PHYSICAL REVIEW A VOLUME 17, NUMBER 6 JUNE 1978

Symmetries of the light scattering processes in low-density fluids

R. Bonneville and D. S. Chemla

Centre National d'Etudes des Télécommunications, 196 rue de Paris, 92220 Bagneux, France

(Received 31 May 1977)

Using the formalism of irreducible spherical tensors, we derive a general expression for the light intensity scattered in a process of any order in a low-density fluid; elastic (both coherent and incoherent) and inelastic (incoherent) scattering are considered. The relevant physical quantities involved are the scalar invariants associated with the irreducible parts of the various scattering tensors; the polarization dependence is governed by $P_0(\cos\eta)$ and $P_2(\cos\eta)$ only, where P_k is the Legendre polynomial of order k and η the angle between the polarizations of the scattered and incident light. Depolarization ratios and molecular selection rules are also given for up to four-photon processes.

I. INTRODUCTION

Angular-distribution and polarization properties of the light scattered by a material medium have been widely investigated.[1] In ordinary scattering experiments, either in the elastic (Rayleigh) case or in the inelastic (Raman) case, each efficient photon of the incident light beam accounts for one scattered photon. Now, the emergence of high-power coherent sources has allowed higher-order effects to be evidenced, such as harmonic scattering (hyper-Rayleigh scattering) or normally forbidden Raman transitions (hyper-Raman scattering): for instance, at first order (first hyperscattering), two incident photons at frequency ω may generate a single scattered photon at frequency 2ω, or $2\omega \pm \omega_M$, where ω_M is some molecular frequency. First hyper-Rayleigh scattering has been observed by Maker, Terhune, and Savage[2] in organic liquids, and theoretically discussed by Maker[3]; first hyper-Raman scattering has been investigated by Cyvin, Rauch, and Decius,[4] who gave the molecular selection rules and depolarization ratios. Higher-order processes can be thought of and, to the best of our knowledge, no unified treatment of light scattering pointing out the symmetry features common to the different processes has yet been presented. It is the purpose of this paper to provide such an analysis in the case of light scattering by an homogeneous low-density fluid (local-field effects in fluids will be investigated in a forthcoming paper). (See Fig. 1 for scattering examples.)

In such an isotropic medium, the relevant physical quantities which characterize a phenomenon from a macroscopic point of view are the scalar invariants formed from the susceptibility tensors describing this effect on the microscopic scale. As an example, the expression of the light amplitude scattered by a single molecule in a process of order r (i.e., involving r photons) depends upon a rank-r scattering tensor T. If one deals with an assembly of molecules, one knows that two types of scattering have to be considered: a coherent process in which one has to sum up the amplitudes of each scattering center and an incoherent process adding up the individual intensities. Now, a way of discerning the coherent process from the incoherent one in an isotropic medium emerges from the decomposition of T into irreducible parts. Indeed, any rank-r Cartesian tensor can be expressed as a sum of irreducible tensors of weight $J \leqslant r$, i.e., $T=\sum_{\tau,J}T^{(\tau,J)}$ (the index τ has been introduced in order to distinguish among the linearly independent irreducible tensors with the same weight which may appear in the reduction process). Summing up the amplitudes reveals one type of invariant: the scalar ($J=0$) irreducible part of T; adding up the intensities evidences another type of invariant: the scalar product (or full contraction) of $T^{(\tau,J)}$ with $T^{(\tau',J)}$. Hence, coherent scattering involves only the scalar irreducible parts of the scattering tensor, while incoherent scattering involves all the various $(T^{(\tau,J)}\cdot T^{(\tau',J)})$ products.

In a previous paper,[5] hereafter referred to as I, we have developed a general formalism in order to express the physical properties of a medium in terms of tensors irreducible under the three-dimensional orthogonal group. The formal reduc-

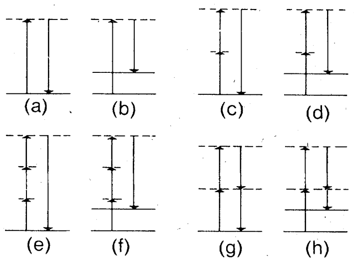

FIG. 1. Some scattering processes. (a): Rayleigh; (b): Raman Stokes; (c) and (d): first hyperscattering; (e)–(h): second hyperscattering.

tion scheme of Cartesian tensors and their transformation to spherical tensors was presented using group theory and spherical tensor algebra. A particular emphasis was put on the geometrical symmetries (rotation and parity) and the intrinsic symmetries (behavior under index permutations) of irreducible spherical tensors. Since irreducible tensors transform in point operations in a much simpler way with the use of spherical rather than Cartesian formalism, molecular symmetries are more easily taken into account, and the relevant physical quantities directly related to their irreducible components. The interest of such an approach is to easily keep track of these symmetries in any change of reference frame, in particular when rotating from the microscopic axes, where the symmetries of the molecular unit are most naturally written, to the macroscopic axes in which the experimental data are collected. This formalism has been applied to the static-electric-field-induced optical effects in rarefied fluids,[6] and it was shown to be very convenient to describe the thermodynamical average over the molecular orientations in the presence of the dc field.

Henceforth, we shall consider the following situation: an assembly of identical atoms or molecules in a gas or a solution is irradiated by an intense monomode light beam; the scattered light at a given frequency is observed in a given direction. With different modes, the above conclusions about the scalar invariants of the susceptibility tensors are still valid; an example of the calculation is given in Sec. IV B for two three-photon processes, for higher orders, the explicit expressions of the scattered intensity become more complicated because of the numerical coefficients involved.

In Sec. II, after a survey of the definition and properties of the scattering tensors, we recall how the distinction between coherent and incoherent scattering appears, pointing out that elastic scattering may have both coherent and incoherent contributions, whereas inelastic scattering is always incoherent. Then, we express the amplitude scattered by a single molecule in a process of order r in terms of the irreducible components of a scattering tensor and those of a tensor collecting all the polarization dependences of the fields.

In Secs. III and IV, the mean scattered intensity is calculated, first in the incoherent case, then in the coherent case, by an averaging procedure over the random molecular orientations, using some well-known properties of Wigner matrices. The polarization dependence and the relevant terms of the scattering tensors are discussed; an explicit computation of the scattered intensities and depolarization ratios is given for $r=2,3,4$.

Finally, we investigate the important case of molecular vibrational scattering and give the selection rules for the most frequently encountered molecular point groups for the different cases $r=2,3,4$.

II. THEORETICAL BACKGROUND

A. Scattering tensors

Let us consider an atom or a molecule interacting with the electromagnetic field.[7] The free (i.e., noninteracting) system Hamiltonian is $H_0 = H_{\mathrm{at}} + H_{\mathrm{ra}}$ (at stands for atom and ra for radiation); if we restrict ourselves to electric dipole transitions, the coupling Hamiltonian is $V = -\vec{\mathrm{p}}\cdot\vec{\mathrm{E}}$ ($\vec{\mathrm{p}}$: electric dipole of the molecule; $\vec{\mathrm{E}}$: electric field). The transition probability amplitude S_{21} from a given eigenstate $|\phi_1\rangle$ of the free system (at + ra), to another eigenstate $|\phi_2\rangle$ can be expressed as a series of the electric field:

$$-(S_{21}) = \mu_i\langle E_i\rangle + \alpha_{ij}^{(2,1)}\langle E_iE_j\rangle + \beta_{ijk}^{(2,1)}\langle E_iE_jE_k\rangle + \gamma_{ijkl}^{(2,1)}\langle E_iE_jE_kE_l\rangle + \cdots \tag{1}$$

(summation is assumed over repeated indices). $\alpha_{ij}^{(2,1)}$, $\beta_{ijk}^{(2,1)}$, and $\gamma_{ijkl}^{(2,1)}$ are the successive scattering tensors; they can be explicitly calculated through diagram methods (Appendix A) and depend upon the final and initial atomic states and on the field frequencies; $\langle E_i\rangle$, $\langle E_iE_j\rangle$, $\langle E_iE_jE_k\rangle$, and so on, are matrix elements of the electric field.

If the initial and final atomic states are the same, and we shall see in Sec. II B that this is precisely the case for coherent scattering, the scattering tensors $\alpha_{ij}^{(2,1)}$, $\beta_{ijk}^{(2,1)}$, $\gamma_{ijkl}^{(2,1)}, \ldots$, coincide with the linear polarizability α_{ij} and the first, second, ..., hyperpolarizabilities $\beta_{ijk}, \gamma_{ijkl}, \ldots$, as they are usually defined in nonlinear optics.[8]

The scattering tensor involved in a process of order r is a rank-r tensor, symmetrical in some permutations of its indices; the frequency of the scattered light is $\omega_S = |\omega \pm \omega \pm \omega \cdots \pm \omega|$, ω appearing $r-1$ times in an elastic (hyper-Rayleigh) process, and $\omega_S = |\omega \pm \omega \pm \omega \cdots \pm \omega| \pm \omega_M$ in an inelastic (hyper-Raman) process, which accounts for harmonic scattering and for apparently forbidden Raman lines. For instance α, β, γ are tensors of rank $r = 2,3,4$, respectively; the linear term α is responsible for the two-photon processes, while the nonlinear terms $\beta, \gamma, \ldots$, account for higher-order scatterings. The Rayleigh tensor $\alpha_{ij}(-\omega, \omega)$ is a symmetrical one, but the Raman tensor $\alpha_{ij}(-\omega_S, \omega)$ with $\omega_S = \omega + \omega_M$ (anti-Stokes) or $\omega_S = \omega - \omega_M$ (Stokes) can give an antisymmetrical contribution.

In a third-order process, the first hyperscattering tensor $\beta_{ijk}(-\omega_S, \omega, \omega)$, with $\omega_S = 2\omega$ (first hyper-Rayleigh) or $\omega_S = 2\omega \pm \omega_M$ (first hyper-Raman), is symmetrical in the permutation of its two last indices j and k; in a fourth-order process, the second hyperscattering tensor $\gamma_{ijkl}(-\omega_S, \omega, \omega, \omega)$ is invariant in any permutation of (jkl) whereas $\gamma_{ijkl}(-\omega_S, \omega, \omega, -\omega)$ is unchanged only when permuting j and k.

Furthermore, if ω and ω_S are within the transparency range of the medium, the scattering tensors are real, and if one neglects the dispersion, they can be assumed to be invariant in the permutation of all their indices (Kleinman's symmetry). For a given atomic transition $a \to b$ in a process of order r, in most cases only the first vanishing term in the above series [Eq. (2)] is to be taken into account. However, at high intensities, further-order contributions may become non-negligible; for instance, in presence of an intense laser field at frequency ω', the net dipole moment of a polar molecule is

$$\mu_i + \beta_{ijk}(0, \omega', -\omega')\langle E_j^{\omega'} E_k^{\omega'*}\rangle + \cdots$$

and in the scattering process $\omega \to \omega_S$, the relevant scattering tensor is

$$\alpha_{ij}(-\omega_S, \omega) + \gamma_{ijkl}(-\omega_S, \omega, \omega', -\omega')\langle E_k^{\omega'} E_l^{\omega'*}\rangle + \cdots .$$

The γ term interfering with the α term will cause Kerr optical effect ($\omega' \neq \omega$) and self-focusing ($\omega' = \omega$); if from selection rules some component of the α term vanishes; however, photons at ω_S can be detected.

B. Coherence and incoherence

Although we deal with an assembly of identical molecules or atoms, we cannot consider as identical the quantum states (with which the matrix elements of the dipole moment are computed) of two of them in the same (nondegenerate) energy level. In fact, the quantum states of an atom are only determined up to an arbitrary phase factor; for instance, in a scattering transition $a \to b$, the amplitude scattered by the qth atom has a phase factor $\exp i(\phi_b^{(q)} - \phi_a^{(q)})$, where $\phi_b^{(q)}$ and $\phi_a^{(q)}$ are the phases of the final and initial states of the atom q (Ref. 9) (the overlap of the wave functions of two molecules is neglected).

We must also take into account the propagation of the electric field, if the dimensions of the active medium are not small compared to the wavelengths; hence, the amplitude scattered by the qth molecule is multiplied by a phase factor $\exp(i\Delta\vec{k} \cdot \vec{R}_q)$, where $\vec{R}_q$ denotes the position of the molecule q and $\Delta\vec{k}$ the wave-vector mismatch:

$$\Delta\vec{k} = \vec{k}_S - (\vec{k} \pm \vec{k} \pm \vec{k} \pm \cdots) \tag{2}$$

($\vec{k}_S$ and $\vec{k}$: wave vectors of the scattered and incident light, respectively).

Now, we assume for the sake of simplicity that the initial atomic state is a pure eigenstate of H_{at} (not a statistical mixture) and that the levels a and b are not degenerate (see Appendix B).

The total scattered amplitude in the $a \to b$ transition is the sum of the amplitudes scattered by each individual molecule, *with their phases*, i.e.,

$$\underline{A}(a \to b) = \sum_q A_q \tag{3a}$$

with

$$A_q = A(\Omega_q) e^{i\Delta\vec{k}\cdot\vec{R}_q} e^{i(\varphi_b^{(q)} - \varphi_a^{(q)})} . \tag{3b}$$

The summation (3a) runs over the N_a individual molecules on level a.

The amplitude $A(\Omega_q)$ scattered by one molecule regardless of the phase factors, depends upon the set of Euler angles $\Omega_q = (\phi_q, \theta_q, \psi_q)$ describing the orientation of the qth molecular frame.

The mean scattered intensity I_S is the square modulus of $\underline{A}$ after averaging over the molecular orientations:

$$I_S(a \to b) = \langle \underline{A}\,\underline{A}^* \rangle \tag{4a}$$

or

$$I_S(a \to b) = \left\langle \sum_{qq'} A(\Omega_q) A(\Omega_{q'}) e^{i\Delta\vec{k}\cdot(\vec{R}_q - \vec{R}_{q'})} \times e^{i(\Delta_\varphi^{(q)} - \Delta_\varphi^{(q')})} \right\rangle . \tag{4b}$$

We have to perform, in a first step, the sum over the molecular positions, noticing that $A(\Omega_q)$ is independent of $\vec{R}_q$, then the average over the molecular orientations. *This separation is possible only because we neglect molecular correlations:* in fact, the presence of other molecules which can belong to the solvent, in the vicinity of a scattering center, will affect its orientation.

In an inelastic scattering process, levels a and b are different and the phase factor $e^{i\Delta\varphi^{(q)}}$ differs from unity; because of these random phase factors in Eq. (4b), the sum over q and q' with $q \neq q'$ vanishes; the sum with $q = q'$ is N_a, and hence we get

$$I_S(a \to b) = N_a \langle A(\Omega) A^*(\Omega) \rangle = I_{\text{incoh}}(a \to b) . \tag{5}$$

The total scattering cross section is then N_a times the cross section of one molecule, and such a process is fully incoherent. (This is *not* the case, for instance, of stimulated Raman scattering which is interpreted as a resonant four-photon *elastic* process ($\omega + \omega \to \omega_S + \omega_{AS}$); the oscillation at the Stokes frequency starts on the noise due to ordinary incoherent Raman scattering).

Conversely, in an elastic process, $e^{i\Delta\varphi^{(q)}} = 1$; if we sum separately over $q = q'$ and $q \neq q'$, the former summation is $N_a\langle A(\Omega)A^*(\Omega)\rangle$, and the latter is

$$\langle A(\Omega)\rangle\langle A^*(\Omega)\rangle\left(\left|\sum_q e^{i\Delta\vec{k}\cdot\vec{R}_q}\right|^2 - N_a\right).$$

The mean scattered intensity hence results from two contributions, i.e., $I_S(a\to a)=I_{\text{coh}}(a\to a)+\Delta I(a\to a)$. The first one,

$$I_{\text{coh}}(a\to a)=\left|\langle A(\Omega)\rangle\right|^2\left|\sum_q e^{i\Delta\vec{k}\cdot\vec{R}_q}\right|^2, \tag{6a}$$

is the coherent term that we should have obtained in adding up the individual amplitudes with their phase, then averaging over all the molecular orientations, then squared.

The residual term

$$\Delta I(a\to a)=N_a[\langle|A(\Omega)|^2\rangle - |\langle A(\Omega)\rangle|^2], \tag{6b}$$

which is proportional to the square variance of $|A|$ and to the number of active centers, is an incoherent contribution due to the random molecular orientations (with rigidly fixed molecules, it would vanish).

If the energy levels are degenerate, the inelastic scattering is still incoherent, but the elastic scattering has both a coherent contribution caused by transitions from one state to the same state and an incoherent contribution resulting from transitions between two different states with the same energy (see Appendix B).

From the above considerations, if follows that in both coherent and incoherent cases, we have to express the amplitude scattered by an arbitrary molecule and then perform an averaging procedure, calculating $\langle A(\Omega)A^*(\Omega)\rangle$ in the incoherent process and $\langle A(\Omega)\rangle\langle A^*(\Omega)\rangle$ in the coherent contribution.

C. Irreducible tensors

Consider an r-photon process, and let T be the rank-r scattering tensor involved, and $(\hat{e}^i,\omega_i)$, $(\hat{\epsilon},\omega_S)$ the polarization unit vector and frequency of the incident and scattered light, respectively $(i=1,2,\ldots,r-1)$. ($\hat{e}$ and $\hat{\epsilon}$ can be *a priori* circular, linear, or elliptic.) The amplitude scattered by one molecule is proportional to the scalar component quantity

$$\underline{T}=\sum_{IJK\cdots R} T_{IJK\cdots R}\,\epsilon_I^* e_J^{r-1}e_K^{r-2}\cdots e_R^1 . \tag{7}$$

In Eq. (7), the subscripts $I,J,K,\ldots,R$ of the Cartesian components of T, $\hat{e}^i$, and $\hat{\epsilon}$ refer to a fixed reference frame XYZ which we take as the laboratory frame. The macroscopic components $T_{IJK\cdots R}$ depend on the orientations of the molecule in the laboratory axes; now, let xyz be a reference frame rigidly linked to the molecule; in the microscopic axes, the components $T_{ijk\cdots r}$ of T are fixed quantities, and the number of independent components depend only upon the molecular symmetries. The transformation of the components of T from the macroscopic (XYZ) axes to the microscopic (xyz) axes in Cartesian coordinates is given by

$$T_{IJK\cdots R}=\sum_{ijk\cdots r}\cos\theta_{iI}\cos\theta_{jJ}\cos\theta_{kK}\cdots\cos\theta_{rR}T_{ijk\cdots r}, \tag{8}$$

where θ_{iI} is the angle between the axes i and I; hence the calculation of the scattered intensity will exhibit tremendous expressions, such as

$$\langle\cos\theta_{iI}\cos\theta_{jJ}\cdots\cos\theta_{rR}\cos\theta_{i'I'}\times\cos\theta_{j'J'}\cdots\cos\theta_{r'R'}\rangle$$

in an incoherent process, and the averaging over all the molecular orientations will be tedious in Cartesian form.

On the contrary, it will be easily performed in the spherical tensor formalism. Let ϕ, θ, ψ be the Euler angles of the rotations changing XYZ into xyz (we adopt the convention of Edmonds[10] according to which θ and ϕ are the polar angles of the z axis in the laboratory frame). The transformation of an irreducible spherical tensor T_M^J is easily performed by use of a Wigner matrix $\mathfrak{D}_{mM}^J(\phi,\theta,\psi)$:

$$T_M^J=\sum_m \mathfrak{D}_{mM}^{(J)}\,T_m^J , \tag{9}$$

and the averaging procedure over all the molecular orientations leads to $\langle\mathfrak{D}_{mM}^{(J)}\mathfrak{D}_{m'M'}^{(J')*}\rangle$, which is quite simple to evaluate using the orthogonality properties of Wigner matrices:

$$\begin{aligned}\langle\mathfrak{D}_{mM}^{(J)}\mathfrak{D}_{m'M'}^{(J')*}\rangle &= \int_0^{2\pi}\frac{d\psi}{2\pi}\int_0^{2\pi}\frac{d\phi}{2\pi}\int_0^{\pi}\frac{\sin\theta\,d\theta}{2}\,\mathfrak{D}_{mM}^{(J)}\mathfrak{D}_{m'M'}^{(J')*}\\ &=\delta_{JJ'}\delta_{mm'}\delta_{MM'}/(2J+1).\end{aligned} \tag{10}$$

Hence, in order to derive the general formulas describing light scattering, we shall now use the formalism of I and express (7) in terms of irreducible spherical tensors.

The transformation from reducible Cartesian tensors to irreducible spherical tensors can be performed in two steps. First, from reducible Cartesian tensors to reducible spherical tensors. Second, by reducing these spherical tensors through spherical tensor algebra. In order to distinguish between Cartesian and spherical subscripts, we use the following notation: a latin letter (k,K) stands for a Cartesian coordinate (X,Y,Z); a greek letter (μ) stands for a spherical coordinate $(-1,0,+1)$. The first step is just a product of unitary transformations [see Eq. (4) of (I)], leading to

$$\underline{T}=\sum_{\lambda\mu\nu\cdots\rho}(-1)^{M}T_{\lambda\mu\nu\cdots\rho}\,\epsilon^{\dagger}_{-\lambda}e_{-\mu}e_{-\nu}\cdots e_{-\rho}\tag{11}$$

with $M=(\lambda+\mu+\nu+\cdots+\rho)$.

All the polarization dependences can be collected in a unique tensor P defined by

$$P=\hat{\epsilon}^{+}\otimes\hat{e}^{r-1}\otimes\hat{e}^{r-2}\otimes\cdots\otimes\hat{e}^{1}\,.\tag{12}$$

Let $T^{\tau J}$ and $P^{\tau J}$ be the irreducible parts of T and P with weight J (the reduction process is analyzed in detail in I). By applying Eq. (47a) of I, Eq. (11) can be cast in the following form:

$$\underline{T}=\sum_{\tau JM}(-1)^{r+J+M}T^{(\tau J)}_{M}P^{\tau J}_{-M}$$

or (13)

$$\underline{T}=\sum_{\tau J}(-1)^{r+J}(T^{\tau J}\cdot P^{\tau J})\,.$$

The amplitude scattered by a single molecule can thus be expressed in terms of the irreducible tensors $P^{\tau J}_{M}$ and $T^{\tau J}_{M}$, but only this last tensor depends upon the molecular orientation and needs to be expressed in terms of the fixed components $T^{\tau J}_{m}$ along a set of molecular axes. The amplitude scattered by a single molecule is thus proportional to

$$\underline{T}=\sum_{\tau J}(-1)^{r+J}\sum_{mM}(-1)^{M}T^{\tau J}_{m}P^{\tau J}_{-M}\mathfrak{D}^{(J)}_{mM}\,.\tag{14}$$

The averaging over all the random molecular orientations can now be performed with the use of Eq. (10) in both coherent and incoherent cases, since in Eq. (14) only the Wigner matrices $\mathfrak{D}^{(J)}_{mM}$ depend upon the Euler angles ϕ, θ, ψ.

III. EXPRESSION OF THE SCATTERED INTENSITY

A. General expression

From Eq. (5), the intensity scattered incoherently by N molecules is

$$I_{\rm inc}=NI_0\langle\underline{T}\,\underline{T}^{*}\rangle,$$

where I_0 is a proportionality constant whose explicit calculation is briefly recalled in Appendix A; from Eq. (14) the intensity scattered by a single molecule is proportional to

$$\underline{T}\,\underline{T}^{*}=\sum_{\substack{\tau JMm\\ \tau' J'M'm'}}(-1)^{J+J'+M+M'}(P^{\tau J}_{-M}{}^{*}P^{\tau' J'}_{-M'})\times(T^{\tau J}_{m}{}^{*}T^{\tau' J'}_{m'})(\mathfrak{D}^{(J)}_{mM}{}^{*}\mathfrak{D}^{(J')}_{m'M'}).$$

The averaging over molecular orientations is performed by use of Eq. (10): the summation over J', m', M' vanishes, and finally one has

$$I_{\rm inc}=NI_0\sum_{\tau\tau' J}(2J+1)^{-1}\left(\sum_{M}P^{\tau J*}_{M}P^{\tau' J}_{M}\right)\left(\sum_{m}T^{\tau J*}_{m}T^{\tau' J}_{m}\right)\,.\tag{15}$$

All orientation dependence has disappeared, which accounts for the isotropy of the scattering process.

In Sec. II, we had obtained the following expression for the coherently scattered intensity [Eq. (6b)]:

$$I_{\rm coh}=|\langle A(\Omega)\rangle|^{2}\left|\sum_{q}e^{i\Delta\vec{k}\cdot\vec{R}_q}\right|^{2}.$$

From Eq. (14) the mean scattered amplitude per molecule is proportional to

$$\langle\underline{T}\rangle=\sum_{\tau JmM}(-1)^{r+J+M}T^{\tau J}_{m}P^{\tau J}_{-M}\langle\mathfrak{D}^{(J)}_{mM}\rangle\,.$$

The mean value of the Wigner matrix is readily obtained from Eq. (10), since $D^{(0)}_{00}=1$,

$$\langle\mathfrak{D}^{(J)}_{mM}\rangle=\delta_{J0}\,\delta_{M0}\,\delta_{m0}.$$

Hence, the mean amplitude scattered coherently by a single molecule depends only on the scalar irreducible parts of the scattering tensor (which in this case is identical to the usual polarizability tensor).

The substitution of the sum over the molecular positions by an integral over the volume of the medium (assuming the mean distance between molecules to be smaller than the wave-lengths), i.e.,

$$\sum_{q}e^{i\Delta\vec{k}\cdot\vec{R}_q}\to\frac{N}{V}\int_{(V)}e^{i\Delta\vec{k}\cdot\vec{R}}d^{3}\vec{R}\,,$$

evidences the function

$$f(V,\vec{k})=N^{2}\sum_{i=x,y,z}\left(\frac{\sin\frac{1}{2}\Delta k_iL_i}{\frac{1}{2}\Delta k_iL_i}\right)^{2},\tag{16}$$

proportional to the square of the number of atoms and involving a phase-matching condition.[12] If a monochromatic incident light wave travels on a length L in the direction of $\vec{k}$ in the medium, $f(V,\vec{k})$ is merely $N^{2}(\sin X/X)^{2}$, where $X=\frac{1}{2}(\Delta\vec{k}\cdot\vec{L})$. If the dispersion of the medium keeps the phase-matching condition from being exactly achieved (i.e., $\Delta\vec{k}=0$), coherently scattered light can yet be observed. One can define a coherence length L_C from $\Delta kL_C=\frac{1}{2}\pi$, i.e., $L_C=\lambda/4[n(p\omega)-n(\omega)]$ if $\omega_S=p\omega$.

Moreover, whereas the Doppler effect and collisions broaden the spectrum of incoherently scattered light, conversely in the coherent case, when phase matching is achieved, no impulsion is transferred to the atomic system so that first-order Doppler effect is eliminated. (The frequency-matching condition $\Sigma\omega = 0$ in the molecular frame implies its fulfillment in the laboratory frame.) If we neglect molecular correlations, the spectral width of the scattered light is then limited by the spectral width of the source (temporal coherence).

Hence, the coherent intensity is given by

$$I_{\text{coh}} = I_0 f(V, \vec{k}) \sum_{\tau\tau'} (T^{\tau 0} T^{\tau' 0 *})(P^{\tau 0} P^{\tau' 0 *}) . \tag{17}$$

We note that by isolating in the expressions of the incoherently scattered intensity Eq. (15) the contributions of the scalar ($J = 0$) irreducible parts of T and replacing N by $f(V, \vec{k})$ gives Eq. (17), while the residual incoherent contribution Eq. (6b) is accounted for by the other-than-scalar terms in Eq. (15).

In both cases, we can write

$$I_{\text{incoh}} = N I_0 \sum_J \chi(J)$$

and

$$I_{\text{coh}} = I_0 f(V, \vec{k}) \chi(0)$$

with

$$\chi(J) = \sum_{\tau\tau'} \frac{(T^{\tau J} \cdot T^{\dagger\tau' J})(P^{\tau J} \cdot P^{\dagger\tau' J})}{2J+1} .$$

Here, $R^{\dagger J}$ denotes the Hermitian conjugate of R^J (i.e., $R^{\dagger J}_M = (-1)^M R^{J*}_{-M}$); if, in Cartesian coordinates, R contains an imaginary part (T near a resonance or P if one of the polarization vectors is circular or elliptical), R^J is not Hermitian ($R^\dagger \neq R$), but can be expressed as the sum of a Hermitian part and an anti-Hermitian one.

In order to end up with practical formulas, we now calculate separately the two scalar products $T^{\tau J} \cdot T^{\dagger\tau' J}$ and $P^{\tau J} \cdot P^{\dagger\tau' J}$. Let us first consider the polarization dependence

$$P^{\tau J} = \{\epsilon^\dagger \otimes s^k\}^J .$$

The unit vector $\hat{\epsilon}$ is an irreducible tensor of weight 1, and s^k is an irreducible tensor of weight k originated from the tensor product

$$s = \hat{e}^{r-1} \otimes \hat{e}^{r-2} \otimes \cdots \otimes \hat{e}^1 .$$

The scalar product $P^{\tau J} \cdot P^{\dagger\tau' J}$ can be transformed in order to couple the $\hat{\epsilon}$ and the s together:

$$\begin{aligned} P^{\tau J} \cdot P^{\dagger\tau' J} &= \{\epsilon^\dagger \otimes s^k\}^J \cdot \{\epsilon \otimes s^{\dagger k'}\}^J \\ &= (2J+1) \sum_l (-1)^{k+1} \begin{Bmatrix} 1 & 1 & l \\ k' & k & J \end{Bmatrix} \\ &\quad \times \{\epsilon^\dagger \otimes \epsilon\}^l \cdot \{s^k \otimes s^{\dagger k'}\}^l . \end{aligned} \tag{18}$$

For sake of simplicity, we now assume the scattered light to be linearly analyzed, and let (θ_S, ϕ_S) be the polar angles of the real polarization $\hat{\epsilon}$. It is well known from the properties of the Racah spherical harmonics (see, e.g., I, Appendix 3) that

$$\hat{\epsilon} = C^{(1)}(\theta_S, \phi_S)$$

and (19)

$$\{\hat{\epsilon} \otimes \hat{\epsilon}\}^l = \langle 11, 00 | l0 \rangle C^{(l)}(\theta_S, \phi_S) .$$

B. Linearly polarized pump beam

If one deals with a single linearly polarized pump beam, let (θ_I, ϕ_I) be the polar angles of the polarization $\hat{e}$. In a similar way, $\hat{e} = C^{(1)}(\theta_I, \phi_I)$; s then reduces to the symmetrical tensor product $(\otimes^{r-1}\hat{e})$. In the irreducible subspace $\mathcal{E}(k)$ with $2k+1$ dimensions, the spherical harmonics $C^k_q(\theta, \phi)$ play the role of unit tensors in the (θ, ϕ) representation, and hence $s^{(k)}_q$ is proportional to $C^{(k)}_q(\theta_I, \phi_I)$:

$$s^{(k)} = \langle \tau | (0) \rangle C^{(k)}(\theta_I, \phi_I) .$$

$\langle \tau | (0) \rangle$ is a proportionality coefficient depending upon the coupling scheme (and then upon τ).

From the coupling scheme adopted in I, i.e.,

$$s^{(k)} = \{e^{r-1} \otimes \{e^{r-2} \otimes \{ \cdots \otimes \{e^2 \otimes e^1\}^{j3}\}^{j4} \cdots \}^{jr-2}\}^{(k)} ,$$

the seniority index τ is $(j_3, j_4, \cdots, j_{r-2}, k)$. It has been shown in I that the proportionality coefficient $\langle \tau | (0) \rangle$ was then equal to a product of Clebsch-Gordan (C-G) coefficients:

$$\langle \tau | (0) \rangle = \langle 11, 00 | j_3 0 \rangle \langle 1 j_3, 00 | j_4 0 \rangle \cdots \langle 1 j_{n-2}, 00 | k0 \rangle .$$

The symmetry properties of the C-G coefficients $\langle j_p 1, 00 | j_{p+1} 0 \rangle$ require the following selection rules: j_{2p+1} must be even and j_{2p} must be odd. The coefficients $\langle \tau | (0) \rangle$ have been tabulated in I up to order 4. Similarly one has

$$s^{(k)} = \langle \tau' | (0) \rangle C^{(k')}(\theta_I, \phi_I)$$

and

$$\{s^k \otimes s^{k'}\}^l = \langle \tau | (0) \rangle \langle \tau' | (0) \rangle \langle kk', 00 | l0 \rangle C^{(l)}(\theta_I, \phi_I) .$$

The polarization dependence of Eq. (18) can now be put in the following form:

$$P^{\tau J}\cdot P^{\tau' J}=(-1)^{k+1}(2J+1)\langle\tau|(0)\rangle\langle\tau'|(0)\rangle \times\langle 11,00|l0\rangle\langle kk',00|l0\rangle \times\sum_{l}\begin{Bmatrix}1 & 1 & l\\ k' & k & J\end{Bmatrix}[C^{(l)}(\omega_S)C^{(l)}(\omega_I)]. \tag{20}$$

(Note that these results would hold if one deals with two or more beams with different frequencies and directions but the same polarization.)

The only relevant angular parameter involved in the process is the angle η, which is between the incident polarization vector $\hat{e}$ and the scattered polarization vector $\hat{\epsilon}$ ($\cos\eta=\hat{e}\cdot\hat{\epsilon}$). In terms of the Legendre polynomials, we have

$$C^l(\theta_S,\phi_S)C^l(\theta_I,\phi_I)=P_l(\cos\eta),$$

leading to

$$P^{\tau J}\cdot P^{\tau' J}=\sum_l A(J,l,\tau,\tau')P_l(\cos\eta), \tag{21a}$$

where $A(J,l,\tau,\tau')$ is a numerical coefficient, easily computed in terms of the Clebsch-Gordan and Wigner 6-j coefficients[11]:

$$A(J,l,\tau,\tau')=(-1)^{1+j_{r-1}}\langle\tau|(0)\rangle\langle\tau'|(0)\rangle\langle 11,00|l0\rangle \times\langle j_{r-1}j'_{r-1},00|l0\rangle\begin{Bmatrix}1 & j_{r-1} & J\\ j'_{r-1} & 1 & l\end{Bmatrix}. \tag{21b}$$

Equation (21a) is absolutely general, and by use of the reduction method of I, can be used to analyze any scattering process of the type considered. The relevant tensorial quantities are the scalar products $T^{\tau J}\cdot T^{\tau' J}$ as was mentioned in the Introduction. An important result is readily obtained from Eq. (21b): Because of the selection rules of the Clebsch-Gordan coefficients, l can only take the value 0 or 2. Thus, whatever the order of the process may be, the dependence of the scattered intensity upon the angle between the incident and scattered polarization only involves an isotropic part $P_0(\cos\eta)$ and a part proportional to

$$P_2(\cos\eta)=\tfrac{1}{2}(3\cos^2\eta-1).$$

This result can be illustrated in the following way. Because the scattered intensity (a scalar quantity) is observed for a given direction of polarization, the dependence on $\hat{\epsilon}$ is a linear function of $(\hat{\epsilon}\otimes\hat{\epsilon})$, i.e., a symmetric rank-2 tensor with only a part of weight 2 and a part of weight 0, which must be coupled with tensors of the same weight to form a scalar. Since the only relevant angle is η, the intensity can depend only on $P_0(\cos\eta)$ and $P_2(\cos\eta)$.

C. Symmetrical case

It is now necessary to study in more detail the influence of the properties of the irreducible components of the scattering tensors on the scattered intensity.

For the sake of simplicity we assume that the scattering tensor T is fully symmetric in any permutation of its Cartesian indices, i.e., the experiment is performed in the transparency range of the medium. In this case, it has been shown in I that T has only one nonvanishing component of weight J, T^J, if $r+J$ is even and none otherwise; moreover, the projection of $T^{\tau J}$ upon the totally symmetric representation of the permutation group S_r is obtained by applying the r-symmetrizer $\sigma(r)$:

$$\sigma(r)T^{\tau J}=\lambda^r_{\tau J}\,T^{\tau J}.$$

The real coefficients

$$\lambda^r_{\tau J}=|\langle\tau|(0)\rangle|\Big/\Big(\sum_\tau\langle\tau J|(0)\rangle^2\Big)^{1/2}$$

have been tabulated up to rank 4 in I. The scalar product $T^{\tau J}\cdot T^{\tau' J}$ is thus directly proportional to the squared norm of the irreducible tensor T^J, i.e., $\|T^J\|^2=T^J\cdot T^J$, and one can write

$$\chi(J)=\sum_{l=0,2}B(J,l)\|T^J\|^2P_l(\cos\eta). \tag{22a}$$

The numerical factor

$$B(J,l)=\sum_{\tau\tau'}\lambda^r_{\tau J}\lambda^r_{\tau' J}A(J,l,\tau,\tau') \tag{22b}$$

is tedious but straightforward to compute. The explicit calculation has been perfromed up to order 4 in the incoherent case, i.e., ordinary Rayleigh and Raman, and first and second hyper-Rayleigh and -Raman scattering, with linearly polarized incident and scattered lights. The results are given below: The fraction of the scattered light polarized parallel to the incident light is I [$\eta=0$, $P_l(\cos\eta)=1$], whereas the fraction polarized perpendicular to the incident light is I [$\eta=\frac{1}{2}\pi$, $P_2(\cos\eta)=-\frac{1}{2}$].

1. Rayleigh-Raman scattering

$$I_{\text{inc}}=\tfrac{1}{9}I_0\{(\alpha^{(0)}\cdot\alpha^{(0)})[1+2P_2(\cos\eta)] +(\alpha^{(2)}\cdot\alpha^{(2)})[1+\tfrac{1}{5}P_2(\cos\eta)]\},$$

$$I_{\parallel}=\tfrac{1}{3}I_0\{\|\alpha^{(0)}\|^2+\tfrac{2}{5}\|\alpha^{(2)}\|^2\},$$

$$I_{\perp}=\tfrac{1}{10}I_0\{\|\alpha^{(2)}\|^2\}.$$

The scalar term is the classical $\cos^2\eta$ law.

2. First hyper-Rayleigh-Raman scattering

$$I_{\text{inc}}=\tfrac{1}{45}I_0\{\tfrac{1}{3}(\beta^{(1)}\cdot\beta^{(1)})[11+16P_2(\cos\eta)] +2(\beta^{(3)}\cdot\beta^{(3)})[1+\tfrac{2}{7}P_2(\cos\eta)]\},$$

$$I_{\parallel}=\tfrac{1}{5}I_0\{\|\beta^{(1)}\|^2+\tfrac{2}{7}\|\beta^{(3)}\|^2\},$$

$$I_{\perp}=\tfrac{1}{45}I_0\{\|\beta^{(1)}\|^2+\tfrac{12}{7}\|\beta^{(3)}\|^2\}.$$

These formulas are essentially the same as those of Maker.[3]

3. *Second hyper-Rayleigh-Raman scattering*

If one deals with centrosymmetrical molecules, β vanishes, and the hyperscattering is due to the cubic polarizability; such an effect, excessively weak, has not yet been observed:

$$\begin{aligned} I_{\text{incoh}} = \tfrac{1}{15} I_0 \{ & (\gamma^{(0)} \cdot \gamma^{(0)})[1 + 2P_2(\cos\eta)] \\ & + (\gamma^{(2)} \cdot \gamma^{(2)})[\tfrac{11}{14} + \tfrac{13}{14} P_2(\cos\eta)] \\ & + (\gamma^{(4)} \cdot \gamma^{(4)})[\tfrac{2}{7} + \tfrac{2}{21} P_2(\cos\eta)] \}, \end{aligned}$$

$$I_{\parallel} = \tfrac{1}{5} I_0 \{ \|\gamma^{(0)}\|^2 + \tfrac{4}{7} \|\gamma^{(2)}\|^2 + \tfrac{8}{63} \|\gamma^{(4)}\|^2 \},$$

$$I_{\perp} = \tfrac{1}{7} I_0 \{ \tfrac{3}{20} \|\gamma^{(2)}\|^2 + \tfrac{1}{9} \|\gamma^{(4)}\|^2 \}.$$

One of the most widely used parameters is the depolarization ratio ρ which is defined from

$$1 - \rho = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}).$$

Table I gives the depolarization ratio for the three configurations analyzed above. The most notable result of this section is the following: if we assume Kleinman's symmetry, the relevant quantities in incoherent scattering processes are the norms of the various irreducible parts of the scattering tensors.

On the other hand, in a coherent process, $\chi(0)$ reduces to

$$\sum_{\tau\tau'} (T^{\tau 0} \cdot T^{\tau' 0}) \sum_{l=0,2} A(0, l, \tau, \tau') P_l(\cos\eta), \tag{23}$$

which can be changed into

$$\sum_{\tau\tau'} (T^{\tau 0} \cdot T^{\tau' 0}) \langle \tau | (0) \rangle \langle \tau' (0) \rangle \left(\frac{P_0 + 2P_2}{9} \right).$$

Since $P_0 = 1$ and $P_2 = \frac{1}{2}(3\cos^2\eta - 1)$, the polarization dependence of the scattered intensity is thus merely the square cosine of the angle between the incident and the scattered light polarizations.

In a second-order coherent process appears the norm of the scalar polarizability $\alpha^{(0)}$. Since the phase-matching condition is fulfilled in the forward direction,

$$I_{\text{coh}} = I_0 f(V, \vec{k}) \|\alpha^{(0)}\|^2 \tfrac{1}{3} \cos^2\eta$$

gives the distribution of the forward scattered Rayleigh intensity. In the incident mode ($\vec{k}_S = \vec{k}$, $\hat{\epsilon} = \hat{e}$) the scattered amplitude interferes destructively with the incident wave, which ensures the total intensity to be conserved. The second hyperpolarizability γ has two scalar irreducible parts,

$$\gamma^{01,0} = \tfrac{1}{3}\sqrt{5}\gamma^{(0)} \quad \text{and} \quad \gamma^{21,0} = \tfrac{2}{3}\gamma^{(0)},$$

which after a short calculation leads to

$$I_{\text{coh}} = \tfrac{1}{5} I_0 f(V, \vec{k}) \|\gamma^{(0)}\|^2 \cos^2\eta.$$

With a monochromatic pump, one fourth-order coherent process can be evidenced: third harmonic generation, i.e., $\omega_S = 3_\omega$ and $\Delta\vec{k} = \vec{k}(3\omega) - 3\vec{k}(\omega)$. With two pump beams at frequencies ω_1 and ω_2, several fourth-order effects have been observed and discussed,[12] such as coherent anti-Stokes Raman scattering ($\omega_3 = 2\omega_1 - \omega_2$) and three-wave mixing ($\omega_3 = 2\omega_1 + \omega_2$).

D. Circularly polarized pump beam

If the pump beam is circularly polarized, we can assume a propagation in the $+z$ direction and a polarization in the xy plane; for a right circular wave, $\hat{e}$ is given by its circular components $e_{+1} = 1$, $e_0 = e_{-1} = 0$. It follows that

$$\{ \overset{r-1}{\otimes} \hat{e} \}_q^{(k)} = \delta_{k,r-1} \delta_{q,r-1},$$

$$\begin{aligned} \{ s^k \otimes s^{\dagger k'} \}_m^l = {} & \delta_{k,r-1} \delta_{k',r-1} \delta_{m,0} \\ & \times \langle r-1\, r-1, r-1\; -r+1 | l0 \rangle, \end{aligned}$$

and hence that

$$\begin{aligned} \chi(J) = \|T^{\tau,J}\|^2 \sum_l (-1)^r & \begin{Bmatrix} 1 & 1 & l \\ r-1 & r-1 & J \end{Bmatrix} P_l(\cos\theta_S) \\ & \times \langle 11, 00 | l0 \rangle \\ & \times \langle r-1\, r-1, r-1\; -r+1 | l0 \rangle. \end{aligned} \tag{24}$$

The only irreducible component appearing in $\chi(J)$ is the one with maximum value of k and k' ($k = k' = r-1$); this implies that except in a linear (two-photon) process, no coherent ($J = 0$) scattering can occur in a fluid with one circularly polarized pump beam. The explicit calculation has been

TABLE I. Depolarization ratios in incoherent scattering.

Depolarization ratio	Raman scattering	First hyper-Raman	Second hyper-Raman
ρ	$6\|\alpha^{(2)}\|^2$ $10\|\alpha^{(0)}\|^2 + 7\|\alpha^{(2)}\|^2$	$7\|\beta^{(1)}\|^2 + 12\|\beta^{(3)}\|^2$ $35\|\beta^{(1)}\|^2 + 15\|\beta^{(3)}\|^2$	$54\|\gamma^{(2)}\|^2 + 40\|\gamma^{(4)}\|^2$ $252\|\gamma^{(0)}\|^2 + 171\|\gamma^{(2)}\|^2 + 42\|\gamma^{(4)}\|^2$

performed below in the symmetric case.

Two-photon process:

$$\frac{I_{\text{coh}}}{I_0}=\frac{\|\alpha^{(0)}\|^2}{6}\sin^2\theta_S f(V,\vec{k}),$$

$$\frac{I}{I_0}=\frac{\|\alpha^{(0)}\|^2}{9}(P_0-P_2)+\frac{\|\alpha^{(2)}\|^2}{9}\left(P_0-\frac{P_2}{10}\right),$$

$$I_z=I_0\frac{\|\alpha^{(2)}\|^2}{10},$$

$$I_x=I_y=I_0\left(\frac{\|\alpha^{(0)}\|^2}{6}+\frac{7\|\alpha^{(2)}\|^2}{60}\right).$$

Three-photon process:

$$\frac{I}{I_0}=\frac{4}{9}\frac{\|\beta^{(1)}\|^2}{15}(P_0-P_2)+\frac{\|\beta^{(3)}\|^2}{15}\left(P_0-\frac{2}{7}P_2\right),$$

$$I_z=I_0\frac{\|\beta^{(3)}\|^2}{21},$$

$$I_x=I_y=I_0\left(\frac{2}{45}\|\beta^{(1)}\|^2+\frac{8}{105}\|\beta^{(1)}\|^2\right).$$

Four-photon process:

$$\frac{I}{I_0}=\frac{3}{10}\frac{\|\gamma^{(2)}\|^2}{21}(P_0-P_2)+\frac{\|\gamma^{(4)}\|^2}{21}\left(P_0-\frac{5}{12}P_2\right),$$

$$I_z=I_0\frac{\|\gamma^{(4)}\|^2}{36},$$

$$I_x=I_y=I_0\left(\frac{3}{140}\|\gamma^{(2)}\|^2+\frac{29}{252}\|\gamma^{(4)}\|^2\right).$$

This provides a way of measuring directly the norm of the irreducible component of highest weight, for instance, $\|\beta^{(3)}\|$. Then one can measure $\|\beta^{(1)}\|$ with different polarizations. These experiments can complete other nonlinear optical experiments, such as dc second-harmonic generation, which allows one to measure $\beta_0^{(1)}$.

IV. OTHER EXAMPLES

In Sec. III, we investigated the case of one single monochromatic linearly polarized pump beam. All of our results [Eqs. (15)–(18)] are still valid in more complex situations, and we shall now give two examples relative to third-order processes: (i) Coherent frequency mixing, with two monochromatic beams, both linearly polarized. (ii) Incoherent hyper-Rayleigh scattering, with one pump beam elliptically polarized.

A. Coherent frequency mixing

Since the (pseudo) scalar part of a rank-3 tensor is fully antisymmetrical in any permutation of its Cartesian indices, no coherent second harmonic generation can occur in a fluid. Now, parametric interactions such as $\omega_3=\omega_1\pm\omega_2$ ($\omega_1\neq\omega_2$) can be evidenced with molecules containing a pseudoscalar quantity in the totally symmetrical representation of their point group. These molecules belong to direct groups (i.e., with no improper point operation) and hence exhibit optical activity, such a frequency mixing, first discussed by Giordmaine,[14] and observed, for example, in solutions of chiral glucides by Rentzepis *et al.*,[15] is weak since it is only allowed as far as frequency dispersion cannot be neglected. If the two fundamental beams are polarized parallel to each other, Eq. (20) gives a zero intensity; however, the scattered intensity is easy to compute from Eq. (17) and is readily written

$$I_{\text{coh}}=I_0 f(V,\vec{k})\|\beta^{(0)}\|^2P^{1,0}P^{1,0*}$$

with

$$P^{1,0}=\{\hat{\epsilon}\otimes\{\hat{e}^1\otimes\hat{e}^2\}^{(1)}\}^{(0)}.$$

Since

$$\{\hat{e}^1\otimes\hat{e}^2\}^{(1)}=(i/\sqrt{2})\hat{e}^1\times\hat{e}^2$$

and

$$\{e\otimes u\}^{(0)}=-(1/\sqrt{3})\hat{\epsilon}\cdot\hat{u},$$

we obtain

$$I_{\text{coh}}=\tfrac{1}{6}I_0 f(V,\vec{k})\|\beta^{(0)}\|^2|\hat{\epsilon}\cdot(\hat{e}^1\times\hat{e}^2)|^2. \tag{25}$$

Indeed, if $\hat{e}^1$ and $\hat{e}^2$ are parallel, $I_{\text{coh}}=0$; if $\hat{e}^1\perp\hat{e}^2$, for instance $\hat{e}^1\parallel x$ and $\hat{e}^2\parallel y$, let θ_S be the angle between $\hat{\epsilon}$ and the $\hat{z}$ axis, we then find that I_{coh} is proportional to $\cos^2\theta_S$.

B. Hyper-Rayleigh scattering

Though no coherent second harmonic generation can occur in a liquid, Rayleigh scattering can still be observed. We suppose that the fundamental beam is elliptically polarized, i.e., a statistical mixing; then, $\hat{e}$ is given by its circular components ($\hat{e}=\cos\lambda\hat{e}^++\sin\lambda\hat{e}^-$).

The generation of a harmonic photon can result from the fusion of two photons belonging either to the same mode, or to orthogonal modes:

$$I/I_0=\cos^4\lambda I(+)+\sin^4\lambda I(-)+4\sin^2\lambda\cos^2\lambda I(\pm). \tag{26}$$

The two first terms account for pure circular waves. The crossed term is readily computed from

$$s_q^{(k)}=\{\hat{e}^+\otimes\hat{e}^-\}_q^{(k)}=\langle 11,1-1|k0\rangle\delta_{q0}$$

and one finds

$$\chi(J)=\sum_l\langle 11,00|l0\rangle P_l(\cos\theta_S)$$
$$\times\sum_{kk'}(-1)^{k+1}\begin{Bmatrix}1 & 1 & l\\ k & k' & J\end{Bmatrix}\langle kk',00|l0\rangle$$
$$\times\langle 11,1-1|k0\rangle\langle 11,1-1|k'0\rangle(\beta^{k,J}\cdot\beta^{k'J}).$$

In the symmetrical case,

$$I_{(\pm)}/I_0 = \tfrac{1}{15}\,\|\beta^{(1)}\|^2[P_0 - \tfrac{14}{9}P_2(\cos\theta_S)] + \tfrac{2}{45}\,\|\beta^{(3)}\|^2[P_0 + \tfrac{2}{7}P_2(\cos\theta_S)]\,. \tag{27}$$

The circular case is given by (26) and (27) with $\cos\lambda = 0$ or $\sin\lambda = 0$; in the linear case, $|\cos\lambda| = |\sin\lambda| = 1/\sqrt{2}$. If one uses $P_2(\cos\hat{\epsilon}\cdot\hat{z}) = -P_2(\cos\eta)$, one finds again the results of Sec. III B. This approach can be generalized for a process of any order, evidencing the squared coefficients of the binomial expansion of $(\cos\lambda + \sin\lambda)^{r-1}$.

V. MOLECULAR SELECTION RULES

Molecular symmetry requires selection rules on the polarizability components, which are not customarily expressed in the formalism of spherical tensors. For sake of completeness we now discuss some symmetry considerations for vibrational Rayleigh or Raman scattering. The correspondence between spherical and fully symmetrical Cartesian tensors is explicitly given in I up to rank 4.

In the Born-Oppenheimer approximation, the wave function of the molecule is written as the product of an electronic and a nuclear wave function. The electronic Hamiltonian as well as the electronic wave function can be developed in series of the normal nuclear coordinates q_p so that the polarizability tensor involved in a process of order r can be developed as

$$T_M^{\tau J}(q_p) = T_M^{\tau J}(0) + \sum_p T_{M;p}^{\tau J} q_p + \cdots\,, \tag{28}$$

where $T_{M;p}^{\tau J} = (\partial T_M^{\tau J}/\partial q_p)_{qp=0}$. The first term in Eq. (27) is purely electronic and accounts for Rayleigh scattering; the second term is responsible for Raman scattering. The occurrence of a Raman transition requires that the corresponding $T_M^{\tau J}$ component symmetry type contains the symmetry of the normal coordinate involved q_p. In particular, a coherent process can only involve normal coordinates transforming like a scalar.

In Table II we give the irreducible components of spherical true and pseudotensors up to $J = 4$ for each representation of the 32 crystallographic point groups and the molecular groups $C_{\infty v}$ and $D_{\infty h}$; the irreducible representations are labeled following Koster *et al.*[16] The qth component of an irreducible tensor of weight k is denoted by D_q^k; if necessary a superscript "+" or "−" indicates the parity of the tensor.

VI. CONCLUSION

We have applied the formalism developed in I to the problem of elastic (always incoherent) light scattering in a low-density fluid. It has been found that the intensity scattered in a given direction depends on one angular parameter, namely, the angle between the polarization of the incident and the scattered light, and can only have an isotropic contribution $P_0(\cos\eta)$ and a deviatoric one $P_2(\cos\eta)$. The scattered intensity is a function of the scalar invariants associated with the various irreducible components $T^{\tau J}$ of the scattering tensor T: the scalar products $(T^{\tau J}\cdot T^{\tau' J})$ in the incoherent case, which are changed into $\|T^{J}\|^2$ if Kleinman's symmetry is assumed, or the scalar irreducible component $T^{\tau 0}$ in the coherent case.

ACKNOWLEDGMENT

We feel very indebted to Dr. J. Jerphagnon for fruitful discussions.

APPENDIX A

We briefly recall how the scattering tensors and the absolute cross sections are calculated explicitly. The transition probability per unit from an eigenstate $|\phi_1\rangle$ with energy W_1 of the free (atom plus radiation) system to another state $|\phi_2\rangle$ under the coupling V is

$$\frac{dp}{dt} = \frac{2\pi}{\hbar}\rho(W_1)|S_{21}|^2\,. \tag{A1}$$

In (A1), $\rho(W)$ is the density of final states, and

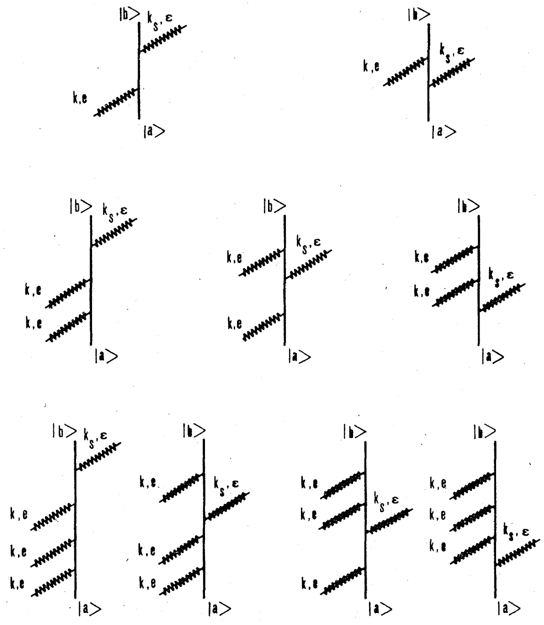

FIG. 2. Perturbation diagrams for computing $\alpha(-\omega_S, \omega)$, $\beta(-\omega_S, \omega, \omega)$, $\gamma(-\omega_S, \omega, \omega, \omega)$.

TABLE II. Molecular selection rules for the most frequently encountered point groups.

(a) Triclinic system

Group C_1 (1)

Γ_1 D_q^k $q: -k, -k+1, \ldots, k-1, k$

Group S_2 $(\bar{1})$

D_q^{k+} is Γ_1^+, D_q^{k-} is Γ_1^-

(b) Monoclinic system

Group C_2 (2)

$$\begin{array}{ll} \Gamma_1 \;\; D_q^k,\ q \text{ even} & \\ & q: -k, -k+1, \ldots, k-1, k \\ \Gamma_2 \;\; D_q^k,\ q \text{ odd} & \end{array}$$

Group C_s (m)

$$D_q^k \text{ is } \Gamma_l \text{ in } C_2 \begin{cases} D_q^{k+}: \text{idem} \\ D_q^{k-}: \Gamma_1 \longleftrightarrow \Gamma_2 \end{cases}$$

Group C_{2h} $(2/m)$

$$D_q^k \text{ is } \Gamma_l \text{ in } C_2 \begin{cases} D_q^{k+} \text{ is } \Gamma_l^+ \\ D_q^{k-} \text{ is } \Gamma_l^- \end{cases}$$

(c) Orthorhombic system

Group D_2 (222)

Γ_1	D_0^0		D_0^2, $D_2^2+D_{-2}^2$	$D_2^3-D_{-2}^3$	D_0^4, $D_2^4+D_{-2}^4$, $D_4^4+D_{-4}^4$
Γ_2		$D_1^1-D_{-1}^1$	$D_1^2+D_{-1}^2$	$D_1^3-D_{-1}^3$, $D_3^3-D_{-3}^3$	$D_1^4+D_{-1}^4$, $D_3^4+D_{-3}^4$
Γ_3		D_0^1	$D_2^2-D_{-2}^2$	D_0^3, $D_2^3+D_{-2}^3$	$D_2^4-D_{-2}^4$, $D_4^4-D_{-4}^4$
Γ_4		$D_1^1+D_{-1}^1$	$D_1^2-D_{-1}^2$	$D_1^3+D_{-1}^3$, $D_3^3+D_{-3}^3$	$D_1^4-D_{-1}^4$, $D_3^4-D_{-3}^4$

Group C_{2v} $(mm2)$

$$D_q^k \text{ is } \Gamma_l \text{ in } D_2 \begin{cases} D_q^{k+}: \text{idem} \\ D_q^{k-}: \Gamma_1 \longleftrightarrow \Gamma_3,\ \Gamma_2 \longleftrightarrow \Gamma_4 \end{cases}$$

Group D_{2h} (mmm)

$$D_q^k \text{ is } \Gamma_l \text{ in } D_2 \begin{cases} D_q^{k+} \text{ is } \Gamma_l^+ \\ D_q^{k-} \text{ is } \Gamma_l^- \end{cases}$$

(d) Trigonal system

Group C_3 (3)

Γ_1	D_0^0	D_0^1	D_0^2	D_{-3}^3, D_0^3, D_3^3	D_{-3}^4, D_0^4, D_3^4
Γ_2		D_1^1	D_{-2}^2, D_1^2	D_{-2}^3, D_1^3	D_{-2}^4, D_1^4, D_4^4
Γ_3		D_{-1}^1	D_{-1}^2, D_2^2	D_{-1}^3, D_2^3	D_{-4}^4, D_{-1}^4, D_2^4

Group S_6 $(\bar{3})$

$$D_q^k \text{ is } \Gamma_l \text{ in } C_3 \begin{cases} D_q^{k+} \text{ is } \Gamma_l^+ \\ D_q^{k-} \text{ is } \Gamma_l^- \end{cases}$$

TABLE II.*(continued)*

Group D_3 (32)

Γ_1	D_0^0		D_0^2	$D_3^3+D_{-3}^3$	D_0^4, $D_3^4-D_{-3}^4$
Γ_2		D_0^1		D_0^3, $D_3^3-D_{-3}^3$	$D_3^4+D_{-3}^4$
Γ_3		$D_{\pm1}^1$	$D_{\pm1}^2$, $D_{\pm2}^2$	$D_{\pm1}^3$, $D_{\pm2}^3$	$D_{\pm1}^4$, $D_{\pm2}^4$, $D_{\pm4}^4$

Group C_{3v} ($3m$)

$$D_q^k \text{ is } \Gamma_l \text{ in } D_3 \begin{cases} D_q^{k^+}: \text{idem} \\ D_q^{k^-}: \Gamma_1 \longleftrightarrow \Gamma_2 \end{cases}$$

Group D_{3d} ($\bar{3}m$)

$$D_q^k \text{ is } \Gamma_l \text{ in } D_3 \begin{cases} D_q^{k^+} \text{ is } \Gamma_l^+ \\ D_q^{k^-} \text{ is } \Gamma_l^- \end{cases}$$

(e) Tetragonal system

Group C_4 (4)

Γ_1	D_0^0	D_0^1	D_0^2	D_0^3	D_{-4}^4, D_0^4, D_4^4
Γ_2			D_{-2}^2, D_2^2	D_{-2}^3, D_2^3	D_{-2}^4, D_2^4
Γ_3		D_1^1	D_1^2	D_{-3}^3, D_1^3	D_{-3}^4, D_1^4
Γ_4		D_{-1}^1	D_{-1}^2	D_{-1}^3, D_3^3	D_{-1}^4, D_3^4

Group S_4 ($\bar{4}$)

$$D_q^k \text{ is } \Gamma_l \text{ in } C_4 \begin{cases} D_q^{k^+}: \text{idem} \\ D_q^{k^-}: \Gamma_1 \longleftrightarrow \Gamma_3,\ \Gamma_2 \longleftrightarrow \Gamma_4 \end{cases}$$

Group C_{4h} ($4/m$)

$$D_q^k \text{ is } \Gamma_l \text{ in } C_4 \begin{cases} D^{k^+} \text{ is } \Gamma_l^+ \\ D_q^{k^-} \text{ is } \Gamma_l^- \end{cases}$$

Group D_4 (422)

Γ_1	D_0^0		D_0^2		D_0^4, $D_4^4+D_{-4}^4$
Γ_2		D_0^1		D_0^3	$D_4^4-D_{-4}^4$
Γ_3			$D_2^2+D_{-2}^2$	$D_2^3-D_{-2}^3$	$D_2^4+D_{-2}^4$
Γ_4			$D_2^2-D_{-2}^2$	$D_2^3+D_{-2}^3$	$D_2^4-D_{-2}^4$
Γ_5		$D_{\pm1}^1$	$D_{\pm1}^2$	$D_{\pm1}^3$, $D_{\pm3}^3$	$D_{\pm1}^4$, $D_{\pm3}^4$

Group C_{4v} ($4mm$)

$$D_q^k \text{ is } \Gamma_l \text{ in } D_4 \begin{cases} D_q^{k^+}: \text{idem} \\ D_q^{k^-}: \Gamma_1 \longleftrightarrow \Gamma_3,\ \Gamma_3 \longleftrightarrow \Gamma_4 \end{cases}$$

Group D_{2d} ($\bar{4}2m$)

$$D_q^k \text{ is } \Gamma_l \text{ in } D_4 \begin{cases} D_q^{k^+}: \text{idem} \\ D_q^{k^-}: \Gamma_1 \longleftrightarrow \Gamma_3,\ \Gamma_2 \longleftrightarrow \Gamma_4 \end{cases}$$

Group D_{4h} ($4/mmm$)

$$D_q^k \text{ is } \Gamma_l \text{ in } D_4 \begin{cases} D_q^{k^+} \text{ is } \Gamma_l^+ \\ D_q^{k^-} \text{ is } \Gamma_l^- \end{cases}$$

TABLE II. *(continued)*

(f) Hexagonal system

Group C_6 (6)

Γ_1	D_0^0	D_0^1	D_0^2	D_0^3	D_0^4
Γ_2			D_{-2}^2	D_{-2}^3	D_{-2}^4, D_4^4
Γ_3			D_2^2	D_2^3	D_{-4}^4, D_2^4
Γ_4				D_{-3}^3, D_3^3	D_{-3}^4, D_3^4
Γ_5		D_1^1	D_1^2	D_1^3	D_1^4
Γ_6		D_{-1}^1	D_{-1}^2	D_{-1}^3	D_{-1}^4

Group C_{3h} $(\overline{6})$

$$D_q^k \text{ is } \Gamma_l \text{ in } C_6 \begin{cases} D_q^{k+}: \text{idem} \\ D_q^{k-}: \Gamma_1 \leftrightarrow \Gamma_4,\ \Gamma_2 \leftrightarrow \Gamma_5,\ \Gamma_3 \leftrightarrow \Gamma_6 \end{cases}$$

Group C_{6h} $(6/m)$

$$D_q^k \text{ is } \Gamma_l \text{ in } C_6 \begin{cases} D_q^{k+} \text{ is } \Gamma_l^+ \\ D_q^{k-} \text{ is } \Gamma_l^- \end{cases}$$

Group D_6 (622)

Γ_1	D_0^0		D_0^2		D_0^4
Γ_2		D_0^1		D_0^3	
Γ_3				$D_3^3 - D_{-3}^3$	$D_3^4 + D_{-3}^4$
Γ_4				$D_3^3 + D_{-3}^3$	$D_3^4 - D_{-3}^4$
Γ_5		$D_{\pm 1}^1$	$D_{\pm 1}^2$	$D_{\pm 1}^3$	$D_{\pm 1}^4$
Γ_6			$D_{\pm 2}^2$	$D_{\pm 2}^3$	$D_{\pm 2}^4$, $D_{\pm 4}^4$

Group C_{6v} $(6mm)$

$$D_q^k \text{ is } \Gamma_l \text{ in } D_6 \begin{cases} D_q^{k+}: \text{idem} \\ D_q^{k-}: \Gamma_1 \leftrightarrow \Gamma_2,\ \Gamma_3 \leftrightarrow \Gamma_4 \end{cases}$$

Group D_{3h} $(6m2)$

$$D_q^k \text{ is } \Gamma_l \text{ in } D_6 \begin{cases} D_q^{k+}: \text{idem} \\ D_q^{k-}: \Gamma_1 \leftrightarrow \Gamma_3,\ \Gamma_2 \leftrightarrow \Gamma_4,\ \Gamma_5 \leftrightarrow \Gamma_6 \end{cases}$$

Group D_{6h} $(6/mmm)$

$$D_q^k \text{ is } \Gamma_l \text{ in } D_6 \begin{cases} D_q^{k+} \text{ is } \Gamma_l^+ \\ D_q^{k-} \text{ is } \Gamma_l^- \end{cases}$$

(g) Cubic system

Group T (23)

Γ_1	D_0^0			$D_2^3 - D_{-2}^3$	$\sqrt{14} D_0^4 + \sqrt{5} (D_4^4 + D_{-4}^4)$
Γ_2			$D_0^2 + i/\sqrt{2} (D_2^2 + D_{-2}^2)$		$\sqrt{10} D_0^4 - \sqrt{7} (D_4^4 + D_{-4}^4) - 2i\sqrt{3} (D_2^4 + D_{-2}^4)$
Γ_3			$D_0^2 - i/\sqrt{2} (D_2^2 + D_{-2}^2)$		$\sqrt{10} D_0^4 - \sqrt{7} (D_4^4 + D_{-4}^4) + 2i\sqrt{3} (D_2^4 + D_{-2}^4)$
Γ_4		D_1^1 D_0^1 D_{-1}^1	$D_2^2 - D_{-2}^2$ $D_{\pm 1}^2$	$D_{\pm 3}^3$ D_0^3, $D_{\pm 2}^3 + D_{-2}^3$ $D_{\pm 1}^3$	$D_{\pm 1}^4$, $D_2^4 - D_{-2}^4$ $D_{\pm 3}^4$, $D_4^4 - D_{-4}^4$

TABLE II.*(continued)*

Group T_h ($m3$)

$$D_q^k \text{ is } \Gamma_l \text{ in } T \begin{cases} D_q^{k+} \text{ is } \Gamma_l^+ \\ D_q^{k-} \text{ is } \Gamma_l^- \end{cases}$$

Group O (432)

Γ_1	D_0^0				$\sqrt{14}D_0^4+\sqrt{5}(D_4^4+D_{-4}^4)$
Γ_2				$D_2^3-D_{-2}^3$	
Γ_3			D_0^2		$\sqrt{10}D_0^4-\sqrt{7}(D_4^4+D_{-4}^4)$
			$D_2^2+D_{-2}^2$		$D_2^4+D_{-2}^4$
Γ_4		D_{-1}^1		$\sqrt{5}D_{-3}^3+\sqrt{3}D_1^3$	$D_{-3}^4+\sqrt{7}D_1^4$
		D_0^1		D_0^3	$D_4^4-D_{-4}^4$
		D_1^1		$\sqrt{5}D_3^3+\sqrt{3}D_{-1}^3$	$D_3^4+\sqrt{7}D_{-1}^4$
Γ_5			D_{-1}^2	$\sqrt{3}D_{-3}^3-\sqrt{5}D_1^3$	$\sqrt{7}D_{-3}^4-D_1^4$
			$D_2^2-D_{-2}^2$	$D_2^3+D_{-2}^3$	$D_2^4-D_{-2}^4$
			D_1^2	$\sqrt{3}D_3^3-\sqrt{5}D_{-1}^3$	$\sqrt{7}D_3^4-D_{-1}^4$

Group T_d ($\overline{4}3m$)

$$D_q^k \text{ is } \Gamma_l \text{ in } O \begin{cases} D_q^{k+} : \text{idem} \\ D_q^{k-} : \Gamma_1 \longleftrightarrow \Gamma_2,\ \Gamma_4 \longleftrightarrow \Gamma_5 \end{cases}$$

Group O_h ($m3m$)

$$D_q^k \text{ is } \Gamma_l \text{ in } O \begin{cases} D_q^{k+} \text{ is } \Gamma_l^+ \\ D_q^{k-} \text{ is } \Gamma_l^- \end{cases}$$

(h) Group $C_{\infty V}$

Σ^+	D_0^{0+}	D_0^{1-}	D_0^{2+}	D_0^{3-}	D_0^{4+}
Σ^-	D_0^{0-}	D_0^{1+}	D_0^{2-}	D_0^3	D_0^{4-}
Π		$D_{\pm1}^1$	$D_{\pm1}^2$	$D_{\pm1}^3$	$D_{\pm1}^4$
Δ			$D_{\pm2}^2$	$D_{\pm2}^3$	$D_{\pm2}^4$
Φ				$D_{\pm3}^3$	$D_{\pm3}^4$
Γ					$D_{\pm4}^4$

Group $D_{\infty h}$

D_q^{k+} is g, D_q^{k-} is u

S_{21} is the transition matrix element (see Sec. II A) $\langle\phi_2|V|\psi_1^+\rangle$ with

$$|\psi_1^+\rangle = |\phi_1\rangle + \lim_{\epsilon\to 0}\frac{1}{W_1-H_0+i\epsilon}|\psi_1^+\rangle\,.$$

An eigenstate of the free system can be expressed as the product of an atomic state by a radiation state; in particular, in an rth-order scattering process

$$|\phi_1\rangle = |a\rangle|N(\vec{k},\vec{e})\rangle$$

and

$$|\phi_2\rangle = |b\rangle|(N-r+1)(\vec{k},\vec{e});1(\vec{k}_s,\vec{\epsilon})\rangle\,.$$

We use the expression of the quantized electric field

$$\vec{E} = \sum_{\vec{k},\vec{e}}\left(\frac{\hbar\omega}{2\epsilon_0 V}\right)^{1/2} i\{a\vec{e}e^{i\vec{k}\cdot\vec{R}} - a^+\vec{e}^{\,*}e^{-i\vec{k}\cdot\vec{R}}\},$$

the relation between the incident intensity I and the mean photon numer $\overline{N}_{k,e}$, assuming the pump beam to be coherent, is

$$I = (\hbar\omega c/V)\overline{N},$$

and

$$\langle N(N-1)\ldots(N-p+1)\rangle = \overline{N}^{p},$$

and $\rho(W)\,d\Omega = V\omega_S^2\,d\Omega/(2\pi c)^3\hbar$. This leads to the cross section per molecule for an rth-order scattering process:

$$\frac{d\sigma}{d\Omega} = \frac{\omega_S^3\omega}{c^4}\left(\frac{2\pi I}{c}\right)^{r-2}\frac{|T_{(r)}^{a\to b}|^2}{(4\pi\epsilon_0)^r}. \tag{A2}$$

ω and ω_S are the incident and scattered frequencies respectively; $T_{(r)}^{a\to b}$ is the scattering tensor component (Eq. 7); these formulas are given in mksa units but the tensors keep the same expression in cgs units ($4\pi\epsilon_0 = 1$). The intensity scattered in a given direction at a distance L is

$$I_S = \frac{\omega_S}{\omega} I \frac{d\sigma}{L^2 d\Omega}. \tag{A3}$$

Through a diagram method (Fig. 2) we obtain the explicit expression of the scattering tensors up to rank 4 (it is worth noting that if q incident photons belong to a same mode, each diagram has to be counted $q!$ times). For instance;

$$\alpha_{ij}^{a\to b}(-\omega_S,\omega) = \sum_m \frac{\langle b|d_i|m\rangle\langle m|d_j|a\rangle}{E_a - E_m + \hbar\omega} + \frac{\langle b|d_j|m\rangle\langle m|d_i|a\rangle}{E_a - E_m + \hbar\omega_S},$$

$$\beta_{ijk}^{a\to b}(-\omega_S,\omega,\omega) = \sum_{m,n} \frac{\langle b|d_i|m\rangle\langle m|d_j|n\rangle\langle n|d_k|a\rangle}{(E_a - E_m + 2\hbar\omega)(E_a - E_n + \hbar\omega)} + \frac{\langle b|d_k|m\rangle\langle m|d_i|n\rangle\langle n|d_j|a\rangle}{(E_a - E_m + \hbar\omega - \hbar\omega_S)(E_a - E_n + \hbar\omega)}$$

$$+ \frac{\langle b|d_j|m\rangle\langle m|d_k|n\rangle\langle n|d_i|a\rangle}{(E_a - E_m + \hbar\omega - \hbar\omega_S)(E_a - E_n - \hbar\omega_S)} + \text{(idem with exchanging } j \text{ and } k).$$

From Eqs. (A2) and (A3), one can find immediately the expression of the proportionality constant I_0 of Eq. (5).

APPENDIX B

In Sec. (IIb), we had assumed that the atomic levels a and b were not degenerate; otherwise, let $g(a)$ be the degeneracy of the initial level, and α and β be the indices labeling the eigenstates of the levels a and b, respectively.

An inelastic $a\to b$ process is still incoherent; the total scattering cross section is obtained in summing over the final states β and averaging over the initial states α which we assume to be unpolarized:

$$I_{\text{incoh}(a\to b)} = \frac{N_a}{g(a)} \sum_{\alpha,\beta} \langle AA^*\rangle_{\alpha\to\beta}. \tag{B1}$$

An elastic $a\to a$ process has both an incoherent contribution due to the $|\alpha\rangle\to|\alpha'\rangle$, with $\alpha\neq\alpha'$, transitions:

$$I_{\substack{\text{inc}\\(a\to a)}} = \frac{N_a}{g(a)} \sum_{\substack{\alpha,\alpha'\\ \alpha\neq\alpha'}} \langle AA^*\rangle_{\alpha\to\alpha'} \tag{B2}$$

and a coherent contribution due to the $|\alpha\rangle\to|\alpha\rangle$ transitions.

Since the initial state of the atomic system is not in general an eigenstate of H_{at}, but a statistical mixing described by a density matrix

$$\rho = \sum_{a,\alpha} p(a,\alpha)\,|a\alpha\rangle\langle a\alpha|,$$

the polarizability tensor $T^{a\alpha\to a\alpha}$ which accounts for a coherent scattering process must be replaced by the average value $\overline{T} = \text{Tr}(\rho T)$, so that the total coherently scattered intensity is given by

$$I_{\text{coh}} = f(V,\vec{k})\left|\sum_{a\alpha} p(a,\alpha)\langle A\rangle_{\alpha\to\alpha}\right|^2. \tag{B3}$$

---

[1] See, for example, *The Raman Effect*, edited by A. Anderson (Dekker, New York, 1971).

[2] R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Lett. 14, 681 (1965).

[3] P. D. Maker, Phys. Rev. A 1, 923 (1970).

[4] S. J. Cyvin, J. E. Rauch, and J. C. Decius, J. Chem. Phys. 43, 4083 (1970).

[5] J. Jerphagnon, D. S. Chemla, and R. Bonneville (unpublished).

[6] D. S. Chemla and R. Bonneville, J. Chem. Phys. (to be published).

[7] A. Messiah, *Mecanique Quantique II* (Dunod, Paris, 1962).

[8] N. Bloembergen, *Nonlinear Optics* (Benjamin, New

York, 1965).

[9] L. Landau and E. Lifshitz, *Théorie Quantique Relativiste* (Mir, Moscow, 1972).

[10] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, N. J., 1960).

[11] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (MIT, Cambridge, Mass., 1959).

[12] J. Ducuing and C. Flytzanis, in *Optical Properties of Solids*, edited by F. Abelès (North-Holland, Amsterdam, 1972).

[13] M. D. Levenson and N. Bloembergen, Phys. Rev. B 10, 4447 (1974).

[14] J. A. Giordmaine, Phys. Rev. A 6, 1599 (1965).

[15] P. M. Rentzepis, J. A. Giordmaine, and K. W. Wecht, Phys. Rev. Lett. 16, 792 (1966).

[16] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-two Point Groups* (MIT, Cambridge, Mass., 1963).