The Dipole Moments and Polarizabilities in the Excited States of Naphthalene from Spectral Solvent Shifts

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Several attempts have been made to estimate dipole moments in excited states of aromatic compounds on the basis of the solvent effects on their electronic spectra.1-5) Recently Abe6) has evolved a theory for solvent effects by means of the application of the van der Waals interaction and has estimated the dipole moment and polarizability in the excited state of nitrobenzene. In the present paper, the dipole moments and polarizabilities in the $^1B_{1u}$- and $^1B_{2u}$-excited states of naphthalene will be estimated by the application of the general expression derived by Abe to the solvent shifts for naphthalene.

The general expression presented by Abe can be written as:

$$\{(\mu_i{}^u)^2-(\mu_0{}^u)^2\} + A\cdot\alpha_i{}^u = B \qquad (1)$$

where:

$$A = \left\{\frac{2}{3\boldsymbol{k}T}\cdot(\mu_0{}^v)^2+\alpha_0{}^v\right\}^{-1} \times\left\{(\mu_0{}^v)^2+\frac{3}{2}\cdot(\alpha_0{}^v)\cdot I_0{}^v\cdot\frac{I_0{}^u-\boldsymbol{hc}\nu^0{}_{i0}}{I_0{}^v+I_0{}^u-\boldsymbol{hc}\nu^0{}_{i0}}\right\}$$

and:

$$\begin{aligned}B = &\left\{\frac{2}{3\boldsymbol{k}T}\cdot(\mu_0{}^v)^2+\alpha_0{}^v\right\}^{-1}\\ &\times\left[\left\{(\mu_0{}^v)^2+\frac{3}{2}\cdot(\alpha_0{}^v)\cdot I_0{}^v\cdot\frac{I_0{}^u}{I_0{}^v+I_0{}^u}\right\}\cdot(\alpha_0{}^u)\right.\\ &-\left\{1.007\times10^{65}(\mathrm{erg}^{-1}\mathrm{cm}^{-1})\times\left(\frac{d^v}{M^v}\right)^{2/3}\right\}^{-1}\\ &\times\left\{\left(\left(\frac{M^u}{d^u}\right)^{1/3}+\left(\frac{M^v}{d^v}\right)^{1/3}\right)^{-4}\right.\\ &+\left(\left(\frac{M^u}{d^u}\right)^{1/3}+3\left(\frac{M^v}{d^v}\right)^{1/3}\right)^{-4}\\ &\left.\left.+\left(\left(\frac{M^u}{d^u}\right)^{1/3}+5\left(\frac{M^v}{d^v}\right)^{1/3}\right)^{-4}\right\}^{-1}\times(\nu_{i0}-\nu^0{}_{i0})\right]\end{aligned}$$

Here $\nu^0{}_{i0}$ and ν_{i0} are the maximum wave numbers in the vapor and in the solution respectively in an absorption transition from the ground state to the ith excited state of an isotropic solute molecule. All the notations refer to Abe's original paper. The notations of $\mu_i{}^u$ and $\alpha_i{}^u$ are the dipole moment and the polarizability in the ith excited state. The values of A and B can be calculated from the observed values, so the plot of B against A should be linear; the slope of the straight line will be equal to $\alpha_i{}^u$, and the intersection of the line at $A=0$ will be equal to $\{(\mu_i{}^u)^2-(\mu_0{}^u)^2]$.

Experimental

Measurements were made with a Hitachi EPS-2 recording spectrophotometer or a Shimazu GE-100

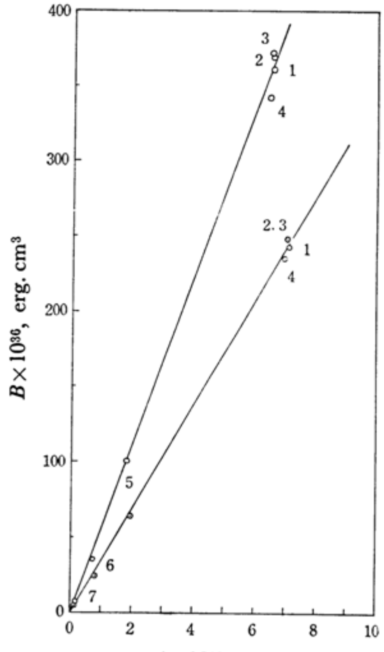

Fig. 1. Plots of B against A.

○ $^1B_{1u}$
⊙ $^1B_{2u}$

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TABLE I. THE $^1B_{1u}$ AND $^1B_{2u}$ TRANSITIONS IN NAPHTHALENE AND THE DATA USED

No.	Solvent	ν_{i0}, cm^{-1} $^1B_{1u}$	ν_{i0}, cm^{-1} $^1B_{2u}$	μ_0[8] D, gas	α_0[8] $\times 10^{25}$ cm^3	I_0 eV.
	Vapor	32456[7]	35919[7]	0	175.2*	8.12[9]
1	*n*-Pentane	32198[7]	35049[7]	0	99.5	10.55[10]
2	*n*-Hexane	32168[7]	35007[7]	0	117.8	10.43[10]
3	*n*-Heptane	32169[7]	35002[7]	0	136.1	10.35[10]
4	Cyclohexane	32160[7]	34965[7]	0	108.7	9.88[9]
5	Ethyl ether	32220	35000	1.18	87.3	9.53[9]
6	Ethanol	32200	34940	1.68	53.1*	10.50[10]
7	Acetonitrile	32190	34730	3.94	44.166**	12.39[11]

* These values were calculated by the use of the observed values[8] for deformation polarizations.

** This value was calculated from the sum of bond refractions.

grating spectrophotograph at room temperature. The results of the measurements of the $^1B_{1u}$ and $^1B_{2u}$ bands of naphthalene in polar solvents are given in Table I. Usually the first reasonably intense vibration band of a transition was measured.

Naphthalene was purified by sublimation after being recrystallized four times, alternately from ethyl ether and from ethanol. Ethanol was twice distilled after being refluxed with 12 N sulfuric acid and with potassium hydroxide and silver nitrate, dried over calcium chloride, and fractionated. Ethyl ether was refluxed with 10% sodium carbonate, distilled, dried over calcium chloride, and distilled over sodium. Acetonitrile was of spectroscopic grade and had been obtained from the Eastman Co.

Results

The first intense vibration bands of the $^1B_{1u}$ and $^1B_{2u}$ transitions in naphthalene and the other data used are listed in Table I. The densities of d at 20°C taken from Lange's table[12] and from another source were used. On the assumption that the temperature is 20°C, that is, that $2/3\boldsymbol{k}T$ is 1.647×10^{13} erg^{-1}, the present authors calculated the values of A and B and plotted B against A, as is shown in Fig. 1. It may be seen in Fig. 1 that the points fall close to the straight lines which approximately pass through the point of origin. The values of $\{(\mu_i{}^u)^2-(\mu_0{}^u)^2\}$ are, therefore, estimated to be zero. Accordingly, both the dipole moments in the $^1B_{1u}$- and $^1B_{2u}$-excited states of naphthalene are estimated to be zero, because the observed value of $\mu_0{}^u$ is zero. From the slopes of the lines in Fig. 1, the polarizabilities in the $^1B_{1u}$- and $^1B_{2u}$-excited states of naphthalene are found to be 345.8×10^{-25} and 556.2×10^{-25} cm^3 respectively.

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