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Citation: The Journal of Chemical Physics **83**, 4975 (1985); doi: 10.1063/1.449761
View online: http://dx.doi.org/10.1063/1.449761
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Self-broadening and self-shifting of ammonia lines in the $2\nu_2$ band around 16 μm

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(Received 12 March 1985; accepted 12 June 1985)

We have measured the pressure broadening and shift of several transition lines of ammonia, $^{14}NH_3$, in the $2\nu_2$ band around 16 μm. Satisfactory agreement is found between the experimental results and a slightly modified version of the Anderson theory. A comparison between the theory and measurements of other authors has also been made.

INTRODUCTION

Recently we investigated in a systematic way the width and shift of several absorption lines of ammonia gas as a function of the pressure of the ammonia itself. We measured the broadening and the shift parameters of 46 lines of the $\nu_2 = 1 \leftarrow 0$ band in the range 868–953 cm^{-1},[1] and of 17 lines of the $\nu_2 = 2a \leftarrow 1s$ band, which fall in the same range of frequency.[2]

A comparison between experimental results and theory was made by using the Anderson approximation[3] extended to calculate the shift as well as the width.[4] The comparison confirms the reliability of the Anderson approach for the calculation of widths and shifts in the rotovibrational spectrum of ammonia.

In the present work we have extended our investigation to several absorption lines of the $\nu_2 = 2s \leftarrow 1a$ band, which fall around 630 cm^{-1}. The experimental results are in agreement with the theoretical expectations.

EXPERIMENTAL AND THEORETICAL DETAILS

The absorption lines of ammonia have been measured at $T \simeq 308$ K by using an infrared spectrometer with tunable diode lasers.[1] Diode lasers emitting around 16 μm were supplied by the Fraunhofer Institute fur Physikalische Meβtechnik in Freiburg, Germany. There were no particular difficulties in performing the measurements,[1,2] aside from those deriving from the closeness of two or more absorption lines. In several cases we had to take into account the absorption of the neighboring transitions in order to obtain the true 100% transmission curve. The accuracy of the broadening measurements is similar to or slightly better than that of the $2sQ$ lines,[2] i.e. $\lesssim 15\%$. An accuracy of $\sim 10\%$ or better has been reached in the shift measurements when the shift is larger than ~ 1 MHz/Torr, by using a method which eliminated the consequences of the frequency drift of the diode laser.

In Fig. 1(a) we report the linewidth and the shift of the $2aQ(6,6)$ line vs the NH_3 pressure. The linewidth measurements have been perturbed by the closeness of the $2aQ(8,7)$ line, $\Delta\nu = 0.232$ cm^{-1}. The scattering of the experimental points around the expected linear slope reflects the perturbation and the necessary correction. An unexpected result was obtained in the linewidth at low pressures, which turned out to be much larger than the expected Doppler width. This discrepancy must have been caused by the instability of the laser frequency, which is estimated to be ~ 130 MHz. This value is an order of magnitude larger than that expected for the diodes used for the measurements at 10 μm.[1] However that width of the laser emission implies an error of $\sim 2\%$ on the broadening parameter, which is negligible in view of the much larger errors originating from the method of measurement itself. In Fig. 1(b) we report the shift of the same line. The logarithmic plot of the experimental points has been fitted with a linear slope, as expected in a theory of binary collision.[1] However, the measurements seem to follow a slope slightly bigger than unity and the same behavior has been noticed in other lines. At the moment it is impossible to state that we are dealing with a nonlinear behavior, mainly because the experimental errors are still comparable to the deviation from linear slope. We therefore report only the best fit to a linear slope, although we feel that a more accurate investigation is desirable.

A detailed description of the theory has been provided in a previous paper.[1] Here we would like to recall a few points needed to explain the results. A central role in the Anderson theory[3] is played by the collision efficiency function $P(b)$ which, assuming dipole–dipole interactions for ammonia, is given by

$$P(b) \sim \frac{1}{b^4} \sum \mu_r^2 D_{rr'}^2 \{\mu_i^2 D_{ii'}^2 [f_{dd}(k_i) + i\phi_{dd}(k_i)] + \mu_f^2 D_{ff'}^2 [f_{dd}(k_f) - i\phi_{dd}(k_f)]\}, \quad (1)$$

where b is the impact parameter, μ is the dipole moment, D is a geometrical factor which is a function of the quantum numbers (J, K) of the levels, f_{dd} and ϕ_{dd} are known functions,[1] and k is a dimensionless parameter proportional to the energy exchanged during the collision. The sum is extended over all the possible inversion-rotation transitions,

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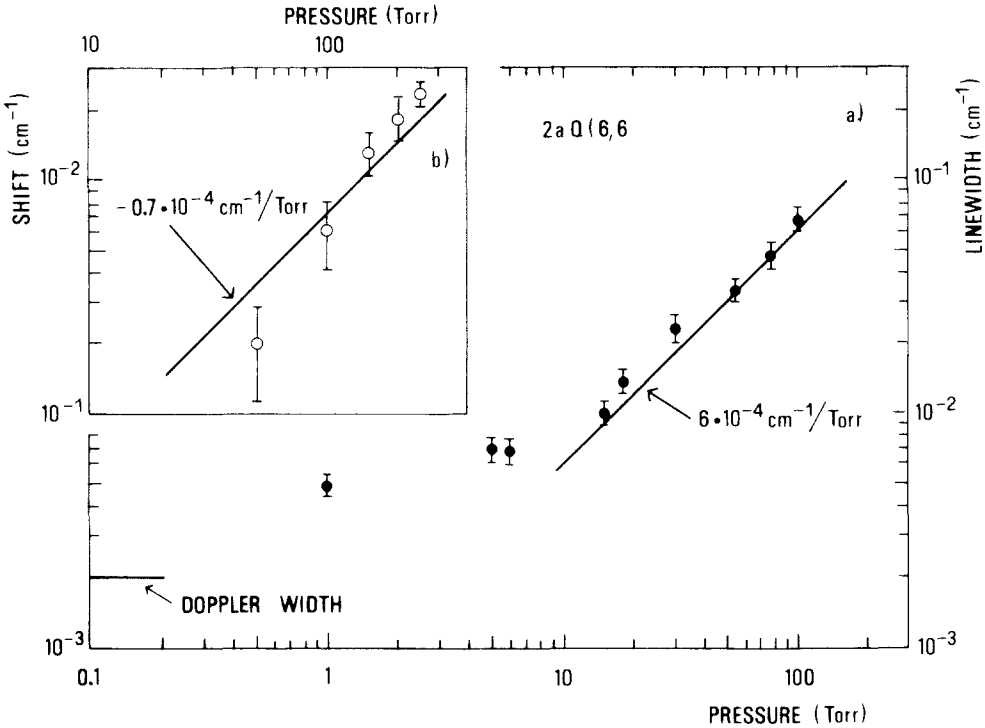

FIG. 1. Linewidth (FWHM) (a) and shift (b) of the $2aQ(6,6)$ transition vs NH_3 pressure.

$r \rightarrow r'$ of the perturbing molecule (mainly in the ground state, $v_2 = 0$) $i \rightarrow i'$ and $f \rightarrow f'$ of the absorbing molecule in the initial state $v_2 = 1$, and final state $v_2 = 2$, respectively.

We have taken into account both the real part, responsible for the broadening, and the imaginary part, responsible for the shift, to calculate the cutoff radius b_0. Recall that b_0 is the impact parameter, below which the collision produces a complete loss of memory of the original state of energy of the molecule. Thus, in order to define the cutoff radius b_0, we have used the truncation procedure T_2 as in the previous papers.[1,2]

The transitions we are dealing with here produce values of the dimensionless parameter k larger than unity, except in a few cases which will be considered below. This is mainly due to the inversion transition in the state $v_2 = 1, \sim 30\ \text{cm}^{-1}$, which is larger than in the ground state, $\sim 0.8\ \text{cm}^{-1}$. Because the function $f_{dd}(k_i)$ in Eq. (1) decays very quickly at high values of k, we expect broadening parameters smaller than in the $v_2 = 1 \leftarrow 0$ transitions[1] and similar to the $v_2 = 2 \leftarrow 1$ previously measured transitions.[2]

As far as the shift is concerned we expect a change of sign with respect to the $2sQ$ transitions.[2] Indeed because of the negative value of the inversion energy jump in the $v_2 = 1a$ level, the parameter k becomes negative as the odd–parity function $\phi_{dd}(k_i)$ in the expression of $P(b)$. The situation is quite different for small values of J, where positive rotational jumps can compete with negative inversion transitions or for small values of the ratio K/J, for which the factor $D_{ii'}$ in the expression of $P(b)$ greatly diminishes the influence of the negative terms. In such cases the shift can be either negative or positive depending on the particular transitions involved.

RESULTS AND DISCUSSION

The measured broadening a and shift b parameters[1] are reported in Table I for 17 Q-branch transitions of the $s2v_2 \leftarrow av_2$ band. The frequencies for the transitions have been measured previously[5] except for $2aQ(4,1)$ and $2aQ(9,6)$ for which new data have been used.[6] The broadening parameters of the transitions $2aQ(3,3)$ and $2aQ(6,5)$ have not been measured because of their closeness, while the shifting parameter of the $2aQ(5,3)$ is not reported because of poor experimental reliability.

TABLE I. Pressure broadening (HWHM) a and pressure shift b in MHz/Torr of rotovibrational transitions in the $2v_2$ band of ammonia $^{14}NH_3$.

Transition	v_0(cm^{-1})	Broadening		Shift	
		a_{meas}	a_{calc}	b_{meas}	b_{calc}
$2aQ(1,1)$	629.443	12.5	13.3	2.2	2.1
$2aQ(2,2)$	629.108	6.5	6.3	−0.5	−0.6
$2aQ(3,1)$	632.491	8.6	7.4	1.3	1.0
$2aQ(3,2)$	630.880	8.0	7.1	−0.7	−0.8
$2aQ(3,3)$	628.348	...	6.8	−3.0	−2.2
$2aQ(4,1)$	635.043	9.6	7.5	0.3	0.2
$2aQ(4,3)$	630.624	8.5	7.8	−1.9	−1.7
$2aQ(4,4)$	627.163	7.0	7.4	−2.2	−2.3
$2aQ(5,3)$	633.644	9.0	8.1	...	−1.3
$2aQ(5,4)$	629.824	8.5	8.1	−1.7	−1.8
$2aQ(5,5)$	625.548	7.5	7.7	−2.2	−2.1
$2aQ(6,5)$	628.423	...	7.9	−2.0	−1.7
$2aQ(6,6)$	623.510	9.0	7.7	−2.1	−1.9
$2aQ(7,5)$	632.280	8.5	7.4	−1.8	−1.7
$2aQ(7,6)$	626.387	10.0	7.6	−2.5	−1.8
$2aQ(8,7)$	623.742	11.5	7.3	−2.2	−1.8
$2aQ(9,6)$	635.672	9.4	7.0	−2.5	−1.9

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TABLE II. Pressure broadening and shift in MHz/Torr of infrared absorptions of ammonia from other authors, compared with theory.

Transition	ν_0(cm^{-1})	Broadening		Shift	
		a_{meas}	a_{calc}	b_{meas}	b_{calc}
$2sR$ (3,1)[a]	1023.203	7.0	8.3	1.3	0.4
$2sR$ (4,3)[a]	1043.156	9.6	8.3	2.0	3.0
aR (0,0)[b]	947.796	12.0	12.0	4.0	3.7

[a] Reference 14.
[b] $^{15}NH_3$, Ref. 13.

The theoretical broadening and shifting parameters have been calculated for $T = 308$ K, and by using the energy levels as given by Taylor.[7] We have not found substantial variations by using the more recent and precise spectroscopic constants of Urban *et al.*[8] The dipole moments of the ammonia molecule have been taken as follows: $\mu(\nu_2 = 0) = 1.47$ D,[9] $\mu(\nu_2 = 1) = 1.25$ D,[9] and $\mu(\nu_2 = 2) = 0.83$ D.[10] We have also performed calculations on the present transitions and on the previous ones[2] by using the recent value $\mu(\nu_2 = 2) = 1.02$ D.[11] We have found differences which are less than 5% for a_{calc}, and seldom larger than 10% for b_{calc}. Thus in the present work we have kept the old value for $\mu(\nu_2 = 2)$ in order to be consistent with the previous papers.[1,2]

A comparison between the measured and calculated values of the broadening and shifting parameters in Table I shows substantial agreement, especially if one takes into account the various errors and uncertainties both in the experiments and in the theory. As expected the width values are smaller than those in the $\nu_2 = 1 \leftarrow 0$ band[1] and similar to each other except for the line $2aQ(1,1)$. This result is explained by the accidental near degeneracy between the $a(1,1)$ and $s(2,1)$ levels in the $\nu_2 = 1$ band. They are separated only by ~ 4 cm^{-1}, and as a consequence the probability function $P(b)$, and hence the width, increases for collisions involving one of these levels. Analogous cases have been observed for the transition $2sP(2,1)$[2] and for the inversion transitions $a(1,1) \leftarrow s(1,1)$ and $a(2,1) \leftarrow s(2,1)$,[1,12] both of which have in common one of the aforementioned levels. For the shifts we expected negative values in the majority of the cases, and this is exactly what we have found. However the transition $2aQ(1,1)$ is a notable exception. Again, as for the width, the energy exchanges during the collisions are small because the rotational jumps are of the same order as the inversion jump, and so the negative contribution of $\phi_{dd}(k_i)$ is not big enough to overcome the positive one. The two transitions $2aQ(3,1)$ and $2aQ(4,1)$ have values of K/J of 0.33 and 0.25, respectively, and so the negative term is decreased by the geometrical factor $D_{ii'} = K^2/[J(J+1)]$.

In addition we report in Table II the measured[13,14] and calculated values for the broadening and shift parameters of two lines from the excited vibrational state of $^{14}NH_3$ and one line from the ground state of $^{15}NH_3$. The frequency in cm^{-1} of the transitions has been taken from Refs 14, 15, and 16, respectively, for the lines $2sR$ (3,1), $2sR$ (4,3), and aR (0,0) ($^{15}NH_3$). The measurements have been performed by measuring the absorption of a CO_2 laser line close, but not coincident, to the ammonia transition to be investigated, as a function of the pressure of the ammonia itself. This method, devised when tunable infrared sources were not easily available,[17–19] usually gives good results, although there are several difficulties arising mainly from the fitting procedures. Note that the value of a_{meas} for the aR (0,0) ($^{15}NH_3$) line is almost equal to that of the more abundant isotope species $^{14}NH_3$,[1] as expected from the Anderson theory. In conclusion, there is a fairly good agreement between measured and calculated values in Table II.

Until a few years ago only a few pressure broadening and shift measurements were available for the infrared transitions of ammonia and it was not possible to make a useful comparison with the theory. Now the large number of transitions studied in this paper and in the previous ones[1,2] give both a satisfactory picture from the experimental point of view and solid confidence in the validity of the Anderson theory.

[1] G. Baldacchini, S. Marchetti, V. Montelatici, G. Buffa, and O. Tarrini, J. Chem. Phys. **76**, 5271 (1982). Table I of this paper contains three errors; a_{meas} for the lines $aP(3,1)$, $sP(5,0)$, and $sP(5,1)$ should be 16, 11, and 12, respectively, instead of the reported values of 10, 15.5, and 16.0.
[2] G. Baldacchini, S. Marchetti, V. Montelatici, V. Sorge, G. Buffa, and O. Tarrini, J. Chem. Phys. 78, 665 (1983). Table I of this work contains two errors; b_{calc} for the lines $2sQ(2,2)$ and $2sQ(6,3)$ should be 3.0 and 2.4 instead of the reported values of 3.9 and 2.8.
[3] P. W. Anderson, Phys. Rev. **76**, 647 (1949).
[4] A. Di Giacomo and O. Tarrini, Nuovo Cimento B **68**, 165 (1970).
[5] G. Baldacchini, S. Marchetti, and V. Montelatici, J. Mol. Spectrosc. **103**, 257 (1984).
[6] J. Hermanussen, A. Bizzari, and G. Baldacchini, Report ENEA and to be published.
[7] F. W. Taylor, J. Quant. Spectrosc. Radiat. Transfer **13**, 1181 (1973).
[8] S. Urban, V. Spirko, D. Papousek, R. S. McDowell, N. G. Nereson, S. P. Belov, L. I. Gershstein, A. V. Maslovskij, A. F. Krupnov, J. Curtis, and K. Narahari Rao, J. Mol. Spectrosc. **79**, 455 (1980).
[9] F. Shimizu, J. Chem. Phys. **51**, 2754 (1969); **52**, 3572 (1970).
[10] W. K. Bischel, P. J. Kelly, and C. K. Rhodes, Phys. Rev. A **13**, 1828 (1976).
[11] M. Takami, H. Jones, and T. Oka, Chem. Phys. **70**, 3557 (1979).
[12] S. P. Belov, L. I. Gershstein, A. F. Krupnov, A. Maslovskij, S. Urban, V. Spirko, and D. Papousek, J. Mol. Spectrosc. **84**, 288 (1980).
[13] M. O. Bulanin, Yu. M. Ladvishchenko, and E. B. Khodos, Opt. Spectrosc. **53**, 119 (1982).
[14] M. O. Bulanin, Yu. M. Ladvishchenko, and Yu. M. Sveshnikov, Opt. Spectrosc. **54**, 116 (1983).
[15] K. J. Siemsen and J. Reid, Appl. Opt. **17**, 3523 (1978).
[16] G. Di Lonardo, L. Fusina, and A. Trombetti, J. Mol. Spectrosc. **92**, 298 (1982).
[17] T. Shimizu, F. O. Shimizu, R. Turner, and T. Oka, J. Chem. Phys. **55**, 2822 (1971).
[18] V. S. Letokhov, A. G. Platova, and O. A. Tumanov, Opt. Spectrosc. **37**, 29 (1974).
[19] V. P. Bulychev, Yu. M. Ladvishchenko, E. B. Khodos, and M. O. Bulanin, Opt. Spectrosc. **41**, 237 (1976).

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