Theory of Solvent Effects on Molecular Electronic Spectra. Frequency Shifts

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Several quantitative theories[1-9] have been presented for solvent effects on electronic spectra. These theories give good theoretical interpretations for observed frequency shifts, but they can be used only with difficulty to calculate general frequency shifts, since their expressions are either very complicated or only applicable to non-polar solvents.

In the present work, by the application of the van der Waals interaction, an attempt has been made to derive a general theoretical expression for the frequency shifts, from which expression the frequency shifts can be calculated by the use of other observed values.

Among the solvent effects on the electronic spectra, there is the important effect of hydrogen bonding between a solute and solvent molecules found by Nagakura and Baba.[10] In the present theory, however, this effect has not been considered.

Theoretical

The method of treatment consists of the application of the van der Waals interaction to the calculation of the electronic interactions among molecules of a solution containing N identical solvent molecules and one solute molecule. The spectra of solutions are usually measured at very low concentrations in the longer wavelength regions in which no solvents absorb. We will, therefore, consider the ith excited electronic state of the solution in which the solute molecule is in its ith excited electronic state and all the solvent molecules are in their ground states. We will suppose that all the spherical molecules have fixed positions. In view of the Franck-Condon principle, the same positions are appropriate to the ground and excited states of the solution.

In the zeroth order of approximation, we consider that all the spherical isotropic molecules do not interact. The zeroth-order electronic state energies are sums of the electronic state energies of the unperturbed component molecules; the energies corresponding to the ground and excited states of the solution are given, respectively, by:

$$E_0^0 = w_0^{\mathrm{u}} + N w_0^{\mathrm{v}}$$

$$E_i^0 = w_i^{\mathrm{u}} + N w_0^{\mathrm{v}}$$

where w denotes the electronic state energy of an unperturbed molecule. Throughout this paper the notations u and v(p) will refer to the solute and the pth solvent molecule, while the subscript zero will indicate the ground electronic state, and i, the ith excited electronic state. Thus, the energy difference in cm^{-1} between the zeroth and ith states of the solute in gas will be expressed by:

$$\nu_{i0}^0 = (w_i^{\mathrm{u}} - w_0^{\mathrm{u}})/\boldsymbol{hc} \qquad (1)$$

where $\boldsymbol{h}$ is the Planck constant and $\boldsymbol{c}$, the velocity of light.

Assuming that there are no strong dipole orientations among the molecules, we represent the energy of the interaction of all the molecules in solution by the energy of the van der Waals interaction,[11] which is given by:

$$\begin{aligned} E_i' = & -\sum_{p=1}^{N} \frac{1}{R_{\mathrm{u}\,\mathrm{v}(p)}^6} \left\{ \frac{2}{3} \cdot \frac{(\mu_i^{\mathrm{u}})^2 (\mu_0^{\mathrm{v}(p)})^2}{\boldsymbol{kT}} \right. \\ & + (\alpha_i^{\mathrm{u}})(\mu_0^{\mathrm{v}(p)})^2 + (\alpha_0^{\mathrm{v}(p)})(\mu_i^{\mathrm{u}})^2 \\ & \left. + \frac{3}{2} \cdot \frac{I_i^{\mathrm{u}} \cdot I_0^{\mathrm{v}(p)}}{I_i^{\mathrm{u}} + I_0^{\mathrm{v}(p)}} \cdot (\alpha_i^{\mathrm{u}})(\alpha_0^{\mathrm{v}(p)}) \right\} \\ & - \frac{1}{2} \sum_{p=1}^{N} \sum_{q=1}^{N} \frac{1}{R_{\mathrm{v}(p)\mathrm{v}(q)}^6} \left\{ \frac{2}{3} \cdot \frac{(\mu_0^{\mathrm{v}(p)})^2 (\mu_0^{\mathrm{v}(q)})^2}{\boldsymbol{kT}} \right. \\ & + (\alpha_0^{\mathrm{v}(p)})(\mu_0^{\mathrm{v}(q)})^2 + (\alpha_0^{\mathrm{v}(q)})(\mu_0^{\mathrm{v}(p)})^2 \\ & \left. + \frac{3}{2} \cdot \frac{I_0^{\mathrm{v}(p)} \cdot I_0^{\mathrm{v}(q)}}{I_0^{\mathrm{v}(p)} + I_0^{\mathrm{v}(q)}} \cdot (\alpha_0^{\mathrm{v}(p)})(\alpha_0^{\mathrm{v}(q)}) \right\} \qquad (2) \end{aligned}$$

where R denotes the distance between two molecules in solution, and I, the ionization potential of an unperturbed molecule in gas.

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[4] W. W. Robertson, O. E. Weigang, Jr., and F. A. Matsen, *J. Mol. Spectry*, **1**, 1 (1957).

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Here $\boldsymbol{k}$ is the Boltzmann constant, and T is the absolute temperature.

The energy of the perturbed ith excited state of the solution, corresponding in the zeroth order of approximation to the unperturbed ith excited state, is given by:

$$E_i = E_i^0 + E_i' \tag{3}$$

A similar expression for the ground state of the solution is obtained by replacing i by 0. The frequency shift, $\varDelta\nu_{i0}$, is given by:

$$\boldsymbol{hc}\cdot\varDelta\nu_{i0} = (E_i - E_0) - (E_i^0 - E_0^0) \tag{4}$$

With the aid of Eq. 3, Eq. 4 can be written:

$$\boldsymbol{hc}\cdot\varDelta\nu_{i0} = E_i' - E_0' \tag{5}$$

The ionization potential of the ith excited state of the solute molecule is approximated as smaller than that for the ground state by $\boldsymbol{hc}\nu_{i0}^0$ erg. We then obtain for $I_i^{\rm u}$ (in erg):

$$I_i^{\rm u} = I_0^{\rm u} - \boldsymbol{hc}\nu_{i0}^0 \tag{6}$$

From the assumption that all the spherical solvent molecules are identical, it follows that they have identical dipole moments of $\mu_0^{\rm v}$ (gas) and identical ionization potentials of $I_0^{\rm v}$. From Eqs. 2, 5 and 6, we find:

$$\begin{aligned}\boldsymbol{hc}\cdot\varDelta\nu_{i0} = &-\Big(\sum_{p=1}^{N} 1/R_{{\rm uv}(p)}^6\Big)\Big[\frac{2}{3}\cdot\frac{(\mu_0^{\rm v})^2}{\boldsymbol{k}T}\{(\mu_i^{\rm u})^2\\ &-(\mu_0^{\rm u})^2\} + (\mu_0^{\rm v})^2\{(\alpha_i^{\rm u}) - (\alpha_0^{\rm u})\} + (\alpha_0^{\rm v})\{(\mu_i^{\rm u})^2\\ &-(\mu_0^{\rm u})^2\} + \frac{3}{2}\cdot(\alpha_0^{\rm v})\cdot I_0^{\rm v}\Big\{\frac{I_0^{\rm u} - \boldsymbol{hc}\nu_{i0}^0}{I_0^{\rm v} + I_0^{\rm u} - \boldsymbol{hc}\nu_{i0}^0}\cdot\\ &(\alpha_i^{\rm u}) - \frac{I_0^{\rm u}}{I_0^{\rm v} + I_0^{\rm u}}\cdot(\alpha_0^{\rm u})\Big\}\Big]\end{aligned} \tag{7}$$

The Reduction of $\big(\sum_{p=1}^{N} 1/R_{{\rm uv}(p)}^6\big)$**.**—If the solute and the solvent molecules are spherical, their radii can be written, respectively, as:

$$r^{\rm u} = (3\,M^{\rm u}/4\pi \boldsymbol{A}_0 d^{\rm u})^{1/3} \tag{8}$$

$$r^{\rm v} = (3\,M^{\rm v}/4\pi \boldsymbol{A}_0 d^{\rm v})^{1/3} \tag{9}$$

Here $\boldsymbol{A}_0$ is the Avogadro number; M, a molecular weight, and d, a liquid density. We then have for the values of $R_{{\rm uv}(p)}$:

$$(r^{\rm u}+r^{\rm v}),\ (r^{\rm u}+3r^{\rm v}),\ (r^{\rm u}+5r^{\rm v}),\cdots$$

The numbers of the solvent molecules at the distances corresponding to the above values of $R_{{\rm uv}(p)}$ may be approximated as, respectively:

$$\frac{4\pi(r^{\rm u}+r^{\rm v})^2}{(2r^{\rm v})^2},\ \frac{4\pi(r^{\rm u}+3r^{\rm v})^2}{(2r^{\rm v})^2},\ \frac{4\pi(r^{\rm u}+5r^{\rm v})^2}{(2r^{\rm v})^2},\cdots$$

We then write:

$$\begin{aligned}\sum_{p=1}^{N}\frac{1}{R_{{\rm uv}(p)}^6} = &\frac{4\pi(r^{\rm u}+r^{\rm v})^2/(2r^{\rm v})^2}{(r^{\rm u}+r^{\rm v})^6}\\ &+\frac{4\pi(r^{\rm u}+3r^{\rm v})^2/(2r^{\rm v})^2}{(r^{\rm u}+3r^{\rm v})^6}\\ &+\frac{4\pi(r^{\rm u}+5r^{\rm v})^2/(2r^{\rm v})^2}{(r^{\rm u}+5r^{\rm v})^6}+\cdots\end{aligned} \tag{10}$$

where we can neglect terms higher than the third, so that we derive, approximately:

$$\begin{aligned}\sum_{p=1}^{N} 1/R_{{\rm uv}(p)}^6 = &\frac{\pi}{(r^{\rm v})^2}\{(r^{\rm u}+r^{\rm v})^{-4}\\ &+(r^{\rm u}+3r^{\rm v})^{-4}+(r^{\rm u}+5r^{\rm v})^{-4}\}\end{aligned} \tag{11}$$

General Formula.—From Eqs. 7, 8, 9 and 11, we obtain, for the frequency shift in an absorption transition from the ground state to the ith excited state of an isotropic molecule:

$$\begin{aligned}\varDelta\nu_{i0} = &-\frac{16\pi^3\boldsymbol{A}_0^2}{9\boldsymbol{hc}}\cdot\Big(\frac{d^{\rm v}}{M^{\rm v}}\Big)^{2/3}\times\Big[\Big\{\Big(\frac{M^{\rm u}}{d^{\rm u}}\Big)^{1/3}\\ &+\Big(\frac{M^{\rm v}}{d^{\rm v}}\Big)^{1/3}\Big\}^{-4}+\Big\{\Big(\frac{M^{\rm u}}{d^{\rm u}}\Big)^{1/3}+3\Big(\frac{M^{\rm v}}{d^{\rm v}}\Big)^{1/3}\Big\}^{-4}\\ &+\Big\{\Big(\frac{M^{\rm u}}{d^{\rm u}}\Big)^{1/3}+5\Big(\frac{M^{\rm v}}{d^{\rm v}}\Big)^{1/3}\Big\}^{-4}\Big]\times\Big[\frac{2}{3}\cdot\\ &\frac{(\mu_0^{\rm v})^2}{\boldsymbol{k}T}\{(\mu_i^{\rm u})^2-(\mu_0^{\rm u})^2\}+(\mu_0^{\rm v})^2\{(\alpha_i^{\rm u})\\ &-(\alpha_0^{\rm u})\}+(\alpha_0^{\rm v})\{(\mu_i^{\rm u})^2-(\mu_0^{\rm u})^2\}+\frac{3}{2}\cdot\\ &(\alpha_0^{\rm v})\cdot I_0^{\rm v}\Big\{\frac{I_0^{\rm u}-\boldsymbol{hc}\nu_{i0}^0}{I_0^{\rm v}+I_0^{\rm u}-\boldsymbol{hc}\nu_{i0}^0}\cdot(\alpha_i^{\rm u})\\ &-\frac{I_0^{\rm u}}{I_0^{\rm v}+I_0^{\rm u}}\cdot(\alpha_0^{\rm u})\Big\}\Big]\end{aligned} \tag{12}$$

where $16\pi^3\boldsymbol{A}_0^2/9\boldsymbol{hc} = 1.007\times10^{65}\ {\rm erg}^{-1}\,{\rm cm}^{-1}$ and $2/3\boldsymbol{k}T = 1.647\times10^{13}\ {\rm erg}^{-1}$ at 20°C.

Approximate Formula.—It is well-known that a molecular deformation polarization is approximately equal to a molecular refraction. We, therefore, have:

$$\alpha_0^{\rm v} = \frac{3}{4\pi\boldsymbol{A}_0}\cdot[R]^{\rm v} \tag{13}$$

where $[R]^{\rm v}$ denotes the molecular refraction of the solvent, which can be calculated as a sum of the atomic refractions from a table.

The values of $\alpha_i^{\rm u}$ and $\mu_i^{\rm u}$ are for the solute molecule in gas. According to the Clausius-Debye equation, we have:

$$\alpha_0^{\rm u} = \frac{3}{4\pi\boldsymbol{A}_0}\cdot\frac{M^{\rm u}}{d_0^{\rm u(g)}}\cdot\frac{\varepsilon_0^{\rm u}-1}{\varepsilon_0^{\rm u}+2} - \frac{(\mu_0^{\rm u})^2}{3\boldsymbol{k}T} \tag{14}$$

$$\alpha_i^{\rm u} = \frac{3}{4\pi\boldsymbol{A}_0}\cdot\frac{M^{\rm u}}{d_i^{\rm u(g)}}\cdot\frac{\varepsilon_i^{\rm u}-1}{\varepsilon_i^{\rm u}+2} - \frac{(\mu_i^{\rm u})^2}{3\boldsymbol{k}T} \tag{15}$$

where $d^{\rm u(g)}$ and $\varepsilon^{\rm u}$ denote the density and the dielectric constant of the solute in gas respectively.

On the assumption that all the molecules have the same positions in the ground and excited states of the solution, we may write:

$$d_0^{\rm u(g)} = d_i^{\rm u(g)} \tag{16}$$

From $I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0<I_0^{\mathrm{u}}$, we may suppose the following inequality, since $I_0^{\mathrm{v}}+I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0>I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0$, although $I_0^{\mathrm{v}}+I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0<I_0^{\mathrm{v}}+I_0^{\mathrm{u}}$:

$$\frac{I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0}{I_0^{\mathrm{v}}+I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0}<\frac{I_0^{\mathrm{u}}}{I_0^{\mathrm{v}}+I_0^{\mathrm{u}}} \tag{17}$$

It may be assumed that the dielectric constant of the excited state of the solute is greater than that for the ground state; that is:

$$\varepsilon_i^{\mathrm{u}}>\varepsilon_0^{\mathrm{u}}$$

From Eqs. 17 and 18, we may assume the following approximation:

$$\frac{I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0}{I_0^{\mathrm{v}}+I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0}\cdot\frac{\varepsilon_i^{\mathrm{u}}-1}{\varepsilon_i^{\mathrm{u}}+2}= \frac{I_0^{\mathrm{u}}}{I_0^{\mathrm{v}}+I_0^{\mathrm{u}}}\cdot\frac{\varepsilon_0^{\mathrm{u}}-1}{\varepsilon_0^{\mathrm{u}}+2} \tag{19}$$

Using Eqs. 13, 14, 15, 16 and 19, we may reduce Eq. 12 approximately to:

$$\begin{aligned}\Delta\nu_{i0}=&-\frac{4\pi^2\boldsymbol{A}_0}{3\boldsymbol{hc}}\cdot\left(\frac{d^{\mathrm{v}}}{M^{\mathrm{v}}}\right)^{2/3}\times\left[\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}\right.\right.\\&\left.+\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+3\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{u}}}\right)^{1/3}\right\}^{-4}\\&\left.+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+5\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}\right]\times\left[\frac{4\pi\boldsymbol{A}_0}{9\boldsymbol{k}T}\cdot\right.\\&(\mu_0^{\mathrm{v}})^2\{(\mu_i^{\mathrm{u}})^2-(\mu_0^{\mathrm{u}})^2\}+[R]^{\mathrm{v}}\{(\mu_i^{\mathrm{u}})^2-(\mu_0^{\mathrm{u}})^2\}\\&-\frac{1}{2\boldsymbol{k}T}\cdot I_0^{\mathrm{v}}\cdot[R]^{\mathrm{v}}\cdot\left\{\frac{I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0}{I_0^{\mathrm{v}}+I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0}\cdot(\mu_i^{\mathrm{u}})^2\right.\\&\left.\left.-\frac{I_0^{\mathrm{u}}}{I_0^{\mathrm{v}}+I_0^{\mathrm{u}}}\cdot(\mu_0^{\mathrm{u}})^2\right\}\right]\end{aligned} \tag{20}$$

where $4\pi^2\boldsymbol{A}_0/3\boldsymbol{hc}=3.992\times10^{40}\ \mathrm{erg}^{-1}\,\mathrm{cm}^{-1}$, $4\pi\boldsymbol{A}_0/9\boldsymbol{k}T=2.078\times10^{37}\ \mathrm{erg}^{-1}$, and $1/2\boldsymbol{k}T=1.236\times10^{13}\ \mathrm{erg}^{-1}$ at 20°C.

Discussion

Assuming that all the molecules in the solution are spherical, we have derived Eqs. 12 and 20. Accordingly, these equations are not applicable to rod-like molecules. For the rod-like molecules, the values of $\sum_{p=1}^{N}1/\mathrm{R}_{\mathrm{uv}(p)}^6$ must be otherwise estimated.

Equations 12 and 20 are limited for use to solutions in which no complete dipole orientations occur between solutes and solvent molecules, because Eq. 2 includes the isotropic polarizabilities. These equation, however, hold for the solutions in which there are strong dipole orientations among the solvent molecules, because Eq. 5 excludes this effect. When there is a complete dipole orientation between a solute and the solvent molecules, anisotropic polarizabilities must be used instead of the isotropic ones and Eq. 11 can not be applied.

When the frequency shifts are small, Eqs. 12 and 20 cannot be applied quantitatively, since the above assumptions do not hold.

When there is a small orientation effect between a solute and the solvent molecules, $\Delta\nu_{i0}^0$ is chiefly governed by the third term of the dispersion effect in the second bracket in Eq. 12. Accordingly, in order to calculate μ_i^{u}, it is better to apply Eq. 12 to the polar solvents, since the first term of the orientation effect in the second bracket is included.

As has been mentioned above, Nagakura and Baba[10] have found that the hydrogen bonding causes the frequency shifts. Since Eqs. 12 and 20 do not include this effect, they will give the deviated $\Delta\nu_{i0}$ from the observed frequency shift for a polar solvent forming a hydrogen bond with a solute. This deviation may be due to the hydrogen bonding.

The Relationship Between $\boldsymbol{\Delta\nu_{i0}}$ and the Refractive Index and the Dielectric Constant of the Solvent. — Considering that all the molecules do not interact in the zeroth order approximation, we have derived Eqs. 12 and 20. When we consider an unperturbed solute molecule and the solvent molecules already interacting with one another in the zeroth order approximation, we must write:

$$\begin{aligned}E_i'=&-\sum_{p=1}^{N}\frac{1}{R_{\mathrm{uv}(p)}^6}\left\{\frac{2}{3}\cdot\frac{(\mu_i^{\mathrm{u}})^2(\mu_0^{\mathrm{v}(p)})^2}{\boldsymbol{k}T}\right.\\&+(\alpha_i^{\mathrm{u}})(\mu_0^{\mathrm{v}(p)})^2+(\alpha_0^{\mathrm{v}(p)})(\mu_i^{\mathrm{u}})^2\\&\left.+\frac{3}{2}\cdot\frac{I_i^{\mathrm{u}}\cdot I_0^{\mathrm{v}(p)}}{I_i^{\mathrm{u}}+I_0^{\mathrm{v}(p)}}\cdot(\alpha_i^{\mathrm{u}})(\alpha_0^{\mathrm{u}(p)})\right\}\end{aligned} \tag{21}$$

where $\mu_0^{\mathrm{v}(p)}$ is the dipole moment, $\mu_0^{\mathrm{v}(1)}$, of the liquid solvent. By the same procedure we obtain the same final formulae as Eqs. 12 and 20. According to Onsager,[12] the dipole moment of the liquid solvent is given approximately by:

$$\begin{aligned}(\mu_0^{\mathrm{v}(1)})^2=&\frac{9\boldsymbol{k}T}{4\pi\boldsymbol{A}_0}\cdot\frac{M_{\mathrm{v}}}{d^{\mathrm{v}}}\cdot\\&\frac{\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\end{aligned} \tag{22}$$

Here ε^{v} and n^{v} denote the static dielectric constant of the solvent, and its refractive index extrapolated to zero frequency, respectively.

It is well-known that the molecular refraction can be expressed by:

$$[R]^{\mathrm{v}}=\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\cdot\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}} \tag{23}$$

For example, by putting Eqs. 22 and 23 into the same form as Eq. 20, we obtain:

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[12] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

TABLE I. THE π-π^* TRANSITION (240 mμ) IN NITROBENZENE

No.	Solvent	ν_{max}(cm^{-1})	μ_0(D, gas)[15]	$\alpha_0\times10^{25}$(cm^3)[15]	I_0(eV.)
	Nitrobenzene (gas)	41680[13]	4.23	129.2	10.15[16]
1	*n*-Heptane	39700[13]	0	136.1	10.35[15]
2	Cycohexane	39540[13]	0	108.7	9.24[17]
3	Carbon tetrachloride	39170[14]	0	105	11.0[15]
4	Dioxane	38650[13]	0	94.4	9.52[17]
5	Chloroform	38150[14]	1.05	82.3	11.5[15]

$$\varDelta\nu_{i0}=-\frac{4\pi^2\boldsymbol{A}_0}{3\boldsymbol{hc}}\cdot\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\times\left[\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+3\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+5\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}\right]\times\left[\frac{\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\cdot\{(\mu_i^{\mathrm{u}})^2-(\mu_0^{\mathrm{u}})^2\}+\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\{(\mu_i^{\mathrm{u}})^2-(\mu_0^{\mathrm{u}})^2\}-\frac{1}{2kT}\cdot\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\cdot I_0^{\mathrm{v}}\left\{\frac{I_0^{\mathrm{u}}+\boldsymbol{hc}\nu_{i0}^0}{I_0^{\mathrm{v}}+I_0^{\mathrm{u}}-\boldsymbol{hc}\nu_{i0}^0}\cdot(\mu_i^{\mathrm{u}})^2-\frac{I_0^{\mathrm{u}}}{I_0^{\mathrm{v}}+I_0^{\mathrm{u}}}\cdot(\mu_0^{\mathrm{u}})^2\right\}\right] \tag{24}$$

where the refractive index may be replaced approximately by the value appropriate to the sodium-D line.

Application

The Application of Eq. 12 to Nitrobenzene.—The frequency shifts of the 239.9 mμ band of nitrobenzene in solvents and the other observed values to be used are listed in Table I. The values of d from Lange's table[18] and other sources were used for 20°C. Assuming that the temperature is 20°C, the author can apply Eq. 12 to nitrobenzene. By means of the least square method, α_i^{u} and μ_i^{u} are estimated as 580.7×10^{-25} cm^3 and 8.18 D respectively. Putting the above values into Eq. 12, the author obtained a good agreement in the frequency shifts between the theoretical and the experimental results, as is indicated in Fig. 1. The finding that the dipole moment of the excited state caused by the 240 mμ transition in nitrobenzene is greater than that for the ground state is consistent with Nagakura and Tanaka's theory.[19] They have interpreted the band of nitrobenzene in terms of the intramolecular charge-transfer involving an excitation of a bonding electron of the highest-occupied orbital of benzene to the vacant orbital of the nitro group. Bayliss and McRae[15,20] have also mentioned that there is a greater dipole moment in the excited state of nitrobenzene.

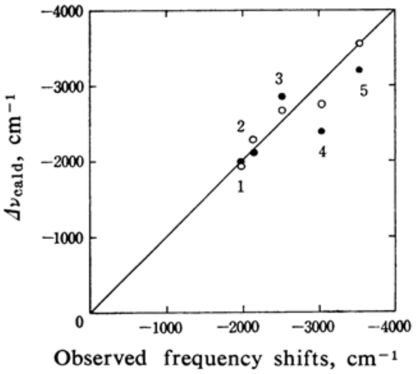

Fig. 1. Calculated vs. observed frequency shifts in the 240 mμ band of nitrobenzene.
○ calculated from Eq. 12
● calculated from Eq. 20

The Application of Eq. 20 to Nitrobenzene.—Equation 20 is applied to the frequency shift of the 240 mμ band of nitrobenzene at 20°C. The values of $[R]^{\mathrm{v}}$ were calculated from a table. By putting the observed shift for *n*-heptane into Eq. 20, the author estimated μ_i^{u} to be 4.67 D, and then, using that value, he calculated the frequency shifts for other solvents, as Fig. 1 indicates. The μ_i^{u} value of 4.67 D is considerably smaller than that obtained from Eq. 12. The points calculated from Eq. 20 are also worse fitted to the full straight line than those calculated from Eq. 12, as is shown in Fig. 1.

The Application of Eq. 20 to Acetophenone.—The frequency shifts of the 231.3 mμ band of acetophenone in non-polar solvents are listed in Table II.

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13) W. M. Schubert, J. Robins and J. L. Haun, ibid., **79**, 910 (1957).

14) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954).

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16) S. Nagakura and J. Tanaka, This Bulletin, **32**, 734 (1959).

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19) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

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TABLE II. THE π-π^* TRANSITIONE IN ACETOPHENONE

Solvent	ν_{max} (cm^{-1})[13]
Acetophenone (gas)	43230
n-Heptane	41980
Cyclohexane	41940

The ionization potential of acetophenone is 9.77 eV.[15] Putting the observed shifts into Eq. 20 at 20°C, the author has estimated μ_0^u and μ_i^u to be 3.81 and 4.42 D respectively. The value of 3.81 D accords fairly with the experimental value of 3.00 D (gas).[15] The result of $\mu_i^u > \mu_0^u$ is consistent with the intramolecular charge-transfer band[19,21,22] and with Bayliss and McRae's interpretation.[20]

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