

Microwave studies of collision-induced transitions between rotational levels. VIII. Collisions between NH₃ and polar molecules

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The technique of four-level microwave double resonance has been applied to the study of rotation-inversion transitions of NH₃, induced by collisions with various polar molecules. H₂O, D₂O, CH₃OH, CH₃X and CHX₃ (X = F, Cl, Br, I), NO, CO, and OCS were used as collision partners. The values of $\eta = \Delta I/I$ observed for many four-level systems which are connected by dipole-type transitions ($\Delta J = \pm 1$, $\Delta K = 0$, parity $+\leftrightarrow -$) are given and qualitatively explained taking into account the long-range dipole-dipole interaction and the pattern of rotational energy levels of the collision partners.

I. INTRODUCTION

Flygare has contributed greatly to our understanding of rotational energy transfer processes through his studies of coherent transient emission and absorption.¹ Together with his collaborators he used the latter phenomena for the measurement of relaxation times T_1 and T_2 . Of particular importance is his work on NH₃,^{2,3} in which T_1 and T_2 were shown to be not equal but $2 \geq T_2/T_1 \geq 1$ for many levels of NH₃. This had been earlier shown by the transient nutation experiment of Schwendeman *et al.* [Ref. 4(a) where t and τ were used for T_1 and T_2] and by the molecular beam experiment of Kukolich *et al.* [Ref. 4(b) where the one-cavity cross section σ_I and the two-cavity cross section σ_{II} were related to T_1 and T_2], but Flygare brought the ratio T_2/T_1 to the fore and showed this relation systematically for many NH₃ inversion lines. Subsequently, Amano and Schwendeman⁵ measured the values of T_2/T_1 accurately by using power broadening. The significant difference between the values of T_1 and T_2 is due to the special arrangement of the NH₃ rotation-inversion levels in which the collision-induced transition rates between closely spaced inversion levels (the β transition in Fig. 1 to be shown later) are much larger than those between much farther separated levels with different J levels (α and γ transitions in Fig. 1). Note that the rate for the β transition appears twice in the expression of $1/T_1$ but only once in that of $1/T_2$.²⁻⁵ Thus, in the extreme case in which we can consider a pair of inversion levels as isolated levels we have $T_2 = 2T_1$, if we neglect the effect of phase changing collisions.

In the present paper we report further studies on NH₃ using polar molecules as collision partners. The dominant interaction in such a case is the long-range dipole-dipole interaction but depending on the energy levels of collision partners remarkable differences in the ratio of the rates for $\Delta J = 0$ β transitions and $\Delta J = \pm 1$ α and γ transition were observed. Three types of molecules were used as collision partners: asymmetric tops H₂O,

D₂O, CH₃OH, symmetric tops CH₃X and CHX₃ (X = F, Cl, Br), CH₃I, and CH₃CN, linear molecules NO, CO, and OCS. Although the experiments were performed several years ago and part of them were referred in a review paper,⁶ publication of the detailed results has been urged in view of the recent revival of activities in this field both in theory⁷⁻¹¹ and in experiment.¹²⁻¹⁵ In particular the results of the recent detailed measurement^{16,17} of cross sections of NH₃ with polar gases using beam masers by the Nijmegen group are relevant to interpretation of our results.

II. FOUR-LEVEL DOUBLE RESONANCE EXPERIMENT

The four level system of NH₃ used for experiments are shown in Fig. 1. The strong pump microwave radiation shown in Fig. 1 with the bold arrow pumps the inversion levels for the J rotational state and equalizes the population between these two levels. This population anomaly is then transferred to the monitoring levels for $J - 1$ due to the parity changing transitions α and parity conserving transitions γ . This transferred population anomaly is dissipated by the transition β between the monitored levels and by the transitions η and ξ (which are assumed to be equal in this paper) which connects the monitored levels to the thermal bath; the latter transitions include all transitions other than α , β , and γ . The variation of the absorption ΔI for the $J - 1$ inversion transition is monitored by the second microwave radiation which is sufficiently weak that it does not itself change the population. A simple first order rate equation analysis^{6,18} gives the fraction of signal change $\Delta I/I$ as

$$\eta = \frac{\Delta I}{I} = \frac{\nu_p}{\nu_s} \cdot \frac{k'_\alpha - k'_\gamma}{k'_\alpha + k'_\gamma + 2k'_\beta + k'_\xi}, \quad (1)$$

where ν_p and ν_s are the frequencies of the pump and signal radiation respectively, k'_α , etc. are rate constants corresponding to the specified transitions, and the arrow in k'_α represents the rate for the transition upward from the $J - 1$ level to the J level. k'_α is related to the rate for the transition downward k''_α by the principle of detailed balancing $k'_\alpha/k''_\alpha = (2J + 1) \exp(-2BJh/kT)/(2J - 1)$ where the rotational constant B of NH₃ is ~ 10 cm⁻¹.

Equation (1) indicates that the large value of η is ob-

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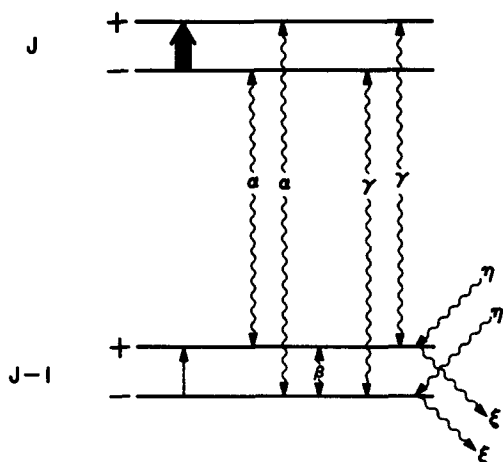


FIG. 1. The four-level system of NH₃ used for the double resonance experiments. A powerful pump microwave radiation (~ 10 W shown with the bold arrow) saturates the inversion transition for the J levels and equalizes the population between the doublet. This nonthermal population is then transferred to the inversion doublet with $J-1$ by collision-induced transitions α (which changes parity) and γ (which conserves parity). The anomalous population introduced is dissipated by the transition β between the doublet and the transition η and ξ which connect the $J-1$ doublet to other levels. A weak signal microwave radiation (~ 10 μ W shown with the thin arrow) probes the variation ΔI of the intensity of the $J-1$ inversion line. The + or - sign beside the levels indicates the parity of the levels. The case with odd K value is shown in this figure; opposite parities should be used for even K .

tained if (a) the transition obeys parity $+\leftrightarrow-$, i. e., $k_\alpha > k_\gamma$ and (b) if rates of the dissipating transition k_β and k_ξ are not much larger than k_α . For pure NH₃ collisions¹⁸ the former is satisfied but the latter is not, especially for levels with $K \sim J$. Thus, η values on the order of 1% were observed for $J-1=K$ levels.¹⁸ Larger η values were observed for $J-1 > K$ levels, the highest value being 8.2% for the $(4, 1)_{\text{pump}} - (3, 1)_{\text{signal}}$ system. We see from the above argument that the reason for a small η value in NH₃ is precisely the reason for a large value of T_2/T_1 . The relation between T_2/T_1 and η have been discussed by Hoke *et al.*³ and by Amano and Schwendeman.⁵ If we neglect the effect of phase changing collisions on T_2 , we have

$$\frac{k_\beta}{k_\alpha - k_\gamma} = \frac{1 - T_1/T_2}{\eta} \quad (2)$$

The details of the apparatus and the experimental procedure can be found elsewhere.¹⁸ In each experiment approximately 10 mTorr of NH₃ were mixed in the microwave cell with one of the polar gases at about 200 mTorr. This mixing ratio (1:20) was sufficient to assure for most polar gases with large dipole moments that the rotational transitions observed are dominantly produced by NH₃-polar gas collisions. The η values were measured at least twice for each four-level system with different mixtures. The observations were made by monitoring particular inversion signals and scanning the pump frequencies until a change in the signal intensity was observed. The uncertainty in the observed value of η is estimated to be $\pm 1\%$.

III. OBSERVED RESULTS AND INTERPRETATION

A. H₂O and D₂O as collision partners

The observed values for the NH₃-H₂O and NH₃-D₂O collisions are listed in Table I together with the NH₃ results for a comparison. The results for the series of four-level systems $(J, K)_p - (J-1, K)_s$ with $J-1=K$ are plotted in Fig. 2 for NH₃-H₂O and NH₃-NH₃. It is remarkable that the values of η for both of the NH₃-H₂O collisions and the NH₃-D₂O collisions are one order of magnitude greater than the corresponding η values for the NH₃-NH₃ collision.

This large increase in η values is most likely due to the decrease of the rate constant k_β in the denominator of Eq. (1). The β transition for which $\Delta J=0$ and parity changes ($+\leftrightarrow-$) is caused by the dipole-dipole interaction between NH₃ and the collision partner, in which the latter also has to change its parity. In order for this to occur efficiently the whole system of NH₃ and the collision partner must conserve total rotational energy before and after the collision; otherwise the transition probability falls off drastically due to the resonance factor of Tsao and Curnutte²⁰ and van Kranendonk.^{21,6} The NH₃ molecule as the collision partner can easily satisfy this condition because of the parity changing transition between inversion doublets but H₂O and D₂O cannot. The parity changing transition in H₂O and D₂O (for which $\Delta K_c = \text{odd}$ and $\Delta K_a = \text{odd}$)²² are always between widely separated levels because of the large value of the A rotational constant (~ 28 cm⁻¹) and cannot "resonate" with the NH₃ inversion β transition. On the other hand, they can resonate with α transitions of NH₃ with the right energy spacing (which are listed in Table I). In order to see this situation the observed far infrared

TABLE I. Observed values of $\eta = \Delta I/I$ for the NH₃-H₂O, NH₃-D₂O, and NH₃-NH₃ collisions.

Pumped doublet $(J, K)_p$	Signal doublet $(J, K)_s$	Separation ^a (cm ⁻¹)	$\Delta I/I$ (%)		
			H ₂ O ^b	D ₂ O ^b	NH ₃ ^c
(2, 1)	(1, 1)	39.7	15.5	14.0	1.46
(3, 2)	(2, 2)	59.6	11.0	10.0	1.19
(4, 3)	(3, 3)	79.4	7.5	7.0	1.06
(5, 4)	(4, 4)	99.3	6.5	6.0	0.80
(6, 5)	(5, 5)	119.1	4.0	4.0	0.63
(7, 6)	(6, 6)	138.8	2.0	2.0	0.35
(3, 1)	(2, 1)	59.6	16.0	16.0	4.43
(4, 2)	(3, 2)	79.4	11.5	11.0	2.50
(5, 3)	(4, 3)	99.2	9.5	8.5	2.02
(6, 4)	(5, 4)	118.9	5.5	4.5	1.56
(7, 5)	(6, 5)	138.6	4.0	3.5	0.88
(8, 6)	(7, 6)	156.2	1.5	2.0	0.56
(4, 1)	(3, 1)	79.4	18.0	16.0	8.22
(5, 2)	(4, 2)	99.1	12.0	12.0	4.62
(6, 3)	(5, 3)	118.8	6.5	...	1.91
(3, 1)	(1, 1)	99.3	-5.0	-4.5	d

^aSeparation of the centers of the pump and the signal levels after Kauppinen's far infrared measurement in Ref. 19.

^bThe uncertainty of the η value is $\pm 1\%$.

^cThe uncertainty of the η value is $\pm 0.2\%$.

^dThe signal was not observed in NH₃-NH₃ collision.

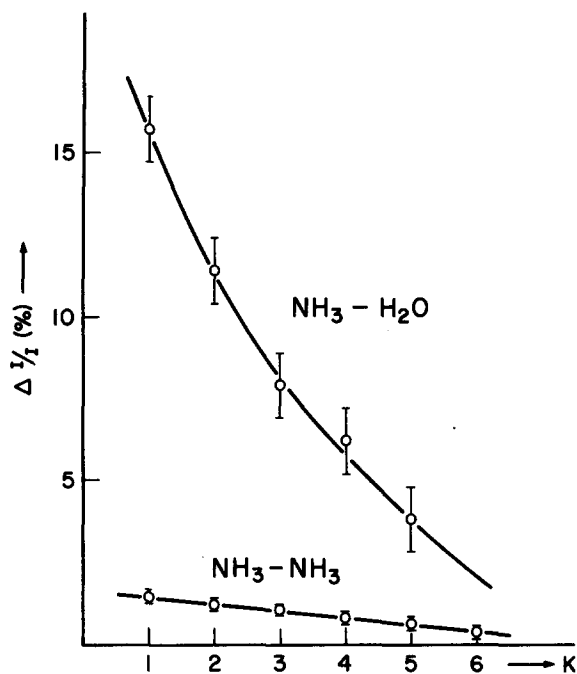


FIG. 2. Comparison of the values of $\eta = \Delta I/I$ for the four level systems $(J, K)_p - (J-1, K)_e$ ($J-1=K$) of NH_3 - H_2O mixture and NH_3 - NH_3 mixture.

spectrum of H_2O^{23} is shown in Fig. 3 in which the energy separations of NH_3 are shown with arrows. It is noticed that $\Delta J=1$ transitions of NH_3 have near coincidences with H_2O rotational transitions. For example, the $(2, 1) \rightarrow (1, 1)$ transitions of NH_3 at 40.536 and 38.976 cm^{-1} are near resonant with the strong H_2O transitions $3_{21} \rightarrow 3_{12}$ at 38.792 cm^{-1} and $3_{03} \rightarrow 3_{02}$ at 36.606 cm^{-1} , and the $(3, 2) \rightarrow (2, 2)$ transitions of NH_3 at 60.387 and 58.835 cm^{-1} are near resonant with H_2O transitions of $5_{32} \rightarrow 5_{23}$ at 62.301 cm^{-1} , $3_{03} \rightarrow 2_{12}$ at 57.269 cm^{-1} , and $2_{12} \rightarrow 1_{01}$ at 55.705 cm^{-1} , etc.

The far infrared spectrum of D_2O is expected to be similar to that of H_2O except for the lower rotational

constants and thus a more closely packed spectrum. Therefore, it had been expected that D_2O would also give high η values but the observed close similarity of η values between NH_3 - H_2O collisions and NH_3 - D_2O was surprising. It would be of great interest to carry out theoretical calculations on these systems using either Anderson's theory^{24,18} or modified Anderson's theory^{16,17} to see if results obtained in this work can be explained quantitatively. Such a calculation will reveal whether the long-range dipole-dipole interaction is sufficient to explain our system quantitatively or the hydrogen bonding force between NH_3 and H_2O has also to be considered.

The decrease of η for the series of double resonance as J increases is due to the decrease of k_α in the numerator of Eq. (1). This is because of the $\sqrt{J^2 - K^2}/J$ factor in the dipole matrix element for $\Delta J=1$.¹⁸

B. CH_3OH , CH_3H ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$), and CF_3H as collision partners

The six molecules CH_3OH , CH_3F , CH_3Cl , CH_3Br , CH_3I , and CF_3H give qualitatively similar values of η ; the observed results are listed in Table II together with their dipole moments and rotational constants.²⁵ The observed results are summarized as follows: (i) For the lowest double resonance system $(2, 1)_p - (1, 1)_e$, CH_3OH , CH_3F , CH_3Cl , and CF_3H give η values which are much smaller than those for H_2O and D_2O but are larger than those for pure NH_3 case. (ii) The η values decrease rapidly as we probe levels with higher J values, and as we use heavier molecules in the series of CH_3X ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). Qualitative interpretation of these trends are given below.

(i) The six molecules studied are different from H_2O and D_2O in that they can resonate with the β transitions of NH_3 through (a) their double parity levels with $K \neq 0$ and (b) their low J $\Delta J \neq 0$ transitions. The former is much more significant than the latter because the percentage of molecules in $K \neq 0$ levels is higher than that

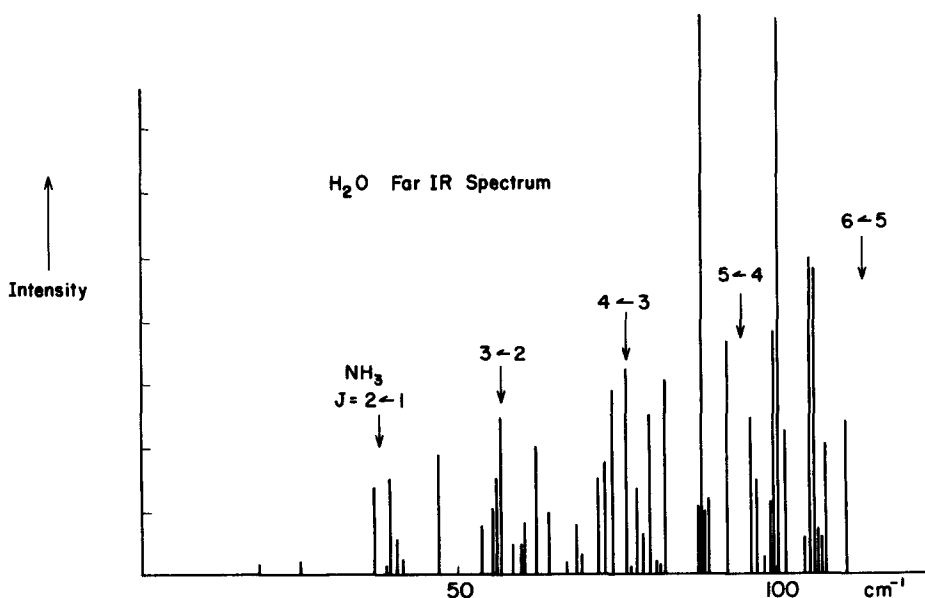


FIG. 3. Rotational spectrum of H_2O reported by Hall and Dowling (Ref. 23). The positions of $\Delta J=1$ transitions NH_3 are shown by arrows. Note the approximate resonance between NH_3 and H_2O .

TABLE II. Observed values of $\eta = \Delta I/I$ for NH₃ mixed with CH₃OH, CH₃F, CH₃Cl, CH₃Br, CH₃I, and CF₃H.

Pumped doublet (J, K) _p	Signal doublet (J, K) _s	$\Delta I/I$ (%)					
		CH ₃ OH ^a	CH ₃ F $\mu = 1.905$ D $B = 25.54$ GHz	CH ₃ Cl $\mu = 1.869$ D $B = 13.293$ GHz	CH ₃ Br $\mu = 1.797$ D $B = 9.568$ GHz	CH ₃ I $\mu = 1.65$ D $B = 7.501$ GHz	CF ₃ H $\mu = 1.64$ D $B = 10.349$ GHz ^b
(2, 1)	(1, 1)	4.0	4.0	3.0	1.5	1.0	3.0
(3, 2)	(2, 2)	1.5	0.5	0.5	0.0	0.0	1.5
For ($J=K+1, K$) _p - ($J=K, K$) _s system with $K \geq 3$ $\eta = 0$							
(3, 1)	(2, 1)	5.0	3.0	1.5	0.0	0.0	5.0
(4, 2)	(3, 2)	2.5	0.0	0.0	0.0	0.0	2.5
For ($J=K+2, K$) _p - ($J=K, K$) _s system with $K \geq 3$ $\eta = 0$							

^aThe dipole moment parallel to CO is 0.885 D, perpendicular to CO is 1.44 D.

^bCH₃CN ($\mu = 3.92$ D, $B = 9.199$ GHz), CHCl₃ ($\mu = 1.2$ D, $B = 3.302$ GHz), and CHBr₃ ($B = 1.248$ GHz) did not produce observable signals.

of molecules in low J levels. We can consider the double parity levels as inversion doublets with very small splittings. CH₃OH is an asymmetric top molecule and has rotational level pattern qualitatively different from other symmetric top molecules but it can resonate with β transitions through the double parity levels in the degenerate torsional state²² and through K -doublet levels with small splittings. Thus, the values of η are lower for these molecules than for H₂O and D₂O because of the larger values of k_β in the denominator of Eq. (1). Compared with pure NH₃ case, the observed η values are higher for the (2, 1)_p - (1, 1)_s system and this is due to the larger values of k_α in the numerator of Eq. (1). The higher value of k_α is explained as due to the fact that CH₃OH, CH₃F, CH₃Cl, and CF₃H has more fraction of molecules (than NH₃) resonating with the $J=2 \rightarrow 1$ α transitions of NH₃. The J number for maximum population at temperature T for a symmetric top molecule with rotational constants A and B is estimated to be

$$J_{\max} \sim (\phi kT/2Bh)^{1/2}, \quad (3)$$

where $\phi = 1$ for a linear molecule or for $A \gg kT$, $\phi = 2$

for a spherical top ($A=B$), and ϕ is larger than two for an oblate top. For the series of symmetric top molecules CH₃F, CH₃Cl, CH₃Br, CH₃I, and CF₃H, the estimated values of J_{\max} are 11, 16, 19, 21, and 27, respectively, and the corresponding rotational separations are 19, 14, 12, 11, and 19 cm⁻¹. The population varies slowly around the maximum value and thus has significant fraction which can resonate with the $J=2 \rightarrow 1$ α transition at 40 cm⁻¹. The fact that k_α is larger for NH₃-CH₃F and NH₃-CF₃H collisions than for NH₃-NH₃ collisions has been also reported more quantitatively by Klaassen *et al.*¹⁷

(ii) The rapid decrease of η values for higher J values is partly due to the matrix element discussed in the previous section but also because of the lack of resonance due to the larger moments of inertia of collision partners. For heavier molecules of the series even the lowest α transition $J=2 \rightarrow 1$ does not resonate with collision partners and η values are very small. CH₃CN, CHCl₃, and CHBr₃ did not produce observable signals.

TABLE III. Observed values of $\eta = \Delta I/I$ for NH₃ mixed with NO, CO, and OCS.

Pumped doublet (J, K) _p	Signal doublet (J, K) _s	$\Delta I/I$ (%)		
		NO $\mu = 0.16$ D $B = 51.08$ GHz	CO $\mu = 0.11$ D $B = 57.90$ GHz	OCS $\mu = 0.709$ D $B = 6.081$ GHz
(2, 1)	(1, 1)	7.0	4.0	1.0
(3, 2)	(2, 2)	3.0	2.5	0.5
(4, 3)	(3, 3)	1.5	1.5	0.0
(5, 4)	(4, 4)	0.5	0.0	0.0
(6, 5)	(5, 5)	0.5	0.0	0.0
(3, 1)	(2, 1)	7.5	6.5	2.0
(4, 2)	(3, 2)	3.5	3.5	0.5
(5, 3)	(4, 3)	3.0	2.0	0.0
(6, 4)	(5, 4)	2.0	0.5	0.0
(7, 5)	(6, 5)	1.0	0.0	0.0
$\Delta J = 2$				
(3, 1)	(1, 1)	-1.5	-1.0	0.0
(4, 2)	(3, 2)	-1.5	-1.0	0.0

C. NO, CO, and OCS as collision partners

The observed η values for NO, CO, and OCS are listed in Table III. The η values for NO and CO are larger than the corresponding η values for nonpolar molecules²⁶ O₂ and N₂ by a factor of 1.3–2.2 but show similar J , K dependence. The η values are larger because of the dipole moments of NO and CO albeit very small. The unpaired electron in NO provides double parity levels which can resonate with the NH₃ β transitions and thus can make η values small. The observed results show, however, that the effect of this is small, probably because of the small dipole matrix elements between the Λ doublets. The η values for NO and CO are comparable to those for symmetric rotors listed in Table V for the lowest double resonance system; this is because the smallness of k_α due to small dipole moments of NO and CO is compensated by the smallness of k_β due to lack of resonance. However, the larger rotational constants of NO and CO make the η values observable for higher J systems. For OCS which has a small rotational constant η values are low.

¹J. C. McGurk, T. G. Schmalz, and W. H. Flygare, *Adv. Chem. Phys.* **25**, 1 (1974).

²W. E. Hoke, J. Ekkers, and W. H. Flygare, *J. Chem. Phys.* **63**, 4075 (1975).

³W. E. Hoke, D. R. Bauer, J. Ekkers, and W. H. Flygare, *J. Chem. Phys.* **64**, 5276 (1976).

⁴(a) A. H. Brittain, P. J. Manor, and R. H. Schwendeman, *J. Chem. Phys.* **58**, 5735 (1973). (b) S. G. Kukolich, J. H. S. Wang, and D. E. Oates, *Chem. Phys. Lett.* **20**, 519 (1973); J. H. S.

Wang, D. E. Oates, A. Ben-Ruben, and S. G. Kukolich, *J. Chem. Phys.* **59**, 5268 (1973).

⁵T. Amano and R. H. Schwendeman, *J. Chem. Phys.* **65**, 5133 (1976).

⁶T. Oka, *Adv. At. Mol. Phys.* **9**, 127 (1973).

⁷S. Green, *J. Chem. Phys.* **64**, 3463 (1976).

⁸S. L. Davis and J. E. Boggs, *J. Chem. Phys.* **69**, 2355 (1978).

⁹S. Green, *J. Chem. Phys.* **73**, 2740 (1980).

¹⁰M. H. Alexander, *J. Chem. Phys.* **77**, 1855 (1982).

¹¹K. L. Peterson, *J. Chem. Phys.* **75**, 5655 (1981).

¹²S. Kano, T. Amano, and T. Shimizu, *J. Chem. Phys.* **64**, 7411 (1976).

¹³N. Morita, S. Kano, Y. Ueda, and T. Shimizu, *J. Chem. Phys.* **66**, 2226 (1977).

¹⁴N. Morita, S. Kano, and T. Shimizu, *J. Chem. Phys.* **68**, 3897 (1978).

¹⁵T. Amano, T. Amano, and R. H. Schwendeman, *J. Chem. Phys.* **73**, 1238 (1980).

¹⁶D. B. M. Klaassen, J. M. H. Reijnders, J. J. ter Meulen, and A. Dymanus, *J. Chem. Phys.* **76**, 3019 (1982).

¹⁷D. B. M. Klaassen, J. J. ter Meulen, and A. Dymanus, *J. Chem. Phys.* **77**, 4972 (1982).

¹⁸T. Oka, *J. Chem. Phys.* **48**, 4919 (1968).

¹⁹S. Urban, V. Spirko, D. Papousek, J. Kauppinen, S. P. Belov, L. I. Gershtein, and A. F. Krupnov, *J. Mol. Spectrosc.* **88**, 274 (1981).

²⁰C. J. Tsao and B. Curnutte, *J. Quant. Spectrosc. Radiat. Transfer* **2**, 41 (1962).

²¹J. Van Kranendonk, *Can. J. Phys.* **41**, 433 (1963).

²²T. Oka, *J. Mol. Spectrosc.* **48**, 503 (1973).

²³R. T. Hall and J. M. Dowling, *J. Chem. Phys.* **47**, 2454 (1967).

²⁴P. W. Anderson, *Phys. Rev.* **76**, 647 (1949).

²⁵C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).

²⁶P. W. Daly and T. Oka, *J. Chem. Phys.* **53**, 3272 (1970).