

Interaction-induced Rayleigh light scattering from molecular fluids by projection operator technique†

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A projection operator technique is applied to study the influence of interaction-induced mechanisms on density fluctuation-induced isotropic (DFIILS) and orientation fluctuation-induced anisotropic (OFIALS) light scattering. Analytical formulae for the integrated intensity of purely interaction-induced isotropic (PIIILS) and purely interaction-induced anisotropic (PIIALS) light scattering are derived. The integrated intensity of PIIILS as well as PIIALS is found in the form of the difference of 'square' and 'cross' contributions. Both terms are calculated numerically for liquid N₂ and CO₂ within the first order approximation of the dipole-induced dipole (DID) model. The same order of magnitude is obtained for the 'square' and 'cross' contributions.

1. INTRODUCTION

Intermolecular interactions give rise to spectra that are forbidden within the framework of conventional single-molecule spectroscopy [1]. In the spectroscopy of scattered radiation, a classical example of this is to be found in the depolarized component of light scattered by media consisting of atoms and spherically symmetric molecules. Such interaction-induced spectra are usually characterized by broad frequency distributions.

Obviously, the same intermolecular interactions are active as well in light scattering processes which are allowed in the absence of interaction-induced mechanisms. The most typical example of an effect of interaction-induced scattering mechanisms on the spectral band shape is provided by spectra containing a broad interaction-induced component underlying a relatively narrow component due to the mechanism leading to the allowed spectrum. This is quite obvious, since the principle governing the interaction-induced transitions which accompany an allowed spectrum is very similar to that underlying the mechanism responsible for forbidden spectra [1, 2]. However, the interaction-induced part of a spectrum is by no means much broader than the allowed spectrum in all cases.

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Results obtained by computer simulation [3, 4] show that, for small molecules, the relaxation times characterizing purely interaction-induced anisotropic light scattering are comparable with the relaxation times of collective orientational fluctuations in molecular anisotropy characterizing anisotropic light scattering. Commonly, however, the separation in time of the two processes is considerable [5].

The influence of interaction-induced scattering mechanisms on the allowed spectrum cannot, however, be described solely as a superposition of allowed and interaction-induced transitions. In fact, a closer analysis shows that the interaction-induced mechanisms also modify the intensities of the allowed spectra [6, 7].

Consequently, the intensity of the interaction-induced component accompanying an allowed spectrum has to be calculated with special care. The present paper is devoted to the problem of calculating the integrated intensity of the interaction-induced part of the spectrum of isotropic and anisotropic Rayleigh light scattering from molecular fluids.

In the absence of interaction-induced processes, isotropic light scattering is solely due to fluctuations in density of the molecules, and anisotropic scattering, to fluctuations in their orientation [2, 8]. In §§2 and 3 we apply a projection operator technique to calculate the influence of interaction-induced effects on the integrated intensity of isotropic density-induced and anisotropic orientation-induced scattering. The method adopted by us is shown to provide analytical formulae for the integrated intensities of the purely interaction-induced isotropic as well as the anisotropic light scattering. Our formulae are found in the form of the difference of two terms. The form of these results is intuitively obvious, since the total intensity due to interaction-induced mechanisms is reduced by the amount which modifies the intensity of the allowed spectrum. Previous analyses of the purely interaction-induced parts of the isotropic [9] and anisotropic [10] scattering spectra extracted from experimental spectra have mostly overlooked the second term of our expression for the integrated intensity.

In §4 we perform numerical calculations for liquid N_2 and CO_2 . The two terms discussed above are found to be of the same order of magnitude. Hence, when calculating the integrated intensity of interaction-induced light scattering accompanying the allowed spectrum, one is not justified in restricting oneself to the first term only. We suggest that the integrated intensities of isotropic and anisotropic scattering for other liquids as well should be analysed on the basis of the complete expressions for these intensities derived here.

The projection operator technique used here has the advantage of permitting, in a physically meaningful and quite natural way, the splitting of the interaction-induced polarizability into the part which modifies the allowed spectrum and the part responsible for the purely interaction-induced component.

2. THE MECHANISMS OF LIGHT SCATTERING AS DEALT WITH IN THE PROJECTION OPERATOR APPROACH

Consider a system composed of N anisotropic interacting molecules. The total polarizability tensor of the fluid has the form [2-5, 11]

$$\pi_{\alpha\beta} = {}^{(0)}\pi_{\alpha\beta} + \Delta\pi_{\alpha\beta}, \quad (1)$$

where

$$\pi_{\alpha\beta} = \sum_{i=1}^N {}_{(i)}\alpha_{\alpha\beta} \quad (2)$$

is the polarizability tensor of the system in the absence of intermolecular interactions whereas $\Delta\pi_{\alpha\beta}$ denotes its variation due to intermolecular interactions. An electromagnetic wave of intensity I_0 and frequency ω_i linearly polarized in the direction \mathbf{e}_i is incident on this system. At a point \mathbf{R} , distant from the centre of the system, the radiation scattered at ω_s is measured on traversal of a polarization analyser \mathbf{n} . The total intensity of scattered radiation is given by the autocorrelation function [12] of

$$\pi = e_\alpha \pi_{\alpha\beta} n_\beta^* \quad (3)$$

If the polarizability tensor of the i th molecule ${}_{(i)}\alpha_{\alpha\beta}$ is symmetric in its indices, it can be written as the sum of a zero-rank isotropic tensor ${}_{(i)}\alpha_{\alpha\beta}^{(0)}$ and an irreducible anisotropic tensor of second rank ${}_{(i)}\alpha_{\alpha\beta}^{(2)}$. Consequently, the total polarizability tensor ${}^{(0)}\pi_{\alpha\beta}$ can be written as

$${}^{(0)}\pi_{\alpha\beta} = {}^{(0)}\pi_{\alpha\beta}^{(0)} + {}^{(0)}\pi_{\alpha\beta}^{(2)} \quad (4)$$

Similarly we can distinguish in $\Delta\pi_{\alpha\beta}$ an isotropic $\Delta\pi_{\alpha\beta}^{(0)}$ and an anisotropic $\Delta\pi_{\alpha\beta}^{(2)}$ part.

${}^{(0)}\pi_{\alpha\beta}^{(0)}$ and ${}^{(0)}\pi_{\alpha\beta}^{(2)}$ are responsible for, respectively, density fluctuation-induced isotropic and orientation fluctuation-induced anisotropic light scattering, both present in our system even in the absence of interaction-induced processes. The integrated intensities of scattered radiation of these types of scattering are given, respectively, by the autocorrelation functions of

$${}^{(0)}\pi_{\text{iso}} = e_\alpha {}^{(0)}\pi_{\alpha\beta}^{(0)} n_\beta^* \quad (5a)$$

and

$${}^{(0)}\pi_{\text{aniso}} = e_\alpha {}^{(0)}\pi_{\alpha\beta}^{(2)} n_\beta^* \quad (5b)$$

when calculated with no shift of time ($\Delta t = 0$).

We now consider the influence of the interaction-induced part of the polarizability tensor $\Delta\pi_{\alpha\beta}$ on both types of scattering.

(i) Isotropic scattering

We define

$$\Delta\pi_{\text{iso}} = e_\alpha \Delta\pi_{\alpha\beta}^{(0)} n_\beta^* \quad (6)$$

With the help of the projection operator [12, 13]

$$\hat{P} = \frac{\langle \cdot, A \rangle}{\langle A, A \rangle} A$$

which projects an arbitrary 'vector' onto A , we set $A = {}^{(0)}\pi_{\text{iso}}$, in order to extract that part of $\Delta\pi_{\text{iso}}$ which behaves like ${}^{(0)}\pi_{\text{iso}}$. That quantity modifies the density fluctuation-induced isotropic light scattering (DFILS). The remaining part of $\Delta\pi_{\text{iso}}$, namely $\Delta\pi_{\text{iso}} - \hat{P}\Delta\pi_{\text{iso}} = \hat{Q}\Delta\pi_{\text{iso}}$ is the projection of $\Delta\pi_{\text{iso}}$ into a subspace orthogonal to ${}^{(0)}\pi_{\text{iso}}$. $\hat{Q}\Delta\pi_{\text{iso}}$ is responsible for a new type of isotropic scattering,

termed purely interaction-induced isotropic light scattering (PIIILS). From what has been said above, the DFIILS is described by the tensor

$${}^{(\text{DF})}\pi_{\alpha\beta}^{(0)} = \left(1 + \frac{\langle \Delta\pi_{\text{iso}}, {}^{(0)}\pi_{\text{iso}} \rangle}{\langle {}^{(0)}\pi_{\text{iso}}, {}^{(0)}\pi_{\text{iso}} \rangle} \right) {}^{(0)}\pi_{\alpha\beta}^{(0)}, \quad (7a)$$

whereas PIIILS by

$${}^{(\text{PII})}\pi_{\alpha\beta}^{(0)} = \Delta\pi_{\alpha\beta}^{(0)} - \frac{\langle \Delta\pi_{\text{iso}}, {}^{(0)}\pi_{\text{iso}} \rangle}{\langle {}^{(0)}\pi_{\text{iso}}, {}^{(0)}\pi_{\text{iso}} \rangle} {}^{(0)}\pi_{\alpha\beta}^{(0)}. \quad (7b)$$

(ii) *Anisotropic scattering*

Let us define

$$\Delta\pi_{\text{aniso}} = e_{\alpha} \Delta\pi_{\alpha\beta}^{(2)} n_{\beta}^*. \quad (8)$$

The projection operator

$$\hat{P} = \frac{\langle \cdot, {}^{(0)}\pi_{\text{aniso}} \rangle}{\langle {}^{(0)}\pi_{\text{aniso}}, {}^{(0)}\pi_{\text{aniso}} \rangle} {}^{(0)}\pi_{\text{aniso}}$$

now enables us to extract that part of $\Delta\pi_{\text{aniso}}$ which modifies orientation fluctuation-induced anisotropic light scattering (OFIALS). The remaining part of $\Delta\pi_{\text{aniso}}$, namely $\hat{Q}\Delta\pi_{\text{aniso}}$ orthogonal to ${}^{(0)}\pi_{\text{aniso}}$ is the source of purely interaction-induced anisotropic light scattering (PIIALS) [3, 4]. Thus OFIALS is described by the tensor

$${}^{(\text{OF})}\pi_{\alpha\beta}^{(2)} = \left(1 + \frac{\langle \Delta\pi_{\text{aniso}}, {}^{(0)}\pi_{\text{aniso}} \rangle}{\langle {}^{(0)}\pi_{\text{aniso}}, {}^{(0)}\pi_{\text{aniso}} \rangle} \right) {}^{(0)}\pi_{\alpha\beta}^{(2)}, \quad (9a)$$

whereas PIIALS is described by

$${}^{(\text{PII})}\pi_{\alpha\beta}^{(2)} = \Delta\pi_{\alpha\beta}^{(2)} - \frac{\langle \Delta\pi_{\text{aniso}}, {}^{(0)}\pi_{\text{aniso}} \rangle}{\langle {}^{(0)}\pi_{\text{aniso}}, {}^{(0)}\pi_{\text{aniso}} \rangle} {}^{(0)}\pi_{\alpha\beta}^{(2)}. \quad (9b)$$

Consider now the integrated intensity of each of the four above discussed types of scattering. In a macroscopically isotropic scattering system, the polarizability tensors of different ranks (zero and two) are not coupled. We then calculate the intensities of isotropic and anisotropic scattering separately as the autocorrelation functions of π_{iso} and π_{aniso} , respectively. Taking into account the orthogonality condition

$$\langle {}^{(\text{DF})}\pi_{\text{iso}}(0), {}^{(\text{PII})}\pi_{\text{iso}}(0) \rangle = 0, \quad (10a)$$

we note that in the case of isotropic scattering we calculate the integrated intensity of DFIILS and PIIILS as the autocorrelation functions of ${}^{(\text{DF})}\pi_{\text{iso}}$ and ${}^{(\text{PII})}\pi_{\text{iso}}$, respectively, where

$${}^{(\text{DF})}\pi_{\text{iso}} = e_{\alpha} {}^{(\text{DF})}\pi_{\alpha\beta}^{(0)} n_{\beta}^*, \quad (11a)$$

$${}^{(\text{PII})}\pi_{\text{iso}} = e_{\alpha} {}^{(\text{PII})}\pi_{\alpha\beta}^{(0)} n_{\beta}^*. \quad (11b)$$

Since

$$\langle {}^{(\text{OF})}\pi_{\text{aniso}}(0), {}^{(\text{PII})}\pi_{\text{aniso}}(0) \rangle = 0, \quad (10b)$$

we can calculate the integrated intensities of anisotropic scattering in an analogous way. Note that the cross-correlation functions (10 *a*) and (10 *b*) are nonzero when calculated for different times. Consequently, they contribute to the spectral distribution of scattered light and are referred to as cross (interference) terms [3–5]. However, (10 *a*) and (10 *b*) show that these terms contribute nothing to the integrated intensity.

Our splitting of the integrated intensity of isotropic and anisotropic scattering into density and orientation fluctuation-induced parts and into purely interaction-induced parts is mathematical in nature. However, in an experimental spectrum, we expect the spectrum of DFIILS to be very narrow in comparison with the spectrum of PIILS [9, 14]. Thus, it should be possible to determine the intensity of PIILS from the experimental curve with good accuracy. A less clear situation exists for the anisotropic spectrum. Only if the decay time of orientational fluctuations of the molecule is much longer than the decay time of fluctuations in its environment can we neglect the dynamical cross-correlations

$$\langle {}^{(OF)}\pi_{\text{aniso}}(t), {}^{(PII)}\pi_{\text{aniso}}(0) \rangle \cong 0. \quad (12)$$

The spectrum of scattered radiation can then be considered as a superposition of an orientational band and an interaction-induced band. Under certain assumptions, both bands can be separated and analysed [15]. The analytical form of the integral intensity of both parts of the spectrum is then important. The integrated intensities of DFIILS [7] and OFIALS [6] have been analysed. Less attention has been devoted to the analytical form of the integral intensity of purely interaction-induced isotropic as well as anisotropic light scattering.

The intensity of both of these parts of the scattered radiation have been analysed successfully by computer simulation. Such calculations allow one to determine the influence of density, temperature, the form of $\Delta\pi_{\alpha\beta}$ and the intermolecular potential on all types of light scattering [3, 4]. Nonetheless, for the analysis of experimental spectra, analytical formulae describing all parts of the intensity are useful.

3. INTENSITY OF SCATTERED LIGHT

Having defined the polarizability tensors (7) and (9) responsible for the individual types of light scattering we are in a position to obtain analytical formulae for the integrated intensity in each case. We shall find it convenient to perform the calculations in spherical coordinates. By (7) and (9) and using spherical tensor algebra, we find the integrated intensity of interactionally-corrected allowed ${}^{(A)}I_n^{(l)}$ and purely interaction-induced ${}^{(PII)}I_n^{(l)}$ light scattering to be

$${}^{(A)}I_n^{(l)} = A_\omega \phi_{ll}^0 \left[1 + \frac{\langle (\Delta\boldsymbol{\pi}^{(l)} \odot {}^{(0)}\boldsymbol{\pi}^{(l)}) \rangle}{\langle ({}^{(0)}\boldsymbol{\pi}^{(l)} \odot {}^{(0)}\boldsymbol{\pi}^{(l)}) \rangle} \right]^2 \langle ({}^{(0)}\boldsymbol{\pi}^{(l)} \odot {}^{(0)}\boldsymbol{\pi}^{(l)}) \rangle, \quad (13 a)$$

$${}^{(PII)}I_n^{(l)} = A_\omega \phi_{ll}^0 \left\{ \langle (\Delta\boldsymbol{\pi}^{(l)} \odot \Delta\boldsymbol{\pi}^{(l)}) \rangle - \frac{[\langle (\Delta\boldsymbol{\pi}^{(l)} \odot {}^{(0)}\boldsymbol{\pi}^{(l)}) \rangle]^2}{\langle ({}^{(0)}\boldsymbol{\pi}^{(l)} \odot {}^{(0)}\boldsymbol{\pi}^{(l)}) \rangle} \right\}, \quad (13 b)$$

where

$$A_\omega = \left(\frac{n_{\omega_i}^2 + 2}{3} \right)^2 \left(\frac{n_{\omega_s}^2 + 2}{3} \right)^2 \frac{I_0}{R^2} \left(\frac{\omega_s}{c} \right)^4.$$

Above, n_{ω_i} and n_{ω_s} are the refractive indices of the scattering medium at the frequencies ω_i and ω_s , respectively, whereas ${}^{(0)}\boldsymbol{\pi}^{(l)}$ and $\boldsymbol{\Delta}\boldsymbol{\pi}^{(l)}$ are irreducible spherical tensors for the polarizability of the system in the absence of molecular interactions and its variation due to intermolecular interactions, respectively. $\langle \rangle$ denotes statistical equilibrium averaging and \odot , the scalar product of two tensors, whereas ϕ_{ll}^0 determines the angular distribution of scattered radiation [11, 16]

$$\phi_{00}^0 = \frac{1}{3}(\mathbf{e} \cdot \mathbf{n})^2, \quad \phi_{22}^0 = \frac{1}{30}[(\mathbf{e} \cdot \mathbf{n})^2 + 3]. \quad (14)$$

(We use the definition of these factors that differs from the ϕ_{ll}^0 of Ben-Reuven and Gershon [16] by a factor of $(2l+1)^{-1/2}$ (cf. Posch [17*b*])). Obviously, with $l=0$, (13*a*) yields the integral intensity of DFILS, and (13*b*) yields that of PIILS. Similarly, if $l=2$, (13*a*) describes the integrated intensity of OFIALS and (13*b*), that of PIALS.

A specification of the source of $\boldsymbol{\Delta}\boldsymbol{\pi}^{(l)}$ constitutes the next problem of the theory. $\boldsymbol{\Delta}\boldsymbol{\pi}^{(l)}$ can be calculated within the DID model [2–4, 11, 18–19]. The results can be refined by taking account of higher-order terms in the multipole expansion [2, 10, 17, 20, 21] and/or molecular nonlinearities [11, 14, 21]. In addition, corrections for the overlap of the electronic wave functions of the interacting molecules have also been suggested as well as empirical polarizability models [22].

Calculating $\Delta\pi_x^{(l)}$ in the first approximation of the DID model, we obtain

$$\begin{aligned} \Delta\pi_0^{(0)} &= (8\pi)^{1/2} \sum_{\substack{p, q \\ (p \neq q)}} \sum_{\substack{f, g \\ \beta, \gamma, \delta, \beta', \gamma'}} (-)^{g-\beta} \Pi_f \begin{Bmatrix} 2 & g & f \\ 1 & 1 & 1 \end{Bmatrix} \begin{Bmatrix} 2 & f & g \\ \delta & \gamma & \beta \end{Bmatrix} \\ &\times D_{\beta\beta'}^{(g)*}(\Omega_p) D_{\gamma\gamma'}^{(f)*}(\Omega_q) Y_{2\delta}(\Omega_{pq}) r_{pq}^{-3} \tilde{a}_{\beta}^{(g)} \tilde{a}_{\gamma'}^{(f)}, \end{aligned} \quad (15 a)$$

$$\begin{aligned} \Delta\pi_x^{(2)} &= (24\pi)^{1/2} \sum_{\substack{p, q \\ (p \neq q)}} \sum_{\substack{f, g, h \\ \beta, \gamma, \delta, \varepsilon, \beta', \gamma'}} (-)^h \Pi_{ghf} \begin{Bmatrix} g & h & 2 \\ 1 & 1 & 1 \end{Bmatrix} \begin{Bmatrix} 2 & h & f \\ 1 & 1 & 1 \end{Bmatrix} \\ &\times \begin{bmatrix} 2 & f & h \\ \delta & \gamma & \varepsilon \end{bmatrix} \begin{bmatrix} g & h & 2 \\ \beta & \varepsilon & \alpha \end{bmatrix} D_{\beta\beta'}^{(g)*}(\Omega_p) D_{\gamma\gamma'}^{(f)*}(\Omega_q) Y_{2\delta}(\Omega_{pq}) r_{pq}^{-3} \tilde{a}_{\beta}^{(g)} \tilde{a}_{\gamma'}^{(f)} \end{aligned} \quad (15 b)$$

where

$$\begin{bmatrix} a & b & c \\ \alpha & \beta & \gamma \end{bmatrix}$$

denote Clebsch–Gordan coefficients,

$$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$$

is a 6- j symbol and $\Pi_{ab\dots f} = [(2a+1)(2b+1)\dots(2f+1)]^{1/2}$. The $D_{mm}^j(\Omega)$ and $Y_{lm}(\Omega)$ stand for Wigner functions and spherical harmonics, respectively, with arguments which denote molecular orientations Ω_p, Ω_q as well as the orientation of the intermolecular vector $\mathbf{r}_{pq}(\Omega_{pq})$ in the laboratory frame [23]. Moreover, \tilde{a}_m^l stands for the m -component of the irreducible l th rank spherical polarizability tensor in the molecular frame. On inserting (15) into (13*a*) we note that the integrated intensities of interactionally-corrected allowed isotropic and anisotropic scattering are described by two- and three-body angular-radial molecular corrections. Since almost nothing is known about the analytical description of

three-body angular-radial correlations in liquids, we use Ladanyi and Keyes' approach [6, 7] which is based on a superposition approximation to the three-body distribution function and a neglect of 'irreducible connected' parts within the three-body term. We average the two-body terms in (13 a) using the invariant space-fixed expansion of the molecular pair correlation function [24]

$$g^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2) = \sum_{l_1, l_2, l} \sum_{m_1, m_2, m} \sum_{n_1, n_2} g(l_1 l_2 l; n_1 n_2; r_{12}) \times \begin{bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{bmatrix} D_{m_1 n_1}^{(l_1)*}(\Omega_1) D_{m_2 n_2}^{(l_2)*}(\Omega_2) Y_{lm}(\Omega_{12}). \quad (16)$$

Equations (13), (15) and (16) hold for molecules of arbitrary shape. However, to simplify the results, we restrict these calculations to axially symmetric molecules. For the integral intensity of the polarized component ($\mathbf{n} \parallel \mathbf{e}$) of DFILS we now have

$${}^{(DF)}I_{\parallel}^{(t=0)} = A_{\omega} N \left\{ a + \frac{8\sqrt{5}}{15} \left[J_3(202; 00) a \gamma - \frac{\sqrt{(14)}}{60} J_3(222; 00) \gamma^2 \right] \right\}^2 \rho k T \beta_T, \quad (17)$$

where a and γ denote, respectively, the isotropic part and the anisotropy of the intrinsic polarizability tensor of the molecule. Moreover, we have introduced the following molecular integrals:

$$J_n(l_1 l_2 l; n_1 n_2) = (4\pi)^{1/2} \rho \int g(l_1 l_2 l; n_1 n_2; r_{12}) r_{12}^{-n+2} dr_{12} \quad (18)$$

with $\rho = N/V$ and $\beta_T =$ isothermal compressibility.

When $l = 2$, equation (13 a) yields for the integrated intensity of the depolarized component of OFIALS ($\mathbf{n} \perp \mathbf{e}$)

$${}^{(OF)}I_{\perp}^{(t=2)} = \frac{A_{\omega} N}{15} \left\{ \gamma + \frac{6\sqrt{5}}{5} \left[J_3(202; 00) \left(a^2 + \frac{a\gamma}{3} + \frac{2}{9} \gamma^2 \right) - \frac{\sqrt{(14)}}{30} J_3(222; 00) \left(a\gamma + \frac{\gamma^2}{3} \right) \right] \right\}^2 (1 + J_A), \quad (19)$$

where the well-known angular correlation parameter [2, 8, 24]

$$J_A = \frac{\sqrt{5}}{25} J_0(220; 00).$$

It should be stressed that equations (17) and (19) agree with the intensities derived by Ladanyi and Keyes for DFILS (see equations (13), (39), (44) and (69) of [7]) and OFIALS (see equations (55), (152), (159) and (157) of [6]) on the basis of fluctuation theory. When comparing our results with those of Ladanyi and Keyes, we have to keep in mind that for linear molecules the following relations between our molecular integrals $J_3(202; 00)$ and $J_3(222; 00)$ and their τ_{20} and τ_{22} hold [24], respectively:

$$J_3(202; 00) = \frac{\sqrt{5}\rho}{5} \tau_{20}, \quad (18a)$$

and

$$J_3(222; 00) = \frac{\sqrt{70}\rho}{35} \tau_{22}. \quad (18b)$$

Moreover, formulae (17) and (19) are very similar to the expressions valid when only the interaction-independent ${}^{(0)}\pi_{\alpha\beta}$ part of the polarizability tensor is considered [2, 8, 12]. Modifications appear only in the expressions placed in curly brackets. In addition to the mean value a and anisotropy γ of the polarizability tensor of an isolated molecule, corrections Δa and $\Delta\gamma$ appear in (17) and (19) due to the $\hat{P}\Delta\pi$ parts of (7a) and (9a). Explicit expressions for these quantities are

$$\Delta a = \frac{8\sqrt{5}}{15} \left[J_3(202; 00)\alpha\gamma - \frac{\sqrt{(14)}}{60} J_3(222; 00)\gamma^2 \right], \quad (20 a)$$

and

$$\Delta\gamma = \frac{6\sqrt{5}}{5} \left[J_3(202; 00) \left(a^2 + \frac{a\gamma}{3} + \frac{2}{9} \gamma^2 \right) - \frac{\sqrt{(14)}}{30} J_3(222; 00) \left(a\gamma + \frac{\gamma^2}{3} \right) \right]. \quad (20 b)$$

Of course, one can define $a_{\text{eff}} = a + \Delta a$ and $\gamma_{\text{eff}} = \gamma + \Delta\gamma$ to be the effective isotropic polarizability and the effective anisotropy for a molecule in a dense system [3, 7, 11, 25]. In the approximation used here (first order DID model), the corrections to the intrinsic polarizability of the molecule given in equations (20) are dependent on the angular-radial molecular correlations and vanish if the molecules are correlated radially but uncorrelated angularly (S -model system [11c]).

The total integrated intensity is the sum of the interactionally-corrected allowed part (13a) and purely interaction-induced part (13b). Thus,

$${}^{(\text{TOT})}I_n^{(l)} = A_\omega \phi_{ll}^0 \langle \langle ({}^{(0)}\boldsymbol{\pi}^{(l)} \odot ({}^{(0)}\boldsymbol{\pi}^{(l)})) \rangle \rangle + 2 \langle \langle (\boldsymbol{\Delta}\boldsymbol{\pi}^{(l)} \odot ({}^{(0)}\boldsymbol{\pi}^{(l)})) \rangle \rangle + \langle \langle (\boldsymbol{\Delta}\boldsymbol{\pi}^{(l)} \odot \boldsymbol{\Delta}\boldsymbol{\pi}^{(l)}) \rangle \rangle. \quad (21)$$

Equation (21) is identical with the expression for the total integral intensity obtained by Kielich [11, 25] and Woźniak and Kielich [26] many years ago. In their approach the scattered light intensity was calculated using the form (1) of the polarizability tensor of the system without splitting it into (7a) and (7b) in the case of isotropic scattering or into (9a) and (9b) in the case of anisotropic scattering.

4. THE INTEGRATED INTENSITIES OF PIIILS AND PIIALS

The analytical expression (13b) for the integrated intensity of PIIILS ($l = 0$) and PIIALS ($l = 2$) constitutes the main result of the present paper. Although these intensities have already been calculated successfully for selected molecules and thermodynamical states by computer simulation [3, 4] analytical formulae are nonetheless useful when it comes to the analysis of experimental spectra in general. The integrated intensity of PIIILS is the result of subtraction of two terms, namely, the 'square' term ${}^{(\text{PII})}I_n^{(l)}(\text{square})$ and the 'cross' term ${}^{(\text{PII})}I_n^{(l)}(\text{cross})$

$${}^{(\text{PII})}I_n^{(l)} = {}^{(\text{PII})}I_n^{(l)}(\text{square}) - {}^{(\text{PII})}I_n^{(l)}(\text{cross}), \quad (22)$$

where

$${}^{(\text{PII})}I_n^{(l)}(\text{square}) = A_\omega \phi_{ll}^0 \langle \langle (\boldsymbol{\Delta}\boldsymbol{\pi}^{(l)} \odot \boldsymbol{\Delta}\boldsymbol{\pi}^{(l)}) \rangle \rangle, \quad (23 a)$$

and

$${}^{(\text{PII})}I_n^{(l)}(\text{cross}) = A_\omega \phi_{ll}^0 \frac{[\langle \langle (\boldsymbol{\Delta}\boldsymbol{\pi}^{(l)} \odot ({}^{(0)}\boldsymbol{\pi}^{(l)})) \rangle \rangle]^2}{\langle \langle ({}^{(0)}\boldsymbol{\pi}^{(l)} \odot ({}^{(0)}\boldsymbol{\pi}^{(l)})) \rangle \rangle}. \quad (23 b)$$

The 'square' term describes the integral intensity of scattered radiation in the case when the process is forbidden in the absence of interaction-induced mechanisms: ${}^{(0)}\pi_{\alpha\beta} = 0$. The second term is of the cross type since its numerator has the form of the scalar product of the polarizability tensor in the absence of interaction-induced mechanisms ${}^{(0)}\boldsymbol{\pi}^{(l)}$ and its variation $\Delta\boldsymbol{\pi}^{(l)}$ due to those mechanisms. This term emerges when we consider the purely interaction-induced part of scattered light for allowed transitions (otherwise ${}^{(0)}\boldsymbol{\pi}^{(l)} = 0$).

Calculating $\Delta\boldsymbol{\pi}^{(l)}$ in the first approximation of the DID model we note that the 'square' term (23 *a*) consists of radial and angular-radial two-, three- and four-body contributions. The cross term (23 *b*), however, is purely angular-radial, similar to the corrections to the intrinsic polarizability of the molecule given in equations (20). ${}^{(PII)}I_n^{(l)}(\text{cross})$ vanishes for an *S*-model system.

The purely interaction-induced spectra accompanying the allowed light scattering from molecular liquids have rarely been analysed experimentally (for molecular gases, see [27]). Much more attention has been devoted to forbidden spectra [28–31] and to the analysis of DFIILS [2, 7, 32] and OFIALS [2, 6, 12, 15]. However, in previous discussions of the purely interaction-induced part of the isotropic [9, 10] and the anisotropic [10] spectrum, the integral intensity formulae used contain only the first 'square' term of our equation (22). As in this paper, $\Delta\boldsymbol{\pi}^{(l)}$ in those studies was calculated in the first approximation of the DID model. These results and ours are in agreement only within the *S*-model, i.e. when ${}^{(PII)}I_n^{(l)}(\text{cross}) = 0$. Within first order DID approximation, the *S*-model implies that there is no interaction-induced correction to the intrinsic polarizability tensor of the molecule. Analyses of computer [3, 4] and laboratory [15 *a*] experiments point to substantial differences between the values of effective polarizability tensors of simple molecules in a liquid and in the dilute gas. This proves the importance of the second ('cross') term (23 *b*) of our formula (22). The numerical calculations presented here also confirm this conclusion.

In order to evaluate the PIIILS and the PIIALS integrated intensities, we must rewrite equations (22), (23 *a*) and (23 *b*) in explicit form. We shall be calculating the 'square' term in (23 *a*) taking into account only the pair-wise angular-radial correlations because, as stated above, almost nothing is known about triplet and quartet angular correlations in molecular liquids. We shall include triplet and quartet molecular correlations in the *S*-model approximation, i.e. taking into account only radial correlations. The complete analytical form of ${}^{(PII)}I_n^{(l)}(\text{square})$ in the pairwise approximation is to be found in our earlier paper [33]. However, we have shown in [33] that the greatest contribution to the scattered light intensity from pairwise angular-radial correlations comes from the first two angle-dependent terms of the series expansion (16) of $g^{(2)}$, namely $g(202; 00; r_{12}) = g(022; 00; r_{12})$.

Closer inspection of the 'cross' term (23 *b*) reveals its connection [14 *a*] with the interaction-induced correlation to the intrinsic polarizability tensor of the molecule (20). We have

$$\frac{\langle(\Delta\boldsymbol{\pi}^{(0)} \odot {}^{(0)}\boldsymbol{\pi}^{(0)})\rangle}{\langle({}^{(0)}\boldsymbol{\pi}^{(0)} \odot {}^{(0)}\boldsymbol{\pi}^{(0)})\rangle} = \frac{\Delta a}{a}, \quad (24 a)$$

$$\frac{\langle(\Delta\boldsymbol{\pi}^{(2)} \odot {}^{(0)}\boldsymbol{\pi}^{(2)})\rangle}{\langle({}^{(0)}\boldsymbol{\pi}^{(2)} \odot {}^{(0)}\boldsymbol{\pi}^{(2)})\rangle} = \frac{\Delta\gamma}{\gamma}. \quad (24 b)$$

Thus we can calculate the 'cross' term (23 *b*) from the simulation results [3, 4] for Δa and $\Delta\gamma$. If no simulations are available, we can use equations (20).

For linear molecules, these approximations lead to an expression for the integrated intensity of the polarized component of PIILS (its reduced intensity $\hat{I} = I/A_\omega N$) which is

$$\begin{aligned} {}^{(\text{PII})}\hat{I}_{\parallel}^{(l=0)} &= {}^{(\text{PII})}\hat{I}_{\parallel}^{(l=0)}(\text{square}) - {}^{(\text{PII})}\hat{I}_{\parallel}^{(l=0)}(\text{cross}) \\ &= \left[\left(\frac{16}{45}a^2\gamma^2 + \frac{28}{2025}\gamma^4 \right) J_6(000) + \frac{16}{45}a^2\gamma^2 J(3b) + \frac{8\sqrt{5}}{45} \right. \\ &\quad \left. \times \left(\frac{4}{9}a^2\gamma^2 + \frac{4}{15}a\gamma^3 - \frac{1}{105}\gamma^4 \right) J_6(200) \right] - (\Delta a)^2 \rho k T \beta_T. \end{aligned} \quad (25 a)$$

For the integrated intensity of the depolarized component of PIILS we obtain

$$\begin{aligned} {}^{(\text{PII})}\hat{I}_{\perp}^{(l=2)} &= {}^{(\text{PII})}\hat{I}_{\perp}^{(l=2)}(\text{square}) - {}^{(\text{PII})}\hat{I}_{\perp}^{(l=2)}(\text{cross}) \\ &= \left\{ \frac{3}{5}a^4 [2J_6(000) + 4J(3b) + J(4b)] + \frac{14}{5}a^2\gamma^2 \right. \\ &\quad \times [J_6(000) + J(3b)] + \frac{44}{1125}\gamma^4 J_6(000) + \frac{2\sqrt{5}}{25} \\ &\quad \left. \times (4a^3\gamma - \frac{1}{3}a^2\gamma^2 + \frac{137}{315}\gamma^4) J_6(200) \right\} - \frac{1}{15}(\Delta\gamma)^2(1 + J_A). \end{aligned} \quad (25 b)$$

By $J(3b)$ and $J(4b)$ we have denoted the molecular integrals involving triplet and quartet radial correlations.

For our numerical calculations we use computer simulation results for the distribution function $g^{(2)}$. Then, the irreducible intermolecular frame expansion of the binary distribution function [34]:

$$g^{(2)}(r_{12}, \Omega_1^{12}, \Omega_2^{12}) = 4\pi \sum_{l_1 l_2 m} g_{l_1 l_2 m}(r_{12}) Y_{l_1 m}(\Omega_1^{12}) Y_{l_2 -m}(\Omega_2^{12}) \quad (26)$$

will be utilized rather than the more general invariant space fixed frame expansion (16) used in §3. Equations (25) have been averaged in the intermolecular frame so as to adapt them to our numerical calculations. The molecular parameters now become

$$J_n(l_1 l_2 m) = 4\pi\rho \int g_{l_1 l_2 m}(r_{12}) r_{12}^{-n+2} dr_{12}. \quad (27)$$

Numerical calculations have been carried out for CO_2 at $\rho^* = 0.422$ and $T^* = 1.345$ with the aid of the computer simulation results of Singer, Taylor and Singer [35] for $g^{(2)}$. In addition, we have treated N_2 at $\rho^* = 0.630$ and $T^* = 2.13$ using Cheung and Powles' results [36] for $g^{(2)}$. We obtain $\Delta\gamma$ by extrapolating Frenkel and McTague's values [3 *b*] for CO_2 to our ρ^* and T^* . However, when calculating Δa , special care is required. Frenkel [3 *a*] and Frenkel and McTague [3 *b*] as well as Ladanyi [4] have computed the effective isotropic polarizability from the Lorentz-Lorenz equation, so that their Δa is proportional to $\langle \Delta\pi^{(0)} \rangle$ and, within the first approximation of the DID model, depends on pair correlations only. However, the effective polarizability for light scattering induced by density fluctuations [7] is proportional ((7 *a*) and (24 *a*)) to the average value of

Table 1. Calculated integrated intensities of PIHLS.

| Molecule | Thermo- dynamic state | $^{(PII)}\hat{I}_{\parallel}^{(l=0)}$ (square) (\AA^6) | $^{(PII)}\hat{I}_{\parallel}^{(l=0)}$ (cross) (\AA^6) | $^{(PII)}\hat{I}_{\parallel}^{(l=0)}$ (\AA^6) | $\frac{^{(PII)}\hat{I}_{\parallel}^{(l=0)}}{^{(TOT)}\hat{I}_{\parallel}^{(l=2)}}$ (per cent) |
|-----------------|-----------------------------------|---|--|---|---|
| N ₂ | $\rho^* = 0.630$ $T^* = 2.13$ | 0.00017 | 0.00003 | 0.00014 | 0.4 (0.4)† |
| CO ₂ | $\rho^* = 0.422$ $T^* = 1.345$ | 0.012 | 0.006 | 0.006 | 1.9 (3.1)‡ (4.0)§ |

† Reference [3] ($\rho^* = 0.630$, $T^* = 2.13$).

‡ Reference [3] ($\rho^* = 0.360$, $T^* = 1.61$).

§ Reference [4] ($\rho^* = 0.460$, $T^* = 1.62$).

the projection of $\Delta\pi^{(0)}$ onto $^{(0)}\pi^{(0)}$. The projection operation generates a three-body correlation term and a factor of 2 within the two-body term. However, when calculating the three-body correlation term of Δa in the superposition approximation and neglecting its 'irreducible connected' parts, the three-body contribution to Δa is completely described by two-body correlations [7]. Thus Δa is described by our equation (20 a). This approximate Δa is greater by a factor of 2 than the Δa defined in [3] and [4]. The factor of 2 results from the presence of two (mutually equivalent) kinds of two-body correlations in our definition (24 a) of Δa whereas, on the contrary, the formulae defining Δa in [3] and [4] involve but one kind of binary correlations. Obviously the difference in the definitions of Δa has an effect on the form of $^{(PII)}\pi^{(0)}$. The detailed analysis of the influence of these divergences on isotropic light scattering requires further investigation. Work on that problem is in progress. We use our approximative equation (20 a) for numerical calculations of Δa . We calculate the $J(3b)$ and $J(4b)$ molecular integrals as in [33].

The calculated integrated intensities of PIHLS are listed in table 1 and those of PIIALS, in table 2. In both cases, the results for the 'square' term and the 'cross' term are listed separately in order to show the substantial value of the 'cross' term. These numerical results show that, except for PIHLS from N₂, both $^{(PII)}I_n^{(l)}$ (square) and $^{(PII)}I_n^{(l)}$ (cross) are of the same order of magnitude. This

Table 2. Calculated integrated intensities of PIIALS.

| Molecule | Thermo- dynamical state | $^{(PII)}\hat{I}_{\perp}^{(l=2)}$ (square) (\AA^6) | $^{(PII)}\hat{I}_{\perp}^{(l=2)}$ (cross) (\AA^6) | $^{(PII)}\hat{I}_{\perp}^{(l=2)}$ (\AA^6) | $\frac{^{(PII)}\hat{I}_{\perp}^{(l=2)}}{^{(TOT)}\hat{I}_{\perp}^{(l=2)}}$ (per cent) |
|-----------------|-----------------------------------|---|--|---|---|
| N ₂ | $\rho^* = 0.630$ $T^* = 2.13$ | 0.0012 | 0.0004 | 0.0008 | 3.2 (3.9)† |
| CO ₂ | $\rho^* = 0.422$ $T^* = 1.345$ | 0.060 | 0.021 | 0.039 | 15.5 (10.8)‡ (14.4)§ |

† Reference [3] ($\rho^* = 0.630$, $T^* = 2.13$).

‡ Reference [3] ($\rho^* = 0.360$, $T^* = 1.61$).

§ Reference [4] ($\rho^* = 0.460$, $T^* = 1.62$).

suggests that when calculating the integrated intensity of purely interaction-induced isotropic as well as anisotropic light scattering for other classes of molecules one should take into account (beside the 'square' term) the hitherto omitted 'cross' term too. In the last column of tables 1 and 2 we have calculated the ratio of the integrated intensity of purely interaction-induced light scattering to the total integrated intensity (21) of anisotropic light scattering. We have compared our results with the values obtained by Frenkel and McTague [3] and Ladanyi [4] from their computer simulations. Good agreement is found between our results and theirs, suggesting that the approximations used in our calculations are reasonable. The numerical significance of the 'cross' term originating in the angular-radial correlations only, as compared with the 'square' term containing i.a. spherically symmetric radial correlations, may seem unexpected, especially for molecules of symmetry so close to spherical as N_2 . In this case the angular-radial correlations are small compared with the spherically symmetric radial correlations. However, when significant cancellation of these radial correlations occurs, as it does in the 'square' term, the angular-radial correlations and consequently the 'cross' term become important, as in the case considered by us.

The contribution of one of us (T. B.) began to take shape on a visit to the Department of Chemistry of The Pennsylvania State University.

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