Absorption Spectra of Nitrobenzene Derivatives. II. Effect of Solvent on Intramolecular Charge Transfer Spectra of Nitrobenzene Derivatives

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In a previous paper[1] intramolecular charge transfer spectra of nitrobenzene derivatives were studied from the viewpoint of Nagakura and Tanaka's theory[2]. These absorption spectra are strongly influenced by solvents and shift toward longer wavelengths for solvents of higher dielectric constant.

Several papers treating of the effect of solvent on the electronic spectra of organic compounds have been published[3]. Recently, Bayliss and McRae[4] discussed the effects in terms of the dipole-, polarization-, and hydrogen bonding forces between solute and solvent molecules. It is not always easy to interpret the solvent effects correctly because these often arise from the resultant of several individual effects reinforcing as well as cancelling each other. It seems certain that hydrogen bonding plays a very important role in the frequency shift, while effects from other origins are no less important, since frequency shifts are observed even in systems containing no hydrogen bonds.

In this paper the role of the electrostatic interaction between solute and solvent molecules in the intramolecular charge transfer spectra of *o*-, *m*- and *p*-nitrophenol, -nitroanisole, -nitroaniline and -nitron-*N*-dimethylaniline was examined on the basis of the general expression proposed by McRae[5] for the solvent effect on absorption spectra. The contribution of hydrogen bonding between solute and solvent molecules was also taken into consideration for some cases.

Experimental

Absorption spectra in the wavelength region 250~400 mμ were obtained by a Hitachi automatic recording spectrophotometer, type EPS-2. Fused quartz cells of 1 cm. path length were used.

Samples of nitrobenzene derivatives were the same ones used in a previous work[1]. Solvents, *n*-hexane, dioxane, cyclohexane, carbon tetrachloride, toluene, benzene, ethyl ether, nitromethane, acetonitrile, methanol, and ethanol, were purified by the method recommended by Weissberger and Proskauer[6], special care having been taken to remove contaminating water.

Result and Discussion

Theoretical Expression for the Solvent Effect. —In current discussions of the solvent effects on electronic absorption spectra the frequency shifts are mainly attributed to dipole, polarization and hydrogen bonding effects. The general formula* derived from the perturbation theory by McRae[5] for solvent-induced spectral shifts can be simplified for the discussion of present results in the following form[7]

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[1] K. Semba, This Bulletin, 33, 1640 (1960).

[2] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955).

[3] For example: N. D. Coggeshell and E. M. Lang, *J. Am. Chem. Soc.*, **70**, 3282 (1948); M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950); H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

[4] N. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002, 1006 (1954).

[5] E. G. McRae, ibid., **61**, 562 (1957).

[6] A. Weissberger and E. S. Proskauer, "Organic Solvent", Interscience Publishers, Inc., New York (1955).

* Y. Ooshika has also given a similar formula: *J. Phys, Soc. Japan*, **9**, 542 (1954).

[7] M. Ito, K. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1317 (1960).

$$\Delta\nu = \text{dispersion term} + B\left[\frac{n_D^2-1}{2n_D^2+1}\right] + C\left[\frac{D-1}{D+2} - \frac{n_D^2-1}{n_D^2+2}\right] + E\left[\frac{D-1}{D+2} - \frac{n_D^2-1}{n_D^2+2}\right]^2 \quad (1)$$

where ***B***, ***C*** and ***E*** are constants characteristic of the solute molecule,

$$B = \frac{1}{hc}\ \frac{(\mathbf{M}_{oo}^{u}) - (\mathbf{M}_{ii}^{u})^2}{a^3} \quad (2)$$

$$C = \frac{2}{hc}\ \frac{(\mathbf{M}_{oo}^{u})\ (\mathbf{M}_{oo}^{u} - \mathbf{M}_{ii}^{u})}{a^3} \quad (3)$$

$$E = \frac{6}{hc}\ \frac{(\mathbf{M}_{oo}^{u})\ (\alpha_o^{u} - \alpha_i^{u})}{a^6} \quad (4)$$

$\mathbf{M}_{oo}^{u}$ and $\mathbf{M}_{ii}^{u}$ represent the vector dipole moments of the solute molecule in its electronic ground and excited states, respectively, and ***a*** is Onsagar's reaction radius of the solute molecule. For the meaning of the various other quantities appearing in these equations McRae's original paper[5] is referred to.

Effect of Electrostatic Interactions.—Absorption maxima (ν_{max}) of *o*-, *m*- and *p*-nitrobenzene derivatives in various solvents are given in Table I, in which refractive indices and dielectric constants are also given. The *p*-derivative shows only one absorption band which is in the near ultraviolet region due to the intramolecular charge transfer transition. On the other hand, the *o*- and *m*-derivatives show two intramolecular charge transfer bands due to the transitions $H_{x1} \to V_s'$ and $H_{x2} \to V_s$, as observed in a previous paper[1]. The bands of *o*- and *m*-derivatives at shorter wavelengths in both toluene and benzene solutions can not be observed, because they are covered by solvent absorption bands, hence only the longer-wavelength bands due to the $H_{x1} \to V_s$ transition are considered.

We shall first consider the effect of non-polar solvents, *n*-hexane, dioxane, carbon tetrachloride, toluene and benzene, in the order of increasing refractive index. It is seen from the table that ν_{max} decreases with the increase in the refractive index of the solvent, with the exception of dioxane. Plots of ν_{max} against $(n_D^2-1)/(2n_D^2+1)$ for these derivatives are shown in Figs. 1—3. For each of these molecules the points for various solvents are approximately on a straight line, with the exception of the point for dioxane.

For non-polar solvents the third and the fourth terms in Eq. 1 may be neglected since $n_D^2 \approx D$, and only the first and the second terms have to be considered. Then, if the first term is much smaller than the second,

TABLE I. ABSORPTION MAXIMA OF *o*-, *m*- AND *p*-NITROBENZENE DERIVATIVES IN VARIOUS SOLVENTS (cm^{-1})

Solvent	n_D	*D*	*o*-Nitrophenol	*o*-Nitroanisole	*o*-Nitroaniline	*m*-Nitrophenol	*m*-Nitroanisole
n-Hexane	1.375	1.890	36400 28810	39800 32510	37160 26870	37850 32040	38200 31200
Dioxane	1.422	2.209	36420 28560	38690 31240	36160 25020	37090 30390	37160 30620
Cyclohexane	1.426	2.023	36700 28650	39670 32350	36390 26270	38160 31440	38080 31440
Carbon tetrachloride	1.460	2.238	36410 28420	— 31740	36750 25900	38010 31440	37560 30900
Toluene	1.497	2.379	— 28120	— 31290	— 25310	— 30390	— 30390
Benzene	1.501	2.284	— 28040	— 31100	— 25310	— 30690	— 30370

Solvent	*m*-Nitroaniline	*m*-Nitro-*N*-dimethylaniline	*p*-Nitrophenol	*p*-Nitroanisole	*p*-Nitroaniline	*p*-Nitro-*N*-dimethylaniline
n-Hexane	38450* 29060	40310 26120	— 35200	— 34120	— 31240	— 28730
Dioxane	35700* 26800	40020 24840	— 32780	— 32720	— 28080	— 26140
Cyclohexane	37030* 28730	40180 26030	— 35020	— 22890	— 30840	— 28160
Carbon tetrachloride	36620 28240	— 25440	— 34060	— 33380	— 30040	— 27430
Toluene	— 27370	— 24810	— 33210	— 32720	— 28940	— 26170
Benzene	— 27390	— 24560	— 33100	— 32560	— 28890	— 26030

* Absorption shoulder

or if the first term is nearly the equal of these solvents, an approximately linear relation between $\nu_{\max}$ and $(n_D^2-1)/(2n_D^2+1)$ should hold. Although the frequency shift of absorption caused by non-polar solvents results from the effects of both the first and the second terms in Eq. 1, the second term mainly determines the amount of the shifts, if the first term is small.

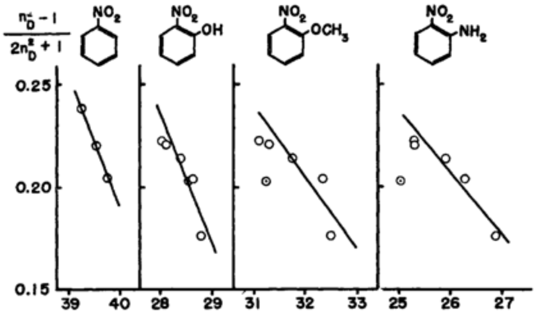

Fig. 1. Relation between $\frac{n_D^2-1}{2n_D^2+1}$ and $\nu_{\max}$ (longer-wavelength bands) for nitrobenzene and *o*-nitrobenzene derivatives. (⊙: dioxane, the value n_D for nitrobenzene was used for 250 mμ)

For these nitrobenzene derivatives B in Eq. 2 is negative, indicating that $(\mathbf{M}_{oo}^{u})^2$ is smaller than $(\mathbf{M}_{ii}^{u})^2$, or that the dipole moment values of these derivatives increase in their electronically excited states reached by the absorption transition. The values of B can be evaluated from slopes of the straight lines as apparent in Figs. 1—3 and Table II. The B value for nitrobenzene is evaluated from the data of Bayliss and McRae[4] obtained for *n*-heptane, cyclohexane and carbon tetrachloride. For *p*-nitrobenzene derivatives the B values decrease with the increasing permanent dipole moments of the solute molecules, but for *o*- and *m*-derivatives these relations are not clearly observed. Spectral shifts are also much greater in nitrobenzene derivatives than nitrobenzene.

The present case of a polar solute dissolved in a non-polar solvent corresponds to the case

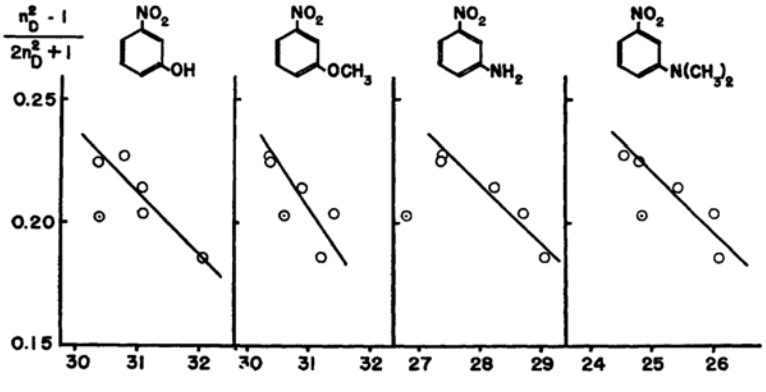

Fig. 2. Ralation between $\frac{n_D^2-1}{2n_D^2+1}$ and $\nu_{\max}$ (longer-wavelength bands) for *m*-nitrobenzene derivatives. (⊙: dioxane)

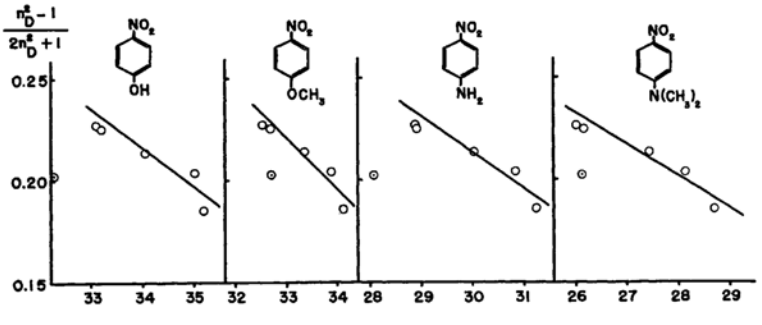

Fig. 3. Relation between $\frac{n_D^2-1}{2n_D^2+1}$ and $\nu_{\max}$ for *p*-nitrobenzene derivatives. (⊙: dioxane)

TABLE II. EVALUATION OF B VALUES (cm^{-1})

Molecule	B	Ground state dipole moment* (Debye units)
Nitrobenzene	−32000**	3.82∼4.00
o-Nitrophenol	−16000	4.10
o-Nitroanisole	−30000	4.83
o-Nitroaniline	−34000	4.26
m-Nitrophenol	−40000	3.90
m-Nitroanisole	−26000	3.86
m-Nitroaniline	−40000	4.72
m-Nitro-*N*-dimethylaniline	−40000	5.06
p-Nitrophenol	−52000	5.05
p-Nitroanisole	−40000	4.75
p-Nitroaniline	−58000	6.32
p-Nitro-*N*-dimethylaniline	−64000	6.87

* See Ref. 10.

** Evaluated from Bayliss and MaRae's data⁴⁾.

III b of Bayliss and McRae's paper⁴⁾, in which the solute dipole moment increases during the transition. According to their theory, the forces contributing to the solvation energy are dispersion and dipole-polarization forces (polarization of solvent molecules by the solute dipoles) and the latter is probably greater than the former. When the solute dipole moment increases as the result of the transition, the solvation energy becomes greater in the excited state than in the ground state, and hence absorption maxima are shifted to the red.

It is well known that dioxane behaves differently from other solvents and it can not be regarded as a non-polar solvent here⁵·⁷·⁸⁾. Nitrophenol and nitroaniline probably from hydrogen bonds with dioxane and in these systems red shifts due to the hydrogen bonding effect may be expected. However, the anomalous shifts are also observed for nitroanisole and nitro-*N*-dimethylaniline in dioxane solutions, where no hydrogen bonding between solute and solvent molecules can be expected.

Absorption frequency shifts $\Delta\nu_{\max}$ due to non-hydrogen bonding polar solvents can be simply expressed in a following form⁷⁾

$$\nu_a-\nu_b=C\left[\frac{D_a-1}{D_a+2}-\frac{D_b-1}{D_b+2}\right]+E\left[\frac{D_a-1}{D_a+2}-\frac{D_b-1}{D_b+2}\right]^2 \qquad (5)$$

where ν_a and ν_b are the $\nu_{\max}$'s of the solutions in solvents a and b, and D_a and D_b are their respective dielectric constant values. To check this relation we chose ethyl ether with $n_D=1.356$ and acetonitrile with $n_D=1.344$ for a and b. Their refractive indices are about the same. Moreover, the absorption spectra of these solvents are similar to each other in the point that they have no strong absorption above 200 mμ, and the dispersion-term contributions from them are expected to be nearly equal⁵⁾. On the other hand, the two solvents have quite different values of dielectric constant, 4.34 for ethyl ether and 37.50 for acetonitrile. Also ethyl ether and nitromethane ($n_D=1.382$, $D=35.87$) were used as solvents for *p*-nitro-*N*-dimethylaniline.

Absorption maxima of nitrobenzene, *o*-, *m*- and *p*-nitroanisole and *m*- and *p*-nitro-*N*-dimethylaniline were measured in solvents consisting of ethyl ether and acetonitrile mixed in various proportions*, in which no hydrogen bonding is expected to arise. The results are shown in Figs. 4—9, where for each solute molecule $\Delta\nu_{\max}$ for ethyl ether and for the mixed solvents are plotted againt $(D-1)/(D+2)$ of the solvents.

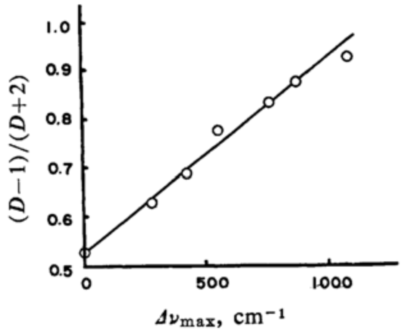

Fig. 4. Relation between $\Delta\nu_{\max}$ and $(D-1)/(D+2)$ for nitrobenzene.

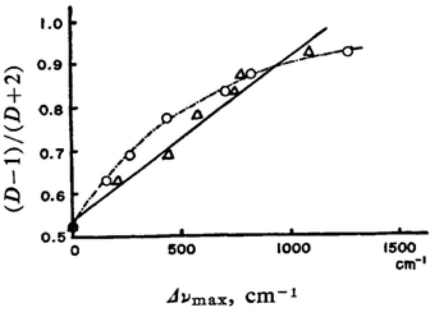

Fig. 5. Relation between $\Delta\nu_{\max}$ and $(D-1)/(D+2)$ for *o*-nitroanisole. (○: $H_{x1}\rightarrow V_s$ transiton; △: $H_{x2}\rightarrow V_s$ transition)

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8) E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955).

* The dielectric constant of a mixed solvent was calculated according to Hoigne and Gaumann⁹⁾ by $D=D_0+bW$, where D_0 is the value of dielectric constant of ethyl ether, b the difference of dielectric constant values of ethyl ether and acetonitrile, and W the weight fraction of acetonitrile in the solution.

9) J. Hoigne and T. Gaumann, *Helv. Chim. Acta*, **41**, 1933 (1958).

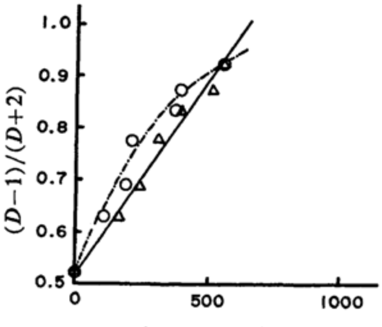

Fig. 6. Relation between $\Delta\nu_{\max}$ and $(D-1)/(D+2)$ for *m*-nitroanisole. (○ : $H_{x1}\rightarrow V_s$ transition; △ : $H_{x2}\rightarrow V_s$ transition)

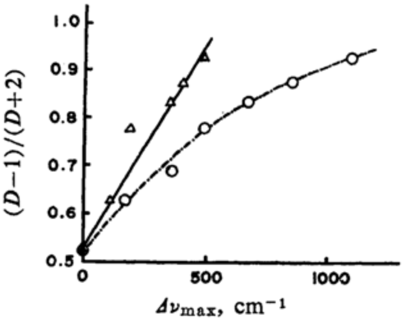

Fig. 7. Relation between $\Delta\nu_{\max}$ and $(D-1)/(D+2)$ for *m*-nitro-*N*-dimethylaniline. (○ : $H_{x1}\rightarrow V_s$ transition; △ : $H_{x2}\rightarrow V_s$ transition)

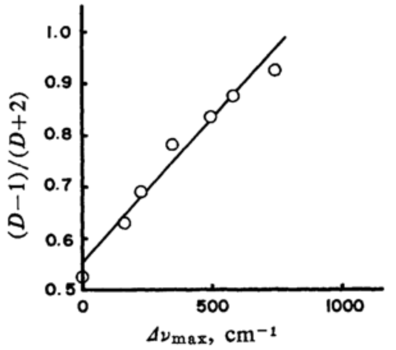

Fig. 8. Relation between $\Delta\nu_{\max}$ and $(D-1)/(D+2)$ for *p*-nitroanisole.

For the shorter-wavelength bands of *o*- and *m*-nitrobenzene derivatives which arise from the $H_{x2}\rightarrow V_s$ transition, and also for the intramolecular charge transfer bands of nitrobenzene and *p*-nitrobenzene derivatives, the linear relation holds approximately. However, for all of the longer-wavelength bands of *o*- and *m*-nitrobenzene derivatives arising from $H_{x1}\rightarrow V_s$ transition the plots show obvious curvatures.

These facts indicate that while for the shorter-wavelength bands the shifts are determined only by the first term in Eq. 5, for the longer-wavelength bands both the first and the second terms would be responsible. In other words, only the interaction between the permanent dipoles of solute and solvent molecules essentially contribute to the spectral shift for the first case, but for the latter case the interaction between the dipole of the solvent molecules and that induced in the solute molecule also makes possibly an important contribution to the shift.

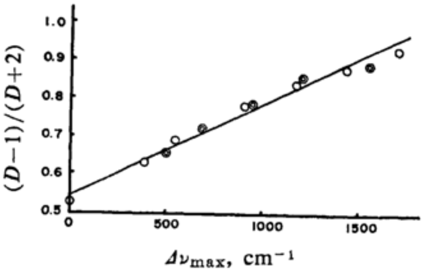

Fig. 9. Relation between $\Delta\nu_{\max}$ and $(D-1)/(D+2)$ for *p*-nitro-*N*-dimethylaniline. (○ : in ethyl ether and acetonitrile; ◎ : in ethyl ether and nitromethane)

The values of *C* in Eq. 5 are easily obtained from the slopes of the straight lines for the shorter-wavelength bands, from which we may calculate* the excited state dipole moment $\mathbf{M}_{11}{}^{u}$, if the values of *a* are known. Similarly, for the longer-wavelength bands $\mathbf{M}_{11}{}^{u}$ as well as he polarizability differerence $(\alpha_0{}^{u}-\alpha_1{}^{u})$ of the solute in its ground and excited states may be estimated from *C* and *E* values.

The polarization effect on the spectral shift is apparent only in the $H_{x1}\rightarrow V_s$ transitions of *o*- and *m*-nitrobenzene derivatives. It could not be observed in all other absorption bands investigated. In all cases *C* and *E* in Eq. 5 are negative, showing that dipole moment and polarizability are greater in the excited state than in the ground state. This indicates that the stabilization energies arising from the electrostatic interactions between the solute and solvent molecules are much greater in the excited state than in the ground state. Thus, the main factor causing the red shift of these absorption band in polar solvents is the great stabilization in the excited state owing to the electrostatic interaction between the solute and solvent molecules. On the other hand, from the consideration of the obviously important resonance forms of these molecules

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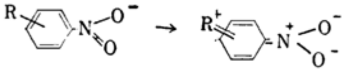
* For example, if we assume that *a* is 4Å for *p*-nitroanisole, the excited state dipole moment $\mathbf{M}_{11}{}^{u}$ can be calculated to be 6.89 D. As its ground state dipole moment is 4.78 D[10], the dipole moment increases by 2.11 D in the excited state.

10) L. G. Wesson, "Tables of Electric Dipole Moments", The Technology Press, M. I. T. (1948).

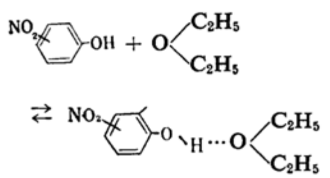
shown below, the optical absorption may well be accompanied by the excitation of the molecule according to the scheme



which would contribute largely to the moment of the excited state.

Effect of Hydrogen Bonding.—The hydrogen bonding plays a very important role in the spectral shift of a solution. The hydrogen bonding effect on the absorption spectra of *m*- and *p*-nitrophenol was observed in mixed solvents consisting of *n*-hexane and ethyl ether.

Figs. 10 and 11 show that the absorption maxima are shifted toward the red with an increasing proportion of ethyl ether in the solvent. In each case an isosbestic point is observed. The following hydrogen bonding reaction may be suggested



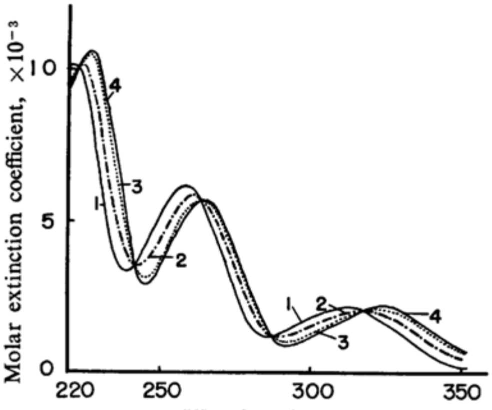


Fig. 10. Absorption curves of *m*-nitrophenol (7.63×10^{-5} mol./l.) in *n*-hexane solution containing ethyl ether at 12°C.
curve 1: *n*-hexane solution (free *m*-nitrophenol)
curve 2: ethyl ether 3.91×10^{-3} mol./l.
curve 3: ethyl ether 7.81×10^{-3} mol./l.
curve 4: calculated curve for bound *m*-nitrophenol

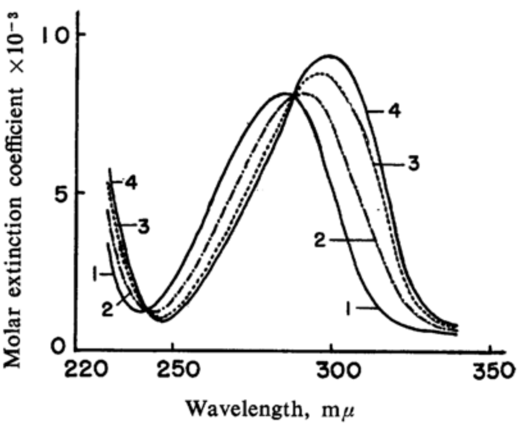


Fig. 11. Absorption curves of *p*-nitrophenol (7.18×10^{-5} mol./l.) in *n*-hexane solution containing ethyl ether at 20°C.
curve 1: *n*-hexane solution (free *p*-nitrophenol)
curve 2: ethyl ether 3.85×10^{-2} mol./l.
curve 3: ethyl ether 1.93×10^{-1} mol./l.
curve 4: calculated curve for bound *p*-nitrophenol

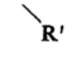
TABLE III. EQUILIBRIUM CONSTANTS AND FREE ENERGY DIFFERENCES FOR *m*- AND *p*-NITROPHENOL

Molecule	Equilibrium constant	Free energy difference (kcal./mol.)
m-Nitrophenol	113.1	−2.6 (12°C)
p-Nitrophenol	24.6	−1.9 (20°C)

From these curves the equilibrium constants* and the free energy differences** are obtained as given in Table III. The equilibrium constant for *m*-nitrophenol is much greater than that for *p*-nitrophenol, indicating that the former requires a very small amount of ethyl ether to reach equilibrium. This may be due to the meta-directing property of the nitro group1).

For *m*- and *p*-nitroaniline no isosbestic point is clearly observed. This indicates that there is no simple equilibrium relation in the hydrogen bonding reaction. However, their absorption maxima are shifted toward the red with an increasing amount of ethyl ether in the solvents.

Next we shall consider the cases of *p*-nitroanisole and *p*-nitro-*N*-dimethylaniline dissolved in methanol and ethanol. In these systems hydrogen bonds may be expected to be formed between the nitro and the hydroxyl groups, the alcohol molecule playing the role of a proton donor according to the scheme



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* The equilibrium constant K is calculated as

$$K=\frac{\varepsilon-\varepsilon_A}{\varepsilon'-\varepsilon}\ \frac{1}{C_B}\quad - \quad\frac{\varepsilon'-\varepsilon_A}{\varepsilon'-\varepsilon}\ \frac{1}{C_B'}$$

where ε_A is the molar extinction coefficient of free *p*-nitrophenol (curve 1), ε and ε' are those of the mixed solvents for curves 2 and 3, and C_B and C_B' are the concentrations of ethyl ether corresponding to the curves 2 and 3.

** The free energy difference ΔF is calculated as $\Delta F=-RT\ \ln K$.

TABLE IV. CALCULATED BLUE-SHIFTS DUE TO $NO_2\cdots H—O$ (cm^{-1})

Solvent (proton donor)	Nitro-benzene	o-Nitro-anisole	m-Nitro-anisole	m-Nitro-N-dimethyl-aniline	p-Nitro-anisole	p-Nitro-N-dimethyl-aniline
Methanol	—	230	150	260	—	—
	130	290	200	330	150	370
Ethanol	—	320	220	250	—	—
	210	270	150	370	280	410

Absorption maxima of *p*-nitroanisole and *p*-nitro-*N*-dimethylaniline are at 32510 and 25540 cm^{-1} in methanol and 32700 and 25700 cm^{-1} in ethanol, respectively. The contribution of electrostatic interactions to the frequency shifts can be evaluated from Eq. 5 as the refractive indices of these alcohols are close to that of ethyl ether or acetonitrile. From the values of C and the dielectric constant for alcohol solutions, the frequency shifts of *p*-nitroanisole relative to the ethyl ether solution can be evaluated as 960 cm^{-1} and as 900 cm^{-1}, and the shifts of *p*-nitro-*N*-dimethylaniline as 1630 and 1520 cm^{-1} for methanol and ethanol, respectively. The experimentally observed shifts for *p*-nitroanisole are 810 and 620 cm^{-1}, and for *p*-nitro-*N*-dimethylaniline 1260 and 1100 cm^{-1}, respectively, for methanol and ethanol. Thus the absorption maximum appears at a shorter wavelength than that expected from only the electrostatic origin in each case. The difference between experimentally observed and calculated frequency shifts may probably be accounted for on the basis of hydrogen bonding between the solute and alcohol molecules. Such differences are observed also for nitrobenzene, *o*- and *m*-nitroanisole, and *m*-nitro-*N*-dimethylaniline as shown in Table IV.

Baba[11] has shown that, if an alcohol molecule plays the role of the proton donor, a blue shift is expected in a $\pi\rightarrow\pi^*$ type transition. The present observed shifts are in good agreement with his theory. Shifts due to hydrogen bonding between the nitro and the hydroxyl groups are estimated as given in Table IV.

Summary

Intramolecular charge transfer spectra of *o*-, *m*- and *p*-nitrobenzene derivatives were measured in solutions with various solvents. Frequency shifts induced by solvents were analyzed on the basis of current theories of solvent effects on absorption spectra. Results show that the frequency shifts in the absorption bands of nitrobenzene derivatives can be interpreted as arising from both the electrostatic and hydrogen bonding interactions.

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11) H. Baba, *Bull. Research Institute of Applied Electricity, Hokkaido University*, 9, 84 (1957).