POLARIZATION STATES AND ANGULAR DISTRIBUTION OF HYPER-RAYLEIGH AND HYPER-RAMAN SCATTERINGS IN TERMS OF STOKES PARAMETERS*

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A theory of polarization effects in integral hyper-Rayleigh and hyper-Raman scatterings for arbitrary scattering angles is developed using Stokes parameters for both the incident and scattered radiations. A detailed discussion of the scattered light, described by the irreducible symmetric and unsymmetric parts of the hyperpolarizability tensor $b_{\alpha\beta\gamma}$ is carried out for linear and circular polarization of the coherent incident light. Such parameters as: the ellipticity, the circularity degree, and the reversal and depolarization ratios are studied. The problem of scattering of natural light and polarized chaotic light is also touched on.

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1. Introduction

Hyper-Rayleigh and hyper-Raman scatterings belong to three-photon processes and consist in the annihilation of two photons ω of the incident light and the spontaneous emission of a third photon with the frequency ω_s fulfilling, with accuracy to the spectral width, the following relation: $\omega_s = 2\omega \pm \omega_{ij}$, where ω_{ij} is a frequency arising from the transition between the quantum molecular states i and j. If $i = j$ we deal with hyper-Rayleigh scattering. If $i \neq j$, hyper-Raman scattering takes place.

Although both types of scattering have already been reviewed from the viewpoint of theory as well as experiment [1–5], and almost twenty years have elapsed since the pioneer experiment of Terhune et al. [6] in which hyper-Rayleigh and hyper-Raman scatterings were observed, they are still interesting topics for research even in their general aspects. In this paper we return to their polarization properties. Since this aspect of scattering is common to both types of the process in question, the two can be discussed jointly.

The subject under consideration has first been discussed by Stanton [7] in terms of Stokes parameters. His discussion, however, was restricted to forward symmetric scattering

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and, chiefly, to ellipticity. We have carried out general investigations for arbitrary angles in the formalism of intensities, in both Cartesian [8, 9] and spherical [10, 11] representations. Recently, we used Stokes parameters to the description of the incident light only [5, 12].

Also recently, some publications giving rather unconventional definitions and interpretations of some parameters characterizing scattered light have appeared. It is our aim to reconcile these definitions with those commonly used and, moreover, to propose an intrinsically consistent interpretation.

2. Three-photon scattered light intensity tensor

As the basis for our considerations we take a macroscopic sample of a gaseous medium. We assume linear dimensions of the molecules much smaller than the incident wavelength; this enables us to neglect interference effects from different parts of one and the same molecule.

The sample is irradiated by an intense plane wave of frequency ω and wave vector k, the electric field of which is taken in the form:

$$E(r, t) = \text{Re} \{E e^{-i(\omega t - k \cdot r)}\}, \tag{1}$$

E is a complex amplitude, fluctuating in general. The efficiency of nonlinear processes strongly depends on the statistical properties of the light causing them. This problem will also be discussed here. For this reason, we have to perform appropriate statistical averaging over the ensemble of the incident amplitudes which replaces time averaging for ergodic processes.

The molecules undergo, in the first order, electric-dipole polarization. In the quadratic approximation relevant to us, this polarization leads to the following incoherent integral intensity tensor of light scattered by N statistically independent molecules [9]:

$$I_{ij} = \frac{c}{4\pi} L' \langle b_{ikl} b_{jmn}^* E_k E_l E_m^* E_n^* \rangle, \tag{2}$$

where L' is a scattering factor dependent on the frequency ω_s^4 and proportional to the number of molecules. We use Latin indices for components with respect to a laboratory frame and Greek indices for a molecule-fixed frame. Einstein's summation convention for repeated indices is applied throughout.

The third-rank hyperpolarizability tensor b_{ijk} of an individual molecule may be expanded in a power series in normal coordinates Q_λ of vibration [13]:

$$b_{ijk} = b_{ijk}(Q) = b_{ijk}(0) + \sum_\lambda b_{ijk}^\lambda Q_\lambda + \dots . \tag{3}$$

$b_{ijk}(0)$ is responsible for hyper-Rayleigh scattering. This type of scattering occurs for molecules without a centre of symmetry in their ground electronic state if, of course, we deal with gaseous media. The derivative b_{ijk}^λ is responsible for hyper-Raman scattering which can be caused even by molecules centrosymmetric in their ground quantum state.

It is approximately possible to assume total index symmetry of the tensor b_{ijk} in the limit of low incident frequencies [3, 14]. But in general this tensor should be considered as symmetric in its last two indices only.

The symbol $\langle\rangle$ in (2) stands for appropriate statistical averagings over molecular orientations, vibrations and complex amplitudes of the incident field in general. In the effects considered here averaging over molecular orientations is related to rotational averaging of the product of six directional cosines connecting the two above mentioned frames as first carried out by Kielich [15]. This procedure leads to:

$$I_{ij} = \frac{c}{4\pi} L\{\alpha\delta_{ij}\langle E_k E_k^* E_l E_l^*\rangle + \beta\delta_{ij}\langle E_k E_k E_l^* E_l^*\rangle$$

$$+\gamma\langle E_i E_j^* E_k E_k^*\rangle + \delta\langle E_i^* E_j E_k E_k^*\rangle + \varepsilon\langle E_i^* E_j^* E_k E_k\rangle + \varepsilon^*\langle E_i E_j E_k^* E_k^*\rangle\}, \tag{4}$$

where $L = L'/105$.

If the scattering tensor is symmetric in its last two indices, the molecular rotational invariants α—ε have the following form:

$$\alpha = \langle 11b_{\alpha\beta\gamma}b_{\alpha\beta\gamma}^* - 6b_{\alpha\beta\gamma}b_{\beta\alpha\gamma}^* - 5b_{\alpha\beta\beta}b_{\alpha\gamma\gamma}^* + 4b_{\alpha\beta\beta}b_{\gamma\gamma\alpha}^* + 4b_{\beta\beta\alpha}b_{\alpha\gamma\gamma}^* - 6b_{\beta\beta\alpha}b_{\gamma\gamma\alpha}^*\rangle,$$

$$\beta = \langle -5b_{\alpha\beta\gamma}b_{\alpha\beta\gamma}^* + 4b_{\alpha\beta\gamma}b_{\beta\alpha\gamma}^* + 8b_{\alpha\beta\beta}b_{\alpha\gamma\gamma}^* - 5b_{\alpha\beta\beta}b_{\gamma\gamma\alpha}^* - 5b_{\beta\beta\alpha}b_{\alpha\gamma\gamma}^* + 4b_{\beta\beta\alpha}b_{\gamma\gamma\alpha}^*\rangle,$$

$$\gamma = 2\langle -3b_{\alpha\beta\gamma}b_{\alpha\beta\gamma}^* + b_{\alpha\beta\gamma}b_{\beta\alpha\gamma}^* + 2b_{\alpha\beta\beta}b_{\alpha\gamma\gamma}^* - 3b_{\alpha\beta\beta}b_{\gamma\gamma\alpha}^* - 3b_{\beta\beta\alpha}b_{\alpha\gamma\gamma}^* + 8b_{\beta\beta\alpha}b_{\gamma\gamma\alpha}^*\rangle,$$

$$\delta = 2\langle -3b_{\alpha\beta\gamma}b_{\alpha\beta\gamma}^* + 8b_{\alpha\beta\gamma}b_{\beta\alpha\gamma}^* + 2b_{\alpha\beta\beta}b_{\alpha\gamma\gamma}^* - 3b_{\alpha\beta\beta}b_{\gamma\gamma\alpha}^* - 3b_{\beta\beta\alpha}b_{\alpha\gamma\gamma}^* + b_{\beta\beta\alpha}b_{\gamma\gamma\alpha}^*\rangle,$$

$$\varepsilon = \langle 4b_{\alpha\beta\gamma}b_{\alpha\beta\gamma}^* - 6b_{\alpha\beta\gamma}b_{\beta\alpha\gamma}^* - 5b_{\alpha\beta\beta}b_{\alpha\gamma\gamma}^* + 11b_{\alpha\beta\beta}b_{\gamma\gamma\alpha}^* + 4b_{\beta\beta\alpha}b_{\alpha\gamma\gamma}^* - 6b_{\beta\beta\alpha}b_{\gamma\gamma\alpha}^*\rangle, \tag{5}$$

where $\langle\rangle$ now refers to hyper-Raman only and denotes averaging related to the normal coordinates of vibrations. α—δ are real parameters.

The tensor $b_{\alpha\beta\gamma}$, partly symmetric in the last two indices, may be decomposed into two parts: a completely symmetric part $b_{\alpha\beta\gamma}^S$ related to permutation of all indices and a residual unsymmetric part $b_{\alpha\beta\gamma}^U$ still symmetric in the indices β and γ — cf. Christie and Lockwood [14]:

$$b_{\alpha\beta\gamma} = b_{\alpha\beta\gamma}^S + b_{\alpha\beta\gamma}^U,$$

$$b_{\alpha\beta\gamma}^S = \tfrac{1}{3}(b_{\alpha\beta\gamma} + b_{\beta\alpha\gamma} + b_{\gamma\alpha\beta}),$$

$$b_{\alpha\beta\gamma}^U = \tfrac{1}{3}(2b_{\alpha\beta\gamma} - b_{\beta\alpha\gamma} - b_{\gamma\alpha\beta}). \tag{6}$$

In other words, the unsymmetricity is related to the permutation of α and whichever of the indices β or γ.

Accordingly, the molecular invariants α—ε may be represented as sums of purely symmetric components α^S—ε^S, purely unsymmetric components α^U—ε^U, whereas some of them will also in general contain a mixed symmetric-unsymmetric component (SU).

Finally we arrive at:

$$\alpha^S = \tfrac{1}{2}\delta^S = 5B_3^S,$$

$$\beta^S = \tfrac{1}{4}\gamma^S = \tfrac{1}{2}\varepsilon^S = \tfrac{1}{2}\varepsilon^{S*} = \tfrac{1}{3}(7B_1^S - 3B_3^S), \tag{7}$$

where the non-negative parameters

$$B_1^S = \tfrac{3}{5} \langle b_{\alpha\beta\beta}^S b_{\alpha\gamma\gamma}^{S*} \rangle,$$

$$B_3^S = \tfrac{1}{5} \langle 5b_{\alpha\beta\gamma}^S b_{\alpha\beta\gamma}^{S*} - 3b_{\alpha\beta\beta}^S b_{\alpha\gamma\gamma}^{S*} \rangle, \tag{8}$$

correspond directly to the square modulus of the irreducible symmetric spherical tensors of weight 1 and 3, respectively [3–6, 11].

$$\alpha^U = -\delta^U = 14B_2^U,$$

$$\beta^U = \gamma^U = -\varepsilon^U = -\varepsilon^{U*} = \tfrac{7}{3}(5B_1^U - 3B_2^U), \tag{9}$$

where

$$B_1^U = \tfrac{3}{4} \langle b_{\alpha\beta\beta}^U b_{\alpha\gamma\gamma}^{U*} \rangle,$$

$$B_2^U = \tfrac{1}{4} \langle 4b_{\alpha\beta\gamma}^U b_{\alpha\beta\gamma}^{U*} - 3b_{\alpha\beta\beta}^U b_{\alpha\gamma\gamma}^{U*} \rangle \tag{10}$$

are also positive-defined parameters corresponding to the squared modulus of the irreducible unsymmetric spherical tensors of weight 1 and 2, respectively [4, 11]. It is seen that the purely symmetric and the purely unsymmetric components of the invariant ε are real.

$$\alpha^{SU} = \delta^{SU} = 0,$$

$$\beta^{SU} = -\tfrac{1}{2}\gamma^{SU} = 2\,\mathrm{Re}\,\varepsilon^{SU} = 7B_1^{SU}, \tag{11}$$

where

$$B_1^{SU} = \tfrac{1}{2} \langle b_{\alpha\beta\beta}^S b_{\alpha\gamma\gamma}^{U*} + b_{\alpha\beta\beta}^{S*} b_{\alpha\gamma\gamma}^U \rangle, \tag{12}$$

and, in principle, can take positive as well as negative values.

Generally,

$$\varepsilon^{SU} = -\tfrac{7}{2} \langle b_{\alpha\beta\beta}^S b_{\alpha\gamma\gamma}^{U*} - 2b_{\alpha\beta\beta}^{S*} b_{\alpha\gamma\gamma}^U \rangle, \tag{13}$$

whence

$$\mathrm{Im}\,\varepsilon^{SU} = \frac{21i}{4} \langle b_{\alpha\beta\beta}^S b_{\alpha\gamma\gamma}^{U*} - b_{\alpha\beta\beta}^{S*} b_{\alpha\gamma\gamma}^U \rangle. \tag{14}$$

In the majority of cases, except elliptical or partly elliptical polarization of the incident light, the final results are dependent on $\mathrm{Re}\,\varepsilon$ only. Then, the initial six invariants $\alpha-\varepsilon$ and ε^* reduce to five: B_1^S, B_3^S, B_1^U, B_2^U and B_1^{SU}, similarly as for real $b_{\alpha\beta\gamma}$.

Ordinary Raman and Rayleigh processes are dependent on the second-order polarizability tensor $a_{\alpha\beta}$. This tensor can be decomposed into isotropic, anisotropic and antisymmetric parts described by appropriate irreducible spherical tensors which do not mix under rotation in space. Hence, the intensity scattered by noninteracting molecules is the additive sum of three intensities related to pure isotropic, anisotropic and antisymmetric contributions. They are briefly said to be isotropic, anisotropic and antisymmetric scatterings [16]. These scatterings have different polarization properties. In three-photon scattering, following the decomposition of $b_{\alpha\beta\gamma}$ into symmetric and unsymmetric components, one can

consider symmetric and unsymmetric contributions to the scattered intensity. However, in general, the scattered intensity is not the simple incoherent sum of these contributions because of the presence of the cross terms B_1^{SU} and $\text{Im } \varepsilon^{SU}$ arising from the symmetric and unsymmetric parts of the irreducible tensor of weight 1 which mix under rotation in space. Although the symmetric and unsymmetric contributions to the scattered intensity do not add incoherently, nonetheless for the sake of simplicity we use here the terms: symmetric and unsymmetric scattering. This is all the more justified as each of these processes can take place individually under certain conditions. The polarization properties of pure unsymmetric scattering are identical with those of antisymmetric scattering in ordinary Rayleigh and Raman.

In the limit of low incident frequencies we deal, in a good approximation, with pure symmetric scattering, dependent generally on the two rotational invariants B_1^S and S_3^S. If the above condition is not fulfilled, unsymmetric scattering appears. In the majority of cases it will accompany symmetric scattering and, in general, all six molecular invariants B_1^S, B_3^S, B_1^U, B_2^U, B_1^{SU} and $\text{Im } \varepsilon^{SU}$ will then intervene. On the other hand, unsymmetricity in $b_{\alpha\beta\gamma}$ can activate vibrations inactive in the case of completely symmetric scattering tensor [14]. This means that for certain point groups of symmetry and kinds of vibrations, pure unsymmetric hyper-Raman scattering can occur alone. Moreover, one can also expect pure unsymmetric hyper-Rayleigh scattering on molecules of symmetry D_4, D_5 and D_6. These molecules do not exhibit hyper-Rayleigh in the symmetric case. Pure unsymmetric scattering depends on B_2^U only. Namely, inspection of the nonvanishing components of the scattering tensor shows that then the components $b_{\alpha\beta\gamma}^U$ with all indices α, β and γ different intervene solely [14, 18]. This in fact leads to $B_1^U = 0$, whereas the nonzero invariant B_2^U equals $\langle |b_{\alpha\beta\gamma}^U|^2 \rangle$. Since this scattering depends on one rotational invariant B_2^U the relative parameters characterizing this process are no longer dependent on B_2^U and may be dependent on the scattering angle.

3. General remarks on the polarization properties of light

Electromagnetic radiation interacting with matter experiences in general changes in the state of its polarization. The quality and magnitude of these changes depend on the kind of interaction and on the molecular and thermodynamical properties of the medium. The statistical properties of scattered light are also modified by comparison with those of the incident radiation.

The most consistent formulation of the subject in question is obtained by the use of Stokes parameters. If we assume the incident light to be propagating along the z-axis, they are [17]:

$$s_0 = E_x E_x^* + E_y E_y^*,$$

$$s_1 = E_x E_x^* - E_y E_y^*,$$

$$s_2 = E_x E_y^* + E_y E_x^*,$$

$$s_3 = i(E_y E_x^* - E_x E_y^*), \tag{15}$$

or, equivalently,

$$s_1 = s_0 \cos 2\phi \cos 2\psi,$$

$$s_2 = s_0 \cos 2\phi \sin 2\psi,$$

$$s_3 = s_0 \sin 2\phi, \tag{16}$$

where ψ denotes the azimuth of the elliptic major axis relative to x, and ϕ is the ellipticity.

For monochromatic light

$$s_0^2 = s_1^2 + s_2^2 + s_3^2, \tag{17}$$

which, in general, is not fulfilled for quasi-monochromatic light with fluctuating intensity.

In linear optics, when describing processes caused by quasi-monochromatic light, we immediately use the parameters (15) averaged over the ensemble of the incident field amplitudes. For nonlinear processes we have to use, in this case, unaveraged parameters (15) or (16). These processes depend on intensity fluctuations of the light causing them. But the final results have to be averaged in the above mentioned sense. If we use the form (16) of the Stokes parameters and if the incident light is unpolarized, then we have to perform additionally averaging over the angles ψ and ϕ.

We denote the Stokes parameters for the scattered light by capital letters. $\sigma = \sqrt{S_1^2 + S_2^2 + S_3^2}$ refers to its completely polarized portion I_p while $S_0 - \sigma$ to its unpolarized portion I_u [17].

One of the relative parameters characterizing the scattered radiation is given by the depolarization ratio ^{p_1}D:

$$^{p_1}D = \frac{^{p_1}S_0 - {}^{p_1}\sigma}{^{p_1}S_0 + {}^{p_1}\sigma}. \tag{18}$$

The superscript preceding D and the Stokes parameters denotes polarization of the incident light.

The polarized portion of the scattered light is described by the azimuth ψ_s and the ellipticity ϕ_s as below [17]:

$$\tan 2\psi_s = \frac{^{p_1}S_2}{^{p_1}S_1}, \tag{19}$$

$$\sin 2\phi_s = \frac{^{p_1}S_3}{^{p_1}\sigma}. \tag{20}$$

In ordinary Rayleigh and Raman the azimuth corresponding to forward and backward purely symmetric scattering is the same as the incident azimuth. In the antisymmetric case it is always changed by $\pi/2$. In the processes under consideration the same situation occurs for purely symmetric and unsymmetric scatterings.

If both scatterings are simultaneously present, the resultant azimuth depends on their magnitude as well as on the magnitude of the cross terms.

When the incident radiation is circularly or elliptically polarized the scattered radiation is often characterized by the degree of circularity [18]

$$^{\pm}C = \frac{^{\pm}S_3}{^{\pm}S_0}, \tag{21}$$

where the superscript $(+)$ before the parameters denotes right-handedness of the incident radiation while $(-)$ — left-handedness, as viewed oppositely to the propagation direction.

One can further introduce the reversal ratio $^{\pm}R$ defined as the ratio of the scattered intensity $^{\pm}I_{\mp}$ transmitted by an optical system accepting the helicity contrary to the helicity of the incident light and the scattered intensity $^{\pm}I_{\pm}$ transmitted by the optical system accepting the same handedness as that of the incident radiation [16]. In terms of the Stokes parameters, the reversal ratio takes the form:

$$^{\pm}R = \frac{^{\pm}S_0 \mp {}^{\pm}S_3}{^{\pm}S_0 \pm {}^{\pm}S_3}. \tag{22}$$

Our definition (22) differs from that proposed by Long [18]:

$$^{\pm}R = \frac{^{\pm}S_0 - |{}^{\pm}S_3|}{^{\pm}S_0 + |{}^{\pm}S_3|}. \tag{23}$$

The definition (23) consistently removes the signs in the numerator and denominator, signs related to the handedness of the incident radiation. But unfortunately, it also removes the sign of the molecular rotational invariant included in S_3. The reversal ratio defined in this way would have its upper limit equal to unity. The definition (23) holds for positive molecular invariants in S_3 whilst its inverse holds for negative invariants. The negative molecular invariants are responsible for helicity reversal of the scattered polarized portion relative to that of the incident radiation. Then $^{\pm}R$ should exceed unity.

From equations (21) and (22) we find:

$$^{\pm}R = \frac{1 \mp {}^{\pm}C}{1 \pm {}^{\pm}C}. \tag{24}$$

Recently, Andrews and Harlow [19] have introduced a parameter p^{-1} representing the fraction of scattered intensity with the same helicity as the incident light: $^{\pm}p^{-1} = (p_{||} + p_{\perp})^{-1} = {}^{\pm}I_{\pm}/I_{\text{total}}$. This can be rewritten as follows:

$$^{\pm}p^{-1} = \tfrac{1}{2}(1 \pm {}^{\pm}C) = \frac{1}{1 + {}^{\pm}R}. \tag{25}$$

We would like to concentrate for a while on the interpretations of $C = 0$ [18, 19]. The authors of Ref. [19] interpret different values of p^{-1}, among others $p^{-1} = 1/2$. But $p^{-1} = 1/2$ involves directly $C = 0$. Long [18] interpretes $C = 0$ as signifying unpolarized scattered light while Andrews and Harlow [19] say that $p^{-1} = 1/2$ means plane polarized scattered light. At first glance, at least one of these interpretations would hardly appear correct. To our mind, $C = 0$ is not a decisive quantity and the two above cited interpretations are

really possible. Moreover one can add a third interpretation according to which $C = 0$ signifies partly plane polarized light. The parameter S_3 of course characterizes the polarized portion. First of all, S_3 equals zero if this portion does not exist at all. Then it directly implies unpolarized scattered light. For a nonzero polarized portion, S_3 reaches zero only if it is plane polarized. The unpolarized portion may exist or not, leading to partly plane polarized or completely plane polarized radiation, respectively. Since $C = 0$ corresponds to these three different polarization states, $C = 0$ is in fact a not univocally decisive quantity. The same conclusion refers to $R = 1$ and $p^{-1} = 1/2$.

4. The Stokes parameters for the light scattered

The scattered light is observed in the $YZ = yz$ plane along the Z-axis at an angle ϑ relative to z. Then, in the most general case of the polarization state of the incoming light, (4) and (15) lead to:

$$^{p_1}S_0(\vartheta) = \tfrac{1}{2} L\{4\alpha\langle s_0^2\rangle + 2\beta[\langle s_0^2\rangle + \langle s_1^2\rangle + \langle s_2^2\rangle - \langle s_3^2\rangle]$$

$$+ (\gamma + \delta)\left[\langle s_0^2\rangle + \langle s_0 s_1\rangle + (\langle s_0^2\rangle - \langle s_0 s_1\rangle)\cos^2\vartheta\right]$$

$$+ \mathrm{Re}\,\varepsilon[\langle s_0^2\rangle + \langle s_1^2\rangle + \langle s_2^2\rangle - \langle s_3^2\rangle + 2\langle s_0 s_1\rangle$$

$$+ (\langle s_0^2\rangle + \langle s_1^2\rangle + \langle s_2^2\rangle - \langle s_3^2\rangle - 2\langle s_0 s_1\rangle)\cos^2\vartheta] + 2\,\mathrm{Im}\,\varepsilon\langle s_2 s_3\rangle \sin^2\vartheta\},$$

$$^{p_1}S_1(\vartheta) = \tfrac{1}{2} L\{(\gamma + \delta)\left[\langle s_0^2\rangle + \langle s_0 s_1\rangle - (\langle s_0^2\rangle - \langle s_0 s_1\rangle)\cos^2\vartheta\right]$$

$$+ \mathrm{Re}\,\varepsilon[\langle s_0^2\rangle + \langle s_1^2\rangle + \langle s_2^2\rangle - \langle s_3^2\rangle + 2\langle s_0 s_1\rangle - (\langle s_0^2\rangle + \langle s_1^2\rangle + \langle s_2^2\rangle - \langle s_3^2\rangle$$

$$- 2\langle s_0 s_1\rangle)\cos^2\vartheta] + 2\,\mathrm{Im}\,\varepsilon\langle s_2 s_3\rangle (1 + \cos^2\vartheta)\},$$

$$^{p_1}S_2(\vartheta) = L\{(\gamma + \delta + 2\,\mathrm{Re}\,\varepsilon)\langle s_0 s_2\rangle - 2\,\mathrm{Im}\,\varepsilon\langle s_1 s_3\rangle\}\cos\vartheta,$$

$$^{p_1}S_3(\vartheta) = L(\gamma - \delta)\langle s_0 s_3\rangle \cos\vartheta. \tag{26}$$

Already from these general forms of the Stokes parameters it is possible to read some properties of three-photon scattered light.

Firstly, for perpendicular observation ($\vartheta = \pi/2$), we have $^{p_1}S_2(\pi/2) = {}^{p_1}S_3(\pi/2) = 0$. This means that if a polarized portion of the scattered light exists, it will be linearly polarized irrespective of the polarization state of the incident light. $^{p_1}S_2(\pi/2) = 0$ corresponds to the azimuths $\psi_s = 0$ or π and $\psi = \pi/2$ which signify that the electric field may oscillate along the X or Y-axis according to the sign of $^{p_1}S_1(\pi/2)$.

Secondly, for forward scattering ($\vartheta = 0$), equations (26) lead to:

$$\tan 2\psi_s(0) = \frac{(\gamma + \delta + 2\,\mathrm{Re}\,\varepsilon)\langle s_0 s_2\rangle - 2\,\mathrm{Im}\,\varepsilon\langle s_1 s_3\rangle}{(\gamma + \delta + 2\,\mathrm{Re}\,\varepsilon)\langle s_0 s_1\rangle + 2\,\mathrm{Im}\,\varepsilon\langle s_2 s_3\rangle}, \tag{27}$$

which, for completely polarized incident light, transforms to:

$$\tan 2\psi_s(0) = \tan 2\psi\,\frac{\gamma + \delta + 2\,\mathrm{Re}\,\varepsilon - 2\,\mathrm{Im}\,\varepsilon \cot 2\psi \sin 2\phi}{\gamma + \delta + 2\,\mathrm{Re}\,\varepsilon + 2\,\mathrm{Im}\,\varepsilon \tan 2\psi \sin 2\phi}. \tag{28}$$

The last terms in the numerator and denominator can vanish either with respect to the polarization state of the incident light or with respect to the conditions leading to Im $\varepsilon = 0$. As to the polarization state of the incident light, they vanish if it is linearly or circularly polarized as well as for unpolarized light.

Then, equation (28) reads:

$$\tan 2\psi_s(0) = \tan 2\psi. \qquad (29)$$

Stanton [7] noticed that this relation means retention of the azimuth relative to that of the incident light. However, this relation admits moreover of a change of the azimuth ψ_s by $\pi/2$ in comparison with ψ. First of all, this will take place for pure unsymmetric scattering. This can also occur if both symmetric and unsymmetric scatterings are simultaneously present.

For elliptical polarization of the incident light, if Im $\varepsilon \neq 0$, the resultant azimuth will also differ from ψ but in the majority of cases not by $\pi/2$. This is a serious discrepancy from the results for ordinary Rayleigh and Raman where this difference is always $\pi/2$.

5. Application to various polarization states of the incident light

At the start we shall assume the incident light to be coherent. Thus, we can omit statistical averaging over the field amplitude, since it is constant, and also take advantage of (17).

5.1. Linearly polarized incident light

Let us assume polarization of the incoming light perpendicular (along x) to the observation plane. Then we have: $s_0 = s_1$, $s_2 = s_3 = 0$ and hence from (26) we get:

$$^{\perp}S_0 = Ls_0^2(2\alpha + 2\beta + \gamma + \delta + 2\,\text{Re}\,\varepsilon),$$

$$^{\perp}S_1 = Ls_0^2(\gamma + \delta + 2\,\text{Re}\,\varepsilon),$$

$$^{\perp}S_2 = {}^{\perp}S_3 = 0, \qquad \phi_s = 0, \qquad (30)$$

irrespective of the scattering angle.

With respect to (7) and (9) for pure symmetric and unsymmetric scatterings we have:

$$^{\perp}S_0^S = \tfrac{10}{3}\,Ls_0^2(7B_1^S + 3B_3^S),$$

$$^{\perp}S_1^S = \tfrac{2}{3}\,Ls_0^2(28B_1^S + 3B_3^S), \qquad (31)$$

$$^{\perp}S_0^U = -{}^{\perp}S_1^U = 7Ls_0^2B_2^U, \qquad (32)$$

where, as already said, purely unsymmetric scattering depends on B_2^U only. This scattering leads to completely linearly polarized light along the direction Y, what, in fact amounts to a change of the azimuth ψ_s^U by $\pi/2$ relative to that of the incident light. As for the symmetric scattering, the azimuth of its polarized portion is preserved, $\psi_s^S = 0$.

At $^{Pi}S_2 = {}^{Pi}S_3 = 0$ the depolarization ratio (18) reduces to the form:

$$^{Pi}D = \frac{^{Pi}S_0 - {}^{Pi}S_1}{^{Pi}S_0 + {}^{Pi}S_1},$$

(33)

for positive $^{Pi}S_1$, and to the form:

$$^{Pi}D = \frac{^{Pi}S_0 + {}^{Pi}S_1}{^{Pi}S_0 - {}^{Pi}S_1}$$

(34)

for negative $^{Pi}S_1$. They are given simply as the ratios of the smaller and greater principal values of the scattered intensity tensor and are ratios of the components I_{YY}/I_{XX} and I_{XX}/I_{YY}, respectively.

For pure symmetric scattering, on insertion of (31) into (33), we find [5]:

$$^{\perp}D^S = \frac{7B_1^S + 12B_3^S}{63B_1^S + 18B_3^S}.$$

(35)

The lower limit of this quantity occurs for $B_3^S = 0$, whereas the upper limit for $B_1^S = 0$. $^{\perp}D^S$ varies within the range:

$$\tfrac{1}{9} \leqslant {}^{\perp}D^S \leqslant \tfrac{2}{3},$$

(36)

in agreement with numerous previous results.

Unsymmetric scattering gives linearly polarized light, hence from (34):

$$^{\perp}D^U = 0.$$

(37)

If both these scatterings take place together we have additionally to take into account the unsymmetric parameter B_1^U as well as the cross term B_1^{SU}, related with the symmetric and unsymmetric parts of the irreducible tensor of weight 1. From (30), (7), (9) and (11) we finally get for total scattering:

$$^{\perp}S_0 - {}^{\perp}S_1 = \tfrac{2}{3} Ls_0^2 (7B_1^S + 12B_3^S + 35B_1^U + 21B_2^U + 21B_1^{SU}),$$

$$^{\perp}S_0 + {}^{\perp}S_1 = 6Ls_0^2 (7B_1^S + 2B_3^S).$$

(38)

The light scattered by a great number of noninteracting statistically independent molecules is completely incoherent. The elementary scattering processes from different molecules are uncorrelated. However, the magnitude of these elementary processes is not in general a simple additive sum of symmetric and unsymmetric contributions owing to the presence of the cross term B_1^{SU}. In other words this, as it were interference term, does not influence the statistical properties of the scattered light but affects only the magnitude of scattering.

As we see, the intensity component X remains purely symmetric. The magnitude of the component Y is the additive sum of the symmetric and unsymmetric contributions resulting from the symmetric and unsymmetric irreducible tensors of weight 3 and 2, respectively:

$$^{\perp}S_0 - {}^{\perp}S_1 = 2Ls_0^2 (4B_3^S + 7B_2^U),$$

(39)

and of a remaining part due to the symmetric and unsymmetric components of the irreducible tensor of weight 1:

$$^{\perp}S_0 - {}^{\perp}S_1 = \tfrac{14}{3} L s_0^2 (B_1^S + 5 B_1^U + 3 B_1^{SU})$$

$$= \tfrac{7}{10} L s_0^2 (2 b_{\alpha\beta\beta}^S + 5 b_{\alpha\beta\beta}^U)(2 b_{\alpha\gamma\gamma}^{S*} + 5 b_{\alpha\gamma\gamma}^{U*}). \tag{40}$$

The cross term B_1^{SU} is positive for certain molecules and kinds of vibrations but negative for some others, leading to a constructive or destructive influence on the scattered intensity component Y. In principle, the destructive influence can totally extinguish the part (40) of this component. This can occur for $2 b_{\alpha\beta\beta}^S = -5 b_{\alpha\beta\beta}^U$. If additionally B_3^S and B_2^U were zero, the scattered light would be linearly polarized in the direction X and would arise from B_1^S only. Generally, the intensity component Y in (38) will differ from zero. Incoherent superposition of two orthogonal, in general unequally intense linearly polarized waves, gives an unpolarized portion and a diminished linearly polarized portion with azimuth determined by the initially greater intensity component. Hence, the resultant azimuth can be the same or can be changed by $\pi/2$ compared with the incident azimuth.

For the sake of simplicity, irrespective of the resultant azimuth, only one of the definitions of depolarization (33) and (34) is applied in practice. On the definition (33), for unsymmetric scattering exceeding symmetric scattering, depolarization may exceed unity. This is so-called anomalous depolarization:

$$^{\perp}D = \frac{7 B_1^S + 12 B_3^S + 35 B_1^U + 21 B_2^U + 21 B_1^{SU}}{63 B_1^S + 18 B_3^S}, \tag{41}$$

and $^{\perp}D$ ranges within [4, 11]:

$$0 \leqslant {}^{\perp}D < \infty, \tag{42}$$

where infinity corresponds to pure unsymmetric scattering since $^{\perp}D$ is the inverse of $^{\perp}D^U$ calculated from (34).

The depolarization ratio (41) is in general a function of the five molecular invariants. Since this parameter is angle-independent, we have no possibility of determining all these invariants simultaneously from angular distribution measurements of the scattered light.

With respect to $^{\perp}S_3 = 0$, independently of the medium $^{\perp}R = 1$, $^{\perp}C = 0$, and $^{\perp}p^{-1} = 1/2$. As shown (42), the scattered light may be completely or partly polarized linearly, and natural as well.

Similarly, one can discuss scattering of light polarized linearly in the observation plane, i.e. along the direction y. The final results depend on the scattering angle. As shown previously [9], very simple relations with the results just presented hold, even in the presence of unsymmetric scattering. For this reason we shall not consider this case here. However, one should mention that, at this geometry of scattering, it is possible to perform five angular distribution measurements permitting the determination of every of the five molecular invariants B_1^S, B_3^S, B_1^U, B_2^U and B_1^{SU}.

5.2. Circular polarization of the incident light

The incident light is now supposed to be circularly polarized. Then $s_3 = \pm s_0$ and $s_1 = s_2 = 0$. From (26) we get:

$$^{\pm}S_0(\vartheta) = \tfrac{1}{2}\, Ls_0^2\{4\alpha + (\gamma + \delta)\,(1 + \cos^2\vartheta)\},$$

$$^{\pm}S_1(\vartheta) = \tfrac{1}{2}\, Ls_0^2(\gamma + \delta)\sin^2\vartheta,$$

$$^{\pm}S_3(\vartheta) = \pm Ls_0^2(\gamma - \delta)\cos\vartheta,$$

$$^{\pm}S_2(\vartheta) = 0. \tag{43}$$

The process depends on three rotational invariants α, γ and δ which, however, are expressed by the five invariants related to the irreducible tensors.

For pure symmetric scattering we find:

$$^{\pm}S_0^{S}(\vartheta) = \tfrac{1}{3}\, Ls_0^2\{14B_1^{S} + 39B_3^{S} + (14B_1^{S} + 9B_3^{S})\cos^2\vartheta\},$$

$$^{\pm}S_1^{S}(\vartheta) = \tfrac{1}{3}\, Ls_0^2(14B_1^{S} + 9B_3^{S})\sin^2\vartheta,$$

$$^{\pm}S_3^{S}(\vartheta) = \pm\tfrac{14}{3}\, Ls_0^2(2B_1^{S} - 3B_3^{S})\cos\vartheta, \tag{44}$$

whereas for pure unsymmetric scattering

$$^{\pm}S_0^{U}(\vartheta) = \tfrac{7}{2}\, Ls_0^2 B_2^{U}(5 - 3\cos^2\vartheta),$$

$$^{\pm}S_1^{U}(\vartheta) = -\tfrac{21}{2}\, Ls_0^2 B_2^{U}\sin^2\vartheta,$$

$$^{\pm}S_3^{U}(\vartheta) = \pm 7Ls_0^2 B_2^{U}\cos\vartheta. \tag{45}$$

The polarized portions of both scatterings are in general ($0 < \vartheta < \pi/2$) elliptically polarized. The major axis related to the symmetric scattering lies along the X-axis. For unsymmetric scattering it lies along the direction Y. In the case of symmetric scattering an exceptional situation occurs for $2B_1^{S} = 3B_3^{S}$: the polarized portion of this scattering is then polarized linearly.

For pure unsymmetric scattering the helicity of the polarized portion is always the same as the incident helicity. The helicity of the symmetric polarized portion may be retained or reversed.

For forward scattering the ellipses generally transform into circles ($^{\pm}S_1^{S}(0) = {}^{\pm}S_1^{U}(0) = 0$), whereas for perpendicular scattering — into straight lines ($^{\pm}S_3^{S}(\pi/2) = {}^{\pm}S_3^{U}(\pi/2) = 0$). The light scattered forwards in the unsymmetric case is completely circularly polarized ($^{\pm}S_0^{U}(0) = \pm\,{}^{\pm}S_3^{U}(0)$) with preserved helicity as already said. The molecules with $2B_1^{S} = 3B_3^{S}$ scatter forwards unpolarized light in the symmetric case.

For the ellipticity we have:

$$\sin 2\phi_s^{U}(\vartheta) = \pm\,\frac{2\cos\vartheta}{\sqrt{9 - 14\cos^2\vartheta + 9\cos^4\vartheta}}\,. \tag{46}$$

For $\vartheta = 0$, this gives $^\pm\phi_s^U(0) = \pm\pi/4$, i.e. circular polarization. For $\vartheta = \pi/2$, $\phi_s^U(\pi/2)$ tends to zero implying linear polarization of the polarized portion.

In the case of symmetric scattering:

$$\sin 2\,^\pm\phi_s^S(\vartheta) = \pm\frac{14(2B_1^S - 3B_3^S)\cos\vartheta}{\{(14B_1^S + 9B_3^S)^2 \sin^4\vartheta + 196(2B_1^S - 3B_3^S)^2 \cos^2\vartheta\}^{1/2}}. \tag{47}$$

The handedness of the polarized portion is dependent on the magnitudes of B_1^S and B_3^S. For $2B_1^S > 3B_3^S$ it is preserved while for $2B_1^S < 3B_3^S$ we deal with reversed handedness in comparison with the incident helicity. For $\vartheta = 0$ and $2B_1^S \neq 3B_3^S$ this equation gives $^\pm\phi_s^S(0) = \pm\pi/4$ or $\mp\pi/4$, i.e. circular polarization. For $\vartheta = \pi/2$ we have linear polarization of this portion similarly as for unsymmetric scattering.

The circularity degree is as follows:

$$^\pm C^U(\vartheta) = \pm\frac{2\cos\vartheta}{5 - 3\cos^2\vartheta}, \tag{48}$$

whence $^\pm C^U(\pi/2) = 0$, whereas for forward scattering this reads: $^\pm C^U(0) = \pm1$.

In the symmetric case:

$$^\pm C^S(\vartheta) = \pm\frac{14(2B_1^S - 3B_3^S)\cos\vartheta}{14B_1^S + 39B_3^S + (14B_1^S + 9B_3^S)\cos^2\vartheta}, \tag{49}$$

whence $^\pm C^S(\pi/2) = 0$ while for forward observation we have:

$$^\pm C^S(0) = \pm\frac{14B_1^S - 21B_3^S}{14B_1^S + 24B_3^S}. \tag{50}$$

For molecules with $B_3^S = 0$ the scattered light is completely circularly polarized with retained handedness, since $^\pm C^S(0) = \pm1$. For all other molecules it will be partly circularly polarized.

Generally, this quantity ranges within:

$$-\tfrac{7}{8} \leqslant\, ^+C^S(0) \leqslant 1,$$
$$-1 \leqslant\, ^-C^S(0) \leqslant \tfrac{7}{8}, \tag{51}$$

where

$$-\tfrac{7}{8} \leqslant\, ^+C^S(0) < 0,$$
$$0 <\, ^-C^S(0) \leqslant \tfrac{7}{8} \tag{52}$$

signify reversed handedness of the polarized portion whereas

$$0 <\, ^+C^S(0) \leqslant 1,$$
$$-1 \leqslant\, ^-C^S(0) < 0 \tag{53}$$

signify retention of the handedness. $^\pm C^S(0) = 0$ means here unpolarized light.

The reversal ratio takes the form:

$$^{\pm}R^U(\vartheta) = \frac{5-2\cos\vartheta-3\cos^2\vartheta}{5+2\cos\vartheta-3\cos^2\vartheta}, \tag{54}$$

and $^{\pm}R^U(\pi/2) = 1$ while $^{\pm}R^U(0) = 0$.

In the symmetric case [5, 9]:

$$^{\pm}R^S(\vartheta) = \frac{14B_1^S+39B_3^S-14(2B_1^S-3B_3^S)\cos\vartheta+(14B_1^S+9B_3^S)\cos^2\vartheta}{14B_1^S+39B_3^S+14(2B_1^S-3B_3^S)\cos\vartheta+(14B_1^S+9B_3^S)\cos^2\vartheta}, \tag{55}$$

whence $^{\pm}R^S(\pi/2) = 1$ and

$$^{\pm}R^S(0) = \frac{45B_3^S}{28B_1^S+3B_3^S}. \tag{56}$$

$^{\pm}R^S(0)$ ranges within the limits [9–11]:

$$0 \leqslant {}^{\pm}R^S(0) \leqslant 15. \tag{57}$$

Finally, let us discuss the parameter $^{\pm}p^{-1}$ [19]. For forward scattering

$$^{\pm}p^{-1U}(0) = 1, \tag{58}$$

and

$$^{\pm}p^{-1S}(0) = \frac{28B_1^S+3B_3^S}{28B_1^S+48B_3^S}, \tag{59}$$

whence

$$\tfrac{1}{16} \leqslant {}^{\pm}p^{-1S}(0) \leqslant 1. \tag{60}$$

The results $^{\pm}p^{-1U}(0) = {}^{\pm}p^{-1S}(0) = 1$ obviously point to completely circularly polarized radiation with preserved incident helicity.

The ranges (57) for $^{\pm}R^S(0)$ and (60) for $^{\pm}p^{-1S}(0)$ can (like (52) and (53)) be divided into two subranges, corresponding to reversed and preserved handedness. The values at the points of division are, respectively, unity and one half. All the values $^{\pm}R^S(0) < 1$ and $^{\pm}p^{-1S}(0) > 1/2$ refer to preserved helicity, whereas $^{\pm}R^S(0) > 1$ and $^{\pm}p^{-1}(0) < 1/2$ to reversed helicity. Both cited values mean here unpolarized light, as already discussed.

In general, $^{\pm}S_3^S(\vartheta)$ and $^{\pm}S_3^U(\vartheta)$ are nonzero. Hence the depolarization ratio is not the ratio of two mutually perpendicular intensity components. For $\vartheta = \pi/2$ it simplifies since $^{\pm}S_3^U(\pi/2) = {}^{\pm}S_3^S(\pi/2) = 0$ and then becomes such a ratio of the two principal components.

Since $^{\pm}S_1^U(\pi/2) < 0$, from the definition (34) we get:

$$^{\pm}D^U\left(\frac{\pi}{2}\right) = \tfrac{1}{4}. \tag{61}$$

For symmetric scattering $^{\pm}S_1^S(\pi/2)$ is non-negative, hence from (33)

$$^{\pm}D^S\left(\frac{\pi}{2}\right) = \frac{15B_3^S}{14B_1^S+24B_3^S}, \tag{62}$$

and varies within [9]:

$$0 \leqslant {}^{\pm}D^{\mathrm{S}}\left(\frac{\pi}{2}\right) \leqslant \tfrac{5}{8}\,. \tag{63}$$

For forward observation, with respect to ${}^{\pm}S_1^{\mathrm{U}}(0) = 0$ and ${}^{\pm}S_0^{\mathrm{U}}(0) = \pm\,{}^{\pm}S_3^{\mathrm{U}}(0)$, we have by (18):

$$\pm D^{\mathrm{U}}(0) = 0, \tag{64}$$

as could be predicted (among others) from ${}^{\pm}C^{\mathrm{U}}(0) = 1$, whereas generally

$$\pm D_1^{\mathrm{S}}(0) = \frac{{}^{\pm}S_0^{\mathrm{S}}(0) - {}^{\pm}S_3^{\mathrm{S}}(0)}{{}^{\pm}S_0^{\mathrm{S}}(0) + {}^{\pm}S_3^{\mathrm{S}}(0)} \tag{65}$$

for positive ${}^{\pm}S_3^{\mathrm{S}}(0)$, and

$$\pm D_2^{\mathrm{S}}(0) = \frac{{}^{\pm}S_0^{\mathrm{S}}(0) + {}^{\pm}S_3^{\mathrm{S}}(0)}{{}^{\pm}S_0^{\mathrm{S}}(0) - {}^{\pm}S_3^{\mathrm{S}}(0)} \tag{66}$$

for negative ${}^{\pm}S_3^{\mathrm{S}}(0)$. The sign of ${}^{\pm}S_3^{\mathrm{S}}(0)$ depends on the helicity of the incident light and on the sign of $2B_1^{\mathrm{S}} - 3B_3^{\mathrm{S}}$. If we decide to introduce a single depolarization ratio, strictly speaking an anomalous depolarization ratio, irrespective of the sign of the difference of the two molecular invariants, then instead of (65) and (66) we get:

$$\pm D^{\mathrm{S}}(0) = \frac{{}^{\pm}S_0^{\mathrm{S}}(0) \mp {}^{\pm}S_3^{\mathrm{S}}(0)}{{}^{\pm}S_0^{\mathrm{S}}(0) \pm {}^{\pm}S_3^{\mathrm{S}}(0)}\,. \tag{67}$$

This depolarization ratio is simply equal to the reversal ratio (22) and ranges within $[0, 15]$, whereas ${}^{\pm}D_1^{\mathrm{S}}(0) \in [0, 1]$ and ${}^{\pm}D_2^{\mathrm{S}}(0) \in [1/15, 1]$.

Previously [9] we had introduced a depolarization parameter directly given as the ratio of the two mutually perpendicular intensity components: ${}^{\pm}\varrho(\vartheta) = I_{YY}/I_{XX}$. Obviously ${}^{\pm}D(\pi/2) = {}^{\pm}\varrho(\pi/2)$. However, in general, ${}^{\pm}\varrho(\vartheta)$ cannot play the role of depolarization in the full meaning of the word. For $\vartheta = 0$, ${}^{\pm}\varrho(0) = 1$ what could lead to the wrong interpretation that the scattered light were then unpolarized. As we bear in mind, for $\vartheta = 0$ the scattered light is partly circularly polarized. For such light ${}^{\pm}\varrho(0)$ also equals unity. An analyzer parallel or perpendicular to the observation plane will transmit the same intensities. But ${}^{\pm}\varrho(\vartheta)$ can still be a useful experimental parameter.

For symmetric scattering, with regard to equations (35), (56) and (2), one can derive simple relations between ${}^{\pm}D^{\mathrm{S}}(\pi/2)$, ${}^{\pm}R^{\mathrm{S}}(0)$ and ${}^{\perp}D^{\mathrm{S}}$[9]. Moreover, by (35), (50) and (59), the following relations hold:

$$\pm C^{\mathrm{S}}(0) = \pm\,\frac{1 - 5\,{}^{\perp}D^{\mathrm{S}}}{4\,{}^{\perp}D^{\mathrm{S}}}\,, \tag{68}$$

$$\pm p^{-1\mathrm{S}}(0) = \frac{1 - {}^{\perp}D^{\mathrm{S}}}{8\,{}^{\perp}D^{\mathrm{S}}}\,. \tag{69}$$

If the symmetric and unsymmetric scatterings are present together, in particular for perpendicular observation one finds from (45), (7), (9) and (11):

$$^{\pm}S_0\left(\frac{\pi}{2}\right) - {}^{\pm}S_1\left(\frac{\pi}{2}\right) = 2Ls_0^2(5B_3^S + 14B_2^U),$$

$$^{\pm}S_0\left(\frac{\pi}{2}\right) + {}^{\pm}S_1\left(\frac{\pi}{2}\right) = \tfrac{1}{3}Ls_0^2(28B_1^S + 48B_3^S + 35B_1^U + 21B_2^U - 42B_1^{SU}). \tag{70}$$

The part of the component X related to the irreducible tensor of weight 1 equals:

$$^{\pm}S_0\left(\frac{\pi}{2}\right) + {}^{\pm}S_1\left(\frac{\pi}{2}\right) = \tfrac{7}{3}Ls_0^2(4B_1^S + 5B_1^U - 6B_1^{SU})$$

$$= \tfrac{21}{20}Ls_0^2(4b_{\alpha\beta\beta}^S - 5b_{\alpha\beta\beta}^U)(4b_{\alpha\gamma\gamma}^{S*} - 5b_{\alpha\gamma}^{U*}). \tag{71}$$

The destructive influence of B_1^{SU} occurs now for $B_1^{SU} > 0$, i.e. when for scattering of linearly polarized light B_1^{SU} acts constructively, and reaches a maximum for $4b_{\alpha\beta\beta}^S = 5b_{\alpha\beta\beta}^U$. The whole component X would then vanish if simultaneously B_3^S and B_2^U were zero. But the latter would imply vanishing of the intensity component Y, i.e. a lack of perpendicular scattering of circularly polarized light. It is an open question whether these conditions are realistic.

The resultant azimuth is as previously determined by the greater of the components (70). Introducing consequently one total depolarization ratio independently of the resultant azimuth, for instance according to the definition (33), we obtain:

$$^{\pm}D\left(\frac{\pi}{2}\right) = \frac{30B_3^S + 84B_2^U}{28B_1^S + 48B_3^S + 35B_1^U + 21B_2^U - 42B_1^{SU}}, \tag{72}$$

whence

$$0 \leqslant {}^{\pm}D\left(\frac{\pi}{2}\right) \leqslant 4 \tag{73}$$

in agreement with [4]. The upper limit corresponds to pure unsymmetric scattering and is the inverse of the value (61).

For forward total scattering we have:

$$^{\pm}S_0(0) \mp {}^{\pm}S_3(0) = 30Ls_0^2B_3^S,$$

$$^{\pm}S_0(0) \pm {}^{\pm}S_3(0) = \tfrac{2}{3}Ls_0^2(28B_1^S + 3B_3^S + 35B_1^U + 21B_2^U - 42B_1^{SU}). \tag{74}$$

The contribution from the irreducible tensor of weight 1 contained in the second of the components (74) is twice as great as for perpendicular scattering (71). Since it is multiplied by a numerical factor only, the same conditions for constructive and destructive influence hold. The first of the intensity components (74) remains purely symmetric.

From (74) we get directly:

$$^{\pm}R(0) = \frac{45B_3^S}{28B_1^S + 3B_3^S + 35B_1^U + 21B_2^U - 42B_1^{SU}}. \tag{75}$$

The forms of $^{\pm}C(0)$ and $^{\pm}p^{-1}(0)$ can easily be obtained from (75) on insertion thereof into the relations (24) and (25). All these three quantities range within the same limits as their purely symmetric counterparts.

5.3. Natural incident light

For the completeness of our discussion, let us mention scattering of natural light. In the early days of three-photon light scattering, the description of nonlinear scattering of natural light was, as it were, borrowed bodily from linear scattering processes. Thus, natural light was treated as a superposition of two modes with perpendicular polarizations and equal constant amplitudes albeit with phases fluctuating independently, which led to Strizhevsky and Klimenko's result [20], or was dealt with as one wave with constant amplitude but with fluctuating polarization direction [7-9, 21, 22]. Already Strizhevsky [23] proved this approach to be inadequate for the correct description of nonlinear scattering of natural light, and the matter was later discussed in Refs [5, 12, 24, 25].

There are three possible ways to define natural light. From the viewpoint of mathematics the simplest way is to define natural light as a superposition of two orthogonal linearly polarized waves with independently fluctuating Gaussian amplitudes of equal mean intensities. A somewhat more complicated way leading to the same final result is to describe natural light as a superposition of two contrary-handed, either circularly or elliptically polarized waves with azimuth differing by $\pi/2$ and equal mean independently fluctuating intensities. Thus we have to perform an appropriate statistical averaging in (26) over the complex amplitudes of the incident light, which as already stated — are time-dependent for quasi-monochromatic light. Considering integral scattering, the calculation of the Stokes parameters (26) involves the use of appropriate second-order correlation functions of the incident amplitudes for zero delay time $\tau = 0$.

On all three definitions:

$$\langle s_0^2 \rangle = 3\langle s_1^2 \rangle = 3\langle s_2^2 \rangle = 3\langle s_3^2 \rangle = \tfrac{3}{2}\langle s_0 \rangle^2,$$

$$\langle s_0 s_1 \rangle = \langle s_0 s_2 \rangle = \langle s_0 s_3 \rangle = \langle s_1 s_3 \rangle = \langle s_2 s_3 \rangle = 0. \tag{76}$$

On insertion of (76) into (26) we arrive at:

$$^{N}S_0(\vartheta) = \tfrac{1}{4} L\langle s_0 \rangle^2 \{12\alpha + 8\beta + (3\gamma + 3\delta + 4\,\mathrm{Re}\,\varepsilon)(1 + \cos^2 \vartheta)\},$$

$$^{N}S_1(\vartheta) = \tfrac{1}{4} L\langle s_0 \rangle^2 (3\gamma + 3\delta + 4\,\mathrm{Re}\,\varepsilon) \sin^2 \vartheta, \tag{77}$$

which with regard to (7) and (9) decompose into:

$$^{N}S_0^S(\vartheta) = \tfrac{1}{6} L\langle s_0 \rangle^2 \{98B_1^S + 93B_3^S + 5(14B_1^S + 3B_3^S) \cos^2 \vartheta\}, \tag{78}$$

$$^{N}S_1^S(\vartheta) = \tfrac{5}{6} L\langle s_0\rangle^2 (14B_1^S + 3B_3^S)\sin^2\vartheta,$$

$$^{N}S_0^U(\vartheta) = \tfrac{7}{4} L\langle s_0\rangle^2 B_2^U(11 - 5\cos^2\vartheta),$$

$$^{N}S_1^U(\vartheta) = -\tfrac{35}{4} L\langle s_0\rangle^2 B_2^U \sin^2\vartheta. \tag{79}$$

Light scattered forwards remains unpolarized in both (symmetric and unsymmetric) cases.

Generally, the azimuths of both scatterings again differ by $\pi/2$. Hence, from (33) and (34) we have, respectively:

$$^{N}D^S(\vartheta) = \frac{14B_1^S + 39B_3^S + 5(14B_1^S + 3B_3^S)\cos^2\vartheta}{84B_1^S + 54B_3^S}, \tag{80}$$

$$^{N}D^U(\vartheta) = \frac{3}{8 - 5\cos^2\vartheta}, \tag{81}$$

whence $^{N}D^S(0) = {}^{N}D^U(0) = 1$ and

$$^{N}D^U\left(\frac{\pi}{2}\right) = \tfrac{3}{8}, \tag{82}$$

$$^{N}D^S\left(\frac{\pi}{2}\right) = \frac{14B_1^S + 39B_3^S}{84B_1^S + 54B_3^S}, \tag{83}$$

which varies within:

$$\tfrac{1}{6} \leqslant {}^{N}D^S\left(\frac{\pi}{2}\right) \leqslant \tfrac{13}{18} \tag{84}$$

in full accordance with [4] and [25] but differs as to the upper limit from [23].

From equations (35), (62) and (83) one finds:

$$^{N}D^S\left(\frac{\pi}{2}\right) = \frac{21^{\perp}D^S - 1}{18^{\perp}D^S + 6}, \tag{85}$$

$$^{N}D^S\left(\frac{\pi}{2}\right) = \frac{1 + {}^{\pm}D^S\left(\dfrac{\pi}{2}\right)}{6\left[1 - {}^{\pm}D^S\left(\dfrac{\pi}{2}\right)\right]}, \tag{86}$$

which differ from the relations for ordinary Rayleigh and Raman processes.

When both symmetric and unsymmetric scatterings take place together, in particular for perpendicular observation, one gets:

$$^{N}S_0\left(\frac{\pi}{2}\right) - {}^{N}S_1\left(\frac{\pi}{2}\right) = \tfrac{1}{3} L\langle s_0\rangle^2 (14B_1^S + 39B_3^S + 70B_1^U + 84B_2^U + 42B_1^{SU}),$$

$$^{N}S_0\left(\frac{\pi}{2}\right) + {}^{N}S_1\left(\frac{\pi}{2}\right) = \tfrac{1}{2} L\langle s_0\rangle^2 (56B_1^S + 36B_3^S + 35B_1^U + 21B_2^U). \tag{87}$$

Again, only one principal intensity component reveals dependence on the cross term B_1^{SU}. The whole part of scattering connected with the irreducible tensor of weight 1 is identical with (40) and the maximum of destructive influence of B_1^{SU} occurs, as previously, for $2b_{\alpha\beta\beta}^S = -5b_{\alpha\beta\beta}^U$. Similarly, the whole component Y can be fully extinguished if simultaneously $B_3^S = B_2^U = 0$. The scattered light would then be linearly polarized in the direction X and would arise from the B_1^S contribution only.

The anomalous depolarization ratio calculated from the definition (33)

$$^N D\left(\frac{\pi}{2}\right) = \frac{28B_1^S + 78B_3^S + 140B_1^U + 168B_2^U + 84B_1^{SU}}{168B_1^S + 108B_3^S + 105B_1^U + 63B_2^U} \tag{88}$$

can range within the limits:

$$0 \leqslant {}^N D\left(\frac{\pi}{2}\right) \leqslant \tfrac{8}{3}, \tag{89}$$

where the upper limit corresponds to pure unsymmetric scattering and is the inverse of the value (82).

5.4. Linearly polarized chaotic incident light

Let us now assume that the initially natural incident light before reaching the medium is linearly polarized along the x-axis. In other words, we consider Gaussian linearly polarized light. Usually, Gaussian light is referred to as chaotic. Then, averaging over the amplitude E gives:

$$\langle s_0^2 \rangle = \langle s_1^2 \rangle = \langle s_0 s_1 \rangle = 2\langle s_0 \rangle^2. \tag{90}$$

Insertion of (90) into (26) leads to:

$$^{\perp}S_0 = 2L\langle s_0 \rangle^2 (2\alpha + 2\beta + \gamma + \delta + 2\,\mathrm{Re}\,\varepsilon),$$

$$^{\perp}S_1 = 2L\langle s_0 \rangle^2 (\gamma + \delta + 2\,\mathrm{Re}\,\varepsilon). \tag{91}$$

Simple inspection of (91) and (30) shows, at equality of the incident chaotic $\langle s_0 \rangle$ and coherent s_0 intensities, that the parameters just calculated are twice greater. The rates of nonlinear processes depend on higher-order coherence degrees of the incident light; the scatterings in question depend on the second-order coherence degree $g^{(2)} = \langle s_0^2 \rangle / \langle s_0 \rangle^2$. This quantity, for polarized chaotic light, is twice greater than for coherent light. Hence, polarized chaotic light is here scattered twice as effectively as coherent light. This was already shown by Shen [26] and first confirmed for second-harmonic generation [27]. The same conclusion has been derived, among others, in [25] for hyper-Raman scattering. Altmann and Strey [25] considered chaotic polarized light as a superposition of an infinite number of identical polarized modes with statistically independent amplitudes. Indeed, the resultant modulated amplitude is then Gaussian [28]. The relations (91) are valid for single-mode filtered polarized chaotic light as well as for multi-mode polarized chaotic light. There is no difference, since for both kinds of light $g^{(2)}(\tau = 0) = 2$.

In studies of the time evolution of three-photon scattered intensity or, equivalently, of spectral broadening one should expect in general different results for single-mode and multi-mode chaotic light depending on the time scale of the molecular relaxations. This is directly related to the time dependence of the second-order coherence degree in the multi-mode case which decays from two for zero delay time to unity for delay times considerably exceeding the coherence time of such light.

If the number of statistically independent molecules is sufficiently great and if the incident light is coherent, the linearly or nonlinearly scattered light will be Gaussian [29, 30]. When the incident light is Gaussian the nonlinearly scattered light does not remain Gaussian. The intensity fluctuations in the scattered light are enhanced; this is reflected by a value of the second-order coherence degree greater than two. In the processes in question this quantity may reach a value of twelve. In the case of second-harmonic generation, which is a coherent process, it can amount to six. Such light is often called superchaotic. The terms: natural light and unpolarized light mean the same in linear optics and are used interchangeably. Unpolarized superchaotic light can no longer be called natural light with respect to its statistics, different from the Gaussian statistics of the latter.

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