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G. Baldacchini, S. Marchetti, V. Montelatici, G. Buffa, and O. Tarrini

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Experimental and theoretical investigation of self-broadening and self-shifting of ammonia transition lines in the ν_2 band

G. Baldacchini, S. Marchetti, and V. Montelatici

Comitato Nazionale Energia Nucleare-Centro di Frascati, C.P. 65-Frascati, Rome, Italy

G. Buffa and O. Tarrini

Insituto di Fisica dell'Università e Gruppo Nazionale di Struttura della Materia, Pisa, Italy
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We have measured self-broadenings and self-shiftings of several rotovibrational transitions of the ν_2 band of NH_3. We have found smaller broadenings and bigger shifts with respect to the known data of the inversion spectrum in the microwave region. The experimental results are compared with the Anderson original line broadening theory, successively extended in order to calculate the shift also. The agreement between experiments and theory is quite good so that it is possible to select the right procedure among those usually adopted in order to avoid divergences occurring in the Anderson's perturbative treatment of the molecular collision matrix.

I. INTRODUCTION

The pressure broadening and shift of radiative transitions are a consequence of collisions between molecules, and their knowledge gives useful insights on molecular interactions.

Ammonia gas has been extensively studied, especially in its microwave inversion spectrum, since the early days of microwave development. Good reviews of these early measurements and of their theoretical interpretation have been made by Townes and Shawlow[1] and later by Birnbaum.[2] Recently, there has been a renewed interest in the microwave region of the spectrum. However, several discrepancies can be found among the experimental results of various authors, especially for the line shifts.[3-6]

These discrepancies are not surprising at all, both for the experimental difficulties to eliminate spurious effects due to the microwaves themselves and for the small shifts exhibited by the line transitions in this region of the spectrum.

On the contrary, only a few infrared transitions have been measured so far,[7-12] mainly for the lack of suitable tunable sources. Smaller linewidths and bigger shifts than those in the microwave region are expected from general considerations and such trends have been really observed in the previous few measurements and in our preliminary systematic study.[13]

In Sec. II, we describe the experimental apparatus and the method used to measure both the broadening and the shift in ammonia gas at room temperature. The peculiar properties of a diode laser source have been fully exploited and a few relevant measurements will be shown.

As far as theory is concerned, Anderson's[14] approximation provides a tool which can be easily extended to the calculation of the linewidths in the infrared spectrum. An extension of the Anderson's theory[15,5] allows, also, the calculation of the shifts.

However, contrary to what happens in the microwave spectrum, in the infrared region different ways[16,17] to interrupt Anderson's perturbative procedure lead to different shift values. In Sec. III, we recall the general features of that theory and we will specialize it for molecules interacting through a force that is mainly dipole–dipole, which is the case of ammonia molecules.

Finally, in Sec. IV, we will make a comparison between experimental results and theoretical calculations. We will see that, putting aside minor discrepancies, there is an overall agreement, especially for the shifts, some of which are much bigger than in the inversion spectrum of the ground state. The comparison between the measured shifts and the calculated ones also allows us to decide which one of the possible perturbative procedures must be used. Our conclusions in this point are in complete agreement with the findings of Boulet *et al.*[17] for the infrared spectrum of the linear molecules HCl, HF, DF, and DCl.

II. EXPERIMENTAL

The absorption spectrum of ammonia has been measured by using a tunable diode laser. The infrared radiation from the diode (Laser Analytics, Inc.) is collected by a lens and sent through a cell containing the ammonia gas at the desired pressure. After traversing a germanium etalon, used for relative calibration of the frequency scale, the radiation is focused to the entrance slit of a spectrometer to filter out spurious emission modes from the laser. Eventually, the infrared radiation is revealed by a copper-doped germanium detector (SBRC Mod. MO-80), cooled at 4.2 K, and the electrical signal sent to an averager (Memory-Display HP 5480B). Usually, hundreds of signals are averaged in order to have a good signal to noise ratio, and the final result is transferred to an $X-Y$ plotter. The frequency of the laser diode is swept across the absorption line under study by modulating linearly the current of the diode, while keeping its temperature constant. So, on the plotter, we have a signal which represents the trans-

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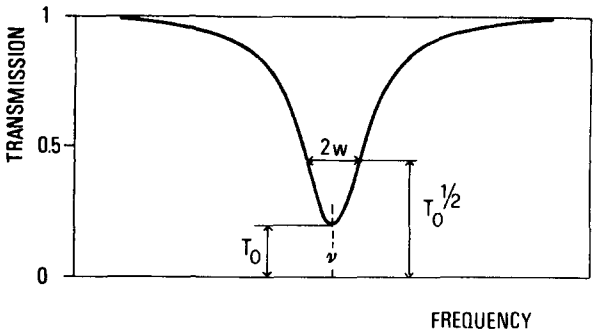

FIG. 1. Schematic drawing of a pressure broadening absorption line with quantities relevant for the measurement of the linewidth.

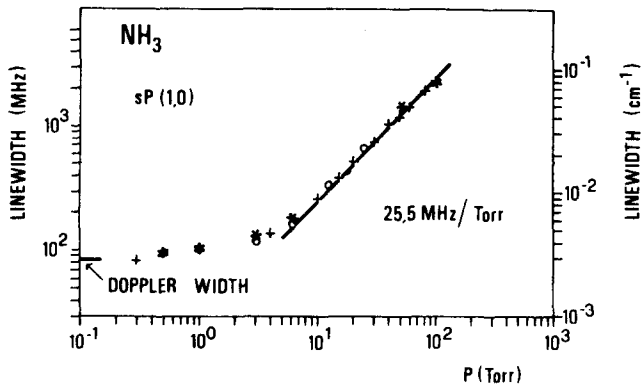

FIG. 3. Linewidth $2w$ of the $sP(1,0)$ transition vs NH_3 pressure. Different symbols refer to various experimental runs.

mission of the absorbing gas in the cell vs the frequency.

In Fig. 1, we have represented schematically the case of a typical absorption line, which is characterized by the center frequency ν and by the linewidth $2w$. For linewidth $2w$, we mean the full width at one-half of the maximum absorption (FWHM). If T_0 is the minimum transmission, corresponding to the maximum absorption α_0 $[\alpha = \log(T^{-1})]$, it is easily shown that $2w$, corresponding to $\frac{1}{2}\alpha_0$, is the width measured at $\sqrt{T_0}$, as shown in Fig. 1.

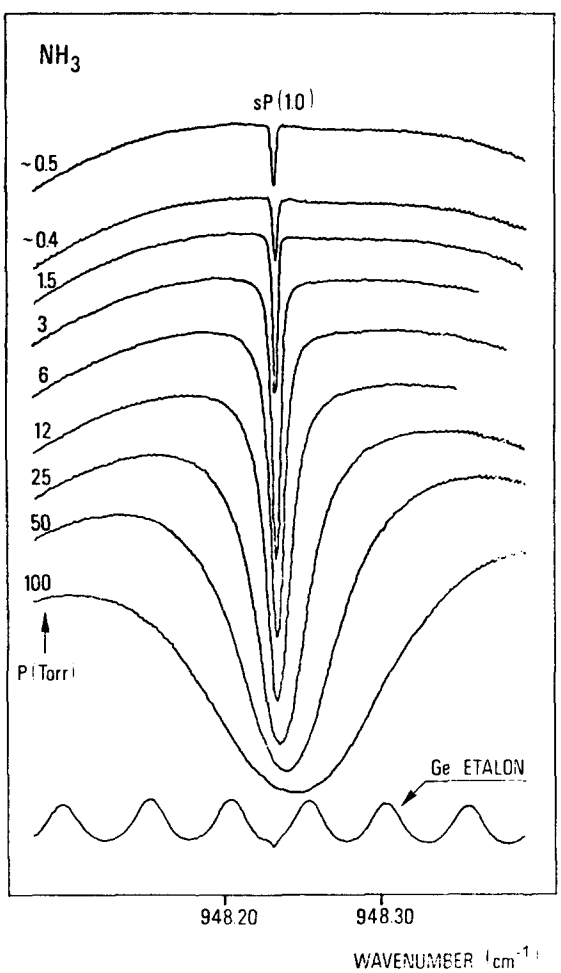

FIG. 2. Lineshape of the $sP(1,0)$ transition at various NH_3 pressures. The interference fringes of the germanium etalon are spaced by 0.0492 cm^{-1}.

However, the determination of w contains some uncertainties which are almost impossible to avoid. The power of the diode emission is not constant vs the frequency, as in Fig. 1. Usually, it is bell shaped and corrections are necessary to reconstruct the form of the absorption. Often, it is not possible to eliminate completely spurious modes which do not contribute to the absorption, but which affect the experimental determination of T_0. Finally, the width of the emission of the diode laser ($\Delta\nu$ laser) can contribute to the width of the absorption line. We have determined this contribution by measuring the width of the ammonia lines at low pressures, where the linewidth is given, essentially, by the Doppler effect

$$2w_D = 0.0214 \sqrt{\frac{T}{M}}\, \bar{\nu}(\mathrm{MHz}), \qquad (1)$$

where $\bar{\nu}$ (cm^{-1}) is the frequency of the transition, $T(K)$ the temperature, and M the molecular weight of the gas. By properly subtracting the Doppler contribution $2w_D$, which is ~85 MHz in our case, from the experimental linewidth, we inferred $\Delta\nu$ (laser) ~10 MHz during the time of a line measurement. Such instability of the laser frequency reported previously by other authors,[18,19] and the other sources of errors discussed previously introduce an uncertainty in the measurement of w which is of the order of 10%. However, the laser frequency instability affects much more the measurement of the line shift $s = \nu - \nu_0$, where ν_0 is the center position of the line at low pressure. Without going into too much detail, it suffices to say that we were able to measure with a reasonable accuracy only shift parameters bigger than ~1 MHz/Torr.

In Fig. 2, we report the line shape of the transition $sP(1,0)$ at various NH_3 pressures. The top curve at 0.5 Torr has been made at the end of the whole run to check again the center position of the line. The bell-shaped mode of the laser is clearly visible and some corrections have been made, especially at high pressures. The linewidth $2w$ of the transition is reported in Fig. 3 vs NH_3 pressure. The linear dependence on the pressure (solid line) after ~6 Torr is in agreement with the theory[14] on the collision broadening. Moreover,

we have analyzed the line shapes of the absorption at pressures below 1 Torr and above 10 Torr, and we have found, within the experimental errors, a Gaussian and a Lorentzian shape, respectively, as expected. Between 1 and 10 Torr, the shape of the absorption is well described by a Voigt profile. The blue shift of the $sP(1,0)$ line is reported in Fig. 4, together with the much smaller red shift of the line $aQ(6,4)$. The expected linear dependence on the pressure is well displayed, but the scattered experimental points are a proof of the large inaccuracy of these kind of measurements. The uncertainty on the value of the pressure, in both width and shift measurements, is of the order of 2% at high pressures, so it does not contribute appreciably to the total error, ~10% for the broadening measurements and even bigger for the shift measurements, as determined before. Some difficulties have been found in measuring w and s of multiplets which are not uncommon in the ν_2 band of ammonia. The single transitions merge in one big absorption at a moderately low pressure,[13] so it is almost impossible to measure the shift of the single lines, which are sucked toward the center of gravity of the multiplet.

In conclusion, we have measured the width and, when possible, the shift of several lines in the ν_2 band of ammonia vs NH_3 pressure. The experiments were carried out at room temperature (293 K). The numerical results will be given in Sec. IV, along with the few measurements made by other authors.

III. THEORY

Details on the theory of pressure shift and pressure broadening in the frame of the impact approximation[20] has been extensively given elsewhere.[5,14-17,21,22] In the following we recall briefly some essential points.

At low pressures, the width w (half-width at half-maximum) and shift s are linear with the number density n of the gas, and are given by

$$w = n \operatorname{Re} \bar{L} , \qquad s = n \operatorname{Im} \bar{L} . \tag{2}$$

$n\bar{L}$ describes the relaxation of the thermal bath on the line and is expressed, in the frame of Anderson[14] approximation, in term of binary collisions with relative velocity v and impact parameter b, by

$$\bar{L} = \left\langle v\pi b_0^2(r,v) + v\int_{b_0}^{\infty} 2\pi b\, db\, P(r,v,b) \right\rangle_{r,v} , \tag{3}$$

r being the internal states of the perturbing molecule and b_0 the cutoff radius, defined by the assumption that collisions with impact parameter smaller than b_0 completely interrupt the process of radiation.

$P(r,v,b)$ can be expressed perturbatively in terms of the intermolecular interaction, that, in our case, is mainly dipole–dipole, by the complex formula

$$P(r,v,b) = \frac{4}{9\hbar^2 v^2 b^4} \sum_{\substack{r',i' \\ J_r',J'}} \mu_r^2 D^2(rJ_r \to r'J_r') \times \{\mu_i^2 D^2(l_iJ_i \to l'J')[f_{dd}(k_i) + i\varphi_{dd}(k_i)] + \mu_f^2 D^2(l_fJ_f \to l'J')[f_{dd}(k_f) - i\varphi_{dd}(k_f)]\} , \tag{4}$$

where the quantum numbers $rJ_r \to r'J_r'$ describe the collisional transition of the perturbing molecule; r and r' summarizing all quantum numbers other than J_r, J_r'; and $l_iJ_i \to l'J'$, $l_fJ_f \to l'J'$ describe the possible collisional transitions from the initial i and final f states of the absorbing molecule; μD is the reduced matrix element of the dipole moment in the transition and μ depends on the vibrational quantum number ν_2 through the subscript r, i, f; μ_r is the dipole moment in the fundamental $\nu_2 = 0$ state, since only a small fraction of the perturbing molecules is vibrationally excited; μ_i is the dipole moment for $\nu_2 = 0$ and μ_f for $\nu_2 = 1$, since we are treating the $\nu_2 = 0 \to 1$ band. f_{dd} and φ_{dd} are, respectively, the function defined by Tsao and Cornutte[22] for the dipole–dipole interaction and its transform[15,17] and they are reported in Fig. 5. Their argument $k_{i,f}$ represents the ratio between the frequency $\omega_{i,f} = \Delta E_{i,f}/\hbar$ involved in the energy jump in the collision and the inverse of the duration of the collision v/b, i.e., $k_{i,f} = \Delta E_{i,f} b/\hbar v$ being $\Delta E_{i,f} = E(l',J') + E(r',J_r') - E(l_{i,f},J_{i,f}) - E(r,J_r)$.

The cutoff radius b_0 of Eq. (3) is defined in the original

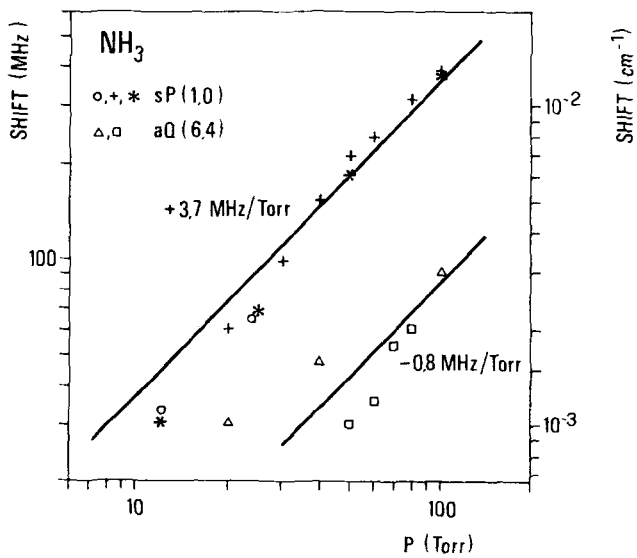

FIG. 4. Frequency shift s of $sP(1,0)$ and $aQ(6,4)$ lines vs NH_3 pressure. Different symbols refer to various experimental runs.

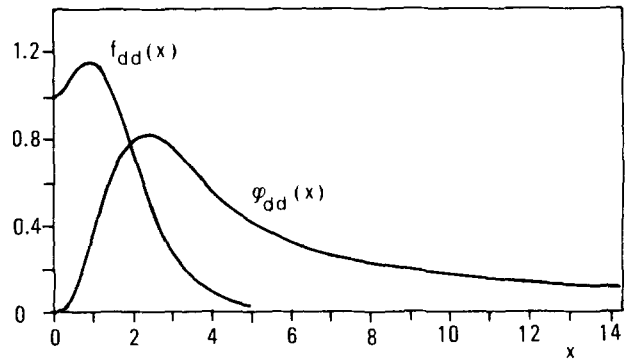

FIG. 5. Shape of the functions f_{dd} and φ_{dd} occurring in the calculation of the width and shift for dipole–dipole interaction.

Anderson line-broadening theory by imposing the unitary bound to $P(r, v, b)$ through

$$\mathrm{Re}\, P(r, v, b_0) = 1 \ . \tag{5}$$

For infrared spectra, for which the condition $\mathrm{Im}\, P \ll \mathrm{Re}\, P$ is not anymore valid,[16,17] it has been suggested that condition (5) should be changed more appropriately to

$$[\mathrm{Re}\, P(r, v, b_0)]^2 + [\mathrm{Im}\, P(r, v, b_0)]^2 = 1 \ . \tag{6}$$

From the above theory, we have performed a numerical computation of the width and shift using both cutoff procedures [Eqs. (5) and (6)], which we shall call truncation 1 ($T1$) and truncation 2 ($T2$), respectively. For the ammonia dipole moment, we have used the values[23] $\mu = 1.47$ D for the ground vibrational state and $\mu = 1.25$ D for $\nu_2 = 1$. Interactions other than dipole–dipole have been neglected, since their contribution represents only a few percent of the total. The energy level structure of the ammonia molecule has been deduced by using the spectroscopic constants reported by Taylor.[24] More precise determinations are available now,[25] but our calculation is not influenced by errors of the order of 0.5 cm^{-1}. Moreover, we have performed an explicit numerical integration over the Maxwellian distribution of the collisional velocities. The simple use of the average velocity $\bar{v}$ would have produced good results for the widths but considerable discrepancies for the shifts.

IV. DISCUSSION AND CONCLUSIONS

In Table I, we report the measured self-broadening a and self-shifting b parameters defined as

$$\begin{aligned} w &= aP \ , \\ s &= bP \ , \end{aligned} \tag{7}$$

where P is the pressure of the gas in Torr, of several transitions from the ground state to the first excited state of the ν_2 band of ammonia. Clearly, the first of Eqs. (7) holds in the region of pressures where the collision broadening processes dominate the Doppler effect (see Fig. 3). The experimental values are compared with those calculated with the theory outlined in the previous section, by using both cutoff procedures $T1$ and $T2$. The position of the transitions have been desumed by the current literature.[13,25–27]

A. Shift

Because of small shifts, or bad power modes of the laser, or the presence of absorption multiplets, we were not able to measure the shift or give an indication of its sign for some transitions. However, the shift parameters b, not reported in Table I, do not exceed a few MHz/Torr at most, otherwise we would have measured them.

A close inspection of the measured shift values and the calculated ones allows us to conclude that the truncation procedure $T2$, which takes into account the imaginary part of $P(b)$, also, must be preferred. This conclusion about the cutoff procedure is in complete agreement with the results which Boulet *et al.*[17] have found for the rotovibrational spectrum of HF and other linear molecules.

The use of $T1$ produces large discrepancies for a number of lines. These discrepancies, which cannot be attributed to experimental errors alone, are particularly evident in the case of the lines $aR(0, 0)$, $aP(2, 0)$, and $sP(1, 0)$.

The agreement which we have found is quite interesting because spectroscopic data from the microwave inversion spectrum of NH_3 in the ground state $\nu_2 = 0$ could lead to doubt the validity of the theory in the calculation of the shifts. Indeed, a number of experiments[3,5,6,28] have found for that spectrum shift values that are in complete disagreement with the calculated ones ($T1$ and $T2$ are, in this case, equivalent). Only one experiment[4] has given for the (13, 13) inversion line at 1.105 cm^{-1} a shift parameter of $+1.9 \pm 0.4$ MHz/Torr, which is compatible with the theoretical value of $+2.5$ MHz/Torr.

However, experiments,[29,30] always in the microwave region of the spectrum, in other molecules such as CH_3Br, CH_3I, CH_3F, and N_2O have given shift values in agreement with the theory. In this conflictual situation, the validity of the previous theory is confirmed from our rotovibration measurements, where the shift to width ratio is large enough for some lines to give reliable shift values.

Recently, shift measurements have been performed by Belov *et al.*[31,32] for some inversion–rotation transitions in the excited vibrational state $\nu_2 = 1$ of ammonia, occurring in the submillimeter frequency region. We have calculated from the theory the width and shift for such lines. As can be seen in Table II, also, in this case, the agreement is good when the cutoff procedure $T2$ is used.

So it is possible to conclude that the theory allows reliable calculation for the shifts even if minor discrepancies remain, which are probably caused by both experimental difficulties and approximation involved in the theory.

B. Width

From Table I, it can be seen that the discrepancy among theory and experiments for most of the lines is of the order of 10%, which can be considered a good agreement because it is of the same order of the experimental errors. Discrepancies of the same order were also found in the microwave inversion spectrum. The agreement is equally good for the rotovibrational lines measured by other authors, some of which are reported in Table III. Three lines in Table I [$aP(3, 1)$, $sP(5, 0)$ and $sP(5, 1)$] show a discrepancy quite larger than 10%. However, they have been measured at the end of very weak laser modes so that the experimental error on the width is far larger than in the other transition lines.

It is interesting to note that in multiplets such as $sP(4, K)$ and $sP(3, K)$, the K dependence on the width is very closely reproduced by theory. This is important

TABLE I. Pressure shift and broadening, in MHz/Torr, of rotovibrational transitions of the ν_2 band of ammonia ($^{14}NH_3$).

Transition	ν_0(cm^{-1})	Broadening			Shift		
		a_{meas}	a_{calc}		b_{meas}	b_{calc}	
			$T1$	$T2$		$T1$	$T2$
$aQ(1,1)$	931.629	22.5	19.4	19.5		−0.2	−0.5
$aQ(2,1)$	932.136	17.5	17.3	17.4		+1.1	+1.1
$aQ(3,1)$	932.880	13.0	13.3	13.6		+1.5	+1.1
$aQ(3,2)$	932.095	16.5	17.9	18.0		−0.3	−0.4
$aQ(3,3)$	930.756	22.0	22.9	23.0	−2.4	−1.5	−1.6
$aQ(4,2)$	933.076	16.5	16.0	16.2	<0	−0.2	−0.5
$aQ(4,3)$	931.771	21.0	19.7	19.8	<0	−0.8	−1.0
$aQ(5,3)$	932.992	20.0	17.7	17.8	−2	−1.0	−1.0
$aQ(6,1)$	936.315	13.0	11.8	12.1		+0.5	+0.1
$aQ(6,3)$	934.381	15.5	16.1	16.2	−1.6	−0.9	−0.9
$aQ(6,4)$	932.636	16.5	18.6	18.7	−1.4	−1.2	−1.2
$aQ(7,1)$	937.741	12	10.5	10.8		+0.8	+0.3
$aQ(7,2)$	937.066	11.5	12.3	12.5		+0.1	−0.2
$aQ(7,5)$	932.008	18.0	19.0	19.2		−1.0	−1.2
$aQ(8,2)$	938.627	11.5	10.6	10.8		+0.4	0.0
$aQ(8,3)$	937.516	12.0	12.6	12.8	−0.6	−0.1	−0.4
$aQ(9,4)$	937.699	15.5	12.9	13.1		−0.2	−0.5
$aQ(9,6)$	933.160	16.0	17.2	17.4	<0	−0.6	−1.0
$aQ(9,9)$	921.255	25.5	23.7	23.9		−0.8	−1.7
$aQ(10,5)$	937.612	13.5	13.4	13.5	<0	−0.3	−0.7
$aQ(10,6)$	935.222	17.0	15.4	15.6	−1.3	−0.4	−0.9
$aQ(10,7)$	932.235	19.0	17.5	17.6	<0	−0.5	−1.0
$aQ(10,10)$	918.621	19.5	23.7	24.0		−0.9	−1.7
$aQ(11,6)$	937.273	13.5	14.0	14.1		−0.5	−0.9
$aQ(11,10)$	921.812	24	21.9	22.1	−3	−0.7	−1.4
$aQ(11,11)$	915.665	21	23.8	24.0		−1.0	−1.8
$aQ(12,12)$	912.385	18	23.8	24.0		−1.0	−1.9
$aQ(13,7)$	938.782	11.5	13.6	13.7		−0.8	−1.1
$aQ(13,9)$	932.291	17.5	16.9	17.0		−0.8	−1.3
$aQ(13,13)$	908.764	22.5	23.8	24.1	<0	−1.1	−1.9
$aR(0,0)$	951.778	12.0	11.4	12.4	+4.5	+7.0	+3.7
$aP(2,0)$	892.158	13.0	10.7	11.4	−2.0	−4.3	−2.4
$aP(2,0)$[a]	888.324	11.2	10.4	11.2	−1.7	−4.3	−2.3
$aP(2,1)$	891.884	15	14.1	14.2	<0	−1.6	−1.5
$aP(3,1)$	872.565	10	16.5	16.6	>0	+1.8	+1.5
$sQ(15,15)$	952.436	21	23.9	24.2		+0.7	+1.8
$sP(1,0)$	948.234	12.5	11.0	12.1	+3.7	+6.9	+3.7
$sP(2,1)$	928.230	20.5	18.1	18.3	−2.2	−2.5	−1.9
$sP(3,0)$	908.200	14.0	10.7	11.7		−7.6	−2.6
$sP(3,1)$	908.178	17.5	13.2	13.5		−2.6	−1.6
$sP(3,2)$	908.115	20.0	17.4	17.6	>0	+0.8	+0.8
$sP(4,1)$	888.084	12.0	12.8	13.1		−1.7	−0.8
$sP(4,2)$	888.003	13.5	16.1	16.3		+0.3	+0.6
$sP(4,3)$	887.877	16.5	19.4	19.6		+1.8	+1.6
$sP(5,0)$	868.001	15.5	10.7	11.1	−1.3	−4.7	−1.0
$sP(5,1)$	867.967	16.0	12.3	12.6	−1.0	−1.6	−0.6

[a] $^{15}NH_3$.

because some experiments[29,33,34] on other symmetric top molecules in the microwave region had led to doubt of the theoretical expectation on the K dependence of the linewidth.

Many $aQ(J,K)$ lines have been measured and for them, too, the J, K dependence of the width is satisfactory reproduced. If we compare these lines with the corresponding (J,K) lines of the microwave inversion spectrum, we find a reduction of the pressure broadening. Indeed, the typical parameter a for the $J=K$ inversion lines is 23–25 MHz/Torr, while, for the $aQ(J,J)$ lines, we find 18–22 MHz/Torr. This reduction is easily understood from Eq. (4). In the rotovibrational spectrum, the transitions allowed by the dipole selection rules from the final state f are all characterized by energy differences of the order of 30 cm^{-1}, and so the values of k_f appearing in Eq. (4) are of the order of five or more. The exponential decrease of the function $f_{dd}(k)$ (see Fig. 5) causes a strong reduction of the

TABLE II. Pressure shift and broadening of inversion and inversion–rotation transitions in the $\nu_2=1$ state of ammonia. Measurements from Belov *et al.* compared with theory.

Transition	$\nu_0(\text{cm}^{-1})$	Broadening			Shift		
		a_{meas}	a_{calc}		b_{meas}	b_{calc}	
			$T1$	$T2$		$T1$	$T2$
$(1,1)^a$	35.579	15[d]	15.2	15.5	−2.4	−2.4	−1.7
$(2,1)^a$	34.796		13.9	14.2	<0	−3.6	−2.8
$(2,2)^a$	35.613	11[d]	8.4	9.5	+1.5	+6.1	+1.8
$(7,5)^a$	32.084		8.8	10.0	>0	+6.7	+2.1
$(8,5)^a$	29.587		8.2	9.2	>0	+4.7	+1.8
$(9,6)^a$	29.198		7.5	8.8	>0	+5.7	+2.0
$s(1,0)\rightarrow a(0,0)^b$	15.553		11.8	13.4	+3.2	+10.7	+4.8
$s(1,0)\rightarrow a(0,0)^{b,c}$	14.350		11.4	13.0	+3.15	+11.0	+4.7
$a(2,0)\rightarrow s(3,0)^a$	25.674		9.7	10.9	+3.6	+7.8	+2.9
$a(2,1)\rightarrow s(3,1)^a$	25.445		9.5	10.4	+3.3	+5.8	+2.4
$a(2,2)\rightarrow s(3,2)^a$	24.743		8.5	8.9	−0.2	−1.3	−0.6

[a]Reference 31.

[b]Reference 32. The values of b_{meas} have been obtained by indirect method, A. F. Krupnov and S. P. BePov, Izv. Vuzov Radiofizika **22**, 901 (1979); from the data of E. N. Karyakin, A. F. Krupnov, D. Papousek, Yu. M. Shchurin, and S. Urban, J. Mol. Spectrosc. **66**, 171 (1977). The correct value of the line-shift parameter is equal to +5.6 MHz/Torr instead of +3.2 MHz/Torr (private communication from A. F. Krupnov).

[c]$^{15}NH_3$. Same as in footnote (b). The correct value of b_{meas} is ~5.6 MHz/Torr instead of 3.15 MHz/Torr.

[d]Deduced by the shift to width ratio reported in Ref. 31.

broadening contribution of the final state, if compared with the final state of the corresponding microwave line, for which an inversion transition is allowed, involving an energy difference of only 0.8 cm^{-1} and $k_f \simeq 0.3$. An upper bound to this reduction can be roughly evaluated, observing that the linewidth is proportional to b_0^2. From Eq. (4), the cutoff condition [Eq. (5)] can be written as

$$1=\text{Re}\,P(b_0)=(\alpha_i+\alpha_f)/b_0^4\,, \tag{8}$$

where α_i represents the contribution of the initial state and α_f the contribution of the final one, for the microwave spectrum $\alpha_i \simeq \alpha_f$. If we consider, for the infrared spectrum, the extreme case $\alpha_f \simeq 0$, this would reduce b_0 by a factor $2^{1/4}$ [Eq. (8)], and consequently the linewidth would be reduced by $2^{1/2}$. The observed reductions (see Table I) are well within this limit.

Far stronger is the reduction expected for the transitions reported in Table II, for which both initial and final states ($\nu_2=1$ for both) involve large energy transitions. It is interesting to note that both lines (1, 1) and (2, 1) have a broadening parameter larger than that of the line (2, 2), exactly the contrary of what happens in the ground state inversion spectrum. This is due to the fortuitous circumstance that, for $\nu_2=1$, the state $a(1,1)$ and $s(2,1)$ are separated by only ~4 cm^{-1}. Transitions between these two states occur in the calculation of the width of the (1, 1) and (2, 1) inversion lines and give a strong contribution to the width. This case shows that the J, K polynomial expansion that is frequently used[24] to approximate the width is not very reliable and that the correct use of Anderson's theory is preferable.

Still a further reduction is expected for transitions from the first excited state $\nu_2=1$ to the second excited state $\nu_2=2$, and some preliminary measurements seem to agree with the theoretical previsions. However, these lines ($2s$ type) are not easily measured, due to their low absorption intensity. Measurements are in progress and the results will be given in a forthcoming paper.

In conclusion, we have shown that Anderson's theory with the right cutoff procedure $T2$, for calculating the impact parameter b_0, predicts correctly the pressure broadening and shifting of the ν_2 transitions of the ammonia molecule. As a consequence, width and shift measurements can also be used as a valid aid for the identification of transitions in some doubtful case. This happened, for instance, with the line $aQ(10,6)$, which is quite near in frequency (~0.77 cm^{-1}) to the line $aQ(5,1)$. The identification was in doubt because we were able to pick up only one of the two lines with the diode laser mode available. However, we measured a width parameter of 17 MHz/Torr and a shift parameter of −1.3 MHz/Torr. Theory gives 15.6 and −0.9 for $aQ(10,6)$ and 12.8 and +0.1 for $aQ(5,1)$, respectively. This allowed us to conclude with almost complete certainty that the observed line was the $aQ(10,6)$ and not the $aQ(5,1)$.

TABLE III. Pressure broadening of infrared absorption of the band ν_2 of ammonia from other authors compared with theory.

Transition	$\nu_0\,(\text{cm}^{-1})$	Broadening		
		a_{meas}	a_{calc}	
			$T1$	$T2$
$aQ(8,7)^a$	927.739	22.7	21.5	21.7
$aQ(9,3)^b$	939.212	12.5	10.9	11.0
$aR(0,0)^c$	947.789	13.3	11.0	12.0

[a]Reference 9. [b]Reference 10. [c]$^{15}NH_3$, Ref. 7.

As a last point, which is of some interest for the knowledge of the Jovian atmosphere, [24,35] let us remark that, by following Anderson's theory, the two isotope species $^{14}NH_3$ and $^{15}NH_3$ are expected to behave in the same manner as far as the pressure broadening and shift are concerned. The few experimental results [$aR(00)$, $aP(2,0)$ and $s(1,0) \rightarrow a(0,0)$], reported in Tables I, II, and III, confirm such expectation. The same conclusion has been reached recently[36] by using pressures larger than in the previous measurements and by measuring the linewidth with instruments having a much lower resolution than that used in this work.

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