





This is to certify that the

dissertation entitled STUDIES IN INFRARED LASER AND MICROWAVE SPECTROSCOPY: I. TWO-PHOTON SPECTROSCOPY OF THE  $v_2$  BANDS OF <sup>14</sup>NH<sub>3</sub> AND <sup>15</sup>NH<sub>3</sub> and  $v_3$  BANDS of <sup>12</sup>CH<sub>3</sub>F and <sup>13</sup>CH<sub>3</sub>F; II. MICROWAVE SPECTROSCOPY OF 3-METHYL-1-BUTENE.

Parvaneh Shoja-Chaghervand

has been accepted towards fulfillment of the requirements for

Ph.D. degree in Chemistry

A. Schwendeman Major professor

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STUDIES IN INFRARED LASER AND MICROWAVE SPECTROSCOPY:

I. TWO-PHOTON SPECTROSCOPY OF THE  $v_2$  BANDS OF  ${}^{14}$ NH<sub>3</sub> AND  ${}^{15}$ NH<sub>3</sub> AND  $v_3$  BANDS of  ${}^{12}$ CH<sub>3</sub>F and  ${}^{13}$ CH<sub>3</sub>F; II. MICROWAVE SPECTROSCOPY OF 3-METHYL-1-BUTENE

Ву

## Parvaneh Shoja-Chaghervand

### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

#### ABSTRACT

#### STUDIES IN INFRARED LASER AND MICROWAVE SPECTROSCOPY:

I. TWO-PHOTON SPECTROSCOPY OF THE  $v_2$  BANDS OF <sup>14</sup>NH<sub>3</sub> AND <sup>15</sup>NH<sub>3</sub> AND  $v_3$  BANDS of <sup>12</sup>CH<sub>3</sub>F and <sup>13</sup>CH<sub>3</sub>F; II. MICROWAVE SPECTROSCOPY OF 3-METHYL-1-BUTENE.

Ву

#### Parvaneh Shoja-Chaghervand

The recently developed technique of infrared-microwave two-photon spectroscopy has been employed to study the  $v_2$ bands of  ${}^{14}$ NH<sub>3</sub> and  ${}^{15}$ NH<sub>3</sub> and the  $v_3$  bands of  ${}^{12}$ CH<sub>3</sub>F and  ${}^{13}$ CH<sub>3</sub>F. A CO<sub>2</sub> or N<sub>2</sub>O laser was used as the infrared source and a backward wave oscillator served as the microwave source. The molecular parameters for the inversion-free ground and  $v_2$ =1 excited states were obtained for both species of ammonia by least-squares fits of the frequencies of the assigned two-photon transitions combined with previously reported frequencies measured relative to CO<sub>2</sub> or N<sub>2</sub>O lasers. The two-photon frequencies in this work have been compared to previous two-photon measurements and infrared frequencies obtained by other methods.

For <sup>12</sup>CH<sub>3</sub>F, the assigned two-photon frequencies were

combined with previous two-photon measurements, with laser stark measurements, with far-infrared rotational frequencies in the ground and  $v_3=1$  states, and with microwave frequencies of the rotational transitions in both states. Least-squares analyses of the data were carried out and the molecular constants in both states were determined.

Molecular parameters of  ${}^{13}\text{CH}_3\text{F}$  were derived by a leastsquares fitting of the frequencies of the two-photon transitions assigned in this work, the two-photon frequencies previously reported, the infrared frequencies obtained by analysis of the laser Stark spectrum, and the frequencies of the J=1+0 rotational transitions in the ground and  $v_3=1$ states measured by microwave spectroscopy.

From relative intensity measurements on several transitions in the ground and first excited torsional states of two conformers of 3-methyl-1-butene, the torsional excitation energies have been estimated to be 90±10 and 104±10 cm<sup>-1</sup> for the species with the double bond trans to the ring and rotated ~120° from the trans position "gauche", respectively. The gauche-trans energy difference has been estimated to be 130±20 cm<sup>-1</sup>. The torsional excitation energies and the gauche-trans energy difference have been used to estimate the torsional potential constants. By analysis of Stark effects, the dipole moments have been determined to be  $\mu_a = 0.312\pm0.003D$ ,  $\mu_b=0$  (assumed),  $\mu_c=0.071\pm0.042D$ , and  $\mu_T= 0.320\pm0.010D$  for the trans conformer. For the gauche conformer, they are  $\mu_a=0.367\pm0.004D$ ,  $\mu_b\approx0,\mu_c=0.154\pm0.006D$ , and  $\mu_T=0.398\pm0.004D$ .

To My Parents

For Their Everlasting Love

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#### CHAPTER I

#### INTRODUCTION

This thesis is concerned with studies of the structural parameters of molecules by two different molecular spectroscopy techniques. In one study, the infrared-microwave two-photon spectra of the  $NH_3$  and  $CH_3F$  molecules have been examined by using an  $N_2O$  or  $CO_2$  infrared gas laser combined with a tunable microwave source. In the second study, the dipole moment and torsional potential function of 3-methyl-1-butene have been determined from an investigation of the microwave spectrum of this molecule.

The theoretical and experimental aspects involved in these two studies are similar. Therefore, Chapters II and III are devoted to discussions of the theory and descriptions of the experiments, respectively. In Chapter II the energy levels, the effect of the application of an electric field to a system of molecules (Stark effect), the selection rules governing one-photon and two-photon transitions, and finally the response of a molecular system irradiated simultaneously from two sources are described.

Chapter III includes a brief description of the infrared-microwave spectrometer and the experimental procedure

employed to observe the vibration-rotation spectrum of ammonia and methyl fluoride. A description of the microwave spectrometer and the experimental procedure used to determine the dipole moments and torsional potential function for 3-methyl-1-butene are also included in this chapter.

The experimental results of the two-photon studies of ammonia and methyl fluoride are presented in Chapter IV, whereas the results of the microwave study of the 3-methyll-butene are covered in Chapter V. Each of these chapters includes a review of previous work and a discussion summarizing the results of the present experiments.

#### CHAPTER II

#### THEORY

### 2.1. Introduction

Molecular spectroscopy is essentially a method for the determination of the energy levels of molecules. The energy of the electromagnetic radiation absorbed by a molecular system is always approximately equal to an energy difference between two allowed states of the molecule. The fundamental equation of spectroscopy is the quantum condition:

$$hv = E_2 - E_1$$
 (2-1)

where: h is Planck's constant;

v is the frequency of the radiation; and  $E_1$  and  $E_2$  are the initial and final energy states or levels of the system absorbing the radiation.

The molecule is considered as a collection of atoms held together by a set of interatomic bonds. The molecule is not a rigid body; electrons move, atoms vibrate relative to each other, and the molecule rotates and translates as

a whole.

The energy of the motion of the electrons and of the rotational and vibrational motions of the nuclei in a molecule can only assume certain discrete values, and so leads to discrete frequencies of transitions. An understanding of molecular motions starts with the total energy expression  $E_T$ . To a high level of accuracy the total energy of a molecule can be expressed as the sum of its electronic  $E_{elec}$ , vibrational  $E_{vib}$ , rotational  $E_{rot}$ , and translational energies  $E_{trans}$ , 1

$$E_{T} = E_{elec} + E_{vib} + E_{rot} + E_{trans}$$
 (2-2)

In some cases it is necessary to add terms to Equation (2-2) which allow for the interaction between the electronic and vibrational motions or between the vibration and rotational motions.

To the same degree of approximation that Equation (2-2) is valid the molecular Hamiltonian may be written as the sum of corresponding operators, and the molecular wave function as a product of separate wave functions, as follows:

$$H = H_{elect} + H_{vib} + H_{rot} + H_{trans}$$
(2-3)

$$\psi = \psi_{\text{elect}} \times \psi_{\text{vib}} \times \psi_{\text{rot}} \times \psi_{\text{trans}}$$
 (2-4)

The terms in Equation (2-3) are related to the corresponding factors in Equation (2-4) by the time independent Schrödinger equation:

$$H\psi = E\psi \quad . \tag{2-5}$$

### 2.2. Energy Levels

# 2.2.a. Rotational Energy Levels.

The rotational energy,  $E_{rot}$ , of a molecule is the solution of Equation (2-5) in which H is the rotational Hamiltonian operator for the system and  $\psi$  is the wave function describing the system. The value of  $E_{rot}$  is a constant which defines the stationary state energy levels of the system.

The rotational Hamiltonian can be expressed in terms of the angular momentum components  $P_a$ ,  $P_b$ , and  $P_c$  about the three principal axes,<sup>2</sup> as follows:

$$H_{rot} = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c}$$
(2-6)

Equation (2-6) may also be written as

$$H_{rot} = \frac{4\pi^2}{h} (AP_a^2 + BP_b^2 + CP_c^2) , \qquad (2-7)$$

where A, B, and C are rotational constants and are defined

$$A = \frac{h}{8\pi^{2}I_{a}}; \quad B = \frac{h}{8\pi^{2}I_{b}}; \quad C = \frac{h}{8\pi^{2}I_{c}}. \quad (2-8)$$

-----

In Equations (2-6) and (2-8)  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia where by convention,

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$$A \ge B \ge C$$
 or  $I_a \le I_b \le I_c$ . (2-9)

i) <u>Symmetric Top Energy Levels</u> - When two moments of inertia are equal, the molecule is a symmetric top. A molecule is considered to be a prolate symmetric top if  $I_a < I_b = I_c$  and an oblate symmetric top if  $I_a = I_b < I_c$ . In terms of the rotational constants the energy for a prolate rotor is

$$E_{rot} = h[BJ(J+1) - (A-B)K^2]$$
 (2-10)

For an oblate top the energy is

$$E_{rot} = h[BJ(J+1) - (C-B)K^2]$$
 (2-11)

It is obvious from Equations (2-10) and (2-11) that each rotational level is specified by two quantum numbers, J and K.

J represents the total rotational angular momentum of

as

the molecule. The quantum number K represents the component of angular momentum about the symmetry axis of the molecule, the a axis for a prolate top or the c axis for an oblate top. The J quantum number takes positive integer values including zero, while the K quantum number takes all the negative and positive values between -J and +J including zero.

The energy for a symmetric rotor is independent of the sign of K; therefore, levels with K > 0 are doubly degenerate. In a prolate rotor the value of (A-B) is positive; this causes an increase in energy level with increase in K for a given J. For an oblate rotor the opposite holds because (C-B) is a negative quantity.

Up to this point, a molecule has been considered as a rigid body. However, in reality a molecule is not rigid. The effects of vibration-rotation interaction including centrifugal distortion should be considered.

For a polyatomic molecule, there are several normal modes of vibration, each with its own vibrational quantum number  $v_i$ . The strongest effect of vibration-rotation interaction can be taken into account by defining effective rotational constants,<sup>3</sup>

$$B_{v} = B_{e} - \sum_{i} \alpha_{i}^{B} (v_{i} + \frac{d_{i}}{2}) \qquad (2-12)$$

Here  $B_{\rho}$  is the hypothetical B rotational constant for the

rigid molecule at equilibrium,  $B_v$  is the effective rotational constant for a given vibrational state, and the sum runs over all of the vibrational modes of the molecule. Also in Equation (2-12)  $d_i$  is equal to one for non-degenerate and two for doubly degenerate modes, respectively, and  $\alpha_i^B$  is called a vibration-rotation coupling constant. Similar expressions exist for the A and C rotational constants.

The centrifugal forces resulting from the rotational motion tend to alter the effective moments of inertia. For rotation about any axis in the molecule, this effect forces the atoms away from the axis of rotation and increases the moment of inertia about that axis. The effect of centrifugal distortion on rotational energies in many cases is small, so it can be treated as a perturbation of the rigid rotor Hamiltonian. The rotational energy including centrifugal distortion constants for a prolate symmetric top is: <sup>4</sup>

$$E(J,K) = BJ(J+1) + (A-B)K^{2}-D_{J}J^{2}(J+1)^{2}-D_{JK}J(J+1)K^{2}$$
$$-D_{K}K^{4} + H_{JJJ}J^{3}(J+1)^{3} + H_{JJK}J^{2}(J+1)^{2}K^{2}$$
$$+ H_{JKK}J(J+1)K^{4} + H_{KKK}K^{6} + \dots \qquad (2.13)$$

Here  $D_J$ ,  $D_{JK}$  and  $D_K$  are the first order distortion constants,  $H_{JJJ}$ ,  $H_{JJK}$ ,  $H_{JKK}$  and  $H_{KKK}$  are the second order distortion

constants, etc. For oblate symmetric tops A is replaced by the C rotational constant.

Experimental values of the centrifugal distortion constants can be combined with values of vibrational wave numbers to determine the force field of a molecule or can be used to check the validity of results obtained from vibrational data alone.<sup>5,6</sup> General formulas relating  $D_J$ ,  $D_{JK}$ and  $D_K$  to the vibrational force constants have been given by Wilson<sup>7</sup> for the case of a molecule with symmetry point group  $C_{3v}$ ;

$$D_{J} = (\hbar^{4}/32I_{B}^{\circ 4}) \qquad \begin{bmatrix} \Sigma & \frac{\partial I_{1}}{\partial S_{i}} & (F^{-1})_{ij} & \frac{\partial I_{1}}{\partial S_{j}} + \\ \vdots, j(A_{1}) & \frac{\partial I_{2}}{\partial S_{i}} & (F^{-1})_{ij} & \frac{\partial I_{2}}{\partial S_{j}} \end{bmatrix} ,$$

 $D_{JK} = -2D_{J} + (\hbar^{4}/8I_{B}^{\circ 2}I_{A}^{\circ 2})$ 

$$\times \left[ \sum_{i,j(A_1)} \frac{\partial I_1}{\partial S_i} (F^{-1})_{ij} \frac{\partial I_3}{\partial S_j} + \right]$$

$$\sum_{i,j(E_{y})} \frac{\partial I_{4}}{\partial S_{i}} (F^{-1})_{ij} \frac{\partial I_{4}}{\partial S_{j}} ,$$

$$D_{K} = -D_{J} - D_{JK} + (\hbar^{4}/8I_{A}^{\circ 4}) \sum_{i,j(A_{1})} \frac{\partial I_{3}}{\partial S_{i}} (F^{-1})_{ij} \frac{\partial I_{3}}{\partial S_{j}}.$$

Here,

$$I_{1} = I_{B} + I_{C} = \sum_{\alpha} m_{\alpha} (x_{\alpha}^{2} + y_{\alpha}^{2} + 2z_{\alpha}^{2}) , (A_{1})$$

$$I_{2} = I_{B} - I_{C} = \sum_{\alpha} m_{\alpha} (x_{\alpha}^{2} - y_{\alpha}^{2}) , (E_{y})$$

$$I_{3} = \sum_{\alpha} m_{\alpha} (x_{\alpha}^{2} + y_{\alpha}^{2}) ,$$

$$I_{4} = 2 \sum_{\alpha} m_{\alpha} y_{\alpha} z_{\alpha} . \qquad (2-14)$$

In these formulas, fi is Planck's constant divided by  $2\pi$ ;  $I_A^{\circ}$  is the moment of inertia about the threefold axis of symmetry (figure axis z);  $I_B^{\circ}$  is the moment of inertia about an axis (y) perpendicular to the z axis;  $S_i$  is an internal symmetry coordinate;  $(F^{-1})_{ij}$  is an element of the matrix inverse to the force constant matrix;  $I_A$ ,  $I_B$ , and  $I_C$  are the instantaneous moments of inertia; x, y, and z are Cartesian coordinates and  $m_{\alpha}$  is the mass of the  $\alpha^{th}$  atom. The derivatives of  $I_1$  and  $I_3$  are non-zero only for internal symmetry coordinates which have the symmetry  $A_1$ . Similarly,  $I_2$  and  $I_4$  derivatives vanish unless the  $S_i$  have symmetry E.

ii) <u>Asymmetric Top Energy Levels</u> - A molecule is considered to be an asymmetric top when it possesses three unequal moments of inertia,  $I_a \neq I_b \neq I_c$ . In contrast to symmetric tops, the rotational energy for an asymmetric

top cannot be given by a simple formula.

For an asymmetric top molecule no component of the total rotational angular momentum along a molecule-fixed axis is a constant of the motion. Therefore, while J and M (M represents the projection of the total rotational angular momentum along a space fixed axis) are still good quantum numbers, K is not. However, K is kept to label the energy levels:  $K_1$  is the value of K for the limiting case of an oblate symmetric top,  $K_{-1}$  for the limiting prolate top. Each level may be labeled by  $J_{K_{-1}K_1}$ .

The asymmetry of a molecule is conveniently described in terms of an asymmetry parameter  $\kappa$  proposed by Ray,  $^8$ 

$$\kappa = \frac{2B - A - C}{A - C} \tag{2-15}$$

The value of  $\kappa$  is between +1 for an oblate top and -1 for a prolate symmetric top.

The rotational Hamiltonian in standard form is given by<sup>9</sup>

$$H = \sum_{p,q,r} h_{pqr} \left( J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p \right)$$
(2-16)

where p + q + r is even;  $J_x$ ,  $J_y$ ,  $J_z$  in units of  $\hbar$  are the components of the total angular momentum vector J projected on molecule-fixed axes. These components satisfy the reversed commutation relations

$$[J_x, J_y] = J_x J_y - J_y J_x = -iJ_z$$
, etc. (2-17)

The coefficients  $h_{pqr}$  are the rotational and distortion constants of the vibrational state under consideration.

The Hamiltonian of Equation (2-16), after a suitable unitary transformation is given as a reduced Hamiltonian.<sup>9</sup> For terms up to sextic in the angular momentum, this reduced Hamiltonian is:

$$\tilde{H} = \tilde{H}_2 + \tilde{H}_4 + \tilde{H}_6$$
 (2-18)

or

$$\begin{split} \tilde{H} &= \left[ I_{2} (x+y) J^{2} + \{ z-I_{2} (x+y) \} J_{z}^{2} - \Delta_{J} (J^{2})^{2} \right] \\ &- \Delta_{JK} J^{2} J_{z}^{2} - \Delta_{K} J_{z}^{4} + H_{J} (J^{2})^{3} + H_{JK} (J^{2})^{2} J_{z}^{2} \\ &+ H_{KJ} J^{2} J_{z}^{4} + H_{K} J_{z}^{6} \right] \\ &+ \left[ I_{2} (x-y) (J_{x}^{2} - J_{y}^{2}) - 2\delta_{J} J^{2} (J_{x}^{2} - J_{y}^{2}) \right] \\ &- \delta_{K} \{ J_{z}^{2} (J_{x}^{2} - J_{y}^{2}) + (J_{x}^{2} - J_{y}^{2}) J_{z}^{2} \} \\ &+ 2h_{y} (J^{2})^{2} (J_{x}^{2} - J_{y}^{2}) + h_{JK} J^{2} \{ J_{z}^{2} (J_{x}^{2} - J_{y}^{2}) \} \\ &+ (J_{x}^{2} - J_{y}^{2}) J_{z}^{2} \} + h_{K} \{ J_{z}^{4} (J_{x}^{2} - J_{y}^{2}) + (J_{x}^{2} - J_{y}^{2}) J_{z}^{4} \} ] \quad . \quad (2-19) \end{split}$$

In this equation: x, y, z are the effective principal rotational constants;  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$ ,  $\delta_K$  are the quartic distortion coefficients;  $H_J$ ,  $H_{JK}$ ,  $H_{KJ}$ ,  $H_K$ ,  $h_J$ ,  $h_{JK}$ ,  $h_K$ , are the sextic distortion coefficients.

The matrix elements of the first bracket are diagonal in K and those of the second bracket have  $\Delta K = \pm 2$ .

The term  $\tilde{H}_2$  represents the effective rigid rotor Hamiltonian, Equation (2-6). The first order contributions to the rigid rotor energy levels are obtained by taking the diagonal matrix elements of  $\tilde{H}_4$  and  $\tilde{H}_6$  in the rigid rotor basis. The rotational energy levels corresponding to the Hamiltonian in Equation (2-19) are computed by evaluating the matrix elements for a given J and diagonalizing the matrix.

### 2.2.b. Vibrational Energy

For a molecule consisting of N atoms, the number of vibrational degrees of freedom is 3N-6 for a non-linear system and 3N-5 for a linear system. The kinetic and potential energy of vibration may be written in terms of 3N-6 or 3N-5 internal coordinates. The kinetic energy T and potential energy V of vibration, in terms of the normal coordinates  $Q_i$  and their conjugate momenta  $P_i$ , are given by the expressions<sup>10</sup>

$$T = \frac{3N-6}{\sum_{i=1}^{N-6} P_{i}^{2}}$$
(2-20)

$$V = \frac{3N-6}{\sum_{i=1}^{N-6} \lambda_i Q_i^2}$$
(2-21)

The vibrational Hamiltonian of a molecular system can be written as

$$H = \frac{1}{2} \begin{bmatrix} \frac{3N-6}{\Sigma} & P_{i}^{2} + \frac{3N-6}{\Sigma} & \lambda_{i}Q_{i}^{2} \end{bmatrix}$$
(2-22)

and the Schrödinger wave equation becomes

$$-\frac{h^2}{8\pi^2} \sum_{i=1}^{3N-6} \frac{\partial^2 \psi}{\partial Q_i^2} + \frac{\lambda}{2} \sum_{i=1}^{3N-6} \lambda_i Q_i^2 \psi = E\psi \qquad (2-23)$$

The advantage of using normal coordinates is obvious from the fact that Equation (2-23) is separable into 3N-6 equations, one for each vibrational mode

$$-\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial Q_i^2}\psi_i + \frac{1}{2}\lambda_i Q_i^2\psi_i = E_i\psi_i \qquad (2-24)$$

Equation (2-24) is the well known harmonic oscillator wave equation. Therefore, the vibrational wave function is a product of harmonic oscillator wave functions, and the vibrational energy is a sum of harmonic oscillator energies.

$$\psi_{vib} = \prod_{i=1}^{3N-6} \psi_i; \quad E_{vib} = \sum_{i=1}^{3N-6} E_i \qquad (2-25)$$

Here  $E_i$  is given by

$$E_{i} = (v_{i} + \frac{1}{2})hv_{i}$$
  $v_{i} = 0, 1, 2, ...$  (2-26)

In Equation (2-26)  $v_i$  is the frequency associated with normal coordinate  $Q_i$  and  $v_i$  is the vibrational quantum number, a positive integer or zero.

By substitution of  $E_i$  from Equation (2-26) into  $E_{vib}$ , Equation (2-25), the vibrational energy of a molecule with several modes of vibration can be written as

$$E_{vib} = (v_1 + \frac{1}{2})hv_1 + (v_2 + \frac{1}{2})hv_2 + \dots + (v_{3N-6} + \frac{1}{2})hv_{3N-6}$$
(2-27)

A vibrational transition is induced by radiation only if the derivative of the dipole moment with respect to a normal coordinate is non-zero at equilibrium. The selection rule for the ith normal mode turns out to be  $\Delta v_i = \pm 1$ ,  $\Delta v_j = 0$ ,  $j \neq i$ .

## 2.2.c. Torsional Levels

Internal rotation occurs when one part of molecule (top) rotates relative to the rest (frame) about a bond connecting the two parts. A simple example is ethane in which one methyl group can rotate with respect to the other about the C-C bond. This torsional motion is not a free rotation; in most molecules a potential energy barrier has to be overcome in turning from one configuration to another. Microwave spectroscopy provides a powerful technique for the determination of potential barriers.

The rotational spectrum will be affected by coupling between internal and overall rotations of the molecule, and the complexity of the spectrum depends on the height of the potential barrier hindering internal rotation and the moment of inertia of the rotating group.

We follow the procedure of Quade and  $\text{Lin}^{11}$  in which the torsional angle  $\alpha$  is assumed to be the only internal degree of freedom. The resulting kinetic energy expression may be written

$$2T = \omega^{+} I \omega \qquad (2-28)$$

or

$$T = P^{\dagger} F P \qquad (2-29)$$

In these equations the transpose of the column matrix  $\underset{\sim}{\omega}$  is defined as

$$\omega^{+} = (\omega_{\mathbf{x}}\omega_{\mathbf{y}}\omega_{\mathbf{z}} \dot{\alpha}) \qquad (2-30)$$

and the transpose of the corresponding momentum matrix as

$$P^{+} = (P_{x}P_{y}P_{z}P) .$$
 (2-31)

The  $\omega_g$  and  $P_g$  are components of the molecular velocity and angular momentum about the g axis, respectively, and p is the momentum conjugate to  $\alpha$ . The matrix F is the inverse of the matrix I/2. After substitution into the usual expression for the Hamiltonian, 10, 12

$$H = I^{-\frac{1}{4}} P^{+} F I^{\frac{1}{2}} P I^{-\frac{1}{4}} + V ; \qquad (2-32)$$

in which I is the determinant of I. After simplification, it is found that  $^{\rm 13}$ 

In this expression  $F_{gg}$ ,  $F_{g\alpha}$ , and  $F_{\alpha\alpha}$  are appropriately defined components of the 4 x 4 matrix F, and V' is a multiplicative operator which remains from the evaluation of the quantum-mechanical kinetic energy operator after separating out the P<sub>a</sub> and p dependent terms. It is found that

$$V' = \frac{1}{4I} \frac{d}{d\alpha} \left( F_{\alpha\alpha} \frac{dI}{d\alpha} \right) - \frac{3}{16I^2} F_{\alpha\alpha} \left( \frac{dI}{d\alpha} \right)^2$$
(2-34)

Fourier expansion of V' leads to terms which simply add to the corresponding terms of V and lead to slightly altered
values of the  $V_n$ , where V represents the potential energy associated with the internal rotation and the  $V_n$  are the potential constants,

$$V = \sum_{n} \frac{V_{n}}{2} (1 - \cos n\alpha)$$
 (2-35)

The first three terms of the Hamiltonian (2-33) lead to an effective Hamiltonian for a rigid rotor with centrifugal distortion, from which the usual rotational energy levels are obtained. The last three terms of the Hamiltonian make up the torsional energy operator, as follows:

$$H_{T} = pF_{\alpha\alpha}p + \overline{V}$$
 (2-36)

in which the Fourier components of  $\overline{V}$  are the sums of the  $V_n$  and the corresponding components of V'.

The torsional energies can be obtained by direct diagonalization of a matrix for  $H_{T}$ . Linear combinations of the free-rotor functions, exp (ima) with m = 0,  $\pm 1$ ,  $\pm 2$ , etc., can be used as basis functions for the calculation.

The potential function for an internal rotor with three fold symmetry (-CH<sub>3</sub>) has three identical minima. If the potential barriers between the minima are high, all energy levels within the minima are triply degenerate.<sup>1</sup> However, as the barrier is reduced, the possibility of quantum mechanical tunnelling increases and the degeneracy is partially removed, giving a non-degenerate A level and a doubly degenerate E level. This causes many microwave transitions to appear as doublets, each component corresponding to a transition between torsional levels of the same symmetry; i.e.,  $A \leftrightarrow A$  or  $E \leftrightarrow E$ . The extent of the splitting is a sensitive function of the potential barrier to internal rotation.

The mode of vibration known as inversion is another hindered motion. This vibration exists, in principle, for all non-planar molecules and usually involves the interchange of two equivalent configurations via a planar intermediate. The potential function has two minima separated by a potential hump.

The energy levels for a particle moving with a harmonic potential are equally spaced. If the potential is distorted by a barrier rising in its center, then pairs of energy levels approach each other. In the limit of a very high potential barrier, the particle again has equally spaced energy levels, but in two sets corresponding to vibration on either side of the barrier. Therefore, the energy levels are doubly degenerate.

Classically, the motion of the particle from one side of the barrier to the other side is forbidden, unless the particle has enough energy to overcome the barrier. But quantum mechanically, the tunnelling effect allows penetration of the particle from one minimum to the other. In NH<sub>2</sub>, the potential barrier is moderately high, and a

transition between the two lowest vibrational levels falls in the microwave region,  $\Delta E \sim 0.8 \text{ cm}^{-1}$ . In  $\text{CH}_3\text{F}$ , the potential barrier is so high that the two lowest vibrational levels coincide.

## 2.3 Stark Effect

When a molecule is subjected to a static electric field, the total rotational angular momentum J is constrained to 2J+1 possible orientations with respect to the electric field direction. These orientations may be identified with a quantum number M which measures the projection of J in the direction of applied field  $\varepsilon$ . The 2J+1 values of M are integer values from +J to -J. In the absence of an electric field, the 2J+1 possible directions of J have the same energy.

The existence of a permanent dipole moment  $\mu$  causes an interaction between the molecule and an electric field. The perturbation of the rotational energy levels of the molecule by this interaction is called the Stark effect, and the 2J+1 degeneracy of the rotational levels can be lifted.

The interaction energy of a molecule subjected to an electric field may be written as

 $H_{e} = -\mu \cdot \varepsilon \tag{2-37}$ 

Since the Stark energies are usually small in comparison

with rotational energies, perturbation theory can be used to calculate the Stark splittings.

For symmetric top molecules a first order perturbation treatment leads to

$$E_{s}^{(1)} = -\mu \varepsilon \frac{kM}{J(J+1)}$$
(2-38)

where k, the signed value of K, is the projection of the angular momentum along the figure axis of the molecule.

The second order Stark energy in a symmetric top is usually much smaller than the first order correction  $E_s^{(1)}$  and is ignored unless k or M = 0, in which case the first order contribution vanishes. A linear molecule may be thought of as a special case of a symmetric top molecule with K = 0. Then, the first order correction to the rotational energy is zero for this calss of molecules and the second order effect is

$$E_{s}^{(2)} = \frac{\mu^{2} \varepsilon^{2}}{2hB} \left[ \frac{J(J+1) - 3M^{2}}{J(J+1)(2J-1)(2J+3)} \right]$$
(2-39)

where B is the rotational constant of the molecule.

Stark effects in asymmetric rotors are usually second order or proportional to  $\epsilon^2$ 

$$E_{J,M}^{(2)} = \epsilon^{2} \sum_{g} \left[ (A_{g} + B_{g}M^{2}) \mu_{g}^{2} \right]$$
(2-40)

In this equation, g = a,b,c; the  $A_g$ 's and  $B_g$ 's are Stark coefficients, which depend on the rotational constants and the quantum numbers of the specific level. At Michigan State University, these coefficients can be calculated by a computer program called "EIGVALS". The second order energy depends only on  $M^2$  and so does not remove the (2J+1) degeneracy completely. It splits the levels into (J+1) components.

Equation (2-40) provides a means by which the dipole moment of a molecule can be obtained from experimental results. The selection rules are  $\Delta M = 0$  or ±1 depending on whether the electric field of the radiation and Stark field are parallel or perpendicular to each other, respectively. For  $\Delta M = 0$  selection rules, the frequency of a transition  $v_M$  can be writter as

$$v_{\rm M} = v_{\rm O} + v_{\rm S} \tag{2-41}$$

where  $v_0$  is zero field frequency and  $v_s$  is the Stark effect contribution to the frequency. From Equation (2-40),  $v_s$  turns out to be

$$\nu_{s} = \varepsilon^{2} \sum_{g} \left[ \left( \Delta A_{g} + \Delta B_{g} M^{2} \right) \mu_{g}^{2} \right] , \qquad (2-42)$$

where  $\Delta A_g$  and  $\Delta B_g$  are the difference in  $A_g$  and  $B_g$  values for the two levels involved in the transition.

The Stark shift in frequency,  $\nu_s$ , can be measured for

different values of the Stark field  $\varepsilon$  for a particular M component. A plot of the Stark contribution  $v_s vs. \varepsilon^2$  will be a straight line whose slope is  $\Sigma(\Delta A_g + \Delta B_g M^2) \mu_g^2$ , from which the  $\mu_g^2$  can be calculated.

#### 2.4. Molecular Spectra

## 2.4.a. One-Photon

i) <u>Symmetric Top Selection Rules</u> - A molecule under certain conditions can interact with electromagnetic radiation and undergo a transition from one state to another. Relations between the quantum numbers of the two states are called selection rules.

Rotational transitions can be induced by radiation provided that the molecule possesses a permanent dipole moment. The selection rules governing rotational transitions in a symmetric top molecule are:

 $\Delta J = 0, \pm 1; \quad \Delta K = 0; \quad \Delta M = 0, \pm 1; + \rightarrow -$  (2.43)

The last selection rule applies to symmetric top molecules, such as NH<sub>3</sub>, in which the inversion degeneracy is removed. In this case transitions are allowed between two inversion levels with opposite symmetry.

For molecules without inversion doubling, the last selection rule is unimportant, because symmetric and

asymmetric inversion levels coincide in pairs. The molecule  $CH_3F$  is an example of this group of molecules for which each level has double parity.

ii) <u>Asymmetric Top Selection Rules</u> - The dipole moment in an asymmetric top molecule is not restricted to lie along a figure axis as in the symmetric top, but may have components  $\mu_a$ ,  $\mu_b$ ,  $\mu_c$  along any or all of the principal axes. Therefore, the spectrum of an asymmetric rotor may be complicated by as many as three different types of rotational transitions. These transitions are called atype, b-type, and c-type transitions depending upon which component of the dipole moment is responsible for the transition. If the dipole moment has three significant components along three principal axes, all three types of transitions will be present in the spectrum.

The selection rules for the J quantum number are:

 $\Delta J = 0, \pm 1;$ 

 $\Delta J = 0$  for Q branch transitions and  $\Delta J = -1$ , and +1 are for P and R branch transitions, respectively.

The selection rules on the quantum number  $K_{-1}$  and  $K_{+1}$  are the following:

a-type transitions:  $\mu_a \neq 0$   $ee \leftrightarrow eo$  $oe \leftrightarrow oo$ 

b-type transitions: 
$$\mu_b \neq 0$$
   
c-type transitions:  $\mu_c \neq 0$    
ee  $\leftrightarrow$  oo   
ee  $\leftrightarrow$  eo   
(2-44)

Here, e and o represent the quantum numbers  $K_{-1}$  and  $K_{+1}$  as even or odd.

2.4.b. Two-Photon

i) <u>Single Parity Levels</u> - The energy levels involved in a microwave-infrared two-photon process can have single parity, like NH<sub>3</sub>, or double parity, as in the case of CH<sub>3</sub>F.

Figure (2-1) is a diagram of some energy levels of NH<sub>3</sub> showing possible two-photon transitions in which a microwave quantum is added (a) or subtracted (b) from an infrared quantum. For this case, the transition moment is given by

$$M_{2} = \frac{\langle 1 | \mu_{p} E_{m} | 2 \rangle \langle 2 | \mu_{v} E_{\ell} | 3 \rangle}{2h \Delta v} . \qquad (2-45)$$

In this equation  $\mu_p$  and  $\mu_v$  are the permanent dipole moment and the vibrational transition moment, respectively;  $E_m$ and  $E_\ell$  are the electric fields of the microwave and the laser radiation, respectively; and  $\Delta v$  is the offset frequency, which is the difference between the laser frequency and the frequency of the allowed transition 3 + 2.



(The microwave radiation  $v_m$  is added (a) or subtracted (b) from the infrared  $v_l$  radiation. The (+) and (-) signs indicate the parity of levels.)

Figure 2-1. Energy-level schemes for IR-MW two-photon processes. Three level system (NH<sub>3</sub>). It is apparent from Equation (2-45) that in order for the two-photon transition 3  $\leftrightarrow$  1 to be allowed, it is necessary that there be at least one third level, 2, such that the one-photon transitions 2  $\div$  1 and 3  $\div$  2 are allowed. It is also apparent from Equation (2-45) that twophoton absorption is favored when  $\mu_p$  and  $\mu_v$  are large, microwave and laser powers are high, and  $\Delta v$  is small. If we compare the transition moment for a two-photon process with that for a single photon process (2-46),

$$M_{1} = \langle 2 | \mu_{v} E_{\ell} | 3 \rangle , \qquad (2-46)$$

we find that a two-photon transition is weaker than a normal vibrational transition by a factor of

$$\left|\frac{M_{2}}{M_{1}}\right|^{2} = \left|\frac{\langle 1 | \mu_{p} E_{m} | 2 \rangle}{2h\Delta \nu}\right|^{2} . \qquad (2-47)$$

However, if microwave radiation of sufficient power is used, this factor is not very small, even for relatively large  $\Delta v$ .

ii) <u>Double Parity Levels</u> - In case II Figure (2-2), where the molecular levels involved in the process are of double parity, a third level is not necessary and we can add or subtract the microwave radiation directly. Whether the microwave frequency has been added or subtracted and the second state of the second state of the second state of the second state of the second second second s



Figure 2-2. Energy-level schemes for IR-MW two-photon processes. Two level system (CH<sub>3</sub>F).

The microwave radiation  $v_m$  is added (c) or subtracted (d) from the infrared  $v_{\ell}$  radiation. The (+) and (-) signs indicate the parity of levels. Each level has double parity (±).



can be easily checked experimentally by manually increasing the frequency of the laser and seeing whether the microwave frequency satisfying the two-photon condition decreases or increases.

For each of the cases for double parity levels there are two processes shown in Figure (2-2), corresponding to whether the required third state is part of the lower level or part of the upper level. Since these two processes are not distinguishable by the experiment, the overall process is a superposition of the two. Unfortunately, this is a destructive interference; the transition dipole is,

$$M_{2 \leftarrow \pm 1} = [ < 1 | \mu E_m | 1 > - < 2 | \mu' E_m | 2 > ] < 1 | \mu_v E_{\ell} | 2 > / 2hv_m , (2-48)$$

where  $\mu$  and  $\mu'$  are permanent dipole moments corresponding to states 1 and 2, respectively, and  $\nu_m$  is the frequency of the microwave radiation required to observe the twophoton transition. (In this case  $\nu_m$  is the same as the offset frequency.)

In Equation (2-48), the microwave matrix element appears in the transition moment as a difference. For a Q branch transition, the magnitude of the microwave matrix element for  $\Delta M = 0$  transitions depends only on the difference between  $\mu$ ' and  $\mu$ , which is normally very small. However, with a correct experimental arrangement,  $\Delta M = \pm 1$  transitions are allowed and we were able to observe Q

branch CH<sub>3</sub>F transitions.

iii) <u>Density Matrix Formulation</u> - The response of the molecules to simultaneously applied infrared and microwave radiation is calculated by the density matrix method.<sup>14</sup>

$$\dot{\rho} = -\frac{i}{b}[H,\rho] - \Gamma(\rho - \rho^{(0)})$$
 (2-49)

in which H is the matrix representation of the complete Hamiltonian and  $\rho$  represents the density matrix. The term  $\Gamma(\rho-\rho^{(O)})$  accounts for the random perturbations that cause relaxation of the system to thermal equilibrium.

We consider a three level system, as in Figure (2-1). The molecules are irradiated with two beams; therefore, the applied field is

$$E = \varepsilon_{m} \cos \omega_{m} t + \varepsilon_{l} \cos \omega_{l} t \qquad (2-50)$$

where  $\varepsilon_{\rm m}$  and  $\varepsilon_{\rm l}$  are the amplitudes of the microwave and infrared laser beams, respectively, and  $\omega_{\rm m}$  and  $\omega_{\rm l}$  are the corresponding angular frequencies ( $\omega = 2\pi\nu$  if  $\nu$  is the circular frequency of the radiation).

The Hamiltonian (2-49) for this system can be written as

 $H = H^{(0)} + H^{(1)}$ (2-51)

In this equation  $H^{(0)}$  is the Hamiltonian for a free molecule and  $H^{(1)}$  is the interaction Hamiltonian due to the applied fields;

$$H^{(1)} = -\mu \cdot E$$
 (2-52)

where  $\mu$  is the molecular dipole moment and E is defined by Equation (2-50). It is assumed that  $\omega_{\rm m} \sim \omega_{21}$  and  $\omega_{\rm l} \sim \omega_{32}$  where  $\omega_{\rm ij} = (H_{\rm ii}^{(0)} - H_{\rm jj}^{(0)})/\hbar$  and  $H_{\rm ii}^{(0)}$  is the energy of the i<sup>th</sup> level.

The matrix elements of H<sup>(1)</sup> are

$$H_{JK}^{(1)} = -\mu_{JK} \left( \varepsilon_{m} \cos \omega_{m} t + \varepsilon_{\ell} \cos \omega_{\ell} t \right)$$
 (2-53)

For the system in Figure (2-1), only  $\mu_{12}$  and  $\mu_{23} \neq 0$ ;  $\mu_{11}$ ,  $\mu_{22}$ , and  $\mu_{33} = 0$ ; and  $H_{JK}^{(1)} = H_{KJ}^{(1)}$ .

We also assume that

$$\rho_{21} = d_{21} e^{-i\omega_{m}t}$$
; (2-54a)

$$\rho_{32} = d_{32} e^{-i\omega_{\ell}t}$$
; and (2-54b)

$$\rho_{31} = d_{31} e^{-i(\omega_m + \omega_\ell)t}$$
 (2-54c)

By using the rotating wave approximation, in which all terms with fast oscillation in time are eliminated, the density matrix elements can be given by

$$\dot{\rho}_{1} = i X_{1} (d_{21} - d_{12}) - \frac{i X_{2}}{2} (d_{32} - d_{23}) - \gamma_{1} (\rho_{1} - \rho_{1}^{(0)}) (2-55a)$$

$$\dot{\rho}_{2} = \frac{i X_{1}}{2} (d_{12} - d_{21}) + i X_{2} (d_{32} - d_{23}) - \gamma_{2} (\rho_{2} - \rho_{2}^{(0)}) (2-55b)$$

$$\dot{d}_{21} = i (\omega_{m} - \omega_{21}) d_{21} + \frac{i}{2} X_{1} \rho_{1} + \frac{i X_{2}}{2} d_{31} - \gamma_{21} d_{21} (2-55c)$$

$$\dot{d}_{32} = i (\omega_{\ell} - \omega_{32}) d_{32} + \frac{i X_{2}}{2} \rho_{2} - \frac{i X_{1}}{2} d_{31} - \gamma_{32} d_{32} (2-55d)$$

$$\dot{d}_{31} = i (\omega_{m} + \omega_{\ell} - \omega_{31}) d_{31} + \frac{i X_{2}}{2} d_{21} - \frac{i X_{1}}{2} d_{32} - \gamma_{31} d_{31} (2-55c)$$

where

 $\rho_1 = \rho_{11} - \rho_{22}, \quad \rho_2 = \rho_{22} - \rho_{33}, \quad X_1 = \mu_{21} \epsilon_m / \hbar$ , and  $X_2 = \mu_{23} \epsilon_0 / \hbar$ .

Equation (2-55) may be solved exactly for the steadystate approximation in which all of the derivatives with respect to the time,  $\dot{\rho}_1$ ,  $\dot{\rho}_2$ ,  $\dot{d}_{21}$ ,  $\dot{d}_{32}$ ,  $\dot{d}_{31}$ , are zero<sup>15</sup>, or they may be solved approximately. One approximate solution is based on the perturbation diagram given in Figure (2-3).<sup>16</sup> The equations are solved by iteration. In the zeroth order of approximation all off-diagonal matrix





elements of  $\rho$  are zero and only  $\rho_1^{(O)}$  and  $\rho_2^{(O)}$  are non-zero.

In order to derive the relation between the absorption coefficient and the density matrix elements, we begin with the expression for the absorption coefficient  $\alpha$  given by Flygare,<sup>17</sup>

$$\alpha = -(4\pi\omega_{\ell}/c) \frac{P_{s}^{(\ell)}}{\varepsilon_{\ell}} . \qquad (2-56)$$

In this equation,  $P_s^{(l)}$  is the coefficient of the sine component of the polarization and  $\varepsilon_l$  is the amplitude of the detected radiation (here the infrared radiation). The induced polarization resulting from two radiation fields in the sample can be written as

$$P = P_{c}^{(\ell)} \cos \omega_{\ell} t - P_{s}^{(\ell)} \sin \omega_{\ell} t + P_{c}^{(m)} \cos \omega_{m} t - P_{s}^{(m)} \sin \omega_{m} t.$$
(2-57)

The polarization is also related to the density matrix elements by the expression

$$P = NTr(\mu\rho)$$
(2-58)

where N is the number of molecules per cubic centimeter. The symbol  $Tr(\mu\rho)$  represents the trace or sum of the diagonal elements of the matrix that is the product of the

dipole moment and density matrices. For our case, Equation (2-58) can be expanded as

$$P = N[\mu_{12}(\rho_{21}+\rho_{12}) + \mu_{23}(\rho_{32}+\rho_{23})] . \qquad (2-59)$$

If we substitute  $\rho_{21}$ ,  $\rho_{32}$ , and their complex conjugates from Equation (2-54) and compare Equation (2-59) and (2-57), we obtain

$$P_s^{(l)} = -iN\mu_{23} (d_{23}-d_{32})$$
 (2-60)

If we write  $d_{32}$  and  $d_{23}$  in terms of their real  $(d'_{32})$  and imaginary  $(d''_{32})$  parts, then

$$P_{s}^{(l)} = -2N\mu_{23}d_{32}^{*} . \qquad (2-61)$$

After substitution for  $P_s^{(l)}$  in Equation (2-56),

$$\alpha = \frac{8\pi N \omega_{\ell}}{c \varepsilon_{\ell}} \mu_{23} d_{32}^{*} . \qquad (2-62)$$

Therefore, the absorption coefficient depends on the imaginary part of  $d_{32}$ . Two-photon absorption turns out to be a third order effect and  $d_{32}^{(3)}$  can be evaluated according to the perturbation scheme Figure (2-3).

$$i \left( d_{23}^{(3)} - d_{32}^{(3)} \right) = \frac{x_2 \rho_2^0}{(\delta_2^2 + \gamma_{32}^2)^2} \begin{cases} \frac{\gamma_{32}^2 x_2^2}{\gamma_2} - \frac{x_1^2}{4} \left[ \frac{2\delta_2 \delta_3 \gamma_{32} + \gamma_{31} (\delta_2^2 - \gamma_{32}^2)}{\delta_3^2 + \gamma_{31}^2} \right] \\ - \frac{x_2 x_1^2 \rho_1^0}{2(\delta_1^2 + \gamma_{21}^2) (\delta_2^2 + \gamma_{32}^2)} \left[ \frac{\gamma_{32} \gamma_{31}}{\gamma_2} \right] \end{cases}$$

$$-\frac{\delta_{1}\delta_{2}\gamma_{31}+\delta_{1}\delta_{3}\gamma_{32}+\delta_{2}\delta_{3}\gamma_{21}+\gamma_{31}\gamma_{21}\gamma_{32}}{2(\delta_{3}^{2}+\gamma_{31}^{2})}\right] \qquad (2-63)$$

In this equation,

$$\delta_1 = \omega_m - \omega_{21}; \quad \delta_2 = \omega_\ell - \omega_{32};$$
$$\delta_3 = \delta_1 + \delta_2 = \omega_m + \omega_\ell - \omega_{31}.$$

Only the second and the fourth terms in Equation (2-63) contribute to the two-photon absorption. Then, since for our experiments,  $\delta_1^2 >> \gamma_{21}^2$ ,  $\delta_2^2 >> \gamma_{32}^2$ , and  $\delta_1 \sim \delta_2$ ,

$$i(d_{23}^{(3)}-d_{32}^{(3)}) \approx \frac{5x_2 x_1^2 \gamma(\rho_2^0-\rho_1^0)}{4\delta_1^2} \frac{1}{(\delta_3^2+\gamma^2)} \quad . \tag{2-64}$$

To obtain this expression  $\gamma_{21}$ ,  $\gamma_{32}$ , and  $\gamma_{31}$  have all been taken to be equal (i.e ,  $\gamma$ ), and  $\gamma^2$  has been ignored relative

to  $\delta_1^2$  wherever it occurs. After substituting in Equation (2-60),

$$P_{s}^{(\ell)} = -N_{\mu_{23}} \frac{5x_{2}x_{1}^{2}\gamma}{4\delta_{1}^{2}} \frac{(\rho_{2}^{0}-\rho_{1}^{0})}{(\delta_{3}^{2}+\gamma^{2})}$$
(2-65)

The absorption of the radiant power will be proportional to the incident power,

$$\frac{\mathrm{dP}}{\mathrm{dx}} = -\mathrm{P}\alpha \tag{2-66}$$

where P is the power, x is the coordinate along the axis of the cell, and  $\alpha$  is the absorption coefficient. From this equation the signal at the detector, the difference in the power with and without sample, turns out to be

Signal = 
$$\Delta P = P_0 - P_f \approx \alpha \ell P_0$$
. (2-67)

In this expression  $P_0$  is the incident power of the radiation,  $P_f$  is the output power after absorption occurred, and  $\ell$  is the length of the cell. If we substitute  $P_0 = P_{\ell} = \frac{C}{8\pi} \varepsilon_{\ell}^2$ , and use  $\alpha$  from Equation (2-56), the signal due to the detection of the infrared will be

Signal = 
$$-\frac{\omega_{\ell}}{2} P_{s}^{(\ell)} \varepsilon_{\ell}$$
, (2-68)

and finally from Equation (2-65), the signal is

1

Signal = 
$$\frac{5N\omega_{\ell}\ell(\rho_{2}^{o}-\rho_{1}^{o})}{2} \frac{\hbar x_{2}^{2}x_{1}^{2}\gamma}{4\delta_{1}^{2}} \frac{1}{(\delta_{3}^{2}+\gamma^{2})}$$
 (2-69)

Since

$$\frac{x_{1}^{2}x_{2}^{2}}{4\delta_{1}^{2}} = \frac{\mu_{21}^{2}\mu_{32}^{2}\varepsilon_{m}^{2}\varepsilon_{\ell}^{2}}{4\hbar^{4}\delta_{1}^{2}}$$

the two-photon signal is proportional to the square of the product of the electric fields of the two radiation fields, is inversely proportional to the square of the offset frequency  $\delta_1$ , and depends on the product of the square of the microwave and infrared transition moments  $\mu_{21}^2 \mu_{32}^2$ .

For the exact solution, used by Dr. R. H. Schwendeman,<sup>15</sup> Equations (2-55) are solved by setting up an eight by eight matrix. In this treatment  $\dot{d}_{21}$ ,  $\dot{d}_{32}$  and  $\dot{d}_{31}$  are separated into real and imaginary parts,

$$d_{21} = d'_{21} + id''_{21}$$
$$d_{32} = d'_{32} + id''_{32}$$
$$d_{31} = d'_{31} + id''_{31}$$

(2 - 70)

Then,

$$\dot{\rho}_{1} = -2x_{1}d_{21}^{"} + x_{2}d_{32}^{"} - \gamma_{1} (\rho_{1} - \rho_{1}^{0})$$

$$\dot{\rho}_{2} = x_{1}d_{21}^{"} - 2x_{2}d_{32}^{"} - \gamma_{2}(\rho_{2} - \rho_{2}^{0})$$

$$\dot{d}_{21}^{'} = -\delta_{1}d_{21}^{"} - \frac{x_{2}}{2}d_{31}^{"} - \gamma_{21}d_{21}^{'}$$

$$\dot{d}_{21}^{"} = \delta_{1}d_{21}^{'} + \frac{x_{1}}{2}\rho_{1} + \frac{x_{2}}{2}d_{31}^{'} - \gamma_{21}d_{21}^{"}$$

$$\dot{d}_{32}^{'} = -\delta_{2}d_{32}^{"} + \frac{x_{1}}{2}d_{31}^{"} - \gamma_{32}d_{32}^{'}$$

$$\dot{d}_{32}^{"} = \delta_{2}d_{32}^{'} + \frac{x_{2}}{2}\rho_{2} - \frac{x_{1}}{2}d_{31}^{'} - \gamma_{32}d_{32}^{"}$$

$$\dot{d}_{31}^{'} = -\delta_{3}d_{31}^{"} - \frac{x_{2}}{2}d_{21}^{"} + \frac{x_{1}}{2}d_{32}^{"} - \gamma_{31}d_{31}^{"}$$

$$\dot{d}_{31}^{"} = \delta_{3}d_{31}^{'} + \frac{x_{2}}{2}d_{21}^{'} - \frac{x_{1}}{2}d_{32}^{'} - \gamma_{31}d_{31}^{"}$$

$$(2-71)$$

The equations of motion for the density matrix elements in Equation (2-71) may be written in matrix notation,

[

$$L = -AL + C$$
 , (2-72)

in which the transposes of the column matrices C and L are

$$\mathbf{L}^{\mathbf{T}} = (\rho_1 \ \mathbf{d}_{21}' \ \mathbf{d}_{21}'' \ \mathbf{d}_{31}'' \ \mathbf{d}_{31}'' \ \rho_2 \ \mathbf{d}_{32}' \ \mathbf{d}_{32}'')$$
(2-73)

$$c^{T} = [(\gamma_{1} \rho_{1}^{0}) \quad 0 \quad 0 \quad 0 \quad 0 \quad (\gamma_{2} \rho_{2}^{0}) \quad 0 \quad 0]$$
 (2-74)

and

$$\mathbf{A} = \begin{bmatrix} \mathbf{y}_{1} & \mathbf{0} & 2\mathbf{x}_{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & -\mathbf{x}_{2} \\ \mathbf{0} & \mathbf{y}_{21} & \delta_{1} & \mathbf{0} & \mathbf{x}_{2/2} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ -\mathbf{x}_{1/2} & -\delta_{1} & \mathbf{y}_{21} & -\mathbf{x}_{2/2} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{x}_{2/2} & \mathbf{y}_{31} & (\delta_{1}+\delta_{2}) & \mathbf{0} & \mathbf{0} & -\mathbf{x}_{1/2} \\ \mathbf{0} & -\mathbf{x}_{2/2} & \mathbf{0} & -(\delta_{1}+\delta_{2}) & \mathbf{y}_{31} & \mathbf{0} & \mathbf{x}_{1/2} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & -\mathbf{x}_{1} & \mathbf{0} & \mathbf{0} & \mathbf{y}_{2} & \mathbf{0} & 2\mathbf{x}_{2} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & -\mathbf{x}_{1/2} & \mathbf{0} & \mathbf{y}_{32} & \delta_{2} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{x}_{1/2} & \mathbf{0} & \mathbf{x}_{2/2} & -\delta_{2} & \mathbf{y}_{32} \end{bmatrix}$$

$$(2-75)$$

L is the time derivative of the column matrix L. The steady state solution of Equation (2-72) can be obtained by setting  $\dot{L} = 0$ , therefore,

$$L = A^{-1}C$$
 (2-76)

 $d_{32}^{"}$  can be evaluated from Equation (2-76) either by approximate methods or by exact solution.

To study the response of a two-level system of double parity levels irradiated by two simultaneous photons, as in Figure (2-2), the method used by Dr. R. H. Schwendeman<sup>15c</sup> will be described. In this treatment the basis functions chosen are the functions of mixed parity, which can be shown to have no dipole matrix elements connecting them. The effect of the microwave radiation is neglected at first, and the density matrix elements are calculated for a two-level one-photon (here, infrared) case. With this assumption  $H^{(1)}$  in Equation (2-51) can be written as

$$H_{JK}^{(1)} = -\mu_{JK} \varepsilon_{\ell} \cos \omega_{\ell} t . \qquad (2-77)$$

where only  $\mu_{ab} = \mu_{ba} \neq 0$ .

The equations of motion can be obtained as follows,

$$\dot{\Delta} = -2Xv - \gamma_{1} (\Delta - \Delta^{\circ})$$
  
$$\dot{u} = -\delta v - \gamma_{2} u$$
  
$$\dot{v} = \delta u + \frac{X}{2} \Delta - \gamma_{2} v \qquad (2-78)$$

In these equations,

$$\delta = \omega_{\ell} - \omega_{ba}$$
,  $X = \mu_{ab} \varepsilon_{\ell} / \hbar$ , and  $\Delta = \rho_{aa} - \rho_{bb}$ . (2-79)

Also, u and v are the real and imaginary parts of d<sub>ba</sub>, respectively, where

$$\rho_{ba} = d_{ba} e$$
, and  $d_{ba} = u + iv$ . (2-80)

The effect of the microwave radiation is introduced as a high frequency Stark effect. In this case of levels of mixed parity the Stark effect can be treated by first-order perturbation theory. Then, even for strong microwave fields,

$$\delta = \delta_{a} + \delta_{b} (e^{i\omega_{m}t} + e^{-i\omega_{m}t})$$
(2-81)

in which

$$\delta_a = \omega_\ell - \omega_{ba}$$

and

$$\delta_{b} = (\mu_{aa} - \mu_{bb}) \epsilon_{m} / 2\hbar$$

Also, although the energies are changed by the perturbation, to a good approximation the eigenfunctions are not. We then let

$$\Delta = \sum_{k} \Delta_{k} e^{ik\omega_{m}t}$$

$$u = \sum_{k} u_{k} e^{ik\omega_{m}t}$$

$$v = \sum_{k} v_{k} e^{ik\omega_{m}t}$$
(2-82)

After substituting the expressions (2-81) and (2-82) into Equation (2-78) and solving for the steady state, v = $u = \Delta = 0$ , the third order expression for  $v_0$  is

$$v_{o}^{(3)} \approx \frac{X\Delta^{o}}{2} \frac{\gamma_{2}}{\delta_{a}^{2}} \frac{\delta_{b}^{2}}{[\gamma_{2}^{2} + (\omega_{m} - \delta_{a})^{2}]}$$
 (2-83)

Only  $v_0^{(3)}$  is needed, as the oscillating components of  $v^{(3)}$  will average to zero as a result of the filtering of the absorption signal.

The imaginary part of the radiation-induced polarization  $P_s^{(l)}$  due to the laser radiation is

$$P_{s}^{(l)} = 2N\mu_{ab} v_{o}$$
 (2-84)

Therefore, the signal at the detector,

Signal 
$$\propto \mu_{ab}^2 (\mu_{aa} - \mu_{bb})^2 = \frac{\epsilon_{\ell}^2 \epsilon_{m}^2}{4\delta_{a}^2}$$
 (2-85)

As for the three level system, the signal is proportional to the product of the squares of the electric fields of the two radiant beams and inversely proportional to the square of the offset frequency  $\delta_a$  (Figure 2-2). The signal is also proportional to the square of the infrared transition moment. It is, however, proportional to the difference in the diagonal matrix elements of the dipole moment for the upper and lower levels. Thus, as mentioned above, some care must be exercised in the experimental arrangement to avoid cancellation of these two terms. ÷...

#### CHAPTER III

## EXPERIMENTAL PROCEDURES

This chapter describes the spectrometers and experimental procedures used for the investigations of the infrared-microwave two-photon spectroscopy of  $^{14}NH_3$ ,  $^{15}NH_3$ ,  $^{12}CH_3F$ , and  $^{13}CH_3F$  and for the study of the microwave spectrum of 3-methyl-l-butene.

# 3.1. Infrared-Microwave Two-Photon Spectroscopy

# 3.1.a. <u>Description of the Spectrometer and Experim-</u> tal Procedure

A block diagram of the spectrometer used in this investigation is shown in Figure (3-1).

Microwave radiation produced by a backward wave oscillator (BWO) is passed through an isolator to reduce microwave reflections and through an attenuator to control the microwave power in the system. The output from the attenuator enters a 3 db directional coupler, where it is divided into two parts. One part is sent to a diode mixermultiplier for comparison with a harmonic of a precisely known reference frequency. The second part is amplitude





Figure 3-1.

modulated by means of a PIN diode controlled by a 10 KHz square wave voltage and amplified in a traveling wave tube amplifier (TWTA). The maximum output power of the TWTA was measured to be about 20 watts. The amplified radiation is sent to the sample cell. A 20 db directional coupler between the TWTA and the cell samples the microwave radiation for power measurement. The radiation that passes through the absorption cell is absorbed by a microwave termination at the end of the cell.

A CO<sub>2</sub> or N<sub>2</sub>O laser creates infrared radiation which leaves the laser cavity through a partially-transmitting The output power of the laser is about 1 watt. mirror. A correctly aligned configuration of 5 mirrors allows the beam to pass through the absorption cell. Mirror 1 in Figure (3-2) can be changed to a combination of two mirrors in order to rotate the plane of the polarization of the radiation by 90°. This causes the electric field of the infrared radiation to oscillate in a plane perpendicular to that of the microwave electric field. A particular laser transition is selected by rotating a plane grating at one end of the laser cavity and in order to identify the transition selected, the laser beam is deflected by inserting a mirror between mirrors 1 and 2 in the diagram. The reflected beam enters an Optical Engineering CO2 Model 16-A laser spectrum Analyzer where its wavelength can be estimated well enough to identify the particular laser transition.



Figure 3-2. Mirror configuration for two-photon experiment.

The beam splitter shown between mirrors 2 and 3 has two uses. One application is to use the reflected component of infrared radiation for power measurements. But the primary use of the beam splitter is to allow insertion of a beam from a He-Ne laser into the infrared optical path for assistance in alignment. For this purpose, a pyroelectric detector is placed between mirror 5 and the absorption cell. The infrared beam is chopped, monitored by this detector, and the detector output is displayed on an oscilloscope. The position and size of the two irises between mirrors 3 and 4 and the position of the detector are changed until the amplitude of the oscilloscope pattern is maximized when the openings of the irises are as small as possible. This shows that the infrared beam is centered at the openings of the two irises. Next the position of the He-Ne laser is adjusted until its beam after reflection from the splitter is exactly aligned through the irises; at this point the He-Ne beam is superimposed on the infrared beam.

Next the detector is removed and by adjustment of mirrors 4 and 5 the beam is sent through the absorption cell. A low-noise, liquid-nitrogen-cooled Barnes Engineering Pb-Sn-Te photovoltaic detector, placed at the exit of the sample cell, is used to monitor the infrared beam. The detected signal is amplified and coherently detected by a Keithley Model 840 Autoloc Amplifier. The reference signal for the phase sensitive detector is obtained from the square wave that drives the PIN switch in the microwave circuit.

The output of the Autoloc Amplifier can be displayed on an oscilloscope, a chart recorder, or can be sent to a Digital Equipment Corporation PDP8/E computer, where the absorption as a function of frequency of the microwave radiation can be recorded on a flexible disk.

The computer program BWOHP, which was written by Dr. Erik Bjarnov, was used to scan the frequency of the microwave radiation in any region of interest. For each single laser line the microwave frequency is scanned in the two ranges of 8-12.4 GHz and 12.4-18 GHz to identify the position of the transitions. Survey spectra were usually recorded at 2 MHz intervals in 800 MHz sections. In order to record a transition, a shorter sweep - 400 MHz in most cases - is used with the transition in the center of the sweep. It is possible to scan over a particular region several times and average the spectra. In this investigation 1 to 3 sweeps were used depending on the strength of the observed transition. Normally, 5 readings at each frequency were averaged during each sweep. The output of the phase sensitive detector was filtered with time constants ranging from 3-30 ms and the time between readings was typically 2-5 time constants. The data were taken in 2 MHz steps; therefore, a 400 MHz sweep included 201 data points.

A second computer program LFIT2, was used for least squares fitting of the line shape of the observed transitions

to a Lorentzian function in order to determine the frequency of the transitions. At the sample pressures used (~1 torr) the lineshapes were some combination of Lorentz and Gauss functions, but the Lorentz fitting provided a rapid and accurate method of obtaining the frequencies of the transitions.

#### 3.1.b. Radiation Sources

It is obvious that in order to be able to carry out an infrared-microwave two-photon experiment, a microwave source and an infrared source are necessary. In the MSU two-photon spectrometer, microwave radiation is produced by one of two Varian Backward Wave Oscillators (BWO). The frequency ranges of the BWO's are 8-12.4 GHz and 12.4-18.0 GHz. The frequency-controlling helix voltage for the BWO is generated by a Kepco Model 2000 Operational Power Supply (OPS) which in turn is driven by a voltage from a D/A converter controlled by the computer. The microwave frequency is brought into the lock range of a phase-sensitive synchronizer by the OPS output. The synchronizer locks the frequency to a synthesized frequency also controlled by the computer.

A flowing gas  $N_2O$  or  $CO_2$  laser is used as the source of infrared radiation for the MSU spectrometer. The  $N_2O$  or  $CO_2$  laser oscillates at single frequencies separated by 1 or 2 cm<sup>-1</sup> throughout the 900-1100 cm<sup>-1</sup> range. The

laser used in this experiment consists of a 2.8 m long water cooled gain cell with an outer diameter of 2.8 cm. The laser tube is sealed with NaCl windows at the Brewster angle at each end; therefore, the output radiation is plane polarized with the electric field of the radiation parallel to the floor.

The laser cavity is about 4.4 m long with a 150 lines/mm plane grating blazed at 10 µm at one end and a concave dielectric-coated, partially-transmitting germanium mirror of 10 m radius at the other end. Mirrors with reflectivity of 80% and 95% are available; which mirror is used depends on the strength of the chosen laser line. This mirror is mounted on a piezoelectric translator. To stabilize the laser the position of the cavity mirror is sinusoidally modulated (520 Hz), causing modulation of the laser cavity length and therefore modulation of laser frequency. The modulated laser output is detected by a Santa Barbara Research Center Hg-Cd-Te detector. The detected signal is preamplified and coherently detected by a Model 80-214 Lansing Lock-in Stabilizer. The output from the stabilizer is a discriminator signal which is zero when the laser is oscillating at the top of its gain profile  $v_{o}$ and non-zero otherwise. This discriminator signal is applied as a DC bias to the piezoelectric translator to stabilize the cavity length, and therefore maintains oscillation of the laser at  $v_{\alpha}$ .

By manual adjustment of the angle of the grating a particular  $CO_2$  or  $N_2O$  vibration-rotation line can be chosen for laser operation. The active medium of the laser is a mixture of helium, nitrogen, and  $CO_2$  or  $N_2O$  with a total pressure of less than 10 torr. The composition of the gas mixture is controlled by five needle values.

3.1.c. Sample cell

Two brass absorption cells were used for the infraredmicrowave two-photon experiments. One cell, a P-band wave quide (0.790 cm x 1.580 cm, i.d.) one meter long was used for microwave frequencies between 12.4 and 18 GHz. The second cell is a 1.5 meter long, X band (1.016 cm x 2.286 cm, i.d.) cell for microwave frequencies in the 8-12.4 GHz range. Figure (3-3) is a top view of the absorption cell. Two holes, 6 mm diameter in X-band cell and 5 mm diameter in the P-band cell, are drilled in positions 1 and 2 in Figure (3-3). The holes are sealed by NaCl windows of about 4 mm thickness to allow transmission of the infrared radiation. At positions 3 and 4 the sample cell is sealed by vacuum tight mica windows and "O" rings. The cell is attached to the vacuum line by a brass or glass tubing through the sample inlet. In all measurements the absorption cell was placed outside the laser cavity.


Diagram of the absorption cell used in infrared-microwave two-photon experiment. Figure 3-3.

3.1.d. Samples

The four samples studied by infrared-microwave twophoton spectroscopy for this thesis include  ${}^{14}NH_3$ ,  ${}^{15}NH_3$ ,  ${}^{12}CH_3F$  and  ${}^{13}CH_3F$ .

The sample of <sup>14</sup>NH<sub>3</sub>, which was purchased from Matheson and had a stated purity of 99.9%, was kindly provided by Professor J. L. Dye's research group at Michigan State University.

The  ${}^{15}\text{NH}_3$  sample, obtained from Prochem was enriched in  ${}^{15}\text{NH}_3$  to 99.8%. A sample of  ${}^{12}\text{CH}_3\text{F}$  was obtained from PCR Research Chemicals, Inc. and  ${}^{13}\text{CH}_3\text{F}$  with 90% enrichment was purchased from Merck & Co., Inc. All of the samples were used as they were received without any further purifications.

#### 3.2. Microwave Spectroscopy

# 3.2.a. Description of the Spectrometer and Experimental Procedure

A Hewlett-Packard 8460A Molecular Rotational Resonance (MRR) Spectrometer was used to study the rotational spectra of 3-methyl-1-butene. This MRR spectrometer uses Stark modulation techniques with a modulation frequency of 33.333 kHz.

The microwave radiation is produced by a backward wave oscillator (BWO), and sent into the Stark cell by means of

the proper wave guide. The frequency of the BWO is controlled by a frequency synthesizer whose frequency can be stepped at rates and step sizes under operator control.

The Stark cell is a 2.5 m long, X band cell. A metal plate inserted in the middle of the cell along its length serves as an electrode or septum. It is parallel to the broad dimension of the cell and insulated from the cell by Teflon strips.

When square-wave 33.333 KHz modulation is applied to the septum, the absorption frequencies of the molecule are modulated by the Stark effect. A modulated absorption signal is detected by a Si crystal diode. The detected signal is preamplified and sent to a phase-sensitive detector, where it is compared against the 33.333 KHz reference signal. The output of the phase sensitive detector is filtered, in order to reduce the noise, and finally displayed on a strip chart recorder. As a result of phase-sensitive detection the zero field transition and its Stark components are recorded in opposite directions with respect to each other. The 8456A sweep control provides a continuous display of the microwave frequency to 1 KHz. The MRR spectrometer can provide markers on the chart paper at selected intervals between 1 KHz to 10 MHz.

To measure the frequency of an MRR absorption line, the microwave frequency is swept up and down over the line at the same rate. The frequency from both traces is

extracted from the markers and an average is taken.

To determine the Stark effect, the frequencies of the Stark components as a function of the electric field are measured. These frequencies are plotted against the square of the electric field. The observed slopes are used to determine the dipole moment components.

Relative intensity measurements were made by recording pairs of transitions at constant crystal current under conditions of low microwave power. For many of the transitions the peak intensities were measured and compared at several pressures and Stark fields. All of the intensity measurements were made with the sample cell surrounded by dry ice. The temperature of the cell at several points was measured by taping a Pt resistance thermometer to the cell walls. The temperature was taken to be the mean of the measured values (204 K).

#### 3.2.b. Sample

The sample studied by microwave spectroscopy for this thesis is 3-methyl-l-butene. This sample was obtained from Chemical Samples Company, Columbus, OH, and used without further purification.

#### CHAPTER IV

TWO-PHOTON SPECTROSCOPY OF AMMONIA AND METHYL FLUORIDE

#### 4.1. Introduction

The invention of the laser<sup>18</sup> provided spectroscopists with a light source of extremely high intensity and extremely narrow bandwidth and has led to the development of the extensive field of laser spectroscopy for characterizing the interaction of radiation with matter. Under low light level conditions, the absorption cross section is linear in the laser intensity. As the laser intensity increases, new phenomena appear that no longer vary linearly with intensity. The two-photon process, which is involved with the excitation of rotational, vibrational, and electronic states of molecules by the simultaneous interaction with two photons, is an example of a non-linear phenomenon.

Two-photon spectroscopy, using both absorption and fluorescence techniques, is now well established in the study of molecular electronic transitions where, because of the operation of different selection rules, information complementary to that from one-photon processes may be obtained.<sup>19-21</sup>

The theory of two-photon absorption was first

investigated by Goppert-Mayer.<sup>22</sup> She was able to extend Dirac's theory of dispersion to cover the case where two photons were absorbed simultaneously in a single process.

In 1970, Oka and Shimizu reported the observation of microwave double-photon absorption in the rotational spectra of  $CD_3CN$  and  $PF_3$ . The double-photon transitions involving quantum numbers  $J = 3 \leftrightarrow 2$  and  $J = 2 \leftrightarrow 0$  in  $CD_3CN$  and  $J = 2 \leftrightarrow 0$  in  $PF_3$  were monitored by using a second microwave field as a probe.<sup>23</sup>

The first infrared-microwave two-photon transition was observed in the  $v_2$  band of  ${}^{15}\text{NH}_3$ . In this technique a tunable microwave frequency is added to, or subtracted from, the fixed laser frequency by using the nonlinearity of the molecular transition process. The P(15), N<sub>2</sub>O laser line was employed to detect the ssQ (4,4) two-photon transition in  ${}^{15}\text{NH}_3$ .<sup>24</sup> This paper demonstrated the possibility of infrared spectroscopy being carried out with a resolution and accuracy of frequency measurement approaching that of microwave spectroscopy.

After observation of infrared-microwave two-photon saturation dips (Lamb dips<sup>25</sup>) by Freund and Oka<sup>26</sup> in 1972, a theoretical explanation of two-photon Lamb-dips was developed by Shimizu.<sup>27</sup>

The first example of systematic spectroscopy carried out by the infrared-microwave two-photon technique was reported by Freund and Oka in their study of the  $v_2$  band

of ammonia with  $N_2O$  and normal  $CO_2$  lasers.<sup>28</sup> An extension of this work was reported by H. Jones in which  ${}^{13}CO_2$  and  $C^{18}O_2$  lasers were used with the cell placed within the laser cavity.<sup>29,30</sup> In addition, a number of two-photon transitions have been observed in fundamental and hotbands of the linear molecules fluoroacetylene (HCCF) and cyanogen fluoride (FCN) by H. Jones.<sup>31</sup>

Recently, Doppler-free infrared-infrared two-photon absorptions have been observed in the  $v_2$  band of NH<sub>3</sub> by using a fixed-frequency CO<sub>2</sub> laser and a diode laser. Beams from the two lasers were passed in opposite directions through the sample cell and the transmitted intensity of the diode laser beam was monitored as a function of its frequency.<sup>32</sup>

In 1979 a computer-controlled infrared-microwave twophoton spectrometer was assembled at Michigan State University. Ammonia was chosen as the first molecule to be studied with this spectrometer. It was chosen because of its large transition dipole moment, and because a number of transitions in the  $v_2$  vibration-rotation band are known to be near CO<sub>2</sub> laser frequencies.<sup>33-35</sup> Furthermore, since this molecule is of considerable astrophysical significance,<sup>36,37</sup> it is important to have as precise information as possible for its energy level structure.

Methyl fluoride was selected as the second molecule to be studied in order to compare the spectra of symmetric

top molecules with (NH<sub>3</sub>) and without (CH<sub>3</sub>F) inversion.

The theory of two-photon spectroscopy was presented in Chapter II and the two-photon spectrometer used in this study was described in Chapter III.

## 4.2. The $v_2$ Bands of $14_{\rm NH_3}$ and $15_{\rm NH_3}$

#### 4.2.a. Introduction

Numerous investigations of the microwave spectrum of ammonia, a pyramidal molecule with  $C_{3v}$  symmetry and the rotational structure of a symmetric top, have been published since the early stages of microwave spectroscopy.<sup>38</sup> The microwave spectrum of ammonia in the centimeter region is the result of transitions between the members of inversion doublets.<sup>39</sup> These doublets result from the fact that the potential barrier to the motion in which the NH<sub>3</sub> pyramid is inverted is relatively low.

At the present time, the most accurate ground state inversion frequencies have been obtained in beam maser studies by Kukolich and co-workers,  $^{40-42}$  but these are limited to a small number of ammonia lines. Poynter and Kakar have measured the frequencies of 119 inversion transitions of  $^{14}NH_3$  in the ground state to high accuracy by conventional microwave spectroscopy. The accuracy of their measurements is reported to be  $\pm 0.005$  MHz. $^{43}$  The frequencies of 15 high J inversion transitions have been measured by Sinha and Smith<sup>44</sup> with an accuracy of ±0.03 MHz by thermally populating higher rotational levels. Accurate measurements (±1 MHz) of the frequencies of the inversion transitions of <sup>14</sup>NH<sub>3</sub> in the  $v_2$  excited state have been carried out by Belov <u>et al.</u><sup>45</sup> The inversion spectrum of NH<sub>3</sub> in the  $v_2 = 1$  state lies in the far-infrared or submillimeter region ( $\sim$ 35 cm<sup>-1</sup>). The most recent published inversion frequencies of <sup>15</sup>NH<sub>3</sub> in the ground vibrational state are measurements made by Sasada.<sup>46</sup> In this work frequencies of 115 microwave lines were measured to an accuracy of ±0.01 MHz.

The analysis of the inversion spectrum of ammonia is based on numerical fits of the frequencies to selected functional forms. In one approach a power series in J(J+1), the square of the total angular momentum, and  $K^2$ , the square of the projection of the angular momentum on the symmetry axis of the molecule, has been used.<sup>47</sup> In a second approach an exponential model due to Costain<sup>48</sup> has been used. More recently, Young and Young used a Padé approximation to fit Poynter and Kakar's measurements with a standard deviation which was close to the accuracy of their experimental measurements.<sup>49</sup>

The vibration-rotation spectrum of NH<sub>3</sub> has also been studied since the early days of infrared spectroscopy.<sup>50</sup> Ammonia is predicted to have 4 fundamental frequencies, two totally symmetric (a<sub>1</sub> symmetry in the C<sub>3v</sub> group) and two doubly degenerate modes (e symmetry), all of them infrared active. The strong  $v_1$  and  $v_2$  bands of  $a_1$  symmetry are near 3 and 10  $\mu$ m, respectively. The very weak  $v_3$  band is close to  $v_1$  in frequency and the very strong  $v_4$  band is near 6  $\mu$ m.

In 1941, Sheng <u>et al</u>. published the results of a study of the 10 µm band, in which a grating spectrometer was used.<sup>51</sup> In 1958, Benedict <u>et al</u>. studied the  $(v_2 + v_3)$ perpendicular and  $(v_1 + v_2)$  parallel combination bands of ammonia which lie between 2.15 and 2.5 µm. They also gave a general analysis of the ammonia vibration-rotation spectra.<sup>52</sup> Later, in a high resolution study of NH<sub>3</sub> and ND<sub>3</sub> over the range of 1750 to 7100 cm<sup>-1</sup> with an effective spectral resolution of 0.1 to 0.2 cm<sup>-1</sup>, they determined the rotational constants and the molecular dimensions of ammonia to be  $r_e = 1.0124$  Å and  $h_e = 0.3816$  Å<sup>53</sup> ( $r_e$  and  $h_e$ are the equilibrium NH bond distance and the distance of the nitrogen atom from the plane of the three hydrogens, respectively).

Measurements and analysis of the  $v_2$  band of ammonia under a resolution of 0.1 cm<sup>-1</sup> were reported by Mould and his co-workers in 1959. They derived the molecular constants of ammonia in the ground and  $v_2$  states.<sup>54</sup> In the same year an independent investigation of ammonia in the regions 510-1280 cm<sup>-1</sup> and 1440-1840 cm<sup>-1</sup> with a vacuum grating spectrometer was carried out.<sup>55</sup> The accuracy of the frequencies of the transitions is reported to be  $\pm 0.03$  cm<sup>-1</sup>

for the 10-16  $\mu$ m region and ±0.05 cm<sup>-1</sup> in the 6  $\mu$ m region. Moreover, a theoretical discussion which involves the Coriolis interaction between the  $\nu_2$  and  $\nu_4$  bands and *l*-type doubling in the  $\nu_4$  band was presented.

Infrared laser Stark spectra of the  $v_2$  bands of  ${}^{14}\text{NH}_3$ and  ${}^{15}\text{NH}_3$  were published by Shimizu in 1970.  ${}^{34,35}$  In these experiments CO<sub>2</sub> and N<sub>2</sub>O lasers were employed as infrared sources, and quite a few coincidences between the ammonia lines and CO<sub>2</sub> or N<sub>2</sub>O laser lines were revealed. Since then, the ammonia spectrum has proved to be a favorite example of infrared transitions for the study of novel methods of laser spectroscopy.

Analysis of the  $v_2$  band of  ${}^{15}\text{NH}_3$  was carried out by Shimizu and Shimizu.<sup>56</sup> In this study the spectrum of  ${}^{15}\text{NH}_3$  was obtained by using an infrared vacuum spectrometer. About 170 absorption lines in the frequency range from 842-1154 cm<sup>-1</sup> were observed. They believe that the error in the frequency determination should be less than 0.02 cm<sup>-1</sup>. Rotational constants and the  $v_2$  band origin were obtained from the least squares analysis of the observed frequencies of  ${}^{15}\text{NH}_3$ .

In 1976 Freund and Oka published a paper<sup>28</sup> in which they presented the result of a high resolution study of the  $v_2$  band of ammonia by two-photon spectroscopy, where the sources of radiation were a tunable microwave source and a fixed frequency CO<sub>2</sub> or N<sub>2</sub>O laser. Both straightforward and Lamb-dip two-photon techniques were used. Thirty-nine

<sup>14</sup>NH<sub>3</sub> and 11 <sup>15</sup>NH<sub>3</sub> transitions were assigned by straightforward two-photon technique and the accuracy of their frequency measurements was estimated to be ±30 MHz. For Lambdip measurements to be carried out, the infrared transition has to be saturated. Therefore, a high power infrared beam is required and in order to satisfy this condition, Freund and Oka placed the sample cell inside the laser cavity. A total of 25 <sup>14</sup>NH<sub>3</sub> transitions and 6 transitions in  $^{15}\mathrm{NH}_3$  were observed with this method and the accuracy of these data is reported to be ±3 MHz and ±6 MHz for measurements done with CO<sub>2</sub> or N<sub>2</sub>O lasers, respectively. Additional measurements of the  $v_2$  band of ammonia by the infrared-microwave two-photon method were made by H. Jones. In these experiments the frequencies of 36 transitions of  $14_{\rm NH_3}^{29}$  and 11 transitions of  $15_{\rm NH_3}^{30}$  were determined with isotopic <sup>13</sup>CO<sub>2</sub> and C<sup>18</sup>O<sub>2</sub> laser lines. By combining these results with those of previous two-photon measurements and laser Stark data, the spectroscopic constants of this band were calculated for  $^{15}NH_3$ .

By employing an infrared heterodyne technique, precision measurements of  $NH_3$  spectral lines near 11 µm have been made.<sup>57,58</sup> Although this technique is very accurate, it is limited by the frequency-tuning range of the laser local oscillator and the intermediate-frequency (IF) bandwidth of the optical mixer.

Diode laser measurements of NH<sub>3</sub> absorption lines in

the 9.6 and 10.6  $\mu m$  region have been performed by different investigators.  $^{59-62}$ 

In 1980 there appeared two papers concerned with the high resolution infrared study of ammonia. One paper is concerned with the laser Stark spectroscopy of the  $v_2$  band of ammonia.<sup>33</sup> In this study the molecular constants for the ground and  $v_2$  vibrational states are obtained by applying a simple Hamiltonian. The dipole moments in the two states were determined for both  $^{14}NH_3$  and  $^{15}NH_3$ . The second paper compiles the results of experiments carried out by a number of investigators. This paper<sup>63</sup> is unique in that it reports for the first time the measured frequencies of the pure inversion and rotation-inversion transitions in the  $v_2$  state of <sup>14</sup>NH<sub>3</sub> in 700-1100 GHz region. A submillimeter wave spectrometer was used for these measurements. A vibration-inversion-rotation Hamiltonian, which was developed previously  $^{64}$  was used for parameterization of the energy levels of ammonia. In this approach, the Coriolis interaction between the  $v_2$  and  $v_4$  states and ltype doubling in the  $v_4$  band were considered. Rotational and centrifugal distortion constants of the molecule in the  $2v_2$ ,  $v_4$ ,  $3v_2$ , and  $(v_2 + v_4)$  states as well as in the ground and  $v_2$  states were derived in this study. In an extension of this work experimental data, including Fourier transform infrared spectra of the inversion-rotation transitions between 40-300 cm<sup>-1</sup>, submillimeter wave spectra of the inversion and inversion-rotation transitions in the

 $v_2$  state of <sup>14</sup>NH<sub>3</sub>, and a few  $\Delta K = \pm 3$  "perturbation-allowed" transition frequencies are combined with the microwave ground-state transition frequencies and  $v_2$  infrared-micro-wave two-photon frequencies and are simultaneously analyzed. The ground state and  $v_2$  state molecular parameters are determined in this analysis.<sup>65</sup>

The IR spectrum of  ${}^{15}$ NH<sub>3</sub> between 510-3040 cm<sup>-1</sup> recorded with a Fourier transform infrared spectrometer has been reported.<sup>66</sup> The  $v_2$ ,  $2v_2$ ,  $3v_2$ ,  $v_4$  and  $v_2 + v_4$  bands were measured and analyzed on the basis of the vibration-rotation Hamiltonian of Ref. 64-d. The molecular parameters for the  $v_2 = 1,2,3$  states were derived in this study.<sup>66</sup> The rotation inversion spectrum in the ground state of  ${}^{15}$ NH<sub>3</sub> has been obtained between 38 and 280 cm<sup>-1</sup> by Fourier transform spectroscopy.<sup>67</sup>

Recently, Sattler <u>et al</u>.<sup>68</sup> have made diode laser heterodyne measurements of the frequencies of a number of transitions in the 9 and 10  $\mu$ m region of NH<sub>3</sub> with an accuracy of ±2 x 10<sup>-4</sup> cm<sup>-1</sup>. Molecular absorption frequencies were determined by heterodyning the emission of the leadsalt diode laser and a reference CO<sub>2</sub> laser and using a spectrum analyzer to measure the beat frequency.

We have reinvestigated the two-photon spectrum of  ${}^{14}_{\rm NH_3}$  and  ${}^{15}_{\rm NH_3}$  by using normal CO<sub>2</sub> and N<sub>2</sub>O lasers and microwave oscillators in the 8-18 GHz region. A least-squares fit of all of the two-photon frequencies measured in this work, all of the previous two-photon frequencies,  ${}^{28-30}$ 

and all of the diode laser heterodyne measurements<sup>68</sup> has been carried out. The microwave, millimeter wave, and submillimeter wave values of the inversion frequencies were assumed in this analysis. For this fitting the simple Hamiltonian that was used by Shimoda <u>et al</u>.<sup>33</sup> was used. A number of simple tests of the accuracy and consistency of the twophoton results have been performed. Rotational and centrifugal distortion constants of the ground states and  $v_2$  states have been determined and are compared with previous results.

4.2.b. <u>14<sub>NH3</sub></u>

The study of the  $v_2$  band of NH<sub>3</sub> by two-photon spectroscopy was begun by calculating approximate frequencies of the possible two-photon transitions. The ground and  $v_2$ vibrational levels of <sup>14</sup>NH<sub>3</sub> are shown in Figure (4-1). Inversion splitting causes a separation between rotational levels (J,K) of approximately 0.7934 cm<sup>-1</sup> in the ground state<sup>70</sup> and 35.6881 cm<sup>-1</sup> in the  $v_2$ =1 state.<sup>71</sup> The rotational energy of the (J,K) state of NH<sub>3</sub> in a particular vibrational state is expressed in the form,

$$E_{rot}(J,K)/h = BJ(J+1) - (B-C)K^{2} - D_{J}J^{2}(J+1)^{2}$$
  
-  $D_{JK}J(J+1)K^{2} - D_{K}K^{4} + H_{J}J^{3}(J+1)^{3}$   
+  $H_{JJK}J^{2}(J+1)^{2}K^{2} + H_{JKK}J(J+1)K^{4} + H_{K}K^{6}$   
(4-1)



Figure 4-1. Energy level diagrams involved in two-photon transitions of NH<sub>3</sub>.

where B and C are rotational constants, and the D's and H's are centrifugal distortion constants. Equation (4-1) is an expression for the rotational energy of a symmetric top molecule. In this equation, the B, C, D's and H's are mean values of the constants for the symmetric (s) and antisymmetric (a) inversion levels.

The two-photon selection rules are the same as vibration-rotation selection rules (i.e., for a parallel band,  $\Delta J = 0, \pm 1, \Delta K=0$ ) with one exception: two-photon transitions are allowed only between s  $\leftrightarrow$ s or a $\leftrightarrow$  a levels while vibrational transitions happen for s  $\leftrightarrow$  a levels. In order to calculate the frequencies of the a $\rightarrow$ a and s $\rightarrow$ s two-photon transitions, the effect of the inversion splitting must be added to Equation (4-1). Therefore,

$$E_{INV-rot}(v,J,K) = E_{rot}(J,K) \pm 1/2\Delta E_{INV}(v,J,K) \quad (4-2)$$

Here + and - signs refer to the a and s states, respectively, and  $\Delta E_{INV}(v,J,K)$  is the energy difference between the members of the (J,K) inversion doublet in the vibrational state v.

By using the  $\Delta K=0$  selection rule and assuming (J",K) and (J',K) as the lower and upper state quantum numbers, respectively, the following expression is obtained for the frequency of an s $\rightarrow$ s or a $\rightarrow$ a two-photon transition.

$$\begin{split} \nu_{\mathrm{TP}} &= \nu_{\mathrm{O}} + B'J'(J'+1) - [(B'-C') - (B''-C'')]K^{2} - D_{J}'J'^{2}(J'+1)^{2} \\ &- D'_{JK}J'(J'+1)K^{2} - (D_{K}'-D_{K}'')K^{4} + H_{J}'J'^{3}(J'+1)^{3} + H_{JJK}'J'^{2}(J'+1)^{2}K^{2} \\ &+ H_{JKK}'J'(J'+1)K^{4} + (H_{K}'-H_{K}'')K^{6} \\ &- B''J''(J''+1) + D_{J}'J''^{2}(J''+1)^{2} + D_{JK}'J''(J''+1)K^{2} \\ &- H_{J}'J''^{3}(J''+1)^{3} - H_{JJK}'J''^{2}(J''+1)^{2}K^{2} - H_{JKK}'J''(J''+1)K^{4} \\ &\pm 1/2[\Delta E_{\mathrm{INV}}(1,J',K) - \Delta E_{\mathrm{INV}}(0,J'',K)] \qquad (4-3) \end{split}$$

Again the + or - sign is used for an  $a \rightarrow a$  or an  $s \rightarrow s$  transition, respectively. In this equation  $v_0$  is the band origin, which is the energy difference between the J" = K" = 0 and J' = K' = 0 states in the absence of inversion splitting.

In Equation (4-3) all of the rotational constants with a prime belong to the upper state and those with a double prime belong to the lower state. To calculate inversion frequencies in the ground state,  $\Delta E_{INV}(0,J^*,K^*)$ , the 21parameter equation and parameters given by Schnable <u>et al</u>.<sup>70</sup> were used. In order to reproduce the required inversion frequencies in the  $v_2$  state,  $\Delta E_{INV}(1,J^*,K^*)$ , a 21-term polynomial in the quantum numbers J and K was used (Table 4-1). These parameters were obtained here by a leastsquares fit of the inversion frequencies in the  $v_2$  state Table 4-1. Polynomial Representation of  $v_{INV}$ , the Inversion Frequency in the  $v_2 = 1$  State of  ${}^{14}NH_3$ . The 21 parameters were obtained by fitting the data from Reference 63.

$$v_{INV} = v_0 + A_1 J (J+1) + A_2 K^2 + A_3 J^2 (J+1)^2 + A_4 J (J+1) K^2$$
  
+  $A_5 K^4 + A_6 J^3 (J+1)^3 + A_7 J^2 (J+1)^2 K^2 + A_8 J (J+1) K^4 + A_9 K^6$   
+  $A_{10} J^4 (J+1)^4 + A_{11} J^3 (J+1)^3 K^2 + A_{12} J^2 (J+1)^2 K^4 + A_{13} J (J+1) K^6$   
+  $A_{14} K^8 + A_{15} J^5 (J+1)^5 + A_{16} J^4 (J+1)^4 K^2 + A_{17} J^3 (J+1)^3 K^4$   
+  $A_{18} J^2 (J+1)^2 K^6 + A_{19} J (J+1) K^8 + A_{20} K^{10}$ 

Parameter Value	Parameter Value
$v_0 = 0.106990428 \cdot 10^7$	
$A_1 = -0.540014712 \cdot 10^4$	$A_{11} = 0.109025839 \cdot 10^{-2}$
$A_2 = 0.754257405 \cdot 10^4$	$A_{12} = -0.271524180 \cdot 10^{-2}$
$A_3 = 0.128582772 \cdot 10^2$	$A_{13} = 0.284822774 \cdot 10^{-2}$
$A_4 = -0.350185240 \cdot 10^2$	$A_{14} = -0.106401210 \cdot 10^{-2}$
$A_5 = 0.236303331 \cdot 10^2$	$A_{15} = 0.105158889 \cdot 10^{-5}$
$A_6 = -0.997400177 \cdot 10^{-2}$	$A_{16} = -0.873631923 \cdot 10^{-5}$
$A_7 = 0.249227152 \cdot 10^{-1}$	$A_{17} = 0.277375789 \cdot 10^{-4}$
$A_8 = -0.104487519 \cdot 10^{-1}$	$A_{18} = -0.424652581 \cdot 10^{-4}$
$A_9 = -0.698633839 \cdot 10^{-2}$	$A_{19} = 0.315335845 \cdot 10^{-4}$
$A_{10} = -0.153245109 \cdot 10^{-3}$	$A_{20} = -0.914279839 \cdot 10^{-5}$

of <sup>14</sup>NH<sub>3</sub> obtained by Belov <u>et al</u>.<sup>63</sup> by submillimeter wave spectroscopy. The K = 3 transitions were excluded from the fit since they are strongly affected by  $\Delta K = \pm 3$  perturbations arising from centrifugal distortion effects.<sup>71</sup>

The rotational parameters obtained by Shimoda et al. 33 (Table (4-2) Column II) for the upper (m') and lower (m") states\* and the calculated inversion frequencies in the ground and  $v_2$  excited states were used as input data for a computer program that uses Equation (4-3) to calculate the two-photon frequencies and compares them to CO<sub>2</sub> and N<sub>2</sub>O laser frequencies. The output of this program is a list of the differences between the frequencies of the two-photon transitions and the nearest laser frequencies,  $v_{\rm m} = v_{\rm TP} - v_{\rm Laser}$ . The MSU spectrometer can detect those  $\boldsymbol{\nu}_m$  frequencies which are in the microwave range of 8 to 18 GHz, provided that the transition has enough intensity. The frequencies of CO2 laser lines were computed by using the rotational parameters of Freed <u>et</u> <u>al</u>.<sup>72</sup>. The N<sub>2</sub>O laser frequencies were derived with the parameters published by Whitford et al. 73

Figure (4-1) shows examples of the energy levels of ammonia and the possible two-photon transitions. The

<sup>&</sup>quot;The symbols m" and m' are used to designate hypothetical levels halfway between the members of an inversion doublet in the ground and first excited states, respectively.

Parameter	This Work <sup>b</sup> I	Ref. 33 <sup>C</sup> II
ν <sub>0</sub>	949.88112(8)	949.88093(18)
в'	9.9801426(432)	9.980194(68)
∆C-∆B	-0.1404435(122)	-0.140441(24)
D'I	9.1479(126)×10 <sup>-4</sup>	9.1757(280)x10 <sup>-4</sup>
	$-1.82866(450) \times 10^{-3}$	$-1.83398(620) \times 10^{-3}$
$D_{K}^{\prime}-D_{K}^{\prime}$	$2.2168(30) \times 10^{-4}$	$2.2026(88) \times 10^{-4}$
H'	$2.7528(1230) \times 10^{-7}$	$3.1131(360) \times 10^{-7}$
H'TTK	-1.1205(456)x10 <sup>-6</sup>	-1.2145(1100)x10 <sup>-6</sup>
H'IKK	1.50067(11152)x10 <sup>-6</sup>	1.5759(1240)x10 <sup>-6</sup>
H <sup>'</sup> <sub>K</sub> -H <sup>"</sup> <sub>K</sub>	$-2.0328(254)\times10^{-7}$	$-1.785(102) \times 10^{-7}$
B"	9.9441342(420)	9.944190(66)
D,,	$8.4042(122)\times 10^{-4}$	$8.4409(260) \times 10^{-4}$
D", TK	$-1.55129(448) \times 10^{-3}$	$-1.55886(600) \times 10^{-3}$
н",	$2.3829(1210) \times 10^{-7}$	$2.8665(346) \times 10^{-7}$
- Н"ЈЈК	-8.5268(4518)x10 <sup>-7</sup>	$-9.925(1080) \times 10^{-7}$
H"JKK	1.06253(11096)×10 <sup>-6</sup>	$1.1953(1220) \times 10^{-6}$
S.D. (MHz)	5.85	11.1

Table 4-2. Ground State and  $v_2$  Excited State Molecular Parameters of  ${}^{14}\mathrm{NH}_3$  (cm<sup>-1</sup>).<sup>a</sup>

<sup>a</sup>The quoted uncertainties for the constants are two times the standard deviations of the least squares fit, given in units of the last digit.

<sup>b</sup>From fit of frequencies in Appendix B. All 16 parameters varied.

<sup>C</sup>Reference 33.

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 $^{14}$ NH<sub>3</sub> sample was used at a pressure ranging from 0.2 to 1.3 torr. By using 18 CO<sub>2</sub> and 11 N<sub>2</sub>O laser lines a total of 63 spectral lines were observed; 44 transitions were assigned and the assignments were confirmed by comparison with the results of other two-photon experiments<sup>28,29</sup> and the known infrared frequencies of <sup>14</sup>NH<sub>3</sub>.<sup>63</sup>

As a result of generally good line shapes, the MSU spectrometer can measure the microwave frequency  $v_{\rm m}$  with an uncertainty of about ±1 MHz. However, because of the uncertainty of the laser frequency arising from our method of stabilization, we estimate the accuracy of our measurements to be ±5 MHz. Figures (4-2) and (4-3) are photographs of oscilloscope displays of the stored data files for two typical two-photon transitions. In both cases the width of the sweep is 400 MHz, corresponding to 200 data points.

The assigned transitions are listed in Tables (4-3), and (4-4) for s→s and a→a transitions, respectively. The second column of these tables gives the laser line involved, where 10 and 9 indicate a  $CO_2$  laser line in the 10 µm and 9 µm region, respectively, and N indicates an N<sub>2</sub>O laser line. The first column of the tables shows the assignment in the form V(J",K) with V = P,Q and R referring to  $\Delta J = -1,0$ , and +1 transitions, respectively. The frequency of the microwave radiation at which the transition occurs is given in the third column with a sign + or - which shows whether the two photons are added together or whether

Figure 4-2. IR-MW two-photon absorption signal. The sQ(5,5) two-photon transition of  $14_{\rm NH_3}$  observed by using the CO<sub>2</sub> P(36) laser line  $(\nu_{\ell} = 929.017435 \text{ cm}^{-1})$  and microwave frequency of  $\nu_{\rm m} = 16651 \text{ MHz}$ . The offset frequency  $\Delta \nu = 7.882 \text{ GHz}$  and the sample pressure was 0.6 torr. The width of the sweep is 400 MHz.

Figure 4-3. IR-MW two-photon absorption signal. The aQ(1,1) two-photon transition of  $14_{\rm NH_3}$  observed by using the CO<sub>2</sub> R(8) line ( $\nu_{\ell}$  = 967.707233 cm<sup>-1</sup>) and microwave frequency of  $\nu_{\rm m}$  = 14987 MHz. The sample pressure was 1.25 torr, and the offset frequency  $\Delta\nu$  = 8.707 GHz. The width of the sweep is 400 MHz.

Table 4-3. Comparison of observed and calculated frequencies of

Transition	laser line	a Microwave <sup>b</sup>	Two-Photon <sup>C</sup>	$b_{u\lambda}$
II and I cion	Duber inte	(MHZ)	$(cm^{-1})$	(GHZ)
Q( 1,1)	10P(32)	-16251.	932.41833(25)	39.95
Q(1,1)	NP(8)	10089.	932.41926(118)	13.61
Q(3,3)	NP(8)	-15881.	931.55298(91)	39.75
Q(3,3)	NP(9)	9956.	931.55333(127)	13.91
Q(3,3)	10P(34)	16548.	931.55341(135)	7.32
Q(4,3)	10P(32)	-12892.	932.53038(-2)	35.58
Q(4,3)	NP(8)	13424.	932.53049(10)	9.26
Q( 4,4)	NP(9)	-15517.	930.70362(29)	39.66
Q( 4,4)	10P(34)	-8935.	930.70341(8)	33.07
Q( 4,4)	NP(10)	10402.	930.70335(2)	13.74
Q( 5,5)	10P(36)	16651.	929.57286(4)	7.88
Q( 6,4)	NP(7)	11848.	933.33605(2)	9.15
Q( 6,6)	NP(12)	-13718.	928.15903(22)	38.77
Q(7,3)	10P(28)	-8956.	936.50501(-200)	26.97
Q( 7 <b>,</b> 6)	NP(11)	13147.	929.92670(16)	9.78
Q(7 <b>,</b> 6)	NP(10)	-12883.	929.92663(9)	35.81
Q(7,7)	10P(38)	-16512.	926.45753(20)	42.23
Q(7,7)	NP(15)	14263.	926.45765(32)	11.45
Q(8,5)	10P(30)	-13222.	934.45346(20)	32.03
Q(8,6)	NP(9)	17753.	931.81338(25)	2.97
Q(8,7)	10P(36)	-15005.	928.51693(-11)	38.24
Q(8,8)	10P(40)	-15290.	924.46395(51)	41.89
Q(9,4)	10P(26)	-14145.	938.21643(-27)	29.67
Q(9,5)	10P(28)	-16067.	936.26781(22)	32.87
Q(9,7)	NP(10)	9174.	930.66240(32)	11.56
Q(11,9)	10P(38)	17360.	92/.58/40(1)	3.71
R(4,2)	9P(34)	16543.	1034.03982(3)	5.16
R(6,1)	9R(16)	13452.	10/6.43654(-2)	4.94
R( 6,5)	AK(IQ)	-10019.	10/1.34942(8)	38.15

s-s two-photon transitions in the  $v_2$  band of <sup>14</sup> NHz.

- $^{a}$  N, 9, 10 refer to N 20, 9  $\mu m$  band of CO  $_{2},$  or 10  $\mu m$  band of CO  $_{2}$  laser, respectively.
- <sup>b</sup> Microwave frequency in MHz. A minus sign indicates that the microwave frequency is subtracted from the laser frequency to obtain the two-photon frequency.
- <sup>C</sup> The numbers in parentheses are observed minus calculated frequencies in multiples of 0.00001 cm<sup>-1</sup>. The parameters for the calculation are in the first column of Table 4-2.
- <sup>d</sup> Absolute value of the difference between the laser frequency and the frequency of the corresponding one-photon allowed transition.

Table 4-4. Comparison of observed and calculated frequencies of

Transition	Laser line <sup>a</sup>	Microwave <sup>b</sup> (MHZ)	Two-Photon <sup>C</sup> (cm <sup>-1</sup> )	<sub>کر</sub> ط (GHZ)
P(2,1) Q(1,1) Q(3,2) Q(3,3) Q(5,2) Q(5,3) Q(5,5) Q(5,5) Q(7,4) Q(9,5) R(3,3) R(5,1) R(5,2) R(5,3) P(5,3)	10P(38) 10R(8) 10R(6) 10R(6) 10R(6) 10R(4) 10R(4) 10R(4) 10R(2) 9P(22) 9R(28) 9R(28) 9R(28)	13581. -14987. 11834. 8987. -13677. -17401. 16900. -12905. -16640. 16688. 14481. 13537. 12122. 16472.	927.46135(-7) 967.20731(-5) 965.64509(-11) 966.55013(117) 965.79414(28) 965.66992(-101) 965.33270(-16) 964.33851(9) 962.70808(-59) 1045.57832(-23) 1083.96181(-13) 1083.93033(19) 1083.88311(15)	36.68 8.71 34.67 32.86 6.69 3.88 41.43 6.31 Ø.16 4Ø.56 34.32 33.91 33.41
R( 5,5)	9R(28)	9060.	1083.78098(7)	33.59

a-a two-photon transitions in the  $v_2$  band of <sup>14</sup> NH<sub>2</sub>.

- $^a$  N, 9, 10 refer to N O, 9  $\mu m$  band of CO  $_2,$  or 10  $\mu m$  band of CO  $_2$  laser, respectively.
- b Microwave frequency in MHz. A minus sign indicates that the microwave frequency is subtracted from the laser frequency to obtain the two-photon frequency.
- <sup>C</sup> The numbers in parentheses are observed minus calculated frequencies in multiples of 0.00001 cm<sup>-1</sup>. The parameters for the calculation are in the first column of Table 4-2.

d Absolute value of the difference between the laser frequency and the frequency of the corresponding one-photon allowed transition.

-

the microwave frequency is subtracted from the laser frequency to obtain the two-photon frequency. The fourth column gives the frequency of the two-photon transition  $(v_{TP} = v_{l} \pm v_{m})$ , whereas the last column lists the offset frequency, which is the difference between the laser frequency and the frequency of the nearest one-photon transition. The intensity of a two-photon transition is proportional to the inverse of the square of  $\Delta v$ , so the smaller  $\Delta v$ , the stronger the transition. We have been able to observe transitions with a  $\Delta v$  as large as  $\sim$ 43 GHz.

In order to analyze the data and derive a set of molecular constants, Equation (4-3) has been rearranged as follows:

$$v_{\rm RV} = v_0 + E(J',K) - E(J'',K)$$
 (4-4)

where  $v_{RV}$  is a hypothetical inversion-free rotationvibration frequency defined as:

$$v_{\rm RV} = v_{\rm TP} + \frac{1}{2} [\Delta E_{\rm INV}(1,J',K) - \Delta E_{\rm INV}(0,J'',K)] \qquad (4-5)$$

with - and + for a  $\rightarrow$  a and s  $\rightarrow$  s two-photon transitions, respectively. The E(J',K) and E(J",K) in Equation (4-4) represent the rotational terms in the upper  $v_2$  and ground state, respectively, as defined in Equation (4-1). For this purpose, the  $\Delta E_{TNV}$ 's were taken from the experimental inversion frequencies of Belov <u>et al</u>.<sup>71</sup> for the  $v_2$  state, and those of Poynter and Kakar<sup>43</sup> for the ground state (Appendix A). The  $v_{\rm TP}$  values were obtained from the laser frequencies and the measured microwave frequencies. In this way values of  $v_{\rm RV}$  were determined experimentally.

A simultaneous least squares fit of the  $v_{\rm RV}$  derived from our two-photon data, from those reported by H. Jones<sup>29</sup> and Freund and Oka,<sup>28</sup> and from diode laser<sup>68</sup> and heterodyne measurements<sup>58</sup> was carried out. Since the transitions reported in Reference 68 and 58, are  $a \rightarrow s$  or  $s \rightarrow a$  one-photon IR transitions, the  $v_{\rm RV}$  corresponding to Equation (4-5) was  $v_{\rm RV} = v_{\rm Sat} \pm \frac{1}{2} [\Delta E_{\rm INV}(1,J',K) + \Delta E_{\rm INV}(0,J'',K)]$ . For these transitions the + and - signs are for transitions from  $a \rightarrow s$  or  $s \rightarrow a$  levels, respectively. All of the frequencies in the fitting were given weights that are inversely proportional to the square of their estimated accuracy. The set of linear equations used in the least squares fitting are

$$\delta v = \sum_{i=1}^{16} \left( \frac{\partial v}{\partial X_i} \right) \delta X_i . \qquad (4-6)$$

where  $\delta v = (v_{exp} - v_{calc})$ ,  $\delta X_i = (X_i)_{exp} - (X_i)_{calc}$ , and  $v_{exp}$  and  $v_{calc}$  are the experimental and calculated frequencies of ro-vibrational transitions. The values of  $v_{calc}$  were obtained by using the parameters of Shimoda <u>et al</u>.<sup>33</sup>

The parameters fitted are:

Each  $(\frac{\partial v}{\partial X_i})$  is the partial derivative of the transition frequency with respect to the i<sup>th</sup> parameter. These derivatives are:

$$(\frac{\partial v}{\partial X_{1}}) = 1$$

$$(\frac{\partial v}{\partial X_{9}}) = J' (J'+1) K^{4}$$

$$(\frac{\partial v}{\partial X_{2}}) = J' (J'+1)$$

$$(\frac{\partial v}{\partial X_{3}}) = K^{2}$$

$$(\frac{\partial v}{\partial X_{4}}) = -J'^{2} (J'+1)^{2}$$

$$(\frac{\partial v}{\partial X_{12}}) = J''^{2} (J'+1)^{2}$$

$$(\frac{\partial v}{\partial X_{12}}) = J''^{2} (J'+1) K^{2}$$

$$(\frac{\partial v}{\partial X_{13}}) = J'' (J'+1) K^{2}$$

$$(\frac{\partial v}{\partial X_{13}}) = J'' (J'+1) K^{2}$$

$$(\frac{\partial v}{\partial X_{14}}) = -J''^{3} (J''+1) K^{2}$$

$$(\frac{\partial v}{\partial X_7}) = J'^3 (J'+1)^3 \qquad (\frac{\partial v}{\partial X_{15}}) = -J'' (J''+1)^2 K^2 (\frac{\partial v}{\partial X_8}) = J'^2 (J'+1)^2 K^2 \qquad (\frac{\partial v}{\partial X_{16}}) = -J'' (J''+1) K^4 (4-8)$$

No inversion transitions involving levels with K = 0are observed, because for K = 0, levels with even values of J are missing in the lower component of inversion doublets (s) and levels with odd values of J are missing in the upper component of inversion doublets (a). The missing levels are a result of the effect of nuclear spin statistics. Therefore, the inversion frequencies of the (J,K) = (5,0) and (6,0) levels in the ground state and the (6,0) and (7,0) levels in  $v_2 = 1$  state were calculated from the parameters given by Schnabel <u>et al</u>.<sup>70</sup> and Belov <u>et al</u>.<sup>71</sup> respectively. These values appear in Appendix A, where all of the inversion frequencies used in our fit are given.

In order to obtain a set of parameters which are able to reproduce the experimental two-photon transitions, a number of fittings were performed. In the first fitting all of the transitions mentioned above, including transitions involving levels with K = 3, were included in the fit; 16 rotational parameters in the ground and  $v_2 = 1$  states were varied. With this fitting, rather large residuals for transitions with K = 3 were obtained and the deviation for these transitions increased with J. The fit was repeated after eliminating the K = 3 transitions; in this case a better standard deviation 26.03 MHz was obtained. In the final fit, in addition to the K = 3 transitions, 10 transitions that showed deviations larger than 34 MHz were eliminated. For this fitting, the standard deviation dropped to 5.85 MHz, Table 4-2, Column I.

The final parameters obtained here are compared to those from the infrared laser Stark study of Shimoda <u>et al</u>. in Table 4-2. A large deviation appears in the value of the band origin,  $v_0$ , which is  $\sim 6$  MHz higher than the Shimoda result when both ground state and  $v_2$  excited state parameters are allowed to vary. The constants C', C", D'\_K, D''\_K, H''\_K and H''\_K can not be determined independently because of the  $\Delta K = 0$  selection rule. A list of all of the frequencies used in the fitting is given in Appendix B.

#### 4.2.c. Some Checks of the Accuracy of the Data

i) <u>Inversion Frequencies in the  $v_2 = 1$  State of</u>  $\frac{14_{\rm NH_3}}{-}$  It is possible to derive the frequency between inversion doublets in the  $v_2$  state of ammonia from the frequencies of two-photon transitions by using the expression,

$$v_{INV}(J,K) = v_{aa}(J,K) - v_{ss}(J,K) + v_0(J,K)$$
 (4-9)

Here,  $v_{\rm INV}$  is the inversion frequency in  $v_2$  state,  $v_{\rm aa}$ and  $v_{\rm ss}$  are two-photon transitions and  $v_0$  is the inversion frequency in the ground state. The  $v_{\rm aa}$  and  $v_{\rm ss}$  values in Tables (4-4) and (4-3) may be combined with the ground state inversion frequencies given by Poynter and Kakar (Appendix A) to determine "experimental"  $v_2$  inversion frequencies. The results are given in Table (4-5) and are compared to the submillimeter wave measurements of Belov et al.<sup>71</sup>.

ii) <u>Difference Between Frequencies of the Laser</u> <u>Lines</u> - In the cases where the same transition has been observed with two different laser lines, the difference in frequency of the two laser lines can be obtained. As an example, Table (4-3) shows that sQ(7,7) has been identified with two different laser lines, P(15) of the N<sub>2</sub>O laser and P(38) of the CO<sub>2</sub> laser in the 10 µm region. The measured microwave frequencies are 14263 MHz and -16512 MHz, respectively.

Therefore,

$$v[NP(15)] + 14263 = v[10P(38)] - 16512$$
 (4-10)

(MHz).
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4-5.
Table

(J,K) <sup>a</sup>	vaa	vs <sup>b</sup>	۷ <mark>, ا</mark> ۷۷ (۲, ۲) <sup>۲</sup>	v <mark>i<sub>NV</sub>(J,K)<sup>d</sup></mark>
(1,1)	28996145.69	27953226.18	23694.496	1066614.0(36.82)
(1,1)	=	27953198.3	=	1066641.9(8.94)
(3,3)	28976443.93	27927268.65	23870.13	1073045.4(5.3)
(3,3)	Ξ	27927266.26	=	1073047.8(2.9)
(3,3)	=	27927255.76	=	1073058.3(7.59
(2,5)	28939946.29	27867893.26	24532.982	1096586.02(5.61)

<sup>a</sup>J and K are the rotational quantum numbers of the inversion doublet.

 $^{
m b}$   $_{
m aa}$  and  $v_{
m ss}$  are the observed frequencies of the two-photon transitions a+a and s+s for levels with the same J and K.

<sup>C</sup>Inversion frequency for the ground state from Reference 43.

 $^d$ Calculated inversion frequency in the  $v_2^{=1}$  state; the numbers in parenthesis are the differences between  $v_{INV}^{1}(J,K)$  of Reference 71 and those obtained in this work. v[10P(38)] - v[NP(15)] = 16512 + 14263 = 30775 MHz.

The calculated difference from References 72 and 73 is 30771.88 MHz. The deviation between the two methods of obtaining the frequency difference is 3.09 MHz.

Table (4-6) contains a list of the transitions that have been observed with more than one laser line. The third column of this table shows the frequency difference  $\Delta v$  of the two laser lines identified in the second column and the last column shows observed minus calculated values. All of the differences are within the estimated error with the exception of [10P(32)-NP(8)] obtained from sQ(1,1)transitions. This is probably due to a less accurate value of the sQ(1,1) frequency determined with the N<sub>2</sub>O laser, as the same discrepancy is seen in the residual columns of Table (4-3) and Table (4-5).

or

Table 4-6. Comparison of Differences in Laser Frequencies Obtained from Duplicate Measurements of <sup>14</sup>NH<sub>3</sub> Two-Photon Frequencies With Differences Calculated from Vibration-Rotation Constants of CO<sub>2</sub><sup>72</sup> or N<sub>2</sub>O.<sup>73</sup>

Transition <sup>a</sup>	Δv1-v2 <sup>b</sup>	c Δν <sub>obs</sub> . (MHz)	$\frac{\Delta v_{obs}}{(MHz)}^{d}$
sQ(1,1)	10P(32)-NP(8)	26340	27.12
s <u>O</u> (3,3)	NP(9)-10P(34) NP(8)-NP(9)	6592. 25837.	2.9 10.02
	NP(8)-10P(34)	32429.	12.92
sQ(4,3)	10P(32)-NP(8)	26316.	3.12
sQ(4,4)	10P(34)-NP(10) NP(9)-10P(34) NP(9)-NP(10)	19337. 6582. 25919.	-1.51 -7.1 -8.61
sQ(7,6)	NP(10)-NP(11)	26030	1.88
sQ(7,7)	10P(38)-NP(15)	30775	3.09

<sup>a</sup>The transition observed with more than one laser line.

 $v_1$  and  $v_2$  are the two laser lines whose frequency difference is determined by two-photon spectroscopy.

 $^{c}\Delta v_{obs} = v_{\ell_1} - v_{\ell_2} = v_{m_2} - v_{m_1}$ .  $v_m$  represent the microwave frequency satisfying the two-photon condition.

 $d_{\Delta\nu}_{calc.}$  is the calculated frequency difference from Ref. 72 and 73 for CO<sub>2</sub> and N<sub>2</sub>O laser lines, respectively.

### 4.2.d. $\frac{15_{\rm NH}}{-2}$

The initial calculation of the frequencies of the twophoton transitions in the  $v_2$  band of  ${}^{15}\text{NH}_3$  was carried out by combination of the vibration-rotation constants reported in Reference 33, and those in Reference 30.

In the present study of the  $v_2$  band of  ${}^{15}\text{NH}_3$ , 28 CO<sub>2</sub> and 14 N<sub>2</sub>O laser lines were employed. A total of 101 transitions were detected and 60 of them were assigned to two-photon transitions of  ${}^{15}\text{NH}_3$ . Most of the transitions were recorded with a sample pressure of approximately 1 torr.

The assignment of the transitions was based both on the results of the initial calculation and on previous twophoton results.<sup>28,30</sup> Tables (4-7) and (4-8) list the assigned <sup>15</sup>NH<sub>3</sub> transitions measured in this work. No direct measurements of the inversion frequencies of  ${}^{15}{}_{\rm NH}{}_{3}$ in the  $v_2 = 1$  vibrational state have been reported so far. Therefore, it is not possible to obtain the mean values of the vibration-rotation parameters in the  $v_2$  state directly from our data, as was done for <sup>14</sup>NH<sub>3</sub>. The present twophoton frequencies were combined with the previous twophoton measurements  $^{28,30}$ , with 7 transitions measured in a laser Stark experiment, transitions measured by a diode laser heterodyne technique,<sup>68</sup> and with the previously measured microwave inversion frequencies in the ground state. 46 These data were used to obtain experimental frequencies from the hypothetical level m" (midway
Table 4-7. Comparison of observed and calculated frequencies of s-s two-photon transitions in the  $v_2^{}$  band of  $^{15}\rm NH_3^{}$ .

Transition	Laser line <sup>a</sup>	Microwave <sup>b</sup> (MHZ)	Two-Photon <sup>C</sup> (cm <sup>-1</sup> )	کرب <sup>d</sup> (GHZ)
$\begin{array}{c} Q(2,1)\\ Q(2,1)\\ Q(2,2)\\ Q(3,2)\\ Q(3,2)\\ Q(3,2)\\ Q(3,2)\\ Q(3,2)\\ Q(3,3)\\ Q(4,2)\\ Q(4,2)\\ Q(4,2)\\ Q(4,2)\\ Q(4,2)\\ Q(4,2)\\ Q(5,5)\\ Q(5,3)\\ Q(5,3)\\ Q(5,3)\\ Q(5,3)\\ Q(5,3)\\ Q(5,4)\\ Q(5,5)\\ Q(6,4)\\ Q(5,5)\\ Q(6,4)\\ Q(7,3)\\ Q(5,5)\\ Q(6,4)\\ Q(7,3)\\ Q(8,7)\\ Q(8,7)\\ Q(8,5)\\ Q(9,6)\\ Q(10,7)\\ Q(10,8)\\ Q(10,8)\\ Q(10,8)\\ Q(10,8)\\ Q(10,9)\\ Q(11,7)\\ Q(11,9)\\ Q(12,7)\\ Q(12,10)\\ Q(13,9)\\ Q(14,12)\\ \end{array}$	NP(12) NP(11) NP(12) NP(11) NP(12) 1ØP(38) NP(11) NP(10) 1ØP(36) NP(11) NP(10) NP(12) NP(16) 1ØP(32) 1ØP(32) 1ØP(32) 1ØP(42) 1ØP(30) 1ØP(34) NP(10) NP(16) 1ØP(32) NP(11) NP(24) NP(23) NP(12) 1ØP(40) 1ØP(22) NP(12) NP(20) 1ØP(32) NP(17) 1ØP(32) NP(12) NP(20) NP(12) NP(25)	9866. -16257. -13719. -17388. 8739. 17669. 11605. -14429. -12547. 9321. -16699. -17864. 16486. 13177. -8728. -10239. 13504. -10759. 8567. -12523. -8838. -13210. -13831. 15258. 13275. -14050. 14614. 15763. 12084. 14476. -12553. 9723. 16662. -10046. 15914. 14006. 17537. 14251.	928.94570(-9) 928.94589(8) 928.15899(2) 928.90816(7) 928.90816(7) 928.90811(1) 927.59770(-22) 929.87527(-8) 929.87507(-27) 928.59891(9) 929.79908(-6) 929.79935(21) 928.02073(40) 925.64688(8) 929.45697(-7) 932.66929(63) 922.57276(-6) 935.34494(19) 930.64255(12) 930.64213(-30) 924.67924(27) 924.67918(21) 934.45386(11) 932.49907(1) 929.99712(-22) 918.34064(-35) 918.34069(-30) 929.10408(-21) 925.50004(14) 921.10526(23) 931.32576(30) 923.87291(-5) 923.87361(65) 933.49125(-35) 921.99117(-23) 929.20158(34) 917.45837(-10)	12.18 $38.30$ $36.37$ $39.17$ $13.05$ $5.12$ $9.08$ $35.11$ $34.19$ $10.95$ $36.97$ $39.46$ $6.94$ $6.81$ $25.83$ $34.79$ $1.30$ $28.61$ $9.29$ $34.66$ $30.97$ $27.89$ $29.74$ $2.29$ $12.97$ $40.29$ $2.72$ $4.05$ $7.73$ $8.58$ $35.61$ $5.33$ $3.35$ $30.06$ $2.99$ $6.30$ $3.00$ $6.96$

Table 4-7 (cont.)

Transition	Laser line <sup>a</sup>	Microwave <sup>b</sup> (MHZ)	Two-Photon <sup>C</sup> (cm <sup>-1</sup> )	∆v <sup>d</sup> (GHZ)
R(1,1) R(2,1) R(4,2) R(4,4) R(5,2) R(5,4) R(5,4) R(6,1) R(6,5) R(7,3) R(7,5) R(7,7)	10R(10) 10R(44) 9P(38) 9P(40) 9P(16) 9P(18) 9R(10) 9R(4) 9R(42) 9R(36) 9R(28)	-15751. -15439. 13696. -9298. 9961. -16925. 11422. -11478. 15279. 10655. -16250.	968.61415(-11) 989.13151(-3) 1029.89894(-8) 1027.07202(15) 1050.77355(5) 1048.09625(-1) 1072.26476(17) 1067.15625(4) 1091.53985(-99) 1088.30372(-1) 1082.93674(27)	38.38 37.48 6.99 32.34 9.43 38.52 6.04 33.15 1.82 9.14 40.80

 $^a$  N, 9, or 10 refer to N2O, 9  $\mu$  m band of CO  $_2,$  or 10  $\mu$  m band of CO  $_2$  laser, respectively.

<sup>b</sup> Microwave frequency in MHz. A minus sign indicates that the microwave frequency is subtracted from the laser frequency to obtain the two-photon frequency.

- <sup>C</sup>The numbers in parentheses are observed minus calculated frequencies in multiples of 0.00001 cm<sup>-1</sup>. The parameters for the calculation are in the first column of Table 4-9.
- d Absolute value of the difference between the laser frequency and the frequency of the corresponding one-photon allowed transition.

Table 4-8. Comparison of observed and calculated frequencies of a-a two-photon transitions in the  $v_2$  band of  ${}^{15}NH_2$ .

Transition	Laser Line <sup>a</sup>	Microwave <sup>b</sup> (MHZ)	Two-Photon <sup>C</sup> (cm <sup>-1</sup> )	∆v <sup>d</sup> (GHZ)
P(2,1)	10P(42)	-16285.	922.37108(24)	5.76
Q(6, 4) Q(7, 5)	10P(2) 10P(2)	14966.	959.89096(54) 959.05741(-31)	34.95
Q(7,7)	10P( 4)	17778.	958.39355(-19)	42.33
Q(8,6)	10P( 4)	8645.	958.08890(14)	28.59
Q(8,8)	10P(4)	-14848.	957.30526(3)	10.48
Q(9, 6)	10P(4)	-11091.	95/.43058(251)	<b>6.</b> 46
Q(10, 5)	10P(4) 10P(6)	-13284	957.22014(-0)	5.40
O(11, 8)	10P( 8)	12852	954,97378 (-5)	30.06
Q(13,13)	10P(14)	11358.	949.85818(0)	43.00

 $^aN$ , 9, 10 refer to  $N_2O$ , 9  $\mu m$  band of CO  $_2$ , or 10  $\mu m$  band of CO  $_2$  laser, respectively.

<sup>b</sup>Microwave frequency in MHz. A minus sign indicates that the microwave frequency is subtracted from the laser frequency to obtain the two-photon frequency.

<sup>C</sup>The numbers in parentheses are observed minus calculated frequencies in multiples of 0.00001 cm<sup>-1</sup>. The parameters for the calculation are in the first column of Table 4-10.

<sup>d</sup>Absolute value of the difference between the laser frequency and the frequency of the corresponding one-photon allowed transition. between the s and a inversion levels in the ground state) to the s and a inversion levels in the  $v_2 = 1$  state. Eighty-five  $v_2 = 1$ , s +  $v_2 = 0$ , m" and 27  $v_2 = 1$ , a +  $v_2 = 0$ , m" frequencies were used.

A least squares analysis of s+m" transitions was carried out to obtain a set of vibration-rotation parameters for the m" ground and  $v_2 = 1$ , s excited states; the final results are given in Table (4-9). The standard deviation of the fit is 6.99 MHz, if all of the transitions with K = 3, two transitions with J,K = 7,7, and one transition with J,K = 5,4, which show rather large residuals, are eliminated from the fit. As for  $^{14}NH_3$ , K = 3 transitions were omitted because they are perturbed by a centrifugal distortion effect. For the least squares calculation, the parameters and derivatives used were the same as those in the previous section (Equation (4-7) and (4-8)) except for the following:

$$X_{3} = C' - C''$$

 $\left(\frac{\partial v}{\partial X_{2}}\right) = J'(J'+1) - K^{2}$   $\left(\frac{\partial v}{\partial X_{11}}\right) = -[J''(J''+1) - K^{2}] \qquad (4-11)$ 

The inversion frequencies used for the present calculation are listed in Appendix A. Appendices C and D list all the transitions used in the fitting for  $^{15}NH_3$ . Vibration-

e Ground State m" and the	
ion Parameters of <sup>15</sup> NH <sub>3</sub> in t	c (s) State (cm <sup>-1</sup> ).
ible 4-9. Vibration-Rotati	$v_2 = 1$ Symmetric

	This	Work	Others	
Parameters	Ia	qII	III <sup>C</sup>	Ref.
0 2	928.07757(24)	928.07746(24)	928.076685	σ
B'	10.0489250(656)	10.0489980(238)	10.04892(14)	ч
c'-c"	-0.1387205(150)	-0.1387179(156)	-0.1386925	ð
- D	11.396(26)x10 <sup>-4</sup>	11.421(6)×10 <sup>-4</sup>	11.51(6)x10 <sup>-4</sup>	Ŧ
DJK	-24.444(68)xl0 <sup>-4</sup>	-24.524(12)x10 <sup>-4</sup>	-24.74(14)x10 <sup>-4</sup>	ч
DK-D"	6.2966(68)x10 <sup>-4</sup>	6.2934(78)x10 <sup>-4</sup>	6.30585x10 <sup>-4</sup>	g
H <mark>,</mark>	0.54904(2804)x10 <sup>-6</sup>	0.59550(382)x10 <sup>-6</sup>	0.70(6)x10 <sup>-6</sup>	ч
НЈЈК	-2.2299(880)×10 <sup>-6</sup>	-2.4508(142)x10 <sup>-6</sup>	-2.55(18)x10 <sup>-6</sup>	Ŧ
H <sup>1</sup> JKK	2.95666(8446)x10 <sup>-6</sup>	3.24446(1830)x10 <sup>-6</sup>	3.00(28)×10 <sup>-6</sup>	Ŧ
H'-H" K	-0.84189(670)x10 <sup>-6</sup>	-0.83999(796)x10 <sup>-6</sup>	-0.8371x10 <sup>-6</sup>	g
в"	9.9198705(578)	מ	9.919955(158)	Ð
D" J	8.432(24)x10 <sup>-4</sup>	q	8.4609(640)x10 <sup>-4</sup>	Ø
D''K	-1.5623(64)x10 <sup>-3</sup>	q	-1.57101(1360)x10 <sup>-3</sup>	Ø
	ورافقه منابع والمقاقات والمنازر تناوان المراجع والمتحافظاتين والمحافظاتين ويراجع والمراوي والمحاولا مناريا			

	This Wo	rk	Others	
Parameters	Ia	qII		Ref.
H <sub>J</sub>	2.3178(2726)×10 <sup>-7</sup>	סי	2.802(780)×10 <sup>-7</sup>	υ
H"JJK	-0.8444(862)x10 <sup>-6</sup>	ס	-1.0710(2240)x10 <sup>-6</sup>	Ð
H <sub>JKK</sub>	1.04805(8290)×10 <sup>-6</sup>	g	1.3416(2740)×10 <sup>-6</sup>	U
S.D.	6.99 MHz	8.44 MHz		
<sup>a</sup> From fit of parentheses	frequencies in Appendix are 2 standard errors.	C. All 16 param	eters varied. The numbers	in
<sup>b</sup> <sub>F</sub> rom fit of fixed at val	frequencies in Appendix ues in Column III.	C. First 10 par	ameters varied; last 6 para	ameters
<sup>C</sup> Results from	other studies. Refere	nces in the last	column.	
d Constrained	to the values in Column	III.		
<sup>e</sup> Reference 33				
f <sub>Reference 30</sub>				
<sup>g</sup> Calculated f	rom parameters in Refer	ence 33.		

Continued.

Table 4-9.

rotation parameters by other workers are included in Table 4-9 for comparison. Again, the major difference is observed for the value of the band origin, a difference of  $\sim$ 27 MHz (0.00090 cm<sup>-1</sup>).

In a second fitting the ground state parameters were constrained to those obtained from the laser Stark data,<sup>33</sup> and upper state parameters were calculated. A comparable difference of  $\sim$ 23 MHz (0.00077 cm<sup>-1</sup>) in the band origin was obtained.

The number of experimental frequencies available for transitions from the ground state to the asymmetric excited state is insufficient to allow determination of 16 parameters. Therefore, a fit of these lines was carried out in which the ground state parameters were constrained to those obtained in the fit of s+m" transitions. The resulting upper state parameters are shown in Table (4-10). In Table (4-11) the inversion frequencies in the  $v_2 = 1$ state that can be calculated from our data are shown. In Table (4-12) the difference in frequency for pairs of laser lines obtained from our experimental data are compared with values calculated from the vibration-rotation parameters of  $CO_2^{72}$  or  $N_2O_2^{73}$ 

Parameter	This Work <sup>C</sup>	Others	Ref.
ν <sub>0</sub>	962.514804(412)	962.5140	b
B'	9.8713084(448)	9.87121(8)	a
C'-C"	-0.0690825(368)	-0.0690695	b
D'J	$7.126(14) \times 10^{-4}$	$7.09(6) \times 10^{-4}$	a
D'JK	$-12.766(36) \times 10^{-4}$	$-12.5(2) \times 10^{-4}$	a
D <mark>''</mark> -D"K	$-1.6116(254)\times10^{-4}$	$-1.74(8) \times 10^{-4}$	a
H'J	0.06058(1182)x10 <sup>-6</sup>	0.0692x10 <sup>-6</sup>	a
H'JJK	-0.3069(254)x10 <sup>-6</sup>	0.139x10 <sup>-6</sup>	a
H'JKK	0.45084(6076)x10 <sup>-6</sup>	0.0927x10 <sup>-6</sup>	a
нк-нк	0.24056(2846)x10 <sup>-6</sup>	0.45x10 <sup>-6</sup>	a
S.D.	8.39 MHz		

Table 4-10. Vibration-Rotation Parameters of  ${}^{15}NH_3$  in the  $v_2 = 1$  Asymmetric (a) State cm<sup>-1</sup>.

<sup>a</sup>From Reference 30.

<sup>b</sup>Calculated from parameters of Reference 33.

<sup>C</sup>The upper state parameters obtained by constraining the ground state parameters to those values in Table 4-9. column I.

Table 4-11. Inversion Frequencies of <sup>15</sup>NH<sub>3</sub> in the v<sub>2</sub>=1 State Calculated From Differences in Two-Photon Frequencies.<sup>a</sup>

Transition	vaa	vss	$v_{INV}(0)^{b}$	v <sub>INV</sub> (v <sub>2</sub> ) <sup>c</sup>
Q(6,4)	28776807.03	27864418.96	19984.32	932372.4
Q(7,7)	28731915.81	27658035.54	24553.43	1098433.7
Q(9,6)	28703046.69	27880612.25	17548.34	839982.8
Q(10,8)	28652420.74	27745785.39	19810.62	926446.0
Q(10,8)	28652420.74	27745793.19	19810.62	926438.2

<sup>a</sup>All frequencies in MHz.

<sup>b</sup>Ground state inversion frequency from Reference 46.

 $v_{\rm INV}(v_2) = v_{\rm aa} - v_{\rm ss} + v_{\rm INV}(0)$ .

Table 4-12. Comparison of Differences in Laser Frequencies Obtained from Duplicate Measurements of Two-Photon Frequencies with Differences Calculated From Vibration-Rotation Constants of  $CO_2$  or  $N_2O$ .

Transition <sup>a</sup>	v <sub>l</sub> 1 <sup>-v<sub>l</sub>2<sup>b</sup></sup>	c Δνobs. (MHz)	$\Delta v_{\rm obs.}$ $\Delta v_{\rm calc.}$ (MHz)
SQ(2,1)	NP(11)-NP(12)	26123.	-5.54
SQ(3,2)	NP(11)-NP(12)	26127.	-1.54
SQ(4,2)	NP(10)-NP(11)	26034.	5.88
SQ(5,3)	NP(10)-NP(11)	26020.	-8.13
SQ(8,5)	10P(34)-NP(10)	19326.	-12.51
SΩ(8,7)	NP(16)-10P(40)	3685.	-1.85
SQ(9,9)	NP(23)-NP(24)	27325.	-1.39
SQ(10,8)	NP(16)-10P(40)	3679.	-7.85
SQ(10,9)	NP(20)-NP(21)	27029.	0.95
SQ(11,9)	NP(17)-NP(18)	26708.	-21.01

 $a_{\text{Two-photon transitions of }}^{15}\text{NH}_3$  observed with more than one laser line.

<sup>b</sup>The two laser lines used to determine the two-photon frequency.

 $c_{\Delta\nu_{obs}} = v_{m_2} - v_{m_1}$  where  $v_{m_1}$  and  $v_{m_2}$  are the microwave frequencies of the transitions for the laser lines  $v_{\ell_2}$  and  $v_{\ell_1}$ , respectively.

 $d_{\Delta v_{calc}} = v_{\ell} - v_{\ell}$  calculated from vibration-rotation constants in Reference 72 and 73.

## 4.2.e. <u>Calculation of Ground State B" Constants for</u> <u>14<sub>NH3</sub> and <sup>15</sup><sub>NH3</sub></u>.

The ground state rotational constants B" for <sup>14</sup>NH<sub>3</sub> and  $^{15}$ NH<sub>3</sub> were calculated by Helminger <u>et al</u>.<sup>74</sup> from the millimeter wave frequency of the J = 1 + 0 rotation-inversion transitions. For this calculation, they used  $D_{\rm J}^{"}$  values obtained from conventional infrared spectroscopy. 54,56 We can follow their procedure, but use our values of  $D_T^{"}$  and  $H_{T,T}^{"}$  given in Tables (4-2) and (4-9) for  $H_{3}^{14}$  and  $H_{3}^{15}$ , respectively. Figure (4-4) shows energy-level diagrams for the (J=0, K=0) and (J=1, K=0) levels of  $NH_3$ . As was mentioned previously, for K = 0 one of the inversion components is missing because of nuclear spin statistics.<sup>39</sup> Therefore, to eliminate the contributions from inversion, hypothetical inversion frequencies must be calculated for these levels. These were calculated from the empirical formulas of Schnable <u>et al.</u><sup>70</sup> for  ${}^{14}NH_3$  and of Sasada<sup>46</sup> for  ${}^{15}NH_3$ . The values obtained are shown in Figure (4-4).

The rotational frequencies of the (J,K) = (1,0) + (0,0)transitions are 572112.78 MHz for  ${}^{15}NH_3$  and 572498.15 MHz for  ${}^{14}NH_3$ .<sup>74</sup> To calculate the rotational constants we need to obtain the frequency at which these transitions would occur if there were no inversion splitting. This can be obtained by adding half the sum of the appropriate inversion frequencies, as shown in Figure (4-4). The hypothetical frequencies obtained in this way are



Figure 4-4. Energy-level diagrams for the J = 0 and J = 1, v = 0 states of  $14_{\rm NH_3}$  and  $15_{\rm NH_3}$  showing the observed transitions and the hypothetical levels corresponding to no inverstion (observed frequencies from Reference 74).

596133.49 MHz and 594680.91 MHz for  $^{14}NH_3$  and  $^{15}NH_3$ , respectively.

Now by using the usual symmetric top rotational energy terms Equation (4-1), the frequency of the (J,K) = (J+1,0)+ (J,0) rotational transition is,

$$v = 2B(J+1) - 4D_{J}(J+1)^{3} + H_{JJJ}(J+1)^{3}[(J+2)^{2}-J^{3}]$$
(4-12)

Here, J refers to the quantum number of the lower state, which in this case is J = 0. Therefore,

$$v = 2B - 4D_{J} + 8H_{JJJ}$$
 (4-13)

or

$$B = \frac{v + 4D_{J} - 8H_{JJJ}}{2}$$
(4-14)

By substitution of the values of  $D_J$ ,  $H_{JJJ}$ , and v, we calculate the ground state B" constants of NH<sub>3</sub> to be 298117.107 MHz for <sup>14</sup>NH<sub>3</sub> and 297390.985 MHz for <sup>15</sup>NH<sub>3</sub>. Comparison of these values with those obtained from our fit of the two-photon data (<sup>14</sup>NH<sub>3</sub>: 298117.64±0.63 MHz and <sup>15</sup>NH<sub>3</sub>: 297390.24±0.87 MHz) shows good agreement.

## 4.2.f. Comparison of the Frequency of the (J=1,0+0,0)Rotation-Inversion Transition of NH<sub>3</sub> with the Value From Microwave Spectroscopy

The frequency of the (J,K=1,0+0,0) rotation-inversion transitions can be calculated using our values of the B",  $D_{\rm J}^{\prime\prime}\text{,}$  and  $H_{\rm J,J,J}^{\prime\prime}$  constants in the ground state given in Table (4-2) and (4-9) for  $14_{\rm NH_3}$  and  $15_{\rm NH_3}$ , respectively. For this purpose, B",  $D_{J}$  and  $H_{JJJ}$  have been substituted in Equation (4-13), in order to calculate the frequency of the hypothetical rotational transition (J=1,0+0,0). Next the effect of the inversion splitting is eliminated by subtracting half of the sum of the frequencies of the hypothetical inversion frequencies of the J,K = 1,0 and 0,0 transitions. The calculation of the inversion frequencies J,K = 1,0 and 0,0 are described in the last section. The same procedure was used to calculate the rotation-inversion frequencies from the parameters of Reference 33. The calculated frequencies and the observed submillimeter frequencies of the J = 1  $\leftarrow$  0 transitions for <sup>14</sup>NH<sub>3</sub> and <sup>15</sup>NH<sub>3</sub> are compared in Table 4-13.

#### 4.2.g. Discussion

The  $v_2$  vibration-rotation bands of  ${}^{14}\text{NH}_3$  and  ${}^{15}\text{NH}_3$ have been reinvestigated in this study. Forty-four twophoton transitions in  ${}^{14}\text{NH}_3$  and 60 two-photon transitions

Table 4-13. Comparison of the Calculated Frequency of the J,K = 1,0+0,0 Rotation-Inversion Transition in  ${}^{14}_{NH_3}$  and  ${}^{15}_{NH_3}$  with the Experimental Value.<sup>a</sup>

		Calculat	ed Value
Molecule	Experiment <sup>b</sup>	This Work	Ref. 33
14 <sub>NH</sub> 3	572498.15±0.15	572499.22	572502.07
15 <sub>NH</sub> 3	572112.78±0.1	572111.30	572115.95

<sup>a</sup>All frequencies in MHz.

<sup>b</sup>Reference 74.

in  ${}^{15}\text{NH}_3$  were assigned. The frequencies of the observed two-photon transitions in each case were combined with all of the previous infrared data that had been measured relative to CO<sub>2</sub> or N<sub>2</sub>O laser lines. By means of least-squares analyses of these data molecular parameters in the ground and v<sub>2</sub> = 1 excited states were derived. The parameters are listed in Table (4-2) for  ${}^{14}\text{NH}_3$  and in Tables (4-9) and (4-10) for  ${}^{15}\text{NH}_3$ .

By combining a two-photon frequency with an appropriate ground state or upper state inversion frequency, the frequency corresponding to a one-photon allowed a + s or s + a transition can be obtained. The one-photon frequencies derived in this way for  $^{15}NH_3$  from the results of the present study and inversion frequencies in the ground state (from Reference 46) are compared in Appendix G to similarly derived frequencies from previous two photon work and to one-photon frequencies obtained by CO<sub>2</sub> laser-based, diodelaser measurements. Also, compared in Appendix G are the results of the theoretical calculation by DiLonardo <u>et al</u>.

A similar comparison has been made for  ${}^{14}NH_3$ ; the results appear in Appendix H. For  ${}^{14}NH_3$ , because experimental inversion frequencies in both the ground and the upper state have been reported (43,71) the frequencies of both the a + s and s + a one-photon transitions can be obtained from the frequency of one, two-photon transition. This has been done for the entries in Appendix H. The results of the theoretical calculations for  ${}^{14}NH_3$  by Urban <u>et al</u>. are also included in this appendix.

Comparison of the same transition measured by different methods provides further verification of the ability to measure the frequencies of Doppler-broadened transitions to a precision of  $\pm 0.0002$  cm<sup>-1</sup> by methods based on the frequencies of CO<sub>2</sub> or N<sub>2</sub>O lasers.

Tables (4-3), (4-4), (4-7), and (4-8) and Appendices G and H provide comparisons of observed frequencies with frequencies calculated according to two-different approaches. We have chosen to express the energies by a double power series expansion in J(J+1) and  $K^2$  (Equation 4-1). In this approach the various perturbations and interactions with other states are assumed to lead to corrections to the energy levels that follow this form. This procedure has the advantage of being easily programmed for the rapid calculations of the frequencies by a computer. It is only useful for those levels (J,K) which are not strongly perturbed. For the range of J and K values shown here, the s + a and a + s one-photon frequencies can be calculated to an accuracy of  $\sim 20$  MHz by means of the constants in Table (4-2) and experimental inversion frequencies in the ground state and  $v_2 = 1$  state for  ${}^{14}NH_3$ , and by constants given in Tables (4-9) and (4-10) and inversion frequencies in the ground state for  $15_{\rm NH_2}$ .

The calculated frequencies compared with experimental

values in Appendices G and H were obtained by considering the interaction between the  $v_2$ ,  $2v_2$ ,  $3v_2$ ,  $v_4$ , and  $v_2$  +  $v_4$  levels explicitly. This approach allows a reasonable calculation of the energies of the strongly perturbed states. The advantage of this approach is that the derived rotational constants and centrifugal distortion constants are more easily related to structural properties. The disadvantage of such a calculation is its complexity.

Tables (4-14) and (4-15) show the frequencies of the infrared transitions measured in Michigan State University for  $^{14}NH_3$  and  $^{15}NH_3$ , respectively. Whenever there has been an infrared measurement by other investigators for the same transition, it is included in these tables. These two tables show that the lineshape method of determining the frequency of Doppler broadened infrared-microwave twophoton transitions used in this investigation gives results that are comparable in accuracy to the measurements of saturation dips when the laser has been stabilized by maximizing the power output. This is probably a result of the fact that in either case the error in determination of the microwave frequency is considerably smaller than the fluctuation in the laser frequency. A real test of the two methods will occur when measurements are made with the laser stabilized to a Doppler-free dip in the fluorescence from a CO<sub>2</sub> or N<sub>2</sub>O sample.

Table 4-14	• Freque	encies of th	e IR transi	tions	in $^{14}$ NH <sub>3</sub> .
===============				======	
Transition <sup>a</sup>	Ref. <sup>b</sup>	IR Frequency <sup>C</sup>	Transition <sup>a</sup>	Ref. <sup>b</sup>	IR Frequency <sup>C</sup>
<pre>sP(2,1) sQ(1,1) sQ(1,1) sQ(3,2) sQ(3,2) sQ(3,2) sQ(3,3) sQ(3,3) sQ(3,3) sQ(3,3) sQ(3,3) sQ(5,2) sQ(5,3) sQ(5,3) sQ(5,3) sQ(5,3)</pre>	SC SC F FL SC F F FL SA SC SC F A HK	891.88171 931.62767 931.62746 931.62773 932.09398 932.09452 930.75701 930.75741 930.75654 930.75697 930.75708 934.25216 932.99231 932.99237 932.99228	<pre>SQ(5,5) SQ(5,5) SQ(7,4) SQ(9,5) SR(3,3) SR(5,1) SR(5,2) SR(5,2) SR(5,2) SR(5,3) SR(5,3) SR(5,3) SR(5,4) SR(5,4) SR(5,5) SR(5,5)</pre>	SC FFL SC SC SC SC FC FC FL FL FL	928.75434 928.75393 928.75432 934.23571 935.70667 1011.20350 1054.91248 1054.25276 1054.25109 1053.13049 1053.13044 1051.51210 1051.51206 1049.34639 1049.34631
aQ(1,1)aQ(1,1)aQ(1,1)aQ(3,3)aQ(3,3)aQ(3,3)aQ(3,3)aQ(4,3)aQ(4,3)aQ(4,4)aQ(4,4)aQ(4,4)aQ(4,4)aQ(4,4)aQ(4,4)aQ(4,4)aQ(4,4)aQ(5,5)aQ(5,5)aQ(5,5)aQ(5,5)aQ(5,5)aQ(6,4)aQ(6,4)aQ(6,6)	SC SC J SC SC SC F SC SC SC SC SC SC SC SC SC SC SC SC SC	967.99798 967.99890 967.99785 967.34610 967.34645 967.34653 967.34502 966.90520 966.90531 966.81505 966.81484 966.81478 966.81477 966.81477 966.15122 966.15053 966.15083 966.15118 965.65207 965.65208 965.65211	aQ(7,6) aQ(7,6) aQ(7,7) aQ(7,7) aQ(7,7) aQ(8,5) aQ(8,5) aQ(8,5) aQ(8,6) aQ(8,6) aQ(8,6) aQ(8,6) aQ(8,7) aQ(8,7) aQ(8,7) aQ(8,7) aQ(8,7) aQ(8,7) aQ(9,4) aQ(9,5) aQ(9,7) aQ(9,7) aQ(11,9)	F SC SC JC JC FS F JC F SC S JC SC S S S S S S S S S S S S S S	964.59561 964.42430 964.42442 964.42442 964.42215 964.04123 964.04152 964.04152 964.04115 963.79644 963.79658 963.79678 963.55855 963.55855 963.55855 963.55853 963.55853 963.55853 963.55853 963.55853 963.55853 963.55853 963.55853 963.55853 963.55853 963.55853 963.55853 963.55853 963.67042 960.01989

Table 4-14	(cont.)					
Transition <sup>a</sup>	Ref. <sup>b</sup>	IR Frequency <sup>C</sup>	Transition <sup>a</sup>	Ref <sup>b</sup>	IR Frequency <sup>C</sup>	
aQ(6,6) aQ(6,6) aQ(7,3) aQ(7,6) aQ(7,6)	J JL SC SC SC	965.35422 965.35415 965.13796 964.59604 964.59597	aQ(11,9) aR(4,2) aR(6,1) aR(6,5) aR(6,5)	FL SC SC SC J	960.01978 1065.58180 1103.48587 1103.43445 1103.43421	
<sup>a</sup> V(J",K) where V = P, Q, or R for ∆J = -1, Ø, or +1, res- pectively. s and a represent transitions from ground state s to upper state a and from ground state a to upper state s ,respectively.						
<sup>b</sup> J, Ref. 29 diode lase <sup>c</sup> All frequen	by Jones r measure ncies are	s; F, Ref. ements by Sa e in cm <sup>-1</sup> .	28 by Freund attler, Ref.	d et al 68; SC	.; SA, C, this work.	

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Table 4-15	. Freq	uencies of	the IR trans	itions	in <sup>15</sup> NH <sub>3</sub> .
Transition <sup>a</sup>	Ref. <sup>b</sup>	IR Frequency	C <sup>Transition<sup>a</sup></sup>	Ref. <sup>b</sup>	IR Frequency <sup>C</sup>
<pre>SP(2,1) SP(2,1) SQ(6,4) SQ(7,5) SQ(7,7) SQ(8,6) SQ(8,8)</pre>	SC J SC SC SC SC SC	923.10640 923.10657 960.55756 959.71764 959.21256 958.74609 958.14996	<pre>SQ(8,8) SQ(9,6) SQ(10,5) SQ(10,8) SQ(10,8) SQ(10,8) SQ(11,8) SQ(13,13)</pre>	D SC SC SC SA SC SC	958.15001 958.01593 957.68709 956.40269 956.39927 955.54763 950.91534
aQ(2,1) aQ(2,2) aQ(3,2) aQ(3,2) aQ(3,2) aQ(3,3) aQ(3,3) aQ(4,2) aQ(4,2) aQ(4,2) aQ(4,2) aQ(4,2) aQ(4,2) aQ(5,3) aQ(5,3) aQ(5,3) aQ(5,3) aQ(5,3) aQ(5,4) aQ(7,7) aQ(7,7) aQ(7,7)	SC SC SC SC SC SC SC SC SC SC SC SC SC S	928.21039 928.21057 927.40348 928.18153 928.18153 928.18148 926.83752 926.83793 926.83771 929.18536 929.18536 929.18536 929.18536 929.12287 929.12287 929.12241 929.12287 929.12241 929.12287 929.12274 927.30030 927.29996 927.29820 924.86560 928.79037 928.79018 932.09898 921.75374 921.75469	aQ(9,5) aQ(9,6) aQ(9,9) aQ(10,7) aQ(10,7) aQ(10,8) aQ(10,9) aQ(10,9) aQ(10,9) aQ(10,9) aQ(11,7) aQ(11,7) aQ(11,7) aQ(11,7) aQ(11,9) aQ(11,9) aQ(11,9) aQ(12,7) aQ(12,7) aQ(12,7) aQ(12,7) aQ(12,7) aQ(12,7) aQ(12,7) aQ(12,7) aQ(12,10) aQ(13,9) aQ(14,12) aR(1,1) aR(1,1) aR(1,1) aR(1,1) aR(2,1) aR(4,4) aR(5,2) aR(5,4)	SC SC SC SC SC SC SC SC SC SC SC SC SC S	931.96844 929.41177 917.46528 917.46532 928.52593 924.83897 924.83923 920.33626 920.33622 920.33613 930.82348 930.82286 923.20546 923.20546 923.20502 933.06019 933.06062 923.20502 933.06062 921.31381 928.71667 916.75101 967.85946 967.85943 988.39620 1029.20904 1026.30329 1050.12685
aQ(8,2) aQ(8,2) aQ(8,5) aQ(8,5)	SA SC SC	934.85127 934.85121 930.04696 930.04654	aR(6,1) aR(6,5) aR(7,3)	SC SA SC SC	1071.68213 1071.68178 1066.43348 1090.96955

Table 4-15 (cont.) Transition<sup>a</sup> Ref.<sup>b</sup> IR Transition<sup>a</sup> Ref.<sup>b</sup> IR Frequency<sup>C</sup> Frequency<sup>C</sup> aQ(8,5) J 930.04671 aR(7,3) J 1090.96971 aQ(8,7) SC 923.94090 aR(7,5) SC 1087.64349 aQ(8,7) SC 923.94084 aR(7,7) SC 1082.11772 aQ(9,4) SC 933.96415 aR(7,7) SA 1082.11719 <sup>a</sup>V(J",K) where V = P, Q, or R for  $\Delta J = -1$ , Ø, or +1 ,respectively. s and a represent transitions from ground state s to upper state a and from ground state a to upper state s ,respectively. <sup>b</sup>J, Ref. 30 by H. Jones; F, Ref. 28 by Freund et al.;FL, Lamb-dip measurements, Ref. 28; SA, diode laser measurements

<sup>C</sup>All frequencies are in cm<sup>-1</sup>.

by Sattler, Ref. 68; SC, this work.

# 4.3. The $v_3$ Bands of ${}^{12}CH_3F$ and ${}^{13}CH_3F$

### 4.3.a. Introduction

Methyl fluoride is a prolate symmetric top with  $C_{3v}$ symmetry. This molecule possesses six fundamental vibrational modes, three totally symmetric and three doubly degenerate, all infrared active.

The frequencies of rotational transitions in  ${}^{12}$ CH<sub>3</sub>F have been measured by Gilliam <u>et al</u>.,<sup>75</sup> Johnson <u>et al</u>.<sup>69</sup> Orville <u>et al</u>.,<sup>76</sup> Winton and Gordy,<sup>77</sup> Sullivan and Frenkel,<sup>78</sup> Tanaka and Hirota,<sup>79</sup> and Hirota <u>et al</u>.<sup>80</sup>. The most precise frequencies were obtained by Lamb dip procedures by Winton and Gordy;<sup>77</sup> Sullivan and Frenkel measured several high J transitions;<sup>78</sup> and Tanaka and Hirota<sup>79</sup> and Hirota <u>et al</u>.<sup>80</sup> measured the J = 1 + 0 transition in excited vibrational states. The frequency of the J = 1 + 0 transition in  ${}^{13}$ CH<sub>3</sub>F was originally measured by Gilliam <u>et al</u>.<sup>75</sup> but their value has been corrected by Tanaka and Hirota,<sup>79</sup> who also measured the frequencies of this transition in the  $v_3$  and  $v_6$  excited states.

A detailed study of the infrared spectrum of  $CH_3F$  was carried out by Yates and Nielsen.<sup>81</sup> Andersen and coworkers reported and analyzed all of the perpendicular fundamentals and discussed the structure of  $CH_3F$ .<sup>82</sup> Smith and Mills<sup>83</sup> re-analyzed the rotational structure of some of the bands, particularly the two fundamentals at 1049 cm<sup>-1</sup> (parallel  $v_3$  band) and 1182 cm<sup>-1</sup> (perpendicular  $v_6$  band). Similarly, Duncan <u>et al</u>. studied the infrared spectrum of  ${}^{13}CH_3F$ .<sup>84</sup> All of this work was performed with conventional grating spectrometers.

The  $v_3$  band of  $CH_3F$ , corresponding to the C-F stretching vibration, lies close to the 9.55  $\mu$ m region of  $CO_2$ laser lines. Therefore, this molecule, like  $NH_3$ , has been used for various laser spectroscopic experiments.

In an optical double-resonance experiment, Brewer determined accurate values for dipole moments in the ground and  $v_3$  states.<sup>85</sup> In this experiment two CO<sub>2</sub> lasers were used as sources of radiation. Chang and Bridges reported the observation of laser action on six rotational transitions in a sample of CH<sub>3</sub>F that was optically pumped by a CO<sub>2</sub> laser.<sup>86</sup> This was the first optically pumped far infrared or submillimeter laser. Several additional optically pumped laser lines were observed later by Chang et al.<sup>87,88</sup>

Laser Stark spectroscopy of the  $v_3$  band of  $CH_3F$  was carried out by Freund <u>et al</u>. by using  $CO_2$  laser lines near 9.4 µm. In this investigation, the dipole moment and vibration-rotation parameters of the  $v_3$  state were determined.<sup>89,90</sup> Doppler-free, two-photon absorption in the  $v_3$  band of  $CH_3F$  has been observed, in which two fixed-frequency infrared radiation sources ( $CO_2$  lasers), in combination with molecular Stark tuning were used.<sup>91</sup> The ground state rotational constant  $A_0$  and the centrifugal distortion constant  $D_K^0$  of  $CH_3F$  were determined by Graner from the frequencies of perturbation-allowed infrared transitions<sup>92</sup> measured with a tunable diode laser. Infrared-radio frequency two-photon and multiphoton Lamb dips have been observed for methylfluoride in the cavity of a  $CO_2$  laser oscillating in the 9.4  $\mu$ m band.<sup>93</sup>

Sattler and Simonis studied the  $\nu_3$  band of  $^{12}\text{CH}_3\text{F}$  by diode laser spectroscopy.<sup>94</sup> They measured frequencies by means of a Ge etalon and therefore only their frequency differences are very precise. Magerl et al.95 measured the frequencies of numerous high J transitions in the  $v_3$  band of <sup>12</sup>CH<sub>3</sub>F by a tunable laser sideband technique. Herlemont et al.96 measured the frequencies of more high J transitions in this band by using heterodyne methods with a diode laser and a waveguide laser. Blumburg et al. 97 used a tunable submillimeter wave source to measure the frequencies of rotational transitions in the  $v_3 = 1$  state of  $^{12}$ CH $_3$ F, but reported only the resulting D $_J$  and D $_{JK}$  values and not the frequencies themselves. Freund <u>et</u> <u>al</u>.  $^{89,90}$ Arimondo and Inguscio, 98 Magerl et al. 95 and Herlemont et <u>al</u>.<sup>96</sup> have all reported the results of fitting the  $v_3$  band transitions to rotational and centrifugal distortion constants.

The  $v_3$  band of methyl fluoride was studied at Michigan State University with the same infrared-microwave twophoton spectrometer that was used for NH<sub>3</sub>. Two-photon transitions were assigned for both species, <sup>12</sup>CH<sub>3</sub>F and <sup>13</sup>CH<sub>3</sub>F. From a least squares analysis of the two-photon

data obtained in this study and from the earlier measurements combined with the data available from microwave, FIR, laser-Stark, and laser infrared investigations of  $^{12}$ CH<sub>3</sub>F, rotational and centrifugal distortion constants in the ground and  $v_3 = 1$  excited states were determined. The molecular constants of the ground and the  $v_3$  fundamental mode were obtained for  $^{13}$ CH<sub>3</sub>F as well. For this fit the two-photon data, the zero-field frequencies obtained from a laser-Stark experiment, and the frequencies of the rotational transitions (J = 1 + 0) in the ground and  $v_3$  states were used.

## 4.3.b. $\frac{12_{CH_3F}}{2}$

Methyl fluoride is an example of a symmetric top molecule in which the inversion splitting of the levels is not resolvable. Therefore, all of the levels with  $K \neq 0$  have double parity and there is no need for a third level to observe a two-photon transition.

A pair of ground and  $v_3$  vibration-rotation levels of  $CH_3F$  are shown in Figure (2-2). In this figure  $v_m$  and  $v_\ell$  are the frequencies of the microwave and laser satisfying the two-photon condition, respectively. The offset frequency - the frequency difference between the laser and the molecular transition - is equal to  $v_m$  in this case.

The study of the  $v_3$  vibrational band of  ${}^{12}CH_3F$  by twophoton spectroscopy was begun by calculating the frequencies of the possible two-photon transitions. For this calculation, the ground state rotational parameters, B", D<sub>J</sub>", and D<sub>JK</sub>, obtained by analysis of the frequencies of millimeterwave Doppler-free spectra,<sup>77</sup> and the vibration-rotation parameters of the  $v_3 = 1$  state, reported in a laser Stark study of CH<sub>3</sub>F,<sup>89</sup> were used.

Since the  $v_3$  band of  $CH_3F$  is a parallel vibrational band, the selection rule for K is  $\Delta K = 0$ . The frequency of a transition from the ground to the  $v_3$  excited state can be obtained by applying the selection rules to Equation (4-4). It should be noted that for  $CH_3F$ ,  $v_{RV}$  in Equation (4-4) corresponds to the frequency of the one-photon as well as to the two-photon transition, and  $v_0$  in the equation is the energy difference between the J' = K' = 0 and J" = K" = 0 states. The primes and double primes mark the levels for the upper and lower states, respectively.

By using eight  $CO_2$  laser lines in the 9.4 µm region, 24 two-photon transitions were observed for  ${}^{12}CH_3F$  in the available microwave range of 8 - 18 GHz; Table (4-16) lists the two-photon transitions and their assignments. The  ${}^{12}CH_3F$  sample was used at a pressure of  $\sim$ l torr.

Figure (4-5) shows a trace of the Q branch two-photon transitions (J = 6, K = 3,4,5,6). These transitions were observed by using the 9P(18) laser line. Since microwave transition moments appear as a difference in Equation (2-48), we were able to see Q branch transitions of  $CH_3F$ 

Table 4-16. Comparison of observed and calculated frequencies of two-photon transitions in the  $v_2$  band of  $^{12}$ CH<sub>2</sub>F.

Transition <sup>a</sup>	Laser Line <sup>b</sup>	Microwave(MHz) <sup>C</sup>	Two-Photon(cm <sup>-1</sup> ) <sup>d</sup>
P(5,2)	9P(28)	15145.	1039.87450(24)
P(5,3)	9P(28)	15385.	1039.88250(20)
P(5,4)	9P(28)	15727.	1039.89391(7)
P(4,1)	9P(26)	11508.	1041.66294(1)
P(4,2)	9P(26)	11651.	1041.66771(6)
P(4,3)	9P(26)	11891.	1041.67571(6)
P(3,1)	9P(24)	8111.	1043.43379(-17)
P(3,2)	9P(24)	8261.	1043.43880(16)
Q(4,2)	9P(18)	-8103.	1048.39052(-9)
Q(5,5)	9P(18)	-10551.	1048.30887(-2)
Q(5,4)	9P(18)	-10965.	1048.29506(-6)
Q(5 <b>,</b> 3)	9P(18)	<u>-</u> 11276.	1048.28468(-11)
Q(6,6)	9P(18)	-14116.	1048.18995(12)
Q(6,5)	9P(18)	-14630.	1048.17281(18)
Q(6,4)	9P(18)	-15036.	1048.15926(10)
Q(6,3)	9P(18)	-15333.	1048.14936(30)
R(2,2)	9P(12)	-9962.	1053.59121(-1)
R(2,1)	9P(12)	-10080.	1053.58727(16)
R(3,2)	9P(10)	-12613.	1055.20435(37)
R(4,4)	9P( 8)	-14701.	1056.80979(8)
R(4,3)	9P( 8)	-14981.	1056.80045(4)
R(4,2)	9P( 8)	-15177.	1056.79391(-5)
R(5,3)	9P( 6)	-17430.	1058.36731(4)
R(5,4)	9P( 6)	-17161.	1058.37629(14)

 $^{a}V(J",K)$  where V = P, Q, or R for  $\Delta J = -1$ , Ø, or +1, respectively.

<sup>b</sup>All the laser lines are in the 9  $\mu$  m region.

<sup>C</sup>Microwave frequency in MHz. A minus sign indicates that the microwave frequency is subtracted from the laser frequency to obtain the two-photon frequency.

<sup>d</sup>The numbers in parentheses are observed minus calculated frequencies in multiples of 0.00001 cm<sup>-1</sup>. The parameters for the calculation are given in Table 4-17.

```
Figure 4-5. Trace of the {}^QQ(6,K), (K = 6,5,4,3) two-
photon transitions in {}^{12}CH_3F. The P(18)
CO_2 laser line in the 9.5 µm region was
used with a microwave sweep from 13900 -
15600 MHz to record this spectrum. The
K values are given at the top of each
transition.
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only when the electric field of the laser and microwave radiation were perpendicular to each other, in which case  $\Delta M = \pm 1$ .

Figure (4-5) shows that for the same J quantum number, transitions with larger K quantum numbers have higher intensity. Another feature of this spectrum is that the transitions involving rotational levels with K = 3n show higher intensity. This higher intensity is associated with the fact that the statistical weight of levels with K = 3n is twice that of levels for which K is not a multiple of three.<sup>39</sup>

To obtain a set of vibration-rotation parameters for  ${}^{12}$ CH<sub>3</sub>F, the two-photon frequencies observed in this study (Table 4-16), the previous two-photon data,<sup>89</sup> the zero field frequencies determined in a laser Stark study<sup>89,90</sup> of the v<sub>3</sub> band of  ${}^{12}$ CH<sub>3</sub>F, the frequencies of the rotational transitions in the ground and v<sub>3</sub> = 1 states,<sup>77,78-80</sup> the rotation-vibration transition P(32,3),<sup>88</sup> the FIR transitions in the ground and v<sub>3</sub> = 1 states,<sup>98</sup> the diode laser and wave guide laser measurements,<sup>96</sup> and the transitions observed with a tunable sideband laser,<sup>95</sup> were combined. The transitions were given weights proportional to the inverse of the square of their reported uncertainties and a simultaneous least squares fitting of the weighted data was carried out. A total of 172 frequencies were used as input data for the least squares fitting; they are given

in Appendix E. The resulting vibration-rotation parameters are given in Table (4-17).

4.3.c.  $\frac{13_{CH_3F}}{2}$ 

Equation (4-4) and the vibration-rotation parameters of the ground state and  $v_3 = 1$  state of  ${}^{13}\text{CH}_3\text{F}$  given in Reference 89 provided the means by which the frequencies of the two-photon transitions of the  $v_3$  band of  ${}^{13}\text{CH}_3\text{F}$  were first calculated.

In this investigation three  $CO_2$  laser lines were used to detect fourteen two-photon transitions in the 9  $\mu$ m region. The frequencies and assignments of the observed two-photon transitions are given in Table (4-18). The pressure of the <sup>13</sup>CH<sub>3</sub>F sample was approximately 1 torr.

The molecular parameters for the ground state and  $v_3$ = 1 excited state of <sup>13</sup>CH<sub>3</sub>F were obtained from a least squares analysis of a combination of two-photon data obtained in this work and by a previous study<sup>89</sup> with zerofield frequencies from a laser Stark study of the  $v_3$ band,<sup>89,90</sup> and with the microwave frequencies of the J = 1 + 0 transitions.<sup>79</sup> The total number of transitions was 44. Since this number was not sufficient to determine all of the 16 parameters in the ground and excited states, the values of the sextic centrifugal distortion constants (H's) were constrained to zero. As a result, 9 parameters $v_0$ , B', [(A'-A")-(B'-B")], D'\_J, D'\_{JK}, (D'\_K-D'\_K), B", D''\_J, and D''\_{JK} -

Parameter <sup>a</sup>	Ground State <sup>b</sup>	$v_3 = 1^b$	
v <sub>0</sub>	0	31436558.6(18)	MHz
В	25536.1500(12)	25197.563(18)	MHz
ΔΑ-ΔΒ	0	44.109(218)	MHz
$D_{J}$	60.26(6)	57.43(20)	KHz
D <sub>JK</sub>	439.47(20)	518.22(222)	KHz
DK-DK	0	-101.35(255)	KHz
н <sub>Ј</sub>	1.2(7)	1.4(10)	Hz
<sup>H</sup> jjk	-9.6(90)	15.6(112)	Hz
<sup>н</sup> јкк	46.3(330)	-119.0(332)	Hz
HK-HK	0	106.3(145)	Hz

Table 4-17. Molecular Parameters of  ${}^{12}CH_3F$  in the Ground State and  $v_3 = 1$  Excited State.

Standard Deviation<sup>C</sup> 5.71 MHz

<sup>a</sup>Prime and double primes refer to the upper and lower state, respectively.

<sup>b</sup>From fit of frequencies in Appendix E. The numbers in parentheses are 2 standard errors in multiples of the last digit in the parameter.

<sup>C</sup>Standard deviation is for observations of unit weight.

Transition <sup>a</sup>	Laser Line <sup>b</sup>	Microwave(MHz) <sup>C</sup>	Two-Photon(cm <sup>-1</sup> ) <sup>d</sup>
P(4,3)	9P(46)	-9461.	1020.74133(9)
P(4,2)	9P(46)	-9638.	1020.73542(3)
Q(6,6)	9P(40)	-8993.	1027.08220(-14)
Q(6,5)	9P(40)	-9358.	1027.07002(-9)
Q(6,4)	9P(40)	-9646.	1027.06042(-10)
Q(6,3)	9P(40)	-9862.	1027.05321(-11)
Q(7,7)	9P(40)	-13053.	1026.94677(2)
Q(7 <b>,</b> 6)	9P(40)	-13500.	1026.93186(-4)
Q(7 <b>,</b> 5)	9P(40)	-13855.	1026.92002(7)
Q(7,4)	9P(40)	-14139.	1026.91055(-4)
Q(7 <b>,</b> 3)	9P(40)	-14349.	1026.90354(-2)
Q(8,8)	9P(40)	-17685.	1026.79226(8)
R(3,2)	9P(34)	12870.	1033.91730(5)
R(3,3)	9P(34)	13014.	1033.92210(22)

Table 4-18. Comparison of observed and calculated frequencies of two-photon transitions in the  $v_3$  band of  $^{13}CH_3F$ .

<sup>a</sup> V(J',K) where V = P, Q, or R for  $\Delta J = -1$ , Ø, or +1, respectively.

 $^{b}$  All the laser lines are in the 9  $_{\mu}\text{m}$  region.

- <sup>C</sup> Microwave frequency in MHz. A minus sign indicates that the microwave frequency is subtracted from the laser frequency to obtain the two-photon frequency.
- <sup>d</sup> The numbers in parentheses are observed minus calculated frequencies in multiples of 0.00001 cm-1. The parameters for the calculation are given in Table 4-19.

were determined. The results are shown in Table (4-19).

Figure (4-6) shows two-photon spectra of the Q type transitions J = 6, K = 6,5,4,3 and possibly K = 2. This spectrum was recorded in the X band microwave region (8700 - 10100 MHz) with the P(40) CO<sub>2</sub> laser line in the 9  $\mu$ m range. In order to observe this spectrum, the electric field of the laser and the microwave radiation must be perpendicular to each other. Higher intensity of the transitions with larger K (for the same J) and with K = 3n is confirmed in Figure (4-6).

### 4.3.d. Discussion

The  $v_3$  vibration-rotation bands of  ${}^{12}\text{CH}_3\text{F}$  and  ${}^{13}\text{CH}_3\text{F}$ have been studied in this experiment. Twenty-four twophoton transitions in  ${}^{12}\text{CH}_3\text{F}$  and fourteen two-photon transitions in  ${}^{13}\text{CH}_3\text{F}$  were assigned.

Even though the intensity of the spectra for the double parity levels in symmetric top molecules without inversion are inversely proportional to the square of the microwave frequency, transitions have been observed with microwave frequencies up to 17 GHz. Considering the fact that the lasers used in this investigation were not particularly high power ( $\sim$ l watt at the sample cell), we can expect that vibrational bands which are considerably weaker than the  $v_3$  band of CH<sub>3</sub>F will be suitable for study, provided that they have close coincidences with the laser lines.

1Hz
1Hz
AH z
KHz
ΚHz
KHz

Table 4-19. Molecular Parameters of  ${}^{13}CH_3F$  in the Ground State and  $v_3 = 1$  Excited State.

Standard Deviation<sup>C</sup> 4.46 MHz

<sup>a</sup>Prime and double primes represent upper and lower state parameters, respectively.

<sup>b</sup>From fit of frequencies in Appendix F. The numbers in parentheses are 2 standard errors.

<sup>C</sup>Standard deviation is for observations of unit weight.
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Figure 4-6. Trace of the {}^{Q}Q(6,K), (K = 6,5,4,3,2) two-
photon transitions in {}^{13}CH_{3}F. The P(40) CO<sub>2</sub>
laser line in the 9.5 µm region was used with
a microwave sweep from 8700 - 10100 MHz to
record this spectrum. The K value is given
at the top of each transition.
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Unlike symmetric tops with inversion or asymmetric tops, the selection rules for two-photon transitions in symmetric tops without inversion are the same as the infrared selection rules. Therefore, two-photon spectra of symmetric top molecules without inversion are directly comparable to infrared spectra.

A comparison of two-photon frequencies and zero-field frequencies derived from laser Stark spectra is shown in Table (4-20). The agreement is seen to be excellent; in only three cases are the differences greater than the expected uncertainty of ±6 MHz.

Comparison of the observed and calculated frequencies, given in Tables 4-16 and 4-18, also shows very good agreement.

Transition	<sup>∨</sup> TP	$^{ u}$ LS
	13 <sub>CH</sub>	I <sub>2</sub> F
P(4,2)	30600878.19	30600876.87
P(4,3)	30601055.19	30601054.22
R(3,2)	30996060.75	30996058.98
R(3,3)	30996204.75	30996199.53
	12 <sub>CH</sub>	<sup>I</sup> 3 <sup>F</sup>
P(3,1)	31281358.15	31281365.56
P(3,2)	31281508.15	31281506.76
P(4,2)	31228412.30	31228410.22
P(4,3)	31228652.30	31228650.06
P(5,3)	31174893.16	31174887.67
P(5,4)	31175235.16	31175234.23
R(2,1)	31585751.80	31585745.44
R(2,2)	31585869.80	31585871.36
R(3,2)	31634230.44	31634218.59
R(4,3)	31682080.48	31682068.46
R(4,4)	31682360.48	31682349.37

Table 4-20. Comparison of Two-Photon Frequencies  $(v_{TP})^a$ and Zero-Field Frequencies Derived from Laser Stark Spectra  $(v_{LS})^b$ .

<sup>a</sup>This work

<sup>b</sup>From References 89 and 90.

<sup>C</sup>All transitions are in MHz.

#### CHAPTER V

### MICROWAVE SPECTRUM OF 3-METHYL-1-BUTENE

### 5.1. Introduction

During the past several years there has been considerable interest in the characterization and comparison of the potential functions for the internal rotation of groups attached to the cyclopropane ring, to the ethylene oxide ring, and to the isopropyl group. Among the molecules in this class are those in which the attached atom is a double-bonded carbon atom such as the carbon atom in an aldehyde or vinyl group. The internal rotation in these molecules is of interest because of the possibility of conjugation between the attached group and the cyclopropyl or ethylene oxide ring. The corresponding molecules in which the same group is attached to an isopropyl group have been studied for comparison. The earliest comparison of this type followed the determination by electron diffraction of the structures of cyclopropanecarboxaldehyde99 and isopropylcarboxaldehyde.<sup>100</sup> It was shown that isopropylcarboxaldehyde occurs in conformations with the CO bond eclipsing either a CC bond or a CH bond in the isopropyl group. These conformations are consistent with

those found in CH<sub>2</sub>COX compounds<sup>101</sup> and most RCH<sub>2</sub>COX molecules.<sup>102</sup> By contrast, cyclopropylcarboxaldehyde was found<sup>99</sup> to occur as an almost 50-50 mixture of conformers with the oxygen atom cis and trans to the ring, and this result was later confirmed by microwave spectroscopy.<sup>103</sup> Since that time cyclopropylcarboxylic acid chloride, <sup>104,105</sup> cyclopropylmethylketone, <sup>104,106</sup> and cyclopropylcarboxylic acid fluoride <sup>107</sup> have all been shown to occur with cis and trans conformers, and therefore have a torsional potential which is dominated by a  $\cos 2\alpha$  term. On the other hand, an electron diffraction investigation of vinylcyclopropane<sup>108</sup> was interpreted in terms of species with the vinyl group trans to the ring and rotated approximately 120° from the trans configuration. A microwave study<sup>109</sup> confirmed only the trans conformer; no transitions from a second conformer were found. In the present work the microwave spectrum of 3-methyl-1-butene was studied and transitions assigned to species with the vinyl group eclipsing the CH bond of the isopropyl group (referred to here as the "trans" configuration) and with the vinyl group rotated approximately 120° from the trans configuration (the "gauche" configuration). The  $v = 0 \rightarrow 1$  torsional excitation energies and the ground state energy difference of the two species have been evaluated by relative intensity measurements and used to estimate the first four coefficients in the torsional potential function.

#### 5.2. <u>3-Methyl-l-Butene</u>

The study of the microwave spectrum of 3-methyl-1-butene in the 18-40 GHz region was begun by R.A. Creswell and M. Pagitsas.<sup>110</sup> The a-type transitions were assigned to species with the vinyl group eclipsing the CH bond of the isopropyl group (referred to here as the "trans" configuration) and with the vinyl group rotated approximately 120° from the trans configuration (the "gauche" configuration). No b or c type transitions could be assigned for either species, presumably due to the small  $\mu_b$  or  $\mu_c$  components of the dipole moment. Figure (5-1) is a projection of trans 3methyl-1-butene in its ac plane of symmetry.

The transitions for each of the species were accompanied by a single intense series of satellite lines, which have been assigned to rotational transitions in the excited states of the torsional motion of the vinyl group relative to the isopropyl group.

### 5.2.a. Dipole Moment

The Stark effects of several transitions for trans-3methyl-1-butene were studied and combined with the results obtained by Creswell and Pagitsas for gauche and trans conformers in order to determine dipole moments for the two species. In each case the slopes of plots of the observed frequencies vs. the square of the field  $\varepsilon^2$  were fit by least squares to



Figure 5-1. Projection of trans 3-methyl-l-butene in its ac plane of symmetry. The angle  $\alpha$  measures internal rotation about the indicated CC bond.

the expression

$$\frac{dv}{d\epsilon^2} = \sum_{g} (\Delta A_g + \Delta B_g M^2) \mu_g^2$$
(5-1)

which contains the squares of the components of the dipole moment,  $\mu_{\mathbf{g}},$  as adjustable parameters, and in each case the result was that  $\mu_b^2$  was found to be a small negative value. For the trans species this is presumably because  $\mu_{\rm b}$  = 0 by symmetry and the negative value of  $\mu_{\rm b}^2$  was a result of experimental error. In the gauche species, however, it is expected that  $\mu_{h} \neq 0$ , and therefore the negative value of  $\mu_{b}^{2}$  is taken to mean that  $\mu_{b}$  is very small. Thus, for each species the fitting of the Stark slopes was repeated with the assumption that  $\mu_{\mathbf{b}} = \mathbf{0}$ . The results of the fittings, including comparisons of observed and calculated Stark slopes, are shown in Tables (5-1) and (5-2). The dipole moments for the trans conformer are  $\mu_{a}$  = 0.312 ±0.003 D,  $\mu_{\rm b}$  = 0 (assumed),  $\mu_{\rm c}$  = 0.071±0.042 D, and  $\mu_{\rm T}$  = 0.320±0.010 D; for the gauche conformer, they are  $\mu_{a}$  = 0.367±0.004 D,  $\mu_b \simeq$  0,  $\mu_c$  = 0.154±0.006 D and  $\mu_T$  = 0.398 ±0.004 D. Here,  $\mu_T^2 = \mu_a^2 + \mu_b^2 + \mu_c^2$  and  $\mu_T$  is the total dipole moment.

The total dipole moments of several compounds that contain a vinyl group were recently compared.<sup>109</sup> If the present species is included in that comparison, it is found that the total dipole moments of the two conformers

Transition	М	$(dv/d\epsilon^2)^a_{obs}$	$(dv/d\epsilon^2)^a_{calc}$
$4_{23} + 3_{22}$	1	1.09	1.10
	2	4.16	4.16 <sup>b</sup>
$4_{22} + 3_{21}$	1	-1.04	-1.05
	2	-4.08	-4.08 <sup>b</sup>
<sup>6</sup> 25 <sup>← 5</sup> 24	2	0.083	0.086
	3	0.196	0.197
	4	0.353	0.353
	5	0.556	0.553
<sup>6</sup> 24 <sup>+ 5</sup> 23	2	-0.080	-0.083
	3	-0.182	-0.183
	4	-0.318	-0.322
	5	-0.509	-0.500
	μ <sub>a</sub> =	0.312±0.003 D	
	μ <sub>b</sub> =	0 (Assumed)	
	μ <sub>c</sub> =	0.071±0.042 D	
	μ <sub>T</sub> =	0.320±0.010 D	

Table 5-1. Stark Coefficients and Dipole Moments for Trans 3-methyl-l-butene.

<sup>a</sup>Units are MHz/(V/cm)<sup>2</sup>.

<sup>b</sup>These slopes were calculated from frequencies obtained by direct diagonalization of the energy matrix. The other slopes were obtained by second-order perturbation.

Transition	М	$(dv/d\epsilon^2)^{a}_{obs}$	$(dv/d\epsilon^2)^{a,b}_{calc}$
<sup>4</sup> 13 <sup>↔ 3</sup> 13	2	0.305	0.314
	3	0.746	0.742
$5_{24} + 4_{23}$	1	1.509	1.515
	2	0.878	0.852
	3	0.383	0.378
	4	0.088	0.094
$5_{23} + 4_{22}$	2	-0.336	-0.350
	3	-0.773	-0.783
	μ <sub>a</sub> =	0.367±0.004 D	
	μ <sub>p</sub>	0	
	μ <sub>c</sub> =	0.154±0.006 D	
	μ <sub>T</sub> =	0.398±0.004 D	

Table 5-2.	Stark	Coefficients	and	Dipole	Moments	for
	Gauche	e 3-methyl-l-h	outer	ne.		

<sup>a</sup>Units are MHz/(V/cm)<sup>2</sup>.

 $^{b}\text{Calculated with }\mu_{b}$  assumed to be zero.

of 3-methyl-1-butene are closer to that of propylene  $(0.364 \text{ D})^{111}$  and methylallene  $(0.401 \text{ D})^{112}$  than to transvinylcyclopropane  $(0.498 \text{ D}).^{109}$ 

### 5.2.b. Internal Rotation

Relative intensity measurements were made on several transitions in the ground and first excited torsional states of both species of 3-methyl-1-butene with the sample cooled in dry ice. The present measurements were combined with the measurements of Creswell and Pagitsis. Analysis of the relative intensities led to the following estimates of the energy differences:

 $E(t,v=1) - E(t,v=0) = \omega_t = 90\pm 10 \text{ cm}^{-1}$   $E(g,v=1) - E(g,v=0) = \omega_g = 104\pm 10 \text{ cm}^{-1}$   $E(g,v=0) - E(t,v=0) = \Delta E_{gt} = 130\pm 20 \text{ cm}^{-1} \quad (5-2)$ 

The excitation energies for the trans  $(\omega_t)$  and gauche  $(\omega_g)$ species were derived from relative intensity measurements on 9 and 8 transitions, respectively, whereas 9 pairs of transitions were studied to obtain  $\Delta E_{gt}$  (energy difference between gauche and trans conformers). The Boltzmann expression was used to derive the three energy differences.<sup>1</sup> Thus,

$$\frac{m_1}{m_2} = g \exp[-\Delta E/kT] , \qquad (5-3)$$

where  $\Delta E$  is the energy difference, k is the Boltzmann constant,  $m_1/m_2$  is the equilibrium population ratio of the two rotational isomers at any temperature, T, and g is the statistical weight ratio of the rotamers. In 3-methyl-1butene, g=1 and 2 for the trans and gauche conformer, respectively.

The three energy differences together with an estimate of the equilibrium torsional angle for the gauche configuration may be used to estimate the first four potential constants in a Fourier expansion of the torsional potential energy, V,

$$V = \sum_{n} \frac{V_n}{2} (1 - \cos n\alpha) . \qquad (5-4)$$

In this equation  $\alpha$  is the torsional angle, which is assumed to be zero in the trans configuration, and the V<sub>n</sub> are the potential constants. Unfortunately, the determination of the equilibrium angle for the gauche configuration offered even more uncertainty than usual. If reasonable values of bond distances and angles are transfered from the known structures of propane<sup>113</sup> and propylene<sup>114</sup> and adjusted slightly, it is possible to compute moments of inertia and rotational constants which agree with those for the trans species. If then the rotational constants are calculated as functions of  $\alpha$ , the plot shown in Figure (5-2) is obtained. The experimental rotational constants for the gauche conformer are indicated in the plot. It is evident that all one can say is that the equilibrium value of  $\alpha$ is near 120°.

The fact that the three rotational constants for the gauche species do not indicate the same equilibrium angle is evidence for either some poor assumptions about the structure for the trans species or a correlation between  $\alpha$  and some other internal coordinate. The two C-C-C angles and the C-C=C angle have been varied to improve the consistency of the predicted  $\alpha$  for the gauche species. By adjusting  $\alpha$  and any two of the mentioned angles, the conclusion is always the same: the angles increase and the torsional angle increases to greater than 120°. This result is most simply interpreted by assuming that as the vinyl group rotates from the trans to the gauche configuration, a steric hindrance causes the molecule to open up. Each of the possible CC distances has been changed by 0.01 Å and the above calculation has been repeated without changing the conclusion. The problem then is that if only the torsional angle is changed, the predicted torsional angle for the gauche conformer is less than 120° (112° is the best compromise). On the other hand if the CCC angles are allowed to vary, the predicted gauche torsional angle



an assumed structure. The vertical scale is in MHz. The crosses mark the experimental values of  $A_g - A_t$ ,  $B_g - B_t$ , and  $C_g - C_t$ . C-C\_0 with torsional angle  $\alpha$  for 3-methyl-l-butene. Here,  $A_0$  ,  $B_0$ and  $C_0$  are constants for the trans configuration calculated for Figure (5-2). A plot of the variation of calculated values of  $A-A_0$ ,  $B-B_0$  and

is 122-125°. As a result of this uncertainty, the torsional angle is kept at 120 and a ±5° uncertainty in this angle is included.

To obtain the torsional energy levels from  $H_T$  (2-36) we have used expressions given by Quade and Lin<sup>11</sup> and by Knopp and Quade<sup>115</sup> for the moments of inertia as functions of torsional angle for molecules with a planar top (here the -CH=CH<sub>2</sub> group) attached to a frame with a plane of symmetry (here the (CH<sub>3</sub>)<sub>2</sub>CH- group). The moment of inertia matrix I was inverted at 10° intervals in  $\alpha$  from 0 -180° and the resulting values of  $F_{\alpha\alpha}$  were fit to a Fourier series of the form

$$F_{\alpha\alpha} = F_{\alpha\alpha}^{(0)} + F_{\alpha\alpha}^{(1)} \cos\alpha + F_{\alpha\alpha}^{(2)} \cos2\alpha . \qquad (5-5)$$

With the  $F_{\alpha\alpha}^{(n)}$  given in Table (5-3) the computed  $F_{\alpha\alpha}$  agree with those obtained by inversion of I to within 0.5% over the entire range of  $\alpha$ .

The torsional energies were obtained by direct diagonalization of a truncated matrix for  $H_T$ , Equation (2-36). The basis functions used were normalized even and odd linear combinations of the free-rotor functions, exp (im $\alpha$ ). Twenty basis functions were found to give the lowest few levels to sufficient accuracy. The potential constants were adjusted in this calculation to match the four items of information in Table (5-3). The effects of varying the

Table 5-3. Parameters Related to the Internal Torsion of the Vinyl Group in 3-Methyl-l-Butene.<sup>a</sup>

ωt	$= 90 \pm 10 \text{ cm}^{-1}$
ωg	$= 104 \pm 10 \text{ cm}^{-1}$
^_ ∆E <sub>qt</sub>	$= 130 \pm 20 \text{ cm}^{-1}$
Fo	$= 1.678 \text{ cm}^{-1}$
Fl	$= 0.022 \text{ cm}^{-1}$
F <sub>2</sub>	$= -0.102 \text{ cm}^{-1}$
vı	= $300\pm100 \text{ cm}^{-1}$ (0.86±0.30 kcal/mole)
v <sub>2</sub>	$= -50\pm100 \text{ cm}^{-1} (-0.14\pm0.30 \text{ kcal/mole})$
v <sub>3</sub>	= $750\pm75 \text{ cm}^{-1}$ (2.14±0.21 kcal/mole)
v <sub>4</sub>	$= -100\pm 50 \text{ cm}^{-1}$ (-0.29±0.15 kcal/mole)

<sup>a</sup>See text for the definitions of the parameters.

input parameters on the calculated energies were analyzed to obtain rough estimates of the uncertainties in the derived potential constants.

The results of this calculation show that the potential function is predominantly three-fold with contributions from the other terms being considerably smaller than from the  $V_3$  term. The  $V_n$  obtained are given in Table (5-3) and a plot of the potential function is shown in Figure (5-3).

### 5.3. Discussion

The most important conclusion from the present study is the predominantly 3-fold character of the potential function for 3-methyl-1-butene. This conclusion follows directly from the existence of trans and gauche conformers in approximately equal concentrations. From the relative intensity measurements two additional conclusions can be drawn. From the trans-gauche intensity ratio it follows that the trans conformer is approximately 370 cal/mole more stable than the gauche species. If this fact is coupled with the fact that the estimated torsional excitation energy for the gauche species (104 cm<sup>-1</sup>) is higher than for the trans species (90 cm<sup>-1</sup>), it is concluded that the gauche-gauche potential barrier is higher than the transgauche barrier. All of these conclusions are confirmed by the numerical analysis of the torsional potential with





the resulting constants given in Table 5-3.

The coefficient of the  $\cos 3\alpha$  term in the potential function for rotation of the vinyl group in 3-methyl-l-butene (2140 cal/mole) is comparable to that in propylene (1978 cal/mole).<sup>111</sup> In addition, the gauche-trans energy difference ( $\Delta E = 370$  cal/mole) is only slightly greater than the closely related cis-skew energy difference in 1-butene  $(\Delta E = 150 \text{ cal/mole})$ .<sup>116</sup> As already indicated, the dipole moments of the two conformers are similar to that of propylene. Thus, from a number of points of view the electronic structure of 3-methyl-l-butene is very similar to that of propylene and 1-butene. One unusual feature of the structure of 3-methyl-1-butene is the evidence presented above for significant steric interaction in the gauche conformation. The molecule appears to become more extended as it moves into the gauche configuration. Also, the gauchegauche energy barrier predicted by the potential function in Table 5-3 is  $\sim 2.7$  kcal/mole whereas the trans-gauche barrier as seen from the trans configuration is  $\sim 2.1$  kcal/ mole. Kondo et al. found a higher barrier for internal rotation of the methyl group in the cis form of 1-butene (analogous to the gauche form of the present molecule) than in the skew form (analogous to the trans form).<sup>116</sup> This difference was attributed to steric hindrance. In addition, they found larger CCC angles in the cis form.

Comparison of the internal rotation of the vinyl group

in 3-methyl-l-butene with that in corresponding compounds containing the cyclopropane or the ethylene oxide ring is difficult. The corresponding 1,2-epoxy-3-butene does not appear to have been studied by either electron diffraction or microwave spectroscopy. An electron diffraction study of vinylcyclopropane<sup>108</sup> was interpreted to favor a mixture of 3 parts trans to one part gauche at 293 K, which would correspond to a 6.5:1 ratio at 204 K. Here trans refers to the conformer with the vinyl group trans to the ring and the gauche conformer is rotated  $120^{\circ}$  from trans. A microwave investigation<sup>109</sup> failed to uncover transitions belonging to another species. Also, as indicated in the introduction, a number of related cyclopropyl derivatives have shown transcis conformers rather than trans-gauche. However, if accepted, the electron diffraction results predict a gauchetrans energy difference of approximately 1 kcal/mole, which is larger than the 0.37 kcal/mole difference determined for 3-methyl-l-butene.

The corresponding aldehyde compounds can be intercompared because all three compounds have been studied. An electron diffraction study of 2-methylpropanal (isopropylcarboxaldehyde)<sup>100</sup> showed that  $\sim$ 10% of the molecules have the oxygen atom trans to the isopropyl group (aldehyde hydrogen trans to isopropyl hydrogen) and  $\sim$ 90% of the molecules are gauche conformers (at 266 K). Electron diffraction <sup>99</sup> and microwave<sup>103</sup> studies of cyclopropanecarboxaldehyde predict an approximately 50-50 mixture (45%-55%)

of species containing the oxygen atom cis and trans to the ring. Thus, the predominantly 3-fold potential in the isopropyl compound becomes a predominantly 2-fold potential when the methyl carbons are joined to form a cyclopropane ring. Finally, in a microwave study of glycidaldehyde, <sup>117</sup> only species with the aldehyde oxygen approximately trans to the ring were found. It was concluded that any other species, if present, occur with considerably lower concentration. Thus, in the aldehyde compounds there is an increase in the relative stability of the trans species in going from isopropyl to cyclopropyl to ethylene oxide group. A corresponding increase in the relative stability of the trans species occurs for the vinyl compounds in going from the isopropyl to the cyclopropyl group. Comparison of the two groups of molecules shows that the relative stability of the trans species is greater in the vinyl compounds than in the aldehydes. We do not at present have a consistent interpretation of these interesting results.

APPENDICES

APPENDIX	A
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Inversion frequencies of ammonia in the ground (v<sub>2</sub> =  $\emptyset$ ) and excited state (v<sub>2</sub> = 1) in MHZ.

Transition	tion 14 <sub>NH</sub>		15 <sub>NH3</sub>
JK	$v_2 = 0^a$	$v_2 = 1^{b}$	v <sub>2</sub> = 0 <sup>°</sup>
$\begin{array}{c} J \\ K \\ \hline 1 \\ 2 \\ 2 \\ 2 \\ 3 \\ 0 \\ 3 \\ 1 \\ 2 \\ 2 \\ 3 \\ 0 \\ 3 \\ 1 \\ 2 \\ 2 \\ 3 \\ 3 \\ 1 \\ 2 \\ 3 \\ 3 \\ 1 \\ 2 \\ 3 \\ 3 \\ 1 \\ 2 \\ 3 \\ 3 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 2$	$v_2 = 0$ 23694.496 23098.815 23722.631 - 22234.504 22834.182 23870.130 21134.311 21703.358 22688.312 24139.417 19663.821 e 19838.346 20371.450 21285.275 22653.022 24532.982 18230.132 e 18391.562 18884.695 - 20994.617 22732.429 25056.025 - 17291.493 18017.337 19218.465 20804.830 22924.940 25715.182	$v_2 = 1$ 1066650.82 1045318.70 1067676.77 - 1014084.00 1035816.20 1073050.70 973826.50 994747.80 1030531.20 1082593.49 d - 925657.40 945604.80 979650.00 1029374.50 1096591.63 d 864695.41 870877.05 d 809710.90 - 968810.00 1032323.00 115083.22 d 805159.23 f 828521.90 858394.20 902459.20 961885.20 1039360.80 1138215.24 d	$v_2 = 0$ 22624.94 22044.24 22649.84 21011.88 9 21202.28 21784.01 22789.45 20131.40 20682.88 21637.73 23046.02 
8 2 8 5 8 6 8 7	15639.761 18808.507 20719.221 23232.238	763583.33 887018.80 958827.90 1050521.50	14799.99 17855.33 19701.85 22134.88

### Appendix A (cont.)

Transitio	n 1	<sup>4</sup> NH <sub>3</sub>	15 <sub>NH</sub> 3
JK	v <sub>2</sub> = Ø <sup>a</sup>	$v_2 = 1^b$	$v_2 = 0^C$
8       8         9       4         9       5         9       6         9       7         9       8         9       9         10       1         10       5         10       6         10       7         10       8         10       9         10       10         11       3         11       7         11       8         11       9         11       10         12       3         12       7         12       10         13       7	26518.981 15523.900 16798.134 18499.390 20735.452 23657.471 12017.172 14822.527 16319.324 	1166172.70 <sup>d</sup> 759001.20 809481.89 875368.80 959569.00 1065868.20 615055.02 <sup>d</sup> 730985.03 <sup>d</sup> 790818.23 964060.30 1237497.36 <sup>d</sup> 580479.16 862810.70 972301.60 1109551.07 <sup>d</sup> 515386.76 <sup>d</sup> 984314.10 <sup>d</sup> 600861.05 <sup>d</sup>	2 14681.19 15907.90 17548.34 26242.76 13998.96 17332.55 19810.62 23054.96 27323.41 15057.77 20009.80 23696.82 12923.03 20306.75
13       9         13       12         13       13         14       11         14       12         14       13         14       13	26654.847 33156.849 	1171597.15 <sup>d</sup> 1387550.49 <sup>d</sup> 1019895.50 1210022.25 <sup>d</sup>	14537.32 - 17312.98 21206.06 -

<sup>a</sup>Ref. 43; <sup>b</sup>Ref. 71; <sup>C</sup>Ref. 46.

<sup>d</sup>Calculated values from Ref. 71.

eCalculated from pparameters given in Ref. 70.

<sup>f</sup>Calculated from parameters given in Ref. 71.

<sup>g</sup>Calculated from parameters given in Ref. 46.

### APPENDIX B

Input data for the least-squares fitting program in  $^{14}\rm NH$  .

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Frequency <sup>a</sup>	Wt <sup>b</sup> Ref	Ty <sup>d</sup>	Trans.	Frequency <sup>a</sup>	Wt <sup>b</sup> Ref?	Ty <sup>d</sup>
Q(4,4) $28431011.53$ $1.00$ SC $1$ $Q(7,4)$ $28468520.88$ $1.00$ SC $2$ Q(4,4) $28431020.20$ $0.10$ F $1$ $Q(1,1)$ $28474667.60$ $1.00$ SC $2$ Q(4,4) $28431011.16$ $0.25$ J $1$ $Q(1,1)$ $28474661.29$ $0.10$ F $2$ Q(5,2) $28491167.63$ $0.25$ J $1$ $P(2,1)$ $27282815.81$ $1.00$ SC $2$ Q(5,3) $28470880.12$ $0.10$ F $1$ $R(2,1)$ $30271494.27$ $0.25$ J $2$ Q(5,3) $28470863.49$ $0.10$ F $1$ $Q(2,2)$ $28466358.93$ $0.10$ F $2$ Q(5,4) $28442037.53$ $0.10$ F $1$ $Q(3,2)$ $28472899.9919.08$ $0.25$ J $2$ Q(5,4) $28442012.38$ $0.25$ J $1$ $Q(3,2)$ $28472815.99$ $0.10$ F $2$ Q(5,5) $28403922.71$ $1.00$ SC $1$ $Q(3,3)$ $28451853.54$ $1.00$ SC $2$ Q(5,5) $2840391.94$ $0.10$ F $1$ $Q(3,3)$ $28451853.54$ $1.00$ SC $2$ Q(5,5) $2840391.50$ $0.25$ J $1$ $Q(3,3)$ $28451865.71$ $0.10$ F $2$ Q(5,5) $2840391.50$ $0.25$ J $1$ $Q(3,3)$ $28451839.47$ $0.10$ F $2$ Q(6,1) $32657460.82$ $0.25$ J $1$ $Q(3,3)$ $28451839.47$ $0.10$ F $2$ Q(6,4) $28454618.46$ $1.00$ SC $1$ $Q(1,1)$ $28474669.29$ $4.00$ FL $2$ Q(6,4)	$\begin{array}{c} Q(1,1)\\ Q(1,1)\\ Q(1,1)\\ Q(1,1)\\ Q(2,2)\\ Q(2,2)\\$	28474676.59 28474704.38 28474704.38 28474672.80 29670838.19 28478971.81 28466383.96 28466371.86 28466371.71 30259929.55 28472808.88 28451846.08 28451856.65 28451856.65 28451858.87 28451813.57 28493353.05 28481144.98 31461684.59 28460479.02 28460482.32 31443769.38 28431019.50 28431013.31 28431011.53 28431011.53 28431011.53 28431011.16 28491167.63 28470880.12 28470863.49 28442037.53 28442012.38 28403922.71 28403921.94 28403911.50 32667019.09 32657460.82 28454618.46	1.00 SC 1.00 SC 0.25 J 0.10 F 0.10 F 0.10 F 0.25 J 4.00 JL 0.10 F 0.25 J 4.00 SC 1.00 SC 0.10 F 0.25 J 1.00 SC 0.10 F 0.25 J 1.00 SC 0.10 F 0.25 J 1.00 SC 0.10 F 0.25 J 1.00 SC 0.10 F 0.25 J 0.10 F 0.25 J 0.00 SC 0.10 F 0.25 J 0.00 SC 1.00 SC 0.10 F 0.10 F 0.10 F 0.25 J 1.00 SC 0.10 SC 0.25 J 1.00 SC	$\begin{array}{c} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 $	$\begin{array}{c} R(5,2)\\ Q(5,3)\\ Q(5,3)\\ Q(5,3)\\ R(5,3)\\ Q(5,4)\\ R(5,4)\\ Q(5,5)\\ Q(5,5)\\ Q(5,5)\\ Q(5,5)\\ R(5,5)\\ Q(6,4)\\ Q(7,3)\\ Q(7,6)\\ Q(7,7)\\ Q(8,7)\\ Q(7,6)\\ Q(7,7)\\ Q(8,7)\\ Q(7,6)\\ Q(7,7)\\ Q(8,7)\\ Q(7,6)\\ Q(7,7)\\ Q(8,7)\\ Q(9,6)\\ Q(9,5)\\ Q(9,6)\\ Q(9,6)\\ Q(9,7)\\ Q(9,6)\\ Q(9,7)\\ Q(9,8)\\ Q(9,6)\\ Q(9,7)\\ Q(1,1)\\ Q(14,12)\\ Q(2,2)\\ Q(3,3)\\ Q(3,3)\\ Q(14,1)\\ Q(2,2)\\ Q(3,3)\\ Q(14,1)\\ Q(2,2)\\ Q(3,3)\\ Q(3,3)\\ Q(14,1)\\ Q(14,12)\\ Q(14,12)$	32060743.95 28470887.76 28470873.55 32043670.75 28441987.32 32019271.24 28403904.74 31987041.32 28454617.07 28495881.48 28386700.50 28330749.74 28349869.93 28284545.58 28464920.29 28422254.73 28370075.71 28306897.39 28172565.83 28283986.22 28110720.59 28110724.39 28468520.88 28474667.60 28474661.29 27282815.81 30271494.27 28466358.93 30259919.08 28472815.99 28472815.99 28451853.54 28451839.47 30842318.81 28474669.29 28466373.53	1.00 SC 0.10 F 1.00 SC 1.00 SC 0.10 F 1.00 SC 0.10 F 1.00 SC 0.10 F 0.10 F 0.25 J 1.00 SC 0.10 F 0.25 J 0.10 F 0.25 J 0.10 F 0.25 J 0.10 F 0.25 J 0.10 F 0.25 J 0.10 F 0.25 J 0.00 SC 0.10 F 0.00 SC 0.00 FL 0.00 SC 0.00 FL 0.00 FL	222222222222222222222222222222222222222

Appendix B (cont.)

Trans.	Frequency <sup>a</sup>	Wt PRef	ту <sup>d</sup>	Trans.	Frequency <sup>a</sup>	Wt <sup>b</sup> Refç	ту <sup>d</sup>
$\begin{array}{c} Q(6,5) \\ R(6,5) \\ R(6,5) \\ Q(6,6) \\ Q(6,6) \\ Q(6,6) \\ Q(6,6) \\ Q(7,2) \\ Q(7,3) \\ Q(7,4) \\ R(7,4) \\ Q(7,6) \\ Q(7,6) \\ Q(7,6) \\ Q(7,7) \\ Q(8,5) \\ Q(8,6) \\ Q(8,6) \\ Q(8,6) \\ Q(8,6) \\ Q(8,7) \\ Q(9,4) \\ Q(9,4) \\ Q(9,4) \\ Q(9,6) \\ Q(9,7) \\ Q(10,6) \\ Q(10,10) \\ Q(11,9) $	28417429.57 32587823.93 32587816.46 28370521.34 28370525.01 28370525.01 28370521.77 28370519.67 33251080.44 28495902.37 28468521.32 33214248.46 28386705.99 28386716.91 28330747.96 28330751.52 28330683.39 28448315.26 28448324.10 28404116.80 28404121.13 28404126.98 28349881.84 28349871.40 28498759.68 28349881.84 28349871.40 28498759.68 28498598 28498598.68 2848598598 2848598598	0.10 F 1.00 SC 0.25 J 1.00 SC 0.10 F 0.25 J 4.00 JL 0.25 J 0.25 J 0.00 SC 1.00 SC 1.00 SC 1.00 SC 0.25 J 1.00 SC 0.25 J 1.00 SC 0.25 J 1.00 SC 0.10 F 1.00 SC 0.10 F 1.00 SC 0.10 F 1.00 SC 0.10 F 1.00 SC 0.25 J 1.00 SC 0.10 F 1.00 SC 0.10 F 1.00 SC 0.25 J 1.00 SC 0.10 F 1.00 SC 0.25 J 1.00 SC 0.10 F 1.00 SC 0.25 J 1.00 SC 0.25 J 0.00 SC 0.10 F 0.25 J 0.00 SC 0.10 F 0.00 SC 0.25 J 0.00 SC 0.10 F 0.00 SC 0.25 J 0.25 J 0.	$1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\$	$\begin{array}{c} R(5,5)\\ Q(5,5)\\ R(5,4)\\ Q(5,4)\\ R(5,3)\\ Q(7,7)\\ Q(7,5)\\ Q(9,6)\\ Q(10,10)\\ Q(11,9)\\ Q(11,9)\\ Q(11,9)\\ Q(11,9)\\ Q(11,9)\\ Q(11,9)\\ Q(12,3)\\ Q(5,1)\\ Q(12,3)\\ Q(5,1)\\ Q(12,3)\\ Q(7,6)\\ Q(7,6)\\ Q(7,4)\\ Q(5,5)\\ Q(7,4)\\ Q(5,5)\\ Q(7,4)\\ Q(5,5)\\ Q(7,4)\\ Q(5,5)\\ Q(7,4)\\ Q(5,5)\\ Q(5,4)\\ Q(5,3)\\ Q(2,2)\\ Q(2,1)\\ R(1,1)\\ R(6,5)\\ R(6,1)\\ R(6,5)\\ R(6,1)\\ R(5,3)\\ R(5,5)\\ R(5,2)\\ R(5,1)\\ R(5,6)\\ Q(12,10)\\ Q(11,9)\\ Q(11,9)\\ Q(11,9)\\ Q(11,8)\\ \end{array}$	31987039.07 28403916.24 32019269.89 28442011.32 32043669.07 28330741.94 28432333.84 28422290.18 28172576.73 28283986.22 28284538.98 28485234.95 28503164.02 28528656.29 28449907.67 28566954.50 28386708.72 28432330.04 28468520.89 28403921.40 28442009.59 28470872.62 28466367.96 28478946.85 29670796.26 32587822.85 32667015.46 32670352.78 32019267.72 32043671.55 31987039.52 32060743.82 32070849.70 32074180.08 28232155.07 28283985.62 2833025.43	4.00 FL 4.00 SA 1.00 SA	222222222244443333334444333333444444
Q(14,12) Q(14,12) R(1,1) Q(2,1)	28202444.52 28110744.83 29670797.19 28478945.81	0.25 J 0.25 J 4.00 FL 4.00 FL	1 1 1	Q(8,6) Q(5,4) Q(5,3) Q(4,2)	28404109.77 28442007.82 28470875.23 28481135.24	1.00 SA 1.00 SA 1.00 SA 1.00 SA	4 4 4 4

Appendix B (cont.)

Trans.	Frequency <sup>a</sup>	Wt. <sup>b</sup> Ref. <sup>C</sup> T	d Y Trans.	Frequency <sup>a</sup>	wt. Ref.	r <sub>Ty</sub> d
Q(3, 2) Q(5, 4) Q(5, 3) Q(5, 3) Q(6, 5) Q(8, 7) Q(8, 6) Q(8, 5) Q(8, 5) Q(9, 8) Q(11, 9) P(4, 1) R(4, 1) P(4, 2) R(4, 2) P(4, 3) R(4, 3) R(4, 4) R(5, 1) Q(5, 2)	28472800.88 28442008.03 28470877.12 28470877.12 28470871.89 28417415.57 28349881.00 28404105.93 28448312.88 28306918.66 28283982.72 26106297.18 31472318.32 26092774.60 31461703.15 26070012.83 31443680.03 31418036.33 32070838.32 28491163.27	4.00 FL 1 4.00 FL 1 0.25 J 2 0.25 J 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Q(9,6) Q(10,1) Q(11,3) Q(14,14) Q(14,13) Q(13,13) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(13,12) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(14,14) Q(13,12) Q(13,12) Q(2,2) P(1,1) Q(2,2) P(1,1) Q(2,2) P(1,1) Q(2,2) P(1,1) Q(2,2) P(1,1) Q(2,2) Q(2,2) P(1,1) Q(2,2) P(1,1) Q(2,2) Q(2,2) Q(2,2) P(1,1) Q(2,2) Q(2,3) Q(2,2) Q(2,3) Q(2,3) Q(2,3) Q(3,3) Q(3,3) Q(3,3) Q(3,4) Q(3,3) Q(3,4) Q(3	28422287.66 28566562.53 28552915.58 27867759.49 27998634.52 27954330.68 28072926.65 28528657.65 28491162.69 28466366.46 31461681.24 29670802.86 28466369.32 26070009.42 28442012.29 28470872.53 28454617.50 28370517.97	1.00 SA 1.00 HK 1.00 HK 1.00 HK 1.00 HK 1.00 HK 1.00 HK	4 4 3 3 3 3 3 3 4 4 3 4 4 4 4 4 4 4 4 4
(J, Z)	3200033.00		. Q(14,13)	21330043.52	TORUN	5

- <sup>a</sup> The frequency of the transition from the inversion free ground state  $(v_2 = \emptyset)$  to the inversion free level in the  $v_2 = 1$  excited state in MHZ.
- <sup>b</sup> Weight for each transition in the least squares fit.
- <sup>C</sup> References as follows: SC, this work; F, Ref. 28; FL, Rcf. 28, Lamb dip; J, Ref. 29; JL, Ref. 29, Lamb dip; SA, Ref. 68; HK, Ref. 58.
- <sup>d</sup> This column shows the type of transition.  $l = two-photon (s \leftarrow s)$ 2 = two-photon (a  $\leftarrow$  a), 3 = IR (a  $\leftarrow$  s) and 4 = IR transition (s  $\leftarrow$  a).

# APPENDIX C

Input data for the least-squares fitting program in  $15_{\rm NH}_3$ .

Trans	5.	Frequency <sup>a</sup>	Wtb Ref 7	īyd	Trans.	Frequencya	Wt. Ref	ту <sup>đ</sup>
Trans P(2, Q(2, Q(2, Q(2, Q(2, Q(2, Q(2, Q(2, Q	1)))))))))))))))))))))))))))))))))))))	Frequency <sup>a</sup> 26633848.870 27838069.605 27838075.002 27814181.843 27860491.683 27837074.294 27837072.496 27797296.932 27797290.336 2789426.452 27866617.642 27866617.642 27866617.642 27866617.642 27876.062 27772075.598 27772076.591 27864539.181 27864539.181 27864534.984 27810552.255 27810499.492 27738500.736 27854426.882 27854421.185 27696401.780 27952173.313	<pre>% tb Ref ? % tb Ref ? % tb Ref ? % % tb Ref ? % % tb Ref ? % % % % % % % % % % % % % % % % % % %</pre>	ryd 1111411141111114111114111141111411114	Trans. Q(8,7) Q(9,4) Q(9,5) Q(9,6) Q(9,9) Q(9,9) Q(10,7) Q(10,8) Q(10,8) Q(10,9) Q(10,9) Q(10,9) Q(10,9) Q(10,9) Q(10,9) Q(10,9) Q(10,9) Q(10,9) Q(10,9) Q(10,9) Q(11,7) Q(11,7) Q(11,7) Q(11,9) Q(11,9) Q(12,7) Q(12,10) Q(12,12) Q(12,12) Q(12,12) Q(12,12) Q(14,12) R(1,1) R(1,1) R(2,1) R(2,2) R(4,2) R(4,4) R(5,2) R(5,4)	Frequency <sup>a</sup> 27710118.784 27710116.985 28006881.240 27947664.734 27871837.928 27518038.458 27518039.957 27845173.488 27735880.250 27735880.250 27735888.044 27602514.277 27602513.378 27602510.679 27912914.891 2791296.304 27687008.083 27687029.069 27686995.192 27978902.209 27978915.100 27630446.540 27257320.050 27849494.096 27494107.226 29027009.320 29027032.404 29027008.120 29642394.797 29619812.031 30865252.131 30779321.719 31491704.746	<pre>wtb Ref l.00 SC l</pre>	$Ty^{d}$
Q(7, Q(7, Q(7, Q(7, Q(7, Q(8,	5) 6) 7) 7) 7) 7)	27751665.222 27751691.004 27645758.739 27645787.220 27645785.121 28033535.787	0.10 F 0.10 F 1.00 SC 0.25 J 0.10 F 1.00 SC	1 1 1 1 1 1	R(5,5) R(5,5) R(6,1) R(6,1) R(6,5) R(7,3) R(7,3)	31346050.281 32136955.549 32136945.056 31981705.626 32714992.882 32714997.678	1.00 SA 1.00 SA 1.00 SC 1.00 SA 1.00 SC 1.00 SC 0.25 J	4 1 4 1 1

Append	ix C (cont.)				
Trans.	Frequency <sup>a</sup>	Wt. Ref <sup>C</sup> Ty <sup>d</sup>	Trans.	Frequency <sup>a</sup>	Wt. <sup>b</sup> Ref <sup>C</sup> Ty <sup>d</sup>
Q(8,2) Q(8,5) Q(8,5) Q(8,5) Q(8,5)	28033534.288 27891034.239 27891021.647 27891026.444	1.00 SA 4 1.00 SC 1 1.00 SC 1 0.25 J 1	R(7,5) R(7,7) R(7,7)	32616627.978 32453349.913 32453334.024	1.00 SC 1 1.00 SC 1 1.00 SA 4
<sup>a</sup> The front to the b	equency of the v <sub>2</sub> = 1 ,s exc for each tran	e transition fr ited state in sition in the	com the inv MHZ. least squa	version free g ares fit.	round state
<sup>C</sup> Referen Lamb d <sup>d</sup> This co , type	nces as follow ip; J, Ref. 30 olumn shows th 4 = IR transi	s; sc, this wo ; SA, Ref. 68; e type of tran tion (s ← a).	ork; F, Ref D, Ref. ( Asition. Ty	f. 28; FL, Ref 66. ype 1 = two-ph	• 28, oton(s ← s)

#### APPENDIX D

Input data for the le	east-squares fitting	program in <sup>15</sup> N	<sup>H</sup> 3•
Trans. Frequency <sup>a</sup>	Wt. Ref. Ty <sup>d</sup> Trans.	Frequency <sup>a</sup>	wt. Ref. <sup>C</sup> Ty <sup>d</sup>
P(2, 1) 27663011.496 P(2, 1) 27663016.592 Q(3, 1) 28837837.580 Q(3, 2) 28835761.518 Q(3, 3) 28832485.386 Q(4, 4) 28816572.702 Q(6, 3) 28792724.212 Q(6, 4) 28786799.114 Q(7, 5) 28761714.579 Q(7, 7) 28744177.620 Q(7, 7) 28744177.620 Q(7, 7) 28744192.310 Q(8, 6) 28732633.512 Q(8, 8) 28711951.430	1.00 SC 2 Q( 8, 8) .25 J 2 Q( 9, 6) 4.00 FL 2 Q(10, 5) 4.00 FL 2 Q(10, 5) 4.00 FL 2 Q(10, 8) .10 F 2 Q(11, 6) 4.00 FL 2 Q(11, 8) .10 F 2 Q(11, 9) 1.00 SC 2 Q(13,13) 1.00 SC 2 R( 3, 1) .10 F 2 R( 3, 2) .10 F 2 R( 3, 3) 1.00 SC 2 R( 6, 5) 1.00 SC 2 R( 6, 6) 1.00 SC 2	28711952.929 28711821.020 28703737.116 28662325.885 28670550.991 28637995.628 28621119.711 28491877.983 31200173.969 31199000.881 31197242.898 32907002.456 32905393.170	1.00 D 3 1.00 SC 2 1.00 SC 2 1.00 SC 2 1.00 D 3 1.00 SC 2 1.00 D 3 1.00 SC 2 1.00 SA 3 1.00 SA 3 1.00 SA 3 1.00 D 3 1.00 D 3

<sup>a</sup>The frequency of the transition from the inversion free ground state to the  $v_2 = 1$ , a excited state in MHZ.

<sup>b</sup>Weight for each transition in the least squares fit.

<sup>C</sup>References as follows; SC, this work; F, Ref. 28; FL, Ref. 28, Lamb dip; J, Ref. 30; SA, Ref. 68; D, Ref. 66.

<sup>d</sup>This column shows the type of transition. Type 2 = two-photon(a  $\leftarrow$  a), type 3 =IR transition (a  $\leftarrow$  s).

## APPENDIX E

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Trans.	Frequency <sup>a</sup>	Wt.b	тус	Trans.	Frequencya	Wt.b	тус
P(5,2)	31174653.158	1.00	2	Q(18, 6)	31321902.500	Ø.36	2
P(5,3)	31174893.158	1.00	2	Q(18, 7)	31322201.500	Ø.36	2
P(5,4)	31175235.158	1.00	2	Q(18, 8)	31322601.500	0.36	2
P(4,1)	31228269.302	1.00	2	Q(18, 9)	31323083.500	Ø.36	2
P(4,2)	31228412.302	1.00	2	Q(18,10)	31323667.500	0.30	2
P(4, 3)	31228052.302	1.00	2	Q(18, 12)	31323233.500	0.30	2
P(3, 1)	31201330+133	1 00	2	Q(10,13)	31320299.500	Ø.30 Ø.36	2
P(3, 2)	31429957 201	1 00	2	P(5, 2)	31174636.000	Ø.36	2
Q(-1, 2) Q(-5, 5)	31427509,201	1.00	2	P(5, 3)	31174878,000	Ø.36	2
O(5, 4)	31427095.201	1.00	2	P(5, 4)	31175223.000	Ø.36	2
0(5,3)	31426784.201	1.00	2	0(6,2)	31422501.000	Ø.18	2
Q(6,6)	31423944.201	1.00	2	Q(6,2)	31422501.000	Ø.18	2
Q(6,5)	31423430.201	1.00	2	Q(6,3)	31422713.000	Ø.36	2
Q(6,4)	31423024.201	1.00	2	Q(6,4)	31423018.000	Ø.36	2
Q(6,3)	31422727.201	1.00	2	Q(6,5)	31423415.000	Ø.36	2
R(2,2)	31585869.798	1.00	2	Q( 6 <b>, 6)</b>	31423934.000	Ø.36	2
R(2,1)	31585751.798	1.00	2	Q(10, 2)	31399484.000	Ø.36	2
R(3,2)	31634230.435	1.00	2	Q(10, 3)	31399650.000	Ø.36	2
R(4,4)	31682360.478	1.00	2	Q(10, 4)	31399928.000	Ø.36	2
R(4,3)	31682080.478	1.00	2	Q(10, 5)	31400281.000	0.36	2
R(4, 2)	31681884.478	1.00	2	Q(10, 6)	31400/29.000	0.30	2
R( <b>5</b> , <b>3</b> )	31/29003.845	1.00	2	Q(10, 7)	31401299.000	0.30	2
R(5, 4)	31/29322.045	1 00	2	Q(14, 4)	31366352 000	0.30	2
P(5, 3)	31174887-674	1.00	2	Q(14, 5)	31366716.000	Ø.36	2
P(5, 4)	31175234,234	1.00	2	0(14, 7)	31367174.000	Ø.36	2
P(4, 2)	31228410,221	1.00	2	0(14.8)	31367729.000	Ø.36	2
P(4,3)	31228650.055	1.00	2	0(14, 9)	31368408.000	Ø.36	2
P(3,1)	31281365.561	1.00	2	Q(14, 10)	31369221.000	Ø.36	2
P(3,2)	31281506.760	1.00	2	Q(14,11)	31370200.000	Ø.36	2
P(2,0)	31333746.499	1.00	2	Q(14,12)	31371396.000	Ø.36	2
P(2,1)	31333787.870	1.00	2	Q(16, 2)	31344776.000	Ø.36	2
Q(12, 2)	31383944.647	9.00	2	Q(16, 3)	31344902.000	Ø.36	2
P( 1, Ø)	31385488.580	1.00	2	Q(16, 4)	31345084.000	Ø.36	2
Q(4,4)	31430495.221	1.00	2	Q(16, 5)	31345323.000	0.36	2
Q(3,3)	31432893.860	1.00	2	Q(16, 6)	31345629.000	Ø.36	2
Q(2,2)	31434706.406	9.00	2	Q(16, 7)	31346023.000	0.36	2
Q(1, 1)	31435926.261	9.00	2	Q(16, 8)	31346503.000	0.36	2
R(0,0)	31486945.430	1.00	2	$\hat{D}(13,11)$	31311220.000	10.30 a 36	2
K( 1, 0)	313300/4.515	1.00	2	Q(19,12)	21211230.000	0.30	2

Input data for the least-squares fitting program in  $^{12}\mathrm{CH}_3\mathrm{F}.$ 

Appendix E (cont.)

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Trans.	Frequencya	wtb	Wt <sup>b</sup> Ty <sup>c</sup> Trans. Frequencya		wtb	Tyc	
R(1,1)	31536714 087	1.00	2	0(19,13)	31312934.000	Ø. 36	2
R(2, 1)	31585745,443	1.00	2	0(19, 14)	31314093.000	Ø.36	2
R(2, 2)	31585871.356	1.00	2	0(19,15)	31315477.000	Ø.36	2
R(3, 2)	31634218,590	1.00	2	R(14, 3)	32120863.000	Ø.36	2
R(3,3)	31634420.646	1.00	2	R(14, 4)	32120963.000	Ø.36	2
R(4,3)	31682068.460	1.00	2	R(14, 5)	32121111.000	Ø.36	2
R(4,4)	31682349.366	1.00	2	R(14, 6)	32121307.000	0.36	2
R(5,5)	31729664.410	1.00	2	R(14, 7)	32121558.000	Ø.36	2
R(12, 1)	663400.000	1.00	Ø	R(14, 8)	32121868.000	Ø.36	2
R(12, 2)	663370.000	1.00	Ø	R(15, 3)	32160948.000	Ø.36	2
R(11, 1)	604333.000	1.00	1	R(15, 4)	32161035.000	Ø.36	2
R(11, 2)	604297.300	225.00	1	R(15, 5)	32161150.000	Ø.36	2
R(10, 1)	554029.000	1.00	1	R(15, 6)	32161304.000	Ø.36	2
R(10, 2)	553995.000	1.00	1	R(15, 7)	32161506.000	Ø.36	2
Q(12, 3)	31384110.120	9.00	2	R(15, 8)	32161779.000	Ø.36	2
Q(18,5)	31321653.500	0.36	2	R(15, 9)	32162125.000	Ø.36	2
P(32, 3)	29477160.810	Ø.Ø4	2	R(16, 5)	32200496.000	Ø.36	2
R(Ø,Ø)	50394.922	90000.00	1	R(16, 6)	32200612.000	Ø.36	2
R( 1, Ø)	100788.340	144.00	1	R(16, 7)	32200766.000	Ø.36	2
Q(1, 1)	31435918.200	0.36	2	R(16, 8)	32200980.000	Ø.36	2
Q(2, 1)	31434562.200	Ø.36	2	R(16, 9)	32201260.000	0.36	2
Q(2,2)	31434696.200	Ø.36	2	R(16,1Ø)	32201629.000	0.36	2
Q(3,1)	31432539.200	Ø.36	2	R(16,11)	32202097.000	Ø.36	2
P(1,0)	31385488.400	Ø.36	2	R(16,12)	32202716.000	Ø.36	2
Q(12, 1)	31383841.400	144.00	2	R(17, 7)	32239330.000	0.36	2
Q(12, 2)	31383938.500	144.00	2	R(17, 8)	32239487.000	0.36	2
Q(12, 4)	31384345.400	Ø.36	2	R(17, 9)	32239696.000	0.36	2
Q(12, 5)	31384675.400	Ø.30	2	R(17,10)	32239992.000	0.30	2
Q(12, 0)	31385090.400	Ø.30	2	R(1/,11)	32240372.000	0.30	2
Q(12, 7)	21202000.400	0.30	2	$R(1/_{12})$	22240007.000	0.30	2
Q(12, 0)	31396003 100	0.30	2	R(1/(1/3))	102102 666	2 25546	2
Q(12, 9)	31387927 100	Ø-36	2	R(1, 0)	102142.000	$2 \cdot 25E + 6$	a
Q(12,10)	31300362 100	Ø-36	2	P(2, 0)	153210 300	$2 \cdot 25E+6$	a
Q(12,12)	31375286 400	Ø 36	2	R(2, 0)	153200.599	$2 \cdot 25E + 6$	a
Q(13, 3)	31375531 100	Ø-36	2	R(2, 1)	153199 843	$2 \cdot 25E + 6$	a
Q(13, 4)	31375829 100	Ø 36	2	P(3 0)	201273 779	2.25E+6	a
0(13, 5)	31376226 400	Ø-30	2	R(3, 0)	204273.773	2.25E+6	a
0(13, 7)	31376718.400	Ø.36	2	R(3, 2)	204270-205	2.25E+6	ด
0(13, 8)	31377320.400	Ø.36	2	R(3, 3)	204232.148	2.25E+6	a
0(13, 9)	31378043.400	Ø.36	2	R(4, 0)	255331.358	90000.0	ā
0(13.11)	31379968.400	Ø-36	2	R(4.1)	255326-986	90000.0	ø
0(13.12)	31381237.400	Ø_36	2	R(4,2)	255313-807	90000.0	ดี
0(18.3)	31321314.500	Ø.36	2	R(4.3)	255291.845	90000.0	ø
Q(18, 4)	31321440.500	Ø.36	2	R(4,4)	255261.098	90000.0	Ø

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Appendix E, Footnotes.

<sup>a</sup>All frequencies are in MHZ.

<sup>b</sup>Weight for each transition in the least squares fit.

<sup>C</sup> Type 2=transitions from the ground state to the  $v_3$ =1 excited state; Type 1=rotational transitions in the  $v_3$ =1 excited state; Type Ø=rotational ransition in the ground state.

### APPENDIX F

Trans.	Frequency <sup>a</sup>	Wt.	Ту	c Trans.	Frequency <sup>a</sup>	Wt.	туС
P(4,3)	30601055.194	1.0	2	P(3,2)	30652526.180	1.0	2
P(4, 2)	30600878.194	1.0 1.0	2	Q(5, 4)	30/94346.060	1.0	2
0(6, 5)	30790784.681	1.0	2	0(3, 2)	30799751,950	25.0	2
$\tilde{O}(6, 4)$	30790496.681	1.0	2	O(3, 3)	30799909.210	25.0	2
Q(6,3)	30790280.681	1.0	2	Q(2,1)	30801580.160	25.0	2
Q(7,7)	30787089.681	1.0	2	Q(2,2)	30801675.340	25.0	2
Q(7,6)	30786642.681	1.0	2	Q( 1, 1)	30802860.880	25.0	2
Q(7,5)	30786287.681	1.0	2	R(Ø,Ø)	30852558.480	1.0	2
Q(7,4)	30786003.681	1.0	2	R( 1, 1)	30901034.690	1.0	2
Q(7,3)	30785793.681	1.0	2	R(3,2)	30996058.980	1.0	2
Q(8,8)	30782457.681	1.0	2	R(3,3)	30996199.530	1.0	2
R(3,2)	30996060.753	1.0	2	R(4,1)	31042483.410	25.0	2
R(3,3)	30996204.753	1.0	2	R(4,2)	31042561.510	25.0	2
P(6,4)	30496133.010	1.0	2	R(4,3)	31042693.680	25.0	2
P(6,5)	30496473.160	1.0	2	R(4,4)	31042883.330	25.0	2
P(5,1)	30548502.120	1.0	2	R(5,4)	31088722.770	1.0	2
P(5,2)	30548607.240	1.0	2	R(5,5)	31088965.690	1.0	2
P(5,3)	30548784.760	1.0	2	Q(1,0)	30802835.910	1.0	2
P(5,4)	30549038.900	1.0	2	Q(2,0)	30801554.990	1.0	2
P(4,2)	30600876.870	1.0	2	R(0,0)	49/25.344	90000.0	Ø
P(4,3)	30601054.220	1.0	2	R(0,0)	49084.309	90000.0	T

Input data for the least-squares fitting program in  $^{13}CH_3F$ .

<sup>a</sup>All frequencies are in MHZ.

<sup>b</sup>Weight for each transition in the least squares fit.

<sup>C</sup> Type 2 = transitions from the ground state to  $v_3 = 1$  excited state; Type 1 = rotational transitio in the  $v_3 = 1$  excited state; Type  $\emptyset$  = rotational transition in the ground state.

### APPENDIX G

Comparison of observed and calculated frequencies in the  $\overset{\nu}{_2}$  band of  $^{15}_{\ \rm NH_3}.$  a

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	J'J'	' K	Ty <sup>b</sup> Ref.	c IR (obs) d	IR(calc) <sup>d</sup>	, <sup>e</sup> x← m(obs) <sup>f</sup>	x∹m(calc) <sup>f</sup>	wt. <sup>g</sup>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1 2	1	2 SC	923.10640	923.10653	922.73874	922.73887	1.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	12	1	2 J	923.10657	923.10653	922.73891	<b>922.</b> 73887	Ø.25
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3 3	1	2 FL	962.28034	962.28045	961.92672	961.92683	4.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3 3	2	2 FL	962.22079	962.22092	961.85747	961.85760	4.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3 3	3	2 F	962.12828	962.12880	961.74819	961.74871	0.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4 4	4	2 FL	961.60176	961.60197	961.21740	961.21760	4.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6 6	3	2 F	960.73525	960.73366	960.42190	960.42031	0.10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 6	4	2 SC	960.55756	960.55699	960.22426	960.22369	1.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		5	2 SC	959./1/64	959./1/92	959.38/53	959.38781	1.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	77		2 F	959.21207	959.21286	958.80256	958.80335	0.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	/ /	/	2 F	959.21321	959.21286	958.80371	958.80335	0.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	/ /		2 50	959.21256	959.21286	958.80305	958.80335	1.00
8       8       2       5C       958.15001       958.15003       957.72766       957.72768       1.00         9       9       6       2       SC       958.01593       958.01452       957.72766       957.72768       1.00         10       10       5       2       SC       958.01593       958.01452       957.72326       957.72768       1.00         10       10       5       2       SC       956.07040       957.68831       957.45361       957.45483       1.00         11       16       3       D       956.57040       956.57043       956.34664       956.34667       1.00         11       18       2       SC       955.03152       955.03145       954.69779       954.69772       1.00         13       13       2       SC       955.03152       950.38675       950.38669       1.00         4       3       3       SA       1041.07940       1041.07962       1040.72578       1040.72600       1.00         4       3       3       SA       1041.00810       1041.00831       1040.62801       1040.62822       1.00         7       6       3       D       1098.02083       1097.6	88	6		958.74609	958./458/	958.41/49	958.41/28	1.00
a       a       b       958.15001       958.15003       957.72766       957.72766       1.00         9       9       6       2       SC       958.01593       958.01452       957.72326       957.72185       1.00         10       10       5       2       SC       957.68709       957.68831       957.45361       957.45483       1.00         10       10       8       2       SC       956.40269       956.40249       956.34664       956.34667       1.00         11       1       6       3       D       955.54763       955.54923       955.26071       955.26231       1.00         11       1       9       3       D       955.03152       955.03145       954.69779       954.69772       1.00         13       13       2       SC       950.91534       950.91527       950.38675       950.38669       1.00         4       3       1       SA       1041.07940       1041.07962       1040.72578       1040.72600       1.00         4       3       3       SA       1041.00810       1040.62801       1040.62822       1.00         7       6       5       D       1098.02083	88	8	2 50	958.14996	958.15003	957.72761	95/./2/08	1.00
9       9       6       2       SC       958.01393       958.01452       957.72320       957.72165       1.00         10       10       5       2       SC       957.68709       957.68831       957.45361       957.45483       1.00         10       10       8       2       SC       956.40269       956.40249       956.07228       956.07208       1.00         11       11       6       3       D       955.54763       955.54923       955.26071       955.26231       1.00         11       11       9       3       D       955.03152       955.03145       954.69779       954.69772       1.00         13       13       2       SC       950.91534       950.91527       950.38675       950.38669       1.00         4       3       1       3 SA       1041.07940       1041.07962       1040.72578       1040.72600       1.00         4       3       3       SA       1041.00810       1041.00831       1040.628201       1040.62822       1.00         7       6       5       3       D       1098.02083       1097.65945       1097.65965       1.00         7       6       3	88	8 C	3 D	958.15001	958.15003	95/./2/00	95/ 12/00	1.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	99	5	2 50	958.01593	958.01452	95/ 12320	95/./2185	1.00
10       10       2       SC       956.40269       956.40249       956.07228       956.07208       1.00         11       11       6       3       D       956.57040       956.57043       955.26071       955.26231       1.00         11       11       8       2       SC       955.54763       955.54923       955.26071       955.26231       1.00         11       11       9       3       D       955.03152       955.03145       954.69779       954.69772       1.00         13       13       2       SC       950.01534       950.01527       950.38675       950.38669       1.00         4       3       1       3       SA       1041.07940       1041.07962       1040.72578       1040.72600       1.00         4       3       3       SA       1041.00810       1041.00831       1040.68665       1040.68687       1.00         4       3       3       SA       1041.00810       1041.00831       1040.62801       1040.62822       1.00         7       6       5       D       1098.00475       1098.00451       1097.65945       1097.65953       1.00         2       1       SC	10 10	2 0	2 50	95/.08/09	95/.08831	957.45301	95/.45483	1.00
11       11       16       3       D       956.57040       956.57043       955.24034       956.34064       956.34064       956.34064       956.34064       100         11       11       18       2       SC       955.03152       955.03145       954.69779       954.69772       1.00         13       13       13       2       SC       950.91534       950.91527       950.38675       950.38669       1.00         4       3       1       3       SA       1041.07940       1041.07962       1040.72578       1040.72600       1.00         4       3       3       SA       1041.04997       1041.05019       1040.62801       1040.62822       1.00         4       3       3       SA       1041.00810       1041.00831       1040.62801       1040.62822       1.00         7       6       5       D       1098.02083       1098.02103       1097.60577       1097.60553       1.00         7       6       6       D       1098.00475       1098.00451       1097.60577       1097.60553       1.00         2       1       1       SC       928.21039       928.21044       928.57805       928.57810       1.00	שב שב	6	2 50	950.40209 056 570A0	950.40249	950.01220	950.07200	1.00
11       11       11       11       11       11       11       11       11       12       12       15       955.03152       955.03145       954.69779       954.69772       1.00         13       13       13       2       SC       950.91534       950.91527       950.38675       950.38669       1.00         4       3       1       3       SA       1041.07940       1041.07962       1040.72578       1040.72600       1.00         4       3       2       3       SA       1041.04997       1041.05019       1040.68665       1040.68687       1.00         4       3       3       SA       1041.00810       1041.00831       1040.62801       1040.62822       1.00         7       6       5       3       D       1098.02083       1097.65945       1097.65965       1.00         7       6       6       3       D       1098.00475       1098.00451       1097.60557       1097.60553       1.00         2       1       1       SC       928.21057       928.21044       928.57805       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.7		0	3 50	950.5/040	900.0/043	950.34004	900.3400/	1.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11 11	0	2 50	955.54/03	900.04923	955.20071	955.20231	1.00
13       13       13       13       13       13       13       141.07940       1041.07962       1040.72578       1040.72600       1.00         4       3       2       3       SA       1041.04997       1041.05019       1040.68665       1040.68667       1.00         4       3       3       SA       1041.00810       1041.00831       1040.68665       1040.68687       1.00         4       3       3       SA       1041.00810       1041.00831       1040.62801       1040.62822       1.00         7       6       5       3       D       1098.02083       1098.02103       1097.65945       1097.65965       1.00         7       6       6       3       D       1098.00475       1098.00451       1097.60577       1097.60553       1.00         1       2       1       1       SC       928.21057       928.21044       928.57805       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       3       1       4       SA       928.97235       928.928.97252       929.32597       929.32614       1.00	12 12	2	2 50	900.000102	900.03140	934.09//9	954.09/12	1.00
4       3       2       3       SA       1041.07940       1041.07902       1040.72576       1040.72660       1.00         4       3       2       3       SA       1041.04997       1041.05019       1040.68665       1040.68667       1.00         4       3       3       SA       1041.00810       1041.00831       1040.62801       1040.62822       1.00         7       6       5       3       D       1098.02083       1098.02103       1097.65945       1097.65965       1.00         7       6       6       3       D       1098.00475       1098.00451       1097.60577       1097.60553       1.00         1       2       1       1       SE8.04191       888.04119       888.40957       888.40885       0.25         2       2       1       1       SC       928.21044       928.57805       928.57810       1.00         2       2       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       3       1       4 <t< td=""><td>12 I2</td><td>13</td><td>2 50</td><td>1011 07010</td><td>101 07062</td><td>1010 72572</td><td>1010 72600</td><td>1 00</td></t<>	12 I2	13	2 50	1011 07010	101 07062	1010 72572	1010 72600	1 00
4       3       3       SA       1041.004397       1041.00819       1041.00831       1040.0300       1040.0300       1.00         7       6       5       3       D       1098.02083       1098.02103       1097.65945       1097.65965       1.00         7       6       6       3       D       1098.00475       1098.00451       1097.60577       1097.60553       1.00         1       2       1       1       SE       928.21039       928.21044       928.57805       928.57810       1.00         2       2       1       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       1       4       SA       928.97235       928.928.5787       928.54484       1.00         3       2       1       SC       928.18152       928.54485       928.54484       1.00         3       2       1       SC       926.83776       927.21761       927.21785       1.00         3       3       1       SC       926.83771       926.83776	4 3	2	3 67	1041.07940	1041.07902	1040.72578	1040.72000	1 00
7       6       5       3       D       1098.02083       1098.02103       1097.65945       1097.65965       1.00         7       6       6       3       D       1098.00475       1098.00451       1097.60577       1097.60553       1.00         1       2       1       1       J       888.04191       888.0419       888.40957       888.40885       0.25         2       2       1       1       SC       928.21039       928.21044       928.57805       928.57810       1.00         2       2       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       3       1       4       SA       928.97235       928.929.32597       929.32614       1.00         3       3       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       3       1	4 3	2	3 67	1041.04997	1041.00019	1040.00000	1040.00007	1 00
7       6       6       3       D       1098.00475       1098.00451       1097.60577       1097.60553       1.00         1       2       1       1       J       888.04191       888.0419       888.40957       888.40885       0.25         2       2       1       1       SC       928.21039       928.21044       928.57805       928.57810       1.00         2       2       1       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       3       1       4       SA       928.97235       928.97252       929.32597       929.32614       1.00         3       3       2       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3	7 6	5	חכנ	1091.00010	1092 02103	1097 65915	1040.02022	1 00
1       2       1       1       J       888.04191       888.04119       888.40957       888.40885       0.25         2       2       1       1       SC       928.21039       928.21044       928.57805       928.57810       1.00         2       2       1       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       3       1       4       SA       928.97235       928.97252       929.32597       929.32614       1.00         3       3       2       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       1       SC       926.83793       926.83776       927.21780       927.21785       1.00         3       3       1       F       926.83771       926.83776       927.21780       927.21785       1.00	7 6	6	ם ג מג	1098.00475	1098 00451	1097.60577	1097 60553	1 00
1211J888.04191888.04119888.40957888.408850.252211SC928.21039928.21044928.57805928.578101.002211SC928.21057928.21044928.57823928.578101.002221SC927.40348937.40340927.78124937.781161.003314SA928.97235928.97252929.32597929.326141.003321SC928.18153928.18152928.54485928.544841.003321SC928.18148928.18152928.54479928.544841.00331SC926.83752926.83776927.21761927.217851.00331F926.83793926.83776927.21780927.217850.10334SA926.83771926.83776927.21780927.217851.00	, 0	U	50	1090.00475	1000.00401	1097.00577	1031.00222	1.00
2       1       1       SC       928.21039       928.21044       928.57805       928.57810       1.00         2       2       1       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       3       1       4       SA       928.97252       929.32597       929.32614       1.00         3       3       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       1       F       926.83793       926.83776       927.21802       927.21785       0.10         3       3       1       F       926.83771       926.83776       927.21780       927.21785       1.00	12	1	Т. Г	888.04191	888.04119	888, 40957	888.40885	0.25
2       1       1       5C       526.21153       526.21153       526.21154       526.57655       526.57615       1.00         2       2       1       1       SC       928.21057       928.21044       928.57823       928.57810       1.00         2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       3       1       4       SA       928.97235       928.97252       929.32597       929.32614       1.00         3       3       2       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       1       F       926.83793       926.83776       927.21802       927.21785       0.10         3       3       1       F       926.83771       926.83776       927.21780       927.21785       1.00	2 2	1		928, 21039	928,21044	928-57805	928 57810	1.00
2       2       1       SC       927.40348       937.40340       927.78124       937.78116       1.00         3       3       1       4       SA       928.97235       928.97252       929.32597       929.32614       1.00         3       3       2       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       928.18148       928.18152       928.54485       928.54484       1.00         3       3       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       1       F       926.83793       926.83776       927.21780       927.21785       0.10         3       3       4       SA       926.83771       926.83776       927.21780       927.21785       1.00	2 2	ī		928,21057	928, 21044	928, 57823	928.57810	1.00
3       3       1       4       SA       928.97235       928.97252       929.32597       929.32614       1.00         3       3       2       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       928.18148       928.18152       928.54485       928.54484       1.00         3       3       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       1       F       926.83793       926.83776       927.21802       927.21785       0.10         3       3       4       SA       926.83771       926.83776       927.21780       927.21785       1.00	2 2	2	1 SC	927,40348	937.40340	927, 781 24	937, 781 16	1.00
3       3       2       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       928.18153       928.18152       928.54485       928.54484       1.00         3       3       2       1       SC       928.18148       928.18152       928.54479       928.54484       1.00         3       3       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       1       F       926.83793       926.83776       927.21802       927.21785       0.10         3       3       4       SA       926.83771       926.83776       927.21780       927.21785       1.00	วิวิ	ĩ	4 SA	928,97235	928,97252	929, 32597	929, 32614	1.00
3       3       2       1       SC       928.18148       928.18152       928.54479       928.54484       1.00         3       3       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       1       F       926.83793       926.83776       927.21802       927.21785       0.10         3       3       4       SA       926.83771       926.83776       927.21780       927.21785       1.00	3 3	2	1 SC	928, 18153	928, 18152	928,54485	928,54484	1.00
3       3       1       SC       926.83752       926.83776       927.21761       927.21785       1.00         3       3       1       F       926.83793       926.83776       927.21802       927.21785       0.10         3       3       4       SA       926.83771       926.83776       927.21780       927.21785       1.00	33	2	1 SC	928, 18148	928, 18152	928,54479	928,54484	1.00
3       3       1       F       926.83793       926.83776       927.21802       927.21785       0.10         3       3       4       SA       926.83771       926.83776       927.21780       927.21785       1.00	33	3	1 SC	926.83752	926.83776	927,2176]	927, 21785	1.00
3 3 3 4 SA 926.83771 926.83776 927.21780 927.21785 1.00	33	3	1 F	926.83793	926.83776	927.21802	927.21785	Ø.10
	3 3	3	4 SA	926.83771	926.83776	927.21780	927.21785	1.00
Appendix G (cont.)

J'	J"	к	Ty Ref. C	IR (obs) <sup>d</sup>	IR(calc) <sup>d,e</sup>	x≁m(obs) <sup>f</sup>	x↔m(calc) <sup>f</sup>	Wt.g
4	4	1	1 J	929.95537	929.95571	930.29113	930.29147	Ø.25
4	4	2	1 SC	929.18536	929.18555	929.53031	929.53050	1.00
4	4	2	1 SC	929.18516	929.18555	929.53012	929.53050	1.00
4	4	2	4 SA	929.18536	929.18555	929.53031	929.53050	1.00
4	4	3	1 SC	927.87716	927.87724	928.23803	928.23812	1.00
4	4	4	1 J	925.99262	925.99248	926.37699	926.37685	Ø.25
4	4	4	1 F	925.99209	925.99248	926.37646	926.37685	0.10
4	4	4		925.99240	925.99248	926.37676	926.37685	4.00
4	4	4	4 D**	925.99241	925.99248	926.37678	926.37685	1.00
5	5	3	1 SC	929.12288	929.12296	929.46098	929.46106	1.00
5	5	3	1 SC	929.12315	929.12296	929.46125	929.46106	1.00
5	5	3	1 F	929.12241	929.12296	929.46051	929.46106	0.10
5	5	3	1 FL	929.12287	929.12296	929.46098	929.46106	4.00
5	5	3	4 SA	929.12274	929.12296	929.46084	929.46106	1.00
5	5	4	1 SC	927.30030	927.30009	927.66052	927.66030	1.00
5	5	4	1 J	927.29996	927.30009	927.66017	927.66030	0.25
5	5	4	1 F	927.29820	927.30009	927.65841	927.66030	0.10
5	5	5	1 SC	924.86560	924.86553	925.25624	925.25617	1.00
5	5	5	1 J	924.86616	924.86553	925.25679	925.25617	0.25
6	6	4	1 SC	928.79037	928.79054	929.12367	929.12384	1.00
6	6	4	1 J	928.79067	928.79054	929.12397	929.12384	Ø.25
6	6	4	4 SA	928.79018	928.79054	929.12348	929.12384	1.00
6	6	6	1 F	923.45354	923.45384	923.85252	923.85282	0.10
7	7	3	1 SC	932.09898	932.09803	932.38414	932.38318	1.00
7	7	6	1 F	925.33155	925.33184	925.69591	925.69620	Ø.1Ø
7	7	6	1 F	925.33241	925.33184	925.69677	925.69620	0.10
7	7	7	1 SC	921.75374	921.75330	922.16325	922.16281	1.00
7	7	7	1 J	921.75469	921.75330	922.16420	922.16281	0.25
7	7	7	lFh	921.75462	921.75330	922.16413	922.16281	0.10
7	7	7	4 D	921.75343	921.75330	922.16294	922.16281	1.00
8	8	2	1 SC	934.85127	934.85307	935.09810	935.09991	1.00
8	8	2	4 SA	934.85121	934.85307	935.09805	935.09991	1.00
8	8	5	1 SC	930.04696	930.04690	930.34476	930.34469	1.00
8	8	5	1 SC	930.04654	930.04690	930.34434	930.34469	1.00
8	8	5	1 J	930.04671	930.04690	930.34450	930.34469	0.25
8	8	7	1 SC	923.94090	923.94057	924.31007	924.30974	1.00
8	8	7	1 SC	923.94084	923.94057	924.31001	924.30974	1.00
9	9	4	1 SC	933.96415	933.96618	934.20900	934.21104	1.00
9	9	5	1 SC	931.96844	931.96940	932.23375	932.23472	1.00
9	9	6	1 SC	929.41177	929.41186	929.70444	929.70453	1.00
9	9	9	1 SC	917.46528	917.46428	917.90296	917.90196	1.00
9	9	9	1 SC	917.46532	917.46428	917.90301	917.90196	1.00
10	10	7	1 SC	928.52593	928.52572	928.81501	928.81480	1.00

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Appendix G (cont.)

J'J"	К	Ту	b Ref.	c IR (obs) d	d,e IR(calc)	x-m(obs)	x-m(calc) <sup>f</sup>	Wt. <sup>g</sup>
			····					
10 10	8	1	SC	924.83897	924.83834	925.16938	925.16875	1.00
10 10	8	1	SC	924.83923	924.83834	925.16964	925.16875	1.00
10 IØ	9	1	SC	920.33626	920.33621	920.72077	920.72073	1.00
10 10	9	1	SC	920.33622	920.33621	920.72074	920.72073	1.00
10 10	9	1	J	920.33613	920.33621	920.72065	920.72073	0.25
10 10	9	4	D <sup>n</sup>	920.33583	920.33621	920.72035	920.72073	1.00
11 11	7	1	SC	930.82348	930.82461	931.07462	931.07575	1.00
11 11	7	4	SA	930.82286	930.82461	931.07400	931.07575	1.00
11 11	9	1	SC	923.20546	923.20458	923.53918	923.53831	1.00
11 11	9	1	SC	923.20616	923.20458	923.53988	923.53831	1.00
11 11	9	4	D	923.20502	923.20458	923.53875	923.53831	1.00
12 12	7	1	SC	933.06019	933.06577	933.27572	<b>933.</b> 281.3Ø	1.00
12 12	7	4	SA	933.06062	933.06577	933.27615	933.28130	1.00
12 12	10	1	SC	921.31381	921.31314	921.65249	921.65182	1.00
12 12	12	4	D	908.70549	908.70514	909.20633	909.20598	1.00
13 13	9	1	SC	928.71667	928.71725	928.95913	928.95971	1.00
14 14	12	1	SC	916.75101	916.75144	917.10470	917.10512	1.00
2 1	1	1	SC	967.85956	967.85961	968.23681	968.23695	1.10
2 1	1	1	F	967.86124	967.85961	968.23758	968.23695	0.10
21	1	4	SA	967.85943	967.85961	968.23677	968.23695	1.00
32	1	1	SC	988.39620	988.39647	988.76386	988.76413	1.00
32	2	1	FL	987.63283	987.63289	988.01058	988.01065	4.00
54	2	1	SC	1029.20904	1029.20974	1029.55399	1029.55469	1.00
54	4	1	SC	1026.30329	1026.30306	1026.68766	1026.68743	1.00
65	2	1	SC	1050.12685	1050.12788	1050.45020	1050.45123	1.00
6 5	4	1	SC	1047.37583	1047.37601	1047.73604	1047.73622	1.00
65	5	4	SĄ	1045.20105	1045.20068	1045.59169	1045.59132	1.00
65	5	4	D	1045.20087	1045.20068	1045.59151	1045.59132	1.00
76	1	1	SC	1071.68213	1071.68411	1071.97345	1071.97543	1.00
76	1	4	SA	1071.68178	1071.68411	1071.97310	1071.97543	1.00
76	5	1	SC	1066.43348	1066.43323	1066.79487	1066.79461	1.00
8 7	3	1	SC	1090.96955	1090.97202	1091.25470	1091.25717	1.00
8 7	3	1	J	1090.96971	1090.97202	1091.25486	1091.25717	Ø.25
8 7	5	1	SC	1087.64349	1087.64388	1087.97360	1087.97399	1.00
8 7	7	1	SC	1082.11772	1082.11520	1082.52723	1082.52471	1.00
87	7	4	SA	1082.11719	1082.11520	1082.52670	1082.52471	1.00

<sup>a</sup>All values in cm<sup>-1</sup>.

<sup>C</sup>Reference: sc = this work; J = Ref. 30; F = Ref. 28; FL = Ref. 28, Lamb dip; D = Ref. 66; SA = Ref. 68. Appendix G (cont.)

<sup>d</sup>IR frequency is a for first group of frequencies, s for second
group.

<sup>e</sup>Calculated values copied from Ref. 66.

<sup>f</sup>x = a for first group of frequencies; x = s for second group.
m = mean of s and a in ground state.

<sup>g</sup>Weight for least squares fitting.

<sup>h</sup>These transitions were not included in the fitting.

## APPENDIX H

Comparison of observed and calculated frequencies in the  $\nu_2$  band of 14  $_{\rm NH_3.}^{\rm a}$ 

J'	J''	ĸ	TY	<sup>b</sup> Ref. <sup>C</sup>	a⁺s(obs)	a≁s(calc) <sup>d</sup>	s←a(obs)	s←a(calc) <sup>d</sup>	Wt. <sup>e</sup>
1	2	1	2	SC	928.23184	928.23205	891.88171	891.88192	1.0
3	4	1	2	J	888.07792	888.07948	853.54676	853.54827	1.0
3	4	2	2	J	887.99880	887.99987	852.72375	852.72481	1.0
3 3	4 4	3 3	2 3	J HK	887.87698 887.87687	887.87685 887.87685	851.32706 851.32695	851.32699 851.32699	1.0 1.0
1 1 1 1 1	1 1 1 1 1	1 1 1 1 1	1 1 2 2 2	SC SC J SC F FL	967.99798 967.99890 967.99785 967.99768 967.99747 967.99773	967.99778 967.99778 967.99778 967.99778 967.99778 967.99778	931.62797 931.62890 931.62784 931.62767 931.62746 931.62773	931.62778 931.62778 931.62778 931.62778 931.62778 931.62778 931.62778	1.0 0.0 1.0 1.0 1.0 4.0
2 2 2	2 2 2	1 1 1	1 1 3	F FL SA	967.77553 967.77467 967.77470	967.77479 967.77479 967.77479	932.13696 932.13609 932.13613	932.13619 932.13619 932.13619	Ø.Ø 4.Ø 1.Ø
2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	1 1 2 2 3 3 4	F J JL F FL SA HK HK	967.73894 967.73854 967.73810 967.73853 967.73811 967.73860 967.73841 967.73836 967.73842 967.73842	967.73844 967.73844 967.73844 967.73844 967.73844 967.73844 967.73844 967.73844 967.73844 967.73844	931.33378 931.3337 931.33294 931.3337 931.33294 931.33343 931.33324 931.33319 931.33325 931.33325	931.33328 931.33328 931.33328 931.33328 931.33328 931.33328 931.33328 931.33328 931.33328 931.33328 931.33328	1.0 1.0 4.0 4.0 4.0 1.0 1.0 1.0
3	3	1	4	SA	967.44909	967.44916	932.88123	932.88125	1.0
3 3 3 3	3 3 3 3	2 2 2 2	1 1 2 2	F FL SC F	967.40706 967.40679 967.40676 967.40730	967.40686 967.40686 967.40686 967.40686	932.09429 932.09402 932.09398 932.09452	932.09408 932.09408 932.09408 932.09408	0.0 4.0 1.0 0.0

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Appendix H (cont.)

J'	J''	к	b TY	Ref. <sup>C</sup>	a≁s(obs)	a←s(calc) <sup>d</sup>	s≁a(obs)	s⊬a(calc) <sup>d</sup>	Wt. <sup>e</sup>
3	3	3	1	SC	967.3461Ø	967.34634	930.75676	930.75706	1.0
ר ר	ר ג	ר ג	1	SC SC	967.34645	967.34634	930.75719	930.75706	1.0
3	3	3	ī	F	967.34502	967.34634	930.75567	930.75706	ø.ø
3	3	3	2	SC	967.34635	967.34634	930.75701	930.75706	1.0
3	3	3	2	F	967.34675	967.34634	930.75741	930.75706	1.0
3	3	3	2	F	967.34588	967.34634	930.75654	930.75706	0.0
3	3	3	2	FL	967.34631	967.34634	930.75697	930.75706	4.0
3	3	3	4	SA	967.34642	967.34634	930.75708	930.75700	1.0
4	4	1	1	J	967.03011	967.03091	933.84179	933.84256	1.0
4	4	2	1	F	966.98132	966.98104	933.07615	933.07587	1.0
4	4	2	4	SA	966.98099	966.98104	933.07583	933.07587	1.0
4	4	3	1	SC	966,90520	966,90520	931,77358	931.77359	1.0
4	4	3	ī	SC	966.90531	966.90520	931.77369	931.77359	1.0
4	4	4	1	SC	966.81505	966.81475	929 <b>.89</b> 841	929.89813	1.0
4	4	4	1	SC	966.81484	966.81475	<b>929.8</b> 982Ø	929.89813	1.0
4	4	4	1	SC	966.81478	966.81475	929.89815	929.89813	1.0
4	4	4	1	F	966.81507	966.81475	929.89843	929.89813	1.0
4	4	4	1	J	966.81477	966.81475	929.89813	929.89813	1.0
5	5	1	4	SA	966.53238	966.53244	934.99404	<b>934.99</b> 4ø8	1.0
5	5	2	1	J	966.47380	966.47370	934.25231	934.25220	1.0
5	5	2	2	SC	966.47366	966.47370	934.25216	934.25220	1.0
5	5	2	3	SA	966.47364	966 <b>.</b> 4737Ø	934.25214	934.25220	1.0
5	5	3	1	F	966.38014	966,38001	932,99253	932,99235	1.0
5	5	3	ī	F	966.37959	966.38001	932.99198	932.99235	ø.ø
5	5	3	1	FL	966.38004	966.38001	932.99243	932.99235	4.0
5	5	3	1	FL	<b>966.379</b> 87	966.38001	932.99226	932.99235	<b>4.</b> Ø
5	5	3	2	F	966.38039	966.38001	932.99279	932.99235	0.0
5	5	3	2	SC	966.37992	966.38001	932.99231	932.99235	1.0
5	5	3	3	SA	966.37989	966.38001	932.99228	932.99235	1.0
2 5	2 5	2	4	5A DA	900.3/990	966 38001	932.99231	932.99235	1.0
5	J	J	-1	111/	300 <b>.</b> 37303	TAROC • 0005	JJL•JJLL0	736•77633	T•10
5	5	4	1	F	966.27018	966.26928	931.17832	931.17737	Ø.Ø
5	5	4	1	J	966.26934	966.26928	931.17748	931.17737	1.0
5	5	4	1	FL	966.26920	966.26928	931.17734	931.17737	4.0
5	5	4	2	F	966.26851	966.26928	931.17665	931.17737	0.0
5	5	4	2	г.Г	966.26931	966.26928	931.17745	931.17737	4.0

Appendix H (cont.)

Wt. <sup>e</sup>	s+a(calc) <sup>d</sup>	s+a(obs)	a+s(calc) <sup>d</sup>	a⊷s(obs)	Ref. <sup>C</sup>	b TY	K	J''	J'
1.0	931, 17737	931, 17739	966,26928	966, 26925	SA	3	4	5	5
1.0	931, 17737	931, 17733	966, 26928	966, 26919	SA	4	4	5	5
1.0	931.17737	931.17748	966.26928	966.26934	НК	3	4	5	5
1.0	928.75449	928.75453	966.15116	966.15122	SC	1	5	5	5
0.0	928.75449	928.75384	966.15116	966.15053	F	1	5	5	5
1.0	928.75449	928.75416	966.15116	966.15085	J	1	5	5	5
1.0	928.75449	928.75434	966.15116	966.15103	SC	2	5	5	5
Ø.Ø	928.75449	928.75393	966 <b>.15116</b>	966.15062	F	2	5	5	5
4.0	928.75449	928.75432	966.15116	966.15101	FL	2	5	5	5
1.0	928.75449	928.75449	966.15116	966.15118	SA	3	5	5	5
1.0	932.63573	932.63574	965.65206	965.65207	SC	1	4	6	6
1.0	932.63573	932.63575	<b>9</b> 65.65206	965.65208	J	1	4	6	6
4.0	932.63573	932.63578	<b>965.65</b> 2Ø6	<b>965.6</b> 5211	JL	1	4	6	6
1.0	932.63573	932.63570	965 <b>.</b> 652Ø6	965.65202	F	2	4	6	6
1.0	932.63573	932.63571	965.65206	965.65204	HK	4	4	6	6
Ø.Ø	930.30663	930.30699	965.49948	965.49985	F	1	5	6	6
4.0	930.30663	930.30652	965.49948	965.49938	FL	1	5	6	6
1.0	927.32303	927.32325	965.35393	965.35420	SC	1	6	6	6
1.0	927.32303	927.32337	965.35393	965.35433	F	1	6	6	6
1.0	<b>927.32</b> 3Ø3	927.32327	<b>9</b> 65 <b>.</b> 35393	965.35422	J	1	6	6	6
4.0	927.32303	927.32320	965.35393	965.35415	JL	1	6	6	6
1.0	927.32303	927.32314	965.35393	<b>9</b> 65 <b>.</b> 35409	HK	4	6	6	6
1.0	935.90391	935.90402	965.13790	965.13796	SC	1	3	7	7
1.0	935.90391	935.90332	965.13790	965.13726	F	2	3	7	7
1.0	934.23583	934.23573	964.97969	964.97958	J	1	4	7	7
1.0	934.23583	934.23571	964.97969	964.97957	SC	2	4	7	7
1.0	934.23583	934.23571	964.97969	964.97957	SA	3	4	7	7
4.0	932.01123	932.01107	<b>964.7</b> 9ø25	964.79008	FL	2	5	7	7
1.0	932.01123	932.01094	964.79025	964.78995	SA	3	5	7	7
1.0	929.16174	929.16157	964.59579	964.59561	F	1	6	7	7
1.0	929.16174	929.16200	964.59579	964.59604	SC	1	6	7	7
1.0	929.16174	929.16193	964.59579	964 <b>.</b> 59597	SC	1	6	7	7
1.0	929.16174	929.16139	964.59579	964.59543	F	2	6	7	7
1.0	929.16174	929.16166	964.59579	964.59570	SA	3	6	7	7
1 a	929.16174	929.16175	964.59579	964.59579	SA	4	6	7	7

Appendix H (cont.)

J'	J''	к	b TY	Ref. <sup>C</sup>	a≁s(obs)	a≁s(calc) <sup>d</sup>	s←a (obs)	s←a(calc) <sup>d</sup>	Wt.e
7	7	7	1	SC SC	964.4243Ø 964.42442	964.42405 964.42405	925.59976 925.59988	925.59961 925.59961	1.0
7	7	7	ī	J	964.42215	964.42405	925.59761	925.59961	ø.ø
7	7	7	2	F	964.42436	964.42405	925.59982	925.59961	1.0
7	7	7	2	FL	964.42410	964.42405	925.59956	925.59961	4.0
8	8	2	4	SA	964.60958	964.61009	938.61750	938.61804	1.0
8	8	2	3	SA	964.60963	964 <b>.6</b> 1009	938.61755	938.61804	1.0
8	8	5	ı	SC	964,04123	964,04128	933,82608	933, 82614	1.0
8	8	5	ī	J	964.04152	964.04128	933.82638	933.82614	ø.ø
8	8	5	1	FL	964.04115	964.04128	933.82600	933.82614	4.0
8	8	6	ı	SC	963, 79644	963, 79623	931,12226	931,12203	1.0
8	8	6	ī	F	963.79658	963.79623	931.12241	931.12203	1.0
8	8	6	1	J	963.79678	963.79623	931.12260	931.122Ø3	0.0
8	8	6	1	FL	963.79608	963.79623	931.12190	931.12203	4.0
8	8	6	4	SA	963.79620	963.79623	931.12203	931.12203	1.0
8	8	7	1	SC	963,55855	963.55858	927.74198	927.74201	1.0
8	8	7	1	F	963.55820	963.55858	927.74164	927.74201	1.0
8	8	7	1	FL	963.55853	963.55858	927.74196	927.74201	4.0
8	8	7	2	F	963.55816	963.55858	927.74159	927.74201	1.0
8	8	8	1	SC	963.36329	963.36273	923.57937	923.57902	1.0
8	8	8	2	F	963.36284	963.36273	923.57893	923.57902	1.0
8	8	8	2	FL	963.36262	963.36273	923.57871	923.57902	4.0
9	9	4	1	SC	963, 53399	963, 53473	937.69861	937,69933	1.0
9	9	4	ī	J	963.53426	963.53473	937.69889	937.69933	1.0
٩	٩	5	۱	SC	063 26022	063 26030	935 707/9	935 70766	าต
9	9	5	2	SC	963.26841	963.26939	935.70667	935.70766	1.0
•	-	•	-				2000.2001	2000.2.00	
9	9	6	1	F	962.97311	962.97370	933.15688	933.15748	0.0
9	9	6	1	F	962.97359	962.97370	933.15736	933.15748	1.0
9	9	6	2	F	962.97249	962.97370	933.15625	933.15748	0.0
9	9	6	2	FL CD	962.9/367	962.9/3/0	933.15743	933.15748	4.0
9	9	b	4	SA	902.9/358	902.9/3/0	22.12/32	933.15/48	1.0
9	9	7	1	SC	962.67017	962.66984	929.97074	929.97048	1.0
9	9	7	1	J	962.67042	962.66984	929.97098	929.97048	1.0
9	9	7	2	F	962.67358	962.66984	929.97415	929.97048	0.0

Appendix H (cont.)

J'	J''	К	b TY	Ref. <sup>C</sup>	a≁s(obs)	a≁s(calc) <sup>d</sup>	s≁a(obs)	s←a(calc) <sup>d</sup>	wt. <sup>e</sup>
9 9 9	9 9 9	8 8 8	1 1 2	F FL F	962.38858 962.38850 962.38779	962.38842 962.38842 962.38842	926.04591 926.04584 926.04513	926.04576 926.04576 926.04576	1.0 4.0 Ø.0
10	10	1	4	SA	963.33640	963.33775	942.41952	942.42117	1.0
10	1Ø	5	1	J	962.48927	962.48956	937.61180	937.61208	1.0
10	10	6	1	J	962.14463	962.14466	935.22142	<b>935.</b> 22146	1.0
1Ø	1Ø	8	1	J	961.41113	961.41104	928.55797	928.55790	1.0
10 10 10	10 10 10	1Ø 1Ø 1Ø	1 2 2	J F FL	960.85357 960.85195 960.85232	960.85230 960.85230 960.85230	918.62095 918.61933 918.61970	918.62058 918.62058 918.62058	Ø.Ø 1.Ø 4.Ø
11	11	3	4	SA	962.27982	<b>963.</b> 28081	942.56567	942.56672	1.0
11	11	8	4	SA	960.44817	960.44829	931.06208	831.06220	1.0
11 11 11 11 11 11 11	11 11 11 11 11 11 11	9 9 9 9 9 9	1 1 2 2 4 1	SC F FL FL SA J	960.01989 960.02063 960.01978 960.01989 960.01989 960.01987 960.01987	960.01993 960.01993 960.01993 960.01993 960.01993 960.01993 950.01993	926.88456 926.88529 926.88444 926.88456 926.88456 926.88454 926.88454	926.88461 926.88461 926.88461 926.88461 926.88461 926.88461 926.88461 926.88461	1.0 0.0 4.0 1.0 4.0 1.0
12	12	3	4	SA	961.66749	961.67016	944.11458	944.11773	1.0
12	12	1Ø	4	SA	958.49669	958.49673	924.94996	924.95002	1.0
13	13	7	4	SA	959.20274	959 <b>.</b> 20281	938.77080	938.77072	1.Ø
13	13	12	3	SA	956.39673	956.39709	916.42735	916.42882	1.0
13	13	13	3	SA	956.15095	956.15139	938.76125	908.76737	1.0
14 14 14	14 14 14	12 12 12	1 2 2	J J JL	955.05637 955.05556 955.05568		920.29067 920.28986 920.28999		Ø.Ø 1.Ø 4.Ø

Appendix H (cont.)

J'	J''	К	b TY	Ref. <sup>C</sup>	a≁s(obs)	a⁺s(calc) <sup>d</sup>	s⁺a(obs)	s≁a(calc) <sup>d</sup>	Wt. e
14 14	14 14	13 13	3 3	SA HK	954.57811 954.57841		913.28973 913.29003		1.Ø 1.Ø
14	14	14	3	SA	954.34693		904.78990		1.0
2	1	1	1	F	1007.54185	1007.54052	971.88341	971.88206	0.0
2	1	1	1	FL	1007.54048	1007.54052	971.88204	971.88206	4.0
2	1	1	4	SA	1007.54045	1007.54052	971.88201	971.88206	1.0
2	1	1	4	HK	1007.54067	1007.54052	971.88223	971.88206	1.0
3	2	1	2	J	1027.04671	1027.04703	992.45001	992.45030	1.0
3	2	2	1	F	1027.03381	1027.03295	991.6914Ø	991.69053	1.Ø
3	2	2	2	J	1027.03346	1027.03295	991.691Ø5	991.69053	1.Ø
4	3	3	2	SC	1046.37454	1046.37468	1011.20350	1011.20366	1.0
5	4	1	2	J	1065.59432	1065.59432	1034.01275	1034.01273	1.0
5	4	2	1	SC	1065.58180	1065.58172	1033.31587	1033.31579	1.0
5	4	2	2	J	1065.58242	1065.58172	1033.31649	1033.31579	1.0
5	4	2	4	SA	1065.58169	1065.58172	1033.31576	1033.31579	1.0
5	4	3	1	J	1065.56845	1065.56552	1032.13404	1032.13106	1.Ø
5	4	3	2	J	1065.56547	1065.56552	1032.13106	1032.13106	1.Ø
5	4	4	2	J	1065.56361	1065.56385	1030.42217	1030.42237	1.0
6	5	1	2	SC	1084.62355	1084.62370	1054.91248	1054.91262	1.Ø
6	5	1	3	SA	1084.62393	1084.62370	1054.91286	1054.91262	1.Ø
6	5	2	2	F	1084.60817	1084.60981	1054.25109	1054.25275	Ø.Ø
6	5	2	2	SC	1084.60984	1084.60981	1054.25276	1054.25275	1.Ø
6	5	2	3	SA	1084.60984	1084.60981	1054.25276	1054.25275	1.Ø
6	5	3	2	SC	1084.59311	1084.59313	1053.13049	1053.13045	1.Ø
6	5	3	2	FL	1084.59306	1084.59313	1053.13044	1053.13045	4.Ø
6	5	3	3	SA	1084.59314	1084.59313	1053.13052	1053.13045	1.Ø
6	5	4	2	SC	1084.58375	1084.58363	1051.51210	1051.51198	1.0
6	5	4	2	FL	1084.58370	1084.58363	1051.51206	1051.51198	4.0
6	5	4	3	SA	1084.58363	1084.58363	1051.51198	1051.51198	1.0

Appendix H (cont.)

J'	J''	к	b TY	Ref. <sup>C</sup>	a←s(obs)	a←s(calc) <sup>d</sup>	s∢a(obs)	s⊷a(calc) <sup>d</sup>	Wt. <sup>e</sup>
6 6 6	5 5 5	5 5 5	2 2 3	SC FL SA	1084.59931 1084.59924 1084.59925	1084.59927 1084.59927 1084.59927	1049.34639 1049.34631 1049.34633	1049.34637 1049.34637 1049.34637	1.0 4.0 1.0
7 7	6 6	1 1	1 4	SC SA	1103.48587 1103.48575	1103.48583 1103.48583	1075.82306 1075.82294	1075.82304 1075.82304	1.0 1.0
7	6	2	1	J	1103.46886	1103.46982	1075.20242	1075.20329	1.0
7 7 7	6 6 6	5 5 5	1 1 4	SC J SA	1103.43445 1103.43421 1103.43442	1103.43435 1103.43435 1103.43435	1070.59115 1070.59090 1070.59111	1070.59104 1070.59104 1070.59104	1.0 1.0 1.0
8	7	2	1	J	1122.16025	1122.16021	1096.11307	1096.11306	1.0
8	7	4	1	J	1122.10436	1122.10406	1093.71179	1093.71150	1.0

<sup>a</sup>All values in cm<sup>-1</sup>.

<sup>b</sup>Type: 1 = s+s two-photon; 2 = a+a two-photon; 3 = a+s infrared; 4 = s+a infrared.

<sup>C</sup> Reference: SC = this work; J = Ref. 29 ; F = Ref. 28; FL = Ref. 28 , Lamb dip; HK = Ref. 57,58 SA = Ref. 68.

<sup>d</sup>Calculated values copied from Ref. 63,65.

<sup>e</sup>Weight for least squares fitting.

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