SYMMETRIC AND ANTISYMMETRIC SECOND-HARMONIC ELASTIC LIGHT SCATTERING AND ITS ANGULAR DEPENDENCES

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By a semi-macroscopic method, general expressions are derived for the symmetric and antisymmetric parts of the intensity tensor of second-harmonic elastic light scattering by statistically inhomogeneous media. In the relevant expressions, a separation is achieved, on the one hand, of the factors accounting for the state of polarisation (linear, circular, elliptical) of the incident light wave and the experimental configuration of scattered light observation and, on the other, of those factors which describe the molecular-statistical properties of the scattering medium. Formulas are derived for the depolarisation ratio and reversal ratio of second-harmonic scattering, and their angular dependences and mutual relationships are discussed. The theory is particularized for media consisting of molecules without a centre of symmetry where, in regions of short-range order, angular correlations, spatial redistribution of molecules and fluctuations of the electric fields of molecular multipoles intervene. The theoretical results are compared with recent measurements of second-harmonic scattering in molecular liquids.

1. Introduction

Second-harmonic (or hyper-Rayleigh) light scattering (SHLS) denotes a process wherein two photons with the same frequency are incident upon a non-centrosymmetric molecule, or assemblage of molecules, which then scatters elastically a third photon, of doubled frequency 2ω. The theory of this novel nonlinear scattering process was first formulated by Kielich [1] for molecular gases and then extended to dense media by Bersohn *et al.* [2], Kielich [3, 4] and Strizhevsky and Klimenko [5].

The earliest experimental observations of nonlinear light scattering were performed by Terhune *et al.* [6] by laser technique in liquids composed of molecules without a centre of symmetry. Weinberg [7] and Maker [8] studied respectively the temperature-dependence of second-harmonic scattering in liquids and the spectral broadening of SHLS.

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Lalanne *et al.* [9] studied co-operative SHLS by regions of short-range order of centro-symmetric non-centrally distributed molecules. Second-harmonic scattering by angular fluctuations near the critical point was observed by Freund [10]. Of late, Dolino *et al.* [11] investigated second-harmonic scattering of laser light by domains in ferroelectric crystals.

Elastic SHLS is a particular case of inelastic SHLS (hyper-Raman scattering), where molecular own-frequencies ω_m superimpose themselves on the doubled frequency 2ω leading to inelastic scattering at frequencies $2\omega \pm \omega_m$. The quantum-mechanical theory of inelastic three-photon scattering was developed independently by Li [12] and by Kielich [1, 13]. Cyvin *et al.* [14] determined the vibrational selection rules for hyper--Raman scattering and showed that lines inactive in infra-red and usual Raman can become active in hyper-Raman; this was confirmed by the spectral work of Verdieck *et al.* [15] on gases with centrosymmetric and non-centrosymmetric molecules. Long and Stanton [16], in the density matrix treatment, have given a discussion of the conditions for hyper--Raman intensity amplification by resonance processes.

Maker [17] suggested the feasibility of observing fine structure in three-photon scattering due to rotational motions of spherical top molecules [18], and performed spectral observations in methane, pressurized to 100 atmospheres. The study of hyper--Rayleigh rotational fine structure has recently been extended by Bancewicz *et al.* [19] to the case of symmetric top molecules (of symmetry C_{3v}) nad linear molecules (symmetry $C_{\infty v}$), and by Ożgo and Kielich [20] to other molecules not having a centre of symmetry.

The preceding brief review shows that the investigation of hyper-Rayleigh and hyper--Raman scattering has developed into a new nonlinear molecular spectroscopy, which has by now become a powerful method of investigating the finer details of the structure of molecules [21, 22] as well as the statistical inhomogeneities of scattering media [23–25] and their correlations with the statistics of photons [26]. Obviously, it is also worth while to study scattering processes involving more than three photons, especially in media consisting of atoms [24, 27].

Existing hyper-Rayleigh and hyper-Raman intensity calculations take into account only totally symmetric scattering. This is correct only with respect to gaseous media in the absence of electronic dispersion and absorption. In the general case, asymmetric and antisymmetric scattering, due essentially to the lack of total symmetricity of the hyperpolarizability tensors, have also to be considered. In the absence of molecular corre-lations, asymmetricity of the hyperpolarizability tensors is a result of their dependence on the light vibration frequency [1, 28] and can moreover be due to the properties of the molecules, if the latter are optically active [29]. In dense media, as we shall show in the course of the present considerations, asymmetricity of hyperpolarizability tensors stems from statistical inhomogeneities of scattering regions (*e.g.* molecular redistribution, effects of molecular fields).

Asymmetric nonlinear light scattering is moreover obtained on taking into account, besides frequency dispersion, also spatial dispersion as well as electric and magnetic multipolar scattering processes [30]. The symmetricity or asymmetricity of the tensor of scattered light intensity [13] depends, too, on the state of polarisation of the incident light wave. Thus, circularly or elliptically polarized light always leads to antisymmetric

light scattering [31, 32]. In the description of the state of polarisation of scattering processes use can be made of Stokes parameters [33], as was done recently by Stanton [34] for hyper-Raman and by Long [35] for stimulated Raman scattering.

In the present paper, we shall calculate the SHLS intensity tensor with regard to both its symmetric and antisymmetric part. We deal with the tensor of second-order nonlinear polarizability as, in general, non-symmetric. We shall discuss the effect, on the scattering tensor, of the state of polarisation of the incident light wave (which can be unpolarized, or polarized linearly, circularly and elliptically) as well as of the experimental configuration at which the scattered light is observed. We shall moreover give with regard to SHLS an analysis of the rôle of molecular angular correlations, molecular redistribution, and fluctuations of molecular fields.

2. The tensor of hyper-Rayleigh scattered intensity

The intensity of light (incident as well as scattered) is described by a tensor of rank 2 resulting from Poynting's vector [33]:

$$I_{ij} = \frac{cn}{8\pi} \langle E_i E_j^* \rangle, \tag{1}$$

where E_i is an electric field component of the electromagnetic wave, of propagation velocity c and refractive index n. The symbol $\langle \ \rangle$ stands for appropriate time-averaging or statistical averaging. The tensor I_{ij} is by definition Hermitian, $I_{ij} = I_{ji}^*$.

We introduce the following symmetric and antisymmetric intensity tensors:

$$I_{ij}^S = I_{(ij)} = \tfrac{1}{2}(I_{ij} + I_{ji}), \tag{2}$$

$$I_{ij}^A = I_{[ij]} = \tfrac{1}{2}(I_{ij} - I_{ji}), \tag{3}$$

where indices ij in round brackets, (ij), denote total symmetricity whereas indices ij in square brackets, $[ij]$, denote antisymmetricity.

We are concerned with hyper-Rayleigh scattering, at the doubled frequency 2ω, for which the intensity tensor in the electric dipole approximation is of the following form [13, 36]:

$$I_{ij}^{2\omega} = L^{2\omega} \langle B_{ikm}^{2\omega}(B_{jln}^{2\omega})^* \rangle E_k E_l^* E_m E_n^*, \tag{4}$$

where, for brevity, we have used the notation:

$$L^{2\omega} = \frac{cn_{2\omega}}{128} \left(\frac{2\omega}{c}\right)^4 \left(\frac{n_{2\omega}^2 + 2}{3}\right)^2 \left(\frac{n_\omega^2 + 2}{3}\right)^4 \tag{5}$$

with refractive indices n_ω and $n_{2\omega}$ at the frequencies ω and 2ω, respectively.

The tensor $B_{ijk}^{2\omega} = B_{ijk}(-2\omega, \omega, \omega)$ of rank 3 denotes at 2ω the second-order nonlinear polarizability (i.e. the hyperpolarizability) of the scattering sample [4, 36]. The

tensor B_{ijk} is not, in general, symmetric, and can be represented in the form [25]:

$$B_{ijk} = B_{(ijk)} + B_{[ijk]} + \tfrac{2}{3}(B_{[ij]k} + B_{[kj]i}) + \tfrac{2}{3}(B_{(ij)k} - B_{k(ij)}), \qquad (6)$$

where the totally symmetric and antisymmetric parts are, respectively:

$$B_{(ijk)} = \tfrac{1}{6}(B_{ijk} + B_{jki} + B_{kij} + B_{jik} + B_{ikj} + B_{kji}),$$

$$B_{[ijk]} = \tfrac{1}{6}(B_{ijk} + B_{jki} + B_{kij} - B_{jik} - B_{ikj} - B_{kji}),$$

and the partially symmetric and antisymmetric parts are:

$$B_{(ij)k} = \tfrac{1}{2}(B_{ijk} + B_{jik}), \qquad B_{[ij]k} = \tfrac{1}{2}(B_{ijk} - B_{jik}).$$

The tensor (6) can equivalently be written as follows [28]:

$$B_{ijk} = B_{ijk}^{S} + B_{ijk}^{NS}, \qquad (6a)$$

where the symmetric and antisymmetric tensors are:

$$B_{ijk}^{S} = \tfrac{1}{3}(B_{ijk} + B_{jki} + B_{kij}),$$

$$B_{ijk}^{NS} = \tfrac{1}{3}(2B_{ijk} - B_{jki} - B_{kij}).$$

In the tensor (6), the symmetric part consists of cyclical as well as anticyclical permutations of the indices i, j, k, whereas in the tensor (6a) only cyclical permutations occur.

When dealing with an isotropic medium, an averaging has to be performed in the right hand term of Eq. (4) over all possible orientations of the electric fields with respect to the axes of laboratory co-ordinates. To this aim, we carry out a transformation of the tensor B_{ijk} from laboratory co-ordinates (Latin indices $i, j, k, l, \ldots$) to a system of co-ordinates $B_{\alpha\beta\gamma}$ (Greek indices $\alpha, \beta, \gamma, \ldots$) rigidly attached to the scattering element:

$$B_{ijk} = c_{i\alpha} c_{j\beta} c_{k\gamma} B_{\alpha\beta\gamma}, \qquad (7)$$

where the transformation coefficients $c_{i\alpha}$, in the case of Cartesian co-ordinate systems, have the meaning of cosines of the angles between the axes $i, \ldots$ and the axes $\alpha, \ldots$ of the two sets of co-ordinates.

In a first approximation, we can operate a separation of the unweighted averaging with respect to external variables (*i.e.* the $c_{i\alpha}$) and the statistical averaging with respect to internal variables (the molecular configuration of the scattering region). Consequently, by (4) and (7), we write:

$$I_{ij}^{2\omega} = L^{2\omega} \langle c_{i\alpha} c_{j\beta} c_{k\gamma} c_{l\delta} c_{m\varepsilon} c_{n\eta} \rangle_{\Omega} \langle B_{\alpha\gamma\varepsilon}^{2\omega} (B_{\beta\delta\eta}^{2\omega})^{*} \rangle E_k E_l^{*} E_m E_n^{*}. \qquad (8)$$

The unweighted averaging of the products of directional cosines over all possible orientations Ω has been performed in invariant form by Kielich [25, 37]:

$$\langle c_{i\alpha} c_{j\beta} c_{k\gamma} c_{l\delta} c_{m\varepsilon} c_{n\eta} \rangle_{\Omega} = \tfrac{1}{210} \sum_{s=1}^{15} X_{\alpha\beta\gamma\delta\varepsilon\eta}^{(s)} \delta_{ij} \delta_{kl} \delta_{mn}, \qquad (9)$$

where in the right hand term we have 15 components, resulting from the permutation

of the 6 indices $i, j, ..., n$; the tensors $X^{(s)}_{\alpha\beta\gamma\delta\epsilon\eta}$ are expressed in terms of appropriate combinations of products $\delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\epsilon\eta}$, with $\delta_{ij}, \delta_{\alpha\beta}, ...$ denoting Kronecker unit tensors.

From (9) and on resorting to Eqs (2), (3) and (8), we obtain the following expressions for the intensity tensors of symmetric and antisymmetric second-harmonic scattering:

$$I^{2\omega}_{(ij)} = L^{2\omega}\{\delta_{ij}(A^{2\omega}_1 E_k E^*_k E_l E^*_l + A^{2\omega}_2 E_k E^*_l E_k E^*_l) +$$

$$+ A^{2\omega}_3 (E_i E^*_j + E_j E^*_i)E_k E^*_k + A^{2\omega}_4 (E_i E^*_k E_j E^*_k + E_k E^*_i E_k E^*_j)\}, \tag{10}$$

$$I^{2\omega}_{[ij]} = L^{2\omega}A^{2\omega}_5 (E_i E^*_j - E_j E^*_i)E_k E^*_k. \tag{11}$$

Above, we have introduced the following quantities characterizing the molecular-statistical properties of the scattering medium:

$$A^{2\omega}_1 = \tfrac{1}{210} \langle B^{2\omega}_{\alpha\gamma\epsilon}(B^{2\omega}_{\beta\delta\eta})^* \rangle \{7\delta_{\alpha\beta}(\delta_{\gamma\delta}\delta_{\epsilon\eta} + \delta_{\eta\eta}\delta_{\delta\epsilon} - 2\delta_{\gamma\epsilon}\delta_{\delta\eta}) +$$

$$+ 4Y_{\alpha\beta\gamma\delta\epsilon\eta} - 3Z_{\alpha\beta\gamma\delta\epsilon\eta}\},$$

$$A^{2\omega}_2 = \tfrac{1}{210} \langle B^{2\omega}_{\alpha\gamma\epsilon}(B^{2\omega}_{\beta\delta\eta})^* \rangle \{21\delta_{\alpha\beta}\delta_{\gamma\epsilon}\delta_{\delta\eta} - 5Y_{\alpha\beta\gamma\delta\epsilon\eta} + 2Z_{\alpha\beta\gamma\delta\epsilon\eta}\},$$

$$A^{2\omega}_3 = \tfrac{1}{420} \langle B^{2\omega}_{\alpha\gamma\epsilon}(B^{2\omega}_{\beta\delta\eta})^* \rangle \{28\delta_{\alpha\beta}\delta_{\gamma\epsilon}\delta_{\delta\eta} - 12Y_{\alpha\beta\gamma\delta\epsilon\eta} + 9Z_{\alpha\beta\gamma\delta\epsilon\eta}\},$$

$$A^{2\omega}_4 = \tfrac{1}{210} \langle B^{2\omega}_{\alpha\gamma\epsilon}(B^{2\omega}_{\beta\delta\eta})^* \rangle \{7\delta_{\delta\eta}(\delta_{\alpha\gamma}\delta_{\beta\epsilon} + \delta_{\alpha\epsilon}\delta_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\epsilon}) + 4Y_{\alpha\beta\gamma\delta\epsilon\eta} - 3Z_{\alpha\beta\gamma\delta\epsilon\eta}\},$$

$$A^{2\omega}_5 = \tfrac{1}{60} \langle B^{2\omega}_{\alpha\gamma\eta}(B^{2\omega}_{\beta\delta\eta})^* \rangle \{\delta_{\gamma\delta}(\delta_{\alpha\epsilon}\delta_{\beta\eta} - \delta_{\alpha\eta}\delta_{\beta\epsilon}) + \delta_{\epsilon\eta}(\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}) +$$

$$+ \delta_{\delta\epsilon}(\delta_{\alpha\gamma}\delta_{\beta\eta} - \delta_{\alpha\eta}\delta_{\beta\gamma}) + \delta_{\gamma\eta}(\delta_{\alpha\epsilon}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\epsilon})\}, \tag{12}$$

using, for brevity, the following notations:

$$Y_{\alpha\beta\gamma\delta\epsilon\eta} = \delta_{\alpha\beta}(\delta_{\gamma\delta}\delta_{\epsilon\eta} + \delta_{\gamma\epsilon}\delta_{\delta\eta} + \delta_{\gamma\eta}\delta_{\delta\epsilon}) + \delta_{\delta\eta}(\delta_{\alpha\gamma}\delta_{\beta\epsilon} + \delta_{\alpha\epsilon}\delta_{\beta\gamma}) + \delta_{\gamma\epsilon}(\delta_{\alpha\delta}\delta_{\beta\eta} + \delta_{\alpha\eta}\delta_{\beta\delta}),$$

$$Z_{\alpha\beta\gamma\delta\epsilon\eta} = \delta_{\gamma\delta}(\delta_{\alpha\epsilon}\delta_{\beta\eta} + \delta_{\alpha\eta}\delta_{\beta\epsilon}) + \delta_{\epsilon\eta}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) +$$

$$+ \delta_{\delta\epsilon}(\delta_{\alpha\gamma}\delta_{\beta\eta} + \delta_{\beta\gamma}\delta_{\alpha\eta}) + \delta_{\gamma\eta}(\delta_{\alpha\delta}\delta_{\beta\epsilon} + \delta_{\alpha\epsilon}\delta_{\beta\delta}).$$

The quantities (12) are of a quite general nature. On certain assumptions regarding the symmetricity of the hyperpolarizability tensor $B_{\alpha\beta\gamma}$, they undergo a considerable simplification. On assuming the decomposition of $B_{\alpha\beta\gamma}$ in the form (6), the following totally symmetric component can be extracted from the quantities (12):

$$_sA^{2\omega}_1 = \tfrac{2}{105} \Gamma^2_{2\omega},$$

$$2_sA^{2\omega}_2 = {}_sA^{2\omega}_4 = \tfrac{2}{525} (63B^2_{2\omega} - 2\Gamma^2_{2\omega}),$$

$$_sA^{2\omega}_3 = \tfrac{2}{175} (21B^2_{2\omega} + \Gamma^2_{2\omega}),$$

$$_sA^{2\omega}_5 = \tfrac{2}{75} (9B^2_{2\omega} - \Gamma^2_{2\omega}), \tag{13}$$

where we have introduced the following nonlinear parameters of an isotropic, and respectively, anisotropic nature:

$$B^2_{2\omega} = \tfrac{1}{9} \langle B^{2\omega}_{(\alpha\beta\beta)}(B^{2\omega}_{(\alpha\gamma\gamma)})^* \rangle, \tag{14}$$

$$\Gamma^2_{2\omega} = \tfrac{1}{2} \langle 5B^{2\omega}_{(\alpha\beta\gamma)}(B^{2\omega}_{(\alpha\beta\gamma)})^* - 3B^{2\omega}_{(\alpha\beta\beta)}(B^{2\omega}_{(\alpha\gamma\gamma)})^* \rangle. \tag{15}$$

Keeping in mind that the totally antisymmetric tensor $B_{[\alpha\beta\gamma]}$ vanishes on contraction in any pair of indices and that $B_{[\alpha\beta\gamma]} = -B_{[\alpha\gamma\beta]}$, *etc.*, one is readily convinced that the purely antisymmetric part of the quantities (12) vanishes. There still remain the mixed symmetric-antisymmetric components, which in general differ from zero. If in particular we assume the tensor $B_{\alpha\beta\gamma}$ as symmetric in the pair of indices β, γ, the non-symmetric parts of the quantities (12) take the following form:

$$_{NS}A_3^{2\omega} = -\tfrac{3}{2}\,_{NS}A_1^{2\omega} = -\tfrac{1}{35}\,\langle 3B_{\alpha\beta\gamma}^{2\omega}(B_{\alpha\beta\gamma}^{2\omega}-B_{\beta\alpha\gamma}^{2\omega})^* + B_{\alpha\beta\beta}^{2\omega}(B_{\gamma\gamma\alpha}^{2\omega}-B_{\alpha\gamma\gamma}^{2\omega})^* +$$

$$+ 3(B_{\alpha\beta\beta}^{2\omega}-B_{\beta\beta\alpha}^{2\omega})\,(B_{\gamma\gamma\alpha}^{2\omega*})\rangle,$$

$$_{NS}A_4^{2\omega} = -\tfrac{3}{2}\,_{NS}A_2^{2\omega} = \tfrac{1}{35}\,\langle 2B_{\alpha\beta\gamma}^{2\omega}(B_{\alpha\beta\gamma}^{2\omega}-B_{\beta\alpha\gamma}^{2\omega})^* + 3B_{\alpha\beta\beta}^{2\omega}(B_{\gamma\gamma\alpha}^{2\omega}-B_{\alpha\gamma\gamma}^{2\omega})^* +$$

$$+ 2(B_{\alpha\beta\beta}^{2\omega}-B_{\beta\beta\alpha}^{2\omega})\,(B_{\gamma\gamma\alpha}^{2\omega*})\rangle,$$

$$_{NS}A_5^{2\omega} = \tfrac{1}{15}\,\langle B_{\alpha\beta\gamma}^{2\omega}(B_{\alpha\beta\gamma}^{2\omega}-B_{\beta\alpha\gamma}^{2\omega})^* - B_{\alpha\beta\beta}^{2\omega}(B_{\alpha\gamma\gamma}^{2\omega})^* + B_{\beta\beta\alpha}^{2\omega}(B_{\gamma\gamma\alpha}^{2\omega})^*\rangle. \tag{16}$$

3. The polarisational properties of SHLS

Let us assume a set-up in which the incident laser light propagates along the z-axis of laboratory co-ordinates xyz. The scattered light is observed in a distinct set of laboratory co-ordinates $x'y'z'$. As the plane of observation, we chose the $y'z'$-plane. Let the $y'z'$-plane coincide with the yz-plane, and let the z'-axis subtend the angle ϑ with the z-axis. Thus, ϑ is our scattering angle.

Generally, we can express the electric vector E of the incident beam as follows:

$$E = E_0(x\,\sin\,\psi + y\,\cos\,\psi\,e^{i\Delta}), \tag{17}$$

where ψ is the angle between E and the yz-plane, and Δ is the phase shift of the y-component of the field.

Less general, but more convenient in our further considerations, is the following form:

$$E = E_0(x\,\sin\,\psi \pm i\,y\,\cos\,\psi). \tag{17a}$$

The sign $\pm$ denotes that the y-component of the field is shifted in phase by $\Delta = \pm\pi/2$ with respect to the x-component. The last formula still covers all possible states of polarisation of the incident wave.

Linear polarisation is obtained if $\psi = 0$ (horizontal to the observation plane) or $\psi = \pi/2$ (vertical). At $\psi = \pi/4$ we have circular polarisation, right circular if the sign is $+$ and left circular if it is $-$ for an observer viewing in the direction opposite to propagation. At intermediate values of the angle ψ the incident light beam is elliptically polarized and the axes of the ellipse always coincide with x and y. At this polarisation description of the incident light, the principal axes of the scattered intensity tensor will in all cases have the same directions, thus permitting the univocal description of scattered light depolarisation.

The unit vector n defining the polarisation of scattered light in co-ordinates $x'y'z'$ can in general be written in a form similar to (17):

$$n = x' \sin \varphi + y' \cos \varphi \, e^{i\delta}. \tag{18}$$

φ is the angle between n and the $y'z'$-plane. δ is the phase shift of the y'-component of the electric field of scattered light.

On transformation of the basis vectors x', y' to co-ordinates x, y, z the expression (18) transforms to:

$$n = x \sin \varphi + (y \cos \varphi \cos \vartheta - z \cos \varphi \sin \vartheta) \, e^{i\delta}. \tag{19}$$

By definition, the scattered intensity component with polarisation given by (19) is:

$$I_{nn}^{2\omega} = I_{ij}^{2\omega} n_i^* n_j. \tag{20}$$

With regard to (20), on insertion of (17a) and (19) into Eqs (10) and (11) we get:

$$I_{(nn)}^{2\omega} = L^{2\omega} E_0^4 \{ A_1^{2\omega} + A_2^{2\omega} \cos^2 2\psi + 2A_3^{2\omega}(\cos^2 \psi \cos^2 \varphi \cos^2 \vartheta +$$

$$+ \sin^2 \psi \sin^2 \varphi) + 2A_4^{2\omega}(\cos^2 \psi \cos^2 \varphi \cos^2 \vartheta - \sin^2 \psi \sin^2 \varphi) \cos 2\psi \}, \tag{21}$$

$$^{\pm}I_{[nn]}^{2\omega} = \pm L^{2\omega} \, ^{\pm}E_0^4 A_5^{2\omega} \sin 2\psi \sin 2\varphi \cos \vartheta \sin \delta. \tag{22}$$

On inspection of (22) one readily notices that the antisymmetric intensity component vanishes in the scattering of linearly polarized as well as natural (unpolarized) light. Obviously, this results already from the more general form (11) of the antisymmetric tensor. In fact, in these cases the electric field amplitude can be represented as a real quantity.

In the processes of scattering of, respectively, right and left circularly and elliptically polarized incident light, the antisymmetric component is positive or negative, as the case may be. This is consistently indicated by the left upper signs $\pm$ at $^{\pm}I_{[nn]}^{2\omega}$ and $^{\pm}E_0$ in Eq. (22).

Furthermore, we see from (21) that the first term of the symmetric part is altogether independent of the state of polarisation of the incident and scattered light waves. The second term is dependent only on the state of polarisation of the incident wave. The remaining two terms are functions of the states of polarisation of the two waves. With regard to the fact that the value of the symmetric component does not depend on the choice of the phase sign in (17a), we have omitted the signs $\pm$ at E_0 and $I_{(nn)}^{2\omega}$.

When determining the depolarisation of scattered light, we are interested solely in the intensity components along the principal axes of the intensity tensor. At the above-stated laboratory geometry of the experimental configuration and polarisation description (17a) of the incident light, the relevant intensity components are those with vibrations of the electric vector parallel ($\varphi = 0$) and perpendicular ($\varphi = \pi/2$) to the plane of observation. We denote them respectively as $H^{2\omega}$ (horizontal component) and $V^{2\omega}$ (vertical component). Eq. (21) now yields:

$$H^{2\omega} = I_{(y'y')}^{2\omega} = L^{2\omega} E_0^4 \{ A_1^{2\omega} + A_2^{2\omega} \cos^2 2\psi + 2(A_3^{2\omega} + A_4^{2\omega} \cos 2\psi) \cos^2 \psi \cos^2 \vartheta \},$$

$$V^{2\omega} = I_{(x'x')}^{2\omega} = L^{2\omega} E_0^4 \{ A_1^{2\omega} + A_2^{2\omega} \cos^2 2\psi + 2(A_3^{2\omega} - A_4^{2\omega} \cos 2\psi) \sin^2 \psi \}. \tag{23}$$

The principal values of the antisymmetric tensor obviously vanish.

(*i*) We begin by an analysis of the scattering of incident linearly polarized light. Eq. (17a) shows that it can be horizontally ($\varphi = 0$) or vertically ($\varphi = \pi/2$) polarized with respect to the plane of observation. We shall denote this, respectively, by a lower index h or v.

Eqs (23) now lead to the following results:

$$H_h^{2\omega}(\vartheta) = L^{2\omega}E_0^4\{A_1^{2\omega}+A_2^{2\omega}+2(A_3^{2\omega}+A_4^{2\omega})\cos^2\vartheta\},$$

$$V_h^{2\omega} = H_v^{2\omega} = L^{2\omega}E_0^4\{A_1^{2\omega}+A_2^{2\omega}\},$$

$$V_v^{2\omega} = H_h^{2\omega}(0) = L^{2\omega}E_0^4\{A_1^{2\omega}+A_2^{2\omega}+2(A_3^{2\omega}+A_4^{2\omega})\}. \tag{24}$$

Here, Krishnan's relation originally established for classical linear scattering by small molecules:

$$H_v^{2\omega} = V_h^{2\omega} = H_h^{2\omega}(\pi/2) \tag{25}$$

is fulfilled.

The depolarisation of scattered light is, by definition:

$$D_v^{2\omega} = \frac{H_v^{2\omega}}{V_v^{2\omega}} = \frac{A_1^{2\omega}+A_2^{2\omega}}{A_1^{2\omega}+A_2^{2\omega}+2(A_3^{2\omega}+A_4^{2\omega})},$$

$$D_h^{2\omega}(\vartheta) = \frac{V_h^{2\omega}}{H_h^{2\omega}(\vartheta)} = \frac{A_1^{2\omega}+A_2^{2\omega}}{A_1^{2\omega}+A_2^{2\omega}+2(A_3^{2\omega}+A_4^{2\omega})\cos^2\vartheta}, \tag{26}$$

leading to the following simple relation between the two depolarisation ratios:

$$D_h^{2\omega}(\vartheta) = \frac{D_v^{2\omega}}{D_v^{2\omega}+(1-D_v^{2\omega})\cos^2\vartheta} \tag{27}$$

which is fulfilled also for *n*-harmonic elastic scattering of arbitrary order [27].

In the case of natural incident light the scattered components $H_u^{2\omega}(\vartheta)$ and $V_u^{2\omega}$ can be derived directly from (25) by way of the formulas $H_u^{2\omega}(\vartheta) = H_h^{2\omega}(\vartheta)+H_v^{2\omega}$ and $V_u^{2\omega} = V_h^{2\omega}+V_v^{2\omega}$. However, we shall refrain from further considering this situation.

(*ii*) In dealing with the scattering of circularly polarized light, we have to put $\psi = \pi/4$ in Eqs (23). We then obtain:

$$H_c^{2\omega}(\vartheta) = L^{2\omega}E_0^4\{A_1^{2\omega}+A_3^{2\omega}\cos^2\vartheta\},$$

$$V_c^{2\omega} = H_c^{2\omega}(0) = L^{2\omega}E_0^4\{A_1^{2\omega}+A_3^{2\omega}\}, \tag{28}$$

where the lower index c denotes circularly polarized incident light.

The depolarisation of scattered light amounts to:

$$D_c^{2\omega}(\vartheta) = \frac{H_c^{2\omega}(\vartheta)}{V_c^{2\omega}} = \frac{A_1^{2\omega}+A_3^{2\omega}\cos^2\vartheta}{A_1^{2\omega}+A_3^{2\omega}}, \tag{29}$$

whence in particular we get $D_c^{2\omega}(0) = 1$ irrespective of the characteristics of the scattering medium.

For $\vartheta = \pi/2$, Eq. (29) yields:

$$D_c^{2\omega}(\pi/2) = \frac{A_1^{2\omega}}{A_1^{2\omega} + A_3^{2\omega}} \, . \tag{30}$$

In the case of circularly polarized incident light, it is of interest to represent the scattered light in the form of the sum of two incoherent waves circularly polarized in mutually inverse senses. In defining the ratio of their intensities, the "reversal ratio" [31] is conveniently resorted to. Presently, an essential rôle belongs to the sense of polarisation of the circular incident light. The reversal ratio is by definition the ratio of that part of the scattered intensity whose sense of circular polarisation is contrary to that of the incident wave and the part whose sense of circular polarisation coincides with the latter. We thus have, quite generally:

$$R^{2\omega}(\vartheta) = \frac{{}^{\pm}I_{nn}^{2\omega}\left(\delta = \mp \dfrac{\pi}{2}, \; \varphi = \dfrac{\pi}{4}\right)}{{}^{\pm}I_{nn}^{2\omega}\left(\delta = \pm \dfrac{\pi}{2}, \; \varphi = \dfrac{\pi}{4}\right)} \, , \tag{31}$$

where it should be kept in mind that, as previously, the upper left signs + and − refer to incident right and left circularly polarized light. Obviously, the choice of the sign of the phase affects the antisymmetric component only.

From Eqs (21) and (22), we obtain:

$$I_{(nn)}^{2\omega}\left(\delta = -\frac{\pi}{2}, \; \varphi = \frac{\pi}{4}\right) = I_{(nn)}^{2\omega}\left(\delta = \frac{\pi}{2}, \; \varphi = \frac{\pi}{4}\right) =$$

$$= 2^{-1}L^{2\omega}E_0^4\{2A_1^{2\omega} + A_3^{2\omega}(1+\cos^2\vartheta)\},$$

$${}^{\pm}I_{[nn]}^{2\omega}\left(\delta = \mp \frac{\pi}{2}, \; \varphi = \frac{\pi}{4}\right) = -\, {}^{\pm}I_{[nn]}^{2\omega}\left(\delta = \pm \frac{\pi}{2}, \; \varphi = \frac{\pi}{4}\right) =$$

$$= -\, L^{2\omega}\,{}^{\pm}E_0^4 A_5^{2\omega}\cos\vartheta. \tag{32}$$

Calculations resorting to Eqs (31) and (32) yield:

$$R^{2\omega}(\vartheta) = \frac{2A_1^{2\omega} + A_3^{2\omega} - 2A_5^{2\omega}\cos\vartheta + A_3^{2\omega}\cos^2\vartheta}{2A_1^{2\omega} + A_3^{2\omega} + 2A_5^{2\omega}\cos\vartheta + A_3^{2\omega}\cos^2\vartheta} \tag{33}$$

and, irrespective of the medium, $R^{2\omega}(\pi/2) = 1$.

For the scattering angle $\vartheta = 0$, we obtain from Eq. (33):

$$R^{2\omega}(0) = \frac{A_1^{2\omega} + A_3^{2\omega} - A_5^{2\omega}}{A_1^{2\omega} + A_3^{2\omega} + A_5^{2\omega}} \, . \tag{34}$$

Obviously, the expressions $H_c^{2\omega}(\vartheta) + V_c^{2\omega}$ (28) and $\pm I_{nn}^{2\omega}(\delta = \mp\pi/2, \varphi = \pi/4) + \pm I_{nn}^{2\omega}(\delta = \pm\pi/2, \varphi = \pi/4)$ (32) are equal to one another, as both represent the total intensity scattered in a given direction at the angle ϑ.

Further on it will be shown that when considering light scattering by rarefied media (gases and vapours) i. e. when scattering on fluctuations of the molecular fields of permanent and induced dipoles can be neglected, simple relationships hold between the depolarisation ratios $D_v^{2\omega}$, $D_c^{2\omega}(\vartheta)$ and the reversal ratio $R^{2\omega}(\vartheta)$. Without entering into the details at this moment, we wish to state that if the medium is transparent for the frequencies ω and 2ω and consists of optically inactive molecules the hyperpolarizability tensor $B_{\alpha\beta\gamma}^{2\omega}$ can be dealt with as symmetric with regard to permutation of all three indices and the scattering factors $A_1^{2\omega} - A_5^{2\omega}$ (13) have exclusively symmetric non-vanishing parts.

(*i*) Here, we shall restrict ourselves to the case of vertically polarized incident light. Eq. (24) now yields:

$$H_v^{2\omega} = \tfrac{1}{525} L^{2\omega} E_0^4 \{8\Gamma_{2\omega}^2 + 63 B_{2\omega}^2\},$$

$$V_v^{2\omega} = \tfrac{1}{175} L^{2\omega} E_0^4 \{4\Gamma_{2\omega}^2 + 189 B_{2\omega}^2\}. \tag{35}$$

The depolarisation ratio $D_v^{2\omega}$ of second-harmonic scattered light is, consequently, given by (26) and (35) in the following form:

$$D_v^{2\omega} = \frac{1}{3} \frac{8\Gamma_{2\omega}^2 + 63 B_{2\omega}^2}{4\Gamma_{2\omega}^2 + 189 B_{2\omega}^2}, \tag{36}$$

showing that the value of the depolarisation ratio is comprised within the interval $D_v^{2\omega} \in [1/9, 2/3]$ and takes the limiting values if one of the molecular factors, $\Gamma_{2\omega}^2$ or $B_{2\omega}^2$, vanishes.

(*ii*) For the scattering of circularly polarized light, we have by Eq. (28):

$$H_c^{2\omega}(\vartheta) = \tfrac{2}{525} L^{2\omega} E_0^4 \{5\Gamma_{2\omega}^2 + 3(\Gamma_{2\omega}^2 + 21 B_{2\omega}^2) \cos^2 \vartheta\},$$

$$V_c^{2\omega} = H_c^{2\omega}(0) = \tfrac{2}{525} L^{2\omega} E_0^4 \{8\Gamma_{2\omega}^2 + 63 B_{2\omega}^2\}, \tag{37}$$

and, by Eqs (36) and (35):

$$V_c^{2\omega} = H_c^{2\omega}(0) = 2H_v^{2\omega} = 2V_h^{2\omega} = 2H_h^{2\omega}\left(\frac{\pi}{2}\right), \tag{38}$$

at equal intensities of linearly polarized and circularly polarized light. The experimental values of $V_c^{2\omega}/H_v^{2\omega}$ of Terhune *et al.* [6] are assentially in accordance with this relation amounting to 2.5 ± 0.3 for water, 2.15 ± 0.15 for fused quartz, and 2.2 ± 0.3 for CH_3CN. Obviously some discrepancy is due to the fact that whereas Eq. (37) was derived for negligible scattering on fluctuations of molecular fields, the above cited values were measured in dense media.

With regard to (37), the depolarisation of scattered light defined by (29) becomes:

$$D_c^{2\omega}(\vartheta) = \frac{5\Gamma_{2\omega}^2 + 3(\Gamma_{2\omega}^2 + 21B_{2\omega}^2)\cos^2\vartheta}{8\Gamma_{2\omega}^2 + 63B_{2\omega}^2}, \tag{39}$$

whence $D_c^{2\omega}(\pi/2) \in [0, 5/8]$. Quite generally, $D_c^{2\omega}(\vartheta) \in [0,1]$.

By (36) and (39), the following relation between the depolarisation ratios is fulfilled for an arbitrary rarefied isotropic medium:

$$D_c^{2\omega}\left(\frac{\pi}{2}\right) = \frac{1}{12}\left\{3(3+\cos^2\vartheta) - \frac{\sin^2\vartheta}{D_v^{2\omega}}\right\}, \tag{40}$$

whence in particular we obtain:

$$D_c^{2\omega}\left(\frac{\pi}{2}\right) = \frac{1}{12D_v^{2\omega}}(9D_v^{2\omega}-1). \tag{41}$$

Now with regard to (13) the expression (33) defining the reversal ratio takes the following form:

$$R^{2\omega}(\vartheta) = \frac{(13+14\cos\vartheta+3\cos^2\vartheta)\Gamma_{2\omega}^2 + 63(1-\cos\vartheta)^2B_{2\omega}^2}{(13-14\cos\vartheta+3\cos^2\vartheta)\Gamma_{2\omega}^2 + 63(1+\cos\vartheta)^2B_{2\omega}^2} \tag{42}$$

whence for the scattering angle $\vartheta = 0$ we obtain:

$$R^{2\omega}(0) = \frac{15\Gamma_{2\omega}^2}{\Gamma_{2\omega}^2 + 126B_{2\omega}^2}, \tag{43}$$

a result derived by us previously [20, 38].

Eqs (36) and (42) lead to the following general relation between the reversal ratio $R^{2\omega}(\vartheta)$ and depolarisation ratio $D_v^{2\omega}$:

$$R^{2\omega}(\vartheta) = \frac{3(7+10\cos\vartheta+\cos^2\vartheta)D_v^{2\omega} - 1 - 6\cos\vartheta + \cos^2\vartheta}{3(7-10\cos\vartheta+\cos^2\vartheta)D_v^{2\omega} - 1 + 6\cos\vartheta + \cos^2\vartheta} \tag{44}$$

whence in particular:

$$R^{2\omega}(0) = \frac{9D_v^{2\omega}-1}{1-D_v^{2\omega}}. \tag{45}$$

Formulas (43) and (45) permit the conclusion that the values of the reversal ratio $R^{2\omega}(0)$ have to lie within the interval [0,15], according to the scattering medium.

Relations between the quantities $R^{2\omega}(\vartheta)$ and $D_c^{2\omega}(\vartheta)$ can be easily derived by calculation of $D_v^{2\omega}$ from (40) and insertion into (44). For example, Eqs (41) and (45) yield:

$$D_c^{2\omega}\left(\frac{\pi}{2}\right) = \frac{2}{3}\frac{R^{2\omega}(0)}{1+R^{2\omega}(0)}. \tag{46}$$

4. The molecular-statistical properties of SHLS

4.1. Scattering on fluctuations of molecular orientation

It was our assumption that the hyperpolarizability tensor of the medium $B_{\alpha\beta\gamma}^{2\omega}$ was, in a first approximation, totally symmetric. This assumption is justifiable provided $B_{\alpha\beta\gamma}^{2\omega}$ can be written in the form [36]:

$$B_{\alpha\beta\gamma}^{2\omega} = \sum_{p=1}^{N} b_{\alpha\beta\gamma}^{2\omega(p)} \exp{(i\Delta k \cdot r_p)}, \tag{47}$$

that is to say, as long as effects of the molecular fields are negligible and the process of second-harmonic scattering is determined by the tensor $b_{\alpha\beta\gamma}^{2\omega}$ of the isolated molecule. It is this tensor which, on previously made assumptions, can be dealt with as totally symmetric and real. Here, $\Delta k = k_{2\omega} - 2k_\omega$, where k_ω and $k_{2\omega}$ are respectively the wave vectors of incident and scattered light and r_p is the radius vector of the p-th scattering molecule. Eq. (47) yields:

$$\langle B_{\alpha\beta\gamma}^{2\omega}(B_{\alpha\beta\gamma}^{2\omega})^*\rangle = \langle \sum_{p=1}^{N} \sum_{q=1}^{N} b_{\alpha\beta\gamma}^{2\omega(p)} b_{\alpha\beta\gamma}^{2\omega(q)} \exp{(i\Delta k \cdot r_{pq})}\rangle,$$

$$\langle B_{\alpha\beta\beta}^{2\omega}(B_{\alpha\gamma\gamma}^{2\omega})^*\rangle = \langle \sum_{p=1}^{N} \sum_{q=1}^{N} b_{\alpha\beta\beta}^{2\omega(p)} b_{\alpha\gamma\gamma}^{2\omega(q)} \exp{(i\Delta k \cdot r_{pq})}\rangle. \tag{48}$$

Above, $|r_{pq}| = |r_p - r_q|$ is the distance between the p-th and q-th molecule. Now, on introducing the binary correlation function $g(\tau_p, \tau_q)$, where τ_p is a variable describing the position r_p and orientation ω_p of the p-th molecule, and keeping in mind that for liquids and gases this function depends on the mutual position of the molecules only, the expression (48) is transformed to:

$$\langle B_{\alpha\beta\gamma}^{2\omega}(B_{\alpha\beta\gamma}^{2\omega})^*\rangle = N b_{\alpha\beta\gamma}^{2\omega} b_{\alpha\beta\gamma}^{2\omega}(1 + J_A^{(1)}),$$

$$\langle B_{\alpha\beta\beta}^{2\omega}(B_{\alpha\gamma\gamma}^{2\omega})^*\rangle = N b_{\alpha\beta\beta}^{2\omega} b_{\alpha\gamma\gamma}^{2\omega}(1 + J_A^{(2)}), \tag{49}$$

where $J_A^{(1)}$ and $J_A^{(2)}$ are angular correlation parameters, describing coherent scattering on fluctuations of the orientations of correlated molecules [2]. They are of the form:

$$J_A^{(1)} = \frac{4\pi\varrho}{b_{\alpha\beta\gamma}^{2\omega} b_{\alpha\beta\gamma}^{2\omega}} \iint b_{\alpha\beta\gamma}^{2\omega(p)} b_{\alpha\beta\gamma}^{2\omega(q)} \frac{\sin{(\Delta k r_{pq})}}{\Delta k r_{pq}} g(r_{pq}, \omega_p, \omega_q) r_{pq}^2 dr_{pq} d\omega_p d\omega_q,$$

$$J_A^{(2)} = \frac{4\pi\varrho}{b_{\alpha\beta\beta}^{2\omega} b_{\alpha\gamma\gamma}^{2\omega}} \iint b_{\alpha\beta\beta}^{2\omega(p)} b_{\alpha\gamma\gamma}^{2\omega(q)} \frac{\sin{(\Delta k r_{pq})}}{\Delta k r_{pq}} g(r_{pq}, \omega_p, \omega_q) r_{pq}^2 dr_{pq} d\omega_p d\omega_q, \tag{50}$$

where ϱ is the number density of molecules.

According to the statistical molecular distribution of the medium, these parameters can be positive or negative. In other words, light scattering by fluctuations of orientation can either enhance or weaken the incoherent light scattering by fluctuations of the hyperpolarizability of individual molecules. At scattering of light of a wavelength λ by mole-

cules whose linear dimensions d fulfil the condition $d \leqslant \lambda/20$, the interference factor $\sin(\Delta k r_{pq})/\Delta k r_{pq}$ can be approximated by 1 and the parameters (50) reduce to a simpler form. In fact, the preceding inequality condition is the criterion of applicability of the theory of electric dipole scattering. If this is not the case, scattering by individual electric quadrupoles can no longer be left unconsidered [39].

At weak angular interaction, or if the molecules are of a shape so highly symmetric that all orientations are equally probable, the parameters (50) can be averaged isotropically over all molecular orientations and vanish.

We now proceed to apply our general expressions to a special case of molecular symmetry. We shall consider tetrahedral molecules of the symmetry T_d, like CCl_4, CH_4, or CF_4. The hyperpolarizability tensor $b_{\alpha\beta\gamma}^{2\omega}$ possesses non-zero tensor elements for $\alpha \neq \neq \beta \neq \gamma$ and is of the form [1,4]:

$$b_{\alpha\beta\gamma}^{2\omega(p)} = b_{123}^{2\omega}[i_\alpha^{(p)}(j_\beta^{(p)}k_\gamma^{(p)} + k_\beta^{(p)}j_\gamma^{(p)}) +$$
$$+ j_\alpha^{(p)}(i_\beta^{(p)}k_\gamma^{(p)} + k_\beta^{(p)}i_\gamma^{(p)}) + k_\alpha^{(p)}(i_\beta^{(p)}j_\gamma^{(p)} + j_\beta^{(p)}i_\gamma^{(p)})], \tag{51}$$

where i, j, k are versors of the axes 1, 2, 3 of molecular co-ordinates, rigidly attached to the molecule under consideration.

With regard to (49) and (51), Eqs (14) and (15) yield:

$$B_{2\omega}^2 = 0,$$
$$\Gamma_{2\omega}^2 = 15N(b_{123}^{2\omega})^2(1 + J_A^{(1)}). \tag{52}$$

The parameter $J_A^{(1)}$ is of the following, rather complicated form:

$$J_A^{(1)} = 4\pi\varrho \iint \{\cos\theta_{11}^{(pq)}\cos\theta_{22}^{(pq)}\cos\theta_{33}^{(pq)} + \cos\theta_{11}^{(pq)}\cos\theta_{23}^{(pq)}\cos\theta_{32}^{(pq)} +$$

$$+ \cos\theta_{22}^{(pq)}\cos\theta_{13}^{(pq)}\cos\theta_{31}^{(pq)} + \cos\theta_{33}^{(pq)}\cos\theta_{12}^{(pq)}\cos\theta_{21}^{(pq)} + \cos\theta_{12}^{(pq)}\cos\theta_{23}^{(pq)}\cos\theta_{31}^{(pq)} +$$

$$+ \cos\theta_{21}^{(pq)}\cos\theta_{32}^{(pq)}\cos\theta_{13}^{(pq)}\}g(r_{pq}, \omega_p, \omega_q)r_{pq}^2 dr_{pq}d\omega_p d\omega_q, \tag{53}$$

where e. g. θ_{12}^{pq} is the angle between the 1-axis of co-ordinates attached to the p-th molecule and the 2-axis of the q-th one.

Obviously, for tetrahedral molecules, one would be justified in putting approximately $J_A^{(1)} = 0$ for reasons stated previously. But even without doing so we get from (35), (39) and (42), successively, expressions which are independent of either the tensor element $b_{123}^{2\omega}$ or the orientational correlation parameter, thus:

$$D_v^{2\omega} = \frac{2}{3}, \quad D_c^{2\omega}(\vartheta) = \frac{5 + 3\cos^2\vartheta}{8},$$

$$R^{2\omega}(\vartheta) = \frac{13 + 14\cos\vartheta + 3\cos^2\vartheta}{13 - 14\cos\vartheta + 3\cos^2\vartheta}. \tag{54}$$

Consequently, the values $D_v^{2\omega} = 2/3$, $D_c^{2\omega}(\pi/2) = 5/8$ and $R^{2\omega}(0) = 15$ are majorants, defined in a previous Section. No wonder, as these were just the values obtained on the

condition $B^{2\omega}_{\alpha\beta\beta} = 0$, as it is the case for tetrahedral molecules in the absence of molecular fields. The result $2/3$, originally derived by Kielich [1], is modified only if one proceeds to take into consideration scattering by statistical fluctuations of molecular fields, since now $\langle B^{2\omega}_{\alpha\beta\beta}(B^{2\omega}_{\alpha\gamma\gamma})^* \rangle \neq 0$.

A discussion of the expressions (49) for other molecular symmetries is to be found in a paper by Kielich [4]; we consequently restrict ourselves to this one example.

4.2. Scattering by fluctuations of molecular fields

When dealing with scattering by dense isotropic media, liquids and compressed gases, one has moreover to consider effects due to fluctuations of molecular fields.

In this approximation, the tensor $B^{2\omega}_{\alpha\beta\gamma}$ has to be written as follows:

$$B^{2\omega}_{\alpha\beta\gamma} = \sum_{p=1}^{N} \left\{ b^{2\omega(p)}_{\alpha\varepsilon\eta} \left(\delta_{\varepsilon\beta} + \frac{\partial F^{(p)}_{\varepsilon}}{\partial E_{\beta}} \right) \left(\delta_{\eta\gamma} + \frac{\partial F^{(p)}_{\eta}}{\partial E_{\gamma}} \right) + c^{2\omega(p)}_{\alpha\beta\gamma\delta} F^{(p)}_{0\delta} + \ldots \right\}, \tag{55}$$

where the fourth-rank tensor $c^{2\omega}_{\alpha\beta\gamma\delta}$ is that of hyperpolarizability of order 4 induced in molecule p by the molecular field F_0 due in general to the other $N-1$ molecules of the medium, in the absence of an externally applied electric field.

Quite generally, the field of permanent molecules is:

$$F^{(p)}_{0\alpha} = - \sum_{\substack{q=1 \\ q \neq p}}^{N} \left\{ T^{(pq)}_{\alpha\beta}\mu^{(q)}_{\beta} - \tfrac{1}{3} T^{(pq)}_{\alpha\beta\gamma}\Theta^{(q)}_{\beta\gamma} + \tfrac{1}{15} T^{(pq)}_{\alpha\beta\gamma\delta}\Omega^{(q)}_{\beta\gamma\delta} - \ldots \right\}, \tag{56}$$

where μ, Θ, and Ω are respectively the permanent electric dipole, quadrupole and octupole moment of the molecule [40]. The tensors $T^{(pq)}_{\alpha\beta}$, $T^{(pq)}_{\alpha\beta\gamma}$ and $T^{(pq)}_{\alpha\beta\gamma\delta}$ are those of binary (pairwise) interaction between molecules p and q respectively of the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole kinds [25] and differ from zero for $p \neq q$.

Now F is the molecular field which appears when an external electric field is applied. It establishes an additional, spatial molecular redistribution, related with Yvon-Kirkwood [41] translational fluctuations. We write the field of induced electric dipoles in the form of the following expansion [25, 40]:

$$F^{(p)}_{\alpha} = - \sum_{\substack{q=1 \\ q \neq p}}^{N} T^{(pq)}_{\alpha\beta} a^{\omega(q)}_{\beta\gamma} E_{\gamma} + \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{\substack{r=1 \\ r \neq q}}^{N} T^{(pq)}_{\alpha\beta} a^{\omega(q)}_{\beta\gamma} T^{(qr)}_{\gamma\delta} a^{\omega(r)}_{\delta\varepsilon} E_{\varepsilon} - \ldots, \tag{57}$$

where $a^{\omega}_{\alpha\beta}$ is the tensor of linear optical polarizability of the molecule.

In (55), we have omitted the influence of this field on the hyperpolarizability $c^{2\omega}_{\alpha\beta\gamma\delta}$. Our calculations led us to this simplification. In fact, fluctuations of the fields F_0 would by no means modify the permutational symmetry of the tensor $B^{2\omega}_{\alpha\beta\gamma}$. Hence, the symmetric terms (13) alone suffice fully for the description of scattering by fluctuations of the fields of permanent multipoles.

The non-symmetric terms (16), however, differ from zero due to scattering by fluctuations of the molecular fields F of induced dipoles. In fact, in the present problem the tensor $B^{2\omega}_{\alpha\beta\gamma}$ can be dealt with as symmetric in the last pair of indices only.

For tetrahedral molecules specifically, on omitting at this stage the effects of variations in molecular fields $\partial F/\partial E = 0$, Eq. (55) yields:

$$B_{\alpha\beta\gamma}^{2\omega} = \sum_{p=1}^{N} \{b_{\alpha\beta\gamma}^{2\omega(p)} + c_{\alpha\beta\gamma\delta}^{2\omega(p)} F_{0\delta}^{(p)} + \ldots\},\tag{58}$$

$$B_{\alpha\beta\beta}^{2\omega} = \sum_{p=1}^{N} c_{\alpha\beta\beta\delta}^{2\omega(p)} F_{0\delta}^{(p)} + \ldots.$$

Keeping in mind that the lowest moment of such molecules is an octupole, we obtain from (56) [40]:

$$F_{0\alpha}^{(p)} = \tfrac{1}{15} \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\alpha\beta\gamma\delta}^{(pq)} \Omega_{\beta\gamma\delta}^{(q)} - \ldots\tag{59}$$

The tensor $c_{\alpha\beta\gamma\delta}^{2\omega}$ in the present case can satisfactorily be dealt with as isotropic, i. e.

$$c_{\alpha\beta\gamma\delta}^{2\omega} = \tfrac{1}{3} c_{2\omega}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\tag{60}$$

with $c_{2\omega} = c_{\alpha\alpha\beta\beta}^{2\omega}/5$ denoting the mean hyperpolarizability, and the octupole moment in the form [40]:

$$\Omega_{\alpha\beta\gamma} = \Omega_{123}[i_{\alpha}(j_{\beta}k_{\gamma} + k_{\beta}j_{\gamma}) + j_{\alpha}(i_{\beta}k_{\gamma} + k_{\beta}i_{\gamma}) + k_{\alpha}(i_{\beta}j_{\gamma} + j_{\beta}i_{\gamma})].\tag{61}$$

We restrict our considerations to pairwise interactions. On averaging over all possible molecular orientations, Eqs (14) and (15) transform to:

$$\Gamma_{2\omega}^2 = 15N b_{123}^{2\omega} b_{123}^{2\omega},$$

$$B_{2\omega}^2 = \tfrac{80}{27} N c_{2\omega}^2 \Omega_{123}^2 R_{10}.\tag{62}$$

The anisotropic factor $\Gamma_{2\omega}^2$ thus does not in the present approximation depend on the fluctuations of the molecular field F_0, whereas the isotropic factor $B_{2\omega}^2$ is now non-zero only as a result of the scattering mechanism considered above. The quantity R_{10} represents the parameter of radial interactions; at $n = 10$, it is defined by the following expression [4]:

$$R_n = 4\pi\varrho \int r_{pq}^{-n+2} g(r_{pq}) dr_{pq},\tag{63}$$

where $g(r_{pq})$ is the binary radial distribution function.

.We now proceed to consider scattering by fluctuations of the molecular fields of induced dipoles. General expressions for the symmetric and non-symmetric scattering factors $A_1^{2\omega} - A_5^{2\omega}$ valid for an arbitrary isotropic medium are adduced in Appendix. Here, we shall discuss some computational steps for tetrahedral molecules.

In the present approximation, we obtain from (55) and (56) at:

$$a_{\alpha\beta}^{\omega} = a_{\omega}\delta_{\alpha\beta}\tag{64}$$

(where $a_\omega = a_{\alpha\alpha}^\omega/3$ is the mean linear molecular polarizability) with an accuracy to within a_ω^2:

$$B_{2\omega}^2 = \frac{4}{9} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{\substack{r=1 \\ r \neq p}}^{N} \sum_{\substack{s=1 \\ s \neq q}}^{N} b_{\alpha\beta\varepsilon}^{2\omega(p)} b_{\alpha\gamma\eta}^{2\omega(q)} a_\omega^{(r)} a_\omega^{(s)} T_{\varepsilon\beta}^{(pr)} T_{\eta\gamma}^{(qs)} \right\rangle. \tag{65}$$

For pairwise interactions only ($p = q$, $r = s$; $p = s$, $q = r$) and on averaging over all possible molecular orientations, this yields with regard to (51):

$$B_{2\omega}^2 = \frac{16}{5} N b_{123}^{2\omega} b_{123}^{2\omega} a_\omega^2 R_6. \tag{66}$$

R_6 is the parameter of translational fluctuations given by (63) at $n = 6$.

In turn, the contribution to $\Gamma_{2\omega}^2$ from scattering on fluctuations of the molecular field F of induced dipoles is:

$$\Gamma_{2\omega}^2 = \frac{744}{5} N b_{123}^{2\omega} b_{123}^{2\omega} a_\omega^2 R_6. \tag{67}$$

On assembling (62), (66) and (67) we obtain, for the symmetric scattering factors (13):

$$_S A_1^{2\omega} = \frac{2}{35} N b_{123}^{2\omega} b_{123}^{2\omega} \{5 + \frac{248}{5} a_\omega^2 R_6\},$$

$$2_S A_2^{2\omega} = _S A_4^{2\omega} = \frac{4}{175} N \{ -b_{123}^{2\omega} b_{123}^{2\omega} (5 + 16 a_\omega^2 R_6) + \frac{280}{9} c_{2\omega}^2 \Omega_{123}^2 R_{10} \},$$

$$_S A_3^{2\omega} = \frac{2}{175} N \{ 3 b_{123}^{2\omega} b_{123}^{2\omega} (5 + 72 a_\omega^2 R_6) + \frac{560}{9} c_{2\omega}^2 \Omega_{123}^2 R_{10} \},$$

$$_S A_5^{2\omega} = \frac{2}{5} N \{ -b_{123}^{2\omega} b_{123}^{2\omega} (1 + 8 a_\omega^2 R_6) + \frac{16}{9} c_{2\omega}^2 \Omega_{123}^2 R_{10} \}. \tag{68}$$

Obviously, the terms proportional to R_6 can as well be derived from Eqs ((D1)–(D4)) on insertion of (55) and (66).

It is the non-symmetric parts of the molecular scattering factors that we obtain from ((D5)–(D7)) with (55) and (64) in the form:

$$_{NS} A_4^{2\omega} = -\frac{3}{2} {}_{NS} A_2^{2\omega} = -\frac{36}{175} N b_{123}^{2\omega} b_{123}^{2\omega} a_\omega^2 R_6,$$

$$_{NS} A_3^{2\omega} = -\frac{3}{2} {}_{NS} A_1^{2\omega} = -\frac{198}{175} N b_{123}^{2\omega} b_{123}^{2\omega} a_\omega^2 R_6,$$

$$_{NS} A_5^{2\omega} = -\frac{9}{25} N b_{123}^{2\omega} b_{123}^{2\omega} a_\omega^2 R_6. \tag{69}$$

Let us now calculate the depolarisation ratios $D_v^{2\omega}$ and $D_c^{2\omega}(\pi/2)$. With regard to (26) and (30), and by (68) and (69), we have:

$$D_v^{2\omega} = \frac{2}{3} \frac{1 + \dfrac{31}{2} a_\omega^2 R_6 + \dfrac{14}{9} \left(\dfrac{c_{2\omega}}{b_{123}^{2\omega}} \right)^2 \Omega_{123}^2 R_{10}}{1 + \dfrac{74}{5} a_\omega^2 R_6 + \dfrac{28}{3} \left(\dfrac{c_{2\omega}}{b_{123}^{2\omega}} \right)^2 \Omega_{123}^2 R_{10}}, \tag{70}$$

$$D_c^{2\omega} \left(\frac{\pi}{2} \right) = \frac{5}{8} \frac{1 + \dfrac{314}{25} a_\omega^2 R_6}{1 + \dfrac{431}{40} a_\omega^2 R_6 + \dfrac{14}{9} \left(\dfrac{c_{2\omega}}{b_{123}^{2\omega}} \right)^2 \Omega_{123}^2 R_{10}}. \tag{71}$$

Eqs (71) and (70) yield, in place of (41),

$$D_c^{2\omega}\left(\frac{\pi}{2}\right) = \frac{9D_v^{2\omega}-1}{12D_v^{2\omega}} \frac{1+\dfrac{314}{25}a_\omega^2 R_6}{1+\dfrac{1}{100}\left(997+\dfrac{63}{D_v^{2\omega}}\right)a_\omega^2 R_6} \cdot \tag{72}$$

The conclusion to be drawn from (70) and (71) is that agreement with experimental results can be obtained only if scattering on fluctuations of the molecular field of octupoles is much stronger than the effects due to molecular redistribution.

In the formulas for $D_v^{2\omega}$ of Refs [4,42] the contributions due to molecular redistribution ($a_\omega^2 R_6$) differed by certain numerical factors from those of Eq. (70) since only the symmetric scattering components (66)–(67) were taken into consideration in those calculations.

The calculation of the next Section will substantiate this.

5. Calculations

In order to evaluate the contributions from the various scattering mechanisms, it is in the first place necessary to have available the values of the translational fluctuation parameters R_6 and R_{10}.

Applying Kirkwood's approximation [40] to the correlation function $g(r_{pq})$, we obtain quite generally for $n \geqslant 4$ [43]:

$$R_n = \frac{4\pi\varrho}{n-3}\left(\frac{\pi}{6v}\right)^{\frac{n-3}{3}}, \tag{73}$$

where v is the molecular volume, $0.6 \leqslant \varrho v \leqslant 0.74$ [40].

Recent, more accurate calculations [44] indicate that the solution of (73) yields experimentally correct values from $n = 8$ onwards. At $n = 6$, the parameters evaluated from (73) are, on the average, some 15 times too large compared with those to be expected from the experimental study of linear anisotropic light scattering [44] and Kerr's effect [43]. The solution [44]:

$$R_6 = \frac{4\pi\varrho}{3e^{\beta\varepsilon}\sigma^3} \sum_{m=0}^{\infty} \sum_{n=0}^{m} \frac{(-1)^{n+2}\binom{m}{n}(4\beta\varepsilon)^m}{m!(2m+2n+1)}\left[1-2^{-\frac{2m+2n+1}{2}}\right] \tag{74}$$

is found to circumvent these deficiencies (ε and σ are constants of the Lennard-Jones potential, and $\beta = 1/kT$). The parameter R_6, computed from (74), is $R_6 = 2.5 \cdot 10^{43}$ cm^{-6} for CCl$_4$, whereas $R_{10} = 5 \cdot 10^{72}$ cm^{-10} from Eq. (73). For CCl$_4$ molecules $a_\omega = 10.5 \cdot 10^{-48}$ cm^3, and the factor $a_\omega^2 R_6 \cong 2.5 \cdot 10^{-3}$ is negligibly small. The largest of the numerical factors preceding the latter in Eqs (70)–(72) are but slightly larger than 10. Hence, in the present case, the redistribution terms can as well be omitted. The reason for the discrep-

ancy between the theoretical and experimental values has to be sought in the predominant rôle of scattering on fluctuations of the octupole fields. It will be remembered that this latter process was described by the symmetric part of the molecular scattering factors only. Thus, for these molecules, the relations (40), (44) and (45) are fulfilled as well as Eq. (41), as one finds immediately from (72) on omission of the redistributional terms. On insertion of the experimental result $D_v^{2\omega} = 0.34$ [6] into Eq. (41), we get $D_c^{2\omega}(\pi/2) = 0.50$. The value measured by Terhune *et al.* [6] amounts to 0.53 ± 0.07. Thus, in this case, the theoretically derived relation (41) is very satisfactorily fulfilled.

We are here led immediately to a conclusion of a more general nature. In fact, the fulfillment or non-fulfillment of the relations (40) and (41) by a set of experimentally measured values of depolarisation ratios provides a direct symptom of the importance or, as the case may be, unimportance of molecular redistribution in SHG. In the latter eventuality, it will be possible to make direct evaluations of the parameters R_6 from relations of the type of (72). For example, with regard to water, insertion of the experimental value [6] $D_v^{2\omega} = 0.117 \pm 0.015$ into (41) yields $D_c^{2\omega}(\pi/2) = 0.04 \pm 0.08$, whereas experimentally $D_c^{2\omega}(\pi/2) = 0.18 \pm 0.02$ [6]. We have adduced so highly accurate values for two reasons: firstly, in order to show how a small error in experimental depolarisation ratio $D_v^{2\omega}$, amounting in this instance to 13 per cent, affects essentially the value of $D_c^{2\omega}(\pi/2)$ to be expected from the relation (41), and secondly, because of the discrepancy apparent between the calculated and measured $D_c^{2\omega}(\pi/2)$-values, even when providing for the interval of error. The source of this discrepancy resides in the large contribution from scattering by fluctuations of the molecular fields of induced dipoles.

For CCl$_4$, at the values $b_{123}^{2\omega} = 3.10^{-32}$ esu [45] and $c_{2\omega} = 3.6 \cdot 10^{-36}$ esu [46] agreement with the experimental value of $D_v^{2\omega}$ is obtained from (70) at $\Omega_{123} = 15 \cdot 10^{-34}$ esu [4,42]. This value is by a half smaller than the one calculated by Weinberg [7].

From Eqs (34) and (68), on omitting terms containing molecular redistribution, we get for the reversal ratio:

$$R^{2\omega}(0) = \frac{15}{1 + \dfrac{224}{9}\left(\dfrac{c_{2\omega}}{b_{123}^{2\omega}}\right)^2 \Omega_{123}^2 R_{10}} \cdot \quad (75)$$

With the calculated value of Ω_{123}, Eq. (43) yields a value of $R^{2\omega}(0) = 3$ *i. e.* five times less than for scattering by a gaseous medium. Obviously, the same value has to result from (44) by insertion of $D_v^{2\omega} = 0.34$ [6].

For CCl$_4$ molecules two more values for $D_v^{2\omega}$ are available from measurements by Maker [8] and Lalanne [9] amounting, respectively, to 0.55 and 0.45. Neither, however, dealt with scattering of circularly polarized light. At the above values, one would have, respectively: from (68) $\Omega_{123} = 6 \cdot 10^{-34}$ esu and $10 \cdot 10^{-34}$ esu; from (41) $D_c^{2\omega}(\pi/2) = 0.6$ and 0.56; and from (45) $R^{2\omega}(0) \cong 8.8$ and 5.6. A repetition of the measurements could possibly decide in favour of one of the sets of values. The discrepancy is seen to be the largest for the reversal ratio.

It should be stressed that the recourse to circularly polarized incident light makes available information inaccessible from studies of the scattering of linearly polarized

light. The relation (27) between the depolarisation ratios $D_v^{2\omega}$ and $D_h^{2\omega}(\vartheta)$ is always fulfilled, since it is density-independent *i. e.* independent of the kind and size of molecular interaction. The relation (46) between the depolarisation ratio $D_c^{2\omega}(\pi/2)$ and reversal ratio $R^{2\omega}(0)$ will hold for all those dense media where scattering by fluctuations of the molecular field of induced dipoles can be neglected; otherwise, it will undergo a modification always only by a redistribution term, proportional to the parameter R_6. This circumstance will permit the direct evaluation of the radial molecular interactions. The effects due to scattering by fluctuations of molecular multipole fields described by the symmetric terms of the molecular scattering factors, are already taken into account by the relation (46).

It would appear still more interesting to perform experiments applying, at the same time, circularly polarized and linearly polarized light. Such measurements would yield simultaneously a larger number of relations between the various parameters (40), (41), (44) and (45), characterizing the scattered light and consequently can be expected to disclose more accurate information concerning the interactions between molecules.

APPENDIX

We here adduce formulas, generally valid for isotropic media and describing the influence of spatial redistribution of molecules on SHLS. In the symmetric factors, we omit the terms accounting for scattering by fluctuations in orientation and fluctuations of molecular fields of permanent multipoles. The non-symmetric terms of the molecular scattering factors $_{NS}A_1^{2\omega} - _{NS}A_5^{2\omega}$ are non-zero only owing to fluctuations of the molecular fields of induced dipoles.

By (13) and (16), with regard to (55) and (57), on restricting our calculations to pairwise interactions, and on performing an averaging over all possible orientations of the molecules, we obtain:

$$_{S}A_1^{2\omega} = \frac{R_6}{2625} N\{7(29b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} - 13b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega} + 3(-123b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} +$$

$$+ 131b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\omega}^2 + 200(5b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\varepsilon}^{2\omega} - 3b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\varepsilon}^{2\omega})a_{\varepsilon\gamma}^{\omega}a_{\omega}^{\omega}\}, \tag{D1}$$

$$_{S}A_4^{2\omega} = 2_{S}A_2^{2\omega} = \frac{2R_6}{2625} N\{-7(3b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} - 11b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega} +$$

$$+ 3(61b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} - 57b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\omega}^2 - 200(b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\varepsilon}^{2\omega} - 2b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\varepsilon}^{2\omega})a_{\varepsilon\gamma}^{\omega}a_{\omega}^{\omega}\}, \tag{D2}$$

$$_{S}A_3^{2\omega} = \frac{R_6}{2625} N\{7(23b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} + 9b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega} +$$

$$+ 3(-b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} + 17b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\omega}^2 + 200(3b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\varepsilon}^{2\omega} + b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\varepsilon}^{2\omega})a_{\varepsilon\gamma}^{\omega}a_{\omega}^{\omega}\}, \tag{D3}$$

$$_sA_5^{2\omega} = -\frac{R_6}{75}\,N\{7(b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} - b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})\,(a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega} - 3a_{\omega}^2) +$$

$$+ 40(b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\varepsilon}^{2\omega} - b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\varepsilon}^{2\omega})a_{\varepsilon\gamma}^{\omega}a_{\omega}\}. \tag{D4}$$

$$_{NS}A_4^{2\omega} = -\frac{3}{2}\,_{NS}A_2^{2\omega} = \frac{R_6}{875}\,N\{(4b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} - 15b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega} +$$

$$- 3(14b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} - 15b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\omega}^2 - 50b_{\alpha\beta\beta}^{2\omega}(b_{\alpha\gamma\varepsilon}^{2\omega}a_{\varepsilon\gamma}^{\omega} - b_{\varepsilon\gamma\gamma}^{2\omega}a_{\varepsilon\alpha}^{\omega})a_{\omega}\}, \tag{D5}$$

$$_{NS}A_3^{2\omega} = -\frac{3}{2}\,_{NS}A_1^{2\omega} = \frac{R_6}{1750}\,N\{(61b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} - 17b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega} +$$

$$+ 3(49b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} - 53b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})a_{\omega}^2 + 200b_{\alpha\beta\beta}^{2\omega}(b_{\alpha\gamma\varepsilon}^{2\omega}a_{\varepsilon\gamma}^{\omega} - b_{\varepsilon\gamma\gamma}^{2\omega}a_{\varepsilon\alpha}^{\omega})a_{\omega}\}, \tag{D6}$$

$$_{NS}A_5^{2\omega} = \frac{R_6}{750}\,N\{3(-b_{\alpha\beta\gamma}^{2\omega}b_{\alpha\beta\gamma}^{2\omega} + b_{\alpha\beta\beta}^{2\omega}b_{\alpha\gamma\gamma}^{2\omega})\,(a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega} + 27a_{\omega}^2) +$$

$$- 200b_{\alpha\beta\beta}^{2\omega}(b_{\alpha\gamma\varepsilon}^{2\omega}a_{\varepsilon\gamma}^{\omega} - b_{\varepsilon\gamma\gamma}^{2\omega}a_{\varepsilon\alpha})a_{\omega}\}, \tag{D7}$$

where $a_{\omega} = a_{\alpha\alpha}^{\omega}/3$ is, as previously, the mean linear polarizability.

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