

MOLECULAR ANGULAR CORRELATIONS AND STRONG OPTICAL NONLINEARITIES IN INTENSE LASER LIGHT PROPAGATION IN LIQUIDS

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A formula is proposed admitting of direct calculations of $2n$ -th nonlinearities in the optical permittivity ϵ_{2n} for liquids consisting of anisotropic molecules. The ϵ_2 values calculated taking into account pairwise molecular angular correlations are in good agreement with measurements of the optical Kerr effect. It is shown that ϵ_4 can be positive or negative according to the sign of the molecular anisotropy and type of angular correlations; this can be of considerable significance for the self-focussing of laser beams.

1. Introduction

Some years ago, for certain macromolecular substances, the Kerr effect has been shown to depend on higher powers of the *DC* electric field strength E when the latter is sufficiently high, leading to saturation of birefringence [1]. Recently [2], [3] optical saturation has been invoked as an important factor in the evolution of self-focussing of laser beams. Such considerations go beyond the quadratic dependence of the refractive index on the laser light amplitude E_0 known from earlier experiments [4–6]. Tentative theoretical analysis of the latter shows at once that — in addition to the weak process of nonlinear optical molecular polarization and the strong effect of molecular reorientation [7–9] — an essential role therein belongs to various angular molecular correlations [8, 10, 11] as well as to the effect of molecular redistribution [8, 10–12].

It is the aim of this paper to give a more detailed analysis of the expression [10]:

$$\epsilon_{\sigma\tau} - \epsilon_0 \delta_{\sigma\tau} = \frac{1}{3} \{AE^2 \delta_{\sigma\nu} + B(3E_\sigma E_\nu - E^2 \delta_{\sigma\nu})\} (\epsilon_{\nu\tau} + 2\delta_{\nu\tau}) \quad (1)$$

for the nonlinear changes undergone by the optical permittivity tensor $\epsilon_{\sigma\tau}$ when intense laser light propagates in a liquid.

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The constants A and B define respectively the isotropic and anisotropic optical properties induced in the medium and account for its structure and thermodynamical state; they are even functions of E_0 . In particular, A is also related with the electrostrictional and electrocaloric effects already discussed in a quadratic approximation [13, 14].

2. Higher-order optical Kerr constants

Here, we shall concentrate on the constant B defining the birefringence induced optically in the medium. Excluding dispersion and absorption, B can be expanded as follows:

$$B = \sum_{n=1}^{\infty} \frac{1}{2^{n-1}} B_{2n} E_0^{2(n-1)}. \quad (2)$$

The coefficients B_{2n} are the following functions of the temperature T :

$$B_{2n} = \sum_{s=0}^n B_{2n}^{(s)} T^s = B_{2n}^{(0)} + \frac{B_{2n}^{(1)}}{T} + \dots + \frac{B_{2n}^{(n)}}{T^n}. \quad (3)$$

The first term $B_{2n}^{(0)}$, not explicitly dependent on T , is related only with nonlinear optical polarization of the molecules (this effect can appear in any medium irrespective of the symmetry of its molecules, thus for the spherical symmetry also [7], [10]). The last, most strongly temperature-dependent term in Eq. (3), $B_{2n}^{(n)}/T^n$, corresponds to the effect of optical molecular reorientation. In the case of substances consisting of anisotropic molecules, it is this term that plays the most essential role and predominates over $B_{2n}^{(0)}$ and the other, mixed terms in the sum of (3). For strongly anisotropic molecules, one can restrict oneself to the purely orientational effect defined for axially-symmetric molecules by the expression (see Appendix)

$$B_{2n} = 2\pi\rho a_n (\alpha_{\parallel} - \alpha_{\perp}) \left(\frac{\alpha_{\parallel} - \alpha_{\perp}}{2kT} \right)^n \left(\frac{\varepsilon + 2}{3} \right)^{2n}, \quad (4)$$

where ρ is the number density of the liquid of optical permittivity $\varepsilon = n^2$, α_{\parallel} and α_{\perp} — the optical polarizabilities parallel and perpendicular to the molecule's symmetry axis, and

$$a_n = \frac{1}{n!(2n+3)} - \sum_{k=1}^n \frac{a_{n-k}}{k!(2k+1)}. \quad (5)$$

For anisotropic molecules with principal polarizabilities $\alpha_1, \alpha_2, \alpha_3$ one obtains instead of Eq. (4) for $n = 1$ and $n = 2$ [10]

$$B_2 = \frac{2\pi\rho}{45kT} \{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2\} \left(\frac{\varepsilon + 2}{3} \right)^2, \quad (6)$$

$$B_4 = \frac{2\pi\rho}{945k^2T^2} \{(\alpha_1 - \alpha_2)^2(\alpha_1 + \alpha_2 - 2\alpha_3) + (\alpha_2 - \alpha_3)^2(\alpha_2 + \alpha_3 - 2\alpha_1) + (\alpha_3 - \alpha_1)^2(\alpha_3 + \alpha_1 - 2\alpha_2)\} \left(\frac{\varepsilon + 2}{3} \right)^4. \quad (7)$$

The expressions (2) and (4) can be applied for direct evaluations of higher-order nonlinearities of various liquids, as apparent from Table I. However, this kind of optical saturation demands fulfillment of the condition $(\alpha_{||} - \alpha_{\perp})E_0^2 < 4kT$. In most anisotropic molecules, this in turn requires that $E_0 \leq 10^5$ e. s. u. This would bring us to the threshold of many-quantum photo-ionization. But even if nonlinearities in the region below 10^5 e. s. u. are small, they may still be strong enough to affect various sensitive processes accompanying *e. g.* self-focussing and self-trapping of light in liquids. From Eq. (4) and Table I, the sign of B_2 is seen to be always positive [15] and that of B_6 negative. B_4 and B_8 can be positive or negative, according to the sign of the anisotropy of the isolated molecule.

We now write Eq. (2) as follows:

$$B = \sum_{n=1}^{\infty} B_{2n} I^{n-1} \quad (8)$$

with $I = E_0^2/2$ denoting the incident laser light intensity; by (4) and (5), the induced optical anisotropy is now given by the series

$$B = B_2 \left(1 + \frac{2b}{21} I - \frac{4b^2}{315} I^2 - \frac{8b^3}{2079} I^3 + \dots \right), \quad (9)$$

where

$$b = \frac{\alpha_{||} - \alpha_{\perp}}{2kT} \left(\frac{\epsilon + 2}{3} \right)^2 \quad (10)$$

is a molecular reorientation parameter.

In the case of colloid systems, higher-order nonlinearities are incomparably larger [16]. For such systems, we get instead of Eq. (4) in satisfactory approximation $B_{2n}^{\text{Coll}} = q^n B_{2n}$, where q is the ratio of volumes of the colloid particle and molecule and lies in the range of $1 \leq q \leq 10^6$. For example, in the case of gold colloid particles in water [16]

$$B^{\text{Au}} = B_2(1 + 6 \times 10^{-6}I - 5 \times 10^{-11}I^2 - 9.4 \times 10^{-16}I^3 + \dots),$$

while for CS_2 from Eq. (8) and the values of Table I

$$B^{\text{CS}_2} = B_2(1 + 14 \times 10^{-12}I - 105 \times 10^{-24}I^2 - 916 \times 10^{-36}I^3 + \dots).$$

As can be seen from Eq. (1) and the above expansions for B^{Au} and B^{CS_2} , after an initial steep increase the refractive index can decrease as negative terms B_6 and B_8 come to play

TABLE I

Calculated values of contributions B_2 , B_4 , B_6 and B_8 to optical saturation in liquids, without angular correlations

Liquid	$B_2 \times 10^{12}$	$B_4 \times 10^{24}$	$B_6 \times 10^{36}$	$B_8 \times 10^{48}$
Carbon disulphide	15.4	211.1	-1618.6	-14104.8
Chloroform	0.52	-1.5	-24.6	47.5
Benzene	3.3	-23.6	-100.4	452.0
Nitrobenzene	6.6	-66.4	-374.1	2375.5

a part. Thus a laser beam propagating in a colloid solution will at first undergo strong narrowing and subsequently exhibit divergence; as a matter of fact, this has been observed recently in gold-water colloid at sufficiently high power of the beam [17].

3. Role of molecular interactions

In order to have better agreement with experiment, one has to take into consideration molecular correlations of the angular type, leading to the equations

$$B_2^* = B_2(1 + \rho J_2), \quad (11)$$

$$B_4^* = B_4(1 + 3\rho J_2 + \rho^2 J_3), \quad (12)$$

with

$$J_2 = \frac{1}{2V} \iint (3 \cos^2 \theta_{pq} - 1) g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (13)$$

$$J_3 = \frac{1}{2V} \iiint \{9 \cos \theta_{pq} \cos \theta_{qr} \cos \theta_{rp} - 3(\cos^2 \theta_{pq} + \cos^2 \theta_{qr} + \cos^2 \theta_{rp}) + 2\} \times \\ \times g^{(3)}(\tau_p, \tau_q, \tau_r) d\tau_p d\tau_q d\tau_r, \quad (14)$$

where θ_{pq} denotes the angle between the symmetry axes of molecules p and q at configurations τ_p and τ_q , and $g^{(2)}$ and $g^{(3)}$ are the binary and ternary correlation functions.

J_2 and J_3 are respectively pairwise and triple angular molecular correlation parameters; their values can be determined from light scattering data [8], [18]. In the present context, it is noteworthy that angular correlations can cause a change in sign of B_4 as well as a decrease or increase in the value of B_2 as compared with B_2 calculated without correlations; as apparent from Table II, this leads to better agreement with experiment [4–6].

The effect of molecular redistribution also plays a part (essentially in liquids consisting of symmetrical molecules [8], [12]); instead of Eq. (6), we now obtain in the absence of angular correlations [19]

$$B_2 = \frac{4\pi\rho}{45kT} \left\{ \delta^2 + \rho \left[9\alpha^4 + \frac{28}{5} \alpha^2 \delta^2 + \frac{2}{3} \alpha \delta^3 + \frac{67}{225} \delta^4 \right] J_R + O(\rho^2) \right\} \left(\frac{\varepsilon + 2}{3} \right)^2, \quad (15)$$

where α is the mean polarizability of the molecule, $\delta = \alpha_{||} - \alpha_{\perp}$ its anisotropy, and

$$J_R = 8\pi \int r_{pq}^{-4} g(r_{pq}) dr_{pq} \quad (16)$$

a pairwise radial correlation parameter whose value can be computed from data on light scattering [8] or calculated directly [12]. If one puts $\delta = 0$, Eq. (15) takes a form appropriate for isotropically polarizable molecules, *e. g.* for CCl_4 and the like.

In the case of substances consisting of axially-symmetric molecules, the effect of molecular redistribution raises the effect of molecular reorientation by about 10–50 per cent.

If both molecular redistribution and angular molecular correlations are taken into account, new mixed contributions to B_2 are obtained, raising or reducing the optical birefringence according to the model assumed [11], [19].

TABLE II

Numerical calculations of B_2^* and B_4^* taking into account angular molecular correlations, and comparison with the experimental data¹

Liquid	ρJ_2 ²⁾	$B_2 \times 10^{12}$	$B_2^* \times 10^{12}$	$B_2^{\text{exp}} \times 10^{12}$	$B_4 \times 10^{24}$	$B_4^* \times 10^{24}$
Carbon disulphide	-0.40	15.41	9.25	9.12 ^a 6.45 ^b 8.17 ^c	211.1	-42.2
Chloroform	-0.36	0.52	0.36	0.42 ^a 0.39 ^b	-1.5	0.1
Acetone	-0.33	0.48	0.37	0.20 ^a 0.25 ^b	-1.1	-0.4
Cyclohexane	-0.76	0.41	0.08	0.11 ^a 0.15 ^b	-1.1	1.5
Benzene	-0.52	3.33	1.60	0.97 ^a 1.25 ^b 1.57 ^c	-23.6	13.2
Toluene	-0.53	4.25	2.00	2.26 ^a 1.44 ^b 2.03 ^c	-36.1	21.3
Chlorobenzene	-0.34	4.03	2.66	2.13 ^b	-33.9	0.8
Bromobenzene	0.23	3.54	4.35	3.00 ^b	-23.7	-40.1
Nitrobenzene	0.04	6.64	6.90	6.73 ^a 5.47 ^b 6.06 ^c	-66.4	-197.9

¹ B_2^{exp} is calculated from the formula $B_2 = 6n\lambda B_\lambda(n^2+2)^2$, which results by Eq. (31) with $n = \sqrt{\epsilon_0}$:

^a B_λ from Paillette's [4] measurements of optical Kerr effect.

^b B_λ from static Kerr effect extrapolated to optical frequencies by Shen [13].

^c Data from Wang's [6] rotatory-power measurements.

² Values J_2 are calculated from the depolarization data [8], [22].

4. Electrostriction

By dielectrics thermodynamics [20], the change in pressure p caused by the effect of a strong electric field E on a liquid of volume V (neglecting the contribution from anisotropy of the stress tensor) is

$$\Delta p = \frac{1}{4\pi V} \int \int_V \rho \left(\frac{\partial \epsilon_{\sigma\tau}}{\partial Q} \right)_T E_\tau dE_\sigma dV. \quad (17)$$

At constant number density of liquid molecules ρ and if the optical permittivity tensor $\epsilon_{\sigma\tau} = \epsilon \delta_{\sigma\tau}$ is isotropic and independent of the electric field strength, Eq. (17) leads immediately to the well-known formula [21]

$$\Delta p = \frac{\rho}{8\pi} \left(\frac{\partial \epsilon}{\partial Q} \right)_T E^2. \quad (18)$$

In the preceding approximation, electrostriction causes changes in refractive index that are isotropic irrespective of other molecular effects (nonlinear polarizability of the

molecules and their optical orientation) contributing to the optical Kerr effect described by the constant B of Eq. (1). In reality, when acted on by the strong laser field E , the liquid becomes both nonlinear and anisotropic (in accordance with Eq. (1)), and consequently the electrostrictional changes occurring therein with some delay [21] will in general also be anisotropic. The part played by electrostriction can become especially apparent in cases when a very intense light beam gives rise to nonlinearities of higher orders in the liquid, involving cross-effects due to interaction between electrostriction and molecular reorientation and molecular redistribution. If the electrostriction is related with a deformation in shape of the specimen [20], a cross-effect is given rise to already in the quadratic approximation resulting in anisotropic changes in refractive index. Isotropic electrostriction, by Eqs (1) and (17), entails anisotropic changes of the refractive index only in approximations higher than quadratic, namely we have

$$\Delta\varepsilon_e = \frac{\beta_T \varrho^2}{16\pi} \left(\frac{\partial\varepsilon}{\partial\varrho} \right)_T \left\{ \left(\frac{\partial\varepsilon}{\partial\varrho} \right)_T + \frac{1}{4} \left(\frac{\partial\varepsilon_2}{\partial\varrho} \right)_T E_0^2 + \dots \right\} E_0^2, \quad (19)$$

where ε_2 is the quadratic change in optical permittivity and β_T the isothermal compressibility coefficient of the liquid.

If experimental values of $(\partial\varepsilon/\partial\varrho)_T$ are not directly available, they can be calculated from the well-known Lorentz-Lorenz formula [13]:

$$\varrho \left(\frac{\partial\varepsilon}{\partial\varrho} \right)_T = (\varepsilon - 1) \left(\frac{\varepsilon + 2}{3} \right), \quad (20)$$

which yields values by 5 to 10 per cent in excess of the experimental results [22].

From the general equation (1), the total nonlinear change in electric permittivity is

$$\Delta\varepsilon = \Delta\varepsilon_e + \Delta\varepsilon_B, \quad (21)$$

where in addition to the variation $\Delta\varepsilon_e$ due to electrostriction, we have the following variation due to optical birefringence:

$$\Delta\varepsilon_B = \sum_{n=1}^{\infty} \frac{1}{2^n} \varepsilon_{2n}^B E_0^{2n} = \sum_{n=1}^{\infty} \varepsilon_{2n}^B I^n, \quad (22)$$

wherein, by Eq. (2) or (8),

$$\varepsilon_{2n}^B = 2 \left(\frac{\varepsilon + 2}{3} \right)^2 B_{2n}. \quad (23)$$

By (19) and (20), the quadratic change in refractive index due to electrostriction is given by [13]:

$$\varepsilon_2^E = \frac{\beta_T \varrho^2}{8\pi} \left(\frac{\partial\varepsilon}{\partial\varrho} \right)_T^2 = \frac{\beta_T}{8\pi} (\varepsilon - 1)^2 \left(\frac{\varepsilon + 2}{3} \right)^2. \quad (24)$$

5. Nonlinear refractive index calculated from light scattering data

Eq. (1), in its mathematical form, can be derived either by the semi-macroscopic method [10] or by the molecular method of the local field (see Appendix). Albeit, within the framework of the semi-macroscopic method the field E has the physical meaning of a field

E^0 applied *ex vacuo*, whereas in the local field molecular method E stands for the mean macroscopic field E^M existing within the medium. By electrostatics, the relationship between the two fields is:

$$3E_\sigma^0 = (\varepsilon_{\sigma\tau} + 2\delta_{\sigma\tau})E_\tau^M. \quad (25)$$

If in particular $\varepsilon_{\sigma\tau} = \varepsilon\delta_{\sigma\tau}$, Eq. (25) reduces to the well-known formula [20]

$$3E^0 = (\varepsilon + 2)E^M. \quad (26)$$

On the other hand, the relation between $\varepsilon_{\sigma\tau}$, E^M and the electric polarization vector \mathbf{P} is of the form

$$(\varepsilon_{\sigma\tau} - \delta_{\sigma\tau})E_\tau^M = 4\pi P_\sigma. \quad (27)$$

Eqs (25) and (27) jointly provide the starting point for deriving the general Eq. (1), whence we obtain the ensuing expressions for the permittivity tensor components in the X - and Z -directions:

$$\frac{\varepsilon_{xx} - 1}{\varepsilon_{xx} + 2} - \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{1}{3}AE^2 + \frac{1}{3}B(3E_x^2 - E^2), \quad (28)$$

$$\frac{\varepsilon_{zz} - 1}{\varepsilon_{zz} + 2} - \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{1}{3}AE^2 + \frac{1}{3}B(3E_z^2 - E^2). \quad (29)$$

On the assumption that ε_x and ε_z differ but little from ε_0 , we can write

$$\varepsilon_{zz} - \varepsilon_{xx} = 3 \left(\frac{\varepsilon_0 + 2}{3} \right)^2 B \left(\overline{E_z^2} - \overline{E_x^2} \right) = 2\lambda\sqrt{\varepsilon_0}B_\lambda \left(\overline{E_z^2} - \overline{E_x^2} \right), \quad (30)$$

where B_λ is the birefringence constant measured in experiment [4]; symbol $\overline{\quad}^t$ denotes the time-average.

In the general case, the Rayleigh ratio R consists of an isotropic part R_{is} and an anisotropic part R_{anis} , the latter being related with B_2 as follows [8], [10]:

$$B_2 = \frac{\lambda^4 R_{\text{anis}}}{26\pi^3 kT}. \quad (31)$$

On the other hand, the depolarization ratio D is expressed by R_{is} and R_{anis} as follows:

$$D = \frac{6R_{\text{anis}}}{13R_{\text{is}} + 7R_{\text{anis}}}. \quad (32)$$

If R_{anis} is not available experimentally, one can recur to the formula

$$B_2 = \frac{\lambda^4 D R_{\text{is}}}{2\pi^3 kT(6 - 7D)} \quad (33)$$

in place of Eq. (31).

With regard to Eq. (32), we have

$$R = R_{\text{is}} + R_{\text{anis}} = \frac{6+6D}{13D} R_{\text{anis}} = \frac{6+6D}{6-7D} R_{\text{is}} \quad (34)$$

and Eq. (31) can be rewritten thus:

$$B_2 = \frac{\lambda^4 DR}{12\pi^3 kT(1+D)}. \quad (35)$$

This formula yields good agreement with the experimental data [14].

Eqs (31), (33) and (35) are valid for arbitrary molecular substances in the condensed state consisting of optically isotropic or optically anisotropic molecules.

On expressing the isotropic part R_{is} of Rayleigh's ratio in thermodynamical form [22]:

$$R_{\text{is}}^3 = \frac{\pi^2}{2\lambda^4} kT\beta_T \varrho^2 \left(\frac{\partial \varepsilon}{\partial \varrho} \right)_T^2 \quad (36)$$

the change in permittivity of Eq. (24) induced by electrostriction can be written as

$$\varepsilon_{21}^E = \frac{\lambda^4 R_{\text{is}}}{4\pi^3 kT}. \quad (37)$$

Similarly, inserting (31) and (35) into Eq. (23) we obtain the formulas

$$\varepsilon_{21}^B = \frac{\lambda^4 R_{\text{anis}}}{13\pi^3 kT} \left(\frac{\varepsilon+2}{3} \right)^2, \quad (38)$$

$$\varepsilon_{21}^B = \frac{\lambda^4 DR}{6\pi^3 kT(1+D)} \left(\frac{\varepsilon+2}{3} \right)^2 \quad (39)$$

enabling us to calculate the quadratic change in electric permittivity due to the optical Kerr effect from light scattering data of liquids.

In Table III, the n_2^E values calculated from Eqs (24) and (37) are seen to agree satisfactorily. Similarly, as seen in Table IV, those of n_2^B calculated from Eqs (38) and (39) agree; however, in the cases of CS_2 and $\text{C}_6\text{H}_5\text{NO}_2$, they are more than twice larger than the values

TABLE III
Calculated values of variations in refractive index due to electrostriction

Liquid	ϱ $10^{21}/\text{cm}^3$	$\beta_T \times 10^{12}$ cm^2/dyne	$n = \sqrt{\varepsilon}$ for λ		$n_2^E = \varepsilon_2^E/2n$ in 10^{-12}		
			5460 Å	6940 Å	5460 Å Eq. (24)	6940 Å Eq. (24)	5460 Å Eq. (37)
Carbon tetrachloride	6.22	106	1.460	1.457	3.49	3.45	3.09
Carbon disulphide	9.99	94	1.634	1.614	7.73	7.03	6.51
Chloroform	7.51	87	1.446	1.430	2.65	2.40	2.67
Benzene	6.74	95	1.503	1.495	4.05	3.89	3.48
Toluene	5.65	92	1.499	1.490	3.85	3.61	3.09
Nitrobenzene	5.89	49	1.560	1.542	2.86	2.56	2.90

calculated from measurements of the optical Kerr effect [4]. In the case of CS₂ Eqs (38) and (39) yield values in accordance with recent results from intensity-induced rotation measurements [24].

TABLE IV

Calculated values of variations in refractive index due to optical Kerr effect¹

Liquid	D	Rayleighs ratios in 10^{-6} cm^{-1} for $\lambda = 5460 \text{ \AA}$			$n_2^B = \epsilon_2^B/2n$ in 10^{-12}			
		R_{is}	R_{anis}	R	Eq. (38)	Eq. (39)	Eq. (11)	Exper [4]
Carbon tetrachloride	0.042	5.09	0.29	5.38	0.10	0.17	—	0.17
Carbon disulphide	0.64	12.00	71.9	83.90	29.07	28.69	13.94	13.89
Chloroform	0.22	4.36	2.80	7.16	0.98	0.91	0.47	0.54
Benzene	0.42	5.90	9.9	15.80	3.62	3.70	2.16	1.30
Toluene	0.48	5.23	13.2	18.43	4.09	4.72	2.69	3.02
Nitrobenzene	0.74	5.10	60.7	65.80	23.18	23.16	9.75	9.43

¹ Values of D and R for chloroform are from Ref. [23], whereas for other liquids from Ref. [22].

6. Conclusions

With light propagating along the Y -axis (its electric vector oscillating in the Z -direction) Eq. (1) leads to the following ratio of changes in optical permittivity in two mutually perpendicular directions:

$$\frac{\Delta\epsilon_{zz}}{\Delta\epsilon_{xx}} = \left(\frac{\epsilon_{zz}+2}{\epsilon_{xx}+2} \right) \left(\frac{A+2B}{A-B} \right). \quad (40)$$

By Eqs (1) and (40), the induced anisotropy B raises the value of $\Delta\epsilon_{zz}$ but lowers $\Delta\epsilon_{xx}$; the latter can be negative if $A < B$, as is the case in such liquids as CS₂ and C₆H₅NO₂.

The generalized relation of Havelock (40) yields -2 if only Langevin's reorientation effect intervenes, since in this case $A = 0$, and a value of 3 if only Voigt's nonlinear deformation effect is present, when $2A = 5B$ [10].

It would be highly desirable to measure ϵ_{zz} and ϵ_{xx} independently of one another and to use the results in conjunction with Eq. (40) for deciding which of the mechanisms predominates in the liquid under consideration: electrostriction, nonlinear polarizability, or molecular reorientation. The last word would then belong to measurements of the temperature-dependence and dispersion of nonlinear changes in refractive index. The information gained in this way could provide better insight into the hitherto not fully clarified details of "small-scale" and "large-scale" beam trapping [2], [3], [21] as well as of stimulated Rayleigh and Raman scattering [21], [25—28].

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APPENDIX

Reorientation of axially symmetric molecules

Consider an isotropic medium, not excessively dense, of number density ρ , subjected to an electric field \mathbf{E} which, if very intense (as is the case of a laser beam) will induce anisotropy given by the permittivity tensor of Eq. (27)

$$(\varepsilon_{\sigma\tau} - \delta_{\sigma\tau}) E_{\tau}^M = 4\pi P_{\sigma} = 4\pi\rho \langle m_{\sigma} \rangle_E, \quad (\text{A1})$$

where

$$\langle m_{\sigma} \rangle_E = \int m_{\sigma} f(\boldsymbol{\Omega}, \mathbf{E}) d\boldsymbol{\Omega} \quad (\text{A2})$$

is the statistical mean value of the dipole moment component induced in a molecule at orientation $\boldsymbol{\Omega}$ with respect to the direction of \mathbf{E} .

In the case of a molecule anisotropic and linearly polarizable in the local Lorentz type field

$$F_{\sigma} = E_{\sigma} + \frac{4\pi}{3} P_{\sigma} = \frac{1}{3} (\varepsilon_{\sigma\tau} + 2\delta_{\sigma\tau}) E_{\tau}^M \quad (\text{A3})$$

we can write

$$m_{\sigma} = \alpha_{\sigma\tau} F_{\tau}, \quad (\text{A4})$$

where $\alpha_{\sigma\tau}$ is the molecule's polarizability tensor.

Inserting (A3) and (A4) into Eq. (A1), we get

$$\varepsilon_{\sigma\tau} - \delta_{\sigma\tau} = \frac{4\pi}{3} \rho \langle \alpha_{\sigma\tau} \rangle_E (\varepsilon_{\nu\tau} + 2\delta_{\nu\tau}). \quad (\text{A5})$$

Assuming the statistical distribution function in a first approximation [10]:

$$f(\boldsymbol{\Omega}, \mathbf{E}) = f(\boldsymbol{\Omega}, 0) \left\{ 1 + \frac{1}{2kT} (\alpha_{\sigma\tau} - \alpha \delta_{\sigma\tau}) F_{\sigma} F_{\tau} + \dots \right\} \quad (\text{A6})$$

one obtains immediately with respect to (A5) an equation of the form (1), where $B = B_2$ is defined by (6).

Since it is our aim here to calculate nonlinearities of higher orders, we have to start from a distribution function in the form

$$f(\boldsymbol{\Omega}, \mathbf{E}) = \frac{\exp \left\{ -\frac{u(\boldsymbol{\Omega}, \mathbf{E})}{kT} \right\}}{\int \exp \left\{ -\frac{u(\boldsymbol{\Omega}, \mathbf{E})}{kT} \right\} d\boldsymbol{\Omega}}, \quad (\text{A7})$$

where the potential energy of an anisotropic molecule is given as

$$u(\boldsymbol{\Omega}, \mathbf{E}) = -\frac{1}{2} \alpha_{\sigma\tau} F_{\sigma} F_{\tau}. \quad (\text{A8})$$

Our further calculations will proceed on the assumption that the molecule is symmetric about its 3-axis (unit vector \mathbf{k}), so that [10]:

$$\alpha_{\sigma\tau} = \alpha \delta_{\sigma\tau} + (\alpha_{\parallel} - \alpha_{\perp}) \left(k_{\sigma} k_{\tau} - \frac{1}{3} \delta_{\sigma\tau} \right). \quad (\text{A9})$$

If the electric field \mathbf{E} acts along the laboratory Z -axis, we have by Eqs (A1) and (A9) for the permittivity along the Z - and X -axes respectively

$$\frac{\varepsilon_{zz}-1}{\varepsilon_{zz}+2} - \frac{\varepsilon_0-1}{\varepsilon_0+2} = \frac{2}{3} \overline{BE_z^2}^t, \quad (\text{A10})$$

$$\frac{\varepsilon_{xx}-1}{\varepsilon_{xx}+2} - \frac{\varepsilon_0-1}{\varepsilon_0+2} = -\frac{1}{3} \overline{BE_z^2}^t, \quad (\text{A11})$$

where we have introduced the constant

$$\overline{BE_z^2}^t = 2\pi Q(\alpha_{\parallel} - \alpha_{\perp}) \left\langle \cos^2 \vartheta - \frac{1}{3} \right\rangle_E, \quad (\text{A12})$$

with ϑ denoting the angle between the symmetry axis of the molecule and the direction of the electric field E_x .

Time averaging of (A8) over the oscillation period of the optical field and taking into consideration (A9) leads to the distribution function now in the form of

$$f(\Omega, I) = \frac{\exp(bI \cos^2 \vartheta)}{2\pi \int_0^\pi \exp(bI \cos^2 \vartheta) \sin \vartheta d\vartheta}, \quad (\text{A13})$$

where b is a reorientation parameter of the molecule given by (10).

We now introduce integrals

$$Y_{2k} = \frac{1}{2} \int_0^\pi \cos^{2k} \vartheta \exp(bI \cos^2 \vartheta) \sin \vartheta d\vartheta = \sum_{n=0}^{\infty} \frac{b^n I^n}{n!} I^n \overline{\cos^{2(k+n)} \vartheta} \quad (\text{A14})$$

with

$$\overline{\cos^{2(k+n)} \vartheta} = \frac{1}{2} \int_0^\pi \cos^{2(k+n)} \vartheta \sin \vartheta d\vartheta = \frac{1}{2(k+n)+1}. \quad (\text{A15})$$

We thus have

$$Y_{2k} = \sum_{n=0}^{\infty} \frac{b^n I^n}{n! [2(k+n)+1]}, \quad (\text{A16})$$

whence by the definitions of Eqs (A2) and (A7)

$$\langle \cos^2 \vartheta \rangle_E = \frac{Y_2}{Y_0} = \frac{\sum_{n=0}^{\infty} \frac{b^n I^n}{n!(2n+3)}}{\sum_{n=0}^{\infty} \frac{b^n I^n}{n!(2n+1)}} = \sum_{n=0}^{\infty} a_n b^n I^n. \quad (\text{A17})$$

Eq. (A17) on insertion into (A12) yields Eqs (4) and (8).

In the case of optical saturation $\langle \cos^2 \vartheta \rangle_E$ has to be calculated without series expansion, as in Refs and [3]:

$$\langle \cos^2 \vartheta \rangle_E = \pm \left\{ \sqrt{y} e^{\mp y} \int_{-\sqrt{y}}^{\sqrt{y}} e^{\pm t^2} dt \right\}^{-1} \mp \frac{1}{2y}, \quad (\text{A18})$$

upper and lower signs relating to positive and negative reorientation parameters $y = bI$.

REFERENCES

- [1] C. T. O'Konski, K. Yoshioka and W. H. Orttung *J. Phys. Chem.* **63**, 1558 (1959); M. J. Shah, *J. Phys. Chem.*, **67**, 2215 (1963); D. N. Holcomb and I. Tinoco, Jr, *J. Phys. Chem.*, **67**, 2691 (1963) and references therein.
- [2] A. Piekara, *J. Quant. Elec.*, **2**, 249 (1966); S. A. Akhmanov, A. P. Sukhorukov and R. V. Khokhlov, *Uspekhi Fiz. Nauk*, **93**, 19 (1967) and references therein.
- [3] R. G. Brewer, J. R. Lifshitz, E. Garmire, R. Y. Chiao and C. H. Townes, *Phys. Rev.*, **166**, 326 (1968); T. K. Gustafson, P. L. Kelley, R. Y. Chiao and R. C. Brewer, *Appl. Phys. Letters*, **12**, 165 (1968).
- [4] G. Mayer and F. Gires, *CR Acad. Sci. (France)*, **258**, 2039 (1964); M. Paillette, *ibid*, **262**, 264 (1966).
- [5] P. D. Maker, R. W. Terhune and C. M. Savage, *Phys. Rev. Letters*, **12**, 507 (1964); P. D. Maker and R. W. Terhune, *Phys. Rev.*, **137**, A801 (1965).
- [6] C. C. Wang, *Phys. Rev.*, **152**, 149 (1966).
- [7] A. D. Buckingham, *Proc. Phys. Soc.*, B **69**, 344 (1956).
- [8] S. Kielich, *Acta Phys. Polon.*, **19**, 149, 573 (1960); **30**, 683 (1966); *J. Chem. Phys.*, **46**, 4090 (1967).
- [9] N. Bloembergen and P. Lallemand, *Phys. Rev. Letters*, **16**, 81 (1966).
- [10] S. Kielich, *Proc. Phys. Soc.*, **90**, 847 (1967); *Acta Phys. Polon.* **31**, 689 (1967).
- [11] M. Takatsuji, *Phys. Rev.*, **165**, 171 (1968).
- [12] R. W. Hellwarth, *Phys. Rev.*, **152**, 156 (1966).
- [13] Y. R. Shen, *Physics Letters*, **20**, 378 (1966).
- [14] S. Kielich, *Physics Letters*, **24A**, 383 (1967); B. Kasprowicz and S. Kielich, *Acta Phys. Polon.* **31**, 787 (1967); **33**, 495 (1968).
- [15] R. Landauer, *Physics Letters*, **25A**, 416 (1967).
- [16] S. Kielich, *Chem. Phys. Letters*, **1**, 675 (1968).
- [17] F. Kaczmarek, *Acta Phys. Polon.*, **32**, 1003 (1967).
- [18] S. Kielich, *Acta Phys. Polon.*, **23**, 819 (1963); *Physics Letters*, **25A**, 153 (1967).
- [19] S. Kielich, *J. Phys. (France)*, **29**, 619 (1968); *Chem. Phys. Letters*, **2**, 112 (1968).
- [20] B. K. P. Scaife, *Proc. Phys. Soc.*, **69B**, 153 (1956); L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Pergamon Press, Inc., New York 1960.
- [21] Y. R. Shen and Y. J. Shaham, *Phys. Rev.*, **163**, 224 (1967).
- [22] D. J. Coumou, E. L. Mackor and J. Hijmans, *Trans. Faraday Soc.*, **60**, 1539, 2244 (1964).
- [23] M. Giurgea, C. Ghita and L. Ghita, *Stud. Cercetari Fiz. (Rumania)*, **13**, 455 (1962).
- [24] P. D. Mc Wane and D. A. Sealer, *Appl. Phys. Letters*, **8**, 278 (1966); F. Shimizu, *J. Phys. Soc. Japan*, **22**, 1070 (1967).
- [25] N. Bloembergen, *Amer. J. Phys.*, **35**, 989 (1967).
- [26] V. S. Starunov, *Trudy Fizicheskogo Instituta A. N. SSSR*, **39**, 151 (1967).
- [27] R. M. Herman, *Phys. Rev.*, **164**, 200 (1967).
- [28] G. Rivoire and J. L. Beaudoin, *J. Phys. (France)*, **29**, 759 (1968).