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creasing vibrational quantum number. The opposite choice of a potential function should produce positive deviations like those we observed.

There are several ways in which one might expect the rudimentary harmonic models to be defective as representations of $3d^n \leftrightarrow 3d^n$ spectra at elevated temperatures. However, there is at present little objective basis for sorting out these defects according to importance. We do not believe that the data presented here necessarily constitute a norm for the temperature dependence of $3d^n \leftrightarrow 3d^n$ spectra of centrosymmetric complexes in general. Clearly, the temperature dependence observed by Holmes and McClure is different from that which we found.

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Second-Order Interactions between Polar Molecules

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The interaction energy between polar molecules is calculated up to second-order perturbation contributions. The essential result is that the dipole-induced-dipole energy calculated by quantum theory differs considerably from the corresponding classical expression. This is confirmed by a variational calculation.

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I. INTRODUCTION

The interaction between molecules with permanent dipole moments is usually written as the sum of three contributions: (1) the first-order dipole–dipole interaction; (2) the dipole–induced-dipole interaction; and (3) the van der Waals–London energy. Generally the van der Waals–London component of the interaction is evaluated, from second-order perturbation theory, without explicitly taking into account the intrinsic dipole moments of the molecules. To this component the classical expressions for the dipole–dipole and the dipole–induced-dipole interactions are then added. Although, apparently, many investigators have been aware of the fact that quantum theory and classical electrostatics yield different results for the dipole–induced-dipole energy, this difference has to our knowledge not been determined explicitly.

In the present article we deduce the quantum theoretical expression for the total interaction between polar molecules including second-order terms. It is shown that the dipole–dipole energy is in agreement with classical electrostatics, that the van der Waals interaction is the same as for nonpolar molecules, but that the formula for the dipole–induced-dipole energy is reduced considerably with respect to the classical result.

Consider two systems (atoms or molecules), both electrically neutral. Without interaction the systems satisfy the equations

\[ H(1) | m\rangle_1 = E_m(1) | m\rangle_1; \]
\[ H(2) | n\rangle_2 = E_n(2) | n\rangle_2. \]  

\[ (1) \]

and

\[ H(1), | m\rangle_1, E_m(1) \text{ and } H(2), | n\rangle_2, E_n(2) \text{ are the } \]

Hamiltonians, the \( m \text{th} \) and \( n \text{th} \) eigenstates and the corresponding energy eigenvalues of Systems 1 and 2. Excluding overlap and exchange the unperturbed states of the total system, i.e., System 1 and System 2 together without interaction, are then

\[ | m, n\rangle = | m\rangle_1 | n\rangle_2. \]

The total Hamiltonian reads as follows:

\[ H(1, 2) = H(1) + H(2) + V(1, 2). \]

\[ (2) \]

The interaction \( V(1, 2) \) is expanded in a series of negative powers of \( R \), where the vector \( R \) connects the centers of charge of Systems 1 and 2. When neutrality is assumed, the first nonvanishing term of the
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$V(1, 2) = \hat{p}_i(1) T_{ij} \hat{p}_j(2) + \cdots$; \hspace{1cm} (3)

$p_i(1)$ and $p_j(2)$ are the operators of the total electric dipole of Systems 1 and 2. $T_{ij}$ is a symmetric tensor of second rank defined by

$T_{ij} = \frac{1}{R^3} (\hat{a}_{ij} - 3\hat{a}_i\hat{a}_j)$, \hspace{1cm} (4)

where $\hat{a}$ is the unit vector in the direction of $R$. The dipole moments of Systems 1 and 2, in their ground states, are then

$\mu_i(1) = \langle 0 | \hat{p}_i(1) | 0 \rangle$;

$\mu_j(2) = \langle 0 | \hat{p}_j(2) | 0 \rangle$. \hspace{1cm} (5)

Higher terms of the series, corresponding to interactions between higher multipoles, are not considered.

### II. PERTURBATION CALCULATION

With $V(1, 2)$ regarded as a perturbation, the expression for the energy becomes, up to second order,

$E = E_0(1) + E_0(2) + \langle 0 | V | 0 \rangle$

$+ \sum_{m,n} \{ (\langle 0 | V | m, n \rangle \langle n, m | V | 0 \rangle - \langle 0 | V | 0 \rangle^2) / [E_0(1) - E_m(1) + E_0(2) - E_n(2)] \}$. \hspace{1cm} (6)

The first-order energy is easily calculated

$e_1 = \langle 0 | V | 0 \rangle = \mu_i(1) T_{ij} \mu_j(2)$; \hspace{1cm} (7)

it corresponds to the classical result.

Introducing an average excitation energy of the total unperturbed system, $I_{total}$, the second-order term can be written as

$e_2 = \sum_{m,n} \{ (\langle 0 | V | m, n \rangle \langle n, m | V | 0 \rangle - \langle 0 | V | 0 \rangle^2) / [E_0(1) - E_m(1) + E_0(2) - E_n(2)] \}$

$= - (1/I_{total}) \langle 0 | V^2 | 0 \rangle - \langle 0 | V | 0 \rangle^2$. \hspace{1cm} (8)

With the help of (3) and (4) we obtain, after some algebra,

$[ \langle 0 | V^2 | 0 \rangle - \langle 0 | V | 0 \rangle^2 ] = T_{ij} T_{kl} \{ \langle 0 | [\hat{p}_i(1) - \mu_i(1)] [\hat{p}_j(1) - \mu_j(1)] | 0 \rangle \langle 0 | [\hat{p}_k(2) - \mu_k(2)] [\hat{p}_l(2) - \mu_l(2)] | 0 \rangle$

$\times (\hat{p}_k(2) - \mu_k(2)) | 0 \rangle + (\hat{p}_l(2) - \mu_l(2)) | 0 \rangle + \langle 0 | [\hat{p}_i(1) - \mu_i(1)] [\hat{p}_j(1) - \mu_j(1)] | 0 \rangle [\hat{p}_k(2) - \mu_k(2)] [\hat{p}_l(2) - \mu_l(2)] | 0 \rangle$. \hspace{1cm} (9)

To see the physical meaning of these terms, we consider the effect of an external electric field $F$ on System 1. The perturbation is then given by $V = \hat{p}_i(1) F_i$ and the energy, up to second-order perturbation terms, by

$E_F = E_0(1) + \mu_i(1) F_i - (1/I_1) F_i \{ \langle 0 | [\hat{p}_i(1) - \mu_i(1)] [\hat{p}_j(1) - \mu_j(1)] | 0 \rangle F_j \}$. \hspace{1cm} (10)

The averaging procedure yielding $I_1$ is carried out only over the excited states of System 1. By comparison with the classical formula for the energy of a polar system in an external field

$E_F = E_0 + \mu_i F_i - \frac{1}{2} F_i \alpha_{ii} F_j$,

we obtain, for the symmetric dipole-polarizability tensor of System 1,

$\alpha_{ii}(1) = \frac{2}{I_1} \langle 0 | [\hat{p}_i(1) - \mu_i(1)] [\hat{p}_j(1) - \mu_j(1)] | 0 \rangle$. \hspace{1cm} (11)

and analogously for System 2,

$\alpha_{jk}(2) = \frac{2}{I_2} \langle 0 | [\hat{p}_j(2) - \mu_j(2)] [\hat{p}_k(2) - \mu_k(2)] | 0 \rangle$. \hspace{1cm} (12)

Substituting (10) into (9), the second-order energy can be expressed completely in measurable quantities

$e_2 = -(I_1^2 / 4 I_{total}) \alpha_{ii}(1) T_{ij} \alpha_{jk}(2) T_{kl}$

$= - \langle I_1 / I_{total} \rangle \mu_i(1) T_{ij} \alpha_{jk}(2) T_{kl} \mu_j(1)$

$- \langle I_2 / I_{total} \rangle \mu_j(2) T_{ij} \alpha_{ik}(1) T_{kl} \mu_k(2)$. \hspace{1cm} (13)

The first term is the van der Waals energy. If one assumes the polarizability to be a scalar, then this expression is transformed into the familiar form

$- \frac{3}{2} I_1 I_2 (I_1 + I_2) [\alpha(1) \alpha(2) / R^6]$, \hspace{1cm} (14)

where $I_{total}$ is approximated by $I_1 + I_2$. The second and third terms correspond to the interaction of the in-

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4 In this article a scalar is denoted by a variable without index, a vector by a variable with one index, and a tensor of second rank by a variable with two indices. In addition, the sum convention is used for repeated indices. A short outline of tensor calculus may be found, e.g., in J. Mathews and R. L. Walker, Mathematical Methods of Physics (W. A. Benjamin, Inc., New York, 1964), Chap. 15.
trinsic dipole moment of System 1 with the induced dipole moment of System 2, and vice versa. Upon comparing these expressions with the classical formulas one notes that the latter are multiplied by the ratio $I_3/I_{total}$, respectively $I_3/I_{total}$, the numerator denoting an average excitation energy of the polarized system alone. The dipole–induced-dipole energy calculated by quantum theory is consequently always smaller than the classical result, in the case of two identical molecules even by a factor of approximately 2.

The reason for this difference is that in classical theory only the effect of the field originating from a molecule on a second one is considered, not the reaction of the field on the first molecule itself. This means that in the second-order energy expression (8), for instance, System 1 is kept in its ground state, not allowing for virtual excitations by the interaction. Using the definition for the polarizability (10), one obtains in this case exactly the classical energy for an induced dipole moment of Molecule 2 in the field of the permanent dipole moment of Molecule 1.

Recently, the interaction between two molecules with permanent electric moments has been treated by Buckingham. The second-order term of the perturbation series is divided into the classical dipole–induced-dipole interaction and the van der Waals–London interaction, plus a correction term which is assumed to be negligible. Upon inspection it appears, however, that the correction cannot, in general, be neglected. Being positive, this term diminishes the second-order energy in qualitative agreement with the present result.

III. VARIATIONAL CALCULATION

Following Kihara, we choose as a trial function

$$|\psi\rangle = (1 + A \chi) |0\rangle$$ (12)

with variation parameter $A$; the expression

$$E = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$$ (13)

is minimized with respect to $A$. The result is

$$E = E_0(1) + E_0(2) + \langle 0 | V | 0 \rangle \quad \text{and} \quad \langle 0 | V^2 | 0 \rangle - \langle 0 | V | 0 \rangle^2 \rangle / \langle 0 | V^2 | 0 \rangle \rangle. \quad (14)$$

The first-order term $\langle 0 | V | 0 \rangle$ is again the classical dipole–dipole interaction energy. To compare the second-order term with the corresponding term of the perturbation series (6), we make some transformations. To this end, the denominator in (14) is written as

$$\text{denominator} = \langle 0 | (V - \langle 0 | V | 0 \rangle) \langle H(1) - E_0(1) + H(2) - E_0(2) \rangle (V - \langle 0 | V | 0 \rangle) | 0 \rangle. \quad (15)$$

Using the closure condition

$$\sum_{n,m} |m,n\rangle \langle m,n| = 1,$$

we obtain

$$\text{denominator} = \sum_{m,n} \[E_m(1) - E_0(1) + E_n(2) - E_0(2) \] \langle 0 | (V - \langle 0 | V | 0 \rangle) \langle m,n\rangle \langle m,n | (V - \langle 0 | V | 0 \rangle) | 0 \rangle \rangle. \quad (16)$$

and averaging over the excitation energies yields

$$\text{denominator} = \langle \Delta E_{total} \rangle_\mu \langle 0 | V^2 | 0 \rangle - \langle 0 | V | 0 \rangle^2 \rangle. \quad (17)$$

The averaging procedure yielding $\langle \Delta E_{total} \rangle_\mu$ must be distinguished from the averaging in the perturbation expression (8). Generally, therefore, $\langle \Delta E_{total} \rangle_\mu$ is not exactly equal to $I_{total}$. Substituting (17) into (14), the second-order term becomes

$$\epsilon_2 = - \langle 1 / \langle \Delta E_{total} \rangle_\mu \rangle \langle 0 | V^2 | 0 \rangle - \langle 0 | V | 0 \rangle^2 \rangle. \quad (18)$$

With the help of (9), and substituting this time the variational expression for the polarizability tensors, we obtain

$$\epsilon_2 = - \langle \langle \Delta E_1 \rangle_\mu \langle \Delta E_2 \rangle_\mu / 4 \langle \Delta E_{total} \rangle_\mu \rangle \alpha_{11}(1) T_{ij} \alpha_{11}(2) T_{kl}$$

$$- \langle \langle \Delta E_2 \rangle_\mu / 2 \langle \Delta E_{total} \rangle_\mu \rangle \mu_{11}(1) T_{ij} \mu_{11}(2) T_{kl} \mu_{11}(1) - \langle \langle \Delta E_1 \rangle_\mu / 2 \langle \Delta E_{total} \rangle_\mu \rangle \mu_{11}(1) T_{ij} \mu_{11}(2) T_{kl} \mu_{11}(1). \quad (19)$$

This result is formally equal to that obtained by perturbation theory (11); only the averages $I_1$, $I_2$, and $I_{total}$ are replaced by $\langle \Delta E_1 \rangle_\mu$, $\langle \Delta E_2 \rangle_\mu$, and $\langle \Delta E_{total} \rangle_\mu$, respectively.

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