

EFFECT OF MOLECULAR SHAPE ON LIGHT SCATTERING AND OPTICAL BIREFRINGENCE IN LIQUIDS

by

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Summary. This paper contains a quantitative analysis of molecular light scattering and optical birefringence in the Lorentz and Onsager local field approach taking into account the ellipsoidal shape of scattering molecules. 10 liquids are selected for numerical analysis, and it is shown that satisfactory agreement between the experimental data and the theory resorting to the ellipsoidal Onsager-Scholte and Lorentz models is achieved for the depolarization ratio and optical birefringence, whereas with regard to the Rayleigh ratio agreement is more satisfactory when resorting to the spherical models. These results point to a larger role of molecular shape in anisotropic light scattering and optical birefringence than in isotropic scattering, and to its unimportance in molecular refraction. It is found that better agreement with experiment is obtained within the framework of statistical-molecular theory taking into consideration (beside fluctuations in number density of molecules and anisotropy of their polarizability) translational fluctuations, fluctuations in molecular field anisotropy, fluctuations in molecular angular correlations, as well as fluctuations in molecular hyperpolarizability.

1. INTRODUCTION

Statistical-molecular theory of anisotropic light scattering in liquids leads, in general, to results that are of a rather highly involved form both in the case of optically isotropic [1 - 4] and optically anisotropic [2 - 8] molecules. The statistical-molecular theory of optically-induced birefringence in liquids [9] is likewise involved. The parameters of molecular correlations intervening in these effects can in fact be determined from other phenomena, thus e.g. from Kerr [10 - 13] or Cotton-Mouton [12, 14] effect; however, such a procedure requires that the electric and magnetic properties of the molecules in question be known beforehand. It is felt that a theory describing the liquid state and at the same time leading to simple expressions convenient for numerical evaluations is worth elaborating. As we hope to show further on, this aim can be achieved by resorting to Lorentz's [15] or Onsager's [16] model taking into account the so-called anisotropy of the local field due to non-sphericity of the cavity (as is the case with the Lorentz model [17]) or to the

shape and anisotropy of the molecule (as is that of the Onsager-Scholte model [7 - 9, 16, 18 - 22]). Obviously, the final results derived with these models are mathematically simple only if short-range molecular correlations are neglected.

2. THE RESPECTIVE LOCAL FIELDS

When a dielectric isotropic medium is acted on by the electric field of a light wave, each of its molecules is acted on by a local field \vec{F} which is the sum of the macroscopic field \vec{E} existing throughout the medium and the field \vec{F}' stemming additionally from neighbouring polarized molecules. There are currently two ways of calculating this local field: one is due to Lorentz [15], and the other to Onsager [16].

According to Lorentz, the supplementary field \vec{F}' is in a first approximation proportional to the dipolar polarization \vec{P} of the medium; if the cavity containing the molecule under consideration is assumed as ellipsoidal, the field component along the principal axis i of the ellipsoid is [17]:

$$F'_i = 4\pi L_i P_i, \quad (1)$$

with L_i a geometrical parameter of shape of the ellipsoid given [19] as:

$$L_i = \frac{1}{2} r_1 r_2 r_3 \int_0^\infty \frac{ds}{(s+r_i^2) \sqrt{(s+r_1^2)(s+r_2^2)(s+r_3^2)}}, \quad (2)$$

r_1, r_2, r_3 being the semi-axes, and $L_1 + L_2 + L_3 = 1$.

Keeping in mind that the polarization vector \vec{P} and electric field vector \vec{E} of the light wave are, in the case of an isotropic medium of index n , related by the formula:

$$4\pi P_i = (n^2 - 1) E_i, \quad (3)$$

we obtain by (1) for the Lorentz local field:

$$F_i = E_i + 4\pi L_i P_i = \{1 + (n^2 - 1) L_i\} E_i. \quad (4)$$

In particular, for a spherical cavity we have $L_1 = L_2 = L_3 = \frac{1}{3}$, and the field (4) reduces to the well-known form:

$$F_i = \frac{n^2 + 2}{3} E_i. \quad (5)$$

With regard to (5), we can rewrite (4) as follows:

$$F_i = \frac{n^2 + 2}{3} E_i + F_i^{\text{anis}}, \quad (6)$$

where

$$F_i^{\text{anis}} = (n^2 - 1) (L_i - \frac{1}{3}) E_i \quad (7)$$

denotes the anisotropy of the local field; this anisotropy, in the Lorentz case, is caused by the deviation of the cavity from the spherical shape. Clearly, for a spherical cavity, the anisotropy (7) vanishes.

If we assume the medium to consist of optically anisotropic molecules having polarizabilities $a_1 \neq a_2 \neq a_3$ in the three principal axis directions 1, 2, 3 of the molecule, the dipole moment induced in a molecule by the local field (4) can be written as:

$$m_i = a_i F_i = a_i^* E_i, \quad (8)$$

where

$$a_i^* = \{1 + (n^2 - 1) L_i\} a_i \quad (9)$$

is the effective polarizability of the molecule.

In Onsager's model, the local field consists of the field G of the cavity and a reaction field R ; the dimensions of the cavity are taken as identical to those of the molecule itself. This model, which was formulated by Onsager for the case of spherical cavity, was subsequently extended by Scholte to that of an ellipsoidal cavity [18] immersed in a continuous medium of refractive index n . The field of the ellipsoidal cavity is [20]:

$$G_i = \frac{n^2}{n^2 + (1 - n^2) L_i} E_i \quad (10)$$

whereas the reaction field is expressed as follows:

$$R_i = f_i m_i, \quad (11)$$

where

$$f_i = \frac{3L_i(1-L_i)(n^2-1)}{\{n^2 + (1-n^2)L_i\}r_1r_2r_3} \quad (12)$$

is a parameter of the reaction field.

The fields (10) and (11) lead to eq. (8), albeit with an effective polarizability of the form

$$a_i^* = \frac{n^2 a_i}{\{n^2 + (1 - n^2) L_i\} (1 - f_i a_i)}, \quad (13)$$

which is readily seen to go over into the Lorentz form (9) on replacing the right hand term by a polarizability given by the formula

$$a_i = \frac{(n^2 - 1) r_1 r_2 r_3}{3 [1 + (n^2 - 1) L_i]}. \quad (14)$$

In particular, for a spherical cavity, the effective polarizabilities (9) and (13) become:

$$\text{in the Lorentz case } a_i^* = \left(\frac{n^2 + 2}{3} \right) a_i, \quad (15)$$

$$\text{in the Onsager case } a_i^* = \frac{3n^2 r^3 a_i}{(2n^2 + 1) r^3 - 2(n^2 - 1) a_i}. \quad (16)$$

Table 1 contains polarizability values as well as dimension and shape parameters for various isolated molecules. The effective polarizabilities calculated with the data of Table 1 and eqs (9) and (15) (Lorentz model) and, respectively, eqs (13) and (16) (Onsager model), are given in Tables 2 and 3.

Table 1

Molecular parameters for several anisotropic molecules

| Molecule | Polarizabilities (10^{-24} cm ³) | | | Semiaxes (Å°) | | | Shape factors | | |
|---|---|-------|-------|-------------------------------|-------|-------|-------------------|-------|-------|
| | a_1 | a_2 | a_3 | r_1 | r_2 | r_3 | L_1 | L_2 | L_3 |
| CS ₂ | 15.14 ^a | 5.54 | 5.54 | 6.8 ^d | 3.7 | 3.7 | 0.19 ^d | 0.405 | 0.405 |
| C ₆ H ₆ | 12.31 ^a | 12.31 | 6.35 | 7.1 ^d | 7.1 | 3.7 | 0.23 ^d | 0.23 | 0.54 |
| C ₃ H ₆ O | 6.96 ^b | 7.22 | 4.82 | 5.4 ^d | 6.7 | 4.0 | 0.31 ^e | 0.24 | 0.45 |
| C ₇ H ₈ | 15.64 ^a | 13.66 | 7.48 | 8.5 ^d | 6.5 | 4.0 | 0.19 ^e | 0.30 | 0.51 |
| CHCl ₃ | 6.68 ^a | 9.01 | 9.01 | 4.6 ^d | 7.1 | 7.1 | 0.46 ^e | 0.27 | 0.27 |
| C ₆ H ₅ Cl | 15.51 ^b | 13.82 | 7.42 | 8.5 ^d | 6.5 | 3.7 | 0.19 ^e | 0.26 | 0.55 |
| C ₆ H ₅ NO ₂ | 17.16 ^b | 14.19 | 7.41 | 8.5 ^d | 6.5 | 3.7 | 0.18 ^e | 0.25 | 0.57 |
| C ₆ H ₅ Br | 16.84 ^c | 12.13 | 9.56 | 8.8 ^d | 6.5 | 3.9 | 0.19 ^e | 0.28 | 0.53 |
| C ₆ H ₅ F | 11.26 ^c | 11.06 | 7.11 | 7.6 ^d | 6.5 | 3.7 | 0.14 ^d | 0.36 | 0.50 |
| C ₅ H ₅ N | 10.84 ^a | 11.88 | 5.78 | 6.6 ^d | 6.5 | 3.7 | 0.30 ^d | 0.23 | 0.47 |

^a Stuart H. A., Die Struktur des Freien Moleküls, Bd. I, Springer - Verlag, Berlin-Göttingen-Heidelberg (1952).

^b Landolt - Börnstein Tabellen, I Bd. 510, 512 (1951).

^c Le Fèvre C. G. and Le Fèvre R. J. W., Rev. Pure Appl. Chem. 5, 261-318 (1955).

^d Yasumi M., Okabayashi H. and Komooka H., Bull. Chem. Soc. Japan, 31, 673 (1958).

^e Ref. 20

Table 2

Computed values of effective polarizabilities, in units 10^{-24} cm³, for the spherical and ellipsoidal Lorentz models

| Molecule | Lorentz spherical | | | Lorentz ellipsoidal | | |
|---|-------------------|---------|---------|---------------------|---------|---------|
| | a_1^* | a_2^* | a_3^* | a_1^* | a_2^* | a_3^* |
| CS ₂ | 23.57 | 8.63 | 8.63 | 19.94 | 9.28 | 9.28 |
| C ₆ H ₆ | 17.48 | 17.48 | 9.02 | 15.87 | 15.87 | 10.67 |
| C ₃ H ₆ O | 8.92 | 9.26 | 6.18 | 8.78 | 8.68 | 6.66 |
| C ₇ H ₈ | 22.15 | 19.34 | 10.59 | 19.35 | 18.77 | 12.24 |
| CHCl ₃ | 9.11 | 12.29 | 12.29 | 10.03 | 11.66 | 11.66 |
| C ₆ H ₅ Cl | 22.30 | 19.87 | 10.67 | 19.37 | 18.53 | 12.78 |
| C ₆ H ₅ NO ₂ | 25.36 | 20.97 | 10.95 | 21.59 | 19.27 | 13.46 |
| C ₆ H ₅ Br | 24.80 | 17.87 | 14.08 | 21.37 | 16.95 | 16.74 |
| C ₆ H ₅ F | 15.53 | 15.25 | 9.80 | 13.05 | 15.58 | 11.15 |
| C ₅ H ₅ N | 15.46 | 16.94 | 8.24 | 14.99 | 15.37 | 9.25 |

The experimental results show that when a medium goes over from the gaseous to the liquid state its optical anisotropy undergoes a change. This is corroborated by the theoretical calculations carried out for different local field models (Tables 2 and 3). The spherical models of Lorentz and Onsager raise the effective polarizability of a molecule as compared with the ellipsoidal models. Indeed, the optical anisotropy values calculated with the spherical Lorentz and Onsager models (Tables 5 and 7) are 2 to 2,5 times larger than those obtained with the ellipsoidal models (Tables 6 and 8) for liquids like C₆H₆, C₃H₆O, C₇H₈, CS₂, C₆H₅F, C₅H₅N, and 3 to 4 times larger for CHCl₃, C₆H₅Cl, C₆H₅NO₂ and C₆H₅Br. With the aim of comparing the theoretical values of effective

Table 3
Computed values of effective polarizabilities, in units 10^{-24} cm³, for the spherical and ellipsoidal
Onsager models

| Molecule | Onsager spherical | | | Onsager-Scholte | | |
|---|-------------------|---------|---------|-----------------|---------|---------|
| | a_1^* | a_2^* | a_3^* | a_1^* | a_2^* | a_3^* |
| CS ₂ | 20.92 | 7.22 | 7.22 | 18.14 | 7.69 | 7.69 |
| C ₆ H ₆ | 15.58 | 15.58 | 7.92 | 14.43 | 14.43 | 9.27 |
| C ₃ H ₆ O | 8.36 | 8.68 | 5.76 | 8.24 | 8.22 | 6.17 |
| C ₇ H ₈ | 19.82 | 17.24 | 9.32 | 17.84 | 16.82 | 10.64 |
| CHCl ₃ | 8.18 | 11.09 | 11.09 | 8.92 | 10.63 | 10.63 |
| C ₆ H ₅ Cl | 19.83 | 17.59 | 9.31 | 17.77 | 16.64 | 11.03 |
| C ₆ H ₅ NO ₂ | 22.27 | 18.27 | 9.39 | 19.67 | 17.10 | 11.42 |
| C ₆ H ₅ Br | 21.73 | 15.48 | 12.14 | 19.39 | 14.85 | 14.25 |
| C ₆ H ₅ F | 14.06 | 13.81 | 8.79 | 12.33 | 14.07 | 9.89 |
| C ₅ H ₅ N | 13.76 | 15.13 | 7.23 | 13.42 | 14.01 | 8.01 |

optical anisotropies, we calculated Δ_{exp}^2 (Table 4) which, on neglecting angular correlations, is of the form [8]:

$$\Delta_{\text{exp}}^2 = \frac{5D}{6-7D} \rho k T \beta_T (\alpha_1 + \alpha_2 + \alpha_3)^2. \quad (16a)$$

The ellipsoidal models yield values of effective optical anisotropies in accordance, to within experimental error, with the experimentally measured ones. Exceptions are: CS₂, for which we get values that are twice larger, and C₅H₅N, for which the values are three times larger.

On the other hand, the spherical models considerably raise the effective anisotropy as compared with the experimental results.

3. RAYLEIGH RATIO AND DEPOLARIZATION RATIO

Statistical-molecular theory of light scattering by liquids leads quite generally to the following equation for the intensity tensor [8]:

$$I_{\sigma\tau}^s = \{S_{\text{is}} e_\sigma e_\tau + S_{\text{anis}} (3\delta_{\sigma\tau} + e_\sigma e_\tau)\} I. \quad (17)$$

Above, $I = \overline{E^2}$ is the incident intensity, and \hat{e} a unit vector in the direction of the electric field \vec{E} . The constants of isotropic and anisotropic light scattering are of the form:

$$S_{\text{is}} = \frac{1}{9} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha} \frac{\partial m_\beta^{(q)}}{\partial E_\beta} \right\rangle, \quad (18)$$

$$S_{\text{anis}} = \frac{1}{90} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N \left(3 \frac{\partial m_\alpha^{(p)}}{\partial E_\beta} \frac{\partial m_\alpha^{(q)}}{\partial E_\beta} - \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha} \frac{\partial m_\beta^{(q)}}{\partial E_\beta} \right) \right\rangle, \quad (19)$$

$m^{(p)}$ being the component of the dipole moment induced in the p -th molecule of the medium, and the symbol $\langle \rangle$ standing for statistical averaging.

Table 4

Experimental data for several liquids

| Liquid | $\rho \cdot 10^{-21}$ [cm ⁻³] | n $\lambda =$ 546 m μ | $\beta_T \cdot 10^{12}$ [$\frac{\text{cm}^2}{\text{dyne}}$] | D | $R_{1s} \cdot 10^6$ [cm ⁻¹] | $R_{\text{anis}} \cdot 10^6$ [cm ⁻¹] | $R \cdot 10^6$ [cm ⁻¹] | $B_\rho \cdot 10^{12}$ | R_m | $d^2 \cdot 10^{48}$ [cm ⁶] | $\delta^2 \cdot 10^{48}$ [cm ⁶] |
|---|--|-----------------------------------|--|--------------------------|--|---|---------------------------------------|------------------------|--------------------|---|--|
| CS ₂ | 9.997 | 1.634 ^a | 94 ^a | 0.65 ^a | 12.0 ^a | 71.9 ^a | 83.9 ^a | 3.83 ^k | 21.54 | 59.11 ⁿ | 92.16 ⁿ |
| | | | | 0.669 ^b | 13.1 ^h | 72.9 ^h | 84.6 ^c | 2.94 ^l | | | |
| | | | | 0.68 ^c | 12.3 ⁿ | 71.6 ⁿ | 86 ^h | 3.08 ^m | | | |
| | | | | 0.62 ^d | 13.23 ^a | 72.37 ^a | 85.6 ^a | | | | |
| | | | | 0.651 ^e | | | | | | | |
| C ₆ H ₆ | 6.736 | 1.503 ^a | 95 ^a | 0.42 ^a | 5.9 ^a | 9.9 ^a | 15.8 ^a | 0.48 ^k | 26.2 ^o | 17.30 ⁿ | 35.52 ⁿ |
| | | | | 0.438 ^b | | | | | | | |
| | | | | 0.40 - 0.42 ^c | 6.03 ^a | 10.27 ^a | 16.3 ^a | 0.62 ^l | | | |
| | | | | 0.428 ^d | 5.67 ⁿ | 10.13 ⁿ | 15.4 ^l | 0.82 ^m | | | |
| | | | | 0.41 ^e | | | 16.1 ^h | | | | |
| C ₃ H ₈ O | 8.202 | 1.359 ^l | 125 ^l | 0.208 ^l | 2.14 ⁿ | 1.46 ⁿ | 3.6 ^e | 0.13 ^k | 16.17 | 3.48 ⁿ | 5.20 ⁿ |
| | | | | 0.231 ^l | | | | 0.15 ^l | | | |
| | | | | 0.236 ^l | | | | | | | |
| | | | | 0.163 ^e | | | | | | | |
| | | | | | | | | | | | |
| C ₇ H ₈ | 5.649 | 1.499 ^a | 92 ^a | 0.48 ^a | 5.23 ^a | 13.17 ^a | 18.4 ^a | 1.11 ^k | 31.3 | 26.14 ⁿ | 54.34 ⁿ |
| | | | | 0.528 ^b | 5.47 ⁿ | 12.93 ⁿ | 17.2 ^l | 0.66 ^l | | | |
| | | | | 0.43 - 0.49 ^c | | | 19.3 ^l | 1.03 ^m | | | |
| | | | | 0.51 ^d | | | | | | | |
| | | | | | | | | | | | |
| CHCl ₃ | 7.510 | 1.446 ^l | 87 ^l | 0.204 ^b | 4.36 ^f | 2.80 ^f | 7.16 ^f | 0.22 ^k | 21.39 | 4.07 ⁿ | 5.43 ⁿ |
| | | | | 0.22 ^e | 4.36 ⁿ | 2.82 ⁿ | 7.45 ^p | 0.21 ^l | | | |
| | | | | 0.225 ^p | | | | | | | |
| | | | | 0.215 ^e | | | | | | | |
| | | | | | | | | | | | |
| C ₆ H ₅ Cl | 5.902 | 1.521 ^l | 75 ^l | 0.58 ^d | 4.22 ⁿ | 16.38 ⁿ | 20.6 ^e | 1.03 ^l | 31.19 ^o | 36.39 ⁿ | 54.63 ⁿ |
| | | | | 0.60 ^l | | | | | | | |
| | | | | 0.575 ^l | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| C ₆ H ₅ NO ₂ | 5.887 | 1.560 ^a | 49 ^a | 0.74 ^d | 5.1 ^a | 60.7 ^a | 65.8 ^a | 3.13 ^k | 33.08 | 79.83 ⁿ | 74.92 ⁿ |
| | | | | 0.652 ^l | 8.09 ⁿ | 62.14 ⁿ | | 2.50 ^l | | | |
| | | | | 0.68 ^l | | | | 2.55 ^m | | | |
| | | | | 0.753 ^e | | | | | | | |
| | | | | | | | | | | | |
| C ₆ H ₅ Br | 5.704 | 1.560 ^l | 65 ^l | 0.57 ^d | | | | 1.37 ^l | 34.15 | 31.71 ⁿ | 40.89 ⁿ |
| | | | | 0.65 ^l | | | | | | | |
| C ₆ H ₅ F | 6.367 | 1.462 ^l | 95 ^l | | | | | | 25.99 | 9.33 ⁿ | |
| C ₃ H ₅ N | 7.486 | 1.509 ^l | 48 ^l | 0.46 ^l | 4.51 ⁿ | 9.69 ⁿ | 14.2 ^a | | 24.02 | 9.89 ⁿ | 31.94 ⁿ |
| | | | | 0.455 ^p | | | 21.85 ^p | | | | |

^a Values taken from ref. 25.

^b Leite R. C. C., Moore R. S., Porto S. P. S., J. Chem. Phys. 40 (1964).

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^d Weill, G., Ann. Physique, 6, 1063 (1961).

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^f Giurgea M., Ghita C., et Ghita L., Studii și Cercetări de Fizică, 3 (1962).

^g Fabelinskiy, I. L., Molekularnoye Rasseyaniye Sveta (Moskva 1965).

^h Deželić GJ. and Vavra, J., Croat. Chem. Acta 38, 35 (1966).

ⁱ Volkenshteyn, M. V., Molekularnaya Optika (Gostekhizdat, Moskva 1951).

^j Landolt-Börnstein Tables, II Band, 8 Teil (Springer-Verlag, Berlin).

^k Paillette M., CR. Acad. Sci. Paris, 262, 264 (1966).

^l Shen, Y., Phys. Letters, 20, 378 (1966).

^m Wang, C. C. Phys. Rev. 152, 149 (1966).

ⁿ Values calculated from formulas (39), (40), (16a).

^o Schmidt R. L., Journal of Colloid and Interface Science, 27, 516 (1968).

^p Malmberg M. S., Lippincott, E. R., Journal of Colloid and Interface Science 27, 591 (1968).

^q Ghita C., Revue Roumaine de Chimie, 13, 1019 - 1025 (1968).

On neglecting in eqs. (18) and (19) molecular correlations of the angular type, and with regard to the relation (8), we obtain in a satisfactory approximation:

$$S_{is} = N \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{a_1^* + a_2^* + a_3^*}{3} \right)^2 \rho k T \beta_T, \quad (20)$$

$$S_{anis} = \frac{N}{45} \left(\frac{2\pi}{\lambda} \right)^4 \Delta^2, \quad (21)$$

where $\rho = N/V$ is the number density of molecules, β_T the isothermal compressibility coefficient, and

$$\Delta^2 = \frac{1}{2} \{ (a_1^* - a_2^*)^2 + (a_3^* - a_1^*)^2 + (a_3^* - a_2^*)^2 \} \quad (22)$$

the effective optical anisotropy of the molecule values of which for several liquids are assembled in Tables 2 and 3.

From the general equation (17) we obtain for the Rayleigh ratio, when the incident light is natural and observation of scattered light is performed perpendicularly to the direction of incidence,

$$R = R_{is} + R_{anis}, \quad (23)$$

with the Rayleigh ratios of isotropic and anisotropic light scattering related with the constants (20) and (21) as follows:

$$R_{is} = \frac{1}{2V} S_{is}, \quad R_{anis} = \frac{13}{2V} S_{anis}, \quad (24)$$

V being the volume of the scattering medium.

At identical conditions of observation, eq. (17) yields for the depolarization ratio:

$$D = \frac{6S_{anis}}{S_{is} + 7S_{anis}}. \quad (25)$$

The expressions (20) - (22) are obviously seen to contain only parameters which are available. Consequently, we can compute numerically the quantities R and D and compare them with the existing experimental data, which are assembled in Tables 4 - 8. Such a comparison shows that the constants of isotropic light scattering are considerably smaller than the experimental values of Table 4 both for the spherical and ellipsoidal models of Lorentz and Onsager. On the other hand, the values of R_{anis} behave variously according to the liquid and the model assumed. Assuming the spherical Lorentz model, we get $R_{anis}^{calc} < R_{anis}^{exp}$ for CS_2 , $CHCl_3$, $C_6H_5NO_2$ and C_6H_5N . For the other liquids, $R_{anis}^{calc} > R_{anis}^{exp}$. Assuming the spherical Onsager model, one has $R_{anis}^{calc} < R_{anis}^{exp}$ in CS_2 , $CHCl_3$, C_6H_5Cl , $C_6H_5NO_2$ and C_6H_5N . Assuming the ellipsoidal models of Lorentz and Onsager, we come to values of the anisotropic light scattering constants which are about twice smaller than the experimental data and indeed five times smaller for $CHCl_3$, three times smaller for C_6H_5Cl , and eight times smaller for $C_6H_5NO_2$.

The preceding analysis permits the conclusion that the approach to light scattering by resorting to models leads to values of isotropic and anisotropic light scattering con-

stants which diverge strongly from the values measured in experiment. Moreover, it has to be stressed that the assumption of a spherical model of the molecule raises the values of R_{is} and R_{anis} with respect to the ellipsoidal model. The calculations of this paper have been performed on neglecting short range angular correlations. This simplification, which renders the numerical computations mathematically easier, overlooks statistical intermolecular interactions in the liquid which essentially affect the value of the optical anisotropy and, consequently, the value of the constant of anisotropic light scattering by the liquid. This explains the divergences between the experimental data and the theoretical values derived here.

The ratio of light depolarization calculated from eq. (25) on the assumption of a spherical shape of the molecule takes values slightly in excess of the experimental ones. The ellipsoidal models lead to values in accordance with experiment.

4. MOLECULAR REFRACTION AND OPTICAL KERR EFFECT

Molecular refraction, given as:

$$R_m = \frac{n^2 - 1}{n^2 + 2} V_m \quad (26)$$

is expressed, with regard to eq. (8), by the formula:

$$R_m = \frac{4\pi}{3} N_A \left(\frac{a_1^* + a_2^* + a_3^*}{n^2 + 2} \right), \quad (27)$$

where V_m is the molar volume, N_A Avogadro's number, and the effective polarizabilities a_i^* are given by eqs. (9) and (13) - (16).

When very intense light is incident on the medium, its refractive index becomes a function of the light intensity I and the medium itself becomes optically anisotropic. The difference between the indices is:

$$n_{||} - n_{\perp} = n B_n I, \quad (28)$$

with B_n - the experimentally measured optical Kerr effect constant, expressed as follows in terms of properties of the medium [8, 21]:

$$B_n = \frac{(n^2 + 2)^4}{54n^2} B_\rho, \quad (29)$$

with

$$B_\rho = \frac{4\pi\rho}{5(n^2 + 2)^2 kT} \Delta^2, \quad (30)$$

the effective optical anisotropy of the molecule being given by eq. (22).

The experimental data for R_m and B_ρ are assembled in Table 4; those computed theoretically for the respective models are to be found in Tables 5 - 8.

Table 5

Values computed with Lorentz's spherical model

| Liquid | $\Delta^2 \cdot 10^{48}$ [cm ⁶] | $R_{1s} \cdot 10^6$ [cm ⁻¹] | $R_{1s}^* \cdot 10^6$ [cm ⁻¹] | $R_{anis} \cdot 10^6$ [cm ⁻¹] | $R \cdot 10^6$ [cm ⁻¹] | $D \cdot 10^2$ | $B_p \cdot 10^{12}$ | R_m [cm ³] |
|---|--|--|--|--|---------------------------------------|----------------|---------------------|-----------------------------|
| CS ₂ | 223.204 | 6.22 | 14.41 | 60.31 | 66.53 | 71.9 | 6.295 | 22.03 |
| C ₆ H ₆ | 71.572 | 3.31 | 6.89 | 12.19 | 15.50 | 57.0 | 1.636 | 26.02 |
| C ₃ H ₆ O | 8.554 | 1.98 | 3.34 | 1.77 | 3.75 | 27.9 | 0.291 | 15.96 |
| C ₇ H ₈ | 109.046 | 3.17 | 6.51 | 15.57 | 18.74 | 62.2 | 2.103 | 30.90 |
| CHCl ₃ | 10.112 | 2.21 | 4.37 | 1.92 | 4.13 | 27.3 | 0.279 | 20.75 |
| C ₆ H ₅ Cl | 112.900 | 2.90 | 6.06 | 16.84 | 19.74 | 64.9 | 2.202 | 30.87 |
| C ₆ H ₅ NO ₂ | 163.660 | 2.21 | 4.99 | 24.35 | 26.56 | 73.4 | 3.015 | 32.55 |
| C ₆ H ₅ Br | 88.68 | 2.71 | 6.62 | 12.79 | 15.50 | 61.5 | 1.583 | 32.37 |
| C ₆ H ₅ F | 35.188 | 2.52 | 5.30 | 5.66 | 8.18 | 46.9 | 0.805 | 24.72 |
| C ₅ H ₅ N | 65.004 | 1.77 | 3.61 | 12.30 | 14.07 | 67.6 | 1.636 | 23.96 |

Table 6

Values computed with Lorentz's ellipsoidal model

| Liquid | $\Delta^2 \cdot 10^{48}$ [cm ⁶] | $R_{1s} \cdot 10^6$ [cm ⁻¹] | $R_{1s}^* \cdot 10^6$ [cm ⁻¹] | $R_{anis} \cdot 10^6$ [cm ⁻¹] | $R \cdot 10^6$ [cm ⁻¹] | $D \cdot 10^2$ | $B_p \cdot 10^{12}$ | R_m [cm ³] |
|---|--|--|--|--|---------------------------------------|----------------|---------------------|-----------------------------|
| CS ₂ | 113.636 | 5.53 | 12.82 | 30.70 | 36.23 | 64.2 | 3.205 | 20.77 |
| C ₆ H ₆ | 27.040 | 3.08 | 6.41 | 4.60 | 7.68 | 38.2 | 0.618 | 25.10 |
| C ₃ H ₆ O | 4.361 | 1.94 | 3.28 | 0.90 | 2.84 | 17.6 | 0.149 | 15.80 |
| C ₇ H ₈ | 46.765 | 2.96 | 6.08 | 6.68 | 9.64 | 47.0 | 0.902 | 29.89 |
| CHCl ₃ | 2.657 | 2.17 | 4.28 | 0.50 | 2.67 | 9.5 | 0.073 | 20.55 |
| C ₆ H ₅ Cl | 38.598 | 2.66 | 5.58 | 5.76 | 8.42 | 46.1 | 0.753 | 29.61 |
| C ₆ H ₅ NO ₂ | 52.617 | 1.99 | 4.49 | 7.83 | 9.82 | 58.2 | 0.969 | 30.88 |
| C ₆ H ₅ Br | 20.464 | 2.55 | 6.23 | 2.95 | 5.50 | 32.9 | 0.365 | 31.40 |
| C ₆ H ₅ F | 14.818 | 2.42 | 5.09 | 2.39 | 4.81 | 29.8 | 0.339 | 24.23 |
| C ₅ H ₅ N | 35.166 | 1.68 | 3.42 | 6.65 | 8.33 | 58.3 | 0.885 | 23.34 |

Table 7

Values computed with Onsager's spherical model

| Liquid | $\Delta^2 \cdot 10^{48}$ [cm ⁶] | $R_{1s} \cdot 10^6$ [cm ⁻¹] | $R_{1s}^* \cdot 10^6$ [cm ⁻¹] | $R_{anis} \cdot 10^6$ [cm ⁻¹] | $R \cdot 10^6$ [cm ⁻¹] | $D \cdot 10^2$ | $B_p \cdot 10^{12}$ | R_m [cm ³] |
|---|--|--|--|--|---------------------------------------|----------------|---------------------|-----------------------------|
| CS ₂ | 187.416 | 4.67 | 7.90 | 50.64 | 55.31 | 73.2 | 5.29 | 19.09 |
| C ₆ H ₆ | 58.676 | 2.62 | 4.37 | 9.99 | 12.61 | 57.6 | 1.34 | 23.13 |
| C ₃ H ₆ O | 7.694 | 1.74 | 2.55 | 1.60 | 3.34 | 28.4 | 0.26 | 14.93 |
| C ₇ H ₈ | 89.816 | 2.51 | 4.16 | 12.83 | 15.34 | 62.9 | 1.73 | 27.52 |
| CHCl ₃ | 8.41 | 1.80 | 2.96 | 1.60 | 3.40 | 27.8 | 0.23 | 18.70 |
| C ₆ H ₅ Cl | 92.123 | 2.27 | 3.77 | 13.74 | 16.01 | 65.6 | 1.80 | 27.31 |
| C ₆ H ₅ NO ₂ | 131.028 | 1.68 | 2.94 | 19.50 | 21.18 | 73.9 | 2.41 | 28.37 |
| C ₆ H ₅ Br | 71.093 | 2.05 | 3.88 | 10.25 | 12.30 | 62.5 | 1.27 | 28.15 |
| C ₆ H ₅ F | 26.517 | 2.06 | 3.56 | 4.27 | 6.33 | 45.2 | 0.61 | 22.33 |
| C ₅ H ₅ N | 53.450 | 1.39 | 2.28 | 10.11 | 11.50 | 68.3 | 1.35 | 21.29 |

Table 8

Values computed with the Onsager-Scholte ellipsoidal model

| Liquid | $\Delta^2 \cdot 10^{48}$ [cm ⁶] | $R_{is} \cdot 10^6$ [cm ⁻¹] | $R_{is}^* \cdot 10^6$ [cm ⁻¹] | $R_{anis} \cdot 10^6$ [cm ⁻¹] | $R \cdot 10^6$ [cm ⁻¹] | $D \cdot 10^2$ | $B_p \cdot 10^{12}$ | R_m [cm ³] |
|---|--|--|--|--|---------------------------------------|----------------|---------------------|-----------------------------|
| CS ₂ | 109.20 | 4.19 | 7.45 | 29.51 | 33.70 | 67.8 | 3.08 | 18.08 |
| C ₆ H ₆ | 26.63 | 2.49 | 4.28 | 4.53 | 7.02 | 42.4 | 0.61 | 22.56 |
| C ₃ H ₆ O | 4.24 | 1.71 | 2.56 | 0.88 | 2.59 | 18.6 | 0.15 | 14.82 |
| C ₇ H ₈ | 45.54 | 2.39 | 4.09 | 6.50 | 8.89 | 50.9 | 0.88 | 26.88 |
| CHCl ₃ | 2.92 | 1.78 | 2.93 | 0.56 | 2.34 | 12.4 | 0.08 | 18.59 |
| C ₆ H ₅ Cl | 38.49 | 2.14 | 3.67 | 5.74 | 7.88 | 50.7 | 0.75 | 26.56 |
| C ₆ H ₅ NO ₂ | 53.47 | 1.57 | 2.88 | 7.96 | 9.53 | 62.7 | 0.99 | 27.38 |
| C ₆ H ₅ Br | 23.70 | 1.97 | 3.82 | 3.42 | 5.39 | 41.4 | 0.42 | 27.65 |
| C ₆ H ₅ F | 13.23 | 2.02 | 3.53 | 2.13 | 4.15 | 31.0 | 0.30 | 22.09 |
| C ₃ H ₅ N | 32.81 | 1.34 | 2.22 | 6.21 | 7.55 | 61.2 | 0.83 | 20.88 |

On confronting the latter with the experimental data we see that the spherical models raise the optical birefringence constant B_p (the Lorentz model does so much more markedly than the Onsager model). The values of B_p calculated with the ellipsoidal models are below the experimental data for CHCl₃, C₆H₅Cl, C₆H₅NO₂ and C₆H₅Br; for the other liquids, they coincide with experiment.

The results of calculations of molecular refraction are generally in accordance with (spherical models) or slightly lower than the experimental data. Of all the quantities calculated in this paper, the molecular refraction R_m is the least sensitive to the assumptions made as to molecular shape and local field.

5. DISCUSSION AND CONCLUSIONS

The results of the present, model-based calculations prove that good accordance with the experimental data requires taking into account short range angular molecular correlations [13, 22]. Independently, the ellipsoidal models make apparent the important rôle of molecular geometrical shape in anisotropic light scattering and optical birefringence.

The formula for R_{is} resulting from the thermodynamical-fluctuational Smoluchowski-Einstein theory is [24]:

$$R_{is}^* = \frac{\pi^2}{2\lambda^4} kT\beta_T \left(\rho \frac{\partial n^2}{\partial \rho} \right)_T, \quad (31)$$

where the quantity $\left(\rho \frac{\partial n^2}{\partial \rho} \right)_T$ is accessible to direct experimental determination [24, 25] or can be calculated theoretically once the equation of state relating the index n and density ρ is available [13].

Using the ellipsoidal Lorentz model, we have by eqs. (9), (26) and (27):

$$\left(\rho \frac{\partial n^2}{\partial \rho} \right)_T = (n^2 - 1) \left\{ 1 + (n^2 - 1) \left(\frac{a_1 L_1 + a_2 L_2 + a_3 L_3}{a_1 + a_2 + a_3} \right) \right\}. \quad (32)$$

This expression, on neglecting the anisotropy of the local field, reduces to the well-known Einstein formula:

$$\left(\rho \frac{\partial n^2}{\partial \rho}\right)_T = (n^2 - 1) \left(\frac{n^2 + 2}{3}\right), \quad (33)$$

which yields values by 5 - 10 per cent in excess of the experimental ones [25].

Anisotropy of the Onsager-Scholte field leads to the formula:

$$\left(\rho \frac{\partial n^2}{\partial \rho}\right)_T = (n^2 - 1) \left(\frac{a_1^* + a_2^* + a_3^*}{A_1 + A_2 + A_3}\right), \quad (34)$$

where we have used the notation:

$$A_i = a_i^* \left\{ 1 - \frac{(n^2 - 1) a_i^* L_i}{n^4 a_i} \left[1 + \frac{3(1 - L_i) a_i}{r_1 r_2 r_3} \right] \right\}. \quad (35)$$

The values of $\left(\rho \frac{\partial n^2}{\partial \rho}\right)_T$ calculated with the respective local field models are assembled in Table 9; the quantity R_{is}^* hence calculated (eq. 31) is given in Tables 5 - 8. The Lorentz

Table 9

Values of $\rho \left(\frac{\partial n^2}{\partial \rho}\right)_T$ for the various electrostatic models

| Liquid | $\rho \left(\frac{\partial n^2}{\partial \rho}\right)_T$ | | | | |
|---|--|-------------------|---------------------|-------------------|------------------|
| | experimental | Lorentz spherical | Lorentz ellipsoidal | Onsager spherical | Onsager -Scholte |
| CS ₂ | 2.37 | 2.60 | 2.45 | 1.93 | 1.87 |
| C ₆ H ₆ | 1.65 | 1.79 | 1.72 | 1.42 | 1.41 |
| C ₃ H ₆ O | | 1.09 | 1.08 | 0.95 | 0.95 |
| C ₇ H ₈ | 1.58 | 1.77 | 1.71 | 1.41 | 1.40 |
| CHCl ₃ | 1.435 | 1.49 | 1.47 | 1.23 | 1.22 |
| C ₆ H ₅ Cl | 1.72 | 1.89 | 1.81 | 1.49 | 1.47 |
| C ₆ H ₅ NO ₂ | 1.875 | 2.12 | 2.01 | 1.63 | 1.61 |
| C ₆ H ₅ Br | | 2.12 | 2.06 | 1.62 | 1.61 |
| C ₆ H ₅ F | | 1.57 | 1.54 | 1.29 | 1.28 |
| C ₅ H ₅ N | | 1.82 | 1.77 | 1.45 | 1.43 |

model, spherical and ellipsoidal, yields results in excess of experiment [25], whereas those from the Onsager and Onsager-Scholte models lie somewhat below the experimental data. The situation is similar with regard to R_{is}^* .

By eqs. (23) - (25), we have

$$\frac{R_{anis}}{R_{is}} = \frac{13D}{6-7D} \quad (36)$$

and the following formulas permitting separate calculations of R_{is} and R_{anis} once R and D are known experimentally:

$$R_{is} = \frac{6-7D}{6+6D} R, \quad (37)$$

$$R_{anis} = \frac{13DR}{6+6D}. \quad (38)$$

The values of R_{is} and R_{anis} calculated from eqs. (37) and (38) are given in Table 4.

6. RÔLE OF MOLECULAR CORRELATIONS

In the statistical-molecular approach, the scattering constants (18) and (19) become [3, 8]:

$$S_{is} = V \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2+2}{3} \right)^2 F_{is}, \quad (39)$$

$$S_{anis} = \frac{V}{5} \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2+2}{3} \right)^2 F_{anis}, \quad (40)$$

with F_{is} and F_{anis} denoting respectively molecular factors of isotropic and anisotropic light scattering which depend on the optical properties of the atoms or molecules and on the micro-structure of the medium. In the general case, these factors are of a mathematically highly involved form [21, 29] but in certain cases expressions well adapted to direct, numerical calculations can be obtained.

a) Rôle of translational fluctuations. For a medium consisting of atoms or isotropically polarizable molecules, one obtains on taking into account spatial redistribution [8, 21]:

$$F_{is} = \rho a^2 (\rho k T \beta_T + 4a^2 J_R + \dots), \quad (41)$$

$$F_{anis} = \rho a^2 (a^2 J_R + \dots). \quad (42)$$

It is thus seen that, in this case, by eq. (41) isotropic scattering of light is caused not only by fluctuations in the number density $\rho k T \beta_T$ of molecules but moreover by translational fluctuations [30, 31] leading to their spatial redistribution which, in a first approximation, is given as $a^2 J_R$, where [14]:

$$J_R = 8\pi\rho \int r^{-4} g(r) dr \quad (43)$$

is a parameter of pairwise radial correlations, described by the radial function $g(r)$. The parameter (43) can be determined experimentally, or calculated directly taking $g(r)$ in Kirkwood's approximation [31] which yields [32]:

$$J_R = \frac{4\pi^2\rho}{9v} \quad (43a)$$

with v — the molecular volume.

Eq. (42) shows that the translational fluctuations not only enhance isotropic scattering but moreover act as a source of anisotropic light scattering by dense atomic liquids or

ones consisting of isotropically polarizable molecules [3, 8, 21]. For CCl_4 , $\rho k T \beta_T = 0.026$, whereas $4a^2 J_R = 0.034$ (with J_R calculated from eq. (43a) for $\rho v = 1$) or $4a^2 J_R = 0.005$ (with the experimentally determined value $J_R = 1.3 \cdot 10^{43} \text{ cm}^{-6}$ [14]). Hence, translational fluctuations contribute at least 20 per cent to isotropic scattering; theoretically (eq. 43a) their contribution can amount to over 100 per cent, according to the model used in the calculations.

b) Rôle of orientational fluctuations. In a liquid consisting of anisotropic molecules, fluctuations in orientational molecular interaction can raise or reduce the anisotropic scattering of light by the liquid. These fluctuations have to be considered distinctly from fluctuations in number density and translational fluctuations. If the molecules present the axial symmetry, the anisotropic scattering factor results, in place of (42), in the form [8, 32]:

$$F_{\text{anis}} = \rho a^2 \left\{ \kappa^2 (1 + J_A) + a^2 \left(1 + \frac{28}{5} \kappa^2 + 2\kappa^3 + \frac{67}{25} \kappa^4 \right) J_R + \dots \right\}, \quad (44)$$

with $\kappa = (a_3 - a_1)/3a$ — a dimensionless anisotropy, and [3, 14]

$$J_A = \frac{\rho}{2} \int (3 \cos^2 \theta - 1) g(\tau) d\tau \quad (45)$$

— a parameter of angular correlations between molecules the symmetry axes of which subtend the angle θ . The angular correlation parameter of eq. (45) can be calculated theoretically for the different models of intermolecular interaction, or can be determined from experimental data [12, 13, 23, 33], and is found to be positive for some liquids but negative for others [23, 33]. This shows how angular correlations act to increase or lower anisotropic scattering.

c) Rôle of molecular hyperpolarizabilities. Light scattering is moreover affected by the molecular hyperpolarizability due to the molecular fields existing in dense media [2, 3, 21]. Resorting to Onsager's model, the processes of molecular hyperpolarizability can be satisfactorily separated in a first approximation from the other statistical-correlational processes, and one obtains [21, 29]:

$$F_{\text{is}} = \rho a^2 k T \beta_T (1 + A_{\text{is}} + H_{\text{is}} + \dots), \quad (46)$$

$$F_{\text{ains}} = \rho a^2 \kappa^2 (1 + J_A) (1 + A_{\text{anis}} + H_{\text{anis}} + \dots), \quad (47)$$

where A_{is} and A_{anis} define contributions from fluctuations in anisotropy of the molecular field, whereas H_{is} and H_{anis} are contributions from molecular hyperpolarizability. The latter contributions have been calculated for dipolar [2, 3, 29] as well as quadrupolar [21] molecules. Numerical evaluations performed in an earlier paper [29] led to participations of molecular field anisotropy ranging from 5 to 90 per cent in the case of CS_2 , and to hyperpolarizability processes amounting to as much as 50 per cent (e. g. in toluene). The hyperpolarizability effects can, too, be calculated by a molecular-statistical procedure [32]. These effects raise the values of F_{is} and F_{ains} if the optical anisotropy of the molecules is positive but lower the values of F_{is} and F_{ains} if it is negative. The above-mentioned contributions, when taken into account jointly, lead to better agreement between the theory and experiment [30 - 34]. However, this involves calculations that are rather tedious. Nevertheless, we think that it may fully be worth the trouble to de-

velop the statistical-molecular theories still further in regard of the high value of the information provided by them concerning the spatial structure of nearest neighbourhoods in dense media [29, 33].

In Shakhparonov's treatment of light scattering [5, 35], the right hand terms of eqs. (39) and (40) contain local field factors of the form $\left(\frac{n^2+2}{3}\right)^4$, whereas according to Coumou [27] isotropic scattering is defined by a factor of the form $\left(\frac{n^2+2}{3}\right)^4$, but anisotropic scattering by one of the form $\left(\frac{n^2+2}{3}\right)^2$ as in our treatment (40). The difference between their approach and ours resides, firstly, in the circumstance that our factor $\left(\frac{n^2+2}{3}\right)^2$ does not result (as is the case with them) from the assumption of a Lorentz local field but rather from the well-known relationship between the mean macroscopic field within the medium and the field outside the medium yielding [21]:

$$I = \left(\frac{3}{n^2+2}\right)^2 I_0. \quad (48)$$

Secondly, in our previous papers [8, 21, 29, 32], account was taken — in addition to fluctuations of the number density and of polarizability anisotropy — of other processes, such as translational fluctuations, fluctuations of the anisotropy of molecular fields, fluctuations of angular correlations, and hyperpolarizability processes. Now, obviously, the contribution of each of these processes to isotropic light scattering is different from its contribution to anisotropic scattering. All in all, though eqs. (39) and (40) contain the same factor $\left(\frac{n^2+2}{3}\right)^2$ in both isotropic and anisotropic scattering, the other statistical-molecular processes will contribute to S_{is} and S_{anis} differently by way of the factors F_{is} and F_{anis} in accordance with several simplest expressions (41) - (47) adduced here. In the light of our considerations, the different local field corrections to the two scatterings S_{is} and S_{anis} as obtained by Coumou [27] appear fully justified.

In concluding this discussion we express the opinion that, in many cases, the theory of light scattering in the Lorentz or Onsager local field approach can be applied with a satisfactory degree of accuracy, though generally better agreement is achieved with the Onsager-Scholte model. In order to obtain good agreement with experiment for a given liquid, one has to resort to statistical-molecular theory taking into account the various additional contributions lying beyond the scope of the formal approach of a mean local field model. For liquids, the statistical-molecular theory at its present stage sets some difficulties in the way of performing the calculations to the final results numerically; for imperfect gases, however, this has been done by the method of virial coefficients [36]. It is to be regretted that as yet measurements of light scattering by gases in function of pressure are not available.

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