NONLINEAR CHANGE IN LIGHT DEPOLARIZATION RATIO DUE TO OPTICAL MOLECULAR REORIENTATION EFFECT

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Formulas for the nonlinear change ΔD in depolarization ratio from optical molecular reorientation are proposed taking into account relaxational as well as pairwise and triple molecular angular interaction processes. Numerical evaluations for liquids show that ΔD is accessible to experimental detection by existing laser techniques, providing a new method for the direct determination of the value and sign of the optical molecular anisotropy.

Second harmonic light scattering in liquids, observed recently by Terhune et al. [1], is due essentially to nonlinear molecular polarization induced by the square of the electric field of intense laser beams [2]. In highly anisotropic molecules, reorientation in strong oscillating fields can become important [3], affecting the depolarization ratio D. Here, we calculate this effect of ΔD, taking into account molecular relaxation [4] as well as angular pairwise and triple correlations.

Assume the weak light beam propagating along the Y-axis of the laboratory system, with electric vector oscillating in the observation plane XY. If the light scattered linearly is observed along the X-axis, one has $D = 1$ [3]. When the medium is moreover acted on by an intense electromagnetic field of frequency ω_L, the depolarization ratio will undergo the following, nonlinear variation:

$$\Delta D = \frac{1}{14kT}\left\{a_{\parallel}^{\omega_L} - a_{\perp}^{\omega_L} + \frac{\mu^2}{kT(1+\mathrm{i}\omega_L\tau_D)}\right\} \times$$

$$\times\left\{1 + \frac{\exp(\mathrm{i}2\,\omega_L t)}{1+\mathrm{i}2\,\omega_L\tau_L}\right\}(F_{0Y}^2 - F_{0Z}^2). \qquad (1)$$

Above, $a_{\parallel}$ and $a_{\perp}$ are respectively linear polarizabilities parallel and perpendicular to the symmetry axis of the molecule of dipole moment μ, and τ_L is a relaxation time characterizing molecular reorientation caused by the local electric field $F(\omega_L)$ and related with Debye's relaxation time τ_D as $\tau_D = 3\tau_L$ [4].

Table 1
Calculated variations in depolarization ratio due to optical molecular reorientation effect.

Liquid	D	J_2	$\frac{\Delta D}{I}\times 10^{10}$	$\frac{\Delta Dc}{I}\times 10^{10}$
Carbon disulphide	0.65	-0.36	0.81	-0.11
Chloroform	0.20	-0.32	-0.15	-0.01
Methyl ethyl ketone	0.16	-0.71	-0.19	0.74
Acetone	0.21	-0.32	-0.13	-0.01
Cyclohexane	0.06	-0.75	-0.15	0.75
Dioxane	0.11	-0.72	-0.17	0.73
Benzene	0.42	-0.52	-0.42	0.49
Toluene	0.48	-0.49	-0.50	0.48
Chlorobenzene	0.56	-0.61	-0.50	1.05
Bromobenzene	0.62	0.29	-0.39	-0.56
Nitrobenzene	0.74	0.31	-0.57	-0.84
Pyridine	0.46	-0.62	-0.22	0.33

For $\omega_L \to 0$, eq. (1) goes over into the well-known result [3, 5], whereas in the other limiting case when both $\tau_D\omega_L$ and $\tau_L\omega_L$ become very large, the following formula results:

$$\Delta D = \frac{a_{\parallel} - a_{\perp}}{7\,kT}\left(\frac{n^2+2}{3}\right)^2 (I_Y - I_Z) \qquad (2)$$

defining the change in D due to intense laser light of intensities I_Y and I_Z with oscillations along the Y- and Z- axes.

Eq. (2) can provide the basis for a new method of determining directly the value and sign of the optical anisotropy of the molecule. Methods based on measurements of such quantities as optically induced birefringence or the depolarization of linearly scattered light permit to determine the square of the optical anisotropy only [3, 4].

Liquids present statistical molecular correlations of the angular kind, which if taken into account lead to the following modification of eq. (2):

$$\Delta D_c = \Delta D\,(1+3\,J_2+J_3)/(1+J_2) \tag{3}$$

In the integral parameter [4]

$$J_2 = \frac{\rho}{2V}\int\!\!\int (3\cos^2\theta_{pq}-1)\,g_2(\tau_p,\tau_q)\,\mathrm{d}\tau_p\,\mathrm{d}\tau_q, \tag{4}$$

g_2 is the binary correlation function of two molecules at configurations τ_p and τ_q subtending the angle θ_{pq} and ρ is the mean number density of molecules in volume V of the medium. J_3 contains the ternary correlation function g_3 [c.f.3]. The pairwise angular correlation parameter J_2 can be determined numerically from the formula of the optically induced birefringence constant or depolarization ratio D [4].

In evaluating numerically ΔD_c from eq. (3), triple correlations can be omitted, restricting calculations to pairwise correlations J_2, as done establishing table 1. On comparing the two last columns one sees that pairwise angular correlations, in addition to an increase or decrease in the numerical value of ΔD_c, lead moreover to a change of its sign. ΔD is mostly of the order of $10^{-10}\,I$ and is thus accessible to experimental detection using a laser beam of intensity 10^5 - 10^6 esu.

References

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