# The Excited-State Dipole Moment of Nitrobenzene Estimated from Solvent Spectral Frequency Shifts

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**Synopsis.** The excited-state dipole moment of nitrobenzene has been estimated to be $33.7\times10^{-30}$ C m from solvent spectral frequency shifts. This value agrees well with that ($(31.7\pm3.3)\times10^{-30}$ C m) determined from an electrooptical absorption measurement.

Many theories[1] have previously been proposed regarding solvent spectral frequency shifts of organic molecules. On the basis of some of these, dipole moments and/or polarizabilities have been estimated for the excited states of organic molecules. As mentioned in a previous paper,[2] comparisons of the excited-state dipole moments and/or polarizabilities estimated from the solvent spectral shifts with those determined from electrooptical measurements are necessary, in part, to justify the theoretical expressions for the solvent spectral frequency shifts. Among the theoretical expressions, those expressions that give excited-state dipole moment and polarizability values that are comparable to those of electrooptical measurements will survive. Recently, Sinha and Yates[3] have reported the excited-state dipole moment of nitrobenzene from an electrooptical measurement. Nitrobenzene is one of the typical molecules used for the study of the solvent spectral frequency shifts, because the shifts of nitrobenzene are large. This paper, therefore, applies Abe's improved equation[2,4] to data for nitrobenzene in order to examine the accuracy of this equation by comparing an excited-state dipole moment estimated from the solvent spectral shifts with that obtained from the electrooptical measurement.

## Results and Discussion

In a previous paper,[2] Abe's improved expression for the solvent spectral frequency shift of a neutral solute molecule in solution is given by

$$A\times(p_{00}^{A}\cos\theta)p_{ii}^{A}+B\times(p_{ii}^{A})^2+C\times\alpha_{ii}^{A}=\sigma_{0i}^{\circ}-\sigma_{0i}+D, \quad (1)$$

where

$$E=\frac{(d^{S}/M_{r}^{S})^{2/3}}{(r_A+r_S)^4}\times\frac{\pi}{hc}\left(\frac{4\pi L}{3}\right)^{2/3}, \quad (2)$$

$$A=E\times\frac{2(p_{00}^{S})^2}{3(4\pi\varepsilon_0)^2kT}, \quad (3)$$

$$B=E\times\frac{\alpha_{00}^{S}}{4\pi\varepsilon_0}, \quad (4)$$

$$C=E\times\left\{\frac{(p_{00}^{S})^2}{4\pi\varepsilon_0}+\frac{3}{2}\times\frac{I_0^{S}I_0^{A}\alpha_{00}^{S}}{I_0^{S}+I_0^{A}}\right\}, \quad (5)$$

and

$$D=E\times\left[\frac{2(p_{00}^{S})^2(p_{00}^{A})^2}{3(4\pi\varepsilon_0)^2kT}+\frac{1}{4\pi\varepsilon_0}\times\{(p_{00}^{S})^2\alpha_{00}^{A}+\alpha_{00}^{S}(p_{00}^{A})^2\}+\frac{3}{2}\times\frac{I_0^{S}I_0^{A}\alpha_{00}^{S}\alpha_{00}^{A}}{I_0^{S}+I_0^{A}}\right]. \quad (6)$$

Here $\sigma_{0i}^{\circ}$ and $\sigma_{0i}$ are the wave numbers of a transition from the ground state to the $i$th-excited state of a molecule in the vapor state and in solution, respectively. The A and S superscripts/subscripts denote the solute and solvent molecules, respectively. The subscripts 00 and $ii$ denote the ground and $i$th-excited states, respectively. The dipole moment and polarizability are denoted by $p$ and $\alpha$, respectively. The angle between $p_{00}^{A}$ and $p_{ii}^{A}$ is denoted by $\theta$. The symbol $c$ is the speed of light in a vacuum, $h$ is Planck's constant, $L$ is Avogadro's constant, $\varepsilon_0$ is the permittivity of a vacuum, $M_r$ is the relative molecular mass, $d$ is the density, and $I_0$ is the ionization potential of the ground state. In applying Eq. 1, the method of detailed calculations was the same as that used in Ref 2.

Macovei[5] has investigated in detail the effects of a solvent on the absorption maximum of the 41820 $cm^{-1}$ band[6] of nitrobenzene in the vapor phase. Data for 13 solvents from his spectral data involving 26 solvents were chosen for this study. Data for protic solvents and for solvents lacking information regarding ionization potentials were excluded. Moreover, data for the solvents 1,2-dichloroethane, acetonitrile, and 1,4-dioxane were excluded. 1,2-Dichloroethane is a mixture of rotational isomers having different dipole moments. The aceonitrile molecule has a large dipole moment (3.92 D, where 1 D=$3.333\times10^{-30}$ C m). In Abe's theory,[4] the solvent molecule is assumed to have a small enough dipole moment that it is not tightly oriented with nitrobenzene (4.21 D). According to Marcus,[7] 1,4-dioxane has a dipole moment of 0.45 D. Which of 0 and 0.45 D should be used as the dipole moment of dioxane is not clear. Therefore, the datum for 1,4-dioxane was excluded. In applying Eq. 1, the temperature was assumed to be 20 °C. Data used for nitrobenzene were $r_A$=0.344 nm, $\alpha_{00}^{A}=126.29\times10^{-25}$ $cm^3$, $I_0^{A}$=9.88 eV, and $\cos\theta=1$.[3] The values of $p_{ii}^{A}$ and $\alpha_{ii}^{A}$ estimated by means of Calculation 1 in Ref. 2 are 10.1 D and $397\times10^{-25}$ $cm^3$, respectively. Even if a value of $-1$ was used for $\cos\theta$, the same excited-state values (i.e., $p_{ii}^{A}=-10.1$ D and $\alpha_{ii}^{A}=397\times10^{-25}$ $cm^3$) were still obtained. This supports the assumption that $p_{00}^{A}$ and $p_{ii}^{A}$ are collinear. By using the $p_{ii}^{A}$ and $\alpha_{ii}^{A}$ values so estimated, one can calculate the frequencies. The correlation between the experimental frequencies ($\sigma_{0i,\,obsd}$) and the calculated ones ($\sigma_{0i,\,calcd}$) is shown in Fig. 1. On the whole, the correlation is good.

The present estimation of $p_{ii}^{A}$=10.1 D closely agrees with the experimental values of (9.5±1)[3] and (9±2)[8] D

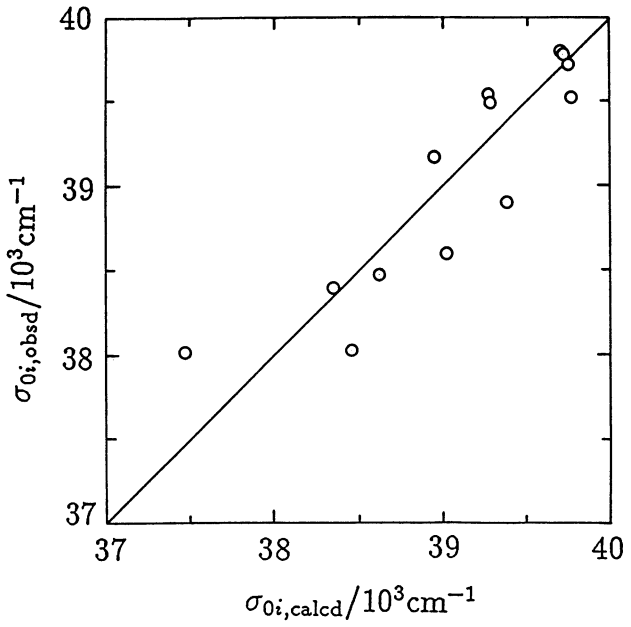


Fig. 1. A plot of $\sigma_{0i,obsd}$ vs. $\sigma_{0i,calcd}$.

determined from the electrooptical measurements. Several values for the excited-state dipole moment of nitrobenzene have hitherto been estimated from the solvent spectral frequency shifts: by applying McRae's equation,[9] Macovei[5] obtained $p_{ii}^{A}=7.19$ D. Using the simple equation based on the Onsager model,[10] Suppan and Ledger[11,12] obtained $p_{ii}^{A}=6.3$ D. Modifying the equation proposed by Amos and Burrows,[13] Millefiori et al.[14] obtained a good result of $p_{ii}^{A}-p_{00}^{A}=4.37$ D. By applying McRae's equation, Prabhumirashi obtained $p_{ii}^{A}=5.84$ D[15] and 7.99 D.[16] A comparable result for nitrobenzene, as determined by the electrooptical measurements and the present analysis, shows that Fq. 1 can be applied for estimating the excited-state dipole moment of a polar solute molecule, as already described in Ref. 2.

## References

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