SYMMETRIC AND ANTISYMMETRIC DYNAMICAL RAYLEIGH LIGHT SCATTERING IN MOLECULAR LIQUIDS*,**

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The problem of symmetric and antisymmetric dynamical Rayleigh scattering of light by interacting systems of anisotropic molecules is discussed, the symmetricity and antisymmetricity bearing on the tensor of light intensity as well as on that of the optical (linear and dipolar) polarizability of the molecule. The resolution of the molecular polarizability tensor into three irreducible parts of various orders, namely an isotropic part of the zeroth order, an anisotropic part of the second order, and an antisymmetric part of the first order leads to the emergence, in the scattered light spectrum, of a number of spectral (Lorentz type) lines, related with three orders of relaxation time: the zeroth (τ_T, translational relaxation time), and the second and first (respectively τ_{2M} and τ_{1M}, rotational relaxation times), the number of these lines depending on the molecular symmetry in the case of each individual molecular system.

1. Introduction

Light scattering is one of the many optical effects providing the basis for methods whereby the parameters characterizing atoms and molecules statically and dynamically, as well as those characterizing their mutual interactions, can be studied profitably [1–3]. The problem of integral light scattering by molecular liquids has been discussed in detail by Kielich [4, 5]. The spectral theory of light scattering by non-spherical molecules was developed by Steele and Pecora [6] applying results of Steele [7] concerning the general statistical theory of such systems. Pecora [8] then extended the theory by having recourse to model approximations of translational and rotational diffusion. Theoretical studies were intensely stimulated by the discovery of a fine structure in the depolarized spectrum [9, 10] due to certain factors of a hydrodynamical nature [11, 12].

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In his theory of Rayleigh scattering and the Raman effect, Placzek [13] first defined the three mechanisms of light scattering: isotropic, anisotropic, and antisymmetric, related with three irreducible parts of the (linear and dipolar) optical polarizability tensor of the molecule.

Our present results are an extension, to dynamical scattering, of those of Kielich [2, 14] derived from his treatment of the three scattering mechanisms in a Cartesian basis. Our results are expressed in a Cartesian as well as a circular-cylindrical basis permitting their direct application to the scattering of linearly polarized and circularly polarized light. Essentially relevant here is the relationship established between the antisymmetric part of the polarizability tensor and rotational relaxation times of the first order τ_{1M}.

2. The symmetric and antisymmetric part of the scattered light intensity tensor

We assume the electric field of incident light (monochromatic wave) existing at the centre of a molecule p (scattering volume V), distant by $\vec{r}_p(t_0)$ at the moment of time t_0 from an arbitrarily chosen origin of coordinates, in the form:

$$\vec{E}^{(p)}(\vec{r}_p, t_0) = \vec{E}_0^{(p)} e^{-i[\omega_0 t_0 - \vec{k}_0 \cdot \vec{r}_p(t_0)]}, \tag{1}$$

with $\vec{E}_0^{(p)}$ the amplitude, ω_0 the vibration frequency, and $\vec{k}_0$ the wave vector.

In the electric-dipole approximation, we define as follows the time-dependent tensor of scattered light intensity [2]:

$$I_{ij}(t) = \left(\frac{\omega_0}{c}\right)^4 \langle M_i(\vec{r}, t_0) M_j^*(\vec{r}, t_0 + t)\rangle_{t_0}, \tag{2}$$

where we have introduced the notation:

$$M_i(\vec{r}, t_0) = \sum_{p=1}^{N} d_i^{(p)}(t_0) e^{i[\Delta\vec{k} \cdot \vec{r}_p(t_0)]}, \tag{3}$$

$d_i^{(p)}(t_0)$ being the i-component of the dipole moment, induced in molecule p, whereas $\Delta\vec{k}$ is the difference in wave vectors of the incident and scattered light; summation extends over all N molecules of the scattering volume. In Eq. (2), the brackets $\langle \ldots \rangle_{t_0}$ denote averaging over the time t_0 and the statistical ensemble.

The scattered light intensity tensor (2) has the properties of a polar Hermitian tensor of rank 2 i.e. $I_{ij} = I_{ji}^*$. Thus, its symmetric part is real and its antisymmetric part imaginary [15]; they are defined as:

$$I_{ij}^{(\pm)}(t) = \tfrac{1}{2}\{I_{ij}(t) \pm I_{ji}(t)\}, \tag{4}$$

the superscripts $(\pm)$ denoting, respectively, the symmetric part $(+)$ and antisymmetric part $(-)$. Accordingly, we write the tensor of scattered light intensity in the form:

$$I_{ij}(t) = I_{ij}^{(+)}(t) + I_{ij}^{(-)}(t). \tag{5}$$

In the case of optically anisotropic molecules, the electric dipole moment is given, in the linear approximation (in the absence of molecular redistribution [4, 5]), as:

$$d_i^{(p)}(t_0) = \alpha_{i\underline{k}}^{\omega_0}[\Omega_p(t_0)]E_k(t_0), \tag{6}$$

where $\alpha_{i\underline{k}}^{\omega_0}[\Omega_p(t_0)]$ is the (dipolar and linear) optical polarizability tensor of molecule p, $\Omega_p(t_0)$ stands for its orientational variables at the moment of time t_0 referred to the laboratory, and the superscript ω_0 expresses the fact that the polarizability is a function of the frequency ω_0 of incident light. The lower index k in (6) is underlined to express its contravariancy with respect to the non-underlined indices.

On insertion of (3) and (6) into Eq. (2) and applying the definition (4), we write:

$$I_{ij}^{(\pm)}(t) = {}_{\mathrm{s}}I_{ij}^{(\pm)}(t) + {}_{\mathrm{d}}I_{ij}^{(\pm)}(t), \tag{7}$$

where

$${}_{\mathrm{s}}I_{ij}^{(\pm)}(t) = \tfrac{1}{4}\left(\frac{\omega_0}{c}\right)^4 N\langle\{\alpha_{i\underline{k}}^{\omega_0}[\Omega_1(0)]\alpha_{j\underline{l}}^{\omega_0 *}[\Omega_1(t)]E_k(0)E_l^*(t)$$

$$\pm\alpha_{j\underline{l}}^{\omega_0}[\Omega_1(0)]\alpha_{i\underline{k}}^{\omega_0 *}[\Omega_1(t)]E_l(0)E_k^*(t)\}\exp\left[i\Delta\vec{k}\cdot(\vec{r}_1(t)-\vec{r}_1(0))\right]\rangle \tag{8}$$

is the "self"-type part, corresponding to incoherent scattering, whereas

$${}_{\mathrm{d}}I_{ij}^{(\pm)}(t) = \tfrac{1}{4}\left(\frac{\omega_0}{c}\right)^4 N(N-1)\langle\{\alpha_{i\underline{k}}^{\omega_0}[\Omega_1(0)]\alpha_{j\underline{l}}^{\omega_0 *}[\Omega_2(t)]E_k(0)E_l^*(t)$$

$$\pm\alpha_{j\underline{l}}^{\omega_0}[\Omega_1(0)]\alpha_{i\underline{k}}^{\omega_0 *}[\Omega_2(t)]E_l(0)E_k^*(t)\}\exp\left[i\Delta\vec{k}\cdot(\vec{r}_2(t)-\vec{r}_1(0))\right]\rangle \tag{9}$$

is the "distinct" part, corresponding to coherent scattering on statistically time- and space-correlated molecules. Since (8) and (9) are already time-averaged over t_0, the brackets $\langle\ldots\rangle$ now denote averaging over the statistical ensemble only, and we have adopted $t_0 = 0$ within the statistical average.

3. Time-dependent distribution of symmetric and antisymmetric light scattering by a system of anisotropic molecules

In order to calculate the statistical averages occurring in Eqs (8) and (9), we have to introduce van Hove's [16] space-time functions of the "self" type, $G_{\mathrm{s}}\{\vec{R}_1(0), \vec{R}_1(t), t\}$ and of the "distinct" type, $G_{\mathrm{d}}\{\vec{R}_1(0), \vec{R}_2(t), t\}$, where $\vec{R}$ stands for the configuration of the molecule (the sets of its positional variables $\vec{r}$ and orientational variables Ω with respect to the laboratory basis). Van Hove's "self" function defines the probability of finding molecule 1 at the moment of time t in the configuration $\vec{R}_1(t)$ if its configuration was $\vec{R}_1(0)$ at the moment of time $t = 0$. The "distinct" function defines the probability of finding molecule 2 at the time t in the configuration $\vec{R}_2(t)$ if, at $t = 0$, molecule 1 was in the configuration $\vec{R}_1(0)$. We now proceed to introduce certain model approximations to simplify further calculations. We make the following assumptions:

(a) The translational and rotational motions of the molecules are mutually independent. This permits the separation of variables: $G_{\mathrm{s}}\{\vec{R}_1(0), \vec{R}_1(t), t\} = G_{\mathrm{s}}\{\Omega_1(0), \Omega_1(t), t\}$,

$\mathcal{G}_s\{\vec{r}_1(0), \vec{r}_1(t), t\}$, and the function $G_s\{\Omega_1(0), \Omega_1(t), t\}$ can be expanded in a series of Wigner matrices [6] with expansion coefficients of a form resulting from the assumption of diffusion of the symmetric top type

$$G_s\{\Omega_1(0), \Omega_1(t), t\} = \sum_{J,M,K} \frac{2J+1}{8\pi^2} e^{-\frac{t}{\tau_{JM}}} D^J_{KM}[\Omega_1(0)] D^J_{KM}[\Omega_1(t)], \tag{10}$$

where the M-th rotation relaxation time of the J-th order is given by: $\tau_{JM}^{-1} = J(J+1)D_1^R + M^2(D_3^R - D_1^R)$, with $D_1^R = D_2^R \neq D_3^R$ — the diagonal elements of the rotational diffusion tensor.

(b) The position of the molecule changes by way of translational diffusion, so that the function $\mathcal{G}_s\{\vec{r}_1(0), \vec{r}_1(t), t\}$ fulfils the equation of translational diffusion in Smoluchowski's form:

$$\mathcal{G}_s(r, t) = \frac{1}{(4\pi D^T t)^{3/2}} \exp\left\{-\frac{r^2}{4D^T t}\right\}, \tag{11}$$

where $r = |\vec{r}_1(t) - \vec{r}_1(0)|$ and D^T is the translational diffusion coefficient.

(c) The molecules interact with one another at the moment of time $t = 0$ only, whereas at $t > 0$ they are statistically independent and obey the laws of translational and rotational diffusion. This approximation is generally referred to as that of the Vineyard convolution [17] since, here, the van Hove "distinct" function is defined by the convolution:

$$G_d\{\vec{R}_1(0), \vec{R}_2(t), t\} = \int g^{(2)}\{\vec{R}_1(0), \vec{R}_2(0)\} G_s\{\vec{R}_2(0), \vec{R}_2(t), t\} d\vec{R}_2(0), \tag{12}$$

where $g^{(2)}\{\vec{R}_1(0), \vec{R}_2(0)\}$ is the pairwise configuration function at equilibrium.

The function $G_d\{\vec{R}_1(0), \vec{R}_2(t), t\}$ can be expanded in a series in Wigner matrices, as follows [18]:

$$G_d\{\vec{R}_1(0), \vec{R}_2(t), t\} = \sum_{\substack{J_1,K_1,M_1 \\ J_2,K_2,M_2}} \sqrt{(2J_1+1)(2J_2+1)}$$

$$\times \tilde{g}^{J_1J_2}_{K_1M_1K_2M_2}\{\vec{r}_2(t) - \vec{r}_1(0), t\} D^{J_1}_{K_1M_1}[\Omega_1^{21}(0)] D^{J_2}_{K_1M_2}[\Omega_2^{21}(t)], \tag{13}$$

where Ω_1^{21}, Ω_2^{21} define the orientation of molecules 1 and 2 in a coordinate system the z-axis of which coincides with the vector $\vec{r}_2(t) - \vec{r}_1(0)$. Similarly, we expand the function $g^{(2)}\{\vec{R}_1(0), \vec{R}_2(0)\}$:

$$g^{(2)}\{\vec{R}_1(0), \vec{R}_2(0)\} = \sum_{\substack{J_1,K_1,M_1 \\ J_2,K_2,M_2}} \sqrt{(2J_1+1)(2J_2+1)}$$

$$\times g^{J_1J_2}_{K_1M_1K_2M_2}\{\vec{r}_2(0) - \vec{r}_1(0)\} D^{J_1}_{K_1M_1}[\Omega_1^{21}(0)] D^{J_2}_{K_2M_2}[\Omega_2^{21}(0)]. \tag{14}$$

The expansion coefficients in (13) and (14) are mutually related by way of the Vineyard approximation (12), as follows:

$$\tilde{g}^{J_1J_2}_{K_1M_1K_2M_2}\{\vec{r}_2(t) - \vec{r}_1(0), t\} = \exp\{-t/\tau_{J_2M_2}\}$$

$$\times \int g^{J_1J_2}_{K_1M_1K_2M_2}\{\vec{r}_2(0) - \vec{r}_1(0)\} \mathcal{G}_s\{\vec{r}_2(0), \vec{r}_2(t), t\} d\vec{r}_2(0). \tag{15}$$

When calculating the averages occurring in (8) and (9) it is convenient to go over from Cartesian polarizability tensor components to spherical components (irreducible form) with simultaneous rotation to the molecular coordinate system. The transition is defined by the following transformation:

$$\alpha_{\underline{ik}}^{\omega_0}[\Omega_1(0)] = \sum_{J_1,K_1,M_1} c_{\underline{ik}}^{(J_1)K_1} D_{K_1M_1}^{J_1}[\Omega_1(0)]\tilde{\alpha}_{M_1}^{(J_1)}, \tag{16}$$

the $c_{\underline{ik}}^{(J_1)K_1}$ being transformation coefficients leading from a Cartesian tensor of rank 2 to a spherical tensor, irreducible with respect to the three-dimensional group of rotations.

By having recourse to the assumptions (a), (b), and the transformation (16), as well as the orthogonal properties of the Wigner matrices [18], we obtain Eq. (8) in the following form:

$$\begin{aligned} {}_sI_{ij}^{(\pm)}(t) = \tfrac{1}{4}\left(\frac{\omega_0}{c}\right)^4 Nh(t) \sum_{J,M,K} \frac{1}{2J+1} \exp\{-t/\tau_{JM}\} \\ \times |\tilde{\alpha}_M^{(J)}|^2 \{c_{\underline{ik}}^{(J)K} c_{\underline{jl}}^{(J)K*} E_k(0)E_l^*(t) \pm c_{\underline{jl}}^{(J)K} c_{\underline{ik}}^{(J)K*} E_l(0)E_k^*(t)\}, \end{aligned} \tag{17}$$

where $h(t) \equiv \exp\{-\Delta k^2 D^T t\} = \exp\{-t/\tau_T\}$, $\tau_T^{-1} = \Delta k^2 D^T$ being the translational relaxation time. When calculating (9) we have to apply, in addition to the assumption (c) and the expressions (13), (15) and (16), the following transformation [18]:

$$D_{KM}^J[\Omega_1^{21}(0)] = \sum_R D_{RM}^J[\Omega_1(0)] D_{RK}^{J*}[\Omega_{21}], \tag{18}$$

leading from the coordinate system attached to the pair of molecules (index 21) to laboratory coordinates, as well as the following expansion [18]:

$$\exp(i\Delta\vec{k}\cdot\vec{r}) = \sum_J i^J(2J+1) j_J(\Delta kr) D_{00}^J[\Omega_{21}], \tag{19}$$

where the $j_J(\Delta kr)$ are spherical Bessel functions of order J.

We now have from (9):

$$\begin{aligned} {}_dI_{ij}^{(\pm)}(t) = \tfrac{1}{4}\left(\frac{\omega_0}{c}\right)^4 Nh(t) \sum_{\substack{J,J_1,K_1,M_1,N_1 \\ J_2,K_2,M_2,N_2}} \frac{i^J(-1)^{K_2-M_2}(2J+1)}{\sqrt{(2J_1+1)(2J_2+1)}} \exp\{-t/\tau_{J_2M_2}\} \\ \times \tilde{\alpha}_{M_1}^{(J_1)} \tilde{\alpha}_{M_2}^{(J_2)*} \begin{pmatrix} J_1 & J_2 & J \\ K_1 & -K_2 & 0 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J \\ -N_1 & -N_2 & 0 \end{pmatrix} 4\pi\varrho \int g_{N_1-M_2N_2M_2}^{J_1J_2}(r) \\ \times j_J(\Delta kr) r^2 dr \{c_{\underline{ik}}^{(J_1)K_1} c_{\underline{jl}}^{(J_2)K_2*} E_k(0)E_l^*(t) \pm c_{\underline{jl}}^{(J_1)K_1} c_{\underline{ik}}^{(J_2)K_2*} E_l(0)E_k^*(t)\}, \end{aligned} \tag{20}$$

where $\begin{pmatrix} J_1 & J_2 & J \\ K_1 & -K_2 & 0 \end{pmatrix}$ and $\begin{pmatrix} J_1 & J_2 & J \\ -N_1 & -N_2 & 0 \end{pmatrix}$ are Wigner 3-J symbols ($\varrho = N/V$). In the

limit $\Delta kr \ll 1$ (short-range correlations), we have $\exp\{i\Delta\vec{k}\cdot\vec{r}\} \approx j_0(\Delta kr) \approx 1$ and Eq. (20) reduces to:

$$
{}_{\mathrm{d}}I_{ij}^{(\pm)}(t) = \tfrac{1}{4}\left(\frac{\omega_0}{c}\right)^4 Nh(t) \sum_{J,M_1,M_2,K} \frac{1}{2J+1} \exp\{-t/\tau_{JM_2}\}
$$

$$
\times \tilde{\alpha}_{M_1}^{(J)}\tilde{\alpha}_{M_2}^{(J)*}\Gamma_{M_1M_2}^{J}\{c_{\underline{ik}}^{(J)K}c_{\underline{jl}}^{(J)K*}E_k(0)E_l^*(t) \pm c_{\underline{jl}}^{(J)K}c_{\underline{ik}}^{(J)K*}E_l(0)E_k^*(t)\}, \tag{21}
$$

where

$$
\Gamma_{M_1M_2}^{J} = \sum_{N} \frac{(-1)^{N-M_1}}{2J+1} 4\pi\varrho \int_0^\infty g_{N-M_1-NM_2}^{JJ}(r)r^2dr \tag{22}
$$

is Steele's radial-angular correlation parameter [19]. For large intermolecular distances one has $\lim_{r\to\infty} g_{N-M_1-NM_2}^{J\ J}(r) = 0$ for $J \neq 0$; the expression (21) vanishes, and only "self"-type scattering (17) remains. In the case of isotropic molecules $J = N = M_1 = M_2 = 0$; the parameter

$$
\Gamma_{00}^{0} = 4\pi\varrho \int_0^\infty \{g_{00}(r)-1\}r^2dr \tag{23}
$$

is related with the radial correlation function of Zernike and Prins [2], and the following limiting condition: $\lim_{r\to\infty} g_{00}(r) = 1$ holds.

The coefficients (16) transforming a Cartesian tensor of rank 2 to irreducible representation are given after Varshalovich et al. [18]. To us, of interest are the products of those coefficients which intervene in the expressions (17) and (21). In the Cartesian basis $(i, j, k, l = x, y, z)$, we have:

$$
\begin{aligned}
c_{ik}^{(0)0}c_{jl}^{(0)0*} &= \tfrac{1}{3}\delta_{ik}\delta_{jl},\\
\sum_K c_{ik}^{(1)K}c_{jl}^{(1)K*} &= \tfrac{1}{2}(\delta_{ij}\delta_{kl}-\delta_{il}\delta_{kj}),\\
\sum_K c_{ik}^{(2)K}c_{jl}^{(2)K*} &= \tfrac{1}{2}(\delta_{ij}\delta_{kl}+\delta_{il}\delta_{kj})-\tfrac{1}{3}\delta_{ik}\delta_{jl},
\end{aligned} \tag{24}
$$

whereas, in the circular-cylindrical basis $(i, j, k, l = 0, \pm 1)$:

$$
\begin{aligned}
c_{\underline{ik}}^{(0)0}c_{\underline{jl}}^{(0)0*} &= \frac{(-1)^{i+j}}{3}\delta_{i,-k}\delta_{j,-l},\\
\sum_K c_{\underline{ik}}^{(1)K}c_{\underline{jl}}^{(1)K*} &= \tfrac{1}{2}(\delta_{ij}\delta_{kl}-\delta_{il}\delta_{kj}),\\
\sum_K c_{\underline{ik}}^{(2)K}c_{\underline{jl}}^{(2)K*} &= \tfrac{1}{2}(\delta_{ij}\delta_{kl}+\delta_{il}\delta_{kj})-\frac{(-1)^{i+j}}{3}\delta_{i,-k}\delta_{j,-l}.
\end{aligned} \tag{25}
$$

In (24), we have omitted the underlining of indices denoting contravariancy as irrelevant in the Cartesian though of importance in the circular basis.

The incident light intensity: ${}_0I_{ij}(t) = \frac{1}{2}E_{0i}E_{0j}^{*}e^{i\omega_0 t}$, is of the form of a polar Hermitian tensor of rank 2. As done above, Eq. (4), we define its symmetric ${}_0I_{ij}^{(+)}(t)$ and antisymmetric ${}_0I_{ij}^{(-)}(t)$ parts. On applying Eqs (7), (17), (21), (24) and (25), we obtain the symmetric and antisymmetric parts of the intensity tensor of scattered light:

(A) in the Cartesian basis $(i, j = x, y, z)$

$$I_{ij}^{(+)}(t) = [A_{\mathrm{IS}}(t)+A_{\mathrm{ANIS}}(t)-A_{\mathrm{ANTIS}}(t)]\ {}_0I_{ij}^{(+)}(t)+[3A_{\mathrm{ANIS}}(t)+A_{\mathrm{ANTIS}}(t)]\delta_{ij}\ {}_0I(t),$$

$$I_{ij}^{(-)}(t) = [A_{\mathrm{IS}}(t)-5A_{\mathrm{ANIS}}(t)+A_{\mathrm{ANTIS}}(t)]\ {}_0I_{ij}^{(-)}(t), \tag{26}$$

(B) in the circular basis $(i, j = 0, \pm 1)$

$$I_{ij}^{(+)}(t) = (-1)^{i+j}[A_{\mathrm{IS}}(t)-2A_{\mathrm{ANIS}}(t)]\ {}_0I_{ij}^{(+)}(t)$$

$$+[3A_{\mathrm{ANIS}}(t)+A_{\mathrm{ANTIS}}(t)]\delta_{ij}\ {}_0I(t)+[3A_{\mathrm{ANIS}}(t)-A_{\mathrm{ANTIS}}(t)]\ {}_0I_{-i,-j}^{(+)}(t)$$

$$I_{ij}^{(-)}(t) = (-1)^{i+j}[A_{\mathrm{IS}}(t)-2A_{\mathrm{ANIS}}(t)]\ {}_0I_{ij}^{(-)}(t)-[3A_{\mathrm{ANIS}}(t)-A_{\mathrm{ANTIS}}(t)]\ {}_0I_{-i,-j}^{(-)}(t). \tag{27}$$

The molecular scattering factors of Eqs (26) and (27) are of the form:

$$A_{\mathrm{IS}}(t) = \tfrac{1}{3}\left(\frac{\omega_0}{c}\right)^4 Nh(t)\,|\tilde{\alpha}_0^{(0)}|^2\{1+\Gamma_{00}^0\}, \tag{28}$$

$$A_{\mathrm{ANIS}}(t) = \tfrac{1}{30}\left(\frac{\omega_0}{c}\right)^4 Nh(t)\sum_{M,M'}\tilde{\alpha}_M^{(2)}\tilde{\alpha}_M^{(2)*}\exp(-t/\tau_{2M})\{\delta_{MM'}+\Gamma_{M'M}^2\}, \tag{29}$$

$$A_{\mathrm{ANTIS}}(t) = \tfrac{1}{6}\left(\frac{\omega_0}{c}\right)^4 Nh(t)\sum_{M,M'}\tilde{\alpha}_{M'}^{(1)}\tilde{\alpha}_M^{(1)*}\exp(-t/\tau_{1M})\{\delta_{MM'}+\Gamma_{M'M}^1\}, \tag{30}$$

with the radial-angular correlation parameter $\Gamma_{MM'}^J$ given by (22). In the limit $r \to \infty$ i.e. at zero intermolecular interactions the molecular factors (28), (29) and (30) reduce to their "self" form.

The time-dependence of (26) and (27) reduces essentially to that of the molecular scattering factors (28)—(30). On going over with (26) to integral scattering, the results take the form of earlier ones [2, 14].

4. Linear optical polarizability and its antisymmetricity

The results derived above — Eqs (26) and (27) — enable us to carry out a discussion of the spectrum of scattered light (applying the well known Fourier transform procedure) for linear as well as circular polarisation of the incident light beam and various geometries of observation.

The molecular scattering factors are related with the square of the optical polarizability of the molecule in the spherical basis. As is well known [18], a tensor of rank 2 resolves into three irreducible parts of the zeroth, first and second order, respectively, so that each of the molecular scattering factors is related with the corresponding order of irreducibility of the polarizability tensor of the molecule:

$$A_{\mathrm{IS}} \sim |\tilde{\alpha}_0^{(0)}|^2, \quad A_{\mathrm{ANIS}} \sim \sum_M |\tilde{\alpha}_M^{(2)}|^2, \quad A_{\mathrm{ANTIS}} \sim \sum_M |\tilde{\alpha}_M^{(1)}|^2, \tag{31}$$

simultaneously dictating the order of the relaxation time for each of the factors. Thus, A_{IS} is related with the translational relaxation time τ_{T}, A_{ANIS} and A_{ANTIS} with the rotational relaxation times τ_{2M} and τ_{1M} respectively (for small molecules).

The linear dipolar optical polarizability of the molecule is $\alpha_{ik}^{\omega_0}$ ($\alpha_{ik}^{\omega_0} \equiv \alpha_{ik}(\omega_0)$). Far from absorption, the tensor is Hermitian, $\alpha_{ik}^{\omega_0} = \alpha_{ki}^{\omega_0 *}$, i.e. its symmetric part is real and its antisymmetric part imaginary. Quantum-mechanical perturbation calculus leads to its frequency-dependence in the Kramers-Heisenberg form:

$$\alpha_{ik}(\omega_0) = \frac{1}{\hbar} \sum_k \left\{ \frac{(d_i)_{mk}(d_k)_{km}}{\omega_{km}+\omega_0} + \frac{(d_i)_{km}(d_k)_{mk}}{\omega_{km}-\omega_0} \right\}, \tag{32}$$

where $\hbar$ is Planck's constant, $(d_i)_{mk}$ are matrix elements of the electric-dipole transition between the states m and k, and ω_{km} is the transition frequency. With (32), we obtain the real and imaginary part as follows:

$$\alpha'_{(ik)}(\omega_0) = \frac{1}{\hbar} \sum_k \frac{\omega_{km}}{\omega_{km}^2-\omega_0^2} \{(d_i)_{km}(d_k)_{mk}+(d_i)_{mk}(d_k)_{km}\}, \tag{33}$$

$$\alpha''_{[ik]}(\omega_0) = \frac{1}{\hbar} \sum_k \frac{\omega_0}{\omega_{km}^2-\omega_0^2} \{(d_i)_{km}(d_k)_{mk}-(d_i)_{mk}(d_k)_{km}\}, \tag{34}$$

(ik) and $[ik]$ denoting, respectively, symmetricity and antisymmetricity in the indices i, k whereas "prime" and "bis" denote an even, or odd function of the frequency ω_0. In irreducible representation, Eq. (32) permits the resolution of the polarizability tensor into the three parts: $\tilde{\alpha}(2\,\mathrm{rank}) \to \tilde{\alpha}^{(0)}, \tilde{\alpha}^{(1)}, \tilde{\alpha}^{(2)}$. Eqs (33) and (34) lead to important time-inversion properties.

The real part of the polarizability tensor, $\alpha'_{(ik)}$, is a polar tensor of the type i (symmetric under time inversion), i.e.

$$\alpha'_{(ik)}(-\omega_0) = \alpha'_{(ik)}(\omega_0), \tag{35}$$

whereas the antisymmetric part $\alpha''_{[ik]}$ is a polar tensor of the type c (antisymmetric under time inversion):

$$\alpha''_{[ik]}(-\omega_0) = -\alpha''_{[ik]}(\omega_0). \tag{36}$$

In general, the polarizability tensor has the following property:

$$\alpha_{ik}(\omega_0) = \alpha_{ki}(-\omega_0). \tag{37}$$

If time inversion is absent in the system (molecule), the polarizability tensor is symmetric and real: $\alpha_{ik}(\omega_0) = \alpha_{ki}(\omega_0)$. With regard to the manner of adjunction of time inversion to the set of directional symmetry elements (rotations, reflections, reflection-rotations, spatial inversion) constituting the point group G_p, one distinguishes three groups [20, 21]:

$$G_R = G_p \times R, \quad G_p, \quad G_{\bar{p}} = G'_p + \{G_p - G'_p\} \times \underline{R}. \tag{38}$$

Above, G'_p is a sub-group of the group G_p, and R the time-inversion group (unit element and time inversion $\underline{R}$). Groups G_R are referred to as non-magnetic classes (they rule out the presence of a permanent magnetic moment); groups G_p are referred to as classical magnetic classes; and groups $G_{\bar{p}}$ in which time inversion $\underline{R}$ occurs in a form coupled to elements of the group G_p not belonging to the sub-group G'_p are termed magnetic classes.

Tensors of the type *i* (symmetric under time inversion) can exist in all 32 non-magnetic classes G_R, in all 32 classical magnetic classes G_p, as well as all 58 magnetic classes $G_{\bar{p}}$. Tensors of the type *c* (antisymmetric under time inversion) can exist only in the 32 classical magnetic classes G_p and 58 magnetic classes $G_{\bar{p}}$ [20, 21]. With regard to the property of *c*-type tensors, the antisymmetric imaginary part of the optical polarizability tensor of the molecule can be non-zero only in one of the 90 magnetic classes (G_p or $G_{\bar{p}}$). This is so because the relation (36) holds for molecules belonging to the magnetic symmetry classes. A molecule can fall into the latter category owing e.g. to internal magnetic perturbations, such as spin-orbit coupling [22].

In the general case, the (linear-dipolar) optical polarizability tensor of the molecule depends moreover on the wave vector of incident light. At weak spatial dispersion, we have [2]:

$$\alpha_{ik}(\omega_0, \vec{k}_0) = \alpha_{ik}(\omega_0) + \eta_{ikl}(\omega_0) k_{0l} + \dots . \tag{39}$$

Since the tensor (39) is Hermitian, its real part is symmetric and its imaginary part antisymmetric in the indices *i*, *k*. Hence, we write the real part as:

$$\alpha'_{(ik)}(\omega_0, \vec{k}_0) = \alpha'_{(ik)}(\omega_0) + \eta''_{(ik)l}(\omega_0) k_{0l} + \dots, \tag{40}$$

and the imaginary part as:

$$\alpha''_{[ik]}(\omega_0, \vec{k}_0) = \alpha''_{[ik]}(\omega_0) + \eta'_{[ik]l}(\omega_0) k_{0l} + \dots, \tag{41}$$

Spatial dispersion (39) leads to natural optical activity of the molecules. In isotropic molecular systems (liquids and gases) free of external orienting perturbations, the tensor $\eta_{ikl}(\omega_0)$ is related with the magnetic-dipole contribution to electric-dipole polarizability [23, 24].

The tensors have the following properties: $\alpha'_{(ik)}(\omega_0)$ and $\eta'_{[ik]l}(\omega_0)$ are polar, of type *i*, whereas $\alpha''_{[ik]}(\omega_0)$ and $\eta''_{(ik)l}(\omega_0)$ are polar, of type *c*[1]. Spatial dispersion thus engenders an antisymmetric part in the polarizability tensor. Likewise, an externally applied magnetic field can engender an antisymmetric part in the case of "non-magnetic" molecules even

[1] In Appendix we discuss the tensors $\alpha'_{(ik)}(\omega_0)$, $\alpha'_{[ik]}(\omega_0)$ and $\eta'_{[ik]l}(\omega_0)$ for various molecular symmetry classes.

in the absence of spatial dispersion (magneto-optical activity). The optical activity tensor $\eta'_{[ik]l}$ has the following irreducible components: $\tilde{\eta}(3 \text{ rank}) \to \tilde{\eta}^{3(1)}, \tilde{\eta}^{3(2)}, \tilde{\eta}^{4(0)}$, the superscripts 3, 4 denoting partly antisymmetric and completely antisymmetric representation, respectively.

The preceding discussion shows that the antisymmetric part of the (linear-dipolar) optical polarizability tensor can differ from zero for molecules with internal magnetic perturbations, or at spatial dispersion (magnetic dipole case). Another factor, also leading to antisymmetricity, can reside in an external static magnetic field (Faraday effect). In this work we have restricted ourselves to the electric-dipole approximation; in general, electric--quadrupole and magnetic-dipole radiation [24] have to be considered as well.

5. Conclusions

The form of the expressions (28)—(30) derived by us for the molecular scattering factors is strictly related with the model assumptions made, namely that of translational and rotational (axial) diffusion and that of the Vineyard convolution. The latter assumption modifies the spectral line intensities only (compared with the spectrum of non-interacting molecules), leaving unaffected the linewidths.

Thus, the rotational relaxation times of the "self" and "distinct" parts are the same. Albeit, the problem is dealt with otherwise within the framework of the Keyes–Kivelson [25] theory, which is based on Mori's molecular-statistical fluctuation theory [26]. We made use of Vineyard's approximation in the above considerations, it being our sole aim to draw attention to the problem.

In this paper, we have left unconsidered the ellipticity effect of scattered light due to optically active molecules resulting from the mixed terms $\tilde{\alpha}^{(0)}\tilde{\eta}^{4(0)}$ (isotropic) and $\tilde{\alpha}^{(2)}\tilde{\eta}^{3(2)}$ (anisotropic) [23, 27]. As to the effect of intermolecular interactions on the spectrum of scattered light, we reduced it to simple calculations of the Vineyard approximation. Recently, the problem has been studied in detail by Gierke [28] and Bertucci et al. [29], albeit not taking into account the antisymmetricity of polarizability.

Apart from the preliminary measurements of Maker [30] for hyper-Rayleigh scattering, there is as yet a lack of complete experimental spectral studies of linearly and circularly polarized light for Rayleigh scattering by liquids. It is our hope that the present results provide convincing proof of the utility of undertaking extensive studies of dynamical Rayleigh scattering for both the linear and circular state of light polarisation.

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APPENDIX

Tables I, II and III contain the non-zero components of the irreducible tensor $\tilde{\alpha}_M^{(J)}$ and $\tilde{\eta}_M^{s(J)}$ corresponding to the i-type polar Cartesian tensor $\alpha'_{(ik)}$, c-type polar Cartesian tensor $\alpha''_{[ik]}$ and polar Cartesian i-tensor $\tilde{\eta}'_{[ik]l}$ for various molecular symmetry classes.

TABLE I

Components of the spherical tensor $\tilde{\alpha}_M^{(J)}$ for the polar Cartesian i-tensor $\alpha'_{(ik)}$ of rank 2, symmetric in the indices i, k, for various (non-magnetic and magnetic) molecular symmetry classes

Symmetry class (international symbols)	Non-zero parameters $\tilde{\alpha}_M^{(J)}$	Spectral lines $L_{JM}(\Delta\omega)$ in Rayleigh scattering
1, $\bar{1}$, $\underline{\bar{1}}$	$\tilde{\alpha}_0^{(0)} = \frac{1}{\sqrt{3}}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$, $\tilde{\alpha}_0^{(2)} = \frac{1}{\sqrt{6}}(\alpha_{xx}+\alpha_{yy}-2\alpha_{zz})$, $\tilde{\alpha}_{-1}^{(2)} = -\alpha_{xz}-i\alpha_{yz}$, $\tilde{\alpha}_1^{(2)} = \alpha_{xz}+i\alpha_{yz}$, $\tilde{\alpha}_{-2}^{(2)} = -\frac{1}{2}(\alpha_{xx}-\alpha_{yy}-2i\alpha_{xy})$, $\tilde{\alpha}_2^{(2)} = -\frac{1}{2}(\alpha_{xx}-\alpha_{yy}+2i\alpha_{xy})$	$L_{00}(\Delta\omega)$, $L_{20}(\Delta\omega)$, $L_{21}(\Delta\omega)$, $L_{22}(\Delta\omega)$
2, $\underline{2}$, m, $\underline{m}$, $2/m$, $\underline{2}/\underline{m}$, $\underline{2}/m$, $2/\underline{m}$	$\tilde{\alpha}_0^{(0)} = \frac{1}{\sqrt{3}}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$, $\tilde{\alpha}_0^{(2)} = \frac{1}{\sqrt{6}}(\alpha_{xx}+\alpha_{yy}-2\alpha_{zz})$, $\tilde{\alpha}_{-2}^{(2)} = -\frac{1}{2}(\alpha_{xx}-\alpha_{yy}-2i\alpha_{xy})$, $\tilde{\alpha}_2^{(2)} = -\frac{1}{2}(\alpha_{xx}-\alpha_{yy}+2i\alpha_{xy})$	$L_{00}(\Delta\omega)$, $L_{20}(\Delta\omega)$, $L_{22}(\Delta\omega)$
222, $\underline{222}$, $mm2$, $\underline{mm}2$, $2\underline{mm}$, mmm, $\underline{mmm}$, $\underline{mmm}$, $mm\underline{m}$	$\tilde{\alpha}_0^{(0)} = \frac{1}{\sqrt{3}}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$, $\tilde{\alpha}_0^{(2)} = \frac{1}{\sqrt{6}}(\alpha_{xx}+\alpha_{yy}-2\alpha_{zz})$, $\tilde{\alpha}_{-2}^{(2)} = \tilde{\alpha}_2^{(2)} = -\frac{1}{2}(\alpha_{xx}-\alpha_{yy})$	$L_{00}(\Delta\omega)$, $L_{20}(\Delta\omega)$, $L_{22}(\Delta\omega)$
4, $\underline{4}$, $\bar{4}$, $\underline{\bar{4}}$, $4/m$, $\underline{4}/m$, $4/\underline{m}$, $\underline{4}/\underline{m}$, 422, $\underline{422}$, $42\underline{2}$, $4mm$, $\underline{4mm}$, $4m\underline{m}$, $\bar{4}2m$, $\underline{\bar{4}2m}$, $\bar{4}\underline{2m}$, $4/mmm$, $\underline{4/mmm}$, $4/m\underline{mm}$, $4/\underline{mmm}$, $4/\underline{mmm}$, $4/m\underline{mm}$, $\underline{4/mmm}$, 3, $\bar{3}$, $\underline{\bar{3}}$, 32, $3\underline{2}$, $3m$, $3\underline{m}$, $\bar{3}m$, $\bar{3}\underline{m}$, $\underline{\bar{3}m}$, $\underline{\bar{3}}m$, 6, $\underline{6}$, $\bar{6}$, $\underline{\bar{6}}$, $6/m$, $\underline{6}/m$, $6/\underline{m}$, $\underline{6}/\underline{m}$, 622, $\underline{622}$, $62\underline{2}$, $6mm$, $\underline{6mm}$, $6m\underline{m}$, $\bar{6}m2$, $\underline{\bar{6}m2}$, $\bar{6}\underline{m2}$, $\bar{6}m\underline{2}$, $6/mmm$, $\underline{6/mmm}$, $6/m\underline{mm}$, $6/\underline{mmm}$, $6/\underline{mmm}$, $\underline{6}/m\underline{mm}$	$\tilde{\alpha}_0^{(0)} = \frac{1}{\sqrt{3}}(2\alpha_{xx}+\alpha_{zz})$, $\tilde{\alpha}_0^{(2)} = \frac{2}{\sqrt{6}}(\alpha_{xx}-\alpha_{zz})$	$L_{00}(\Delta\omega)$, $L_{20}(\Delta\omega)$
23, $m3$, $\underline{m}3$, 432, $43\underline{2}$, $43m$, $\bar{4}3\underline{m}$, $m3m$, $m3\underline{m}$, $m\underline{3}m$, $\underline{m}3m$	$\tilde{\alpha}_0^{(0)} = \frac{3}{\sqrt{3}}\alpha_{xx}$	$L_{00}(\Delta\omega)$

TABLE II

Non-zero components of the spherical tensor $\tilde{\alpha}_M^{(J)}$ for the polar Cartesian c-tensor $\alpha'_{[ik]}$ of rank 2, antisymmetric in the indices i, k, for various magnetic classes of molecular symmetry

Symmetry class (international symbols)	Non-zero parameters $\tilde{\alpha}_M^{(J)}$	Spectral lines $L_{JM}(\Delta\omega)$ in Rayleigh scattering
1, $\bar{1}$	$\tilde{\alpha}_0^{(1)} = -\frac{2i}{\sqrt{2}}\alpha_{xy}$ $\tilde{\alpha}_{-1}^{(1)}\alpha_{xz} - i\alpha_{yz}$, $\tilde{\alpha}_1^{(1)}\alpha_{xz} + i\alpha_{yz}$	$L_{10}(\Delta\omega)$, $L_{11}(\Delta\omega)$
2, m, 2/m	$\tilde{\alpha}_{-1}^{(1)} = \alpha_{xz} - i\alpha_{yz}$, $\tilde{\alpha}_1^{(1)} = \alpha_{xz} + i\alpha_{yz}$	$L_{11}(\Delta\omega)$
2, m, 2/m, 222, $mm2$, 2mm, mmm, 4, $\underline{4}$, $\bar{4}$, $\underline{\bar{4}}$, 4/m, $\underline{4}/m$, 422, 4/mm, $\bar{4}2m$ 4/mmm, 3, $\bar{3}$, 32, 3m, $\bar{3}m$, 6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}m2$, 6/mmm	$\tilde{\alpha}_0^{(1)} = -\frac{2i}{\sqrt{2}}\alpha_{xy}$	$L_{10}(\Delta\omega)$

In the other 56 magnetic classes all components vanish.

TABLE III

Non-zero components of the spherical tensor $\tilde{\eta}_M^{s(J)}$ for the polar Cartesian i-tensor $\eta'_{[ik]l}$ of rank 3, antisymmetric in the indices i, k, for various (non-magnetic and magnetic) classes of molecular symmetry

Symmetry class (international symbols)	Non-zero components $\tilde{\eta}_M^{s(J)}$
1	$\tilde{\eta}_0^{3(1)} = i(\eta_{yzy}+\eta_{xzx})$, $\tilde{\eta}_{\pm1}^{3(1)} = \frac{1}{\sqrt{2}}[\eta_{xyx}+\eta_{zyz} \mp i(\eta_{yxy}+\eta_{zxz})]$, $\tilde{\eta}_0^{3(2)} = \frac{1}{\sqrt{3}}(\eta_{xzy}+\eta_{zyx}-2\eta_{yxz})$, $\tilde{\eta}_{\pm1}^{3(2)} = \frac{1}{\sqrt{2}}[\mp\eta_{xyx}\pm\eta_{zyz}+i(\eta_{yxy}-\eta_{zxz})]$, $\tilde{\eta}_{\pm}^{3(2)} = \frac{1}{\sqrt{2}}[\eta_{xzy}-\eta_{zyx} \mp i(\eta_{yzy}-\eta_{xzx})]$, $\tilde{\eta}_0^{4(0)} = \frac{2}{\sqrt{6}}(\eta_{yxz}+\eta_{xzy}+\eta_{zyx})$
2, $\underline{2}$	$\tilde{\eta}_0^{3(1)} = i(\eta_{yzy}+\eta_{xzx})$, $\tilde{\eta}_0^{3(2)} = \frac{1}{\sqrt{3}}(\eta_{xzy}+\eta_{zyx}-2\eta_{yxz})$, $\tilde{\eta}_{\pm2}^{3(2)} = \frac{1}{\sqrt{2}}[\eta_{xzy}-\eta_{zyx} \mp i(\eta_{yzy}-\eta_{xzx})]$, $\tilde{\eta}_0^{4(0)} = \frac{2}{\sqrt{6}}(\eta_{yxz}+\eta_{xzy}+\eta_{zyx})$

TABLE III (continued)

Symmetry class (international symbols)	Non-zero components $\tilde{\eta}^{s(J)}_M$
m, $\underline{m}$	$\tilde{\eta}^{3(1)}_{\pm1} = \frac{1}{\sqrt{2}}[\eta_{xyx}+\eta_{zyz} \mp i(\eta_{yxy}+\eta_{zxz})]$, $\tilde{\eta}^{3(2)}_{\pm1} = \frac{1}{\sqrt{2}}[\mp\eta_{xyx} \pm \eta_{zyz} - i(\eta_{yxy}-\eta_{zxz})]$
222, $\underline{222}$	$\tilde{\eta}^{3(2)}_{0} = \frac{1}{\sqrt{3}}(\eta_{xzy}+\eta_{zyx}-2\eta_{yxz})$, $\tilde{\eta}^{3(2)}_{\pm2} = \frac{1}{\sqrt{2}}(\eta_{xzy}-\eta_{zyx})$, $\tilde{\eta}^{4(0)}_{0} = \frac{2}{\sqrt{6}}(\eta_{yxz}+\eta_{xzy}+\eta_{zyx})$
$mm2$, $\underline{mm}2$, $2\underline{mm}$	$\tilde{\eta}^{3(1)}_{0} = i(\eta_{yzy}+\eta_{xzx})$, $\tilde{\eta}^{3(2)}_{\pm2} = \frac{\mp i}{\sqrt{2}}(\eta_{yzy}-\eta_{xzx})$
4, $\underline{4}$, 3, 6, $\underline{6}$	$\tilde{\eta}^{3(2)}_{0} = \frac{2}{\sqrt{3}}(\eta_{xzy}-\eta_{yxz})$, $\tilde{\eta}^{3(2)}_{\pm2} = \mp\frac{2i}{\sqrt{2}}\eta_{xzx}$, $\tilde{\eta}^{4(0)}_{0} = \frac{2}{\sqrt{6}}(\eta_{yxz}+2\eta_{xzy})$
$\bar{4}$, $\underline{\bar{4}}$	$\tilde{\eta}^{3(2)}_{\pm2} = \frac{2}{\sqrt{2}}(\eta_{xzy} \pm i\eta_{xzx})$
422, $\underline{422}$, $4\underline{22}$, 32, $3\underline{2}$, 622, $\underline{622}$, $62\underline{2}$	$\tilde{\eta}^{3(2)}_{0} = \frac{2}{\sqrt{3}}(\eta_{xzy}-\eta_{yxz})$, $\tilde{\eta}^{4(0)}_{0} = \frac{2}{\sqrt{6}}(\eta_{yxz}+2\eta_{xzy})$
$4mm$, $\underline{4mm}$, $4\underline{mm}$, $3m$, $3\underline{m}$, $6mm$, $\underline{6mm}$, $6\underline{mm}$	$\tilde{\eta}^{3(1)}_{0} = 2i\eta_{xzx}$
$\bar{4}2m$, $\underline{\bar{4}2m}$, $\bar{4}2\underline{m}$, $\underline{\bar{4}}m2$, $\underline{\bar{4}2m}$	$\tilde{\eta}^{3(2)}_{\pm2} = \frac{2}{\sqrt{2}}\eta_{xzy}$
23, 432, $\underline{432}$	$\tilde{\eta}^{4(0)}_{0} = \sqrt{6}\eta_{yxz}$

In the other 14 non-magnetic and 50 magnetic classes all components vanish.

Tables I and II moreover contain Lorentzian spectral lines (for small molecules and in the approximation of translational and rotational diffusion for the symmetric top), occurring in the spectrum of scattered light, of the form:

$$L_{JM}(\Delta\omega) = \frac{\tau_{JM}}{1+(\Delta\omega\tau_{JM})^2},$$

with $J > 0$, $M > 0$. A change in frequency by ω_0 occurs ($\Delta\omega = \omega - \omega_0$). $L_{00}(\Delta\omega)$ is the line due to translational motions, with τ_T.

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