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STUDIES IN MOLECULAR SPECTROSCOPY:

- I. INFRARED LASER STARK SPECTRUM OF METHYLACETYLENE;
- II. DETERMINATION OF ROTATIONAL RELAXATION PARAMETERS  
FOR OCS IN  $H_2$ ,  $CO_2$  and  $CH_3F$ ;
- III. MICROWAVE SPECTRUM OF ISOPROPENYLCYCLOPROPANE  
presented by

Patricia M. Thrash

has been accepted towards fulfillment  
of the requirements for

Ph.D. degree in Chemistry

A handwritten signature in cursive script, reading "R. H. Schwendeman".

Major professor

Date July 23, 1979



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By

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## ABSTRACT

### STUDIES IN MOLECULAR SPECTROSCOPY:

- I. INFRARED LASER STARK SPECTRUM OF METHYLACETYLENE
- II. DETERMINATION OF ROTATIONAL RELAXATION PARAMETERS  
FOR OCS IN  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CH}_3\text{F}$
- III. MICROWAVE SPECTRUM OF ISOPROPENYLCYCLOPROPANE

By

Patricia M. Thrash

The  $\nu_5$  band of methylacetylene was studied by microwave and laser Stark spectroscopy. The rotational constant  $B_5$  and the centrifugal distortion constants  $D_{JK}^{(5)}$  and  $D_J^{(5)}$  were determined from the microwave spectrum to be  $8508.119 \pm 0.003$  MHz,  $169 \pm 1$  kHz, and  $1.8 \pm 0.2$  kHz, respectively. The dipole moments for the ground and  $\nu_5$  excited states were also determined from the microwave spectrum to be  $\mu_0 = 0.7839 \pm 0.0010$  D and  $\mu_5 = 0.7954 \pm 0.0010$  D. The laser Stark spectrum of methylacetylene was obtained by using  $\text{CO}_2$  and  $\text{N}_2\text{O}$  lasers. The molecular parameters were obtained from least squares fit of the assigned laser Stark frequencies. The molecular constants obtained include the band center  $\nu_0 = 930.2749 \pm 0.0004$   $\text{cm}^{-1}$ ; the difference in the A rotational constants for the  $\nu_5$  excited vibrational state and ground state,  $A_5 - A_0 = -206 \pm 7$  MHz; the corresponding

difference in the centrifugal distortion constants,  $D_K^{(5)} - D_K^{(0)} = 4.8 \pm 0.7$  MHz, and the difference in the dipole moments,  $\mu_5 - \mu_0 = 0.0110 \pm 0.0006$  D.

Microwave lineshapes have been studied under conditions of low and moderate incident power for dilute gaseous samples of OCS in  $H_2$ ,  $CO_2$ , and  $CH_3F$ . The  $J = 2 \leftarrow 1$  transition near 24326 MHz was studied for each of the samples. From the low-power lineshapes, values of the linewidth parameters,  $\Delta\nu/p$ , were obtained as follows: OCS/ $H_2$ ,  $6.07 \pm 0.09$  MHz/torr; OCS/ $CO_2$ ,  $5.26 \pm 0.08$  MHz/torr; and OCS/ $CH_3F$ ,  $11.45 \pm 0.17$  MHz/torr. The power-broadened lineshapes were analyzed in two ways. By fitting the lines to a superposition of power-broadened M components values of  $(T_1/T_2)_0 = 1.05 \pm 0.10$ ,  $1.03 \pm 0.10$ , and  $0.97 \pm 0.10$  were obtained for OCS in  $H_2$ ,  $CO_2$ , and  $CH_3F$ , respectively. By fitting the lineshapes to a single Lorentzian, corresponding values of  $q T_1/T_2 = 1.32 \pm 0.13$ ,  $1.30 \pm 0.13$ , and  $1.23 \pm 0.12$  were obtained.

The microwave spectrum of isopropenylcyclopropane was studied in the 18-40 GHz region. Transitions were assigned to a species with rotational constants  $A = 6287.089 \pm 0.600$  MHz,  $B = 2647.222 \pm 0.028$  MHz, and  $C = 2235.061 \pm 0.024$  MHz. Comparison of these constants with values calculated from assumed structures of isopropenylcyclopropane with a variety of torsional orientations of the isopropenyl group relative to the cyclopropane ring showed that the rotational constants of a single species are not sensitive enough to the torsional angle to determine the torsional conformation

responsible for the assigned species. No assignment for another species could be obtained in the very weak microwave spectrum of this compound.

To Bob

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PART I  
INFRARED LASER STARK SPECTRUM OF METHYLACETYLENE

CHAPTER I  
INTRODUCTION

Methylacetylene is a prolate symmetric top molecule with  $C_{3v}$  symmetry. It has 15 normal modes: 5 nondegenerate vibrations and 5 doubly degenerate vibrations. The rotational structure of the  $\nu_5$  band falls in the same frequency range as the  $CO_2$  and  $N_2O$  laser transitions. The  $\nu_5$  vibration is primarily the C-C stretch of the methylacetylene molecule.

Methylacetylene has been studied both by microwave and infrared spectroscopy. Gordy and coworkers obtained the B rotational constant and the  $D_J$  and  $D_{JK}$  centrifugal distortion constants of the ground state.<sup>1-3</sup> The ground state dipole moment was measured accurately by Muentert and Laurie.<sup>4</sup> Dubrulle and coworkers determined the quartic and sextic centrifugal distortion constants.<sup>5</sup> Thompson and coworkers made several studies of the fundamental vibrational bands of methylacetylene,<sup>6-8</sup> while several other investigators have looked at the  $\nu_1$  fundamental, hot bands, and overtones.<sup>9,10</sup> Duncan and coworkers have studied the Fermi and Coriolis interactions between the  $\nu_4$  and  $\nu_7$ ,  $\nu_{8+10}$  band system.<sup>11</sup> Duncan, et al. have also examined the harmonic force field of methylacetylene.<sup>12</sup>

In this investigation of the ground state and  $\nu_5$  vibrational state of methylacetylene, both conventional microwave spectroscopy and the more recent technique of laser Stark spectroscopy have been used. The work was undertaken in part to acquaint ourselves with the use of lasers in vibration-rotation spectroscopy. After the laser Stark spectrum of the gas molecule had been analyzed, it was hoped that several transitions might be found which would be suitable for infrared transient effect spectroscopy which could be used to measure the relaxation parameters  $T_1$  and  $T_2$  for vibration-rotation transitions and rotational transitions in excited vibrational states. As a result of the extremely low absorption coefficients of the available transitions, this does not appear to be possible with currently available equipment. Consequently, this work is concerned entirely with the spectroscopic analysis of the  $\nu_5$  band.

## CHAPTER II

### THEORY

Molecular motion can be divided into several categories. Molecules undergo translation in space and rotate end over end; the atoms within molecules vibrate; and the electrons constantly move around. A certain amount of energy is required to excite each type of motion. Energy in the microwave region with a frequency of 1 to 1000 GHz is sufficient to excite rotational motion, whereas excitation of vibrational motion requires frequencies of  $1 \times 10^3 - 1 \times 10^5$  GHz. An infrared laser Stark spectrum contains transitions between the rotational energy levels of two different vibrational energy levels. In this section, the molecular Hamiltonian will be discussed first. Then, rotational energy levels, vibrational energy levels, and finally laser Stark spectroscopy will be described.

#### The Molecular Hamiltonian

To find the energies of molecules, their molecular motions must be described. Equations of motion are written for the molecule and converted to the Hamiltonian function for the total energy of the system. The Hamiltonian includes contributions from the kinetic energy

and the potential energy:

$$H(\underline{p}, \underline{q}, t) = T(\underline{p}, \underline{q}) + V(\underline{q}, t). \quad (1)$$

The kinetic energy,  $T$ , is expressed in terms of the coordinates,  $q_i$ , and conjugate momenta,  $p_i$ , of the system; the potential energy,  $V$ , is a function of the coordinates and possibly the time.<sup>13</sup> The Hamiltonian operator,  $\hat{H}$ , is used in the Schrödinger equation to derive the molecular energies,  $E_n$ ,

$$\hat{H}\psi_n = E_n\psi_n. \quad (2)$$

Here,  $\psi_n$  is the wavefunction which defines the state of the system in which the energy is  $E_n$ .

The Hamiltonian contains terms involving both the nuclei and electrons of the atoms in the molecule and can be written

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN}, \quad (3)$$

where  $T_N$  is the kinetic energy of all the nuclei and  $T_e$  is the kinetic energy of the electrons. Of the potential energy terms,  $V_{Ne}$  is the attraction of the nuclei for the electrons,  $V_{ee}$  is the electron-electron repulsion term, and  $V_{NN}$  is the repulsion between the nuclei. An

approximation can be made in which it is assumed that the nuclei are fixed in position relative to the motion of the electrons. This Born-Oppenheimer approximation allows the molecular Hamiltonian to be separated into two parts, an equation for the electrons and one for the nuclei.<sup>14</sup> Thus, the Schrödinger equation can be written as two equations,

$$\hat{H}_N \psi_N = E \psi_N \quad (4)$$

and

$$\hat{H}_e \psi_e = E_e \psi_e. \quad (5)$$

The electronic Hamiltonian is

$$\hat{H}_e = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee}, \quad (6)$$

whereas the Hamiltonian for nuclear motion is

$$\hat{H}_N = \hat{T}_N + \hat{V}_{NN} + E_e, \quad (7)$$

and  $E$  is the total energy of the molecule. Therefore, the electronic energy,  $E_e$ , which is an eigenvalue of  $\hat{H}_e$  for a given set of nuclear coordinates, contributes directly to the potential energy for nuclear motion.

### Rotational Energy - Rigid Rotor

The nuclear Hamiltonian is the sum of kinetic energy and potential energy terms,<sup>15</sup>

$$H_N = T_{\text{trans}} + T_{\text{vib}} + T_{\text{rot}} + T_{\text{vib-rot}} + V. \quad (8)$$

The kinetic energy of the molecule can be written as the sum of the translational motion of the center of mass plus the kinetic energy of the motion of the atoms relative to the center of mass. In free space, the two motions can be treated separately. In the rigid rotor approximation there are no vibrations, and the  $T_{\text{vib}}$  and  $T_{\text{vib-rot}}$  terms are zero. In center-of-mass coordinates, the Hamiltonian then contains only the kinetic energy of rotation, which depends on the moments of inertia and on the angular momenta of the molecule.

The moment of inertia for a rigid rotor is

$$I = \sum_i m_i r_i^2, \quad (9)$$

where  $m_i$  is the mass of the  $i$ th atom and  $r_i$  is the distance between the center of mass and the  $i$ th atom. The moment of inertia matrix,  $I$ , may be written<sup>16</sup>

$$I = \begin{pmatrix} I_{xx'} & I_{xy'} & I_{xz'} \\ I_{yx'} & I_{yy'} & I_{yz'} \\ I_{zx'} & I_{zy'} & I_{zz'} \end{pmatrix}, \quad (10)$$

where  $I_{xx'} = \sum_i m_i (y_i'^2 + z_i'^2)$  and  $I_{xy'} = - \sum_i m_i x_i' y_i'$ . The other terms can be formed by a permutation of  $x'$ ,  $y'$  and  $z'$ . Again,  $m_i$  is the mass of the particle and  $x'$ ,  $y'$  or  $z'$  are the position coordinates in a rectangular molecule-fixed coordinate system that has its origin at the center of mass of the molecule. One orientation of this coordinate system will cause the diagonal elements of the moment-of-inertia matrix to have either maximum or minimum values and the off-diagonal elements to vanish. This is the principal inertial matrix whose diagonal elements, the principal moments of inertia, are the roots of the cubic equation,

$$\begin{vmatrix} I_{xx'} - I & I_{xy'} & I_{xz'} \\ I_{yx'} & I_{yy'} - I & I_{yz'} \\ I_{zx'} & I_{zy'} & I_{zz'} - I \end{vmatrix} = 0. \quad (11)$$

If the three roots are designated  $I_x$ ,  $I_y$ , and  $I_z$ , the rotational Hamiltonian becomes

$$H = \frac{1}{2} \left( \frac{P_x^2}{I_x} + \frac{P_y^2}{I_y} + \frac{P_z^2}{I_z} \right), \quad (12)$$

where  $P_x$ ,  $P_y$ , and  $P_z$  are components of the rotational angular momentum projected on the molecule-fixed principal axes of inertia.

The Hamiltonian and hence the energy equations are different for different types of molecules. If all three moments of inertia are the same, the molecule has very high symmetry and is called a spherical rotor. If only two of the moments are the same, it is a symmetric rotor, and if all three moments of inertia are different and none equals zero, the molecule is an asymmetric rotor.

Methylacetylene is a symmetric top molecule because two of its principal moments of inertia are equal. A symmetric top has one rotational axis of  $C_3$  or higher symmetry. One of the principal inertial axes always lies along this axis, and corresponds with the unique moment of inertia. The three principal axes are mutually perpendicular and are conventionally labelled  $I_a$ ,  $I_b$ , and  $I_c$ . Two cases exist for symmetric tops: the moment of inertia about the symmetry axis is either larger or smaller than the other two moments. If it is larger ( $I_a = I_b < I_c$ ), the molecule is an oblate symmetric top. If it is smaller ( $I_a < I_b = I_c$ ), the molecule is a prolate symmetric top. Methylacetylene is a prolate symmetric top. The Hamiltonian

operator for a prolate rigid rotor is<sup>16</sup>

$$H_r = \frac{P^2}{2I_b} + \frac{1}{2} \left( \frac{1}{I_a} - \frac{1}{I_b} \right) P_a^2, \quad (13)$$

where

$$P^2 = P_a^2 + P_b^2 + P_c^2. \quad (14)$$

To find the energies of the rigid rotor, the Schrödinger equation for  $H_r$  must be solved. The Hamiltonian operator for the symmetric top contains constants and angular momentum operators. Since the matrix elements of the angular momentum operators are well known, the matrix elements of the Hamiltonian operator can be easily found.

### Angular Momenta

The angular momentum of a single particle is  $\tilde{P} = \tilde{r} \times \tilde{p}$ , where  $\tilde{r}$  is the vector from the origin and  $\tilde{p}$  is the linear momentum of the particle. The angular momentum can be expanded and written in terms of its components  $P_X$ ,  $P_Y$ , and  $P_Z$  which lie along the direction of the space-fixed axes. These components can be expressed as follows:<sup>16</sup>

$$\begin{aligned} P_X &= Yp_Z - Zp_Y, \\ P_Y &= Zp_X - Xp_Z, \\ P_Z &= Xp_Y - Yp_X, \end{aligned} \quad (15)$$

and

$$P^2 = P_X^2 + P_Y^2 + P_Z^2. \quad (16)$$

It is easily shown that  $P^2$  commutes with  $P_X$ ,  $P_Y$ , and  $P_Z$ ;

$$P^2 P_X - P_X P^2 = 0, \text{ etc.} \quad (17)$$

However, the components of the angular momenta do not commute among themselves;

$$\begin{aligned} P_X P_Y - P_Y P_X &= i\hbar P_Z, \\ P_Y P_Z - P_Z P_Y &= i\hbar P_X, \\ P_Z P_X - P_X P_Z &= i\hbar P_Y. \end{aligned} \quad (18)$$

The angular momentum can also be expanded and written in terms of its components  $P_x$ ,  $P_y$ , and  $P_z$ , which lie along the molecule-fixed axes. Again,

$$P^2 = P_x^2 + P_y^2 + P_z^2, \quad (19)$$

and  $P^2$  commutes with  $P_x$ ,  $P_y$ , and  $P_z$ ; they do not, however, commute among themselves,

$$\begin{aligned}
P_x P_y - P_y P_x &= -i\hbar P_z, \\
P_y P_z - P_z P_y &= -i\hbar P_x, \\
P_z P_x - P_x P_z &= -i\hbar P_y.
\end{aligned}
\tag{20}$$

With the aid of these commutation rules it is possible to derive eigenvalue equations for angular momenta as follows:<sup>17</sup>

$$\begin{aligned}
P^2 \psi_{Jkm} &= \hbar^2 J(J+1) \psi_{Jkm} \\
P_z \psi_{Jkm} &= \hbar m \psi_{Jkm} \\
P_z \psi_{Jkm} &= \hbar k \psi_{Jkm}.
\end{aligned}
\tag{21}$$

The square of the total rotational angular momentum is  $J(J+1)\hbar^2$  where  $J = 0, 1, 2, 3, \dots$ , while the projection of the angular momentum on the space-fixed  $Z$  axis is  $m\hbar$ ;  $m$  is an integer with permitted values  $J \geq m \geq -J$ . The projection of the total angular momentum on the molecule-fixed  $z$  axis is  $k\hbar$  where  $k$  is an integer equal to or between  $-J$  and  $J$ . Left multiplication of both sides of the eigenvalue equations by an eigenfunction and integration yields the non-zero matrix elements of the angular momenta in the eigenfunction basis, as follows:

$$\begin{aligned}
\langle J,k,m | P^2 | J,k,m \rangle &= \hbar^2 J(J+1) \\
\langle J,k,m | P_z | J,k,m \rangle &= \hbar m \\
\langle J,k,m | P_z^2 | J,k,m \rangle &= \hbar^2 k^2.
\end{aligned} \tag{22}$$

The rigid rotor Hamiltonian for the prolate symmetric top is given by Equation (13). The Hamiltonian depends upon only the molecule-fixed coordinates, so the energies have no  $m$  dependence. The  $m$  degeneracy is removed, however, when a space-fixed electric field is applied. The energies for the rigid rotor are the eigenvalues of the Hamiltonian operator,

$$E_r = \langle J,k | H_r | J,k \rangle = \frac{\hbar^2}{2I_b} J(J+1) + \frac{\hbar^2}{2} \left( \frac{1}{I_a} - \frac{1}{I_b} \right) K^2, \tag{23}$$

where  $K = |k|$ . Generally,  $\frac{h}{8\pi^2 I_b}$  is written as a rotational constant  $B$  and  $\frac{h}{8\pi^2 I_a}$  as  $A$ ; therefore,

$$E_r = h[BJ(J+1) + (A-B)K^2]. \tag{24}$$

Figure 1 shows a plot of the energy levels of methylacetylene, a prolate symmetric top. Since  $K$  is squared in the energy expression, all of the energy levels except  $K = 0$  are doubly degenerate. Perturbations outside the molecule, such as application of an electric field, cannot lift this  $K$  degeneracy. Normally, the Hamiltonian does not include an angular momentum term that depends on the

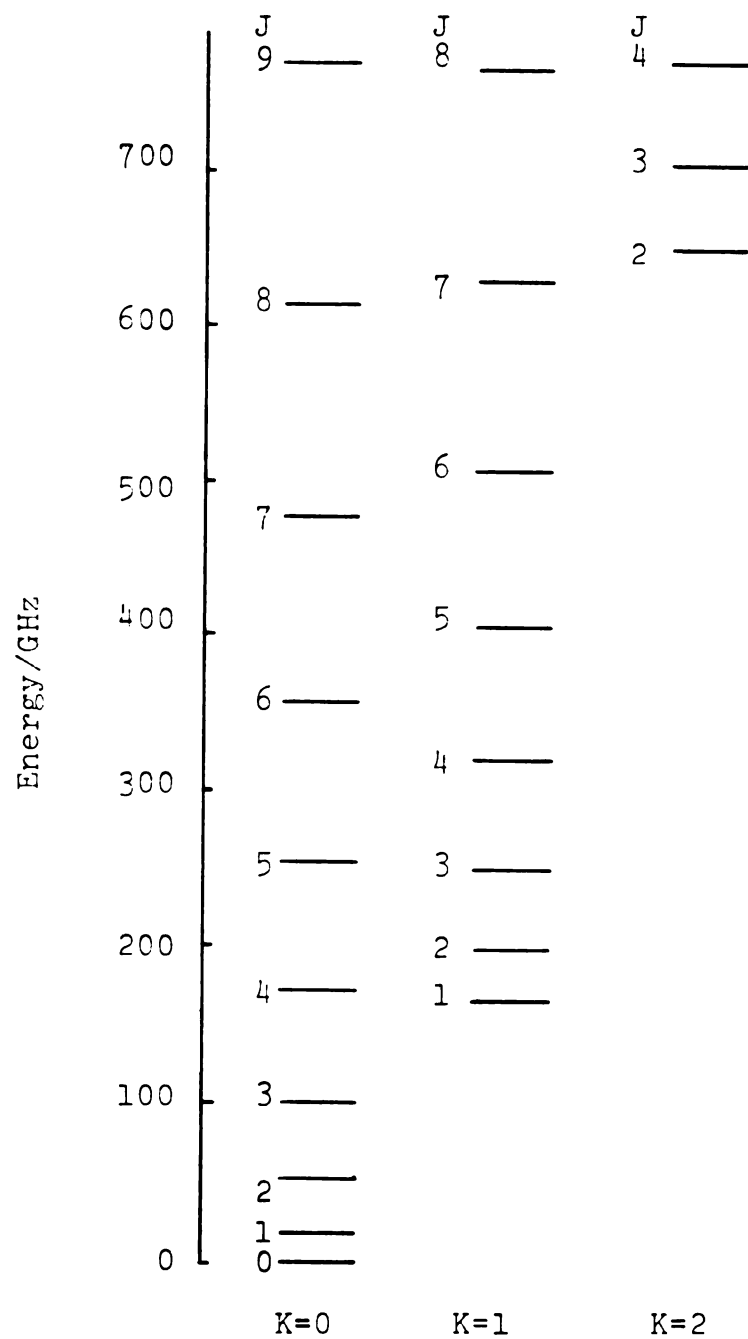


Figure 1. Plot of the rotational energy levels of the prolate symmetric top, methylacetylene.

relative orientation of the molecule-fixed and space fixed-axes. Therefore, the energy levels also possess a  $(2J+1)$ -fold degeneracy in  $m$ . This degeneracy is lifted in the presence of an electric field and will be discussed in the Stark effect section.

### Centrifugal Distortion

A molecule is not really rigid. As it spins about an axis the atoms are pushed out away from that axis, changing the moments of inertia. The effect of centrifugal distortion can be added to the rigid rotor Hamiltonian as a perturbation. The centrifugal distortion Hamiltonian is given by<sup>18</sup>

$$H_d = \frac{\hbar^4}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta, \quad (25)$$

where  $\alpha, \beta, \gamma$ , and  $\delta$  refer to the principal inertial axes  $x$ ,  $y$ , and  $z$ . The centrifugal distortion is determined by the angular momenta and the constants  $\tau_{\alpha\beta\gamma\delta}$ , which are functions of the force constants and the moments of inertia of the molecule.<sup>16</sup> The centrifugal distortion energies can be found by using first-order perturbation theory, in which the energy is expressed as

$$E_d = \langle J, K | H_d | J, K \rangle. \quad (26)$$

The centrifugal distortion Hamiltonian is averaged over the rigid rotor wave functions. Terms that contain odd powers of the angular momentum average to zero. The centrifugal distortion Hamiltonian can be simplified by use of the commutation rules and the fact that many of the  $\tau_{\alpha\beta\gamma\delta}$  constants are equivalent.<sup>19</sup> By using these relations and first-order perturbation theory, the centrifugal distortion energy of a symmetric rotor is found to be<sup>16,20</sup>

$$E_d = -D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4, \quad (27)$$

where

$$\begin{aligned} D_J &= \left(-\frac{\hbar^4}{4}\right)\tau_{xxxx} \\ D_{JK} &= -2D_J - \left(\frac{\hbar^4}{2}\right)\{\tau_{xxzz} + 2\tau_{xzxz}\} \\ D_K &= -D_J - D_{JK} - \left(\frac{\hbar^4}{4}\right)\tau_{zzzz}. \end{aligned} \quad (28)$$

### Stark Effect

When a rotating molecule is placed in an electric field, the molecular dipole moment interacts with the field, removing the  $m$  degeneracy of the energy levels. This splitting of the rotational energy levels by an electric field is known as the Stark effect. The Stark effect causes additional lines to be seen in the

rotational spectrum of a molecule and hence is useful in identifying transitions. It is also used to determine the value of the molecular dipole moment.

Generally, the electric field is held constant and fixed in space. For Stark effect calculations the electric dipole moment,  $\mu$ , is assumed to be constant in the molecule-fixed coordinate system. The interaction between the dipole moment and the electric field is expressed as

$$H_S = -\mu \cdot \tilde{\epsilon}. \quad (29)$$

Here,  $H_S$  is the Hamiltonian for the Stark effect and  $\tilde{\epsilon}$  is the electric field vector, which is normally in a constant direction and defined in the space-fixed coordinate system. To express both of these vectors in the same coordinate system, a means of relating the molecule-fixed and space-fixed systems is needed. This relation is given by the cosines of the angles between the two systems. If the electric field is along the space-fixed Z-axis, the Stark Hamiltonian becomes

$$H_S = -\epsilon \sum_{g=x,y,z} \mu_g \phi_{Zg}, \quad (30)$$

where  $\epsilon$  is the magnitude of the electric field and the  $\phi_{Zg}$  are direction cosines of the molecule-fixed x, y, and z axes relative to the space-fixed Z axis.<sup>16</sup> Only the

dipole interaction will be considered here. The interaction of the field and the polarizability will be neglected since its effect is quite small. For the symmetric rotor, the Stark Hamiltonian simplifies to

$$H_S = -\epsilon \mu_z \Phi_{ZZ}, \quad (31)$$

because  $|\tilde{\mu}| = \mu_z$  and  $\mu_x = \mu_y = 0$ . Exact expressions for the eigenvalues of the combined Hamiltonian  $H_r + H_S$  cannot be obtained. However, the eigenvalues can be determined by numerical methods. The matrix elements for  $\Phi_{ZZ}$  can be obtained from commutation rules between the angular momentum operators and the direction cosines.<sup>22</sup> For a symmetric rotor, the diagonal elements of the Stark effect matrix are

$$\langle J, k, m | H_S | J, k, m \rangle = -\epsilon \langle J, k, m | \Phi_{ZZ} | J, k, m \rangle \quad (32)$$

$$= -\frac{\epsilon k m}{J(J+1)}, \quad (33)$$

while the matrix elements off-diagonal in  $J$  are

$$\langle J, k, m | H_S | J+1, k, m \rangle = -\epsilon \langle J, k, m | \Phi_{ZZ} | J+1, k, m \rangle \quad (34)$$

$$= -\frac{\epsilon}{(J+1)} \left( \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(2J+1)(2J+3)} \right)^{1/2}. \quad (35)$$

Notice that the matrix has diagonal elements and elements one off the diagonal; all other matrix elements are zero. To obtain the spectroscopic frequencies in a Stark field, the matrices for  $H_r + H_s$  that contain the  $J$ ,  $k$ , and  $m$  quantum numbers needed for both the upper and lower energy levels of the transition are truncated at some high  $J$  value and diagonalized, after which the appropriate difference in eigenvalues is taken.

Rather than solving for the Stark energies numerically, perturbation theory may be employed when the energy level shift due to the Stark effect is smaller than the spacing between the rotational levels. The Stark energies obtained from the first-order and second-order perturbation theory are accurate enough for most microwave applications. Perturbation theory yields first-order Stark energies given by

$$E_s^{(1)} = \int \psi_j^{(0)} H_s \psi_j^{(0)} d\tau, \quad (36)$$

where  $\psi_j^{(0)}$  is the limiting wavefunction of the symmetric rigid rotor as the field goes to zero. The first-order Stark energy for a symmetric top is

$$E_s^{(1)} = -\mu \epsilon k m / J(J+1). \quad (37)$$

The second-order term for a symmetric top molecule is

$$E_s^{(2)} = \sum_{J' \neq J} \frac{|\langle J, k, m | H_s | J', k, m \rangle|^2}{E_{J, k} - E_{J', k}}, \quad (38)$$

which may be shown to be<sup>16</sup>

$$E_s^{(2)} = \frac{\mu^2 \epsilon^2}{2hB} \left( \frac{(J^2 - K^2)(J^2 - M^2)}{J^3(2J-1)(2J+1)} - \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(J+1)^3(2J+1)(2J+3)} \right). \quad (39)$$

The total rotational energy in a Stark field is  $E_r + E_d + E_s^{(1)} + E_s^{(2)}$ . As before, the frequencies of the transitions are equal to differences in this total energy.

A plot of the frequency of one of the Stark transitions against the electric field will result in a straight line for symmetric rotor molecules if one of the levels in the transition has  $k$  and  $m$  different from zero. These molecules are said to exhibit a first-order Stark effect. If  $k$  or  $m$  is equal to zero for both levels in the transition, the leading field-dependent term is proportional to  $\epsilon^2$ . Such transitions are said to have a second-order Stark effect. At the same field, first-order Stark shifts are much larger than second-order ones. At low pressures, it takes only a few tens of volts per centimeter to separate the  $m$  components of a transition with a first-order Stark effect, while a field of several hundred volts per centimeter is needed to separate the components when the Stark shift is second-order. Second-order Stark shifts are

superimposed upon first-order shifts. However, since they are much smaller at low fields than first-order shifts, they are usually not noticed unless the field is very high.

The J and k selection rules for a rotational transition in an electric field are determined by the type of molecule. For a symmetric top molecule,  $\Delta J = 0, \pm 1$  and  $\Delta k = 0$ . The values allowed for  $\Delta m$  are 0 or  $\pm 1$ . If the electric vector of the radiation is parallel to the applied electric field,  $\Delta m = 0$  selection rules apply, and if the electric vector of the radiation is perpendicular to the electric field,  $\Delta m = \pm 1$ . In microwave spectroscopy the usual arrangement of the sample cell employs a metal septum running down the length of the cell in its center, and parallel to its broad face. The electric vector of the radiation is then parallel to the Stark field and the allowed transitions are those for which  $\Delta m = 0$ . These spectra are much easier to interpret than  $\Delta m = \pm 1$  spectra. Both  $\Delta m = 0$  and  $\Delta m = \pm 1$  transitions are not normally seen in the same spectrum, because different experimental setups are needed for each. In the microwave region a parallel plate sample cell or a split waveguide sample cell is used to obtain  $\Delta m = \pm 1$  spectra. In laser Stark spectroscopy a parallel plate sample cell is used and the plane of polarization of the laser light may be selected to obtain either  $\Delta m = 0$  or  $\Delta m = \pm 1$  transitions. When the Stark effect is first order, the levels for  $+k$  and  $+m$  have the same energy as those

with  $-k$  and  $-m$ . When the Stark effect is second order, the levels for  $\pm k$  and  $\pm m$  are degenerate, except for  $m = 0$ , for which only the  $\pm k$  degeneracy holds, or for  $k = 0$  for which only the  $\pm m$  degeneracy holds. The levels with  $k = 0$  and  $m = 0$  are non-degenerate.

The number of Stark components, spacing between the components, and their relative intensities can be used to assign the transitions. The intensity of each Stark component is proportional to the square of the appropriate direction cosine matrix element. For  $\Delta m = 0$  and  $\Delta J = 0$ , the intensity of each Stark peak is proportional to  $M^2$ , so the peaks with the largest intensity are those with the greatest absolute value of  $m$ . The  $m = 0$  component will be missing. For  $\Delta m = 0$  and  $J + 1 \leftarrow J$ , the opposite is true. The largest values of  $|m|$  have the smallest intensity, since the intensity is proportional to  $[(J+1)^2 - M^2]$ . In this case, no component has zero intensity since  $J$  is always at least as large as  $M$ . When looking at the relative intensities of second-order Stark components, the calculated value for the  $M \neq 0$  transitions should be multiplied by 2, since the degeneracy of these levels is twice that for  $M = 0$ . The frequency spacing between the Stark components of a transition increases with increasing value of  $M$ . Various patterns of spacing and intensity of Stark components are shown in reference 16.

### Selection Rules

Molecules can undergo only certain transitions as a result of interaction with radiation. To see when stimulated absorption will occur, the time dependence of the interaction of the radiation with the molecule must be examined. By using time-dependent perturbation theory, it may be shown that the probability of a transition per unit time to state  $n$  by a molecule in state  $m$  is<sup>23</sup>

$$\rho_{m \rightarrow n} = \frac{8\pi^3}{3h^2} \langle m | \mu_F | n \rangle^2 \rho(\nu_{mn}) \quad (40)$$

for unpolarized radiation. Here,  $\langle m | \mu_F | n \rangle$  is the dipole moment matrix element of the molecule, and  $\rho(\nu_{mn})$  is the radiation density. An allowed transition, then, is one for which the square of the dipole moment matrix element does not vanish. After expansion,

$$\langle m | \mu_F | n \rangle = \mu_x \int \psi_m^* \phi_{Fx} \psi_n d\tau + \mu_y \int \psi_m^* \phi_{Fy} \psi_n d\tau + \mu_z \int \psi_m^* \phi_{Fz} \psi_n d\tau, \quad (41)$$

where  $\phi_{Fg}$  are the direction cosines.

In a rigid symmetric top molecule, the dipole moment lies along the symmetry axis so that  $\mu = \mu_z$  and  $\mu_x = \mu_y = 0$ . Therefore the general dipole moment matrix element becomes

$$\int \psi_m^* \mu_F \psi_n d\tau = \mu_z \int \psi_m^* \phi_{Fz} \psi_n d\tau . \quad (42)$$

From the table of direction cosine matrix elements, it can be seen that the dipole moment matrix elements of a symmetric rotor are non-zero when  $\Delta J = 0, \pm 1$ ;  $\Delta k = 0$ ; and  $\Delta m = 0, \pm 1$ . Which  $\Delta m$  selection rule is observed depends upon the situation. In the absence of a Stark field, the direction of the electric vector of the exciting radiation defines the space-fixed F direction. Then, F may be set equal to Z and the dipole moment matrix element is non-zero only if  $\Delta m = 0$ . If an applied Stark field is also in the Z direction,  $\Delta m = 0$  selection rules again apply. However, if the applied Stark field is reasonably large and perpendicular to the electric vector of the radiation, then F = X or Y and the dipole moment matrix element is non-zero only if  $\Delta m = \pm 1$ .

### Dipole Moments From Microwave Spectra

The measurement of Stark shifts in microwave spectroscopy is one of the most accurate methods for the determination of molecular dipole moments. Some problems encountered in other methods for determining dipole moments are not sources of difficulty in microwave spectroscopy. These dipole moments are unaffected by impurities in the sample since measurements are made on known microwave transitions.

Thus, the dipole moments of molecules which decompose rapidly may be obtained since the decomposition rates will not affect the dipole determination. Solids and liquids with sufficient vapor pressure can be studied in the gas phase by microwave spectroscopy, since so little sample is needed. Dipole moments obtained from these measurements will be independent of solvent effects which would otherwise affect them. Dipole moments are obtained for distinct vibrational and rotational states, rather than averaged over all states as in other methods. And, finally, small dipole moments can be measured with almost the same accuracy as large dipole moments.<sup>24</sup>

The best microwave transitions to use are those with a Stark shift which is as large and purely first- or second-order as possible. The lines should be sharp and should not be complicated with hyperfine structure. The electric field employed must be uniform to obtain sharp Stark components and its value must be well known in order to obtain accurate dipole moments.

The first-order Stark energy is given in Equation (37). Thus, the first-order Stark shift in frequency is given by

$$\Delta\nu_1 = - \frac{2\mu\epsilon}{h} \frac{km}{J(J+1)(J+2)} \quad (43)$$

for the case  $J + 1 \leftarrow J$ ,  $\Delta k = 0$ , and  $\Delta m = 0$ . Also,  $\epsilon$  is

the electric field,  $\mu$  is the dipole moment, and  $h$  is Planck's constant.

The second-order Stark energy is shown in Equation (39) and the second-order Stark shift in frequency for a symmetric top,  $\Delta k = 0$ , with  $k = 0$ ,  $J + 1 \leftarrow J$ , and  $\Delta m = 0$  is<sup>25</sup>

$$\Delta \nu_2 = \frac{\mu^2 \epsilon^2}{h^2 \nu_0} \frac{3M^2(16J^2 + 32J + 10) - 8J(J+1)^2(J+2)}{J(J+2)(2J-1)(2J+1)(2J+3)(2J+5)} \quad (44)$$

where  $\nu_0$  is the zero-field frequency and  $\Delta \nu_2$  is the difference between the Stark component frequency and  $\nu_0$ . This equation can also be used for a linear molecule since a linear molecule can be thought of as the special case of a symmetric top with  $k = 0$ . The  $\Delta m = 0$  selection rule implies that the electric vector of the microwave radiation is parallel to the electric field. This is the case for most microwave spectrometers in which the sample cell waveguide contains a septum as one of the electrodes. The cell used in this investigation is of this type.

When the Stark effect measurements are made at high electric field strengths, higher order corrections to the energy must be included.<sup>4</sup> For a first-order Stark effect the energy is then

$$E = E^{(1)} + E^{(2)} + E^{(3)} + \dots \quad (45)$$

For a second-order Stark shift - i.e., when the first-order effect is zero - all higher odd-order terms vanish,<sup>26</sup> so the energy becomes:

$$E = E^{(2)} + E^{(4)} + \dots \quad (46)$$

and the Stark shift is of the form

$$\Delta v = A_D \mu^2 \epsilon^2 + B_D \mu^4 \epsilon^4 + \dots \quad (47)$$

In Equation (47)  $A_D$  and  $B_D$  are constants for a microwave transition and can be found from perturbation energy expressions. For example,  $A_D$  may be obtained from Equation (44).

### Vibration-Rotation Spectra

Molecular vibrational spectra usually occur in the infrared region between 10 and 10,000  $\text{cm}^{-1}$ . However, overtones may be found in the visible region. With the laser Stark technique the rotational fine structure of the vibrational bands can be observed. This work is done with gaseous samples. Infrared spectra of liquids and solids do not show rotational structure. In the simplest approximation, the energy of a vibrating and rotating molecule is just the sum of the vibrational energy and the rotational energy. In the next approximation, the interaction between

the vibration and rotation is taken into account. Since the moments of inertia of the molecule change during the vibration, the vibrationally-averaged rotational constants A, B, C, etc. are slightly different in each vibrational state of the molecule. Even the constants in the lowest vibrational state differ from the equilibrium values, since the energy of the lowest vibrational level does not equal zero. It may be shown that the energy associated with each vibrational mode of the molecule is approximately equal to that of a harmonic oscillator,

$$E_v = (v + \frac{1}{2})h\nu_0, \quad (48)$$

where  $v = 0, 1, 2, \dots$ ,  $\nu_0$  is the classical frequency of the system, and  $h$  is Planck's constant. A molecule with several classical frequencies has a vibrational energy of<sup>15</sup>

$$E_v = (v_1 + \frac{1}{2})h\nu_1 + (v_2 + \frac{1}{2})h\nu_2 + \dots + (v_{3N-6} + \frac{1}{2})h\nu_{3N-6}, \quad (49)$$

where a quantum number  $v_k$  and classical frequency  $\nu_k$  are associated with each normal coordinate  $Q_k$  of the molecule. Anharmonicities and other perturbations are added to the vibrational energy of the simple harmonic oscillator to approximate the energy levels of a real molecule. These coordinates will not be discussed; in this investigation of  $\text{CH}_3\text{C}\equiv\text{CH}$  only the fundamental ( $v = 1 \leftarrow v = 0$ ) of a single

vibration-rotation band was studied. As a result, the only purely vibrational parameter determined was the band center,  $\nu_0$ . More data would be needed to determine the difference between  $\nu_0$  and the vibrational frequency,  $\nu$ .

The fine structure of a vibration-rotation band can form several patterns. A symmetric top molecule which has a symmetry axis of  $C_3$  or higher can have two types of fundamental vibrational bands. When the change in the electric moment of the molecule during vibration is parallel to the symmetry axis, the vibrational band is termed a parallel band. When  $k$  does not equal zero, the selection rules for parallel bands are

$$k \neq 0: \quad \Delta J = 0, \pm 1 \quad \Delta k = 0. \quad (50)$$

If  $k$  equals zero, the selection rules are

$$k = 0: \quad \Delta J = \pm 1 \quad \Delta k = 0. \quad (51)$$

For a perpendicular band, the change in the electric moment is perpendicular to the symmetry axis. These transitions are allowed when<sup>27</sup>

$$\Delta J = 0, \pm 1 \quad \Delta k = \pm 1. \quad (52)$$

An accidentally symmetric top or some overtone or combination gives rise to a hybrid band. These are bands in which both components of the electric moment exist, so the hybrid band has characteristics of parallel and perpendicular bands.

The band observed in this study of methylacetylene was a parallel band. The band structure of a parallel band is simpler than that of perpendicular or hybrid bands. The energy levels for a prolate symmetric top in zero Stark field were found to be

$$E_r = BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4. \quad (53)$$

By using the selection rules for a parallel band and adding the vibrational band center frequency  $\nu_0$ , the frequency for each line of the P and R branches is written as<sup>27</sup>

$$\begin{aligned} \nu^{P,R} = \nu_0 &+ (B'+B'')\bar{m} + (B'-B''-D_J'+D_J'')\bar{m}^2 - 2(D_J'+D_J'')\bar{m}^3 \\ &- (D_J'-D_J'')\bar{m}^4 + \{[(A'-A'') - (B'-B'')] - (D_{JK}'-D_{JK}'')\bar{m} \\ &- (D_{JK}'-D_{JK}'')\bar{m}^2\}K^2 - (D_K'-D_K'')K^4 \end{aligned} \quad (54)$$

where  $\bar{m}$  is a running index with  $\bar{m} = J + 1$  for the R branch and  $\bar{m} = -J$  for the P branch. In Equation (54) J refers to

the value of  $J$  in the lower energy level and the single prime indicates an excited state parameter while the double prime indicates a lower state parameter. The frequency of a Q branch transition is given by<sup>27</sup>

$$\begin{aligned} \nu^Q = \nu_0 + [(A'-B') - (A''-B'')]K^2 - (D_K'-D_K'')K^4 \\ + (B'-B'')J(J+1) - (D_J'-D_J'')J^2(J+1)^2 - (D_{JK}'-D_{JK}'')J(J+1)K^2. \end{aligned} \quad (55)$$

The transitions of the parallel band can be separated into sets - each set containing lines with the same value of  $K$ . Figure 2a shows the sets  $K = 0$  through  $K = 4$  for the  $\nu_5$  band of methylacetylene. In Figure 2b, these sets are plotted together as actually seen in the spectrum. Notice that for  $K = 0$  there is no Q branch line. Also, for sets of increasing values of  $K$ , lines are missing from the beginning of the branches since  $J$  must be greater than or equal to  $K$  for any energy level. In Figure 2b, where all the sets are plotted together, it can be seen that the lines from each set do not lie exactly on top of one another. Thus the  $K$  components are resolved in the P, Q, and R branches. The lines in each set do not exactly coincide, because the spacings between the energy levels of the upper state are different from the spacings between the lower state energy levels.

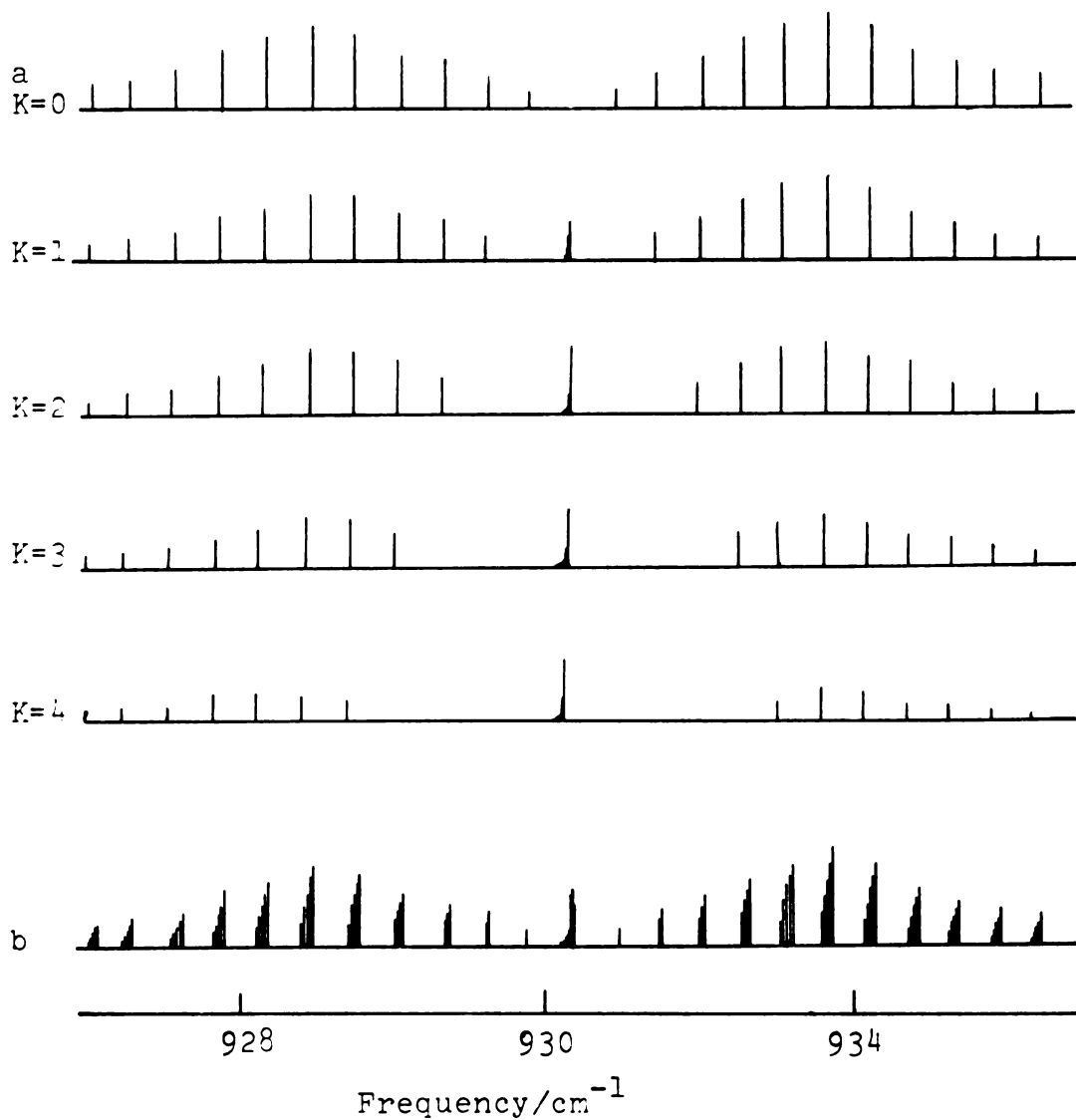


Figure 2. Plot of the transitions of the parallel band  $\nu_5$  in methylacetylene. The lines can be separated into sets; one for each value of  $K$ . Figure 2a shows the sets  $K=0$  through  $K=4$ . In Figure 2b these sets are plotted together.

### Laser Stark Spectroscopy

The first working laser was built in 1960 by T. H. Maiman.<sup>28,29</sup> It was a three-level ruby laser, pumped by a xenon flash lamp. In the following years, the number and types of lasers greatly increased and the uses to which they were put covered many fields. They soon made their way into spectroscopy, where they were used as light sources in the infrared and visible regions. Lasers can be made monochromatic, unlike conventional light sources. Some lasers, such as dye lasers, have continuously variable frequencies, while others can be made to oscillate only at a number of particular frequencies.

Most lasers which operate in the infrared are not continuously tunable. It was found that the application of a magnetic field to the He-Ne and He-Xe lasers could shift their energy levels by means of the Zeeman effect and cause the laser to be tunable over several gigahertz.<sup>30</sup> It is possible to observe the rotation-vibration transitions of a number of molecules in this limited range. Recently, tunable diode lasers, color-center lasers, and difference dye lasers have been used as tunable laser sources in the infrared region.

Molecular lasers in the infrared, however, cannot be tuned over a very large range. An individual CO<sub>2</sub> line can only be tuned about 50 MHz across its linewidth. Since the laser frequency cannot be tuned, the molecular frequency

is tuned to bring it into resonance with the laser line. In 1968 Uehara, Shimizu, and Shimoda reported the use of the Stark effect to tune the molecular frequency.<sup>31</sup> This technique is known as laser Stark spectroscopy or laser electric resonance. As described earlier, the application of an electric field to the sample splits the  $m$  degeneracy of the molecular energy levels, separates the Stark components, and may bring one of the Stark components into resonance with the laser frequency. In laser Stark spectroscopy, fields as high as 70 kV/cm have been used. Some first-order Stark components have been shifted as much as 28,990 MHz, or about  $1\text{ cm}^{-1}$ . The separation between adjacent  $\text{N}_2\text{O}$  laser lines is about  $1\text{ cm}^{-1}$  and that between two adjacent  $\text{CO}_2$  laser lines is about  $2\text{ cm}^{-1}$ .

The information gained from laser Stark spectroscopy includes molecular parameters such as the band origin, excited state rotational constants, centrifugal distortion constants, upper and lower state dipole moments, and, for perpendicular transitions, Coriolis coupling constants and  $\ell$ -type doubling constants. The technique of laser Stark spectroscopy is limited to molecules with a significant permanent dipole moment. Molecules most suited to laser Stark spectroscopy with  $\text{CO}_2$  or  $\text{N}_2\text{O}$  lasers are those which have a sizable Stark shift since the laser lines are one or two wavenumbers apart. At lower fields, first-order Stark shifts are much faster than second-order Stark shifts,

so symmetric top or near symmetric top molecules are likely candidates. Of course, the molecule must have an infrared active band in the range of the laser frequencies, which for the  $\text{N}_2\text{O}$  and  $\text{CO}_2$  lasers is about  $900\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$ . Table 1 lists the molecules which have been studied to date by laser Stark spectroscopy.

Although laser Stark spectroscopy is not applicable to all molecules, it has several advantages over conventional spectroscopy. The laser is used as the frequency standard, so there is no frequency calibration problem. Since the frequencies of the laser are well known and the instability of the laser is only a few megahertz, the technique is remarkably accurate and precise. Laser Stark spectroscopy is quite sensitive. Shimoda has estimated that the minimum detectable number of molecules in the beam is  $10^2$  to  $10^{6.72}$ . For  $\text{H}_2\text{CO}$ , Johns and McKellar estimate that less than  $10^7$  molecules are involved in the transitions they observed, and that  $10^6$  molecules are responsible for the Lamb dips seen.<sup>50</sup> This sensitivity allows detection of weak transitions. The technique is also useful for looking at short-lived molecules such as  $\text{HCO}$ .<sup>37</sup> Because of the sensitivity, sample pressures as low as several mtorr can be used so that the transition linewidth is not broadened by collisions. The resolution of laser Stark spectroscopy is limited only by the Doppler width of the molecule. The laser has enough power to saturate the transition, so that Lamb-dip and level-

Table 1. Molecules which have been studied by laser Stark spectroscopy.

|                               |                     |                                  |        |
|-------------------------------|---------------------|----------------------------------|--------|
| OCS                           | 32, 33 <sup>a</sup> | CH <sub>4</sub>                  | 55     |
| HCN                           | 34                  | CH <sub>3</sub> Br               | 56     |
| FCN                           | 35                  | CH <sub>3</sub> Cl               | 57     |
| D <sub>2</sub> O              | 36                  | CD <sub>3</sub> Cl               | 58     |
| HDO                           | 36                  | CH <sub>3</sub> F                | 59, 60 |
| HCO                           | 37                  | <sup>13</sup> CH <sub>3</sub> F  | 59     |
| NH <sub>3</sub>               | 31, 38-43           | CD <sub>3</sub> F                | 61, 62 |
| <sup>15</sup> NH <sub>3</sub> | 43                  | CD <sub>3</sub> I                | 63, 64 |
| NH <sub>2</sub> D             | 45, 46              | CH <sub>2</sub> F <sub>2</sub>   | 65     |
| PH <sub>3</sub>               | 47                  | SiH <sub>4</sub>                 | 66     |
| H <sub>2</sub> CO             | 48-51               | POF <sub>3</sub>                 | 67     |
| HDCO                          | 52                  | CH <sub>3</sub> OH               | 68     |
| D <sub>2</sub> CO             | 49, 53              | C <sub>2</sub> H <sub>3</sub> Cl | 69     |
| FC≡CH                         | 54                  | CH <sub>2</sub> CF <sub>2</sub>  | 70,71  |

<sup>a</sup>The numbers refer to references in the list at the end of this thesis.

crossing spectroscopy can be done. The linewidth of these transitions may be less than the Doppler width.<sup>58</sup> Lamb-dip studies have enabled Van Stryland and Shoemaker to observe nuclear quadrupole coupling in an excited vibrational state of  $\text{NH}_2\text{D}$ ,<sup>45</sup> with linewidths as small as 700 kHz. As in microwave spectroscopy, the position and intensity of the Stark components can aid in identifying the transitions. And, finally, information is obtained about the dipole moment of both the lower and excited states of the molecule.

A symmetric top such as methylacetylene exhibits predominately a first-order Stark effect. A schematic plot of the energy versus electric field of the  $J = 1$  energy levels of the ground state and an excited vibrational state of a symmetric top molecule is shown in Figure 3. The rotational constants of the upper and lower vibrational levels are different, so the splitting of the lower and upper state energy levels is different. The transitions shown are for the selection rules  $\Delta J = 0$ ,  $\Delta m = -1$ . The difference between an  $m$  level in a lower and upper vibrational state corresponds to the frequency of the transition. It is easily seen that scanning across the electric field strength causes the frequency of the molecular transition to vary. It may be possible to find a particular electric field strength for which the molecular transition frequency equals the laser frequency. The length of the solid vertical lines in the figure correspond to the

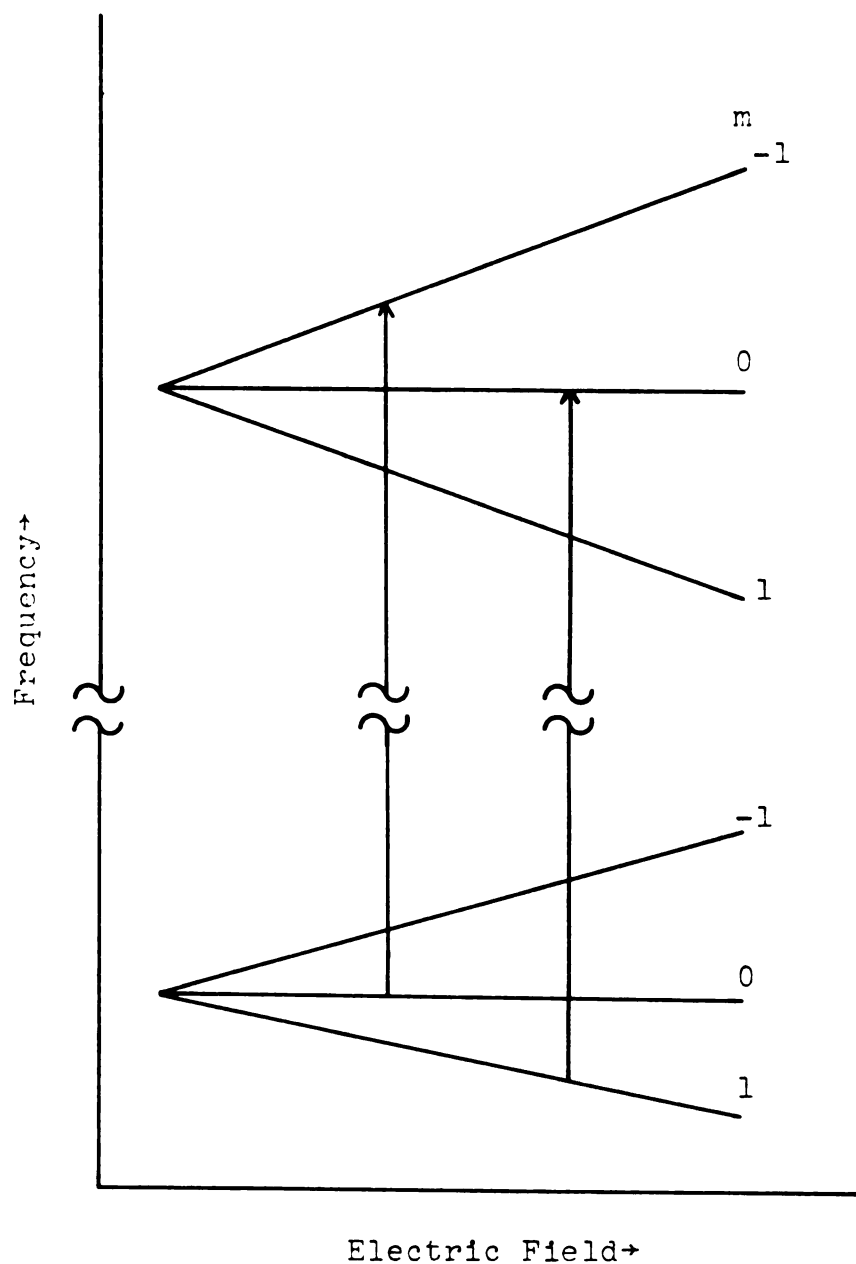


Figure 3. A schematic plot of the energy versus electric field for the  $J=1$  energy levels of the ground state and an excited vibrational state of a symmetric top molecule. The transitions shown are for the selection rules  $\Delta J=0$ ,  $\Delta m=-1$ . The length of the solid vertical lines correspond to the laser frequency.

laser frequency. The difference in electric field strength between the two lines corresponds to the difference in dipole moments of the upper and lower vibrational states. Energy level diagrams of this type may be calculated and drawn for all of the transitions.

Clues such as relative intensity, linewidth, and the sign of  $\partial\nu/\partial\epsilon$  are useful in the assignment of laser Stark transitions. The rules for identifying Stark components are also helpful. When a first-order Stark effect is expected and the  $\Delta m = 0$  selection rule holds,  $m$ -component transitions from the same parent transition usually occur in a series at electric fields proportional to  $m^{-1}$ . In other words, the electric field times the value of  $m$  is equal to a constant for transitions with the same  $J$  and  $k$  quantum numbers. For  $\Delta m = \pm 1$  transitions, patterns are more difficult to see.

Although the absolute intensities of the transitions are difficult to determine experimentally, the relative intensities of the transitions seen with a single laser line can be measured. The relative transition intensity is proportional to the square of the dipole moment matrix element and can be calculated. If the rotational and vibrational motions are assumed to be independent, the component of the electric dipole moment along the molecule-fixed  $x$ -axis can be expressed as<sup>27</sup>

$$\mu_x = \mu_x^0 + \sum_k \left( \frac{\partial \mu_x}{\partial Q_k} \right)_{Q_k=0} Q_k + \dots \quad (56)$$

where  $\mu_x^0$  is the permanent electric dipole moment along the molecule-fixed x-axis and  $Q_k$  is the kth normal coordinate of vibration. The components of the electric dipole moment along the molecule-fixed y and z axes can be expressed in a similar manner. As discussed in the section on the Stark effect, the direction cosines relate the molecule-fixed and space-fixed coordinate systems, so that the dipole moment along the space-fixed axis is written

$$\mu_F = \sum_g \phi_{Fg} \mu_g . \quad (57)$$

If the rotational and vibrational motions are independent, the Hamiltonian can be written  $H = H_r + H_v$ . Thus, the energy can be written in two parts,  $E = E_r + E_v$ , and the wavefunction is expressed as the product of the rotational and vibrational wavefunctions,  $\psi = \psi_r \psi_v$ . The electric dipole moment matrix element is

$$\int \psi'^* \mu_F \psi'' d\tau = \int \psi_v'^* \psi_r'^* \mu_F \psi_r'' \psi_v'' d\tau_r d\tau_v . \quad (58)$$

After substitution of Equation (56) and Equation (57) into Equation (58), the dipole moment matrix element becomes

$$\begin{aligned}
& \sum_g \mu_g^0 \int \psi_r'^* \Phi_{Fg} \psi_r'' d\tau_r \int \psi_v'^* \psi_v'' d\tau_v \\
& + \sum_g \sum_k \int \psi_v'^* \left( \frac{\partial \mu_x}{\partial Q_k} \right)_0 Q_k \psi_v'' d\tau_v \int \psi_r'^* \Phi_{Fg} \psi_r'' d\tau_r . \quad (59)
\end{aligned}$$

This equation has two independent terms;<sup>27</sup> because of the orthonormality of vibrational wave functions in a given electronic state, the first term is for a rotational transition occurring within one vibrational energy state:

$$\sum_g \mu_g^0 \int \psi_r'^* \Phi_{Fg} \psi_r'' d\tau_r . \quad (60)$$

The second term is for a transition between two rotational states, each in a different vibrational state:

$$\sum_g \sum_k \left( \frac{\partial \mu_g}{\partial Q_k} \right)_0 Q_k \int \psi_v'^* \psi_v'' d\tau_v \int \psi_r'^* \Phi_{Fg} \psi_r'' d\tau_r . \quad (61)$$

Equation (61) is of interest in laser Stark spectroscopy, while Equation (60) applies to microwave spectroscopy. The intensities of rotational spectra are proportional to  $(\mu_g^0)^2$ , whereas the intensities of vibration rotation transitions are proportional to  $\left( \frac{\partial \mu_g}{\partial Q_k} \right)^2$ . The laser Stark spectrum generally contains transitions between many rotational energy levels, but only two vibrational levels. Thus the vibrational part of the matrix element is a constant for all the rotational transitions in a particular vibrational band. Therefore, the relative intensities of

the laser Stark transitions are given by the squares of the direction cosine matrix elements and any symmetry considerations. Table 2 shows the contribution of the direction cosine matrix elements to the intensity. Because of the K degeneracy in symmetric top molecules, the transitions arising from the  $K \neq 0$  energy levels must have their intensity contributions from the direction cosines multiplied by 2.

It is useful to know whether the frequency of the laser line lies above or below the zero field frequency of the transition. In other words, is the slope of the transition frequency with respect to the electric field,  $\partial\nu/\partial\epsilon$ , positive or negative? It should, of course, correspond in sign to the experimental slope.

The experimental linewidths can be compared to the calculated linewidth of the transition. An expression for the linewidth is derived in Appendix B. The full width of the line at half height is expressed as

$$\Delta\nu = \left(\frac{2}{\ln 2}\right)^{1/2} \frac{\Delta\nu_D}{(\partial\nu/\partial\epsilon)_\epsilon} \quad (62)$$

where  $\Delta\nu_D$  is the Doppler width of the transition and  $(\partial\nu/\partial\epsilon)_\epsilon$  is the slope, at an electric field value  $\epsilon$ , of the transition frequency plotted against electric field.

Table 2. Contribution of the direction cosine matrix elements to the intensity of a vibration-rotation transition in a symmetric top molecule. All of the intensity contributions shown are for transitions in which  $\Delta K = 0$ . The values for J and M are those of the lower state.

| $\Delta J$ | $\Delta M$ | Square of the Direction Cosine Matrix Element                             |
|------------|------------|---------------------------------------------------------------------------|
| 0          | 0          | $\frac{K^2 M^2}{J^2 (J+1)^2}$                                             |
| 0          | $\pm 1$    | $\frac{K^2 (J \mp m) (J \pm m + 1)}{4 J^2 (J+1)^2}$                       |
| -1         | 0          | $\frac{(J^2 - K^2) (J^2 - M^2)}{J^2 (4 J^2 - 1)}$                         |
| -1         | $\pm 1$    | $\frac{(J^2 - K^2) (J \mp m) (J \mp m - 1)}{4 J^2 (4 J^2 - 1)}$           |
| +1         | 0          | $\frac{(J+k+1)(J-k+1)(J+m+1)(J-m+1)}{(J+1)^2 (2J+1)(2J+3)}$               |
| +1         | $\pm 1$    | $\frac{(J+k+1)(J-k+1)(J \pm m + 1)(J \pm m + 2)}{4 (J+1)^2 (2J+1)(2J+3)}$ |

<sup>a</sup>P. C. Cross, R. M. Hainer, and G. C. King, J. Chem. Phys., 12, 210 (1944).

### Lamb Dip

At the very low pressures used in laser Stark spectroscopy, the transition linewidth is due mainly to Doppler broadening. This type of broadening occurs because molecules traveling at different velocities absorb radiation corresponding to a particular transition at slightly different frequencies. The gas molecules do not all travel at the same velocity, but rather a Maxwell velocity distribution exists. The molecular velocity vectors can be thought of as having two components, one parallel to the propagation of the laser radiation in the  $z$  direction and another component perpendicular to it. Since the molecules are moving with respect to the incident radiation, the frequency at which the molecule appears to absorb will be Doppler shifted by an amount  $\pm \frac{v_z}{c}$ , where  $v_z$  is the molecular velocity component in the  $z$  direction. Each group of molecules with velocity  $v_1$  will then absorb radiation centered about either  $\nu_0 + \frac{v_{1z}}{c}$  or  $\nu_0 - \frac{v_{1z}}{c}$  depending whether the molecule is traveling toward or away from the radiation, respectively. When the narrow Lorentzian lineshapes of each velocity group are superimposed, an inhomogeneous Doppler-broadened lineshape is the result. In the infrared region, the Doppler broadening is tens of megahertz. Under certain conditions, a narrow dip can be seen in the center of a Doppler broadened lineshape. These "Lamb dips" may occur in atomic as well as molecular gas systems. They

were first observed<sup>73,74</sup> in 1963 and were named after Willis E. Lamb who investigated the dips mathematically.<sup>75</sup>

For a Lamb dip to occur, the sample must be simultaneously irradiated from both the forward and reverse directions. These conditions occur inside a laser cavity. The sample gas may also be placed in a cell outside the laser cavity. In this case, a mirror is placed at the end of the sample cell so the laser radiation traverses the sample cell and is reflected back through the sample cell by the mirror.

The Lamb dip is a saturation effect of an inhomogeneously broadened line. Saturation occurs when the power of the radiation is so high that the molecules absorb power and undergo a transition to an excited state at a faster rate than they can return to the lower state by means of available relaxation processes. Thus, the population difference between the two states becomes smaller than it would be at thermal equilibrium. As there are now fewer molecules available in the lower state to absorb the radiation and more in the upper state to emit radiation, the intensity of the peak decreases.

When monochromatic radiation of high power traverses forward and back through the sample cell, those molecules in the velocity group  $v_z = 0$  (those molecules traveling perpendicular to the direction of the propagation of the radiation) will be saturated by both radiation beams.

Therefore, the incident power appears doubled to this velocity group and these molecules will experience more saturation than the rest of the molecules in the sample. Thus a dip appears in the lineshape as shown in Figure 4. Furthermore, because molecules with a velocity component  $v_z = 0$  absorb radiation at frequency  $\nu_0$ , the center frequency of the transition, the Lamb dip will appear at the center frequency of the transition.

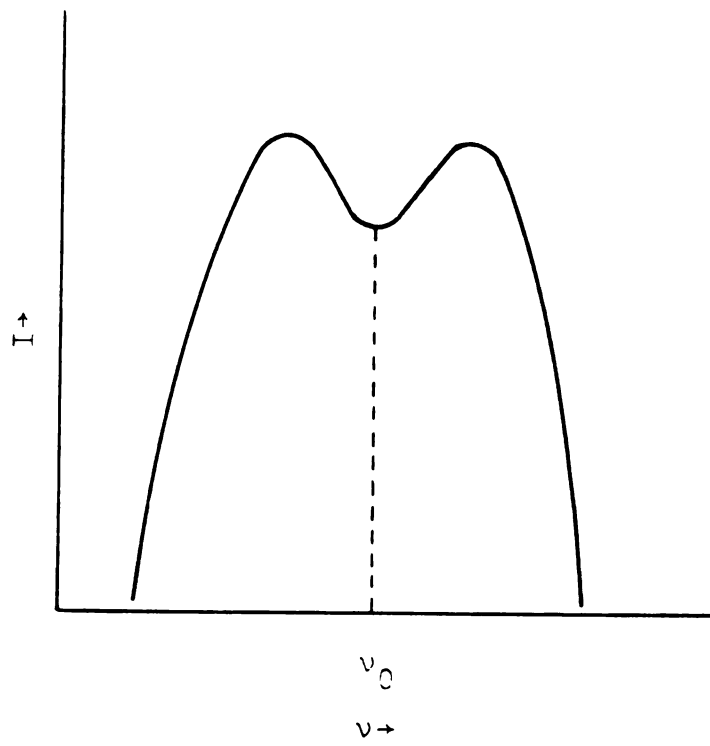


Figure 4. Lamb dip, centered at the transition frequency  $\nu_0$ .

## CHAPTER III

### EXPERIMENTAL

#### Methylacetylene

The methylacetylene was purchased from the Linde Division of Union Carbide Corporation, New York, NY. An infrared spectrum of the sample was obtained which showed some acetylene to be present. After vacuum distillation, the very strong  $730\text{ cm}^{-1}$  line of acetylene could no longer be seen in the methylacetylene infrared spectrum. Even so, the  $\nu_5$  vibrational band of methylacetylene studied absorbs at about  $930\text{ cm}^{-1}$ ; acetylene does not absorb between about  $825$  and  $1200\text{ cm}^{-1}$ . The infrared spectra of methylacetylene and acetylene have been published.<sup>76</sup>

#### Microwave Experiment

##### Equipment

The Hewlett Packard MRR spectrometer used to take the microwave measurements is described in Part II of this thesis.

## Procedure

Ground State Methylacetylene Dipole Moment - Rather than measuring the voltage and the spacing between the electrodes each time a dipole moment is to be obtained, a molecule with a well-known dipole moment is used to calibrate the field. In the R band where the methylacetylene spectrum was obtained, OCS is generally used as the calibrant.

Second-order Stark shifts of the  $J = 3 \leftarrow 2$  transition of OCS and the  $J = 2 \leftarrow 1$  transition of methylacetylene were obtained at five different fields with a sample which contained approximately 50% OCS and 50%  $\text{CH}_3\text{C}\equiv\text{CH}$ . The frequencies of the OCS transitions at one electric field setting were measured. Then, without changing the field, the frequencies of the methylacetylene transitions were obtained. The field was changed and the next set of OCS and methylacetylene frequencies were obtained, and so on.

Excited State Methylacetylene Dipole Moment - The first-order Stark shifts of the  $J = 2 \leftarrow 1$  transitions of methylacetylene in the ground state and  $\nu_5 = 1$  excited vibrational state were obtained at 15 different fields. The sample contained pure methylacetylene. Again, all of the ground state and excited state transition frequencies were obtained at one field setting; then, the field setting was

changed and the next group of transition frequencies were measured.

## Laser Stark Experiment

### Equipment

In the laser Stark experiments, a  $\text{CO}_2$  or  $\text{N}_2\text{O}$  plane-polarized laser beam was passed between parallel electrodes inside a sample cell and onto an infrared detector. A block diagram of the apparatus is shown in Figure 5. A discussion of the laser used in this experiment can be found in Appendix C.

Stark Electrodes - The sample cell contains two parallel electrodes. These electrodes are nickel plates, 40 cm long, 5 cm wide, and 2.5 cm thick. The plates are flat to better than  $\pm 0.5$  microns, and all the edges and corners are rounded. Five quartz spacers, one-quarter inch in diameter, are used to separate the electrodes. The spacers are about 1 mm thick and were ground to be flat, parallel and of equal thickness to within  $\pm 0.2$  microns. The Stark plates and spacers are surrounded on four sides by glass plates. There are no glass plates on the two sides where the laser beam enters and exits the sample cell. The electrodes are held in an aluminum cradle which rests on the bottom of the sample cell.

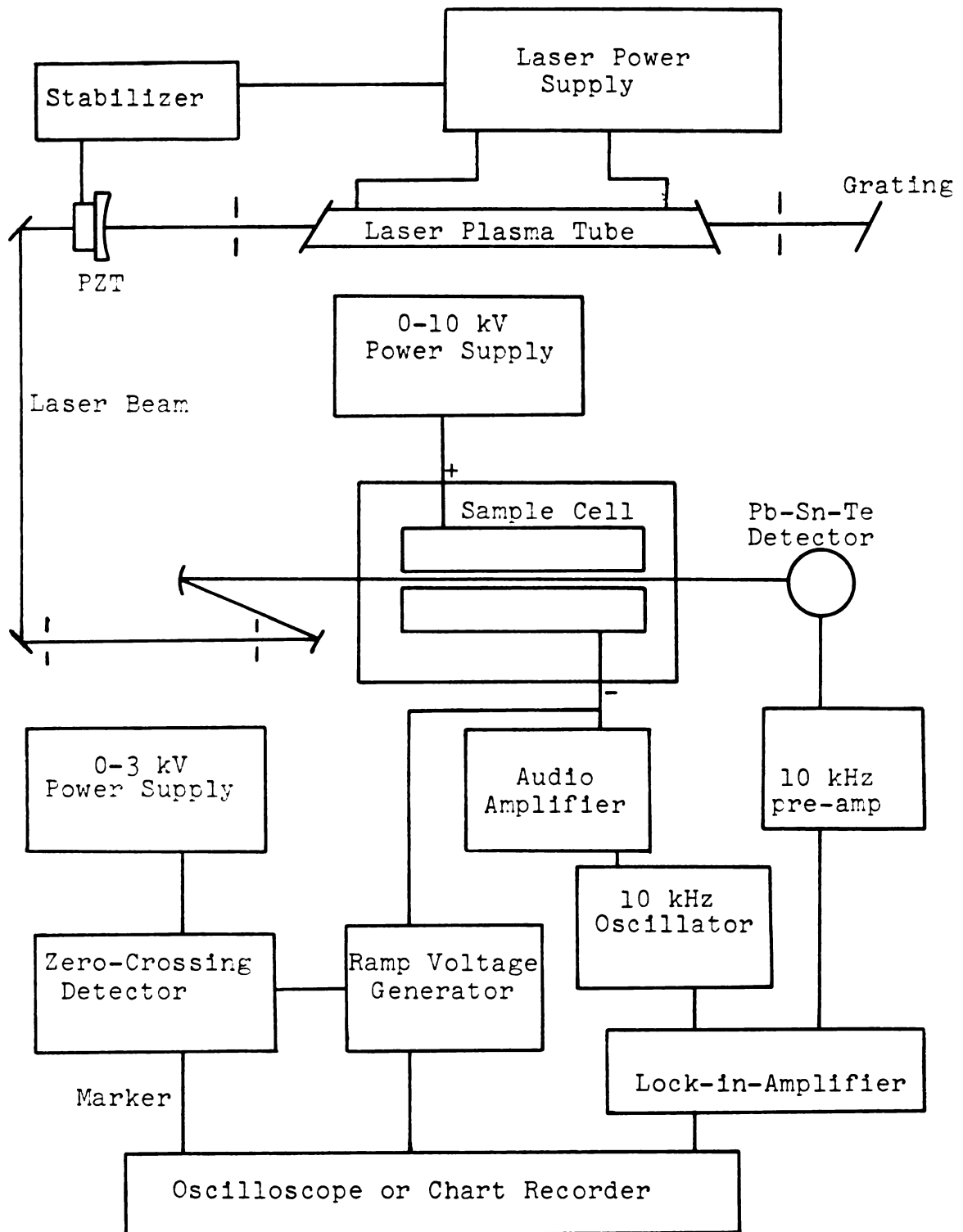


Figure 5. Block diagram of the laser Stark spectrometer.

Sample Cell - The sample cell is a six inch diameter glass "T", the outside of which is covered with wire mesh. Aluminum plates are clamped to the three openings of the cell. Large rubber gaskets are used between the metal and glass. The two side plates have holes in the center, covered with NaCl windows, to pass the laser light. The top plate contains the gas inlet and exit, electrical connections for the electrodes, and a Hastings DV-6M pressure gauge. Inside the cell, about one foot of #20 braided wire connects a separate high voltage bnc connector on the cover plate to each electrode. A brass plug was soldered to one end of each wire. This plug was inserted snugly into a hole in the electrode to make electrical contact. The end of the high voltage, high vacuum bnc adaptor was covered with heat shrink teflon tubing, and the whole length of the wire was covered with teflon tubing to help eliminate electrical discharge upon application of high voltage.

Assembly of the Sample Cell - When the sample cell is assembled, everything must be very clean. Any dust, grease, or fingerprints may cause discharge paths to form under application of high voltage. Care must be taken not to scratch the surface of the Stark plates. To assemble the Stark plates, the cradle is laid on its side, with the five screws on top. Two pieces of glass and an electrode are

set in the cradle. A drop of methanol is placed directly beneath each screw and a spacer is placed on each methanol drop. This procedure floats away minute particles of dust. A drop of methanol is placed on top of each spacer and the other electrode is eased on. Another glass plate is placed on the electrode. A piece of 2 mm thick teflon is placed between each screw tip and the glass plate. The five screws are tightened to hold the assembly together.

Electronics - A block diagram of the laser Stark spectrometer is shown in Figure 5. A high voltage Fluke Model 410B power supply applies a DC voltage to one of the electrodes. This voltage can be changed in varying steps from 0 to 10,000 volts and is stable to  $\pm 0.005\%$  per hour after warm up and to  $\pm 0.02\%$  per day. A ramp voltage is applied to the other electrode by a Kepco Model 2000 operational power supply (OPS). The width of the ramp can be varied from 0 to 1500 volts. A Wavetek Model 112 function generator is used to drive the ramp output of the OPS. The ramp voltage and the voltage from another high voltage power supply, a Fluke Model 412B, are compared in a zero-crossing detector circuit. The large voltages of the OPS and Fluke 412B power supply are reduced in magnitude by five 200 k $\Omega$  resistors. For calibration purposes, the 20 k $\Omega$  potentiometer shown in Figure 6 is set so that the resistance across the OPS equals the resistance across the

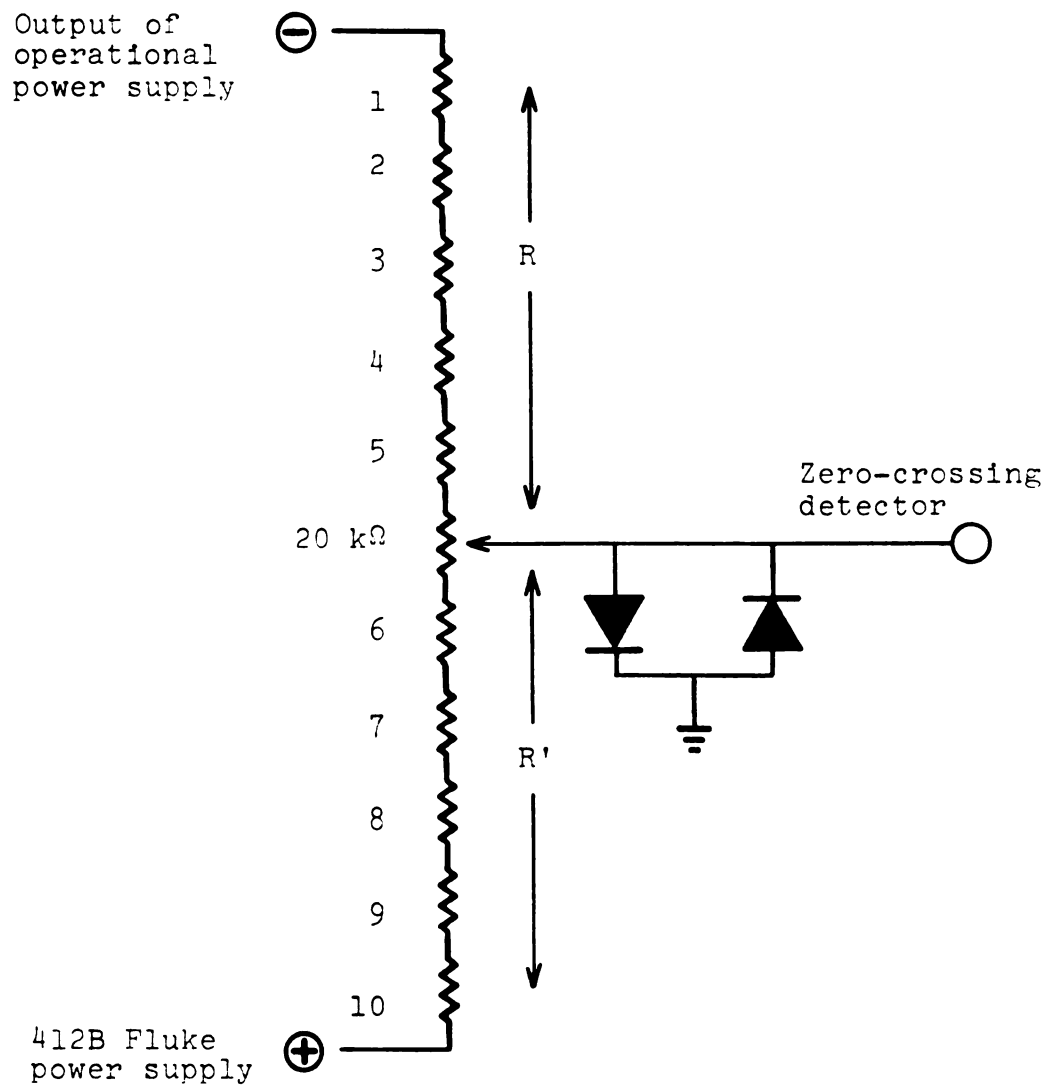


Figure 6. Schematic diagram of the circuit used to protect the zero-crossing detector. The ten numbered resistors are 200 kΩ each.

Fluke 412B power supply when their voltages are equal in magnitude (but opposite in sign). For good precision, the 200 k $\Omega$  resistors have low and equal temperature variation. The two diodes keep the voltage entering the zero-crossing detector within the range of  $\pm 0.5$  volts to protect it. When the output voltage of the OPS equals the Fluke 412B voltage, a marker is generated. It is possible to change the time width of the marker. If this is done, the zero difference of the voltages is at the leading edge of the marker. The field across the electrodes at the time of a marker can be obtained from the sum of the voltage settings of the Fluke 410B and the Fluke 412B power supplies.

An amplified 10 kHz sine wave voltage from a Hewlett Packard Model 651A Test Oscillator is used to modulate the ramp voltage. The sine wave voltage is amplified by a Bogen Sound Systems Model DB10 audio amplifier. A Cal-electro Corporation G. C. Electronics transformer steps up the voltage from the audio amplifier.

The laser beam is detected by a Barnes Pb-Sn-Te photovoltaic detector. The output voltage of the detector is amplified by a 10 kHz tuned amplifier. A Keithley Model 840 Autoloc Amplifier is used as a phase sensitive detector. The output is seen as a first derivative line-shape on an oscilloscope or chart recorder.

Polarization of Laser Light - The infrared radiation leaving the laser is plane polarized with its electric vector parallel to the floor. Since the electric field across the Stark electrodes is also parallel to the floor, spectra with the selection rule  $\Delta m = 0$  can be observed. To observe spectra under the selection rule  $\Delta m = \pm 1$ , the polarization of the electric vector of the radiation must be perpendicular to the electric field between the Stark plates. The electric vector of the laser light can be rotated  $90^\circ$  by reflection between two appropriately placed mirrors. This mirror configuration is shown in Figure 7. The net movement of the laser beam is to raise the beam up and to turn a corner  $90^\circ$ .

### Procedure

#### Alignment of the CO<sub>2</sub> Laser Beam Through the Sample

Cell - A He-Ne laser is used to help in the positioning of mirrors to send the infrared laser light through the sample cell. The two irises within the CO<sub>2</sub> laser should be positioned in the apparent center of the plasma tube. The position of the CO<sub>2</sub> beam varies slightly, depending upon which laser line is oscillating and whether or not it is oscillating at the top of its gain profile. Thus, the conditions for the particular CO<sub>2</sub> laser line must be optimized.

If none of the mirrors in Figure 8 are in position

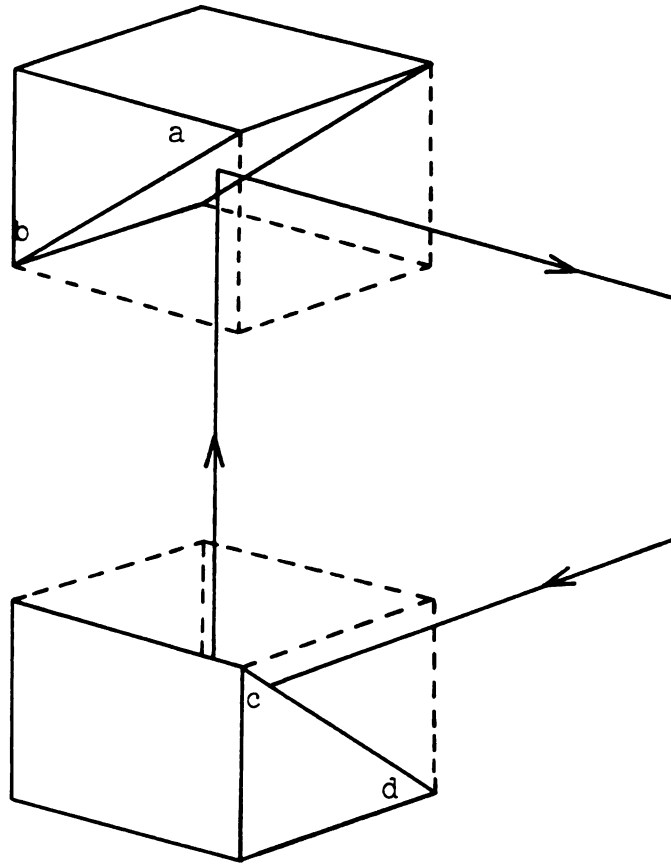


Figure 7. The appropriate mirror configuration to rotate by  $90^\circ$  the electric vector of the laser radiation. The two cubes, shown by the solid and dotted lines lie directly above one another. The angles  $a$ ,  $b$ ,  $c$ , and  $d$  are each  $45^\circ$ . The arrows show the direction of the beam.

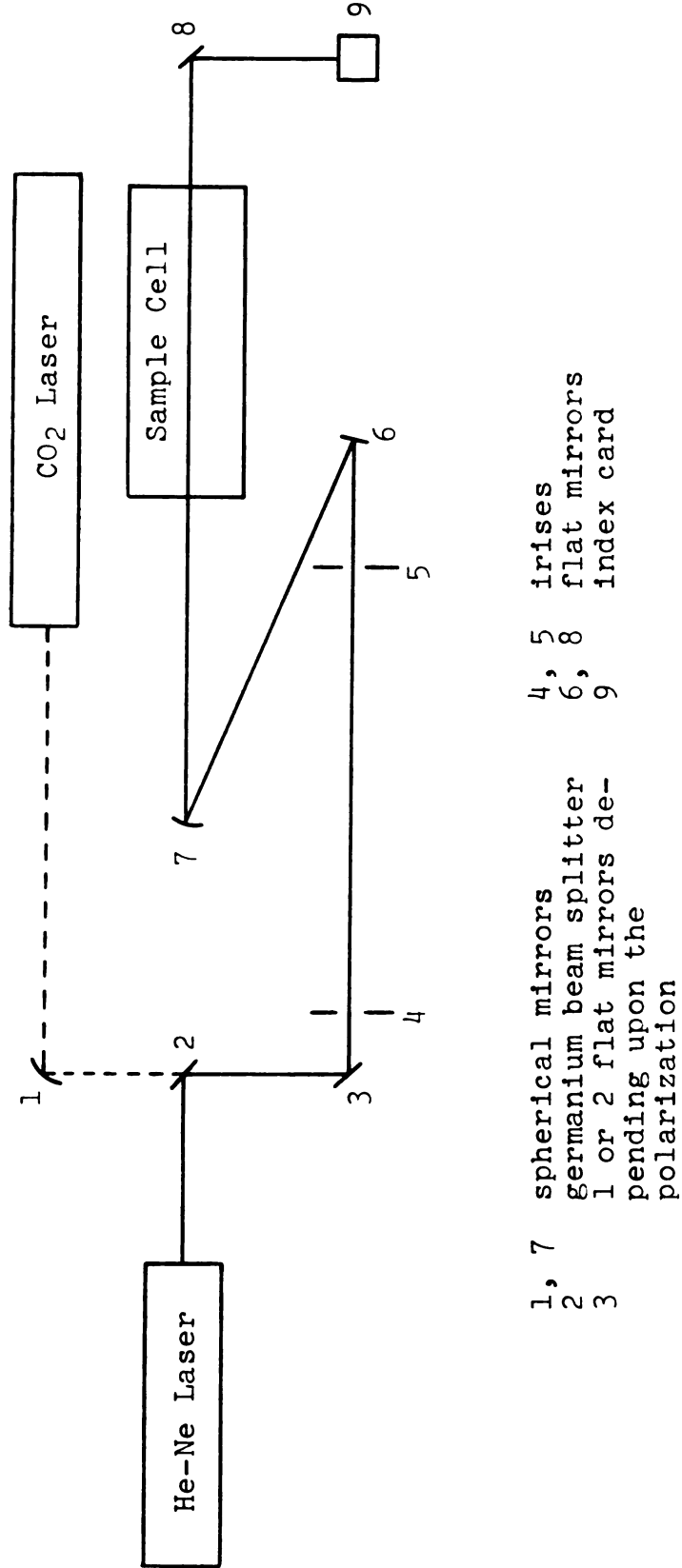


Figure 8. Arrangement of the optics for the laser Stark spectrometer.

yet, mirror 3 is replaced by an iris and an infrared detector is placed behind it. The position of the He-Ne laser is adjusted until its beam is superimposed upon the CO<sub>2</sub> laser beam. The He-Ne laser beam can now be used to position the mirrors and irises in Figure 8. With the exception of mirror 8, all irises and mirrors should be mounted on translation stages and secured to the table. (Room should be saved to place a detector between iris 5 and mirror 6.)

Alignment of the CO<sub>2</sub> beam through the sample cell is begun by placing a detector between iris 5 and mirror 6. The two irises are centered about the CO<sub>2</sub> beam and the position of the He-Ne laser is adjusted until its beam is colinear with the CO<sub>2</sub> laser beam. The detector is removed and a mirror is placed at position 8. Mirrors 6 and 7 are adjusted until the He-Ne beam passes through the sample cell and makes one small symmetric spot on the index card, 9. Mirror 8 is replaced by a detector. The CO<sub>2</sub> laser beam should pass through the sample cell and strike it.

### Calibration of the Plate Spacing

The quartz spacers in our sample cell were ground at the same time, so they would be the same thickness. Since the plate spacing may change slightly each time the plates are put together, the plate separation must be determined each time this happens. The resonant voltages of Lamb

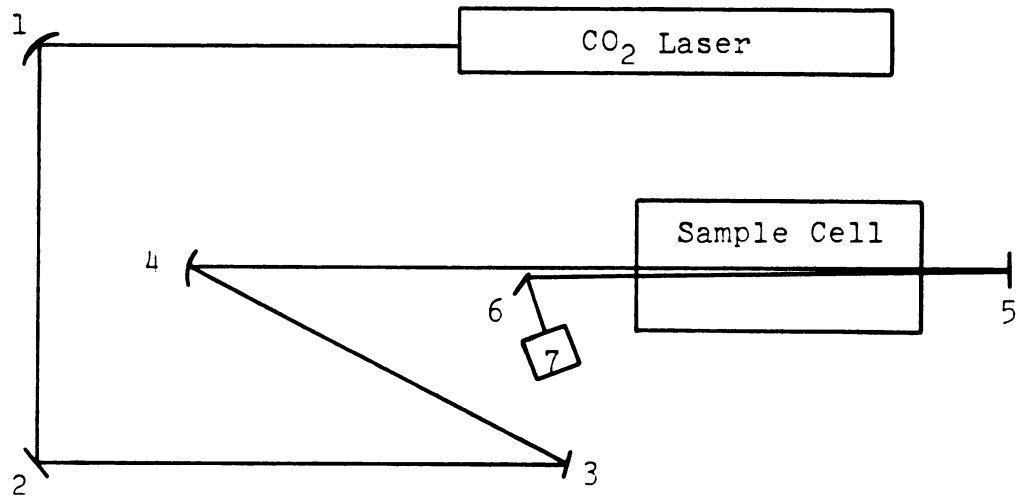
dips observed for several lines of methylfluoride were measured and compared to voltages obtained by Freund, et al.<sup>59</sup> The transitions compared were a doublet and a quartet which absorb the P(18) line of the 9.6  $\mu$  band of the CO<sub>2</sub> laser when the electric vector of the radiation is aligned to be perpendicular to the electric field. These transitions and the voltages obtained by Freund, et al. are given in Table 3. The average of the ratio of our voltage to the voltage of Freund, et al. for the above six transitions was then multiplied by their reported plate spacing of 0.1002851 cm to obtain our plate spacing.

In order to obtain these voltages to the accuracy required, the technique of Lamb dip spectroscopy was employed. The mirrors and detector were set as shown in Figure 9. In this arrangement, the path of the returning beam was about 3 mm below the incoming beam so that it could be reflected from the edge of a flat rectangular mirror into the detector. The modulation voltage was very low, about 3 volts out of the audio amplifier. With the irises wide open to saturate the transition, a dip was seen in the CH<sub>3</sub>F transition. Because of the small amplitude Stark modulation, the dip appeared as a first derivative lineshape that was 180° out of phase with respect to the main transition. Figure 10 shows Lamb dips for the  $J = 1 \leftarrow 1$ ,  $k = 1 \leftarrow 1$ ,  $m = -1 \leftarrow 0$  and  $m = 0 \leftarrow 1$  transitions of CH<sub>3</sub>F.

Table 3. The resonant voltages of several transitions of methylfluoride measured by Freund, et al.<sup>a</sup> These transitions were used to calibrate the plate spacing. For these transitions  $\Delta k=0$ .

| Voltage | Quantum Numbers |       |     |      |       |
|---------|-----------------|-------|-----|------|-------|
|         | $J'$            | $J''$ | $k$ | $m'$ | $m''$ |
| 444.82  | 1               | 1     | 1   | -1   | 0     |
| 459.96  | 1               | 1     | 1   | 0    | 1     |
| 1019.13 | 2               | 2     | 2   | -2   | -1    |
| 1050.75 | 2               | 2     | 2   | -1   | 0     |
| 1084.12 | 2               | 2     | 2   | 0    | 1     |
| 1119.29 | 2               | 2     | 2   | 1    | 2     |

<sup>a</sup>S. M. Freund, G. Duxbury, M. Römheld, J. T. Tiedje and T. Oka, J. Mol. Spectrosc. 52, 38 (1974).



- 1, 4 spherical mirrors
- 2 1 or 2 mirrors depending upon polarization
- 3, 5 flat mirrors
- 6 flat rectangular mirror
- 7 detector

Figure 9. Arrangement of the optics for Lamb dip spectroscopy.

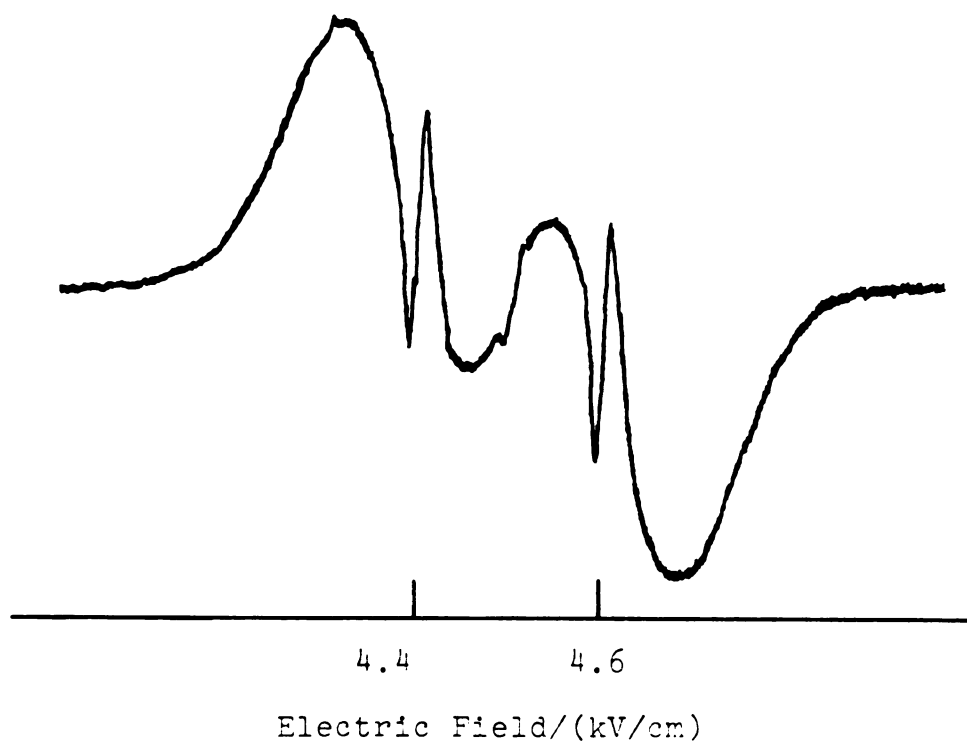


Figure 10. Lamb dips for the  $J=1 \leftarrow 1$ ,  $k=1 \leftarrow 1$ ,  $m=-1 \leftarrow 0$  and  $m=0 \leftarrow -1$  transitions of  $\text{CH}_3\text{F}$ .

## CHAPTER IV

### RESULTS AND DISCUSSION

#### Microwave Spectrum

##### Ground State Rotational Constant, B"

The frequency of a microwave transition in a symmetric top molecule in a vibrational state of A symmetry is

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2, \quad (63)$$

where J is the angular momentum value of the lower state. For a  $J = 2 \leftarrow 1$  transition, this equation becomes

$$\nu = 4B - 32 D_J - 4D_{JK}K^2. \quad (64)$$

Since the centrifugal distortion constants are known, the ground state B rotational constant can be calculated and is shown in Table 4.

##### $\nu_5$ Excited State Rotational Constant, B'

A microwave spectrum of methylacetylene was taken between 33800 and 34550 MHz. Table 5 lists the frequencies of those lines which were assigned. It was of

Table 4. The calculated ground state B rotational constant of methylacetylene.

| K | $\nu$ /MHz | $B''$ /MHz               | avg $B''$ /MHz | Other $B''$           |
|---|------------|--------------------------|----------------|-----------------------|
| 0 | 34183.413  | 8545.877(1) <sup>b</sup> | 8545.877       | 8545.877 <sup>a</sup> |
| 1 | 34182.762  | 8545.877(1) <sup>b</sup> |                |                       |

based on  $D_J'' = 0.00298^a$  MHz

$D_{JK}'' = 0.1629^a$  MHz

<sup>a</sup>C. A. Burrus and W. Gordy, J. Chem. Phys. 26, 391 (1957).

<sup>b</sup>The number in parenthesis shows the error of the last significant figure.

Table 5. Microwave transitions of methylacetylene. All these transitions are  $J = 2 \leftarrow 1$  and  $\Delta K = 0$ .

| $\nu$ /MHz | Assignment                                    |
|------------|-----------------------------------------------|
| 34031.7    | $\nu_5=1 \quad K=1$                           |
| 34032.3    | $\nu_5=1 \quad K=0$                           |
| 34168.6    | $\text{CH}_3^{13}\text{CCH} \quad K=1^a$      |
| 34169.1    | $\text{CH}_3^{13}\text{CCH} \quad K=0^a$      |
| 34182.7    | $K=1^a$                                       |
| 34183.3    | $K=0^a$                                       |
| 34187.2    | $\nu_9=1 \quad K=\pm 1 \quad \ell=\mp 1^b$    |
| 34202.9    | $\nu_9=1 \quad K=\pm 1 \quad \ell=\pm 1^b$    |
| 34204.1    | $\nu_9=1 \quad K=0 \quad \ell=\pm 1^b$        |
| 34223.3    | $\nu_9=1 \quad K=\pm 1 \quad \ell=\mp 1^b$    |
| 34246.2    | $\nu_{10}=1 \quad K=\pm 1 \quad \ell=\mp 1^a$ |
| 34277.1    | $\nu_{10}=1 \quad K=\pm 1 \quad \ell=\pm 1^a$ |
| 34279.1    | $\nu_{10}=1 \quad K=0 \quad \ell=\pm 1^a$     |
| 34313.3    | $\nu_{10}=1 \quad K=\pm 1 \quad \ell=\mp 1^a$ |
| 34386.9    | $\nu_4=1 \quad K=\pm 1$                       |
| 34387.8    | $\nu_4=1 \quad K=0$                           |

<sup>a</sup>R. Trambarulo and W. Gordy, J. Chem. Phys. 18, 1613 (1950).

<sup>b</sup>Frequency difference between  $K=\ell=\pm 1$  lines  $\sim 2q(J+1)$  where where  $q \sim 2B^2/\omega$ .

particular interest to identify the vibrationally excited  $\nu_5$   $J = 2 \leftarrow 1$  line. The intensity of a vibrationally excited transition relative to the corresponding ground state transition, is given by

$$\frac{I_{\text{ex}}}{I_{\text{gr}}} = \frac{g_{\text{ex}}}{g_{\text{gr}}} e^{-\Delta E/k_B T}, \quad (65)$$

where  $g_{\text{ex}}$  is the degeneracy of the excited state,  $g_{\text{gr}}$  is the degeneracy of the ground state,  $\Delta E$  is the energy difference between the vibrationally excited state and the ground vibrational state,  $k_B$  is Boltzmann's constant, and  $T$  is the absolute temperature. Table 6 lists the intensities of the rotational transitions in the vibrational excited states relative to the ground state. The  $\nu_5$  excited state transition is about 100 times less intense than the ground state. However, transitions of methylacetylene with one  $^{13}\text{C}$  are also 100 times less intense than the species with only  $^{12}\text{C}$ . To be certain that the transition assigned to  $\nu_5$  was not one due to methylacetylene with  $^{13}\text{C}$ , the spectrum was taken under dry ice conditions. The relative intensity of the  $^{13}\text{C}$  peaks remained the same, while the relative intensities of peaks due to excited vibrational states decreased. The frequencies of the rotational transitions in the  $\nu_5$  excited state were found to be as follows:

Table 6. Intensities of the rotational transitions in the vibrational excited states relative to the ground state.

| Vibrationally<br>Excited State | $\Delta E/\text{cm}^{-1}\text{a}$ | $\frac{I_{\text{ex}}}{I_{\text{gr}}}$ |
|--------------------------------|-----------------------------------|---------------------------------------|
| $\nu_1$                        | 3335.1                            | $1 \times 10^{-7}$                    |
| $\nu_2$                        | 2941                              | $7 \times 10^{-7}$                    |
| $\nu_3$                        | 2142                              | $3 \times 10^{-5}$                    |
| $\nu_4$                        | 1390.6                            | $1 \times 10^{-3}$                    |
| $\nu_5$                        | 930.1                             | $1 \times 10^{-2}$                    |
| $\nu_6$                        | 2980.8                            | $1 \times 10^{-8}$                    |
| $\nu_7$                        | 1450.9                            | $2 \times 10^{-3}$                    |
| $\nu_8$                        | 1036.0                            | $1 \times 10^{-2}$                    |
| $\nu_9$                        | 638.6                             | $1 \times 10^{-1}$                    |
| $\nu_{10}$                     | 329.2                             | $4 \times 10^{-1}$                    |

<sup>a</sup>T. Shimanouchi, N5RDS-NBS 39, Tables of Molecular Vibrational Frequencies Consolidated Volume I. (U.S. Government Printing Office, 1972.)

<sup>b</sup> $T = 298^\circ\text{K}.$

$$J = 1 \leftarrow 0 \quad K = 0 \quad \nu = 17016.231 \text{ MHz}$$

$$J = 2 \leftarrow 1 \quad K = 0 \quad \nu = 34032.416 \text{ MHz}$$

$$J = 2 \leftarrow 1 \quad K = 1 \quad \nu = 34031.744 \text{ MHz.}$$

Theoretical expressions for these transitions are as follows:

$$J = 1 \leftarrow 0 \quad K = 0 \quad \nu = 2B - 4D_J$$

$$J = 2 \leftarrow 1 \quad K = 0 \quad \nu = 4B - 32 D_J$$

$$J = 2 \leftarrow 1 \quad K = 1 \quad \nu = 4B - 32 D_J - 4D_{JK}.$$

By the appropriate combination of these equations, the  $\nu_5$  vibrationally excited state  $B$ ,  $D_J$ , and  $D_{JK}$  are calculated to be:

$$B_5 = 8508.119 \pm 0.003 \text{ MHz}$$

$$D_J^{(5)} = 1.8 \pm 0.2 \text{ kHz}$$

$$D_{JK}^{(5)} = 169 \pm 1 \text{ kHz.}$$

#### Ground State Methylacetylene Dipole Moment

Tables 7 and 8 contain the second-order Stark shifts for OCS and  $\text{CH}_3\text{C}\equiv\text{CH}$ . The Stark voltage was found to differ from the voltage indicated on the dial by an amount that was not constant as a function of dial reading. The

Table 7. Frequencies (MHz) of M components of the J=3+2 transition in OCS measured as a function of dial setting on the H. P. spectrometer.<sup>a,b</sup>

| Dial Setting<br>(volts) | M = 0     |               | M = 1     |               | M = 2     |               |
|-------------------------|-----------|---------------|-----------|---------------|-----------|---------------|
|                         | $\nu$     | $\Delta\nu^c$ | $\nu$     | $\Delta\nu^c$ | $\nu$     | $\Delta\nu^c$ |
| 800                     | 36488.068 | -0.745        | 36488.603 | -0.210        | 36490.208 | 1.395         |
| 1000                    | 36487.670 | -1.143        | 36488.492 | -0.321        | 36490.953 | 2.140         |
| 1200                    | 36487.192 | -1.621        | 36488.357 | -0.456        | 36491.847 | 3.034         |
| 1400                    | 36486.635 | -2.178        | 36488.203 | -0.610        | 36492.896 | 4.083         |
| 1600                    | 36486.002 | -2.811        | 36488.025 | -0.788        | 36494.076 | 5.263         |

<sup>a</sup>The measured zero-field frequency for the transition is 36488.813±0.005 MHz.

<sup>b</sup>The estimated uncertainty in the measured frequencies relative to the zero-field frequency is ±0.005 MHz.

<sup>c</sup> $\Delta\nu$  is the difference in MHz between the measured frequency in the field and in zero field.

Table 8. Frequencies (MHz) of M components of the J=2+1 transition in  $\text{CH}_3\text{C}\equiv\text{CH}$  measured as a function of dial setting on the H. P. spectrometer.<sup>a,b</sup>

| Dial Setting<br>(Volts) | K = 0, M = 0 |               | K = 0, M = 1 |               |
|-------------------------|--------------|---------------|--------------|---------------|
|                         | $\nu$        | $\Delta\nu^c$ | $\nu$        | $\Delta\nu^c$ |
| 800                     | 34179.596    | -3.817        | 34186.514    | 3.101         |
| 1000                    | 34177.573    | -5.840        | 34188.161    | 4.748         |
| 1200                    | 34175.145    | -8.268        | 34190.134    | 6.721         |
| 1400                    | 34172.322    | -11.091       | 34192.447    | 9.034         |
| 1600                    | 34169.084    | -14.329       | 34195.067    | 11.654        |

<sup>a</sup>The measured zero-field frequency for the transition is 34183.413±0.005 MHz.

<sup>b</sup>The estimated uncertainty in the measured frequencies relative to the zero-field frequency is ±0.005 MHz.

<sup>c</sup> $\Delta\nu$  is the difference in MHz between the measured frequency in the field and in zero field.

variation of the Stark voltage is discussed in Appendix A. Since the OCS and  $\text{CH}_3\text{C}\equiv\text{CH}$  frequencies were measured at exactly the same field, the square of the field was calculated from Equation (44), the second-order Stark shift equation for a linear molecule, by using the OCS Stark shifts and the known OCS dipole moment of 0.71519 D.<sup>77</sup> These results are given in Table 9. The  $M = 1$  Stark lobe of OCS was not included since the line is asymmetric, due to its proximity to the zero-field line. The asymmetry of the line makes the determination of its center frequency difficult and uncertain.

A second-order Stark shift with higher order corrections can be expressed as

$$\Delta\nu = A_D\mu_D^2\epsilon^2 + B_D\mu_D^4\epsilon^4 + \dots \quad (66)$$

where  $\epsilon$  is the electric field and  $A_D$  and  $B_D$  are constants. After dividing by  $A_D\epsilon^2$ , the equation becomes,

$$\frac{\Delta\nu}{A_D\epsilon^2} = \mu_D^2 + \frac{B_D\mu_D^4\epsilon^2}{A_D} \quad (67)$$

Plotting  $\Delta\nu/A_D\epsilon^2$  versus  $\epsilon^2$  yields a straight line with  $\mu_D^2$  as the intercept. To obtain the methylacetylene dipole moment, the fields calculated from the OCS  $M = 0$  transitions were averaged with the fields calculated from the OCS  $M = 2$  transitions. The methylacetylene Stark shifts were

Table 9. Calculated value of the electric field determined from the OCS second-order Stark shifts.

| Dial Setting<br>(Volts) | M = 0                  |                                | M = 2                  |                                |
|-------------------------|------------------------|--------------------------------|------------------------|--------------------------------|
|                         | $\Delta\nu/\text{MHz}$ | $\epsilon^2/(\text{kVolt/cm})$ | $\Delta\nu/\text{MHz}$ | $\epsilon^2/(\text{kVolt/cm})$ |
| 800                     | - .745                 | 2.752                          | 1.395                  | 2.749                          |
| 1000                    | -1.143                 | 4.223                          | 2.140                  | 4.216                          |
| 1200                    | -1.621                 | 5.988                          | 3.034                  | 5.978                          |
| 1400                    | -2.178                 | 8.046                          | 4.083                  | 8.045                          |
| 1600                    | -2.811                 | 10.384                         | 5.263                  | 10.369                         |

used for  $\Delta\nu$ , and  $A_D$  was calculated from Equation (44), the equation for the second-order Stark shift. The pairs of  $\Delta\nu/A_D\epsilon^2$  versus  $\epsilon^2$  were fit by the method of least squares to a straight line for the  $K = 0, M = 0$  Stark shifts and for the  $K = 0, M = 1$  Stark shifts of methylacetylene. Thus, the methylacetylene ground state dipole moments for the  $J = 2 \leftarrow 1$  transitions were:

for  $K = 0, M = 0, \mu_D = 0.78395 \text{ D};$

for  $K = 0, M = 1, \mu_D = 0.78381 \text{ D}$

with the average dipole moment equal to  $0.7839 \pm 0.0010 \text{ D}$ . This may be compared to  $\mu_D = 0.7840 \pm 0.0023 \text{ D}$  derived from the value found by Muentner and Laurie<sup>4</sup> after correction for the more recent value of the dipole moment of OCS.<sup>77</sup>

#### The Dipole Moment of Methylacetylene in the $\nu_5$ Excited State

First-order Stark effect frequencies for the ground state and the  $\nu_5 = 1$  excited state of the  $k = \pm 1, m = \pm 1$  and  $k = \pm 1, m = \mp 1$  transitions of methylacetylene are shown in Table 10. The transitions in a Stark field,  $\epsilon$ , are found at frequencies of

$$\nu = \nu_0 - \frac{km}{J(J+1)} (\mu_D \epsilon) = \nu_0 - \frac{\mu_D km}{J(J+1)} \left( \frac{V}{S} \right), \quad (68)$$

Table 10. First-order Stark effect frequencies (MHz) for the ground state and the  $\nu_5$  excited state of the  $k=1$ ,  $m=1$  and  $k=1$ ,  $m=1$  components of the  $J=2+1$  transitions of methylacetylene.

| Dial Setting<br>(Volts) | Ground State Frequencies |               | $\nu_5$ Excited State Frequencies |               |
|-------------------------|--------------------------|---------------|-----------------------------------|---------------|
|                         | $k=1$ , $m=1$            | $k=1$ , $m=1$ | $k=1$ , $m=1$                     | $k=1$ , $m=1$ |
| 0                       | 34182.76                 | 34182.76      | 34031.74                          | 34031.74      |
| 50                      | 34202.64                 | 34162.92      | 34051.90                          | 34011.58      |
| 60                      | 34205.32                 | 34160.26      | 34054.62                          | 34008.91      |
| 70                      | 34207.96                 | 34157.61      | 34057.28                          | 34006.22      |
| 80                      | 34210.59                 | 34154.99      | 34059.94                          | 34003.58      |
| 90                      | 34213.18                 | 34152.44      | 34062.58                          | 34000.96      |
| 100                     | 34215.87                 | 34149.72      | 34065.31                          | 33998.22      |
| 110                     | 34218.45                 | 34147.13      | 34067.93                          | 33995.58      |
| 120                     | 34221.13                 | 34144.46      | 34070.64                          | 33992.88      |
| 130                     | 34223.76                 | 34141.81      | 34073.31                          | 33990.19      |
| 140                     | 34226.36                 | 34139.14      | 34075.96                          | 33987.49      |
| 150                     | 34229.02                 | 34136.55      | 34078.74                          | 33984.84      |
| 160                     | -----                    | 34133.92      | -----                             | 33982.24      |
| 170                     | 34234.33                 | 34131.34      | -----                             | 33979.60      |
| 180                     | 34236.90                 | 34128.67      | 34086.66                          | 33976.79      |

where  $\nu_0$  is the zero-field frequency of the transition,  $V$  is the applied voltage and  $S$  is the cell spacing. A straight line is obtained when  $\nu$  versus  $V$  is plotted. However, in our instrument the voltage obtained from the dial setting is not the true voltage - there is an offset which appears to be constant at these low fields. (The offset is discussed in Appendix A.) In this case, the Stark field can be written as

$$\epsilon = \left( \frac{V_d + V_o}{S} \right), \quad (69)$$

where  $V_d$  is the voltage from the dial,  $V_o$  is the voltage offset, and  $S$  is the cell spacing. Thus the first-order Stark frequency is

$$\nu = \nu_0 - \frac{\mu_D^{km}}{J(J+1)} \left( \frac{V_d + V_o}{S} \right). \quad (70)$$

This equation can be rearranged to

$$\nu = \left( \nu_0 - \frac{\mu_D^{km}}{J(J+1)} \frac{V_o}{S} \right) - \frac{\mu_D^{km}}{J(J+1)S} V_d. \quad (71)$$

Thus, when  $\nu$  is plotted versus  $V_d$  a straight line is still obtained but the y-intercept is now

$$\nu_0 - \frac{\mu_D^{km}}{J(J+1)} \frac{V_o}{S}.$$

The frequencies and dial voltages were fit to a straight line by the method of least squares. These results are shown in Table 11.

The excited state dipole moment of methylacetylene can be found from the ratio of the slopes of the ground and excited states and from the ground state dipole moment as follows:

$$\mu_{\text{ex}} = \mu_{\text{gr}} \left( \frac{\text{slope}_{\text{ex}}}{\text{slope}_{\text{gr}}} \right) . \quad (72)$$

The dipole moment for the  $\nu_5$  state of methylacetylene was found to be  $0.7954 \pm 0.0010$  Debye.

### Laser Stark Spectrum

#### Calculation of the Laser Stark Spectrum

In order to calculate the frequencies of the laser Stark transitions, the vibration-rotation energy levels of the molecule must be calculated. Then, the Stark splitting of each energy level must be taken into account. The transition frequency is given by the difference between two molecular energy levels. The vibration-rotation transition frequencies (i.e., the transition frequencies at zero field) are given for a symmetric top in Equation (54) and Equation (55). As mentioned before, when the fields are low, the Stark shifts of the transitions can be found by

Table 11. The corrected voltages versus the first-order Stark effect frequencies of the ground state and  $\nu_5$  excited state of the  $J = 2 \leftarrow 1$  transition of methylacetylene fit to a straight line by the method of least squares.

|                        | Slope     | Zero Field Frequency/MHz |
|------------------------|-----------|--------------------------|
| ground state           |           |                          |
| $k = \pm 1, m = \mp 1$ | 0.263516  | 34182.76                 |
| $k = \pm 1, m = \pm 1$ | -0.263419 | 34182.76                 |
| $\nu_5$ excited state  |           |                          |
| $k = \pm 1, m = \mp 1$ | 0.267449  | 34031.74                 |
| $k = \pm 1, m = \pm 1$ | -0.267219 | 34031.74                 |

perturbation methods. Since the electric fields used in laser Stark spectroscopy can be very high, the Stark shifts approach the magnitude of the spacing between the rotational energy levels, and the perturbation equations are not sufficiently accurate. Therefore, the rotational energies, including the Stark shifts, were calculated by diagonalizing the matrix of the Hamiltonian,

$$H = H_r - \mu \cdot \xi . \quad (73)$$

The diagonal matrix elements are<sup>22</sup>

$$\begin{aligned} \langle J, k, m | H | J, k, m \rangle = & B J(J+1) + (A-B) K^2 - D_K K^4 - D_{JK} K^2 J(J+1) \\ & - D_J J^2 (J+1)^2 - [k m / J(J+1)] \mu_D \epsilon, \end{aligned} \quad (74)$$

while the off-diagonal matrix elements are

$$\langle J, k, m | H | J+1, k, m \rangle = -\frac{1}{(J+1)} \left( \frac{[(J+1)^2 - M^2][(J+1)^2 - K^2]}{(2J+1)(2J+3)} \right)^{1/2} \mu_D \epsilon. \quad (75)$$

A program written for the CDC 6500 computer calculates the laser Stark transition frequencies at nine different electric field values. Since the Hamiltonian matrix is diagonal in  $k$  and  $m$ , a matrix was set up for every  $m$  value

for each value of  $k \geq 0$ . One set of matrices was generated for the lower vibrational state and one set for the excited vibrational state. The matrices were truncated at  $J_{\text{matrix}} = J_{\text{transition}} + 5$  and diagonalized. The laser Stark frequencies are then equal to

$$\nu = \nu_0 + E'(J', k', m') - E''(J'', k'', m'') \quad (76)$$

where  $E'$  and  $E''$  are eigenvalues of the matrices for the upper and lower states, respectively, and  $\nu_0$  is the frequency of the vibrational band center.

Another program written for the CDC 6500 computer uses a least squares routine to fit frequencies of experimental laser Stark transitions to calculated frequencies and to determine the band center and rotational constants. The equation

$$\nu_p^{(e)} - \nu_p^{(c)} = \sum_i \left( \frac{\partial \nu_p}{\partial \alpha_i} \right)_c (\alpha_i^{(e)} - \alpha_i^{(c)}) \quad (77)$$

is used to fit the transitions and determine the parameters. The experimental frequency of a transition is  $\nu_p^{(e)}$  and the calculated frequency of that transition is  $\nu_p^{(c)}$ . The fitting parameters are  $\alpha_i$ . There are eleven parameters in this case, which are listed in Table 12.

Since the energy is found from Equation (74) and Equation (75) it can be seen that the derivative of the

Table 12. The eleven parameters that can be fit from the laser Stark transitions and the derivatives of the frequency with respect to these parameters.

| $\alpha_i$    | Parameter    | $\partial \nu_p / \partial \alpha_i$ |
|---------------|--------------|--------------------------------------|
| $\alpha_1$    | $\nu_0$      | 1                                    |
| $\alpha_2$    | $B'$         | $\tilde{T}'[J'(J'+1) - K^2]T'$       |
| $\alpha_3$    | $B''$        | $\tilde{T}''[J''(J''+1) - K^2]T''$   |
| $\alpha_4$    | $\Delta A$   | $K^2$                                |
| $\alpha_5$    | $\Delta D_K$ | $-K^4$                               |
| $\alpha_6$    | $D_{JK'}$    | $\tilde{T}'[-K^2 J'(J'+1)]T'$        |
| $\alpha_7$    | $D_{JK''}$   | $\tilde{T}''[-K^2 J''(J''+1)]T''$    |
| $\alpha_8$    | $D_{J'}$     | $\tilde{T}'[-J'^2(J'+1)^2]T'$        |
| $\alpha_9$    | $D_{J''}$    | $\tilde{T}''[-J''^2(J''+1)^2]T''$    |
| $\alpha_{10}$ | $\mu'$       | $\tilde{T}'\mu'T'$                   |
| $\alpha_{11}$ | $\mu''$      | $\tilde{T}''\mu''T''$                |

frequency with respect to B for a particular value of the quantum numbers is given by the matrix element,

$$\frac{\partial v_p}{\partial B} = \{\tilde{T}[J(J+1)-K^2]T\}_{pp}. \quad (78)$$

In Equation (78),  $[J(J+1)-K^2]$  is used to denote a diagonal matrix with diagonal values given by the expression in brackets; T is the matrix used to diagonalize the Hamiltonian for the total rotational energy. The derivative  $\partial v_p/\partial B$  is the p,p matrix element of the matrix product indicated. The derivatives  $\partial v_p/\partial \Delta A$ ,  $\partial v_p/\partial \Delta D_K$ , and  $\partial v_p/\partial v_0$  can be computed without matrix transformation. By contrast, the derivatives with respect to the dipole moments require transformation of a matrix that has both diagonal and off-diagonal elements. All of these derivatives are listed in Table 12.

To obtain the fitted parameters, a set of parameters is assumed. The transition frequencies  $v_p^{(c)}$  are calculated from these assumed parameters. For each transition, two calculations are made. The difference  $v_p^{(e)} - v_p^{(c)}$  is computed and the set of derivatives  $(\partial v_p/\partial \alpha_1)$  is computed for each parameter  $\alpha_1$ . The linear system of Equations (77) is solved for  $(\alpha_1^{(e)} - \alpha_1^{(c)}) = \Delta_1$ . The values for the experimental parameters are found from

$$\alpha_1^{(e)} = \alpha_1^{(c)} + \Delta_1. \quad (79)$$

The set of parameters  $\alpha_i^{(e)}$  is used in place of the assumed values of  $\alpha_i^{(c)}$  and the procedure is repeated. The iteration is stopped when the  $\alpha_i^{(e)} - \alpha_i^{(c)}$  are all below some preset tolerance.

### Observed Laser Stark Spectrum

The  $\nu_5$  band of the methylacetylene spectrum is very weak. It is weaker than the hot band  $2\nu_3 + \nu_3$  of  $\text{CH}_3\text{F}$  observed by Freund, *et al.*<sup>59</sup> Recently, the infrared absorption intensities of methylacetylene have been studied.<sup>78</sup> The integrated intensity for the  $\nu_5$  band of methylacetylene was measured to be  $1 \text{ km mol}^{-1}$  as compared to  $95 \text{ km mol}^{-1}$  for the  $\nu_3$  band of  $\text{CH}_3\text{F}$ .<sup>79</sup> Since the  $\nu_5$  laser Stark spectrum of methylacetylene is sparse in the area of the laser lines and very weak, few lines were seen at all. The methylacetylene  $\nu_5$  transitions were much too weak to be able to use the Lamb dip technique to help locate the line center.

The transitions were assigned by observing patterns for the case of the Q-branch lines by comparing the observed and calculated spectrum and by comparing the observed and calculated linewidths and relative intensities. For some of the transitions, it was possible to watch the line move to a higher or lower voltage as the cavity length, and hence the laser frequency, was changed slightly. If

the cavity length is increased and the line moves to a lower field, the zero-field frequency of the transition lies below the frequency of the laser line. However, if they both increase, the zero-field frequency of the transition lies above the frequency of the laser line. The fields and quantum numbers of the assigned lines are then fit to Equations (54), (55), (74), and (75) to obtain the molecular parameters.

Several observed laser Stark absorption lines of methylacetylene are shown in Figures 11 and 12. In Figure 11 both transitions were shifted into resonance with the P(32) line of the 001-100 band of the CO<sub>2</sub> laser. Both transitions have  $J = 5 \leftarrow 4$ ,  $k = 3$ , and  $\Delta m = +1$ . For the upper trace  $m'' = -3$  while for the lower trace  $m'' = -2$ . A Q-branch doublet of methylacetylene is shown in Figure 12. The transitions are  $J = 1$ ,  $k = 1$ , and  $\Delta m = -1$ , with  $m'' = 0$  for the lower field transition and  $m'' = 1$  for the higher field transition. These transitions are in resonance with the P(10) line of the N<sub>2</sub>O laser. The spectra in Figures 11 and 12 were taken with a time constant of 1 sec and a sample pressure of 7 mtorr, although lower pressures sometimes were used at high fields to avoid electrical discharge in the sample gas. The scanning rate (determined by the cycle rate of the ramp and its maximum amplitude) was adjusted in conjunction with the time constant to optimize the appearance of the spectra. A modulation amplitude of

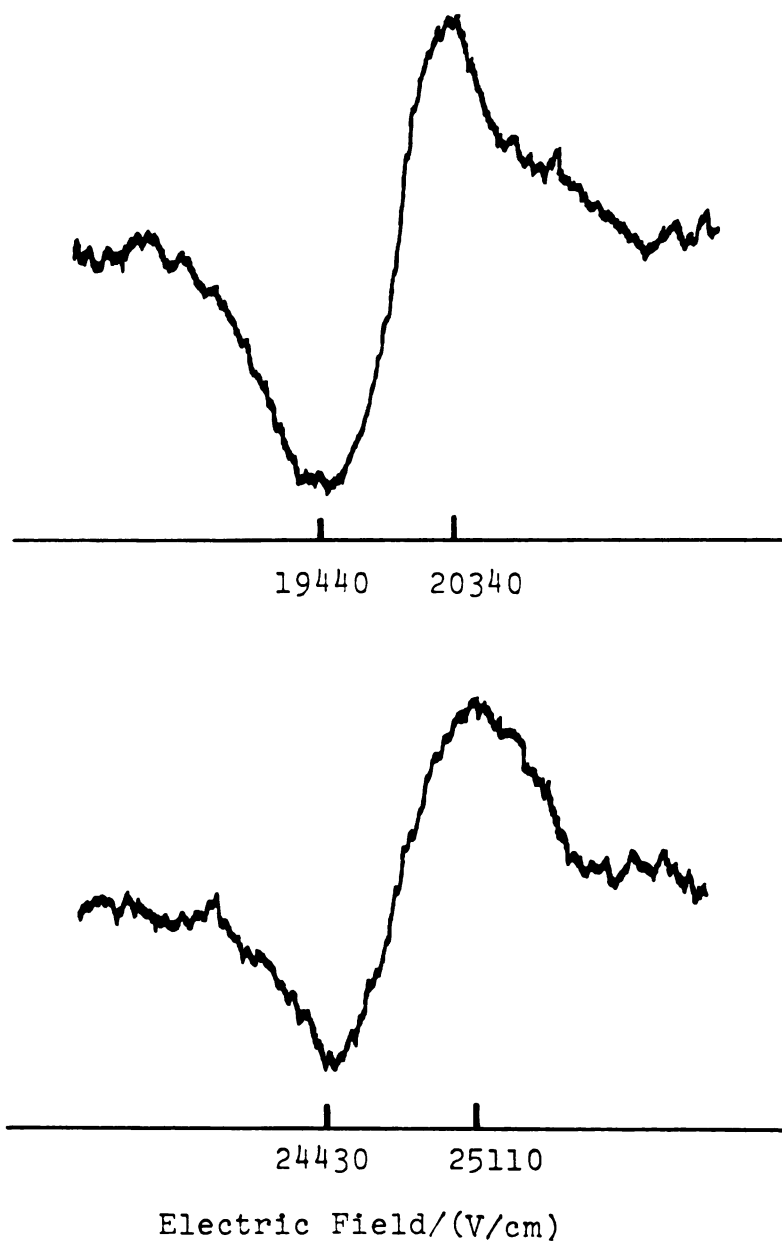


Figure 11. Observed laser Stark absorption lines of methylacetylene. Both transitions were shifted into resonance with the P(32) line of the 001-100 band of the  $\text{CO}_2$  laser. The assignments of the transitions are  $J=5+4$ ,  $k=3$ , and  $\Delta m=+1$ . For the upper trace  $m''=-3$  while for the lower trace  $m''=-2$ .

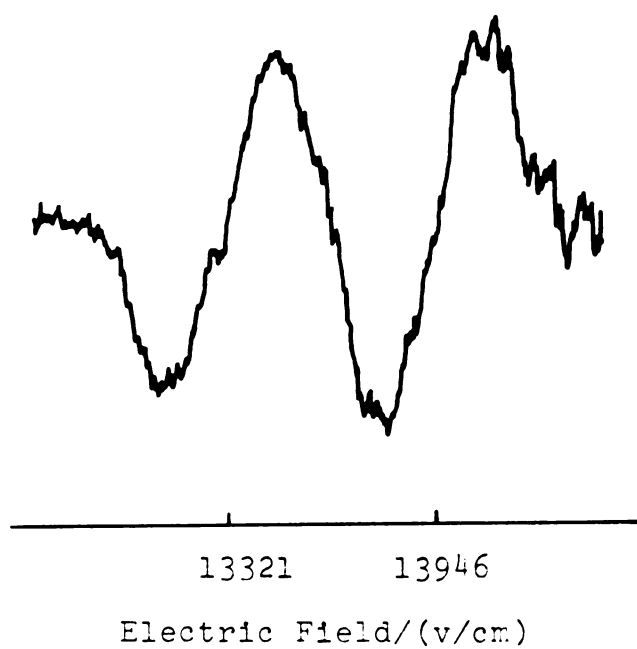


Figure 12. A Q-branch doublet of methylacetylene. The transitions are  $J=1$ ,  $k=1$ , and  $\Delta m=-1$ , with  $m''=0$  for the lower field transition and  $m''=1$  for the higher field transition. These transitions are in resonance with the P(10) line of the  $N_2O$  laser.

40 to 60 volts was used to observe the spectra. With the configuration for  $\Delta m = 0$  selection rules, lines P(24) through P(46) of the 001-100 band of the  $\text{CO}_2$  laser were scanned between 0 and 32,000 v/cm. In addition, lines P(5), P(7), P(12), P(15), and P(17) of the  $\text{N}_2\text{O}$  laser were scanned up to 22,000 v/cm. With the configuration for  $\Delta m = \pm 1$  selection rules, P(30) through P(40) of the 001-100 band of the  $\text{CO}_2$  laser and lines P(6) through P(16) of the  $\text{N}_2\text{O}$  laser were scanned. The upper limit for scanning the electric field, which varied between 30,000 and 50,000 v/cm, was determined by the field strength which caused electric discharge through the sample. Tables 13 and 14 list the observed transitions for each laser line. The assigned transitions are listed in Table 14, and lines for which approximate fields have been determined are listed in Table 13. At most, only one or two transitions were observed with each laser line. The calculated spectra for each of these laser lines show only one or two transitions with intensities strong enough to be likely to be observed. The calculated spectra only include values of J up to 10. Table 13 also lists the calculated field and probable assignment of these transitions. (To ascertain that the assignment is correct, more precise fields for the transitions need to be obtained.) Table 14 lists the assignment of twenty lines and includes the laser lines they absorbed, and the fields needed to Stark shift the transitions into resonance

Table 13. Approximate fields of the observed transitions between the  $\nu_5$  excited state and the ground state of methylacetylene. The fields in parenthesis are calculated fields where a "strong" transition is to occur. The calculation includes J values up to J=10. Transitions for which accurate fields have been measured and assignment made are listed in Table 14.

| Laser Line   | $\Delta m$ | Electric Field Value of<br>Observed Transitions/(kV/cm) |
|--------------|------------|---------------------------------------------------------|
| $N_2O$ P(11) | $\pm 1$    | 7.7                                                     |
| $N_2O$ P(12) | $\pm 1$    | 39.0 (38.96)                                            |
| $CO_2$ P(30) | $\pm 1$    | many lines                                              |
| $CO_2$ P(32) | $\pm 1$    | 46.6 52.0(51.91) 55.0                                   |
| $CO_2$ P(34) | $\pm 1$    | 31.4 33.9 52.7                                          |
| $CO_2$ P(40) | $\pm 1$    | 46.2                                                    |
| $CO_2$ P(30) | 0          | 28.6                                                    |
| $CO_2$ P(32) | 0          | 19.5 26.0(26.05)                                        |
| $CO_2$ P(34) | 0          | 17.3                                                    |
| $CO_2$ P(36) | 0          | 22.4(22.54)                                             |
| $CO_2$ P(38) | 0          | 28.7                                                    |
| $CO_2$ P(40) | 0          | 21.4(21.31)                                             |

Table 14. Assigned transitions between the  $\nu_5$  excited vibrational state and the ground state of methylacetylene.

| Laser Line             | J'K'M' + J''K''M'' | Field/(Volt/cm) | ( $\nu_m^0 - \nu_e$ )/MHz |
|------------------------|--------------------|-----------------|---------------------------|
| N <sub>2</sub> O P(10) | 1 1-1+1 1 0        | 13321           | -2689.93                  |
|                        | 1 1 0+1 1 1        | 13946           |                           |
|                        | 2 2-2+2 2-1        | 24601           | -3405.54                  |
|                        | 2 2-1+2 2 0        | 25454           |                           |
|                        | 2 2 0+2 2 1        | 26337           |                           |
|                        | 2 2 1+2 2 2        | 27241           |                           |
|                        | 3 3-3+3 3-2        | 45163           | -4788.65                  |
|                        | 3 3-2+3 3-1        | 46504           |                           |
|                        | 3 3-1+3 3 0        | 47923           |                           |
|                        | 3 3 0+3 3 1        | 49372           |                           |
|                        | 3 3 1+3 3 2        | 50856           |                           |
|                        | 3 3 2+3 3 3        | 52365           |                           |
| CO <sub>2</sub> P(32)  | 5 3-2+4 3-3        | 19925           | 1922.97                   |
|                        | 5 3-1+4 3-2        | 24771           |                           |
|                        | 5 3 0+4 3-1        | 33135           |                           |
| CO <sub>2</sub> P(36)  | 1 1 0+2 1-1        | 32527           | 3433.43                   |
|                        | 1 1 1+2 1 2        | 41685           |                           |
|                        | 1 0 1+2 0 0        | 50413           | 3266.8                    |
| CO <sub>2</sub> P(40)  | 7 7 1+8 7 2        | 25483           | -778.63                   |
|                        | 7 7-5+8 7-6        | 34066           |                           |

with the laser. The differences between the frequencies of the laser line and the zero-field frequency of the transition are also listed. Table 15 compares the molecular parameters obtained by fitting the laser Stark frequencies to two sets of parameters: set I includes the values of the band center, difference in A rotational constants, difference in  $D_K$  centrifugal distortion constants, and the excited state dipole moment; set II includes the parameters of set I and the ground state dipole moment. The values of the other parameters were assumed from the microwave study. The errors listed for the parameters of column I and II are twice the standard deviation of each parameter obtained from the fit. They reflect the precision but not accuracy of the numbers. Although the parameters in column II are more precise than those in column I, the ground state dipole moment given in column II differs from that obtained from the microwave data. Hence, the parameters in column II are considered to be less accurate than those in column I. The difference between the experimental and calculated frequencies of methylacetylene for these two cases are compared in Table 16.

The band center obtained from the laser Stark spectrum is  $930.2749 \pm 0.0004 \text{ cm}^{-1}$ . A value of  $-206 \pm 7 \text{ MHz}$  was obtained for the difference between the ground state and  $v_5 = 1$  excited state A rotational constant. The ground state rotational constant  $A_0$  has been measured by Thomas

Table 15. Rotation-vibration parameters of  $\text{CH}_3\text{C}\equiv\text{CH}$ . In columns I and II are the parameters obtained from the laser Stark experiments. The parameters in column I were obtained by letting  $\nu_0$ ,  $\Delta A$ ,  $\Delta D_K$ , and  $\mu'$  vary in the fitting routine while those in column II were obtained by varying  $\nu_0$ ,  $\Delta A$ ,  $\Delta D_K$ ,  $\mu'$  and  $\mu''$ . The primes refer to the  $\nu_5$  vibrational state while the double primes refer to the ground vibrational state.

| Parameter                | I             | II           | (This Laboratory) Microwave | Other                 |
|--------------------------|---------------|--------------|-----------------------------|-----------------------|
| $\nu_5/\text{MHz}$       | 27888944.(13) | 27888935.(6) |                             |                       |
| $\nu_5/\text{cm}^{-1}$   | 930.2749(4)   | 930.2746(2)  |                             | 930.07 <sup>a</sup>   |
| $B''/\text{MHz}$         |               |              | 8545.877(1)                 | 8545.877 <sup>b</sup> |
| $B'/\text{MHz}$          |               |              | 8508.119(3)                 |                       |
| $\alpha_5/\text{MHz}$    |               |              | 37.757 (4)                  | 39 <sup>a</sup>       |
| $A'-A''/\text{MHz}$      | -205.6 (70)   | -199.0 (10)  |                             |                       |
| $D_K^I-D_K''/\text{MHz}$ | 4.8 (7)       | 5.4 (1)      |                             |                       |
| $D_J^I/\text{kHz}$       |               |              | 1.8 (2)                     |                       |
| $D_J''/\text{kHz}$       |               |              |                             | 2.96 <sup>b</sup>     |
| $D_{JK}^I/\text{kHz}$    |               |              | 169.(1)                     |                       |
| $D_{JK}''/\text{kHz}$    |               |              |                             | 162.9 <sup>b</sup>    |
| $\mu'/D$                 | 0.7949(6)     | 0.7935(1)    | 0.7954(10)                  |                       |
| $\mu''/D$                |               | 0.7825(1)    | 0.7839(10)                  | 0.7840 <sup>c</sup>   |

<sup>a</sup>R. K. Thomas and H. W. Thompson, Spectrochim. Acta, 24A, 1337 (1968). <sup>b</sup>C. A. Burrus and W. Gordy, J. Chem. Phys. 26, 391 (1957). <sup>c</sup>J. S. Muentner and V. W. Laurie, J. Chem. Phys. 45, 855 (1966); corrected to  $\mu(\text{OCS}) = 0.71519$  D.

Table 16. Comparison of the difference between the experimental and calculated frequencies of the methylacetylene transitions for the two cases in Table 15.

| Transition<br>J'K'M'+J''K''M'' | I <sup>a</sup><br>( $\nu^e - \nu^c$ )/MHz | II <sup>a</sup><br>( $\nu^e - \nu^c$ )/MHz |
|--------------------------------|-------------------------------------------|--------------------------------------------|
| 1 1-1+1 1 0                    | -8.4                                      | -0.7                                       |
| 1 1 0+1 1 1                    | -9.0                                      | -1.1                                       |
| 2 2-2+2 2-1                    | 6.8                                       | 4.1                                        |
| 2 2-1+2 2 0                    | 4.0                                       | 1.6                                        |
| 2 2 0+2 2 1                    | 0.6                                       | -1.5                                       |
| 2 2 1+2 2 2                    | -2.0                                      | -3.8                                       |
| 3 3-3+3 3-2                    | -4.4                                      | -1.4                                       |
| 3 3-2+3 3-1                    | -1.9                                      | 1.4                                        |
| 3 3-1+3 3 0                    | -3.4                                      | 0.4                                        |
| 3 3 0+3 3 1                    | -3.8                                      | 0.5                                        |
| 3 3 1+3 3 2                    | -3.4                                      | 1.4                                        |
| 3 3 2+3 3 3                    | -1.3                                      | 4.0                                        |
| 5 3-2+4 3-3                    | 10.8                                      | 5.7                                        |
| 5 3-1+4 3-2                    | 2.5                                       | -5.5                                       |
| 5 3 0+4 3-1                    | 3.1                                       | -4.8                                       |
| 1 1 0+2 1-1                    | -1.7                                      | -6.6                                       |
| 1 1 1+2 1 2                    | -4.4                                      | -6.6                                       |
| 1 0 1+2 0 0                    | 15.6                                      | 12.8                                       |
| 7 7 1+8 7 2                    |                                           | 1.2                                        |
| 7 7-5+8 7-6                    |                                           | -1.3                                       |
| Standard Deviation             | 9.8                                       | 6.6                                        |

<sup>a</sup>The parameters included in sets I and II are listed in Table 15.

and Thompson to be  $5.31 \text{ cm}^{-1}$  (159,000 MHz).<sup>8</sup> The laser Stark experiments also lead to a value of  $4.8 \pm 0.7 \text{ MHz}$  for the difference between the ground state and  $v_5 = 1$  excited state centrifugal distortion constant  $D_K$ . Duncan has calculated the ground state centrifugal distortion constant  $D_K$  of methylacetylene to be  $2.98 \text{ MHz}$ .<sup>12</sup> The ground state dipole moment of  $0.7839 \pm 0.001$  Debye determined from the microwave measurements of the  $J = 2 \leftarrow 1$  transition is in excellent agreement with that of Muentner and Laurie.<sup>4</sup> The difference between the ground state and excited state dipole moments obtained from the laser Stark spectrum compares very well with that obtained from the microwave measurements. This good agreement supports the quality of the other constants determined from the laser Stark spectrum

The weakness of the laser Stark spectrum of the  $v_5$  band of methylacetylene made it difficult at times to obtain accurate resonant fields for the transitions. It also led us to question for some time whether the observed transitions were assigned correctly to the fundamental  $v_5$  band. In support of this assignment is the unmistakable appearance of the Q-branch multiplets and the strong correlation between the infrared laser Stark and the microwave data. Also, as already mentioned, conventional infrared intensity measurements have shown that this band is extremely weak.

The transitions of the  $\nu_5$  band of methylacetylene are too weak to use for good linewidth measurements. It should be possible, though, to interface the ramp voltage of the laser Stark spectrometer with a minicomputer in order to average a large number of scans of each transition. In this way, it might be possible to obtain the molecular parameters more accurately.

PART II  
DETERMINATION OF ROTATIONAL RELAXATION PARAMETERS  
FOR OCS IN  $H_2$ ,  $CO_2$ , AND  $CH_3F$

CHAPTER V  
INTRODUCTION

All spectroscopic transitions have a finite linewidth that is a result of many different effects. Contributions to the linewidth include the natural linewidth, as well as line broadening due to the Doppler effect, pressure broadening, saturation broadening, wall collision broadening, and instrumentation problems. For gaseous samples at pressures above  $\sim 20$  mtorr, the major contribution to the linewidth of microwave transitions is the collisions between the molecules. Perturbation of the rotational energy levels of molecules by collisions (or near collisions) with other molecules causes an increase in the width and a shift in the frequency of the molecular transitions. Thus, the linewidth of a rotational transition can provide information about intermolecular collisions. In addition to the investigation of the physical phenomena responsible for them, lineshapes are studied in several ways for a number of reasons. Astronomers need to know the effects of line broadening since spectral lines are collision broadened in the atmosphere of some planets. In the atmosphere of Jupiter, the linewidth of methane

is broadened by other methane molecules and by ammonia,<sup>80-83</sup> and in the atmosphere of Mars, CO is broadened by CO<sub>2</sub>.<sup>84</sup> Lineshape data are also useful for developing measurement techniques for atmospheric pollutants,<sup>85</sup> and knowledge of the pressure-induced linewidths and frequency shifts are needed for the design, operation, and frequency determination of gas lasers.<sup>86</sup>

Microwave lineshapes have been studied both experimentally and theoretically for many years. The theoretical approach is to identify and use the forces between the radiating molecule and the molecules colliding with it to account for the molecular lineshape. Review articles by Rabitz<sup>87</sup> and by Birnbaum<sup>88</sup> discuss the results of theoretical calculations of microwave linewidths. For treatment of the experimental data, it is sufficient to assume that the collisions act as a first-order relaxation process to return the populations of the states and the polarization of the molecules which have absorbed radiation back to their equilibrium values. The lineshape expected as a result of this assumption will be described in the next chapter.

The studies in this thesis were undertaken to apply the experimental methods recently developed at Michigan State University for the determination of the population relaxation time,  $T_1$ , and the polarization relaxation time,  $T_2$ . The system of OCS in CH<sub>3</sub>F was studied to try to resolve

apparently conflicting values of the ratio of the relaxation parameters. A transient effect experiment by Mäder, et al.<sup>89</sup> showed that  $T_2/T_1$  was almost 1 ( $T_1^{-1} = 0.079 \pm 0.009 \text{ } \mu\text{sec}^{-1} \text{ mtorr}^{-1}$ ,  $T_2^{-1} = 0.077 \pm 0.002 \text{ } \mu\text{sec}^{-1} \text{ mtorr}^{-1}$ ), whereas a molecular beam experiment by Wang, et al.<sup>90</sup> showed that the cross sections  $\sigma_I$  and  $\sigma_{II}$ , which are closely related to  $T_1^{-1}$  and  $T_2^{-1}$ , respectively, were significantly different ( $\sigma_I = 990 \text{ } \text{\AA}^2$ ,  $\sigma_{II} = 750 \text{ } \text{\AA}^2$ ). The system OCS-CH<sub>3</sub>F is that of a linear molecule perturbed by a polar symmetric top molecule. For comparison purposes, it was decided to study OCS-H<sub>2</sub>, a linear molecule perturbed by a non-polar diatomic molecule, and OCS-CO<sub>2</sub>, a linear molecule perturbed by a non-polar linear molecule. As indicated, the ultimate goal of measurements of the relaxation times is two-fold. The data can be used to test theories of intermolecular interactions and also for theoretical treatments of interstellar, atmospheric, or laser phenomena.

## CHAPTER VI

### THEORY

In these experiments, the values of the relaxation parameters,  $T_1$  and  $T_2$ , were desired. The following sections describe how these parameters can be obtained from the width of the molecular transition.

#### Interaction of Radiation with the Sample

The microwave radiation used to excite the sample is a beam of electromagnetic radiation that is monochromatic (to better than 1 part in  $10^8$ ), coherent, and plane polarized. The electric field of the radiation may be expressed as

$$E(z) = \epsilon_0 \cos(\omega t - kz), \quad (80)$$

where  $\epsilon_0$  is the amplitude of the field,  $\omega$  is the angular frequency, and  $k$  is the wave number. The beam travels in the  $+z$  space-fixed direction and the direction of the field will be taken to be the  $x$  direction. This electric field induces an oscillating polarization in the sample molecules of the form

$$P = P_r \cos (\omega t - kz) - P_i \sin (\omega t - kz). \quad (81)$$

In this expression  $P_r$  and  $P_i$  are the amplitudes of the components of the polarization that are in phase and in quadrature with the radiation, respectively. The polarization oscillates at the same frequency as the radiation, but with a phase shift when  $P_i \neq 0$ . The electric polarization is the macroscopic dipole density of the sample. It is the result of molecular dipole moments tending to align themselves with the electric field. The electric field creates a stress in the molecules as a result of their non-uniform charge distribution. This stress manifests itself as an orientation of the molecules in space or as a stretching and bending of the molecular bonds, all of which contribute to the polarization. The electric field of the radiation can also alter the charge distribution of the electrons relative to the nuclei.

The amplitude of the electric field of the incident radiation is assumed to be constant in space along its direction of propagation and therefore the polarization is uniform throughout the sample. However, it oscillates at the same frequency as the electric field. The oscillating polarization of the sample creates an oscillating electric field that has the same phase relative to the exciting field through the sample. Thus, the intensity of the induced electric field appears to increase with distance

through the sample, since each volume of sample  $dx\ dy\ dz$  contributes to it.

At the end of the sample the detector monitors the change in intensity of a combination of the incident and induced electric fields. In this picture, absorption or emission of the radiation depends on the phase of the induced electric field. If the phase of the induced field is opposite that of the incident radiation, the amplitude of the combined electric field at the exit of the cell will be less than at the entrance. Then, absorption is said to have occurred. Emission occurs when the induced and incident fields have the same phase.

#### Relation Between the Absorption Coefficient and $P_i$

If the radiation is strong enough to be described as a classical wave, Maxwell's wave equations can be used to explain its behavior. These equations will be written in the Gaussian system of units. In a non-conducting, non-magnetic medium, the electric field,  $E$ , and the magnetic induction,  $B$ , are related as follows:<sup>91</sup>

$$\nabla \times \vec{E} = - \frac{1}{c} \frac{\partial \vec{B}}{\partial t}, \quad (82)$$

where

$$\nabla = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}, \quad (83)$$

c is the speed of light, and t is time. Thus,

$$\nabla_{\lambda} \times (\nabla_{\lambda} \times \mathbf{E}) = - \frac{1}{c} \frac{\partial}{\partial t} (\nabla_{\lambda} \times \mathbf{B}). \quad (84)$$

To find an expression for  $\nabla_{\lambda} \times \mathbf{B}$ , substitute

$$\mathbf{B} = \mu \mathbf{H} \quad (85)$$

and

$$\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} \quad (86)$$

into Maxwell's equation,

$$\nabla_{\lambda} \times \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}, \quad (87)$$

to obtain

$$\nabla_{\lambda} \times \mathbf{B} = \frac{1}{c} \left( \frac{\partial \mathbf{E}}{\partial t} + 4\pi \frac{\partial \mathbf{P}}{\partial t} \right). \quad (88)$$

In Equation (88) the permeability of the gas sample,  $\mu$ , is assumed to be unity. Also,  $\mathbf{D}$  is the electric displacement and  $\mathbf{P}$  is the polarization of the molecular sample;  $\mathbf{H}$  is the magnetic field of the radiation. Therefore

$$\nabla_{\lambda} \times (\nabla_{\lambda} \times \mathbf{E}) = - \frac{1}{c^2} \left( \frac{\partial^2 \mathbf{E}}{\partial t^2} + 4\pi \frac{\partial^2 \mathbf{P}}{\partial t^2} \right). \quad (89)$$

Since microwave radiation in a rectangular waveguide is plane polarized, let

$$\vec{E} = \hat{z} E(z) \quad (90)$$

so that the direction of propagation is along the  $z$  axis and the electric field vector oscillates in the  $xz$  plane. Then,

$$\nabla \times \vec{E} = \hat{z} \frac{\partial E(z)}{\partial z} \quad (91)$$

and

$$\nabla \times (\nabla \times \vec{E}) = -\hat{z} \frac{\partial^2 E(z)}{\partial z^2}. \quad (92)$$

Upon comparing Equations (89) and (92), it is apparent that

$$\vec{P} = \hat{z} P, \quad (93)$$

the other components of  $\vec{P}$  being zero. With this in mind, Equations (89) and (92) are combined to obtain

$$-\frac{\partial^2 E}{\partial z^2} + \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = -\frac{4}{c^2} \frac{\partial^2 P}{\partial t^2}. \quad (94)$$

The electric field of the incident radiation induces a polarization in the sample as expressed in Equation (81).

If the change in  $P_r$  and  $P_1$  with time is very slow compared to the frequency of the radiation, differentiation of Equation (81) gives

$$\frac{\partial^2 P}{\partial t^2} \approx -\omega^2 P . \quad (95)$$

Equation (94) then becomes

$$\frac{\partial^2 E}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = - \frac{4\pi\omega^2 P}{c^2} . \quad (96)$$

The next step is to evaluate the derivatives of  $E$ , as given by Equation (80) with respect to  $t$  and  $z$ . The left and right sides of Equation (96) then each become a sum of a sine and a cosine term with slowly varying coefficients. After equating the coefficients of the sine terms, it is found that

$$\frac{\partial \epsilon_0}{\partial z} + \frac{1}{c} \frac{\partial \epsilon_0}{\partial t} = \frac{2\omega\pi}{c} P_1 . \quad (97)$$

However, as shown by Flygare and his coworkers,<sup>92</sup>

$$\frac{1}{c} \left| \frac{\partial \epsilon_0}{\partial t} \right| \ll \frac{\partial \epsilon_0}{\partial z} , \quad (98)$$

so that

$$d\epsilon_0 \approx \frac{2\pi\omega}{c} P_1 dz . \quad (99)$$

The absorption coefficient is defined in terms of the fractional energy lost to the system by the radiation,

$$\gamma dz \equiv - \frac{dW}{W} . \quad (100)$$

Here,  $\gamma$  is the absorption coefficient and  $W$  is the energy. The energy per unit area of the radiation flowing into the system can be calculated from the Poynting vector to be

$$W = \frac{\epsilon_0^2 c}{8\pi} . \quad (101)$$

Hence,

$$\frac{dW}{W} = \frac{2d\epsilon_0}{\epsilon_0} . \quad (102)$$

By combining Equations (99) and (102) it can be seen that the absorption coefficient is proportional to the amplitude of the in-quadrature part of the polarization,<sup>92</sup>

$$\gamma = - \frac{4\pi\omega}{c} \frac{P_1}{\epsilon_0} . \quad (103)$$

### The Optical Bloch Equations

The optical Bloch equations have been derived for a two-level system in the presence of radiation.<sup>92</sup> The

Hamiltonian for the two-level system without collisions is

$$H = H^0 - \mu \cdot E , \quad (104)$$

where  $H^0$  is the Hamiltonian for the field-free system and the interaction between the radiation and the sample is given by the dot product of the molecular dipole moment and the electric field of the radiation. The normalized wavefunction for the  $\alpha^{\text{th}}$  molecule of a system of  $N$  molecules is expanded in terms of eigenfunctions of  $H^0$  to give

$$\psi^{(\alpha)} = \sum_a c_a^{(\alpha)} \phi_a^0 . \quad (105)$$

Then, the population of state  $a$  is defined to be

$$N_a = \sum_{\alpha=1}^N c_a^{(\alpha)*} c_a^{(\alpha)} , \quad (106)$$

whereas the contribution to the polarization from the states  $a$  and  $b$  is

$$P_{ab} = \sum_{\alpha=1}^N \mu_{ab}^{(x)} (c_a^{(\alpha)*} c_b^{(\alpha)} + c_b^{(\alpha)*} c_a^{(\alpha)}) \quad (107)$$

if the electric field of the radiation is in the  $x$  direction;  $\mu_{ab}^{(x)}$  has been assumed to be real. If the energy

difference between states a and b is approximately  $\hbar\omega$ , and if there are no other pairs of states for which this is true, then to a good approximation  $P = P_{ab}$ . It may be shown that with suitable approximations the time-dependent Schrödinger equation for the system of N molecules is equivalent to the following set of equations:<sup>92</sup>

$$\frac{d}{dt} (\hbar\Delta N) + \epsilon_0 P_i = 0 \quad (108)$$

$$\frac{dP_r}{dt} - \delta P_i = 0 \quad (109)$$

$$\frac{dP_i}{dt} - \left| \frac{\mu_{ab}^{(x)}}{\hbar} \right|^2 \epsilon_0 (\hbar\Delta N) + \delta P_r = 0. \quad (110)$$

In these equations  $\Delta N$  is the difference in populations of states a and b,  $\delta$  is equal to the resonant frequency of the system minus the driving frequency of the electric field, and  $\mu_{ab}^{(x)}$  is the dipole moment matrix element which connects states a and b. Equations (108)-(110) are similar to the Bloch equations for NMR.<sup>93</sup> To account for the effect of collisions, phenomenological first-order relaxation terms are added so that the optical Bloch equations for a set of two-level systems with collisions are as follows:<sup>92</sup>

$$\frac{d}{dt} (\hbar\Delta N) + \epsilon_0 P_i + \hbar \frac{(\Delta N - \Delta N^0)}{T_1} = 0 \quad (111)$$

$$\frac{d}{dt} P_r - \delta P_i + \frac{P_r - P_r^0}{T_2} = 0 \quad (112)$$

$$\frac{d}{dt} P_i - \left| \frac{\mu_{ab}^{(x)}}{\hbar} \right|^2 \epsilon_0 (\hbar \Delta N) + \delta P_r + \frac{P_i - P_i^0}{T_1} = 0. \quad (113)$$

The phenomenological relaxation terms  $T_1$  and  $T_2$  will be discussed in the next section. The quantities  $P_i^0$ ,  $P_r^0$ , and  $\Delta N^0$  are the equilibrium values of  $P_i$ ,  $P_r$  and  $\Delta N$ ; ordinarily,  $P_i^0 = P_r^0 = 0$ .

#### Meaning of $T_1$ and $T_2$

Originally,  $T_1$  and  $T_2$  were introduced into the optical Bloch equations phenomenologically. In the two level system,  $T_1$  is the relaxation time for the difference in the populations of the two energy levels of the molecules under study to return to its equilibrium value. Thus,  $T_1^{-1}$  is a measure of the rate at which the population difference between the two levels returns to its equilibrium value after the radiation perturbation is introduced. The relaxation rate  $T_2^{-1}$  is a measure of the rate at which the components of the polarization return to their equilibrium values.

It is of interest to determine what kinds of collisions contribute to the relaxation of the population difference and polarization. The relaxation times have been interpreted in several ways. Liu and Marcus<sup>94</sup> obtain expressions

for  $T_1$  and  $T_2$  in terms of the scattering matrix elements. Expressions for  $T_1$  and  $T_2$  can also be obtained by application of the Bloch-Wangsness-Redfield theory<sup>95</sup> that has been used to characterize relaxation in NMR. In this theory the relaxation times are interpreted as combinations of time correlation functions of a random perturbation  $H^{(r)}$  that is introduced to describe the collisional processes. It turns out that for a two-state system,<sup>96</sup>

$$T_1^{-1} = 2\Gamma_{12} + \Gamma' , \quad (114)$$

and

$$T_2^{-1} = \Gamma_{12} + \Gamma' + \Gamma_a , \quad (115)$$

where

$$\Gamma_a = \frac{1}{\hbar^2} \int_0^\infty [H_{11}^{(r)}(t) - H_{22}^{(r)}(t)][H_{11}^{(r)}(t-\tau) - H_{22}^{(r)}(t-\tau)] d\tau, \quad (116)$$

$$\Gamma_{12} = \frac{1}{2}(W_{12} + W_{21}) , \quad (117)$$

$$\Gamma' = \frac{1}{2} \sum_{k \neq 1,2} (W_{1k} + W_{2k}) , \quad (118)$$

$$W_{mn} = \frac{1}{\hbar^2} \int_{-\infty}^\infty H_{mn}^{(r)}(t) H_{nm}^{(r)}(t-\tau) e^{i\omega_{nm}\tau} d\tau \quad (119)$$

and in which

$$\omega_{mn} = (E_m^0 - E_n^0)/\hbar .$$

These equations were derived for non-degenerate energy levels where levels 1 and 2 are connected by the radiation;  $E_m^0$  and  $E_n^0$  are unperturbed energies of levels m and n, respectively.

Expressed in this way,  $T_1$  and  $T_2$  have a physical interpretation. The constant  $W_{mn}$  can be thought of as the rate constant for collision-induced transitions from level m to level n. Thus,  $\Gamma_{12}$  is the mean rate constant for collision-induced transitions between states 1 and 2, while  $\Gamma'$  is the combined rate constant for collision-induced transitions between states 1 or 2 and any other state. The constant  $\Gamma_a$  can be thought of as the rate constant for adiabatic processes such as reorientation or phase changing collisions. These adiabatic collisions do not change the populations of the levels, so they are not included in the expression for the relaxation time  $T_1$ . Also, it should be noted that a transition between levels 1 and 2 causes the population difference between the two states to increase by two or decrease by two. Thus, one transition between levels 1 and 2 should cause the population difference to change by two and the polarization to change by one. From Equations (114) and (115) it is easy to see that transitions between levels 1 and 2 are twice as effective in changing  $T_1^{-1}$  than in changing  $T_2^{-1}$ .

The ratio of the relaxation parameters can be expressed in terms of the time correlation functions as follows:

$$\frac{T_2}{T_1} = \frac{2\Gamma_{12} + \Gamma'}{\Gamma_{12} + \Gamma' + \Gamma_a} \quad . \quad (120)$$

The variation of  $T_2/T_1$  for different values of the time correlation functions can be investigated.<sup>96</sup> If  $\Gamma_a$  is very small, the value of  $T_2/T_1$  will be between 1 and 2. If  $\Gamma_a$  is small and  $\Gamma_{12} \gg \Gamma'$ , as would be the case when collisional transitions involving molecules in states 1 or 2 are due predominately to transitions between states 1 and 2, then  $T_2/T_1 \sim 2$ . However, if  $\Gamma_a$  is small and the collisional transitions which involve molecules in states 1 and 2 are mostly those between states 1 or 2 and some other state, as is the case when  $\Gamma' \gg \Gamma_{12}$ , then  $T_2/T_1 \sim 1$ . So far it has been assumed that  $\Gamma_a$ , the rate constant for adiabatic relaxation processes, is small. If  $\Gamma_a$  is very large,  $T_2/T_1 \sim 0$ . Thus,  $T_2/T_1$  can range in value from 0 through 2, depending upon which type of relaxation process predominates.

The expressions just given for  $T_1^{-1}$  and  $T_2^{-1}$  for non-degenerate levels have been extended to the case of  $m$  degeneracy, which always occurs in the absence of Stark or Zeeman fields. For this case,

$$T_1^{-1} = \frac{1}{2} \sum_m \sum_{m'} \left( \frac{1}{2J_1+1} (2w_{J_f m J_1 m'} + \sum_{J \neq J_1, J_f} w_{J m' J_1 m} \right. \\ \left. + \frac{1}{2J_f+1} (2w_{J_1 m J_f m'} + \sum_{J \neq J_1, J_f} w_{J m' J_f m}) \right) \quad (121)$$

and

$$T_2^{-1} = \text{Re} \left( \frac{1}{2} \sum_m f(m) \sum_{J'} \sum_{m'} (w_{J' m' J_f m} + w_{J' m' J_1 m}) \right. \\ \left. - 3 \sum_m \sum_{m'} (-1)^{m+m'} \begin{pmatrix} J_f & J_1 & 1 \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} J_f & J_1 & 1 \\ m' & -m' & 0 \end{pmatrix} \phi_{J_f m' J_1 m} \right), \quad (122)$$

where

$$w_{J_1 m_1 J_f m_f} = \frac{\int_{-\infty}^{\infty} \langle J_1 m_1 | H^{(r)}(t) | J_f m_f \rangle \langle J_f m_f | H^{(r)}(t+\tau) | J_1 m_1 \rangle e^{-i w_{J_1 m_1 J_f m_f} \tau} d\tau, \quad (123)$$

$$\phi_{J_f m' J_1 m} = \frac{\int_{-\infty}^{\infty} \langle J_f m' | H^{(r)}(t) | J_f m \rangle \langle J_1 m' | H^{(r)}(t+\tau) | J_1 m \rangle d\tau, \quad (124)$$

and

$$w_{J_1 m_1 J_f m_f} = \langle J_1 m_1 | H^{(m)} | J_1 m_1 \rangle - \langle J_f m_f | H^{(m)} | J_f m_f \rangle. \quad (125)$$

The factor  $f(m)$  is three times a Wigner 3-j coefficient;<sup>97</sup>  
i.e.,

$$f(m) = 3 \begin{pmatrix} J_f & J_1 & 1 \\ m & -m & 0 \end{pmatrix} . \quad (126)$$

The  $w_{J_f m_f J_1 m_1}$  can be interpreted as the rate constants for collisionally induced transitions from state  $J_1 m_1$  to state  $J_f m_f$ . Thus, all the contributions to  $T_1^{-1}$  are rate constants for a change of state. As before, any collisions between level  $J_1$  and  $J_f$  contribute to  $T_1^{-1}$  approximately twice as much as collisions between level  $J_1$  or level  $J_f$  and any other  $J$  level. The relaxation term  $T_2^{-1}$ , however, contains contributions from collisions which cause a change in state as well as contributions from adiabatic collisions. In this case collisions between level  $J_1$  and level  $J_f$ , collisions between level  $J_1$  or  $J_f$  and any other level  $J$ , and simple reorientation collisions  $J_f m \rightarrow J_f m'$  or  $J_1 m \rightarrow J_1 m'$ , occur with the same weight factor. The second term in Equation (122) for  $T_2^{-1}$  contains adiabatic contributions.

### Steady State Solutions to the Optical Bloch Equations

A long time (several relaxation times) after the onset of the radiation, it is assumed that steady state conditions have been reached. In the steady state,  $d(\Delta N)/dt = 0$ ,  $dP_1/dt = 0$ , and  $dP_r/dt = 0$ . Under these circumstances, the Bloch equations become

$$\epsilon_0 P_1 + \hbar \frac{(\Delta N - \Delta N^0)}{T_1} = 0 , \quad (127a)$$

$$- \delta P_1 + \frac{P_r}{T_2} = 0 , \quad (127b)$$

and

$$\delta P_1 - \kappa^2 \epsilon_0 (\hbar \Delta N) + \frac{P_1}{T_2} = 0, \quad (127c)$$

where

$$\kappa = \frac{|\mu_{ab}^{(x)}|}{\hbar}. \quad (128)$$

These equations may be solved to yield

$$P_1 = \frac{\kappa^2 \epsilon_0 \hbar \Delta N^0 / T_2}{\delta^2 + (1/T_2)^2 + \kappa^2 \epsilon_0^2 (T_1/T_2)}. \quad (129)$$

It was shown earlier, (Equation (103)) that the in-quadrature component of the polarizability is related to the absorption coefficient,

$$\gamma = - \frac{4\pi\omega}{c} \frac{P_1}{\epsilon_0}.$$

Therefore, by combination of Equations (103) and (129),

$$\gamma = \frac{4\pi\omega}{c} \frac{\kappa^2 \hbar \Delta N^0 / T_2}{\delta^2 + (1/T_2)^2 + \kappa^2 \epsilon_0^2 (T_1/T_2)}. \quad (130)$$

Low Power

When the power of the radiation is very low, that is, as  $\epsilon_0 \rightarrow 0$ , Equation (130) becomes

$$\gamma = \frac{4\pi\omega\kappa^2\hbar\Delta N^0}{c} \left( \frac{1/T_2}{\delta^2 + (1/T_2)^2} \right). \quad (131)$$

This is the equation for a Lorentzian line shape centered about  $\delta = 0$  and with the half-width at half-height given by

$$\Delta\omega = \frac{1}{T_2}, \quad (132)$$

or

$$\Delta\nu = \frac{1}{(2\pi T_2)}. \quad (133)$$

Hence, Equation (131) can be expressed as

$$\gamma = \frac{4\pi\omega\kappa^2\hbar\Delta N^0}{c} \left( \frac{\Delta\omega}{(\omega - \omega_0)^2 + \Delta\omega^2} \right). \quad (134)$$

Thus, under steady state conditions, the relaxation time  $T_2$  can be obtained from the linewidth of the transition when the radiation power is low.

### Moderate Power

Under conditions of moderate radiation power, the term proportional to  $\epsilon_0^2$  is not negligible and the absorption coefficient is expressed by Equation (130). Under conditions of uniform moderate power, Equation (130) still represents a Lorentzian line shape centered about  $\delta = 0$  and with a half-width at half-height of

$$\Delta\omega = \sqrt{(1/T_2)^2 + \kappa^2 \epsilon_0^2 (T_1/T_2)} \quad . \quad (135)$$

If  $T_2$  is known, the ratio  $T_1/T_2$  can be obtained from this equation.

The signal at the input of the preamplifier of a microwave spectrometer is proportional to the mean difference in the current of the detector crystal in the presence and in the absence of sample. The change in the current at any time is proportional to the change in the microwave power,  $\bar{W}$ , as seen at the detector. It may be shown that the change in the microwave power is proportional to  $\epsilon_0 P_1$ ; <sup>92</sup> hence, it is proportional to  $\gamma \epsilon_0^2$ . Unfortunately,  $\epsilon_0$  is not constant throughout the sample. Therefore, to obtain  $d\bar{W}$  it is necessary to integrate over an assumed distribution for  $\epsilon_0$  so that

$$d\bar{W} = \frac{\Delta N_0^0 \hbar \omega}{2T_2} \frac{\kappa^2 \epsilon_0^2 dx dy dz}{\delta^2 + \kappa^2 \epsilon_0^2 T_1/T_2 + (1/T_2)^2} \quad . \quad (136)$$

In Equation (136)  $d\bar{W}$  is the contribution to the change in power that results from absorption in a box of volume  $dx dy dz$  located at  $x, y, z$  where  $\epsilon = \epsilon_0 \cos(\omega t - kz)$ .

The power distribution in the sample cell is assumed to be the power of a  $TE_{10}$  microwave mode, attenuated by ohmic losses in the walls of the cell; thus, as discussed more fully in the next section,

$$\epsilon_0^2 = \epsilon_m^2 \sin^2 \left( \frac{\pi y}{b} \right) e^{-\beta z} \quad (137)$$

where  $\beta$  is the cell attenuation coefficient and  $\epsilon_m$  is the peak electric field of the radiation at the entrance of the cell. After substituting for the power distribution and integrating over  $x, y$ , and  $z$ , Equation (136) becomes

$$d\bar{W} = \frac{\Delta N^0 \hbar \omega ab}{T_2^\beta} \ln \frac{\sqrt{C_0^2 + C_1^2 + C_0}}{\sqrt{C_0^2 + C_1^2 e^{-\beta \ell} + C_0}}, \quad (138)$$

where  $a$  and  $b$  are the width and height of the sample cell,  $\ell$  is its length,  $\Delta\bar{W}$  is the difference in the power at the inlet and outlet of the sample cell,

$$C_0^2 = \delta^2 + \left( \frac{1}{T_2} \right)^2, \quad (139)$$

and

$$C_1^2 = \frac{T_1}{T_2} \kappa^2 \epsilon_m^2 . \quad (140)$$

In the presence of an electric field many molecular transitions are split into several components. Equation (138) is the power broadened line shape of one such  $m$  component. At zero Stark field, when the transition is degenerate in  $m$ , the usual procedure has been to follow the work of Karplus and Schwinger and consider the line-shape to be a simple superposition of power broadened line shapes.<sup>98</sup> Recently, it has been shown by a number of workers<sup>94, 99-103</sup> that under conditions of partial saturation the  $m$  components of the transition are not completely uncoupled in the zero field experiment. Liu and Marcus<sup>94</sup> have shown that the power broadened line shape collapses to a single Lorentzian when certain assumptions are made about the populations of the  $m$  states. Schwendeman and Amano<sup>104</sup> have shown that the assumption Liu and Marcus made about the population of the  $m$  states was inadequate and made a different assumption. These results still lead to a line shape for the power broadened transition that is approximately a single Lorentzian.

In the work by Schwendeman and Amano the absorption coefficient times the power was found to be

$$\gamma \bar{W} = \frac{K \epsilon_m^2}{(\omega - \omega_0)^2 + (1/T_2)^2 + \gamma_s^2 T_1/T_2} . \quad (141)$$

where K is a constant. In this expression  $\gamma_s$  is defined as

$$\gamma_s^2 = q \times \mu_{f1}^{-2} \epsilon_m^2 / \hbar^2 , \quad (142)$$

where

$$X = \frac{J_1 + J_f + 1}{3(2J_1+1)(2J_f+1)} , \quad (143)$$

and  $J_1$  and  $J_f$  are the J values for the lower and upper states, respectively; q is a parameter that will be discussed below.

For a transition of the type  $J_f = J + 1 \leftarrow J_1 = J$ ,

$$X = \frac{2}{3} \frac{(J+1)}{(2J+1)(2J+3)} . \quad (144)$$

The averaged dipole moment matrix element is expressed as

$$\mu_{f1}^{-2} = 3 \sum_m |\langle J_f m | \mu_z | J_1 m \rangle|^2 , \quad (145)$$

and for the  $J + 1 \leftarrow J$  transition,

$$|\langle J+1, m | \mu_z | J, m \rangle|^2 = \frac{(J+1)^2 - M^2}{(2J+1)(2J+3)} \mu_0^2 . \quad (146)$$

Thus, the averaged dipole moment matrix element becomes,

$$\bar{\mu}_{f1}^2 = 3 \left( \frac{(2J+1)(J+1)^2}{(2J+1)(2J+3)} - \frac{\sum M^2}{(2J+1)(2J+3)} \right) \mu_0^2 . \quad (147)$$

Since

$$\sum_{m=-J}^J M^2 = \frac{1}{3} J(J+1)(2J+1) , \quad (148)$$

the averaged dipole moment matrix element is equal to

$$\bar{\mu}_{f1}^2 = (J+1)\mu_0^2 . \quad (149)$$

The parameter  $q$  in Equation (142) is defined as follows:

$$q = \frac{\sum_m f(m) [\Delta\rho(J_1 m, J_1 m) - \Delta\rho(J_f m, J_f m)]}{(\Delta\bar{\rho}_1 - \Delta\bar{\rho}_f)} \quad (150)$$

where  $\Delta\rho(J_m, J_m) = \rho(J_m, J_m) - \rho^0(J_m, J_m)$ , the term  $\rho^0(J_m, J_m)$  is the equilibrium value of the density matrix element  $\rho(J_m, J_m)$ , and  $\Delta\bar{\rho}_1$  and  $\Delta\bar{\rho}_f$  are the mean deviations of the density matrix elements from their equilibrium values.

If the frequency variation of the parameter  $q$  is ignored, Equation (141) is a single Lorentzian function that may be power averaged to give a function of the

form,

$$S(\omega) = AN \ln \frac{\sqrt{c_0^2 + c_1^2} + c_0}{\sqrt{c_0^2 + c_1^2} e^{-\beta l} + c_0} . \quad (151)$$

In this equation,

$$c_1^2 = \gamma_s^2 \frac{T_1}{T_2} = \frac{2}{3} \left( \frac{(J+1)^2}{(2J+1)(2J+3)} \right) \frac{\mu_0^2 \epsilon_0^2}{\hbar^2} \left( q \frac{T_1}{T_2} \right) , \quad (152)$$

$$c_0^2 = (\omega - \omega_0)^2 + (\Delta\omega)^2 , \quad (153)$$

and

$$N = \left( \ln \frac{\sqrt{(\Delta\omega)^2 + c_1^2} + \Delta\omega}{\sqrt{(\Delta\omega)^2 + c_1^2} e^{-\beta l} + \Delta\omega} \right)^{-1} . \quad (154)$$

### Microwave Power

The value of  $T_1$  may be determined from the linewidth equation under conditions of saturation. This occurs when the microwave power is high enough so that  $\epsilon_m$ , the peak amplitude of the electric field of the radiation is not negligible.

Consider a rectangular waveguide, as shown in Figure 13,

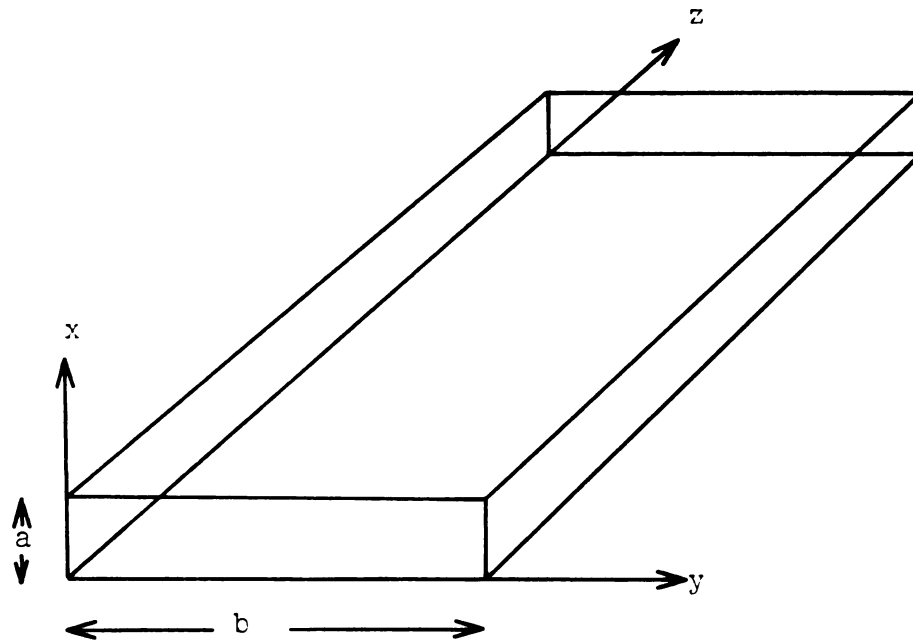


Figure 13. Rectangular hollow metal pipe waveguide.

where  $a$  is the length of the waveguide along the  $x$  axis and  $b$  is its length along the  $y$  axis. The radiation propagates along the  $z$  axis. Wave equations for the electric and magnetic part of the radiation can be derived from Maxwell's equations. After solving the wave equations for a lossless waveguide, the components of the electric field and the magnetic field for the  $TE_{10}$  mode are written<sup>105</sup>

$$\epsilon_0(z) = \epsilon_m \sin\left(\frac{\pi y}{b}\right) e^{i(\omega t - z/\lambda_g)} \quad (155)$$

$$\epsilon_y = \epsilon_x = H_z = 0 \quad (156)$$

$$H_y = \frac{\epsilon_m}{\omega \mu_0 \lambda_g} \sin\left(\frac{\pi y}{b}\right) e^{i(\omega t - z/\lambda_g)} \quad (157)$$

$$H_x = \frac{\epsilon_0 \pi}{\omega \mu_0 b} \cos\left(\frac{\pi y}{b}\right) e^{i[\omega t - 1/\lambda_g(z + \lambda_g/4)]} \quad (158)$$

where

$$\lambda_g = \frac{\lambda_0}{\{1 - (\frac{\lambda_0}{2b})^2\}^{1/2}} \quad (159)$$

In these equations  $\epsilon_m$  is the amplitude of the electric field,  $\omega$  is the angular velocity of the radiation,  $\mu_0$  is the permeability of a vacuum,  $\lambda_0$  is the wavelength of the radiation in free space,  $\lambda_g$  is the guided wavelength of the radiation, and  $\lambda_g = \lambda_0/2\pi$ . When the free-space wavelength of the

radiation is greater than  $2b$ , the radiation will not propagate along the waveguide. Thus,  $\lambda_c = 2b$  is the cut-off wavelength.

The propagation of radiation in a hollow rectangular waveguide is discussed in books on microwave theory and on electromagnetic theory.<sup>106</sup> It can be shown that the amount of energy passing through unit area per unit time can be obtained from the real part of the Poynting vector. The time average of the Poynting vector in mks units is expressed

$$S_{av} = \frac{1}{2}(\vec{E} \times \vec{H}^*)_{av} , \quad (160)$$

where  $\vec{E}$  is the electric field vector and  $\vec{H}^*$  is the complex conjugate of the magnetic field vector. Thus, in a rectangular waveguide, the real part of the time averaged Poynting vector<sup>105</sup> is

$$R_e(S_{av}) = \frac{1}{2} R_e(-E_x H_z^* + E_z H_x^*)_{av} , \quad (161)$$

or

$$R_e(S_{av}) = \frac{\epsilon_0^2}{2\omega\mu_0\lambda_g} \sin^2\left(\frac{\pi y}{b}\right)_{av} . \quad (162)$$

To obtain the transmitted power,  $W$ , the time averaged Poynting vector must be integrated over the surface area,

$$W = \int_{x=0}^{x=a} \int_{y=0}^{y=b} \frac{\epsilon_0^2}{2\omega\mu_0\lambda_g} \sin^2\left(\frac{\pi y}{b}\right) dx dy \quad (163)$$

$$W = \frac{\epsilon_0^2 ab}{4\omega\mu_0\lambda_g} \quad (164)$$

Since  $\omega = \frac{c}{\lambda_0}$ ,

$$W = \frac{\epsilon_0^2 ab}{4c\mu_0} \left(1 - \left(\frac{\lambda_0}{\lambda_c}\right)^2\right)^{1/2} \quad (165)$$

Thus

$$\epsilon_0 = W^{1/2} \left(\frac{4c\mu_0}{ab}\right)^{1/2} \left(1 - \left(\frac{\lambda_0}{\lambda_c}\right)^2\right)^{-1/4} \quad (166)$$

and

$$\kappa\epsilon_0 = W^{1/2} \left(\frac{4c\mu_0}{ab}\right)^{1/2} \frac{|\mu_{if}|}{\hbar} \left(1 - \left(\frac{\lambda_0}{\lambda_c}\right)^2\right)^{-1/4} \quad (167)$$

The dipole moment matrix element,  $|\mu_{if}|$ , can be expressed as the dipole moment  $\mu_D$  times the direction cosine matrix element. For the  $J + 1 \leftarrow J$ ,  $\Delta M = 0$  transition of a linear molecule, the direction cosine matrix element is expressed

$$f_M = \left( \frac{(J+1)^2 - M^2}{(2J+1)(2J+3)} \right)^{1/2} \quad (168)$$

Thus, in an X-band waveguide in which  $a = 1.016$  cm and  $b = 2.286$  cm,  $\kappa\epsilon_0$  in rad/ $\mu$ sec is given by

$$\kappa\epsilon_0(\text{rad/ sec}) = 2.548 \mu_D(\text{Debye}) f_M[W(\text{mW})]^{1/2} \left(1 - \left(\frac{\omega_c}{\omega_0}\right)^2\right)^{-1/4}, \quad (169)$$

when the dipole moment  $\mu_D$  is expressed in Debye and the power is given in milliwatts.

### The Natural Linewidth

The smallest contribution to the width of a microwave spectral line is called the natural linewidth. It arises from the uncertainty principle,

$$\Delta t \cdot \Delta E \approx \hbar. \quad (170)$$

Thus there is an energy spread and a spread in the lifetime associated with each excited state of the molecule. Since frequency is equal to energy divided by Planck's constant, a spread in the frequency of each transition also exists. This is the natural linewidth. The frequency spread is expressed as<sup>107</sup>

$$\Delta\nu = \frac{32\pi^3 \nu_{mn}^3}{3hc^3} \langle m|\mu|n\rangle^2, \quad (171)$$

where  $\nu_{mn}$  is the transition frequency and  $\langle m|\mu|n\rangle$  is the dipole moment matrix element from state  $m$  to state  $n$ . For a frequency of 30 GHz and a dipole moment matrix element of 1 Debye, the natural linewidth is roughly  $10^{-7}$  Hz. Such a linewidth is negligible compared to the other linewidth contributions. Most of the other line broadening mechanisms increase the linewidth by amounts on the order of kHz.

### Broadening by Collisions with the Walls

Collisions of sample molecules with the cell walls cause a broadening of spectral transitions which becomes a significant factor when the sample pressure is so low that the mean free path of the molecules approximates the cell dimensions. It is assumed that a collision between a sample molecule and a cell wall interrupts the radiation process. The collisions return the molecules to a Boltzmann distribution. According to theory, the contribution to the total lineshape differs slightly from a Lorentz line shape.<sup>108</sup> The full width at half-maximum in kHz is given approximately by<sup>107</sup>

$$2\Delta\nu \approx 1.16 \left( \frac{1}{a} + \frac{1}{b} + \frac{1}{c} \right) \left( \frac{T}{M} \right)^{1/2}, \quad (172)$$

where  $a$ ,  $b$ , and  $c$  are the dimensions of the sample cell in cm,  $T$  is the absolute temperature of the gas, and  $M$  is

its molecular mass. In an X-band waveguide at room temperature, the half-width at half maximum due to wall collision broadening is about 7 kHz for OCS.

### Doppler Broadening

At thermal equilibrium gas molecules in the sample cell are moving in random directions and have a Maxwell-Boltzmann distribution of velocities. In each molecule-fixed frame of reference the frequency of a beam of radiation differs from the laboratory frequency  $\omega$ . If a molecule has a component of its velocity in the direction of the radiation, the radiation appears to have a frequency  $\omega_a = \omega(1 - \frac{v}{c})$ , where  $v$  is the velocity component in the direction of propagation of the radiation and  $c$  is the velocity of the radiation. Thus, if the molecule is moving with the radiation, its frequency appears to be lower than the laboratory frequency. A molecule moving towards the radiation sees a higher frequency, while a molecule moving in a direction perpendicular to the direction of propagation of the radiation sees a frequency equal to the laboratory value.

To see the effect of Doppler broadening on the line-shape, it is useful to consider Equations (111)-(113) from which it is seen that  $\Delta N$ ,  $P_i$ , and  $P_r$  depend on the velocity of the molecules only in the frequency difference,  $\delta = \omega - \omega_0$ . The molecules can be divided into velocity

groups each of which contains molecules with velocities between  $v$  and  $v + dv$ . The fractional number of molecules in each group is

$$F(v)dv = \left(\frac{M}{2\pi k_B T}\right)^{1/2} e^{-Mv^2/2k_B T} dv, \quad (173)$$

where  $M$  is the molecular mass,  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature. The frequency of the radiation seen by the molecules in a given group is  $\omega(1 - \frac{v}{c})$  so that

$$\delta = \omega(1 - \frac{v}{c}) - \omega_0 \quad (174)$$

for each group. Thus the velocity-averaged  $P_1$  is found from

$$\bar{P}_1 = \int_{-\infty}^{\infty} P_1(v)F(v)dv. \quad (175)$$

Similar equations can be written for  $P_r$  and  $\Delta N$ . It has already been shown in Equation (103) that the absorption coefficient is proportional to  $P_1$ , so that

$$\bar{\gamma} = \int_{-\infty}^{\infty} \gamma(v)F(v)dv. \quad (176)$$

From Equations (130), and (173), the average absorption coefficient is found to be

$$\bar{\gamma} = \frac{4\pi\omega\kappa^2\hbar\Delta N^0}{cT_2} \left( \frac{M}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{\infty} \frac{e^{-Mv^2/2k_B T} dv}{\left( \omega - \frac{\omega v}{c} - \omega_0 \right)^2 + \left( \frac{1}{T_2} \right)^2 + \left( \frac{\kappa^2 \epsilon_0^2 T_1}{T_2} \right)} \quad (177)$$

To integrate Equation (177), let

$$x = \omega - \frac{\omega v}{c} - \omega_0. \quad (178)$$

Then,

$$dx = - \frac{\omega}{c} dv, \quad (179)$$

and

$$v^2 = (\omega - \omega_0 - x)^2 \left( \frac{c}{\omega} \right)^2. \quad (180)$$

If the microwave power and the sample pressure are very low,

$$\Delta^2 = \left( \frac{1}{T_2} \right)^2 + \frac{\kappa^2 \epsilon_0^2 T_1}{T_2}$$

is small. In this case, the Lorentzian in the denominator will fall and rise much faster than the Gaussian in the numerator. Under these circumstances,  $x$  can be set equal

to zero in the numerator and removed from the integral,  
which becomes

$$\bar{\gamma} = \frac{c}{\omega} e^{-\frac{Mc^2}{2k_B T \omega^2} (\omega - \omega_0)^2} \int_{-\infty}^{\infty} \frac{dx}{x^2 + \Delta^2}, \quad (181)$$

or

$$\bar{\gamma} = \frac{\pi c}{\omega \Delta} e^{-\frac{Mc^2 (\omega - \omega_0)^2}{2k_B T \omega^2}}. \quad (182)$$

The Doppler half-width occurs when

$$e^{-\frac{Mc^2 (\omega - \omega_0)^2}{2k_B T \omega^2}} = 1/2 \quad (183)$$

or

$$(\omega - \omega_0)^2 = \frac{(\ln 2) 2k_B T \omega^2}{Mc^2}. \quad (184)$$

Thus, the Doppler half-width is

$$\Delta \omega_D = \left( \frac{2k_B T \ln 2}{M} \right)^{1/2} \frac{\omega}{c}. \quad (185)$$

The other limiting case occurs when  $\Delta$  is much larger than  $\Delta\omega_D$ . In this case the Gaussian numerator rises and falls much faster than the Lorentzian denominator. It is then sufficient to set  $v = 0$  in the denominator of Equation (177) and remove the denominator from the integral. The integral then becomes equal to 1 and  $\bar{\gamma}$  reverts to the expression for  $\gamma$  given by Equation (130). For intermediate cases, i.e., when  $\Delta \sim \Delta\omega_D$ , Equation (177) must be integrated numerically, as there are no suitable analytical expressions or approximations. For the OCS  $J = 2 \leftarrow 1$  transition at 298°K,  $\Delta\omega_D \sim 19$  kHz. Since the linewidths in this work are all greater than  $\sim 200$  kHz, the extra broadening due to the Doppler effect is negligible and has been ignored.

## CHAPTER VII

### EXPERIMENTAL

#### Sample

The OCS sample was obtained from the Linde Division of Union Carbide Corporation, the  $H_2$  and  $CO_2$  were obtained from Matheson Chemical Co., and  $CH_3F$  was obtained from Peninsular Chemical Research Company. The OCS was analyzed at room temperature by means of a Beckman GC-2 gas chromatograph with a six foot silicone column. The sample was found to contain 1.8%  $CO_2$ . The sample was not purified, but corrections for the  $CO_2$  impurity were calculated by assuming that  $\Delta\nu/P$  for OCS/ $CO_2$  is 5.3 MHz/torr.<sup>109</sup> The correction was necessary in the case of a pure OCS sample, but was insignificant for the gas mixture which contained about 3% OCS. Gas chromatography applied to the  $CO_2$  and  $CH_3F$  samples showed no impurities. The  $H_2$  sample was advertised as being 99.95% pure and was not checked.

#### Pressure Meter

The sample pressures were measured by an MKS Baratron 77M-XR pressure meter with a 77H1 pressure measuring head; the Baratron is a capacitance manometer. With this system,

sample pressures can be measured to 0.01 mtorr and the accuracy of pressure measurements above 10 mtorr appears to be of the order of 1%. Some of the transitions were recorded over a period of about 4 minutes, during which the pressure varied by a maximum of 0.04 mtorr. Others were recorded over a 7 minute period with a maximum pressure variation of 0.09 mtorr. The majority of the pressure variation was attributed to a slow leak in the sample cell.

#### Microwave Spectrometer

The spectrometer used for the linewidth measurements was a Hewlett-Packard 8460A Molecular Rotational Resonance (MRR) spectrometer. Its radiation source is a backward wave oscillator, the frequency of which is stabilized to harmonics of the output of a frequency synthesizer by means of phase-lock loops. Stark modulation of 33.33 kHz and phase sensitive detection are used to increase the sensitivity.

Just before and just after the sample cell, the radiation power was sampled through 20 db directional couplers. Microwave power measurements were obtained by using two Hewlett-Packard Model K486A thermister mounts with a Hewlett-Packard Model 432A power meter. This combination is capable of measuring power between 1 $\mu$ W and 10 mW with a maximum uncertainty of about 4% in the 0.03 mW

range. The power meter and thermister mount are designed so that the power measurements are free from drifts due to changes in the ambient temperature.

The sample cell was X-band waveguide, 6 feet long, which encloses a metal septum. The microwave radiation was rectified and filtered by a crystal detector, and the resulting DC crystal current was passed through a resistor in a preamplifier. A low pass filter was placed in front of the detector to remove the effects of the  $J = 4 \leftarrow 3$  transition of OCS. The frequency of this transition is approximately twice that of the  $J = 2 \leftarrow 1$  OCS transition and the transition occurs when the molecules absorb the second harmonic of the microwave radiation. The line-shape was observed under conditions of low and moderate radiant power. To insure that the crystal detector would always sense the same microwave power, attenuators were placed before and after the sample cell. The two attenuators were adjusted so that the sum of their attenuations was always the same.

The lineshapes were acquired in digital form by means of a Digital Equipment Corporation PDP-8/E computer. The computer was interfaced to the spectrometer through a Heath EU-801E analog-digital-designer and an interface card designed by Steven Brown. The analog-to-digital (A/D) converter was a Heath EU-900-EB 10 bit system. The computer program averaged the results of an optional number of

readings of the A/D converter at each frequency for an optional number of sweeps through the spectrum. The time delay before making the first reading at each frequency and the time between readings at each frequency could also be selected by the operator. The results of thorough tests of the apparatus with pure OCS as a sample have been described.<sup>109</sup>

### Experimental Procedure

Linewidth measurements were made for OCS mixed with various other gases. The samples were 3.1% OCS in  $\text{CH}_3\text{F}$ , 1.6% OCS in  $\text{CO}_2$ , and 1.9% OCS in  $\text{H}_2$ . The relative amounts of the different gases were determined by pressure measurements with a mercury manometer in a particular section of a vacuum line.

Before the linewidths were obtained, the best Stark voltage for recording the OCS transition had to be found. A Stark voltage of 1600 volts was used because at this voltage the Stark components do not overlap the zero-field transition. The lineshape of the  $J = 2 \leftarrow 1$  transition in the ground state of OCS was scanned from 24321 MHz to 24331 MHz at 50 kHz intervals. When  $\text{CH}_3\text{F}$  was used as the perturbing gas, the A/D converter was read 10 times at each frequency with a 200 msec pause between readings. The initial reading at each frequency was made after a pause of 100 msec from the last reading at the previous frequency.

The spectrum was scanned once and the average readings were recorded on magnetic tape. When  $\text{CO}_2$  or  $\text{H}_2$  was used as the perturber, the spectrum was scanned once, the A/D converter was read 20 times at 50 msec intervals, and there was a 200 msec pause before the initial readings at each frequency. For all of the systems, the time constant of the lock-in amplifier was 10 msec.

Each of the three samples was studied at various total pressures between 20 and 120 mtorr. The OCS transition was recorded seven times at each pressure. The second, fourth, and sixth recordings were taken with approximately 10 m watts of microwave power entering the sample cell. The other four recordings were obtained under conditions of low incident power, about 22 db below the power level of the three high power recordings. For each lineshape recorded, the time of day, sample cell temperature, sample pressure, and temperature of the Baratron head were obtained.

Before the linewidths of the transition were analyzed, some properties of the spectrometer were checked. The linearity of the attenuator and synchronous detector was checked. For the high power measurements it was necessary to determine the attenuation of the sample cell and other components of the spectrometer waveguide. This was done by sampling the microwave power before and after the waveguide components by means of directional couplers. The ratios of the input and output microwave power with and without the element under consideration were compared.

## CHAPTER VIII

### RESULTS

#### Low Power Linewidths

The low-power lineshapes were fit to a Lorentz function of the form

$$S(\nu) = \frac{A(\Delta\nu)^2}{(\nu-\nu_0)^2 + (\Delta\nu)^2} + B_0 + B_1(\nu-\nu_0) , \quad (186)$$

where  $A$ ,  $B_0$ ,  $B_1$ ,  $\nu_0$  and  $\Delta\nu$  are the adjustable parameters. In Equation (186),  $A$  is the amplitude of the transition,  $\nu$  is the microwave frequency,  $\nu_0$  is the center frequency of the transition,  $B_0$  is the background voltage, and  $B_1$  corrects for any slope of the background. The background corrections are introduced to account for variations in the output of the lock-in amplifier, which result from differences in electronic pickup at various microwave frequencies. Variation of the crystal current with frequency could also contribute to the background, but this effect was found to be negligible for our instrument.<sup>109</sup>

It has been found that the linewidth of the OCS  $J = 2 \leftarrow 1$  transition is nearly inversely proportional to temperature near 298 K.<sup>109</sup> All of the lineshapes were

recorded at room temperature and throughout the day the temperatures varied by several degrees. Therefore, all linewidths were corrected to 298°K by multiplying the room temperature linewidth by  $T/298$ , where  $T$  was the measured temperature in degrees Kelvin.

The sample cell had a slow leak of less than one micron per hour. Figure 14 shows a plot of pressure versus time for the linewidth measurements of OCS in  $\text{CH}_3\text{F}$  at a total pressure of about 34 microns. For each set of linewidth measurements at one pressure, the pressure was plotted against the time and, by using the method of least squares, the sample pressure was found at the time the sample cell was closed (and hence no longer pumped on). This pressure was subtracted from the measured pressure at any time to yield the pressure of air in the sample cell at that time. The contribution to the linewidth from the air was found by multiplying the pressure of air by 4.41 MHz/torr,<sup>88</sup> the linewidth parameter for  $\text{N}_2$ , since nitrogen is the main component of air. The linewidth of OCS in the perturbing gas was found by subtracting the linewidth due to air from the measured, temperature-corrected linewidth.

Four low-power linewidths were observed at each pressure. After temperature corrections and corrections for air were made, the four linewidths were averaged. Table 17 lists the corrected linewidth and pressure without air for OCS in  $\text{CH}_3\text{F}$ , OCS in  $\text{CO}_2$  and OCS in  $\text{H}_2$ . These points

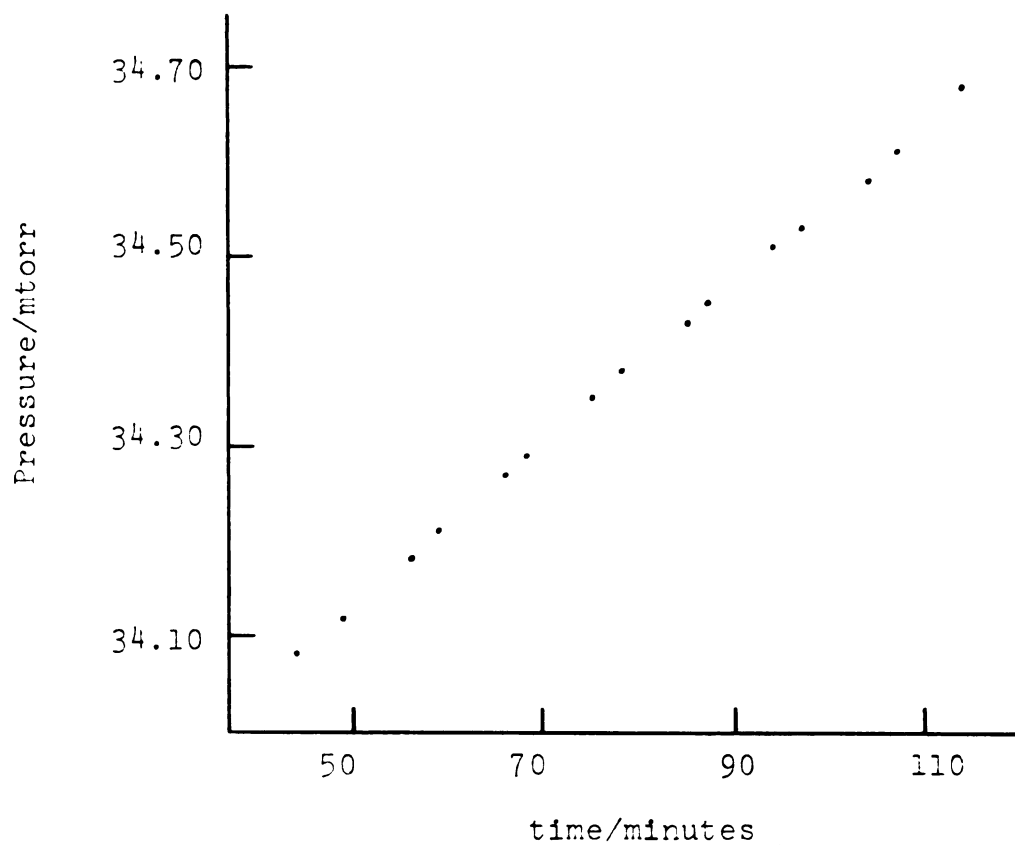


Figure 14. Plot of pressure versus time for the line-width measurements of OCS in  $\text{CH}_3\text{F}$  at a pressure of 34 microns.

Table 17. Average linewidth and pressure for the  $J = 2 + 1$  transition of OCS in  $\text{CH}_3\text{F}$ ,  $\text{CO}_2$  or  $\text{H}_2$ . Corrections have been made for the effects of temperature variation and the addition of air.

| OCS in $\text{CH}_3\text{F}$ |                 |
|------------------------------|-----------------|
| Linewidth/kHz                | Pressure/ $\mu$ |
| 212.6                        | 17.94           |
| 229.4                        | 19.38           |
| 322.9                        | 27.70           |
| 393.2                        | 33.69           |
| 480.9                        | 41.80           |
| 577.9                        | 50.52           |
| 668.6                        | 58.30           |
| 760.1                        | 66.71           |
| 962.2                        | 84.02           |
| OCS in $\text{CO}_2$         |                 |
| Linewidth/kHz                | Pressure/ $\mu$ |
| 210.6                        | 38.29           |
| 261.8                        | 48.07           |
| 342.7                        | 63.38           |
| 452.9                        | 84.33           |
| 506.6                        | 94.64           |
| 582.1                        | 108.86          |
| 633.9                        | 118.47          |
| OCS in $\text{H}_2$          |                 |
| Linewidth/kHz                | Pressure/ $\mu$ |
| 175.4                        | 26.84           |
| 236.6                        | 36.98           |
| 281.5                        | 44.58           |
| 362.7                        | 58.10           |
| 398.4                        | 64.02           |
| 453.0                        | 72.87           |
| 531.3                        | 85.69           |
| 659.8                        | 106.60          |

were least squares fit to a straight line,

$$\Delta\nu = \Delta\nu_0 + (\Delta\nu/p)p, \quad (187)$$

where  $\Delta\nu_0$  is the limiting linewidth at zero pressure and  $\Delta\nu/p$  is the linewidth parameter.

One way to perform this experiment would be to use a constant pressure of OCS and to vary the pressure of the foreign gas. The linewidth of the transition can then be plotted against the pressure of the foreign gas. This will result in a straight line, the slope of which is the linewidth parameter of OCS with this collision partner. The intercept of the line will be the linewidth due to collisions of OCS with the wall and the linewidth contribution due to OCS colliding with other OCS molecules. However, in our experiment the sample always had the same percentage of OCS mixed with the foreign gas. Changing the pressure of the sample would change the amount of OCS as well as the amount of the foreign gas. In this case, a plot of the linewidth against the total pressure would again yield a straight line. The intercept, however, is the linewidth due only to collisions of OCS with the wall. Therefore, the slope of the line in this case, will contain contributions both from the linewidth parameter due to OCS-OCS collisions and the linewidth parameter due to collisions between OCS and the foreign gas. Thus, the contribution due to OCS-OCS

collisions must be removed from the linewidth parameter of the gas mixture.

To remove the effect of self-broadening, the linewidth is expressed as follows:

$$\Delta\nu_T = \Delta\nu_{\text{wall}} + p_1\left(\frac{\Delta\nu}{p}\right)_1 + p_2\left(\frac{\Delta\nu}{p}\right)_2 \quad (188)$$

where  $p_1$  is the pressure of the OCS,  $p_2$  is the pressure of the foreign gas,  $\left(\frac{\Delta\nu}{p}\right)_1$  is the linewidth parameter for collisions between OCS molecules and  $\left(\frac{\Delta\nu}{p}\right)_2$  is the linewidth parameter for collisions between OCS and the foreign gas. Equation (188) can be rearranged to

$$\left(\frac{\Delta\nu}{p}\right)_2 = \frac{\Delta\nu_T - \Delta\nu_{\text{wall}}}{p_T} - \frac{p_1}{p_T} \left[ \left(\frac{\Delta\nu}{p}\right)_1 - \left(\frac{\Delta\nu}{p}\right)_2 \right], \quad (189)$$

where  $p_T = p_1 + p_2$  and  $\frac{\Delta\nu_T - \Delta\nu_{\text{wall}}}{p_T}$  is the slope from the plot of the linewidth against total pressure. Table 18 lists the linewidth parameters taken from the slopes, the corrected linewidth parameters for collisions between OCS and the foreign gas, and the linewidth contribution due to collisions of OCS with the wall.

### Power-Broadened Linewidths

The power-broadened transitions were fit by the two different methods which were discussed in the theory chapter. In one method the power broadened lineshapes were

Table 18. Linewidth parameters and linewidths due to wall collisions for the  $J = 2 \leftarrow 1$  transition of OCS in a foreign gas. The slope is from the plot of linewidth versus pressure. It contains the linewidth parameter due to OCS-OCS collisions and that due to collisions of OCS with the foreign gas. The column  $(\Delta\nu/p)$  contains only the linewidth parameter due to OCS-foreign gas collisions.

| Perturber         | Slope/(MHz/torr) <sup>a</sup> | $(\Delta\nu/p)$ /(MHz/torr)                 | $\Delta\nu_w$ /kHz <sup>a</sup> |
|-------------------|-------------------------------|---------------------------------------------|---------------------------------|
| CH <sub>3</sub> F | 11.29                         | 11.45(17) <sup>a</sup><br>11.9 <sup>d</sup> | 9.9                             |
| CO <sub>2</sub>   | 5.27                          | 5.26(8) <sup>a</sup><br>5.13 <sup>d</sup>   | 8.4                             |
| H <sub>2</sub>    | 6.07                          | 6.07(9) <sup>a</sup><br>6.10 <sup>d</sup>   | 11.2                            |
| OCS               |                               | 6.03                                        |                                 |

<sup>a</sup>This work.

<sup>b</sup>H. Mäder, J. Ekkers, W. Hoke, and W. H. Flygare, J. Chem. Phys., 62, 4380 (1975).

<sup>c</sup>OCS,  $J = 1 \leftarrow 0$  transition.

<sup>d</sup>B. Th. Berendts and A. Dymanus, J. Chem. Phys., 48, 1361 (1968).

<sup>e</sup>R. A. Creswell, S. R. Brown, R. H. Schwendeman, J. Chem. Phys., 64, 1820 (1976).

fit to the following equation, which assumes that the absorption coefficient is the sum of power broadened Lorentzian lineshapes for each  $m$  component of the transition:

$$S(\omega) = NA \sum_m \ln \frac{\sqrt{c_0^2 + c_1^2} + c_0}{\sqrt{c_0^2 + c_1^2 e^{-\beta \ell}} + c_0} + B_1(\omega - \omega_0) + B_0, \quad (190)$$

where

$$N = \left( \sum_m \ln \frac{\sqrt{T_2^{-2} + c_1^2} + T_2^{-1}}{\sqrt{T_2^{-2} + c_1^2 e^{-\beta \ell}} + T_2^{-1}} \right)^{-1}, \quad (191)$$

$$c_0^2 = (\omega - \omega_0)^2 + T_2^{-2}, \quad (192)$$

$$c_1^2 = T_1 T_2^{-1} \mu^2 \epsilon_0^2 n^2, \quad (193)$$

and the sum is over all the  $m$  components of the transition. The value for  $T_2$  is obtained from the average of the low power linewidth just before and just after the high power recording. The quantities  $A$ ,  $B_0$ ,  $B_1$ ,  $\omega_0$ , and  $T_1/T_2$  are the adjustable parameters. As before,  $A$  is the amplitude of the transition,  $\omega$  is the angular frequency of the microwave radiation,  $\omega_0$  is the center frequency of the transition,  $B_0$  is the background value, and  $B_1$  is the slope of the

background. The sample cell length is  $\ell$  and its attenuation is  $\beta$ . Inclusion of the factor  $N$  improved the convergence and stability of the iteration procedure. Both the low-power and moderate-power transitions were analyzed on the PDP8 minicomputer.

At each pressure, three moderate-power transitions were recorded. Each transition was fit to the power broadened lineshape. The ratio  $T_1/T_2$  was obtained from the fitted parameter,  $E_p$ , defined as follows:

$$C_1^2 = \frac{E_p[(J+1)^2 - M^2]}{[(2J+1)(2J+3)]^2} = \mu^2 \epsilon_0^2 \frac{T_1}{T_2} . \quad (194)$$

The quantity  $E_p$  is called the "effective power".

Figures 15, 16, and 17 show plots of the effective power versus pressure for OCS mixed with  $\text{CH}_3\text{F}$ , OCS mixed with  $\text{CO}_2$ , and OCS mixed with  $\text{H}_2$ . As mentioned, three linewidths were analyzed at each pressure. All three values for the effective power are shown. The bars indicate the size of the standard deviations of the fitted parameter. As there is no clear indication of a pressure dependence, all of the values of the effective power were averaged for each of the three gas mixtures and  $T_1/T_2$  was determined for each sample. The results are shown in Table 19.

The same power broadened lines were also fit to a single Lorentzian lineshape from which the parameter

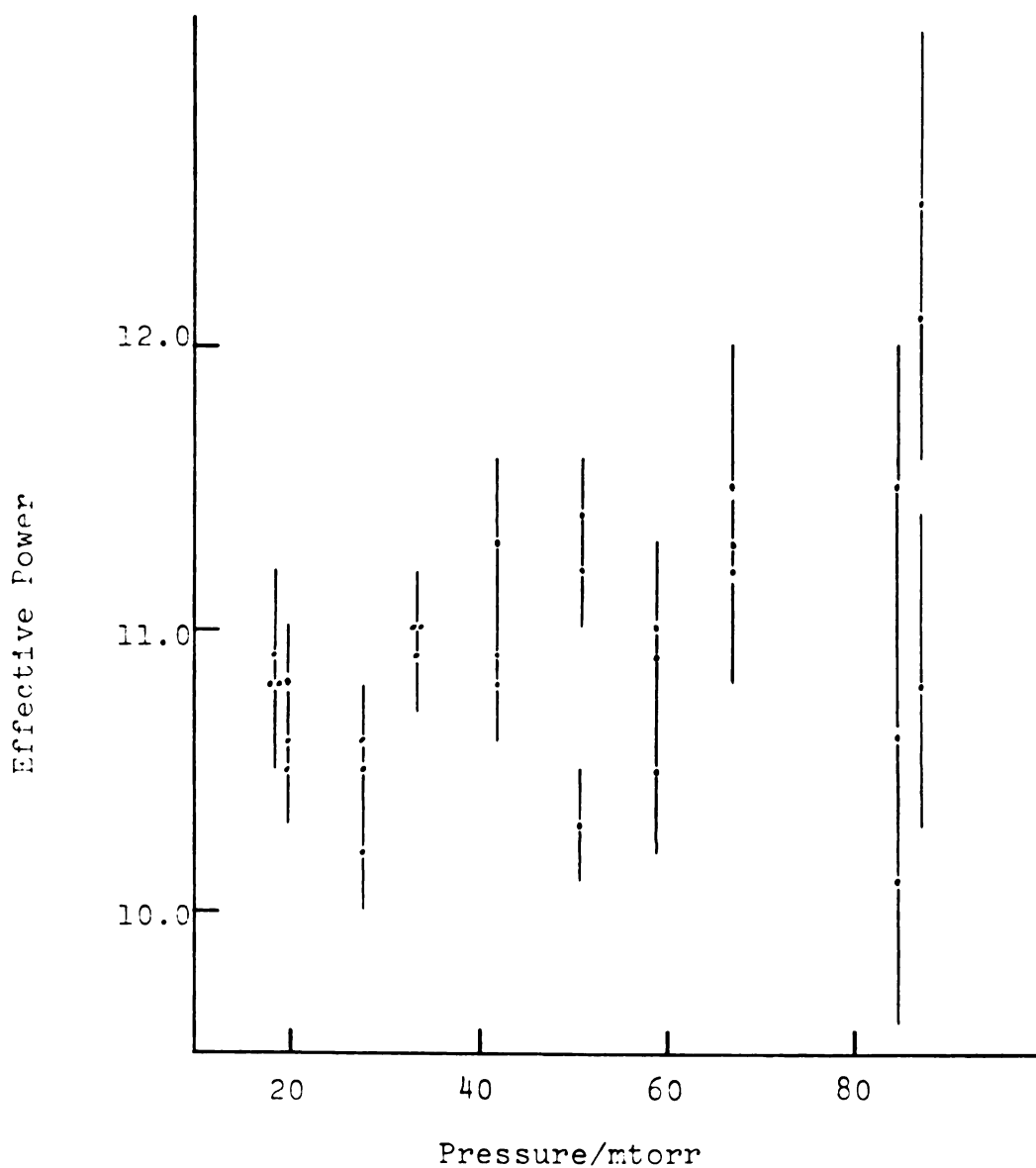


Figure 15. Plot of effective power versus pressure for OCS mixed with  $\text{CH}_3\text{F}$ . Three linewidths were analyzed at each pressure. All three values for the effective power are shown. The bars indicate the size of the standard deviation of the fitted parameter.

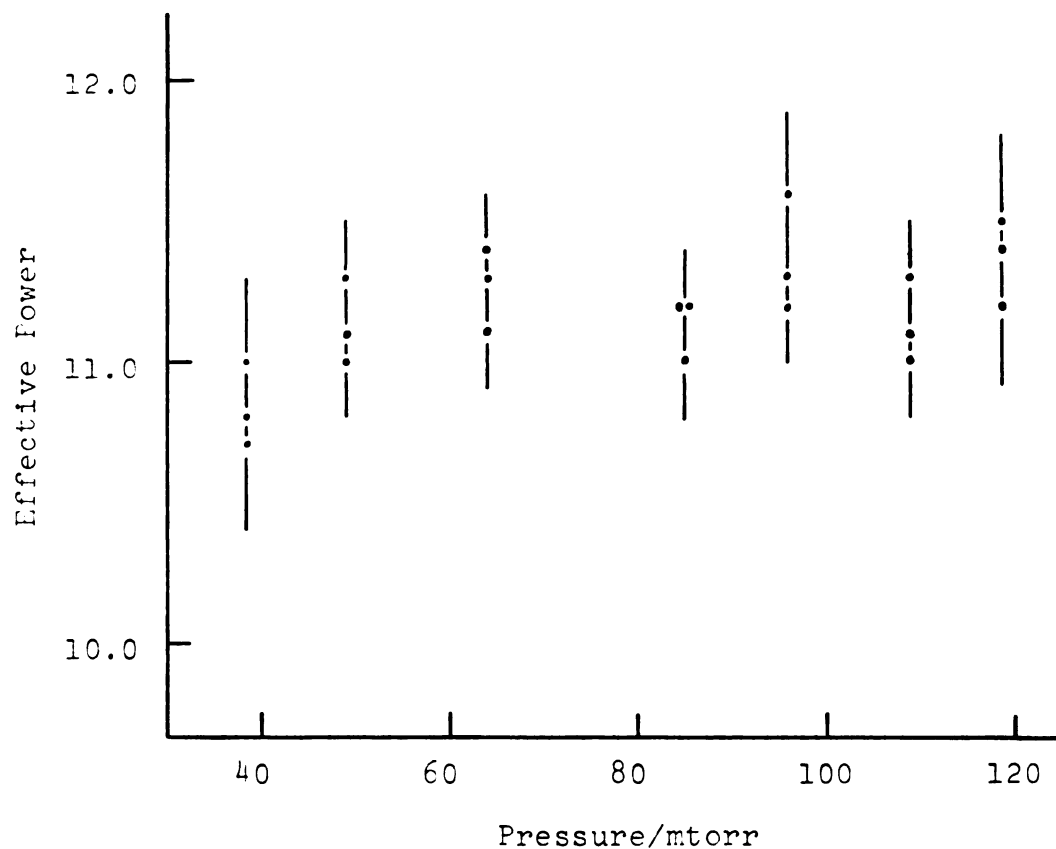


Figure 16. Plot of effective power versus pressure for OCS mixed with CO<sub>2</sub>. Three linewidths were analyzed at each pressure. All three values for the effective power are shown. The bars indicate the size of the standard deviation of the fitted parameter.

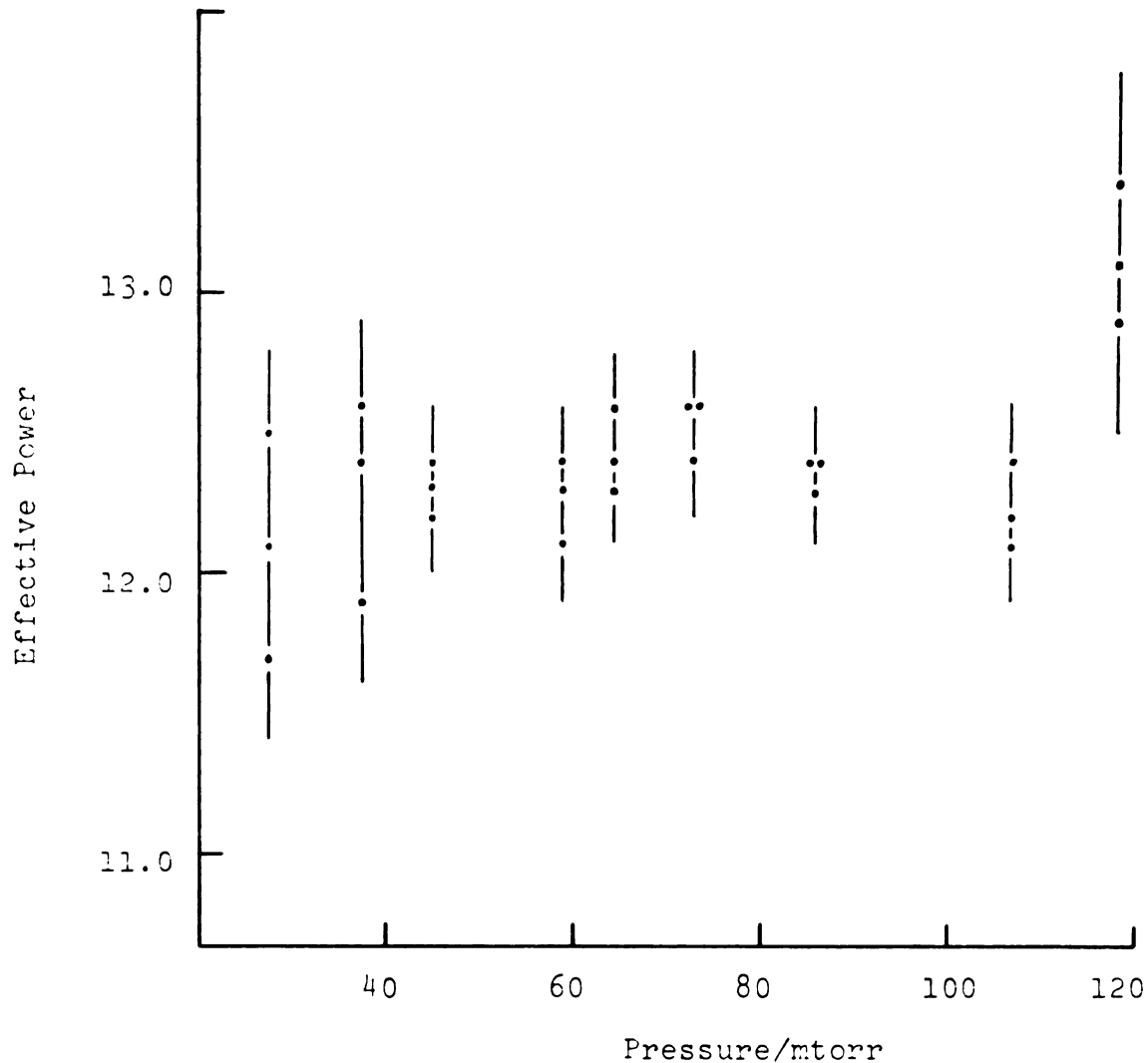


Figure 17. Plot of effective power versus pressure for OCS mixed with  $H_2$ . Three linewidths were analyzed at each pressure. All three values for the effective power are shown. The bars indicate the size of the standard deviation of the fitted parameter.

Table 19. Average values for  $(T_1/T_2)_0$  and  $(q T_1/T_2)$  measured for the  $J = 2 \leftarrow 1$  transition of OCS mixed with various foreign gases. All of the parameters were obtained at zero Stark field.

| Perturber         | $(T_1/T_2)_0$ | $(q T_1/T_2)$ |
|-------------------|---------------|---------------|
| CH <sub>3</sub> F | 0.97±0.10     | 1.23±0.12     |
| CO <sub>2</sub>   | 1.03±0.10     | 1.30±0.13     |
| H <sub>2</sub>    | 1.05±0.10     | 1.32±0.13     |

( $q T_1/T_2$ ) was obtained. In this case the power broadened lineshapes are fit to a function of the form

$$S(\omega) = AN \ln \frac{\sqrt{c_0^2 + c_1^2} + c_0}{\sqrt{c_0^2 + c_1^2} e^{-\beta \ell} + c_0} + B_1(\omega - \omega_0) + B_0 . \quad (195)$$

In Equation (195)  $c_1^2 = \gamma_s^2 \frac{T_1}{T_2}$ , or

$$c_1^2 = \frac{2}{3} \frac{(J+1)^2}{(2J+1)(2J+3)} \frac{\mu_0^2 \epsilon_0^2}{\hbar^2} \left( q \frac{T_1}{T_2} \right) . \quad (196)$$

The results for  $T_1/T_2$  and  $q T_1/T_2$  for the various collision partners of OCS, taken at zero field, are given in Table 19. Neither the power broadened lines which were fit to a single Lorentzian nor those fit to a sum of Lorentzian lineshapes showed a significant shift in the center frequency with pressure.

## CHAPTER IX

### DISCUSSION

The values of  $T_2$  obtained from the low-power linewidth measurements of the  $J = 2 \leftarrow 1$  transition of OCS in a sample of OCS mixed with foreign gases compare favorably with those measured previously in the same mixtures by Berendts. These  $T_2$  values are known slightly less well than the  $T_2$  relaxation constant for a pure OCS sample, since the mixtures contain only 3% or less of OCS and the linewidths were observed in the same pressure range.

The results of the low-power linewidth study of these same mixtures is shown in Table 18. The uncertainties in the linewidth parameter are probably dominated by an estimated  $\pm 1.5\%$  uncertainty in the measurement of the absolute pressures. The linewidth parameter for the OCS- $H_2$  mixture is not much different from the linewidth parameter for OCS self broadening. The same result was found for the linewidth of another linear molecule,  $N_2O$ .<sup>88</sup> The linewidth parameter for the  $N_2O$ - $H_2$  mixture was found to be 5.15 MHz/torr, and for  $N_2O$  self broadening it was found to be 5.22 MHz/torr. When  $H_2$  was used as the perturbing gas for non-linear molecules, however, the linewidth parameter was found to be much different for the mixture and for self broadening.<sup>88</sup> Also, our value for the linewidth parameter for

the OCS-CH<sub>3</sub>F mixture lies between that for pure OCS at 6.03 MHz/torr and that for pure CH<sub>3</sub>F at about 20 MHz/torr.<sup>88</sup>

Effective cross-sections for collisions,  $\sigma$ , and effective collision diameters,  $b$ , were computed using the expressions<sup>107</sup>

$$\sigma = 2\pi\Delta v/N \bar{v}_{\text{rel}} , \quad (197)$$

and

$$b^2 = \sigma/\pi . \quad (198)$$

In Equation (197),  $N$  is the number of molecules per cm<sup>3</sup> and  $\bar{v}_{\text{rel}}$  is the mean relative velocity of OCS and the perturbing molecule. The effective collision diameter for OCS perturbed by H<sub>2</sub> is 4.56 Å,  $b$  for OCS perturbed by CO<sub>2</sub> is 8.07 Å,  $b$  for OCS perturbed by OCS is 9.01 Å and  $b$  for OCS perturbed by CH<sub>3</sub>F is 11.45 Å. As expected, the effective collision diameters increase for increasing size and increasing dipole moment of the perturber.

The high-power linewidths yield the ratio  $T_2/T_1$ . In Chapter VI,  $T_2/T_1$  was shown to be related to collisional rate constants, as follows:

$$\frac{T_2}{T_1} = \frac{2\Gamma_{12} + \Gamma'}{\Gamma_{12} + \Gamma' + \Gamma_a} .$$

As mentioned previously, the rate constant due to adiabatic processes,  $\Gamma_a$ , is expected to be small for microwave transitions. Therefore, since the experimental values of  $T_2/T_1$  for the gas mixtures studied here are approximately one, collisional transitions involving the states  $J = 1$  and  $J = 2$  are dominated by transitions to and from other states. This might well be expected for a molecule such as OCS, in which the energy separations of the rotational levels are small compared to the collisional energy. This may be contrasted to a system such as  $\text{NH}_3$ , in which pairs of rotational energy levels, the inversion doublets, are separated by energies corresponding to microwave radiation, and are separated from other pairs of levels by energies corresponding to far-infrared radiation. Work done in this laboratory has shown that for  $\text{NH}_3$ ,  $T_1 \neq T_2$ . In fact,  $1 < T_2/T_1 < 2$ . It would be useful for future work to examine the rotational relaxation constants  $T_1$  and  $T_2$  for other quasi two-level systems such as formaldehyde or HCN as well as for a molecule with a typical level structure such as  $\text{SO}_2$ , to see if the value of  $T_2/T_1$  is near 2 for two level systems and near 1 for multilevel systems.

Mäder et al.<sup>89</sup> found that  $T_1/T_2$  was almost equal to 1 for the  $J = 1 \leftarrow 0$  transition of OCS in a mixture of OCS and  $\text{CH}_3\text{F}$ . This result was obtained from a transient experiment in which a  $\pi$ - $\tau$ - $\pi/2$  microwave pulse sequence was applied to the sample. The ratio of the peak absorption at the

end of the  $\pi/2$  pulse to the peak absorption in the middle of the  $\pi$  pulse was plotted against  $\tau$  to obtain  $T_1$ . The rotational relaxation parameter  $T_2$  was obtained from the envelope of the decay of the transient emission following a  $\pi/2$  pulse. In a molecular beam experiment, Wang et al.<sup>90</sup> found the cross sections  $\sigma_I$  and  $\sigma_{II}$  (which are thought to be closely related to  $T_1^{-1}$  and  $T_2^{-2}$ , respectively) to be quite different for the  $J = 2 \leftarrow 1$  transition of OCS in a mixture of OCS and  $\text{CH}_3\text{F}$ . Our value of  $T_1/T_2$  for the  $J = 2 \leftarrow 1$  transition of OCS in a mixture of OCS and  $\text{CH}_3\text{F}$  was very close to Flygare's value - near 1.

The values of  $T_1/T_2$  found by Mader, et al., by Wang, et al., and in our laboratory are listed in Table 20. Upon comparison of the  $T_1/T_2$  value from our linewidth measurements of the  $J = 2 \leftarrow 1$  transition of OCS for the OCS- $\text{CH}_3\text{F}$  mixture to the  $\sigma_{II}/\sigma_I$  value from the molecular beam experiment, it is apparent that two different quantities are being measured. Apparently, the ratio of the molecular beam cross sections,  $\sigma_{II}/\sigma_I$ , can be significantly different from  $T_1/T_2$ . The zero field linewidth value of  $(T_1/T_2)_0$  obtained here for the  $J = 2 \leftarrow 1$  transition is, however, essentially the same as the  $T_1/T_2$  value obtained by the transient effect measurements for the  $J = 1 \leftarrow 0$  transition.

A comparison of the  $(T_1/T_2)_0$  values for the mixtures OCS- $\text{H}_2$ , OCS- $\text{CO}_2$ , and OCS- $\text{CH}_3\text{F}$  is shown in Table 19.

Table 20. Comparison of the rotational relaxation parameters of OCS in a mixture of OCS and CH<sub>3</sub>F found by transient effect, molecular beam, and linewidth measurements.

| Transient Effect, J=1+0 <sup>a</sup><br>T <sup>-1</sup> <sub>1</sub> /μsec <sup>-1</sup> mtorr <sup>-1</sup> |                              | Molecular Beam, J=2+1 <sup>b</sup><br>σ/Å <sup>2</sup> |                | Linewidth, J=2+1 <sup>c</sup>                                                                        |
|--------------------------------------------------------------------------------------------------------------|------------------------------|--------------------------------------------------------|----------------|------------------------------------------------------------------------------------------------------|
| T <sup>-1</sup> <sub>1</sub>                                                                                 | T <sup>-1</sup> <sub>2</sub> | T <sub>1</sub> /T <sub>2</sub>                         | σ <sub>I</sub> | σ <sub>II</sub><br>σ <sub>II</sub> /σ <sub>I</sub><br>(T <sub>1</sub> /T <sub>2</sub> ) <sub>0</sub> |
| 0.079                                                                                                        | 0.077                        | 0.97                                                   | 990            | 750<br>0.76<br>0.97                                                                                  |

<sup>a</sup>H. Mäder, J. Ekkers, W. Hoke, and W. H. Flygare, J. Chem. Phys., 62, 4380 (1975).

<sup>b</sup>J. H. S. Wang, D. E. Oates, A. Ben-Reuven, and S. G. Kukolich, J. Chem. Phys., 59, 5268 (1975).

<sup>c</sup>This work.

The uncertainty in the values of  $(T_1/T_2)_0$  from our moderate-power linewidth studies is estimated to be  $\pm 10\%$ . Most of the error is due to uncertainty in the magnitude and distribution of the microwave power. The values of  $(T_1/T_2)_0$  are nearly equal for all three of the mixtures. The trend in  $(T_1/T_2)_0$ , however, might be more accurate than the absolute magnitudes of the ratios since the power uncertainties are unaffected by the gas mixture and are therefore the same for all three gases. Hence, the slight differences in  $(T_1/T_2)_0$  may be real.

For the same experimental lineshapes of the three different mixtures, the ratios of the rotational relaxation times were calculated in two different ways. The discussion just given referred to the calculation of  $(T_1/T_2)_0$ , the value of  $T_1/T_2$  at zero field when the lineshape is fit to a sum of power-broadened Lorentzian lines. This calculation followed the procedure first described by Karplus and Schwinger. Recently, it has been shown that it is more correct to fit the lineshapes to a single power-broadened Lorentzian, from which it is possible to extract the single parameter  $q T_1/T_2$ . This calculation has been performed and the values of  $q T_1/T_2$  for each gas mixture are shown in Table 19. No method of interpretation of  $q T_1/T_2$  exists as yet; however, C. Bottcher has stated privately that he has estimated  $q$  to be about 1.3, which is what we obtain if  $T_1/T_2 \cong 1$ . More theoretical work must be done before experimental  $q T_1/T_2$  values can be interpreted.

## PART III

### MICROWAVE SPECTRUM OF ISOPROPENYLCYCLOPROPANE

#### CHAPTER X

##### Introduction

The internal rotation of various groups attached to cyclopropane has been studied by microwave spectroscopy in this laboratory and elsewhere. These compounds have also been studied by electron diffraction. As an extension of this work, we wanted to compare the internal rotation of the isopropenyl group with the internal rotation in vinylcyclopropane,<sup>110</sup> cyclopropanecarboxaldehyde,<sup>111</sup> cyclopropanecarboxylic acid fluoride,<sup>112</sup> and cyclopropylmethylketone.<sup>113</sup> Two conformations were found by electron diffraction<sup>114</sup> and by microwave spectroscopy for cyclopropanecarboxaldehyde<sup>111</sup> and by microwave spectroscopy for cyclopropanecarboxylic acid fluoride.<sup>112</sup> In one configuration the oxygen atom is trans to the cyclopropane ring, and in the other the oxygen is cis to the ring. It has been hypothesized that trans and cis conformers, rather than the expected trans and gauche conformers, are found in these compounds because of conjugation across the C-C bond between the ring and the carbonyl double bond. Vinylcyclopropane

was studied to see if the conjugation to the ring would occur when the attached  $\pi$ -system was a  $-C=C-$  group.<sup>110</sup> Unfortunately, only the trans species of vinylcyclopropane could be assigned in the microwave spectrum. However, an electron diffraction investigation has indicated that vinylcyclopropane occurs as trans and gauche conformers,<sup>115</sup> and this result has been confirmed by ab initio calculations.<sup>116</sup> A recent study of 3-methyl-1-butene has shown that the conformers in this molecule have the vinyl group trans and gauche to the plane of the isopropane carbons.<sup>117</sup> Hence, it was of some interest to try to determine the conformations in isopropenylcyclopropane. Unfortunately, as described below, the study of the microwave spectrum of this molecule proved even less conclusive than that of vinylcyclopropane. Only one species could be assigned in the very weak spectrum obtained, and it does not appear to be possible to identify the conformation in this species. Because of the overall weakness of the spectrum, it did not appear to be worthwhile to continue this investigation further. The results obtained prior to termination of the study are reported in this chapter.

### Theory

When none of the three principal moments of inertia of a molecule is equal to zero - and no two of the moments are equal - the molecule is an asymmetric rotor.

Isopropenylcyclopropane is such a molecule. As for the symmetric top case described previously, the moments of inertia are ordered such that  $I_a < I_b < I_c$ . In the asymmetric rotor there are two limiting cases: that of the near-prolate symmetric top when  $I_b$  approaches  $I_c$ , and that of the near-oblate symmetric top when  $I_b$  approaches  $I_a$ . The closer  $I_b$  approaches either  $I_a$  or  $I_c$ , the more symmetric the molecule is. A parameter  $\kappa$  is used to quantitatively describe the amount of asymmetry;<sup>16</sup>

$$\kappa = \frac{2B - A - C}{A - C}, \quad (199)$$

where A, B, and C are the rotational constants of the molecule. The parameter  $\kappa \rightarrow \pm 1$  as the molecules approach the limiting cases of an oblate or prolate top, respectively;  $\kappa = 0$  for the case of maximum asymmetry. In a symmetric rotor, the energy levels are doubly degenerate in K. There is no such degeneracy in an asymmetric rotor, so that there are  $(2J+1)$  rotational energy levels for each value of J. Since K is not a good quantum number for an asymmetric rotor, it is necessary to find a way to identify these energy levels. Two systems are now in use. King, Hainer, and Cross<sup>118</sup> designate each level by the symbol  $^J_{K_{-1}K_{+1}}$ . The subscript  $K_{-1}$  is the K value the energy level would have in the limiting case of the prolate symmetric rotor, while the subscript  $K_{+1}$  is the K value the energy

level would have in the limiting case of the oblate symmetric top. The energy levels can also be identified by another system where each energy level is designated by  $J_\tau$  where  $-J \leq \tau \leq J$  and  $\tau$  increases in the order of increasing energy of the levels for a given  $J$ . It may be shown that the two quantum number schemes are connected by the relation  $\tau = K_{-1} - K_{+1}$ .

The Hamiltonian for the asymmetric top molecule in the rigid rotor approximation is

$$H_a = AP_a^2 + BP_b^2 + CP_c^2, \quad (200)$$

where  $P_a$ ,  $P_b$ , and  $P_c$  are the components of the rotational angular momentum projected on the molecule-fixed principal axes of inertia. For an asymmetric rotor, it is not in general possible to obtain direct solutions to the Schrödinger equation. The procedure usually followed is to expand the eigenfunctions in terms of an orthogonal set of wavefunctions such as those of the symmetric top. In this procedure, the asymmetric top wavefunction,  $\psi_{J_\tau M}$ , is a linear combination of the symmetric rotor wavefunctions  $\psi_{JKM}$ ,

$$\psi_{J_\tau M} = \sum_{JKM} a_{JKM} \psi_{JKM}, \quad (201)$$

where the  $a_{JKM}$ 's are numerical constants. Substitution of Equation (201) into the Schrödinger equation yields

$$\sum_{JKM} a_{JKM} H \psi_{JKM} = E \sum_{JKM} a_{JKM} \psi_{JKM} . \quad (202)$$

After left multiplying both sides of the equation by the complex conjugate of  $\psi_{JK'M}$ , integrating over all the coordinates, and rearranging, one obtains

$$\sum_{K=-J}^J (H_{K',K} - \delta_{K',K} \lambda) a_{JKM} = 0 . \quad (203)$$

Here  $K' = -J, \dots, +J$ ;  $H_{K',K} = \langle JK'M | H | JKM \rangle$ ,  $\delta_{K',K}$  is the Kronecker delta, and  $\lambda$  is an eigenvalue. The non-zero matrix elements in the symmetric top basis are found to be<sup>16</sup>

$$\langle J, K, M | H | J, K, M \rangle = \frac{\hbar^2}{4} [J(J+1) \left( \frac{1}{I_a} + \frac{1}{I_b} \right) + K^2 \left( \frac{2}{I_c} - \frac{1}{I_a} - \frac{1}{I_b} \right)] \quad (204)$$

and

$$\begin{aligned} \langle J, K, M | H | J, K \pm 2, M \rangle &= \frac{\hbar^2}{8} [J(J+1) - K(K \pm 1)]^{1/2} \\ &\times [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2} \left( \frac{1}{I_b} - \frac{1}{I_a} \right) . \end{aligned} \quad (205)$$

Since the Hamiltonian for the asymmetric rotor does not commute with  $P_z$ , it is not diagonal in the symmetric top JMK representation. However, the asymmetric rotor Hamiltonian

does commute with  $P^2$  and  $P_z$ ; hence, the Hamiltonian matrix elements are diagonal in  $J$  and  $M$ . The set of equations, Equation (203), can be solved for  $\lambda$ , the allowed energy levels of an asymmetric rotor, by solving the secular determinant. Note that this matrix has elements on the diagonal and two off the diagonal. The matrix is infinite because of the infinite possible values of  $J$ . However, since it is diagonal in  $J$ , it can be factored into blocks along the diagonal, one for each value of  $J$ . Each submatrix has  $(2J+1)$  rows and columns, but it is possible to factor the matrix further from knowledge of symmetry properties of the asymmetric rotor.

The ellipsoid of inertia of an asymmetric rotor is symmetric with respect to the identity operator  $E$ , of course, but also to a  $C_2$  symmetry operation about each of its principal axes of rotation. These symmetry operations:  $E$ ,  $C_2^a$ ,  $C_2^b$ ,  $C_2^c$  form a group known as the Four-group. As a result of these properties of the ellipsoid of inertia, the Hamiltonian for an asymmetric rotor commutes with the operations of the Four-group. If the wavefunctions used to calculate the rotational energies belonged to this group, each one would be classified according to the way it behaves under the four symmetry operations. Since the Four-group contains four irreducible representations, there are four different symmetry species that the wavefunction can be classified under. Since the Hamiltonian operator is

invariant under all four symmetry operations, the only non-zero matrix elements of the Hamiltonian,  $\langle \psi_i | H | \psi_j \rangle$ , allowed by symmetry are those for which the two wavefunctions,  $\psi_i$  and  $\psi_j$ , are of the same species. Therefore the matrix can be factored into four parts, one for each symmetry species. If this is done, there are four matrices for each  $J$ ; the order of each is about  $J/2$ .

The symmetric rotor wavefunctions,  $\psi_{JKM}$ , do not belong to the Four-group; however, the Wang linear combinations of symmetric rotor wavefunctions have this symmetry.<sup>16</sup> Hence, before diagonalization of the Hamiltonian matrix, the symmetric rotor wavefunctions are usually transformed to a new basis, as follows:<sup>16</sup>

$$S = X\psi , \quad (206)$$

where  $S$  is the new set of wavefunctions,  $\psi$  is the set of symmetric rotor wavefunctions, and the Wang transformation is

$$X = X^{-1} = \frac{1}{\sqrt{2}} \begin{bmatrix} \ddots & -1 & 0 & 0 & 0 & 1 & \ddots \\ 0 & -1 & 0 & 1 & 0 & & \\ 0 & 0 & \sqrt{2} & 0 & 0 & & \\ 0 & 1 & 0 & 1 & 0 & & \\ \ddots & 1 & 0 & 0 & 0 & 1 & \ddots \end{bmatrix} . \quad (207)$$

The four submatrices which result from the Wang transformation of a submatrix for a given  $J$  are labeled  $E^+$ ,  $0^+$ ,  $0^-$ , and  $E^-$ , and the eigenvalues of each of these submatrices are often labeled accordingly.

Allowed transitions are those for which the dipole moment matrix element does not vanish. As for the symmetric rotor, the allowed changes in  $J$  are

$$\Delta J = 0, \pm 1. \quad (208)$$

However, in the case of the asymmetric rotor, all three of these changes may cause absorption of radiation. The usefulness of the  $K_{-1}$ ,  $K_{+1}$ , notation is that the changes in  $K_{-1}$  and  $K_{+1}$  for allowed transitions are easily stated for each component of the dipole moment. Table 21 shows the selection rules in terms of changes in the subscripts  $K_{-1}$  and  $K_{+1}$ .

### Experimental, Results, and Discussion

The sample of isopropenylcyclopropane was obtained from Chemical Samples Company, Columbus, OH, and was used as received. The spectra were obtained with the 33 kHz Stark-modulated Hewlett Packard Model 8460A microwave spectrometer discussed in Part II of this thesis. The reported molecular structures of propylene<sup>119</sup> and methylcyclopropane<sup>120</sup> were used as a basis to guess a probable

Table 21. Selection rules of the asymmetric rotor for permitted changes in the values of  $K_{-1}$  and  $K_{+1}$ .<sup>a</sup>

| Type of Transition | Dipole Moment Component <sup>b</sup> | $\Delta K_{-1}$       | $\Delta K_{+1}$       |
|--------------------|--------------------------------------|-----------------------|-----------------------|
| a                  | $\mu_a \neq 0$                       | $0, \pm 2, \dots$     | $\pm 1, \pm 3, \dots$ |
| b                  | $\mu_b \neq 0$                       | $\pm 1, \pm 3, \dots$ | $\pm 1, \pm 3, \dots$ |
| c                  | $\mu_c \neq 0$                       | $\pm 1, \pm 3, \dots$ | $0, \pm 2, \dots$     |

<sup>a</sup>W. Gordy and R. L. Cook, Microwave Molecular Spectra: Chemical Applications of Spectroscopy, Part II in Technique of Organic Chemistry, A. Weissberger, editor (Interscience Publishers, New York, 1970).

<sup>b</sup> $\mu_a$  lies along  $I_a$ ,  $\mu_b$  lies along  $I_b$ , and  $\mu_c$  lies along  $I_c$ , where  $I_a < I_b < I_c$ .

structure for isopropenylcyclopropane; the structure obtained is shown in Figure 18. The microwave spectrum was observed in the R band between 30000 and 40000 MHz. By comparison with calculated spectra, it was possible to assign a number of R-branch transitions, all of which were a-type transitions. The frequencies of the assigned transitions are listed in Table 22. The frequencies were fit to the eigenvalues of the following non-rigid rotor Hamiltonian given by Watson:<sup>121</sup>

$$\begin{aligned}
 H = & \frac{1}{2} (B+C)P^2 + [A - \frac{1}{2} (B+C)]P_a^2 \\
 & + \frac{1}{2} (B-C)(P_b^2 - P_c^2) - \Delta_J P^4 \\
 & - \Delta_{JK} P^2 P_a^2 - \Delta_K P_a^4 - 2\delta_J P^2 (P_b^2 - P_c^2) \\
 & - \delta_K [P_a^2 (P_b^2 - P_c^2) + (P_b^2 - P_c^2) P_a^2] \quad . \quad (209)
 \end{aligned}$$

In this equation A, B, and C are the rotational constants, and  $\Delta_J$ ,  $\Delta_K$ ,  $\Delta_{JK}$ ,  $\delta_J$ , and  $\delta_K$  are quartic centrifugal distortion constants. Table 22 also shows the difference in the observed and calculated frequencies from this fit. The rotational constants and centrifugal distortion constants obtained from the fit to the Watson Hamiltonian are shown in Table 23.

No transitions from another conformation were assigned.

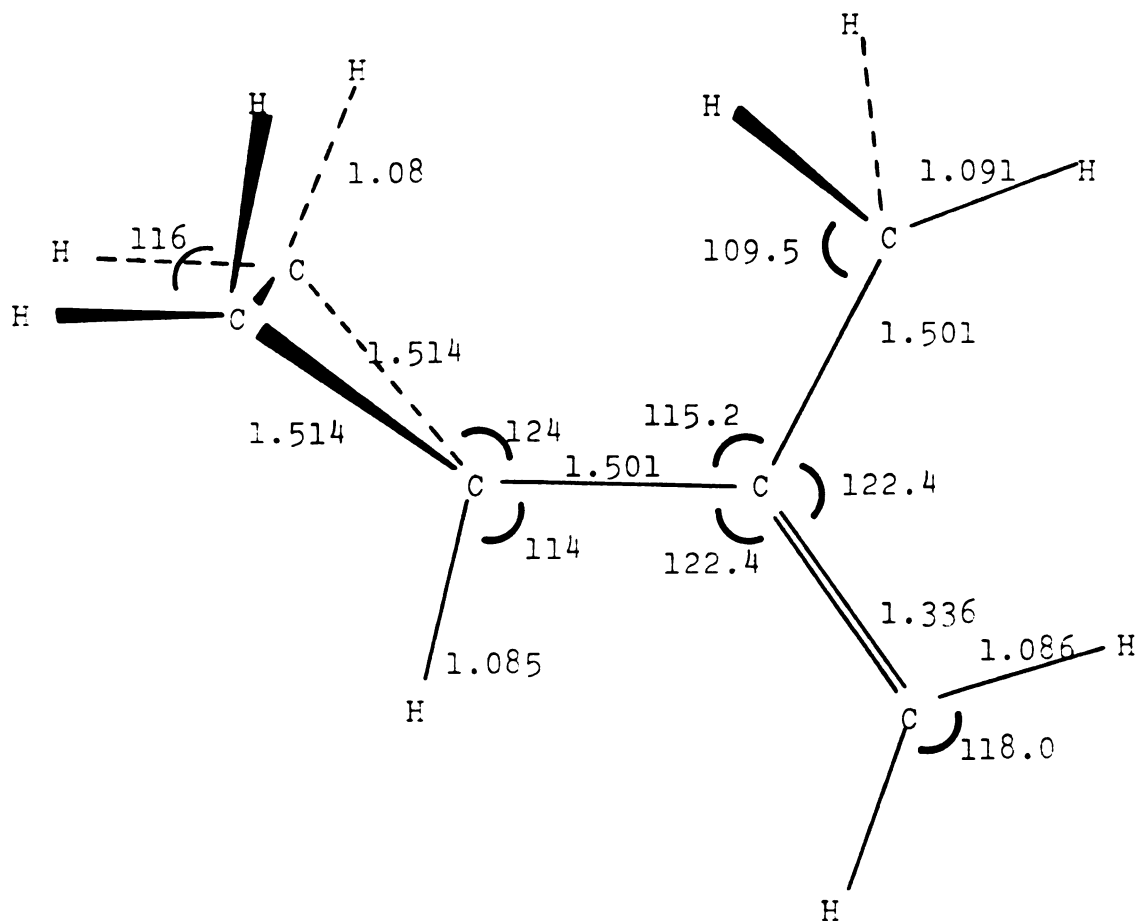


Figure 18. Possible structure for isopropenylcyclopropane as determined from bond distances and bond angles of propylene and methylcyclopropane.

Table 22. Comparison of observed and calculated frequencies of isopropenylcyclopropane.

| Transition                 | Observed<br>Frequency <sup>a</sup> /MHz | Obs-calc/MHz |
|----------------------------|-----------------------------------------|--------------|
| $6_{16} \leftarrow 5_{15}$ | 27887.90                                | -0.01        |
| $6_{06} \leftarrow 5_{05}$ | 28362.50                                | -0.01        |
| $6_{51} \leftarrow 5_{50}$ | 29549.27                                | -0.05        |
| $6_{52} \leftarrow 5_{51}$ | 29549.27                                | -0.01        |
| $6_{43} \leftarrow 5_{42}$ | 29582.05                                | 0.10         |
| $6_{42} \leftarrow 5_{41}$ | 29585.21                                | 0.02         |
| $6_{15} \leftarrow 5_{14}$ | 30413.33                                | -0.02        |
| $7_{17} \leftarrow 6_{16}$ | 32445.01                                | 0.01         |
| $7_{07} \leftarrow 6_{06}$ | 32807.46                                | 0.01         |
| $7_{26} \leftarrow 6_{25}$ | 34074.31                                | 0            |
| $7_{61} \leftarrow 6_{60}$ | 34469.40                                | 0.03         |
| $7_{62} \leftarrow 6_{61}$ | 34469.40                                | 0.03         |
| $7_{53} \leftarrow 6_{52}$ | 34497.70                                | -0.06        |
| $7_{52} \leftarrow 6_{51}$ | 34497.91                                | -0.05        |
| $7_{44} \leftarrow 6_{43}$ | 34547.32                                | 0.08         |
| $7_{35} \leftarrow 6_{34}$ | 34563.67                                | -0.05        |
| $7_{43} \leftarrow 6_{42}$ | 34557.95                                | 0.01         |
| $7_{34} \leftarrow 6_{33}$ | 34802.99                                | -0.02        |
| $7_{16} \leftarrow 6_{15}$ | 35280.09                                | 0.02         |
| $7_{25} \leftarrow 6_{24}$ | 35620.86                                | -0.01        |
| $8_{18} \leftarrow 7_{17}$ | 36977.96                                | 0            |
| $8_{08} \leftarrow 7_{07}$ | 37233.36                                | -0.01        |
| $8_{71} \leftarrow 7_{70}$ | 39389.69                                | 0.02         |
| $8_{72} \leftarrow 7_{71}$ | 39387.69                                | 0.02         |
| $8_{62} \leftarrow 7_{61}$ | 39414.81                                | -0.04        |
| $8_{63} \leftarrow 7_{62}$ | 39414.81                                | -0.03        |
| $8_{45} \leftarrow 7_{44}$ | 39525.49                                | 0.02         |
| $8_{44} \leftarrow 7_{43}$ | 39554.50                                | 0.03         |

<sup>a</sup>Estimated accuracy of 0.05 MHz.

Table 23. Rotational constants and centrifugal distortion constants<sup>a</sup> of isopropenylcyclopropane.

| Parameter          | Value    | Standard Error |
|--------------------|----------|----------------|
| A/MHz              | 6287.089 | 0.30           |
| B/MHz              | 2674.222 | 0.014          |
| C/MHz              | 2235.061 | 0.012          |
| $\Delta_J$ /kHz    | 0.02     | 0.06           |
| $\Delta_{JK}$ /kHz | 4.09     | 0.29           |
| $\Delta_K$ /kHz    | 29.      | 96             |
| $\delta_J$ /kHz    | 0.03     | .05            |
| $\delta_K$ /kHz    | -18.0    | 3.6            |

<sup>a</sup>Determined in an  $I^R$  axis representation:  $A \leftrightarrow Z$ ,  $B \leftrightarrow X$ ,  $C \leftrightarrow Y$ .

In order to identify the conformation observed, the rotational constants for the assumed structure were calculated for every ten degrees of rotation about the dihedral angle. Figure 19 shows a plot of the rotational constants versus the dihedral angle. The horizontal dotted lines in the figure are the fitted rotational constants obtained from the observed transitions. It is apparent that the variation in rotational constants with angle and the derived constants are such that it is not possible to determine the configuration of the molecule from these data alone.

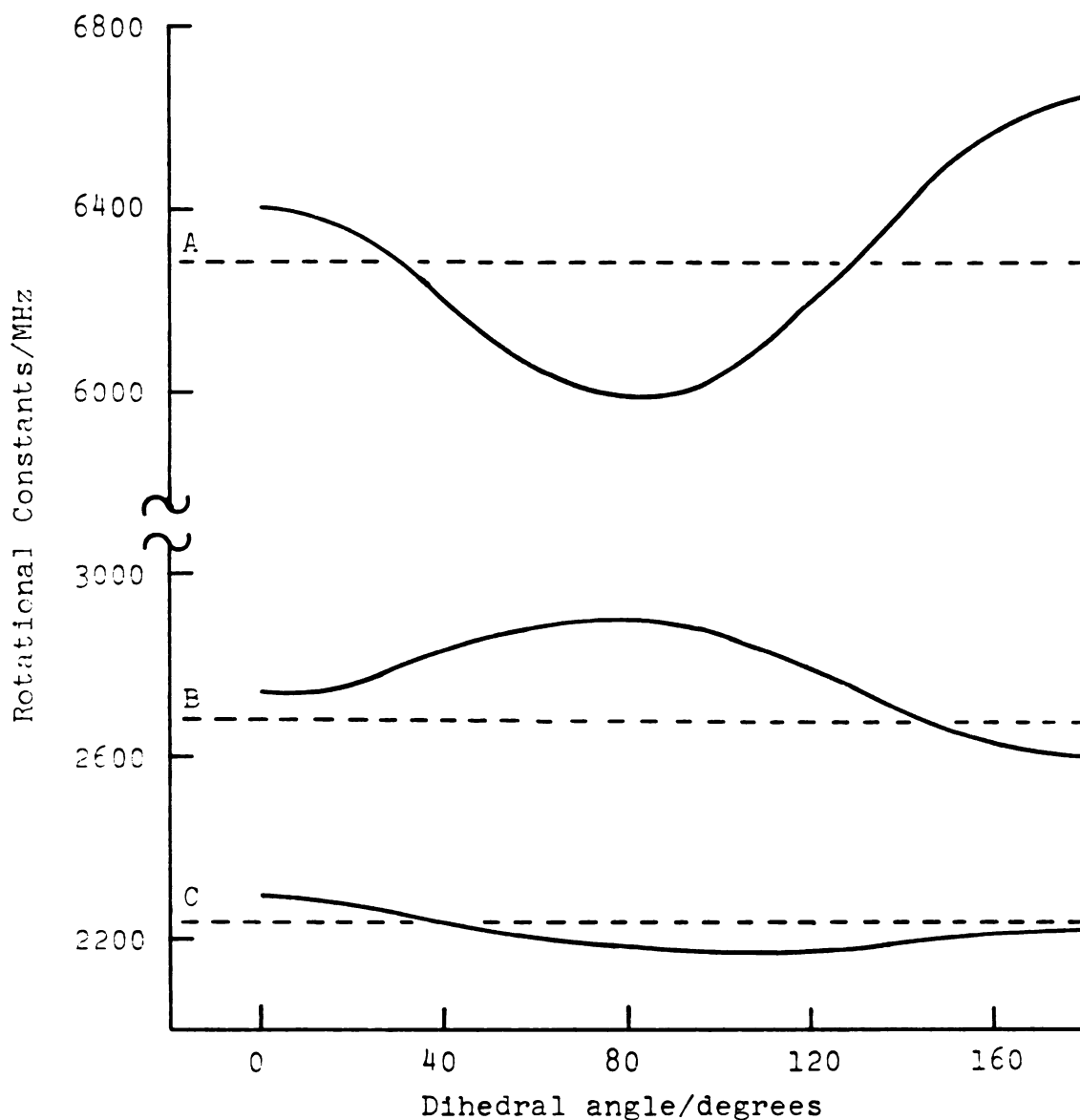


Figure 19. Rotational constants versus dihedral angle of isopropenylcyclopropane. The horizontal dotted lines in the figure are the rotational constants obtained from the fit of the observed transitions.

## APPENDICES

## APPENDIX A

### THE VOLTAGE VARIATION OF THE STARK FIELD IN THE MICROWAVE SAMPLE CELL

The Stark voltage was found to differ from the voltage indicated on the dial by an amount which was not constant as a function of the dial reading. This voltage variation will be discussed for both high and low Stark fields.

#### Low Fields

First-order Stark effects for the ground state and  $\nu_5 = 1$  excited state of methylacetylene were measured at Stark fields corresponding to voltages - as read from the dial - between 0 and 180 volts. To calculate the correct voltage, the first-order Stark effect transitions were fit to a straight line by the method of least squares. If the x-axis is the dial voltage and the y axis is the transition frequency, the intercept and slope are shown in Table A-1. These slopes along with the measured frequencies and a zero-field frequency of 34182.78 MHz for the ground state and 34031.74 MHz for the  $\nu_5$  excited state were used in the straight line equation to calculate the voltages. These calculated voltages are shown in Table A-2. The actual voltage appears to be greater than the dial voltage

Table A-1. Least squares fit to a straight line of the dial setting versus the first-order Stark effect frequencies of the ground state and  $\nu_5$  excited state of the  $J = 2 \leftarrow 1$  transition of methyl-acetylene.

|                          | Slope     | Frequency<br>Intercept/MHz |
|--------------------------|-----------|----------------------------|
| ground state             |           |                            |
| $k=\pm 1, m=\bar{\pm} 1$ | 0.263519  | 34189.48                   |
| $k=\pm 1, m=\pm 1$       | -0.263420 | 34176.08                   |
| $\nu_5$ excited state    |           |                            |
| $k=\pm 1, m=\bar{\pm} 1$ | 0.267451  | 34038.54                   |
| $k=\pm 1, m=\pm 1$       | -0.267213 | 34024.95                   |

Table A-2. Voltages of the first-order Stark effect of the  $J = 2 + 1$  transition of the ground and  $v_5$  excited states of methylacetylene. The voltages have been corrected to include the offset of the dial reading.

| Dial<br>Setting<br>(Volts) | Calculated Voltages/Volts |                    |                     |                    |
|----------------------------|---------------------------|--------------------|---------------------|--------------------|
|                            | Ground State              |                    | $v_5$ Excited State |                    |
|                            | $k=\pm 1, m=\mp 1$        | $k=\pm 1, m=\pm 1$ | $k=\pm 1, m=\mp 1$  | $k=\pm 1, m=\pm 1$ |
| 50                         | 75.44                     | 75.32              | 75.38               | 75.45              |
| 60                         | 85.61                     | 85.42              | 85.55               | 85.44              |
| 70                         | 95.63                     | 95.47              | 95.49               | 95.58              |
| 80                         | 105.61                    | 105.42             | 105.44              | 105.38             |
| 90                         | 115.44                    | 115.10             | 115.31              | 115.19             |
| 100                        | 125.64                    | 125.43             | 125.52              | 125.44             |
| 110                        | 135.44                    | 135.26             | 135.31              | 135.32             |
| 120                        | 145.61                    | 145.40             | 145.45              | 145.43             |
| 130                        | 155.59                    | 155.46             | 155.43              | 155.41             |
| 140                        | 165.45                    | 165.59             | 165.34              | 165.60             |
| 150                        | 175.55                    | 175.42             | 175.73              | 175.51             |
| 160                        | -----                     | 185.41             | -----               | 185.24             |
| 170                        | 195.70                    | 195.20             | -----               | 195.12             |
| 180                        | 205.45                    | 205.34             | 205.35              | 205.64             |
| $V_{\text{calc}} - V_d$    | 25.55                     | 25.43              | 25.44               | 25.41              |

by a near constant 25.4 volts. The measured frequencies and voltages of the dial reading plus 25.4 volts were then fit to a straight line with the results shown in Table 11. Again, the  $\nu_5$  excited state dipole moment is calculated to be 0.7954 Debye.

### High Fields

Second-order Stark effect measurements were obtained with dial voltages between 800 and 1600 volts. In this range the offset is no longer constant, but appears to increase with increasing field.

The frequency shift for a second-order Stark effect can be expressed as

$$\Delta\nu_2 = \mu_D^2 A_D \epsilon^2 \quad (\text{A-1})$$

where  $A_D$  depends upon the quantum numbers and rotational constants. After expressing the electric field as the total voltage divided by the cell spacing, the frequency shift becomes

$$\Delta\nu_2 = A_D \mu_D^2 \left( \frac{V_d + V_o}{S} \right)^2 \quad (\text{A-2})$$

or

$$\frac{S^2 \Delta v_2}{A_D \mu_D^2} = V_d^2 + 2V_d V_o + V_o^2 . \quad (A-3)$$

For the molecule OCS, the dipole moment is known and  $A_D$  can be calculated. The Stark shifts were measured at different dial voltages. The only unknowns are the offset voltage and the cell spacing. By using the  $M = 0$  Stark shifts for dial voltages of 800 volts and 1000 volts, the two simultaneous equations can be solved to yield an offset voltage of 38 volts. Repeating the process for 1400 volts and 1600 volts yields an offset voltage of 71 volts. It is apparent that at high Stark fields the difference between the dial setting and the apparent voltage is not constant.

## APPENDIX B

### LINEWIDTH OF THE LASER STARK TRANSITIONS

A Doppler-broadened Gaussian lineshape,  $I$ , can be expressed as

$$I = Ae^{-\gamma(\nu_i - \nu_\epsilon)^2} \quad (B-1)$$

where  $A$  and  $\gamma$  are constants for each transition. The half width at half height,  $\Delta\nu_D$ , can be found from

$$\frac{1}{2} = e^{-\gamma(\Delta\nu_D)^2}, \quad (B-2)$$

which can be rewritten as

$$\ln 2 = \gamma(\Delta\nu_D)^2. \quad (B-3)$$

The frequency of a transition at an electric field  $\epsilon$  can be expressed as

$$\nu_\epsilon = \nu_0 + \left(\frac{\partial \nu_0}{\partial \epsilon}\right)_\epsilon (\epsilon - \epsilon_0), \quad (B-4)$$

where  $\nu_0$  is the transition frequency at electric field  $\epsilon_0$ . Therefore

$$(\nu_1 - \nu_\epsilon)^2 = [\nu_1 - \nu_0 - (\frac{\partial \nu}{\partial \epsilon})_\epsilon (\epsilon - \epsilon_0)]^2 . \quad (\text{B-5})$$

If  $\nu_0$  is chosen to be equal to  $\nu_1$ ,

$$(\nu_1 - \nu_\epsilon)^2 = (\frac{\partial \nu}{\partial \epsilon})_\epsilon^2 (\epsilon - \epsilon_0)^2 . \quad (\text{B-6})$$

The lineshape function, Equation (B-1), then becomes

$$I = Ae^{-\gamma (\frac{\partial \nu}{\partial \epsilon})_\epsilon^2 (\epsilon - \epsilon_0)^2} \quad (\text{B-7})$$

or

$$I = Ae^{-\beta (\epsilon - \epsilon_0)^2} , \quad (\text{B-8})$$

where

$$\beta = \gamma (\frac{\partial \nu}{\partial \epsilon})_\epsilon^2 . \quad (\text{B-9})$$

Thus,

$$\frac{1}{2} = e^{-\beta \Delta \epsilon_D^2} , \quad (\text{B-10})$$

where  $\Delta \epsilon_D$  is found to be

$$\Delta \epsilon_D = \frac{\Delta \nu_D}{(\frac{\partial \nu}{\partial \epsilon})_\epsilon} . \quad (\text{B-11})$$

A first-derivative lineshape was used in the laser Stark experiment. The first derivative of I is given by

$$\frac{\partial I}{\partial \epsilon} = -2\beta(\epsilon - \epsilon_0)Ae^{-\beta(\epsilon - \epsilon_0)^2}. \quad (B-12)$$

The points of maximum and minimum intensity,  $\epsilon_p$  and  $\epsilon'_p$ , can be found by setting the derivative  $\frac{\partial^2 I}{\partial \epsilon^2}$  equal to zero,

$$\frac{\partial^2 I}{\partial \epsilon^2} = [-2\beta + 4\beta^2(\epsilon - \epsilon_0)^2]Ae^{-\beta(\epsilon - \epsilon_0)^2}, \quad (B-13)$$

and  $\frac{\partial^2 I}{\partial \epsilon^2}$  equals zero when

$$-2\beta + 4\beta^2(\epsilon - \epsilon_0)^2 = 0 \quad (B-14)$$

Therefore

$$\epsilon_p - \epsilon_0 = \pm \sqrt{\frac{1}{2\beta}}. \quad (B-15)$$

Substitution of Equation (B-3) into Equation (B-9) yields

$$\beta = \frac{\ln 2 \left(\frac{\partial \nu}{\partial \epsilon}\right)^2_{\epsilon}}{(\partial \nu_D)^2}, \quad (B-16)$$

So that the full linewidth is expressed by

$$\epsilon_p - \epsilon'_p = \left(\frac{2}{\ln 2}\right)^{1/2} \frac{\partial \nu_D}{\left(\frac{\partial \nu}{\partial \epsilon}\right)_{\epsilon}}. \quad (B-17)$$

## APPENDIX C

### THE CO<sub>2</sub> AND N<sub>2</sub>O GAS LASERS

#### Introduction

Lasers that have been used to excite sample gases in laser Stark spectroscopy include as the active gas: CO, CO<sub>2</sub>, N<sub>2</sub>O, D<sub>2</sub>O, HCN, He-Xe, He-Ne, and some carbon-13 species. In this study a CO<sub>2</sub> laser and an N<sub>2</sub>O laser were used.

A laser<sup>122,123</sup> consists of two basic components, the active medium and an optical cavity. The active medium in this case is the CO<sub>2</sub> or N<sub>2</sub>O gas and the optical cavity is made of two reflectors, one mounted on either side of the active medium. Initially, the CO<sub>2</sub> or N<sub>2</sub>O molecules are excited by an external source of energy. Photons are emitted which in turn stimulate the emission and absorption of photons by the gas molecules. If the external energy source excites more molecules to an upper state than a lower state, population inversion is achieved and laser action occurs. Because of the design of the laser cavity and because stimulated emission is involved, laser radiation has some rather unique properties. The CO<sub>2</sub> and N<sub>2</sub>O lasers used emit power continuously and can be made to be monochromatic - i.e., emit radiation at one frequency. Also, the laser emission is coherent so that the divergence of

the output beam is very small and the radiation is all in phase. Hence, a small beam of radiation can be passed through a long distance and accurately aimed at a small target. The laser can be designed so that the radiation is plane polarized.

### Theory of the CO<sub>2</sub> Laser

The active medium of a CO<sub>2</sub> laser is a gas mixture consisting of about 5% CO<sub>2</sub>, 15% N<sub>2</sub>, and 80% He. The nitrogen gas is used to excite the carbon dioxide. A partial energy level diagram for CO<sub>2</sub> and N<sub>2</sub> is shown in Figure C-1. The rotational levels have been left out for simplicity. An electric discharge raises the N<sub>2</sub> molecules to excited vibrational levels. Because N<sub>2</sub> has no oscillating dipole moment, vibrationally-excited N<sub>2</sub> in the ground electronic state cannot decay through electric dipole radiation. Deactivation must occur through collisions with other molecules and with the walls. The energy difference between the 001 level of CO<sub>2</sub> and the  $v = 1$  level of N<sub>2</sub> is only  $\sim 18 \text{ cm}^{-1}$ , so the excited N<sub>2</sub> molecules can easily transfer their energy to the CO<sub>2</sub> molecules upon collision. Any CO<sub>2</sub> molecules in the 001 level may decay with emission of radiation to the 100 or 020 energy level and from there to the 010 level. Collisions with helium help depopulate the 010 level. With enough excitation it is possible to have more molecules in the 001 state than in either the

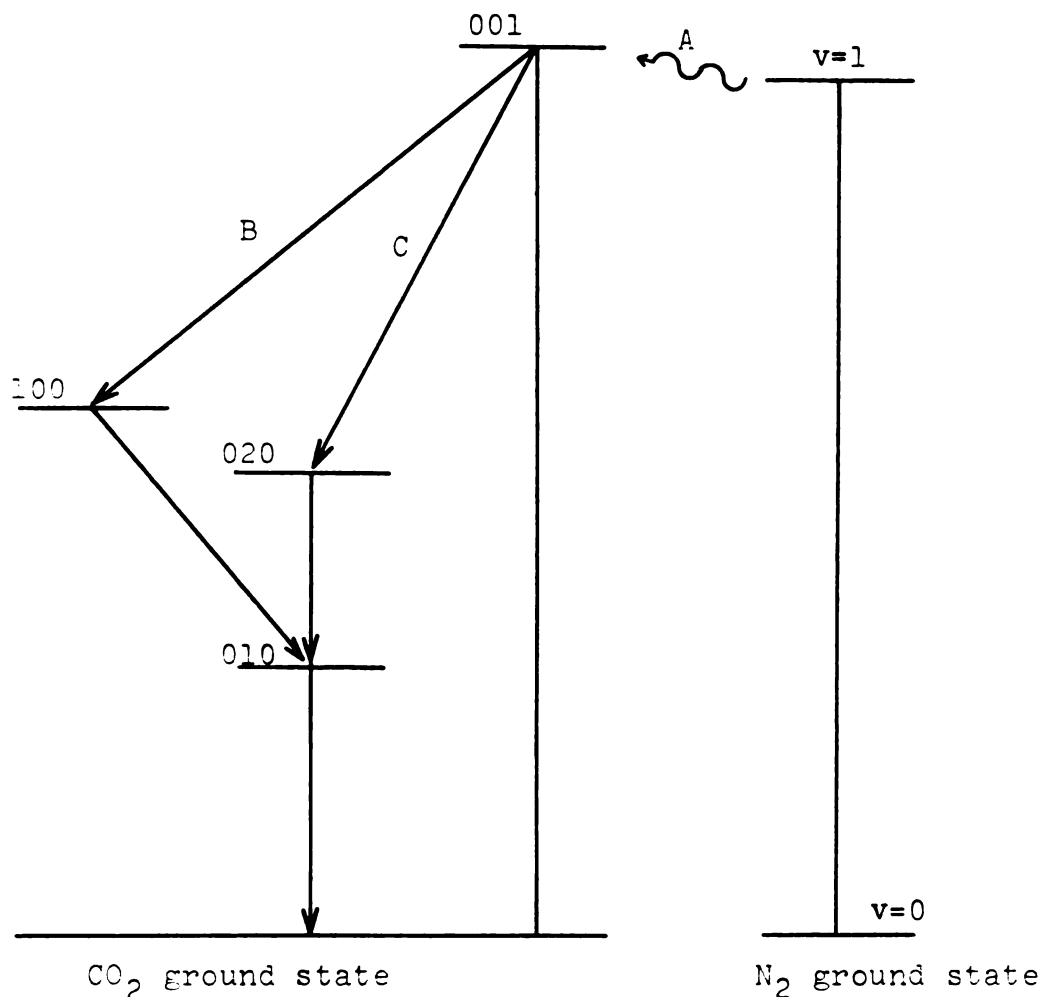


Figure C-1. Diagram of the  $\text{CO}_2$  and  $\text{N}_2$  vibrational energy levels which are of interest for the  $\text{CO}_2$  laser. The energy difference labeled A is  $\sim 18 \text{ cm}^{-1}$ . The laser transitions corresponding to label B are centered around  $961.0 \text{ cm}^{-1}$  and those corresponding to label C are centered around  $1063.8 \text{ cm}^{-1}$ .

100 or the 020 states. At this point, population inversion is achieved. When a  $\text{CO}_2$  molecule undergoes spontaneous emission from the 001 to the 100 level, the photon given off stimulates another molecule to undergo this transition and the effect snowballs. The laser transitions are from individual rotational levels in the 001 vibrational state to individual rotational levels in the 100 state at a frequency near  $961\text{ cm}^{-1}$  or from a rotational level in the 001 state to a level in the 020 state at a frequency near  $1064\text{ cm}^{-1}$ . The transitions near  $961\text{ cm}^{-1}$  have higher gain and will undergo laser action unless conditions are made to favor a  $1064\text{ cm}^{-1}$  transition.

Stimulated emission is in the same direction and has the same phase as the stimulating radiation. Photons which hit one of the mirrors at either end of the laser may be reflected back into the optical cavity. Photons which never strike a mirror eventually leave the optical cavity and are lost. Thus, the only photons which survive to stimulate a large number of new photons are those which travel back and forth between the mirrors. Output from the laser is achieved when some of these photons are allowed to escape through a small hole at the center of one mirror or through one mirror which is partially transmitting.

The output of the laser just described would probably not be monochromatic, since the radiation would arise from transitions between many rotational energy levels. To

obtain monochromatic laser radiation, one of the mirrors may be replaced by a diffraction grating. By changing the angle of the grating, different laser frequencies can be selected. The  $\text{CO}_2$  and  $\text{N}_2\text{O}$  lasers have transitions spaced every 1 or 2  $\text{cm}^{-1}$  covering most of the 9-11  $\mu$  region. The intensities of the transitions vary according to the Boltzmann distribution of the rotational levels. The most intense transitions are those near P(18) or R(18) of each band. Tables C-1 and C-2 contain lists of the  $\text{CO}_2$  and  $\text{N}_2\text{O}$  laser lines used in this investigation. Their frequencies are given in megahertz and wavenumbers. By adjusting the length of the optical cavity, an individual  $\text{CO}_2$  or  $\text{N}_2\text{O}$  laser line can be continuously tuned by about  $\pm 25$  MHz. This is the only manner in which these lasers are continuously tunable.

#### Description of the $\text{CO}_2/\text{N}_2\text{O}$ Laser Used in this Study

Figure C-2 is a schematic diagram of the laser used in this investigation. The laser may be used with either  $\text{CO}_2$  or  $\text{N}_2\text{O}$  as the active gas. The gas mixture, pressure, and the method of stabilization employed are different for the two gases. In either case, the laser gas mixture flows through the system and is rapidly pumped away. The plasma tube confining the gases is made of pyrex, 2.8 cm in diameter and 2.6 m long. It is surrounded by a water jacket with a

Table C-1. List of the CO<sub>2</sub> laser lines of the 001-100 band used in this experiment. Their frequencies are given in wavenumbers<sup>a</sup> and megahertz.<sup>b</sup>

| Laser Line | Frequency/MHz | Frequency/cm <sup>-1</sup> |
|------------|---------------|----------------------------|
| P(24)      | 28196922.584  | 940.5481026                |
| P(26)      | 28141165.954  | 938.6882616                |
| P(28)      | 28084669.777  | 936.8037519                |
| P(30)      | 28027431.849  | 934.8945002                |
| P(32)      | 27969449.737  | 932.9604251                |
| P(34)      | 27910720.770  | 931.0014376                |
| P(36)      | 27851242.035  | 929.0174405                |
| P(38)      | 27791010.378  | 927.0083287                |
| P(40)      | 27730022.394  | 924.9739885                |
| P(42)      | 27668274.428  | 922.9142981                |
| P(44)      | 27605762.565  | 920.8291267                |
| P(46)      | 27542782.627  | 918.7183352                |

<sup>a</sup>c = 299,792,456.2 ± 1.1 m/sec.

<sup>b</sup>The frequencies of the CO<sub>2</sub> laser were calculated with the parameters determined by K. M. Evenson, J. S. Wells, R. F. Petersen, B. L. Danielson and W. G. Day, Appl. Phys. Lett. 22, 192 (1973) and F. R. Petersen, D. G. McDonald, J. D. Cupp, and B. L. Danielson, Phys. Rev. Lett. 31, 573 (1973).

Table C-2. List of the N<sub>2</sub>O laser lines used in this experiment. Their frequencies are given in megahertz<sup>a</sup> and wavenumbers.<sup>b</sup>

| Laser Line | Frequency/MHz | Frequency/cm <sup>-1</sup> |
|------------|---------------|----------------------------|
| P(5)       | 28020012.994  | 934.647034                 |
| P(6)       | 27994488.534  | 933.795629                 |
| P(7)       | 27968863.122  | 932.940858                 |
| P(8)       | 27943136.871  | 932.082722                 |
| P(9)       | 27917309.890  | 931.221227                 |
| P(10)      | 27891382.284  | 930.356375                 |
| P(11)      | 27865354.160  | 929.488170                 |
| P(12)      | 27839225.620  | 928.616616                 |
| P(13)      | 27812996.763  | 927.741716                 |
| P(14)      | 27786667.689  | 926.863472                 |
| P(15)      | 27760238.493  | 925.981889                 |
| P(16)      | 27733709.268  | 925.096969                 |
| P(17)      | 27707080.105  | 924.208716                 |

<sup>a</sup>B. G. Whitford, K. J. Siemsen, H. D. Riccius, and G. R. Hanes, Opt. Comm. 14, 70 (1975).

<sup>b</sup>c = 299,792,456.2 ± 1.1 m/sec.

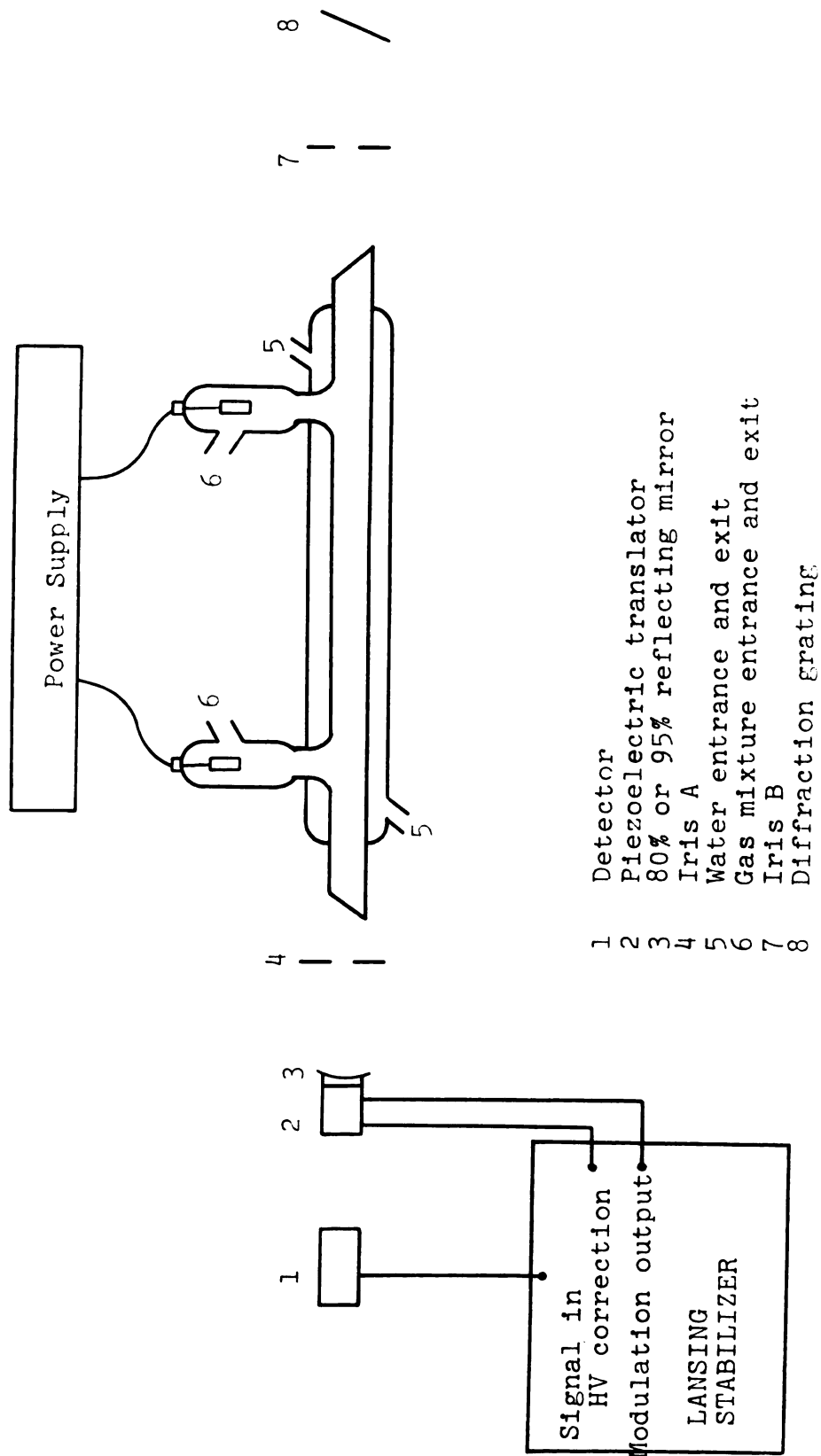


Figure C-2. Schematic diagram of the  $\text{CO}_2/\text{N}_2\text{O}$  laser used in this study.

5 cm outside diameter. Attached to the plasma tube about 20 cm from each end are ground glass joints to which the electrode compartments are sealed with black wax. Each electrode is a hollow stainless steel cylinder attached to a 1.3 mm tungsten rod. The tungsten rod carries the electrical connection through the glass wall of the electrode compartment. Attached to each end of the plasma tube are NaCl windows, purchased from the Harshaw Company. The windows are 5.1 cm in diameter, 6 mm thick, flat to within  $\pm 1 \mu\text{m}$  and the faces on each are parallel to 30 seconds of arc. These windows are oriented at Brewster's angle,<sup>124</sup> so that the output radiation is plane polarized with the plane of the electric vector parallel to the floor. At one end of the optical cavity is a PTR Optics ML 303 original diffraction grating that is flat, has 150 grooves/mm, and has first order reflective efficiency of about 95%. A partially-transmitting germanium mirror is at the other end of the optical cavity. This mirror has a 10 m radius of curvature, a front surface which is 80% reflecting at a wavelength of  $10.6 \mu\text{m}$ , and an antireflection-coated rear surface. (A 95% reflecting mirror is also available.) The length of the optical cavity is 398 cm and can be changed slightly by applying a voltage to a piezoelectric crystal which can be controlled by a Lansing Research Model 80-214 laser stabilizer. The laser is supported by three 4.14 m long Invar rods which are 3.2 cm in diameter. The

rods are held in place at each end by "U"-shaped aluminum blocks. Three sets of smaller aluminum blocks support the Invar rods at one-quarter, one-half, and three-quarters of their length. The power supply for the laser is a 30 kV, 50 ma unit manufactured by the Megavolt Corporation. The current regulator was designed for our use by Martin Rabb.

The laser may be run on a commercially available gas mixture which contains 5% of either  $\text{CO}_2$  or  $\text{N}_2\text{O}$ , 15%  $\text{N}_2$ , 80% He, and in the case of the  $\text{N}_2\text{O}$  laser, a small amount of CO. However, the intensity of a laser line depends in part upon the gas mixture. Consequently, the gases were mixed at the inlet to the laser tube. By mixing the gases ourselves, it was possible to obtain laser output on a weak line which would not lase with premixed gases. The laser was designed as a free-flowing system. Copper tubing connects the gas tanks to fine metering valves, one each for  $\text{N}_2$ , He, and CO, and one for either  $\text{CO}_2$  or  $\text{N}_2\text{O}$ . A fifth metering valve can close the plasma tube to all the gases. The gas mixture enters the plasma tube at one electrode and leaves at the other. A Precision Scientific Company Vac Torr 1000 (1000 $\ell$ /sec) pump was used to keep the gas flowing. PVC reinforced tubing and Pyrex tubing is used for all the connections between the micrometer valves and the laser.

Alignment of the Laser at 10.6 $\mu$ \*

Alignment of the laser is begun by insuring that the centers of both irises inside the cavity lie along the apparent center of the plasma tube. To do this, one iris is closed, covered with a Kimwipe, and illuminated from behind by a flashlight. A mirror is placed at the opposite end of the laser in order to be able to look down the plasma tube. The position of the second iris is changed until it is centered around the white circle of light. The same procedure is then used to center the other iris.

Once the irises are centered, a He-Ne laser is used to align the mirror and diffraction grating. The partially transmitting mirror of the CO<sub>2</sub> laser is removed. The He-Ne laser is set outside the optical cavity of the CO<sub>2</sub> laser and adjusted so that the He-Ne radiation shines down the center of the plasma tube, through both irises, and onto the diffraction grating. The lines of the diffraction grating should be vertical and the grating itself placed at such an angle that the reflection of the He-Ne beam off the grating forms a horizontal row of spots. The brightest spot is the thirteenth-order reflection. The grating is rotated until the seventeenth-order reflection is

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\*In the operation of any laser, it should be remembered that laser radiation can be harmful to human tissue, especially the eye. Therefore suitable precautions must be taken.

superimposed upon the incoming He-Ne laser beam. The radiation from the seventeenth-order reflection now travels back toward the He-Ne laser, strikes its mirror and is reflected back toward the diffraction grating. If the alignment has been well done, this very faint spot can be seen on the diffraction grating and is moved on top of the primary spot.

The partially transmitting mirror of the CO<sub>2</sub> laser is replaced without disturbing the position of the He-Ne laser. Two spots from the He-Ne laser can be seen on the back of the CO<sub>2</sub> mirror. The strong spot is the He-Ne beam striking the mirror. The other is the light from the He-Ne laser reflected from the CO<sub>2</sub> mirror to the He-Ne mirror and back. The partially transmitting mirror of the CO<sub>2</sub> laser is adjusted until the weak spot is superimposed upon the stronger one.

### Operation of the CO<sub>2</sub> Laser

The alignment for the seventeenth line of the He-Ne laser is very close to the alignment needed to cause lasing on the P(36) line of the 001-100 band of the CO<sub>2</sub> laser. Before the laser is started, the irises within the optical cavity should be open and the stabilizer set to fast sweep. Slightly more than one torr CO<sub>2</sub> and about 6 torr He are added to the plasma tube. (The pressure meter

is between the plasma tube and the pump, so the pressures given may not be those in the plasma tube.) The high voltage power supply is turned up to 20 k volts and the current to 20 m amps. As the pressure of  $N_2$  is slowly increased to a few torr, the plasma color changes from violet to rose and lasing should occur. The output beam of the laser is conveniently observed by chopping the beam and observing the detected beam by means of an oscilloscope. Sometimes a slight displacement of the diffraction grating is needed for the laser to lase. The PZT voltage is manually adjusted to the top of the gain profile and He is added to the plasma tube until the total pressure is about 10 torr. The  $CO_2$ ,  $N_2$ , and He pressures are adjusted to give the maximum laser power. The intracavity irises should be closed as small as possible and the diffraction grating and partially-transmitting mirror adjusted to give the maximum signal. This process is repeated until the irises can be closed no farther without losing the signal, even after the grating and mirror are adjusted. The cross-sectional shape of the laser beam should be the simple circle of the  $TEM_{00}$  mode. The following is a sample of different mode patterns:



If one of the other modes is obtained, the simple mode may be restored by decreasing the size of the irises. If necessary, the laser power can be increased by increasing the gas pressure.

### Operation of the N<sub>2</sub>O Laser

It is slightly more difficult to operate the N<sub>2</sub>O laser than the CO<sub>2</sub> laser. The frequency of the P(32) line of the 001-100 band of the CO<sub>2</sub> laser at 932.9569 cm<sup>-1</sup> is almost the same as the frequency of the P(7) line of the 001-100 band of the N<sub>2</sub>O laser at 932.9368 cm<sup>-1</sup>. Hence, this is an easy place to change over from the CO<sub>2</sub> to the N<sub>2</sub>O laser. To operate the N<sub>2</sub>O laser, the irises should be completely open. A very small amount of N<sub>2</sub>O and about 5 torr of He are added to the plasma tube. The high voltage of the power supply is turned up to 20 kV, while the current is increased to 10 ma. The discharge should glow blue if there is little or no N<sub>2</sub>O. More N<sub>2</sub>O is added until the plasma is deep purple. If too much N<sub>2</sub>O has been added, a gap - a clear space - forms in the plasma near the grounded electrode. (Lasing will not occur when too much N<sub>2</sub>O is present.) The addition of a little N<sub>2</sub> will cause the N<sub>2</sub>O laser to lase. The amounts of N<sub>2</sub>O, N<sub>2</sub> and He are adjusted until the maximum signal is obtained with the total pressure about 7 torr. Then CO is added until the signal is

maximized; it will just about double in size. Again, the laser is aligned by adjusting the diffraction grating, mirror, and irises.

### Laser Stabilization

The frequency of a laser is determined by the active medium - in this case, the  $\text{CO}_2$  or  $\text{N}_2\text{O}$  gas - and the cavity length. When lasing occurs, a standing wave pattern is set up between the mirror and the diffraction grating. Excluding the end surfaces, there are  $n-1$  nodal planes in the standing wave pattern. Large changes in the cavity length will change the number of nodes in the standing wave. When this happens the laser is said to change modes. The frequency within a given mode is inversely proportional to the cavity length,

$$\frac{\nu}{n} = \frac{c}{2L} \quad , \quad (\text{C-1})$$

where  $\nu$  is the frequency,  $n-1$  the number of nodes (excluding those at the boundary),  $c$  is the speed of light, and  $L$  is the cavity length. When the cavity length is slightly changed, the frequency changes in inverse proportion. Therefore, to stabilize the laser, the cavity length must be kept such that the laser oscillates at the top of the gain profile for the mode that it is in.

The stabilization system is shown in Figure C-2. The length of the cavity is varied by sinusoidally modulating the position of the mirror. As the cavity length varies, the laser frequency and hence the laser power varies as shown in Figure C-3. The modulated component of the laser power is detected by a pyroelectric detector and enters the Lansing stabilizer where it is preamplified and observed by means of phase sensitive detection. This provides a discriminator signal which is zero when the cavity length allows the laser to oscillate at the top of its gain profile; that is, at its maximum power. This occurs at frequency  $\nu_0$ , when the slope of the laser power vs frequency equals zero. The discriminator signal is appreciably large at frequencies larger or smaller than  $\nu_0$ , and the slope of power vs frequency is positive for frequencies smaller than  $\nu_0$  and negative for frequencies larger than  $\nu_0$ . The stabilizer produces a correction voltage to be applied to the piezoelectric crystal to change the length of the laser cavity. The result is to stabilize the cavity length so that lasing occurs at the top of the gain profile at frequency  $\nu_0$ .

A slight variation of this method can also be used to stabilize the  $\text{CO}_2$  laser. Modulation of the cavity length causes a modulation in the output power of the laser, which causes the impedance of the plasma tube to oscillate. Thus, rather than detecting the modulation of the laser power,

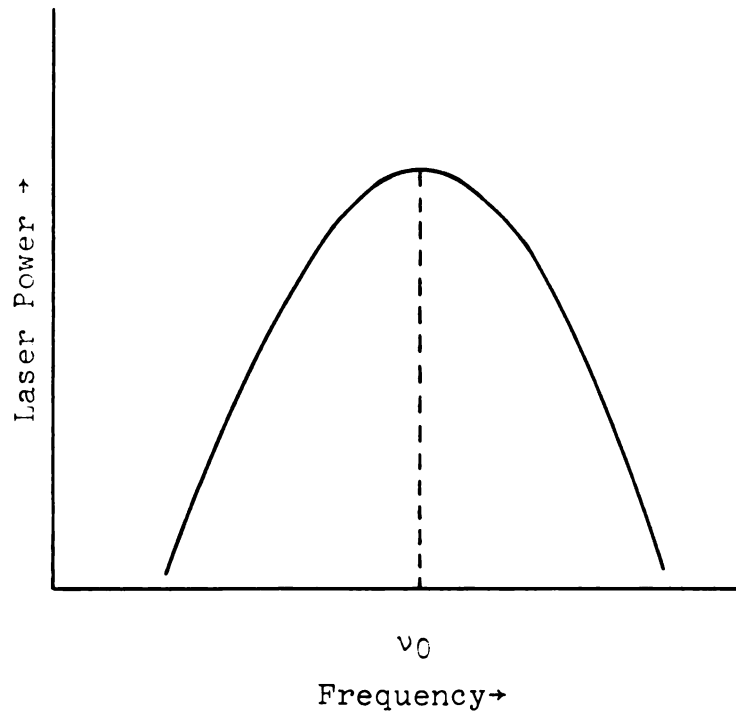


Figure C-3. Variation of the laser power with laser frequency for a single longitudinal mode.

the modulation of the plasma tube impedance can be detected.<sup>125</sup>

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