Takayoshi Amano, Takako Amano, and R. H. Schwendeman

Articles you may be interested in

Variational transitionstate theory calculation using the direct dynamics method: NH3+H→NH2+H2 reaction
J. Chem. Phys. **101**, 1333 (1994); 10.1063/1.467826

Product branching ratios in the reaction of O(1D2) with NH3
J. Chem. Phys. **73**, 5381 (1980); 10.1063/1.439927

Optical phonons line broadening at the first order phase transition of (C2H5NH3)2CdCl4: A spin–phonon coupled system
J. Chem. Phys. **71**, 2732 (1979); 10.1063/1.438602

Determination of T 2/T 1 for inversion transitions in NH3 by analysis of powerbroadened line shapes
J. Chem. Phys. **65**, 5133 (1976); 10.1063/1.433053

Linewidths of HCl Broadened by H2, D2, and HCN
J. Chem. Phys. **53**, 4303 (1970); 10.1063/1.1673937

Determination of linewidths and T_1/T_2 ratios for inversion transitions in NH₃ broadened by H₂[a]

Takayoshi Amano, Takako Amano, and R. H. Schwendeman

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824
(Received 20 March 1980; accepted 15 April 1980)

A computer-coupled microwave spectrometer has been used to record the line shapes of 11 inversion transitions in ^{15}NH₃ in mixtures of a small amount of ^{15}NH₃ in a large excess of H₂. The steady-state absorptions were recorded as a function of frequency under conditions of low and moderate microwave powers. From the low power line shapes, values of $\Delta\nu$ were obtained and used as input data for the analysis of power-broadened line shapes, from which values of $(T_1/T_2)_0$ and qT_1/T_2 were obtained. The $(T_1/T_2)_0$ values are all closer to 1 than the results previously reported for NH₃·NH₃ collisions. The difference in $(T_1/T_2)_0$ ratios for the two sets of data decreases with increasing J and K and is explained as being the result of increased importance of collisions that change rotational states of NH₃ molecules in states of low J and K in NH₃·H₂ mixtures. The pressure dependence of shifts in center frequencies of the transitions are reported and are very small for all of the transitions studied.

I. INTRODUCTION

There has been considerable recent interest in the determination of the rates of energy transfer by collision in low pressure gases. The traditional method of determination of these rates has been by measurement of the pressure dependence of the linewidths and line shifts of unsaturated rotational or inversion transitions in the microwave and infrared regions.[1] In current terminology, the half-width at half-height of an unsaturated transition, $\Delta\nu = 1/2\pi T_2$, where T_2 is the relaxation time for the radiation-induced macroscopic polarization of the sample.[2] In order to obtain additional information concerning the energy transfer process, we have been measuring linewidths of rotational and inversion transitions under conditions of partial saturation where the widths are known to depend on T_1, the relaxation time for the return to equilibrium of the difference in population of the two levels involved in the transition.[2,3]

The relaxation times T_1 and T_2 have also been measured by a variety of transient effect experiments in microwave and infrared spectroscopy.[4] The inversion transitions of NH₃ have been the subject of a number of studies, because the unusual energy level structure in this molecule led to predictions that $T_1 \neq T_2$ for the inversion transitions.[5] Hoke *et al.*, by means of free induction decay and π, τ, $\pi/2$ pulse-sequence methods, demonstrated that T_2 is definitely longer than T_1 for several transitions in ^{15}NH₃.[6,7] Subsequently, by analysis of line shapes under conditions of low and moderate microwave power input, we confirmed the result that $T_2 > T_1$ for most of the transitions studied by Hoke *et al.* and obtained a similar result for several other transitions.[8] The T_2 values obtained by the linewidth and transient effect measurements agree very well, but the agreement between the T_1 values obtained by the two methods appeared to be poor. This has now been traced to the fact that the transient effect results were obtained for samples in an electric field of sufficient magnitude to separate the M components of the transitions, whereas the linewidth measurements were on samples in zero field. This difference has two consequences. First, the relaxation times in samples in a Stark field have been shown to have different definitions from those for zero field.[9] We now call the relaxation times for transitions in the presence of a field T_{1m} and T_{2m}. The second field–no field difference is that methods for the determination of T_{1m} by analysis of either line shape or transient effect results are well established, whereas the best method of determination of T_1 by either method has not yet been clearly resolved.

Our first method of analysis of power-broadened line shapes was based on the simple assumption that the degenerate transition at zero field was a linear superposition of contributions from the M components.[10] Each M component was assumed to be power broadened by an amount that is proportional to the product of the square of the appropriate dipole moment matrix element, the microwave power, and a quantity that we now call $\langle T_1/T_2\rangle_0$. We developed equations for integrating over an assumed microwave power distribution in the sample cell.[3] When Hoke *et al.* showed that T_{1m} depends on M for NH₃ transitions,[11] we followed the lead of Pickett,[12] Bottcher,[13] Liu and Marcus,[14] and Coombe and Snider[15] and looked more carefully at the theory of power broadening for the case of zero-field spatial degeneracy. Our first result was to show that, subject to certain approximations, the power-broadened line shape could be represented as a single Lorentz line, power broadened by an amount that was proportional to the product of the line strength for the zero-field transition, the microwave power, and qT_1/T_2.[9] The new parameter, q, was shown to depend on the ratio of a second-order tensorial combination of the populations of the states involved to a sum of the differences between the populations of the states and their equilibrium values. The first application of the new theory to analysis of experimental line shapes was to the $J = 2 \leftarrow 1$ transition in OCS in mixtures in H₂, CO₂, and CH₃F.[16] In that work, it was shown that qT_1/T_2 closely parallels $(T_1/T_2)_0$. It was also shown that $(T_1/T_2)_0$ and qT_1/T_2 were both essentially independent of pressure for a given microwave power. These results

led us to reanalyze the previously reported data for NH$_3$·NH$_3$ collisions and also to apply the new theory to the present data for NH$_3$·H$_2$ mixtures. The result was that we found a small pressure dependence of $(T_1/T_2)_0$ and a considerably larger pressure dependence for qT_1/T_2. This suggested that there might be more validity to the procedure for obtaining $(T_1/T_2)_0$ than was obvious from the existing theories.

Recently, we have reexamined the theory of power broadening in transitions between spatially degenerate levels and have been able to derive an expression for the line shape that is essentially free of serious approximations.[17] This expression, which is in the form of a continued fraction, depends on the relaxation rates for spherical tensorial combinations of the density matrix elements. For a $J \rightarrow J$ transition, the rates involved are a_n for $n = 1, 3, \ldots, 2J - 1$, and b_n for $n = 0, 2, \ldots, 2J$. The a_n are relaxation parameters for off-diagonal elements of the density matrix, and the b_n are parameters for differences between the diagonal elements of the density matrix corresponding to lower and upper state populations. The n's are the orders of the tensorial combinations. For $J \rightarrow J$ transitions, $T_1^{-1} = b_0$ and $T_2^{-1} = a_1$. It was shown that if the a_n are all equal, and the b_n are all equal, then $(T_1/T_2)_0 = T_1/T_2$.[17]

The new expression was used together with assumed parameters to calculate theoretical line shapes. These line shapes were numerically averaged over the power distribution in the sample and fit to obtain $(T_1/T_2)_0$ by the same computer program that was used to analyze the experimental data. The result was to show, for experimental conditions close to those in this work, that the line shape is an order of magnitude more dependent on b_0 and a_1 than on b_2 and a_3, and even less dependent on the higher order parameters. The results also showed that pressure dependence of $(T_1/T_2)_0$ at fixed power is evidence that the conditions under which $(T_1/T_2)_0 = T_1/T_2$ are not satisfied. Since some pressure dependence appears in the present work, the dependence should be analyzed to obtain values closer to T_1/T_2 than are obtained by simply using $(T_1/T_2)_0$. However, the best method of analysis is not yet worked out, so that only qualitative statements are made below. Nevertheless, we believe that the model errors in the use of $(T_1/T_2)_0$ to approximate T_1/T_2 are well within the ±10% uncertainty in $(T_1/T_2)_0$ that results from difficulty in pressure measurement.

In the next section the experimental and theoretical details of the line shape measurement and numerical fitting process are described. The results and discussion are presented in the final section of the paper.

II. EXPERIMENTAL AND THEORETICAL DETAILS

A. Apparatus

With the exception of the sample preparation, the experimental procedure was the same as that described previously.[8] Essentially, a Digital Equipment Corporation PDP8/E computer was used to control the frequency and read the output of a Hewlett-Packard Model 8460A Stark-modulated microwave spectrometer and to record

the data on magnetic tape for subsequent analysis. The microwave power was measured by means of Hewlett-Packard Model 432A power meters with Model K486A thermistor mounts. The gas pressure was monitored by means of a calibrated MKS Baratron Type 77 pressure gauge with a Type 77H1 pressure sensing head. At each gas pressure, the line shape was recorded 7 times in quick succession; the second, fourth, and sixth recordings were taken under conditions of maximum available microwave power (~15 mW), while the other recordings were taken at 35 db below maximum power. The power was adjusted with calibrated attenuators before and after the cell so that the detector crystal current was the same for all recordings of a given spectral line. A typical spectrum consisted of a single sweep over 201 points spaced 100 kHz apart with five readings of the phase-sensitive detector averaged at each point.

B. Spectral fitting functions

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

$$S(\nu) = \frac{A_0(\Delta\nu)^2}{(\nu - \nu_0)^2 + (\Delta\nu)^2} + B_0(\nu - \nu_0) + D_0 . \quad (1)$$

In this expression, $S(\nu)$ is the voltage at the output of the phase-sensitive detector at spectral frequency ν; A_0 is the maximum amplitude, ν_0 is the resonant frequency, and $\Delta\nu$ is the linewidth of the transition. The term including $B_0(\nu - \nu_0)$ is a correction for possible slope of the background and D_0 is the background voltage. The recorded values of $S(\nu)$ were fit by least squares to the function in Eq. (1) with A_0, ν_0, $\Delta\nu$, B_0, and D_0 as adjustable parameters. A typical standard deviation of observed minus calculated points was 10–20 on a scale on which the maximum amplitude was 3500.

The power-broadened data were fit by the two methods alluded to in the Introduction. In these methods, the spectral line shape is assumed to be either that of a single power-broadened Lorentzian or a sum of power-broadened Lorentzians. Each Lorentz component is averaged over an assumed power distribution in the sample cell (TE_{10} mode). If a sum of Lorentzians is assumed, the functional form for the spectrum is[3]

$$S(\nu) = A_1 N_1 \sum_M \ln \left(\frac{C_0 + (C_0^2 + C_1^2)^{1/2}}{C_0 + (C_0^2 + C_1^2 f)^{1/2}} \right) + B_1(\nu_1 - \nu_0) + D_1 .$$

$$(2)$$

In this equation, $f = e^{-\beta l}$ is the cell attenuation,

$$N_1^{-1} = \sum_M \ln \left(\frac{\Delta\nu + [(\Delta\nu)^2 + C_1^2]^{1/2}}{\Delta\nu + [(\Delta\nu)^2 + C_1^2 f]^{1/2}} \right) , \quad (3)$$

$$C_0^2 = (\nu - \nu_0)^2 + (\Delta\nu)^2 , \quad (4)$$

and

$$C_1^2 = [KM\mu_0 \epsilon_0 / J(J+1)]^2 (T_1/T_2)_0 . \quad (5)$$

In Eq. (5), J, K, and M are the usual quantum numbers for an inversion transition, μ_0 is the dipole moment (1.469 D),[18] and ϵ_0 is the peak value of the microwave field. The normalization factor N_1 was included in Eq. (2) to improve the convergence of the results. In fitting data to Eq. (2), the value of $\Delta\nu$ was taken to be the

average of the values obtained from analyses of the low-power line shapes taken just before and just after the power-broadened data, and the fitting parameters were A_1, B_1, D_1, ν_0, and $(T_1/T_2)_0$.

In the second method of analysis of the power-broadened data the functional form for the spectrum was[9,16]

$$S(\nu) = A_2 N_2 \ln \left(\frac{C_0 + (C_0^2 + C_2^2)^{1/2}}{C_0 + (C_0^2 + C_2^2 f)^{1/2}} \right) + B_2(\nu - \nu_0) + D_2 .$$

(6)

In this equation

$$N_2^{-1} = \ln \left(\frac{\Delta\nu + [(\Delta\nu)^2 + C_2^2]^{1/2}}{\Delta\nu + [(\Delta\nu)^2 + C_2^2 f]^{1/2}} \right) ,$$

(7)

and

$$C_2^2 = [K^2 \mu_0^2 \epsilon_0^2 / 3J(J+1)] (qT_1/T_2) .$$

(8)

Again, $\Delta\nu$ was taken to be the mean of low-power linewidths and in this case the fitting parameters were A_2, B_2, D_2, ν_0, and qT_1/T_2.

C. Sample preparations

The gas mixtures were prepared from $^{15}NH_3$, which was purchased from Bio-Rad Laboratories, and "prepurified" H_2, which was obtained from Matheson Gas Products; the gases were used as received. To prepare the mixtures, a small amount of $^{15}NH_3$ was introduced into the gas cell and the pressure was monitored until a stationary value was reached. Then, H_2 was added to the desired total pressure and the peak intensity of a $^{15}NH_3$ absorption was allowed to reach a stable value. "Mixing ratios" were calculated from pressures measured before and after the addition of H_2, a procedure that neglects any change in the amount of adsorbed NH_3 brought about by the addition of H_2. For most of the measurements, the mixtures were prepared at pressures above the highest pressure desired and stored in a 14-l stainless steel tank attached to the vacuum system. The tank was then closed off from the cell and the pressure in the cell was adjusted by pumping. When new samples were needed, the cell was evacuated, the tank valve opened and closed, and the cell pressure again adjusted by pumping. Mixing ratios of $H_2 : NH_3$ from 36 : 1 to 213 : 1 were used, with the bulk of the measurements made at the higher ratio.

D. Corrections and uncertainties

Preliminary values of $\Delta\nu/p$ were obtained from the slopes of plots of $\Delta\nu$ versus p for the mixtures. For the final values of $\Delta\nu/p$, the $\Delta\nu$ values were corrected for the effects of $NH_3 \cdot NH_3$ collisions by calculating the partial pressures of NH_3 from the mixing ratios and the total pressure and by assuming $\Delta\nu/p$ values from our previous work.[8] The final values of $\Delta\nu/p$ were 1%-3% smaller than the uncorrected values. No corrections were employed in the data analysis for the $(T_1/T_2)_0$ and qT_1/T_2 ratios, as the corrections are expected to be much smaller in this case.

If the parameters $(T_1/T_2)_0$ and qT_1/T_2 are assumed to be defined by the operations used to obtain them, the largest source of uncertainty in these parameters is the uncertainty in the measurement of microwave power and the assumption of a TE_{10} power mode in the absorption cell. We estimate approximately 10% uncertainty in $(T_1/T_2)_0$ and qT_1/T_2 from this source alone. However, the contribution of this uncertainty to the comparison of results for $NH_3 \cdot NH_3$ collisions with that for $NH_3 \cdot H_2$ collisions for a given transition should be considerably smaller, because the power measurements were made in the same microwave system at the same set of frequencies for the two sets of measurements. As a result, direct comparison of values of $(T_1/T_2)_0$ or qT_1/T_2 obtained for pure NH_3 to corresponding values obtained for the $NH_3 \cdot H_2$ mixtures ought to be valid to 3% or 4%.

E. Theoretical line shape calculations

In the discussion in the next section, reference is made to calculations based on the recently derived equation for the line shape. For these calculations, the absorption coefficient was assumed to be of the form[17]

$$\alpha(\nu) = \frac{A}{L_1 + f_2^2[L_3 + f_4^2 /(L_5 + \cdots)]^{-1}} ,$$

(9)

in which A is a collection of constants,

$$L_n = (\Delta\nu_n^2 / a_n) + a_n + x^2(C_{n-1,n}^2 / b_{n-1} + C_{n+1,n}^2 / b_{n+1}) ,$$

(10)

$$\Delta\nu_n = \nu - \nu_0 - \delta_n ,$$

(11)

$$x = 0.4055 [(2J+1)/J(J+1)]^{1/2}$$
$$\times K(1 - \lambda_0^2/\lambda_c^2)^{-1/4} (\mu_0/D)(P/mW)^{1/2} ,$$

(12)

$$f_n = x^2 C_{n,n-1} C_{n,n+1} / b_n ,$$

(13)

and

$$C_{n,n-1} = C_{n-1,n} = (-1)^n n^{1/2} \begin{Bmatrix} n-1 & n & 1 \\ J & J & J \end{Bmatrix} ,$$

(14)

The last denominator in the continued fraction, Eq. (9), is L_n for $n = 2J$. In Eq. (10)–(13), δ_n and a_n, for $n = 1$, $3, \ldots, 2J-1$, and b_n, for $n = 0, 2, \ldots, 2J$, are the relaxation parameters mentioned in the introduction and defined by Eq. (31), (33), and (57) in Ref. 17, where it is shown that $b_0 = T_1^{-1}$ and $a_1 = T_2^{-1}$. In Eq. (11), ν_0 is the resonance frequency, and in Eq. (12), P is the microwave power in mW. The last factor in Eq. (14) is a Wigner $6-j$ symbol. At each ν, the absorption coefficient was calculated by means of Eq. (9) at a series of x values corresponding to an assumed power distribution in the absorption cell. The values of the absorption coefficient were then summed to obtain the line shape function, which was fit by means of the same programs used to analyze the experimental data.

III. RESULTS AND DISCUSSION

A. Low-power linewidths

Table I is a comparison of $\Delta\nu/p$ values for $NH_3 \cdot H_2$ mixtures, as obtained in the present work, with $\Delta\nu/p$ values for the same transitions for $NH_3 \cdot NH_3$ collisions, as given in our previous work. The entries for $NH_3 \cdot H_2$ in Table I were obtained by the method described in the previous section and are believed to be known to within $\pm 3\%$.

TABLE I. Comparison of linewidth parameters at 298 K for $^{15}NH_3$ inversion transitions in pure $^{15}NH_3$ and dilute $^{15}NH_3$ in H_2. Line shift parameters for $^{15}NH_3 \cdot H_2$.

	$(\Delta\nu/p)/(MHz/Torr)$[a]		$(d\nu_0/dp)/(MHz/Torr)$
J, K	$^{15}NH_3 \cdot H_2$[b]	$^{15}NH_3$[c]	$^{15}NH_3 \cdot H_2$[d]
1,1	3.79	21.6	−0.14
2,1	3.51	14.6	0.13
3,2	3.56	17.5	0.00
3,3	3.26	24.4	−0.01
4,3	3.36	20.6	−0.10
5,3	3.09	18.4	−0.06
5,4	3.18	22.0	0.06
5,5	3.04	24.6	0.05
7,6	2.92	21.8	0.06
7,7	2.87	24.1	−0.03
8,7	2.81	23.7	0.19

[a]Uncertainty estimated to be ± 3%.
[b]This work.
[c]Reference 8.
[d]Uncertainty estimated to be ± 0.03 MHz/Torr.

Previous published linewidth measurements in the $NH_3 \cdot H_2$ system are confined to low-power linewidths for the $(J, K) = (3, 3)$, $(4, 4)$, and $(6, 6)$ transitions of $^{14}NH_3$. The $(4, 4)$ and $(6, 6)$ transitions were not included in the present study.[19] In the older work, values were often reported as collision diameters. After conversion to linewidth parameters where necessary, the previous results for the $(J, K) = (3, 3)$ line are $\Delta\nu/p$ =3.71 MHz/Torr,[20] 2.64 MHz/Torr,[21] 3.26 MHz/Torr,[22] and 3.05 MHz/Torr[19] (temperatures, which are not given, are assumed to be 298 K for these comparisons). These results may be compared with the value of 3.26 ± 0.10 MHz/Torr given in Table I for $^{15}NH_3 \cdot H_2$.

The values of $\Delta\nu/p$ for $NH_3 \cdot H_2$ are seen to be much smaller than for $NH_3 \cdot NH_3$. In addition, the $NH_3 \cdot H_2$ numbers generally decrease with increasing J and K, whereas the $NH_3 \cdot NH_3$ data show a more complicated dependence on the quantum numbers. Theories of the broadening of the NH_3 inversion transitions by nonpolar diatomic molecules, including H_2, have been given by Anderson[23] and by Murphy and Boggs.[24] The essential point of Anderson's theory is that quadrupole–induced dipole interaction is more important than dipole–induced dipole interaction. As a result, $\Delta J = \pm 1$ contributions to T_2^{-1} were neglected. Anderson's theory explained the dependence on foreign gas of the widths of the NH_3 (J, K) = (3, 3) line, the only values available at that time. However, the dependence of $\Delta\nu/p$ on J and K, as calculated from Eq. (14) of Ref. 23, is not that of the data in Table I. Murphy and Boggs assume dipole–quadrupole interaction, but calculate $\Delta\nu/p$ for only the (J, K) = (3, 3) line.

B. Low-power line shifts

The slopes of plots of the center frequencies of the low-power line shapes as a function of pressure for $NH_3 \cdot H_2$ are given in Table I. The line shift parameters are very small, many of them are barely outside the experimental uncertainty. In addition, it should be pointed out that the

fitting procedure contains a variable parameter for the slope of the background $[B_0$ in Eq. (1)]. Inclusion of this term affects the value of the center frequency obtained and we have routinely included a slope correction since our discovery that it removed inconsistencies in the determination of center frequencies of the $J = 2 - 1$ transition in OCS.[3]

C. Determination of T_1/T_2

In Table II, values of $(T_1/T_2)_0$ and qT_1/T_2 are compared for $NH_3 \cdot NH_3$ and $NH_3 \cdot H_2$ collisions. Also given are values of the slopes of the best least-squares straight lines through values of $(T_1/T_2)_0$ and qT_1/T_2 plotted against $\Delta\nu = (2\pi T_2)^{-1}$ for $NH_3 \cdot H_2$. These slopes are not given for $NH_3 \cdot NH_3$ because the pressure range used for measurement of $(T_1/T_2)_0$ and qT_1/T_2 was not large enough in our earlier work to obtain meaningful results. Because there is a variation in pressure for many of the entries in Table II, we have chosen to present the best values at the pressure at which $\Delta\nu = (2\pi T_2)^{-1} = 0.5$ MHz. For the reasons given in the Introduction, we interpret the $(T_1/T_2)_0$ given in Table II as being within ± 10% of the actual values of T_1/T_2 and within ± 3% of the values of T_1/T_2 for purposes of comparison between the two gas samples.

For the transitions in Table II, $(T_1/T_2)_0$ for $NH_3 \cdot NH_3$ collisions is generally less than the corresponding value for $NH_3 \cdot H_2$ collisions. In our previous study we concluded from the values of $(T_1/T_2)_0$ for $NH_3 \cdot NH_3$ collisions that the ratio of adiabatic collisions to all diabatic collisions is 0.35.[8] This value has been criticized by Hoke et al.[11] and by McMahon[25] as being too large. On the basis of a comparison of observed and calculated T_{2m}/T_{1m} values for the Stark-separated M states of the

TABLE II. Comparison of $(T_1/T_2)_0$ and qT_1/T_2 values for $^{15}NH_3$ transitions in pure $^{15}NH_3$ and in dilute $^{15}NH_3$ in H_2.

	$(T_1/T_2)_0$[a]			qT_1/T_2[a]		
J, K	$^{15}NH_3$[b]	$^{15}NH_3 \cdot H_2$[c]	Deriv[d]	$^{15}NH_3$[b]	$^{15}NH_3 \cdot H_2$[c]	Deriv[e]
1,1	0.98	1.00	−0.03	1.47	1.50	−0.06
2,1	0.84	0.97	f	1.25	1.39	f
3,2	0.83	0.94	0.15	1.17	1.27	0.57
3,3	0.71	0.80	−0.03	0.89	1.09	0.12
4,3	0.71	0.85	−0.01	0.96	1.11	0.35
5,3	0.75	0.86	0.11	1.13	1.21	0.58
5,4	0.70	0.80	−0.01	0.94	1.05	0.33
5,5	0.64	0.75	−0.07	0.83	0.89	0.31
7,6	0.65	0.78	−0.13	0.93	0.98	0.24
7,7	0.74	0.74	−0.01	0.95	0.96	0.40
8,7	0.72	0.69	0.09	0.91	0.86	0.51

[a]The values of $(T_1/T_2)_0$ and qT_1/T_2 are the predicted values at $\Delta\nu = 0.500$ MHz. See text for details. Absolute uncertainty estimated to be ± 10%; relative uncertainty estimated to be ± 4%.
[b]Obtained by reanalysis of the data from Ref. 8.
[c]This work.
[d]$d(T_1/T_2)_0/d(\Delta\nu)$ in MHz^{-1} for $^{15}NH_3 \cdot H_2$ obtained from linear least squares fit. Estimated uncertainty is ± 0.05.
[e]$d(qT_1/T_2)/d(\Delta\nu)$ in MHz^{-1} for $NH_3 \cdot H_2$ obtained from linear least squares fit. Estimated uncertainty is ± 0.10.
[f]Insufficient data to compute derivative.

$(J, K) = (2, 2)$ and $(3, 3)$ transitions, Hoke et al. concluded that "...there is no direct evidence for phase changing collisions in NH_3".[11] On the basis of a comparison of our $(T_1/T_2)_0$ results for resonant transitions and the results of Bleaney and Loubser[26] for the non-resonant line shape, McMahon[25] estimated that the ratio of adiabatic to diabatic collisions is ≤ 0.23, rather than the 0.35 that we reported.

Our previous conclusion was based on an interpretation of T_1 and T_2 in terms of collisional rate constants that are defined to be time-correlation integrals over the interaction Hamiltonian [Eqs. (16)–(19) of Ref. 8]. Unfortunately, a two-state theory that does not properly account for the M degeneracy was used. We have since extended the theory to take the M degeneracy into account.[9] If the extended theory is used to analyze the data for NH_3, the ratio of adiabatic to diabatic collisions is found to be considerably smaller than 0.35; as will be seen, additional calculations are needed to determine the final result.

To see why inclusion of consideration of M degeneracy reduces the apparent contribution from adiabatic collisions, we rewrite Eqs. (89) and (96) of Ref. 9 in the following form for a $J \rightarrow J$ transition:

$$T_1^{-1} = 2\Gamma_{if}^{(1)} + \Gamma_b^{(1)} , \tag{15}$$

$$T_2^{-1} = \Gamma_{if}^{(2)} + \Gamma_b^{(2)} + \Gamma_a . \tag{16}$$

In these equations,

$$\Gamma_{if}^{(\ell)} = \frac{1}{2} \sum_M f_\ell(M) \sum_{M'} (w_{J_f M, J_i M'} + w_{J_i M, J_f M'}) , \tag{17}$$

and

$$\Gamma_b^{(\ell)} = \frac{1}{2} \sum_M f_\ell(M) \sum_{M'} \sum_{J' \neq J_i, J_f} (w_{J'M', J_i M} + w_{J'M', J_f M}) , \tag{18}$$

where

$$f_1(M) = (2J+1)^{-1} \tag{19}$$

and

$$f_2(M) = 3M^2/J(J+1)(2J+1) . \tag{20}$$

The weighting factors $f_1(M)$ and $f_2(M)$ are each normalized so that $\sum f_\ell(M) = 1$; the different weightings are a result of the different tensorial order of the relaxations represented by T_1^{-1} and T_2^{-1}. In Eq. (17) and (18), $w_{J'M', JM}$ is a time correlation integral over the interaction Hamiltonian and is defined by Eqs. (B2) and (B10) of Ref. 9. For most purposes, $w_{J'M', JM}$ may be interpreted to be the rate constant for collisionally induced transitions between state J, M and state $J'M'$. In writing Eq. (16) we have assumed the w's to be real. Finally, in Eq. (16), Γ_a is the sum of contributions to T_2^{-1} from phase-changing and adiabatic reorientation collisions.

Since $T_1/T_2 = T_2^{-1}/T_1^{-1}$, we may use Eq. (15) and (16) to write

$$T_1/T_2 = (\Gamma_{if}^{(2)} + \Gamma_b^{(2)} + \Gamma_a)/(2\Gamma_{if}^{(1)} + \Gamma_b^{(1)}) . \tag{21}$$

Oka[27] and Daly and Oka[28] have concluded from the results of their four-level double-resonance experiments, that

Γ_{if} processes (Oka's β processes[29]) are much more frequent than Γ_b processes (Oka's α processes[29]). The four-level double-resonance measurements are not sensitive to Γ_a processes. If we assume $\Gamma_b^{(\ell)} \ll \Gamma_{if}^{(\ell)}$, then $T_1/T_2 = (\Gamma_{if}^{(2)} + \Gamma_a)/2\Gamma_{if}^{(1)}$.

In a two-state system with no consideration of the effects of spatial degeneracy, $\Gamma_{if}^{(1)} = \Gamma_{if}^{(2)}$, and under these circumstances, $T_1/T_2 = 0.5 + \Gamma_a/2\Gamma_{if}$. By contrast, when the M degeneracy is taken into account for NH_3, it appears that $\Gamma_{if}^{(2)} > \Gamma_{if}^{(1)}$. This is because the probability of $\Delta M = 0$ transitions has an M^2 dependence for dipole selection rules, and $f_2(M)$ increases as M^2. The probability of $\Delta M = \pm 1$ transitions decreases with M, but the dependence on M is smaller and the individual transition probabilities are smaller than for $\Delta M = 0$ transitions. A rough calculation, based on the assumption that the probabilities for collision-induced transitions are proportional to the squares of the appropriate dipole moment matrix elements, gives, for the J values of interest here, $\Gamma_{if}^{(2)}/2\Gamma_{if}^{(1)} = 0.60$. If 0.60 is used for $\Gamma_{if}^{(2)}/2\Gamma_{if}^{(1)}$ rather than 0.50, the experimental values of T_1/T_2 lead to considerably smaller contributions from phase-changing collisions than previously predicted.

To carry this analysis one step further, we note from Table II that $(T_1/T_2)_0 \simeq 0.70$ for the higher J transitions in pure NH_3. If it is assumed that Γ_a and $\Gamma_b^{(\ell)}$ are considerably smaller than $\Gamma_{if}^{(\ell)}$, then to first order

$$T_1/T_2 = (\Gamma_{if}^{(2)}/2\Gamma_{if}^{(1)}) + (\Gamma_a/2\Gamma_{if}^{(1)})$$
$$+ (\Gamma_b^{(1)}/2\Gamma_{if}^{(1)})(\Gamma_b^{(2)}/\Gamma_b^{(1)} - \Gamma_{if}^{(2)}/2\Gamma_{if}^{(1)}) . \tag{22}$$

If $\Gamma_{if}^{(2)}/2\Gamma_{if}^{(1)} = 0.60$ and $\Gamma_b^{(2)}/\Gamma_b^{(1)} = 0.93$, as obtained by again assuming transition probabilities proportional to the squares of the appropriate dipole matrix elements, then $T_1/T_2 = 0.70$ leads to

$$(\Gamma_a + 0.33\Gamma_b^{(1)})/2\Gamma_{if}^{(1)} = 0.10 . \tag{23}$$

Johns et al.[30] have shown, by analysis of the intensities of collision-induced Lamb dips, that the ratio of $\Delta M = \pm 1$ adiabatic reorientation collisions to all diabatic collisions is about 0.15 for the $(J, K) = (9, 9)$ and $(10, 10)$ transitions in pure NH_3. If we take $\Gamma_a = \Gamma_\phi + \Gamma_r$ and let $\Gamma_r/\Gamma_{if}^{(1)} = 0.15$, we conclude that $(\Gamma_\phi + 0.33\Gamma_b^{(1)})/\Gamma_{if}^{(1)}$ is about 0.05. Thus, the $(T_1/T_2)_0$ data for high J and K transitions are compatible with an estimate of 5% for the combined contribution from phase-changing collisions and collisions that change the rotational state in NH_3.

The lower J transitions in NH_3 and nearly all of the transitions in $NH_3 \cdot H_2$ have $(T_1/T_2)_0$ values greater than 0.7. For these transitions the contributions from phase-changing and rotational-state-changing collisions are predicted to be greater than 5%. For example, for $(T_1/T_2)_0 = 0.8$, these contributions are predicted to total 20% of all of the collisions. In the four-level double-resonance studies, increased double-resonance effects are attributed to increased contributions of $\Delta J \neq 0$ transitions (Γ_n or α processes) relative to $\Delta J = 0$ transitions (Γ_{if} or β processes).[27-29] Comparison of the four-level double-resonance results for NH_3 and $NH_3 \cdot H_2$ shows larger double resonance effects for smaller J, K in NH_3 and consistently larger effects for $NH_3 \cdot H_2$ than for NH_3

for the same transition, provided that K is less than about 3 or 4. Comparison with our results for NH_3 and $NH_3 \cdot H_2$ shows somewhat greater differences in T_1/T_2 to higher K values than the double-resonance data would predict, although the trends are the same. The reason or reasons for this quantitative discrepancy between the two sets of data is difficult to assess at present. Even though the resonant line shape data now appear to be in good qualitative agreement and reasonable quantitative agreement with four-level double-resonance, transient-effect, and nonresonant line shape studies, theoretical calculations of the individual rate constants would be useful both for checking the validity of the assumption that $(T_1/T_2)_0 = T_1/T_2$ and for determining the proper values of $\Gamma_{if}^{(2)}/\Gamma_{if}^{(1)}$ and $\Gamma_b^{(2)}/\Gamma_b^{(1)}$.

D. Higher order relaxation rates

The possibility of using power-broadened line shape data for estimation of relaxation rates for higher order tensorial combinations of the diagonal or off-diagonal density matrix elements is intriguing. Unfortunately, the present experimental data were taken before the existence of this possibility was discovered.[17] As a result, the necessary systematic collection of highly precise data as a function of both pressure and power has not been done. Nevertheless, in the third and sixth columns of Table II the slopes of the best straight lines through $(T_1/T_2)_0$ and qT_1/T_2 values plotted against $\Delta\nu$ are presented. Many of the values in the third column are near zero, which indicates that either the ratios of relaxation coefficients, a_3/a_1 and b_2/b_0, are near unity or that they take on values that fortuitously compensate one another. An indication of the experimental uncertainty is provided by the slope for the $(J, K) = (1, 1)$ transition (-0.03). This transition has a single component for $|m| = 1$ and should therefore have a slope of zero. Line shapes have been calculated by means of Eq. (9) for the $(J, K) = (3, 2)$ and $(J, K) = (5, 3)$ transitions with parameters close to the experimental values. The theoretical line shapes were power averaged and analyzed by the same programs that were used for the experimental data. For these transitions, the experimental slopes for $(T_1/T_2)_0$ and qT_1/T_2 can be predicted by assuming that $b_2/b_0 \sim 0.75$. The reliability of this prediction is difficult to assess at present. It is based on the assumption that all a_n and all δ_n are equal for these levels. In addition, there is the problem of experimental uncertainty. The large uncertainty in $(T_1/T_2)_0$ and qT_1/T_2 that results from uncertainty in the measure-

ment of absolute microwave power should not affect the slopes, because the same method of power measurement is used at each pressure, and there is almost no day-to-day variation in measurement of the maximum microwave power available at a given frequency. Nevertheless, the scatter in individual $(T_1/T_2)_0$ values at a given pressure was of the order of $0.01-0.03$ for $NH_3 \cdot H_2$ and this scatter should be reduced to achieve reliable determination of $d(T_1/T_2)_0/d(\Delta\nu)$.

[1]H. Rabitz, Ann. Rev. Phys. Chem. 25, 155 (1974).
[2]J. C. McGurk, T. G. Schmalz, and W. H. Flygare, Adv. Chem. Phys. 25, 1 (1974).
[3]R. A. Creswell, S. R. Brown, and R. H. Schwendeman, J. Chem. Phys. 64, 1820 (1976).
[4]R. H. Schwendeman, Ann. Rev. Phys. Chem. 29, 537 (1978).
[5]T. Oka (private communication).
[6]W. Hoke, J. Ekkers, and W. H. Flygare, J. Chem. Phys. 63, 4075 (1975).
[7]W. E. Hoke, D. R. Bauer, J. Ekkers, and W. H. Flygare, J. Chem. Phys. 64, 5276 (1976).
[8]T. Amano and R. H. Schwendeman, J. Chem. Phys. 65, 5133 (1977).
[9]R. H. Schwendeman and T. Amano, J. Chem. Phys. 70, 962 (1979).
[10]R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).
[11]W. E. Hoke, D. R. Bauer, and W. H. Flygare, J. Chem. Phys. 67, 3454 (1977).
[12]H. M. Pickett, J. Chem. Phys. 61, 1923 (1974).
[13]C. Bottcher, Chem. Phys. Lett. 34, 143 (1975).
[14]W. Liu and R. A. Marcus, J. Chem. Phys. 63, 272 (1975); J. Chem. Phys. 63, 290 (1975).
[15]D. A. Coombe and R. F. Snider, J. Chem. Phys. 67, 2659 (1977); J. Chem. Phys. 67, 2668 (1977).
[16]P. M. Thrash and R. H. Schwendeman, J. Chem. Phys. 71, 5196 (1979).
[17]R. H. Schwendeman, J. Chem. Phys. (to be published).
[18]B. J. Orr and T. Oka, J. Mol. Spectrosc. 66, 302 (1977).
[19]R. L. Legan, J. A. Roberts, E. A. Rinehart, and C. C. Lin, J. Chem. Phys. 43, 4337 (1965).
[20]B. Bleaney and R. P. Penrose, Proc. Phys. Soc. London 60, 540 (1948).
[21]R. R. Howard and W. V. Smith, Phys. Rev. 79, 128 (1950).
[22]J. Weber, Phys. Rev. 83, 1058 (1951).
[23]P. W. Anderson, Phys. Rev. 80, 511 (1950).
[24]J. S. Murphy and J. E. Boggs, J. Chem. Phys. 50, 3320 (1969).
[25]D. R. A. McMahon, J. Chem. Phys. 71, 3135 (1979).
[26]B. Bleaney and J. H. N. Loubser, Proc. Phys. Soc. London Ser. A 63, 483 (1950).
[27]T. Oka, J. Chem. Phys. 48, 4919 (1968).
[28]P. W. Daly and T. Oka, J. Chem. Phys. 53, 3272 (1970).
[29]T. Oka, Adv. At. Mol. Phys. 9, 127 (1973).
[30]J. W. C. Johns, A. R. W. McKellar, T. Oka, and M. Römheld, J. Chem. Phys. 62, 1488 (1975).