Spectral distribution of scattered light by fluid mixtures of correlated atoms and molecules

S. KIELICH, T. BANCEWICZ, AND S. WOŹNIAK

Nonlinear Optics Division, Institute of Physics, A. Mickiewicz University, 60-780 Poznań, Poland

Received January 29, 1981

A stochastic theory of the spectral distribution of light scattered by mixtures of atoms and molecules, colliding in time and space, is proposed. New time-correlation functions $C^{(0)}(t)$ and $C^{(2)}(t)$ are introduced describing respectively the statistical microscopic mechanisms of isotropic and anisotropic coherent scattering, related with changes in the first and second perturbation of the molecular polarizability tensor due to the long-range fields of induced molecular electric multipoles. In this way, not only anisotropic but also isotropic scattering is shown to have a rotational spectral structure due to orientational motions and angular collisions of the polar molecules. The hitherto not considered cross approximations 0.1 and 0.2 of the functions $C^{(0)}(t)$ and $C^{(2)}(t)$ involve the first power of the dipole–quadrupole, dipole–octupole, and quadrupole–quadrupole tensors thus permitting first determinations of the signs of the successive multipolar molecular polarizabilities.

On donne une théorie stochastique de la répartition spectrale de la lumière diffusée par des mélanges d'atomes et de molécules en collisions dans le temps et dans l'espace. De nouvelles fonctions $C^{(0)}(t)$ et $C^{(2)}(t)$ sont introduites, décrivant respectivement les mécanismes microsco-piques-statistiques de la diffusion cohérente isotrope et anisotrope liée aux variations de la première et deuxième perturbation du tenseur de polarisabilité moléculaire due aux champs à longue portée des multipôles électriques moléculaires induits. On montre ainsi que non seulement la diffusion anisotrope mais aussi la diffusion isotrope possède une structure spectrale de rotation due aux mouvements d'orientation et aux collisions angulaires des molécules polaires. Les approximations mixtes 0,1 et 0,2 jusqu'à présent non considérées des fonctions $C^{(0)}(t)$ et $C^{(2)}(t)$ contiennent les premières puissances des tenseurs de la polarisabilité dipolaire-quadrupolaire, dipolaire-octupolaire et quadrupolaire-quadrupolaire ce qui, pour la première fois, permet de déterminer les signes des polarisabilités multipolaires successives des molécules.

[Traduit par le journal]

1. Introduction

Owing to laser light, scattering spectra have become an effective tool in the study of structural and dynamical subtleties of statistical media, composed of atoms, molecules, and particles (1–3). Yvon (4) was the first to show that translational fluctuations of binary and ternary atomic correlations of dipolar types cause a depolarization of the scattered light. However, quite generally, variations in the polarizability of atoms arise not only as the result of electric fields of the dipolar type (DID) but moreover in higher, multipole orders; this is apparent in molecular refraction (5, 6) and, hence, in light scattering (7, 8). Although the experimental observations of recent years point to the dipole approximation as sufficiently accurate with regard to atomic fluids (9–12) complete agreement with experiment requires the inclusion of other mechanisms, e.g., multiple-scattering effects (13–15) or short-range collisional effects (9–12).

In molecular fluids the situation is more complex due to the coexistence of many mechanisms (3). Even in the case of highly (tetrahedrally and octa-hedrally) symmetric molecules one has to proceed

beyond the dipolar field approximation to higher multipolar approximations (6–8, 17–20). In that of low-symmetry molecules with intrinsic optical anisotropy, e.g., N_2, CO_2, C_6H_6, etc., the calculations become much more complicated, as not only translational but also translational–orientational and orientational fluctuations strongly affecting the scattered light depolarization have to be taken into account (7, 21–25). For polar molecules, agreement between the theory and scattered light observations can be enhanced by considering binary and ternary correlation factors (7, 22–28), of great importance in Kerr's effect and other, nonlinear effects (7, 29–31). Also, highly relevant are local field models (24, 32, 33).

This paper is aimed at presenting a stochastic treatment (2, 3, 34) of the spectral distribution of light, scattered by many-component systems of atoms and molecules, correlated in time and space. Our approach is of sufficient generality to comprise various processes of fluctuations of the multipolar molecular fields as well as many-body atomic-molecular correlations of the dispersional, electro-static, and inductional types. We have hitherto con-

ﬁﬂered these mechanisms for the integral scattered light intensity in mixtures (7, 21, 35, 36); spectral theories have, as yet, not analyzed them explicitly and sufficiently generally, though first attempts have been made by us with respect to one-component systems in the spherical tensor approach in the DID approximation (37, 38).

2. Scattering Correlation Tensor

We consider a spherical sample of volume V and electric permittivity ε_ω immersed in an isotropic continuous medium of permittivity ε_0. The well known relation $(\varepsilon_\omega + 2\varepsilon_0)E(t) = 3\varepsilon_0 E_0(t)$ holds between the mean macroscopic electric field $E(t)$ within the scattering sample and the field $E_0(t)$ outside the sample. The volume V is considered to contain $N = \sum_i N_i$ molecules (N_i is the number of those of the ith species), the position and orientation of molecule p of species i being given at the moment of time t by the variables $r_{pi}^{(t)}$ and $\Omega_{pi}^{(t)}$. Restricting the problem to electric-dipole scattering in the wave zone, we write the time-dependent intensity tensor for the multi-component system in the form:

$$I_{\sigma\tau}(t) = \tfrac{1}{2}D_\omega \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \Pi_{\sigma\nu}(r_{pi}^0, \Omega_{pi}^0)^* \Pi_{\tau\rho}(r_{qj}{}', \Omega_{qj}{}') \exp[iu\cdot(r_{qj}{}' - r_{pi}^0)] \right\rangle E_\nu(0)^* E_\rho(t)$$

where we have used the notation:

$$D_\omega = \left(\frac{\omega_s}{c}\right)^4 \left(\frac{\varepsilon_{\omega_s} + 2\varepsilon_0}{3\varepsilon_0}\right)^2 \left(\frac{\varepsilon_\omega + 2\varepsilon_0}{3\varepsilon_0}\right)^2 \simeq \left(\frac{\omega}{c}\right)^4 \left(\frac{n^2+2}{3}\right)^4$$

with $\varepsilon_\omega \simeq n^2$ and $\varepsilon_{\omega_s} \simeq n^2$ the electric permittivities for the incident and scattered light frequencies, respectively, and $u = k - k_s$ is the difference between the propagation vectors of the incident k and scattered k_s waves. Generally the form of D_ω is dependent on the shape of the sample and the conditions of observation of the scattered light (3, 24, 32, 33).

On decomposing the effective polarizability tensor into three irreducible tensors (2): $\Pi_{\sigma\tau}^{(0)} = \Pi\delta_{\sigma\tau}$ (isotropic tensor), $\Pi_{\sigma\tau}^{(1)} = (\Pi_{\sigma\tau} - \Pi_{\tau\sigma})/2$ (antisymmetric tensor), and $\Pi_{\sigma\tau}^{(2)} = (\Pi_{\sigma\tau} + \Pi_{\tau\sigma})/2 - \Pi\delta_{\sigma\tau}$ (anisotropic tensor or deviator), and on performing an averaging in [1] over all possible orientations of the molecules, we obtain respectively:

$$I_{\sigma\tau}^{(0)}(t) = \frac{D_\omega}{6} C^{(0)}(t) E_\sigma(0)^* E_\tau(t)$$

$$I_{\sigma\tau}^{(1)}(t) = \frac{D_\omega}{12} C^{(1)}(t)[\delta_{\sigma\tau} E_\nu(0)^* E_\nu(t) - E_\sigma(0)E_\tau(t)^*]$$

$$I_{\sigma\tau}^{(2)}(t) = \frac{D_\omega}{60} C^{(2)}(t)[3\delta_{\sigma\tau} E_\nu(0)^* E_\nu(t) + 3E_\sigma(0)E_\tau(t)^* - 2E_\sigma(0)^* E_\tau(t)]$$

Above, we have introduced the time-dependent correlation functions ($h = 0, 1, 2$)

$$C^{(h)}(t) = \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \Pi_{\alpha\beta}^{(h)}(r_{pi}^0, \Omega_{pi}^0)^* \Pi_{\alpha\beta}^{(h)}(r_{qj}{}', \Omega_{qj}{}') \exp[iu\cdot(r_{qj}{}' - r_{pi}^0)] \right\rangle$$

characterizing the molecular-statistical dynamics of isotropic ($h = 0$), antisymmetric ($h = 1$), and anisotropic ($h = 2$) scattering.

3. Effective Polarizability Tensor

If the N molecules in volume V interact with one another, a given molecule p of species i is acted on (in addition to the field $E(t)$ of the light wave) by the field $F(r_{pi}{}')$, produced by the induced multipole electric moments of the other $N - 1$ molecules. Accordingly, the total dipole moment, induced in molecule p of species i, amounts in an approximation linear in $E(t)$ to:

$$M_\alpha(r_{pi}{}', \Omega_{pi}{}') = A_{\alpha\beta}(\Omega_{pi}{}')E_\beta(t) + \sum_{m=1}^\infty \frac{1}{(2m-1)!!} A_{\alpha:\alpha_1\ldots\alpha_m}(\Omega_{pi}{}')F_{\alpha_1\ldots\alpha_m}(r_{pi}{}', \Omega_{pi}{}')$$

where $A_{\alpha\beta}(\Omega_{pi}{}')$ is the second-rank tensor of linear dipole–dipole polarizability in the absence of a molecular field $F(r_{pi}{}')$. Similarly, the $(1 + m)$th rank tensor $A_{\alpha:\alpha_1\ldots\alpha_m}(\Omega_{pi})$ defines the linear polarizability of dipole – 2^m-pole type.

The 2^m-pole electric field, produced at r_{pi} by the 2^n-pole induced electric multipoles $M_{\beta_1...\beta_n}(r_{qj}')$ of the $N - 1$ surrounding molecules, is (6, 20):

[7] $F_{\alpha_1...\alpha_m}(r_{pi}', \Omega_{pi}') = \sum_j \sum_{q \neq p}^{N_j} \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n-1)!!} T_{\alpha_1...\alpha_m\beta_1...\beta_n}(r_{piqj}') M_{\beta_1...\beta_n}(r_{qj}', \Omega_{qj}')$

where the $(m + n)$-rank tensor (5, 20)

[8] $T_{\alpha_1...\alpha_m\beta_1...\beta_n}(r_{piqj}') = \nabla_{\alpha_2}^p...\nabla_{\alpha_m}\nabla_{\beta_2}^q...\beta_n(\nabla_{\alpha_1}^p\nabla_{\beta_1}^q - k^2\delta_{\alpha_1\beta_1})r_{piqj}^{-1} \exp(ikr_{piqj}')$

describes the (2^m-pole) – (2^n-pole) dynamic interactions between molecules p_i and q_j, separated by a distance r_{piqj}.

By [6] and [7] we obtain in a satisfactory approximation the effective polarizability tensor in the form:

[9] $\Pi_{\alpha\beta} = \overset{(0)}{\Pi}_{\alpha\beta} + \overset{(1)}{\Pi}_{\alpha\beta} + \overset{(2)}{\Pi}_{\alpha\beta} + ...$

where, in the zeroth approximation,

$\overset{(0)}{\Pi}_{\alpha\beta} = A_{\alpha\beta}(\Omega_{pi}')$

while the first- and second-order approximations are of the form:

[10] $\overset{(1)}{\Pi}_{\alpha\beta}(r_{pi}', \Omega_{pi}') = \sum_j \sum_{q \neq p}^{N_j} \sum_{m,n=1}^{\infty} (-1)^n c_{mn} A_{\alpha:\alpha_1...\alpha_m}(\Omega_{pi}') T_{\alpha_1...\alpha_m\beta_1...\beta_n}(r_{piqj}') A_{\beta_1...\beta_n:\beta}(\Omega_{qj}')$

[11] $\overset{(2)}{\Pi}(r_{pi}', \Omega_{pi}') = \sum_{jk} \sum_{q \neq p}^{N_j} \sum_{r \neq q}^{N_k} \sum_{m...w=1}^{\infty} (-1)^{n+w} c_{mnuw} A_{\alpha:\alpha_1...\alpha_m}(\Omega_{pj}') T_{\alpha_1...\alpha_m\beta_1...\beta_n}(r_{piqj}') A_{\beta_1...\beta_n:\gamma_1...\gamma_u}(\Omega_{qj}')$

$\times T_{\gamma_1...\gamma_u\delta_1...\delta_w}(r_{qjrk}') A_{\delta_1...\delta_w:\beta}(\Omega_{rk}')$

with the notation

$c_{m...w} = \frac{1}{(2m-1)!!} \cdots \frac{1}{(2w-1)!!}$

4. Time-correlation Functions

With regard to [9]–[11], the time-correlation functions [5] take the form of a series expansion in power of the molar fractions $x_i = N_i/N$:

[12] $C^{(h)}(t) = \sum_i x_i C_i^{(h)}(t) + \sum_{ij} x_i x_j C_{ij}^{(h)}(t) + \sum_{ijk} x_i x_j x_k C_{ijk}^{(h)}(t) + \sum_{ijkl} x_i x_j x_k x_l C_{ijkl}^{(h)}(t) + ...$

with the $C_i^{(h)}(t)$, self-correlation functions, describing incoherent light scattering by statistically independent atoms or molecules. The other correlation functions $C_{ij}^{(h)}(t)$, $C_{ijk}^{(h)}(t)$, $C_{ijkl}^{(h)}(t)$ refer to binary, ternary and quaternary assemblages of molecules moving interdependently in time and space. These functions describe how $C^{(h)}(t)$ deviates from additivity and account for coherent scattering of light.

We shall now discuss the various terms of [12] for several models of molecular systems.

4.1. Statistically Independent Molecules

Excluding antisymmetric light scattering from our further considerations we obtain from [5], in the absence of all molecular correlations, the following self-correlation functions of isotropic and anisotropic scattering:

[13] $C_i^{(0)}(t)_{0,0} = 3\rho|A_i|^2 \iiint \exp[iu \cdot (r_p' - r_p^0)] G_i^{(2)}(r_p^0, r_p', \Omega_p^0) \, dr_p' \, d\Omega_p^0 \, d\Omega_p'$

[14] $C_i^{(2)}(t)_{0,0} = \frac{\rho}{3} \int \int \int \{3A_{\alpha\beta}^{(i)}(\Omega_p^0)^*A_{\alpha\beta}^{(i)}(\Omega_p') - A_{\alpha\alpha}^{(i)}(\Omega_p^0)^*A_{\beta\beta}^{(i)}(\Omega_p')\} \exp[iu \cdot (r_p' - r_p^0)]$

$\times G_i^{(2)}(r_p^0, r_p', \Omega_p^0, \Omega_p') \, dr_p' \, d\Omega_p^0 \, d\Omega$

where $G_i^{(2)}(r_p', r_p^0, \Omega_p', \Omega_p^0)$ is the generalized Van Hove space–time ordinary (self) correlation function, ρ the average number density of the fluid, and $A_i = A_{\alpha\alpha}^{(i)}/3$ the mean polarizability of a molecule of species i.

Obviously, [13] and [14] are results analogous to those derived for a one-component system (2, 39), and we shall not stop to discuss them.

4.2. Correlated Molecules without Change of Polarizability

If the molecules are correlated statistically but if we neglect the changes in their polarizabilities caused by the molecular fields (the zeroth approximation of [9]), we obtain by [5], for the distinct-correlation functions,

$$[15] \quad C_{ij}^{(0)}(t)_{0,0} = 3\rho^2 A_i{}^* A_j \int \int \int \int \exp[i\boldsymbol{u}\cdot(r_q' - r_p^0)]G_{ij}^{(2)}(r_p^0, r_q', \Omega_p^0, \Omega_q')\,dr_p^0\,dr_q'\,d\Omega_p^0\,d\Omega_q'$$

$$[16] \quad C_{ij}^{(2)}(t)_{0,0} = \frac{\rho^2}{3} \int \int \int \int \{3A_{\alpha\beta}^{(i)}(\Omega_p^0)^* A_{\alpha\beta}^{(j)}(\Omega_q') - A_{\alpha\alpha}^{(i)}(\Omega_p^0)^* A_{\beta\beta}^{(j)}(\Omega_q')\}\exp[i\boldsymbol{u}\cdot(r_q' - r_p^0)]$$
$$\times\, G_{ij}^{(2)}(r_p^0, r_q', \Omega_p^0, \Omega_q')\,dr_p^0\,dr_q'\,d\Omega_p^0\,d\Omega_q'$$

where $G_{ij}^{(2)}(r_p^0, r_q', \Omega_p^0, \Omega_q')$ is the generalized Van Hove space–time binary correlation function (40).

4.3. Dipole – Induced Dipole Approximation

We shall now consider the cross term of the (0,1) approximation: $\langle \overset{(0)}{\Pi}_{\alpha\beta}{}^{(h)}(0) * \overset{(1)}{\Pi}_{\alpha\beta}{}^{(h)}(t)\rangle$ restricting ourselves in [10] to collisions of the dipole – induced dipole type. For binary correlations, the correlation function $C_{ij}^{(h)}(t)_{0,1} = C_{ij}^{(h)}(t)_{1,0}$ has been discussed by Bancewicz (38) (see also refs. 21–25) and we shall not consider it here. We prefer to give the results for ternary molecular correlations:

$$[17] \quad C_{ijk}^{(0)}(t)_{0,1} = -\frac{\rho^3}{3}\int \cdots \int A_{\alpha\alpha}^{(i)}(\Omega_p^0)^* A_{\beta\gamma}^{(j)}(\Omega_q')A_{\delta\delta}^{(k)}(\Omega_r')T_{\gamma\delta}^{(i)}(r_{qr}')\exp[i\boldsymbol{u}\cdot(r_q' - r_p^0)]$$
$$\times\, G_{ijk}^{(3)}(r_p^0, r_q', r_r', \Omega_p^0, \Omega_q', \Omega_r')\,dr_p^0 \cdots d\Omega_r'$$

$$[18] \quad C_{ijk}^{(2)}(t)_{0,1} = -\frac{\rho^3}{3}\int \cdots \int \{3A_{\alpha\beta}^{(i)}(\Omega_p^0)^* A_{\alpha\gamma}^{(j)}(\Omega_q')A_{\delta\beta}^{(k)}(\Omega_r') - A_{\alpha\alpha}^{(i)}(\Omega_p^0)^* A_{\beta\gamma}^{(j)}(\Omega_q')A_{\delta\beta}^{(k)}(\Omega_r')\}$$
$$\times\, T_{\gamma\delta}^{(ij)}(r_{qr}')\exp[i\boldsymbol{u}\cdot(r_q' - r_p^0)]G_{ijk}^{(3)}(r_p^0, r_q', r_r', \Omega_p^0, \Omega_q', \Omega_r')\,dr_p^0 \cdots d\Omega_r'$$

where $G_{ijk}^{(3)}(r_p^0, r_q', r_r', \Omega_p^0, \Omega_q', \Omega_r')$ is the generalized Van Hove space–time ternary correlation function (3, 41), defining the probability that two molecules q_j and r_k shall be at the configurations (r_{qj}', Ω_{qj}') and (r_{rk}', Ω_{rk}') in the moment of time t under the condition that a third molecule, p_i, was in the configuration $(r_{pi}^0, \Omega_{pi}^0)$ at the moment of time $t = 0$.

Similarly, we calculate the (1,1) approximation of the function $\langle \overset{(1)}{\Pi}_{\alpha\beta}{}^{(h)}(0) * \overset{(1)}{\Pi}_{\alpha\beta}{}^{(h)}(t)\rangle$, which splits into the binary contribution $C_{ij}^{(h)}(t)_{1,1}$ and ternary contribution $C_{ijk}^{(h)}(t)_{1,i}$ discussed previously for various models (7, 21, 36), and quaternary contributions of the following form:

$$[19] \quad C_{ijkl}^{(0)}(t)_{1,1} = \frac{\rho^4}{3}\int \cdots \int A_{\alpha\gamma}^{(i)}(\Omega_p^0)^* A_{\beta\epsilon}^{(j)}(\Omega_q')A_{\delta\alpha}^{(k)}(\Omega_r^0)^* A_{\eta\beta}^{(l)}(\Omega_s')T_{\gamma\delta}^{(ik)}(r_{pr}^0)^* T_{\epsilon\eta}^{(jl)}(r_{qs}')$$
$$\times\, \exp[i\boldsymbol{u}\cdot(r_q' - r_p^0)]G_{ijkl}^{(4)}(r_p^0, r_q', r_r^0, r_s', \Omega_p^0, \Omega_q', \Omega_r^0, \Omega_s')\,dr_p^0 \cdots d\Omega_s'$$

$$[20] \quad C_{ijkl}^{(2)}(t)_{1,1} = \frac{\rho^4}{3}\int \cdots \int A_{\alpha\gamma}^{(i)}(\Omega_p^0)^*\{3A_{\alpha\epsilon}^{(j)}(\Omega_q')A_{\delta\beta}^{(k)}(\Omega_r^0)^* - A_{\beta\epsilon}^{(j)}(\Omega_q')A_{\delta\alpha}^{(k)}(\Omega_r^0)^*\}$$
$$\times\, A_{\eta\beta}^{(l)}(\Omega_s')T_{\gamma\delta}^{(ik)}(r_{pr}^0)^* T_{\epsilon\eta}^{(jl)}(r_{qs}')\exp[i\boldsymbol{u}\cdot(r_q' - r_p^0)]G_{ijkl}^{(4)}(r_p^0, r_q', r_r^0, r_s', \Omega_p^0, \Omega_q', \Omega_r^0, \Omega_s')$$
$$\times\, dr_p^0 \cdots d\Omega_s'$$

where $G_{ijkl}^{(4)}(r_p^0, r_q', r_r^0, r_s', \Omega_p^0, \Omega_q', \Omega_r^0, \Omega_s')$ is the generalized Van Hove space–time quaternary correlation function defined in (3, 42).

In order to achieve complete results in this approximation we still have to reach back to the second-order perturbation of [11] and calculate contributions of the type $\langle \overset{(0)}{\Pi}_{\alpha\beta}{}^{(h)}(0) * \overset{(2)}{\Pi}_{\alpha\beta}{}^{(h)}(t)\rangle$ and $\langle \overset{(2)}{\Pi}_{\alpha\beta}{}^{(h)}(0) * \overset{(0)}{\Pi}_{\alpha\beta}{}^{(h)}(t)\rangle$ discussed previously for integral scattering (7).

4.4. Dipole – Induced Quadrupole Approximation

In the expansion [10] we now have recourse to the terms related with the third-rank tensors $A_{\gamma:\alpha\beta}$ and $A_{\alpha\beta:\gamma}$ describing dipole–quadrupole and quadrupole–dipole polarizabilities respectively. For the correlation functions [5] and in the approximation (0,1) we now obtain:

$$[21] \quad C^{(0)}(t)_{0,1} = \frac{1}{9} \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r \neq q}^{N_k} A_{\alpha\alpha}(\Omega_{pi}{}^0)^* [A_{\beta\gamma}(\Omega_{qj}{}') A_{\delta\epsilon:\beta}(\Omega_{rk}{}') - A_{\beta:\gamma\delta}(\Omega_{qj}{}') A_{\epsilon\beta}(\Omega_{rk}{}')] T_{\gamma\delta\epsilon}(r_{qjrk}{}') \right.$$
$$\left. \times \exp[i\boldsymbol{u}\cdot(\boldsymbol{r}_{qj}{}' - \boldsymbol{r}_{pi}{}^0)] \right\rangle$$

$$[22] \quad C^{(2)}(t)_{0,1} = \frac{1}{9} \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r \neq q}^{N_k} \{ 3A_{\alpha\beta}(\Omega_{pi}{}^0)^* [A_{\alpha\gamma}(\Omega_{qj}{}') A_{\delta\epsilon:\beta}(\Omega_{rk}{}') - A_{\alpha:\gamma\delta}(\Omega_{qj}{}') A_{\epsilon\beta}(\Omega_{rk}{}')] \right.$$
$$\left. - A_{\alpha\alpha}(\Omega_{pi}{}^0)^* [A_{\beta\gamma}(\Omega_{qj}{}') A_{\delta\epsilon:\beta}(\Omega_{rk}{}') - A_{\beta:\gamma\delta}(\Omega_{qj}{}') A_{\epsilon\beta}(\Omega_{rk}{}')] \} T_{\gamma\delta\epsilon}(r_{qjrk}{}') \exp[i\boldsymbol{u}\cdot(\boldsymbol{r}_{qj}{}' - \boldsymbol{r}_{pi}{}^0)] \right\rangle$$

As above, we can decompose the functions [21] and [22] into binary components $C_{ij}{}^{(h)}(t)_{0,1}$ and ternary components $C_{ijk}{}^{(h)}(t)_{0,1}$, which play a very important role with regard to molecules possessing an intrinsic electric dipole or quadrupole and contribute proportionally to $\langle r_{ij}{}^{-8} \rangle$ (see ref. 20). The relevance of the functions [21] and [22] consists in the fact that they contain the dipole–quadrupole polarizability tensors $A_{\gamma:\alpha\beta}$ and $A_{\alpha\beta:\gamma}$ in the first power, in contradistinction to the (1.1) contribution $C^{(h)}(t)_{1,1}$, which contains products of these tensors. The effect of the latter approximation on binary collisional scattering of light by tetrahedral molecules has been discussed recently by Buckingham and Tabisz (17) and Posch (18) (see also ref. 19). For molecules of arbitrary symmetry, these contributions in relation to binary and ternary collisions have been calculated recently for integral scattering (20) together with a higher approximation of the type (0, 2), based on the expansion [11]. We refrain from writing here the explicit form of the correlation functions $C^{(h)}(t)_{1,1}$ and $C^{(h)}(t)_{0,2} = C^{(h)}(t)_{2,0}$ or their contributions, proportional to $\langle r_{ij}{}^{-8} \rangle$ and $\langle r_{ij}{}^{-4} r_{jk}{}^{-4} \rangle$, to the expansion [12].

4.5. Quadrupole–Quadrupole Polarizability Effect

In the case of centrosymmetric molecules the dipole–quadrupole polarizability tensor components $A_{\alpha:\beta\gamma}$ vanish. As a consequence of this, for such molecules (atoms), the nonvanishing quadrupole–quadrupole polarizability tensors $A_{\alpha\beta:\gamma\delta}$ occurring in the second perturbation [11] for $m = w = 1$ and $n = u = 2$ become very important. The correlation functions [5] now become

$$[23] \quad C^{(0)}(t)_{0,2} = -\frac{1}{27} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r \neq q}^{N_k} \sum_{s \neq r}^{N_l} A_{\alpha\alpha}(\Omega_{pi}{}^0)^* A_{\beta\gamma}(\Omega_{qj}{}') A_{\delta\epsilon:\eta\lambda}(\Omega_{rk}{}') A_{\mu\beta}(\Omega_{sl}{}') \right.$$
$$\left. \times T_{\gamma\delta\epsilon}(r_{qjrk}{}') T_{\eta\lambda\mu}(r_{rksl}{}') \exp[i\boldsymbol{u}\cdot(\boldsymbol{r}_{qj}{}' - \boldsymbol{r}_{pi}{}^0)] \right\rangle$$

$$[24] \quad C^{(2)}(t)_{0,2} = -\frac{1}{27} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r \neq q}^{N_k} \sum_{s \neq r}^{N_l} \{ 3A_{\alpha\beta}(\Omega_{pi}{}^0)^* A_{\alpha\gamma}(\Omega_{qj}{}') - A_{\alpha\alpha}(\Omega_{pi}{}^0) A_{\beta\gamma}(\Omega_{qj}{}') \} A_{\delta\epsilon:\eta\lambda}(\Omega_{rk}{}') A_{\mu\beta}(\Omega_{sl}{}') \right.$$
$$\left. \times T_{\gamma\delta\epsilon}(r_{qjrk}{}') T_{\eta\lambda\mu}(r_{rksl}{}') \exp[i\boldsymbol{u}\cdot(\boldsymbol{r}_{qj}{}' - \boldsymbol{r}_{pi}{}^0)] \right\rangle$$

In particular, for atoms, the correlation function of anisotropic light scattering [24] vanishes whereas that of isotropic scattering [23] reduces to:

$$[25] \quad C^{(0)}(t)_{0,2} = -\frac{1}{9} \sum_{ijkl} A_i{}^* A_j Q_k A_l \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r \neq q}^{N_k} \sum_{s \neq r}^{N_l} T_{\alpha\beta\gamma}(r_{qjrk}{}') T_{\alpha\beta\gamma}(r_{rksl}{}') \exp[i\boldsymbol{u}\cdot(\boldsymbol{r}_{qj}{}' - \boldsymbol{r}_{pi}{}^0)] \right\rangle$$

where $Q_k = A_{\alpha\beta:\alpha\beta}{}^{(k)}/5$ is the mean quadrupole–quadrupole polarizability of an atom of the species k.

The correlation functions [23]–[25] give binary, ternary, and quaternary contributions to the expansion [12] proportional, respectively, to the statistical averages $\langle r_{ij}{}^{-8} \rangle$ and $\langle r_{ij}{}^{-4} r_{jk}{}^{-4} \rangle$. Characteristically, these functions contain the quadrupole–quadrupole polarizability in the first power thus permitting the determination of its sign.

4.6. Dipole–Octupole Polarizability Effect

Finally, we shall consider the effect due to terms of [10] with $m = 1$, $n = 3$ and $m = 3$, $n = 1$, related with the tensors $A_{\delta:\alpha\beta\gamma}$ and $A_{\alpha\beta\gamma:\delta}$ of dipole–octupole and octupole–dipole polarizability. In the $(0, 1)$ approximation the correlation functions now assume the form:

$$[26] \quad C^{(0)}(t)_{0,1} = -\frac{1}{45} \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r \neq q}^{N_k} A_{\alpha\alpha}(\Omega_{pi}{}^0)^* \{ A_{\beta\gamma}(\Omega_{qj}{}')A_{\delta\epsilon\eta:\beta}(\Omega_{rk}{}') + A_{\beta:\gamma\delta\epsilon}(\Omega_{qj}{}')A_{\eta\beta}(\Omega_{rk}{}') \} \right.$$

$$\left. \times\ T_{\gamma\delta\epsilon\eta}(r_{qjrk}{}')\ \exp\left[i\boldsymbol{u}\cdot(r_{qj}{}' - r_{pi}{}^0)\right] \right\rangle$$

$$[27] \quad C^{(2)}(t)_{0,1} = -\frac{1}{45} \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r \neq q}^{N_k} \{ 3A_{\alpha\beta}(\Omega_{pi}{}^0)^*[A_{\alpha\gamma}(\Omega_{qj}{}')A_{\delta\epsilon\eta:\beta}(\Omega_{rk}{}') + A_{\alpha:\gamma\delta\epsilon}(\Omega_{qj}{}')A_{\eta\beta}(\Omega_{rk}{}')] \right.$$

$$\left. -\ A_{\alpha\alpha}(\Omega_{pi}{}^0)^*[A_{\beta\gamma}(\Omega_{qj}{}')A_{\delta\epsilon\eta:\beta}(\Omega_{rk}{}') + A_{\beta:\gamma\delta\epsilon}(\Omega_{qj}{}')A_{\eta\beta}(\Omega_{rk}{}')] \}\ T_{\gamma\delta\epsilon\eta}(r_{qjrk}{}')\ \exp\left[i\boldsymbol{u}\cdot(r_{qj}{}' - r_{pi}{}^0)\right] \right\rangle$$

These functions give nonzero contributions for an appropriately chosen distribution function, e.g., involving electrostatic intrinsic quadrupole–quadrupole interaction, when [27] contributes proportionally to $\langle r_{ij}{}^{-10}\rangle$ for binary correlations.

Since [26] and [27] contain the tensors $A_{\delta:\alpha\beta\gamma}$ and $A_{\alpha\beta\gamma:\delta}$ in the first power, we are able to determine their sign. By analogy, a discussion can be carried out for the $(1, 1)$ approximation, involving products of the tensors $A_{\delta:\alpha\beta\gamma}$ and $A_{\alpha\beta\gamma:\delta}$, as done by Buckingham and Tabisz (17) for octahedral molecules.

5. Discussion and Conclusions

The time-correlation functions [12]–[27] derived above have now to be applied to the concrete experimental situations one deals with in spectral and integral observations of scattered light. This is a rather straightforward procedure, consisting, in each case, in the determination of the form of the multipole polarizability tensors occurring in the expansions [10] and [11] for various molecular (point group) symmetries, and in the calculation of the analytical shape of the many-body correlation functions. It can be performed in Cartesian basis (29) or by having recourse to the formalism of spherical tensors (43). The latter representation is highly advantageous, the irreducible representation of spherical tensors of arbitrary order (3, 44) leading to final results of great clarity. However, it was not our aim to give here that complete, mathematically complex analysis of the correlation functions [12]–[27]; nonetheless, their practical value when it comes to gaining a complete, uniform description of light scattering experiments (9–12, 16–19, 25–27) is worth stressing.

One notes immediately from the general outline of our theory that, besides the hitherto considered correlation functions $C^{(h)}(t)_{1,1}$ in the $(1, 1)$ approx-

imation, an essential role belongs to the cross correlation functions $C^{(h)}(t)_{0,1} = C^{(h)}(t)_{1,0}$ and $C^{(h)}(t)_{0,2} = C^{(h)}(t)_{2,0}$ which, for certain molecular models, give not only numerical contributions to integral scattering, but moreover, additional contributions to the rotational structure of the scattered light spectrum.

Especially noteworthy is the circumstance that, on taking into account the changes in molecular polarizabilities caused by the electric fields of induced multipoles [7], the isotropic scattering is found to possess a spectral structure, related not only with translational but also with orientational motions as has been proved beyond doubt by us (45) for Raman spectra in the DID approximation.

Interesting results are obtained when applying the new correlation functions [17]–[27] derived by us to mixtures of two and three components, one of which consists of atoms and the others of simple axially symmetric molecules (N_2, CO_2), tetrahedral molecules (CH_4), or octahedral ones (SF_6). In this case the spectral structure is described by novel radial-angular functions, differing from those analyzed hitherto and expressed by Legendre polynomials (46).

As to the stochastic aspect of our approach, it involves generalized Van Hove many-body space-time correlation functions $G_{ij}{}^{(2)}$, $G_{ijk}{}^{(3)}$, $G_{ijkl}{}^{(4)}$, ... and thus provides new information concerning them and their relation to the equilibrium many-body correlation functions (3). In this way, similar to intermolecular infrared spectroscopy (47), intermolecular Rayleigh and Raman spectroscopy becomes a strong tool for investigations leading beyond the structure of individual atoms and molecules into the domain of their translational and rotational motions as well as their many-body collisional effects.

1. I. L. FABELINSKII. Molecular scattering of light. Plenum Press, New York, NY. 1968.
2. A. BEN-REUVEN and N. D. GERSHON. J. Chem. Phys. 51, 893 (1969).
3. S. KIELICH. Molecular nonlinear optics. Izd. Nauka, Moscow, U.S.S.R. 1981.
4. J. YVON. La propagation et la diffusion de la lumiére. Actualités Scientifiques et Industrielles. No. 543. Herman et Cie, Paris, France. 1937.
5. R. K. BULLOUGH. Philos. Trans. R. Soc. London, Ser. A, 254, 397 (1962).
6. S. KIELICH. Mol. Phys. 9, 549 (1965); Acta Phys. Pol. 27, 305 (1965); 28, 459 (1965).
7. S. KIELICH. Chem. Phys. Lett. 10, 516 (1971); J. Phys. 29, 619 (1968).
8. R. A. PASMANTER, R. SAMSON, and A. BEN-REUVEN. Phys. Rev. A, 14, 1238 (1976).
9. M. THIBEAU, G. C. TABISZ, B. OKSENGORN, and B. VODAR. J. Quant. Spectrosc. Radiat. Transfer. 10, 839 (1970); C. G. GRAY and H. I. RALPH. Phys. Lett. A, 33, 165 (1970); J. P.McTAGUE and G. BIRNBAUM. Phys. Rev. A, 3, 1376 (1971); H. I. RALPH and C. G. GRAY. Mol. Phys. 27, 1683 (1974).
10. M. BÉRARD and P. LALLEMAND. Mol. Phys. 34, 251 (1977); B. J. ALDER, J.C. BEERS, H. L. STRAUSS, and J. J. WEIS. J. Chem. Phys. 70, 4091 (1979); Y. LE DUFF. Phys. Rev. A, 20, 48 (1979).
11. F. BAROCCHI and M. ZOPPI. Phys. Lett. A, 69, 187 (1978); U. BALUCANI, V. TOGNETTI, and R. VALLAURI. Phys. Rev. A, 19, 177 (1979); L. FROMMHOLD and M. H. PROFFITT. Mol. Phys. 35, 681 (1978).
12. S. C. AN, L. FISHMAN, T. A. LITOVITZ, C. J. MONTROSE, and H. A. POSCH. J. Chem. Phys. 70, 4626 (1979); A. J. C. LADD, T. A. LITOVITZ, and C. J. MONTROSE. J. Chem. Phys. 71, 4242 (1979).
13. H. M. BOOTS, D. BEDEAUX, and P. MAZUR. Physica A, 79, 397 (1975).
14. T. KEYES, B. M. LADANYI, and P. A. MADDEN. Chem. Phys. Lett. 64, 479 (1979).
15. W. M. GELBART. Philos. Trans. R. Soc. London, Ser. A, 293, 359 (1979).
16. F. BAROCCHI, M. ZOPPI, D. P. SHELTON, and G. C. TABISZ. Can. J. Phys. 55, 1962 (1977); F. D. MADINA and W. B. DANIELS. Phys. Rev. A, 17, 1474 (1978).
17. A. D. BUCKINGHAM and G. C. TABISZ. Mol. Phys. 36, 583 (1978).
18. H. A. POSCH. Mol. Phys. 37, 1059 (1979).
19. D. P. SHELTON and G. C. TABISZ. Mol. Phys. 40, 285 (1980); 40, 299 (1980).
20. S. KIELICH. Opt. Commun. 34, 367 (1980).
21. S. KIELICH. Acta Phys. Pol. 19, 711 (1960).
22. S. KIELICH, J. R. LALANNE, and F. B. MARTIN. J. Phys. 33, C1-191 (1972).

23. T. KEYES, D. KIVELSON, and J. P.McTAGUE. J. Chem. Phys. 55, 4096 (1971).
24. T. KEYES and B. M. LADANYI. Mol. Phys. 33, 1099 (1977).
25. D. FRENKEL and J. P. McTAGUE. J. Chem. Phys. 72, 2801 (1980).
26. G. R. ALMS, T. D. GIERKE, and W. H. FLYGARE. J. Chem. Phys. 61, 4083 (1974).
27. D. R. BAUER, J. I. BRAUMAN, and R. PECORA. J. Chem. Phys. 63, 53 (1975).
28. S. WOŹNIAK and S.KIELICH. J. Phys. 36, 1305 (1975).
29. S. KIELICH. Dielectric and related molecular processes. Vol. 1. Edited by M. Davies. Chemical Society of London, Engl. 1972. Chapt. 7.
30. M. R. BATTAGLIA, T. I. COX, and P. A. MADDEN. Mol. Phys. 37, 1413 (1979).
31. P. P. HO and R. R. ALFANO. Phys. Rev. A, 20, 2170 (1979).
32. A. K. BURNHAM, G. R. ALMS, and W. H. FLYGARE. J. Chem. Phys. 62, 3289 (1975).
33. D. E. SULLIVAN and J. M. DEUTCH. J. Chem. Phys. 64, 3870 (1976).
34. G. J. GABRIEL. Phys. Rev. A, 8, 963 (1973).
35. S. KIELICH. Acta Phys. Pol. 33, 63 (1968).
36. S. KIELICH and S. WOŹNIAK. Acta Phys. Pol. A, 45, 163 (1974); S. WOŹNIAK and S. KIELICH. Acta Phys. Pol. A, 52, 863 (1977).
37. K. KNAST and S. KIELICH. Acta Phys. Pol. A, 55, 319 (1979).
38. T. BANCEWICZ. Acta Phys. Pol. A, 56, 431 (1979).
39. L. A. NAFIE and W. L. PETICOLAS. J. Chem. Phys. 57, 3145 (1972).
40. W. A. STEELE and R. PECORA. J. Chem. Phys. 42, 1863 (1965).
41. P. A.EGELSTAFF. C. G. GRAY, and K. E. GUBBINS. Phys. Lett. A, 37, 321 (1971); K. E. GUBBINS, C. G. GRAY, and P. A. EGELSTAFF. Mol. Phys. 35, 315 (1978).
42. J. D. POLL. Proc. Int. School of Physics "Enrico Fermi", 1978. Course 75. Intermolecular spectroscopy. Edited by J. Van Kranendonk. North-Holland. 1980. p. 45; K. KNAST, W. CHMIELOWSKI, and S. KIELICH. Proc. Int. Conference Lasers '79, Orlando, Florida, USA. Edited by V. J. Corcoran. STS Press. McLean, VA. 1980. p. 304.
43. C. G. GRAY and B. W. N. LO. Chem. Phys. 14, 73 (1976).
44. Z. OŻGO and S. KIELICH. Physica, 72, 191 (1974); Physica C, 81, 151 (1976); J. JERPHAGNON, D. CHEMLA, and R. BONNEVILLE. Adv. Phys. 27, 609 (1978).
45. T. BANCEWICZ and S. KIELICH. Proceedings VIIth Int. Conf. Raman Spectroscopy. Ottawa, Ont. 1980. Edited by W. F. Murphy. North Holland. Amsterdam. 1980. p. 290; J. Chem. Phys. 75, 107 (1981).
46. J. S. HØYE and G. STELL. J. Chem. Phys. 66, 795 (1977).
47. J. VAN KRANENDONK. Physica, 73, 156 (1974).