Van der Waals Forces Between Symmetrical Rotators

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Work of F. London on the van der Waals forces between linear dipole molecules has been extended to polyatomic molecules which are representable as symmetrical tops. The results obtained by a second-order perturbation calculation are compared with those of a variational calculation for the specific case of the interaction between two tops in one-quantum states.

IN a recent paper by Margenau and Warren[1] the first-order perturbation energy between symmetrical top molecules carrying permanent dipole moments along their figure axes was calculated. The results were applied to the pressure broadening of the near infra-red spectral lines of ammonia, and qualitative agreement with experiment obtained. This indicates that these long range forces play a significant role in line broadening even at atmospheric pressure. It was there assumed that the second-order forces would be negligibly small over the range for which their calculation was valid, a conclusion based on the results of London[2] for linear dipole molecules. In the present work, the second-order perturbation to the van der Waals forces is calculated for symmetrical top molecules. The results show that the second-order effect is indeed negligible in line broadening. Actually the addition of another degree of freedom (spin about the figure axis) to the calculation for linear molecules reduces the second-order interaction. An independent calculation of the effect is made by the variation method.

The Schrödinger second-order perturbation formula may be used to find the energy change, averaged over degenerate states, resulting from the approach of two molecules carrying dipole moments μ along their figure axes:

$$\langle \Delta E_i \rangle_{\text{Av}}^{(2)} = \frac{1}{g_i} \sum_i' \frac{\sum_{\lambda,\mu} |V_{\lambda\mu}{}^{ij}|^2}{E_i{}^0 - E_j{}^0}. \qquad (1)$$

$V_{\lambda\mu}{}^{ij}$ is the matrix element of the perturbing potential V between the degenerate states λ and μ belonging to the energy states i and j respec-

tively, g_i is the degree of degeneracy of the ith state. The perturbing potential (interaction of the dipole moments) is

$$V = -(\mu^2/R^3)[2 \cos \theta_1 \cos \theta_2 \\ - \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)]$$

where the orientations of the molecules are expressed in the Eulerian angles θ, ϕ, χ relative to the line joining them, and R is the separation of the two molecules. A state j is characterized by the product of two unperturbed symmetrical top eigenfunctions, each of which is dependent on the three quantum numbers J, K, M. Since the energy of the symmetrical top is

$$E = \frac{h^2}{8\pi^2} \left\{ \frac{J(J+1)}{A} + \left(\frac{1}{C} - \frac{1}{A} \right) K^2 \right\}, \qquad (2)$$

where A and C are the moments of inertia about the principal axes, summing over degenerate states involves summing the numerator of (1) over permissible values of the M's (from $-J$ to $+J$) and the two possible values of the K's. If the quantum numbers of the two molecules belonging to the ith state are denoted by J_i, K_i, M_i and J_i', K_i', M_i' the numerator of Eq. (1) becomes

$$\sum \left| V \begin{matrix} J_i K_i M_i ; J_i' K_i' M_i' \\ J_j K_j M_j ; J_j' K_j' M_j' \end{matrix} \right|^2$$

$$= \frac{6\mu^4}{R^6} \sum \left(\cos \theta_1 \begin{matrix} J_i, K_i, M_i ; J_i', K_i', M_i' \\ J_j, K_j, M_j ; J_j', K_j', M_j' \end{matrix} \right)^2$$

$$\cdot \left(\cos \theta_2 \begin{matrix} J_i, K_i, M_i ; J_i', K_i', M_i' \\ J_j, K_j, M_j ; J_j', K_j', M_j' \end{matrix} \right)^2. \qquad (3)$$

The summation in (3) is over degenerate quantum numbers of both initial and final states. It

[1] H. Margenau and D. T. Warren, Phys. Rev. **51**, 748 (1937).

[2] F. London, Zeits. f. Physik **63**, 245 (1930).

has been carried out over degenerate quantum numbers of the final state (j) in calculations on transition probabilities, for example, in the work of Dennison.[3] Because the result at this stage is independent of the degenerate quantum numbers of the initial state (i), the remainder of the summation yields only the degeneracy factor, g_i. In terms of Dennison's transition probabilities

$$\sum \left(\cos \theta \,\frac{J_i K_i M_i}{J_j K_j M_j} \right)^2 = \frac{g_i}{3} \left(A\,\frac{J_i K_i}{J_j K_j} \right)^2.$$

The factor $\frac{1}{3}$ arises from the three possibilities of polarization which contribute equally to the total transition probability A^2. Expressed in these terms, the numerator of (1) becomes

$$\frac{2\mu^4}{3R^6} g_i g_{i'} \left(A\,\frac{J_i K_i}{J_j K_j} \right)^2 \left(A\,\frac{J_i' K_i'}{J_j' K_j'} \right)^2$$

and

$$\langle \Delta E_i \rangle_{\mathrm{Av}}^{(2)} = \frac{2\mu^4}{3R^6} \sum_j' \frac{\left(A\,\dfrac{J_i K_i}{J_j K_j} \right)^2 \left(A\,\dfrac{J_i' K_i'}{J_j' K_j'} \right)^2}{E_i{}^0 - E_j{}^0}.$$

The elements A^2 are different from zero only when $\Delta J = 0$, ± 1 and $\Delta K = 0$ (selection rules for $\parallel$-type bands). With Dennison's[3,4] expressions for the A's, the final result is

$$\langle \Delta E \rangle_{\mathrm{Av}}^{(2)} = -\frac{\mu^4}{3R^6 B} \left\{ \frac{(J+1)^2 - K^2}{(J+1)(2J+1)} \left[\frac{(J'+1)^2 - K'^2}{(J'+1)(2J'+1)(J+J'+2)} + \frac{K'^2}{J'(J'+1)(J+1)} \right. \right.$$

$$+ \frac{J'^2 - K'^2}{J'(2J'+1)(J-J'+1)} \left] + \frac{K^2 K'^2}{J(J+1) J'^2 (J'+1)^2} + \frac{J^2 - K^2}{J(2J+1)} \left[\frac{(J'+1)^2 - K'^2}{(J'+1)(2J'+1)(1+J'-J)} \right. \right.$$

$$\left. \left. - \frac{K'^2}{J J' (J'+1)} - \frac{J'^2 - K'^2}{J'(2J'+1)(J+J')} \right] \right\}, \quad (3)$$

where the subscripts i have been dropped throughout. Table I gives a few values of this expression. It is seen that an increase in K, the "spin" quantum number, weakens the interaction between molecules of fixed J and J'. Since this energy perturbation would be described classically as the tendency of one dipole molecule to line up its neighbors, it may be said that an increase in the "spin" energy of a top strengthens its resistance to orientation.

If K is set equal to zero, the wave functions of the symmetrical top go over into those of the linear molecule. If the K's in (3) are allowed to vanish, the resulting expression is identical with that obtained for linear dipole molecules by F. London.[2] It is to be noted that (3) has the familiar form of the $1/R^6$ law which is characteristic of this effect. It does not apply, of course, to cases of close approach where the numerators of terms in (1) become comparable to the denominators. For a typical molecule, calculations indicate that Eq. (3) is quite accurate for distances of separation greater than 9 or 10A.

Since the first-order splitting of levels is symmetrical, the "center of gravity" of a degenerate group of levels is unchanged by this interaction. Hence Eq. (3) contains the total average effect of these long range forces.

An upper bound to the energy of interaction can be found by the variation method, by using a linear combination of unperturbed wave functions. The mathematical complexity, how-

TABLE I. *Values of $\langle \Delta E \rangle_{\mathrm{Av}}^{(2)}$ for various energy states.*

Energy State	$\langle \Delta E \rangle_{\mathrm{Av}}^{(2)}$ in Units of $\mu^4/R^6 B$	Energy State	$\langle \Delta E \rangle_{\mathrm{Av}}^{(2)}$ in Units of $\mu^4/R^6 B$
$J = J'$ $\quad$ $K = K' = 0$	$-\dfrac{1}{6}$	$J = 1$ $\quad J' = 2$ $\quad$ $K = 1$ $\quad K' = 2$	$-\dfrac{23}{270}$
$J = 1 = J'$ $\quad$ $K = 1 = K'$	$-\dfrac{5}{48}$	$J = 2$ $\quad J' = 2$ $\quad$ $K = 2$ $\quad K' = 2$	$-\dfrac{1}{18}$
$J = 0$ $\quad J' = 1$ $\quad$ $K = 0$ $\quad K' = 0$	$-\dfrac{2}{27}$	$J = 2$ $\quad J' = 2$ $\quad$ $K = 1$ $\quad K' = 1$	-0.158
$J = 0$ $\quad J' = 1$ $\quad$ $K = 0$ $\quad K' = 1$	$-\dfrac{2}{9}$		

[3] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[4] The expressions given by Dennison are here to be multiplied by 4.
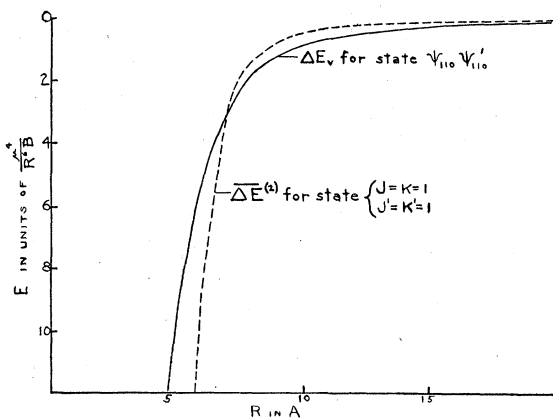
Fig. 1. Energies of state as functions of R.

ever, prevents an explicit calculation for the general case. It has been carried out for the special case where both interacting molecules are in the state $J=1$, $K=1$, $M=0$. Here the variation function suggested by the problem is a linear combination of the ten unperturbed wave functions with which the given state $(\psi_{110}\psi'_{110})$ combines, i.e.,

$$\psi_{111}\ \psi'_{11-1},\quad \psi_{11-1}\psi'_{111},\quad \psi_{211}\ \psi'_{21-1},$$

$$\psi_{111}\ \psi'_{21-1},\quad \psi_{210}\ \psi'_{210},\quad \psi_{21-1}\psi'_{211},$$

$$\psi_{11-1}\psi'_{211},\quad \psi_{211}\ \psi'_{11-1},\quad \psi_{21-1}\psi'_{111}.$$

Minimizing the energy of the system with respect to the constants in the variation function leads to a secular determinant of ten rows and columns, but which possesses only four distinct roots, reducing to an equation of the fourth degree in E_v, the variation energy. The various matrix elements in the secular equation were constructed from a table of integrals involving symmetrical top wave functions published by Reiche and Rademacher.[5] The resulting fourth degree equation was solved numerically for various values of the molecular separation, R, using reasonable values of the molecular constants ($\mu=1.5\times10^{-18}$ e.s.u., $A=3\times10^{-40}$ g cm^2, from which B, the separation of the rotational levels$=1.8\times10^{-15}$ ergs, or about 0.001 ev.). The lowest root of the secular equation is an upper bound to the energy of the given state. This energy is shown in Fig. 1 as a function of R. Included for comparison is a plot of $\langle\Delta E\rangle_{Av}{}^{(2)}$ for the energy state $J=|K|=J'=|K'|=1$. Neglecting the effect on E_v of averaging over degenerate states, it is seen that it is larger than the second-order perturbation for $R>8$A, since E_v contains also the first-order effect, which obeys a $1/R^3$ law. At distances less than about 8A, the second-order perturbation diverges markedly. This shows that Eq. (3) is valid only for R greater than this value.

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[5] F. Reiche and H. Rademacher, Zeits. f. Physik **41**, 453 (1927).