

Pressure Broadening Measurement of the $\nu_2[{}^qR_-(0, 0)]$ Transition of ${}^{15}\text{NH}_3$ by a CO_2 Laser

TADAO SHIMIZU,* FUMIKO O. SHIMIZU,† R. TURNER,‡ AND TAKESHI OKA
Division of Physics, National Research Council of Canada, Ottawa 7, Ontario, Canada
 (Received 11 May 1971)

The near coincidence of the $P(16)$ line of the CO_2 laser in $10.6\ \mu\text{m}$ and the $\nu_2[{}^qR_-(0, 0)]$ line of ${}^{15}\text{NH}_3$ was used to measure the pressure broadening and the absolute absorption coefficient of the latter transition. The pressure broadening parameter was determined to be $\Delta\nu_p = 13.3 \pm 1.2\ \text{MHz/torr}$, and the transition dipole moment of the ν_2 vibrational transition was determined to be 0.23_D .

I. INTRODUCTION

Recent development of the infrared lasers has provided strong and monochromatic cw sources for infrared spectroscopy. Since the oscillation frequencies of the molecular infrared lasers (such as CO_2 and N_2O lasers) are not tunable, molecular absorption lines to be studied are "tuned in" to the laser lines by Stark shift¹⁻⁴ or by pressure broadening.⁵⁻⁷ The former method gives the accurate frequency differences between the laser line and the absorption line and provides information on the dipole moment, whereas the latter method gives the pressure broadening parameter and provides information on intermolecular interaction. The present paper is concerned with the latter method.

It has been found by conventional infrared spectroscopy⁸ that the frequency of the $\nu_2[{}^qR_-(0, 0)]$ transition of ${}^{15}\text{NH}_3$ is close to that of the $P(16)$ CO_2 laser line of the $10.6\text{-}\mu\text{m}$ band. Since the $\nu_2[{}^qR_-(0, 0)]$ line is well isolated from other strong absorption lines of ${}^{15}\text{NH}_3$, this near coincidence is ideal for a precise study of the collision broadening. Also the measurement gives a value for the collision time of rotational levels of NH_3 with $K=0$ which has never been measured by microwave pressure broadening. It has been stated empirically or theoretically that the pressure broadening

parameter of NH_3 is proportional to $[K^2/J(J+1)]^{1/n}$ with $n=2$ or 3 .⁹⁻¹² The measurement of pressure broadening for $K=0$ levels is of particular interest since the above formula gives zero for these levels.

II. EXPERIMENTAL

A stable CO_2 laser which oscillates in a single mode was used for the precise measurement of the absorption coefficient. The laser consisted of a 39-cm-long discharge tube with a water-cooling jacket and a semi-spherical mirror system which was supported by an Invar frame. The laser power was taken out through an Irtran concave mirror with partially transmitting dielectric coating; the output beam of the laser was rather divergent. Typical output power of the CO_2 $P(16)$ line was 300 mW. The variation of the output power of the laser was less than 5% over several hours of free running in the air-conditioned room; the frequency stability of the laser was estimated to be of the order of $10\ \text{MHz}/^\circ\text{C}$. The laser was tuned to various CO_2 lines by moving the concave mirror with a pressure spring; excellent tunability and resettability were obtained. A mixture of CO_2 (5%), N_2 (15%), and He (80%) was passed through the discharge tube at a pressure of about 10 torr.

The absorption cell was 31.85 cm long and 2 cm in diameter and was sealed with two NaCl windows. Longer absorption cells (up to 2 m in length) were also used for low-pressure measurements. The absorption cell and other gas-handling systems were all made of glass, and greaseless stopcorks were used for vacuum handling to avoid absorption of ammonia. The pressure of the gas was measured by a sensitive mercury manometer and an oil manometer. The $^{15}\text{NH}_3$ gas with more than 99% abundance of ^{15}N was used for the measurement.

The laser light after being transmitted through the absorption cell and a monochromator was detected by the use of a Golay cell. The resolution of the monochromator, which had a grating and a prism for dispersion, was better than 0.5 cm^{-1} . The reading of the monochromator was calibrated against a high-resolution infrared spectrometer referred to neon standard lines. The radiation of the laser was chopped at 10 Hz, detected by a phase-sensitive detector and displayed on a chart recorder.

III. OBSERVATION

Absorption of the $P(16)$ line of the CO_2 laser by the $\nu_2[{}^9\text{R}_L(0,0)]$ line of $^{15}\text{NH}_3$ was observed as a function of gas pressure. A strong absorption was observed indicating that the coincidence of the lines is fairly good as expected from the infrared spectroscopy. For example, a decrease of 7% in the transmitted power resulted from absorption in $^{15}\text{NH}_3$ at a pressure of 1 torr in a cell 32 cm long. At the higher pressure of 20 torr, the absorption was 98%. Care was taken to avoid saturation of the absorption in the low-pressure region. Because of the relatively large cross section of the laser beam the saturation effect was not appreciable if the pressure was 1 torr or higher. The transition moment $\mu E/h$ for the laser power density of 100-mW/cm^2 is less than 1 MHz while the pressure broadening width is 15 MHz at the pressure of 1 torr.

A. Self-Broadening

The pressure dependence of the absorption by pure $^{15}\text{NH}_3$ gas was measured at more than 100 points of

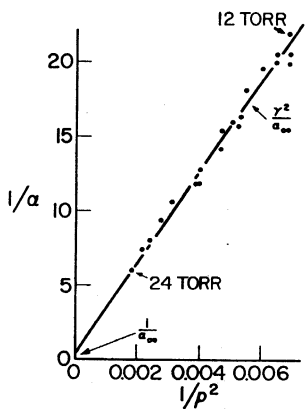


FIG. 1. Plot of observed $1/\alpha$ (cm) vs $1/p^2$ (torr^{-2}) where α is the absorption coefficient and p is the pressure of NH_3 . The deviation from the straight line at low pressures demonstrates that the absorption curve is not Lorentzian in this pressure region. The value of α_∞ and $\gamma = |\nu_L - \nu_0| / \Delta\nu_p$ is determined from the observed values in high-pressure regions.

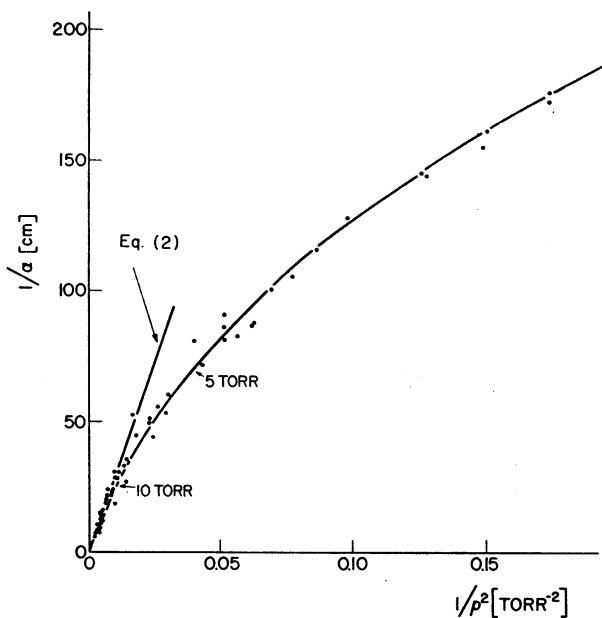


FIG. 2. Plot of observed $1/\alpha$ (cm) vs $1/p^2$ (torr^{-2}) in the high-pressure region.

pressure between 0.2 and 50 torr. The inverse of the measured absorption coefficient ($1/\alpha$) is plotted as a function of the inverse of the pressure squared ($1/p^2$) in Fig. 1. The observed points are on a straight line at pressure higher than 10 torr as expected for a Lorentzian line shape,

$$\alpha = A \{ \nu_L N \Delta\nu / [(\nu_L - \nu_0)^2 + (\Delta\nu)^2] \}, \quad (1)$$

where A is a constant, N is the density of molecule, $\Delta\nu$ is the pressure broadening, and ν_0 and ν_L are the frequencies of the center of absorption and of the laser oscillation, respectively. Since both $N (=np)$ and $\Delta\nu (= \Delta\nu_p p)$ are proportional to pressure, Eq. (1) can be rewritten as

$$\alpha^{-1} = (\alpha_\infty)^{-1} [1 + (\gamma^2/p^2)], \quad (2)$$

where $\alpha_\infty = A\nu_L N / \Delta\nu_p$ and $\gamma = |\nu_L - \nu_0| / \Delta\nu_p$. α_∞ represents the absorption coefficient at infinitely large pressure and is very close to the maximum absorption coefficient α_0 which is obtained from Eq. (1) by putting $\nu_L = \nu_0$. The observed values of α^{-1} deviate from the straight line in the low-pressure range ($p < 10$ torr); this means that the line shape is no longer a simple Lorentzian at the tail of the absorption. Whether this deviation is caused by the Doppler effect or by relatively large duration of collision so that the impact theory is no longer applicable, or by other weaker absorption lines of ammonia has not been made clear. We leave this interesting question as a future problem. The linear part of Fig. 1 is magnified in Fig. 2. The intersection of the straight line with the abscissa gives $1/\alpha_\infty$ and the slope of the straight line γ^2/α_∞ . The values of these parameters are listed in Table I.

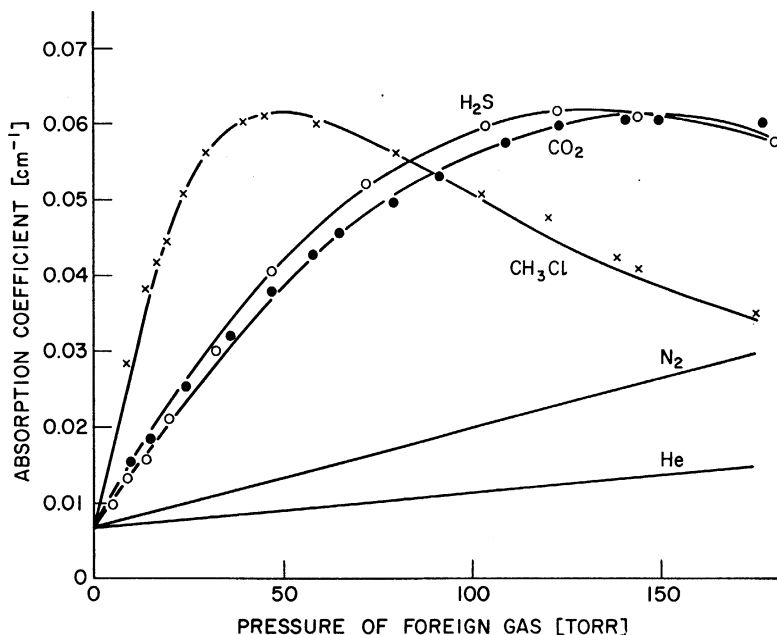


FIG. 3. Observed absorption coefficient α (cm^{-1}) vs foreign gas pressure. The pressure of $^{15}\text{NH}_3$ is 3.2 torr.

B. Foreign Gas Broadening

The pressure broadening of the $\nu_2[{}^aR_-(0, 0)]$ line caused by several foreign gases— CH_3Cl , SO_2 , CO_2 , N_2 , and He —was observed. The pressure of $^{15}\text{NH}_3$ was kept constant at about 3 torr and the pressure of the foreign gas was varied 0–200 torr. An example of the observed results is shown in Fig. 3. In general as the pressure of foreign gas was increased, the absorption also increased, reached a maximum, and then decreased with further increase of the pressure. The maximum point was reached only for CH_3Cl , SO_2 , and CO_2 which have relatively large cross sections for collisions with $^{15}\text{NH}_3$. This general behavior is understood as the result of “tuning in” the molecules by pressure broadening in the low-pressure region and subsequent flattening of the absorption profile at the high-pressure region.

For more quantitative discussion we substitute the following formula into Eq. (1):

$$\Delta\nu = \Delta\nu_p p_p + \Delta\nu_f p_f,$$

where $\Delta\nu_p$ and $\Delta\nu_f$ are the pure gas and foreign gas broadening parameters, respectively, and p_p and p_f are the pressures of ammonia and foreign gas, respec-

TABLE I. Molecular constants determined from the laser spectroscopy.

$(\alpha_\infty)^{-1} = 0.29 \text{ cm}$	$\alpha_\infty = 3.8 \pm 0.5 \text{ cm}^{-1}$
$\gamma/\alpha_\infty = 26.0 \text{ torr} \cdot \text{cm}$	$\gamma = \nu_0 - \nu_L /\Delta\nu_p = 104 \pm 10 \text{ torr}$
$\gamma^2/\alpha_\infty = 2971 \text{ torr}^2 \cdot \text{cm}$	
$\partial\mu/\partial Q = 139 \pm 15 \text{ esu}$	
$\Delta\nu_p = 13.3 \pm 1.2 \text{ MHz/torr}$	

tively. We obtain the expression for the absorption coefficient as

$$\alpha = \alpha_\infty p_p (p_p + R p_f) / \gamma^2 + (p_p + R p_f)^2, \quad (3)$$

where $R = \Delta\nu_f/\Delta\nu_p$. The maximum absorption α_{max} and the foreign gas pressure $(p_f)_{\text{max}}$, at which the maximum absorption is obtained, can be determined from Eq. (3) as

$$\alpha_{\text{max}} = \alpha_\infty p_p / 2\gamma$$

and

$$(p_f)_{\text{max}} = (\gamma - p_p) / R. \quad (4)$$

It is noted that the maximum absorption α_{max} is independent of which foreign gas is used. In addition to the two expressions containing α_∞ and γ in pure gas experiments, the foreign gas experiment gives one further quantity

$$\gamma/\alpha_\infty = p_p / 2\alpha_{\text{max}}$$

which can be obtained from the measurement of α_{max} . The constancy of this expression for various foreign gases is seen in Table II. The weighted mean value of the observed values of γ/α_∞ is given in Table I.

The accurate determination of $(p_f)_{\text{max}}$ was rather

TABLE II. Determination of γ/α_∞ from foreign gas broadening.

Foreign gas molecules	α_{max} (cm^{-1})	P_{NH_3} (torr)	γ/α_∞ (torr \cdot cm)
CH_3Cl	6.20×10^{-2}	3.20	25.8
SO_2	4.20×10^{-2}	2.20	26.0
CO_2	6.00×10^{-2}	3.10	25.8

difficult because of the broad peak of the observed curves shown in Fig. 3.

IV. RESULTS

As shown in Table I three independent quantities $1/\alpha_\infty$, γ/α_∞ , and γ^2/α_∞ have been determined from the pure gas and foreign gas broadening measurement. The value of α_∞ and γ are determined from these measured values to be

$$\alpha_\infty = 3.8 \pm 0.4 \text{ cm}^{-1} \quad (5)$$

and

$$\gamma = |\nu_0 - \nu_L| / \Delta\nu_p = 104 \pm 10 \text{ torr}. \quad (6)$$

In order to obtain the pressure broadening parameter $\Delta\nu_p$, the value of $|\nu_0 - \nu_L|$ is needed. The accurate determination of this quantity was attempted by applying an electric field and tuning the molecular absorption into the laser line. However, the highest electric field which is applicable to the molecule without discharge breakdown in the gas was not enough to shift the molecular line to the laser line because the second-order Stark shift of the [$^qR_-(0,0)$] line is rather small [$3 \times 10^{-8} \text{ MHz}/(\text{V}/\text{cm})^2$]. Recently the infrared spectrum of ¹⁵NH₃ in the 10- μm region has been analyzed by conventional high-resolution infrared spectroscopy⁸ and by laser-Stark spectroscopy.⁴ The accuracy of the latter method is so high that most of the frequencies of the observed transition are within 0.003 cm^{-1} from the calculated frequencies using a set of molecular constants. We adopt the calculated frequency of 947.789 cm^{-1} as ν_0 . On the other hand the absolute frequency of the $P(18)$ CO₂ laser line¹³ and the frequency difference between the $P(16)$ line and the $P(18)$ line¹⁴ have been accurately measured with the frequency beating method. From these data the frequency of the $P(16)$ line is calculated to be 947.743 cm^{-1} .¹⁵ Therefore the frequency difference between the ¹⁵NH₃ line and the laser line is

$$\nu_0 - \nu_L = 0.046 \pm 0.003 \text{ cm}^{-1}.$$

Using this value with the experimentally determined γ in Eq. (6) we obtain the pressure broadening parameter

$$\Delta\nu_p = 13.3 \pm 1.2 \text{ MHz/torr}. \quad (7)$$

In order to confirm that the process of deriving α_∞ and $\Delta\nu_p$ is correct, the value of α_0 and $\Delta\nu_p$ were measured with a conventional high-resolution spectrometer. A 2-m vacuum grating spectrometer^{16,17} with the resolution of about 0.1 cm^{-1} was used. The maximum absorption coefficient was determined to be $\alpha_0 = 3.4 \text{ cm}^{-1}$ from the observation of the spectral line at various pressures. The linewidth of the ν_2 [$^qR_-(0,0)$] line was measured in the pressure range 53–713 torr. Three cells with various lengths of absorption (1 cm, 4 mm, and 1 mm) were used. By measuring the slope of the linewidth-vs-pressure curve which is a straight line at high-pressure range, the pressure broadening parameter was deter-

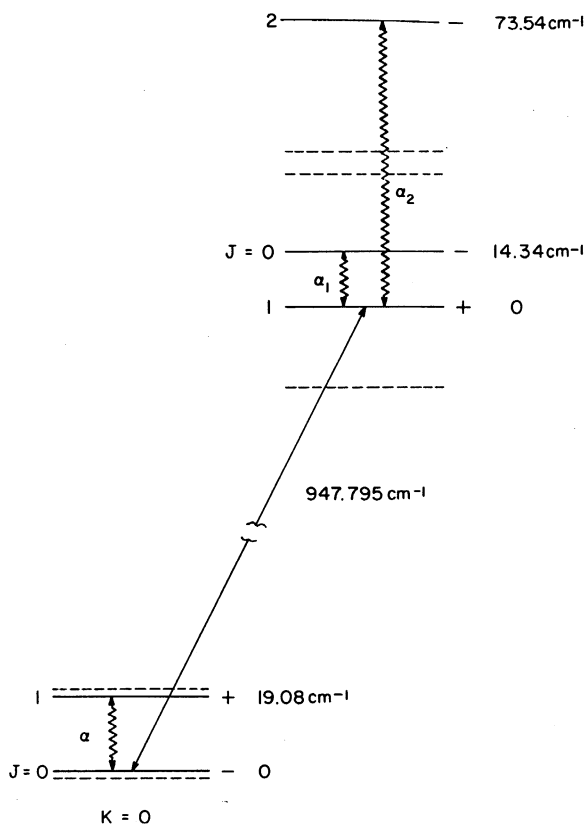


FIG. 4. Rotational levels of NH₃ relevant for the discussion of pressure broadening.

mined to be $\Delta\nu_p = 15.0 \text{ MHz/torr}$. Although the values determined in this way are less accurate than the values determined from laser spectroscopy, the agreement between the two sets of values confirms the correctness of the procedure.

V. DISCUSSION

It has been demonstrated that the laser spectroscopy described in this paper gives accurate values of $\alpha_\infty \sim \alpha_0$ and $\gamma = |\nu_0 - \nu_L| / \Delta\nu_p$. The value of α_∞ gives the transition dipole moment $(\partial\mu/\partial Q)Q_{01}$ and the dipole-moment derivative $\partial\mu/\partial Q$, and the value of γ combined with known value of $|\nu_0 - \nu_L|$ gives the pressure broadening parameter $\Delta\nu_p$. The value of the transition dipole moment $\delta\mu = (\partial\mu/\partial Q)Q_{01}$ is determined from the following formula¹⁸:

$$\alpha_\infty \sim \alpha_0 = \frac{8\pi^2 n_f f_{J,K} (\Phi_{JK}^{J'K'} \delta\mu)^2 \nu_0}{3ch \Delta\nu_p} \left[1 - \exp\left(-\frac{h\nu_0}{kT}\right) \right], \quad (8)$$

where $f_v = \prod_s [1 - \exp(-h\nu_s/kT)]^{2s} = 0.990$ is the inverse of the vibrational partition function, $f_{J,K} = \frac{3}{2} [B^2 C h^2 / \pi (kT)^3]^{1/2} = 0.00703$ is the fraction of the number of molecules in the $J=0$ and $K=0$ level, n is the number of molecules per cubic centimeter per torr at

the room temperature, ν is the frequency of the infrared transition, and $\Delta\nu_p$ is the pressure broadening parameter. $\Phi_{JK}^{J'K'}$ is the direction cosine matrix element between the two rotational levels which for NH_3 is expressed as

$$\Phi_{J,K}^{J'+1,K} = [(J+1)^2 - k^2] / (J+1)(2J+1).$$

Using the observed value of $\alpha_\infty = 3.8$ we obtain the transition dipole moment $\delta\mu = 0.239 \pm 0.02$ D and the dipole-moment derivative of $\partial\mu/\partial Q = 139$ esu. The latter value agrees very well with the value reported by McKean and Schatz,¹⁹ $\partial\mu/\partial Q = 138.5$ esu. The large vibrational transition moment makes the vibrational transition useful for various infrared experiments.^{4,20-22}

The pressure broadened width of the spectral line is expressed in terms of the lifetime of the upper rotational level τ_u and that of the lower rotational level τ_l as follows²³:

$$\Delta\nu = (4\pi)^{-1} [(\tau_u)^{-1} + (\tau_l)^{-1}]. \quad (9)$$

The rotational energy levels relevant for discussing the pressure broadening measured in this paper is shown in Fig. 4. Because of the "selection rules" ($\Delta K = 0$) governing the rotational transition induced by NH_3 - NH_3 collision²⁴ only the $K=0$ rotational levels are considered. The $K=0$ levels of NH_3 are different from $K \neq 0$ levels in that one component of the inversion doublet is absent because of the Pauli exclusion principle. Therefore the $\Delta J = 0$ transition (β transition) which contributes dominantly to the pressure broadening of microwave spectral lines ($K \neq 0$) is absent and the $\Delta J = \pm 1$ $\Delta K = 0$ transitions (α transition) indicated by wavy arrows in Fig. 4 are the most important transitions. Relatively large dipole matrix elements and the close spacing between the $J=0$ and $J=1$ levels in both upper and lower vibrational states make the probabilities of the $J=1 \leftarrow 0$ transition in the ground state (α transition) and the $J=0 \leftarrow 1$ transition in the excited state (α_1 transition) rather large to give $\Delta\nu_p = 13.3$ MHz/torr determined in this paper. The semi-empirical formula $\Delta\nu_p = [k^2/J(J+1)]^{1/n}$ (with $n=2$ or 3) obviously does not work in this case. Although the determination of the probabilities of individual transitions is not possible from this experiment, we can consider that the value of $2\pi\Delta\nu$ gives an approximate transition probability for the $J=1 \leftarrow 0$ transition in the ground state.

The method of pressure broadening measurement by the use of a laser will be generally applicable to many other molecules if (i) the absorption line to be studied is reasonably isolated from the other lines and (ii) the coincidence between the laser and the molecular absorption line is close.

ACKNOWLEDGMENTS

We wish to thank J. G. Potter and E. K. Pfitze for the design and construction of the stable CO_2 laser used in this paper, R. N. Jones for his helpful advice on infrared equipment, and J. W. C. Johns for his loan of the high-resolution spectrometer.

* Present address: Department of Physics, University of Tokyo, Tokyo, Japan.

† Present address: Sophia University, Tokyo, Japan.

‡ Present address: National Physical Research Laboratories, Pretoria, South Africa.

¹ K. Uehara, T. Shimizu, and K. Shimoda, *IEEE J. Quantum Electron.* **QE-4**, 728 (1968).

² T. Shimizu, K. Shimoda, and A. Minoh, *J. Phys. Soc. Japan* **24**, 1185 (1968).

³ R. G. Brewer, M. J. Kelly, and A. Javan, *Phys. Rev. Letters* **25**, 559 (1969).

⁴ F. Shimizu, *J. Chem. Phys.* **51**, 2754 (1969); **52**, 3572 (1970).

⁵ C. Borde and L. Henry, *IEEE J. Quantum Electron.* **QE-4**, 874 (1968).

⁶ T. K. McCubbin, Jr., and T. R. Mooney, *J. Quant. Spectry. Radiative Transfer* **8**, 1255 (1968).

⁷ T. Shimizu, Y. Ueda, and K. Shimoda, *Bull. Am. Phys. Soc.* **14**, 622 (1969).

⁸ F. O. Shimizu and T. Shimizu, *J. Mol. Spectry.* **36**, 94 (1970).

⁹ B. Bleary and R. P. Penrose, *Proc. Phys. Soc. (London)* **60**, 540 (1968).

¹⁰ H. Margenau, *Phys. Rev.* **76**, 121 (1969).

¹¹ W. V. Smith, *J. Chem. Phys.* **25**, 510 (1955).

¹² R. L. Legan, J. A. Robarts, E. A. Rinehart, and C. C. Lin, *J. Chem. Phys.* **43**, 4337 (1965).

¹³ K. M. Evenson, J. S. Wells, and L. M. Matarrese, *Appl. Phys. Letters* **16**, 251 (1970).

¹⁴ T. J. Bridges and T. Y. Chang, *Phys. Rev. Letters* **22**, 811 (1969).

¹⁵ T. Y. Chang, *Opt. Commun.* **2**, 77 (1970).

¹⁶ A. E. Douglas and D. Sharma, *J. Chem. Phys.* **21**, 448 (1953).

¹⁷ J. W. C. Johns, H. F. Shurvell, and J. K. Tyler, *Can. J. Phys.* **47**, 893 (1969).

¹⁸ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).

¹⁹ D. C. McKean and P. N. Schatz, *J. Chem. Phys.* **24**, 316 (1959).

²⁰ T. Shimizu and T. Oka, *Phys. Rev. A* **2**, 1177 (1970).

²¹ T. Y. Chang, T. J. Bridges, and E. G. Burkhardt, *Appl. Phys. Letters* **17**, 357 (1970).

²² T. Oka and T. Shimizu, *Appl. Phys. Letters* (to be published).

²³ V. W. Weisskopf and E. Wigner, *Z. Physik* **63**, 54 (1930).

²⁴ T. Oka, *J. Chem. Phys.* **48**, 4919 (1968).