TWO PHOTON TRANSITIONS IN
LASER PUMPED SUBMILLIMETER LASERS

by

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B.S., University of California at Los Angeles
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SUBMITTED IN PARTIAL FULFILLMENT
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Submitted to the Department of Physics
on February 28, 1978 in partial fulfillment of
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ABSTRACT

This thesis describes the first detailed investigation
of the gain spectrum and saturation behavior of infrared
laser pumped submillimeter wavelength lasers in the
homogeneously broadened regime. A single mode CO\textsubscript{2} laser
was used to pump a single mode tunable cavity and amplifier
of the submillimeter laser. In this way, for the first time
data were obtained allowing detailed comparison with theoretical models. The model used in this work is based on the
density matrix formalism treating the interaction of two
near resonant coherent fields with a three-level system.
We have extended this model to include the M-level space
degeneracy and thus obtained a complete theory capable of
predicting gain spectrum and polarization and saturation
properties at any field strengths. These results are crucial
for designing submillimeter laser systems for applications.

Experimental measurements were performed on the CO\textsubscript{2}
laser pumped 385 \textmu m transition in D\textsubscript{2}O and 496 \textmu m transition
in CH\textsubscript{3}F. Small signal gain versus frequency was measured
as a function of pressure and pump power. Saturation
behavior was also investigated. Very good agreement was
obtained between theory and experiment in all respects
except for small correction factors in the absolute gain
amplitudes. Part of those factors was qualitatively explained
on the basis of other models.

Thesis Supervisors: Benjamin Lax, Professor of Physics
Director, F. Bitter National Magnet Laboratory; and
Richard J. Temkin, Project Leader
F. Bitter National Magnet Laboratory
I dedicate this thesis to
my parents
Krystyna and Adam Drozdowicz
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I. INTRODUCTION

This thesis concerns itself with the spectral and saturation characteristics of the gain in laser pumped submillimeter (SMM) lasers in the homogeneously broadened regime.

This field was opened in 1970 with the discovery of lasing action in CO$_2$ laser pumped CH$_3$F gas by Chang and Bridges.$^1$ This discovery bridged the gap between the microwaves and the infrared in the spectrum of available sources of coherent radiation. Since then many other polar molecular gases with vibrational-rotational transitions matching the output frequencies of the existing infrared lasers have produced radiation with wavelengths ranging from $12 \, \mu$m$^2$ to over 2 mm.$^3$-$^5$ Both in the original discovery$^1$ and in a number of following works$^6$-$^{12}$ low power CW or Q-switched lasers have been utilized as the sources of pump radiation. Later on high power pulsed infrared lasers have been used to produce kilowatt type outputs in the SMM region.$^{13,14}$ Since then megawatt level peak powers have been achieved.$^{15}$

The development of these lasers has been spurred on by the possibility of their various applications. Those include the measurement of plasma parameters such as the density, the ion temperature, and the impurity content in the Tokamak machines.$^{16-18}$ The knowledge of these parameters
is vital to the progress of the controlled thermonuclear fusion effort. Other applications include spectroscopy and material science utilizing the high intensity per unit frequency made available for the first time in the SMM regime at frequencies other than those of the few lines of the electrically excited lasers like the H$_2$O and HCN$^{19}$ ones. There also exists a good chance that the new lasers will find application in the laser detecting and ranging (lidar) thanks to the atmospheric windows around 1 mm.$^{20}$

To develop good lasers for these and other applications it is necessary to understand the basics of their operation. Careful measurements of laser parameters, like gain and saturation intensity, need to be performed and compared with theoretical treatments. There are no reports in the literature, to the best of our knowledge, of high power pulsed laser parameter measurements which were done under conditions characterized well enough to produce meaningful comparison with the theoretical predictions.

As for the theoretical treatments, the early analyses of the new lasers confined themselves to the rate equation type of approach.$^{21-25}$ These yielded good agreement for the CW laser pumped SMM lasers$^{22,23}$ and even correctly accounted for the absorption of the pump
radiation in the case of high power pulsed pump lasers. Soon however it was realized that a laser pumped SMM laser is essentially a two-photon device. This was manifestly shown in the work of Skribanowitz et al. dealing with the anisotropic gain caused by the interaction between the pump radiation and the laser transition in a fully Doppler-broadened regime. The explanation of this phenomenon was based on a two quantum process first considered for three level gas masers. Soon thereafter treatments allowing for interaction between two fields of high intensity and a three level system appeared.

Experimentally it was observed that some high power SMM lasers pumped slightly off resonance lase at the Raman or the submillimeter transition frequency depending on the exact operating conditions. It was then decided that the spectral behavior of these systems merits a close investigation and this thesis applies itself to this task.

The thesis is organized in the following manner: In Part II, following this Introduction, the theories of the optically pumped SMM lasers in the homogeneously broadened regime are reviewed and our new contributions are introduced. The new parts deal with the relative polarization of the submillimeter and the pump beams and also with the saturation properties of the
gain. In Part III a short summary of our past efforts utilizing multimode pump lasers is given. Part IV concerns itself with the final experimental setup in which a single mode hybrid CO$_2$ laser$^{36,37}$ was used to pump a single mode tunable submillimeter cavity and a submillimeter amplifier. The experimental results are presented in this section. The discussion and comparison with the theory are also included. Conclusions are offered in Part V.
II. A. LASER MEDIUM

A laser is a device whose operation most commonly requires a medium in which population inversion has been achieved. For the laser pumped submillimeter lasers this medium is provided by a gas, the molecules of which possess a permanent dipole moment. An infrared laser pump provides the population inversion by increasing the population of a particular rational level within an excited vibrational level of the molecules in the gas.

In our work we dealt with two kinds of molecules. The first kind are called symmetric-top molecules due to the fact that two of their principal moments of inertia are equal. The second kind are called asymmetric-top molecules and are characterized by having three unequal principal moments of inertia. The energy levels of these molecules have been discussed at length by various authors \(^{38-40}\) and therefore we will introduce here only some essentials.

In typical treatments, the vibrational motion involving the interatomic bonds and the rotational motion of the whole molecule are treated separately, their interaction treated as a higher order perturbation. The vibrational motion is treated in terms of normal modes, each of which has a quantum number \(v_i\) associated with it. The subscript \(i\) indentified the normal mode and \(v\) describes
the amount of excitation in this mode. Consecutive, vibrational levels are typically separated by energies falling into the infrared region of the spectrum and this is the reason for using infrared lasers, like CO$_2$, for pumping our submillimeter lasers.

Each vibrational level is subdivided into energy levels associated with the rotational motion. The separation of these levels falls typically into the microwave region in ground vibration state and into the submillimeter region in the excited vibrational state. The rotational wavefunctions and energy levels of symmetric top molecules are described in terms of three quantum numbers: $J$, $K$, $M$. $J$ describes the total angular momentum, $K$ gives its projection onto the molecular axis of symmetry, and $M$ gives its projection onto some space fixed axis, usually denoted by $z$. The rotational levels of an asymmetric top molecule are also described by the quantum numbers $J$ and $M$, however, since there is no axis of symmetry, $K$ is no longer a good quantum number and various notations are used to distinguish between the levels associated with the different possible orientations of the total angular momentum with respect to the molecule. We will adopt the $J_{K-1}K_1$ notation as described in Townes and Schawlow.$^{40}$ Ray's parameter of asymmetry $\kappa$.$^{40}$, which is $\pm1$ for a symmetric-top molecule and $-1<\kappa<1$ for an asymmetric-top
one, will be used to describe the extent of asymmetry.

Once the energy levels of a molecule are known, we can predict what wavelengths will be associated with the transitions between any pair of vibrational-rotational levels. The probabilities of these transitions occurring are provided by quantum mechanics. The interaction between electromagnetic waves and any medium can be treated by expansion in terms of the contributions from various multipoles. The strongest of these, if non-zero, are the dipole interactions. It is for this reason, i.e. to have dipole allowed transitions, that we worked with molecules possessing permanent dipole moment. Purely rotational transitions, which are the source of the SMM lasing action, are dipole allowed only for such molecules.

The probability of the occurrence of any dipole allowed transition is proportional to the square of the matrix element of the transition dipole moment, \( |\mu_{ij}|^2 \), where

\[
\mu_{ij} = \int \psi_j^* \mu \psi_i \, d\tau
\]  

(2-A-1)

where \( \psi_i \) is the initial state, \( \psi_j \) the final state, and \( \mu \) the dipole moment associated with a given transition. \( \mu \) is the permanent dipole moment for the purely rotational transitions and the induced dipole moment for the vibrational-
rotational transitions.\textsuperscript{38-39} We will discuss the form of the transition matrix element in some detail in Section II-E.

II. B. RATE EQUATION MODEL

One standard way of treating laser problems is through the use of rate equations.\textsuperscript{82} In such treatments populations of the various levels involved in the lasing process are calculated and this can yield information about the gain. In this section we will solve a set of equations identical to those of Temkin and Cohn,\textsuperscript{25} the new solutions being different by the fact that the level degeneracy factors and the population of the excited vibrational state are explicitly taken into account. It will be later shown that the rate equation treatment, while giving the right order of magnitude estimates, is never fully correct in describing the lineshape of the gain of the SMM lasers. This is due to the fact that the coherence effects, introduced by the interacting fields are not accounted for in these equations.

The system which we want to analyze is shown in Fig. II-B-1. The infrared laser pump (optical pump) causes a transition between the rotational level 1 of the ground vibrational state of the molecule and the level 3 in the excited vibrational state and thus creates population inversion between the rotational levels 3 and 2 in
Fig. II-B-1 -- Level diagram for a laser pumped FIR laser.
the excited vibrational state. Far infrared (FIR) lasing can then occur between these levels. In the equations that follow we neglect the vibrational-vibrational and vibrational-translational relaxation channels as at the typical operating pressures of a few Torr these occur on time scales longer than the high power laser pulses (<200 nsec).\textsuperscript{41,42} The same treatment is afforded to the collisional de-excitation of the higher vibration states. A single collision frequency is assumed for establishing rotational equilibrium between the levels within each vibrational manifold.

With the above assumptions, we can then write

\[
\frac{dN_1}{dt} = N_{31} W_p + \left( f_1 N_{v0} - N_1 \right) W_c
\]

\[
\frac{dN_3}{dt} = -N_{31} W_p - N_{32} W_f + \left( f_3 N_{v1} - N_3 \right) W_c
\]

\[
\frac{dN_2}{dt} = N_{32} W_f + \left( f_2 N_{v1} - N_2 \right) W_c
\]

\[
\frac{dN_{v0}}{dt} = N_{31} W_p
\]

\[
\frac{dN_{v1}}{dt} = -N_{31} W_p
\]

\[
N_{v0} + N_{v1} = N
\]  \hspace{1cm} (2-B-1)
where

\[ N_{i,j} = N_i - \frac{g_i}{g_j} N_j \]

with \( g_i(j) \) being the degeneracy factor of level \( i(j) \).

\( N_i \) is the population of the level \( i \). \( N_{V0}(N_{V1}) \) is the total population of the ground (excited) vibrational level. \( \omega_c \), the collisional frequency, is given by \( \pi \Delta \nu \), where \( \Delta \nu \) is the Lorentzian linewidth of the pressure broadened rotational transition; \( f_i \) is the Boltzmann factor for the level \( i \) within the vibrational level;

\( W_p \) and \( W_f \) are the induced transition rates for optical pumping and stimulated far infrared (FIR will be used interchangeably with SMM throughout this thesis) emission.

\( W \) is given by

\[ W(\nu) = \frac{\lambda^2}{8 \pi h \nu t_{sp}} \frac{I(\nu)}{g(\nu)} \]  

(2-B-2)

where \( \lambda \) and \( \nu \) are the wavelength and frequency, respectively; \( g(\nu) \) is a lineshape function; \( I(\nu) \) is the beam intensity; \( t_{sp} \) is the spontaneous emission time for transition from the upper to the lower level which includes the degeneracy factor for the lower level.

Anticipating results below, we define saturation intensity constants for optical pumping, \( I_{ps} \), and stimulated emission, \( I_{fs} \), where
We can now solve equations (2-B-1) in adiabatic approximation. We will assume that the total populations of the vibrational levels are changing slowly enough so that at each point in time they can be considered as constant factors in evaluating the absorption and gain factors.

In this approximation, we look for steady state solutions for the rotational level populations. We do it by setting their time derivatives equal to zero in (2-B-1):

\[ 0 = N_{31} \frac{W_p}{W_c} + (f_1 N_{v0} - N_1) W_c \]
\[ 0 = -N_{31} \frac{W_p}{W_c} - N_{32} \frac{W_f}{W_c} + (f_3 N_{v1} - N_3) W_c \]
\[ 0 = N_{32} \frac{W_f}{W_c} + (f_2 N_{v1} - N_2) W_c \]

After some uninteresting algebra one obtains:

\[ N_{32} = \frac{A \frac{I_p}{I_f}}{W_c (1 + g_{13})(I_p + I_{f5}) (R_p I_f + I_{f5})} \]
\[ N_{31} = -\frac{A \frac{I_{f5}}{I_p}}{g_{13} (R_p I_p + I_{f5}) W_c} + N_{v1} \frac{I_{f5}}{I_p} (f_2 - g_{23} f_3) \frac{l + g_{13}}{g_{13} g_{23}} \]
where

\[ R_P = \frac{1 + \kappa}{1 + \frac{I_P}{I_{ps}}} \]

\[ R_f = \frac{1 + \kappa}{1 + \frac{I_f}{I_{fs}}} \]

\[ K = \frac{(1 + g_0)(1 + g_{23}^2) - g_{13}g_{23}^3}{(1 + g_{13})(1 + g_{23})} \]

\[ A = W_c \left( g_f N_{v_0} - F N_{v_1} \right) \]

\[ F = g_{13} f_3 + (1 + \frac{I_{ps}}{I_P})(1 + g_{13}) \frac{f_2 - g_{23} f_3}{g_{23}} \]

Having found the population differences we can calculate the absorption and gain coefficients for the pump and the SMM frequencies respectively.

The absorption coefficient can be written as:

\[ \lambda_p = \frac{1}{I_p} \frac{dI_p}{dz} \]

\[ = \frac{1}{I_p} N_{3,1} W_p h \nu_p \]

Using equations 2-B-3 and 2-B-5 we obtain

\[ \lambda_p = - \frac{A h \nu_p}{(1 + g_{13})(R_f I_p + I_{ps})} + N_{v_1} \frac{W_c h \nu_p (f_2 - g_{23} f_3)}{g_{23} I_p} \quad (2-B-6) \]

In a similar fashion we obtain the FIR gain coefficient

\[ \lambda_f = \frac{A h \nu_f I_p}{(1 + g_{13})(1 + g_{23})(I_p + I_{ps})(R_f I_f + I_{fs})} \quad (2-B-7) \]

Equations 2-B-6 and 2-B-7 correctly reduce to those of Temkin and Cohn when the following approximations
are made:

\[ g_1 = g_2 = g_3 = 1; \quad g_1 \approx g_2 \approx g_3 \approx \frac{1}{J}; \quad N_{v_1} \approx 0; \quad N_{v_0} \approx N \]

The next point of interest is the time evolution of the absorption and gain coefficients due to the changing populations of the vibrational manifolds. This is especially important in the cases where high power pump lasers are used since with the very high pumping rates a large number of molecules may be transferred to the upper vibrational state and this will cut down the magnitude of both the gain and the absorption coefficients.

From equations (2-B-1) we find

\[ \frac{d}{dt} N_{v_0} = - \frac{d}{dt} N_{v_1} = N_{31} \mu_p \]

and \( N_{31} \) is given by (2-B-5). In a typical laser pumped SMM laser the following approximate equalities hold:

\[ g_1 \approx g_2 \approx g_3 \equiv \frac{1}{J} \]

\[ g_{13} \approx g_{23} \approx 1 \]

With the above assumptions and using (2-B-1) one finds

\[ N_{31} = - \frac{I_{ps} \frac{1}{J} \left( \frac{2 N_{v_0} - N}{R_g I_p + I_{ps}} \right)}{} \]

Inserting (2-B-10) and (2-B-3) into (2-B-8) we finally obtain
where

\[
\frac{dN_{v_0}}{dt} = -W_u \left( N_{v_0} - \frac{1}{2} N \right) \tag{2-B-11}
\]

We will now assume an initially empty excited vibrational state, which is a very good approximation for levels 1000 cm\(^{-1}\) or more above the ground state at room temperature which corresponds to about 200 cm\(^{-1}\). Using this initial condition the expressions for the vibrational level populations become:

\[
N_{v_0} = \frac{1}{2} N \left( 1 + e^{-W_u t} \right)
\]

\[
N_{v_1} = \frac{1}{2} N \left( 1 - e^{-W_u t} \right) \tag{2-B-12}
\]

We can see now that our assumption of the vibrational level population changes being slow compared to other processes was correct. The rate of change \(W_u\), defined in (2-B-11), is close to zero for unsaturated pumping and becomes at most \(f W_c\) for a very strong pump. \(f\) is the Boltzmann factor for the rotational levels of interest and even for the most populated ones it never exceeds a few per cent.

We can now insert (2-B-12) into the absorption (2-B-6) and gain (2-B-7) expressions to find out about their time evolution. For simplicity we will again
utilize the approximations of (2-B-9) to obtain

\[ \lambda_p(t) = \lambda_p(0) e^{-\omega \nu t} \quad (2-B-13) \]

where \( \lambda_p(0) \) is the absorption coefficient when the excited vibrational level is empty. We can see then that the absorption goes down in time and therefore to keep the laser operating efficiently one should try to use pump pulses short compared to

\[ t_{cv} \equiv \frac{1}{\nu \omega_c} \quad (2-B-14) \]

To obtain the expression for the time dependence of the gain coefficient we will relax one of the assumptions of (2-B-9) and allow \( f_2 \neq f_3 \). This will lead to the possibility of negative gain, i.e., absorption, when the upper vibrational level is strongly filled up and thermalized. The energy separation of the levels 2 and 3, Fig. II-B-1, is typically on the order of 10 to 50 cm\(^{-1}\), much less than \( kT \). Therefore their equilibrium population difference is given by

\[
\mathcal{J}_2 - \mathcal{J}_3 = \frac{e^{-\frac{\hbar \nu_2}{kT}} - e^{-\frac{\hbar \nu_3}{kT}}}{Z} \quad (2-B-15)
\]

\[ \approx \frac{\mathcal{J}_{Av}}{Z} \frac{\hbar \nu_j}{kT} \]
where
\[ j_{AV} = \frac{-\hbar \frac{\nu_s + \nu_2}{2}}{e^{\frac{\nu_s + \nu_2}{2kT}} - 1} \]

\[ \nu_f = \nu_3 - \nu_2 \]

Within the above approximations we then obtain
\[ a_f(t) = a_f(0) e^{-\frac{W_c t}{2kT}} - \frac{j_{AV} \frac{1}{2} N(1 - e^{-\frac{W_c t}{kT}}) W_c \hbar^2 \nu_f^2}{2 k T (R_p I_g + I_{f_3})} \] (2-B-16)

Again, \( a_f(0) \) is the gain coefficient when the excited vibrational level is empty. From expression (2-B-16) we find that under a condition of strong pumping the gain will become negative after approximately a time
\[ t = \frac{1}{j_{AV}} \ln \left( \frac{kT}{\hbar \nu_f} \right) \] (2-B-17)

This time it is just a little bit longer than \( t_{cv} \) of (2-B-14).

As we mentioned before, the rate equation approach is good for the order of magnitude estimates but does not properly reflect the spectral characteristics of the gain. This will become apparent in the section that follows.
II. C. DENSITY MATRIX TREATMENT

To correctly predict the spectral response we will treat the interaction of a three-level system with two near resonant radiation fields in some more detail. The semiclassical approach which we will use, i.e. quantized molecular system interacting with classical electromagnetic fields, takes into account the coherence between the states 1, 3, and 2 introduced by the presence of the two laser fields, the pump and the SMM ones. These effects, about which we can think as mixing or modulation of the molecular wave functions by the near resonant fields, produce changes in the molecular response spectrum commonly known as the AC (or dynamic) Stark effect, Rabi splitting, or Autler-Townes effect. Javan presented the first quantum mechanical calculation for a homogeneously broadened three-level laser system using the time dependent Schrodinger equation. His results are valid in the case of weak FIR field intensity. For strong FIR field his results are valid only for both fields on resonance or if both are off resonance by the same amount. Recently there have been a number of publications extending the results to arbitrary field intensities and offsets utilizing the ensemble averaged density matrix formalism. Panock and Temkin have provided extensive discussion of the results rather than simply writing out the solutions and therefore
here we will reproduce their results using their notation. Extensions and applications of these results are presented in subsequent sections. The appropriate level diagram and symbol definitions are shown on Fig. II-C-1. The pump field of amplitude $E_p$ and of angular frequency $\omega_p$ is incident on the molecular system whose levels 3 and 1 are separated by angular frequency $\omega_{31}$. The pump offset

$$\delta_p = \omega_p - \omega_{31}$$

is assumed to be much smaller than either of the level separations $\omega_{31}$ or $\omega_{32}$. The transition between levels 3 and 2 is probed by a signal field of amplitude $E_s$ and of angular frequency $\omega_s$. The signal offset

$$\delta_s = \omega_s - \omega_{32}$$

is again assumed much smaller than either $\omega_{31}$ or $\omega_{32}$. We are dealing then with near resonant interactions. The transitions are assumed to be electric dipole allowed and the respective matrix elements of the transition dipole moments are denoted by $\mu_{13}$ and $\mu_{32}$. It is also convenient to introduce the symbols

$$\varrho_{13} = \frac{\mu_{13} \cdot E_p}{2 \hbar}$$

and

$$\varrho_{32} = \frac{\mu_{32} \cdot E_s}{2 \hbar}$$
OPTICALLY PUMPED LASER

\[ \beta_{13} \equiv |\mu_{13}| \frac{E_p}{2\hbar} \]
\[ \delta_p \equiv \omega_p - \omega_{31} \]
\[ \beta_{32} \equiv |\mu_{32}| \frac{E_s}{2\hbar} \]
\[ \delta_s \equiv \omega_s - \omega_{32} \]

FIGURE II-C-1
which are equal to one-half of what is commonly called the Rabi frequency.

The time evolution of the density matrix is governed by the following equation:

\[
\dot{\rho}_{mn} = \frac{i}{\hbar} [\rho, H]_{mn}
\]  

(2-C-4)

If all the interactions of the system are known accurately they can be explicitly included in the Hamiltonian. It is however often more convenient to treat certain disturbances in a phenomenological way. We find that the interacting fields can be easily included in the Hamiltonian but that the collisional interactions are best handled by phenomenological decay constants. Our work concentrates on systems which are homogeneously broadened. For such systems we can rewrite (2-C-4) as

\[
\dot{\rho}_{mm} = -\tau^{-1}_{mm} (\rho_{mm} - \rho^0_{mm}) + \frac{i}{\hbar} [\rho, H]_{mm}
\]

\[
\dot{\rho}_{mn} = -\tau^{-1}_{mn} \rho_{mn} + \frac{i}{\hbar} [\rho, H]_{mn}
\]  

(2-C-5)

where \(\rho^0_{mm}\) are the values of the diagonal density matrix elements, corresponding to the level populations, in the absence of the applied fields. \(\tau_{mn}\) and \(\tau_{mm}\) account for the changes in populations and the destruction of coherence between the molecular states due to collisions.
is the Hamiltonian of the unperturbed system plus the terms accounting for the dipole interactions with the fields:

\[ H = H_0 - \mu \cdot E(t) \]  

(2-C-6)

with

\[ \int \psi^*_n H \psi_m d\tau = E_m \delta_{mn} - \mu_{mn} \cdot E(t) \]  

(2-C-7)

In our further derivations we will assume that \( \mu_{nn} E(t) = 0 \). This is not true for molecules with permanent dipole moments, but \( \mu_{nn} \neq 0 \) does not directly affect emission or absorption of radiation at frequency \( \omega_p \) or \( \omega_s \) and we can drop this term at the outset. We will also allow \( \mu_{12} = 0 \) since we assume that no radiation at the frequency \( \omega_{12} \) is present.

We will now define population differences to be

\[ r_{13} = \rho_{11} - \rho_{33} \]

\[ r_{32} = \rho_{33} - \rho_{22} \]  

(2-C-8)

Equations (2-C-5) then become:

\[ \dot{r}_{13} = -\left( r_{13} - r_{13}^* \right) \tau^{-1} + \frac{i}{\hbar} \left[ 2 \left( \mu_{13} g_{31} - \mu_{31} g_{13} \right) - \left( \mu_{32} g_{23} - \mu_{23} g_{32} \right) \right] E(t) \]  

\[ \dot{r}_{32} = -\left( r_{32} - r_{32}^* \right) \tau^{-1} + \frac{i}{\hbar} \left[ \left( \mu_{31} g_{13} - \mu_{13} g_{31} \right) + 2 \left( \mu_{32} g_{23} - \mu_{23} g_{32} \right) \right] E(t) \]
\[
\begin{align*}
(\frac{d}{dt} + \tau^{-1} - i\omega_{31})\rho_{12} &= \frac{i}{\hbar} \left( \mu_{13} \rho_{32} - \mu_{32} \rho_{13} \right) E(t) \\
(\frac{d}{dt} + \tau^{-1} - i\omega_{31})\rho_{13} &= -\frac{i}{\hbar} \left( \mu_{13} \rho_{13} + \mu_{23} \rho_{12} \right) E(t) \\
(\frac{d}{dt} + \tau^{-1} + i\omega_{22})\rho_{32} &= \frac{i}{\hbar} \left( \mu_{32} \rho_{32} - \mu_{31} \rho_{12} \right) E(t)
\end{align*}
\]

where for simplicity we have allowed all the relaxation constants to be equal. This approximation usually holds well for systems in which the energy level separations are much less than the room temperature energy \(kT\).

To obtain steady state solutions we will set \(\dot{\rho}_{13} = \dot{\rho}_{32} = 0\) and thus obtain two time independent equations for the population differences and three time dependent equations for the off-diagonal matrix elements.

Since our interest lies in the nearly resonant terms we will take the electric field to be a sum of two components oscillating at \(\omega_p = \omega_{31}\) and \(\omega_s = \omega_{32}\):

\[
E(t) = E_p \cos(\omega_p t + \phi_p) + E_s \cos(\omega_s t + \phi_s)
\]

which in complex notation becomes

\[
E(t) = \frac{1}{2} \left[ E_p e^{i\phi_p} e^{i\omega_p t} + E_s e^{i\phi_s} e^{i\omega_s t} + c.c. \right]
\]
After a rather lengthy algebraic manipulation of equations (2-C-9) one obtains, in the steady state population limit, the following results:

\[
\mathcal{S}_{13} = \frac{\mu_{13}}{2 \hbar} \left\{ \frac{\mathcal{R}_{13}}{L_{13}} + \mathcal{Q}_{32}^2 R \left[ \frac{\mathcal{R}_{13}}{L_{13}} - \frac{\mathcal{R}_{32}}{L_{32}} \right] \right\} \mathcal{E}_p e^{i \phi_e} e^{i \omega_p t}
\]

\[
\mathcal{S}_{32} = \frac{\mu_{32}}{2 \hbar} \left\{ \frac{\mathcal{R}_{32}}{L_{32}} - \mathcal{Q}_{13}^2 R \left[ \frac{\mathcal{R}_{13}}{L_{13}} - \frac{\mathcal{R}_{32}}{L_{32}} \right] \right\} \mathcal{E}_s e^{i \phi_s} e^{i \omega_s t}
\]

where

\[
L_{13} = \omega_{31} - \omega_p + \frac{i}{\tau}
\]

and

\[
L_{32} = \omega_5 - \omega_{32} + \frac{i}{\tau}
\]

are, upon squaring, the Lorenzian lineshapes, and

\[
R = (R_1 - i R_2) \tau
\]

where

\[
R_1 = \left( 1 + \delta_s^2 \tau^2 \right) \left( 1 + \delta_p^2 \tau^2 \right) \left[ A / (A^2 + B^2) \right]
\]

\[
R_2 = \left( 1 + \delta_s^2 \tau^2 \right) \left( 1 + \delta_p^2 \tau^2 \right) \left[ B / (A^2 + B^2) \right]
\]

and where

\[
A = \delta_s \tau \left( 1 + \delta_p^2 \tau^2 \right) \left( 1 + \delta_s^2 \tau^2 - \mathcal{Q}_{13}^2 \tau^2 \right)
- \delta_p \tau \left( 1 + \delta_s^2 \tau^2 \right) \left( 1 + \delta_p^2 \tau^2 - \mathcal{Q}_{32}^2 \tau^2 \right)
\]

\[
B = \left( 1 + \delta_s^2 \tau^2 \right) \left( 1 + \delta_p^2 \tau^2 \right) + \mathcal{Q}_{13}^2 \tau^2 \left( 1 + \delta_p^2 \tau^2 \right)
+ \mathcal{Q}_{32}^2 \tau^2 \left( 1 + \delta_s^2 \tau^2 \right)
\]
We can now obtain the expressions for the steady state population differences using (2-C-9) and (2-C-12) to (2-C-15):

\[
\begin{align*}
\Gamma_{13} &= r_{13}^0 \left[ \begin{array}{c} \Gamma_4 \ / \ (\Gamma_1 \Gamma_4 - \Gamma_2 \Gamma_3) \end{array} \right] \\
\Gamma_{32} &= r_{13}^0 \left[ \begin{array}{c} \Gamma_3 \ / \ (\Gamma_1 \Gamma_4 - \Gamma_2 \Gamma_3) \end{array} \right] \\
\Gamma_{12} &= \Gamma_{13} + \Gamma_{32}
\end{align*}
\]  

(2-C-16)

where

\[
\begin{align*}
\Gamma_1 &= 1 + \frac{4 \theta_{13} \tau^2}{1 + \delta^2 \tau^2} \left\{ \begin{array}{c} 1 - \theta_{32} \tau^2 \left[ \frac{\alpha_1}{1 + \delta^2 \tau^2} + \frac{\alpha_2}{2 (1 + \delta^2 \tau^2)} \right] \end{array} \right\} \\
\Gamma_2 &= \frac{2 \theta_{32} \tau^2}{1 + \delta^2 \tau^2} \left\{ \begin{array}{c} 1 + 2 \theta_{13} \tau^2 \left[ - \frac{\alpha_2}{1 + \delta^2 \tau^2} + \frac{\alpha_3}{2 (1 + \delta^2 \tau^2)} \right] \end{array} \right\} \\
\Gamma_3 &= \frac{2 \theta_{13} \tau^2}{1 + \delta^2 \tau^2} \left\{ \begin{array}{c} 1 - \theta_{32} \tau^2 \left[ \frac{2 \alpha_2}{1 + \delta^2 \tau^2} + \frac{\alpha_4}{1 + \delta^2 \tau^2} \right] \end{array} \right\} \\
\Gamma_4 &= 1 + \frac{4 \theta_{32} \tau^2}{1 + \delta^2 \tau^2} \left\{ \begin{array}{c} 1 + \theta_{13} \tau^2 \left[ \frac{\alpha_4}{1 + \delta^2 \tau^2} - \frac{\alpha_2}{2 (1 + \delta^2 \tau^2)} \right] \end{array} \right\} \\
\alpha_1 &= (1 - \delta^2 \tau^2) R_2 + 2 \delta \tau R_1 \\
\alpha_2 &= (\delta - \delta_s) \tau R_1 + (1 + \delta \delta_s \tau^2) R_2 \\
\alpha_3 &= 2 \delta_s \tau R_1 - (1 - \delta_s^2 \tau^2) R_2
\end{align*}
\]  

(2-C-17)
In obtaining (2-C-16) we have assumed that \( r_{32} = 0 \). This is similar to the assumption following equation (2-B-11) and is based on the same rationale, i.e. essentially empty excited vibrational state.

To obtain the expectation value of any operator using the ensemble averaged density matrix formalism one only has to find the trace of the product of the matrix representing this operator and the density matrix. The induced polarization can then be calculated as

\[
\mathcal{P} = \text{Tr} \left( \mu \varrho \right) \quad (2-C-18)
\]

which for the system under discussion becomes

\[
\mathcal{P} = 2 \text{Re} \left( \mu_{31} \varrho_{13} \right) + 2 \text{Re} \left( \mu_{32} \varrho_{23} \right) \quad (2-C-19)
\]

From (2-C-12) we see that the time dependence of \( \rho_{13} \) is just a factor of \( e^{i \omega_p t} \) and that the time dependence of \( \rho_{23} \) \( (= \rho_{32}^* \) is just \( e^{i \omega_s t} \). Thus we can write the total polarization as the sum of an induced polarization at frequency \( \omega_p \) and an induced polarization at frequency \( \omega_s \) where \( \mathcal{P}(\omega_p) = 2 \text{Re} \left( \mu_{31} \varrho_{13} \right) \), \( \mathcal{P}(\omega_s) = 2 \text{Re} \left( \mu_{32} \varrho_{23} \right) \). These expressions can be rewritten in the form \( \mathcal{P} = \text{Re} \left( \chi \mathcal{E} e^{i \omega_p t} e^{i \omega_s t} \right) \) where the susceptibility \( \chi \) is complex. The imaginary part of the susceptibility is responsible for amplifica-
tion and absorption. Utilizing the usual notation \( \chi = \chi' + i\chi'' \) we can write for the rate of change of intensity with distance

\[
\frac{dI}{dz} = P \cdot E
\]

\[
= \frac{1}{2} \omega |E|^2 \chi''(\omega)
\]

(2-C-20)

where the bar over the product \( P \cdot E \) indicates time average.

The solutions for the imaginary part of the susceptibility at frequencies \( \omega_s \) and \( \omega_p \) are found to be

\[
\chi''(\omega_s) = \frac{|\mu_{13}|^2}{\kappa} \frac{\tau}{1 + \delta_s^2 \tau^2} \left\{ r_{32} \left[ 1 + \theta_{13}^2 \tau^2 \left( \frac{\alpha_2}{i + \delta_s \tau^2} + \frac{\alpha_3}{i + \delta_s \tau^2} \right) \right] + r_{12} \left( \beta_{13} \tau^2 \frac{\alpha_2}{i + \delta_s \tau^2} \right) \right\}
\]

(2-C-21)

\[
\chi''(\omega_p) = -\frac{|\mu_{13}|^2}{\kappa} \frac{\tau}{1 + \delta_f \tau^2} \left\{ r_{13} \left[ 1 - \theta_{32}^2 \tau^2 \left( \frac{\alpha_1}{i + \delta_f \tau^2} + \frac{\alpha_2}{i + \delta_f \tau^2} \right) \right] + r_{12} \left( \theta_{32} \tau^2 \frac{\alpha_2}{i + \delta_f \tau^2} \right) \right\}
\]

(2-C-22)

where population differences are given by (2-C-16) and \( \alpha_1, \alpha_2, \alpha_3 \) are defined in (2-C-17).

In the expressions (2-C-21) and (2-C-22) two types of processes can be recognized. The terms proportional to \( r_{32} \) and \( r_{13} \) represent single photon transitions since these are population differences between the levels connected by the SMM and pump transitions respectively.
The terms proportional to $r_{12}$ represent two-photon processes since we have assumed $\mu_{12}=0$, which means that no direct electric dipole allowed transition is possible between the levels 1 and 2 (see Fig. II-C-1). Panock and Temkin\cite{31} show that the two-photon process, in both $\chi''(\omega_s)$ and $\chi''(\omega_p)$, has a resonance when $R_1=0$, which for small field intensities becomes $\delta_s = \delta_p$. This is just an energy conservation condition for an ordinary Raman process. These authors further show that if $R = (R_1-iR_2)\tau$ is set equal to zero one obtains the rate equation results\cite{21,25} for $\chi''(\omega_s)$ and $\chi''(\omega_p)$. An inspection of equations (2-C-14) and (2-C-15) shows however that $R_2$ can never be equal to zero and therefore the rate equation treatment is never correct, as pointed out by the same authors.\cite{31} They go on further to demonstrate that in the limit of a very weak FIR intensity, $\beta_{32}\tau \ll 1$, $\chi''(\omega_p)$ as given by (2-C-22) is in good agreement with the rate equation model due to the fact that there are very few transitions to level 2, see Fig. II-C-1, and therefore the system reduces basically to a two-level one. However, as they point out, under no conditions is the rate equation model correct in its predictions for $\chi''(\omega_s)$. The two-photon processes are as strong as the single photon ones for $\beta_{32}\tau = 0$ and are stronger than the latter ones for $\beta_{32}\tau > 0$. This is to say that under all
practical conditions the two photon processes dominate the SMM response of the system.

To check on the correctness of their solutions Panock and Temkin\textsuperscript{31} took their expressions to the limit of very weak SMM field, $\beta_{32}^\tau \ll 1$, which has been previously described by Javan.\textsuperscript{45} The results which they obtained:

\begin{align}
\Gamma_{13} &= \Gamma_{13}^0 \frac{1 + \delta_p \tau^2}{1 + \delta_p \tau^2 + 4 \theta_{13} \tau^2} \\
\Gamma_{32} &= \Gamma_{13}^0 \frac{2 \theta_{13} \tau^2}{1 + \delta_p \tau^2 + 4 \theta_{13} \tau^2} \\
\chi''(\omega_p) &= \frac{|\mu_{13}|^2}{\hbar} \tau \frac{\Gamma_{13}^0 \theta_{13}^2}{1 + \delta_p \tau^2 + 4 \theta_{13} \tau^2} \\
\chi''(\omega_s) &= \frac{|\mu_{23}|^2}{4 \hbar} \tau \Gamma_{13}^0 \theta_{13}^2 \left\{ \frac{1}{1 + (\gamma - \Omega)^2 \tau^2} \right\} \\
&\quad + \frac{1}{1 + (\gamma + \Omega)^2 \tau^2} \\
&\quad + \frac{2 (\gamma^2 - \Omega^2) \tau^2 (1 + 2 \gamma^2 \tau^2) - 2}{(1 + 4 \gamma^2 \tau^2)[1 + (\gamma - \Omega)^2 \tau^2][1 + (\gamma + \Omega)^2 \tau^2]}
\end{align}

where

\begin{align}
\Omega &= \frac{1}{2} \delta_p - \delta_s \\
\gamma &= \frac{1}{2} (\delta_p^2 + 4 \theta_{13}^2) \frac{1}{2}
\end{align}

agree with the corresponding results presented by Javan.\textsuperscript{45}

It is interesting to note that the absorption lineshape is a simple Lorentzian of full-width at half maximum (FWHM) $\Delta \omega = 2(1 + 4 \beta_{13}^2 \tau^2)^{1/2}/\tau$, i.e. a combina-
tion of homogeneous \((1/\tau)\) and power \((4\beta_{13}^2 \tau^2)\) broadening. This is the same result as that of the rate equations. By contrast, the emission lineshape as given by (2-C-25) is never a Lorentzian, which is what the rate equation model predicts. Some typical SMM lineshapes are shown on Fig. II-C-2.

In Fig. II-C-2(a), on resonance pumping, we can see the emission lineshape to be a single peak, higher than a Lorentzian, for small values of the pump parameter, \(\beta_{13}\). As the pump parameter increases, the peak grows in height and width. The maximum occurs for \(\beta_{13}^2 \tau^2 = 1/2\), after which the peak starts decreasing in height but keeps on increasing in width until, at \(\beta_{13}^2 \tau^2 = 5/7\), it splits into two peaks. For large values of \(\beta_{13} \tau\) the two peaks become quite distinct and located at \(\delta s \tau = \pm \beta_{13} \tau\), each of them having an almost Lorentzian lineshape of FWHM=\(\frac{2}{\tau}\). This splitting of the lineshape is, as we mentioned previously, called AC (or dynamic) Stark effect or Rabi splitting with the two peaks separated by the Rabi frequency (\(=2 \beta_{13}\)). Figure II-C-2(b) represents the case of off-resonance pumping with the detuning parameter, \(\delta p \tau\), equal to -5. This case is quite different from resonant pumping in that the lineshape, for \(|\delta p \tau| > 1\), consists of two peaks even for a very weak pump parameter,
FIGURE II-C-2 — Normalized $\chi''(\omega_s)$ is plotted for several values of the pump parameter, $\beta_{13} \tau$, versus the SMM frequency offset, $\delta_s$, normalized to the collision time, $\tau$, for weak SMM intensity, $\beta_{32} \tau \ll 1$, and for

(a) on resonance pumping, $\delta_p \tau = 0$

(b) off resonance pumping, $\delta_p \tau = -5$
\[ \delta_s \tau \ll 1. \] In this limit the two peaks are located at
\[ \delta_s = 0 \] and \[ \delta_s = \delta_p, \] i.e. at line center and at Raman frequency. For higher pump intensities the peaks separate further, their location given by
\[ (\delta_s \tau)^2 = \frac{1}{2} \delta_p \tau \pm \left( \delta_p^2 \tau^2 + 4 \Theta_{13} \tau^2 \right)^{1/2} \] (2-C-27)

The height of the peaks, all other parameters being the same, is smaller for off-resonant pumping as compared to on resonance case. These results, for small SMM intensities, have been reviewed in more detail by Shimoda and Shimizu.\(^{48,49}\)

When both the pump and the FIR fields are strong, \( \beta_{ij} \tau \gg 1, \) we find even more departures from the rate equation model predictions. We will use again the work of Panock and Temkin.\(^{31}\) In the strong field limit it is more illustrative to work with \( dI/dz \) than with \( \chi^\prime. \) In Fig. II-C-3 the normalized values of \( dI(\omega_s)/dz \) versus SMM frequency offsets are plotted for on resonance pumping, \( \delta_p = 0. \) The outstanding features are that for strong pumping the increasing SMM intensity first causes the peaks to broaden and then merge into a single peak at \( \delta_s = 0. \) This happens when \( \beta_{32} \approx \beta_{13}. \) As the intensity of the emission field is increased further, the peak height actually decreases, while its width keeps on increasing. This is a very important result in terms of
FIGURE II-C-3 -- Normalized $\frac{dI(\omega_s)}{dz}$ plotted for several values of the SMM emission parameter, $\beta_{32} \tau$, versus the SMM frequency offset, $\delta_s \tau$, normalized to the collision time, $\tau$, for on resonance pumping, $\delta_p = 0$, and for pump parameter.

(a) $\beta_{13} \tau = 5$

(b) $\beta_{13} \tau = 2$
FIGURE II-C-3 -- Normalized $dI(\omega_s)/dz$ is plotted for several values of the SMM emission parameter, $\beta_{32}\tau$, versus the SMM frequency offset, $\delta_s$, normalized to the collision time, $\tau$, for on resonance pumping, $\delta_p=0$, and for pump parameter (c) $\beta_{13}\tau=1$, (d) $\beta_{13}\tau=.5$. 
optimization of the performance of the laser pumped lasers and is quite different from the predictions of the rate equation model, i.e. $dI/dz$ monotonically increasing with both the pump and emission intensities. Panock and Temkin\textsuperscript{31} obtain an exact expression for the emission parameter which optimizes $dI(\omega_s)/dz$ for on resonance pumping:

$$\left( \frac{\beta^2}{\tau^2} \right)_{\text{max}} = \frac{1}{2} \left[ \left( 1 + \frac{\beta^2}{\tau^2} \right) \left( 1 + 4 \frac{\beta^2}{\tau^2} \right) \right]^{1/2}$$

(2-C-28)

which becomes $\beta_{32} \approx \beta_{13}$ for $\beta_{13}^2 \tau^2 \gg 1$ (strong pumping).

An investigation of the behavior of $(dI(\omega_s)/dz)_{\text{max}}$ as a function of $\beta_{13}^2 \tau$ reveals that it monotonically increases and asymptotically approaches the value of $3/8 (\hbar \omega_s/\tau) r_{13}^o$.

Figures II-C-4 and II-C-5 show some results for off resonant pumping. One of the interesting features is the different saturation behavior of the two peaks which will be discussed in more detail in Section II-D. Also visible is the shift in the peak positions with increasing value of the emission parameter $\beta_{32}^{2}\tau$ until they merge into a single peak. Again, for every value of $\delta_p$ and $\beta_{13}$ parameters there exists a value of $\beta_{32}$ optimizing the emission efficiency. No analytic formulas are available due to the complexity of the expressions in the off-resonant pumping case. Interested reader is referred to the work of Panock and Temkin\textsuperscript{31} for a discus-
FIGURE II-C-4 -- Normalized $\chi''(\omega_s)$ is plotted versus the signal offset, $\delta_s$, normalized to the collision time, $\tau$, for various values of the offset parameter, $\delta_p \tau$, for $\beta_{13} \tau = 10$ and (a) $\beta_{32} \tau = 1$, (b) $\beta_{32} \tau = 5$. 
FIGURE II-C-5 -- Normalized $dI(\delta_s)/dz$ is plotted versus the signal offset, $\delta_s$, normalized to the collision time, $\tau$, for various values of the emission parameter, $\beta_{32}\tau$, for pump offset parameter $\delta_p\tau = -5$ and for (a) $\beta_{13}\tau = 5$, (b) $\beta_{13}\tau = 2$. 
sion of numerical methods of finding the optimizing values. One interesting result of their work is that off-resonant pumping produces higher values of \(dI(\omega_s)/dz\) than resonant one for the same values of other parameters. This seems to have been confirmed in the recent experiments of Woskoboinikow et al. \(^53\) They observed that the \(4_{22} \rightarrow 4_{13}, 385 \mu m\), transition in \(D_2O\) vapor pumped by the 9.26 \(\mu m\) R22 line of \(CO_2\) has the highest conversion efficiency of pump to FIR radiation when the pump frequency, normally about 318 MHz \(^51,52\) below the absorbing line is tuned even further away from that line.

II. D. SATURATION BEHAVIOR

In Section II. C. we have encountered the phenomenon that when the emission intensity increases the spectral response of the laser pumped gain medium (off resonant pumping) becomes asymmetric, see Figs. II-C-4 and II-C-5. This indicates different saturation properties of the two emission components, the line center and the Raman. We will find below that the line center component saturates easier than the Raman one. It will be shown, for the first time, that the saturation intensity for the line center frequency is the same, in some limits, as that given by the rate equation model while the saturation intensity for the
Raman line is a function of both the pump offset and intensity. The physical reason for this difference in behavior can be explained as follows. The line center emission is basically a single photon process involving only two levels and is thus well described by the rate equation model. The Raman frequency emission involves both the pump and the SMM fields and utilizes a virtual level at some offset, $\delta_P$, from the real level. It is for that reason that the two field intensities appear in the saturation expression in a similar manner, their joint power broadening effect acting to overcome the frequency difference between the virtual and real levels.

We will start our treatment by looking at the line center behavior. We find, starting from (2-C-21), that we are able, in a limiting case to be described below, to obtain the following expression:

$$\chi''(\omega_{32}) = \frac{r_3^0 \tau |\mu_{31}|^2}{\hbar} \frac{Q_{33}^2 \tau^2}{\delta_P^2 \tau^2} \frac{1}{1 + 4 \Theta_{32}^2 \tau^2}$$  \hspace{1cm} (2-D-1)$$

The saturating E-field is then derived from the condition

$$4 \Theta_{32}^2 \tau^2 = 1$$  \hspace{1cm} (2-D-2)$$
which gives

$$\frac{\mu_{32} \cdot E_s}{\kappa} \tau = 1$$

(2-D-3)

exactly as in the rate equation model. The conditions under which we were able to derive these results were as follows:

$$\delta_s^2 \tau ^2 \ll 1 \Rightarrow \text{SMM frequency close to the line center}$$

$$\delta_p^2 \tau ^2 \gg 1 \Rightarrow \text{large pump offset}$$

$$\delta_p^2 \tau ^2 \gg 4\beta_{13}^2 \tau ^2 \Rightarrow \text{negligible AC Stark shifts}$$

$$\delta_p^2 \tau ^2 \gg \beta_{13}^4 \tau ^4 \Rightarrow \text{needed to drop some terms}$$

(2-D-4)

Numerical results seem to indicate that this result is valid over a much broader range of parameters than the ones stated above. We can see in Figures II-D-1 (a) through (c) that as the pump power increases the saturation intensity of the line center peak, even when it is AC stark shifted by a very large amount as in Figure II-D-1(c), remains almost constant (there is only a slight increase).

Let's now look at the Raman line. It is easier to deal with since for the signal offset equal to the pump offset, $\delta_s = \delta_p$, we can use the much simpler formulation of Javan.\textsuperscript{45} We will continue to use the notation of Panock and Temkin.\textsuperscript{31} In the limit of non-zero emission signal, $\beta_{32} \neq 0$, expression (2-C-25) becomes
FIGURE II-D-1 -- Saturation behavior I.

Normalized $\chi''(\omega_s)$ is plotted versus signal offset, $\delta_s \tau$, for $\delta_p \tau = -5$. Each of the figures contains a plot in the small signal limit (higher one), $\beta_{32} \tau \ll 1$, and a plot with $\beta_{32} \tau = 1/2$ (lower one), which is the saturation value predicted by the rate equations.

(a) $\beta_{13} \tau = 0.1$ weak pumping; $\chi''(\omega_s)$ plotted for $\delta_s \tau$ between -10 and 5 and its maximum value is $4.18 \times 10^{-4}$.

(b) $\beta_{13} \tau = 5; \delta_s \tau$ between -15 and 10; $\chi''(\omega_s)_{\max} = 0.2$

(c) $\beta_{13} \tau = 25; \delta_s \tau$ between -32 and 32; $\chi''(\omega_s)_{\max} = 0.25$
\[ \chi''(\omega_s) = \frac{1}{4} \left( \frac{m_{13}^2}{h} \right)^2 \tau_{13}^{\prime 0} \frac{\phi_{13}^2}{\delta^2} \left\{ \frac{1}{1 + (\nu - \nu')^2 \tau^2} + \frac{1}{1 + (\nu + \nu')^2 \tau^2} \right\} \]

\[ + \frac{2 \left( \nu^2 - \nu'^2 \right) \tau^2 \left( 1 + 2 \nu^2 \tau^2 \right) - 2 \left( 1 + 4 \nu^2 \tau^2 \right) \left[ 1 + (\nu - \nu')^2 \tau^2 \right] \left[ 1 + (\nu + \nu')^2 \tau^2 \right] \right\} \]  \hspace{1cm} \text{(2-D-5)}

where

\[ \Omega = \frac{1}{2} \delta_p - \delta_s \quad \text{and} \quad \gamma = \frac{1}{2} \left[ \delta_p^2 + 4 \left( \phi_{13}^2 + \phi_{32}^2 \right) \right]^{1/2} \]  \hspace{1cm} \text{(2-D-6)}

We will notice that the only difference appears in the form of the parameter \( \gamma \) which now includes, on equal footing, both \( \beta_{13} \) and \( \beta_{32} \). The contribution from the third term in the parenthesis in expression (2-D-5) can be neglected for off-resonant pumping, \( \delta_p \gg 1 \), since it mainly affects the spectral region between the Raman and line center frequencies. Of the other two terms in the parenthesis only one is resonant at the Raman frequency, depending on the sign of the pump offset. For the sake of simplicity, without affecting the generality of this discussion, we will assume a negative pump offset. In this case only the first term in the parenthesis of (2-D-5) is of importance at \( \delta_s = \delta_p \) and we can write

\[ \chi''(\omega_{32} + \delta_p) = \frac{1}{4} \left( \frac{m_{13}^2}{h} \right)^2 \tau_{13}^{\prime 0} \frac{\phi_{13}^2}{\delta^2} \frac{1}{4 \left[ \delta_p^2 + 4 \left( \phi_{13}^2 + \phi_{32}^2 \right) \right]^{1/2} + \frac{1}{2} \delta_p^2} \tau^2 \]  \hspace{1cm} \text{(2-D-7)}
We note again in (2-D-7) the similar treatment of the pump and the FIR intensities as far as the FIR saturation is concerned. We will stop here the analytic treatment of the Raman line. This is because for the high pump powers, which are of interest to us, the position of the Raman peak shifts away from $\delta_s = \delta_p$ due to the AC Stark effect and the behavior of $\chi''$ at $\omega = \omega_{32} + \delta_p$, where (2-D-7) is valid, is no longer of interest. In place of an analytic treatment we can see the saturation behavior using the results of some numerical work, as shown on Fig. II-D-1. The rate equation model would have us believe that the saturation E-field at $\delta_s = \delta_p$ would be $E_s = E_s^0 (1 + \delta_p^2 r^2)^{1/2}$ which means that for $\delta_p \tau >> 1$ the Raman component would be much harder to saturate under all pumping conditions. Fig. II-D-1 however shows that a strong pump makes the saturation of the now also AC Stark shifted Raman line almost as easy as the saturation of the line center. This is another example of the failure of the rate equation model in the treatment of a three-level laser pumped system.

Yet another departure from the rate equation model is illustrated by Fig. II-D-2. Here, in the weak pump regime, $\beta_{13} \tau = 0.1$ and $\delta_p \tau = -5$, we have plotted the system response for three values of $\beta_{32} \tau$, i.e. the
FIGURE II-D-2 -- Saturation behavior II.
Normalized $\chi''(\omega_s)$ is plotted versus signal offset, $\delta_s \tau$, for $\delta_p \tau = -5$ and $\beta_{13} \tau = 0.1$.

Horizontal scale: $\delta_s \tau = -10$ to $\delta_s \tau = 5$.

The three curves, in order of decreasing amplitude, correspond to $\beta_{32} \tau = 0$, $\beta_{32} \tau = 2.5$, and $\beta_{32} \tau = 5$ respectively. The peak heights are $4.18 \times 10^{-4}$, $2.60 \times 10^{-4}$, and $0.99 \times 10^{-4}$ respectively.
signal parameter.

The curve with the highest amplitude and double peak structure corresponds to the small signal limit, the same as in Fig. II-D-1(a). As we increase $\beta_{32}\tau$, the line center component goes down to half its amplitude at $\beta_{32}\tau = .5$, see Fig. II-D-1(a), while the Raman component reacts to a much smaller degree. As the signal power is increased further, $\beta_{32}\tau = 2.5$, we see a single peak down to a little over one-half of the small signal limit's amplitude and shifted away from the Raman position and toward the line center position. For $\beta_{32}\tau = 5$ we find the single, now quite broad, peak at the line center position. Its amplitude is down to about 1/4 of that of the small signal limit.

The signal offset, $\delta_{SR}$, corresponding to the peak of the Raman transition is given by

$$\delta_{SR} \tau \left( 1 + \delta_{P}^{2} \tau^{2} \right) \left( 1 + \delta_{SR}^{2} \tau^{2} - Q_{IS}^{2} \tau^{2} \right) = \delta_{P} \tau \left( 1 + \delta_{SR}^{2} \tau^{2} - Q_{IS}^{2} \tau^{2} \right)$$

which comes directly from the Raman resonance condition of $R_{1} = 0$ (see eq. 2-C-14). Numerical solutions of (2-D-8) show that for strong FIR fields the Raman peak approaches the $\delta_{S} = 0$ position. For very large $\beta_{32}\tau$ values however, eq. (2-D-8) does not have a solution.
II. E. POLARIZATION PROPERTIES

In our treatment so far we have dealt with an idealized three-level system. In a real gas however the molecules are randomly oriented in space. Polarization of the pump and SMM fields removes the space isotropy in a sense that molecules with different magnetic sub-level quantum numbers $M$ will have different transition probabilities associated with them. This follows from the fact that the strength of the interaction between the field and the molecule depends on the dot product $\mu \cdot \mathbf{E}$ and the direction of $\mu$ is a function of the quantum number $M$.

In this section we will derive, for the first time for the homogeneously broadened regime, analytical expressions for the gain for the FIR fields polarized parallel and perpendicular with respect to the pump polarization. We will show that these are applicable both to the symmetric-top and the asymmetric-top molecules.

Let us first consider the matrix elements involved in the dipole allowed transitions. We will assume that there is no interaction between the rotational and the vibrational motions of the molecule. Under this assumption the total wavefunction can be separated
into a product of rotational and vibrational wavefunctions:

\[ \psi = \psi_V \psi_R \]  \hspace{1cm} (2-E-1)

We will now associate, without any loss of generality, a space fixed \( \hat{z} \)-axis with the direction of polarization of the field. With this choice only the \( z \)-component of the transition dipole moment will be responsible for the transition.

Let us first consider symmetric top molecules. We can separate the dipole moment into two components, one parallel and one perpendicular to the direction of the molecular axis of symmetry:

\[ \vec{\mu} = \vec{\mu}_\parallel + \vec{\mu}_\perp \]  \hspace{1cm} (2-E-2)

With the above definitions in mind we can write the \( z \)-component of the matrix element of the transition as

\[ \mu_z = \int \psi_V^* \psi_R^* (\vec{\mu}_\parallel + \vec{\mu}_\perp) \cdot \hat{z} \psi_V \psi_R \, d\tau_V \, d\tau_R \]  \hspace{1cm} (2-E-3)

where \( d\tau_V \) is the infinitessimal element of the integration space over the normal coordinates of molecular vibrations and \( d\tau_R \) gives the infinitessimal integration volume over the angles associated with the molecular rotation. In the integral (2-E-3) we can express the dot product in terms of Eulerian angles:
where \( \theta \) is the angle between the molecular axis of symmetry and the space fixed \( \hat{z} \)-axis and \( \chi \) is the angle of rotation about the molecular axis of symmetry. Making the above substitutions we obtain

\[
\vec{\mu} \cdot \hat{z} = \mu_{\parallel} \cos \theta
\]
\[
\vec{\mu} \cdot \hat{z} = \mu_{\perp} \sin \theta \cos \chi
\] (2-E-4)

For the purely rotational transitions, \( \psi_j^i = \psi_v^i \), only the permanent dipole moment, \( \mu_0 \), is of importance. \( 38-40 \) In molecules with any type of symmetry axis \( \mu_0 \) is always parallel to this axis and thus we obtain

\[
\mu_{\text{rot.}} = \mu_0 \int \psi_v^* \psi_v^i \ d\tau \int \psi_R^* \psi_R^i \cos \theta \ d\tau_R
\] (2-E-5)

The first integral in (2-E-6) is equal to unity since the wavefunctions are assumed to be normalized. The value of the second integral can be found in many references \( 38-40 \) and is also listed in Table II-E-1 under its commonly used name of "Direction-cosine Matrix Element". In this table, fashioned after Townes and Schawlow, \( 40 \) the total matrix element is written as
\[ \mu_{\text{transition}} = \mu \delta_{j j'} \delta_{k k'} \delta_{m m'} \]  

(2-E-7)

where \( J, K, M \) and \( J', K', M' \) are the quantum numbers of the initial and final states respectively.

In the case of vibrational - rotational transitions only the induced dipole moment is active\textsuperscript{38,39} and we will denote its integral by \( \mu_v \). The induced dipole moment may have components both parallel and perpendicular to the axis of molecular symmetry depending on which normal modes of vibration are excited. With this in mind we obtain

\[ \mu_{\text{vib.-rot}}^i_{j} = \mu_v \int \psi_R^i \psi_R^j \cos \Theta d\tau_R + \mu_v \int \psi_R^i \psi_R^j \sin \Theta \cos \chi d\tau_R \]  

(2-E-8)

and again the values of the integrals can be obtained from the Table II-E-1.

If we choose some arbitrary direction of polarization the total transition probability will be the sum of probabilities given for each of its projections onto the space fixed coordinate axes.

Before we go any further we will show that the derivations below will describe both the symmetric-top and asymmetric-top molecules. The symmetric-top molecular wavefunctions form a complete set and therefore any rotational wavefunction, specifically that of an asym-
### TABLE II-E-1 -- VALUES OF FACTORS OF THE DIRECTION-COSINE MATRIX ELEMENTS

The dipole moment matrix element is
\[ \phi_{JJ'} \phi_{JKJ'} \phi_{JMJ'} \] Subscript a applies to cases where \( \mu \) is along the molecular axis, b or c to cases where \( \mu \) is perpendicular to this axis. Subscripts x, y, or z apply for \( \mu_x, \mu_y, \) or \( \mu_z, \) which are the appropriate elements for polarization along the x, y, or z directions, respectively. Matrix elements listed are appropriate for a prolate symmetric top (with a the symmetry axis). For an oblate symmetric top, \( \phi_a \) should be replaced by \( \phi_c, \) \( \phi_c \) by \( \phi_b, \) and \( \phi_b \) by \( \phi_a. \)

<table>
<thead>
<tr>
<th>Matrix element factor</th>
<th>Value of J'</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J + 1</td>
</tr>
<tr>
<td>( \phi_{JJ'} )</td>
<td>[ \frac{4 (J + 1)}{(2J + 1)(2J + 3)} ]^{-1}</td>
</tr>
<tr>
<td>( \phi_a ) ( J K J' K' )</td>
<td>2 ( \sqrt{J + 1}^2 - K^2 )</td>
</tr>
<tr>
<td>( \phi_b ) or ( \pm i \phi_b ) ( J K J' K' )</td>
<td>[ \pm \frac{[(J \pm K + 1) (J \pm K + 2)]^{1/2}}{(J \pm K)(J \pm K+1)} ] ( \sqrt{J \pm K}(J \pm K+1) ) [ \pm \sqrt{J \pm K}(J \pm K-1) ]</td>
</tr>
<tr>
<td>( \phi_e ) ( J M J' M' )</td>
<td>2 ( \sqrt{(J + 1)^2 - M^2} )</td>
</tr>
<tr>
<td>( \phi_x ) or ( \mp i \phi_x ) ( J M J' M' )</td>
<td>[ \pm \frac{[(J \pm M + 1) (J \pm M + 2)]^{1/2}}{(J \pm M)(J \pm M+1)} ] ( \sqrt{J \pm M}(J \pm M+1) ) [ \pm \sqrt{J \pm M}(J \pm M-1) ]</td>
</tr>
</tbody>
</table>
metric-top molecule, can be expressed as a combination of them. Using the formalism explained in Section II. A.
we can write

\[ \psi_{JK, \Gamma, M} = \sum_{K} a_{JKM} \psi_{JKM} \]  

(2-E-9)

where \( \psi_{JKM} \) are the symmetric-top wavefunctions. We sum only over the internal projection quantum number \( K \) since the total angular momentum, \( J \), and its projection on an arbitrary space fixed axis, \( M \), are good quantum numbers for any isolated system. We will further note that in the absence of external fields all molecular orientations are equally probable and therefore the expansion coefficients \( a_{JKM} \) can only be functions of \( J \) and \( K \).

Therefore, we write

\[ \psi_{JK, \Gamma, M} = \sum_{K} a_{JK} \psi_{JKM} \]  

(2-E-10)

Let us again choose, for the sake of simplicity, a space fixed coordinate system whose z-axis is parallel to the field's polarization vector. With this choice again only the z-component of the matrix element of the transition is active. We can therefore write

\[ M_{z}^{i} = \mu \int \cos \theta \ \psi_{j_{1}K_{1}K_{11}M_{1}}^{*} \psi_{j_{1}K_{1}K_{11}M_{1}} \ d\tau_{R} \]  

(2-E-11)

where \( \mu \) is the permanent dipole moment for a rotational transition or the induced dipole moment vibrational
matrix element for a vibrational-rotational transition. \( \theta \) is the angle between the space fixed \( \hat{z} \)-axis and the dipole moment. Substituting (2-E-10) into (2-E-11) and using (2-E-6) we obtain

\[
\mu_{ij}^{\hat{z}} \equiv \sum_{K_i K_i} a_{ji K_i} a_{ji K_i} \mu_{ij \text{sym.-top}}^{\hat{z}}
\]

(2-E-12)

With the help of equation (2-E-7) we finally write

\[
\mu_{ij}^{\hat{z}} = \mu \varphi_{ji} \varphi_{ji} \mathcal{K}_{ji} \sum_{K_i K_i} a_{ji K_i} a_{ji K_i} \varphi_{ji} \varphi_{ji}
\]

(2-E-13)

The dependence of the molecular response to the incident radiation's polarization is confined to the \( \varphi_{ji} \mathcal{K}_{ji} \) factor since only this factor contains the information about the molecular orientation in the space fixed coordinate system. From (2-E-7) and (2-E-13) we see that this factor enters in exactly the same way into the transition dipole moment matrix elements for the symmetric- and the asymmetric-top molecules. Therefore, the results to be derived below will apply to both types of molecules.

There are three limits which lend themselves to analytical treatment. In all of them the SMM field is assumed small so that equation (2-C-25) rather than (2-C-21) can be used as a starting point. The three limits are differentiated by the relative sizes of \( \gamma_{13} \tau \) and \( \delta_{p} \tau \). 


parameters. We will find that the cases of weak pumping field, $\beta_1^2 \tau^2 \ll 1$, and strong pumping field, $\delta_p^2 \tau^2 \gg 4\beta_1^2 \tau^2 \gg 1$, are identical in their polarization behavior, while the strong pump case of $4\beta_1^2 \tau^2 \gg \delta_p^2 \tau^2 \gg 1$ differs from them.

In order to obtain the aforementioned results we will extend the density matrix treatment of Section II. C. to include the space degeneracy of the system with $(2J+1)$ rotational M sublevels. The system response is governed by its susceptibility, the imaginary part of which is of main interest to us. The total response of the system will be assumed to be a sum of responses of the subsystems characterized by different M quantum numbers. This is analogous to the treatment of Skribanowitz, et al.\textsuperscript{54} in the Doppler broadened regime. Even though recent measurements of Leite, et al.\textsuperscript{55} show that M changing collisions can be as fast as the dipole allowed ones in the excited vibrational state of NH\textsubscript{3}, this is true only for inverting molecules which, in the excited vibrational state, invert on a time scale comparable to the collisional interaction time thus reducing the probability of dipole-dipole interactions.\textsuperscript{56} For most molecules we can neglect the M changing collisions\textsuperscript{57,58} especially for larger J values, and treat the M-subsystems as being uncoupled. With the above assumptions the total response
of the system is described by

\[ \chi''(\omega_s) = \sum_{M_1, M_2, M_3} \chi''(\omega_s; \mu_{13}(M_1, M_3); \mu_{32}(M_3, M_2)) \] (2-E-14)

where now we would use equation (2-C-25) for each

\[ \chi''(\omega_s; \mu_{13}(M_1, M_3); \mu_{32}(M_3, M_2)) \]
with \( r_{13} \) replaced by \( r_{13} \cdot (M_1, M_3) \)

and representing the population difference for the given

M-subsystem. Typically

\[ r_{13}^0 (M_1, M_3) \approx \frac{1}{2} \frac{r_{13}^0}{j+1} \] (2-E-15)

Let us now start the first limiting case, that of two weak fields interacting with the ensemble of three level systems. In this case, \( \beta_{13} / 1, \chi''(\omega_s) \) has a single peak at line center, \( \delta_s = 0 \), if \( \delta_p / 1 \) or two peaks, at \( \delta_s = 0 \) and \( \delta_s = \delta_p \) if \( \delta_p / 1 \). We can therefore look only at the peak at \( \delta_s = 0 \) remembering that for \( \delta_p / 1 \) there is another and equal peak at \( \delta_s = \delta_p \). With the help of (2-C-25) we obtain

\[ \chi''(\omega_{31}) = \frac{3}{2} \mu_{31}^2 \tau r_{13}^0 \frac{\delta_{13}^2 \tau^2}{\gamma} \] (2-E-16)

for \( \delta_p^2 \tau^2 \ll \beta_{13}^2 \tau^2 \ll 1 \), which is 3/2 of the rate equation result, and

\[ \chi''(\omega_{31}) = \frac{1}{2} \mu_{31}^2 \tau r_{13}^0 \frac{\delta_{13}^2 \tau^2}{\gamma} \] (2-E-17)

for \( \beta_{13}^2 \tau^2 \ll 1 \ll \delta_p^2 \tau^2 \), which is 1/2 of the rate equation result. We can see then that regardless of the
pump offset the peak value of the imaginary part of the susceptibility is proportional to the product $|\mu_{13}|^2 |\mu_{32}|^2$, i.e.

$$\chi''(\omega_{32}) \sim |\mu_{13}|^2 |\mu_{32}|^2$$  \hspace{1cm} (2-E-18)

and it is this product which contains the polarization dependence.

Let us define $|\mu_{12}|^2$ as

$$|\mu_{12}|^2 \overset{\text{def.}}{=} |\mu_{13}|^2 |\mu_{32}|^2$$  \hspace{1cm} (2-E-19)

and specialize to the case of symmetric-top molecules. We will remember, as discussed previously, that the final results will also apply to asymmetric top molecules. With the help of equations (2-E-7) and remembering that we are interested in a sum of contributions like the one in (2-E-14) we can write $|\mu_{12}|^2$ as

$$|\mu_{12}|^2 = \sum_{M_1, M_2, M_3} |\mu_{12}(M_1, M_2, M_3)|^2$$

$$= \sum_{M_1, M_2, M_3} \rho_{J_1J_3}^2 \rho_{J_1K_1J_3K_3}^2 \rho_{J_3K_3J_2K_2}^2 \rho_{J_3M_3J_2M_2}^2$$

$$\times \sum_{M_1, M_2, M_3} \rho_{J_1M_1J_3M_3}^2 \rho_{J_3M_3J_2M_2}^2$$  \hspace{1cm} (2-E-20)
ordinarily ignored. In this approach $|\mu_{13}(M)|^2$ and $|\mu_{32}(M)|^2$ are both first averaged over $M$ and then multiplied together. In the usual approach

$$M_{13}^{\text{av}} = \frac{3}{2J_z+1} \sum M_i \phi_{J_z J_3}^2 \phi_{J_z J_2}^2 \phi_{J_z K_z K_3}^2 \sum \phi_{J_z M_z J_z M_z}^2$$

$$M_{32}^{\text{av}} = \frac{3}{2J_z+1} \sum M_3 \phi_{J_z J_3}^2 \phi_{J_z J_2}^2 \phi_{J_z K_z K_3}^2 \sum \phi_{J_z M_z J_z M_z}^2$$

(2-E-21)

where in each case, for simplicity, we have assumed the field to be polarized along the $\hat{z}$-axis thus yielding the $\Delta M=0$ selection rule for each transition. In the process of space averaging we lose the directional information and the direction of polarization loses its significance. With the above definitions, the gain coefficient is then proportional to

$$\lambda \sim r_{13}^o \frac{M_{13}^{\text{av}}}{3} \frac{M_{32}^{\text{av}}}{3}$$

(2-E-22)

Using (2-E-15) we may define

$$M_{12}^{\text{av}} = (2J_z+1) \frac{M_{13}^{\text{av}}}{3} \frac{M_{32}^{\text{av}}}{3}$$

(2-E-23)

and then

$$\lambda \sim r_{13}^o (M_1, M_3) \frac{M_{12}^{\text{av}}}{3}$$

(2-E-24)

If we now define a quantity $F(J_1 J_3 J_2)$

$$F(J_1 J_3 J_2) = \frac{M_{12}^2}{M_{12}^{\text{av}}}$$

(2-E-25)
where $\mu_{ir}$ is the induced dipole moment associated with the infrared pump transition and $\mu$ is the permanent dipole moment associated with the FIR signal emission. The values of the factors of the direction-cosine matrix element are listed in Table II-E-1 and those not listed are equal to zero due to the dipole transition selection rules. We can see that the only transitions allowed are those which change the total angular momentum quantum number $J$ by 0 or ±1. We will use spectroscopic notation, i.e. we treat all transitions as if they were absorptions, to describe the transitions. Table II-E-2 lists those transitions with level 3, see Fig. II-C-1, used as a reference.

\[
\begin{array}{ccc}
J_i = & J_3 + 1 & J_3 & J_3 - 1 \\
Transition & P & Q & R \\
\end{array}
\]

$i = 1$ for pump, $=2$ for FIR transition

For noninverting molecules the FIR transition is always an R transition $(J_3 + J_3 - 1)$. However, for the sake of completeness we will evaluate all of the cases.

First we will review some usual results for two photon transitions in which polarization effects are
then finally the gain becomes proportional to
\[ \alpha \sim r_{13}^0 \frac{\mu_{13}^2}{3} \frac{\mu_{32}^2}{3} F(J_1, J_3, J_2) \]  
(2-E-26)

This expression is easy to work with since quantities $\mu_{13}^2$ and $\mu_{32}^2$ are tabulated in Townes and Schawlow for symmetric-top molecules and numerical tables are provided for asymmetric-top ones. The quantity $F(J_1, J_3, J_2)$ contains then all of the information about the changes introduced into the model by inclusion of the different molecular orientations. Since both pump and probe transitions may be of the P, Q, or R variety, we will have nine cases, each of them subdivided further into parallel (\( \| \)) and perpendicular (\( \perp \)) relative polarizations of the two fields. If the $\Delta J$'s of both the probe and pump field transitions are specified, then $J_1$ and $J_2$ are determined if $J_3$ is given. Hence $F(J_1, J_3, J_2)$ is given in terms of $J_3$ only. The values of $F(J_1, J_3, J_2)$ are given in Table II-E-3.

To the best of our knowledge there has been only one previous work which presented results similar to those in Table II-E-3. This work by Beterov, et al. presented only numerical values of a parameter equivalent to $1/3 F(J_1, J_3, J_2)$ for one particular case of $J_3 = 1$ and parallel polarization.
TABLE II-E-3

Values of \( F(J_3) \) [defined in (2-E-25)] for \( J_3 \gg 1 \) and for \( J_3 = 0 \) in PP case (\( J_3=0 \) in other cases gives zero transition probability for one of the transitions)

(a) Beams Parallel \( \langle E_p | \langle E_s \rangle \)

<table>
<thead>
<tr>
<th>Probe Transition</th>
<th>( P )</th>
<th>( Q )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump transition</td>
<td>( \frac{3}{5} ) ( \frac{4J_3^2 + 8J_3 + 5}{(J_3+1)(2J_3+3)} )</td>
<td>( \frac{3}{5} ) ( \frac{J_3 + 2}{J_3 + 1} )</td>
<td>6/5</td>
</tr>
<tr>
<td>( Q )</td>
<td>( \frac{3}{5} ) ( \frac{J_3 + 2}{J_3 + 1} )</td>
<td>( \frac{3}{5} ) ( \frac{3J_3^2 + 3J_3 - 1}{J_3 (J_3 + 1)} )</td>
<td>( \frac{3}{5} ) ( \frac{J_3 - 1}{J_3} )</td>
</tr>
<tr>
<td>( R )</td>
<td>6/5</td>
<td>( \frac{3}{5} ) ( \frac{J_3 - 1}{J_3} )</td>
<td>( \frac{3}{5} ) ( \frac{4J_3^3 + 1}{J_3 (2J_3 - 1)} )</td>
</tr>
</tbody>
</table>

(b) Beams Perpendicular \( \langle E_p \perp E_s \rangle \)

<table>
<thead>
<tr>
<th>Probe Transition</th>
<th>( P )</th>
<th>( Q )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump transition</td>
<td>( \frac{3}{10} ) ( \frac{(J_3+2)(6J_3 + 5)}{(J_3+1)(2J_3+3)} )</td>
<td>( \frac{3}{10} ) ( \frac{4J_3 + 3}{J_3 + 1} )</td>
<td>9/10</td>
</tr>
<tr>
<td>( Q )</td>
<td>( \frac{3}{10} ) ( \frac{4J_3 + 3}{J_3 + 1} )</td>
<td>( \frac{3}{10} ) ( \frac{2J_3^2 + 2J_3 + 1}{J_3 (J_3 + 1)} )</td>
<td>( \frac{3}{10} ) ( \frac{4J_3 + 1}{J_3} )</td>
</tr>
<tr>
<td>( R )</td>
<td>9/10</td>
<td>( \frac{3}{10} ) ( \frac{4J_3 + 1}{J_3} )</td>
<td>( \frac{3}{10} ) ( \frac{(J_3-1)(6J_3 + 1)}{J_3 (2J_3 - 1)} )</td>
</tr>
</tbody>
</table>
Although there are eighteen values listed in Table II-E-3 many of them coincide for large $J_3$. Let $AB(||)$ and $AB(\perp)$ denote transitions with a type A(A=P, Q, or R) pump transition, a type B(B=P, Q, or R) probe transition and either $||$ or $\perp$ relative polarizations.

Then for large $J_3$, $J_3 \gg 1$, we find only 3 cases:

**Case 1:** $\Delta J = \pm 1$ for both transitions:

- $PP(\perp)$, $PR(\perp)$, $RP(\perp)$, $RR(\perp)$
  
  yield $F_{\perp}(J_3 \gg 1) = \frac{9}{10}$

- and $PP(\parallel)$, $PR(\parallel)$, $RP(\parallel)$, $RR(\parallel)$
  
  yield $F_{\parallel}(J_3 \gg 1) = \frac{6}{5}$

Therefore

$$\frac{F_{\parallel}}{F_{\perp}} = \frac{4}{3} \quad \text{and} \quad \frac{1}{2} (F_{\parallel} + F_{\perp}) = \frac{21}{20}$$

**Case 2:** $\Delta J = \pm 1$ for one transition, $\Delta J = 0$ for the other one. The $PQ$, $QP$, $RQ$, $QR$ transitions yield

$$F_{\perp} = \frac{6}{5} \quad , \quad F_{\parallel} = \frac{3}{5}$$

$$\frac{F_{\parallel}}{F_{\perp}} = \frac{1}{2} \quad , \quad \frac{1}{2} (F_{\parallel} + F_{\perp}) = \frac{9}{10}$$

**Case 3:** $\Delta J = 0$ for both transitions ($QQ$):

$$F_{\perp} = \frac{3}{5} \quad , \quad F_{\parallel} = \frac{9}{5}$$

$$\frac{F_{\parallel}}{F_{\perp}} = 3 \quad , \quad \frac{1}{2} (F_{\parallel} + F_{\perp}) = \frac{6}{5}$$
We can summarize the main results for large $J_3$ as follows. In all of the cases the small signal gain for randomly polarized probe radiation is not equal to that ordinarily calculated using $\mu_{12}^2$. However, the maximum error is 20% (Case 3). In Case 1, the small signal gain is $4/3$ times larger for parallel than for perpendicular relative polarizations. This considerably differs from Chang's estimate of 3:1. In Case 3, the perpendicular polarization has twice the small signal gain of the parallel polarization, in agreement with Chang. For Case 3, parallel polarization is favored 3:1.

We can now state a following rule, a variation of Chang's work, regarding the relative polarizations of the pump and FIR beams. If the sum of the $\Delta J$'s for the pump and FIR transitions is even, parallel polarization predominates. If it is odd, perpendicular polarization is stronger.

We might also comment here that the recent statements by Lipton, et al. in regard to the dependence of relative polarizations on the signs of the changes of the $K_+$ and $K_-$ numbers for $D_2O$ are incompatible with our theory and furthermore we will present in Section III experimental results contradicting their predictions and measurements.
We will now specialize to the strong pump regime. We will first treat the case where even though the pump is strong, $\beta_{13}^2 \tau^2 >> 1$, the Rabi frequency it produces (or power broadening) is less than the pump offset, $\delta_p^2 \tau^2 >> 4\beta_{13}^2 \tau^2$. In this case the peaks are again located at $\delta_s = 0$ and $\delta_s = \delta_p$, $\gamma$ of (2-C-26) becomes $\delta_p/2$ and thus instead of eq. (2-C-25) we obtain

\[
\chi''(\Omega_s) = \sum_M \frac{\mu_{32}^2}{4 \hbar} \tau \ r_{13}^o(M) \ \frac{4 Q_{13}^2}{\delta_p^2} \left\{ \frac{1}{1 + \delta_s^2 \tau^2} + \frac{1}{1 + (\delta_p - \delta_s)^2 \tau^2} \right\}
\]

LHS

\[
= \frac{\tau \ r_{13}^o(M)}{\hbar \delta_p^2} \left\{ \frac{1}{1 + \delta_s^2 \tau^2} + \frac{1}{1 + (\delta_p - \delta_s)^2 \tau^2} \right\} \sum_M \frac{\mu_{32}^2}{4 \hbar} Q_{13}^2
\]

(2-E-27)

Therefore this case is identical to the case of weak pumping, $\beta_{13}^2 \tau^2 << 1$. This was really to be expected since for off-resonant pumping the parameter that determines the pump's strength is not the pressure broadening but rather the pump offset and $4\beta_{13}^2 \tau << \delta_p^2 \tau^2$ means basically also weak pumping (even though $\beta_{13}^2 \tau^2 >> 1$).

Let us now look at the very strong pumping regime, $4\beta_{13}^2 \tau^2 >> \delta_p^2 \tau^2 >> 1$. In this case the peaks are located at approximately $\delta_s = \pm \beta_{13}$ and $\gamma$ of (2-C-26) is just $\beta_{13}$. Therefore instead of (2-C-25) we obtain

\[
\chi''(\Omega_s) = \sum_M \frac{\mu_{32}^2}{4 \hbar} \tau \ r_{13}^o(M) \ \left\{ \frac{1}{1 + (\beta_{13} - \delta_s)^2 \tau^2} + \frac{1}{1 + (\beta_{13} + \delta_s)^2 \tau^2} \right\}
\]

(2-E-28)
In this case, there are \(2(J_3 - 1), 2J_3, \) or \(2(J_3 + 1)\) peaks. Peak locations depend on \(M\) via

\[
\delta^\pm_5 = \pm \frac{1}{2} \frac{|\mu_{13}(M)|}{E_p} \tag{2-E-29}
\]

The number of peaks for each set of transitions is listed in Table II-E-4, which is identical to that of Skribanowitz, et al.\(^{54}\) This Table is a result of the selection rules applied to the \(M\) levels. If, for convenience, we associate the \(z\)-axis with the direction of polarization of the pump radiation, then \(\Delta M = 0\) for pump transitions and for probe transitions with parallel relative polarization, \(\Delta M = \pm 1\) for probe transitions with perpendicular relative polarization. A careful inspection of equation (2-E-28) reveals that in the limit of very strong pumping the intensities of the peaks are functions of \(|\mu_{32}(M)|^2\) only while their positions depend only on \(|\mu_{13}(M)|\). We will find it convenient to define new quantities

\[
\mu_{13}^2 \overset{\text{def.}}{=} \frac{\mu_{13}^2}{3} \quad ; \quad \mu_{32}^2 \overset{\text{def.}}{=} \frac{\mu_{32}^2}{3} \tag{2-E-30}
\]

where \(\mu_{13}^2\) and \(\mu_{32}^2\) were defined in (2-E-21) and are the quantities used in all microwave absorption works.\(^{40}\) All these definitions may be somewhat confusing. However, this is the simplest notation we could come up with. The problem comes from the way the quantities \(\mu_{ij}^2\) are
### TABLE II-E-4 -- NUMBER OF PAIRS OF PEAKS

**PROBE TRANSITION**

<table>
<thead>
<tr>
<th>Pump Transition</th>
<th><strong>P</strong></th>
<th><strong>Q</strong></th>
<th><strong>R</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P</strong></td>
<td>(J_3 + 1)</td>
<td>(J_3)</td>
<td>(J_3)</td>
</tr>
<tr>
<td><strong>Q</strong></td>
<td>(J_3)</td>
<td>(J_3)</td>
<td>(J_3 - 1)</td>
</tr>
<tr>
<td><strong>R</strong></td>
<td>(J_3)</td>
<td>(J_3 - 1)</td>
<td>(J_3)</td>
</tr>
</tbody>
</table>
defined. If one carefully follows their derivation one finds that these quantities are three times the average value of $\mu_{ij}^2(M)$ as calculated using the expressions from Table II-E-1. Townes and Schawlow compensate for this in their absorption coefficient expressions by introducing an extra factor of 1/3. We feel that $\mu_{ij}$'s, as defined in eq. 2-E-30, are more physically meaningful than Townes and Schawlow's $\mu_{ijav}$'s. We can now relate the transition probabilities for each particular M level to our newly defined quantities. Table II-E-5 lists the ratio of $\mu_{ij}^2(M)/\mu_{ij}^2$ where we have arbitrarily chosen the $\hat{z}$-axis to be parallel to the pump polarization vector. Again we have nine cases to treat, each with two possible relative polarizations. For a general discussion we will specialize to large $J_3$ values which greatly simplifies the expressions of Table II-E-5. First we will note that in Table II-E-5(a) the quantum number M always appears in the form of $M^2$. We can therefore conclude that peaks associated with $+M$ and $-M$ will always coincide. Therefore, even though some of the expressions in Table II-E-5(b) have maxima for $M=0$, the system response will have a maximum for $M=1$ since it has twice the population ($M=+1$ and $M=-1$) of $M=0$.

Let us now look at some specific cases.
### TABLE II-E-5

(a)

<table>
<thead>
<tr>
<th>Pump transition</th>
<th>$P$</th>
<th>$Q$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\mathcal{J}<em>{13}^2 (M)}{\mathcal{J}</em>{13}^2}$</td>
<td>$\frac{3 \left[ \left( J_3+1 \right)^2 - M^2 \right]}{(J_3+1) (2J_3+1)}$</td>
<td>$\frac{3 M^2}{J_3 (J_3+1)}$</td>
<td>$\frac{3 \left( J_3^2 - M^2 \right)}{J_3 (2J_3+1)}$</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Probe transition</th>
<th>$P$</th>
<th>$Q$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\mathcal{J}<em>{32}^2 (M)}{\mathcal{J}</em>{32}^2}$</td>
<td>$\frac{3 \left[ \left( J_3+1 \right)^2 - M^2 \right]}{(J_3+1) (2J_3+1)}$</td>
<td>$\frac{3 \left[ J_3 (J_3+1) - M^2 \right]}{2 J_3 (J_3+1)}$</td>
<td>$\frac{3 \left( J_3^2 - M^2 \right)}{J_3 (2J_3+1)}$</td>
</tr>
<tr>
<td>$\frac{M^2}{J_3 (J_3+1)}$</td>
<td>$\frac{3 M^2}{J_3 (J_3+1)}$</td>
<td>$\frac{3 \left[ J_3^2 - M^2 \right]}{J_3 (2J_3-1)}$</td>
<td>$\frac{3 \left( J_3^2 - J_3 + M^2 \right)}{2 J_3 (2J_3-1)}$</td>
</tr>
</tbody>
</table>
CASE 1: \( PR \)

\( PR(\|) \) will have maximum peak for \( M=1 \) with relative height of \( \frac{M_{32}(1)}{M_{31}^2} + \frac{M_{32}(-1)}{M_{32}^2} \) which for large \( J_3 \) becomes 3.

\( PR(\perp) \) has its maximum at \( M = J_3 \) with the relative height also going to 3 in the limit of large \( J_3 \).

Hence for well resolved peaks the peak gain value is the same for parallel and perpendicular polarizations. This peak height is \( \frac{3}{2J_3+3} \) times the peak height in the absence of peak splitting. The factor of 3 comes from the relative height considerations above while the factor of \( \frac{1}{2J_3+3} \) comes from the fact that each \( M \) level has \( \frac{1}{2J_1+1} \) the population of the whole level \( J_1 \). Now, the peak spacings will be different for different \( M \)'s and, as we will see, below, it is often very difficult to have them all separated. For a \( P \) pump transition the peaks that will be the closest to each other are those that belong to \( M=0 \) and \( |M|=1 \) levels. To be able to distinguish them we must demand that

\[
\frac{M_{13}(0) \cdot E_P}{2 \hbar} - \frac{M_{13}(1) \cdot E_P}{2 \hbar} > \frac{1}{\tau}
\]

(2-E-31)

which, for large \( J_3 \), becomes

\[
\theta_{13} \tau > 1.63 \cdot \frac{j_3^2}{\hbar}
\]

(2-E-32)
This condition is very severe at large $J_3$, and ordinarily will not be met. The peaks the most separated from each other, for a $P$ pump transition, are those associated with $|M|=J_3$ and $|M|=J_3-1$. The condition for their distinguishability becomes, for large $J_3$,

$$c_{13} \tau > 1.39 \sqrt{J_3}$$  \hspace{1cm} (2-E-33)

which is much easier to accomplish experimentally.

For a moderate pump power then we can conclude that in the PR case the perpendicular polarization, which peaks for large values of $M$, will have the highest peaks resolved while the parallel polarization transitions, peaking for small values of $M$, will not be resolved. The net effect will be that of parallel polarization having higher peak gain. We found previously the same to be true when the $M$ levels were totally unresolved (weak pumping case). If all $M$ peaks are resolved the peak gains are the same for both polarizations.

$PP$, $RP$, $RR$ cases are similar to the PR case discussed above, except that for $RP$ and $RR$ cases $M=J_3$ is not allowed. Otherwise the conclusions are the same in the large $J_3$ limit.

**CASE 2: PQ**

$PQ(\|\|)$: Maximum at $|M|=J_3$ with relative peak height becoming 6 for large $J_3$. 
PQ(\perp): Maximum at \(|M|=1\) with relative peak height becoming 3 for large \(J_3\). Hence when peaks are fully resolved, parallel polarization predominates. This is opposite of the weak field case. When peaks are partially resolved, the parallel polarization becomes weaker than the perpendicular one. Since the pump transition, \(P\), is the same in this case as in Case 1, the peak separations are governed by the rules discussed previously.

RQ transition is similar, except that \(|M|\neq J_3\) is not allowed.

**CASE 3: QP**

QP(\parallel): Maximum at \(|M|=1\) of relative height 3/2.

QP(\perp): Maximum at \(|M|=J_3\) of relative height 3/2.

Hence for well resolved peaks the peak gain is the same for both polarizations.

For a Q pump transition the peaks are evenly spaced and for large \(J_3\) the condition for separation becomes

\[
\beta_{13} \tau \geq \frac{J_3}{13}
\]

For a weak pump field, we remember, we found the perpendicular polarization to dominate. QR case is found to be very
similar except $M=J_3$ is not allowed.

**CASE 4: QQ**

QQ$(\parallel \parallel)$: Maximum at $|M|=J_3$ of relative height 6.

QQ$(\perp \perp)$: Maximum at $|M|=1$ of relative height 3.

Hence parallel polarization is favored for the widely resolved case, the same as in the weak field case.

The peak separation is the same as described in **CASE 3**.

A summary of the results is given in Table II-E-6. We will notice that PQ and RQ transitions are the only ones that change preferred polarization as $\beta_{13} \tau$ is increased.

To demonstrate some of the relations about which we talked in this section results of a numerical calculation, utilizing equation (2-E-21), are plotted on Fig. II-E-(a)-(i) for the nine cases. Each of the pictures, (a)-(i), shows the normalized $\chi''(\omega_s)$ for parallel and perpendicular polarizations. Also plotted, for reference, is $\chi''(\omega_s)$ calculated using $\mu_{12}^{2 \text{av}}$. The numbers used were $J_3=4$, $\beta_{13} \tau = 10$, $\beta \tau = 0$, $\delta_p = 0$.

We can compare these figures with our previous predictions. Case 1 (PR, PP, RP, RR) is represented by Figs. II-E-1 (a)-(d) and indeed we see that the parallel polarization peak has basically unresolved M peaks and their sum gives a
TABLE II-E-6

SUMMARY: Parallel/perpendicular polarization ratios for large $J_3$ values. Preferred polarization in parenthesis.

(a) Weak pump and probe

<table>
<thead>
<tr>
<th>Probe</th>
<th>P</th>
<th>Q</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>$\frac{4}{3}$ (</td>
<td></td>
<td>)</td>
</tr>
<tr>
<td>Q</td>
<td>$\frac{1}{2}$ (\perp)</td>
<td>3 (</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>$\frac{4}{3}$ (</td>
<td></td>
<td>)</td>
</tr>
</tbody>
</table>

(b) Strong pump, but not all peaks resolved, weak probe (qualitative)

<table>
<thead>
<tr>
<th>Probe</th>
<th>P</th>
<th>Q</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>(</td>
<td></td>
<td>)</td>
</tr>
<tr>
<td>Q</td>
<td>*</td>
<td>(</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>(</td>
<td></td>
<td>)</td>
</tr>
</tbody>
</table>

*has to be determined for a particular set of numbers

(c) Strong pump, all peaks resolved, weak probe

<table>
<thead>
<tr>
<th>Probe</th>
<th>P</th>
<th>Q</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1</td>
<td>2 (</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>1</td>
<td>2 (</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>1</td>
<td>2 (</td>
<td></td>
</tr>
</tbody>
</table>

(d) Strong probe - numerical work necessary
FIGURE II-E-1 (a)-(d) -- Normalized χ"(ωₜ) plotted for two polarizations and for μ²₁₂₉ (narrowest). The polarization with higher peak gain is marked in parenthesis, next to each figure. The type of pump and signal transitions is marked on top of the figures. The horizontal scale extends from δₜ=−20 to δₜ=+20. Parameters used were β₁₃τ=10, β₃₂τ=0, δₜτ=0, J₃=4.
FIGURE II-E-1 (e)-(g) -- Normalized $\chi''(\omega_s)$ plotted for two polarizations and for $\mu_{12av}^2$ (narrowest). The polarization with higher peak gain is marked, in parenthesis, next to each figure. Parameters used were $\beta_{13} \tau = 10$, $\beta_{32} \tau = 0$, $\delta_p \tau = 0$, $J_3 = 4$. The horizontal scale extends from $\delta_s \tau = -20$ to $\delta_s \tau = 20$. The type of pump and signal transitions is marked on top of the figures.
FIGURE II-E-1 (h), (i). Normalized $\chi''(\omega_s)$ plotted for two polarizations and for $\nu_{12\text{av}}$ (narrowest). The polarization with higher peak gain is marked, in parenthesis, next to each figure. The horizontal scale extends from $\delta_s \tau = -20$ to $\delta_s \tau = 20$. Parameters used were $\beta_{13} \tau = 10, \beta_{32} \tau = 0, \delta_p \tau = 0, J_3 = 4$. The type of pump and signal transition is marked on top of the figures.
high peak gain than that of perpendicular polarization with its semi-resolved highest peaks. Case 2 (PQ, RQ) is represented by Figures II-E-1 (h) and (i). We predicted, for fully resolved peaks, that parallel polarization will dominate but on the pictures the perpendicular polarization has a higher gain (especially the RQ case). The reason for that is twofold. First, the peaks are not well resolved at this pump power and when the $\beta_{13}$ parameter is increased to about 30 the parallel polarization does get larger than the perpendicular one for the PQ transition. The other reason has to do with the size of $J_3$. $J_3 = 4$ is by no means a really large value. The importance of its size comes from the fact that especially for an R pump transition only $M = 0$ to $M = J_3 - 1$ components are excited and for a Q signal transition the parallel polarization will have a strongest component proportional to $(J_3 - 1)^2$ and the perpendicular polarization to $1/2 [J_3 (J_3 + 1) - 1]$. Comparison of the two shows that we can call $J_3$ truly large only if it is 5 or more. Cases 3 and 4 (QP, QR, QQ) are shown on Figs. II-E-1 (e)-(g). We immediately notice the equal spacing of the peaks characteristic of the Q pump transition. The QP and QR cases have almost equal peak gains on the two polarizations and QQ has parallel polarization almost twice as large as the perpendicular
one. This is just as was predicted for well-resolved peaks.

Another point may be worth making here with regard to the importance of including explicitly $M$ levels in gain considerations. The $\Delta M$ selection rules quite frequently exclude part of the population from taking part in the absorption or gain process and this is especially important for small values of $J_3$. As an example let us consider the $J_3 = 1$ and $P$ pump transition ($J_1 = 2$) case. Due to the $\Delta M = 0$ selection rule only $M=0$ and $M=\pm 1$ will participate thus decreasing the gain (absorption) by a factor of $3/5$. Were we to use average values of matrix elements, the full population difference would have been used.

We also would like to mention here that in our numerical work we were limited by the small core size of the available PDP-11 computer and thus were unable to go to much larger values of the pump parameter required to show full splitting of all peaks on all transitions.

II. F. THEORY -- $D_2O 385 \mu m$ TRANSITION

The theoretical results of the previous sections allow us, for the first time, to calculate the theoretical gain for many optically pumped laser systems, assuming their parameters, like dipole moments, frequencies and relaxation rates, are known. These parameters are in fact
known for many systems under current investigation such as the 385 μm transition in D₂O, treated in this section, and the 496 μm transition in CH₃F, with which we deal in the subsequent section. The theoretical predictions of this and the following sections will be compared with our experimental results in Chapter IV.

We should mention here that we will be applying the results derived for homogeneously broadened systems to gases even at very low pressures. This will be correct as long as the pump offsets are larger than the Doppler half width of the transitions and we find this to be the case for most pulsed FIR systems.

Figure II-F-1 shows the D₂O energy levels and the wavelengths of the respective transitions of importance to the 385 μm emission.³¹,⁵⁹ The 9.26 μm R22 line of the CO₂ laser pumps the (000)₅₃₃ to (010)₄₂₂ transition of D₂O, ν₂ vibrational mode, with the pump line about 320 MHz smaller than the absorption line.⁵¹,⁵² The 385 μm FIR emission occurs between the 4₁₂₂ and 4₁₁₃ rotational levels in the first excited vibrational ν₂ level. In mirrorless systems the cascade 359 μm line between levels 4₁₁₃ and 4₀₄ is also frequently observed. D₂O is a molecule of the asymmetric-top kind with Ray's asymmetry parameter⁴⁰

\[ k \approx -0.5 \]  
(2-F-1)
FIGURE II-F-1 -- Energy levels of D₂O
The strength of various transitions can be calculated using

\[
\mu_{J_k, \kappa, \kappa'}^2 \frac{S_{J_k, \kappa, \kappa'} J_{K_k, \kappa, \kappa'} (K)}{2 J+1} \]

(2-F-2)

where \( \mu_{J_k, \kappa, \kappa'}^2 \) is the asymmetric-top equivalent of the quantities defined in (2-E-21) for symmetric-top molecules. \( \mu \) is \( \mu_{ir} \) (or \( \mu_{permanent} \)) for vibrational-rotational (or purely rotational) transitions. The quantity \( S_{J_{K-1}K, J_{K'}K'-1} (K) \) is tabulated by various authors. Since we are discussing a three-level system, we will disregard the \( 4^0_0 \) level and the \( 359 \mu m \) transition in this treatment. The two transition strengths of interest are then found to be

\[
\begin{align*}
S_{33} & \quad q_{zz} (-0.5) = 2.3609 \times 10^{-4} \\
S_{42} & \quad q_{zz} (-0.5) = 3.6119 \times 10^{-4}
\end{align*}
\]

(2-F-3)

The approximate population factors are found according to

\[
\mathcal{J} = \frac{(2J+1) e^{-W_{j_{K-1}K} / kT}}{\sqrt{\frac{\pi}{\lambda BC^3 \left( \frac{kT}{\hbar} \right)^3}}} S(I,K) \]

(2-F-4)

where \( W_{j_{K-1}K} \) is the rotational level energy within its vibrational manifold, \( A, B, C \) are the rotational constants in Hz, associated with the molecule, and \( S(I,K) \) is the
nuclear statistics factor. For D₂O, the constants A, B, C are found in Townes and Schawlow while the energies of the levels can be found in Williamson. These are as follows

\[
\begin{align*}
A &= 4.6149 \times 10^{11} \text{ Hz} \\
B &= 2.1774 \times 10^{11} \text{ Hz} \\
C &= 1.4546 \times 10^{11} \text{ Hz} \\
W_{533} (v_2 = 0) &= 267.5 \text{ cm}^{-1} \\
W_{422} (v_2 = 1) &= 169.1 \text{ cm}^{-1} \\
W_{413} (v_2 = 1) &= 143.1 \text{ cm}^{-1}
\end{align*}
\]

(2-F-5)

The respective populations, with the nuclear spin statistics factor of 4/3 included, are then

\[
\begin{align*}
f_{533} &= 1.8\% \\
f_{422} &= 2.5\% \\
f_{413} &= 2.8\%
\end{align*}
\]

(2-F-6)

We will assume the pressure broadening coefficient to be \(\Delta v_{\text{FWHM}} = 40 \text{ Mhz/Torr}\) (see Petuchowski, et al. for discussion of various works). We found that this coefficient gives the best fit to our experimental data. The Doppler broadening is 88 MHz FWHM for the pump transition and 2.2 Mhz for the FIR one. The permanent dipole moment, (000) vibrational state, is 1.87 Debye and we will use it for the excited state too. The infrared transition induced dipole moment can be deduced
from the data of Keilman et al.\textsuperscript{51} and was also found from similar measurements by Petuchowski et al.\textsuperscript{35} Its value is

\[ \mu_{ir} = 0.12 \text{ Debye} \quad (2-F-7) \]

The rate equation model of Section II-B predicts the small signal gain of the 385 \( \mu \)m transition to be, under the condition of saturated pumping,

\[ \alpha = 2.1 \text{ cm}^{-1} \quad (2-F-8) \]

at line center and the saturation intensity

\[ I_{gs} = 4.5 \beta_{13}^2 \left( \frac{W}{cm^2 \text{ Torr}^2} \right) \quad (2-F-9) \]

Numerical results illustrating various phenomena discussed in Sections II-C to II-E are shown on the figures that follow.

The M-level structure is demonstrated under the conditions of very intense pumping, 2.5 MW/cm\(^2\) at 0.3 Torr pressure, in Figure II-F-2. \( \beta_{13} \tau(M) \) pump parameters vary from 75 for \( M=0 \) to 45 for \( M=4 \). The pump offset parameter is \( \delta_p \tau = -54 \). The small signal gain on the plots is multiplied by a factor of 10,000 due to the requirements of the plotting routine. The gain spectrum is typical of the PQ transition. The parallel polarization produces peaks with greatest heights on the "inside"
FIGURE II-F-2 -- D₂O - 385 μm: Small signal gain for both polarizations showing the M level structure under very strong pumping (M = 1 level produces the two peaks with the largest separation for the parallel polarization, while M = 0, which gives largest separation for the perpendicular polarization case, is absorbed into the outside wings of the M = 1 peaks, which are almost twice the size of the M = 0 peaks).
of the spectrum, and they are the most separated ones. The perpendicular polarization has the largest peaks on the "outside" and the separation between them is the smallest. The separation between the M=0 and M=1 peaks is so small that the M=0 peaks are absorbed into the wings of the twice their size, due to twice the population, M=1 peaks. It is worth also noticing that parallel polarization has a higher peak gain here as opposed to the unresolved peak situation.

The next Figure, II-F-3, represents the effects that different pressure broadening coefficients have on the small signal gain amplitude and spectrum. As we mentioned before, 40 MHz/Torr FWHM coefficient gave the best spectral fit to our data.

Some typical small signal gain spectra, obtained using $\Delta v_{FWHM} = 40$ MHz/Torr, are presented in Fig. II-F-4. Perpendicular and parallel relative polarizations are plotted on the same figures, the perpendicular being the higher of the two. Figure II-F-4(a) shows the weak pumping case, 10 Kw/cm$^2$ at 1 Torr, with the pump parameter, $\beta_{13} \tau (M)$, varying from 1.4 for M=0 to 0.85 for M = 4. The pump offset parameter is $\delta_p \tau = -16$ and so even though $\beta_{13} \tau \approx 1$ we still have $4\beta_{13}^2 \tau << \delta_p^2 \tau^2$ or weak pumping as discussed in Section II E. The peaks
FIGURE II-F-3 -- D$_2$O - 385μm: Influence of pressure broadening coefficient on the small signal gain amplitude and spectrum. The three curves correspond, in decreasing amplitude, to $\Delta v_{\text{FWHM}}$ of 26 MHz/Torr, 40 MHz/Torr, and 60 MHz/Torr.
Figure II-F-4 -- \( \text{D}_2\text{O} - 385\mu \text{m} \): Typical small signal gain spectra. Perpendicular (higher) and parallel (lower) polarizations under three sets of circumstances.

(a) 10 kW/cm\(^2\) pump intensity: \( \chi_{\perp, \text{max}} = 0.0226 \text{ cm}^{-1} \)

(b) 0.85 MW/cm\(^2\) pump intensity: \( \chi_{\perp, \text{max}} = 0.556 \text{ cm}^{-1} \)

(c) 0.85 MW/cm\(^2\) pump intensity: \( \chi_{\perp, \text{max}} = 0.667 \text{ cm}^{-1} \)

The horizontal scales are -400 to 100 MHz in (a) and -1000 to 500 MHz in (b) and (c).
are located at 0 (line center) and -320 (Raman) MHz and perpendicular polarization is 1.58 times stronger than parallel one. This is exactly as predicted by Table II-E-3 for the case of $J_3 = 4$ and a PQ transition. Figures II-F-4(b) and (c) show the spectrum for reasonably strong pumping conditions at 3 and 10 Torr respectively. The pump power was chosen to be 0.85 MW/cm$^2$. The peaks on these pictures are noticeably offset from their weak pumping positions of 0 and -320 MHz due to the AC Stark effect. For the 3 Torr case $\beta_{13} \tau$ varies from 4.4 to 2.6 while $\delta_p \tau = -5.3$ and for the 10 Torr case $\beta_{13} \tau$ changes from 1.3 to 0.78 while $\delta_p \tau = -1.6$. It is also interesting to observe the difference between the peak positions for the two polarizations. The perpendicular polarization peaks further out even though the pump parameters, $\beta_{13} \tau(M)$, are the same for both cases. This is due to the different dependence of the peak heights on $M$ for the two cases as discussed following Figure II-F-2.

Figure II-F-5 shows some of the saturation properties as discussed in Section II D and now applied to $D_2O$. In the weak pump case, Figure II-F-5(a), the line center peak saturates with an FIR power level predicted by the rate equation approach, see Section II D. The Raman peak remains essentially unaltered by this level of signal radiation. The situation is different when the
FIGURE II-F-5 -- $\text{D}_2\text{O}$ - 385 $\mu$m: FIR saturation properties

(a) 10 MW/cm$^2$ pump power; 0 and 5 W/cm$^2$ FIR power
(Notice different vertical scales for the two polarizations).

(b) 0.5 MW/cm$^2$ pump power; 0 and 5 W/cm$^2$ FIR power.
pump field becomes stronger as shown in Figure II-F-5(b). Here the line center still saturates with approximately the same intensity while the Raman line saturates with only a little bit higher FIR intensity. This is also in agreement with the discussion in Section II. D.

II. G. THEORY - CH$_3$F 496 µm TRANSITION

We will conclude the theory chapter with a discussion of the 496 µm transition in CH$_3$F. It is one of the strongest SMM lines and was also the first one to be discovered.$^1$ Figure II-G-1 shows some of the energy levels and transition wavelengths for CH$_3$F. CH$_3$F is of the symmetric-top kind and its spectrum shows the typical ordering of levels. Each vibrational level is subdivided into many rotational levels, denoted by the total angular momentum quantum number J. These rotational levels are further subdivided according to the quantum number K associated with the projection of the total angular momentum vector onto the molecular axis of symmetry. On Figure II-G-1 we find energy levels corresponding to K=0, 1, and 2. For strong pumping, as we will find soon, even levels of K=7 and higher can participate in the absorption and therefore also the lasing action. We will leave the discussion of the participating K levels until later. Now, we will introduce
CH$_3$F LASER

496 μm (SPLITTING ~ 40 MHz)

$\begin{align*}
    v = 1 &: \{ J = 12, J = 11, J = 10 \} \\
    v = 0 &: \{ J = 13, J = 12, J = 11 \}
\end{align*}$

FIGURE II-G-1 -- Energy levels of CH$_3$F
some basic data. As is seen on Figure II-G-1, the 9.55 µm P20 line of CO₂ pumps the \((v_3=0, J=12, K=1, 2\ldots)\) to \((v_3=1, J=12, K=1, 2\ldots)\) transitions in CH₃F. The 496 µm emission comes from transitions in the \(v_3=1\) vibrational state: \((J=12, K)+(J=11, K)\). Refilling and cascade lines, two of which are shown on Figure II-G-1, are also quite often present in CH₃F lasers. We will disregard them here, since we are treating only three-level systems. Due to the \(\Delta K=0\) selection rule for the transitions involved in the CH₃F lasing action⁴⁰ and the low frequency of the K changing collisions, which are not dipole allowed, we can treat each set of molecules of quantum number K as an independent three-level system. The gain spectrum of the CH₃F laser will then consist of a sum of the contributions from the K=1, 2, \ldots systems. Each of these will be characterized by a slightly different absorption frequency, emission frequency, and also by different transition matrix elements. The population differences will also be different. We will now list the appropriate quantities taken or deduced from a number of references.¹,⁴⁰,⁶¹,⁶² Let us start with the pump transition frequencies. We calculate them according to

\[
\mathcal{Q}(12, K) = [\text{CO}_2 \ \text{P}(20)]
\]

\[
= -53.6 + 23.43 K^2 + 0.15 K^4 \quad (\text{MHz}) \quad (2-G-1)
\]
where the CO$_2$ frequency was provided by Baird, et al.\textsuperscript{63}

The emission frequencies, referenced to K=0 (even though it does not participate in the laser action due to the K\neq0 selection rule for the pump transition) are given by

\[ \nu(J,K) - \nu(J,0) = -12.96 K^2 \text{ (MHz)} \]  \text{(2-G-2)}

The resulting values of equus. (2-G-1) and (2-G-2) are presented in Table II-G-1.

The population factors calculated using data of Freund et al.\textsuperscript{61} in eq. (2-F-4) and including appropriate nuclear statistics factors\textsuperscript{40} are listed in Table II-G-2. These population factors include the degeneracy of the K levels (W$K = W_{-K}$).

Doppler broadening is 66 MHz FWHM for the pump transition and 1.3 MHz for the FIR one. The pressure broadening coefficient is 41.3±1.0 MHz/Torr.\textsuperscript{64}

The infrared transition dipole moment, derived from the data of Hodges, et al.\textsuperscript{62} is

\[ \mu_{ir} = 0.205 \text{ Debye} \]  \text{(2-G-3)}

and

\[ \mu_{13av}(K) = \mu_{ir}^2 \frac{K^2}{J_3(J_3+1)} \]  \text{(2-G-4)}

for a Q pump transition.

The permanent dipole moment in the first excited
TABLE II-G-1

Absorption and emission frequencies of CH$_2$F

<table>
<thead>
<tr>
<th>$K$</th>
<th>Absorption $Q_Q(12,K) - [CO_2 P(20)]$ (MHz)</th>
<th>Emission $\nu(J,K) - \nu(J,0)$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-30</td>
<td>-13</td>
</tr>
<tr>
<td>2</td>
<td>42</td>
<td>-52</td>
</tr>
<tr>
<td>3</td>
<td>169</td>
<td>-117</td>
</tr>
<tr>
<td>4</td>
<td>359</td>
<td>-207</td>
</tr>
<tr>
<td>5</td>
<td>626</td>
<td>-324</td>
</tr>
<tr>
<td>6</td>
<td>984</td>
<td>-467</td>
</tr>
<tr>
<td>7</td>
<td>1454</td>
<td>-635</td>
</tr>
</tbody>
</table>

TABLE II-G-2

<table>
<thead>
<tr>
<th>$K$</th>
<th>Level Population (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.71</td>
</tr>
<tr>
<td>2</td>
<td>0.66</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>0.43</td>
</tr>
<tr>
<td>6</td>
<td>0.67</td>
</tr>
<tr>
<td>7</td>
<td>0.26</td>
</tr>
</tbody>
</table>
\( \nu_3 \) vibrational state is\(^6\):

\[ \mu_s = 1.905 \text{ Debye} \quad (2-G-5) \]

and \( \mu_{32}^2 (K) \) is given by\(^{40}\)

\[ \mu_{32}^2 (K) = \mu_0^2 \frac{J_3^2 - K^2}{J_3 (2J_3 + 1)} \quad (2-G-6) \]

for an R SMM transition. \( j_3 = 12 \) in the case of \( CH_3F \) and \( K \) is confined to small values (like 1 to 7). Therefore, all the FIR transitions are essentially equally strongly.

The rate equation model of Section II. B. predicts a small signal gain, under saturated pumping conditions, of 1.3 cm\(^{-1}\) for \( K = 3 \) and about 0.5 cm\(^{-1}\) for other nearby \( K \) levels. The FIR saturation intensity is expected to be about 5 W/cm\(^2\) Torr\(^2\) for each \( K \) level on its line center.

We will again demonstrate some of the phenomena discussed in Sections II.C. to II. E. in the figures that follow.

Figure II-G-2 shows the small signal gain for each of the seven \( K \) levels and then their sum for the two polarizations. The pictures are for 1 Torr pressure and 0.5 MW/cm\(^2\) pump power. The 1 to 12 \( M \) levels hidden in each picture are not resolved. In general the perpendicular polarization has a higher gain with the ratio of perpendicular to parallel polarization gain for \( K = 7 \).
FIGURE II-G-2 -- CH₃F-496 μm: Small signal gain. 1 Torr, 0.5 MW/cm² pump power.

The picture numbers correspond to the K levels and relative polarizations (2⊥ means K=2, perpendicular polarization).

Horizontal scales: -600 to 600 MHz for K=1
-1200 to 800 MHz for K=2

1∥: \( \alpha_{\text{max}} = 0.203 \, \text{cm}^{-1} \)
1⊥: \( \alpha_{\text{max}} = 0.214 \, \text{cm}^{-1} \)
2∥: \( \alpha_{\text{max}} = 0.134 \, \text{cm}^{-1} \)
2⊥: \( \alpha_{\text{max}} = 0.129 \, \text{cm}^{-1} \)
FIGURE II-G-2 -- CH$_3$F - 496 μm: Small signal gain. 1 Torr, 0.5 MW/cm$^2$ pump power. The picture numbers correspond to the K levels and relative polarizations ($4_{\parallel}$ means K=4 and parallel polarization).

Horizontal scales: -1200 to 800 MHz for K=3
-2000 to 800 MHz for K=4

$3_{\parallel}$: max = 0.121 cm$^{-1}$
$3_{\perp}$: max = 0.152 cm$^{-1}$
$4_{\parallel}$: max = 0.0296 cm$^{-1}$
$4_{\perp}$: max = 0.0437 cm$^{-1}$
FIGURE II-G-2 -- CH$_3$F - 496 μm: Small signal gain. 1 Torr, 0.5 MW/cm$^2$ pump power. The picture numbers correspond to the K levels and relative polarizations (5$_\perp$ means K=5 and perpendicular polarization).

Horizontal scales: -2000 to 800 MHz for K=5
                -2400 to 800 MHz for K=6

5$_\parallel$ : $\alpha_{\text{max}} = 0.015$ cm$^{-1}$
5$_\perp$ : $\alpha_{\text{max}} = 0.025$ cm$^{-1}$
6$_\parallel$ : $\alpha_{\text{max}} = 0.0145$ cm$^{-1}$
6$_\perp$ : $\alpha_{\text{max}} = 0.026$ cm$^{-1}$
FIGURE II-G-2 -- CH₃F - 496 μm: Small signal gain. 1 Torr, 0.5 MW/cm² pump power. The picture numbers correspond to the K levels and relative polarizations (\( \sum_{K=1}^{7} \)) means a sum of contributions from levels K=1 to K=7 and parallel polarization).

Horizontal scales: -3000 to 500 MHz for K=7
-3000 to 1000 MHz for \( \sum_{K=1}^{7} \)

\[ \begin{align*}
7_{||} : & \quad \alpha_{\text{max}} = 0.0035 \text{ cm}^{-1} \\
7_{\perp} : & \quad \alpha_{\text{max}} = 0.0066 \text{ cm}^{-1} \\
\sum_{K=1}^{7} \parallel : & \quad \alpha_{\text{max}} = 0.442 \text{ cm}^{-1} \\
\sum_{K=1}^{7} \perp : & \quad \alpha_{\text{max}} = 0.463 \text{ cm}^{-1}
\end{align*} \]
being 1.9 while Table II-E-3 gives 2.2 for a weak pump. Since $\beta_{13} \tau (M)$ varies for $K=7$ from 2.2 for $M=1$ to 26 for $M=12$ with $\delta_p \tau = -70$, we are almost in the weak pump regime and expect a pretty good agreement which we indeed obtain. One interesting departure from the general rule occurs for $K=2$ for which the parallel polarization is just a bit stronger than the perpendicular one. This can be explained by the fact that the parallel polarization peaks for small values of $M$, which are on the inside, and thus the two peaks reinforce each other in the area of the overlap. The perpendicular polarization peaks for large $M$ values and so the highest peaks end up farthest away from each other. Some typical pump parameters are $\beta_{13} \tau (K=1)$ from 0.3 for $M=1$ to 3.7 for $M=12$ with $\delta_p (K=1) \tau = 1.4$, i.e. strong pump on the average; $\beta_{13} \tau (K=3)$ from 0.9 to 11 and with $\delta_p (K=3) \tau = -8$, i.e., the pump not quite so strong. When we get to $K=7$ the pump is already weak. This variation is due to the fact that the pump transition intensity is proportional to $K^2$, see Eq. (2-G-4), while the pump offset has a $K^4$ dependence, see Eq. (2-G-1).

Figure II-G-3 shows small signal gain for a different set of parameters: 5 Torr and 1 MW/cm² pump power. There is not that much difference between Figures II-G-2 and II-G-3. Figure II-G-3 corresponds to twice the pump power and has approximately twice the amplitude. It also corre-
FIGURE II-G-3 -- CH₃F - 496 μm: Small signal gain, 5 Torr, 1 MW/cm² pump power. The picture numbers correspond to the K levels and relative polarizations (l∥ means K=1 and parallel polarization).

Horizontal scales: -600 to 600 MHz for K=1
-1200 to 800 MHz for K=2

l∥: α_max = 0.295 cm⁻¹
1⊥: α_max = 0.385 cm⁻¹
2∥: α_max = 0.301 cm⁻¹ max
2⊥: α_max = 0.285 cm⁻¹ max
FIGURE II-G-3 -- CH₃F - 496 μm: Small signal gain. 5 Torr, 1 MW/cm² pump power. The picture numbers correspond to the K levels and relative polarizations (3⊥ means K=3 and perpendicular polarization).

Horizontal scales:  -1200 to 800 MHz for K=3
                 -2000 to 800 MHz for K=4

3∥:  α_{max} = 0.308 cm⁻¹
3⊥:  α_{max} = 0.353 cm⁻¹
4∥:  α_{max} = 0.0805 cm⁻¹
4⊥:  α_{max} = 0.107 cm⁻¹
FIGURE II-G-3 -- CH₃F - 496 μm. Small signal gain. 5 Torr, 1 MW/cm² pump power. The picture numbers correspond to the K levels and relative polarizations (6∥ means K=6 and parallel polarization).

Horizontal scales: -2000 to 800 MHz for K=5
   -2400 to 800 MHz for K=6

5∥ : α_max = 0.0436 cm⁻¹
5⊥ : α_max = 0.0647 cm⁻¹
6∥ : α_max = 0.0437 cm⁻¹
6⊥ : α_max = 0.0706 cm⁻¹
FIGURE II-G-3 -- CH$_3$F - 496 μm: Small signal gain. 5 Torr, 1 MW/cm$^2$ pump power. The picture numbers correspond to the K levels and relative polarizations ($\sum_{K=1}^{7}$ means a sum over the contributions from levels K=1 to K=7 and perpendicular polarization).

Horizontal scales: -3000 to 500 MHz for K=7
-3000 to 1000 MHz for $\sum_{K=1}^{7}$

$7_H$: $\alpha_{\text{max}} = 0.0107$ cm$^{-1}$
$7_L$: $\alpha_{\text{max}} = 0.0186$ cm$^{-1}$
$\sum_{K=1}^{7}$ $H$: $\alpha_{\text{max}} = 0.964$ cm$^{-1}$
$\sum_{K=1}^{7}$ $L$: $\alpha_{\text{max}} = 1.19$ cm$^{-1}$
sponds to five times the pressure and so all the features are broader. Parallel polarization still persists in being higher for K=2. The maximum gain is about 1.2 cm\(^{-1}\) which can be compared with \(\alpha \approx 2.5\) cm\(^{-1}\) corresponding to the contributions of K=1, K=2 and K=3 from the rate equation model. We see that, as usual, the rate equation model gives about twice the answer (no split peaks there).

Figure II-G-4 illustrates the saturation behavior of the CH\(_3\)F laser. Each picture contains two curves, the higher corresponding to the small signal gain, the lower corresponding to the gain saturated somewhat by the 10 W/cm\(^2\) FIR power. The pressure was chosen to be 1 Torr and the pump power to be 0.5 MW/cm\(^2\). For K=1 and 2 the 10W/cm\(^2\) is enough to saturate both the line center and the Raman line, while for K=7 only line center noticeably responds. This can be again understood in terms of the treatment of Section II. D. For K=1 and 2, with their small pump offsets, 0.5 MW/cm\(^2\) constitutes strong pumping and so we expect the Raman line to saturate almost as easily as the line center. For K=7, as we discussed following Figure II-G-2, 0.5 MW/cm\(^2\) constitutes weak pumping and therefore the 10W/cm\(^2\) FIR power is not sufficient to saturate the Raman line.

We will see in Chapter IV that 10W/cm\(^2\), at 1 Torr, is indeed close to the saturating power experimentally too.
FIGURE II-G-4 -- CH$_3$F - 496 µm: Saturation behavior. 1 Torr, 0.5 MW cm$^{-2}$ pump power, 0 W/cm$^2$ (higher) and 10 W/cm$^2$ (lower) FIR power on each picture.
FIGURE II-G-4 -- CH$_3$I - 496 μm: Saturation behavior. 1 Torr, 0.5 mW/cm$^2$ pump power, 0W/cm$^2$ (higher) and 10W/cm$^2$ (lower) FIR power on each picture.
FIGURE II-G-4 -- CH$_3$F - 496 nm: Saturation behavior. 1 Torr, 0.5 MW/cm$^2$ pump power, 0W/cm$^2$ (higher) and 10W/cm$^2$ (lower) FIR power on each picture. The last set of pictures represents the sums of the contributions from the seven K levels.
However, our previous measurements\textsuperscript{65} reported kW/cm\textsuperscript{2} and higher FIR saturation intensities. These were measured by observing the amplification of the output of typically multimode FIR cavities in very long amplifiers. The beams were spatially and temporally very nonuniform and the CO\textsubscript{2} pump beam was self-mode locked. The frequencies of the FIR outputs were not known at all. A combination of all of these factors must have been responsible for the high measured value of the saturation intensity. A paper by Brown, et al.\textsuperscript{66} put an upper limit of 400 W/cm\textsuperscript{2} on the saturation intensity.

We would like to end this section with a comparison of our results with the recent approximate treatment of Chang\textsuperscript{67} in which he attempts to explain the spectrum of the high power ASE type CH\textsubscript{3}F lasers using the small signal theory of Javan.\textsuperscript{45} Figure II-G-5 shows a comparison of small signal gain, on a logarithmic scale predicted by our (solid line) and Chang's\textsuperscript{67} (broken line) theories. There are discrepancies both in amplitude and shape. Chang's\textsuperscript{67} approach is to divide all of the molecules into three groups and assign them to three mutually orthogonal orientations of the total angular momentum vector. Thus he has three instead of \((2J+1)\) orientations to deal with. Since both the rigorous treatment, as done here, and his approach require a computer
FIGURE II-G-5 -- CH₃F - 496 µm: Small signal gain. Comparison of this author's theory (solid line) with that of Chang⁶⁷ (broken line). 2 Torr, perpendicular relative polarization.
for the final results, there is really no reason to use his approach: there is only a small saving in computer time and the results obtained are inaccurate. Furthermore, his treatment excludes all the saturation effects which are known to affect the spectral content of ASE type lasers. \textsuperscript{68,31}
III. EXPERIMENTS WITH MULTIMODE CO$_2$ PUMP LASERS

In this Chapter we will provide a review of our earlier work connected with the operation of laser pumped submillimeter lasers.

Our first work\textsuperscript{69} was concerned with the measurement of the absorption and emission characteristics of an amplified spontaneous emission (ASE) methyl fluoride laser pumped by a high power multimode CO$_2$ laser (Lumonics model 103). One of the important findings of this work was the fact that with a strong pump the number of molecules pumped up to the excited vibrational levels was much larger than the number of molecules originally in the levels being directly excited. This phenomenon was successfully explained on the basis of very fast collisional repopulation of these initial levels. The results of this work were analyzed later on by Temkin and Cohn\textsuperscript{25} with the help of their rate equation model. Figure III-1 shows the fit between their theory and the experimental data\textsuperscript{69} on saturated absorption. A very good agreement was obtained considering that no adjustable parameters were used in the model.

The objective of most of the research described in this section was the development of a high power and narrow linewidth source of FIR radiation. To this end a CH$_3$F oscillator\textsuperscript{70} and then amplifier\textsuperscript{65} were developed.
FIGURE III-1 -- Comparison of the rate equation theory (solid lines) to the experimental data\textsuperscript{69} on saturated absorption of 100\,\mu\text{s} pulses of 9.55\,\mu\text{m} CO\textsubscript{2} laser radiation in CH\textsubscript{3}F gas at pressure P.
Both of these devices were pumped by the CO\textsubscript{2} beam in a zig-zag fashion and in this way the need for optical components applicable to both the 10 \( \mu \)m and 500 \( \mu \)m wavelength regime was avoided. The FIR cavity was shown to produce output whose spectral width was less than 30 MHz FWHM and the amplifier essentially preserved that spectrum. From the amplifier data an FIR saturation intensity of about 2kW/cm\textsuperscript{2} at 1 Torr was deduced. This, as we now know, is two orders of magnitude larger than the true value of \( I_{f,s} \) for each of the K levels separately on their line center frequencies. The position of the cavity output frequency with respect to the CH\textsubscript{3}F line centers was unknown. For a homogeneously broadened transition, the saturation intensity has a

\[ I_{f,s}(\nu) = I_{f,s}(\nu_0) \left[ 1 + \frac{4(\nu - \nu_0)^2}{\Delta \nu^2} \right] \]  

dependence\textsuperscript{25} on frequency. Since the cavity output frequency can be at most on resonance with one of the K line centers, then the others will respond much more weakly and this will manifest itself in a much higher overall saturation intensity. The small value of the small signal gain obtained in this early work\textsuperscript{65} is due to the very poor suitability of this system to small signal gain measurements. With a small signal gain of about 0.2 cm\textsuperscript{-1}, as we now know it, only a few centimeters
of gain medium are necessary to perform this measurement. The 2 m long amplifier was certainly not the tool for such a measurement. However, as we mentioned before, our goal was a high power system and this required large dimensions for the laser.

In our quest for higher FIR output powers we obtained a larger CO₂ pump laser and designed a larger FIR system. While this work was in progress we investigated the operation of a 1.2 mm isotopic methyl fluoride, \(^{13}\text{CH}_3\text{F}\), laser pumped by the 9.63 \(\mu\text{m}\) P32 line of CO₂ laser (again Lumonics 103 was used).\(^{71}\) Over 5kW peak output power was obtained from a 3 m long ASE type system. Besides the main, \(v_3=1\): \(J_3=5\) to \(J_2=4\), transition, three refilling transition in the ground vibrational state, \(J=5\) to \(J=4\), \(J=6\) to \(J=5\), and \(J=7\) to \(J=6\), were also observed and assigned. All of these were in the 1 mm wavelength regime. This was the first time that such high powers were obtained from a laser in the millimeter region.

After our new CO₂ pump system was completed, a Lumonics 103 oscillator with a Lumonics 601 amplifier used in a three-pass arrangement, we continued our work leading toward megawatt power levels in the FIR for plasma diagnostics. Our results were described by Woskoboinikow, et al.\(^{72}\) and summarized by Drozdowicz,
et al. and here we will discuss only some of them.

The large FIR system consisted again of a cavity-amplifier arrangement and various geometries for the two components were tried out. In the course of experiments various gases, like CH₃I and D₂O, were tried, pumped by the appropriate lines of the CO₂ laser. Of the various lasing media D₂O was found to give the highest outputs for the same pump parameters. The investigation of CH₃F was then set aside and our efforts concentrated on the 385 μm line of D₂O. Various short cavities were used to produce single mode FIR radiation and axially pumped amplifiers, up to 8 m long, were used to produce almost 200 kW peak power FIR outputs. A Restrahlen band of crystal quartz around 9 μm was put to use by utilizing a quartz crystal at 45° angle as a reflector for CO₂ and a window for FIR in the long amplifiers. To increase the cavity power output while retaining good mode control a Fox-Smith mode selector was used in a longer cavity with good results.

In the course of one of our gain measurements on D₂O, on June 2, 1976, we accidentally allowed the gas pressure in the amplifier to drop much below its usual pressure of 2 Torr. To our surprise we noticed that when the amplifier was allowed to lase in ASE mode its output frequency was about 350 MHz higher than the
frequency of optimum cavity output, the cavity being operated at 2.5 Torr D₂O pressure. We investigated this phenomenon in more detail in a smaller ASE type laser and found out that a number of gases pumped by the CO₂ laser suddenly change their emission frequency when the pressure is dropped to very low values. The difference between the two frequencies was always close to but also a little bit larger than the pump frequency offset from the absorption line. The two emission frequencies were therefore assigned to the Raman type, at higher pressure, and line center, at lower pressures, processes. The difference between the measured frequency shift and the pump offset was assigned to the AC Stark effect. The reason that Raman emission usually dominates lies probably in three factors. First, this process is more efficient in that one-to-one pump-to-FIR photon conversion is theoretically possible while line center allows only two-to-one conversion efficiency. Another factor is associated with the higher saturation intensity of the Raman line thus allowing its gain to remain larger than losses up to higher intensities. Also losses are higher at line center since it can be resonantly absorbed in a single photon transition which is in direct competition with the emission process, when the upper vibrational state becomes significantly populated. At low pressures, however, the FIR radiation buildup time
can be as long as the 100 nsec pump pulse and therefore most of the FIR emission occurs after the pump field is gone. This makes a two-photon Raman process impossible and causes the emission frequency to switch to the line center frequency at low pressure.

We would like to end this Chapter with a few of our unpublished results.

During our search for strong submillimeter lines various gases were introduced into a 3 m long ASE type laser and pumped with about 1MW/cm$^2$ CO$_2$ beam, the exact intensity depending on the particular line. One of the more unusual outputs was obtained when methyl acetylene, CH$_3$CCH, was introduced into the system and pumped with the 10.59 µm P20 CO$_2$ line. The output wavelength of a CW system was previously reported as 798.55 µm$^7$. When pumped with the high power CO$_2$ laser, we measured this output to be at 684 ±14 µm and therefore a different transition must be responsible for the CW and pulsed cases. The laser worked very weakly when the CO$_2$ laser was run without N$_2$ in the mixture thus having only the 100 nsec gain switched peak. When N$_2$ was added to the CO$_2$ mixture the output of the FIR laser increased more than tenfold to about 80 µJ/pulse at 2.7 Torr pressure. A Schottky diode picture of the output is presented on Figure III-2. A very unusual time structure, quite
FIGURE III-2 -- CH$_3$CCH - 684 um: Shottky diode picture of the output pulse of a 3 m ASE laser at 2.7 Torr. 200 nsec/div. The three major peaks separated by approximately 140 nsec from each other.
unlike the outputs of other transitions we studied, can be seen there. The three major peaks are separated by about 140 nsec from each other. The CO₂ pump pulse consisted of a 100 nsec gain switched peak, containing about 25% of pulse energy, and a 2 - 3 μsec long nitrogen tail containing the rest of the pulse energy (about 4 Joules total). The polarization of the FIR output was parallel to the CO₂ pump beam's polarization. Scanning the output at 2.7 Torr with a mesh mirror Fabry-Perot produced a single strong line with less than 35 MHz FWHM width and a second one, at least ten times weaker, lower in frequency by 115 ±10 MHz. The assignments of these lines are unknown to us. The absorption of the CO₂ beam was very weak, which might be due either to a large pump offset or a very small population factor of the level. Since most of the FIR emission occurred while the CO₂ pump was in its lower power nitrogen tail area we would tend to believe that a low population is responsible for the poor pump absorption.

There is one point we would like to make in this section and it concerns the relative polarizations of the FIR and the CO₂ beam. We have already mentioned in Section II. E. that we believe both the rules and the measurements presented in the paper by Lipton and Nicholson⁵⁰ to be in error. Their claim is that when the K⁺ and
K_ numbers change by the same (opposite) sign the relative polarizations occur parallel (perpendicular) to each other. They list a number of transitions they observed in D_2O when pumped by their single mode, etalon tunable CO_2 laser and all of them follow this rule. We take issue with one of their measurements: the 6_{24} to 5_{33} refilling line associated with the 385 μm laser. They claim that the relative polarization of this line is perpendicular, i.e. the same as that of the 385 μm line. Our own measurements on an ASE type laser indicate that typically the 385 μm line is polarized perpendicular to the CO_2 beam with a ratio of about 2:1 while the opposite was true for the 239 μm, 6_{24} to 5_{33} transition. This transition will then violate their rule experimentally. Theoretically we are unaware of any reason for this rule, as our own treatment demonstrates that there is no dependence on the internal quantum numbers.

We will close this Chapter with the mention that we have observed yet another refilling transition for the 385 μm line. This was 5_{42} to 5_{33} transition with wavelength measured to be 158±2 μm and predicted 60 to be 157.3 μm.
IV. EXPERIMENTS WITH SINGLE MODE PUMP AND FIR LASERS

In this Chapter the results of our latest set of experiments will be presented. These involved the investigation of the small signal gains and saturation intensities of the 385 μm D_2O transition and the 496 μm CH_3F transition. Single mode CO_2 pump and FIR cavity were used. The equipment will be described in Section IV. A. together with our data collection techniques. Sections IV. B. and IV. C. will contain the results for D_2O and CH_3F respectively. These sections will also include a comparison of the experimental results with the theoretical predictions.

A. Equipment and Data Collection Methods

We will start this Section by describing our CO_2 pump laser. This laser was of a hybrid type, i.e., contained low pressure and TEA gain sections within one cavity. This cavity was created by a 150 lines per millimeter grating, mounted in an auto collimation arrangement, and a 10 m radius, 36% reflective front germanium mirror. The cavity was 250 cm long. The cavity was forced to oscillate in TEM_{00} mode by two apertures located one near the grating and the other near the front mirror. Their diameters were set to 3 w_0 and 3 w_1 respectively, where w_0 and w_1 are the radii of the Gaussian beam near these components. The values of w_0 and w_1 were calculated to be 3.7 mm and 4.3 mm respectively.
The outside surface of the germanium output window was AR coated and had a 7.5 m radius of curvature. The output beam just after leaving the cavity had then \( w = 4.3 \text{ mm} \) and infinite radius of curvature (i.e. plane wavefront). The grating was used to tune the cavity to one of the many CO\(_2\) laser lines. The function of the low pressure CO\(_2\) gain section was to initiate oscillations of only one of the possible longitudinal cavity modes. This mode then could grow very fast when the TEA section was excited and saturate the gain before other modes got a chance to establish oscillations. The net result was a high power single mode output.

The low pressure section consisted of 3/4" i.d. Pyrex tube closed at the ends by Brewster angle Na\( \text{Cl} \) windows. The length of the discharge volume was 90 cm. The electrical discharge circuit, modeled after Loy\(^{37}\), consisted of 16 \( \mu \text{f} \) capacitor charged up to 300 to 400 V which was discharged through the primary winding of a Delco D523 ignition coil when an SCR (2N688) was triggered. The secondary winding of this coil was connected across the discharge tube. The particular coil used was found to have the best impedance match to the discharge. A typical output pulse of the low pressure section alone is shown on Figure IV-A-1 for a 10 Torr pressure, 350 V on the capacitor and approximately 6:1:1 mixture of He:CO\(_2\):N\(_2\).
FIGURE IV-A-1 -- Low pressure CO\textsubscript{2} laser output (lower trace) and voltage across the discharge (upper trace).

200 \textmu s/div horizontal
10 kV/div upper trace
Approx. 25 watts/div lower trace.
This output was monitored with an approximately 100 nsec risetime pyroelectric detector. The pulse was 120 μsec FWHM long and, with 4mJ/pulse energy, had 20 watt peak power. This low pressure section was reported to be capable of 1kW peak power outputs. For our applications we were interested in a few watts type of power levels so that the gain switched peak of the TEA section would not be decreased significantly in power. We achieved the lowered power levels in the low pressure section by running it at low pressures, 7 to 8 Torr, and voltages, about 300 V.

The TEA section of our CO₂ laser was similar to that described by Chang and Wood. Two capacitors of 0.05 μF and 0.07 μF each, arranged to form an LC inversion generator, were charged to ~30kV, the discharge taking place between a pair of Rogowski profile electrodes, 60 cm long and separated by ~1.9 cm. The laser typically operated on input energies of 300-400 J/l for an approximately 78:12:10 mixture of He:CO₂:N₂. The photopreionization of the laser was provided by a flashboard which was fired approximately 1 μsec before the main discharge. The flashboard was powered by a separate LC inversion generator consisting of two 2700 pF capacitors for each half of it. The adjustable delay between the flashboard and main discharges allowed for optimization of the laser's operation for various gas mixtures. The TEA section was closed
with two ZnSe Brewster windows.

All the components of the CO₂ laser were mounted on an aluminum table. This created some problems with thermal stability since with the large coefficient of thermal expansion of aluminum, \( \alpha = 23.4 \times 10^{-6} \, (°C)^{-1} \), it took less than 0.1°C change in temperature to make the laser go through its full free spectral range (FSR) of 60 MHz. These thermal fluctuations were observable when the output of the CO₂ laser, operating with both gain sections on, was monitored with a photon drag germanium detector. This output was observed to go through cycles of single mode - two modes - single mode operation, the changes occurring on a few minute time scale. Some typical outputs of the laser are displayed on Figure IV-A-2. Figure IV-A-2 (a) and (b) show typical single mode outputs on 200 and 50 nsec/div scales respectively. Figure IV-A-2(c) shows a typical output for two longitudinal modes oscillating simultaneously. Note the approximately 16 nsec spacing between the peaks corresponding to the 60 MHz longitudinal mode separation. Using pictures like Figure IV-A-2(a) the pulse energy, ~0.3 Joule in TEM₀₀ mode, was found to be divided approximately 50:50 between the gain switched peak and the nitrogen tail of the pulse. The peak power was then calculated to be ~1.5 MW for the ~100 nsec FWHM gain switched peak of the 9.26 μm R22 line. Figure IV-A-3
FIGURE IV-A-3 -- Burn pattern produced by the single mode laser, 3.3 m away from the output mirror, on a 3 M Company's Thermo-Fax brand Infrared Copy Paper.
shows the burn pattern produced by the single mode laser 3.3 m away from the output mirror, on a 3M Company's Thermo-Fax brand Infrared Copy Paper. It is another indication, besides the absence of slow mode beating in time resolved pictures, that the laser was operating essentially in TEM\textsubscript{00} mode.

We should mention here that throughout our measurements of the FIR laser parameters the CO\textsubscript{2} laser output was monitored with the photon drag detector and data was taken only during the single mode cycles of this laser.

The FIR cavity, shown on Figure IV-A-4, was built inside 4" i.d., 6" long Pyrex glass tube. Metal meshes, which act as semitransparent mirrors if the wavelength of the radiation is longer than the mesh constant,\textsuperscript{80} were used to define the cavity. It was found that 400 lines per inch Ni mesh, with transmission of about 9\% at 385 \textmu m, 5\% at 496 \textmu m, and 70\% at the CO\textsubscript{2} wavelengths (the last of which were also strongly diffracted with about 4.3° half angle of diffraction), gave very good results for both the D\textsubscript{2}O and CH\textsubscript{3}F lasers. One of the meshes was mounted in a gimbal mount, to allow for angular alignment of the cavity, while the other was mounted on a miniature precision translation stage, to allow cavity frequency tuning. The meshes were stretched over ~1.5" dia. rings. Mesh mirror separation was about 11.5 cm thus yielding 1.3 GHz FSR
FIGURE IV-A-4 -- FIR CAVITY
for an empty cavity. The cavity FSR was kept so high in order to avoid any chance of more than one longitudinal mode oscillating at one time. We depended on high diffraction losses of the plane-plane cavity to inhibit the oscillation of higher order transverse modes and have not used any extra apertures. The CO$_2$ beam, diffracted by the passage through one of the mesh mirrors from ~1 cm dia. at the input to ~2 cm. dia. at the output mesh, defined the size of the gain medium and thus provided its own aperturing. The AR coated ZnSe input window for the CO$_2$ beam and the crystal quartz FIR output window were mounted at offset angles to avoid double cavity effects.

The FIR amplifier is shown on Figure IV-A-5. The FIR beam from the cavity entered the amplifier through an offset mounted crystal quartz window. This window was offset to avoid creating a cavity effect between the input and the output windows. After entering the amplifier part of the FIR beam was reflected toward the output window by a 45° mounted germanium window, AR coated for CO$_2$ wavelengths. The CO$_2$ pump beam entered the amplifier through the Ge window and the two beams co-propagated inside the 7.5 cm long amplifier. The diameter of the FIR beam was much larger than the approximately 1 cm diameter of the CO$_2$ beam. In this way the overlap of the two beams was always assured.
FIGURE IV-A-5 -- FIR AMPLIFIER
The spectrum and frequency changes, with the cavity tuning, of the FIR radiation were measured using a metal mesh mirror scanning Fabry-Perot interferometer with variable free spectral range. Pyroelectric detectors, made by Laser Precision Corporation, were used to measure the FIR pulse energy. A Schottky diode detector provided time resolved pictures of the FIR pulses with bandwidth of hundreds of MHz. These were observed on Tektronix 7904 (500 MHz) and 7844 (dual beam, 400 MHz) oscilloscopes. The energy of the CO$_2$ beam was measured using a GenTec joulemeter, after proper attenuation, while its time structure was observed with a photon drag detector. Pressures were measured using capacitive pressure gauge. The output beam of the CO$_2$ laser was split into three components by an Na Cl beam splitter with a 3° wedge. In a typical arrangement, at ~70° angle of incidence, about 50% of the beam was transmitted and used to pump the cavity, about 30% was reflected from the front surface of the beam splitter and used to pump the amplifier, and about 10% was reflected from the second surface of the beam splitter, at an angle different by 3°, and sent to the photon drag detector to assure data collection only when the CO$_2$ pulses were indeed single mode.

A typical arrangement of equipment setup for gain measurements is shown on Figure IV-A-6. The output of the
FIGURE IV-A-6 -- Experimental Setup

M  - mirror
M1 - large radius of curvature mirror
B.S.1 - Na Cl beam splitter with 3° wedge
B.S.2 - 150 l.p.i. Cu mesh beam splitter
P.D. - Photon Drag detector
D1 - Pyroelectric detector, 5 mm dia input
D2 - Reference pyroelectric detector
single mode CO$_2$ laser is split into three beams by the NaCl beam splitter (B.S.1). The transmitted beam pumps the FIR cavity, one of the reflected beams is monitored by the photon drag detector (P.D.), while the second reflected beam is sent around the setup and used to pump the FIR amplifier. The output of the FIR cavity is first collimated by a slightly focusing mirror (M1) and then split into two beams by a metal mesh beam splitter (B.S.2). The reflected beam is measured by the reference pyroelectric detector (D2) while the transmitted one enters the FIR amplifier. The output of the amplifier is measured by the pyroelectric detector (D1) which is located right next to the amplifier's output window. This was done so as to avoid any losses associated with diffraction of the small diameter amplified beam. This beam has the diameter of its CO$_2$ pump beam, $\sim$1 cm, and for wavelength on the order of 0.5 mm the diffraction angle can be quite large.

The pyroelectric detector D1 consists of a highly polished metal cone which collects radiation from an area of 5 mm diameter and focuses it down into the 2 mm diameter detector element. We chose to increase the effective area of the detector, through the use of the cone, in order to improve the signal to noise ratio. We had to work with signals of magnitude $\sim$1$\times$10$^{-7}$ J/cm$^2$ ($\sim$1 Watt/cm$^2$ in 100 nsec pulse) in order to avoid saturation of the FIR transitions.
On the other hand we were looking for effects depending on the magnitude of the pump's E-field (AC Stark effect) and thus wanted to collect signal from area pumped by essentially constant $E_{\text{pump}}$. The 5 mm diameter collecting cone gave us sufficient amount of signal while, for our specific CO$_2$ beam, the pump's E-field was smaller on the edges only by a factor of $\sqrt{\frac{1}{2}}$. This detector, D1, was calibrated against another, 1 cm$^2$ area, pyroelectric joule meter. This calibration was good to ±20%. However, the calibration of our "standard" detector was uncertain to within a factor of 2 due to the uncertainty in the absorption of very long wavelengths by the detector's coating. This uncertainty will show up in the saturation intensity values which will be presented later on in this Chapter.

The CO$_2$ pump laser could be pulsed about once every two seconds. To smooth out the pulse-to-pulse signal variations the outputs of the pyroelectric detectors were fed into linear gates, ORTEC Brookdeal model 9415, for a "box-car integration" processing. The outputs of the linear gates were then displayed by a two-pen chart recorder. The amplification factor was obtained by blocking and unblocking the CO$_2$ pump beam going to the FIR amplifier. The ratio of the signals from the 5 mm dia. pyroelectric detector, D1, for the two cases gave us the amplification
factor. The reference pyroelectric detector, D2, was used to monitor the output of the FIR cavity to make sure that no sudden changes in intensity occurred during any of the amplification measurements. For saturation intensity measurements, when the amplification factor could be as small as 10%, we used a differential amplifier set to unity gain. The output of the reference detector was subtracted from the output of the 5 mm dia. one. One of the electrical signals was attenuated so that when the CO₂ pump beam going to the amplifier was blocked the output of the differential amplifier was zero. The signal from the differential amplifier when the pump beam was unblocked corresponded then to the increase in the FIR signal due to amplification. This, together with the knowledge of the signal amplitude before amplification, gave us all the information necessary to obtain the amplification factor.

IV. B. D₂O Experimental Results

In this section we will present the results of the small signal gain and saturation intensity measurements for the 385 μm D₂O transition. These will be followed by the presentation of some of the more interesting features of the cavity operation which include strong frequency pulling effects, response to the gain modulation
when the CO$_2$ pump contains more than a single mode, and some other spectral effects.

We remember from Section 7.I.D. that the minimum value of the saturation intensity is given by its value predicted by the rate equation model. This number is, from equation 2-F-9, 4.5 W/cm$^2$ Torr$^{-2}$. We took all of our small signal gain data at 3 and 10 Torr pressures with the corresponding saturation intensities of 40 and 450 W/cm$^2$ respectively. We kept the FIR intensity in the 1 to 2 Watts/cm$^2$ range at all times and thus were able to use the small signal limit formalism. In this limit

$$I_{out} = I_{in} \cdot e^{A \cdot l}$$

(4-B-1)

and the small signal gain, $\alpha_o$, is obtained from amplifier measurements as

$$\alpha_o = \frac{l}{l} \ln \frac{I_{out}}{I_{in}}$$

(4-B-2)

where $l$ is the length of the gain medium.

Since equation 4-B-2 contains only a ratio of intensities the uncertainty in the detector calibration does not affect the results to be presented.

Figure IV-B-1 shows the experimental results for the weak pump case at 3 Torr pressure. The 35 kW/cm$^2$ pump power gave the pump parameter, $\beta_{13} \tau$, of between .5 and .9 while $\delta_p \tau = -5.4$. Easily noticeable is the double
Figure IV-B-1 -- D$_2$O - small signal gain. 3 Torr, 35 kW/cm$^2$ pump power.

- $x$ - experimental
- continuous line - theory scaled down vertically by a factor of 2
peak structure, one of the peaks located at $\delta_s=0$, the other around $-320$ MHz. The first peak is then the line center emission, while the other is due to the Raman transition. The continuous lines are the results of numerical predictions based on the density matrix model with the M-level degeneracy folded in. The amplitudes of the theoretical curves were found to be about two times as large as the measured ones. When the theoretical curves were scaled down uniformly by a factor of 2, the same for the parallel and perpendicular relative polarizations, the fit shown on Figure IV-B-1 was obtained. It is important to notice that our theoretical model accounts very well for the spectral dependence of the small signal gain and also for the relative strength of the two polarizations. The only major discrepancy arises in the predictions concerning the amplitude of the gain.

We will come back to this point later on in this Section. The maximum gain measured for this pump power was about $0.034 \text{ cm}^{-1}$ for the perpendicular polarization.

As the pump power increases we expect to see increase in gain and a shift in peak positions due to the AC Stark effect. These are demonstrated in Figure IV-B-2, which shows the measured small signal gain for 3 Torr pressure and 500 kW/cm$^2$ pump power. The pump parameter, $\beta_{13} t$, was between 2 and 3.3, for the different M levels,
Signal offset from line center frequency

FIG. IV-B-2 -- D₂O - small signal gain. 3 Torr, 500 kW/cm² pump power.
  x - experimental
  continuous line - theory scaled down vertically by a factor of 3.
with $\delta_p \tau = -5.4$ again. We can see the shift of the line center peak from its weak pumping position of $\delta_s = 0$. The Raman peak is also shifted away from its energy conserving position $\delta_s = \delta_p$. The agreement between the predicted and the observed spectra is again very good for both polarizations. The ratio between the predicted and the measured gain has now increased to 3. We will again leave the discussion of this point until later.

The highest gain measured here was 0.14 cm$^{-1}$ for the perpendicular polarization. Figure IV-B-3 shows the small signal gain for 10 Torr pressure and 500 kW/cm$^2$ pump power. The line center and Raman peaks are essentially merged into a single broad peak due to the large pressure broadening. The best fit of the theory and data was obtained when the theoretical small signal gain was scaled down by a factor of 3.75. The highest gain measured was 0.155 cm$^{-1}$ for the perpendicular polarization.

The overall highest gain measured was $\sim0.21$ cm$^{-1}$ for 10 Torr pressure and $\sim1$ MW/cm$^2$ pump power. This gain was for the perpendicular relative polarization.

Thus far we have found that our theoretical considerations provide good agreement with our experimental data as far as spectral content and relative strengths of the two polarizations are concerned. As for the amplitude of the gain, we find that the theory and experiment diverge.
Signal offset from the line center frequency

FIGURE IV-B-3 -- D$_2$O - small signal gain. 10 Torr, 500 kW/cm$^2$ pump power.

x - experimental
continuous line - theory scaled down vertically by a factor of 3.75.
Let us first take a look at the changing ratio of the theoretical and experimental gains as we vary the pump power and gas pressure. We found \( \frac{\alpha_{\text{theory}}}{\alpha_{\text{experiment}}} \) to be: 2 for 35 kW/cm\(^2\) pump power at 3 Torr, 3 for 500 kW/cm\(^2\) pump power at 3 Torr, and 3.75 for 500 kW/cm\(^2\) pump power at 10 Torr. Equation 2-B-17, dealing with the time necessary to obtain zero gain under conditions of strongly saturating pump field may provide the explanation for this phenomenon. We find that this time is about 300 nsec at 3 Torr and 90 nsec at 10 Torr. Now, 500 kW/cm\(^2\) is a strong pump but not really highly saturating one. Therefore with ~100 nsec pump pulse we do not expect to reach the point of zero or negative gain. However, some gain reduction is expected due to the filling up and thermalization of the excited vibrational state. It seems to us that that is what we are observing here since the theoretical curves of Figures IV-B-1 to IV-B-3 were derived with the assumption of an empty upper vibrational state.

In case of weak pumping we expected to find a good agreement between the theory and experiment since the upper vibrational state does indeed remain essentially empty. We found however a factor of 2 difference. Part of that can be ascribed to the fact that the pump pulse is not flat in time. Its rising and falling edges will
have smaller contributions to the overall gain than its high power central section and therefore in the spectrum we mostly see the contributions from the latter one. However, since we are measuring gain integrated over the whole pulse length, the overall value will be lowered somewhat. We suspected also diffraction losses to be responsible for a part of the difference since the gain medium had only ~1 cm diameter and we were dealing with ~0.5 mm wavelengths. However, when we pumped the amplifier with the CO$_2$ beam expanded to ~3 cm dia. the same type of theory to experiment factors were observed.

The saturation behavior of the gain was observed for perpendicular relative polarization at 1 Torr pressure and under conditions of weak pumping, 35 kW/cm$^2$. The pump power was kept low in order to avoid AC Start effect and the associated shift in peak positions for the various M levels. The results are presented in Figure IV-B-4.

The difference in gain behavior at the line center and Raman frequencies is immediately obvious. The line center data was easily fitted by a usual saturation equation, like 2-D-1, with the saturation intensity equal to one-half of the maximum available FIR intensity at this frequency. The latter one was measured to be between 9.5 and 19 Watts/cm$^2$, the uncertainty stemming from the previously described problems with detector
FIGURE IV-B-4 -- D₂O - saturation behavior. 1 Torr, 35 kW/cm² pump power. \( I_{\text{max}} \) is between 9.5 and 19 Watts/cm² (uncertainty due to detector calibration).

(a) Line center data fitted with saturation intensity equal to \( \frac{1}{2} I_{\text{max}} \).

(b) Raman data - no saturation observable up to the maximum obtainable FIR intensity.
calibration, yielding

\[ 4.75 \leq I_{fs} \leq 9.5 \text{ W/cm}^2 \] (4-B-3)

This is in very good agreement with our prediction of 4.5 Watts/cm\(^2\) at 1 Torr pressure. We could tune into the line center position only to within ±15 MHz which in view of the dependence of the saturation intensity on frequency:

\[ I_{fs}(v) = I_{fs}(v_0) \left[ 1 + \frac{(v-v_0)^2}{(\Delta v/2)^2} \right] \] (4-B-4)

could lead us to a measurement equal to almost twice the value of saturation intensity on line center (Δν=40 MHz).

For the Raman frequency gain component we were unable to see any saturation effects with the available FIR power. This is again in line with the predictions of Section II.D. We found the gain at Raman frequency to be about 1/2 of that at line center at 1 Torr, see Figure IV-B-4. We believe that this is due to the frequency fluctuations of the CO\(_2\) pump laser. As we mentioned in an earlier part of this Chapter the CO\(_2\) laser was not thermally stabilized and its frequency was drifting within ±30 MHz (1/2 of its FSR) of its line center. This caused the frequency of the Raman line, tied to the pump frequency through \(\omega_{pump} - \omega_{Raman} = \omega_{21}\), to drift within the same range while the probe frequency was fixed by the cavity setting.
We were then in effect measuring some average value of gain within ±30 MHz of the 40 MHz FWHM Raman peak. The factor of one half seems very reasonable in view of the above comments.

We are now ready to present some of the more interesting aspects of the operation of the FIR cavity. Figures IV-B-5 and IV-B-6 show the dependence of the cavity output on cavity length at 2 Torr and 10 Torr pressures respectively. The free spectral range of an empty cavity was 1.3 GHz, as marked on the Figures. At 2 Torr a double peak feature was observed, the peaks separated by about 325 MHz. One of the peaks, the one at lower frequency, was about ten times stronger than the other one. We assigned those two peaks to the Raman and line center transitions, as marked on Figure IV-B-5, based on their relative frequencies. This assignment was further confirmed by their relative heights, the Raman transition being responsible for the higher peak. The physical reason for this is as follows. The two transitions have the same small signal gains but the Raman transition has a much higher saturation intensity. It takes therefore much more FIR intensity to cut the Raman gain down to its threshold value than it does for the line center gain. This is reflected in the cavity outputs at these two frequencies.
FIGURE IV-B-5

$D_2O$ - cavity output versus length. 2 Torr pressure.
FIGURE IV-B-6

$D_2O$ - cavity output versus length.
10 Torr pressure.
For most of our experiments the cavity was operated at 10 Torr pressure. This pressure yielded optimum cavity operation as far as tunability and output amplitude was concerned. We can see in Figure IV-B-6 that pressure broadening plus the dependence of the saturation intensity on pressure (\( \sim p^2 \) for the line center) caused the output of the cavity to become a single broad peak, as the cavity length is scanned. The 500 MHz tuning range marked on Figure IV-B-6 corresponds to empty cavity tuning. Frequency pulling effects, to be described later on in this section, caused it to be only \( \sim 600 \) MHz.

The high \( \text{D}_2\text{O} \) pressure, 10 Torr, was also instrumental in fast quenching of cavity oscillations after the gain switched peak of the pump pulse was over. This facilitated the analysis of the amplifier data since we did not have to worry about the effects of the long, low power nitrogen tail in the pump pulse. Figure IV-B-7 shows some typical FIR pulses, with their corresponding pump pulses, for a cavity setting near the line center frequency and a 10 Torr pressure. Figure IV-B-7 (a) shows a typical cavity output when pumped by a single mode pulse from the \( \text{CO}_2 \) laser. The cavity output is also single mode, its width at \( \sim 60 \) nsec FWHM, slightly smaller than that of the pump pulse, at \( \sim 100 \) nsec FWHM. Figures IV-B-7 (b) and (c) show the response of the cavity to a two mode, (b),
FIGURE IV-B-7 -- D$_2$O

Time resolved cavity output. 10 Torr, Near line center frequency. Upper trace: FIR pulse observed with a Schottky diode. Lower trace: CO$_2$ pump pulse observed with a photon drag detector.

(a) Single mode CO$_2$ pump pulse

(b) Two mode CO$_2$ pump pulse

(c) Multimode CO$_2$ pump pulse.
and multimode, (c), pump pulse. The cavity output seems to capable to follow the amplitude of the pump pulse with a response time on the order of a few nanoseconds. The temporal structure in the CO$_2$ pump pulse is due to beating between a number of longitudinal modes offset from each other by 60 MHz intervals. However, the longitudinal modes of the FIR cavity are separated by 1.3 GHz and this cannot be responsible for the 16 nsec oscillation in the output intensity. Gain modulation by the oscillating pump intensity coupled with a fast relaxation time, less than 1 nsec at 10 Torr, and a short cavity decay time must be responsible for this behavior. We will show shortly in our analysis of the cavity tuning curve, that the cavity is very lossy and therefore the cavity decay time is indeed on the order of a nanosecond.

Figure IV-B-8 shows again the time resolved picture, this time with a 20 nsec/div. horizontal scale, of the FIR (top) and CO$_2$ (bottom) pulses. Cavity, at 10 Torr, was set to a position corresponding to frequency ~ -280 MHz from the line center, i.e. close to the Raman frequency. The point we want to make with this Figure is that the cavity output is essentially smooth suggesting a single mode operation, the same as the one on Figure IV-B-7 (a). The importance of this point becomes apparent when we look at Figure IV-B-9 which shows the output of a scanning Fabry-Perot interferometer. This output was obtained as
FIGURE IV-B-8 -- D$_2$O - time resolved cavity output.
FIR - top trace
CO$_2$ - bottom trace
20 nsec/div horizontal scale.
FIGURE IV-B-9 -- D$_2$O - Cavity output analyzed by a scanning Fabry-Perot interferometer
(a) Line center frequency, multimode pump; (b) line center position, single mode pump;
(c) near Raman frequency, single mode pump.
follows. The Fabry-Perot, with 300 l.p.i. Ni mesh mirrors and 500 MHz FSR, was allowed to run continuously. Peaks marked (a) were obtained with the cavity being pumped by multimode CO₂ pulses (the low pressure gain section of the hybrid pump laser was switched off). Peaks marked (b) and (c) were obtained with the cavity being pumped by single mode pulses. Peaks (a) and (b) were obtained at cavity setting corresponding to the line center frequency, while peaks (c) were obtained with the cavity set near the Raman frequency. There are two immediately noticeable features in Figure IV-B-9. One of them is the sudden change in peak spacing between the (b) and (c) pairs, which corresponds to a change in the lasing frequency of the cavity as its length is changed. Peaks (c) were found to correspond to a frequency ~280 MHz lower than that of the preceding peaks and thus they represent the same cavity setting as the time resolved picture on Figure IV-B-8. The other outstanding feature is the much larger width of peaks (c) compared to (b) even though both seem to represent single mode cavity outputs. One possible explanation of the increased width of peaks (c) is that the strong frequency pulling effects, which we will describe right after this discussion, are dependent on the location of the Raman frequency and thus will vary from shot to shot due to the pump frequency drifts. A
comparison between peaks (a) and (b) shows that the former show more spectral structure. We can associate this with the sidebands due to the modulation of the output power. We should also mention here two other points. The first one is that of the 60 MHz FWHM of peaks (b) at least 30 MHz is due to the instrumental width of the Fabry-Perot interferometer. The other point is that in none of the Fabry-Perot scans did we observe any cascade or refilling lines and therefore the three level theory, as presented in the earlier Chapters, should apply without any corrections for other levels.

We now come to the tuning characteristics of the FIR cavity. Figure IV-B-10 shows the measured cavity tuning versus the one expected for an empty cavity of the same length. This data was obtained in a following manner. The Fabry-Perot interferometer was continuously scanned through two to three consecutive peaks at cavity setting corresponding to the line center frequency. After the last peak the cavity length was suddenly changed to a new position with the Fabry-Perot still scanning continuously. Two to three more peaks were recorded at this new cavity setting and then the cavity was returned to its line center frequency position. This routine was repeated for every new cavity length setting. The amount of tuning achieved was measured by observing the amount of shift of
FIGURE IV-B-10 -- $D_2O$ - cavity tuning curve. 10 Torr pressure. The 45° broken line is drawn for reference through a point halfway between the line center (0 MHz) and Raman (-320 MHz) frequencies.
the peaks associated with a given cavity setting with respect to those corresponding to the line center frequency. The error bars on Figure IV-B-10 arose from a combination of the Fabry-Perot instrumental width and pulse-to-pulse variation of the cavity output frequency. The latter was responsible for a larger part of the error bars of the points at large negative offsets (Raman frequency and beyond). The 45° broken line in Figure IV-B-10 was drawn for reference to show the tuning curve of a "cold" cavity. Departures from this line are due to frequency pulling effects. These are caused by the effect that the resonance of the imaginary part of the susceptibility, $\chi''$, has on its corresponding real part, $\chi'$, and therefore on the medium's index of refraction. Yariv shows one typical treatment of this effect and obtains, for an oscillating cavity whose gain medium has a single, Lorentzian shaped resonance, the following expression:

$$\nu \approx \nu_m - (\nu - \nu_0) \frac{\Delta \nu_{1/2}}{\Delta \nu}$$

(4-B-5)

where $\nu$ is the frequency of oscillation, $\nu_m$ is the frequency of "cold" cavity, $\nu_0$ is the resonance frequency, $\Delta \nu_{1/2}$ is the full width of the cavity response curve (i.e., $\frac{1}{\pi t_c}$, where $t_c$ is the cavity decay time), and $\Delta \nu$ is the FWHM of the homogeneously broadened gain curve. As long as the cavity losses are not frequency dependent and the pulling
effect is not too strong this equation should describe any oscillating cavity disregardless of the number of resonances. This is because the threshold gain is constant throughout the region of oscillation and this is the quantity that leads to equation 4-B-5. If one tries to fit a straight line through the experimental points in Figure IV-B-10 one finds that it is well fitted by a ratio

\[
\frac{\Delta \nu_{\nu_2}}{\Delta \nu} \approx \frac{3}{4}
\]  

(4-B-6)

Now, since \( \Delta \nu \approx 400 \text{ MHz} \) at 10 Torr then \( \Delta \nu_{1/2} \approx 300 \text{ MHz} \) and the cavity decay time is less than 1 nsec. For a symmetric cavity, \( R_1 = R_2 = R \), the cavity loss coefficient is given by

\[
\alpha = \frac{2\pi n \Delta \nu_{\nu_2}}{c} + \frac{1}{l} \ln R
\]  

(4-B-7)

In our case \( l = 11.5 \text{ cm} \), \( R = .91 \), and therefore

\[
\alpha = 5.5 \times 10^{-2} \text{ cm}^{-1}
\]  

(4-B-8)

which causes the loss per pass, \( L = 1 - e^{-\alpha l} \), to become 46%. This very large loss is due mostly to diffraction and is a penalty we had to pay for working with a plane-plane cavity.

We will conclude this section by presenting the spatial profile, Figure IV-B-11, of the cavity output. This data was taken with the detector mounted on an x-y translation stage driven by two different pitch screws. When each of these screws was in turn driven by a single speed synchronous motor the curves of Figure IV-B-11 resulted. We believe
FIGURE IV-B-11 -- D₂O - cavity spatial profile. 10 Torr.
that the structure visible in this curve is due at least in part to occasional problems with the CO₂ pump laser. We base this on the fact that even though the general shapes of these curves were reproducible from scan to scan, the structure was not.

IV. C. CH₃F - Experimental Results

The presentation of our experimental results for CH₃F will follow along the same lines as for D₂O, in the preceding section. First small signal gain and saturation intensity will be presented. The description of cavity operation will follow.

Discussion presented in this section will be shorter since most major considerations are the same in the case of CH₃F as they were for D₂O. There are a few differences, though, which we would like to mention here. The foremost of these is the fact that, with the M level degeneracy neglected, D₂O was a simple 3-level system while CH₃F is a combination of 3-level systems associated with the various K quantum numbers. The frequencies of emission of these systems form an irregular "comb" and with the limited spectral resolution, of 20 to 30 MHz, we could not have hoped to be able to isolate the individual K level contributions to the spectrum. Therefore, we chose to work only under conditions under which the spectral features
would be broadened enough to form one continuous gain curve. This was achieved by using moderately strong pumping and higher pressures. Another difference arises from the fact that in CH$_3$F the perpendicular polarization dominates the parallel one to such a degree that no parallel polarization emission from the cavity was measured at any time (in D$_2$O about 30% of the energy was coming out with parallel polarization). It was therefore necessary to use external optical elements to obtain some power in the parallel polarization so that the small signal gain could be measured. A quarter-wave quartz plate, available in the laboratory, was used for this purpose.

We recall from Section II. G. that the saturation intensity for line center of each K level is about 5 Watts/cm$^2$ Torr$^2$. We again kept the FIR intensity at or below 1 Watt/cm$^2$ in order to avoid saturation effects in the small signal gain measurements.

Figure IV-C-1 shows the measured and predicted small signal gains for the two polarizations. These represent 500 kW/cm$^2$ pump power and 5 Torr pressure. The theoretical curves, as in Section II. G. came from summation over contributions from K=1 to K=7 levels. 0 MHz corresponds to the line center frequency of the K=0 transition, absent from the picture due to K≠0 selection rule for
FIGURE IV-C-1 -- CH$_3$F - small signal gain.
5 Torr, 500 kW/cm$^2$ pump power
x - experimental
Continuous line - theory scaled down vertically by a factor of 5.4
the pump transition. Theoretical predictions had to be scaled down by a factor of 5.4 to achieve the fit of Figure IV-C-1. However, a good fit to the spectral and relative polarization strength data was again achieved. The highest gain measured was $0.21 \text{ cm}^{-1}$ for perpendicular relative polarization. The pump parameter, $\beta_1 \tau$, varied from 0.06 to 0.75 for the $M$ levels of $K=1$ to 0.44 to 5.2 for the $M$ levels of $K=7$ while $\delta_p \tau$ varied from 0.29 for $K=1$ to -14 for $K=7$.

Figure IV-C-2 shows the small signal gain for the perpendicular relative polarization at 500 kW/cm$^2$ pump power and 1 Torr pressure. The signal to noise ratio made the measurement of small signal gain for the parallel polarization impossible. The highest gain measured for this set of parameters was $0.09 \text{ cm}^{-1}$. The theoretical curve had to be scaled down again by a factor of 5.4. This is rather puzzling since we would have expected, based on the model of filling up upper vibrational state, that at lower pressure the ratio of our theoretical predictions to the measured values would go down. Here we find that approximately the same scale factor gives us a good fit to both the 5 Torr and 1 Torr data. We have no explanation for this phenomenon at this time.

Figure IV-C-3 shows the saturation data we obtained at 1 Torr pressure, 500 kW/cm$^2$ pump power, and perpendicular
FIGURE IV-C-2 -- CH$_3$F - small signal gain.

1 Torr, 500 kW/cm$^2$ pump power.

$\times$ - experimental

Continuous line - theory scaled down vertically by a factor of 5.4.
FIGURE IV-C-3 -- CH₃F - saturation behavior.
1 Torr, 500 kW/cm² pump power, perpendicular polarization.

\( I_{\text{max}} \) is between 6 and 12 watts/cm².
Data fitted with saturation intensity equal to 1.6 \( I_{\text{max}} \).
relative polarization. The data was taken at a frequency of \(-50\text{ MHz}\), i.e., somewhere in between \(K=1\) and \(K=2\) line center frequencies. This data seems to follow a curve given by \(I_{fs} = 1.6 I_{\text{max}}\), where \(I_{\text{max}}\) was the maximum available FIR power and was measured to be between 6 and 12 watts/cm\(^2\). This uncertainty was again due to detector calibration. In reality we did not expect the data to follow the typical saturation curve

\[
\lambda = \lambda_0 \frac{1}{1 + \frac{1}{I_{fs}}}
\]

since the gain curve in this region is a combination of contributions from line centers and Raman components of \(K=1\) to \(K=3\). Numerical analysis shows that the gain will saturate, i.e. reach \(1/2\) of its small signal value, at \(-12.5\) watts/cm\(^2\) FIR intensity at 1 Torr and this agrees well with our measured limits of

\[
10 \leq I_{fs} \leq 20 \text{ W/cm}^2
\]

at 1 Torr.

The FIR cavity operating with CH\(_3\)F exhibited certain similar features to the ones observed when it was operated with D\(_2\)O. Figure IV-C-4 shows the cavity output versus frequency calibrated cavity length for 1 Torr pressure. The average pump power was estimated to be 200 kW/cm\(^2\) when the diffraction by the mesh mirror was taken into
FIGURE IV-C-4 -- CH$_3$F - cavity output versus frequency.

1 Torr pressure.
account. The FIR power inside the cavity was estimated to be ~100 W/cm². -290 MHz point is the approximate position of the Raman peak of K=3 level. Figure IV-C-4 should be compared with Figure IV-C-5 which shows the results of numerical modeling, using the theory developed in previous chapters, applied to the conditions stated above, i.e. 1 Torr pressure, 200 kW/cm² pump power, 100 W/cm² FIR power, and perpendicular relative polarization. The similarity between the spectral shape of the cavity output and the spectral shape of the theoretical gain is quite striking. In Figure IV-C-5 the highest peak is due to a combination of contributions from the line centers and Raman components of the K=1 and K=2 levels plus the line center contribution of K=3 level. The sharper, slightly lower peak around -300 MHz is due to the Raman component of the K=3 level.

For most of our measurements the cavity was operated at 6 Torr pressure. At that pressure the output amplitude and tuning range were optimized. The output versus frequency looked similar to that shown, for D₂O, in Figure IV-B-6, except that the tuning range was somewhat smaller.

When the cavity output was monitored with a Schottky diode detector, Figure IV-C-6, it was found that it was essentially single mode, Figure IV-C-6(a), at all cavity
FIGURE IV-C-5 -- CH₃F - theoretical gain spectrum for conditions similar to those encountered inside the FIR cavity at 1 Torr pressure, 200 kw/cm² pump power, 100 w/cm² FIR power, perpendicular relative polarization. Horizontal scale: -3000 MHz to 1000 MHz.
FIGURE IV-C-6 -- CH$_3$F -- time resolved cavity output.
positions which produced reasonable output power levels. When the CO$_2$ pump contained more than one frequency component, the FIR cavity, like for D$_2$O, followed the intensity of the pump beam, Figure IV-C-6(b).

Figure IV-C-7 shows the output of our scanning Fabry-Perot interferometer for two cavity settings, one, near the optimum cavity output setting, at $\sim -175$ MHz from our reference point of the line center of K=0 level, the other at $\sim -360$ MHz. This Figure is similar to Figure IV-B-9 for D$_2$O in that even though the Schottky diode pictures show lack of temporal structure in the FIR beam for both cavity settings, Fabry-Perot scan indicates that there are many more frequencies present for the cavity setting at $-360$ MHz. The peaks in Figure IV-C-7(a) are narrower than the corresponding peaks in Figure IV-B-9(b) which we believe to be due to a smaller contribution from the instrumental width of the Fabry-Perot. Its 300 l.p.i. mesh mirrors had 80% reflectivity at 385 $\mu$m and 88% at 496 $\mu$m.

Again, as for D$_2$O, we did not observe, in any of the Fabry-Perot scans, any signs of refilling or cascade transitions and so the three-level theory is expected to apply here as well.

The tuning characteristics of the cavity run with CH$_3$F,
FIGURE IV-C-7 -- CH$_3$F - Cavity output analyzed by a scanning Fabry-Perot interferometer.  
(a) frequency ~ -175 MHz from K=0;  (b) frequency ~ -360 MHz from K=0.
Figure IV-C-8, were again similar to those for D$_2$O. For CH$_3$F we find again

\[ \frac{\Delta \nu_{1/2}}{\Delta \nu} \approx \frac{3}{4} \quad (4-C-3) \]

which with $\Delta \nu = 240$ MHz and $R = 0.95$ gives a 32% loss per pass. This is lower than the 46% loss per pass found for D$_2$O and opposite of what we would expect. Diffraction losses associated with a longer wavelength, CH$_3$F, should be larger than those associated with a shorter wavelength, D$_2$O. This might mean that equation 4-B-5 does not hold very well for high lossy cavities with complicated gain spectrum. This may be due to the fact that the Kramers-Kronig relations do not hold for systems under saturation$^{47}$ and therefore we cannot use them to derive $\chi'$ from $\chi''$ under those conditions.

As a last point we would like to mention that a \( \sim 0.1 \text{ cm}^{-1} \) small signal gain in CH$_3$F, was measured by Semet et al.$^{81}$ under the conditions of very strong, power unspecified, multimode pumping at 4 Torr pressure and at some unspecified but optimized frequency. This would tend to indicate that no large systematic errors were made in our measurements which would lead to much lower measured small signal gain values, their maximum gain value being one-half of the one we measured. This indicates to us that some strong loss mechanism, not included in our theoretical model, is responsible for the large ratio of the predicted to measured small signal gain.
FIGURE IV-C-8 -- CH$_3$F - cavity tuning curve. 6 Torr pressure. The 45° broken line is drawn for reference through a point corresponding to the strongest output (-175 MHz on vertical scale).
V. CONCLUSION

This thesis contains the first comprehensive theoretical and experimental study of the basic properties of the homogeneously broadened infrared laser pumped submillimeter laser.

In the theoretical section the density matrix treatment has been extended to include explicitly the space degeneracy of the molecular states, as expressed by the magnetic quantum number M. With this extension a complete theory for predicting gain of the laser pumped submillimeter lasers has been obtained. It can be used to predict performance of SMM laser oscillators and amplifiers at all power levels. It will be therefore useful in the design of practical SMM laser systems of current interest for various applications. The general polarization rules, derived in this thesis, are valid not only for the submillimeter lasers but also for any three level system interacting with two coherent fields and thus can be used for two photon absorption studies and for the new optically pumped near infrared lasers of interest for isotope separation and other applications. These rules are also valid in the Doppler broadened regime if the pump field is strong enough so that the Rabi frequency exceeds the Doppler width.

The detailed discussion of the laser saturation
behavior, presented here, should help the understanding of the operation of the high SMM power systems.

Experimentally, a set of careful measurements of gain and saturation intensity has been performed for the 385 \( \mu m \) transition in \( \text{D}_2\text{O} \) and the 496 \( \mu m \) transition in \( \text{CH}_3\text{F} \). The experimental data has been compared to the theoretical predictions and very good agreement was found in the spectral behavior of the gain and also in the relative gain amplitudes for the two possible polarizations. The measured saturation intensities were also, within the experimental error, in agreement with the theory. The theory predicted however larger gain than the measured one. This was much more pronounced for \( \text{CH}_3\text{F} \) than for \( \text{D}_2\text{O} \). No explanation is available for this phenomenon at this time.

Suggested extensions of this work would include further tests of the gain spectrum. In particular, the one parameter not varied was the pump frequency. This variation is of practical importance because it can lead to wide tunability in the SMM region through the Raman process emission. It is also of theoretical interest since the density matrix treatment predicts a higher conversion efficiency, pump to SMM photons, for off resonance pumping. This problem is being presently pursued experimentally by Woskoboinikow, et al.\textsuperscript{53}
Two more points, brought up by Professor M. S. Feld, will be worth looking into. Symmetric top molecules have non-zero permanent dipole moment in the space fixed frame of reference and the changes brought into the density matrix treatment by $\mu_{nn} \neq 0$ should be investigated. The other point concerns itself with the relative strength of the M-changing collisions. These are usually weaker than the electric dipole allowed collisions (J-changing) but may not be that much weaker as to be totally neglected. Their influence on gain spectra should also be investigated.
REFERENCES


19. e.g.: see the Journal of the Optical Society of America 67, July 1977, containing some of the papers presented at the Second International Conference and Winter School on Submillimeter Waves and Their Applications, San Juan, Puerto Rico, 6-11 December 1976.


47. For a good discussion of the density matrix formalism see for example Dietrich Marcuse, Engineering Quantum Electrodynamics (Harcourt, Brace and World, Inc., New York, 1970).


BIOGRAPHICAL NOTE

The author was born in Warsaw, Poland, on April 9, 1949. He received his elementary and high school education in Warsaw, Poland. He was graduated, Summa cum Laude, from the University of California at Los Angeles with a Bachelor of Science Degree in Physics in June 1972. He was a co-recipient of the E. Lee Kinsey award for the best academic record in mathematics and physics courses. He was also made a member of the Phi Beta Kappa Society.

The author was invited to pursue his graduate education at the Massachusetts Institute of Technology as the Physics Department's Karl T. Compton Predoctoral Fellow. His research work there concentrated on the development of high power, spectrally pure laser pumped submillimeter lasers for plasma diagnostics and then on the investigation of single and two photon effects and their influence on the gain spectra and saturation behavior in those lasers.

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PUBLICATIONS


MEETING SPEECHES (INVITED TALK)


OTHER MEETING SPEECHES


