

OPTICALLY INDUCED BIREFRINGENCE CALCULATED FROM LIGHT SCATTERING DATA OF LIQUIDS

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Optically induced birefringence is calculated numerically from simple formulae involving the experimentally measured Rayleigh and depolarization ratios of light scattered by liquids. Values of nonlinear variations in refractive index due to optical birefringence are compared with variations from electrostriction and the electrocaloric effect.

Recently, Shen [1] calculated numerically the changes in refractive index induced in liquids by electrostrictive pressure and the optical Kerr effect, thus admitting a preliminary analysis of the role of these effects in the self-focussing of laser beams in liquids and of their part in other nonlinear optical processes discussed recently by a number of authors [2,3]. Also, the first successful measurements of light intensity-induced rotation [4] and optically induced birefringence [5] in liquids have been reported. Hence, this is the time to proceed to a more detailed, quantitative analysis of these novel optical effects on the basis of formulae as simple as possible and yielding directly numerical results. With this in mind, we propose to calculate the optically induced birefringence from formulae involving only measurable quantities accessible from work on light scattering in liquids [6]*.

Let us consider an isotropic medium of volume V at temperature T on which a light beam of high intensity $I_0 = EE^*$ and electric vector E is incident. The nonlinear variation in refractive index is now

$$\Delta n(V, T, E) = \Delta n_V + \Delta n_T + \Delta n_E, \quad (1)$$

where Δn_V and Δn_T are respectively due to electrostriction and the electrocaloric effect, and are given thermodynamically as

$$\Delta n_V = \frac{1}{8\pi\beta_T} \left(\frac{\partial n}{\partial p} \right)_T \left\{ 2n \left(\frac{\partial n}{\partial p} \right)_T - (n^2 - 1)\beta_T \right\} \left(\frac{n^2 + 2}{3} \right)^2 I, \quad (2)$$

* In ref. 1, the optical birefringence is calculated from a relationship involving the anisotropic part of the d.c. Kerr constant.

$$\Delta n_T = -\frac{T\gamma}{8\pi C_p} \left(\frac{\partial n}{\partial T} \right)_p \left\{ 2n \left(\frac{\partial n}{\partial T} \right)_p + (n^2 - 1)\alpha_p \right\} \left(\frac{n^2 + 2}{3} \right)^2 I. \quad (3)$$

Above, β_T is the isothermal compressibility coefficient, α_p and C_p are the thermal expansion coefficient and specific heat at constant pressure p , and $I = 9I_0 / (n^2 + 2)^2$ is the light intensity existing within the medium of refractive index n .

The last term Δn_E in eq. (1) accounts for the change in refractive index due to the influence of the optical field E on the molecular properties of the medium. In the general case, we have [7]:

$$\Delta n_E = A_n I + (\cos^2 \Omega - \frac{1}{3}) n B I, \quad (4)$$

Ω being the angle between the electric vectors of the measuring beam and the intense beam, which polarizes the medium nonlinearly; A_n is a constant related with optical deformation of the molecules of an isotropic nature, and B a constant describing the optical anisotropy induced in the medium. Indeed, by eqs. (1) and (4) we have

$$\Delta n_B = \Delta n_{\parallel} - \Delta n_{\perp} = n B I \quad (5)$$

for the change in refractive index resulting solely by the optical birefringence of the isotropic medium.

The molecular - statistical form of the optical birefringence constant B is rather involved [7,8]; in the case of dense media with considerable molecular correlations, it is hardly convenient for direct numerical evaluations. However, restricting oneself to the effect resulting from optical molecular orientation, which in most molecular liquids predominates with regard to the small ef-

Table 1
Comparison of calculated variations in refractive index due to optical birefringence and variations due to electrostriction and electrocaloric effect*.

	n	$\beta_T \times 10^{12}$	D	$R \times 10^6 \text{ cm}^{-1}$	$\Delta n_B / I = nB \times 10^{12}$			$\frac{\Delta n_V}{I} \times 10^{12}$	$-\frac{\Delta n_T}{I} \times 10^{12}$
	$\lambda=5460 \text{ \AA}$	(cm^2/dyn)		$\lambda=5460 \text{ \AA}$	eq. (6)	eq. (7)	experim.		
Benzene	1.503	95	0.42	15.8	5.50	3.29	1.95 ^a	1.67	0.39
Toluene	1.499	92	0.48	18.4	7.01	4.13	4.54 ^a	1.31	0.30
Cyclohexane	1.426	112	0.049	4.56	0.24	0.16	0.20 ^a	0.95	0.23
Iso-octane	1.391	152	0.047	5.15	0.25	0.16		0.90	
n-Hexane	1.374	170	0.073	5.32	0.39	0.26	0.36 ^b	0.80	0.16
n-Octane	1.398	125	0.12	4.85	0.57	0.40	0.47 ^b	0.84	0.16
n-Decane	1.413	105	0.15	4.95	0.71	0.47	0.56 ^b	0.89	0.13
n-Hexadecane	1.435	83	0.26	5.75	1.33	0.88		0.85	
Carbon tetrachloride	1.460	106	0.042	5.38	0.25	0.16	0.25 ^a	1.30	0.33
Carbon disulphide	1.634	94	0.65	83.9	43.07	20.83	20.40 ^a	4.70	1.26
Methyl ethyl ketone	1.379	108	0.16	4.18	0.62	0.43	3.33 ^b	0.66	
Nitrobenzene	1.560	49	0.74	65.8	34.45	15.18	14.15 ^a	1.98	0.19
Water	1.334	46	0.108	0.99	0.10	0.08	0.14 ^a	0.10	0.01
Chloroform	1.446	87	0.20	5.64	1.06	0.70	0.81 ^a	0.45	0.51
Acetone	1.359	125	0.208	4.06	0.74	0.59	0.37 ^a	0.27	0.08
Chlorobenzene	1.521	75	0.575	23.1	10.08	6.16	6.34 ^b	1.70	
Aniline	1.586	45	0.60	16.0	7.53	5.90		2.27	
Ethyl alcohol	1.362	110	0.056	2.81	0.16	0.11	0.11 ^b	0.25	
Methyl alcohol	1.328	127	0.049	2.31	0.11	0.09	0.08 ^b	0.17	
Piridine	1.509	48	0.46			2.09	13.92 ^b	1.02	

* Values of n , β_T , D and R are from refs. 6 and 10.

^a Calculated from Paillette's measurements [5].

^b Calculated from eq. (9) and the experimental Kerr constant of ref. 10.

fect of nonlinear optical deformation [7], we obtain the following relation [8]:

$$B = \frac{\lambda^4 R D}{8\pi^3 k T (1+D)} \left(\frac{n^2+2}{3n} \right)^2 \quad (6)$$

wherein all quantities are directly measurable in light scattering, namely the Rayleigh ratio R and depolarization ratio D . Eq. (6) holds for isotropic bodies irrespective of their state of condensation, molecular symmetries, and molecular statistical correlations.

On the other hand, B can be expressed with sufficient accuracy as follows [7]:

$$B = \frac{6\pi\beta_T D}{6-7D} \left(\frac{n^2-1}{4\pi} \right)^2 \left(\frac{n^2+2}{3n} \right)^2, \quad (7)$$

this formula being of less generality than (6), but presenting the advantage of applicability in cases when the experimental Rayleigh ratio R is not available.

In cases when the anisotropic part of the latter, R_{anis} , can be determined independently, eq. (6) can be replaced by the simpler formula

$$B = \frac{3\lambda^4 R_{\text{anis}}}{52\pi^3 k T} \left(\frac{n^2+2}{3n} \right)^2 \quad (8)$$

relating directly the effects of optically induced birefringence and anisotropic light scattering in liquids [8].

One can moreover express B by the anisotropic part of the Kerr constant, K_{anis} , by way of the approximate relation [8]

$$B = \frac{(n^2-1)(n^2+2)}{(\epsilon_\infty-1)(\epsilon_\infty+2)} K_{\text{anis}}, \quad (9)$$

where ϵ_∞ is the high-frequency dielectric constant. Eq. (9) is of advantage in the case of non-dipolar substances only, when it yields sufficient accuracy. In the dipolar case, K_{anis} has to be determined as the difference $K_{\text{anis}} = K - K_{\text{dip}}$ between the total Kerr constant K and its dipolar part K_{dip} . However, for liquids, their determination separately raises great difficulties and can only be performed approximately.

Table 1 gives the values of variations of refractive index, Δn_B , as calculated from eqs. (5) - (7)

and available experimental data for R and D [6]. Also, it contains the values of Δn_B calculated from available measurements [5]. For the sake of comparison, we give the variations Δn_V and Δn_T calculated previously [9] from eqs. (2) and (3).

From table 1, the Δn_B - values calculated from eq. (6) are in all cases seen to be (on the average about twice) larger than those from eq. (7), the latter being in better agreement with the experimental Δn_B - values resulting from present optical birefringence measurements [5] and earlier data from the Kerr effect [10]. As to the values of the variations Δn_V due to electrostriction, they exceed Δn_B in weakly birefringent liquids, but are smaller than Δn_B in strongly birefringent ones. The variations Δn_T due to the electrocaloric effect are negative and smaller in absolute value than Δn_V and Δn_B .

Thus, eqs. (6) and (7) lead smoothly and directly to Δn_B - values which are both reasonable and in accordance with nonlinear optical measurements [4,5]. In this way, and on the other hand recurring to formulae for B in molecular-statistical form [7,8], we can gain valuable information regarding both molecular optical anisotropy and molecular correlations in dense systems. Hence, work on the various nonlinear changes in refractive index should profitably proceed in conjunction with research on molecular light scattering in liquids [8]. The phenomena discussed above, together with the experimental [11] and theoretical [12] investigation of multi-harmonic

light scattering, provide the basis of nonlinear molecular optics.

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