The Dipole Moment and Polarizability in the Excited State of *p*-Nitroaniline from Spectral Solvent Shifts

Takehiro ABE

College of General Education, Tohoku University, Kawauchi, Sendai

(Received November 2, 1967)

The absorption spectrum of *p*-nitroaniline in vapor has not yet been reported on, although there have been many data on the solvent effects. This paper will aim to estimate the dipole moment and polarizability in the π-π^* excited state of *p*-nitroaniline by a method similar to that used in previous papers[1,2] without a spectral datum on the absorption transition of *p*-nitroaniline in vapor.

Considering an unperturbed solute molecule and the solvent molecules already interacting with one another in the zeroth-order approximation, one may write an absorption frequency in cm^{-1} in a transition from the ground state to the *i*th excited state of the solute molecule in the solution as follows by the same procedure as was used in Ref. 1:

$$\begin{aligned}\nu_{i0} = \nu_{i0}^0 &- 1.007\times10^{65}(\mathrm{erg^{-1}cm^{-1}})\times(d^v/M^v)^{2/3}\\ &\times[\{(M^u/d^u)^{1/3}+(M^v/d^v)^{1/3}\}^{-4}+\{(M^u/d^u)^{1/3}\\ &+3(M^v/d^v)^{1/3}\}^{-4}+\{(M^u/d^u)^{1/3}\\ &+5(M^v/d^v)^{1/3}\}^{-4}]\times[(2/3\boldsymbol{k}T)\\ &\times(\mu_1^v)^2\{(\mu_i^u)^2-(\mu_0^u)^2\}+3.963\times10^{-25}\\ &\times(M^v/d^v)\times\{(n^v)^2-1\}/\{(n^v)^2+2\}\\ &\times\{(\mu_i^u)^2-(\mu_0^u)^2\}+(\mu_1^v)^2\{(\alpha_i^u)-(\alpha_0^u)\}\\ &+5.945\times10^{-25}\times(M^v/d^v)\\ &\times\{(n^v)^2-1\}/\{(n^v)^2+2\}\times I_0^v\\ &\times\{(I_0^u-\boldsymbol{hc}\nu_{i0}^0)/(I_0^v+I_0^u-\boldsymbol{hc}\nu_{i0}^0)\times(\alpha_i^u)\\ &-I_0^u/(I_0^v+I_0^u)\times(\alpha_0^u)\}] \qquad (1)\end{aligned}$$

where M is the molecular weight, d is the liquid density, n is the refractive index, I is the ionization potential, μ is the permanent dipole moment, α is the isotropic polarizability, and $\boldsymbol{k}$, $\boldsymbol{c}$, and T have the usual meanings. Here ν_{i0}^0 is the frequency in the vapor, and μ_1 is the liquid dipole moment. The notations u and v refer to the solute and the solvent respectively. The subscript zero indicates the ground electronic state.

The procedure of calculation is as follows: Taking the value of $(I_0^u-\boldsymbol{hc}\nu_{i0}^0)$ which has been calculated with an arbitrary value for ν_{i0}^0, one applies Eq. (1) to the observed frequencies for various solvents and estimates the values of ν_{i0}^0, μ_i^u, and α_i^u by the least-squares method. Next, using the new value of ν_{i0}^0 estimated above, one recalculates the value of $(I_0^u-\boldsymbol{hc}\nu_{i0}^0)$ and continues the iterative process until the value of ν_{i0}^0 no longer changes.

In applying Eq. (1), the temperature was assumed to be 20°C. The values of d and n were taken from tables.[3,4] The value of 6.13 D[5] was used for μ_0^u (gas). The value of α_0^u was calculated as 157×10^{-25} cm^3 from a combination of the bond refractions and the value[5] observed for a deformation polarization of nitrobenzene. Neglecting α_0^u and α_i^u in Eq. (1), the author preliminarily obtained 33420 cm^{-1} and 20.9 D for ν_{i0}^0 and μ_i^u respectively. Starting with these values, the author has finally estimated as follows; $\nu_{i0}^0=33740$ cm^{-1}, $\mu_i^u=10.26$ D, and $\alpha_i^u=729.8\times10^{-25}$ cm^3. By putting the above values into Eq. (1), the author has calculated the frequencies for the solutions listed in Table 1.

The ν_{i0}^0 value of 33740cm^{-1} is larger than the value of 32300 cm^{-1} calculated by Tanaka.[7] According to Tanaka,[7] the absorption band is a charge-transfer one and is polarized along the two-fold symmetry axis of the molecule. The large dipole moment in the excited state may be due to the charge transfer. The μ_i^u value of 10.26 D is smaller than

1) T. Abe, This Bulletin, **38**, 1314 (1965).
2) T. Abe, *ibid.*, **39**, 936 (1966).
3) Chem. Soc. Japan, "Kagaku-Binran (Chemical Table)," Elementary Sec. I and II, Maruzen, Tokyo (1966).
4) N. A. Lange, "Handbook of Chemistry," 10th Ed., McGraw-Hill, New York (1961).
5) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Vol. 1, Part 3, 6th Ed., Springer, Berlin (1951), pp. 463, 517.
6) A. D. Buckingham and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1952**, 1932.
7) J. Tanaka, This Bulletin, **36**, 833 (1963).

TABLE 1. SOLVENT EFFECTS ON ABSORPTION SPECTRUM OF *p*-NITROANILINE

Solvent	$\nu_{i0,\text{obs.}}$ cm^{-1}	$\nu_{i0,\text{cald.}}$ cm^{-1}	I_0, eV[3]	μ_1^v, *D*
(*p*-Nitroaniline)	—	—	(8.85)	—
n-Hexane	31200	31180	10.46	0
n-Heptane	31130	31220	10.41	0
Cyclohexane	30690	30630	10.79	0
Methylcyclohexane	30990	30940	10.19	0
Carbon tetrachloride	30380	30240	11.47	0
Chloroform	28670	29080	11.42	0.975[6]
Methylene chloride	28300	28080	11.35	1.145[6]

the value of 14 *D* obtained by Czekalla and Wick[8] from the measurement of dichroism under a high electric field.

8) J. Czekalla and G. Wick, *Z. Elektrochem.*, **65**, 727 (1961).

Experimental

p-Nitroaniline was recrystallized twice from water. All the solvents used were of a spectroscopic grade. The absorption spectra were obtained at room temperature by means of a Hitachi 139 spectrophotometer.