

## Collision induced transitions of ammonia calculation of relaxation times $T_1$ and $T_2$ , line widths, line shifts, and the double resonance effect

K TANAKA\*, J E BOGGS\*\* and S C MEHROTRA†

\*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka, Japan

\*\*Department of Chemistry, University of Texas at Austin, Austin, Texas, 78712 USA

†Department of Physics, Marathwada University, University Campus, Aurangabad 431 004, India

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**Abstract.** The longitudinal relaxation time  $T_1$  and the transverse relaxation time  $T_2$  for the inversion levels of the  $\text{NH}_3$  molecule have been calculated for  $\text{NH}_3 - \text{NH}_3$ ,  $\text{NH}_3 - \text{N}_2$  and  $\text{NH}_3 - \text{H}_2$  collisions. The ratio  $T_2/T_1$  lies between 1 and 2 which agrees well with the experiment. The phase shift effect on  $T_2$  and on the collision-induced line shift  $\delta\omega$  under the framework of the Mehrotra-Boggs theory have also been evaluated. The change in the line intensity  $\Delta I/I$ , in four-level double resonance experiments was also calculated, and the significance of higher order interaction terms has been pointed out.

**Keywords.** Relaxation time; rotational energy transfer; molecular-collisions; line widths; collision induced shift, ammonia calculation; double resonance effect.

### 1. Introduction

Since Fourier transform spectroscopic techniques in microwave and IR regions have been recently developed to measure the longitudinal and the transverse relaxation times,  $T_1$  and  $T_2$  respectively, many theoretical attempts have been made to understand their physical meaning. These concepts may be in simple analogy with those used in nuclear magnetic resonance (NMR) where Redfield or Bloch equations are applied to two-level systems. Since the energy levels in the gaseous molecules are more complicated than in the spin system, the physical conditions must be critically examined to adopt the concepts of relaxation times as used in NMR.

Early studies of rotational relaxation in gas phase molecule gave  $T_1 \simeq T_2$  for a number of molecules. The  $\text{NH}_3$  molecule has been extensively studied (Brittain *et al* 1973; Wang *et al* 1973; Jetter *et al* 1973; McGurk *et al* 1974; Weatherly *et al* 1974; Mäder *et al* 1975; Hoke *et al* 1976). It presents a special case because one inversion doublet is largely isolated from the other rotational levels so that the two-level approximation for the population relaxation holds to a certain extent. The values of  $T_1$  and  $T_2$  have recently been measured by a  $(\pi, \tau, \pi/2)$  pulse technique and free induction decay (Hoke *et al* 1975, 1976). The ratio  $T_2/T_1$  lies between 1 and 2 for the system, and is appreciably higher than for other molecules where the relaxation times are

essentially equal. Similar results were reported earlier from the scattering cross-section of  $\text{NH}_3$  in a beam maser experiment (Kukolich *et al* 1973; Wang *et al* 1973b) and also from the power-broadened line shape (Amano and Schwendeman 1976). The  $T_2/T_1$  values can be attributed to the approximate two-level nature of the inversion-rotation levels of  $\text{NH}_3$ , and some qualitative interpretations have been given (Amano and Schwendeman 1976).

Liu and Marcus (1975) presented a theory for  $T_1$  and  $T_2$  using a relaxation matrix and calculated the crosssections for OCS-rare gas collisions. A modified Anderson theory has also been given for the calculation of relaxation times  $T_1$  and  $T_2$  (Hoke *et al* 1976).

Murphy and Boggs (1967) presented a theory for rotational linewidths and applied it to various molecules. This approach has also been used to interpret the steady-state four-level double resonance experiments (Prakash and Boggs 1972; Oka 1968). Mehrotra and Boggs (1977) presented a theory which has been successfully applied to explain not only collision-induced widths, but also collision-induced shifts. In this paper, the theory is extended to compute the relaxation time  $T_1$ . The longitudinal and transverse relaxation times,  $T_1$  and  $T_2$ , together with the lineshifts are computed for  $\text{NH}_3\text{-NH}_3$ ,  $\text{NH}_3\text{-N}_2$ , and  $\text{NH}_3\text{-H}_2$  collisions in terms of the intermolecular potential. The intensity changes  $\Delta I/I$ , for the double resonance experiment are also computed.

## 2. Theory

A molecular system interacting with a coherent radiation field is described by the Hamiltonian

$$H(t) = H^{(0)} + H^{(c)}(t) + H^{(r)}(t) \quad (1)$$

where  $H^{(0)}$ ,  $H^{(c)}(t)$ , and  $H^{(r)}(t)$  denote the isolated molecule, the effects of the random collisions and the coherent radiation respectively.

The time-dependent behaviour of the system is given using the time evolution operator  $\rho(t_0, t)$  as

$$\rho_I(t) = T_I(t, t_0) \rho_I(t_0) T_I^{-1}(t, t_0), \quad (2)$$

where  $\rho_I$  is the density matrix operator in the interaction representation. The effect of the random collision process can be treated as a perturbation, expanding the diagonal element of the  $T$  operator in an exponential form as

$$T_{nn}(-\infty, \infty) = \exp(-A_{nn}), \quad (3)$$

$$A_{nn} = - \sum_j (i/\hbar)^j A_{nn}^{(j)}.$$

The expansion coefficients  $A_{nn}^{(j)}$ , are identical with those of the Born approximation up to the third order, and the series remains unitary even if it is cut off at a finite

order. This treatment of the molecular collision has been successfully applied to calculate the line widths of various molecules by Murphy and Boggs (1967, 1968, 1969).

The coherent radiation field is considered next. The frequency of the radiation is near resonance with the separation of an inversion doublet of ammonia,  $\omega \simeq \omega_{21}$ , and linear polarization,  $H'(t) = -\mu E_0 \cos \omega t$  is assumed. Including this coherent term, variation of the density matrix with time is given in the Schrödinger representation as

$$d\rho_{nn} | dt = (-i | \hbar) (H_{nm}^c \rho_{mn} - \rho_{nm} H_{mn}^c) - P_n \rho_{nn} + \sum_k' P_{nk} \rho_{kk}, \quad (4)$$

$$d\rho_{nm} | dt = (-i | \hbar) H_{nm}^c (\rho_{mm} - \rho_{nn}) - T_{nm} \rho_{nm} - i \omega_{nm} \rho_{nm},$$

where  $P_n$  and  $T_{nm}$  are the transition probabilities of the density matrix due to the collisional relaxation process, given from (3) as

$$P_n = \sum_k P_{kn} = 1 - \exp(-2 \operatorname{Re} A_{nn})$$

$$T_{nm} = 1 - \exp[-(A_{nn} + A_{mm}^*)]$$

and  $P_{kn}$  denotes the transition probability from state  $n$  to state  $k$ .

Using the pseudo-vector defined as  $\rho = [\rho_{21} + \rho_{12}, i(\rho_{21} - \rho_{12}), (\rho_{22} - \rho_{11})]$  and the rotating wave approximation, (4) can be reduced to the Bloch equation,

$$\partial \rho' / \partial t = \begin{pmatrix} -1/T_2 & \omega_{21} + \delta & \omega_{21} - \omega & 0 \\ \omega - (\omega_{21} + \delta) & -1/T_2 & X & \\ 0 & -X & -1/T_1 & \end{pmatrix} \rho' + \begin{pmatrix} 0 \\ 0 \\ \rho^0/T_1 \end{pmatrix} \quad (6)$$

where  $\rho'$  is the equilibrium value of the population difference,  $X = \mu E_0 / \hbar$  and  $\tilde{\mu}$  is the matrix element of the dipole moment. The following assumption, used to get the two-level coupling formula,

$$\frac{1}{2} (P_2 - P_1 - P_{12} - P_{21}) (\rho_{22} + \rho_{11}) + \sum_k' (P_{2k} - P_{1k}) \rho_{kk} = 0$$

may be expected to be a good approximation considering the isolated situation of an inversion doublet from the others.

The phenomenological relaxation times,  $T_1$  and  $T_2$  and line shift,  $\delta\omega_{21}$  are given explicitly as

$$1/T_1 = \frac{1}{2} [2 - \exp(-2 \operatorname{Re} A_{11}) - \exp(-2 \operatorname{Re} A_{22}) + P_{12} + P_{21}] \quad (7a)$$

$$1/T_2 = 1 - \exp[-\operatorname{Re}(A_{11} + A_{22})] \cos[\operatorname{Im}(A_{22} - A_{11})] \quad (7b)$$

$$\delta\omega_{21} = \exp [-\operatorname{Re} (A_{11} + A_{22})] \sin [\operatorname{Im} (A_{22} - A_{11})] \quad (7c)$$

equations (7a) and (7b) are obtained earlier (Mehrotra and Boggs 1977).

### 3. Computation and results

The values of  $T_1$ ,  $T_2$  and  $\delta\omega_{21}$  have been computed using the expressions given in (7). The computational technique was similar to the one used earlier (Mehrotra and Boggs 1977).

#### 3.1 Self broadening of $\text{NH}_3$

$T_1$ ,  $T_2$  and  $\delta\omega_{21}$  were calculated for  $\text{NH}_3$  self-broadening in the many-level and in the two-level resonant approximations, which are quoted as (a) and (c) respectively. In a many-level system, every possible collisional transition was considered, but in the two-level resonant approximation, the transition between the inversion doublet was treated separately from the rotational transitions. The physical meaning and the formulation of this approximation were given earlier (Murphy and Boggs 1969).

Both (a) and (c) were calculated to second order. The dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions were taken into account with  $\mu = 1.468$  Debye and  $Q = 1.3$  Debye Å. In a separate calculation, (e), the third order term of the perturbation expansion and the quadrupole type transitions were treated as two successive dipolar transitions. This approximation was previously applied to the four-level double resonance experiment in HCN and  $\text{H}_2\text{CO}$  (Prakash and Boggs 1974).

The transition probabilities for the population relaxation and the phase relaxation are plotted in figure 1. The inelastic collision out of the initial state, especially the transition between members of the inversion doublet, is dominant in all regions of the impact parameter  $b$ . On the other hand, the phase shift effect has a value comparable to the real cross-section in the long interaction range.

$T_1$  was calculated using (7a) and the  $T_2/T_1$  values are given in table 1 along with recent experimental results. The two different calculations, (a) and (c), gave almost identical values, so only (a) is shown. However, with the inclusion of third-order

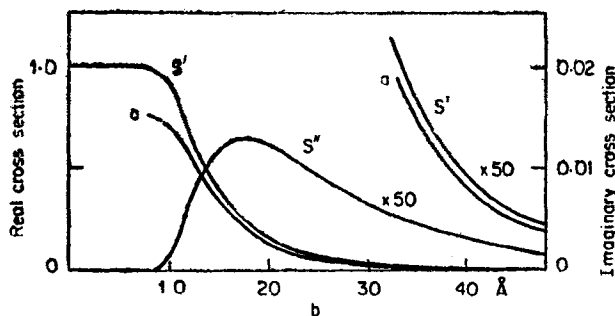


Figure 1. The transition probability from the initial level,  $S'$ , and the probability of the phase shift,  $S''$ , as a function of impact parameter  $b$ . The line shown as  $a$  denotes the transition probability between members of the inversion doublet. The initial states of the absorber and the perturber are assumed to be  $(J, K) = (3, 3)$  and  $(4, 3)$ , respectively. The calculation is based on procedure (a).

Table 1. Calculated ratios of  $T_2/T_1$  for  $\text{NH}_3\text{--NH}_3$  collisions.

$J$	$K$	Calculation		Experiment	
		(a) <sup>a</sup>	(e) <sup>b</sup>		
1	1	1.819	1.695	1.4(1) <sup>c</sup> ,	1.11(6) <sup>d</sup>
2	1	1.627	1.468	1.1(1) <sup>c</sup> ,	1.22(5) <sup>d</sup>
2	2	1.857	1.758	1.4(1) <sup>c</sup>	
3	2	1.704	1.555	1.6(1) <sup>c</sup> ,	1.25(7) <sup>d</sup> , 1.45 <sup>e</sup>
4	2	1.583	1.399	1.26(5) <sup>d</sup>	
3	3	1.866	1.779	1.8(2) <sup>c</sup> ,	1.42(6) <sup>d</sup>
4	3	1.729	1.577	1.7(1) <sup>c</sup> ,	1.41(9) <sup>d</sup>
5	3	1.651	1.477	1.32(9) <sup>d</sup>	
6	3	1.611	1.426	1.31(7) <sup>d</sup>	
4	4	1.879	1.799	1.8(2) <sup>c</sup>	
5	4	1.760	1.613	1.43(7) <sup>d</sup>	
5	5	1.897	1.838	1.58(9) <sup>d</sup>	
7	6	1.830	1.689	1.46(11) <sup>d</sup> ,	1.83 <sup>e</sup>
7	7	1.930	—	1.42(5) <sup>d</sup>	
8	7	1.865	1.739	1.16(10) <sup>c</sup> ,	1.42(13) <sup>d</sup>

<sup>a</sup>Multilevel system including quadrupole interactions; <sup>b</sup>Multilevel system including third order interactions; <sup>c</sup>Hoke *et al* 1976; <sup>d</sup>Amano *et al* 1976; <sup>e</sup>Wang *et al* 1973a,b.

terms, case (e), the values were 0.1—0.2 times smaller than in the other two cases. This indicates that the higher order terms *i.e.*  $V_{d\alpha}$ ,  $V_{d\beta}$ ,  $V_{d\gamma}$  and  $V_{q\alpha}$ ,  $V_{q\beta}$ ,  $V_{q\gamma}$  have an appreciable effect on  $T_2/T_1$ . The present calculations agree with the pulse experiments of Hoke *et al* (1976) but are a little larger than the results given by the line shape analysis of Amano and Schwendeman (1976).

The linewidths,  $\Delta\omega = (2\pi T_2 P)^{-1}$ , calculated by (a) and (c) are summarised in figure 2, which shows fairly good agreement with experiment, not only for the relative variation with the quantum numbers  $J$  and  $K$ , but also for the absolute values. The overestimation of  $1/T_2$  in case (a) may be caused by neglect of the higher order terms which allow the reverse transition back to the initial state.

The effect of the phase shift on the transverse relaxation time, which in the Born approximation corresponds to  $\phi_{21}^2/2$  was calculated from (7b) as

$$(1/T_2)_{el} = \exp [-\text{Re}(A_{11} + A_{22})] \{1 - \cos [\text{Im}(A_{22} - A_{11})]\}.$$

The effect of this term was in every case less than 0.5% of the linewidth, so the influence of the phase shift on  $1/T_2$  was negligibly small.

This evaluation of the phase-shift was supported by the pressure-induced lineshift calculation, which is first order in the phase-shift effect. The calculated results are shown for  $J = K$  levels in figure 3 along with available experimental data (Shimoda 1957; Matura 1960; Parsons *et al* 1972; Hewitt and Parsons 1973; Kakar and Poynter 1975). The present results are reasonably good as an evaluation of the sign and magnitude of the effect. The quantitative agreement is not yet clear since the accuracy of the experimental results has not been confirmed. However, it is clear that the elastic term of the transverse relaxation time is not very much greater than that given by the present calculation.

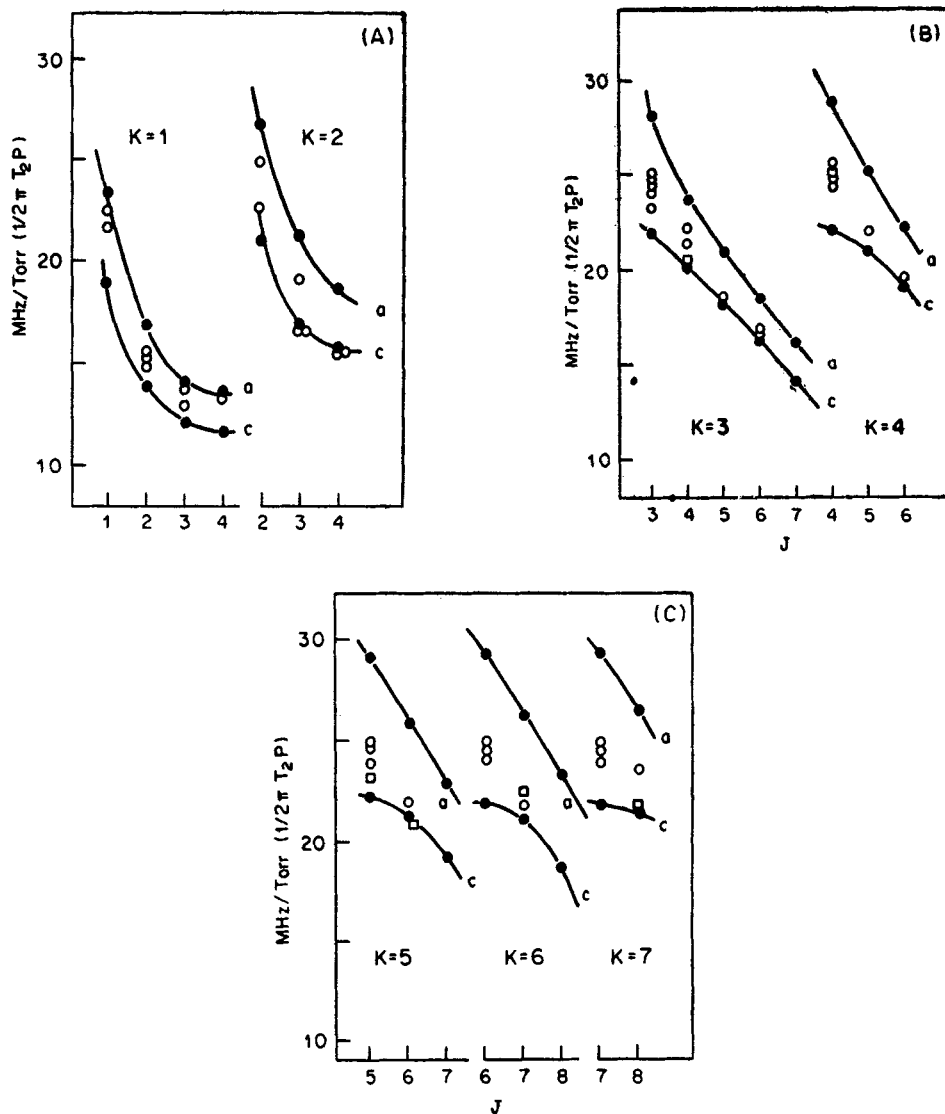


Figure 2. The transverse relaxation time  $T_2$  as a function of  $J$  and  $K$ . The solid lines denoted  $a$  and  $c$  are the calculated results. (O)—Recent experimental results  $\square$  Hoke *et al* 1976 and Wang *et al* 1973 respectively.

### 3.2 Broadening of $\text{NH}_3$ lines by nonpolar linear molecules

$T_1$ ,  $T_2$  and  $\delta\omega$  were also calculated for the  $\text{NH}_3\text{-N}_2$  and  $\text{NH}_3\text{-H}_2$  systems in the manner described above. The dipole-quadrupole and quadrupole-quadrupole interactions were taken into account with  $Q = 1.56$  and  $0.60$  Debye  $\text{\AA}$  for  $\text{N}_2$  and  $\text{H}_2$ , respectively (Stogryn and Stogryn 1966; Bloom *et al* 1965).

The  $T_2/T_1$  values are shown in table 2. Here again the values lie between 1 and 2, but are smaller than those obtained in the ammonia self-broadening case. This indicates that the transition between members of the inversion doublet of  $\text{NH}_3$  becomes less important in the case of broadening by collisions with  $\text{N}_2$  or  $\text{H}_2$ .

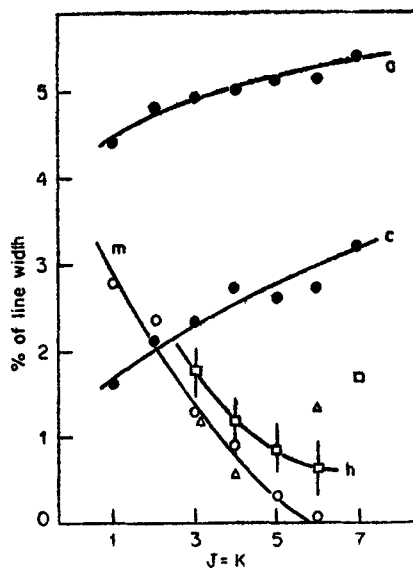


Figure 3. The line shift, as a percent of the linewidth for various transitions with  $J = K$ . The lines denoted as *a* and *c* are the calculated results based on the many-level and the two-level resonance systems, respectively. The experimental results, shown as *m* and *h*, are given by Matura 1960 and Hewitt and Parsons 1973 respectively.

Table 2. Calculated ratios of  $T_2/T_1$  for  $\text{NH}_3-\text{N}_2$  and  $\text{NH}_3-\text{H}_2$  collisions.

<i>J</i>	<i>K</i>	$\text{NH}_3 - \text{N}_2$		$\text{NH}_3 - \text{H}_2$	
		( <i>a</i> ) <sup>a</sup>	( <i>e</i> ) <sup>b</sup>	( <i>a</i> ) <sup>a</sup>	( <i>e</i> ) <sup>b</sup>
1	1	1.450	1.324	1.347	1.298
2	1	1.240	1.162	1.129	1.211
3	1	1.182	1.118	1.116	1.103
4	1	1.167	1.136	1.101	1.091
2	2	1.544	1.414	1.431	1.376
3	2	1.346	1.232	1.252	1.211
4	2	1.297	1.119	1.200	1.170
3	3	1.609	1.483	1.492	1.443
4	3	1.428	1.288	1.319	1.523
5	3	1.403	1.258	1.268	1.227
6	3	1.423	1.358	1.245	1.217
4	4	1.670	1.603	1.539	1.497
5	4	1.512	1.424	—	—
6	4	1.507	1.431	1.323	1.276
5	5	1.726	1.676	—	—
6	6	1.777	1.742	1.606	1.580
7	6	1.670	1.610	1.457	1.414
8	7	1.734	1.691	—	—
9	8	1.784	1.755	—	—

<sup>a</sup>Multilevel system including quadrupole interactions; <sup>b</sup>Multilevel system including third order interactions.

The  $\sigma_1/\sigma_2$  ratios of two different scattered cross-sections, reported for  $\text{NH}_3\text{-N}_2$  collisions by beam maser experiment (Wang *et al* 1973b) are 1.16 and 1.19 for the  $J, K = 3, 2$  and  $7, 6$  states, respectively. The present  $T_2/T_1$  value agrees with the experimental values for  $J, K = 3, 2$ , if it is allowed to compare  $T_2/T_1$  with  $\sigma_1/\sigma_2$ , where  $\sigma_1/\sigma_2$  is the ratio of two different scattered cross-sections as measured by the beam maser experiment (Wang *et al* 1973), but is about 30% higher in the case of  $J, K = 7, 6$ . No experimental data are available yet for the  $\text{NH}_3\text{-H}_2$  system.

The calculated line shifts were of the order of 0.1% of the linewidths, and the elastic term of the transverse relaxation time was negligibly small. This means that short range interactions through the quadrupole moment permit more contribution from inelastic collisions. Parson *et al* (1972) reported the lineshift of  $J, K = 12, 12$  level of the  $\text{NH}_3\text{-N}_2$  to be  $-8.2\%$  of the linewidth, but the present result is only  $-0.2\%$ . If the experimental result is correct, the disagreement may be due to the straight path model which neglects the phase shift effect caused by the first order term of (3).

### 3.3 Double resonance effect

In comparison with the other types of experiment, the four-level double resonance effect of  $\text{NH}_3$  was calculated. The relative intensity change  $\Delta I/I$  was written using  $T_1$  according to the formulation given by Oka (1968), Lees and Oka (1968) Daly and Oka (1970) as

$$\Delta I/I = (\gamma_p/\gamma_s) (K_{a\uparrow} - K_{a\downarrow}) T_2$$

where  $K_{a\uparrow}$  and  $K_{a\downarrow}$  are the dipole and the quadrupole type transition rates averaged between members of the inversion doublet. The results are plotted in figure 5 for the (a) and (e) calculations as a function of  $J$  and  $K$ . The ratio  $\Delta I/I$  was larger by 3.5% than the experimental results in (a) and (c), but quite satisfactory in (e). When third-order terms such as  $V_{da} V_{d\beta} V_{d\gamma}$  were taken into account, the inversion transition rate,  $k_\beta$ , decreased by 10–20%, while the quadrupole type transition,

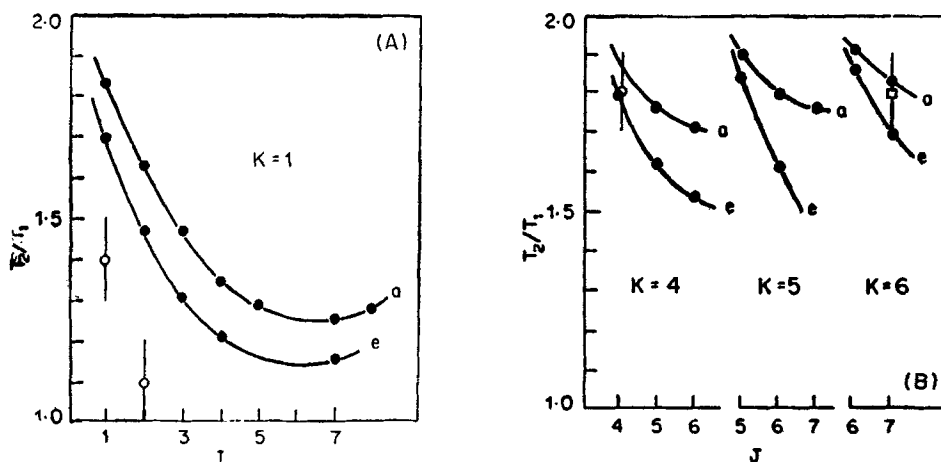


Figure 4. The ratio of the longitudinal and the transverse relaxation times of  $\text{NH}_3$ . The lines denoted as a and e are the calculated results and the white circles and squares are the experimental results of Hoke *et al* 1976, and Wang *et al* 1973 respectively.



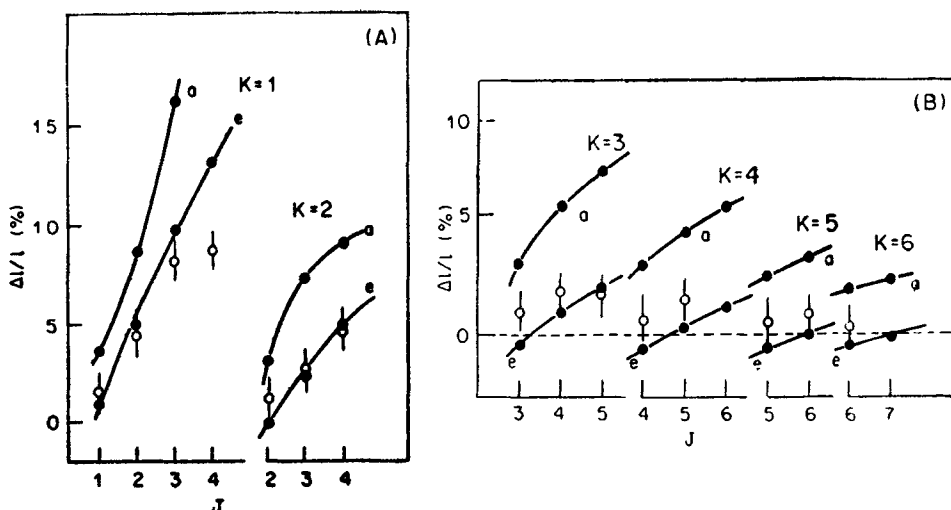


Figure 5. The four-level double resonance effect,  $\Delta I/I$ . The inversion doublet of  $(J+1, K)$  is pumped and that of  $(J, K)$  is observed. The calculations are by procedures (a) and (e). The white circles are the experimental results of Oka 1968.

$k_\gamma$ , increased. Consequently, the  $\Delta I/I$  and the  $T_2/T_1$  ratios were reduced. The effect of these higher order terms was neglected in the second-order treatment, but the present results suggest that the effect is important in the  $\text{NH}_3$  case where the inversion separation is small.

#### 4. Discussion

In the limit of the Born approximation, the ratio of  $T_2$  and  $T_1$  may be written as

$$\frac{T_2}{T_1} - 1 \simeq \frac{P_{21} + P_{12} - \phi_{21}^2}{T_1 + T_2 + \phi_{21}^2}.$$

If the phase-shift effect is neglected, the fraction shows the ratio of the transition rate between the inversion levels to the total transition rate,  $1/T_2$ . The ratio has the  $J$  and  $K$  dependence shown in figure 4, and it decreases with  $J$  for a given  $K$ . This tendency can be explained qualitatively in the following manner. The dipolar transition moment between the inversion levels is given by

$$\begin{pmatrix} J & 1 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{K^2}{(2J+1)(2J+1)J}$$

which has a maximum value at  $J = K$ , but decreases rapidly with  $J$  when  $K$  is constant. On the other hand, the transition between the rotational levels has the dipole transition moment shown by

$$\begin{pmatrix} J & 1 & J+1 \\ -K & 0 & K \end{pmatrix} = \frac{(J+1)^2 - K^2}{(2J+3)(2J+1)(J+1)}$$

This has a minimum value when  $J = K$ , but increases with  $J$  in the same  $K$  series. As the result of the two competitive processes, the inversion is dominant, giving  $T_2/T_1$  near 2 when  $J$  is close to  $K$ . On the contrary, if  $J$  is much larger than  $K$ , the transitions between rotational levels are significant, and the ratio becomes nearly 1. The experimental results and the present calculation agree well with this schematic aspect, and these considerations will not be affected significantly even if the higher order multipole moments are taken into account. On the other hand, when the phase-shift term  $\phi_{21}$  is considered, the  $T_2/T_1$  ratio can be  $\lesssim 1$ .

Mehrotra and Boggs (1975) have shown that the time-dependent transition probability (TDTP) has two different behaviours. One of these is a simple decay with time, and the change around the collisional region is monotone. The other type of TDTP curve has at least one peak; more generally, it oscillates around the position of the perturber. The former type has been defined as a weak collision and the latter as a strong collision. The present perturbation method ignores the behaviour within the duration of the collision, every transition being considered as a weak collision, so we cannot distinguish between the two different processes.

The other serious approximation in the present calculation was the use of the classical or straight path model. According to the beam maser experiment (Wang *et al* 1973a, b), an appreciable cross-section was observed which should be attributed to a nonclassical trajectory. We believe, however, that even if the straight path model is not a universally good approximation, the effect of the phase shift on the ratio  $T_2/T_1$ , will not be significant, as the line shift effect is known not to be too much larger than the calculated value in the case of  $\text{NH}_3\text{-NH}_3$  collisions.

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### References

- Amano T and Schwendeman R H 1976 *J. Chem. Phys.* **65** 5133  
Brittain A H, Manor P J and Schwendeman R H 1973 *J. Chem. Phys.* **58** 5735  
Bloom M, Openheim I, Lipcicas M, Wode C G and Yarness C F 1965 *J. Chem. Phys.* **43** 1036  
Daly P W and Oka T 1970 *J. Chem. Phys.* **53** 3272  
Gordon R G 1966 *J. Chem. Phys.* **44** 3083  
Hewitt P L and Parsons R W 1973 *Phys. Lett.* **A45** 27  
Hoke W E, Ekkers J and Flygare W H 1975 *J. Chem. Phys.* **63** 4075  
Hoke W E, Bauer D R, Ekkers J and Flygare W H 1976 *J. Chem. Phys.* **64** 5276  
Jetter H, Pearson E F, Norris C L, McGurk J C and Flygare W H 1973 *J. Chem. Phys.* **59** 1796  
Kakar R K and Poynter R L 1975 *J. Mol. Spectrosc.* **54** 475  
Kukulich S G, Wang J H S and Oates D E 1973 *Chem. Phys. Lett.* **20** 519  
Lees R M and Oka T 1968 *J. Chem. Phys.* **49** 4233  
Liu W K and Marcus J 1975 *J. Chem. Phys.* **63** 272, 290  
Mäder H, Ekkers J, Hoke W E and Flygare W H 1975 *J. Chem. Phys.* **62** 4380  
McGurk J C, Mäder H, Hofmann R T, Schmalz T G and Flygare W H 1974 *J. Chem. Phys.* **61** 3759  
Mehrotra S C and Boggs J E 1975a *J. Chem. Phys.* **62** 1453  
Mehrotra S C and Boggs J E 1975b *J. Chem. Phys.* **63** 4618  
Mehrotra S C and Boggs J E 1977 *J. Chem. Phys.* **66** 5306

- Murphy J S and Boggs J E 1967 *J. Chem. Phys.* **47** 691  
Murphy J S and Boggs J E 1968 *J. Chem. Phys.* **49** 3333  
Murphy J S and Boggs J E 1969 *J. Chem. Phys.* **50** 3320  
Matsura K 1960 *Res. Electrotech. Lab.* **24** 579  
Oka T 1968 *J. Chem. Phys.* **48** 4919  
Prakash V and Boggs J E 1972 *J. Chem. Phys.* **57** 2599  
Prakash V and Boggs J E 1974 *J. Chem. Phys.* **60** 2163  
Parsons R W, Metchnik V I and Story I C 1972 *J. Phys.* **B5** 1221  
Shimoda K 1957 *J. Phys. Soc. Jpn.* **12** 558  
Stogryn D E and Stogryn A P 1966 *Mol. Phys.* **11** 371  
Wang J H S, Levy J W, Kukolich S G and Steinfeld J I 1973a *Chem. Phys.* **1** 141  
Wang J H S, Oates D E, Ben-Reuven A and Kukolich S G 1973b *J. Chem. Phys.* **59** 5268  
Weatherly T L, Williams Q and Tsai F 1974 *J. Chem. Phys.* **61** 2925