QUANTUM BEAT SPECTROSCOPY OF ACETYLENE

by

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ABSTRACT

The excited singlet state S_1 of acetylene is embedded in a dense manifold of vibrational triplet levels T_1. An applied magnetic field causes the S_1 and T_1 levels to tune relative to one another. Using a pulsed laser, closely spaced S_1 and T_1 levels are coherently excited in the 225nm region, resulting in anticrossings and quantum beats. In this work, it was determined that quantum beats can arise from a polarization effect, as well as arising from anticrossings. From the polarization quantum beats, a g value of ~0.05 was calculated for the excited singlet.

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INTRODUCTION

The technique of quantum beat spectroscopy is used to study acetylene (C_2H_2) in highly excited vibrational states. Much work has already been performed on this subject [1]. The following project constitutes part of ongoing studies of acetylene, and is primarily concerned with the effects of excitation polarization on the quantum beats.

When two uncoupled levels (i.e. matrix elements between the states are zero) of an excited molecule are tuned to the same energy, a level crossing occurs. If there is a coupling between the two states, then at nearly degenerate energy levels, these states will repel each other. This is known as an anticrossing; it results in the production of quantum beats, an oscillatory variation in the fluorescence.

In acetylene, the excited singlet S_1 is coupled to a dense manifold of vibrational triplet levels T_1. The T_1 states do not fluoresce to the ground state $\tilde{X}$ via the electric dipole transition; hence little is known about them. But by tuning the energy of a T_1 level via an external magnetic field, one can induce the anticrossing effect and study the resulting quantum beats. Thus, anticrossings serve as a window to the vibrational T_1 levels. Furthermore, the high resolution (~0.1 MHz) provided by a pulsed laser enables one to examine regions with a high density of states.

A specific goal of this project is to determine whether quantum beats can result from a polarization effect, in addition to arising from singlet-triplet anticrossings. Moreover, it is necessary to provide a framework for distinguishing the polarization beats from anticrossing beats. Finally, the effects of incident polarization on the excited levels is studied.

THEORY

Acetylene

The ground electronic state S_0 ($\tilde{X}\ ^1\Sigma_g^+$) of acetylene is linear and belongs to the point group $D_{\infty h}$. In this experiment we excite to v_3' of the first excited singlet S_1, which corresponds to the $\tilde{A}\ ^1A_u$ state. It is trans-bent planar and belongs to the C_{2h} point group. See Figure 1 for bond lengths and angles [1]. The two lowest triplet levels T_1 and T_2 lie at energies between S_0 and S_1. We tune a level of T_1 with a magnetic field to the energy of an S_1 level to produce the anticrossings and quantum beats. Figure 2 shows a diagram of the various geometries of the two lowest singlet and triplet surfaces, and their approximate electronic energies [3].

The rotational structure of the $\tilde{A}$ state is that of a near-symmetric prolate top. The electronic transition moment is perpendicular to the plane of the trans-bent molecule and leads to a selection rule of $\Delta K = \pm 1$ [1]. In the $\tilde{X}$ state, $K = \ell''$ and in the $\tilde{A}$ state $K = K_a'$; ℓ is the vibrational total angular momentum quantum number and K_a is the component of K along the principal inertial a-axis. The parity under inversion of the total wavefunction is also a good quantum number and must change sign with an electric dipole transition.

Anticrossings

Consider two closely spaced levels $|a\rangle$ and $|b\rangle$ that are eigenstates of the Hamiltonian H. Let W denote a general symmetry operator that commutes with H so that $[W,H]=0$. This symmetry refers to total parity, vibrational and nuclear permutation symmetries, etc. Then,

$$\langle a|[W,H]|b\rangle = 0.$$

Expanding the expression :

$$\langle a|WH - HW|b\rangle = 0$$

$$\langle a|H|b\rangle w_a - \langle a|H|b\rangle w_b = 0$$

$$\langle a|H|b\rangle(w_a - w_b) = 0$$

Solution 1: $\langle a|H|b\rangle=0$, $w_a \neq w_b$

If $w_a \neq w_b$, the levels are of different symmetry. Since $\langle a|H|b\rangle=0$, there is no coupling between the two states. If one level is tuned in energy (via a magnetic field, for example) with the other level, a level crossing occurs. At the point of crossing, the levels are degenerate with energy $E_a = E_b$.

Solution 2: $\langle a|H|b\rangle \neq 0$, $w_a = w_b$

If $w_a = w_b$, the levels are of the same symmetry. Since $\langle a|H|b\rangle \neq 0$, there will be an off-diagonal matrix element V coupling the states $|a\rangle$ and $|b\rangle$. Then,

$$H = H^o + H'$$

$$= \begin{bmatrix} E_a & 0 \\ 0 & E_b \end{bmatrix} + \begin{bmatrix} 0 & V \\ V & 0 \end{bmatrix}$$

$$= \begin{bmatrix} E_a & V \\ V & E_b \end{bmatrix}$$

The eigenvalues of the complete Hamiltonian are no longer E_a and E_b, and the new eigenstates $|1\rangle$ and $|2\rangle$ are different from the zero order states $|a\rangle$ and $|b\rangle$. When tuned to near degeneracy, the levels will be prevented from crossing by the presence of the perturbation V, and instead will repel one another. This is the phenomenon of anticrossing. It was first observed experimentally by Eck et. al. in 1963 [6].

At the region near the anticrossing, the wavefunctions $|1\rangle$ and $|2\rangle$ are described by a superposition of the states $|a\rangle$ and $|b\rangle$:

$$|1\rangle = \alpha|a\rangle + \beta|b\rangle$$

$$|2\rangle = -\beta|a\rangle + \alpha|b\rangle$$

$$\text{where } \alpha^2 + \beta^2 = 1$$

At the center of the anticrossing, there is an equal superposition of the states $|a\rangle$ and $|b\rangle$. Far from the anticrossing, the levels are virtually unaffected by the perturbation (since the energy separation $E_a - E_b$ becomes much greater than V) and can be described by the original basis states $|a\rangle$ and $|b\rangle$. Far from the anticrossings the levels must also be unaffected by the occurrence of the anticrossing (and must behave the same whether a level crossing or an anticrossing occurred).

As found above, the two levels must be of the same symmetry in order for the anticrossing to occur. For the Zeeman effect, M_J provides a good symmetry label since the Hamiltonian is invariant under rotation about the magnetic field axis. Therefore, we conclude that $\Delta M_J=0$ must be satisfied for an anticrossing to occur. This selection rule is valid for all field strengths, since M_J remains a good quantum number at all fields.

Quantum Beats

If two nondegenerate states are coherently excited, and if both states have non-zero transition probabilities to a common final state, then the emitted radiation is modulated. This modulation is known as quantum beats.

Consider the zero-order basis states of the singlet and triplet in acetylene, $|S\rangle$ and $|T\rangle$. It is insignificant whether the two levels are closely spaced by chance, or were brought together by tuning a magnetic field. For levels of the same symmetry ($\Delta M_J=0$), the eigenstates of the complete Hamiltonian H are :

$$|1\rangle = a|S\rangle + b|T\rangle$$

$$|2\rangle = -b|S\rangle + a|T\rangle$$

where $a^2 + b^2 = 1$

See Figure 3. The corresponding eigenenergies E_1 and E_2 are :

$$E_{1,2} = \frac{(E_S+E_T) \pm \sqrt{(E_S-E_T)^2 + 4V^2}}{2}$$

If a pulsed laser with a coherence width greater than E_1-E_2 coherently excites these two eigenstates from S_0, the wavefunction of the excited states at t=0 is:

$$\psi(0) = a|1\rangle - b|2\rangle$$

The excited state $\psi(0)$ is not an eigenstate of the Hamiltonian. Because of spontaneous decay to a level $|X\rangle$ of the ground singlet state $\tilde{X}$, the wavefunction evolves in time according to :

$$\psi(t) = e^{-\gamma_1 t/2}\, a|1\rangle e^{-iE_1 t/\hbar} - e^{-\gamma_2 t/2}\, b|2\rangle e^{-iE_2 t/\hbar}$$

where γ_i = the decay constant of the states $|1\rangle$, $|2\rangle$.

The fluorescence intensity is given by :

$$I(t) = |\langle X|\mu|\psi(t)\rangle|^2$$

where μ = electric dipole operator.

Since the triplet has negligible oscillator strength to the ground singlet state, assume that $|\langle X|\mu|T\rangle|=0$.

$$I(t) = \left|a e^{-\gamma_1 t/2} \langle X|\mu|1\rangle e^{-iE_1 t/\hbar} - b e^{-\gamma_2 t/2} \langle X|\mu|2\rangle e^{-iE_2 t/\hbar}\right|^2$$

$$= \left|a^2 e^{-\gamma_1 t/2} \langle X|\mu|S\rangle e^{-iE_1 t/\hbar} + b^2 e^{-\gamma_2 t/2} \langle X|\mu|S\rangle e^{-iE_2 t/\hbar}\right|^2$$

$$I(t) = \mu^2_{xs} \left|a^4 e^{-\gamma_1 t} + b^4 e^{-\gamma_2 t} + 2a^2 b^2 e^{-(\gamma_1+\gamma_2)t/2} \cos(\Delta E\ t/\hbar)\right|$$

where $\mu^2_{xs} = \langle X|\mu|S\rangle$ and $\Delta E = |E_1 - E_2|$

Note that the interference between $|1\rangle$ and $|2\rangle$ causes an averaging of their lifetimes, as seen in the exponential factor of the oscillatory term above. At the center of the anticrossing, $a=b=1/\sqrt{2}$, $\gamma_1=\gamma_2=\gamma$, and the fluorescence consists of an oscillation superimposed on an exponential decay :

$$I(t) = \frac{1}{2}\mu^2_{xs} e^{-\gamma t} \left[1 + \cos(\Delta E\ t/\hbar)\right]$$

We emphasize that the levels $|1\rangle$ and $|2\rangle$ must be prepared coherently. The transitions $|1\rangle \rightarrow |X\rangle$ and $|2\rangle \rightarrow |X\rangle$ are thus not distinguishable. This leads to interference between the quantum amplitudes of $|1\rangle$ and $|2\rangle$ and results in the quantum beat pattern. This is an example of the general principle in quantum mechanics that, for indistinguishable processes, individual amplitudes add, not individual probabilities. Hence, the quantum beat phenomenon is analogous to Young's double slit interference experiment.

The previous equation for eigenenergies dealt with static basis levels. Now consider what occurs when a triplet basis state |T> is tuned across a stationary singlet basis state |S> by the application of a magnetic field B. From previous studies of acetylene it was found that the field strengths in this experiment (up to 2.5 kGauss) are insufficient to decouple the rotational angular momentum R̲ from the electronic spin S̲ [1]. Thus, the Zeeman energy shift is described by the "weak-field" case. The energy of |T> then is:

$$\begin{aligned} E'_T &= E_T + g_T \mu_B B M_J \\ &= E_S + g_T \mu_B (B-B_o) M_J \qquad (2) \end{aligned}$$

where :

g_T = Lande g factor of the triplet

μ_B = Bohr magneton (1.4 MHz/Gauss)

B_o = magnetic field at center of anticrossing

and :

$$g_T = \frac{3J(J+1) + S(S+1) - R(R+1)}{2J(J+1)}$$

Substituting equation (2) into (1) yields :

$$(3) \quad E_{1,2} = \frac{E_S + g_T \mu_B (B-B_o) \pm \sqrt{g_T^2 \mu_B^2 (B-B_o)^2 + 4V^2}}{2}$$

The beat frequency ν is :

$$\nu = \frac{E_1 - E_2}{h} \qquad (4)$$

Combining (3) and (4) yields :

$$\nu^2 = \frac{g_T^2 \mu_B^2 B^2 (B-B_o)^2 + 4V^2}{h^2}$$

which has the functional form of a hyperbola for ν vs. B.

Polarization Quantum Beats

Consider an R(0) transition [$J=1 \leftarrow J=0$] with excitation polarized parallel (π) to the magnetic field axis. Only the $M=0$ Zeeman component is populated, and the anticrossing occurs between $M=0$ of the singlet and $M=0$ of the triplet, producing $\Delta M=0$ quantum beats (all values of M refer to M_J). If however, R(0) is excited with light polarized perpendicular to the field, the $M=1$ and $M=-1$ substates are prepared coherently. The anticrossing can occur between $M=1$ of the singlet and $M=1$ of the triplet. Because of the $\Delta M=0$ selection rule for anticrossings, the $M=-1$ of the singlet cannot participate in the anticrossing. However, it will be coherently excited at an energy between that of the two $M=1$ levels (see Figure 4). Since quantum beats can occur if levels are coherently excited, the $M=-1$ level of the singlet will beat with both $M=1$ levels, producing two $\Delta M=2$ beats. These $\Delta M=2$ beats are what we call the polarization quantum beats. They should appear in the fluorescence along with the $\Delta M=0$ anticrossing beat if both π and σ fluorescence is detected (as was done in this experiment).

We now consider a quantitative discussion of the polarization beats, using the simplest case of the R(0) transition, with σ polarization. From Figure 4, let the eigenstates $|1\rangle$, $|2\rangle$, and $|3\rangle$ be represented by :

$$|1\rangle = a|S_1\rangle + c|T\rangle$$

$$|2\rangle = |S_{-1}\rangle$$

$$|3\rangle = -c|S_1\rangle + a|T\rangle$$

where: $a^2 + c^2 = 1$

Here, the subscripts on S refer to the M value of that state. Since $|2\rangle$ does not participate in the anticrossing, there is no mixing of zero-order states, and $|2\rangle$ retains pure singlet character. The wavefunction of the excited state is:

$$\psi(0) = \alpha|1\rangle + \beta|2\rangle + \gamma|3\rangle$$

$$\psi(t) = \alpha|1\rangle e^{-iE_1t/\hbar} + \beta|2\rangle e^{-iE_2t/\hbar} + \gamma|3\rangle e^{-iE_3t/\hbar}$$

where: $\alpha^2 + \beta^2 + \gamma^2 = 1$

We ignore the exponential decay factor of each state to simplify the discussion. α, β, γ represent the the probability amplitude that the light pulse prepared the states $|1\rangle$, $|2\rangle$, $|3\rangle$. To write α, β, γ in terms of a, b, c, we note two facts: The proportion of each eigenstate excited is equal to the proportion of singlet character in each; with σ polarization, half of the probability amplitude goes into the M=+1 level, and the other half into the M=-1 level. Therefore:

$$\alpha^2 = \frac{a^2}{a^2 + c^2} \cdot \frac{1}{2}$$

$$\beta^2 = 1 \cdot \frac{1}{2}$$

$$\gamma^2 = \frac{(-c)^2}{a^2 + c^2} \cdot \frac{1}{2}$$

Since $a^2+c^2=1$, we get:

$$\alpha = \frac{a}{\sqrt{2}}, \quad \beta = \frac{1}{\sqrt{2}}, \quad \gamma = \frac{-c}{\sqrt{2}}$$

Assume that $\langle X|\mu|T\rangle=0$ and that $\langle X|\mu|S_1\rangle=\langle X|\mu|S_{-1}\rangle=\mu_{XS}$. The fluorescence intensity is:

$$I(t) = |\alpha\langle X|\mu|1\rangle e^{-iE_1t/\hbar} + \beta\langle X|\mu|2\rangle e^{-iE_2t/\hbar} + \gamma\langle X|\mu|3\rangle e^{-iE_3t/\hbar}|^2$$

$$= |\frac{a}{\sqrt{2}}\langle X|u|S_1\rangle e^{-iE_1t/\hbar} + \frac{1}{\sqrt{2}}\langle X|\mu|S_{-1}\rangle e^{-iE_2t/\hbar} + \frac{c}{\sqrt{2}}\langle X|\mu|S_1\rangle e^{-iE_3t/\hbar}|^2$$

$$= \mu_{xs}^2\{\frac{a^4}{2}+\frac{c^4}{2}+\frac{1}{2}+a^2\underbrace{\cos[(E_1-E_2)\frac{t}{\hbar}]}_{\Delta M=2} + c^2\underbrace{\cos[(E_2-E_3)\frac{t}{\hbar}]}_{\Delta M=2} + a^2c^2\underbrace{\cos[(E_1-E_3)\frac{t}{\hbar}]}_{\Delta M=0}\}$$

Each term has its own exponential decay factor which has been ignored. Since a<1 and c<1, the amplitude of the ΔM=0 beats is always greater than that of the ΔM=0 beat (at a given magnetic field). Also, since the ΔM=2 beat involves the state |2> of pure singlet character, the lifetime of these beats is shorter than that of the ΔM=0 beat. This is explained by the following: The fluorescence lifetime of the |T> basis state is much longer than that of |S>. When mixing occurs, there will be an increase in the lifetime as |T> character is mixed into a predominantly |S> level. Levels |1> and |3> both have the triplet character that translates into longer lifetime for the ΔM=0 beat between those two levels. Note also that we always have the sum of two frequencies equaling a third.

At the center of the anticrossing $a=c=1/\sqrt{2}$, and $(E_1-E_2)=(E_2-E_3)$

$$I(t) = \mu_{xs}^2\ [\frac{3}{4} + \cos[(E_1-E_2)\frac{t}{\hbar}] + \frac{1}{4}\cos[2(E_1-E_2)\frac{t}{\hbar}]$$

The two previous ΔM=2 beats combine to form a single beat at the center of the anticrossing. The ΔM=2 beat now has half the frequency and four times the amplitude of the ΔM=0 beat. To find the relative lifetimes note that $\gamma_1=\gamma_3=\gamma_2/2$, where γ_i

are the decay constants of states $|i\rangle$. The lifetime is inversely proportional to the decay rate. This yields the result that the lifetime of the $\Delta M=2$ beat is two-thirds that of the $\Delta M=0$ beat.

We proceed to determine qualitatively the expected shape of the ν vs. B curve when both $\Delta M=2$ and $\Delta M=0$ beats are present. From Figure 5 note that the $\Delta M=0$ beat will produce a hyperbola as shown previously. In addition, there will be a curve which starts at zero frequency and increases with increasing B, and another curve that starts at a high frequency and decreases to zero. These two curves correspond to the $\Delta M=2$ beats. See Figure 6 for a sketch. In contrast, a three-level anticrossing (i.e. three levels with identical M values) results in three hyperbolas. Thus, the shape of a ν vs. B curve provides one way to distinguish the case with polarization beats from that containing only anticrossing beats. The expected relative amplitudes and lifetimes provide additional criteria.

DISCUSSION and RESULTS

Procedure

We chose to excite to the $v_3'=2$, $K_a'=1$ vibrational level. The density of anticrossings per Gauss increases significantly with higher v_3', leading to greater complexity [1]. It was not possible to excite to $v_3'=1$ or $v_3'=0$ with the current apparatus. In addition, we restricted the experiment to low J values (namely J'=1) to keep the analysis as straightforward as possible.

Figure 6 shows the M levels that are populated with π or σ polarized excitation for the R(0), Q(1), and P(2) lines. For σ polarization the solid lines indicate the Zeeman substates that are coherently prepared. The dashed lines represent incoherent population; these do not concern us since they cannot produce quantum beats. To locate a two-level anticrossing (either both M=1 or both M=-1) we consider two approaches.

The first approach involves studying Q(1) quantum beats. We first locate a Q(1)π beat of single frequency, as seen on the transient digitizer. This corresponds to an anticrossing between two levels, both of which have M=1 or M=-1 ($\Delta J=0$, $M=0\to0$ interactions are forbidden for the Zeeman Hamiltonian). If we now switch to Q(1)σ, both M=1 and M=-1 should be excited coherently and we should see two additional beats that correspond to $\Delta M=2$. The purpose of this approach is to avoid the multiple level anticrossings and thus be able to detect $\Delta M=2$ beats easily. Unfortunately, no clear single frequency Q(1)π beats were found in a region up to 5000 Gauss. This was probably due to a high density of states cluttering the region.

It was then decided to study R(0) quantum beats and use P(2) for comparison. We first tune the magnetic field to a P(2)π single frequency beat. This corresponds to a two-level anticrossing in which both levels have M=1, or M=0, or M=-1. The M=1 or M=-1 anticrossing is necessary for observing ΔM=2 beats. To determine which case is present, we switch to R(0)π. If the anticrossing is between M=1 or M=-1, R(0)π should exhibit no quantum beats, since only the the M=0 level is populated in R(0)π. Once the appropriate case is found, we can switch to R(0)σ and record data at several field strengths to search for ΔM=0 beats. Several two-level anticrossings were found with this approach. We could not switch from R(0)π to R(0)σ directly because no diagnostic for locating a M=1 or M=-1 anticrossing would then be provided. The only anticrossing observed with R(0)π excitation involves M=0 whereas we are interested in M=±1 levels. Since the M levels of the triplet are presumed to be non-degenerate (because they should have significant g values) the center of the R(0)π anticrossing would not correspond to that of a related R(0)σ anticrossing. Once we tune the magnetic field, other triplet levels may be tuned into resonance and we have defeated the purpose of trying to locate a two-level anticrossing between M=1 or M=-1 |S> and |T> levels. We also could not use Q(1) as a comparison for R(0); Q and R transitions populate different J=1 levels, corresponding to levels of opposite parity.

It was presumed previous to this work that the M levels of the singlet are degenerate and do not tune with the magnetic field, owing to a negligible g value. However, to test this, R(0) was examined at low fields to determine whether the singlet splits and produces quantum beats among its own M substates. This in fact was observed and led to interesting results.

Data Analysis

In order to determine the quantum beat frequencies, a simple exponential decay was fitted to and subsequently subtracted from the fluorescence trace. The result was Fourier transformed to yield the approximate component frequencies. Using these as starting values the trace was fit to :

$$I(t) = Ae^{-\Gamma t} + \sum_{i} a_i e^{-\gamma_i t} \cos(2\pi\nu_i t+\phi_i)$$

The index i corresponds to a sum over the frequencies present. The fits were done using a a non-linear least squares algorithm. There was an unresolved problem fitting the decay constants. In some cases these decay constants changed markedly depending on the starting position of the fit, and thus the accuracy for this parameter was less than ideal. Some unexplained background variation may have been present. In any case, the frequencies were well determined by the fit and were accurate to within ±0.1 MHz.

Results

The most interesting observation was that of a single frequency quantum beat at low magnetic fields with R(0)σ (Figure 7 shows such a case). We conclude for the following reasons that this demonstrates a singlet level splitting into its Zeeman substates, thereby producing the beat between M=1 and M=-1 of the singlet:

1) If an anticrossing were occurring with a triplet state and a degenerate singlet, there must be a minimum of three frequencies present (with σ polarization).
2) The ν vs. B curve is quite linear, while an anticrossing produces a hyperbola.
3) Neither R(0)π nor P(2)π exhibited beats in the same range of the magnetic field.
4) The observed beats were present over a broad range in the field (300 Gauss). Beats from anticrossings are typically present for only 50 to 100 Gauss since the triplet, with its relatively large g value, tunes faster with the field than does a singlet.

Thus, the quantum beats detected are concluded to be $\Delta M=2$ polarization beats. This Zeeman splitting of the singlet enables us to calculate its g value using a linear least-squares fit of the equation:

$$\Delta E = (g\mu_B \Delta M)B$$

where the slope $= g\mu_B(\Delta M) = 2g\mu_B$

The data points were weighted equally with no constraints. The plot is given is Figure 8. The fitted line did not go through the origin. This was probably due to inaccurate zeroing of the magnet caused by extreme sensitivity of the gaussmeter probe to its exact orientation. But the slope is the relevant parameter, yielding a g value of:

$$g_{|s\rangle} = 0.049 \pm .002$$

The singlet probably acquired its nonzero g value from perturbations by a nearby triplet (presumably, by a second order perturbation interaction with a "remote" perturber). The apparent linearity of the Zeeman splitting implies that the Zeeman tuning of the nearby triplet is small compared to the singlet-triplet splitting and zero field.

Even though the singlet splits at low fields it is not clear that it must remain so at higher fields. Perturbations and anticrossings could cause the g value to change significantly.

At higher fields, with R(0)σ, single frequency beats were found in one case, near B=2500 Gauss. These are presumed to be singlet-triplet anticrossing beats between a singlet M=+1 substate and a triplet substate with the same M value, because the curve is hyperbolic. See Figure 9. This curve is not a complete hyperbola; the beats lose amplitude faster on the high field side. This is probably due to a perturbation from a nearby level. The presence of only one frequency implies that the singlet is non-degenerate here. The M level is not known since σ polarization populates both M=1 and M=-1. An approximate value was calculated for Δg, the difference in g values for the singlet and triplet, by approximating the outer part of the hyperbola as a straight line. This yielded $\Delta g \simeq 0.25 \pm 0.01$

In another case, near B=950 Gauss, two frequencies were detected. See Figure 10. Again, this is presumed due to a $\Delta M=0$ anticrossing (in this case, among three levels). The slope of the outer part of the main hyperbola gave $\Delta g \simeq 0.25 \pm 0.01$. It would seem from Figures 9 and 10 that the singlet remains split at higher fields, at least up to 2500 Gauss.

Summary

Although $\Delta M=2$ beats between a singlet and triplet were not observed, $\Delta M=2$ beats were observed between singlet substates, verifying that σ polarization can produce extra quantum beats. A g value of ~0.05 was calculated for the excited singlet.

Further Suggestions

It would be interesting to discover whether $g=0.05$ is typical for singlet levels in this energy region. By using the appropriate frequency doubling crystal, one can excite to $v_3'=1$ and $v_3'=0$ and study this region.

Circular polarization (σ^+, σ^-) could be used to determine the M_J sublevel of the triplet in an anticrossing, since circular light populates only one M level at a time: $M=+1$ <u>or</u> $M=-1$ (in $J'=1$). It could also unambiguously verify the splitting of the singlet at low fields, since the $R(0)\sigma$ beats should disappear with σ^+ or σ^- polarization. Circular polarization was not readily available with the set-up in this experiment.

EXPERIMENTAL

The experimental apparatus is depicted in Figure 11. A tunable dye laser pumped by a YAG laser was the excitation source. Figure 12 shows a schematic of the excitation and fluorescence directions relative to the magnetic field.

The pulsed, Nd:YAG laser (Molectron MY 34-20) used a third harmonic crystal to mix its fundamental (1064nm) and second harmonic (532nm) components to generate ~30 mJ per pulse of 355nm light. The mixing is a phenomenon of nonlinear optics, where higher order electric field intensities play a significant role. The pulses were 18ns in duration, with a repetition frequency of 20 Hz. The coherence width $\Delta\nu$ of a laser with a Gaussian pulse profile is: $\Delta\nu \approx 1/\Delta T$, where ΔT is the pulse duration. This yields $\Delta\nu = 55$ MHz for the YAG pulse. In reality the YAG pulse is not Gaussian but may be described by a superposition of several 5ns pulses. The resulting coherence width is estimated to be 100 MHz.

The 355nm light pumped a tunable dye laser (Lambda Physik FL-2002E) to give ~3 mJ of tunable light. The oscillator contained 0.13 g of Coumarin 440 dye dissolved in 400 ml of methanol and the amplifier contained the same quantity of dye dissolved in 800 ml of methanol. The grating in the dye laser cavity was used to tune to a wavelength of 450nm. An intracavity etalon was used to obtain nearly monochromatic light and high spectral resolution (bandwidth at FWHM=0.05 cm^{-1}). The emerging beam was directed through a frequency doubling KPB crystal to produce 225nm light (necessary for excitation to the $v_3'=2$ band) with a conversion efficiency of 2 % .

The 225nm and 450nm light were initially collinear, and were separated with a 60° prism. The 450nm light was used to monitor the beam quality. The interference fringes produced by the etalon were projected onto a card, and monitored to keep the grating and etalon modes aligned. The free spectral range of the etalon is 1 cm^{-1} .

The 225nm light was directed through a quarter-wave plate to produce the required parallel or perpendicular polarization. A Wollaston prism was used to determine the polarization. This prism is a birefringent crystal, and passes two beams of orthogonal polarization diverging from each other by ~2° . The birefringence is caused by the optical anisotropy of the material. By rotating the quarter-wave plate appropriately either of the two beams could be made to disappear. The Wollaston was moved out of the way once the polarization was set; otherwise there would have been two different optical paths for the different polarizations. Next, the beam passed through a collimating lens of 0.5m focal length and was directed into the cell.

The cell was made of Pyrex, and quartz windows were glued on with an epoxy (Torr Seal). The windows were positioned at Brewster's angle θ_B to optimize the transmittance of desired polarizations at the input window and to minimize the back reflection from the exit window. The component polarized parallel to the surface is reflected at θ_B, equal to 56° for the air-quartz interface.

The cell was placed between the 12" diameter poles (separated by 9 cm.) of an electromagnet (Harvey Wells) capable of producing a homogeneous field of up to 8.5 kGauss. A digital multimeter was connected to a Gaussmeter (Bell 620) to measure the field strength to a precision of 1 Gauss. However, the Gaussmeter probe was sensitive to its exact orientation and could give a reading of up to 20 Gauss away from the true field strength. This was not a serious problem since the relative values of the magnetic field were more important than absolute ones.

The acetylene was purified with several freeze-thaw cycles using liquid nitrogen. At the liquid N_2 temperature (-196 °C) the acetylene and acetone were frozen, and other impurities (nitrogen etc.) were pumped out. The acetylene was then sublimed at -130 °C using a pentane-liquid N_2 slush. The vapor pressure of acetylene is high enough at -130 °C to fill the cell, while that of acetone is negligible. The cell was evacuated to 0.01 mTorr and then filled with 50 (±5) mTorr of acetylene, as measured with a digital multimeter connected to a Baratron gauge.

A schematic of the optics for collecting fluorescence is shown in Figure 13. The photomultiplier tube (PMT) had to placed 2 meters away to avoid the effects of the magnetic field; therefore it was necessary to use several lenses to image the fluorescence onto the PMT. About a 10mm region of the fluorescence from the cell was imaged onto the PMT. The F/1 imaging system consisted of four lenses: two collimating lenses L1 and L2, a field lens L3, and a final focussing lens L4. The magnification from the collimating lenses to the field lens was about 8; from the field lens to the PMT it was about 1/6. The PMT was usually operated at -1400 volts.

Since acetylene fluoresces mainly in the 230-410 nm region [2], a filter (Schott UG-5) that transmits only in that range was tested. However, its transmission was appreciably less than 100% and the signal was reduced beyond its already weak value. As a result it was decided not to use the filter. Even without the filter, no extraneous visible laser light (450nm) reached the PMT. The only unwanted light was 225nm scatter, but this was compensated for in the curve fits.

For recording a spectrum of acetylene, it was necessary to pressure scan the dye laser with nitrogen because the grating provided only a coarse adjustment. The change in pressure in the laser cavity changes the optical path length (since the refractive index is pressure dependent), thus producing a different wavelength. The signal from the PMT was sent through an amplifier to a boxcar (gated integrator), which was triggered to start integrating counts after the scattered light had decayed. The boxcar integrated 15ns of the signal and sent the output to a chart recorder. Although the lifetime of the fluorescence is several hundred nanoseconds, 15ns provided enough signal to record the various transitions. The resulting spectrum was compared with an existing calibration spectrum.

To record the quantum beats of a specific transition, the laser was set on a line and the magnetic field was tuned to a particular value. The signal from the PMT was sent through the amplifier to a transient digitizer (Tektronix 7912AD). Fluorescence on a 1μs time scale was collected in a trace of 512 bins, yielding a resolution of ~2ns. Data was recorded at 5-10 field strengths per anticrossing. An IBM PC was used to average successive laser shots and record the data. Usually, 512 laser pulses were averaged at each field. The data was transferred to a VAX 11/780 for analysis.

With so many shots averaged, a sufficient number of photons reached the PMT to render random noise negligible. There was instrumental noise present from the digitizer, due to slightly varying sensitivities of the diodes over the entire screen. This contributed a 1% fluctuation in the signal. Scattered 225nm light from the acetylene cell was present, but its lifetime (~20ns) was much shorter than that of the fluorescence (~300ns), and its amplitude was smaller by a factor of 30. To avoid fitting excessive scatter, the fits were usually started after the first 30 nanoseconds of the fluorescence.

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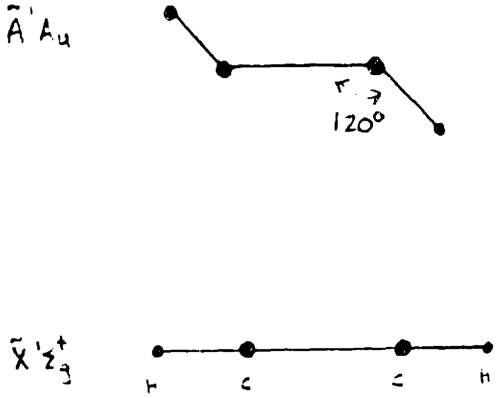
Figure 1 : Bond lengths and angles Ref. (1)



C-C length = 1.38 Å
C-H length = 1.06 Å

C-C length = 1.20 Å
C-H length = 1.06 Å

Figure 2 : Various geometries of C_2H_2 Ref. (3)

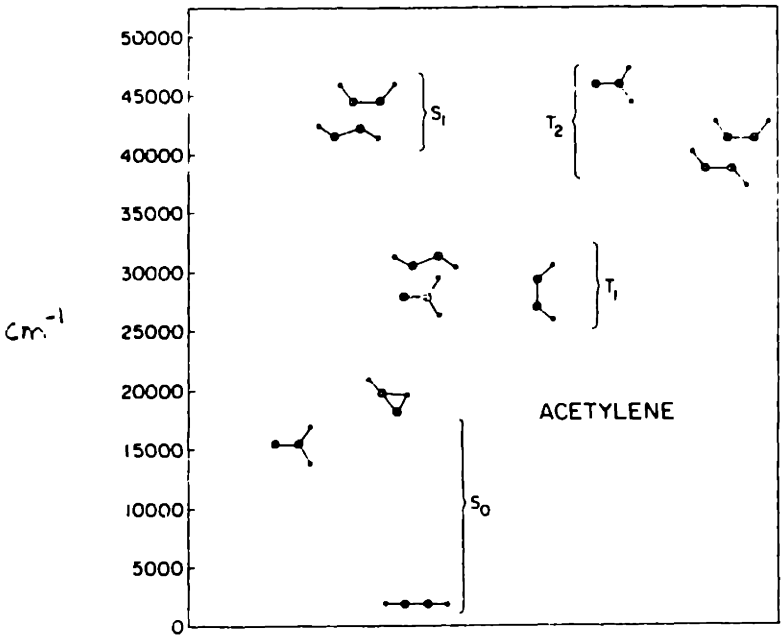


Figure 3 : Simple Anticrossing

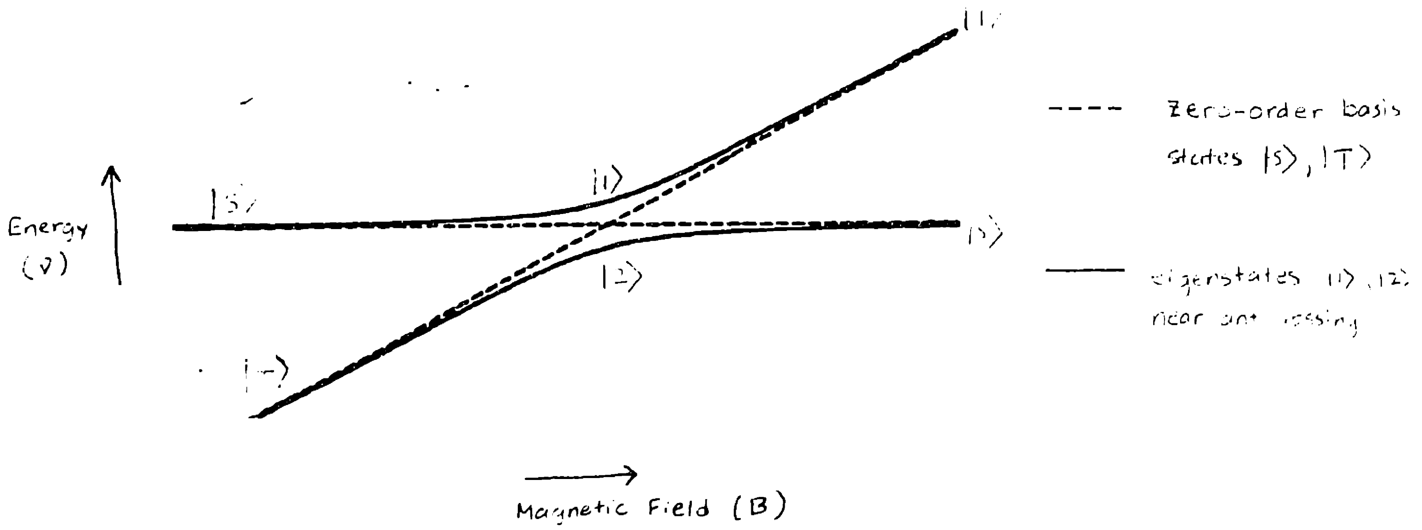


Figure 4

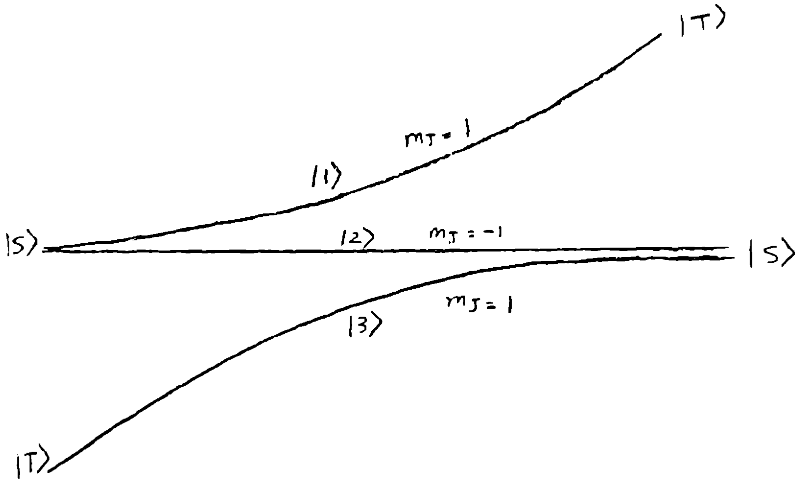


Figure 5

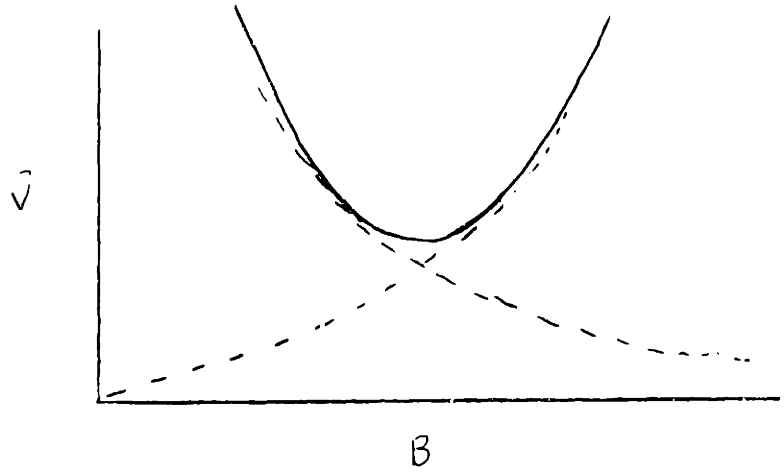


Figure 6

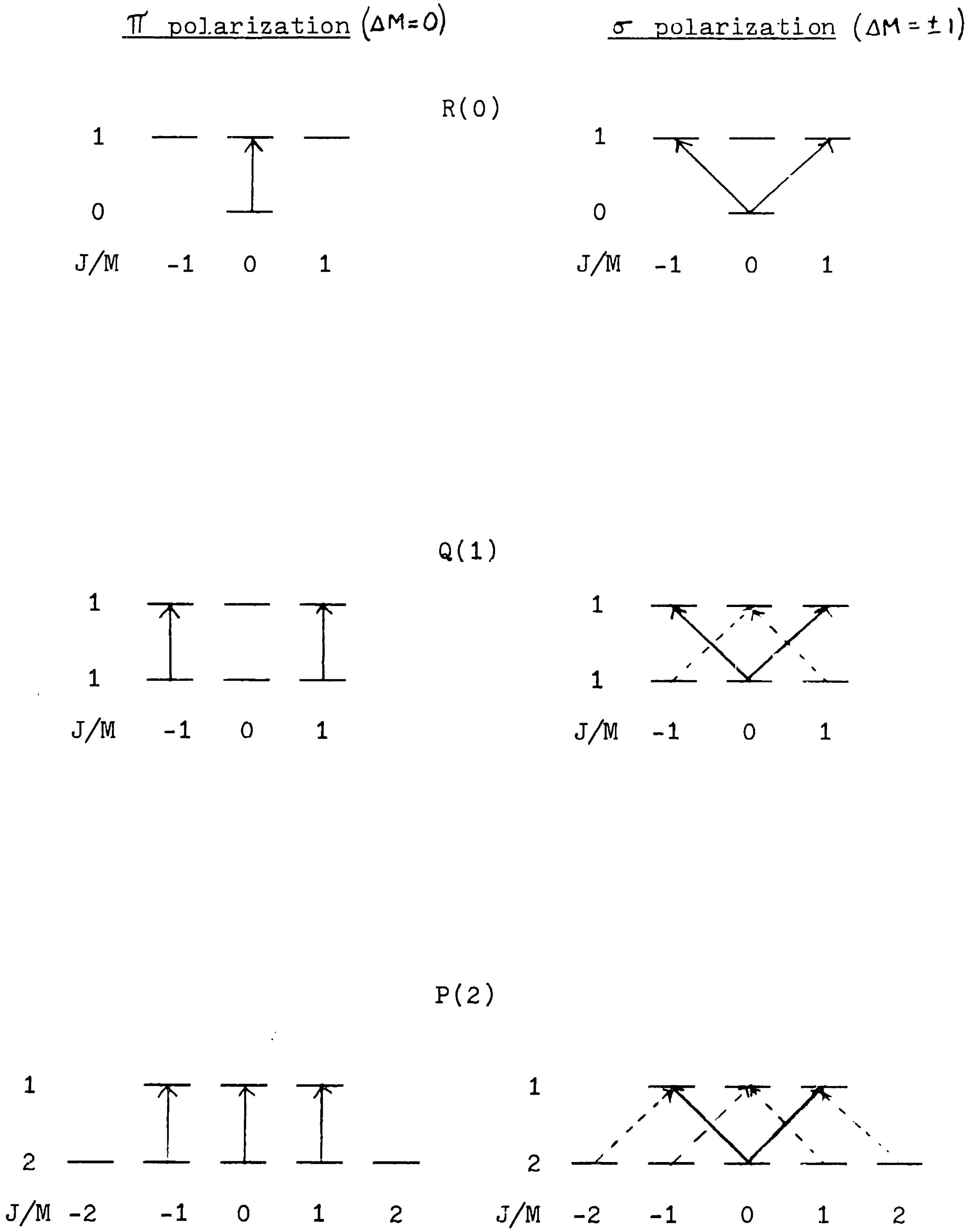

π polarization (ΔM=0)
σ polarization (ΔM=±1)
R(0)
1
0
J/M -1 0 1
1
0
J/M -1 0 1
Q(1)
1
1
J/M -1 0 1
1
1
J/M -1 0 1
P(2)
1
2
J/M -2 -1 0 1 2
1
2
J/M -2 -1 0 1 2

Figure 7 : Singlet - Singlet Quantum Beat

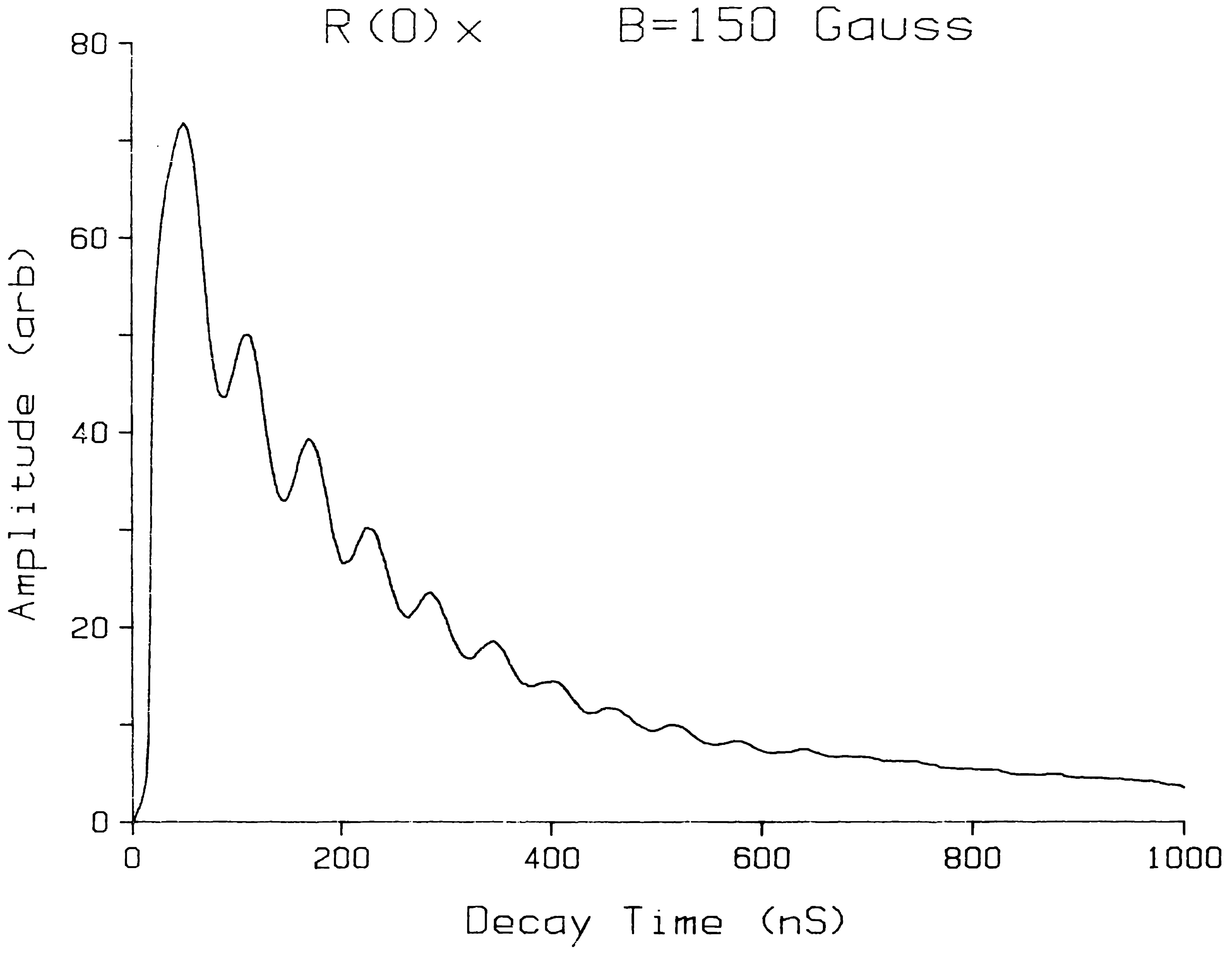


Figure 8 : Zeeman Splitting of Singlet

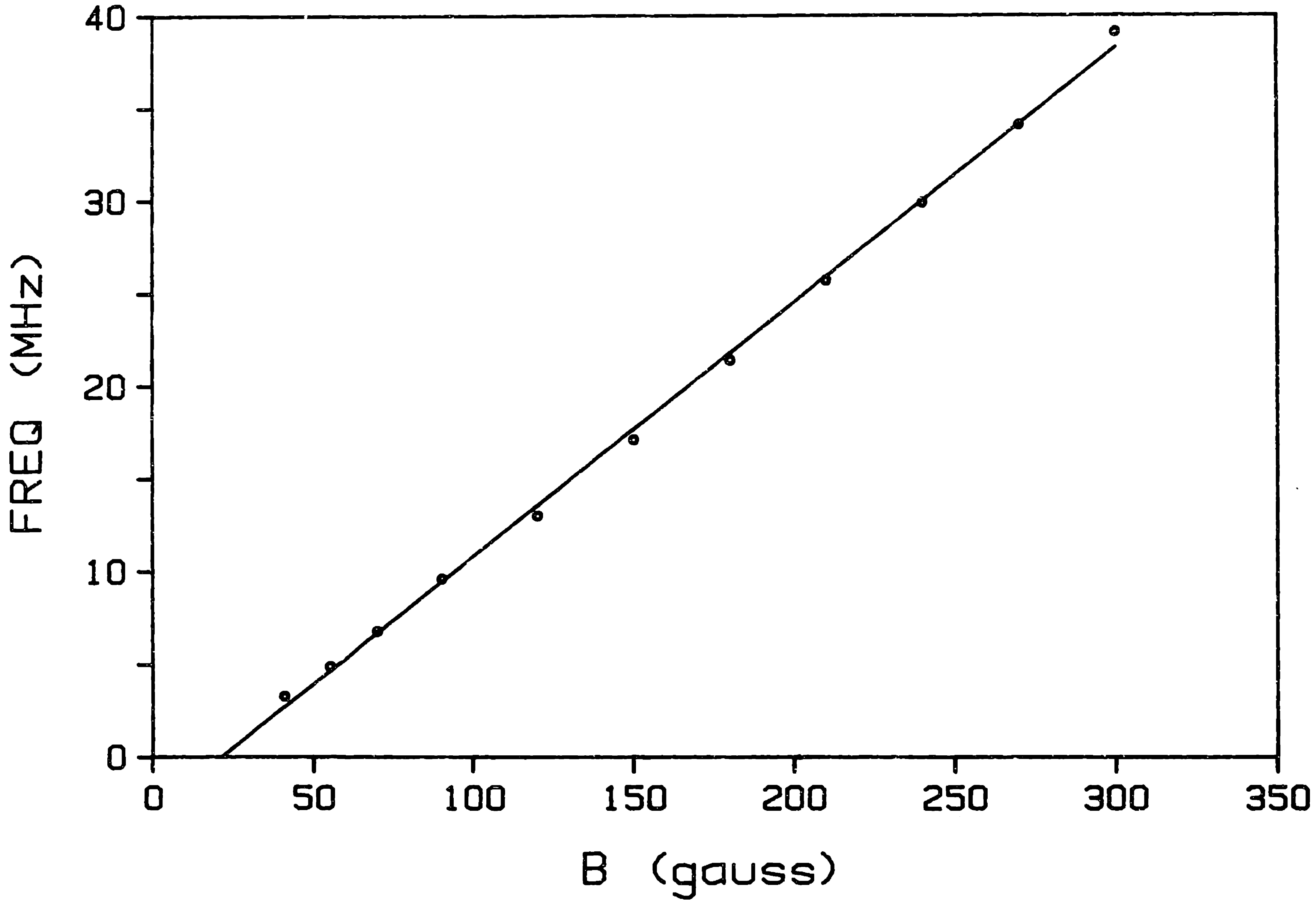


Figure 9: Singlet - Triplet Anticrossing

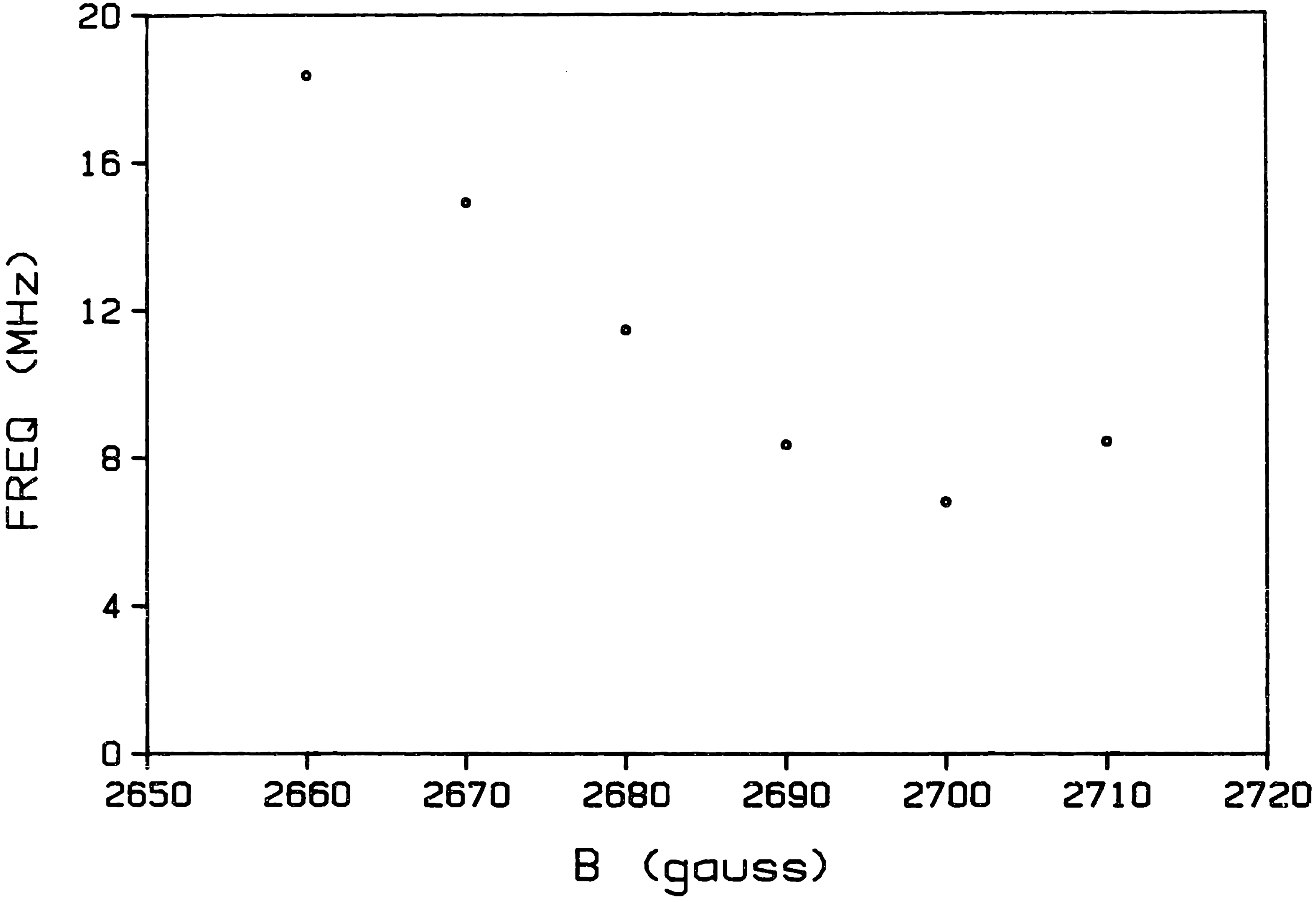


Figure 10 : Singlet - Triplet Anticrossing

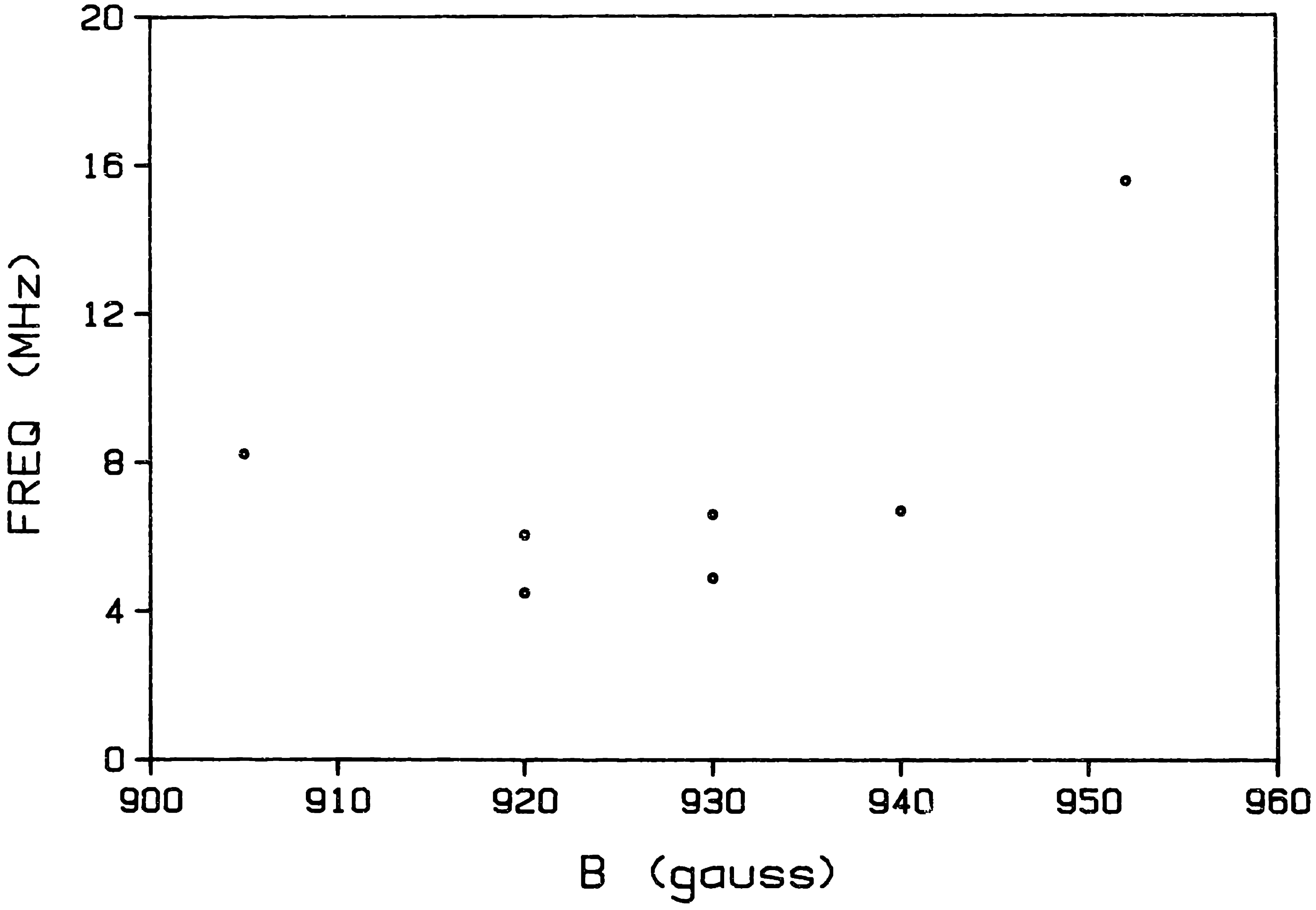
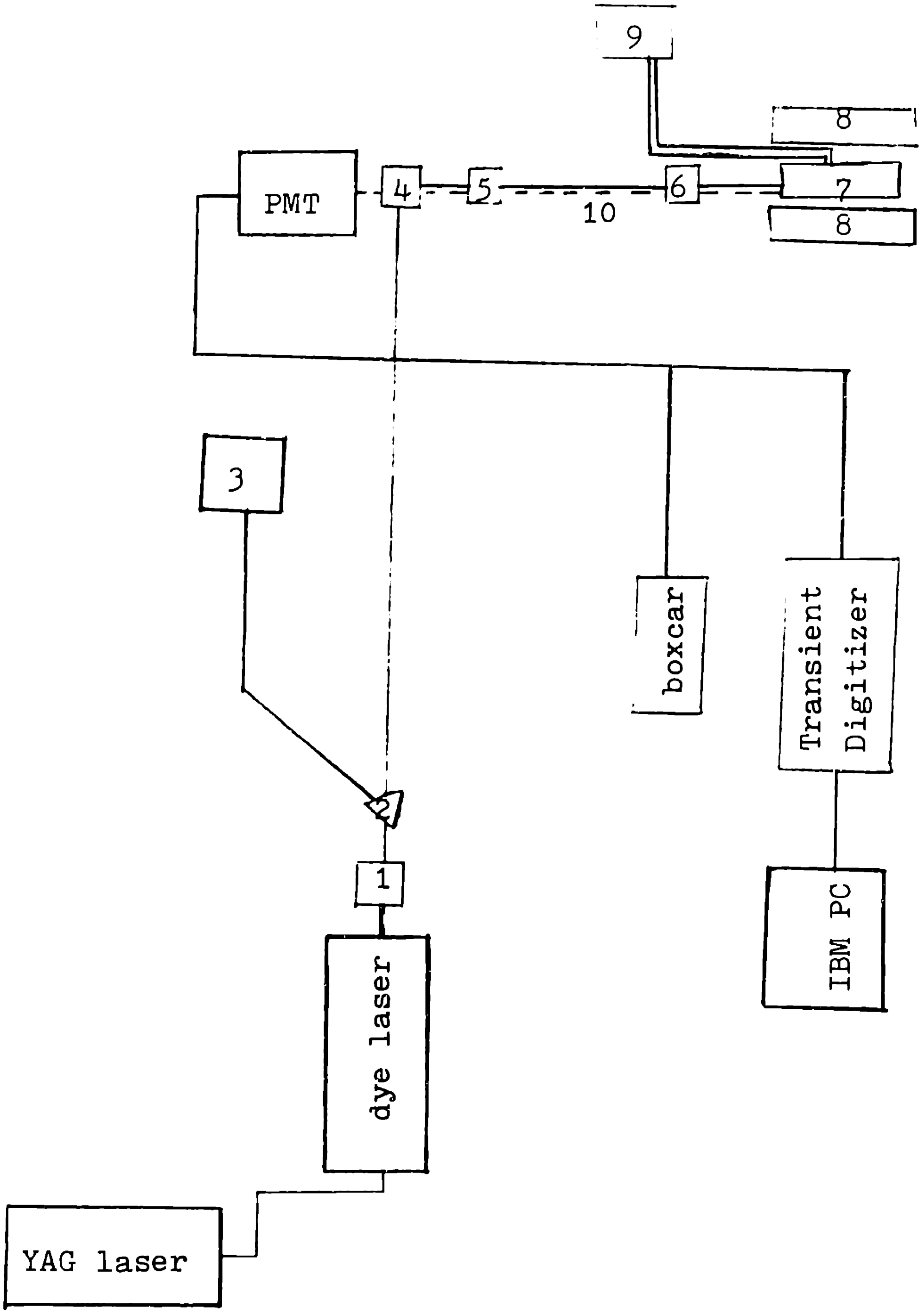


Figure 11 : Experimental Set-Up



1: doubling crystal
2: 60 prism
3: card to monitor fringes
4: $\frac{1}{4}$ wave plate
5: Wollaston prism (movable)

6: collimating lens ($\frac{1}{2}$m. fl)
7: cell
8: magnet
9: vacuum line
10: collection optics (see Fig. 14

Figure 12 : Detection Geometry

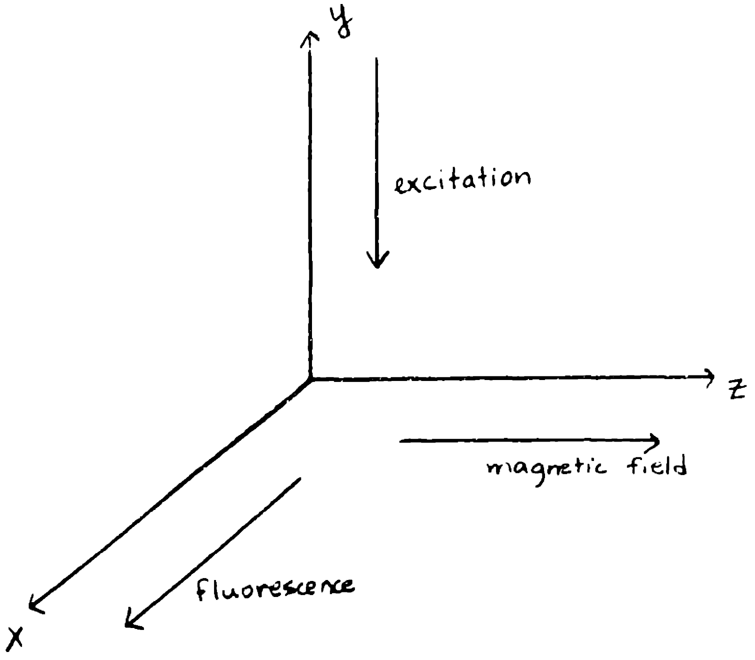
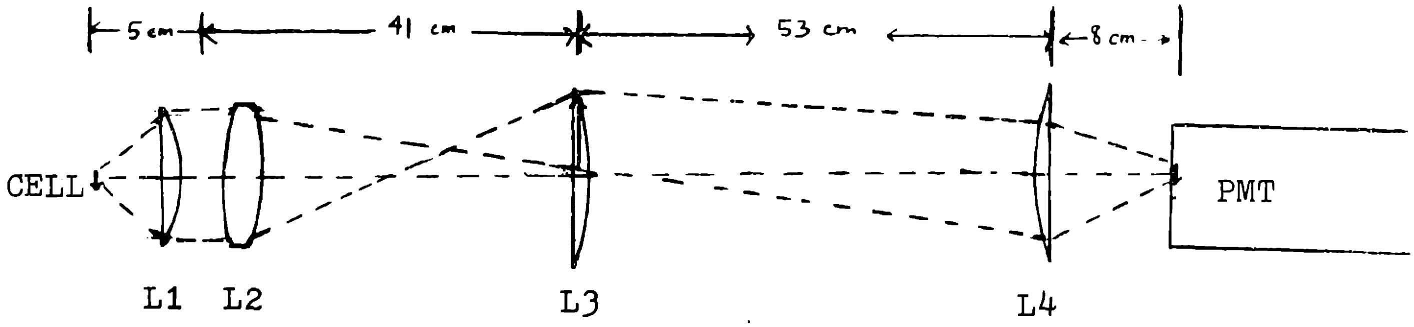


Figure 13 : Collection Optics



L1:	Plano-convex	2" diam.	3" fl
L2:	Bi-convex	2" diam.	5" fl
L3:	Plano-convex	3" diam.	9" fl
L4:	Plano-convex	3" diam.	6" fl