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SPECTRUM**

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ABSTRACT

The shift parameters for self-broadened lines in the ammonia inversion spectrum have been calculated using the convergent approach of Cattani. A good agreement is found between theory and experiment.

As pointed out in preceding papers,¹⁻³ considerable efforts have been devoted to explain the width and shift parameters for the self-broadened lines in the ammonia inversion spectrum. Many calculations, that have been performed using the current line shape theories, were not able to give a good description of the experimental results. Only recently Cattani and Yamamoto¹⁻³ were able to explain satisfactorily the line widths assuming that the NH_3 molecules is essentially a two-level system. In our works¹⁻³ no attempt has been done to calculate the shifts. In this paper, using the convergent approach developed by Cattani,⁴ we show how to describe satisfactorily the experimental shift parameters.

According to the general impact theory of Baranger⁵ and Kolb and Griem,⁶ the half half-width ω and the shift d , for an isolated Lorentzian line, measured in rad/s, are given by $\omega = \text{Re}(H_{if})$ and $d = -\text{Im}(H_{if})$, where the indices i and f refer to the initial and final states of the line, respectively,

$$\begin{aligned} H_{if} &= \langle 1 - S_{if} S_{if}^{\dagger} \rangle = \\ &= 2\pi N \int_0^{\infty} dv v F(v) \int_0^{\infty} db b \sum_n \rho_n \langle n | \left[1 - \langle i | S(b, v) | i \rangle \langle f | S^{\dagger}(b, v) | f \rangle \right] | n \rangle , \end{aligned} \quad (1.1)$$

N the density of perturbing particles, b the impact parameter, v the relative velocity, $F(v)$ the Maxwell-Boltzmann velocity distribution, ρ_n the probability of finding the perturbing molecule in the state $|n\rangle$, S the scattering matrix between emitting and perturbing molecules, $|i\rangle$ and $|f\rangle$ the initial and final states of the emitting molecule.

Adopting the many level convergent theory,⁴ and taking into account that only diagonal scattering matrix elements contribute to the linewidths and shifts, one can easily verify that ω and d are given by

$$\omega = 2\pi N \sum_n \rho_n \int_0^\infty dv v F(v) \int_0^\infty db b \left\{ 1 - \cos [\phi_{ifn}(b,v)] \exp[-\Gamma_{ifn}(b,v)/2] \right\} \quad (1.2)$$

and

$$d = -2\pi N \sum_n \rho_n \int_0^\infty dv v F(v) \int_0^\infty db b \sin [\phi_{ifn}(b,v)] \exp[-\Gamma_{ifn}(b,v)/2] \quad (1.3)$$

where

$$\phi_{ifn}(b,v) = \phi_{in}(b,v) - \phi_{fn}(b,v) \quad (1.4)$$

and

$$\Gamma_{ifn}(b,v) = \Gamma_{in}(b,v) + \Gamma_{fn}(b,v) \quad (1.5)$$

The functions $\phi_{kn}(b,v)$ and $\Gamma_{kn}(b,v)$, with $k = i$ or f , are given by⁷

$$\phi_{kn}(b,v) = \left[\frac{1}{2\pi\hbar^2} \right] \sum_{m\ell} P \int_{-\infty}^{+\infty} \frac{d\omega}{\omega_{kn,m\ell} - \omega} |\langle k | \langle n | G(\omega) | m \rangle | \ell \rangle|^2_{Av}$$

and

$$\Gamma_{kn}(b,v) = \frac{1}{\hbar^2} \sum_{m\ell} |\langle k | \langle n | G(\omega_{kn,m\ell}) | m \rangle | \ell \rangle|^2_{Av}$$

where $|m\rangle$ and $|\ell\rangle$ are the intermediate states of the emitting and perturbing molecules, respectively, the symbol Av means an average over all possible values of the z components of the molecular angular momenta, $\omega_{kn,m\ell}$ the energy difference between the states $|k\rangle|n\rangle$ and $|m\rangle|\ell\rangle$, $G(\omega) = \int_{-\infty}^{+\infty} dt V(t) \exp(i\omega t)$, and $V(t)$ the interaction potential between emitting and perturbing molecules as a function of the time t .

2. AMMONIA SELF-BROADENING

The ammonia states can be specified by their parities (\pm) and by the quantum numbers J , K and M if we ignore vibrational and electronic degrees of freedom. Thus, assuming that the widths and shifts of the ammonia inversion lines are produced essentially by the electric dipole-dipole interaction between the ammonia molecules we can show that Eqs. (1.4) and (1.5) are written as⁸⁻¹⁰

$$\phi_{if2}(b,v) = C_\mu \left[\sum_{J_1'K_1'J_2'K_2'} D(J_1K_1, J_1'K_1') \cdot D(J_2K_2, J_2'K_2') h_1(k_1) - \sum_{J_1'K_1'J_2'K_2'} D(J_1K_f, J_1'K_f') \cdot D(J_2K_2, J_2'K_2') h_1(k_f) \right] \quad (2.1)$$

and

$$\Gamma_{if2}(b,v) = 2C_\mu \left[\sum_{J_1'K_1'J_2'K_2'} D(J_1K_1, J_1'K_1') \cdot D(J_2K_2, J_2'K_2') f_1(k_1) + \sum_{J_1'K_1'J_2'K_2'} D(J_1K_f, J_1'K_f') \cdot D(J_2K_2, J_2'K_2') f_1(k_f) \right] \quad (2.2)$$

where the indice 2 denotes the perturbing molecules, $C_\mu = \left[\frac{2\mu^2}{3\hbar^2 v} \right]^2$, μ the ammonia dipole moment,

$D(JK, J'K') = |(JK \| d \| J'K')|^2 = \left[\frac{K^2}{J(J+1)} \delta_{J,J'} + \frac{J^2 - K^2}{J(2J+1)} + \delta_{J-1, J'} + \frac{(J+1)^2 - K^2}{(2J+1)(J+1)} \delta_{J+1, J'} \right] \delta_{K', K}$
the squared dipole matrix elements, that are zero between states of the same parity (the

parities of the states $|JKM_{\pm}\rangle$ have been omitted for simplicity), $f_1(k) = (k^4/4)\{K_2^2(k) + 4K_1^2(k) + 3K_0^2(k)\}$, $h_1(k) = (\pi k^4/4)\{K_2(k)I_2(k) - 4K_1(k)I_1(k) + 3K_0(k)I_0(k)\}$, $K_n(k)$ and $I_n(k)$ are modified Bessel functions of integer order, $k = (b/\hbar v)[E(JK) + E(J_2K_2) - E(J'K') - E(J_2'K_2')]$; $E(JK)$ the energy of the states $|JK_{\pm}\rangle$.

Let us indicate by $\hbar\omega(JK)$ the energy differences¹ due to the inversion transitions, where $\omega(JK)$ is the inversion frequency between states of different parities as a function of J and K (cf. Townes and Schawlow¹¹). The energy differences due to rotational transitions will be indicated by $\hbar\omega_{rot} = 2\pi\hbar B[J(J+1) + J_2(J_2+1) - J'(J'+1) - J_2'(J_2'+1)]$, remembering that $K=K'$ and $K_2=K_2'$ for dipole transitions and that $B = 298 \times 10^3$ Mhz is the rotational constant of the ammonia molecule.

As in our preceding paper,¹ the densities of the perturbing molecules in the states (+) and (-) will be represented here by N_+ and N_- , respectively. For (+) molecules we verify that,

$$k_i^{(+)} = \hbar\omega_i^{(+)} / bv = (\hbar/bv) [\omega_+ + \omega_{rot}]$$

and

$$k_f^{(+)} = \hbar\omega_f^{(+)} / bv = (\hbar/bv) [-\omega_- + \omega_{rot}]$$

where, $\omega_+ = \omega(J_1K_1) + \omega(J_2K_2)$ and $\omega_- = \omega(J_1K_1) - \omega(J_2K_2)$, taking into account that $J_1=J_1'$ and $K_1=K_1'$. For (-) we see that

$$k_i^{(-)} = \hbar\omega_i^{(-)} / bv = (\hbar/bv) [\omega_- + \omega_{rot}]$$

and

$$k_f^{(-)} = \hbar\omega_f^{(-)} / bv = (\hbar/bv) [-\omega_+ + \omega_{rot}]$$

In these conditions, the functions $\phi_{if2}(b,v)$ and $\Gamma_{if2}(b,v)$, defined by Eqs. (2.1) and (2.2), are written as

$$\phi_{12}^{(\pm)}(b,v) = C_{\mu} \sum_{J_1'K_1'J_2'K_2'} D(J_1K_1, J_1'K_1') \cdot D(J_2K_2, J_2'K_2') [h_1(k_i^{(\pm)}) - h_1(k_f^{(\pm)})] \quad (2.3)$$

and

$$\Gamma_{12}^{(\pm)}(b,v) = 2C_{\mu} \sum_{J_1'K_1'J_2'K_2'} D(J_1K_1, J_1'K_1') \cdot D(J_2K_2, J_2'K_2') [f_1(k_i^{(\pm)}) + f_1(k_f^{(\pm)})] \quad (2.4)$$

As the energy differences $\hbar\omega(JK)$ are very small compared with $\hbar\omega_{rot}$ we can put

$$h_1(k_i^{\pm}) - h_1(k_f^{\pm}) \cong 2k(J_1K_1) \left(\frac{\partial h_1(k)}{\partial k} \right)_{k=k_{rot}}$$

and

$$f_1(k_i^{\pm}) + f_1(k_f^{\pm}) \cong 2f_1(k_{rot})$$

where $k(J_1K_1) = \hbar\omega(J_1K_1)/bv$ and $k_{rot} = \hbar\omega_{rot}/bv$. With these approximations the functions $\phi_{12}(b,v)$ and $\Gamma_{12}(b,v)$, defined by Eqs. (2.3) and (2.4), becoming independent of the parities (+) and (-), are written as

$$\phi_{12}(b,v) = 2k(J_1K_1) C_{\mu} \sum_{J_1'K_1'J_2'K_2'} D(J_1K_1, J_1'K_1') \cdot D(J_2K_2, J_2'K_2') \left[\frac{\partial h_1(k)}{\partial k} \right]_{k=k_{rot}} \quad (2.5)$$

and

$$\Gamma_{12}(b,v) = 4C_{\mu} \sum_{J_1'K_1'J_2'K_2'} D(J_1K_1, J_1'K_1') \cdot D(J_2K_2, J_2'K_2') f_1(k_{rot}) \quad (2.6)$$

Substituting Eqs. (2.5) and (2.6) into Eq. (1.3) we get

$$d_{\pm}(J_1K_1) = -2\pi N_{\pm} \sum_{J_2K_2} \rho(J_2K_2) \int_0^{\infty} dv F(v) v \int_0^{\infty} db b \sin[\phi_{12}(b,v)] \exp[-\Gamma_{12}(b,v)/2] \quad (2.7)$$

Since $N_+ \cong N_- \cong N/2$ we see that $d_+ \cong d_- \cong d/2$. Taking, in Eq. (2.7), $\sin[\phi_{12}(b,v)] \cong \phi_{12}(b,v)$ and performing the integrations over the relative velocities v and the impact parameters b ,¹ the shift $d(J_1K_1) = d_+ + d_-$ is given, in good approximation, by

$$d(J_1K_1) = -2\pi N \beta \omega(J_1K_1) \sum_{J_2K_2} \rho(J_2K_2) \psi(J_1K_1, J_2K_2, Q) \quad (2.8)$$

where $\beta = (4/\pi)^{3/4} \times \frac{\sqrt{2}}{\hbar^{1/2}} \frac{\mu}{\bar{v}^{3/2}}$, \bar{v} the mean relative velocity,

$$\psi(J_1K_1, J_2K_2, Q) = \sum_{J_1'K_1' J_2'K_2'} D(J_1K_1, J_1'K_1') \cdot D(J_2K_2, J_2'K_2') g(Q) ,$$

$g(Q) = \int_0^{\infty} \frac{dy}{\sqrt{y}} (\partial h_1(z)/\partial z) \exp[-y^2 f_1(Q/\sqrt{y})]$, $z = Q/\sqrt{y}$ and $Q = \beta \omega_{\text{rot}}$. The function $g(Q)$ is calculated numerically and tabulated as a function of the parameter Q .

Our results for $d(J_1K_1)$, per unit pressure P , are given in Table 1 and Fig. 1, where they are also compared with the more recent experimental results of Hewitt and Parsons.¹²

(INSERT TABLE 1 AND FIGURE 1)

From Table 1 and Fig. 1, we see that, in view of the experimental uncertainties found in lineshift measurements,¹² there is a good agreement between theory and experiment.

It is important to note that, taking into account only the inversion transitions, the lineshift predictions are equal to zero. On the other hand, considering only the rotational transitions we verified that the predicted shifts are about ten times larger^{8,9} than the experimental results. Both inversion and rotational contributions are important to the lineshifts, as seen in Eq. (2.8), justifying for these calculations the use of a many level approach.

Finally, we must observe that the linewidths obtained with Eqs. (2.2) and (2.3) are about 27% larger than the experimental results. As pointed out before,¹⁻³ this occurs because the widths are essentially generated by inversion transitions that can be satisfactorily estimated only by using a two-level formalism.

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REFERENCES

1. M. Cattani and Y. Yamamoto, *JQRST* **27**, 563 (1982).
2. M. Cattani, *JQRST* **34**, 453 (1985).
3. M. Cattani, *JQRST* **42**, 83 (1989).
4. M. Cattani, *Phys. Lett.* **38A**, 147 (1972).
5. M. Baranger, *Phys. Rev.* **112**, 855 (1958).
6. A.C. Kolb and H.R. Griem, *Phys. Rev.* **111**, 514 (1958).
7. J.S. Murphy and J.E. Boggs, *J. Chem. Phys.* **47**, 691 (1967).
8. B.S. Frost, *J. Phys.* **B9**, 1001 (1976).
9. P.L. Hewitt, *JQRST* **16**, 499 (1976).
10. M. Cattani, *J. Chem. Phys.* **52**, 4566 (1970).
11. C.H. Townes and A.L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill, New York (1955).
12. P.E. Hewitt and R.W. Parsons, *Phys. Lett.* **45A**, 21 (1973).

FIGURE CAPTIONS

Fig. 1 - The theoretical predictions (•) for $d(J_1K_1)/P$ are compared with the experimental results (+) of Hewitt and Parsons.¹²

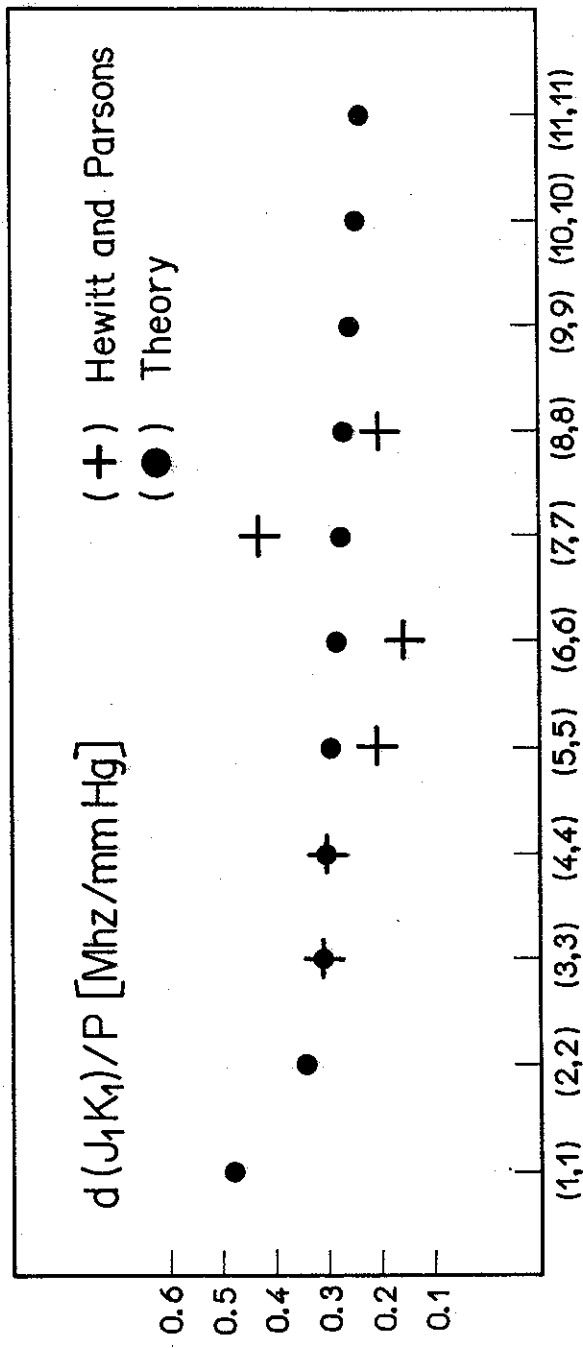


Table 1. Theoretical and experimental results for lineshifts of the NH_3 inversion spectrum. The shifts, per unit pressure P , $d(J_1, K_1)/P$, are given in Mhz/mmHg.

Transition	$d(J_1, K_1)/P$	Experimental values ¹²
(1,1)	0.48	
(2,2)	0.34	
(3,3)	0.31	0.31 ± 0.04
(4,4)	0.30	0.30 ± 0.08
(5,5)	0.29	0.21 ± 0.07
(6,6)	0.28	0.16 ± 0.04
(7,7)	0.27	0.43 ± 0.09
(8,8)	0.26	0.20 ± 0.08
(9,9)	0.25	
(10,10)	0.23	
(11,11)	0.22	