

THEORY OF MULTIPOLAR INTERACTION-INDUCED CONTRIBUTIONS TO RAYLEIGH INTENSITY SCATTERED BY FLUIDS WITH LINEAR CENTROSYMMETRIC MOLECULES ^{*}

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Received 6 April 1988

The multipolar theory of light Rayleigh scattered by linear centrosymmetric molecules is derived using spherical tensors. Analytical forms are given for the binary and ternary radial and angular–radial terms describing the integrated intensity. Particular attention is devoted to the ternary angular–radial terms. Using available computer simulation results for the spherical components $g_{l_1 l_2 m}(r_{12})$ of the pair distribution function for molecules of liquid N_2 , the dipolar and octopolar contributions to the integrated intensity are computed. The reasons why the quadratic terms of the scattered radiation are so well described within the S model are considered.

1. Introduction

For many years, light scattering has been a highly useful means for studies of the microscopic properties of simple molecular systems [1,2]. Numerous papers have been devoted to qualitative and quantitative analyses of the scattered light intensity [3–18].

In a liquid, the magnitude of the moment induced in a molecule is dependent (in addition to the external perturbation) on the internal field originating in its neighbourhood. In a first approximation, its existence is due to the dipole moments induced in the neighbouring molecules by the light wave incident on the medium. Within the volume of a molecule the field is strongly inhomogeneous and its gradients are essentially important. Inclusion of the gradients into the theory is equivalent to taking into consideration the multipolar polarizabilities of the molecules in the scattering process [4]. Here we deal with light scattering by fluids with linear centrosymmetric molecules. Therefore, all the electric multipole polarizability tensors of odd rank vanish, so that the dipole–induced octopole scattering mechanism is the first multipolar correction term (immediately after the dipole–induced dipole mechanism). Consequently, this paper is devoted chiefly to the influence of the dipole–induced octopole mechanism on the Rayleigh scattering by fluids with linear centrosymmetric molecules. We have derived analytical formulae describing the various parts of the scattered intensity. Particular attention is devoted to the ternary angular–radial terms. As an example, we have performed numerical calculations for fluid N_2 . To our knowledge, the complete set of dipolar and octopolar polarizability tensor components is available for N_2 only. Since we are dealing here with the integrated intensity our calculations will be performed in non-projection scheme [16,18].

Our calculations will proceed as follows: in section 2, we give the multipole theory of light scattering in terms of spherical tensors. In section 3, using computer simulation results for the spherical components $g_{l_1 l_2 m}(r_{12})$ of the pair distribution function for molecules of liquid N_2 , we calculate numerically the individual terms of the integrated intensity. The appendices summarize briefly (A) the multipole theory of

^{*} Work carried out under Research Project of the Polish Academy of Sciences CPBP 01.12.5.7.

the collective polarizability in spherical and Cartesian coordinates, (B) the analytical results for the DID model, and (C) problems related with the ternary angular–radial terms describing the intensity of the scattered radiation.

2. Multipole theory of the integrated scattered intensity

Present theories of light scattering [3,4] agree that the time-decay of the intensity of light Rayleigh scattered by a dense medium is proportional to the fluctuation autocorrelation function of a dynamical variable S , called the source function:

$$I_{\alpha\alpha}(t) \propto \langle \delta S_{\alpha}(0) \delta S_{\alpha}(t) \rangle, \quad (1)$$

where the source function S is defined in ref. [3] as follows:

$$S = P - [(\langle \epsilon \rangle - 1)/4\pi] E, \quad (2)$$

and P is the polarization of the fluid and E the electric field existing within it. In (2), $\langle \epsilon \rangle$ is the equilibrium value of the dielectric permittivity of the medium.

After Ladanyi [5], eq. (1) can be expressed by way of the collective polarizability Π of the medium, the Lorentz local field factor $[(n^2 + 2)/3]^4$, and a geometrical factor G [19]:

$$I(t) \propto [(n^2 + 2)/3]^4 G \langle \Pi(0) \odot \Pi(t) \rangle, \quad (3)$$

with \odot denoting the scalar tensorial product.

For multipolar interactions, we can write Π as the sum of two components

$$\Pi = {}^{(0)}_{(M)}\Pi + {}_{(DIM)}\Pi, \quad (4)$$

where ${}^{(0)}_{(M)}\Pi$, henceforth to be referred to as the molecular component, is the sum of the molecular polarizability tensors in the absence of intermolecular interactions, whereas ${}_{(DIM)}\Pi$ is an excess interaction-induced polarizability of the system due to the dipole-induced multipole mechanisms. In a first approximation ${}_{(DIM)}\Pi$ can be expressed in terms of a multipole series expansion (see appendix A):

$${}_{(DIM)}\Pi = {}_{(DID)}\Pi + {}_{(DIQ)}\Pi + {}_{(DIO)}\Pi + \dots, \quad (5)$$

where the first term is the dipole–induced dipole (DID) contribution well known from the Yvon–Kirkwood theory, and the second and third terms represent, respectively, the dipole–induced quadrupole (DIQ) and dipole–induced octopole (DIO) contributions. In our paper we use the multipole expansion (5) for the collective polarizability assuming approximately that the individual intrinsic molecular properties (multipole moments, polarizabilities) are not changed during interactions.

At this point, we introduce expressions for the dipole–induced multipole polarizability in spherical coordinates (see appendix A). Below, we give formulae for ${}_{(DIM)}\Pi_{J\alpha}$ in two different coupling schemes:

$$\begin{aligned} {}_{(DIM)}\Pi_{J\alpha} = & \sum_{pq} \sum_{J_1 J_2 J_3 l_1 l_2} (-1)^{J_1 + J_2 - J_3} \left(\frac{2^N}{(2l_1)!(2l_2)!} \right)^{1/2} \Pi_{J_1 J_2 J_3 N} \begin{Bmatrix} J & J_1 & J_3 \\ l_1 & 1 & 1 \end{Bmatrix} \begin{Bmatrix} J_2 & N & J_3 \\ l_1 & 1 & l_2 \end{Bmatrix} \\ & \times \left\{ \mathbf{A}_{J_1}^{(1l_1)}(p) \otimes \left[\mathbf{T}_N(pq) \otimes \mathbf{A}_{J_2}^{(1l_2)}(q) \right]_{J_3} \right\}_{J\alpha}, \end{aligned} \quad (6a)$$

$$\begin{aligned}
{}_{(\text{DIM})}^{(1)}\Pi_{J\alpha} &= \sum_{pq} \sum_{J_1 J_2 J_3 l_1 l_2} (-1)^{J_1+N} \left(\frac{2^N}{(2l_1)!(2l_2)!} \right)^{1/2} \Pi_{J_1 J_2 J_3 N} \begin{Bmatrix} J_1 & J_2 & J_3 \\ 1 & 1 & J \\ l_1 & l_2 & N \end{Bmatrix} \\
&\times \left\{ \mathbf{T}_N(pq) \otimes \left[\mathbf{A}_{J_1}^{(l_1)}(p) \otimes \mathbf{A}_{J_2}^{(l_2)}(q) \right]_{J_3} \right\}_{J\alpha},
\end{aligned} \tag{6b}$$

where

$$\Pi_{ab\dots f} = [(2a+1)(2b+1)\dots(2f+1)]^{1/2}, \quad \text{and} \quad l_1 + l_2 = N.$$

Quite obviously, either scheme presents specific advantages according to the approach taken in the calculations [20]. The left-hand superscript 1 at ${}_{(\text{DIM})}^{(1)}\Pi$ stands for a polarizability in the first approximation of perturbation theory. The expressions for the polarizability in higher approximations are bulky and highly involved. Thus, though we have derived a general formula expressing arbitrary dipole-induced multipole polarizabilities in spherical coordinates in the second order of perturbation calculus [21], we refrain from writing it out in analytical form here and restrict ourselves to discuss their numerical contributions to the scattered intensity (contributions of the type ${}^{(20+02)}C_2$ [4]).

These analytical expressions (6) hold for systems of molecules of arbitrary symmetry. Our present work, however, is mainly concerned with an analysis of the integrated intensity scattered by fluids with linear centrosymmetric molecules. In this case, tensors of odd rank vanish in the electric approximation. The most essential consequence of this is the vanishing of the dipole-induced quadrupole polarizability: ${}^{(1)}A_{\alpha\beta\gamma}^{(2)} \equiv 0$. This, in the first order of perturbation (iteration), causes the vanishing of the dipole-induced quadrupole contribution to the polarizability (5), ${}_{(\text{DIO})}^{(1)}\Pi \equiv 0$, and the collective polarizability Π of eq. (4) becomes the sum of three components: the molecular component M, DID and DIO. When calculating the scattered light intensity as the scalar product (3) of the collective polarizability of the system one easily notes that the total integrated intensity is the sum of terms of two types: quadratic, and cross. There are three quadratic terms:

(a) molecular,

$${}_{(\text{M})}^{(00)}C_2 = \left\langle {}_{(\text{M})}^{(0)}\Pi_2 \odot {}_{(\text{M})}^{(0)}\Pi_2 \right\rangle, \tag{7a}$$

(b) DID,

$${}_{(\text{DID})}^{(11)}C_2 = \left\langle {}_{(\text{DID})}^{(1)}\Pi_2 \odot {}_{(\text{DID})}^{(1)}\Pi_2 \right\rangle, \tag{7b}$$

(c) DIO,

$${}_{(\text{DIO})}^{(11)}C_2 = \left\langle {}_{(\text{DIO})}^{(1)}\Pi_2 \odot {}_{(\text{DIO})}^{(1)}\Pi_2 \right\rangle, \tag{7c}$$

and three cross terms:

(a) M–DID,

$${}_{(\text{M-DID})}^{(10+01)}C_2 = 2 \left\langle {}_{(\text{M})}^{(0)}\Pi_2 \odot {}_{(\text{DID})}^{(1)}\Pi_2 \right\rangle, \tag{8a}$$

(b) M–DIO,

$${}_{(\text{M-DIO})}^{(10+01)}C_2 = 2 \left\langle {}_{(\text{M})}^{(0)}\Pi_2 \odot {}_{(\text{DIO})}^{(1)}\Pi_2 \right\rangle, \tag{8b}$$

(c) DID–DIO,

$${}_{(\text{DID-DIO})}^{(11)}C_2 = 2 \left\langle {}_{(\text{DID})}^{(1)}\Pi_2 \odot {}_{(\text{DIO})}^{(1)}\Pi_2 \right\rangle. \tag{8c}$$

Table 1

The numerical values for N_2 used here for the spherical components of the dipole–dipole $\tilde{A}_{j_0}^{(11)}$, quadrupole–quadrupole $\tilde{A}_{j_0}^{(22)}$, and dipole–octopole $\tilde{A}_{j_0}^{(13)}$ polarizabilities

J	$\tilde{A}_{j_0}^{(11)}$ (\AA^3)	$\tilde{A}_{j_0}^{(13)}$ (\AA^5)	$\tilde{A}_{j_0}^{(22)}$ (\AA^5)
0	–2.850 ^{a)} –2.944 ^{b)}	0	4.683 ^{a)} 2.120 ^{b)}
2	0.843 ^{a)} 0.629 ^{b)}	–1.809 ^{a)} –1.786 ^{b)}	–1.650 ^{a)} –0.683 ^{b)}
4	0	–0.359 ^{a)} –0.341 ^{b)}	–0.413 ^{a)} –0.368 ^{b)}

^{a)} From ref. [23]. ^{b)} From ref. [24].

We have denoted by C_2 the “molecular part” of the integrated intensity given by the scalar tensorial product in eq. (3). It will be the subject of our further analysis. The subscript 2 means that we are analyzing the anisotropic part of the scattered radiation.

When analyzing the successive components of the integrated scattered intensity (7) and (8) we readily distinguish the well known molecular component ${}^{(00)}C_2$ [1,2,22] as well as the similarly discussed [16] quadratic (7b) and cross (8a) components of the first and second approximation of the dipole–induced dipole (DID) model. Their analytical formulae are summarized in appendix B. Moreover for each of them we shall calculate, in continuation of our earlier work [16], the contribution from ternary angular–radial correlations (see appendix C). The next three are new components, hitherto not discussed numerically for liquids (though analytical calculations have been performed [4,10,13]). Here, we have a purely octopolar quadratic term (7c), a molecular–octopolar cross term (8b), and a specific dipole–octopole cross term (8c) occurring, in contradistinction to the other cross terms, in the second approximation of statistical perturbation calculus.

To derive the collective dipole–octopole polarizability of eq. (6) in analytical form we have to put $l_1 = 1$, $l_2 = 3$ and $l_1 = 3$, $l_2 = 1$ (obviously, for the dipole–dipole polarizability $l_1 = 1$, $l_2 = 1$). On insertion of the expression thus obtained into (7c), (8b) and (8c) we get formulae for the contributions to the scattered light from the octopolar mechanism. As stated above, our numerical calculations will concern N_2 – a system composed of molecules with symmetry $D_{\infty h}$. From the symmetry conditions it results that, in the coordinate system of molecular axes, only two irreducible components of the dipole–octopole polarizability tensor are non-zero, namely $\tilde{A}_{20}^{(13)}$ and $\tilde{A}_{40}^{(13)}$. Their numerical values, calculated ab initio for N_2 by Mulder et al. [23] as well as Maroulis and Bishop [24], are given in table 1 together with those of $\tilde{A}_{00}^{(11)}$ and $\tilde{A}_{20}^{(11)}$. Moreover, table 1 contains the numerical values of the non-zero components of the quadrupole–quadrupole polarizability tensor ($l_1 = 2$, $l_2 = 2$) appearing if one calculates Π with accuracy to the second order of perturbation calculus.

The cross term (8a) is determined by binary and ternary angular–radial correlations. It is zero if angular correlations are neglected [4,16]. Similarly, the dipole–octopole cross terms (8b) vanishes if the molecules of the liquid are assumed to be correlated radially but uncorrelated angularly (the S model, [11–13,15]). On the S model, only the quadratic components give non-zero contributions; so does the term ${}^{(20+20)}C_2$ (not discussed here in full analytical detail), where we have taken into account the quadrupole–quadrupole polarizability tensor [4,21].

In general, the expressions for the quadratic terms (7c) and (8c) are determined by binary, ternary and quaternary angular–radial correlations. Within the framework of the S model, due to the absence of the irreducible zero-rank tensor component $\tilde{A}_{00}^{(13)} \equiv 0$ of dipole–octopole polarizability, the quadratic quaternary octopole–octopole term (7c) is zero. Analytical methods for the study of quaternary

angular–radial correlations are as yet unavailable. Terms like these will not be dealt with in what follows. We shall, however, carry out calculations of the binary and ternary radial and angular–radial contributions to the scattered intensity. The terms given by binary correlations will be averaged using the spherical components $g_{l_1 l_2 m}(r_{12})$ of the pair distribution function [25] calculated by the method of computer simulation [26]:

$$g(r_{12}, \Omega_1^{12}, \Omega_2^{12}) = 4\pi \sum_{l_1 l_2 m} g_{l_1 l_2 m}(r_{12}) Y_{l_1 m}(\Omega_1^{12}) Y_{l_2 -m}(\Omega_2^{12}). \quad (9)$$

In this way, we obtain for the general molecular–multipole cross term of the type (8a), (8b) of scattered light intensity:

$$\begin{aligned} {}_{(M-DIM)}^{(10+01)} C_2 &= 4\sqrt{5} \rho N_A \sum_{J_1 J_2 N X} \sum_{l_1 l_2} \Pi_{J_1} \left(\frac{(2N)!}{(2l_1)!(2l_2)!} \right)^{1/2} \begin{Bmatrix} J_2 & N & X \\ l_1 & 1 & l_2 \end{Bmatrix} \begin{Bmatrix} l_1 & 1 & X \\ 2 & J_1 & 1 \end{Bmatrix} \\ &\times \tilde{A}_{J_2 0}^{(l_2)} \{ \tilde{\mathbf{A}}_{J_1}^{(l_1)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{X0} \sum_{\alpha} \begin{bmatrix} J_2 & X & N \\ \alpha & -\alpha & 0 \end{bmatrix} 4\pi \int g_{XJ_2 \alpha}(r_{12}) r_{12}^{-N+1} dr_{12}, \end{aligned} \quad (10)$$

where $[{}_{\alpha\beta\gamma}^{abc}]$ stands for the Clebsch–Gordan coefficient, N_A is the number of scatterers in the medium, $\rho = N_A/V$, and the tilde denotes the molecular dipole–multipole polarizability tensor in the molecular frame.

The expression (10) gives the cross term between the intrinsic molecular polarizability and the polarizability induced in the medium due to the first approximation of the DID model at $l_1 = l_2 = 1$ [16], as well as the cross contribution between the molecular polarizability and that caused by the DIO mechanism at $l_1 = 1$, $l_3 = 3$ and $l_1 = 3$, $l_3 = 1$; $N = 4$. On expanding the sums in (10) for DIO, we get:

$$\begin{aligned} {}_{(M-DIO)}^{(10+01)} C_2 &= -\frac{4}{15}\sqrt{5} N_A \rho \left\{ \left[\sqrt{3} \tilde{A}_{20}^{(13)} \{ \tilde{\mathbf{A}}_0^{(11)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{20} + \frac{1}{2}\sqrt{21} \tilde{A}_{20}^{(13)} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{20} \right. \right. \\ &+ \left. \frac{1}{35}\sqrt{35} \tilde{A}_{20}^{(11)} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{20} + \sqrt{7} \tilde{A}_{20}^{(11)} \{ \tilde{\mathbf{A}}_4^{(13)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{20} \right] \\ &\times [3J_5(220) + 4J_5(221) + J_5(222)] \\ &+ \frac{5}{9} \left[\sqrt{7} \tilde{A}_{40}^{(13)} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{00} + \sqrt{3} \tilde{A}_{00}^{(11)} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{40} + \frac{1}{4}\sqrt{22} \tilde{A}_{00}^{(11)} \{ \tilde{\mathbf{A}}_4^{(13)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{40} \right] \\ &\times J_5(400) \Big\}, \end{aligned} \quad (11)$$

where we have introduced the following integral molecular parameter

$$J_n(l_1 l_2 m) = 4\pi \int g_{l_1 l_2 m}(r_{12}) r_{12}^{-n+2} dr_{12}. \quad (11a)$$

Even the simplest term, ${}_{(M-DIO)}^{(10+01)} C_2$, is rather complicated. We are thus forced to discuss the other components (7c) and (8c) having recourse to certain simplifying assumptions. We first give the expression for the quadratic term (7c) in the approximation of the S model on the assumption that the molecules are correlated radially but uncorrelated angularly, meaning that in the expansion (9) we retain the terms $g_{000}(r_{12})$ only. De Santis, Sampoli and Vallauri [18] have proved by computer simulation the beautiful applicability of the S model to describe the quadratic DID term (7b) of the integrated intensity for N_2 . We obtain

$$\begin{aligned} {}_{(DIO)}^{(11)} C_2^{(2R)} &= N_A \rho \left[\frac{16}{3}\sqrt{5} \{ \tilde{\mathbf{A}}_0^{(11)} \otimes \tilde{\mathbf{A}}_0^{(11)} \}_{00} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_2^{(13)} \}_{00} + \frac{110}{27} \{ \tilde{\mathbf{A}}_0^{(11)} \otimes \tilde{\mathbf{A}}_0^{(11)} \}_{00} \{ \tilde{\mathbf{A}}_4^{(13)} \otimes \tilde{\mathbf{A}}_4^{(13)} \}_{00} \right. \\ &+ \frac{28}{3} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{00} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_2^{(13)} \}_{00} + \frac{308}{27}\sqrt{5} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{00} \{ \tilde{\mathbf{A}}_4^{(13)} \otimes \tilde{\mathbf{A}}_4^{(13)} \}_{00} \\ &\left. + \frac{8}{3} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(13)} \}_{00} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{00} \right] J_{10}(000). \end{aligned} \quad (12)$$

We calculate the three-molecule contribution to (7c) in the S model approximation with the radial part of the ternary correlation function in Kirkwood's approximation $g_R^{(3)}(1, 2, 3) = g_{000}^{(2)}(r_{12})g_{000}^{(2)}(r_{13})g_{000}^{(2)}(r_{23})$, thus obtaining

$${}_{(\text{DIO})}C_2^{(3R)} = N_A \rho^2 \tilde{A}_{00}^{(11)} \tilde{A}_{00}^{(11)} \left[\frac{2}{315} \sqrt{5} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_2^{(13)} \}_{00} + \frac{11}{2268} \{ \tilde{\mathbf{A}}_4^{(13)} \otimes \tilde{\mathbf{A}}_4^{(13)} \}_{00} \right] \langle \{ \mathbf{T}_4(12) \otimes \mathbf{T}_4(13) \}_{00} \rangle_{g_R^{(3)}}, \quad (13)$$

with

$$280 \quad \langle \{ \mathbf{T}_4(12) \otimes \mathbf{T}_4(13) \}_{00} \rangle_{g_R^{(3)}} = 2\sqrt{70} \langle r_{12}^{-5} r_{13}^{-5} P_4(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13}) \rangle_{g_R^{(3)}}$$

and [28]:

$$\begin{aligned} \langle r_{12}^{-5} r_{13}^{-5} P_4(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13}) \rangle_{g_R^{(3)}} &= 8\pi^2 \int_{-1}^1 d(\cos \beta) \int \frac{dr_{12}}{r_{12}^3} \int \frac{dr_{13}}{r_{13}^3} \frac{1}{8} (35 \cos^4 \beta - 30 \cos^2 \beta + 3) \\ &\times g_{000}^{(2)}(r_{12}) g_{000}^{(2)}(r_{13}) g_{000}^{(2)}(r_{23}). \end{aligned} \quad (14)$$

As shown above, the term described by quaternary radial correlations within the S model is zero in the case of the quadratic DIO contribution.

When analyzing the binary angular-radial correlations we shall restrict ourselves, however, to the lowest non-zero angular radial correlations, i.e. to those between the orientation of a single molecule and the centre of mass of the other, thus retaining only the coefficients $g_{200}(r) = g_{020}(r)$ in the expansion (9). This approximation is well justified [3,6]. In fact, it coincides with the dielectric cavity theory for an anisotropic molecule interacting with a continuous dielectric medium. For the cross term (8c) we now get

$$\begin{aligned} {}_{(\text{DID-DIO})}C_2 &= N_A \rho \left[\frac{20}{21} \sqrt{5} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_0^{(11)} \}_{20} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(13)} \}_{00} + \frac{172}{1225} \sqrt{35} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{20} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(13)} \}_{00} \right. \\ &+ \frac{32}{7} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_0^{(11)} \}_{20} \{ \tilde{\mathbf{A}}_0^{(11)} \otimes \tilde{\mathbf{A}}_0^{(11)} \}_{00} + \frac{32}{49} \sqrt{7} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{20} \{ \tilde{\mathbf{A}}_0^{(11)} \otimes \tilde{\mathbf{A}}_0^{(11)} \}_{00} \\ &+ \frac{220}{441} \sqrt{21} \{ \tilde{\mathbf{A}}_4^{(13)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{20} \{ \tilde{\mathbf{A}}_0^{(11)} \otimes \tilde{\mathbf{A}}_0^{(11)} \}_{00} + \frac{148}{175} \sqrt{5} \{ \tilde{\mathbf{A}}_2^{(13)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{20} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{00} \\ &\left. + \frac{9361}{9261} \sqrt{105} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_4^{(13)} \}_{20} \{ \tilde{\mathbf{A}}_2^{(11)} \otimes \tilde{\mathbf{A}}_2^{(11)} \}_{00} \right] J_8(200). \end{aligned} \quad (15)$$

Computer simulations as well as analytical studies of the scattered light intensity [18,27,42] and the absorption induced by interactions [28,29] point to an essential role of ternary angular-radial correlations in these processes. An analytical method enabling to take these correlations into account in numerical computations has been proposed by Ladanyi and Keyes [6]. In spite of restrictions imposing the omission of "irreducible connected" terms, their method enables one to bring out the constant of ternary angular-radial correlations. They applied it to the expressions we refer to as cross terms, since only such terms occur in their theory. Madden and Tildesley [27] drew attention to the possibility of applying this approach to terms of the quadratic type. We shall take ternary angular-radial correlations into account in all the components occurring in our calculations by having recourse to the Ladanyi-Keyes method.

Following Ladanyi and Keyes, for cross molecular-multipolar terms like (8a) and (8b) we obviously have

$$\left\langle \sum_{\substack{pqr \\ p \neq q \neq r}} \left[{}_{(\text{M})}^{(0)}\Pi_2(r) \odot {}^{(1)}\Pi_2(pq) \right] \right\rangle = {}_{(\text{M-DIM})}^{(10+01)}C_2 \rho f, \quad (16)$$

where ${}_{(M-DIM)}^{(10+01)}C_2$ is given by (10), whereas f ($\rho f = J_A$) is the well known parameter of binary angular correlations (otherwise denoted as J_A [2]), defined as follows by the coefficients of the expansion (9):

$$f = \frac{4}{5}\pi \sum_m (-1)^m \int g_{22m}(r_{12}) r_{12}^2 dr_{12}. \quad (16a)$$

General expressions for the ternary dipole–multipole cross terms (8c) and quadratic multipole–multipole terms (7b) and (7c) are given in appendix C. Here, we restrict ourselves to giving but the leading terms of the respective expressions in explicit form; thus, as in the case of angular–radial binary correlations, we retain only the lowest non-zero correlations between the centre of mass of one molecule and the orientations of the others, restricting ourselves in the expansion (9) to those terms for which $g_{200} = g_{020}$. With regard to the fact that this problem has hitherto not been dealt with in detail even in the DID approximation, we adduce here moreover the relevant DID analytical expression.

For the quadratic DID–DID term (7b), we have:

$$\begin{aligned} {}_{(DID-DID)}^{(11)}C_2^{(3AR)} &= 4 \left\langle \sum_{\substack{pqs \\ p \neq q \neq s}} \left[{}_{(DID)}^{(1)}\Pi_2(pq) \odot {}_{(DID)}^{(1)}\Pi_2(ps) \right] \right\rangle_{h(pq)h(ps)} \\ &= 4N_A \rho^2 \left(\frac{6}{5}a^4 + \frac{4}{5}a^3\gamma + \frac{2}{3}a^2\gamma^2 + \frac{8}{45}a\gamma^3 + \frac{8}{135}\gamma^4 \right) [J_3(200)]^2. \end{aligned} \quad (17)$$

Similar expressions hold for the dipole–octopole cross term:

$$\begin{aligned} {}_{(DID-DIO)}^{(11)}C_2^{(3AR)} &= N_A \rho^2 \frac{64}{9} \sqrt{14} \tilde{A}_{00}^{(11)} \tilde{A}_{00}^{(11)} \left[\sqrt{2/245} \{ \tilde{\mathbf{A}}_0^{(11)} \otimes \mathbf{A}_2^{(13)} \}_{20} + \frac{5}{126} \sqrt{6/5} \{ \tilde{\mathbf{A}}_0^{(11)} \otimes \mathbf{A}_4^{(13)} \}_{40} \right] \\ &\quad \times J_3(200) J_5(400). \end{aligned} \quad (18)$$

3. Numerical computations and discussion

We applied the analytical results of the preceding section for numerical computations of the individual terms (7) and (8) of the integrated intensity of light Rayleigh scattered by liquid nitrogen, at the same time making use of the computer simulation results of Streett and Tildesley [26] for the coefficients $g_{l_1 l_2 m}(r_{12})$ of the expansion (9). The results of our computations are given in table 2, whereas the values of the dipole, quadrupole and octopole polarizability components used by us are given in table 1. We had recourse to the polarizability components calculated ab initio by Mulder et al. [23]. Noteworthy is their relatively high value of the anisotropy of the dipole polarizability tensor, $\gamma = 1.03 \text{ \AA}^3$, as compared with the commonly applied value $\gamma = 0.69 \text{ \AA}^3$ of Bridge and Buckingham [31]; this essentially raises the values of the molecular component ${}_{(M)}^{(00)}C_2$ as well as the cross components ${}_{(M-DID)}^{(10+01)}C_2$ and ${}_{(M-DIO)}^{(10+01)}C_2$ of the integral scattered intensity. We also have used the polarizability components calculated recently ab initio by Maroulis and Bishop [24]. Their anisotropy $\gamma = 0.77 \text{ \AA}^3$ is in better agreement with ref. [31]. A comparison of the magnitudes of the various interaction-induced scattered intensity components convinces us all the more strongly [16] that for both sets of values [23,24] of the multipolarizabilities components (if the intensity is analyzed in non-projection scheme) the decisive, numerically negative contribution to the scattered intensity comes from the cross term ${}_{(M-DID)}^{(10+01)}C_2$. When analyzing the magnitudes of the individual components of the quadratic DID term and, jointly, the binary, ternary and quaternary terms in the S model ${}^{(11)}C_2^{(S)}$, as well as the binary angular–radial term ${}^{(11)}C_2^{(2AR)}$ and the ternary angular-radial term ${}^{(11)}C_2^{(3AR)}$, one immediately notes an almost complete mutual cancellation of the last two terms. Here,

Table 2

Values for the individual terms of the molecular part C_2 of the integrated intensity (per one molecule) of light Rayleigh scattered by liquid nitrogen^{a)}. The true values are multiplied by a factor of 10

Approximation	Term	Multipolarizability	
		ref. [23]	ref. [24]
M	$^{(00)}C_2$	6.255 ^{b)}	3.478 ^{b)}
DID	$^{(10+01)}C_2$	-1.698 ^{b)}	-1.257 ^{b)}
	$^{(11)}C_2^{(S)}$	0.142	0.137
	$^{(11)}C_2^{(2AR)}$	-0.141	-0.118
	$^{(11)}C_2^{(3AR)}$	0.135	0.129
	$^{(20+02)}C_2$	0.005 ^{b)}	0.010 ^{b)}
DIO	$^{(10+01)}C_2$	0.113 ^{b)}	0.081 ^{b)}
	$^{(11)}C_2^{(S)}$	0.006	0.006
	$^{(11)}C_2^{(2AR)}$	-0.080	-0.085
	$^{(11)}C_2^{(3AR)}$	0.054	0.060
DIO + QIQ	$^{(20+02)}C_2$	0.008	0.014

^{a)} Thermodynamical state: $\rho^* = 0.659$, $T^* = 1.79$, where $\rho^* = \rho\sigma^3$, $T^* = k_B T/\epsilon$ ($\sigma = 3.31 \text{ \AA}$, $\epsilon/k_B = 37.3 \text{ K}$).

^{b)} Use was made of the value $\rho f = -0.12$, determined in ref. [38] for the angular correlation parameter.

obviously, the cancellation of $^{(11)}C_2^{(S)}$ and $^{(11)}C_2^{(2AR)}$ is fortuitous, as one easily concludes from an analysis of the DIO mechanism. The strong reduction of the binary and ternary angular-radial correlations explains once again why the quadratic terms of the scattered and absorbed light intensity [15,18,27,29,42] are so highly adequately accounted for within the framework of the S model.

We shall now proceed to an analysis of the various multipole contributions, starting with the dipole-induced octopole mechanism. Here, similarly as in the DID mechanism, the contribution of the molecular-octopole cross term (8a), (11) is predominant. It is positive (though not so in the DID mechanism) chiefly due to the negative values of the tensor components of dipole-octopole polarizability $\tilde{A}_{20}^{(13)}$ and $\tilde{A}_{40}^{(13)}$ (table 1). The extreme smallness of $^{(11)}C_2^{(S)}$ (DIO-DIO) is due to the cancellation of the radial binary correlations (12) and radial ternary correlations (13) as well as the lack, in $^{(11)}C_2^{(S)}$ (DIO-DIO), of a term originating in quaternary radial correlations (cf., section 2). Moreover, it is our opinion that the Kirkwood model [2,32], with regard to the ternary correlation function $g^{(3)}$, overestimates the negative radial three-body terms leading to too much cancellation of binary and ternary radial correlations.

From our calculations, the predominant contribution to the cross term (02), $^{(02+20)}C_2$, comes from the quadrupole-quadrupole polarizability. This contribution, as shown by Kielich [4,33], differs from zero already in the approximation of the S model.

The overall contribution resulting from the dipole-induced octopole and quadrupole-quadrupole mechanisms in the case of the multipole polarizabilities components from [23] amounts to $0.101 \times 10^{-1} \text{ \AA}^6$, which makes 2.1% of the total intensity of the light Rayleigh scattered by liquid nitrogen. If the multipole polarizabilities components are taken after ref. [24], the multipole mechanisms produce $0.076 \times 10^{-1} \text{ \AA}^6$, which makes 3.1% of the total intensity. This DIO contribution is positive in both cases, in contradistinction to the overall contribution from the dipole-induced dipole mechanisms. The dipole-induced octopole mechanism is responsible for the rise in intensity compared with its rather drastic decrease due to the changes caused by the first approximation of the DID model. Ladanyi [34] calculated the changes due to higher-order terms in DID interactions on the depolarized light scattering intensity in liquid oxygen, finding that the higher than first-order contributions to polarizability also give a positive (by contrast to the first-order) contribution to the scattered intensity. Ladanyi estimates them at 2.8% of the total scattered light. The changes due to the DIO mechanism are of the same order of magnitude.

Computer calculations for larger molecules [35] with high polarizability (CS_2) show that as much as 10–50% of the integrated scattered intensity is contributed by first- and higher-order terms of the dipole polarizability expansion. Calculations for water and H_2S [30,36,37] point to a highly essential role of multipole mechanisms. If the anisotropy of the system is low, almost the whole contribution to the depolarized intensity component of scattered radiation comes from interaction-induced mechanisms.

The scattered light intensity due to multipolar mechanisms in fluids of simple molecules, though not great quantitatively, entails an important consequence with regard to the spectral description of the scattered radiation. We immediately note that the dipole–octopole scattering mechanism is responsible for rotational transitions governed by the following selection rules: $\Delta J_1 = 0, \pm 2$; $\Delta J_2 = \pm 2, \pm 4$. Then a substantial part of the octopolar intensity is located on the far wings of the spectral line. Moreover multipolar mechanisms strongly influence the spectral distribution of the isotropic part $C_0(\omega)$ of the scattered radiation. Careful spectral measurements [39,40] indicate a substantial decrease in the depolarization ratio at the wings of the spectral line. That behaviour of the frequency dependence of the depolarization ratio in N_2 and O_2 cannot be explained within the DID model [39,40]. Assuming approximately that the overall intensity due to the octopole mechanism is located at the wings of the spectral line, we calculate the depolarization ratio of the wings as:

$$\eta(\omega_{\text{wing}}) = \left(\frac{4}{3} + I_{\text{VV}}^{\text{iso}}/I_{\text{VH}}^{\text{aniso}} \right)^{-1}, \quad (19)$$

where the polarized isotropic $I_{\text{VV}}^{\text{iso}}$ as well as the depolarized anisotropic $I_{\text{VH}}^{\text{aniso}}$ parts of scattered radiation are due to the DIO mechanism. Performing numerical calculations for N_2 we get $\eta(\omega_{\text{wing}}) = 0.69$. The DID model leads to $\eta(\omega_{\text{wing}}) = 0.74$. The inclusion of the DIO mechanism considerably improves the degree of agreement between the theoretically predicted and the experimental value of the depolarization ratio of the wings.

Appendix A

The Hamiltonian of a system of two molecules p and q subjected to an external electric field of frequency ω and interacting with each other by way of multipolar forces can be written as follows:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \quad (\text{A.1})$$

where \hat{H}_0 is the Hamiltonian in the absence of the interactions and \hat{H}_{int} describes the interactions [32]:

$$\begin{aligned} \hat{H}_{\text{int}} = & \sqrt{3} \left[\{ \mathbf{E}_1 \otimes \hat{\mathbf{M}}_1(p) \}_{00} + \{ \mathbf{E}_1 \otimes \hat{\mathbf{M}}_1(q) \}_{00} \right] \cos \omega t \\ & + \sum_{l_1 l_2} (-1)^{l_2} \left(\frac{2^{l_1+l_2}}{(2l_1)!(2l_2)!} \right)^{1/2} \sqrt{ \{ \{ \hat{\mathbf{M}}_{l_1}(p) \otimes \hat{\mathbf{T}}_N(pq) \}_{l_2} \otimes \hat{\mathbf{M}}_{l_2}(q) \}_{00} }, \end{aligned} \quad (\text{A.2})$$

with $\hat{\mathbf{T}}_N$ being the spherical multipole interaction tensor, $\hat{\mathbf{M}}_l$ the irreducible spherical operator of the l th order multipole moment, and \mathbf{E}_1 the external electric field. The symbol \otimes denotes an irreducible tensor product.

Dealing with \hat{H}_{int} as a perturbation, we can write the dipole moment of the p th molecule in the form of the sum

$$\mathbf{M}_1(p) = {}^{(0)}\mathbf{M}_1(p) + {}^{(1)}\mathbf{M}_1(p) + {}^{(2)}\mathbf{M}_1(p) + \dots, \quad (\text{A.3})$$

where the ${}^{(k)}\mathbf{M}_1(p)$ are corrections to the value of the dipole moment corresponding to successive approximations of perturbation calculus.

On taking into account the appropriate terms of the sum (A.3) resulting from the second order of perturbation calculus and linear in E_1 , we get

$${}^{(2)}\mathbf{M}_1(p) = \sum_{J_1 J_2 J_3} \sum_{l_1 l_2} \left(\frac{2^{l_1+l_2}}{(2l_1)!(2l_2)!} \right)^{1/2} \frac{(-1)^{1+J_1+J_2+J_3}}{\sqrt{3}} \Pi_{J_1 J_2 J_3 N} \begin{Bmatrix} N & l_1 & l_2 \\ 1 & J_3 & J_1 \end{Bmatrix} \\ \times \begin{Bmatrix} J_3 & l_2 & 1 \\ 1 & J & J_2 \end{Bmatrix} \left\{ \left\{ \left\{ \mathbf{A}_{J_1}^{(l_1)}(p) \otimes \mathbf{T}_N(pq) \right\}_{J_3} \otimes \mathbf{A}_{J_2}^{(l_2)}(q) \right\}_J \otimes \mathbf{E}_1 \right\}_1, \quad (\text{A.4})$$

with $\left\{ \begin{smallmatrix} a & b & c \\ d & e & f \end{smallmatrix} \right\}$ being the 6- j Wigner symbol and $\mathbf{A}_J^{(l)}$ the irreducible J -rank spherical tensor of multipole polarizability defined as:

$$\mathbf{A}_J^{(l)} = \sum_{\phi} \frac{1}{\hbar} \left(\frac{\langle 0 | \hat{\mathbf{M}}_1 | \phi \rangle \langle \phi | \hat{\mathbf{M}}_l | 0 \rangle}{\omega_{\phi 0} - \omega} + \frac{\langle 0 | \hat{\mathbf{M}}_l | \phi \rangle \langle \phi | \hat{\mathbf{M}}_1 | 0 \rangle}{\omega_{\phi 0} + \omega} \right). \quad (\text{A.5})$$

With regard to (A.4), summing over all the molecules, and on performing the appropriate operations of spherical tensor algebra [41] we finally obtain the first interaction-induced correction to the collective polarizability in the form

$${}^{(1)}\Pi_{J\alpha} = \sum_{p=1}^{N_A} \sum_{q \neq p} \sum_{l_1 l_2} \sum_{J_1 J_2 J_3} (-1)^{N+J_1} \left(\frac{2^N}{(2l_1)!(2l_2)!} \right)^{1/2} \Pi_{J_1 J_2 J_3 N} \begin{Bmatrix} J_1 & J_2 & J_3 \\ 1 & 1 & J \\ l_1 & l_2 & N \end{Bmatrix} \\ \times \left\{ \mathbf{T}_N(pq) \otimes \left\{ \mathbf{A}_{J_1}^{(l_1)}(p) \otimes \mathbf{A}_{J_2}^{(l_2)}(q) \right\}_{J_3} \right\}_{J\alpha}, \quad (\text{A.6})$$

where $\left\{ \begin{smallmatrix} a & b & c \\ c & e & f \\ g & h & j \end{smallmatrix} \right\}$ is the 9- j Wigner coefficient.

We feel, however, that it is easier to gain insight into the origin of the collective polarizability Π by considering the above mechanisms in Cartesian coordinates as well. In these coordinates we have [4,29]

$${}^{(1)}\Pi_{\alpha\beta} = \sum_{p=1}^N \sum_{q \neq p} \sum_{m,n=1}^{\infty} (-1)^n C_{mn} \left[\begin{smallmatrix} (1) \mathbf{A}^{(m)} \\ (p) \end{smallmatrix} [m] \begin{smallmatrix} (m) \mathbf{G}_{pq}^{(n)} \\ (n) \end{smallmatrix} [n] \begin{smallmatrix} (n) \mathbf{A}^{(1)} \\ (q) \end{smallmatrix} \right]_{\alpha\beta}, \quad (\text{A.7})$$

where the $(c+d)$ th rank Cartesian tensor $\begin{smallmatrix} (c) \\ (p) \end{smallmatrix} \mathbf{A}^{(d)}$ determines the linear polarizability of the 2^c pole of molecule p due to the d -degree local electric field $\mathbf{L}^{(d)} = \nabla^{(d-1)} \mathbf{L}$ at molecule p , whereas the Green tensor of rank $(m+n)$, which is

$$\begin{smallmatrix} (m) \\ (p) \end{smallmatrix} \mathbf{G}_{pq}^{(n)} = \nabla_p^{(m-1)} \nabla_q^{(n-1)} (\nabla_p \nabla_q - k^2 \mathbf{U}) r_{pq}^{-1} \exp(ikr_{pq}), \quad (\text{A.8})$$

determines the 2^m -pole- 2^n -pole dynamic interactions between molecules p and q , separated by a distance r_{pq} . Since our considerations bear on liquids far from the critical point, the correlations are short-range and the dynamical Green tensor $\begin{smallmatrix} (m) \\ (p) \end{smallmatrix} \mathbf{G}_{pq}^{(n)}$ occurring in (A.7) and (A.8) can be replaced by the tensor $\begin{smallmatrix} (m) \\ (p) \end{smallmatrix} \mathbf{T}_{pq}^{(n)} = \nabla_p^{(m)} \nabla_q^{(n)} r_{pq}^{-1}$ of the respective static interactions.

For the collective polarizability, restricting our considerations to the dipole and octopole mechanism (when ${}^{(1)}\mathbf{A}^{(2)} = 0$), we have:

$${}^{(1)}\Pi_{\alpha\beta} = \sum_{p=1}^N \sum_{q \neq p} \left\{ \left[\begin{smallmatrix} (1) \mathbf{A}^{(1)} \\ (p) \end{smallmatrix} \cdot \begin{smallmatrix} (1) \mathbf{T}_{pq}^{(1)} \\ (1) \end{smallmatrix} \cdot \begin{smallmatrix} (1) \mathbf{A}^{(1)} \\ (q) \end{smallmatrix} \right]_{\alpha\beta} \right. \\ \left. + \frac{1}{15} \left[\begin{smallmatrix} (1) \mathbf{A}^{(1)} \\ (p) \end{smallmatrix} \cdot \begin{smallmatrix} (1) \mathbf{T}_{pq}^{(3)} [3] \\ (1) \end{smallmatrix} \cdot \begin{smallmatrix} (3) \mathbf{A}^{(1)} \\ (q) \end{smallmatrix} + \begin{smallmatrix} (3) \mathbf{A}^{(3)} [3] \\ (p) \end{smallmatrix} \cdot \begin{smallmatrix} (3) \mathbf{T}_{pq}^{(1)} \\ (3) \end{smallmatrix} \cdot \begin{smallmatrix} (1) \mathbf{A}^{(1)} \\ (q) \end{smallmatrix} \right]_{\alpha\beta} \right\}. \quad (\text{A.9})$$

The first component of the sum (A.9) originates in the Yvon–Kirkwood dipole polarizability expansion, whereas the other two components are due to dipole–octopole effects.

Appendix B

We summarize here the analytical formulae [4,11,12,15–17] describing the respective terms, as given in table 2, of the integrated intensity within the molecular and DID models. In our previous paper [16] we presented only the resultant formulae for the total integrated intensity. It is important, however, to have each of them available separately. We have (per one molecule):

(a) for the molecular term

$${}_{(M)}^{(00)}C_2 = \frac{2}{3}\gamma^2(1 + \rho f) = |\tilde{A}_{20}^{(11)}|^2(1 + \rho f), \quad (\text{B.1})$$

(b) for the cross molecular-induced dipole term (within the lowest angular–radial correlations)

$${}^{(10+01)}C_2 = \left[\frac{8}{5}\sqrt{5}\rho\gamma(a^2 + \frac{1}{3}a\gamma + \frac{2}{9}\gamma^2)J_3(200) \right](1 + \rho f), \quad (\text{B.2})$$

(c) for the quadratic term within the S model (binary, ternary and quaternary correlations jointly)

$${}^{(11)}C_2^{(S)} = \rho \left\{ 6a^4 [2J_6(000) + J(3b) + J(4b)] + \frac{28}{15}a^2\gamma^2 [J_6(000) + J(3b)] + \frac{88}{225}\gamma^4 J_6(000) \right\}, \quad (\text{B.3})$$

(d) for the quadratic term to within the lowest binary angular–radial correlations,

$${}^{(11)}C_2^{(2AR)} = \frac{4}{5}\sqrt{5}\rho \left(4a^3\gamma - \frac{1}{7}a^2\gamma^2 + \frac{137}{315}\gamma^4 \right) J_6(200), \quad (\text{B.4})$$

(e) for the (02) term within the S model

$${}^{(20+02)}C_2^{(S)} = 4\rho \left\{ \frac{7}{3}a^2\gamma^2 [J_6(000) + J(3b)] + \frac{2}{7}a\gamma^3 J_6(000) + \frac{1}{675}\gamma^4 J_6(000) \right\}, \quad (\text{B.5})$$

(f) for the (02) term to within the lowest binary angular–radial correlations

$${}^{(20+02)}C_2^{(2AR)} = \frac{8}{5}\sqrt{5}\rho \left(a^3\gamma + \frac{2}{7}a^2\gamma^2 + \frac{23}{45}a\gamma^3 + \frac{74}{945}\gamma^4 \right) J_6(200), \quad (\text{B.6})$$

(g) the leading result for the (02) term for ternary angular–radial correlations

$${}^{(20+02)}C_2^{(3AR)} = 4\rho a^3\gamma \left[\frac{2}{3}\sqrt{5}J_6(200)\rho f - \frac{3}{125}\rho\tau_{22}\tau_{20} \right]. \quad (\text{B.7})$$

Between spherical and Cartesian molecular invariants the following relations hold

$$\tilde{A}_{20}^{(11)} = \sqrt{2/3}\gamma, \quad \tilde{A}_{00}^{(11)} = -\sqrt{3}a, \quad (\text{B.8})$$

where a denotes the mean value of the dipole polarizability tensor and γ its anisotropy, whereas τ_{22} and τ_{20} are the molecular angular–radial parameters introduced by Keyes and Ladanyi [3,6].

Obviously, for the normalized integrated intensity [16] of the depolarized component of scattered light we have:

$$\hat{I}_{\perp} = \frac{1}{10}C_2. \quad (\text{B.9})$$

Appendix C

When calculating the scattered light intensity, the essential problem resides in the calculation of a correlation function of the type

$$\left\langle \left({}_{(DIM)}^{(1)}\Pi_2(12) \right) \odot \left({}_{(DIM)}^{(1)}\Pi_2(13) \right) \right\rangle_{g^{(3)}(123)} \quad (\text{C.1})$$

determined by the radial-angular molecular correlations. On expressing the ternary radial-angular correlation function $g^{(3)}$ in the Kirkwood approximation [2,3,32] as

$$g^{(3)}(123) = g^{(2)}(12)g^{(2)}(13)g^{(2)}(23) \quad (\text{C.2})$$

and on introducing

$$h(12) = g^{(2)}(12) - 1 \quad (\text{C.3})$$

it is readily shown that (C.1) possesses a rather simple analytical form if $g^{(3)}$ in (C.1) is replaced by the product $h(12)h(13)$. In place of (C.1) we now have

$$\left\langle \binom{(1)}{(\text{DIM})}\Pi_2(12) \odot \binom{(1)}{(\text{DIM})}\Pi_2(13) \right\rangle_{h(12)h(13)}. \quad (\text{C.4})$$

However, if one takes the other terms of $g^{(3)}$ into consideration, the situation tends to become much more complicated. Ladanyi and Keyes [3,6] call the remaining terms "irreducible connected" and propose to disregard them. Madden and Tildesley [27] also neglect them arguing that (C.4) contains the lowest number of h -bonds. Here, we too shall apply a similar approximation. It thus remains for us to calculate the value of (C.4) for the product of two arbitrary multipolar polarizabilities. Our experience suggests that the easiest way to do this is to have recourse to the second coupling scheme (6b) for the spherical representation of the multipole polarizability tensor and to expand the two distribution functions h of (C.4) in a series of spherical harmonics in the laboratory system of coordinates [32]:

$$h(r_{pq}, \Omega_p, \Omega_q) = \sum_{\substack{l_1 l_2 l \\ m_1 m_2 m}} h(l_1 l_2 l, r_{pq}) \begin{bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{bmatrix} Y_{l_1 m_1}(\Omega_p) Y_{l_2 m_2}(\Omega_q) Y_{l m}^*(\Omega_{pq}). \quad (\text{C.5})$$

One thus arrives at

$$\begin{aligned} & \left\langle \binom{(1)}{(\text{DIM})}\Pi_2(12) \odot \binom{(1)}{(\text{DIM})}\Pi_2(13) \right\rangle \\ &= \frac{N\rho^2}{4\pi} \sum_{KRL} \sum_{K'R'L'} (-1)^R \Pi_{KK'RR'NN'} \left(\frac{2^{N+N'}}{(2l_1)!(2l_2)!(2l'_1)!(2l'_2)!} \right)^{1/2} \\ & \times \begin{bmatrix} K & R & 2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} K' & R' & 2 \\ 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} L & N & R \\ l_1 & 1 & l_2 \end{Bmatrix} \begin{Bmatrix} 2 & K & R \\ l_1 & 1 & 1 \end{Bmatrix} \begin{Bmatrix} L' & N' & R' \\ l'_1 & 1 & l'_2 \end{Bmatrix} \begin{Bmatrix} 2 & K' & R' \\ l'_1 & 1 & 1 \end{Bmatrix} \\ & \times \hat{T}_{N0} \hat{T}_{N'0} H_{N+1}(RLN) H_{N'+1}(R'L'N') \tilde{A}_{K0}^{(l_1)} \tilde{A}_{L0}^{(l_2)} \tilde{A}_{K'0}^{(l'_1)} \tilde{A}_{L'0}^{(l'_2)}, \end{aligned} \quad (\text{C.6})$$

where

$$\hat{T}_{N0}(r_{pq}) = \tilde{T}_{N0}(r_{pq}) r_{pq}^{N+1} = (-1)^N [(2N)!/2^N]^{1/2}.$$

\tilde{T}_{N0} is the zeroth spherical component of the irreducible spherical interaction tensor of the N th rank in a coordinate system with z -axis parallel to r_{pq} , whereas

$$H_M(l_1 l_2 l) = 4\pi \int h(l_1 l_2 l, r_{12}) r_{12}^{-M+2} dr_{12} \quad (\text{C.7})$$

is a molecular parameter strictly related with the parameter (11a) introduced by us in the text. In fact for angular-radial correlations:

$$H_M(l_1 l_2 l) = \sum_m \left(\frac{4\pi}{2l+1} \right)^{1/2} \begin{bmatrix} l_1 & l_2 & l \\ m & -m & 0 \end{bmatrix} J_M(l_1 l_2 m). \quad (\text{C.8})$$

In particular

$$H_M(202) = \left(\frac{4}{3}\pi\right)^{1/2} J_M(200); \quad (\text{C.9})$$

moreover, for $M = 3$,

$$H_3(202) = \frac{1}{3}\sqrt{4\pi}\tau_{20}, \quad H_3(222) = \sqrt{4\pi}\sqrt{2/35}\tau_{22}, \quad (\text{C.10})$$

whereas, for $M = 0$

$$H_0(222) = \sqrt{4\pi}\sqrt{5}f. \quad (\text{C.11})$$

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