

## LETTERS TO THE EDITOR

NUMERICAL CALCULATIONS OF OPTICAL KERR CONSTANT  
FOR SEVERAL LIQUIDS

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Molecular optical Kerr constants calculated taking into account the effect of angular correlations on molecular reorientation are found to be in satisfactory agreement with recent measurements of laser light-induced optical birefringence of the liquids.

Laser techniques provide new possibilities of studying the optical Kerr effect, which consists in the induction of optical birefringence  $n_{||} - n_{\perp}$  in a fluid by intense laser light [1], [2]. One has [3]

$$n_{||} - n_{\perp} = n_1 B_{n_1} I_2 = \lambda_1 B_{\lambda_1} I_2, \quad (1)$$

with  $n_1$  — the refractive index at the wavelength  $\lambda_1$  used in the measurement (thus, a gas laser emitting  $\lambda_1 = 4880 \text{ \AA}$  [2]), and  $I_2$  the laser light intensity. The measured optical Kerr constants are related to the molecular constant  $B_m$  as follows [3]:

$$B_{n_1} = \frac{\lambda_1}{n_1} B_{\lambda_1} = \frac{3}{2} \left( \frac{n_1^2 + 2}{3n_1} \right)^2 \left( \frac{n_2^2 + 2}{3} \right)^2 \frac{B_m}{V_m}, \quad (2)$$

where  $n_2$  is the refractive index for intense light of wavelength  $\lambda_2$  (thus, from a ruby laser emitting  $\lambda_2 = 6943 \text{ \AA}$ ) inducing birefringence in a medium of molar volume  $V_m$ .

In general,  $B_m$  consists of a part [3], [4]

$$B_m^{NL} = \frac{4\pi}{9} N_A c \quad (3)$$

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linked with nonlinear polarization  $c$  of the molecule, and a part

$$B_m^{OR} = \frac{4\pi N_A}{45 kT} \delta^2 \quad (4)$$

due to the effect of optical orientation of molecules possessing the optical anisotropy

$$\delta^2 = \frac{1}{2} \{(a_1 - a_2)^2 + (a_2 - a_3)^2 + (a_3 - a_1)^2\}, \quad (5)$$

where  $a_1, a_2, a_3$  are linear polarizabilities in the directions of the three principal molecular axes (for simplicity, the polarizabilities are assumed the same for  $\lambda_1$  and  $\lambda_2$ ).

In liquids, various molecular correlations have to be considered [3]. These modify eqs (3) and (4). The most strongly affected is the orientational part (4), which can be written as [3]

$${}_C B_m^{OR} = B_m^{OR} (1 + J_A). \quad (6)$$

$J_A$  denoting the angular correlations parameter

$$J_A = \frac{1}{2} \varrho \delta^{-2} \sum_{s,t=1}^3 a_s a_t \int (3 \cos^2 \theta_{st}^{(pq)} - 1) g(\tau_{pq}) d\tau_{pq}; \quad (7)$$

here,  $\theta_{st}^{(pq)}$  is the angle between the principal axes  $s, t$  of molecules  $p$  and  $q$  at mutual configuration  $\tau_{pq}$  and correlation function  $g(\tau_{pq})$ .

TABLE I

Angular correlations parameter  $J_A$  determined from experimental data of depolarization ratio  $D$  for several liquids

Liquid	Polarizabilities in $10^{-24}$ cm <sup>3</sup>			$\delta^2 \times 10^{18}$ (cm <sup>6</sup> )	$\varrho \times 10^{-21}$ (cm <sup>-3</sup> )	$\beta_T \times 10^{12}$ (dyn/cm <sup>2</sup> )	$D$	$J_A$
	$a_1$	$a_2$	$a_3$					
Carbon disulphide	15.14	5.54	5.54 <sup>1</sup>	92.16	9.99	94 <sup>3</sup>	0.64 <sup>3</sup>	-0.40
Chloroform	6.68	9.01	9.01 <sup>1</sup>	5.43	7.51	87 <sup>4</sup>	0.20 <sup>4</sup>	-0.36
Acetone	6.96	7.22	4.82 <sup>2</sup>	5.20	8.21	125 <sup>4</sup>	0.21 <sup>4</sup>	-0.33
Cyclohexane	11.68	11.68	9.25 <sup>1</sup>	5.90	5.55	112 <sup>3</sup>	0.06 <sup>4</sup>	-0.76
Benzene	12.31	12.31	6.35 <sup>1</sup>	35.52	6.74	95 <sup>3</sup>	0.42 <sup>3</sup>	-0.52
Toluene	15.64	13.66	7.48 <sup>1</sup>	54.35	5.65	92 <sup>3</sup>	0.48 <sup>3</sup>	-0.53
Chlorobenzene	15.51	13.82	7.42 <sup>2</sup>	54.63	5.92	75 <sup>4</sup>	0.58 <sup>4</sup>	-0.34
Bromobenzene	16.84	12.13	9.56 <sup>2</sup>	40.88	5.73	65 <sup>4</sup>	0.65 <sup>4</sup>	0.23
Nitrobenzene	17.16	14.19	7.41 <sup>2</sup>	74.92	5.89	49 <sup>3</sup>	0.74 <sup>3</sup>	0.04

Values of  $a_1, a_2, a_3$  are from: <sup>1</sup> H. A. Stuart, *Die Struktur des freien Moleküls* (Springer-Verlag, Berlin 1952); <sup>2</sup> M. Yasumi, H. Okabayashi and H. Komooka, *Bull. Chem. Soc. Japan*, **31**, 673 (1958).

Values of  $\beta_T$  and  $D$  are from: <sup>3</sup> D. J. Coumou, E. L. Mackor and J. Hijmans, *Trans. Faraday Soc.*, **60**, 1539, 2244 (1964); <sup>4</sup> I. L. Fabelinskiy, *Molekularnoye Rassieyaniye Sveta* (Gostekhizdat, Moskva 1951); *Landolt-Börnstein Tables* (Springer-Verlag, Berlin).

The numerical value of the parameter [7] can be obtained by measuring the degree of depolarization of scattered light  $D$  [5], [6] from the relation

$$1 + J_A = \frac{45a^2 \rho k T \beta_T D}{\delta^2 (6 - 7D)}, \quad (8)$$

where  $\beta_T$  is the isothermal compressibility coefficient of the medium, and  $\rho = N_A/V_m$ .

The values of  $J_A$  calculated from eq. (8) are assembled in Table I, whereas those of  $B_m^{OR}$  and  $C_m^{BOR}$  calculated from eqs (4) and (6) — in Table II. Agreement is seen to be satisfactory between the values of  $C_m^{BOR}$  calculated when taking into account molecular angular correlations and those determined from optical birefringence measurements [2], though not so good with those from other experiments [7], [8].

TABLE II

Comparison of calculated and experimental values of the molecular optical Kerr constants for various liquids

Liquid	$n_\lambda$ for $\lambda$ in Å			$V_m$ cm <sup>3</sup> /mol	$B_\lambda^{exp} \times 10^9$	Molecular optical Kerr constants in 10 <sup>12</sup> esu		
	4880	5893	6943			$B_m^{OR}$	$C_m^{BOR}$	$B_m^{exp}$
Carbon disulphide	1.654	1.630	1.614	60.2	418.0 <sup>1</sup>	383.4	230.0	230.3 <sup>1</sup>
					326.0 <sup>2</sup>			177.1 <sup>2</sup>
Chloroform	1.453	1.447	1.430	80.2	16.5 <sup>1</sup>	22.6	14.5	17.9 <sup>1</sup>
					17.0 <sup>2</sup>			16.7 <sup>2</sup>
Acetone	1.363	1.359	1.350	73.4	7.3 <sup>1</sup>	21.6	14.5	8.3 <sup>1</sup>
					10.3 <sup>2</sup>			11.1 <sup>2</sup>
Cyclohexane	1.432	1.426	1.421	108.5	4.1 <sup>1</sup>	24.5	5.9	6.3 <sup>1</sup>
					7.8 <sup>2</sup>			10.8 <sup>2</sup>
Benzene	1.513	1.501	1.495	89.4	40.0 <sup>1</sup>	147.7	70.9	43.1 <sup>1</sup>
					57.3 <sup>2</sup>			55.5 <sup>2</sup>
Toluene	1.508	1.496	1.490	106.6	93.0 <sup>1</sup>	226.1	106.3	118.1 <sup>1</sup>
					65.5 <sup>2</sup>			70.1 <sup>2</sup>
Chlorobenzene	1.538	1.525	1.518	101.7	99.3 <sup>2</sup>	227.3	150.0	104.7 <sup>2</sup>
Bromobenzene	1.574	1.559	1.550	105.1	143.5 <sup>2</sup>	170.1	209.2	144.5 <sup>2</sup>
Nitrobenzene	1.572	1.553	1.542	102.3	290.0 <sup>1</sup>	311.7	324.1	320.7 <sup>1</sup>
					264.0 <sup>2</sup>			255.6 <sup>2</sup>

Values of  $n$  are from International Critical Tables Vol. VII (McGraw-Hill Book Company, Inc. New York 1930),  $n$ -values for  $\lambda = 6943$  Å are extrapolated.

<sup>1</sup>  $B_\lambda$  from Paillette's [2] measurements of optical Kerr effect ( $\lambda_1 = 4880$  Å and  $\lambda_2 = 6943$  Å).

<sup>2</sup>  $B_\lambda$  from static Kerr effect extrapolated to  $\lambda_1 = \lambda_2 = 5893$  Å by Shen [7].

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