BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1571—1574 (1967)

The Dipole Moments and Polarizabilities in the Excited States of Four Benzene Derivatives from Spectral Solvent Shifts

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(Received January 5, 1967)

According to Abe's expressions for the spectral solvent shifts (*Bull. Chem. Soc. Japan*, **39**, 936 (1966)), the dipole moments, polarizabilities, and solvation energies in the excited states of nitrobenzene, anisole, acetophenone, and *p*-chloroacetophenone have been estimated. The large dipole moments of 6.78 and 4.23 *D* for the excited states of nitrobenzene and acetophenone respectively have supported Nagakura and Tanaka's theory of the intramolecular charge-transfer band.

In previous papers,[1-3] the present author has undertaken to estimate the dipole moments and polarizabilities in the excited states of three organic molecules, using his expressions for spectral solvent shifts. In the present paper, by the method described in Ref. 3, the dipole moments, isotropic polarizabilities, and solvation energies in the excited states of nitrobenzene, anisole, acetophenone, and *p*-chloroacetophenone will be estimated in order to obtain knowledge of their excited states.

The Method of Calculation

The dipole moment, μ_i^u, and the polarizability, α_i^u, in the ith excited state of a solute molecule were calculated by the following expression from Ref. 3:

$$\{(\mu_i^u)^2-(\mu_0^u)^2\}+(\alpha_i^u)A=B$$

The subscript zero indicates the ground electronic state. The values of A and B can be calculated from the observed values, and the plot of B against A should be linear; the slope of the straight line will then be equal to α_i^u, and the intersection of the line at $A=0$ will be equal to $\{(\mu_i^u)^2-(\mu_0^u)^2\}$. The solvation energy, E_i', in the ith excited state was calculated by the expression in Ref. 3. The expressions for the spectral solvent shifts in Refs. 1 and 3, derived by applying the van der Waals equation to the calculation of the electronic interactions among molecules, are restricted for use to the large, spherical solute and to solvent molecules with no strong dipole-orientation power, because the van der Waals equation used is derived on the assumption that distances among the molecules with no orientation power are larger than the radii of the molecules. The present author, therefore, used the solvent shift data for the large solvent molecules which were not rod-like, except for acetonitrile.

The rod-like molecule of acetonitrile has the large dipole moment of 3.94 *D*. There may, therefore, be strong orientation strains between acetonitrile and solutes. The above expressions will not sufficiently hold for the case of acetonitrile, as has been reported in a previous paper.[3] In the case of acetonitrile, therefore, the author used the expression of zE_i' for the solvation energy. Here z is the empirical parameter. The frequency shift, $\Delta\nu_{i0}$, is then given by $z(E_i'-E_0')/\boldsymbol{hc}$ for the case of acetonitrile. Accordingly, for the case of acetonitrile the author used $\Delta\nu_{i0}/z$ and $1.198\ z\times10^{41}$ $\mathrm{erg^{-1}cm^{-1}}$ in place of $\Delta\nu_{i0}$ and $1.198\times10^{41}\ \mathrm{erg^{-1}\cdot cm^{-1}}$ in the expressions for B and $\Delta\nu_{i0}$ respectively in Ref. 3. The author chose the z value of 0.2805 as best placing the B value for acetonitrile on the straight line in the plot of B against A for nitrobenzene.

The equations in Ref. 3 utilize Onsager's approximate expression for a polar-solvent dipole moment. Onsager's expression is, however, limited for use to spherical molecules and so is unsatisfactory for alcohols forming hydrogen bonds. Therefore, in calculations of the frequency shifts for the benzene derivatives in alcohols, the author used the general expression in Ref. 1, with the values of α_i^u and μ_i^u determined above. From the difference between the calculated and the observed frequency shifts, the frequency shift due to the formation of the hydrogen bond was estimated by $\Delta=\Delta\nu_{i0,\ \mathrm{cald}}-\Delta\nu_{i0,\ \mathrm{obs}}$, as has been described in previous papers.[1,3]

The data measured by Schubert *et al.*[4-7] for the principal bands of nitrobenzene, anisole, acetophenone, and *p*-chloroacetophenone in solvents of isopentane, cyclohexane, chloroform, *t*-butyl chloride, ethyl ether, acetonitrile, methanol, ethanol, and

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[1] T. Abe, This Bulletin, **38**, 1314 (1965).

[2] T. Abe, Y. Amako, T. Nishioka and H. Azumi, *ibid.*, **39**, 845 (1966).

[3] T. Abe, *ibid.*, **39**, 936 (1966).

[4] W. M. Schubert, J. Robins and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957).

[5] W. M. Schubert, H. Steadly and J. M. Craven, *ibid.*, **82**, 1353 (1960).

[6] W. M. Schubert and J. M. Craven, *ibid.*, **82**, 1357 (1960).

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

butanol were used.

In applying the expressions for the frequency shift and the solvation energy in Ref. 3, the temperature was assumed to be 20°C. The values of the ionization potentials, the dipole moments, and the deformation polarizabilities used are listed in Tables 1—3. The ground-state polarizabilities of the benzene derivatives were calculated from the sums of the bond refractions. The polarizabilities of the alcohols were calculated by the use of the values[8] observed for deformation polarizations.

Table 1. IONIZATION POTENTIALS USED, eV

Nitrobenzene	10.18[9]
Anisole	8.83[9]
Acetophenone	9.32[10]
p-Chloroacetophenone	9.47[10]
Isopentane	10.10[11]
Cyclohexane	9.24[12]
Chloroform	11.5[8]
t-Butyl chloride	10.20[13]
Ethyl ether	9.72[12]
Acetonitrile	12.39[12]
Methanol	10.95[12]
Ethanol	10.60[12]
t-Butanol	9.92[14]

TABLE 2. THE DEFORMATION POLARIZATIONS AND DIPOLE MOMENTS OF ALCHOHOLS[8]

	Deformation Polarization cm^3	μ_0(gas) D
Methanol	9.5	1.705
Ethanol	14.2	1.680
t-Butanol	23.1*	1.66**

* The value for isobutanol
** The value in benzene

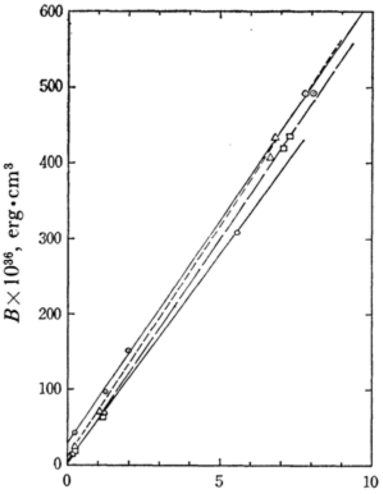

Fig. 1. Plots of B against A.
⊙: Nitrobenzene ○: Anisole
△: Acetophenone
□: *p*-Chloroacetophenone

Results

The plots of B against A for the four benzene derivatives in the solvents with no hydrogen bonding power are shown in Fig. 1. It may be seen in Fig. 1 that all the points fall close to the corresponding straight lines. From the intersections and slopes of the lines in Fig. 1, the values of the dipole moments and polarizabilities in the excited states are found to be as indicated in Table 3. By putting the values for the excited states in Table 3 into the expressions for $\Delta\nu_{i0}$ and E_i' in Ref. 3, the author has calculated the frequency shifts and the solvation energies; they are shown in Figs. 2 and 3. In Fig. 2 there is a good agreement between the theoretical and the experimental results. The results of the calculation of the frequency shifts due to the

TABLE 3. THE RESULTS OF CALCULATION OF DIPOLE MOMENTS AND POLARIZABILITIES IN EXCITED STATES

	ν_{io}^0, cm^{-1}*	μ_o^u, D[8]	μ_i^u, D	$\alpha_i^u\times10^{25}$, cm^3	α_i^u/α_o^u
Nitrobenzene	41820	4.23	6.78	587.8	4.66
Anisole	46510	1.35	2.37	549.2	4.25
Acetophenone	43460	3.00	4.23	613.8	4.37
p-Chloroacetophenone	41440	2.23**	2.68	591.9	3.71

* The absorption frequencies in the gas states[4-6]
** The value in benzene

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8) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Vol. 1, Part 3, 6th Ed., Springer, Berlin (1951), pp. 386, 395, 509.

9) G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

10) A. Foffani, S. Pignataro, B. Cantone and F. Grasso, *Z. Physik. Chem. (Frankfurt)*, **42**, 221 (1964).

11) M. B. Koffel and R. A. Lad, *J. Chem. Phys.*, **16**, 420 (1948).

12) J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952).

13) D. P. Stevenson and J. A. Hipple, *J. Am. Chem. Soc.*, **64**, 2766 (1942).

14) I. Omura, H. Baba and K. Higasi, This Bulletin, **28**, 147 (1955).

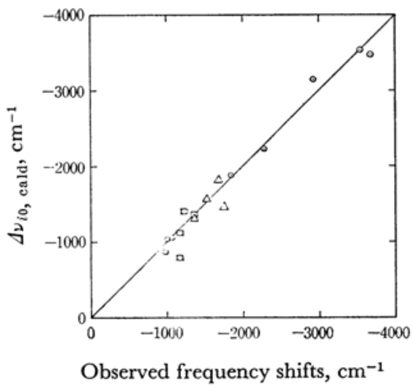


Fig. 2. Calculated *vs.* observed frequency shifts in the principal bands.
⊙: Nitrobenzene ○: Anisole
△: Acetophenone
□: *p*-Chloroacetophenone

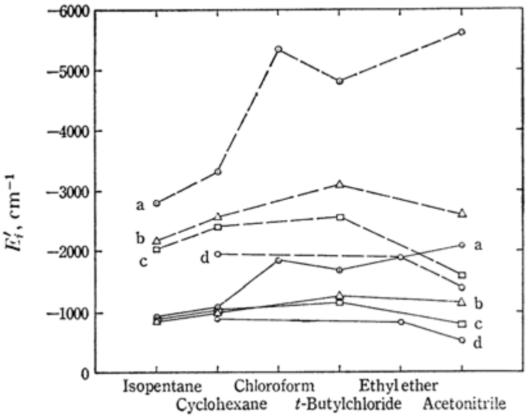


Fig. 3. Solvation energies of the ground- (——) and excited- (— —) states of nitrobenzene (a), acetophenone (b), *p*-chloroacetophenone (c) and anisole (d) in various solvents.

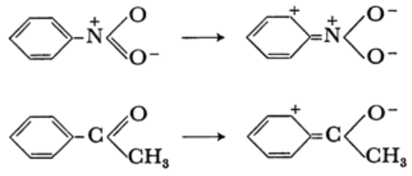
formation of the hydrogen bonds between the benzene derivatives and the alcohols are listed in Table 4. Here the positive value of Δ means a blue shift.

Discussion

In a previous paper[1] the dipole moment and polarizability in the excited state of nitrobenzene were estimated to be 8.18 *D* and 580.7×10^{-25} cm^3 respectively. These values are somewhat different from the corresponding values in Table 3. The previous values are not accurate, however, since a polar solvent was used in computing them.[1]

The 41820 and 43460 cm^{-1} bands of nitrobenzene and acetophenone respectively have been interpreted by Nagakura and Tanaka[15–18] in terms of the intramolecular charge-transfer involving the excitation of an electron of the highest-occupied orbital of the benzene ring to a vacant orbital of the nitro- or the acetyl group. The finding that the dipole moments of the excited states caused by the 41820 and 43460 cm^{-1} transitions in nitrobenzene and acetophenone respectively are greater than the corresponding moments for their ground states supports Nagakura and Tanaka's theory.

The transitions in nitrobenzene and acetophenone are represented by Bayliss and McRae[7,19] by:



The above representations can also account for the larger dipole moment in the excited state. In the representations, the negative charge on the substituent group in the excited state of nitrobenzene is greater than that for acetophenone. This leads to the interpretation that the excited-state dipole moment of nitrobenzene is greater than that for acetophenone.

It can be easily seen from the results of calculation by the simple LCAO MO method that the oxygen atom in the methoxy group in anisole has a greater positive charge in the excited state than in the ground state. From this it can be expected that the dipole moment of anisole will be greater in the excited state than in the ground. Kimura and Nagakura[20] have reported that the excited state caused by the 46510 cm^{-1} transition in anisole consists mainly of the B_{1u}-excited configuration of benzene. Accordingly, the increase in the dipole moment of the excited state of anisole will be relatively small, as is indicated in Table 3.

In the previous paper[1] the excited-state polarizability of nitrobenzene was estimated to be 580.7×10^{-25} cm^3. This value is in accordance with the present one (Table 3). It is known from Table 3 that the polarizabilities considerably increase in the excited states. The values of $(\mu_i^u-\mu_0^u)$ increase with the increasing values of α_i^u/α_0^u. This may be accounted for by the fact that the excited states are polarized more easily than the ground ones as the values of α_i^u/α_0^u increase.

It can be known from Fig. 3 that the excited-

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

[16] J. Tanaka, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **79**, 1114 (1958).

[17] S. Nagakura, M. Kojima and Y. Maruyama, *J. mol. Spectroscopy*, **13**, 174 (1964).

[18] J. Tanaka, S. Nagakura and M. Kobayashi, *J. Chem. Phys.*, **24**, 311 (1956).

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

[20] K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).

TABLE 4. FREQUENCY SHIFTS DUE TO HYDROGEN BONDINGS

Substance	Solvent	$\Delta\nu_{io, \mathrm{obs}}$, cm^{-1}	$\Delta\nu_{io, \mathrm{cald}}$, cm^{-1}	Δ, cm^{-1}
Nitrobenzene	Methanol	38540[4]	35690	2850
	Ethanol	38580[7]	37180	1400
	t-Butanol	38790[4]	38510	280
Anisole	Methanol	45640[4]	44560	1080
	Ethanol	45570[6]	44890	940
Acetophenone	*t*-Butanol	41420[5]	41510	−90
p-Chloroacetophenone	*t*-Butanol	39820[5]	39920	−100

state solvation energy of each derivative is greater than that for the ground state, and that the dispersion effect can not be neglected, since the solvation energies for the nonpolar solvents, due only to the effect, are quite large. From Table 3 and Fig. 3 it may be seen that the solvation energies of the derivatives become large with the increase in the values of the dipole moment in the ground and excited states.

It can be seen from Table 4 that the blue shifts due to hydrogen bonding are great in the order of methanol, ethanol, and *t*-butanol in the cases of nitrobenzene and anisole. Table 4 also shows that the hydrogen-bond formation of *t*-butanol with acetophenone or *p*-chloroacetophenone shifts the absorption frequency towards red by *ca.* 100 cm^{-1}. The red shifts are not certain, however, since the magnitude of the shifts are perhaps within the limits of error of the present calculation, as is shown by Fig. 2. The red shifts are, however, consistent with Baba's theory.[21] According to Baba[21] the formation of a hydrogen bond between acetophenone and alcohols will shift the absorption frequency towards red.

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[21] H. Baba, *Bull. Research Institute of Applied Electricity, Hokkaido Univ.*, **9**, 84 (1957).