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Theory of Solvent Effects on Oscillator Strengths for Molecular Electronic Transitions

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A theoretical expression has been presented for an oscillator strength of an electronic transition in a solute molecule immersed in an isotropic dielectric continuum of solvent. It is assumed that a charged particle in the solute is subjected to a force due to a cavity field. The approximate expression derived on the basis of a quantum-mechanical perturbation theory has been successfully tested for nitrobenzene and acetone.

Many theoretical expressions have recently been presented for solvent effects on frequency shifts in electronic absorption spectra. There are, however, few theoretical expressions relating to solvent effects on intensities of electronic transitions in solute molecules. The only explicit expression relating an oscillator strength of solution to that of vapor was given by Chako¹⁾ who used the classical dispersion theory. Schuyer²⁾ gave a classical extension relating a molar extinction coefficient of solution to that of vapor. Weigang³⁾ and Liptay⁴⁾ independently presented expressions of an integrated intensity.

In the present work, attempts are made to present a new expression for the oscillator strength of solution on the basis of a quantum-mechanical theory, and to compare the result with previous theories. The approximate expression is applied to the data for nitrobenzene and acetone.

Theoretical

Spectra of solutions are usually measured at very low concentrations. Let us consider a solution containing numerous solvent molecules and one neutral solute molecule, and assume that the solute molecule is contained within a spherical cavity in an isotropic continuous medium of the solvent. According to the Franck-Condon principle the same molecular configurations are assumed for the ground and excited states of the solute. The present theory does not include specific effects like hydrogen bonding and complexing.

Solution spectra are commonly measured by using transparent solvents. Thus we can assume that the electronic absorption region of the solvent is at shorter wavelengths than that of the solute.

We consider an electromagnetic radiation field of frequency ν with an electric field $\vec{E}$. The change of field $\vec{E}$ with time t may be written as

$$\vec{E}(\nu) = -\frac{1}{\sqrt{\varepsilon(\nu)}\,\{c/n(\nu)\}} \times \frac{\partial}{\partial t}\vec{A} \qquad (1)$$

where $\vec{A}$ is a vector potential, $\boldsymbol{c}$ is the velocity of light in a vacuum, and $n(\nu)$ and $\varepsilon(\nu)$ are the refractive index and dielectric constant of the solvent at ν, respectively. In Eq. (1) a scalar potential is neglected, since the wavelength of the radiation is much longer than the diameter of the cavity. In electromagnetic theory a radiation density $\rho(\nu)$ is given by:

$$\rho(\nu) = \frac{\varepsilon(\nu)}{4\pi} \times \overline{E^2(\nu)} \qquad (2)$$

Applying the Onsager cavity field, the author assumes that a particle of charge e_j in the solute molecule immersed in the solvent in the presence of the electromagnetic field is subjected to the force

$$\vec{F} = e_j \times \frac{3n^2(\nu)}{2n^2(\nu)+1} \times \vec{E}(\nu) \qquad (3)$$

Reaction field is neglected herewith, assuming that the effect of the reaction field is much smaller than that of the cavity field. The effect of magnetic intensity of light is also neglected, since the velocity of electrons in the solute is small compared to that of light.

Starting from Eq. (3) and calculating in the same way as Eyring, Walter and Kimball,⁵⁾ we can approximately write the Einstein transition probability coefficient $B_{0\to i}$ for an electronic transition from the ground state to the ith-excited state in the solute molecule as

$$B_{0\to i} = \frac{8\pi^3}{3\boldsymbol{h}^2} \times \frac{9n_{\mathrm{D}}^2}{(2n_{\mathrm{D}}^2+1)^2} \times |\overrightarrow{\mu_{0i}^0}|^2 \qquad (4)$$

where $\boldsymbol{h}$ is the Planck constant, n_{D} is the refractive index of the solvent at the frequency of sodium-D line, and $\overrightarrow{\mu_{0i}^0}$ is the transition moment from the ground state to the ith-excited state for the free solute molecule. In Eq. (4) $n(\nu)$ is replaced approximately by n_{D}.

By the definition of oscillator strength, we find the theoretical expression for the oscillator strength of the transition of the solute molecule in solution from Eq. (4) as

$$f_{0\to i}^{\mathrm{theor}}(\mathrm{soln}) = \frac{\boldsymbol{mhc}\tilde{\nu}_{0i}}{\pi \boldsymbol{e}^2} \times B_{0\to i}$$
$$= \frac{8\pi^2\boldsymbol{cm}}{3\boldsymbol{he}^2} \times \frac{9n_{\mathrm{D}}^2}{(2n_{\mathrm{D}}^2+1)^2} \times \tilde{\nu}_{0i}|\overrightarrow{\mu_{0i}^0}|^2 \qquad (5)$$

where $\boldsymbol{e}$ and $\boldsymbol{m}$ are the charge and mass of an electron, respectively, and $\tilde{\nu}_{0i}$ is the transition energy of the solute in solution in unit of cm^{-1}. From Eq. (5), we find the relation

$$f_{0\to i}^{\mathrm{theor}}(\mathrm{soln})/f_{0\to i}^{\mathrm{theor}}(\mathrm{vap}) = \frac{9n_{\mathrm{D}}^2}{(2n_{\mathrm{D}}^2+1)^2} \times \frac{\tilde{\nu}_{0i}^0}{\tilde{\nu}_{0i}^0} \qquad (6)$$

where $\tilde{\nu}_{0i}^0$ is the transition energy of the free solute.

When the traditional Lorentz field is used instead of the Onsager cavity field, we can derive the following approximate expression by the same method as described above.

$$B_{0\to i} = \frac{8\pi^3}{3\boldsymbol{h}^2} \times \frac{1}{n_{\mathrm{D}}^2} \times \left(\frac{n_{\mathrm{D}}^2+2}{3}\right)^2 \times |\overrightarrow{\mu_{0i}^0}|^2 \qquad (7)$$

Thus we have

$$f_{0\to i}^{\mathrm{theor}}(\mathrm{soln}) = \frac{8\pi^2\boldsymbol{cm}}{3\boldsymbol{he}^2} \times \frac{(n_{\mathrm{D}}^2+2)^2}{9n_{\mathrm{D}}^2} \times \tilde{\nu}_{0i}|\overrightarrow{\mu_{0i}^0}|^2 \qquad (8)$$

Accordingly, we have the relation

$$f_{0\to i}^{\mathrm{theor}}(\mathrm{soln})/f_{0\to i}^{\mathrm{theor}}(\mathrm{vap}) = \frac{(n_{\mathrm{D}}^2+2)^2}{9n_{\mathrm{D}}^2} \times \frac{\tilde{\nu}_{0i}}{\tilde{\nu}_{0i}^0} \qquad (9)$$

Experimental Expression for Solution Oscillator Strength. The experimental oscillator strength for the solute molecule in solution has been customarily determined by

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1) N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

2) J. Schuyer, *Rec. Trav. Chim. Pays-Bas*, **72**, 933 (1953).

3) O. E. Weigang, Jr., *J. Chem. Phys.*, **41**, 1435 (1964).

4) W. Liptay, *Z. Naturforsch.*, **21A**, 1605 (1966).

5) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons, Inc., New York (1949), p. 107.

$$\bar{f}^{\text{exp}}_{0\to i}(\text{soln}) = \frac{10^3 \ln 10\cdot m\boldsymbol{c}^2}{\pi \boldsymbol{e}^2\boldsymbol{N}}\int \kappa(\tilde{\nu})\mathrm{d}\tilde{\nu} \tag{10}$$

where $\boldsymbol{N}$ is the Avogadro number, and $k(\tilde{\nu})$ is a molar extinction coefficient. Equation (10) has been derived on the assumption that the velocity of light in the solution is equal to that in a vacuum. When the velocity of light in the solution is considered by replacing $\boldsymbol{c}$ by $\boldsymbol{c}/n(\nu)$, as pointed out by Baba,[6] we can approximately write

$$f^{\text{exp}}_{0\to i}(\text{soln}) = \frac{10^3 \ln 10\cdot m\boldsymbol{c}^2}{\pi \boldsymbol{e}^2\boldsymbol{N}}\times\frac{1}{n_{\text{D}}^2}\int \kappa(\tilde{\nu})\mathrm{d}\tilde{\nu} \tag{11}$$

Thus we can relate $\bar{f}^{\text{exp}}_{0\to i}(\text{soln})$ to $f^{\text{exp}}_{0\to i}(\text{soln})$ as

$$f^{\text{exp}}_{0\to i}(\text{soln}) = (1/n_{\text{D}}^2)\times \bar{f}^{\text{exp}}_{0\to i}(\text{soln}) \tag{12}$$

Discussion

The Onsager cavity model is adopted in the present theory. Any deviation of the cavity from spherical symmetry would result in a great difference between the observed and theoretical ratios of the oscillator strength of solution to that of vapor. It is, however, probable that a thermal motion makes the cavity nearly spherical.

If the Onsager reaction field is considered in Eq. (3), the expression for the oscillator strength will differ from Eq. (5), but the difference will not be great.

Equations (5) and (8) show that the effective microscopic fields and the dielectric constant of the solvent at ν_{0i} have important roles for the solvent effects on the oscillator strength. It is, of course, better to use the refractive index measured at the frequency of ν_{0i}, although n_{D} was used herewith for the sake of convenience.

Previous Theories. *(1) Chako's Formula.* Chako's formula[1] based on the classical dispersion theory is usually written as

$$f^{\text{theor}}_{0\to i}(\text{soln})/f^{\text{theor}}_{0\to i}(\text{vap}) = (n_{\text{D}}^2+2)^2/9n_{\text{D}} \tag{13}$$

(2) Schuyer's Theory. An original formula (Eq. (29) in Ref. 2) derived by Schuyer[2] from the theory of Onsager-Böttcher may be approximately written as

$$\frac{(2n_{\text{D}}^2+1)(n_{\text{D}}^2+1)}{6n_{\text{D}}^3}\times\kappa(\tilde{\nu}_{0i}) = \text{constant} \tag{14}$$

Combining Eq. (14) with $k^0(\tilde{\nu}_{0i}) = \text{constant}$ for $n_{\text{D}} = 1$, we have

$$\kappa(\tilde{\nu}_{0i}) = \frac{6n_{\text{D}}^3}{(2n_{\text{D}}^2+1)(n_{\text{D}}^2+1)}\times\kappa^0(\tilde{\nu}_{0i}) \tag{15}$$

Putting Eq. (15) into Eq. (11), we obtain after some calculation

$$f_{0\to i}(\text{soln})/f_{0\to i}(\text{vap}) = 6n_{\text{D}}/(2n_{\text{D}}^2+1)(n_{\text{D}}^2+1) \tag{16}$$

Assuming the simple relation $f_{0\to i}(\text{soln})/f_{0\to i}(\text{vap}) = k(\tilde{\nu}_{0i})/k^0(\tilde{\nu}_{0i})$ on the basis of Schuyer's theory, Bayliss and Wills-Johnson[7] presented a formula different from Eq. (16).

(3) Weigang's Theory. Applying Moffitt and Moscowitz's formula[8] for dispersion, Weigang[3] presented the expression

$$\int\frac{\kappa(\nu)}{\nu}\mathrm{d}\nu = \frac{8\pi^3\boldsymbol{N}}{3\times 10^3\ln 10\cdot\boldsymbol{hc}}\times\frac{\{n^2(\nu)+2\}^2}{9n(\nu)}\times\frac{|\overrightarrow{\mu_{0i}}|^2}{k} \tag{17}$$

where k is the number of the solute molecules contained in a small cavity, and $\overrightarrow{\mu_{0i}}$ is the transition moment for the solute molecule in solution. The Lorentz condition is included in Eq. (17). Using Weigang's expression[3] for $\overrightarrow{\mu_{0i}}$, we may write $B_{0\to i}$ as follows

$$\begin{aligned} B_{0\to i} &= \frac{10^3\ln 10\cdot(\boldsymbol{c}/n_{\text{D}})}{\boldsymbol{hN}}\int\frac{\kappa(\nu)}{\nu}\mathrm{d}\nu \\ &= \frac{8\pi^3}{3\boldsymbol{h}^2}\times\frac{(n_{\text{D}}^2+2)^2}{9n_{\text{D}}^2}\times|\overrightarrow{\mu^0_{0i}}|^2\times\left\{1+A\times\frac{n_{\text{D}}^2-1}{2n_{\text{D}}^2+1}\right. \\ &\quad\left.+B\times\frac{n_{\text{D}}^2-1}{2n_{\text{D}}^2+1}-C\left(\frac{\varepsilon_0-1}{\varepsilon_0+2}-\frac{n_{\text{D}}^2-1}{n_{\text{D}}^2+2}\right)\right\}^2 \end{aligned} \tag{18}$$

where the coefficients of A, B and C are characteristic of the solute, the cavity radius and the absolute temperature. Equation (18) may be approximated to Eq. (7). Thus we obtain the relation identical to Eq. (9) from Weigang's theory.

(4) Liptay's Theory. Liptay[4] presented the following formula.

$$\begin{aligned} \int\frac{\kappa(\tilde{\nu})}{\tilde{\nu}}\mathrm{d}\tilde{\nu} &= \frac{8\pi^3\boldsymbol{N}}{2.303\times 10^3\times 3\boldsymbol{h}(\boldsymbol{c}/n_{\text{D}})}\times|\overrightarrow{\mu^0_{0i}}|^2 \\ &= \frac{8\pi^3\boldsymbol{N}}{2.303\times 10^3\times 3\boldsymbol{h}(\boldsymbol{c}/n_{\text{D}})}\times[|\overrightarrow{\mu^0_{0i}}|^2+\tilde{R}\overrightarrow{F}_{\text{RW}} \\ &\quad+\tilde{F}_{\text{RW}}(\overrightarrow{P}+\overrightarrow{Q})\overrightarrow{F}_{\text{RW}}+2\boldsymbol{Re}\{\tilde{\mu}^0_{0i}\overrightarrow{W}_{0i}\}f'] \end{aligned} \tag{19}$$

Here the notations refer to Liptay's original paper. In Eq. (19), $\boldsymbol{c}$ in the original formula of Liptay is replaced by $\boldsymbol{c}/n_{\text{D}}$. Carrying out the same calculation as in the case of Weigang's theory, we obtain approximately

$$f_{0\to i}(\text{soln})/f_{0\to i}(\text{vap}) = \tilde{\nu}_{0i}/\tilde{\nu}^0_{0i} \tag{20}$$

It is obvious from Eq. (19) that Liptay did not consider any effective microscopic field such as the Onsager cavity or Lorentz field.

Application

Equations (6), (9), (13), (16) and (20) were applied to the 240 mμ band of nitrobenzene and to the 280 mμ band of acetone. The results are summarized in Tables 1 and 2.

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[6] H. Baba, "Zikkenkagaku Koza," Ser. 11, ed. by Chem. Soc., Japan, Maruzen, Tokyo (1965), p. 22.

[7] N. S. Bayliss and G. Wills-Johnson, *Spectrochim. Acta*, **24A**, 551 (1968).

[8] W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).

TABLE 1. THE π-π^* TRANSITION OF NITROBENZENE

Solvent	$\tilde{\nu}_{\rm max}$ cm^{-1}	$\bar{f}^{\rm exp}$	$\frac{f^{\rm exp}({\rm soln})}{f^{\rm exp}({\rm vap})}$	$\frac{f^{\rm theor}({\rm soln})}{f^{\rm theor}({\rm vap})}$				
				Eq. (6) (Abe)	Eq. (9) (Abe, Weigang)	Eq. (13) (Chako)	Eq. (16) (Schuyer)	Eq. (20) (Liptay)
Vapor	41670$^{9)}$	0.17$^{9)}$	1	1	1	1	1	1
n-Heptane	39740$^{10)}$	0.23$^{10)}$	0.70$_3$	0.702	0.848	1.23	0.587	0.954
Cyclohexane	39540$^{10)}$	0.26$^{10)}$	0.75$_2$	0.677	0.844	1.27	0.556	0.949
Chloroform	38150$^{10)}$	0.25$^{10)}$	0.70$_4$	0.642	0.814	1.29	0.542	0.916

TABLE 2. THE n-π^* TRANSITION OF ACETONE

Solvent	$n_{\rm D}^{20}$	$\tilde{\nu}_{\rm max}$$^{7)}$ cm^{-1}	$\frac{f^{\rm exp}({\rm soln})}{f^{\rm exp}({\rm vap})}$		$\frac{f^{\rm theor}({\rm soln})}{f^{\rm theor}({\rm vap})}$				
			Ref. 7	Ref. 10	Eq.(6)	Eq.(9)	Eq.(13)	Eq.(16)	Eq.(20)
Vapor	1	36100	1	1	1	1	1	1	1
n-Heptane	1.3876	35800	0.636	0.654	0.730	0.882	1.23	0.587	0.992
Isooctane	1.3915	35800	0.584	—	0.728	0.882	1.24	0.584	0.992
Cyclohexane	1.4262	35700	0.502	0.708	0.705	0.879	1.27	0.556	0.989
Benzene	1.5011	35450	0.471	—	0.657	0.876	1.34	0.503	0.982
Carbon tetrachloride	1.4604	35650	0.618	0.896	0.683	0.879	1.30	0.531	0.988
Chloroform	1.4457(19°)	36250	0.626	0.761	0.704	0.893	1.29	0.542	1.004
Dichloromethane	1.4237	36300	0.594	—	0.718	0.894	1.27	0.558	1.006
Diethylether	1.3497 (24.8°)	36050	0.780	—	0.759	0.890	1.20	0.618	0.999

TABLE 3. RATIOS OF CUSTOMARY OSCILLATOR STRENGTHS OF NITROBENZENE

Solvent	$n^{10)}$ 2800 Å	$\frac{\bar{f}^{\rm exp}({\rm soln})}{\bar{f}^{\rm exp}({\rm vap})}$ (from Refs. 9 and 10)	$\frac{n^2 f^{\rm theor}({\rm soln})}{f^{\rm theor}({\rm vap})}$ (Eq. (6) $\times n^2$)
Vapor	—	1	1
n-Heptane	1.42	1.3$_5$	1.38
Cyclohexane	1.47	1.5$_3$	1.41
Chlororoform	1.50	1.4$_7$	1.38

The ratio of the customary experimental oscillator strength of solution to that of vapor can be directly compared with the theoretical value. Using Eq. (6) and values of refractive indexes for 2800 Å, the values of $\bar{f}^{\rm exp}({\rm soln})/\bar{f}^{\rm exp}({\rm vap})$ were compared with those of $n^2 f^{\rm theor}({\rm soln})/f^{\rm theor}({\rm vap})$, as indicated in Table 3.

The values of $\bar{f}^{\rm exp}$ by Bayliss and Wills-Johnson were computed by assuming the spectra to be symmetric about absorption maxima.[7] As Bayliss and Wills-Johnson[7] mentioned, the determination of oscillator strength is complicated by the fact that the transitions under investigation are overlapped by other transitions. In view of the above discussion, Tables 1—3 seem to show that Eq. (6) best reproduces the experimental results among the five theoretical formulas.

The author is particularly indebted to Professor Yoshito Amako for discussion.

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9) S. Nagakura, M. Kojima and Y. Maruyama, *J. Mol. Spectrosc.*, **13**, 174 (1964).

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