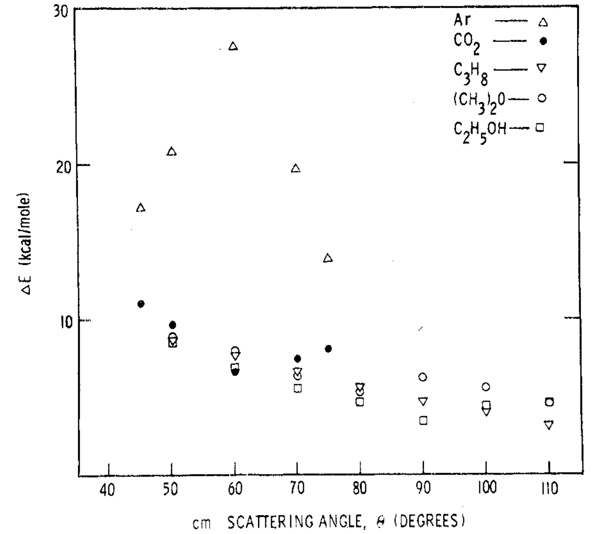

Figure 8. Characteristic energy transfer, ΔE, as a function of cm scattering angle for the scattering of $KBr^{\dagger}$ by Ar, CO_2, C_3H_8, $(CH_3)_2O$, and C_2H_5OH.

tween the relative translational energy corresponding to the maximum intensity in the high-velocity region and the initial relative translational energy. This quantity is designated ΔE and is plotted as a function of θ in Figure 8 for all the partners having molecular weights between 40 and 46. Within the experimental uncertainty, the ΔE's for all the molecular partners are the same at a given cm scattering angle. This observation coupled with the remarks at the end of the preceding section suggests that it may well be possible to find a fairly general quasi-statistical theory which will treat collision dynamics in systems not involving atomic collision partners or complex formation.

In this Account we have tried to indicate why energy transfer warrants thorough investigation. We have illustrated one set of techniques appropriate for studying vibrational energy transfer at the single collision level and have showed how scattering distributions in prototype systems can be interpreted qualitatively. A discussion of the quantitative interpretation of data in simple systems dominated by either attractive or repulsive forces was given and the features present in more complicated systems were discussed briefly. We have tried to show how molecular beam studies can yield a worthwhile reward in terms of an improved understanding of the mechanisms responsible for vibrational energy transfer.

We are greatly indebted to our colleagues in the investigations discussed here: Drs. T. Donohue, H. B. Bente, M. S. Chou, and M. K. Matzen. The experiments discussed were conducted in the Chemistry Department at Cornell University and supported in part by the National Science Foundation. The trajectory study was supported by the U.S. Energy Research and Development Administration.

An Atom Dipole Interaction Model for Molecular Optical Properties

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A simple way to understand the origin of various optical effects in many substances is based on an atom dipole interaction model. The atoms in a molecule are regarded as isotropic particles which interact by way of the dipole moments induced in them by an external field. Since the dipole fields are anisotropic, the molecule as a whole becomes anisotropic. This model was first proposed by Gray[1] in 1916 to account for optical rotation and by Silberstein[2] in 1917 to account for molecular anisotropies exhibited by the depolarization of scattered light and by the electrooptical Kerr effect. The qualitative predictions of Silberstein's theory provided an important insight during the early part of this century, and served as a basis for correlating anisotropy data with molecular structure in the work of Cabannes,[3] Stuart,[4] and others. Before the advent of electronic computers, however, it was difficult to treat the model quantitatively for polyatomic molecules. Consequently, the model has until recently played little role in the quantitative theory of molecular properties, and little was known about its quantitative validity.

From the early studies it could be expected that the model would provide some information on molecular optical properties outside of absorption bands. It might, therefore, be a useful alternative to quantum mechanical dispersion theory in such cases, since the latter requires a detailed knowledge of many electronic transitions in order to make calculations analogous to those which can be performed with relatively little empirical information for the atom dipole interaction model. In recent years we have found that the model is approximately valid for many polyatomic molecules. Thus it is possible to predict signs and approximate magnitudes of properties (e.g., optical rotations and

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(1) F. Gray, *Phys. Rev.*, 7, 472 (1916).

(2) L. Silberstein, *Phil. Mag.*, 33, 92 (1917).

(3) J. Cabannes, "La diffusion moléculaire de la lumière", Les Presses universitaires de France, Paris, 1929.

(4) H. A. Stuart, "Molekülstruktur", Verlag von Julius Springer, Berlin, 1934.

Kerr constants) of compounds for which this information is sufficient to distinguish among possible structures. The model serves to predict other information which is not usually available from experiment, such as the quadrupole polarizability and the signs of polarizability derivatives which govern Raman scattering. The model should prove useful in predicting properties of functional groups in a molecule (e.g., dipole and higher multipole polarizability tensors) where this information is needed for calculations of interactions with other groups or other molecules.

The choice of atoms, rather than bonds or other groups, as the interacting units in a molecule was made in this study because the locations of the atoms could be assigned with little ambiguity and their polarizabilities could be regarded as isotropic in a first approximation. Other assignments of interacting units would be possible within the same formalism, though these have not yet been as fully explored.

The purpose of this Account is to give some examples of recent applications of the model, and at the same time to describe the mechanisms by which the model exhibits the various properties.

The Atom Dipole Interaction Model[5]

We regard the molecule as being made up of N atoms, each of which acts as a point particle located at the nucleus and responds to an electric field only by the induction of a dipole moment which is a linear function of the local field. If the field at atom i due to a light wave or external charges is $\mathbf{E}_i$, then the induced moment μ_i in atom i is

$$\mu_i = \alpha_i \cdot (\mathbf{E}_i - \sum_{\substack{j=1 \\ j \neq i}}^{N} \mathbf{T}_{ij} \cdot \mu_j) \qquad (1)$$

where α_i is the polarizability of atom i and $\mathbf{T}_{ij}$ is the dipole field tensor, $\mathbf{T}_{ij} = r_{ij}^{-3}\mathbf{I} - 3r_{ij}^{-5}\mathbf{r}_{ij}\mathbf{r}_{ij}$, with $\mathbf{I}$ the unit tensor and $\mathbf{r}_{ij}$ the vector from atom i to atom j. The expression in parentheses in eq 1 is the total electric field at atom i, consisting of the external field plus the fields of all of the other induced dipoles in the molecule. Equation 1 can be rearranged in the form

$$\sum_{j=1}^{N} \mathbf{A}_{ij} \cdot \mu_j = \mathbf{E}_i \qquad (2)$$

where

$$\mathbf{A}_{ij} = \alpha_i^{-1} \qquad (3a)$$

and

$$\mathbf{A}_{ij} = \mathbf{T}_{ij}, \; i \neq j \qquad (3b)$$

The solution to eq 2, which may be obtained by matrix inversion, is

$$\mu_i = \sum_{j=1}^{N} \mathbf{B}_{ij} \cdot \mathbf{E}_j \qquad (4)$$

$\mathbf{B}_{ij}$ is a useful tensor which we call a "relay tensor", because it expresses the dipole moment relayed to atom i by the external field applied to atom j. $\mathbf{B}_{ij}$ can be calculated when the polarizabilities and coordinates of the atoms are given. The most immediate useful consequence of eq 4, applied to the case of a uniform field, is that the molecular polarizability tensor α is

$$\alpha = \sum_{i,j} \mathbf{B}_{ij} \qquad (5)$$

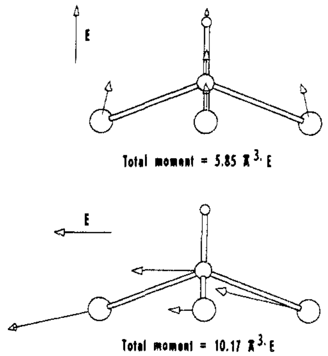

Figure 1. Induced atom dipole moments in $CHCl_3$ placed in a uniform field **E**. Arrows show the total moments induced by the external field and the fields of the other atom dipoles.

Polarizability and Its Anisotropy

Figure 1 illustrates the application of the model to the $CHCl_3$ molecule placed in a uniform field **E**, which may be regarded as the field of a light wave whose wavelength is very long compared to molecular dimensions. Arrows show the dipole moments induced in the atoms; these include the effects of **E** and of the induced moments in all of the other atoms and were calculated by eq 4 using atom polarizabilities obtained as described below. For "vertical" **E** the local dipole fields tend to oppose the applied field, while for "horizontal" **E** the local dipole fields enhance the applied field. Thus the molecule has its greatest polarizability in the horizontal direction. This behavior of $CHCl_3$ was deduced by Stuart long ago[6] from a qualitative extension of Silberstein's theory. However, Figure 1 illustrates an additional effect which has not been generally recognized. The induced atom dipoles are not all mutually parallel according to this model, and hence the net induced molecular dipole moment does not fully represent the charge distortions induced by the field; i.e., higher multipole moments are also induced. We will return to this point at the end of this Account.

The dipole polarizability, α, is related to three extensively measured quantities. The first is the molar refraction, R, given by

$$R = \frac{n^2 - 1}{n^2 + 2}\frac{M}{d} = \frac{4}{3}\pi N_A \bar{\alpha} \qquad (6)$$

where the mean polarizability $\bar{\alpha}$ is

$$\bar{\alpha} = {}^1/_3(\alpha_1 + \alpha_2 + \alpha_3) \qquad (7)$$

and α_1, α_2, α_3 are the principal polarizability components, n is the refractive index, M is the molecular weight, d is the density, and N_A is Avogadro's number.

The second is the depolarization ratio, ρ_l, for light scattered in a direction perpendicular to both the direction of propagation and the direction of polarization of the incident light, given by[7] eq 8, where the an-

$$\rho_l = 3\gamma^2/(45\bar{\alpha}^2 + 4\gamma^2) \qquad (8)$$

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(5) J. Applequist, J. R. Carl, and K.-K. Fung, *J. Am. Chem. Soc.*, **94**, 2952 (1972).

(6) Reference 4, p 224.

Table I
Atom Polarizabilities at 5893 Å and Their Derivatives with Respect to Bond Lengths

Atom	α, Å^3	$d\alpha/dR$, Å^2
H (alkane)	0.135 ± 0.006	0.746
H (alcohol)	0.135	
H (aldehyde)	0.167 ± 0.001	
H (amide)	0.161 ± 0.005	
H (amine)	0.155 ± 0.005	
C (alkane)	0.878 ± 0.014	0.023
C (carbonyl)	0.616 ± 0.008	
C (nitrile)	0.36	
N (amide)	0.530 ± 0.006	
N (amine)	0.618 ± 0.02	
N (nitrile)	0.52	
O (alcohol)	0.465	
O (ether)	0.465	
O (carbonyl)	0.434 ± 0.010	
F (halomethanes)	0.32 ± 0.01	1.09
Cl (halomethanes)	1.91 ± 0.02	3.18
Br (halomethanes)	2.88 ± 0.05	3.73
I (halomethanes)	4.69 ± 0.07	

Table II
Calculated and Observed Mean Polarizabilities, Depolarization Factors, and Kerr Constants of Gaseous Substances[a]

Compd	$\bar{\alpha}$, Å^3	$\rho_l \times 10^2$ [b]	$K \times 10^{15}$, esu[c]
CH_3Cl	4.41 ± 0.04 (4.55)	2.3 ± 0.2 (0.766)	67 ± 3 (36.5)
CH_2Cl_2	6.65 ± 0.08 (6.82)	2.7 ± 0.2 (1.124	−8.5 ± 0.3 (−5.6)
$CHCl_3$	8.73 ± 0.13 (8.53)	1.6 ± 0.1 (0.652)	−13.4 ± 0.4 (−7.7)
CH_3Br	5.39 ± 0.08 (5.61)	2.3 ± 0.2	70 ± 4 (45.5)
$CHBr_3$	11.89 ± 0.26 (11.84)[d]	1.5 ± 0.1 (1.5)[e]	−26.4 ± 0.8
CHF_3	2.78 ± 0.07 (2.81)	0.02 ± 0.03 (0.050)	−2.6 ± 1.6 (−2.9)
CH_3OCH_3	5.22 (5.24)	1.7 (0.7)	−15.9 (−5.0)
CH_3COCH_3	6.44 (6.39)[d]	0.72 (0.8)	31.3 (32.1)
C_2H_6	4.47 (4.48)	0.75 (0.198)	0.63 (0.59)

[a] Sources of experimental data, shown in parentheses, are cited in ref 5 except as noted. [b] Where ρ_n (natural incident light) was reported, a conversion was made using $\rho_l = \rho_n/(2 - \rho_n)$. [c] Temperature and pressure are those of experimental measurements; dipole moments used in calculations are from A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963. [d] From liquid-phase refractivity. [e] I. R. Rao, *Indian J. Phys.*, 2, 61 (1927).

isotropy γ is defined by eq 9.

$$\gamma^2 = {}^1/_2[(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_2 - \alpha_3)^2] \tag{9}$$

The third is the electrooptical Kerr constant, K, which expresses the birefringence, Δn, produced by a static field E by the relation $\Delta n = KnE^2$. For a dilute ideal gas at pressure p and temperature T, K is given by[4,8]

$$K = \frac{3\pi p}{kT}(\beta_1 + \beta_2) \tag{10}$$

where k is Boltzmann's constant and

$$\beta_1 = \frac{1}{45kT}[(\alpha_1{}^0 - \alpha_2{}^0)(\alpha_1 - \alpha_2) + (\alpha_2{}^0 - \alpha_3{}^0) \times (\alpha_2 - \alpha_3) + (\alpha_3{}^0 - \alpha_1{}^0)(\alpha_3 - \alpha_1)] \tag{11}$$

$$\beta_2 = \frac{1}{45k^2T^2}[(\mu_1{}^2 - \mu_2{}^2)(\alpha_1 - \alpha_2) + (\mu_2{}^2 - \mu_3{}^2) \times (\alpha_2 - \alpha_3) + (\mu_3{}^2 - \mu_1{}^2)(\alpha_3 - \alpha_1)] \tag{12}$$

where the superscript zero indicates polarizabilities in a static field and μ_k is the permanent dipole moment component along the kth principal optical axis.

Table I lists the atom polarizabilities that have been determined thus far,[5,9] including those that were used for all calculations described in this paper. The values were obtained by optimizing $\bar{\alpha}$ calculated for the atom dipole interaction model to fit experimental $\bar{\alpha}$ for over 40 substances. Additive values for atom polarizabilities are generally larger than those in Table I and have been found to be unsuitable for use with this model.[5,10] The standard deviations shown were estimated in the optimization process and are useful for estimating uncertainties in the predictions.

Table II lists the calculated and observed $\bar{\alpha}$, ρ_l, and K for several gaseous substances. The principal polarizability components for these cases have been listed elsewhere[5] and are omitted here since ρ_l and K show more directly than the components the extent to which the model accounts for properties which depend on anisotropy. The uncertainties in the calculated values are those propagated by the uncertainties in atom polarizabilities, and do not include other sources of error, such as errors in structural parameters. The comparison in Table II shows that $\bar{\alpha}$ is predicted satisfactorily and that there is a reasonable correlation between theory and experiment for ρ_l and K. However, there are a number of substantial discrepancies for the latter quantities. This is probably due in part to oversimplicity of the model and in part to the fact that ρ_l and K are sensitive to differences between components of α, so that errors in these components become magnified. In addition, the calculation of K by eq 10–12 is an approximation in which hyperpolarizability terms are neglected. It has recently been shown by Buckingham and Orr[11] that the error in this approximation is in the range of 20–40% in some typical cases. It seems fair to conclude that the calculations in Table II are reasonable first approximations, indicating that fairly good polarizability tensors are predicted by the model.

The cases where the model seems to work are primarily saturated molecules, though the results for acetone (Table II) and some amides and nitriles are equally good.[5] However, the model does not appear to fit the data for ethylene or benzene; i.e., any set of atom polarizabilities which give the correct $\bar{\alpha}$ for these cases give out-of-plane polarizabilities which are too small by a factor of 2–3.[9] The delocalization of electrons in π orbitals may be the reason for this failure, since our model treats the atoms as if their electrons were strongly localized.

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(7) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955, p 47.

(8) C. J. F. Böttcher, "Theory of Electric Polarization", Elsevier, Amsterdam, 1952, p 287.

(9) K.-K. Fung and J. Applequist, unpublished results.

(10) J. Applequist, *J. Am. Chem. Soc.*, **95**, 8255 (1973).

(11) A. D. Buckingham and B. J. Orr, *Trans. Faraday Soc.*, **65**, 673 (1969).

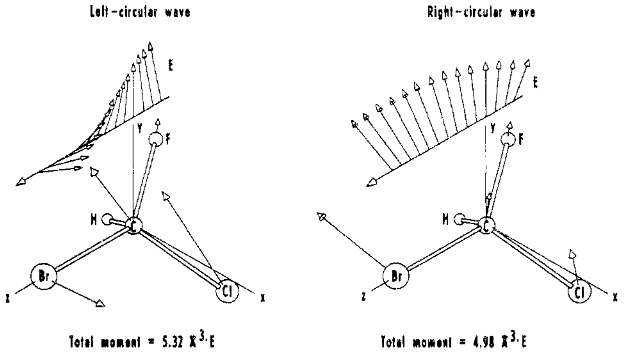

Figure 2. Atom dipole moments in CHFClBr induced by left and right circularly polarized light waves traveling parallel to the *z* axis. A short wavelength (12 Å) was used in this calculation to emphasize the distinction between the two cases.

Optical Rotation

Figure 2 illustrates the mechanism by which the atom dipole interaction model produces optical rotation in a chiral molecule, taking CHFClBr as an example. The molecule is shown in the presence of left and right circularly polarized light waves, which may be thought of as the resolved components of a plane polarized wave. Fresnel[12] showed in 1822 that the plane of polarization is rotated if the refractive index of the medium differs for left and right circularly polarized waves. The induced atom dipole moments calculated by eq 4 are shown in Figure 2. As in Figure 1, these moments are affected by local dipole fields; thus their directions and magnitudes are not simply related to the field **E**. For example, at the C atom **E** is the same in both waves, yet the induced moment is very different in the two. This is because another atom, such as Br, sees different **E** vectors in the two waves (since the molecular dimensions are not negligible compared with the wavelength) and hence has a different effect on C in each wave. The total molecular moments are thus different in the two waves; this means that the molecular polarizability, and hence the refractive index, differs in the two waves, as required to produce optical rotation.

The actual magnitude of the rotation is influenced by two additional considerations.[13] (i) The oscillations of the induced electric dipoles in the atoms constitute a circulating electric current which gives rise to an oscillating magnetic dipole moment. The calculation of the refractive index from Maxwell's equations shows that this magnetic moment makes an additional contribution to the optical rotation exactly equal to that produced by the induced electric dipole moment. (ii) The induced moments in Figure 2 hold only for the particular configurations of the molecule and wave shown; for an isotropic fluid medium the moments must be averaged over all orientations of the molecule. This averaging would result in a vanishing of the difference in molecular polarizability in the two waves if for every configuration of the molecule plus left circular wave there were a possible configuration of the molecule plus right circular wave with the same induced moment. However, in order for this to be generally true, the latter configuration would have to be the mirror image of the former, and this is not possible for a chiral molecule. Hence a medium of randomly oriented chiral molecules is optically active.

Equation 4 leads to an expression for rotation when one substitutes for $\mathbf{E}_j$ the terms $\mathbf{E}_0 + \mathbf{r}_j\cdot\nabla\mathbf{E}$ from a series expansion of the field of the wave about an arbitrary origin near the molecule.[14] Taking into account the magnetic moment contribution as well and performing the averaging over all orientations, one finds for the intrinsic molar rotation, $[m]$, at wavelength λ

$$[m] = (48\pi^2 N_A/\lambda^2) \sum_{i<j} \mathbf{r}_{ij}\cdot\mathbf{b}_{ij} \tag{13}$$

where $\mathbf{b}_{ij}$ is a vector formed from the relay tensor in the manner

$$\mathbf{b}_{ij} = (B_{ij}^{32} - B_{ij}^{23}, B_{ij}^{13} - B_{ij}^{31}, B_{ij}^{21} - B_{ij}^{12}) \tag{14}$$

where superscripts denote Cartesian components. $[m]$ is related to the conventional specific rotation, $[\alpha]$, by $[m] = [\alpha](M/100)[3/(n^2 + 2)]$.

The theory of optical rotation just outlined has its origins in the early work of Gray,[1] de Malleman,[15] and Boys.[16] The latter authors were able to show that the mechanism is capable of producing rotations comparable to those observed experimentally. However, the important goal of establishing a link between the sign of the observed rotation and the absolute configuration of a chiral molecule proved elusive because accurate calculations for polyatomic molecules were difficult to carry out. Kirkwood[17] reduced the problem to relatively simple calculations involving only the pairwise dipole interactions between anisotropic groups in a molecule. By this method Wood, Fickett, and Kirkwood[18] were able to make correct assignments of absolute configurations of some simple molecules. The pairwise approximation is, however, not justified in general because it neglects significant higher order contributions.[10,14] CHFClBr is a special case in which the approximation breaks down because of the tetrahedral arrangement of the axes of the groups; in such a case each pair of groups has a plane of symmetry, and hence contributes nothing to the rotation. Since our model includes the simultaneous interaction of all atoms, it predicts $[m]_D$ in the range +2 to +16 deg cm²/dmol for *S*-CHFClBr (illustrated).[14] This prediction has not been confirmed, though progress in resolving the compound has been reported.[19]

A comparison between theory and experiment has been made for two molecules having a tetrahedral arrangement of the substituent axes, namely, α-bromopropionitrile (BPN) and 3-methyl-5-bromo-1-cyanoadamantane (MBCA).[10,20] The ± sign for MBCA indicates that the configuration of the experimental compound was not known independently. The sign of the calculated rotation suggests a configurational assignment, though this may be questionable for MBCA since the sign of the calculated rotation for MBCA was

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(12) A. Fresnel, "Oeuvres Complètes", Vol. 1, Imprimerie Impériale, Paris, 1866, p 749.

(13) W. Kauzmann, "Quantum Chemistry", Academic Press, New York, N.Y., 1957, p 616 ff.

(14) J. Applequist, *J. Chem. Phys.*, **58**, 4251 (1973).

(15) R. de Malleman, *Trans. Faraday Soc.*, **26**, 281 (1930).

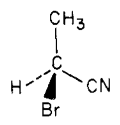
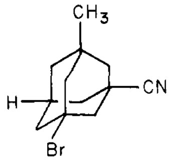
(16) S. F. Boys, *Proc. R. Soc. London, Ser. A*, **144**, 655 (1934).

(17) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

(18) W. W. Wood, W. Fickett, and J. G. Kirkwood, *J. Chem. Phys.*, **20**, 561 (1952).

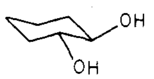
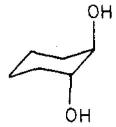
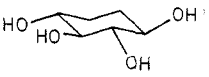
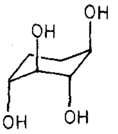
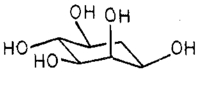
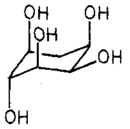
(19) M. K. Hargreaves and B. Modarai, *J. Chem. Soc. C*, 1013 (1971).

(20) J. Applequist, P. Rivers, and D. E. Applequist, *J. Am. Chem. Soc.*, **91**, 5705 (1969).

	 *S*-BPN	 *S*-MBCA
$[m]_D$ (calcd)	−74°	−0.84°
$[m]_D$ (exptl)	(−19°)	(±0.82°)

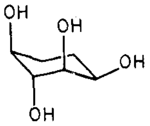
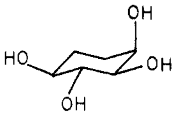
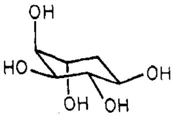
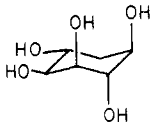
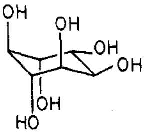
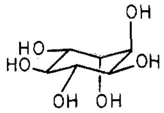
found to be sensitive to deviations of the CCN group from the assumed linearity. These data show that our model is consistent with the order-of-magnitude decrease in rotation as the distance between groups is increased.

A more demanding test of the model is its application to the cyclohexanepolyols, a large family of relatively rigid molecules having 22 enantiomorphic pairs. Calculations have been carried out for all of these,[21] and some examples will be cited here. In the following cases, both chair forms (*C*1 and 1*C*) are predicted to have similar rotations, so that there is no ambiguity in correlating calculated and observed signs. Positional numbers of the substituents are given, in which substituents "above" and "below" the plane of the ring are separated by a slash. Experimental $[m]_D$ are in parentheses.

	*C*1		1*C*
1/2	 −89° ± 25°	(−43°)	 −84° ± 48°
1,3/2,4	 −79 ± 22°	(−34°)	 −65 ± 38°
1,2,3,5/4	 −36 ± 17°	(−7°)	 −31 ± 15°

For these calculations an isotropic OH group was used in place of the two atoms, a procedure which was found to give results similar to those obtained by conformational averaging of the two-atom OH group. The large theoretical uncertainties, which are propagated by rather small uncertainties in the input parameters (Table I), indicate that predictions of this type are inherently limited by their sensitivity to these parameters. However, the approximate magnitudes, and especially the signs, of $[m]_D$ are given correctly in the above cases and suggest that absolute configurations of members of this series could be established from the predicted rotations.

The following are examples in which the two chair forms have substantially different predicted rotations, and we assign the observed rotation to the chair form to whose calculated rotation it comes closest. Interestingly, the chair form to which the experimental rotation is assigned in each case is the one with the least number of axial substituents. This is the form which is expected to be most stable from estimates of the free-energy excess (1–5 kJ/mol) of the axial vs. equatorial OH in cyclohexanol.[22] It should be noted that the empirical rules of Whiffen for predicting rotations have led to the same conclusions regarding the most stable conformation.[23] These rules, however, required independent information about the absolute configurations and the conformations of at least some of the compounds, while our predictions do not.

	*C*1	1*C*
1,2,4/3	 +29 ± 10°	 −108 ± 45° (−45°)
1,3,4/2,5	 +34 ± 6° (+34°)	 −106 ± 28°
1,2,4/3,5,6	 +134 ± 32°	 −140 ± 33° (−93°)

These examples show that the atom dipole interaction model is valid for predicting signs and approximate magnitudes of optical rotations of relatively rigid, primarily saturated molecules. With care in examining the uncertainty in the predictions, the model is of potential value in interpreting experimental rotations in terms of structure.

Raman Scattering Parameters

According to both the classical and quantum mechanical theories of vibrational Raman scattering, when light of frequency ν_0 is scattered by molecules having a vibrational frequency ν_t, the scattered light has weak components at frequencies $\nu_0 \pm \nu_t$ if the molecular polarizability tensor is a function of the positions of the nuclei.[24] The atom dipole interaction model has this functionality built in, and it is therefore of interest to see whether the model is capable of predicting intensities of Raman scattering.

The derivative α' of α with respect to a vibrational normal coordinate Q_t is, for our model,[21,25]

$$\alpha' = -\sum_{i,j,k,l} \mathbf{B}_{ij}\cdot\mathbf{A}_{jk}'\cdot\mathbf{B}_{kl} \qquad (15)$$

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[22] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965, p 437.

[23] D. H. Whiffen, *Chem. Ind.* (*London*), 964 (1956).

[24] (a) M. Born, "Optik", Springer-Verlag, Berlin, 1933, p 390 ff; (b) ref 7, p 48 ff.

[25] J. Applequist and C. O. Quicksall, *J. Chem. Phys.*, in press.

Table III
Raman Scattering Parameters for Totally Symmetric Vibrations of Methanes and Halomethanes

Compd	Coord	ν_t, cm^{-1}	$\bar{\alpha}'$, Å^2 amu$^{-1/2}$ Calcd	$\bar{\alpha}'$, Å^2 amu$^{-1/2}$ Exptl	γ', Å^2 amu$^{-1/2}$ Calcd	γ', Å^2 amu$^{-1/2}$ Exptl
CH_4	Q_1	2914	2.08	±2.10	0	0
CD_4	Q_1	2090	1.47	±1.39	0	0
CHF_3	Q_1	3033	1.00	±1.13	3.05	±1.64
CH_3Cl	Q_1	2965	1.77	±1.79	−0.85	±0.82
$CHCl_3$	Q_1	3023	0.69	±0.78	3.11	±0.68
CH_3Br	Q_1	2862	1.76	±1.71	−0.51	±0.77
CH_2Cl_2	Q_1	3003	1.31	±1.35	±2.36	±2.3
$CFCl_3$	Q_1	1090	0.23	±0.17	−0.36	
	Q_2	535	0.58	±0.53	0.84	±0.81
	Q_3	350	−0.45	±0.25	0.37	±0.48

where $\mathbf{A}_{jk}'$ is the derivative of $\mathbf{A}_{jk}$ with respect to Q_t. For any normal coordinate whose transformation to Cartesian coordinates is known, $\mathbf{A}_{jk}'$ can be calculated from eq 3b for $j \neq k$. In our treatment, terms in $\mathbf{A}_{jj}'$ also contribute (see eq 3a) because the atom polarizabilities are regarded as functions of the bond lengths. This dependence is expressed as

$$\alpha_j = \alpha_j(0) + \sum_n (\mathrm{d}\alpha_j/\mathrm{d}R_n)R_n \qquad (16)$$

where R_n is the displacement of the nth bond length from its rest value and $\alpha_j(0)$ is the atom polarizability at the rest configuration of the molecule. Equation 16 represents an additional hypothesis in our model, but is reasonable in view of the fact that the electronic wave function of a molecule depends on the nuclear positions. Both our calculations and earlier calculations by Matossi[26] for di- and triatomic molecules showed that the atom dipole interaction model is not adequate without this hypothesis.

From α' calculated by eq 15 one obtains the mean polarizability derivative, $\bar{\alpha}'$, and the anisotropy, γ', which are defined by eq 7 and 9 when the principal components are replaced by their derivatives. The magnitudes (but not the signs) of $\bar{\alpha}'$ and γ' are determined experimentally from measurements of intensities and depolarization ratios of Raman lines under conditions where ν_0 is much greater than ν_t but much less than the lowest electronic absorption frequency.[24] A compilation by Murphy et al.[27] for gaseous substances was the major source of such data for our recent study,[25] whose findings will be described here by means of selected examples.

Since the $\mathrm{d}\alpha_j/\mathrm{d}R_n$ values were not known from other information, we chose to optimize these quantities for five atoms to fit the experimental values of $\bar{\alpha}'$ for 29 normal vibrations of a set of methanes and halomethanes. The optimum values so determined are listed in Table I. The values of $\alpha_j(0)$ were taken as those determined from molecular polarizabilities at 5893 Å (Table I).

Table III compares the calculated and experimental values of $\bar{\alpha}'$ and γ' for some of the molecules used in the optimization procedure. The entries for all molecules except $CFCl_3$ are for vibrations involving primarily C–H or C–D stretching. These are of particular interest because they correspond to relatively intense Raman lines, for which the experimental data are presumably most accurate. For present purposes the signs of the Q_1 normal coordinates of CH_3Cl, $CHCl_3$, CH_3Br, and $CFCl_3$ have been reversed from those used in our original paper,[25] so that in every case increasing Q_1 corresponds to increasing bond length. It is seen that the calculated $\bar{\alpha}'$ values are generally satisfactory. The fact that they are positive means that the mean molecular polarizability increases with increasing C–H bond length in all of these compounds. This conclusion, which is suggested but not proven by these calculations, could not be reached on the basis of the experimental data alone; it is, however, consistent with Bell's conclusion from a study of the isotope effect on the molar refraction of CH_4.[28] The fit to the experimental γ' values is less satisfactory, but a rough correlation exists nevertheless. The agreement found here is good enough to support the validity of the atom dipole interaction model as a first approximation.

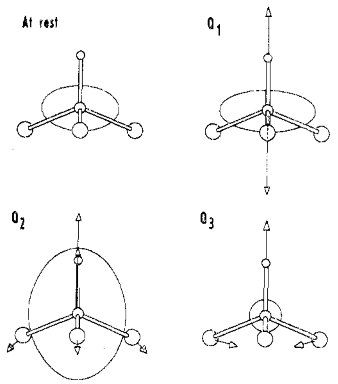

Figure 3. Nuclear displacements and polarizability ellipsoid distortions for the totally symmetric vibrations of $CFCl_3$.

The significance of $\bar{\alpha}'$ and γ' is illustrated in Figure 3 for the totally symmetric modes of $CFCl_3$. Arrows indicate nuclear displacements calculated for Q_t = 10 Å amu$^{1/2}$ from Holzer's transformation matrices.[29] For small displacements the polarizability is $\alpha = \alpha(0) + \alpha' Q_t$, and is represented in each diagram by a polarizability ellipsoid. Thus if $\bar{\alpha}'$ is positive, the mean dimensions of the ellipsoid increase (cf. Table III). These vibrations each have a threefold symmetry axis, and in such a case the anisotropy reduces to $\gamma' = \alpha'_{\parallel} - \alpha'_{\perp}$ where subscripts denote components parallel and perpendicular to the symmetry axis. Thus, according to our model, γ' is negative for Q_1 because $\alpha'_{\parallel} < 0 < \alpha'_{\perp}$; for Q_2 γ' is positive because $\alpha'_{\parallel} > \alpha'_{\perp} > 0$; and for Q_3 γ' is positive because $0 > \alpha'_{\parallel} > \alpha'_{\perp}$. These effects originate, according to our model, in the mutually counteracting effects of decreasing atom dipole interactions and increasing atom polarizabilities with increasing bond lengths.

Quadrupole Polarizability

In connection with Figure 1, we have noted that a uniform field **E** induces charge displacements other than those described by the molecular dipole moments, according to our model. It is of interest to see whether this behavior of the model is consistent with experi-

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(26) F. Matossi, *J. Chem. Phys.*, **19**, 1007 (1951).

(27) W. F. Murphy, W. Holzer, and H. J. Bernstein, *Appl. Spectrosc.*, **23**, 211 (1969).

(28) R. P. Bell, *Trans. Faraday Soc.*, **38**, 422 (1942).

(29) W. Holzer, Doctoral Dissertation, University of Munich, 1967.

Table IV
Quadrupole Polarizability of CH_4

Q, Å^4	Source
1.57	This work
2	IR line broadening in CH_4-Ar[a]
2.71	Proton spin relaxation in CH_4-He[b]
0.88	Proton spin relaxation in CH_4-Ne[b]
0.89	Proton spin relaxation in CH_4-Ar[b]

[a] C. G. Gray, *J. Chem. Phys.*, **50**, 549 (1969). [b] S. Rajan, K. Lalita, and S. V. Babu, *J. Magn. Reson.*, **16**, 115 (1974).

mental data on the induced quadrupole moment. The quadrupole moment Θ of a system of charges e_k located at positions $\mathbf{r}_k$ can be defined, following Buckingham,[30] by eq 17. In our model, the ith atom may be assigned

$$\Theta = {}^1/_2 \sum_k e_k(3\mathbf{r}_k\mathbf{r}_k - \mathbf{r}_k{}^2\mathbf{I}) \tag{17}$$

a charge e_i at position $\mathbf{r}_i + \delta\mathbf{r}_i$ and a charge $-e_i$ at $\mathbf{r}_i$, so that the induced atom dipole moment is $\boldsymbol{\mu}_i = e_i\delta\mathbf{r}_i$. Then the induced quadrupole moment can be expressed in terms of the induced atom dipole moments. Defining the quadrupole polarizability $\mathbf{Q}$ by $\Theta = \mathbf{Q}\cdot\mathbf{E}$, we find

$$\mathbf{Q} = \sum_{i,j} (\frac{3}{2}\mathbf{r}_i\mathbf{B}_{ij} + \frac{3}{2}\overset{\cap}{\mathbf{r}_i\mathbf{B}_{ij}} - \mathbf{I}\mathbf{r}_i\cdot\mathbf{B}_{ij}) \tag{18}$$

where $\cap$ indicates transposition of the first and second coordinate indices of $\mathbf{r}_i\mathbf{B}_{ij}$.

For the CH_4 molecule one scalar quantity Q is sufficient to specify $\mathbf{Q}$ when the H atoms are located at (d,d,d), $(d,-d,-d)$, $(-d,d,-d)$, and $(-d,-d,d)$, where $d = r_{CH}/3^{1/2}$.[30] The value of Q calculated from eq 18 using the atom polarizabilities in Table I is given in Table IV along with experimental values estimated from data on collisional interactions of CH_4 with rare gas atoms. The agreement is encouraging and suggests once again that the atom dipole interaction model is capable of reproducing some of the rather subtle charge distortions experienced by real molecules in electric fields.

Conclusions and Outlook

The variety of molecular properties which are accounted for at least approximately suggests that the atom dipole interaction model is a reasonable facsimile of real molecules. The model is appealing because it requires relatively little information for practical calculations. It is to be expected that further research on this model will lead to refinements and extensions to other properties. For example, Sundberg[31] has recently extended the theory to include effects due to the nonlinear response of atoms to an applied field. Buckingham and Stiles[32] have considered the role of higher multipole interactions in optical rotation. Both of these developments may well have significant effects on the properties discussed here.

Note Added in Proof. An important test of the atom dipole interaction model which was not mentioned above is its application to the collisional polarizability anisotropy of inert gases. Buckingham and Dunmur[33] have applied the model with partial success to this effect as it applies to the density dependence of the Kerr constant. Oxtoby and Gelbart[34] have improved the predictions of atom pair anisotropies in a related context by replacing point polarizabilities with polarizability densities which are spread over the whole atom.

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Chemically Induced Nuclear Spin Polarization in the Study of Carbene Reaction Mechanisms

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Among the synthetically useful intermediates of organic chemistry there are four classes with carbon atoms in other than tetravalent states. In three of these, carbanions, carbon radicals, and carbocations, carbon is trivalent. The fourth class is that of the carbenes, intermediates containing one divalent carbon atom with two nonbonding electrons, i.e., with an electron sextet. Formally, the recorded interest in divalent carbon species goes back to Dumas' attempts to dehydrate methanol;[1] of course, these experiments were carried out well before the quadrivalence of carbon was recognized. Authentic carbene reactions were observed as early as three-quarters of a century ago by Buchner and

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(1) J. B. Dumas, *Ann. Chim. Phys.*, [2] **58**, 28 (1835).