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III

MULTI-PHOTON SCATTERING MOLECULAR SPECTROSCOPY

BY

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CONTENTS

§ 1. Historical Developments and Outline of the Present Review

Light scattering – one of the most important aspects of interaction between electromagnetic radiation and material systems – poses theoretical and experimental problems which, to this day, are unceasingly in the forefront of scientific investigation. The qualitative and quantitative evolution of numerous processes of light scattering is determined not only by the statistics and thermodynamical state of the scattering medium, but moreover – and, perhaps, chiefly – by the statistics of the incident light wave and the state of its polarization. This has become evident especially since the application of rapidly developing laser techniques in studies of light scattering.

1.1. THE DEFINITION OF SPONTANEOUS MULTI-PHOTON SCATTERING

In a quantal approach, some of the incident photons interact with the microsystems (electrons, atoms, molecules, particles, etc.) of the medium, or with collective excitations (phonons, excitons, magnons, polaritons, plasmons, etc.). As a result of this interaction the microsystem absorbs a photon of frequency $\omega_1(\boldsymbol{k}_1)$, and simultaneously emits a photon $\omega_2(\boldsymbol{k}_2)$, thus performing a transition from the initial quantum state $|\mathrm{i}\rangle$, by way of an intermediate state $|k\rangle\langle k|$, to the final quantum state $\langle \mathrm{f}|$. The energy conservation law requires that

$$\hbar(\omega_1-\omega_2)=E_\mathrm{f}-E_\mathrm{i}=\hbar\omega_{\mathrm{fi}}, \tag{1.1}$$

with an accuracy determined by the width of the line emitted.

If, during the transition, the final state $\langle \mathrm{f}|$ and initial state $|\mathrm{i}\rangle$ are identical, $E_\mathrm{f}=E_\mathrm{i}$, one has, with regard to eq. (1.1)

$$\omega_2=\omega_1 \tag{1.1a}$$

meaning that, in this scattering process, the photon frequency remains unchanged although the direction of its motion generally undergoes a

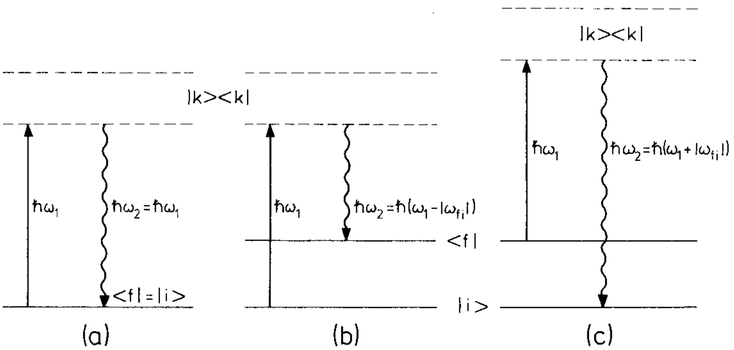

Fig. 1.1. Two-photon energy transitions: (a) Rayleigh, (b) Stokes Raman, and (c) anti-Stokes Raman.

change, $\boldsymbol{k}_1 \neq \boldsymbol{k}_2$. The elastic scattering process described above is referred to as Rayleigh scattering (Fig. 1.1).

If the energy of the emitted photon E_f differs from that of the incident photon E_i, the process is inelastic and is referred to as Raman scattering. In the quantal picture proposed by Smekal in 1923, if $\omega_2 = \omega_1 - |\omega_{fi}|$ we deal with a Stokes process, whereas if $\omega_2 = \omega_1 + |\omega_{fi}|$ we have an anti-Stokes process; i.e. by eq. (1.1):

$$\omega_2 = \omega_1 \mp |\omega_{fi}|. \tag{1.1b}$$

As the microsystem is acted on by the complex analytic signal

$$\boldsymbol{E}(t) = \boldsymbol{E}(\omega_1) \exp(-\mathrm{i}\omega_1 t) \tag{1.2}$$

of the light wave vibrating at the circular frequency ω_1, and if the electric field is not excessively strong, the electric dipole moment for the transition $\langle f| \leftarrow |i\rangle$ is (in the case of linear response)

$$\boldsymbol{D}_{fi}^{(1)}(t) = \boldsymbol{a}_{fi}^{(1)}(-\omega_2, \omega_1) \cdot \boldsymbol{E}(\omega_1) \exp[-\mathrm{i}(\omega_1 + \omega_{fi})t], \tag{1.3}$$

where $\boldsymbol{a}_{fi}^{(1)}(-\omega_2, \omega_1)$ is a tensor of the second rank determining the linear electric polarizability of the microsystem.

One hundred and ten years have elapsed since Lord Rayleigh laid the foundations of the microscopic theory of light scattering and, at the same time, explained why we perceive the sky as blue on a cloudless day. Much later, the statistical-thermodynamical theory of Rayleigh scattering was formulated by Smoluchowski in 1908 and Einstein in 1910, based on the stochasticity of light scattering on thermal fluctuations of density and, in solutions, of the concentration. The next step was made by Brillouin in

1922, who showed that time-variable statistical fluctuations of density cause a modulation of the spectrum of scattered light. In addition to the central Rayleigh–Smoluchowski line (due to isobaric fluctuations of density), two symmetrically disposed lines due to adiabatic fluctuations of density appear. This Brillouin–Mandelshtam doublet was detected in liquids by Gross in 1930. These matters have been discussed in numerous monographs (see, for example, FABELINSKII [1968] and KIELICH [1980a]).

Just over half a century ago Raman and Krishnan, and Landsberg and Mandelshtam, brought into being in 1928 what is now generally referred to as Raman spectroscopy. In these days of laser techniques, Raman scattering and the spectroscopic methods based on it have been generally accepted as a potent instrument of study, revealing to us the properties of atoms, molecules and macromolecules, as well as the microscopic structure of gases, liquids and solids. This completely autonomous discipline has been dealt with comprehensively in a number of books (see, for example, KONINGSTEIN [1972], LONG [1977], CARDONA [1975], and HAYES and LOUDON [1978]).

Equations (1.1) and (1.3) determine a two-quantum process (one incident photon and one scattered photon). When a microsystem is in a radiation field with a high density of the photons, processes involving more than two photons can take place. Thus, as early as 1931, Göppert-Mayer considered theoretically three-photon processes involving the emission or absorption of two photons. Extending her theory BLATON [1931], and later NEUGEBAUER [1963] showed that a quantal system can produce elastic scattering at the doubled frequency 2ω. GÜTTINGER [1932] analyzed the possibility of inelastic three-photon scattering at the frequencies $\omega_3 = \omega_1 + \omega_2 \mp \omega_{\mathrm{fi}}$ (Fig. 1.2). The quantum-mechanical foundations of three- and four-photon Raman scattering have been formulated by KIELICH [1964b] for molecular systems of arbitrary symmetry.

Accordingly, a molecular system in a strong electric field (1.2) generally exhibits a nonlinear response when its electric dipole moment of the nth order for a transition $\langle \mathrm{f}| \leftarrow |\mathrm{i}\rangle$ is

$$\begin{aligned} \boldsymbol{D}_{\mathrm{fi}}^{(n)}(t) = \boldsymbol{K}(\omega_{n+1})\, \boldsymbol{a}_{\mathrm{fi}}^{(n)}(-\omega_{n+1}, \omega_n, \ldots, \omega_1) \\ \times [n]\, \boldsymbol{E}(\omega_n) \cdots \boldsymbol{E}(\omega_1) \exp[-\mathrm{i}(\omega_n + \cdots + \omega_1 + \omega_{\mathrm{fi}})t], \end{aligned} \tag{1.4}$$

where $\boldsymbol{a}_{\mathrm{fi}}^{(n)}(-\omega_{n+1}, \omega_n, \ldots, \omega_1)$ is a tensor of the $(n+1)$th rank determining the nth order polarizability of the scatterer. In eq. (1.4), the symbol $[n]$ stands for n-fold contraction of two tensors of rank n, whereas $K(\omega_{n+1})$ is a numerical expansion and frequency degeneracy coefficient.

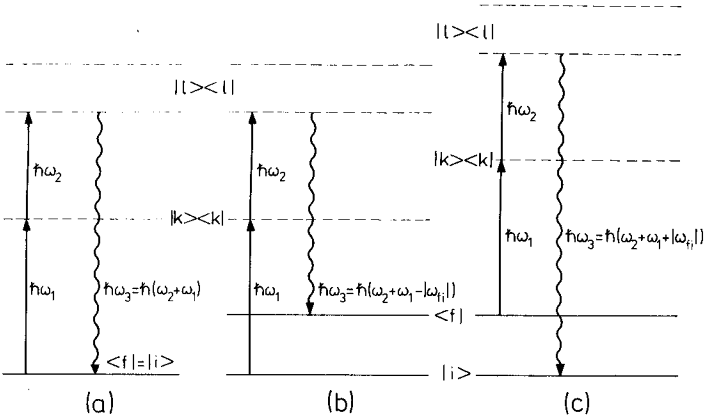

Fig. 1.2. Three-photon energy transitions: (a) hyper-Rayleigh, (b) Stokes hyper-Raman, and (c) anti-Stokes hyper-Raman.

Equation (1.4) shows that, if n photons with different frequencies $\omega_1, \ldots, \omega_n$ are incident on the microsystem, then an $(n+1)$th photon, having one of the frequencies

$$\omega_{n+1} = \omega_n + \cdots + \omega_1 \mp |\omega_{\mathrm{fi}}|, \tag{1.5}$$

is scattered in the quantal transition of transition frequency ω_{fi}.

Equations (1.4) and (1.5) define $(n+1)$-photon spontaneous Raman scattering, also referred to as non-degenerate hyper-Raman scattering of the $(n-1)$th order, with $n \geqslant 2$. In particular, if the photons have the same frequency ω, we have for $(n-1)$th order degenerate hyper-Raman scattering:

$$\omega_{n+1} = n\omega \mp |\omega_{\mathrm{fi}}|. \tag{1.6}$$

The process, described by eq. (1.6), is also referred to as n-harmonic Raman scattering.

For the case $\omega_{\mathrm{fi}} = 0$, eqs. (1.5) and (1.6) give the following frequencies:

$$\omega_{n+1} = \omega_n + \cdots + \omega_1, \tag{1.5a}$$

$$\omega_{n+1} = n\omega, \tag{1.6a}$$

determining respectively spontaneous non-degenerate $(n+1)$-photon Rayleigh scattering, and degenerate spontaneous Rayleigh (or $(n-1)$-order hyper-Rayleigh) scattering.

Although various review articles on multi-photon spectroscopy have

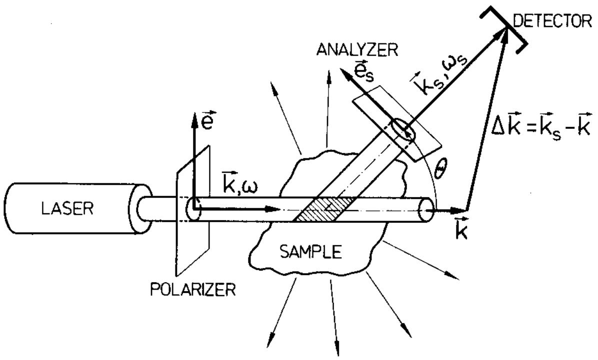

Fig. 1.3. Typical experimental geometry for the study of scattered light, of frequency ω_s, propagation vector $\boldsymbol{k}_s$ and polarization vector $\boldsymbol{e}_s$. The incident laser light wave has the frequency ω, propagation vector $\boldsymbol{k}$ and polarization vector $\boldsymbol{e}$.

already appeared (see, for example, PETICOLAS [1967], VOGT [1974], FRENCH and LONG [1976], and KIELICH [1977, 1980b]), we cannot refrain from giving a brief and in some respects actualized discussion of the matter. The laser light scattering experiment is represented in Fig. 1.3.

1.2. SPONTANEOUS HYPER-RAYLEIGH LIGHT SCATTERING STUDIES

The earliest experimental detection of Rayleigh nonlinear scattering at the frequency 2ω is due to TERHUNE, MAKER and SAVAGE [1965], who used the light beam of a giant ruby laser and scattering liquids like CCl_4 and H_2O with non-centrosymmetric molecules, as suggested by the theory (KIELICH [1964a]). BERSOHN, PAO and FRISCH [1966], KIELICH [1964c, 1968a], and KIELICH and KOZIEROWSKI [1974] have analyzed the influence of radial and angular correlations of the scatterers in hyper-Rayleigh scattering by liquids. The preliminary observations of WEINBERG [1967] nonetheless led to a rather weak dependence on temperature of hyper-Rayleigh scattering in the case of CCl_4 and H_2O, pointing to an insignificant role of angular correlations. This, in fact, could have been expected; the theory predicts that in liquids whose molecules lack a centre of inversion, incoherent three-photon scattering is the predominant effect, against the background of which a slight coherent (temperature-dependent) effect is weakly perceptible.

Only liquids with molecules that have a centre of symmetry provide the appropriate test of the role of correlations in hyper-Rayleigh scattering since for them incoherent three-photon Rayleigh scattering is forbidden in the electric-dipole approximation. In such liquids, only coherent three-photon scattering due to cooperative molecular effects in short-range regions (KIELICH [1968b]), or to molecular field inhomogeneities (SAMSON and PASMANTER [1974]) is possible. The demonstration of cooperative three-photon Rayleigh scattering by liquids such as cyclohexane, benzene and carbon disulphide has been provided by KIELICH, LALANNE and MARTIN [1971, 1973]. The effect has also been analyzed theoretically by PASMANTER, SAMSON and BEN-REUVEN [1976].

In simple molecular liquids in the normal state, cooperative hyper-Rayleigh scattering is weak. Obviously, it can be expected to become stronger as the liquid approaches a critical point, when critical opalescence due to anomalous density fluctuations (according to Smoluchowski), or concentrational fluctuations (according to Einstein), sets in. With regard to nonlinear scattering, LAJZEROWICZ [1965] drew attention to this circumstance, suggesting that very considerable critical scattering can occur in liquids exhibiting phase transitions. The effect was first observed by FREUND [1967, 1968] for polycrystalline NH_4Cl at temperatures near the second-kind phase transition. Subsequent work by FREUND and KOPF [1970], and LUBAN, WISER and GREENFIELD [1970] has permitted the utilization of critical second-harmonic scattering as a source of information on order–disorder phase transitions.

DOLINO, LAJZEROWICZ and VALLADE [1969, 1970] and DOLINO [1972] initiated studies of laser second-harmonic scattering on domain structures of ferro-electric crystals (triglycine sulphate). INOUE [1974], and WEINMANN and VOGT [1974] have carried out a detailed investigation of the second-harmonic of light, scattered in $NaNO_2$ crystals, whereas VOGT and NEUMAN [1978] have pursued the same work in single crystals of $NaNO_3$. Second-harmonic scattering in the electric dipole-quadrupole approximation has been observed by ORTMANN and VOGT [1976] in the centrosymmetric crystal $NaNO_3$, and by DENISOV, MAVRIN, PODOBEDOV, STERIN and VARSHAL [1980] in non-centrosymmetric TiO_2 crystal. KOSOLOBOV and SOKOLOVSKY [1977] have observed second-harmonic scattering on defects of $LiIO_3$ crystal structure. This type of light scattering by centrosymmetric crystals had been predicted by RABIN [1969].

To MAKER [1970] are due the earliest line broadening observations for three-photon "quasi-elastic" scattering due to rotational-translational motions in molecular liquids. He simultaneously worked out the theory of its incoherent component, whereas the theory of the coherent component related with space-time angular molecular correlations has been proposed by BANCEWICZ and KIELICH [1976].

TANAŚ and KIELICH [1975] have considered second-harmonic scattering of light by a two-level system at two-photon resonance with the radiation field, when, in addition to the central line at 2ω, two side lines appear with frequencies $2\omega \pm \delta$, where δ is the level splitting, dependent on the beam intensity in the case of two-photon resonance.

1.3. SPONTANEOUS HYPER-RAMAN SCATTERING STUDIES

The work of PLACZEK [1934] provided the foundations of the polarizability theory of Raman scattering. His ideas have later been applied to the multi-photon case (KIELICH [1964b], AKHMANOV and KLYSHKO [1965], STRIZHEVSKY and KLIMENKO [1967], and LONG and STANTON [1970]). The selection rules for hyper-Raman scatterings differ from those of infrared absorption and usual Raman scattering. Those of vibrational transitions in three-photon Raman scattering have been established by CYVIN, RAUCH and DECIUS [1965] for all point groups and types of vibrations.

The theoretical formulation of hyper-Raman scattering is given in Cartesian representation, based on eq. (1.4) (see KIELICH [1964b], CYVIN, RAUCH and DECIUS [1965], and ANDREWS and THIRUNAMACHANDRAN [1978]), as well as in spherical tensor representation (see, for example, OŻGO [1975b]). Specifically, the methods of Racah algebra are well adapted to the description of hyper-Raman spectroscopy. They lead to general and at the same time clear results, comprising the angular dependences and different states of polarization of the incident and scattered photons (see CHIU [1970], KIELICH and OŻGO [1973], OŻGO and KIELICH [1974, 1976], JERPHAGNON, CHEMLA and BONNEVILLE [1978], and CHEMLA and BONNEVILLE [1978]).

BANCEWICZ, OŻGO and KIELICH [1973a, 1975] have calculated the rotational structure of hyper-Raman lines of gases consisting of spherical as well as symmetric top molecules. ALEXIEWICZ, BANCEWICZ, KIELICH and OŻGO [1974] have worked out the theory of three-photon Raman line broadening caused by the rotational diffusional motion of molecules. The theory has been extended to multi-photon Raman scattering by KIELICH, KOZIEROWSKI and OŻGO [1977]. Quite recently, MANAKOV and OVSIANNIKOV [1980] have given a discussion of non-degenerate three-photon Raman scattering by atomic gases.

The resonantial amplification of hyper-Raman scattering discussed by KIELICH [1965a] and, on a numerical basis, by LONG and STANTON [1970], has been analyzed anew by BEN-ZEEV, WILSON and FRIEDMANN [1977] for real coherent pulse shapes, causing the emergence of a novel resonance peak and a saturation effect such as Stark splitting, Stark shifts and optical nutation. AGARWAL [1979] has performed an analysis of saturation effects in hyper-Raman scattering by a four-level system at three-photon resonance (see also ARUTYUNIAN, PAPAZIAN, CHILINGARIAN, KARMENIAN and SARKISIAN [1974]).

ALTMANN and STREY [1977] have analyzed the increase in intensity of hyper-Raman scattering due to the statistical properties of the field of radiation (cf. MANDEL and WOLF [1965]). PEŘINOVA, PEŘINA, SZLACHETKA and KIELICH [1979], and SZLACHETKA, KIELICH, PEŘINA and PEŘINOVA [1980]), have formulated a complete quantal theory of hyper-Raman scattering, in which they give an analysis of the dynamics of photon correlation and anti-correlation for arbitrary initial states. The effect of photon anti-bunching is purely quantal in nature (see WALLS [1979]). It has been detected by KIMBLE, DAGENAIS and MANDEL [1977] in resonance fluorescence, in accordance with the predictions of CARMICHAEL and WALLS [1976]. Previously, SIMAAN [1978] considered the quantum statistical properties of Stokes hyper-Raman scattering using the master equation and Fock states (see LOUDON [1980]).

In their first experiment TERHUNE, MAKER and SAVAGE [1965] observed, in addition to hyper-Rayleigh lines, hyper-Raman spectra for water. VERDIECK, PETERSON, SAVAGE and MAKER [1970] observed hyper-Raman spectra in some gases. Soon afterwards, SAVAGE and MAKER [1971], and FRENCH and LONG [1975] succeeded in perfecting the technique of recording hyper-Raman spectra, thus considerably shortening the time of exposition. FRENCH and LONG [1975] constructed a special spectrometer, operating on one or many channels, with which they recorded hyper-Raman spectra for the liquids H_2O, $CHCl_3$ and CCl_4 and later (DINES, FRENCH, HALL and LONG [1976]), for a whole family of liquids comprising chloromethanes, bromomethanes and tetrachlorides. SCHMID and SCHRÖTTER [1977] have observed vibrational hyper-Raman spectra in solutions of C_2Cl_4 and CCl_4.

The past few years have witnessed an increase in the amount of work devoted to the hyper-Raman phenomenon in solids, the theory of which is due to STRIZHEVSKY and OBUKHOVSKY [1970]. With regard to scattering on phonons in ionic crystals the theory is due to JHA and WOO [1971] and, for polaritons in molecular crystals, to ZAVOROTNEV and OVANDER [1975]. BANCEWICZ, KIELICH and OŻGO [1975] have given a discussion of three- and four-photon electric dipole and quadrupole Raman scattering for crystals with symmetry O_h. OŻGO, BANCEWICZ and KIELICH [1978] have analyzed the symmetry of the hyperpolarizability tensor for all symmetry classes and types of vibrations of crystals. BALAGUROV and VAKS [1978] have pointed out that intense critical hyper-Raman scattering can be observed in ferroelectrics.

TERHUNE, MAKER and SAVAGE [1965], in their pioneering work, observed a hyper-Raman spectrum in molten quartz. SAVAGE and MAKER [1971], using a many-channel spectrograph, recorded a hyper-Raman spectrum from NH_4Cl single crystals (see also DINES, FRENCH, HALL and LONG [1976]). Of great importance is the report of YU and ALFANO [1975] announcing the observation of three- and four-photon Raman spectra in diamonds. POLIVANOV and SAYAKHOV [1978] have observed hyper-Raman scattering on optical phonons in calcite crystals. VOGT and NEUMANN [1976, 1979] have performed systematic studies of such spectra for crystals of CsI, CsBr, RbI and $SrTiO_3$. INOUE and SAMESHIMA [1979] and INOUE, ASAI and SAMESHIMA [1980, 1981], studying $SrTiO_3$ crystals, have proved hyper-Raman to be a simple and promising method for observing the phonon polariton mode. POLIVANOV and SAYAKHOV [1979a, b] have reported the first observation of hyper-Raman scattering on optical phonons in CdS. Quite recently, DENISOV, MAVRIN, PODOBEDOV, STERIN and VARSHAL [1980] have published observations of both two-phonon and polariton hyper-Raman scattering in TiO_2 crystals subsequent to the results of DENISOV, MAVRIN, PODOBEDOV and STERIN [1978] for $LiNbO_3$ crystals. SCHREY, LYSSENKO, KLINGSHIRN and HÖNERLAGE [1979] in CdS and, more recently HÖNERLAGE, RÖSSLER, PHACH, BIVAŠ and GRUN [1980] in CuBr, have observed hyper-Raman scattering via virtually excited biexcitons. Hyper-Raman resonance scattering associated with excitonic molecules in CuCl was observed by NAGASAWA, MITA and UETA [1976], HENNEBERGER, HENNEBERGER and VOIGT [1977], and recently by GRUN [1980].

1.4. THE PURPOSE OF THIS PAPER

This review article is restricted to spontaneous multi-photon Rayleigh and Raman scattering. We dare not enter the vast, rapidly developing domain of stimulated Raman, Rayleigh or Brillouin scattering effects (see, for example, Bloembergen [1967, 1977], Fabelinskii [1968], and Schubert and Wilhelmi [1978]). Nor shall we deal with higher-order stimulated Raman processes (Compaan, Wiener-Avnear and Chandra [1978]), Rayleigh and Raman resonant scattering by intense beams (Prakash, Chandra and Vachaspati [1976], Cohen-Tannoudji and Reynaud [1977], Agarwal and Jha [1979], Ballagh and Coope [1980], Fiutak and Van Kranendonk [1980], and Knight [1980]), Doppler-free multiphotonic spectroscopy (Grynberg and Cagnac [1977]), or the parametric scattering of beams discussed in the monograph of Klyshko [1980].

It is our intention to give a quantitative account of spontaneous multi-photon scattering in a uniform classical and semi-classical treatment, applying Cartesian representation for the description of integral scattering and irreducible spherical representation for spectral scattering. The formulae derived for the tensors of multi-photon scattering are adapted to the concrete particular cases encountered in actual experimental situations. In addition to considering the role of the nonlinear optical properties of free molecules apparent in incoherent scattering, we concentrate primarily on the stochastic aspects related to time-space correlations of the molecules and their translational-rotational motion within the scattering volume. We also expose the role played in dense media by electric molecular fields, the time and spatial fluctuations of which give rise to cooperative three-photon scattering. We adduce the essential experimental observations of the various scattering effects. Our discussion, moreover, comprises the angular distribution of integral intensities for arbitrary states of polarization (linear, circular and elliptical) of the incident and scattered photons, making no attempt to avoid the thorny problem of the choice of a univocal model of a natural light which, in application to nonlinear processes, is still controversial.

§ 2. Nonlinear Molecular Raman Polarizabilities

The quantum-mechanical theory of nonlinear Raman polarizabilities has been developed previously in the electric-dipole approximation (Kielich [1964b]), and electric magnetic-multipole approximation (Kielich [1965a]) for free molecules. Here, the problem will be extended to damping effects (Bloembergen [1965], Butcher [1965], and Kielich

[1966b]). The problem is sometimes formulated in a very simple manner within the framework of classical Lorentz–Voigt electron theory, permitting the calculation of non-linear polarizabilities, taking into account the damping of electron vibrations as well as effects of nuclear vibrations (see, for example, KASPROWICZ-KIELICH and KIELICH [1975], and FLYTZANIS and BLOEMBERGEN [1976]).

2.1 THE MULTIPOLE INTERACTION HAMILTONIAN

We consider a microsystem composed of s point particles (nuclei and electrons), with electric charges e_j, masses m_j, and positional vectors $\boldsymbol{r}_j$ referred to the centre Q of the micro-system (Fig. 2.1). Its electromagnetic field is observed at a point P, distant by $\boldsymbol{R}$ from Q; we denote the vector connecting P with a charge e_j as $\boldsymbol{R}_j = \boldsymbol{R} + \boldsymbol{r}_j$.

The Hamiltonian of the spinless microsystem, in the nonrelativistic case, is (HEITLER [1954]):

$$H = \sum_{j=1}^{s} \{e_j \Phi(\boldsymbol{R}_j, t) + (2m_j)^{-1} [\boldsymbol{p}_j - (e_j/c) \mathbf{A}(\boldsymbol{R}_j, t)]^2\} \tag{2.1}$$

in which $\Phi(\boldsymbol{R}_j, t)$ and $\mathbf{A}(\boldsymbol{R}_j, t)$ are the scalar and vector potentials of the electromagnetic field at the time t and point $\boldsymbol{R}_j$ of the jth particle, having the generalized momentum operator $\boldsymbol{p}_j$.

In eq. (2.1) we have neglected the potential-energy term of Coulomb interactions between the particles.

We suppose that the microsystem is subjected to external space- and

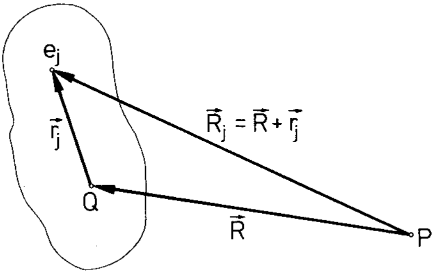

Fig. 2.1. System of electric point charges of linear dimensions very small compared with the distance $|\boldsymbol{R}| \gg |\boldsymbol{r}_j|$ at which the field of the system is studied.

time-dependent electric and magnetic fields at the point $(\boldsymbol{R}, t)$

$$\begin{aligned} \boldsymbol{E}(\boldsymbol{R}, t) &= -(1/c)\,\partial \boldsymbol{A}(\boldsymbol{R}, t)/\partial t - \boldsymbol{\nabla}\Phi(\boldsymbol{R}, t), \\ \boldsymbol{H}(\boldsymbol{R}, t) &= \boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{R}, t). \end{aligned} \tag{2.2}$$

At the present stage, we do not specify a particular gauge.

Quite generally, when the potentials $\Phi(\boldsymbol{R}_j, t)$ and $\boldsymbol{A}(\boldsymbol{R}_j, t)$ are not constant within the region of the microsystem, one can expand these potentials at $\boldsymbol{R}_j = \boldsymbol{R} + \boldsymbol{r}_j$ in a series in powers of $\boldsymbol{r}_j$ (KIELICH [1966a]):

$$\begin{aligned} \Phi(\boldsymbol{R}+\boldsymbol{r}_j, t) &= \sum_{n=0}^{\infty} (n!)^{-1}\, \boldsymbol{r}_j^n[n]\, \boldsymbol{\nabla}^n\, \Phi(\boldsymbol{R}, t), \\ \boldsymbol{A}(\boldsymbol{R}+\boldsymbol{r}_j, t) &= \sum_{n=0}^{\infty} (n!)^{-1} \boldsymbol{r}_j^n[n]\, \boldsymbol{\nabla}^n\, \boldsymbol{A}(\boldsymbol{R}, t), \end{aligned} \tag{2.3}$$

where $\boldsymbol{\nabla}$ is the spatial differential operator at the position $\boldsymbol{R}$.

After an appropriate canonical gauge transformation (see, for example, FIUTAK [1963] and POWER [1978]) we have, with respect to eqs. (2.1)–(2.3):

$$H = H_0 + H'(t) = H_{\mathrm{e}} + H_{\mathrm{e}}^{(1)}(t) + H_{\mathrm{m}}^{(1)}(t) + H_{\mathrm{m}}^{(2)}(t) + \cdots, \tag{2.4}$$

where H_0 is the Hamiltonian of the non-perturbated microsystem, its first-order perturbation Hamiltonian being (KIELICH [1965a])

$$H_{\mathrm{e}}^{(1)} = -\sum_{n=1}^{\infty} [(2n-1)!!]^{-1}\, \boldsymbol{M}_{\mathrm{e}}^{(n)}[n]\, \boldsymbol{E}^{(n)}(\boldsymbol{R}, t), \tag{2.5}$$

$$H_{\mathrm{m}}^{(1)}(t) = -\sum_{n=1}^{\infty} [(2n-1)!!]^{-1}\, \boldsymbol{M}_{\mathrm{m}}^{(n)}[n]\, \boldsymbol{H}^{(n)}(\boldsymbol{R}, t) \tag{2.6}$$

with $\boldsymbol{E}^{(n)}(\boldsymbol{R}, t) = \boldsymbol{\nabla}^{n-1}\boldsymbol{E}(\boldsymbol{R}, t)$ and $\boldsymbol{H}^{(n)}(\boldsymbol{R}, t) = \boldsymbol{\nabla}^{n-1}\, \boldsymbol{H}(\boldsymbol{R}, t)$.

We have introduced above the following 2^n-pole electric moments of the microsystem

$$\boldsymbol{M}_{\mathrm{e}}^{(n)} = \sum_{j=1}^{s} e_j r_j^n\, \boldsymbol{Y}^{(n)}(r_j) \tag{2.7}$$

and 2^n-pole magnetic moments of the microsystem

$$\boldsymbol{M}_{\mathrm{m}}^{(n)} = n[(n+1)c]^{-1} \sum_{j=1}^{s} e_j r_j \boldsymbol{Y}^{(n)}(\boldsymbol{r}_j) \times \dot{\boldsymbol{r}}_j, \tag{2.8}$$

wherein the vector operator $\boldsymbol{Y}^{(n)}$, of degree n (its properties resemble those of spherical harmonic functions), is given by

$$\boldsymbol{Y}^{(n)}(\boldsymbol{r}_j) = (-1)^n\, (n!)^{-1}\, r_j^{n+1}\, \boldsymbol{\nabla}_j^n(r_j^{-1}). \tag{2.9}$$

The higher-order Hamiltonians of interaction between the microsystem and a strong classical electromagnetic field occurring in eq. (2.4) have been given in earlier papers (KIELICH [1965, 1966a]).

In commonly discussed problems it is sufficient to take only the first terms of the Hamiltonians (2.5) and (2.6):

$$H_{\mathrm{e}}^{(1)} = -\boldsymbol{D}^{\mathrm{e}} \cdot \boldsymbol{E}(\boldsymbol{R}, t) - \tfrac{1}{3}\boldsymbol{Q}^{\mathrm{e}} : \boldsymbol{\nabla}\boldsymbol{E}(\boldsymbol{R}, t) - \dots, \tag{2.5a}$$

$$H_{\mathrm{m}}^{(1)} = -\boldsymbol{D}^{\mathrm{m}} \cdot \boldsymbol{H}(\boldsymbol{R}, t) - \dots, \tag{2.6a}$$

where $\boldsymbol{D}_{\mathrm{e}} = \boldsymbol{M}_{\mathrm{e}}^{(1)}$ and $\boldsymbol{Q}_{\mathrm{e}} = \boldsymbol{M}_{\mathrm{e}}^{(2)}$ are operators of the electric dipole and quadrupole moments respectively, and $\boldsymbol{D}_{\mathrm{m}} = \boldsymbol{M}_{\mathrm{m}}^{(1)}$ is the magnetic dipole moment operator.

Obviously, in this approximation, one should take into consideration the first term of the Hamiltonian $H_{\mathrm{m}}^{(2)}$. It is given as follows (KIELICH [1965a]):

$$H_{\mathrm{m}}^{(2)} = -\tfrac{1}{2}\boldsymbol{H}(\boldsymbol{R}, t) \cdot \boldsymbol{\chi}_{\mathrm{m}} \cdot \boldsymbol{H}(\boldsymbol{R}, t), \tag{2.10}$$

where

$$\boldsymbol{\chi}_{\mathrm{m}} = (4c^2)^{-1} \sum_{j=1}^{s} (e_j^2/m_j)\,(\boldsymbol{r}_j\boldsymbol{r}_j - r_j^2\boldsymbol{U}) \tag{2.11}$$

is the operator of the magnetic polarizability of the microsystem and $\boldsymbol{U}$ the second-rank unit tensor.

Similarly, one can calculate multipolar contributions to the electric and magnetic polarizabilities (KIELICH [1965a, 1966a] and DE GROOT [1969]).

2.2. THE EQUATION OF MOTION FOR THE VECTOR OF STATE

The expectation value of a dynamic operator $\boldsymbol{M}(t)$ for a quantum transition $\langle \mathrm{f}| \leftarrow |\mathrm{i}\rangle$, under the influence of a perturbation, is

$$\boldsymbol{M}_{\mathrm{fi}}(t) = \langle \psi_{\mathrm{f}}(t)|\, \boldsymbol{M}\, |\psi_{\mathrm{i}}(t)\rangle, \tag{2.12}$$

where motion of the vector of state $|\psi_{\mathrm{i}}(t)\rangle$ in Hilbert space is given by the Schrödinger equation

$$\mathrm{i}\hbar(\partial/\partial t)\, |\psi_{\mathrm{i}}(t)\rangle = \{H_0 + H'(t)\}\, |\psi_{\mathrm{i}}(t)\rangle \tag{2.13}$$

the Hamiltonian of the microsystem being given by (2.4).

We express the wave function of the perturbated system $\psi_{\mathrm{i}}(\boldsymbol{r}, t)$ in terms of the following expansion, involving known wave functions $\psi_{\mathrm{i}}(\boldsymbol{r}, 0)$

of stationary states of the non-perturbated system:

$$\psi_i(\boldsymbol{r}, t) = \sum_l c_{li}(t)\, \psi_l(\boldsymbol{r}, 0) \exp(-i\omega_l t), \tag{2.14}$$

with $\omega_l = E_l/\hbar$ being the circular vibration frequency corresponding to the eigen-energy E_l of the quantal state l of the non-perturbated system. The transition coefficients for a transition of the quantal system from the state $|i\rangle$ to the state $\langle l|$, under the influence of the perturbation $H'(t)$, are functions of time and can be expanded in a series as follows:

$$c_{li}(t) = c_{li}^{(0)}(t) + c_{li}^{(1)}(t) + c_{li}^{(2)}(t) + \cdots = \sum_{n=0}^{\infty} c_{li}^{(n)}(t). \tag{2.15}$$

The solution of the problem is dependent on the initial conditions assumed, defining the state of the system while still not acted on by the perturbation. This reduces to finding the zeroth approximation of the expansion (2.15). Sometimes, one can assume the ideal situation when the levels of the states of the "isolated" microsystem are of zero width; then $c_{li}^{(0)}(t) = \delta_{li}$ is independent of time. Regrettably, however, this situation is unrealistic, since even in the "isolated" case the levels almost always possess a non-zero width for various reasons (e.g. polarization of vacuum, heat reservoir, external fields, etc.). In fact, this finite width of the levels is the factor ensuring spontaneous emission – the action of the external electromagnetic field reducing to cause time-variations of the pre-existing level widths. We have thus in the zeroth approximation (LOUISELL [1973])

$$c_{li}^{(0)}(t) = \delta_{li} \exp(-\Gamma_l t/2), \tag{2.16}$$

where Γ_l^{-1} is the lifetime of the quantum state l and Γ is real.

With regard to the condition (2.16) we obtain, by (2.13)–(2.15), the following equation determining the transition coefficients for $n = 1, 2, 3, \ldots$ (PŁÓCINICZAK [1980]):

$$i\hbar(\partial/\partial t)c_{li}^{(n)}(t) = -i\hbar(\Gamma_l/2)c_{li}^{(n)}(t) + \sum_k H'_{lk}(t)\, c_{ki}^{(n-1)}(t) \exp(-i\omega_{kl} t), \tag{2.17}$$

where the matrix elements of the perturbation Hamiltonian $H'_{lk}(t)$ are defined as usual.

The equations of motion (2.17) represent a modification of the approach of ORR and WARD [1971], as well as the respective equation of motion for the density matrix operator of a system in the presence of damping (see BLOEMBERGEN [1965], AGARWAL [1973], and APANASEVICH [1977]).

In order to derive the transition coefficients for $n = 1, 2, 3, \ldots$ one has to know the perturbation Hamiltonian in analytical form, or rather its explicit dependence on the time. From eq. (2.5), the first-order perturbation Hamiltonians are seen to be linear functions of the electromagnetic field which, in turn, can be expressed as a superposition of different monochromatic waves in Fourier representation

$$\boldsymbol{E}(\boldsymbol{R}, t) = \frac{1}{2} \sum_{\lambda} \{\boldsymbol{E}(\boldsymbol{R}, \omega_\lambda) \exp(-\mathrm{i}\omega_\lambda t) + \boldsymbol{E}(\boldsymbol{R}, \omega_\lambda)^* \exp(\mathrm{i}\omega_\lambda t)\}, \tag{2.18}$$

where summation extends over all discrete vibration frequencies, with $\boldsymbol{E}(\boldsymbol{R}, \omega_\lambda)^* = \boldsymbol{E}(\boldsymbol{R}, -\omega_\lambda)$.

Restricting our considerations to the Hamiltonian of first-order perturbation, with time-dependence of the type (2.18), we obtain, with regard to the solution of the inhomogeneous linear differential equation (2.17), the following first-order transition coefficients:

$$\begin{aligned} c_{l\mathrm{i}}^{(1)}(t) = \frac{1}{2} \sum_{\lambda} \{ & c_{l\mathrm{i}}^{(1)}(\omega_\lambda) \exp(-\mathrm{i}\omega_\lambda t) \\ & + c_{l\mathrm{i}}^{(1)}(-\omega_\lambda) \exp(\mathrm{i}\omega_\lambda t)\} \exp[\mathrm{i}(\omega_{l\mathrm{i}} + \mathrm{i}\Gamma_\mathrm{i}/2)t], \end{aligned} \tag{2.19}$$

where the transition coefficient amplitudes are of the form

$$c_{l\mathrm{i}}^{(1)}(\pm\omega_\lambda) = -\frac{1}{\hbar} \frac{\langle l| H(\pm\omega_\lambda) |\mathrm{i}\rangle}{\omega_{l\mathrm{i}} \mp \omega_\lambda - \mathrm{i}\Gamma_{l\mathrm{i}}}. \tag{2.19a}$$

Above, $\Gamma_{l\mathrm{i}} = (\Gamma_l - \Gamma_\mathrm{i})/2$ are the difference level widths of the system for transitions $\langle l| \leftarrow |\mathrm{i}\rangle$.

Similarly, we obtain the transition coefficients for higher and higher approximations. Quite generally, in the nth order we have

$$\begin{aligned} c_{l\mathrm{i}}^{(n)}(t) = 2^{-n} \sum_{\lambda_1 \cdots \lambda_n} \{ & c_{l\mathrm{i}}^{(n)}(\omega_{\lambda_n} + \cdots + \omega_{\lambda_1}) \exp[-\mathrm{i}(\omega_{\lambda_n} + \cdots + \omega_{\lambda_1})t] \\ & + (2^n - 1) \text{ terms}\} \exp[\mathrm{i}(\omega_{l\mathrm{i}} + \mathrm{i}\Gamma_\mathrm{i}/2)t] \end{aligned} \tag{2.20}$$

with the nth order transition coefficient amplitude

$$\begin{aligned} & c_{l\mathrm{i}}^{(n)}(\pm\omega_{\lambda_n} \cdots \pm \omega_{\lambda_1}) = (-1)^n \hbar^{-n} \\ & \qquad \times \sum_{k_1 \cdots k_{n-1}} \frac{\langle l| H(\omega_{\lambda_n}) |k_{n-1}\rangle \cdots \langle k_1| H(\omega_{\lambda_1}) |\mathrm{i}\rangle}{\prod_{u=1}^{n} (\omega_{k_{n-u}\mathrm{i}} \mp \omega_{\lambda_u} - \cdots - \mathrm{i}\Gamma_{k_{n-u}\mathrm{i}})} \end{aligned} \tag{2.20a}$$

and $k_0 = l$.

By eqs. (2.14) and (2.15), the transition operator (2.12) can be written in the form of the series

$$\boldsymbol{M}_{\mathrm{fi}}(t)=\sum_{n=0}^{\infty}\boldsymbol{M}_{\mathrm{fi}}(t)^{(n)}, \tag{2.21}$$

where the approximations of successive orders are

$$\boldsymbol{M}_{\mathrm{fi}}(t)^{(n)}=\sum_{u=0}^{n}\sum_{kl}c_{k\mathrm{f}}^{(u)}(t)^{*}\,\boldsymbol{M}_{kl}\,c_{l\mathrm{i}}^{(n-u)}(t)\exp\left(\mathrm{i}\omega_{kl}t\right). \tag{2.22}$$

In particular, in the zeroth approximation, we hence have for the transition operator

$$\boldsymbol{M}_{\mathrm{fi}}(t)^{(0)}=\boldsymbol{M}_{\mathrm{fi}}\exp\left[\mathrm{i}(\omega_{\mathrm{fi}}+\mathrm{i}\Gamma_{\mathrm{fi}}^{+})t\right]. \tag{2.23}$$

The above operator describes spontaneous emission and absorption. Here, however, $\Gamma_{\mathrm{fi}}^{+}=(\Gamma_{\mathrm{f}}+\Gamma_{\mathrm{i}})/2$ is the summation level width.

The transition matrix in the first-order approximation is, by eqs. (2.16), (2.19) and (2.22),

$$\begin{aligned}\boldsymbol{M}_{\mathrm{fi}}(t)^{(1)}=\frac{1}{2}\sum_{\lambda}\sum_{k}\{&[\boldsymbol{M}_{\mathrm{f}k}c_{k\mathrm{i}}^{(1)}(\omega_{\lambda})+c_{\mathrm{f}k}^{(1)}(\omega_{\lambda})^{*}\,\boldsymbol{M}_{k\mathrm{i}}]\exp\left(-\mathrm{i}\omega_{\lambda}t\right)\\&+[\boldsymbol{M}_{\mathrm{f}k}c_{k\mathrm{i}}^{(1)}(-\omega_{\lambda})+c_{\mathrm{f}k}^{(1)}(-\omega_{\lambda})^{*}\,\boldsymbol{M}_{k\mathrm{i}}]\exp\left(\mathrm{i}\omega_{\lambda}t\right)\}\exp\left[\mathrm{i}(\omega_{\mathrm{fi}}+\mathrm{i}\Gamma_{\mathrm{fi}}^{+})t\right].\end{aligned} \tag{2.24}$$

We likewise express the transition matrices of higher orders, including the nth (2.22).

2.3. NONLINEAR POLARIZABILITIES IN THE ELECTRIC-DIPOLE APPROXIMATION

We shall now consider the quantum transition matrices (2.22), restricting ourselves to the electric-dipole approximation in the perturbation Hamiltonian (2.5). In this procedure, we obtain by (2.24), for the component σ (in a Cartesian reference system X, Y, Z) of the electric dipole transition moment, the following first-order approximations:

$$\begin{aligned}D_{\sigma\mathrm{fi}}^{\mathrm{e}}(t)^{(1)}=\frac{1}{2}\sum_{\lambda}\{&a_{\sigma\tau}^{\mathrm{fi}}(\omega_{\lambda})\,E_{\tau}(\omega_{\lambda})\exp\left(-\mathrm{i}\omega_{\lambda}t\right)\\&+a_{\sigma\tau}^{\mathrm{fi}}(-\omega_{\lambda})\,E_{\tau}(-\omega_{\lambda})\exp\left(\mathrm{i}\omega_{\lambda}t\right)\}\exp\left[\mathrm{i}(\omega_{\mathrm{fi}}+\mathrm{i}\Gamma_{\mathrm{fi}}^{+})t\right],\end{aligned} \tag{2.25}$$

where the second-rank tensors of the linear polarizability of the microsystem for the transition $\langle \mathrm{f}| \leftarrow |\mathrm{i}\rangle$ have the form

$$a^{\mathrm{fi}}_{\sigma\tau}(\pm\omega_\lambda) = \frac{1}{\hbar}\sum_{k}\left\{\frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_{\sigma}\, |k\rangle\langle k|\, D^{\mathrm{e}}_{\tau}\, |\mathrm{i}\rangle}{\omega_{k\mathrm{i}} \mp \omega_\lambda - \mathrm{i}\Gamma_{k\mathrm{i}}} + \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_{\tau}\, |k\rangle\langle k|\, D^{\mathrm{e}}_{\sigma}\, |\mathrm{i}\rangle}{\omega_{k\mathrm{f}} \pm \omega_\lambda + \mathrm{i}\Gamma_{k\mathrm{f}}}\right\}. \tag{2.25a}$$

The preceding quantum-mechanical expressions proceed beyond the WEISSKOPF–WIGNER theory [1930] and, in the absence of damping, go over into the well known KRAMERS–HEISENBERG result [1925] (see EBERLY [1980]). By (2.25), the scattered frequencies are $\pm\omega_\lambda + \omega_{\mathrm{fi}} + \mathrm{i}\Gamma^{+}_{\mathrm{fi}}$.

Proceeding along similar lines we obtain, by eqs. (2.20) and (2.22), the second-order transition matrix of the electric dipole moment

$$D^{\mathrm{e}}_{\sigma\mathrm{fi}}(t)^{(2)} = \frac{1}{8}\sum_{\lambda\mu}\{b^{\mathrm{fi}}_{\sigma\tau\nu}(\omega_\mu, \omega_\lambda)\, E_\tau(\omega_\mu)\, E_\nu(\omega_\lambda)$$
$$\times \exp\left[-\mathrm{i}(\omega_\mu + \omega_\lambda)t\right] + 3 \text{ terms}\}\exp\left[\mathrm{i}(\omega_{\mathrm{fi}} + \mathrm{i}\Gamma^{+}_{\mathrm{fi}})t\right], \tag{2.26}$$

where we have introduced the third-rank tensors $b^{\mathrm{fi}}_{\sigma\tau\nu}$, defining the second-order nonlinear polarizabilities for the transition $\langle \mathrm{f}| \leftarrow |\mathrm{i}\rangle$:

$$b^{\mathrm{fi}}_{\sigma\tau\nu}(\omega_\mu, \omega_\lambda) = \frac{S_2}{\hbar^2}\sum_{kl}\left\{\frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_{\sigma}\, |l\rangle\langle l|\, D^{\mathrm{e}}_{\tau}\, |k\rangle\langle k|\, D^{\mathrm{e}}_{\nu}\, |\mathrm{i}\rangle}{(\omega_{l\mathrm{i}} - \omega_\mu - \omega_\lambda - \mathrm{i}\Gamma_{l\mathrm{i}})(\omega_{k\mathrm{i}} - \omega_\lambda - \mathrm{i}\Gamma_{k\mathrm{i}})}\right.$$
$$+ \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_{\tau}\, |k\rangle\langle k|\, D^{\mathrm{e}}_{\sigma}\, |l\rangle\langle l|\, D^{\mathrm{e}}_{\nu}\, |\mathrm{i}\rangle}{(\omega_{k\mathrm{f}} + \omega_\mu + \mathrm{i}\Gamma_{k\mathrm{f}})(\omega_{l\mathrm{i}} - \omega_\lambda - \mathrm{i}\Gamma_{l\mathrm{i}})}$$
$$\left. + \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_{\nu}\, |l\rangle\langle l|\, D^{\mathrm{e}}_{\tau}\, |k\rangle\langle k|\, D^{\mathrm{e}}_{\sigma}\, |\mathrm{i}\rangle}{(\omega_{l\mathrm{f}} + \omega_\lambda + \mathrm{i}\Gamma_{l\mathrm{f}})(\omega_{k\mathrm{f}} + \omega_\mu + \omega_\lambda + \mathrm{i}\Gamma_{k\mathrm{f}})}\right\}. \tag{2.27}$$

Here, S_2 denotes the symmetrizing operation, which indicates that the expressions following it are to be summed over the 2! possible permutations of the pairs $\tau\omega_\mu$ and $\nu\omega_\lambda$.

The third-order electric dipole transition moment is:

$$D^{\mathrm{e}}_{\sigma\mathrm{fi}}(t)^{(3)} = \frac{1}{48}\sum_{\lambda\mu\varepsilon}\{c^{\mathrm{fi}}_{\sigma\tau\nu\rho}(\omega_\varepsilon, \omega_\mu, \omega_\lambda)$$
$$\times E_\tau(\omega_\varepsilon)\, E_\nu(\omega_\mu)\, E_\rho(\omega_\lambda)\exp\left[-\mathrm{i}(\omega_\varepsilon + \omega_\mu + \omega_\lambda)t\right]$$
$$+ 7 \text{ terms} \cdots\}\exp\left[\mathrm{i}(\omega_{\mathrm{fi}} + \mathrm{i}\Gamma^{+}_{\mathrm{fi}})t\right], \tag{2.28}$$

where the fourth-rank tensors $c^{\mathrm{fi}}_{\sigma\tau\nu\rho}$, defining the third-order nonlinear polarizabilities for the transition $\langle \mathrm{f}| \leftarrow |\mathrm{i}\rangle$, are

$$
\begin{aligned}
c^{\mathrm{fi}}_{\sigma\tau\nu\rho}(\omega_\varepsilon, \omega_\mu, \omega_\lambda) &= \hbar^{-3} S_3 \\
&\times \sum_{klm} \left\{ \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_\sigma\, |m\rangle\langle m|\, D^{\mathrm{e}}_\tau\, |l\rangle\langle l|\, D^{\mathrm{e}}_\nu\, |k\rangle\langle k|\, D^{\mathrm{e}}_\rho\, |\mathrm{i}\rangle}{(\omega_{m\mathrm{i}} - \omega_\varepsilon - \omega_\mu - \omega_\lambda - \mathrm{i}\Gamma_{m\mathrm{i}})(\omega_{l\mathrm{i}} - \omega_\mu - \omega_\lambda - \mathrm{i}\Gamma_{l\mathrm{i}})(\omega_{k\mathrm{i}} - \omega_\lambda - \mathrm{i}\Gamma_{k\mathrm{i}})} \right. \\
&+ \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_\tau\, |k\rangle\langle k|\, D^{\mathrm{e}}_\sigma\, |m\rangle\langle m|\, D^{\mathrm{e}}_\nu\, |l\rangle\langle l|\, D^{\mathrm{e}}_\rho\, |\mathrm{i}\rangle}{(\omega_{k\mathrm{f}} + \omega_\varepsilon + \mathrm{i}\Gamma_{k\mathrm{f}})(\omega_{m\mathrm{i}} - \omega_\mu - \omega_\lambda - \mathrm{i}\Gamma_{m\mathrm{i}})(\omega_{l\mathrm{i}} - \omega_\lambda - \mathrm{i}\Gamma_{l\mathrm{i}})} \\
&+ \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_\nu\, |m\rangle\langle m|\, D^{\mathrm{e}}_\tau\, |k\rangle\langle k|\, D^{\mathrm{e}}_\sigma\, |l\rangle\langle l|\, D^{\mathrm{e}}_\rho\, |\mathrm{i}\rangle}{(\omega_{m\mathrm{f}} + \omega_\mu + \mathrm{i}\Gamma_{m\mathrm{f}})(\omega_{k\mathrm{f}} + \omega_\varepsilon + \omega_\mu + \mathrm{i}\Gamma_{k\mathrm{f}})(\omega_{l\mathrm{i}} - \omega_\lambda - \mathrm{i}\Gamma_{l\mathrm{i}})} \\
&+ \left. \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_\rho\, |m\rangle\langle m|\, D^{\mathrm{e}}_\nu\, |l\rangle\langle l|\, D^{\mathrm{e}}_\tau\, |k\rangle\langle k|\, D^{\mathrm{e}}_\sigma\, |\mathrm{i}\rangle}{(\omega_{m\mathrm{f}} + \omega_\lambda + \mathrm{i}\Gamma_{m\mathrm{f}})(\omega_{l\mathrm{f}} + \omega_\lambda + \omega_\mu + \mathrm{i}\Gamma_{l\mathrm{f}})(\omega_{k\mathrm{f}} + \omega_\varepsilon + \omega_\mu + \omega_\lambda + \mathrm{i}\Gamma_{k\mathrm{f}})} \right\}.
\end{aligned}
\tag{2.29}
$$

The other 7 tensors of eq. (2.28) are hence derived by successively changing the signs at the frequencies ω_ε, ω_μ and ω_λ.

Finally, by (2.22) and (2.20), we have for the nth order electric dipole transition moment (cf. KIELICH [1966b]):

$$
\begin{aligned}
D^{\mathrm{e}}_{\sigma\mathrm{fi}}(t)^{(n)} = (2^n n!)^{-1} \sum_{\lambda_1 \cdots \lambda_n} \{ & a^{\mathrm{fi}}_{\sigma\sigma_1 \cdots \sigma_n}(\omega_{\lambda_1}, \ldots, \omega_{\lambda_n})\, E_{\sigma_1}(\omega_{\lambda_1}) \cdots E_{\sigma_n}(\omega_{\lambda_n}) \\
& \times \exp[-\mathrm{i}(\omega_{\lambda_1} + \cdots + \omega_{\lambda_n})t] + (2^n - 1) \text{ terms}\} \exp[\mathrm{i}(\omega_{\mathrm{fi}} + \mathrm{i}\Gamma^{+}_{\mathrm{fi}})t],
\end{aligned}
\tag{2.30}
$$

where the $(n+1)$th rank tensor of nonlinear nth order polarizability for the transition $\langle \mathrm{f}| \leftarrow |\mathrm{i}\rangle$ has the form

$$
\begin{aligned}
a^{\mathrm{fi}}_{\sigma\sigma_1 \cdots \sigma_n}(\omega_{\lambda_1}, \ldots, \omega_{\lambda_n}) &= \hbar^{-n} \sum_{s=0}^{n} S_n \\
&\times \sum_{k_1 \cdots k_n} \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_{\sigma_1}\, |k_1\rangle \cdots \langle k_s|\, D^{\mathrm{e}}_{\sigma}\, |k_{s+1}\rangle \cdots \langle k_n|\, D^{\mathrm{e}}_{\sigma_n}\, |\mathrm{i}\rangle}{\prod_{u=1}^{s} (\omega_{k_u\mathrm{f}} + \omega_{\lambda_1} + \cdots + \omega_{\lambda_u} + \mathrm{i}\Gamma_{k_u\mathrm{f}}) \prod_{u=s+1}^{n} (\omega_{k_u\mathrm{i}} - \omega_{\lambda_u} - \cdots - \omega_{\lambda_n} - \mathrm{i}\Gamma_{k_u\mathrm{i}})}.
\end{aligned}
\tag{2.31}
$$

Here, S_n is a symmetrizing operator, implying summation over all $n!$ permutations of $\sigma_1\omega_{\lambda_1}, \ldots, \sigma_n\omega_{\lambda_n}$.

As we see, the transition dipole moments (2.30) are in general complex quantities; to obtain their real parts, determining classical radiation of real dipole moments, one can have recourse to the postulate of KLEIN [1927] (see also PLACZEK [1934]).

In the non-resonance case, the nonlinear polarizabilities induced by vibrational transitions can be described by the method proposed by Placzek [1934] (see Kielich [1964b]). Recently, Pandey and Santry [1980] have evaluated vibrational contributions to the polarizabilities and hyper-polarizabilities of some simple molecules (CO, HCN and H_2O).

2.4. MULTIPOLE ELECTRIC AND MAGNETIC POLARIZABILITIES

Electric dipole transitions of even orders are forbidden for certain molecular symmetries, and one has to consider electric quadrupole or still higher multipole transitions. To deal with these situations, we insert the multipolar Hamiltonian (2.5) into the transition moment (2.24). This leads to the first-order electric multipole moment for the transition $\langle \mathrm{f}| \leftarrow |\mathrm{i}\rangle$

$$\begin{aligned} {}_{\mathrm{e}}\boldsymbol{M}_{\mathrm{fi}}^{(n)}(t)^{(1)} = \frac{1}{2} \sum_{\lambda_1} \sum_{n_1=1}^{\infty} [(2n_1-1)!!]^{-1} \{ {}^{(n)}_{\mathrm{e}}\mathbf{A}_{\mathrm{efi}}^{(n_1)}(\omega_{\lambda_1}) [n_1] \boldsymbol{E}^{(n_1)}(\boldsymbol{R}, \omega_{\lambda_1}) \\ \times \exp(-\mathrm{i}\omega_{\lambda_1} t) + {}^{(n)}_{\mathrm{e}}\mathbf{A}_{\mathrm{efi}}^{(n_1)}(-\omega_{\lambda_1}) [n_1] \boldsymbol{E}^{(n_1)}(\boldsymbol{R}, \omega_{\lambda_1})^* \exp(\mathrm{i}\omega_{\lambda_1} t)\} \\ \times \exp[\mathrm{i}(\omega_{\mathrm{fi}} + \mathrm{i}\Gamma_{\mathrm{fi}}^{+})t], \end{aligned} \tag{2.32}$$

where the tensors of rank $n+n_1$ determine the linear multipole electric-electric polarizabilities (Kielich [1965a, 1975]):

$${}^{(n)}_{\mathrm{e}}\mathbf{A}_{\mathrm{efi}}^{(n_1)}(\pm\omega_{\lambda_1}) = \frac{1}{\hbar} \sum_k \left\{ \frac{\langle \mathrm{f}| \boldsymbol{M}_{\mathrm{e}}^{(n)} |k\rangle\langle k| \boldsymbol{M}_{\mathrm{e}}^{(n_1)} |\mathrm{i}\rangle}{\omega_{k\mathrm{i}} \mp \omega_{\lambda_1} - \mathrm{i}\Gamma_{k\mathrm{i}}} + \frac{\langle \mathrm{f}| \boldsymbol{M}_{\mathrm{e}}^{(n_1)} |k\rangle\langle k| \boldsymbol{M}_{\mathrm{e}}^{(n)} |\mathrm{i}\rangle}{\omega_{k\mathrm{f}} \pm \omega_{\lambda_1} + \mathrm{i}\Gamma_{k\mathrm{f}}} \right\}. \tag{2.33}$$

Strictly, (2.33) is the tensor of 2^n-pole electric polarizability induced by 2^{n_1}-pole electric transitions.

Obviously, for $n=1$ and $n_1=1$ eqs. (2.32), (2.33) reduce to (2.25).

In a similar way, one can write the tensors ${}^{(n)}_{\mathrm{e}}\mathbf{A}_{\mathrm{mfi}}^{(n_1)}$ and ${}^{(n)}_{\mathrm{m}}\mathbf{A}_{\mathrm{efi}}^{(n_1)}$ defining the tensors of 2^n-pole electric polarizability induced by 2^{n_1}-pole magnetic transitions, and vice versa. Also, the magnetic multipole Hamiltonian (2.6) permits the calculation of the tensor ${}^{(n)}_{\mathrm{m}}\mathbf{A}_{\mathrm{mfi}}^{(n_1)}$ determining the 2^n-pole magnetic polarizabilities, induced in 2^{n_1}-pole magnetic transitions (see Kielich [1965a]).

By having recourse to the expressions (2.20) and (2.22), we obtain, for the second-order 2^n-pole moment, induced in multipole electric transitions (2.5) and magnetic transitions (2.6) (KIELICH [1965a, 1966b]),

$$
\begin{aligned}
{}_{\mathrm{e}}\boldsymbol{M}_{\mathrm{fi}}^{(n)}(t)^{(2)} = \frac{1}{8} \sum_{\lambda_1\lambda_2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} & [(2n_1-1)!!\,(2n_2-1)!!]^{-1} \\
& \times \{[{}^{(n)}_{\mathrm{e}}\boldsymbol{B}_{\mathrm{eefi}}^{(n_1+n_2)}(\omega_{\lambda_1}, \omega_{\lambda_2})\,[n_1+n_2]\,\boldsymbol{E}^{(n_1)}(\boldsymbol{R}, \omega_{\lambda_1})\,\boldsymbol{E}^{(n_2)}(\boldsymbol{R}, \omega_{\lambda_2}) \\
& + {}^{(n)}_{\mathrm{e}}\boldsymbol{B}_{\mathrm{emfi}}^{(n_1+n_2)}(\omega_{\lambda_1}, \omega_{\lambda_2})\,[n_1+n_2]\,\boldsymbol{E}^{(n_1)}(\boldsymbol{R}, \omega_{\lambda_1})\,\boldsymbol{H}^{(n_2)}(\boldsymbol{R}, \omega_{\lambda_2}) \\
& + {}^{(n)}_{\mathrm{e}}\boldsymbol{B}_{\mathrm{mefi}}^{(n_1+n_2)}(\omega_{\lambda_1}, \omega_{\lambda_2})\,[n_1+n_2]\,\boldsymbol{H}^{(n_1)}(\boldsymbol{R}, \omega_{\lambda_1})\,\boldsymbol{E}^{(n_2)}(\boldsymbol{R}, \omega_{\lambda_2}) \\
& + {}^{(n)}_{\mathrm{e}}\boldsymbol{B}_{\mathrm{mmfi}}^{(n_1+n_2)}(\omega_{\lambda_1}, \omega_{\lambda_2})\,[n_1+n_2]\,\boldsymbol{H}^{(n_1)}(\boldsymbol{R}, \omega_{\lambda_1})\,\boldsymbol{H}^{(n_2)}(\boldsymbol{R}, \omega_{\lambda_2})] \\
& \times \exp[-\mathrm{i}(\omega_{\lambda_1}+\omega_{\lambda_2})t] + \cdots\} \exp[\mathrm{i}(\omega_{\mathrm{fi}}+\mathrm{i}\Gamma_{\mathrm{fi}}^{+})t],
\end{aligned}
\tag{2.34}
$$

where, as an example, we write out the quantum-mechanical form of the $(n+n_1+n_2)$-rank pseudo-tensor:

$$
\begin{aligned}
{}^{(n)}_{\mathrm{e}}\boldsymbol{B}_{\mathrm{emfi}}^{(n_1+n_2)}(\omega_{\lambda_1}, \omega_{\lambda_2}) = \hbar^{-2} S(n_1\omega_{\lambda_1}, n_2\omega_{\lambda_2}) & \\
\times \sum_{kl} \Bigg\{ & \frac{\langle \mathrm{f}|\,\boldsymbol{M}_{\mathrm{e}}^{(n)}\,|l\rangle \langle l|\,\boldsymbol{M}_{\mathrm{e}}^{(n_1)}\,|k\rangle \langle k|\,\boldsymbol{M}_{\mathrm{m}}^{(n_2)}\,|\mathrm{i}\rangle}{(\omega_{l\mathrm{i}}-\omega_{\lambda_1}-\omega_{\lambda_2}-\mathrm{i}\Gamma_{l\mathrm{i}})(\omega_{k\mathrm{i}}-\omega_{\lambda_2}-\mathrm{i}\Gamma_{k\mathrm{i}})} \\
& + \frac{\langle \mathrm{f}|\,\boldsymbol{M}_{\mathrm{e}}^{(n_1)}\,|k\rangle \langle k|\,\boldsymbol{M}_{\mathrm{e}}^{(n)}\,|l\rangle \langle l|\,\boldsymbol{M}_{\mathrm{m}}^{(n_2)}\,|\mathrm{i}\rangle}{(\omega_{k\mathrm{f}}+\omega_{\lambda_1}+\mathrm{i}\Gamma_{k\mathrm{f}})(\omega_{l\mathrm{i}}-\omega_{\lambda_2}-\mathrm{i}\Gamma_{l\mathrm{i}})} \\
& + \frac{\langle \mathrm{f}|\,\boldsymbol{M}_{\mathrm{m}}^{(n_2)}\,|l\rangle \langle l|\,\boldsymbol{M}_{\mathrm{e}}^{(n_1)}\,|k\rangle \langle k|\,\boldsymbol{M}_{\mathrm{e}}^{(n)}\,|\mathrm{i}\rangle}{(\omega_{l\mathrm{f}}+\omega_{\lambda_2}+\mathrm{i}\Gamma_{l\mathrm{f}})(\omega_{k\mathrm{f}}+\omega_{\lambda_2}+\omega_{\lambda_1}+\mathrm{i}\Gamma_{k\mathrm{f}})} \Bigg\}
\end{aligned}
\tag{2.35}
$$

determining the 2^n-pole electric second-order nonlinear polarizability, induced by 2^{n_1}-pole electric and 2^{n_2}-pole magnetic transitions. Clearly, by the interchange of $\boldsymbol{M}_{\mathrm{m}}^{(n_2)}$ and $\boldsymbol{M}_{\mathrm{e}}^{(n_2)}$ in eq. (2.35) one arrives at the quantum-mechanical expression for the tensor ${}^{(n)}_{\mathrm{e}}\boldsymbol{B}_{\mathrm{eefi}}^{(n_1+n_2)}(\omega_{\lambda_1}, \omega_{\lambda_2})$. Similar interchanges lead to the other tensors of the expansions (2.34). It is worth noting in particular that the second-order electric dipole transition moment (2.26) results from (2.34) for $n = n_1 = n_2 = 1$. Likewise, eqs. (2.34) and (2.35) lead to the quadrupole and higher electric and electromagnetic transition moments.

We have seen how expressions are derived for third-order and higher-order electric or magnetic multipole moments. However, in the calculations, one has to keep in mind the fact that, from the second-order approximation upwards, Hamiltonians of the second order and, in the relativistic case, Hamiltonians of higher orders, should be taken when calculating the vectors of state (2.27) (see KIELICH [1965a, 1966a]). In some cases, the contributions from the second-order Hamiltonian (2.10) are highly essential, e.g. in nonlinear optical activity, as well as in the nonlinear Faraday effect of diamagnetic gases (KIELICH, MANAKOV and OVSIANNIKOV [1978], and MANAKOV, OVSIANNIKOV and KIELICH [1980]).

In particular, we get for the second-order electric dipole moment induced by a direct magnetic transition (2.10):

$$D^{\mathrm{e}}_{\sigma\mathrm{fi}}(t)^{(2)} = \frac{1}{8}\sum_{\lambda\mu}\{b^{\mathrm{emfi}}_{\sigma:\tau\nu}(\omega_\mu, \omega_\lambda)\, H_\tau(\omega_\mu)\, H_\nu(\omega_\lambda) \times \exp[-\mathrm{i}(\omega_\mu + \omega_\lambda)t] + \cdots\} \exp[\mathrm{i}(\omega_{\mathrm{fi}} + \mathrm{i}\overset{+}{\Gamma}_{\mathrm{fi}})t], \tag{2.36}$$

where we have introduced the third-rank pseudo-tensor (KIELICH [1965a])

$$b^{\mathrm{emfi}}_{\sigma:\tau\nu}(\omega_\mu, \omega_\lambda) = \frac{1}{\hbar}\sum_k \left\{\frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_\sigma\, |k\rangle\langle k|\, \chi^{\mathrm{m}}_{\tau\nu}\, |\mathrm{i}\rangle}{\omega_{k\mathrm{i}} - \omega_\mu - \omega_\lambda - \mathrm{i}\Gamma_{k\mathrm{i}}} + \frac{\langle \mathrm{f}|\, \chi^{\mathrm{m}}_{\nu\tau}\, |k\rangle\langle k|\, D^{\mathrm{e}}_\sigma\, |\mathrm{i}\rangle}{\omega_{k\mathrm{f}} + \omega_\mu + \omega_\lambda + \mathrm{i}\Gamma_{k\mathrm{f}}}\right\}, \tag{2.37}$$

determining the second-order nonlinear electric polarizability induced by a magnetic transition, due to the square of the magnetic field strength H^2 (quadratic transition).

The third-order electric dipole moment, induced by a simultaneous electric dipole transition (2.5a) and magnetic transition (2.10), has the form

$$D^{\mathrm{e}}_{\sigma\mathrm{fi}}(t)^{(1,2)} = \frac{1}{16}\sum_{\lambda\mu\varepsilon}\{c^{\mathrm{eemfi}}_{\sigma\tau:\nu\rho}(\omega_\varepsilon, \omega_\mu, \omega_\lambda)\, E_\tau(\omega_\varepsilon)\, H_\nu(\omega_\mu)\, H_\rho(\omega_\lambda) \times \exp[-\mathrm{i}(\omega_\varepsilon + \omega_\mu + \omega_\lambda)t] + \cdots\} \exp[\mathrm{i}(\omega_{\mathrm{fi}} + \mathrm{i}\overset{+}{\Gamma}_{\mathrm{fi}})t], \tag{2.38}$$

where the fourth-rank tensor

$$\begin{aligned} c^{\mathrm{eemfi}}_{\sigma\tau:\nu\rho}(\omega_\varepsilon, \omega_\mu, \omega_\lambda) &= \hbar^{-2} S_2 \\ &\times \sum_{kl}\left\{\frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_\sigma\, |l\rangle\langle l|\, D^{\mathrm{e}}_\tau\, |k\rangle\langle k|\, \chi^{\mathrm{m}}_{\nu\rho}\, |\mathrm{i}\rangle}{(\omega_{l\mathrm{i}} - \omega_\varepsilon - \omega_\mu - \omega_\lambda - \mathrm{i}\Gamma_{l\mathrm{i}})\,(\omega_{k\mathrm{i}} - \omega_\mu - \omega_\lambda - \mathrm{i}\Gamma_{k\mathrm{i}})}\right. \\ &+ \frac{\langle \mathrm{f}|\, D^{\mathrm{e}}_\tau\, |k\rangle\langle k|\, D^{\mathrm{e}}_\sigma\, |l\rangle\langle l|\, \chi^{\mathrm{m}}_{\nu\rho}\, |\mathrm{i}\rangle}{(\omega_{k\mathrm{f}} + \omega_\varepsilon + \mathrm{i}\Gamma_{k\mathrm{f}})\,(\omega_{l\mathrm{i}} - \omega_\mu - \omega_\lambda - \mathrm{i}\Gamma_{l\mathrm{i}})} \\ &+ \left.\frac{\langle \mathrm{f}|\, \chi^{\mathrm{m}}_{\rho\nu}\, |l\rangle\langle l|\, D^{\mathrm{e}}_\tau\, |k\rangle\langle k|\, D^{\mathrm{e}}_\sigma\, |\mathrm{i}\rangle}{(\omega_{l\mathrm{f}} + \omega_\lambda + \omega_\mu + \mathrm{i}\Gamma_{l\mathrm{f}})(\omega_{k\mathrm{f}} + \omega_\varepsilon + \omega_\mu + \omega_\lambda + \mathrm{i}\Gamma_{k\mathrm{f}})}\right\} \end{aligned} \tag{2.39}$$

determines the third-order nonlinear electric polarizability, induced by electric dipole and magnetic quadratic transitions (2.10).

§ 3. Incoherent and Nonresonant Multi-Photon Scattering by Free Molecules

3.1. THE ELECTRIC AND MAGNETIC FIELDS OF THE SCATTERED WAVE

We consider the molecular system defined in Fig. 2.1. Since we are concerned with the field in the wave zone, i.e. at distances from the radiating molecular system considerably exceeding the light wavelength ($R \gg \lambda$), we can write (see HEITLER [1954]), at the space-time point ($\boldsymbol{R}$, t):

$$\boldsymbol{E}_S(\boldsymbol{R}, t) = (1/R^3c^2)\{\boldsymbol{R}\times[\boldsymbol{R}\times\ddot{\boldsymbol{Z}}(t')\}, \tag{3.1}$$

$$\boldsymbol{H}_S(\boldsymbol{R}, t) = -(1/R^2c^2)\{\boldsymbol{R}\times\ddot{\boldsymbol{Z}}(t')\}, \tag{3.2}$$

where

$$\boldsymbol{Z}(t') = \sum_j e_j\, \boldsymbol{r}_j(t'_j) \tag{3.3}$$

is the Hertz vector at the retarded moment of time

$$t'_j = t - (R_j/c) = t - c^{-1}\,|\boldsymbol{R}+\boldsymbol{r}_j|, \tag{3.4}$$

since $\boldsymbol{R}_j = \boldsymbol{R}+\boldsymbol{r}_j$ (Fig. 2.1).

On expanding the vector (3.3) in a series in powers of $\boldsymbol{r}_j$, and taking into consideration (3.4), we obtain (KIELICH [1965a]):

$$\boldsymbol{Z}(t') = \boldsymbol{Z}_e(t-R/c) + \boldsymbol{Z}_m(t-R/c), \tag{3.5}$$

where the first term of the Hertz vector,

$$\boldsymbol{Z}_e(t-R/c) = \sum_{n=1}^{\infty} [(2n-1)!!\,(Rc)^{n-1}]^{-1}\, \boldsymbol{R}^{n-1}[n-1](\partial^{n-1}/\partial t^{n-1})\, \boldsymbol{M}_e^{(n)}(t-R/c) \tag{3.5a}$$

describes electric multipole radiation and the second,

$$\boldsymbol{Z}_m(t-R/c) = -\sum_{n=1}^{\infty} [(2n-1)!!\,R^n c^{n-1}]^{-1}\, \boldsymbol{R}^{n-1}[n-1] \times\{\boldsymbol{R}\times(\partial^{n-1}/\partial t^{n-1})\}\, \boldsymbol{M}_m^{(n)}(t-R/c) \tag{3.5b}$$

describe magnetic multipole radiation (see eqs. (2.7) and (2.8)).

By the definition of the Poyntings vector of electromagnetic radiation:

$$\boldsymbol{S}(\boldsymbol{R}, t) = (c/4\pi)\,\boldsymbol{E}_S(\boldsymbol{R}, t)\times\boldsymbol{H}_S(\boldsymbol{R}, t)$$

and with regard to eqs. (3.1) and (3.2), we obtain for the mean value:

$$\langle\boldsymbol{S}(\boldsymbol{R}, t)\rangle = (c/4\pi R^5)\,(R^2\delta_{\sigma\tau} - R_\sigma R_\tau)I^S_{\sigma\tau}\boldsymbol{R}. \tag{3.6}$$

Above, we have introduced the intensity tensor of light scattered by the molecular system:

$$I^{S}_{\sigma\tau} = (N/2c^4)\langle \ddot{Z}_\sigma(t-R/c)^* \, \ddot{Z}_\tau(t-R/c)\rangle_{\Omega,E}, \tag{3.7}$$

where the symbol $\langle\ \rangle_{\Omega,E}$ denotes appropriate averaging over the orientations Ω of the molecules and averaging over the states of the incident field of light $\boldsymbol{E}$, whereas N is the number of molecules, reorienting freely in the scattering volume. The geometry of scattered light observation is shown in Fig. 1.3.

3.2. HARMONIC ELECTRIC-DIPOLE ELASTIC SCATTERING PROCESSES

We shall first consider the electric-dipole approximation, on the assumption of monochromatic incident light sufficiently intense to cause nonlinear polarization of the molecule. Taking into account purely harmonic terms, with frequencies ω, 2ω, $3\omega, \ldots$, we obtain

$$Z_\sigma(t-R/c) = \sum_{n=1}^{\infty} D_\sigma(n\omega)\cos[n\omega(t-R/c)], \tag{3.8}$$

where the amplitude of the nth harmonic of the electric dipole moment induced in the molecule is

$$D_\sigma(n\omega) = (2^{n-1}n!)^{-1}\, a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n} E_{\sigma_1}(\omega)\cdots E_{\sigma_n}(\omega). \tag{3.9}$$

The $(n+1)$th rank tensor $a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n}$ defining the nth order nonlinear polarizability can be dealt with as completely symmetric in the nonresonant case.

On the insertion of (3.8) into (3.7) we have:

$$I^{S}_{\sigma\tau} = \sum_{n=1}^{\infty} I^{n\omega}_{\sigma\tau} = I^{\omega}_{\sigma\tau} + I^{2\omega}_{\sigma\tau} + I^{3\omega}_{\sigma\tau} + \cdots, \tag{3.10}$$

where

$$I^{n\omega}_{\sigma\tau} = 2^{-1}(n\omega/c)^4 N\langle D^*_\sigma(n\omega)\, D_\tau(n\omega)\rangle_{\Omega,E} \tag{3.11}$$

is the intensity tensor of the light scattered at the nth harmonic frequency; with regard to eq. (3.9), it has the following, explicit form:

$$\begin{aligned} I^{n\omega}_{\sigma\tau} &= N[2^{2n-1}(n!)^2]^{-1}\,(n\omega/c)^4 \\ &\quad \times\langle a^{-n\omega}_{\sigma\sigma_1\cdots\sigma_n} a^{n\omega}_{\tau\tau_1\cdots\tau_n} E^*_{\sigma_1}(\omega)\cdots E^*_{\sigma_n}(\omega)\, E_{\tau_1}(\omega)\cdots E_{\tau_n}(\omega)\rangle_{\Omega,E}. \end{aligned} \tag{3.12}$$

The averaging of the Cartesian tensor products of (3.12) is readily performed for $n=1,2,3$ (KIELICH [1961], and ANDREWS and THIRUNAMACHANDRAN [1977a]), but is in general a highly complex affair if $n \geqslant 4$. However, (3.12) is easy to calculate for arbitrary n if the incident beam is assumed to be linearly polarized, since in this case one obtains (KIELICH [1967a, 1968b], see also Appendix B):

$$I_{\sigma\tau}^{n\omega} = (n\omega/c)^4\,(\delta_{\sigma\tau}F_{n\omega} + e_\sigma e_\tau G_{n\omega})I^n g^{(n)} \tag{3.13}$$

with: $I = \langle |E|^2 \rangle/2$ the intensity of incident linearly polarized light, and $\boldsymbol{e}$ the unit vector in the direction of the field $\boldsymbol{E}$.

Equation (3.13) involves two molecular parameters of elastic n-harmonic scattering (KIELICH and KOZIEROWSKI [1972]):

$$F_{n\omega} = N a_{\alpha\alpha_1\cdots\alpha_n}^{-n\omega}\, a_{\beta\beta_1\cdots\beta_n}^{n\omega}\, f_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n}, \tag{3.14a}$$

$$G_{n\omega} = N a_{\alpha\alpha_1\cdots\alpha_n}^{-n\omega}\, a_{\beta\beta_1\cdots\beta_n}^{n\omega}\, g_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n}, \tag{3.14b}$$

where the tensor operators: $f_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n}$ and $g_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n}$ are defined in Appendix B.

We have also introduced in eq. (3.13) the degree of nth order coherence of the incident linearly polarized beam

$$g^{(n)} = \langle |E(\omega)|^{2n} \rangle_E / \langle |E(\omega)|^2 \rangle_E^n, \tag{3.15}$$

leading to (MANDEL and WOLF [1965])

$$g^{(n)} = \begin{cases} 1 & \text{for coherent light,} \\ n! & \text{for chaotic light.} \end{cases} \tag{3.15a}$$

The molecular parameters (3.14) are valid for all symmetries of the tensor $a_{\alpha\alpha_1\cdots\alpha_n}^{n\omega}$. In the case of completely symmetric nonlinear polarizability tensors, the final results simplify considerably, and can be expressed in terms of the least number of irreducible invariants for the rank $n+1$ under consideration.

(i) Rayleigh scattering. In particular, for linear Rayleigh scattering ($n=1$) we have:

$$F_\omega = (N/10)\,|a_\omega^{(2)}|^2, \qquad G_\omega = (N/3)[|a_\omega^{(0)}|^2 + (1/10)\,|a_\omega^{(2)}|^2] \tag{3.16}$$

involving the parameters of isotropic and anisotropic scattering

$$|a_\omega^{(0)}|^2 = a_{\alpha\alpha}^{-\omega} a_{\beta\beta}^{\omega}/3, \qquad |a_\omega^{(2)}|^2 = (3a_{\alpha\beta}^{-\omega} a_{\alpha\beta}^{\omega} - a_{\alpha\alpha}^{-\omega} a_{\beta\beta}^{\omega})/3. \tag{3.17}$$

(ii) Second-harmonic Rayleigh scattering. Similarly, on applying eq. (3.14) to second-harmonic scattering ($n = 2$) we have, for a completely symmetric tensor of second-order nonlinear polarizability $a^{2\omega}_{\alpha\beta\gamma} = b^{2\omega}_{\alpha\beta\gamma}$

$$F_{2\omega} = (N/2520)(7\,|b^{(1)}_{2\omega}|^2 + 12\,|b^{(3)}_{2\omega}|^2), \tag{3.18a}$$

$$G_{2\omega} = (N/1260)(28\,|b^{(1)}_{2\omega}|^2 + 3\,|b^{(3)}_{2\omega}|^2), \tag{3.18b}$$

with the two irreducible molecular parameters (Kielich and Ożgo [1973])

$$|b^{(1)}_{2\omega}|^2 = (3/5) b^{-2\omega}_{\alpha\beta\beta} b^{2\omega}_{\alpha\gamma\gamma}, \tag{3.19a}$$

$$|b^{(3)}_{2\omega}|^2 = (1/5)(5 b^{-2\omega}_{\alpha\beta\gamma} b^{2\omega}_{\alpha\beta\gamma} - 3 b^{-2\omega}_{\alpha\beta\beta} b^{2\omega}_{\alpha\gamma\gamma}). \tag{3.19b}$$

(iii) Third-harmonic Rayleigh scattering. We shall still consider third-harmonic elastic scattering ($n = 3$). Here, for a completely symmetric tensor of third-order nonlinear polarizability $a^{3\omega}_{\alpha\beta\gamma\delta} = c^{3\omega}_{\alpha\beta\gamma\delta}$, we obtain (Kozierowski [1970])

$$F_{3\omega} = (N/181444)(27\,|c^{(2)}_{3\omega}|^2 + 20\,|c^{(4)}_{3\omega}|^2), \tag{3.20a}$$

$$G_{3\omega} = (N/60480)(84\,|c^{(0)}_{3\omega}|^2 + 39\,|c^{(2)}_{3\omega}|^2 + 4\,|c^{(4)}_{3\omega}|^2), \tag{3.20b}$$

where the following three irreducible molecular parameters, introduced by Ożgo [1975a], intervene:

$$|c^{(0)}_{3\omega}|^2 = (1/5) c^{-3\omega}_{\alpha\alpha\beta\beta} c^{3\omega}_{\gamma\gamma\delta\delta}, \tag{3.21a}$$

$$|c^{(2)}_{3\omega}|^2 = (2/7)(3 c^{-3\omega}_{\alpha\beta\gamma\gamma} c^{3\omega}_{\alpha\beta\delta\delta} - c^{-3\omega}_{\alpha\alpha\beta\beta} c^{3\omega}_{\gamma\gamma\delta\delta}), \tag{3.21b}$$

$$|c^{(4)}_{3\omega}|^2 = (1/35)(35 c^{-3\omega}_{\alpha\beta\gamma\delta} c^{3\omega}_{\alpha\beta\gamma\delta} - 30 c^{-3\omega}_{\alpha\beta\gamma\gamma} c^{3\omega}_{\alpha\beta\delta\delta} + 3 c^{-3\omega}_{\alpha\alpha\beta\beta} c^{3\omega}_{\gamma\gamma\delta\delta}). \tag{3.21c}$$

The irreducible molecular parameters (3.17), (3.19) and (3.21) are, in practice, immediately applicable to various symmetries of the molecule, since tables giving the nonzero and mutually independent components of the tensors $a_{\alpha\beta}$, $b_{\alpha\beta\gamma}$ and $c_{\alpha\beta\gamma\delta}$ for all point groups are available (see, for example, Kielich [1972a, b, 1980a]). The parameters react individually to the presence of various elements of symmetry in the molecule. If, for example, the latter, when in its ground state, possesses a centre of symmetry, the parameters (3.19) vanish, meaning that no second-harmonic scattering can take place in the electric-dipole approximation considered. Centrosymmetric molecules can give rise to second-harmonic scattering only if we go over to the electric-quadrupole approximation (see Kielich, Kozierowski, Ożgo and Zawodny [1974]).

3.3. MULTI-PHOTON VIBRATIONAL RAMAN SCATTERING (CLASSICAL APPROACH)

We shall now consider scattering processes due to the vibrations of molecular nuclei in the classical treatment of PLACZEK's [1934] polarizability theory, which can be extended rather easily to second- and third-harmonic Raman scattering (KIELICH [1964b], STRIZHEVSKY and KLIMENKO [1967], and LONG and STANTON [1970]). According to Placzek, the polarizability of a molecule is not constant, but varies with time, for example as a result of the vibrations of its nuclei. Let $Q_m(t)$, with $m = 1, 2, \ldots, 3N-6$, denote the normal coordinates of the displacements of the nuclei with respect to their equilibrium position. Then, for harmonic vibrations with the frequency ω_m and phase shift φ_m, we have:

$$Q_m(t) = Q_m(0) \exp\left[\mathrm{i}(\omega_m t + \varphi_m)\right], \tag{3.22}$$

where $Q_m(0)$ is the amplitude of the mth normal vibrational mode. In the expansion (3.9) the nonlinear polarizability tensors are now functions of the normal coordinates $a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n}(Q)$, of an (in general) unknown analytical form. For small vibration amplitudes, however, one can write the following expansion:

$$a^{n\omega}_{\sigma\sigma_1\cdots\tau_n}(Q) = a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n}(0) + \sum_m a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n:m} Q_m + \ldots, \tag{3.23}$$

where we have used the notation

$$a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n:m} \equiv (\partial a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n}/\partial Q_m)_{Q=0}.$$

Hence, by eqs. (3.7)–(3.9) and (3.22), (3.23), we have for n-harmonic Raman scattering:

$$\begin{aligned} I^{n\omega\mp\omega_m}_{\sigma\tau} &= N[2^{2n-1}(n!)^2]^{-1}\left[(n\omega\mp\omega_m)/c\right]^4 \\ &\quad \times \langle a^{-n\omega}_{\sigma\sigma_1\cdots\sigma_n:m}\, a^{n\omega}_{\tau\tau_1\cdots\tau_n:m}\, |Q_m|^2\rangle_\Omega \\ &\quad \times \langle E^*_{\sigma_1}(\omega)\cdots E^*_{\sigma_n}(\omega)\, E_{\tau_1}(\omega)\cdots E_{\tau_n}(\omega)\rangle_E. \end{aligned} \tag{3.24}$$

Above, $a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n:m}$ is the first derivative of the nonlinear polarizability tensor with respect to the normal coordinate Q_m.

Concerning the calculation of the tensor (3.24), we proceed as follows: we average over the orientations of the molecule Ω in the representation of spherical tensors, leaving the average over the fields in Cartesian basis. Transforming from laboratory Cartesian coordinates to the spherical basis we write;

$$a^{n\omega}_{\sigma\sigma_1\cdots\sigma_n:m} = \sum_{JKL} R^{JKL}_{\sigma\sigma_1\cdots\sigma_n}\, a^{(J)L}_{K:m}(n\omega), \tag{3.25}$$

where the $R^{JKL}_{\sigma\sigma_1\cdots\sigma_n}$ are transformation coefficients between the two representations. $a^{(J)L}_{K:m}(n\omega)$ is the Kth component of the irreducible tensor of Jth order, with components transforming from the laboratory to the molecular system of coordinates in accordance with the relation:

$$a^{(J)L}_{K:m} = \sum_{M=-J}^{+J} D^J_{KM}(\Omega)\, \tilde{a}^{(J)L}_{M:m} \tag{3.26}$$

the $D^J_{KM}(\Omega)$ denoting elements of the unitary Wigner rotation matrix possessing the property:

$$\langle D^J_{KM}(\Omega)^*\, D^{J'}_{K'M'}(\Omega)\rangle_\Omega = (2J+1)^{-1}\, \delta_{JJ'}\delta_{KK'}\delta_{MM'}. \tag{3.27}$$

With regard to the expressions (3.24)–(3.27) we finally obtain

$$\begin{aligned} I^{n\omega\mp\omega_m}_{\sigma\tau} &= [2^{n-1}(n!)^2]^{-1}\, [(n\omega\mp\omega_m)/c]^4\, N\, |Q_m|^2\, I^n g^{(n)} \\ &\times \sum_{JKLM} (2J+1)^{-1}\, |\tilde{a}^{(J)L}_{M:m}(n\omega)|^2\, \Phi^{JKL}_{\sigma\tau}, \end{aligned} \tag{3.28}$$

where we have introduced the following tensor:

$$\Phi^{JKL}_{\sigma\tau} = R^{*JKL}_{\sigma\sigma_1\cdots\sigma_n} R^{JKL}_{\tau\tau_1\cdots\tau_n} \langle e^*_{\sigma_1}\cdots e^*_{\sigma_n}\, e_{\tau_1}\cdots e_{\tau_n}\rangle \tag{3.29}$$

accounting for arbitrary polarization states of the incident and scattered light, and arbitrary geometries of observation.

The coefficients $R^{JKL}_{\sigma\sigma_1\cdots\sigma_n}$ of the rotational transformation have been tabulated by MAKER [1970] for $n=2$ and by OŻGO [1975a] and STONE [1975] for $n=3$.

Like eq. (3.13), the tensor of n-harmonic vibrational Raman scattering (3.28) is applicable to first-, second-, third- and higher-harmonic light scattering processes. However, eq. (3.28) is more general than (3.13) in that, thanks to the tensor (3.29), it is valid for arbitrary polarization states of the fields.

3.4. ROTATIONAL, VIBRATIONAL AND ROTATIONAL-VIBRATIONAL MULTI-PHOTON SCATTERING PROCESSES (SEMI-CLASSICAL APPROACH)

When proceeding to the quantal (or rather semi-classical) treatment of multi-harmonic scattering, we wish to draw attention to the following three aspects relating to the tensor (3.7). First, we have to deal with the matrix element Z_σ^{fi} of the transition from the initial quantum state $|\mathrm{i}\rangle$ to the final state $\langle\mathrm{f}|$. Second, in place of N we now have N_i, the number of freely orienting molecules in the initial state $|\mathrm{i}\rangle$, since only these molecules take part in scattering, accompanied by a change in quantum state from $|\mathrm{i}\rangle$ to $\langle\mathrm{f}|$. And third, averaging over the molecular orientations Ω has to be performed in a different way, since the rotational motion of the molecule is quantized so that it can only be in rotational states such that the projection of its angular momentum $\boldsymbol{J}$ onto the z-axis, shall be equal to M, with $-J \leqslant M \leqslant J$. Thus, instead of unweighted integration $\langle\ \rangle_\Omega$ over all possible values of the Euler angles, we now have to carry out a summation over all the permitted quantum numbers M_i and M_f of the initial and final states of the molecule. We denote this average by the symbol $\langle(\cdot\cdot\cdot)\rangle_M \equiv (2J+1)^{-1}\sum_{M_\mathrm{i}M_\mathrm{f}}(\cdot\cdot\cdot)$ since, with regard to spatial degeneracy, each of the rotational levels is $(2J+1)$-fold degenerate.

With the above in mind, we have in place of (3.7) the following intensity tensor of light, scattered in the quantum transition $\langle\mathrm{f}| \leftarrow |\mathrm{i}\rangle$:

$$I_{\sigma\tau}^{\mathrm{fi}} = (N_\mathrm{i}/2c^4)\,\langle \ddot{Z}_\sigma^{\mathrm{fi}}(t-R/c)^*\, \ddot{Z}_\tau^{\mathrm{fi}}(t-R/c)\rangle_{M,E}. \tag{3.30}$$

In the case of inelastic multi-harmonic electric-dipole scattering (3.8) we have an expansion of the type (3.10) where, now, the transition tensor for the nth scattered harmonic is:

$$\begin{aligned} I_{\sigma\tau}^{\mathrm{fi}}(n\omega) = {} & N_\mathrm{i}[2^{n-1}(n!)^2]^{-1}\,[(n\omega \mp \omega_{\mathrm{if}})/c]^4 I^n \\ & \times \langle a_{\sigma\sigma_1\cdots\sigma_n}^{\mathrm{fi}}(n\omega)^*\, a_{\tau\tau_1\cdots\tau_n}^{\mathrm{fi}}(n\omega)\rangle_M\, g_{\sigma_1\cdots\sigma_n\tau_1\cdots\tau_n}^{(n)}. \end{aligned} \tag{3.31}$$

In (3.31), we have introduced the tensor of the nth order degree of coherence of the incident beam:

$$g_{\sigma_1\cdots\sigma_n\tau_1\cdots\tau_n}^{(n)} = \langle E_{\sigma_1}^*(\omega)\cdots E_{\sigma_n}^*(\omega)\, E_{\tau_1}(\omega)\cdots E_{\tau_n}(\omega)\rangle_\mathrm{E}\langle|E(\omega)|^2\rangle_\mathrm{E}^{-n}. \tag{3.32}$$

In further discussions, for the sake of clarity, we shall apply certain simplifying assumptions which, by the way, have already been used by PLACZEK [1934] in his treatment of usual Raman scattering.

(i) In our description of the wave function ψ_i of the molecule in the state $|\mathrm{i}\rangle$, we apply the adiabatic Born–Oppenheimer approximation, permitting the factorization

$$\psi_\mathrm{i} = \psi_{\mathrm{E}^\mathrm{i}}(r, q)\,\psi_{\mathrm{V}^\mathrm{i}}(Q)\,\psi_{\mathrm{R}^\mathrm{i}}(\Omega)\,\psi_{I^\mathrm{i}}(\sigma), \tag{3.33}$$

with: $\psi_{\mathrm{E}^\mathrm{i}}(r, q)$ the electron wave function, dependent on the coordinates r

of the electrons and q of the nuclei; $\psi_{V^{\mathrm{i}}}(Q)$ the vibrational wave function, dependent on the normal coordinates Q of the vibrations and the vibrational quantum number V^{i}; $\psi_{R^{\mathrm{i}}}(\Omega)$ the rotational wave function, dependent on the Euler angles Ω and the set of rotational quantum numbers $R^{\mathrm{i}}=(J^{\mathrm{i}}, \tau^{\mathrm{i}}, M^{\mathrm{i}})$; and $\psi_{I^{\mathrm{i}}}(\sigma)$ the spin wave function, dependent on the spin coordinates σ and spin quantum numbers I^{i} of the nuclei.

(ii) The vibration frequency of the incident light wave is far remote from regions of resonance, and is so high that the vibrational and rotational transition frequencies can be omitted in the denominators of the transition polarizabilities (2.27) and (2.29).

(iii) In the act of scattering, the ground electron state g of the molecule remains unchanged; moreover, the state g is non-degenerate.

On these assumptions, we are able to perform the summation over all the intermediate vibrational states V and rotational states R in the expressions (2.27) and (2.29) for the hyperpolarizability tensors; i.e., going over to the spherical basis, (3.25)–(3.26), we may write

$$a^{\mathrm{fi}}_{\sigma\sigma_1\cdots\sigma_n}(n\omega)=\sum_{JKLM} R^{JKL}_{\sigma\sigma_1\cdots\sigma_n} \times\langle R^{\mathrm{f}}|\, D^{J}_{KM}(\Omega)\,|R^{\mathrm{i}}\rangle\langle V^{\mathrm{f}}|\,\tilde{a}^{(J)L}_{M}(n\omega, Q)\,|V^{\mathrm{i}}\rangle. \quad (3.34)$$

Consider first the matrix element of vibrational transitions. In the harmonic oscillator approximation (3.23) it can be written, by analogy to linear Raman scattering (see LONG [1977]), in the form

$$\langle V^{\mathrm{f}}|\,\tilde{a}^{(J)L}_{M}(n\omega, Q)\,|V^{\mathrm{i}}\rangle=\tilde{a}^{(J)L}_{M}(n\omega)\langle V^{\mathrm{f}}\mid V^{\mathrm{i}}\rangle +\sum_{m}\tilde{a}^{(J)L}_{M:m}(n\omega)\langle V^{\mathrm{f}}_{m}|\,Q_m\,|V^{\mathrm{i}}_{m}\rangle+\cdots \quad (3.34a)$$

In the latter approximation, these matrix elements have the following properties (LONG [1977]) for Rayleigh lines:

$$\langle V^{\mathrm{f}}\mid V^{\mathrm{i}}\rangle=\begin{cases}0 & \text{for } V^{\mathrm{f}}\neq V^{\mathrm{i}},\\ 1 & \text{for } V^{\mathrm{f}}=V^{\mathrm{i}},\end{cases} \quad (3.34b)$$

and for Raman lines:

$$\langle V^{\mathrm{f}}|\,Q_m\,|V^{\mathrm{i}}_{m}\rangle=\begin{cases}0 & \text{for } V^{\mathrm{f}}_{m}=V^{\mathrm{i}}_{m},\\ (V^{\mathrm{i}}_{m}+1)^{1/2}(\hbar/2\omega_m)^{1/2} & \text{for } V^{\mathrm{f}}_{m}=V^{\mathrm{i}}_{m}+1,\\ (V^{\mathrm{i}}_{m})^{1/2}(\hbar/2\omega_m)^{1/2} & \text{for } V^{\mathrm{f}}_{m}=V^{\mathrm{i}}_{m}-1,\end{cases} \quad (3.34c)$$

since the selection rules for the vibrational quantum number are: $V^{\mathrm{f}}_m = V^{\mathrm{i}}_m + 1$ for Stokes lines $n\omega - \omega_m$ and $V^{\mathrm{f}}_m = V^{\mathrm{i}}_m - 1$ for anti-Stokes lines $n\omega + \omega_m$, with $m = 0, 1, 2 \ldots$.

We determine the vibrational and rotational wave functions of (3.34) by methods of quantum mechanics, applying the solutions of Schrödinger's equation for the Hamiltonian of the quantal system. The rotational quantum numbers $R = (J, \tau, M)$ correspond to the solutions for molecules of the freely rotating asymmetric top kind. Henceforth, we shall be considering symmetric top molecules, for which the quantum number $\tau = K$ describes the projection of the angular momentum onto its symmetry axis. In this case, the solution of the Schrödinger equation gives the following rotational wave function:

$$|\psi_{JKM}(\Omega)\rangle = \mathrm{i}^{J-K}\left(\frac{2J+1}{\Omega}\right)^{1/2} D^J_{KM}(\Omega) = \mathrm{i}^{J-K}\bar{D}^J_{KM}(\Omega). \tag{3.35}$$

Although these functions are of the same form for the spherical top and symmetric top, the respective eigenvalues of the Hamiltonian operator H_R are different. For the spherical top we have

$$E_J = \hbar^2 AJ(J+1), \tag{3.35a}$$

whereas for the symmetric top

$$E_{JK} = \hbar^2\{BJ(J+1) + (A-B)K^2\}, \tag{3.35b}$$

with A, B the rotational constants (Long [1977]).

The selection rules for the rotational and rotational-vibrational transitions in Raman scattering have been discussed by Placzek and Teller [1933], Altmann and Strey [1972], and Koningstein [1972], as well as by Chiu [1970], who moreover considered magnetic-dipole and electric-quadrupole transitions.

When calculating the intensities related to rotational transitions, one has to apply the formulae (Edmonds [1957])

$$\langle D^{J_1}_{K_1M_1} D^{J_2}_{K_2M_2} D^{J_3}_{K_3M_3}\rangle_\Omega = \begin{pmatrix} J_1 & J_2 & J_3 \\ K_1 & K_2 & K_3 \end{pmatrix}\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}, \tag{3.36}$$

where the $3J$ Wigner coefficients fulfill the orthogonality condition

$$\sum_{J_3K_3} (2J_3+1)\begin{pmatrix} J_1 & J_2 & J_3 \\ K_1 & K_2 & K_3 \end{pmatrix}\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & K_3 \end{pmatrix} = \delta_{K_1M_1}\,\delta_{K_2M_2}. \tag{3.36a}$$

Only those molecules act as scatterers for the transition $V^{\mathrm{f}}R^{\mathrm{f}} \leftarrow V^{\mathrm{i}}R^{\mathrm{i}}$

which are in the initial state given by the Boltzmann distribution

$$N_{V^i_m R^i} = N g(V^i_m R^i)\, g_I\, Z^{-1}_{VR} \exp\left(-E_{V^i_m R^i}/kT\right), \tag{3.37}$$

where $g(V^i_m R^i)$ is the degree of degeneracy of the initial level, g_I the nuclear statistical weight, and Z_{VR} the vibrational-rotational partition function. A discussion of (3.37) for particular cases is to be found in handbooks, for example by Koningstein [1972] and Long [1977].

3.4.1. *Three-photon Raman scattering*

We begin with three-photon Raman scattering. We have, by eq. (3.31),

$$I^{fi}_{\sigma\tau}(2\omega) = (N_i/8)[(2\omega \mp \omega_{fi})/c]^4 I^2 \langle b^{fi}_{\sigma\nu\rho}(2\omega)^* \, b^{fi}_{\tau\lambda\mu}(2\omega)\rangle_M g^{(2)}_{\nu\rho\lambda\mu}. \tag{3.38}$$

This tensor is readily averaged in the Cartesian basis. In the general case of a non-symmetric tensor $b^{fi}_{\sigma\nu\rho}(2\omega)$ one has to deal with five molecular parameters, of a rather complicated analytical form (see Kielich [1964b], Andrews and Thirunamachandran [1978], and Strey [1980]). We refrain from adducing them here, preferring to go over to a discussion of the case of completely symmetric $b^{fi}_{\sigma\nu\rho}(2\omega)$ in the treatment of spherical tensors proposed by Bancewicz, Ożgo and Kielich [1973a, 1975], and omitting the polarizational aspects and angular relationships discussed by Ożgo and Kielich [1974].

In order to simplify the discussion we assume the geometry shown in Fig. 3.1. On going over in eq. (3.38) to the spherical representation (3.25)

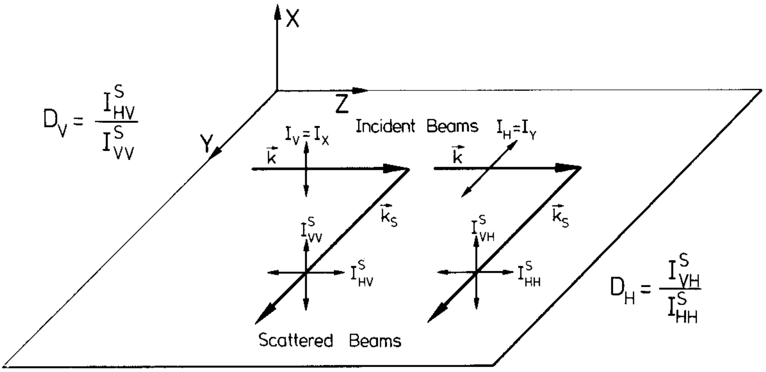

Fig. 3.1. Geometry for the determination of the vertical and horizontal intensity components of scattered light observed in the YZ-plane, for vertically polarized I_V and horizontally polarized I_H incident light.

we obtain, for the vertical scattered (polarized) component and horizontal (depolarized) component (if the incident light wave was polarized vertically) (Bancewicz, Ożgo and Kielich [1973b])

$$\begin{aligned} I^{\mathrm{fi}}_{\mathrm{VV}}(2\omega) &= (N_{\mathrm{V^iJ^iK^i}}/280)[(2\omega \mp \omega_{\mathrm{fi}})/c]^4 I^2_{\mathrm{V}} g^{(2)}_{\mathrm{V}} \\ &\quad \times (2J^{\mathrm{f}}+1)\left\{7\begin{pmatrix} J^{\mathrm{f}} & 1 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\langle V^{\mathrm{f}}|\, \tilde{b}^{(1)}_s(Q)\,|V^{\mathrm{i}}\rangle|^2 \right. \\ &\quad \left. +2\begin{pmatrix} J^{\mathrm{f}} & 3 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\langle V^{\mathrm{f}}|\, \tilde{b}^{(3)}_s(Q)\,|V^{\mathrm{i}}\rangle|^2 \right\}, \end{aligned} \tag{3.39a}$$

$$\begin{aligned} I^{\mathrm{fi}}_{\mathrm{HV}}(2\omega) &= (N_{\mathrm{V^iJ^iK^i}}/2520)[(2\omega \mp \omega_{\mathrm{fi}})/c]^4 I^2_{\mathrm{V}} g^{(2)}_{\mathrm{V}} \\ &\quad \times (2J^{\mathrm{f}}+1)\left\{7\begin{pmatrix} J^{\mathrm{f}} & 1 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\langle V^{\mathrm{f}}|\, \tilde{b}^{(1)}_s(Q)\,|V^{\mathrm{i}}\rangle|^2 \right. \\ &\quad \left. +12\begin{pmatrix} J^{\mathrm{f}} & 3 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\langle V^{\mathrm{f}}|\, \tilde{b}^{(3)}_s(Q)\,|V^{\mathrm{i}}\rangle|^2 \right\}. \end{aligned} \tag{3.39b}$$

These expressions are for purely rotational hyper-Raman lines if $Q=0$ and rotational-vibrational hyper-Raman lines if $Q \neq 0$. The properties of the $3j$ Wigner coefficients in eq. (3.39) impose the following selection rules on the rotational quantum numbers in hyper-Raman scattering: $\Delta J = J^{\mathrm{f}} - J^{\mathrm{i}} = 0, \pm 1, \pm 2, \pm 3$ and $\Delta K = 0, \pm 1, \pm 2, \pm 3$. For linear molecules (CO, NO), if $K^{\mathrm{i}} = K^{\mathrm{f}} = 0$, the only permitted transitions are those with $\Delta J = \pm 1, \pm 3$ (Bancewicz, Ożgo and Kielich [1973a, 1975]).

The symmetry of the molecule and the symmetry of the vibration decide which of the nonlinear molecular parameters $|\langle V^{\mathrm{f}}|\, b^{(J)}_{\mathrm{M}}(Q)\,|V^{\mathrm{i}}\rangle|^2$ of eq. (3.39) are nonzero for $J=1, 3$. Hence, moreover, we obtain the selection rules for the quantum number K, since the relation $\Delta K = M$ has to hold always.

It is noteworthy that in three-photon scattering no isotropic intensity component, related to a spherical tensor of order zero, occurs. A Q-branch appears only if the selection rules $\Delta J = 0$, $\Delta K = 0$ are permitted, in the part described by spherical tensors of the ranks 1 and 3. At two-photon (linear) scattering, the intensity of the line for the transition $J^{\mathrm{f}}K^{\mathrm{f}} \leftarrow J^{\mathrm{i}}K^{\mathrm{i}}$ depends (for any ΔJ and well-defined ΔK) only on the one molecular parameter $|\tilde{a}^{(2)}_{\mathrm{M}}|^2$ (see Koningstein [1972]). Whereas at three-photon scattering we have two parameters, $|\tilde{b}^{(1)}_{\mathrm{M}}|^2$ and $|b^{(3)}_{\mathrm{M}}|^2$, for the symmetric top; one $|\tilde{b}^{(3)}_3|^2$, for the symmetries $D_{3\mathrm{h}}$ and $C_{3\mathrm{h}}$; and one, $|\tilde{b}^{(3)}_2|^2$, for the symmetries $D_{2\mathrm{d}}, \mathrm{T}, \mathrm{T_d}$. The expressions for the molecular parameters $|\tilde{b}^{(J)}_{\mathrm{M}}|^2$ for all point group symmetries have been tabulated by

Bancewicz, Kielich and Ożgo [1975] and Alexiewicz, Bancewicz, Kielich and Ożgo [1974]. Stanton [1973] has given a complete discussion of the selection rules governing rotational hyper-Raman transitions.

(i) The rotational structure of the lines

Let us now introduce, with regard to eq. (3.39a), the parameter of purely rotational structure for the vertical component of the lines ($2\omega + \omega_{R^fR^i}$)

$$\begin{aligned} F_V(J^fK^f, J^iK^i) &= \exp(-E_{J^iK^i}/kT)(g_{I^i,K^i}/35Z_{R^i}) \\ &\times(2J^f+1)(2J^i+1)\left\{7\begin{pmatrix} J^f & 1 & J^i \\ -K^f & s & K^i \end{pmatrix}^2 |\tilde{b}_s^{(1)}|^2\right. \\ &\left.+2\begin{pmatrix} J^f & 3 & J^i \\ -K^f & \mathrm{s} & K^i \end{pmatrix}^2 |\tilde{b}_s^{(3)}|^2\right\}, \end{aligned} \tag{3.40}$$

where Z_{R^i} denotes the rotational sum of states and g_{I^i,K^i} the nuclear statistical weighting factor, whereas $E_{J^iK^i}$ is given by (3.35b).

We apply the rotational structure factor (3.40) to bi-atomic molecules (C_∞), when $K = 0$

$$\begin{aligned} F_V(J^f, J^i) &= (hB/35kT)\exp[-hBJ^i(J^i+1)/kT] \\ &\times(2J^f+1)(2J^i+1)\left\{7\begin{pmatrix} J^f & 1 & J^i \\ 0 & 0 & 0 \end{pmatrix}^2 |\tilde{b}_0^{(1)}|^2 + 2\begin{pmatrix} J^f & 3 & J^i \\ 0 & 0 & 0 \end{pmatrix}^2 |\tilde{b}_0^{(3)}|^2\right\}, \end{aligned} \tag{3.40a}$$

and molecules having the symmetry C_{3v}

$$\begin{aligned} F_V(J^fK^f, J^iK^i) &= [g_{I^i,K^i}/35(4I^{i2}+4I^i+1)] \\ &\times[AB^2h^3/\pi(kT)^3]^{1/2}\exp(-E_{J^iK^i}/kT)(2J^f+1) \\ &\times(2J^i+1)\left\{7\begin{pmatrix} J^f & 1 & J^i \\ -K^f & 0 & K^i \end{pmatrix}^2 |\tilde{b}_0^{(1)}|^2 + 2\begin{pmatrix} J^f & 3 & J^i \\ -K^f & 0 & K^i \end{pmatrix}^2\right. \\ &\times|\tilde{b}_0^{(3)}|^2 + 2\begin{pmatrix} J^f & 3 & J^i \\ -K^f & 3 & K^i \end{pmatrix}^2 |\tilde{b}_3^{(3)}|^2 \\ &\left.+2\begin{pmatrix} J^f & 3 & J^i \\ -K^f & -3 & K^i \end{pmatrix}^2 |\tilde{b}_{-3}^{(3)}|^2\right\}. \end{aligned} \tag{3.40b}$$

The spectral density distributions $S_V(\Delta\omega_R)$, calculated from eqs. (3.40a) and (3.40b) by Bancewicz, Kielich and Ożgo [1975], are plotted in Figs. 3.2 and 3.3. The purely rotational band distributions are strongly dependent on the value and sign of the hyperpolarizability tensor components

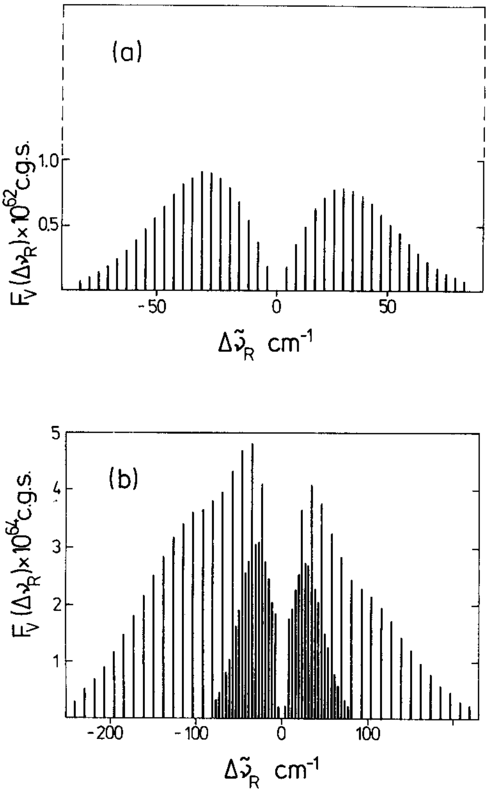

Fig. 3.2. Rotational structure of the spectrum calculated theoretically (Bancewicz, Kielich and Ożgo [1975]) for the molecule CO applying hyperpolarizability component values of (a) O'Hare and Hurst [1967], and (b) Hush and Williams [1972].

$b^{2\omega}_{\alpha\beta\gamma}$ for linear molecules. Herein we see an experimental method for checking the theoretically calculated quantum-mechanical values of the components $b^{2\omega}_{\alpha\beta\gamma}$. It should also be stressed that the cross sections $d\sigma(2\omega)$, calculated for CO and NH_3, are considerably in excess of those of CH_4, for which Maker [1966] performed observations of the rotational hyper-Rayleigh line structure (Fig. 3.4). The latter circumstance should be an encouragement to further experimental studies of the rotational structure of three-photon scattering processes in molecular gases.

(ii) Vibrational hyper-Rayleigh and hyper-Raman lines

With regard to eqs. (3.36a) and (3.37), we can carry out the summation in (3.39) over all the permitted rotational transitions $J^fK^f \leftarrow J^iK^i$, thus

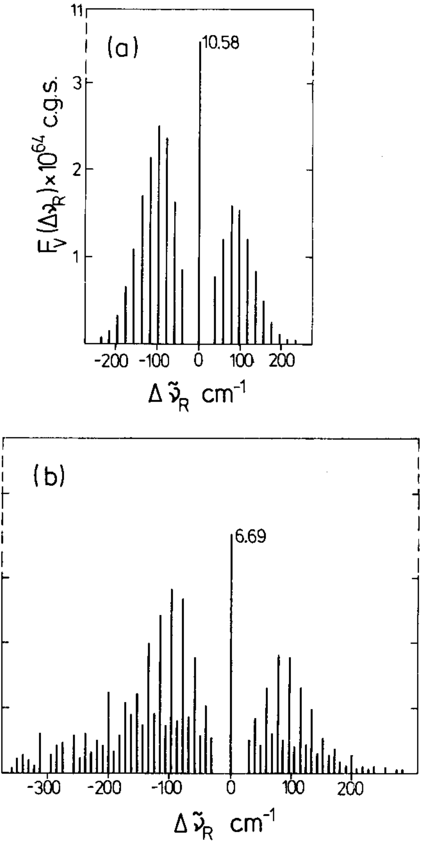

Fig. 3.3. Rotational structure calculated by BANCEWICZ, KIELICH and OŻGO [1975] for the molecule NH_3, applying hyperpolarizability components after (a) HUSH and WILLIAMS [1972], and (b) ARRIGHINI, MAESTRO and MOCCIA [1968].

obtaining the integral intensities of the purely vibrational lines in three-photon scattering

$$I^{fi}_{VV}(2\omega)=(N_{V^i}/280)[(2\omega+\omega_{V^fV^i})/c]^4 I_V^2 g_V^{(2)} \times\sum_s\{7\,|\langle V^f|\,\tilde{b}_s^{(1)}(Q)\,|V^i\rangle|^2+2\,|\langle V^f|\,\tilde{b}_s^{(3)}(Q)\,|V^i\rangle|^2\}, \tag{3.41a}$$

$$I^{fi}_{HV}(2\omega)=(N_{V^i}/2520)[(2\omega+\omega_{V^fV^i})/c]^4 I_V^2 g_V^{(2)} \times\sum_s\{7\,|\langle V^f|\,\tilde{b}_s^{(1)}(Q)\,|V^i\rangle|^2+12\,|\langle V^f|\,\tilde{b}_s^{(3)}(Q)\,|V^i\rangle|^2\}. \tag{3.41b}$$

In the harmonic oscillator approximation (3.34a), and with regard to

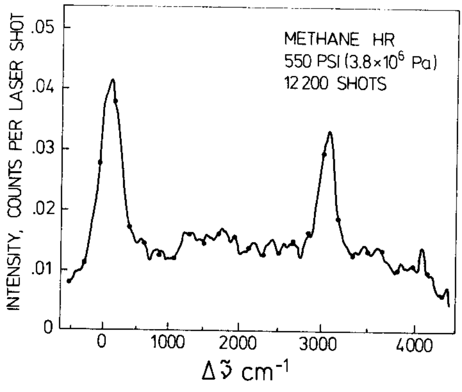

Fig. 3.4. The hyper-Raman spectrum of methane according to VERDIECK, PETERSON, SAVAGE and MAKER [1970]. Horizontal scale is the hyper-Raman shift $\Delta\tilde{\nu} = 2\nu - \nu_s$. The predominant line, centered about $100\,\text{cm}^{-1}$, referring to the pure rotational hyper-Raman spectrum, was predicted and observed earlier by MAKER [1966]. The other prominent line, centered about $3050\,\text{cm}^{-1}$, corresponds to the hyper-Raman shift due to the C–H stretching frequency $\nu_3(F_2)$.

(3.34b), the preceding expressions refer to hyper-Rayleigh lines at $Q = 0$ and to vibrational hyper-Raman lines for $Q \neq 0$ when, taking (3.34c) and the selection rules into account, we can write

$$I^{\text{fi}}_{\text{VV}}(2\omega) = (N/280)[(2\omega \mp \omega_m)/c]^4 I^2_{\text{V}} g^{(2)}_{\text{V}} f^{\mp}_m \sum_s \{7\,|\tilde{b}^{(1)}_{s:m}|^2 + 2\,|\tilde{b}^{(3)}_{s:m}|^2\}, \tag{3.42a}$$

$$I^{\text{fi}}_{\text{HV}}(2\omega) = (N/2520)[(2\omega \mp \omega_m)/c]^4 I^2_{\text{V}} g^{(2)}_{\text{V}} f^{\mp}_m \sum_s \{7\,|\tilde{b}^{(1)}_{s:m}|^2 + 12\,|\tilde{b}^{(3)}_{s:m}|^2\}, \tag{3.42b}$$

where, applying (3.37) and (3.34c), we have introduced the statistical distributions for Stokes and anti-Stokes lines (see LONG [1977]):

$$f^{\mp}_m = \pm(\hbar/2\omega_m)[1 - \exp(\mp\hbar\omega_m/kT)]^{-1}. \tag{3.43}$$

KIELICH and OŻGO [1973] have calculated the line intensities for the case of right-circularly polarized incident light. At forward scattering (Fig. 3.5), they obtained for the right- and left-circularly polarized scattered components

$$I^{\text{fi}}_{+1+1}(2\omega) = (N/2520)[(2\omega \mp \omega_m)/c]^4 I^2_{+1} g^{(2)}_{+1} f^{\mp}_m \sum_s \{28\,|\tilde{b}^{(1)}_{s:m}|^2 + 3\,|\tilde{b}^{(3)}_{s:m}|^2\}, \tag{3.44a}$$

$$I^{\text{fi}}_{-1+1}(2\omega) = (N/56)[(2\omega \mp \omega_m)/c]^4 I^2_{+1} g^{(2)}_{+1} f^{\mp}_m \sum_s |\tilde{b}^{(3)}_{s:m}|^2. \tag{3.44b}$$

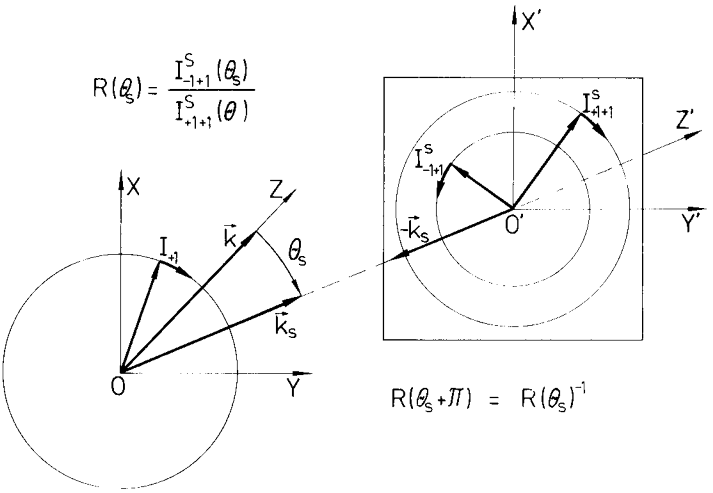

Fig. 3.5. Observation of the Reversal Ratio, on the angular momentum convention. Under the action of incident light, circularly polarized in the right sense, I_{+1}, two circularly polarized components appear in the scattered light, the one right-circular I_{+1+1}, and the other left-circular I_{-1+1}.

Here, it is worth noting that the component (3.44b) is dependent only on the one molecular parameter $|\tilde{b}^{(3)}_{s:m}|^2$, providing the opportunity of an independent determination of its value and sign in experiment.

The nonzero values of all these molecular parameters have been tabulated for all point groups and vibration symmetries by Alexiewicz, Bancewicz, Kielich and Ożgo [1974]. Cyvin, Rauch and Decius [1965] have discussed the selection rules for the vibrational transition frequencies of molecules and lattice vibration frequencies of crystals. A new, complete classification of the hyper-Raman spectral lines has been given by Andrews and Thirunamachandran [1978]. Earlier, Ożgo [1975a], and more recently Strey [1980], have proposed a systematic discussion of rotational and vibrational selection rules, as well as a method for the determination of the five irreducible molecular parameters $|\tilde{b}^{(J)L}_{M}|^2$ (for the asymmetric tensor $b_{\alpha\beta\gamma}$), from appropriate measurements of the intensity and depolarization ratio of three-photon scattering for various states of polarization of the incident and scattered photons. Ożgo and Kielich [1974], as well as Ożgo [1975b], have proposed a complete analysis of the polarization state and angular dependence of three-photon scattering, applying methods of Racah algebra. Ilyinsky and Taranukhin [1974, 1975] have studied the problem with regard to hyper-Raman scattering,

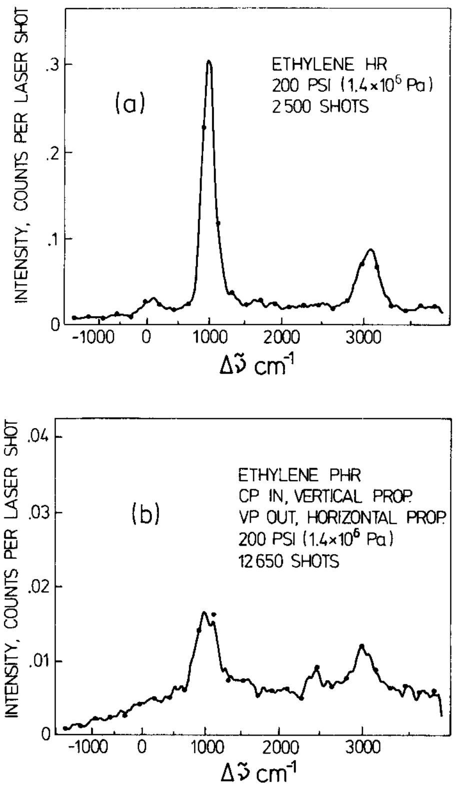

Fig. 3.6. The hyper-Raman spectra of ethylene observed by Verdieck, Peterson, Savage and Maker [1970] under different polarization conditions: (a) represents non-analyzed output scattering, (b) incident light circularly polarized and scattered light analyzed with horizontal polarization.

resonantially stimulated in IR (see also Blok, Krochik and Kronopulos [1979]).

Figure 3.6 shows the hyper-Raman spectrum of ethylene observed by Verdieck, Peterson, Savage and Maker [1970], whereas Fig. 3.7 permits a comparison of the normal Raman spectra of (liquid) carbon tetrachloride and the hyper-Rayleigh and hyper-Raman spectra obtained by French and Long [1975].

Our considerations concern electric-dipole scattering only, but can be extended to electric and magnetic multipole transitions on the basis of eq. (3.5). As shown recently by Andrews and Thirunamachandran [1979], the contributions from these transitions are particularly important

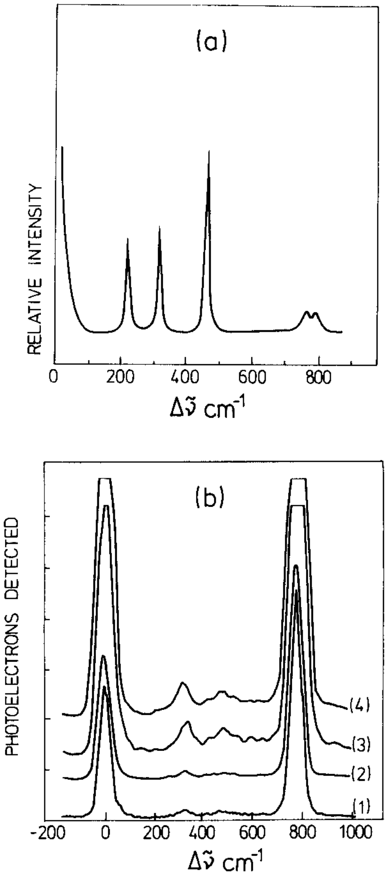

Fig. 3.7. Spectra of liquid carbon tetrachloride: (a) for normal Raman scattering, and (b) hyper-Rayleigh and Stokes hyper-Raman scattering observed by French and Long [1975] with multi-channel devices. The spectra labelled (1)–(4) correspond to virgin data, obtained for various numbers of channels and laser shots.

in the case of chirial molecules, for which, beside the vibrational hyper-Raman intensities calculated above, there appear additional cross-terms for electric-dipole ↔ magnetic-dipole as well as electric-dipole ↔ electric-quadrupole (and vice versa) transitions. The contributions from electric-quadrupole ↔ electric-quadrupole transitions calculated earlier by Kielich, Kozierowski, Ożgo and Zawodny [1974] are insignificant in the visible range, but grow for UV and X-rays. They become significant in second-harmonic Rayleigh scattering, when the latter is permitted even for atoms and centrosymmetric molecules, but is forbidden in the electric dipole approximation.

(iii) Vibrational-rotational hyper-Raman lines

Returning once again to eq. (3.39), and taking into account the harmonic term of the expansion (3.34a), we get, for the intensity of vibrational-rotational three-photon Raman lines (Bancewicz [1976]),

$$\begin{aligned} I^{\mathrm{fi}}_{\mathrm{VV}}(2\omega) &= (N_{J^{\mathrm{i}}K^{\mathrm{i}}}/280)[(2\omega \mp \omega_m + \omega_{R^{\mathrm{f}}R^{\mathrm{i}}})/c]^4 I^2_{\mathrm{V}} g^{(2)}_{\mathrm{V}} \\ &\times (2J^{\mathrm{f}}+1) f^{\mp}_m \left\{ 7 \begin{pmatrix} J^{\mathrm{f}} & 1 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\tilde{b}^{(1)}_{s:m}|^2 \right. \\ &\left. + 2 \begin{pmatrix} J^{\mathrm{f}} & 3 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\tilde{b}^{(3)}_{s:m}|^2 \right\}, \end{aligned} \tag{3.45a}$$

$$\begin{aligned} I^{\mathrm{fi}}_{\mathrm{HV}}(2\omega) &= (N_{J^{\mathrm{i}}K^{\mathrm{i}}}/2520)[(2\omega \mp \omega_m + \omega_{R^{\mathrm{f}}R^{\mathrm{i}}})/c]^4 I^2_{\mathrm{V}} g^{(2)}_{\mathrm{V}} \\ &\times (2J^{\mathrm{f}}+1) f^{\mp}_m \left\{ 7 \begin{pmatrix} J^{\mathrm{f}} & 1 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\tilde{b}^{(1)}_{s:m}|^2 \right. \\ &\left. + 12 \begin{pmatrix} J^{\mathrm{f}} & 3 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\tilde{b}^{(3)}_{s:m}|^2 \right\}. \end{aligned} \tag{3.45b}$$

Similarly, we obtain for circular polarization (Kielich and Ożgo [1973])

$$\begin{aligned} I^{\mathrm{fi}}_{+1+1}(2\omega) &= (N_{J^{\mathrm{i}}K^{\mathrm{i}}}/2520)[(2\omega \mp \omega_m + \omega_{R^{\mathrm{f}}R^{\mathrm{i}}})/c]^4 I^2_{+1} g^{(2)}_{+1} \\ &\times (2J^{\mathrm{f}}+1) f^{\mp}_m \left\{ 28 \begin{pmatrix} J^{\mathrm{f}} & 1 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\tilde{b}^{(1)}_{s:m}|^2 \right. \\ &\left. + 3 \begin{pmatrix} J^{\mathrm{f}} & 3 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\tilde{b}^{(3)}_{s:m}|^2 \right\}, \end{aligned} \tag{3.46a}$$

$$\begin{aligned} I^{\mathrm{fi}}_{-1+1}(2\omega) &= (N_{J^{\mathrm{i}}K^{\mathrm{i}}}/56)[(2\omega \mp \omega_m + \omega_{R^{\mathrm{f}}R^{\mathrm{i}}})/c]^4 I^2_{+1} g^{(2)}_{+1} \\ &\times (2J^{\mathrm{f}}+1) f^{\mp}_m \begin{pmatrix} J^{\mathrm{f}} & 3 & J^{\mathrm{i}} \\ -K^{\mathrm{f}} & s & K^{\mathrm{i}} \end{pmatrix}^2 |\tilde{b}^{(3)}_{s:m}|^2. \end{aligned} \tag{3.46b}$$

If a vibration ω_m belongs to a representation $\Gamma^{(m)}$, of dimension $k_m > 1$, it is degenerate; then, several normal coordinates $Q^{(j)}_m$, $j = 1, 2, \ldots, k_m$ correspond to the same frequency. In such cases the harmonic term in eq. (3.23) is given by the sum $\sum_{j=1}^{k_m} \tilde{b}^{(k)(j)}_{s:m} Q^{(j)}_m$, where $\tilde{b}^{(k)(j)}_{s:m}$ is the sth component of the spherical tensor of order k, related to the jth normal coordinate of a mode of the type m, belonging to the irreducible representation $\Gamma^{(m)}$ of the molecule. Accordingly, the molecular parameter $|\tilde{b}^{(k)}_{s:m}|^2$ related to the mode in question (neglecting coupling between rotational and vibrational motion) can be calculated from the formula (Poulet and Mathieu [1970]):

$$|\tilde{b}^{(k)}_{s:m}|^2 = \sum_{j=1}^{k_m} |\tilde{b}^{(k)(j)}_{s:m}|^2. \tag{3.47}$$

The nonzero molecular parameters (3.47) resulting from the vibrational selection rules have been tabulated by Alexiewicz, Bancewicz, Kielich and Ożgo [1974] as quadratic functions of the Cartesian components of the tensor $b_{\alpha\beta\gamma}$, for all point group symmetries and for all types of vibrations of symmetric top and spherical top molecules. Pascaud and Poussique [1978] have performed a detailed analysis of the vibrational-rotational hyper-Raman spectra of tetrahedral molecules.

On defining the depolarization ratio D_V of a spectral line of scattered light as that of its horizontal component I_{HV}, and vertical component I_{VV}, we arrive with regard to eq. (3.45), at Bancewicz's formula [1976]

$$D^{fi}_V(2\omega) = \frac{7\begin{pmatrix} J^f & 1 & J^i \\ -K^f & s & K^i \end{pmatrix}^2 |\tilde{b}^{(1)}_{s:m}|^2 + 12\begin{pmatrix} J^f & 3 & J^i \\ -K^f & s & K^i \end{pmatrix}^2 |\tilde{b}^{(3)}_{s:m}|^2}{63\begin{pmatrix} J^f & 1 & J^i \\ -K^f & s & K^i \end{pmatrix}^2 |\tilde{b}^{(1)}_{s:m}|^2 + 18\begin{pmatrix} J^f & 3 & J^i \\ -K^f & s & K^i \end{pmatrix}^2 |\tilde{b}^{(3)}_{s:m}|^2} \tag{3.48}$$

for vibrational-rotational (as well as vibrational and rotational) lines. It will be remembered that, in linear scattering, the depolarization ratio of any line equals 3/4 (see Placzek [1934] and Koningstein [1972]). From eq. (3.48), we note that, for second harmonic scattering, the depolarization ratio is in general a function of J and K. However, for all rotational lines with $\Delta K = \pm 2, \pm 3$ the depolarization ratio amounts to 2/3. Of special interest are vibrations for which only one of the molecular parameters (3.47) for $k = 3$ is nonzero, since here the depolarization ratio of any rotational line is 2/3. At the same time, for such a vibration, provided that it is completely symmetric, the depolarization ratio of the vibrational band or hyper-Rayleigh line is also equal to 2/3 (Kielich [1964a]).

Defining the reversal ratio as $I^{fi}_{-1+1}(2\omega)/I^{fi}_{+1+1}(2\omega)$ (see Fig. 3.5), and with regard to (3.46), one obtains in the case of forward scattering (Kielich and Ożgo [1973])

$$R^{fi}(2\omega) = \frac{45\begin{pmatrix} J^f & 3 & J^i \\ -K^f & s & K^i \end{pmatrix}^2 |\tilde{b}^{(3)}_{s:m}|^2}{28\begin{pmatrix} J^f & 1 & J^i \\ -K^f & s & K^i \end{pmatrix}^2 |\tilde{b}^{(1)}_{s:m}|^2 + 3\begin{pmatrix} J^f & 3 & J^i \\ -K^f & s & K^i \end{pmatrix}^2 |\tilde{b}^{(3)}_{s:m}|^2}. \tag{3.49}$$

For molecules with the point group symmetries T_d, D_{3h} and C_{3h} only one parameter $|\tilde{b}^{(3)}_{s:m}|^2$ differs from zero and the reversal ratio (3.49) assumes the values 15. In general, one has

$$0 \leqslant R^{\rm fi}(2\omega) \leqslant 15. \tag{3.50a}$$

By comparison, in the case of usual Raman scattering (see LONG [1977])

$$0 \leqslant R^{\rm fi}(\omega) \leqslant 6. \tag{3.50b}$$

3.4.2. *Four-photon scattering*

We now apply the tensor (3.31) to four-photon Raman scattering:

$$I^{\rm fi}_{\sigma\tau}(3\omega) = (N_i/144)[(3\omega+\omega_{\rm fi})/c]^4 I^3 \langle c^{\rm fi}_{\sigma\nu\rho\lambda}(3\omega)^* \, c^{\rm fi}_{\tau\mu\varepsilon\eta}(3\omega)\rangle_M \, g^{(3)}_{\nu\rho\lambda\mu\varepsilon\eta}. \tag{3.51}$$

The tensor has been averaged in Cartesian basis for arbitrary symmetries of $c_{\sigma\nu\rho\lambda}$ for linearly polarized (KOZIEROWSKI [1970]), as well as circularly polarized light (KOZIEROWSKI [1974]). We refrain, however, from adducing these highly complex results but restrict ourselves to writing out the vertical and horizontal component of (3.51) as obtained by OŻGO [1975b], in spherical basis for linearly polarized light

$$\begin{aligned} I^{\rm fi}_{\rm VV}(3\omega) &= (N_{V^iJ^iK^i}/45360)[(3\omega+\omega_{\rm fi})/c]^4 I^{(3)}_{\rm V} g^{(3)}_{\rm V} \\ &\quad \times (2J^{\rm f}+1)\left\{63\begin{pmatrix} J^{\rm f} & 0 & J^{\rm i} \\ -K^{\rm f} & 0 & K^{\rm i}\end{pmatrix}^2 |\langle V^{\rm f}|\,\tilde{c}^{(0)}_0(Q)\,|V^{\rm i}\rangle|^2 \right. \\ &\quad +36\begin{pmatrix} J^{\rm f} & 2 & J^{\rm i} \\ -K^{\rm f} & s & K^{\rm i}\end{pmatrix}^2 |\langle V^{\rm f}|\,\tilde{c}^{(2)}_s(Q)\,|V^{\rm i}\rangle|^2 \\ &\quad \left. +8\begin{pmatrix} J^{\rm f} & 4 & J^{\rm i} \\ -K^{\rm f} & s & K^{\rm i}\end{pmatrix}^2 |\langle V^{\rm f}|\,\tilde{c}^{(4)}_s(Q)\,|V^{\rm i}\rangle|^2\right\}, \end{aligned} \tag{3.52a}$$

$$\begin{aligned} I^{\rm fi}_{\rm HV}(3\omega) &= (N_{V^iJ^iK^i}/181440)[(3\omega+\omega_{\rm fi})/c]^4 I^3_{\rm V} g^{(3)}_{\rm V} \\ &\quad \times (2J^{\rm f}+1)\left\{27\begin{pmatrix} J^{\rm f} & 2 & J^{\rm i} \\ -K^{\rm f} & s & K^{\rm i}\end{pmatrix}^2 |\langle V^{\rm f}|\,\tilde{c}^{(2)}_s(Q)\,|V^{\rm i}\rangle|^2 \right. \\ &\quad \left. +20\begin{pmatrix} J^{\rm f} & 4 & J^{\rm i} \\ -K^{\rm f} & s & K^{\rm i}\end{pmatrix}^2 |\langle V^{\rm f}|\,\tilde{c}^{(4)}_s(Q)\,|V^{\rm i}\rangle|^2\right\}. \end{aligned} \tag{3.52b}$$

These components define the structure of the rotational lines as well as that of the vibrational-rotational lines at four-photon scattering. The matter is well adapted to a discussion similar to that of the components (3.39) of three-photon scattering.

Equations (3.52) lead to the selection rules, discussed by IEVLEVA and KARAGODOVA [1967], OŻGO [1968], and CHRISTIE and LOCKWOOD [1971] for vibrational transitions, and by OŻGO [1975] for rotational transitions. ALEXIEWICZ, OŻGO and KIELICH [1975] have tabulated the molecular parameters $|\tilde{c}_{\mathrm{M}}^{(J)}|^2$ as quadratic functions of the Cartesian tensor elements $c_{\alpha\beta\gamma\delta}$ for all molecular symmetry point groups.

Equations (3.52) show that the only permitted rotational transitions are those with $\Delta J = 0, \pm 1, \pm 2, \pm 3, \pm 4$ and $\Delta K = s$. The permitted values of s are to be had from the condition of non-vanishing of the molecular parameters $|c_{s:\mathrm{m}}^{(k)}|^2$ for the vibrational transitions $V_{\mathrm{m}}^{\mathrm{f}} \leftarrow V_{\mathrm{m}}^{\mathrm{i}} \pm 1$ under consideration. The branches with $\Delta J = \pm 3$, ± 4 are dependent on the parameters $|\tilde{c}_{s:m}^{(4)}|^2$ only. In the case of linear molecules only branches with even ΔJ can occur. Especially easy to analyze are those types of scattering which are dependent on only one molecular parameter (e.g. for K, Y, $\mathrm{K_h}$ and $\mathrm{Y_h}$), or two (e.g. T, $\mathrm{T_h}$, $\mathrm{T_d}$, O and $\mathrm{O_h}$).

On performing the summation in eqs. (3.52) over rotational transitions $J^{\mathrm{f}}K^{\mathrm{f}} \leftarrow J^{\mathrm{i}}K^{\mathrm{i}}$, one obtains the integral intensities of the bands due to vibrational transitions $V^{\mathrm{f}} \leftarrow V^{\mathrm{i}} \pm 1$ only:

$$I_{\mathrm{VV}}^{\mathrm{fi}}(3\omega) = (N_{\mathrm{V^i}}/45360)[(3\omega + \omega_{\mathrm{V^fV^i}})/c]^4 I_{\mathrm{V}}^3 g_{\mathrm{V}}^{(3)} \Big\{ 63\, |\langle V^{\mathrm{f}}|\, \tilde{c}_0^{(0)}(Q)\, |V^{\mathrm{i}}\rangle|^2 + \sum_s [36\, |\langle V^{\mathrm{f}}|\, \tilde{c}_s^{(2)}(Q)\, |V^{\mathrm{i}}\rangle|^2 + 8\, |\langle V^{\mathrm{f}}|\, \tilde{c}_s^{(4)}(Q)\, |V^{\mathrm{i}}\rangle|^2] \Big\}, \tag{3.53a}$$

$$I_{\mathrm{HV}}^{\mathrm{fi}}(3\omega) = (N_{\mathrm{V^i}}/181440)[(3\omega + \omega_{\mathrm{V^fV^i}})/c]^4 I_{\mathrm{V}}^3 g_{\mathrm{V}}^{(3)} \times \sum_s \{27\, |\langle V^{\mathrm{f}}|\, \tilde{c}_s^{(2)}(Q)\, |V^{\mathrm{i}}\rangle|^2 + 20\, |\langle V^{\mathrm{f}}|\, \tilde{c}_s^{(4)}(Q)\, |V^{\mathrm{i}}\rangle|^2\}. \tag{3.53b}$$

OŻGO [1975b] derived, as well, the vibration band intensities for circularly polarized light

$$I_{+1+1}^{\mathrm{fi}}(3\omega) = (N_{\mathrm{V^i}}/181440)[(3\omega + \omega_{\mathrm{V^fV^i}})/c]^4 I_{+1}^3 g_{+1}^{(3)} \times \sum_s \{54\, |\langle V^{\mathrm{f}}|\, \tilde{c}_s^{(2)}(Q)\, |V^{\mathrm{i}}\rangle|^2 + 5\, |\langle V^{\mathrm{f}}|\, \tilde{c}_s^{(4)}(Q)\, |V^{\mathrm{i}}\rangle|^2\}, \tag{3.54a}$$

$$I_{-1+1}^{\mathrm{fi}}(3\omega) = (N_{\mathrm{V^i}}/1296)[(3\omega + \omega_{\mathrm{V^fV^i}})/c]^4 I_{+1}^3 g_{+1}^{(3)} \sum_s |\langle V^{\mathrm{f}}|\, \tilde{c}_s^{(4)}(Q)\, |V^{\mathrm{i}}\rangle|^2. \tag{3.54b}$$

Thus, at circular polarization of the incident light wave, the parameter $|\tilde{c}_0^{(0)}|^2$ defining isotropic four-photon scattering does not intervene.

Equations (3.53) and (3.54) give for the depolarization and, respectively, reversal ratio of vibrational lines in four-photon scattering processes (Ożgo [1975a])

$$D_V(3\omega \mp \omega_m) = \frac{\sum_s \{27\,|\tilde{c}^{(2)}_{s:m}|^2 + 20\,|\tilde{c}^{(4)}_{s:m}|^2\}}{252\,|\tilde{c}^{(0)}_{0:m}|^2 + 16\sum_s \{9\,|\tilde{c}^{(2)}_{s:m}|^2 + 2\,|\tilde{c}^{(4)}_{s:m}|^2\}}, \tag{3.55}$$

$$R(3\omega \mp \omega_m) = \frac{140 \sum_s |\tilde{c}^{(4)}_{s:m}|^2}{\sum_s \{54\,|\tilde{c}^{(2)}_{s:m}|^2 + 5\,|\tilde{c}^{(4)}_{s:m}|^2\}}, \tag{3.56}$$

from which we have the following ranges of variability for the respective ratios:

$$0 \leq D(3\omega \mp \omega_m) \leq 5/8, \tag{3.55a}$$

$$0 \leq R(3\omega \mp \omega_m) \leq 28. \tag{3.55b}$$

The same ranges of variability result as well for elastic scattering, both with regard to the depolarization ratio (Kielich and Kozierowski [1970]) and reversal ratio (Kozierowski [1974]).

The decomposition of all tensors $c_{\alpha\beta\gamma\delta}$, in irreducible representations of all point groups, has been given by Ożgo and Zawodny [1970]. The

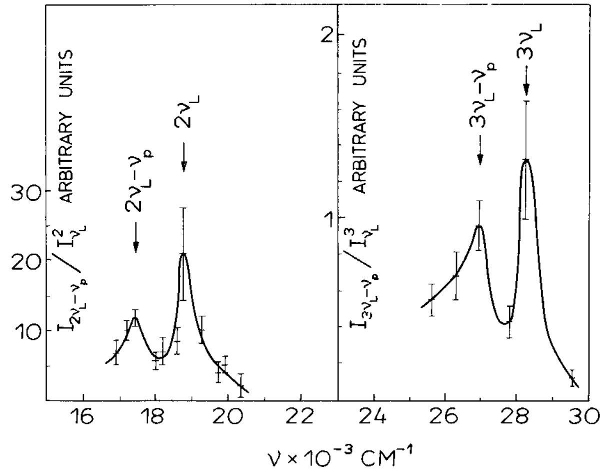

Fig. 3.8. Observations of Yu and Alfano [1975], representing relative intensities of three- and four-photon scattering versus the frequency ν_L from diamond upon the passage of intense picosecond laser pulses (20 or more laser shots), with ν_p, the optical phonon frequency of the diamond lattice.

properties of the tensors up to the fourth rank inclusively have been analyzed in full detail for the case of icosahedral molecules by Boyle and Ożgo [1973] and Boyle and Schäffer [1974]. Atoms and molecules of icosahedral symmetry cannot scatter circularly polarized light elastically ($m=0$), since in their case the parameters $|\tilde{c}^{(2)}_{s:m}|^2$ and $|\tilde{c}^{(4)}_{s:m}|^2$ vanish. However, they cause four-photon scattering induced by linearly polarized light, since the parameter $|\tilde{c}^{(0)}_0|^2$, occurring in eq. (3.53), is nonzero.

Hitherto, spontaneous four-photon scattering by molecular substances has not been observed. The only report by Yu and Alfano [1975] concerns three- and four-photon elastic and inelastic scattering from diamond crystal upon the passage of intense picosecond laser pulses (Fig. 3.8).

§ 4. Linewidth Broadening in Quasi-Elastic Multi-Photon Scattering by Correlated Molecules

4.1 THE ELECTRIC FIELD AND CORRELATION TENSOR OF SCATTERED LIGHT

We consider a macroscopic sample of volume V and electric permittivity ε in an isotropic continuous medium of electric permittivity ε_e. The macroscopic electric field (Maxwellian field) $\boldsymbol{E}$ existing in the sample differs in general from the external field $\boldsymbol{E}^e$, acting throughout the surrounding medium. The relation between the two fields is dependent on the structure and shape of the sample; in the particular case of an isotropic spherical sample it takes the form well known from electrostatics

$$\boldsymbol{E}^e = \frac{\varepsilon + 2\varepsilon_e}{3\varepsilon_e}\boldsymbol{E} = R\boldsymbol{E}. \tag{4.1}$$

If the external field $\boldsymbol{E}^e$ is sufficiently strong the sample becomes electrically anisotropic and its permittivity is tensorial, $\varepsilon_{\sigma\tau}$. Instead of the vectorial relation (4.1) we now have the tensorial formula (Kasprowicz-Kielich [1975]):

$$E^e_\sigma = R_{\sigma\tau}E_\tau. \tag{4.2}$$

The tensor relating the field components E^e_σ and E_τ is, in general, for a dielectric ellipsoidal sample

$$R_{\sigma\tau} = \varepsilon_e^{-1}[\varepsilon_e\delta_{\sigma\tau} + (\varepsilon_{\sigma\nu} - \varepsilon_e\delta_{\sigma\nu})L_{\nu\tau}], \tag{4.3}$$

where $L_{\sigma\tau}$ is a field depolarization tensor, dependent on the shape of the dielectric sample, and defined so that its trace shall equal unity $L_{\sigma\sigma} = L_{xx} + L_{yy} + L_{zz} = 1$.

In particular, for a spherical sample $L_{\sigma\tau} = \delta_{\sigma\tau}/3$ and the tensor (4.3) becomes

$$R_{\sigma\tau} = (\varepsilon_{\sigma\tau} + 2\varepsilon_e\delta_{\sigma\tau})/3\varepsilon_e. \tag{4.3a}$$

If, moreover, the sample is electrically isotropic, then (4.3a) becomes an isotropic tensor:

$$R_{\sigma\tau} = R\delta_{\sigma\tau}, \tag{4.3b}$$

where R is given by eq. (4.1).

The above holds also for the electric fields $\boldsymbol{E}(t)$ of the incident light wave, and $\boldsymbol{E}_s(t)$ of the scattered wave. However, the permittivities now become functions of the frequencies ω and ω_s.

We now assume that the scattering sample (volume V) contains N molecules, correlated in time and space. The electric field of the light scattered by the sample, and observed at a large distance $\boldsymbol{R}$ in the surrounding medium, is

$$\boldsymbol{E}_s^e(\boldsymbol{R}, t) = R(\omega_s) \sum_{p=1}^{N} \boldsymbol{E}_s^{(p)}(\boldsymbol{R}, t), \tag{4.4}$$

where, for an isotropic spherical sample, we have by eq. (4.3b),

$$R(\omega_s) = \frac{\varepsilon(\omega_s) + 2\varepsilon_e}{3\varepsilon_e} \tag{4.5}$$

with $\varepsilon(\omega_s)$ the electric permittivity of the sample at the vibration frequency ω_s of the scattered light wave.

The electric field strength vector of the light scattered by the pth molecule of the sample is, in the wave zone at the space-time point $(\boldsymbol{R}, t)$,

$$\boldsymbol{E}_s^{(p)}(\boldsymbol{R}, t) = (c^2R_p^3)^{-1}\{\boldsymbol{R}_p \times [\boldsymbol{R}_p \times \ddot{\boldsymbol{Z}}(t_p)]\}, \tag{4.6}$$

where $\boldsymbol{Z}(t_p)$ is the Hertz vector for the pth molecule at the retarded time $t_p = t - R_p/c$, and

$$R_p = |\boldsymbol{R} - \boldsymbol{r}_p| = R - \boldsymbol{s} \cdot \boldsymbol{r}_p + \cdots \tag{4.6a}$$

$\boldsymbol{r}_p$ denoting the radius vector of molecule p, and $\boldsymbol{s}$ the unit vector in the direction of propagation (observation) of the scattered light, $\boldsymbol{R} = R\boldsymbol{s}$.

Similarly to the integral intensity tensor of scattered light we can introduce, on the basis of eqs. (4.4) and (4.6), the tensor of time-correlation of the scattered light electric field (for processes stationary in time)

$$I^s_{\sigma\tau}(\boldsymbol{R}, t) = \tfrac{1}{2}c^{-4}\,|R(\omega_s)|^2 \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \ddot{Z}_\sigma(t_p)^* \, \ddot{Z}_\tau(t_q + t) \right\rangle. \tag{4.7}$$

With regard to the theorem of Wiener and Khinchin, the Fourier transform of the time-correlation tensor (4.7) defines the spectral density

$$S_{\sigma\tau}(\Delta \boldsymbol{k}, \Delta\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} \mathrm{d}t \, I^s_{\sigma\tau}(\boldsymbol{R}, t) \exp(\mathrm{i}\omega_s t). \tag{4.8}$$

The range of applicability of this spectral approach to time-dependent processes has recently been the subject of an analysis by EBERLY and WÓDKIEWICZ [1977].

We now proceed to define the Hertz vector in the electric dipole approximation, taking into account only time-dependent nonlinear components at harmonic frequencies. We thus write in complex analytic representation

$$\begin{aligned} Z^{n\omega}_\sigma(t_p) = {} & (2^{n-1} n!)^{-1} R^n(\omega) A^{n\omega}_{\sigma\sigma_1\cdots\sigma_n}(\boldsymbol{r}'_p, \Omega'_p) \\ & \times E_{\sigma_1}(\omega, \boldsymbol{k}) \cdots E_{\sigma_n}(\omega, \boldsymbol{k}) \exp[\mathrm{i}n(\boldsymbol{k}\cdot\boldsymbol{r}'_p - \omega t_p)], \end{aligned} \tag{4.9}$$

where the positional variables $\boldsymbol{r}'_p$ and orientational variables Ω'_p determining the configuration of the molecule are taken at the retarded moment of time t_p. The tensors $A^{n\omega}_{\sigma\sigma_1\cdots\sigma_n}$ now define effective nonlinear polarizabilities, dependent in general on the electric fields of neighboring molecules (KIELICH [1965b, c] and BEDEAUX and BLOEMBERGEN [1973]).

By eqs. (4.7) and (4.9), the tensor of time-correlation of the electric field of n-harmonically scattered light is

$$\begin{aligned} I^{n\omega}_{\sigma\tau}(\boldsymbol{R}, t) = {} & Q_{n\omega} I^n \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} A^{n\omega}_{\sigma\sigma_1\cdots\sigma_n}(\boldsymbol{r}^0_p, \Omega^0_p)^* \right. \\ & \left. \times A^{n\omega}_{\tau\tau_1\cdots\tau_n}(\boldsymbol{r}^t_q, \Omega^t_q) \exp[\mathrm{i}\Delta\boldsymbol{k}_n \cdot (\boldsymbol{r}^0_p - \boldsymbol{r}^t_q)] \right\rangle_K \\ & \times g^{(n)}_{\sigma_1\cdots\sigma_n\tau_1\cdots\tau_n} \exp(-\mathrm{i}n\,\omega t), \end{aligned} \tag{4.10}$$

where the parameter $Q_{n\omega}$ is:

$$Q_{n\omega} = \frac{1}{2^{n-1}(n!)^2} \left(\frac{n\omega}{c}\right)^4 \left|\frac{\varepsilon(n\omega) + 2\varepsilon_e}{3\varepsilon_e}\right|^2 \left|\frac{\varepsilon(\omega) + 2\varepsilon_e}{3\varepsilon_e}\right|^{2n}. \tag{4.11}$$

In (4.10), we have introduced the following tensor of the degree of nth order coherence of the incident electric light field

$$g^{(n)}_{\sigma_1\cdots\sigma_n\tau_1\cdots\tau_n} = \langle E^*_{\sigma_1}(\omega, \boldsymbol{k}) \cdots E^*_{\sigma_n}(\omega, \boldsymbol{k})\, E_{\tau_1}(\omega, \boldsymbol{k}) \cdots E_{\tau_n}(\omega, \boldsymbol{k})\rangle_E \\ \times \langle |\boldsymbol{E}(\omega, \boldsymbol{k})|^2\rangle_E^{-n}. \tag{4.12}$$

When going over from eq. (4.7) to eq. (4.10) we assumed that, in a first approximation, statistical averaging over the configurations K of the molecules in the scattering medium (denoted by the symbol $\langle\ \rangle_K$) can be carried out independently of the averaging over the states of the incident light field amplitudes (denoted by $\langle\ \rangle_E$) (see LOUDON [1973]).

The difference between the propagation vectors of the scattered wave and incident wave amounts to $\Delta\boldsymbol{k}_n = \boldsymbol{k}_{n\omega} - n\boldsymbol{k}_\omega$, and its module (Fig. 1.3) amounts to:

$$\Delta k_n = [(k_{n\omega} - nk_\omega)^2 + 4nk_{n\omega}k_\omega \sin^2(\theta_n/2)]^{1/2}, \tag{4.13}$$

where θ_n is the angle between the vectors $\boldsymbol{k}_{n\omega}$ and $\boldsymbol{k}_\omega$.

4.2. LINEAR SCATTERING

Although a detailed discussion of the spectral theory of linear light scattering would lie beyond the scope of our present aims, we nonetheless adduce the equations which result from eq. (4.10), in order to provide a simple illustration of certain complex aspects of light scattering on correlated clusters of molecules. Accordingly, eq. (4.10) leads to

$$I^\omega_{\sigma\tau}(\boldsymbol{R}, t) = Q_\omega I \Big\langle \sum_{p=1}^{N} \sum_{q=1}^{N} A^\omega_{\sigma\nu}(\boldsymbol{r}^0_p, \Omega^0_p)^* A^\omega_{\tau\rho}(\boldsymbol{r}^t_q, \Omega^t_q) \\ \times \exp[\mathrm{i}\Delta\boldsymbol{k}\cdot(\boldsymbol{r}^0_p - \boldsymbol{r}^t_q)] \Big\rangle_K g^{(1)}_{\nu\rho} \exp(-\mathrm{i}\omega t), \tag{4.14}$$

where Q_ω is given by eq. (4.11), with $n=1$.

A tensor of the second rank decomposes into three irreducible components: isotropic, antisymmetric and anisotropic (Appendix A)

$$A_{\sigma\nu} = A^{(0)}_{\sigma\nu} + A^{(1)}_{\sigma\nu} + A^{(2)}_{\sigma\nu}.$$

Thus, on isotropic averaging (see Appendix B) eq. (4.14) can be reduced to the following form:

$$I^\omega_{\sigma\tau}(\boldsymbol{R}, t) = \tfrac{1}{30} Q_\omega I \{10 A^\omega_0(\Delta\boldsymbol{k}, t)\, g^{(1,0)}_{\sigma\tau} \\ + 5 A^\omega_1(\Delta\boldsymbol{k}, t)\, g^{(1,1)}_{\sigma\tau} + A^\omega_2(\Delta\boldsymbol{k}, t)\, g^{(1,2)}_{\sigma\tau}\} \exp(-\mathrm{i}\omega t), \tag{4.15}$$

where we now have to deal with the following time-correlation functions $(h=0,1,2)$:

$$A_h^\omega(\Delta \boldsymbol{k}, t)=\left\langle \sum_{p=1}^{N}\sum_{q=1}^{N} A_{\alpha\beta}^{(h)}(\boldsymbol{r}_p^0, \Omega_p^0)^* A_{\alpha\beta}^{(h)}(\boldsymbol{r}_q^t, \Omega_q^t) \exp[\mathrm{i}\Delta \boldsymbol{k}\cdot(\boldsymbol{r}_p^0-\boldsymbol{r}_q^t)]\right\rangle_K \tag{4.16}$$

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

The tensors of the degree of first order coherence are

$$\begin{aligned} g_{\sigma\tau}^{(1,0)} &= \langle E_\sigma^* E_\tau\rangle_E/\langle|\boldsymbol{E}|^2\rangle_E, \\ g_{\sigma\tau}^{(1,1)} &= \langle \delta_{\sigma\tau}\, |\boldsymbol{E}|^2 - E_\sigma E_\tau^*\rangle_E/\langle|\boldsymbol{E}|^2\rangle_E, \\ g_{\sigma\tau}^{(1,2)} &= \langle 3\delta_{\sigma\tau}\, |\boldsymbol{E}|^2 + 3E_\sigma E_\tau^* - 2E_\sigma^* E_\tau\rangle_E/\langle|\boldsymbol{E}|^2\rangle_E. \end{aligned} \tag{4.17}$$

If the linear polarizability tensor is symmetric $A_{\alpha\beta}^\omega = A_{\beta\alpha}^\omega$, antisymmetric scattering vanishes $(A_1(t)=0)$, whereas the time-correlation functions of isotropic and anisotropic light scattering become, with regard to eq. (4.16),

$$A_0^\omega(\Delta \boldsymbol{k}, t)=\frac{1}{3}\left\langle \sum_{p=1}^{N}\sum_{q=1}^{N} A_{\alpha\alpha}^\omega(\boldsymbol{r}_p^0, \Omega_p^0)^* A_{\beta\beta}^\omega(\boldsymbol{r}_q^t, \Omega_q^t) \exp[\mathrm{i}\Delta \boldsymbol{k}\cdot(\boldsymbol{r}_p^0-\boldsymbol{r}_q^t)]\right\rangle_K, \tag{4.18}$$

$$\begin{aligned} A_2^\omega(\Delta \boldsymbol{k}, t)=\frac{1}{3}\Bigg\langle \sum_{p=1}^{N}\sum_{q=1}^{N} \{&3A_{\alpha\beta}^\omega(\boldsymbol{r}_p^0, \Omega_p^0)^* A_{\alpha\beta}^\omega(\boldsymbol{r}_q^t, \Omega_q^t) \\ &-A_{\alpha\alpha}^\omega(\boldsymbol{r}_p^0, \Omega_p^0)^* A_{\beta\beta}^\omega(\boldsymbol{r}_q^t, \Omega_q^t)\} \exp[\mathrm{i}\Delta \boldsymbol{k}\cdot(\boldsymbol{r}_p^0-\boldsymbol{r}_q^t)]\Bigg\rangle_K. \end{aligned} \tag{4.19}$$

4.2.1. *Isotropic incoherent and coherent scattering*

To start with, we assume that the polarizabilities of the molecules are not dependent on the distances between the latter (i.e. we assume the approximation of isolated molecule polarizabilities), so that the correlation function of isotropic scattering (4.18) can be written in the form

$$A_0^\omega(\Delta \boldsymbol{k}, t)=3N\,|a_\omega|^2\, F(\Delta \boldsymbol{k}, t), \tag{4.20}$$

with $a_\omega = a_{\alpha\alpha}^\omega/3$ the mean polarizability of the isolated molecule, and

$$F(\Delta \boldsymbol{k}, t)=N^{-1}\left\langle \sum_{p=1}^{N}\sum_{q=1}^{N} \exp[\mathrm{i}\Delta \boldsymbol{k}\cdot(\boldsymbol{r}_p^0-\boldsymbol{r}_q^t)]\right\rangle_K \tag{4.21}$$

the intermediate scattering correlation function, discussed in the theory of neutron scattering (see Copley and Lovesey [1975]).

After Van Hove [1954], we introduce the space-time binary correlation function:

$$G(\boldsymbol{r},\boldsymbol{r}',t)=G_{\mathrm{S}}(\boldsymbol{r}_{\mathrm{p}}^{0},\boldsymbol{r}_{\mathrm{p}}^{t},t)+G_{\mathrm{D}}(\boldsymbol{r}_{\mathrm{p}}^{0},\boldsymbol{r}_{q}^{t},t), \tag{4.22}$$

where the self-correlation function $G_{\mathrm{S}}\,(\boldsymbol{r}_{\mathrm{p}}^{0},\boldsymbol{r}_{\mathrm{p}}^{t},t)$ determines the probability of finding a (selected) molecule p in the point $\boldsymbol{r}_{\mathrm{p}}^{t}$ at the moment of time t, if it is known to have occupied the point $\boldsymbol{r}_{\mathrm{p}}^{0}$ at the moment of time $t=0$. Similarly, the distinct correlation function $G_{\mathrm{D}}(\boldsymbol{r}_{\mathrm{p}}^{0},\boldsymbol{r}_{q}^{t},t)$ expresses the probability of finding a molecule q in the point $\boldsymbol{r}_{q}^{t}$, if the fixed molecule p was in $\boldsymbol{r}_{\mathrm{p}}^{0}$ at $t=0$.

The evolution in time of the functions $G_{\mathrm{S}}(t)$ and $G_{\mathrm{D}}(t)$ differs according to the time interval considered. Usually, we distinguish three different intervals, corresponding respectively to the short times of molecular collisions $t_{\mathrm{c}}<10^{-13}\,\mathrm{s}$, the intermediate times of molecular relaxations $10^{-13}<t_{\mathrm{r}}<10^{-6}\,\mathrm{s}$, and the very long times of hydrodynamical relaxations $t_{\mathrm{h}}>10^{-6}\,\mathrm{s}$. It is important to find a reasonable and physically plausible analytical construction of G_{S} and, especially, G_{D}. In spite of the progress achieved, the problem of time-many-body correlation functions for the different time intervals has hitherto not been solved satisfactorily (see, for example, Berne [1971], Rowlinson and Evans [1975], and Evans [1977]). Here, of essential interest to us is the interval of times t_{r}, for which one may apply the solution based on the model of diffusion of translational and rotational molecular motion.

By having recourse to the Van Hove function (4.22) we can split the intermediate scattering correlation function into two parts (see Powles [1973]): a self-correlation part, describing incoherent scattering ($p=q$)

$$\begin{aligned}F_{\mathrm{inc}}(\Delta\boldsymbol{k},t)&=\langle\exp[\mathrm{i}\Delta\boldsymbol{k}\cdot(\boldsymbol{r}_{\mathrm{p}}^{0}-\boldsymbol{r}_{\mathrm{p}}^{t})]\rangle\\&=V^{-1}\iint\exp[\mathrm{i}\Delta\boldsymbol{k}\cdot(\boldsymbol{r}_{\mathrm{p}}^{0}-\boldsymbol{r}_{\mathrm{p}}^{t})]\,G_{\mathrm{S}}(\boldsymbol{r}_{\mathrm{p}}^{0},\boldsymbol{r}_{\mathrm{p}}^{t},t)\,\mathrm{d}\boldsymbol{r}_{\mathrm{p}}^{0}\,\mathrm{d}\boldsymbol{r}_{\mathrm{p}}^{t}\end{aligned} \tag{4.21a}$$

and a "distinct" part, describing coherent scattering on stochastically correlated molecules ($p\neq q$)

$$\begin{aligned}F_{\mathrm{coh}}(\Delta\boldsymbol{k},t)&=\left\langle\sum_{q\neq \mathrm{p}}^{N}\exp[\mathrm{i}\Delta\boldsymbol{k}\cdot(\boldsymbol{r}_{\mathrm{p}}^{0}-\boldsymbol{r}_{q}^{t})]\right\rangle\\&=(\rho/V)\iint\exp[\mathrm{i}\Delta\boldsymbol{k}\cdot(\boldsymbol{r}_{\mathrm{p}}^{0}-\boldsymbol{r}_{q}^{t})]\,G_{\mathrm{D}}(\boldsymbol{r}_{\mathrm{p}}^{0},\boldsymbol{r}_{q}^{t},t)\,\mathrm{d}\boldsymbol{r}_{\mathrm{p}}^{0}\,\mathrm{d}\boldsymbol{r}_{q}^{t}\end{aligned} \tag{4.21b}$$

with ρ being the average number density of molecules.

On the assumption of Einstein and Smoluchowski's free translational diffusion model, we have

$$G_S(\boldsymbol{r}_p^0, \boldsymbol{r}_p^t, t) = (4\pi D_T t)^{-3/2} \exp(-|\boldsymbol{r}_p^t - \boldsymbol{r}_p^0|^2/4D_T t). \tag{4.23}$$

Thus, the correlation function (4.21a) finally takes the form

$$F_{\text{inc}}(\Delta\boldsymbol{k}, t) = \exp(-|\Delta\boldsymbol{k}|^2 D_T t), \tag{4.24}$$

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

The calculation of the coherent scattering function (4.21b) is by no means simple for a lack of the analytical form of the correlation function $G_D(\boldsymbol{r}_p^0, \boldsymbol{r}_q^t, t)$. In some cases use can be made of VINEYARD's convolution approximation [1958]

$$G_D(\boldsymbol{r}_p^0, \boldsymbol{r}_q^t, t) = \int g(\boldsymbol{r}_{pq}^0)\, G_S(\boldsymbol{r}_q^0, \boldsymbol{r}_q^t, t)\, \mathrm{d}\boldsymbol{r}_q^0, \tag{4.25}$$

where $g(\boldsymbol{r}_{pq}^0)$ is the (equilibrium) radial correlation function of two molecules p and q, the centres of which are distant by $\boldsymbol{r}_{pq}^0$.

The convolution approximation of Vineyard (4.25) has been criticized for a number of reasons i.a. because it does not lead to the Mandelshtam–Brillouin doublet, which appears in the hydrodynamical treatment (SINGWI and SJÖLANDER [1964]). Nonetheless, it is satisfactorily fulfilled within the interval of intermediate times t_r, when the solution of the free diffusion equation can be applied to the description of the self-correlation function G_S.

Applying the correlation functions (4.23) and (4.25), we reduce the coherent scattering function (4.21b) to the following form (cf. NIJBOER and RAHMAN [1966]):

$$F_{\text{coh}}(\Delta\boldsymbol{k}, t) = \Gamma(\Delta\boldsymbol{k})\, F_{\text{inc}}(\Delta\boldsymbol{k}, t) \tag{4.26}$$

involving the integral parameter

$$\Gamma(\Delta\boldsymbol{k}) = 4\pi\rho \int_0^\infty g(r_{pq}) \frac{\sin \Delta k\, r_{pq}}{\Delta k\, r_{pq}} r_{pq}^2\, \mathrm{d}r_{pq} \tag{4.27}$$

introduced by ZERNIKE and PRINS [1927] in their theory of X-ray scattering by liquids.

4.2.2. *Anisotropic incoherent and coherent scattering*

In § 4.2.1 we have proved that, in the approximation of the polarizability of isolated molecules, the dynamics of isotropic light scattering is restricted to translational motion of the molecules. We shall now show that, within the same approximation, the anisotropic scattering function (4.19) requires moreover the intervention of rotational molecular motion. However, here, eq. (4.22) can be replaced by generalized correlation functions, involving additionally the molecular orientations Ω:

$$G(\boldsymbol{r}, \boldsymbol{r}'; \Omega, \Omega', t) = G_{\mathrm{S}}(\boldsymbol{r}_{\mathrm{p}}^{0}, \boldsymbol{r}_{\mathrm{p}}^{t}; \Omega_{\mathrm{p}}^{0}, \Omega_{\mathrm{p}}^{t}, t) + G_{\mathrm{D}}(\boldsymbol{r}_{\mathrm{p}}^{0}, \boldsymbol{r}_{q}^{t}; \Omega_{\mathrm{p}}^{0}, \Omega_{q}^{t}, t). \tag{4.28}$$

Regrettably, as yet, not much is known concerning the analytical form of eq. (4.28) and hardly anything concerning G_{D}. Nonetheless, by having recourse to a procedure due to STEELE and PECORA [1965], one can expand eq. (4.28) in a series in spherical Wigner functions:

$$G_{\mathrm{S}}(\boldsymbol{r}_{\mathrm{p}}^{0}, \boldsymbol{r}_{\mathrm{p}}^{t}; \Omega_{\mathrm{p}}^{0}, \Omega_{\mathrm{p}}^{t}, t) = \sum_{JKMM'} f_{MM'}^{J}(\boldsymbol{r}_{\mathrm{pp}}^{t}, t) \bar{D}_{KM}^{J}(\Omega_{\mathrm{p}}^{0})\, \bar{D}_{KM'}^{J}(\Omega_{\mathrm{p}}^{t})^{*}, \tag{4.28a}$$

$$G_{\mathrm{D}}(\boldsymbol{r}_{p}^{0}, \boldsymbol{r}_{q}^{t}; \Omega_{\mathrm{p}}^{0}, \Omega_{q}^{t}, t) = \sum_{J_{\mathrm{p}}K_{\mathrm{p}}M_{\mathrm{p}}} \sum_{J_{q}K_{q}M_{q}} g_{K_{\mathrm{p}}M_{\mathrm{p}},\, K_{q}M_{q}}^{J_{\mathrm{p}}J_{q}}(\boldsymbol{r}_{pq}^{t}, t) \times \bar{D}_{K_{\mathrm{p}}M_{\mathrm{p}}}^{J_{\mathrm{p}}}({}^{pq}\Omega_{\mathrm{p}}^{0}) \bar{D}_{K_{q}M_{q}}^{J_{q}}({}^{pq}\Omega_{q}^{t})^{*}. \tag{4.28b}$$

In eq. (4.28b), ${}^{pq}\Omega_{p}^{0}$ and ${}^{pq}\Omega_{q}^{t}$ determine the orientations of the molecules p and q in a system of coordinates pq, defined so that its positive z-axis coincides with $\boldsymbol{r}_{pq}^{t} = \boldsymbol{r}_{q}^{t} - \boldsymbol{r}_{\mathrm{p}}^{0}$.

The analytical form of the functions $f_{MM'}^{J}(\boldsymbol{r}_{pq}^{t}, t)$ and $g_{K_{\mathrm{p}}M_{\mathrm{p}},\, K_{q}M_{q}}^{J_{\mathrm{p}}J_{q}}(\boldsymbol{r}_{pq}^{t}, t)$ can be specified for a given model of the molecular motions, the simplest model of this kind being that of translational-rotational diffusion.

The correlation function of anisotropic scattering (4.19) has to be expressed in the same spherical representation as that used for the distribution function (4.28). With regard to the transformations (3.25) and (3.26), eq. (4.19) becomes

$$A_{2}^{\omega}(\Delta\boldsymbol{k}, t) = \sum_{KMM'} \tilde{a}_{M}^{(2)*}\, \tilde{a}_{M'}^{(2)} \Big\langle \sum_{\mathrm{p}=1}^{N} \sum_{q=1}^{N} D_{KM}^{2}(\Omega_{\mathrm{p}}^{0})^{*} \times D_{KM'}^{2}(\Omega_{q}^{t}) \exp\left[\mathrm{i}\Delta\boldsymbol{k} \cdot (\boldsymbol{r}_{\mathrm{p}}^{0} - \boldsymbol{r}_{q}^{t})\right] \Big\rangle, \tag{4.29}$$

where we have assumed, for the sake of simplicity, that the polarizability tensors $\tilde{a}_{M}^{(J)}$, in the system of reference of the molecule, are not dependent explicitly on the radial and angular variables of the other molecules.

Obviously, the interference factor of eq. (4.29) has also to be written in the spherical representation, given by the Rayleigh expansion (ROSE

[1957])

$$\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) = 4\pi \sum_{JM} \mathrm{i}^J j_J(kr)\, Y^J_M(\Omega_k)\, Y^J_M(\Omega_r)^* \tag{4.30}$$

where j_J is a spherical Bessel function and the Y^J_M are harmonic functions.

The form of eqs. (4.28)–(4.30) is such as to convince us that the time-dependent problem of anisotropic light scattering is still, at this stage, enormously complex and that its effective solution requires the assumption of some model of stochastic molecular motion.

(i) Incoherent scattering

When dealing with incoherent scattering one is justified in applying the free diffusion model and assuming that the translation motions of the molecules are stochastically independent of their rotational motions. In this case, the expansion coefficients of the function (4.28a) can be expressed as follows:

$$f^J_{MM'}(\boldsymbol{r}^t_{\mathrm{pp}}, t) = \delta_{MM'}\, G_{\mathrm{S}}(\boldsymbol{r}^t_{\mathrm{pp}}, t) \exp(-t/\tau^J_M), \tag{4.31}$$

where $G_{\mathrm{S}}(\boldsymbol{r}^t_{\mathrm{p}}, t)$ is defined by eq. (4.23) and τ^J_M denotes the Mth component of the rotational relaxation time of the Jth order which, for the symmetric top, is given by

$$\tau^J_M = \{J(J+1)D^{\mathrm{R}}_{11} + M^2(D^{\mathrm{R}}_{33} - D^{\mathrm{R}}_{11})\}^{-1}, \tag{4.31a}$$

D^{R}_{11} and D^{R}_{33} being the principal values of the rotational diffusion tensor $D^{\mathrm{R}}_{\alpha\beta}$.

From eq. (4.29), by having recourse to the functions (4.28a) and (4.31), we derive the time-correlation function of incoherent anisotropic scattering (cf. Knast and Kielich [1979])

$$A^{\omega}_2(\Delta\boldsymbol{k}, t)_{\mathrm{inc}} = NF_{\mathrm{inc}}(\Delta\boldsymbol{k}, t) \sum_{M=-2}^{+2} |\tilde{a}^{(2)}_M|^2 \exp(-t/\tau^2_M). \tag{4.32}$$

(ii) Coherent scattering

The expansion coefficients of (4.28b) can be expressed in the following way (Steele and Pecora [1965]):

$$g^{J_pJ_q}_{K_pM_p,\,K_qM_q}(\boldsymbol{r}^t_{pq}, t) = \exp(-t/\tau^{J_q}_{M_q}) \int g^{J_pJ_q}_{K_pM_p,\,K_qM_q}(\boldsymbol{r}_{pq})\, G_{\mathrm{S}}(\boldsymbol{r}^0_q, \boldsymbol{r}^t_q, t)\, \mathrm{d}\boldsymbol{r}^0_q, \tag{4.33}$$

where the equilibrium function of radial-angular correlations for two molecules is, in general, defined as

$$g^{J_pJ_q}_{K_pM_p,\,K_qM_q}(\boldsymbol{r}_{pq}) = \Omega^{-2} \iint g^{(2)}(\boldsymbol{r}_{pq}, \Omega_p^{pq}, \Omega_q^{pq}) \times \bar{D}^{J_p}_{K_pM_p}(\Omega_p^{pq})^* \, \bar{D}^{J_q}_{K_qM_q}(\Omega_q^{pq}) \, \mathrm{d}\Omega_p^{pq} \, \mathrm{d}\Omega_q^{pq}. \quad (4.34)$$

In eqs. (4.28b) and (4.34), we moreover have to keep in mind the multiplication law for Wigner functions (EDMONDS [1957]):

$$D^{J_p}_{K_pM_p}(\Omega_p^{pq}) = \sum_L D^{J_p}_{K_pL}(\Omega_p) \, D^{J_p}_{LM_p}(\Omega_{pq}). \quad (4.34a)$$

Thus, applying the function (4.28b) together with (4.23), (4.33) and (4.34) as well as (4.30) for $J=0$, we obtain the coherent part of the time-correlation function of anisotropic scattering (4.29) (KNAST and KIELICH [1979]):

$$A_2^{\omega}(\Delta\boldsymbol{k}, t)_{\mathrm{coh}} = NF_{\mathrm{inc}}(\Delta\boldsymbol{k}, t) \sum_{M,\,M'} \Gamma^{(2)}_{MM'}(\Delta\boldsymbol{k}) \, \tilde{a}_M^{(2)*} \, \tilde{a}_{M'}^{(2)} \exp\left(-t/\tau_M^2\right), \quad (4.35)$$

where we have introduced a generalized STEELE and PECORA [1965] radial-angular correlation parameter:

$$\Gamma^{(J)}_{MM'}(\Delta\boldsymbol{k}) = \sum_N \frac{(-1)^{N-M}}{2J+1} 4\pi\rho \int_0^{\infty} g^{JJ}_{N,\,-M,\,-N,\,M'}(\boldsymbol{r}_{pq}) \frac{\sin \Delta k \, r_{pq}}{\Delta k \, r_{pq}} \, r_{pq}^2 \, \mathrm{d}r_{pq}. \quad (4.36)$$

In the particular case of $J=M=M'=N=0$, it reduces to the parameter (4.27) for isotropic coherent light scattering.

If $\Delta k \, r \ll 1$ (short-range correlation), eq. (4.36) reduces to the STEELE parameter [1965]:

$$\Gamma^{(J)}_{MM'}(0) = \sum_N \frac{(-1)^{N-M}}{2J+1} 4\pi\rho \int_0^{\infty} g^{JJ}_{N,\,-M,\,-N,\,M'}(\boldsymbol{r}_{pq}) \, r_{pq}^2 \, \mathrm{d}r_{pq} \quad (4.36a)$$

which has been calculated numerically for concrete models of molecular interactions (see, for example KIELICH [1968c, 1972a], ANANTH, GUBBINS and GRAY [1974], and HØYE and STELL [1977]).

4.3. THREE-PHOTON SCATTERING

Let us now apply the tensor (4.10) to three-photon scattering, assuming for simplicity the tensor $A^{2\omega}_{\sigma\nu\rho} = B^{2\omega}_{\sigma\nu\rho}$ as completely symmetric. We finally obtain (see Appendix B):

$$
\begin{aligned}
I_{\sigma\tau}^{2\omega}(\boldsymbol{R}, t) = \tfrac{1}{315}\, Q_{2\omega} I^2 \{ & 7 B_1^{2\omega}(\Delta \boldsymbol{k}_2, t)\, g_{\sigma\tau}^{(2,1)} \\
& + 3 B_3^{2\omega}(\Delta \boldsymbol{k}_2, t)\, g_{\sigma\tau}^{(2,3)} \} \exp(-\mathrm{i}\, 2\omega t),
\end{aligned}
\tag{4.37}
$$

where we have introduced the time-correlation functions

$$
\begin{aligned}
B_1^{2\omega}(\Delta \boldsymbol{k}_2, t) = \frac{3}{5} \Big\langle \sum_{p=1}^{N} \sum_{q=1}^{N} & B_{\alpha\beta\beta}^{2\omega}(\boldsymbol{r}_p^0, \Omega_p^0)^* \\
& \times B_{\alpha\gamma\gamma}^{2\omega}(\boldsymbol{r}_q^t, \Omega_q^t) \exp[\mathrm{i} \Delta \boldsymbol{k}_2 \cdot (\boldsymbol{r}_p^0 - \boldsymbol{r}_q^t)] \Big\rangle_K,
\end{aligned}
\tag{4.38}
$$

$$
\begin{aligned}
B_3^{2\omega}(\Delta \boldsymbol{k}_2, t) = \frac{1}{5} \Big\langle \sum_{p=1}^{N} \sum_{q=1}^{N} & \{ 5 B_{\alpha\beta\gamma}^{2\omega}(\boldsymbol{r}_p^0, \Omega_p^0)^* B_{\alpha\beta\gamma}^{2\omega}(\boldsymbol{r}_q^t, \Omega_q^t) \\
& - 3 B_{\alpha\beta\beta}^{2\omega}(\boldsymbol{r}_p^0, \Omega_p^0)^*\, B_{\alpha\gamma\gamma}^{2\omega}(\boldsymbol{r}_q^t, \Omega_q^t) \} \\
& \times \exp[\mathrm{i} \Delta \boldsymbol{k}_2 \cdot (\boldsymbol{r}_p^0 - \boldsymbol{r}_q^t)] \Big\rangle_K
\end{aligned}
\tag{4.39}
$$

characterizing the molecular-stochastic aspects of second-harmonic scattering in dense fluids.

The tensors of the degree of second-order coherence occurring in eq. (4.37) are of the form

$$
g_{\sigma\tau}^{(2,1)} = \frac{\langle \delta_{\sigma\tau}\, |\boldsymbol{E}^2|^2 + 2 E_\sigma^* E_\tau^* \boldsymbol{E}^2 + 2 E_\sigma E_\tau \boldsymbol{E}^{*2} + 4 E_\sigma^* E_\tau\, |\boldsymbol{E}|^2 \rangle_E}{\langle |E|^2 \rangle_E^2},
$$

$$
g_{\sigma\tau}^{(2,3)} = \frac{\begin{gathered}\langle \delta_{\sigma\tau}(5\,|\boldsymbol{E}|^4 - |\boldsymbol{E}^2|^2) - 2 E_\sigma^* E_\tau^* \boldsymbol{E}^2 \\ - 2 E_\sigma E_\tau \boldsymbol{E}^{*2} + 2(5 E_\sigma E_\tau^* - 2 E_\sigma^* E_\tau)\, |\boldsymbol{E}|^2 \rangle_E\end{gathered}}{\langle |E|^2 \rangle_E^2.}\,.
\tag{4.40}
$$

We shall give a discussion of these tensors in § 7.

When discussing in detail the correlation functions (4.38) and (4.39) we proceed as in § 4.2 for linear scattering.

(i) Incoherent scattering

For incoherent scattering of second-harmonic light we have, by eqs. (4.38) and (4.39) for $J = 1, 3$ (with $\boldsymbol{r}_t = \boldsymbol{r}_p^t - \boldsymbol{r}_p^0$)

$$
B_J^{2\omega}(\Delta \boldsymbol{k}_2, t)_{\text{inc}} = N \sum_{MM'} \Big\langle f_{MM'}^J(\boldsymbol{r}_t, t) \frac{\sin \Delta k_2\, r_t}{\Delta k_2\, r_t}\, \tilde{b}_M^{(J)*} \tilde{b}_{M'}^{(J)} \Big\rangle.
\tag{4.41}
$$

On the free translational-rotational diffusion model, for which the distribution (4.31) is valid, we finally obtain

$$B_J^{2\omega}(\Delta \mathbf{k}_2, t)_{\mathrm{inc}} = N F_{\mathrm{inc}}(\Delta \mathbf{k}_2, t) \sum_{M} |\tilde{b}_M^{(J)}|^2 \exp(-t/\tau_M^J). \tag{4.42}$$

Taking, on the basis of eq. (4.8), the Fourier transforms of eqs. (4.37) and (4.42) we obtain the spectral expression first applied by MAKER [1970] to determine the relaxation times τ_0^1 and τ_0^3 from spectral linewidth measurements of "quasi-elastic" second-harmonic light scattering (see Fig. 4.1).

ALEXIEWICZ [1975] has extended Maker's theory to asymmetric top molecules, characterized in general by relaxation times τ_M^J. The problem

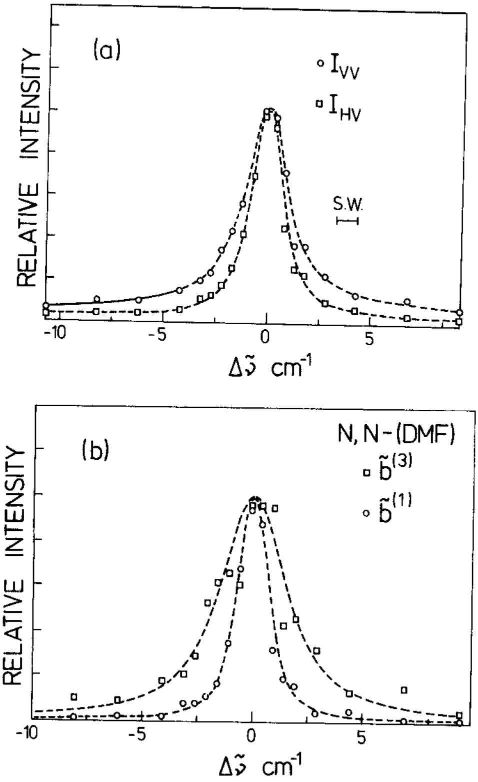

Fig. 4.1. Spectral width of "elastic" second-harmonic light scattering observed by MAKER [1970], for N,N-dimethylformamide at room temperature: (a) Vertical and horizontal scattered intensity, the measured points being connected by a smooth line, (b) The molecular parameters $\tilde{b}^{(1)}$ and $\tilde{b}^{(3)}$ derived from the data (a), together with the best fit Lorentzian convolution.

simplifies considerably if only one of the molecular parameters of eq. (4.42) differs from zero corresponding to one relaxation time, e.g. τ_3^3 for the molecular symmetries D_3, D_{3h} and C_{3h}, or τ_2^3 for the symmetries T, T_d and D_{2d}.

(ii) Coherent scattering

The coherent parts of eqs. (4.38) and (4.39) have been analyzed in detail by Bancewicz and Kielich [1976]. Here, we restrict ourselves to giving the results ($J = 1, 3$):

$$B_J^{2\omega}(\Delta \boldsymbol{k}_2, t)_{\text{coh}} = NF_{\text{inc}}(\Delta \boldsymbol{k}_2, t) \sum_{M, M'} \Gamma_{MM'}^{(J)}(\Delta \boldsymbol{k}_2)\, \tilde{b}_M^{(J)*}\, \tilde{b}_{M'}^{(J)} \exp(-t/\tau_M^J). \tag{4.43}$$

Above, the radial-angular correlation parameter has the form (4.36) on insertion of $\Delta \boldsymbol{k}_2$ for $\Delta \boldsymbol{k}$. In particular, it is analogical to that derived by Bersohn, Pao and Frisch [1966] for hyper-Rayleigh scattering in liquids.

Obviously, in order to calculate the parameter (4.36), one has to have available the molecular correlation function (4.34) in analytical form. In a satisfactory approximation, one may write (see Kielich [1972a])

$$g^{(2)}(r_{pq}, \Omega_{pq}) = g(r_{pq}) \sum_{m=0}^{\infty} (m!)^{-1} (-U_{pq}/kT)^m, \tag{4.44}$$

where $U_{pq} = U(r_{pq}, \Omega_{pq})$ is the potential energy of mutual radial-angular interaction of two molecules p and q, and has to be expressed by spherical harmonics (Gray [1968] and Moraal [1976]).

Assuming for $U(r_{pq}, \Omega_{pq})$ in eq. (4.44) intrinsic dipole-intrinsic dipole interaction only, one obtains the first nonzero terms of the parameter (4.36) (Bancewicz [1976]):

$$\Gamma_{00}^{(1)}(0) = \frac{2}{75}\left(\frac{d^2}{kT}\right)^3 \langle r_{pq}^{-9}\rangle, \qquad \Gamma_{00}^{(3)}(0) = -\frac{2}{3675}\left(\frac{d^2}{kT}\right)^3 \langle r_{pq}^{-9}\rangle \tag{4.45}$$

involving the following radial averages

$$\langle r_{pq}^{-n}\rangle = 4\pi\rho \int_0^{\infty} r_{pq}^{2-n}\, g(r_{pq})\, \mathrm{d}r_{pq} \tag{4.46}$$

accessible to calculation for well defined molecular models (Kielich [1972a] and Stell and Weis [1977]).

In the approximation considered, we finally obtain, with regard to eq.

(4.43), the results (Bancewicz and Kielich [1976]):

$$B_1^{2\omega}(0, t)_{\mathrm{coh}} = \frac{2N}{75}\left(\frac{d^2}{kT}\right)^3 \langle r_{pq}^{-9}\rangle\, |\tilde{b}_0^{(1)}|^2 \exp(-t/\tau_0^1), \tag{4.43a}$$

$$B_3^{2\omega}(0, t)_{\mathrm{coh}} = -\frac{2N}{3675}\left(\frac{d^2}{kT}\right)^3 \langle r_{pq}^{-9}\rangle |\tilde{b}_0^{(3)}|^2 \exp(-t/\tau_0^3), \tag{4.43b}$$

which, for integral scattering, go over into those of Kielich [1968a].

It is of interest to note that, on the model assumed, the coherent scattering parameter (4.43b) is negative; whereas, for incoherent scattering, the respective parameter resulting directly from (4.42) is always positive.

Similar calculations of the parameters (4.36) can be carried out for other models of correlated molecules, leading in all cases to a stronger or weaker influence of temperature on the spectrum observed. Studies of

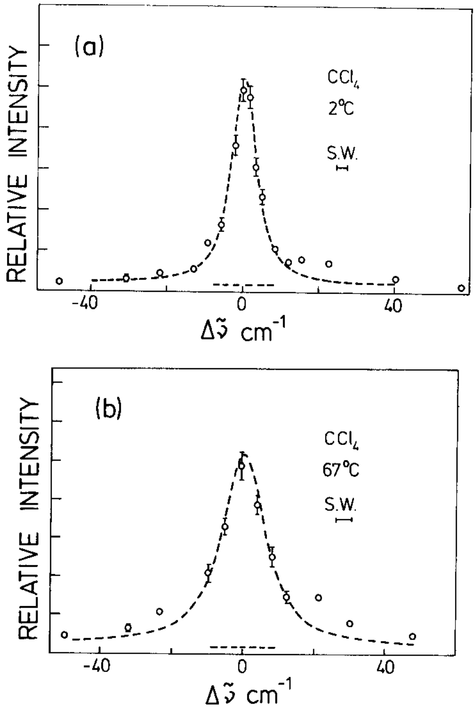

Fig. 4.2. Spectral width of "elastic" second-harmonic light scattering measured by Maker [1970] for CCl_4 as a function of temperature from 2° to 67°C.

this kind have been performed by MAKER [1970] for CCl_4, comparing his results with the earlier integral observations by WEINBERG [1967], who found a rather weak dependence on temperature (Fig. 4.2).

Finally, it may be worth mentioning that ALEXIEWICZ [1976] succeeded in applying Mori's formalism to the description of the spectrum of hyper-Rayleigh coherent scattering, i.e. as was done by KEYES and KIVELSON [1971] for usual Rayleigh scattering in liquids (see also KEYES and LADANYI [1977]).

4.4. FOUR-PHOTON SCATTERING

Applying the tensor (4.10) to four-photon scattering ($n=3$), and assuming the tensor $A^{3\omega}_{\sigma\tau\nu\lambda}=C^{3\omega}_{\sigma\tau\nu\lambda}$ as completely symmetric, one obtains (see Appendix B)

$$\begin{aligned}I^{3\omega}_{\sigma\tau}(\boldsymbol{R},t)=(Q_{3\omega}/1260)I^3\{252C_0^{3\omega}(\Delta\boldsymbol{k}_3,t)\,g^{(3,0)}_{\sigma\tau}+9C_2^{3\omega}(\Delta\boldsymbol{k}_3,t)\,g^{(3,2)}_{\sigma\tau}\\+C_4^{3\omega}(\Delta\boldsymbol{k}_3,t)\,g^{(3,4)}_{\sigma\tau}\}\exp(-\mathrm{i}\,3\omega t).\end{aligned}\tag{4.47}$$

The stochastic molecular mechanisms are determined by the following three irreducible time-correlation functions:

$$\begin{aligned}C_0^{3\omega}(\Delta\boldsymbol{k}_3,t)=\frac{1}{5}\Big\langle\sum_{p=1}^{N}\sum_{q=1}^{N}C^{3\omega}_{\alpha\alpha\beta\beta}(\boldsymbol{r}_p^0,\Omega_p^0)^*\\\times C^{3\omega}_{\gamma\gamma\delta\delta}(\boldsymbol{r}_q^t,\Omega_q^t)\exp[\mathrm{i}\Delta\boldsymbol{k}_3\cdot(\boldsymbol{r}_p^0-\boldsymbol{r}_q^t)]\Big\rangle_K,\end{aligned}\tag{4.48}$$

$$\begin{aligned}C_2^{3\omega}(\Delta\boldsymbol{k}_3,t)=\frac{2}{7}\Big\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\{3C^{3\omega}_{\alpha\beta\gamma\gamma}(\boldsymbol{r}_p^0,\Omega_p^0)^*\,C^{3\omega}_{\alpha\beta\delta\delta}(\boldsymbol{r}_q^t,\Omega_q^t)\\-C^{3\omega}_{\alpha\alpha\beta\beta}(\boldsymbol{r}_p^0,\Omega_p^0)^*\,C^{3\omega}_{\gamma\gamma\delta\delta}(\boldsymbol{r}_q^t,\Omega_q^t)\}\exp[\mathrm{i}\Delta\boldsymbol{k}_3\cdot(\boldsymbol{r}_p^0-\boldsymbol{r}_q^t)]\Big\rangle_K,\end{aligned}\tag{4.49}$$

$$\begin{aligned}C_4^{3\omega}(\Delta\boldsymbol{k}_3,t)=\frac{1}{35}\Big\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\{35C^{3\omega}_{\alpha\beta\gamma\delta}(\boldsymbol{r}_p^0,\Omega_p^0)^*\,C^{3\omega}_{\alpha\beta\gamma\delta}(\boldsymbol{r}_q^t,\Omega_q^t)\\-30C^{3\omega}_{\alpha\beta\gamma\gamma}(\boldsymbol{r}_p^0,\Omega_p^0)^*\,C^{3\omega}_{\alpha\beta\delta\delta}(\boldsymbol{r}_q^t,\Omega_q^t)\\+3C^{3\omega}_{\alpha\alpha\beta\beta}(\boldsymbol{r}_p^0,\Omega_p^0)^*\,C^{3\omega}_{\gamma\gamma\delta\delta}(\boldsymbol{r}_q^t,\Omega_q^t)\}\exp[\mathrm{i}\Delta\boldsymbol{k}_3\cdot(\boldsymbol{r}_p^0-\boldsymbol{r}_q^t)]\Big\rangle_K.\end{aligned}\tag{4.50}$$

The tensors of the degree of third-order coherence and polarization of the incident and scattered photons corresponding to the individual correlation functions (4.48)–(4.50) are of the form

$$\begin{aligned}
g_{\sigma\tau}^{(3,0)} &= \langle E_\sigma^* E_\tau \, |\boldsymbol{E}^2|^2 \rangle_\mathrm{E} / \langle |E|^2 \rangle_\mathrm{E}^3, \\
g_{\sigma\tau}^{(3,2)} &= \langle (3\delta_{\sigma\tau} \, |\boldsymbol{E}|^2 - 5E_\sigma^* E_\tau) \, |\boldsymbol{E}^2|^2 + 6(E_\sigma^* E_\tau \, |\boldsymbol{E}|^2 + E_\sigma^* E_\tau^* \boldsymbol{E}^2 \\
&\quad + E_\sigma E_\tau \boldsymbol{E}^{*2}) \, |\boldsymbol{E}|^2 \rangle_\mathrm{E} / \langle |E|^2 \rangle_\mathrm{E}^3, \\
g_{\sigma\tau}^{(3,4)} &= \langle 5\delta_{\sigma\tau} (7 \, |\boldsymbol{E}|^4 - 3 \, |\boldsymbol{E}^2|^2) \, |\boldsymbol{E}|^2 + 15(7E_\sigma E_\tau^* - 2E_\sigma^* E_\tau) \, |\boldsymbol{E}|^4 \\
&\quad - \tfrac{3}{2}(37 E_\sigma^* E_\tau - 35 E_\sigma E_\tau^*) \, |\boldsymbol{E}^2|^2 \\
&\quad - 30(E_\sigma^* E_\tau^* \boldsymbol{E}^2 + E_\sigma E_\tau \boldsymbol{E}^{*2}) \, |\boldsymbol{E}|^2 \rangle_\mathrm{E} / \langle |\boldsymbol{E}|^2 \rangle_\mathrm{E}^3.
\end{aligned} \qquad (4.51)$$

In the approximation of invariable molecular polarizabilities, the time-correlation function of isotropic scattering (4.48) can be expressed in the form

$$C_0^{3\omega}(\Delta \boldsymbol{k}_3, t) = 5N \, |c_{3\omega}|^2 \, F(\Delta \boldsymbol{k}_3, t), \qquad (4.52)$$

where $c_{3\omega} = c_{\alpha\alpha\beta\beta}^{3\omega}/5$ is the mean nonlinear polarizability of the isolated molecule, and $F(\Delta \boldsymbol{k}_3, t)$ the "intermediate" scattering correlation function, which takes the form (4.21) if $\Delta \boldsymbol{k}$ is replaced by $\Delta \boldsymbol{k}_3$.

The parameters (4.49) and (4.50) are well adapted to an analysis similar to that carried out for the parameters (4.38) and (4.39). However, with regard to volume, we refrain from pursuing the subject.

§ 5. Cooperative Three-Photon Scattering

5.1. FLUCTUATIONAL VARIATIONS OF THE NONLINEAR MOLECULAR POLARIZABILITIES

In § 4, when considering multi-photon scattering processes in dense media, we wrote the Hertz vector in the form (4.9), where $A_{\sigma\sigma_1 \cdots \sigma_n}^{n\omega}(\boldsymbol{r}_p, \Omega_p)$ stood for the tensor of a certain effective nonlinear polarizability, differing in general from the polarizability $a_{\sigma\sigma_1 \cdots \sigma_n}^{n\omega}(\Omega_p)$ of the isolated molecule. The difference is due to the fact that, in statistically inhomogeneous media, the nearest neighborhood of a molecule presents regions of quasi-ordering engendered by various mechanisms of a microscopic or semi-macroscopic nature. We shall not, however, consider effects of short-range interactions, but shall concentrate essentially on the changes in polarizability of the molecule caused by fluctuations of the long-range electric multipole fields of the molecules surrounding it (see, for example, KIELICH [1965b, 1972a] and VAN KRANENDONK and SIPE [1977]).

In a stochastic medium, the Hertz vector can be written in the form

$$\boldsymbol{Z}(t_p) = \boldsymbol{Z}(t') + \delta \boldsymbol{Z}(t_p), \tag{5.1}$$

where $\boldsymbol{Z}(t')$ describes the electromagnetic properties of an individual microscopic scattering centre, whereas $\delta \boldsymbol{Z}(t_p)$ moreover describes the variation in Hertz vector due to various processes, such as collisions and many-body interactions, or fluctuations of the molecular electric fields $\boldsymbol{F}(\boldsymbol{r}, t)$ in time and space.

When determining the variations $\delta \boldsymbol{Z}(t_p)$, characterizing the stochastic regions of correlated scatterers, we shall restrict our considerations to contributions from long-range electric fields $\boldsymbol{F}(\boldsymbol{r}, t)$. At the centre of a molecule p, the field due to the polarized electric multipoles of the $N-1$ surrounding molecules is (KIELICH [1965b])

$$\boldsymbol{F}^{(n)}(\boldsymbol{r}_\mathrm{p}, t_\mathrm{p}) = \sum_{s \neq \mathrm{p}}^{N} \sum_{n_1=1}^{\infty} (-1)^{n_1}[(2n_1-1)!!]^{-1}\, {}^{(n)}\boldsymbol{T}^{(n_1)}(r_{ps}, \omega)[n_1]\boldsymbol{M}_\mathrm{e}^{(n_1)}(\boldsymbol{r}_\mathrm{s}, t_\mathrm{s}), \tag{5.2}$$

where the tensor of rank $(n+n_1)$

$${}^{(n)}\boldsymbol{T}^{(n_1)}(r_{ps}, \omega) = \boldsymbol{\nabla}_{ps}^{n-1}\boldsymbol{\nabla}_{ps}^{n_1-1}[\boldsymbol{\nabla}_\mathrm{p}\boldsymbol{\nabla}_s - (\omega/c)^2\boldsymbol{U}]r_{\mathrm{ps}}^{-1} \exp[\mathrm{i}(\omega/c)r_{\mathrm{ps}}] \tag{5.3}$$

describes the (2^n-pole)–(2^{n_1}-pole) interactions between the molecules p and s, separated by a distance r_{ps}.

The 2^n-pole electric moment of (3.5a), induced in molecule p by the total electric field $\boldsymbol{E}_\mathrm{e}^{(n)}(\boldsymbol{r}_p^t) + \boldsymbol{F}^{(n)}(\boldsymbol{r}_p, t_p)$ is, in h-order approximation (KIELICH [1965b]),

$$\begin{aligned}\boldsymbol{M}_\mathrm{e}^{(n)}(\boldsymbol{r}_\mathrm{p}, t_\mathrm{p})^{(h)} = \frac{1}{h!}\sum_{n_1=1}^{\infty} \cdots \sum_{n_h=1}^{\infty} C_{n_1 \cdots n_h}\, {}^{(n)}\mathbf{A}^{(n_1+\cdots+n_h)}(\boldsymbol{r}_\mathrm{p}^t, \Omega_\mathrm{p}^t) \\ \times[n_1+\cdots+n_h][\boldsymbol{E}_\mathrm{e}^{(n_1)}(\boldsymbol{r}_p^t) + \boldsymbol{F}^{(n_1)}(\boldsymbol{r}_p, t_p)]\cdots \\ \times[\boldsymbol{E}_\mathrm{e}^{(n_h)}(\boldsymbol{r}_p^t) + \boldsymbol{F}^{(n_h)}(\boldsymbol{r}_p, t_p)]\end{aligned} \tag{5.4}$$

with $C_{n_1 \cdots n_h} = [(2n_1-1)!!]^{-1} \cdots [(2n_h-1)!!]^{-1}$.

The expressions (5.2) and (5.4) can be evaluated by the method of successive approximations, thus leading to the fluctuational contributions of (5.1) (for the linear multipole polarizability, see KIELICH [1980c]). Since we shall be dealing only with three-photon scattering, given by the parameters (4.38) and (4.39), we are justified in writing the tensor of second-order nonlinear multipole polarizability (neglecting spatial dispersion, i.e. assuming the electric field of the incident light wave as homogeneous throughout the region of the molecule) in the form (KIELICH [1980d])

$$ {}^{(n)}\boldsymbol{B}_{2\omega}^{(1+1)}(\boldsymbol{r}_{\mathrm{p}}^{t}, \Omega_{\mathrm{p}}^{t}) = {}^{(n)}\boldsymbol{b}_{2\omega}^{(1+1)}(\Omega_{\mathrm{p}}^{t}) + \delta\, {}^{(n)}\boldsymbol{B}_{2\omega}^{(1+1)}(\boldsymbol{r}_{\mathrm{p}}^{t}, \Omega_{\mathrm{p}}^{t}), \tag{5.5} $$

where the tensor ${}^{(n)}\boldsymbol{b}_{2\omega}^{(1+1)}$ of rank $n+2$ refers to the (isolated molecule) single-body approximation (in particular, for $n = 1$, it becomes the tensor ${}^{(1)}\boldsymbol{b}_{2\omega}^{(1+1)} = b_{\alpha\beta\gamma}^{2\omega}$). The variation caused in the tensor (5.5) by fluctuations of the electric multipole fields contains, in general, many-body contributions and, in the two-body interaction approximation, has the form

$$ \begin{aligned} \delta\, {}^{(n)}\boldsymbol{B}_{2\omega}^{(1+1)}(\boldsymbol{r}_{\mathrm{p}}^{t}, \Omega_{\mathrm{p}}^{t})_2 = \sum_{s\neq \mathrm{p}}^{N} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} (-1)^{n_2} C_{n_1 n_2} \big[& {}^{(n)}\boldsymbol{b}_{2\omega}^{(1+n_1)}(\Omega_{\mathrm{p}}^{t}) \\ & + {}^{(n)}\boldsymbol{b}_{2\omega}^{(n_1+1)}(\Omega_{\mathrm{p}}^{t})\big][n_1]^{(n_1)}\boldsymbol{T}^{(n_2)}(\boldsymbol{r}_{\mathrm{ps}}^{t})[n_2]^{(n_2)}\boldsymbol{a}_{\omega}^{(1)}(\Omega_{s}^{t}), \end{aligned} \tag{5.6} $$

where ${}^{(n_1)}\boldsymbol{T}^{(n_2)}(\boldsymbol{r}_{ps}^{t}) = {}^{(n_1)}\boldsymbol{T}^{(n_2)}(r_{ps}, \omega) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ps}^{t})$.

It turns out that, in atomic fluids, essentially important are the three-body interaction contributions

$$ \begin{aligned} \delta^{(n)}\boldsymbol{B}_{2\omega}^{(1+1)}(\boldsymbol{r}_{\mathrm{p}}^{t}, \Omega_{\mathrm{p}}^{t})_3 = \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} C_{n_1 \cdots n_4} \sum_{s\neq \mathrm{p}}^{N} \Bigg\{ & \sum_{u\neq s}^{N} (-1)^{n_2+n_4} \\ & \times \big[{}^{(n)}\boldsymbol{b}_{2\omega}^{(1+n_1)}(\Omega_{\mathrm{p}}^{t}) + {}^{(n)}\boldsymbol{b}_{2\omega}^{(n_1+1)}(\Omega_{\mathrm{p}}^{t})\big][n_1]^{(n_1)}\boldsymbol{T}^{(n_2)}(\boldsymbol{r}_{ps}^{t}) \\ & \times [n_2]^{(n_2)}\boldsymbol{a}_{\omega}^{(n_3)}(\Omega_{s}^{t})[n_3]^{(n_3)}\boldsymbol{T}^{(n_4)}(\boldsymbol{r}_{su}^{t})[n_4]^{(n_4)}\boldsymbol{a}_{\omega}^{(1)}(\Omega_{u}^{t}) \\ & + \sum_{u\neq \mathrm{p}}^{N} (-1)^{n_3+n_4}\, {}^{(n)}\boldsymbol{b}_{2\omega}^{(n_1+n_2)}(\Omega_{\mathrm{p}}^{t})[n_1+n_2]^{(n_1)}\boldsymbol{T}^{(n_3)}(\boldsymbol{r}_{\mathrm{ps}}^{t}) \\ & \times [n_3]^{(n_3)}\boldsymbol{a}_{\omega}^{(1)}(\Omega_{s}^{t})\, {}^{(n_2)}\boldsymbol{T}^{(n_4)}(\boldsymbol{r}_{\mathrm{p}u}^{t})[n_4]^{(n_4)}\boldsymbol{a}_{\omega}^{(1)}(\Omega_{u}^{t}) \Bigg\}. \end{aligned} \tag{5.7} $$

The two- and three-body multipole contributions (5.6) and (5.7), derived above by the molecular-statistical method, are consistent with the results of the quantum-mechanical method developed by PASMANTER, SAMSON and BEN-REUVEN [1976].

In addition to the variations (5.6) and (5.7) due to multipole moments (5.4) of the first and second order, one has still to take into account many-body contributions from multipole moments of the third-order. Here, we shall restrict ourselves to the second-order approximation of nonlinear electric dipole polarizability (KIELICH [1968a])

$$\delta\, {}^{(1)}\boldsymbol{B}_{2\omega}^{(1+1)}(\boldsymbol{r}_{p}^{t}, \Omega_{p}^{t}) = {}^{(1)}\boldsymbol{C}_{2\omega}^{(1+1+1)}(\Omega_{p}^{t}) \cdot \boldsymbol{F}(\boldsymbol{r}_{p}^{t}) + \cdots, \tag{5.8}$$

where, by expression (5.2), the field of electrically polarizable multipoles (in the absence of external fields) is (KIELICH [1965c])

$$\begin{aligned}\boldsymbol{F}(\boldsymbol{r}_{p}^{t}) = {} & \sum_{s\neq p}^{N} \sum_{n_1=1}^{\infty} (-1)^{n_1} C_{n_1}\, {}^{(1)}\boldsymbol{T}^{(n_1)}(\boldsymbol{r}_{ps}^{t})[n_1]\boldsymbol{M}_{e}^{(n_1)}(\Omega_{s}^{t}) \\ & + \sum_{s\neq p}^{N} \sum_{u\neq s}^{N} \sum_{n_1=1}^{\infty} \cdot \sum_{n_3=1}^{\infty} (-1)^{n_1+n_3} C_{n_1\cdot n_3}\, {}^{(1)}\boldsymbol{T}^{(n_1)}(\boldsymbol{r}_{ps}^{t}) \\ & \times [n_1]\, {}^{(n_1)}\boldsymbol{a}_{\omega}^{(n_2)}(\Omega_{s}^{t})[n_2]\, {}^{(n_2)}\boldsymbol{T}^{(n_3)}(\boldsymbol{r}_{su}^{t})[n_3]\boldsymbol{M}_{e}^{(n_3)}(\Omega_{u}^{t}) + \cdots\end{aligned} \tag{5.9}$$

$\boldsymbol{M}_{e}^{(n_1)}(\Omega_{s}^{t})$ denoting the intrinsic 2^{n_1}-pole electric moment of molecule s.

5.2. THE TIME-CORRELATION FUNCTION FOR INTERACTING ATOMS AND CENTROSYMMETRIC MOLECULES

We have seen that, in the general case, when the nonlinear polarizabilities have the form (5.5) for $n = 1$, the time-correlation functions (4.38) and (4.39) split into three parts. The first is related with the intrinsic polarizability of the molecules $b_{\alpha\beta\gamma}^{2\omega}$, and has been discussed in § 4.3. The second part is related to the cross terms

$$b_{\alpha\beta\gamma}^{2\omega}(\Omega_{p}^{0})^{*}\ \delta B_{\alpha\beta\gamma}^{2\omega}(\boldsymbol{r}_{q}^{t}, \Omega_{q}^{t}) + \delta B_{\alpha\beta\gamma}^{2\omega}(\boldsymbol{r}_{p}^{0}, \Omega_{p}^{0})^{*}\ b_{\alpha\beta\gamma}^{2\omega}(\Omega_{q}^{t})$$

and vanishes if $b_{\alpha\beta\gamma}^{2\omega}(\Omega_{p}^{t}) = 0$, as in fact is the case for molecules possessing a centre of symmetry. Obviously, in this case the first part also vanishes. As a consequence of this, for systems composed of centrosymmetric molecules, the time-correlation functions (4.38) and (4.39) take the form

$$\begin{aligned}B_{1}^{2\omega}(\Delta\boldsymbol{k}_2, t)_{\mathrm{coh}} = \frac{3}{5}\Big\langle & \sum_{p=1}^{N} \sum_{q=1}^{N} \delta B_{\alpha\beta\beta}^{2\omega}(\boldsymbol{r}_{p}^{0}, \Omega_{p}^{0})^{*} \\ & \times \delta B_{\alpha\gamma\gamma}^{2\omega}(\boldsymbol{r}_{q}^{t}, \Omega_{q}^{t}) \exp[\mathrm{i}\Delta\boldsymbol{k}_2 \cdot (\boldsymbol{r}_{p}^{0} - \boldsymbol{r}_{q}^{t})]\Big\rangle,\end{aligned} \tag{5.10}$$

$$\begin{aligned}B_{3}^{2\omega}(\Delta\boldsymbol{k}_2, t)_{\mathrm{coh}} = \frac{1}{5}\Big\langle & \sum_{p=1}^{N} \sum_{q=1}^{N} \{5\delta B_{\alpha\beta\gamma}^{2\omega}(\boldsymbol{r}_{p}^{0}, \Omega_{p}^{0})^{*}\delta B_{\alpha\beta\gamma}^{2\omega}(\boldsymbol{r}_{q}^{t}, \Omega_{q}^{t}) \\ & - 3\delta B_{\alpha\beta\beta}^{2\omega}(\boldsymbol{r}_{p}^{0}, \Omega_{p}^{0})^{*}\ \delta B_{\alpha\gamma\gamma}^{2\omega}(\boldsymbol{r}_{q}^{t}, \Omega_{q}^{t})\} \exp[\mathrm{i}\Delta\boldsymbol{k}_2 \cdot (\boldsymbol{r}_{p}^{0} - \boldsymbol{r}_{q}^{t})]\Big\rangle.\end{aligned} \tag{5.11}$$

Since variations $\delta B_{\alpha\beta\gamma}^{2\omega}$ exist only in the presence of well defined many-body molecular interactions, the time-correlation functions (5.10) and

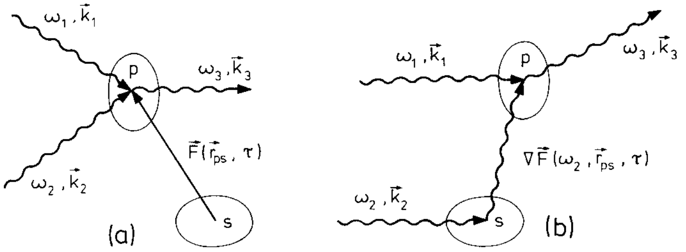

Fig. 5.1. Models of coherent three-photon scattering: (a) the electric field $\boldsymbol{F}(\boldsymbol{r}_{ps}, t)$ of molecule s removes the inversion centre of molecule p, which now produces scattering at ω_3 (Kielich [1968a, 1977]), (b) the dipole moment induced at the frequency ω_2 in molecule s gives rise to the electric field gradient $\boldsymbol{\nabla F}(\omega_2, \boldsymbol{r}_{ps})$ in molecule p, which performs an electric dipole–quadrupole transition and produces a photon at ω_3 (Pasmanter, Samson and Ben-Reuven [1976]).

(5.11) describe solely and exclusively three-photon coherent scattering, caused by cooperative effects in regions of quasi-ordering.

We now proceed to discuss the two simple models shown in Fig. 5.1.

5.2.1. *Many-body atomic multipole interaction*

Samson and Pasmanter [1974] have drawn attention to the fact that mixed interaction between a dipole induced in one atom, and the electric field gradient produced by the dipole induced in another atom (see Fig. 5.1b), causes three-photon coherent elastic light scattering. This effect is contained in our expansion (5.6) for $n = 1$, $n_1 = 2$ and $n_2 = 1$:

$$\delta B^{2\omega}_{\alpha\beta\gamma}(\boldsymbol{r}^t_p, \Omega^t_p) = -\frac{1}{3}\sum_{s\neq p}^{N} [b^{2\omega}_{\alpha\beta:\delta\varepsilon}(\Omega^t_p) + b^{2\omega}_{\alpha:\delta\varepsilon:\beta}(\Omega^t_p)]\, T_{\delta\varepsilon\eta}(\boldsymbol{r}^t_{ps})\, a^{\omega}_{\eta\gamma}(\Omega^t_s), \tag{5.6a}$$

where the fourth-rank tensor $b^{2\omega}_{\alpha\beta:\delta\varepsilon}$ describes the second-order nonlinear electric-dipole polarizability induced by a mixed electric dipole-electric quadrupole transition. This tensor is of interest in that it is non-zero for atoms and centrosymmetric molecules. Its nonzero and mutually independent components have been tabulated by Kielich, Kozierowski, Ożgo and Zawodny [1974] for all point group symmetries. The tensor $T_{\delta\varepsilon\eta}(\boldsymbol{r}_{ps})$ describes quadrupole–dipole interaction ${}^{(2)}\boldsymbol{T}^{(1)}(\boldsymbol{r}_{ps})$.

Let us consider the simplest case of atoms and molecules with the point group symmetries Y and K. The expression (5.6a) now reduces to

$$\delta B^{2\omega}_{\alpha\beta\gamma}(\boldsymbol{r}^t_{\mathrm{p}}) = -2 \sum_{s\neq \mathrm{p}}^{N} q^{2\omega}_{\mathrm{p}} a^{\omega}_{\mathrm{s}} T_{\alpha\beta\gamma}(\boldsymbol{r}^t_{\mathrm{ps}}), \tag{5.12}$$

where $a_\omega = \frac{1}{3} a^{\omega}_{\alpha\alpha}$ and $q^{2\omega} = \frac{1}{15} b^{2\omega}_{\alpha\beta:\alpha\beta}$.

For the model considered in the approximation (5.12) the correlation function (5.10) vanishes, whereas the function (5.11) assumes the form

$$B^{2\omega}_3(\Delta \boldsymbol{k}_2, t)_{\mathrm{coh}} = 4\Big\langle \sum_{\mathrm{p}=1}^{N} \sum_{q=1}^{N} \sum_{s\neq \mathrm{p}}^{N} \sum_{u\neq q}^{N} q_{\mathrm{p}}^{-2\omega} q_{\mathrm{q}}^{2\omega} a_{\mathrm{s}}^{-\omega} a_u^{\omega} \times T_{\alpha\beta\gamma}(\boldsymbol{r}^0_{\mathrm{ps}})^* \, T_{\alpha\beta\gamma}(\boldsymbol{r}^t_{qu}) \exp[\mathrm{i}\Delta \boldsymbol{k}_2 \cdot (\boldsymbol{r}^0_{p} - \boldsymbol{r}^t_{q})] \Big\rangle. \tag{5.13}$$

The two-body contribution

$$B^{2\omega}_3(\Delta \boldsymbol{k}_2, t)_{\mathrm{coh}} = 4\Big\langle \sum_{\mathrm{p}=1}^{N} \sum_{s\neq \mathrm{p}}^{N} \{|q^{2\omega}_{\mathrm{p}} a^{\omega}_{s}|^2 \exp[\mathrm{i}\Delta \boldsymbol{k}_2 \cdot (\boldsymbol{r}^0_{p} - \boldsymbol{r}^t_{\mathrm{p}})] \, T_{\alpha\beta\gamma}(\boldsymbol{r}^0_{ps})^* \, T_{\alpha\beta\gamma}(\boldsymbol{r}^t_{ps}) + q_p^{-2\omega} a_p^{\omega} q_s^{2\omega} a_s^{-\omega} \exp[\mathrm{i}\Delta \boldsymbol{k}_2 \cdot (\boldsymbol{r}^0_{p} - \boldsymbol{r}^t_{s})] T_{\alpha\beta\gamma}(\boldsymbol{r}^0_{ps})^* T_{\alpha\beta\gamma}(\boldsymbol{r}^t_{sp})\} \Big\rangle \tag{5.13a}$$

occurring in (5.13) vanishes for like atoms ($a_{\mathrm{p}} = a_{\mathrm{s}} = a$; $q_{\mathrm{p}} = q_{\mathrm{s}} = q$) in the absence of interference effects when $T_{\alpha\beta\gamma}(\boldsymbol{r}^t_{ps}) = -T_{\alpha\beta\gamma}(\boldsymbol{r}^t_{sp})$.

The three- and four-body contributions occurring in eq. (5.13) are in general nonzero even if the atoms are of the same species. However, evaluations are difficult, since the time many-body correlation functions are not available (see GROOME, GUBBINS and DUFTY [1976] and KNAST, CHMIELOWSKI and KIELICH [1980]).

On applying eq. (5.7) to atoms we obtain the three-body contribution of interest to us:

$$\delta B^{2\omega}_{\alpha\beta\gamma}(\boldsymbol{r}^t_{\mathrm{p}}, \Omega^t_{\mathrm{p}}) = 2 \sum_{s\neq \mathrm{p}}^{N} q^{2\omega}_{\mathrm{p}} a^{\omega}_{\mathrm{s}} \left\{ \sum_{u\neq s}^{N} a^{\omega}_u \, T_{\alpha\beta\delta}(\boldsymbol{r}^t_{\mathrm{ps}}) \, T_{\delta\gamma}(\boldsymbol{r}^t_{su}) + \sum_{u\neq \mathrm{p}}^{N} a^{\omega}_u \, T_{\alpha\gamma\delta}(\boldsymbol{r}^t_{\mathrm{ps}}) \, T_{\delta\beta}(\boldsymbol{r}^t_{pu}) \right\} \tag{5.7a}$$

which now gives nonzero contributions to the two correlation functions (5.10) and (5.11). These many-body contributions to three-photon scattering by atomic systems have been analyzed and evaluated numerically by SAMSON and PASMANTER [1974]. Also, GELBART [1973] has considered the possibility of three-photon scattering by three-body clusters of atoms, taking into consideration electronic cloud distortion effects. Contributions from long-range interactions of unlike atoms can be calculated as well (see GALATRY and GHARBI [1980]).

Under normal non-resonance conditions, such predominantly collisional three-photon scattering effects are rather weak and their observation is beset with difficulties, as shown by the first and, hitherto, only attempts of MAKER [1972] in the liquids nitrogen, argon, oxygen, etc. Hitherto, only observations and studies of two-photon collisional Rayleigh and Raman scattering have been successful (see, for example, MCTAGUE and BIRNBAUM [1971], KNAAP and LALLEMAND [1975], FRENKEL and MCTAGUE [1980], and TABISZ [1979]).

5.2.2. *Molecules with centre of inversion destroyed by the field of electric multipoles*

KIELICH, LALANNE and MARTIN [1971] have proposed yet another mechanism leading to three-photon scattering by fluids composed of centrosymmetric molecules. It originates in the changes in polarizability determined by eq. (5.8), and resides in the fact that the time and spatially fluctuating electric field $\boldsymbol{F}$ of the intrinsic multipole moments lowers the symmetry of the molecule; if the latter possessed a centre of symmetry in its ground state, it loses its centre of symmetry under the influence of the field $\boldsymbol{F}$, and is endowed with the ability to cause three-photon scattering (Fig. 5.1a). Generally speaking, the molecular field $\boldsymbol{F}$ not only lowers the natural symmetry of the molecule by way of the nonlinear polarizability of the latter but, due to its very existence, causes the region of short-range ordering to become anisotropic, with no local centre of symmetry. To provide a simple demonstration of the aforesaid, we neglect in a first approximation the anisotropy of the tensor ${}^{(1)}\boldsymbol{c}_{2\omega}^{(1+1+1)} \equiv c_{\alpha\beta\gamma\delta}^{2\omega}$ in eq. (5.8) so that, now, the correlation function (5.10) is nonzero

$$B_1^{2\omega}(\Delta\boldsymbol{k}_2, t)_{\mathrm{coh}} = \tfrac{5}{9}|c_{2\omega}|^2 \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \boldsymbol{F}(\boldsymbol{r}_p^0)^* \cdot \boldsymbol{F}(\boldsymbol{r}_q^t) \exp\left[\mathrm{i}\Delta\boldsymbol{k}_2 \cdot (\boldsymbol{r}_p^0 - \boldsymbol{r}_q^t)\right] \right\rangle, \tag{5.14}$$

whereas the correlation function (5.11) vanishes.

One sees that, on this model, coherent three-photon scattering is in fact caused by the square of the time and spatially fluctuating electric multipole molecular fields, determined generally by eq. (5.9).

(i) Quadrupolar molecules

For centrosymmetric molecules with an intrinsic quadrupole moment $\boldsymbol{M}_e^{(2)} = \boldsymbol{\Theta}$ (neglecting hexadecapole moments) we obtain, by eqs. (5.9) and (5.14),

$$B_1^{2\omega}(\Delta \boldsymbol{k}_2, t)_{\mathrm{coh}} = \tfrac{5}{81}|c_{2\omega}|^2 \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{s\neq p}^{N} \sum_{u\neq q}^{N} T_{\alpha\beta\gamma}(\boldsymbol{r}_{ps}^0)^* \right.$$
$$\left. \times T_{\alpha\delta\varepsilon}(\boldsymbol{r}_{qu}^t)\, \Theta_{\beta\gamma}(\Omega_s^0)^*\, \Theta_{\delta\varepsilon}(\Omega_u^t) \exp\left[\mathrm{i}\Delta \boldsymbol{k}_2 \cdot (\boldsymbol{r}_p^0 - \boldsymbol{r}_q^t)\right] \right\rangle. \quad (5.15)$$

The function (5.15) leads to a result noteworthy for its simplicity when we consider integral scattering. Thus, for axially symmetric molecules having a quadrupole $\boldsymbol{\Theta} = \boldsymbol{\Theta}_{33}$, we obtain in the approximation of two-body correlations (KIELICH, LALANNE and MARTIN [1971])

$$B_1^{2\omega}(0)_{\mathrm{coh}} = \tfrac{5}{3}\, |c_{2\omega}|^2\, \Theta^2\, N\langle r_{pq}^{-8}\rangle, \quad (5.16)$$

where the radial parameter $\langle r_{pq}^{-8}\rangle$ is given by (4.46).

Dropping the assumption of isotropicity of the tensor $c_{\alpha\beta\gamma\delta}^{2\omega}$ we obtain by eqs. (5.8), (5.10) and (5.11) in the integral case (KIELICH [1968a, 1980a])

$$B_1^{2\omega}(0)_{\mathrm{coh}} = (2/25)N(5c_{\alpha\beta\beta\delta}^{-2\omega}\, c_{\alpha\gamma\gamma\delta}^{2\omega}\, \Theta_{\varepsilon\eta}\, \Theta_{\varepsilon\eta} - 3c_{\alpha\beta\beta\gamma}^{-2\omega}\, \Theta_{\alpha\gamma}\, c_{\delta\varepsilon\varepsilon\eta}^{2\omega}\, \Theta_{\delta\eta})\, \langle r_{pq}^{-8}\rangle, \quad (5.17)$$

$$B_3^{2\omega}(0)_{\mathrm{coh}} = (2/3675)\, N\{245(5c_{\alpha\beta\gamma\delta}^{-2\omega}\, c_{\alpha\beta\gamma\delta}^{2\omega}$$
$$- 3c_{\alpha\beta\beta\delta}^{-2\omega}\, c_{\alpha\gamma\gamma\delta}^{2\omega})\, \Theta_{\varepsilon\eta}\, \Theta_{\varepsilon\eta} - 9c_{\alpha\beta\beta\gamma}^{-2\omega}\, \Theta_{\alpha\gamma}\, c_{\delta\varepsilon\varepsilon\eta}^{2\omega}\, \Theta_{\varepsilon\eta}\}\langle r_{pq}^{-8}\rangle. \quad (5.18)$$

These formulae are applicable to various symmetries of quadrupole molecules.

(ii) Multipole molecules

The use of the time-correlation function (5.14) is especially justified in the case of molecules of a high degree of symmetry, e.g. tetrahedral, octahedral etc. molecules. Taking into account the multipole field (5.9), we now obtain for two-body correlation (KIELICH [1965c, 1968a])

$$B_1^{2\omega}(0)_{\mathrm{coh}} = \tfrac{5}{3}|c_{2\omega}|^2\, N \sum_{n=1}^{\infty} \frac{(n+1)!}{(2n-1)!!}\, \boldsymbol{M}_e^{(n)}\, [n]\, \boldsymbol{M}_e^{(n)}\, \langle r_{pq}^{-2(n+2)}\rangle. \quad (5.19)$$

For quadrupole molecules, eq. (5.19) immediately leads to the result (5.16).

For tetrahedral molecules (CH_4, CCl_4), with an octupole moment

$M_e^{(3)} = \Omega_{123}$, and a hexadecapole moment $M_e^{(4)} = \Phi_{1133}$, we obtain, with regard to eq. (5.19),

$$B_1^{2\omega}(0)_{\mathrm{coh}} = 16\,|c_{2\omega}|^2\,N\{\Omega_{123}^2\langle r_{pq}^{-10}\rangle + (25/7)\Phi_{1133}^2\langle r_{pq}^{-12}\rangle\}. \qquad (5.19a)$$

Obviously, one should keep in mind that tetrahedral molecules cause, in the first place, incoherent three-photon scattering (3.12).

In octahedral molecules (SF_6), the first nonzero moment is a hexadecapole, and eq. (5.19a) leads to

$$B_1^{2\omega}(0)_{\mathrm{coh}} = (400/7)\,|c_{2\omega}|^2\,N\,\Phi_{1133}^2\langle r_{pq}^{-12}\rangle. \qquad (5.19b)$$

Since, at present, we have available the numerical values of the nonlinear polarizabilities $c_{2\omega}$, as well as the quadrupole, octupole and hexadecapole moments of various simpler molecules (Stogryn [1966] and Kielich [1972a, 1980a]), the formulae (5.16)–(5.18), (5.19a) and (5.19b) are directly applicable for numerical evaluation. The three-photon cooperative scattering evaluated in this way is, in some cases, by two orders of magnitude greater than the scattering effects caused by the many-body collisional effects discussed in § 5.2.1. The collisional contributions to three-photon scattering are accessible to evaluation for tetrahedral molecules, since the numerical values of their multipole polarizabilities are known (Amos [1979]).

(iii) The depolarization ratio

Going over in eq. (4.37) to integral scattering, we obtain, for the depolarization ratio of three-photon cooperative scattering

$$D_V^{2\omega} = \frac{7B_1^{2\omega}(0) + 12B_3^{2\omega}(0)}{63B_1^{2\omega}(0) + 18B_3^{2\omega}(0)}. \qquad (5.20)$$

As mentioned in § 3, $B_1^{2\omega} = 0$ for incoherent scattering by tetrahedral molecules, so that (5.20) gives $D_V^{2\omega} = \frac{2}{3}$ (Kielich [1964a]). For coherent scattering and the model described by eq. (5.19), the depolarization ratio (5.20) gives $D_V^{2\omega} = \frac{1}{9}$. We see that, depending on the type of scattering and the molecular model assumed, the depolarization ratio (5.20) takes a value ranging from $\frac{1}{9}$ to $\frac{2}{3}$ (Kielich, Lalanne and Martin [1973]):

$$\tfrac{1}{9} = 0.11 \leq D_V^{2\omega} \leq \tfrac{2}{3} = 0.66. \qquad (5.20a)$$

Table 5.1 shows that the theoretical relation (5.20a) is satisfactorily confirmed by the existing experimental results for three-photon scattering, both for liquids composed of molecules without a centre of symmetry and for ones composed of centrosymmetric molecules.

TABLE 5.1

Experimental values of the depolarization ratio D_V^{ω} for linear scattering and $D_V^{2\omega}$ for second-harmonic scattering by molecular liquids

Liquid	Point group	D_V^{ω}	$D_V^{2\omega}$	Authors
H_2O	C_{2v}	0.057	0.116	TERHUNE, MAKER, SAVAGE [1965]
CCl_4	T_d	0.02	0.345	TERHUNE, MAKER, SAVAGE [1965]
			0.51	MAKER [1970]
			0.45	KIELICH, LALANNE, MARTIN [1972]
$CHCl_3$	C_{3v}	0.11	0.65	MAKER [1970]
$C_4H_{10}O$		0.038	0.16	MAKER [1970]
C_7H_{14}	C_s	0.058	0.10	MAKER [1970]
CH_3OH	C_{3v}	0.025	0.17	MAKER [1970]
n-C_3H_7OH	C_s	0.025	0.45	MAKER [1970]
iso-C_3H_7OH		0.02	0.21	MAKER [1970]
C_6H_{12}	D_{3d}	0.025	0.12	KIELICH, LALANNE, MARTIN [1971, 1972]
C_2Cl_4	D_{2h}		0.20	KIELICH, LALANNE, MARTIN [1971]
$C_2H_2Cl_2$	C_{2h}	0.25	0.24	KIELICH, LALANNE, MARTIN [1971]
C_6H_6	D_{6h}	0.27	0.17	KIELICH, LALANNE, MARTIN [1973, 1972]
CS_2	$D_{\infty h}$	0.48	0.21	KIELICH, LALANNE, MARTIN [1973, 1972]
CH_3CN	$C_{\infty v}$		0.10	TERHUNE, MAKER, SAVAGE [1965]

LALANNE, MARTIN and KIELICH [1975] have applied the earlier discovered and studied cooperative three-photon scattering (KIELICH, LALANNE and MARTIN [1971, 1972, 1973]) to the numerical determination of the quadrupole moments of centrosymmetric molecules from eqs. (5.16)–(5.18). Maybe in the near future eqs. (5.19a) and (5.19b) can be used to determine molecular octupoles and hexadecapoles, as hitherto done with success on the basis of collision-induced far infrared absorption (see, for example, GRAY [1971] and BIRNBAUM and COHEN [1975]) and dielectric measurements (KIELICH [1965b, c] and ISNARD, ROBERT and GALATRY [1980]).

Quite recently, TELLE and LAUBEREAU [1980] have observed a sharp increase of second-harmonic generation of picosecond laser pulses, suggesting this increase may be caused by a cooperative mechanism of clusters due to hydrogen bonding in water. In our approach, when dealing with this case, all successive contributions from intrinsic dipoles, quadrupoles and octupoles, the numerical values of which are available for H_2O (see STOGRYN [1966]), have to be taken into account in eq. (5.19), and the function $B_3^{2\omega}(0)_{\mathrm{coh}}$ (containing, like eq. (5.18) quadrupole contributions only) has to be calculated.

Wołejko and Kielich [1975] have analyzed the influence exerted on three-photon scattering by statistical molecular reorientation induced by an intense laser beam. Nitsolov [1977] has considered the influence of thermal fluctuations of density on three-photon scattering of the dipole-quadrupole type.

Kielich, Kozierowski and Lalanne [1975] have developed a theory of three-photon scattering in solutions consisting of atoms and molecules with electric multipoles. The only hitherto known observations by Lalanne, Kielich, Kozierowski and Planner [1976] concern CCl_4–C_6H_{12} solutions. Studies of solutions of this kind are highly relevant, since in CCl_4 we deal chiefly with incoherent three-photon scattering, whereas (as we have seen) C_6H_{12} gives rise to coherent three-photon scattering only. It is worth noting that Schmid and Schrötter [1977] have reported observations of hyper-Raman spectra from CCl_4–C_2Cl_4 solutions.

Andrews [1979a] has analyzed hyper-Raman scattering by oriented molecules in liquid and molecular crystals.

Four-photon scattering is less sensitive to cooperative effects, as was confirmed recently by Kildal and Brueck [1980] when studying third-harmonic generation in cryogenic liquids.

§ 6. Raman Line Broadening in Multi-Photon Scattering (Classical Treatment)

The discussions in §§ 4 and 5 make it clear that, in general, not only incoherent scattering on free molecules but moreover – and in some cases primarily – coherent scattering on statistically correlated molecules has to be taken into consideration. Mathematically, however, the description of coherent scattering processes, though formally feasible, is beset with difficulties when it comes to concrete numerical evaluations, chiefly for a lack of the analytical form of the many-body correlation functions. Luckily the situation is quite different with regard to the analysis of Raman multi-photon spectra since, in this case, coherent scattering may be neglected with sufficient accuracy. This is so because the normal vibrations of molecules (even in certain liquids) can be treated as statistically independent (Bartoli and Litovitz [1972] and Nafie and Peticolas [1972]). Within this approximation Raman line shape studies provide information regarding the translational and rotational motions of the individual molecules in contradistinction to Rayleigh scattering, where molecular correlations play an outstanding role and may not be neglected, expecially in liquids (see, for example, § 5 for a discussion of cooperative scattering).

As in the case of usual Raman scattering, the normal vibrations are responsible for the vibrational hyper-Raman lines, whereas the translational and rotational motions of the molecules broaden the lines by $\Delta\omega_n$ about the central values $n\omega \pm \omega_m$ of the latter. In order to prove the aforesaid we have recourse to the classical treatment of § 3.3, which led us to the scattering tensor (3.28). In the spectral case of § 4 it takes the form

$$\begin{aligned} I^{n\omega\mp\omega_m}_{\sigma\tau}(\boldsymbol{R}, t) &= [N f^{\mp}_m/2^{n-1}(n!)^2]\,[(n\omega \mp \omega_m)/c]^4\, I^n g^{(n)} \\ &\quad \times \langle |Q^t_m|^2\rangle C_m(t)\, K^{n\omega\mp\omega_m}_{\sigma\tau}(\boldsymbol{R}, t), \end{aligned} \tag{6.1}$$

where we have introduced the normalized vibrational autocorrelation function

$$C_m(t) = \langle Q^{0*}_m Q^t_m\rangle / \langle |Q^t_m|^2\rangle \tag{6.2}$$

and the tensor of translational-rotational and polarizational autocorrelations

$$\begin{aligned} K^{n\omega\mp\omega_m}_{\sigma\tau}(\boldsymbol{R}, t) = \sum_{JKLMM'} &(2J+1)^{-1}\,\langle f^J_{MM'}(\boldsymbol{r}_t, t) \exp(-\mathrm{i}\Delta\boldsymbol{k}_n \cdot \boldsymbol{r}_t)\rangle \\ &\times \tilde{a}^{(J)L}_{M:m}(n\omega)^*\, \tilde{a}^{(J)L}_{M':m}(n\omega)\, \Phi^{JKL}_{\sigma\tau} \\ &\times \exp[-\mathrm{i}(n\omega \mp \omega_m)t] \end{aligned} \tag{6.3}$$

with $\Phi^{JKL}_{\sigma\tau}$ given by eq. (3.29). On calculating the Fourier transform of (6.3) we obtain, by (4.8), the spectral density tensor of multi-photon Raman scattering with the frequency change $\Delta\omega_n = \omega_s - (n\omega \mp \omega_m)$

$$\begin{aligned} S^{n\omega\mp\omega_m}_{\sigma\tau}(\Delta\boldsymbol{k}_n, \Delta\omega_n) = \sum_{JKLMM'} &(2J+1)^{-1}\, f^J_{MM'}(\Delta\boldsymbol{k}_n, \Delta\omega_n) \\ &\times \tilde{a}^{(J)L}_{M:m}(n\omega)^*\, \tilde{a}^{(J)L}_{M':m}(n\omega)\, \Phi^{JKL}_{\sigma\tau}, \end{aligned} \tag{6.4}$$

where we have introduced the following spectral function:

$$\begin{aligned} f^J_{MM'}(\Delta\boldsymbol{k}_n, \Delta\omega_n) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}t \int_{-\infty}^{\infty} &\mathrm{d}\boldsymbol{r}_t f^J_{MM'}(\boldsymbol{r}_t, t) \\ &\times \exp[\mathrm{i}(\Delta\omega_n t - \Delta\boldsymbol{k}_n \cdot \boldsymbol{r}_t)]. \end{aligned} \tag{6.5}$$

After Gordon [1965], for Raman processes, the spectral function (6.5) can be calculated separately for molecular motion at short and long times.

On taking STEELE and PECORA's solution [1965] for the short-time approximation we can write (6.5) in the form

$$f^J_{MM'}(\Delta \boldsymbol{k}_n, \Delta\omega_n) = \delta_{MM'}\, G^J_M(\Delta \boldsymbol{k}_n, \Delta\omega_n), \tag{6.6}$$

where, for a molecule of mass m and inertia moment I,

$$G^J_M(\Delta \boldsymbol{k}_n, \Delta\omega_n) = \{2\pi m I/kT[mJ(J+1)+I\,|\Delta \boldsymbol{k}_n|^2]\}^{\frac{1}{2}}$$
$$\times \exp\{-|\Delta\omega_n|^2\,[mI/2kT[mJ(J+1)+I\,|\Delta \boldsymbol{k}_n|^2]]\}. \tag{6.6a}$$

In particular, for $\Delta k_n \to 0$ and $J=0$, we have

$$\lim_{\Delta k_n \to 0} G^J_M(\Delta k_n, \Delta\omega_n) = 2\pi\delta(\Delta\omega_n). \tag{6.6b}$$

Thus, in the present case, the total scattered spectrum consists of a sum of Gaussian shape functions centered about $\Delta\omega_n$, with width determined by the mass and moments of inertia of the scatterer.

The properties of the function (6.5) at long times may be simulated by a stochastic (Markov) process. As mentioned in § 4, the sole stochastic model for which the complete analytical form of $f^J_{MM'}(\boldsymbol{r}_t, t)$ is known is that of free diffusion of translational-rotational motions of Brownian particles, giving eqs. (4.23) and (4.31). In spite of numerous objections the model is still in common use due to its heuristic value and simplicity, permitting the expression of (6.5) in the form

$$f^J_{MM'}(\Delta \boldsymbol{k}_n, \Delta\omega_n) = \delta_{MM'}\, L^J_M(\Delta \boldsymbol{k}_n, \Delta\omega_n). \tag{6.7}$$

Above, we have introduced the generalized Lorentz function for the translational-rotational shape of the spectrum

$$L^J_M(\Delta \boldsymbol{k}_n, \Delta\omega_n) = \frac{1}{\pi}\,\frac{1/\tau^J_M + |\Delta \boldsymbol{k}_n|^2 D_{\mathrm{T}}}{(\Delta\omega_n)^2 + (1/\tau^J_M + |\Delta \boldsymbol{k}_n|^2 D_{\mathrm{T}})^2}. \tag{6.7a}$$

The half-width of the preceding Lorentzian lines amounts to $(\Delta\omega_n)_{1/2} = 2(1/\tau^J_M + |\Delta \boldsymbol{k}_n|^2 D_{\mathrm{T}})$. Under normal experimental conditions $1/\tau^J_M \gg |\Delta \boldsymbol{k}_n|^2 D_{\mathrm{T}} = \tau_{\mathrm{T}}^{-1}$ (e.g. for molecules $\tau_{\mathrm{T}} \sim 10^{-5}$ s), whereas $\tau^J_M \sim 10^{-12}$ s and the effect of translational motion of the molecules in broadening the spectral lines is determined by their rotation relaxation times τ^J_M only:

$$L^J_M(0, \Delta\omega_n) = \frac{1}{\pi}\,\frac{\tau^J_M}{1+(\Delta\omega_n \tau^J_M)^2}, \tag{6.7b}$$

where, now, $(\Delta\omega_n)_{1/2} = 1/\tau^J_M$.

In fact, the spectral functions (6.5)–(6.7) are applicable both to multi-photon Raman scattering processes and to the incoherent Rayleigh scattering processes discussed in § 4. In this sense, the applicability of the diffusion model (6.7) can be justified by arguments put forward by STARUNOV [1965], who considers the broadening of the central part of the spectrum of the depolarized component of Rayleigh scattering, adjacent on the central line and extending to 3–15 cm^{-1} on both sides of the latter, to be due to rotational Brownian motions. All the other processes taking place in the liquid (in short-time approximation) affect the shape and fine structure of the wings. Maybe, in some cases, it would be profitable to replace the model of continuous diffusion (4.31) by some other model of molecular motion, e.g. that of "diffusion by jumps" (see VALIYEV and IVANOV [1973]), or the J- or M-diffusion model (see, for example, STEELE [1976] and MCCLUNG [1977]). However, distribution functions for jumpwise diffusion models applicable to molecular spectroscopy are available, strictly speaking, for the spherical top only; in the long run, they too lead to a Lorentzian spectral distribution, albeit with other relaxation times.

Hence, on the free diffusion model and with regard to eq. (6.7), the spectral density tensor (6.4) for the nth order hyper-Raman is, finally,

$$S_{\sigma\tau}^{n\omega\mp\omega_n}(\Delta\boldsymbol{k}_n, \Delta\omega_n) = \sum_{JKLM} (2J+1)^{-1}\, L_M^J(\Delta\boldsymbol{k}_n, \Delta\omega_n)\, |\tilde{a}_{M:m}^{(J)L}(n\omega)|^2\, \Phi_{\sigma\tau}^{JKL}. \tag{6.8}$$

The preceding spectral theory of hyper-Raman scattering differs essentially from the theory of incoherent "quasi-elastic" multi-photon scattering processes of § 4 in two ways. First, the molecular parameters $|\tilde{a}_{M:m}^{(J)L}(n\omega)|^2$ of eq. (6.8) are defined via the nonzero components of the spherical nonlinear Raman polarizability tensor, related to the normal vibration Q_m of frequency ω_m. Their selection rules are dependent on the symmetry of the molecule and type $\Gamma^{(m)}$ of the vibration considered (cf. eq. (3.47)). Second, to determine the Fourier transform of (6.1), one has to be in a position to separate the intrinsic shape of the natural vibrational line, determined by the correlation function (6.2), from the observed nth order Raman spectrum.

The vibrational autocorrelation functions (6.2) are accessible to determination from IR absorption and usual Raman scattering measurements by measuring the spectral distribution, whence the part related with vibrations of the molecule can be separated (NAFIE and PETICOLAS [1972]):

$$C_m(\Delta\omega_m) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}t\, C_m(t) \exp(\mathrm{i}\Delta\omega_m t). \tag{6.9}$$

This Fourier transform is a function of the intrinsic vibrational line shape. Its independent determination from three- and five-photon scattering is not possible because, as we know, processes with even harmonics produce no isotropic scattering; the latter, however, does take place in processes involving odd harmonics.

Hence, having available the total correlation tensor (6.1) or Fourier transform of the hyper-Raman scattering spectrum observed and, independently, the vibrational functions (6.2) or (6.9), one is able to determine the translational-rotational tensor (6.3) and its Fourier transform (6.4) or (6.8).

Kielich, Kozierowski and Ożgo [1977] have proposed a more general treatment of the problem taking into account, among other things, the fact that one has to consider the Fourier transform of the total tensor (6.1) which, generally, is not a product of the spectral density tensor (6.4) or (6.8) and Fourier transform of the vibrational functions (6.9). In other words, we have in general a convolution of the intrinsic vibration line shape with the translational-vibrational spectrum (see, for example, Bartoli and Litovitz [1972]).

Equations (6.1)–(6.8) are applicable to two-, three-, four- and more-photon Raman scattering.

6.1. THREE-PHOTON RAMAN SCATTERING

For the sake of simplicity, we shall discuss the spectral density tensor (6.8) only. In the three-photon case it becomes

$$S_{\sigma\tau}^{2\omega\mp\omega_m}(\Delta\boldsymbol{k}_2, \Delta\omega_2) = \frac{1}{21} \sum_{KM} \{7L_M^1(\Delta\boldsymbol{k}_2, \Delta\omega_2)|\tilde{b}_{M:m}^{(1)}|^2\, \Phi_{\sigma\tau}^{1\boldsymbol{K}} + 3L_M^3(\Delta\boldsymbol{k}_2, \Delta\omega_2)\,|\tilde{b}_{M:m}^{(3)}|^2\, \Phi_{\sigma\tau}^{3K}\}. \tag{6.10}$$

Here, we have assumed the nonlinear polarizability tensor $\tilde{b}_{M:m}^{(J)L}$ in the simpler, completely symmetric form $\tilde{b}_{M:m}^{(J)}$.

We note that the hyper-Raman line shape (6.10) is in general a superposition of several Lorentz lines (6.7a), among which one can distinguish spectra for $J = 1$ and $J = 3$. If the anisotropy of the rotational diffusion tensor in (4.31a) is considerable for the molecule under consideration, several lines with different M-values appear within the same value of J. The nonzero molecular parameters $|\tilde{b}_{M:m}^{(J)}|^2$ for all groups of molecular symmetry and all types of vibrations, active in hyper-Raman, are to be found in tabulated form in papers by Alexiewicz, Bancewicz, Kielich and Ożgo [1974] and Bancewicz [1976].

For linearly polarized incident light, the spectral density tensor (6.10) becomes

$$S_{\mathrm{VV}}^{2\omega\mp\omega_m}(\Delta\boldsymbol{k}_2, \Delta\omega_2) = \frac{1}{35}\sum_M \{7L_M^1(\Delta\boldsymbol{k}_2, \Delta\omega_2)\,|\tilde{b}^{(1)}_{M:m}|^2 + 2L_M^3(\Delta\boldsymbol{k}_2, \Delta\omega_2)\,|\tilde{b}^{(3)}_M|^2\}, \tag{6.11a}$$

$$S_{\mathrm{HV}}^{2\omega\mp\omega_m}(\Delta\boldsymbol{k}_2, \Delta\omega_2) = \frac{1}{315}\sum_M \{7L_M^1(\Delta\boldsymbol{k}_2, \Delta\omega_2)\,|\tilde{b}^{(1)}_{M:m}|^2 + 12L_M^3(\Delta\boldsymbol{k}_2, \Delta\omega_2)\,|\tilde{b}^{(3)}_{M:m}|^2\}, \tag{6.11b}$$

whereas for light circularly polarized in the right sense

$$S_{+1+1}^{2\omega\mp\omega_m}(\Delta\boldsymbol{k}_2, \Delta\omega_2) = \frac{1}{315}\sum_M \{28L_M^1(\Delta\boldsymbol{k}_2, \Delta\omega_2)\,|\tilde{b}^{(1)}_{M:m}|^2 + 3L_M^3(\Delta\boldsymbol{k}_2, \Delta\omega_2)\,|\tilde{b}^{(3)}_{M:m}|^2\}, \tag{6.12a}$$

$$S_{-1+1}^{2\omega\mp\omega_m}(\Delta\boldsymbol{k}_2, \Delta\omega_2) = \frac{1}{7}\sum_M L_M^3(\Delta\boldsymbol{k}_2, \Delta\omega_2)\,|\tilde{b}^{(3)}_{M:m}|^2. \tag{6.12b}$$

When studying the rotational motion of the molecules of a liquid, special importance should be attached to those normal vibrations to which only one molecular parameter $|\tilde{b}^{(J)}_{M:m}|^2$ corresponds, since in this case the line-width is dependent on one relaxation time τ_M^J only, and the latter can be determined from eq. (6.7). For example, such is the case of the molecules of C_2H_6 (point group symmetry D_{6h}) and their vibrations of the types B_{1u}, B_{2u} and E_{2u}, for which eqs. (6.11) and (6.12) lead to the relation

$$S_{\mathrm{VV}}^{2\omega\mp\omega_m} = \tfrac{3}{2}S_{\mathrm{HV}}^{2\omega\mp\omega_m} = 6S_{+1+1}^{2\omega\mp\omega_m} = \tfrac{2}{5}S_{-1+1}^{2\omega\mp\omega_m} = \tfrac{4}{35}L_M^3\,|\tilde{b}^{(3)}_{M:m}|^2, \tag{6.13}$$

where one has to put $M=3$ for $m=B_{1u}$ and $m=B_{2u}$, and $M=2$ for $m=E_{2u}$. In this way we derive from eq. (6.7) the rotational relaxational times τ_3^3 or τ_2^3. In the case of the group C_{6h}, one can also determine τ_3^3 for vibrations of the type B_2 and τ_2^3 for E_{2u}. Similarly, τ_M^1 and τ_M^3 are accessible to determination for appropriately selected types of vibrations and molecular symmetries.

The hyper-Raman lines of molecules without a centre of inversion are much weaker than the hyper-Rayleigh line (cf. Fig. 3.4), and are thus more difficult to observe. However, the outlooks become quite promising in the case of centro-symmetric molecules for which elastic three-photon scattering is forbidden in the electric-dipole approximation. Here, one can observe, solely or chiefly, hyper-Raman lines (see Fig. 3.6); and certain of them are forbidden in IR spectroscopy or in the spectroscopy of usual Raman scattering, which provides information on the relaxation times τ_M^2 only. Also, the complete absence or faintness of coherent scattering is a factor in favor of hyper-Raman, as compared to hyper-Rayleigh, spectroscopy.

6.2. FOUR-PHOTON RAMAN SCATTERING

On the assumption of a completely symmetric tensor $\tilde{a}^{(J)L}_{M:m}(3\omega) = \tilde{c}^{(J)}_{M:m}$, eq. (6.8) leads to the following spectral density tensor of four-photon Raman scattering:

$$\begin{aligned} S^{3\omega\mp\omega_m}_{\sigma\tau}(\Delta \boldsymbol{k}_3, \Delta\omega_3) = {} & L_0^0(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(0)}_{0:m}|^2\, \Phi^{00}_{\sigma\tau} \\ & + \frac{1}{45} \sum_{MK} \{9 L_M^2(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(2)}_{M:m}|^2\, \Phi^{2K}_{\sigma\tau} \\ & + 5 L_M^4(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(4)}_{M:m}|^2\, \Phi^{4K}_{\sigma\tau}\}. \end{aligned} \tag{6.14}$$

With the values, tabulated by OŻGO [1975a], of the transformation coefficients $R^{JK}_{\sigma\nu\rho\lambda}$ occurring in the tensor (3.29), we obtain, by (6.14), for incident linearly polarized light

$$\begin{aligned} S^{3\omega\mp\omega_m}_{\mathrm{VV}}(\Delta \boldsymbol{k}_3, \Delta\omega_3) = \Big\{ & \tfrac{1}{5} L_0^0(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(0)}_{0:m}|^2 \\ & + \frac{4}{315} \sum_{M} [9 L_M^2(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(2)}_{M:m}|^2 \\ & + 2 L_M^4(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(4)}_{M:m}|^2] \Big\}, \end{aligned} \tag{6.15a}$$

$$\begin{aligned} S^{3\omega\mp\omega_m}_{\mathrm{HV}}(\Delta \boldsymbol{k}_3, \Delta\omega_3) = \frac{1}{1260} \sum_{M} \{ & 27 L_M^2(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(2)}_{M:m}|^2 \\ & + 20 L_M^4(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(4)}_{M:m}|^2\}, \end{aligned} \tag{6.15b}$$

and for light circularly polarized in the right sense

$$\begin{aligned} S^{3\omega\mp\omega_m}_{+1+1}(\Delta \boldsymbol{k}_3, \Delta\omega_3) = \frac{1}{1260} \sum_{M} \{ & 54 L_M^2(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(2)}_{M:m}|^2 \\ & + 5 L_M^4(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(4)}_{M:m}|^2\}, \end{aligned} \tag{6.16a}$$

$$S^{3\omega\mp\omega_m}_{-1+1}(\Delta \boldsymbol{k}_3, \Delta\omega_3) = \frac{1}{9} \sum_{M} L_M^4(\Delta \boldsymbol{k}_3, \Delta\omega_3)\, |\tilde{c}^{(4)}_{M:m}|^2. \tag{6.16b}$$

Equation (6.15a) conveys to us that third-harmonic Raman, like linear Raman, contains isotropically scattered light, related to the parameter $|c^{(0)}_{0:m}|^2$. This enables us to separate the contribution to the spectral line shape due to vibrational motion of the molecules (6.9). The component (6.16b) is also of interest, since it involves only one term, permitting the determination of the new rotational relaxation time τ^4_M hitherto inaccessible by other methods.

By comparison, in usual Raman the intensity of isotropic scattering can be determined from the relation (Bartoli and Litovitz [1972])

$$I_{\rm is}^{\omega\mp\omega_m} = I_{\rm VV}^{\omega\mp\omega_m} - \tfrac{4}{3} I_{\rm HV}^{\omega\mp\omega_m}. \tag{6.17}$$

Similarly, for third-harmonic Raman we get, by eqs. (6.1), (6.15) and (6.16), the relation

$$I_{\rm is}^{3\omega\mp\omega_m} = I_{\rm VV}^{3\omega\mp\omega_m} - \tfrac{16}{3} I_{\rm HV}^{3\omega\mp\omega_m} + \tfrac{8}{15} I_{-1+1}^{3\omega\mp\omega_m} \tag{6.18}$$

permitting the determination of the isotropic third-harmonic scattering component, and hence the vibration function (6.2). In particular, for spherical top molecules $|c^{(2)}_{M:m}|^2 = 0$ and eqs. (6.15) and (6.16) lead to the relation

$$7 I_{\rm HV}^{3\omega\mp\omega_m} = I_{-1+1}^{3\omega\mp\omega_m} = 28 I_{+1+1}^{3\omega\mp\omega_m} \tag{6.19}$$

with regard to which the relation (6.18) reduces to (see Kielich, Kozierowski and Ożgo [1977]):

$$I_{\rm is}^{3\omega\mp\omega_m} = I_{\rm VV}^{3\omega\mp\omega_m} - \tfrac{8}{5} I_{\rm HV}^{3\omega\mp\omega_m}. \tag{6.20}$$

The determination of the isotropic component of third-harmonic scattering, in this case, requires the measurement of two components only, as in that of the usual Raman scattering effect given by the relation (6.17).

§ 7. Angular Distribution and Polarization States of Multi-Photon Scattered Light

7.1. THE SCATTERING TENSORS IN TERMS OF STOKES PARAMETERS

The state of polarization of a plane quasi-monochromatic light wave, propagating along the Z-axis with electric vector

$$\boldsymbol{E}(t) = \boldsymbol{E}_x(t) + \boldsymbol{E}_y(t), \tag{7.1}$$

is usually expressed in terms of the Stokes parameters (Born and Wolf [1968]):

$$S_0 = E_x^* E_x + E_y^* E_y, \qquad S_1 = E_x^* E_x - E_y^* E_y,$$
$$S_2 = E_x^* E_y + E_y^* E_x, \qquad S_3 = \mathrm{i}(E_y^* E_x - E_x^* E_y). \tag{7.2}$$

These, in fact, are integral Stokes parameters. By analogy, one can introduce spectral Stokes parameters (see Peřina [1972]). Of the four parameters, only three are mutually independent, since the identity

$$S_0^2 = S_1^2 + S_2^2 + S_3^2$$

is fulfilled. With regard to (7.2), we obtain (see Born and Wolf [1968]):

$$E_x^* E_x = \tfrac{1}{2}(S_0 + S_1), \qquad E_y^* E_y = \tfrac{1}{2}(S_0 - S_1),$$
$$E_x^* E_y = \tfrac{1}{2}(S_2 + \mathrm{i}S_3), \qquad E_y^* E_x = \tfrac{1}{2}(S_2 - \mathrm{i}S_3). \tag{7.3}$$

We apply this relation to express the multi-photon scattered intensities in terms of Stokes parameters.

The versors of the incident and scattered wave fields are now, respectively (Fig. 7.1),

$$\boldsymbol{e} = \boldsymbol{x} \sin \psi + \mathrm{e}^{\mathrm{i}\delta}\, \boldsymbol{y} \cos \psi, \tag{7.4}$$

$$\boldsymbol{e}_\mathrm{s} = \boldsymbol{x} \sin \varphi + \mathrm{e}^{\mathrm{i}\delta_\mathrm{s}}(\boldsymbol{y} \cos \Theta - \boldsymbol{z} \sin \Theta) \cos \varphi, \tag{7.5}$$

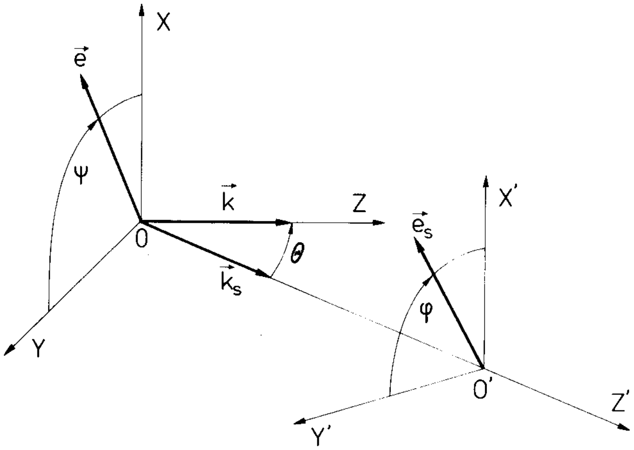

Fig. 7.1. Systems for the calculation of the angular distribution and polarization states of scattered light.

where $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$ are unit vectors in the direction of the axes X, Y and Z of the coordinate system attached to the vector $\boldsymbol{E} = E\boldsymbol{e}$ of the incident light wave.

Here, obviously, we have $\boldsymbol{e} \cdot \boldsymbol{e}^* = 1$ and $\boldsymbol{e}_{\mathrm{s}} \cdot \boldsymbol{e}_{\mathrm{s}}^* = 1$. Equations (7.4) and (7.5) account for all possible states of polarization of incident and scattered light. For example, at $\delta = 0$ the incident wave is linearly polarized at an arbitrary angle to the plane of observation YZ, and we have

$$\boldsymbol{e} = \boldsymbol{x} \sin \psi + \boldsymbol{y} \cos \psi. \tag{7.4a}$$

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

$$\boldsymbol{e}_{\pm} = \boldsymbol{x} \sin \psi \pm \mathrm{i}\boldsymbol{y} \cos \psi. \tag{7.4b}$$

With regard to the angular momentum convention a phase shift $+\pi/2$ refers to right elliptical polarization of the wave and $-\pi/2$ to left elliptical polarization. If, in addition, $\psi = \pi/4$, then eq. (7.4b) gives, for a circularly polarized wave,

$$\boldsymbol{e}_{\pm} = 2^{-1/2}(\boldsymbol{x} \pm \mathrm{i}\boldsymbol{y}). \tag{7.4c}$$

It is our aim to determine the angular distribution and polarization state of the scattered wave. They are given by the intensity tensor components, measured by the analyzer:

$$I^{\mathrm{s}}_{e_s e}(t) = e_{\mathrm{s}\sigma}\, I^{\mathrm{s}}_{\sigma\tau}(t)\, e^*_{\mathrm{s}\tau}, \tag{7.6}$$

where the scattering tensor in Cartesian representation is given by eq. (4.10). Thus, the problem reduces essentially to an analysis of the coherence degree tensor (4.12) or, rather, of its components

$$g^{(n,h)}_{e_s e} = e_{\mathrm{s}\sigma}\, g^{(n,h)}_{\sigma\tau}\, e^*_{\mathrm{s}\tau}, \tag{7.7}$$

where the irreducible components for $n = 1$, 2 and 3 are given respectively by eqs. (4.17), (4.40) and (4.51).

Thus, by (4.37) and (7.6), we obtain the intensity of integral second-harmonic scattering in the form

$$I^{2\omega}_{e_s e}(0) = (Q_{2\omega} I^2/315)\{7B_1^{2\omega}(0)\, g^{(2,1)}_{e_s e} + 3B_3^{2\omega}(0)\, g^{(2,3)}_{e_s e}\}. \tag{7.6a}$$

With regard to the aforesaid, we express the polarization tensors of linear scattering (4.17) in terms of Stokes parameters:

$$\begin{aligned} g_{e_se}^{(1,0)} &= (2\langle S_0\rangle)^{-1}\,\langle (S_0+S_1)\sin^2\varphi+(S_0-S_1)\cos^2\theta\cos^2\varphi \\ &\quad +(S_2\cos\delta_s+S_3\sin\delta_s)\cos\theta\sin 2\varphi\rangle, \\ g_{e_se}^{(1,1)} &= (2\langle S_0\rangle)^{-1}\,\langle 2S_0-(S_0+S_1)\sin^2\varphi-(S_0-S_1)\cos^2\theta\cos^2\varphi \\ &\quad -(S_2\cos\delta_s-S_3\sin\delta_s)\cos\theta\sin 2\varphi\rangle, \\ g_{e_se}^{(1,2)} &= (2\langle S_0\rangle)^{-1}\,\langle 6S_0+(S_0+S_1)\sin^2\varphi+(S_0-S_1)\cos^2\theta\cos^2\varphi \\ &\quad +(S_2\cos\delta_s-5S_3\sin\delta_s)\cos\theta\sin 2\varphi\rangle, \end{aligned} \tag{7.8}$$

and, similarly, those of symmetric three-photon scattering (4.40):

$$\begin{aligned} g_{e_se}^{(2,1)} &= \langle S_0\rangle^{-2}\,\langle S_0^2-S_3^2+2(2S_0^2+2S_0S_1-S_3^2)\sin^2\varphi \\ &\quad +2(2S_0^2-2S_0S_1-S_3^2)\cos^2\theta\cos^2\varphi \\ &\quad +2S_0\,(2S_2\cos\delta_s+S_3\sin\delta_s)\cos\theta\sin 2\varphi\rangle, \\ g_{e_se}^{(2,3)} &= \langle S_0\rangle^{-2}\,\langle 4S_0^2+S_3^2+(S_0^2+S_0S_1+2S_3^2)\sin^2\varphi \\ &\quad +(S_0^2-S_0S_1+2S_3^2)\cos^2\theta\cos^2\varphi \\ &\quad +S_0\,(S_2\cos\delta_s-7S_3\sin\delta_s)\cos\theta\sin 2\varphi\rangle. \end{aligned} \tag{7.9}$$

We now proceed to consider the polarization parameters (7.8) and (7.9) for various states of polarization of the incident $\boldsymbol{e}$ and scattered $\boldsymbol{e}_s$ photons.

7.2. NATURAL INCIDENT LIGHT

Hitherto, no unequivocal model of natural light is available (see, for example, Prakash and Chandra [1971]). We shall accordingly consider some plausible models (Wołejko, Kozierowski and Kielich [1978]):

(a) On the traditional model, natural light is considered to be a superposition of two waves, linearly polarized, or polarized circularly in opposite senses, with amplitudes equal and constant but with uncorrelated phases. This is the equivalent of a single wave with fluctuating direction of polarization and constant amplitude (see, for example, Born and Wolf [1968]). In this case, by (7.4a), one has for the linear Stokes parameters:

$$\langle S_0\rangle = \langle |E|^2\rangle, \qquad \langle S_1\rangle = \langle S_2\rangle = \langle S_3\rangle = 0, \tag{7.10}$$

and for the nonzero nonlinear Stokes parameters:

$$\langle S_0^2\rangle = 2\langle S_1^2\rangle = 2\langle S_2^2\rangle = \langle S_0\rangle^2, \tag{7.11a}$$

so that the parameters (7.8) reduce to the form well known from the literature:

$$\begin{aligned} g_{e_s u}^{(1,0)} &= \tfrac{1}{2}(\sin^2\varphi + \cos^2\varphi\cos^2\theta), \\ g_{e_s u}^{(1,2)} &= \tfrac{1}{2}(6 + \sin^2\varphi + \cos^2\varphi\cos^2\theta). \end{aligned} \tag{7.8a}$$

On the same model the nonlinear scattering parameters (7.9) take the form

$$\begin{aligned} g_{e_s u}^{(2,1)} &= 1 + 4(\sin^2\varphi + \cos^2\varphi\cos^2\theta), \\ g_{e_s u}^{(2,3)} &= 4 + \sin^2\varphi + \cos^2\varphi\cos^2\theta. \end{aligned} \tag{7.9a}$$

With regard to eq. (7.6a), this leads to the results of CYVIN, RAUCH and DECIUS [1965] (see also KIELICH and KOZIEROWSKI [1972]).

(b) Natural light is treated as the superposition of two waves with mutually orthogonal polarizations, equal amplitudes, and independently fluctuating phases (STRIZHEVSKY and KLIMENKO [1967]), so that the linear Stokes parameters have the form (7.10), whereas the nonzero nonlinear ones take the form

$$\langle S_0^2\rangle = 2\langle S_2^2\rangle = 2\langle S_3^2\rangle = \langle S_0\rangle^2. \tag{7.11b}$$

In this case, the linear parameters (7.8) have the form (7.8a), whereas the nonlinear ones (7.9) assume the following form:

$$\begin{aligned} g_{e_s u}^{(2,1)} &= \tfrac{1}{2}\{1 + 6(\sin^2\varphi + \cos^2\varphi\cos^2\theta)\}, \\ g_{e_s u}^{(2,3)} &= \tfrac{1}{2}\{9 + 4(\sin^2\varphi + \cos^2\varphi\cos^2\theta)\}, \end{aligned} \tag{7.9b}$$

and eq. (7.6a) leads to the formulae of STRIZHEVSKY and KLIMENKO [1967] for the depolarization ratios and their angular dependence.

(c) Natural light is a superposition of two waves, orthogonally (linearly or circularly) polarized, with independently fluctuating phases and mutually independent Gaussian amplitudes. One now has, in addition to (7.10), the following nonzero nonlinear Stokes parameters:

$$\langle S_0^2\rangle = 3\langle S_1^2\rangle = 3\langle S_2^2\rangle = 3\langle S_3^2\rangle = \tfrac{3}{2}\langle S_0\rangle^2. \tag{7.11c}$$

Equation (7.8a) still holds, whereas the nonlinear polarizational parameters have the form:

$$\begin{aligned} g_{e_s u}^{(2,1)} &= 1 + 5(\sin^2\varphi + \cos^2\varphi\cos^2\theta), \\ g_{e_s u}^{(2,3)} &= \tfrac{1}{2}[13 + 5(\sin^2\varphi + \cos^2\varphi\cos^2\theta)], \end{aligned} \tag{7.9c}$$

and, for the depolarization ratios, one has the ANDREWS–THIRUNAMACHANDRAN [1977b] relation.

(d) Natural light is a multi-mode light (ALTMAN and STREY [1977] and STREY [1980]). On the assumption that all N incoherent modes have the same intensity, and that N is infinite, this model leads to the same results as the model (c). This is so because, as shown by PRAKASH and CHANDRA [1971], if two orthogonally polarized components of unpolarized light are statistically independent, the radiation is necessarily chaotic.

We note that, in linear scattering, all four models of natural light lead to identical results; however, nonlinear scattering is strongly model-sensitive and can be considered as a test of the correctness of the natural light model assumed.

7.3. LINEARLY POLARIZED INCIDENT LIGHT

(i) Incident light, polarized in the vertical plane ($E_x \neq 0$, $E_y = 0$) is, with regard to (7.2), characterized by the following Stokes parameters:

$$S_0 = S_1 = |E_x|^2, \qquad S_2 = S_3 = 0, \tag{7.2a}$$

causing the polarizational parameters of linear scattering (7.8) to take the form:

$$g_{e_s V}^{(1,0)} = \sin^2 \varphi; \qquad g_{e_s V}^{(1,2)} = 3 + \sin^2 \varphi, \tag{7.12}$$

and those of nonlinear scattering (7.9) to become

$$g_{e_s V}^{(2,1)} = g_V^{(2)}(1 + 8 \sin^2 \varphi), \qquad g_{e_s V}^{(2,3)} = g_V^{(2)}(4 + 2 \sin^2 \varphi). \tag{7.13}$$

These parameters take the following values for the vertical scattered component ($\varphi = 90°$):

$$g_{VV}^{(1,0)} = 1, \qquad g_{VV}^{(1,2)} = 4, \tag{7.12a}$$

$$g_{VV}^{(2,1)} = 9 g_V^{(2)}, \qquad g_{VV}^{(2,3)} = 6 g_V^{(2)}, \tag{7.13a}$$

and, for the horizontal scattered component ($\varphi = 0°$),

$$g_{HV}^{(1,0)} = 0, \qquad g_{HV}^{(1,2)} = 3, \tag{7.12b}$$

$$g_{HV}^{(2,1)} = g_V^{(2)}, \qquad g_{HV}^{(2)} = 4 g_V^{(2)}. \tag{7.13b}$$

In this case, by (7.6a), the depolarization ratio is given by (5.20).

(ii) For incident light, polarized in the horizontal plane ($E_x = 0$, $E_y \neq 0$), the Stokes parameters (7.1) take the values

$$S_0 = -S_1 = |E_y|^2, \qquad S_2 = S_3 = 0. \tag{7.2b}$$

In this case, the polarizational parameters of linear (7.8) and nonlinear

(7.9) scattering assume the form:

$$\mathrm{g}_{e_s\mathrm{H}}^{(1,0)}=\cos^2\varphi\cos^2\theta,\qquad \mathrm{g}_{e_s\mathrm{H}}^{(1,2)}=3+\cos^2\varphi\cos^2\theta,\tag{7.14}$$

$$\mathrm{g}_{e_s\mathrm{H}}^{(2,1)}=\mathrm{g}_{\mathrm{H}}^{(2)}(1+8\cos^2\varphi\cos^2\theta),\qquad \mathrm{g}_{e_s\mathrm{H}}^{(2,3)}=\mathrm{g}_{\mathrm{H}}^{(2)}(4+2\cos^2\varphi\cos^2\theta).\tag{7.15}$$

One obtains, for the vertical scattered component ($\varphi=90°$)

$$\mathrm{g}_{\mathrm{VH}}^{(1,0)}=0,\qquad \mathrm{g}_{\mathrm{VH}}^{(1,2)}=3,\tag{7.14a}$$

$$\mathrm{g}_{\mathrm{VH}}^{(2,1)}=\mathrm{g}_{\mathrm{H}}^{(2)},\qquad \mathrm{g}_{\mathrm{VH}}^{(2,3)}=4\mathrm{g}_{\mathrm{H}}^{(2)},\tag{7.15a}$$

and for the horizontal scattered component ($\varphi=0°$)

$$\mathrm{g}_{\mathrm{HH}}^{(1,0)}=\cos^2\theta,\qquad \mathrm{g}_{\mathrm{HH}}^{(1,2)}=3+\cos^2\theta,\tag{7.14b}$$

$$\mathrm{g}_{\mathrm{HH}}^{(2,1)}=\mathrm{g}_{\mathrm{H}}^{(2)}(1+8\cos^2\theta),\qquad \mathrm{g}_{\mathrm{HH}}^{(2,3)}=\mathrm{g}_{\mathrm{H}}^{(2)}(4+2\cos^2\theta).\tag{7.15b}$$

Defining the depolarization ratio as $D_{\mathrm{H}}^{2\omega}=I_{\mathrm{VH}}^{2\omega}/I_{\mathrm{HH}}^{2\omega}$, we have by eq. (7.6a) (Kielich [1968a]):

$$D_{\mathrm{H}}^{2\omega}(\theta)=\frac{7B_1^{2\omega}(0)+12B_3^{2\omega}(0)}{7B_1^{2\omega}(0)+12B_3^{2\omega}(0)+2[28B_1^{2\omega}(0)+3B_3^{2\omega}(0)]\cos^2\theta}\tag{7.16}$$

yielding, at perpendicular observation, $D_{\mathrm{H}}^{2}(90°)=1$.

7.4. CIRCULARLY POLARIZED INCIDENT LIGHT

In the case of circularly polarized incident light, eq. (7.4c) leads to only two Stokes parameters,

$$S_0=|E_+|^2+|E_-|^2,\qquad S_3=|E_-|^2-|E_+|^2.\tag{7.17}$$

When calculating the reversal ratio for incident light circularly polarized in the right sense only ($e=+1$), one has to put $\delta_s=\mp\pi/2$, $\varphi=\pi/4$, and $e_s=\pm1$ in eqs. (7.8) for forward scattering. This leads to the following results, well known from the literature, referring to isotropic, antisymmetric, and anisotropic scattering (see Placzek [1934]):

$$\mathrm{g}_{-1+1}^{(1,0)}/\mathrm{g}_{+1+1}^{(1,0)}=\mathrm{tg}^4\theta/2,\tag{7.18a}$$

$$\mathrm{g}_{-1+1}^{(1,1)}/\mathrm{g}_{+1+1}^{(1,1)}=\frac{1-\cos^4\theta/2}{1-\sin^4\theta/2},\tag{7.18b}$$

$$\mathrm{g}_{-1+1}^{(1,2)}/\mathrm{g}_{+1+1}^{(1,2)}=\frac{13+10\cos\theta+\cos^2\theta}{13-10\cos\theta+\cos^2\theta}.\tag{7.18c}$$

Let us return to the nonlinear polarization parameters (7.9). By (7.17), for right-circularly polarized incident light, they take the form

$$g^{(2,1)}_{e_s+1} = 2g^{(2)}_{+1}(\sin^2\varphi + \cos^2\theta\cos^2\varphi - \sin\delta_s\cos\theta\sin 2\varphi),$$
$$g^{(2,3)}_{e_s+1} = g^{(2)}_{+1}[5 + 3(\sin^2\varphi + \cos^2\theta\cos^2\varphi) + 7\sin\delta_s\cos\theta\sin 2\varphi]. \quad (7.19)$$

(i) Depolarization ratio

At $\delta_s = 0$, the expressions (7.19) take the following form for the vertical ($\varphi = 90°$) and horizontal ($\varphi = 0°$) component, respectively:

$$\begin{aligned} g^{(2,1)}_{V+1} &= 2g^{(2)}_{+1}, & g^{(2,3)}_{V+1} &= 8g^{(2)}_{+1}, \\ g^{(2,1)}_{H+1} &= 2g^{(2)}_{+1}\cos^2\theta, & g^{(2,3)}_{H+1} &= g^{(2)}_{+1}(5 + 3\cos^2\theta), \end{aligned} \quad (7.19a)$$

from which (7.6a) now leads to the depolarization ratio of circularly polarized incident light (KIELICH and KOZIEROWSKI [1974]):

$$D^{2\omega}_{+1}(\theta) = \frac{15B^{2\omega}_3(0) + [14B^{2\omega}_1(0) + 9B^{2\omega}_3(0)]\cos^2\theta}{14B^{2\omega}_1(0) + 24B^{2\omega}_3(0)}. \quad (7.20)$$

In the particular case of tetrahedrally symmetric molecules in the absence of cooperative scattering $B^{2\omega}_1(0) = 0$, and the depolarization ratio (7.19) becomes

$$D^{2\omega}_{+1}(\theta) = (5 + 3\cos^2\theta)/8. \quad (7.20a)$$

At perpendicular observation of the scattered light ($\theta = 90°$) we obtain the value $D^{2\omega}_{+1}(90°) = 5/8$, to be considered as the upper limit.

For cooperative three-photon scattering one has generally $B^{2\omega}_1(0) \gg B^{2\omega}_3(0)$, so that eq. (7.19) leads to the simple result

$$D^{2\omega}_{+1}(\theta) \simeq \cos^2\theta, \quad (7.20b)$$

signifying that, in the cooperative case, vertically scattered ($\theta = 90°$) light is completely polarized, whereas light scattered into the propagation direction of the incident wave ($\theta = 0°$) is unpolarized.

With regard to (7.19a) and (7.19b), the range of variability of the scattered light depolarization ratio for circularly polarized incident light is

$$0 \leqslant D^{2\omega}_{+1}(90°) \leqslant 5/8. \quad (7.20c)$$

(ii) Reversal ratio

On putting $\varphi = \pi/4$ and $\delta_s = \mp\pi/2$ in (7.19), one obtains

$$\begin{aligned} g^{(2,1)}_{\pm 1+1} &= g^{(2)}_{+1}(1 \pm \cos\theta)^2, \\ g^{(2,3)}_{\pm 1+1} &= \tfrac{1}{2} g^{(2)}_{+1}(13 \mp 14\cos\theta + 3\cos^2\theta) \end{aligned} \tag{7.19b}$$

from which, by (7.6a), one gets, for the angular dependence of the reversal ratio (KIELICH and KOZIEROWSKI [1974]):

$$R^{2\omega}_{+1}(\theta) = \frac{56B^{2\omega}_1(0)\sin^4\theta/2 + 3(13 + 14\cos\theta + 3\cos^2\theta)\,B^{2\omega}_3(0)}{56B^{2\omega}_1(0)\cos^4\theta/2 + 3(13 - 14\cos\theta + 3\cos^2\theta)\,B^{2\omega}_3(0)}. \tag{7.21}$$

In particular, at $\theta = 0°$, eq. (7.21) leads to

$$R^{2\omega}_{+1}(0°) = \frac{45B^{2\omega}_3(0)}{28B^{2\omega}_1(0) + 3B^{2\omega}_3(0)} \tag{7.21a}$$

corresponding to the previously discussed formula (3.49).

For $B^{2\omega}_3(0) \simeq 0$, formula (7.21) leads to

$$R^{2\omega}_{+1}(\theta) = \mathrm{tg}^4\theta/2. \tag{7.21b}$$

In the opposite case of $B^{2\omega}_1(0) \simeq 0$, one obtains

$$R^{2\omega}_{+1}(\theta) = \frac{13 + 14\cos\theta + 3\cos^2\theta}{13 - 14\cos\theta + 3\cos^2\theta}. \tag{7.21c}$$

Thus, the reversal ratio (7.21b) is the same as for the case of isotropic linear scattering (7.18a). In particular $R^{2\omega}_{+1}(0°) = 0$, meaning that cooperatively scattered light is polarized circularly. Equations (7.21b) and (7.21c) lead to the relation (3.50a).

7.5. FOUR-PHOTON LIGHT SCATTERING

The rapid progress achieved recently in the domain of various four-photon spectroscopies stimulates us to supplement this article with an analysis of the angular and polarizational properties of light, scattered in the four-photon processes described by the tensors (4.51). With regard to eqs. (7.3) and (7.7), the latter assume the form

$$\begin{aligned} g_{e_s e}^{(3,0)} &= (4\langle S_0\rangle^3)^{-1} \langle [2S_0 (S_0^2+S_0S_1-S_3^2)+S_1(S_2^2-S_3^2)] \sin^2\varphi \\ &\quad +[2S_0 (S_0^2-S_0S_1-S_3^2)-S_1 (S_2^2-S_3^2)] \cos^2\theta \cos^2\varphi \\ &\quad +2(S_0^2-S_3^2)(S_2 \cos\delta_s+S_3 \sin\delta_s) \cos\theta \sin 2\varphi\rangle, \\ g_{e_s e}^{(3,2)} &= (4\langle S_0\rangle^3)^{-1} \langle 12S_0 (S_0^2-S_3^2) \\ &\quad +[2S_0 (13S_0^2+13S_0S_1-7S_3^2)-5S_1 (S_2^2-S_3^2)] \sin^2\varphi \\ &\quad +[2S_0 (13S_0^2-13S_0S_1-7S_3^2)+5S_1 (S_2^2-S_3^2)] \cos^2\theta \cos^2\varphi \\ &\quad +2[(13S_0^2+5S_3^2) S_2 \cos\delta_s+(S_0^2+5S_3^2) S_3 \sin\delta_s] \cos\theta \sin 2\varphi\rangle, \\ g_{e_s e}^{(3,4)} &= (4\langle S_0\rangle^3)^{-1} \langle 20S_0 (4S_0^2+3S_3^2)+3[2S_0 (4S_0^2+4S_0S_1+21S_3^2) \\ &\quad -S_1(S_2^2-S_3^2)] \sin^2\varphi+3[2S_0 (4S_0^2-4S_0S_1+21S_3^2) \\ &\quad +S_1(S_2^2-S_3^2)] \cos^2\theta \sin^2\varphi+6[(4S_0^2+S_3^2) S_2 \cos\delta_s \\ &\quad -9(7S_0^2-2S_3^2) S_3 \sin\delta_s] \cos\theta \sin 2\varphi\rangle. \end{aligned} \tag{7.22}$$

(i) Vertical polarization

For vertically polarized incident light one has (7.2a), from which the nonlinear parameters (7.22) become

$$\begin{aligned} & g_{e_s\mathrm{V}}^{(3,0)} = g_{\mathrm{V}}^{(3)} \sin^2\varphi, \qquad g_{e_s\mathrm{V}}^{(3,2)} = g_{\mathrm{V}}^{(3)}(3+13 \sin^2\varphi), \\ & g_{e_s\mathrm{V}}^{(3,4)} = 4g_{\mathrm{V}}^{(3)} (5+3 \sin^2\varphi), \end{aligned} \tag{7.22a}$$

so that, in this case, the expression (4.47) gives a formula for the depolarization ratio $D_{\mathrm{V}}^{3\omega}$ analogical to eq. (3.55) (cf. KIELICH and KOZIEROWSKI [1970]).

(ii) Horizontal polarization

With regard to eq. (7.8b), we bring the nonlinear polarizational parameters (7.22) to the form

$$\begin{aligned} g_{e_s\mathrm{H}}^{(3,0)} &= g_{\mathrm{H}}^{(3)} \cos^2\theta \cos^2\varphi, \\ g_{e_s\mathrm{H}}^{(3,2)} &= g_{\mathrm{H}}^{(3)} (3+13 \cos^2\theta \cos^2\varphi), \\ g_{e_s\mathrm{H}}^{(3,4)} &= 4g_{\mathrm{H}}^{(3)} (5+3 \cos^2\theta \cos^2\varphi). \end{aligned} \tag{7.22b}$$

Thus, the depolarization ratio of four-photon scattered light at horizontal polarization of the incident light wave is (KIELICH and KOZIEROWSKI

[1970])

$$D_{\mathrm{H}}^{3\omega}(\theta) = \tag{7.23}$$

$$\frac{27\,C_2^{3\omega}(0)+20\,C_4^{3\omega}(0)}{27\,C_2^{3\omega}(0)+20\,C_4^{3\omega}(0)+[252\,C_0^{3\omega}(0)\,+117\,C_2^{3\omega}(0)+12\,C_4^{3\omega}(0)]\cos^2\theta}.$$

In particular, at perpendicular observation $D_{\mathrm{H}}^{3\omega}(90°)=1$.

(iii) Circular polarization

Applying the nonlinear parameters (7.22) to circular polarization of the incident light wave, we obtain

$$\begin{gathered} g_{e_s+1}^{(3,0)}=0, \qquad g_{e_s+1}^{(3,2)}=3\,g_{+1}^{(3)}\,(\sin^2\varphi+\cos^2\theta\cos^2\varphi-\sin\delta_s\cos\theta\sin 2\varphi),\\ g_{e_s+1}^{(3,4)}=\tfrac{5}{2}g_{+1}^{(3)}\,[14+15\,(\sin^2\varphi+\cos^2\theta\cos^2\varphi)+27\sin\delta_s\cos\theta\sin 2\varphi]. \end{gathered} \tag{7.22c}$$

Insertion of these parameters into eq. (4.47) leads to the following depolarization ratios for the vertical and horizontal component (cf. Kozierowski [1974]):

$$D_{+1}^{3\omega}(\theta)=\frac{70\,C_4^{3\omega}(0)+3\,[18\,C_2^{3\omega}(0)+25\,C_4^{3\omega}(0)]\cos^2\theta}{54\,C_2^{3\omega}(0)+145\,C_4^{3\omega}(0)}, \tag{7.24}$$

from which, at perpendicular observation

$$D_{+1}^{3\omega}(90°)=\frac{70\,C_4^{3\omega}(0)}{54\,C_2^{3\omega}(0)+145\,C_4^{3\omega}(0)}, \tag{7.24a}$$

whereas at collinear observation ($\theta=0°$) $D_{+1}^{3\omega}(0°)=1$, proving that the scattered light is natural light.

Similarly, we calculate with eqs. (4.47) and (7.22c) the reversal ratio of four-photon scattering (cf. Kozierowski [1974])

$$R_{+1}^{3\omega}(\theta)=\frac{216\,C_2^{3\omega}(0)\sin^4\theta/2+5\,(43+54\cos\theta+15\cos^2\theta)\,C_4^{3\omega}(0)}{216\,C_2^{3\omega}(0)\cos^4\theta/2+5\,(43-54\cos\theta+15\cos^2\theta)\,C_4^{3\omega}(0)}. \tag{7.25}$$

This leads, for observation at $\theta=0°$, to a result corresponding to the formula of Ożgo (3.56), whereas, for observation at $\theta=90°$, it leads to $R_{+1}^{3\omega}(90°)=1$ for arbitrary media.

In cases of incoherent scattering by atoms in their ground state

$C_0^{3\omega}(0) \neq 0$ and $C_2^{3\omega}(0) = C_4^{3\omega}(0) = 0$, showing that, here, four-photon scattering of circularly polarized incident light cannot occur. In the case of cooperative scattering due to many-body interaction the situation is quite different (see the discussion in § 5).

7.6. RECIPROCITY RELATIONS

With regard to the definition (7.6), the tensor of n-harmonic scattering (3.13) may be written as follows:

$$I_{e_se}^{n\omega} = (n\omega/c)^4 \left[F_{n\omega} + (\boldsymbol{e}_s \cdot \boldsymbol{e})^2 G_{n\omega}\right] I^n g^{(n)}, \tag{7.26}$$

where, by (7.4a) and (7.5), one has for linearly polarized light ($\delta_s = 0$, see Fig. 7.1):

$$\boldsymbol{e}_s \cdot \boldsymbol{e} = \sin\varphi \sin\psi + \cos\theta \cos\varphi \cos\psi.$$

Hence, the four components take the form (see Fig. 3.1)

$$I_{VV}^{n\omega} = (n\omega/c)^4 (F_{n\omega} + G_{n\omega}) I_V^n g_V^{(n)}, \tag{7.26a}$$

$$I_{VH}^{n\omega}/I_H^n g_H^{(n)} = I_{HV}^{n\omega}/I_V^n g_V^{(n)} = (n\omega/c)^4 F_{n\omega}, \tag{7.26b}$$

$$I_{HH}^{n\omega}(\theta) = (n\omega/c)^4 (F_{n\omega} + \cos^2\theta\, G_{n\omega}) I_H^n g_H^{(n)}. \tag{7.26c}$$

Thus, at perpendicular observation, the Rayleigh–Krishnan reciprocity relation holds for all scattered harmonics:

$$I_{VH}^{n\omega}/I_H^n g_H^{(n)} = I_{HH}^{n\omega}(90°)/I_H^n g_H^{(n)} = (n\omega/c)^4 F_{n\omega}. \tag{7.27}$$

Equation (7.26), moreover, leads to the following relation between the depolarization ratios of arbitrary scattered harmonics (Kielich and Kozierowski [1972]):

$$D_H^{n\omega}(\theta) = D_V^{n\omega} \{D_V^{n\omega} + (1 - D_V^{n\omega}) \cos^2\theta\}^{-1}, \tag{7.28}$$

where

$$D_V^{n\omega} = F_{n\omega}/(F_{n\omega} + G_{n\omega}), \tag{7.28a}$$

$$D_H^{n\omega}(\theta) = F_{n\omega}/(F_{n\omega} + \cos^2\theta\, G_{n\omega}). \tag{7.28b}$$

Similarly, for unpolarized incident light, one has the relation (Kielich and Kozierowski [1972])

$$D_U^{n\omega}(\theta) = D_U^{n\omega}(90°) + [1 - D_U^{n\omega}(90°)] \cos^2\theta. \tag{7.29}$$

Obviously, in the case of linear scattering, the relations (7.28) and

(7.29) are fulfilled unrestrictedly; in addition, the following relation also holds:

$$D_{\mathrm{U}}^{\omega}(90°) = 2D_{\mathrm{V}}^{\omega}/(1+D_{\mathrm{V}}^{\omega}). \tag{7.30}$$

ANDREWS and THIRUNAMACHANDRAN [1977b, 1978] have shown that, at nonlinear scattering, no immediate relation of the type (7.30) exists between $D_{\mathrm{U}}^{n\omega}$ and $D_{\mathrm{V}}^{n\omega}$, since the circularly-polarized light intensity has to be taken into account. Let us consider the matter more closely for the case of second-harmonic scattering. We obtain from eqs. (7.6a) and (7.9c), for unpolarized incident light:

$$\begin{aligned}
I_{\mathrm{VU}}^{2\omega} &= \tfrac{1}{105}[14\, B_1^{2\omega}(0) + 9\, B_3^{2\omega}(0)] I_{\mathrm{U}}^2,\\
I_{\mathrm{HU}}^{2\omega}(\theta) &= \tfrac{1}{630}\{14\, B_1^{2\omega}(0) + 39\, B_3^{2\omega}(0)\\
&\quad + 5\,[14\, B_1^{2\omega}(0) + 3\, B_3^{2\omega}(0)] \cos^2\theta\} I_{\mathrm{U}}^2.
\end{aligned} \tag{7.31}$$

On the other hand, from eqs. (7.6a), (7.13a), (7.13b), (7.15a), (7.15b) and (7.19a) we obtain

$$\begin{aligned}
I_{\mathrm{VV}}^{2\omega} &= \tfrac{1}{35}[7\, B_1^{2\omega}(0) + 2\, B_3^{2\omega}(0)]\, I_{\mathrm{V}}^2\, g_{\mathrm{V}}^{(2)},\\
I_{\mathrm{HV}}^{2\omega}/I_{\mathrm{V}}^2\, g_{\mathrm{V}}^{(2)} &= I_{\mathrm{VH}}^{2\omega}/I_{\mathrm{H}}^2\, g_{\mathrm{H}}^{(2)} = I_{\mathrm{VC}}^{2\omega}/I_{\mathrm{C}}^2\, g_{\mathrm{C}}^{(2)}\\
&= \tfrac{1}{315}[7B_1^{2\omega}(0) + 12\, B_3^{2\omega}(0)],\\
I_{\mathrm{HH}}^{2\omega}(\theta) &= \tfrac{1}{315}\{7\, B_1^{2\omega}(0) + 12\, B_3^{2\omega}(0) + 2\,[28\, B_1^{2\omega}(0)\\
&\quad + 3\, B_3^{2\omega}(0)] \cos^2\theta\}\, I_{\mathrm{H}}^2\, g_{\mathrm{H}}^{(2)},\\
I_{\mathrm{HC}}^{2\omega}(\theta) &= \tfrac{1}{315}\{15\, B_3^{2\omega}(0) + [14\, B_1^{2\omega}(0)\\
&\quad + 9\, B_3^{2\omega}(0)] \cos^2\theta\}\, I_{\mathrm{C}}^2\, g_{\mathrm{C}}^{(2)}.
\end{aligned} \tag{7.32}$$

Since $g_{\mathrm{V}}^{(2)} = g_{\mathrm{H}}^{(2)} = g_{\mathrm{C}}^{(2)} = g^{(2)}$, $I_{\mathrm{V}} = I_{\mathrm{H}} = I_{\mathrm{C}} = I_{\mathrm{U}}$, we have, with regard to (7.31) and (7.32),

$$\begin{aligned}
I_{\mathrm{VU}}^{2\omega} &= \frac{1}{2g^{(2)}}(I_{\mathrm{VV}}^{2\omega} + I_{\mathrm{VH}}^{2\omega} + I_{\mathrm{VC}}^{2\omega}),\\
I_{\mathrm{HU}}^{2\omega}(\theta) &= \frac{1}{2g^{(2)}}\{I_{\mathrm{HV}}^{2\omega} + I_{\mathrm{HH}}^{2\omega}(\theta) + I_{\mathrm{HC}}^{2\omega}(\theta)\},
\end{aligned} \tag{7.33}$$

where $g^{(2)} = 2$ for chaotic light and $g^{(2)} = 1$ for coherent light.

By (7.32) and (7.33) we obtain the following relations for perpendicular observation:

$$D_{\mathrm{U}}^{2\omega}(90°) = \frac{I_{\mathrm{HU}}^{2\omega}(90°)}{I_{\mathrm{VU}}^{2\omega}} = 2D_{\mathrm{V}}^{2\omega}\,\frac{1 + D_{\mathrm{C}}^{2\omega}(90°)}{1 + 3D_{\mathrm{V}}^{2\omega}}. \tag{7.34}$$

This proves that, in second-harmonic scattering, the relation between $D_{\mathrm{U}}^{2\omega}(90°)$ and $D_{\mathrm{V}}^{2\omega}$ involves, additionally, $D_{\mathrm{C}}^{2\omega}(90°)$ as determined by eq. (7.20) for $\theta = 90°$.

Obviously, on the light model (c), and with regard to (7.16) and (5.20), the relation (7.28) as well as (7.29) are fulfilled, with (cf. ANDREWS and THIRUNAMACHANDRAN [1977b]):

$$D_{\mathrm{U}}^{2\omega}(90°) = \frac{14\, B_1^{2\omega}(0) + 39\, B_3^{2\omega}(0)}{84\, B_1^{2\omega}(0) + 54\, B_3^{2\omega}(0)}\,. \tag{7.35}$$

A similar analysis can be performed for the reciprocity relations of the third-harmonic scattering effects, discussed in § 7.5.

For a complete polarizational analysis, it is very important to know the symmetry properties and selection rules for nonlinear responses of matter to circularly or elliptically polarized light, as determined by TANG and RABIN [1971], and OŻGO and KIELICH [1976], on the basis of group theory and irreducible spherical tensors.

§ 8. Concluding Remarks, and Outlook

As we have seen, the investigation of spontaneous multi-photon incoherent scattering processes provides direct information concerning the nonlinear polarizabilities of atoms and molecules. This data can be compared with that derived from studies of optically induced birefringence (KIELICH [1958, 1972a, b] and HELLWARTH [1977]), DC second-harmonic generation of laser beams (LEVINE [1977] and KIELICH [1979]), third-harmonic generation (WARD and NEW [1969]), and n-harmonic generation by free molecules (ANDREWS [1980]), as well as theoretical calculations (LEULIETTE-DEVIN and LOCQUENEUX [1975], HAMEKA [1977] and SUNDBERG [1977]). Particularly valuable are studies of three-photon scattering effects, which are highly sensitive to the ground state symmetry of the molecules.

Coherent multi-photon scattering by stochastic inhomogeneous media are a source of information concerning the many-body correlation function. Of special importance are cooperative scattering effects, caused by fluctuations of the molecular fields, as a source of data for the electric multipoles and polarizabilities of molecules with various point group symmetries for which the components are known in spherical representation (GRAY and LO [1976]). This type of cooperative scattering constitutes a fine example of a self-organizing process (HAKEN [1978]). In the description of cooperative scattering, it appears that the consequences of the Ewald–Oseen "extinction theorem" have to be taken into account explicitly. This by now classical problem (see BORN and WOLF [1968]) has been considered in a new light by PATTANAYAK and WOLF [1972] as well as DE GOEDE and MAZUR [1972] and, more recently, by many others (SEIN [1975], PATTANAYAK [1975] and VAN KRANENDONK and SIPE [1977]).

Statistical-fluctuation processes exert a strong influence on spontaneous multi-photon scattering. In fact, molecular field fluctuations are sometimes its sole origin, for example, in the case of cooperative three-photon scattering effects. Under extremal conditions, nonlinear light scattering is a particularly potent method of investigation, as when occurring in optical inhomogeneities near a critical point, in phase transitions, and in the domain structure of a ferroelectric, as well as in defects of crystal structure.

The truly unlimited possibilities provided by laser techniques will permit a fuller investigation of multi-photon elastic, as well as inelastic, scattering processes as sources of data concerning translational and rotational stochastic molecular motion. In addition to the first-order correlation tensor of scattering electric fields discussed in this article, one can analyze second-order correlation tensors of multi-photon scattering (KIELICH, KOZIEROWSKI and TANAŚ [1975]) which provide finer information on the stochastic motions of molecules. Three- and more-photon incoherent spontaneous Raman scattering effects provide new information on the structure of rotational, vibrational and rotational-vibrational spectra, since the latter obey selection rules other than those of usual Raman and absorption in the infrared. Much is to be expected from the coherent hyper-Raman scattering processes recently analyzed by BONNEVILLE and CHEMLA [1978], BJARNASON, HUDSON and ANDERSEN [1979], and BJARNASON, ANDERSEN and HUDSON [1980].

To keep within the space allotted to the present review, we refrain from discussing the theory of multi-photon scattering by molecular crystals and, in general, solids. The subject has to be dealt with by the methods of crystal lattice dynamics discussed in the comprehensive monograph of BIRMAN [1974], and applied to infrared absorption and Raman scattering.

We have refrained from an analysis of non-degenerate multi-photon scattering processes in which the scattering frequencies are given by sum frequencies (1.5) or difference frequencies (see KIELICH [1964b, 1965a, 1966b], PEŘINOVA, PEŘINA, SZLACHETKA and KIELICH [1979], ANDREWS [1979b], and MANAKOV and OVSIANNIKOV [1980]). Nor have we considered the hyper-parametric scatterings discussed in the monograph of KLYSHKO [1980] (see also SCHUBERT and WILHELMI [1980]).

We hope to have given a detailed analysis of spontaneous hyper-Raman scattering processes. However, the work on its stimulated electronic counterpart in metal vapors, initiated by BADALJAN, IRADJAN and MOVSESJAN [1968] and YATSIV, ROKNI and BARAK [1968] and developed in the past few years (VREHEN and HIKSPOORS [1977], COTTER, HANNA, TUTTLEBEE and YURATICH [1977], REIF and WALTHER [1978], HARTIG [1978] and BERGER [1978]), should not be left unmentioned. This novel type of scattering has already been applied for obtaining infrared and far infrared radiation (KIM and COLEMAN [1980]), as well as in studies of ultra-short laser pulse propagation in nonlinear media (HERMAN and THOMPSON [1981]). DNEPROVSKY, KARMENIAN and NURMINSKY [1972] and PENZKOFER, LAUBEREAU and KAISER [1973] observed stimulated hyper-Raman scattering in water. Perhaps, too, studies of higher-order Brillouin scattering can achieve a similar status, as suggested by BAROCCHI [1971].

Since multi-photon scattering processes are of a stochastic nature (GABRIEL [1973] and SPOHN [1980]) their complete quantitative description has to include the statistics of matter as well as the statistics of the radiation field in conjunction with a model of its state of polarization. When treated on a quantum-theoretical basis, the statistical and polarizational properties of the electromagnetic field should be described in terms of the nth order correlation tensors introduced by GLAUBER [1963]. They represent a generalization to quantal fields of the correlation tensors of WOLF [1954] and MANDEL and WOLF [1965] for classical fields. In the quantal case, the polarization density matrix for n photons can be extracted from the nth order correlation tensors and then put in a relationship with the Stokes parameters (ATKINS and WILSON [1972] and TANAŚ [1979]).

Although this review does not deal with the results of quantum theories of stimulated Raman scattering, we nonetheless have to mention the fundamental papers of SHEN [1967], WALLS [1973], MCNEIL and WALLS [1974], SIMAAN [1975] and, more recently, GUPTA and MOHANTY [1980]. Here, the difference between spontaneous and stimulated coherent Raman scattering should be kept in mind (see DESIDERIO and HUDSON [1979]). SIMAAN [1978] and, independently, SZLACHETKA and KIELICH

[1978] have drawn attention to the possibility of photon antibunching occurring in hyper-Raman scattering. Effects of correlation and anticorrelation of incident and scattered photons in the presence of phonon fluctuations have been analyzed closely by PEŘINOVA, PEŘINA, SZLACHETKA and KIELICH [1979] and SZLACHETKA, KIELICH, PEŘINA and PEŘINOVA [1979, 1980], for various initial statistical properties of laser and Stokes or anti-Stokes modes, e.g. coherent, chaotic or in vacuum state.

The dynamics of photon antibunching, in processes of multi-photon scattering as well as in processes of nonlinear light propagation, are largely dependent on the photon polarization state (not only on the field statistics) (ATKINS and WILSON [1972], TANAŚ and KIELICH [1979], and RITZE [1980]). Under certain conditions, antibunching of laser photons in spontaneous hyper-Raman scattering processes occurs in a similar way to their antibunching in harmonic generation processes (WALLS and TINDLE [1971], KOZIEROWSKI and TANAŚ [1977], MOSTOWSKI and RŻĄŻEWSKI [1978], KIELICH, KOZIEROWSKI and TANAŚ [1978], DRUMMOND, MCNEIL, and WALLS [1979], SZLACHETKA, KIELICH, PEŘINA and PEŘINOVA [1980], and PEŘINA [1980]).

Although the spontaneously scattered multi-photon intensities are, under normal conditions, weaker than those scattered at stimulation, the labor spent on their observation is nonetheless highly rewarding, due to the importance of the information gained. This is so because the essence of spontaneous light scattering resides in the very foundations of stochastic physics as well as quantum mechanics and electrodynamics (see, for example, KLAUDER and SUDARSHAN [1968], RISKEN [1970], MEHTA [1970], SENITZKY [1978], MANDEL [1976] and SPOHN [1980]). Accordingly, the spontaneous effects discussed provide a test of the correctness of those foundations, e.g. of the purely quantal structure of light apparent in the phenomenon of photon anticorrelation (antibunching) (WALLS [1979] and LOUDON [1980]).

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Appendix A. Irreducible Cartesian Tensors

A Cartesian tensor $T^{(n)}$ of the nth rank has 3^n components $T_{i_1 \dots i_n}$. Since a tensor has to be independent of the coordinate system XYZ, its components have to obey the following transformation law when we go over from one coordinate system to another (rotated) system:

$$T_{i_1 \dots i_n} = R_{i_1 \alpha_1} \cdots R_{i_n \alpha_n} T_{\alpha_1 \dots \alpha_n}. \qquad \text{(A.1)}$$

The transformation (rotation) coefficients $R_{i\alpha}$ are functions of the mutual orientation of the two systems of reference.

An important operation on tensors consists in expressing the components of an nth rank Cartesian tensor in weight-J irreducible representation in terms of their $2J+1$ independent components (COOPE, SNIDER and MCCOURT [1965], COOPE and SNIDER [1970], and JERPHAGNON, CHEMLA and BONNEVILLE [1978]).

Thus, we have the representation of a second-rank tensor in the form of the sum of three irreducible components:

$$T_{ij} = T_{ij}^{(0)} + T_{ij}^{(1)} + T_{ij}^{(2)}, \qquad \text{(A.2)}$$

where

$$T_{ij}^{(0)} = \tfrac{1}{3} T_{kk}\, \delta_{ij} \qquad \text{(A.2a)}$$

is an isotropic tensor of the second rank (trace of the tensor) obtained by unweighted averaging of (A.2) over all directions in space. The antisymmetric part of the tensor is

$$T_{ij}^{(1)} = \tfrac{1}{2}(T_{ij} - T_{ji}) \qquad \text{(A.2b)}$$

and its anisotropic part (or deviator) is

$$T_{ij}^{(2)} = \tfrac{1}{2}(T_{ij} + T_{ji}) - \tfrac{1}{3} T_{kk}\, \delta_{ij}. \qquad \text{(A.2c)}$$

A tensor of the third rank has $3^3 = 27$ independent components and can be represented as the sum of one pseudo-scalar ($J=0$), three vectors

$(J=1)$, two pseudo-deviators $(J=2)$, and one septor $(J=3)$ (see, for example, JERPHAGNON, CHEMLA and BONNEVILLE [1978]). In particular, a completely symmetric tensor of the third rank has ten independent components and is the sum of one vector (3) and one septor (7):

$$T_{ijk} = T^{(1)}_{ijk} + T^{(3)}_{ijk}, \tag{A.3}$$

where

$$T^{(1)}_{ijk} = \tfrac{1}{5}(\delta_{ij}\, T_{kll} + \delta_{jk}\, T_{ill} + \delta_{ki}\, T_{jll}), \tag{A.3a}$$

$$T^{(3)}_{ijk} = T_{ijk} - T^{(1)}_{ijk}. \tag{A.3b}$$

A tensor T_{ijkl}, which in general has $3^4 = 81$ independent components, has only fifteen in the completely symmetric case, and is the sum of one scalar $(J=0, 2J+1=1)$, one deviator $(J=2, 2J+1=5)$, and one nonor $(J=4, 2J+1=9)$ (JERPHAGNON, CHEMLA and BONNEVILLE [1978]):

$$T_{ijkl} = T^{(0)}_{ijkl} + T^{(2)}_{ijkl} + T^{(4)}_{ijkl}, \tag{A.4}$$

where

$$T^{(0)}_{ijkl} = \tfrac{1}{15} T_{mmnn}\, \sigma_{ijkl}, \tag{A.4a}$$

$$\begin{aligned} T^{(2)}_{ijkl} = \tfrac{1}{7}(&\delta_{ij}\, T_{klmm} + \delta_{ik}\, T_{jlmm} + \delta_{il}\, T_{jkmm} \\ &+ \delta_{jk}\, T_{ilmm} + \delta_{jl}\, T_{ikmm} + \delta_{kl}\, T_{ijmm} - \tfrac{2}{3} T_{mmnn}\, \sigma_{ijkl}), \end{aligned} \tag{A.4b}$$

$$T^{(4)}_{ijkl} = T_{ijkl} - T^{(2)}_{ijkl} - T^{(0)}_{ijkl}, \tag{A.4c}$$

with the notation

$$\sigma_{ijkl} = \delta_{ij}\, \delta_{kl} + \delta_{ik}\, \delta_{jl} + \delta_{il}\, \delta_{jk}. \tag{A.5}$$

More complete information concerning irreducible Cartesian tensors and the transition leading from Cartesian to spherical tensors is to be found in the original papers (see, for example, COOPE [1970], STONE [1975], OŻGO and KIELICH [1974, 1976], OŻGO [1975b], and JERPHAGNON, CHEMLA and BONNEVILLE [1978]).

Appendix B. Isotropic Averaging of Cartesian Tensors

If the systems of coordinates in which the tensors $T_{i_1 \ldots i_n}$ and $T_{\alpha_1 \ldots \alpha_n}$ are expressed are both orthogonal, the rotation transformation coefficients $R_{i\alpha}$ are directional cosines, i.e. cosines of the angles between the axes i and α of the two systems of coordinates. Thus, isotropic averaging of

Cartesian tensors reduces to the averaging of products of the directional cosines, and we have, with regard to (A.1),

$$\langle T_{i_1 \dots i_n} \rangle_\Omega = \langle R_{i_1 \alpha_1} \cdots R_{i_n \alpha_n} \rangle_\Omega \, T_{\alpha_1 \dots \alpha_n}, \tag{B.1}$$

where the symbol $\langle \; \rangle_\Omega$ stands for unweighted averaging over all orientations:

$$\langle R_{i_1 \alpha_1} \cdots R_{i_n \alpha_n} \rangle_\Omega = \frac{1}{\Omega} \int R_{i_1 \alpha_1} \cdots R_{i_n \alpha_n} \, \mathrm{d}\Omega. \tag{B.2}$$

If $n \leqslant 4$, the averaging procedure is trivial, but becomes complicated starting from $n = 5$ (Kielich [1968d] and Healy [1975]) and has been carried out generally for $n = 6$ (Kielich [1961] and McClain [1972]) and $n = 7$ (Andrews and Thirunamachandran [1977a]). The results are of a high degree of complexity, and shall not be given here.

The procedure of eq. (B.1) is also applicable when it comes to the isotropic averaging of a product of tensors. For example, the following result is obtained for the isotropic average of the product of two second-rank tensors:

$$\begin{aligned} \langle A_{ij} A_{kl} \rangle_\Omega &= \tfrac{1}{3} A_0^2 \, \delta_{ij} \, \delta_{kl} + \tfrac{1}{6} A_1^2 (\delta_{ik} \, \delta_{jl} - \delta_{il} \, \delta_{jk}) \\ &\quad + \tfrac{1}{30} A_2^2 (3\delta_{ik} \, \delta_{jl} + 3\delta_{il} \, \delta_{jk} - 2\delta_{ij} \, \delta_{kl}), \end{aligned} \tag{B.3}$$

where we have the following irreducible components:

$$\begin{aligned} A_0^2 &= A_{\alpha\beta}^{(0)} A_{\alpha\beta}^{(0)} = \tfrac{1}{3} A_{\alpha\alpha} A_{\beta\beta}, \\ A_1^2 &= A_{\alpha\beta}^{(1)} A_{\alpha\beta}^{(1)} = \tfrac{1}{4} (A_{\alpha\beta} - A_{\beta\alpha}) (A_{\alpha\beta} - A_{\beta\alpha}), \\ A_2^2 &= A_{\alpha\beta}^{(2)} A_{\alpha\beta}^{(2)} = \tfrac{1}{4} (A_{\alpha\beta} + A_{\beta\alpha}) (A_{\alpha\beta} + A_{\beta\alpha}) - \tfrac{1}{3} A_{\alpha\alpha} A_{\beta\beta}. \end{aligned} \tag{B.4}$$

The isotropic average of the product of two symmetric third-rank tensors is

$$\langle B_{ijk} \, B_{lmn} \rangle_\Omega = \tfrac{1}{45} B_1^2 \, \sigma_{ijklmn}^{(1)} + \tfrac{1}{210} B_3^2 \, \sigma_{ijklmn}^{(3)}, \tag{B.5}$$

where we have introduced the isotropic tensors:

$$\begin{aligned} \sigma_{ijklmn}^{(1)} &= \delta_{ij} \, \sigma_{klmn} + \delta_{ik} \, \sigma_{jlmn} + \delta_{jk} \, \sigma_{ilmn}, \\ \sigma_{ijklmn}^{(3)} &= 5[\delta_{il} \, (\delta_{jm} \, \delta_{kn} + \delta_{jn} \, \delta_{km}) + \delta_{im} \, (\delta_{kl} \, \delta_{jn} + \delta_{kn} \, \delta_{jl}) \\ &\quad + \delta_{in} \, (\delta_{jm} \, \delta_{kl} + \delta_{jl} \, \delta_{km})] - 2\sigma_{ijklmn}^{(1)}. \end{aligned} \tag{B.6}$$

The irreducible components have the form

$$\begin{aligned} B_1^2 &= B_{\alpha\beta\gamma}^{(1)} B_{\alpha\beta\gamma}^{(1)} = \tfrac{3}{5} B_{\alpha\beta\beta} \, B_{\alpha\gamma\gamma}, \\ B_3^2 &= B_{\alpha\beta\gamma}^{(3)} B_{\alpha\beta\gamma}^{(3)} = \tfrac{1}{5} (5 \, B_{\alpha\beta\gamma} \, B_{\alpha\beta\gamma} - 3 \, B_{\alpha\beta\beta} \, B_{\alpha\gamma\gamma}). \end{aligned} \tag{B.7}$$

Similarly, we find the isotropic average of a product of two symmetric tensors of the fourth rank:

$$\langle C_{ijkl}\, C_{mnop}\rangle_{\Omega} = \tfrac{1}{45} C_0^2\, \sigma^{(0)}_{ijklmnop} + \tfrac{1}{1260}\, C_2^2\, \sigma^{(2)}_{ijklmnop} + \tfrac{1}{7560}\, C_4^2\, \sigma^{(4)}_{ijklmnop}, \tag{B.8}$$

where we have introduced the isotropic tensors

$$\begin{aligned}
\sigma^{(0)}_{ijklmnop} &= \sigma_{ijkl}\, \sigma_{mnop},\\
\sigma^{(2)}_{ijklmnop} &= 3\,(\delta_{ij}\, \sigma_{klmnop} + \delta_{ik}\, \sigma_{jlmnop} + \delta_{il}\, \sigma_{jkmnop}\\
&\qquad + \delta_{jk}\, \sigma_{ilmnop} + \delta_{jl}\, \sigma_{ikmnop} + \delta_{kl}\, \sigma_{ijmnop}) - 14\sigma^{(0)}_{ijklmnop},\\
\sigma^{(4)}_{ijklmnop} &= 35\,(\delta_{ij}\, \sigma_{klmnop} + \delta_{ik}\, \sigma_{jlmnop} + \delta_{il}\, \sigma_{jkmnop}\\
&\qquad + \delta_{im}\, \sigma_{jklnop} + \delta_{in}\, \sigma_{jklmop} + \delta_{io}\, \sigma_{jklmnp} + \delta_{ip}\, \sigma_{jklmno})\\
&\qquad - 15\, \sigma^{(2)}_{ijklmnop} - 147\, \sigma^{(0)}_{ijklmnop},
\end{aligned} \tag{B.9}$$

with

$$\sigma_{ijklmn} = \delta_{ij}\, \sigma_{klmn} + \delta_{ik}\, \sigma_{jlmn} + \delta_{il}\, \sigma_{jkmn} + \delta_{im}\, \sigma_{jkln} + \delta_{in}\, \sigma_{jklm},$$

and irreducible components

$$\begin{aligned}
C_0^2 &= C^{(0)}_{\alpha\beta\gamma\delta}\, C^{(0)}_{\alpha\beta\gamma\delta} = \tfrac{1}{5} C_{\alpha\alpha\beta\beta}\, C_{\gamma\gamma\delta\delta},\\
C_2^2 &= C^{(2)}_{\alpha\beta\gamma\delta}\, C^{(2)}_{\alpha\beta\gamma\delta} = \tfrac{2}{7}(3\, C_{\alpha\beta\gamma\gamma}\, C_{\alpha\beta\delta\delta} - C_{\alpha\alpha\beta\beta}\, C_{\gamma\gamma\delta\delta}),\\
C_4^2 &= C^{(4)}_{\alpha\beta\gamma\delta}\, C^{(4)}_{\alpha\beta\gamma\delta} = \tfrac{1}{35}(35\, C_{\alpha\beta\gamma\delta}\, C_{\alpha\beta\gamma\delta} - 30\, C_{\alpha\beta\gamma\gamma}\, C_{\alpha\beta\delta\delta} + 3\, C_{\alpha\alpha\beta\beta}\, C_{\gamma\gamma\delta\delta}).
\end{aligned} \tag{B.10}$$

Isotropic averaging (B.2) becomes highly complicated for $n \geqslant 8$. However, the general solution can be derived for the following isotropic average (KIELICH and KOZIEROWSKI [1972]):

$$\langle R_{\sigma\alpha}\, R_{\tau\beta}\, e_{\alpha_1} \cdots e_{\alpha_n} e_{\beta_1} \cdots e_{\beta_n}\rangle_{\Omega} = \delta_{\sigma\tau}\, p_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n} + e_{\sigma}\, e_{\tau}\, q_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n}, \tag{B.11}$$

where we have introduced the unit tensor operators:

$$\begin{aligned}
p_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n} &= [2(2n+3)!!]^{-1}\, [(2n+3)\, \delta_{\alpha\beta}\, \sigma_{\alpha_1\beta_1\cdots\alpha_n\beta_n} - \sigma_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n}],\\
q_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n} &= [2(2n+3)!!]^{-1}\, [3\sigma_{\alpha\beta\alpha_1\beta_1\cdots\alpha_n\beta_n} - (2n+3)\, \delta_{\alpha\beta}\, \sigma_{\alpha_1\beta_1\cdots\alpha_n\beta_n}]
\end{aligned} \tag{B.12}$$

e being a real unit vector.

We have made use of (B.11) when going over from the scattering tensor (3.12) to (3.13). Thus, performing on (3.12) the tensorial transformation (A.1) and then putting $E^*_{\sigma_1} = E^* e_{\sigma_1}$, we have

$$\begin{aligned} &\langle a^{-n\omega}_{\sigma\sigma_1 \cdots \sigma_n} a^{n\omega}_{\tau\tau_1 \cdots \tau_n} E^*_{\sigma_1} \cdots E^*_{\sigma_n} E_{\tau_1} \cdots E_{\tau_n} \rangle_{\Omega, E} \\ &\quad = a^{-n\omega}_{\alpha\alpha_1 \cdots \alpha_n} a^{n\omega}_{\beta\beta_1 \cdots \beta_n} \langle R_{\sigma\alpha} R_{\tau\beta} e_{\alpha_1} \cdots e_{\alpha_n} e_{\beta_1} \cdots e_{\beta_n} \rangle_\Omega \langle |E|^{2n} \rangle_E \end{aligned} \tag{B.13}$$

and with regard to (B.11) we arrive at (3.13), on having introduced the tensors

$$\begin{aligned} f_{\alpha\beta\alpha_1\beta_1 \cdots \alpha_n\beta_n} &= [2^{n-1}(n!)^2]^{-1} p_{\alpha\beta\alpha_1\beta_1 \cdots \alpha_n\beta_n}, \\ g_{\alpha\beta\alpha_1\beta_1 \cdots \alpha_n\beta_n} &= [2^{n-1}(n!)^2]^{-1} q_{\alpha\beta\alpha_1\beta_1 \cdots \alpha_n\beta_n}, \end{aligned} \tag{B.14}$$

into the molecular parameters (3.14).

From (B.11) we easily find the useful expression

$$\langle e_{\alpha_1} \cdots e_{\alpha_n} e_{\beta_1} \cdots e_{\beta_n} \rangle_\Omega = [(2n+1)!!]^{-1} \sigma_{\alpha_1\beta_1 \cdots \alpha_n\beta_n} \tag{B.15}$$

with the isotropic tensor

$$\begin{aligned} \sigma_{\alpha_1\beta_1 \cdots \alpha_n\beta_n} &= \delta_{\alpha_1\beta_1} \sigma_{\alpha_2\beta_2 \cdots \alpha_n\beta_n} + \delta_{\alpha_1\beta_2} \sigma_{\alpha_2\beta_1 \cdots \alpha_n\beta_n} \\ &\quad + \cdots \delta_{\alpha_1\beta_n} \sigma_{\alpha_2\beta_2 \cdots \alpha_n\beta_{n-1}} + \cdots \end{aligned} \tag{B.16}$$

and $(2n+1)!! = 1 \cdot 3 \cdot 5 \cdots (2n+1)$.

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