ON THE RELATION BETWEEN NONLINEAR REFRACTIVE INDEX
AND MOLECULAR LIGHT SCATTERING IN LIQUIDS

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A direct relationship is shown to hold between light scattering in liquids and nonlinearity of the refractive index due to reorientation of molecules in the strong optical field of a laser. A discussion is given of the role, in either effect, of molecular translational fluctuations and electric fields of dipoles and quadrupoles, causing nonlinear polarization of molecules immersed in a dense medium.

The molecular-statistical theory of dipolar light scattering in liquids leads to the following equation for the scattered intensity tensor [1]:

$$I^S_{\sigma\tau} = \left(\frac{\omega}{c}\right)^4 \{e_\sigma e_\tau F_{\text{is}} + \tfrac{1}{5}(3\delta_{\sigma\tau} + e_\sigma e_\tau)F_{\text{anis}}\}I; \quad (1)$$

$I = EE^*$ being the intensity of the incident light with electric field E oscillating at frequency ω, with unit vector e. The indices σ and τ relate to axes X, Y, Z of the laboratory reference frame, and $\delta_{\sigma\tau}$ is the unit Kronecker tensor.

The factors F_{is} and F_{anis} define respectively scattering of the isotropic and anisotropic kinds; in the absence of absorption and internal interference, when the sizes of the molecules and their mutual distances are small compared with the light wavelength λ, they are of the form [1]

$$F_{\text{is}} = \frac{1}{9V}\langle \triangle \sum_{p=1}^{N} \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha} \triangle \sum_{q=1}^{N} \frac{\partial m_\beta^{(q)}}{\partial E_\beta}\rangle, \quad (2)$$

$$F_{\text{anis}} = \frac{1}{18V}\langle \sum_{p=1}^{N}\sum_{q=1}^{N}\left(3\frac{\partial m_\alpha^{(p)}}{\partial E_\beta}\frac{\partial m_\alpha^{(q)}}{\partial E_\beta} - \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha}\frac{\partial m_\beta^{(q)}}{\partial E_\beta}\right)\rangle, \quad (3)$$

where $m_\alpha^{(p)}$ is a component of the dipole moment induced by the electric field in molecule p of the medium (of volume V and containing N molecules); the brackets $\langle \rangle$ indicate statistical averaging and $\triangle$ a fluctuation.

In the case when an intense laser beam is incident on the medium, its refractive index becomes dependent on I according to the formula [2]

$$n^2_{\sigma\tau} - \delta_{\sigma\tau} = \{R_L\delta_{\sigma\nu} + \tfrac{1}{3}[A\,\delta_{\sigma\nu} + \\ + B(3e_\sigma e_\nu - \delta_{\sigma\nu})]I\}(n^2_{\nu\tau} + 2\delta_{\nu\tau}), \quad (4)$$

where [3]

$$R_L = \frac{4\pi}{9V}\langle \sum_{p=1}^{N} \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha}\rangle = \frac{n^2 - 1}{n^2 + 2} \quad (5)$$

is the Lorentz-Lorenz function.

The constants A and B in eq. (4) define respectively the isotropic and anisotropic variations of the optical permittivity tensor $n_{\sigma\tau}$ induced by strong light of intensity I. At this point it is especially noteworthy that, if solely changes due to the effect of reorientation of molecules in the optical field are taken into consideration [4], the constants A and B can be expressed directly in terms of the factors (2) and (3):

$$A_R = \frac{2\pi}{kT}F_{\text{is}}, \quad (6)$$

$$B_R = \frac{4\pi}{5kT}F_{\text{anis}}. \quad (7)$$

These relations remain valid irrespective of the molecular symmetry and the state of condensation of the isotropic medium. The structural factors (2) and (3) were discussed previously for several molecular models [1]; here, we shall discuss them for some models not considered then. Firstly, we shall refer to earlier work of others proving that the dependence of the Lorentz-Lorenz function (5) on the number density $\rho = N/V$ and

temperature T of the fluid can be explained on the basis of statistical translational fluctuations [5], variations in linear polarizability induced by molecular interactions [6], as well as nonlinear variations in polarizability and multipole interactions [3,7]. Since the experimentally observed density-dependent changes in R_L are but insignificant [8], the roles of various statistical fluctuations are not easily rendered apparent. We shall show that a quantity highly sensitive to translational fluctuations and other molecular correlations is to be found in the anisotropic factor (3).

Let us assume, in the first place, that the molecules are linearly polarizable and that they possess anisotropic optical properties described by a symmetric polarizability tensor $\alpha_{\alpha\beta}$. In the case when the medium is sufficiently dense, as a result of Yvon-Kirkwood statistical fluctuations [5] we can write, without taking into account the Jansen-Mazur effect [6] and to within dipole interactions [3],

$$\frac{\partial m_\alpha^{(p)}}{\partial E_\beta} = \alpha_{\alpha\beta}^{(p)} - \sum_{q=1}^{N} \alpha_{\alpha\gamma}^{(p)} T_{\gamma\delta}^{(pq)} \alpha_{\delta\beta}^{(q)} +$$
$$+ \sum_{q=1}^{N} \sum_{l=1}^{N} \alpha_{\alpha\gamma}^{(p)} T_{\gamma\delta}^{(pl)} \alpha_{\delta\epsilon}^{(l)} T_{\epsilon\eta}^{(lq)} \alpha_{\eta\beta}^{(q)} - \ldots , \quad (8)$$

with the tensor

$$T_{\alpha\beta}^{(pq)} = - r_{pq}^{-5}(3r_{pq\alpha} r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta}), \quad p \neq q \quad (9)$$

of dipole-dipole interaction between molecules p and q at mutual distance $r_{pq} \ll \lambda$.

On inserting into eq. (3) the expression of the zeroth approximation of the expansion (8), and on omitting molecular correlations of the angular kind, we obtain

$$F_{\text{anis}}^{(0)} = \frac{\rho}{18}\{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2\}, \quad (10)$$

where we have introduced the principal polarizabilities α_1, α_2, α_3 of the isolated molecule. Hence, for the case of isotropically polarizable molecules ($\alpha_1 = \alpha_2 = \alpha_3 = \alpha$), the anisotropic factor $F_{\text{anis}}^{(0)}$ vanishes and, in accordance with eqs. (1), (4) and (7), neither anisotropic scattering nor optical birefringence occurs.

On the other hand, if one inserts into (3) the full expansion (8), the contribution from the first approximation (the terms linear in the dipole interaction tensor (9)) vanishes by averaging over all possible orientations of the molecules, and it is the contribution from the second approximation that is non-zero. This, for the case of axially symmetric molecules, and to within pairwise

correlations, is of the form

$$F_{\text{anis}}^{(2)} = 2\alpha^4 \rho \left(1 + \frac{28}{5}\kappa^2 + 2\kappa^3 + \frac{67}{25}\kappa^4\right)\langle r^{-6}\rangle ; \quad (11)$$

here $\kappa = (2\alpha_3 - \alpha_1 - \alpha_2)/6\alpha$ is the optical anisotropy and

$$\langle r^{-m}\rangle = \rho \int_0^\infty r_{pq}^{-m} g(r_{pq}) \mathrm{d} r_{pq} , \quad (12)$$

where $g(r_{pq})$ is the distribution function of radial molecular correlations.

The contribution of eq. (11) presents a result of particular interest, since it does not vanish even if the isolated molecule is not anisotropic optically, $\kappa = 0$. In other words, owing to translational fluctuations, an assemblage of mutually correlating atoms or isotropic molecules presents a non-zero effective optical anisotropy [1] giving rise to anisotropic light scattering and optical birefringence.

On closer inspection it is found that, on inserting into (3) the first approximation of (8) and on carrying out statistical averaging with a Boltzmann factor $\exp(-W/kT)$ containing the potential energy W of dipole-dipole interaction [1]

$$W = \frac{1}{2} \sum_{p=1}^{N} \sum_{q=1}^{N} \mu_\alpha^{(p)} T_{\alpha\beta}^{(pq)} \mu_\beta^{(q)} \quad (13)$$

the following contribution is obtained:

$$F_{\text{anis}}^{(1)} = \frac{4\alpha^3 \kappa \mu^4 \rho}{75 k^2 T^2}(5 + 4\kappa + 9\kappa^2)\langle r^{-9}\rangle \quad (14)$$

with μ denoting the permanent dipole moment of the molecule.

The contribution of eq. (14) is seen to be negative for molecules presenting negative optical anisotropy $\kappa < 0$. Takatsuji [9] recently obtained a reduction in effective optical anisotropy in liquids by recurring to a particularized model of two parallelly oriented nondipolar molecules.

Numerical calculations of the contributions (11) and (14) involve computing the mean values of eq. (12). This can be achieved with sufficient accuracy for the case of real gases by using a radial correlation function with the Lennard-Jones potential [3,7]. In a number of cases, evaluations for liquids can be usefully made using a model of hard spheres of diameter d, when [5]

$$g(r_{pq}) = \begin{cases} 0 \text{ for } r_{pq} < d, \\ 1 \text{ for } r_{pq} > d, \end{cases}$$

and one now obtains for $m \geq 4$

$$\langle r^{-m} \rangle = \frac{4\pi\rho}{m-3}\left(\frac{\pi}{6v}\right)^{\frac{1}{3}(m-3)}, \qquad (15)$$

$v = \pi d^3/6$ being the volume of the molecule.

On the other hand, the anisotropic factor F_{anis} can be determined experimentally by means of the following formula resulting from eq. (1):

$$F_{anis} = \frac{15\lambda^4 R\, D}{16\pi^4(n^2+2)^2(1+D)}, \qquad (16)$$

which contains the Rayleigh ratio R and depolarization ratio D directly measurable in experiments on light scattering [1].

F_{anis} can moreover be determined from measurements of the optical birefringence induced in a liquid by intense laser light [10] recurring to the formula of the optical Kerr constant

$$B_\lambda = \frac{6\pi n}{15\lambda kT}\left(\frac{n^2+2}{3n}\right)^2\left(\frac{n_L^2+2}{3}\right)^2 F_{anis}, \qquad (17)$$

where n and n_L are, respectively, the refractive indices for the wavelength λ of the weak measuring light beam and for that ($\lambda_L = 6943$ Å) of the intense laser beam. Eq. (17) is readily seen to be a direct consequence of eqs. (4) and (7).

As obvious from table 1, the theoretical model used here leads to values for F_{anis} that are considerably larger than those determined from measurements of light scattering [1] and of the optical Kerr effect [10]. Our theoretical calculations based on the model of eq. (15) were carried out on the assumption that $\rho v = 0.6$, which is true for most liquids. An assumption of $\rho v = 1$ would have led to theoretical results closer to the experimental ones. It seems, however, that the divergence between the values in table 1 is due not only to the approximate nature of the model of eq. (15) but moreover to the omission of other molecular factors [3,6,7], which are able to lower the value of F_{anis}.

One such factor can reside in the nonlinear variation caused in the effective polarizability tensor by fluctuations of the electric fields of the dipoles or quadrupoles of neighbouring molecules. Namely, we have [3]

$$\frac{\partial m_\alpha^{(p)}}{\partial E_\beta} = \alpha_{\alpha\beta}^{(p)} + \beta_{\alpha\beta\gamma}^{(p)}F_\gamma^{(p)} + \tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}^{(p)}F_\gamma^{(p)}F_\delta^{(p)} + \dots, \qquad (18)$$

where $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are tensors of the hyperpolarizability of molecules [11].

If we take into account the electric field due to dipolar molecules of the medium [1]:

$$F_\alpha^{(p)} = -\sum_{q=1}^{N} T_{\alpha\beta}^{(pq)}\mu_\beta^{(q)}, \qquad (19)$$

then by eqs. (3), (13) and (18) we have in a first approximation, on neglecting anisotropy of the hyperpolarizability tensor,

$$F_{anis}^{(1)} = \frac{4\alpha\kappa}{75kT}\beta\mu^3\rho\langle r^{-6}\rangle, \qquad (20)$$

where $\beta = (\beta_{113}+\beta_{223}+\beta_{333})/3$ is the mean hyperpolarizability of the first order.

Likewise, considering molecules having a quadrupole moment Θ only, we obtain [1,12]

$$F_\alpha^{(p)} = \tfrac{1}{3}\sum_{q=1}^{N} T_{\alpha\beta\gamma}^{(pq)}\Theta_{\beta\gamma}^{(q)} \qquad (21)$$

and, in a second approximation for axially-symmetric molecules

$$F_{anis}^{(2)} = \frac{20}{21}\alpha\kappa\gamma\Theta^2\rho\langle r^{-8}\rangle, \qquad (22)$$

where $\gamma = \gamma_{\alpha\alpha\beta\beta}/5$ is the mean hyperpolarizability of the second order.

Elsewhere [13], calculations have been made of yet other contributions to F_{anis} from dispersional and inductional interactions; however, these are of secondary importance.

Table 1

A comparison of the theoretically calculated values of the anisotropic factor F_{anis}, in 10^{26} cm^3, and the values found by recurring to experimental results [1,10].

| Liquid | Theoretical values of F_{anis}^{theor} | | | | Experimental values | |
	$F_{anis}^{(0)}$ eq. [10]	$F_{anis}^{(1)}$ eq. [14]	$F_{anis}^{(2)}$ eq. [11]	F_{anis}^{theor}	Eq. [16]	Eq. [17]
Carbon tetrachloride	0	0	2.13	2.13	0.11	0.11
Chloroform	0.45	−0.13	1.48	1.81	0.65	0.34
Carbon disulphide	10.22	0	8.77	18.32	12.72	6.16
Benzene	2.65	0	3.22	5.67	2.20	0.77
Toluene	3.41	−0.87	3.61	6.14	2.72	1.72
Nitrobenzene	4.90	−2.64	5.25	7.51	12.15	5.22

As we see, the additionally calculated factors (20) and (22) are negative for molecules with negative anisotropy κ. It is to be regretted that, as yet, approximate values of β and γ are known only for some few molecules [11], among which the molecules noted in table 1 are not. Attributing the divergences of table 1 to nonlinear polarization of molecules, it would be feasible to recur to formulas (20) and (22) for gaining estimative information regarding β and γ. In this way, simultaneous investigation of anisotropic light scattering and the optical Kerr effect in liquids can provide data on the nonlinear optical properties and electric moments of molecules and on the molecular structure of the medium.

References

[1] S. Kielich, J. Chem. Phys. 46 (1967) 4090.
[2] S. Kielich, Proc. Phys. Soc. 90 (1967) 847.
[3] S. Kielich, Physica 28 (1962) 1116;
    Acta Phys. Polon. 22 (1962) 477; 24 (1963) 389;
    25 (1964) 39.
[4] A. D. Buckingham, Proc. Phys. Soc. B69 (1956) 344.
[5] J. Yvon, Compt. Rend. 202 (1936) 35;
    J. G. Kirkwood, J. Chem. Phys. 4 (1936) 592.
[6] L. Jansen and P. Mazur, Physica 21 (1955) 193, 208;
    J. Heinrichs, Chem. Phys. Letters 1 (1967) 467.
[7] A. D. Buckingham, Trans. Faraday Soc. 52 (1956) 747, 1035.
[8] R. Beaume, R. Nacasch and R. Coulon, J. Phys. Radium 26 (1965) 597, and references therein.
[9] M. Takatsuji, Phys. Rev. 165 (1968) 171.
[10] M. Paillette, Compt. Rend. 262 (1966) 264.
[11] A. D. Buckingham and B. J. Orr, Quarterly Reviews 21 (1967) 195.
[12] L. Jansen, Phys. Rev. 110 (1958) 661.
[13] S. Kielich, J. Phys. Radium 29 (1968), to be published.