

Intermolecular light scattering

STANISŁAW KIELICH

Nonlinear Optics Division, Institute of Physics, A. Mickiewicz University, Grunwaldzka 6,
60-780 Poznań, Poland.

1. Introduction

The theoretical foundations of molecular light scattering are due to the insight of Lord Rayleigh, Smoluchowski and Einstein. The subject has since been dealt with in a number of monographs (Cabannes 1929; Born 1933; Fabelinskii 1968; Crosignani *et al* 1975; Berne and Pecora 1976; Long 1977; Kielich 1981). The scientific relevance of elastic light scattering resides in the ease with which it permits the elucidation of the molecular-statistical structure of matter.

1.1 *Studies of integral light scattering*

As predicted by Lord Rayleigh, light scattering by gases and rarefied systems is a source of information regarding the electronic structure of the individual atoms and molecules. The fundamental results of Smoluchowski (1908) and Einstein (1910) have disclosed the stochastic mechanisms of light scattering consisting of spontaneous fluctuations in number density or concentration as well as those of other thermodynamical properties. The fluctuations are generally isotropic in nature; hence, the light scattering process too is isotropic, conserving not only the frequency of the incident light wave, but also its state of polarisation.

Depolarisation of scattered light is caused essentially by anisotropic fluctuations. According to Born (1933) and Cabannes (1929), such fluctuations are due to intrinsic anisotropy of the optical polarizability of the molecules or, after Yvon (1936, 1937), to anisotropy induced in the polarizability of correlated atoms (see Fixman 1955; Theimer and Paul 1965; Macrakis 1967). In a given thermodynamical state of the substance, the two preceding mechanisms leading to anisotropic light scattering are modified by angular correlations between the molecules (Benoit and Stockmayer 1956; Kielich 1958, 1960a).

According to Yvon (1937), statistical translational fluctuations of the dipolar type modify the polarizability of an atom in a fluid causing it to become a function of the density as the result of two- and three-body radial correlations. In addition to these modifications due to long-range forces (Mazur and Mandel 1956; Linder and Kromhout 1970; Frommhold and Proffitt 1978), one generally has to deal with changes in the polarizability of a pair of atoms caused by a short-range overlap effect (Levine and Birnbaum 1971; Lim *et al* 1970; O'Brien *et al* 1973; Oxtoby and Gelbart 1975; Hilton and Oxtoby 1981). These binary collision-induced variations in polarizability of the atoms lead to collision-induced light scattering as first observed by Thibeau *et al* (1968) and by McTague and Birnbaum (1968, 1971). This new kind of collisional

scattering by gases will be considered briefly, since reviews on the subject have been written recently by Gelbart (1974), Knaap and Lallemand (1975), Tabisz (1979), and Frommhold (1981).

When Yvon's theory is extended to molecules having intrinsic optical anisotropy, orientational as well as cross translational-orientational fluctuations have to be taken into account, considerably affecting the depolarisation of scattered light (Kielich 1960a,b, 1968a,b, 1971a,b). In the case of polar molecules, agreement between theory and experiment can be enhanced by taking into consideration angular dispersive, electrostatic and inductive binary and ternary interactions (Kielich 1967, 1968a,b; Kielich *et al* 1972; Kielich and Woźniak 1974; Woźniak and Kielich 1975, 1977).

In recent years, numerous authors have discussed anew the applicability of the dipolar approximation of the electric molecular field and its utility for the interpretation of the newest experimental observations of scattered light in dense fluids (Felderhof 1974; Ladanyi and Keyes 1976, 1977a,b, 1978; Keyes 1979).

Moreover, the scattered light intensity has been studied though its dependence on the local field model (Kielich and Pieczyńska 1970; Burnham *et al* 1975; Sullivan and Deutch 1976; Keyes and Ladanyi 1977; Ladanyi and Keyes 1979; Breuer 1980) and multiple scattering (Frisch and McKenna 1965; Boots *et al* 1975; Gelbart 1979; Keyes *et al* 1979; Hynne 1980).

Undeniably, with regard to atomic gases, the electric-dipole approximation suffices to achieve an acceptable degree of accordance with experiment though *e.g.* for helium gas considerable discrepancies (Barocchi *et al* 1978) and good agreement (Le Duff 1979) have both been reported. However, this is no longer the case when one deals with molecular substances, and higher multipole contributions from the molecular electric field, causing additional variations of the molecular polarizability, have to be included in the calculations. This has first been done by Bullough (1962) for molecular refraction and by Kielich (1965a,b) for distortional electric polarization and more recently, for light scattering, by Pasmanter *et al* (1976) and Kielich (1980). In general, one cannot neglect the contributions from nonlinear multipole polarizabilities (Kielich 1965b, 1980; Hunt 1980; Hunt K L C, Zilles B A and Bohr J E 1981, private communication).

1.2 Studies of spectral light scattering

Beside the integral intensity studies touched on in the preceding sections dealing with the influence of molecular correlations on the process of light scattering, recent years have witnessed rapid progress in the domain of the spectral distribution of scattered light. Thus, beside intermolecular infrared absorption spectroscopy (Van Kranendonk 1974), a new field of intermolecular scattering spectroscopy has arisen (Van Kranendonk 1980) and become a source of valuable information concerning, in addition to translational and rotational motions of the individual molecules, the dynamics of momentary assemblages of molecules correlated in time and space.

The stochastic foundations of the spectral theory of light scattering are, in fact, those of Van Hove's (1954) and Vineyard's (1958) theory of neutron scattering by atomic fluids (Powles 1973; Copley and Lovesey 1975) extended by Steele and Pecora (1965) to the case of x-ray and slow neutron scattering from fluids composed of non-spherical molecules. Here, the problem consists in the formulation of one-, two- and many-body space-time correlation functions, permitting the determination of the dynamical fluctuations in number density, the stochastic treatment of which is due to

Smoluchowski (1906, 1915) in his kinetic theory of translational Brown motions, and has been extended by Chandrasekhar (1943) and Kac (1959) and, more recently, by Brenner *et al* (1978). Besides the kinetic-microscopic treatment of light scattering (Gabriel 1973), thermodynamical-hydrodynamical approaches also exist (Mountain 1977); the two points of view merge in the general theory of irreversible processes, proposed by Mori (1965).

The detailed studies of Starunov *et al* (1967) as well as Stegeman and Stoicheff (1968), of the fine structure of the lines of light scattered from a laser beam in molecular liquids, have disclosed the presence of a doublet in the depolarized part of the spectrum. Laser spectroscopy has made it possible to carry out precise observations of the doublet in the scattered spectrum in numerous liquids consisting of optically anisotropic molecules. For an extensive discussion of these studies we refer the reader to the monographs by Fabelinskii (1968) and Atakhodzhayev and Tukhvatulin (1981) and the reviews by Fleury and Boon (1973) and Ytarova (1980); also, we refer to the experimental results of Stegeman and Stoicheff (1973), Alms *et al* (1973a,b), Dardy *et al* (1973), Bruining and Clarke (1976), and Fröhlich and Posch (1978).

According to the thermodynamical theory of Leontovich (1941) and Rytov (1957), the occurrence of the Rayleigh wing and its doublet is due to light scattering on fluctuations of anisotropy and on deformations of shearing waves in liquids. Starunov and Fabelinskii (1974) have performed an analysis of the complete structure of the scattered light spectrum on the basis of Rytov's theory (1970), involving two anisotropy relaxation times.

Ben-Reuven and Gershon (1969) have formulated a molecular-statistical spectral theory and have applied it in their description of the depolarisation of the Rayleigh line wing on the microscopic level. Other forms of the theory have been proposed by Anderson and Pecora (1971), Keyes and Kivelson (1971, 1972) and Gierke (1976). In liquids, rotational molecular motion is dependent on correlations between the molecules and, in accordance with the Keyes-Kivelson theory, the reorientational relaxation time in the presence of binary correlations, τ_c , is related to the uncorrelated single-particle reorientational time τ_s , as follows:

$$\frac{\tau_c}{\tau_s} = \frac{1 + fN}{1 + gN},$$

where f and g are, respectively, the static and dynamic pair orientational correlations parameters. The above relationship is the subject of numerous studies (Bauer *et al* 1974, 1975; Patterson and Griffiths 1975; Wang *et al* 1976; Cheung *et al* 1976; Rouch *et al* 1976; Jones and Wang 1977; Alms and Patterson 1978; Higashigaki *et al* 1978; Perrot *et al* 1978; Lund *et al* 1979; Hilbert *et al* 1979; Cox *et al* 1979).

The effect of molecular fields on the spectral distribution has also been discussed (Hellwarth 1970; Keyes *et al* 1971; Keyes and Ladanyi 1977; Bancewicz 1979), as well as that of angular correlations (Knast and Kielich 1979; Głaz 1981) and other mechanisms (Bucaro and Litovitz 1971; Van Konynenburg and Steele 1972; Dill *et al* 1975; Rosenthal and Strauss 1976; Bancewicz and Kielich 1981).

Also, spectral research has proceeded in simple gases under pressure (Thibeau *et al* 1970; Keijser *et al* 1974; Berrue *et al* 1976; Madden 1978; Medina and Daniels 1978; Alder *et al* 1979; Ladd *et al* 1979; Posch 1979, 1980; Ghaem-Maghani and May 1980; Guillot *et al* 1980; De Santis *et al* 1980; Medina 1981), in atomic liquids and ones composed of spherical-top molecules (McTague *et al* 1969; Fleury and McTague 1969;

Gornal *et al* 1970; Ho and Tabisz 1973; Schoen *et al* 1975; Posch and Litovitz 1976; Ladd *et al* 1980; Varshneya *et al* 1981), and in liquid mixtures (Tabisz *et al* 1972; Ackerson and Hanley 1980).

1.3 Outline of the present review

The above is ample evidence that theoretical and experimental work on light scattering in atomic and molecular media proceeds untiringly and that the number of papers and communications on its various aspects is increasing. Since some results are still theoretically and experimentally controversial, there is an urgent need for a comprehensive, general theory of light scattering well suited to concrete situations in which various molecular correlations are apparent. Accordingly, we shall attempt to propose a uniform though rather formal approach to the foundations of integral and spectral scattering theory. To insure generality and compactness of the mathematics, we shall essentially make use of Cartesian tensor formalism in the approach initiated by Jansen (1958) in his theory of electrostatic multipole interactions and extended by others (Kielich 1965a–f, 1966a, b; De Groot 1969; Stogryn 1971, 1972).

Similarly, as in the complete electromagnetic theory of the refractive index (Vezzetti and Keller 1967; Kielich 1965c, 1966a) and optical activity (Kielich 1975), we consider in general, multipolar electric and magnetic scattering processes separating the intensities into irreducible isotropic, antisymmetric and anisotropic parts. With this aim, we give a systematically developed theory of interactions between electric and magnetic multipoles and external as well as internal electromagnetic fields. This enables us to determine generally the changes in multipolar electric and magnetic polarizabilities of molecules induced by space- and time-fluctuations of the multipole fields. These changes, resulting in general from many-body correlations, are determined by the perturbation method. The procedure outlined permits the calculation of pure contributions of the type 00, 11, 22, 33 etc. and, moreover, of cross contributions 01, 02 and so forth to the scattered light intensity. Especially relevant to antisymmetric scattering are the mixed electro-magnetic and magneto-electric multipolar polarizabilities. In addition to this direct influence of molecular correlations, light scattering is indirectly dependent on them by way of the statistical distribution function, permitting the determination of the mean scattered intensity. These indirect temperature-dependent contributions are calculated by thermodynamical perturbation calculus. The results are expressed in a notation applicable to systems of N like, as well as N unlike scattering centres.

2. Interaction of electric and magnetic multipoles with electromagnetic field

We consider an assembly of N interacting microsystems (atoms, molecules or ions) subjected to an electromagnetic field with electric and magnetic vectors at the position \mathbf{r} and time t :

$$\mathbf{E}(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}(\mathbf{r}, t) - \nabla \Phi(\mathbf{r}, t),$$

$$\mathbf{H}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t), \quad (1)$$

where $\Phi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ are the scalar and vector potentials at the space-time point (\mathbf{r}, t) and ∇ is the derivation operator.

Let the i th microsystem consist of n_i point particles (nuclei and electrons) with electric charges e_{si} , masses m_{si} and positional vectors \mathbf{R}_{si} ($s = 1, 2, \dots, n_i$, $i = 1, 2, \dots, N$). For convenience, we introduce the set of independent coordinates

$$\mathbf{r}_i = \sum_s m_{si} \mathbf{R}_{si} / \sum_s m_{si} \quad \text{and} \quad \mathbf{r}_{si} = \mathbf{R}_{si} - \mathbf{r}_i, \quad (2)$$

where \mathbf{r}_{si} is the (relative) position vector of the s th particle with respect to the center of mass of the microsystem i whose position is \mathbf{r}_i (figure 1).

The Hamiltonian of the spinless microsystem i , in the nonrelativistic classical case, is (Heitler 1954):

$$H_i = \sum_{s=1}^{n_i} \left\{ e_{si} \Phi(\mathbf{R}_{si}, t) + \frac{1}{2c^2 m_{si}} [c \mathbf{p}_{si} - e_{si} \mathbf{A}(\mathbf{R}_{si}, t)]^2 \right\}, \quad (3)$$

in which \mathbf{p}_{si} is the generalized momentum operator of the s th particle of the microsystem i .

The total Hamiltonian of an assembly of N microsystems is

$$HN = \sum_{i=1}^N H_i. \quad (4)$$

The Hamiltonian (3) can, in the well known manner, be resolved into a nonperturbed part $H_i^{(0)}$ and perturbed Hamiltonians of the first and second order of the form

$$H_i^{(1)} = -\frac{1}{2c} \sum_{s=1}^{n_i} \frac{e_{si}}{m_{si}} [\mathbf{p}_{si} \cdot \mathbf{A}(\mathbf{R}_{si}, t) + \mathbf{A}(\mathbf{R}_{si}, t) \cdot \mathbf{p}_{si}] + \sum_{s=1}^{n_i} e_{si} \Phi(\mathbf{R}_{si}, t), \quad (5)$$

$$H_i^{(2)} = \frac{1}{2c^2} \sum_{s=1}^{n_i} \frac{e_{si}^2}{m_{si}} \mathbf{A}(\mathbf{R}_{si}, t) \cdot \mathbf{A}(\mathbf{R}_{si}, t). \quad (6)$$

In the general case when the scalar and vector potentials are not constant within the region of the microsystem (the field is generally nonhomogeneous throughout

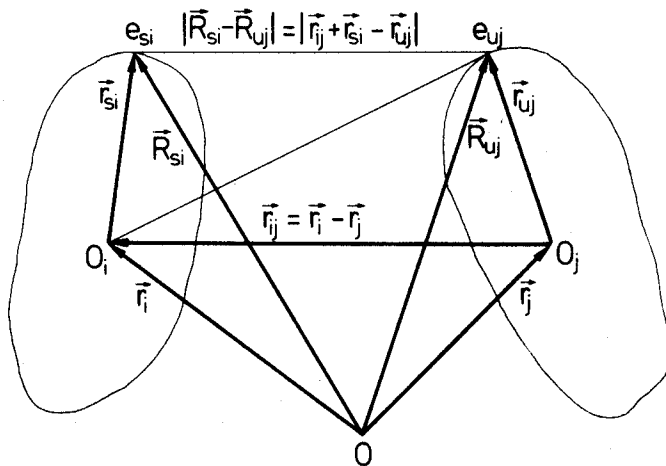


Figure 1. Interaction of two non-overlapping microsystems i and j separated by the vector distance $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and of linear dimensions very small compared with the distances $|\mathbf{r}_i| \gg |\mathbf{r}_{si}|$ and $|\mathbf{r}_j| \gg |\mathbf{r}_{sj}|$ at which the electric field is studied.

the region of a microsystem), one can expand $\Phi(\mathbf{R}_{si}, t)$ and $\mathbf{A}(\mathbf{R}_{si}, t)$ in series in powers of $\vec{\mathbf{r}}_{si}$ ($|\mathbf{r}_{si}| \ll |\mathbf{r}_i|$):

$$\begin{aligned}\Phi(\mathbf{r}_i + \mathbf{r}_{si}, t) &= \sum_{n=0}^{\infty} \frac{1}{n!} \mathbf{r}_{si}^n [n] \nabla_i^n \Phi(\mathbf{r}_i, t), \\ \mathbf{A}(\mathbf{r}_i + \mathbf{r}_{si}, t) &= \sum_{n=0}^{\infty} \frac{1}{n!} \mathbf{r}_{si}^n [n] \nabla_i^n \mathbf{A}(\mathbf{r}_i, t),\end{aligned}\quad (7)$$

where the symbol $[n]$ in Jansen's (1958) notation denotes n -fold scalar contraction of the product of two n th rank vectors \mathbf{r}_{si}^n and ∇_i^n .

By the expansions (7), the first-order perturbation Hamiltonian (5) can be represented in the form of a multipole expansion (Kielich 1966a):

$$\begin{aligned}H_i^{(1)} &= \sum_{s=1}^{n_i} e_{si} \Phi(\mathbf{r}_i, t) - \sum_{n=0}^{\infty} \frac{1}{(2n-1)!!} \left\{ \mathbf{M}_{ei}^{(n)} [n] \mathbf{E}^{(n)}(\mathbf{r}_i, t) + \right. \\ &\quad \left. + \mathbf{M}_{mi}^{(n)} [n] \mathbf{H}^{(n)}(\mathbf{r}_i, t) \right\},\end{aligned}\quad (8)$$

in which the first term represents the potential energy of the total charge of the microsystem in a scalar potential $\Phi(\mathbf{r}_i, t)$. The second term describes interaction between the 2^n -pole intrinsic electric moment of the microsystem i

$$\mathbf{M}_{ei}^{(n)} = \sum_{s=1}^{n_i} e_{si} \mathbf{r}_{si}^n \mathbf{Y}^{(n)}(\mathbf{r}_{si}) \quad (9)$$

and electric field vector of degree n at the point (\mathbf{r}_i, t)

$$\mathbf{E}^{(n)}(\mathbf{r}_i, t) = \nabla_i^{n-1} \mathbf{E}(\mathbf{r}_i, t). \quad (1a)$$

In the definition (9), $\mathbf{Y}^{(n)}(\mathbf{r})$ is an operator of degree n having the properties of spherical harmonics and determined as follows (Kielich 1965c):

$$\begin{aligned}\mathbf{Y}^{(n)}(\mathbf{r}) &= \frac{1}{n! r^n} \left\{ (2n-1)!! \mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_n - (2n-3)!! r^2 \sum \mathbf{U}_{12} \mathbf{r}_3 \dots \mathbf{r}_n \right. \\ &\quad \left. + \dots + (-1)^k (2n-2k-1)!! r^{2k} \right. \\ &\quad \left. \sum \mathbf{U}_{12} \dots \mathbf{U}_{2k-1, 2k} \mathbf{r}_{2k+1} \dots \mathbf{r}_n + \dots \right\}\end{aligned}\quad (10)$$

where \mathbf{U}_{12} denotes the unit tensor of rank two, and $\sum \mathbf{U}_{12} \mathbf{r}_3 \dots \mathbf{r}_n$, etc. are sums of the terms obtained from the one written out by interchanging the suffixes 1, 2, \dots , n . The number of terms in the last sum in (10) is equal to $n! / \{2^k (n-2k)! k!\}$.

The third term in the Hamiltonian (8) represents interaction between the 2^n -pole intrinsic magnetic moment of the microsystem i (Kielich 1965c):

$$\mathbf{M}_{mi}^{(n)} = \frac{n}{(n+1)c} \sum_{s=1}^{n_i} e_{si} \mathbf{r}_{si}^n \mathbf{Y}^{(n)}(\mathbf{r}_{si}) \times \dot{\mathbf{r}}_{si} \quad (11)$$

and the magnetic field vector of degree n at the point (\mathbf{r}_i, t)

$$\mathbf{H}^{(n)}(\mathbf{r}_i, t) = \nabla_i^{n-1} \mathbf{H}(\mathbf{r}_i, t) = \nabla_i^n \times \mathbf{A}(\mathbf{r}_i, t). \quad (1b)$$

With respect to (7), the second-order perturbation Hamiltonian (6) is obtained as follows (Kielich 1965c):

$$H_i^{(2)} = -\frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{(2n_1-1)!!(2n_2-1)!!} \mathbf{H}^{(n_1)}(\mathbf{r}_i, t) [n_1] {}^{(n_1)}\mathbf{A}_{mi}^{(n_2)} [n_2] \mathbf{H}^{(n_2)}(\mathbf{r}_i, t), \quad (12)$$

where we have introduced the tensor of rank $n_1 + n_2$

$${}^{(n_1)}\mathbf{A}_{mi}^{(n_2)} = \frac{n_1 n_2}{(n_1+1)(n_2+1)c^2} \sum_{s=1}^{n_1} \frac{e_{si}}{m_{si}} r_{si}^{n_1+n_2} \{ \mathbf{Y}^{(n_1)}(\mathbf{r}_{si}) \mathbf{Y}^{(n_2)}(\mathbf{r}_{si}) - \mathbf{Y}^{(n_1)}(\mathbf{r}_{si}) \cdot \mathbf{Y}^{(n_2)}(\mathbf{r}_{si}) \mathbf{U} \} \quad (13)$$

determining the multipole (dia) magnetic polarizability operator of the microsystem i .

Our multipole expansion Hamiltonians (8) and (12) obtained by the Cartesian tensor method can be given immediately in spherical tensor representation (Gray 1976; Gray and Stiles 1976).

3. Long-range multipole forces

We shall now discuss the perturbation Hamiltonians (5) and (6) from internal fields existing in an assembly of interacting microsystems. Neglecting retarded time effects, we have for the scalar and vector potentials

$$\begin{aligned} \Phi^{\text{int}}(\mathbf{R}_{si}) &= \sum_{j \neq i}^N \sum_{u=1}^{n_j} \frac{e_{uj}}{|\mathbf{R}_{si} - \mathbf{R}_{uj}|}, \\ \mathbf{A}^{\text{int}}(\mathbf{R}_{si}) &= \frac{1}{c} \sum_{j \neq i}^N \sum_{u=1}^{n_j} \frac{e_{uj} \dot{\mathbf{R}}_{uj}}{|\mathbf{R}_{si} - \mathbf{R}_{uj}|}, \end{aligned} \quad (14)$$

where, by (2) (also see figure 1):

$$|\mathbf{R}_{si} - \mathbf{R}_{uj}| = |\mathbf{r}_{ij} + \mathbf{r}_{si} - \mathbf{r}_{uj}|. \quad (2a)$$

In the special case of nonoverlapping microsystems when $|\mathbf{r}_{si} + \mathbf{r}_{uj}| < |\mathbf{r}_{ij}|$ we can expand (14) in the form of a double Taylor series (Jansen 1958):

$$|\mathbf{R}_{si} - \mathbf{R}_{uj}|^{-1} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{(-1)^{n_2+1}}{n_1! n_2!} \mathbf{r}_{si}^{n_1} [n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)} [n_2] \mathbf{r}_{uj}^{n_2}, \quad (14a)$$

wherein the tensor of rank $n_1 + n_2$

$${}^{(n_1)}\mathbf{T}_{ij}^{(n_2)} = -\nabla_i^{n_1} \nabla_j^{n_2} |\mathbf{r}_{ij}|^{-1} = (-1)^{n_1+n_2} {}^{(n_2)}\mathbf{T}_{ji}^{(n_1)} \quad (15)$$

describes $(2^{n_1}$ -pole) $-(2^{n_2}$ -pole)-type interactions between microsystems i and j distant by \mathbf{r}_{ij} .

With regard to (4), (5), (14) and (14a) we obtain for the total first-order perturbation Hamiltonian resulting from internal long-range forces (Kielich 1965c, 1966a):

$$\begin{aligned} H_{\text{int}}^{(1)} &= -\frac{1}{2} \sum_{i=1}^N \left\{ \sum_{n=0}^{\infty} \frac{1}{(2n-1)!!} \mathbf{M}_{ei}^{(n)} [n] \mathbf{F}_{0e}^{(n)}(\mathbf{r}_i) + \right. \\ &\quad \left. + \sum_{n=0}^{\infty} \frac{1}{(2n-1)!!} \mathbf{M}_{mi}^{(n)} [n] \mathbf{F}_{0m}^{(n)}(\mathbf{r}_i) \right\}, \end{aligned} \quad (16)$$

where we have introduced the electric internal field of degree n at the centre of the microsystem i due to the intrinsic electric multipoles of the $N - 1$ surrounding microsystems of the assembly:

$$\mathbf{F}_{0e}^{(n)}(\mathbf{r}_i) = \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1 - 1)!!} {}^{(n)}\mathbf{T}_{ij}^{(n_1)}[n_1] \mathbf{M}_{ej}^{(n_1)}. \quad (17)$$

Similarly, the magnetic internal field of degree n at the centre of the microsystem i is (Kielich 1962, 1966a)

$$\mathbf{F}_{0m}^{(n)}(\mathbf{r}_i) = \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1 - 1)!!} {}^{(n)}\mathbf{T}_{ij}^{(n_1)}[n_1] \mathbf{M}_{mj}^{(n_1)}. \quad (18)$$

On substituting in (16) the fields (17) and (18), we obtain in explicit form the Hamiltonian (Kielich 1966a):

$$H_{\text{int}}^{(1)} = -\frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{(-1)^{n_2}}{(2n_1 - 1)!! (2n_2 - 1)!!} \cdot \{ \mathbf{M}_{ei}^{(n_1)}[n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}[n_2] \mathbf{M}_{ej}^{(n_2)} + \mathbf{M}_{mi}^{(n_1)}[n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}[n_2] \mathbf{M}_{mj}^{(n_2)} \}, \quad (19)$$

where the first term arises from electrostatic interaction between the intrinsic electric multipoles of an assembly of N micro-systems and the second term arises from magnetostatic interaction between the intrinsic magnetic multipoles of the micro-systems (see also Chiu 1979).

In the same way, we obtain expressions for the higher-order intermolecular Hamiltonians (Kielich 1965e; Stogryn 1971, 1972).

The application of these general expressions, such as (19), to concrete special cases is a rather straightforward procedure and the results are given in many papers (see *e.g.* Kielich 1972; Isnard *et al* 1976; Galatry and Gharbi 1980). Tables of non-zero and independent tensor elements of the electric quadrupole, octopole and hexadecapole moments for all point groups have been published by Kielich and Zawodny (1971) (see also Kielich 1972, 1981). Also, the numerical values of these multipoles for various simpler molecules are available (Stogryn and Stogryn 1966; Kielich 1972; Birnbaum and Cohen 1975, 1976; Isnard *et al* 1980; Birnbaum and Sutter 1981).

Expressions for the molecular interaction Hamiltonians in terms of irreducible spherical multipole tensors have been given by Gray (1968), Riera and Meath (1973), Moraal (1976) and Leavitt (1980).

4. Multipole electro-magnetic polarizabilities

4.1 Induced multipole moments of a microsystem

Let us consider a microsystem acted on by the electric and magnetic fields

$$\begin{aligned} \mathbf{E}(\mathbf{r}, t) &= \mathbf{E}(\omega, \mathbf{k}) \exp \{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} + \text{C.C.}, \\ \mathbf{H}(\mathbf{r}, t) &= \mathbf{H}(\omega, \mathbf{k}) \exp \{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} + \text{C.C.} \end{aligned} \quad (20)$$

of a monochromatic light wave vibrating with the frequency ω and having the propagation vector \mathbf{k} .

Assume the microsystem, previous to applying the fields (20), to have occupied one of its energy levels $E_g = \hbar\omega_g$. We assume this as the ground state and denote the eigenfunction corresponding thereto by $\psi_g^0(\mathbf{r})$. The quantum state of the microsystem in the presence of the fields (20) is given by the vector of state $|\psi_g(\mathbf{r}, t)\rangle$, which has to fulfil the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi_g(\mathbf{r}, t)\rangle = \{H^{(0)} + H^{(1)} + H^{(2)} + \dots\} |\psi_g(\mathbf{r}, t)\rangle, \quad (21)$$

where the perturbation Hamiltonians of the microsystem are given by (8) and (12).

We express the wave function of the perturbed microsystem $\psi_g(\mathbf{r}, t)$ in terms of the following expansion:

$$\psi_g(\mathbf{r}, t) = \sum_k c_{kg}(t) \psi_k^{(0)}(\mathbf{r}) \exp(-i\omega_k t), \quad (22)$$

where the coefficients for a transition of the microsystem from the quantum state $|g\rangle$ to the state $|k\rangle$ under the influence of the perturbation are functions of time and can be expanded in a series, as follows:

$$c_{kg}(t) = c_{kg}^{(0)}(t) + c_{kg}^{(1)}(t) + c_{kg}^{(2)}(t) + \dots = \sum_{p=0}^{\infty} c_{kg}^{(p)}(t). \quad (22a)$$

The solution of the problem is dependent on the initial conditions assumed, and we write in the zeroth approximation (Louisell 1973)

$$c_{kg}^{(0)}(t) = \delta_{kg} \exp(-\Gamma_k t/2), \quad (22b)$$

since even in the isolated case the levels of the microsystems almost always possess a finite width for various reasons; Γ_k^{-1} is the lifetime of the quantum state $|k\rangle$.

With regard to the initial condition (22b) we obtain, by (21) and (22), the following equation determining the transition coefficients for $p = 1, 2, 3 \dots$ (Płóciniczak 1980):

$$i\hbar \frac{\partial}{\partial t} c_{kg}^{(p)}(t) = -i\hbar (\Gamma_k/2) c_{kg}^{(p)} + \sum_l \{H_{kl}^{(1)}(t) + H_{kl}^{(2)}(t) + \dots\} c_{lg}^{(p-1)}(t) \exp(i\omega_{kl} t), \quad (23)$$

where the matrix elements of the perturbation Hamiltonians $H_{kl}^{(1)}(t), \dots$ are defined as usual.

The form of the equation of motion (23) is consistent with the approach of Orr and Ward (1971).

Now our problem consists in calculating the electric or magnetic multipole moment $\mathbf{M}_{e,m}^{(n)}(t)$ induced in the microsystems by the fields (20). By quantum-mechanical statistics we have

$$\mathbf{M}_{e,m}^{(n)}(\mathbf{r}, t) = \sum_g \rho_g \int \Psi_g^*(\mathbf{r}, t) \mathbf{M}_{e,m}^{(n)} \Psi_g(\mathbf{r}, t) d\tau, \quad (24)$$

where ρ_g is the statistical matrix in the quantum state g .

By the definition (24) and expression (22), the induced electric or magnetic multipole moment can be expanded as follows:

$$\mathbf{M}_{e,m}^{(n)}(\mathbf{r}, t) = \sum_{p=0}^{\infty} \mathbf{M}_{e,m}^{(n)}(\mathbf{r}, t)^{(p)}, \quad (25)$$

where the p th order induced moments are given by

$$\mathbf{M}_{e,m}^{(n)}(\mathbf{r}, t)^{(p)} = \sum_{q=0}^p \sum_{gkl} \rho_g c_{kg}^{(q)}(t)^* \langle k | \mathbf{M}_{e,m}^{(n)} | l \rangle c_{lg}^{(p-q)}(t). \tag{26}$$

Restricting our present considerations to the first-order Hamiltonian (8) with time-dependent fields of the type (20), we obtain from (23):

$$c_{kg}^{(1)}(t) = -\frac{1}{\hbar} \frac{\langle k | H^{(1)}(\omega) | g \rangle}{\omega_{kg} - \omega - i\Gamma_{kg}} \exp [i(\omega_{kg} - \omega + i\Gamma_g/2)t] + \text{C.C.}, \tag{23a}$$

where $H^{(1)}(\omega)$ is the Fourier frequency transform of the Hamiltonian (8) and $\Gamma_{kg} = (\Gamma_k - \Gamma_g)/2$ determines the level widths of the microsystem for the transition $\langle k | \leftarrow | g \rangle$.

By (23a) with (8) we obtain from (26) for the linear (first-order) electric multipole moment of the microsystem (Kielich 1965c, 1975)

$$\begin{aligned} \mathbf{M}_e^{(n)}(\mathbf{r}, t)^{(1)} = & \sum_{n_1=1}^{\infty} \frac{1}{(2n_1 - 1)!!} \{ {}^{(n)}_e \mathbf{A}_e^{(n_1)}(\omega) [n_1] \mathbf{E}^{(n_1)}(\mathbf{r}, t) + \\ & + {}^{(n)}_e \mathbf{A}_m^{(n_1)}(\omega) [n_1] \mathbf{H}^{(n_1)}(\mathbf{r}, t) \}, \end{aligned} \tag{27}$$

where the tensor of rank $n + n_1$

$$\begin{aligned} {}^{(n)}_e \mathbf{A}_e^{(n_1)}(\omega) = & \frac{1}{\hbar} \sum_{gk} \rho_g \left\{ \frac{\langle g | \mathbf{M}_e^{(n)} | k \rangle \langle k | \mathbf{M}_e^{(n_1)} | g \rangle}{\omega_{kg} - \omega - i\Gamma_{kg}} + \right. \\ & \left. + \frac{\langle g | \mathbf{M}_e^{(n_1)} | k \rangle \langle k | \mathbf{M}_e^{(n)} | g \rangle}{\omega_{kg} + \omega + i\Gamma_{kg}} \right\} \exp(-\Gamma_g t) \end{aligned} \tag{28}$$

defines the linear 2^n -pole electric polarizability induced in the microsystem by 2^{n_1} -pole electric transitions.

Similarly, the tensor ${}^{(n)}_e \mathbf{A}_m^{(n_1)}(\omega)$ determines the linear 2^n -pole electric polarizability induced in the microsystem by 2^{n_1} -pole magnetic transitions and can be obtained immediately from (28) on replacing therein $\mathbf{M}_e^{(n_1)}$ by $\mathbf{M}_m^{(n_1)}$.

On replacing in the expression (27) the index e by m and m by e as well as $\mathbf{E}^{(n_1)}$ by $\mathbf{H}^{(n_1)}$ and vice versa, we obtain automatically the expression for the linear magnetic multipole moment.

4.2 Variations in polarizability tensor due to multipolar fields

Generally, in a condensed system such as a compressed gas or a liquid, even in the absence of external fields (20), molecular multipole fields (17) and (18) exist owing to the presence of intrinsic or induced multipole moments (9) and (11). In the presence of external fields $\mathbf{E}_0(\mathbf{r}, t)$ and $\mathbf{H}_0(\mathbf{r}, t)$, the molecular fields $\mathbf{F}_{0e}(\mathbf{r})$ and $\mathbf{F}_{0m}(\mathbf{r})$ undergo a change as the result of polarization of the microsystems of the medium, and have to be replaced by molecular fields

$$\begin{aligned} \mathbf{F}_e^{(n)}(\mathbf{r}_i, t) = & \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1 - 1)!!} {}^{(n)} \mathbf{T}_{ij}^{(n_1)}(\omega) [n_1] \mathbf{M}_e^{(n_1)}(\mathbf{r}_j, t), \\ \mathbf{F}_m^{(n)}(\mathbf{r}_i, t) = & \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1 - 1)!!} {}^{(n)} \mathbf{T}_{ij}^{(n_1)}(\omega) [n_1] \mathbf{M}_m^{(n_1)}(\mathbf{r}_j, t) \end{aligned} \tag{29}$$

which, in general, are functions of $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$.

In (29), the interaction tensor has the form

$${}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega) = -\nabla_i^{n_1-1} \nabla_j^{n_2-1} \left[\nabla_i \nabla_j - \left(\frac{\omega}{c}\right)^2 \mathbf{U} \right] |\mathbf{r}_{ij}|^{-1} \exp\left(i\frac{\omega}{c} |\mathbf{r}_{ij}|\right), \quad (30)$$

which, for $(\omega/c) |\mathbf{r}_{ij}| \ll 1$, reduces to (15).

Hence, in a condensed medium, each (*e.g.* the *i*th) microsystem is acted on, in addition to the external fields $\mathbf{E}(\mathbf{r}_i, t)$ and $\mathbf{H}(\mathbf{r}_i, t)$, by the multipole fields (29). Consequently, the total multipole moments of the *i*th microsystem are now functions of the effective fields $\mathbf{E}_0(\mathbf{r}, t) + \mathbf{F}_e(\mathbf{r}, t)$ and $\mathbf{H}_0(\mathbf{r}, t) + \mathbf{F}_m(\mathbf{r}, t)$. On restricting ourselves to a linear approximation we have by (27) and (29) for the total electric multipole moment of the *i*th microsystem (neglecting inhomogeneity of the external electric field *i.e.* writing $\mathbf{E}^{(n)} = 0$ for $n \geq 2$ and external magnetic field $\mathbf{H}^{(n)} = 0$):

$$\begin{aligned} \mathbf{M}_e^{(n)}(\mathbf{r}_i, t) = & \mathbf{M}_{0e}^{(n)}(\mathbf{r}_i) + {}^{(n)}\mathbf{A}_{ei}^{(1)}(\omega) \cdot \mathbf{E}_0(\mathbf{r}_i, t) + \sum_{n_1=1}^{\infty} \frac{1}{(2n_1-1)!!} \times \\ & \times \{ {}^{(n)}\mathbf{A}_{ei}^{(n_1)}(\omega) [n_1] \mathbf{F}_e^{(n_1)}(\mathbf{r}_i, t) + {}^{(n)}\mathbf{A}_{mi}^{(n_1)}(\omega) [n_1] \mathbf{F}_m^{(n_1)}(\mathbf{r}_i, t) \}, \quad (31) \end{aligned}$$

where the total multipole electric and magnetic fields are of the form (for simplicity, we have omitted the higher order terms) (Kielich 1965a):

$$\begin{aligned} \mathbf{F}_e^{(n)}(\mathbf{r}_i, t) = & \mathbf{F}_e^{(n)}(\mathbf{r}_i) + \sum_{j \neq i} \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1-1)!!} \times \\ & \times {}^{(n)}\mathbf{T}_{ij}^{(n_1)}(\omega) [n_1] {}^{(n_1)}\mathbf{A}_{ej}^{(1)}(\omega) \cdot \mathbf{E}(\mathbf{r}_j, t) + \dots \quad (32) \end{aligned}$$

$$\begin{aligned} \mathbf{F}_m^{(n)}(\mathbf{r}_i, t) = & \mathbf{F}_m^{(n)}(\mathbf{r}_i) + \sum_{j \neq i} \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1-1)!!} \times \\ & \times {}^{(n)}\mathbf{T}_{ij}^{(n_1)}(\omega) [n_1] {}^{(n_1)}\mathbf{A}_{mj}^{(1)}(\omega) \cdot \mathbf{E}(\mathbf{r}_j, t) + \dots \quad (33) \end{aligned}$$

The expressions (31)–(33) lead, for the electric dipole moment induced in the *i*th microsystem immersed in a dense medium, to

$$\mathbf{M}_e(\mathbf{r}_i, t) = \mathbf{\Pi}_{ei}(\omega) \cdot \mathbf{E}_0(\mathbf{r}_i, t), \quad (34)$$

where

$$\mathbf{\Pi}_{ei}(\omega) = \mathbf{\Pi}_{ei}(\omega)^{(0)} + \mathbf{\Pi}_{ei}(\omega)^{(1)} + \mathbf{\Pi}_{ei}(\omega)^{(2)} + \dots = \sum_{p=0}^{\infty} \mathbf{\Pi}_{ei}(\omega)^{(p)} \quad (35)$$

is the second-rank tensor of linear electric dipole polarizability of the *i*th microsystem in the presence of fluctuations of the multipolar electric and magnetic fields.

In the zeroth approximation we assume no long-range multipole field to be present, so that the second-rank tensor

$$\mathbf{\Pi}_{ei}(\omega)^{(0)} = {}^{(1)}\mathbf{A}_{ei}^{(1)}(\omega) \equiv {}_e\mathbf{A}_{ei}(\omega) \quad (35a)$$

represents the linear electric-dipole polarizability of an individual microsystem (one-body contribution).

The successive terms of the expansion (35) determine variations in dipole polarizability of the first, second, . . . etc. order perturbations due to the action of the electric and magnetic multipole fields (many-body interaction contributions). In the first-order perturbation we have (two-body interaction contribution)

$$\begin{aligned} \Pi_{ei}(\omega)^{(1)} &= \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!!(2n_2-1)!!} \times \\ &\times \left\{ {}_e^{(1)}\mathbf{A}_{ei}^{(n_1)}(\omega)[n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega)[n_2] {}_e^{(n_2)}\mathbf{A}_{ej}^{(1)}(\omega) + \right. \\ &\left. + {}_e^{(1)}\mathbf{A}_{mi}^{(n_1)}(\omega)[n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega)[n_2] {}_m^{(n_2)}\mathbf{A}_{ej}^{(1)}(\omega) \right\}. \end{aligned} \quad (36)$$

In the second-order approximation the linear dipole polarizability variations are given by (three-body interactions contribution)

$$\begin{aligned} \Pi_{ei}(\omega)^{(2)} &= \sum_{j \neq i}^N \sum_{k \neq j}^N \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_2+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \times \\ &\left\{ {}_e^{(1)}\mathbf{A}_{ei}^{(n_1)}(\omega)[n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega)[n_2] {}_e^{(n_2)}\mathbf{A}_{ej}^{(n_3)}(\omega) + \right. \\ &\left. + {}_e^{(1)}\mathbf{A}_{mi}^{(n_1)}(\omega)[n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega)[n_2] {}_m^{(n_2)}\mathbf{A}_{ej}^{(n_3)}(\omega) + \dots \right\} \\ &\times [n_3] {}^{(n_3)}\mathbf{T}_{jk}^{(n_4)}(\omega)[n_4] {}_e^{(n_4)}\mathbf{A}_{ek}^{(1)}(\omega). \end{aligned} \quad (37)$$

The perturbation expansion (35) with (36) and (37) in the electric-dipole approximation represents the well-known result of Yvon (1936, 1937) and Kirkwood (1936).

4.3 Contributions from nonlinear multipole polarizabilities

We now consider the further contributions to the effective polarizability (35) from induced dipole moments of the second and third orders given by (26) for $p = 2$ and $p = 3$, respectively. The electric multipole moment resulting from second-order perturbation theory is given, at the frequency ω , by:

$$\begin{aligned} \mathbf{M}_e^{(n)}(\mathbf{r}_i, t)^{(2)} &= \frac{1}{2} \sum_{n_1=1}^{\infty} \frac{1}{(2n_1-1)!!} \left\{ {}_e^{(n)}\mathbf{B}_{eei}^{(1+n_1)}(\omega) + \right. \\ &\left. + {}_e^{(n)}\mathbf{B}_{eei}^{(n_1+1)}(\omega) \right\} [1+n_1] \mathbf{E}_0(\mathbf{r}_i, t) \mathbf{F}_e^{(n_1)}(\mathbf{r}_i) + \\ &+ \frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{(2n_1-1)!!(2n_2-1)!!} {}_e^{(n)}\mathbf{B}_{eei}^{(n_1+n_2)}(\omega)[n_1+n_2] \\ &\times \left\{ \widehat{\mathbf{F}}_e^{(n_1)}(\mathbf{r}_i, t) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i) + \mathbf{F}_e^{(n_1)}(\mathbf{r}_i) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i, t) \right\}, \end{aligned} \quad (38)$$

where the $n+n_1+n_2$ -rank tensor ${}_e^{(n)}\mathbf{B}_{eei}^{(n_1+n_2)}(\omega)$ defines the second-order nonlinear 2^n -pole electric polarizability induced in the microsystem by $2^{n_1+n_2}$ -pole electric transitions.

The electric multipole field existing at the centre of the i th microsystem immersed in the medium when the external field is absent is now of the form (Kielich 1965a)

$$\begin{aligned} \mathbf{F}_e^{(n)}(\mathbf{r}_i) &= \mathbf{F}_{0e}^{(n)}(\mathbf{r}_i) + \sum_{j \neq i}^N \sum_{k \neq i}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \times \\ &\times \frac{(-1)^{n_1+n_3}}{(2n_1-1)!!(2n_2-1)!!(2n_3-1)!!} \\ &\times {}^{(n)}\mathbf{T}_{ij}^{(n_1)}[n_1] {}_e^{(n_1)}\mathbf{A}_{ej}^{(n_2)}(\omega)[n_2] {}^{(n_2)}\mathbf{T}_{jk}^{(n_3)}[n_3] \mathbf{M}_e^{(n_3)}(\mathbf{r}_k), \end{aligned} \quad (39)$$

where $\mathbf{F}_{0e}^{(n)}(\mathbf{r}_i)$ is given by (17).

We see from (38) that the external electric field $\mathbf{E}_0(\mathbf{r}, t)$ in cooperation with the

multipole electric field (17) or multipole electric fields (32) and (17) causes nonlinear multipole polarizabilities which lead to an additional contribution to the linear effective polarizability (35) (Kielich 1965, 1980), namely to the two-body contribution

$$\begin{aligned} \Pi_{ei}(\omega)_{NL}^{(1)} = & \frac{1}{2} \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!!(2n_2-1)!!} \{ {}^{(1)}\mathbf{B}_{eei}^{(1+n_1)}(\omega) + \\ & + {}^{(1)}\mathbf{B}_{eei}^{(n_1+1)}(\omega) \} [n_1]^{(n_1)} \mathbf{T}_{ij}^{(n_2)} [n_2] \mathbf{M}_e^{(n_2)}(\mathbf{r}_j), \end{aligned} \quad (40a)$$

as well as the three-body contribution

$$\begin{aligned} \Pi_{ei}(\omega)_{NL}^{(2)} = & \frac{1}{2} \sum_{j \neq i}^N \sum_{k \neq j}^N \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_2+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \times \\ & \times \{ {}^{(1)}\mathbf{B}_{eei}^{(1+n_1)}(\omega) + {}^{(1)}\mathbf{B}_{eei}^{(n_1+1)}(\omega) \} [n_1]^{(n_1)} \mathbf{T}_{ij}^{(n_2)} [n_2] \times \\ & \times {}^{(n_2)}\mathbf{A}_{ej}^{(n_3)} [n_3] {}^{(n_3)}\mathbf{T}_{jk}^{(n_4)} [n_4] \mathbf{M}_e^{(n_4)}(\mathbf{r}_k) + \\ & + \frac{1}{2} \sum_{j \neq i}^N \sum_{k \neq j}^N \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_3+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} {}^{(1)}\mathbf{B}_{eei}^{(n_1+n_2)}(\omega) \\ & \times [n_1+n_2] \{ {}^{(n_1)}\mathbf{T}_{ij}^{(n_3)}(\omega) [n_3] {}^{(n_3)}\mathbf{A}_{ej}^{(1)}(\omega) {}^{(n_2)}\mathbf{T}_{jk}^{(n_4)} [n_4] \mathbf{M}_e^{(n_4)}(\mathbf{r}_k) + \\ & + {}^{(n_1)}\mathbf{T}_{ij}^{(n_3)} [n_3] \mathbf{M}_e^{(n_3)}(\mathbf{r}_j) {}^{(n_2)}\mathbf{T}_{jk}^{(n_4)}(\omega) [n_4] {}^{(n_4)}\mathbf{A}_{ek}^{(1)}(\omega) \}. \end{aligned} \quad (40b)$$

Similarly, the expression (26) leads to the third-order electric multipole moment induced at the frequency ω :

$$\begin{aligned} \mathbf{M}_e^{(n)}(\mathbf{r}_i, t)^{(3)} = & \frac{1}{12} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{S(1, n_1, n_2)}{(2n_1-1)!!(2n_2-1)!!} \times \\ & \times {}^{(n)}\mathbf{C}_{eeei}^{(1+n_1+n_2)}(\omega) [1+n_1+n_2] \mathbf{E}_0(\mathbf{r}, t) \mathbf{F}_e^{(n_1)}(\mathbf{r}_i) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i) + \\ & + \frac{1}{12} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \frac{S(n_1, n_2, n_3)}{(2n_1-1)!!(2n_2-1)!!(2n_3-1)!!} \times \\ & \times {}^{(n)}\mathbf{C}_{eeei}^{(n_1+n_2+n_3)}(\omega) [n_1+n_2+n_3] \mathbf{F}_e^{(n_1)}(\mathbf{r}_i, t) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i) \mathbf{F}_e^{(n_3)}(\mathbf{r}_i), \end{aligned} \quad (41)$$

where $S(n_1, n_2, n_3, \dots)$ is a symmetrizing operator consisting in summation over all permutations n_1, n_2, n_3, \dots .

In (41) the $(n+n_1+n_2+n_3)$ -rank tensor ${}^{(n)}\mathbf{C}_{eeei}^{(n_1+n_2+n_3)}$ describes the third-order nonlinear 2^n -pole electric polarizability produced by $2^{n_1+n_2+n_3}$ -pole electric transitions.

In particular, we obtain by (39) and (41) for the second-order contributions

$$\begin{aligned} \Pi_{ei}(\omega)_{NL}^{(2)} = & \frac{1}{12} \sum_{j \neq i}^N \sum_{k \neq i}^N \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{S(1, n_1, n_2)(-1)^{n_3+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \\ & \times {}^{(1)}\mathbf{C}_{eeei}^{(1+n_1+n_2)}(\omega) [n_1+n_2] {}^{(n_1)}\mathbf{T}_{ij}^{(n_3)} [n_3] \mathbf{M}_e^{(n_3)}(\mathbf{r}_j) {}^{(n_2)}\mathbf{T}_{ik}^{(n_4)} \times \\ & \times [n_4] \mathbf{M}_e^{(n_4)}(\mathbf{r}_k). \end{aligned} \quad (42)$$

4.4 Cross magneto-electric contributions

Generally, one has to take into consideration in the equations of motion (23) both the electric and magnetic parts of the perturbation Hamiltonian. As a result, in addition to

the induced purely electric and magnetic multipole moments $\mathbf{M}_e^{(n)}(\mathbf{r}, t)$ and $\mathbf{M}_m^{(n)}(\mathbf{r}, t)$ one obtains, respectively, the additional mixed multipole moments $\mathbf{M}_{em}^{(n)}(\mathbf{r}, t)$ and $\mathbf{M}_{me}^{(n)}(\mathbf{r}, t)$. In second-order approximation, $\mathbf{M}_{em}^{(n)}(\mathbf{r}, t)^{(2)}$ consists of a part dependent only on the square of the magnetic field strength and a cross part dependent on the electric and magnetic fields simultaneously. The latter contribution is of the form

$$\begin{aligned} \mathbf{M}_{em}^{(n)}(\mathbf{r}_i, t)^{(2)} = & \frac{1}{2} \sum_{n_1=1}^{\infty} \frac{1}{(2n_1-1)!!} \{ {}^{(n)}_e \mathbf{B}_{emi}^{(1+n_1)}(\omega) + \\ & + {}^{(n)}_e \mathbf{B}_{mei}^{(n_1+1)}(\omega) \} [1+n_1] \mathbf{E}_0(\mathbf{r}_i, t) \mathbf{F}_m^{(n_1)}(\mathbf{r}_i) + \\ & + \frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{(2n_1-1)!!(2n_2-1)!!} \{ {}^{(n)}_e \mathbf{B}_{emi}^{(n_1+n_2)}(\omega) [n_1+n_2] \times \\ & \times \mathbf{F}_e^{(n_1)}(\mathbf{r}_i, t) \mathbf{F}_m^{(n_2)}(\mathbf{r}_i) + {}^{(n)}_e \mathbf{B}_{mei}^{(n_1+n_2)}(\omega) [n_1+n_2] \times \\ & \times \mathbf{F}_m^{(n_1)}(\mathbf{r}_i) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i, t) \}, \end{aligned} \quad (43)$$

where the $(n+n_1+n_2)$ -rank tensor ${}^{(n)}_e \mathbf{B}_{emi}^{(n_1+n_2)}$ defines the second-order nonlinear 2^n -pole electric polarizability due to 2^{n_1} -pole electric and 2^{n_2} -pole magnetic transitions.

By (18) and (43) we obtain one of the more important cross electro-magnetic contributions to the first-order variation in electric polarizability:

$$\begin{aligned} \mathbf{\Pi}_{ei}(\omega)_{NL}^{(1)} = & \frac{1}{2} \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!!(2n_2-1)!!} \{ {}^{(1)}_e \mathbf{B}_{emi}^{(1+n_1)} + \\ & + {}^{(1)}_e \mathbf{B}_{mei}^{(n_1+1)}(\omega) \} [n_1] {}^{(n_1)} \mathbf{T}_{ij}^{(n_2)} [n_2] \mathbf{M}_m^{(n)}(\mathbf{r}_j). \end{aligned} \quad (44)$$

Analogously, one obtains multipolar mixed electro-magnetic contributions in the third approximations of perturbation theory (see Kielich 1965b).

5. Fundamentals of the statistical-molecular theory of light scattering

5.1 The electric and magnetic multipole fields of the scattered wave

The Liénard-Wiechert potentials generated by a point particle s of the microsystem i at the space-time point (\mathbf{R}_{si}, t) are (De Groot 1969)

$$\begin{aligned} \Phi(\mathbf{R}_{si}, t) &= \frac{e_{si}}{R_{si} + (\mathbf{R}_{si} \cdot \dot{\mathbf{R}}_{si})/c} \Big|_{\text{Ret}}, \\ \mathbf{A}(\mathbf{R}_{si}, t) &= \frac{1}{c} \frac{e_{si} \dot{\mathbf{R}}_{si}}{R_{si} + (\mathbf{R}_{si} \cdot \dot{\mathbf{R}}_{si})/c} \Big|_{\text{Ret}}, \end{aligned} \quad (45)$$

where the subscript 'Ret' indicates that the position \mathbf{R}_{si} and velocity $\dot{\mathbf{R}}_{si}$ must be taken at the retarded moment of time (see figure 1)

$$t' = t - R_{si}(t')/c = t - |\mathbf{r}_i(t') + \mathbf{r}_{si}(t')|/c. \quad (45a)$$

On expanding the potentials (45) in a series in powers of r_{si} and taking into consideration (45a) we obtain by (1) for the electric and magnetic radiation fields in the wave zone *i.e.* at distances from the radiating microsystem considerably exceeding the

light wavelength ($r_i \gg \lambda$) (Heitler 1954; Born and Wolf 1968):

$$\mathbf{E}^S(\mathbf{r}_i, t) = \frac{1}{c^2 r_i^2} \{ \vec{\mathbf{r}}_i \times [\mathbf{r}_i \times \ddot{\mathbf{Z}}(t_i)] \}_{\text{Ret}},$$

$$\mathbf{H}^S(\mathbf{r}_i, t) = -\frac{1}{c^2 r_i} \{ \mathbf{r}_i \times \ddot{\mathbf{Z}}(t_i) \}_{\text{Ret}}, \quad (46)$$

where

$$t_i = t - r_i/c. \quad (46a)$$

The Hertz vector

$$\mathbf{Z}(t_i) = \mathbf{Z}_e(t_i) + \mathbf{Z}_m(t_i) \quad (47)$$

consists in general of a part accounting for electric multipole radiation (Kielich 1965c)

$$\mathbf{Z}_e(t_i) = \sum_{n=1}^{\infty} \frac{1}{(2n-1)!! r_i^n c^{n-1}} \mathbf{r}_i^{n-1} [n-1] \frac{\partial^{n-1}}{\partial t^{n-1}} \mathbf{M}_e^{(n)}(t_i), \quad (47a)$$

and a part accounting for magnetic multipole radiation

$$\mathbf{Z}_m(t_i) = - \sum_{n=1}^{\infty} \frac{1}{(2n-1)!! r_i^{n+1} c^{n-1}} \mathbf{r}_i^{n-1} [n-1] \left\{ \mathbf{r}_i \times \frac{\partial^{n-1}}{\partial t^{n-1}} \mathbf{M}_m^{(n)}(t_i) \right\}. \quad (47b)$$

5.2 Relation between electric fields in a medium and in vacuum

In the semi-macroscopic approach, we consider a macroscopic sample of volume V , electric permittivity tensor $\boldsymbol{\varepsilon}$ and magnetic permittivity tensor $\boldsymbol{\mu}$ immersed in an isotropic continuous medium with the scalar permittivities ε_0 and μ_0 . The electric field of the light wave in the surrounding medium being $\mathbf{E}_0(\mathbf{r}, t)$, the mean macroscopic (Maxwellian) field $\mathbf{E}(\mathbf{r}, t)$ existing in the sample will in general differ from $\mathbf{E}_0(\mathbf{r}, t)$. The relation between the two fields is dependent on the structure and shape of the sample and the conditions in which the scattered light is observed. Generally, the two fields are related by the tensor $\mathbf{R}_e(\omega)$ as follows (Kielich 1972):

$$\mathbf{E}_0(\mathbf{r}, t) = \mathbf{R}_e(\omega) \cdot \mathbf{E}(\mathbf{r}, t), \quad (48)$$

where

$$\mathbf{R}_e(\omega) = \varepsilon_0^{-1} \{ \varepsilon_0 \mathbf{U} + \mathbf{L} \cdot [\boldsymbol{\varepsilon}(\omega) - \varepsilon_0 \mathbf{U}] \}. \quad (48a)$$

Here, \mathbf{L} is a symmetric field depolarization tensor, dependent on the shape of the sample, and defined so that its trace shall equal unity: $\mathbf{L} : \mathbf{U} = L_{xx} + L_{yy} + L_{zz} = 1$. Its principal values are ($\sigma = x, y, z$):

$$L_\sigma = \frac{1}{2} \int_0^\infty \frac{r_x r_y r_z ds}{(r_\sigma^2 + S) [(r_x^2 + S)(r_y^2 + S)(r_z^2 + S)]^{1/2}},$$

r_x, r_y and r_z denoting the principal semi-axes of the ellipsoid. In particular, for a spherical sample $r_x = r_y = r_z = r$ and $\mathbf{L} = \frac{1}{3} \mathbf{U}$, whence the tensor (48a) reduces to

$$\mathbf{R}_e(\omega) = [\boldsymbol{\varepsilon}(\omega) + 2\varepsilon_0 \mathbf{U}] / 3\varepsilon_0. \quad (48b)$$

If moreover the permittivity of the sample is isotropic $\boldsymbol{\varepsilon} = \varepsilon \mathbf{U}$, one has the well known relation:

$$\mathbf{R}_e(\omega) = [\varepsilon(\omega) + 2\varepsilon_0] \mathbf{U} / 3\varepsilon_0 = \mathbf{R}_e(\omega) \mathbf{U}. \quad (48c)$$

If the sample is a cylinder, the axis of which is directed along the x -axis, one has $L_x = 0$ and $L_y = L_z = 1/2$. For a circular oblate disc $L_x = L_y = 0$ and $L_z = 1$.

By analogy to (48) we define the relation tensor $\mathbf{R}_m(\omega)$ between the magnetic vectors $\mathbf{H}_0(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$.

We now assume that the scattering sample of volume V contains N microsystems, correlated stochastically in time and space. The electric field of light scattered by the spherical sample and observed at a large distance r in the surrounding medium is (in a satisfactory approximation)

$$\mathbf{E}_0^S(\mathbf{r}, t) = \mathbf{R}_e(\omega_S) \sum_{i=1}^N \mathbf{E}^S(\mathbf{r}_i, t) = \left[\frac{\varepsilon(\omega_S) + 2\varepsilon_0}{3\varepsilon_0} \right] \sum_{i=1}^N \mathbf{E}^S(\mathbf{r}_i, t), \quad (49)$$

where $\varepsilon(\omega_S)$ is the electric permittivity of the isotropic sample at the vibration frequency ω_S of the scattered light wave.

5.3 Intensity of scattered light

We shall now consider the integral intensity of the light scattered by the volume V in order to determine the component thereof transmitted by an analyzer at the point of observation (figure 2). Let the direction of the vibration transmitted by the analyzer be that determined by the unit vector \mathbf{e}_s perpendicular to the vector of observation \mathbf{r} . Since now $\mathbf{e}_s \cdot \mathbf{r} = 0$, the component of the electric field (49) in the direction of the unit vector \mathbf{e}_s is, by (46),

$$\mathbf{E}_0^S(\mathbf{r}, t) \cdot \mathbf{e}_s = -\frac{1}{c^2} R_e(\omega_S) \sum_{i=1}^N \ddot{\mathbf{Z}}(t_i) \cdot \mathbf{e}_s. \quad (49a)$$

The intensity of the light scattered by the volume V and transmitted by an analyzer outside the sample at r is defined as follows:

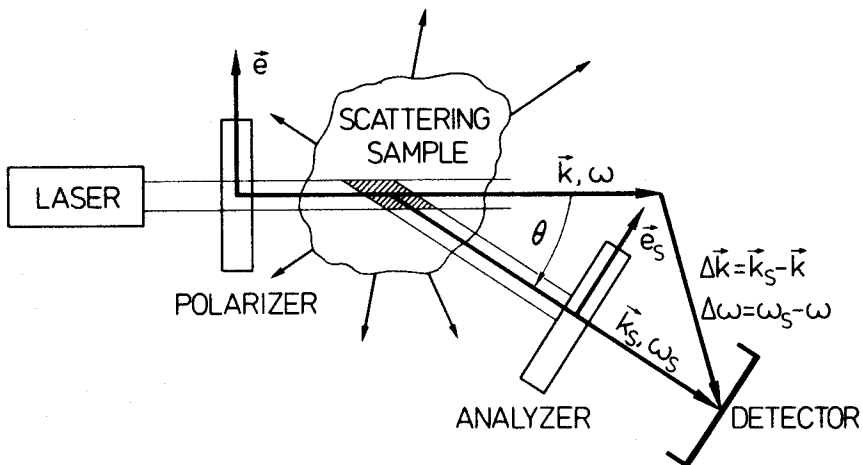


Figure 2. Laser light scattering experiment. The incident laser light beam has the frequency ω , propagation vector \mathbf{k} and polarization vector \mathbf{e} , whereas the scattered beam has the frequency ω_s , propagation vector \mathbf{k}_s and polarization vector \mathbf{e}_s ; $\Delta \mathbf{k} = \mathbf{k}_s - \mathbf{k}$ is the scattering vector and θ the scattering angle.

$$I_{e_s}(r) = \frac{c}{8\pi} \langle \mathbf{e}_s \cdot \mathbf{E}_0^s(\mathbf{r}, t) \mathbf{E}_0^s(\mathbf{r}, t) \cdot \mathbf{e}_s^* \rangle, \quad (50)$$

where the symbol $\langle \rangle$ denotes appropriate statistical averaging.

Substituting (49a) in (50), the fundamental equation for the scattered intensity takes the form

$$I_{e_s}(r) = \frac{R_e^2(\omega_s)}{8\pi c^3} \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{e}_s \cdot \ddot{\mathbf{Z}}(t_i) \mathbf{Z}(t_j) \cdot \mathbf{e}_s^* \right\rangle, \quad (50a)$$

where the Hertz vector is given by (47).

Since by assumption $V \ll \lambda^3$, we can restrict our considerations to light scattering of the electric dipolar type. We now have by (34), (47) and (50a):

$$I_{e_s e}(r) = Q(\omega_s) I_0 \left\langle \sum_{i=1}^N \sum_{j=1}^N [\mathbf{e}_s \cdot \mathbf{\Pi}_{ei}(\omega) \mathbf{e}_s^*] \times \right. \\ \left. \times [\mathbf{e} \cdot \mathbf{\Pi}_{ej}(\omega) \cdot \mathbf{e}_s^*] \exp(i\Delta\mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (50b)$$

where I_0 is the incident light intensity existing within the scattering sample and $Q(\omega_s) = (1/r^2)(\omega_s/c)^4 R_e^2(\omega_s) R_e^2(\omega)$.

In the case of an isotropic medium and when the external field is absent, the probability for all directions of the unit vectors \mathbf{e} and \mathbf{e}_s is the same, so it is useful first to perform unweighted averaging in (50b) over all possible orientations of \mathbf{e} and \mathbf{e}_s with respect to the fixed system of reference (X, Y, Z):

$$I_{e_s e}(r) = I_{e_s e}^{is} + I_{e_s e}^{antis} + I_{e_s e}^{anis}, \quad (51)$$

where we have the intensities of isotropic, antisymmetric and anisotropic scattering, respectively, in the form

$$I_{e_s e}^{is} = \frac{1}{3} Q(\omega_s) I_0 S^{is} |\mathbf{e}_s \cdot \mathbf{e}^*|^2, \quad (51a)$$

$$I_{e_s e}^{antis} = \frac{1}{6} Q(\omega_s) I_0 S^{antis} (1 - |\mathbf{e}_s \cdot \mathbf{e}^*|^2), \quad (51b)$$

$$I_{e_s e}^{anis} = \frac{1}{30} Q(\omega_s) I_0 S^{anis} (3 + 3|\mathbf{e}_s \cdot \mathbf{e}^*|^2 - 2|\mathbf{e}_s \cdot \mathbf{e}^*|^2). \quad (51c)$$

Above, we have introduced the constants

$$S^{is} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{\Pi}_{ei}(\omega) \mathbf{\Pi}_{ej}(\omega) \exp(i\Delta\mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (52)$$

$$S^{antis} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{\Pi}_{ei}^{antis}(\omega) \mathbf{\Pi}_{ej}^{antis}(\omega) \exp(i\Delta\mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (53)$$

$$S^{anis} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \{ \mathbf{\Pi}_{ei}(\omega) \mathbf{\Pi}_{ej}(\omega) - 3\mathbf{\Pi}_{ei}(\omega) \mathbf{\Pi}_{ej}(\omega) \} \exp(i\Delta\mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (54)$$

characterizing the molecular-statistical mechanism of isotropic, antisymmetric and anisotropic scattering.

Here, we have introduced a scalar polarizability:

$$\mathbf{\Pi}_{ei} = \frac{1}{3} \mathbf{\Pi}_{ei} : \mathbf{U}. \quad (52a)$$

The mathematical form of the scattering constants (52)–(54) follows from the definition ($h = 0, 1, 2$):

$$S^{(h)} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{(h)}(\omega)^* : \Pi_{ej}^{(h)}(\omega) \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle \quad (55)$$

in agreement with the fact that a second-rank tensor can be represented in the form of the sum of three irreducible components:

$$\Pi = \Pi^{(0)} + \Pi^{(1)} + \Pi^{(2)} = \sum_{h=0}^2 \Pi^{(h)},$$

where $\Pi^{(0)} = \Pi U$ is an isotropic tensor ($h = 0$), $\Pi^{(1)}$ an antisymmetric tensor ($h = 1$) and $\Pi^{(2)}$ an anisotropic tensor ($h = 2$). So, in this way, we can denote $S^{\text{is}} = S^{(0)}$, $S^{\text{antis}} = S^{(1)}$ and $S^{\text{anis}} = S^{(2)}$ (see Placzek 1934).

With regard to the perturbation expansion of the polarizability tensor (35), we rewrite the scattering constants (55) as follows:

$$S^{(h)} = \sum_{p=0}^{\infty} S_p^{(h)} = S_0^{(h)} + S_1^{(h)} + S_2^{(h)} + \dots, \quad (55a)$$

where

$$S_p^{(h)} = \sum_{q=0}^p \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{(h)}(\omega)^{(q)} : \Pi_{ej}^{(h)}(\omega)^{(p-q)} \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle \quad (55b)$$

is the h -scattering constant of the n th approximation. In general, the above statistical averaging should be performed with the grand canonical statistical ensemble

$$f(\mathbf{r}^N, \Omega^N) = Q_N \exp\{- (U^N + H^N)/kT\}, \quad (56)$$

where, in addition to the long-range interaction Hamiltonian of multipole interactions of N microsystems, we have the potential energy U^N of short-range interactions of the N multipolar microsystems.

The various kinds of molecular energies have recently been reviewed by Ratajczak and Orville-Thomas (1980).

6. Angular distribution and polarization states of scattered light

Let us assume a set-up in which the incident light propagates along the Z -axis of laboratory coordinates XYZ , attached to the centre of the scattering volume V (figure 3). The scattered light is observed in a distinct set of laboratory co-ordinates $X'Y'Z'$. As the plane of observation we chose the $Y'Z'$ -plane, which coincides with the YZ -plane. Thus, Θ is our scattering angle, subtended by the axes Z and Z' .

Generally, we express the versor \mathbf{e} of the incident wave electric field $\mathbf{E} = E\mathbf{e}$ as follows:

$$\mathbf{e} = x \sin \Psi + e^{i\Delta} y \cos \Psi, \quad (57)$$

where Ψ is the angle between \mathbf{e} and the YZ -plane, and Δ is the phase shift of the Y -component of the field \mathbf{E} ($\mathbf{x}, \mathbf{y}, \mathbf{z}$ are unit vectors in the direction of the axes X, Y, Z of the laboratory frame).

The unit vector \mathbf{e}_s , defining the polarization of the scattered beam in co-ordinates X, Y, Z can in general be written in a form similar to (57):

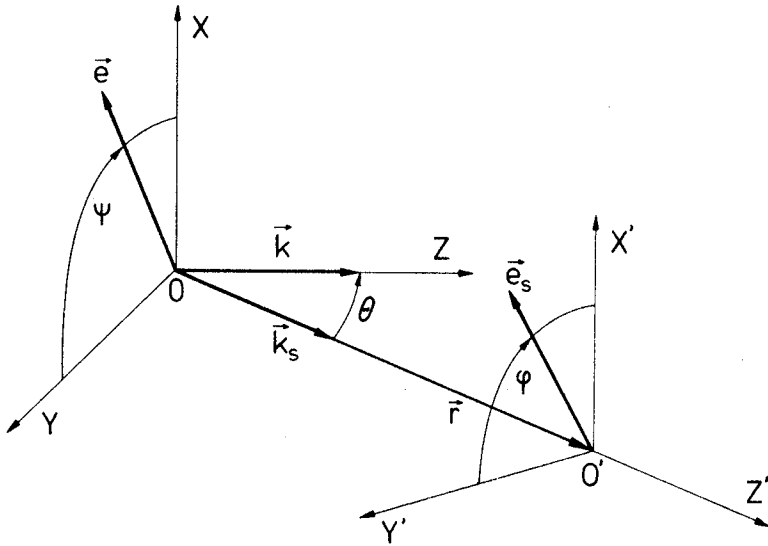


Figure 3. Systems for the determination of the angular distribution and polarization states of scattered beams.

$$\mathbf{e}_s = x \sin \varphi + e^{i\delta} (y \cos \Theta - z \sin \Theta) \cos \varphi, \quad (58)$$

φ being the angle between \mathbf{e}_s and the $Y'Z'$ plane.

Equations (57) and (58) account for all possible states of polarization of the incident and scattered light. For example, at $\Delta = 0$ the incident wave is linearly polarized at an arbitrary angle

$$\mathbf{e} = x \sin \Psi + y \cos \Psi. \quad (57a)$$

If the y -component of the field is shifted in phase by $\Delta = \pm \pi/2$, we have for elliptical polarization

$$\mathbf{e}_{\pm} = x \sin \Psi \pm iy \cos \Psi, \quad (57b)$$

where with regard to the angular momentum convention a phase shift $+\pi/2$ refers to right circular polarization of the wave and $-\pi/2$ to left circular polarization. If in addition $\Psi = \pi/4$, then (57b) gives for a circularly polarized wave

$$\mathbf{e}_{\pm} = (x \pm iy) / \sqrt{2}. \quad (57c)$$

It is our aim to determine the angular distribution and polarization state of the intensity scattering components (51a)–(51c).

6.1 Linearly polarized incident light

For linearly polarized incident light, we have by (57a) and (58)

$$\begin{aligned} |\mathbf{e}_s \cdot \mathbf{e}^*|^2 = |\mathbf{e}_s \cdot \mathbf{e}|^2 = & \sin^2 \varphi \cos^2 \Psi + \cos^2 \Theta \cos^2 \varphi \cos^2 \Psi + \\ & + \frac{1}{2} \sin 2\varphi \sin 2\Psi \cos \delta \end{aligned} \quad (51c)$$

and obtain from (51a)–(51c) for the vertical and horizontal scattered intensity components (see figure 4)

$$I_{VV}^{\text{is}} = \frac{1}{3} Q(\omega_s) S^{(0)}, \quad I_{HV}^{\text{is}} = I_{VH}^{\text{is}} = 0, \\ I_{HH}^{\text{is}} = \frac{1}{3} Q(\omega_s) S^{(0)} \cos^2 \Theta, \quad (59a)$$

$$I_{VV}^{\text{antis}} = 0, \quad I_{HV}^{\text{antis}} = I_{VH}^{\text{antis}} = \frac{1}{6} Q(\omega_s) S^{(1)}, \\ I_{HH}^{\text{antis}} = \frac{1}{6} Q(\omega_s) S^{(1)} (1 - \cos^2 \Theta), \quad (59b)$$

$$I_{VV}^{\text{anis}} = \frac{2}{15} Q(\omega_s) S^{(2)}, \\ I_{HV}^{\text{anis}} = I_{VH}^{\text{anis}} = \frac{1}{10} Q(\omega_s) S^{(2)}, \\ I_{HH}^{\text{anis}} = \frac{1}{30} Q(\omega_s) S^{(2)} (3 + \cos^2 \Theta). \quad (59c)$$

Defining the depolarization rates as $D_V = I_{HV}^i / I_{VV}^i$ and $D_H = I_{VH}^i / I_{HH}^i$ for incident light polarized vertically ($\Psi = 90^\circ$) or horizontally ($\Psi = 0^\circ$), respectively, we obtain by (59a)–(59c):

$$D_V = \frac{3S^{(2)} + 5S^{(1)}}{10S^{(0)} + 4S^{(2)}}, \quad (60a)$$

$$D_H(\Theta) = \frac{3S^{(2)} + 5S^{(1)}}{10S^{(0)} \cos^2 \Theta + 5S^{(1)} (1 - \cos^2 \Theta) + S^{(2)} (3 + \cos^2 \Theta)}. \quad (60b)$$

Equation (60a) is similar to the result derived by Placzek (1934) for Raman scattering.

6.2 Circularly polarized incident light

In the case of circularly polarized incident light (57c) we obtain by (58) from (51a)–(51c):

$$I_{e_s, \pm 1}^{\text{is}} = \frac{1}{6} Q(\omega_s) S^{(0)} (\sin^2 \varphi + \cos^2 \Theta \cos^2 \varphi \pm \cos \Theta \sin 2\varphi \sin \delta), \quad (61a)$$

$$I_{e_s, \pm 1}^{\text{antis}} = \frac{1}{12} Q(\omega_s) S^{(1)} (2 - \sin^2 \varphi - \cos^2 \Theta \cos^2 \varphi \pm \cos \Theta \sin 2\varphi \sin \delta), \quad (61b)$$

$$I_{e_s, \pm 1}^{\text{anis}} = \frac{1}{60} Q(\omega_s) S^{(2)} (6 + \sin^2 \varphi + \cos^2 \Theta \cos^2 \varphi \mp 5 \cos \Theta \sin 2\varphi \sin \delta). \quad (61c)$$

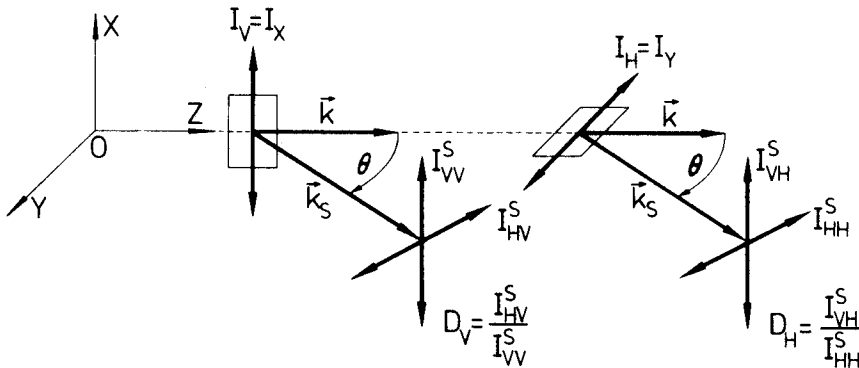


Figure 4. The incident light beam propagates along the Z-axis with intensities I_V or I_H , where the indices V and H denote vertical and horizontal polarization, respectively. Scattered light observation is performed along the Y-axis, with first indices V or H standing for the vertical and horizontal component of the scattered beam intensity I^S .

The depolarization ratio is usually defined as the ratio of the lowest $I_{H\pm 1}^S$ and highest $I_{V\pm 1}^S$ possible values of the scattered intensity (see Born 1933). We obtain by (61) at $\delta = 0$ and $\varphi = 0^\circ$ or $\varphi = 90^\circ$:

$$D_{\pm 1}(\Theta) = \frac{10S^{(1)} + 6S^{(2)} + (10S^{(0)} - 5S^{(1)} + S^{(2)})\cos^2 \Theta}{10S^{(0)} + 5S^{(1)} + 7S^{(2)}}. \quad (62)$$

For incident light circularly polarized in the right sense only ($e = +1$), we obtain by eqs (61) for $\delta = \pm \pi/2$, $\varphi = \pi/4$ and $e_s = \pm 1$:

$$I_{\pm 1, \pm 1}^{is} = \frac{1}{12} Q(\omega_s) S^{(0)} (1 \pm \cos \Theta)^2, \quad (63a)$$

$$I_{\pm 1, \pm 1}^{antis} = \frac{1}{24} Q(\omega_s) S^{(1)} [4 - (1 \mp \cos \Theta)^2], \quad (63b)$$

$$I_{\pm 1, \pm 1}^{anis} = \frac{1}{120} Q(\omega_s) S^{(2)} (13 \mp 10 \cos \Theta + \cos^2 \Theta). \quad (63c)$$

The reversal ratio is by definition the ratio of that part of the scattered intensity whose sense of circular polarization is contrary to that of the incident wave and the part whose sense of circular polarization coincides with the latter (see figure 5). We thus have, quite generally,

$$R_{\pm 1} = \frac{I_{\mp 1, \pm 1}^S}{I_{\pm 1, \pm 1}^S},$$

and obtain by (63) for right-circularly polarized incident light:

$$R_{+1}(\Theta) = \frac{40S^{(0)} \sin^4 \Theta/2 + 20S^{(1)}(1 - \cos^4 \Theta/2) + S^{(2)}(13 + 10 \cos \Theta + \cos^2 \Theta)}{40S^{(0)} \cos^4 \Theta/2 + 20S^{(1)}(1 - \sin^4 \Theta/2) + S^{(2)}(13 - 10 \cos \Theta + \cos^2 \Theta)}. \quad (64)$$

In the case of forward scattering ($\Theta = 0^\circ$), eq. (64) reduces to (see Placzek 1934)

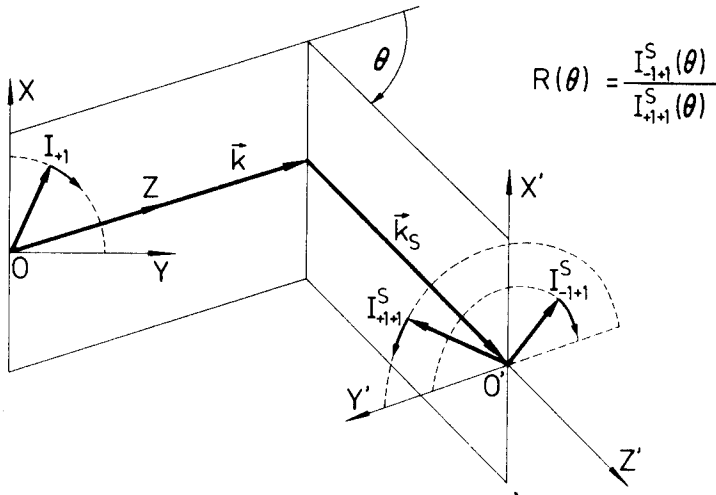


Figure 5. Geometry for the determination of the reversal ratio, on the angular momentum convention. Under the action of the right circularly polarized incident beam I_{+1} propagating along the Z-axis, two circularly polarized components appear in the scattered beam, the one right-circular $I_{+1, +1}^S$ and the other left-circular $I_{-1, +1}^S$.

$$R_{+1}(0^\circ) = \frac{6S^{(2)}}{10S^{(0)} + 5S^{(1)} + S^{(2)}}, \quad (64a)$$

which in some special cases yields results well known from the literature (Born 1933; Long 1977).

7. Application to isotropic scattering

The subsequent discussion of our theory consists in applications of the scattering constants (52)–(54) to particular situations, disclosing the optical properties of the microsystems as such, as well as the micro-structure and thermodynamical state of various substances. We first proceed to consider the isotropic scattering constant (52).

7.1 Microsystems exhibiting constant polarizability

If the scattering medium is but a moderately condensed one, the effect of the long range intermolecular field on the polarizability tensor of the microsystem may be neglected in the expansion (35), and the expression (52) may be written in the zeroth approximation as follows:

$$S_0^{\text{is}} = 3 \left\langle \sum_{i=1}^N \sum_{j=1}^N A_{ei}^* A_{ej} \exp(i\Delta\mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (65)$$

where A_{ei} denotes the mean electric polarizability of the isolated i th microsystem.

We decompose the scattering constant (65) into an incoherent part ($i = j$)

$$S_{0,\text{inc}}^{\text{is}} = 3 \sum_{i=1}^N |A_{ei}|^2 \quad (65a)$$

describing scattering by statistically independent microsystems, and a coherent part ($i \neq j$)

$$S_{0,\text{coh}}^{\text{is}} = 3 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* A_{ej} \frac{\sin \Delta k r_{ij}}{\Delta k r_{ij}} \right\rangle \quad (65b)$$

describing scattering by stochastically correlated microsystems.

If all the microsystems present within the scattering volume V are of one kind $A_{ei} = A_{ej} = A_e$, then (65a) and (65b) may be rewritten as follows:

$$S_{0,\text{inc}}^{\text{is}} = 3N |A_e|^2, \quad (65c)$$

$$S_{0,\text{coh}}^{\text{is}} = S_{0,\text{inc}}^{\text{is}} \Gamma(\Delta\mathbf{k}), \quad (65d)$$

where we have the integral parameter

$$\Gamma(\Delta\rho) = \mathbf{k} \int_0^\infty \iint \left\{ g^{(2)}(r_{12}, \Omega_1, \Omega_2) - 1 \right\} \frac{\sin \Delta k r_{12}}{\Delta k r_{12}} \mathrm{d}r_{12} \mathrm{d}\Omega_1 \mathrm{d}\Omega_2, \quad (66)$$

introduced by Zernike and Prins (1927) in their theory of x-ray scattering by liquids. Above, $g^{(2)}(r_{12}, \Omega_1, \Omega_2)$ is the binary correlation function for microsystems 1 and 2 having orientations Ω_1 and Ω_2 at the distance r_{12} , and $\rho = N/V$ is the number density of microsystems.

In the absence of phase interference (when the wavelength is large with respect to the intermolecular distance) (66) yields

$$\Gamma(0) = N^{-1} \langle (\Delta N)^2 \rangle - 1, \tag{66b}$$

where the mean square fluctuation of the number of microsystems is given by the Smoluchowski-Einstein formula

$$\langle (\Delta N)^2 \rangle = V \rho^2 kT \beta_T$$

with β_T —the isothermal compressibility coefficient of the medium.

In the case of compressed gases, we have by (66) the relation

$$\Gamma(0) = -\frac{1}{2} B(T) \tag{66c}$$

between $\Gamma(0)$ and the second virial coefficient of the equation of state of the real gas

$$B(T) = -\frac{2\Pi N}{\Omega^2} \int_0^\infty \int \{ \exp[-u(r_{12}, \Omega_1, \Omega_2)/kT] - 1 \} r_{12}^2 dr_{12} d\Omega_1, d\Omega_2, \tag{67}$$

where $u(r_{12}, \Omega_1, \Omega_2)$ denotes the total potential energy of interaction of the two microsystems.

Hence, it is obvious that coherent isotropic scattering is accounted for directly by the second virial coefficient (67) only if the microsystems exhibit a polarizability that is unaffected by the presence of their neighbours. Perturbation series expansions of the second virial coefficient (67) for general multipole interactions have, of course, been considered by many authors (see *eg* Kielich 1965f; Stogryn 1969; Moraal 1976; Singh and Singh 1976; Isnard *et al* 1980).

7.2 Microsystems with variable polarizability

In a sufficiently condensed medium, the polarizability of a microsystem is affected by the presence of the intrinsic fields of its neighbours.

Let us first calculate the contribution to (52) for the case when the statistical averaging is performed with the distribution function (56) in the absence of tensorial interaction

$$f(\mathbf{r}^N, \Omega^N) = \Omega^{-N} f(\mathbf{r}^N), \tag{56a}$$

so we have only radial molecular interactions described by the potential energy $U_0(\mathbf{r}^N)$.

Under the assumption of (56a), the first approximation of (55b) vanishes. In the second approximation we have by (52) and (55b):

$$S_{0, \text{coh}}^{\text{is}} = S_{02}^{\text{is}} + S_{11}^{\text{is}} + S_{20}^{\text{is}}, \tag{68}$$

where we have, in the absence of interference effects,

$$S_{02}^{\text{is}} = 3 \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{(0)*} \Pi_{ej}^{(2)} \right\rangle, \tag{68a}$$

$$S_{11}^{\text{is}} = 3 \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{(1)*} \Pi_{ej}^{(1)} \right\rangle, \tag{68b}$$

and S_{20}^{is} is defined similarly to S_{02}^{is} .

7.2a. *Linear multipole polarizabilities:* By (37) we obtain from (68a) for the cross 02 approximation for the two-body correlations contribution (omitting for simplicity the magneto-electric terms)

$$\begin{aligned}
 {}_2S_{02}^{is} = & \sum_{n=1}^{\infty} \sum_{u=1}^{\infty} \frac{2^{n+u} (n! u!)^2 (2n+2u)!}{(2n)! (2n+1)! [(2u)!]^2} \times \\
 & \times \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ A_{ei}^{(2u)} ({}^{(1)}\mathbf{A}_{ej}^{(n)} [n+1]^{(n)} \mathbf{A}_{ej}^{(1)}) + \right. \\
 & \left. + A_{ej}^{(2u)} ({}^{(1)}\mathbf{A}_{ei}^{(n)} [n+1]^{(n)} \mathbf{A}_{ei}^{(1)}) \} r_{ij}^{-2(n+u+1)} \right\rangle, \quad (69)
 \end{aligned}$$

and, for the three-body correlations contribution:

$$\begin{aligned}
 {}_3S_{02}^{is} = & \sum_{n=1}^{\infty} (n+1)! (2n+1) \frac{2^n n!}{(2n)!} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \times \right. \\
 & \times (A_{ei}^* + A_{ej}^* + A_{ek}^*) A_{ei} A_{ej}^{(2n)} A_{ek} (r_{ij} r_{jk})^{-(n+2)} P_{n+1} \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \Bigg\rangle \\
 & + \sum_{n=1}^{\infty} \sum_{u=1}^{\infty} \frac{2^{n+u} (n! u!)^2 (2n+2u)!}{(2n)! (2n+1)! [(2u)!]^2} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \times \right. \\
 & \times A_{ei}^* \{ {}^{(1)}\mathbf{A}_{ej}^{(n)} [n+1]^{(n)} \mathbf{A}_{ej}^{(1)} \} A_{ek}^{(2u)} r_{jk}^{-2(n+u+1)} \Bigg\rangle. \quad (70)
 \end{aligned}$$

Here,

$$A_{ei}^{(2n)} = \frac{1}{2n+1} ({}^{(n)}\mathbf{A}_{ei}^{(n)} [2n] \mathbf{U}^n) \quad (71)$$

is the mean value of the 2^n -pole electric polarizability of the i th microsystem and P_{n+1} is a Legendre polynomial of degree $n+1$.

The contribution (69) is similar to that obtained previously by Kielich (1965a, b) for molecular refraction and distortional electric polarization but the contribution (70) differs by the last term, proportional to $r_{jk}^{-2(n+u+1)}$.

If the higher-order terms are neglected, we obtain from (69)

$$\begin{aligned}
 {}_2S_{02}^{is} = & 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ [A_{ei}(\mathbf{A}_{ej} : \mathbf{A}_{ej}) + (\mathbf{A}_{ei} : \mathbf{A}_{ei}) A_{ej}] r_{ij}^{-6} + \right. \\
 & + [A_{ei} ({}^{(1)}\mathbf{A}_{ej}^{(2)} : {}^{(2)}\mathbf{A}_{ej}^{(1)}) + ({}^{(1)}\mathbf{A}_{ei}^{(2)} : {}^{(2)}\mathbf{A}_{ei}^{(1)}) A_{ej}] r_{ij}^{-8} + \\
 & + \frac{4}{3} [A_{ei} ({}^{(1)}\mathbf{A}_{ej}^{(3)} : {}^{(3)}\mathbf{A}_{ej}^{(1)}) + ({}^{(1)}\mathbf{A}_{ei}^{(3)} : {}^{(3)}\mathbf{A}_{ei}^{(1)}) A_{ej}] r_{ij}^{-10} + \\
 & + \frac{5}{3} [A_{ei}^{(4)} (\mathbf{A}_{ej} : \mathbf{A}_{ej}) + (\mathbf{A}_{ei} : \mathbf{A}_{ei}) A_{ej}^{(4)}] r_{ij}^{-8} + \\
 & \left. + \frac{28}{9} [A_{ei}^{(4)} ({}^{(1)}\mathbf{A}_{ej}^{(2)} : {}^{(2)}\mathbf{A}_{ej}^{(1)}) + ({}^{(1)}\mathbf{A}_{ei}^{(2)} : {}^{(2)}\mathbf{A}_{ei}^{(1)}) A_{ej}^{(4)}] r_{ij}^{-10} + \dots \right\rangle, \quad (69a)
 \end{aligned}$$

where $({}^{(1)}\mathbf{A}_{ei}^{(2)})$ and $({}^{(2)}\mathbf{A}_{ei}^{(1)})$ are the linear electric dipole-quadrupole and quadrupole-dipole polarizabilities and, by (71), $A_{ei}^{(4)}$ is the mean electric quadrupole-quadrupole polarizability.

As a particular case of some interest we shall consider that of axially-symmetric molecules with centers of inversion for which (69a) yields in a good approximation

$${}_2S_{02}^{is} = 6 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ A_{ei} A_{ej} [A_{ei} (1 + 2\kappa_i^2) + A_{ej} (1 + 2\kappa_j^2)] r_{ij}^{-6} + \right. \\
 \left. + \frac{2}{3} [A_{ei}^{(4)} A_{ej}^2 (1 + 2\kappa_j^2) + A_{ei}^2 (1 + 2\kappa_i^2) A_{ej}^{(4)}] r_{ij}^{-8} + \dots \right\rangle, \quad (69b)$$

where $\kappa \doteq (A_{\parallel} - A_{\perp})/3A$ is a parameter determining the anisotropy of dipole polarizability with A_{\parallel} and A_{\perp} , respectively, the polarizability in the directions parallel and perpendicular to the molecule's symmetry axis.

In the same manner we can particularize the three-body contribution (70); e.g. we have for the electric dipole approximation

$${}_3S_{02}^{is} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \left\{ 3(A_{ei}^* + A_{ej}^* + A_{ek}^*) A_{ei} A_{ej} A_{ek} \cdot \right. \right. \\
 \left. \left. \times (r_{ij} r_{jk})^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) + A_{ei}^* A_{ek} (A_{ej} : A_{ej}) r_{jk}^{-6} \right\} \right\rangle. \quad (70a)$$

In the calculation of the contribution (68b) we restrict ourselves to the electric dipole-dipole approximation in the multipole expansion (36) and obtain for the two- and three-body interactions

$${}_2S_{11}^{is} = \frac{1}{75} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ 60[|A_{ei}|^2 (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) + (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) |A_{ej}|^2] + \right. \\
 \left. + 7(\mathbf{D}_{ei}^* : \mathbf{D}_{ei})(\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \} r_{ij}^{-6} \right\rangle, \quad (72a)$$

$${}_3S_{11}^{is} = \frac{4}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \{ A_{ei}^* A_{ek} + A_{ei} A_{ek}^* \} (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \times \right. \\
 \left. \times (r_{ij} r_{jk})^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \quad (72b)$$

with

$$\mathbf{D}_e = \mathbf{A}_e - A_e \mathbf{U} \quad (71a)$$

the deviation tensor of linear dipole-dipole electric polarizability.

Applying the preceding expression to axially-symmetric molecules, we obtain:

$${}_2S_{11}^{is} = \frac{12}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N |A_{ei}|^2 |A_{ej}|^2 (2\kappa_i^2 + 2\kappa_j^2 + \frac{7}{3}\kappa_i^2 \kappa_j^2) r_{ij}^{-6} \right\rangle, \quad (72c)$$

$${}_3S_{11}^{is} = \frac{24}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N (A_{ei}^* A_{ek} + A_{ei} A_{ek}^*) |A_{ej}|^2 \kappa_j^2 \times \right. \\
 \left. \times (r_{ij} r_{jk})^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle. \quad (72d)$$

In the approximation (11), the four-body contribution is zero:

$${}_4S_{11}^{is} = 0, \quad (72e)$$

whereas in the approximation (02) we have:

$$\begin{aligned}
{}_4S_{02}^{\text{is}} = & 6 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \sum_{l \neq k \neq j \neq i}^N A_{ei}^* A_{ej} A_{ek} A_{el} \times \right. \\
& \left. \times r_{jk}^{-3} r_{kl}^{-3} P_2 \left(\frac{\mathbf{r}_{jk} \cdot \mathbf{r}_{kl}}{r_{jk} r_{kl}} \right) \right\rangle. \quad (72f)
\end{aligned}$$

On proceeding to the next higher dipole-quadrupole approximation in the expansion (36) we obtain, beside the two-body contribution provided by (69a):

$$\begin{aligned}
{}_2S_{02}^{\text{is}} = & 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ |A_{ei}|^2 ({}^{(1)}\mathbf{A}_{ej}^{(2)} : {}^{(2)}\mathbf{A}_{ej}^{(1)}) + \right. \\
& \left. + ({}^{(1)}\mathbf{A}_{ei}^{(2)} : {}^{(2)}\mathbf{A}_{ei}^{(1)}) A_{ei}^* A_{ej} \} r_{ij}^{-8} \right\rangle, \quad (69c)
\end{aligned}$$

the following contributions arising from (68b) for the two- and three-body interactions (Kielich 1980)*

$${}_2S_{11}^{\text{is}} = \frac{40}{21} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ |A_{ei}|^2 G_j^{(3,3)} + \frac{2}{25} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) K_j^{(3,3)} \} r_{ij}^{-8} \right\rangle \quad (72f)$$

$${}_3S_{11}^{\text{is}} = -\frac{40}{21} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N A_{ei}^* G_j^{(3,3)} A_{ek} \cdot r_{ij}^{-4} r_{jk}^{-4} P_3 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \quad (72g)$$

$${}_4S_{11}^{\text{is}} = 0, \quad (72h)$$

where the molecular parameters $G_j^{(3,3)}$ and $K_j^{(3,3)}$ are in general rather highly complicated combinations of scalar products of the tensors ${}^{(1)}\mathbf{A}_j^{(2)}$ and ${}^{(2)}\mathbf{A}_j^{(1)}$ and we refrain from adducing them in explicit form. We shall consider these formulae again in §8.

7.2b. *Nonlinear multipole polarizabilities:* We now consider the higher contributions to (68) from the nonlinear multipole polarizabilities (40) and (42). By (42) we obtain for the two-body contribution (Kielich 1965b)

$$\begin{aligned}
{}_2S_{02}^{\text{is}} = & \frac{1}{2} \sum_{n=1}^{\infty} \sum_{u=1}^{\infty} \frac{2^{n+u} (n! u!)^2 (2n+2u)! (2n+3)}{(2n)! (2n+1)! (2u)! (2u+1)!} \times \\
& \times \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ C_{ei}^{2(n+1)} (\mathbf{M}_{ej}^{(u)} [u] \mathbf{M}_{ej}^{(u)}) + \right. \\
& \left. + (\mathbf{M}_{ei}^{(u)} [u] \mathbf{M}_{ei}^{(u)}) C_{ej}^{2(n+1)} \} r_{ij}^{-2(n+u+1)} \right\rangle, \quad (73)
\end{aligned}$$

where

$$C_{ei}^{2(n+1)} = \frac{1}{2n+3} \mathbf{U} : {}^{(1)}_e \mathbf{C}_{eee}^{(1+n+n)} [2n] \mathbf{U}^n \quad (74)$$

is the mean nonlinear (third-order) multipole electric polarizability.

* The scattering constants defined by (52) and (54) as applied here are in excess of those used in a previous paper (Kielich 1980) by factors of 3 and 30, respectively.

In the case of axially-symmetric molecules possessing only the third-order mean dipole-dipole polarizability $C_e^{(4)}$, the expression (73) becomes

$${}_2S_{02}^{is} = \frac{5}{6} \sum_{n=1}^{\infty} (n+1) \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ C_{ei}^{(4)} (M_{ej}^{(n)})^2 + (M_{ei}^{(n)})^2 C_{ej}^{(4)} \} r_{ij}^{-2(n+2)} \right\rangle, \quad (73a)$$

where, by (9),

$$M_{ei}^{(n)} = \sum_{s=1}^{n_i} e_{si} r_{si}^n P_n(\cos \Theta_s) \quad (9a)$$

is the 2^n -pole scalar electric moment of an axially symmetric i th molecule.

By (40b), we obtain for nonlinearly polarizable dipolar and quadrupolar molecules, respectively (Kielich 1980)

$${}_2S_{02}^{is} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* (A_{ei} + A_{ej}) (\mathbf{U} : {}^{(1)}_e \mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)}) r_{ij}^{-6} \right\rangle, \quad (75a)$$

$${}_2S_{02}^{is} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* (A_{ei} + A_{ej}) (\mathbf{U} : {}^{(1)}_e \mathbf{B}_{eej}^{(1+2)} : \mathbf{M}_{ej}^{(2)}) r_{ij}^{-8} \right\rangle. \quad (75b)$$

The molecular parameter $\mathbf{U} : {}^{(1)}_e \mathbf{B}_{ee}^{(1+1)} \cdot \mathbf{M}_e^{(1)}$ intervenes in DC electric field-induced second-harmonic light generation (Kielich 1969, 1979; Hauchecorne *et al* 1971) permitting the determination of the value of the nonlinear (second-order) dipole-dipole electric polarizability tensor ${}^{(1)}_e \mathbf{B}_{ee}^{(1+1)}$, if the intrinsic electric dipole moment $\mathbf{M}_e^{(1)}$ is known. The new contributions (75a) and (75b) are of interest as containing the first power of the tensors ${}^{(1)}_e \mathbf{B}_{ee}^{(1+1)}$ and ${}^{(1)}_e \mathbf{B}_{ee}^{(1+2)}$ and not their square, as it is the case for the S_{11}^{is} contribution (Kielich 1960, 1968). So the formula (75b) provides an indirect method for the determination of the value and sign of the second-order nonlinear dipole-quadrupole electric polarizability or the intrinsic quadrupole electric moment $\mathbf{M}_e^{(2)}$.

7.3 Temperature-dependent contributions arising from electrostatic multipole interaction

Hitherto, in the foregoing calculations, we considered the approximation (56a) when the distribution function depended only on the positional variables \mathbf{r}^N of the molecules. Generally, the total interaction energy consists, besides $U_0(\mathbf{r}^N)$, also of that part of $V_{\Omega}^N = V(\mathbf{r}^N, \Omega^N)$ which depends both on the positional and orientational variables \mathbf{r} and Ω of the molecules. In the case of weak tensorial interactions between the microsystems, i.e. when simultaneously $V_{\Omega} \ll U_0$ and $V_{\Omega} < kT$, the Boltzmann factors in (56) can be expanded in power series in V_{Ω}/kT . In particular, restricting the problem to the first approximation of statistical perturbation calculus, the exact distribution function (56) can be replaced by:

$$f(\mathbf{r}^N, \Omega^N) = \Omega^{-N} f(\mathbf{r}^N) \left\{ 1 - \frac{1}{kT} (V_{\Omega} - \langle V_{\Omega} \rangle) + \dots \right\}. \quad (56b)$$

This expansion leads to further contributions to the scattering constant (52), which are dependent explicitly on temperature. However, we shall restrict these supplementary calculations to the first approximation resulting from (55b):

$$S_1^{is} = S_{01}^{is} + S_{10}^{is}. \quad (76)$$

Usually, electrostatic multipole interactions in (19) play the predominant role and we obtain for dipole-quadrupole type interactions with regard to (36) and (56b) (Kielich 1980)

$${}^2S_{01(1)}^{\text{is}} = -\frac{1}{5kT} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N (A_{ei}^* + A_{ej}^*) (\mathbf{D}_{ei} : \mathbf{M}_{ei}^{(2)}) \times \right. \\ \left. \times [\mathbf{U} : ({}^{(1)}\mathbf{A}_{ej}^{(2)} + {}^{(2)}\mathbf{A}_{ej}^{(1)}) \cdot \mathbf{M}_{ej}^{(1)}] r_{ij}^{-8} \right\rangle. \quad (77)$$

The above contributions attract our attention because they involve the first power of the tensors ${}^{(1)}\mathbf{A}_e^{(2)}$ and ${}^{(2)}\mathbf{A}_e^{(1)}$ and not their product, as it is the case for the contribution (69a).

On inserting (19) into (56a) one obtains by (40a) for the two-body contributions (Kielich 1965b)

$${}^2S_{01(1)}^{\text{is}} = \frac{1}{kT} \sum_{n=1}^{\infty} \sum_{u=1}^{\infty} \frac{2^{n+u} (n!u!)^2 (2n+2u)!}{(2n)! (2n+1)! (2u)! (2u+1)!} \cdot \\ \cdot \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ (\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+n)} [n] \mathbf{M}_{ei}^{(n)}) (\mathbf{M}_{ej}^{(u)} [u] \mathbf{M}_{ej}^{(u)}) + \right. \\ \left. + (\mathbf{M}_{ei}^{(u)} [u] \mathbf{M}_{ei}^{(u)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+n)} [n] \mathbf{M}_{ej}^{(n)}) \} r_{ij}^{-2(n+u+1)} \right\rangle. \quad (78)$$

On expanding this general expression to within the term in quadrupole moments we have

$${}^2S_{01(1)}^{\text{is}} = \frac{2}{3kT} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ [(\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{M}_{ej}^{(1)} \cdot \mathbf{M}_{ej}^{(1)}) \right. \\ + (\mathbf{M}_{ei}^{(1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)})] r_{ij}^{-6} + \\ + [(\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)}) + \\ + (\mathbf{M}_{ei}^{(2)} : \mathbf{M}_{ei}^{(2)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)}) + (\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+2)} : \mathbf{M}_{ei}^{(2)}) (\mathbf{M}_{ej}^{(1)} \cdot \mathbf{M}_{ej}^{(1)}) + \\ + (\mathbf{M}_{ei}^{(1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)} : \mathbf{M}_{ej}^{(2)})] r_{ij}^{-8} + \\ + \frac{28}{5} [(\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+2)} : \mathbf{M}_{ei}^{(2)}) (\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)}) + \\ \left. + (\mathbf{M}_{ei}^{(2)} : \mathbf{M}_{ei}^{(2)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)} : \mathbf{M}_{ej}^{(2)})] r_{ij}^{-10} \right\}. \quad (78a)$$

In a similar way we can calculate some other contributions to S_p^{is} , also dependent on T^{-p} for $p \geq 2$ (Kielich 1960b).

8. Application to anisotropic (depolarized) scattering

8.1 Zeroth approximation of the theory

In the zeroth approximation the polarizability tensor of a microsystem is independent of the electric field of the surrounding, neighbouring microsystems, and the anisotropic scattering constant (54) becomes

$$S_0^{\text{anis}} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{D}_{ei}^* : \mathbf{D}_{ej} \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (79)$$

where the deviator defined by (71a) differs from zero only if the molecule is, intrinsically, optically anisotropic.

In the absence of interference effects we obtain immediately from (79) for the incoherent and coherent parts of the anisotropic scattering constant

$$S_{0,\text{inc}}^{\text{anis}} = \sum_{i=1}^N \mathbf{D}_{ei}^* : \mathbf{D}_{ei} = 6 \sum_{i=1}^N |A_{ei}|^2 \kappa_i^2, \quad (79a)$$

$$S_{0,\text{coh}}^{\text{anis}} = \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \mathbf{D}_{ei}^* : \mathbf{D}_{ej} \right\rangle, \quad (79b)$$

where

$$\kappa_i^2 = \frac{\mathbf{D}_{ei}^* : \mathbf{D}_{ei}}{6|A_{ei}|^2}, \quad (80)$$

is the parameter of optical anisotropy polarizability of the i th molecule.

The expressions of (79) and (80) are valid for any molecular symmetry, whereas they undergo considerable simplification if the scattering molecules are assumed to possess the axial symmetry:

$$S_{0,\text{coh}}^{\text{anis}} = 3 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* A_{ej} \kappa_i \kappa_j (3 \cos^2 \Theta_{ij} - 1) \right\rangle \quad (81)$$

with Θ_{ij} denoting the angle between the axes of symmetry of two mutually interacting molecules having the orientations Ω_i and Ω_j .

Obviously, in the absence of molecular interactions, the coherent scattering constants (79b) and (81) vanish.

For molecules of the same species (81) reduces to the well-known result

$$S_0^{\text{anis}} = S_{0,\text{inc}}^{\text{anis}} J_A, \quad (81a)$$

where

$$S_{0,\text{inc}}^{\text{anis}} = 6N |A_e|^2 \kappa^2,$$

and

$$J_A = \frac{1}{2} \rho \iint (3 \cos^2 \Theta_{12} - 1) g^{(2)}(r_{12}, \Omega_1, \Omega_2) d\mathbf{r}_{12} d\Omega_1 d\Omega_2 \quad (82)$$

is the angular molecular pair correlation parameter.

The influence of various angular molecular correlations (dispersional, electrostatic, inductional, etc.) on anisotropic light scattering has been discussed by many authors (Benoit and Stockmayer 1956; Kielich 1960a, 1967, 1968b; Pecora and Steele 1965; Kielich and Woźniak 1974; Woźniak and Kielich 1975; Gray and Gubbins 1975; Høyve and Stell 1977; Ladanyi *et al* 1980). On the other hand, the parameter (82) accounting for these correlations is accessible to determination from experimental data (Deželić 1966; Kasprowicz and Kielich 1968; Lalanne 1969; Fechner 1969; Lucas and Jackson 1971; Kielich *et al* 1972; Alms *et al* 1974; Wróż 1975; Tancrede *et al* 1977a, b; Bertucci *et al* 1977; Battaglia *et al* 1979; Madden *et al* 1980; Vereshchagin 1980).

8.2 First approximation of the theory

We now restrict our considerations to the dipole induced dipole approximation in (36) and obtain by (54) for arbitrary molecular symmetry

$$S_{01}^{\text{anis}} = - \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq j}^N \mathbf{D}_{ei}^* : (\mathbf{A}_{ej} \cdot {}^{(1)}\mathbf{T}_{jk}^{(1)} \cdot \mathbf{A}_{ek}) \exp(i \Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle. \quad (83)$$

For molecules possessing the axial symmetry (83) yields for two-body contributions (Kielich 1971a; Kielich and Woźniak 1974)

$$S_{01}^{\text{anis}} = 3 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ 2A_{ei}^* A_{ej} \kappa_i (1 - \kappa_j) [A_{ei} (1 + \kappa_i) - A_{ej} \kappa_j] (3 \cos^2 \Theta_i - 1) r_{ij}^{-3} + 2A_{ei}^* A_{ej} \kappa_i \kappa_j [A_{ei} (1 + \kappa_i) + A_{ej} (1 + \kappa_j)] (3 \cos \theta_i \cos \theta_j \cos \Theta_{ij} - \cos^2 \Theta_{ij}) r_{ij}^{-3} \} \right\rangle, \quad (83a)$$

where θ_i and θ_j denote the angles between the symmetry axes of molecules i or j and the vector \mathbf{r}_{ij} . The three-body contribution is calculated in the paper of Kielich and Woźniak (1974).

In the case of a one-component system, (83a) reduces to

$$S_{01}^{\text{anis}} = 12A_e^3 \kappa N \{ (1 - \kappa) J_{RA} + 2\kappa (1 + \kappa) K_{RA} \}, \quad (83b)$$

where the radial-angular binary correlation parameters (Kielich 1971a)

$$J_{RA} = \frac{1}{2} \rho \iint (3 \cos^2 \Theta_1 - 1) r_{12}^{-3} g^{(2)}(r_{12}, \Omega_1, \Omega_2) d\mathbf{r}_{12} d\Omega_1 d\Omega_2,$$

$$K_{RA} = \frac{1}{2} \rho \iint (3 \cos \Theta_1 \cos \Theta_2 \cos \Theta_{12} - \cos^2 \Theta_{12}) \times$$

$$\times r_{12}^{-3} g^{(2)}(r_{12}, \Omega_1, \Omega_2) d\mathbf{r}_{12} d\Omega_1 d\Omega_2 \quad (84)$$

have been calculated for special molecular models (Kielich *et al* 1972; Woźniak and Kielich 1975). Obviously, the above parameters are defined so as to vanish in the absence of angular correlations.

Similarly to (77), we obtain for the dipole-quadrupole approximation (Kielich 1980):

$${}_2S_{01(1)}^{\text{anis}} = - \frac{2}{5kT} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ [\mathbf{D}_{ei}^* : (\mathbf{A}_{ei} \cdot \mathbf{M}_{ei}^{(2)})] [\mathbf{U} : ({}^{(1)}\mathbf{A}_{ej}^{(2)} + {}^{(2)}\mathbf{A}_{ej}^{(1)}) \cdot \mathbf{M}_{ej}^{(1)}] + [\mathbf{D}_{ei}^* : ({}^{(1)}\mathbf{A}_{ei}^{(2)} + {}^{(2)}\mathbf{A}_{ei}^{(1)}) \cdot \mathbf{M}_{ei}^{(1)}] \times$$

$$\times (\mathbf{D}_{ej} : \mathbf{M}_{ej}^{(2)}) \} r_{ij}^{-8} \right\rangle. \quad (85)$$

By (40a) and (19) we obtain for dipolar nonlinearly polarizable molecules (Kielich 1960b, 1968a):

$${}_2S_{01(1)}^{\text{anis}} = \frac{2}{75kT} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ (\mathbf{M}_{ei}^{(1)} \cdot \mathbf{D}_{ei}^* \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{U} : ({}^{(1)}\mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)})) +$$

$$+ 25 (\mathbf{D}_{ei}^* : ({}^{(1)}\mathbf{B}_{eei}^{(1+1)} \cdot \mathbf{M}_{ei}^{(1)})) (\mathbf{M}_{ej}^{(1)} \cdot \mathbf{M}_{ej}^{(1)}) \} r_{ij}^{-6} \right\rangle. \quad (85a)$$

Analogous calculations, somewhat less complicated, can be carried out for other models of correlating polar molecules (Kielich 1960b, 1968a, b; Kielich and Woźniak 1974; Woźniak and Kielich 1975; Frenkel and McTague 1980).

8.3 Second approximation of the theory

8.3a. *Contribution from linear multipole polarizabilities:* We shall now proceed a step further, and shall take into account the Yvon–Kirkwood translational fluctuation effect for molecules with intrinsic anisotropy. We obtain, by (36) and (37) in the electric dipole approximation for the two-body contribution:

$$\begin{aligned}
 {}_2S_{11}^{\text{anis}} &= \left\langle \sum_{i=1}^N \sum_{j=1}^N \left\{ 12 |A_{ei} A_{ej}|^2 + \frac{7}{5} [|A_{ei}|^2 (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) + \right. \right. \\
 &\quad \left. \left. + (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) |A_{ej}|^2 \right\} + \frac{22}{25} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \right\} r_{ij}^{-6} \right\rangle, \\
 {}_2S_{02}^{\text{anis}} &= \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ 2 [\mathbf{D}_{ei}^* : (\mathbf{D}_{ei} \cdot \mathbf{D}_{ei}) + 2 A_{ei} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei})] A_{ej} + \right. \right. \\
 &\quad \left. \left. + \frac{1}{5} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) A_{ej}^2 + \frac{1}{150} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \right\} r_{ij}^{-6} \right\rangle. \quad (86)
 \end{aligned}$$

Similarly, we have for the three-body contribution

$$\begin{aligned}
 {}_3S_{11}^{\text{anis}} &= 12 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N (A_{ei}^* A_{ek} + A_{ei} A_{ek}^*) [|A_{ej}|^2 + \right. \\
 &\quad \left. + \frac{7}{60} (\mathbf{D}_{ej}^* : \mathbf{D}_{ej})] r_{ij}^{-3} r_{jk}^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \\
 {}_3S_{02}^{\text{anis}} &= \frac{1}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \left\{ 20 (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) A_{ej} + A_{ei} (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \right\} A_{ek} \times \right. \\
 &\quad \left. \times r_{ij}^{-3} r_{jk}^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \quad (87)
 \end{aligned}$$

and for the four-body contribution

$$\begin{aligned}
 {}_4S_{11}^{\text{anis}} &= 6 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \sum_{l \neq k \neq j \neq i}^N A_{ei}^* A_{ej} A_{ek}^* A_{el} \times \right. \\
 &\quad \left. \times r_{ij}^{-3} r_{jl}^{-3} P_2 \left(\frac{\mathbf{r}_{ik} \cdot \mathbf{r}_{jl}}{r_{ik} r_{jl}} \right) \right\rangle, \quad (88a)
 \end{aligned}$$

$${}_4S_{02}^{\text{anis}} = 0. \quad (88b)$$

On addition of (86) and (87) as well as the respective contributions ${}_2S_{20}^{\text{anis}}$ and ${}_3S_{20}^{\text{anis}}$ we obtain the previously derived results for $S_{02}^{\text{anis}} + S_{11}^{\text{anis}} + S_{20}^{\text{anis}}$ (Kielich 1968a, equations A.8–A.10).

For axially-symmetric molecules (86) and (87) reduce to a simpler form:

$$\begin{aligned}
{}_2S_{11}^{\text{anis}} &= 6 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N |A_{ei} A_{ej}|^2 \left\{ 2 + \frac{7}{3} (\kappa_i^2 + \kappa_j^2) + \frac{132}{25} \kappa_i^2 \kappa_j^2 \right\} r_{ij}^{-6} \right\rangle, \\
{}_2S_{02}^{\text{anis}} &= \frac{6}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N |A_{ei}|^2 \left\{ (20A_{ei} + A_{ej}) A_{ej} \kappa_i^2 + \right. \right. \\
&\quad \left. \left. + 10A_{ei} A_{ej} \kappa_i^3 + \frac{1}{3} A_{ej}^2 \kappa_i^2 \kappa_j^2 \right\} r_{ij}^{-6} \right\rangle, \quad (86a) \\
{}_3S_{11}^{\text{anis}} &= 12 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N (A_{ei}^* A_{ek} + A_{ei} A_{ek}^*) |A_{ej}|^2 \times \right. \\
&\quad \left. \times \left(1 + \frac{7}{10} \kappa_j^2 \right) r_{ij}^{-3} r_{jk}^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \\
{}_3S_{02}^{\text{anis}} &= \frac{6}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \left\{ 20 |A_{ei}|^2 A_{ej} \kappa_i^2 + A_{ei} |A_{ej}|^2 \kappa_j^2 \right\} \cdot \right. \\
&\quad \left. \cdot r_{ij}^{-3} r_{jk}^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle. \quad (87a)
\end{aligned}$$

The contributions (86a) and (87a) jointly give the results derived by Kielich (1968a) for liquid mixtures. Applied to one-component fluids, they give the formulae evaluated numerically by Woźniak and Kielich (1975).

Recently, Cox and Madden (1980), applying the spherical tensor method, have calculated the contributions S_{11}^{is} and S_{11}^{anis} only, for the case of a one-component fluid. Their formulae, compared with those resulting from (72a) and (72b) for S_{11}^{is} and (88), (86a) and (87a) for S_{11}^{anis} , as applied to molecules having identical real polarizabilities $\alpha = A_i = A_j = A_k$ and anisotropies $\gamma = 3A_i \kappa_i = 3A_j \kappa_j = A_{\parallel} - A_{\perp}$, are found to differ only in numerical factors at the term $\gamma^4 = (3AK)^4$. Obviously, for weakly optically anisotropic molecules, this term is of no relevance.

Taking into account the terms with dipole-quadrupole polarizability in the expansions (36) and (57) we arrive at the following binary and ternary contributions (Kielich 1980):

$${}_2S_{11}^{\text{anis}} = \frac{16}{7} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ |A_{ei}|^2 P_j^{(3,3)} + \frac{73}{90} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) Q_j^{(3,3)} \right\} r_{ij}^{-8} \right\rangle, \quad (89a)$$

$${}_2S_{02}^{\text{anis}} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ \mathbf{D}_{ei}^* : ({}^{(1)}\mathbf{A}_{ei}^{(2)} : {}^{(2)}\mathbf{A}_{ei}^{(1)}) A_{ej} + \frac{1}{105} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) W_j^{(3,3)} \right\} r_{ij}^{-8} \right\rangle, \quad (89b)$$

$${}_3S_{11}^{\text{anis}} = \frac{-16}{7} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N A_{ei}^* P_j^{(3,3)} A_{ek} r_{ij}^{-4} r_{jk}^{-4} P_3 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \quad (89c)$$

where the molecular parameters $P_j^{(3,3)}$, $Q_j^{(3,3)}$ and $W_j^{(3,3)}$ are given by appropriate combinations of products of the tensors ${}^{(1)}\mathbf{A}_{ej}^{(2)}$ and ${}^{(2)}\mathbf{A}_{ej}^{(1)}$.

For tetrahedrally-symmetric molecules (e.g. CH_4) we have:

$$G_j^{(3,3)} = K_j^{(3,3)} = P_j^{(3,3)} = Q_j^{(3,3)} = W_j^{(3,3)} = 6(A_{xyz}^{(j)})^2,$$

so that formulae (72f) and (89a) go over into those of Buckingham and Tabisz (1978) derived for binary collision-induced rotational Raman scattering by tetrahedral

molecules. It is noteworthy that the contributions (72g) and (89c) can be positive or negative, depending on the three-body interaction model applied and thus can cancel or raise the two-body interaction contributions (72f) and (89a). It is also of interest that the cross contributions (69c) and (89b) are non-zero only for two-body interactions; thus, they can play an important role if (72f) and (72g), as well (89a) and (89c), cancel out mutually.

In the case of anisotropic axially-symmetric molecules of one species (*e.g.* CO₂), (72b) and (39a) lead to the recent results of Amos *et al* (1980) for the binary collision-induced Raman scattering.

If the terms with the quadrupole-quadrupole polarizability tensor ⁽²⁾A_i⁽²⁾ are taken into account in the expansion (37), one obtains by (55b) for two- and three-body interactions (Kielich 1980):

$$\begin{aligned}
 {}_2S_{02}^{\text{anis}} &= \frac{4}{7} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ [|A_{ei}|^2 + \frac{1}{30} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei})] [(\mathbf{D}_{ej}^* : {}^{(2)}\mathbf{A}_{ej}^{(2)}) : \mathbf{U}] + \right. \\
 &\quad \left. + \frac{35}{6} [\mathbf{D}_{ei}^* : (\mathbf{D}_{ei} \cdot \mathbf{D}_{ei}) + 2A_{ei}^* (\mathbf{D}_{ei} : \mathbf{D}_{ei})] A_{ej}^4 \right\} r_{ij}^{-8} \right\rangle, \\
 {}_3S_{02}^{\text{anis}} &= -\frac{4}{7} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \left\{ A_{ei}^* [(\mathbf{D}_{ei} : {}^{(2)}\mathbf{A}_{ei}^{(2)}) : \mathbf{U}] + \right. \\
 &\quad \left. + \frac{35}{3} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) A_{ej}^{(4)} \right\} r_{ij}^{-4} r_{jk}^{-4} P_3 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle. \tag{90}
 \end{aligned}$$

8.3b *Contributions from nonlinear multipole polarizabilities:* For nonlinearly polarizable molecules with an intrinsic dipole moment $\mathbf{M}_{ei}^{(1)}$ the first approximation of (40a) leads to previously calculated results for S_{11} (Kielich 1960b, 1968a); however, the second approximation of (40b) yields the following two-body contribution (Kielich 1980):

$$\begin{aligned}
 {}_2S_{02}^{\text{anis}} &= 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ A_{ei}^* (\mathbf{D}_{ei} : {}^{(1)}\mathbf{B}_{eei}^{(1+1)} \cdot \mathbf{M}_{ei}^{(1)}) + \right. \\
 &\quad \left. + \frac{1}{225} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)}) \right\} r_{ij}^{-6} \right\rangle. \tag{91}
 \end{aligned}$$

For molecules having an intrinsic quadrupole moment $\mathbf{M}_{ei}^{(2)}$ and the nonlinear dipole-quadrupole polarizability ${}^{(1)}\mathbf{B}_{eei}^{(1+2)}$, (40a), (40b) lead, in the two-body approximation (Kielich 1980), to

$$\begin{aligned}
 {}_2S_{11}^{\text{anis}} &= \frac{56}{135} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ [3 {}^{(1)}\mathbf{B}_{eei}^{(1+2)} * \dots * {}^{(1)}\mathbf{B}_{eei}^{(1+2)} - \right. \\
 &\quad - (\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+2)}) * : (\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+2)})] (\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)}) + \\
 &\quad + \frac{8}{49} [(3\mathbf{U}_{13} : {}^{(1)}\mathbf{B}_{eei}^{(1+2)} - \mathbf{U}_{12} : {}^{(1)}\mathbf{B}_{eei}^{(1+2)}) * : \mathbf{M}_{ei}^{(2)}] [(3\mathbf{U}_{13} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)} - \\
 &\quad - \mathbf{U}_{12} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)}) : \mathbf{M}_{ej}^{(2)}] \right\} r_{ij}^{-10} \right\rangle, \\
 {}_2S_{02}^{\text{anis}} &= 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ A_{ei}^* (\mathbf{D}_{ej} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)} : \mathbf{M}_{ej}^{(2)}) + \frac{1}{315} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) \times \right. \\
 &\quad \left. \times (3\mathbf{U}_{13} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)} - \mathbf{U}_{12} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)}) : \mathbf{M}_{ej}^{(2)} \right\} r_{ij}^{-8} \right\rangle. \tag{92}
 \end{aligned}$$

The last formulae provide an indirect method for the determination of the sign of the intrinsic quadrupole moment $M_e^{(2)}$.

By the expansion (42), similar calculations yield successively for the two-body contribution from interaction between an intrinsic dipole or quadrupole moment and induced third-order dipole moment (Kielich 1960b, 1968a):

$${}_2S_{02}^{\text{anis}} = \frac{1}{15} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ C_{ei}^{(4)}(\mathbf{M}_{ej}^{(1)} \cdot \mathbf{D}_{ej}^* \cdot \mathbf{M}_{ej}^{(1)}) + 5(\mathbf{D}_{ei}^* : {}^{(1)}_e C_{eeei}^{(1+1+1)} : \mathbf{U})(\mathbf{M}_{ej}^{(1)} \cdot \mathbf{M}_{ej}^{(1)}) \} r_{ij}^{-6} \right\rangle, \quad (93)$$

$${}_2S_{02}^{\text{anis}} = \frac{1}{21} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ 20C_{ei}^{(4)}[\mathbf{D}_{ej}^* : (\mathbf{M}_{ej}^{(2)} \cdot \mathbf{M}_{ej}^{(2)})] + 7(\mathbf{D}_{ei}^* : {}^{(1)}_e C_{eeei}^{(1+1+1)} : \mathbf{U})(\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)}) \} r_{ij}^{-8} \right\rangle. \quad (94)$$

9. Linewidth broadening in quasi-elastic scattering by correlated microsystems

This section is aimed at presenting a stochastic treatment of the spectral distribution of light scattered by systems of atoms and molecules, correlated in time and space.

9.1 Time-correlations intensity of scattered light

Similarly to the integral intensity of scattered light (50) we can introduce the following time-correlation intensity of scattered light (for processes stationary in time)

$$I_{e_s}(\mathbf{r}, t) = \frac{R_e^2(\omega_s)}{8\pi c^3} \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{e}_s \cdot \ddot{\mathbf{Z}}(t_i) \ddot{\mathbf{Z}}(t_j + t) \cdot \mathbf{e}_s^* \right\rangle. \quad (95)$$

With regard to the theorem of Wiener and Khinchin, the Fourier transform of the time-correlation intensity (95) determines the spectral density

$$S_{e_s}(\Delta \mathbf{k}, \omega) = (2\pi)^{-4} \int \int_{-\infty}^{+\infty} I_{e_s}(\mathbf{r}, t) \exp[i(\omega_s t - \Delta \mathbf{k} \cdot \mathbf{r})] dt d\mathbf{r}. \quad (95a)$$

The range of applicability of this theorem to time-dependent spectral processes has been the subject of an analysis by Eberly and Wódkiewicz (1977).

Restricting the problem to electric-dipole scattering in the wave zone, we write (95) in the form

$$I_{e_s e}(\mathbf{r}, t) = Q(\omega_s) I_0(\mathbf{r}, t) \left\langle \sum_{i=1}^N \sum_{j=1}^N [\mathbf{e}_s \cdot \Pi_e(r_i^0, \Omega_i^0) \cdot \mathbf{e}_s^*] \times [\mathbf{e}_s^* \cdot \Pi_e(r_j^t, \Omega_j^t) \cdot \mathbf{e}] \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle, \quad (96)$$

where the position and orientation of a microsystem i is given at the moment of time t by the variables \mathbf{r}_i^t and Ω_i^t , and

$$I_0(\mathbf{r}, t) = I_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)].$$

On decomposing the effective polarizability tensor $\Pi(\mathbf{r}, \Omega)$ into three irreducible tensors and on averaging in (96) over all possible orientations of the microsystems, we obtain respectively for isotropic, antisymmetric and anisotropic scattering (Kielich *et al* 1981)

$$I_{e,e}^{(0)}(\mathbf{r}, t) = \frac{1}{3} Q(\omega_s) I_0(\mathbf{r}, t) S^{(0)}(\Delta \mathbf{k}, t) |\mathbf{e}_s \cdot \mathbf{e}^*|^2, \quad (96a)$$

$$I_{e,e}^{(1)}(\mathbf{r}, t) = \frac{1}{6} Q(\omega_s) I_0(\mathbf{r}, t) S^{(1)}(\Delta \mathbf{k}, t) (1 - |\mathbf{e}_s \cdot \mathbf{e}|^2), \quad (96b)$$

$$I_{e,e}^{(2)}(\mathbf{r}, t) = \frac{1}{30} Q(\omega_s) I_0(\mathbf{r}, t) S^{(2)}(\Delta \mathbf{k}, t) (3 + 3|\mathbf{e}_s \cdot \mathbf{e}|^2 - 2|\mathbf{e}_s \cdot \mathbf{e}^*|^2). \quad (96c)$$

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

$$S^{(h)}(\Delta \mathbf{k}, t) = \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_e^{(h)}(\mathbf{r}_i^0, \Omega_i^0)^* : \Pi_e^{(h)}(\mathbf{r}_j^t, \Omega_j^t) \exp [i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle \quad (97)$$

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

9.2 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), we obtain from (97)

$$S^{(h)}(\Delta \mathbf{k}, t) = \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{A}_e^{(h)}(\Omega_i^0)^* : \mathbf{A}_e^{(h)}(\Omega_j^t) \exp [i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle. \quad (98)$$

In particular, for anisotropic scattering, we get:

$$S^{(2)}(\Delta \mathbf{k}, t) = \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{D}_e(\Omega_i^0)^* : \mathbf{D}_e(\Omega_j^t) \exp [i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle. \quad (98a)$$

9.2a *Correlation function of isotropic scattering:* In the case of atoms and isotropically polarizable molecules we have by (98) isotropic scattering only, with the correlation function

$$S^{(0)}(\Delta \mathbf{k}, t) = 3 \left\langle \sum_{i=1}^N \sum_{j=1}^N A_{ei}^* A_{ej} \exp [i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle \quad (99)$$

which, for like correlating microsystems, reduces to

$$S^{(0)}(\Delta \mathbf{k}, t) = 3N |A_e|^2 F(\Delta \mathbf{k}, t). \quad (99a)$$

Here, we have introduced the well known intermediate scattering correlation function

$$F(\Delta \mathbf{k}, t) = N^{-1} \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp [i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle \quad (100)$$

discussed in the theory of neutron scattering.

After Van Hove (1954), we introduce the space-time binary correlation function

$$G^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) = G_s(\mathbf{r}_1^0, \mathbf{r}_1^t, t) + G_D(\mathbf{r}_1^0, \mathbf{r}_2^t, t), \quad (101)$$

where the self-correlation function $G_s(\mathbf{r}_i^0, \mathbf{r}_i^t, t)$ determines the probability of finding a

selected molecule i at the point \mathbf{r}_i^t at the moment of time t if it is known to have occupied the point \mathbf{r}_i^0 at the moment of time $t = 0$. Similarly, the distinct correlation function $G_D(\mathbf{r}_i^0, \mathbf{r}_j^t, t)$ expresses the probability of finding a molecule j at the point \mathbf{r}_j^t if the fixed molecule i was at \mathbf{r}_i^0 at $t = 0$.

By having recourse to the Van Hove function (101) we can split (100) into two parts (see Powles 1973), a self-correlation part, describing incoherent scattering

$$F_{\text{inc}}(\Delta\mathbf{k}, t) = V^{-1} \iint \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_i^t)] G_S(\mathbf{r}_i^0, \mathbf{r}_i^t, t) d\mathbf{r}_i^0 d\mathbf{r}_i^t \quad (100a)$$

and a distinct part, describing coherent scattering on stochastically correlated molecules

$$F_{\text{coh}}(\Delta\mathbf{k}, t) = \frac{\rho}{V} \iint \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] G_D(\mathbf{r}_i^0, \mathbf{r}_j^t, t) d\mathbf{r}_i^0 d\mathbf{r}_j^t. \quad (100b)$$

It is important to find a reasonable and physically plausible analytical construction of G_S and—especially— G_D . Here, of essential interest to us is the interval of intermediate times of molecular relaxations ($10^{-13} < t < 10^{-6}$ sec), for which one may apply the solution on the model of diffusion of translational or rotational molecular motion.

On the assumption of the Einstein–Smoluchowski free translational model, we have

$$G_S(\mathbf{r}_i^0, \mathbf{r}_i^t, t) = (4\pi D_T t)^{-3/2} \exp(-|\mathbf{r}_i^0 - \mathbf{r}_i^t|^2/4D_T t). \quad (102)$$

Thus, the incoherent scattering function (100a) finally takes the form

$$F_{\text{inc}}(\Delta\mathbf{k}, t) = \exp(-|\Delta\mathbf{k}|^2 D_T t), \quad (103)$$

where D_T is the coefficient of translational diffusion of Brownian particles.

The calculation of the coherent scattering function (100b) is by no means simple for a lack of the analytical form of the distinct correlation function G_D . In some cases use can be made of Vineyard's (1958) convolution approximation

$$G_D(\mathbf{r}_i^0, \mathbf{r}_j^t, t) = \int g^{(2)}(\mathbf{r}_{ij}^0) G_S(\mathbf{r}_j^0, \mathbf{r}_j^t, t) d\mathbf{r}_j^0 \quad (104)$$

and we reduce the coherent scattering function (100b) to the following form (see *e.g.* Nijboer and Rahman 1966):

$$F_{\text{coh}}(\Delta\mathbf{k}, t) = \Gamma_{00}^0(\Delta\mathbf{k}) F_{\text{inc}}(\Delta\mathbf{k}, t), \quad (105)$$

where the integral parameter $\Gamma_{00}^0(\Delta\mathbf{k})$ is given by (66).

By (99a), (103) and (105) we can write finally

$$S^{(0)}(\Delta\mathbf{k}, t) = 3N |A_e|^2 F_{\text{inc}}(\Delta\mathbf{k}, t) [1 + \Gamma_{00}^0(\Delta\mathbf{k})]. \quad (106)$$

9.2b Correlation functions of antisymmetric and anisotropic scattering: In the case of anisotropic molecules we have to replace the Van Hove function (101) by the generalized space-time correlation functions;

$$G^{(2)}(\mathbf{r}_1, \Omega_1^0, \mathbf{r}_2, \Omega_2, t) = G_S(\mathbf{r}_i^0, \Omega_i^0; \mathbf{r}_i^t, \Omega_i^t, t) + G_D(\mathbf{r}_i^0, \Omega_i^0; \mathbf{r}_j^t, \Omega_j^t, t). \quad (107)$$

involving additionally the molecular orientation variables Ω_i and Ω_j .

Regrettably, as yet, not much is known concerning the analytical form of (28) and hardly anything concerning G_D (Rowlinson and Evans 1975; Evans 1977; Williams

1978). We now proceed to introduce certain model assumptions to simplify our further calculations:

(i) the translational and rotational motions of the molecules are mutually independent,

(ii) after Vineyard (1958), the molecules interact with one another at the moment of time $t = 0$ only, whereas at $t > 0$ they are statistically independent and move in conformity with the laws of self-diffusion.

With the above assumptions and applying a procedure due to Steele and Pecora (1965), one can expand (107) in a series in spherical Wigner functions $D_{KM}^J(\Omega)$:

$$G_S(\mathbf{r}_i^0, \Omega_i^0; \mathbf{r}_i^t, \Omega_i^t, t) = \sum_{JKMM'} f_{MM'}^J(\mathbf{r}_{ii}^t, t) \bar{D}_{KM}^J(\Omega_i^0) \bar{D}_{KM'}^J(\Omega_i^t)^*, \quad (107a)$$

$$G_D(\mathbf{r}_i^0, \Omega_i^0; \mathbf{r}_j^t, \Omega_j^t, t) = \sum_{J,K_i M_i} \sum_{J,K_j M_j} g_{K_i M_i, K_j M_j}^{J_i J_j}(\mathbf{r}_{ij}^t, t) \times \bar{D}_{K_i M_i}^{J_i}({}^{ij}\Omega_i^0) \bar{D}_{K_j M_j}^{J_j}({}^{ij}\Omega_j^t)^*, \quad (107b)$$

where

$$\bar{D}_{KM}^J(\Omega) = \left(\frac{2J+1}{\Omega} \right)^{1/2} D_{KM}^J(\Omega).$$

The analytical form of the functions

$$f_{MM'}^J(\mathbf{r}_{ii}^t, t) \quad \text{and} \quad g_{K_i M_i, K_j M_j}^{J_i J_j}(\mathbf{r}_{ij}^t, t)$$

can be specified for a given model of the molecular motions, the simplest model of this kind being that of translational-rotational diffusion. In this case we have

$$f_{MM'}^J(\mathbf{r}_{ii}^t, t) = \delta_{MM'} G_S(\mathbf{r}_i^0, \mathbf{r}_i^t, t) \exp(-t/\tau_M^J), \quad (108)$$

where $G_S(\mathbf{r}_i^0, \mathbf{r}_i^t, t)$ is given by (102) and τ_M^J denotes the M th component of the rotational relaxation time of the J th order which, for symmetric top molecules, is given by

$$\tau_M^J = \{J(J+1)D_{11}^R + M^2(D_{33}^R - D_{11}^R)\}^{-1} \quad (109)$$

D_{11}^R and D_{33}^R being the principal values of the rotational diffusion tensor.

The expansion coefficients of (108b) can be expressed as follows (Steele and Pecora 1965):

$$g_{K_i M_i, K_j M_j}^{J_i J_j}(\mathbf{r}_{ij}^t, t) = \exp(-t/\tau_M^J) \int g_{K_i M_i, K_j M_j}^{J_i J_j}(\mathbf{r}_{ij}^0) G_S(\mathbf{r}_j^0, \mathbf{r}_j^t, t) d\mathbf{r}_j^0. \quad (110)$$

Our problem becomes quite simple on transforming the Cartesian tensor $A_e^{(h)}(\Omega)$ occurring in (98) to spherical representation and we obtain by (107)–(109) for the antisymmetric and anisotropic scattering functions (Knast and Kielich 1979).

$$S^{(1)}(\Delta\mathbf{k}, t) = N F_{\text{inc}}(\Delta\mathbf{k}, t) \sum_{MM'} (A_{eM}^{(1)})^* A_{eM'}^{(1)} \exp(-t/\tau_M^1) [\delta_{MM'} + \Gamma_{MM'}^1(\Delta\mathbf{k})], \quad (111)$$

$$S^{(2)}(\Delta\mathbf{k}, t) = N F_{\text{inc}}(\Delta\mathbf{k}, t) \sum_{MM'} (A_{eM}^{(2)})^* A_{eM'}^{(2)} \exp(-t/\tau_M^2) [\delta_{MM'} + \Gamma_{MM'}^2(\Delta\mathbf{k})], \quad (112)$$

where we have introduced a generalized Steele and Pecora (1965) radial-angular correlation parameter,

$$\Gamma_{MM'}^J(\Delta\mathbf{k}) = \sum_N \frac{(-1)^{N-M}}{2J+1} \int_0^\infty g_{N,-M,-N,M'}^{JJ}(\mathbf{r}_{12}) \frac{\sin \Delta k r_{12}}{\Delta k r_{12}} d\mathbf{r}_{12}. \quad (113)$$

If $\Delta\mathbf{k} \cdot \mathbf{r} \ll 1$ (short-range correlation), (113) reduces to the Steele (1965) parameter

$$\Gamma_{MM'}^J(0) = \sum_N \frac{(-1)^{N-M}}{2J+1} \int_0^\infty g_{N,-M,-N,M'}^{JJ}(r_{12}) d\mathbf{r}_{12}, \quad (113a)$$

which has been calculated numerically for concrete models of interacting molecules (see *e.g.* Kielich 1967, 1972; Ananth *et al* 1974; Woźniak and Kielich 1975; Høye and Stell 1977; Głaz 1981).

In the absence of molecular interactions, the parameters (113) vanish and the time correlation functions (111) and (112) describe incoherent antisymmetric and anisotropic light scattering

$$S_{\text{inc}}^{(1)}(\Delta\mathbf{k}, t) = N F_{\text{inc}}(\Delta\mathbf{k}, t) \sum_M |A_{eM}^{(1)}|^2 \exp(-t/\tau_M^1), \quad (111a)$$

$$S_{\text{inc}}^{(2)}(\Delta\mathbf{k}, t) = N F_{\text{inc}}(\Delta\mathbf{k}, t) \sum_M |A_{eM}^{(2)}|^2 \exp(-t/\tau_M^2). \quad (112a)$$

9.3 Contributions from multipole polarizabilities

The results of recent experimental and theoretical spectral studies are evidence of the importance of contributions from multipolar polarizabilities (see *e.g.* Kielich 1963, 1968; Pasmanter *et al* 1976; Buckingham and Tabisz 1978; Tabisz 1979; Posch 1979, 1980; Shelton and Tabisz 1980; Cox and Madden 1980; Amos *et al* 1980; Kielich *et al* 1981). These contributions bear on the anisotropic as well as the isotropic scattering, inherent in the time-correlation functions (97) and are determined with complete generality by the expressions derived for effective polarizabilities derived in §4. Since the latter, in spite of the compact Cartesian tensor notation applied, are rather complex mathematically, we shall restrict ourselves here to writing the lower-order contributions to the correlation function of isotropic scattering. By (97), it can be written explicitly in the form:

$$S^{(0)}(\Delta\mathbf{k}, t) = \frac{1}{3} \left\langle \sum_{i=1}^N \sum_{j=1}^N \{ \Pi_e(\mathbf{r}_i^0, \Omega_i^0) : \mathbf{U} \}^* \times \right. \\ \left. \times \{ \Pi_e(\mathbf{r}_j^t, \Omega_j^t) : \mathbf{U} \} \exp [i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle \quad (114)$$

With regard to (36) we thus arrive at the following contributions from linear multipole polarizabilities (on neglecting magneto-electric terms):

$$S_{01}^{(0)}(\Delta\mathbf{k}, t) = \sum_{n_1=1}^\infty \sum_{n_2=1}^\infty \frac{(-1)^{n_2}}{(2n_1-1)!!(2n_2-1)!!} \times \\ \times \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq j}^N A_e^*(\Omega_i^0) \{ {}^{(1)}_e \mathbf{A}_e^{(n_1)}(\Omega_j^t) [n_1]^{(n_1)} \mathbf{T}_{jk}^{(n_2)} \} \times \right. \\ \left. \times [n_2]^{(n_2)} \mathbf{A}_e^{(1)}(\Omega_k^t) \} : \mathbf{U} \exp [i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle, \quad (115)$$

$$\begin{aligned}
 S_{11}^{(0)}(\Delta\mathbf{k}, t) = & \frac{1}{3} \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_2+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \times \\
 & \times \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq i}^N \sum_{l \neq j}^N \{ {}^{(1)}_e \mathbf{A}_e^{(n_1)}(\Omega_i^0)[n_1] {}^{(n_1)}\mathbf{T}_{ik}^{(n_2)}[n_2] \times \right. \\
 & \times {}^{(n_2)}_e \mathbf{A}_e^{(1)}(\Omega_k^0) \}^* : \mathbf{U} \{ {}^{(1)}_e \mathbf{A}_e^{(n_3)}(\Omega_j^t)[n_3] {}^{(n_3)}\mathbf{T}_{jl}^{(n_4)}[n_4] \times \\
 & \left. \times {}^{(n_4)}_e \mathbf{A}_e^{(1)}(\Omega_l^t) \} : \mathbf{U} \exp [i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle. \quad (116)
 \end{aligned}$$

To derive the coherent contributions to (114) of the same order of magnitude one has to take into account, beside the currently considered contribution (116), moreover mixed contributions originating in the second-order change in the effective polarizability (37) (omitting magneto-electric terms):

$$\begin{aligned}
 S_{02}^{(0)}(\Delta\mathbf{k}, t) = & \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_2+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \times \\
 & \times \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq j}^N \sum_{l \neq k}^N A_e^*(\Omega_i^0) \{ {}^{(1)}_e \mathbf{A}_e^{(n_1)}(\Omega_j^t)[n_1] \times \right. \\
 & \times {}^{(n_1)}\mathbf{T}_{jk}^{(n_2)}[n_2] {}^{(n_2)}_e \mathbf{A}_e^{(n_3)}(\Omega_k^t)[n_3] {}^{(n_3)}\mathbf{T}_{kl}^{(n_4)}[n_4] \times \\
 & \left. \times {}^{(n_4)}_e \mathbf{A}_e^{(1)}(\Omega_l^t) \} : \mathbf{U} \exp [i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle. \quad (117)
 \end{aligned}$$

Obviously, the contribution $S_{20}^{(0)}(\Delta\mathbf{k}, t)$ is of a similar form.

All these contributions determine isotropic coherent light scattering and can be split in the standard manner into components due to two-, three- and four-body interactions. Obviously, in this way, the spectral distribution is determined by new angular correlation functions. The only complete to-the-end analyses are, hitherto, those of Bancewicz (1979, 1980) and Frenkel and McTague (1980) for axially symmetric molecules in the dipole-induced dipole approximation and of Pošch (1980) for tetrahedral ones in the dipole-quadrupole approximation. A discussion of the angular correlation functions for higher dipole-quadrupole, quadrupole-quadrupole and dipole-octupole approximations has been given quite recently by Kielich *et al* (1981).

As in the case of integral scattering, an important role is played by contributions from nonlinear multipole polarizabilities in that of spectral scattering. As an example, we adduce the following first-order contribution which, by (40a) and (114), has the form

$$\begin{aligned}
 S_{01}^{(0)}(\Delta\mathbf{k}, t) = & \frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!! (2n_2-1)!!} \times \\
 & \times \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq j}^N {}_e A_e^*(\Omega_i^0) \{ \mathbf{U} : {}^{(1)}_e \mathbf{B}_{ee}^{(1+n_1)}(\Omega_j^t) + \right. \\
 & \left. + {}^{(1)}_e \mathbf{B}_{ee}^{(n_1+1)}(\Omega_j^t) \} [n_1] {}^{(n_1)}\mathbf{T}_{jk}^{(n_2)}[n_2] \mathbf{M}_e^{(n_2)}(\Omega_k^t) \times \right. \\
 & \left. \times \exp [i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle. \quad (118)
 \end{aligned}$$

(and likewise for $S_{10}^{(0)}$).

The expansions (40b), (42) and (43) permit the determination of second- and higher-order contributions to (114) due to the nonlinear multipole polarizabilities.

Finally, it may be worth stressing that the correlation functions of isotropic scattering (115)–(118) and analogical functions of anisotropic light scattering (not given explicitly in this review) contain all multipolar contributions, readily adaptable to various molecular symmetries of the spherical top and symmetric top kind. On applying reasonable model assumptions their mathematical form simplifies considerably. Their numerical evaluation is easy to perform since, as stated above, the numerical values of the electric multipoles and nonlinear polarizabilities of many of the simpler molecules (see *e.g.* Kielich 1972, 1981) as well as their multipole polarizabilities (Amos 1979; Rivail and Cartier 1979; Espinoza *et al* 1979) are known.

The angular dependence of the correlation functions (115)–(118) assume a simple and at the same time elegant form if the Cartesian tensors are written in irreducible spherical tensor representation. With the spherical representation of the many-body distribution functions *e.g.* (107a, b) available, the calculations can be easily carried out to the end leading to results which are well adapted to numerical treatment. Nonetheless, the analytical expressions for the individual contributions are still mathematically bulky and we refrain from adducing them here.

10. Concluding remarks

Sections 7–9 contain but some of the more important applications of the general theory formulated in §5 comprising material hitherto not discussed in detail. The general expressions, of a high degree of complication from the mathematical viewpoint, reduce to a simpler form when one or another model is adopted. We then have to deal with rather straightforward problems, the concrete solutions of which are dependent on specific data available from the literature, thus (i) the mutually independent and non-zero tensor components of the intrinsic multipole moment and multipole polarizabilities for the various point groups in Cartesian representation (see *e.g.* Kielich 1972, 1981) or irreducible tensor representation (Gray and Lo 1976), and (ii) the possibility of calculating the radial binary, ternary averages $\langle r_{ij}^{-n} \rangle$, $\langle r_{ij}^{-n} r_{jk}^{-n} \rangle$, etc. for concrete models of the equilibrium correlation functions $g_{ij}^{(2)}$, $g_{ijk}^{(3)}$, . . . , considered in the statistical theory of fluids (Ananth *et al* 1974; Blum and Narten 1976; Stell and Weis 1977; Larsen *et al* 1977; Wertheim 1980; Steinhäuser and Neumann 1980; Haile and Gray 1980). Such concrete light scattering calculations have been carried out for atomic fluids and ones composed of spherical top molecules (Kielich 1960b, 1971b; Ralph and Gray 1974; Graben *et al* 1975; Alder *et al* 1979; Balucani *et al* 1979) as well as liquids with polar molecules (Woźniak and Kielich 1975, 1977).

The detailed treatment of these problems involves the finer fluctuational effects discussed on an advanced level in recently proposed molecular–statistical theories of the electric polarization of atomic and molecular fluids (see *e.g.* Titulaer and Deutch 1974; Høye and Stell 1980; Høye and Bedeaux 1977; Wertheim 1978, 1979; Felderhof 1979; Fulton 1979).

With regard to spectral studies, a considerable difficulty in the way of concrete applications of the formulae given in §§7–9 consists in the lack of analytical expressions for the time-space many body correlation function. Since Vineyard (1958) proposed his well known approximation of the binary correlation function, attempts have been

made recently aimed at determining the three- and four-body space-time correlation functions analytically (see *e.g.* Groome *et al* 1976; Gubbins *et al* 1978; Knast *et al* 1980). Our stochastic approach to scattered spectra taking into account changes in polarizability induced by space and time fluctuations of multipole fields involving, beside $G_{ij}^{(2)}(\mathbf{r}, t)$, the higher many-body correlation functions $G_{ijk}^{(3)}(\mathbf{r}, t)$, $G_{ijkl}^{(4)}(\mathbf{r}, t)$ enables us to gain simultaneously information regarding these functions inaccessible from other studies.

We have given considerable attention to the analysis of the cross contributions S_{01} , S_{02} , . . . , often neglected when analyzing experimental results. We have shown them to be of the same order of magnitude as S_{11} ; they are all the more interesting since they can be positive or negative, according to the electrical structure of the molecule and the model of ternary molecular correlations adopted. Obviously, we have by no means given all the possible contributions (*e.g.* the magneto-electric contributions, discussed in §4, are omitted) it being our sole aim to point out the potentialities inherent in the theory outlined above. The latter proves especially efficient in applications to two- and three-component systems, one component of which is composed of atoms and the others of spherical top (*e.g.* tetrahedral CCl_4 or octahedral SF_6), symmetric top (axially symmetric N_2 , CO_2 , C_6H_6 etc.), or asymmetric top molecules. In these cases, the spectral structure is described by new time-correlation functions. Clearly, the study of the Fourier transforms of these correlation functions is made easier by the use of the elegant formalism of irreducible spherical tensors (Chiu 1970; Ożgo and Kielich 1976; Jerphagnon *et al* 1978; Tough and Stone 1979).

The by now well tested intermolecular (linear or two-photon) light scattering spectroscopy discussed above provides the foundations for the multiphoton scattering molecular spectroscopy developed more recently (Kielich 1981, 1983).

References

- Ackerson B J and Hanley H J M 1980 *J. Chem. Phys.* **73** 3568
Alder B J, Beers J C, Strauss H L and Weis J J 1979 *J. Chem. Phys.* **70** 4091
Alms G R, Bauer D R, Brauman J I and Pecora R 1973a *J. Chem. Phys.* **58** 5570
Alms G R, Bauer D R, Brauman J I and Pecora R 1973b *J. Chem. Phys.* **59** 5304, 5310
Alms G R, Gierke T D and Flygare W H 1974 *J. Chem. Phys.* **61** 4083
Alms G R and Patterson G D 1978 *J. Chem. Phys.* **68** 3440
Amos R D 1979 *Mol. Phys.* **38** 33
Amos R D, Buckingham A D and Williams J H 1980 *Mol. Phys.* **39** 1519
Ananth M S, Gubbins K E and Gray C G 1974 *Mol. Phys.* **28** 1005
Anderson H C and Pecora R 1971 *J. Chem. Phys.* **54** 2584
Atakhodzhayev A K and Tukhvatullin F Kh 1981 Spectral intensity distribution in the wing of the light scattering lines of liquids and solutions, *Izd. Uzbetskoi SSR, Tashkent*
Balucani U, Tognetti V and Vallauri R 1979 *Phys. Rev.* **A19** 177
Bancewicz T 1979 *Acta Phys. Pol.* **A56** 431
Bancewicz T 1980 *J. Mol. Struct.* **61** 125
Bancewicz T and Kielich S 1981 *J. Chem. Phys.* **75** 107
Barocchi F, Mazzinghi P and Zoppi M 1978 *Phys. Rev. Lett.* **41** 1785
Battaglia M R, Cox T I and Madden P A 1979 *Mol. Phys.* **37** 1413
Bauer D R, Alms G R, Brauman J I and Pecora R 1974 *J. Chem. Phys.* **61** 2255
Bauer D R, Brauman J I and Pecora R 1975 *J. Chem. Phys.* **63** 53
Benoit H and Stockmayer W H 1956 *J. Phys. Radium* **17** 21
Ben-Reuven A and Gershon N D 1969 *J. Chem. Phys.* **51** 893
Berne B J and Pecora R 1976 *Dynamic light scattering* (New York: John Wiley)

- Berrue J, Chave A, Dumon B and Thibeu M 1976 *J. Phys. (Paris)* **37** 845
- Bertucci S J, Burnham A K, Alms G R and Flygare W H 1977 *J. Chem. Phys.* **66** 605
- Birnbaum G and Cohen E R 1975 *J. Chem. Phys.* **62** 3807
- Birnbaum G and Cohen E R 1976 *Mol. Phys.* **32** 161
- Birnbaum G and Sutter H 1981 *Mol. Phys.* **42** 21
- Blum L and Narten A H 1976 *Adv. Chem. Phys.* **34** 203
- Boots H M, Bedeaux D and Mazur P 1975 *Physica* **A79** 397
- Born M 1933 *Optik* (Berlin: Springer-Verlag)
- Born M and Wolf E 1968 *Principles of optics* (4th ed.) (Oxford: Pergamon Press)
- Brenner S L, Nossal R J and Weiss G H 1978 *J. Stat. Phys.* **18** 1
- Breuer G 1980 *Mol. Phys.* **41** 747
- Bruining J and Clarke J H R 1976 *Mol. Phys.* **31** 1425
- Bucaro J A and Litovitz T A 1971 *J. Chem. Phys.* **54** 3846
- Buckingham A D and Tabisz G C 1978 *Mol. Phys.* **36** 583
- Bullough R K 1962 *Philos. Trans. R. Soc. London* **A254** 397
- Burnham A K, Alms G R and Flygare W H 1975 *J. Chem. Phys.* **62** 3289
- Cabannes J 1929 *La diffusion de la lumière* (Paris: Presses universitaires de France)
- Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
- Cheung C K, Jones D R and Wang C H 1976 *J. Chem. Phys.* **64** 3567
- Chiu Y N 1970 *J. Chem. Phys.* **52** 3641, 4950
- Chiu Y N 1979 *Phys. Rev.* **A20** 32
- Copley J R D and Lovesey S W 1975 *Prog. Phys.* **38** 461
- Cox T I, Battaglia M R and Madden P A 1979 *Mol. Phys.* **38** 1539
- Cox T I and Madden P A 1980 *Mol. Phys.* **39** 1487
- Crosignani B, DiPorto P and Bertolotti M 1975 *Statistical properties of scattered light* (New York: Academic Press)
- Dardy H D, Volterra V and Litovitz T A 1973 *J. Chem. Phys.* **59** 4491
- De Groot S R 1969 *The Maxwell equations* (Amsterdam: North-Holland)
- De Santis A, Nardone M and Sampoli M 1980 *Mol. Phys.* **41** 769
- Deželić G 1966 *J. Chem. Phys.* **45** 185
- Dill J F, Litovitz T A and Bucaro J A 1975 *J. Chem. Phys.* **62** 3839
- Eberly J H and Wódkiewicz K 1977 *J. Opt. Soc. Am.* **67** 1253
- Einstein A 1910 *Ann. Phys. (Leipzig)* **33** 1275
- Espinoza L L, Toro A and Fuentealba P 1979 *Int. J. Quantum Chem.* **16** 399
- Evans M W 1977 in *Dielectric and related molecular processes* (ed.) M Davies (London: Chemical Society) Vol 3 Chap 1
- Fabelinskii I 1968 *Molecular scattering of light* (New York: Plenum)
- Farinato R S and Rowell R L 1976 *J. Chem. Phys.* **65** 593
- Fechner B M 1969 *Acta Phys. Pol.* **36** 297
- Felderhof B U 1974 *Physica* **A76** 486
- Felderhof B U 1979 *Physica* **A95** 572
- Fixman M 1955 *J. Chem. Phys.* **23** 2074
- Fleury P A and McTague J P 1969 *Opt. Commun.* **1** 164
- Fleury P A and Boon J P 1973 *Adv. Chem. Phys.* **24** 1
- Frenkel D and McTague J P 1980 *J. Chem. Phys.* **72** 2801
- Frisch H L and McKenna J 1965 *Phys. Rev.* **A68** 139
- Frommhold L and Profitt M H 1978 *Mol. Phys.* **35** 681
- Frommhold L 1981 *Adv. Chem. Phys.* **46** 1
- Fröhlich P and Posch H A 1978 *Mol. Phys.* **36** 1421
- Fulton R L 1979 *Physica* **A97** 189
- Gabriel G J 1973 *Phys. Rev.* **A8** 963
- Galatry L and Gharbi T 1980 *Chem. Phys. Lett.* **75** 427
- Gelbart W M 1974 *Adv. Chem. Phys.* **26** 1
- Gelbart W M 1979 *Philos. Trans. R. Soc. London* **A293** 359
- Ghaem-Maghani V and May A D 1980 *Phys. Rev.* **A22** 692, 698
- Gierke T D 1976 *J. Chem. Phys.* **65** 3873
- Giż W 1981 *Acta Phys. Pol.* **A60** 419
- Gornal W S, Howard-Lock H E and Stoicheff B P 1970 *Phys. Rev.* **A1** 1288

- Graben H W, Rushbrooke G S and Stell G 1975 *Mol. Phys.* **30** 373
Gray C G 1968 *Can. J. Phys.* **46** 135
Gray C G 1976 *Can. J. Phys.* **54** 505
Gray C G and Lo B W N 1976 *Chem. Phys.* **14** 73
Gray C G and Stiles P J 1976 *Can. J. Phys.* **54** 513
Gray C G and Gubbins K E 1975 *Mol. Phys.* **30** 1481
Groome L, Gubbins K and Dufty J 1976 *Phys. Rev.* **A13** 437
Gubbins K E, Gray C G and Egelstaff P A 1978 *Mol. Phys.* **35** 315
Guillot B, Bratos S and Birnbaum G 1980 *Phys. Rev.* **A22** 2230
Haile J M and Gray C G 1980 *Chem. Phys. Lett.* **76** 583
Hauchecorne G, Kerhervé K and Mayer G 1971 *J. Phys. (Paris)* **32** 47
Heitler W 1954 *The quantum theory of radiation* (Oxford: Clarendon)
Hellwarth R W 1970 *J. Chem. Phys.* **52** 2128
Higashigaki Y, Whittenburg S L and Wang C H 1978 *J. Chem. Phys.* **69** 3297
Hilbert R, Langer H and Versmold H 1979 *Mol. Phys.* **38** 2107
Hilton P R and Oxtoby D W 1981 *J. Chem. Phys.* **74** 1824
Ho J H K and Tabisz G C 1973 *Can. J. Phys.* **51** 2025
Høye J S and Bedeaux D 1977 *Physica* **A87** 288
Høye J S and Stell G 1977 *J. Chem. Phys.* **66** 795
Høye J S and Stell G 1980 *J. Chem. Phys.* **73** 461
Hunt K L C 1980 *Chem. Phys. Lett.* **70** 336
Hynne F 1980 *Mol. Phys.* **41** 583
Isnard P, Robert D and Galatry L 1976 *Mol. Phys.* **31** 1789
Isnard P, Robert D and Galatry L 1980 *Mol. Phys.* **39** 501
Jansen L 1958 *Phys. Rev.* **110** 661
Jerphagnon J, Chemla D and Bonneville R 1978 *Adv. Phys.* **27** 609
Jones D R and Wang C H 1977 *J. Chem. Phys.* **66** 1659
Kac M 1959 *Probability and related topics in physical science* (New York: Interscience)
Kasproicz B and Kielich S 1968 *Acta Phys. Pol.* **33** 495
Keijser R A J, Van Den Hout K D, De Groot M and Knaap H F P 1974 *Physica* **A75** 515
Keyes T 1979 *J. Chem. Phys.* **70** 5438
Keyes T and Kivelson D 1971 *J. Chem. Phys.* **54** 1786
Keyes T and Kivelson D 1972 *J. Chem. Phys.* **56** 1057
Keyes T, Kivelson D and McTague J P 1971 *J. Chem. Phys.* **55** 4096
Keyes T and Ladanyi B M 1977 *Mol. Phys.* **33** 1099
Keyes T, Ladanyi B M and Madden P A 1979 *Chem. Phys. Lett.* **64** 479
Kielich S 1958 *Bull. Acad. Pol. Sci. Cl.* **3** 6 215
Kielich S 1960a *Acta Phys. Pol.* **19** 149
Kielich S 1960b *Acta Phys. Pol.* **19** 711
Kielich S 1962 *Acta Phys. Pol.* **22** 299
Kielich S 1963 *Acta Phys. Pol.* **24** 389
Kielich S 1965a *Acta Phys. Pol.* **27** 305
Kielich S 1965b *Mol. Phys.* **9** 549
Kielich S 1965c *Proc. Phys. Soc.* **86** 709
Kielich S 1965d *Acta Phys. Pol.* **27** 395
Kielich S 1965e *Acta Phys. Pol.* **28** 459
Kielich S 1965f *Physica* **31** 444
Kielich S 1966a *Physica* **32** 385
Kielich S 1966b *Acta Phys. Pol.* **30** 683
Kielich S 1967 *J. Chem. Phys.* **46** 4090
Kielich S 1968a *J. Phys. (Paris)* **29** 619
Kielich S 1968b *Acta Phys. Pol.* **33** 63
Kielich S 1969 *IEEE J. Quantum Electron.* **QE5** 562
Kielich S 1971a *Chem. Phys. Lett.* **10** 516; Erratum *ibid* 1973 **19** 609
Kielich S 1971b *Opt. Commun.* **4** 135
Kielich S 1972 in *Dielectric and related molecular processes* (ed.) M Davies (London: Chemical Society) Vol 1 p. 192
Kielich S 1975 *Chem. Phys. Lett.* **33** 79

- Kielich S 1979 *Nonlinear behaviour of molecules, atoms and ions in electric, magnetic or electromagnetic fields* (Amsterdam: Elsevier) p. 111
- Kielich S 1980 *Opt. Commun.* **34** 367
- Kielich S 1981 *Molecular nonlinear optics* (Moscow: Izd. Nauka)
- Kielich S 1983 *Progress in optics* (ed.) E Wolf (Amsterdam: North Holland Publ. Co.) Vol 20 p. 155
- Kielich S, Bancewicz T and Woźniak S 1981 *Can. J. Phys.* **59** 1620
- Kielich S and Zawodny R 1971 *Chem. Phys. Lett.* **12** 20
- Kielich S, Lalanne J R and Martin F B 1972 *J. Phys.* **33** C1-191
- Kielich S and Woźniak S 1974 *Acta Phys. Pol.* **A45** 163
- Kielich S and Pieczyńska J 1970 *Bull. Soc. Amis Sci. Lett. Poznań* **B22** 31
- Kirkwood J G 1936 *J. Chem. Phys.* **4** 592
- Knaap H F P and Lallemand P 1975 *Annu. Rev. Phys. Chem.* **26** 59
- Knast K and Kielich S 1979 *Acta Phys. Pol.* **A55** 319
- Knast K, Chmielowski W and Kielich S 1980 *Proceedings of the International Conference on Lasers '79, Orlando, Florida, USA*, (ed.) V J Corcoran (McLean V A: STS Press) p. 304
- Ladanyi B M and Keyes T 1976 *Mol. Phys.* **31** 1685
- Ladanyi B M and Keyes T 1977a *Mol. Phys.* **33** 1063
- Ladanyi B M and Keyes T 1977b *Mol. Phys.* **33** 1247
- Ladanyi B M and Keyes T 1978 *J. Chem. Phys.* **68** 3217
- Ladanyi B M and Keyes T 1979 *Mol. Phys.* **37** 1809
- Ladanyi B M, Keyes T, Tildesley D J and Streett W B 1980 *Mol. Phys.* **39** 645
- Ladd A J C, Litovitz T A and Montrose C J 1979 *J. Chem. Phys.* **71** 4242
- Ladd A J C, Litovitz T A, Clarke J H R and Woodcock L V 1980 *J. Chem. Phys.* **72** 1759
- Lalanne J R 1969 *J. Phys. (Paris)* **30** 643
- Larsen B, Rasaiah J C and Stell G 1977 *Mol. Phys.* **33** 987
- Leavitt R P 1980 *J. Chem. Phys.* **72** 3472
- Le Duff Y 1979 *Phys. Rev.* **A20** 48
- Leontovich M A 1941 *Izv. Akad. Nauk SSSR, Ser. Fiz.* **5** 148
- Levine H B and Birnbaum G 1971 *J. Chem. Phys.* **55** 2914
- Lim T K, Linder B and Kromhout R A 1970 *J. Chem. Phys.* **52** 3831
- Linder B and Kromhout R A 1970 *J. Chem. Phys.* **52** 1615
- Long D A 1977 *Raman spectroscopy* (New York: McGraw-Hill)
- Louisell W H 1973 *Quantum statistical properties of radiation* (New York: John Wiley)
- Lucas H C and Jackson D A 1971 *Mol. Phys.* **20** 801
- Lund P-A, Whittenburg S L, Wang C H and Christensen D H 1979 *Mol. Phys.* **37** 749
- Macrakis M S 1967 *J. Appl. Phys.* **38** 2278
- Madden P A 1978 *Mol. Phys.* **36** 365
- Madden P A, Battaglia M R, Cox T I, Pierens R K and Champion J 1980 *Chem. Phys. Lett.* **76** 604
- Mazur P and Mandel M 1956 *Physica* **22** 289, 299
- McTague J P and Birnbaum G 1968 *Phys. Rev. Lett.* **21** 661
- McTague J P and Birnbaum G 1971 *Phys. Rev.* **A3** 1376
- McTague J P, Fleury P A and DuPré D B 1969 *Phys. Rev.* **188** 303
- Medina F D and Daniels W B 1978 *Phys. Rev.* **A17** 1474
- Medina F D 1981 *Phys. Lett.* **A81** 139
- Moraal H 1976 *Physica* **A83** 33, 57
- Moraal H 1981 *Physica* **A105** 286, 297, 303
- Mori H 1965 *Prog. Theor. Phys.* **33** 423
- Mountain R D 1977 *Adv. Mol. Relaxation Processes* **9** 225
- Nijboer B R A and Rahman A 1966 *Physica* **32** 415
- O'Brien E F, Gutschick V P, McKoy V and McTague J P 1973 *Phys. Rev.* **A8** 690
- Orr B J and Ward J F 1971 *Mol. Phys.* **20** 513
- Ozgo Z and Kielich S 1976 *Physica* **C81** 151
- Oxtoby D W and Gelbart W M 1975 *Mol. Phys.* **30** 535
- Pasmanter R A, Samson R and Ben-Reuven A 1976 *Phys. Rev.* **A14** 1238
- Patterson G D and Griffiths J E 1975 *J. Chem. Phys.* **63** 2406
- Pecora R and Steele W A 1965 *J. Chem. Phys.* **42** 1872
- Perrot M, Devaure J and Lascombe J 1978 *Mol. Phys.* **36** 921
- Placzek G 1934 *Handb. Radiol.* **6** 205

- Plóćiniczak K 1980 Abstracts, IX Conf. Quantum Electronics and Nonlinear Optics Poznań April 23–26 Section B, p. 41
- Posch H A 1979 *Mol. Phys.* **37** 1059
- Posch H A 1980 *Mol. Phys.* **40** 1137
- Posch H A and Litovitz T A 1976 *Mol. Phys.* **32** 1559
- Powles J G 1973 *Adv. Phys.* **22** 1
- Ralph H I and Gray C G 1974 *Mol. Phys.* **27** 1683
- Ratajczak H and Orville-Thomas W J 1980 in *Molecular Interactions* (eds) H Ratajczak and W J Orville-Thomas (New York: John Wiley) Chap 1
- Riera A and Meath W J 1973 *Int. J. Quantum Chem.* **7** 959
- Rivail J-L and Cartier A 1979 *Chem. Phys. Lett.* **61** 469
- Rosenthal L C and Strauss H L 1976 *J. Chem. Phys.* **64** 282
- Rouch J, Chabart J P, Letamendia L, Marcou A and Vaucamps C 1976 *Acta Phys. Pol.* **A50** 503
- Rowlinson J S and Evans M 1975 *Annu. Rep.* **A72** 5
- Rytov S M 1957 *Zh. Eksp. Teor. Fiz.* **33** 514
- Rytov S M 1970 *Zh. Eksp. Teor. Fiz.* **59** 12
- Samson R and Ben-Reuven A 1976 *J. Chem. Phys.* **65** 3586
- Schoen P E, Cheung P S Y, Jackson D A and Powles J G 1975 *Mol. Phys.* **29** 1197
- Shelton D P and Tabisz G C 1980 *Mol. Phys.* **40** 285, 299
- Singh S and Singh Y 1976 *Physica* **A83** 339
- Smoluchowski M 1906 *Ann. Phys.* **21** 756
- Smoluchowski M 1908 *Ann. Phys.* **25** 205
- Smoluchowski M 1915 *Ann. Phys.* **48** 1103
- Starunov V S and Fabelinskii I L 1974 *Zh. Eksp. Teor. Fiz.* **66** 1740
- Starunov V S, Tiganov E V and Fabelinskii I L 1967 *Zh. Eksp. Teor. Fiz. Pisma v Red.* **5** 317
- Steele W A 1965 *J. Chem. Phys.* **43** 2598
- Steele W A and Pecora R 1965 *J. Chem. Phys.* **42** 1863
- Stegeman G I A and Stoicheff B P 1968 *Phys. Rev. Lett.* **21** 202
- Stegeman G I A and Stoicheff B P 1973 *Phys. Rev.* **A7** 1160
- Steinhauser O and Neumann M 1980 *Mol. Phys.* **40** 115
- Stell G and Weis J J 1977 *Phys. Rev.* **A16** 757
- Stogryn D E 1969 *J. Chem. Phys.* **50** 4967
- Stogryn D E 1971 *Mol. Phys.* **22** 81
- Stogryn D E 1972 *Mol. Phys.* **23** 897
- Stogryn D E and Stogryn A P 1966 *Mol. Phys.* **11** 371
- Sullivan D E and Deutch J M 1976 *J. Chem. Phys.* **64** 3870
- Tabisz G C, Wall W R and Shelton D P 1972 *Chem. Phys. Lett.* **15** 387
- Tabisz G C 1979 in *Molecular spectroscopy* (eds) Barrow *et al* (London: Chem. Soc.) Vol 6 Chap. 4
- Tancrede P, Bothorel P, De St. Romain P and Patterson D 1977a *J. Chem. Soc. Faraday Trans. II* **73** 15
- Tancrede P, Patterson D and Bothorel P 1977b *J. Chem. Soc. Faraday Trans. II* **73** 29
- Theimer O and Paul R 1965 *J. Chem. Phys.* **42** 2508
- Thibeau M M, Oksengorn B and Vodar B 1968 *J. Phys. (Paris)* **29** 287
- Thibeau M, Tabisz G C, Oksengorn B and Vodar B 1970 *J. Quant. Spectrosc. Radiat. Transfer* **10** 839
- Titulaer U M and Deutch J M 1974 *J. Chem. Phys.* **60** 2703
- Tough R J A and Stone A J 1979 *Mol. Phys.* **37** 1469
- Van Hove L 1954 *Phys. Rev.* **95** 249
- Van Kranendonk J 1974 *Physica* **73** 156
- Van Kranendonk J (ed.) 1980 *Intermolecular spectroscopy and dynamical properties of dense systems*, (Amsterdam: North-Holland)
- Van Konynenburg P and Steele W A 1972 *J. Chem. Phys.* **56** 4776
- Varshneya D, Shirron S F, Litovitz T A, Zoppi M and Barocchi F 1981 *Phys. Rev.* **A23** 77
- Vereshchagin A N 1980 *The polarizability of molecules* (Moskva: Izd. Nauka)
- Vezzetti D J and Kellèr J B 1967 *J. Math. Phys.* **8** 1861
- Vineyard G H 1958 *Phys. Rev.* **110** 999
- Wang C H, Jones D R and Christensen D H 1976 *J. Chem. Phys.* **64** 2820
- Wertheim M S 1978 *Mol. Phys.* **36** 1217
- Wertheim M S 1979 *Mol. Phys.* **37** 83
- Wertheim M S 1980 *J. Chem. Phys.* **73** 1398

Williams G 1978 *Chem. Soc. Rev.* **7** 84

Woźniak S and Kielich S 1975 *J. Phys. (Paris)* **36** 1305

Woźniak S and Kielich S 1977 *Acta Phys. Pol.* **A52** 863

Wróż T 1975 *Opt. Appl.* **5** 3

Ytarova T M 1980 *Trudy Fiz. Inst. Akad. Nauk SSSR* **118** 3

Yvon J 1936 *C.R. Acad. Sci. (Paris)* **202** 35

Yvon J 1937 *La propagation et la diffusion de la lumière, Actualités scientifiques et industrielles, Herman et Cie, Paris, No. 543*

Zernike F and Prins J H 1927 *Z. Phys.* **41** 184