Pressure Broadening of the Ammonia Inversion Line by Foreign Gases: Quadrupole-Induced Dipole Interactions

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The broadening of the 3,3 line of the inversion spectrum of ammonia by foreign gases which are not expected to have dipole or quadrupole moments has been measured accurately by Smith and Howard. This broadening is greater than that previously computed by the author using the interaction of the molecule's dipole moment with the induced dipole on the foreign gas atom. In this paper the broadening is explained quantitatively using the interaction of the induced dipole on the foreign gas atom with the quadrupole moment of ammonia. It is concluded that a model of the ammonia molecule using bond dipoles of the appriate size to give the known dipole moment, or a model with point charges at the atoms, again adjusted to give the correct dipole moment, both give quadrupole moments which explain the broadening cross sections with good accuracy.

I. INTRODUCTION

THE pressure-broadening cross sections of many foreign gas atoms and molecules for the NH_3 inversion lines have been observed to be anomalously high.[1-3] In several cases, in which these cross sections are considerably greater than kinetic theory cross sections, Smith and Howard[2] have successfully ascribed this broadening to the interaction between the NH_3 dipole moment and the quadrupole moment of the foreign gas molecule.

In other cases, usually of atoms or molecules which could be expected to have little or no quadrupole moment, such as argon, Smith and Howard[2] found that the broadening cross section, although comparable with the kinetic theory cross section, showed little correlation with the latter and was instead well correlated with the polarizability of the foreign gas. The relationship between broadening cross section and polarizability is the same as that predicted by the dipole-induced dipole broadening theory of the author.[3] However, the cross sections are considerably greater in magnitude than those predicted by this theory.

The reason why the author's theory[3] gives such low cross sections for this broadening is that the interaction potential between a polarizable atom and a dipolar molecule is

$$H = (\alpha\mu^2/r^6)(1+3\cos^2\theta). \tag{1}$$

θ is the angle between the dipole μ of NH_3 and the interatomic distance r; α is the polarizability of the perturber. This expression contains only even powers of $\cos\theta$. $\cos\theta$ has matrix elements only of the form $(+|\cos\theta|-)$, where the $+$ and $-$ designate the two states connected by the inversion transition. Thus $\cos^2\theta$ can have only diagonal matrix elements in the inversion coordinate, of the form $(+|\cos^2\theta|+)$, and the interaction (1) cannot cause the inversion, and, because of the wide spacing of the NH_3 rotational levels, cannot

cause any transition among quantum states other than the spacially degenerate states of different M quantum number.

It has been shown[3,4] that in this case the broadening cross section is greatly reduced from that one obtains in case non-adiabatic transitions between non-degenerate quantum states can be caused by the collision interaction. Transitions among quantum states which are not degenerate were shown to have the effect of breaking off the radiation completely; transitions merely among degenerate quantum states have a considerably smaller effect on the radiation, which can be thought of as a minor phase or amplitude change.

The reduction, due to this fact, in the quantity S_2 of reference 3 is of the order $(4J^2)^{-1}$, where J is the total angular momentum quantum number. Thus one can see that, since S_2 is proportional to the squared "transition probability" a_{jk} of reference 2, and

$$a_{jk} \sim \text{const}/b^5 = \frac{1}{2}$$

is the rough condition on the broadening diameter b, that b is reduced by a factor $(2J)^{-1/6}$, which is considerable for the $J=3$ line measured by Smith and Howard.

However, at the close distances of approach which enter into the particular broadening under consideration (~ 3.5A) the dipole-dipole forces are not the only ones which need to be considered. For instance, one would expect that the NH_3 molecule has a quadrupole moment which corresponds roughly to that of the known dipole moment at a distance at least $h/2 \simeq 0.2$A (h is the height of the pyramid) from the center of rotation. Then the ratio of the potential (1) between the two configurations in which this dipole is pointed toward the perturber and away from the perturber is $[(3.5+0.2)/(3.5-0.2)]^6 = 1.97$. This means that there is a potential, odd in the angle function $\cos\theta$, of practically the magnitude of the potential (1), due to interaction between the induced dipole on the perturber and the quadrupole on NH_3. It is this potential which turns

[1] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. London **59**, 424 (1948).
[2] W. V. Smith and R. Howard, Phys. Rev. **79**, 132 (1950).
[3] P. W. Anderson, Phys. Rev. **76**, 647 (1949).
[4] P. W. Anderson, thesis, Harvard, 1948, unpublished.
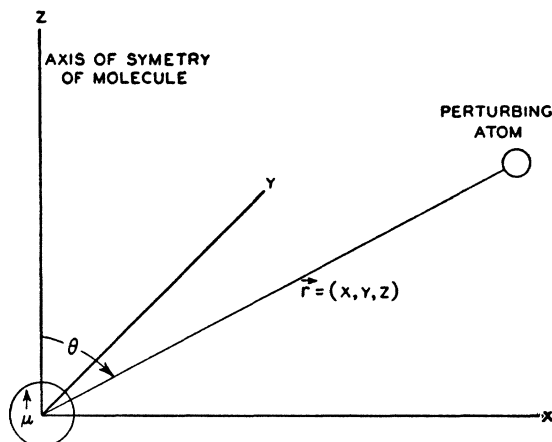
FIG. 1. Coordinates for computation of H.

out to give good agreement with the experimental broadening.

II. COMPUTATION OF THE INTERACTION ENERGY

First let us compute the interaction energy between a molecule, having both a dipole and a quadrupole moment, and a polarizable isotropic atom at a distance r from this molecule. The electrostatic potential at the polarizable atom (the coordinates are shown in Fig. 1.) is

$$V=-\frac{\mu z}{r^3}+\frac{1}{2}\left(\frac{3z^2-r^2}{r^5}\right)(Q_{zz}-Q_{xx}) \qquad (2)$$

where the quadrupole moments (assuming that the molecule has an axis of symmetry) are defined by

$$Q_{xx}=\sum_{\text{mole}}\rho_i x_i^2=Q_{yy},$$
$$Q_{zz}=\sum_{\text{mole}}\rho_i z_i^2. \qquad (3)$$

Since the molecule has a dipole moment these quadrupoles are not independent of the choice of origin; we must use as origin the center of rotation of the molecule; i.e., the center of mass. Let

$$Q=Q_{zz}-Q_{xx}. \qquad (4)$$

Then the field at the polarizable atom is

$$E=\nabla V \qquad (5)$$

of which a typical component is

$$E_z=-\frac{\mu}{r^3}\left(1-\frac{3z^2}{r^2}\right)+\frac{1}{2}\frac{Q}{r^4}\left[\frac{9z}{r}-\frac{15z^3}{r^3}\right]. \qquad (5a)$$

The interaction energy is, most simply
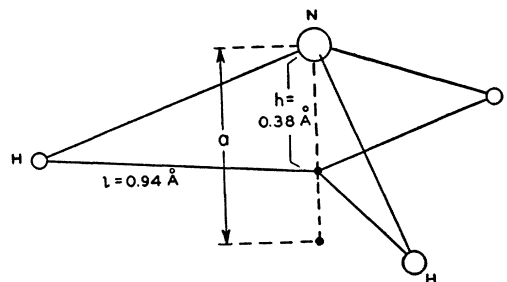
$$H=\tfrac{1}{2}\alpha(E_x^2+E_y^2+E_z^2), \qquad (6)$$

α is the polarizability of the perturbing atom. H can be easily computed and is

$$H=-(6\alpha\mu Q/r^7)\cos^3\theta, \qquad (7)$$

where

$$\cos\theta=z/r.$$

We have included here only the μQ cross term, since the other two terms are both even in $\cos\theta$, and can have

little effect, even though in actual magnitude they must be greater than (7).

III. THE QUADRUPOLE MOMENT OF NH₃

The quadrupole moments of NH_3 about the center of mass can be computed using two models, one with charges on each of the atoms sufficient to give the observed dipole moment, or one with dipoles aligned along the three bonds, again just sufficiently large to give the observed dipole moment. Both models give the same quadrupole moment. Figure 2 shows the model of NH_3 we are using.[5] We choose our origin at a distance a from the nitrogen atom (where a will later be chosen to be 0.07A, or the position of the center of mass). Then, if $-q$ is the charge on the hydrogen,

$$Q_{zz}=3q(a^2)-3q(a-h)^2$$
$$=-3q(h^2-2ah).$$

Since

$$\mu=3qh,$$
$$Q_{zz}=\mu(2a-h). \qquad (8a)$$

On the other hand,

$$Q_{xx}=-q[l^2+2(\tfrac{1}{2}l)^2],$$
$$Q_{xx}=-\mu\left(\frac{l^2}{2h}\right). \qquad (8b)$$

Then

$$Q=\mu\left[2a-h+\frac{l^2}{2h}\right]$$

$$=0.92\times10^{-8}\mu$$

$$=1.325\times10^{-26}\text{e.s.u.-cm}^2. \qquad (8c)$$

We shall find that the value (8c) for Q gives good results for the broadening, which fact seems to confirm sig-

FIG. 2. The NH₃ molecule.
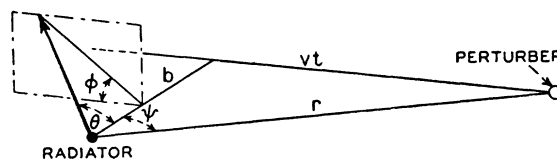
FIG. 3. Coordinates for computation of the transition matrix P.

[5] The interatomic distances are from G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 439.

nificantly that the charge distribution on NH_3 is not greatly different from that which we have assumed.

IV. THEORY OF THE BROADENING

As has been shown in references 2 and 3, the broadening depends on the "transition and phase-shift" matrix P, where

$$P = \int H dt/\hbar. \qquad (9)$$

The integral is taken over the collision path; no energy factors need be considered, since at these distances, and with only the small energy of the inversion transition involved, the energy for the transition comes easily from the kinetic energy of translation. The coordinate system is shown in Fig. 3.

$$P = \frac{6\alpha\mu Q}{\hbar} \int \frac{dt}{r^7} [\cos\theta \cos\psi + \sin\theta \sin\psi \cos\varphi]^3$$

$$= \left(\frac{6\alpha\mu Q}{\hbar}\right) \frac{5\pi}{128 b^6 v} \left[\frac{3}{2}\cos\theta + \frac{11}{2}\cos^3\theta\right.$$

$$\left. + \frac{3}{2}\sin^2\theta \cos\theta \cos 2\varphi\right]. \qquad (10)$$

The matrix elements of P are easily derived, using, for instance

$$(JKM, + |\cos\theta| JKM, -) = KM/J(J+1). \qquad (11)$$

It turns out that the contribution to the broadening of the last term in (10) is quite negligible; then we can give the only matrix element of P which is of importance:

$$(JKM, + |P| JKM, -)$$

$$= \left(\frac{6\alpha\mu Q}{\hbar}\right) \frac{5\pi}{128 b^6 v} \left[\frac{3}{2} \frac{KM}{J(J+1)} + \frac{11}{2} \frac{K^3 M^3}{J^3(J+1)^3}\right]. \qquad (12)$$

The next step in computing broadening cross sections is to compute the quantity S_2, which in the case occurring here is merely a mean square of the matrix elements of P

$$S_2 = \frac{1}{2}(1/2J+1)\sum_{l, M}$$
$$\times [|(i, M|P|l)|^2 + (f, M|P|l)|^2] \qquad (13)$$

where l are all the possible final states for the transition caused by the collision (here only the one state $(J, K, M\pm)$) and i and f designate the initial and final states of the radiative transition. Here this reduces

TABLE I. Broadening of the NH_3 3,3 line by several foreign gases.

Foreign gases	b(Theoretical)	b(Experimental)
H_2	2.57±0.1	2.71
He	2.15±0.1	2.00
A	3.42±0.2	3.73
O_2	3.35±0.2	3.86
(N_2)	(3.39±0.2)	(5.54)

simply to

$$S_2 = (1/2J+1)\sum_M |(JKM + |P| JKM -)|^2. \qquad (13a)$$

This has been computed. It is

$$S_2 = \left(\frac{5\pi}{128 b^6 v}\right)^2 \left(\frac{6\alpha\mu Q}{\hbar}\right)^2 \frac{3}{4} \frac{K^2}{J(J+1)}$$

$$\times \left[1 + \frac{22}{5}\frac{K^2}{J(J+1)} + \frac{121}{21}\frac{K^4}{J^2(J+1)^2} - \frac{K^2}{3J^2(J+1)^2}\right.$$

$$\left. \times \left(\frac{22}{5} + \frac{121}{7}\frac{K^2}{J(J+1)}\right) + \frac{K^4}{J^4(J+1)^4}\frac{121}{63}\right]. \qquad (14)$$

In the case $K=3$, $J=3$ this is

$$S_2 = (5\pi/128 b^6 v)^2 (6\alpha\mu Q/\hbar)^2 (4.05). \qquad (14a)$$

The quantity which is equivalent to the phase-shift of normal impact theories,[6] or to the transition probability a_{jk} of Smith's simplified version[2] of the author's theory is

$$P_{r.m.s.} = (2S_2)^{\frac{1}{2}}. \qquad (15)$$

Smith's criterion for the broadening diameter b is

$$P_{r.m.s.} = A/b^6 = \frac{1}{2}.$$

Where this equation defines A. Then the broadening diameter is

$$b = 2^{1/6}A^{1/6} = 1.12A^{1/6} \qquad (16a)$$

our own criterion[3] gives

$$\sigma = \pi b^2 = 1.1\pi A^{\frac{1}{3}},$$
$$b = (1.1)^{\frac{1}{2}}A^{1/6} = 1.05A^{1/6}. \qquad (16b)$$

These two criteria give slightly different answers; since the second is a lower limit, we shall increase it slightly to give a somewhat better answer, and take ±5 percent as the rough theoretical error. Thus we choose

$$b = 1.08A^{1/6} = 1.08[b^6(2S_2)^{\frac{1}{2}}]^{1/6} ± 5 \text{ percent}, \qquad (17)$$

where S_2 is given by (14a). Table I shows the results given by formula (17) for several gases broadening the NH_3 3,3 line, compared with Smith's experimental results.[2] N_2 is included in order to show that certainly some extra source of broadening must be coming in here, even using our present theory. Thus Smith's computation of the quadrupole moment of N_2 is certainly sound. O_2 also shows a slight hint of having a quadrupole moment. The A value is a little disturbing, since the experimental error is probably considerably less than 0.1A. However, the general agreement seems to be excellent, and to indicate that our estimate for the quadrupole moment of NH_3 is not off by more than 20 to 30 percent.

I should like to express my thanks to Dr. W. V. Smith for the correspondence which led to the work of this paper.

[6] See, for instance, H. Margenau and W. W. Watson, Rev. Mod. Phys. 8, 22 (1936).