[December, 1985] © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 3415—3422 (1985)

Comparison of the Excited-state Dipole Moments and Polarizabilities Estimated from Solvent Spectral Shifts with Those from Electrooptical Measurements

Takehiro Abe* and Idowu Iweibo†
College of General Education, Tohoku University, Kawauchi, Sendai 980

(Received June 3, 1985)

On the assumption that the average energy for all transitions from a low-lying excited state to all other states was approximately the same as that for all transitions from the ground state to all excited states, Abe's improved expression for the solvent spectral frequency shift (*Bull. Chem. Soc. Jpn.*, **54**, 327 (1981)) was applied to spectral data for some neutral organic molecules in solution in order to estimate their excited-state dipole moments and polarizabilities. The changes in the dipole moments and/or polarizabilities of these molecules upon excitation were compared with those obtained from electrooptical measurements. Both methods give results that are consistent.

Many theories[1–11] have hitherto been proposed regarding solvent spectral frequency shifts of organic molecules. On the basis of some of these, dipole moments and polarizabilities have been estimated for the excited states of organic molecules. Such detailed information, which essentially leads to knowledge regarding excited-state structures of organic molecules, may help in the understanding of the photophysics and photochemistry of such molecules. Alternatively, changes in the dipole moments and/or polarizabilities upon excitation have been obtained for many organic molecules in the vapor phase, in solution, or in a crystalline host from electrooptical measurements. In particular, the magnitudes of the changes in the dipole moments of some substituted benzenes, directly determined by a technique involving the optical Stark effect[12] in the gas phase, seem to be very reliable. On the basis of a few assumptions, the values of the excited-state dipole moments and/or polarizabilities of molecules in solution or in a crystalline host have been obtained using electric-field perturbation techniques. Recently, Morales,[13] Prabhumirashi *et al.*,[14,15] and Koutek[16] have tried to compare their results, which were obtained from solvent spectral shifts, with those obtained from electrooptical measurements. Their comparisons appear, however, to be insufficient as will be shown below.

Until now, there has been no detailed and systematic study comparing the excited-state dipole moments and/or polarizabilities estimated from the solvent spectral shifts with those determined from electrooptical measurements. Such comparisons are necessary, in part, to justify the theoretical expressions for the solvent spectral frequency shifts and, in part, to confirm the reliability of the electrooptical measurements or to reveal any inadequacies leading to discrepancies in both methods of measurement and in their variants. Electrooptical measurements are, in general, difficult. In particular, the most reliable technique regarding the optical Stark effect in the gas phase is confined to vaporizable substances, while measurements of solvent spectral shifts are easy and widely applied. It is, therefore, desirable to find a solvent spectral shift theory that gives excited-state dipole moment and polarizability values that are comparable to those of electrooptical measurements. This paper applies Abe's generalized equation,[4] which includes all interaction modes, to data for a representative group of compounds. There is, generally, reasonable agreement between the results of the present type analysis and those for electrooptical measurements. This shows that the use of a multiple linear regression analysis to compute the excited-state dipole moment and polarizability without introducing solvent macroscopic parameters, such as the relative permittivity and the refractive index, is certainly an advantage.

Theory

According to Abe's improved theory,[4] the wave number (σ_{i0}) of a transition from the ground state to the ith-excited state of a neutral solute molecule in solution is given by:

$$\sigma_{i0} = \sigma_{i0}^{\circ} + A \times \frac{(d^{\mathrm{s}}/M_{\mathrm{r}}^{\mathrm{s}})^{2/3}(p_{00}^{\mathrm{s}})^2}{(r_{\mathrm{A}}+r_{\mathrm{s}})^4} + B \times \frac{(d^{\mathrm{s}}/M_{\mathrm{r}}^{\mathrm{s}})^{2/3}\alpha_{00}^{\mathrm{s}}}{(r_{\mathrm{A}}+r_{\mathrm{s}})^4}, \tag{1}$$

where

$$r_{\mathrm{A}} = (3M_{\mathrm{r}}^{\mathrm{A}}/4\pi L d^{\mathrm{A}})^{1/3}, \tag{2}$$

$$r_{\mathrm{S}} = (3M_{\mathrm{r}}^{\mathrm{s}}/4\pi L d^{\mathrm{s}})^{1/3}, \tag{3}$$

$$A = \frac{\pi}{hc}\left(\frac{4\pi L}{3}\right)^{2/3} \times \left[\frac{2\{(p_{00}^{\mathrm{A}})^2 - p_{00}^{\mathrm{A}}p_{ii}^{\mathrm{A}}\cos\theta\}}{3(4\pi\varepsilon_0)^2kT} + \frac{(\alpha_{00}^{\mathrm{A}} - \alpha_{ii}^{\mathrm{A}})}{4\pi\varepsilon_0}\right], \tag{4}$$

and

$$B = \frac{\pi}{hc}\left(\frac{4\pi L}{3}\right)^{2/3}\frac{1}{4\pi\varepsilon_0} \times \left[\{(p_{00}^{\mathrm{A}})^2 - (p_{ii}^{\mathrm{A}})^2\} + \frac{3}{2} \times \left(\frac{\Delta E_0^{\mathrm{A}}\alpha_{00}^{\mathrm{A}}}{1+\Delta E_0^{\mathrm{A}}/\Delta E_0^{\mathrm{s}}} - \frac{\Delta E_i^{\mathrm{A}}\alpha_{ii}^{\mathrm{A}}}{1+\Delta E_i^{\mathrm{A}}/\Delta E_0^{\mathrm{s}}}\right)\right]. \tag{5}$$

---

†Present address: Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

The corresponding transition energy (in cm^{-1}) of the molecule in a vapor state is denoted by σ°_{i0}. For example, the superscripts/subscripts (A and s) denote the solute and solvent molecules, respectively. The symbol c is the speed of light in vacuum, h the Planck constant, L the Avogadro constant, ε_0 the permittivity of a vacuum, M_r the relative molecular mass, and d the density. Moreover, p_{00} and α_{00} denote the electric dipole moment and the electric isotropic polarizability, respectively, for the ground state. The corresponding values for the ith-excited state are p_{ii} and α_{ii}. The angle between p^{A}_{00} and p^{A}_{ii} is denoted by θ. In addition, ΔE_0 and ΔE_i denote the average transition energies for all transitions from the ground state and the ith-excited state, respectively, to all other excited states. The average transition energy (ΔE_0) is usually replaced by the ionization potential (I_0) of the ground state. Similarly ΔE_i is replaced by the ionization potential of the excited state as given by $\Delta E^{A}_{i}=I^{A}_{0}-hc\sigma^{\circ}_{i0}$.[4,17] However, Amos and Burrows[1a,18] stated that the average transition energies in Abe's previous expression[17] should be approximately the same for transitions from a ground state and an excited one. In applying Eq. 1, therefore, we have adopted this assumption of Amos and Burrows:

$$\Delta E^{A}_{i} = \Delta E^{A}_{0} = I^{A}_{0}. \tag{6}$$

As is described in a previous paper,[4] Eq. 1 has been derived on the assumption that a spherical solute molecule exhibits no effective hydrogen bonds or complexes with spherical solvent molecules.

Explicitly, we can rewrite Eq. 1 with the use of Eq. 6 as

$$C \times (p^{A}_{00}\cos\theta)p^{A}_{ii} + D \times (p^{A}_{ii})^2 + E \times \alpha^{A}_{ii} = \sigma^{\circ}_{i0} - \sigma_{i0} + F, \tag{7}$$

where

$$G = \frac{(d^{s}/M^{s}_{r})^{2/3}}{(r_A+r_s)^4} \times \frac{\pi}{hc}\left(\frac{4\pi L}{3}\right)^{2/3}, \tag{8}$$

$$C = G \times \frac{2(p^{s}_{00})^2}{3(4\pi\varepsilon_0)^2 kT}, \tag{9}$$

$$D = G \times \frac{\alpha^{s}_{00}}{4\pi\varepsilon_0}, \tag{10}$$

$$E = G \times \left\{\frac{(p^{s}_{00})^2}{4\pi\varepsilon_0} + \frac{3}{2} \times \frac{I^{s}_{0}I^{A}_{0}\alpha^{s}_{00}}{I^{s}_{0}+I^{A}_{0}}\right\}, \tag{11}$$

and

$$F = G \times \left[\frac{2(p^{s}_{00})^2(p^{A}_{00})^2}{3(4\pi\varepsilon_0)^2 kT} + \frac{1}{4\pi\varepsilon_0} \times \{(p^{s}_{00})^2\alpha^{A}_{00} + \alpha^{s}_{00}(p^{A}_{00})^2\} + \frac{3}{2} \times \frac{I^{s}_{0}I^{A}_{0}\alpha^{s}_{00}\alpha^{A}_{00}}{I^{s}_{0}+I^{A}_{0}}\right]. \tag{12}$$

Unfortunately, except for nonpolar solute molecules, we can not obtain directly reliable values for p^{A}_{ii} and α^{A}_{ii} by means of a least-squares analysis of data regarding solvent spectral shifts by means of Eq. 7. This is because a cubic equation with respect to p^{A}_{ii} must be solved in the case of polar solute molecules. Solving the equation is not practicable. We, therefore, proceed to obtain values of p^{A}_{ii} and α^{A}_{ii} by the following method for a polar solute molecule.

Calculation 1. At first we assumed $(p^{A}_{00}\cos\theta)p^{A}_{ii}(1)=\{(p^{A}_{ii}(1)\}^2$ in Eq. 7 and obtained the first approximate values of $p^{A}_{ii}(1)$ and $\alpha^{A}_{ii}(1)$ by the least-squares method. Next, we wrote the second approximate values as $p^{A}_{ii}(2)=p^{A}_{ii}(1)+\Delta(p)$ and $\alpha^{A}_{ii}(2)=\alpha^{A}_{ii}(1)+\Delta(\alpha)$ in Eq. 7. On the assumption that $2p^{A}_{ii}(1) \gg \Delta(p)$, values of $\Delta(\alpha)$ and $\Delta(p)$ were then obtained by the least-squares method as well as those of $p^{A}_{ii}(2)$ and $\alpha^{A}_{ii}(2)$. The same calculation was repeated until both values for $\Delta(p)$ and $\Delta(\alpha)$ became smaller than 10^{-4} of a unit of measurement of the electric dipole moment or the polarizability.

On the other hand, we adopted the following (Calculations 2 and 3) for a nonpolar solute molecule having no dipole moments in either the ground or the excited states.

Calculation 2. When the value of σ°_{i0} was known, we obtained a value for α^{A}_{ii} by averaging the values of α^{A}_{ii} for all solvents by means of Eq. 7.

Calculation 3. When the σ°_{i0} value was unknown, at first we arbitrarily assumed the first appropriate approximate value of $\sigma^{\circ}_{i0}(1)$ for σ°_{i0} in Eq. 7 and obtained a first approximate value of $\alpha^{A}_{ii}(1)$ by the least-squares method. The second approximate values for σ°_{i0} and α^{A}_{ii} were then given as $\sigma^{\circ}_{i0}(2)=\sigma^{\circ}_{i0}(1)+\Delta(\sigma)$ and $\alpha^{A}_{ii}(2)=\alpha^{A}_{ii}(1)+\Delta(\alpha)$ and the final values for σ°_{i0} and α^{A}_{ii} were obtained by repeating the iterative procedure adopted in Calculation 1.

In applying Eq. 7, we always assumed the temperature to be 20 °C and, unless it is otherwise stated, that all the electric dipole moments and ionization potentials for molecules in the vapor phase were taken from Refs. 19 and 20. Values for α_{00} were calculated from sums of bond refractions. Moreover, we excluded data for solvents lacking information regarding their dipole moments and ionization potentials and of solvents which are capable of forming hydrogen bonds and complexes with solutes. We used the spectral data reported by the same authors for solutes.

Results and Discussion

Benzene, Naphthalene, and Anthracene. The solvent effects on the position of the ^1L_b transition of benzene were investigated by Macovei.[21] We have assumed Macovei's value of 39539 cm^{-1} for σ°_{i0} and have chosen data for 13 solvents (out of his reported total of 27 solvents) by excluding hydrogen bonding solvents. This is because benzene is low in the scale regarding hydrogen-bond acceptor strength determined by Kamlet and Taft.[22] Similarly, we chose data for only 10 and 9 solvents for the ^1L_b and ^1L_a transitions, respectively, in naphthalene from the data of Weigang and Wild.[23,24] For calculations regarding anthracene, data for 25 solvents were taken from the report of Nicol *et al.*[25] The values of α^{A}_{ii} (estimated by Calculation 2) are listed in Table 1, where $\Delta\alpha=\alpha^{A}_{ii}-\alpha^{A}_{00}$.

Except for the expression for the dipole–dipole interaction term between the solute and solvent molecules in Eq. 1, the latter is essentially the same as Abe's previous expression.[17] Accordingly, the application of Eq. 7 to a nonpolar solute gives the same correlation between the experimental frequencies and

TABLE 1. THE $\Delta\alpha$ VALUES FOR NONPOLAR SOLUTE MOLECULES

Molecule	Method	α_{00}^{A} 10^{-24} cm^3	r_A nm	α_{ii}^{A} 10^{-24} cm^3	$\Delta\alpha$ 10^{-24} cm^3
Benzene					
^1L_b	Calcd 2	10.38	0.328	13.96	3.58
	Obsd	—	—	—	$1.2\pm0.6^{a,b)}$
Naphthalene					
^1L_b	Calcd 2	17.04	0.354	22.13	5.09
	Obsd	—	—	—	$1.9\pm0.3^{a)}$
^1L_a	Calcd 2	17.04	0.354	28.36	11.32
	Obsd	—	—	—	$9.8\pm1.6^{a)}$
Anthracene					
^1L_a	Calcd 2	23.69	0.384	42.89	19.2
	Obsd	—	—	—	$16.7\pm2.3^{a,c)}$
Lycopene					
	Calcd 3	72.06	$0.7^{d)}$	312.1	240.0
	Obsd	—	—	—	$246\pm22^{e)}$

a) Ref. 26. b) This experimental value was reduced under the assumption that no change in polarizability occurred in the direction perpendicular to the molecular plane. c) Ref. 27. d) Ref. 29. e) Ref. 28.

the frequencies calculated by Eq. 7 as was found using Abe's previous expression. The latter correlation was discussed in detail by Nicol *et al.*[25)]

The observed $\Delta\alpha$ values for the aromatic hydrocarbon molecules in Table 1 are those measured by Mathies and Albrecht[26)] for molecules dissolved in a rigid solution of 3-methylpentane at 77 K and by Liptay *et al.*[27)] for anthracene in cyclohexane at 25 °C by means of electric field techniques.

Table 1 shows that the large $\Delta\alpha$ values estimated using Eq. 7 for the ^1L_a transitions of naphthalene and anthracene roughly approach those determined by electrooptical measurements. The difference was a maximum of 16%, and the small $\Delta\alpha$ values estimated using Eq. 7 for the ^1L_b transitions of benzene and naphthalene were higher by a factor of *ca.* 3 than those of the electrooptical measurements. The significantly large differences in the $\Delta\alpha$ values for the ^1L_b transitions obtained by using the two different methods may be due to a number of causes: (1) The present theoretical model for the solvent shift assumes spherical shapes for the solute and solvent molecules. The estimation of r_A using Eq. 2 may, therefore, be inappropriate for plane hydrocarbon molecules whose shapes considerably deviate from the spherical model. This is why we consider it inappropriate to extend the application of Eq. 7 to largely plane polynuclear hydrocarbons such as tetracene and perylene, although the $\Delta\alpha$ values for these molecules have been obtained from electrooptical measurements.[27)] An arbitrary choice of smaller r_A values for benzene and naphthalene in our calculations minimized the differences in the $\Delta\alpha$ values obtained from both methods. (2) It has been reported that some excited-state polarizabilities vary with solvents to some extent.[27,28)] The $\Delta\alpha$ values of Mathies and Albrecht are those for the hydrocarbons in 3-methylpentane at 77 K, while the $\Delta\alpha$ values in our present estimation correspond to those for the hydrocarbons in a vapor phase at 20 °C. Moreover, the electrooptical measurements of Mathies and Albrecht contain a few assumptions. Accordingly, some difference in the $\Delta\alpha$ values obtained by both methods may be unavoidable. (3) The differences may also result, in part, from the present assumption regarding Eq. 6.

In Table 1, the application of Eq. 7 gives $\Delta\alpha$ values which are larger than those determined by Mathies and Albrecht by less than 3×10^{-24} cm^3. This means that the excited-state polarizabilities estimated using Eq. 7 may be larger than those of Mathies and Albrecht by less than 3×10^{-24} cm^3. Compared to the polarizability values, the difference of *ca.* 3×10^{-24} cm^3 is small. Thus, we may conclude that our present application of Eq. 7 gives a reasonable estimation of the excited-state polarizabilities for the aromatic hydrocarbon molecules and that the estimation is better with a larger $\Delta\alpha$ value.

Lycopene. The r_A value of lycopene was taken to be 0.7 nm, the value that Myers and Birge[29)] estimated for β-carotene from crystallographic data, as both lycopene and β-carotene have the same molecular formula ($C_{40}H_{56}$) and are similar in shape. The ionization potential of the ground state of a lycopene molecule having 11 conjugated double bonds was extrapolated to be 7.48 eV (1 eV=1.602×10^{-19} J) from the linear relationship[30)] between the observed ionization potentials and the Hückel HOMO energy levels for ethylene, *s-trans*-1,3-butadiene and hexatriene. We used the reported spectral data[31)] for the first transition in lycopene. The σ_{i0}^{o} value of 23050 cm^{-1} and the $\Delta\alpha$ value in Table 1 were estimated according to Calculation 3. Obviously, the $\Delta\alpha$ value so estimated from solvent frequency shifts closely agrees with that obtained from the electric field-induced spectral change of lycopene in 3-methylpentane at 25 °C by Seibold *et al.*[28)] (Table 1).

Chlorobenzene. Macovei[32)] has investigated in detail the effects of a solvent on the 0-0 vibrational component[33)] of the 37052-cm^{-1} π-π^* band of chloro-

TABLE 2. THE DIPOLE MOMENTS AND POLARIZABILITIES OF THE FIRST EXCITED STATES OF CHLOROBENZENE AND FLUOROBENZENE

	Chlorobenzene	Fluorobenzene
P^A_{00}/D	1.782	1.66
$\alpha^A_{00}/10^{-24}\,\mathrm{cm}^3$	12.30	10.29
$\cos\theta$	1	1
P^A_{ii}/D	1.47	1.42
$\alpha^A_{ii}/10^{-24}\,\mathrm{cm}^3$	16.11	13.48
Δp/D	−0.31	−0.24
$\lvert\Delta p\rvert_{\mathrm{obsd}}$/D	0.24±0.08[a)]	0.30±0.07[b)]
$\Delta\alpha/10^{-24}\,\mathrm{cm}^3$	3.81	3.20

a) Ref. 12e. b) Ref. 12d.

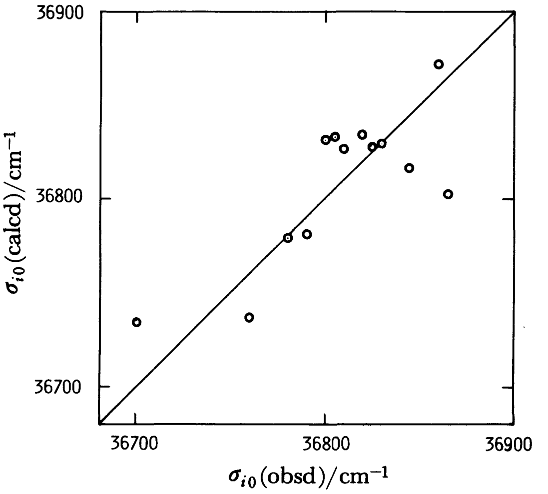

Fig. 1. A plot of the experimental frequency of the 0-0 band of the first transition of chlorobenzene *vs.* the frequency calculated.

benzene in the vapor phase. We chose data for 13 solvents from his spectral data involving 27 solvents. The data for carbon tetrachloride as a solvent were excluded since this molecule forms weak donor-acceptor complexes with benzene and substituted benzenes.[34)] The values of p^A_{ii} and α^A_{ii} estimated by means of Calculation 1 are shown in Table 2. Even if a value of −1.0 was used for $\cos\theta$, we still obtained the same excited-state values recorded in Table 2, where $\Delta p=|p^A_{ii}|-|p^A_{00}|$. By using the p^A_{ii} and α^A_{ii} values so estimated, one can calculate the frequencies according to Eq. 1. We show in Fig. 1 the correlation between the experimental frequencies (σ_{i0} (obsd)) and the calculated ones (σ_{i0} (calcd)) for the ^1L_b band of chlorobenzene, as a representative example for the polar solutes. On the whole, the correlation is good.

The observed $|\Delta p|$ values (Table 2) determined by Lombardi *et al.*[12)] by means of the optical Stark effect in the vapor phase are very reliable. As Lombardi[12a,c)] clearly described, however, the sign of Δp cannot be determined using their experimental method. In the case of chlorobenzene, therefore, the two possible values of 2.03 and 1.55 D (1 D=3.333×10^{-30} Cm) are consistent with each measured splitting.[12e)] By comparing the changes in rotational constants upon excitation, Wu and Lombardi[12e)] expected the larger value for p^A_{ii}=2.03 D to be correct one. Their choice of 2.03 D, however, is not consistent with the theoretical results predicted by Kimura and Nagakura[35)] by means of an MO calculation. Their theoretical results showed that the electron density on the chlorine atom in the first excited state of chlorobenzene should be slightly less than that of the chlorine atom in the ground state. This means that the value of p^A_{ii} is slightly less than that of p^A_{00}, since the substituent is the negative end of the dipole in both the ground and the excited states. Accordingly, the smaller value of p^A_{ii}=1.55 D should be the preferred experimental value of Wu and Lombardi. Our estimation of p^A_{ii}=1.47 D closely agrees with their reliable experimental value. By applying McRae's equation[36)] to the solvent spectral frequency data for chlorobenzene, Macovei[32)] also obtained a good result of p^A_{ii}=1.526 D. Thus, the comparable results on chlorobenzene, as determined by the electrooptical measurement and our present analysis, show that upon the assumption of Eq. 6, Eq. 1 can be applied for estimating the excited-state dipole moment of a polar solute molecule.

Fluorobenzene. There is a limited amount of data regarding polar solvents which do not form hydrogen bonds with fluorobenzene. Unfortunately, no desirable data regarding solvent effects for the 0-0 band (37829 cm^{-1})[37)] of the first π-π^* transition in fluorobenzene in a vapor state are available. We were, therefore, restricted to using the undesirable data of Bowden and Braude[38)] who reported that fluorobenzene in both cyclohexane and ethanol showed the 0-0 band to be at the same position (37590 cm^{-1}).

We wrote an equation for each solvent (cyclohexane or ethanol) according to Eq. 7. By solving the two equations simultaneously, we first obtained the two possible p^A_{ii} values, 1.42 and 242.70 D. For probabilistic reasons, however, the smaller value (1.42 D) was adopted as p^A_{ii} and the α^A_{ii} value was obtained as shown in Table 2. Huang and Lombardi[12d)] determined the two possible excited-state dipole moments to be 1.37 and 1.96 D. They selected the larger value of 1.96 D as they did for chlorobenzene. According to Kimura and Nagakura,[35)] the theoretical results regarding fluorobenzene are similar to those for chlorobenzene. If, by the same reasoning as we adopted in the case of chlorobenzene, we select their smaller value of 1.37 D as the experimental excited-state dipole moment of fluorobenzene, the p^A_{ii} value of 1.42 D estimated by the present method agrees well with the experimental value of 1.37 D.

Aniline. We chose the solvent spectral data of Mataga[39)] for the first absorption band (35490 cm^{-1})[37)] of aniline in vapor: 34800 (cyclohexane), 34700 (1,2-dichloroethane) and 34600 cm^{-1} (acetonitrile). In the present case, the angle θ between p^A_{00} and p^A_{ii} was

Table 3. Changes in the dipole moment and polarizability on excitation in aniline[a)]

$\cos\theta$	P_{ii}^{A}/D	$\Delta p/\mathrm{D}$	$\Delta\alpha/10^{-24}\,\mathrm{cm}^3$
1.0	1.35	−0.13	9.56
0.8	1.69	0.21	9.46
0.5845	2.33	0.85	9.22
0.4	3.48	2.00	8.60
0.2	8.19	6.71	3.50
0.0	8.43	6.95	37.42
−0.2	−8.07	6.59	3.98
−0.4	−3.48	2.00	8.61
−0.5845	−2.33	0.85	9.22
−0.8	−1.69	0.21	9.46
−1.0	−1.35	−0.13	9.56

a) r_A=0.331 nm, P_{00}^{A}=1.48 D, and α_{00}^{A}=11.73×10^{-24} cm^3.

unknown. Consequently, we calculated the excited-state values for the possible values of $\cos\theta$ according to Calculation 1 and give examples of the results in Table 3. By varying r_A in steps over a range from 0.2 to 0.4 nm, we found that Δp varies little with our choice for r_A. However, $\Delta\alpha$ depends on r_A considerably. According to Lombardi's experimental result of $|\Delta p|_{\mathrm{obsd}}$= 0.85±0.15 D,[12a)] the value for p_{ii}^{A} should be either 0.63 or 2.33 D. In Table 3, the larger value (2.33 D) was reproducible by the present method to give $\cos\theta=\pm0.5845$. The angle of p_{ii}^{A} when the value of the moment is 2.33 D and $\cos\theta=0.5845$ is the same as when the p_{ii}^{A} moment is −2.33 D and $\cos\theta=-0.5845=\cos(180°-54.23°)$. However, the direction of the former moment is different from that of the latter moment, as are shown in Fig. 2. Table 3 shows that the application of Eq. 7 gives no excited-state dipole moment smaller than 1.35 D in absolute value. Accordingly, the smaller (0.63 D) of the two possible experimental values proposed by Lombardi may be discarded on the basis of disagreement with the results of the solvent spectral-shift method. Lombardi[12a)] also explained his preference for the larger value of the excited-state dipole moment. Thus, the angle between $\boldsymbol{p}_{00}^{A}$ and $\boldsymbol{p}_{ii}^{A}$ is expected to be 54.23°. There is, therefore, two possible directions for the excited-state dipole moment as are shown by $p_{ii}^{A}=\pm2.33$ D in Fig. 2. The frequencies calculated using estimated values of p_{ii}^{A} and α_{ii}^{A} for $\cos\theta=\pm0.5845$ were 34820 (obsd, 34800), 34680 (obsd, 34700) and 34600 cm^{-1} (obsd, 34600 cm^{-1}) for the solvents of cyclohexane, 1,2-dichloroethane, and acetonitrile, respectively.

The ground-state dipole moment of aniline was calculated by Hehre *et al.*[40)] to be 1.44 D by means of *ab initio* MO theory. Their calculated components for the dipole moment and the direction of the ground-state dipole moment (p_{00}^{A}) are shown in Fig. 2. All the MO calculations of Baba,[41)] Mataga,[39)] and Hirota and Nagakura[42)] show a decrease in the π-electron density at the nitrogen atom in the excited state of aniline. This decrease only increases the magnitude of the excited-state dipole moment component parallel to the plane containing both the benzene ring and the nitrogen atom in the same direction as that of the corresponding ground-state dipole moment component. Accordingly, the positive and negative terminals of the dipole moment component in question will not change sign upon excitation. In Fig. 2, only the positive moment (p_{ii}^{A}=2.33 D) of the two possible moments of ±2.33 D for p_{ii}^{A} does clearly not change the sign of the dipole moment component. Thus, the direction of the excited-state dipole moment may be predicted as shown by p_{ii}^{A}=2.33 D in Fig. 2.

The p_{ii}^{A} value for aniline has been estimated by Mataga (2—2.5 D),[39)] Murrell (5 D),[43)] Iweibo *et al.* (a value nearly equal to p_{00}^{A}),[44)] Suppan (5.2 D),[5)] and Prabhumirashi *et al.* (2.12 D)[14,15)] from solvent shifts of absorption and/or fluorescence spectra. Mataga and Murrell used an equation for solvent shifts of absorption and fluorescence spectra.[45,46)] Suppan used a similar equation. Iweibo *et al.* and Prabhumirashi *et al.* used an approximation (Eq. 46 of Ref. 1a) of McRae's general expression.[36)] Since such an ap-

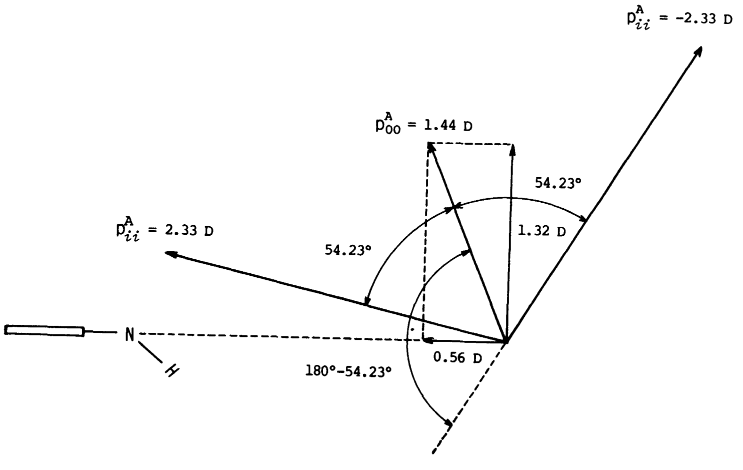

Fig. 2. The predicted directions of the ground- and excited-state dipole moments of aniline. The direction of the arrow denotes a moment from a positive charge to a negative one.

TABLE 4. THE EXCITED-STATE DIPOLE MOMENT AND POLARIZABILITY OF RETINAL

	Present work[a)]	Ponder and Mathies[b)]	
		solid matrix[c)]	gas phase
$\alpha_{ii}^{A}/10^{-24}\,\mathrm{cm}^3$	102.26		
$\Delta\alpha/10^{-24}\,\mathrm{cm}^3$	66.37	180±20	60[e)]
$\Delta\alpha_x^{d)}/10^{-24}\,\mathrm{cm}^3$		600±100	200±20
P_{ii}^{A}/D	7.82	19.8±0.7	7±1

a) $\alpha_{00}^{A}=35.89\times10^{-24}\,\mathrm{cm}^3$ and cos $\theta=1$. b) Ref. 48. c) In poly(methyl methacrylate) films. d) A change in a long-axis polarizability on excitation. e) We so estimated this value that the ratios of $\Delta\alpha_x/\Delta\alpha$ became the same for both the solid matrix and the gas phase.

proximation obviously neglects the dispersion effect, the excited-state dipole moments estimated from such measurements will, for less polarized molecules, show sufficient departure from those of the electrooptical measurements. The fortuitously good estimate of Prabhumirashi *et al.* seems to be due to their choice of a rather small value of 0.146 nm for r_A. Except for Suppan, all of the above authors assumed collinear ground- and excited-state dipole moments. In view of the molecular structure[47)] and the *ab initio* calculation[40)] of the ground-state dipole moment for aniline, it seems difficult to assume such collinear dipole moments.

Retinal. Recently, Ponder and Mathies[48)] have obtained the excited-state dipole moment and polarizability of *all-trans*-retinal from measurements of electric-field-induced changes in its optical absorption spectrum. We attempt to estimate the values of p_{ii}^{A} and α_{ii}^{A} for retinal by applying Eq. 7 to the available spectral data of Corsetti *et al.*[49)] We chose 9 data points including those of 5 polar solvents from a total of 16 data points. From an extrapolation of a good linear relationship between absorption maxima (in cm^{-1}) of retinal in various nonpolar solvents and refractive indices of the solvents, we estimated the σ_{i0}^{0} value of retinal to be 29210 cm^{-1}. The ionization potential of the retinal was estimated to be 8.31 eV as in the case of lycopene where parameters of the coulomb and resonance integrals for an oxygen atom were those referred to in Ref. 30. We used values of 4.55 D for p_{00}^{A} and 0.458 nm for r_A. These values were obtained by Myers and Birge[50)] upon assuming a spherical model. Following Ponder and Mathies,[48)] we assumed that both p_{00}^{A} and p_{ii}^{A} were parallel. Listed in Table 4 are the values of p_{ii}^{A} and $\Delta\alpha$ estimated by means of Calculation 1, in addition to the experimental results of Ponder and Mathies. The former values which were estimated by the present analysis agree well with the latter ones which were obtained from electrooptical measurements in a gas phase.

Azulene. The excited-state dipole moments and/or polarizabilities of azulene were obained from electrooptical measurements[51—55)] as listed in Table 5. Hochstrasser and Noe,[51)] Barker *et al*,[52)] and Clark and Small[55)] applied the Stark spectroscopy of mixed molecular crystals to the absorption systems of azulene. Mathies and Albrecht[52)] adopted electric field broadening experiments for the absorption spectrum of azulene in 3-methylpentane at 77 K. Using reaction fields, Baumann[54)] analyzed data obtained from electrooptical absorption and dielectric measurements for azulene in cyclohexane at 298 K.

We estimated the first and second excited-state dipole moments and polarizabilities of azulene by applying Calculation 1 to the available spectral data[23,24)] as shown in Table 5. We chose 11 data points including 6 for nonpolar solvents and 5 for polar ones. For r_A we used the value of 0.308 nm, whose cube was already estimated by Baumann[54)] for the spherical model of the azulene molecule. In the case of azulene, cosθ obviously takes a value of either 1 or -1. Setting cos$\theta=1$, yielded negative excited-state dipole moments. We, therefore, assumed that cos$\theta=-1$.

As shown in Table 5, the present analysis gives the first and second excited-state dipole moments that are opposite in direction to that of the ground state. This result agrees with that obtained from the electrooptical measurements. The present analysis gives a far smaller decrease in the polarizability of the first excitation than do the measurements of Baumann. The first excited-state dipole moment estimated in the present analysis agrees roughly with those obtained from the electrooptical measurements. However, the present analysis shows that the magnitude of the second excited-state dipole moment is larger than that of the first excited state; electrooptical measurements show a reverse situation. The above differences between the present solvent shift method and the electrooptical

TABLE 5. THE EXCITED-STATE DIPOLE MOMENTS[a)] AND POLARIZABILITIES OF AZULENE

	Present work[b)]	Baumann[c)]	Clark and Small[d)]	Mathies and Albrecht[e)]	Hochstrasser, Noe *et al.*[f)]
The first excited state					
P_{ii}^{A}/D	−0.817	−0.564	−0.26	—	−0.42
$\alpha_{ii}^{A}/10^{-24}\,\mathrm{cm}^3$	15.80	11.44	—	—	—
The second excited state					
P_{ii}^{A}/D	−2.124	−0.348	−0.17	−0.44	−0.31
$\alpha_{ii}^{A}/10^{-24}\,\mathrm{cm}^3$	22.00	—	—	—	—

a) The signs of P_{ii}^{A} were determined relative to P_{00}^{A}. b) $r_A=0.308\,\mathrm{nm}$, $P_{00}^{A}=0.795\,\mathrm{D}$, $\alpha_{00}^{A}=16.664\times10^{-24}\,\mathrm{cm}^3$, and cos $\theta=-1$. c) Ref. 54: $\alpha_{00}^{A}=15.52\times10^{-24}\,\mathrm{cm}^3$. d) Ref. 55. e) Ref. 53. f) Refs. 51 and 52.

Table 6. The excited-state dipole moment and polarizability of *p*-nitroaniline

$\cos\theta$	Present work[a)]		Electrooptical measurements
	P_{ii}^{A}	α_{ii}^{A}	P_{ii}^{A}
	D	$10^{-24}\,\mathrm{cm}^3$	D
1.0	9.21	62.39	14[b)], 15.5±2.8[c)]
0.9	10.32	60.40	
0.8	11.75	57.51	
0.7	13.68	53.05	
0.6	16.41	45.59	
0.5	20.59	31.57	

a) $P_{00}^{A}=6.29$ D, $\alpha_{00}^{A}=13.983\times10^{-24}\,\mathrm{cm}^3$ and $r_A=0.336$ nm. b) Ref. 56. c) Ref. 57.

measurements may be ascribed to the same reasons preferred for the aromatic hydrocarbons above. More reliable excited-state dipole moments for azulene must wait for determinations regarding the optical Stark effect in the gas phase.

p-Nitroaniline. From the electrooptical absorption measurements, Czekalla and Wick[56)] and Liptay *et al.*[57)] obtained the p_{ii}^{A} values listed in Table 6. In order to make a comparison with their values, we applied Eq. 7 to the solvent spectral shift data of Kamlet and Taft[22)] for the observed 34210 cm^{-1} absorption maximum[58)] of *p*-nitroaniline in a vapor phase. We chose 7 data points relative to their 9 non-hydrogen-bonding solvents. The value of 6.29 D[59)] was used for p_{00}^{A}. The direction of the ground-state dipole moment may obviously not lie in the plane of the benzene ring of *p*-nitroaniline for the same reason as described in the case of aniline. In using Calculation 1, therefore, we changed the value of $\cos\theta$ to be within the range of 0.5—1.0. The results of the calculation are shown in Table 6.

The electrooptical measurements made by both Czekalla and Wick[56)] and Liptay *et al.*[57)] assumed that the ground- and excited-state dipole moments were parallel to each other. With this assumption, the results of their measurements can be compared with our present calculation only when $\cos\theta=1$. Their values are considerably higher than that estimated by the present analysis. Czekalla and Wick completely neglected the effects of the ground- and excited-state polarizabilities of *p*-nitroaniline, while Liptay *et al.* neglected only the contribution of its excited-state polarizability. The large difference in the p_{ii}^{A} value using the two methods seems to be mainly due to their neglect of the contributions due to these polarizabilities. Thus, at the present stage, we have no reliable value for an electrooptically determined excited-state dipole moment in the case of *p*-nitroaniline.

The p_{ii}^{A} value has been estimated by Abe (10.26 D),[60)] Suppan (16.3 D),[61)] Millefiori *et al.* (10.13—10.50 D),[58,62)] and Koutek (15.5 D)[16)] from solvent spectral-shift theories. Koutek has applied the local reaction fields of Block and Walker[63)] and Wertheim[64)] to the already presented equations based on McRae's theory.[36)] The expressions used by Suppan and Millefiori *et al.* lack any consideration of the polarizabilities and are based on the assumption that the ground- and excited-state dipole moments were parallel to each other. Koutek's treatments are also insufficient regarding these points. Thus, much weight cannot be credited to results from such computations.

References

1) Almost all references concerning the solvent effects on the frequency shifts of electronic spectra up to 1975, are cited in the following reviews: a) A. T. Amos and B. L. Burrows, *Adv. Quant. Chem.*, **7**, 289 (1973); b) M. F. Nicol, *Appl. Spectrosc. Rev.*, **8**, 183 (1974); c) C. N. R. Rao, S. Singh, and V. P. Senthilnathan, *Chem. Soc. Rev.*, **5**, 297 (1976).

2) A. E. Lutskii, A. V. Shepel, and M. R. Kreslavskii, *Opt. Spektrosk.*, **40**, 150 (1976).

3) K. Hirano, *Nippon Kagaku Kaishi*, **1978**, 481.

4) T. Abe, *Bull. Chem. Soc. Jpn.*, **54**, 327 (1981).

5) P. Suppan, *Chem. Phys. Lett.*, **94**, 272 (1983).

6) A. Botrel, F. Corre, and A. le Beuze, *Chem. Phys.*, **74**, 383 (1983).

7) R. G. E. Morales, *Spectrosc. Lett.*, **16**, 899 (1983).

8) K. S. Schweizer and D. Chandler, *J. Chem. Phys.*, **78**, 4118 (1983).

9) A. Raudino, F. Zuccarello, and G. Buemi, *J. Chem. Soc., Faraday Trans. 2*, **79**, 1759 (1983).

10) R. Constanciel and R. Contreras, *Theor. Chim. Acta*, **65**, 1 (1984).

11) R. Bonaccorsi, R. Cimiraglia, and J. Tomasi, *J. Mol. Struct.*, **107**, 197 (1984).

12) a) J. R. Lombardi, *J. Chem. Phys.*, **50**, 3780 (1969); b) K.-T. Huang and J. R. Lombardi, *J. Chem. Phys.*, **51**, 1228 (1969); c) J. R. Lombardi, *J. Am. Chem. Soc.*, **92**, 1831 (1970); d) K.-T. Huang and J. R. Lombardi, *J. Chem. Phys.*, **52**, 5613 (1970); e) C. Y. Wu and J. R. Lombardi, *J. Chem. Phys.*, **55**, 1997 (1971).

13) R. G. E. Morales, *J. Phys. Chem.*, **86**, 2550 (1982).

14) L. S. Prabhumirashi, *Spectrochim. Acta*, **39A**, 91 (1983).

15) a) L. S. Prabhumirashi, D. K. N. Kutty, and A. S. Bhide, *Spectrochim. Acta*, **39A**, 663 (1983); b) L. S. Prabhumirashi and R. S. Satpute, *Spectrochim. Acta*, **40A**, 953 (1984).

16) B. Koutek, *Collect. Czech. Chem. Commun.*, **43**, 1680 (1984).

17) T. Abe, *Bull. Chem. Soc. Jpn.*, **38**, 1314 (1965).

18) A. T. Amos and B. L. Burrows, *Theor. Chim. Acta*, **29**, 139 (1973).

19) "Kagaku Binran," ed by the Chemical Society of Japan, Maruzen Publishing Co., Tokyo (1975), Kisohen (Fundamental Part), II, pp. 1275, 1279, 1404.

20) "CRC Handbook of Chemistry and Physics, 61st Edition (1980—1981)," ed by R. C. Weast and M. J. Astle, CRC Press, p. E-64.

21) V. Macovei, *Rev. Roum. Chim.*, **20**, 1413 (1975).

22) M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).

23) O. E. Weigang, Jr., *J. Chem. Phys.*, **33**, 892 (1960).

24) O. E. Weigang, Jr. and D. D. Wild, *J. Chem. Phys.*, **37**, 1180 (1962).

25) M. Nicol, J. Swain, Y. -Y. Shum, R. Merin, and R. H. H. Chen, *J. Chem. Phys.*, **48**, 3587 (1968).

26) R. Mathies and A. C. Albrecht, *J. Chem. Phys.*, **60**, 2500 (1974).

27) W. Liptay, G. Walz, W. Baumann, H. -J. Schlosser, H. Deckers, and N. Detzer, *Z. Naturforsch.*, **26a**, 2020 (1971).

28) K. Seibold, H. Navangul, and H. Labhart, *Chem. Phys. Lett.*, **3**, 275 (1969).

29) A. B. Myers and R. R. Birge, *J. Chem. Phys.*, **73**, 5314 (1980).

30) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists, " John Wiley and Sons, New York (1961), pp. 135, 192.

31) F. Feichtmayr, E. Heilbronner, A. Nürrenbach, H. Pommer, and J. Schlag, *Tetrahedron*, **25**, 5383 (1969).

32) V. Macovei, *Rev. Roum. Chim.*, **21**, 193 (1976).

33) H. Sponer and S. H. Wollam, *J. Chem. Phys.*, **9**, 816 (1941).

34) C. N. R. Rao, S. N. Bhat, and P. C. Dwivedi, *Appl. Spectrosc. Rev.*, **5**, 1 (1972).

35) K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).

36) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

37) W. W. Robertson and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5252 (1950).

38) K. Bowden and E. A. Braude, *J. Chem. Soc.*, **1952**, 1068.

39) N. Mataga, *Bull. Chem. Soc. Jpn.*, **36**, 1607 (1963).

40) W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).

41) H. Baba, *Bull. Chem. Soc. Jpn.*, **34**, 76 (1961).

42) F. Hirota and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **43**, 1010 (1970).

43) J. N. Murrell, *Tetrahedron*, **19**, Suppl. 2, 277 (1963).

44) I. Iweibo, R. A. Oderinde, and J. A. Faniran, *Spectrochim. Acta*, **38A**, 1 (1982).

45) N. Mataga, Y. Kaifu, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **28**, 690 (1955); **29**, 465 (1956).

46) a) E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955); b) E. Lippert, *Z. Elektrochem.*, **61**, 962 (1957).

47) D. G. Lister and J. K. Tyler, *J. Chem. Soc., Chem. Commun.*, **1966**, 152.

48) M. Ponder and R. Mathies, *J. Phys. Chem.*, **87**, 5090 (1983).

49) J. P. Corsetti and B. E. Kohler, *J. Chem. Phys.*, **67**, 5237 (1977).

50) A. B. Myers and R. R. Birge, *J. Am. Chem. Soc.*, **103**, 1881 (1981).

51) R. M. Hochstrasser and L. J. Noe, *J. Chem. Phys.*, **50**, 1684 (1969).

52) J. W. Barker, L. J. Noe, and A. P. Marchetti, *J. Chem. Phys.*, **59**, 1304 (1973).

53) R. Mathies and A. C. Albrecht, *J. Chem. Phys.*, **60**, 1420 (1974).

54) W. Baumann, *Chem. Phys.*, **20**, 17 (1977).

55) R. Clark and G. J. Small, *J. Chem. Phys.*, **66**, 1779 (1977).

56) J. Czekalla and G. Wick, *Z. Elektrochem.*, **65**, 727 (1961).

57) W. Liptay, W. Eberlein, H. Weidenberg, and O. Elflein, *Ber. Bunsengeselshaft Phys. Chem.*, **71**, 548 (1967).

58) S. Millefiori, F. Zuccarello, and G. Buemi, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 849.

59) A. L. McClellan, "Table of Experimental Dipole Moments," Freeman, San Francisco (1963).

60) T. Abe, *Bull. Chem. Soc. Jpn.*, **41**, 1260 (1968).

61) a) M. B. Ledger and P. Suppan, *Spectrochim. Acta*, **23A**, 641 (1967); b) P. Suppan, *J. Chem. Soc. (A)*, **1968**, 3125.

62) S. Millefiori, G. Favini, A. Millefiori, and D. Grasso, *Spectrochim. Acta*, **33A**, 21 (1977).

63) M. Block and S. M. Walker, *Chem. Phys. Lett.*, **19**, 363 (1973).

64) M. S. Wertheim, *Mol. Phys.*, **25**, 211 (1973).