

DEPOLARIZATION OF LIGHT SCATTERING BY ATOMIC AND MOLECULAR SOLUTIONS WITH STRONGLY ANISOTROPIC TRANSLATIONAL-ORIENTATIONAL FLUCTUATIONS

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Translational-orientational fluctuations are shown to raise or lower the depolarization of light scattered by solutions according to the structure of the near-order region of anisotropic molecules. In solutions of atoms, translational fluctuations induce anisotropic scattering already described in the bi-molecular radial correlations approximation; in accordance with the latest experiments, this scattering undergoes an increase or decrease depending on ternary radial correlations. A general expression for the effective optical anisotropy of the near-order region in solutions is applied to the dilute case permitting, in a novel manner, determination of both the *value and sign* of the anisotropy for isolated solute molecules.

1. Introduction

Depolarization of light scattered by an interaction-less gas is known to be due solely to the intrinsic anisotropy of the isolated molecule [1]. In real gases, liquids [2] and real solutions [3], the depolarizing agent generally resides in an effective optical anisotropy of the region of near ordering, where various statistical fluctuations take place. On neglecting internal interference as well as frequency and spatial dispersion, this effective anisotropy can be defined, for multi-component systems, as [3, 4]:

$$\Gamma_m^2 = \frac{3}{2N} \sum_{ij} \langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} D_{\alpha\beta}^{(pi)} D_{\alpha\beta}^{(qj)} \rangle, \quad (1)$$

where we have introduced the deviation tensor of optical molecular polarizability:

$$D_{\alpha\beta}^{(pi)} = \frac{1}{2} \left(\frac{\partial m_{\alpha}^{(pi)}}{\partial E_{\beta}} + \frac{\partial m_{\beta}^{(pi)}}{\partial E_{\alpha}} \right) - \frac{1}{3} \delta_{\alpha\beta} \left(\frac{\partial m_{\gamma}^{(pi)}}{\partial E_{\gamma}} \right). \quad (2)$$

Above, $m^{(pi)}$ is the electric dipole moment induced in molecule p of species i (immersed in a medium with a total number of molecules $N = \sum_i N_i$) by the electric field E of the incident light wave; $\delta_{\alpha\beta}$ is Kronecker's unit tensor, the summation is over recurring indices α and β , and $\langle \rangle$ stands for statistical averaging in the presence of molecular correlations.

The deviation tensor (2) is defined to vanish for isolated atoms and isotropically polarizable molecules i.e. when a linear vector function $m^{(pi)} = a_{pi} E$ holds, where a_{pi} denotes the scalar optical polarizability of molecule p of

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species i . The deviation tensor (2) and consequently the effective anisotropy (1) differ from zero only if:

- (i) the molecules are intrinsically anisotropic in the ground state,
- (ii) if isotropically polarizable atoms or molecules interact subject to translational Kirkwood - Yvon fluctuations, or if the molecular interactions perturb their intrinsic polarizabilities [2] in accordance with the Jansen - Mazur [5] model, and
- (iii) if the atoms or molecules are subject to non-linear polarizability in the time- and spatially fluctuating electric field of neighbouring molecules [3, 6].

2. Angular correlations

For optically inactive molecules with intrinsic anisotropy given by the linear polarizability tensor $a_{\alpha\beta}^{(pi)}$, the deviation tensor (1) becomes simply, in the absence of molecular fields,

$$D_{\alpha\beta}^{(pi)}(0) = a_{\alpha\beta}^{(pi)} - a_{pi} \delta_{\alpha\beta}, \quad (3)$$

whence the effective anisotropy (1) can be written in the form of an expansion:

$$\Gamma_{mA}^2 = \sum_i f_i \gamma_i^2 + \sum_{ij} f_i f_j \gamma_i \gamma_j J_{ij}^A, \quad (4)$$

where

$$\gamma_i^2 = \frac{1}{2} \{ (a_{11}^{(i)} - a_{22}^{(i)})^2 + (a_{22}^{(i)} - a_{33}^{(i)})^2 + (a_{33}^{(i)} - a_{11}^{(i)})^2 \} \quad (5)$$

is the optical anisotropy of the isolated molecule of component i at molar fraction f_i .

The parameter J_{ij}^A describes angular correlations between molecules of species i and j . For simplicity, we adduce it for the case of axially-symmetric molecules (when $a_{11}^{(i)} = a_{22}^{(i)} \neq a_{33}^{(i)}$ and $\gamma_i = a_{33}^{(i)} - a_{11}^{(i)}$) [3]:

$$J_{ij}^A = \frac{\rho}{2V} \iint (3 \cos^2 \theta_{ij}^{(pq)} - 1) g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (6)$$

$g_{ij}^{(2)}(\tau_p, \tau_q)$ denoting the binary correlation function for molecules p and q of species i and j at configurations τ_p and τ_q with their symmetry axes subtending the angle $\theta_{ij}^{(pq)}$; $\rho = N/V$ is the number density of molecules in the medium of volume V .

The expansion (4) applied to a two-component solution yields [3]:

$$\Gamma_{mA}^2 = f_1 \gamma_1^2 + f_2 \gamma_2^2 + f_1^2 \gamma_1^2 J_{11}^A + 2f_1 f_2 \gamma_1 \gamma_2 J_{12}^A + f_2^2 \gamma_2^2 J_{22}^A, \quad (7)$$

whence the anisotropy of the solution is found to be an additive property only as long as angular correlations are absent. If present between like molecules (J_{11}^A and J_{22}^A) or between ones of different species (J_{12}^A), angular correlations cause a deviation from additivity in Γ_m^2 proportional to the square of the molar fractions.

Numerically, the angular-correlation parameters J_{ij}^A can be determined experimentally in pure liquids [7-9] and solutions [10-13] and calculated theoretically for weak correlations [2, 3] and for the very strong angular correlations existing in benzene and nitrobenzene [4]. In the two limiting cases [14] of molecules correlated

- (i) into parallel pairs (paratropism, $J_{ij}^A = z$) and
- (ii) into pairs of mutually perpendicular partners (diatropism, $J_{ij}^A = -z/2$), one can gain information regarding the number z of nearest neighbours.

3. Translational-orientational fluctuations

The tensor expressed in the form of eq. (3) led to our obtaining a non-zero effective anisotropy (1), reducible to an additive anisotropy of isolated molecules (5) and a non-additive anisotropy (6) of angularly pairwise-interacting molecules. In this approximation, multi-molecular (triple and higher) correlations become apparent only indirectly by way of the two-molecule correlation function $g_{ij}^{(2)}$. We obtain a direct expression of the influence of multimolecular correlations on Γ^2 by writing the deviation tensor (2) in a form taking into account translational and orientational fluctuations

$$D_{\alpha\beta}^{(pi)} = D_{\alpha\beta}^{(pi)}(0) - \sum_k \sum_{s=1}^{N_k} (a_{\alpha\gamma}^{(pi)} a_{\delta\beta}^{(sk)} - \frac{1}{3} \delta_{\alpha\beta} a_{\epsilon\gamma}^{(pi)} a_{\delta\epsilon}^{(sk)}) T_{\gamma\delta}^{(ps)} + \dots, \quad (8)$$

where $T_{\gamma\delta}^{(ps)} = -r_{ps}^{-5} (3r_{ps\gamma} r_{ps\delta} - r_{ps}^2 \delta_{\gamma\delta})$ is the tensor of interaction between dipoles induced in molecules p and s at distance r_{ps} .

Insertion of eq. (8) into eq. (1) yields, in addition to the anisotropy (4), yet another anisotropy due to translational and orientational fluctuations:

$$\Gamma_{mF}^2 = \sum_{ij} f_i f_j (\Gamma_{RAij}^2 + \Gamma_{Rij}^2) + \sum_{ijk} f_i f_j f_k (\Gamma_{RAijk}^2 + \Gamma_{Rijk}^2) + \dots \quad (9)$$

For axially symmetric molecules and pairwise correlations (in a first approximation with respect to the interaction tensor \mathbf{T}) we get:

$$\Gamma_{RAij}^2 = \frac{2}{3} [\gamma_i (3a_j - \gamma_j) (3a_i + \gamma_i - \gamma_j) + \gamma_j (3a_i - \gamma_i) (3a_j + \gamma_j - \gamma_i)] J_{ij}^{RA} + \frac{4}{3} \gamma_i \gamma_j (3a_i + 3a_j + \gamma_i + \gamma_j) K_{ij}^{RA} \quad (10)$$

involving the new cross parameters of pairwise radial-angular correlations:

$$J_{ij}^{RA} = \frac{\rho}{4V} \iint (3 \cos^2 \theta_{pi} + 3 \cos^2 \theta_{qj} - 2) r_{pq}^{-3} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (11)$$

$$K_{ij}^{RA} = \frac{\rho}{2V} \iint (3 \cos \theta_{pi} \cos \theta_{qj} - \cos \theta_{ij}^{(pq)}) \cos \theta_{ij}^{(pq)} r_{pq}^{-3} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q; \quad (12)$$

θ_{pi} and θ_{qj} denoting the angles between the symmetry axes of molecules p and q (of species i and j) and the vector r_{pq} , respectively.

On considering the form of the correlation factors (11) and (12) we note that the contribution (10) is non-zero only if correlations of the orientational kind are present and that this contribution is positive or negative according to whether the molecules tend to combine into roughly paratropic or diatropic pairs [4].

The anisotropy Γ_{RAijk}^2 is given explicitly in the appendix.

4. Translational fluctuations

The second approximation will be considered here only after neglecting intrinsic anisotropy i.e. when the deviation (3) vanishes; in eq. (8) the sole contribution to the effective anisotropy (1) is then due to purely translational fluctuations:

$$\Gamma_{Rij}^2 = 9a_i^2 a_j^2 J_{ij}^R, \quad (13)$$

involving the bi-molecular radial correlation factor

$$J_{ij}^R = \frac{2\rho}{V} \iint r_{pq}^{-6} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (14)$$

which is subject to calculation using Kirkwood's rigid-sphere model [6] and the general Lennard-Jones potential [15].

The next contribution, that with three-molecule correlations, is (neglecting anisotropy) of the form:

$$\Gamma_{Rijk}^2 = 6(a_i a_j a_k^2 + a_i a_j^2 a_k + a_i^2 a_j a_k) J_{ijk}^R, \quad (15)$$

with the ternary radial correlation parameter of the form:

$$J_{ijk}^R = \frac{\rho^2}{V} \iiint [3(\mathbf{r}_{pq} \cdot \mathbf{r}_{qs})^2 - r_{pq}^2 r_{qs}^2] r_{pq}^{-5} r_{qs}^{-5} g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_s) d\tau_p d\tau_q d\tau_s; \quad (16)$$

$g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_s)$ denoting the ternary correlation function for three molecules p, q and s of species i, j and k at configurations τ_p, τ_q and τ_s .

The ternary correlation parameter (16) deserves particular attention since it can be positive or negative, whereas the parameter (14) is always positive. When the vectors \mathbf{r}_{pq} and \mathbf{r}_{qs} are approximately parallel (asymmetric structure of nearest ordering), J_{ijk}^R is positive, raising the effective anisotropy. If \mathbf{r}_{pq} is almost perpendicular on \mathbf{r}_{qs} or subtending the angle $\pi/3$ (symmetric structure of nearest ordering), J_{ijk}^R is negative thus lowering the effective anisotropy. The latter case is close to reality (especially in atomic substances) since with increasing density the structure of near order tends to become more and more symmetrical, and effective anisotropy has to decrease. This conclusion is confirmed by the latest measurements of the spectrum of the depolarized light scattered by liquefied [16–18] and highly compressed [19] rare gases.

5. Dilute solutions

By combining eqs. (4) and (9) we obtain a general expression for the effective anisotropy of multi-component systems:

$$\Gamma_m^2 = \sum_i f_i \gamma_i^2 + \sum_{ij} f_i f_j \Gamma_{ij}^2 + \sum_{ijk} f_i f_j f_k \Gamma_{ijk}^2 + \dots, \quad (17)$$

where the first term expresses the additivity of anisotropies of the isolated molecules of the components in mixture. The higher terms define deviations from additivity in the effective anisotropy arising from bi-molecular, tri-molecular and multi-molecular correlations of the radial and angular kinds.

On applying expansion (17) to dilute solutions as done by us in the Kerr-effect theory of multi-component systems [20], one obtains for infinitely high dilution:

$$\left(\frac{\partial \Gamma_m^2}{\partial f} \right)_{f \rightarrow 0} = \gamma_2^2 - \gamma_1^2 + \left\{ \frac{\partial}{\partial f} (\Gamma_{11}^2 + \Gamma_{111}^2 + \dots) + 2(\Gamma_{12}^2 - \Gamma_{11}^2) + 3(\Gamma_{112}^2 - \Gamma_{111}^2) + \dots \right\}_{f \rightarrow 0}, \quad (18)$$

where $f = f_2$ is the molar fraction of solute.

If the solvent (index 1) consists of intrinsically non-anisotropic molecules ($\gamma_1 = 0$), eq. (18) yields with regard to the previous results (6), (10), (13) and (15),

$$\left(\frac{\partial \Gamma_m^2}{\partial f}\right)_{f \rightarrow 0} = \gamma_2^2 + \left\{ 9a_1^4 \frac{\partial}{\partial f} (J_{11}^R + 2J_{111}^R) + 18a_1^2 (a_2^2 J_{12}^R - a_1^2 J_{11}^R) + 2a_1 \gamma_2 [2(3a_2 + \gamma_2) J_{12}^{RA} + 3a_1 J_{112}^{RA}] \right. \\ \left. + 18a_1^2 [a_2(2a_1 + a_2) J_{112}^R - 3a_1^2 J_{111}^R] \right\}_{f \rightarrow 0} \quad (19)$$

Since $J_{12}^R/J_{11}^R = J_{112}^R/J_{111}^R \approx \rho_2/\rho_1$, when considering cases in which $a_1 \approx a_2$ the effects of pure redistribution cancel out mutually and we obtain by eq. (19), for the optical anisotropy of a solute molecule at infinite dilution,

$$\gamma_{2\infty}^2 = \left(\frac{\partial \Gamma_m^2}{\partial f}\right)_{f \rightarrow 0} - 2a_1 \gamma_2 [2(3a_2 + \gamma_2) J_{12}^{RA} + 3a_1 J_{112}^{RA}] \quad (20)$$

Consequently, in determinations of values of the optical anisotropy of axially symmetric molecules from measurements of light scattering by infinitely dilute solutions, an important role belongs to solvent-solute molecular translational-orientational cross fluctuations whose positive or negative contribution to $\gamma_{2\infty}^2$ is considerable. Moreover, obviously, eq. (20) can provide a new method for determining not only the value but also the sign of the optical anisotropy of axially symmetric molecules, since J_{12}^R can be positive or negative [4].

In fact, as confirmed by the latest experiments, anisotropic molecules while continually regrouping themselves in the fluctuational region of near ordering, at the same time reorient themselves with respect to each other causing an increase or decrease in the depolarization of scattered light. In atomic and molecular solutions lacking intrinsic optical anisotropy, the effective anisotropy induced by fluctuations in bi-molecular regrouping can undergo a lowering or an enhancement under the influence of multi-molecular regroupings in the near order region.

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Appendix

Since the polarizability tensor for molecules with axial symmetry (unit vector S) is

$$a_{\alpha\beta}^{(pi)} = (a_{pi} - \frac{1}{3}\gamma_{pi}) \delta_{\alpha\beta} + \gamma_{pi} S_{\alpha}^{(pi)} S_{\beta}^{(pi)}, \quad (A.1)$$

we get with regard to eqs. (1) and (8) (in an approximation linear in the interaction tensor T):

$$\Gamma_m^2 = \frac{1}{2N} \sum_{ij} \gamma_i \gamma_j \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} (3 \cos^2 \theta_{ij}^{(pq)} - 1) \right\rangle \\ - \frac{1}{6N} \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \{ (3a_i - \gamma_i) \gamma_j [(3a_k - \gamma_k) S_{\alpha}^{(qi)} S_{\beta}^{(qi)} + \gamma_k (3S_{\alpha}^{(qi)} \cos \theta_{jk}^{(qr)} - S_{\alpha}^{(rk)}) S_{\beta}^{(rk)}] T_{\alpha\beta}^{(pr)} \right. \\ \left. + (3a_j - \gamma_j) \gamma_i [(3a_k - \gamma_k) S_{\alpha}^{(pi)} S_{\beta}^{(pi)} + \gamma_k (3S_{\alpha}^{(pi)} \cos \theta_{ik}^{(pr)} - S_{\alpha}^{(rk)}) S_{\beta}^{(rk)}] T_{\alpha\beta}^{(qr)} + \right.$$

$$\begin{aligned}
& + \gamma_i \gamma_j (3a_k - \gamma_k) [(3S_\alpha^{(qj)} \cos \theta_{ij}^{(pq)} - S_\alpha^{(pi)}) T_{\alpha\beta}^{(pr)} S_\beta^{(pi)} + (3S_\alpha^{(pi)} \cos \theta_{ij}^{(pq)} - S_\alpha^{(qj)}) T_{\alpha\beta}^{(qr)} S_\beta^{(qj)}] \\
& + \gamma_i \gamma_j \gamma_k [(3 \cos \theta_{ij}^{(pq)} \cos \theta_{jk}^{(qr)} - \cos \theta_{ik}^{(pr)}) S_\alpha^{(pi)} T_{\alpha\beta}^{(pr)} S_\beta^{(rk)} \\
& + (3 \cos \theta_{ij}^{(pq)} \cos \theta_{ik}^{(pr)} - \cos \theta_{jk}^{(qr)}) S_\alpha^{(qj)} T_{\alpha\beta}^{(qr)} S_\beta^{(rk)}] \} \} .
\end{aligned} \tag{A.2}$$

In bi-molecular correlation approximation we obtain from eq. (A.2) expressions (4), (6) and (9)–(12). In the case of a solution where the molecules of component 1 have zero intrinsic anisotropy and those of component 2 are axially symmetric eq. (A.2) leads to the contribution

$$\Gamma_{RA\ 112}^2 = 2a_1^2 \gamma_2 J_{112}^{RA} \tag{A.3}$$

occurring in eqs. (18)–(20) with parameter

$$J_{112}^{RA} = \frac{\rho^2}{2V} \iiint (3 \cos^2 \theta_{p2} - 1) r_{ps}^{-3} g_{112}^{(3)}(\tau_p, \tau_q, \tau_s) d\tau_p d\tau_q d\tau_s \tag{A.4}$$

describing ternary correlations between two isotropic molecules and one anisotropic one.

Thus, $\Gamma_{RA\ 12}^2$ and $\Gamma_{RA\ 112}^2$ define the influence of a solvent on the optical anisotropy of molecules in solution.

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