February, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **54**, *327—334 (1981)*

Theoretical Treatment of Solvent Effects on the Frequency Shifts of Electronic Spectra of Anions

Takehiro Abe

College of General Education, Tohoku University, Kawauchi, Sendai 980

(Received March 13, 1980)

A theoretical expression for the spectral solvent shifts of an anion has been presented by assuming the system to consist of a large anion, its counter cations, and numerous solvent molecules. In the zeroth-order all the component particles in the system do not interact with one another. The interaction energy among the particles for the *i*th-excited state of the system, in which only the anion is in the *i*th-excited state, is calculated by the second-order perturbation treatment as the sum of electrostatic interaction energies between pairs of particles. The expression derived from the difference between the interaction energies of the ground and excited states of the system contains the dipole-dipole and dipole-induced dipole interaction terms and the dispersion force terms and is somewhat different from the previous results for neutral solutes (*Bull. Chem. Soc. Jpn.*, **38**, 1314 (1965)). Effects of the counter cations are discussed. This expression is applied to the spectral shifts of an Eosin-Y^{2-} anion, a Meisenheimer complex, and Janovsky complexes.

Many theories have hitherto been proposed for spectral solvent shifts of neutral organic molecules.[1] There are, however, only a few theories relating to anions.[2,3] Miertuš and Kyseľ[2] have calculated frequencies of some anion radicals in solvents by incorporating the solvent effects into the Hamiltonian operator for the radicals in the restricted SCF MO method. Hirano[3] has extended McRae's theory[4] for neutral molecules to organic anions by considering the effects of their counter cations. Hirano has obtained a general expression involving no dipole-dipole and dipole-induced dipole interaction terms but only the dispersion force contribution. According to his theory, the effects of the counter cations can be ignored.

In order to compare results with Hirano's expression, the author has attempted to derive an expression for the spectral solvent shifts of anions on the basis of the previous theory[5,6] for neutral molecules. The previous expressions[5,6] will be somewhat improved. Moreover, an attempt has been made to clarify the similaritities and differences between McRae's theory[4] and the author's.[5,6]

Theoretical

Model. Electronic spectra of solutions are generally measured at very low concentrations of solutes. Let us, therefore, consider a system consisting of a large anion (A^{n-}), its n counter cations (M^+), and N identical neutral solvent molecules. The anion is not an anion radical or a small anion solvated by coordination of solvent molecules. The cations are monatomic. In the zeroth-order, all the component particles in the system do not interact with one another. Let us consider the ion-pair formation between the anion and the n monovalent cations, because such formation is well-known. The solvent molecules are assumed to form no hydrogen bonds and no complexes with the anion and to have small enough dipole moments that they are not tightly oriented with respect to each other. For convenience, let the origin of the coordinates be the center of mass of the anion. In the spectral measurements of solutes in solutions, one usually chooses solvents that absorb light at much shorter wavelengths than the solutes do. The monovalent cations such as Na^+ and K^+ require transition energies considerably higher than those of the anion and the solvent molecule. One therefore assumes that the solvent molecules and the cations remain in their ground states when a transition from the ground state to the ith excited state occurs in the anion.

The Wave Functions and Energies of the System. Let us write the ith electronic state of the system in the zeroth-order as follows:

$$\Phi_i^\circ = \phi_i^A \prod_{c=1}^{n} \phi_0^c \prod_{s=1}^{N} \phi_0^s. \qquad (1)$$

Here the zeroth-order wave functions of ϕ_i^A, ϕ_0^c, and ϕ_0^s denote the ith state of the anion, the ground state of the cth counter cation, and the ground state of the sth solvent molecule, respectively. In the present paper, the suffices and shoulders of A, c and s denote the anion, the cth cation, and the sth solvent molecule, respectively. The ground state of the system is obtained by replacing i by 0 in Eq. 1. Let us assume orthonormality for all the zeroth-order wave functions.

The energy of the ith state of the system in which all the particles interact with one another can be written by the second-order perturbation theory as

$$E_i = E_i^\circ + (\Phi_i^\circ{}^*|H'|\Phi_i^\circ) + \sum_{m \neq i} \frac{(\Phi_m^\circ{}^*|H'|\Phi_i^\circ)(\Phi_i^\circ{}^*|H'|\Phi_m^\circ)}{E_i^\circ - E_m^\circ}, \qquad (2)$$

where E_i° is the unperturbed energy corresponding to Φ_i°, E_m° is an unperturbed energy of the mth excited state of the system, and H' is the perturbation due to the interactions among the particles in the system. It may be sufficient to consider transitions only in the anion and the solvent molecules for the mth excited states of the system, because the cation requires much high transition energies, as mentioned above.

A General Expression for the Spectral Solvent Shift. The transition energies from the ground state to the ith excited state of the anion in the vapor and in the solution are denoted by the frequencies of ν_{i0}° and ν_{i0}, respectively. The total interaction energy among the particles in the system of the ith state is obtained by $(E_i - E_i^\circ)$ according to Eq. 1. The difference between $(E_i - E_i^\circ)$ and $(E_0 - E_0^\circ)$ is equal to that between stabilization energies of the ith-excited and ground states of the anion in the solution, because all the counter cations and the solvent molecules are in their ground states in both the ground and ith-excited states of the system. The spectral solvent shift $(\nu_{i0}-\nu_{i0}^{\circ})$ of the anion is due to the difference between the stabilization energies of the ith-excited and ground states of the anion. Accordingly, the spectral solvent shift is given by $(1/h)\{(E_i-E_i^{\circ})-(E_0-E_0^{\circ})\}$, where h is the Planck constant.

The Frank-Wen model[7] has been accepted for hydration in aqueous solutions. However, solvation numbers of the large picrate anion in organic solvents such as methanol, acetone, acetonitrile, and 1,2-dichloroethane are zero at 25 °C.[8] As described above, the solvent molecules are assumed not to be oriented with respect to each other. The value of $(E_i-E_i^{\circ})$ for the large anion may, therefore, be averaged over all orientations of all the solvent molecules. Thus, one obtains the following expression for the spectral solvent shift:

$$\nu_{i0}-\nu_{i0}^{\circ}=\frac{1}{h}\{\langle E_i-E_i^{\circ}\rangle_{\mathrm{av}}-\langle E_0-E_0^{\circ}\rangle_{\mathrm{av}}\}, \tag{3}$$

where $\langle\ \rangle_{\mathrm{av}}$ denotes the average over all orientations of all the solvent molecules.

An Expression for the Perturbation of H'. According to Böttcher *et al.*,[9] the general expression for the electrostatic interaction energy W_{12} between two unpolarizable particles denoted by 1 and 2 is written as

$$W_{12}=\frac{1}{4\pi\varepsilon_0}\left\{\frac{Q_1Q_2}{R_{12}}-(Q_1\boldsymbol{p}_2-Q_2\boldsymbol{p}_1)\cdot\frac{\boldsymbol{R}_{12}}{R_{12}}-(Q_1\boldsymbol{\theta}_2-\boldsymbol{p}_1\boldsymbol{p}_2+Q_2\boldsymbol{\theta}_1):\boldsymbol{T}_{12}\right\}, \tag{4}$$

where ε_0 is the permittivity of vacuum, Q_1, $\boldsymbol{p}_1$, and $\boldsymbol{\theta}_1$ are the electric charge, permanent dipole moment, and quadrupole moment of particle 1, respectively, and R_{12} is the distance between the centers of masses of the two particles. Here $\boldsymbol{T}_{12}$ is the charge-quadrupole and dipole-dipole interaction tensor of $R_{12}^{-3}(\boldsymbol{I}-3R_{12}^{-2}\boldsymbol{R}_{12}\boldsymbol{R}_{12})$ where $\boldsymbol{I}$ is a unit tensor and $\boldsymbol{R}_{12}$, the position vector from 1 to 2. The dipole and quadrupole moments of the monatomic cation are zero.

On the assumption of the two-body interaction among the particles in the system, one can write H' as

$$H'=H'_{\mathrm{AS}}+H'_{\mathrm{AC}}+H'_{\mathrm{SS}}+H'_{\mathrm{CS}}+H'_{\mathrm{CC}}. \tag{5}$$

Here H'_{AS}, H'_{AC}, H'_{SS}, H'_{CS}, and H'_{CC} are perturbations due to the anion-solvent, anion-cation, solvent-solvent, cation-solvent, and cation-cation interactions, respectively. From Eq. 4, these perturbations can be written as follows:

$$H'_{\mathrm{AS}}=\frac{1}{4\pi\varepsilon_0}\sum_{s=1}^{N}\left\{\frac{ne}{R_s^3}\times\tilde{\boldsymbol{p}}_s\cdot\boldsymbol{R}_s+ne\,\tilde{\boldsymbol{\theta}}^s:\boldsymbol{T}_{\mathrm{A}s}+\tilde{\boldsymbol{p}}_{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\tilde{\boldsymbol{p}}^s\right\} \tag{6}$$

$$H'_{\mathrm{AC}}=\frac{1}{4\pi\varepsilon_0}\sum_{c=1}^{n}\left\{-\frac{ne^2}{R_c}+\frac{e}{R_c^3}\times\tilde{\boldsymbol{p}}_{\mathrm{A}}\cdot\boldsymbol{R}_c-e\tilde{\boldsymbol{\theta}}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right\} \tag{7}$$

$$H'_{\mathrm{SS}}=\frac{1}{8\pi\varepsilon_0}\sum_{s=1}^{N}\sum_{t=1}^{N}\tilde{\boldsymbol{p}}_s\cdot\boldsymbol{T}_{st}\cdot\tilde{\boldsymbol{p}}_t \tag{8}$$

$$H'_{\mathrm{CS}}=\frac{1}{4\pi\varepsilon_0}\sum_{c=1}^{n}\sum_{s=1}^{N}\left\{-\frac{e}{R_{cs}^3}\times\tilde{\boldsymbol{p}}_s\cdot\boldsymbol{R}_{cs}-e\tilde{\boldsymbol{\theta}}^s:\boldsymbol{T}_{cs}\right\} \tag{9}$$

$$H'_{\mathrm{CC}}=\frac{1}{8\pi\varepsilon_0}\sum_{c=1}^{n}\sum_{d=1}^{n}\frac{e^2}{R_{cd}}. \tag{10}$$

Here e is the elementary charge, a ripple mark denotes an operator, R_s and R_c are the distances from the anion to the sth solvent molecule and the cth cation, respectively, R_{st} is the distance from the sth solvent molecule to the tth solvent one, and R_{cd}, the distance from the cth cation to the dth cation.

Average Values of the Second and Third Terms in Eq. 2. Using Eqs. 5—10, one can calculate average values of the second and third terms on the right hand side of Eq. 2 as below. Here the suffix of double zeros, such as p_{00} and θ_{00}, denotes the moment of the ground state, and p_{ii} and θ_{ii} denote the dipole and quadrupole moments of the ith state. All the dipole moments of the solvent molecules are the same as p_{00}^{s}.

In the calculation of $\langle E_i-E_i^{\circ}\rangle_{\mathrm{av}}$, one may always neglect terms containing powers higher than the sixth power of $1/R$, because contributions of these terms to the whole are probably negligible. Moreover, for convenience one writes only terms contributing to the frequency shift. The terms are restricted to those surviving through the calculation of $\langle E_i-E_i^{\circ}\rangle_{\mathrm{av}}-\langle E_0-E_0^{\circ}\rangle_{\mathrm{av}}$. Common terms appearing in both $\langle E_0-E_0^{\circ}\rangle_{\mathrm{av}}$ and $\langle E_i-E_i^{\circ}\rangle_{\mathrm{av}}$ will vanish through the calculation and may be omitted in the expression of $\langle E_i-E_i^{\circ}\rangle_{\mathrm{av}}$. In the calculation of $\langle E_i-E_i^{\circ}\rangle_{\mathrm{av}}$, the Boltzmann factor for the ground state of the system is applied even to the distribution of orientations of solvent molecules for the ith-excited state of the system, because the electronic transition in the anion is much faster than reorientations of the solvent molecules according to the Franck-Condon principle.

Paying attention to the assumption of orthonormality for all the zeroth-order wave functions, one obtains

$$\begin{aligned}(\Phi_i^{\circ *}|H'|\Phi_i^{\circ})
&=\frac{1}{4\pi\varepsilon_0}\sum_{s=1}^{N}\left\{\frac{ne}{R_s^3}\times\boldsymbol{p}_{00}^{s}\cdot\boldsymbol{R}_s+ne\boldsymbol{\theta}_{00}^{s}:\boldsymbol{T}_{\mathrm{A}s}+\boldsymbol{p}_{ii}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{00}^{s}\right\}\\
&\quad+\frac{1}{4\pi\varepsilon_0}\sum_{c=1}^{n}\left\{-\frac{ne^2}{R_c}+\frac{e}{R_c^3}\times\boldsymbol{p}_{ii}^{\mathrm{A}}\cdot\boldsymbol{R}_c-e\boldsymbol{\theta}_{ii}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right\}\\
&\quad+\frac{1}{8\pi\varepsilon_0}\sum_{s=1}^{N}\sum_{t=1}^{N}\boldsymbol{p}_{00}^{s}\cdot\boldsymbol{T}_{st}\cdot\boldsymbol{p}_{00}^{t}\\
&\quad-\frac{1}{4\pi\varepsilon_0}\sum_{c=1}^{n}\sum_{s=1}^{N}\left\{\frac{e}{R_{cs}^3}\times\boldsymbol{p}_{00}^{s}\cdot\boldsymbol{R}_{cs}+e\boldsymbol{\theta}_{00}^{s}:\boldsymbol{T}_{cs}\right\}\\
&\quad+\frac{1}{8\pi\varepsilon_0}\sum_{c=1}^{n}\sum_{d=1}^{n}\frac{e^2}{R_{cd}}.\end{aligned} \tag{11}$$

Then one obtains

$$\begin{aligned}&\langle(\Phi_i^{\circ *}|H'|\Phi_i^{\circ})\rangle_{\mathrm{av}}\\
&\quad=\langle(\Phi_i^{\circ *}|H'_{\mathrm{AS}}|\Phi_i^{\circ})\exp\{-(\Phi_0^{\circ *}|H'|\Phi_0^{\circ})/kT\}\rangle_{\mathrm{av}}\\
&\qquad+(\Phi_i^{\circ *}|H'_{\mathrm{AC}}|\Phi_i^{\circ})\\
&\qquad+\langle(\Phi_i^{\circ *}|H'_{\mathrm{SS}}|\Phi_i^{\circ})\exp\{-(\Phi_0^{\circ *}|H'|\Phi_0^{\circ})/kT\}\rangle_{\mathrm{av}}\\
&\qquad+\langle(\Phi_i^{\circ *}|H'_{\mathrm{CS}}|\Phi_i^{\circ})\exp\{-(\Phi_0^{\circ *}|H'|\Phi_0^{\circ})/kT\}\rangle_{\mathrm{av}}\\
&\qquad+(\Phi_i^{\circ *}|H'_{\mathrm{CC}}|\Phi_i^{\circ}),\end{aligned} \tag{12}$$

where k is the Boltzmann constant and T is the thermodynamic temperature. For example, calculation of the first term on the right hand side of Eq. 12 is performed first by expanding the exponential part in a Taylor series and then by averaging all the resulting terms over all orientations of the solvent molecules. Thus one obtains

$$
\begin{aligned}
&<(\mathit{\Phi}_i^{\circ *}|H'|\mathit{\Phi}_i^\circ)>_{\mathrm{av}} \\
&\approx -\frac{1}{(4\pi\varepsilon_0)^2 kT}\sum_{s=1}^{N}<(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{00}^{s})(\boldsymbol{p}_{ii}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{00}^{s})>_{\mathrm{av}} \\
&\quad+\frac{1}{4\pi\varepsilon_0}\sum_{c=1}^{n}\left\{\frac{e}{R_c^3}\times\boldsymbol{p}_{ii}^{\mathrm{A}}\cdot\boldsymbol{R}_c-e\boldsymbol{\theta}_{ii}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right\} \\
&=-\frac{2(p_{00}^{\mathrm{S}})^2(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{p}_{ii}^{\mathrm{A}})}{3(4\pi\varepsilon^0)^2 kT}\sum_{s=1}^{N}\frac{1}{R_s^6} \\
&\quad+\frac{e}{4\pi\varepsilon_0}\sum_{c=1}^{n}\left\{\frac{\boldsymbol{p}_{ii}^{\mathrm{A}}\cdot\boldsymbol{R}_c}{R_c^3}-\boldsymbol{\theta}_{ii}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right\}. \qquad (13)
\end{aligned}
$$

In view of the mode of transition from the ith state to the mth-excited state, the average value of $I=<\sum_{m\neq i}(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ)(\mathit{\Phi}_i^{\circ *}|H'|\mathit{\Phi}_m^\circ)/(E_i^\circ-E_m^\circ)>_{\mathrm{av}}$ is calculated as the sum of three values, *i.e.*, $I=I_1+I_2+I_3$. Each value results from a different mode of transition and is calculated individually in the manner described below.

The first case is a transition mode in which the anion is excited from the ith-excited state to the jth-excited state and all the other particles remain in their ground states: Let us denote the average of all values of $(E_j^{\mathrm{A}}-E_i^{\mathrm{A}})$ by ΔE_i^{A}, where E_j^{A} is the energy of the jth state $(\mathit{\Phi}_j^{\mathrm{A}})$ of the anion except for $j=i$. In this case one obtains $E_i^\circ-E_m^\circ=E_i^{\mathrm{A}}-E_j^{\mathrm{A}}$ and

$$
\begin{aligned}
&(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ) \\
&=\frac{1}{4\pi\varepsilon_0}\sum_{s=1}^{N}\boldsymbol{p}_{ij}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{00}^{s}+\frac{e}{4\pi\varepsilon_0}\sum_{c=1}^{n}\left\{\frac{\boldsymbol{p}_{ij}^{\mathrm{A}}\cdot\boldsymbol{R}_c}{R_c^3}-\boldsymbol{\theta}_{ij}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right\}, \qquad (14)
\end{aligned}
$$

where $\boldsymbol{p}_{ij}^{\mathrm{A}}=(\phi_i^{\mathrm{A}*}|\tilde{\boldsymbol{p}}^{\mathrm{A}}|\phi_j)$ and $\boldsymbol{\theta}_{ij}^{\mathrm{A}}=(\phi_i^{\mathrm{A}}|\tilde{\boldsymbol{\theta}}^{\mathrm{A}}|\phi_j^{\mathrm{A}})$. Here one denotes an isotropic electric polarizability of the anion in the ith state by $\alpha_{ii}^{\mathrm{A}}=(2/3)\sum_{j\neq i}(|\boldsymbol{p}_{ij}^{\mathrm{A}}|^2/4\pi\varepsilon_0\Delta E_i^{\mathrm{A}})$ in the units of m³. Then one obtains

$$
\begin{aligned}
I_1&=-<\sum_{j\neq i}\frac{1}{\Delta E_i^{\mathrm{A}}}(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ)^2\exp\{-(\mathit{\Phi}_0^{\circ *}|H'|\mathit{\Phi}_0^\circ)/kT\}>_{\mathrm{av}} \\
&\approx-\sum_{j\neq i}\frac{1}{(4\pi\varepsilon_0)^2\Delta E_i^{\mathrm{A}}}\left[\sum_{s=1}^{N}<(\boldsymbol{p}_{ij}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{00}^{s})^2>_{\mathrm{av}}\right. \\
&\quad\left.+e^2\sum_{j\neq i}\left\{\sum_{c=1}^{n}\left(\frac{\boldsymbol{p}_{ij}^{\mathrm{A}}\cdot\boldsymbol{R}_c}{R_c^3}-\boldsymbol{\theta}_{ij}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right)\right\}^2\right] \\
&=-\frac{(p_{00}^{\mathrm{S}})^2\alpha_{ii}^{\mathrm{A}}}{4\pi\varepsilon_0}\sum_{s=1}^{N}\frac{1}{R_s^6} \\
&\quad-\frac{e^2}{(4\pi\varepsilon_0)^2\Delta E_i^{\mathrm{A}}}\sum_{j\neq i}\left\{\sum_{c=1}^{n}\left(\frac{\boldsymbol{p}_{ij}^{\mathrm{A}}\cdot\boldsymbol{R}_c}{R_c^3}-\boldsymbol{\theta}_{ij}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right)\right\}^2. \qquad (15)
\end{aligned}
$$

The second case is a transition mode in which the anion remains in the ith state and one of the N solvent molecules is excited to the lth-excited state: Let us write the average of all values of $(E_l^{\mathrm{S}}-E_0^{\mathrm{S}})$ as ΔE_0^{S}, where E_0^{S} and E_l^{S} are energies of the ground and lth-excited states, respectively, of the solvent molecule. One obtains $E_i^\circ-E_m^\circ=E_0^{\mathrm{S}}-E_l^{\mathrm{S}}$ and

$$
\begin{aligned}
&(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ) \\
&=\frac{1}{4\pi\varepsilon_0}\sum_{s=1}^{N}\left\{\frac{ne}{R_s^3}\times\boldsymbol{p}_{0l}^{s}\cdot\boldsymbol{R}_s+ne\boldsymbol{\theta}_{0l}^{s}:\boldsymbol{T}_{\mathrm{A}s}+\boldsymbol{p}_{ii}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{0l}^{s}\right\} \\
&\quad+\frac{1}{8\pi\varepsilon_0}\sum_{s=1}^{N}\sum_{t=1}^{N}\boldsymbol{p}_{0l}^{s}\cdot\boldsymbol{T}_{st}\cdot\boldsymbol{p}_{00}^{t} \\
&\quad-\frac{e}{4\pi\varepsilon_0}\sum_{c=1}^{n}\sum_{s=1}^{N}\left\{\frac{\boldsymbol{p}_{0l}^{s}\cdot\boldsymbol{R}_{cs}}{R_{cs}^3}+\boldsymbol{\theta}_{0l}^{s}:\boldsymbol{T}_{cs}\right\}. \qquad (16)
\end{aligned}
$$

Then one obtains

$$
\begin{aligned}
I_2&\approx-\frac{1}{(4\pi\varepsilon_0)^2\Delta E_0^{\mathrm{S}}}<\sum_{m\neq i}(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ)^2>_{\mathrm{av}} \\
&=-\frac{1}{(4\pi\varepsilon_0)^2\Delta E_0^{\mathrm{S}}}\sum_{s=1}^{N}\sum_{l\neq 0}<(\boldsymbol{p}_{ii}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{0l}^{s})^2>_{\mathrm{av}} \\
&=-\frac{(p_{ii}^{\mathrm{A}})^2\alpha_{00}^{\mathrm{S}}}{4\pi\varepsilon_0}\sum_{s=1}^{N}\frac{1}{R_s^6}, \qquad (17)
\end{aligned}
$$

where α_{00}^{S} is the isotropic electric polarizability of the solvent molecule in the ground state.

When any two of the N solvent molecules are simultaneously excited, no terms contributing to the frequency shift appear, because $(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ)=(1/8\pi\varepsilon_0)\sum_{s=1}^{N}\sum_{t=1}^{N}\boldsymbol{p}_{0l}^{s}\cdot\boldsymbol{T}_{st}\cdot\boldsymbol{p}_{0l}^{t}$ in this case. When more than two of the solvent molecules are simultaneously excited, $(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ)$ is always zero according to Eqs. 5—10.

The third case is a transition mode in which the anion in the ith state and one of the N solvent molecules in the ground states are simultaneously excited: Since $E_i^\circ-E_m^\circ=E_i^{\mathrm{A}}-E_j^{\mathrm{A}}+E_0^{\mathrm{S}}-E_l^{\mathrm{S}}$ and

$$
(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ)=\frac{1}{4\pi\varepsilon_0}\sum_{s=1}^{N}\boldsymbol{p}_{ij}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{0l}^{s}, \qquad (18)
$$

in this case, one obtains

$$
\begin{aligned}
I_3&\approx-\frac{1}{(4\pi\varepsilon_0)^2(\Delta E_0^{\mathrm{S}}+\Delta E_i^{\mathrm{A}})} \\
&\quad\times<\sum_{j\neq i}\sum_{l\neq 0}\left(\sum_{s=1}^{N}\boldsymbol{p}_{ij}^{\mathrm{A}}\cdot\boldsymbol{T}_{\mathrm{A}s}\cdot\boldsymbol{p}_{0l}^{s}\right)^2>_{\mathrm{av}} \\
&=-\frac{3\Delta E_0^{\mathrm{S}}\Delta E_i^{\mathrm{A}}\alpha_{00}^{\mathrm{S}}\alpha_{ii}^{\mathrm{A}}}{2(\Delta E_0^{\mathrm{S}}+\Delta E_i^{\mathrm{A}})}\sum_{s=1}^{N}\frac{1}{R_s^6}. \qquad (19)
\end{aligned}
$$

Simultaneous excitations of more than two of the N solvent molecules together with the excitation of the anion lead to $(\mathit{\Phi}_m^{\circ *}|H'|\mathit{\Phi}_i^\circ)=0$.

An Expression for ν_{i0}. From Eqs. 3, 13, 15, 17, and 19, one obtains

$$
\begin{aligned}
&h(\nu_{i0}-\nu_{i0}^\circ) \\
&=\frac{e}{4\pi\varepsilon_0}\sum_{c=1}^{n}\left\{\left(\frac{\boldsymbol{p}_{ii}^{\mathrm{A}}\cdot\boldsymbol{R}_c}{R_c^3}-\boldsymbol{\theta}_{ii}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right)-\left(\frac{\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{R}_c}{R_c^3}-\boldsymbol{\theta}_{00}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right)\right\} \\
&\quad+\frac{1}{(4\pi\varepsilon_0)^2}\times\left[\frac{e^2}{\Delta E_0^{\mathrm{A}}}\sum_{j\neq 0}\left\{\sum_{c=1}^{n}\left(\frac{\boldsymbol{p}_{0j}^{\mathrm{A}}\cdot\boldsymbol{R}_c}{R_c^3}-\boldsymbol{\theta}_{0j}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right)\right\}^2\right. \\
&\quad\left.-\frac{e^2}{\Delta E_i^{\mathrm{A}}}\sum_{j\neq i}\left\{\sum_{c=1}^{n}\left(\frac{\boldsymbol{p}_{ij}^{\mathrm{A}}\cdot\boldsymbol{R}_c}{R_c^3}-\boldsymbol{\theta}_{ij}^{\mathrm{A}}:\boldsymbol{T}_{\mathrm{A}c}\right)\right\}^2\right] \\
&\quad+\frac{2(p_{00}^{\mathrm{S}})^2\{(p_{00}^{\mathrm{A}})^2-(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{p}_{ii}^{\mathrm{A}})\}}{3(4\pi\varepsilon_0)^2 kT}\sum_{s=1}^{N}\frac{1}{R_s^6}
\end{aligned}
$$

$$+\frac{(p_{00}^{\mathrm{S}})^2(\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}})}{4\pi\varepsilon_0}\sum_{s=1}^{N}\frac{1}{R_s^6}+\frac{\alpha_{00}^{\mathrm{S}}(p_{00}^{\mathrm{A}}-p_{ii}^{\mathrm{A}})}{4\pi\varepsilon_0}\sum_{s=1}^{N}\frac{1}{R_s^6}$$

$$+\frac{3}{2}\times\left\{\frac{\Delta E_0^{\mathrm{S}}\Delta E_0^{\mathrm{A}}\alpha_{00}^{\mathrm{S}}\alpha_{00}^{\mathrm{A}}}{\Delta E_0^{\mathrm{S}}+\Delta E_0^{\mathrm{A}}}-\frac{\Delta E_0^{\mathrm{S}}\Delta E_i^{\mathrm{A}}\alpha_{00}^{\mathrm{S}}\alpha_{ii}^{\mathrm{A}}}{\Delta E_0^{\mathrm{S}}+\Delta E_i^{\mathrm{A}}}\right\}\sum_{s=1}^{N}\frac{1}{R_s^6}. \tag{20}$$

Both the first and second terms on the right hand side of Eq. 20 are due to the anion-cation interactions and are independent of the solvent. The second term is probably much smaller than the first, because the former contains coefficients of the sixth power of $1/R_c$, while coefficients of the latter are of the third power. The second term may therefore be ignored. The third, fourth, fifth and sixth terms are due to the anion dipole-solvent dipole interactions, the solvent dipole-anion induced dipole ones, the anion dipole-solvent induced dipole ones, and the anion-solvent dispersion forces, respectively. All these terms relating to the solvent contain coefficients of R_s^{-6}. Therefore, the solvent molecules mainly contributing to the frequency shift are attributed to those around the anion. Here one may approximately consider only the closely neighboring solvent molecules. According to the previous treatment,[5,6] this approximation leads to

$$\sum_{s=1}^{N}\frac{1}{R_s^6}\approx\frac{\pi}{(r_{\mathrm{A}}+r_{\mathrm{S}})^4}\times\left(\frac{4\pi N_{\mathrm{A}}}{3}\right)^{2/3}\left(\frac{d^{\mathrm{S}}}{M_r^{\mathrm{S}}}\right)^{2/3}, \tag{21}$$

where N_{A} is Avogadro's number, r_{A} and r_{S} are radii of the anion and the solvent molecule, respectively, and d^{S} and $M_{\mathrm{r}}^{\mathrm{S}}$, the relative density and molecular weight, respectively, of the solvent. For example, r_{S} is given by

$$r_{\mathrm{S}}=\left(\frac{3M_r^{\mathrm{S}}}{4\pi N_{\mathrm{A}}d^{\mathrm{S}}}\right)^{1/3}. \tag{22}$$

Thus, Eq. 20 is reduced to

$$\nu_{i0}=\nu'_{i0}+A\times\frac{(d^{\mathrm{S}}/M_{\mathrm{r}}^{\mathrm{S}})^{2/3}(p_{00}^{\mathrm{S}})^2}{(r_{\mathrm{A}}+r_{\mathrm{S}})^4}+B\times\frac{(d^{\mathrm{S}}/M_{\mathrm{r}}^{\mathrm{S}})^{2/3}\alpha_{00}^{\mathrm{S}}}{(r_{\mathrm{A}}+r_{\mathrm{S}})^4}, \tag{23}$$

where

$$\nu'_{i0}=\nu_{i0}^{\circ}+\frac{1}{4\pi\varepsilon_0}\sum_{c=1}^{n}\frac{e}{R_c^3}\left\{(\boldsymbol{p}_{ii}^{\mathrm{A}}-\boldsymbol{p}_{00}^{\mathrm{A}})\cdot\boldsymbol{R}_c+(\boldsymbol{\theta}_{00}^{\mathrm{A}}-\boldsymbol{\theta}_{ii}^{\mathrm{A}}):\left(\boldsymbol{I}-\frac{3}{R_c^2}\boldsymbol{R}_c\boldsymbol{R}_c\right)\right\} \tag{24}$$

$$A=\frac{\pi}{h}\left(\frac{4\pi N_{\mathrm{A}}}{3}\right)^{2/3}\times\left[\frac{2\times\{(p_{00}^{\mathrm{A}})^2-(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{p}_{ii}^{\mathrm{A}})\}}{3(4\pi\varepsilon_0)^2kT}+\frac{(\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}})}{4\pi\varepsilon_0}\right], \tag{25}$$

and

$$B=\frac{\pi}{h}\left(\frac{4\pi N_{\mathrm{A}}}{3}\right)^{2/3}\times\left[\frac{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2}{4\pi\varepsilon_0}+\frac{3}{2}\times\left(\frac{\Delta E_0^{\mathrm{A}}\alpha_{00}^{\mathrm{A}}}{1+\Delta E_0^{\mathrm{A}}/\Delta\bar{E}_0^{\mathrm{S}}}-\frac{\Delta E_i^{\mathrm{A}}\alpha_{ii}^{\mathrm{A}}}{1+\Delta E_i^{\mathrm{A}}/\Delta\bar{E}_0^{\mathrm{S}}}\right)\right]. \tag{26}$$

Although ΔE_0^{S} varies with the solvent, ΔE_0^{S} is for convenience replaced by the average $\Delta\bar{E}_0^{\mathrm{S}}$ of values of ΔE_0^{S} in Eq. 26. Then, A and B may be approximately characteristic of the anion. Equation 24 indicates that ν'_{i0} is independent of the solvent. According to Eq. 23, therefore, values of ν'_{i0}, A, and B can be estimated by the least-squares method from experimental frequencies of the anion in several solutions. From Eq. 24, effects of the ion pairings between the anion and its cations are shown by the second term in Eq. 24 and can be regarded as being involved at a constant magnitude in the experimental frequency (ν_{i0}).

Discussion

As shown by Eq. 20, the solvent shift is due to the dipole-dipole interactions, the induced dipole-dipole ones, and the dispersion forces between the anion and the solvent molecules, because the first and second terms are independent of the solvent. On the other hand, Hirano's expression for the same shift involves only the dispersion force terms.[3] The essential difference between the present treatment and Hirano's seems to arise from the different results of calculations of the first- and second-order terms of Eq. 2. Moreover, according to Hirano, the effects of the counter cations on the frequency shift can be approximately ignored, while in the present treatment the effects are included approximately at a constant magnitude in the experimental frequency. The difference may be attributed to the operation of averaging over all orientations of the counter cations. Hirano has performed this operation; it is not done in the present treatment.

Equation 23 can be applied not only to the large anions but also to neutral molecules, because the effects of charge of the anion are not involved in Eqs. 25 and 26 and ν'_{i0} is equal to ν_{i0}° in the absence of the counter cations. The previous expressions[5,6] have been derived from assuming van der Waals' equation at the beginning for interactions between the neutral solute molecule in the *i*th state and the solvent molecules. The present treatment is the theoretical basis of the previous theory:[5,6] If the first and second terms are omitted and $(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{p}_{ii}^{\mathrm{A}})$ is replaced by $(p_{ii}^{\mathrm{A}})^2$ in Eq. 20, Eq. 20 is essentially the same as the previous expressions. Accordingly, the previous expressions can be derived in the same way as in the present treatment, if the Boltzmann factor of $\exp\{-(\Phi_i^{\circ *}|H'|\Phi_i^{\circ})/kT\}$ is used instead of that of $\exp\{-(\Phi_0^{\circ *}|H'|\Phi_0^{\circ})/kT\}$ for the *i*th-excited state of the system. This leads to the conclusion that the Franck-Condon principle has not been considered in the previous expressions. When the principle is considered in the previous expressions,[5,6] the value of $(p_{ii}^{\mathrm{A}})^2$ appearing in the solute dipole-solvent dipole interaction terms should be replaced by $(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{p}_{ii}^{\mathrm{A}})$.

In McRae's theory[4] the Hamiltonian operator in Eq. 2 consists of instantaneous dipole-dipole interactions between two neutral molecules in the system. In the case of the neutral solute molecule (U), H' is written from Eq. 4 as

$$H'=\sum_{\mathrm{S}=1}^{N}\tilde{\boldsymbol{p}}^{\mathrm{U}}\cdot\boldsymbol{T}_{\mathrm{U}s}\cdot\tilde{\boldsymbol{p}}^{s}. \tag{27}$$

Equation 27 is the dipole-dipole interaction operator. Accordingly, the previous treatment[5,6] is fundamentally similar to that of McRae, as also described by Amos and Burrows.[1a] An essential difference between McRae's theory[4] and that of the present author lies in the following point: In McRae's theory the second and third terms in Eq. 2 have been concretely calculated by using reaction fields of the Onsager type,[10] while in the present treatment these terms have been consistently obtained in terms of the two-body interactions among the particles of the system. Although the value of local relative permittivity in the neighborhood of the solute differs from that of the bulk relative permittivity of the solvent, the local permittivity is not considered at all in deriving the Onsager reaction field. In order to consider the local permittivity, the Block-Walker reaction field[11] should be used instead of the Onsager one in McRae's theory for the neutral molecule. For the description of experimental results for solvent effects on several phenomena, the Block-Walker reaction field is much superior to the Onsager one.[12] In McRae's theory,[4] another problem arises due to the following assumption: A time average of a square field at the solute dipole owing to the presence of permanent dipoles of surrounding solvent molecules is arbitrarily assumed to be equal to three times the squared value of the reaction field. On the other hand, the present treatment is not accompanied by such problems, because the relative permittivity and the reaction field are not used.

Hirano[3] has extended McRae's theory for the neutral molecule to the anion, using the Onsager reaction field. Both the Onsager reaction field and the Block-Walker one are derived from the assumption that the solute molecule has no excess charge and from solving Laplace equations. These reaction fields can not be applied to the anion, because a reaction field for the anion must be derived by solving a Poisson equation. Instead of the Onsager reaction field, the Kirkwood reaction field[13,14] consisting of the Born charging energy[15] and the Onsager reaction field should be used for the anion, but this field is also derived after neglecting the local relative permittivity. Beveridge and Schnuelle[14] have theoretically treated the polarization energy of a charged solute and have presented a general expression definitely containing the local relative permittivity. One, however, finds difficulty in applying the expression, because it is hard to determine values of the local relative permittivity and thickness of a local solvent shell. These values are necessary for applying the expression. Thus, the solvent shift of the anion has been studied by the present treatment.

In the present calculation of the interaction energies between the solute and the solvent molecules, a serious problem arises from the evaluation of the "average energies" such as ΔE_0^A, ΔE_i^A, and ΔE_0^S. It is found that ΔE_0^A and ΔE_0^S are approximately equal to ionization potentials (I_0^A and I_0^S) of the solute and solvent molecules, respectively, in their ground states.[16] The replacement of the average energy by the ionization potential has not been justified theoretically.[1a,17] At the present stage, however, there is no approach to this problem other than the replacement. The value of ΔE_i^A may be replaced by $I_i^A = I_0^A - hc\nu_{i0}^\circ$ as in the previous papers,[5,6] where c is the speed of light *in vacuo* and I_i^A, an ionization potential of the anion in the ith state. Amos and Burrows[1a,17] have stated that approximately the same average energies should be taken for both the ground and excited states. So far as the average energy is assumed to be approximated by the ionization potential, the assumption of $I_i^A = I_0^A - hc\nu_{i0}^\circ$ is valid for a low-lying excited state: The energy of the ground state of the solute molecule is denoted by $E(^1\Psi_0)$. The energy of the ith-excited state ($^1\Psi_{i0}$) resulting from a transition of an electron from the highest occupied MO (ϕ_0) to the ith vacant MO (ϕ_i) is written as

$$E(^1\Psi_{i0}) = E(^1\Psi_0) + hc\nu_{i0}^\circ. \tag{28}$$

According to Roothaan,[18] a singly ionized state ($^2\Psi_0$) obtained by removing either of the two electrons occupying ϕ_0 has an energy given by

$$E(^2\Psi_0) = E(^1\Psi_0) - \varepsilon_0(\Psi_0) = E(^1\Psi_0) + I_0, \tag{29}$$

where $\varepsilon_0(\phi_0)$ is the energy of ϕ_0, and I_0 is the ionization potential of the ground state of the molecule. From Eqs. 28 and 29, one can write the ionization potential of $^1\Psi_{i0}$ as

$$I_i = E(^2\Psi_0) - E(^1\Psi_{i0}) = I_0 - hc\nu_{i0}^\circ. \tag{30}$$

If the anion is small and is solvated by coordination of the solvent molecules, the second and third terms in Eq. 2 must be calculated without the operation of averaging over all the orientations of all the solvent molecules. Of course, Eq. 23 can not be applied to such a small anion. In the case of a small solvated anion, one may calculate the second and third terms by considering only the solvating solvent molecules surrounding the anion.

Since a molecule generally has a dipole moment larger than its quadrupole moment, Eq. 24 may be approximated by

$$\nu'_{i0} = \nu_{i0}^\circ + \Delta\nu_C, \tag{31}$$

where

$$\Delta\nu_C = \frac{e}{4\pi\varepsilon_0}\sum_{c=1}^{n}\frac{(\boldsymbol{p}_{ii}^A - \boldsymbol{p}_{00}^A)\cdot\boldsymbol{R}_C}{R_c^3}. \tag{32}$$

Here $\Delta\nu_C$ is a frequency shift due to the ion pairings between the anion and its counter cations. Equation 32 shows that $\Delta\nu_C$ becomes smaller with increasing values of R_c, *i.e.*, with an increasing radius of the cation. As described above, $\Delta\nu_C$ is contained in the experimental frequency (ν_{i0}). Consequently, as the radius of cation increases in the same solvent, a wavelength corresponding to ν_{i0} will shift to the red if $(\boldsymbol{p}_{ii}^A - \boldsymbol{p}_{00}^A)\cdot\boldsymbol{R}_c > 0$, because $\Delta\nu_C$ decreases in this case. If $(\boldsymbol{p}_{ii}^A - \boldsymbol{p}_{00}^A)\cdot\boldsymbol{R}_c < 0$, the shift of the wavelength will be toward the blue, because $\Delta\nu_C$ increases. Because of the negative charge, the dipole moment of the anion varies with the way of setting the origin of the coordinates,[19] and often takes a minus sign, as exemplified below. Accordingly, the minus sign as well as a plus one must be considered for values of p_{00}^A and p_{ii}^A which satisfy an inequality of $(\boldsymbol{p}_{ii}^A - \boldsymbol{p}_{00}^A)\cdot\boldsymbol{R}_c \lessgtr 0$. Such red shifts seem to be seen in the cases of xanthene and thioxanthene in 2-methyltetrahydrofuran.[20] For example, xanthene shows absorption maxima at 413, 436, 470, and 482 nm owing to the ion pairings with Li^+, Na^+, K^+, and Cs^+, respectively.[20]

The ion pairings of 4,4-dimethoxy-1,3,5-trinitro-2,5-cyclohexadienide anion with $(n\text{-}C_4H_9)_4N^+$, Na^+, Ca^{2+}, and Ba^{2+} in methanol show the first bands at 480, 490, 490, and 500 nm, respectively, and the second bands at 418, 412, 404, and 405 nm, respectively.[21] The first and second bands tend to shift to the red and to the blue, respectively, with an increasing radius of the cation. In the solution the counter cation is probably held by the four oxygen atoms of two methoxyl groups and two nitro groups on the 3,5-positions.[21] Moreover, a symmetrical structure of crystalline potassium salt of the anion has been determined by the X-ray method.[22] In view of the symmetrical structure of the ion pair between the anion and its cation, all $\boldsymbol{p}^{\rm A}_{00}$, $\boldsymbol{p}^{\rm A}_{ii}$, and $\boldsymbol{R}_c$ probably lie along the same axis of the C_{2v}-symmetry. In the anion, the position vector of the center of negative-charge distribution is much greater in magnitude than that of the positive-charge distribution, though the former magnitude depends on the way of setting the origin. The dipole moment of the anion may, therefore, be in the direction opposite to that of the neutral molecule. One may, therefore, assume that $\boldsymbol{p}^{\rm A}_{00}$ and $\boldsymbol{p}^{\rm A}_{ii}$ are in the opposite direction of $\boldsymbol{R}_c$ in this case. Consequently, one obtains inequalities of $P^{\rm A}_{00} > P^{\rm A}_{ii}$ and $P^{\rm A}_{ii} > P^{\rm A}_{00}$ from the red and blue shifts, respectively. Thus, the dipole moment of the ground state of the anion may be larger than that of the first-excited state but may be smaller than that of the second-excited state.

Equation 32 also shows that, in the case of the same solvent, the shift does not vary with the cation if $P^{\rm A}_{00} \simeq 0$ and $P^{\rm A}_{ii} \simeq 0$ or if $P^{\rm A}_{00} \simeq P^{\rm A}_{ii}$. Such behavior seems to appear in the case of the triiodide anion.[23] The first and second excited states of the triiodide anion as well as its ground state are likely to be nonpolar since their structures consist of three identical iodine atoms. For example, the triiodide anion in diethyl ether shows the first absorption bands at 366.5, 366.7, and 366.4 nm owing to the ion pairings with $(C_2H_5)_4N^+$, $(C_2H_5)_3AsI^+$, and Cs^+, respectively.[23]

In applying Eq. 23, it is convenient to use a wave number σ_{i0} instead of ν_{i0}, because the former is calculated with somewhat greater ease than the latter from the λ_{i0} wavelength observed. Then, ν'_{i0} and ν°_{i0} are replaced by σ'_{i0} and σ°_{i0}. The value of λ_{i0} measured with a spectrophotometer is not a wavelength in the solution but is approximately converted into a wavelength *in vacuo*. In Eq. 23, therefore, ν_{i0} can be replaced by $c\sigma_{i0}$. If λ_{i0} is a value in the solution, ν_{i0} should be replaced by $(c/n_{\rm S})\sigma_{i0}$, where $n_{\rm S}$ is the refractive index of the solvent.

Applications

All the dipole moments and polarizabilities of the anion and the solvent molecule in Eqs. 23—26 are values measured in vapors, because in the zeroth-order approximation all the particles in the system are assumed not to interact with one another. In applying Eq. 23, the temperature was always assumed to be 20 °C and the dipole moments ($p^{\rm S}_{00}$) of the solvent molecules in vapors were taken from Refs. 24 and 25. Dipole moments of *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, dimethyl sulfoxide, 1,2-dimethoxyethane and diethyloxalate were values measured in benzene,[26] since their moments in vapors were not found. Values of $\alpha^{\rm S}_{00}$ were calculated from sums of bond refractions. Unfortunately, few systematic experimental studies have been reported on the spectral solvent shifts of anions.

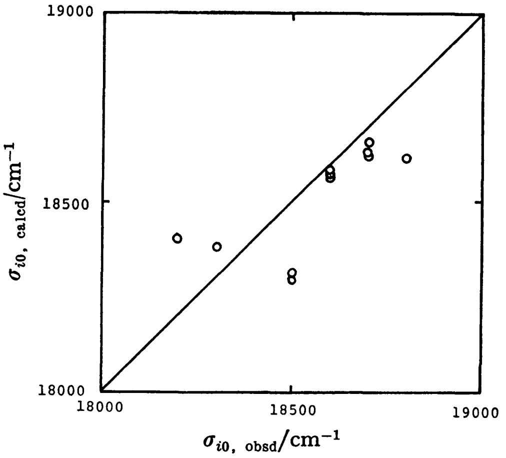

Fig. 1. Correlation of $\sigma_{i0,\,\rm calcd}$ with $\sigma_{i0,\,\rm obsd}$ for the first band of Eosin-Y^{2-} anion.

Eosin-Y²⁻ Anion. Values used for σ_{i0} of Eosin-Y^{2-} were those measured by Hirano.[3] He did not report the kind of counter cation used. The value of $r_{\rm A}$ was assumed to be 0.56 nm from the molecular volume (0.7—0.8 nm³) estimated in footnote 25 in Ref. 3. These results were obtained: $\sigma'_{i0} = 18990$ cm^{-1}, $A = 5.60 \times 10^{12}$ J^{-1} m^2, and $B = -5.75 \times 10^{-6}$ m^2. The frequencies ($\sigma_{i0,\rm calcd}$) calculated by using these values are plotted in Fig. 1 against the $\sigma_{i0,\rm obsd}$ observed. The correlation of $\sigma_{i0,\rm calcd}$ with $\sigma_{i0,\rm obsd}$ is as good as that in the application of Hirano.[3] The value of σ'_{i0} is smaller than that of σ°_{i0} (19300 cm^{-1}) obtained by Hirano, though σ'_{i0} is interpreted to involve a constant shift due to the ion pairings with cations.

The Meisenheimer Complex of 1,3,5-Trinitrobenzene with Cyanide Ion. An application was made to spectral solvent shifts of the first and second absorption bands of the tetrabutylammonium salt of 4-cyano-1,3,5-trinitro-2,5-cyclohexadienide (**1**).[27] The value of $r_{\rm A}$ was assumed to be 0.44 nm from crystal data[22] of the potassium salt of 4,4-dimethoxy-1,3,5-trinitro-2,5-cyclo-

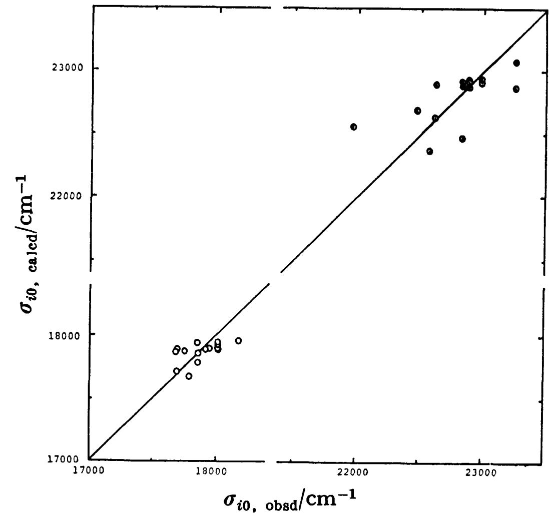

Fig. 2. Correlations of $\sigma_{i0,\,\rm calcd}$ with $\sigma_{i0,\,\rm obsd}$ for the first (○) and second (⊙) bands of **1**.

hexadienide. These results were obtained: $\sigma'_{i0}=18200$ cm^{-1}, $A=-9.32\times10^{11}$ J^{-1} m^2, and $B=-2.271\times10^{-6}$ m^2 for the first band, and $\sigma'_{i0}=23260$ cm^{-1}, $A=-1.153\times10^{13}$ J^{-1} m^2, and $B=-2.571\times10^{-6}$ m^2 for the second band. The frequencies calculated by using these values of σ'_{i0}, A, and B are roughly correlated with thcse observed, as shown in Fig. 2.

Putting the above values of A and B for the first band into Eqs. 25 and 26, respectively, one obtains the following equations:

$$\{(p_{00}^{\mathrm{A}})^2-(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{p}_{ii}^{\mathrm{A}})\}+6.17\times10^{-21}\,\mathrm{J}\times(\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}})$$
$$=-0.20\times10^{-49}\,\mathrm{J\,m^3} \tag{33}$$

$$\{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2+1.5\times\left(\frac{\Delta E_0^{\mathrm{A}}\alpha_{00}^{\mathrm{A}}}{1+\Delta E_0^{\mathrm{A}}/\Delta\bar{E}_0^{\mathrm{S}}}-\frac{\Delta E_i^{\mathrm{A}}\alpha_{ii}^{\mathrm{A}}}{1+\Delta E_i^{\mathrm{A}}/\Delta\bar{E}_0^{\mathrm{S}}}\right)$$
$$=-77.49\times10^{-49}\,\mathrm{J\,m^3}. \tag{34}$$

Generally, upon an electronic excitation from a ground state to an excited one, an increase in polarizability might be expected, because an orbital of the excited state is larger and more diffuse than that of the ground state. Actually, such increases in polarizabilities have been confirmed experimentally for several neutral molecules.[28] An inequality of $\alpha_{ii}^{\mathrm{A}}>\alpha_{00}^{\mathrm{A}}$ may also be expected for the anion under consideration. Since (1 Debye)$^2=1.000\times10^{-49}$ J m^3, -77.49×10^{-49} J m^3 in Eq. 34 is rather large. This large negative value is probably due not only to $\alpha_{ii}^{\mathrm{A}}>\alpha_{00}^{\mathrm{A}}$ but also to $|p_{ii}^{\mathrm{A}}|>|p_{00}^{\mathrm{A}}|$, because ΔE_0^{A} is larger than ΔE_i^{A}, according to Eq. 30, and the second term on the left hand side of Eq. 34 is probably not so large that the value can be attributed to it alone. On the other hand, the absolute value of -0.20×10^{-49} J m^3 in Eq. 33 is relatively very small. This small negative value should be due to cancellation between the first and second terms on the left hand side of Eq. 33. This leads to the inequality of $\{(p_{00}^{\mathrm{A}})^2-(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{p}_{ii}^{\mathrm{A}})\}>0$, since $\alpha_{ii}^{\mathrm{A}}>\alpha_{00}^{\mathrm{A}}$. Changes in dipole moments between the ground and excited states of the anion are probably due to those of the π-electron system of 1,3,5-trinitro-2,4-pentadien-1-ide. In view of the symmetric structure of the π-electron system, both p_{00}^{A} and p_{ii}^{A} are approximately in the same direction. Therefore, the inequality of $\{(p_{00}^{\mathrm{A}})^2-(\boldsymbol{p}_{00}^{\mathrm{A}}\cdot\boldsymbol{p}_{ii}^{\mathrm{A}})\}>0$ comes probably from the relation of $p_{00}^{\mathrm{A}}>0$ and $0>p_{ii}^{\mathrm{A}}$, since $|p_{ii}^{\mathrm{A}}|>|p_{00}^{\mathrm{A}}|$. Thus, the positive dipole moment of the ground state of **1** is larger than the negative dipole moment of the first-excited state, while the absolute value of the latter is larger than the former. In a similar way the relative large values of both A and B for the second band lead to the opposite conclusion, that the dipole moment of the second-excited state is larger than that of the ground state.

These conclusions are supported by the results ($p_{00}^{\mathrm{A}}>p_{ii}^{\mathrm{A}}$ (the first-excited state) and $p_{00}^{\mathrm{A}}<p_{ii}^{\mathrm{A}}$ (the second-excited state)) obtained above from the red and blue shifts due to the ion pairings of 4,4-dimethoxy-1,3,5-trinitro-2,5-cyclohexadienide anion, because the changes in the dipole moments between the ground and excited states of both the anions can be attributed approximately to those of the same π-electron system of 1,3,5-trinitro-2,4-pentadien-1-ide.

The conclusions obtained above from the spectral solvent shifts of **1** are also supported by calculating the dipole moments of the π-electron system. Hosoya *et al.*[29] have reported the SCF MO's and atomic coordinates for the π-electron system of 1,3,5-trinitro-2,4-pentadien-1-ide anion. Using their MO's and coordinates, one obtains the dipole moments of -7.2, -12.2, and -0.8 Debyes for the ground, first-excited, and second-excited states, respectively, of the π-electron system in the same direction of the y axis (the axis of $\mathrm{C_{2v}}$ symmetry). When the values of these dipole moments are divided by $-e$, centers of negative-charge distributions may be approximately obtained, because the magnitude of the position vector of the center of the negative-charge distribution is much greater than that of the positive-charge distribution in the anion, as described above. Even if the origin is shifted by y_0, the positions of these centers of the negative-charge distributions do not change and their coordinates only change by y_0. The center of mass of **1** is apparently located above the origin set by Hosoya *et al.* at the position of 1-carbon. When their origin is shifted upward by 0.16 nm along the y axis, one obtains the dipole moments of 0.5, -4.5 and 6.9 Debyes for the ground, first-excited, and second-excited states, respectively. These dipole moments of the π-electron system can explain the conclusions obtained from the spectral solvent shifts of **1**.

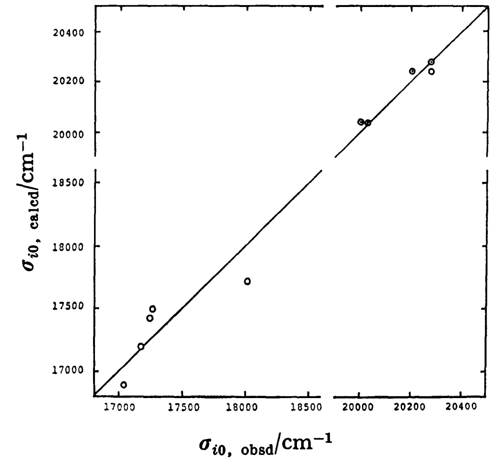

Fig. 3. Correlations of $\sigma_{i0,\,\mathrm{calcd}}$ with $\sigma_{i0,\,\mathrm{obsd}}$ for the first bands of **2** (○) and **3** (◉).

Janovsky Complexes. Applications were tried to the first absorption bands of the Janovsky complexes of the potassium salts of 4-acetonyl-1,3-dinitro-2,5-cyclohexadienide (**2**) and 4-acetonylidene-1,3-dinitro-2,5-cyclohexadienide (**3**). As in the case of **1**, r_{A} was assumed to be 0.44 nm. The values of $\sigma'_{i0}=18170$ cm^{-1}, $A=-2.434\times10^{13}$ J^{-1} m^2 and $B=-2.636\times10^{-6}$ m^2 were obtained for **2** and those of $\sigma'_{i0}=20560$ cm^{-1}, $A=6.43\times10^{11}$ J^{-1} m^2 and $B=-2.453\times10^{-6}$ m^2 were obtained for **3**. The correlation of $\sigma_{i0,\mathrm{calcd}}$ with $\sigma_{i0,\mathrm{obsd}}$ is fairly good, as shown in Fig. 3. The magnitudes of A for **3** and **2** correspond to those of the first and second bands of **1**, respectively. Accordingly, in a similar way as in the case of **1**, one will arrive at the conclusions that in the case of **3** the dipole moment of the ground state may be larger than that of the first-excited state, while in the case of **2** the latter is larger than the former.

References

1) For example, see the following reviews and recent paper: 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.*, **15**, 297 (1976); d) I. Fischer-Hjalmars, A. Henriksson-Enflo, and C. Herrmann, *Chem. Phys.*, **24**, 167 (1977).

2) S. Miertuš and O. Kysel̆, *Chem. Phys.*, **21**, 33, 47 (1977).

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

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

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

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

7) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

8) E. S. Amis and J. F. Hinton, "Solvent Effects on Chemical Phenomena," Academic Press, New York (1973), Vol. 1, p. 65.

9) C. J. F. Böttcher, O. C. van Belle, P. Bordewijk, and A. Rip, "Theory of Electric Polarization," Elsevier Scientific Publishing Co., Amsterdam (1973), Vol. 1, p. 113.

10) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

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

12) J. -L. M. Abboud and R. W. Taft, *J. Phys. Chem.*, **83**, 412 (1979).

13) J. G. Kirkwood, *J. Chem. Phys.*, **1**, 351 (1934).

14) D. L. Beveridge and G. W. Schnuelle, *J. Phys. Chem.*, **79**, 2562 (1975).

15) M. Born, *Z. Phys.*, **1**, 45 (1920).

16) For example: a) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York (1967), p. 963; b) H. Margenau and N. R. Kestner, "Theory of Intermolecular Forces," 2nd ed, Pergamon Press, Oxford (1971), p. 28.

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

18) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

19) D. W. Davies, "The Theory of the Electric and Magnetic Properties of Molecules," John Wiley and Sons, London (1967), p. 77.

20) H. W. Vos, G. G. A. Rietveld, C. MacLean, and N. H. Velthorst, *J. Chem. Soc., Faraday Trans. 2*, **1976**, 1636.

21) M. R. Crampton and H. A. Khan, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1103.

22) H. Ueda, N. Sakabe, J. Tanaka, and A. Furusaki, *Bull. Chem. Soc. Jpn.*, **41**, 2866 (1968).

23) C. Detellier and P. Laszlo, *J. Phys. Chem.*, **80**, 2503 (1976).

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

25) T. Shimozawa, "Yudenritsu no Kaishaku (Interpretation of Relative Permittivities)," Kyoritsu Publishing Co., Tokyo (1967), p. 83.

26) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York (1970).

27) A. R. Norris, *Can. J. Chem.*, **45**, 2703 (1967).

28) a) K. Seibold, H. Navangul, and H. Labhart, *Chem. Phys. Lett.*, **3**, 275 (1969); b) J. W. Barker and L. J. Noe, *J. Chem. Phys.*, **58**, 5192 (1973); c) R. Mathies and A. C. Albrecht, *J. Chem. Phys.*, **60**, 2500 (1974); d) G. C. Causley and B. R. Russell, *J. Chem. Phys.*, **68**, 3797 (1978).

29) H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, **12**, 117 (1968).

30) M. Kimura, M. Kawata, and M. Nakadate, *Chem. Ind. (London)*, **1965**, 2065.