Electro-Optics
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RELATION BETWEEN ELECTRIC FIELD-INDUCED OPTICAL RECTIFICATION AND

ELECTRO-OPTIC KERR EFFECT IN MACROMOLECULAR SOLUTIONS

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The conditions for a relationship between the new effect of
Electric Field-Induced Optical Rectification (EFIOR) and the
Electro-Optical Kerr Effect (EOKE) are analyzed. Measurements
of the two effects yield the same information only in the case
of molecular substances, acted on by a static electric field
of not excessive strength. We show that in solutions of macro-
molecules exhibiting considerable reorientation effects of
permanent and induced electric dipoles, the above relation
between the two methods does not hold since, under external
conditions, optical saturation of macromolecular alignment takes
place in EFIOR whereas it is electric saturation in EOKE. We
prove however that the measurement of laser light - induced
electric anisotropy leads to identical results as EFIOR in the
molecular as well as macromolecular case.

Strong light can cause nonlinear changes in the electric permit-
tivity of media (1) measurable as optically induced electric aniso-
tropy (2) or as electric field-induced optical rectification (EFIOR)
(3,4). Recently, Ward and Guha (3) have shown the nonlinear suscepti-
bility tensor components $\chi_{ijkl}(0,0,\omega,-\omega)$, determined by the EFIOR
method for nitrobenzene, to be the same as the respective components
$\chi_{1kji}(-\omega,\omega,0,0)$, determined from electro-optical Kerr effect
(EOKE) measurements, in accordance with permutation symmetry. Now
this relation holds prevalently in molecular substances, where pro-
cesses of electric dipole reorientation are not too intense. Here,
it is our aim to show that the relation in question is not in general
valid in macromolecular solutions, in which both electric reorienta-
tion (5) and optical reorientation of the macromolecules (6) can attain
a state of complete ordering, i.e. electric or optical saturation.

We assume the solution to be sufficiently dilute for interactions between the macromolecules to be negligible. The molecules have a permanent electric dipole moment μ_i as well as anisotropic electric (α_{ij}) and optical (a_{ij}) polarizabilities. If the static electric field E(0) is not too strong, and omitting nonlinear polarizabilities, we have for the i-component of the total dipole moment of the macro-molecule:

$$m_i = \mu_i + \alpha_{ij} F_j (0) \qquad (1)$$

In the same approximation, its potential energy is:

$$u (E_o, E_\omega) = - \mu_i F_i (0) - \frac{1}{2} a_{ij} \langle F_i (\omega) F_j (\omega) \rangle_t \qquad (2)$$

The brackets $\langle \ \rangle_t$ indicate time-averaging over the oscillation period of the electric field of the highly intense laser light wave. Denoting by ρ the number density of macromolecules, the electric dipole polarisation is, by definition,

$$P_i (E_o, E_\omega) = \rho \langle m_i \rangle_{E_o, E_\omega} \qquad (3)$$

For axially symmetric macromolecules, eq. 3 becomes:

$$P_y (E_o, E_\omega) = \rho (\alpha + \frac{\mu^2}{3kT}) F_y (0) +$$

$$+ \frac{\rho}{3} (\gamma + \frac{\mu^2}{kT}) \langle 3 \cos^2\theta - 1 \rangle_{E_\omega} F_y (0), \qquad (4)$$

where $\alpha = (\alpha_{33} + 2\alpha_{11})/3$ is the mean value and $\gamma = \alpha_{33} - \alpha_{11}$ the anisotropy of the polarizability of the macromolecules, with their axis of symmetry subtending an angle θ with the direction of the static field $E_y(0)$, acting along the Y-axis.

Let the laser beam propagate along the Z-axis and the angle between the fields $E(\omega)$ and $E_y(0)$ be Ω. From eqs. 2 and 4, the change in polarization component is now:

$$\Delta P_y (E_o, E_\omega) = \frac{2}{3} \rho (\frac{\varepsilon + 2}{3})^2 (\pm |\gamma| + \frac{\mu^2}{kT}) \Phi (\pm q_\Omega^\omega) E_y(0), \qquad (5)$$

where (5,6)

$$\Phi (\pm q_\Omega^\omega) = \frac{1}{2} \langle 3 \cos^2\theta - 1 \rangle_{E_\omega} = \frac{3}{2} L_2 (\pm q_\Omega^\omega) - \frac{1}{2} \qquad (6)$$

is the functio of macromolecular reorientation in the optical field; the parameter q_Ω^ω of the reorientation being

$$q_\Omega^\omega = - \frac{|a_{33}^\omega - a_{11}^\omega|}{4kT} (\frac{n_\omega^2 + 2}{3})^2 (3 \cos^2\Omega - 1) \langle E_\omega^2 \rangle_t. \qquad (7)$$
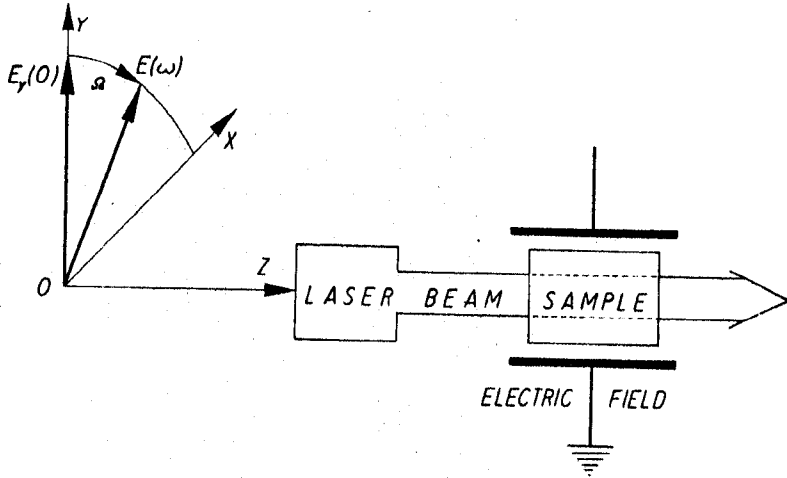
Fig. 1.   The laser beam propagates along the Z-axis, its electric
          vector $\vec{E}(\omega)$ subtending an angle Ω with the Y-axis.
          The static electric field $E_Y(0)$ acts along Y.

In eqs. 5 and 6 the positive sign is for macromolecules having posi-
tive optical anisotropy ($a_{33} > a_{11}$) i.e. for cigar-shaped particles,
whereas the minus sign refers to disc-shaped macromolecules with
negative anisotropy ($a_{33} < a_{11}$).

    If optical reorientation of the macromolecules is weak, eq. 5
gives:

$$\Delta P_y(\Omega) = \frac{\rho(3\cos^2\Omega - 1)}{45\,kT}\,(\,|\gamma| \pm \frac{\mu^2}{kT}\,)\,|a_{33}^\omega - a_{11}^\omega|\,\times$$

$$(\frac{\epsilon + 2}{3})^2\,(\frac{n_\omega^2 + 2}{3})^2\langle E_\omega^2\rangle_t \tag{8}$$

    If the optical reorientation is extremely strong, leading to
complete alignment of the macromolecules, eq. 5 gives for cigar- and
disc-shaped particles, respectively:

$$\Delta P_y(E_0,\infty) = \frac{2}{3}\,\rho\,(\frac{\epsilon + 2}{3})^2\,(\,|\gamma| + \frac{\mu^2}{kT}\,)\,E_y(0), \tag{9}$$

$$\Delta P_y(E_0,\infty) = \frac{1}{3}\,\rho\,(\frac{\epsilon + 2}{3})^2\,(\,|\gamma| - \frac{\mu^2}{kT}\,)\,E_y(0). \tag{10}$$

    Hence we note that formulae 8 to 10 can be useful for deter-
minations of the anisotropy in polarizability, and the permanent
dipole moment, of macromolecules.

For comparison we adduce the formula of O'Konski et al. (5) for the electro-optical birefringence of a macromolecular solution.

$$n_{||} - n_{\perp} = \pm 2\pi\rho n \left(\frac{n^2+2}{3n}\right)^2 \left| a_{33}^\omega - a_{11}^\omega \right| \Phi(p, \pm q), \quad (11)$$

where $\Phi(p, \pm q)$ is the electric reorientation function of macromolecules with the Langevin-Benoit parameters:

$$p = \frac{\mu}{kT} \left(\frac{\varepsilon+2}{3}\right) E_o; \qquad q = \frac{|\delta|}{2kT} \left(\frac{\varepsilon+2}{3}\right)^2 E_o^2. \quad (12)$$

One sees that in the general case of strong optical (eq.5) or electric (eq.11) macromolecular reorientation, no direct relationship between the methods of EOKE and EFIOR occurs. In the case of weak reorientation only, we obtain the following relationship, resulting from formulae 8 and 11:

$$6\pi \Delta P_y(\Omega) E_y(0) = n(n_{||} - n_{\perp}) (3\cos^2\Omega - 1) \langle E_\omega^2 \rangle_t. \quad (13)$$

Consequently, in this approximation, the two methods of EOKE and EFIOR provide the same information regarding the macromolecular parameters.

Since by definition

$$\Delta\varepsilon_y(\Omega) E_y(0) = 4\pi \Delta P_y(\Omega) \quad (14)$$

with regard to eq. 13 the change in electric permittivity due to intense light is related as follows (1) with the Kerr constant K:

$$\Delta\varepsilon_y(\Omega) = \frac{2}{3} n^2 (3\cos^2\Omega - 1) K \langle E_\omega^2 \rangle_t. \quad (15)$$

This relation provides another experimental procedure for gaining information concerning the electro-optical properties of macromolecules. This has been attempted for nitrobenzene (7).

If an AC electric field of frequency below the Debye dispersion is applied instead of the static field, no direct analytical relation exists between the three above-discussed methods even in the approximation of weak reorientation (4,8,9).

In statistically inhomogeneous fluids, yet other fluctuational processes take place (e.g. fluctuations in density, concentration, molecular fields, etc.) which affect the above discussed EFIOR and EOKE effects to varying degrees (10). In particular, in a quadratic approximation, these fluctuational processes are of an isotropic nature. They are independent of the angle Ω and involve an additional variation in electric permittivity:

$$\Delta \mathcal{E} = \frac{2\pi}{9VkT} \left(\frac{\mathcal{E}+2}{3}\right)^2 \left(\frac{n^2+2}{3}\right)^2 \left\langle \left(\underset{\iota}{A} + \frac{1}{kT}\Delta M^2\right)\Delta A^\omega\right\rangle x$$

$$\left\langle E_\omega^2 \right\rangle_t . \tag{16}$$

Here, ΔA and ΔA^ω are the statistical fluctuations in electric polarizability of the whole sample of volume V, whereas ΔM^2 is the fluctuation of the squared electric moment of the sample in the absence of external fields. The effects due to statistical fluctuations (eq. 16), can be detected only by measuring the absolute variation $\Delta \mathcal{E}$ and do not intervene in measurements of optically induced electric anisotropy (2) or Kerr effect.

The preceding theory can be extended to comprise various radial and angular macromolecular correlations as well as statistical-fluctuational processes (10). The theory of the EFIOR and EOKE methods can also be developed for liquid crystals, intensely studied of late by new measuring techniques involving lasers (11-18).

REFERENCES

1   Piekara A and Kielich S, J. Chem. Phys., 29, (1958) 1297.
     Kielich S and Piekara A, Acta Physica Polonica, 18, (1959) 439.
2   Kielich S, Physica, 34, (1967) 586.
3   Ward J F and Guha J K, Appl. Phys. Lett., 30 (1977) 276.
4   Buchert J, Kasprowicz-Kielich B and Kielich S, Adv. Mol. Relax.
          Interaction Processes, 11 (1977) 115.
5   O'Konski C T, Yoshioka K and Orttung W H, J. Phys. Chem., 63,
          (1959) 1558.
6   Kielich S, J. Colloid Interface Sci., 33, (1970) 142.
7   Drobnik A, Piekara A and Kaczmarek F, Second Conference on
          Coherence and Quantum Optics, Rochester 1966, Abstract
          p. 156.
8   Kasprowicz-Kielich B and Kielich S, Adv. Mol. Relax. Proc., 7,
          (1975) 275.
9   Alexiewicz W, Buchert J and Kielich S, Acta Phys. Polonica,
          A52, (1977) 445.
10   Kielich S, in "Dielectric and Related Molecular Processes",
          Ed. M. Davies (Wright, London, 1972) Vol.1 p.192.
11   Prost J and Lalanne J R, Phys. Rev. A8, (1973) 2090.
12   Wong G K L and Shen Y R, Phys. Rev. A10, (1974) 1277.
13   Coles H J and Jennings B R, Mol. Phys. 31, (1976) 571; 1225.
14   Jennings B R and Coles H J, Proc. Roy. Soc. London, A348, (1976)
          525.
15   Hanson E G, Shen Y R and Wong G K L, Phys. Rev. A14, (1976) 1281.
16   Lalanne J R, Martin B, Pouligny B and Kielich S, Optic Comm. 19,
          (1976) 440; Mol. Cryst., Liquid Cryst. 42, (1977) 153.
17   Schadt M, J. Chem. Phys., 67 (1977) 210.
18   Filippini J C and Poggi Y, Phys. Letters, 65A, (1978) 30.