On the Pressure Shift of the Inversion Frequency of Ammonia

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Recently those who are working with Maser have found a definite amount of shift in the inversion frequency of ammonia which is proportional to pressure and to the width of resonance. In this letter we note that this shift is due to the second order non-adiabatic effect of the electric dipole-dipole interaction between ammonia molecules.
In our previous letter,\textsuperscript{4} which will be referred to as I, we discussed the equivalence between the line width and the rate of energy relaxation by using the relaxation function method.\textsuperscript{3} According to this method the relaxation function $\phi_a(t)$ of the electric dipole moment of the molecule having the inversion frequency $\omega_a$ is given by

$$\phi_a(t) = \exp \{ i \omega_a t - \psi_a(t) \}, \quad (1)$$

and

$$\psi_a(t) = \sum \sum \langle \sigma_{aM}^2(b) \rangle_* \times \int_0^t (t-\tau) e^{i \omega_a \tau} f_M(\nu \tau/b) d\tau, \quad (2)$$

where $\sigma_{aM}^2(b)$ is the second moment of the intermolecular interaction (eq. (5) of I), $f_M(\nu \tau/b)$ is the correlation function of the radial part of it (eq. (6) of I). $\nu$ is the average velocity of the molecule, $b$ is the impact parameter, and $\langle \rangle_*$ denotes the summation over the number and type of collision (eq. (4) of I). In the case of self-broadening the energy change $b \omega_r$ associated with the second order effect is equal to $b (\omega_a \pm \omega_{a'})$, where $\omega_{a'}$ is the inversion frequency of the perturbing molecule.

When the pressure is not very high, say below 10 mm Hg, we have a condition $\sigma_{aM}^2(b) \ll \nu/b$ which assures the validity of the impact approximation. In this case $\psi_a(t)$ becomes proportional to $t$, and is written as

$$\psi_a(t) = t \sum \sum \langle \sigma_{aM}^2(b) (b/\nu) F_M(b \omega_r/\nu) \rangle_* = t (\Phi_\omega - i \sigma), \quad (3)$$

where

$$F_M(b \omega_r/\nu) = \int_0^\infty d\tau' e^{i(b \omega_r/\nu) \tau'} f_M(\tau'). \quad (4)$$

Here $\Phi_\omega$ is the damping constant which is measured as line width, and $\sigma$ denotes the persistent cloud effect which should be detected as shift in the resonance frequency. This latter effect was dropped out in Anderson's treatment\textsuperscript{6} when he assumed the commutability of the interactions at different times, however it is not really negligible in the case of ammonia as we show in the following. If we assume $f_M(\tau')$ to be given by $\exp \{ - (\nu \tau'/b) \}$ for a fixed value of the impact parameter $b$, then we have

$$a = D/\Phi_\omega = b \omega_r/\nu \simeq b (\text{Å}) \times (0.035). \quad (5)$$

This is not actually negligible as compared with unity for the value of $b$ around 10 Å for which we have the dominant contribution to the width. In view of this situation we have performed a straightforward calculation of the functions $f_M(\tau')$ by adopting the dipole-dipole interaction as the perturbation. In order to perform the integration over the impact parameter $b$, we can resort to the characteristic situation in the case of pressure broadening, i.e. that the spectrum is fairly insensitive to the behaviour of the radiator and the perturber inside a certain range. The reason is that the radiation emitted and absorbed by the radiator is seriously disturbed and is not observed as resonance inside an intermolecular distance $b_r$ which is far greater than the kinetic radius $b_k$. Based on this consideration we have introduced a method of cutting off the contribution of the irrelevant region to the shift, which is similar to that proposed for width by Anderson\textsuperscript{5}. The cut-off radii are 12.6 Å for the width and 5.1 Å for the shift.
The final results are listed in Table I together with the observed value of shift and width.

Table I. The width and the shift of 3–3 inversion line of ammonia (in the unit of megacycles per mm Hg)

<table>
<thead>
<tr>
<th></th>
<th>Theory</th>
<th>Experiment</th>
</tr>
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<tbody>
<tr>
<td>Width</td>
<td>31.9</td>
<td>27.</td>
</tr>
<tr>
<td>Shift</td>
<td>5.9</td>
<td>1.0–0.5</td>
</tr>
</tbody>
</table>

The ratio $\alpha$ of shift to width is found to be 0.18 which is definitely larger than the observed ratio of 0.04–0.02. The reason for this discrepancy may be traced back to the assumption of the straight line motion with uniform velocity. Although it should be allowed for the calculation of width, it may not be so in the case of shift, for the cut-off distance is actually comparable with the kinetic radius, i.e. $4.4\,\text{Å}$. It seems, therefore, that we have to take into account the effect of deflection and velocity change in the relative motion of the radiator and perturber. The details and the possible refinement will be published soon.

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2) I. Takahashi, M. Yamano, and A. Hirai, private communication.
3) K. Shimoda, private communication.
4) K. Tomita, Prog. Theor. Phys. 17 (1957), 513