have also been the subject of a number of classical trajectory studies.[14] LEPS surfaces were used in these studies and were adjusted to reproduce the known experimental data. For the abstraction reaction the height of the barrier obtained in this manner is $\sim 4\frac{1}{2}$ kcal/mole[14]; this is to be compared to the 8.1 kcal/mole calculated here. The LEPS surfaces also predict that for the abstraction reaction $R_{\mathrm{HH}} \sim 0.97-0.99$ Å and $R_{\mathrm{HCl}} \sim 1.40-1.41$ Å, i.e., that at the saddle point R_{HCl} is less extended than R_{HH}. In contrast to this the present calculations predict that the transition state lies closer to the products than to the reactants.

For the exchange reaction the above LEPS surfaces actually predict a shallow well at the transition state as compared to the calculated barrier of 25.3 kcal/mole. *Assuming* that the barrier for abstraction is as given by the LEPS surface, we would predict the barrier for exchange to be 21.7 kcal/mole if the error in the calculated barrier is additive $[25.3+(4.5-8.1)]$ and 14.1 kcal/mole if it is multiplicative $[25.3\times(4.5/8.1)]$. It is unlikely that the barrier to exchange is lower than ~14 kcal/mole and may well be closer to 22 kcal/mole in line with the calculations of Botschwina and Meyer.[13]

The calculations will be presented in greater detail in a later paper.

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The relation between structure of van der Waals molecular dimers and dielectric second virial coefficients*

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(Received 24 September 1976)

One motivation for undertaking electric deflection and spectroscopic measurements on van der Waals molecular dimers is to obtain information about pair anisotropic intermolecular forces. A similar motivation holds for the measurement of dielectric virial coefficients of polar and nonpolar gases. The purpose of this note is to draw attention to how both electric deflection and dielectric virial coefficient measurements can be used to complement one another and to indicate the implications of the results of spectroscopic studies of van der Waals molecules for dielectric virial experiments and *vice versa*.

Up to the present, the most important implication of electric deflection results on van der Waals molecular dimers is that pair interactions based on classical electrostatic interactions of permanent and induced electrical moments may not be either adequate or efficient for predicting the geometry of molecular dimers.[1] This is not surprising when one realizes that the characteristic equilibrium separation of the dimer is of the order of the dimensions of the molecular partners, so that a far field electrostatic expansion is not necessarily useful. For example, a nonpolar dimer formed of polar monomers is unexpected from dipole-dipole interactions. However, all theories[2] for the dielectric virial coefficient are based on classical electrostatic potentials of interaction.

Here we present modifications of the conventional theory that permit the possibility of permanent dipole moment and pair interaction $u(1, 2)$ variations due to molecular overlaps that are not easily produced in the electrostatic picture. At the level of the second virial

The Journal of Chemical Physics, Vol. 66, No. 6, 15 March 1977

coefficient, an adequate representation of the net dipole moment $\mu_{\text{net}}(\mathbf{R}^N)$ of the sample of N molecules is

$$\mu_{\text{net}}(\mathbf{R}^N) = \sum_i \mu(i) + \sum_{\substack{i<j \\ 1}}^{N} \delta\mu(i,j) \ , \tag{1}$$

where $\delta\mu(i,j)$ denotes the difference between the permanent dipole moment of a pair of molecules $\mu_{\text{DIM}}(i,j)$ at a specified separation and orientation from the infinite dilution gas phase value; thus

$$\mu_{\text{DIM}}(1,2) = \mu(1) + \mu(2) + \delta\mu(1,2) \ . \tag{2}$$

Modifications to the standard theory[3] for the dielectric virial coefficient $B_\epsilon(T) = B_\alpha + B_\mu(T)$ lead to the result:

$$B_\mu(T) = (6k_BT)^{-1} \int \frac{d\omega_1}{\Omega_1}\frac{d\omega_2}{\Omega_2} \int d\mathbf{R}_{12} \exp\left[\frac{-u(1,2)}{k_BT}\right] \times [\mu_{\text{DIM}}(1,2)\cdot\mu_{\text{DIM}}(1,2) - \mu(1)^2 - \mu(2)^2] \tag{3}$$

where ω_i refers to the orientation of molecule i and $\Omega_i = \int d\omega_i$. The quantity B_α depends upon the difference in average polarizability of the dimer and constituent molecules; it does not exhibit the dominant T^{-1} dependence of $B_\mu(T)$.

In general the well depths of dimers are of the order of 1 to 10 times room temperature, and support a number of bound states. While a quantum theory of the dielectric constant would seem at first to be most closely connected to structural measurements, this would require a vast amount of structural data. The structural data, including numerical values of the dipole moment, exist in general only for the ground vibrational level of the dimer. It is highly likely that each vibrational level, all of which will be populated, has a different dipole moment. In addition, for excited vibrational levels it is likely that effects of nonrigidity are quite severe, making Van Vleck's high and low frequency separation nonapplicable. Thus, without this detailed knowledge of the electronic and mechanical properties of the dimer, a quantum mechanical theory at present would not be more physically correct than the above classical treatment.

The expression Eq. (3) may be used to investigate those cases that differ most markedly from predictions based on the electrostatic multipole picture. For example, for nonpolar molecules $B_\mu(T)$ takes the form

$$B_\mu(T) = (6k_BT)^{-1} \int \frac{d\omega_1}{\Omega_1}\frac{d\omega_2}{\Omega_2} \times \int d\mathbf{R}_{12} \exp\left[\frac{-u(1,2)}{k_BT}\right] \delta\mu(1,2)^2 \ . \tag{4}$$

If electric beam deflection measurements indicate that the ground state of the van der Waals dimer is polar, as in the case of $(Cl_2)_2$ or $(C_6H_6)_2$, $B_\mu(T)$ is predicted to decrease with increasing T, in agreement with the conventional theory. However, if the molecular beam electric deflection measurements indicate that the ground state of the dimer is nonpolar, as in the case of $(C_2H_4)_2$, then the possibility exists for $B_\mu(T)$ to *increase* with increasing T. In this case, $\delta\mu$ will vanish at the potential minimum but there can be an appreciable contribution from $\delta\mu(1,2)^2$ in Eq. (4) from more energetic conformations.

While in principle such a possibility is permissible within the conventional electrostatic picture, it requires the introduction of a fortuitous agreement of quadrupole moments and anisotropic induced polarizability.

In fact original measurements for $B_\mu(T)$ on ethylene indicated that $B_\mu(T)$ increased with increasing T.[4,5] However, the interpretation of more recent experiments has reversed this finding.[6,7] We predict this effect should be readily observed in the isoelectronic species formaldehyde. H_2CO is polar while its dimer is observed by electric deflection to be nonpolar. The connection between the electric deflection studies of van der Waals dimers and dielectric virial coefficients is evident: an anomalous temperature dependence for $B_\mu(T)$ of a nonpolar gas implies a nonpolar van der Waals dimer ground state, while molecular beam electric deflection evidence for a nonpolar van der Waals molecular dimer indicates possible dielectric anomaly.

In conclusion, spectroscopic studies of van der Waals molecules and gas phase dielectric measurements (or by analogy, Kerr effect virial coefficients) usefully complement one another. Both these measurements are probing the anisotropic intermolecular potential and involve μ_{DIM}.[1,2] Systems which especially deserve study are those that test the conventional miltipolar interaction picture. An example is the pair CH_3CN/CH_3NC, both of which have a similar dipole moment, quadrupole moment, polarizability anisotropy and shape.[8]

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*Supported in part by the National Science Foundation.

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