KERR EFFECT INDUCED IN LIQUID ARGON AND CARBON TETRACHLORIDE BY FLUCTUATIONAL-STATISTICAL PROCESSES

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The Kerr effect induced in atomic and molecular liquids by binary radial correlations is shown to be strongly modified by ternary and higher correlations as well as by fluctuations of molecular fields in the range of near ordering. Numerical evaluations are performed to the end for liquids argon and CCl_4; for the latter, reasonable agreement with measurement is obtained.

Optical birefringence, induced in liquids by a DC electric field E_0, is given by the expression [1]:

$$n_{\parallel}^{\omega} - n_{\perp}^{\omega} = \frac{3}{2n_{\omega}} \left(\frac{n_{\omega}^2 + 2}{3} \right)^2 \left(\frac{\varepsilon + 2}{3} \right)^2 KE_S^2, \tag{1}$$

with n_{ω} — the refractive index at frequency ω of the measuring light beam, ε the electric permittivity, and E_S the mean macroscopic field existing in the liquid specimen.

The Kerr constant K consists in general of two parts: K^{NL} due to the nonlinear polarizability of the molecules (Voigt-Born effect) and K^{SF} due to fluctuational-statistical Langevin-Yvon-Kirkwood processes. K^{SF} consists of the following two contributions [1]:

$$K_1^{SF} = \frac{2\pi}{15kTV} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} D_p^{\omega} : D_q^{0} \right\rangle, \tag{2}$$

$$K_2^{SF} = \frac{2\pi}{15k^2T^2V} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{r=1}^{N} D_p^{\omega} : m_q^0 m_r^0 \right\rangle, \tag{3}$$

where V is the liquid volume, containing N molecules, and the brackets $\langle \, \rangle$ stand for statistical averaging in the presence of molecular correlations.

In Eq. (2), D_p^ω is the deviation tensor (of rank 2) of the optical polarizability of molecule p immersed in the medium,

$$D_p^\omega = \frac{\partial m_p^\omega}{\partial E_\omega} - \frac{1}{3} u \left(\frac{\partial m_p^\omega}{\partial E_\omega} : u \right) \tag{4}$$

with m_p^ω the dipole moment induced in molecule p by the electric field E_ω of the measuring beam, and u Kronecker's unit tensor. The electric polarizability deviation tensor D_q^0 is defined likewise to (4) for $\omega = 0$. In Eq. (3), m_q^0 is the total electric dipole moment in the absence of an external electric field.

On taking into account the Kirkwood-Yvon translational statistical fluctuations in the dipole approximation, we have for isotropically polarizable molecules:

$$\frac{\partial m_p^\omega}{\partial E_\omega} = a_p^\omega \left\{ u - \sum_{q=1}^{N} T_{pq} a_q^\omega + \sum_{q=1}^{N} \sum_{r=1}^{N} T_{pq} \cdot T_{qr} a_q^\omega a_r^\omega \ldots \right\}, \tag{5}$$

where $T_{pq} = -r_{pq}^{-5}(3r_{pq}r_{pq} - r_{pq}^2 u)$ is the interaction tensor between dipoles induced in molecules p and q, separated by r_{pq} and having scalar polarizabilities a_p^ω and a_q^ω.

Applying known methods of classical statistical mechanics, we obtain to a good approximation from (2), (4) and (5):

$$K_1^{SF} = \frac{8\pi \varrho}{5kT} (a^\omega a^0)^2 \{ \langle r_{pq}^{-6} \rangle + \langle r_{pq}^{-3} r_{qs}^{-3} \rangle + \langle r_{ps}^{-3} r_{sq}^{-3} \rangle + \ldots$$

$$+ (a^\omega + a^0)(\langle r_{pq}^{-9} \rangle + \langle r_{pq}^{-3} r_{qs}^{-3} r_{sp}^{-3} \rangle + \langle r_{pq}^{-6} r_{qs}^{-3} \rangle +$$

$$+ \langle r_{ps}^{-3} r_{sq}^{-6} \rangle + \langle r_{pq}^{-3} r_{ps}^{-6} \rangle + \ldots) + \ldots \}, \tag{6}$$

where $\varrho = N/V$ is the number density of molecules, and where we have introduced the following statistical averages:

$$\langle r_{pq}^{-n} \rangle = \frac{\varrho}{V} \iint r_{pq}^{-n} g^{(2)}(r_p, r_q) dr_p dr_q, \tag{7}$$

$$\langle r_{pq}^{-n} r_{qs}^{-m} \rangle = \frac{\varrho^2}{4V} \iiint \{ 3(r_{pq} \cdot r_{qs})^2 - r_{pq}^2 r_{qs}^2 \} \times$$

$$\times \{ r_{pq}^{-n+2} r_{qs}^{-m+2} + r_{pq}^{-m+2} r_{qs}^{-n+2} \} g^{(3)}(r_p, r_q, r_s) dr_p dr_q dr_s, \tag{8}$$

$$\langle r_{pq}^{-3} r_{qs}^{-3} r_{sp}^{-3} \rangle = \frac{\varrho^2}{2V} \iiint \{ 9(r_{pq} \cdot r_{qs})(r_{qs} \cdot r_{sp})(r_{sp} \cdot r_{pq}) -$$

$$- 3r_{pq}^2(r_{qs} \cdot r_{sp})^2 - 3r_{qs}^2(r_{sp} \cdot r_{pq})^2 - 3r_{sp}^2(r_{pq} \cdot r_{qs})^2 +$$

$$+ 2r_{pq}^2 r_{qs}^2 r_{sp}^2 \} r_{pq}^{-5} r_{qs}^{-5} r_{sp}^{-5} g^{(3)}(r_p, r_q, r_s) dr_p dr_q dr_s. \tag{9}$$

Here $g^{(2)}(r_p, r_q)$ is the binary correlation function of two molecules at r_p and r_q, and $g^{(3)}(r_p, r_q, r_s)$ the ternary correlation function of three molecules at r_p, r_q and r_s.

The expression (6) to within the first term $\langle r_{pq}^{-6}\rangle$ represents an earlier result of this author [1] stating that binary radial correlations of atoms or isotropically polarizable molecules induce an optical anisotropy in the range of near ordering. The higher correlation parameters (8) and (9) modify the induced anisotropy raising or lowering it, according to the type of ternary correlations [2, 3]. Thus, the parameter (8) is positive when the vectors r_{pq} and r_{qs} subtend an angle between 0° and 180°, without the region from 54° to 126°, for which it becomes negative.

The constant (3), too, is in general non-zero in the presence of the translational fluctuation deviation tensor (5) and molecular fields F fluctuating in the range of near ordering (in the absence of external fields) which induce, in a linear approximation, the dipole moment $m_q^0 = a_q^0 F_q + ...$; we obtain:

$$K_2^{SF} = -\frac{2\pi}{15k^2T^2V}\left\langle \sum_{pqrs}^{N} a_p^\omega a_q^0 a_r^0 a_s^\omega T_{ps} : (F_q F_r)\right\rangle + ... \tag{10}$$

TABLE I

Comparison of calculated and experimental Kerr constant in liquids

Liquid	Kerr Constant, in 10^{-14} e.s.u.				
	K^{NL}	K_1^{SF}	K_2^{SF}	K_{calc}	K_{exp}
Argon (85°K)	2.2[a]	35.0[b]		37.2	
Carbon	2.8[c]	145.0[b]	7.5[b]	155.3	11.8[f]
tetrachloride	2.8[c]	7.3[d]	0.4[d]	10.5	12.6[g]
(293°K)				9.1[e]	12.0[h]

[a] This result was calculated with the value $c^\omega = 0.59\times 10^{-36}$ e.s.u. of A. D. Buckingham, D. A. Dunmur, *Trans. Faraday Soc.*, **64**, 1776 (1968).

[b] Calculated theoretically by us, with correlation parameters (7)-(9) evaluated numerically on the assumption of Kirkwood's rigid sphere model [5].

[c] These results were calculated with the value $c^\omega = 3.3\times 10^{-36}$ e.s.u. of S. Kielich, J. R. Lalanne, F. B. Martin, *C.R. Acad. Sci.* (France), B **272**, 731 (1971).

[d] Calculated theoretically by us, with correlation parameters (7)-(9) determined from the depolarization ratio of light scattering [1].

[e] Value calculated by J. A. Brace, J. V. Champion, *J. Phys. C*, **2**, 2408 (1969).

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Tetrahedral molecules can serve as an example of isotropically polarizable molecules, the fields of whose permanent electric octopole and hexadecapole moments induce dipole moments in neighbouring molecules. The constant (10) is now non-zero, and we have in a binary correlation approximation:

$$K_2^{SF} = \frac{64\pi\varrho}{35k^2T^2}(a^\omega a^0)^2 \Omega_{123}^2 \langle r_{pq}^{-13}\rangle + ..., \tag{11}$$

with Ω_{123} the electric octopole moment component of the tetrahedral molecule [4].

In the general case, atoms and molecules polarize nonlinearly in the external electric field as well as in the molecular field and we have the contribution:

$$K^{NL} = \frac{4\pi}{9} \varrho c^{\omega} \left(1 + \frac{48}{5} a^2 \langle r_{pq}^{-6} \rangle + \dots \right), \tag{12}$$

where c^{ω} stands for the mean third-order nonlinear polarizability due to the external electric field [1].

All the statistical averages of formulas (7)–(9) are accessible to numerical calculation, with the various models of binary correlation and ternary correlation functions [2–5]. Consequently since the other optical and electric molecular parameters are available in the literature [6], we were able to evaluate the above contributions to the Kerr constant. The calculated results for liquid argon and CCl_4 are in Table I. In liquid argon, nonlinear polarizability contributes but 6%, translational fluctuations 94%. In CCl_4, the fluctuation contributions, calculated with Kirkwood's rigid sphere model, prove too large by over 1 order of magnitude; good agreement with experiment is achieved if the radial correlation parameters (7)–(9) are determined from the depolarization ratio of light scattering [1]. In the latter case, nonlinear polarizability contributes 27%, translational fluctuations 69%, and molecular field fluctuations 4%.

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