Fourier transform linewidths measurements in NH3 in the vibrational ground state

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Fourier transform linewidths measurements in NH_3 in the vibrational ground state

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We have measured linewidths of several pure rotational transitions in the vibrational ground state in the far infrared ($80–200$ cm^{-1}). The experiments were conducted by using a Fourier transform spectrometer and gases (NH_3 diluted by H_2 or He) contained in a 15 cm absorption cell at room temperature. The aim of our study is to discuss the vibrational effect by comparing our measurements with those done in the infrared, 3 and 6 μm regions (v_3 and v_4 bands) and to find evidence for vibrational dependence. The measured pressure broadening cross sections were typically found to be 26 Å^2 for the NH_3–H_2 collisions and 16 Å^2 for the NH_3–He collisions, by comparing these values with those obtained for the v_4 mode, 35 Å^2 for the H_2 perturber and 17 Å^2 for the He perturber, we see a vibrational effect for the NH_3–H_2 collisions but not significant for the NH_3–He ones. Our measurements are in good agreement with the theoretical calculations done by Billing by using the semiclassical coupled states method.

INTRODUCTION

NH_3 molecules are relatively abundant in interstellar regions, being the first polyatomic molecule found there.[1] They hence provide excellent probes of astrophysical regions. Since many astrophysical environments are not in thermal equilibrium, the knowledge of collisional cross sections is needed for the interpretation of the observed line intensities. In fact, Townes[2] have made the initial suggestion, which now generally accepted, that collisions with H_2 molecules represent the primary mechanism of excitation of rotation and inversion states of NH_3 in dense interstellar clouds. To know the collisional cross sections, it is necessary to determine the intermolecular potential and particularly the anisotropic part of this potential, which is responsible for the rotational relaxation. Accurate measurements of cross sections done in laboratory permit us to test this potential, then calculations could be done referring to the interstellar conditions.

Total collision cross sections for NH_3 have been studied for some time through collisional broadening in microwave region[3] as well as in crossed molecular beams experiments,[4,5] but there is actually little information for state to state transitions induced by NH_3–H_2 and NH_3–He collisions. Recently Das and Townes have undertaken an infrared microwave double resonance method to measure rates for inelastic collision-induced rotation–inversion transitions in NH_3 colliding with He and N_2.[6] Their measurements are consistent with Oka's saturation experiments.[6,7]

In previous papers[9,10] we have measured pressure broadening cross sections in NH_3 perturbed with H_2 and He in the v_3 and v_4 bands, and we have discussed some vibrational dependence of the intermolecular potential when comparing the microwave measurements done by Townes[11] on the one hand, and v_3 and v_4 results on the other hand. In the present paper we report measurements of pressure broadening cross sections done at room temperature in the vibrational ground state (pure rotational transitions which lie in the far infrared) by using a Fourier Transform spectrometer. We attempt to emphasize the dependence of collisional processes on the vibrational modes and to resolve earlier difference[10] between experimental and theoretical calculations done by Billing[12] which significantly improve the fit with experimental results.

The study of pressure broadening in the far infrared is different from similar studies in the microwave region. However, lines in the microwave spectra of NH_3 can attain pressure broadening widths comparable to their resonance frequencies at rather low pressures, and a significant contribution to the spectrum is attributed to so-called negative resonance terms.[13] In our measurements done in the far infrared region (frequencies vary from 80 to 200 cm^{-1}) the pressure broadening widths are very small compared with the resonance frequencies. Thus we did not have to separate the effects of inversion relaxation from the rotational lines. The only known experiments concerning the pressure broadening cross section on ammonia colliding with He and H_2 in the vibrational ground state were made in the microwave region.[3,7,11,14,15] To our knowledge we present in this

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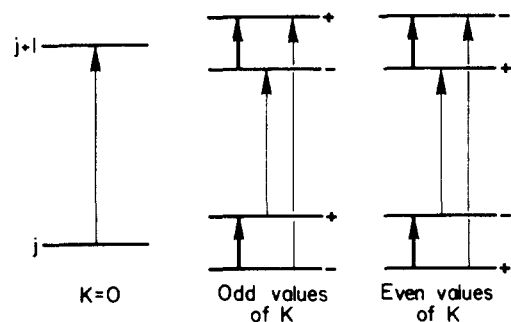[b] Professeur Invité par l'Université de Paris-Sud.

FIG. 1. Inversion–rotation levels in the ground vibrational state: inversion → microwave region; rotation → far infrared region.

paper the first results of pressure broadening cross sections in the far infrared region.

The pure rotation spectrum studied here obeys the symmetric-top selection rule $\Delta j = 0,1$, $\Delta k = 0$, and $+ \leftrightarrow -$. Transitions between rotational levels $\Delta j = +1$, $\Delta k = 0$ occur in the far IR. Transitions between inversion levels with $\Delta j = 0$, $\Delta k = 0$ occur in the microwave region near 1 cm^{-1}. The doubling of each level due to inversion produces a doubling of rotational lines. This rotational transition lies in the far infrared (see Fig. 1). The far infrared absorption spectrum of ammonia was measured with resolution of 0.010 cm^{-1} of resolution, by Urban *et al.*[16] by using the Fourier transform method.

EXPERIMENTAL ARRANGEMENT

This work was done with a resolution of about 0.03 cm^{-1} by using a commercial Fourier transform spectrometer "Brucker IFS 113V" equipped with a DTGS detector (polyethylene window). The source is a globar and a $12 \mu\text{m}$ leaf of mylar as BMS. The spectrum obtained by a 200 scans accumulation is calculated with the trapezoidal apodization function and a zero filling of 16 for the interpolation. The sample and background interferogram were recorded and the spectra were determined by Fourier transformation with a digital computer. The logarithm of their ratio produced the absorption profile. The mixing gas was contained in a 15 cm cell with polyethylene windows. Spectrum with a good signal-to-noise ratio is obtained in 8 h. The pressure of ammonia is 3 Torr and the pressure for helium varies from 100 to 700 Torr and from 100 to 350 Torr for hydrogen. All the results are obtained at room temperature. Figure 2 shows the typical spectrum obtained for two rotational transitions. We observe directly the absorption profile in terms of pressure. The computer makes the deconvolution of the pure Lorentzian profile with the instrumental one. In these experiments we have assumed that the Doppler linewidth (0.001 cm^{-1}) contribution is negligible with regard to the instrumental one (0.03 cm^{-1}). In addition the pressure of ammonia is so low that the contribution of the self-broadening is negligible.

EXPERIMENTAL DATA

Table I shows the results obtained at room temperature for several transitions of ammonia perturbed by helium and Table II shows the same for ammonia perturbed by hydro-

FIG. 2. Deconvoluted observed spectrum for the ${}^Q_4R(8)$ and ${}^Q_5R(8)$ transitions.

TABLE I. Pressure broadening parameters for the NH_3–He system at 300 K.

Transition $(j,k)_{\pm}$ [c]	γ^a (MHz/Torr)	σ^b (Å^2)
(3.2) +	1.1	15
(4.3) +	1.1	15
(4.4) +	1.2	17
(5.4) −	1.0	14
(5.4) +	1.3	18
(5.5) −	1.1	15
(5.5) +	1.1	15
(6.1) +	1.3	18
(6.3) +	1.3	18
(6.4) +	1.1	15
(6.5) +	1.2	17
(6.6) −	1.2	17
(6.6) +	1.1	15
(7.2) −	1.1	15
(7.2) +	1.1	15
(7.3) −	1.1	15
(7.3) +	1.0	14
(7.4) −	1.1	15
(7.4) +	1.1	15
(7.5) −	1.2	17
(7.5) +	1.1	15
(8.3) −	1.1	15
(8.3) +	1.1	15
(8.4) −	1.1	15
(8.5) −	1.1	15
(8.5) +	1.1	15
(8.6) −	1.1	15
(8.6) +	1.2	17
(8.7) +	1.1	15
(8.8) +	1.1	15
(9.7) +	1.1	15

[a] Pressure broadening coefficient.
[b] Pressure broadening cross section.
[c] $(j,k)_{\pm}$ are lower level in a $\Delta j = +1$, $\Delta k = 0$, $+ \leftrightarrow -$ transition.
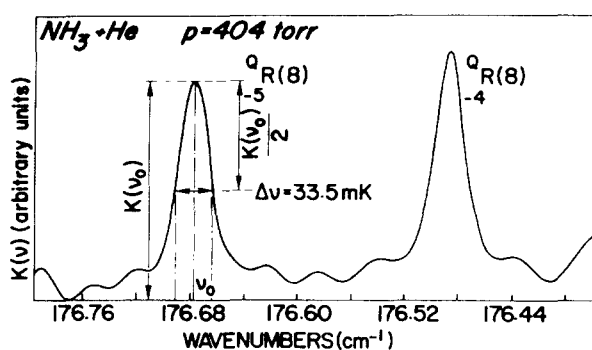
TABLE II. Pressure broadening cross sections for the NH$_3$–H$_2$ system at 300 K.

Transition $(j.k)_{\pm}$ [c]	γ[a] (MHz/Torr)	σ[b] (Å^2)
(3.1) −	2.4	25
(3.2) +	2.4	25
(3.3) −	2.4	25
(3.3) +	2.3	24
(4.1)	2.3	24
(4.2) −	2.3	24
(4.2) +	2.3	24
(4.3) −	2.3	24
(4.3) +	2.2	23
(4.4) −	2.4	25
(4.4) +	2.4	25
(5.2) −	2.3	24
(5.3) −	2.3	24
(5.4) −	2.4	25
(5.4) +	2.4	25
(5.5) −	2.5	26
(5.5) +	2.6	27
(6.1) +	2.5	26
(6.2) +	2.3	24
(6.3) −	2.3	24
(6.4) −	2.4	25
(6.5)	2.6	27
(6.6) −	2.7	28
(6.6) +	2.6	27
(7.2) +	2.6	27
(7.3) −	2.6	27
(7.4) −	2.4	25
(7.5) ±	2.6	27
(7.6) +	2.7	28
(8.1) +	2.3	24
(8.2) −	2.5	26
(8.2) +	2.5	26
(8.3) −	2.3	24
(8.3) +	2.4	25
(8.4) +	2.4	25
(8.5) +	2.4	25
(8.6) +	2.6	27
(8.7) +	2.4	25
(9.1) −	2.5	26
(9.2) −	2.4	25
(9.3) −	2.5	26
(9.6) +	2.7	28
(9.9) +	2.5	26

[a] Pressure broadening coefficient.
[b] Pressure broadening cross section.
[c] $(j.k)_{\pm}$ are lower level in a $\Delta j = +1$, $\Delta k = 0$, $+ \leftrightarrow -$ transition.

gen. We observe that the change of the pressure broadening cross sections in terms of j and k is very smooth. This effect is probably due to the precision of the data which is about 7%.

THEORETICAL CALCULATIONS

The theoretical values have been obtained using the semiclassical coupled states method[17] and details have been given in previous publications.[12] In order to obtain the pressure broadening cross section as a function of temperature we calculate the cross section at a number [3–4] of kinetic energies and average over a Boltzmann distribution. For a given line $jk_+ \rightarrow j'k'_-$ (each level eventually in different rotational states of NH$_3$) we compute the elastic and the total inelastic probability for NH$_3$ initially in either the jk_+ or the $j'k'_-$ state colliding with He or H$_2$. For the cross relaxation cross section we furthermore need the probability for transition to the inversion doublet level, i.e., $jk_+ \rightarrow jk_-$ and $j'k'_- \rightarrow j'k'_+$. In order to obtain convergence for these cross sections it is necessary to include a sufficient number of jk levels in NH$_3$ and rotational levels of H$_2$. However, within the coupled states approximation the coupling becomes diagonal in the m-quantum numbers of NH$_3$ and it is then possible to calculate the cross sections at high j values. Thus a $jk \rightarrow j'k'$ pressure broadening cross section was calculated using levels in the manifolds $j_s = 1,..., j+1$ or $j'+1$ for pNH$_3$. The cross sections were calculated for $m = 0, 1,..., j$ and the averaging over m states performed when calculating the pressure broadening cross sections. For H$_2$ as the perturber it turned out that the cross sections were sensitive to the initial H$_2$ rotational state. Thus the calculations were carried out with $j_{H_2} = 0, 1$, and 2 and the appropriate Boltzmann weighting introduced. For H$_2$ ($j = 0$) and H$_2$ ($j = 2$) the $0 \rightarrow 2$ and $2 \rightarrow 0$ H$_2$ rotational excitation/deexcitation was found to be important. Thus a number of rotational excited H$_2$ states was added to the basis [3]. For H$_2$ in $j = 1$ the 1 to 3 energy gap is so large that the probability for this transition could be neglected.

DISCUSSION

Firstly we show a good agreement between experimental and calculated pressure broadening cross sections.

TABLE III. Comparison between far infrared, ν_4 band, experimental and theoretical pressure broadening cross sections.

NH$_3$ transitions $j.k.\epsilon \rightarrow j'.k'.\epsilon$	(Å^2)	NH$_3$–He 300 K			NH$_3$–H$_2$ normal 300 K			
		Theory	Experimental		Theory		Experimental	
			ν_4	far IR	$j = 0,1,2$	$j = 0$	far IR	ν_4
2.1 + → 1.0 −	σ_{PB}[a]				30.1	21.2		40
3.2 + → 2.1 −	σ_{PB}			15	29.5	21.3	25	
4.4 + → 3.3 −	σ_{PB}	18	17	17	29.6	20.9	25	
5.5 + → 4.4 −	σ_{PB}	17.4	17	15	26.9	17.6	26	35
6.6 + → 5.5 −	σ_{PB}	17	17	15	25	13.6	27	33

Comparing the cross sections for He–NH_3 with those for nH_2–NH_3 we see that the experimental measurements show $\sigma_{PB} \approx 14$–18 Å^2 for He and $\sigma_{PB} \approx 23$–28 Å^2 for nH_2. Due to the longer range of the H_2–NH_3 potential we could expect this result. However a lower mass of the collider usually decreases the cross section, i.e., a compensing effect. Indeed we see that for H_2 ($j = 0$) we only find a theoretically σ_{PB} of about 14–21 Å^2, i.e., not much larger than the He–NH_3 cross sections. The reason for the larger H_2 cross sections therefore must be due to something else and Table III shows that the cross section increases with the j-quantum number of the perturber, i.e., H_2 and only by including this effect we get the somewhat larger cross sections mentioned above. Furthermore the even larger cross section measured in the ν_4 mode (Table III) indicate that the vibrational state of NH_3 is also important. Thus the σ_{PB} increases with the vibrational quantum number of the molecule. Although not much is known about rotational cross section in vibrational excited states, a semiclassical calculation performed by G. D. Billing[18] showed that the rotational excitation of vibrational excited H_2 colliding with He was larger than in the ground state. Then it appears that something similar holds for vibrationally excited NH_3.

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