

SECOND HARMONIC LIGHT SCATTERING BY DENSE ISOTROPIC MEDIA

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A semi-macroscopic method is applied to derive the intensity tensor $I_{\sigma\tau}^s$ of light elastically scattered in the general case by a dense isotropic medium on which an intense (laser) beam of intensity I is incident: $I_{\sigma\tau}^s = (P^\omega + P^{2\omega}I + P^{3\omega}I^2 + \dots) I \delta_{\sigma\tau} + (Q^\omega + Q^{2\omega}I + Q^{3\omega}I^2 + \dots) I_{\sigma\tau}$; P^ω , Q^ω denote linear Rayleigh scattering with the ground frequency ω , whereas $P^{2\omega}$, $Q^{2\omega}$, etc. define nonlinear scattering with the double frequency 2ω and higher harmonics 3ω , etc. The angular dependence of nonlinear scattering is discussed, and Krishnan's reciprocity relation is shown to hold. A molecular-statistical discussion of the quantities $P^{2\omega}$ and $Q^{2\omega}$ is given involving bi-molecular radial and orientational correlation functions. Applications to special cases, in particular to interacting tetrahedrally- and axially-symmetric as well as dipolar, quadrupolar and octupolar molecules, are given. A detailed analysis of the results allows to predict that second harmonic scattering measurements will provide information concerning molecular correlations, anisotropy of nonlinear polarizability of isolated molecules, and their quadrupole or octupole moments.

1. Introduction

Recently, Terhune *et al* [1] and Maker [2], recurring to laser techniques, detected second harmonic light scattering by liquids and compressed gases. These first successful experiments, in conjunction with theoretical calculations [3]—[7], provide a new method of studying the nonlinear optical properties of atoms and isolated molecules as well as of intermolecular interactions in dense media [7]—[9].

Here, a semi-macroscopic method, initiated by Kirkwood [10] in dielectrics theory, will be applied for a quantitative description of nonlinear elastic light scattering in isotropic dense media. Kirkwood's method has proved efficient in many a problem *i.a.* with regard to both linear [11], [12] and nonlinear light scattering [8], [9]. This semi-macroscopic approach has the advantage of yielding directly, by a formal and at the same time simple procedure, quite general expressions that hold for arbitrarily condensed, isotropic media, and any conditions of observation. These expressions can then be specialized in a molecular-statistical treatment to various cases, disclosing the acting microscopic mechanism of non-

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linear light scattering. Beside radial and orientational molecular correlations, particular attention will be given to the part played by molecular fields, whose existence in dense media can contribute to the appearance of second-order nonlinear scattering even in a medium consisting of molecules presenting a centre of inversion (*e.g.* quadrupolar molecules).

Also, nonlinear scattering will be investigated in detail in its dependence on the angle of observation (a problem already discussed in part in refs [5], [9] and [13]), and Krishnan's reciprocity relation will be shown to hold, as for linear scattering [11].

With regard to simplicity, however, we shall refrain here from considering explicitly nonlinear dispersion and absorption, scattering with summation field frequencies, and quantum transition frequencies, these having been discussed quantum-mechanically by various authors (see refs [3]—[7] and [14].) With these restrictions, it will be possible to give a complete formulation of the present theory on a classical level, admitting of a solution of the problem of correlations in nonlinear light scattering with sufficient generality by way of simple methods of classical statistical mechanics and microscopic electrodynamics. In this respect, the present theoretical considerations go much further than those of Terhune *et al* [1], Cyvin *et al* [6], Bersohn *et al* [7], and this author [5], [8], [9], in that most of the molecular correlation factors describing nonlinear light scattering in liquids are shown to be accessible if one recurs to other, experimentally investigated molecular effects. The latter circumstance would seem highly important for the development of the nonlinear molecular optics of condensed systems.

II. General semi-macroscopic theory

Consider a medium of volume V , macroscopically isotropic in the absence of external forces on which a light wave with electric vector $\mathbf{E} = \mathbf{E}_0 \cos \omega t$ oscillating at frequency ω is incident. In a first approximation, \mathbf{E} induces in V a dipole electric moment \mathbf{M} , which in the classical linear case is of the form [11]

$$\mathbf{M} = \sum_{p=1}^N \mathbf{m}^{(p)}(t) \exp [i(\mathbf{k} - \mathbf{k}_s) \cdot \mathbf{r}_p], \quad (1)$$

with $\mathbf{m}^{(p)}(t)$ denoting the dipole moment induced in molecule p distant by \mathbf{r}_p from the centre of the scattering volume, and \mathbf{k} , \mathbf{k}_s the wave vectors of incident and scattered light, respectively.

We introduce the intensity tensor of scattered light $I_{\sigma\tau}^s$, which for dipolar scattering in the wave zone, is of the form [9]

$$I_{\sigma\tau}^s = (c^4 V)^{-1} \left\langle \frac{d^2 M_\sigma}{dt^2} \frac{d^2 M_\tau}{dt^2} \right\rangle_E. \quad (2)$$

The symbol $-'$ stands for averaging over the time t , whereas the brackets $\langle \rangle_E$ denote statistical averaging in the presence of the electric field \mathbf{E} .

We furthermore assume for simplicity that the incident wavelength λ is large as compared with intermolecular distances and that ω lies outside the absorption bands of the medium. Also, \mathbf{E} is assumed homogeneous, with intensity sufficiently large for the isotropic medium

to become optically nonlinear. \mathbf{M} is now in general a nonlinear function of \mathbf{E} , and can be satisfactorily approximated by the expansion [15]

$$M_{\sigma} = A_{\sigma\tau}E_{\tau} + \frac{1}{2} B_{\sigma\tau\nu}E_{\tau}E_{\nu} + \frac{1}{6} C_{\sigma\tau\nu\varrho}E_{\tau}E_{\nu}E_{\varrho} + \dots, \quad (3)$$

whose first term describes the linear properties of the medium as given by its optical polarizability tensor $A_{\sigma\tau}$. The remaining terms of (3) account for the optical nonlinearity induced in the medium by the strong field \mathbf{E} , and contain the tensors $B_{\sigma\tau\nu}$, $C_{\sigma\tau\nu\varrho}$ and so forth of second, third and higher order polarizabilities.

By assumption, we have excluded dispersion and absorption from our considerations. This makes it unnecessary to consider the tensors $A_{\sigma\tau}$, $B_{\sigma\tau\nu}$ etc. in their explicit dependence on ω . With the above assumptions, we can write with regard to Eqs (2) and (3)

$$I_{\sigma\tau}^* = I_{\sigma\tau}^{\omega} + I_{\sigma\tau}^{2\omega} + I_{\sigma\tau}^{3\omega} + \dots, \quad (4)$$

where

$$I_{\sigma\tau}^{\omega} = \frac{1}{V} \left(\frac{\omega}{c} \right)^4 \langle A_{\sigma\nu}^{\omega} A_{\tau\varrho}^{-\omega} \rangle I_{\nu\varrho} \quad (5)$$

is the intensity tensor of light linearly scattered at the frequency ω of the incident light beam of intensity $I_{\nu\varrho} = E_{0\nu}E_{0\varrho}/2$. The higher terms in (4) define nonlinear light scattering; here, we shall restrict considerations to second-harmonic scattering given by the tensor

$$I_{\sigma\tau}^{2\omega} = \frac{1}{8V} \left(\frac{2\omega}{c} \right)^4 \langle B_{\sigma\nu\lambda}^{2\omega} B_{\tau\varrho\mu}^{-2\omega} \rangle I_{\nu\varrho} I_{\lambda\mu}. \quad (6)$$

On averageing over all possible molecular orientations in the right hand terms of Eqs (5) and (6), we obtain (see Appendix A)

$$I_{\sigma\tau}^{\omega} = P^{\omega} I \delta_{\sigma\tau} + Q^{\omega} I_{\sigma\tau}, \quad (7)$$

$$I_{\sigma\tau}^{2\omega} = (P^{2\omega} I \delta_{\sigma\tau} + Q^{2\omega} I_{\sigma\tau}) I, \quad (8)$$

where we have introduced the notation:

$$P^{\omega} = \frac{1}{30V} \left(\frac{\omega}{c} \right)^4 (5\delta_{\alpha\beta}\delta_{\gamma\delta} - \sigma_{\alpha\beta\gamma\delta}) \langle A_{\alpha\gamma} A_{\beta\delta} \rangle, \quad (9)$$

$$Q^{\omega} = \frac{1}{30V} \left(\frac{\omega}{c} \right)^4 (3\sigma_{\alpha\beta\gamma\delta} - 5\delta_{\alpha\beta}\delta_{\gamma\delta}) \langle A_{\alpha\gamma} A_{\beta\delta} \rangle, \quad (10)$$

$$P^{2\omega} = \frac{1}{1680V} \left(\frac{2\omega}{c} \right)^4 (7\delta_{\alpha\beta}\sigma_{\gamma\delta\epsilon\eta} - \sigma_{\alpha\beta\gamma\delta\epsilon\eta}) \langle B_{\alpha\gamma\epsilon} B_{\beta\delta\eta} \rangle, \quad (11)$$

$$Q^{2\omega} = \frac{1}{1680V} \left(\frac{2\omega}{c} \right)^4 (3\sigma_{\alpha\beta\gamma\delta\epsilon\eta} - 7\delta_{\alpha\beta}\sigma_{\gamma\delta\epsilon\eta}) \langle B_{\alpha\gamma\epsilon} B_{\beta\delta\eta} \rangle \quad (12)$$

(the tensors $\sigma_{\alpha\beta\gamma\delta}$ and $\sigma_{\alpha\beta\gamma\delta\epsilon\eta}$ are defined in Appendix A).

By (7) and (8), the tensors of both linear and nonlinear scattering are seen to consist of two parts: a part independent of the state of polarisation of the incident beam, and a part dependent thereon as well as on the conditions of observation. In order to make this fact apparent, let us assume that the incident light propagates along the Y -axis with electric vector oscillating in the XZ -plane at an angle ψ to the plane of observation XY :

$$\mathbf{E} = (\mathbf{x} \cos \psi + \mathbf{z} \sin \psi) E, \quad (13)$$

$\mathbf{x}, \mathbf{y}, \mathbf{z}$ being unit vectors on the axes X, Y, Z of the laboratory frame attached to the centre of V ; the scattered light is observed in the XY -plane at an angle ϑ to the direction of incidence (Y -axis), the point of observation having attached to it the reference frame X', Y', Z' with unit vectors,

$$\mathbf{x}' = \mathbf{x} \sin \vartheta + \mathbf{y} \cos \vartheta, \quad \mathbf{y}' = -\mathbf{x} \cos \vartheta + \mathbf{y} \sin \vartheta, \quad \mathbf{z}' = \mathbf{z}. \quad (14)$$

The horizontal (H) and vertical (V) scattering tensor components are now by definition

$$H = I_{\sigma\tau}^s y'_\sigma y'_\tau \quad \text{and} \quad V = I_{\sigma\tau}^s z'_\sigma z'_\tau \quad (15)$$

i.e. by (7), (8), (13) and (14) we get for linear light scattering:

$$\begin{aligned} H^\omega(\psi, \vartheta) &= (P^\omega + Q^\omega \cos^2 \vartheta \cos^2 \psi) I, \\ V^\omega(\psi) &= (P^\omega + Q^\omega \sin^2 \psi) I, \end{aligned} \quad (16)$$

and for nonlinear second harmonic light scattering:

$$\begin{aligned} H^{2\omega}(\psi, \vartheta) &= (P^{2\omega} + Q^{2\omega} \cos^2 \vartheta \cos^2 \psi) I^2, \\ V^{2\omega}(\psi) &= (P^{2\omega} + Q^{2\omega} \sin^2 \psi) I^2. \end{aligned} \quad (17)$$

Hence, quite generally, by analogy to linear scattering [11], [16] we obtain from Eq. (17) the following components of nonlinear light scattering according to whether the incident beam oscillates in the horizontal or vertical plane (lower indices h and v at the capital letters H and V):

$$\begin{aligned} H_h^{2\omega}(\vartheta) &= (P^{2\omega} + Q^{2\omega} \cos^2 \vartheta) I^2, \\ H_h^{2\omega} &= V_h^{2\omega} = P^{2\omega} I^2, \\ V_v^{2\omega} &= (P^{2\omega} + Q^{2\omega}) I^2. \end{aligned} \quad (18)$$

Thus, in the case of nonlinear light scattering too, Krishnan's reciprocity relation $H_v^{2\omega} = V_h^{2\omega}$ is fulfilled.

By (18), the depolarisation ratio for the two polarisations of the incident light beam are:

$$D_v^{2\omega} = \frac{H_v^{2\omega}}{V_v^{2\omega}} = \frac{P^{2\omega}}{P^{2\omega} + Q^{2\omega}}, \quad (19)$$

$$D_h^{2\omega} = \frac{V_h^{2\omega}}{H_h^{2\omega}} = \frac{P^{2\omega}}{P^{2\omega} + Q^{2\omega} \cos^2 \vartheta}. \quad (20)$$

For unpolarized incident light, we get the scattered light components in the form:

$$\begin{aligned} H_u^{2\omega}(\vartheta) &= H_v^{2\omega} + H_h^{2\omega} = (2P^{2\omega} + Q^{2\omega} \cos^2 \vartheta)I^2, \\ V_u^{2\omega} &= V_v^{2\omega} + V_h^{2\omega} = (2P^{2\omega} + Q^{2\omega})I^2, \end{aligned} \quad (21)$$

and the depolarisation ratio

$$D_u^{2\omega}(\vartheta) = \frac{H_u^{2\omega}}{V_u^{2\omega}} = \frac{2P^{2\omega} + Q^{2\omega} \cos^2 \vartheta}{2P^{2\omega} + Q^{2\omega}}. \quad (22)$$

The expressions (16)–(22) provide a full and quantitative description of the angular dependence of both linear and nonlinear light scattering for an isotropic medium irrespective of its state of condensation and molecular structure (in the absence of internal interference, when the exponential factor in (1) can be put equal to unity).

III. Molecular-statistical theory

The quantities (9)–(12), which account for the optical properties of the scattering medium and for its molecular structure, will now be discussed. First, Eqs (9) and (10) can be rewritten thus:

$$P^\omega = \frac{3}{5} \left(\frac{\omega}{c} \right)^4 F_{\text{anis}}, \quad Q^\omega = \left(\frac{\omega}{c} \right)^4 \left(F_{\text{is}} + \frac{1}{5} F_{\text{anis}} \right), \quad (23)$$

where the quantities

$$F_{\text{is}} = \frac{1}{9V} \langle A_{\alpha\alpha} A_{\beta\beta} \rangle, \quad F_{\text{anis}} = \frac{1}{18V} \langle 3A_{\alpha\beta} A_{\alpha\beta} - A_{\alpha\alpha} A_{\beta\beta} \rangle, \quad (24)$$

which respectively define isotropic and anisotropic linear scattering of light, have been discussed in a molecular-statistical approach in earlier papers [11], [17]. In proceeding from the strict formulas (9) and (10) to (23) and (24), we assumed the optical polarizability tensor of the medium $A_{\alpha\beta}$ as totally symmetric (this is so for optically inactive bodies in the absence of dispersion and absorption).

By analogy to (23), one can transform Eqs (11) and (12) as follows:

$$P^{2\omega} = \frac{3(2\omega)^4}{280 c^4} G_{\text{anis}}, \quad Q^{2\omega} = \frac{(2\omega)^4}{40 c^4} \left(G_{\text{is}} + \frac{5}{7} G_{\text{anis}} \right), \quad (25)$$

where the quantities

$$G_{\text{is}} = \frac{1}{9V} (\sigma_{\alpha\beta\gamma\delta\epsilon\eta} - 4\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta}) \langle B_{\alpha\gamma\epsilon} B_{\beta\delta\eta} \rangle, \quad (26)$$

$$G_{\text{anis}} = \frac{1}{18V} (7 \delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} - \sigma_{\alpha\beta\gamma\delta\epsilon\eta}) \langle B_{\alpha\gamma\epsilon} B_{\beta\delta\eta} \rangle, \quad (27)$$

define the isotropic and anisotropic parts of nonlinear light scattering.

If moreover one assumes for simplicity the nonlinear polarizability tensor $B_{\alpha\beta\gamma}$ as totally symmetric, Eqs (26) and (27) reduce to

$$G_{is} = \frac{1}{9V} \langle 5B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} - 2B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle, \quad (28)$$

$$G_{anis} = \frac{1}{9V} \langle 4B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} - B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle, \quad (29)$$

On substituting the relations (25) and quantities (28), (29) into the depolarisation ratio (19) we get

$$D_v^{2\omega} = \frac{3G_{anis}}{7G_{is} + 8G_{anis}} = \frac{4\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle - \langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle}{6\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle + 9\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle}. \quad (30)$$

We shall discuss the above expression for a medium of N molecules, when by (1) and (3) we have

$$B_{\alpha\beta\gamma} = \left(\frac{\partial^2 M_\alpha}{\partial E_\beta \partial E_\gamma} \right)_0 = \sum_{p=1}^N \left(\frac{\partial^2 m_\alpha^{(p)}}{\partial E_\beta \partial E_\gamma} \right)_0, \quad (31)$$

wherein in the general case [11]

$$\begin{aligned} m_\alpha^{(p)} = & a_{\alpha\beta}^{(p)}(E_\beta + F_\beta^{(p)}) + \frac{1}{2} b_{\alpha\beta\gamma}^{(p)}(E_\beta + F_\beta^{(p)})(E_\gamma + F_\gamma^{(p)}) + \frac{1}{3} q_{\alpha\beta\gamma}^{(p)}(E_{\beta\gamma} + F_{\beta\gamma}^{(p)}) + \\ & + \frac{1}{6} c_{\alpha\beta\gamma\delta}^{(p)}(E_\beta + F_\beta^{(p)})(E_\gamma + F_\gamma^{(p)})(E_\delta + F_\delta^{(p)}) + \frac{1}{3} q_{\alpha\beta\gamma\delta}^{(p)}(E_\beta + F_\beta^{(p)})(E_{\gamma\delta} + F_{\gamma\delta}^{(p)}) + \dots \end{aligned} \quad (32)$$

In this expansion $a_{\alpha\beta}^{(p)}$ is the tensor of linear, $b_{\alpha\beta\gamma}^{(p)}$, $c_{\alpha\beta\gamma\delta}^{(p)}$ those of nonlinear dipolar, and $q_{\alpha\beta\gamma}^{(p)}$, $q_{\alpha\beta\gamma\delta}^{(p)}$ those of quadrupolar optical polarizability of the p -th isolated molecule. $F_\alpha^{(p)}$ is the molecular electric field acting on the latter in the presence of the external field E_α , whereas $E_{\alpha\beta}$ and $F_{\alpha\beta}^{(p)}$ are their gradients, which induce quadrupolar polarizability.

A. Tetrahedral molecules.

In a first approximation, for a not too dense medium, the action of the molecular field can be neglected and by (31), (32) we have with satisfactory accuracy

$$B_{\alpha\beta\gamma} = \sum_{p=1}^N b_{\alpha\beta\gamma}^{(p)}. \quad (33)$$

In the case of molecules having the point group symmetry T_d , the tensor $b_{\alpha\beta\gamma}$ presents only 6 non-zero components b_{123} and can be written as follows [8], [9]:

$$b_{\alpha\beta\gamma}^{(p)} = b_{123} \{ i_\alpha^{(p)} (j_\beta^{(p)} k_\gamma^{(p)} + k_\beta^{(p)} j_\gamma^{(p)}) + j_\alpha^{(p)} (k_\beta^{(p)} i_\gamma^{(p)} + i_\beta^{(p)} k_\gamma^{(p)}) + k_\alpha^{(p)} (i_\beta^{(p)} j_\gamma^{(p)} + j_\beta^{(p)} i_\gamma^{(p)}) \} \quad (34)$$

(i, j, k are unit vectors along the axes 1, 2, 3 of molecular coordinates).

By (33) and (34), we have

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = 0, \quad \langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = \left\langle \sum_{p=1}^N \sum_{q=1}^N b_{\alpha\beta\gamma}^{(p)} b_{\alpha\beta\gamma}^{(q)} \right\rangle. \quad (35)$$

This expression can be transformed to

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = 6V\varrho b_{123}^2 + \varrho^2 \iint b_{\alpha\beta\gamma}^{(p)} b_{\alpha\beta\gamma}^{(q)} g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (36)$$

by recurring to the binary correlation function $g^{(2)}(\tau_p, \tau_q)$ of molecules p and q having the configurations τ_p and τ_q , respectively.

In the absence of orientational correlations, the second term of (36) vanishes and we get simply

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = 6V\varrho b_{123}^2 \quad (37)$$

a result that holds for light scattering by isolated tetrahedral molecules.

On substituting the result of (36) into Eq. (30) we obtain in the above approximation [3] $D_v^{2\omega} = 2/3$, irrespective of a specification of the statistical correlations. Measurements [1] in liquefied CCl_4 yield $D_v^{2\omega} \simeq 1/3$, a value almost twice smaller than that calculated on the preceding approximation.

The foregoing calculations can, however, be rendered more exact by taking into consideration the effect of the molecular field, which in the case of tetrahedral molecules, isotropically polarizable in a linear approximation, can be represented by the expansion [11]

$$F_\alpha^{(p)} = F_{0\alpha}^{(p)} - \sum_{\substack{q=1 \\ q \neq p}}^N a_q T_{\alpha\beta}^{(pq)} E_\beta + \sum_{\substack{q=1 \\ q \neq p}}^N \sum_{\substack{r=1 \\ r \neq q}}^N a_q a_r T_{\alpha\beta}^{(pq)} T_{\beta\gamma}^{(qr)} E_\gamma - \dots, \quad (38)$$

where the tensor

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5} (3r_{pq} a_r r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta}) \quad (39)$$

defines dipole-dipole type interaction between molecules p and q distant by r_{pq} .

On neglecting in (32) higher-order nonlinear polarizabilities, we can replace (33) with regard to (31) by the expansion

$$B_{\alpha\beta\gamma} = \sum_{p=1}^N \left\{ b_{\alpha\beta\gamma}^{(p)} + 2b_{\alpha\beta\epsilon}^{(p)} \frac{\partial F_\epsilon^{(p)}}{\partial E_\gamma} + b_{\alpha\epsilon\eta}^{(p)} \frac{\partial F_\epsilon^{(p)}}{\partial E_\beta} \frac{\partial F_\eta^{(p)}}{\partial E_\gamma} + \dots \right\}, \quad (40)$$

which, significantly, implies in general the non-vanishing of the term $\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle$ also. Indeed, we have to within a^2

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = 4 \left\langle \sum_{p=1}^N \sum_{\substack{q=1 \\ r \neq q}}^N \sum_{\substack{r=1 \\ s \neq q}}^N b_{\alpha\beta\epsilon}^{(p)} b_{\alpha\gamma\eta}^{(q)} a_r a_s T_{\epsilon\beta}^{(pr)} T_{\eta\gamma}^{(qs)} \right\rangle, \quad (41)$$

or, on averaging over all molecular orientations and on restricting considerations to the contribution from pairwise correlations only,

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = \frac{24}{5} V\varrho a^2 b_{\alpha\beta\gamma} b_{\alpha\beta\gamma} R_6, \quad (42)$$

where we have introduced the following integral parameter [17] for $n = 6$:

$$R_n = \varrho \int r_{pq}^{-n} g(r_{pq}) dr_{pq} \quad (43)$$

containing the radial correlation function $g(r_{pq})$.

In the same approximation, we obtain instead of (37)

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = V\varrho b_{\alpha\beta\gamma} b_{\alpha\beta\gamma} \left(1 + \frac{82}{5} a^2 R_6 \right). \quad (44)$$

By (42) and (44), the depolarization ratio (30) now assumes the value

$$D_v^{2\omega} = \frac{2}{3} \frac{1 + \frac{76}{5} a^2 R_6}{1 + \frac{118}{5} a^2 R_6} \cong \frac{2}{3} \left(1 - \frac{42}{5} a^2 R_6 \right), \quad (45)$$

which is slightly smaller than the previous $2/3$ owing to radial interactions between the induced dipole moments given by (43).

In addition to the indirect effect of the molecular field $F^{(p)}$ calculated above, one has in general to consider also that of the molecular field $F_0^{(p)}$, which exists in very dense media even if no external field E is acting. In this case, we have by (31) and (32)

$$B_{\alpha\beta\gamma} = \sum_{p=1}^N (b_{\alpha\beta\gamma}^{(p)} + c_{\alpha\beta\gamma\delta}^{(p)} F_{0\delta}^{(p)} + \dots) \quad (46)$$

and, for tetrahedral molecules, we can write

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = \left\langle \sum_{p=1}^N \sum_{q=1}^N c_{\alpha\beta\beta\delta}^{(p)} c_{\alpha\gamma\gamma\epsilon}^{(q)} F_{0\delta}^{(p)} F_{0\epsilon}^{(q)} \right\rangle. \quad (47)$$

Restricting ourselves as above to pairwise correlations, we obtain after averaging over all possible molecular orientations

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = \frac{25}{3} c^2 V\varrho \langle F_0^2 \rangle, \quad (48)$$

where $c = c_{\alpha\alpha\beta\beta}/5$ is the mean third-order polarizability, and

$$\langle F_0^2 \rangle = \frac{1}{3} \varrho \int \langle F_{0\alpha}^{(p)} F_{0\alpha}^{(q)} \rangle_{\omega} g(r_{pq}) dr_{pq} \quad (49)$$

is the orientationally-averaged square of the molecular field $F_0^{(p)}$ produced at the centre of molecule p by the charge distribution of its neighbour q .

Similarly and with the same accuracy we have in place of (37)

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = V\varrho (6b_{123}^2 + 5c^2 \langle F_0^2 \rangle). \quad (50)$$

By substitution of (48) and (50) into Eq. (30), we get the depolarisation ratio of tetrahedral molecules in the form:

$$D_v^{2\omega} = \frac{2b_{123}^2 + \frac{35}{36} c^2 \langle F_0^2 \rangle}{3b_{123}^2 + \frac{35}{4} c^2 \langle F_0^2 \rangle}, \quad (51)$$

wherein the presence of the parameter $\langle F_0^2 \rangle$ still further lowers the $D_v^{2\omega}$ value with regard to 2/3.

Since the lowest octupolar moment of a tetrahedral molecule is given by the octupole moment Ω_{123} , the parameter (49) is expressed as follows if interaction is assumed to be of the induced dipole-permanent octupole kind (see Appendix B)

$$\langle F_0^2 \rangle = \frac{16}{5} \Omega_{123}^2 R_{10}, \quad (52)$$

where R_{10} is defined by (43) for $n = 10$.

Above, in the case of the tetrahedral symmetry T_d , the tensor of the octupole moment is expressed as follows:

$$\Omega_{\alpha\beta\gamma} = \Omega_{123} \{i_\alpha(j_\beta k_\gamma + j_\beta k_\gamma) + j_\alpha(k_\beta i_\gamma + k_\beta i_\gamma) + k_\alpha(i_\beta j_\gamma + j_\beta i_\gamma)\} \quad (53)$$

with

$$\Omega_{123} = \frac{5}{2} \sum_i e_i r_{1i} r_{2i} r_{3i} \quad (54)$$

where e_i is the i -th electric charge of the molecule and \mathbf{r}_i is its radius vector.

B. Axially-symmetric molecules.

On assuming that the tensor $b_{\alpha\beta\gamma}$ is totally symmetric, we get for the case of molecules having the axial symmetry with regard to the molecular 3-axis [9]:

$$b_{\alpha\beta\gamma}^{(p)} = b(1 - \kappa_b)(k_\alpha^{(p)} \delta_{\beta\gamma} + k_\beta^{(p)} \delta_{\gamma\alpha} + k_\gamma^{(p)} \delta_{\alpha\beta} - 2k_\alpha^{(p)} k_\beta^{(p)} k_\gamma^{(p)}) + 3b\kappa_b k_\alpha^{(p)} k_\beta^{(p)} k_\gamma^{(p)} \quad (55)$$

with

$$b = (b_{333} + 2b_{113})/3 \quad \text{and} \quad \kappa_b = (b_{333} - b_{113})/3b \quad (56)$$

denoting the mean nonlinear polarizability and its anisotropy.

Assuming in a first step the approximation (33), we have by (55)

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = 9b^2 \langle \sum_{p=1}^N \sum_{q=1}^N \cos \theta_{pq} \rangle, \quad (57)$$

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = 3b^2(1 + 4\kappa_b - 5\kappa_b^2) \langle \sum_{p=1}^N \sum_{q=1}^N \cos \theta_{pq} \rangle + b^2(2 - 5\kappa_b)^2 \langle \sum_{p=1}^N \sum_{q=1}^N \cos^3 \theta_{pq} \rangle, \quad (58)$$

θ_{pq} being the angle between the symmetry axis of molecule p and that of molecule q .

Recurring to the bi-molecular correlation function we have

$$\langle \sum_{p=1}^N \sum_{q=1}^N \cos^n \theta_{pq} \rangle = V_Q(1 + J_n), \quad (59)$$

where

$$J_n = \frac{\rho}{V} \int \int \cos^n \theta_{pq} g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (60)$$

is an integral parameter of angular correlations. In particular, for $n = 1$, Eq. (60) gives the well-known Kirkwood correlation parameter [10] for the dielectric polarisation of dipolar liquids.

Substitution of (57) and (58) into Eq. (30) yields the depolarisation ratio for axially-symmetric molecules in the form

$$D_v^{2\omega} = \frac{3(1+16\kappa_b-20\kappa_b^2)(1+J_1)+4(2-5\kappa_b)^2(1+J_3)}{9(11+8\kappa_b-10\kappa_b^2)(1+J_1)+6(2-5\kappa_b)^2(1+J_3)}; \quad (61)$$

in the absence of angular correlations, when $J_1 = J_3 = 0$, this reduces to

$$D_v^{2\omega} = \frac{19-32\kappa_b+40\kappa_b^2}{3(41-16\kappa_b+20\kappa_b^2)}. \quad (62)$$

In the case of chloroform [9] $\kappa_b = -0.074$, and Eq. (62) yields approximately $D_v^{2\omega} \simeq 0.13$. Measurements by Terhune *et al* [1] for CH_3CN led to a depolarisation of about 0.1.

The angular correlations parameters (60) can be calculated numerically if one makes the approximation [17]

$$g^{(2)}(\tau_p, \tau_q) = \Omega^{-2} g(r_{pq}) \exp(-\beta v_{pq}), \quad (63)$$

$v_{pq} = v_{pq}(\mathbf{r}_{pq}, \boldsymbol{\omega}_p, \boldsymbol{\omega}_q)$ being the potential energy of angular interaction between two molecules having orientations $\boldsymbol{\omega}_p$ and $\boldsymbol{\omega}_q$, with $\Omega = \int d\boldsymbol{\omega}_p = \int d\boldsymbol{\omega}_q$ and $\beta = 1/kT$.

In particular for molecules with a permanent dipole moment μ we have

$$v_{pq} = -\mu^2(3 \cos \theta_p \cos \theta_q - \cos \theta_{pq})r_{pq}^{-3}, \quad (64)$$

so that with regard to (60) and (63) one obtains

$$J_1 = \frac{2\mu^6}{75} \beta^3 \left(R_9 + \frac{8\mu^4}{49} \beta^2 R_{15} + \frac{5\mu^8}{441} \beta^4 R_{21} + \dots \right), \quad (65)$$

$$J_3 = \frac{58\mu^6}{3675} \beta^3 \left(R_9 + \frac{44\mu^4}{261} \beta^2 R_{15} + \dots \right) \quad (66)$$

with R_9 , R_{15} and R_{21} given by Eq. (43) for $n = 9, 15, 21$ respectively.

C. Molecules of arbitrary symmetry.

We finally proceed to consider the general case of arbitrarily symmetric molecules, for which in the approximation of Eq. (33) we have, to within pairwise correlations,

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = V \rho b_{\alpha\beta\beta} b_{\alpha\gamma\gamma} + \rho^2 \iint b_{\alpha\beta\beta}^{(p)} b_{\alpha\gamma\gamma}^{(q)} g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (67)$$

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = V \rho b_{\alpha\beta\gamma} b_{\alpha\beta\gamma} + \rho^2 \iint b_{\alpha\beta\gamma}^{(p)} b_{\alpha\beta\gamma}^{(q)} g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q. \quad (68)$$

Taking into account the tensor components $b_{\alpha\beta\gamma}$ appropriate to each point group symmetry [5]—[7], one can apply the expressions (67) and (68) to various experimentally studied cases. Thus *e.g.* in dealing with dipolar molecules, the energy (64) is conveniently replaced by

$$v_{pq} = \mu_\alpha^{(p)} T_{\alpha\beta}^{(pq)} \mu_\beta^{(q)} \quad (69)$$

and on retaining the approximation (63) one gets by Eqs (67) and (68)

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = V_Q b_{\alpha\beta\beta} b_{\delta\gamma\gamma} \left(\delta_{\alpha\delta} + \frac{2\mu^4}{75} \beta^3 \mu_\alpha \mu_\delta R_9 + \dots \right), \quad (70)$$

$$\begin{aligned} \langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = V_Q b_{\alpha\beta\gamma} b_{\delta\epsilon\eta} \left\{ \delta_{\alpha\delta} \delta_{\beta\epsilon} \delta_{\gamma\eta} + \frac{\beta^3}{3675} \mu_\alpha \mu_\delta (57\mu^4 \delta_{\beta\gamma} \delta_{\epsilon\eta} + \right. \\ \left. + 6\delta_{\beta\gamma} \mu^2 \mu_\epsilon \mu_\eta - 5\mu_\beta \mu_\gamma \mu_\epsilon \mu_\eta) R_9 + \dots \right\}. \end{aligned} \quad (71)$$

In particular, for dipolar axially-symmetric molecules the preceding formulae lead to the results (57)—(66) with an accuracy to within β^3 .

Similarly, one can effect calculations of the quantities (67) and (68) with a correlation function (63) containing other types of interactions, thus dipole-quadrupole, dipole-octupole, octupole-octupole interaction, or the like. But these being of rather involved form (see Appendix B), effective calculations tend to become very tedious, and results are intricate. Recently, Bersohn *et al* [7] dealt with the problem, for liquids, by recurring to an approximation which consisted in assuming such a form of the orientational part of the correlation function as to obtain a non-zero result from the averaging procedure, in the first approximation of perturbation calculus (term βv_a). Compared to theirs, the present, dipole model based on Eqs (63) and (69) yields a non-zero contribution only in the third approximation with β^3 .

Now let us consider the expansion of Eq. (46), starting with the assumption that the molecular field $F^{(p)}$ appearing therein is due to odd order electric moments (dipoles, octupoles, *etc.*) Restricting the problem to pairwise correlations, one gets in a satisfactory approximation

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = V_Q (b_{\alpha\beta\beta} b_{\alpha\gamma\gamma} + c_{\alpha\beta\beta\delta} c_{\alpha\gamma\gamma\delta} \langle F_0^2 \rangle), \quad (72)$$

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = V_Q (b_{\alpha\beta\gamma} b_{\alpha\beta\gamma} + c_{\alpha\beta\gamma\delta} c_{\alpha\beta\gamma\delta} \langle F_0^2 \rangle), \quad (73)$$

where with regard to (49) we have (see, Appendix B)

$$\langle F_0^2 \rangle = \frac{2}{3} \mu^2 R_6 + \frac{8}{15} \Omega_{\alpha\beta\gamma} \Omega_{\alpha\beta\gamma} R_{10} + \dots \quad (74)$$

$\Omega_{\alpha\beta\gamma}$ denoting the molecular octupole moment tensor.

For molecules having a quadrupole moment tensor $\Theta_{\alpha\beta}$, one obtains by (46), in place of Eqs (72) and (73),

$$\langle B_{\alpha\beta\beta} B_{\alpha\gamma\gamma} \rangle = V_Q \left\{ b_{\alpha\beta\beta} b_{\alpha\gamma\gamma} + \frac{2}{15} (5c_{\alpha\beta\beta\delta} c_{\alpha\gamma\gamma\delta} \Theta_{\epsilon\eta} \Theta_{\epsilon\eta} - 3c_{\alpha\beta\beta\gamma} \Theta_{\alpha\gamma} c_{\delta\epsilon\epsilon\eta} \Theta_{\delta\eta}) R_8 \right\}, \quad (75)$$

$$\langle B_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \rangle = V_Q \left\{ b_{\alpha\beta\gamma} b_{\alpha\beta\gamma} + \frac{2}{147} (49c_{\alpha\beta\gamma\delta} c_{\alpha\beta\gamma\delta} \Theta_{\epsilon\eta} \Theta_{\epsilon\eta} - 18c_{\alpha\beta\beta\gamma} \Theta_{\alpha\gamma} c_{\delta\epsilon\epsilon\eta} \Theta_{\delta\eta}) R_8 \right\}. \quad (76)$$

This latter result is of interest inasmuch as the expressions (75) and (76) applied to molecules with a centre of inversion as well as a quadrupole moment are non-zero and, in the case of the axial symmetry, take the form

$$\langle B_{\alpha\beta\beta}B_{\alpha\gamma\gamma} \rangle = \frac{25}{3} c^2 V_Q \left(1 - \kappa_c + \frac{19}{125} \kappa_c^2 \right) \Theta^2 R_8, \quad (77)$$

$$\langle B_{\alpha\beta\gamma}B_{\alpha\beta\gamma} \rangle = 5c^2 V_Q \left(1 + \frac{51}{245} \kappa_c^2 \right) \Theta^2 R_8, \quad (78)$$

where $\kappa_c = (c_{3333} - c_{1111})/3c$ defines the anisotropy of third-order nonlinear polarizability.

On inserting (77) and (78) into Eq. (30), the depolarisation ratio results as

$$D_v^{2\omega} = \frac{7 + \kappa_c + \frac{612}{245} \kappa_c^2}{9 \left(7 - \kappa_c + \frac{133}{175} \kappa_c^2 \right)} \cong \frac{1}{9} \left(1 + \frac{2}{7} \kappa_c \right). \quad (79)$$

On neglecting the anisotropy of nonlinear polarizability κ_c , the depolarization ratio amounts to 1/9, which is just the value derived previously from Eq. (51) with $b_{123} = 0$ for atomic substances.

IV. Discussion and conclusions.

The general, semi-macroscopic theory of nonlinear light scattering by isotropic bodies developed in this paper is seen to yield, in a first approximation of the molecular-statistical approach, when no molecular correlations intervene, results that are valid for gases whose atoms or molecules retain their individual optical properties affected only by interaction with the strong electromagnetic field of the light wave. Thus, investigation of second- or higher-order light scattering in gases provides direct information on the nonlinear optical properties of their molecules.

In condensed media such as compressed gases or liquids, nonlinear light scattering is to a larger or lesser extent influenced by various molecular interactions, ultimately leading to the emergence of radial correlation parameters R_n . The latter, as defined by Eq. (43), can be effectively computed only in the case of real gases [19] on the assumption of *e.g.* a general Lennard-Jones potential. In that of liquids, their computation presents difficulties since an analytically given radial correlation function $g(r)$ is not available. Luckily, however, these difficulties can be circumvented if other, actually measurable effects involving the parameters R_n are taken into account. Thus, in studying substances consisting of isotropic, linearly polarizable molecules, the parameter R_6 can be determined from:

(i) the formula for molecular polarisation [20] or molecular refraction [11]

$$R_m = \frac{4\pi}{3} \rho a (1 + 2a^2 R_6), \quad (80)$$

(ii) the formula for the molecular Kerr constant [11] or optical birefringence [21]

$$B_m = \frac{8\pi\rho}{5kT} \alpha^4 R_6, \quad (81)$$

or

(iii) the formula for the depolarisation ratio of linearly scattered light [11]

$$D_u = \frac{12a^2 R_6}{5\rho kT \kappa_T + 14a^2 R_6}, \quad (82)$$

(κ_T being the isothermal compressibility).

Similarly, the other parameters, such as R_8 , R_{10} and so forth, can be determined from the expression for the molecular orientational polarisation of multipolar substances [22]

$$P_m^o = \frac{8\pi\rho\alpha^2}{9kT} \left\{ \Theta_{\alpha\beta} \Theta_{\alpha\beta} R_8 + \frac{4}{5} \Omega_{\alpha\beta\gamma} \Omega_{\alpha\beta\gamma} R_{10} + \frac{4}{7} \Phi_{\alpha\beta\gamma\delta} \Phi_{\alpha\beta\gamma\delta} R_{12} + \dots \right\} \quad (83)$$

if the molecules have only isotropic dipole polarizability α .

Thus, considering separately spherical, quadrupolar, octupolar, and other kinds of molecules, and basing on various measurable effects, one can determine numerically the quantities R_n and hence evaluate the contributions to nonlinear scattering resulting on the assumption of a particular molecular model. One can then make conclusions about the values of molecular multipoles and compare the results with those obtained by other methods, as reviewed recently by Stogryn and Stogryn [23]. In this context, special attention should be drawn to the role of molecular fields in nonlinear scattering. *E.g.* in the case of substances consisting of tetrahedral molecules, the depolarisation ratio does not in the least depend on statistical orientational correlations (thus, with the present model, on the energy of induced dipole-octupole, or octupole-octupole interaction), but is constant, amounting to 2/3. It is only when molecular fields are taken into account that the depolarisation ratio is in general dependent on the density, temperature and molecular structure of the medium as rendered by Eq. (45) or (51). At normal conditions, in CCl_4 , the effect of the molecular field upon $D_v^{2\omega}$ as given by Eq. (45) amounts to several per cent if Eq. (82) is resorted to.

It is a main point of interest that the role of molecular fields is not restricted to contributing quantitative corrections, but that they lead to the emergence of new scattering effects, which otherwise could not be expected to take place. *E.g.* by Eqs (72) and (73) if applied to molecules for which in the ground state $b_{123} = 0$, the anisotropic component of second harmonic scattering (18) and depolarisation ratio (30) is non-zero.

In principle, isolated molecules with a centre of inversion do not (in the absence of mutual interactions) give rise to second harmonic scattering, but can cause third harmonic scattering whose ratio, however, with regard to the one-photon process is of the order of $10^{-24} I^2$. This would be accessible to observation only by using a very strong laser beam ($I \simeq 10^9$ cgs).

Similarly, as seen from Eqs (77) and (78), some amount of second harmonic scattering can occur in liquids of centro-symmetrical molecules if the latter have a permanent quadrupole moment. Significantly, both scattering processes mentioned above are anisotropic and thus depolarize the scattered light nonlinearly.

Although it is too early to make far-reaching conclusions in the present, initial phase of nonlinear light scattering investigation, both experimental and theoretical, it can nevertheless be said with assurance that such studies will provide much interesting information concerning the nonlinear properties of isolated molecules and their mutual correlations in condensed media. Most certainly, the study of multi-photon scattering processes in gases and liquids is a basic factor in the rapid development of nonlinear molecular optics.

APPENDIX A

Averageing of directional cosines

The scattering tensor (2) and dipole moment (3) components are referred to the laboratory axes, which are labelled $\sigma, \tau, \nu \dots$. We introduce another system of coordinate axes, labelled $\alpha, \beta, \gamma, \dots$, mobile and attached to a given point of the body (*e.g.* to the centre of one of its molecules). We next proceed to a transformation of the various tensors in expansion (3) from laboratory to mobile coordinates, as follows:

$$A_{\sigma\tau} = \omega_{\sigma\alpha}\omega_{\tau\beta}A_{\alpha\beta}, \quad B_{\sigma\tau\nu} = \omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}B_{\alpha\beta\gamma}, \dots \quad (\text{A.1})$$

With Cartesian reference frames, the transformation coefficients $\omega_{\sigma\alpha}, \omega_{\tau\beta} \dots$ have the meaning of cosines of the angles between the respective axes and fulfil the orthonormality conditions

$$\omega_{\sigma\alpha}\omega_{\sigma\beta} = \delta_{\alpha\beta} \quad \text{and} \quad \omega_{\sigma\alpha}\omega_{\tau\alpha} = \delta_{\sigma\tau}. \quad (\text{A.2})$$

Thus, in going over from (5), (6) to (7), (8), calculations reduce to the averaging of appropriate products of directional cosines over all possible orientations of the mobile axes with respect to the laboratory axes. For the intensity tensor of linear scattering, the following mean value [24] is relevant:

$$\begin{aligned} \langle \omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\rho\delta} \rangle_{\omega} &= \frac{1}{30} \{ (4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma})\delta_{\sigma\tau}\delta_{\nu\rho} + \\ &+ (4\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta})\delta_{\sigma\nu}\delta_{\tau\rho} + (4\delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta})\delta_{\sigma\rho}\delta_{\tau\nu} \}, \end{aligned} \quad (\text{A.3})$$

which, denoting the components of the unit vector of \mathbf{E} by e_{ν} , yields

$$\langle \omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\rho\delta} \rangle_{\omega} e_{\nu}e_{\rho} = \frac{1}{30} \{ 5\delta_{\alpha\beta}\delta_{\gamma\delta} (\delta_{\sigma\tau} - e_{\sigma}e_{\tau}) + \sigma_{\alpha\beta\gamma\delta} (3 e_{\sigma}e_{\tau} - \delta_{\sigma\tau}) \}, \quad (\text{A.4})$$

where we have used the notation

$$\sigma_{\alpha\beta\gamma\delta} = \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}. \quad (\text{A.5})$$

By means of (A.1) and (A.4), Eq. (5) transforms directly to (7).

Nonlinear second-order scattering as given by the tensor (6) involves the averaging of $\langle \omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\rho\delta}\omega_{\lambda\epsilon}\omega_{\mu\eta} \rangle_{\omega}$. The general result of this averaging procedure is to be found in a previous paper [24], and leads to the here relevant expression

$$\langle \omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\rho\delta}\omega_{\lambda\epsilon}\omega_{\mu\eta} \rangle_{\omega} e_{\nu}e_{\rho}e_{\lambda}e_{\mu} = \frac{1}{210} \{ 7\delta_{\alpha\beta}\sigma_{\gamma\delta\epsilon\eta} (\delta_{\sigma\tau}^{\eta\eta} - e_{\sigma}e_{\tau}) + \sigma_{\alpha\beta\gamma\delta\epsilon\eta} (3 e_{\sigma}e_{\tau} - \delta_{\sigma\tau}) \}, \quad (\text{A.6})$$

where we have introduced the notation

$$\sigma_{\alpha\beta\gamma\delta\epsilon\eta} = \delta_{\alpha\beta\sigma\gamma\delta\epsilon\eta} + \delta_{\alpha\gamma}\sigma_{\delta\epsilon\eta\beta} + \delta_{\alpha\delta}\sigma_{\epsilon\eta\beta\gamma} + \delta_{\alpha\epsilon}\sigma_{\eta\beta\gamma\delta} + \delta_{\alpha\eta}\sigma_{\beta\gamma\delta\epsilon}. \quad (\text{A.7})$$

In this case also, (A.1) together with the mean value (A.6) transforms the tensor (6) into Eq. (8).

APPENDIX B.

Mean square of the fields of molecular multipoles

The discussion given in Section III shows that if anisotropy of nonlinear third-order polarizability is neglected, the effect of the molecular field F_0 on second-order nonlinear scattering is expressed in a first approximation as

$$\langle B_{\alpha\beta\beta}B_{\alpha\gamma\gamma} \rangle_{F_0} = \frac{25}{3} c^2 V_Q \langle F_0^2 \rangle, \quad (\text{B.1})$$

$$\langle B_{\alpha\beta\gamma}B_{\alpha\beta\gamma} \rangle_{F_0} = 5c^2 V_Q \langle F_0^2 \rangle, \quad (\text{B.2})$$

with the mean square of the molecular field defined by (49).

The electric field existing at the centre of molecule p as induced by the electric multipoles of molecule q is [19, 25]

$$\mathbf{F}_0^{(pq)} = \sum_{n=0}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} {}^{(1)}\mathbf{T}_{pq}^{(n)} [n] \mathbf{M}_q^{(n)}, \quad (\text{B.3})$$

where

$$\mathbf{M}_q^{(n)} = \sum_j e_{qj} r_{qj}^n \mathbf{Y}_{qj}^{(n)} \quad (\text{B.4})$$

is the 2^n -pole electric moment of molecule q , which is assumed to consist of charges e_{qi} with radius-vector \mathbf{r}_{qj} ;

$$\mathbf{Y}_{qj}^{(n)} = \frac{(-1)^n}{n!} r_{qj}^{n+1} \nabla^n \left(\frac{1}{r_{qj}} \right) \text{ and } {}^{(1)}\mathbf{T}_{pq}^{(n)} = -\nabla^{1+n} \left(\frac{1}{r_{pq}} \right); \quad (\text{B.5})$$

the symbol $[n]$ in Jansen's notation [25] denotes n -fold contraction of the product of the tensors ${}^{(1)}\mathbf{T}_{pq}^{(n)}$ and $\mathbf{M}_q^{(n)}$.

The square of the field (B.3), averaged over all possible orientations of molecule q with respect to molecule p , amounts to [19]

$$\langle \mathbf{F}_0^{(pq)} \cdot \mathbf{F}_0^{(pq)} \rangle_{\omega} = \sum_{n=0}^{\infty} \frac{2^n (n+1) (n!)^2}{(2n)!} \mathbf{M}_q^{(n)} [n] \mathbf{M}_q^{(n)} r_{pq}^{-2(n+2)}. \quad (\text{B.6})$$

In particular, if the multipolar molecule q is axially-symmetric, Eq. (B.6) reduces to

$$\begin{aligned} \langle \mathbf{F}_0^{(pq)} \cdot \mathbf{F}_0^{(pq)} \rangle_{\omega} &= \sum_{n=0}^{\infty} (n+1) \{M_q^{(n)}\}^2 r_{pq}^{-2(n+2)} \\ &= 2\mu_q^2 r_{pq}^{-6} + 3\Theta_q^2 r_{pq}^{-8} + 4\Omega_q^2 r_{pq}^{-10} + 5\Phi_q^2 r_{pq}^{-12} + \dots, \end{aligned} \quad (\text{B.7})$$

where μ , Θ , Ω , Φ , *etc.* stand for the dipolar, quadrupolar, octupolar, hexadecapolar, *etc.* molecular moment.

In the case when molecule q is tetrahedrally symmetric, the general expression (B.6) becomes

$$\langle \mathbf{F}_0^{(pq)} \cdot \mathbf{F}_0^{(pq)} \rangle_\omega = \frac{48}{5} \Omega_{123}^2 r_{pq}^{-10} + \frac{240}{7} \Phi_{1133}^2 r_{pq}^{-12}. \quad (\text{B.8})$$

Clearly, it would still be desirable to consider how the molecular multipoles affect nonlinear scattering by way of the energy v_{pq} , which appears in the bi-molecular correlation function (63) and is in general defined as follows (on neglecting inductive interactions) [19, 25]:

$$v_{pq} = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^{m+1} \frac{2^{n+m} n! m!}{(2n)! (2m)!} \mathbf{M}_p^{(n)} [n] {}^{(n)}\mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_q^{(m)}. \quad (\text{B.9})$$

However, simple results are obtained in the dipolar approximation only, as seen from (65) and (66).

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