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The Calculation of Dipole Polarizability and Anisotropy by the CNDO Method

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The dipole polarizabilities and the anisotropies of small linear molecules have been calculated according to a formula in which the frequency of the incident light is taken into account, as derived by the time-dependent perturbation theory. The wave functions and the energies were calculated by the CNDO method, involving the configuration interaction treatment. The effect of the parametrization in the CNDO method on the calculated polarizability and anisotropy has also been discussed. The method has been used to calculate the variations in the anisotropy, the polarizability, α, and its derivatives, $(\partial\alpha/\partial S_i)_0$ and $(\partial^2\alpha/\partial S_i^2)_0$, with the frequency of the incident light, where S_i is the appropriate symmetry coordinate of the molecular vibration.

There have been published several reports in which the polarizability has been investigated theoretically.[1-6] The variational-perturbation method has been applied to calculate the polarizability by several investigators. From the results of this treatment using the LCAO–MO functions of the Roothaan type for the zero-order wave functions, O'Hare and Hurst[1] suggested that the calculated polarizability can be used to determine whether or not the wave functions are appropriate, since the theoretical polarizability is sensitive to the zero-order wave functions. Liebmann and Moskowitz[2] discussed the results of the calculations for the polarizabilities of many compounds by this method. They compared the polarizabilities calculated by the use of different types (Slater- and Gaussian-types) of atomic orbitals with each other. Also, Sadlej[3] calculated the polarizability by the variational-perturbation method, using the complete neglect of differential overlap (CNDO) version, and compared the results of his calculations with those of the non-empirical calculations. He concluded that the CNDO version can be adapted for the calculation of the polarizability.

Davies[4] discussed the theoretical polarizability calculated from the first-order perturbed wave functions in the self-consistent perturbation theory within the framework of the CNDO approximation. From a comparison between the results of calculations in which the 2p orbitals of the hydrogen atom are and are not considered, he concluded that the valence orbital basis set, which is generally used in the LCAO–MO method, was inadequate for the representation of the perturbed wave functions. In the method described above, the perturbing term in the molecular Hamiltonian which arises from the interaction between the molecule and the uniform electric field, $\mathbf{E}$, is $H' = -e\sum_i \mathbf{r}_i\cdot\mathbf{E}$, where $\mathbf{r}_i$ is the position vector of the i-th electron.

The finite perturbation theory has been used by Hush and Williams[5,6] to investigate the polarizability and the anisotropy. In this method, the SCF calculation was performed for an appropriate system including an molecule plus a fixed charge on the molecular axis.

Although the polarizability is dependent upon the frequency of the incident light, all the theoretical treatments described above do not take the contribution of the frequency of the incident light into account. In this work, however, an approximate method which is dependent upon the frequency of the incident light has been used to calculate the polarizability of several small molecules. The total wave function used to calculate the polarizability has been obtained by the CNDO method,[7-11] involving the configuration interaction treatment. The dependence of the values of the polarizability and the anisotropy on the frequency of the incident light has been discussed. Moreover, the effect of the parametrization in the CNDO method on the calculated polarizability has been discussed. Furthermore, for example, this approximate method has been used to estimate the dependence of the polarizability derivatives, $(\partial\alpha/\partial S_i)_0$ and $(\partial^2\alpha/\partial S_i^2)_0$, on the frequency of the incident light, where α is the molecular polarizability, and S_i, an appropriate symmetry coordinate.

Methods of Calculation

The Molecular Polarizability. The perturbed wave function (Ψ_a) of the system in the electromagnetic field is represented by the wave functions (Ψ^0's) of the system in the absence of the field:[12]

$$\Psi_a = \Psi_a{}^0 + \sum_b C_b \Psi_b{}^0, \tag{1}$$

where, if the energy of the incident light is $\varepsilon(=h\nu)$, the C_b is given by the relation:

$$C_b = \frac{iE_{ba}}{2c\hbar}\mathbf{A}_0{}^0\cdot\langle\Psi_b{}^0|e\sum_i\mathbf{r}_i|\Psi_a{}^0\rangle\left\{\frac{\exp(i(E_{ba}+\varepsilon)t/\hbar)}{E_{ba}+\varepsilon} + \frac{\exp(i(E_{ba}-\varepsilon)t/\hbar)}{E_{ba}-\varepsilon}\right\} + \text{constant}, \tag{2}$$

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[1] J. M. O'Hare and R. P. Hurst, *J. Chem. Phys.*, **46**, 2356 (1967).

[2] S. P. Liebmann and J. W. Moskowitz, *ibid.*, **54**, 3622 (1971).

[3] A. J. Sadlej, *Theor. Chim. Acta*, **21**, 159 (1971).

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[9] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[10] J. D. Bene and H. H. Jaffé, *ibid.*, **48**, 1807 (1968).

[11] J. D. Bene and H. H. Jaffé, *ibid.*, **48**, 4050 (1968).

[12] H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons, New York (1944), p. 118.

where $E_{\mathrm{ba}}=E_{\mathrm{b}}-E_{\mathrm{a}}$ $(=h\nu_{\mathrm{ba}})$ and where $\mathbf{A}_0{}^0$ is the vector relating to the electric field, $\mathbf{E}_0$: $\mathbf{E}_0=\varepsilon/c\hbar\ \mathbf{A}_0{}^0 \sin \varepsilon/h\ t$.

The dipole moment $(\mathbf{R}_{\mathrm{a}})$ associated with the Ψ_{a} state as a function of the electric field is:

$$\mathbf{R}_{\mathrm{a}} = \langle \Psi_{\mathrm{a}}{}^0 | e\sum_i \mathbf{r}_i | \Psi_{\mathrm{a}}{}^0 \rangle + \frac{2}{h}\sum_b \frac{\nu_{\mathrm{ba}}}{\nu_{\mathrm{ba}}^2-\nu^2} \langle \Psi_{\mathrm{a}}{}^0 | e\sum_i \mathbf{r}_i | \Psi_{\mathrm{b}}{}^0 \rangle \langle \Psi_{\mathrm{b}}{}^0 | e\sum_i \mathbf{r}_i | \Psi_{\mathrm{a}}{}^0 \rangle \cdot \boldsymbol{E}_0. \tag{3}$$

The first term on the right-hand side in Eq. (3) is the permanent dipole moment of the system. By averaging the vector quantities over all the orientations of the system with respect to the field, the second term can be rewritten as follows:

$$\frac{2}{3h}\sum_b \frac{\nu_{\mathrm{ba}} |\langle \Psi_{\mathrm{a}}{}^0 | e\sum_i \mathbf{r}_i | \Psi_{\mathrm{b}}{}^0 \rangle|^2}{\nu_{\mathrm{ba}}^2-\nu^2} \mathbf{E}_0 = \alpha \mathbf{E}_0. \tag{4}$$

Thus, the polarizability, α, can be calculated from the quantum-mechanical expression, Eq. (4).

The Molecular Anisotropy. The molecular anisotropy, κ, which determines the depolarization of light scattered by the molecule, is expressed by the components of the polarizability tensor as follows:

$$\kappa^2 = \{(\alpha-\alpha_1)^2+(\alpha-\alpha_2)^2+(\alpha-\alpha_3)^2\}/6\alpha^2, \tag{5}$$

where α_1, α_2, and α_3 are the principal polarizabilities of the molecule. In the case of linear molecules, Eq. (5) can be simplified as follows:

$$\kappa = (\alpha_{/\!/}-\alpha_{\perp})/3\alpha = \Delta\alpha/3\alpha, \tag{6}$$

where $\alpha_{/\!/}=\alpha_1$, $\alpha_{\perp}=\alpha_2=\alpha_3$.

The Molecular Wave Functions. In this calculation, the molecular wave functions, Ψ^0's, in Eq. (1) are described as the antisymmetrized products of one-electron functions and the excited state, $\Psi_{\mathrm{b}}{}^0$, is described as a linear combination of the excited configurations $(\Phi_{\mathrm{i-k}})$ obtained by the configuration interaction (CI) treatment. The wave functions and energies of the excited states were improved by these CI treatments, but the improvement of the ground state by considering doubly-excited configurations was abridged to avoid tedious computations.

The one-electron wave functions were determined by means of the CNDO method, that is, the approximate self-consistent molecular orbital method with complete neglect of differential overlap. In an effort to determine the effect of the parametrization in the CNDO method on the theoretical polarizability and anisotropy three different types of calculations were performed.

Method I. The calculation followed the original CNDO/2 method proposed by Pople *et al.*[7-9]

Method II. The calculation was performed according to the modified CNDO method proposed by Bene and Jaffé.[10,11]

Method III. In this method, the calculation was performed under the same approximation as Method II except for the evaluation of the bonding parameter. The distinction in estimating the bonding parameters for the pi-type and for sigma-type interaction was avoided, and the bonding parameter referring to the sigma-type interaction was approximated by the adoption of the method for the pi-type interaction. The numerical values of the parameters are indicated in Table 1.

Table 1. Parameter values (eV)

	Atom	H	C	N	O
β_{A}^0 [a]	Method I	−9	−21	−25	−31
	Method II	−12	−17	−26	−45
γ_{AA} [b]	Method I[c]	20.40	16.06	19.27	22.48
	Method II[d]	12.85	11.11	12.01	13.00

a) Bonding parameter.

b) One-center electron-repulsion integral.

c) Calculated as a Coulomb repulsion integral over Slater's functions. (Z': H(1s) 1.2, C(2s) 3.25, N(2s) 3.9 and O(2s) 4.55).

d) Calculated as a difference between the ionization potential and electron affinity of 1s for H atom and of 2p for C, N, and O atoms.

In order to obtain the excited states, $\Psi_{\mathrm{b}}{}^0$'s, required to describe the perturbed wave function by means of Eq. (1), the SCF calculations described above were followed by CI treatment. In the CI treatment, all singly-excited configurations were considered. By the use of the coefficients ($c^{(\mathrm{b})}$'s) of the configurations and the transition moment between the ground state and each excited configuration, the integral in Eq. (4) could be calculated as follows:

$$\langle \Psi_{\mathrm{a}}{}^0 | e\sum_i \mathbf{r}_i | \Psi_{\mathrm{b}}{}^0 \rangle = \sum_i^{\mathrm{occ}} \sum_k^{\mathrm{unocc}} c_{(i-k)}^{(\mathrm{b})} \langle \Psi_{\mathrm{a}}{}^0 | e\sum_i \mathbf{r}_i | \Phi_{i-k} \rangle. \tag{7}$$

The X-component of the integral on the right-hand side of the above equation is expressed by:

$$\langle \Psi_{\mathrm{a}}{}^0 | e\sum_i X_i | \Phi_{i-k} \rangle = -\sqrt{2}\sum_{\mathrm{A}} \{2.5416 X_{\mathrm{A}} \sum_{\mu} d_{i\mu}^{(\mathrm{A})} d_{k\mu}^{(\mathrm{A})} + 7.3370 (d_{i(2\mathrm{s})}^{(\mathrm{A})} d_{k(2\mathrm{p_x})}^{(\mathrm{A})} + d_{i(2\mathrm{p_x})}^{(\mathrm{A})} d_{k(2\mathrm{s})}^{(\mathrm{A})}) / Z_{\mathrm{A}}'\} \text{ (Debye)}, \tag{8}$$

where $d_{\mathrm{i}\mu}^{(\mathrm{A})}$ is the coefficient of the atomic orbital, χ_{μ}, on the A atom in the molecular orbital, φ_{i}; where X_{A} is the X-component of the position vector (atomic unit) of the atom A, and where Z_{A}' is the orbital exponent of the A atom. The Y- and Z-components of the integral can be obtained in the same manner by replacing $d_{i(2\mathrm{p_x})}$ in Eq. (8) with $d_{i(2\mathrm{p_y})}$ and with $d_{i(2\mathrm{p_z})}$ respectively, and by replacing X_{A} with Y_{A} and with Z_{A} respectively.

The Polarizability Derivatives. The molecular polarizabilities were calculated for the molecule distorted in the manner dictated by the appropriate symmetry coordinate. The desired values were obtained by fitting the calculated polarizabilities to a cubic function with respect to the symmetry coordinate and by taking the first and second derivatives.

Results and Discussion

The calculated polarizabilities are, in Table 2, listed and compared with the theoretical and observed values reported by other investigators. The values calculated by Method I were similar in magnitude to those calculated by Hush[5] and Davies.[4] Generally, they were smaller than the experimental results. The calculated polarizabilities were improved by the use of Methods II and III. From a comparison between the results of different calculations, it has been found that the transition energies and transition moments along the

TABLE 2. SUMMARY OF CALCULATED POLARIZABILITIES[a] (Å^3)

Molecule	I[b]	II[b]	III[b]	R1[c]	R2[d]	Obsd[e]
N_2	0.754	1.183	1.281	0.647	0.633	1.77
CO	0.933	1.229	1.368	0.829		1.97
CO_2	1.189	1.823	1.960	0.879		2.63
C_2H_2	1.028	1.727	2.190	0.707		3.49
C_2H_4	1.497	2.137	3.068		1.333	4.22
C_2H_6	1.376	1.355	2.655		1.240	4.47

a) Calculated under the condition that the energy of the incident light was equal to zero.
b) Calculated by Methods I, II, and III in this work.
c) From Ref. 5.
d) From Ref. 4.
e) From Ref. 13.

bond axis vary widely from method to method, while the transition moments perpendicular to the bond axis remain unaltered. Moreover, it seems reasonable to conclude that a direct basic cause of the results for the theoretical polarizabilities being different from those found by different approximate methods is the differences between energy levels which are affected by the bonding parameter in the CNDO calculation.

TABLE 3. SUMMARY OF CALCULATED ANISOTROPIES[a]

Molecule	I[b]	II[b]	III[b]	R1[c]	R2[d]	Obsd[e]
N_2	0.472	0.595	0.568	0.391	0.369	0.131
CO	0.236	0.339	0.356	0.145		0.090
CO_2	0.727	0.826	0.754	0.634		0.266
C_2H_2	0.683	0.748	0.697	1.000		0.178
C_2H_4[f]	0.446	0.552	0.420			0.143
C_2H_6	−0.019	−0.071	−0.015		0.008	0.058

a), b), c), d), and e) References to footnotes are the same as those in Table 2.
f) The anisotropy was calculated from Eq. (5).

The calculated anisotropies are summarized in Table 3. Generally, they were larger than the experimental results. However, the order of magnitude in the theoretical values for the molecules was in satisfactory agreement with that obtained from the observed results, such as $CO_2 > C_2H_2 > N_2 > CO > C_2H_6$. The values calculated by Method I were slightly improved as compared to those from Methods II and III. Of course, the values of the $\Delta\alpha$'s showed the same tendencies. However, Method II was adapted for the calculation of the polarizability, as has been stated above. This change in the results can be explained by the facts that the $\alpha_{//}$'s calculated by Method II increased remarkably in comparison with those from Method I, but there was not very much change for the values of $\alpha_{\perp}$'s in these different types of calculations. Thus, an approximate method which provides appropriate values for both the α and $\Delta\alpha$ must be found. Furthermore, the effect of the inner-shell electrons and the consideration of the atomic vacant orbitals, such as the 2p orbital for hydrogen introduced by Davies,[4] remain subjects for future study.

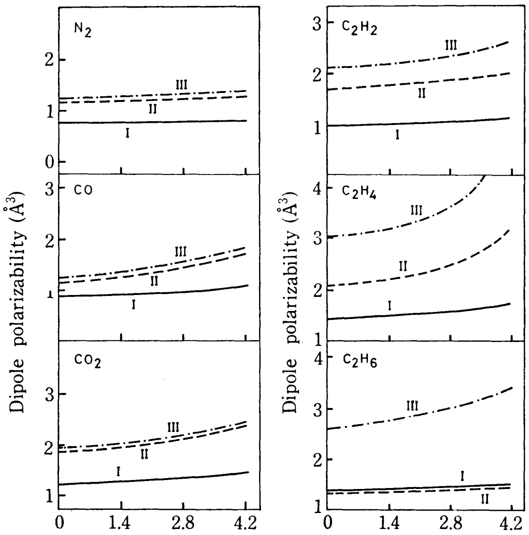

Fig. 1. The variation of the polarizability as a function of the energy of the incident light.
I, II, and III indicate the values calculated by the methods I, II, and III respectively.

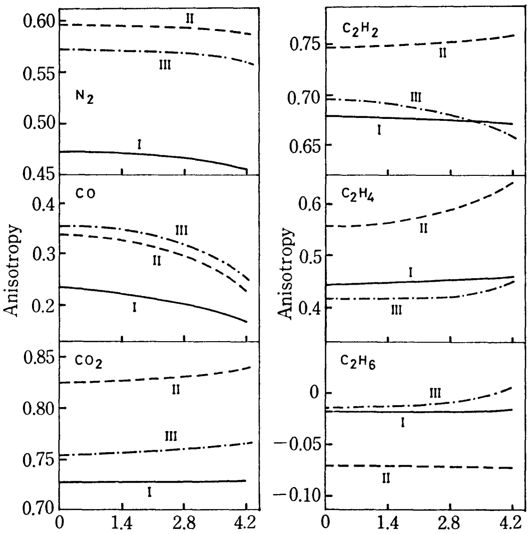

Fig. 2. The variation of the anisotropy as a function of the energy of the incident light.
I, II, and III indicate the values calculated by the methods I, II, and III respectively.

The approximate method for the polarizability calculation in this work is characterized by the introduction of the frequency of the incident light. As an example of the application of this method, variations in the polarizability and anisotropy with the frequency of the incident light were calculated. The results of the calculations are shown in Figs. 1 and 2. These figures show that the calculated values vary with the decrease in the difference between the energy of the incident light and the calculated energy for the first absorption band which is allowed for the electron transition. Furthermore, the polarizability derivatives, $\alpha' = (\partial\alpha/\partial S_1)_0$ and $\alpha'' = (\partial^2\alpha/\partial S_1^2)_0$, with respect to the symmetric stretching coordinate, S_1, were calculated for NH_3 and CO_2 by the use of the wave functions and energies calculated by Method I. The variations in

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Table 4. SUMMARY OF POLARIZABILITY DERIVATIVES

Energy of incident light (eV)	CO_2[a),b)]		NH_3[a),b)]	
	α'(Å^2)	α''(Å)	α'(Å^2)	α''(Å)
0	1.704	0.829	0.991	0.953
2	1.743	0.883	1.017	0.993
4	1.875	1.082	1.109	1.139
6	2.158	1.600	2.605	2.997
8	2.793	3.211	4.013	6.695
9			7.088	20.563
10	4.820	12.085		
12	34.304	459.015		

a) $\alpha'=\left(\frac{\partial\alpha}{\partial S_i}\right)_0$, and $\alpha''=\left(\frac{\partial^2\alpha}{\partial S_i^2}\right)_0$.

where $S_i=\frac{1}{\sqrt{2}}(\Delta r'_{CO}+\Delta r''_{CO})$ for CO_2,

and $S_i=\frac{1}{\sqrt{3}}(\Delta r'_{NH}+\Delta r''_{NH}+\Delta r'''_{NH})$ for NH_3.

b) Calculated energyies for the first absorption bands were 12.78 eV and 9.98 eV for CO_2 and NH_3 respectively.

the polarizability derivatives with the energy of the incident light were also calculated; they are indicated in Table 4. The α''/α' ratio was calculated as a function with respect to the energy of the incident light; it is shown in Fig. 3. Such a treatment as has been described above can be used for the analysis of the resonance and pre-resonance Raman intensities[14,15] in a manner similar to that used in the infrared region: the dipole-moment derivative, $(\partial\mu/\partial S_i)_0$ and $(\partial^2\mu/\partial S_i^2)_0$, obtained by the CNDO calculation are effective for the theoretical calculation of the infrared absorption intensity of the vibration band.[16-18]

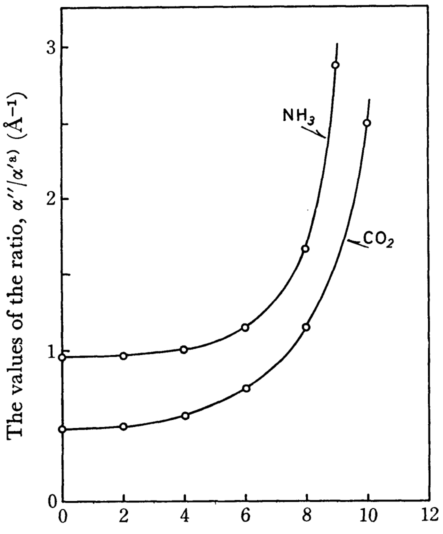

Fig. 3. The variation of the ratio, α''/α',[a)] as a function of the energy of the incident light.

a) $\alpha'=(\partial\alpha/\partial S_i)_0$. $\alpha''=(\partial^2\alpha/\partial S_i^2)_0$, where S_i is the symmetry coordinate.

Conclusion

The dipole polarizabilities, α's, and the anisotropies, κ's, of small linear molecules were calculated according to a formula derived from the time-dependent perturbation theory. The method of the calculation in this work is characterized by the introduction of the frequency of the incident light. The calculated polarizabilities were generally smaller than the experimental results. However, the calculated anisotropies and $\Delta\alpha$'s were larger than the observed results. These results of the calculations were discussed on the basis of the values of $\alpha_{//}$ and $\alpha_{\perp}$ calculated with different parametrizations. As an example of the application of this method, the variations in the polarizability and anisotropy with the frequency of the incident light were calculated. Moreover, the polarizability derivatives, $(\partial\alpha/\partial S_i)_0$ and $(\partial^2\alpha/\partial S_i^2)_0$, with respect to the symmetric stretching coordinate, S_i, were calculated for NH_3 and CO_2. Furthermore, the variations in the polarizability derivatives with the energy of the incident light were calculated.

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