+^0\rangle - |\psi_-^0\rangle \right)
\]

The expectation values for the \( p^{th} \) component of the molecular dipole moment in these states of mixed parity are given by:

\[
\langle T_p^1(\mu) \rangle_a = \langle \psi_a^0 | T_p^1(\mu) | \psi_a^0 \rangle = \text{Re} \left( \langle \psi_-^0 | T_p^1(\mu) | \psi_+^1 \rangle \right) \neq 0
\]

\[
\langle T_p^1(\mu) \rangle_b = \langle \psi_b^0 | T_p^1(\mu) | \psi_b^0 \rangle = -\text{Re} \left( \langle \psi_-^0 | T_p^1(\mu) | \psi_+^1 \rangle \right) \neq 0
\]

The presence of degenerate eigenstates has thus resulted in a nonzero value for the space-fixed components of the electric dipole moment. In actual practice, this degeneracy can occur either accidentally, as is the case in the hydrogenic atoms where states of different angular quantum number \( l \) (for a given principal quantum number \( n \)) can have the same energy, or for symmetry related reasons, as in a true symmetric top molecule for which all levels with angular momentum quantum number \( K > 0 \) are doubly degenerate [58]. The \((2J+1)\)-fold degeneracy associated with the magnetic quantum numbers, \( M \), does not alter this situation. For a state of given total angular momentum, all of the \( M \) sublevels have the same parity.

The application of an electric field to the system produces an entirely new set
of circumstances. Since the inversion operator will not invert the fixed charges producing the external field, it will no longer commute with the effective molecular Hamiltonian. As a result, parity is no longer a strictly valid symmetry label for the eigenstates. This implies that:

\[ \langle T_p^1(\mu) \rangle_n = \langle \Psi_n | T_p^1(\mu) | \Psi_n \rangle \neq 0 \]

where \( |\Psi_n \rangle \) represents a state of ill-defined parity which exists in the presence of a nonzero electric field. The destruction of parity which accompanies the application of an external electric field can thus lead to an induced, space-fixed component of the electric dipole moment.

The discussion presented above illustrates a basic fact of nature, namely that no electric multipole moments of odd order can exist in the absence of a degeneracy [39, 57]. This has several implications for electric dipole moments measurements in an asymmetric rotor, such as formaldehyde, where there are no systematic degeneracies between states of opposite parity. Due to the lack of a permanent electric moment at zero-field, the Stark effect will initially be second order (viz proportional to the square of the applied field). This can be classically rationalized in terms of an induction process in which the external field must induce a moment in the molecular system with which it can subsequently interact. However, once the electric field is large enough to cause the mixing of states having opposite parity (e.g. the members of an asymmetry doublet) the Stark perturbation can be transformed into an effect which is linearly proportional to the magnitude of the applied field. This behavior is clearly illustrated in figure 1-2 where the linearity of the Stark shifts associated with individual \( J = 2 \) eigenstates is found to be correlated with the size of the asymmetry splitting (i.e. a smaller asymmetry
splitting results in the onset of linearity at a lower value of the applied electric field). Since the $2_{0,2}$ level is not a member of a $K_a$-doublet, it retains a small second order Stark effect until the electric field perturbation becomes large enough to mix adjacent rotational states (i.e. states of different $J$ and/or $K$).

1.3 Quantum Beat Spectroscopy

1.3.1 Introduction

Since their inception in 1960 [58], lasers have revolutionized nearly all aspects of science and technology. Nowhere is this more apparent than in the area of optical spectroscopy where the unique properties of laser light, viz. exceptional monochromaticity, extreme intensity, and unprecedented spatial and temporal coherence, have brought about a renaissance in a once nearly stagnant field. As a result, the methodology of the modern, high-resolution spectroscopist has been redefined, with concepts intrinsic to once-novel techniques such as quantum beat spectroscopy assuming key roles in everyday experiments.

Quantum beat spectroscopy, as applied to the work presented in this Chapter, provides a means of performing ultrahigh-resolution optical spectroscopy in excited electronic states of gas phase molecules. Although the first quantum beat experiments were accomplished with conventional light sources [59, 60, 61], the transformation of these techniques from theoretical curiosities to practical spectroscopic tools has occurred only recently with the introduction of readily tunable dye lasers, capable of producing intense, short pulses with near Fourier transform limited spectral bandwidths, and high-speed detection electronics. Nevertheless, the methods of quantum beat spectroscopy and other time-resolved coherent optical techniques have rapidly evolved into an important branch of high-resolution laser spectroscopy.
In order to define exactly what is meant by the term "quantum beat", consider an experiment in which a pulsed source of excitation, e.g. a laser, is used to induce transient spontaneous emission from a sample of molecules. Even in the absence of quantum beat effects, analysis of the resulting time-resolved fluorescence signal can provide considerable insight into the spectroscopic and dynamical properties of the molecular system. Most notably, such time domain measurements readily permit the extraction of lifetimes for excited electronic states.

However, if the pulsed excitation is performed in an appropriate manner, a coherent superposition of nondegenerate eigenstates can be created in the excited electronic state of the molecule. In this case, there exists the possibility of observing amplitude modulations in the resulting time-resolved fluorescence signal with modulation frequencies corresponding to the energy separations between pairs of coherently-prepared levels in the excited state. These oscillations are referred to as quantum beats since they can be explained in terms of a quantum mechanical interference effect between the different channels for spontaneous emission available to the constituent levels of the superposition state. Analysis of the beat frequencies, perhaps as a function of some external perturbation (e.g. an applied electric or magnetic field), provides a convenient method for measuring, with extremely high resolution, small energy splittings in excited electronic states.

1.3.2 A Simple Model of Quantum Beat Phenomena

Considerable insight into the nature of the interference effects responsible for the appearance of quantum beats can be obtained by considering the hypothetical molecular energy level diagram illustrated in figure 1-3. This ideal four-level system consists of an initially populated ground state, designated by |0⟩, a set of closely spaced levels in an excited electronic state, viz. |1⟩ and |2⟩, and a final lower level.
Figure 1-3: Phenomenological Model for Quantum Beat Effects.

This figure illustrates the hypothetical four-level system utilized for our analysis of quantum beat effects. A coherent superposition is created between levels $|1\rangle$ and $|2\rangle$ by a short resonant laser pulse, of duration $\Delta t$, which has a Fourier transform bandwidth, $\Delta \nu$, comparable to the energy separation in the excited state ($\text{viz. } E_2 - E_1$). The time-resolved signal observed through spontaneous emission into a common lower level (i.e. $|3\rangle$) will therefore be a summation of the individual exponentially decaying fluorescence amplitudes ($\text{viz. } A_1 e^{-\Gamma_1 t} + A_2 e^{-\Gamma_2 t}$) and the oscillatory term ($\text{viz. } A_b e^{-\Gamma_0 t} \cos (\omega_0 t + \Phi_0)$) associated with the quantum mechanical interference phenomenon of quantum beats.
Excitation Pulse:

Fourier Transform

Detected Signal:

\[ I(t) = A_1 e^{-r_1 t} + A_2 e^{-r_2 t} + A_3 e^{-r_3 t} \cos(\omega_0 t + \Phi_0) \]
i.e. \(|3\rangle\), into which the excited states can relax via spontaneous emission of a photon. In anticipation of what is to follow, the nearly degenerate states \(|1\rangle\) and \(|2\rangle\) might represent, for instance, the Stark split \(M\) components of a single rotation-vibration level in the \(\tilde{A}^1\!A_2\) state of formaldehyde.

Assume that at time \(t = 0\) a short, resonant laser pulse irradiates this hypothetical molecule, thereby inducing the simultaneous and coherent transfer of population from the single ground state \(|0\rangle\) into both of the nondegenerate levels of the excited state. For such a concurrent preparation of the eigenstates \(|1\rangle\) and \(|2\rangle\) to occur, the Fourier transform spectral bandwidth (i.e. coherence bandwidth), \(\Delta \nu\), of the excitation source must be comparable to the energy splittings present in the excited electronic state:

\[
\Delta \nu \geq \frac{E_{21}}{h} = \nu_{21}
\]

(1.11)

where

\[E_{21} = E_{2} - E_{1}\]

is the energy separation between state \(|2\rangle\) of energy \(E_{2}\) and state \(|1\rangle\) of energy \(E_{1}\),

\[\nu_{21} = E_{21}/h\]

is the frequency corresponding to the excited state energy splitting.

The Fourier transform limited bandwidth corresponding to an excitation pulse of duration \(\Delta \tau\) can be written in the following form:

\[
\Delta \nu = \frac{1}{\eta \Delta \tau}
\]

(1.12)

where \(\eta\) is a constant which depends upon the functional form of the excitation pulse in the time domain (e.g. for a Gaussian pulse shape, \(\eta = \pi/(4\ln 2)\), and for a Lorentzian profile, \(\eta = 2\pi\).}
By substituting expression (1.12) into equation (1.11), the pulse duration required for coherent excitation of both levels in the excited state is found to be:

\[
\Delta \tau \leq \frac{1}{\eta v_{21}}
\]  

(1.13)

It is interesting to note that, by defining a characteristic time period for the molecule in terms of \( \Delta T = 1/v_{21} \), equation (1.11) can be recast in the familiar form of a quantum mechanical time-energy uncertainty principle:

\[
\Delta T \Delta E \geq \hbar
\]

where \( \Delta E = \hbar \Delta \nu \).

Thus, immediately following preparation by an appropriate excitation pulse, the state vector of the molecular system, \( |\Psi(t=0)\rangle \), can be represented in terms of a coherent superposition of the eigenstates \( |1\rangle \) and \( |2\rangle \):

\[
|\Psi(0)\rangle = a|1\rangle + b e^{-i\delta}|2\rangle
\]  

(1.14)

where \( a \), \( b \), and \( \delta \) are real quantities which depend upon the details of the excitation process.

In general, the coefficients appearing in front of the eigenvectors in equation (1.14) will be proportional to the matrix elements of the quantum mechanical transition moment operator, \( D_{ab} \), which describes the absorption of a photon by the molecule:
\[ a \approx |(1|D_{ab}|0)| \]
\[ b \approx |(2|D_{ab}|0)| \]

(1.15)

In this context, \( \delta \) is related to the phase difference between the two, generally complex, transition moment matrix elements.

It is important to realize that equation (1.14) represents a rather exceptional situation which is crucial for the appearance of quantum interference effects. Creation of such a coherent superposition necessitates that the component levels be populated by optical pumping from a single, common lower state (viz. \( |0\rangle \)). Otherwise, an exact phase relationship will not exist between the constituents and a statistical mixture, rather than a linear superposition, of eigenstates will result.

Provided that the excitation pulse is sufficiently short with respect to the excited state lifetimes, i.e. \( \Delta \tau \ll \tau_1 \) and \( \Delta \tau \ll \tau_2 \) where \( \tau_j \) denotes the lifetime of level \( j \), the state vector of the molecular system will evolve freely in time such that:

\[ |\Psi(t)\rangle = a e^{-iE_{13}t/\hbar - \Gamma_1 t/2}|1\rangle + b e^{-iE_{23}t/\hbar - i\delta - \Gamma_2 t/2}|2\rangle \]

(1.16)

where

\[ \Gamma_j = 1/\tau_j \quad \text{is the decay rate for state } j \text{ which phenomenologically accounts for spontaneous emission processes,} \]

\[ E_{j3} = E_j - E_3 \quad \text{is the energy separation between the excited state } |j\rangle \text{ and the lower level } |3\rangle \text{ into which it relaxes via spontaneous emission.} \]

The time-dependent fluorescence intensity, \( I(t) \), emitted by the excited molecule as it relaxes to the lower level \( |3\rangle \), is given by:

\[ I(t) \approx |(3|D_{em}|\Psi(t))|^2 \]

(1.17)
where $D_{em}$ signifies the quantum mechanical operator describing the spontaneous emission process. The operators $D_{em}$ and $D_{ab}$ are essentially identical except for the spatial and polarization characteristics of the emitted or absorbed photons.

The temporal dependence of the spontaneous emission produced by the coherently excited four-level molecule can be obtained by substitution of expression (1.16) into equation (1.17):

$$I(t) \approx a^2| \langle 3| D_{em}|1 \rangle |^2 e^{-\Gamma_1 t} + b^2| \langle 3| D_{em}|2 \rangle |^2 e^{-\Gamma_2 t}$$

$$+ 2Re \left( a b \langle 3| D_{em}|2 \rangle \langle 3| D_{em}|1 \rangle^* \times e^{-i(E_{23} - E_{13}) t / \hbar} - i \delta e^{-\gamma_1 t} e^{-\gamma_2 t} / 2 \right)$$

(1.18)

By expressing the matrix elements, which are generally complex, in exponential form:

$$\langle 3| D_{em}|1 \rangle = | \langle 3| D_{em}|1 \rangle | e^{-i \Theta_{31}}$$

$$\langle 3| D_{em}|2 \rangle = | \langle 3| D_{em}|2 \rangle | e^{-i \Theta_{32}}$$

equation (1.18) can be rewritten as:
\[
I(t) \approx a^2 |\langle \mathbf{D}_{em}|1\rangle|^2 e^{-\Gamma_1 t} + b^2 |\langle \mathbf{D}_{em}|2\rangle|^2 e^{-\Gamma_2 t} \\
+ 2 \left( a b |\langle \mathbf{D}_{em}|1\rangle| |\langle \mathbf{D}_{em}|2\rangle| \right) \\
\times e^{-(\Gamma_1 + \Gamma_2) t/2} \cos (\omega_{21} t + \delta + \theta_{32} - \theta_{31})
\]

where \( \omega_{21} = E_{21}/\hbar = (E_{23} - E_{21})/\hbar \).

A final collection and redefinition of the terms in equation (1.19) yields:

\[
I(t) \approx A_1 e^{-\Gamma_1 t} + A_2 e^{-\Gamma_2 t} + A_3 e^{-\Gamma_3 t} \cos (\omega_b t + \phi_b)
\]

Consequently, as illustrated in figure 1-3, the observed time domain signal is a summation of three separate factors. The first two components are exponentially decaying functions which describe the spontaneous emission resulting from the independent (i.e. incoherent) excitation of levels \( |1\rangle \) and \( |2\rangle \) respectively. These terms are identical to those encountered in time-resolved fluorescence experiments devoid of any quantum interference effects.

The final term in equations (1.19) and (1.20), a cross product between the spontaneous emission probability amplitudes corresponding to the eigenstates \( |1\rangle \) and \( |2\rangle \), is the origin of the quantum beat phenomenon. A careful examination of this time dependent fluorescence signal reveals several important details regarding the creation, detection, and interpretation of such quantum interference effects:

1. The radial oscillation frequency of the quantum beat, \( \omega_b \), is given by:

\[
\omega_b = \omega_{21} = 2\pi \nu_{21}
\]
Consequently, the modulations occur at a frequency which \textit{exactly} corresponds to the energy level splitting in the excited electronic state.

2. The modulation amplitude for the quantum beat, $A_b$, can be expressed as follows:

\begin{equation}
A_b = 2ab \left| \langle 3 | \mathbf{D}_{em} | 1 \rangle \right| \left| \langle 3 | \mathbf{D}_{em} | 2 \rangle \right| \tag{1.22}
\end{equation}

This amplitude depends upon the details of both the preparation step \textit{(viz. through a and b)} and the detection process \textit{(viz. through the matrix elements for $\mathbf{D}_{em}$)}. In particular, the coherent superposition in the excited state \textbf{must} be created by optical pumping from a \textit{single initial level} and observed in emission to a \textit{common final level}.

By utilizing equation (1.22) in conjunction with the spontaneous emission amplitudes expected in the absence of any quantum interference effects, the relative modulation depth of the quantum beat, $A_m$, is found to be:

\begin{equation}
A_m = \frac{A_b}{A_1 + A_2} = \frac{2ab \left| \langle 3 | \mathbf{D}_{em} | 1 \rangle \right| \left| \langle 3 | \mathbf{D}_{em} | 2 \rangle \right|}{a^2 \left| \langle 3 | \mathbf{D}_{em} | 1 \rangle \right|^2 + b^2 \left| \langle 3 | \mathbf{D}_{em} | 2 \rangle \right|^2} \tag{1.23}
\end{equation}

3. The collision-free decay rate for the quantum beat, $\Gamma_b = 1/\tau_b$, is given by:

\begin{equation}
\Gamma_b = \frac{1}{2} (\Gamma_1 + \Gamma_2)
\end{equation}

This is obviously the average depopulation rate for the eigenstates \textit{(i.e. $|1\rangle$ and $|2\rangle$)} which give rise to the quantum beat. In the presence of collisions, an additional term, $\Gamma_\phi$, must be incorporated to account for processes \textit{(viz. pure dephasing collisions [62])} which destroy molecular coherence without affecting the population of energy levels:
\[ \Gamma_b = \frac{1}{2} (\Gamma_1 + \Gamma_2) + \Gamma_\phi \]

or

\[ \Gamma_b \geq \frac{1}{2} (\Gamma_1 + \Gamma_2) \] (1.24)

4. The phase of the quantum beat signal, \( \Phi_b \), can be expressed by:

\[ \Phi_b = \delta + \Theta_{32} - \Theta_{31} \] (1.25)

Therefore, the phase of the quantum beat modulations also depends upon the details of both the excitation step (viz. through \( \delta \)) and the observation process (viz. through \( \Theta_{32} \) and \( \Theta_{31} \)).

A physical interpretation for quantum beats can be obtained from an analogy with Young's double slit experiment in optics [63]. Here the coherently excited states \(|1\rangle \) and \(|2\rangle \) constitute the slits through which photons will be scattered by means of spontaneous emission. In a similar manner, the temporal modulation of the detected fluorescence light assumes the role of the spatial intensity pattern normally associated with optical interference effects.

Provided that the total fluorescence signal is monitored, there is no way to distinguish between the channels \(|1\rangle \to |3\rangle \) and \(|2\rangle \to |3\rangle \) when the coherently excited molecule spontaneously emits a photon. In complete agreement with the double slit experiment, any attempt to resolve these emission pathways, whether by spectral dispersion, polarized detection, or other means, will necessarily result in the destruction of any interference effect. The postulates of quantum mechanics stipulate that the total probability amplitude for two indistinguishable processes must be calculated by summation of the corresponding individual amplitudes. As a
result, the time-resolved fluorescence signal, defined in equation (1.17) by the square of the total probability amplitude, will contain the cross terms which are responsible for the manifestation of quantum beats.

As demonstrated in the four-level model presented above, the temporally modulated spontaneous emission, which characterizes the phenomenon of quantum beats, can provide a means of performing spectroscopic measurements in excited electronic states. The inherent simplicity of these time-resolved experiments is underscored by the fact that they are relatively immune to artifacts, such as those induced by saturation effects [64, 65], which tend to plague similar optical pumping techniques. In short, the versatility and elegance of these methods can best be illustrated by comparing a molecule involved in a quantum beat measurement with a brass bell. From this viewpoint, the pulsed excitation source represents the clapper which induces the bell (i.e. the molecule) to resound with its characteristic resonance frequencies. All that the high-resolution laser spectroscopist need do is to record and analyze the ensuing molecular reverberation.

1.3.3 The Resolution of Quantum Beat Spectroscopy

Aside from their conceptual and experimental simplicity, the utility of quantum beat techniques derives from the fact that they permit unparalleled resolution and precision in spectroscopic measurements. This is of special importance for cases in which excitation sources having a relatively low degree of monochromaticity (i.e. pulsed lasers) are used to probe inhomogeneously broadened molecular systems (e.g. Doppler broadened, gas phase molecules). Here quantum beat methods can improve resolution many orders of magnitude beyond that obtainable by more conventional means.

For typical gas phase optical experiments, spectroscopic transitions are
inhomogenously broadened well beyond their natural linewidths \( i.e. \Delta \nu^{(L)} = 1/\pi \tau \) where \( \tau \) is the radiative lifetime of the excited state) due to the statistical thermal motion of molecules. Consequently, the so-called Doppler width of a molecular transition, \( \Delta \nu^{(D)} \), at an absolute temperature \( T \), is given by:

\[
\Delta \nu^{(D)} = \frac{2\nu_0}{c} \left( \frac{2kT}{m} \ln 2 \right)^{1/2} = 2\sqrt{\ln 2} \frac{\nu_{mp}}{c} \quad (1.26)
\]

where

- \( \nu_0 \) is the center frequency of the transition,
- \( \nu_{mp} \) is the most probable molecular velocity,
- \( m \) is the molecular mass,
- \( k \) is the Boltzmann constant.

In the case of the formaldehyde-\( \text{H}_2 \cdot 4^1 \) vibronic band, which has its origin at \( \nu_0 = 8.49 \times 10^{14} \text{Hz} \), equation (1.26) implies that, at 298 °K, \( \Delta \nu^{(D)} = 1.92 \times 10^9 \text{Hz} \) (i.e. \( 6.39 \times 10^{-2} \text{cm}^{-1} \)) and \( \Delta \nu^{(D)}/\nu_0 \approx 2 \times 10^{-6} \). This is to be contrasted with the natural linewidth of \( \Delta \nu^{(L)} \approx 6.4 \times 10^4 \text{Hz} \) derived from the reported radiative lifetime of \( \sim 5 \mu s \) [66, 67, 68]. Consequently, small splittings in the excited state, such as those induced by the Stark effect, would be, at best, very difficult to measure in Doppler-limited experiments.

Now consider the situation which arises in a quantum beat experiment where, as indicated in figure 1-3, a direct measurement is performed of the difference frequency, \( \nu_{21} = \nu_{23} - \nu_{13} \), between two coherently excited transitions in the same molecule. If this molecule is moving with a velocity \( v \), each transition has its own Doppler shift as given by equation (1.26):
\[ \Delta \nu_{13} = 2 \sqrt{\ln 2} \ \nu_{13} \frac{v}{c} \]

\[ \Delta \nu_{23} = 2 \sqrt{\ln 2} \ \nu_{23} \frac{v}{c} \]

Consequently, the Doppler broadening associated with the measured quantum beat frequency, \( \Delta \nu_{21} \), is:

\[ \Delta \nu_{21} = \Delta (\nu_{23} - \nu_{13}) = \Delta \nu_{23} - \Delta \nu_{13} \]

\[ = 2 \sqrt{\ln 2} (\nu_{23} - \nu_{13}) \frac{v}{c} \]

\[ = 2 \sqrt{\ln 2} \ \nu_{21} \frac{v}{c} \]

(1.27)

By assuming typical values for the formaldehyde-\( \text{H}_2 \) 41\( _0 \) band, viz. \( v \approx v_{mp} \) and \( \nu_{21} \approx 100 \text{MHz} \), the inhomogeneous Doppler broadening is found to be only \( \Delta \nu_{21}^{(D)} \approx 190 \text{Hz} \).

Equation (1.27) demonstrates that the Doppler shifts associated with the two interfering transitions in a single, coherently excited molecule effectively cancel one another. Consequently, each molecule, regardless of its velocity vector, will contribute with nearly the same oscillation frequency, \( \nu_{21} \), to the resulting modulated fluorescence emission. Quantum beat techniques thus provide an expeditious means for increasing spectroscopic resolution to the point where inhomogeneous Doppler broadening is negligible compared to other linewidth limiting factors such as the natural lifetime of the excited molecular state (i.e. lifetime broadening). For the 41\( _0 \) formaldehyde-\( \text{H}_2 \) example discussed above, this implies that quantum beat spectroscopy can achieve a limiting resolution of \( \Delta \nu / \nu \approx \Delta \nu^{(L)} / \nu_0 \approx 7 \times 10^{-11} \).
1.3.4 Stark Induced Quantum Beat Spectroscopy in Formaldehyde

The energy level scheme in figure 1-4 summarizes the spectroscopic details for a typical quantum beat measurement performed in conjunction with our dipole moment studies. This diagram depicts an experiment designed to examine Stark effects within the $2_{1,1}$, $v_4 = 1$ rotation-vibration level of $\tilde{A}^1A_2$ formaldehyde. A specific rotational transition ($\text{viz. } 2_{1,1} \leftarrow 2_{0,2}$) within the $4_0^1$ vibronic band is illustrated.

As previously mentioned, the application of an external electric field lifts spatial degeneracy and separates each formaldehyde rovibronic level of total angular momentum $J$ into $J+1$ sublevels designated by the absolute value of the magnetic quantum number $M$. Therefore, the $J = 2$ states illustrated in figure 1-4 each split into three components labeled by $M = 0$, $|M| = 1$, and $|M| = 2$. The tuning of the magnetic sublevels in an electric field is related in a precise manner (i.e. through the Stark Hamiltonian) to the magnitude of the electric dipole moment associated with the rovibronic eigenstate.

By choosing the polarization of the optical excitation source to be perpendicular to the applied electric field, the selection rule $\Delta M = \pm 1$ is obtained. Therefore, the $M = 0$ and $|M| = 2$ sublevels of the lower state can each be excited only into the $|M| = 1$ sublevel of the upper state. On the other hand, figure 1-4 illustrates that the $|M| = 1$ component of the ground state can be used to prepare simultaneously the $M = 0$ and $|M| = 2$ sublevels of the excited state.

Consequently, if the coherent bandwidth of the pulsed excitation source exceeds the magnitude of the Stark splitting, the $M = 0$ and $|M| = 2$ sublevels of the excited state can be prepared concurrently with an exact phase relationship between them. Interference terms in the fluorescence amplitude radiated from this coherent superposition state produce a time-resolved emission intensity having the
Figure 1-4: Energy Level Scheme for Stark Induced Quantum Beats.
STARK INDUCED QUANTUM BEATS
IN
H$_2$CO

$\tilde{A}^1A_2$ 2$_{1,1}$

$\tilde{X}^1A_1$ 2$_{0,2}$

ELECTRIC FIELD
form of a modulated exponential decay. These oscillations, the result of a quantum mechanical interference phenomenon analogous to that discussed previously, are here referred to as Stark quantum beats.

Since the oscillation frequency derived from the modulated fluorescence decay profile is *exactly* equal to the energy separation of the coherently prepared sublevels, quantum beat spectroscopy provides a direct means of measuring Stark splittings with sub-Doppler resolution (*i.e.* with respect to the optical transition). Subsequent modelling of the observed frequencies as a function of the applied electric field can be used to extract the dipole moment for a specific rotation-vibration target level in the excited electronic state.

In a less obvious fashion, figure 1-4 also illustrates several important points regarding the use of quantum beat techniques to measure Stark effects in a molecule such as formaldehyde:

1. The use of $J = 2$ rotation-vibration eigenstates as target levels in the excited electronic state represents the most straightforward method of creating a *single frequency* $\Delta M = 2$ coherence (*viz.* between $M = 0$ and $|M| = 2$).

   In contrast, the larger number of Stark components present in states of higher angular momentum would lead to more complicated, multiple frequency quantum beat patterns. On the other hand, eigenstates of lower $J$ are not capable of supporting even a single, usable $\Delta M = 2$ coherence.

2. A simple transition moment calculation indicates that Q branch transitions provide the most efficient means of preparing molecules in the $M = 0$ and $|M| = 2$ sublevels of the target rovibronic eigenstate (the levels responsible for the quantum beat signal) with minimal excitation of the $|M| = 1$ component (*the* level producing an unmodulated fluorescence background).

The results of this calculation also reveal that R branch rovibronic transitions should be least effective in producing such $\Delta M = 2$ coherences with P branch transitions falling somewhere between the Q
and R limits.

3. In a similar manner, it can be shown that a maximum quantum beat amplitude is obtained when the detected fluorescence emission proceeds via a Q branch transition.

The most intense vibronic bands in the formaldehyde $\tilde{A} \leftrightarrow \tilde{X}$ system have been shown to involve a transition moment directed along the molecular $b$-axis [69, 70]. The selection rules for $b$-type rovibronic transitions [56] indicate that $2_{1,1}$ rotational levels are the only $J = 2$ states which will support two Q branches (viz. $2_{1,1} \rightarrow 2_{0,2}$ and $2_{1,1} \rightarrow 2_{2,0}$). Therefore, the undispersed fluorescence accompanying coherent excitation of $2_{1,1}$ rotation-vibration eigenstates in $\tilde{A}^1A_2$ formaldehyde should exhibit quantum beat modulations with larger amplitudes than those encountered for other $J = 2$ levels.

In light of the arguments presented above, all of the quantum beat measurements performed in conjunction with the formaldehyde dipole moment studies were designed to examine $J = 2$ target levels within the excited electronic state. Whenever possible, Q branch transitions were employed in the preparation step with particular attention directed towards excitation of the $2_{1,1}$ eigenstate.

In order to ascertain the polarization properties of the Stark quantum beats observed during the formaldehyde studies, it is essential to remember that two intimately related steps are involved in such time-resolved experiments:

- **Rapid preparation** of a coherent superposition of eigenstates in the excited state from a single, common initial level.

- **Time-resolved detection** of the fluorescence emitted by the constituents of the superposition state as they undergo spontaneous emission to a single, common final level.

By analogy between the preparation and detection steps, the $\Delta M = 2$ coherences created in $J = 2$ rovibronic levels of $\tilde{A}^1A_2$ formaldehyde will produce modulations in the time-resolved fluorescence signal only when spontaneous emission
proceeds via $\Delta M = \pm 1$ processes ($|M| = 2 \rightarrow |M| = 1$ and $M = 0 \rightarrow |M| = 1$). For this reason, only the radiation emitted with a polarization perpendicular to the direction of the applied electric field will exhibit quantum beats.

1.4 Experimental

The experimental apparatus utilized in the quantum beat measurements is shown schematically in figure 1-5. The second harmonic of a pulsed Nd:YAG laser (Quanta Ray DCR-1A; $\sim 150$mJ/pulse, $\sim 7$ns FWHM pulse duration, 10Hz repetition rate) was used to pump a single dye laser (Quanta Ray PDL-1) configured in the Hansch-Klauminzer design (viz. oscillator with intracavity prism beam expander in conjunction with travelling-wave preamplifier and amplifier stages). This commercially available dye laser was modified by incorporating an optical delay of $\sim 3$ns for the YAG pump beam between the oscillator and preamplifier/amplifier in order to suppress amplified spontaneous emission. Various laser dyes, dissolved in spectroscopic grade methanol, were employed depending upon which formaldehyde vibronic transition was to be investigated: LDS 751 for the $4^1_0$ band, LDS 750 for the $4^1_1$ band, and LDS 698 for the $4^3_0$ band (all dyes from Exciton Chemical Company). The dye laser, operated with a custom designed air-spaced intracavity etalon (Tech Optics; 0.75 cm$^{-1}$ FSR, $\sim 30$ reflectivity finesse @700nm, $\lambda/150$ plate flatness, $\lambda/50$ plate parallelism), possessed a measured linewidth of $\sim 0.03$cm$^{-1}$ FWHM and a pulse duration of $\sim 6$ns FWHM. Frequency tuning of the laser output was accomplished by pressure scanning with prepurified nitrogen. This permitted $\sim 3.5$cm$^{-1}$ of tuning (i.e. $\sim 7$cm$^{-1}$ at frequency doubled wavelengths) for the 0 to 800 torr pressure change utilized in these experiments.

The dye laser output at $\sim 700$nm was frequency doubled to $\sim 350$nm by means of an extracavity angle-tuned KD$^*$P crystal (Quanta Ray, 76° cut) with an
Figure 1-5: Experimental Apparatus for Quantum Beat Measurements
overall conversion efficiency of 20-25%. Separation of the copropagating fundamental and doubled light was accomplished by a set of S1-UV 60° prisms (Esco) each adjusted so that the incoming laser beam was at the minimum deviation angle. This use of prisms permitted efficient isolation of the collinear UV and visible beams with negligible loss of UV power (i.e. the doubled light, polarized perpendicular to the initial vertical output of the dye laser, was incident on the prisms at near Brewster's angle). The resulting UV beam had a spectral width of \( \sim 0.06 \text{cm}^{-1} \) FWHM, a pulse duration of \( \sim 5\text{ns} \) FWHM, and an energy of \( \sim 5\text{mJ/pulse} \). A portion of the fundamental dye laser output, viz. the light reflected from the first 60° prism, was directed into a monitor etalon (Molectron; \( \sim 0.56 \text{cm}^{-1} \) FSR) which provided a visual assessment for the single mode performance of the dye laser. Some of this reflected light was also sent to a heated iodine absorption cell (\( \sim 250^\circ\text{C} \)) which provided a convenient absolute frequency calibration when used in conjunction with the Fourier Transform atlas of Gerstenkorn and Lec [71].

The UV output was subsequently sent through a Keplerian telescope where it was spatially filtered by means of a sapphire pinhole (Richard H. Bird & Company; \( \sim 200\mu\text{m} \)) in order to improve beam quality and reduce the effects of spatial laser fluctuations. The resulting beam, now nearly collimated with a diameter of \( \sim 4\text{mm} \), was directed though a 352.5nm halfwave retardation plate (Virgo Optics) and a Glan-Laser calcite prism (Karl Lambrecht MGLA-DW-8) before entering the Stark region of the fluorescence cell. The orientation of the calcite prism was selected such that the emerging light would be polarized perpendicular to the Stark electric field. The halfwave retarder was adjusted, by means of both rotation and tilting, to achieve maximum throughput in the Glan-Laser prism.

The fluorescence cell utilized in these quantum beat measurements was
originally designed for Stark-SEP experiments [11] on formaldehyde. The cell was constructed of glass with metal baffles designed to reduce scattered light from the UV laser beam. It had an ultimate vacuum pressure of $\sim 5 \times 10^{-6}$ Torr with a leak rate of $\leq 10^{-4}$ Torr/hour. Sample pressures in the fluorescence cell were monitored by means of a 0 to 1 Torr capacitance manometer (*MKS Baratron* model 220B).

The Stark electrode assembly consisted of two circular stainless steel plates (10 cm diameter, 0.5 cm thickness), precision ground and polished to a flatness better than $\pm 1 \mu$m, separated by four quartz spacers. These were cut from a single optical flat (*Spectra Physics*) with surfaces parallel to less than 1 s of arc and possessed a mean thickness of $0.25702 \pm 0.00015$ inches as measured by a mechanical micrometer (*L. S. Starrett Co.* No 231-F). The beam path for the pulsed UV laser was carefully designed to be more than two plate separations away from any of these spacers since they might induce local perturbations in the electric field homogeneity. Lastly, the resulting Stark electrode assembly was rigidly held together by a set of *Kel-F* (*Dupont*) clamps in order to maintain the integrity of the plate spacing over the time period (*viz.* $\sim 5$ weeks) required for completion of these quantum beat experiments.

The apparatus used to create and monitor the electric field in the fluorescence cell is schematically illustrated in figure 1-6. The voltage for the Stark electrodes was provided by one of two D.C. power supplies:

1. A *Fluke* 335A voltage standard (0 to 1100 volts) [72].
   - Ripple and Noise: $< 40 \mu$V rms.
   - Stability: $\pm (0.001\% + 20 \mu$V) per month.
   - Accuracy of Output: $\leq \pm 0.005\%$.

2. A *Fluke* 410B DC power supply (0 to 10,000 volts) [73].
   - Ripple and Noise: $< 1 \mu$V rms.
   - Stability: $\pm 0.005\%$ per hour.
   - Accuracy of Output: N/A
Figure 1-6: Apparatus used to create and monitor Stark Field.
In practice, the less accurate Fluke 410B power supply was employed only when required voltages exceeded the maximum output of the Fluke 335A voltage standard (1100 volts).

The applied voltage was monitored by means of a stabilized voltage divider, consisting of two high voltage resistors (Caddock Electronics MG780 Series) immersed in a temperature controlled oil bath (Gulf transformer oil Transcrest HI) maintained at 37.5°C and a precision digital voltmeter (Systron Donner model 7115). The Fluke 335A voltage standard served as a primary voltage reference and was checked daily against a set of twelve standard cells enclosed in a temperature stabilized housing (Guildline Instruments Ltd. Standard Cell Enclosure Type 9152T/12). In this manner, fluctuations of less than 20ppm were observed in the Fluke 335A over the period of time required for completion of the quantum beat measurements. The voltage divider assembly, which was essential for the accurate measurement of voltages produced by the intrinsically less stable Fluke 410B power supply (i.e. voltages greater than 1100V), was calibrated each day by applying known voltages from the Fluke 335A standard. As a result, recorded voltages are believed to be accurate to roughly one part in 10^5.

The undispersed molecular fluorescence produced by interaction of the UV laser pulse with a formaldehyde sample in the Stark cell was detected, at 90° to the incoming beam, by means of a two inch diameter end-on photomultiplier tube (RC'A 4501/V4, ~5ns rise time) coupled directly to a high speed preamplifier (LeCroy VV100B, DC to 250MHz Bandwidth, x10 gain). To ensure that the detected signal originated from regions free of electric field edge effects (viz. from the Stark plates), an f/1 UV imaging system (Unique Optical; 2.5X magnification) was employed, in conjunction with a slit in front of the PMT. This restricted the collected fluorescence to the central 0.8 centimeter region of the Stark electrodes. Two low fluorescence
380nm cutoff filters (Oriel Corporation 5125) were used in front of the PMT slit to eliminate residual scattered laser light. Polarized detection was accomplished by utilizing a UV polarizing filter (Polaroid Corporation HNP'-B) oriented with its polarization vector perpendicular to the electric field applied in the Stark cell.

The preamplified output from the photomultiplier was sent directly to a high speed, programmable transient digitizer (Tektronix 7912AD, 7B92A time base, 7A29 amplifier, DC to 500MHz Bandwidth) to permit signal averaging and then to a microcomputer (DEC LSI-11/03) for further processing and analysis. For the quantum beat experiments, the transient digitizer was instructed to average over 1024 laser pulses, thereby yielding time-resolved fluorescence profiles possessing signal to noise ratios typically exceeding 1000:1. In order to eliminate temporal jitter, the digitizer was triggered by means of a high speed photodiode (EG&G FND-100; 90V reverse bias) which monitored a back reflection from the pulsed dye laser beam. All signal-carrying connections between instruments were accomplished with double-shielded coax cable (RG223), with careful attention being paid to preservation of 50Ω transmission line characteristics.

Since the quantum beat measurements necessitated a high degree of accuracy and linearity in the time-resolved fluorescence profiles that were acquired, the horizontal and vertical scales of the transient digitizer were calibrated at the completion of each day of data collection. Calibration of the horizontal or time scale was accomplished through digitization of sine waves generated by a frequency synthesizer (Hewlett Packard 3320A with high stability option 02). The high accuracy to which the period of these sinusoids were known (i.e. better than 1 part in 10⁶) permitted their use as a time standard for the horizontal scale. In a similar manner, calibration of the vertical or amplitude scale was achieved through measurement of accurately known voltages produced by the previously mentioned
*Fluke* 335A voltage standard. By digitizing several traces obtained with various applied voltages, a linearization of the vertical scale could be easily performed.

The formaldehyde utilized in these experiments was prepared by the pyrolysis of either paraformaldehyde-\(h_2\) (*Aldrich*) or paraformaldehyde-\(d_2\) (*MSD Isotopes*; 98% atom percent) followed by two fractional distillations. Typical fluorescence cell pressures were \(\leq 1\text{mTorr}\) except in the case of the \(4^0_1\) hot bands where, due to lower signal levels, pressures of \(\sim 10\text{mTorr}\) and \(\sim 3\text{mTorr}\) were required for \(\text{H}_2\text{CO}\) and \(\text{D}_2\text{CO}\) respectively. Such low pressures were necessary both to prevent electrical breakdown between the Stark electrodes and to minimize the effects of dephasing collisions on the quantum beat signals.

The initial step in an actual quantum beat experiment entailed the acquisition of a fluorescence excitation spectrum so as to locate spectroscopic transitions terminating on the target rovibronic level in the excited electronic state. This was accomplished by connecting the preamplified output of the fluorescence cell photomultiplier to a gated integrator/boxcar averager (*SRI* SR250). At the same time, the output of a photodiode (*EG&G* UV-215BQ), monitoring the UV laser power, was directed to an identical boxcar module. Division of these two averaged data channels (*SRI* SR235 Analog Processing Module) resulted in a power normalized excitation spectrum which was recorded, as a function of dye laser frequency, on a strip chart recorder (*Linear Instruments* model 595) along with the fringes of a monitor etalon (\(\sim 0.56\text{cm}^{-1}\) FSR) for relative frequency calibration and the spectral lines from an iodine absorption cell for absolute frequency calibration. In order to minimize the effects of formaldehyde lifetime fluctuations (*i.e.* fluctuations in the fluorescence quantum yield) on the excitation spectrum, a narrow time gate, typically 3ns or less, was used on the gated integrator of the boxcar. Consequently, the resulting spectra closely mimic those that would be obtained in a
conventional absorption experiment.

A typical excitation spectrum from the $4^1_0$ band of formaldehyde–$h_2$ is illustrated in part (a) of figure 1-7. For the cold bands (viz. $4^1_0$ and $4^3_0$), assignment of the excitation spectra was greatly facilitated by the use of the extended ASYROT program of Birss and Ramsay [74] which permitted the calculation of line lists and spectral simulations from spectroscopic constants. Part (b) of figure 1-7 shows the results of such a computer simulation and table 1-I presents a list of expected spectroscopic transitions in this region. The definitive nature of the spectral assignments is clearly demonstrated by comparison of the two diagrams in figure 1-7. In the case of the $4^0_1$ rovibronic transitions of both $H_2CO$ and $D_2CO$, however, simulations from spectroscopic constants were complicated due to Coriolis perturbations in the $v_4=1$ levels of the ground electronic states [75, 76, 10, 77]. Consequently, these hot bands necessitated the use of published lists of absolute frequencies and their assignments [78, 79]. Table 1-II presents a compilation of all transitions utilized in the quantum beat experiments.

By means of excitation spectra assigned in the manner discussed above, the dye laser frequency could readily be tuned into resonance with molecular transitions terminating on target rotation-vibration levels in the $\tilde{A}$ state of formaldehyde. The photomultiplier output was subsequently reconnected to the transient digitizer in order to permit the acquisition of time-resolved fluorescence signals for various values of the applied Stark field.
The transition frequencies and intensities generated by the extended ASYROT program of Birss and Ramsay [74] were employed for calculation of the simulated spectrum. Rotational and centrifugal distortion constants were obtained from reference [50]. A gaussian lineshape profile, with a FWHM of 0.07\,cm$^{-1}$, was utilized in the simulation.
<table>
<thead>
<tr>
<th>Rotational Level</th>
<th>Rotational Level</th>
<th>Relative Transition Intensity</th>
<th>Calculated Transition Frequency</th>
</tr>
</thead>
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</table>

\(^a\) In cm\(^{-1}\).

**Table 1-I:** Portion of the Spectral Line List for \(^1\) formaldehyde-\(h_x\)
<table>
<thead>
<tr>
<th>$\tilde{A}$ Rotational Level</th>
<th>$\tilde{X}$ Rotational Level</th>
<th>Relative Transition Intensity</th>
<th>Calculated Transition Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>7,3,5</td>
<td>8,2,6</td>
<td>0.53</td>
<td>28320.856</td>
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<td>16,3,13</td>
<td>3.23</td>
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<td>13,0,13</td>
<td>3.38</td>
<td>28320.064</td>
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<td>1,1</td>
<td>1,0</td>
<td>1.48</td>
<td>28320.008</td>
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<td>13,3,10</td>
<td>13,2,11</td>
<td>1.89</td>
<td>28319.923</td>
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<td>2,0,2</td>
<td>2.39</td>
<td><strong>28319.537</strong></td>
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<td>28316.137</td>
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</table>

$^a$ In cm$^{-1}$.

Table 1-I, concluded.
### Transitions Utilized in Formaldehyde-\( \text{H}_2 \) Experiments.

<table>
<thead>
<tr>
<th>Vibronic Transition</th>
<th>( \tilde{A} , ^1A_2 ) Rotational Level</th>
<th>( \tilde{X} , ^1A_1 ) Rotational Level</th>
<th>Transition Frequency(^a)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4^1_1 )</td>
<td>2(_{1,1})</td>
<td>2(_{2,0})</td>
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<td>[78]</td>
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<td>[50]</td>
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</table>

\(^a\) In cm\(^{-1}\).

Table 1-II: Transitions Utilized in Quantum Beat Experiments on Formaldehyde
b. Transitions Utilized in Formaldehyde-$d_2$ Experiments.

<table>
<thead>
<tr>
<th>Vibronic Transition</th>
<th>$\tilde{A}  ^1A_2$ Rotational Level</th>
<th>$\tilde{X}  ^1A_1$ Rotational Level</th>
<th>Transition Frequency$^a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td>28376.10</td>
<td>[80]</td>
</tr>
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<td>[80]</td>
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<td>$2_{1,1}$</td>
<td>$2_{0,2}$</td>
<td>28972.49</td>
<td>[78]</td>
</tr>
</tbody>
</table>

$^a$ In cm$^{-1}$.

Table 1-II, concluded.
1.5 Data Analysis

The preceding sections have attempted to define and characterize the coherent interactions which form the cornerstone of the work presented in this Chapter. The physical manifestation of such quantum interference effects can best be illustrated by reference to figure 1-8. The two plots presented in this diagram contrast the time-resolved total fluorescence signals observed subsequent to the abrupt excitation of $\tilde{A}^1A_2$ formaldehyde-$h_2$ at zero field and at an electric field strength of $1531.79 \pm 0.89$ Volts/cm (one standard deviation uncertainty). These data correspond to the selective and coherent preparation of the $z_{1,1}$ rotational eigenstate within the $v_4 = 1$ out-of-plane bending mode of the excited electronic state. Each curve in this figure consists of 512 discrete points obtained concurrently by instructing a high-speed transient digitizer to signal average over 1024 laser pulses. The amplitude modulations, which constitute the phenomenon of quantum beats, are clearly visible on the non-zero field trace. As previously indicated, the frequency of these oscillations provides a direct measure of the Stark splitting induced by the applied electric field between the $M = 0$ and $|M| = 2$ subcomponents of the target rovibronic level. The sub-Doppler resolution afforded by the technique of quantum beat spectroscopy is demonstrated by the fact that an energy separation on the order of 12MHz can be precisely determined from analysis of figure 1-8 while the inhomogeneous (i.e. Doppler) broadening associated with the corresponding optical transition is in excess of 0.07cm$^{-1}$ (viz 2100MHz).

The relative modulation depth of the quantum beats in figure 1-8 is somewhat smaller than the value predicted by equation (1.20). This is most probably a consequence of the undispersed fluorescence method utilized in these experiments. The nonselective nature of this detection scheme implies that the recorded signals will be a superposition of spontaneous emission from both the coherently prepared
Figure 1-8: Quantum Beats in $2_{1,1} v_4=1$ level of $\tilde{A}^1A_2$ formaldehyde-$h_g$
target level (viz. modulated emission) and the manifold of adjacent rovibronic eigenstates which are incoherently populated through collisions (viz. unmodulated emission). This undesired background fluorescence translates into a reduction of the relative oscillation amplitude observed in the time-resolved decay profiles. The collisional transfer of coherence and other cascade quantum beat phenomena [81, 82] did not play any role in our measurements due to the rather special conditions that are required for the appearance of these relatively small effects.

The polarization properties of quantum beats are demonstrated in figure 1-9 for the $2_{1,1}$ $v_4=1$ rotation-vibration level of $\tilde{A}^1A_2$ formaldehyde-$h_2$. The three decay curves presented in this diagram contrast the time-resolved fluorescence signals obtained (a) without polarized detection, (b) with detection polarized perpendicular to the applied electric field, and (c) with detection polarized parallel to the applied electric field. In each case, the excitation pulse propagated parallel to the Stark plates and was polarized perpendicular to the applied electric field in order to produce the requisite $\Delta M = 2$ molecular coherence. Spontaneous emission was monitored at an angle of 90°, with respect to the incoming laser beam, in the plane defined by the flat surfaces of the Stark electrode assembly.

As previously mentioned, quantum beats should appear on the fluorescence decay profile of a coherently excited $J = 2$ rovibronic level only when the spontaneous emission proceeds via a $\Delta M = \pm 1$ pathway (viz. $|M| = 2 \rightarrow |M| = 1$ and $M = 0 \rightarrow |M| = 1$ transitions must occur simultaneously). Therefore, as demonstrated by parts (b) and (c) of figure 1-9, only the radiation emitted with a polarization perpendicular to the direction of the applied electric field (i.e. $\Delta M = \pm 1$ selection rule) exhibits the desired quantum interference phenomenon. From this point of view, the oscillations observed in the absence of polarization-selective filters can be rationalized in terms of a superposition between the modulated (i.e.
Figure 1-0: Polarization Properties of Quantum Beat Signals.

This figure illustrates the polarized nature of quantum beat phenomena through comparison of the time resolved fluorescence decay profiles obtained (a) without polarized detection, (b) with detection polarized perpendicular to the applied electric field, and (c) with detection polarized parallel to the applied electric field.
perpendicular polarization) and unmodulated (i.e. parallel polarization) fluorescence signals. All of our Stark measurements were performed with perpendicularly polarized detection in order to take advantage of the enhanced quantum beat amplitudes that could be attained in this manner.

Figure 1-10 illustrates the evolution of our quantum beat signals as a function of three related experimental parameters: the normalized spontaneous emission intensity, the fluorescence decay time, and the applied electric field strength. Each curve in this three-dimensional plot represents the results of a single time-resolved total fluorescence measurement performed, at a given value of the electric field, upon the $2_{1,1} v_4=1$ rotation-vibration level in $\tilde{A}^1A_2$ formaldehyde-$h_2$. The frequency of the amplitude modulations corresponds to the energy separation between the coherently prepared $M = 0$ and $|M| = 2$ components within the $2_{1,1}$ rovibronic eigenstate. This frequency is observed to increase with increasing electric field exactly as expected on the basis of the Stark tuning curves displayed in figure 1-2. Although it might appear that the phase of the oscillations is also being affected by variations in the magnitude of the applied electric field, this is nothing more than an illusion created by the associated frequency changes. A careful analysis of the quantum beat profiles has demonstrated that each data set has an initial phase approximately equal to $\pi$ (see equations (1.20) and (1.25)). This is consistent with the excitation and detection geometries employed in our experiments.

As indicated by equation (1.20), the oscillations in the time-resolved quantum beat signal can be effectively isolated from the unmodulated portion of the fluorescence through subtraction of the exponentially decaying background. The sinusoidal waveform obtained in this manner can subsequently be Fourier analyzed to determine rough estimates for the modulation frequencies and, therefore, for the energy separations between the coherently prepared levels in the excited electronic
Figure 1-10: Evolution of Quantum Beat Signals in $v_4=1$ formaldehyde-$h_2$

Quantum beats in the $2_{1,1}$, $v_4 = 1$ rovibronic level of $\tilde{A}^1\text{A}_2$ formaldehyde-$h_2$ are depicted as a function of three experimental parameters: the normalized spontaneous emission amplitude (arbitrary units), the fluorescence decay time (ranging from 0 to 2 µs), and the electric field strength (ranging from 0 to 3.1 KV/cm). Successive time-resolved decay profiles represent a 50V increase in the voltage applied to the Stark electrode assembly (Stark plate spacing: 0.65283(38)cm).
\[ \text{Intensity (arb)} \]
state. This procedure was applied to the data of figure 1-10 in order to produce the three-dimensional Fourier transform presented in figure 1-11.

In addition to its vivid illustration of the electric field dependence associated with the quantum beat frequency, figure 1-11 also demonstrates the evolution of modulation amplitudes observed for the $2_{1,1}$ rovibronic level. This provides an indication of constraints imposed upon the range of energy separations that can be measured through the techniques of quantum beat spectroscopy. The low frequency (or small separation) limit is defined by the molecular system in terms of the fluorescence lifetime for the excited electronic state. The high frequency (or large separation) limit, on the other hand, is determined by the experimental apparatus through the coherent (i.e. Fourier transform limited) bandwidth of the laser pulse utilized in the excitation process.

In order to precisely measure the Stark splittings produced within the excited electronic state of formaldehyde, each quantum beat decay profile (e.g. those shown in figure 1-8) was fit, by means of a nonlinear least squares regression procedure based upon the Marquardt algorithm [83], to the functional form suggested by equation (1.20). For the purposes of our data analysis, this expression was slightly reformulated in terms of a summation over $N_{exp}$ exponential terms (i.e. responsible for unmodulated exponentially decaying fluorescence background) and $N_{osc}$ oscillatory terms (i.e. responsible for quantum beat oscillations). The time-dependent fluorescence emission, $I(t)$, observed subsequent to the pulsed excitation of $\tilde{A}^1A_2$ formaldehyde was therefore parameterized as follows:
Figure 1-11: Fourier Transform of Beat Signals in $v_4 = 1$ formaldehyde-$h_\Sigma$

The Fourier transform of the coherent oscillations appearing on the time-resolved spontaneous emission from the $2_{1,1}^\Sigma$, $v_4 = 1$ rovibronic level in $\tilde{A}^1A_2$ formaldehyde-$h_\Sigma$ is illustrated as a function of three parameters: the normalized amplitude (arbitrary units), the quantum beat frequency (ranging from 0 to 75 MHz), and the electric field strength (ranging from 0 to 3.1 KV/cm). Successive Fourier transforms represent a 50V increase in the voltage applied to the Stark electrode assembly (Stark plate spacing: 0.65283(38)cm).
\[ I(t-t_0) = B + \sum_{k=1}^{N_{exp}} A_k e^{-\Gamma_k (t-t_0)} \]
\[ + \sum_{j=1}^{N_{osc}} A_{b,j} e^{-\Gamma_{b,j} (t-t_0)} \cos (\omega_{b,j} (t-t_0) + \Phi_{b,j}) \]  

(1.28)

where

- \( t_0 \) denotes the time origin utilized in the regression procedure.
- \( A_k \) represents the amplitude associated with the \( k^{th} \) exponential term.
- \( A_{b,j} \) represents the amplitude of the quantum beats associated with the \( j^{th} \) oscillatory term.
- \( B \) represents a constant background level,
- \( \Gamma_k = 1/\tau_k \) signifies the decay rate associated with the \( k^{th} \) exponential term.
- The corresponding fluorescence lifetime is given by \( \tau_k \).
- \( \Gamma_{b,j} = 1/\tau_{b,j} \) signifies the decay rate of the quantum beat amplitude associated with the \( j^{th} \) oscillatory term. The corresponding lifetime of the quantum beat is given by \( \tau_{b,j} \).
- \( \omega_{b,j} \) denotes the radial modulation frequency of the quantum beat associated with the \( j^{th} \) oscillatory term,
- \( \Phi_{b,j} \) denotes the initial phase of the quantum beat associated with the \( j^{th} \) oscillatory term.

The number of exponential terms, \( N_{exp} \), utilized in the fitting procedure was determined by analysis of the decay profiles obtained at zero applied electric field (where \( N_{osc} = 0 \)). Especially in the case of formaldehyde-\( h_2 \), the time resolved fluorescence signals observed under these conditions often consisted of a superposition of several exponentially decaying components, each possessing a radically different lifetime. This phenomenon, which is the subject of the work
presented in the following Chapter of this thesis, can be attributed to the randomly fluctuating collisionless decay rates (viz. resulting from nonadiabatic interactions with predissociated rotation-vibration levels of the $\tilde{X}^1A_1$ state) and large collision-induced energy transfer cross sections associated with individual rovibronic levels within the $\tilde{A}^1A_2$ state [19].

Since the coherently prepared levels within the $\tilde{A}^1A_2$ state are magnetic components of the same rovibronic eigenstate, they can normally be expected to have identical spontaneous emission lifetimes [84]. The first two terms of equation (1.20) would therefore coalesce into a single term with an increased amplitude and a common fluorescence decay rate. This situation is not always strictly correct, however, in view of the nonadiabatic couplings which exist between the electronic states of the formaldehyde system. In particular, the relative Stark tuning of the $\tilde{A}^1A_2$ and $\tilde{X}^1A_1$ rovibronic manifolds can dramatically alter the influence of $S_I \sim S_0$ interactions upon radiative and nonradiative molecular processes. Among other consequences; this can produce a substantial electric field dependence in the fluorescence lifetimes of individual M states associated with a single rovibronic level of $\tilde{A}^1A_2$ formaldehyde [24, 22, 23]. Therefore, at a given nonzero value of the applied electric field, the nondegenerate magnetic components may no longer have identical decay rates. The results of one such occurrence, which was observed in the $2_{0,2}$ rotational level of $4^1$ formaldehyde-h$_2$, will be discussed later in this Chapter.

In order to determine the number of oscillatory terms, $N_{osc}$, to be incorporated into the nonlinear fitting procedure, a Fourier analysis was performed on the amplitude modulations in each time-resolved fluorescence decay profile. The value of $N_{osc}$ could thus be easily determined by counting the number of distinct non-zero frequencies present in the resulting Fourier transform. This process also provided initial values of $\omega_{b,j}$, $\phi_{b,j}$, and $A_{b,j}$ for the subsequent least squares
regression.

For most of the data sets analyzed in the course of this investigation, a single oscillatory term (i.e. \( N_{osc} = 1 \)) was required. This situation, which is demonstrated by the collection of curves shown in figure 1-11, is exactly that expected on the basis of a lone \( \Delta M = 2 \) coherence being prepared in a \( J = 2 \) rotation-vibration eigenstate. In the case of the \( 2_{2,0} \) and \( 2_{2,1} \) rovibronic levels of \( 4^1 \) formaldehyde-\( d_2 \), however, overlapping spectroscopic transitions in the preparation step resulted in the creation of an additional coherent superposition within a high angular momentum state. Consequently, a second, independent amplitude modulation was observed in the time-resolved fluorescence signals. Since this additional quantum beat frequency could readily be distinguished from that associated with the target \( J = 2 \) level, its appearance had no effect whatsoever on the ultimate precision achieved in these measurements. A more significant manifestation of multiple quantum beat frequencies was encountered in the Stark measurements performed within the \( v_4 = 3 \) vibrational level of formaldehyde-\( d_2 \). As will be discussed at a later point in this Chapter, these oscillations can be attributed to nuclear hyperfine interactions in the \( \tilde{A}^{1}A_2 \) state.

Figure 1-12 illustrates typical time-resolved fluorescence decay profiles obtained for the \( 2_{1,1} v_4 = 1 \) rotation-vibration levels in the \( \tilde{A}^{1}A_2 \) electronic states of both formaldehyde-\( h_2 \) and formaldehyde-\( d_2 \). Also shown are the results of performing a least squares regression of these experimental data to the functional form provided by equation (1.28). In each case, the fitting procedure has incorporated a convolution with the temporal response function for our detection electronics. A comparison between the deuterated and nondeuterated data sets presented in this diagram demonstrates that a dramatic difference in fluorescence lifetime exists between the two molecular systems. This effect can be explained
Figure 1-12: Experimental and Calculated Quantum Beat Profiles.
$\text{H}_2\text{CO} \quad \tilde{A}^1\tilde{A}_2 \quad v_4=1 \quad 2_{1,1}$

**Experimental**
1455.20(85) Volts/cm

**Simulated**

Decay Time (ns)
through the isotopic dependence of the nonradiative relaxation pathways made available to $\tilde{A}^1A_2$ rovibronic levels by $S_I \sim S_0$ nonadiabatic interactions [85, 86, 22].

Table 1-III summarizes the results of the nonlinear least squares analyses depicted in figure 1-12. The quantum beat frequencies, which provide a direct measurement of Stark splittings within the excited electronic state, are determined with a precision significantly better than 1 part in $10^3$. This compilation of regression parameters also indicates that the decay rate of the amplitude modulations (i.e. $\Gamma_6$) is always faster than that predicted from the lifetimes of the eigenstates involved in the coherent superposition. As suggested by equation (1.24), this can be explained by the presence of pure dephasing processes which destroy the molecular coherence without disrupting the corresponding rovibronic level populations.

The even more rapid decay rate of the amplitude modulations observed for the case of formaldehyde-$d_g$ is most probably a consequence of the larger hyperfine interactions present in this isotopic species [46, 3]. Although the hyperfine structure is barely at the limits of our experimental resolution, its presence is revealed though an apparent increase in quantum beat dephasing processes. This is brought about by the superposition of several slightly different (incommensurate) modulation frequencies associated with the hyperfine subcomponents of the Stark split rovibronic levels.

Figure 1-13 presents the Stark tuning curves obtained for the $2_{1,1} \nu_4=1$ rotation-vibration levels in the $\tilde{A}^1A_2$ states of formaldehyde-$h_\gamma$ and formaldehyde-$d_g$. Each point on these plots of quantum beat frequency (or Stark splitting) versus applied electric field is the result of a least squares regression procedure identical to those summarized in table 1-III. The data clearly exhibit the
<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Parameter Units</th>
<th>Formaldehyde-$h_2$ Results</th>
<th>Formaldehyde-$d_2$ Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied Voltage</td>
<td>Volts</td>
<td>950.000(10)</td>
<td>700.000(10)</td>
</tr>
<tr>
<td>Electric Field</td>
<td>Volts/cm</td>
<td>1455.20(85)</td>
<td>1072.25(63)</td>
</tr>
<tr>
<td>B</td>
<td>Arb</td>
<td>13.74(21)</td>
<td>7.926(84)</td>
</tr>
<tr>
<td>$A_1$</td>
<td>Arb</td>
<td>219.61(23)</td>
<td>252.0(1.6)</td>
</tr>
<tr>
<td>$\Gamma_1$</td>
<td>$\mu$sec$^{-1}$</td>
<td>1.2806(45)</td>
<td>0.1793(13)</td>
</tr>
<tr>
<td>$A_2$</td>
<td>Arb</td>
<td>125.27(37)</td>
<td>43.8(1.5)</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>$\mu$sec$^{-1}$</td>
<td>11.38(63)</td>
<td>0.954(32)</td>
</tr>
<tr>
<td>$\Gamma_{b,1}$</td>
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<td>1.606(14)</td>
<td>0.3840(61)</td>
</tr>
<tr>
<td>$A_{b,1}$</td>
<td>Arb</td>
<td>20.66(13)</td>
<td>16.04(16)</td>
</tr>
<tr>
<td>$\omega_{b,1}$</td>
<td>MHz</td>
<td>11.416(12)</td>
<td>4.2904(81)</td>
</tr>
<tr>
<td>$\Phi_{b,1}$</td>
<td>Radians</td>
<td>2.913(19)</td>
<td>2.794(17)</td>
</tr>
</tbody>
</table>

$^a$ Arb refers to arbitrary units.

$^b$ One standard Deviation uncertainties for last two significant digits in parentheses.

**Table 1-III:** Regression Parameters for Quantum Beat Decay Profiles.
Figure 1-13: Experimental Stark Tuning Curves for $2_{1,1}$ $4^1$ Formaldehyde.

The Stark tuning curves obtained for the $2_{1,1}$, $v_4 = 1$ rovibronic levels in formaldehyde-$h_2$ and formaldehyde-$d_2$ are illustrated. The solid line represents the results of a nonlinear least squares analysis via an asymmetric rotor Stark Hamiltonian. The two sets of data presented for H$_2$CO (viz. triangles and circles) denote independent measurements which were performed at both the beginning and the end of our quantum beat studies.
$\tilde{\text{A}}^{1}A_{2} \text{ H}_{2}\text{CO}$

$v_4 = 1 \quad 2_{1,1}$

$\mu_a = 1.48785(35) \text{D}$

$\tilde{\text{A}}^{1}A_{2} \text{ D}_{2}\text{CO}$

$v_4 = 1 \quad 2_{1,1}$

$\mu_a = 1.46926(33) \text{D}$
expected field dependence (*cf.* figure 1-2) for the Stark splitting induced between the $M = 0$ and $|M| = 2$ magnetic components of the target rovibronic level.

The consistency and precision inherent in our determination of excited state Stark splittings is demonstrated by the duplicate points plotted in figure 1-13 for the case of formaldehyde-$h_\alpha$. These data sets were collected, under identical experimental conditions, at both the beginning and the end of our quantum beat studies (*viz.* a time period of $\sim 5$ weeks). The diagram indicates that the independent measurements are in excellent agreement. A close inspection of the actual quantum beat frequencies confirms that the two Stark experiments yield results which are identical to well within the statistical uncertainties imposed by the least squares regression procedure.

The solid line passing through the data points in figure 1-13 is the result of a nonlinear least squares fit to an asymmetric rotor Hamiltonian (*cf.* Appendix B) containing Stark matrix elements for a single component of the dipole moment along the molecular $a$-axis (*i.e.* $\sim \text{C}=\text{O}$ bond direction). The dipole moment components determined in this fashion are shown in the figure. A discussion of this fitting procedure and its implications will be the subject of the following section.

Appendix C presents a compilation of all quantum beat frequencies measured in the course of our dipole moment studies in electronically excited formaldehyde. The corresponding one standard deviation uncertainties are also tabulated.

### 1.6 Results and Discussion

Previous sections of this Chapter have concentrated upon the methodology of quantum beat spectroscopy and its application to the measurement of dipole moments in electronically excited formaldehyde. As indicated by equations (1.6),
(1.7), and (1.9), the spherical tensor formalism of Appendix A provides a computationally expedient means for analyzing the Stark data obtained from our experiments. In this way, the vibronic dipole moment components, \( \langle \gamma | T^1_q (\mu) | \gamma \rangle \), for the various \( \tilde{A}^1 \text{A}_2 \) rotation-vibration eigenstates can be readily determined. These are the molecular parameters which are of primary concern in the present study.

For the discussion and interpretation of molecular properties which will be provided in the present section, it will prove convenient to reformulate the Stark Hamiltonian of equation (1.6) in terms of the Cartesian components of the dipole moment, \( \{ \mu_g; g=x, y, z \} \), in the body-fixed system of coordinates (cf. Appendix A). From this viewpoint, the interaction between a molecular dipole moment and a static external electric field oriented along the space-fixed \( z \)-axis, \( \mathbf{E} = \mathcal{E} \hat{e}_z \), can be recast into the following form:

\[
H_{\text{Stark}} = -\mu_z \mathcal{E} = -\mathcal{E} \sum_g \Phi_{zg} \mu_g
\]

where \( \Phi_{zg} \) denotes the conventional direction cosine operators [56, 48] which provide the transformation between the space-fixed (i.e. \( \mu_z \)) and body-fixed (e.g. \( \mu_g \)) Cartesian components of the dipole moment. In the Cartesian formalism, the \( \Phi_{zg} \) operators serve the same purpose as the Wigner rotation operators (i.e. \( D^{(1)}_{pq}(\Omega) \)) employed in the spherical tensor approach developed in Appendix A. The two sets of transformations can be readily interconverted.

There are several ways in which the body-fixed \( x, y, \) and \( z \) axes of equation (1.29) can be correlated with the inertial axis system of the molecular framework. The ensuing discussion of formaldehyde will adopt the widely-accepted \( \text{I}^l \) convention [87, 88] in which \( x \equiv a, y \equiv b, \) and \( z \equiv a. \) For the case of a planar nuclear configuration, this indicates that the \( z \) axis is directed along the \( \text{C} - \text{O} \) bond.
while the $x$ axis is oriented perpendicular to the molecular plane. In the interest of notational convenience, the vibronic dipole moment in the Cartesian formalism, $\langle \gamma | \mu_y | \gamma \rangle$, will often be denoted simply by $\mu_y$. The vibronic averaging symbolized by $\langle \gamma | \cdots | \gamma \rangle$ is always implied.

The ensuing section will present the results of our Stark quantum beat experiments and attempt to rationalize them in terms of the objectives stated at the beginning of the Chapter. The measured $a$-axis components of the dipole moment in the first excited singlet manifold of formaldehyde will be tabulated and their dependence upon electronic, vibrational, and rotational degrees of freedom, as well as upon isotopic modification, will be examined. The nature of the out-of-plane dipole moment component associated with the inversion doubling of the $\tilde{A}^1A_2$ state will subsequently be discussed. This will naturally lead into an investigation of the origins for the nonplanar nuclear configuration encountered in electronically excited formaldehyde. Here the semiempirical molecular orbital rules of Walsh [17] will be contrasted with the recent vibronic coupling model proposed by Innes [18]. Finally, two of the unexpected effects observed in these studies, an $M$-specific $S_I \sim S_\theta$ anticrossing (i.e. in the $2_{0,2}$ level of $4^1$ H$_2$CO) and the appearance of large hyperfine structure (i.e. in the $2_{1,1}$ level of $4^3$ D$_2$CO), will be briefly considered.

1.6.1 The $a$-Axis Component of the Dipole Moment

In its ground electronic potential surface (viz. the $\tilde{X}^1A_1$ state), formaldehyde is known to possess an equilibrium nuclear configuration which is rigorously planar. In this case, the permanent dipole moment is constrained, by symmetry, to lie along the C–O bond (i.e. $\mu_a \neq 0$ but $\mu_b = \mu_c = 0$). High resolution electric beam resonance experiments [3] performed upon the vibrationless levels of $\tilde{X}^1A_1$ formaldehyde-$h_2$ and formaldehyde-$d_2$ have measured $\mu_a$ values of 2.33168(1)D and 2.347122(2)D
respectively with the dipole moment oriented such that the oxygen atom constitutes the more negative end of the molecule (i.e. \( ^+\text{C-O}^- \)).

Numerous spectroscopic studies \([14, 89, 80]\) have unequivocally established that the \( \tilde{A}^1\text{A}_2 \) state, which is the focus of our quantum beat investigations, supports a nonplanar equilibrium geometry characterized by a double minimum potential surface along the \( \nu_4 \) out-of-plane bending coordinate. The origin of this pyramidal nuclear distortion and its relationship to the electronic configuration of the excited state will be explored at a later point in this discussion. Figures 1-14 and 1-15 illustrate the effective inversion potentials for formaldehyde-\( h_2 \) and formaldehyde-\( d_2 \) as obtained by Jensen and Bunker \([90]\) in their recent semi-rigid inveror calculations. This approach combines a simultaneous treatment of rotational and inversonal degrees of freedom with an explicit variation of internal molecular parameters (i.e. bond lengths and angles) as a function of the out-of-plane angle, \( \rho \), in order to provide a viable model for the experimentally observed rovibronic structure within the \( \nu_4 \) manifold. Based upon their analysis, Jensen and Bunker concluded that the equilibrium out-of-plane distortion angles, \( \rho_e \), appropriate for \( \text{H}_2\text{CO} \) and \( \text{D}_2\text{CO} \) are 34.01° and 33.31° respectively.

In principle, the pyramidal distortion of electronically excited formaldehyde will have several repercussions with regards to our quantum beat studies. By utilizing the structural parameters derived from the Jensen and Bunker semi-rigid inveror model, the relationship between the inertial axes and the nuclear geometry of the \( \tilde{A} \) state can be readily ascertained. The results of such an analysis, performed at the equilibrium value for the out-of-plane bending coordinate, \( \rho_e \), are schematically illustrated in figure 1-16 for both formaldehyde-\( h_2 \) and formaldehyde-\( d_2 \). For a rigid nonplanar configuration, symmetry constraints would dictate that permanent dipole moment components can exist along both the \( a \) and \( c \)
Figure 1-14: Effective Potential Surface for H₂CO.
Figure 1-15: Effective Potential Surface for D₂CO.
**Figure 1-16:** Inertial Coordinate Systems in $\tilde{A}^1 A_2$ Formaldehyde.
$\tilde{A}^{1}A_{2}$ H$_2$CO

\[ \rho_0 = 34.01^\circ \]

$\rightarrow \leftarrow 0.1 \text{ Ångstrom}$

$\tilde{A}^{1}A_{2}$ D$_2$CO

\[ \rho_0 = 33.31^\circ \]
molecular axes (i.e. $\mu_a \neq 0$ and $\mu_c \neq 0$ but $\mu_b = 0$). Since the $a$ axis deviates only slightly from the C–O bond (deviation angle $\sim 3.55^\circ$ in $\text{H}_2\text{CO}$ and $\sim 5.54^\circ$ in $\text{D}_2\text{CO}$), the value of $\mu_a$ can be approximately correlated with the carbonyl bond moment. In contrast, $\mu_c$ is related to the pyramidal distortion of the molecular framework and can therefore be termed the out-of-plane component of the dipole moment.

The nonrigidity of formaldehyde in its $\tilde{A} \, ^1\text{A}_2$ state is characterized by a rapid inversion of the molecular framework between two oppositely oriented pyramidal configurations. The symmetric nature of this inversion process, which entails the momentary passage through a planar geometry, is evinced by the two structures illustrated for each isotope in figure 1-16. Consequently, to lowest order, the quantity determined in a Stark measurement will be the $a$-axis component of the dipole moment, $\mu_a$, averaged over the inversion degree of freedom. The out-of-plane contribution to the dipole moment, $\mu_c$, will be essentially averaged to zero by the molecular inversion: This situation will persist until the perturbation introduced by the external electric field becomes large enough to substantially mix the inversion levels associated with the double minimum potential surface. The higher order effects encountered under these conditions, which include the possible manifestation of $\mu_c$, will be discussed in some depth later in this section. For the present analysis, it will justifiably be assumed that a good representation for the total dipole moment can be obtained from the vibrationally averaged component along the molecular $a$-axis.

The quantum beat frequencies obtained from our formaldehyde studies provide a direct measure of the Stark splittings induced between the $M = 0$ and $|M| = 2$ magnetic components of specific rovibronic levels within the $\tilde{A} \, ^1\text{A}_2$ state. This situation is to be contrasted with that encountered in more prevalent
frequency-domain techniques which are based upon the spectral resolution of modifications produced in a spectroscopic transition by application of an external electric field. While such methods furnish a measurement of the difference in dipole moment between the upper and lower levels of the transition under consideration, the quantum beat scheme has the distinct advantage of only depending upon the individual dipole moment of the target level within the excited electronic state.

The reduction of data obtained from our quantum beat studies was based upon the numerical diagonalization of an asymmetric rotor Stark Hamiltonian expressed in terms of a \( \Pi' \) symmetric rotor basis set [56]. The general form for the matrix elements utilized in this procedure are contained in Appendix B. Incorporation of the Stark interaction terms (cf. equation (1.9)) associated with a single component of the dipole moment along the molecular \( a \)-axis introduces an explicit coupling between basis states differing in total angular momentum, \( J \), by \( \pm 1 \). The exact representation of the total molecular Hamiltonian would therefore require the use of an infinite basis set. For the present measurements, which were confined to \( J=2 \) eigenstates of \( \tilde{A} \,^1A_2 \) formaldehyde at field strengths of less than 10KV/cm, computer simulations have conclusively demonstrated that the Hamiltonian matrix can be conveniently truncated at \( J=4 \) with absolutely no effect (i.e. less than 1 part in \( 10^8 \)) upon the calculated eigenvalues of interest. Rotational and centrifugal distortion constants for individual vibronic manifolds in the \( \tilde{A} \) state were obtained from reference [50] and are compiled in table 1-IV.

The final determination of the \( a \)-axis dipole moments was accomplished through an iterative non-linear least squares procedure, based upon the Marquardt algorithm [83], in which the value of \( \mu_a \) was systematically varied in order to minimize the weighted sum of squares of the deviations between the experimentally observed and numerically calculated Stark splittings. If all data from a given isotope
### Table 1-IV: Rotational and Centrifugal Distortion Constants for $\tilde{A}$ State.

**a. Rotational Constants\(^a\) for $\tilde{A}^1A_2$ Formaldehyde-$h_\varepsilon$**

<table>
<thead>
<tr>
<th>Constant</th>
<th>$v_4=0$</th>
<th>$v_4=1$</th>
<th>$v_4=3$</th>
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<tbody>
<tr>
<td>$A$</td>
<td>8.9519</td>
<td>8.75194</td>
<td>8.5384</td>
</tr>
<tr>
<td>$B$</td>
<td>1.1239</td>
<td>1.12501</td>
<td>1.11774</td>
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<tr>
<td>$C$</td>
<td>1.0044</td>
<td>1.01142</td>
<td>1.01839</td>
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<tr>
<td>$10^4\Delta_K$</td>
<td>6.51</td>
<td>4.995</td>
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<td>6.77</td>
<td>6.58</td>
<td>11.97</td>
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<td>2.59</td>
<td>3.09</td>
</tr>
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<td>$10^5\delta_K$</td>
<td>...</td>
<td>2.07</td>
<td>1.97</td>
</tr>
<tr>
<td>$10^7\delta_J$</td>
<td>...</td>
<td>20.5</td>
<td>5.70</td>
</tr>
</tbody>
</table>

\(^a\) All values in cm\(^{-1}\).
b. Rotational Constants\(^a\) for \(\tilde{A}^1A_2\) Formaldehyde-\(d_2\)

<table>
<thead>
<tr>
<th>Constant</th>
<th>(v_4=0)</th>
<th>(v_4=1)</th>
<th>(v_4=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>4.5134</td>
<td>4.4690</td>
<td>4.2634</td>
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<tr>
<td>(B)</td>
<td>0.9558</td>
<td>0.9563</td>
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</tr>
<tr>
<td>(C)</td>
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<td>(10^5\delta_K)</td>
<td>\ldots \ldots</td>
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</tr>
<tr>
<td>(10^7\delta_J)</td>
<td>\ldots \ldots</td>
<td>\ldots \ldots</td>
<td>\ldots \ldots</td>
</tr>
</tbody>
</table>

\(^a\) All values in cm\(^{-1}\).

Table 1-IV, concluded.
were simultaneously fit assuming a single dipole moment for each vibrational state. Unacceptably large residuals were obtained. Consequently, an effective dipole moment was determined for each rotation-vibration level in the two isotopic modifications of formaldehyde examined in the present study.

The $a$-axis dipole moments determined from the $A^1A_2$ formaldehyde studies are presented in Table 1-V along with their corresponding one standard deviation uncertainties. Each tabulated value of $\mu_a$ is the result of a least-squares regression procedure performed simultaneously upon several data points (i.e. typically $> 25$) obtained at different electric field strengths. The quality of the fit between observed and calculated Stark splittings has been illustrated in Figure 1-13 for the $2_{1,1} v_4 = 1$ rotation-vibration levels of $H_2CO$ and $D_2CO$. Measurements repeated at both the beginning and the end of the quantum beat experiments confirm that the precision ascribed to the reported dipole moments is in the sub-milliDebye range (i.e. $\sim 5$ parts per $10^5$). Due to uncertainty in the absolute spacing of the Stark electrode assembly, the accuracy associated with the $\mu_a$ measurements is limited to approximately 5 parts per 1000.

Two qualifications to the above statements regarding the measurement precision attained in the present experiments merit further attention. For the $2_{1,1} v_4 = 3$ level of $A^1A_2$ formaldehyde-$d_2$, where unusually large hyperfine structure was detected, the reported $\mu_a$ value in Table 1-V is the result of an analysis performed upon the intensity weighted average of the observed quantum beat frequencies. In the case of the $2_{0,2} v_4 = 1$ level of $A^1A_2$ formaldehyde-$h_2$, the identification of a nonadiabatic interaction between the $S_1$ and $S_0$ potential surfaces necessitated that only data points far removed from the region of anticrossing be utilized in the final regression procedure. Both of these effects, which are discussed at greater length later in this Chapter, will produce an overall increase in the
<table>
<thead>
<tr>
<th>Vibrational Level</th>
<th>Rotational Level</th>
<th>( \text{H}_2\text{CO} ) Dipole Moment(^a)</th>
<th>( \text{D}_2\text{CO} ) Dipole Moment(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_4=0 )</td>
<td>( 2_{1,1} )</td>
<td>1.47845(66)D</td>
<td>1.46975(60)D</td>
</tr>
<tr>
<td>( v_4=1 )</td>
<td>( 2_{2,0} )</td>
<td>1.45256(40)D</td>
<td>1.46879(18)D</td>
</tr>
<tr>
<td>( v_4=1 )</td>
<td>( 2_{2,1} )</td>
<td>1.45384(40)D</td>
<td>1.46882(20)D</td>
</tr>
<tr>
<td>( v_4=1 )</td>
<td>( 2_{1,1} )</td>
<td>1.46785(35)D</td>
<td>1.46926(23)D</td>
</tr>
<tr>
<td>( v_4=1 )</td>
<td>( 2_{1,2} )</td>
<td>1.46316(24)D</td>
<td>1.46833(14)D</td>
</tr>
<tr>
<td>( v_4=1 )</td>
<td>( 2_{0,2} )</td>
<td>1.45550(58)D</td>
<td>1.46410(87)D</td>
</tr>
<tr>
<td>( v_4=3 )</td>
<td>( 2_{1,1} )</td>
<td>( \ldots )</td>
<td>1.47857(68)D</td>
</tr>
</tbody>
</table>

\(^a\) One standard deviation uncertainties in parentheses.

**Table 1-V:** \( a \)-axis Dipole Moments Measured in \( \tilde{A} \) \( ^1\text{A}_2 \) Formaldehyde.
-115-

experimental uncertainty ascribed to the corresponding $a$-axis dipole moment components.

Table 1-VI presents a compilation of previous theoretical and experimental attempts to ascertain the dipole moment of $\tilde{A}^1A_2$ formaldehyde-$h_\alpha$. As suggested by comparison with our quantum beat results (cf. table 1-V), the $ab\ initio$ work has been quite successful in determining the $a$-axis dipole moment component for the excited state. In contrast, the theoretical computations are found to be in rather poor agreement with the measured value of $\mu_a$ in the $\tilde{X}^1A_1$ ground potential surface (viz. $\mu_a \approx 2.33$D [3]). Since these calculations are usually much better at predicting relative changes in molecular properties between electronic manifolds as opposed to absolute quantities corresponding to a single state (e.g. electronic transition energies rather than absolute electronic energies), it is somewhat surprising that $\tilde{A}^1A_2$ parameters are accurately determined while those for the $\tilde{X}^1A_1$ state are not. High resolution UV absorption experiments performed by Freeman and Klemperer [12, 13] upon the rotational transitions within the $2^1_0^1$ vibronic band (i.e. the 3390Å band) have indicated an $a$-axis dipole moment of $1.56 \pm 0.07$D. This measurement seems to be too large in magnitude (as compared with our quantum beat results) even when the variation in $\mu_a$ with vibrational excitation, as observed in the ground electronic state [11], is taken into account.

The decrease in dipole moment magnitude accompanying the electronic excitation of formaldehyde (viz. from $\sim 2.33$D to $\sim 1.47$D) can be qualitatively interpreted in terms of a simple molecular orbital scheme for electronic structure such as that depicted in figure 1-17. For the $\tilde{X}^1A_1$ ground electronic state all molecular orbitals up to and including the $2b_2\pi(O)$ orbital are doubly occupied in accordance with the restrictions imposed by the Pauli exclusion principle [51]. The assignment of the $\tilde{A}^1A_2 \leftrightarrow \tilde{X}^1A_1$ system as an $\pi^* \leftrightarrow \pi$ transition corresponds to
a. *Ab Initio* Work.

<table>
<thead>
<tr>
<th>$\mu_a \bar{X}^1A_1$</th>
<th>$\mu_a \bar{A}^1A_2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.859D</td>
<td>1.470D</td>
<td>[15]</td>
</tr>
<tr>
<td>1.94D</td>
<td>1.45D</td>
<td>[91]</td>
</tr>
<tr>
<td>...</td>
<td>1.50D</td>
<td>[92]</td>
</tr>
</tbody>
</table>

b. Experimental Work.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Transition</th>
<th>$\mu_a \bar{A}^1A_2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Absorption</td>
<td>3390Å Band $(2^14^1_{0^0})$</td>
<td>1.56(7)D</td>
<td>[13]</td>
</tr>
<tr>
<td>EFS$^a$</td>
<td>...</td>
<td>1.4(1)D</td>
<td>[93]</td>
</tr>
</tbody>
</table>

$a$ Electric-Field-Induced Spectroscopy. This technique is based upon the phase-sensitive detection of a Stark-modulated absorption spectrum; see reference [93] for experimental details.

**Table 1-VI**: Previous Work on Dipole Moments in $\bar{A}^1A_2$ Formaldehyde.
Figure 1-17: Molecular Orbital Diagram for Formaldehyde.
the promotion of a single electron from the $2b_2 n(O)$ nonbonding orbital, which, in this primitive picture, is essentially a $p_y$ atomic orbital localized on the oxygen atom, to the antibonding $2b_1 \pi^* (CO)$ orbital which is centered over the C–O bond (cf. transition arrow in figure 1-17). By assuming a constant carbonyl bond length of 1.2072Å, as determined through microwave studies of the vibrationless level in the ground electronic potential surface [94], the excitation process (viz. the transfer of one electronic charge by $(1.2072/2)$Å from the oxygen atom to the midpoint of the C–O bond) will entail a reduction in the dipole moment by $\sim 2.9$D.

The inability of the primitive molecular orbital scheme to provide a quantitative assessment of the dipole moment change accompanying electronic excitation can be attributed to several basic shortcomings associated with this oversimplified picture of electronic structure. In the first place, minimal basis SCF calculations [95, 96, 97] performed upon the formaldehyde system have indicated that the "nonbonding" orbital, rather than being completely isolated on the oxygen atom, contributes significantly to the sigma bonding character of the molecular framework. This delocalization of the $2b_2 n(O)$ orbital will reduce the predicted dipole moment change for the $\pi^* \leftarrow n$ transition. In addition, the molecular orbital approach has utilized identical one-electron orbitals for the description of the $\tilde{A}^1A_2$ and $\tilde{X}^1A_1$ manifolds even though large structural differences are known to exist between the two electronic states. Recent ab initio work [98, 99] has suggested that the net positive hole produced on the oxygen atom as a result of the $n$ to $\pi^*$ electron transfer can greatly enhance the polarization of the $\pi$ orbitals in the excited state. The doubly occupied $1b_1 \pi(CO)$ orbital will become more localized on the oxygen while the centroid of the singly occupied $2b_1 \pi^* (CO)$ orbital will tend to move towards the carbon end of the molecule. This provides a cooperative mechanism for reducing the large dipole moment change anticipated from calculations based upon
an invariant set of molecular orbitals.

Studies performed within the ground electronic potential surface of formaldehyde have demonstrated that vibrational degrees of freedom principally involving displacement of the hydrogen atoms will cause a decrease in the dipole moment while C=O stretching motion will lead to a net increase [50]. Therefore, by analogy with the $\tilde{X}^1A_1$ state, the dipole moments determined from our quantum beat experiments are expected to exhibit an overall reduction in magnitude as the degree of excitation within the $\nu_4$ out-of-plane bending mode is augmented. Although such a trend is observed between the $v_4=0$ and $v_4=1$ levels of H$_2$CO, its appearance is much less certain in the case of D$_2$CO, especially when the $v_4=3$ level is taken into account. A plausible explanation for this aberrant behavior might be found in the barrier to inversion which characterizes the $\nu_4$ coordinate in the pyramidal distortion $\tilde{A}^1A_2$ electronic manifold. An analysis of this effect in terms of a vibronic coupling model is discussed later in the present section.

The Stark matrix elements of equations (1.7) and (1.9) were derived under the implicit assumption of a rigid nuclear configuration in which rotational motion could be completely isolated from all other internal coordinates. This separability permitted definition of vibronic dipole moment components, $\langle \gamma | T^1_q(\mu) | \gamma \rangle$ (viz. $\mu_a$, $\mu_b$, and $\mu_c$), which contain no explicit dependence upon rotational quantum numbers. In the case of a nonrigid molecule, however, interaction between the vibrational and rotational degrees of freedom can drastically alter this situation. In particular, centrifugal distortion of the molecular framework will introduce an additional, twofold contribution of rotational motion to the dipole moment. First, centrifugal forces will alter the molecular moments of inertia thereby producing a slight modification in the observed energy level structure as compared to that present in the rigid rotor. This effect, which will translate into a change in Stark tuning rates
for individual rovibronic states, can be taken into account by incorporating centrifugal distortion parameters into the zero field Hamiltonian as was done for our least squares analyses (cf. Appendix B). Of greater significance is the fact that the structural variations induced by centrifugal interactions will produce changes in the electric dipole moment which depend upon the magnitude and orientation of the total angular momentum within the molecular framework. Centrifugal distortion therefore provides a mechanism by which the measured dipole moment can be made to vary from one rotational level to the next. Although similar effects can be produced through Coriolis coupling, previous spectroscopic studies (cf. references in [50]) have demonstrated that this rotation-vibration interaction does not play a significant role for the rovibronic levels examined in the present quantum beat experiments.

The rotational dependence of the dipole moment has been investigated in the ground electronic state of formaldehyde through both molecular beam electric resonance [3] and laser-microwave double resonance [5] techniques. These studies have indicated that rather small variations on the order of $5 \times 10^{-4} \text{D}$ can be expected between adjacent rotational levels. In particular, Tanaka et. al. [5] have confirmed that the effective dipole moment, $\mu_{\text{eff}}(J,K_a)$, associated with rotational levels having total angular momentum $J$ and prolate projection quantum number $K_a$ can be represented by:

$$
\mu_{\text{eff}}(J,K_a) = \mu_0 + \mu_J J(J+1) + \mu_K K_a^2
$$

(1.30)

where the parameters $\mu_0$, $\mu_J$, and $\mu_K$ are constants which can be determined, for a given vibronic level, from the harmonic force field and first derivative of the dipole moment with respect to the normal coordinates [100]. The derivation of equation (1.30) depends upon the relative isolation of $K_a$-type doublets in formaldehyde.
from all other rotational levels. Under such circumstances, the observed Stark effects will be predominantly governed by interactions between the members of an asymmetry doublet. Since \( K_a = 0 \) levels do not exhibit asymmetry doubling, the applicability of expression (1.30) to these rotational eigenstates is somewhat dubious.

From their analysis of the vibrationless and \( \nu_2 \) fundamental bands in \( \tilde{X}^1A_1 \) formaldehyde-\( h_2 \), Tanaka et. al. concluded that \( \mu_J = -1.169 \times 10^{-6}D \) and \( \mu_K = -50.573 \times 10^{-6}D \) with uncertainties of 200\% and 10\% respectively. These numbers are in qualitative agreement with a crude bond moment description of \( H_2CO \) in which the charge separations for the individual bonds are specified by \( ^+C-H^- \) and \( ^+C-O^- \) [101, 102]. Since the \( K_a \) dependence of the dipole moment is of special concern in our quantum beat studies, a brief discussion of the \( \mu_K \) parameter is warranted. The near prolate nature of formaldehyde implies that an increase in \( K_a \) will be accompanied by enhanced rotation about the C–O bond (i.e. the molecular \( a – \)axis). Since centrifugal distortion effects will induce a concomitant expansion in the H–C–H angle, the bond moment model suggests that a slight decrease in dipole moment can be expected with increasing \( K_a \). This prediction is borne out by the negative value of \( \mu_K \) presented above.

Table 1-V contains the dipole moments measured for individual \( J=2 \) rotational levels within the \( \nu_4=1 \) vibrational manifold of \( \tilde{A}^1A_2 \) formaldehyde. The dependence of the observed dipole moments on the \( K_a \) quantum number is considerably more pronounced than that reported in any previous study of the formaldehyde system. The deuterated species exhibits an approximate increase in dipole moment with \( K_a \) (i.e. \( \mu_{\text{eff}}(2,2) \approx \mu_{\text{eff}}(2,1) > \mu_{\text{eff}}(2,0) \)). Provided that \textit{ab initio} calculations [102] are correct in their assertion that the \( \tilde{A} \) state bond moments should be polarized in the same direction as those in the ground electronic potential surface (\textit{viz.} \( ^+C-H^- \) and \( ^+C-O^- \)), this behavior is completely at
variance with the predictions of a crude bond moment model. The near equality of the $K_a = 2$ and $K_a = 1$ moments is also inconsistent with the quadratic $K_a$ dependence indicated in equation (1.30). In the case of formaldehyde-$\tilde{h}_n$, the quantum beat experiments reveal an exceptionally large variation in the dipole moment (i.e. $> 10^{-2}$ Debye) as a function of $K_a$ with no apparent pattern in the deviations from one rovibronic level to the next. Muenter and coworkers [103, 104, 3] have stressed that the manifestation of rotation-vibration interactions in molecular dipole moment functions is often complicated and overshadowed by the presence of higher-order Stark perturbations from induced moments (cf. discussion following equation (1.6)). It would appear, however, that any analysis based upon such polarization anisotropy arguments is incapable of explaining the large magnitude of the rotational effects observed in $\tilde{A} \, ^1A_2$ formaldehyde.

A possible explanation for the anomalous rotational dependence of the measured dipole moments in $\tilde{A} \, ^1A_2$ formaldehyde can be deduced on the basis of the variations present between members of an asymmetry doublet. In the case of a near prolate molecule such as formaldehyde, the centrifugal distortion mechanism would predict virtually no difference in $\mu_a$ for levels possessing the same $J$ and $K_a$ quantum numbers (cf. equation (1.30)). However, our quantum beat results suggest that, for a given value of $J$ (viz. $J = 2$), the dipole moment difference between asymmetry components increases with $K_a$. Since the energy separation for an asymmetry doublet also increases with $K_a$, this behaviour can be correlated with the energy gap between the pair of rovibronic levels. The dipole moment variations are seen to be considerably more pronounced in $\text{H}_2\text{CO}$ than in $\text{D}_2\text{CO}$.

Time-resolved fluorescence studies [19] performed upon individual rotation-vibration eigenstates of $\tilde{A} \, ^1A_2$ (i.e. $S_1$) formaldehyde have demonstrated the
prevalent nature of nonadiabatic interactions with highly excited predissociative levels in the \( \tilde{X}^1A_1 \) (i.e. \( S_0 \)) state. These \( S_1 \sim S_0 \) couplings entail a mixing of rovibronic character between levels in the ground and excited electronic potential surfaces which can manifest itself in several ways. Perhaps of greatest significance is the fact that these interactions can provide a mechanism for the irreversible, radiationless relaxation of molecules from the electronically excited manifold. Experiments have shown that \( \tilde{A} \) state rotational levels (in particular, members of an asymmetry doublet) separated by more than \( \sim 5 \times 10^{-4}\text{cm}^{-1} \) can exhibit radically different collision-free decay rates [21]. This behaviour can be correlated with the random distribution (i.e. random with respect to \( S_1 \) rovibronic structure) of lifetime-broadened levels which characterize the highly excited regions of the \( S_0 \) state.

In light of the discussion presented above, it is quite possible that the aberrant rotational behavior exhibited by the \( \tilde{A}^1A_2 \) dipole moments is yet another manifestation of the random distribution and magnitude of \( S_1 \sim S_0 \) interactions. The rovibronic mixing which accompanies these nonadiabatic perturbations could provide a mechanism for the mixing of dipole moment character between ground and excited electronic states. This would account for the greater variation observed between members of an asymmetry doublet as the value of \( K_a \) (i.e. the energy separation) increases. Further justification for this argument is provided by the \( S_1 \sim S_0 \) anticrossings detected in the \( 2_{0,2} \) \( v_4=1 \) level of formaldehyde-\( h_2 \) (cf. subsequent discussion). The isotopic dependence of the nonadiabatic coupling mechanism [105] would also suggest that much smaller dipole moment deviations should occur in the case of \( D_2\text{CO} \) as opposed to those present in \( H_2\text{CO} \). This supposition is supported by the experimental results compiled in table 1-V.

One additional point regarding the rotational dependence of the dipole
moments in $\tilde{A}^1A_2$ formaldehyde merits discussion. Although our measurements of Stark splittings entailed the use of a high resolution spectroscopic probe (viz. quantum beat spectroscopy), the rotational and centrifugal distortion constants associated with the individual vibronic bands (cf. table 1-IV) were derived from conventional UV absorption techniques [50]. Consequently, a lack of precision in the molecular constants utilized for the reduction of the raw Stark data to dipole moments could contribute to the anomalous variations observed between adjacent rotational levels. However, computer simulations have suggested that substantial changes in the centrifugal distortion parameters, which are not well determined from the traditional spectral analyses, would produce relatively small modifications in the calculated $\mu_a$ values (i.e. $\sim 5 \times 10^{-4}$D change for a 100% variation in the centrifugal distortion constants). Furthermore, the largest dipole moment deviations are encountered in the $v_4 = 1$ vibrational level of formaldehyde-$h_2$ for which the most highly refined molecular constants are available.

1.6.2 The Out-of-Plane Component of the Dipole Moment

The preceding analysis has concentrated upon the $a$-axis contribution to the dipole moment in $\tilde{A}^1A_2$ formaldehyde and has completely neglected the existence of the out-of-plane component $\mu_c$. While the justification for this approach will be provided below, the possibility of utilizing the extraordinary resolution afforded by quantum beat spectroscopy in order to determine $\mu_c$ experimentally represents one of the goals stated in the introductory remarks to the present Chapter. This section will therefore describe our attempts to measure the $c$-axis component of the dipole moment in electronically excited formaldehyde. The ensuing discussion will demonstrate that the manifestation of $\mu_c$ is intimately related to the large amplitude inversion motion which characterizes the $\tilde{A}$ state. The out-of-plane dipole moment
component is therefore completely analogous to the transition dipole moments encountered in ammonia [106, 107] which, in many respects constitutes the prototypical molecular inversion system.

The origin and manifestation of the out-of-plane dipole moment component in $\tilde{A}^1A_2$ formaldehyde can best be understood through an examination of the symm properties which characterize the nonrigid molecular framework encountered in this excited state. Figure 1-13 schematically illustrates the dependence of the energy levels within the $\nu_4$ vibrational manifold upon the magnitude of the barrier to inversion in the electronic potential surface. The right-hand side of this diagram shows the evenly spaced pattern of energy levels associated with the harmonic out-of-plane vibration of a molecule possessing a rigid, planar equilibrium geometry (viz. no barrier to inversion). The symmetry labels affixed to the individual eigenstates are consistent with those of a $b_1$ vibrational mode (i.e. $\nu_4$) described in terms of the $C_{2v}$ point group which is appropriate for planar formaldehyde. The left-hand side of figure 1-18 presents the doubly degenerate vibrational structure corresponding to a rigid, nonplanar molecular system in which two equivalent, but oppositely oriented, pyramidal configurations are separated by an infinite barrier to inversion. The $C_5$ point group, which provides a suitable classification scheme for the pyramidally distorted nuclear framework, indicates that all energy levels will be designated by the $a'$ symmetry label (i.e. both $a_1$ and $b_1$ in $C_{2v}$ correlate with the totally symmetric $a'$ representation of $C_5$).

The correlation diagram of figure 1-18 indicates that, as the magnitude of the barrier to inversion increases (viz. proceeding from right to left in the diagram), pairs of $a_1$ and $b_1$ levels from the evenly spaced vibrational structure of the rigid planar molecule will coalesce to form a single doubly degenerate level in the rigid
Figure 1-18: Vibrational Energy and Symmetry as a Function of Barrier Height.
nonplanar system. For regions between the rigid planar and nonplanar limiting cases, the energy splitting between the members of the lowest inversion doublets (i.e. each pair of merging \( a_1 \) and \( b_1 \) levels) will be quite small. As the top of the barrier is surpassed, however, this energy splitting will increase rapidly, ultimately becoming equal to half of the separation between adjacent levels. When a finite barrier is present, the individual eigenstates can be specified in terms of a single number, corresponding to their vibrational parentage in the rigid pyramidal distorted geometry, with a superscript of (+) or (−) signifying the symmetric or antisymmetric nature of the molecular wavefunction with respect to inversion about the planar configuration. (i.e. ± correlated to the \( a_1 \) and \( b_1 \) representations of the \( \sigma(yz) \) reflection operator in the \( C_{2v} \) point group). The effective potential curves illustrated in figures 1-14 and 1-15 demonstrate that both formaldehyde-\( h_2 \) and formaldehyde-\( d_2 \) fall into this intermediate category with reported barrier heights on the order of 350 cm\(^{-1} \) [90].

In order to obtain a valid symmetry classification for the vibrational levels in the presence of a finite, non-zero barrier, it is necessary to examine the molecule in terms of a nonrigid framework undergoing a large amplitude inversion motion. Under these circumstances, the rigorous description for the molecular system is provided by the complete nuclear permutation-inversion or CNPI group as discussed by Bunker [48]. In the case of formaldehyde, the appropriate CNPI group, termed \( G_4 \), contains the following four symmetry elements: the identity \( E \), the inversion (through the center of mass) \( E^* \), the permutation (of the hydrogen nuclei) \( (12) \), and the permutation-inversion \( (12)^* \). Since \( G_4 \) is conveniently isomorphic with the \( C_{2v}(M) \) molecular symmetry group, it is possible to label the vibrational structure of nonrigid formaldehyde in terms of the same irreducible representations utilized for the rigid planar configuration. This classification scheme, which has been used in
figure 1-18, is analogous to treating $\tilde{A}^1A_2$ formaldehyde as a planar molecule with a highly anharmonic out-of-plane distortion coordinate. The individual eigenstates can therefore be designated by an inversion quantum number, $v_{inv}$, such that $v_{inv}=0 \leftrightarrow 0^+$, $v_{inv}=1 \leftrightarrow 0^-$, $v_{inv}=2 \leftrightarrow 1^+$, \ldots. The relatively low magnitude of the barrier to inversion in the $\tilde{A}$ state has led to the association of $v_{inv}$ with the more traditional $v_4$ vibrational quantum number.

The group theoretical considerations presented above can be utilized in order to ascertain the nature of Stark interactions occurring in the rapidly inverting $\tilde{A}^1A_2$ state of formaldehyde. The conventional treatment [48, 90, 108] of such nonrigid molecular frameworks entails an explicit partitioning of the coordinate(s) responsible for the large amplitude motion (i.e. in formaldehyde; the out-of-plane distortion angle $\rho$) from all other nuclear degrees of freedom (i.e. small amplitude vibrational coordinates $Q$). The symmetry-based arguments to follow will assume that all nuclear/electronic spin effects can justifiably be neglected. Provided that a Born-Oppenheimer adiabatic separation between electronic (i.e. $r$) and nuclear (i.e. $Q$ and $\rho$) coordinates is possible, the complete eigenfunctions for the nonrigid molecular system, $\Psi_{total}(r,Q,\rho,\Omega)$, can be expressed as a product of several factors:

$$\Psi_{total}(r,Q,\rho,\Omega) = \Psi_{elec}(r,Q,\rho) \Psi_{inv}(\rho) \Psi_{vib}(Q,\rho) \Psi_{rot}(\Omega)$$  \hspace{1cm} (1.31)

where successive terms represent the electronic, inversional, vibrational, and rotational portions of the total wavefunction. The separation of $\Psi_{rot}(\Omega)$, which depends only upon the set of Euler rotation angles $\Omega$ (c.f. Appendix A), from the inversion degree of freedom (i.e. $\Psi_{inv}(\rho)$) rests upon the assumption that the molecular moments of inertia are relatively independent of the large amplitude distortion coordinate $\rho$. While this supposition may not be completely justifiable in
the case of \( \tilde{A}^1A_2 \) formaldehyde \([90]\), it will not affect the validity of the ensuing analysis.

The eigenstates for the nonrigid molecular system can now be conveniently specified by the quantum numbers associated with the various degrees of freedom under consideration:

\[
|\Psi_{\text{total}}\rangle = |\gamma_{\text{inv}}^{v_{\text{vib}}} J K_a K_c M\rangle = |\gamma_{\text{inv}}^{v_{\text{vib}}} R\rangle
\]

(1.32)

where

- \( \gamma \) signifies the set of quantum numbers required to label the electronic degrees of freedom,
- \( v_{\text{inv}} \) represents the quantum number associated with the large amplitude inversion motion \((i.e. \, v_4)\),
- \( v_{\text{vib}} \) represents the set of quantum numbers corresponding to the small amplitude nuclear displacements \((i.e. \, the \, normal \, vibrations)\),
- \( R \) denotes the set of quantum numbers \((viz. \, J, K_a, K_c, \, and \, M)\) required to fully specify the rotational degrees of freedom in an asymmetric rotor.

By utilizing the Cartesian expansion of the Stark Hamiltonian as presented in equation (1.29) with the nonrigid molecular eigenstates of expression (1.32), the interaction matrix elements which govern the manifestation of the dipole moment components in \( \tilde{A}^1A_2 \) formaldehyde can be written as follows:

\[
<\gamma^{'v_{\text{inv}}}^{v_{\text{vib}}} R'|H_{\text{Stark}}|\gamma_{\text{inv}}^{v_{\text{vib}}} R\rangle
\]

(1.33)

\[
= -\mathcal{E} \sum_g \langle R'|\Phi_g |R\rangle <\gamma^{'v_{\text{inv}}}^{v_{\text{vib}}} |\mu_g(r, \Omega, \rho)|\gamma_{\text{inv}}^{v_{\text{vib}}} >
\]

where use has been made of the fact that the direction cosine operators, like the Wigner rotation matrices of Appendix A, depend solely upon the rotational
quantum numbers $R$. Note that the dipole moment components are explicitly functions of both the electronic (i.e. $r$) and nuclear (i.e. $Q$ and $\rho$) coordinates.

In order to isolate the effects of vibrational and inversionsal degrees of freedom upon the molecular dipole moment, it will prove convenient to expand $\mu_g(r, Q, \rho)$ in terms of a Taylor series about a reference nuclear configuration in which all small amplitude displacement coordinates are set equal to zero (i.e. $Q = Q_0$):

$$\mu_g(r, Q, \rho) = \mu_g(r, Q_0, \rho) + \sum_n \left( \frac{\partial \mu_g(r, Q, \rho)}{\partial Q_n} \right)_0 Q_n + \cdots \quad (1.34)$$

By retaining only the first term in this dipole moment expansion, the Stark interaction matrix element of equation (1.33) becomes:

$$\langle \gamma'^{v'_\text{inv}} v'_\text{vib} | R \rangle [H_{\text{Stark}} | \gamma^{v_{\text{inv}}} v_{\text{vib}} | R \rangle$$

$$\approx -\mathcal{E} \delta_{v'_\text{vib} v_{\text{vib}}} \sum_g \langle R | \Phi_{zg} | R \rangle \langle \gamma'^{v'_\text{inv}} | \mu_g(r, Q_0, \rho) | \gamma^{v_{\text{inv}}} \rangle \quad (1.35)$$

where the delta function $\delta_{v'_\text{vib} v_{\text{vib}}}$ arises from the fact that the first term in the dipole moment expansion, $\mu_g(r, Q_0, \rho)$, does not depend upon the vibrational (i.e. non-inversionsal) degrees of freedom.

Previous symmetry related arguments have indicated that the $\tilde{A}^1A_2$ state of formaldehyde can support permanent dipole moment components only along the $a$ and $c$ molecular axes. Equation (1.35) can therefore be rewritten as a sum of two independent terms:
\[
\langle \gamma'_{\text{inv}}, \gamma'_{\text{vib}}, R | H_{\text{Stark}} | \gamma_{\text{inv}}, \gamma_{\text{vib}}, R \rangle \approx -\mathcal{E} \delta_{\gamma'_{\text{vib}}, \gamma_{\text{vib}}} \\
\times \left( \langle R'| \Phi_{\text{za}} | R \rangle \langle \gamma'_{\text{inv}} | \mu_a(r, Q_0, \rho) | \gamma_{\text{inv}} \rangle \\
+ \langle R'| \Phi_{\text{zc}} | R \rangle \langle \gamma'_{\text{inv}} | \mu_c(r, Q_0, \rho) | \gamma_{\text{inv}} \rangle \right)
\]  

(1.36)

The \( C_{2v}(M) \) molecular symmetry labels associated with the inversion levels (cf. figure 1-18) and dipole moment components (i.e. \( \Gamma(\mu_a) = a_1 \), \( \Gamma(\mu_b) = b_2 \), and \( \Gamma(\mu_c) = b_1 \) of \( \tilde{A} \) \( ^1A_2 \) formaldehyde can now be utilized in order to determine exactly how each of the terms in equation (1.36) will manifest itself in the course of a Stark experiment. A rather straightforward analysis results in the following first order selection rules for the interactions derived from \( \mu_a \) and \( \mu_c \):

1. For \( \mu_a \):
   \[ \Delta v_{\text{inv}} = 0 , \quad \Delta J = 0, \pm 1 \quad \Delta K_a = 0 \quad \Delta K_c = \pm 1 \quad \Delta M = 0 \]

2. For \( \mu_c \):
   \[ \Delta v_{\text{inv}} = \pm 1 \quad \Delta J = 0, \pm 1 \quad \Delta K_a = \pm 1 \quad \Delta K_c = 0 \quad \Delta M = 0 \]

The selection rules derived for the large amplitude degree of freedom constitute the most significant result obtained from the group theoretical treatment of nonrigid \( \tilde{A} \) \( ^1A_2 \) formaldehyde. While \( \mu_a \) can exist within a single inversion level (i.e. \( \Delta v_{\text{inv}} = 0 \)), the manifestation of the \( c \)-axis dipole moment component requires an interaction between adjacent inversion eigenstates (i.e. \( \Delta v_{\text{inv}} = \pm 1 \)). The most substantial coupling induced by the \( \mu_c \) matrix elements will occur between member levels of an inversion doublet which, as illustrated in figure 1-18, can be separated by relatively small energy gaps. From this viewpoint, the out-of-plane component of the dipole moment is more akin to a vibrational transition moment connecting
inversion levels rather than a permanent moment within a given inversion eigenstate. Note that the orthogonal orientations of \( \mu_a \) and \( \mu_c \) within the body-fixed coordinate system give rise to a completely different dependence upon the \( K_a \) and \( K_c \) projection numbers. These selection rules (viz. for \( \mu_a \): \( \Delta K_a = 0, \Delta K_c = \pm 1 \); for \( \mu_c \): \( \Delta K_a = \pm 1, \Delta K_c = 0 \)) are consistent with those corresponding to type-\( a \) and type-\( c \) spectroscopic transitions [56].

The distinctly different behavior of \( \mu_a \) and \( \mu_c \) can be rationalized in terms of the influence which an electric field exerts upon the wavefunctions of the nonrigid molecular system. In the absence of an external perturbation, the large amplitude inversional motion of \( \tilde{A}^1A_2 \) formaldehyde will tend to average any out-of-plane component of the dipole moment to zero. In contrast, the value of \( \mu_a \) is relatively unaffected by this vibrational averaging. The application of an electric field will be accompanied by a mixing of adjacent inversion levels (i.e. members of inversion doublets) through the \( \mu_c \) matrix elements presented in equation (1.36). These field-induced interactions will produce new molecular eigenstates which can be characterized as the in phase and out of phase linear combination of the two levels within each inversion doublet. Since the inversion wavefunctions alternate between being symmetric and antisymmetric with respect to the inversion coordinate \( \rho \) (c.f. \( \pm \) superscripts in figure 1-18), each linear superposition state will correspond to a preferential distortion of the molecular framework towards one of the configurations associated with the double minimum potential surface. In this manner, a \( c \)-axis dipole moment component can be simultaneously created and observed through the Stark effect.

As indicated above, the principal mechanism responsible for the manifestation of the out-of-plane dipole moment component in \( \tilde{A}^1A_2 \) formaldehyde is the field-induced interaction and partitioning of character among adjacent inversion states.
In terms of a first-order perturbative description, the degree of mixing produced between the molecular eigenfunctions will depend upon the ratio of the Stark matrix element \( i.e. \sim \mu_c \mathcal{E} \) to the energy separation between the inversion levels. The magnitude of the electric field in our quantum beat studies is limited to \( \leq 5 \text{KV/cm} \) by both practical (\( e.g. \) breakdown) and experimental (\( viz. \) total Stark splitting must be between 1MHz and 60MHz for detection through quantum beat spectroscopy) constraints. For the \( \text{ab initio} \) value of \( \mu_c = 0.523D \) [15], this maximum field strength corresponds to a Stark interaction of \( \sim 4.3 \times 10^{-2} \text{cm}^{-1} \). In contrast, the energy gaps associated with the lowest inversion doublets in \( \text{H}_2\text{CO} \) and \( \text{D}_2\text{CO} \) (\( cf. \) figures 1-14 and 1-15) are 125.4cm\(^{-1}\) and 67.0cm\(^{-1}\) respectively. Therefore, the size of the effect produced by the \( c \)-axis dipole moment component is predicted to be extremely small. This provides a justification for our analysis of the quantum beat measurements in terms of \( \mu_a \) only.

Notwithstanding the above arguments, the extraordinary resolution afforded by quantum beat spectroscopy prompted a reexamination of our Stark data in an attempt to determine the out-of-plane component of the dipole moment in \( \tilde{\text{A}}^1\text{A}_2 \) formaldehyde. As discussed earlier, the manifestation of \( \mu_c \) depends upon the field-induced mixing of adjacent vibrational levels within the \( \nu_4 \) manifold. Accordingly, our Stark analysis programs were modified to encompass two vibrational states, each possessing its own \( a \)-axis dipole moment component, coupled by the \( \mu_c \) interaction terms. All matrix elements were evaluated in a \( \Gamma' \) symmetric rotor basis set using the spherical tensor formalism developed in Appendix A (\( nb. \) the \( \Gamma' \) representation ensures that the matrix elements for both \( \mu_a \) and \( \mu_c \) are real [109]). With appropriate truncation of the doubly infinite matrix (as determined via numerical experiments), reliable eigenvalues could be obtained through standard numerical diagonalization procedures. The present treatment was restricted to the
member levels of the lowest inversion doublet (i.e. $v_4 = 0$ and $v_4 = 1$) in both H$_2$CO and D$_2$CO. Due to their relative proximity in energy as compared to all other inversion eigenstates (cf. figures 1-14 and 1-15), these levels are expected to exhibit the largest effects (at a given electric field strength) from the out-of-plane component of the dipole moment.

Figure 1-19 presents a computer simulation of the manner in which the out-of-plane dipole moment will manifest itself in electronically excited formaldehyde-$d_2$ and formaldehyde-$h_2$. For each calculation, the ab initio values [15] of $\mu_a = 1.470D$ (identical for both vibrational levels) and $\mu_c = 0.513D$ were utilized in order to determine the Stark splittings associated with the $J = 2$ rotational eigenstates in the $v_4 = 0$ and $v_4 = 1$ vibrational levels of the $\tilde{A}$ state. The diagram illustrates the changes in quantum beat frequency produced by a non-zero component of the dipole moment along the molecular $c$-axis (i.e. quantum beat frequency with $\mu_c = 0.513D$ minus quantum beat frequency with $\mu_c = 0.0D$). It must be emphasized that the coherent spectroscopic techniques employed in our Stark experiments provided a direct measurement of the field-induced separations between the $|M| = 2$ and $M = 0$ magnetic subcomponents within a target $\tilde{A}^1A_2$ rovibronic level.

For the 0 to 10 kilovolt per centimeter range of electric field illustrated in figure 1-19, the variations produced in the quantum beat frequency by the out-of-plane dipole moment are, at most, $\sim 1.2$MHz in formaldehyde-$d_2$ and $\sim 0.6$MHz in formaldehyde-$h_2$. This factor of two discrepancy between the isotopic species reflects the smaller inversion doublet splitting in D$_2$CO (viz. 67.0cm$^{-1}$) as opposed to that in H$_2$CO (viz. 124.5cm$^{-1}$). The predicted magnitude for the changes induced by the $\mu_c$ interaction is to be compared with the 50-100KHz resolution attained in our quantum beat studies. It must be realized, however, that the large Stark effects associated with the $a$-axis dipole moment component in $\tilde{A}^1A_2$ formaldehyde will
Figure 1-19: Manifestation of $\mu_\epsilon$ in $\tilde{A}^1A_2$ Formaldehyde.
a. Out-of-Plane Dipole Moment in $\text{D}_2\text{CO}$

\[ \tilde{A}^1A_2 \nu_4 = 1 \]

\[ \tilde{A}^1A_2 \nu_4 = 0 \]

Difference Frequency (MHz)

Applied Field (Kilovolts/cm)
b. Out-of-Plane Dipole Moment in $\text{H}_2\text{CO}$

$\tilde{A}^1A_2 \nu_4 = 1$

$\tilde{A}^1A_2 \nu_4 = 0$

Difference Frequency (MHz)

Applied Field (Kilovolts/cm)
impose firm constraints upon the maximum field strength at which coherent oscillations can be experimentally detected (i.e. the $\sim 60\text{MHz}$ upper frequency limit determined by the laser pulse duration). As suggested by figure 1-2, these limitations will be strongly dependent upon the $K_a$ quantum number of the target $J = 2$ rovibronic eigenstate (i.e. for $K_a = 2$; $\mathcal{E} \leq 200\text{V/cm}$, $K_a = 1$: $\mathcal{E} \leq 2.5\text{KV/cm}$, and $K_a = 0$; $\mathcal{E} \leq 5.0\text{KV/cm}$)

Figure 1-19 also indicates that the $\mu_c$ effects produced within the $v_4 = 0$ and $v_4 = 1$ vibrational levels of $\tilde{A}^1\text{A}_2$ formaldehyde display a near mirror image relationship to one another. The behavior can be correlated with the in phase and out of phase linear combinations of inversion eigenfunctions resulting from the interaction of the $c$-axis dipole moment component with the applied electric field. The averaged molecular structures corresponding to the member levels of the inversion doublet therefore experience oppositely oriented pyramidal distortions (i.e. one level distorts with positive $\rho$, the other with negative $\rho$) as the field strength increases.

Despite the encouraging predictions provided by the computer simulations of figure 1-19, attempts to simultaneously analyze the quantum beat measurements in terms of both $\mu_a$ and $\mu_c$ met with only very limited success. Although several different combinations of our experimental Stark data sets were incorporated into the fitting procedure, excessive correlations between the dipole moment parameters always prevented the least-squares regression procedure from achieving the required convergence criteria. However, our results indicate that an upper limit of $\sim 0.65\text{D}$ can be realistically associated with the $c$-axis dipole moment in $\tilde{A}^1\text{A}_2$ formaldehyde. This value is in reasonable agreement with the \textit{ab initio} calculations of Garrison and Schaefer [15] which suggest that $\mu_c = 0.513\text{D}$ for a fixed pyramidal distortion of the molecular framework corresponding to $\rho = 31^\circ$. 
1.6.3 The Nonplanarity of the $\tilde{A}^1A_2$ State

The relationship between electronic structure and nuclear geometry in molecular systems has long been a subject of concern and speculation within the chemical physics community. For diatomic molecules, this interest has led to the development and successful exploitation of numerous Aufbau or build-up principles [110] based upon the assumption of an adiabatic variation in electronic configuration as a function of the internuclear distance. By means of such techniques, electronic states for first row diatomics can readily be characterized with regards to their energy ordering, intrinsic stability, spectroscopic transition intensities, and chemical reactivity. Similar considerations can be applied to polyatomic species where the more robust and varied nature of the available internal coordinates suggests the possibility of further correlating alterations in nuclear configuration (e.g. those accompanying spectroscopic transitions) with corresponding changes in the electronic structure of the molecule. The measurement of observables which explicitly depend upon the charge distribution over the entire molecular framework (viz. dipole moments) can provide some insight into the origin of this interplay between nuclear geometry and electronic structure.

In a landmark series of papers [111, 112, 113, 114, 115, 17, 116, 117], A. D. Walsh proposed an empirical, but, nevertheless, quite successful, approach for the correlation of polyatomic electronic structure with well-defined alterations in the geometry of the molecular framework. This treatment, which is primarily concerned with (symmetry-reducing) bending degrees of freedom, seeks to establish the functional dependence of one-electron orbital energies (e.g. molecular orbital energies) upon systematic variations in one or more of the nuclear coordinates. Once these functional relationships have been ascertained, qualitative predictions can be made for the relative stabilities of various nuclear geometries in a given electronic
state. This ability to predict the shape of a molecular framework on the basis of a simple molecular orbital picture of electronic structure has important ramifications in the field of polyatomic spectroscopy where the intensities of vibronic transitions are related to corresponding changes in the nuclear configuration through the Franck-Condon principle [118]. In fact, the application of the Walsh formalism to the \( \tilde{A}^1\text{A}_2 \) state of formaldehyde [17] provided one of the first indications that the anomalous vibrational frequencies observed in the \( \nu_4 \) out-of-plane bending mode [14] (cf. figures 1-14 and 1-15) could be explained in terms of the inversion doubling associated with a nonplanar equilibrium geometry.

Application of the Walsh formalism to a polyatomic system begins with the construction of nonlocalized, symmetry-adapted molecular orbitals from linear combinations of the valence atomic orbitals in the free atoms. Usually the inner closed-shell electrons are left in their respective atomic orbitals and are assumed not to participate in the molecular bonding process. This procedure is repeated for two distinct reference geometries which constitute the extreme limits of the nuclear displacement to be considered in the ensuing analysis. The results of such calculations, which yield molecular orbitals that can be classified according to the symmetry properties of the individual reference configurations, is illustrated in figure 1-17 for the case of planar formaldehyde. A so-called Walsh diagram, consisting of a plot of molecular orbital energies as a function of variations in the nuclear coordinates, can now be constructed by correlating the lowest available molecular orbitals between the two reference configurations according to the following rules:

1. A molecular orbital does not change its classification respect to symmetry elements common to both reference configurations.

2. The (adiabatic) correlation curves for molecular orbitals of the same symmetry do not intersect.
3. The relative energy of a molecular orbital is lowered (i.e. the molecular orbital contains a more tightly bound electron) if, on variation of the nuclear configuration, the linear combination of atomic orbitals which constitutes the molecular orbital assumes more $s$-character and less $p$-character.

The first two of these principles follow from the well-known restrictions associated with correlations between the different symmetry groups of the reference configurations [119] and the non-crossing rule for adiabatic potential surfaces [118]. Analogous concepts are used in the determination of electronic state manifolds for diatomic systems on the basis of the separated and united atom limiting cases (i.e. reference configurations) [110].

The third of the rules presented above, which forms the cornerstone of the postulates put forth by Walsh in his original work [111], provides a method for correlating the relative energy separations and orderings between the molecular orbitals in the two reference configurations. This principle can be rationalized in terms of the enhanced bonding (or increased bond strength) which accompanies $sp$ hybridization (i.e. the mixing of $s$ and $p$ atomic orbitals) in contrast to that afforded by a pure $p$-orbital valency. Secondary effects, associated with electrostatic repulsion in the molecular charge distribution, can lead to additional modifications in the orbital energies as the nuclear coordinates are varied. Based upon the crude assumption that the total electronic energy is the sum of that for all the occupied molecular orbitals, a Walsh diagram will therefore indicate which electronic states will undergo a distortion in nuclear geometry so as to attain a minimum energy configuration.

On the basis of the above postulates, the dependence of the molecular orbital energies in formaldehyde upon variations in the out-of-plane bending coordinate, $\rho$, can readily be ascertained [17, 88]. The results of such an analysis are summarized
Figure 1-20: Walsh Diagram for Formaldehyde.
by the Walsh diagram in figure 1-20 which schematically illustrates the correlation between the planar (viz. C\textsubscript{2v} symmetry; ρ=0°) and pyramidal (viz. C\textsubscript{s} symmetry; ρ=90°) reference configurations. With one exception (viz. the 2b\textsubscript{1}π\textsuperscript{*}(C=O) orbital), each molecular orbital undergoes a small increase in energy (i.e. a decrease in binding strength) as the out-of-plane distortion becomes larger. This can be rationalized through the loss of sp\textsuperscript{2} hybridization which accompanies this particular modification of the nuclear configuration. Therefore, in the pyramidal molecular framework, the bonding associated with these orbitals is expected to be more suggestive of a pure p-type valency.

The 2b\textsubscript{1}π\textsuperscript{*}(C=O) orbital, which is an antibonding linear combination of the p\textsubscript{z} orbitals on the carbon and oxygen in the planar nuclear configuration (cf. figure 1-17), correlates to essentially a nonbonding 2s carbon atomic orbital in the pyramidal geometry. On the basis of the Walsh postulates, this mixing of s and p character can be expected to substantially reduce the corresponding molecular orbital energy as the out-of-plane bending coordinate increases. This situation is clearly illustrated in figure 1-20. Since only the 2b\textsubscript{1}π\textsuperscript{*}(C=O) orbital becomes more bonding with increasing nonplanarity, it follows that only those electronic configurations of formaldehyde which occupy this orbital will display a tendency to distort from the planar geometry in order to attain a minimum energy situation. In such cases, the degree of distortion actually observed will be governed by secondary factors including the electrostatic repulsion between the electrons in various molecular orbitals.

The electronic configuration corresponding to the ground electronic potential surface of formaldehyde can be obtained by placing the 12 valence electrons into the six lowest molecular orbitals of the Walsh diagram in a manner consistent with the Pauli exclusion principle [51]. This results in a complete filling of the manifold of
one-electron states up to and including the nonbonding \(2b_2\) \(n(O)\) orbital. The Walsh diagram clearly indicates that the \(\tilde{X}^1A_1\) electronic configuration (viz. \((3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2\)) generated by this procedure can be expected to support a planar nuclear geometry since all of the occupied molecular orbitals exhibit an energy increase in response to an out-of-plane distortion. The planarity of the ground electronic state in formaldehyde has been unequivocally confirmed through high resolution microwave spectroscopy [120, 121, 94, 122].

As previously indicated, the first two excited electronic states in formaldehyde, the \(\tilde{A}^1A_2\) and \(\tilde{a}^3A_2\) states, can be attributed to the promotion of a single nonbonding electron from the \(2b_2\) \(n(O)\) orbital to the antibonding \(2b_1\pi^*(CO)\) orbital. This electronic excitation process, which corresponds to the \(\pi^* \leftrightarrow n\) spectroscopic transition utilized throughout the present work, is illustrated by the arrow appearing in figure 1-20. The Walsh diagram suggests that the electronic configurations associated with these excited manifolds (viz. \((3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)(2b_1)\)) will be stabilized (i.e. undergo a net reduction in total electronic energy) by distortion from the planar nuclear geometry which characterizes the ground state of formaldehyde. The predicted nonplanarity has been spectroscopically verified for both the \(\tilde{A}^1A_2\) [89, 14, 80] and \(\tilde{a}^3A_2\) [123] states through the identification of symmetric double minimum potential surfaces along their out-of-plane bending coordinates (c.f. figures 1-14 and 1-15).

The semiempirical molecular orbital approach discussed above has proven to be an extremely powerful and widely applicable technique for determining the qualitative relationship between electronic configuration and nuclear structure in polyatomic systems. However, this formalism provides no means of quantifying its predictions so as to correlate specific molecular properties with variations in the electronic and nuclear degrees of freedom. For the case of \(\tilde{A}^1A_2\) formaldehyde, the
Walsh postulates have indicated that a pyramidal distortion of the molecular framework will occur in order to stabilize the electronic configuration of this excited state. While this prediction constitutes a fundamentally important step in the understanding of molecular structure, very little additional information can be obtained as to the effect of such nuclear and electronic modifications upon experimentally observable quantities (e.g. vibrational frequencies, transition intensities, and molecular dipole moments). These deficiencies have prompted several researchers to explore more quantitative treatments for the correspondence between electronic configuration and nuclear geometry.

In a recent paper [18], K. K. Innes has proposed a completely different formalism for explaining the subtle interplay between electronic and nuclear degrees of freedom that is responsible for the pyramidal distortion of formaldehyde in the \( \tilde{A}^1A_2 \) and \( \tilde{a}^3A_2 \) states. The Innes model suggests that the double minimum potential wells which characterize these excited electronic manifolds can be interpreted in terms of a vibronic interaction between two zero-order adiabatic potential surfaces. The concept of vibronic coupling is by no means alien to the formaldehyde system where it has been well established both theoretically [124, 125, 20] and experimentally [69, 70] that most of the intensity in the \( \tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1 \pi^* \leftarrow n \) transition (at 3500 Å) derives from the considerably stronger \( \tilde{B}^1B_2 \leftarrow \tilde{X}^1A_1 \ 3s \leftarrow n \) Rydberg transition (at 1750 Å) through a mixing of \( \tilde{A} \) and \( \tilde{B} \) character induced by the \( \nu_4 \) out-of-plane bending vibration. The primary advantage of the Innes approach stems from the fact that it offers the possibility of providing \textit{quantitative} predictions regarding observable molecular properties.

In an attempt to understand the physical manifestation of correlations between electronic and nuclear degrees of freedom, Innes initially applied his formalism to an analysis of the vibrational structure exhibited by the first excited
electronic states of formaldehyde (viz. the $\tilde{A}^1A_2$ and $\tilde{\tilde{a}}^3A_2$ states). The vibronic coupling model demonstrated that interactions between adiabatic potential curves could explain the existence of double minimum potential surfaces along the out-of-plane bending coordinates (i.e. $\nu_4$) in these excited states. By performing a least-squares adjustment of various modelling parameters, the "anomalous" (i.e. inversion doubled) vibrational spacings observed within the $\nu_4$ mode of electronically excited $\text{H}_2\text{CO}$, $\text{D}_2\text{CO}$, and $\text{HDCO}$ could be reproduced to within the uncertainty of experimental measurements. Perhaps of even greater significance is the fact that the Innes approach has been able to verify and rationalize the difference in the barrier heights to inversion between the $\tilde{A}^1A_2$ and $\tilde{\tilde{a}}^3A_2$ states of formaldehyde. Although spectroscopic studies have unequivocally established the triplet state barrier to be $\sim 2.4$ times larger than that associated with the singlet potential surface (i.e. 776.60cm$^{-1}$ vs. 350.33cm$^{-1}$ [90, 50]), the most sophisticated $\textit{ab initio}$ calculations [16] performed to date have failed to reproduce or account for this substantial difference. The vibronic coupling parameters derived from the Innes model are also in excellent agreement with those predicted on the basis of the borrowed transition intensity in the $\tilde{A} \leftrightarrow \tilde{X}$ electronic system [69, 70].

The vibronic coupling scheme has proven to be extremely useful for the analysis of molecular properties (e.g. vibrational frequencies) in the excited electronic states of formaldehyde. The unmitigated success of the Innes model has led us to consider its predictions regarding the dipole moment measurements performed in the present work. The influence of vibronic coupling upon molecular moments has long been a subject of considerable interest in the photophysics and spectroscopy of large polyatomic systems [126, 127]. Both theoretical and experimental studies have demonstrated that several significant effects can be attributed to such interactions between nuclear and electronic degrees of freedom.
In particular, anomalous variations in molecular dipole moments [128, 129], as a function of both vibrational excitation and isotopic modification, have been rationalized through vibronic coupling formalisms analogous to that proposed by Innes.

The mathematical details for the Innes formalism, as well as a justification for the terminology employed in the following discussion, have been summarized in Appendix D and will not be repeated at the present time. The conceptual foundations for this vibronic coupling scheme can best be understood by reference to figure 1-21. The dashed curves in this diagram denote two crude adiabatic potential surfaces, labeled as 1 and 2, which are together assumed to provide an adequate zero-order picture for the excited electronic states under consideration. As drawn, the potential surfaces are symmetric in the \( \nu_4 \) out-of-plane bending coordinate which is the only nuclear degree of freedom involved in the present treatment. The ensuing analysis will demonstrate how vibrationally induced electronic mixing between these zero-order manifolds will transform them into representations for the \( \tilde{A}^1A_2 \) and \( \tilde{B}^1B_2 \) states of formaldehyde as indicated by the solid lines in figure 1-21. The eigenvalues resulting from this vibronic coupling mechanism will provide evidence for a pyramidal distortion in the \( \tilde{A} \) state while the eigenvectors will enable predictions to be made for the dipole moments associated with the individual vibrational levels.

By definition (c.f. Appendix D), the crude adiabatic vibronic wavefunctions associated with the potential surfaces of figure 1-21, \( \psi_{j,t}^{CA}(r,Q) \), can be formulated as the simple product of a static electronic function, \( \psi_j (r,Q_0) \), and a crude adiabatic vibrational function, \( \chi_{j,t}^{CA}(Q) \):

\[
\psi_{j,t}^{CA}(r,Q) = \psi_j^{0}(r,Q_0) \chi_{j,t}^{CA}(Q)
\]  

(1.37)
Figure 1-21: The Innes Vibronic Coupling Model.
State 2
\((\tilde{B}^1B_2)\)

State 1
\((\tilde{A}^1A_2)\)

Out-of-Plane Distortion \((Q)\)
where \( r \) and \( Q \) represent the sets of coordinates required to describe the electronic and nuclear degrees of freedom respectively. The indices on the vibronic wavefunction, \( \psi_{j}^{CA}(r,Q) \), denote its association with electronic potential surface \( j \) (i.e. \( j = 1 \) or \( 2 \) for the two potential curves employed in the Innes model) and vibrational state \( t \) (i.e. \( t = 0, 1, 2, \ldots \) for the single vibrational mode considered in the Innes scheme). In contrast to the crude adiabatic vibronic and vibrational functions, the static electronic wavefunctions, \( \psi_{j}^{0}(r,Q_{0}) \), are expressed in terms of a fixed molecular framework (viz. \( Q_{0} \)). This reference nuclear configuration is defined to be at the minima of the crude adiabatic potential curves illustrated in figure 1-21 (i.e. at the point of zero displacement in the out-of-plane distortion coordinate).

In the approximation that vibronic interactions between electronic potential surfaces can be neglected, the crude adiabatic wavefunctions will form the eigenbasis for what might be termed the crude adiabatic representation of the total molecular Hamiltonian, \( H_{total}^{CA}(r,Q) \):

\[
\{ \psi_{ks}^{CA}(r,Q) | H_{total}^{CA}(r,Q) | \psi_{jt}^{CA}(r,Q) \} = E_{jt}^{CA} \delta_{kj} \delta_{st}
\] (1.38)

where \( E_{jt}^{CA} \) denotes the vibronic energy (i.e. vibrational plus electronic energy) corresponding to the crude adiabatic wavefunction \( \psi_{j}^{CA}(r,Q) \). As described in Appendix D, the brackets \( \{ \cdots | \cdots | \cdots \} \) signify an integration over both electronic and nuclear coordinates (viz. over vibronic coordinates).

For the Innes model (cf. figure 1-21), both crude adiabatic potential surfaces are assumed to be harmonic with a common vibrational frequency \( \nu \). With the zero of energy defined by the bottom of the lower potential curve (i.e. state 1), the matrix elements of equation (1.38) become:
\[
\{\psi_{ks}^{CA}(r,Q)|H_{\text{total}}^{CA}(r,Q)|\psi_{1t}^{CA}(r,Q)\} = h\nu \left(t + \frac{1}{2}\right) \delta_{1k} \delta_{st} \tag{1.39}
\]

\[
\{\psi_{ks}^{CA}(r,Q)|H_{\text{total}}^{CA}(r,Q)|\psi_{2t}^{CA}(r,Q)\} = \left(h\nu \left(t + \frac{1}{2}\right) + \Delta E\right) \delta_{1k} \delta_{st} \tag{1.40}
\]

where \(\Delta E\) denotes the electronic energy gap separating the minima of the one-dimensional potential curves corresponding to states 1 and 2. Therefore, provided that vibronic coupling can be justifiably neglected, the Innes model consists of two isolated electronic manifolds each of which contains an identical harmonic vibrational structure. Although the use of identical harmonic potential curves might appear to be overly restrictive, the entire formalism can readily be extended to more realistic multi-dimensional potential surfaces which could be rotated and/or displaced from one another in order to account for differences in the equilibrium nuclear coordinates between the electronic states [126, 130].

The Innes model is based upon the premise that the true molecular Hamiltonian, \(H_{\text{total}}(r,Q)\), contains vibronic interaction terms which, through their explicit coupling of nuclear and electronic degrees of freedom, are responsible for the physical properties (e.g. vibrational frequencies) observed in the electronically excited states of formaldehyde. The crude adiabatic wavefunctions defined by equation (1.37) can now be utilized as a basis set of orthonormal functions in which \(H_{\text{total}}(r,Q)\) can be conveniently expanded (n.b. the \(\psi_{ks}^{CA}(r,Q)\) are \textit{not} eigenfunctions of the total molecular Hamiltonian). The required matrix elements for the total molecular Hamiltonian have been derived in Appendix D and are repeated here for the special case of a single nuclear displacement coordinate \(Q\):
\[
\{ \psi_{ks}^{CA}(r,Q) | H_{total}(r,Q) | \psi_{jt}^{CA}(r,Q) \} = E_{jt}^{CA} \delta_{kt} \delta_{st} 
\]

\[
+ \langle \psi_{k}^{0}(r,Q_{0}) | \left( \frac{\partial U(r,Q)}{\partial Q} \right)_{0} \psi_{j}^{0}(r,Q_{0}) \rangle \langle \chi_{ks}^{CA}(Q) | Q | \chi_{jt}^{CA}(Q) \rangle [ 1 - \delta_{kj} ]
\]

where \( U(r,Q) \) represents the total Coulombic potential energy for the molecule. The derivation of equation (1.41) has employed the intrinsic separability of the crude adiabatic wavefunctions in order to reformulate the vibronic integral in terms of individual integrations over nuclear and electronic coordinates (\( i.e. \) denoted by \( \cdots | \cdots | \cdots \) and \( \cdots | \cdots | \cdots \), respectively). A comparison of this expression with equation (1.38) indicates the presence of an additional term which couples the two electronic potential surfaces (\( \text{viz.} \) the \( 1 - \delta_{kj} \) term which is explicitly off-diagonal in the electronic state indices).

Due to the identical harmonic nature of the crude adiabatic potential surfaces utilized in the Innes model, equation (1.41) can be rewritten as follows:

\[
\{ \psi_{ks}^{CA}(r,Q) | H_{total}^{CA}(r,Q) | \psi_{1t}^{CA}(r,Q) \} = \hbar \nu \left( t + \frac{1}{2} \right) \delta_{1k} \delta_{st} 
\]

\[
+ \beta \left( \sqrt{t+1} \delta_{s,t+1} + \sqrt{t} \delta_{s,t-1} \right) [ 1 - \delta_{1k} ]
\]

\[
\{ \psi_{ks}^{CA}(r,Q) | H_{total}^{CA}(r,Q) | \psi_{2t}^{CA}(r,Q) \} = \left( \hbar \nu \left( t + \frac{1}{2} \right) + \Delta E \right) \delta_{2k} \delta_{st}
\]

\[
+ \beta \left( \sqrt{t+1} \delta_{s,t+1} + \sqrt{t} \delta_{s,t-1} \right) [ 1 - \delta_{2k} ]
\]

where the off-diagonal vibrational matrix elements of \( Q \) have been evaluated in the usual manner [131] and all portions of the vibronic interaction term not explicitly dependent upon vibrational quantum numbers have been incorporated into the
coupling parameter $\beta$.

The matrix representation for the total Hamiltonian defined by equations (1.42) and (1.43) can subsequently be diagonalized in order to determine the eigenvalues, $E_{j\ell}$, and eigenfunctions, $\Psi_{j\ell}(r,Q)$, for the molecular system. As a consequence of the basis set utilized in the expansion of $H_{\text{total}}(r,Q)$, the eigenstates will be obtained in the form of a linear combination of the crude adiabatic wavefunctions:

$$\Psi_{j\ell}(r,Q) = \sum_{k\alpha} c_{k\alpha,j\ell} \psi_{k\alpha}^A(r,Q) = \sum_{k\alpha} c_{k\alpha,j\ell} \psi_{k\alpha}^0(r,Q_0) x_{k\alpha}^A(Q)$$  \hspace{1cm} (1.44)

where $c_{k\alpha,j\ell}$ denotes a real numerical coefficient which describes the amount of $\psi_{k\alpha}^A(r,Q)$ basis function character contained in the exact molecular eigenfunction $\Psi_{j\ell}(r,Q)$.

Strictly speaking, the matrix defined by equations (1.42) and (1.43) will require a basis set of infinite dimension for its exact representation. In practice, however, the low energy eigenstates in each potential surface can be calculated to a preselected accuracy by truncating the Hamiltonian matrix at a finite size determined through numerical experimentation.

As indicated by equations (1.42) and (1.43), the eigenvalues and eigenfunctions obtained from the Innes formalism will be dependent upon three parameters: (1) the electronic energy gap $\Delta E$, (2) the vibronic coupling strength $\beta$, and (3) the harmonic frequency $\nu$. An estimate for $\Delta E$ is readily provided by the measured energy separation between the $\tilde{B}^1B_2$ and $\tilde{A}^1A_2$ electronic manifolds (i.e. $\Delta E \approx 28992\text{cm}^{-1}$ [88]). Similarly, the oscillator strength for the $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ transition, which derives mostly from the vibronic mixing of the $\tilde{B}$ and $\tilde{A}$ electronic states induced by the $\nu_4$ vibration [70], can be used to approximate the
coupling parameter (i.e. $\beta \sim 3000 \text{cm}^{-1}$ [124, 125, 20]). Based on these initial values and an assumed harmonic frequency, Innes was able to perform a least-squares adjustment of all three modelling parameters so as to exactly reproduce the observed vibrational structure in the $\tilde{A}^1A_2$ states of formaldehyde-$h_2$ and its isotopic modifications.

The final parameters reported by Innes [18] for his analysis of $\tilde{A}^1A_2$ H$_2$CO and D$_2$CO are presented in table 1-VII. In order to fully comprehend how the vibronic coupling mechanism should manifest itself in the measurement of molecular dipole moments, figures 1-22 and 1-23 display the effects of varying the interaction strength, $\beta$, while maintaining all other model parameters fixed at the values suggested by Innes (c.f. table 1-VII). The variations induced in both the eigenvalues and eigenfunctions corresponding to the six lowest levels in each of the two formaldehyde-$h_2$ potential surfaces are illustrated.

In figure 1-22, which corresponds to the lower potential curve (i.e. the $\tilde{A}^1A_2$ state) of the Innes model, the first plot displays the dependence of the six lowest energy eigenvalues upon the magnitude of the vibronic coupling parameter $\beta$. For zero interaction strength (viz. $\beta=0$), the vibrational levels are, as expected, harmonically displaced with a frequency of $\nu=1125 \text{cm}^{-1}$ (c.f. table 1-VII). As the vibronic coupling between the electronic manifolds increases, the eigenvalues of this active vibration (viz. $\nu_4$) decrease rapidly and develop a large positive anharmonicity [132]. When the interaction strength has attained sufficient proportions, pairs of molecular energy levels merge in a pattern which closely resembles the inversion doubling structure observed in $\tilde{A}^1A_2$ formaldehyde. This behavior can be rationalized by the formation of a barrier to inversion in the lower electronic potential surface (i.e. the creation of a symmetric double minimum potential well) as a result of the vibronic interaction. The vertical line at
<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Symbol</th>
<th>( \text{H}_2\text{CO} ) Value(^a)</th>
<th>( \text{D}_2\text{CO} ) Value(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic Energy Gap</td>
<td>( \Delta E )</td>
<td>29035</td>
<td>28381</td>
</tr>
<tr>
<td>Vibronic Interaction Strength</td>
<td>( \beta )</td>
<td>3138</td>
<td>2810</td>
</tr>
<tr>
<td>Harmonic Frequency</td>
<td>( \nu )</td>
<td>1125</td>
<td>894</td>
</tr>
</tbody>
</table>

\(^a\) Values optimized by Innes (in cm\(^{-1}\)).

**Table 1-VII:** Parameters Utilized in the Innes Vibronic Coupling Model.
Figure 1-22: Vibronic Coupling in the $\tilde{A}^1A_2$ State of H$_2$CO.
\[ \tilde{A}^1A_2 \mathrm{H}_2\mathrm{CO} \]

![Graph showing energy levels and state characters vs. vibronic coupling parameter](image-url)
Figure 1-23: Vibronic Coupling in the $\tilde{B} ^1B_2$ State of H$_2$CO.
$\tilde{\Sigma}^{1}B_{2} H_2CO$

![Graph showing the relationship between energy (cm$^{-1}$) and vibronic coupling parameter (cm$^{-1}$) for $\tilde{\Sigma}^{1}B_{2} H_2CO$. The graph includes multiple curves representing different states, with state labels 0 to 5 along the vertical axis. The x-axis represents the vibronic coupling parameter in cm$^{-1}$.](image-url)
\[ \beta = 3138 \text{cm}^{-1} \] in figure 1-22 indicates the optimum value for the coupling strength as determined by Innes in his least squares analysis.

The second and third plots in figure 1-22 demonstrate the variations induced in the molecular eigenstates by the vibronic interaction. These graphs respectively indicate the fractional amount of crude adiabatic basis state 1 and basis state 2 character contained in a given eigenfunction of the total Hamiltonian as a function of the coupling strength \( \beta \). From equation (1.44), the quantities of interest in this diagram can be defined by:

\[
(C_{k,j})^2 = \sum_s |c_{k,s,j}|^2
\]  \hspace{1cm} (1.45)

where \( C_{k,j} \) is the parentage coefficient which describes the total amount of crude adiabatic basis state \( k \) character (i.e. \( k=1 \) or \( k=2 \) as per figure 1-21) which is contained in the exact molecular eigenstate \( \Psi_{j}(r,Q) \). Due to the intrinsic separability of the crude adiabatic wavefunctions (cf. equation (1.41)), \( (C_{k,j})^2 \) can also be interpreted as the relative contribution of the \( k^{th} \) static electronic function, \( \psi_{k}^{0}(r,Q_{0}) \), to the eigenfunction \( \Psi_{j}(r,Q) \). The restriction of the present analysis to only two crude adiabatic manifolds ensures that the following conservation principle will hold:

\[
\sum_{k} (C_{k,j})^2 = (C_{1,j})^2 + (C_{2,j})^2 = 1
\]  \hspace{1cm} (1.46)

In the absence of vibronic interactions (viz. \( \beta=0 \)), the eigenfunction plots of figure 1-22 display the pattern suggested by equation (1.39). Under these conditions, all eigenstates for the lower potential surface retain unity character from crude adiabatic basis state 1 (i.e. \( C_{1,l}=1 \)) and zero character from basis state 2 (i.e. \( C_{2,l}=0 \)). As the coupling strength increases, however, the degree of mixing...
between the two electronic manifolds increases monotonically, but not uniformly, for each of the energy levels. Provided that physical characteristics (e.g. dipole moments) can be associated with the crude adiabatic basis states, this disparate behavior suggests that vibronic interactions could result in the manifestation of large differences in molecular properties from one vibrational level to the next. At sufficiently high values of the coupling parameter, the levels begin to "cross" with respect to their fractional parentage in the crude adiabatic basis set. This phenomenon, which is exhibited by vibrational levels 1 and 2 in the vicinity of the optimum vibronic interaction strength proposed by Innes (viz. $\beta=3138\text{cm}^{-1}$), will lead to still greater irregularities in the vibrational dependence of molecular properties. A similar analysis performed upon formalddehyde-$d_2$ indicates even more pronounced variations in basis character distribution. This behavior is clearly demonstrated by the values of the $(C_{k,i})^2$ coefficients which have been compiled in table 1-VIII. The large discrepancies which exist between the parentages of $\text{H}_2\text{CO}$ and $\text{D}_2\text{CO}$ vibrational levels imply that anomalous isotopic effects could result from such vibronic interactions.

Figure 1-23 illustrates the vibronic coupling dependence of eigenvalues and eigenfunctions corresponding to the upper potential curve (i.e. the $\tilde{B}^1\text{B}_2$ state) of the Innes model for formaldehyde-$h_2$. As the magnitude of the coupling parameter $\beta$ increases, the energy levels are characterized by an increase in vibrational frequency and the development of a (more typical) negative anharmonicity. This behavior can be rationalized in terms of a vibronically induced modification of the potential surface away from the harmonic form assumed in the crude adiabatic basis. In contrast to the situation depicted in figure 1-22 (i.e. for the lower potential surface), the eigenstates of the upper potential surface exhibit much smaller and more uniform variations in their fractional parentage as a function of the vibronic
a. \((C_{k,jt})^2\) Fractional Parentage Coefficients for Formaldehyde-\(h_2\)

<table>
<thead>
<tr>
<th>t</th>
<th>((C_{1,tt})^2)</th>
<th>((C_{2,tt})^2)</th>
<th>((C_{1,2t})^2)</th>
<th>((C_{2,2t})^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.93604</td>
<td>0.06396</td>
<td>0.00888</td>
<td>0.99122</td>
</tr>
<tr>
<td>1</td>
<td>0.90296</td>
<td>0.09704</td>
<td>0.02380</td>
<td>0.97620</td>
</tr>
<tr>
<td>2</td>
<td>0.91441</td>
<td>0.08559</td>
<td>0.03718</td>
<td>0.96282</td>
</tr>
<tr>
<td>3</td>
<td>0.89006</td>
<td>0.10994</td>
<td>0.04928</td>
<td>0.95072</td>
</tr>
<tr>
<td>4</td>
<td>0.88021</td>
<td>0.11979</td>
<td>0.06030</td>
<td>0.93970</td>
</tr>
<tr>
<td>5</td>
<td>0.86974</td>
<td>0.13026</td>
<td>0.07039</td>
<td>0.92961</td>
</tr>
</tbody>
</table>

b. \((C_{k,jt})^2\) Fractional Parentage Coefficients for Formaldehyde-\(d_{2}\)

<table>
<thead>
<tr>
<th>t</th>
<th>((C_{1,tt})^2)</th>
<th>((C_{2,tt})^2)</th>
<th>((C_{1,2t})^2)</th>
<th>((C_{2,2t})^2)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>0.93278</td>
<td>0.06722</td>
<td>0.00686</td>
<td>0.99314</td>
</tr>
<tr>
<td>1</td>
<td>0.90777</td>
<td>0.09223</td>
<td>0.01882</td>
<td>0.98118</td>
</tr>
<tr>
<td>2</td>
<td>0.92660</td>
<td>0.07340</td>
<td>0.02977</td>
<td>0.97023</td>
</tr>
<tr>
<td>3</td>
<td>0.90027</td>
<td>0.09973</td>
<td>0.03986</td>
<td>0.96014</td>
</tr>
<tr>
<td>4</td>
<td>0.89202</td>
<td>0.10798</td>
<td>0.04921</td>
<td>0.95079</td>
</tr>
<tr>
<td>5</td>
<td>0.88193</td>
<td>0.11807</td>
<td>0.05789</td>
<td>0.94211</td>
</tr>
</tbody>
</table>

Table 1-VIII: \((C_{k,jt})^2\) Parentage Coefficient from the Innes Model.
coupling strength.

For each vibronic state, ψ_{jl}(r,Q), the corresponding dipole moment, μ_{jl}, is defined by the expectation value of the dipole moment operator μ(r,Q). By utilizing the results of the Innes model to expand the exact molecular eigenstates as a linear combination of the crude adiabatic wavefunctions (cf. equation (1.44)), the measured values for these physical observables can be formulated in the following manner:

\[ μ = \{ψ_{jl}(r,Q)|μ(r,Q)|ψ_{jl}(r,Q)\} \]

\[ = \sum_{kσ} \sum_{iσ} (c_{kσ,jl})^* c_{iσ,jl} \{ψ_{kσ}^{CA}(r,Q)|μ(r,Q)|ψ_{iσ}^{CA}(r,Q)\} \]

\[ = \sum_{kσ} \sum_{iσ} (c_{kσ,jl})^* c_{iσ,jl} (χ_{kσ}^{CA}(Q)|ψ_{kσ}^0(r,Q_0)|μ(r,Q)|ψ_{iσ}^0(r,Q_0)|χ_{iσ}^{CA}(Q)) \]  

(1.47)

where the separability of the crude adiabatic functions has been employed to decouple the integrations over nuclear and electronic coordinates.

An approximate separation between nuclear and electronic degrees of freedom in the dipole moment operator, μ(r,Q), can be accomplished by performing a Taylor series expansion, in the displacement coordinate Q, about the reference configuration Q_0:

\[ μ(r,Q) = μ(r,Q_0) + \left(\frac{∂μ(r,Q)}{∂Q}\right)_0 Q + \frac{1}{2} \left(\frac{∂^2μ(r,Q)}{∂Q^2}\right)_0 Q^2 + \cdots \]  

(1.48)

where the partial derivatives, evaluated at Q = Q_0, are dependent only upon the electronic coordinates. Equation (1.48) constitutes an expression for the electrical
anharmonicity [133] associated with the charge distribution in the molecular framework. The effects of mechanical anharmonicity [133], which stem from the shape of the electronic potential surface used to constrain the nuclear degrees of freedom, are embodied in the wavefunction expansion coefficients (cf. equation (1.44)) determined via the Innes vibronic coupling model.

Substitution of expansion (1.48) into equation (1.47) and separation of integrations over nuclear degrees of freedom from those which involve only electronic coordinates, yields the following expression for the dipole moment in vibronic state \( \psi_{jt}(r,Q) \):

\[
\mu_{jt} = \{ \psi_{jt}(r,Q)|\mu(r,Q)|\psi_{jt}(r,Q) \} \\
= \sum_{ks} \sum_{i} (c_{ks,jt})^* c_{is,jt} \langle \psi_k^0(r,Q_0)|\mu(r,Q_0)|\psi_i^0(r,Q_0) \rangle \\
+ \sum_{ks} \sum_{i} (c_{ks,jt})^* \langle \psi_k^0(r,Q_0)| \left( \frac{\partial \mu(r,Q)}{\partial Q} \right)_0 |\psi_i^0(r,Q_0) \rangle \\
\times \frac{1}{\sqrt{2T}} \left( \sqrt{s+1} c_{is+1,jt} + \sqrt{s} c_{is-1,jt} \right) \\
+ \sum_{ks} \sum_{i} (c_{ks,jt})^* \langle \psi_k^0(r,Q_0)| \left( \frac{\partial^2 \mu(r,Q)}{\partial Q^2} \right)_0 |\psi_i^0(r,Q_0) \rangle \\
\times \frac{1}{2T} \left( \frac{\sqrt{(s+1)(s+2)}}{2} c_{is+2,jt} \\
+ \frac{s+1}{2} c_{is,jt} \\
+ \frac{\sqrt{s(s-1)}}{2} c_{is-2,jt} \right) 
\] (1.49)
where the identical harmonic structure of the crude adiabatic potential surfaces employed in the Innes model has permitted evaluation of the matrix elements for \( Q \) in terms of the well-known harmonic oscillator expressions [131] (n.b. \( T=2\pi\nu/\hbar \)).

By restricting attention to the first term in equation (1.49), which corresponds to complete neglect of the electrical anharmonicity within the molecular framework, the dipole moment of vibronic state \( \psi_{jt}(r, Q) \) can be reformulated as follows:

\[
\mu_{jt} = \sum_{k_0} |c_{k_0, j}\|^2 \mu_{kk}^0 + \sum_{k_0} \sum_{i \neq k} (c_{i_0, j})^* c_{i_0, j} \mu_{ki}^0
\]

\[
= \sum_{k} (C_{k, j})^2 \mu_{kk}^0 + \sum_{k_0} \sum_{i \neq k} (c_{i_0, j})^* c_{i_0, j} \mu_{ki}^0
\]

(1.50)

where \( \mu_{kk}^0=\langle \psi_k^0(r, Q) | \mu(r, Q_0) | \psi_k^0(r, Q_0) \rangle \) is the permanent electric dipole moment for crude adiabatic state \( k \) and \( \mu_{ki}^0=\langle \psi_k^0(r, Q_0) | \mu(r, Q_0) | \psi_i^0(r, Q_0) \rangle \) denotes a dipole transition moment between crude adiabatic states \( k \) and \( i \). The \( (C_{k, j})^2 \) fractional parentage coefficients have been defined in equation (1.45) and their values, determined via the Innes model, are compiled in table 1-VIII. Expression (1.50) suggests that the dipole moments observed in the \( \tilde{A}^1\textrm{A}_2 \) and \( \tilde{B}^1\textrm{B}_2 \) electronic manifolds are derived from vibronically-induced mixing of permanent and transition dipole moment character between the crude adiabatic potential surfaces.

Equation (1.50), when applied to the two crude adiabatic potential surfaces of the Innes vibronic coupling model, suggests that the observed dipole moments in the \( \nu_4 \) out-of-plane bending mode of formaldehyde will be given by:
\[ \mu_{1t} = (C_{1,1t})^2 \mu_{11}^0 + (C_{2,1t})^2 \mu_{22}^0 + 2 \text{Re} \left( \mu_{12}^0 \sum_s (c_{1s,1t}^s)^* c_{2s,1t}^s \right) \]  

(1.51)

for the \( \tilde{A}^1A_2 \) state (i.e. state 1) and

\[ \mu_{2t} = (C_{1,2t})^2 \mu_{11}^0 + (C_{2,2t})^2 \mu_{22}^0 + 2 \text{Re} \left( \mu_{12}^0 \sum_s (c_{1s,2t}^s)^* c_{2s,2t}^s \right) \]  

(1.52)

for the \( \tilde{B}^1B_2 \) state (i.e. state 2).

The dipole moment expressions can be further simplified by recognizing that the vibronic interaction between the crude adiabatic potential surfaces (cf. equation (1.41)) is antisymmetric with respect to the nuclear displacement (i.e. vibrational) coordinate \( Q \). Consequently, a rigorous set of *selection rules* will be obtained for the \( c_{k_0,j} \) coefficients utilized in the expansion of the exact molecular eigenstates:

for \( k = j \):

\[ c_{k_0,j} = 0 \quad \text{if} \quad s = t \pm 1, t \pm 3, \ldots \]  

(1.53)

for \( k \neq j \):

\[ c_{k_0,j} = 0 \quad \text{if} \quad s = t, t \pm 2, \ldots \]

These *selection rules* are readily verified by examination of the eigenvectors obtained through diagonalization of the total Hamiltonian matrix defined in equations (1.42) and (1.43).

The \( c_{k_0,j} \) *selection rules* suggest that the final terms in equations (1.51) and (1.52), which will always satisfy one of the conditions stipulated in expression (1.53), are rigorously zero. Therefore, in the absence of electrical anharmonicity, the dipole moments for the vibrational levels in the \( \tilde{A}^1A_2 \) and \( \tilde{B}^1B_2 \) electronic states of formaldehyde will be given by:
\[ \mu_{1t} = (C_{1,1t})^2 \mu_{11}^0 + (C_{2,1t})^2 \mu_{22}^0 \]  

(1.54)

and

\[ \mu_{2t} = (C_{1,2t})^2 \mu_{11}^0 + (C_{2,2t})^2 \mu_{22}^0. \]  

(1.55)

In order for equations (1.54) and (1.55) to be of use, the crude adiabatic dipole moments \( \mu_{11}^0 \) and \( \mu_{22}^0 \) must be determined. Since our primary concern is with the predictions which the Innes model will provide for the vibrational dependence of the dipole moment function, the measured dipole moments in the vibrationless levels of the \( \tilde{A}^1A_2 \) and \( \tilde{B}^1B_2 \) electronic manifolds \( \text{(viz. } \mu_{10} \text{ and } \mu_{20} \text{)} \) can be utilized for the evaluation of the \( \mu_{kk}^0 \) parameters. As a result, all calculated vibronic dipole moments, \( \mu_{jk} \), will be normalized (\( i.e. \) scaled) with respect to the experimental values for \( \mu_{k0}^0 \).

The work discussed in this Chapter has provided extremely precise dipole moments for the vibrationless levels \( \text{(viz. } v_4 = 0) \) of \( \tilde{A}^1A_2 \) formaldehyde-\( h_2 \) and formaldehyde-\( d_2 \). On the basis of our quantum beat investigations, the values of \( \mu_{10} \) for \( H_2CO \) and \( D_2CO \) are found to be \( \sim 1.48D \) and \( \sim 1.47D \) respectively. In a spectroscopic study based upon the phenomenon of electrochromism [134, 135, 136], Causley and Russell [137, 138] have determined that the dipole moment of the \( \tilde{B}^1B_2 \) state \( \text{(i.e. } \mu_{10} \text{)} \) is \(-0.33 \pm 0.14D. \) The negative sign indicates that the moment is oppositely oriented with respect to that of the \( \tilde{X}^1A_1 \) ground state \( \text{(i.e. the electron density has moved from the oxygen end of the molecule towards the hydrogens). Although this experimental measurement is considerably smaller than the } -3.07D \text{ value predicted by Harding and Goddard [139] in their recent } ab \text{ initio calculations, the large magnitude of the dipole moment change between the } \tilde{B}^1B_2 \)
and $\widetilde{X}^1A_1$ states (viz. $-0.33D$ vs. $2.33D$) appears to confirm the assignment of the $\widetilde{B}$ electronic manifold as a molecular Rydberg state [88].

The values of $\mu_{j0}$ specified above, together with the $(C_{k,j0})^2$ fractional parentage coefficients presented in table 1-VIII, transform equations (1.54) and (1.55) into a system of two coupled algebraic equations in two unknowns (viz. $\mu_{11}^0$ and $\mu_{22}^0$). Solution of this set of linear equations for the crude adiabatic dipole moments in states 1 and 2 yields:

$$\begin{align*}
\text{for } H_2CO: & \quad \mu_{11}^0 = 1.60D \quad \mu_{22}^0 = -0.33D \\
\text{for } D_2CO: & \quad \mu_{11}^0 = 1.60D \quad \mu_{22}^0 = -0.34D
\end{align*}$$ (1.58)

With these values for the crude adiabatic $\mu_{kk}^0$ parameters, the vibrational dependence of the dipole moment function, as predicted by the Innes vibronic coupling formalism, can be readily determined via equations (1.54) and (1.55). Table 1-IX contains the $\widetilde{A}^1A_2$ and $\widetilde{B}^1B_2$ dipole moments calculated for the six lowest vibrational levels in the $\nu_4$ out-of-plane bending modes of $H_2CO$ and $D_2CO$. Figure 1-24 highlights the variations in the vibronic dipole moments which would be expected for the $\widetilde{A}$ state Stark measurements discussed in this Chapter.

Table 1-IX demonstrates that the calculated dipole moments for the $\widetilde{A}^1A_2$ electronic manifold exhibit an overall decrease in magnitude as the degree of excitation in the $\nu_4$ out-of-plane bending mode increases. This trend, illustrated by the downward sloping lines in figure 1-24, is consistent with that observed in the $\widetilde{X}^1A_1$ ground electronic potential surface of formaldehyde [50]. Indeed, the predicted dipole moment variations for the higher vibrational levels of the $\widetilde{A}$ state agree semi-quantitatively with those suggested on the basis of a Taylor series
a. Calculated Dipole Moments<sup>a</sup> in Formaldehyde-$h_2$

<table>
<thead>
<tr>
<th>$v_4$ Quanta</th>
<th>$\tilde{A}^1A_2$ State</th>
<th>$\tilde{B}^1B_2$ State</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.48</td>
<td>-0.33</td>
</tr>
<tr>
<td>1</td>
<td>1.42</td>
<td>-0.30</td>
</tr>
<tr>
<td>2</td>
<td>1.43</td>
<td>-0.27</td>
</tr>
<tr>
<td>3</td>
<td>1.39</td>
<td>-0.25</td>
</tr>
<tr>
<td>4</td>
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<td>-0.23</td>
</tr>
<tr>
<td>5</td>
<td>1.35</td>
<td>-0.21</td>
</tr>
</tbody>
</table>

<sup>a</sup> Normalized to experimental values (in Debye) for $v_4=0$ in $\tilde{A}^1A_2$ and $\tilde{B}^1B_2$ states.

**Table 1-IX:** Dipole Moments Predicted by the Innes Model.
b. Calculated Dipole Moments\(^a\) in Formaldehyde-\(_2^d\) 

<table>
<thead>
<tr>
<th>(v_4) Quanta</th>
<th>(\tilde{A} ,^1A_2) State</th>
<th>(\tilde{B} ,^1B_2) State</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>-0.33</td>
</tr>
<tr>
<td>1</td>
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<td>-0.29</td>
</tr>
<tr>
<td>3</td>
<td>1.41</td>
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<tr>
<td>4</td>
<td>1.39</td>
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</tr>
<tr>
<td>5</td>
<td>1.37</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

\(^a\) Normalized to experimental values (in Debye) for \(v_4=0\) in \(\tilde{A} \,^1A_2\) and \(\tilde{B} \,^1B_2\) states.

Table 1-IX, concluded.
Figure 1-24: Predicted $\tilde{A}^1A_2$ State Dipole Moments.

The vibrational dependence of the $\tilde{A}^1A_2$ dipole moments predicted by the Innes vibronic coupling model is illustrated for both formaldehyde-$h_e$ and formaldehyde-$d_e$. The solid line is only meant as a guide to indicate the general trends associated with the calculated dipole moments.
The diagram shows the relationship between vibrational quanta and dipole moment for two different isotopologues of H$_2$CO:

- $\tilde{A}^1A_2$ H$_2$CO
- $\tilde{A}^1A_2$ D$_2$CO

The dipole moment is measured in Debye, and the vibrational quanta range from 0 to 5.
expansion performed along the $\nu_4$ coordinate of the $\tilde{X}$ state (viz. a decrease of $\sim 0.02\text{D}$ per quantum of $\nu_4$ excitation) [11].

In contrast to the monotonic dipole moment variations predicted for both the $\tilde{B}$ state and the higher energy regions of the $\tilde{A}$ state, the Innes model suggests that the lower vibrational levels of $\tilde{A}\,^1A_2$ formaldehyde will exhibit drastic changes in the molecular dipole moment from one vibrational level in the $\nu_4$ manifold to the next. This anomalous behavior has been rationalized above in terms of the "crossings" which can occur among the $(C_{k,j})^2$ fractional parentage coefficients (c.f. figure 1-22) as a result of the vibronic coupling mechanism. Figure 1-24 indicates that the dipole moments have become so perturbed that they should display a staggered pattern in which $\mu_{11} < \mu_{10} \approx \mu_{12}$. The expected fluctuations in the dipole moment function tend to subside as the degree of excitation in the $\nu_4$ mode increases. This effect can be correlated with the fact that the higher vibrational levels are further removed from the barrier to inversion introduced by vibronic interaction into the $\tilde{A}\,^1A_2$ potential surface (c.f. energy level diagrams in figures 1-14 and 1-14). Table 1-IX also indicates that an unusually large isotopic dependence of the $\tilde{A}\,^1A_2$ dipole moments (i.e. $0.02 \sim 0.03$ Debye) can be expected for $\nu_4 \geq 2$.

The dipole moments derived from the Stark quantum beat studies fail to quantitatively follow the predictions of the Innes model. Although vibronic coupling arguments would suggest a dipole moment decrease of $\sim 0.06\text{D}$ between the $\nu_4=0$ and $\nu_4=1$ levels of $\tilde{A}\,^1A_2$ formaldehyde, our measurements indicate a change of only $\sim 0.02\text{D}$ in $\text{H}_2\text{CO}$ and even less in its deuterated analog. Nonetheless, the experimental dipole moments do exhibit variations which cannot be accounted for in terms of a Taylor series expansion (i.e. of the dipole moment) along the $\nu_4$ out-of-plane bending coordinate [11]. This point will be examined further in the ensuing
discussion. According to the calculations summarized in table I-IX, the effects of
the vibronic interaction upon the molecular dipole moment function should be most
clearly exhibited by the \( v_4 = 2 \) vibrational level of formaldehyde-\( d_2 \). Unfortunately,
the lack of any reported spectroscopic assignments for the \( D_2CO \ 4^2 \) band precluded
its examination in the present quantum beat experiments.

The inability of the Innes model to account for the measured dipole moments
in formaldehyde is quite surprising in view of the extraordinary success which this
approach has demonstrated in explaining the distorted vibrational structure of the
\( \tilde{\Delta} \ A_{2} \) electronic manifold. This failure is all the more puzzling when one considers
that completely analogous vibronic coupling schemes have been widely exploited in
the analysis of molecular moments for intrinsically more complicated (viz. larger)
polyatomic systems [128, 129, 127]. At least part of the responsibility for this lack
of quantitative agreement between theory and experiment might be attributed to
the complete neglect of electrical anharmonicity (cf. equation (1.49)) which was
made in order to derive the simplified dipole moment expressions in equations (1.54)
and (1.55). Incorporation of these additional factors would tend to smooth out the
gross variations in the dipole moment function predicted by the above calculations.

One additional point regarding the applicability of the Innes vibronic coupling
model merits consideration. The previous analysis has depended upon experimental
measurements for the dipole moments in the vibrationless levels of the \( \tilde{\Delta} \ A_{2} \) and
\( \tilde{\Delta} \ B_{2} \) electronic manifolds (viz. \( \mu_{10} \) and \( \mu_{20} \) respectively) in order to provide a
viable method for determining the crude adiabatic \( \mu_{kk}^{0} \) parameters (cf. equation
(1.56)). All predicted dipole moments, \( \mu_{j0} \), were therefore scaled with respect to
these \( \mu_{j0} \) quantities. However, the Causley and Russell [137] value for \( \mu_{20} \),
\(-0.33 \pm 0.14 \)D, differs significantly from that suggested by \textit{ab initio} calculations (i.e.
\(-3.07 \)D [139]).
An alternative procedure for the evaluation of the crude adiabatic $\mu_{kk}^0$ parameters relies on the measured dipole moments in the first two vibrational levels of formaldehyde-$h_2$ (viz. $\mu_{10} \sim 1.478$D and $\mu_{11} \sim 1.468$D from the $2_{1,1}$ rotational levels). By substituting these experimentally-determined quantities and the corresponding fractional parentage coefficients (cf. table I-IX) into the system of algebraic equations contained in expression (1.54), one obtains the following values:

$$\mu_{11}^0 = 1.497D \quad \text{and} \quad \mu_{22}^0 = 1.195D$$

(1.57)

The vibronic dipole moments associated with the $\bar{A}^1A_2$ and $\bar{B}^1B_2$ electronic manifolds of formaldehyde can now be determined from equations (1.54) and (1.55). The values suggested on the basis of the crude adiabatic parameters in expression (1.57) have been compiled in table 1-X.

A close inspection of the calculated dipole moments in table 1-X, which are all scaled with respect to the experimental $\mu_{10}$ and $\mu_{11}$ values for $H_2CO$, reveals a vibrational dependence which closely mimics the patterns observed in the quantum beat studies. In particular, the prediction for the $v_4 = 0$, $v_4 = 1$, and $v_4 = 3$ levels of formaldehyde-$d_2$ agree quite well with the results of our Stark measurements. It is interesting to note that the gross vibrational and isotopic variations in the dipole moment function indicated by our previous analysis no longer appear when the crude adiabatic parameters of expression (1.57) are utilized.

The results summarized in table 1-X suggest that the dipole moment associated with the upper electronic potential surface in the vibronic coupling scheme is $\sim 1.20$D. This value is seriously at variance with the widely accepted assignment of the $\bar{B}^1B_2$ manifold as a molecular Rydberg state (cf. reference [88] for a synopsis of the experimental observations which support this assignment).
a. Calculated Dipole Moments\textsuperscript{a} in Formaldehyde-$\textit{h}_e$

<table>
<thead>
<tr>
<th>$v_4$ Quanta</th>
<th>$\tilde{A}^1A_2$ State</th>
<th>$\tilde{B}^1B_2$ State</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.478</td>
<td>1.198</td>
</tr>
<tr>
<td>1</td>
<td>1.468</td>
<td>1.202</td>
</tr>
<tr>
<td>2</td>
<td>1.471</td>
<td>1.206</td>
</tr>
<tr>
<td>3</td>
<td>1.464</td>
<td>1.210</td>
</tr>
<tr>
<td>4</td>
<td>1.461</td>
<td>1.213</td>
</tr>
<tr>
<td>5</td>
<td>1.458</td>
<td>1.216</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Normalized to experimental values (in Debye) for $v_4=0$ and $v_4=1$ in $\tilde{A}^1A_2$ $\textit{H}_2\textit{CO}$.

\textbf{Table 1-X:} Predicted Dipole moments in $\tilde{A}^1A_2$ and $\tilde{B}^1B_2$ Formaldehyde.
b. Calculated Dipole Moments\(^a\) in Formaldehyde-\(d_x\)

<table>
<thead>
<tr>
<th>(\nu_4) Quanta</th>
<th>(\tilde{A} , ^1A_2) State</th>
<th>(\tilde{B} , ^1B_2) State</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.477</td>
<td>1.197</td>
</tr>
<tr>
<td>1</td>
<td>1.469</td>
<td>1.201</td>
</tr>
<tr>
<td>2</td>
<td>1.475</td>
<td>1.204</td>
</tr>
<tr>
<td>3</td>
<td>1.467</td>
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<tr>
<td>4</td>
<td>1.465</td>
<td>1.210</td>
</tr>
<tr>
<td>5</td>
<td>1.462</td>
<td>1.213</td>
</tr>
</tbody>
</table>

\(^a\) Normalized to experimental values (in Debye) for \(\nu_4=0\) and \(\nu_4=1\) in \(\tilde{A} \, ^1A_2\) \(H_2CO\).

**Table 1-X**, concluded.
However, on the basis of perturbations appearing in their electrochromism measurements of the $\tilde{B}^1B_2 \leftarrow \tilde{X}^1A_1$ (3s $\leftarrow$ n) transition, Causley and Russell [137, 138] have asserted that additional excited states of identical electronic symmetry (viz. $^1B_2$) must exist in the same energy region as the $\tilde{B}$ Rydberg state. The presence of other electronic manifolds has also been indicated by spectroscopic experiments [140] performed under conditions which suppress the intense Rydberg transition (i.e. high-pressure gas phase or condensed phase studies). It is possible that these unidentified $^1B_2$ electronic states play a significant role in the Innes model for the $\tilde{A}^1A_2$ potential surface. Since the predicted 1.20D dipole moment is quite reasonable for a valence state in the formaldehyde system, further investigations might be able to correlate the present dipole moment studies with the position of the $^1B_2 \leftarrow ^1A_1 \sigma^* \leftarrow n$ transition which, despite numerous ab initio calculations [141, 142, 99], has eluded all attempts at experimental identification.

1.6.4 Additional Effects Observed

The quantum beat techniques exploited in the formaldehyde studies have provided the unique ability to examine, with an unparalleled degree of precision, small energy separations within excited electronic states. The extraordinary resolution afforded by this coherent spectroscopic probe is affirmed through the $\leq 50\text{KHz}$ residuals typically obtained in the regression of our Stark measurements to molecular dipole moments. However, in the case of the $^2_0,2$ rotational eigenstate within the $v_4 = 1$ vibrational level of $\tilde{A}^1A_2$ H$_2$CO, the electric field dependence of the quantum beat frequency exhibits an abrupt deviation (i.e. $> 300\text{KHz}$) from the monotonically increasing pattern expected on the basis of a simple dipole moment analysis. As illustrated in figure 1-25, this anomaly occurs in the vicinity of 2.4KV/cm and extends over a relatively narrow range of applied field (i.e.
Figure 1-25: Anomalous Quantum Beat Frequencies in the $2_{0,2}$ Rovibronic Level.
\[ H_2CO \quad \tilde{A}^1A_2 \quad \nu_4 = 1 \quad 2_{0.2} \]
< 500V/cm). The solid line in this diagram represents the Stark tuning curve calculated for an a-axis dipole moment of 1.45550(58)D which was determined from the data sets far removed from the region of aberrant behavior.

A careful examination of the time-resolved quantum beat data for the 2_{0,2} rovibronic eigenstate revealed that the frequency deviations at \( \mathcal{E}_2 = 2.4 \text{KV/cm} \) (nb. the subscript will be explained below) were accompanied by an abrupt enhancement in the fluorescence decay rate. A similar lifetime anomaly was discovered at \( \mathcal{E}_1 = 4.8 \text{KV/cm} \), although no departure from the expected pattern of coherent oscillations could be detected at this point. Figure 1-26 contrasts the time-resolved signals obtained at \( \mathcal{E}_1 \) and \( \mathcal{E}_2 \) with that observed at zero applied electric field. Additional experiments [143] indicated a dramatic decrease in the fluorescence quantum yield at both \( \mathcal{E}_1 \) and \( \mathcal{E}_2 \). All of the aberrant behavior exhibited by the 2_{0,2} level (i.e. enhanced decay rate, diminished quantum yield, and quantum beat anomalies) was demonstrated to have a strong dependence upon the polarization characteristics of the excitation and detection processes.

A viable explanation for the anomalies encountered in the 2_{0,2} eigenstate can be derived from the prevalent \( S_1 \sim S_0 \) nonadiabatic interactions which are known to exist within the \( v_4 = 1 \) vibrational manifold of \( \widetilde{A}^1A_2 \) formaldehyde-\( h_2 \) [19]. From this viewpoint, the dramatic variations in fluorescence lifetime and quantum yield observed as a function of the applied electric field can be interpreted in terms of the relative Stark tuning between the rovibronic structure of the \( \widetilde{A}^1A_2 \) (i.e. \( S_1 \)) state and the background of highly-excited, predissociative levels from the \( \widetilde{X}^1A_1 \) (i.e. \( S_0 \)) ground state [24, 22, 25]. By shifting \( S_1 \) and \( S_0 \) levels into resonance with one another, the Stark effect can greatly enhance the coupling between the two electronic potential surfaces. The resulting admixture of \( S_0 \) character into \( S_1 \) eigenstates provides a mechanism whereby the radiative and nonradiative properties
Figure 1-26: Lifetime Variations in the $2_{0,2}$ Rovibronic Level.

The field dependent lifetime variations encountered in the $2_{0,2}$, \(v_4 = 1\) rovibronic level of $\tilde{A}^1A_2$ formaldehyde-\(h_2\) are illustrated. The dashed line denotes the time-resolved fluorescence signal observed at zero applied field. These data were obtain with unpolarized detection. The double exponential decay can be attributed both to a slight overlap in the pump spectroscopic transition and to collisional relaxation processes (cf. Chapter 2).
E = 2401.48(42) Volts/cm

E = 4812.67(82) Volts/cm
of $\tilde{A}^1A_2$ rovibronic levels can be drastically altered. The abrupt nature and polarization dependence of the aberrant behavior associated with the $2_{0,2}$ eigenstate suggests the occurrence of $M$-specific interactions with a single $S_0$ background level.

The anomalous behavior exhibited by the $2_{0,2}$ eigenstate can be rationalized in terms of the energy level scheme presented in figure 1-27. Since the ground electronic state of formaldehyde has a dipole moment considerably larger than that associated with the first excited singlet state (viz. $\sim 2.33$D vs. $\sim 1.46$D), the application of an electric field can lead to quite different displacements of the rovibronic structure within the $S_1$ and $S_0$ manifolds. This will enable the Stark effect to tune individual $M$-components from the two electronic potential surfaces into resonance with one another. Provided that the rigorous $\Delta M = 0$ selection rule is satisfied, the magnetic sublevels will undergo avoided crossings (at the points of resonance) with the concomitant admixture of substantial $S_0$ character into the $S_1$ state. Since the highly excited $\tilde{X}^1A_1$ rotation-vibration levels are predissociative and incapable of relaxing via spontaneous emission (i.e. on a reasonably short time scale), these nonadiabatic $S_1 \sim S_0$ interactions will translate into significant field-dependent variations in the fluorescence lifetime and quantum yield observed from the $\tilde{A}$ state.

Figure 1-27 depicts the influence of the Stark effect on the coupling of the $2_{0,2}$ rovibronic eigenstate with a single rotation-vibration level from the ground electronic potential surface. As suggested by the above discussion, the $S_1 \sim S_0$ interactions between the $|M| = 2$ and $|M| = 1$ sublevels, which occur at field strengths of $\mathcal{E}_2 = 2.4$KV/cm and $\mathcal{E}_1 = 4.8$KV/cm respectively (nb. the correlation between $|M|$ and the subscripts on $\mathcal{E}_1$ and $\mathcal{E}_2$), will be accompanied by a substantial reduction in the fluorescence lifetime and quantum yield observed from the $\tilde{A}$ state.
Figure 1-27: Energy Level Diagram for $S_1 \sim S_0$ Interaction.
The polarization characteristics of the experimentally detected anomalies, as well as the dependence of the Stark tuning rates on the magnetic quantum number, substantiate the correlation of \( \mathcal{E}_2 \) with the \(|M| = 2\) resonance and \( \mathcal{E}_1 \) with the \(|M| = 1\) resonance. Since the \(|M| = 2\) components of the \(2_{0,2}\) level are involved in the coherent superposition which produces the quantum beat signal, a deviation from the normal pattern of quantum beat frequencies will be expected in the vicinity of the \( \mathcal{E}_2 \) anticrossing. In contrast, no aberrant quantum beat behaviour should be encountered for the \(|M| = 1\) resonance at \( \mathcal{E}_1 \) (i.e. the \(|M| = 1\) levels are not involved in the \( \Delta M = 2\) quantum beat coherence). While nonadiabatic coupling of the \( M = 0 \) sublevels is permitted, the exceptionally small Stark shifts associated with these magnetic components (c.f. figure 1-2) makes it quite improbable that a suitable \( S_1 \sim S_0 \) resonance condition will be attained. Note that the crossing between the \( M = 0 \) and \(|M| = 1\) levels, which occurs at \( \mathcal{E} \approx 4\text{KV/cm} \), does not lead to any observable consequences since mixing of rovibronic character is strictly prohibited by the \( \Delta M = 0 \) selection rule.

The most significant aspect of the anomalies encountered in the present study of the \( 2_{0,2} \) rovibronic level stems from the fact that they provide a "window" through which the unique spectroscopic and dynamical properties of highly excited \( \tilde{X}^1A_1 \) eigenstates can be examined. By performing a suitable modelling [23] of the fluorescence lifetime, quantum yield, and quantum beat data, the magnitude of the \( S_1 \sim S_0 \) nonadiabatic coupling parameter and the linewidth of the predissociatively-broadened \( S_0 \) rotation-vibration level can be directly determined. The lifetime of the highly excited \( \tilde{X} \) state can be correlated with the tunneling rate for dissociation of formaldehyde to \( \text{H}_2 \) and \( \text{CO} \). In this manner, the height of the barrier to dissociation, a quantity of considerable interest to both theoreticians [144, 86, 145, 146, 147] and experimentalists [148, 149, 19], can be
ascertained. The results of an analysis based upon the energy level scheme in figure 1-27 are discussed at greater length in references [23] and [150].

The time-resolved fluorescence decay curves obtained during our Stark measurements on the $2_{1,1}$ rovibronic eigenstate in the $v_4 = 3$ vibrational level of $\tilde{A}^1A_2$ formaldehyde-$d_8$ exhibited unmistakable evidence for the presence of several, slightly incommensurate quantum beat frequencies (viz. the quantum beat pattern seemed to dephase and rephase on the $5\mu$s time scale of the observations). This supposition was confirmed by Fourier analysis of the oscillatory structure superimposed upon the exponentially damped fluorescence background. Although two or more independent modulation frequencies were indicated by the Fourier transforms, in most cases their vastly different amplitudes prohibited convergence of our least squares regression procedure for more than two cosine terms (i.e. $N_{osc} = 2$ in equation (1.28)).

Figure 1-28 illustrates the electric field dependence for the pair of quantum beat frequencies determined from the $2_{1,1}$ $v_4 = 3$ Stark measurements in $\tilde{A}^1A_2$ formaldehyde-$d_8$. The separation between the two oscillations averages $\sim 391$KHz and exhibits a slight increase as a function of the applied field strength. A linear least-squares regression performed upon the splittings suggests a zero-field intercept of $\sim 236$KHz with a differential tuning rate of $0.16$KHz/(V/cm). For each data set (i.e. each value of the applied electric field), the high frequency component has a relative amplitude (viz. $A_{\beta,j}$ in equation (1.28)) of $\sim 0.2$ as compared to that of the lower frequency modulation. Attempts to incorporate a third quantum beat into the analysis were not entirely successful but did suggest the presence of an additional low frequency oscillation (i.e. $\sim 100$KHz below the low frequency component ascribed to each data set) with $\sim 50$ times less intensity than the most pronounced modulation.
Figure 1-28: Multiple Quantum Beat Frequencies in $v_4 = 3 \tilde{A} {^1A}_2 D_2 CO$. 
While a detailed analysis of the multiple quantum beats encountered in the $v_4 = 3$ level was not attempted at the present time, it is almost certain that this behavior can be attributed to nuclear hyperfine structure within the target rovibronic eignestate (viz. $2_{1,1}$). The principal mechanism for hyperfine coupling in a spinless molecule such as formaldehyde-$d_2$ entails electrostatic interaction of the deuteron quadrupole moments with the surrounding nonspherical distribution of electronic charge [46]. When properly interpreted [45, 151], the small spectral modification induced by hyperfine interactions can provide considerable insight into the local (e.g. bond specific) electronic structure of the coupled nuclei [43]. For polyatomic systems, this information is complementary to that determined from electric dipole moment measurements which are sensitive to the global charge distribution within the molecular framework. Hyperfine perturbations in the vibrationless level of $\tilde{X}^1A_1$ formaldehyde have been extensively examined through molecular beam resonance techniques [46, 3]. However, the lack of high resolution (viz. sub-Doppler) spectroscopic probes in the UV-optical region has hampered the study of intrinsically small deuterium quadrupole effects in excited electronic manifolds of polyatomic species.

The nature of the nuclear coupling responsible for the hyperfine structure in formaldehyde-$d_2$ can be appreciated from the multipole expansion derived in equation (1.4). For the present situation, the spherical tensors $T^k(M)$ and $T^k(F)$ must be interpreted as the $k^{th}$ multipole moments for the nuclear and electronic (i.e. extra-nuclear) charge distributions. From this viewpoint, the lowest order term in the expansion (i.e. $k = 0$ or monopole) represents the spherically symmetric Coulombic interaction normally considered in the theory of atomic structure and binding. However, since symmetry restrictions (i.e. parity) strictly prohibit nuclei from possessing permanent electric dipole moments (viz. $T^1(M)$ must be zero) [57].
the next term in the interaction energy is given by:

\[ V^{(2)} = T^2(\Theta) \cdot T^2(\nabla \nabla \Phi) = -(T^2(\Theta) \cdot T^2(\nabla \Phi)) \]  \hspace{1cm} (1.58)

which represents the coupling of the second moment of the nuclear charge distribution, the nuclear quadrupole moment \( \Theta \), with the gradient of the electric field, \( \nabla \Phi = -\nabla \nabla \Phi \), induced by the external distribution of electronic charge. Note that this interaction will vanish if either the nuclear or electronic charge distribution is spherically symmetric (i.e. if \( T^2(M) = 0 \) or \( T^2(F) = 0 \)).

From a classical perspective, the interaction defined by equation (1.58) exerts a torque [2] upon the nucleus which tends to reorient its spin moment in the direction of the field gradient. As a result, the nuclear spin axis will begin to precess about the resultant field gradient. The spectral modifications introduced by the quadrupole coupling can therefore be ascribed to the precessional frequency of the nucleus. Since the local value of the field gradient at the coupling nucleus will depend upon rotational, vibrational, and electronic degrees of freedom, the observed hyperfine structure will vary between individual rovibronic eigenstates.

The presence of resolvable hyperfine structure in the \( v_4 = 3 \) level of \( ^1 \Lambda_2 \rightarrow ^1 \Lambda_2 \) formaldehyde-\( d_2 \) (and not in the \( v_4 = 0 \) and \( v_4 = 1 \) levels) can be rationalized in terms of an increase in the local field gradient experienced by the deuterons (cf. equation (1.58)). A plausible explanation for this change in the electronic charge distribution at the deuterium nuclei can be found in the large amplitude inversion motion which characterizes the first excited singlet state. The effective inversion potentials depicted in figures 1-14 and 1-15 provide a means of determining the structural modifications which accompany the pyramidal distortion of the molecular framework. In particular, the analytical expression for these potential surfaces [90]
permits the turning points for the individual vibrational levels to be associated with an out-of-plane deformation angle, $\rho_{\text{max}}$. Table 1-XI contains a compilation of the $\rho_{\text{max}}$ values calculated, in this manner, for the six lowest vibrational levels in the $\nu_4$ manifolds of $\text{H}_2\text{CO}$ and $\text{D}_2\text{CO}$.

Classical mechanics stipulates that the turning points will be characterized by the complete conversion of kinetic energy into potential energy with a concomitant reduction of the velocity to zero [152]. Therefore, from a classical viewpoint, a molecular system will spend a considerable portion of its vibrational period in the vicinity of the turning points. For $\tilde{\tilde{\text{A}}}$ $^1\text{A}_2$ formaldehyde, this translates into a pronounced tendency for the molecular framework to exist in a pyramidal distortion configuration which places the hydrogen nuclei in close proximity to the $\pi$ electron cloud of the $\text{C}=\text{O}$ bond (cf. molecular orbital diagram in figure 1-17). The values of $\rho_{\text{max}}$ contained in table 1-XI indicate that enhanced vibrational excitation in the $\nu_4$ coordinate will be accompanied by a rapid increase in the degree of nonplanarity exhibited at the turning points (e.g. $\rho_{\text{max}}$ increases by $\sim 12^\circ$ between $\nu_4 = 0$ and $\nu_4 = 3$ in $\text{D}_2\text{CO}$). In the case of formaldehyde-$d_2$, this provides a mechanism whereby the local field gradient at the deuterons and, therefore, the magnitude of the quadrupole hyperfine interaction can be augmented as a function of $\nu_4$ excitation. Similar effects will not be observed in formaldehyde-$h_2$ since the protons, with nuclear spin of $\frac{1}{2}$, cannot support a permanent quadrupole moment [57].
<table>
<thead>
<tr>
<th>$v_4$ Quanta</th>
<th>$\text{H}_2\text{CO}^a$ Turning Point</th>
<th>$\text{D}_2\text{CO}^a$ Turning Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>47.5</td>
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<td>66.6</td>
<td>60.8</td>
</tr>
<tr>
<td>5</td>
<td>70.6</td>
<td>64.2</td>
</tr>
</tbody>
</table>

<br>

$^a$ Out-of-plane deformation angle ($\rho_{max}$ in degrees) at the turning points of potential curve.

**Table 1-XI:** Turning Points in the $v_4$ Manifold of $\tilde{A}^1\text{A}_2$ Formaldehyde.
Chapter 2

Rotational Relaxation in $\tilde{A}^1A_2$ Formaldehyde

2.1 Introduction

The characteristic properties exhibited by electronically excited molecules have attracted considerable attention from researchers involved in various aspects of the physical sciences. In the case of molecular physics, the past two decades have witnessed a renaissance in the study of excited electronic states brought about by the development of powerful new experimental and theoretical methods. The formaldehyde molecular system, the smallest neutral species containing the chemically significant carbonyl chromophore, has assumed a key role in many of these fundamental investigations. Formaldehyde owes this unique position to the fact that, while it is still small enough to be quite amenable to detailed spectroscopic and theoretical analysis, it can nevertheless behave as a prototype for the photochemical and photophysical processes observed in much larger molecules. Formaldehyde has thus become a proving ground for newly developed techniques in many branches of molecular physics ranging from pure spectroscopy to nonradiative transition theory.

The first excited singlet state of formaldehyde, the $\tilde{A}^1A_2$ or $S_f$ state, is among the first for which photophysical and photochemical processes have been examined at the level of individual rovibronic eigenstates [19]. Of primary importance in these studies was elucidation of the mechanisms responsible for the collision-induced and collision-free decay of specific rotation-vibration levels within the $\tilde{A}$ state. In particular, it has been experimentally determined that zero-pressure
lifetimes of single rotational levels in the $v_4=1$ out-of-plane bending mode of $S_1$ formaldehyde-$h_2$ vary, in what appears to be essentially a random fashion, by an astounding factor of 200, from 25ns to 4.2$\mu$s [22, 153]. These values are to be contrasted with the $ab\ initio$ calculated radiative lifetime of 3.4$\mu$s [154, 68].

As a result of work performed by numerous research groups utilizing the most sophisticated theoretical and experimental techniques available, it has now been firmly established that photophysical and photochemical processes in the $\tilde{A}^1A_2$ state of formaldehyde are dominated by nonadiabatic interactions with highly-excited predissociative rotation-vibration levels from the $\tilde{X}^1A_1$ or $S_0$ ground electronic potential surface [19]. The short lifetimes ($\sim 25$ns [23]) associated with these perturbing $S_0$ levels provides a viable explanation for the rapid collision-free decay often observed for individual rovibronic levels in $S_1$ formaldehyde.

The lifetime-broadened spectral widths for highly-excited $S_0$ states have been determined, through both theory [155] and experiment [24, 22, 23], to be substantially smaller than their associated energy spacings. In addition, the interelectronic coupling between the $\tilde{A}$ and $\tilde{X}$ states, which arises from a breakdown of the Born-Oppenheimer approximation, is believed to be quite small in magnitude ($i.e.$ $\sim 10^{-4}$cm$^{-1}$ [20, 105]). Consequently, the degree of interaction between a single rovibronic level in $S_1$ formaldehyde and a perturbing rotation-vibration state from the $S_0$ potential surface will be strongly dependent upon their relative separation in energy. In the language of perturbation theory, the $S_1 \sim S_0$ couplings are dominated by $^*$energy denominator$^*$ effects rather than by variations in the interaction matrix element. Since the rovibronic fine structure within the $\tilde{A}$ and $\tilde{X}$ electronic manifolds can be expected to be uncorrelated (in energy) with respect to one another, the seemingly random variations observed in zero-pressure $S_1$ decay rates can be rationalized in terms of such energy gap arguments.
The collision-induced photophysical processes occurring in the $\tilde{A}^1A_2$ state also seem to exhibit several unanticipated features that further distinguish formaldehyde from other molecular systems. One of the most spectacular of these pressure-dependent anomalies is illustrated in figure 2-1 which is taken from the doctoral thesis of J. C. Weisshaar [156]. This figure presents the Stern-Volmer plots obtained by time-resolving the undispersed spontaneous emission accompanying abrupt excitation of individual rotational levels within the $v_4=1$ out-of-plane bending mode of $\tilde{A}^1A_2$ formaldehyde-$h_\gamma$. These graphs of inverse effective lifetime or total fluorescence decay rate versus formaldehyde pressure should be straight lines with a slope equal to the collisional depopulation rate and a zero-pressure intercept equal to the reciprocal of the collision-free lifetime [157]. Figure 2-1, however, displays two dramatic deviations from the expected behavior:

1. The zero-pressure decay rates (and therefore the collision-free lifetimes) vary in an erratic manner from one rotational level to the next.

2. Even at low pressures, large curvatures, both positive and negative, are observed in what should be linear plots.

On the basis of the arguments presented above, the apparently random fluctuations of the collision-free lifetimes can be rationalized in terms of the nonadiabatic couplings which occur between the $\tilde{A}$ and $\tilde{X}$ electronic states. Although several tentative explanations have been advanced to account for the non-Stern-Volmer kinetic behavior displayed by the pressure dependence of figure 2-1 (cf. ensuing discussion), no direct experimental evidence existed, prior to the work reported in this thesis, either to support or to refute these claims.

The fundamental goal of the work presented in this Chapter was to ascertain the nature of the collision-induced processes responsible for the pressure-dependent relaxation of individual rotation-vibration levels in $\tilde{A}^1A_2$ formaldehyde-$h_\gamma$. In
Figure 2-1: Stern-Volmer Plots for $v_4 = 1 \tilde{A}^1A_2$ formaldehyde-$h_2$
\[ \langle T \rangle^{-1} (\mu \text{sec}^{-1}) \]

Graph (a): 
- \( \Delta rR_{7}(8) \)
- \( \bullet rR_{3}(9) \)
- \( \square rR_{3}(4) \)
- \( \circ rQ_{1}(13) \)
- \( \triangle pQ_{1}(1) \)

Graph (b): 
- \( \frac{4}{0} \text{H}_2\text{CO} \)

\[ P_{\text{H}_2\text{CO}} \text{ (Torr)} \]

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particular, the elucidation of collisional depopulation channels available to electronically excited formaldehyde could provide some insight into the anomalies (e.g. the non-Stern-Volmer behavior in figure 2-1) observed in previous time-resolved kinetic studies.

In view of the pervasive $S_1 \sim S_0$ nonadiabatic interactions encountered in the $\tilde{A}^1A_2$ state of formaldehyde, the unusual kinetic behavior exhibited by individual rotation-vibration levels within this electronically excited manifold had previously been interpreted in terms of two collision-induced processes [19, 156]:

1. Collision-induced rotational and/or vibrational energy transfer within the $\tilde{A}^1A_2$ electronic state.

The study of collision-induced rotational and vibrational energy transfer has provided considerable insight into the mechanisms responsible for the flow of energy within polyatomic systems [158, 159, 160]. In particular, these investigations have led to the formulation of numerous propensity rules which characterize the various collisional pathways available for molecular relaxation processes.

Such inelastic relaxation mechanisms are especially important for the $\tilde{A}^1A_2$ state of formaldehyde where, as a result of the nonadiabatic interactions with highly-excited predissociative $S_0$ states, individual rovibronic levels exhibit large fluctuations in their zero-pressure lifetimes. In the presence of efficient collision-induced rotational and vibrational energy transfer processes, the time-resolved undispersed spontaneous emission accompanying abrupt excitation of a specific $\tilde{A}^1A_2$ rovibronic level will therefore be a complex superposition of several exponentially decaying components. Such convoluted signals result from the concurrent detection of fluorescence both from the initially prepared level and from the manifold of adjacent states which have been populated through collisions. The pressure dependence of this effect can lead to several consequences including the manifestation of non-Stern-Volmer kinetic behavior.

2. Collision-induced energy transfer out of the $\tilde{A}^1A_2$ electronic state.

As is the case for numerous molecular systems, one relaxation pathway
available to the first excited singlet state of formaldehyde entails direct collisonal quenching into the ground state by means of an intermolecular electronic coupling mechanism (e.g. a resonant dipolar interaction) [157, 161]. However, from the viewpoint of the work to be discussed in the present Chapter, a more important collision-induced process is to be found in the nonadiabatic interactions which exist between the electronic states of formaldehyde. In particular, collisions may shift or broaden rotation-vibration levels within the $S_0$ potential surface such that they are effectively brought into resonance with an initially prepared $\tilde{A}^1A_2$ rovibronic eigenstate. This would provide the energy conservation required for interelectronic couplings to induce an irreversible decay of population from the $S_I$ manifold [19]. In the language of radiationless transition theory [162, 163], these collision-induced internal conversion processes can be understood in terms of a pressure-dependent mechanism which hastens the conversion of a small or intermediate case molecular system (e.g. formaldehyde) to the limit of large molecule statistical behavior.

A simple model for collision-induced internal conversion is based upon the fact that nonadiabatic couplings will result in isolated molecular eigenstates of mixed electronic parentage [164]. Collisonal interactions between molecules possessing mixed eigenstates are expected to be qualitatively different from those involving molecular systems with pure electronic states (e.g. although negligible collisional couplings may exist between the pure states, such coupling can be present between the mixed states).

Freed and coworkers [164, 165, 166] have suggested that collisional relaxation for rovibronic levels of mixed electronic parentage can exhibit non-Stern-Volmer kinetic behavior with a limiting high-pressure rate which is essentially independent of the structural details associated with the collision partner. In the case of formaldehyde, this high-pressure saturation effect would occur when collision-induced broadening and shifting of rotation-vibration levels within the $S_0$ manifold becomes comparable to the average energy separations which characterize highly excited regions of the ground electronic potential surface. Through numerical calculations performed upon the photodissociation dynamics of formaldehyde, Heller, et. al. [167] have confirmed that $S_I \sim S_0$ interactions can introduce a nonlinear pressure dependence into the collisional depopulation rates measured for individual rovibronic levels within the $\tilde{A}^1A_2$ state.
The collisional relaxation pathways described above provide two plausible explanations for the anomalous kinetic behavior exhibited by rotation-vibration levels in $\tilde{A}^1A_2$ formaldehyde. While the applicability of the first process would seem to depend more upon the deficiencies associated with the nonselective nature of undispersed fluorescence detection, the latter mechanism represents an intrinsic feature of the formaldehyde electronic system and its nonadiabatic interactions.

The traditional methods for examining the collisional relaxation pathways associated with a specific rovibronic level in $\tilde{A}^1A_2$ formaldehyde-$h_2$ are based upon time-resolved detection of the spectrally dispersed spontaneous emission accompanying abrupt excitation of a preselected rotation-vibration eigenstate. Such studies are hampered, however, by the substantial demands on both sensitivity and resolution imposed by the inherent characteristics of the formaldehyde system. In particular, the fluorescence quantum yields for single rotational levels in the $v_4=1$ state of $\tilde{A}^1A_2$ formaldehyde-$h_2$ have been determined to be as low as 0.006 [168, 169]. An additional complication arises from the distorted equilibrium configuration encountered in the electronically excited state. As a result of this change in geometrical structure, the relatively weak spontaneous emission will be spread over a large number of Franck-Condon allowed vibronic transitions. To achieve the desired objective, one of these vibronic bands would have to be monitored with sufficient temporal and spectral resolution to observe the evolution in time of the rotational fine structure. These experimental difficulties have prevented time-resolved detection of dispersed molecular fluorescence from being a tractable approach for the elucidation of collision-induced photophysical processes in the first excited singlet state of formaldehyde-$h_2$. The situation is perhaps somewhat better for the lowest vibronic states of $\tilde{A}^1A_2$ formaldehyde-$d_2$ where fluorescence quantum yields approaching unity have been measured [169]. However, the more
congested rotational structure [50] and longer lifetimes [19] exhibited by the deuterated species introduce additional impediments into the investigation of collisional relaxation channels through the methods of dispersed molecular fluorescence (e.g. D₂CO would require enhanced spectral resolution at lower overall sample pressures).

To avoid the problems associated with dispersed fluorescence detection, the work presented in this Chapter has utilized the recently developed technique of Transient Gain Spectroscopy [170] in which a single frequency laser serves as a probe of molecular relaxation processes with a sensitivity and resolution far exceeding that attainable with more conventional spectroscopic methods. These time-resolved investigations have permitted, for the first time, the experimental determination of several kinetic parameters which are intimately connected to the collision-induced photophysical pathways occurring in the \( \tilde{A}^1A_2 \) state of formaldehyde-\( h_g \). In particular, our studies have provided:

1. A direct measurement of the true collisional depopulation rate for a single rotation-vibration level in \( \tilde{A}^1A_2 \) formaldehyde-\( h_g \).

2. A direct measurement of state-to-state energy transfer cross sections between individual rotational levels in \( \tilde{A}^1A_2 \) formaldehyde-\( h_g \).

These measurements, which were performed upon specific rotational levels in the \( v_4=1 \) out-of-plane bending mode of \( \tilde{A}^1A_2 \) formaldehyde-\( h_g \), have provided the first direct experimental evidence that large rotational relaxation cross sections, collisionally coupling states of widely different zero-pressure decay rates, are responsible for the non-Stern-Volmer kinetic behavior observed in previous studies. The curvature displayed by the plots in figure 2-1 can therefore be explained through the non-selective nature of the undispersed fluorescence techniques employed in these kinetic investigations. In addition, our state-to-state experiments
have indicated that the dominant collisional relaxation mechanism in electronically excited formaldehyde is pure rotational energy transfer. Collision-induced internal conversion appears to play a negligible role for the depopulation of individual rovibronic levels in \( \tilde{A}^1A_2 \) formaldehyde-\( h_\alpha \).

The following sections will first review the basic techniques employed in the kinetic investigations of \( \tilde{A}^1A_2 \) formaldehyde-\( h_\alpha \). After a discussion of the experimental details, the results of our transient gain measurements will be presented. Finally, the collisional depopulation rates and state-to-state energy transfer cross sections obtained in these studies will be interpreted in terms of the photophysical processes occurring in electronically excited formaldehyde.

2.2 Techniques

2.2.1 Introduction

The main thrust of the present Chapter is a study of relaxation processes occurring in the first excited singlet state of formaldehyde-\( h_\alpha \). The transient gain techniques employed in these investigations required that a coincidence exist between a fixed frequency PROBE laser (viz. a single mode argon ion laser) and an assigned rovibronic transition in the \( \tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1 \) electronic system. As a result, the energy transfer experiments had to be preceded by a spectroscopic search for appropriate resonant transitions.

Since the lowest energy cold bands in the \( \tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1 \) system of formaldehyde-\( h_\alpha \) are located in the ultraviolet region of the spectrum, the visible PROBE laser utilized in the relaxation studies was constrained to transitions which terminated on highly excited rotation-vibration levels of the ground electronic potential surface. These regions of extreme excitation are not readily accessible to
traditional spectroscopic methods, due in part to the exceedingly small absorption cross sections from thermally populated lower levels. Even if conventional spectroscopy could be performed, the rotational and vibrational congestion associated with such highly excited molecules would preclude assignment of the observed spectral features.

The recently developed double resonance technique of Stimulated Emission Pumping [171, 172] provides a convenient means of spectroscopically characterizing such highly excited molecular systems and, in turn, locating the frequency coincidences required for our energy transfer experiments. The discussion which follows will therefore review the method of Stimulated Emission Pumping Spectroscopy before considering the transient gain technique employed in the kinetic study of relaxation processes.

2.2.2 Stimulated Emission Pumping

Figure 2-2 schematically illustrates the Stimulated Emission Pumping or SE technique which makes possible the state-selective preparation and spectroscopic characterization of highly excited molecular systems. As indicated in this diagram, SEP is basically a folded variant of Optical-Optical Double Resonance (OODR) in which molecules are transferred from an initial, thermally populated level, via an excited electronic state, to target rotation-vibration levels of the ground electronic state.

The upward and downward excitation steps in SEP are driven by two, narrow-band pulsed dye lasers designated respectively as the PUMP and the DUMP. The PUMP laser is tuned into resonance with a specific rovibronic transition originating from a single, thermally populated level in the ground electronic state and terminating on a selected rotation-vibration level in the excited electronic state.
Figure 2-2: Energy Level Scheme for Stimulated Emission Pumping.
The population prepared by the PUMP pulse in this intermediate level can be sensitively monitored by observing the resulting molecular fluorescence.

As the frequency of the DUMP laser is tuned, coincidences occur with rovibronic transitions originating from the single rotation-vibration level prepared by the PUMP and terminating on highly excited target levels in the ground electronic state. At these points of resonance, the DUMP stimulates molecules downward resulting in a concomitant decrease of the spontaneous emission from the excited electronic state. It is this decrease in the observed fluorescence intensity which constitutes the measured SEP signal.

Stimulated Emission Pumping thus provides a means of preparing a chemically significant population of highly excited molecules with near perfect rotation-vibration state selectivity. Furthermore, by taking advantage of the differences in nuclear geometry between two electronic states, SEP permits characterization of highly excited target levels possessing radically different vibrational properties from those present in the vibrationless equilibrium configuration of the ground electronic potential surface. In the case of formaldehyde, such Franck-Condon considerations [118] indicate that Stimulated Emission Pumping should be able to probe vibrational states with substantial amplitude in the C=O stretching (i.e. \( \nu_2 \)) and out-of-plane bending (i.e. \( \nu_4 \)) coordinates. These highly-distorted levels are not readily accessible by other techniques.

Of greater significance to the high-resolution spectroscopist, however, is the fact that the double resonance nature of Stimulated Emission Pumping effectively eliminates the complexity normally associated with resolved spectra of moderately sized molecules. As with other OODR methods [173], this is accomplished by selecting a single, upward rovibronic transition to a specific intermediate level from
which only a very limited number of downward rotational transitions are possible by rovibronic selection rules. This enormous spectral simplification, along with sub-Doppler, laser linewidth limited resolution, makes SEP a powerful spectroscopic probe for polyatomic systems. These properties are of special importance for the study of highly excited molecules in which the vibrational density of states is expected to rise dramatically as the degree of excitation increases.

2.2.3 Transient Gain Spectroscopy

Figure 2-3 illustrates the energy level scheme appropriate for the transient gain measurements of total depopulation rates in $\tilde{A}1A_2$ formaldehyde-$h_\gamma$. The experimental configuration is basically a folded variant of Optical-Optical Double Resonance which has much in common with both Stimulated Raman Gain Spectroscopy [174, 175, 176, 177] and the previously mentioned Stimulated Emission Pumping technique [171, 178]. Here the signal-carrying PROBE beam is provided by a single mode, continuous wave argon ion laser, operated on the 488.0nm line, which was found to coincide with the $\nu_1^0\nu_4^0\nu_1^1\nu_2^1\nu_1^0\nu_1^0 \rightarrow \nu_1^1\nu_2^0\nu_1^1\nu_1^0$ rovibronic transition of the $\tilde{A}1A_2 \rightarrow \tilde{X}1A_1$ system. Although this frequency coincidence will be discussed later, it should be mentioned that this vibronic band, with a calculated oscillator strength of $< 10^{-5}$ [178], represents one of the weakest transitions observed in the SEP experiments performed on formaldehyde [180]. The PUMP beam, produced by a frequency doubled pulsed dye laser, was tuned into resonance with the $4_0^1 \nu_2^1 \rightarrow \nu_3^1\nu_1^1$ rovibronic transition at $\sim 28242 \text{cm}^{-1}$.

Before arrival of the PUMP pulse, neither the upper nor the lower level of the PROBE transition is populated. The PROBE beam thus passes through the formaldehyde sample without any interaction. The pulsed PUMP abruptly populates the $13_{2,12}$ level of the $\tilde{A}$ state (i.e. $\sim 10^{11}$ molecules/cm$^3$/Torr), thereby
Figure 2-3: Energy Level Scheme for Transient Gain Spectroscopy.
$\tilde{A}^1A_2$ \{ \\
\hspace{1cm} $\tilde{X}^1A_1$ \\
\hspace{1cm} $\tilde{A}^1A_2$ \}

PUMP

$\sim 353\text{nm}$
pulsed dye

$4^1_0$

PROBE

488.0nm
cw Argon ion

$2^0_1 3^0_1 4^1_4$

$\sim 7830\text{cm}^{-1}$

$13_{2,12}$

$13_{1,13}$

$13_{3,11}$
producing a population inversion in the PROBE transition. The cw PROBE, now
propagating through a transitory gain medium, is amplified by stimulated emission
in proportion to the population of the excited 13,2,12 rovibronic level. Thus, by
directly monitoring the transient gain appearing on the PROBE beam, one can
observe the temporal evolution of a specific rotation-vibration level in the excited
electronic state. This use of a cw probe, in conjunction with a high-speed transient
digitizer, permits acquisition of the entire time-resolved molecular decay profile for
each pulse of the PUMP laser, thereby greatly augmenting the quality and
collection rate of the data.

The parallels between this pulsed-cw method, which is designated Transient
Gain Spectroscopy or TGS, and the Stimulated Emission Pumping technique should
be quite apparent. Both are inverted forms of Optical-Optical Double Resonance
which differ only in terms of the detection scheme used to identify coincidences
between the frequency of a laser (viz. the DUMP in SEP and the PROBE in TGS)
and linked downward rovibronic transitions. In each case the observed signals
depend upon the competition that exists between concurrent spontaneous and
stimulated emission processes. While SEP relies upon the resulting decrease in the
spontaneous molecular fluorescence accompanying the DUMP pulse, TGS directly
monitors the copropagating photon emission induced by the cw PROBE beam.
Nevertheless, both techniques are capable, with appropriate modifications, of
providing comparable information in either the time or frequency domains.
2.3 Experimental

2.3.1 Stimulated Emission Pumping

The method of fluorescence-detected Stimulated Emission Pumping, as developed in our laboratories [171], is based upon a dual-beam, null-detection scheme which provides a considerable enhancement in both the sensitivity and resolution afforded by the technique. In this experimental configuration, the gas cell, which contains the molecular system under investigation, is divided into two optically isolated regions designated as the SIGNAL and the REFERENCE. The PUMP laser is separated into two beams, one of which is directed through the SIGNAL portion of the cell while the other propagates through the REFERENCE section. The spontaneous emission resulting from the interaction of these beams with the sample molecules is simultaneously monitored with two matched photomultiplier tubes. By adjusting the relative intensities of the two PUMP beams and balancing the PMT bias voltages, the observed time-resolved photocurrents, which are proportional to the molecular fluorescence intensities, can be made identical in both shape and magnitude. A fast analog subtraction of these signals thus produces a null which constitutes the background level for an SEP experiment.

The DUMP beam is sent only through the SIGNAL portion of the gas cell in a direction which is counterpropagating and colinear with respect to the PUMP. In the absence of a resonant downward rovibronic transition, the DUMP laser passes through the molecular sample without any interaction. Therefore, the time-resolved fluorescence intensities from the SIGNAL and REFERENCE regions remain identical and the null is maintained. However, when the DUMP frequency coincides with a transition between the PUMP-prepared rovibronic level in the excited state and a highly excited rotation-vibration level in the ground state, the situation is
drastically altered. The DUMP now stimulates molecules downward with a concomitant decrease in the intensity of spontaneous emission produced in the SIGNAL region only. This fluorescence loss offsets the sensitive balance created by the subtraction circuitry, thereby producing a departure from the null condition which signifies the detection of an SEP signal.

For many experiments involving pulsed lasers, the ultimate sensitivity and resolution is grossly limited by the large pulse-to-pulse amplitude fluctuations (e.g. > 20%) associated with such excitation sources. In this context, the utility of the dual-beam configuration described above can easily be appreciated by realizing that amplitude fluctuations in the PUMP beam are essentially cancelled in the null detection process. Since frequency jitter and spatial instabilities of the PUMP ultimately translate into amplitude variations in the observed spontaneous emission, the double beam technique also provides a means of compensating for these effects. As a result, the Stimulated Emission Pumping experiments performed on formaldehyde-$h_2$ have been able to detect signals corresponding to roughly a 0.5% change in fluorescence intensity despite pulse-to-pulse PUMP laser noise on the order of 10%.

The apparatus employed in the Stimulated Emission Pumping experiments on formaldehyde-$h_2$ is illustrated in figure 2-4. Since the SEP technique necessitates the temporal synchronization of two independent excitation sources, a single pulsed Nd:YAG laser (Quanta Ray DCR-1A; 10Hz repetition rate) was used to pump the two tunable dye lasers which served as the PUMP and the DUMP. In practice, an optical delay of $\sim 5\text{ns}$ was incorporated between these beams in order to avoid coherence effects that might accompany concurrent interaction with the molecular sample [181]. The ability of a Nd:YAG system to simultaneously produce radiation at second and third harmonic wavelengths was of great utility in these
Figure 2-4: Apparatus for Stimulated Emission Pumping.
formaldehyde spectroscopic measurements, where the PUMP required a (frequency-doubled) red dye (best pumped by 532nm second harmonic) and the DUMP usually a blue dye (best pumped by 355nm third harmonic).

The PUMP and DUMP beams were produced by two pulsed dye lasers (Quanta Ray PDL-1) of the Hansch-Klauminzer design. In order to reduce amplified spontaneous emission and thereby improve spectral resolution, these commercially available units were each modified by installing $\sim 3$ns of optical delay for the YAG pump between the oscillator and preamplifier/amplifier stages. Both lasers were operated with air-spaced intracavity etalons (PUMP: Tech Optics 0.75cm$^{-1}$ FSR; DUMP: Molelectron 1.0cm$^{-1}$ FSR) which resulted in measured (fundamental) bandwidths of $\sim 0.03$cm$^{-1}$ FWHM. For the PUMP, which was usually maintained at a fixed wavelength during an SEP measurement, pressure scanning with prepurified nitrogen provided $\sim 3.5$cm$^{-1}$ of tuning (i.e. $\sim 7$cm$^{-1}$ at doubled frequencies) for the 0 to 800 Torr pressure change utilized. In the case of the DUMP laser, which was required to scan over larger distances, pressure tuning with instrument grade SF$_6$ (Matheson) over a range of 0 to 2 atmospheres permitted $\sim 35$cm$^{-1}$ of continuous frequency adjustment.

For the $4^1_0$ rovibronic PUMP transitions employed in the SEP experiments on formaldehyde-$h_\gamma$, approximately 80mJ of second harmonic Nd:YAG radiation was used to excite a dye laser containing LDS 750 dye (Exciton Chemical Company) dissolved in spectroscopic grade methanol. The resulting tunable red light was frequency doubled to $\sim 28300$cm$^{-1}$ by an extracavity, angle-tuned KD$^*$P crystal (Quanta Ray, 76° cut). After separation from the colinear fundamental dye output by means of a set of 60° S1-UV prisms (Esco), the ultraviolet beam was spatially filtered through a sapphire pinhole (Richard H. Bird & Company; $\sim 150$μm) and recollimated to a diameter of $\sim 3$mm. This horizontally polarized PUMP had a
spectral bandwidth of $\sim 0.06\text{cm}^{-1}$, a pulse duration of $\sim 5\text{ns}$, and a pulse energy of $\geq 2\text{mJ}$. At the same time, a back reflection from the undoubled dye laser was directed through a monitor etalon (Molelectron; $\sim 0.56\text{cm}^{-1}$ FSR) to provide a visual assessment for the single mode performance of the dye laser.

The separation of the PUMP into two beams, as necessitated by the null detection scheme employed in our SEP experiments, was accomplished by the use of polarization techniques. The PUMP was first directed through a 352.5nm halfwave retardation plate (Virgo Optics) which, by appropriate rotation, permitted transformation of the horizontally polarized UV light into any other linear polarization. The beam subsequently passed through a calcite Glan-Laser prism (Karl Lambrecht MGLA-DW-8) which was oriented to resolve a given input polarization into horizontal and vertical components (i.e. components parallel and perpendicular to the optical axis of the negative uniaxial calcite crystal). In short, the horizontal component propagated straight through the prism while the vertical component underwent total internal reflection and emerged from the calcite crystal at an angle $\geq 90^\circ$. An additional halfwave retarder in front of the Glan-Laser prism enabled the undeviated beam to be rotated back to vertical polarization.

Thus, two vertically polarized PUMP beams were created with their relative intensities readily adjusted (without introducing an angular deviations) by rotation of the input polarization to the calcite prism (i.e. by rotation of the first halfwave retarder). These UV beams were subsequently directed into the SIGNAL and REFERENCE regions of the sample cell.

For the rovibronic DUMP transitions of concern in the present Chapter (viz. target rotation-vibration levels with $\sim 8000\text{cm}^{-1}$ of excitation in the $\tilde{X}^1A_1$ state of formaldehyde-$h_2$), a dye laser containing either Coumarin 480 or Coumarin 500 dye (Exciton Chemical Company), dissolved in spectroscopic grade methanol, was
pumped by \( \sim 100 \text{mJ} \) of third harmonic Nd:YAG radiation. The tunable blue light generated in this manner was passed through a Keplerian telescope where it was spatially filtered by means of a sapphire pinhole (Richard H. Bird & Company; \( \sim 200 \mu\text{m} \)) and recollimated to a diameter of \( \sim 4 \text{mm} \). The resulting DUMP had a spectral bandwidth of \( \sim 0.03 \text{cm}^{-1} \) FWHM, a pulse duration of \( \sim 6 \text{ns} \) FWHM, and an energy of \( \sim 10 \text{mJ/pulse} \). Back reflections from this beam were sent through a monitor etalon (Molelectron; \( \sim 0.55 \text{cm}^{-1} \) FSR), to evaluate the single mode operation of the dye laser, and through a heated tellurium absorption cell (\textit{i.e.} \( ^{130}\text{Te}_2; \sim 500 \, ^\circ\text{C} \)) which provided a convenient absolute frequency reference when used in conjunction with the Fourier Transform atlas of Cariou and Luc [182]. Finally, the DUMP was directed into the SIGNAL portion of the sample cell where it spatially overlapped with the counterpropagating PUMP beam.

The sample cell utilized in the Stimulated Emission Pumping experiments is the one employed for the quantum beat studies of the previous Chapter. This glass cell contained two separately baffled beam paths which defined the SIGNAL and REFERENCE regions associated with our null detection scheme. For SEP spectroscopic measurements, an opaque teflon insert was placed in the center of the Stark electrode assembly, thereby optically isolating the two halves of the cell while still allowing for the free passage of molecules between them. In this configuration, the sample cell had an ultimate vacuum pressure of \( < 1 \times 10^{-5} \) Torr and a leak rate of \( \sim 10^{-4} \) Torr/hour. Pressures within the cell were accurately monitored by means of a 0 to 1 Torr capacitance manometer (MKS Baratron Model 220B).

The formaldehyde-\( \text{H}_2 \) was prepared by pyrolysis of paraformaldehyde-\( \text{H}_2 \) (Aldrich) followed by two fractional distillations. Typical cell pressures were \( \sim 40\text{-}80 \) mTorr depending upon the relative intensity of the PUMP transition. In the course of an actual experiment, the formaldehyde sample was changed
frequently (every 1 ~ 2 hours) to minimize signal deterioration brought about by laser induced photochemical processes.

The spontaneous emission produced by the PUMP beams in the SIGNAL and REFERENCE regions was separately monitored by a matched pair of two inch diameter, end-on photomultiplier tubes (RCA 4501/V4, ~5ns rise time) directly coupled to individual high-speed preamplifiers (LeCroy VV100B, DC to 250MHz bandwidth, x10 gain). A set of identical f/1.0 UV imaging systems (Unique Optical, x2.5 magnification) was employed, in conjunction with various optical slits, to ensure that both detectors observed comparable 2cm long strips of laser induced fluorescence. To minimize residual scattered light produced by the PUMP and the DUMP, each PMT was preceded by a 395nm cut-off filter (Schott) and a 440nm short pass filter (Ditric Optics).

The preamplified photomultiplier outputs were directed, through matched lengths of cable, to a high-speed differential amplifier (LeCroy MVL100TB, DC to >100MHz bandwidth, x10 gain) and then into a gated integrator/boxcar averager (either PAR Model 162/165 or SRI Model SR250). The resulting full-detected SEP signals were recorded as a function of DUMP laser frequency on a strip chart recorder (Linear Instruments 595) along with the fringes from a monitor etalon (Molelectron; ~0.55cm⁻¹ FSR) for relative frequency calibration and with the absorption spectrum of $^{130}$Te₂ for absolute frequency calibration. All connections between instruments were made with double shielded coax cable (RG223) with precautions taken to ensure that 50Ω transmission line characteristics were maintained.

In a typical Stimulated Emission Pumping experiment, the PUMP laser was first scanned into resonance with a preselected upward rovibronic transition. This was accomplished, as described in the previous Chapter, by recording a
formaldehyde excitation spectrum. Briefly, the laser induced fluorescence produced in the SIGNAL region of the sample cell (with the DUMP laser blocked) was monitored as a function of the PUMP frequency. In this manner, the appropriate spectral feature could be identified and the PUMP laser readily tuned into coincidence. Once brought into resonance with a transition, the PUMP frequency would usually remain fixed, without trouble, for several hours. The differential amplifier, which provided the subtraction required for our null detection scheme, was subsequently reconnected to the SIGNAL photomultiplier. SEP spectroscopic measurements could then be performed by scanning the DUMP laser frequency in search of linked downward transitions terminating on highly excited rotation-vibration levels of the ground electronic state.

2.3.2 Transient Gain Spectroscopy

The apparatus utilized in the transient gain studies of relaxation processes in \( \tilde{A}^1A_2 \) formaldehyde-\( h_g \) is illustrated in figure 2-5. In many respects, the experimental configuration is quite similar to those employed for conventional absorption spectroscopy with the exception that our scheme relies on observing a transitory negative absorption or gain signal. As in any absorption method, however, the ultimate sensitivity depends upon the magnitude and frequency of the intrinsic fluctuations present in the interrogating light beam. To alleviate these source-noise problems many ingenious methods based on restricted bandwidth detection (e.g. lock-in detection) or null-detection (e.g. dual beam differential detection) have been developed and successfully exploited. The wide-band, high-speed requirements of our time-resolved investigations precluded the use of such techniques.

The oscillation of the cw PROBE laser on a single longitudinal and transverse
Figure 2-5: Apparatus for Transient Gain Spectroscopy.
cavity mode was found to be a critical factor for eliminating source-related noise problems in the transient gain studies. Without such single frequency performance, the coherently related laser modes present in the PROBE beam would have interfered with one other in our square-law detector (i.e. a photodiode). The high frequency sinusoids produced by such "mode beating" effects would have severely degraded the sensitivity and temporal resolution afforded by our detection scheme. Even with single mode operation, elimination of lower frequency acoustic noise necessitated the use of some electronic filtering in the measurement process.

The PROBE beam employed in the transient gain measurements was produced by a commercial argon ion laser (Spectra Physics Model 164/03) which was operated on the 488.0nm line by replacing the rear high reflector with a prism assembly. Single frequency operation was achieved by constraining laser oscillations to an individual longitudinal cavity mode with an intracavity, angle-tuned etalon (Spectra Physics Model 589-11; 10GHz FSR). The vertically polarized output of this cw source, which was continuously monitored by means of a spectrum analyzer (Tropel Model 240 1.5GHz FSR & Burleigh Model RC-42 ramp generator), had an instantaneous spectral bandwidth of \( \sim 1\text{MHz} \) with a short time frequency jitter \( \leq 20\text{MHz} \). No attempt was made to stabilize the argon laser in either amplitude or frequency. After passing through a Galilean telescope, the PROBE beam, now approximately collimated with a diameter of \( \sim 3\text{mm} \), was directed through the center of the sample cell. All manipulations of the signal-carrying PROBE were performed with dielectric mirrors (Newport Research Corporation) in order to minimize signal attenuation due to reflection losses.

The PUMP for the transient gain studies was produced by the same Nd:YAG pumped, pulsed dye laser utilized as the PUMP in the Stimulated Emission Pumping experiments. The details of this tunable light source have been thoroughly
discussed in the previous section and will not be repeated here. After spatial filtering and recollimation to a diameter of $\sim 4\text{mm}$, the frequency doubled output of the dye laser had a spectral bandwidth of $\sim 0.06\text{cm}^{-1}$ FWHM, a pulse duration of $\sim 5\text{ns}$ FWHM, and an energy of $\sim 2\text{mJ/pulse}$. The resulting PUMP beam was sent through a 350nm halfwave retardation plate (Virgo Optics) and a Glan-Laser calcite prism (Karl Lambrecht MGLA-SW-8) oriented so as to rotate the linear polarization vector of this ultraviolet radiation into coincidence with that of the PROBE (vertical polarization).

The vertically polarized PUMP was subsequently directed through the sample cell at a slight angle (viz. $\leq 6.0$ milliradians) to the copropagating PROBE beam. In this manner, maximum spatial overlap of the two beams could be obtained without requiring them to simultaneously reflect from or pass through the same optical elements. Initial transient gain measurements were based on a completely colinear geometry of the PUMP and PROBE lasers which necessitated the use of a beam combining optic. This scheme, while increasing the total signal level through enhanced spatial coincidence, was soon abandoned when it became apparent that the interaction of the powerful ultraviolet PUMP pulse with optical coatings and substrates (i.e. the beam combiner) resulted in unacceptable transient artifacts on the PROBE beam.

After traversing the sample cell, the PROBE was further isolated from the copropagating PUMP by means of an S1-UV dispersing prism (Esco). The PROBE beam was subsequently directed along a well baffled and filtered optical path, in order to minimize residual scattered light from the pulsed lasers, and ultimately impinging upon a high-speed photodiode (EG&G FND-100, 90V reverse bias, 800ps rise time). Although the diode specifications indicated an exceedingly high threshold for DC saturation (viz. 100W/cm$^2$ [183]), it was found that the transient response of
this detector could be severely degraded by irradiation with an intense cw source, even in the absence of DC saturation. For this reason, the argon ion laser power was maintained at a relatively low level (viz. ≤ 60mW) throughout the course of the relaxation studies. Such low intensities also avoided any optical pumping or saturation effects which might occur in the PROBE transition.

The photodiode output was selectively attenuated with a custom-built high-pass filter (a five-pole Butterworth filter [184], 50Ω input/output, 15KHz 3db point) and then sent to a low noise current amplifier (Analogue Modules LNCA, 8000V/A transimpedance, DC to 500MHz bandwidth, 10nV/Hz noise figure). The particular filter employed in this detection scheme was designed to eliminate the large, kiloHertz frequency amplitude fluctuations which existed in the output of the argon ion laser while producing negligible distortion on the time scale of importance to the present investigations. The amplified signal was subsequently directed into a high-speed transient digitizer (Tektronix 7912AD, 7B92A time base, 7A19 amplifier, DC to 500MHz bandwidth) to permit signal averaging and then to a microcomputer (DEC LSI-11/03) for further processing and analysis. In order to exclude any artifacts associated with timing jitter, the digitizer was triggered by means of a high-speed photodiode (EG&G FND-100, 90V reverse bias) which monitored a back reflection from the PUMP beam.

The radio frequency pulse which accompanied the firing of the Nd:YAG laser employed in these experiments necessitated that all detection equipment be shielded by means of copper gauze and tinned braid. All signal connections between instruments were performed with double shielded coax cable (RG223) with careful attention being directed to the preservation of 50Ω transmission line characteristics. This essentially eliminated artifacts due to interference from external sources and impedance mismatch.
The cell utilized in the transient gain experiments was constructed from a single one meter section of two inch diameter pyrex conical tubing (Corning) which was reduced at both ends to one inch diameter by means of o-ring sealed pyrex unions (Corning). Each end was butted against o-ring containing grooves in black anodized aluminum flanges. Finally, the windows (Easco S1-UV, 3/8 inch thick, 1.25 inch diameter) were directly mounted on o-rings protruding from the outer surface of the metal flanges and were held in place only by the pressure differential between the interior and exterior of the sample cell. The resulting optical path length was approximately 120 cm. Four glass/teflon stopcocks (Ace Glass, 0-5 mm) were fused into the cell body, thereby providing a means of attaching an ionization gauge (Veeco Instruments Inc. Model RGS-7) to measure residual background pressures and a 0 to 1 Torr capacitance manometer (MKS Baratron Model 220B) for accurately monitoring sample pressures. In this configuration, the cell had an ultimate vacuum pressure of \( \sim 10^{-6} \) Torr with a leak rate of \( \leq 10^{-4} \) Torr/hour.

The windows utilized on the sample cell had to be fabricated of extremely high quality S1-UV material so as to avoid the creation of transient artifacts by the powerful ultraviolet PUMP pulse. The method employed for mounting of the windows, namely pressure differential, is the most birefringence-free way of doing such and was especially important for the polarization sensitive detection techniques described in later Chapters. Despite all precautions, laser-induced photochemical processes within the sample gas gradually deposited an unidentifiable residue upon the windows which required that they be replaced periodically.

The formaldehyde-\( \text{H}_2 \) utilized in the transient gain experiments was prepared in the same way as that discussed for Stimulated Emission Pumping Spectroscopy. To ensure the purity of the material used in these kinetic studies, a third fractional distillation of the monomeric \( \text{H}_2\text{CO} \) was performed. All time-resolved measurements
were obtained at room temperature (i.e. 22±3°C) with sample pressures ranging from 0 to 400 milliTorr.

A typical transient gain measurement began in much the same manner as that employed in Stimulated Emission Pumping Spectroscopy, namely, by acquiring an excitation spectrum of formaldehyde-\textit{h}_2 in order to locate a preselected PUMP transition. This was accomplished by removing a kinematically supported beam steering optic thereby permitting the PUMP to enter the cell utilized in the SEP experiments. An undispersed fluorescence spectrum was then recorded in a fashion identical to that described in the previous section. Once the PUMP frequency had been pressure tuned to the appropriate spectral feature the kinematic mount was replaced to redirect the PUMP beam back into the 120cm long absorption cell. The PUMP laser frequency usually remained fixed on the designated transition, without difficulty, for several hours.

With the PUMP tuned to the desired transition, the PROBE beam could be directed through the formaldehyde-containing absorption cell and onto the photodiode detector. The frequency of the PROBE laser was manually adjusted by angle-tuning the intracavity etalon until a maximum gain signal appeared. The transient digitizer was subsequently programmed to average over 1024 pulses of the PUMP. After subtracting a background trace obtained with the argon ion laser detuned from the PROBE transition, the decay profiles had signal to noise ratios typically exceeding 500:1. These were stored on floppy disks for later processing and analysis. In order to minimize the influence of photoproducts in the kinetic studies, the formaldehyde sample was replaced after each measurement (i.e. after acquiring each set of data and background traces).

The transient gain signals displayed large amplitude variations from one PUMP pulse to the next. Although totally eliminated by the signal averaging
process, the origin of these fluctuations was initially a matter of great concern. Basically they can be attributed to the PUMP dye laser which, despite operation in a single etalon mode (viz. $\sim 0.03 \text{cm}^{-1}$ FWHM at fundamental wavelengths), typically oscillated on two or three cavity modes (viz. $\sim 60 \text{MHz}$ Fourier transform limited bandwidth) each separated by $\sim 0.01 \text{cm}^{-1}$. This structure in the PUMP frequency profile, which varied unpredictably from shot to shot, was effectively translated into a structured velocity distribution of molecules prepared in the upper level of the PUMP transition. In contrast, the argon ion PROBE beam, with an instantaneous bandwidth of $\sim 1 \text{MHz}$ (i.e. $\sim 3 \times 10^{-5} \text{cm}^{-1}$), was essentially a delta function on this scale of frequency. Consequently, the pulse to pulse fluctuations resulted from the randomly occurring overlap of the single frequency PROBE with the cavity mode structure present in the PUMP.

The time-resolved signals observed in the depopulation studies often had what appeared to be a "spike" at the beginning of the expected exponential decay. This is thought to be due to coherent coupling between the PUMP and PROBE beams during the time interval (i.e. the PUMP pulse duration) when they concurrently interacted with the molecular sample [181]. In any event, these artifacts, which never occurred in the collisional energy transfer experiments, did not present any problems in the final analysis of the data.

2.4 Results and Discussion

2.4.1 The Search for Coincidences

Our kinetic studies had to be preceded by a spectroscopic search for coincidences between one of the slightly-tunable emission lines available from the single mode argon ion PROBE laser and a rovibronic transition in the $\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1$ electronic system of formaldehyde-$h_2$. A careful examination of
previous Stimulated Emission Pumping measurements performed on formaldehyde [180] suggested that three vibronic transitions offered a reasonable chance of providing the required frequency overlap:

<table>
<thead>
<tr>
<th>Vibronic Transition</th>
<th>Vibrational Origin</th>
<th>Argon Ion Line</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3_1^0 \rightarrow 4^1_1^0$</td>
<td>8397.23 cm$^{-1}$</td>
<td>501.7 nm</td>
</tr>
<tr>
<td>$^2_1^0 \rightarrow 3^0_1^1$</td>
<td>7832.34 cm$^{-1}$</td>
<td>488.0 nm</td>
</tr>
<tr>
<td>$^1_1^0 \rightarrow 4^1_1^0$</td>
<td>7372.46 cm$^{-1}$</td>
<td>476.5 nm</td>
</tr>
</tbody>
</table>

Preliminary Stimulated Emission Pumping experiments, together with the high-power and relatively straightforward single mode operation afforded by the 488.0 nm emission line, indicated that rotational transitions within the $^2_1^0 \rightarrow 3^0_1^1$ vibronic band would provide the best opportunity for identification of a usable frequency coincidence. The candidate vibronic transitions presented above are among the weakest observed in the pulsed SEP studies of formaldehyde-$h_2^+$. 

With the tentative selection of the $^2_1^0 \rightarrow 3^0_1^1$ vibronic band as the PROBE transition, an exact determination of the associated PROBE laser frequency had to be performed. By utilizing the absorption spectrum of $^{130}$Te$_2$ together with the Fourier transform atlas of Cariou and Luc [182], the argon ion 488.0 nm emission line was found to have a central frequency of 20486.646 cm$^{-1}$ with a tuning range of $\sim \pm 0.118$ cm$^{-1}$. This is to be contrasted with the reported frequencies of 20486.5 cm$^{-1}$ from a handbook of laser wavelengths [185] and 20486.656 cm$^{-1}$ calculated from a table of ionic energy levels [186]. Discrepancies between the published and measured values are most probably due to the small spectral modifications induced by the magnetic field which encompasses the argon ion plasma tube.

A systematic investigation of the rotational structure within the $^2_1^0 \rightarrow 3^0_1^1$
vibronic band was subsequently performed. The Stimulated Emission Pumping
technique permitted identification of two rovibronic transitions in the
\( \tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1 \) electronic system of formaldehyde-\( h_2 \) which coincide with the
argon ion 488.0nm line:

<table>
<thead>
<tr>
<th>Vibronic Transition</th>
<th>Rotational Transition</th>
<th>Transition Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2^0_1^0 0^1_4 )</td>
<td>( 13^1_{2,12} \rightarrow 13^1_{1,13} )</td>
<td>20486.710cm(^{-1})</td>
</tr>
<tr>
<td>( 2^0_1^3 0^1_4 )</td>
<td>( 16^1_{1,16} \rightarrow 15^0_{0,15} )</td>
<td>20486.558cm(^{-1})</td>
</tr>
</tbody>
</table>

Due to its greater intensity and superior frequency overlap with the argon ion
488.0nm emission line, the \( 13^1_{2,12} \rightarrow 13^1_{1,13} \) rovibronic transition was selected as the
PROBE transition for the transient gain experiments.

2.4.2 Depopulation Studies

Figure 2-6 presents a typical time-resolved decay profile obtained during our
measurements of depopulation processes within the \( v_4 = 1 \) vibrational manifold of
\( \tilde{A}^1A_2 \) formaldehyde-\( h_2 \) \((c.f. \text{ Figure } 2-3)\). The actual data, represented by the
individual black dots, are obtained by directly monitoring the transitory gain signal
appearing on the cw PROBE beam subsequent to rapid excitation of the \( 13^1_{2,12} \)
rovibronic level by the pulsed PUMP. This trace was acquired by programming a
high-speed transient digitizer to signal average over 1024 pulses of the PUMP laser.
Similar curves were obtained for various formaldehyde pressures ranging from 0 to
300 mTorr with the magnitude of the observed gain signals never exceeding 1 part
in 1000 for the 120cm long sample path length utilized in these experiments.

The solid curve in figure 2-6 represents the results of fitting the transient gain
data to a single exponential decay convoluted with the temporal response function.
Figure 2-8: Typical Decay Curve from Transient Gain Spectroscopy.
$H_2CO \overset{\tilde{A}}{\overset{1}{A}} \overset{1}{A}_2 \; \overset{v}{v}_4 = 1 \; 13_2^{12}$

Transient Gain Signal

$P = 0.1465$ Torr

$\tau = 51.3 \pm 1.3$ ns

Decay Time (ns)

Amplitude (arb)
of our apparatus. A lifetime of $51.3 \pm 1.3\text{ns}$ (one standard deviation uncertainty) is measured for the indicated formaldehyde pressure of $\sim 150\text{ mTorr}$.

The dependence of the measured depopulation rates upon the pressure of the formaldehyde sample is illustrated in figure 2-7. This diagram contrasts the Stern-Volmer plots obtained by monitoring (1) the undispersed fluorescence and (2) the transient gain signal following abrupt excitation of the $\tilde{A}^1\Sigma_g^+ v_4 = 1$ rotation-vibration level in $\tilde{A}^1\Pi_2$ formaldehyde.

The curvature observed in the undispersed fluorescence data, which masks the true rate of population removal, has been interpreted in terms of a rapid collision-induced transfer of molecules from the initially prepared level to several adjacent levels possessing radically different decay rates [187, 19]. The undispersed fluorescence results thus measure a lifetime-weighted, average depopulation rate for the manifold of fluorescing states into which the $13_{2,12}$ rovibronic level collisionally relaxes. Despite the complicated multiple-level kinetics associated with the time-resolved fluorescence decay signals, the recorded data were well represented by a single exponential over the entire pressure region studied.

The transient gain signal, however, shows a linear Stern-Volmer plot over the entire 0 to 300 mTorr pressure range yielding a zero-pressure lifetime of $279 \pm 10\text{ns}$ and a depopulation rate of $110.5 \pm 3.1\mu\text{sec}^{-1}\text{Torr}^{-1}$. This rate, corresponding to a velocity averaged cross section of $526 \pm 10\text{Å}^2$, is in good agreement with that suggested by scaling the results of microwave line-broadening experiments [183, 189], performed in the vibrationless level of the ground electronic potential surface, by the ratio of the electric dipole moments in the $\tilde{X}$ and $\tilde{A}$ electronic states. Kinetic modelling of undispersed fluorescence data in $\text{H}_2\text{CO}$ [187, 156] and dispersed fluorescence measurements in $\text{D}_2\text{CO}$ [190] have also indicated similar collisional depopulation rates.
Figure 2-7: Stern-Volmer Plots for $13_{2,12} v_4 = 1 A_2^1$ Formaldehyde $h_g$
\( \text{H}_2\text{CO} \quad \tilde{A}^1\text{A}_2 \quad \nu_4=1 \quad 13_{2.12} \)

- **Fluorescence Decay Data**
- **TGS Decay Data**

\[ \tau_0 = 279 \pm 10 \text{ ns} \]
\[ k_T = 110.5 \pm 3.1 \quad \mu\text{sec}^{-1} \text{ Torr}^{-1} \]
\[ \sigma_T = 526 \pm 10 \quad \text{Å}^2 \]

**Decay Rate (μsec\(^{-1}\))**

**Formaldehyde Pressure (Torr)**
The depopulation experiments performed upon $\tilde{A}^1A_2$ formaldehyde have conclusively demonstrated that the anomalous curvature encountered in previous Stern-Volmer kinetic studies is an artifact produced by the nonselective nature of undispersed fluorescence detection. By replacing the slits and gratings of a conventional monochromator with a narrow-band PROBE laser, the double resonance technique of Transient Gain Spectroscopy has enabled observation of the temporal evolution for a single rovibronic level within the $\tilde{A}$ state. In this manner the complications introduced by collisional energy transfer among neighboring rotation-vibration eigenstates are essentially eliminated without the considerable deterioration of signal that would accompany traditional dispersed fluorescence measurements.

2.4.3 State-to-State Energy Transfer Experiments

Having succeeded in measuring the true removal rate for a single rotation-vibration level in the $\tilde{A}^1A_2$ state, we now directed our attention towards elucidation of the specific collisional relaxation channels available to electronically excited formaldehyde molecules. First of all, the large cross section for depopulation of the $13_{2,12}$ rovibronic level indicates that a rather long-range interaction is involved in the relaxation process. This rapid removal rate, together with the large permanent electric dipole moments measured in both the ground and excited electronic states of formaldehyde (2.33D [3] and 1.46D respectively), suggests that the predominant self-relaxation mechanism entails a dipole-dipole interaction.

Both theoretical and experimental studies have established rotational energy transfer as the most probable inelastic collisional process, typically occurring with $\sim 50$ times the likelihood of vibrationally inelastic events and nearly two orders of magnitude greater frequency than electronic energy exchange [157]. Although
exceptions to these generalizations have been documented [191, 192], their existence usually depends upon a breakdown in the separability between rotational, vibrational, and electronic degrees of freedom. In short, the mixing of rovibronic character which accompanies the interaction of a pair of zeroth-order vibrational or electronic manifolds can significantly enhance the state-to-state cross sections by enabling collisional relaxation to proceed through essentially a purely rotational mechanism. From this viewpoint, the prevalent nonadiabatic perturbations between the $S_1$ and $S_0$ potential surfaces of formaldehyde could provide the impetus for efficient depopulation of individual rotation-vibration levels within the $\tilde{A}^1A_2$ state via an internal conversion pathway [167].

Experiments performed within the $\tilde{A}^1A_2$ state of formaldehyde have indicated that vibrational relaxation between the $v_4 = 1$ and $v_4 = 0$ levels proceeds with $\sim 2$-3 times the efficiency of gas kinetic encounters [193, 194]. This unusually rapid state-to-state rate (i.e. vibration-to-vibration collisional processes typically occur with less than gas kinetic efficiency [157]) can be rationalized in terms of the small energy gap (viz. 67.0 cm$^{-1}$ in D$_2$CO and 124.5 cm$^{-1}$ in H$_2$CO) which separates the lowest levels in the $v_4$ mode. However, the exceptionally large total removal cross section (i.e. $\geq 10$ times gas kinetic) determined by our transient gain measurements suggests that the depopulation of individual rovibronic eigenstates entails an even more efficient mechanism. In view of the discussion presented above, pure rotation changing processes within the $v_4 = 1$ manifold can be expected to be the most probable collisional relaxation pathway available to the levels examined in the present kinetic study (i.e. provided that the distinction between electronic, vibrational, and rotational degrees of freedom is maintained).

At the long ranges which characterize collision-induced depopulation of formaldehyde (cf. large total removal cross section determined for 13$_{2,12}$ level), the
intermolecular potential can be conveniently expressed in terms of the electrostatic interactions between permanent and induced molecular multipole moments [195, 196, 197]. The application of this formalism to the study of rotational relaxation in polyatomic systems has been thoroughly reviewed by Oka [180]. In the case of formaldehyde, the first nonzero electric moment of the charge distribution is the dipole [2]. Therefore, to lowest order, the self-relaxation of formaldehyde can be expected to occur primarily through the mutual coupling of dipole moments between the colliding molecules. The propensity rules for pure rotation changing processes induced by a permanent electric dipole moment along the molecular a-axis of an asymmetric rotor (e.g. formaldehyde) can be expressed by [180]:

$$\Delta J = 0, \pm 1 \quad \Delta K_a = 0 \quad \Delta K_c = \pm 1$$  \hspace{1cm} (2.1)$$

where \(J\) denotes the total rotational angular momentum which has approximate projection quantum numbers of \(K_a\) and \(K_c\) along the \(a\) and \(c\) molecular axes. These first order propensity rules neglect interactions due to induction and dispersion forces as well as those derived from higher order permanent multipole moments (e.g. dipole-quadrupole, quadrupole-quadrupole, etc.). These additional factors, which are expected to play a relatively small role in the strongly dipolar formaldehyde-formaldehyde collision system, will slightly modify the predicted propensities most notably by the inclusion of larger \(|\Delta J|\) changes [198].

On the basis of the dipole-dipole propensity rules in equation (2.1), the \(13_{2,12}\) level, which forms the upper state for the PROBE transition in the transient gain studies, should exhibit a strong propensity to undergo collisional relaxation to three adjacent rovibronic levels within the \(v_4 = 1\) manifold of \(\tilde{A}^1A_2\) formaldehyde. These pathways, which are illustrated in figure 2-8, can be specified both in terms of the
Figure 2-8: Dipole-Dipole Propensity Rules for Rotation Changing Collisions.
Permanent Dipole Moment along
the molecular γ-axis
(ΔK_a=0 Manifold)
angular momentum change, \( \Delta J \), and rotational energy gap, \( \Delta E_{\text{rot}} \), involved in the collisional exchange process:

\[
\begin{align*}
13_{2,12} &\rightarrow 12_{2,11} & \Delta J &= -1 & \Delta E_{\text{rot}} &= -27.7 \text{cm}^{-1} \\
13_{2,12} &\rightarrow 13_{2,11} & \Delta J &= 0 & \Delta E_{\text{rot}} &= +1.25 \text{cm}^{-1} \\
13_{2,12} &\rightarrow 14_{2,13} & \Delta J &= +1 & \Delta E_{\text{rot}} &= +29.8 \text{cm}^{-1}
\end{align*}
\]

In addition, a simple calculation based on dipole selection rules indicates that depopulation via either the \( \Delta J = +1 \) or \( \Delta J = -1 \) pathway should be a factor of twenty times more probable than the \( \Delta J = 0 \) relaxation mechanism. Note that all of the rotational energy gaps are considerably smaller than the translational energies available at room temperature (i.e. \( kT \sim 200 \text{cm}^{-1} \)).

To assess the relative importance of pure rotational relaxation in comparison to other depopulation processes, the energy transfer experiment depicted in figure 2-9 was performed. Due to the restricted tunability of the the argon ion PROBE (\( \sim 7 \text{ GHz} \)), these state-to-state measurements had to be performed in a somewhat reversed fashion. The PUMP laser was now tuned to coincide with \( 4_0^1 \) rovibronic transitions terminating on specific rotational levels that could be collisionally coupled to the \( 13_{2,12} \) upper state of the PROBE transition. Illustrated in figure 2-0 is the \( \Delta J = -1, \Delta K_a = 0 \) process between the \( 13_{2,12} \) and \( 12_{2,11} \) rotational levels, which is expected to be highly probable on the basis of dipole–dipole propensity rules. The observed transient gain signals should now rise as collisions transfer molecules into the \( 13_{2,12} \) level and subsequently decay as the \( 13_{2,12} \) level depopulates.

Figure 2-10 illustrates typical experimental energy transfer profiles obtained by exciting either the \( 12_{2,11} \) or \( 14_{2,13} \) rovibronic level and monitoring, through
Figure 2-9: Energy Level Scheme for Rotational Relaxation Studies.
\[ \tilde{A}^1A_2 \left\{ \begin{array}{c} \tilde{X}^1A_1 \\ \end{array} \right\} \]

PUMP
\[ \sim 353 \text{nm} \]
\[ \text{pulsed dye} \]

\[ \sim 27.7 \text{cm}^{-1} \]

\[ 12_{2,11} \]

PROBE
\[ 488.0 \text{nm} \]
\[ \text{cw Argon ion} \]

\[ 2^0_13^0_34^1_4 \]

\[ 13_{1,13} \]

\[ \sim 7830 \text{cm}^{-1} \]

\[ 11_{1,10} \]

\[ 13_{1,13} \]
**Figure 2-10**: Rotational Energy Transfer in $\tilde{A}^1A_2$ Formaldehyde.
$13_2,12 \leftarrow 12_2,11$
0.1120 Torr

$k_{13-12} = 31 \pm 8 \mu\text{sec}^{-1} \text{ Torr}^{-1}$

$13_2,12 \leftarrow 14_2,13$
0.1203 Torr

$k_{13-14} = 40 \pm 6 \mu\text{sec}^{-1} \text{ Torr}^{-1}$
Transient Gain Spectroscopy, the population of the $13_{2,12}$ level (cf. figure 2-8). The actual data, denoted by the individual black dots, is the result of averaging the transitory gain signal appearing on the cw PROBE beam over 1024 pulses of the PUMP laser. Similar time-resolved curves were obtained over a wide range of formaldehyde pressures (viz. 0 to 250mTorr) with collisional transfer still quite visible at $\leq$ 30mTorr.

In addition to the collisional processes illustrated in figure 2-10, rotational energy transfer experiments were attempted by excitation of the $14_{2,12}$, $12_{2,10}$, and $13_{2,11}$ rovibronic levels within the $v_4=1$ vibrational manifold of $\tilde{A}^1A_2$ formaldehyde (cf. figure 2-8). Even at quite high sample pressures (viz. $> 200$ mTorr), no transient gain signals could be detected for any of these cases. As suggested by the propensity rules in equation (2.1), the strongly dipolar nature of formaldehyde-formaldehyde encounters will not favor the direct transfer of population between either the $14_{2,12}$ or $12_{2,10}$ levels and the upper state of the PROBE transition (viz. $13_{2,12}$). The absence of signal in the $13_{2,11} \rightarrow 13_{2,12}$ collisional pathway can be attributed, at least in part, to the lower probability ascribed to the $\Delta J = 0$ mechanism on the basis of simple dipole-dipole interactions.

Kinetic modelling of the time-resolved energy transfer measurements is required in order to interpret our results in terms of specific state-to-state relaxation cross sections. Therefore, the analysis of the transient gain data was based upon a system of coupled first order differential equations with rate parameters which could be adjusted to account for the temporal evolution of the molecular populations within the various rotational levels of the $v_4=1$ manifold. In this treatment, the population of the $i^{th}$ rovibronic level, $N_i(t)$, is given by:
\[
\frac{\partial N_i(t)}{\partial t} = \sum_j (1 - 2\delta_{ji}) k_{ji} N_j(t) + A_i(t - t_0) \\
= -k_{ii} N_i(t) + \sum_{j \neq i} k_{ji} N_j(t) + A_i(t - t_0)
\] (2.2)

where

- \( k_{ii} \) denotes the total depopulation rate for the \( i^{th} \) level,
- \( k_{ji} \) denotes the rate of population transfer from level \( j \) to level \( i \),
- \( A_i(t - t_0) \) represents the time dependent pumping term corresponding to the \( i^{th} \) level. For the single rovibronic state actually excited in a given energy transfer experiment, \( A_i(t - t_0) \) is basically the temporal profile of the PUMP laser pulse scaled by the appropriate PUMP transition strength. All other (umpumped) rovibronic levels would have \( A_i(t - t_0) = 0 \),
- \( t_0 \) signifies the reference time at which the PUMP pulse begins to interact with the formaldehyde sample.

Since our transient gain measurements were performed in an excited electronic state which is strongly perturbed by nonadiabatic interactions, both spontaneous emission and radiationless relaxation processes play a significant role in the depopulation of individual rovibronic eigenstates. Therefore, the total removal rate for the \( i^{th} \) level, \( k_{ii} \), will contain contributions from both collision-free, \( k_i^0 \), and collision-induced, \( k_i \), mechanisms:

\[
k_{ii} = k_i^0 + \rho k_i
\] (2.3)

where \( \rho \) denotes the density (i.e. \( \sim \) pressure) of the pure formaldehyde sample under consideration. Provided that all collisionally-coupled rovibronic levels are incorporated into the kinetic model, the collision-induced parameters, \( k_i \), will satisfy
a population conservation criterion (\textit{viz.} \( k_i = \sum_{j \neq i} k_{ij} \)). Equation (2.3) constitutes a definition for the decay rate that would be observed in a Stern-Volmer kinetic scheme [157].

The limited data obtained in the state-to-state relaxation studies required that several simplifying assumptions be incorporated into the kinetic scheme embodied in equations (2.2) and (2.3). The inability to detect any collisional transfer signals for the \( \Delta J = 0 \) process \( \text{13}_{2,12} \leftrightarrow \text{13}_{2,11} \) suggested that the present analysis could be constrained to the \( \Delta J = \pm 1 \) pathways. Therefore, to first order, the transient gain signals observed within the \text{13}_{2,12} \text{PROBE} transition subsequent to excitation of either the \text{14}_{2,13} \text{or} \text{12}_{2,11} \text{rovibronic levels can be described in terms of separate three level model systems (c.f. figure 2-8):}

\[
\text{13}_{2,12} \leftrightarrow \text{14}_{2,13} \leftrightarrow \text{15}_{2,14}
\]

\[
\text{13}_{2,12} \leftrightarrow \text{12}_{2,11} \leftrightarrow \text{11}_{2,10}
\]

The rates for the two collisional transitions associated with each of the pumped levels (i.e. \text{14}_{2,13} \text{and} \text{12}_{2,11}) were taken to be equal except for scaling factors related to level degeneracy and rotational energy gap.

An additional assumption incorporated into the present analysis concerns the total removal rates, \( k_{ii} \), attributed to individual levels within the kinetic scheme (\textit{c.f.} equation (2.3)). Each of the collision-free decay constants, \( k_i^0 \), was fixed at the value determined through low pressure time-resolved fluorescence measurements (\textit{i.e.} except for the \text{13}_{2,12} \text{level where the TGS value of} k_i^0 \text{was utilized}). In contrast, the collision-induced parameters, \( k_i \), were all set equal to the depopulation rate determined from our transient gain studies of the \text{13}_{2,12} \text{rovibronic level (\textit{viz.}} \text{ } k_i = 110.5 \mu \text{sec}^{-1} \text{Torr}^{-1} = 3.412 \times 10^{-9} \text{cm}^3\text{molec}^{-1}\text{sec}^{-1}). \text{In effect, this procedure}
partially accounts for the presence of background states which are not explicitly considered in the three level model.

The optimum state-to-state rate constants were determined through a least squares regression procedure in which the temporal profiles calculated for the $^{13}_2,^{12}$ PROBE level on the basis of the kinetic model were compared to the experimental transient gain signals. This analysis yielded values of $31 \pm 8 \mu \text{sec}^{-1} \text{Torr}^{-1}$ and $40 \pm 6 \mu \text{sec}^{-1} \text{Torr}^{-1}$ for the $^{13}_2,^{12} \Delta J = -1$ and $\Delta J = +1$ processes respectively. The quality of the fits resulting from the energy transfer modelling are demonstrated by the solid curves presented in figure 2-10. It should be stressed that the relatively short time scales encountered in the present collisional studies necessitated that the response function for our apparatus (e.g. the $A_1(t - t_0)$ terms in equation (2.2)), be explicitly taken into account.

The state-to-state relaxation rates determined from our transient gain signals are in relatively good agreement with the dipole-scaled results of recent kinetic measurements performed by Orr and coworkers [199, 200, 201] in the ground electronic state of formaldehyde-$d_x$. The velocity averaged cross sections for the observed relaxation channels, $\sigma_{13 \rightarrow 12} = 143 \pm 38 \text{Å}^2$ and $\sigma_{13 \rightarrow 14} = 190 \pm 29 \text{Å}^2$, also compare favorably with the values calculated by van Hulst [202] on the basis of an adiabatically corrected variant of the sudden approximation (viz. calculated cross sections: $\sigma_{13 \rightarrow 12} = 171 \text{Å}^2$ and $\sigma_{13 \rightarrow 14} = 157 \text{Å}^2$). The crucial point derived from these energy transfer studies is that pure rotation changing processes, in particular the $\Delta J = \pm 1$ pathways examined above, can account for a substantial portion of the collisional depopulation rates attributed to individual rovibronic levels in the $\tilde{A}^1\text{A}_2$ state. The presence of nonadiabatic perturbations between the $S_{1/2}$ and $S_{3/2}$ electronic manifolds would appear to have little influence, if any, upon the collision-induced relaxation of electronically excited formaldehyde-$h_x$.
2.4.4 Concluding Remarks

The results presented in this Chapter have conclusively demonstrated the utility of Transient Gain Spectroscopy for situations in which the competition between nonradiative and collisional relaxation pathways precludes the application of more traditional kinetic probes (viz. those based upon dispersed molecular fluorescence). In the case of $\tilde{A}^1A_2$ formaldehyde-$h_g$, our measurements have provided the first definitive evidence linking the non-Stern-Volmer behavior observed in previous depopulation studies with the pervasive nature of pure rotation-changing collisions in the electronically excited manifold. Furthermore, the propensities observed in the state-to-state energy transfer experiments support the predominance of dipole-dipole interactions in the self-relaxation of formaldehyde. The major limitation associated with the current formulation of the TGS technique, the restricted tunability of the argon ion PROBE laser, will be addressed in subsequent Chapters of this thesis.
Chapter 3

Polarization Probes of $\tilde{A}^1A_2$ Formaldehyde-$h_2$

3.1 Introduction

The transient gain experiments of the previous Chapter have provided considerable insight into the collision-induced photochemical and photophysical processes which occur in $\tilde{A}^1A_2$ formaldehyde-$h_2$. The immunity of this double resonance technique to the non-Stern-Volmer kinetic behavior associated with earlier time-resolved studies has also permitted accurate determination of collision-free lifetimes through linear extrapolation of measured decay rates to zero pressure. As presently formulated, however, the method of Transient Gain Spectroscopy is severely limited by the requirement that a coincidence in frequency exist between the single mode emission of a barely tunable cw PROBE laser (viz. an argon ion laser) and a rovibronic transition within the $\tilde{A} \rightarrow \tilde{X}$ band system. Although the substantial density of rotation-vibration eigenstates encountered in highly excited regions of the ground electronic potential surface might appear to greatly augment the number of suitable PROBE-resonant rovibronic transitions, their location and spectroscopic assignment is still, at best, a most laborious and somewhat uncertain proposition. These constraints make it virtually impossible to utilize this technique in a systematic investigation of relaxation pathways for individual rovibronic levels within the $\tilde{A}$ state.

The principal goal of the work presented in this Chapter was to extend the previous kinetic studies to encompass other rotational eigenstates within the $v_4 = 1$ out-of-plane bending mode of $\tilde{A}^1A_2$ formaldehyde-$h_2$. These measurements, which
necessitated the development of a new time-resolved detection scheme, were crucial for ascertaining the general applicability of our earlier results (i.e. rotational relaxation rates and propensities) to the description of collision-induced photophysical processes in the first excited singlet state of formaldehyde. In addition, the successful outcome of these investigations was an essential prelude for ensuing experiments which were designed to probe the relaxation mechanisms available to highly excited rotation-vibration eigenstates within the ground electronic potential surface of formaldehyde (c.f. Chapter 4).

An obvious solution to the limitations imposed by the restricted tunability of the argon ion PROBE beam was to replace it with a tunable continuous wave dye laser. In this manner, the PROBE frequency could be easily scanned into resonance with virtually any rovibronic transition in the $\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1$ electronic system. A systematic investigation of collisional processes within the first excited singlet state of formaldehyde could therefore be performed in essentially the same fashion as that employed for the TGS measurements. While this is, in theory, the correct approach, attempts to implement it were severely hampered by the large power fluctuations encountered in the output of a single mode cw dye laser. The origin of this amplitude noise, which extended over a broad frequency spectrum, can be attributed to two rather distinct features of continuous wave dye laser technology:

1. Instabilities in the dye laser jet stream.

Most commercially available cw dye lasers depend upon the use of a laminar-flow jet stream in order to rapidly translate the dye solution through the excitation region of the resonator. This permits a uniform and uninterrupted supply of fresh gain medium to be introduced into the laser cavity in a manner which minimizes thermal lensing induced by the tightly focussed pump radiation.

However, from the viewpoint of our transient gain measurements, the major difficulty associated with such jet stream technology arises as a result of microscopic bubbles within the dye solution. When these
micron-sized air pockets pass through the excitation region of the resonator, they can cause a momentary extinction of laser oscillation. These occlusion events, which occur randomly on a microsecond to sub-microsecond time scale for typical flow rates, translate into a substantial amplitude fluctuation on the cw output with an approximately $1/f$ frequency spectrum that extends to well beyond 10MHz. Additional noise problems are produced by lower frequency variations in the macroscopic dimensions of the dye stream itself.

2. Interference between cavity mode structure in the pump beam.

The conventional method for generating tunable cw radiation employs the multimode output of a gas ion laser, operating in either a single line or all line configuration, to excite the gain medium within a dye laser resonator. By utilizing various intracavity optical elements, the resulting dye laser emission can be forced to oscillate on an individual cavity mode.

However, multimode operation of the ion laser will result in gain modulation of the active medium within the dye laser resonator [176]. This effect, which originates from the interference between coherently related mode structures in the excitation beam, ultimately translates into power fluctuations on the cw output of the dye laser. The frequency spectrum of this amplitude noise is constrained to distinct, relatively well-defined values which correspond to the separation of longitudinal and/or transverse cavity modes within the pump laser.

Although problems introduced by multimode excitation can, in principle, be alleviated by utilizing a single mode TEM$_{00}$ pump beam, the difficulties associated with the dye jet stream represent an intrinsic and unavoidable consequence of present-day dye laser technology. These instabilities translate into a substantial increase in both the size and bandwidth of amplitude fluctuations encountered in the output of a dye laser. In fact, it has been estimated [203, 175] that such dye laser systems exhibit over three orders of magnitude more total noise (i.e. averaged over a 0 to 100 MHz detection Bandwidth) than a comparable fixed-frequency cw gas laser such as the argon ion PROBE employed in the previously described transient gain measurements.
Despite the power fluctuations encountered in the output of the cw dye laser, initial experiments with this tunable radiation source as the PROBE were conducted in essentially the same manner as that employed for the TGS measurements of the previous Chapter. Although marginal transient gain signals could be observed on the strongest PROBE rovibronic transitions, the degree of electronic filtering (both high and low pass) required to obtain reasonable signal-to-noise ratios produced severe distortions in the time-resolved decay profiles. Indeed, the amplitude noise on the dye laser not only exceeded normally anticipated signal levels but, oftentimes, even transcended the dynamic range of our detection equipment.

It soon became apparent that the successful outcome of our extended kinetic studies would necessitate modification of the transient gain detection scheme to compensate for the amplitude fluctuations present on the output of the cw dye laser. The methods currently available for suppressing the effects of excess PROBE noise can be classified into two broad categories depending upon which aspects of the problem they address:

1. Methods designed to reduce the amplitude noise on the cw dye laser itself.

The most direct solution to the problem of excessive PROBE noise was to drastically reduce the magnitude of power fluctuations in the dye laser output. With such a *quiet* cw source, the transient gain measurements could proceed in essentially the same manner as described previously except now the PROBE radiation would be completely tunable.

Consequently, a commercial noise reduction system (*Coherent model 307 Noise-eater*), which consisted of an electro-optic light modulator controlled by an amplitude-locked feedback circuit, was utilized in an attempt to produce a *quiet* cw PROBE beam. This approach met with only very limited success, however, since the amplitude stabilizing electronics, which had a 10MHz gain-bandwidth product, tended to transform low frequency power fluctuations (*i.e.* < 1MHz) into high
frequency noise (i.e. > 1MHz). This was totally unacceptable in view of the wide bandwidth requirements (i.e. approximately 0.1 to 100 MHz) imposed by our time-resolved kinetic experiments.

Reports have recently appeared in the literature [204] regarding the use of wide bandwidth amplitude and frequency stabilization systems for cw dye lasers. However, the time that would be required for the implementation of these instruments precluded their use in our kinetic investigations.

2. Methods designed to reduce the noise observed by the detection electronics.

A less direct approach for alleviating the problems caused by amplitude fluctuations on the cw dye laser PROBE was to essentially decrease the total amount of noise observed. The two most obvious means for accomplishing this depend upon either (a) reduction of the detector bandwidth or (b) utilization of a null detection scheme. As previously mentioned, attempts to reduce the detection bandwidth, through electronic filtering, did not prove to be a tractable solution from the viewpoint of our time-resolved measurements.

The concept of null detection (i.e. no detector response unless a true signal is present) has been successfully exploited for many years in the form of fluorescence excitation spectroscopy [205]. However, this technique, which is the most prevalent of the zero-background detection schemes, is not applicable in the present situation. In short, cw excited spontaneous emission (i.e. PROBE-induced emission from either a highly excited rotation-vibration eigenstate in the ground electronic potential surface or, more likely, from a higher excited electronic state) would necessarily result in an unacceptable convolution of the desired transient gain signal with the fluorescence lifetime of the terminal level in the PROBE transition. This difficulty could be overcome by utilizing a pulsed PROBE laser which is capable of being independently time-delayed, in a precise fashion, with respect to the PUMP [199, 201, 206, 207]. Kinetic information would thus be obtained by scanning the time interval between the PUMP and PROBE pulses while simultaneously monitoring the relative intensity of the PROBE-induced spontaneous emission. The implementation of this experimental scheme, which has its own intrinsic set of problems (e.g. experimental conditions may not remain constant during the time interval required to complete a full PUMP/PROBE delay cycle), was not technically feasible at the time that these kinetic studies were being performed.
A much less frequently exploited means for performing zero-background measurements is provided by the technique of polarization spectroscopy [208, 209]. This null detection scheme, which is based upon observation of the birefringence and dichroism induced in a molecular sample by optical pumping, was well suited to the pulsed PUMP, cw PROBE configuration which characterized our previous transient gain experiments. For this reason, and for the enhanced sensitivity which this method promised to afford, polarization spectroscopy was adopted for our extended kinetic studies of $\tilde{A} \, ^1A_2$ formaldehyde-$h_2$.

The sections which follow will first review the methodology of polarization spectroscopy with particular emphasis on its application to our time-resolved measurements. A rather complete discussion of both the conceptual and technical foundations of this null detection scheme will be provided. After a description of experimental details, the results of the kinetic studies in formaldehyde-$h_2$ will be presented and interpreted in the context of the photophysical processes occurring within the $\tilde{A} \, ^1A_2$ state.

3.2 Conceptual and Theoretical Foundations of Polarization Spectroscopy

3.2.1 Introduction

The method of laser polarization spectroscopy was first developed and exploited by Wieman and Hansch in the mid 1970s [210]. Since that time, numerous workers have been attracted by the high-sensitivity and sub-Doppler resolution afforded by this relatively simple double resonance technique. The ability of polarization spectroscopy to monitor specifically a preselected group of molecules has provided a powerful tool for numerous spectroscopic and kinetic studies ranging from the simplification of complex molecular spectra [211, 212, 213, 214] to the elucidation of fundamental collisional relaxation processes [215].
Polarization spectroscopy utilizes the polarization properties of light in order to selectively label and subsequently detect a specific group of gas phase molecules. The molecular sample is first oriented or aligned (cf. discussion below) by optical pumping with the polarized emission from an intense PUMP laser. The spatial anisotropy created within the molecular system by such polarized excitation can be sensitively monitored through its depolarizing effect on a relatively weak PROBE beam. It is this change in the polarization state of the PROBE radiation (i.e. induced by the anisotropic molecular sample) which constitutes the signal for an experiment based upon the technique of polarization spectroscopy.

The conceptual foundations of laser polarization spectroscopy are best illustrated by reference to the experimental diagram presented in figure 3-1. A sample of the molecular system under investigation is placed between a set of crossed polarization optics such as Glan-Laser calcite prisms [216]. A relatively weak, linearly polarized PROBE beam is subsequently directed down the axis defined by the polarization optics and ultimately impinges upon a sensitive photon detector. An intense PUMP laser beam traverses the gaseous sample at a slight angle to the counterpropagating PROBE.

Propagation through the first calcite prism greatly enhances the polarization contrast ratio of the PROBE beam so that it can be effectively cancelled by the second polarization analyzing prism. Consequently no light reaches the photon detector and no signal is recorded. This situation persists as long as the molecules remain spatially isotropic so that the polarization characteristics of the PROBE are unaltered by passage through the gaseous molecular sample. For the double resonance technique of polarization spectroscopy, such zero-signal conditions can exist only when the PUMP and PROBE beams are incapable of interacting with a common group of molecules.
Figure 3-1: Experimental Scheme for Polarization Spectroscopy.
a. Interaction with different groups of molecules.

Isotropic Molecular System

b. Interaction with same group of molecules.

Anisotropic Molecular System
For experiments based upon radiation sources with bandwidths comparable to the inhomogeneous Doppler broadening of the molecular sample, the zero-signal conditions of polarization spectroscopy can be satisfied only if the rotation-vibration levels of the PROBE transition are distinct from those of the PUMP. In the case a sub-Doppler measurement (viz. one that utilizes narrow-band laser sources), however, the absence of signal can persist even for linked PUMP and PROBE rovibronic transitions provided that the two beams do not simultaneously interact with molecules possessing the same axial velocity.

When the PUMP and PROBE beams interact with the same group of molecules, however, the situation is drastically altered. If the PUMP polarization is selected properly (i.e. either circularly polarized or linearly polarized in a direction neither parallel nor perpendicular to the PROBE polarization), the molecular sample will no longer be isotropic. In short, the polarized nature of the PUMP radiation results in a differential excitation of the degenerate angular momentum components (i.e. the sublevels designated by the magnetic quantum number $M$) present in the rovibronic levels of the PUMP transition. This nonuniform population of the degenerate magnetic sublevels translates into an induced optical anisotropy with respect to the PROBE beam.

The optically anisotropic molecular system is both birefringent and dichroic for the incident, linearly polarized PROBE light. As a result, the plane of polarization and the ellipticity of the PROBE beam are slightly altered by propagation through the gaseous sample. The polarization component of the "rotated" PROBE orthogonal to that of the incident radiation passes through the second polarization analyzing calcite prism and enters the photon detector, thereby producing a signal. The depolarization of the PROBE beam thus serves to indicate that a double resonance condition exists between the PUMP and the PROBE (i.e.
they interact with the same group of molecules).

Since the crossed polarization optics transmit the PROBE laser only when a signal is present, polarization spectroscopy permits background-free spectroscopic measurements to be performed on gas phase molecular systems. This is especially important for situations in which the random intensity fluctuations of the interrogating light source would severely limit the ultimate sensitivity achieved in an experiment. The sub-Doppler aspect of the polarization technique can be appreciated by realizing that if the PUMP and PROBE beams are derived from the same narrow band laser and are counterpropagating they will simultaneously interact only with the group of molecules having essentially zero axial velocity. The inhomogeneously broadened Doppler profiles normally encountered in gas phase spectra will therefore be reduced to a single, nearly laser linewidth limited feature located at the center frequency of the molecular transition.

The central role which polarization spectroscopy plays in both the present and the succeeding Chapters necessitates that the reader be familiar with the origins and the characteristics of signals observed in such experiments. The following sections will therefore discuss the theoretical foundations of polarization-based detection schemes with particular emphasis on how the results of these methods are expected to differ from those obtained with traditional absorption techniques (or less conventional gain techniques). In the context of the work presented in this thesis, the signal to noise ratio and temporal response of polarization spectroscopy will be topics of principal concern.

3.2.2 Absorption and Dispersion

Due to the importance of absorption and dispersion phenomena in the creation of polarization signals, a short review of wave propagation in a sourceless, linear
medium will be presented. Manipulation of Maxwell's equations results in the following differential expression for the electric field vector, \( \mathbf{E} \), associated with an electromagnetic wave:

\[
\nabla^2 \mathbf{E} = -\mu \frac{\partial^2 \mathbf{D}}{\partial t^2}
\]

(3.1)

where

\( \mathbf{D} \) represents the electric displacement field vector,

\( \mu \) represents the magnetic permeability of the medium.

The transverse nature of the electromagnetic wave has removed the divergence term (i.e. \( \nabla(\nabla \cdot \mathbf{E}) \)) which would normally appear in equation (3.1).

The electric displacement field can be expressed in terms of the polarization vector, \( \mathbf{P} \), for the medium:

\[
\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}_{nr} + \mathbf{P}_r
\]

\[
= \varepsilon \mathbf{E} + \mathbf{P}_r
\]

(3.2)

where

\( \varepsilon_0 \) represents the electric permittivity of free space,

\( \varepsilon \) represents the electric permittivity of the medium,

\( \mathbf{P}_r \) represents the resonant component of the polarization due to a specific molecular transition within the medium,

\( \mathbf{P}_{nr} \) represents all nonresonant contributions to the polarization.

For a linear, isotropic medium, the resonant component of the polarization is found to be proportional to the electric field vector:

\[
\mathbf{P}_r = \varepsilon_0 \chi(\omega) \mathbf{E}
\]

(3.3)
where $\chi(\omega)$ signifies the frequency dependent linear susceptibility associated with the specific molecular transition within the medium.

Substitution of expressions (3.2) and (3.3) into equation (3.1) yields a new differential equation which has solutions of the form:

$$E = E_0 e^{i(\kappa y - \omega t)}$$  \hspace{1cm} (3.4)

This represents a monochromatic plane wave of angular frequency $\omega$ and amplitude $|E_0|$ propagating along the $+y$ axis with a wavector $\kappa$. The transverse nature of electromagnetic radiation ensures that the vector $E_0$, which describes the polarization characteristics of the wave, will have components only along the $x$ and $z$ axes. The complex notation utilized in equation (3.4) is only for the sake of clarity and convenience. In this and all subsequent expressions, it is to be understood that the real part of the complex term is always implied.

In order for equation (3.4) to be a valid solution for the electric field vector, the value of the wavevector, $\kappa$, must be related to the linear susceptibility, $\chi(\omega)$, in the following manner:

$$\kappa = \sqrt{\mu \varepsilon \omega} \left(1 + \frac{\varepsilon_0}{\varepsilon} \chi(\omega)\right)^{1/2}$$

$$\approx k \left(1 + \frac{\chi(\omega)}{2n^2}\right)$$

where

$$k = \omega \sqrt{\mu \varepsilon}$$

represents the wavevector for an electromagnetic wave of frequency $\omega$ in a medium having magnetic permeability $\mu$ and electric permittivity $\varepsilon$. This would be the wavevector for propagation far from resonance with the molecular transition.
\[ n = \sqrt{\varepsilon/\varepsilon_0} \] represents the index of refraction of the medium far from resonance with the molecular transition.

In the complex notation of equation (3.4), the susceptibility can have both real and imaginary components:

\[ \chi(\omega) = \chi'(\omega) + i\chi''(\omega) \quad (3.5) \]

The electric field vector thus becomes:

\[
\begin{align*}
E &= E_0 e^{-k\chi''(\omega)y/2n^2} e^{ik\chi'(\omega)y/2n^2} e^{i(ky-\omega t)} \\
&= E_0 e^{-\alpha(\omega)y/2} e^{i\eta(\omega)y/2} e^{i(ky-\omega t)} \quad (3.6)
\end{align*}
\]

where

\[ \alpha(\omega) = k\chi''(\omega)/n^2 \] represents the absorption coefficient associated with the resonant transition within the medium,

\[ \eta(\omega) = k\chi'(\omega)/n^2 \] is related to the dispersion or index of refraction associated with the resonant transition within the medium.

The electromagnetic wave is thus seen to undergo both an exponential attenuation (described by \( \alpha(\omega) \)) and a phase shift (described by \( \eta(\omega) \)) as it propagates through the medium. The ensuing discussion will demonstrate that the differential absorption and differential dispersion along two orthogonal axes in an optically anisotropic molecular system are responsible for the signals observed in polarization spectroscopy.

Near resonance (viz. \( \omega \approx \omega_0 \)), the absorption coefficient \( \alpha(\omega) \) and dispersion term \( \eta(\omega) \) can be succinctly described in terms of a normalized spectral lineshape function, \( g(\omega - \omega_0) \), defined by:
\[
\int_{-\infty}^{\infty} g(\omega - \omega_0) \, d\omega = 1
\]

With this definition, the frequency dependence for the absorption and dispersion of a medium can be expressed as follows:

\[
\alpha(\omega) = \alpha^0 \, g(\omega - \omega_0) \tag{3.7}
\]

\[
\eta(\omega) = \eta^0 (\omega - \omega_0) \, g(\omega - \omega_0) \tag{3.8}
\]

where

\[
\alpha_0 \text{ and } \eta_0 \text{ are frequency independent coefficients which depend upon the characteristics of the molecular transition,}
\]

\[
\omega_0 \text{ is the resonance frequency for the molecular transition.}
\]

Finally, recall that the dispersion and absorption associated with a particular molecular transition are related through the complex linear susceptibility \( \chi(\omega) \). Therefore, \( \eta(\omega) \) and \( \alpha(\omega) \) can be expressed in terms of one another by means of the Kramers-Kronig relations [217].

3.2.3 General Description of Polarization Spectroscopy Signals

In order to obtain the appropriate form for the signals expected in a polarization spectroscopy measurement, consider a monochromatic electromagnetic wave, \( \mathbf{E}_{inp} \), propagating along the +y axis. Assume that this input wave is linearly polarized with its direction of polarization oriented at an angle \( \theta \) with respect to the z axis:

\[
\mathbf{E}_{inp} = E \cos \theta \, \hat{e}_z + E \sin \theta \, \hat{e}_x \tag{3.9}
\]
where \( E = E_0 e^{i(ky - \omega t)} \) with \( E_0 = |E_{\text{inp}}| \).

This wave represents the PROBE beam in our polarized detection experiments with the \( z \) axis being defined by the direction of polarization associated with the linearly polarized PUMP laser.

Assume that the electromagnetic wave traverses a medium, of length \( l \), having a differential absorption, \( \Delta \alpha(\omega) \), and a differential dispersion, \( \Delta \eta(\omega) \), along the two axes orthogonal to the direction of propagation:

\[
\begin{align*}
\Delta \alpha(\omega) &= \alpha_z(\omega) - \alpha_x(\omega) \neq 0 \\
\Delta \eta(\omega) &= \eta_z(\omega) - \eta_x(\omega) \neq 0
\end{align*}
\tag{3.10}
\tag{3.11}
\]

where
\( \alpha_z(\omega) \) and \( \alpha_x(\omega) \) represent the absorption coefficients for light polarized along the \( z \) and \( x \) axes as defined in equation (3.6),
\( \eta_z(\omega) \) and \( \eta_x(\omega) \) represent the dispersion for light polarized along the \( z \) and \( x \) axes as defined by equation (3.6).

Equations (3.10) and (3.11) denote an optically anisotropic medium which is both dichroic (\( \Delta \alpha(\omega) \neq 0 \)) and birefringent (\( \Delta \eta(\omega) \neq 0 \)) for the incident electromagnetic wave. This rather special situation can be induced in a gas phase sample of molecules by optically pumping the degenerate \( M \) sublevels of a rovibronic molecular transition with polarized light (\textit{viz.} the PUMP laser). The frequency dependence for the differential absorption and dispersion can be inferred by reference to expressions (3.7) and (3.8), respectively.

The electromagnetic wave emerging from the optically anisotropic medium, \( E_{\text{out}} \), can be described, with the assistance of equation (3.6), as follows:
\[ E_{\text{out}} = E \cos \theta e^{-(\alpha_x(\omega) + i \eta_x(\omega))l/2} e^{-ib_z \hat{e}_z} \]

\[ + E \sin \theta e^{-(\alpha_x(\omega) + i \eta_x(\omega))l/2} e^{-ib_x \hat{e}_x} \]  \hspace{1cm} (3.12)

where \( b_z \) and \( b_x \) are real quantities which account for any phase shift induced by the transparent boundaries of the anisotropic medium (e.g. the windows of the cell containing the gaseous molecular sample).

Equation (3.12) indicates that propagation through the optically anisotropic medium has produced a relative phase shift, \( \Delta \phi \), and a relative amplitude variation, \( \Delta E \), between the \( z \) and \( x \) components of the emerging electromagnetic wave:

\[ \Delta \phi = \text{Arg} (E_{\text{out}} \cdot \hat{e}_z) - \text{Arg} (E_{\text{out}} \cdot \hat{e}_x) \]

\[ = \left( \frac{\eta_z(\omega)l}{2} + b_x \right) - \left( \frac{\eta_x(\omega)l}{2} + b_z \right) \]

\[ \Delta E = |E_{\text{out}} \cdot \hat{e}_z| - |E_{\text{out}} \cdot \hat{e}_x| \]

\[ = E_0 \left( \cos \theta e^{-\alpha_z(\omega)l/2} - \sin \theta e^{-\alpha_x(\omega)l/2} \right) \]

The amplitude variation translates into a slight rotation of the polarization axis associated with the incident electromagnetic wave while the phase difference introduces a small ellipticity into the initial polarization. Equation (3.12) also demonstrates that both of these depolarizing effects will disappear if the polarization vector of the PROBE electromagnetic wave is either parallel or perpendicular to the \( z \) axis (i.e. if \( \theta = 0 \) or \( \theta = \pi/2 \)).

From the point of view of polarization spectroscopy, both the amplitude
variation and the phase shift produced by interaction with the optically anisotropic medium will result in a polarization component of the PROBE electromagnetic wave orthogonal to that of the incident radiation. It is this additional component which is monitored in polarization-based detection schemes. The restrictions placed on the angle $\theta$ indicate that, for a nonzero polarization signal to be observed, the PROBE beam polarization axis must be neither parallel to ($i.e.$ $\theta \neq 0$) nor perpendicular to ($i.e.$ $\theta \neq \pi/2$) that of the PUMP laser.

It will prove convenient to recast equation (3.12) into a form which explicitly contains the differential absorption and dispersion terms:

$$E_{out} = E e^{-ib/2} e^{-(\alpha(\omega) + i\eta(\omega))l/4} \left(\cos \theta e^{-i(\Delta \alpha(\omega) + i\Delta \eta(\omega))l/4} e^{-i\Delta b/2} \hat{e}_z + \sin \theta e^{i(\Delta \alpha(\omega) + i\Delta \eta(\omega))l/4} e^{i\Delta b/2} \hat{e}_x\right) \tag{3.13}$$

where

$\alpha(\omega) = \alpha_z(\omega) + \alpha_x(\omega)$ represents the total absorption coefficient associated with the resonant molecular transition,

$\eta(\omega) = \eta_z(\omega) + \eta_x(\omega)$ represents the total dispersion associated with the resonant molecular transition,

$b = b_z + b_x$ represents the total birefringence induced by the boundaries of the medium,

$\Delta b = b_z - b_x$ represents the differential birefringence induced by the boundaries of the medium.

Assume that, after traversing the optically anisotropic medium, the electromagnetic wave impinges upon a polarization analyzer which is oriented at an angle $\beta$ with respect to the $z$ axis:

$$\hat{e}_{pol} = \cos \beta \hat{e}_z + \sin \beta \hat{e}_x \tag{3.14}$$
where $|\hat{e}_{pol}| = \cos^2 \beta + \sin^2 \beta = 1$.

In a typical polarization-based detection scheme, the analyzer orientation would be approximately orthogonal to the direction corresponding to the linear polarization of the incident PROBE radiation (i.e. $\beta \approx \theta + \pi/2$).

Propagation through the polarization analyzer projects out the component of the electromagnetic wave along the direction $\hat{e}_{pol}$. The electric field vector, $E_\phi$, associated with the PROBE radiation which emerges from the analyzer is thus given by:

$$
E_\phi = (E_{out} \cdot \hat{e}_{pol}) \hat{e}_{pol}
$$

$$
= E \hat{e}_{pol} e^{-i\phi/2} e^{-\left(\alpha(\omega) + i \Delta \eta(\omega)\right)/4} e^{-i\Delta b/2} \left( \cos \theta \cos \beta e^{-\left(\Delta \alpha(\omega) + i \Delta \eta(\omega)\right)/4} e^{-i\Delta b/2} + \sin \theta \sin \beta e^{\left(\Delta \alpha(\omega) + i \Delta \eta(\omega)\right)/4} e^{i\Delta b/2} \right)
$$

(3.15)

If this electromagnetic wave is subsequently monitored by a square law detector, the observed signal intensity, $I_\phi(\omega)$, can be expressed as follows:

$$
I_\phi(\omega) \approx |E_\phi|^2
$$

$$
= E_0^2 e^{-\alpha(\omega)/2} \left( \cos^2 \theta \cos^2 \beta e^{-\Delta \alpha(\omega)/2} + \sin^2 \theta \sin^2 \beta e^{\Delta \alpha(\omega)/2}ight.

+ \left. \frac{\sin 2\theta \sin 2\beta}{2} \cos \left(\Delta \eta(\omega)\right)/2 + \Delta b\right)
$$

(3.16)

Equation (3.16) is the fundamental expression for describing any polarization-
selective detection scheme designed to probe a medium in which an optical anisotropy exists along the \( z \) and \( x \) axes. The dependence of the observed signal intensity on both the incident and analyzed directions of polarization is explicitly indicated (through \( \theta \) and \( \beta \)). Before proceeding, it will prove useful to consider three special cases of equation (3.16) which correspond to the more conventional technique of absorption spectroscopy:

1. Pure absorption detected along the \( z \) axis (\( \theta = \beta = 0 \)):

\[
I_z^{abs}(\omega) \approx E_0^2 e^{-\alpha(\omega)l/2} e^{-\Delta\alpha(\omega)l/2} = E_0^2 e^{-\alpha_z(\omega)l} \\
\approx I_0 (1 - \alpha_z(\omega)l) \tag{3.17}
\]

where \( I_0 \) signifies the intensity of the incident electromagnetic wave and the exponential term has been expanded in the limit of small absorption. This is essentially an expression of Beer's Law for linear absorption [208].

2. Pure absorption detected along the \( x \) axis (\( \theta = \beta = \pi/2 \)):

\[
I_x^{abs}(\omega) \approx E_0^2 e^{\alpha(\omega)l/2} e^{-\Delta\alpha(\omega)l/2} = E_0^2 e^{-\alpha_x(\omega)l} \\
\approx I_0 (1 - \alpha_x(\omega)l)
\]

3. Crossed absorption detected along an orthogonal axis (\( \theta = 0 \) and \( \beta = \pi/2 \) or \( \theta = \pi/2 \) and \( \beta = 0 \)):

\[
I_z^{abs}(\omega) = 0
\]

Each of these absorption techniques orients the polarization axes for both the incident PROBE radiation and the analyzer in such a way that they are either
parallel or perpendicular to the linear polarization of the PUMP beam (viz. the z axis). As mentioned previously, this essentially eliminates any effects induced by the optical anisotropy which exists along the z and x directions.

Consider the situation normally encountered in polarization spectroscopy, where only the polarization component of the PROBE radiation orthogonal to that of the incident wave reaches the detector. In terms of equations (3.9) and (3.14), this necessitates that the orientation of the polarization analyzer be specified by $\beta = \theta + \pi/2$. With this substitution, expression (3.16) can be manipulated into the following form:

$$I_s(\omega) \approx \frac{E_0^2}{2} e^{-\alpha(\omega)t} \sin^2 \theta \sin^2 \theta$$

$$\times \left( \cosh (\Delta \alpha(\omega)t/2) - \cos (\Delta \eta(\omega)t/2 + \Delta b) \right)$$

(3.18)

The optimum orientation for the linear polarization of the PROBE with respect to that of the PUMP (i.e. the value of $\theta$ which maximizes the observed signal) can easily be obtained from equation (3.18). It is found that $\theta = \pi/4$ produces a maximum signal intensity with the dependence upon the anisotropic absorption and dispersion in the medium being expressed by:

$$I_s(\omega) \approx \frac{E_0^2}{2} e^{-\alpha(\omega)t} \left( \cosh (\Delta \alpha(\omega)t/2) - \cos (\Delta \eta(\omega)t/2 + \Delta b) \right)$$

(3.19)

From the point of view of the experimentalist, however, a more convenient expression for the expected polarization signal can be obtained by expanding equation (3.16) in a multiple-variable Taylor series about $\beta = \theta + \pi/2 = 3\pi/4$. 
\[ \Delta \alpha(\omega) = 0, \Delta \eta(\omega) = 0, \text{ and } \Delta b = 0. \] In the limit of small total absorption, where
\[ E_0^2 e^{-\alpha(\omega)t} \approx I_0, \] this procedure yields:

\[
I_s(\omega) \approx I_0 \left( \xi + \delta^2 + \frac{\Delta b}{4} - \frac{\Delta \alpha(\omega)t}{2} \delta \right.
\]

\[
\left. + \frac{\Delta b}{4} \Delta \eta(\omega)t + \frac{1}{4} \left( \Delta \alpha(\omega)t \right)^2 + \right)
\]

(3.20)

where \( \delta = \frac{3\pi}{4} - \beta. \)

An additional term, \( I_0 \xi, \) has been incorporated into this expression in order to account for the finite extinction coefficient \( (\text{viz. } \xi) \) associated with the polarization analyzer. Since \( \Delta \alpha(\omega) \) and \( \Delta \eta(\omega) \) are related through the complex susceptibility and the Kramers-Kronig relationship, the frequency dependence of equation (3.20) could be recast solely in terms of either the differential absorption or the differential dispersion.

The derivation presented above was for the case of a linearly polarized PROBE beam propagating through a medium having an optical anisotropy with respect to the orthogonal \( z \) and \( x \) axes \( (\text{viz. anisotropy created by excitation with a linearly polarized PUMP}). \) An expression analogous to equation (3.20) can be obtained for the situation in which the molecular sample possesses a differential absorption and differential dispersion for right and left circularly polarized light \( (\text{viz. anisotropy created by excitation with a circularly polarized PUMP}) \). Since linearly polarized radiation can be represented as a superposition of right and left circular polarizations, the medium will, once again, be both dichroic and birefringent with respect to the incident PROBE beam. In the limit of small total absorption, the expected polarization signal is given by:
\[ I_s(\omega) \approx I_0 \left( \xi + \delta^2 + \frac{(\Delta b)^2}{4} - \frac{\Delta \eta(\omega)l}{2} \delta \right. \\
\left. + \frac{\Delta b}{4} \Delta \eta(\omega)l + \frac{1}{4} (\Delta \alpha(\omega)l)^2 + \cdots \right) \] (3.21)

where

\[ \Delta \alpha(\omega) = \alpha_+(\omega) - \alpha_-(\omega) \]
represents the differential absorption for right and left circularly polarized light,

\[ \Delta \alpha(\omega) = \alpha_+(\omega) - \alpha_-(\omega) \]
represents the differential dispersion for right and left circularly polarized light,

\( \alpha_+(\omega) \) and \( \eta_+(\omega) \) are the absorption and dispersion for right circularly polarized light (by convention [218], +1 helicity),

\( \alpha_-(\omega) \) and \( \eta_-(\omega) \) are the absorption and dispersion for left circularly polarized light (by convention [218], -1 helicity).

The discrepancies between expressions (3.20) and (3.21) stem from subtle differences in the nature of the optical anisotropy created by optical pumping with circularly polarized radiation. In contrast to the discussion accompanying equation (3.12), it is now the differential absorption which introduces a slight ellipticity into the PROBE beam while the differential dispersion induces a small polarization rotation. Although most of the work presented in both this and the following Chapters has entailed the use of a linearly polarized PUMP beam, some mention will be made of results obtained with circularly polarized excitation.

Through careful optimization of various experimental factors, the differential birefringence associated with the cell windows, \( \Delta b \), and the detuning angle of the polarization analyzer, \( \delta \), can be reduced to essentially insignificant proportions. Under these circumstances, both equations (3.20) and (3.21) simplify to the following form:
\[ I_{\omega}^{pol}(\omega) = I_0 \left( \xi + \frac{1}{4} (\Delta \alpha(\omega) l)^2 \right) \] (3.22)

where the notation \(I_{\omega}^{pol}(\omega)\) indicates that this is the pure polarization signal devoid of any contributions from the heterodyne terms which exist only for nonzero values of \(\delta\) and \(\Delta b\).

This expression depends upon the square of the differential absorption and will therefore lead to small signals in the event that \(\Delta \alpha(\omega) l \ll 1\). The following sections will demonstrate that, even with the inherent disadvantage of a reduction in the observed signal intensity, the pure polarization detection scheme defined by equation (3.22) was still the method of choice for our time-resolved kinetic measurements in formaldehyde-\(h_2\).

3.2.4 Signal and Noise in Polarization Spectroscopy

For the work presented in this thesis, the most important feature of polarization spectroscopy is the enhancement in signal-to-noise ratio that can be achieved, even in the event of an extremely noisy PROBE laser. This is due to the fact that the crossed polarization optics employed in such experiments greatly diminishes the amount of PROBE radiation which eventually reaches the detector. Since random amplitude variations of the interrogating light source are responsible for a considerable portion of the noise associated with absorption-based spectroscopic measurements, the reduction in the number of background photons translates into a substantial improvement in both sensitivity and resolution.

The origin of this background suppression can be appreciated by reformulating equations (3.17) and (3.22), which describe the expected pure absorption and pure polarization signals respectively, in terms of the observed
background, \( I_{\text{background}} \), and the detected signal, \( I_{\text{signal}} \):

\[
I_s^{\text{abs}}(\omega) = I_0 + (\alpha_s(\omega)l)I_0 = I_{\text{background}}^{\text{abs}} + I_{\text{signal}}^{\text{abs}}
\]

\[
I_s^{\text{pol}}(\omega) = I_0 \xi + \frac{1}{4} (\Delta \alpha(\omega)l)^2 I_0 = I_{\text{background}}^{\text{pol}} + I_{\text{signal}}^{\text{pol}}
\]

Comparison of these expressions demonstrates that the background level encountered in polarization spectroscopy is suppressed, relative to that of conventional absorption techniques, by a factor equal to the extinction coefficient, \( \xi \), of the polarization analyzer. Since typical values of \( \xi \) for high quality Glan-Laser calcite prisms can approach \( 10^{-7} \), the reduction in unwanted PROBE radiation can be quite significant. The enhancement in the observed signal to noise ratio can also be related to the extinction coefficient \( \xi \) by defining \( I_{s/n} \approx I_{\text{signal}} / I_{\text{background}} \):

Both equations (3.22) and (3.24) indicate that the pure polarization signal is proportional to the square of the differential absorption created by optical pumping of the molecular sample. Therefore, a situation in which \( \Delta \alpha(\omega)l \ll 1 \) will necessarily lead to rather small signal levels. To overcome this problem, numerous workers [219, 203, 209] have stressed the use of a finite detuning angle for the polarization analyzer (i.e. \( \delta \neq 0 \)) so as to permit the heterodyne terms, which are linearly proportional to the induced optical anisotropy, to dominate in the detected signal. Expression (3.20) indicates that, in the case of a linearly polarized PUMP beam, the observed intensity, \( I_s^{\text{het}} \), will be of the form:

\[
I_s^{\text{het}}(\omega) = I_0 \left( \xi + \delta^2 \right) + \frac{I_0}{2} \Delta \alpha(\omega)l \delta
\]

\[
= I_{\text{background}}^{\text{het}} + I_{\text{signal}}^{\text{het}}
\]
where terms involving $\Delta b$ and $(\Delta \alpha(\omega)l)^2$ have been neglected.

The signal to noise ratio (viz. $I_{s/n} \approx I_{signal}/I_{background}$) for the situation described by equation (3.25) is related to the quantity $\xi/(\xi + \delta^2)$, which has a maximum value at $\delta = \sqrt{\xi}$. Therefore, for an ideal (noise-free) photon detector, an enhancement in the overall sensitivity afforded by polarization spectroscopy can be achieved by detuning the polarization analyzer by an angle comparable to the square root of its extinction coefficient. Although this technique has been successfully exploited in conventional spectroscopic probes of molecular systems, the complications which might accompany the temporal response of such heterodyne terms argued against their use in our time resolved studies.

3.2.5 Calculation of Polarization Signals

Equation (3.22) indicates that the magnitude of a pure polarization signal is principally determined by the value of the differential absorption, $\Delta \alpha(\omega)$, produced within the molecular sample by optical pumping. This is also true for the more general types of polarization signals defined by expressions (3.20) and (3.21) since the differential dispersion term, $\Delta \eta(\omega)$, can be reformulated in terms of $\Delta \alpha(\omega)$ with the assistance of the Kramers-Kronig relations [217]. The present section is concerned with computation of the differential absorption associated with a given set of PUMP and PROBE rovibronic transitions. Particular attention will be directed towards determination of the important relationship between $\Delta \alpha(\omega)$ and the rotational quantum numbers of the molecular system. This crucial dependence of the differential absorption upon the rotational degrees of freedom can be appreciated from the fact that the interaction between a beam of polarized light and a spinning molecule will be strongly affected by the relative orientation of the...
molecular rotation axis. As a result, the rotational energy levels and rovibronic transitions employed in a polarization spectroscopy measurement can be expected to influence profoundly the characteristics of the observed signals.

A rigorous theoretical treatment of the induced optical anisotropy would utilize the density matrix approach [220, 221, 218] in order to describe the interaction of polarized PUMP and PROBE radiation fields with the molecular sample. Instead, our analysis will be based upon a rate equation formalism first exploited by Teets, et. al. [222] for the normally encountered situation of moderately saturated spectroscopic transitions. This pedagogical approach yields all of the essential results obtained from more sophisticated calculations while, at the same time, providing the additional benefits associated with its inherent conceptual simplicity.

Figure 3-2 presents the hypothetical molecular energy level diagram which will provide the framework for our theoretical characterization of polarization spectroscopy signals. This diagram depicts an experimental scheme designed to probe an excited state, |1⟩, through the creation and subsequent observation of an optical anisotropy among its degenerate magnetic sublevels. Each state in this ideal three-level system (nb. the states are actually 2J+1-fold degenerate) is designated by a set of symmetric rotor quantum numbers. Provided that rotational and vibrational-electronic degrees of freedom are separable, these eigenstate labels are:

\[ J \] which represents the total angular momentum of the state,

\[ K \] which represents the projection of the total angular momentum on the body-fixed z axis,

\[ M \] which represents the projection of the total angular momentum on the space-fixed z axis,

and \( \gamma \) which denotes all other vibronic quantum numbers required to fully describe the molecular system.
Figure 3-2: Model Three-Level System for Polarization Signal Calculations.
where:

\[ |0\rangle = \{ |\gamma J K M \rangle; M = -J, \ldots J \} \]
\[ |1\rangle = \{ |\gamma_1 J_1 K_1 M_1 \rangle; M_1 = -J_1, \ldots J_1 \} \]
\[ |2\rangle = \{ |\gamma_2 J_2 K_2 M_2 \rangle; M_2 = -J_2, \ldots J_2 \} \]

Two Polarization Cases:

a) Linear PUMP; Linear PROBE (@ 45°).
b) Circular PUMP; Linear PROBE.
For the calculations discussed in this section, it will be assumed that the molecular eigenstates can be well described by the corresponding symmetric rotor eigenfunctions. This proves to be an exceptionally good approximation for the near-prolate geometrical configuration encountered in the formaldehyde system. In general, however, the wavefunctions of an asymmetric top molecule would have to be expanded as a linear combination of symmetric rotor eigenfunctions each having a different value of the quantum number $K$. Since polarization spectroscopy is principally concerned with the anisotropy created within the magnetic subcomponents (i.e. $M$ levels) of the target rovibronic level, this approximation, whereby $\gamma$, $J$, and $M$ serve as valid state labels, will not alter the results of the ensuing analysis.

The rovibronic transitions illustrated in figure 3-2 can be viewed in terms of the two intimately related steps required for the successful completion of a polarization spectroscopy measurement:

1. Preparation of the Optical Anisotropy with the PUMP Laser.

A short, resonant laser pulse is used to optically pump the $|1\rangle \leftarrow |0\rangle$ rovibronic transition thereby producing a nonuniform population distribution among the degenerate magnetic sublevels of the excited state. The creation of this optical anisotropy can be accomplished through the use of either linearly or circularly polarized PUMP radiation.

2. Detection of the Optical Anisotropy with the PROBE Laser.

The excited state optical anisotropy is monitored through its depolarizing effects on a weak laser beam resonant with the $|1\rangle \rightarrow |2\rangle$ rovibronic transition. The incident PROBE radiation, which can be either continuous wave or pulsed, is always linearly polarized. Equation (3.18) indicates that, in the case of a linearly polarized PUMP, a maximum signal magnitude is obtained for a 45° orientation of the PROBE polarization (i.e. with respect to the direction of the PUMP polarization).
For the most part, the discussion which follows will attempt to characterize the polarization signals expected for the case of a linearly polarized PUMP beam. The situation corresponding to the use of circularly polarized PUMP radiation will be considered only briefly. Since our main purpose is to provide an indication of expected signal magnitudes and their dependence upon rotational quantum numbers, neither elastic nor inelastic collisional processes have been explicitly taken into account. It will also be assumed that spontaneous emission from the excited state \( |1\rangle \) has a negligible influence upon the populations of the lower levels \( |0\rangle \) and \( |2\rangle \).

Our discussion will begin with an analysis of the second step in a polarization spectroscopy experiment, the detection of the induced optical anisotropy. In this manner, the required concepts and formulations of polarization-specific molecule-field interactions can be most succinctly presented. Assume that an optical anisotropy has been abruptly created within the target rovibronic level (viz. \( |1\rangle \)) by excitation with a short resonant pulse of linearly polarized laser radiation. This implies that the population of the degenerate magnetic subcomponents within the excited state, \( \{ N_{\gamma_1 J_1 K_1 M_1}; M_1 = -J_1, \ldots, J_1 \} \), is not uniformly distributed (i.e. \( N_{\gamma_1 J_1 K_1 M_1} \neq N_{\gamma_1 J_1 K_1 M'_1} \) where \( M_1 \neq M'_1 \)). The problem reduces to evaluation of the differential absorption, \( \Delta \alpha(\omega) \), experienced by the PROBE beam as it propagates through the dichroic molecular sample. From equation (3.10):

\[
\Delta \alpha(\omega) = \alpha_z(\omega) - \alpha_x(\omega) \\
= (\alpha_z^0 - \alpha_x^0) g(\omega - \omega_{12}) \\
= \Delta \alpha_0^0 g(\omega - \omega_{12})
\]

(3.26)

where expression (3.7) has been employed in order to reformulate \( \Delta \alpha(\omega) \) in terms of a frequency integrated differential absorption, \( \Delta \alpha_0^0 = \alpha_z^0 - \alpha_x^0 \), and a frequency
normalized lineshape function, $g(\omega - \omega_{12})$, centered on the PROBE rovibrionic transition (viz. $\omega_{12} = E_1 - E_2$).

Note that the quantization axis or space-fixed $z$ axis for the ensuing calculations has been defined along the linear polarization direction of the PUMP radiation. The rationale for this definition stems from the fact that the polarization characteristics of the PUMP are responsible for destroying the isotropy of the molecular system.

Equation (3.26) indicates that, for a given lineshape function, the frequency integrated differential absorption, $\Delta \alpha^0$, will govern the amount of depolarization experienced by the PROBE radiation as it interacts with the anisotropic molecular sample. In the case of an induced dichroism created within the excited state, $|1\rangle$, of our model three-level system, the quantity of interest is given by:

$$\Delta \alpha^0(|1\rangle \rightarrow |2\rangle) = \alpha^0_2(|1\rangle \rightarrow |2\rangle) - \alpha^0_2(|1\rangle \rightarrow |2\rangle)$$

or in terms of the appropriate sets of quantum numbers:

$$\Delta \alpha^0(|1\rangle \rightarrow |2\rangle) = \sum_{M_1M_2} \left( \alpha^0_2(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) 
- \alpha^0_2(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) \right)$$

(3.27)

where the summation over the magnetic quantum numbers indicates that all possible $|1\rangle \rightarrow |2\rangle$ transitions between the degenerate subcomponents are being considered.

To account explicitly for the nonuniform population distribution among the magnetic subcomponents of the excited state, the frequency integrated absorption
coefficient, \( \alpha^0 \), must be reformulated in terms of the frequency integrated cross section, \( \sigma^0 \), for the spectroscopic transition [223]:

\[
\alpha^0(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) = N_{\gamma_1 J_1 K_1 M_1} \sigma^0(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) \tag{3.28}
\]

Equation (3.27) thus becomes:

\[
\Delta \alpha^0(|1\rangle \rightarrow |2\rangle) = N_{\gamma_1 J_1 K_1 M_1} \left( \sigma^0(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) - \sigma^0(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) \right) \tag{3.29}
\]

In order to evaluate the frequency integrated differential absorption from equation (3.29), the cross sections must be recast in terms of the matrix elements for the transition dipole moment operator, \( \mu \). The relationship between these two quantities is given by [223]:

\[
\sigma^0_2(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) = \frac{\pi \omega_{12}}{3 \epsilon_0 \hbar c} |\langle \gamma_2 J_2 K_2 M_2 | \mu_z | \gamma_1 J_1 K_1 M_1 \rangle|^2 \tag{3.30}
\]

\[
\sigma^0_2(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) = \frac{\pi \omega_{12}}{3 \epsilon_0 \hbar c} |\langle \gamma_2 J_2 K_2 M_2 | \mu_x | \gamma_1 J_1 K_1 M_1 \rangle|^2 \tag{3.31}
\]

Note that the \( z \) and \( x \) subscripts which appear in these expressions refer to Cartesian projections along the space-fixed axis system. However, the computation of the required matrix elements is greatly facilitated by conversion of the transition moment operator from cartesian coordinates to the more convenient spherical
coordinate formalism [41]:

\[
    \mu_z = T^1_0(\mu) \\
    \mu_z = \frac{\sqrt{2}}{2} \left( T^1_{-1}(\mu) - T^1_{+1}(\mu) \right)
\]

where \( T^1_p(\mu) \) signifies the \( p^{th} \) space-fixed spherical component of the rank one spherical tensor which represents the transition dipole moment operator \( \mu \).

The mathematical techniques required for evaluation of the spherical tensor matrix elements are demonstrated in Appendix A. Application of these procedures to equations (3.30) and (3.31) yields:

\[
    \sigma^0_z = \sigma^0(\gamma_1 \rightarrow \gamma_2) (2J_1+1)(2J_2+1) \left( \begin{array}{cc}
        J_2 & 1 \\
        -K_2 & K_2 - K_1 
    \end{array} \right) \left( \begin{array}{cc}
        J_1 & 1 \\
        -M_2 & 0 
    \end{array} \right)^2 \left( \begin{array}{cc}
        J_2 & 1 \\
        -M_2 & 1 
    \end{array} \right)^2 \tag{3.32}
\]

\[
    \sigma^0_z = \frac{\sigma^0(\gamma_1 \rightarrow \gamma_2)}{2} (2J_1+1)(2J_2+1) \left( \begin{array}{cc}
        J_2 & 1 \\
        -K_2 & K_2 - K_1 
    \end{array} \right)^2 \\
    \times \left( \begin{array}{cc}
        J_1 & 1 \\
        -M_2 & 1 
    \end{array} \right)^2 \tag{3.33}
\]

where all factors which do not explicitly depend upon angular momentum quantum numbers (e.g. the reduced matrix elements of the transition moment operator) have been incorporated into \( \sigma^0(\gamma_1 \rightarrow \gamma_2) \).

The frequency integrated differential absorption defined in equation (3.29) can now be reformulated in a manner which explicitly demonstrates its dependence upon the rotational degrees of freedom:
\[ \Delta \alpha^0(|1 \rightarrow |2\rangle) = \sigma^0(\gamma_1 \rightarrow \gamma_2)(2J_1+1)(2J_2+1) \left( \begin{array}{c} J_2 \\ J_1 \end{array} \right)^2 \left( \begin{array}{c} 1 \\ -K_2 \\ K_2 \\ -K_1 \\ K_1 \end{array} \right)^2 \]

\[ \times \sum_{M_1M_2} N_{\gamma_1 J_1 K_1 M_1} \left( \begin{array}{c} J_2 \\ J_1 \end{array} \right)^2 \left( \begin{array}{c} 0 \\ -M_2 \end{array} \right) \]

\[ - \frac{1}{2} \left( \left( \begin{array}{c} J_2 \\ J_1 \end{array} \right) \left( \begin{array}{c} 1 \\ -M_2 \end{array} \right) \right)^2 \left( \begin{array}{c} J_2 \\ J_1 \end{array} \right)^2 \left( \begin{array}{c} 1 \\ M_1 \end{array} \right) \left( \begin{array}{c} 0 \\ 1 \\ M_1 \end{array} \right) \right) \] (3.34)

Still unaccounted for in expression (3.34) are the various populations for the degenerate subcomponents within the excited state \(|1\rangle\). These quantities, the distribution of which constitute the optical anisotropy being probed, can readily be determined from a rate equation model [222] under the assumption that the PUMP radiation is produced by a non-saturating resonant laser pulse linearly polarized along the space fixed \(z\) axis. Provided that the pulse duration, \(\tau_{pump}\), is substantially shorter than the lifetimes associated with the individual states of the three-level system, the expected values of \(N_{\gamma_1 J_1 K_1 M_1}\) can be related to the \(|1 \rightarrow |2\rangle\) transition cross section as follows:

\[ N_{\gamma_1 J_1 K_1 M_1} = \frac{N_{\gamma J K}}{2J+1} \sum_M \sigma^0(\gamma_1 J_1 K_1 M_1 \leftarrow \gamma J K M) \frac{I_{pump} \tau_{pump}}{\hbar \omega_{10}} \] (3.35)

where

- \(I_{pump}\) represents the intensity of the PUMP laser,
- \(\omega_{10}\) represents the radial frequency of the PUMP transition (i.e. \(\hbar \omega_{10} = E_1 - E_0\)),
- \(N_{\gamma J K}\) represents the initial population of the ground state \(|0\rangle\) (viz. \(N_{\gamma J K} = \sum_M N_{\gamma J K M}\)).
Equation (3.35) has been derived under the assumption that the initial population within the lower level of the PUMP transition (i.e. |0⟩) is isotropically distributed among the degenerate magnetic subcomponents (viz. before the PUMP pulse, \( N_{\gamma J KM} \equiv N_{\gamma J K M'} \) where \( M \neq M' \)). Consequently, the summation over all possible transitions from the \( 2J+1 \) sublevels of the lower state, \( \{|\gamma J KM\}; M = -J, \ldots, J\} \), to the target level in the excited state, \( |\gamma J 1 K 1 M_1⟩ \), must be performed. This expression can be reformulated in terms of the dipole moment operator in order to indicate explicitly its dependence upon the rotational degrees of freedom:

\[
N_{\gamma J 1 K 1 M_1} = \frac{N_{\gamma J K I_{pump}} I_{pump}}{\hbar \omega_{10}} \sigma^0(\gamma_1 \leftarrow \gamma)(2J+1) \left( \begin{array}{cc} J_1 & 1 \\ -K_1 & K-K_1 \end{array} \right)^2 \\
\times \sum_M \left( \begin{array}{cc} J_1 & 1 \\ -M_1 & 0 \end{array} \right)^2
\]  

(3.36)

where all portions of the cross section not explicitly depending upon the angular momentum quantum numbers have been collected into \( \sigma^0(\gamma_1 \leftarrow \gamma) \).

The nonuniform population distribution prepared within the magnetic sublevels of the excited state by linearly polarized PUMP radiation is illustrated in figure 3-3 for the case of \( J_1 = 10 \). The molecular system resulting from such optical pumping is said to be aligned since degenerate sublevels differing only in the sign of the magnetic quantum number (viz. \( |\gamma_1 J 1 K 1 M_1⟩ vs. |\gamma_1 J 1 K 1 -M_1⟩ \)) are equally populated.

Substitution of expression (3.36) into equation (3.34) yields:
Figure 3-3: Magnetic Sublevel Populations for Linearly Polarized PUMP.
\( \Delta J = 0 \)

\( \Delta J = +1 \)

\( \Delta J = -1 \)

Population \( (N_{J,K,M_J}) \) vs Magnetic Sublevel \( (M_L) \)
\[ \Delta \alpha^0(|1\rangle \rightarrow |2\rangle) = \frac{N_{\gamma J K} I_{\text{pump}}^r \sigma^0(\gamma_1 \leftarrow \gamma) \sigma^0(\gamma_1 \rightarrow \gamma_2)}{\hbar \omega_{10} (2J+1)(2J_1+1)} \]

\[ \times S_{J J_1}^{KK_1(\text{PUMP})} S_{J_1 J_2}^{K_1 K_2(\text{PROBE})} \zeta_{J J_1 J_2}^{\text{linear}} \]  

(3.37)

where

\[ S_{J J_1}^{KK_1(\text{PUMP})} = \frac{(2J+1)(2J_1+1)}{3} \left( \begin{array}{ccc} J_1 & 1 & J_1 \\ -K_1 & K_1 & K_1 \end{array} \right)^2 \]  

(3.38)

and

\[ S_{J_1 J_2}^{K_1 K_2(\text{PROBE})} = \frac{(2J_1+1)(2J_2+1)}{3} \left( \begin{array}{ccc} J_2 & 1 & J_1 \\ -K_2 & K_1 & K_1 \end{array} \right)^2 \]  

(3.39)

represent the symmetric rotor line strength factors [56, 106] corresponding to the PUMP and PROBE spectroscopic transitions.

The \( \zeta_{J J_1 J_2}^{\text{linear}} \) factor which appears in equation (3.37) results from the summation over all magnetic quantum numbers and is given by [222]:

\[ \zeta_{J J_1 J_2}^{\text{linear}} = 9(2J_1+1) \sum_{M M_1 M_2} \left( \begin{array}{ccc} J_1 & 1 & J \\ -M_1 & 0 & M \end{array} \right)^2 \]

\[ \times \left( \left( \begin{array}{ccc} J_2 & 1 & J_1 \\ -M_2 & 0 & M_1 \end{array} \right)^2 - \frac{1}{2} \left( \left( \begin{array}{ccc} J_2 & 1 & J_1 \\ -M_2 & -1 & M_1 \end{array} \right) - \left( \begin{array}{ccc} J_2 & 1 & J_1 \\ -M_2 & 1 & M_1 \end{array} \right) \right)^2 \right) \]  

(3.40)

This factor depends upon the polarization characteristics of the PUMP laser (i.e. the superscript \( \text{linear} \)) as well as on the angular momenta associated with the PUMP and PROBE transitions. It can be interpreted as a measure of the depolarization experienced by the PROBE radiation as it propagates through the
anisotropic molecular sample. The actual computation of the $\zeta_{J_1J_2}$ terms involves
the straightforward, albeit tedious, evaluation of the summation over Wigner 3-j
symbols. These quantities have essentially been calculated in reference [222] and are
presented, for the case of a linearly polarized PUMP beam, in part (a) of table 3-I.

The evaluation of $\Delta \alpha(\omega)$ for the case of a circularly polarized PUMP beam
proceeds in basically the same fashion as indicated above for linear polarization. As
demonstrated in equation (3.21), the polarization properties of the PUMP radiation,
which define the quantization axis for the ensuing calculation, necessitate that the
linearly polarized PROBE be interpreted as a superposition of right-handed and
left-handed circularly polarized light. The frequency integrated absorption is
therefore given by:

$$\Delta \alpha^0(|1 \rightarrow |2)) = \alpha^0_+ (|1 \rightarrow |2)) - \alpha^0_- (|1 \rightarrow |2))$$

$$= \sum_{M_1M_2} \left( \alpha^0_+ (\gamma_1J_1K_1M_1 \rightarrow \gamma_2J_2K_2M_2)$$

$$- \alpha^0_- (\gamma_1J_1K_1M_1 \rightarrow \gamma_2J_2K_2M_2) \right)$$

$$= \sum_{M_1M_2} N_{\gamma_1J_1K_1M_1} \left( \sigma^0_+ (\gamma_1J_1K_1M_1 \rightarrow \gamma_2J_2K_2M_2)$$

$$- \sigma^0_- (\gamma_1J_1K_1M_1 \rightarrow \gamma_2J_2K_2M_2) \right)$$

(3.41)

Once again, the frequency integrated cross sections, $\sigma^0_{\pm}$, can be related to the
matrix elements for the spherical representation of the transition dipole moment
operator:
a. $\zeta JJ_1 J_2$

\[
\begin{array}{ccc}
J_2 = J_1 - 1 & J_2 = J_1 & J_2 = J_1 + 1 \\
J = J_1 - 1 & \frac{3(J_1 + 1)(2J_1 + 3)}{10J_1(2J_1 - 1)} & \frac{-3(2J_1 + 3)}{10J_1} & \frac{3}{10} \\
J = J_1 & \frac{-3J_1(2J_1 + 3)}{10J_1} & \frac{3(2J_1 - 1)(2J_1 + 3)}{10J_1(J_1 + 1)} & \frac{-3(2J_1 - 1)}{10(J_1 + 1)} \\
J = J_1 + 1 & \frac{3}{10} & \frac{-3(2J_1 - 1)}{10(J_1 + 1)} & \frac{3J_1(2J_1 - 1)}{10(J_1 + 1)(2J_1 + 3)}
\end{array}
\]

b. $\zeta JJ_1 J_2$

\[
\begin{array}{ccc}
J_2 = J_1 - 1 & J_2 = J_1 & J_2 = J_1 + 1 \\
J = J_1 - 1 & \frac{3(J_1 + 1)}{2J_1} & \frac{3}{2J_1} & \frac{-3}{2} \\
J = J_1 & \frac{3}{2J_1} & \frac{3}{2J_1(J_1 + 1)} & \frac{-3}{2(J_1 + 1)} \\
J = J_1 + 1 & \frac{-3}{2} & \frac{-3}{2(J_1 + 1)} & \frac{3J_1}{2(J_1 + 1)}
\end{array}
\]

Table 3-I: Depolarization Factors for Polarization Spectroscopy.
\[
\sigma^0_{\pm}(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) = \frac{\pi \omega_{12}}{3 \epsilon_0 \hbar c} |\langle \gamma_2 J_2 K_2 M_2 | T^{\pm}_{\pm} (\mu) | \gamma_1 J_1 K_1 M_1 \rangle|^2
\]

\[
= \sigma^0(\gamma_1 \rightarrow \gamma_2)(2J_1+1)(2J_2+1)
\times \left( \begin{array}{cc} J_2 & 1 \\ -K_2 & K_1 \end{array} \right) \left( \begin{array}{cc} J_1 \\ -M_2 \pm 1 \end{array} \right)^2
\]

(3.42)

where the techniques presented in Appendix A have been utilized in the evaluation of the required matrix elements.

For a right-handed circularly polarized PUMP beam, the rate equation formalism provides the following expression for the population distribution within the excited state:

\[
N_{\gamma_1 J_1 K_1 M_1} = \frac{N_{\gamma JK}}{2J+1} \sum_M \sigma^0_{+}(\gamma_1 J_1 K_1 M_1 \leftarrow \gamma JK M) \frac{I_{\text{pump}} T_{\text{pump}}}{\hbar \omega_{10}}
\]

(3.43)

The nonuniform population distribution prepared within the magnetic sublevels of the excited state by the circularly polarized PUMP radiation is illustrated in figure 3-4 for the case of \( J_1 = 10 \). The resulting molecular system is said to be oriented since degenerate sublevels differing only in the sign of the magnetic quantum number are no longer equally populated. The unique nature of the optical anisotropy created by a linearly polarized and a circularly polarized PUMP beam can be appreciated by contrasting the histograms presented in figures 3-3 and 3-4.

By substituting equation (3.43) into equation (3.41) and utilizing the cross-section definition of expression (3.42), the frequency integrated absorption
Figure 3-4: Magnetic Sublevel Populations for Circularly Polarized PUMP.
The calculated values of the $\zeta$ factors for circularly polarized PUMP radiation are presented in part (b) of table 3-I.
### Table 3-II: High-$J_1$ Limits for Depolarization Factors.

<table>
<thead>
<tr>
<th></th>
<th>$J_2=J_1-1$</th>
<th>$J_2=J_1$</th>
<th>$J_2=J_1+1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J=J_1-1$</td>
<td>$\frac{3}{10}$</td>
<td>$-\frac{3}{5}$</td>
<td>$\frac{3}{10}$</td>
</tr>
<tr>
<td>$J=J_1$</td>
<td>$\frac{-3}{5}$</td>
<td>$\frac{6}{5}$</td>
<td>$\frac{-3}{10}$</td>
</tr>
<tr>
<td>$J=J_1+1$</td>
<td>$\frac{3}{10}$</td>
<td>$\frac{-3}{5}$</td>
<td>$\frac{3}{10}$</td>
</tr>
</tbody>
</table>

### a. Linear

$\xi_{JJ_1 J_2}$

### b. Circular

$\xi_{JJ_1 J_2}$
increasing values of the $\varsigma$ parameter.

Table 3-II indicates that the depolarization factors associated with a linearly polarized PUMP beam, $\varsigma_{J J_1 J_2}^{linear}$, approach $3/10$ if neither the PUMP nor the PROBE transition entails $\Delta J = 0$, $3/5$ if either one of the two transitions has $\Delta J = 0$, and $6/5$ if both transitions have $\Delta J = 0$. Therefore, for linearly polarized PUMP radiation, the largest polarization signals will be obtained when all rovibronic transitions proceed via $Q$ branches. This is especially important in view of the fact that linearly polarized light was utilized for the PUMP in most of the formaldehyde experiments discussed in this and the following Chapters.

The high-$J_1$ limits presented in table 3-II demonstrate that the depolarization factors corresponding to a circularly polarized PUMP, $\varsigma_{J J_1 J_2}^{circular}$, approach a maximum value of $3/2$ only if both the PUMP and PROBE transitions have $\Delta J = \pm 1$. For $\Delta J = 0$ spectroscopic transitions, the depolarization parameter is found to decrease rapidly with increasing $J_1$. This behavior, which is complementary to that indicated above for the case of linearly polarized PUMP radiation, implies that optical pumping with circularly polarized light will produce the largest polarization signals when all rovibronic transitions proceed via $R$ or $P$ branches.

The difference in magnitude of the polarization signals observed with linear and circular PUMP radiation has provided a viable means for identification of $P$, $Q$, and $R$ branches in congested molecular spectra [211, 212]. In addition, the relative signs associated with the depolarization factors of table 3-II can be used to provide a rough estimate for the value of $\Delta J$ in a given spectroscopic transition.
3.2.6 Temporal Response of Polarization Spectroscopy

The work presented in this Chapter of the thesis has utilized polarization spectroscopy as a probe of relaxation processes in $\tilde{A}^1A_2$ formaldehyde. The temporal characteristics of signals derived from such polarization-based detection schemes is of primary importance for both the analysis and interpretation of our time-resolved kinetic experiments. The ensuing discussion will therefore examine polarization spectroscopy in the time domain with particular emphasis on the differences between this technique and more conventional transient absorption (or transient gain) methods.

The mathematical treatment of polarization spectroscopy presented in earlier sections has completely neglected the temporal evolution of the optical anisotropy created within the molecular sample by the PUMP pulse (cf. figure 3-1). This anisotropy, which constitutes the quantity actually measured in any polarization-based detection scheme, is expected to decay exponentially in time as a result of various collision-induced (e.g. energy transfer) and collision-free (e.g. spontaneous emission) relaxation processes. Nevertheless, the appropriate temporal dependence can be readily incorporated into the previous analysis through a slight modification in the notation ascribed to various observables. In particular, the pure polarization signal, $I_{signal}^{pol}$, defined in equation (3.23) can be reformulated as follows:

$$I_{signal}^{pol}(\omega; t) = \frac{1}{4} (\Delta\alpha(\omega; t) l)^2 I_0$$  \hspace{1cm} (3.46)

where the $(\omega; t)$ functional dependence refers to the temporal evolution of observables (e.g. the pure polarization signal $I_{signal}^{pol}(\omega; t)$ and the differential absorption $\Delta\alpha(\omega; t)$) induced within the molecular sample by the resonant PUMP pulse at time $t = 0$ and subsequently monitored via the cw PROBE beam at
spectral frequency $\omega$ (cf. figure 3-2). Equation (3.46) constitutes the mathematical statement for the time-resolved signals expected from our kinetic studies of $\tilde{A}^1A_2$ formaldehyde.

Equation (3.26) can now be utilized in order to recast the pure polarization signal in terms of the frequency integrated differential absorption, $\Delta\alpha^0(1 \rightarrow 2); t)$, and the frequency normalized lineshape function, $g(\omega - \omega_{12})$, corresponding to the $|1 \rightarrow 2)$ PROBE transition:

$$I_{signal}^{pol}(\omega; t) = \frac{1}{4} \left( \Delta\alpha^0(1 \rightarrow 2); t) \cdot g(\omega - \omega_{12}) \right)^2 I_0$$

where, as suggested by the $\Delta\alpha^0(1 \rightarrow 2); t)$ notation, the evolution of the polarization signal in time is completely governed by the temporal dependence of the frequency integrated differential absorption (i.e. the optical anisotropy).

The time dependence of the frequency integrated differential absorption coefficient can be related to the temporal evolution of the molecular population distribution prepared, by the PUMP pulse, within the magnetic components of the target rovibronic level (i.e. $\{ N_{\gamma_1 J_1 K_1 M_1} (t); M_1 = -J_1, \ldots, J_1 \}$). Equations (3.29) and (3.35) indicate that:

$$\Delta\alpha^0(1 \rightarrow 2); t) = \sum_{M_1 M_2} N_{\gamma_1 J_1 K_1 M_1} (t)$$

$$\times \Delta\sigma^0(|\gamma_1 J_1 K_1 M_1) \rightarrow |\gamma_2 J_2 K_2 M_2)$$

where $\Delta\sigma^0(|\gamma_1 J_1 K_1 M_1 \rightarrow |\gamma_2 J_2 K_2 M_2))$ denotes the time-independent cross section for the differential absorption in the PROBE transition.
Equation (3.48) indicates that the temporal characteristics of the induced optical anisotropy are completely determined by evolution of the molecular population prepared within the target rovibronic level (*i.e.* |l). The unique nature of time-resolved polarization spectroscopy can be succinctly demonstrated through consideration of the special case in which elastic collisional processes that transfer molecules either into or among the magnetic components of the target level (*viz.* \{ |\gamma_1 J_1 K_1 M_1 \}; \; M_1 = -J_1, \ldots, J \}) are neglected. Under these circumstances, the individual \( N_{\gamma_1 J_1 K_1 M_1} (t) \) functions can be expected to follow simple first order depopulation kinetics:

\[
\frac{\partial N_{\gamma_1 J_1 K_1 M_1} (t)}{\partial t} = -k_{\gamma_1 J_1 K_1 M_1} N_{\gamma_1 J_1 K_1 M_1} (t) \tag{3.49}
\]

where \( k_{\gamma_1 J_1 K_1 M_1} \) represents the decay rate corresponding to the depopulation of |\gamma_1 J_1 K_1 M_1 \rangle into the manifold of background states.

The set of uncoupled differential equations denoted by expression (3.49) can be readily solved, subject to the initial boundary condition that \( N_{\gamma_1 J_1 K_1 M_1} (t=0) = N_{\gamma_1 J_1 K_1 M_1} (0) \), in order to determine the temporal dependence for the magnetic component populations within the target rovibronic level:

\[
N_{\gamma_1 J_1 K_1 M_1} (t) = N_{\gamma_1 J_1 K_1 M_1} (0) e^{-k_{\gamma_1 J_1 K_1 M_1} t} = N_{\gamma_1 J_1 K_1 M_1} (0) e^{-k_{\gamma_1 J_1 K_1} t} \tag{3.50}
\]

where the assumed absence of \( M \)-specific depopulation processes (*e.g.* \( M \)-changing collisions) ensures that the decay rates for all of the magnetic sublevels will be identical (*viz.* \( k_{\gamma_1 J_1 K_1 M_1} = k_{\gamma_1 J_1 K_1 M_1'} = k_{\gamma_1 J_1 K_1} \) where \( M_1 \neq M_1' \)). The
appropriate values for the $N_{\gamma_1 J_1 K_1 M_1}(0)$ population factors can be determined on the basis of the rate equation formalism presented in the previous section (cf. equations (3.35) and (3.43)).

The time dependence of the frequency integrated differential absorption coefficient is obtained by substituting expression (3.50) into equation (3.48):

$$\Delta \alpha^0(|1) \rightarrow |2); t = e^{-k_1 J_1 K_1} t$$

$$\times \sum_{M_1 M_2} N_{\gamma_1 J_1 K_1 M_1}(\eta) \Delta \sigma^0(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2)$$

$$= e^{-k_1 J_1 K_1} t \Delta \alpha^0(|1) \rightarrow |2); 0)$$  \hspace{1cm} (3.51)

where $\Delta \alpha^0(|1) \rightarrow |2); 0)$, the differential absorption induced in the PROBE transition by the PUMP pulse at time $t = 0$, is given by equations (3.37) and (3.44).

Expressions (3.47) and (3.51) can now be utilized in order to determine the temporal dependence of the pure polarization signals expected under the special circumstances embodied in equation (3.50):

$$I_{signal}^{pol}(\omega; t) = \frac{1}{4} (\Delta \alpha^0(|1) \rightarrow |2); 0) g(\omega - \omega_{12}) t )^2 I_0 e^{-2k_1 J_1 K_1} t$$

$$= I_{signal}^{pol}(\omega; 0) e^{-f^{obs}_{\gamma_1 J_1 K_1} t}$$  \hspace{1cm} (3.52)

where $I_{signal}^{pol}(\omega; 0)$ is equivalent to the time-independent pure polarization signal derived in previous sections and $f^{obs}_{\gamma_1 J_1 K_1} = 2k_1 J_1 K_1$ denotes the exponential decay rate that would actually be observed in the course of an experiment.
Expression (3.52) indicates that, even in the absence of external perturbations (e.g. $M$-specific collisional processes), the detected pure polarization signal will decay with twice the rate attributed to the depopulation of the target rovibronic level (viz. $2k\gamma_1J_1K_1$ vs. $k\gamma_1J_1K_1$). In contrast, the pure absorption signal defined in equation (3.23) is directly proportional to $N_{\gamma_1J_1K_1M_1}(t)$ and will therefore decrease exponentially in time with the rate $k_{\gamma_1J_1K_1}$ (i.e. half of the rate observed in a pure polarization experiment). As will be demonstrated shortly, the introduction of additional polarization dephasing processes, such as certain types of $M$-changing collisions, will further enhance the decay rate of the polarization signal as compared to that measured through pure absorption techniques.

In order for the effects of state-to-state energy transfer processes to be explicitly incorporated into the analysis of the pure polarization signals, the temporal evolution of the nonuniform population distribution prepared by the PUMP pulse must be determined. The population of the individual magnetic components in the target level is now described by a coupled system of first order differential equations:

$$
\frac{\partial N_{\gamma_1J_1K_1M_1}(t)}{\partial t} = -k_{\gamma_1J_1K_1M_1} N_{\gamma_1J_1K_1M_1}(t)
$$

$$
+ \sum_{\gamma'JK'M'} k(\gamma'JK'M' \rightarrow \gamma_1J_1K_1M_1) N_{\gamma'JK'M'}(t)
$$

(3.53)

where $k(\gamma'JK'M' \rightarrow \gamma_1J_1K_1M_1)$ denotes the rate of collision-induced energy transfer from state $|\gamma'JK'M'\rangle$ to the individual magnetic components of the target level $|\gamma_1J_1K_1M_1\rangle$.

Equation (3.53) can be slightly reformulated in a manner which distinguishes
between the various pathways available for molecular energy transfer:

\[
\frac{\partial N_{\gamma_1 J_1 K_1 M_1}(t)}{\partial t} = -k_{\gamma_1 J_1 K_1 M_1} N_{\gamma_1 J_1 K_1 M_1}(t)
\]

\[+
\sum_{\gamma' \neq \gamma_1} \sum_{J'K'M'} k(\gamma' J' K' M' \rightarrow \gamma_1 J_1 K_1 M_1) N_{\gamma' J' K' M'}(t)
\]

\[+
\sum_{J'_1 \neq J_1} \sum_{K'_1 M'_1} k(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_1 J'_1 K'_1 M'_1) N_{\gamma_1 J_1 K_1 M_1}(t)
\]

\[+
\sum_{M'_1} k(\gamma_1 J_1 K_1 M'_1 \rightarrow \gamma_1 J_1 K_1 M_1) N_{\gamma_1 J_1 K_1 M'_1}(t)
\]

(3.54)

where successive summations denote rovibronic, pure rotational, and pure reorientational (i.e. \(M\)-changing) collisional channels.

The solution of the system of differential equations presented in expression (3.54) is a quite formidable task for which explicit knowledge of a large number of state-to-state cross sections is required. However, the \(M\)-specific rate constants, as well as the pure reorientational effects embodied in the final summation, clearly indicate that collisional processes will produce a redistribution of population within the magnetic sublevels of the target rovibronic eigenstate. Since random molecular encounters cannot, \textit{a priori}, be expected to enhance the \(M\)-distributions (\textit{cf.} figures 3-3 and 3-4) initially created within the excited state (\textit{viz.} [1]) by the PUMP radiation, the collision-induced relaxation channels will introduce an additional mechanism through which the optical anisotropy of the molecular sample is disrupted.

The temporal dephasing of the polarization signal which will accompany
collisional energy transfer processes can be phenomenologically described by rewriting the observed decay rate, \( I_{\gamma_1 J_1 K_1}^{\text{obs}} \), in equation (3.52) as a sum of two terms:

\[
I_{\gamma_1 J_1 K_1}^{\text{obs}} = 2 \left( I_{\gamma_1 J_1 K_1}^{\text{depop}} + I_{\gamma_1 J_1 K_1}^{\text{depol}} \right)
\]  

(3.55)

where \( I_{\gamma_1 J_1 K_1}^{\text{depop}} \) and \( I_{\gamma_1 J_1 K_1}^{\text{depol}} \) denote the decay rates corresponding to pure depopulation and pure depolarization processes respectively. The factor of two appearing in equation (3.55) is consistent with the previous derivation of the pure polarization signal.

The distinction between \( I_{\gamma_1 J_1 K_1}^{\text{depop}} \) and \( I_{\gamma_1 J_1 K_1}^{\text{depol}} \) may, at first, seem somewhat artificial. It must be recalled, however, that the optical anisotropy monitored in time-resolved polarization spectroscopy is brought about by the abrupt creation of a nonuniform distribution of molecules among the degenerate magnetic components of the target rovibronic level. The term depolarization thus refers to reorientation processes (e.g. pure \( M \)-changing \textit{elastic} collisions, \( M \)-specific perturbations, \textit{etc.}) which tend to equilibrate the magnetic sublevel populations and thereby destroy the induced anisotropy within the molecular system. In contrast, the word depopulation implies all mechanisms (e.g. \textit{inelastic} collisions, radiationless transitions, \textit{etc.}) which completely remove the molecular population from the target rovibronic level. Note that although depopulation can be considered to be a special form of depolarization, the converse is definitely not true.

As indicated by equation (3.55), the decay rates measured in time-resolved polarization spectroscopy can be augmented beyond the values attributed to simple depopulation of the target rovibronic eigenstate. The collision-induced depolarization effects responsible for this enhanced relaxation will display a strong
dependence upon the rotational degrees of freedom associated with the level under consideration. Although substantial theoretical and experimental progress has been made in the interpretation of reorientation channels in atom-diatomic molecule scattering \[224\], the propensity rules which govern the analogous processes in polyatomic systems are still a matter of considerable speculation.

In the case of the strongly dipolar formaldehyde-formaldehyde collision system, the results presented later in this Chapter will demonstrate that pure depolarization processes play a negligible role in the measured relaxation rates. This fact provides the basis for our utilization of polarization spectroscopy as a kinetic probe for the collision-induced depopulation of individual rotation-vibration levels within the \( ^1A_2 \) electronic manifold.

The temporal characteristics associated with other variants of polarization spectroscopy should be briefly mentioned. In particular, equation (3.25) has suggested that the heterodyne terms in the polarization signal expansion (c.f. expressions (3.20) and (3.21)) offer the possibility of enhanced sensitivity due to their linear dependence upon the optical anisotropy of the molecular sample. This direct proportionality to the differential absorption will also translate into a time-domain response which is similar to that encountered in conventional absorption (or gain) techniques. Therefore, the time-resolved heterodyne signals will decay exponentially with rates equal to half of those observed in pure polarization measurements.
3.3 Techniques

A typical energy level scheme for the polarization spectroscopy measurements of total depopulation rates in $\tilde{A}^1A_2$ formaldehyde-$h_2$ is illustrated in figure 3-5. The similarity between this folded double resonance technique, which is designated Polarized Transient Gain Spectroscopy or PTGS, and the direct transient gain methods of the previous Chapter should be quite apparent. In the present case, however, the PROBE beam is provided by a single-mode cw dye laser which can, in theory, be tuned into resonance with virtually any rovibronic transition in the formaldehyde $\tilde{A} \rightarrow \tilde{X}$ band system. This permits a systematic investigation of both collision-induced and collision-free relaxation processes to be performed upon individual rotation-vibration levels within the excited electronic state.

The experimental scheme illustrated in figure 3-5 represents an attempt to determine the total depopulation rate for the $4_{0,4}$ rotational level within the $v_4=1$ out-of-plane bending mode of $\tilde{A}^1A_2$ formaldehyde-$h_2$. In order to perform these measurements, the cw PROBE laser, which is linearly polarized at an angle of 45° with respect to the vertical, is tuned into resonance with the $2_4^14_{0,4} \rightarrow 1_{1,3}$ rovibronic transition. The lower level of this PROBE transition is a single rotation-vibration eigenstate located some 11300 cm$^{-1}$ above the zero point energy of the ground electronic potential surface. The location and assignment of this spectroscopic transition was accomplished through the use of the Stimulated Emission Pumping technique [171, 172]. The vertically polarized PUMP beam, produced by a frequency-doubled pulsed dye laser, is coincident with the $1_0^{1}4_{0,4} \rightarrow 1_{1,3}$ rovibronic transition at $\sim$ 28300 cm$^{-1}$.

Before arrival of the PUMP pulse, neither level of the PROBE transition is populated. The PROBE beam thus passes through the spatially isotropic
Figure 3-5: Typical Energy Level Diagram for PTGS Experiments.
PUMP: vertical polarization

PROBE: $\pi/4$ polarization
formaldehyde sample without any interaction. The pulsed PUMP abruptly populates the $4_{0,4}$ level of the $\tilde{A}$ state, thereby producing a population inversion in the PROBE transition. The cw PROBE, now propagating through a transitory gain medium, is amplified by stimulated emission in proportion to the excited state population. This sequence of events is completely analogous to that occurring in the TGS experiments of the previous Chapter.

Of greater importance from the viewpoint of our present experiments, is the fact that the linearly polarized nature of the PUMP beam results in the creation of an anisotropic population distribution in the upper level of the PROBE transition. This transitory optical anisotropy is characterized by a net alignment of the molecules within the degenerate magnetic components of the excited $4_{0,4}$ rovibronic level. The polarization properties of the PROBE radiation are therefore altered by the birefringence and dichroism which accompany the stimulated emission process. In the absence of elastic $M$-changing collision, the magnitude of this depolarization effect is directly proportional to the decaying population of the $4_{0,4}$ level.

Thus, by monitoring the transitory depolarization of the PROBE beam induced by optical pumping of the molecular system, the temporal evolution of a specific rotation-vibration level in the excited state can be observed. The use of a cw PROBE, in conjunction with a high-speed transient digitizer, permits acquisition of the entire time-resolved molecular decay profile for each pulse of the PUMP laser. This greatly augments both the quality and collection rate of the experimental data.
3.4 Experimental

3.4.1 Stimulated Emission Pumping

Before the PTGS kinetic studies could begin, the appropriate PROBE transitions had to be located and identified. This was accomplished by utilizing the Stimulated Emission Pumping technique in order to search for rovibronic transitions between a preselected rotational eigenstate in the \( v_4 = 1 \) level of \( ^3 \text{A} \text{A}_2 \) formaldehyde and highly excited rotation-vibration levels in the ground electronic potential surface. The experimental configuration employed for these spectroscopic studies was fully discussed in the Chapter 2 and will not be repeated here.

The only noteworthy differences in the SEP measurements preceeding the polarized transient gain experiments are related to the DUMP wavelength. Constraints imposed by the tunability and output efficiency of the continuous wave PROBE laser necessitated that PROBE transitions be located in the vicinity of \( \sim 17000 \text{cm}^{-1} \). For kinetic studies in the \( v_4 = 1 \) vibrational level of \( ^3 \text{A} \text{A}_2 \) formaldehyde (term energy \( \sim 27300 \text{cm}^{-1} \)), this required that appropriate PROBE transitions would terminate on rotation-vibration eigenstates possessing \( \sim 11300 \text{cm}^{-1} \) of excitation above the zero point energy of the ground electronic potential surface.

In order to produce tunable light in the vicinity of 590nm, a mixture [225, 226] of Coumarin 540A and Rhodamine 6G dyes (Exciton Chemical Company) dissolved in spectroscopic grade methanol (Omnisolve) were employed in the DUMP dye laser. With 355nm third harmonic Nd:YAG radiation as the pump source, this resulted in a pressure-scanable output having a spectral bandwidth of \( \sim 0.03 \text{cm}^{-1} \) FWHM, a pulse duration of \( \sim 6 \text{ns} \) FWHM, and an energy of \( \sim 10 \text{mJ/pulse} \). Although several advantages in terms of both power and dye lifetime could have be
realized by pumping a pure Rhodamine 6G dye solution with the 532nm second harmonic radiation of a Nd:YAG laser, this was not technically feasible at the time that these experiments were performed. The absolute frequency of the DUMP beam was conveniently determined by using a room temperature iodine absorption cell in conjunction with the Fourier transform atlas of Gerstenkorn and Luc [71].

3.4.2 Polarized Transient Gain Spectroscopy

The apparatus utilized for the polarized transient gain studies of $\tilde{A}^1A_2$ formaldehyde-$h_2$ is illustrated in figure 3-6. The correspondence between this diagram and the general configuration for polarization spectroscopy shown in figure 3-1 should be readily apparent. A great similarity, in design as well as concept, also exists between these polarization experiments and the TGS measurements presented in the previous Chapter. In the interest of brevity, the discussion which follows will therefore concentrate specifically upon those areas where the two methods (i.e. PTGS and TGS) differ from one another.

The PROBE beam for the polarized transient gain measurements was produced by utilizing $\sim 3.0$ watts of all-line emission from a continuous-wave argon ion laser (Spectra Physics model 164/03) to pump a commercial standing-wave dye laser (Coherent Radiation CR599-21) containing Rhodamine 6G dye (Exciton Chemical Company) dissolved in ethylene glycol (Fisher Scientific). Single frequency operation was achieved by constraining laser oscillations to an individual longitudinal cavity mode by means of a frequency stabilized and locked intracavity etalon assembly. This resulted in a short time frequency jitter of $\leq 1$MHz and an overall drift rate of $\sim 10$MHz/hour. The vertically polarized output of this cw source, which was constantly monitored by means of a confocal spectrum analyzer (Spectra Physics model 480, 2.0GHz FSR & Burleigh model
Figure 3-6: Apparatus for Polarized Transient Gain Experiments.
RC-42 ramp generator), had an average power of \( \sim 200 \text{mW} \) and could be electronically scanned over any contiguous 1cm\(^{-1}\) interval within the limits imposed by the dye tuning curve (for Rhodamine 6G dye: 570nm \( \sim 620 \text{nm} \)).

After being approximately collimated to a diameter of 3nm by means of a Galilean telescope, the cw PROBE beam was directed through an achromatic half wave retarder (Special Optics model R8-9015) and a calcite Glan-Laser prism (Karl Lambrecht MGLA-8). These optical elements enabled the linear polarization of the PROBE radiation to be precisely oriented at an angle of 45\(^\circ\) with respect to that of the PUMP (\textit{viz.} 45\(^\circ\) with respect to vertical). The tunable cw light subsequently propagated down the center of the sample cell without passing through or reflecting from any additional optical components which might compromise its high polarization contrast ratio.

The PUMP for the polarization experiments was produced by the same Nd:YAG pumped, pulsed dye laser utilized in the transient gain studies of the previous Chapter. The details of this pressure-tunable light source will not be repeated here except to mention that the frequency doubled output (at \( \sim 350 \text{nm} \)) had a spectral bandwidth of \( \sim 0.06 \text{cm}^{-1} \) FWHM, a pulse duration of \( \sim 5 \text{ns} \) FWHM, and an energy of \( \sim 2 \text{mJ/pulse} \). After spatial filtering and recollimation to a diameter of \( \sim 4 \text{mm} \), the PUMP beam propagated through a 350nm half wave retardation plate (Virgo Optics) and a Glan-Laser calcite prism (Karl Lambrecht MGLA-8-SW) so as to ensure that the linear polarization of this ultraviolet radiation was vertically oriented. The PUMP was subsequently directed through the sample cell at a slight angle (\textit{viz.} \( \leq 6.0 \text{ milliradians} \)) with respect to the copropagating PROBE beam.

After traversing the sample cell, the PROBE beam, separated from the copropagating (but not collinear) PUMP by means of an aperture, immediately
entered a Glan-Laser calcite prism (Karl Lambrecht MGLA-8-SW) which functioned as the analyzer in these experiments. This optical component was mounted in a high precision rotation stage (Klinger TR80; $3 \times 10^{-4}$ radian resolution) so that its orientation could be carefully adjusted to effectively null the incident cw radiation. As a result of the transitory optical anisotropy induced in the molecular sample by the PUMP pulse, a small portion of the PROBE will be transmitted through the analyzer. This signal-carrying beam was spectrally dispersed by means of an S1-UV Pellin-Broca prism (Optics for Research) and an Amici direct vision prism (Physitec) in order to remove any residual scattered light originating from the pulsed lasers. The isolated signal photons were subsequently directed through a well-baffled flight tube and eventually impinged upon a high-speed photomultiplier tube (Hamamatsu R1635; 0.8ns rise time) which served as the detector for our time-resolved measurements.

The photomultiplier output was directed, without additional amplification or filtering, into a high-speed transient digitizer (Tektronix 7912AD, 7B92A time base, 7A19 amplifier, DC to 500MHz bandwidth) to permit signal averaging and then to a microcomputer (DEC LSI-11/03) for further processing and analysis. To exclude artifacts associated with timing jitter, the digitizer was triggered by means of a fast photodiode (EG&G FND-100, 90V reverse bias) which monitored a back reflection from the PUMP laser. All signal connections between instruments were performed with double shielded coax cable (RG223) with particular attention to the preservation of 50Ω transmission line characteristics.

The cell utilized in these polarization experiments was the same one employed for the transient gain measurements of Chapter 2. Basically, it was constructed of a 120cm long section of pyrex conical tubing (Corning) into which several glass/teflon stopcocks (Ace Glass) had been fused. Windows (Esco S1-UV, 3/8 inch thick, 1.25
inch diameter) were mounted upon o-ring seals at both ends and held in place only by the pressure differential between the interior and exterior of the cell. Pressures could be accurately monitored by means of either an ionization gauge (Veeco Instruments Inc. model RGS-7) or a 0 to 1 Torr capacitance manometer (MKS Baratron model 220B).

The technique of polarization spectroscopy is based upon the detection of a relatively small anisotropy induced in a molecular system by optical pumping. It was therefore essential that the windows employed on the sample cell be free of any dichroic or birefringent properties which might compromise the polarization characteristics of the PROBE beam and undermine the ultimate sensitivity attained in our time-resolved measurements. In this context, the successful outcome of these experiments required that two conditions be satisfied:

1. The windows were required to be relatively thick and had to be mounted by the most stress-free means available. As a result, they were secured to their o-ring seals only by the pressure differential between the interior and exterior of the sample cell. In this manner, stress-induced optical birefringence in the cell windows could be minimized.

2. The windows had to be fabricated from extremely high quality S1-UV substrates in order to avoid the creation of transient artifacts by the powerful ultraviolet PUMP pulse. The exceptional transparency afforded by such optical material was also essential for the elimination of dichroic interactions between the PROBE radiation and the cell windows.

Despite all precautions, a small residual birefringence usually remained in the cell windows thereby greatly impairing the degree to which the cw PROBE radiation could be nulled. The origin of these problems is best illustrated by reference to equation (3.20) where, for the present set of circumstances, the differential birefringence, $\Delta b$, would be nonzero. It was found that this situation could be dramatically improved by pressing the edge of one sample cell window with the tip of a differential micrometer. By careful adjustment of the force applied
to the window, an additional stress was introduced which effectively cancelled the undesired birefringence terms (i.e. the $\Delta b$ terms) of expression (3.20).

In order to achieve the best possible extinction coefficient in the PTGS measurements, it was necessary for the PROBE beam to propagate, as closely as possible, through the center of all optical elements critical to the polarization detection scheme (viz. calcite prisms and cell windows). In this manner, the detrimental effects of stress-induced birefringence, arising from the mounting of optical components, could be minimized. Similarly, a decrease in the diameter of the PROBE beam significantly enhanced the effectiveness of the nulling process. However, since a reduction in beam dimensions also diminished the number of molecules detected, a compromise had to be made with respect to selection of the PROBE diameter.

The formaldehyde-$h_2$ utilized in the PTGS experiments was prepared by pyrolysis of paraformaldehyde-$h_2$ (Aldrich) followed by two fractional distillations. All time-resolved measurements were performed at room temperature (i.e. $22 \pm 3^\circ C$) with sample pressured ranging from 0 to 400 milliTorr.

A typical polarized transient gain experiment began by tuning the cw dye laser to within one wavenumber (i.e. the range of one electronic scan) of the desired PROBE transition. This process was greatly facilitated by utilizing a room temperature iodine absorption cell in conjunction with the table of absolute frequencies provided by the Fourier transform atlas of Gerstenkorn and Luc [71]. The servo-electronics and external reference cavity of the cw PROBE laser enabled it to remain frequency locked to within 10MHz/hour.

The pulsed PUMP beam was initially directed into a separate fluorescence cell in order to acquire a formaldehyde excitation spectrum for the purpose of identifying a preselected PUMP transition. The PUMP laser frequency was
subsequently pressure scanned into resonance with the appropriate spectral feature where it usually remained, without operator intervention, for several hours. The PUMP was then redirected back towards the apparatus utilized in the polarized transient gain experiments.

The sample cell was filled with the desired pressure of formaldehyde vapor and isolated from the rest of the vacuum line. With the PUMP blocked, the PROBE beam was permitted to traverse the gaseous sample and impinge upon the Glan-Laser polarization analyzer. Only after this calcite prism had been approximately adjusted to transmit light with a polarization orthogonal to that of the incident PROBE radiation, could the shutter of the photomultiplier detector be opened.

The final nulling of the PROBE beam was accomplished by monitoring the output current of the photomultiplier with a picoammmeter (Keithley Instruments Inc. model 600A electrometer) while simultaneously adjusting the orientation of the polarization analyzing Glan-Laser prism as well as the force with which the differential micrometer pressed against the edge of the cell window. By carefully searching for the conditions which resulted in a minimum PMT output current, extinction coefficients better than $10^{-7}$ (for small PROBE beam diameters) could readily be achieved. It was extremely important that no part of the sample cell be touched at this time otherwise the optical birefringence induced by stress within the cell windows could permit an excessive amount of PROBE light to impinge upon the photon detector. This would have a catastrophic effect in the case of the photomultiplier tube utilized in our experiments.

The pulsed PUMP was finally permitted to enter the sample cell in order to produce the transitory optical anisotropy required by the polarized detection scheme. Fine tuning of the cw laser frequency, to bring it into resonance with the
PROBE transition, could easily be performed by maximizing the observed polarization signal. With this accomplished, the transient digitizer was instructed to signal average over 1024 pulses of the PUMP. After subtracting a background trace (also a 1024 shot average) obtained with the PROBE laser detuned, the time-resolved data curves typically had signal-to-noise ratios in excess of 100:1. These data were stored on floppy disks for later processing and analysis. The formaldehyde sample was replaced following the acquisition of each set of signal and background traces in order to minimize the effects of photoproducts in the kinetic studies.

The polarization signals observed in these time-resolved studies typically displayed large amplitude variations from one PUMP pulse to the next. As described in the previous Chapter for the case of transient gain measurements, these fluctuations can be attributed to the randomly occurring frequency overlap between the single mode output of the PROBE laser and the cavity mode structure present in the PUMP beam. The "coherent spiking" behavior discussed in Chapter 2 was also observed in the polarization experiments, but to a much lesser extent.

3.5 Results and Discussion

3.5.1 Stimulated Emission Pumping

The Stimulated Emission Pumping spectroscopy performed in conjunction with the PTGS energy transfer studies was specifically designed to locate intense PROBE transitions through which the collision-induced relaxation of preselected \( \tilde{A}^1A_2 \) eigenstates could be examined. For such time-resolved measurements of depopulation processes in electronically excited formaldehyde, the exact identity of the PROBE transition, in particular the rotation-vibration quantum numbers ascribed to the terminal level within the \( \tilde{X}^1A_1 \) ground state (cf. Figure 3-5), was
not a prerequisite. A possible exception to this statement can be found in the theoretical signal magnitudes expected from polarization sensitive detection schemes. For the case of linearly polarized PUMP radiation, the angular momentum expressions contained in table 3-1 indicate that the depolarization of the PROBE beam will attain a maximum value in Q branch rovibronic transitions. The desire to optimize the observed PTGS signals, as well as the critical role which the present SEP data play in the $\tilde{\chi}^1A_1$ kinetic experiments discussed in the following Chapter, required that a careful analysis be performed on the spectra obtained from the highly excited regions of the ground electronic potential surface.

The cw dye laser utilized as the PROBE in the PTGS studies could be most conveniently operated with Rhodamine 6G dye which has a maximum conversion efficiency at $\sim 590\text{nm}$ [227]. Consequently, all SEP experiments had to be performed with DUMP frequencies in the vicinity of $17000\text{cm}^{-1}$. This constraint, together with the ultimate goal of examining collision-induced relaxation processes in the $v_4=1$ level of $\tilde{\alpha}^1A_2$ formaldehyde, translated into a search for PROBE transitions which terminate on single rotation-vibration eigenstates located $\sim 11300\text{cm}^{-1}$ above the zero point energy of the ground electronic potential surface. Table 3-III contains a compilation of all PUMP transitions which were employed in the present spectroscopic investigation of vibrationally excited formaldehyde. In each case, the DUMP laser was pressure-scanned over the nominal range of $16850-17050\text{cm}^{-1}$.

Previous SEP studies [180] have examined eigenstates in the ground electronic potential surface of formaldehyde with less than $10000\text{cm}^{-1}$ of excitation above the zero point. The spectroscopic transitions observed in these low energy regimes are characterized by their rotational and vibrational simplicity. Each resonance could be associated with a definitive set of rotational and, more importantly, vibrational
<table>
<thead>
<tr>
<th>Vibronic Transition</th>
<th>Rotational Transition</th>
<th>Transition(^a) Energy</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4_0^1)</td>
<td>(2_{1,1} \rightarrow 2_{0,2})</td>
<td>28319.537</td>
<td>2.30</td>
</tr>
<tr>
<td>(4_0^1)</td>
<td>(2_{0,2} \rightarrow 3_{1,3})</td>
<td>28296.687</td>
<td>5.40</td>
</tr>
<tr>
<td>(4_0^1)</td>
<td>(4_{0,4} \rightarrow 4_{1,3})</td>
<td>28300.622</td>
<td>11.00</td>
</tr>
<tr>
<td>(4_0^1)</td>
<td>(5_{0,5} \rightarrow 5_{1,4})</td>
<td>28298.739</td>
<td>12.50</td>
</tr>
<tr>
<td>(4_0^1)</td>
<td>(6_{0,6} \rightarrow 6_{1,5})</td>
<td>28296.474</td>
<td>13.40</td>
</tr>
<tr>
<td>(4_0^1)</td>
<td>(13_{2,12} \rightarrow 13_{3,11})</td>
<td>28242.349</td>
<td>5.00</td>
</tr>
</tbody>
</table>

\(^a\) Calculated values (cm\(^{-1}\)) from rotational constants in reference [50].

**Table 3-III:** PUMP Transitions for SEP at \(\sim 11300\)cm\(^{-1}\).
quantum numbers, thereby permitting the accurate determination of both band origins and rotational constants [228]. This behavior is consistent with the usual notion that adjacent vibrational levels (viz. levels specified by distinct sets of vibrational quantum numbers) should exhibit significantly different chemical, structural, and dynamical properties.

In contrast to the simple behavior documented in low energy regimes, the present SEP studies exhibit a substantially more complicated pattern of resonances. The spectral congestion encountered in our spectroscopic study of rotation-vibration eigenstates at \( \sim 11300 \text{cm}^{-1} \) of excitation virtually eliminates any possibility of labelling individual transitions with vibrational and, in some instances, rotational quantum numbers. The qualitative difference between the high and low energy regions of \( \tilde{X}^1A_1 \) formaldehyde can be readily appreciated through consideration of the two stick spectra illustrated in figure 3-7. In each case, the PUMP laser was tuned into coincidence with the \( 4^1_0 \leftrightarrow 4^1_{0,4} \) rovibronic transition at \( 28300.622 \text{cm}^{-1} \). The stick spectra denote the actual SEP signals observed by scanning the DUMP wavelength in the vicinity of either 422nm or 590nm. This permits examination of rotation-vibration structure within the ground electronic potential surface at energies of \( \sim 4660 \text{cm}^{-1} \) and \( \sim 11370 \text{cm}^{-1} \), respectively.

The lower stick spectrum in figure 3-7 shows the SEP resonances observed for \( \sim 4660 \text{cm}^{-1} \) of excitation in the ground electronic potential surface. The intensities and spacings exhibited by the spectroscopic data are characteristic of the expected \( R \) (i.e. \( 4^1_{0,4} \leftrightarrow 3^1_{1,3} \)), \( Q \) (i.e. \( 4^1_{0,4} \leftrightarrow 4^1_{1,3} \)), and \( P \) (i.e. \( 4^1_{0,4} \leftrightarrow 5^1_{1,5} \)) rotational structure within a single \( b \)-type vibronic band [56]. Such \( b \)-type electric dipole transitions account for nearly 75% of the total oscillator strength attributed to the formaldehyde \( \tilde{A} \leftrightarrow \tilde{X} \) electronic system [69, 70]. In the case of a transition originating from the \( v_4 = 1 \) level of \( \tilde{A}^1A_2 \) formaldehyde, \( b \)-type selection rules
Figure 3-7: Stick Spectra for SEP Resonances in Formaldehyde-$h_z$. 
Region of $2_4^4_4$

$\rho_{\text{vib}} = 0.42/\text{cm}^{-1}$

PUMP: $4_{0,4} v_4 = 1$

Region of $4_4$

$\rho_{\text{vib}} = 0.03/\text{cm}^{-1}$

PUMP: $4_{0,4} v_4 = 1$

$4_{1,3} (Q)$

$3_{1,3} (R)$

$5_{1,4} (P)$
stipulate that the terminal vibrational level in the ground state must transform as the $a_1$ irreducible representation of the $C_{2v}(M)$ molecular symmetry group [48]. This symmetry restriction, together with the rather small density of vibrational states encountered in such low energy regimes (viz. $\rho_{vib} \approx 0.03$/cm$^{-1}$), permits the vibrational character for the depicted DUMP transition to be unambiguously assigned as $4_{4}^{1}$. A careful analysis of the rotational structure associated with this vibronic band permitted the origin for the $v_4 = 4$ vibrational level in $\tilde{X}^1A_1$ formaldehyde to be established at 4629.8±0.5cm$^{-1}$ [180]. The enormous spectral simplification afforded by the Stimulated Emission Pumping technique is clearly demonstrated by the limited number of rovibronic transitions permitted, by rotational selection rules, from the single rotation-vibration level prepared by the PUMP in the excited electronic state to the $v_4 = 4$ vibrational level in the ground electronic state.

The SEP signals depicted in the upper portion of figure 3-7 correspond to eigenstates of $\tilde{X}^1A_1$ formaldehyde which possess $\sim 11370$cm$^{-1}$ of excitation distributed among their vibrational and rotational degrees of freedom. This region of the ground electronic potential surface, which is of particular concern in the present PTGS kinetic studies, supports a total density of vibrational states (i.e. $\rho \approx 0.6$/cm$^{-1}$) which is over an order of magnitude greater than that encountered in the low energy regime probed by the $4_{4}^{1}$ DUMP transition (cf. lower portion of figure 3-7). The large number of resonances contained in the SEP spectrum confirms that the separation between adjacent vibrational levels has decreased to the point that it is comparable to the characteristic energy spacings for rotational fine structure. Nevertheless, the transitions observed at $\sim 11370$cm$^{-1}$ display several basic traits in common with the data recorded at $\sim 4660$cm$^{-1}$ including the presence of an intense Q branch feature flanked by what appear to be doubled P
and R branches. Similar patterns of spectral lines (viz. strong Q branch with
doubled P and R branches) were also found in the experiments performed from the
$2_{0,2}$, $5_{0,5}$, and $6_{0,6}$ rovibronic levels of the $\tilde{A}$ state (cf. table 3-III). It should be
noted that some of the weaker resonances exhibited in the high energy stick
spectrum of figure 3-7, in particular the lines at 11371cm$^{-1}$, might be attributed to
an unavoidable overlap in the PUMP transition (cf. reference [172]).

The rotational character (viz. R, Q, or P) for the SEP rovibronic transitions
illustrated in figure 3-7 can be determined through the use of similar spectroscopic
measurements performed from the $2_{0,2}$ and $6_{0,6}$ eigenstates of $\tilde{A}$ $^1A_2$
formaldehyde (cf. table 3-III). For a single vibronic DUMP transition, the P branch in the SEP
spectrum from the $2_{0,2}$ level will terminate on the same lower rotational eigenstate
as the R branch from the $4_{0,4}$ level. An analogous situation exists between the P
branch derived from the $4_{0,4}$ level and the R branch associated with the $6_{0,6}$ level.
A comparison of the term values derived from the $2_{0,2}$ and $6_{0,6}$ SEP data with those
depicted in figure 3-7 for the $4_{0,4}$ eigenstate confirmed that the doublet structures
at 11357.1cm$^{-1}$ and 11378.1cm$^{-1}$ could be correlated with doubled R and P branch
transitions, respectively.

The pattern of spacings and intensities exhibited by the stick spectrum in the
upper portion of figure 3-7, together with the relatively large oscillator strengths
attributed to individual spectral features in this high energy regime (e.g. the
strongest transitions can be rather easily saturated by the DUMP laser), suggests
the presence of a $b$-type vibronic band. Under this assumption, the pronounced
SEP resonance at $\sim$ 11367.3cm$^{-1}$ can be correlated with a Q branch DUMP
transition which terminates on a $4_{1,3}$ rotational eigenstate within a highly excited $a_1$
vibration level of the ground electronic potential surface. This assignment in terms
of a $\Delta J = 0$ rovibronic transition was confirmed through comparison of polarization
spectroscopy measurements performed under conditions of linearly polarized and circularly polarized PUMP radiation (cf. depolarization factors compiled in tables 3-I and 3-II). The rotational energy for the $4_{1,3}$ level is estimated to be $\sim 33 \text{cm}^{-1}$ from the spectroscopic constants reported for the vibrationless level of $\tilde{X}^1A_1$ formaldehyde–$h_2$ [50]. Therefore, the vibrational band origin for the spectral features depicted in figure 3-7 should be in the vicinity of $11335 \text{cm}^{-1}$.

Table 3-IV contains a compilation of vibrational levels predicted, via the constants of Reisner, et. al. [228], to occur in the vicinity of $11335 \text{cm}^{-1}$ above the zero point energy of the ground electronic potential surface. Only those vibrational levels which would support reasonably intense SEP resonances have been tabulated. Also presented are the vibronic oscillator strengths for DUMP transitions originating from either the $v_4 = 1$ or $v_4 = 3$ level of $\tilde{A}^1A_2$ formaldehyde. These values, determined from the ab initio one-dimensional overlap integrals of van Dijk [179], are consistent with expectations derived from the Franck-Condon principle [110, 118]: Since the $\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1$ transition entails a substantial increase in the carbonyl bond length as well as a pyramidal distortion of the molecular framework, the vibronic spectrum will be dominated by progressions based upon the $\nu_2$ C=O stretching and the $\nu_4$ out-of-plane bending coordinates. It should be noted that the SCF-CI calculations of van Dijk consistently overestimate the intensity of transitions involving the $\nu_3$ symmetric $\text{CH}_2$ deformation mode [180].

A tentative vibrational assignment for the $4_{0,4}$ SEP data depicted in figure 3-7 can be made by recognizing that these spectral features constitute the most intense resonances observed in the $16850-17050 \text{cm}^{-1}$ range scanned by the DUMP laser. This frequency interval translates into a spectroscopic examination of rotation-vibration eigenstates possessing between $11450 \text{cm}^{-1}$ and $11250 \text{cm}^{-1}$ of excitation.
<table>
<thead>
<tr>
<th>Vibrational Level</th>
<th>Term Value</th>
<th>Vibrational Symmetry</th>
<th>Transition Type</th>
<th>$4^1$ DUMP Oscillator Strength</th>
<th>$4^3$ DUMP Oscillator Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1_1^21_2^31_4^41_5^1$</td>
<td>11242.3</td>
<td>$a_2$</td>
<td>c</td>
<td>$8.26 \times 10^{-10}$</td>
<td>$9.23 \times 10^{-10}$</td>
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<td>$2_1^14_4^46_4$</td>
<td>11252.6</td>
<td>$a_1$</td>
<td>b</td>
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<td>$2_3^31_4^43_4^36_1$</td>
<td>11256.6</td>
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<td>$2_2^23_4^15_1^16_2$</td>
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<td>$3.60 \times 10^{-9}$</td>
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<td>$2_2^24_2^52_2$</td>
<td>11299.4</td>
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<td>$1_1^21_2^46_2$</td>
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<td>b</td>
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<td>$2_3^33_4^55_1$</td>
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<tr>
<td>$4_{10}$</td>
<td>11386.5</td>
<td>$a_1$</td>
<td>b</td>
<td>$(1.8 \times 10^{-5})$</td>
<td>$(2.4 \times 10^{-5})$</td>
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<td>$1.95 \times 10^{-8}$</td>
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<td>$b_1$</td>
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<td>$(2.2 \times 10^{-10})$</td>
<td>$(3.8 \times 10^{-10})$</td>
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<td>$a_2$</td>
<td>c</td>
<td>$7.46 \times 10^{-10}$</td>
<td>$8.34 \times 10^{-10}$</td>
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</tbody>
</table>

$^a$ In cm$^{-1}$.

$^b$ DUMP transition type referred to either $4^1$ or $4^3$ PUMP.

$^c$ Values in parentheses estimated from lower energy vibrational levels.

**Table 3-IV:** Calculated Formaldehyde-$h_2$ Vibrational Levels Near 11335cm$^{-1}$. 


above the zero point of the ground electronic potential surface. As suggested by the oscillator strengths contained in table 3-IV, two plausible candidates for the lower vibrational level of the DUMP transition are to be found in the $2_{4}^{4}$ and $4_{10}$ levels which have calculated term values of $11379.8\text{cm}^{-1}$ and $11386.5\text{cm}^{-1}$ respectively. The difference between these term energies and the band origin of $\sim 11340\text{cm}^{-1}$ predicted on the basis of the Q branch frequency in figure 3-7 is not significant. Such discrepancies can be attributed to the constants utilized for evaluation of the vibrational energies in table 3-IV. In short, these spectroscopic parameters were based upon experiments performed in much less energetic regimes (i.e. $< 9300\text{cm}^{-1}$) and do not explicitly take into account the effects of resonant perturbations (e.g. Fermi and Coriolis interactions).

The above analysis has suggested two $b$-type vibronic transitions, $2^{0}_{4}^{4}$ and $4^{1}_{4}$, which could account for the rotational structure and overall intensity exhibited by the high energy SEP data in figure 3-7. The presence of both of these resonances could provide an explanation for the doublets encountered in the R and P branches although such reasoning would also necessitate the appearance of two Q branches. It is quite probable that some form of resonance interaction (i.e. a Coriolis or Fermi perturbation) is responsible for the doubling observed in the $\Delta J = \pm 1$ rovibronic transitions. Further attempts to clarify the vibrational character of the DUMP transition (e.g. through examination of rotational structure) did not prove to be successful. In addition, SEP studies performed from the $13_{2,12}$ rovibronic level of the \(\tilde{A}\) state (cf. table 3-III) revealed a substantially greater number of spectral lines than encountered in the $J_{0,J}$ measurements (i.e. $2_{0,2}'$, $4_{0,4}'$, $5_{0,5}'$, and $6_{0,6}'$). This behavior can be rationalized in terms of the breakdown of rotation-vibration separability in highly excited $\tilde{X}^{1}A_{1}$ formaldehyde brought about by rotation-dependent Coriolis interactions [56]. Dai, et. al. [143] have demonstrated that
rotational motion can significantly diminish the structural differences between neighboring vibrational levels and can promote an averaging of vibrational character with the concomitant destruction of the \( K_a \) quantum number. From this viewpoint, the larger number of resonances observed from the \( 13_{2,12} \) level can be regarded as a manifestation of the rotation-induced mixing of vibronic oscillator strength among adjacent vibrational levels.

The PTGS experiments utilized intense \( Q \) branch resonances, identified through SEP measurements performed upon various \( \tilde{A}^1A_2 \) rotational levels, as PROBE transitions through which relaxation phenomena in electronically excited formaldehyde could be monitored. On the basis of the calculated oscillator strengths compiled in table 3-IV, the ensuing discussion will assume that the most pronounced spectral features can be nominally attributed to the \( 2_{4,4} \) vibrational level within the ground electronic state. Table 3-V presents a detailed description of the PUMP and PROBE transitions which were employed for the kinetic studies of individual rotation-vibration eigenstates. Note that all of the tabulated PROBE transitions were confirmed to be \( Q \) branches through the behavior of their polarization spectroscopy signals following excitation with linearly polarized and circularly polarized PUMP radiation.

### 3.5.2 PTGS As a Spectroscopic Probe

Before describing the kinetic measurements which form the basis for the work presented in this Chapter, it is worthwhile to consider briefly the use of polarization-detected transient gain as a spectroscopic probe for molecules in regions of extreme vibrational excitation. Although the energy level scheme depicted in figure 3-6 has been specifically designed for the investigation of collisional relaxation processes in \( \tilde{A}^1A_2 \) formaldehyde, the same three level system, in conjunction with a
### a. PUMP Transitions.

<table>
<thead>
<tr>
<th>Target Level</th>
<th>Vibronic Transition</th>
<th>Rotational Transition</th>
<th>Transitiona</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>40</td>
<td>20,2 ↔ 21,1</td>
<td>28303.240</td>
<td></td>
</tr>
<tr>
<td>40.4</td>
<td>40</td>
<td>40,4 ↔ 41,3</td>
<td>28300.622</td>
<td></td>
</tr>
<tr>
<td>50.5</td>
<td>40</td>
<td>50,5 ↔ 51,4</td>
<td>28298.730</td>
<td></td>
</tr>
<tr>
<td>60.6</td>
<td>40</td>
<td>60,6 ↔ 61,5</td>
<td>28296.474</td>
<td></td>
</tr>
<tr>
<td>132,12</td>
<td>40</td>
<td>132,12 ↔ 133,11</td>
<td>28242.349</td>
<td></td>
</tr>
</tbody>
</table>

### b. PROBE Transitions.

<table>
<thead>
<tr>
<th>Target Level</th>
<th>Vibronicb</th>
<th>Rotational Transition</th>
<th>Transitiona</th>
<th>Termc</th>
<th>Energy</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>204,1</td>
<td>20,2 → 21,1</td>
<td>16968.442</td>
<td>11350.527</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.4</td>
<td>204,1</td>
<td>40,4 → 41,3</td>
<td>16966.636</td>
<td>11367.269</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.5</td>
<td>204,1</td>
<td>50,5 → 51,4</td>
<td>16965.326</td>
<td>11379.235</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.6</td>
<td>204,1</td>
<td>60,6 → 61,5</td>
<td>16963.780</td>
<td>11393.554</td>
<td></td>
<td></td>
</tr>
<tr>
<td>132,12</td>
<td>204,1</td>
<td>132,12 → 133,?</td>
<td>16938.262</td>
<td>11590.056</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a In cm⁻¹.

b Tentative vibronic assignment for PROBE transition.

c Term value for lower level of PROBE transition in cm⁻¹.

**Table 3-V**: Transitions Utilized in PTGS Studies of \( \tilde{1}A_2 \) Formaldehyde.
tunable PROBE laser, provides a means by which highly excited rotation-vibration eigenstates in the ground electronic potential surface can be located and identified. While this application of the PTGS technique has much in common with Stimulated Emission Pumping, it affords several distinct advantages which will be discussed below.

The unique spectroscopic capabilities of PTGS are demonstrated by the spectral line profile presented in Figure 3-8. This diagram illustrates the magnitude of the pure polarization signal obtained by scanning the PROBE laser in the vicinity of 16966.6cm\(^{-1}\) while simultaneously creating an optical anisotropy within the formaldehyde sample through optical pumping of the \(4_0^1 4_{0,4} \leftarrow 4_{1,3}\) rovibronic transition (cf. Figure 3-6). The frequency-dependent depolarization experienced by the PROBE radiation clearly indicates the position of the \(2_{4,4}^1 4_{0,4} \rightarrow 4_{1,3}\) transition which terminates on a single rotation-vibration eigenstate located 11367.27cm\(^{-1}\) above the zero-point energy of the ground electronic potential surface. A portion of the \(I_2\) absorption spectrum, recorded concurrently as an absolute frequency reference, is also displayed. The signal-to-noise ratio exhibited by the data in figure 3-8 exceeds that attained by conventional Stimulated Emission Pumping under similar conditions.

The most significant spectroscopic advantage of the PTGS technique follows from the use of a frequency-stabilized, single mode cw dye laser as the source of PROBE radiation. This provides an extraordinary degree of spectral resolution as demonstrated by the detailed shape of the line profile which appears in figure 3-8. The pattern of spikes, which varies randomly from one scan to the next but always retains the same characteristic energy spacing (viz. \(\sim 0.008\text{cm}^{-1}\)), represents the cavity mode structure within the single etalon mode of the pulsed dye laser employed as the PUMP. Therefore, by combining the PTGS detection scheme with
Figure 3-8: PTGS as a Spectroscopic Probe for Highly Excited $\text{H}_2\text{CO}$. 

~50mTorr $\text{H}_2\text{CO}$

PUMP: $4^1_0 \quad 4_{0,4} \leftrightarrow 4_{1,3}$

PROBE: $2^0_4 \quad 4_{0,4} \rightarrow 4_{1,3}$
a narrow-band PUMP laser (e.g. a pulse amplified cw dye laser), high resolution. Fourier transform-limited spectroscopy could be performed upon vibrationally excited polyatomic systems. This capability is of special importance in regimes of extreme excitation where the density of rotation-vibration eigenstates far exceeds that encountered in lower, less congested regions of the potential surface.

A further advantage afforded by the PTGS technique stems directly from the polarized nature of this detection scheme. As suggested by the theoretical discussion of polarization spectroscopy presented above, comparison of the relative signal magnitudes derived from linearly polarized and circularly polarized PUMP radiation permits a distinction to be made between $\Delta J = 0$ and $\Delta J = \pm 1$ transitions. Since the intermediate level prepared by the PUMP pulse is usually well characterized, this unique capability can be applied to identification of the PROBE transitions which terminate on highly excited rotation-vibration eigenstates in the ground electronic potential surface. Such polarization measurements provide a quite useful tool for the analysis of spectra obtained from regions in which the separation between adjacent vibrational levels has become comparable to the characteristic spacing for rotational fine structure. The PROBE transition depicted in figure 3-8 was determined to be a Q branch by examination of its behavior under conditions of linearly and circularly polarized optical pumping.

### 3.5.3 Depopulation Studies

Figure 3-9 depicts a typical time-resolved decay profile recorded during our PTGS studies of collisional depopulation processes in $\tilde{\tilde{A}}^1{A}_2$ formaldehyde-$h_x$. The target for this particular measurement was the $4_{0,4}$ rotational eigenstate in the $v_4 = 1$ vibrational level (cf. figures 3-6 and 3-8). The actual data, denoted by the fine black line, were obtained by directly monitoring the transitory depolarization of
Figure 3-9: PTGS for $\tilde{A}^1A_2 v_4 = 1 4_{0,4}$ Formaldehyde.
$H_2CO$ \text{ $^1A_2$} \quad v_4 = 1 \quad 4_{0,4}$

- \text{P} = 0.0525 \text{ Torr}

$\Gamma^{\text{obs}} = 12.42 \pm 0.23 \mu \text{sec}^{-1}$

$\Gamma = 6.21 \pm 0.12 \mu \text{sec}^{-1}$

$\tau = 161.1 \pm 3.0 \text{ ns}$

Decay Time (ns)

Signal Amplitude (arb)
the cw PROBE beam subsequent to abrupt optical pumping of the molecular sample via the $4_{0}^{1} 4_{0,4} \leftrightarrow 4_{1,3}$ rovibronic PUMP transition. This trace was acquired by programming a high-speed transient digitizer to signal average over 1024 pulses of the PUMP laser. Similar curves were recorded at various formaldehyde pressures ranging from 0 to 250 mTorr.

The thick curve in figure 3-9 represents the result of fitting the PTGS data to a single exponential decay convoluted with the temporal response function for our detection apparatus. This least squares regression procedure yields a decay rate of $12.42 \pm 0.23 \mu\text{sec}^{-1} \text{Torr}^{-1}$ (one standard deviation uncertainty) for the indicated formaldehyde pressure of $\sim 0.050$ Torr. As previously demonstrated, the time-domain behavior of pure polarization spectroscopy is such that, in the absence of external perturbations (e.g. pure elastic reorientation), the observed decay rates, $I_{\gamma_{1}J_{1}K_{1}}^{\text{obs}}$, will correspond to exactly twice the true rate of population removal, $I_{\gamma_{1}J_{1}K_{1}}^{\text{depop}}$ (c.f. equations (3.52) and (3.55)). This supposition, which will be justified for the special case of formaldehyde self-relaxation in the ensuing discussion, suggests that the data in figure 3-9 can be associated with a collision-limited lifetime of $\tau = 1/I_{\gamma_{1}J_{1}K_{1}}^{\text{depop}} = 2/I_{\gamma_{1}J_{1}K_{1}}^{\text{obs}} = 161.1 \pm 3.0 \text{ns}$.

The pressure dependence for the collisional relaxation of the $4_{0,4}$ target level is illustrated by the Stern-Volmer plot in figure 3-10. The PTGS decay rates are found to be directly proportional to the density (viz. $\sim$ pressure) of the formaldehyde sample. A linear least squares analysis yields $k_{T} = \frac{1}{2} k_{\text{obs}} = 102.3 \pm 3.0 \mu\text{sec}^{-1} \text{Torr}^{-1}$ as the collision-induced depopulation rate for the $4_{0,4}$ rovibronic eigenstate (nb. the factor of $\frac{1}{2}$ associated with the observed rate, $k_{\text{obs}}$, follows from the temporal characteristics of pure polarization spectroscopy). This total removal rate, which corresponds to a velocity averaged
Figure 3-10: Stern-Volmer Plot for $4_{0,4}$ the Rovibronic Level.
H$_2$CO PTGS Data

$\tilde{A}^1A_2 \ v_4=1 \ 4_{0,4}$

$\begin{align*}
  k_T &= 102.3 \pm 3.0 \ \mu\text{sec}^{-1} \ \text{Torr}^{-1} \\
  \sigma_T &= 487 \pm 15 \ \text{Å}^2 \\
  \tau_0 &= 719 \pm 94 \ \text{ns}
\end{align*}$
cross section of \(487 \pm 15 \text{Å}^2\), indicates that collisional relaxation of the \(4_{0,4}\) target level proceeds with roughly seven times the efficiency suggested by gas kinetic encounters [157]. The collision-free lifetime, \(\tau_0\), derived from the data in figure 3-10 is

\[\tau_0 = \frac{2}{k_{\text{obs}}^0} = 719 \pm 94 \text{ns}\]

where \(k_{\text{obs}}^0\) denotes the observed decay rate extrapolated to zero sample pressure.

Table 3-VI presents a compilation of the depopulation rates, total removal cross sections, and zero pressure lifetimes determined for various rotational eigenstates in the \(v_4 = 1\) vibrational level of \(\tilde{A} 1A_2\) formaldehyde. All of the tabulated values have been scaled by the appropriate factor of two in order to account for the temporal characteristics of the pure polarization detection scheme utilized in the PTGS experiments.

Table 3-VII contrasts the zero-pressure lifetimes determined from the PTGS studies of electronically excited formaldehyde with those measured by other research groups via time-resolved detection of undispersed molecular fluorescence. The tabulated lifetimes were obtained through the selective excitation of single \(\tilde{A} 1A_2\) rovibronic levels in both low pressure static cells and molecular beams. Our zero pressure results compare quite favorably with those reported under the collision-free conditions of a hypersonic jet expansion [153]. This quantitative agreement confirms that, in the absence of external perturbations (e.g. collisions), the pure polarization signals decay with exactly twice the depopulation rate of the target level (cf. equation (3.52)).

The influence of pure polarization dephasing processes (e.g. elastic \(M\)-changing collisions) upon the PTGS signals was examined by performing experiments on the the \(13_{2,12}, v_4 = 1\) rovibronic eigenstate in \(\tilde{A} 1A_2\) formaldehyde. The collisional depopulation of this target level has been previously investigated (cf. Chapter 2) through the polarization insensitive method of Transient Gain Spectroscopy.
<table>
<thead>
<tr>
<th>Rotational Level</th>
<th>Collision-Free Decay Rate$^a$</th>
<th>Collisional Depopulation Rate$^b$</th>
<th>Collisional Depopulation Cross Section$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2_{0,2}$</td>
<td>$1.18 \pm 0.14$</td>
<td>$88.7 \pm 1.8$</td>
<td>$422 \pm 10$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(2.738 \pm 0.061)$</td>
<td></td>
</tr>
<tr>
<td>$^4_{0,4}$</td>
<td>$1.39 \pm 0.27$</td>
<td>$102.3 \pm 3.0$</td>
<td>$487 \pm 15$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(3.159 \pm 0.096)$</td>
<td></td>
</tr>
<tr>
<td>$^5_{0,5}$</td>
<td>$1.48 \pm 0.13$</td>
<td>$113.7 \pm 1.9$</td>
<td>$541 \pm 10$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(3.510 \pm 0.064)$</td>
<td></td>
</tr>
<tr>
<td>$^6_{0,6}$</td>
<td>$3.30 \pm 0.27$</td>
<td>$127.3 \pm 6.4$</td>
<td>$606 \pm 32$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(3.93 \pm 0.20)$</td>
<td></td>
</tr>
<tr>
<td>$^{13}_{2,12}$</td>
<td>$3.36 \pm 0.39$</td>
<td>$106.2 \pm 3.8$</td>
<td>$506 \pm 19$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(3.28 \pm 0.12)$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In $\mu$sec$^{-1}$.

$^b$ In $\mu$sec$^{-1}$Torr$^{-1}$ (Value in parentheses in cm$^3$molec$^{-1}$sec$^{-1}\times10^9$).

$^c$ In Å$^2$.

**Table 3-VI:** PTGS Determined Depopulation Rates and Zero-Pressure Lifetimes.
<table>
<thead>
<tr>
<th>Rotational Level</th>
<th>PTGS Lifetime(^a)</th>
<th>Beam Lifetime(^b)</th>
<th>Bulb Lifetime(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2_{0,2})</td>
<td>850±98</td>
<td>875</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>(4_{0,4})</td>
<td>719±94</td>
<td>700</td>
<td>563</td>
</tr>
<tr>
<td>(5_{0,5})</td>
<td>674±59</td>
<td>(\ldots)</td>
<td>409</td>
</tr>
<tr>
<td>(6_{0,6})</td>
<td>303±50</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>(13_{2,12})</td>
<td>297±34</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
</tr>
</tbody>
</table>

\(^a\) PTGS Lifetimes (in ns) from present work.

\(^b\) Hypersonic Jet Lifetimes (in ns) from reference [229].

\(^c\) Bulb Lifetimes (in ns) from reference [21]; Note that these lifetimes are contaminated by overlapping pump transitions.

**Table 3-VII:** Comparison of Zero-Pressure Lifetimes.
Therefore, a comparison of the removal cross sections obtained from these two techniques should indicate the extent to which collision-induced depolarization contributes to the observed PTGS decay rates (cf. Equation (3.55)). The kinetic parameters measured for the $13_{2,12}$ target level, scaled by the appropriate factor of two in order to account for the temporal characteristics of pure polarization detection, are contained in table 3-VI.

As might be expected on the basis of the comparisons presented in table 3-VII, the PTGS zero pressure lifetime for the $13_{2,12}$ level, $297\pm34\text{ns}$, is in quantitative agreement with the polarization-insensitive value of $279\pm10\text{ns}$ reported in Chapter 2. In addition, the observed collisional decay rate of $106.2\pm3.8\mu\text{sec}^{-1}\text{Torr}^{-1}$ compares quite favorably with the total population removal rate of $110.5\pm3.1\mu\text{sec}^{-1}\text{Torr}^{-1}$ determined through Transient Gain Spectroscopy. These results suggest that, for the special case of formaldehyde self-relaxation, collision-induced depolarization channels contribute insignificantly to the decay rates obtained from pure polarization measurements. In essence, the molecules display a much greater propensity to relax via inelastic energy transfer, characterized by a complete change in rotation-vibration quantum numbers, rather than to undergo an isoenergetic reorientation of their angular momentum (i.e. elastic $M$-change). This behavior provides the justification for our utilization of time-resolved polarization spectroscopy as a kinetic probe for depopulation processes in $\tilde{A}^1A_2$ formaldehyde.

The inability of the PTGS decay rate measurements to detect the presence of pure elastic reorientation processes can be rationalized in terms of the strongly dipolar nature of formaldehyde self-relaxation. Oka [160] has derived propensity rules for collision-induced changes in rotational and magnetic quantum numbers based upon the interaction between leading multipole moments of the individual collision partners. For the special case of formaldehyde-formaldehyde encounters.
the results presented in Chapter 2 have demonstrated that long range coupling of permanent dipole moments constitutes the predominant mechanism for collisional relaxation. Provided that the effects of dispersive and inductive forces, as well as the interactions associated with higher permanent moments, can be justifiably neglected, a simple first order dipole-dipole analysis yields the selection rule $\Delta M = 0, \pm 1$. In addition, a restriction of $+ \leftrightarrow -$ is indicated for the parity change accompanying a dipolar collision.

The time-resolved polarization signals detected in the PTGS experiments arise from the transitory depolarization of the cw PROBE beam as it propagates through the molecular sample. The optical anisotropy responsible for this polarization destruction has its origins in the nonuniform distribution of molecules created among the magnetic components of the target level through optical pumping (cf. figures 3-3 and 3-4). The relatively small $M$ changes (i.e. $\Delta M = 0, \pm 1$) attributed to dipole-dipole interactions suggests that an eigenstate possessing a large rotational angular momentum $J$ (i.e. $2J+1$ magnetic components) will require many elastic collisional events in order to produce a significant redistribution of population among its magnetic sublevels. This could explain the absence of any pure reorientational effects in the kinetic studies performed on the $13_2,12$ rovibronic level. From this viewpoint, however, it might also be argued that the PTGS measurements should exhibit enhanced decay rates at low $J$ values where the disruptive influence of $\Delta M = 0, \pm 1$ processes will be much more pronounced. While such $J$-dependent behavior has been demonstrated by Shoemaker, et. al. [230] in the case of CH$_3$F self-relaxation, the formaldehyde data presented in table 3-VI clearly show exactly the opposite trend (viz. a reduction in decay rate with decreasing $J$).

A viable explanation for the absence of pure reorientation channels in the self-relaxation of formaldehyde follows from the parity restrictions associated with
dipolar interactions (viz. \( + \leftrightarrow - \)). Each rovibronic eigenstate of formaldehyde (and all of the magnetic sublevels contained therein) has a definite parity as specified by the behavior of the molecular wavefunction under the spatial inversion of all coordinates through the center of mass [48]. Consequently, first order dipole-dipole propensity rules will prohibit elastic \( M \)-changing processes (viz. parity conserving processes where \( \Delta \gamma = 0, \Delta J = 0, \Delta K_a = 0, \Delta K_c = 0, \) and \( \Delta M \neq 0 \) from occurring in the formaldehyde-formaldehyde collision system. This constraint will be partially mitigated by the presence of higher order interactions [198] arising from permanent multipole moments as well as from dispersive and inductive forces. In addition, the strict validity of parity labels in the strongly perturbed environment which characterizes an intermolecular encounter (e.g. abrupt and substantial variations in electric field) is somewhat speculative.

The experiments performed by Shoemaker, et. al. [230] on the strongly dipolar methyl fluoride—methyl fluoride collision system have indicated that cross sections for pure depolarization processes (i.e. elastic \( M \)-changing collisions) can approach \( 100 \AA^2 \) with a pronounced dependence upon the rotational angular momentum (viz. \( M \) degeneracy) of the target level. The extraordinary efficiency of \( M \)-changing collisions in the depopulation of methyl fluoride can be quite succinctly explained in terms of the parity constraints imposed by dipole-dipole selection rules. Since \( \text{CH}_3\text{F} \) is a symmetric top, all rovibronic levels having \( K \neq 0 \) are doubly degenerate with double parity (i.e. both \(+\) and \(-\)). Therefore, what appears to be a substantial propensity to undergo elastic reorientation (i.e. \( \Delta J = 0, \Delta K = 0, \) and \( \Delta M \neq 0 \)) may actually be a manifestation of efficient collisional population transfer between the members of the \( K \)-doublet (i.e. \( \Delta J = 0, \Delta K \neq 0, \) and \( \Delta M \neq 0 \)).

In a series of elegant Lamb dip measurements, based upon the high-resolution technique of Laser Stark Spectroscopy, Johns, et. al. [231] have examined the
collision-induced reorientation of formaldehyde molecules in their ground electronic potential surface. This work has indicated a substantial propensity for self-relaxation to proceed via elastic $M$-changing processes (e.g. $\Delta M = \pm 1$ processes account for $\sim 14\%$ of the total removal rate attributed to individual magnetic components in the $J = 1$, $K_a = 1$ rotational levels). On the basis of their spectroscopic investigations, Johns and coworkers also suggested that rather large reorientations of angular momentum, characterized by $|\Delta M| > 1$, could occur during a single collisional event. However, these experiments depend upon the application of an external electric field to the molecular sample in order to Stark tune individual magnetic sublevels into resonance with the infrared probe laser. As discussed in Chapter 1, the manifestation of the Stark effect in formaldehyde necessitates that rovibronic levels of opposite parity (e.g. the members of an asymmetry doublet) be mixed by the electric field. In view of the important role that parity considerations play in dipole-dipole interactions, the mixed-parity conditions under which these Laser Stark studies were performed makes their precise interpretation in terms of unperturbed (i.e. zero field) selection rules problematic.

3.5.4 Energy Transfer Studies

The PTGS technique can also be exploited for the study of state-to-state energy transfer cross sections in electronically excited molecules. The use of a tunable cw dye laser as the source of PROBE radiation in this detection scheme enables a systematic investigation of the propensity rules which govern population relaxation channels. In addition, the unique capabilities of time-resolved polarization spectroscopy (viz. its sensitivity to the distribution of molecules among magnetic sublevels) permits examination of the spatial reorientation of angular momentum which occurs during collision-induced changes in rovibronic quantum numbers.
Detailed studies of alignment and orientation transfer [232, 233, 234] between rotation-vibration eigenstates can therefore be realized. These $M$-changing processes, which are a consequence of torques exerted upon the rotating molecule through the anisotropic portion of the intermolecular potential, provide an indication of steric constraints which accompany collisional interaction. As such, inelastic reorientation events can be of considerable importance in determining the specificity of elementary chemical reactions [224].

Figure 3-11 presents typical time-resolved profiles derived from our state-to-state measurements of rotational energy transfer processes in the $v_4 = 1$ level of $\tilde{A}^1A_2$ formaldehyde. Each trace was obtained by directly monitoring the transitory depolarization of the cw PROBE beam subsequent to optical pumping of a rovibronic eigenstate which is collisionally coupled to the upper level of the PROBE transition. The actual data, denoted by the fine black lines, were acquired through a high-speed transient digitizer which had been programmed to signal average over 1024 pulses of the PUMP laser.

The upper portion of figure 3-11 depicts the time-resolved polarization signal obtained by monitoring the $2^0_{14} 5_{0,5} \rightarrow 5_{1,4}$ transition subsequent to the abrupt creation of a net alignment of molecules (cf. figure 3-3) within the degenerate magnetic sublevels of the $6_{0,6}$ rovibronic eigenstate (cf. table 3-V for a detailed description of the transitions). Dipole-dipole propensity rules (cf. Chapter 2 and reference [180]) suggest that collision-induced energy transfer between the $6_{0,6}$ and $5_{0,5}$ rotational levels of $\tilde{A}^1A_2$ formaldehyde should constitute an efficient pathway for self-relaxation. Therefore, the depolarization of the PROBE beam is found to increase as collisions transfer molecules from the $6_{0,6}$ eigenstate into the $5_{0,5}$ level and subsequently to decay as the $5_{0,5}$ level depopulates. The mere observation of such state-to-state PTGS signals indicates that the nonuniform population
Figure 3-11: State-to-State PTGS Signals in $\tilde{A}^1A_2$ Formaldehyde.
PUMP: $6_{0.6} \leftrightarrow 6_{1.5}$  \[ \begin{array}{c} 4_0^1 \\ 2_{44}^0 \\ 4_4^1 \end{array} \\
PROBE: $5_{0.5} \rightarrow 5_{1.4}$  \[ \begin{array}{c} 2_{44}^0 \\ 4_4^1 \end{array} \\
P = 0.303 \text{ Torr}

PUMP: $5_{0.5} \leftrightarrow 5_{1.4}$  \[ \begin{array}{c} 4_0^1 \\ 2_{44}^0 \\ 4_4^1 \end{array} \\
PROBE: $6_{0.6} \rightarrow 6_{1.5}$  \[ \begin{array}{c} 2_{44}^0 \\ 4_4^1 \end{array} \\
P = 0.296 \text{ Torr}

Decay Time (ns)
distribution initially prepared among the magnetic sublevels of the $6_{0,6}$ rovibronic eigenstate must be at least partially preserved as molecules are transferred to the upper level of the PROBE transition (viz. $5_{0,5}$). The data illustrated in the lower portion of figure 3-11 represent the reverse process in which the $6_{0,6}$ eigenstate is monitored while the $5_{0,5}$ level undergoes optical pumping. The two traces were acquired under similar experimental conditions with a formaldehyde sample pressure of $\sim 300$ mTorr.

The thick curves in figure 3-11 represent the result of fitting the state-to-state PTGS measurements to a sum of two exponentials (i.e. to account for the rise and fall of the signal) convoluted with the temporal response function for our apparatus. This deconvolution procedure, which was essential for the relatively fast time scales that characterize the kinetic data, produced the following rate parameters:

<table>
<thead>
<tr>
<th>Energy Transfer Process</th>
<th>Formaldehyde Pressure</th>
<th>Rate of Signal Rise</th>
<th>Rate of Signal Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6_{0,6} \rightarrow 5_{0,5}$</td>
<td>$302.7 \pm 3.3$</td>
<td>$56.9 \pm 1.8$</td>
<td>$16.85 \pm 0.37$</td>
</tr>
<tr>
<td>$6_{0,6} \leftarrow 5_{0,5}$</td>
<td>$296.1 \pm 4.6$</td>
<td>$50.7 \pm 2.3$</td>
<td>$19.04 \pm 0.64$</td>
</tr>
</tbody>
</table>

where the pressures are reported in millitorr and the rates in $\mu$sec$^{-1}$. The deconvolution procedures utilized for determination of the tabulated rate parameters have explicitly taken into account the squared temporal response (cf. equation (3.52)) of pure polarization spectroscopy.

While a systematic investigation of rotational energy transfer in $\tilde{A}^1A_2$ formaldehyde was not attempted at the present time, the data depicted in figure 3-11 can provide some insight into these kinetic processes. Before proceeding, however, a brief examination of the PTGS techniques with regard to the
measurement of state-to-state cross sections is warranted. The theoretical discussion of polarization spectroscopy presented above has indicated that the temporal characteristics of this detection scheme are governed by the evolution of molecular population within individual magnetic sublevels. The system of coupled differential equations which describes this time-domain behavior is contained in expression (3.54).

A careful inspection of the differential equations presented in expression (3.54) reveals several important points regarding the study of state-to-state kinetics via polarization sensitive detection schemes. First of all, the magnitude of the energy transfer signals observed in polarization spectroscopy will be determined by the efficiency of the reorientation processes which accompany collision-induced changes in rovibronic quantum numbers. This provides the basis for the series of steady-state experiments performed by McCaffery and coworkers [235, 236, 84, 237, 238] as a means of examining the collisional transfer of orientation (cf. figure 3-4) between rotational eigenstates. Suitable modeling of the signal amplitudes obtained in these studies can provide some insight into the propensity rules which govern the evolution of magnetic sublevel populations during inelastic encounters.

Provided that pure elastic reorientation processes can be justifiably neglected, the differential equations contained in expression (3.54) suggest that the temporal profile observed in polarized state-to-state measurements will reflect the bulk transfer of population (i.e. regardless of magnetic sublevel distributions) between the collisionally coupled eigenstates. Our depopulation studies have conclusively demonstrated that elastic $M$-changing collisions play a negligible role in the strongly dipolar self-relaxation of formaldehyde. Therefore, the kinetic parameters derived from the time-resolved PTGS data in figure 3-11 can be utilized in order to examine rotational energy transfer in the $v_4 = 1$ level of the $\tilde{A}$ state.
A detailed analysis of the PTGS state-to-state measurements was not attempted. However, some insight into the rotational energy transfer cross sections which govern the self-relaxation of $\tilde{A}^1\text{A}_2$ formaldehyde can be derived from a simple two level kinetic model which incorporates a manifold of background states in order to provide a channel for irreversible collision-induced depopulation. The set of coupled differential equations which describes this system can be solved analytically [157], subject to the boundary condition that only one of the levels (viz. level 1) is initially populated. This yields the following expressions for the rate of rise, $I_2^{\text{rise}}$, and fall, $I_2^{\text{fall}}$, observed in the state populated through collisions (viz. level 2):

\[ 2I_2^{\text{rise}} = I_1^{\text{depop}} + I_2^{\text{depop}} + \left( (I_2^{\text{depop}} - I_1^{\text{depop}})^2 + 4\Gamma_{12}\Gamma_{21} \right)^{1/2} \]  \hspace{1cm} (3.56)

\[ 2I_2^{\text{fall}} = I_1^{\text{depop}} + I_2^{\text{depop}} - \left( (I_2^{\text{depop}} - I_1^{\text{depop}})^2 + 4\Gamma_{12}\Gamma_{21} \right)^{1/2} \]  \hspace{1cm} (3.57)

where

$I_1^{\text{depop}}$ and $I_2^{\text{depop}}$ denote the depopulation rates for the individual members of the two level kinetic model (viz. levels 1 and 2),

$\Gamma_{12}$ denotes the energy transfer rate from level 1 to level 2,

$\Gamma_{21}$ denotes the energy transfer rate from level 2 to level 1.

Note that the phenomenological rate parameters which appear in equations (3.56) and (3.57) are implicit functions of the formaldehyde sample pressure.

Equations (3.56) and (3.57) can now be solved simultaneously in order to obtain the rate of collision-induced population transfer between the two levels:
\[
\Gamma_{12} \Gamma_{21} = \frac{(\Gamma_{12}^{\text{rise}} - \Gamma_{21}^{\text{fall}})^2 - (\Gamma_{12}^{\text{depop}} - \Gamma_{21}^{\text{depop}})^2}{4}
\]  
(3.58)

The kinetic parameters derived from analysis of the PTGS depopulation and state-to-state experiments can now be substituted into equation (3.58) in order to determine energy transfer cross sections. By utilizing the principle of microscopic reversibility to relate \(\Gamma_{12}\) and \(\Gamma_{21}\), the rate of collision induced population transfer between the \(6_{0,6}\) and \(5_{0,5}\) rotational eigenstates in the \(v_4 = 1\) level of \(\tilde{A}^1A_2\) formaldehyde is found to be \(\sim 50 \mu\text{sec}^{-1}\text{Torr}^{-1}\) with an uncertainty of \(\pm 30\%\).

The \(\Delta J = \pm 1\) rate constant derived on the basis of equation (3.58) is \(\sim 25\%\) larger than that obtained by more sophisticated kinetic modeling performed upon the \(13_{2,12}\) eigenstate (cf. Chapter 2). This discrepancy can be rationalized, at least in part, by the absence of \(\Delta J = 0\) depopulation pathways in \(J_{0,J}\) levels (i.e. the \(13_{2,12}\) level can relax to the \(13_{2,11}\) level but similar \(\Delta J = 0\) processes are not possible for \(5_{0,5}\) and \(6_{0,6}\)). Nevertheless, the state-to-state results still suggest that an appreciable portion of the total removal rate measured for individual rovibronic eigenstates in \(\tilde{A}^1A_2\) formaldehyde can be attributed to pure rotational relaxation via the \(\Delta J = \pm 1\) channels predicted by first order dipole-dipole propensity rules [160].

3.5.5 Concluding Remarks

The work presented above has demonstrated the utility of Polarization-detected Transient Gain spectroscopy as a probe of collision-induced and collision-free relaxation phenomena in \(\tilde{A}^1A_2\) formaldehyde. Theoretical considerations have suggested that, in the absence of perturbations (e.g. collisions), time-resolved pure polarization signals should decay with exactly twice the rate of population removal
from the target level. This supposition was confirmed through comparison of the zero-pressure lifetimes determined for various rovibronic eigenstates with those previously measured under the collision-free conditions of a molecular beam expansion.

Our kinetic studies suggest that, for the special case of formaldehyde self-relaxation, elastic reorientation of rotational angular momentum (i.e. pure $M$—changing collisions) occurs with much less efficiency than other collision-induced processes (e.g. rotational energy transfer). This behavior, which can be rationalized through the first order propensity rules for dipole-dipole interactions, provides the justification for the interpretation of our polarization spectroscopy measurements in terms of pure population removal cross sections. In addition, state-to-state experiments have demonstrated that collisional energy transfer between adjacent $\tilde{A}^1A_2$ rovibronic levels is accompanied by a pronounced tendency to preserve the distribution of molecules within the corresponding magnetic sublevels.

In conclusion, the present studies have provided the foundation for future experiments which will exploit the versatility and unique capabilities afforded by Transient Gain Spectroscopy (with tunable PROBE radiation) in order to systematically examine relaxation pathways in electronically excited molecules. Since the PTGS technique is sensitive to collision-induced changes in the population distribution among magnetic sublevels, it should permit detailed investigations of reorientation processes (e.g. as a function of collision partner, etc.) to be realized. Finally, when coupled with a narrow-band PUMP laser, variants of PTGS might enable high resolution spectroscopic measurements to be performed upon polyatomic systems in regions of extreme vibrational excitation.
Chapter 4

Depopulation Studies in $X^1A_1$ Formaldehyde-$h_2$

4.1 Introduction

The past decade has witnessed the development of considerable interest within the chemical physics community regarding the structural and dynamical properties exhibited by highly excited polyatomic molecules in their ground electronic potential surfaces. The term "highly excited" can be roughly interpreted as referring to those regimes in which the amount of rotation-vibration energy deposited into a molecular framework approaches chemically significant proportions. Recent advances in both theoretical and experimental techniques have motivated a substantial effort towards the characterization of such energetic species.

The numerous reasons for studying highly excited polyatomic molecules reflect the diversity of phenomena which have been attributed to them. Aside from the manifest importance that these transitory chemical species have in various aeronomic and combustion related problems, the high energy regime in which they exist provides an opportunity to reassess conventional scientific thought while simultaneously indicating appropriate directions for future research. From the viewpoint of traditional molecular physics, these regions of extreme excitation are expected to be characterized by the eventual breakdown of well-known precepts regarding molecular structure and dynamics. Many principles firmly established in the repertoire of present-day chemistry and physics, including the ubiquitous notion of normal modes of vibration, rest upon the assumption of small deviations from a reference or equilibrium configuration. The validity of such approaches to the
description of highly excited molecular systems, in which exceedingly large
amplitude motions can occur, is a matter of considerable speculation and concern.
Furthermore, the substantial increase in the density of rotation-vibration levels
encountered in regions of extreme excitation, together with the small, but numerous,
coupling terms which exist between the zero-order rovibronic states, can lead to a
serious failure of the various adiabatic approximations utilized in the separation of
electronic, vibrational, and rotational degrees of freedom from one another. Under
these circumstances, the conventional description of a molecular system in terms of
a set of spectroscopically distinct energy levels, each of which can be uniquely
labeled in terms of well-defined structural and dynamical properties, would be
abrogated by the presence of pervasive intramolecular interactions.

The destruction of rovibronic separability in highly excited polyatomic
molecules will also have significant repercussions for collision-induced phenomena in
these systems. Current theories depend upon the distinction between rotational,
vibrational, and electronic degrees of freedom as a means of assessing the overall
efficiencies and state-to-state propensities which characterize collisional relaxation
processes [157]. This suggests that a careful reconsideration of the subtle
relationship between intermolecular (i.e. collisional) and intramolecular (i.e.
rovibronic mixing) dynamics will be required for the appropriate description of
collision events between highly excited molecules. Insofar as a collision can be
interpreted as representing the simplest of all chemical reactions, the extent of
intramolecular rovibronic interactions encountered in regions of extreme excitation
may also profoundly influence the degree to which energetic chemical reagents can
be manipulated and controlled.

The consequences which accompany the destruction of rovibronic separability
(viz. in highly excited molecules) are reminiscent of the behavior postulated by the
RRKM theory [239] for unimolecular reactions. This statistical hypothesis, which has been extensively utilized in the interpretation of infrared multiphoton excitation studies, stipulates that the coupling of internal modes (e.g. vibrational mixing) in a molecule leads to rapid intramolecular energy randomization on a time scale short relative to the mean lifetime of the decomposing species. The mechanisms responsible for this rapid energy randomization are often collectively designated as Intramolecular Vibrational Redistribution (or IVR) processes [240]. IVR constitutes a prevalent and critically important collision-free relaxation pathway for highly excited polyatomic systems in which a large density of vibrational levels prohibits the preparation of individual molecular eigenstates.

The onset of IVR phenomena, which are in many ways suggestive of radiationless transitions in excited electronic states (i.e. the mathematical formulation is identical, only the names of the levels and nature of the couplings have been changed) [241], can have a dramatic effect upon the rates of all other dynamical pathways (e.g. isomerization, predissociation, and even chemical reaction) within a molecule. Brought to an extreme, such energy randomization processes could provide the impetus for conversion of well-organized molecular motion into the so-called ergodic regime [239]. In this case, the molecule has essentially lost all memory of its initial boundary conditions (e.g. the vibrational modes of the nuclear framework) and is capable of exploring all of the phase space hypersurface consistent with the constraints of conserved total energy and total angular momentum. Although many numerical calculations performed upon model systems [242] have provided evidence for a transition in classical dynamics from largely quasiperiodic (i.e. stable or regular) behavior at lower energies to predominantly chaotic (i.e. stochastic, ergodic, or irregular) behavior at high energies, the nature of the corresponding transition in quantum mechanics is
presently a matter of considerable controversy [243, 244, 245]. The fact that classical motion must represent a limiting case of quantum mechanical behavior (viz. the Correspondence Principle [51]) has directed substantial effort towards observation of the transformation between regular and irregular dynamics in molecular systems. The concepts of ergodicity and IVR also play a significant role in the collisional relaxation (or chemical reaction) of highly excited polyatomic systems, not only in the characterization of the initial states for the energetic collision partners (or reactants), but also in orchestrating the intramolecular "energy transfer" processes which would be required to accommodate any short-lived collision complex (or transition state) that might be formed [239].

Despite the strong and pervasive intramolecular coupling that has been predicted to occur between zero-order vibrational states at high level densities, recent experiments have conclusively demonstrated that some forms of well-organized molecular dynamics can still exist for highly excited polyatomic systems. In particular, studies based upon the sensitive technique of overtone spectroscopy [246] have indicated that concerted motions resembling well-defined molecular displacements (e.g. C-H local modes) are present even when the amount of rotation-vibration energy deposited into a molecule becomes comparable to that required for dissociation of the ground electronic state. This behavior, which is in complete contradiction to that predicted by a naive interpretation of the statistical RRKM theory, suggests the presence of constraints (e.g. "hidden" constants of the motion) which somehow limit the region of energy-accessible phase space that the highly excited molecules are able to explore. Consequently, chemically and structurally significant differences can persist between adjacent levels (or groups of levels) in such regimes of extreme excitation.

Provided that the energy deposited into a molecule is able to remain localized
in a well-defined concerted motion for a sufficient length of time, the possibility exists for mode specific chemistry to be observed subsequent to non-thermal molecular excitation. This suggests that selective preparation of highly excited molecules, perhaps through some complex orchestration of extremely specific laser fields, could result in a chemically significant reaction which would not otherwise have occurred for the same amount of energy randomly distributed over all molecular degrees of freedom. The feasibility of any mode specific chemistry is critically dependent upon the relative rate of relaxation mechanisms (e.g. IVR) which would tend to degrade the initially well-localized molecular excitation. A systematic investigation of inelastic collisional processes (viz. the simplest of all chemical reactions) in regions of extreme excitation could therefore provide considerable insight into the nature and limitations of such mode specific behavior.

The quest for mode specific chemical processes, as well as the desire to characterize the transition between quasiperiodic and ergodic molecular behavior, has led to the development of powerful new spectroscopic probes designed to examine the structural and dynamical properties of highly excited molecules. Due to the important role that the incipient localization of energy plays in these studies, considerable effort has been directed towards the preparation of well-defined initial states, perhaps even individual molecular eigenstates, the properties of which could be monitored as a function of the degree of excitation. In particular, the double resonance method of Stimulated Emission Pumping, first developed in our laboratories [171, 172], provides a means of preparing and characterizing single rotation-vibration target levels in the ground electronic state of moderately-sized polyatomic systems with unprecedented control over both the magnitude and type of initial excitation. Recent application of this high-resolution technique has provided conclusive evidence for the onset of rotation-induced vibrational mixing
effects in highly excited formaldehyde [143] as well as what might be the first documented example of chaotic intramolecular dynamics in the case of acetylene excited ~ 28000cm\(^{-1}\) above its zero-point energy [247].

The work presented in this Chapter constitutes an attempt to elucidate the collision-induced relaxation pathways available to highly excited formaldehyde molecules in their ground electronic potential surface (i.e. the \(\tilde{X}^1A_1\) state). By utilizing a triple resonance scheme based upon the unique preparative capabilities of Stimulated Emission Pumping, these preliminary experiments have been able to monitor the temporal evolution of individual rotation-vibration eigenstates in regions of excitation where the separation between adjacent vibrational levels is comparable to the energy spacings of the corresponding rotational fine structure. Application of this powerful technique to the well-studied [180] formaldehyde system provides the extraordinary opportunity to examine, in an extremely specific manner, kinetic processes for a wide variety of spectroscopically well-characterized energy levels with a tremendous range in both the magnitude and type of excitation deposited into the molecular framework.

Both theoretical and experimental studies have conclusively demonstrated that, in low energy regimes, rotational energy transfer constitutes the most predominant inelastic collisional process, occurring with normally ~ 100 times the frequency of vibrationally inelastic events and with several orders of magnitude more probability than any available (collision-induced) electronic relaxation channels. For the vibrationless level of \(\tilde{X}^1A_1\) formaldehyde, microwave-microwave double resonance techniques [248] have permitted the examination of state-to-state cross sections for collision-induced changes in rotational quantum numbers. The propensities observed in these experiments can be well accounted for by long range interactions between the permanent electric multipole moments of the colliding
molecules [160]. Increasingly more sophisticated techniques, including the utilization of molecular beam technology [249, 202] in order to precisely define the incipient conditions for the collision event, have enabled a detailed examination of rotationally inelastic processes to be performed as a function of scattering angle and translational energy in addition to the more customary parameters of initial and final rotational state selection. The wealth of information provided by such investigations, together with the important position which formaldehyde kinetics assume in the modeling of interstellar media [250, 251, 252, 253], has prompted the application of powerful ab initio computational techniques [254, 255] in an attempt to characterize the anisotropic intermolecular potential surface for this dipolar molecular system.

In contrast to the vast and well documented body of information which exists regarding pure rotation changing collisions in the vibrationless state of formaldehyde, very little is known about the corresponding processes in vibrationally excited manifolds. In a series of elegant time-resolved infrared-ultraviolet double resonance experiments, Orr and coworkers [256, 199, 200, 201] were recently able to examine rotationally inelastic processes within the $v_4 = 1$ vibrational level of $\tilde{X}^1A_1$ formaldehyde-$d_2$. These kinetic studies demonstrated the dominance of pure rotational relaxation over other energy transfer pathways and suggested that the only rigorous propensity rule derives from the difficulty associated with collisional interconversion of the two nuclear spin modifications in $D_2CO$.

Perhaps of greater significance for the work described in this Chapter are recent measurements performed by Haub and Orr [191] upon the rate of mode-to-mode relaxation between two coupled vibrational levels (viz. $\nu_4$ and $\nu_6$) in the ground electronic state of formaldehyde-$d_2$. These kinetic studies indicate that
vibrational mode mixing induced by a rotation-dependent Coriolis perturbation [56] can significantly augment the cross section for collision-induced vibrational energy transfer. From the viewpoint of the discussion presented above, this enhancement can be rationalized in terms of the local breakdown of the distinction between rotational and vibrational degrees of freedom which accompanies a Coriolis interaction. This results not only in a loss of validity for the vibrational state labels but also in a partial destruction of the rotational quantum numbers (viz. $K_a$ and $K_c$) which define the projections of the total angular momentum upon the body-fixed axis system. The collisional energy exchange between the rovibrational states, which are now of mixed vibrational parentage (i.e. as a result of the Coriolis interaction), can therefore proceed through what amounts to an efficient pure rotational relaxation channel.

The present time-resolved studies, which examined total depopulation rates for highly excited rotation-vibration levels in $\tilde{X}^1A_1$ formaldehyde-$h_\nu$, were designed to ascertain the functional dependence of relaxation cross sections upon the density of background states (i.e. the vibrational density of states) and the initial localization of excitation within the molecular framework (i.e. the type and purity of vibrational mode initially prepared). In particular, these measurements attempted to determine whether or not significant differences in kinetic behavior could exist between adjacent rovibrational eigenstates in regions of extreme excitation. Since rotational motion has been shown to be effective in promoting the onset of vibrational mode mixing [143] and related IVR processes [257, 258], the influence of rotational degrees of freedom upon collision-induced molecular dynamics was also of considerable interest.

Although Knight and coworkers [206, 207] have performed an impressive series of collisional studies on highly excited $p$-difluorobenzene in its ground
electronic state, the initial excitation in their experiments was randomly distributed over a group of $\sim 300$ rotational levels. This ill-defined excitation obviously precludes any possibility of examining the critically important rotational dependence of intermolecular and intramolecular dynamical processes in such energetic species. The present work, by virtue of the exceptional specificity achieved in both the preparation and detection stages, represents the first direct examination of collision-induced relaxation mechanisms in completely characterized states of extreme excitation.

4.2 Techniques

4.2.1 Introduction

Figure 4-1 presents a typical energy level diagram for our depopulation studies of highly excited rotation-vibration levels within the ground electronic state of formaldehyde-$h_\chi$. The depicted triple resonance scheme, which is designated Transient Absorption Polarization Spectroscopy or TAPS, combines the inherent capabilities of several previously mentioned experimental techniques to create a kinetic probe for molecular systems in regions of extreme vibrational excitation. First, the exceptional state-specificity afforded by the method of Stimulated Emission Pumping [171, 172] is exploited in order to prepare a substantial number of molecules in a preselected eigenstate of the ground electronic potential surface. The polarized nature of the PUMP and DUMP radiation utilized in this preparation step ensures that a nonuniform population distribution (i.e. a spatial anisotropy) will be created among the degenerate magnetic subcomponents of the target level. The temporal evolution of the highly excited molecules is subsequently monitored through the depolarization of a cw PROBE beam, in much the same manner as that employed in conventional polarization spectroscopy.
Figure 4-1: Level Diagram for Transient Absorption Polarization Spectroscopy.
PUMP and DUMP: vertical polarization
PROBE: $\pi/4$ polarization
Figure 4-1 depicts an experimental scheme designed to examine collision-induced depopulation of the $5_{1,4}$ rotational eigenstate in the $2_{4,4}^4$ vibrational level of $\tilde{X}^1A_1$ formaldehyde-$h_\nu$. In order to perform these time-resolved measurements, the cw PROBE laser, which is linearly polarized at an angle of $45^\circ$ with respect to the vertical, is tuned into resonance with the $2_{4,4}^05_{0,5} \leftrightarrow 5_{1,4}$ rovibronic transition at \( \sim 16967 \text{cm}^{-1} \). The lower level of this PROBE transition, the target of our experiments, is a single rotation-vibration eigenstate located \( \sim 11380 \text{cm}^{-1} \) above the zero point energy of the ground electronic potential surface. The linearly polarized PUMP and DUMP beams, which are produced by separate pulsed dye lasers, are coincident with the $4_{30}^35_{0,5} \leftrightarrow 5_{1,4}$ and $9_{4,4}^05_{0,5} \rightarrow 5_{1,4}$ rovibronic transitions, respectively. The use of different vibrational levels within the excited electronic state for the preparation (viz. $4^1$) and detection (viz. $4^3$) steps ensures that collisional energy transfer processes in $\tilde{A}^1A_2$ formaldehyde will not influence the outcome of the kinetic measurements.

Before arrival of the PUMP and DUMP pulses, neither the upper nor the lower level of the PROBE transition is populated. The PROBE beam thus passes through the spatially isotropic formaldehyde sample without any interaction. The PUMP/DUMP pulse sequence abruptly populates the $2_{4,4}^45_{1,4}$ rotation-vibration level of the $\tilde{X}$ state. The cw PROBE, now propagating through a transitory loss medium, is attenuated by absorption in proportion to the population of the highly excited rotation-vibration eigenstate.

The polarized nature of the PUMP and DUMP beams also results in the creation of a nonuniform population distribution among the degenerate magnetic components in the lower level of the PROBE transition. This net alignment of molecules within the highly excited $5_{1,4}$ target level constitutes an optical anisotropy. The polarization properties of the PROBE radiation will therefore be
altered by the birefringence and dichroism (cf. Chapter 3) which accompany the transitory absorption process. Provided that energetically elastic reorientation collisions (i.e. M-changing collisions) can be neglected, the time-resolved magnitude of this depolarization effect will be directly proportional to the decaying population of the $5_{1,4}$ level.

Thus, by directly monitoring the transitory depolarization of the PROBE radiation, induced by optical pumping of the molecular sample with the PUMP and DUMP beams, the temporal evolution of a specific rotation-vibration level in the ground state of formaldehyde can be observed. The use of a cw PROBE, in conjunction with a high-speed transient digitizer, permits acquisition of the entire time-resolved decay profile for each PUMP/DUMP pulse sequence. Compared with more conventional techniques (e.g. a boxcar averager with a scanning gate), this ability to instantaneously record the complete temporal response of the molecular system provides a significant enhancement in both the quality and collection rate of the experimental data.

By combining the extraordinary specificity of Stimulated Emission Pumping in the preparation step with the high sensitivity afforded by polarized detection, TAPS has permitted investigation of collision-induced relaxation processes in highly excited $\tilde{X}^1A_1$ formaldehyde-$h_2$ at the level of individual molecular eigenstates. The use of tunable laser sources to drive each rovibronic transition in the triple resonance scheme enables virtually any rotation-vibration level within the ground electronic potential surface to be examined.

The preliminary work presented in this Chapter can be grouped into two categories depending upon the amount of energy placed into the molecular system in order to reach the target rotation-vibration level:
1. \( \sim 11300 \text{cm}^{-1} \) above the \( \tilde{X}^1A_1 \) zero point energy.

\[
\text{PUMP}: 4^3_0 \quad \text{DUMP}: 2^0_4 4^3_4 \quad \text{PROBE}: 2^0_4 4^1_4
\]

2. \( \sim 11900 \text{cm}^{-1} \) above the \( \tilde{X}^1A_1 \) zero point energy.

\[
\text{PUMP}: 4^1_0 \quad \text{DUMP}: 2^0_3 4^1_6 \quad \text{PROBE}: 2^0_3 4^3_6
\]

Due to the substantial density of vibrational states (i.e. \( \rho_{\text{vib}} \approx 0.5/\text{cm}^{-1} \)) and the pronounced mixing of vibrational character [143] encountered in such high energy regimes, only tentative vibrational assignments can be made for \( \tilde{X}^1A_1 \) levels involved in the DUMP and PROBE rovibronic transitions. The discussion accompanying the results of our Stimulated Emission Pumping experiments will provide further clarification of this point.

### 4.2.2 Signal Calculation

The TAPS technique exploits a form of time-resolved polarization spectroscopy in order to monitor the temporal evolution of a selectively prepared group of molecules. The signals derived from this kinetic probe can be expected to exhibit qualitative similarities (i.e. in both magnitude and dependence upon rovibronic state labels) with those obtained from the polarized transient gain studies discussed in the previous Chapter. In particular, the theoretical analysis presented in Chapter 3 suggests that the pure polarization signals, \( I^\text{pol}_{s}(\omega) \), detected during a TAPS measurement will be given by:

\[
I^\text{pol}_{s}(\omega) \approx I_0 \left( \xi + (\Delta \alpha(\omega)t)^2 \right) \quad (4.1)
\]
where $I_0$ represents the incident intensity of the PROBE beam, $\xi$ denotes the extinction coefficient of the polarization analyzer, and $\Delta \alpha(\omega)$ represents the differential absorption coefficient, per unit sample length (i.e. $l$), induced in the PROBE transition by optical pumping. This expression, which is valid for either linearly polarized or circularly polarized PUMP and DUMP radiation (i.e. provided that the appropriate definition for $\Delta \alpha(\omega)$ is utilized), assumes that the differential birefringence of the sample cell windows and the detuning angle of the polarization analyzer have been reduced to insignificant proportions (cf. equations (3.20) and (3.21)).

The signals obtained in the TAPS experiments can therefore be completely characterized in terms of the induced differential absorption within the PROBE transition. The expected magnitude of $\Delta \alpha(\omega)$ and its dependence upon rotational degrees of freedom can be readily determined by extending the rate equation formalism of the previous Chapter to the four level system illustrated in figure 4-2. This figure depicts a hypothetical TAPS experiment designed to probe a highly excited rotation-vibration target level (i.e. $|2\rangle$) in the ground electronic potential surface through the creation and subsequent observation of an optical anisotropy among its degenerate magnetic components. Each state in this molecular energy level diagram (nb. the states are actually $2J+1$-fold degenerate) is designated by a set of symmetric rotor quantum numbers denoting the total angular momentum, $J$, and its projection upon the body-fixed and space-fixed z axes ($K$ and $M$ respectively). Since it is assumed that rotational and vibrational-electronic degrees of freedom are separable, all additional quantum numbers required to fully specify an individual eigenstate can be grouped together in a single symbol (viz. $\gamma$).

The rovibronic transitions illustrated in figure 4-2 can be interpreted in terms of the two steps required for the successful completion of a TAPS measurement:
Figure 4-3: Energy Level Diagram for TAPS Calculations.
where:

\[ |0\rangle = \{ |\gamma J K M \rangle; M = -J, ... J \} \]

\[ |1\rangle = \{ |\gamma_1 J_1 K_1 M_1 \rangle; M_1 = -J_1, ... J_1 \} \]

\[ |2\rangle = \{ |\gamma_2 J_2 K_2 M_2 \rangle; M_2 = -J_2, ... J_2 \} \]

\[ |3\rangle = \{ |\gamma_3 J_3 K_3 M_3 \rangle; M_3 = -J_3, ... J_3 \} \]

Two short resonant laser pulses (*viz.* the PUMP and the DUMP) are used to optically pump the $|1\rangle \rightarrow |0\rangle$ and $|1\rangle \rightarrow |2\rangle$ rovibronic transitions, thereby producing a nonuniform population distribution among the degenerate magnetic components of the target level $|2\rangle$. This optical anisotropy can be created with either linearly or circularly polarized radiation. For reasons of pedagogical and experimental simplicity, the ensuing analysis will assume that the PUMP and DUMP beams have the same polarization characteristics. The extension to the more general case of mixed polarizations is quite straightforward.


The optical anisotropy created in the target level is monitored through its depolarizing effects upon a weak PROBE laser beam resonant with the $|3\rangle \rightarrow |2\rangle$ rovibronic transition. The incident PROBE radiation, which can be either cw or pulsed, is always linearly polarized. For the case of linearly polarized PUMP and DUMP beams, a $45^\circ$ orientation of the PROBE polarization direction (i.e. with respect to the common polarization of the PUMP and DUMP) can be shown to yield the largest signal magnitude (*cf.* Chapter 3).

The principal goal of the present section is to indicate the expected TAPS signal magnitudes and their dependence upon rovibronic quantum numbers. The discussion which follows will therefore not explicitly consider the effects of collisional processes. As a result, our analysis will be able to deal exclusively with frequency integrated quantities (*e.g.* frequency integrated absorption coefficients, $\alpha^0$, and cross sections, $\sigma^0$) which can be related to their frequency dependent spectroscopic counterparts through the use of a normalized lineshape function (*cf.* equations (3.26) and (3.28)). It will also be assumed that spontaneous emission from the electronically excited states, $|1\rangle$ and $|3\rangle$, has a negligible influence upon the molecular populations within the lower levels $|0\rangle$ and $|2\rangle$. Of special importance for the validity of these model triple resonance calculations is the assumption that the
time delay between the PUMP and DUMP pulses be much shorter than the natural
lifetime of the common excited state [1]. Coherent interactions between the various
laser fields have been neglected.

Our theoretical discussion of the polarization signals expected from a TAPS
experiment will begin with an analysis of the nonuniform population distribution,
\( \{ N_{\gamma_2 J_2 K_2 M_2}; M_2 = -J_2, \ldots, J_2 \} \), created among the degenerate magnetic
components of the target level (viz. [2]) by the polarized PUMP and DUMP
radiation. This distribution, which constitutes the spatial anisotropy probed by the
polarization sensitive detection scheme, can be determined through extension of the
rate equation formalism (cf. Chapter 3 and reference [222]) to the two rovibronic
transitions employed in the preparation step of a TAPS kinetic measurement.

Assume that the PUMP and DUMP transitions are driven by two slightly
saturating resonant laser pulses, with pulse durations (i.e. \( \tau_{\text{pump}} \) and \( \tau_{\text{dump}} \))
substantially shorter than the typical lifetimes associated with the hypothetical four-
level system. The populations created within the individual magnetic sublevels of
states \( |1\rangle \) and \( |2\rangle \) can be related to the frequency integrated cross sections as follows:

\[
N_{\gamma_1 J_1 K_1 M_1} = \frac{N_{\gamma JK}}{2J+1} \sum_M \sigma^0_p(\gamma_1 J_1 K_1 M_1 \leftrightarrow \gamma J K M) \frac{I_{\text{pump}} \tau_{\text{pump}}}{\hbar \omega_{10}}
\]  

(4.2)

\[
N_{\gamma_2 J_2 K_2 M_2} = \sum_M N_{\gamma_1 J_1 K_1 M_1}
\]

\[
\times \sigma^0_p(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) \frac{I_{\text{dump}} \tau_{\text{dump}}}{\hbar \omega_{12}}
\]  

(4.3)

where

\( I_{\text{pump}} \) represents the intensity of the PUMP beam,

\( I_{\text{dump}} \) represents the intensity of the DUMP beam,
\(\omega_{10}\) denotes the radial frequency of the PUMP transition 
\((\hbar \omega_{10} = E_1 - E_0)\),

\(\omega_{12}\) denotes the radial frequency of the DUMP transition 
\((\hbar \omega_{12} = E_1 - E_2)\),

\(N_{\gamma JK}\) signifies the total population of the ground state \(|0\rangle\) (viz. 
\[N_{\gamma JK} = \sum_M N_{\gamma JKM}\].

The subscript \(p\) which appears on the frequency integrated absorption cross sections in expression (4.2) and (4.3) characterizes the polarization properties of the PUMP and DUMP beams which drive the rovibronic transitions (cf. Chapter 3 and Appendix A). Equation (4.2) has assumed that the initial population in the lower level of the PUMP transition (viz. \(|0\rangle\)) is isotropically distributed throughout the associated magnetic components (i.e. before the PUMP pulse, \(N_{\gamma JKM} = N_{\gamma JKM'}\) where \(M \neq M'\)).

Equations (4.2) and (4.3) can be combined to yield an expression for the molecular population, \(N_{\gamma J_2 K_2 M_2}\), created within the individual magnetic components of the target level \(|2\rangle\) by the PUMP and DUMP radiation:
\[ N_{\gamma_2 J_2 K_2 M_2} = \frac{N_{\gamma JK} I_{\text{pump}}^\tau_{\text{pump}} I_{\text{dump}}^\tau_{\text{dump}}}{2J+1} \frac{\hbar \omega_{10}}{\hbar \omega_{12}} \times \sum_{MM_1} \sigma_p^0(\gamma_1 J_1 K_1 M_1 \leftrightarrow \gamma J K M) \sigma_p^0(\gamma_1 J_1 K_1 M_1 \rightarrow \gamma_2 J_2 K_2 M_2) \]

\[ = N_{\gamma JK} \frac{I_{\text{pump}}^\tau_{\text{pump}} I_{\text{dump}}^\tau_{\text{dump}}}{\hbar \omega_{10}} \frac{\hbar \omega_{12}}{2J+1} \times S_{JJ_1}^{KK_1}(\text{PUMP}) S_{J_1 J_2}^{K_1 K_2}(\text{DUMP}) \]

\[ \times \sum_{MM_1} \left( \frac{J_2}{-M_2} \frac{1}{-p} \frac{J_1}{M_1} \right)^2 \left( \frac{J_1}{-M_1} \frac{1}{-p} \frac{J}{M} \right)^2 \]

(4.4)

where relationships derived in the previous Chapter have been utilized in order to express the absorption cross sections in terms of their symmetric rotor line strength factors (viz. \( S_{JJ_1}^{KK_1}(\text{PUMP}) \) and \( S_{J_1 J_2}^{K_1 K_2}(\text{DUMP}) \)). All portions of the PUMP and DUMP cross sections not explicitly depending upon angular momentum quantum numbers have been collected into the \( \sigma_p^0(\gamma_1 \leftarrow \gamma) \) and \( \sigma_p^0(\gamma_1 \rightarrow \gamma_2) \) terms respectively.

The nonuniform population distributions prepared within the magnetic subcomponents of the target level, [2], by Stimulated Emission Pumping are illustrated in figure 4-3 for the case of \( J_2 = 10 \). The situations appropriate for both linearly polarized and right-handed circularly polarized pulsed beams are presented. As might be expected, the polarization properties of the driving radiation profoundly influence the nature of the anisotropy created within the target level. In particular, linear polarization leads to a net molecular alignment (i.e.
Figure 4-3: Anisotropic Population Distributions Produced by SEP.
a) Linearly Polarized PUMP and DUMP.

\[ J_1 = J_2 - 1 \quad J_1 = J_2 \quad J_1 = J_2 + 1 \]

\[ J = J_1 - 1 \]

\[ J = J_1 \]

\[ J = J_1 + 1 \]

Magnetic Sublevels ($M_\ell$)
b) Circularly Polarized PUMP and DUMP.

\[ J_1 = J_2 - 1 \quad J_1 = J_2 \quad J_1 = J_2 + 1 \]

\[ J = J_1 - 1 \]
\[ J = J_1 \]
\[ J = J_1 + 1 \]

Magnetic Sublevels \((M_S)\)
\( N_{\gamma_2J_2K_2M_2} = N_{\gamma_2J_2K_2-M_2} \) while circular polarization results in an orientation of the molecular system (i.e. \( N_{\gamma_2J_2K_2M_2} \neq N_{\gamma_2J_2K_2-M_2} \)).

As a result of the two polarized transitions required to prepare the target level in a TAPS experiment, the nonuniform population distribution created among the magnetic subcomponents can be significantly enhanced relative to that produced by optical pumping with a single resonant transition. This effect can be readily appreciated by comparing figure 4-3 with similar histograms presented in the previous Chapter for the PTGS technique (cf. figures 3-3 and 3-4). Since the magnitude of a polarization signal is intimately related to the degree of optical anisotropy induced within the molecular sample, appropriate selection of the preparatory scheme utilized in a TAPS measurement can greatly increase the observed signal levels.

Figure 4-3 also suggests several qualitative features regarding the types of rotational transitions employed in the preparatory PUMP/DUMP pulse sequence. In particular, linear polarization produces the largest anisotropy (i.e. the largest polarization signals) through \( Q \) branch rovibronic transitions, while \( R \) or \( P \) branches are most favorable for experiments based upon circularly polarized excitation.

With the population distribution of the magnetic subcomponents in the target level determined via equation (4.4), the evaluation of the frequency integrated differential absorption coefficient for the PROBE transition can proceed in the same manner as described in the previous Chapter. For the case of linearly polarized PUMP and DUMP radiation (i.e. \( p=0 \) in equation (4.4)), the required value of \( \Delta \alpha^0 \) can be expressed by:
\[
\Delta \alpha^0(|3| \leftrightarrow |2|) = \alpha^0_2(|3| \leftrightarrow |2|) - \alpha^0_2(|3| \leftrightarrow |2|) \\
= \sum_{M_2M_3} \left( \alpha^0_2(\gamma_3J_3K_3M_3 \leftrightarrow \gamma_2J_2K_2M_2) \\
- \alpha^0_2(\gamma_3J_3K_3M_3 \leftrightarrow \gamma_2J_2K_2M_2) \right) \\
= \sum_{M_2M_3} N_{\gamma_2J_2K_2M_2} \left( \sigma^0_2(\gamma_3J_3K_3M_3 \leftrightarrow \gamma_2J_2K_2M_2) \\
- \sigma^0_2(\gamma_3J_3K_3M_3 \leftrightarrow \gamma_2J_2K_2M_2) \right) \tag{4.5}
\]

The quantization axis for these expressions is defined by the polarization properties of the pulsed radiation which induces the optical anisotropy within the molecular sample. The space-fixed z axis has therefore been oriented along the common direction of (linear) polarization associated with the PUMP and DUMP beams. The optimum signal situation, in which the PROBE linear polarization is at 45° with respect to that of the PUMP and DUMP (cf. equations (3.18) and (3.19)), is being considered.

By substituting expression (4.4) into equation (4.5) and reformulating the PROBE absorption cross sections in order to explicitly display their dependence upon rotational quantum numbers, the frequency integrated differential absorption becomes:
\[
\Delta \alpha^0(\vert 3 \rangle \leftrightarrow \vert 2 \rangle) = N_{\gamma JK} \frac{I_{\text{pump}} \tau_{\text{pump}}}{\hbar \omega_{10}} \frac{I_{\text{dump}} \tau_{\text{dump}}}{\hbar \omega_{12}}
\times \frac{\sigma^0(\gamma_1 \rightarrow \gamma) \sigma^0(\gamma_1 \rightarrow \gamma_2) \sigma^0(\gamma_2 \leftarrow \gamma_3)}{(2J+1)(2J_1+1)(2J_2+1)}
\times S_{J_1 J_2}^{K_1}(\text{PUMP}) S_{J_1 J_2}^{K_2}(\text{DUMP}) S_{J_1 J_2}^{K_3}(\text{PROBE})
\times \zeta_{\gamma JJ_1 J_2 J_3}^{\text{lin,lin}}
\] (4.6)

where the \(\zeta_{\gamma JJ_1 J_2 J_3}^{\text{lin,lin}}\) term, which results from a summation over all magnetic quantum numbers associated with the hypothetical four-level molecular system, is given by:

\[
\zeta_{\gamma JJ_1 J_2 J_3}^{\text{lin,lin}} = \frac{27(2J_1+1)(2J_2+1)}{MM_1 M_2 M_3} \sum \left( \begin{array}{c} J_2 \\ J_1 \\ J \end{array} \right) \left( \begin{array}{c} 1 \\ 0 \\ M_1 \end{array} \right)^2 
\left( \begin{array}{c} M_2 \\ 0 \\ M_1 \end{array} \right)^2
\times \left( \begin{array}{c} J_3 \\ J_2 \\ J \end{array} \right) \left( \begin{array}{c} 1 \\ 0 \\ M_2 \end{array} \right)^2
\times \frac{1}{2} \left( \left( \begin{array}{c} J_3 \\ J_2 \\ J \end{array} \right) \left( \begin{array}{c} 1 \\ 0 \\ M_2 \end{array} \right) - \left( \begin{array}{c} J_3 \\ J_2 \\ J \end{array} \right) \left( \begin{array}{c} 1 \\ 0 \\ M_2 \end{array} \right) \right)^2
\] (4.7)

These factors depend upon the polarization characteristics of both the PUMP and DUMP beams (i.e. the superscript "\text{lin,lin}" as well as on the angular momentum quantum numbers associated with the PUMP, DUMP, and PROBE transitions. They can be interpreted as a measure of the depolarization experienced by the PROBE radiation as it propagates through the optical anisotropy created in the molecular sample by the PUMP/DUMP pulse sequence. The values of \(\zeta_{\gamma JJ_1 J_2 J_3}^{\text{lin,lin}}\)
corresponding to a linearly polarized PUMP and DUMP excitation scheme are presented in table 4-I.

The determination of the frequency integrated differential absorption coefficient for circularly polarized PUMP and DUMP radiation proceeds in essentially an identical fashion to that described above for the case of linear polarization. By considering the linearly polarized PROBE beam to be a superposition of right-handed and left-handed circularly polarized light, the appropriate definition of $\Delta \alpha^0$ becomes:

$$\Delta \alpha^0(\vert 3 \rangle \rightarrow \vert 2 \rangle) = \alpha^0_+(\vert 3 \rangle \rightarrow \vert 2 \rangle) - \alpha^0_-(\vert 3 \rangle \rightarrow \vert 2 \rangle)$$

$$= \sum_{M_2 M_3} \left( \alpha^0_+ (\gamma_3 J_3 K_3 M_3 \rightarrow \gamma_2 J_2 K_2 M_2) - \alpha^0_- (\gamma_3 J_3 K_3 M_3 \rightarrow \gamma_2 J_2 K_2 M_2) \right)$$

$$= \sum_{M_2 M_3} N_{\gamma_2 J_2 K_2 M_2} \left( \sigma^0_+ (\gamma_3 J_3 K_3 M_3 \rightarrow \gamma_2 J_2 K_2 M_2) - \sigma^0_- (\gamma_3 J_3 K_3 M_3 \rightarrow \gamma_2 J_2 K_2 M_2) \right)$$

The quantization axis for these expressions has been defined with respect to the helicity basis which characterizes the circular polarization of the PUMP and DUMP radiation.

By substituting expression (4.4) (with $p=+1$ for right-handed circularly polarized PUMP and DUMP beams) into equation (4.8) and recasting the PROBE transition cross sections in a manner which exhibits their dependence upon
Table 4-I: $^{lin,lin}_{\textit{J}_1,\textit{J}_2,\textit{J}_3}$ Depolarization Factors.
a. $\langle j_1 j_2 j_3 \rangle$ for $J_3 = J_2 - 1$.

<table>
<thead>
<tr>
<th>$J_1 = J_2 - 1$</th>
<th>$J_1 = J_2$</th>
<th>$J_1 = J_2 + 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = J_1 - 1$</td>
<td>$\frac{18(J_2+1)(2J_2+3)}{35J_2(2J_2-1)}$</td>
<td>$\frac{-9(J_2-1)(J_2-5)(2J_2+3)}{70J_2^2(2J_2-1)}$</td>
</tr>
<tr>
<td>$J = J_1$</td>
<td>$\frac{-9(J_2-5)(J_2+1)(2J_2+3)}{70J_2^2(2J_2-1)}$</td>
<td>$\frac{9(2J_2+3)(6J_2^2+6J_2-5)}{70J_2^2(J_2+1)}$</td>
</tr>
<tr>
<td>$J = J_1 + 1$</td>
<td>$\frac{9(J_2+1)(2J_2+3)(8J_2^2-6J_2+5)}{70J_2^2(2J_2-1)(2J_2+1)}$</td>
<td>$\frac{-9(J_2+2)(J_2+6)}{70J_2(J_2+1)}$</td>
</tr>
</tbody>
</table>

b. $\langle j_1 j_2 j_3 \rangle$ for $J_3 = J_2$.

<table>
<thead>
<tr>
<th>$J_1 = J_2 - 1$</th>
<th>$J_1 = J_2$</th>
<th>$J_1 = J_2 + 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = J_1 - 1$</td>
<td>$\frac{-18(J_2+3)}{35J_2}$</td>
<td>$\frac{9(J_2-1)(J_2-5)(2J_2+3)}{70J_2^2(J_2+1)}$</td>
</tr>
<tr>
<td>$J = J_1$</td>
<td>$\frac{9(2J_2-5)(J_2+3)}{70J_2^2}$</td>
<td>$\frac{9(2J_2-1)(2J_2+3)(6J_2^2+6J_2-5)}{70J_2^2(J_2+1)^2}$</td>
</tr>
<tr>
<td>$J = J_1 + 1$</td>
<td>$\frac{-9(2J_2+3)(8J_2^2-6J_2+5)}{70J_2^2(2J_2+1)}$</td>
<td>$\frac{9(J_2+2)(J_2+6)(2J_2-1)}{70J_2(J_2+1)^2}$</td>
</tr>
</tbody>
</table>
\[ \langle J_{1}, J_{2}, J_{3} \rangle \text{ for } J_{3} = J_{2} + 1. \]

<table>
<thead>
<tr>
<th>( J = J_{1} - 1 )</th>
<th>( J_{1} = J_{2} - 1 )</th>
<th>( J_{1} = J_{2} )</th>
<th>( J_{1} = J_{2} + 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_{1} = J_{2} - 1 )</td>
<td>( -9(J_{2} - 1)(J_{2} - 5) )</td>
<td>( \frac{9J_{2}(2J_{2} - 1)(8J_{2}^{2} + 22J_{2} + 19)}{70J_{2}(2J_{2} + 1)} )</td>
<td>( \frac{9J_{2}(2J_{2} - 1)(8J_{2}^{2} + 22J_{2} + 19)}{70(J_{2} + 1)^{2}(2J_{2} + 1)(2J_{2} + 3)} )</td>
</tr>
<tr>
<td>( J = J_{1} )</td>
<td>( \frac{18}{35} )</td>
<td>( \frac{-9(2J_{2} - 1)(6J_{2}^{2} + 6J_{2} - 5)}{70J_{2}(J_{2} + 1)^{2}} )</td>
<td>( \frac{-9J_{2}(J_{2} + 6)(2J_{2} - 1)}{70(J_{2} + 1)^{2}(2J_{2} + 3)} )</td>
</tr>
<tr>
<td>( J_{1} = J_{2} + 1 )</td>
<td>( \frac{9(8J_{2}^{2} - 6J_{2} + 5)}{70J_{2}(2J_{2} + 1)} )</td>
<td>( \frac{-9(J_{2} + 2)(J_{2} + 6)(2J_{2} - 1)}{70J_{2}(J_{2} + 1)^{2}(2J_{2} + 3)} )</td>
<td>( \frac{18J_{2}(2J_{2} - 1)}{35(J_{2} + 1)(2J_{2} + 3)} )</td>
</tr>
</tbody>
</table>
rotational degrees of freedom, the frequency integrated differential absorption becomes:

\[
\Delta \alpha^0(\ket{3} \rightarrow \ket{2}) = N_{JK} \frac{I_{pump} \tau_{pump}}{\hbar \omega_{10}} \frac{I_{dump} \tau_{dump}}{\hbar \omega_{12}} \times \frac{\sigma^0(\gamma_1 \rightarrow \gamma_1) \sigma^0(\gamma_1 \rightarrow \gamma_2) \sigma^0(\gamma_3 \rightarrow \gamma_2)}{(2J+1)(2J_1+1)(2J_2+1)} \times S^{KK_1}_{JJ_1} \left( \text{PUMP} \right) S^{K_1K_2}_{JJ_2} \left( \text{DUMP} \right) S^{K_2K_3}_{JJ_3} \left( \text{PROBE} \right) \times \zeta^{r_{cp},r_{cp}}_{JJ_1J_2J_3} \tag{4.9}
\]

where the depolarization factors, \( \zeta^{r_{cp},r_{cp}}_{JJ_1J_2J_3} \), corresponding to right-handed circularly polarized (i.e. rcp) PUMP and DUMP radiation, are given by:

\[
\zeta^{r_{cp},r_{cp}}_{JJ_1J_2J_3} = 27(2J_1+1)(2J_2+1) \sum_{MM_1M_2M_3} \left( \begin{array}{cc} J_2 & 1 \\ M_2 & -1 \end{array} \right) \left( \begin{array}{cc} J_1 & 1 \\ M_1 & -1 \end{array} \right) ^2 \times \left( \begin{array}{cc} J_3 & 1 \\ M_3 & -1 \end{array} \right) ^2 - \left( \begin{array}{cc} J_3 & 1 \\ M_3 & -1 \end{array} \right) ^2 \left( \begin{array}{cc} J_3 & 1 \\ M_3 & -1 \end{array} \right) ^2 \tag{4.10}
\]

The calculated values of the \( \zeta_{JJ_1J_2J_3} \) depolarization factors for right-handed circularly polarized PUMP and DUMP beams are presented in table 4-II.

The rotational dependence and relative magnitudes of the polarization signals observed in our TAPS experiments are completely characterized by the \( \zeta_{JJ_1J_2J_3} \) depolarization factors compiled in tables 4-I and 4-II. The trends suggested by these
Table 4-II: $^{r_{cp}, r_{cp}} s_{J_1 J_2 J_3}$ Depolarization Factors.
### a. $J_{J_{1}J_{2}J_{3}}^{rep,rep}$ for $J_{3} = J_{2} - 1$.

<table>
<thead>
<tr>
<th>$J = J_{1} - 1$</th>
<th>$J_{1} = J_{2} - 1$</th>
<th>$J_{1} = J_{2}$</th>
<th>$J_{1} = J_{2} + 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-18(J_{2} + 1)$</td>
<td>$-9(J_{2} - 1)(J_{2} + 3)$</td>
<td>$-9(2J_{2} - 1)$</td>
</tr>
<tr>
<td></td>
<td>$5J_{2}$</td>
<td>$10J_{2}^{2}$</td>
<td>$10(J_{2} + 1)(2J_{2} + 1)$</td>
</tr>
<tr>
<td>$J = J_{1}$</td>
<td>$-9(J_{2} + 1)(J_{2} + 3)$</td>
<td>$-9(2J_{2} - 1)(2J_{2} + 3)$</td>
<td>$9(J_{2} - 2)$</td>
</tr>
<tr>
<td></td>
<td>$10J_{2}^{2}$</td>
<td>$10J_{2}^{2}(J_{2} + 1)$</td>
<td>$10(J_{2} + 1)$</td>
</tr>
<tr>
<td>$J = J_{1} + 1$</td>
<td>$-9(J_{2} + 1)(2J_{2} + 3)$</td>
<td>$9(J_{2} - 2)(J_{2} + 2)$</td>
<td>$18$</td>
</tr>
<tr>
<td></td>
<td>$10J_{2}^{2}(2J_{2} + 1)$</td>
<td>$10J_{2}(J_{2} + 1)$</td>
<td>$5$</td>
</tr>
</tbody>
</table>

### b. $J_{J_{1}J_{2}J_{3}}^{rep,rep}$ for $J_{3} = J_{2}$.

<table>
<thead>
<tr>
<th>$J = J_{1} - 1$</th>
<th>$J_{1} = J_{2} - 1$</th>
<th>$J_{1} = J_{2}$</th>
<th>$J_{1} = J_{2} + 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-18$</td>
<td>$-9(J_{2} - 1)(J_{2} + 3)$</td>
<td>$-9(2J_{2} - 1)$</td>
</tr>
<tr>
<td></td>
<td>$5J_{2}$</td>
<td>$10J_{2}^{2}(J_{2} + 1)$</td>
<td>$10(J_{2} + 1)^2(2J_{2} + 1)$</td>
</tr>
<tr>
<td>$J = J_{1}$</td>
<td>$-9(J_{2} + 3)$</td>
<td>$-9(2J_{2} - 1)(2J_{2} + 3)$</td>
<td>$9(2J_{2} - 2)$</td>
</tr>
<tr>
<td></td>
<td>$10J_{2}^{2}$</td>
<td>$10J_{2}^{2}(J_{2} + 1)^2$</td>
<td>$10(J_{2} + 1)^2$</td>
</tr>
<tr>
<td>$J = J_{1} + 1$</td>
<td>$-9(2J_{2} + 3)$</td>
<td>$9(J_{2} - 2)(J_{2} + 2)$</td>
<td>$18$</td>
</tr>
<tr>
<td></td>
<td>$10J_{2}^{2}(2J_{2} + 1)$</td>
<td>$10J_{2}(J_{2} + 1)^2$</td>
<td>$5(J_{2} + 1)$</td>
</tr>
</tbody>
</table>
c. \( \zeta_{J_1 J_2 J_3}^{rcp, rcp} \) for \( J_3 = J_2 + 1 \).

<table>
<thead>
<tr>
<th>( J = J_1 - 1 )</th>
<th>( J = J_1 )</th>
<th>( J = J_1 + 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_1 = J_2 - 1 )</td>
<td>( \frac{18}{5} )</td>
<td>( \frac{9(J_2-1)(J_2+3)}{10J_2(2J_2+1)} )</td>
</tr>
<tr>
<td>( J = J_1 )</td>
<td>( \frac{9(J_2+3)}{10J_2} )</td>
<td>( \frac{9(2J_2-1)(2J_2+3)}{10J_2(J_2+1)^2} )</td>
</tr>
<tr>
<td>( J = J_1 + 1 )</td>
<td>( \frac{9(2J_2+3)}{10J_2(2J_2+1)} )</td>
<td>( \frac{-9(J_2-1)(J_2+2)}{10(J_2+1)^2} )</td>
</tr>
</tbody>
</table>
analytical angular momentum expressions are perhaps better illustrated by referring to their high-$J_2$ limits which are summarized in table 4-III. As demonstrated by equations (4.6) and (4.9), the polarization signal intensity should increase in proportion to the value of the $\zeta$ parameter.

Part (a) of table 4-III presents the high-$J_2$ limits for the depolarization factors, $\xi_{JJ'_1J'_2J'_3}^{lin,lin}$, associated with linearly polarized PUMP and DUMP radiation. For this case, the $\zeta$ parameter attains a maximum value of $108/35$ when all rovibronic transitions (viz. PUMP, DUMP, and PROBE) proceed via Q branches. As R or P branch transitions are incorporated into the TAPS scheme, however, the degree of depolarization experienced by the PROBE beam (i.e. the signal magnitude) can be expected to decrease substantially.

The high-$J_2$ limits contained in part (b) of table 4-III demonstrate that the depolarization factors corresponding to right-handed circularly polarized PUMP and DUMP beams, $\xi_{JJ'_1J'_2J'_3}^{rcp,rcp}$, approach a maximum value of $18/5$ when all rovibronic transitions proceed via either R or P branches. The incorporation of Q branches into the TAPS scheme, especially in the DUMP and PROBE stages, results in a $\zeta$ parameter which decreases rapidly with increasing total angular momentum in the target level (i.e. increasing $J_2$). Special attention must be directed to the rather low depolarization factors encountered when both R and P branches are employed in the PUMP/DUMP pulse sequence. As illustrated in figure 4-2, the circularly polarized nature of the radiation utilized in the preparation step tends to destroy the desired molecular anisotropy (i.e. the net molecular orientation) if a $\Delta J = \pm 1$ transition is followed by a $\Delta J = \mp 1$ transition.
a. High-$J_2$ Limits for $\sigma_{J_1 J_2 J_3}^{lin, lin}$.

| $|\sigma_{J_1 J_2 J_3}^{lin, lin}|$ | PUMP Transition | DUMP Transition | PROBE Transition |
|----------------------------------|-----------------|-----------------|-----------------|
| 108/35                           | Q               | Q               | Q               |
| 54/35                            | Q               | Q               | P or R          |
| 9/35                             | Q               | P or R          | Q               |
| 9/70                             | Q               | P or R          | P or R          |

**Table 4-III**: High-$J_2$ Limits for Depolarization Factors.
### a. High-$J_2$ Limits for $\gamma_{J1J2J3}$

<table>
<thead>
<tr>
<th>$\gamma_{J1J2J3}$</th>
<th>PUMP Transition</th>
<th>DUMP Transition</th>
<th>PROBE Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{9}{35}$</td>
<td>P or R</td>
<td>Q</td>
<td>Q</td>
</tr>
<tr>
<td>$\frac{9}{70}$</td>
<td>P or R</td>
<td>Q</td>
<td>P or R</td>
</tr>
<tr>
<td>$\frac{36}{35}$</td>
<td>P or R</td>
<td>P or R</td>
<td>Q</td>
</tr>
<tr>
<td>$\frac{18}{35}$</td>
<td>P or R</td>
<td>P or R</td>
<td>P or R</td>
</tr>
</tbody>
</table>

**Table 4-III, continued.**
b. High-\(J_2\) Limits for \(\zeta_{JJ_1J_2J_3}^{rcp,rcp}\).

| \(|\zeta_{JJ_1J_2J_3}^{rcp,rcp}\)| | PUMP Transition | DUMP Transition | PROBE Transition |
|---|---|---|---|
| \(\frac{18}{5J_2}\) | Q | Q | Q |
| \(\frac{18}{5J_2}\) | Q | Q | P or R |
| \(\frac{9}{10J_2}\) | Q | P or R | Q |
| \(\frac{9}{10}\) | Q | P or R | P or R |

*Table 4-III*, continued.
b. High-\(J_2\) Limits for \(\xi_{J_1,J_2,J_3}^{rcp,rcp}\):

<table>
<thead>
<tr>
<th>(\xi_{J_1,J_2,J_3}^{rcp,rcp})</th>
<th>PUMP Transition</th>
<th>DUMP Transition</th>
<th>PROBE Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{9}{10J_2})</td>
<td>P or R</td>
<td>Q</td>
<td>Q</td>
</tr>
<tr>
<td>(\frac{9}{10})</td>
<td>P or R</td>
<td>Q</td>
<td>P or R</td>
</tr>
<tr>
<td>(\frac{18}{5})</td>
<td>R(P)</td>
<td>R(P)</td>
<td>P or R</td>
</tr>
<tr>
<td>(\frac{9}{10J_2})</td>
<td>R(P)</td>
<td>P(R)</td>
<td>P or R</td>
</tr>
<tr>
<td>(\frac{18}{5J_2})</td>
<td>R(P)</td>
<td>R(P)</td>
<td>Q</td>
</tr>
<tr>
<td>(\frac{9}{10J_2^2})</td>
<td>R(P)</td>
<td>P(R)</td>
<td>Q</td>
</tr>
</tbody>
</table>

**Table 4-III**, concluded.
4.3 Experimental

4.3.1 Stimulated Emission Pumping

The TAPS kinetic studies had to be preceded by a search for rovibronic transitions which would provide access to highly excited target levels within the \( \tilde{X}^1A_1 \) state of formaldehyde. The spectroscopic probe employed for these investigations was the double resonance technique of Stimulated Emission Pumping [171, 172]. The conceptual and technical details of this dual-beam, null detection scheme were fully discussed in earlier Chapters and will not be repeated at the present time.

The only noteworthy differences in the SEP experiments which preceded our kinetic investigations are related to the operation of the pulsed dye lasers themselves. As presently formulated, the TAPS scheme necessitates that rovibronic transitions linking a common \( \tilde{X}^1A_1 \) rotation-vibration eigenstate be located from both the \( v_4 = 1 \) and \( v_4 = 3 \) vibrational levels of the excited electronic state (cf. figure 4-1). SEP spectroscopic measurements were therefore performed from each of these vibronic levels in order to identify the appropriate DUMP and PROBE transitions. For the two regions of the \( \tilde{X}^1A_1 \) potential surface examined in the course of these preliminary TAPS studies, table 4-IV presents a compilation of the experimental parameters associated with the operation of the pulsed dye lasers.

All of the dyes listed in table 4-IV were obtained from \textit{Exciton Chemical Company} and dissolved in spectroscopic grade methanol (\textit{Omnisolve}). Although greater DUMP efficiencies could have been achieved, in the case of the measurements at \( \sim 11300\text{cm}^{-1} \), by pumping appropriate red dyes with the 532nm second harmonic output of a Nd:YAG laser, the technical means for accomplishing this (\textit{viz.} optical components) did not exist at the time that these experiments were
Table 4-IV: Parameters for Pulsed Dye Laser Operation.
<table>
<thead>
<tr>
<th>Energy above $\tilde{X}^{1}A_1$ zero point:</th>
<th>~11300 cm⁻¹</th>
<th>~11900 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PUMP Transition:</strong></td>
<td>$\tilde{4}_0^1$</td>
<td>$\tilde{4}_0^3$</td>
</tr>
<tr>
<td>PUMP Wavelength:</td>
<td>~353 nm</td>
<td>~343 nm</td>
</tr>
<tr>
<td>PUMP Dye:</td>
<td>LDS 750</td>
<td>LDS 698</td>
</tr>
<tr>
<td>Excitation Wavelength:</td>
<td>532 nm</td>
<td>532 nm</td>
</tr>
<tr>
<td></td>
<td>75 mJ/pulse</td>
<td>75 mJ/pulse</td>
</tr>
<tr>
<td>PUMP Energy:</td>
<td>12 mJ/pulse</td>
<td>15 mJ/pulse</td>
</tr>
<tr>
<td><strong>DUMP Transition:</strong></td>
<td>$\tilde{2}_4^04_4^1$</td>
<td>$\tilde{2}_4^04_4^3$</td>
</tr>
<tr>
<td>DUMP Wavelength:</td>
<td>~589 nm</td>
<td>~562 nm</td>
</tr>
<tr>
<td>Excitation Wavelength:</td>
<td>532 nm</td>
<td>532 nm</td>
</tr>
<tr>
<td></td>
<td>100 mJ/pulse</td>
<td>100 mJ/pulse</td>
</tr>
<tr>
<td>DUMP Energy:</td>
<td>10 mJ/pulse</td>
<td>10 mJ/pulse</td>
</tr>
</tbody>
</table>

*a* Refers to frequency doubled output.

*b* Typical DUMP transitions for indicated $\tilde{X}^{1}A_1$ energy region.

4.3.2 Transient Absorption Polarization Spectroscopy

Figure 4-4 illustrates the apparatus employed for the TAPS kinetic studies of collisional relaxation processes in highly excited $\tilde{X}^1A_1$ formaldehyde. As expected, there is a great similarity in design, as well as concept, between this experimental configuration and those depicted in previous Chapters for the SEP and PTGS techniques. The ensuing discussion will therefore concentrate upon those details which are particularly relevant to the present time-resolved measurements.

The PROBE beam for the TAPS experiments was produced by employing $\sim 3.0$ watts of all-line emission from a continuous wave argon ion laser (Spectra Physics model 164/03) to pump a commercial standing-wave dye laser (Coherent CR599-21) containing Rhodamine 6G dye (Exciton Chemical Company) dissolved in ethylene glycol (Fisher Scientific). Single frequency operation was achieved by restricting laser oscillation to an individual longitudinal cavity mode through use of a frequency stabilized and locked intracavity etalon assembly. This resulted in a short time frequency jitter of $\leq 1$MHz and an overall drift rate of $\sim 10$MHz/hour. The vertically polarized output of this cw source, which was constantly monitored by means of a confocal spectrum analyzer (Spectra Physics model 480; 2.0GHz FSR & Burleigh model RC-42 ramp generator), had an average power of $\sim 200$mW and could be electronically scanned over any contiguous 1cm$^{-1}$ interval within the limits imposed by the dye tuning curve (i.e. for Rhodamine 6G: 570nm $\sim 620$nm). For the preliminary TAPS measurements presented in this Chapter, the PROBE laser was operated in two distinct spectral regions, either at $\sim 16960$cm$^{-1}$ (region of $2_1^14_4^1$) or at $\sim 17260$cm$^{-1}$ (region of $2_3^34_6^1$), depending upon the upper vibronic level of the PROBE transition as well as the amount of rotation-vibration energy deposited into
Figure 4-4: Apparatus for TAPS Experiments.
the $\tilde{X}^1A_1$ levels under investigation.

After being approximately collimated to a diameter of 3mm by means of a Galilean telescope, the cw PROBE beam was directed through an achromatic half wave retarder (*Special Optics* model R8-9015) and a calcite Glan-Laser prism (*Karl Lambrecht* MGLA-8). These optical components permitted the linear polarization of the PROBE radiation to be precisely oriented at an angle of 45° with respect to that of the vertically polarized PUMP and DUMP pulses. The tunable cw light subsequently propagated down the center of the formaldehyde sample cell without passing through or reflecting from any optical elements which might compromise its high polarization contrast ratio.

The PUMP and DUMP beams for the TAPS studies were produced by two, Nd:YAG-pumped, pulsed dye lasers (*Quanta Ray* PDL-1) of the Hansch-Klauminzer design (*viz.* oscillator with intracavity prism beam expander in conjunction with travelling-wave preamplifier and amplifier stages). In order to reduce amplified spontaneous emission and thereby improve spectral resolution, these commercial dye units were each modified by installing $\sim$3ns of optical delay for the YAG pump radiation between the oscillator and preamplifier/amplifier sections. Both lasers were operated with air-spaced intracavity etalons (PUMP: *Tech Optics* 0.75cm$^{-1}$ FSR; DUMP: *Molecron* 1.0cm$^{-1}$ FSR) which resulted in measured bandwidths (at fundamental output frequencies) of $\sim$0.03cm$^{-1}$ FWHM. The PUMP was pressure scanned with prepurified nitrogen (*Matheson*) in order to attain $\sim$3.5cm$^{-1}$ of continuous tuning (i.e. $\sim$7cm$^{-1}$ at doubled frequencies) for a 0 to 800 Torr change in the (intracavity) pressure. In the case of the DUMP laser, pressure tuning with instrument grade SF$_6$ (*Matheson*) over a range of 0 to 2 atmospheres permitted $\sim$35cm$^{-1}$ of continuous frequency adjustment. Table 4-IV summarizes the experimental parameters pertinent to the operation of the pulsed PUMP and DUMP
dye lasers.

The light generated by the PUMP laser was frequency doubled with an extracavity KD*P crystal (Quanta Ray, 76° cut) in order to produce the ultraviolet radiation required for the formaldehyde $\tilde{A}^1A_2 \leftrightarrow \tilde{X}^1A_1$ electronic transition. After separation from the colinear fundamental dye output by means of a set of 60° S1-UV prisms (Esco), the ultraviolet beam was spatially filtered through a sapphire pinhole (Richard H. Bird & Company; $\sim 200\mu m$) and recollimated to a diameter of $\sim 4mm$. At the same time, a back reflection from the undoubled PUMP was sent through a monitor etalon (Mollectron $\sim 0.55cm^{-1}$ FSR) to provide a visual assessment for the single mode performance of the dye laser.

At this point, the horizontally polarized ultraviolet radiation had a spectral bandwidth of $\sim 0.06cm^{-1}$ FWHM, a pulse duration of $\sim 5ns$ FWHM, and an energy $\geq 2mj/pulse$. This PUMP beam was propagated through a half wave retardation plate (Virgo Optics) and a Glan-Laser calcite prism (Karl Lambrecht MGLA-8-SW) in order to rotate its linear polarization vector to a vertical orientation. The PUMP was subsequently directed through the formaldehyde sample cell at a slight angle (viz. $\leq 6.0$ milliradians) to the copropagating PROBE beam.

The tunable pulsed radiation generated by the DUMP laser was directed through a Keplerian telescope where it was spatially filtered by means of a sapphire pinhole (Richard H. Bird & Company; $\sim 200\mu m$) and approximately recollimated to a diameter of 4mm. The resulting vertically-polarized light had a spectral bandwidth of $\sim 0.03cm^{-1}$ FWHM, a pulse duration of $\sim 6ns$ FWHM, and an energy in excess of 10mJ/pulse. Back reflections from this DUMP beam were sent through a monitor etalon (Mollectron $\sim 0.55cm^{-1}$ FSR), to evaluate the single mode performance of the dye laser, and through a room temperature iodine absorption
cell, which provided a convenient absolute frequency reference when used in conjunction with the Fourier transform atlas of Gerstenkorn and Luc [71].

The DUMP radiation made two passes through a set of $60^\circ$ heavy flint prisms (Physitec) in order to remove any amplified spontaneous emission which might be present at the PROBE frequency. This procedure, designed to eliminate residual scattered laser light in the signal detection process, was especially important in the case of the Coumarin 540A/Rhodamine 6G dye mixture utilized for the TAPS experiments conducted at $\sim 11300\text{cm}^{-1}$ above the zero point energy of the $\tilde{X}$ state (cf. table 4-IV). The DUMP subsequently propagated through a Glan-Laser calcite prism (Karl Lambrecht MGLA-SW-8), to enhance its vertical polarization contrast ratio, before being sent into the sample cell in a direction which was colinear and copropagating with respect to the PUMP beam. Considerable effort was made to ensure that the DUMP radiation entered the formaldehyde vapor only after interaction with the PUMP beam had been completed. This necessitated that a delay of $\leq 5\text{ns}$ be incorporated between the arrival times of the PUMP and DUMP pulses at the center of the sample cell.

After traversing the formaldehyde sample cell, the PROBE beam, separated from the PUMP and DUMP radiation by means of an aperture, immediately entered a Glan-Laser calcite prism (Karl Lambrecht MGLA-8-SW) which functioned as the analyzer for these polarization-detected experiments. This optical component was mounted in a high precision rotation stage (Klinger TR80; $3\times10^{-4}$ radian resolution) so that its orientation could be carefully adjusted to null the incident cw radiation. As a result of the transitory optical anisotropy induced in the molecular sample by the PUMP/DUMP pulse sequence, a small portion of the PROBE will be transmitted through the analyzer. This signal-carrying beam was spectrally dispersed by means of an S1-UV Pellin-Broca prism (Optics for Research) and an
Amici direct vision prism (Physitec) in order to eliminate residual scattered light from the pulsed lasers. The isolated signal photons were subsequently directed through a well-baffled flight tube and eventually impinged upon a high-speed photomultiplier tube (Hamamatsu R1635; 0.8ns rise time) which served as the detector for our time-resolved measurements.

The output of the photomultiplier was directed into a high-speed transient digitizer (Tektronix 7912AD, 7B92A time base, 7A19 Amplifier, DC to 500MHz bandwidth) to permit signal averaging. The TAPS decay profiles obtained in this manner were subsequently sent to a microcomputer (DEC LSI-11/03) for further processing and analysis. To exclude artifacts associated with timing jitter, the digitizer was triggered by means of a fast photodiode (EG&G FND-100, 90V reverse bias) which monitored a back reflection from the DUMP laser. All signal connections between instruments were performed with double shielded coax cable (RG223) with particular attention to the preservation of 50Ω transmission line characteristics.

The cell utilized for the TAPS experiments was the same one employed for the TGS and PTGS studies of the previous Chapters. Pressures within the sample cell could be accurately monitored by means of either an ionization gauge (Veeco Instruments Inc. model RGS-7) or a 0 to 1 Torr capacitance manometer (MKS Baratron model 220B).

Considerable effort was made during the course of the TAPS measurements to ensure that the cell windows were as free as possible of any birefringent or dichroic properties which might compromise the polarization characteristics of the PROBE radiation. In particular, the windows were held in place only by the pressure differential between the interior and exterior of the sample cell so as to minimize stress-induced birefringence associated with the mounting process. As described in
the discussion of the PTGS experiments (cf. Chapter 3), any remaining birefringence could be significantly reduced by utilizing a differential micrometer to create a counterbalancing stress within the window substrates.

The formaldehyde-$h_2$ sample used in the TAPS experiments was prepared by pyrolysis of paraformaldehyde-$h_2$ (Aldrich) followed by two fractional distillations. All time-resolved measurements were performed at room temperature (i.e. $22\pm3^\circ C$) with sample pressures ranging from 0 to 400 milliTorr.

A typical TAPS measurement began by tuning the cw dye laser to within one wavenumber (i.e. the range of one electronic scan) of the desired PROBE transition. This process was greatly facilitated by simultaneously recording the room temperature absorption spectrum of molecular iodine. The Fourier transform atlas of Gerstenkorn and Luc [71] could then be used in order to provide an absolute frequency reference. Once set, the servo-electronics and external reference cavity of the cw PROBE laser enabled it to remain frequency locked to within 10MHz/hour.

The pulsed PUMP and DUMP beams were initially directed into a separate sample cell where Stimulated Emission Pumping experiments were performed in order to locate the preselected PUMP and DUMP rovibronic transitions. The frequency of each laser could then be pressure scanned into resonance with the appropriate spectral features so as to prepare the highly excited target level within the $\tilde{X}^1A_1$ state. Once set, the pulsed lasers usually remained fixed, without operator intervention, for several hours. After this initial frequency adjustment, both beams were redirected back towards the apparatus utilized in the TAPS measurements.

The sample cell was filled with the desired pressure of formaldehyde vapor and isolated from the rest of the vacuum line. With both the PUMP and DUMP beams blocked, the PROBE was permitted to traverse the gaseous sample and
impinge upon the Glan-Laser polarization analyzer. Once this calcite prism had been approximately adjusted to null the incident cw radiation, the shutter on the photomultiplier detector could be opened. The final nulling of the PROBE beam could then be accomplished by monitoring the output current of the photomultiplier with a picoammeter (Keithley Instruments Inc. model 600A electrometer) while simultaneously adjusting the orientation of the Glan-Laser prism and the force applied to the edge of the cell window via the differential micrometer. In this manner, the portion of the PROBE transmitted through the polarization analyzer could typically be reduced (in intensity) to less than 1 part in $10^7$ of the incident radiation.

The pulsed PUMP and DUMP beams were now directed through the sample cell in order to create the transitory optical anisotropy required by the polarization detection scheme. Fine tuning of the cw laser frequency could be readily performed by maximizing the observed polarization signals. With this accomplished, the transient digitizer was instructed to average over 1024 PUMP/DUMP pulse sequences. After subtracting a background trace (1024 shot average) obtained with the PROBE detuned, the time-resolved data curves had typical signal-to-noise ratios in excess of 50:1. These were stored on floppy disk for later processing and analysis. The formaldehyde sample was replaced following the acquisition of each set of signal and background traces in order to minimize the effects of photoproducts in the kinetic studies.

As with the other forms of transient gain spectroscopy (viz. TGS and PTGS) discussed in previous Chapters, the TAPS signals obtained in these time-resolved studies displayed large amplitude variations from one shot of the pulsed lasers to the next. These fluctuations can be attributed to the random frequency overlap which occurs between the single mode output of the PROBE laser and the cavity mode.
structure present in the PUMP and DUMP beams. Although the triple resonance nature of the TAPS experiments might appear to exacerbate this problem, the signal averaging process employed in these studies eliminated any deleterious effects which might be induced by such pulse-to-pulse variations.

4.4 Results and Discussion

4.4.1 Stimulated Emission Pumping

The Stimulated Emission Pumping technique, by virtue of its unique ability to selectively prepare a significant population of highly excited molecules, plays a crucial role for the TAPS studies of relaxation processes in $\tilde{X} \, ^1A_1$ formaldehyde. However, before the kinetic investigations could begin, SEP had to be utilized as a spectroscopic probe for locating and identifying target levels within the ground electronic state. The present section will discuss these spectroscopic measurements with particular emphasis on characterization of the rotation-vibration eigenstates which were employed in the TAPS experiments. The two distinct energy regions of the $\tilde{X} \, ^1A_1$ potential surface explored in the present work (viz. $\sim 11300\text{cm}^{-1}$ and $\sim 11900\text{cm}^{-1}$ of excitation) will be examined separately.

In theory, specification of both the DUMP and PROBE transitions in the TAPS experimental scheme (cf. figure 4-1) requires that the same energy region in the ground electronic potential surface be examined from two separate vibrational levels of the $\tilde{A}$ state (viz. 4$^1$ and 4$^3$). Fortunately, the $\tilde{X} \, ^1A_1$ term values determined from one vibrational level, in conjunction with the spectroscopic constants reported for $\tilde{A} \, ^1A_2$ formaldehyde [50], enabled accurate calculation of rovibronic transition frequencies for the other vibrational level. Therefore, SEP studies of highly excited rotation-vibration eigenstates were only performed from a single $\tilde{A} \, ^1A_2$ vibrational level.
The SEP studies performed in the vicinity of \( \sim 11300 \text{cm}^{-1} \) of excitation have been discussed in Chapter 3 and will be mentioned only briefly at the present time. Careful analysis of the spectral data obtained in this energy region suggests that the most intense resonances can be attributed to \( b \)-type vibronic bands which terminate on either the 244 or 410 vibrational levels. Further clarification of the vibrational character for the \( \tilde{X}^1A_1 \) eigenstates did not prove to be feasible. Rotational assignments could be readily performed in most instances (\textit{nb. DUMP} transitions from the \( 13_2,12 \) level could only be designated as \( \Delta J = 0 \) or \( \Delta J = \pm 1 \) on the basis of polarization studies). These spectroscopic measurements also revealed that the \( P \) and \( R \) branches which accompany pronounced \( Q \) branch features display an unexpected doubling (\textit{cf.} upper portion of figure 3-7). This behavior can almost certainly be attributed to the presence of resonance interactions (\textit{viz. Coriolis or Fermi perturbations}) which result in a mixing of vibronic oscillator strength among adjacent vibrational levels.

The rotation-vibration eigenstates examined during the course of the TAPS kinetic measurements at \( \sim 11300 \text{cm}^{-1} \) of excitation are summarized in table 4-V along with their observed term values. As indicated, each of the target levels is associated with a symbol of the form "TAPS-#". This provides a convenient shorthand notation for specifying the various experiments performed in the present study (\textit{e.g.} TAPS-1 designates the investigation of relaxation processes in the \( 5_{1,4} \) \( 244 \) eigenstate via the energy level scheme illustrated in figure 4-1). Note that the labels TAPS-2, TAPS-3, and TAPS-4 denote spectral features which are depicted in the stick spectrum of figure 3-7. In particular, the latter two designations (\textit{i.e.} TAPS-3 and TAPS-4) refer to the individual members of the doubled \( P \) branch structure which was observed in the SEP measurements performed from the \( 4_{0,4} \) \( v_4 = 1 \) eigenstate of \( \tilde{A}^1A_2 \) formaldehyde. For these experiments (\textit{i.e.} the \( P \)
<table>
<thead>
<tr>
<th>Designation</th>
<th>( \widetilde{X} ,^1A_1 ) Target(^a) Level</th>
<th>Term(^b) Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAPS-1</td>
<td>( 5_{1,4} )</td>
<td>11379.235</td>
</tr>
<tr>
<td>TAPS-2</td>
<td>( 4_{1,3} )</td>
<td>11367.269</td>
</tr>
<tr>
<td>TAPS-3</td>
<td>( 5_{1,5} )</td>
<td>11377.620</td>
</tr>
<tr>
<td>TAPS-4</td>
<td>( 5_{1,5} )</td>
<td>11378.618</td>
</tr>
<tr>
<td>TAPS-5</td>
<td>( 6_{1,5} )</td>
<td>11393.554</td>
</tr>
<tr>
<td>TAPS-6</td>
<td>( 13_{r,r} )</td>
<td>11599.056</td>
</tr>
</tbody>
</table>

\(^a\) Tentative vibrational assignment: \( 2_4,4_4 \).

\(^b\) In cm\(^{-1}\).

**Table 4-V:** Target \( \widetilde{X} \,^1A_1 \) Levels Near 11300 cm\(^{-1}\).
branches), circularly polarized DUMP radiation was utilized in order to maximize the amplitude of the time-resolved signals.

Table 4-VI contains a detailed compilation of the PUMP, DUMP, and PROBE transitions which were employed in the TAPS kinetic studies of rotation-vibration eigenstates at \( \sim 11300\text{cm}^{-1} \) of excitation. The set of four energy levels required for each depopulation experiment (cf. figure 4-1) are conveniently designated by the "TAPS-#" notation as defined in table 4-V.

The \( 11900\text{cm}^{-1} \) region of excitation in \( \tilde{\Delta} \, ^1A_2 \) formaldehyde was selected for additional TAPS experiments since it offered the opportunity to examine eigenstates possessing appreciably different vibrational character from that encountered in the studies at \( \sim 11300\text{cm}^{-1} \). In particular, considerable effort was directed towards identification of pure \( \nu_2 \) (i.e. C\(=\)O stretching) modes which, as demonstrated by Dai, et. al. [143], have a pronounced tendency to remain unaffected by Coriolis perturbations. Kinetic measurements performed upon such levels would permit a systematic investigation of the influence which rotation-induced vibrational mixing exerts upon relaxation processes in highly excited formaldehyde.

The cw dye laser utilized in the TAPS experiments was operated with Rhodamine 6G dye in order to obtain convenient and efficient single mode performance. The limitations on tunability imposed by the dye gain profile (viz. single mode tuning range: \( 570 \sim 620\text{nm} \) [259]), in conjunction with the ultimate objective of examining \( \tilde{X} \, ^1A_1 \) eigenstates with \( \sim 11900\text{cm}^{-1} \) of excitation, necessitated that PROBE transitions terminate within the \( v_4 = 3 \) vibrational level of the \( \tilde{\Delta} \) state. Therefore, SEP studies were performed with DUMP transitions originating from individual rotational eigenstates in the \( v_4 = 3 \) level of electronically excited formaldehyde. Table 4-VII contains a compilation of all PUMP transitions which were employed in the present spectroscopic measurements. In each case, the
**Table 4-VI:** Transition Data for TAPS at $\sim 11300\text{cm}^{-1}$. 
<table>
<thead>
<tr>
<th>Designation</th>
<th>PUMP b Transition</th>
<th>Energy</th>
<th>DUMP c Transition</th>
<th>Energy</th>
<th>PROBE d Transition</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAPS-1</td>
<td>5_0→5_1,4</td>
<td>29125.092</td>
<td>5_0→5_1,4</td>
<td>17786.782</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAPS-2</td>
<td>4_0→4_1,3</td>
<td>29123.971</td>
<td>4_0→4_1,3</td>
<td>17789.885</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAPS-3</td>
<td>4_0→4_1,3</td>
<td>29123.971</td>
<td>4_0→4_1,5</td>
<td>17777.834</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAPS-4</td>
<td>4_0→4_1,5</td>
<td>29123.971</td>
<td>4_0→4_1,5</td>
<td>17778.836</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAPS-5</td>
<td>6_0→6_1,5</td>
<td>29119.833</td>
<td>6_0→6_1,5</td>
<td>17787.830</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAPS-6</td>
<td>12_2,12→12_3,11</td>
<td>29084.874</td>
<td>13_2,12→13_3,11</td>
<td>17760.788</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a PUMP Vibronic Transition: \( ^1A_2 \rightarrow \tilde{X}^1A_1 \); \( ^3 \)
b in cm\(^{-1} \)
c DUMP Vibronic Transition: \( ^1A_2 \rightarrow \tilde{X}^1A_1 \); \( ^3 \)
d PROBE Vibronic Transition: \( ^1A_2 \rightarrow \tilde{X}^1A_1 \); \( ^3 \)
<table>
<thead>
<tr>
<th>Vibronic Transition $^3$4$^0$</th>
<th>Rotation Transition $^1_0,1 \rightarrow ^1_{1,0}$</th>
<th>Transition Energy 29127.345</th>
<th>Relative Intensity 4.27</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4$4$^0$</td>
<td>$^2_0,2 \rightarrow ^2_{1,1}$</td>
<td>29126.596</td>
<td>6.90</td>
</tr>
<tr>
<td>$^4$4$^0$</td>
<td>$^4_0,4 \rightarrow ^4_{1,3}$</td>
<td>29123.971</td>
<td>14.12</td>
</tr>
<tr>
<td>$^4$4$^0$</td>
<td>$^5_0,5 \rightarrow ^5_{1,4}$</td>
<td>29122.092</td>
<td>12.56</td>
</tr>
<tr>
<td>$^4$4$^0$</td>
<td>$^6_0,6 \rightarrow ^6_{1,5}$</td>
<td>29119.833</td>
<td>13.51</td>
</tr>
</tbody>
</table>

$^a$ Calculated values (in cm$^{-1}$) from rotational constants in reference [50].

**Table 4-VII:** PUMP Transitions for SEP Experiments at $\sim 11900$cm$^{-1}$. 
DUMP laser was pressure-scanned over the nominal range of 17150–17300 cm\(^{-1}\). This translates into an investigation of rotation-vibration structure located between 12000 cm\(^{-1}\) and 11850 cm\(^{-1}\) above the zero point energy of the ground electronic potential surface.

Figure 4-5 presents a stick spectrum corresponding to the SEP spectroscopic data obtained by pumping the \(4_{0,4} \rightarrow 3\) level of \(\tilde{A}^1A_2\) formaldehyde (i.e. term energy: 29157.254 cm\(^{-1}\)) and scanning the DUMP laser near 17260 cm\(^{-1}\) in search of linked downward rovibronic transitions. The depicted resonances correspond to individual eigenstates in the ground electronic potential surface with \(\sim 11900\) cm\(^{-1}\) of excitation distributed among their vibrational and rotational degrees of freedom. As evinced by the large number of observed transitions, the separation between adjacent vibrational levels in this region (\(\rho_{vib} \approx 0.52/\text{cm}^{-1}\)) is predicted to be quite comparable to the energy gaps which characterize the rotational fine structure of formaldehyde. Nevertheless, the SEP measurements illustrated in this figure comprise a rather isolated set of spectral features with no pronounced resonances appearing for nearly 15 cm\(^{-1}\) to higher or lower energies. This behavior suggests that significant structural differences can exist between adjacent vibrational levels with regards to their vibronic oscillator strengths.

A comparison of the term values depicted in figure 4-5 with those determined from SEP experiments performed upon the \(2_{0,2}\) and \(6_{0,6}\) eigenstates of \(\tilde{A}^1A_2\) formaldehyde (cf. table 4-VII) permitted identification of three pairs of R and P branches. The procedures employed for making such assignments have been described in Chapter 3 and will not be repeated here. The resonances characterized in this manner are labeled as P or R in the stick spectrum. Therefore, at least three vibronic bands are required in order to account for the observed pattern of SEP transitions.
Figure 4-5: SEP Stick Spectrum Near 11900 cm$^{-1}$ of Excitation in $\tilde{X}^1A_1$ H$_2$CO.
H₂CO SEP Resonances Near 11,900 cm⁻¹

PUMP: ⁴⁰ ⁴₀ ⁴₀,₄⁻⁴₁,₃

ρ_{vib} ≈ 0.52/cm⁻¹

SEP Signal Amplitude (arb)

Term Energy (cm⁻¹)

11880. 11885. 11890. 11895. 11900. 11905.
On the basis of signal magnitudes derived from polarization spectroscopy measurements, several of the more pronounced spectral lines in figure 4-5 could be identified as Q branch DUMP transitions. The resonances assigned in this manner are labeled as Q in the stick spectrum. Of particular interest are the two nearly degenerate transitions which correspond to $\tilde{X}^1A_1$ eigenstates possessing $\sim 11898.5 \text{ cm}^{-1}$ of excitation. Since both of these features are designated as Q branches, they must correspond to rovibronic DUMP transitions which terminate upon distinct $J = 4$ rotational levels in adjacent vibrational states.

The relatively high intensities of the spectral lines in figure 4-5 suggests the presence of $b$-type vibronic DUMP transitions. These vibronic bands are known to account for approximately 75% of the total oscillator strength in the formaldehyde $\tilde{A} \leftrightarrow \tilde{X}$ electronic system [69, 70]. Under this assumption, the pronounced Q branch features at 11895.2 cm$^{-1}$ of excitation can be correlated with $4_{1,3}$ rotational eigenstates in highly excited vibrational levels. The rotational energy associated with a $4_{1,3}$ eigenstate is estimated to be $\sim 33 \text{ cm}^{-1}$ on the basis of spectroscopic constants derived from the vibrationless level of $\tilde{X}^1A_1$ formaldehyde [50]. Therefore, the strong resonances in the SEP spectrum can be ascribed to vibrational states with band origins in the vicinity of 11860 cm$^{-1}$. These arguments will also hold true for $c$-type vibronic bands which are responsible for nearly all of the remaining oscillator strength in the $\tilde{A} \leftrightarrow \tilde{X}$ transition [69]. However, $c$-type rovibronic selection rules stipulate that the Q branch resonances terminate upon $4_{1,4}$ rotational eigenstates (i.e. estimated rotational energy: $\sim 32 \text{ cm}^{-1}$).

Table 4-VIII contains a compilation of vibrational levels predicted, on the basis of the constants derived by Reisner, et. al. [228], to be in the vicinity of 11860 cm$^{-1}$. Only those vibrational states which would support reasonably strong DUMP transitions from the $v_4 = 3$ level of $\tilde{A}^1A_2$ formaldehyde are presented. The
<table>
<thead>
<tr>
<th>Vibrational Level</th>
<th>Term&lt;sup&gt;a&lt;/sup&gt; Value</th>
<th>Vibrational Symmetry</th>
<th>Transition&lt;sup&gt;b&lt;/sup&gt; Type</th>
<th>$4^1$ DUMP Oscillator&lt;sup&gt;c&lt;/sup&gt; Strength</th>
<th>$4^3$ DUMP Oscillator&lt;sup&gt;c&lt;/sup&gt; Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2_2^2 3_1^4 6_6$</td>
<td>11766.3</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$4.47 \times 10^{-6}$</td>
<td>$1.01 \times 10^{-5}$</td>
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<tr>
<td>$1_2^2 2_1^4 4_4$</td>
<td>11771.5</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$1.65 \times 10^{-9}$</td>
<td>$4.45 \times 10^{-10}$</td>
</tr>
<tr>
<td>$2_7$</td>
<td>11804.6</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$(1.1 \times 10^{-6})$</td>
<td>$(1.3 \times 10^{-6})$</td>
</tr>
<tr>
<td>$4_6^6 6_4$</td>
<td>11816.2</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$1.43 \times 10^{-9}$</td>
<td>$3.24 \times 10^{-9}$</td>
</tr>
<tr>
<td>$2_2^3 1_4^5 6_1$</td>
<td>11838.7</td>
<td>$a_2$</td>
<td>$c$</td>
<td>$1.23 \times 10^{-7}$</td>
<td>$1.41 \times 10^{-7}$</td>
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<tr>
<td>$2_1^3 1_4^5 5_1^6_2$</td>
<td>11854.8</td>
<td>$a_2$</td>
<td>$c$</td>
<td>$2.58 \times 10^{-9}$</td>
<td>$3.50 \times 10^{-11}$</td>
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<tr>
<td>$2_1^4 4_5^5_2$</td>
<td>11857.0</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$3.91 \times 10^{-9}$</td>
<td>$1.06 \times 10^{-9}$</td>
</tr>
<tr>
<td>$1_1^4 8$</td>
<td>11861.4</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$(2.8 \times 10^{-7})$</td>
<td>$(6.4 \times 10^{-7})$</td>
</tr>
<tr>
<td>$1_3^3 1_4^4 2_2$</td>
<td>11868.5</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$1.90 \times 10^{-10}$</td>
<td>$4.56 \times 10^{-11}$</td>
</tr>
<tr>
<td>$2_3^3 3_4^4 2_2$</td>
<td>11877.4</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$4.77 \times 10^{-8}$</td>
<td>$1.14 \times 10^{-8}$</td>
</tr>
<tr>
<td>$2_3^3 3_4^4 1_6_1$</td>
<td>11880.4</td>
<td>$a_2$</td>
<td>$c$</td>
<td>$1.35 \times 10^{-9}$</td>
<td>$1.51 \times 10^{-9}$</td>
</tr>
<tr>
<td>$2_3^3 3_4^4 1_5_1$</td>
<td>11882.8</td>
<td>$a_2$</td>
<td>$c$</td>
<td>$2.39 \times 10^{-9}$</td>
<td>$2.56 \times 10^{-9}$</td>
</tr>
<tr>
<td>$1_1^2 2_4^4 2_2$</td>
<td>11892.5</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$6.07 \times 10^{-7}$</td>
<td>$1.45 \times 10^{-7}$</td>
</tr>
<tr>
<td>$2_2^2 3_1^4 6_2$</td>
<td>11907.3</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$1.03 \times 10^{-7}$</td>
<td>$2.78 \times 10^{-8}$</td>
</tr>
<tr>
<td>$2_2^4 5_1$</td>
<td>11914.3</td>
<td>$a_2$</td>
<td>$c$</td>
<td>$8.99 \times 10^{-7}$</td>
<td>$1.02 \times 10^{-6}$</td>
</tr>
<tr>
<td>$1_1^4 7 6_1$</td>
<td>11927.9</td>
<td>$a_2$</td>
<td>$c$</td>
<td>$(7.8 \times 10^{-9})$</td>
<td>$(8.9 \times 10^{-9})$</td>
</tr>
<tr>
<td>$1_1^2 4_4^4 6_1$</td>
<td>11940.7</td>
<td>$a_2$</td>
<td>$c$</td>
<td>$1.71 \times 10^{-8}$</td>
<td>$1.92 \times 10^{-8}$</td>
</tr>
<tr>
<td>$2_3^4 6$</td>
<td>11956.4</td>
<td>$a_1$</td>
<td>$b$</td>
<td>$1.89 \times 10^{-5}$</td>
<td>$4.28 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

<sup>a</sup> In cm<sup>-1</sup>.

<sup>b</sup> DUMP transition type referred to either $4^1$ or $4^3$ PUMP.

<sup>c</sup> Values in parentheses estimated from lower energy vibrational levels.

**Table 4-VIII:** Vibrational Levels Near 11860 cm<sup>-1</sup> of Excitation.
tabulated oscillator strengths were determined from the \textit{ab initio} one-dimensional overlap integrals of van Dijk [179]. Previous SEP studies [180] have demonstrated that these SCF-CI calculations consistently overestimate the intensities of resonances involving the \( \nu_3 \) symmetric CH\(_2\) deformation mode.

The assignment of definitive \( \tilde{X}^1A_1 \) vibrational quantum numbers to the DUMP transitions depicted in figure 4-5 is severely complicated by the large density of vibrational levels predicted in the region of 12000cm\(^{-1}\). Indeed, there has been considerable speculation as to whether it is even appropriate to attribute distinct vibrational labels to individual rotation-vibration eigenstates in such high energy regimes [260, 261, 143]. Nevertheless, tentative vibrational assignments can be obtained through consideration of vibronic transition moments. The oscillator strengths presented in table 4-VIII, in conjunction with the intensity patterns derived from SEP measurements performed at much lower energies [180], suggest that the resonances in figure 4-5 can be identified with four candidate vibrational levels from the \( \tilde{X} \) state: \( 27, 2_{14}5_2, 2_{14}4_2, \text{ and } 1_{12}4_2 \). The discrepancies between the tabulated band origins and the value of 11860cm\(^{-1}\) determined from the Q branch rotational structure of the SEP data are not significant given the uncertainties associated with the calculated term energies. Attempts to exploit rotational constants as a means of further refining the vibrational character for the highly excited eigenstates did not prove to be successful.

The TAPS kinetic studies at 11900cm\(^{-1}\) of excitation concentrated upon the pronounced Q branch features depicted in the stick spectrum of figure 4-5. For \( b \)-type, DUMP transitions, each of these SEP resonances will correspond to a single \( 4_{1,3} \) rotational level in one of the \( a_1 \) vibrational modes located in this region of the \( \tilde{X}^1A_1 \) potential surface. The rotation-vibration eigenstates examined during the course of these experiments are tabulated in table 4-IX along with their observed
<table>
<thead>
<tr>
<th>Designation</th>
<th>$\tilde{X}^1A_1$ Target&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Term&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAPS-7</td>
<td>$^4_{1,3}$</td>
<td>11888.101</td>
</tr>
<tr>
<td>TAPS-8</td>
<td>$^4_{1,3}$</td>
<td>11892.504</td>
</tr>
<tr>
<td>TAPS-9</td>
<td>$^4_{1,3}$</td>
<td>11892.647</td>
</tr>
</tbody>
</table>

<sup>a</sup> See text for tentative vibrational assignments.

<sup>b</sup> In cm<sup>-1</sup>.

**Table 4-IX:** Target $\tilde{X}^1A_1$ Levels Near 11900 cm<sup>-1</sup>.
term values. As discussed above, each of the target levels is designated by the "TAPS-#" notation in order to distinguish between the various four level schemes (cf. figure 4-1) employed in the present time-resolved experiments.

Table 4-X contains a detailed compilation of the PUMP, DUMP, and PROBE transitions which were employed in the TAPS kinetic studies at \( \sim 11900 \text{ cm}^{-1} \). The vibrational character for the highly excited \( \tilde{X}^1A_1 \) eigenstates cannot be precisely defined but is limited to one of the small subset of possibilities suggested on the basis of the above analysis. All of the tabulated DUMP and PROBE resonances were confirmed to be \( Q \) branch transitions through polarization spectroscopy measurements.

4.4.2 Depopulation Studies

Figure 4-6 presents a typical time-resolved decay profile recorded during our investigation of depopulation processes in highly excited \( \tilde{X}^1A_1 \) formaldehyde-\( h_g \). The target for this particular measurement was the \( 5_{1,4}^1 \rightarrow 4_4^1 \) rotation-vibration level (cf. TAPS-1 in tables 3-III and 3-IV) — a single molecular eigenstate located \( \sim 11380 \text{ cm}^{-1} \) above the zero point energy of the ground electronic potential surface. The actual data, denoted by the fine black line, were obtained by directly monitoring the transitory depolarization of the cw PROBE beam subsequent to the abrupt creation of an optical anisotropy within the target level by the PUMP and DUMP radiation. This trace was acquired through a high-speed transient digitizer which had been programmed to signal average over 1024 repetitions of the PUMP/DUMP pulse sequence. Similar curves were obtained for various formaldehyde pressures ranging from 0 to 350 mTorr.

The thick curve in figure 4-6 represents the results of a non-linear least squares regression procedure in which a single exponential decay, having adjustable
Table 4-X: Transition Data for TAPS at $\sim 11900\text{cm}^{-1}$. 
<table>
<thead>
<tr>
<th>Designation</th>
<th>PUMP(^a) Transition</th>
<th>PUMP(^a) Energy</th>
<th>DUMP(^c) Transition</th>
<th>DUMP(^b) Energy</th>
<th>PROBE(^d) Transition</th>
<th>PROBE(^b) Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAPS-7</td>
<td>(4_0,1 \leftrightarrow 4_{1,3})</td>
<td>28333.905</td>
<td>(4_0,1 \rightarrow 4_{1,3})</td>
<td>16445.804</td>
<td>(4_0,1 \leftrightarrow 4_{1,3})</td>
<td>17269.153</td>
</tr>
<tr>
<td>TAPS-8</td>
<td>(4_0,1 \leftrightarrow 4_{1,3})</td>
<td>28333.905</td>
<td>(4_0,1 \rightarrow 4_{1,3})</td>
<td>16441.401</td>
<td>(4_0,1 \leftrightarrow 4_{1,3})</td>
<td>17264.750</td>
</tr>
<tr>
<td>TAPS-9</td>
<td>(4_0,1 \leftrightarrow 4_{1,3})</td>
<td>28333.905</td>
<td>(4_0,1 \rightarrow 4_{1,3})</td>
<td>16441.259</td>
<td>(4_0,1 \leftrightarrow 4_{1,3})</td>
<td>17264.607</td>
</tr>
</tbody>
</table>

\(^a\) PUMP Vibronic Transition: \(\tilde{A}^1A_2 \leftrightarrow \tilde{X}^1A_1\); \(4^1_0\).

\(^b\) In cm\(^{-1}\).

\(^c\) DUMP Vibronic Transition: \(\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1\); see text for vibrational assignment.

\(^d\) PROBE Vibronic Transition: \(\tilde{A}^1A_2 \leftrightarrow \tilde{X}^1A_1\); see text for vibrational assignments.
Figure 4-6: TAPS Data for $5_{1.4} 2_{4.4}$ Target Level.
$\text{H}_2\text{CO} \quad \tilde{X}^1\text{A}_1 \quad 2_{44} \quad 5_{1,4}$

$E_{\text{vib-rot}} = 11,379.24 \text{ cm}^{-1}$

$P = 0.0582 \text{ Torr}$

$\Gamma_{\text{obs}} = 13.51 \pm 0.25 \mu\text{sec}^{-1}$

$\Gamma = 6.76 \pm 0.12 \mu\text{sec}^{-1}$

$\tau = 148.3 \pm 2.7 \text{ ns}$
lifetime and amplitude parameters, was convoluted with the temporal response function for our experimental apparatus. A decay rate of $13.51 \pm 0.25 \mu\text{sec}^{-1}$ (one standard deviation uncertainty) is measured for the indicated formaldehyde pressure of $\sim 58 \text{mTorr}$. As discussed in Chapter 3, the time-domain behavior of pure polarization spectroscopy dictates that, in the absence of external perturbations, the observed decay rates, $I^{\text{obs}}$, will correspond to exactly twice the true rate of population removal, $I^{\text{depop}}$ (cf. equations (3.52) and (3.55)). Therefore, provided that the depolarizing effects of reorientation collisions can be neglected, the data illustrated in figure 4-6 can be associated with a collision-limited lifetime of $\tau = 1/I^{\text{depop}} = 2/I^{\text{obs}} = 148 \pm 2.7 \text{ns}$. The work presented in the previous Chapter has provided ample justification for ignoring the influence of pure $M$-changing processes in the case of strongly dipolar formaldehyde self-relaxation.

The Stern-Volmer plot presented in figure 4-7 summarizes the pressure dependence for the observed decay rates in the highly excited $5_{1,4}$ eigenstate. The decay parameters determined from the least squares analysis of our time-resolved TAPS measurements are found to be directly proportional to the density (i.e. pressure) of the formaldehyde sample. A linear regression performed upon these data yields $k_T = \frac{1}{2} k_{\text{obs}} = 115.1 \pm 3.0 \mu\text{sec}^{-1} \text{Torr}^{-1}$ as the collision-induced depopulation rate for the target level (nb. the factor of $\frac{1}{2}$ associated with the observed rate constant, $k_{\text{obs}}$, follows from the temporal characteristics of pure polarization spectroscopy). This rate of total population removal, which corresponds to a velocity averaged cross section of $548 \pm 15 \text{Å}^2$, is more than an order of magnitude larger than the value suggested by hard sphere gas kinetic encounters [157]. Unfortunately, a reliable zero-pressure lifetime for the highly excited molecular system could not be obtained from the present kinetic measurements. Since this collision-free parameter corresponds to the radiative
Figure 4-7: Stern-Volmer Plot for $5_{1,4} 2_{4,4}$ Target Level.
$H_2CO \quad \tilde{X}^1A_1 \quad 2_4^4_4 \quad 5_{1,4}$

$E_{vib\text{-}rot} = 11,379.24 \text{ cm}^{-1}$

$k_T = 115.1 \pm 3.0 \text{ \mu sec}^{-1} \text{ Torr}^{-1}$

$\sigma_T = 548 \pm 15 \text{ A}^2$
lifetime for a rotation-vibration eigenstate, it can be estimated from transition moments to be on the order of a millisecond [157].

Table 4-XI contains a compilation of the depopulation rates and total removal cross sections determined for various highly excited rotation-vibration eigenstates in $\tilde{X}^1A_1$ formaldehyde-$h_\nu$. The measured values are grouped according to their energy above the zero point of the ground electronic state and are designated by the "TAPS-#" notation applied to the target levels in tables 4-V and 4-IX.

The kinetic parameters compiled in table 4-XI indicate that collision-induced depopulation of $\tilde{X}^1A_1$ rotation-vibration levels proceeds with rates which are at least ten times faster than the value of $10 \mu \text{sec}^{-1} \text{Torr}^{-1}$ predicted on the basis of hard sphere encounters [157]. This behavior suggests that collisional relaxation for individual eigenstates in high energy regions of the ground electronic potential surface is dominated by pure rotation-to-rotation energy transfer channels. The long range dipolar interactions which govern rotation changing processes in the formaldehyde-formaldehyde collision system (cf. Chapters 2 and 3) can readily account for the large total removal cross sections observed in the TAPS studies.

The predominant role which pure rotational relaxation plays in the depopulation of highly excited formaldehyde supports the conventional notion of rotation-to-rotation energy transfer as the most probable of all inelastic collision-induced processes [157]. From this viewpoint, the temporal evolution of the molecules initially prepared in a single rotation-vibration eigenstate of the $\tilde{X}^1A_1$ potential surface can be characterized by the rapid establishment of an equilibrium among the collisionally-coupled rotational levels within the target vibrational level. The metastable distribution of rovibrational population created in this manner subsequently relaxes through much less efficient collisional channels (e.g. vibration-to-vibration energy transfer). This rapid equilibration of molecules among rotational
<table>
<thead>
<tr>
<th>Designation</th>
<th>Rotational Level</th>
<th>Term Energy$^a$</th>
<th>Depopulation Rate$^b$</th>
<th>Depopulation Cross Section$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAPS-1</td>
<td>$5_{1,4}$</td>
<td>11379.235</td>
<td>115.1±3.0</td>
<td>548±15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(3.553±0.097)</td>
<td></td>
</tr>
<tr>
<td>TAPS-2</td>
<td>$4_{1,3}$</td>
<td>11367.269</td>
<td>108.3±5.7</td>
<td>515±28</td>
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<tr>
<td></td>
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<td></td>
<td>(3.34±0.18)</td>
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</tr>
<tr>
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<td>$5_{1,5}$</td>
<td>11377.620</td>
<td>106.8±6.0</td>
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<td></td>
<td>(3.30±0.19)</td>
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<td>$5_{1,5}$</td>
<td>11378.818</td>
<td>105.4±6.8</td>
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<td>(3.25±0.21)</td>
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<tr>
<td>TAPS-5</td>
<td>$6_{1,5}$</td>
<td>11393.554</td>
<td>114.2±2.2</td>
<td>543±11</td>
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<td></td>
<td>(3.525±0.074)</td>
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<tr>
<td>TAPS-6</td>
<td>$13_{1,1}$</td>
<td>11599.056</td>
<td>127.2±3.8</td>
<td>605±19</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>(3.93±0.12)</td>
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<tr>
<td>TAPS-7</td>
<td>$4_{1,3}$</td>
<td>11888.101</td>
<td>128.5±6.4</td>
<td>612±19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(3.97±0.20)</td>
<td></td>
</tr>
<tr>
<td>TAPS-8</td>
<td>$4_{1,3}$</td>
<td>11892.504</td>
<td>148±15</td>
<td>704±72</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>(4.57±0.46)</td>
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</tr>
<tr>
<td>TAPS-9</td>
<td>$4_{1,3}$</td>
<td>11892.647</td>
<td>146±14</td>
<td>693±66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(4.49±0.43)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In cm$^{-1}$.

$^b$ In μsec$^{-1}$Torr$^{-1}$ (value in parentheses in cm$^3$molec$^{-1}$sec$^{-1}$ × 10$^9$).

$^c$ In Å$^2$.

**Table 4-XI:** Depopulation Data for Highly Excited $\tilde{X}^1A_1$ Formaldehyde.
eigenstates was exploited by Lawrance and Knight [206, 207] for their studies of vibrational relaxation cross sections in the ground electronic state of \( p \)-difluorobenzene. However, the ensuing discussion will demonstrate, through comparison of the total removal rates determined for differing amounts of rotational and vibrational excitation, that the manifold of background states (i.e. vibrational states other than the one initially populated) can exert a measurable effect upon the collisional deactivation of individual rotation-vibration levels in \( \tilde{X} \) \(^1\)A\(_1\) formaldehyde. This behavior suggests that the efficiency, as well as the number, of depopulation channels available to formaldehyde in regions of extreme excitation is slightly dependent upon the magnitude and type of internal motion deposited into the molecular framework.

It will prove instructive to compare the the depopulation rates determined for highly excited rotation-vibration eigenstates in \( \tilde{X} \) \(^1\)A\(_1\) formaldehyde-\( h_2 \) (cf. Table 4-XI) with the results obtained from microwave pressure-broadening measurements performed in the vibrationless level. Both theory [262] and experiments [188, 189] suggest that the linewidth parameters, \( \Delta \nu_p \), associated with the self-relaxation of formaldehyde are typically in excess of 25MHz/Torr. These spectral quantities can be readily converted into a total collisional removal rate, \( k_T \), through the following Fourier transform equality:

\[
k_T = \frac{1}{\tau_p} = 2\pi \Delta \nu_p
\]  

(4.11)

where \( \tau_p \) denotes the characteristic relaxation time for the pressure broadening measurement. This equation assumes that the spectral lineshape for the microwave transition is well represented by a Lorentzian profile.

Application of equation (4.11) to the self-broadening linewidth parameters of
formaldehyde yields a depopulation rate of \( k_T \approx 160 \mu \text{sec}^{-1} \text{Torr}^{-1} \). This value is significantly larger than any total removal rate measured in the present investigation. Therefore, provided that microwave pressure-broadening can be justifiably interpreted in terms of the collisional relaxation of an individual eigenstate (cf. following discussion), the TAPS results suggest that the selective deposition of more than 11000 cm\(^{-1}\) of rotation-vibration energy into formaldehyde is accompanied by an overall reduction in the rate of collision-induced depopulation processes. Despite the fact that the energy regime examined in our experiments supports a density of vibrational states which exceeds the density of the corresponding rotational fine structure, the highly excited formaldehyde molecules appear to be relaxing with less efficiency than that encountered in the vibrationless level.

The precise relationship of microwave pressure-broadening to the rates of collision-induced depopulation for individual eigenstates has been a subject of considerable speculation. Although some controversy still exists with regard to the modelling of linewidth parameters in terms of specific state-to-state energy transfer channels, there is universal agreement that pressure-broadening is primarily governed by the total cross section for inelastic collisions. Gordon [263, 264] has suggested that a small portion of experimentally measured linewidths might be attributed to pure reorientation processes (i.e. \( M \)-changing collisions) which produce a modulation in the amplitude of observed spectral lines without altering the populations within rotational levels. This mechanism has been proposed by Oka [160] as a possible source of discrepancies between direct time-resolved and indirect pressure-broadening studies of molecular relaxation phenomena.

The TAPS technique is based upon a time-resolved variant of polarization spectroscopy which should be quite sensitive to the depolarizing effects that
accompany collision-induced reorientation. Therefore, elastic $M$-changing processes can not account for the discrepancy between our depopulation rates and those inferred from microwave pressure-broadening. However, in contrast to the TAPS measurements, linewidth parameters can be influenced by pure phase-interrupting collisions [265, 266]. This collisional mechanism can broaden and shift spectral lines through an abrupt disruption of the oscillating dipole moment associated with a spectroscopic transition. The phase change which is collisionally introduced into the coherence train of the dipole oscillator translates into a decrease in the effective lifetime of the transition (e.g. a decrease of $\tau_p$ in equation (4.11)) while the populations within individual rovibronic levels remain unaltered. Although such phase-interrupting processes have been observed in optical transitions [267, 268], the role which they play in the microwave and infrared regions has not been firmly established. Infrared coherent transient experiments performed by Brewer and coworkers [269] on the strongly dipolar $^{13}$CH$_3$F collision system have indicated that phase-changing collisions represent a completely negligible relaxation channel. Van Stryland and Shoemaker [270] have reported similar conclusions from their collisional studies of $^{15}$NH$_3$.

It is interesting to note that the total removal cross sections compiled in table 4-XI are, for the most part, closer in magnitude to the values determined for $\tilde{X}^1A_2$ formaldehyde (cf. Chapters 2 and 3) than those inferred from microwave pressure-broadening measurements performed in the vibrationless level of the $\tilde{X}^1A_1$ potential surface. Since the probability for dipole-dipole interactions scales as the square of the permanent electric dipole moment present in each collision partner [160], the difference in rotational relaxation efficiency between the $\tilde{A}$ and $\tilde{X}$ manifolds can be attributed to the smaller dipole moment associated with the electronically excited state (viz. 1.46D vs. 2.33D).
In view of the arguments presented above, the depopulation rates derived from the TAPS studies might be rationalized in terms of target rotation-vibration eigenstates which possess substantially smaller dipole moments than the value of 2.33D which characterizes the vibrationless level of the ground electronic state. However, previous spectroscopic investigations [11] indicate that the vibrational dependence of the \( \tilde{X}^1A_1 \) dipole moment is not large enough to account completely for the differences between the total removal cross sections measured in highly excited formaldehyde and those inferred from pressure-broadening in the vibrationless level. Ultimately, these discrepancies suggest that the precise relationship of the linewidth parameter, \( \Delta \nu_p \), for a microwave transition to the collisional relaxation rate for an individual molecular eigenstate is in need of further theoretical clarification.

The TAPS studies performed upon the \( K_a = 1 \) rotational eigenstates at \( \sim 11300 \text{cm}^{-1} \) of excitation (viz. TAPS-1 thru TAPS-5) all indicate collisional depopulation rates on the order of \( 110 \mu \text{sec}^{-1} \text{Torr}^{-1} \). A notable exception to this pattern is to be found in the kinetic parameters derived from the \( J = 13 \) level (i.e. TAPS-6) which exhibit a somewhat larger total removal cross section. This behavior can be rationalized in terms of vibrational mode mixing induced by rotation-dependent Coriolis perturbations [56]. Dai, et. al. [143] have demonstrated that such rotation-vibration couplings can significantly diminish the structural differences between neighboring vibrational levels and promote a local averaging of vibrational character together with a partial destruction of the \( K_a \) quantum number. These interactions are expected to become more pervasive as the density of vibrational states and the degree of rotational excitation increases.

The rotation-vibration coupling associated with Coriolis interactions provides a mechanism through which a local breakdown in the distinction between rotational
and vibrational degrees of freedom can be realized. As a result, energy transfer between individual rovibrational states, which are of mixed vibrational parentage due to the Coriolis perturbation, can proceed via efficient pure rotational relaxation channels (e.g. long range coupling of permanent multipole moments). This phenomenon explains the rapid mode-to-mode vibrational energy transfer observed by Orr and coworkers [191, 192] between the $\nu_6$ (i.e. antisymmetric CH$_2$ rock; $E_{vib} \approx 989cm^{-1}$) and $\nu_4$ (i.e. out-of-plane bend; $E_{vib} \approx 938cm^{-1}$) fundamentals in $\tilde{X}^1A_1$ formaldehyde-$d_2$. For the TAPS studies, the presence of these additional, rotation-induced depopulation channels can account for the enhanced total removal rate measured for the $J = 13$ eigenstate. The other kinetic experiments performed at $\sim 11300cm^{-1}$ of excitation entail target levels with substantially smaller rotational quantum numbers (i.e. in both $J$ and $K_a$) which will not support pronounced Coriolis interactions.

The TAPS experiments performed upon the $4_{1,3}$ eigenstates at $\sim 11900cm^{-1}$ of excitation (viz. TAPS-7 thru TAPS-9) indicate collisional depopulation rates which are $\sim 25\%$ larger than that determined for the identical rotational level (i.e. TAPS-2) at $\sim 11350cm^{-1}$. The discrepancy in the total removal cross sections can be qualitatively correlated with the difference in the calculated density of vibrational states associated with the 11350cm$^{-1}$ and 11900cm$^{-1}$ regions of the ground electronic potential surface (viz. $\rho_{vib} \approx 0.42/cm^{-1}$ at 11350cm$^{-1}$ and $\rho_{vib} \approx 0.52/cm^{-1}$ at 11900cm$^{-1}$). This behavior strongly suggests that the collision-induced processes which govern depopulation of highly excited target levels in $\tilde{X}^1A_1$ formaldehyde are sensitive to the manifold of vibrational background states. Although pure rotation-to-rotation channels constitute the predominant self-relaxation mechanism (as evinced by the $\sim 10$ times gas kinetic depopulation rates), the total removal rate is definitely influenced by the presence of surrounding
vibrational levels. From this viewpoint, the enhanced cross section measured for the $J = 13$ eigenstate during the TAPS-6 study can be interpreted as another manifestation of an effective increase in the density of collisionally-coupled background states, this time brought about by rotation-dependent Coriolis perturbations.

As mentioned in conjunction with the SEP stick spectrum presented in figure 4-5, the target levels at $\sim 11900\text{cm}^{-1}$ of excitation (viz. TAPS-7 thru TAPS-9) can be nominally assigned to $4_{1,3}$ rotational eigenstates in three separate vibrational levels. Since these levels possess identical rotational quantum numbers (i.e. similar Coriolis interactions) and are located in the same region of the $\tilde{X}^1A_1$ potential surface (i.e. influenced by nearly identical manifolds of background states), their collisional properties are expected to be quite similar. However, the kinetic parameters contained in table 4-XI indicate that the collision-induced depopulation rates ascribed to these target levels display substantial differences. In particular, the two nearly degenerate eigenstates at $\sim 11899\text{cm}^{-1}$ (viz. TAPS-8 and TAPS-9) display total removal cross sections which are roughly 15% larger than the value determined for the TAPS-7 target level.

It must be stressed that the variations in the depopulation rates observed at $\sim 11900\text{cm}^{-1}$ of excitation are barely above the level of statistical significance. This fact, together with the nearly overlapping nature of the spectral features examined at $11899\text{cm}^{-1}$ (i.e. TAPS-8 and TAPS-9), casts some doubt on the validity of the differences measured in the total removal cross sections. However, it is interesting to speculate that such deviations, if substantiated by future experiments, could indicate that a given energy region of the $\tilde{X}^1A_1$ potential surface can support vibrational levels which exhibit quite different collisional relaxation properties. This vibrational specificity would have important repercussions in many area of chemical
physics and might provide some insight into the use of selective rotation-vibration excitation as a means of controlling the outcome of chemical processes.

In conclusion, the TAPS experiments have demonstrated that the selective deposition of substantial rotation-vibration energy (viz. $> 11000 \text{ cm}^{-1}$) into $\tilde{X}^1A_1$ formaldehyde does not produce a drastic variation in the measured rates for collision-induced depopulation (i.e. as compared to lower energy regions). This behavior can be rationalized in terms of the predominant role which pure rotation changing collisions play in the self-relaxation of formaldehyde. Although some evidence was obtained for depopulation processes which depend upon the surrounding manifold of vibrational states, the primary collision-induced relaxation channel for individual, highly excited eigenstates in $\tilde{X}^1A_1$ formaldehyde is believed to entail rotation-to-rotation energy transfer within a single vibrational level (viz. the target vibrational level initially prepared). Corroboration of this supposition, as well as the identification of any special collisional properties which characterize such regimes of extreme excitation, will have to await future experiments specifically designed to examine state-to-state kinetic pathways.
Appendix A
Calculation of Dipole Matrix Elements

Many problems in molecular physics require explicit computation of the interaction energy between a molecular electric dipole moment and an electric field. Two examples of special importance for the work presented in this Thesis involve the analysis of Stark effects and the determination of spectroscopic transition intensities. These calculations are complicated by the fact that the molecular moments of interest are defined in the body-fixed axis system while the perturbing electric field is described in terms of space-fixed coordinates. It is the purpose of this Appendix to illustrate how the matrix elements of such interaction terms can be evaluated in the basis set of a symmetric rotor. As might be expected, the ensuing calculations will necessitate that a transformation be made between the molecule-fixed and laboratory-fixed reference frames.

The quantum-mechanical operator, $H_{\text{int}}$, describing the interaction between a molecular dipole moment and an external electric field can be formulated in terms of a scalar product between two rank one spherical tensors (cf. Chapter 1):

$$H_{\text{int}} = -T^1(\mu) \cdot T^1(E)$$  \hspace{1cm} (A.1)

where

$T^1(\mu)$ represents the molecular dipole moment vector,

$T^1(E)$ represents the external electric field vector.

Expansion of this scalar product yields the following equation:
\[ H_{\text{int}} = -\sum_p (-1)^p T_p^1(\mu) T_{-p}^1(E) \] (A.2)

where the superscript \( p \) denotes components of the irreducible spherical tensors referred to the space-fixed coordinate system in which the applied electric field is defined.

Since the molecular dipole moment of interest is defined in the molecule-fixed (i.e. body-fixed) frame of reference, a transformation into this coordinate system must be performed:

\[ T_p^1(\mu) = \sum_q \rho_{pq}^{(1)}(\Omega)^* T_q^1(\mu) \] (A.3)

where

- \( \Omega \) represents the set of Euler angles that specify the relative orientation of the space-fixed and body-fixed reference frames,
- \( \rho_{pq}^{(1)}(\Omega)^* \) denotes the complex conjugate of the \( (p,q)^{th} \) element in the Wigner rotation matrix of rank 1 [40]. This function of the Euler angles, \( \Omega \), is essentially a matrix representation of the rotation operator connecting the space-fixed and body-fixed coordinate systems.

The \( q \) subscripts which appear in equation (A.3) denote components referred to the molecule-fixed coordinate system while, as mentioned above, \( p \) is defined with respect to the space-fixed axes.

Substitution of expression (A.3) into the interaction Hamiltonian of equation (A.2) gives:

\[ H_{\text{int}} = -\sum_p \sum_q (-1)^p \rho_{pq}^{(1)}(\Omega)^* T_q^1(\mu) T_{-p}^1(E) \] (A.4)
The matrix elements of this interaction Hamiltonian can now be evaluated in a basis set of symmetric rotor eigenfunctions which are designated by the quantum numbers $J$, $K$, $M$, and $\gamma$:

\[
\langle \gamma J'K'M' | H_{int} | \gamma JK M \rangle = -\sum_p \sum_q (-1)^p \langle J'K'M' | D^{(1)}_{p,q}(\Omega) \rangle^* | JKM \rangle \\
\times \langle \gamma | T^1_q(\mu) | \gamma \rangle T^1_{-p}(E)
\]

where $K$ and $M$ denote the projection of the total angular momentum $J$ along the molecule-fixed and space-fixed $z$ axes respectively and $\gamma$ represents all other quantum numbers (e.g. quantum numbers for vibrational and electronic degrees of freedom) required to describe the molecular system.

It should be apparent that equation (A.5) has assumed an explicit separability of rotational motion from other molecular degrees of freedom. Since $\langle \gamma | T^1_q(\mu) | \gamma \rangle$ denotes a constant (i.e. the $q^{th}$ spherical component of the dipole moment in vibronic state $\gamma$), the problem has been reduced to evaluation of the matrix elements for the Wigner rotation functions $D^{(1)}(\Omega)$.

Evaluation of the $D^{(1)}(\Omega)$ matrix elements in equation (A.5) begins by realizing that the wavefunctions of a symmetric rotor can be described in terms of the Wigner rotation functions [271]:

\[
|JKM\rangle = \left( \frac{2J+1}{8\pi^2} \right)^{1/2} D^J_{MK}(\Omega)^* \]
For the general case of a $k^{th}$ rank rotation function, $D^{(k)}(\Omega)$, the required matrix element thus becomes:

\[
\langle J K' M' | D^{(k)}_{p q}(\Omega) | J K M \rangle = \frac{\sqrt{(2J'+1)(2J+1)}}{8\pi^2} \times \int_{\Omega} D^{(J')}_{M' K'}(\Omega) D^{(k)}_{p q}(\Omega) \ast D^{(J)}_{M K}(\Omega) \ast d\Omega
\]

\[
= \frac{\sqrt{(2J'+1)(2J+1)}}{8\pi^2} (-1)^{p-q+M-K} \times \int_{\Omega} D^{(J')}_{M' K'}(\Omega) D^{(k)}_{-p-q}(\Omega) D^{(J)}_{-M-K}(\Omega) d\Omega
\]  

(A.7)

where use has been made of the following symmetry property for the Wigner rotation functions [40]:

\[
D^{(k)}_{p q}(\Omega) \ast = (-1)^{p-q} D^{(k)}_{-p-q}(\Omega)
\]

Now the Clebsch-Gordan series [41] provides a means of contracting the product of two Wigner rotation functions possessing the same set of Euler angles $\Omega$:

\[
D^{(J)}_{-M-K}(\Omega) D^{(k)}_{-p-q}(\Omega) = \sum_{J''} \begin{pmatrix} J & k & J'' \\ -M-p & M+p & -K-q K+q \end{pmatrix} D^{(J'')}_{M+p K+q}(\Omega) \ast
\]

(A.8)

where the quantities enclosed in the large parentheses denote Wigner 3-j symbols [271].
Substitution of this expression into equation (A.7) and use of the orthogonality relationship for the Wigner rotation functions [41],

\[ \int_{\Omega} D_{M'}^{(j)}(\Omega) D_{M+p}^{(j')}^{*}(\Omega) \, d\Omega = \frac{8\pi^2}{2J'+1} \delta_{M',M+p} \delta_{J',J} \delta_{M+p+q,J'+q}, \]  

\[ (j'k'M')D_{p q}(\Omega)^{*} |JKM \rangle = (-1)^{M'-K'} \sqrt{(2J'+1)(2J+1)} \times \left( \begin{array}{c} j' \ k \ J \\ -M' \ p \ M \end{array} \right) \left( \begin{array}{c} j' \ k \ J \\ -K' \ q \ K \end{array} \right), \]  

(A.10)

The matrix elements of the interaction Hamiltonian presented in equation (A.4) are thus given by:

\[ \langle \gamma j'k'M' |H_{int}|\gamma JKM \rangle = (-1)^{M'-K'} \sqrt{(2J'+1)(2J+1)} \times \sum_{p} \sum_{q} (-1)^{p} \left( \begin{array}{c} J' \ 1 \ J \\ -M' \ p \ M \end{array} \right) \left( \begin{array}{c} J' \ 1 \ J \\ -K' \ q \ K \end{array} \right) \langle \gamma |T_q^{1}(\mu)|\gamma \rangle T^{-1}_{-p}(E), \]  

(A.11)

The rotational selection rules imposed upon the matrix elements of \( H_{int} \) can be readily obtained from this equation. By utilizing the symmetry properties associated with the Wigner 3-j symbols one finds:

\[ \Delta J = 0, \pm 1 \quad \Delta K = 0, \pm 1 \quad \Delta M = 0, \pm 1 \]

It is important to realize that the use of equation (A.11) with either right-
handed or left-handed circularly polarized radiation (i.e. $T^1_{+1}(E)$ and $T^1_{-1}(E)$ respectively) necessitates that the appropriate value of the index $p$ be incorporated into the first 3-j symbol (viz. $T^1_{\pm 1}(E)$ corresponds to $p=\mp 1$). For calculations involving multiple radiation fields (e.g. double and triple resonance experiments), the distinction between counterpropagation and copropagation, as well as between absorption and emission processes, must be taken into account [272, 273].

For many problems in molecular physics, the perturbing electric field is oriented along a single direction in space which can be defined as the quantization axis or laboratory-fixed $z$ axis for the ensuing calculations. In the spherical tensor representation, this suggests that:

$$T^1_{\pm 1}(E) = \frac{\mp 1}{\sqrt{2}} (E_x \pm iE_y) = 0$$

$$T^1_0(E) = E_z = \mathcal{E}$$  \hspace{1cm} (A.12)

where the subscripts $x$, $y$, and $z$ refer to the space-fixed axis system.

Under these circumstances, the matrix elements of the interaction Hamiltonian are given by:

$$\langle \gamma' J' K'M' \mid H_{\text{int}} \mid \gamma J K M \rangle = -(-1)^{M' - K'} \sqrt{(2J' + 1)(2J + 1)} \mathcal{E}$$

$$\times \left( \begin{array}{cc} J' & 1 \ J \\ -M' & 0 \ M \end{array} \right) \sum_q \left( \begin{array}{cc} -K' & q \ K \end{array} \right) \langle \gamma \mid T^1_q(\mu) \mid \gamma \rangle$$  \hspace{1cm} (A.13)

The symmetry properties of the first 3-j symbol in this expression indicate that, for the case of an electric field oriented along a specific spatial direction, the
interaction Hamiltonian will be diagonal in the magnetic quantum number $M$. The summation over the index $q$ has been retained in equation (A.13) to allow for the fact that the dipole moment, whether it be a permanent moment or a transition moment, can have nonzero components along all three of the molecule-fixed axes.
Appendix B
Stark Hamiltonian

The effective Hamiltonian, $H_{\text{eff}}(\mathcal{E})$, utilized for analysis of the Stark quantum beat measurements in Chapter 1 can be formulated as follows:

$$H_{\text{eff}}(\mathcal{E}) = H_0 + H_{\text{Stark}}(\mathcal{E}) \quad (B.1)$$

where $H_0$ denotes the (field-independent) rotational Hamiltonian for an asymmetric rotor [56] and $H_{\text{Stark}}(\mathcal{E})$ represents the (field-dependent) Stark Hamiltonian for an asymmetric rotor [274, 275].

In a $I'$ symmetric rotor basis set (viz. $|\gamma JKM\rangle$) the nonvanishing matrix elements for the rotational and Stark Hamiltonians are given by:

$$\langle \gamma JKM | H_0 | \gamma JKM \rangle = \frac{1}{2} (B' + C') J(J+1) \quad (B.2)$$

$$+ \left( A' - \frac{1}{2} (B' + C') \right) K^2$$

$$- \Delta_K^J K^4 - \Delta_{JK}^J K^2 J(J+1) - \Delta_J^J J^2(J+1)^2$$

$$+ H_K^J K^6 + H_{KJ}^J K^4 J(J+1) + H_{JK}^J K^2 J^2(J+1)^2 + H_J^J J^3(J+1)^3$$
\[ 
\langle \gamma J+1 M | H_0 | \gamma J-1 M \rangle = \frac{1}{4} (B^{\gamma} - C^{\gamma}) f(J,K) 
\]

\[ 
- \left( \delta_{J}^{\gamma} J(J+1) + \delta_{K}^{\gamma} (K^2+1) \right) f(J,K) 
\]

\[ 
+ \left( h_{J}^{\gamma} J^2(J+1)^2 + h_{K}^{\gamma} J(J+1)(K^2+1) + h_{K}^{\gamma} (K^4+6K^2+1) \right) f(J,K) 
\]

\[ 
\langle \gamma J K M | H_{Stark}(\mathcal{E}) | \gamma J K M \rangle = - \mu_0 \mathcal{E} \frac{K M}{J(J+1)} 
\]

\[ 
\langle \gamma J K M | H_{Stark}(\mathcal{E}) | \gamma J-1 K M \rangle = - \frac{\mu_0 \mathcal{E}}{J} \left( \frac{(J^2-K^2)(J^2-M^2)}{4J^2-1} \right)^{1/2} 
\]

where

\[ 
f(J,K) = \left( \left( J(J+1) - K(K+1) \right) \left( J(J+1) - K(K-1) \right) \right)^{1/2} 
\]

The superscript "\( \gamma \)" is appended to the rotational and centrifugal distortion constants in order to emphasize their dependence upon vibronic quantum numbers. These spectroscopic parameters correspond to a reduced asymmetric rotor Hamiltonian as derived by Watson [276]. The Stark Hamiltonian matrix elements presented in equations (B.4) and (B.5) denote the interaction of an \( a \)-axis dipole moment component (\( \text{viz. } \mu_0 \)) with an external electric field directed along the space-fixed \( z \) axis (\( \text{viz. } \mathcal{E} \)). No attempt has been made to incorporate the effects of centrifugal distortion into the Stark perturbation [100].
Appendix C
Stark Quantum Beat Data

The following pages present a compilation of the Stark quantum beat data which was obtained in conjunction with the dipole moment measurements of Chapter 1. Three experimental parameters (and their corresponding one standard deviation uncertainties) are tabulated for each rovibronic level examined in the $\tilde{A}^1\text{A}_2$ states of formaldehyde-$h_2$ and formaldehyde-$d_2$:

1. The voltage (in volts) applied to the Stark electrode assembly.

2. The electric field (in volts/cm) calculated on the basis of a Stark electrode separation of 0.65283(38) cm.

3. The quantum beat frequency (in MHz) determined through least squares analysis of the time-resolved fluorescence decay profiles.
**Stark Quantum Beat Data:** \( \text{H}_2\text{CO} \quad \tilde{A} \quad ^1\text{A}_2 \quad v_4 = 0 \quad 2_{1,1} \)

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Appendix D
Vibronic Coupling

Innes [18] has recently proposed a model, based upon vibronic coupling between two adiabatic electronic manifolds, to explain the origin of the nonplanar geometry encountered in the $\widetilde{A}^1A_2$ state of formaldehyde. In order to comprehend the implications of this treatment, especially with respect to the dipole moment measurements analyzed in the first Chapter of this thesis, an exact mathematical definition for the term "vibronic coupling" [277] must be presented. This will necessitate a somewhat detailed examination of the formal solutions for the molecular Schrödinger equation with particular emphasis upon the various adiabatic approximations utilized in the decoupling of nuclear (i.e. vibrational) and electronic degrees of freedom. In keeping with the pedagogical nature of the ensuing discussion, it will be assumed that rotational motion is completely separable from other internal coordinates and can therefore be neglected. Under these conditions, the total vibrational-electronic (i.e. vibronic) Hamiltonian, $H_{total}$, for a molecular system is given by:

$$H_{total}(r,Q) = T_e(r) + T_N(Q) + U(r,Q) + V(Q) \quad (D.1)$$

where

- $r$ denotes the set of electronic coordinates required for description of the molecular electronic degrees of freedom,
- $Q$ denotes the set of mass-weighted nuclear displacement coordinates describing the displacement of the molecular structure from a reference configuration (viz. $Q_0$),
- $T_e(r)$ signifies the electronic kinetic energy operator,
- $T_N(Q)$ signifies the nuclear kinetic energy operator,
$U(r,Q)$ represents the total Coulombic potential energy associated with the nuclei and electrons. $U(r,Q)$ also incorporates any other potential energy terms which are functions of electronic coordinates (e.g. spin-orbit coupling),

$V(Q)$ represents the potential energy associated with the nuclei.

The kinetic energy operators in equation (D.1) can be expressed in terms of derivatives with respect to the appropriate molecular coordinates:

$$T_e(r) = - \frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial r_i^2}$$  \hspace{1cm} (D.2)

$$T_N(Q) = - \frac{\hbar^2}{2} \sum_n \frac{\partial^2}{\partial Q_n^2}$$  \hspace{1cm} (D.3)

where $m$ represents the mass of an electron.

The Schrödinger equation corresponding to the total vibronic Hamiltonian of expression (D.1) is given by:

$$[H_{total}(r,Q) - E_t] \Psi_t(r,Q) = 0$$  \hspace{1cm} (D.4)

where $\Psi_t(r,Q)$ represents the exact molecular eigenstate (assumed to be nondegenerate) associated with the vibronic energy $E_t$.

Unfortunately, the intrinsic non-separability of nuclear and electronic degrees of freedom in the total Hamiltonian precludes an exact solution to the molecular Schrödinger equation. As a result, various assumptions are normally incorporated into the analysis so as to obtain an approximate representation for the exact molecular eigenfunctions and eigenvalues. The usual practice is to collect all terms in $H_{total}(r,Q)$ which depend explicitly upon electronic coordinates into an electronic
Hamiltonian, \( H_{\text{elec}} \), which is a parametric function of the nuclear motion:

\[
H_{\text{elec}}(r,Q) = T_e(r) + U(r,Q) \\
= T_e(r) + U(r,Q_0) + \Delta U(r,Q) \\
= H_{\text{elec}}(r,Q_0) + \Delta U(r,Q) \tag{D.5}
\]

where \( \Delta U(r,Q) = U(r,Q) - U(r,Q_0) \) represents the deviation of the total Coulombic potential energy from that encountered in the reference configuration of the nuclei (denoted by \( Q_0 \)).

Depending upon whether \( H_{\text{elec}}(r,Q) \) or \( H_{\text{elec}}(r,Q_0) \) is utilized as the Hamiltonian, two different types of electronic Schrödinger equations, denoted as the dynamical and static equations respectively [126], can now be derived:

\[
[H_{\text{elec}}(r,Q) - \epsilon_i(Q)] \psi_i(r,Q) = [T_e(r) + U(r,Q) - \epsilon_i(Q)] \psi_i(r,Q) \\
= 0 \tag{D.6}
\]

\[
[H_{\text{elec}}(r,Q_0) - \epsilon_i^0(Q_0)] \psi^0_i(r,Q_0) = [T_e(r) + U(r,Q_0) - \epsilon_i^0(Q_0)] \psi^0_i(r,Q_0) \\
= 0 \tag{D.7}
\]

where

\( \psi_i(r,Q) \) represents the dynamical electronic wavefunction associated with the electronic energy \( \epsilon_i(Q) \),

\( \psi^0_i(r,Q_0) \) represents the static electronic wavefunction associated with the electronic energy \( \epsilon_i^0(Q_0) \).

It is important to note that both the wavefunctions and energies appearing in
the electronic Schrödinger equations presented above are parametrically dependent upon the nuclear coordinates.

Since \( \{ \psi_i(r,Q); i = 0, 1, \ldots \} \) and \( \{ \psi_0^0(r,Q_0); i = 0, 1, \ldots \} \) each constitute a complete orthonormal set of functions, the eigenstates of the total molecular Hamiltonian, \( H_{total}(r,Q) \), can be expanded in terms of either type of electronic wavefunction. In keeping with the intial formulation of the Innes vibronic model [278, 132, 18] for the \( \overset{1}{A}_2 \) state of formaldehyde, the following discussion will be based upon use of the static electronic Schrödinger equation. The restrictions and pitfalls associated with this selection will be briefly examined after the completion of the present analysis. The exact molecular eigenstates, \( \Psi_t(r,Q) \), can now be expressed by:

\[
\Psi_t(r,Q) = \sum_k \psi_k^0(r,Q_0) \chi_{kt}(Q) \tag{D.8}
\]

where the expansion coefficients, \( \chi_{kt}(Q) \), will eventually be related to the vibrational wavefunctions for the molecular system.

Substitution of this expanded form for the exact molecular eigenstates into the total molecular Schrödinger equation of expression (D.4) yields:

\[
0 = [H_{total}(r,Q) - E_t] \sum_k \psi_k^0(r,Q_0) \chi_{kt}(Q)
\]

\[
= \sum_k [T_M(Q) + H_{elec}(r,Q_0) + \Delta U(r,Q) + V(Q) - E_t] \psi_k^0(r,Q_0) \chi_{kt}(Q)
\]

\[
= \sum_k [T_M(Q) + \epsilon_k^0(Q_0) + \Delta U(r,Q) + V(Q) - E_t] \psi_k^0(r,Q_0) \chi_{kt}(Q) \tag{D.9}
\]
where equation (D.7) has been utilized in order to write:

\[ H_{\text{elec}}(r,Q_0)\psi_k^0(r,Q_0)\chi_{kt}(Q) = \epsilon_k^0(Q_0)\psi_k^0(r,Q_0)\chi_{kt}(Q) \]  
(D.10)

By multiplying expression (D.9) on the left with \( \psi_j^0(r,Q_0)^* \), integrating over all electronic coordinates, and utilizing the orthonormality of the static electronic wavefunctions, the following set of coupled differential equations is obtained for the expansion coefficients \( \chi_{kt}(Q) \):

\[
\begin{align*}
[T_{N}(Q) + \epsilon_j^0(Q_0) + V(Q) + \langle \psi_j(r,Q_0)|\Delta U(r,Q)|\psi_j(r,Q_0) \rangle - E_t] \chi_j(Q) \\
+ \sum_{k \neq j} \langle \psi_j(r,Q_0)|\Delta U(r,Q)|\psi_k(r,Q_0) \rangle \chi_{kt}(Q) = 0
\end{align*}
\]  
(D.11)

where \( \langle \cdots | \cdots | \cdots \rangle \) denotes an integration over only the electronic coordinates \( r \). The derivation of this expression depends upon the fact that the static electronic wavefunctions, \( \psi_k^0(r,Q_0) \), are constants with respect to the nuclear kinetic energy operator, \( T_N(Q) \), defined in equation (D.3).

In order to achieve the desired separation between the vibrational and electronic degrees of freedom, the following adiabatic approximation, which amounts to neglecting all coupling terms in equation (D.11), is usually made:

\[
\langle \psi_j^0(r,Q_0)|\Delta U(r,Q)|\psi_k^0(r,Q_0) \rangle = 0 \quad \text{for} \quad k \neq j
\]  
(D.12)

This assumption effectively decouples the set of differential equations in expression (D.11) and implies that the coefficients \( \chi_{kt}(Q) \), utilized for the expansion of the exact molecular eigenstates in terms of the complete set of static electronic
wavefunctions (cf. equation (D.8)), are all zero except for \( k = j \). Expressed in spectroscopic terminology, this suggests that the exact molecular eigenstates, \( \Psi_{\ell}(r,Q) \), can, within the approximation defined by equation (D.12), be well represented by the product of a single static electronic wavefunction, \( \psi_j^0(r,Q_0) \), with a single function of the nuclear coordinates, \( \chi_{\ell\ell}(Q) \) (i.e. a vibrational wavefunction):

\[
\psi^\text{CA}_{\ell\ell}(r,Q) = \psi_j^0(r,Q_0) \chi^\text{CA}_{\ell\ell}(Q)
\]  

(D.13)

where the subscript \( j \) is added to the exact molecular eigenstate, \( \psi^\text{CA}_{\ell\ell}(r,Q) \), in order to explicitly denote its association with the electronic wavefunction \( \psi_j^0(r,Q_0) \). The superscript \('CA'\) indicates that the assumptions made in the derivation of equation (D.13) (viz. use of the static electronic Hamiltonian in conjunction with the adiabatic approximations embodied in expression (D.12)) correspond to what is commonly called the Crude Adiabatic approximation [277, 126].

The coefficient \( \chi^\text{CA}_{\ell\ell}(Q) \) for the crude adiabatic wavefunction is obtained by substituting the decoupling approximation of expression (D.12) into equation (D.11). This procedure yields:

\[
[ T_N(Q) + \epsilon_j^0(Q_0) + V(Q) + \langle \psi_j^0(r,Q_0) | \Delta U(r,Q) | \psi_j^0(r,Q_0) \rangle - E^\text{CA}_{\ell\ell} ] \chi^\text{CA}_{\ell\ell}(Q) = 0
\]  

(D.14)

By defining an effective crude adiabatic potential, \( V_j^\text{CA} \), which depends only upon the mass-weighted nuclear coordinates, by:

\[
V_j^\text{CA}(Q) = V(Q) + \epsilon_j^0(Q_0) + \langle \psi_j^0(r,Q_0) | \Delta U(r,Q) | \psi_j^0(r,Q_0) \rangle
\]  

(D.15)
it can readily be demonstrated that expression (D.14) is the Schrödinger equation for a nuclear eigenstate $\chi^{CA}_{j\ell}(Q)$ corresponding to the eigenvalue $E^{CA}_{j\ell}$. Consequently, $\{ \chi^{CA}_{j\ell}(Q); \ell=0,1,\ldots \}$ can be identified as the set of vibrational wavefunctions associated with the static electronic state $\psi^0_j(r, Q_0)$. In this context, $\psi^{CA}_{j\ell}(r, Q)$ can be defined as the crude adiabatic vibronic wavefunction derived from the electronic state $\psi^0_j(r, Q_0)$ and the vibrational state $\chi^{CA}_{j\ell}(Q)$.

The expansion of the total molecular eigenstates as a product of individual electronic and vibrational wavefunctions (cf. equation (D.13)) constitutes the starting point for much of traditional molecular physics and spectroscopy. With further refinements, the entire theoretical framework (e.g. normal modes of vibration) used for the conventional description of molecular structure and dynamics could readily be developed. It should be noted, however, that the crude adiabatic approximation utilized, in the present analysis, to effect the decoupling between nuclear and electronic degrees of freedom is by no means unique. In fact, completely analogous adiabatic separations could be performed on the basis of the dynamical electronic wavefunctions defined in equation (D.6) [277, 126].

The derivation of the adiabatic approximation outlined above proceeded via expansion of the exact molecular eigenstates in terms of a complete set of electronic wavefunctions. This treatment can be related [279] to the original 1927 work of Born and Oppenheimer [280] which relied upon a perturbation expansion in terms of $\left(\frac{m}{M}\right)^{1/4}$ where $m$ and $M$ denote the electron mass and average nuclear mass respectively. In particular, the effective potential defined in expression (D.15) embodies the fundamental supposition of the Born-Oppenheimer approach which states that the electronic energy can assume the role of a potential surface for the characteristically slower motion of the nuclei. Indeed, the entire field of molecular spectroscopy is based upon the notion that electronic potential surfaces are tangible
entities which serve to constrain the nuclear degrees of freedom.

The concept of vibronic coupling, which forms the basis for the Innes model of \( \tilde{A}^1A_2 \) formaldehyde, refers to a breakdown in the assumptions utilized to effect the separation between electronic and nuclear degrees of freedom. It should be obvious that the adiabatic scheme presented above will remain valid only if the various effective electronic potential surfaces, \( \{ V_j^A(Q); j = 0, 1, \ldots \} \), are sufficiently well isolated from each other such that the coupling terms in expression (D.11) can be justifiably neglected. When this is no longer true, the formulation of the exact molecular eigenstates as a simple product of an electronic and a vibrational wavefunction (\textit{c.f.} the crude adiabatic approximation of equation (D.13)) does not provide an adequate description for the molecular system. Stated in spectroscopic terms, the entire concept of a (distinct) potential surface for the nuclear motion has meaning if and only if the adiabatic separation, defined (in our particular case) by expression (D.13), is a sufficiently good representation of the molecular states under consideration.

For situations in which vibronic coupling precludes any approximate separation between electronic and nuclear degrees of freedom, the crude adiabatic wavefunctions, \( \psi_j^A(r, Q) = \psi_j^0(r, Q_0) \chi_j^A(Q) \), provide a convenient basis for expansion of the total molecular Hamiltonian, \( H_{\text{total}}(r, Q) \). In this treatment, which was adopted by Innes for his discussion of \( \tilde{A}^1A_2 \) formaldehyde, the quantities of principal concern are the matrix elements given by [281]:

\[
\{ \psi_k^A(r, Q) | H_{\text{total}}(r, Q) | \psi_j^A(r, Q) \} \tag{D.16}
\]

where \( \{ \ldots | \ldots | \ldots \} \) denotes an integration over both electronic \textit{and} nuclear coordinates (\textit{i.e.} over vibronic coordinates). Diagonalization of the matrix defined in
expression (D.16), through either analytical or (more typically) numerical methods, yields the eigenfunctions and eigenvalues associated with the nonadiabatic (i.e. vibronically coupled) description of the molecular system. It should be noted that the total Hamiltonian will often require an infinite basis set for its exact representation. For the lowest energy states, however, excellent results can usually be obtained by truncating the matrix at a convenient size as determined through numerical experimentation.

By utilizing equations (D.1) and (D.5), the matrix elements for the total molecular Hamiltonian in the crude adiabatic basis set can be reformulated as follows:

\[
\{\psi_{ks}^{CA}(r,Q)|H_{total}(r,Q)|\psi_{jt}^{CA}(r,Q)\} = (x_{ks}^{CA}(Q)|(\psi_{k}^{0}(r,Q_{0})|[T_{N}(Q) + H_{elec}(R,Q_{0})]
+ \Delta U(r,Q) + V(Q)|\psi_{j}^{0}(r,Q_{0})| x_{jt}^{CA}(Q)) \tag{D.17}
\]

where the decoupled nature of the crude adiabatic wavefunctions has been employed in order to rewrite the vibronic integrals in terms of separate integrations over nuclear and electronic coordinates (i.e. denoted by \((\cdots|\cdots|\cdots)\) and \((\cdots|\cdots|\cdots)\) respectively).

This expression can be simplified through successive application of the Schrodinger equations for the crude adiabatic electronic and nuclear wavefunctions as defined in equations (D.7) and (D.14):
\[ \{ \psi^{CA}_{ks}(r, Q)|H_{\text{total}}(r, Q)|\psi^{CA}_{jt}(r, Q) \} \]

\[ = (\chi^{CA}_{ks}(Q)||T_N(Q) + \epsilon_j^0(Q_0) + (\psi_j^0(r, Q_0)|\Delta U(r, Q)|\psi_j^0(r, Q_0)) + V(Q)||\chi^{CA}_{jt}(Q)) \delta_{kj} \]

\[ + (\chi^{CA}_{ks}(Q)||\psi_k^0(r, Q_0)|\Delta U(r, Q)|\psi_j^0(r, Q_0))|\chi^{CA}_{jt}(Q)) [1 - \delta_{kj}] \]

\[ = E^{CA}_{jt} \delta_{kj} \delta_{st} \] \hspace{1cm} (D.18)

\[ + (\chi^{CA}_{ks}(Q)||\psi_k^0(r, Q_0)|\Delta U(r, Q)|\psi_j^0(r, Q_0))|\chi^{CA}_{jt}(Q)) [1 - \delta_{kj}] \]

where use has been made of the orthonormality associated with the crude adiabatic wavefunctions:

\[ \{ \psi^{CA}_{ks}(r, Q)|\psi^{CA}_{jt}(r, Q) \} = \delta_{kj} \delta_{st} \] \hspace{1cm} (D.19)

or

\[ (\psi_k^0(r, Q_0)|\psi_j^0(r, Q_0)) = \delta_{kj} \quad \text{and} \quad (\chi^{CA}_{js}(Q)||\chi^{CA}_{jt}(Q)) = \delta_{st} \] \hspace{1cm} (D.20)

To proceed further with equation (D.18), an explicit form for the matrix elements of \( \Delta U(r, Q) \) must be obtained. This can be partially accomplished by expanding the total Coulombic potential energy of the molecule, \( U(r, Q) \), as a Taylor series in the mass-weighted nuclear coordinates about the reference nuclear configuration \( Q_0 \):
\[ U(r, Q) = U(r, Q_0) + \sum_n \left( \frac{\partial U(r, Q)}{\partial Q_n} \right)_0 Q_n \]

\[ + \frac{1}{2} \sum_n \sum_m \left( \frac{\partial^2 U(r, Q)}{\partial Q_n \partial Q_m} \right)_0 Q_n Q_m + \ldots \]

where the differential terms are evaluated at the reference configuration and are therefore functions only of the electronic coordinates \( r \).

From the definition implied in equation (D.5), the first order approximation to \( \Delta U(r, Q) \) is thus given by:

\[ \Delta U(r, Q) = U(r, Q) - U(r, Q_0) \]

\[ \approx \sum_n \left( \frac{\partial U(r, Q)}{\partial Q_n} \right)_0 Q_n \]  \hspace{1cm} (D.21)

With this substitution, the matrix elements for the total molecular Hamiltonian in a basis set of crude adiabatic wavefunctions can be recast into the following form:

\[ \langle \psi^C_A(r, Q)|H_{total}(r, Q)|\psi^C_A(r, Q) \rangle = E^C_{ij} \delta_{kj}\delta_{st} \]  \hspace{1cm} (D.22)

\[ + \sum_n \langle \psi^0_k(r, Q_0)| \left( \frac{\partial U(r, Q)}{\partial Q_n} \right)_0 |\psi^0_j(r, Q_0) \rangle \langle \chi^C_{ks}(Q)|Q_n|\chi^C_{jt}(Q) \rangle [1 - \delta_{kj}] \]

This equation constitutes the mathematical foundation for the Innes model of the nonplanarity encountered in the first excited singlet state of formaldehyde. The two terms in expression (D.22) can be rationalized through a hypothetical
partitioning of the total molecular Hamiltonian into two distinct portions:

\[ H_{total} = H_{total}^{CA}(r,Q) + H'(r,Q) \]  \hspace{1cm} (D.23)

where \( H_{total}^{CA}(r,Q) \) denotes the crude adiabatic molecular Hamiltonian while \( H'(r,Q) \) contains all terms which are required to correct for the nonadiabatic nature of the exact total molecular Hamiltonian.

Expansion of \( H_{total}(r,Q) \) in the eigenbasis of the crude adiabatic Hamiltonian ensures that the first portion of equation (D.23) (viz. \( H_{total}^{CA}(r,Q) \)) will be completely diagonal in vibronic state labels (cf. the \( \delta_{kj} \delta_{et} \) term in expression (D.22)). In contrast, the nonadiabatic correction terms (viz. \( H'(r,Q) \)) are expected to be off diagonal with respect to the static electronic wavefunctions (cf. the \( 1 - \delta_{kj} \) term in expression (D.22)) so as to account for the partial breakdown in the separation of nuclear and electronic coordinates.

A final comment needs to be made with respect to the choice of the static electronic wavefunctions (i.e. equation (D.7)) for the analysis presented above. It has been legitimately argued [282] that the adiabatic approximations (viz. the crude adiabatic approximation) based upon this choice result in electronic potential surfaces which are both unreasonable and prone to breakdown of the underlying assumptions responsible for their very existence. Indeed, the justification for the crude adiabatic approximation, as stipulated in equation (D.12), depends upon the somewhat dubious omission of coupling terms (viz. \( \Delta U(r,Q) \) matrix elements) which represent deviations in molecular properties from those encountered in the reference nuclear configuration. This alone suggests that augmented nuclear motion (e.g. increased vibrational excitation) will rapidly erode the validity of the assumed separation between nuclear and electronic degrees of freedom. These facts
notwithstanding, it has been demonstrated [126] that the present approach to vibronic coupling can be extended to encompass the more realistic dynamical electronic wavefunctions defined by expression (D.6). This necessitates the construction of entirely new forms of the adiabatic approximation [277] which are no longer constrained by association with a reference nuclear configuration.
Appendix E
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