Inverse polarization of asymmetric hyper-Raman lines

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Index asymmetry in the scattering tensor b_{ijk}, related to permutation of i and whichever of the indices j or k, makes active vibrations inactive in the case of a completely symmetric tensor leading to new selection rules for hyper-Raman scattering and to the emergence of new vibrational lines in the scattered spectrum. These purely asymmetric lines correspond to the asymmetric irreducible part of weight 2 of the tensor b_{ijk}. This scattering, similarly to antisymmetric Raman, is shown to exhibit the phenomenon of inverse polarization. A detailed discussion of angular distribution and of various polarization parameters for all polarization states of the incident light is given in terms of Stokes parameters.

I. INTRODUCTION

Three-photon light scattering was predicted in the early days of quantum mechanics. The history of these early investigations has been widely presented by Altmann and Strey.[1] The invention of the laser and the progress achieved in detection techniques has rendered possible the observation of three-photon scattering and has also given a new impulse to its discussion.[2] This stage of investigation soon culminated in the pioneering experiment of Terhune *et al.*[3] in which hyper-Raman and hyper-Rayleigh scatterings were first observed. The theoretical and experimental achievements in the field of hyper-Raman have already been reviewed in some books and articles.[1,4–7]

In the classical description of scattering phenomena, a molecule in a strong electromagnetic field generally undergoes nonlinear polarization. This polarization is a source of new electromagnetic waves with frequencies that are multiples of the incident frequency and, in the case of hyper-Raman processes, with field amplitudes modulated by the vibrations of the molecules.

We assume the incident field in the form $E_i(\mathbf{r},t) = E_i \exp\{-i(\omega t - \mathbf{k}\cdot\mathbf{r})\}$. In the quadratic approximation with respect to $E_i(\mathbf{r},t)$ the electric dipole moment on the Stokes $2\omega - \omega_Q$ and anti-Stokes $2\omega + \omega_Q$ frequency is

$$m_i^{2\omega\mp\omega_Q}(t) = \tfrac{1}{2} b_{ijk} E_j E_k Q \times \exp\{-i[(2\omega \mp \omega_Q)t + \varphi_Q - 2\mathbf{k}\cdot\mathbf{r}]\}. \tag{1}$$

The incident amplitude E_i can in general be time dependent. The final results have to be averaged over the ensemble of incident field amplitudes replacing time averaging for ergodic processes. $\mathbf{k}$ denotes the incident wave vector, whereas $\mathbf{r}$ represents the position of the molecule. Q is a normal coordinate of vibration, where ω_Q and φ_Q are the vibrational frequency and phase, respectively, corresponding to this coordinate. Italic indices i,j,k for components are used with respect to the laboratory frame and the summation convention over repeated indices is applied throughout.

The hyper-Raman third-rank scattering tensor b_{ijk} is by definition symmetric in its last two indices only, since they are associated with the same frequency ω. In the hyper-Raman theories of the 1960's the tensor b_{ijk} was approximately treated as having full index symmetry (symmetric approximation).[8–12] This simplification is by no means always justified. It fails for paramagnetic molecules or when the incident ω or scattered $2\omega \pm \omega_Q$ frequency approaches an electronic transition frequency ω_e of the molecule. Zhu[13] and Christie and Lockwood[14] have shown this tensor to be completely symmetric for diamagnetic molecules if ω/ω_e and $(2\omega \pm \omega_Q)/\omega_e \ll 1$. In the majority of experimental situations these ratios are but slightly less than unity. Hence, the realistic description of hyper-Raman scattering requires the use of a partly j,k symmetric scattering tensor. Index dissymetry in b_{ijk} leads to new selection rules for hyper-Raman and new hyper-Raman lines appear in the scattered spectrum. In general, this tensor should also be considered as a complex tensor, particularly in the case of paramagnetic molecules and resonance scattering.

The earliest description of hyper-Raman scattering on the assumption of a b_{ijk} tensor symmetric in j and k only and deriving irreducible forms of the asymmetric spherical tensors has been given in the paper.[15] Some aspects of scattering have been developed by Andrews and his co-workers,[16,17] Minard *et al.*,[18] as well as by Altmann and Strey[1] also using the methods of irreducible tensors. In the papers[1,16] the striking polarization properties of the scattering process in question are however touched on but briefly. We consider also asymmetric scattering of elliptically polarized light. This state of polarization was in fact assumed by Stanton[11] and Bonneville and Chemla[19] albeit in the symmetric approximation.[7]

This abovementioned uniqueness of the polarization properties of asymmetrically scattered light is related with the change in azimuth of the scattered polarized portion by $\pi/2$ relative to the azimuth generated in the symmetric approximation. For forward and backward scattering the scattered azimuth is also perpendicular to the incident azimuth, and at appropriately chosen condition of observation it almost always remains perpendicular to the latter irrespective of the scattering angle. This is called inverse polarization. The polarization properties of asymmetric hyper-Raman scattering are similar to those of antisymmetric ordinary Raman scattering.

II. THE SCATTERED LIGHT INTENSITY TENSOR

The integral intensity tensor I_{ij} of the light scattered incoherently by N noninteracting randomly oriented molecules requires unweighted averaging over the molecular orientations Ω. Since $I_{ij} \simeq \langle \ddot{m}_i(t)\ddot{m}_j(t)^* \rangle_{\Omega,E}$, it results from Eq. (1) that this procedure involves averaging of the product of six directional cosines as first performed by Kielich.[20] On averaging, one has[21]

$$I_{ij} = \frac{c}{4\pi} L\{\alpha\delta_{ij}\langle E_k E_k^* E_l E_l^*\rangle_E + \beta\delta_{ij}\langle E_k E_k E_l^* E_l^*\rangle_E + \gamma\langle E_i E_j^* E_k E_k^*\rangle_E + \delta\langle E_i^* E_j E_k E_k^*\rangle_E + \lambda\langle E_i^* E_j^* E_k E_k + E_i E_j E_k^* E_k^*\rangle_E + \mu\langle E_i^* E_j^* E_k E_k - E_i E_j E_k^* E_k^*\rangle_E\}, \quad (2)$$

where $\langle\ \rangle_E$ refers to averaging over the ensemble of the incident field amplitudes and L is a scattering factor of the form

$$L = \frac{N(2\omega \mp \omega_Q)^4 Q^2}{420c^4}. \quad (3)$$

The six parameters α–μ are molecular rotational invariants comprising appropriate combinations of various products of the $b_{\alpha\beta\gamma}$ tensor components. The invariants α–λ are real, whereas μ is purely imaginary. The invariants λ and μ are directly related with the invariant ϵ used in Ref. 21, namely, $\lambda = \mathrm{Re}\,\epsilon$ and $\mu = i\,\mathrm{Im}\,\epsilon$. Except for elliptical polarization of the incident light, the invariant μ intervenes nowhere.

According to Christie and Lockwood[14] the partly symmetric (in its last two indices) tensor $b_{\alpha\beta\gamma}$ can be decomposed into two parts: a fully symmetric part $b^S_{\alpha\beta\gamma}$ with respect to permutation of all indices and a remaining asymmetric (but not antisymmetric in general) part $b^A_{\alpha\beta\gamma}$ which, however, is still symmetric in β and γ (the Greek indices α,β,γ already refer to the fixed molecular frame):

$$b_{\alpha\beta\gamma} = b^S_{\alpha\beta\gamma} + b^A_{\alpha\beta\gamma},$$
$$b^S_{\alpha\beta\gamma} = \tfrac{1}{3}(b_{\alpha\beta\gamma} + b_{\beta\gamma\alpha} + b_{\gamma\alpha\beta}), \quad (4)$$
$$b^A_{\alpha\beta\gamma} = \tfrac{1}{3}(2b_{\alpha\beta\gamma} - b_{\beta\gamma\alpha} - b_{\gamma\alpha\beta}).$$

The fully symmetric tensor $b^S_{\alpha\beta\gamma}$ can further be decomposed into two spherical irreducible sets of weight 1 ($b^{1S}_{\alpha\beta\gamma}$) and 3($b^{3S}_{\alpha\beta\gamma}$) with three and seven components, respectively.[6,7,15,16,22] The remaining asymmetric tensor $b^A_{\alpha\beta\gamma}$ can also be represented by the two spherical irreducible sets of weight 1($b^{1A}_{\alpha\beta\gamma}$) and 2($b^{2A}_{\alpha\beta\gamma}$) having three and five components, respectively.[6,15,16,22] The tensors of the same weight mix under rotation in space. In other words one can in general expect cross contributions to certain scattered lines due to the products of irreducible symmetric and asymmetric tensors of weight 1. By Eqs. (4) and with respect to $b^{3S}_{\alpha\beta\beta} = b^{2A}_{\alpha\beta\beta} = 0$ the form of the six molecular invariants is as follows:

$$\alpha = 5B^S_3 + 14B^A_2,$$
$$\beta = \tfrac{7}{3}B^S_1 - B^S_3 + \tfrac{35}{3}B^A_1 - 7B^A_2 + 7\,{}^1B^A_{11},$$
$$\gamma = \tfrac{28}{3}B^S_1 - 4B^S_3 + \tfrac{35}{3}B^A_1 - 7B^A_2 - 14\,{}^1B^{SA}_{11},$$
$$\delta = 10B^S_3 - 14B^A_2,$$
$$\lambda = \tfrac{14}{3}B^S_1 - 2B^S_3 - \tfrac{35}{3}B^A_1 + 7B^A_2 + \tfrac{7}{2}\,{}^1B^{SA}_{11},$$
$$\mu = \frac{21i}{2}\,{}^2B^{SA}_{11}, \quad (5)$$

where

$$B^S_1 = |b^{1S}_{\alpha\beta\gamma}|^2, \quad B^A_1 = |b^{1A}_{\alpha\beta\gamma}|^2,$$
$$B^S_3 = |b^{3S}_{\alpha\beta\gamma}|^2, \quad B^A_2 = |b^{2A}_{\alpha\beta\gamma}|^2,$$
$${}^1B^{SA}_{11} = \tfrac{1}{2}(b^{1S}_{\alpha\beta\beta} b^{1A*}_{\alpha\gamma\gamma} + b^{1S*}_{\alpha\beta\beta} b^{1A}_{\alpha\gamma\gamma}),$$
$${}^2B^{SA}_{11} = \frac{i}{2}(b^{1S}_{\alpha\beta\beta} b^{1A*}_{\alpha\gamma\gamma} - b^{1S*}_{\alpha\beta\beta} b^{1A}_{\alpha\gamma\gamma}). \quad (6)$$

At elliptical polarizaiton of the incident light all six parameters (6) can intervene in general. For other polarization states their number reduces to five; thus, the parameter ${}^2B^{SA}_{11}$ does not appear. This parameter is responsible for new recently discussed polarization effects: electric dipole elliptical differential scattering,[23] and rotation of the polarization ellipse[24] in resonance hyper-Raman scattering.

Obviously, the number of molecular parameters can be reduced with regard to molecular and vibrational symmetries. In particular, a hyper-Raman line can even be described by one parameter: B^S_3 or B^A_2. This is precisely pure asymmetric hyper-Raman scattering that is represented by the invariant B^A_2. All vibrational modes related to $b^{2A}_{\alpha\beta\gamma}$ are inactive in IR and fall in three classes with regard to their activity in ordinary Raman scattering. Vibrations responsible for pure asymmetric hyper-Raman scattering and their Raman activity are listed in Table I.

Except for the mode E of the cubic groups, the only nonzero components of the tensor $b^{2A}_{\alpha\beta\gamma}$ are[14]

$$b^{2A}_{123} = b^{2A}_{132} = -b^{2A}_{213} = -b^{2A}_{231} \quad (7)$$

and one readily notes that this tensor is moreover antisymmetric in the indices 1 and 2. In this case pure asymmetric scattering can also be termed antisymmetric. With regard to Eq. (7), the molecular invariant B^A_2 equals

$$B^A_2 = 4|b^{2A}_{123}|^2. \quad (8)$$

In the case of the cubic groups, vibrational modes E are described by the following nonvanishing components:

$$b^{2A}_{123}(1) = b^{2A}_{132}(1) = b^{2A}_{213}(1) = b^{2A}_{231}(1) = -\tfrac{1}{2}b^{2A}_{321}(1) = -\tfrac{1}{2}b^{2A}_{312}(1),$$
$$b^{2A}_{123}(2) = -b^{2A}_{213}(2) = \sqrt{3}b^{2A}_{123}(1), \quad (9)$$

where the symbols (1) and (2) in parentheses refer to the first and second component of the double-degenerate vibrational mode E. Now, the only component (2) is antisymmetric in the indices 1 and 2. The molecular invariant B^A_2 for the E mode is

$$B^A_2 = 18|b^{2A}_{123}|^2. \quad (10)$$

III. STOKES PARAMETERS FOR LIGHT SCATTERED

Assuming propagation of the incident radiation along the direction z and observation in the plane $YZ = yz$ along the direction Z at an angle ϑ to Z, the Stokes parameters[25]

$$S_0 = \frac{4\pi}{c}(I_{XX} + I_{YY}),$$
$$S_1 = \frac{4\pi}{c}(I_{XX} - I_{YY}),$$
$$S_2 = \frac{4\pi}{c}(I_{XY} + I_{YX}),$$
$$S_3 = \frac{4\pi i}{c}(I_{YX} - I_{XY}), \quad (11)$$

TABLE I. Vibrational modes leading to pure asymmetric hyper-Raman and their activity in ordinary Raman.

Point group	Symmetric (Modes \ Raman activity)	Antisymmetric (Modes \ Raman activity)	Point group	Modes Raman inactive
D_4, D_5, D_6	A_1		D_{3h}, D_{5h}	A_1''
D_{2d}	B_1		D_{4h}, D_{6h}, D_{5d}	A_{1u}
$T, T_a, 0$	E		D_{4d}, D_{6d}	B_1
C_{4v}, C_{5v}, C_{6v}		A_2	$D_{\infty h}$	$\Sigma u'$
$C_{\infty v}$		Σ^-	T_h, O_h	E_u

for the asymmetric hyper-Raman are, by Eq. (2),

$$\begin{aligned} S_0^A(\vartheta) &= \tfrac{7}{2}LB_2^A\{3\langle s_0^2\rangle_E + 2\langle s_3^2\rangle_E - \langle s_0 s_1\rangle_E \\ &\quad - [\langle s_0^2\rangle_E + 2\langle s_3^2\rangle_E - \langle s_0 s_1\rangle_E]\cos^2\vartheta\}, \\ S_1^A(\vartheta) &= -\tfrac{7}{2}LB_2^A\{\langle s_0^2\rangle_E + 2\langle s_3^2\rangle_E + \langle s_0 s_1\rangle_E \\ &\quad - [\langle s_0^2\rangle_E + 2\langle s_3^2\rangle_E - \langle s_0 s_1\rangle_E]\cos^2\vartheta\}, \\ S_2^A(\vartheta) &= -7LB_2^A\langle s_0 s_2\rangle_E \cos\vartheta, \\ S_3^A(\vartheta) &= 7LB_2^A\langle s_0 s_3\rangle_E \cos\vartheta, \end{aligned} \tag{12}$$

where a lower-case s_i denotes a Stokes parameter for the incident light. To obtain the above parameters, we assumed $\langle s_0^2\rangle_E = \langle s_1^2\rangle_E + \langle s_2^2\rangle_E + \langle s_3^2\rangle_E$. This relation does not hold for partly polarized incident light. In other words, the Stokes parameters (12) describe scattering of completely polarized radiation albeit of arbitrary statistics, and scattering of natural light as well.

Using for the incident light the following form of the Stokes parameters[25]:

$$\begin{aligned} s_1 &= s_0 \cos 2\phi \cos 2\psi, \\ s_2 &= s_0 \cos 2\phi \sin 2\psi, \\ s_3 &= s_0 \sin 2\phi, \end{aligned} \tag{13}$$

where $-\pi/4<\phi<\pi/4$ denotes its ellipticity and $0<\psi<\pi$ the azimuth of the elliptic major axis relative to x, we rewrite the parameters (12) as follows:

$$\begin{aligned} S_0^A(\vartheta) &= \Gamma\{2 + (1 + 2\sin^2 2\phi \\ &\quad - \cos 2\phi \cos 2\psi)\sin^2\vartheta\}, \\ S_1^A(\vartheta) &= -\Gamma\{(1 + 2\sin^2 2\phi)\sin^2\vartheta \\ &\quad + \cos 2\phi \cos 2\psi(1 + \cos^2\vartheta)\}, \\ S_2^A(\vartheta) &= -2\Gamma \cos 2\phi \sin 2\psi \cos\vartheta, \\ S_3^A(\vartheta) &= 2\Gamma \sin 2\phi \cos\vartheta. \end{aligned} \tag{14}$$

For the sake of brevity we have introduced the notation

$$\Gamma = \tfrac{7}{2}LB_2^A\langle s_0\rangle_E^2\, g^{(2)}, \tag{15}$$

where

$$g^{(2)} = \langle s_0^2\rangle_E / \langle s_0\rangle_E^2 \tag{16}$$

is the second-order coherence degree of the incident light. The parameters (14) can still be applied to the description of scattering of natural light. Then, we have additionally to perform in Eq. (14) unweighted averaging over the angles ψ and ϕ.

IV. POLARIZATION PROPERTIES OF LIGHT SCATTERED

The Stokes parameters (14) permit the reading of certain general polarization properties of the asymmetrically scattered light irrespective of the polarization state of the incident radiation.

In particular, for forward observation ($\vartheta = 0$) one gets

$$\begin{aligned} S_0^A(0) &= 2\Gamma, \\ S_1^A(0) &= -S_0^A(0)\cos 2\phi \cos 2\psi, \\ S_2^A(0) &= -S_0^A(0)\cos 2\phi \sin 2\psi, \\ S_3^A(0) &= S_0^A(0)\sin 2\phi. \end{aligned} \tag{17}$$

For polarized incident light the above equations give

$$S_0^A(0)^2 = S_1^A(0)^2 + S_2^A(0)^2 + S_3^A(0)^2, \tag{18}$$

meaning that the light asymmetrically scattered forward remains fully polarized. This is not satisfied for other hyper-Raman lines.

For natural incident light, with respect to $\langle\cos 2\phi\rangle = \langle\sin 2\phi\rangle = \langle\cos 2\psi\rangle = \langle\sin 2\psi\rangle = 0$, only $S_0^A(0)$ differs from zero. This signifies unpolarized scattered light.

For backward scattering ($\vartheta = \pi$) of polarized light a relation similar to Eq. (18) holds. Hence, the light scattered backwards is also completely polarized. At natural incident light, backward scattering gives unpolarized radiation too.

For perpendicular scattering ($\vartheta = \pi/2$ or $3\pi/2$), only $S_0^A(\pi/2)$ and $S_1^A(\pi/2)$ differ from zero, and in general $S_0^A(\pi/2) \neq S_1^A(\pi/2)$ suggesting partly linearly polarized scattered light.

The polarized portion of the scattered light is characterized by ellipticity. One of the equations determining it reads

$$\sin 2\phi_s(\vartheta) = \frac{S_3^A(\vartheta)}{\sqrt{S_1^A(\vartheta)^2 + S_2^A(\vartheta)^2 + S_3^A(\vartheta)^2}}. \tag{19}$$

On insertion of Eq. (14) into Eq. (19) the equation becomes rather complicated. Hence, we further restrict our attention to particular angles ϑ only.

The azimuth of the polarized portion of the scattered radiation is to be had from

$$\tan 2\psi_s(\vartheta) = \frac{S_2^A(\vartheta)}{S_1^A(\vartheta)}, \tag{20}$$

where, with regard to Eq. (14),

$$\tan 2\psi_s(\vartheta) = \frac{2\cos 2\phi \sin 2\psi \cos\vartheta}{(1 + 2\sin^2 2\phi)\sin^2\vartheta + \cos 2\phi \cos 2\psi(1 + \cos^2\vartheta)}. \tag{21}$$

Equation (21) implies rotation of the scattered azimuth as a function of ϑ. This purely geometrical rotation is related to changes in the magnitudes of the projections of the elliptic axes on the observation plane with varying angle ϑ. However, this rotation can be eliminated at appropriately chosen incident azimuth. The above is achieved for $\psi = 0$ or π and $\psi = \pi/2$. Such azimuths ensure that either the greater or smaller principal component of the scattered intensity tensor shall lie in the observation plane irrespective of ϑ.

For forward scattering, Eq. (19) reads

$$\sin 2\phi_s(0) = \sin 2\phi, \tag{22}$$

whereas Eq. (21) becomes

$$\tan 2\psi_s(0) = \tan 2\psi. \tag{23}$$

Thus, asymmetric hyper-Raman scattering in the forward direction exhibits no change in ellipticity relative to the incident radiation. This conclusion does not hold generally for other lines, what in the symmetric approximation was shown by Stanton[11] when even the handedness may be reversed. As for the azimuth, the same relation as Eq. (23) has been derived in the symmetric approximation by Stanton.[11] Then, the above relation signifies retention of the azimuth, the only acceptable solution is $\psi_s = \psi$. The other solution of Eq. (23) signifies a change of the azimuth ψ_s by $\pi/2$ relative to the incident azimuth. Indeed, this takes place for pure asymmetric scattering. The signs of $S_1^A(0)$ and $S_2^A(0)$ in Eq. (17) are opposite to the signs of s_1 and s_2 in Eq. (13) which in fact reflects the abovementioned change. This is so-called inverse polarization. One should mention here that azimuth of the lines to which both symmetric and asymmetric parameters contibute can also be inverted. Then, however, the light scattered forward is partly polarized; this case, in ordinary Raman, is termed anomalous polarization.

For backward scattering, Eq. (19) yields

$$\sin 2\phi_s(\pi) = -\sin 2\phi, \tag{24}$$

i.e., complete reversal of the incident handedness but at preserved magnitude of the ellipticity. The parameter S_3 behaves as a pseudoscalar since it changes its sign under an inversion of the coordinates, hence such a relation (24).

V. APPLICATION TO VARIOUS POLARIZATION STATES OF THE INCIDENT LIGHT

To start with, we remain at elliptical polarization. But we chose the incident azimuth as $\psi = 0$, i.e., we assume that the elliptic major axis is normal to the observation plane. Then

$$^{EV}S_2^A(\vartheta) = 0$$

and

$$^{EV}S_0^A(\vartheta) = \Gamma\{2 + (1 + 2\sin^2 2\phi - \cos 2\phi)\sin^2\vartheta\},$$
$$^{EV}S_1^A(\vartheta) = -\Gamma\{(1 + 2\sin^2 2\phi)\sin^2\vartheta + \cos 2\phi(1 + \cos^2\vartheta)\}, \tag{25}$$
$$^{EV}S_3^A(\vartheta) = 2\Gamma \sin 2\phi \cos\vartheta.$$

The superscript (EV) preceding the Stokes parameters denotes elliptical (E) polarization of the incident light with vertically (V) oriented elliptic major axis.

As it is obvious from Eq. (25), the parameter $^{EV}S_1^A(\vartheta)$ can never become zero. This implies that the polarized portion is elliptically polarized (except for right-angled scattering with $^{EV}S_3^A = 0$). Its ellipticity depends on the scattering angle, and can easily be found from Eq. (19). The sign of $^{EV}S_1^A(\vartheta)$ is always the opposite of that of s_1, suggesting inversion of the azimuth irrespective of ϑ.

For right-angled scattering we have

$$^{EV}S_0^A(\pi/2) = \Gamma(3 + 2\sin^2 2\phi - \cos 2\phi),$$
$$^{EV}S_1^A(\pi/2) = -\Gamma(1 + 2\sin^2 2\phi + \cos 2\phi). \tag{26}$$

At $S_2 = S_3 = 0$ and negative parameter S_1, the depolarizaiton ratio is calculated from the definition

$$D = \frac{S_0 + S_1}{S_0 - S_1}. \tag{27}$$

Thus, owing to Eq. (26), one gets

$$^{EV}D^A\left(\frac{\pi}{2}\right) = \frac{1 - \cos 2\phi}{2(1 + \sin^2 2\phi)}, \tag{28}$$

where

$$0 < {}^{EV}D^A(\pi/2) < 1/4. \tag{29}$$

As already said, the polarized portion of the scattered light is, for right angle, polarized linearly, but the magnitude of depolarization depends on the incident ellipticity.

The reversal ratio R, being a ratio of intensities transmitted by a device that accepts circularly polarized light the handedness of which is contrary to the incident handedness and the same as the incident handedness, respectively, is in terms of the Stokes parameters[21]:

$$R = \frac{S_0 \mp S_3}{S_0 \pm S_3}. \tag{30}$$

The upper signs preceding S_3 go with $\phi > 0$, whereas the lower of them $\phi < 0$. $\phi > 0$ refers to right-handed polarization in the optical convention.

On insertion of S_0 and S_3 from Eq. (25) into Eq. (30) we arrive at

$$^{EV}R(\vartheta) = \frac{2 + (1 + 2\sin^2 2\phi - \cos 2\phi)\sin^2\vartheta - 2|\sin 2\phi|\cos\vartheta}{2 + (1 + 2\sin^2 2\phi - \cos 2\phi)\sin^2\vartheta + 2|\sin 2\phi|\cos\vartheta}, \tag{31}$$

where for forward scattering, as should be expected from Eq. (22),

$$^{EV}R^A(0) = \frac{1 - |\sin 2\phi|}{1 + |\sin 2\phi|} \tag{32}$$

is identical with R for the incident light. This quantity does not exceed unity because of retention of the handedness of the light scattered in this direction. Generally, the handedness is preserved for scattering angles $0 < \vartheta < \pi/2$ and $3\pi/2 < \vartheta < 2\pi$ and reversed for others (except right-angled scattering when ellipses always transform into straight lines). This conclusion is not fully satisfied in the symmetric approximation. Thus, for pure B_3^S modes or for modes with $2B_1^S < 3B_3^S$ the opposite situation can occur regarding handedness.[21]

For backward scattering one has

$$^{EV}R^{A}(\pi)=\frac{1+|\sin 2\phi|}{1-|\sin 2\phi|} \tag{33}$$

and, certainly,

$$^{EV}R^{A}(\pi)={}^{EV}R^{A}(0)^{-1}. \tag{34}$$

Let us now assume the incident azimuth as $\psi=\pi/2$. So, the elliptic major axis is horizontally (H) oriented. From Eq. (14) one gets

$$\begin{aligned}
^{EH}S_0^A(\vartheta) &= \Gamma\{2+(1+2\sin^2 2\phi \\
&\quad +\cos 2\phi)\sin^2\vartheta\},\\
^{EH}S_1^A(\vartheta) &= -\Gamma\{(1+2\sin^2 2\phi)\sin^2\vartheta \\
&\quad -\cos 2\phi(1+\cos^2\vartheta)\},\\
^{EH}S_3^A(\vartheta) &= 2\Gamma\sin 2\phi\cos\vartheta,
\end{aligned} \tag{35}$$

where one easily finds that the parameter $^{EH}S_1^A(\vartheta)$ can change its sign periodically. Namely, for certain angles ϑ, $^{EH}S_1^A$ vanishes. These angles are determined by the equation

$$\sin^2\vartheta=\frac{2\cos 2\phi}{1+2\sin^2 2\phi+\cos 2\phi}, \tag{36}$$

which has the four solutions ϑ_c, $\pi\pm\vartheta_c$, and $2\pi-\vartheta_c$ where $0<\vartheta_c<\pi/2$. Vanishing of $^{EH}S_1^A$ means at $^{EH}S_2^A=0$ that the polarized portion is then polarized circularly (C). $^{EH}S_1^A$ is positive for angles $\pi-\vartheta_c<\vartheta<\pi+\vartheta_c$ and $2\pi-\vartheta_c<\vartheta<2\pi+\vartheta_c$, signifying an inverted azimuth. For $\vartheta_c<\vartheta<\pi-\vartheta_c$ and $\pi+\vartheta_c<\vartheta<2\pi-\vartheta_c$ is negative and the scattered azimuth is coplanar with the incident azimuth but normal to that in the symmetric approximation.[21]

For perpendicular scattering,

$$\begin{aligned}
^{EH}S_0^A(\pi/2) &= \Gamma(3+2\sin^2 2\phi+\cos 2\phi),\\
^{EH}S_1^A(\pi/2) &= -\Gamma(1+2\sin^2 2\phi-\cos 2\phi).
\end{aligned} \tag{37}$$

Since $^{EH}S_1^A(\pi/2)$ is negative, in order to calculate the depolarization we have to apply Eq. (27) which leads to

$$^{EH}D^{A}\left(\frac{\pi}{2}\right)=\frac{1+\cos 2\phi}{2(1+\sin^2 2\phi)}, \tag{38}$$

ranging within

$$1/4<{}^{EH}D^{A}(\pi/2)<1. \tag{39}$$

The reversal ratio (30) now takes the form

$$^{EH}R^{A}(\vartheta)=\frac{2+(1+2\sin^2 2\phi+\cos 2\phi)\sin^2\vartheta-2|\sin 2\phi|\cos\vartheta}{2+(1+2\sin^2 2\phi+\cos 2\phi)\sin^2\vartheta+2|\sin 2\phi|\cos\vartheta}, \tag{40}$$

where for forward scattering $^{EH}R^A(0)$ reduces to the form of $^{EV}R^A(0)$ [Eq. (32)], as could be predicted. For the scattering angles for which $^{EH}S_1^A=0$ the reversal ratio (40) simultaneously plays the role of depolarization ratio of the scattered light.

We now assume circular polarization of the incident light. Thus, we have to take $\phi=\pm\pi/4$. From Eq. (28) or (38) one readily finds

$$^{C}D^{A}(\pi/2)=1/4. \tag{41}$$

Next, from Eq. (31) or (40),

$$^{C}R^{A}(\vartheta)=\frac{5-2\cos\vartheta-3\cos^2\vartheta}{5+2\cos\vartheta-3\cos^2\vartheta}, \tag{42}$$

where $^{C}R^A(0)=0$, pointing to completely circularly polarized radiation with preserved incident handedness.

The incident light is supposed to be polarized linearly (L) along the x axis, i.e., vertically to the observation plane. Linear polarization requires that $\phi=0$. Hence, from Eq. (25) we get

$$\begin{aligned}
^{LV}S_0^A &= 2\Gamma,\\
^{LV}S_1^A &= -{}^{LV}S_0^A,
\end{aligned} \tag{43}$$

irrespective of the scattering angle. The latter equation (43) signifies that the scattered light is completely polarized linearly along the direction Y, what in fact means inverse polarization, and $^{LV}D^A=0$ for all angles.

For incident light polarized in the observation plane, Eqs. (35) lead to

$$\begin{aligned}
^{LH}S_0^A(\vartheta) &= 2\Gamma(1+\sin^2\vartheta),\\
^{LH}S_1^A(\vartheta) &= 2\Gamma\cos^2\vartheta.
\end{aligned} \tag{44}$$

Since now $^{LH}S_1^A(\vartheta)>0$, in order to calculate the depolarization instead of Eq. (27) we have to use the definition

$$D=\frac{S_0-S_1}{S_0+S_1}, \tag{45}$$

where, with regard to Eq. (44),

$$^{LH}D^{A}(\vartheta)=\sin^2\vartheta. \tag{46}$$

Right angled scattering causes unpolarized light; then $^{LH}D^A(\pi/2)=1$. As in the vertical case the scattered azimuth is, for all angles, normal to that produced in symmetric scattering.

To end our discussion of asymmetric hyper-Raman scattering of completely polarized light let us notice that chaotic (i.e., with Gaussian distribution of amplitudes) completely polarized light is scattered twice as effectively as coherent light, as was first pointed out by Shen.[26] This is so because $g^{(2)}=2$ for polarized chaotic light, whereas $g^{(2)}=1$ for coherent radiation. Strong chaotic light can, for example, be obtained via transmission of coherent light by a rotating mat glass disk.

Let us now consider asymmetric hyper-Raman scattering of natural (N) light.

In the theory of linear light scattering all the models of natural light, treated as a superposition of two orthogonal waves linearly, circularly, or elliptically polarized with constant intensities and independently fluctuating phases or as a single wave albeit with randomly fluctuating direction of polarization, give the same results. But when adopted bodily to the description of nonlinear scatterings of natural light in the early days of studies, they turned out to be completely inadequate, as leading to different results. Already Strizhevskii[27] showed how to describe this problem correctly, and it has been further developed in the papers.[5,7,16,28,29]

Natural light is indeed an incoherent superposition of two orthogonal linearly, circularly, or elliptically polarized waves the amplitudes of which, however are not constant but are fluctuating Gaussian amplitudes. For all three models $g^{(2)} = 3/2$. Hence, at $g^{(2)} = 3/2$ in Γ, after averaging Eqs. (14) over the angles ψ and ϕ, or from Eq. (12) at

$$\langle s_0^2 \rangle_E = 3\langle s_3^2 \rangle_E = \tfrac{3}{2}\langle s_0 \rangle_E^2,$$
$$\langle s_0 s_1 \rangle_E = \langle s_0 s_2 \rangle_E = \langle s_0 s_3 \rangle_E = 0, \quad (47)$$

we arrive at

$$^{N}S_0^A(\vartheta) = \tfrac{1}{3}\Gamma(11 - 5\cos^2\vartheta),$$
$$^{N}S_1^A(\vartheta) = -\tfrac{5}{3}\Gamma\sin^2\vartheta. \quad (48)$$

From Eq. (27) one gets

$$^{N}D^A(\vartheta) = \frac{3}{8 - 5\cos^2\vartheta}, \quad (49)$$

where $^{N}D^A(0) = 1$, meaning unpolarized scattered light, and

$$^{N}D^A(\pi/2) = \tfrac{3}{8}. \quad (50)$$

Had we adopted to the calculation of depolarization the definitions of depolarization ratios commonly used in the symmetric approximation, i.e., strictly the definition (45) instead of Eq. (27) and vice versa, we would have obtained for pure asymmetric scattering so-called anomalous values of depolarization exceeding unity; thus, $^{LV}D^A = \infty$, $^{C}D^A(\pi/2) = 4$, and $^{N}D^A(\pi/2) = \tfrac{8}{3}$. All these values correspond directly to the upper limits of the total depolarization ratios given by Altmann and Strey.[1]

It is worth noting that pure asymmetric hyper-Rayleigh scattering can also be expected. Namely, molecules of the point symmetries D_3, D_4, and D_6 exhibit no hyper-Rayleigh intensity in the symmetric approximation, but can do so in the purely asymmetric case. Our results are readily adapted to the hyper-Rayleigh process by putting $\omega_Q = 0$ and omitting Q^2 in the factor Γ. The parameter B_2^A is simply given by Eq. (9) where, formally, we have to replace the hyper-Raman scattering tensor by its hyper-Rayleigh counterpart. Some aspects of hyper-Rayleigh scattering by molecules with electronic degeneracy have recently been discussed by Ostrowski *et al.*[30] Hyper-Raman scattering by such molecules has been considered in detail by Churcher,[31] who moreover established respective selection rules.

VI. CONCLUSIONS

For all we know, no experimental paper has so far announced inverse polarization of certain hyper-Raman lines.[4,5,7] In almost all previous theoretical papers, except for the papers of Refs. 1, 15, 16, and 31, the polarization properties of hyper-Raman have been considered on the assumption of full index symmetry in the scattering tensor. This has led to incomplete sets of selection rules which failed to predict the activity of vibrations responsible for inverse polarization. In other words, no theoretical predictions suggesting this polarization effect had appeared prior to the papers.[1,16] However, even these papers touch on this problem rather briefly. The observation of the purely asymmetric lines is particularly important in the case of modes which are both IR and Raman inactive. One should stress that each of the relative polarization parameters characterizing the pure asymmetric hyper-Raman line takes the same value for all vibrational modes and for all molecules.

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