ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 5

NONLINEAR OPTICAL ACTIVITY IN LIQUIDS

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(Received February 9, 1969)

Strong laser light induces a measurable nonlinear variation of the optical rotation. This variation is calculated, and is shown to provide information on the anisotropy of gyrotropic properties of molecules.

We shall extend Born's [1, 2] molecular theory of natural optical activity to the case when the medium is acted on by strong laser light with the electric vector $\boldsymbol{E}^{\omega_L}$ oscillating at a frequency ω_L. In this situation, the angle of optical rotation per unit length of the medium

$$\theta = \frac{\pi}{\lambda}(n_- - n_+) \tag{1}$$

(λ — vacuum wavelength of the light, n_- and n_+ — refractive indices for left and right circularly polarized light) undergoes a nonlinear variation to an amount dependent on the intensity of the laser beam [3, 4], and the medium becomes opitcally anisotropic.

Assuming the probe light with amplitudes $E_\pm = (E_x \pm iE_y)/\sqrt{2}$ to propagate along the z-axis of coordinates, the rotation angle of Eq. (1) undergoes the following quadratic variation in the presence of the laser field E^{ω_L}:

$$\theta = \theta_0 + \theta_2^{\mathrm{is}} \langle E_\sigma^{\omega_L} E_\sigma^{\omega_L} \rangle_t + \theta_2^{\mathrm{anis}} \langle 3E_z^{\omega_L} E_z^{\omega_L} - E_\sigma^{\omega_L} E_\sigma^{\omega_L} \rangle_t, \tag{2}$$

where

$$\theta_0 = \frac{4\pi^2}{3\lambda V}\left(\frac{n^2+2}{3n}\right)\left\langle \sum_{i=1}^{N} g_{\alpha\alpha}^{(i)} \right\rangle \tag{3}$$

is the natural optical rotation in the absence of laser light; n denotes the refractive index of a medium of volume V containing N molecules, whose optical activity is described by Born's [1] gyration tensor $g_{\alpha\beta}$; the symbols $\langle\rangle$ and $\langle\rangle_t$ respectively denote statistical and time averageing over one oscillation period of the laser field.

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The isotropic variation of θ is given as:

$$\theta_2^{is} = \frac{2\pi^2}{9\lambda V}\left(\frac{n^2+2}{3n}\right)\left(\frac{n_L^2+2}{3}\right)^2\left\{\left\langle\sum_{i=1}^{N} d_{\alpha\alpha\beta\beta}^{(i)}\right\rangle + \frac{1}{kT}\left\langle\Delta\sum_{i=1}^{N} g_{\alpha\alpha}^{(i)}\Delta\sum_{j=1}^{N} a_{\beta\beta}^{(j)}\right\rangle\right\} \tag{4}$$

and consists of a temperature-independent part involving the nonlinear gyration tensor $d_{\alpha\beta\gamma\delta} = \partial^2 g_{\alpha\beta}/\partial E_\gamma \partial E_\delta$ as well as a temperature-dependent part related with fluctuations of the number of molecules, ΔN, and of their mean polarizability tensor $g_{\alpha\beta}$ and $a_{\alpha\beta}$. The refractive index n_L is for the laser frequency.

The anisotropic variation of the rotation angle θ is given by the expression:

$$\theta_2^{anis} = \frac{\pi^2}{45\lambda V}\left(\frac{n^2+2}{3n}\right)\left(\frac{n_L^2+2}{3}\right)^2 \chi_{\alpha\beta\gamma\delta}\left\langle\sum_{i=1}^{N} d_{\alpha\beta\gamma\delta}^{(i)} + \frac{1}{kT}\sum_{i=1}^{N}\sum_{j=1}^{N} g_{\alpha\beta}^{(i)} a_{\gamma\delta}^{(j)}\right\rangle, \tag{5}$$

which contains a part accounting for nonlinear variations in optical activity of the molecules and a temperature-dependent part resulting by reorientation of anisotropic molecules in the electric field of the laser beam; $\chi_{\alpha\beta\gamma\delta} = 3\delta_{\alpha\gamma}\delta_{\beta\delta}+3\delta_{\alpha\delta}\delta_{\beta\gamma}-2\delta_{\alpha\beta}\delta_{\gamma\delta}$.

Particularized for a laser beam propagating along the z-axis *i.e.* parallel to the probe light, by Eq. (2) the variation in optical rotation angle becomes:

$$\theta-\theta_0 = (\theta_2^{is}-\theta_2^{anis})\langle E_x^{\omega_L} E_x^{\omega_L} + E_y^{\omega_L} E_y^{\omega_L}\rangle_t, \tag{6}$$

whereas for laser light oscillations, E^{ω_L} parallel to the z-axis, we have:

$$\theta-\theta_0 = (\theta_2^{is}+2\theta_2^{anis})\langle E_z^{\omega_L} E_z^{\omega_L}\rangle_t. \tag{7}$$

If in Eqs (4) and (5) one neglects terms in the nonlinear gyration tensor $d_{\alpha\beta\gamma\delta}$ and assumes $g_{11} = g_{22} \neq g_{33}$ and $a_{11} = a_{22} \neq a_{33}$, the following expressions, which are well adapted for numerical evaluations, results:

$$\theta_2^{is} = \frac{\beta_T}{8\pi}\,\theta_0(n_L^2-1)\left(\frac{n_L^2+2}{3}\right), \tag{8}$$

$$\theta_2^{anis} = \left(\frac{2\pi}{n^2+2}\right)\left(\frac{g_{33}-g_{11}}{a_{33}-a_{11}}\right)B_\lambda, \tag{9}$$

with β_T — the isothermal compressibility coefficient, and B_λ — the optical Kerr constant of the liquid determined experimentally by the laser technique [5].

Thus, studies of nonlinear variation of the optical rotation angle should permit direct determinations of the amount and sign of the anisotropy $g_{33}-g_{11}$ of the molecular gyration tensor. The present theory can be extended to cases when magneto-optical and multipolar contributions have to be considered as well [6].

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