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# Solvent Effects on the n$\pi$* and $\pi\pi$* Absorption Intensities of Some Organic Molecules

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Recently proposed experimental and theoretical expressions for the molecular electronic oscillator strength in a solution (*J. Chem. Phys.*, **83**, 1546 (1985)) have been succesfully applied to the spectral data of some nonpolar and polar organic molecules (benzoquinones, ketones, nitroalkanes, $\beta$-carotene, and substituted benzenes). In an application of the theoretical expression, the transition moment of a nonpolar solute molecule in various solvents was assumed to be approximately constant, while that of a polar solute molecule was developed on the assumptions of a first-order perturbation of the wave function and a Block-Walker reaction field. The ratio of the oscillator strength in a solution to that either in a vapor or a specified solvent was computed from both experimental data and theoretically from the transition moments. The results of the two computational modes are, generally, in good agreement for the range of compounds studied.

For an electronic transition from the ground state to the $i$th excited state in a solute molecule, we have recently proposed the following equations[1] for the experimental and theoretical oscillator strengths in a solution:

$$f^{\mathrm{exp}}(\mathrm{soln}) = \frac{4n}{(1+n)^2} \times \frac{10^3(\ln 10)m_e c^2}{\pi e^2 L}\int \varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu} \tag{1}$$

and

$$f^{\mathrm{theor}}(\mathrm{soln}) = \frac{36n^4}{(1+n)^2(2n+1)^2} \times \frac{8\pi^2 m_e c}{3he^2} \times \tilde{\nu}_{0i}|\mu_{0i}(\mathrm{soln})|^2, \tag{2}$$

where $n$ is the refractive index of the solvent, $c$ the speed of light in a vacuum, $h$ the Planck constant, $e$ the charge of a proton, $m_e$ the mass of an electron, and $L$ Avogadro's constant. Here, $\tilde{\nu}_{0i}$ is the wave number of the transition, $\varepsilon(\tilde{\nu})$ the molar absorption coefficient at a wave number $\tilde{\nu}$, and $\mu_{0i}$(soln) the transition moment of a solute molecule in a solution. Then, the ratio of the oscillator strength in, for example, two solvents (denoted by subscripts 1 and 2), i.e., $f^{\mathrm{exp}}$(soln 2)/$f^{\mathrm{exp}}$(soln 1), gives a ratio of the energies absorbed per unit time by the transitions, as described in a previous paper.[1]

Here, by either assuming a constant value for $\mu_{0i}$(soln) or using first-order perturbation theory to find an approximate expression for $\mu_{0i}$(soln), we apply Eqs. 1 and 2 to the n$\pi$*- and $\pi\pi$*-absorption spectral data which are available for several compounds and demonstrate that our previously proposed expressions for the oscillator strength of a molecule in a solution give fairly good results.

## Theory

We can write the oscillator strength of a gaseous absorbing system as $f$(vap), and the usual experimental oscillator strength in a solution ($n$=1) as $\bar{f}^{\mathrm{exp}}$(soln). Then, from Eqs. 1 and 2 the following equations can be derived:

$$\frac{f^{\mathrm{exp}}(\mathrm{soln})}{f^{\mathrm{exp}}(\mathrm{vap})} = \frac{4n}{(1+n)^2} \times \frac{\bar{f}^{\mathrm{exp}}(\mathrm{soln})}{f^{\mathrm{exp}}(\mathrm{vap})} \tag{3}$$

and

$$\frac{f^{\mathrm{theor}}(\mathrm{soln})}{f^{\mathrm{theor}}(\mathrm{vap})} = \frac{36n^4}{(1+n)^2(2n^2+1)^2} \times \frac{\tilde{\nu}_{0i}|\mu_{0i}(\mathrm{soln})|^2}{\tilde{\nu}^{\circ}_{0i}|\mu^{\circ}_{0i}|^2}, \tag{4}$$

where $\tilde{\nu}^{\circ}_{0i}$ and $\mu^{\circ}_{0i}$ are the transition energy (in cm$^{-1}$) and the transition moment, respectively, of the isolated solute molecule. In a case where there are no data in the literature for $f^{\mathrm{exp}}$(vap), we used equations corresponding to $f^{\mathrm{exp}}$(soln 2)/$f^{\mathrm{exp}}$(soln 1) and $f^{\mathrm{theor}}$(soln 2)/$f^{\mathrm{theor}}$(soln 1) instead of Eqs. 3 and 4, respectively.

In the present analysis, $\mu_{0i}$(soln) are not transition moments like those formulated by Weigang[2] and Myers and Birge[3] for a system that includes a solute and many solvent molecules, but rather for a single solute molecule in a solution. Even Liptay's generalized expression[4] for $\mu_{0i}$(soln) is still difficult to apply practically. We have, however, found an approximate expression for $\mu_{0i}$(soln) in the following two ways:

**Approximation of $\mu_{0i}$(soln) for Nonpolar Solute Molecules.** Since, in this case, there is usually no data in the literature for $f^{\mathrm{exp}}$(vap), we have adopted an equation corresponding to the expression $f^{\mathrm{theor}}$(soln 2)/$f^{\mathrm{theor}}$(soln 1) instead of Eq. 4. Further, for a nonpolar solute molecule, we assumed that the values of $\mu_{0i}$(soln) in various solvents are approximately constant, since a solute molecule has no dipole moment. From this assumption, it follows from Eq. 2 that

$$\frac{f^{\mathrm{theor}}(\mathrm{soln\ 2})}{f^{\mathrm{theor}}(\mathrm{soln\ 1})} = \frac{F(\mathrm{soln\ 2})\tilde{\nu}_{0i}(\mathrm{soln\ 2})}{F(\mathrm{soln\ 1})\tilde{\nu}_{0i}(\mathrm{soln\ 1})}, \tag{5}$$

where $F(\mathrm{soln}\ i)=36n^4/(1+n)^2(2n^2+1)^2$ and $\tilde{\nu}_{0i}(\mathrm{soln}\ i)$ are, respectively, the solvent correction factor and the transition wave number for the $i$th solvent. By using

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Eq. 3, we obtained experimental values for $f^{\mathrm{exp}}$(soln 2)/$f^{\mathrm{exp}}$(soln 1); these results could be compared with those of Eq. 5.

**Approximation of $\mu_{0i}$(soln) for Polar Solute Molecules.** For a polar solute molecule, we formulated an approximate expression for $\mu_{0i}$(soln) by using the Block–Walker reaction field.[5)]

The ground and $i$th excited state of a neutral solute molecule are denoted by the wave functions $\Psi_0$ and $\Psi_i$, respectively. According to first-order perturbation theory, $\Psi_i$, for example, can be written as

$$\Psi_i = \Psi_i^\circ + \sum_{k\neq i} \frac{(\Psi_k^{\circ *}|H'|\Psi_i^\circ)}{E_i^\circ - E_k^\circ}\Psi_k^\circ, \tag{6}$$

where $E_k^\circ$ is the energy of the $k$th excited state ($\Psi_k^\circ$) for an isolated solute molecule. The perturbation operator $H'$ is written as[6,7)]

$$H' = -\sum_j e_j \boldsymbol{R}\cdot\boldsymbol{r}_j. \tag{7}$$

Here, $e_j$ and $\boldsymbol{r}_j$ are the charge and position vector of the $j$th charged particle in the solute molecule, and $\boldsymbol{R}$ is the reaction field. The expression $\Psi_0$ is similarly obtained by replacing $i$ with 0 in Eq. 6. We denote, for example, the average of all values of $(E_k^\circ - E_i^\circ)$ by $\Delta E_i$ and assume that $\Delta E_i = \Delta E_0 = I_0$, as was done in a previous paper,[8)] where $I_0$ denotes the ionization potential of the ground state of an isolated solute molecule. We then obtain the following approximate expression for $\mu_{0i}$(soln):

$$\begin{aligned}
\mu_{0i}(\mathrm{soln}) &= (\Psi_i^*|\Sigma e_j\boldsymbol{r}_j|\Psi_0) \\
&\approx \mu_{0i}^\circ - \frac{1}{I_0}\{\sum_{k\neq 0}(\Psi_0^{\circ *}|H'|\Psi_k^\circ)(\Psi_k^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_i^\circ) \\
&\qquad + \sum_{k\neq i}(\Psi_i^{\circ *}|H'|\Psi_k^\circ)(\Psi_k^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_0^\circ)\} \\
&\quad + \frac{1}{I_0^2}\sum_{l\neq i}\sum_{k\neq 0}(\Psi_0^{\circ *}|H'|\Psi_k^\circ)(\Psi_i^{\circ *}|H'|\Psi_l^\circ)(\Psi_l^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_k^\circ) \\
&= \mu_{0i}^\circ + \frac{\boldsymbol{R}}{I_0}[\{\sum_k^{\mathrm{all}}(\Psi_0^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_k^\circ)(\Psi_k^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_i^\circ) \\
&\qquad - (\Psi_0^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_0^\circ)(\Psi_0^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_i^\circ)\} \\
&\qquad + \{\sum_k^{\mathrm{all}}(\Psi_i^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_k^\circ)(\Psi_k^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_0^\circ) \\
&\qquad - (\Psi_i^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_i^\circ)(\Psi_i^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_0^\circ)\}] \\
&\quad + \frac{R^2}{I_0^2}\sum_{l\neq i}\sum_{k\neq 0}\left\{\frac{\boldsymbol{R}}{R}(\Psi_0^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_k^\circ)\right\} \\
&\qquad \times \left\{\frac{\boldsymbol{R}}{R}(\Psi_i^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_l^\circ)\right\} \times (\Psi_l^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_k^\circ) \\
&= \mu_{0i}^\circ + \frac{\boldsymbol{R}}{I_0}\times(2Q_{0i}^\circ - \mu_{0i}^\circ\boldsymbol{p}_0^\circ - \mu_{0i}^\circ\boldsymbol{p}_i^\circ) + \frac{R^2}{I_0^2}\times \boldsymbol{R}_{0k,il}^\circ,
\end{aligned} \tag{8}$$

where $\boldsymbol{p}_0^\circ$ and $\boldsymbol{p}_i^\circ$ are the ground- and $i$th-excited-state electric dipole moments, respectively, of the isolated solute molecule and

$$Q_{0i}^\circ = \sum_k^{\mathrm{all}}(\Psi_0^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_k^\circ)(\Psi_k^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_i^\circ) = (\Psi_i^{\circ *}|(\Sigma e_j\boldsymbol{r}_j)^2|\Psi_0^\circ) \tag{9}$$

and

$$\begin{aligned}
\boldsymbol{R}_{0k,il}^\circ = \sum_{l\neq i}\sum_{k\neq 0}&\left\{\frac{\boldsymbol{p}_0^\circ}{p_0^\circ}(\Psi_0^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_k^\circ)\right\} \\
&\times\left\{\frac{\boldsymbol{p}_0^\circ}{p_0^\circ}(\Psi_i^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_l^\circ)\right\}\times(\Psi_l^{\circ *}|\Sigma e_j\boldsymbol{r}_j|\Psi_k^\circ).
\end{aligned} \tag{10}$$

If the Block-Walker reaction field[5)] is written as

$$\boldsymbol{R} = \frac{\theta(\varepsilon_\mathrm{r})}{a^3}\boldsymbol{p}_0^\circ, \tag{11}$$

where

$$\theta(\varepsilon_\mathrm{r}) = \frac{3\varepsilon_\mathrm{r}\ln\varepsilon_\mathrm{r}}{\varepsilon_\mathrm{r}\ln\varepsilon_\mathrm{r} - \varepsilon_\mathrm{r} + 1} - \frac{6}{\ln\varepsilon_\mathrm{r}} - 2 \tag{12}$$

and $a$ and $\varepsilon_\mathrm{r}$ are the cavity radius of the solute molecule and the relative permittivity of the solvent, respectively, the following expression for $\mu_{0i}$(soln) is obtained from Eq. 8:

$$\mu_{0i}(\mathrm{soln}) = \mu_{0i}^\circ\{1 + \theta(\varepsilon_\mathrm{r})\times A + \theta^2(\varepsilon_\mathrm{r})\times B\}. \tag{13}$$

Here, $A$ and $B$ are characteristic of a solute molecule and are expressed as

$$A = \frac{\boldsymbol{p}_0^\circ}{a^3 I_0}\left\{\frac{2\mu_{0i}^\circ Q_{0i}^\circ}{(\mu_{0i}^\circ)^2} - \boldsymbol{p}_0^\circ - \boldsymbol{p}_i^\circ\right\} \tag{14}$$

and

$$B = \frac{(\boldsymbol{p}_0^\circ)^2\mu_{0i}^\circ\boldsymbol{R}_{0k,il}^\circ}{a^6 I_0^2(\mu_{0i}^\circ)^2}. \tag{15}$$

Substituting Eq. 13 into Eq. 4 makes $f^{\mathrm{theor}}$(soln)/$f^{\mathrm{theor}}$(vap) a determinable quantity from experimental data, i.e., $f^{\mathrm{theor}}$(soln)/$f^{\mathrm{theor}}$(vap)=$f^{\mathrm{exp}}$(soln)/$f^{\mathrm{exp}}$(vap), so that alternatively

$$\frac{f^{\mathrm{exp}}(\mathrm{soln})}{f^{\mathrm{exp}}(\mathrm{vap})} = F(\mathrm{soln})\times\frac{\tilde{\nu}_{0i}}{\tilde{\nu}_{0i}^\circ}\times\{1 + \theta(\varepsilon_\mathrm{r})\times A + \theta^2(\varepsilon_\mathrm{r})\times B\}^2. \tag{16}$$

For relative $f$ values in two solvents, Eq. 16 can be transformed into

$$\begin{aligned}
\frac{f^{\mathrm{exp}}(\mathrm{soln\ 2})}{f^{\mathrm{exp}}(\mathrm{soln\ 1})} &= \frac{F(\mathrm{soln\ 2})}{F(\mathrm{soln\ 1})}\times\frac{\tilde{\nu}_{0i}(\mathrm{soln\ 2})}{\tilde{\nu}_{0i}(\mathrm{soln\ 1})} \\
&\quad\times\frac{\{1+\theta(\varepsilon_\mathrm{r}\ 2)\times A + \theta^2(\varepsilon_\mathrm{r}\ 2)\times B\}^2}{\{1+\theta(\varepsilon_\mathrm{r}\ 1)\times A + \theta^2(\varepsilon_\mathrm{r}\ 1)\times B\}^2},
\end{aligned} \tag{17}$$

where $\theta(\varepsilon_\mathrm{r}\ i)$ and $\tilde{\nu}_{0i}$ (soln $i$) are the Block–Walker parameter for the $i$th solvent and the transition energy (cm$^{-1}$) in the $i$th solvent. The squared, bracketed term $\{1+\theta(\varepsilon_\mathrm{r})\times A+\theta^2(\varepsilon_\mathrm{r})\times B\}^2$ in Eq. 16 comes from the calculation of $|\mu_{0i}(\mathrm{soln})|^2/|\mu_{0i}^\circ|^2$ $(=|\mu_{0i}^\circ|^2|1+\theta(\varepsilon_\mathrm{r})\times A+\theta^2(\varepsilon_\mathrm{r})\times B|^2/|\mu_{0i}^\circ|^2)$ in the derivation of Eq. 16. As should be clear from Eq. 13, the second and third terms in the brackets are due to the perturbation of the transition moment by the solvent. Accordingly, on the assumption that the perturbation is small, we assume that $|\theta(\varepsilon_r)\times A+\theta^2(\varepsilon_r)\times B|<1$, i.e., that the bracketed term is always positive. Thus, a data analysis of the square roots of both sides of Eq. 16 by a multiple linear regression permits an evaluation of the constants $A$ and $B$. A similar simultaneous solution of $A$ and $B$ in Eq. 17 also follows from the substitution of experimental values of $f^{\text{exp}}(\text{soln 2})/f^{\text{exp}}(\text{soln 1})$ and of the refractive indices in the square roots of both sides of Eq. 17.

As has already been pointed out in a previous paper,[6] the present treatment neglects dispersion effects. Consequently, Eqs. 16 and 17 cannot be applied to solute molecules with no electric dipole moments.

In applying Eqs. 5, 16, and 17, we always assumed a temperature of 20 °C and excluded data of solvents which were capable of forming hydrogen bonds or complexes with solutes, since such specific interactions were not considered in the derivations of these equations. Moreover, we used the spectral data reported for a solute by the same authors, since experimental values of oscillator strengths considerably vary with different authors.

## Results and Discussion

**nπ* Transitions.** We first test the applicability of Eqs. 5, 16, and 17 from the data of some compounds whose weak electronic spectral bands are assigned to nπ* transitions. These bands are advantageous in the present consideration because of their relatively small overlaps with bands of other transitions in the spectral profiles of these compounds.

**(i) *p*-Benzoquinone, 2,5-Di-*t*-butyl-*p*-benzoquinone and 4,5,5-Trimehtyl-4-phenyl-1,3-dithiolane-2-thione:** Obviously 4,5,5-trimethyl-4-phenyl-1,3-dithiolane-2-thione ought to have a dipole moment owing to its molecular structure. A small experimental dipole moment of 0.81 D[9] (1 D=$3.333\times10^{-30}$ Cm) has been reported for 2,5-di-*t*-butyl-*p*-benzoquinone. This value can be predicted from a resolution of the bond moments of the substituents. Experimentally, *p*-benzoquinone does not have a dipole moment in the vapor phase but has small dipole moments (0.63—0.69 D) in a solution; it varies slightly in such solvents as hexane, dioxane, carbon tetrachloride and benzene.[10] The small and slightly varying dipole moment of *p*-benzoquinone in solvents is probably due to its molecular structure, which is not strictly planar but has a slightly chair form.[11] Accordingly, Eq. 17 was applied to the oscillator strength data of Kuboyama and his coworkers[12] on these compounds. The results are shown in Fig. 1. For each compound, the ratios of the oscillator strengths calculated to that of the standard value in a solvent are in good agreement with those observed.

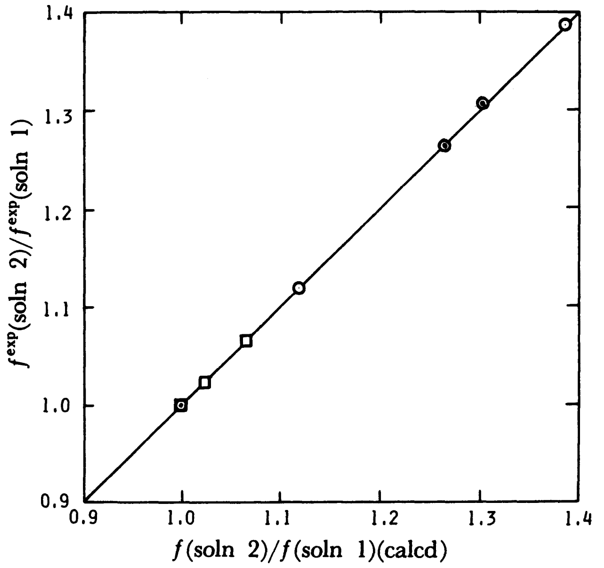

Fig. 1. Correlations between the observed and calculated values of $f$(soln 2)/$f$(soln 1) for *p*-benzoquinone (○) with heptane as the standard solvent ($A$=−8.584 and $B$=44.939), 2,5-*t*-butyl-*p*-benzoquinone (□) with cyclohexane as the standard solvent ($A$=−4.955 and $B$=−23.903) and 4,5,5-trimethyl-4-phenyl-1,3-dithiolane-2-thione (⊙) with cyclohexane as the standard solvent ($A$=4.153 and $B$=60.873).

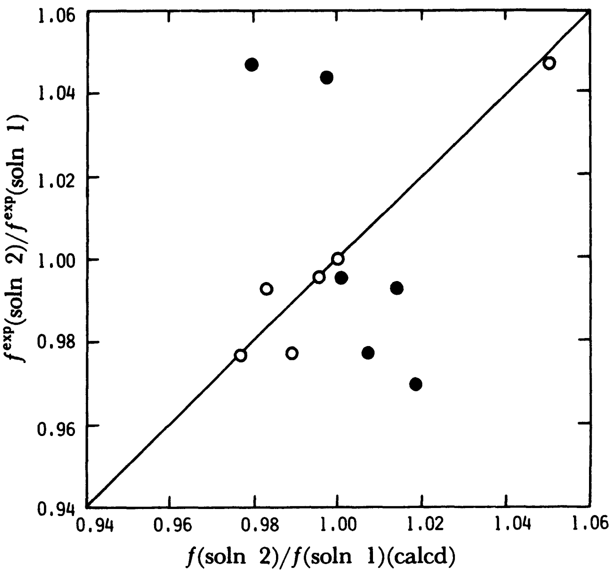

Fig. 2. Correlations between the observed and calculated values of $f$(soln 2)/$f$(soln 1) for pyrazine with cyclohexane as the standard solvent. The plots (○) denote those obtained according to Eq. 17 ($A$=−2.107 and $B$=16.989). The plots (●) denote those obtained according to Eq. 5.

**(ii) Pyrazine:** The experimental dipole moment of pyrazine has been reported as 0.66 D[13] in dioxane, 0.15 D[14] in carbon tetrachloride, and 0.34 D[14] in cyclohexane. Both Eqs. 5 and 17 were, therefore, applied to the reported data[3] for the nπ* absorption intensities of pyrazine. The results are shown in Fig. 2. The figure shows that calculations with Eq. 17 give a good correlation between the experimental and

Table 1. Values of $f$(soln)/$f$(vap) for Ketones

| Ketone | Solvent | | | | | | | $A$ | $B$ |
|---|---|---|---|---|---|---|---|---|---|
| | Heptane | 2,2,4-trimethylpentane | Cyclohexane | Carbon tetrachloride | Chloroform | Dichloromethane | Diethyl ether | | |
| Acetone | | | | | | | | | |
| Obsd | 1.19 | 1.10 | 0.991 | 1.27 | — | 1.17 | 1.26 | | |
| Calcd | 1.15 | 1.15 | 1.14 | 1.14 | — | 1.18 | 1.23 | 0.984 | −2.23 |
| Ethyl methyl ketone | | | | | | | | | |
| Obsd | 1.20 | 1.17 | 1.24 | 1.25 | — | 1.29 | 1.03 | | |
| Calcd | 1.17 | 1.17 | 1.16 | 1.17 | — | 1.20 | 1.25 | 1.05 | −2.40 |
| Diethyl ketone | | | | | | | | | |
| Obsd | 1.18 | 1.07 | 1.00 | 1.23 | 1.10 | 1.15 | 1.08 | | |
| Calcd | 1.11 | 1.11 | 1.09 | 1.09 | 1.13 | 1.12 | 1.16 | 0.648 | −1.48 |
| Methyl propyl ketone | | | | | | | | | |
| Obsd | 1.06 | 1.09 | 1.03 | 1.24 | — | 1.18 | 1.03 | | |
| Calcd | 1.08 | 1.08 | 1.08 | 1.07 | — | 1.14 | 1.15 | 0.517 | −0.917 |
| Dipropyl ketone | | | | | | | | | |
| Obsd | 1.17 | 1.10 | 1.09 | 1.22 | 1.30 | 1.36 | 1.16 | | |
| Calcd | 1.14 | 1.13 | 1.13 | 1.13 | 1.26 | 1.34 | 1.27 | 0.628 | −0.390 |
| Diisopropyl ketone | | | | | | | | | |
| Obsd | 1.14 | 1.21 | 1.19 | 1.27 | 1.29 | 1.41 | 1.15 | | |
| Calcd | 1.16 | 1.16 | 1.16 | 1.17 | 1.30 | 1.34 | 1.31 | 0.974 | −1.36 |
| Dibutyl ketone | | | | | | | | | |
| Obsd | 1.19 | 1.18 | 1.24 | 1.44 | 1.29 | 1.34 | 1.21 | | |
| Calcd | 1.23 | 1.23 | 1.23 | 1.23 | 1.31 | 1.28 | 1.34 | 1.32 | −2.86 |
| Diisobutyl ketone | | | | | | | | | |
| Obsd | 1.13 | 1.16 | 1.11 | 1.32 | 1.22 | 1.39 | 1.15 | | |
| Calcd | 1.14 | 1.15 | 1.14 | 1.15 | 1.26 | 1.32 | 1.28 | 0.778 | −0.857 |
| Cyclohexanone | | | | | | | | | |
| Obsd | 1.35 | 1.43 | 1.35 | 1.77 | 1.73 | 1.53 | 1.51 | | |
| Calcd | 1.45 | 1.45 | 1.46 | 1.48 | 1.63 | 1.53 | 1.66 | 2.59 | −5.94 |

calculated ratios of the oscillator strengths to the value selected as a standard; calculations with Eq. 5 give a poor correlation. Thus, it seems that the pyrazine molecule in solution does have a small dipole moment.

**(iii) Ketones:** In applying the equations developed in this paper to the data of Bayliss and Wills-Johnson[15] on the effects of solvents on the usual oscillator strengths of $n\pi^*$ bands of ketones and nitroalkanes, we have selectively avoided solute–solvent systems with strong tendencies to form a hydrogen bond (e.g., acetone–chloroform, water, and alcohol systems[16]) or a weak donor-acceptor complex (e.g., acetone–benzene complex[17]). Moreover, Nakashima et al.[18] have pointed out that their data for benzene were likely to contain large errors. Accordingly, for the ketones we have chosen data for 6 or 7 solvents out of a reported total of 11. By applying Eq. 16 to the data, we obtained values for $A$ and $B$ (Table 1) from which we calculated the ratios of $f$(soln)/$f$(vap) (Table 1) together with the observed ratios. Considering the difficulties that may attend a determination of the oscillator strengths from the experimental estimates of the values of the integral, $\int\varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu}$, and the inherent approximations in the development of the present treatment, we found that all of the correlations between the observed and calculated ratios of $f$(soln)/$f$(vap) in the case of these ketones were good.

**(iv) Nitroalkanes:** For computations of the nitroalkanes, we chose 6 data points from a total of 11 found by Bayliss and Wills-Johnson.[15] The data gathered for benzene as a solvent were excluded since benzene forms donor-acceptor complexes with nitromethane and nitroethane.[17] The results of calculations by means of Eq. 16 are shown in Table 2. Correlations between the observed and calculated ratios of $f$(soln)/$f$(vap) are reasonably good, but are generally worse than those for the ketones. This may be due to the relatively large overlaps with bands of other transitions in the spectral profiles of these nitroalkanes.

**$\pi\pi^*$ Transitions.** There are only a few advantageous examples of the bands assigned to the $\pi\pi^*$ transitions because of their relatively large overlaps with bands of other $\pi\pi^*$ and/or $n\pi^*$ transitions.

**(i) $\beta$-Carotene:** Myers and Birge[3] have reported relative oscillator-strength values for $\beta$-carotene in various solvents. From their total of 21 data points we chose 19, excluding data points of hexadecane and decalin (mixed isomers). The relative permittivity for hexadecane is unknown. We applied Eq. 5 to these selected data points and obtained the results shown in Fig. 3. This figure shows that the correlation between the observed and calculated ratios of oscillator strengths to those for the benzene solvent is fairly good. However, all the points in Fig. 3 have a tendency to fit a steeper line. This may be due to a neglect of the dispersion effect and the solute-induced dipole (solvent dipole interaction) in the derivation of Eq. 5.

**(ii) Benzene:** Considering that benzene is a weak hydrogen-bonding acceptor,[16] we chose 11 data points from Macovei's total[19] of 17 for the solvent effects on

Table 2. Values of $f$(soln)/$f$(vap) for Nitroalkanes

| Nitroalkane | | Solvent | | | | | | $A$ | $B$ |
|---|---|---|---|---|---|---|---|---|---|
| | | Heptane | 2,2,4-trimethyl-pentane | Cyclohexane | Carbon tetrachloride | Dichloro-methane | Diethyl ether | | |
| Nitromethane | | | | | | | | | |
| | Obsd | 1.56 | 1.65 | 1.68 | 2.11 | 1.95 | 1.97 | | |
| | Calcd | 1.70 | 1.70 | 1.72 | 1.78 | 1.91 | 2.09 | 3.96 | −8.66 |
| Nitroethane | | | | | | | | | |
| | Obsd | 1.68 | 1.59 | 1.69 | 1.91 | 1.98 | 1.92 | | |
| | Calcd | 1.66 | 1.67 | 1.69 | 1.74 | 1.94 | 2.06 | 3.68 | −7.75 |
| 1-Nitropropane | | | | | | | | | |
| | Obsd | 1.86 | 2.07 | 1.73 | 2.03 | 2.09 | 1.87 | | |
| | Calcd | 1.82 | 1.83 | 1.84 | 1.91 | 1.96 | 2.21 | 4.48 | −10.25 |
| 2-Nitropropane | | | | | | | | | |
| | Obsd | 1.45 | 1.62 | 1.59 | 1.77 | 1.81 | 1.44 | | |
| | Calcd | 1.52 | 1.52 | 1.53 | 1.56 | 1.68 | 1.79 | 2.93 | −6.33 |
| 2-Nitro-2-methylpropane | | | | | | | | | |
| | Obsd | 1.51 | 1.68 | 1.59 | 1.93 | 1.75 | 1.67 | | |
| | Calcd | 1.61 | 1.61 | 1.62 | 1.67 | 1.68 | 1.89 | 3.49 | −8.12 |

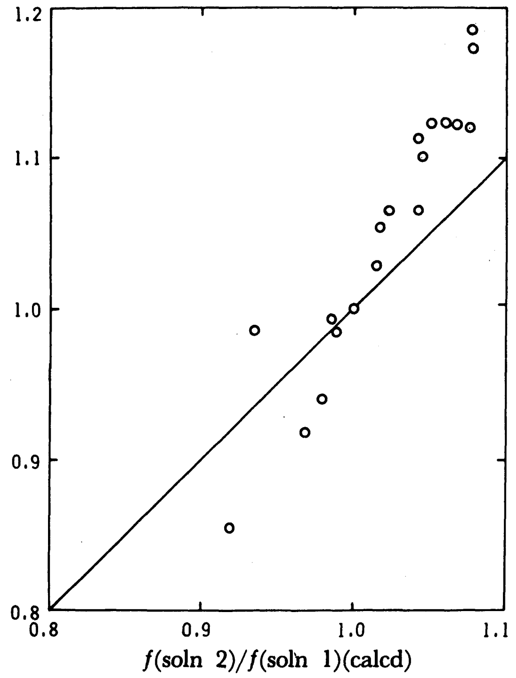

Fig. 3. Correlation between the observed and calculated values of $f$(soln 2)/$f$(soln 1) for $\beta$-carotene with benzene as the standard solvent.

the electronic spectra of benzene and applied Eq. 5 to these data points. Values for the experimental and calculated ratios of oscillator strengths to those for the cyclohexane solvent are given in Table 3. The calculated ratios agree to a gross approximation with the corresponding observed values.

**(iii) Chlorobenzene:** Since chlorobenzene is a weak hydrogen-bonding acceptor,[16] we chose 10 data points from Macovei's total[20] of 19 for solvent effects on the spectral intensities of this molecule. Using $f^{\text{exp}}(\text{vap})=5\times10^{-3}$ for chlorobenzene,[21] we applied Eq. 16 to these selected data points. The results of the calculations are summarized in Fig. 4. The figure shows that the correlation between the observed and calculated values for $f$(soln)/$f$(vap) is also fairly good.

Table 3. Values of $f$(soln 2)/$f$(soln 1) for Benzene

| Solvent | $f$(soln 2)/$f$(soln 1)[a] | |
|---|---|---|
| | Obsd | Calcd |
| Cyclopentane | 1.03 | 1.00 |
| Pentane | 0.780 | 1.02 |
| Cyclohexane | 1.00 | 1.00 |
| Hexane | 0.980 | 1.01 |
| Heptane | 1.03 | 1.01 |
| Octane | 1.02 | 1.01 |
| Decane | 1.07 | 1.00 |
| Dodecane | 1.04 | 1.00 |
| Diethyl ether | 0.833 | 1.02 |
| Acetonitrile | 1.07 | 1.02 |
| 1,4-Dioxane | 1.14 | 1.00 |

a) The oscillator strength in cyclohexane is selected as $f$(soln 1).

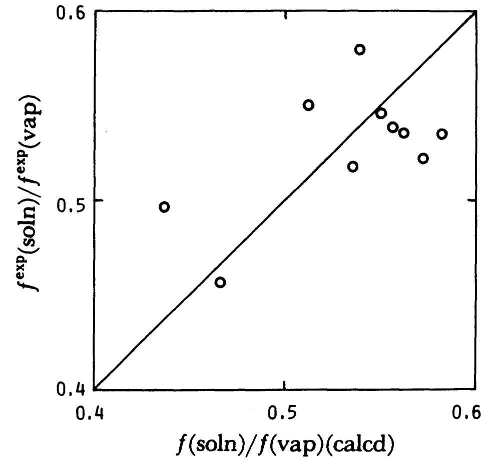

Fig. 4. Correlation between the observed and calculated values of $f$(soln)/$f$(vap) for chlorobenzene ($A$=−3.108 and $B$=7.154).

**(iv) Nitrobenzene:** Macovei[22] has reported the effects of a solvent on the oscillator strength of the principal band of nitrobenzene in the near-ultraviolet region. Of his total of 22 data points, we chose only 9;

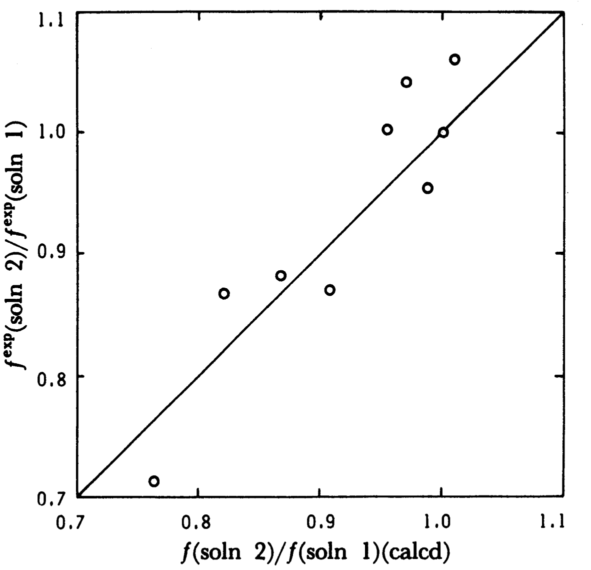

Fig. 5. Correlation between the observed and calculated values of $f$(soln 2)/$f$(soln 1) for nitrobenzene ($A$=−1.584 and $B$=2.654).

the excluded data being those of nonpolar solvents whose molecular shapes are too much long and plane. The principal band of nitrobenzene at 240 nm overlaps a weak band at 288 nm and a strong band at 193 nm.[23,24] In particular, a weak band of nitrobenzene in a solution is hidden in the principal band (Fig. 1 of Ref. 24). Macovei's data for the oscillator strengths in a solution seem not to have been corrected for a contribution from such an overlaps with the weak band. The application of Eq. 17, therefore, to Macovei's data yields the results shown in Fig. 5. The correlation between the observed and calculated values of $f$(soln 2)/$f$(soln 1) is good.

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