Estimation of Electric Polarizabilities of Organic π-Electron Systems from Kerr Effect Measurements

A. Schweig

Physikalisch-Chemisches Institut der Universität Marburg

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A method to estimate the principal polarizabilities of π-electron clouds embedded in a continuous uniform medium of dielectric constant $\varepsilon_0 = 2$ is described and applied to determine these polarizabilities in the case of aromatic hydrocarbons.

It was assumed[1] that the π-electrons of an organic molecule dissolved in a saturated hydrocarbon see the σ-electrons of the molecule and the σ-electrons of the solvent medium as a continuous uniform medium of dielectric constant $\varepsilon_0 = n_1^2 = 2$, where n_1 is the refractive index of the solvent. Therefore an aromatic organic molecule in a saturated hydrocarbon may be considered approximately to be a cloud of π-electrons in a continuous uniform medium of dielectric constant 2.

If a light beam passes through such a solution the polarization per cm³ $(n_{12}^2 - 1) E/4\pi$ produced by the electric field E of the light wave in the solution contains a contribution of the uniform medium $(\varepsilon_0 - 1) E/4\pi$ and a contribution due to the π electron clouds of the solute molecules $\nu_2 \alpha_0 E$ where n_{12} is the refractive index of the solution, ν_2 the number per cm³ of solute molecules. $\alpha_0 = (b_\alpha + b_\beta + b_\gamma)/3$ is the mean polarizability and b_α, b_β and b_γ are the principal electro-optical polarizabilities due to the molecular π-electron cloud embedded in the uniform σ-medium[2].

Thus one obtains[2]

$$n_{12}^2 - \varepsilon_0 = 4\pi \nu_2 \alpha_0 = \frac{4\pi}{3} \nu_2 (b_\alpha + b_\beta + b_\gamma). \tag{1}$$

If a uniform electric field of field strength F is applied to the solution ν_2 changes by $\Delta\nu_2$ because of electrostriction while α_0 changes by α. Thus n_{12} changes by Δn_{12}. Δn_{12} can be found by differentiating (1)

$$\Delta n_{12} = \frac{n_{12}^2 - \varepsilon_0}{2\, n_{12}} \left(\frac{\Delta\nu_2}{\nu_2} + \frac{\Delta\alpha}{\alpha_0} \right). \tag{2}$$

The magnitudes of $\Delta\alpha$ parallel ($\|$) and perpendicular ($\perp$) to the applied field are different and were obtained[3, 4] to be

$$(\Delta\alpha)_{\|} = 2 (\Theta_\mathrm{p} + \Theta_\mathrm{d}) \tfrac{1}{2} F^2, \tag{3}$$

$$(\Delta\alpha)_{\perp} = -(\Theta_\mathrm{p} + \Theta_\mathrm{d}) \tfrac{1}{2} F^2, \tag{4}$$

where

$$\Theta_\mathrm{p} = \frac{1}{45\, k\, T} [(a_\alpha - a_\beta)(b_\alpha - b_\beta) + (a_\beta - a_\gamma)(b_\beta - b_\gamma) + (a_\gamma - a_\alpha)(b_\gamma - b_\alpha)], \tag{5}$$

$$\Theta_\mathrm{d} = \frac{1}{45\, k^2\, T^2} [(\mu_\alpha^2 - \mu_\beta^2)(b_\alpha - b_\beta) + (\mu_\beta^2 - \mu_\gamma^2)(b_\beta - b_\gamma) + (\mu_\gamma^2 - \mu_\alpha^2)(b_\gamma - b_\alpha)]. \tag{6}$$

T is the absolute temperature, k the Boltzmann constant, a_α, a_β and a_γ denote the principal electrostatic polarizabilities and μ_α, μ_β and μ_γ the components of the permanent dipole moment along the principal polarizability axes of a π-electron cloud in the uniform medium of dielectric constant ε_0.

As usually defined, the Kerr constant B_{12} is[4, 5]

$$B_{12} = \frac{[(n_{12})_{\|} - (n_{12})_{\perp}]}{\lambda F^2}, \tag{7}$$

where λ is the wave-length of the light beam and $(n_{12})_{\|}$ and $(n_{12})_{\perp}$ are the refractive indices of the solution parallel and perpendicular to the applied field.

By introducing Eqs. (3) and (4) into (2) one finds $(\Delta n_{12})_{\|}$ and $(\Delta n_{12})_{\perp}$. These expressions, Eq. (1) and $\nu_2 = (N_\mathrm{A}\, w_2)/(M_2\, v_{12})$ (N_A Avogadro's number, w_2 weight fraction and M_2 molecular weight of the solute, v_{12} specific volume of the solution) are introduced into (7) and (8) is obtained.

$$B_{12} = \frac{3\pi N_\mathrm{A}}{\lambda\, n_{12}\, v_{12}\, M_2} (\Theta_\mathrm{p} + \Theta_\mathrm{d})\, w_2. \tag{8}$$

The assumption is made that (9) and (10) may apply to solutions at sufficiently high dilution

$$B_{12} = \delta w_2, \tag{9}$$

$$n_{12} = n_1 + \gamma\, w_2. \tag{10}$$

By equating (8) and (9) and by restricting the resulting expression to solutions of low concentration (under this restriction n_{12} and v_{12} become practically equal to n_1 and v_1, respectively) one finally has

$$\Theta_\mathrm{p} + \Theta_\mathrm{d} = \frac{n_1\, v_1\, \lambda\, M_2}{3\pi N_\mathrm{A}} \delta. \tag{11}$$

The preceding Eqs. (1) to (8) are valid for the ideal case: π-electron clouds are dissolved in an isotropic continuous medium. For such a medium the Kerr constant according to (7) is zero. To deal with the real case of, say, n-heptane solvent which has itself a non-zero Kerr constant it is assumed that the value of this constant applies to the solution σ-medium independent of the concentration of the solute. If in (2) Δn_{12} and

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in (7), (8) and (9) B_{12} are replaced by

$$\Delta n_{12}{}^* = \Delta n_{12} - \Delta n_1 \quad \text{and} \quad B_{12}{}^* = B_{12} - B_1 \,,$$

where Δn_1 and B_1 refer to the solvent medium, then after equating (8) and (9) the final Eq. (11) remains unchanged.

δ and γ were calculated in the cases of benzene, naphthalene, phenanthrene and diphenyl using the experimental data[6, 7] of B_{12} and n_{12} obtained in n-heptane solutions at various values of w_2. Since Θ_{d} is zero for non-polar molecules considered here[8], Θ_{p} may easily be evaluated from (11).

b_γ is defined arbitrarily to be the principal polarizability perpendicular to the molecular plane. The electrostatic polarizabilities a_α, a_β and a_γ are assumed to be the same as the electro-optical polarizabilities b_α, b_β and b_γ[9]. Thus, in (5) there remain three unknowns b_α, b_β and b_γ to be determined and to calculate this unknowns, besides (5), two further equations are required.

One further equation is supplied from (1). Introducing into this equation $\nu_2 = (N_{\mathrm{A}}\, w_2)/(M_2\, v_{12})$ and Eq. (10) for solutions restricted to low concentration one obtains

$$b_\alpha + b_\beta + b_\gamma = \frac{3\, M_2\, v_1\, n_1}{2\, \pi\, N_{\mathrm{A}}}\, \gamma \,. \qquad (12)$$

In the case of benzene the required third equation is $b_\alpha = b_\beta$ on symmetry grounds. Using the three equations described $b_\alpha = b_\beta$ and b_γ were calculated to be 6.4 ± 0.3 Å^3 and -0.2 ± 0.7 Å^3, respectively. This result confirms Coulson's[10] assumption that the polarizability of a π-electron system perpendicular to the molecular plane is approximately zero.

To calculate the principal polarizabilities b_α and b_β of naphthalene and phenanthrene the equation $b_\gamma = 0$ was assumed to be justified by the results obtained for benzene. In the case of diphenyl meaningful results could only be obtained on the assumption that the polarizability due to the π-electrons gives rise to a component $b_\gamma \neq 0$, a result which indicates that in solution also this molecule is non-planar[11].

The principal polarizabilities obtained by the method described above are given in the table. These values were compared with values obtained from quantum theory in a previous paper[12].

molecule	i	b_i (10^{-24} cm^3)
benzene	α	6
	β	
naphthalene	α	14
	β	20
phenanthrene	α	25
	β	30
diphenyl	α	12
	β	23

Table 1. Estimated principal π-electron polarizabilities referred to a medium of dielectric constant 2.

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[8] There is experimental evidence indicating that phenanthrene, too, is non-polar. For references see: A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman and Company, San Francisco—London 1963, p. 456.

[9] One may show that due to the experimental conditions chosen by Briegleb (see Ref. [7]) this assumption is valid, the relations $a_\alpha/b_\alpha = a_\beta/b_\beta = a_\gamma/b_\gamma$ extending between the limits 0.8 and 1.1.

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Rotationsspektrum des Chloroforms in angeregten Schwingungszuständen

Adalbert Goertz

Department of Physics, Pennsylvania State University
Mont Alto, Pa. 17237, USA

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Some vibrational fine structure lines of chloroform are measured at around 66 GHz and 72 GHz. They correspond to the rotational transitions J: 9 → 10, and J: 10 → 11. Some rotation-vibration interaction constants α_i are determined, others are predicted for bromoform and methylfluoride. Electric quadrupole hyperfine structure is not resolved.

Chloroform $HCCl_3{}^{35}$ ist das zweite Molekül[1] in der Reihe der Haloforme HCX_3, für welches Rotationsübergänge in schwingungsangeregten Molekülen bekannt geworden sind[2]. Das Spektrometer war eine 1 Meter lange elektrisch aufheizbare Starkzelle (X-Band). Die Hyperfeinstruktur des Kernquadrupolmoments der drei Chlorkerne Cl^{35} wurde nicht aufgelöst. Bei etwa 4 mm Wellenlänge wurden folgende Absorptionsfrequenzen gemessen (v_i = Schwingungsquantenzahl des i-ten Schwingungszustandes):

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