Estimation of Electric Polarizabilities of Organic \( \pi \)-Electron Systems from Kerr Effect Measurements

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A method to estimate the principal polarizabilities of \( \pi \)-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 \( \pi \)-electrons of an organic molecule dissolved in a saturated hydrocarbon see the \( \sigma \)-electrons of the molecule and the \( \sigma \)-electrons of the solvent medium as a continuous uniform medium of dielectric constant \( \varepsilon_0 = 2 \), where \( \varepsilon_0 \) is the refractive index of the solvent. Therefore an aromatic or organic \( \pi \)-electron cloud may be considered approximately to be a cloud of \( \pi \)-electrons in a continuous uniform medium of dielectric constant 2. If a light beam passes through such a solution the electric field \( E \) of the light wave in the solution contains a contribution of the uniform medium \( (\varepsilon_0 - 1)/\varepsilon_0 \) and a contribution due to the \( \pi \)-electron clouds of the solute molecules \( \nu_2 \lambda_0 \) where \( \nu_2 \) is the refractive index of the solution, \( \lambda_0 \) the wave-length of the light beam and \( \nu_2/b_0 = b_y/b_x \) is the ratio of the components of the molecular \( \pi \)-electronic polarizabilities to the molecular \( \pi \)-electron polarizability in the uniform \( \sigma \)-medium. Thus one obtains

\[
n_2 \lambda_0^2 - \varepsilon_0 = 4 \pi \nu_2 \lambda_0 = \frac{4 \pi}{3} \nu_2 (b_x + b_y + b_0) \quad (1)
\]

where

\[
\nu_2 = \frac{n_2}{n_1} = 1 + \frac{2}{3} \left( b_x + b_y + b_0 \right)^2
\]

If a uniform electric field \( F \) is applied to the solution \( \nu_2 \lambda_0 \) changes by \( \Delta \lambda_0 \) because of electro-striction while \( \lambda_0 \) changes by \( \Delta \lambda_0 \). Thus \( \nu_2 \lambda_0 \) changes by \( 2 \nu_2 \lambda_0 \)yn. \( \Delta \lambda_0 \) can be found by differenciating (1)

\[
\Delta \lambda_0 = \frac{n_2}{n_1} \Delta \nu_2 = \frac{1}{2} \frac{\Delta \lambda_0}{\nu_2} \quad (2)
\]

The magnitudes of \( \lambda_0 \) parallel (\( || \)) and perpendicular (\( \perp \)) to the applied field are then obtained \(^3\) to be

\[
\langle \lambda_0 || \rangle = 2 (\Theta_0 + \Theta_0) \frac{1}{2} F^2, \quad (3)
\]

\[
\langle \lambda_0 \perp \rangle = - (\Theta_0 + \Theta_0) \frac{1}{2} F^2, \quad (4)
\]

where

\[
\Theta_0 = \frac{1}{45 k T} \left[ (a_x - a_0) (b_x - b_0) + (a_y - a_0) (b_y - b_0) + (a_z - a_0) (b_z - b_0) \right], \quad (5)
\]

\[
\Theta_0 = \frac{1}{45 k T} \left[ (\mu_x^2 - \mu_0^2) (b_x - b_0) + (\mu_y^2 - \mu_0^2) (b_y - b_0) + (\mu_z^2 - \mu_0^2) (b_z - b_0) \right]. \quad (6)
\]

\( T \) is the absolute temperature, \( k \) the Boltzmann constant, \( a_x, a_y \) and \( a_z \) denote the principal electrostatic polarizabilities and \( \mu_x, \mu_y \) and \( \mu_z \) the components of the permanent dipole moment along the principal polarizability axes of a \( \pi \)-electron cloud in the uniform medium of dielectric constant \( \varepsilon_0 \).

As usually defined, the Kerr constant \( B_{12} \) is

\[
B_{12} = \frac{\langle \lambda_0 \perp \rangle - \langle \lambda_0 || \rangle}{\lambda \nu_2^2}, \quad (7)
\]

where \( \lambda \) is the wave-length of the light beam and \( \langle \lambda_0 \perp \rangle \) and \( \langle \lambda_0 || \rangle \) are the refractive indices of the solution parallel and perpendicular to the applied field.

By introducing Eqs. (3) and (4) into (2) one finds

\[
B_{12} = \frac{3 \pi N_\Lambda}{\lambda n_1 \nu_1 M_2} (\Theta_0 + \Theta_0) \frac{w_2}{w_3}, \quad (8)
\]

The assumption is made that \( n_2 \) and \( \nu_2 \lambda_0 \) become practically equal to \( n_1 \) and \( \nu_1 \lambda_0 \), respectively, one finally has

\[
\Theta_0 + \Theta_0 = \frac{n_1 \nu_1 \lambda_0 M_2}{3 \pi N_\Lambda} \delta. \quad (11)
\]

A. KUHN

Chimia 9, 237 [1955].


M. BORN, Ann. Physik 55, 177 [1918].


2. J. KERR, Phil. Mag. 50, 337, 446 [1875].

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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 $\Delta n_1$ and $B_1$ refer to the solvent medium, then after equating (8) and (9) the final Eq. (11) remains unchanged.

$\Delta$ and $\gamma$ were calculated in the cases of benzene, naphthalene, phenanthrene and diphenyl using the experimental data of $B_{12}$ and $n_{12}$ obtained in n- heptane solutions at various values of $w_2$. Since $\Theta_\beta$ is zero for non-polar molecules considered here, $\Theta_\beta$ may easily be evaluated from (11).

$b_\lambda$ is defined arbitrarily to be the principal polarization perpendicular to the molecular plane. The electrostatic polarizabilities $a_\lambda$, $a_\beta$ and $a_\gamma$ are assumed to be the same as the electro-optical polarizabilities $b_\lambda$, $b_\beta$ and $b_\gamma$. Thus, in (5) there remain three unknowns $b_\alpha$, $b_\beta$ and $b_\gamma$ 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 $v_\lambda = (N_\lambda w_2) / (M v_\pi v_\pi)$ and Eq. (10) for solutions restricted to low concentration one obtains

$$ b_\lambda + b_\beta + b_\gamma = \frac{3 M_\pi v_\pi n_1}{2 \pi N_\lambda} \gamma. \quad (12) $$

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

To calculate the principal polarizabilities $b_\alpha$ and $b_\beta$ 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 $\pi$-electrons gives rise to a component $b_\gamma \neq 0$, a result which indicates that in solution also this molecule is non-planar\(^9\).

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\(^{12}\).

<table>
<thead>
<tr>
<th>molecule</th>
<th>$i$</th>
<th>$b_i$ (10$^{-24}$ cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>$\beta$</td>
<td>6</td>
</tr>
<tr>
<td>naphthalene</td>
<td>$\beta$</td>
<td>14</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>$\beta$</td>
<td>25</td>
</tr>
<tr>
<td>diphenyl</td>
<td>$\beta$</td>
<td>12</td>
</tr>
</tbody>
</table>

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

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\(^{7}\) G. Briegleb, Z. phys. Chem. B 16, 249, 276 [1932].


\(^{9}\) One may show that due to the experimental conditions chosen by Briegleb (see Ref. 5) this assumption is valid, the relations $a_{\alpha}/b_\alpha = a_{\beta}/b_\beta = a_{\gamma}/b_\gamma$ extending between the limits 0.9 and 1.1.

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Rotationspektrum des Chloroforms in angeregten Schwingungszuständen

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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 $J : 9 \rightarrow 10$, and $J : 10 \rightarrow 11$. Some rotation-vibration interaction constants $\omega_2$ are determined, others are predicted for bromoform and methylfluoride. Electric quadrupole hyperfine structure is not resolved.

Chloroform HCCl$_3$ is das zweite Molekül\(^1\) in der Reihe der Haloforme HCX$_3$, für welches Rotations-übergänge in schwingungss angeregten Molekülen bekannt geworden sind\(^2\). Das Spectrometer war eine 1 Meter lange elektrisch aufheizbare Starkzelle (X-Band). Die Hyperfeinstruktur des Kernquadrupolmoments der drei Chlorkerne Cl$^3$ wurde nicht aufgelöst. Bei etwa 4 mm Wellenlänge wurden folgende Absorptionsfrequenzen gemessen ($\nu_{\pi}$ = Schwingungsquantenzahl des $i$-ten Schwingungszustandes):

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