

SECOND-HARMONIC ELECTRIC QUADRUPOLEAR ELASTIC SCATTERING BY ATOMS AND CENTRO-SYMMETRIC MOLECULES

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Atoms and centro-symmetric molecules, for which second-harmonic elastic scattering is forbidden in the electric dipole approximation, are shown to cause double photon scattering in the electric quadrupole approximation. The process is described by a 4-th rank tensor of quadrupolar polarizability $q_{ij,kl}^{2\omega}$ whose non-zero and independent elements are available in tabulated form for all point groups. General formulae are derived for the light intensity components quadrupolarly scattered at 2ω as well as for their depolarization ratios, which are shown to depend on the scattering angle otherwise than in the case of electric dipole scattering. The theory is applied to atomic gases and ones with molecules of simpler symmetry.

1. Introduction

By using light from a giant pulsed ruby laser, Terhune [1] and Maker [2] performed the first observations of second-harmonic scattering (SHS) in liquids consisting of molecules without a centre of symmetry (H_2O , CCl_4 , etc.).

Different aspects of this three-photon scattering process have been elucidated by Blaton [3], Neugebauer [4], Kielich [5], Cyvin *et al.* [6], and Bersohn *et al.* [7]. In the electric-dipole approximation in the absence of molecular correlations, elastic SHS is described by a nonlinear polarizability tensor $b_{ijk}^{2\omega}$ [5] having non-zero elements for molecules without a centre of symmetry.

From the very beginning, Terhune *et al.* [1] noted the presence of weak SHS from the liquid trans-dichloroethylene, the molecules of which are centro-symmetric (in the cis-isomer of $C_2H_2Cl_2$, whose molecules lack a centre of inversion, the intensity was 20 times larger). These facts led Kielich [8] to work out a theory of SHS by centro-symmetric, strongly correlated molecules. SHS by centro-symmetric molecules occurs when, in condensed phases, their symmetry undergoes degradation under the action of the electric fields of

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their neighbours. This new kind of SHS has been studied in detail recently in C_6H_6 and CS_2 by Lalanne, Martin and Kielich [9], who employed ruby and neodymium lasers in their experiment.

In this paper, we show that in the electric-quadrupole approximation even individual centro-symmetric molecules cause SHS. Strictly speaking, this scattering comes from two sources, namely: (i) scattering of the dipole kind albeit induced by inhomogeneities of the electric field of the light wave within a molecule (the electric field gradient of the wave produces a change in dipole polarizability [10, 11]) and (ii) electric-quadrupole scattering (a strong electric field induces electric quadrupole moments). The investigation of this type of scattering in gaseous systems is bound to provide new data on the tensors of quadrupolar polarizability of atoms as well as centro-symmetric molecules.

2. Fundamentals of the theory

We are concerned with the electric and quadrupole radiation fields at a large distance $R = sR$ from the scattering atom or molecule,

$$E_D(R) = \frac{1}{Rc^2} \{s \times (s \times \ddot{D})\}_{t-R/c}, \quad (1)$$

$$E_Q(R) = \frac{1}{3Rc^3} \{s \times [s \times (\ddot{Q})]\}_{t-R/c}, \quad (2)$$

where the electric dipole moment and electric quadrupole tensor of the molecule are, by definition:

$$D = \sum_v e_v r_v, \quad (3)$$

$$Q = \frac{1}{2} \sum_v e_v (3r_v r_v - r_v^2 U), \quad (4)$$

e_v is the v -th electric charge with radius vector r_v , and U the symmetric unit tensor.

We define the intensity of light scattered with oscillations given by the unit vector n (such that $n \cdot s = 0$) by a medium of number density ϱ as follows:

$$I_n = \varrho \langle [E(R) \cdot n]^2 \rangle_{\Omega, t}. \quad (5)$$

The averaging has to be performed here over all possible molecular orientations Ω and time t .

On inserting (1) and (2) into (5), we obtain respectively for the intensities of electric dipolar and electric quadrupolar scattering [12]:

$${}^D I_n = \frac{\varrho}{R^2 c^4} \langle \ddot{D}_i \ddot{D}_j n_i n_j \rangle_{\Omega, t}, \quad (6)$$

$${}^Q I_n = \frac{\varrho}{9R^2 c^6} \langle \ddot{Q}_{ik} \ddot{Q}_{jl} n_i n_j s_k s_l \rangle_{\Omega, t}. \quad (7)$$

It is our aim to calculate the intensities of SHS caused by an intense electric field of strength

$$\mathbf{E}(r, t) = \mathbf{e}E(r) \cos \omega t,$$

where \mathbf{e} is a unit vector in the field direction \mathbf{E} .

The components of the electric dipole moment D_i and quadrupole tensor moment Q_{ij} , induced in the molecule at the frequency 2ω , are [11]

$$D_i^{2\omega} = \frac{1}{2} \left\{ \frac{1}{2} b_{ijk}^{2\omega} E_j(r) E_k(r) + \frac{1}{3} q_{ij,kl}^{2\omega} E_j(r) E_k(r) + \dots \right\} \cos 2\omega t, \quad (8)$$

$$Q_{ij}^{2\omega} = \frac{1}{4} q_{kl,ij}^{2\omega} E_k(r) E_l(r) \cos 2\omega t + \dots, \quad (9)$$

where $b_{ijk}^{2\omega}$ is the tensor of nonlinear dipole polarizability of order 2 induced by the square of a uniform electric field, E^2 . The tensor $q_{ij,kl}^{2\omega}$ describes quadrupolar nonlinear polarizability of order 2.

In the case of molecules without a centre of symmetry there exist non-zero tensor elements $b_{ijk}^{2\omega}$, and we deal with the intense dipole-dipole SHS discussed in detail in earlier papers [5–7]. For molecules with a centre of inversion in their ground state all $b_{ijk}^{2\omega}$ vanish and, in the above approximation, SHS is forbidden. Nevertheless, for centro-symmetric molecules too, SHS is allowed in the quadrupolar approximation described by the tensor $q_{ij,kl}^{2\omega}$ having, for the ground state also, non-zero tensor elements irrespective of the type of symmetry, including the spherical symmetry. The non-zero and mutually independent elements of the quadrupole-polarizability tensor $q_{ij,kl}^{2\omega}$ are listed in Table I for all point groups.

By inserting the expansion (8) into (6), and (9) into (7), we obtain for dipolar SHS (in the quadrupole approximation) and quadrupolar SHS (in the dipole approximation):

$${}^D I_n(2\omega) = K_{2\omega} q_{in,mk}^{2\omega} q_{jp,ol}^{2\omega} \langle n_i n_j s_k^0 s_l^0 e_m e_n e_o e_p \rangle_\Omega, \quad (10)$$

$${}^Q I_n(2\omega) = K_{2\omega} q_{mn,ik}^{2\omega} q_{op,jl}^{2\omega} \langle n_i n_j s_k^0 s_l^0 e_m e_n e_o e_p \rangle_\Omega. \quad (11)$$

Above, we have introduced the notation $K_{2\omega} = \left(\frac{2\omega}{c}\right)^6 \frac{Q I^2}{72 R^2}$ and assumed the incident light intensity as $I = E_0^2/2$. s^0 is the unit vector in the propagation direction of the incident beam ($s^0 \cdot \mathbf{e} = 0$).

3. Electric quadrupole scattering by individual molecules

Note that in Eq. (10), as compared with (11), we have performed a pairwise interchange of indices: $k \leftrightarrow n$ and $l \leftrightarrow p$, so as to conform to the order of indices in Eqs (8) and (9). We thus achieve a simplification of the results of isotropic averaging.

The averaging procedures in both (10) and (11) are identical. The general result for the product $n_i n_j p_k p_l e_m e_n e_o e_p$ is given in the Appendix. For dipole radiation, we have to insert $\mathbf{p} = \mathbf{s}^0$ and $\mathbf{s}^0 \cdot \mathbf{e} = 0$; for quadrupole radiation $\mathbf{p} = \mathbf{s}$ and $\mathbf{s} \cdot \mathbf{n} = 0$.

Consider specifically the case with \mathbf{s}^0 parallel to the y -axis and observation taking place in the xy -plane in a direction subtending an angle ϑ with \mathbf{s}^0 . The laboratory xyz

TABLE I

Non-zero and independent elements of the quadrupole hyper-polarizability tensor $q_{ij,kl}$ for all point groups

Group	Number of non-zero elements	Number of independent elements	Elements of $q_{ij,kl}$ (denoted only by their subscripts $i, j, k, l = x, y, z$)
C_1 and $C_i(S_2)$	81	30	$A = xxxx = -(xxyy + xxzz), yyyz = -(yxxz + yzzz), zzzz = -(zzxx + zzyy),$ $xyyx = xxyx = yxyx = yxxz = xzzx = zxxx = zzzz = zzyz = zyzy = zyyz;$ $B = xyzz = yxzz = -(xyyy + yxxx), xyyz = yxyy, yxxx = xyxx, yyyx = yxyx, xxxy = xxyx,$ $zzyx = zzxy, xzzy = xzyz = zxyx = zxyz, yzzx = yzxx = zyxz = zyxz;$ $C = xzpy = zxyy = -(xzxx + zxxx), yzxx = zyxz = -(yzzz + zpyy), xzzz = zxxx, zxxx = xzxx,$ $yzzz = zyzz, zyyy = yzyy, xxyz = xxzy, zzzz = zzzz, xxxz = xzzx, zzzz = zzyz, yyyz = yzyy,$ $yyxz = yyxz, xyyz = xyzy = yxzy, zyyx = zyxy = yzyx = yzxy,$ $yxxz = yxzx = xyxz = xyzx, zxyx = xzyx = xzxy = xzyx;$
C_2, C_3 and C_{2h}	41	16	A and B
C_{2v}, D_2 and D_{2h}	21	9	A
C_4, S_4 and C_{4h}	37	8	$D = xxxx = yyyz = -(xxyy + xxzz), zzzz = -(zxxx + zzyy), xxyy = yxxx, xzzz = yvzz, zxxx = zzyy,$ $xyyx = xxyx = yxyx = yxxz = xzzx = zxxx = zzzz = zzyz = zyzy = zyyz = zyyz;$ $E = xxxy = xxyx = -yyyz = -yxyx, xyyy = yxyy = -yxxy = -yxxy = -xyxx,$ $xzzy = xzyz = zxyx = zyxz = -yzzz = -yzzz = -zyzx = -zyzx;$

C_{4v}, D_4, D_{2d} and D_{4h}	21	5	D
C_3 and S_6	69	10	$F = xxxx = yyyy = -(xxyy + xxzz), zzzz = -(zzxx + zzyy), xxzz = yzzz = -2(xxyy + xyyx),$ $xyyy = yyxx, zxxx = zzyy, xyxx = xpyx = yxyx = yxyx,$ $xxxx = xxzx = zxzx = zxxz = yzyz = zyzy = zyyz;$ $G = xxyy = xpyx = -yyyx = -yyxy = xpyy = yxyy = -yxxx = -xyxx,$ $zzzy = xzyz = zxyx = xpyz = -yzzx = -yxzx = -zyzx = -zyxz;$ $H = xzyy = zpyx = zpyx = yzyx = yzxy = -zxxx = -zxzx,$ $yxxz = yyzx = xpyz = yxyx = yxyx = -xxxx = -xxzx;$ $J = yzxx = zpyx = zpyx = xzyx = xzyx = -zyyy = -zyyy,$ $xxyz = xxzy = yxxz = yxxz = xpyz = xpyz = -yyyz = -yyyz;$
C_{3v}, D_3 and D_{3d}	37	6	F and J
C_6, C_{3h}, C_{6h} C_{∞} and $C_{\infty h}$	37	6	F and G
$D_6, C_{6v}, D_{3h},$ $D_{6h}, C_{\infty v}$ and $D_{\infty h}$	21	4	F
T and T_h	21	3	$xxxx = yyyz = zzzz = -(xxyy + xxzz), xxyy = yzzz = zxxx, xxzz = zzyy = yyxx,$ $xpyx = xpyx = yxyx = yxyx = xzzx = xzzx = zxxz = yzyz = yzyz = zyyz;$
T_d, O and O_h	21	2	$xxxx = yyyz = zzzz = -(xxyy + xxzz), xxyy = yzzz = zxxx = zzyy = yyxx,$ $xpyx = xpyx = yxyx = yxyx = xzzx = xzzx = zxxz = yzyz = yzyz = zyyz;$
Y, Y_h, K and K_h	21	1	$xxxx = yyyz = zzzz = -(xxyy + xxzz),$ $xpyx = xpyx = yxyx = yxyx = xzzx = xzzx = zxxz = yzyz = yzyz = zyyz =$ $= zyyz = -\frac{2}{3}xxyy = -\frac{2}{3}yxyx = -\frac{2}{3}xxzz = -\frac{2}{3}zxxx = -\frac{2}{3}yzzz = -\frac{2}{3}zzyy.$

co-ordinate system is rigidly attached to the centre of the scattering volume. With this configuration, we can distinguish the following four situations: the unit vector \mathbf{e} can be assumed to be parallel to x or to z , and similarly, the unit vector \mathbf{n} can be parallel or perpendicular to the xy -plane. These yield the 4 components of scattered light H_v, V_v, H_h, V_h , where the subscript (v stands for vertical and h for horizontal) describes the state of polarization of the incident light wave relative to the plane of observation.

For dipole radiation, we have

$${}^D H_v^{2\omega} : \mathbf{n} \cdot \mathbf{e} = 0, \quad (\mathbf{n} \cdot \mathbf{s}^0)^2 = \sin^2 \vartheta; \quad {}^D H_h^{2\omega} : (\mathbf{n} \cdot \mathbf{e})^2 = \cos^2 \vartheta, \quad (\mathbf{n} \cdot \mathbf{s}^0)^2 = \sin^2 \vartheta, \quad (12)$$

$${}^D V_v^{2\omega} : (\mathbf{n} \cdot \mathbf{e})^2 = 1, \quad \mathbf{n} \cdot \mathbf{s}^0 = 0; \quad {}^D V_h^{2\omega} : \mathbf{n} \cdot \mathbf{e} = \mathbf{n} \cdot \mathbf{s}^0 = 0,$$

and for quadrupole radiation

$$\begin{aligned} {}^Q H_v^{2\omega} : \mathbf{n} \cdot \mathbf{e} = \mathbf{s} \cdot \mathbf{e} = 0; \quad {}^Q H_h^{2\omega} : (\mathbf{n} \cdot \mathbf{e})^2 = \cos^2 \vartheta, \quad (\mathbf{s} \cdot \mathbf{e})^2 = \sin^2 \vartheta, \\ {}^Q V_v^{2\omega} : (\mathbf{n} \cdot \mathbf{e})^2 = 1, \quad \mathbf{s} \cdot \mathbf{e} = 0; \quad {}^Q V_h^{2\omega} : \mathbf{n} \cdot \mathbf{e} = 0, \quad (\mathbf{s} \cdot \mathbf{e})^2 = \sin^2 \vartheta. \end{aligned} \quad (13)$$

With regard to (A.2) and (10) and the previously stated conditions Eq. (12) yields:

$${}^D V_h^{2\omega} = \frac{K_{2\omega}}{7560} \Delta_{ijklmnop} q_{in,mk}^{2\omega} q_{jp,ol}^{2\omega}$$

$${}^D V_v^{2\omega} = \frac{K_{2\omega}}{1890} \{9\delta_{kl}\sigma_{idmnp} - \sigma_{ijklmnop}\} q_{in,mk}^{2\omega} q_{jp,ol}^{2\omega} \quad (14)$$

$${}^D H_h^{2\omega}(\vartheta) = {}^D V_v^{2\omega} + \left\{ \frac{K_{2\omega}}{210} (7\delta_{ij}\delta_{kl}\sigma_{mnop} - \delta_{ij}\sigma_{klmnop}) q_{in,mk}^{2\omega} q_{jp,ol}^{2\omega} - {}^D V_h^{2\omega} - 2{}^D V_v^{2\omega} \right\} \sin^2 \vartheta,$$

$${}^D H_v^{2\omega}(\vartheta) = {}^D H_h^{2\omega}(\vartheta) + ({}^D V_h^{2\omega} - {}^D V_v^{2\omega}) \cos^2 \vartheta,$$

where we have used the notation:

$$\begin{aligned} \Delta_{ijklmnop} = 252\delta_{ij}\delta_{kl}\sigma_{mnop} - 63\sigma_{ijkl}\sigma_{mnop} + 27\delta_{ij}\sigma_{klmnop} - 27\delta_{kl}\sigma_{idmnp} + \sigma_{ijklmnop} + \\ + 9\delta_{ik}\sigma_{jlmnp} + 9\delta_{il}\sigma_{jkmnp} + 9\delta_{jk}\sigma_{ilmnp} + 9\delta_{jl}\sigma_{ikmnp}. \end{aligned}$$

For quadrupole radiation, with regard to (A.2) and (13), we obtain from Eq. (11):

$${}^Q H_v^{2\omega} = \frac{K_{2\omega}}{7560} \Delta_{ijklmnop} q_{mn,ik}^{2\omega} q_{op,jl}^{2\omega}$$

$${}^Q V_v^{2\omega} = \frac{K_{2\omega}}{1890} \{9\delta_{kl}\sigma_{ijmnp} - \sigma_{ijklmnop}\} q_{mn,ik}^{2\omega} q_{op,jl}^{2\omega} \quad (15)$$

$${}^Q V_h^{2\omega}(\vartheta) = {}^Q V_v^{2\omega} + ({}^Q H_v^{2\omega} - {}^Q V_v^{2\omega}) \cos^2 \vartheta,$$

$${}^Q H_h^{2\omega}(\vartheta) = {}^Q V_v^{2\omega} + \frac{K_{2\omega}}{7560} \sin^2 \vartheta \cos^2 \vartheta \Omega_{ijklmnop} q_{mn,ik}^{2\omega} q_{op,jl}^{2\omega}$$

where, in deriving the form of ${}^QV_h^{2\omega}(\vartheta)$ and ${}^QH_h^{2\omega}(\vartheta)$, we made use of the obvious fact that the combinations $\delta_{ij}\sigma_{klmnop}$ and $\delta_{kl}\sigma_{ijmnop}$, acting on the tensor product $q_{mn,ik}^{2\omega}q_{op,jl}^{2\omega}$, yield the same result, whereas the tensor $\Omega_{ijklmnop}$ is of the form:

$$\begin{aligned}\Omega_{ijklmnop} = & 63\sigma_{ijkl}\sigma_{mnop} + 35\sigma_{ijklmnop} - 90\delta_{kl}\sigma_{ijmnop} - 45\delta_{ik}\sigma_{jlmnop} - 45\delta_{il}\sigma_{jkmnop} - \\ & - 45\delta_{jk}\sigma_{ilmnop} + 45\delta_{jl}\sigma_{ikmnop}.\end{aligned}$$

From Eqs (14) and (15), we derive the following reciprocity relations between the components:

$${}^D V_v^{2\omega} = {}^D H_h^{2\omega}(0^\circ), \quad {}^D V_h^{2\omega} = {}^D H_v^{2\omega}(0^\circ), \quad {}^D H_v^{2\omega}(90^\circ) = {}^D H_h^{2\omega}(90^\circ), \quad (16a)$$

$${}^Q H_v^{2\omega} = {}^Q V_h^{2\omega}(0^\circ), \quad {}^Q V_v^{2\omega} = {}^Q H_h^{2\omega}(90^\circ) = {}^Q H_h^{2\omega}(90^\circ) = {}^Q H_h^{2\omega}(0^\circ). \quad (16b)$$

These reciprocity relations obviously differ from those of Krishnan, which hold for dipole radiation due to the square of an electric field and have the well-known form [8, 13]

$${}^D H_v^{2\omega} = {}^D V_h^{2\omega} = {}^D H_h^{2\omega}(90^\circ).$$

The formulae quite generally derived above for the intensity of scattered light can be particularized for various molecular symmetries. To achieve this, the relations between the non-zero elements of the quadrupole hyper-polarizability tensor $q_{ij,kl}^{2\omega}$ have to be available. These relations have been found by standard methods of group theory [14] and are listed in Table I.

4. Application and discussion

In atoms and molecules possessing icosahedral symmetry, the tensor $q_{ij,kl}^{2\omega}$ has but one independent tensor element and takes the form [11]

$$q_{ij,kl}^{2\omega} = \frac{1}{4} q_{2\omega} [3(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - 2\delta_{ij}\delta_{kl}], \quad (17)$$

where the parameter $q_{2\omega} = \frac{2}{15} q_{ij,ij}^{2\omega}$ is the mean hyper-polarizability; in the present case $q_{2\omega} = q_{zzzz}^{2\omega}$.

Insertion of (17) into Eqs (14) and (15) transforms them into:

$${}^D V_v^{2\omega} = {}^D V_h^{2\omega} = {}^Q H_v^{2\omega} = {}^Q V_v^{2\omega} = {}^Q V_h^{2\omega}(\vartheta) = 0,$$

$${}^D H_v^{2\omega}(\vartheta) = {}^D H_h^{2\omega}(\vartheta) = \left(\frac{2\omega}{c}\right)^6 \frac{\varrho I^2}{128R^2} q_{2\omega}^2 \sin^2 \vartheta,$$

$${}^Q H_h^{2\omega}(\vartheta) = \left(\frac{2\omega}{c}\right)^6 \frac{\varrho I^2}{32R^2} q_{2\omega}^2 \sin^2 \vartheta \cos^2 \vartheta. \quad (18)$$

The two kinds of radiation under discussion can be easily distinguished from one another owing to the circumstance that the component $H_v^{2\omega}$ has its source in dipole radiation exclusively. A supplementary factor helping to distinguish between them is to be found in the different angular dependences of the components $H_h^{2\omega}$.

For molecules having the symmetry O_h , the tensor $q_{ij,kl}^{2\omega}$ presents the two independent tensor elements $q_{zzzz}^{2\omega}$ and $q_{zzzx}^{2\omega}$, and takes the form:

$$q_{ij,kl}^{2\omega} = \frac{1}{4} q_{2\omega} [3(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - 2\delta_{ij}\delta_{kl}] + \frac{1}{2} q_{2\omega} \kappa_q [5(\hat{x}_i\hat{x}_j\hat{x}_k\hat{x}_l + \hat{y}_i\hat{y}_j\hat{y}_k\hat{y}_l + \hat{z}_i\hat{z}_j\hat{z}_k\hat{z}_l) - \sigma_{ijkl}], \quad (19)$$

where $q_{2\omega} = \frac{2}{5}(q_{zzzz}^{2\omega} + 2q_{zzzx}^{2\omega})$ and κ_q is a dimensionless anisotropy parameter, $\kappa_q = \frac{3q_{zzzz}^{2\omega} - 4q_{zzzx}^{2\omega}}{5q_{2\omega}}$.

The unit vectors \hat{x} , \hat{y} , \hat{z} point in the directions of the axes x , y , z of laboratory co-ordinates. For dipolar scattering by (19) in the quadrupole approximation, Eqs (14) and (15) yield:

$$\begin{aligned} {}^D V_v^{2\omega} &= 2^D V_h^{2\omega} = \left(\frac{2\omega}{c}\right)^6 \frac{5\rho I^2}{3024R^2} q_{2\omega}^2 \kappa_q^2, \\ {}^D H_h^{2\omega}(\vartheta) &= \left(\frac{2\omega}{c}\right)^6 \frac{\rho I^2}{24192R^2} q_{2\omega}^2 [40\kappa_q^2 + 7(27 - \frac{4}{7} \kappa_q^2) \sin^2 \vartheta], \\ {}^D H_v^{2\omega}(\vartheta) &= \left(\frac{2\omega}{c}\right)^6 \frac{\rho I^2}{24192R^2} q_{2\omega}^2 [20\kappa_q^2 + (189 + 1 \frac{1}{6} \kappa_q^2) \sin^2 \vartheta], \end{aligned} \quad (20)$$

whereas for quadrupolar scattering in the dipole approximation:

$$\begin{aligned} {}^Q V_v^{2\omega} &= 2^Q H_v^{2\omega} = \left(\frac{2\omega}{c}\right)^6 \frac{5\rho I^2}{3024R^2} q_{2\omega}^2 \kappa_q^2, \\ {}^Q V_h^{2\omega}(\vartheta) &= \left(\frac{2\omega}{c}\right)^6 \frac{5\rho I^2}{6048R^2} q_{2\omega}^2 \kappa_q^2 (2 - \cos^2 \vartheta), \\ {}^Q H_h^{2\omega}(\vartheta) &= \left(\frac{2\omega}{c}\right)^6 \frac{\rho I^2}{6048R^2} q_{2\omega}^2 [10\kappa_q^2 + (189 + \kappa_q^2) \sin^2 \vartheta \cos^2 \vartheta]. \end{aligned} \quad (21)$$

It may be worth noting that for $\kappa_q = 0$, *i.e.* for $q_{zzzx}^{2\omega} = \frac{3}{4} q_{zzzz}^{2\omega}$, formulae (20) and (21) reduce to the relations (18).

Similar calculations can be effected for other symmetries. Obviously, these will involve other elements of the hyper-polarizability tensor.

In the analysis of scattered light it is convenient to resort to depolarization ratios. Since we are dealing here with two kinds of scattering of similar magnitude, the depolarization can be defined for both simultaneously or for each separately. Using Krishnan's definition $D_v = H_v/V_v$ and $D_h = V_h/H_h$, this can be done easily by resorting to the relations (14) and (15) or, with regard to the symmetries considered here, to Eqs (18), (20) and (21).

We shall now assess the ratio of quadrupole second-harmonic intensity ${}^Q I(2\omega)$ and usual linear intensity ${}^D I(\omega)$ numerically. In particular, for a gas, we have the Rayleigh

formula, ${}^D I(\omega) \approx \left(\frac{\omega}{c}\right)^4 a_\omega^2 I$, where a_ω is the linear polarizability of the atom. Omitting any consideration of the polarization state and angular dependences, we have for atomic gases the approximate formula [11]

$$\frac{{}^Q I(2\omega)}{{}^D I(\omega)} \approx \frac{1}{4} \left(\frac{2\omega}{c}\right)^2 \left(\frac{q_{2\omega}}{a_\omega}\right)^2 I.$$

For xenon, $a_\omega = 4.11 \times 10^{-24} \text{ cm}^3$ and [16] $q = -1.08 \times 10^{-38}$ e. s. u. whence

$$\frac{{}^Q I(2\omega)}{{}^D I(\omega)} \approx 10^{-27} \lambda^{-2} I.$$

At the ruby laser wavelength ($\lambda = 6943 \text{ \AA}$), the ratio of these intensities is of the order of $10^{-19} I$, which is too low for experimental detection. The only hope of detecting the effect in atomic gases lies in strong UV lasers and future lasers operating in the X-ray region.

Let us now make an assessment of the ratio of electric quadrupole scattering ${}^Q I(2\omega)$ and dipole scattering ${}^D I(b_{ijk}^{2\omega})$. In the case of tetrahedrally symmetric molecules, this ratio is approximately

$$\frac{{}^Q I(2\omega)}{{}^D I(2\omega)} \approx \frac{35}{192} \left(\frac{2\omega}{c}\right)^2 \left(\frac{q_{2\omega}}{b_{123}^{2\omega}}\right)^2,$$

where $b_{123}^{2\omega}$ is the only non-zero tensor element $b_{ijk}^{2\omega}$ for the symmetry T_d . For methane, $b_{123}^{2\omega} = 10^{-32}$ e. s. u. [17] and $q = -1.2 \times 10^{-38}$ e. s. u. [18], whence

$$\frac{{}^Q I(2\omega)}{{}^D I(2\omega)} \approx 10^{-11} \lambda^{-2}.$$

In the visible range, the above ratio is of the order of several per cent, but grows for UV and shorter wavelengths.

Obviously, the role of SHS increases in the case of strongly quadrupolar molecules (like CS_2) and macromolecules of dimensions smaller than the incident wavelength.

APPENDIX

The result of isotropic averaging of the 8-th rank tensor $n_i n_j p_k p_l e_m e_n e_o e_p$ over all possible directions of the vectors \mathbf{n} , \mathbf{p} and \mathbf{e} with respect to the laboratory axes xyz has to be expressed in terms of appropriate combinations of the unit tensor $\delta_{ij}, \delta_{kl}, \delta_{mn}, \delta_{op} \dots$. This can be written as follows:

$$\begin{aligned} \langle n_i n_j p_k p_l e_m e_n e_o e_p \rangle_\Omega = & A_1 \delta_{ij} \delta_{kl} \sigma_{mnop} + A_2 \sigma_{ijkl} \sigma_{mnop} + A_3 \delta_{ij} \sigma_{klmnop} + A_4 \delta_{kl} \sigma_{ijmnop} + \\ & + A_5 \sigma_{ijklmnop} + A_6 [\delta_{ik} \sigma_{jlmnop} + \delta_{il} \sigma_{jkmnop} + \delta_{jk} \sigma_{ilmnop} + \delta_{jl} \sigma_{ikmnop}]. \end{aligned} \quad (\text{A.1})$$

In establishing the final form of (A.1), we resorted to the pairwise equivalence of the indices

i and j ; k and l ; m and n ; and o and p ; in other words, to the equality of the respective expansion coefficients.

The tensor $\sigma_{ijklmnop}$ consists of seven permutational combinations of the form $\delta_{ij}\sigma_{klmnop}$, and the tensor σ_{klmnop} of five combinations of the form $\delta_{kl}\sigma_{mnop}$. Hence, finally,

$$\sigma_{mnop} = \delta_{mn}\delta_{op} + \delta_{mo}\delta_{np} + \delta_{mp}\delta_{no}.$$

By consecutive contraction of the tensor (A.1) in the pairs of indices $i = j$; $k = l$, $m = n$; $o = p$; and $i = k$; $j = l$; $m = n$; $o = p$; ... etc., and keeping in mind that

$$n_i p_i = \mathbf{n} \cdot \mathbf{p}, \quad n_i e_i = \mathbf{n} \cdot \mathbf{e}, \quad p_i e_i = \mathbf{p} \cdot \mathbf{e},$$

and $n_i n_i = p_i p_i = e_i e_i = 1$,

we obtain a set of 6 equations for the coefficients $A_1 \dots A_6$, the solutions of which, inserted into (A.1), yield:

$$\begin{aligned} \langle n_i n_j p_k p_l e_m e_n e_o e_p \rangle_\Omega = & \frac{1}{7560} \{ 252 [1 - (\mathbf{n} \cdot \mathbf{p})^2 - (\mathbf{n} \cdot \mathbf{e})^2 - (\mathbf{p} \cdot \mathbf{e})^2 + \\ & + 2(\mathbf{n} \cdot \mathbf{p})(\mathbf{n} \cdot \mathbf{e})(\mathbf{p} \cdot \mathbf{e})] \delta_{ij} \delta_{kl} \sigma_{mnop} + 63 [-1 + 2(\mathbf{n} \cdot \mathbf{p})^2 + (\mathbf{n} \cdot \mathbf{e})^2 + (\mathbf{p} \cdot \mathbf{e})^2 + \\ & + (\mathbf{n} \cdot \mathbf{e})^2 (\mathbf{p} \cdot \mathbf{e})^2 - 4(\mathbf{n} \cdot \mathbf{p})(\mathbf{n} \cdot \mathbf{e})(\mathbf{p} \cdot \mathbf{e})] \sigma_{ijkl} \sigma_{mnop} + 9 [-3 + 2(\mathbf{n} \cdot \mathbf{p})^2 + \\ & + 7(\mathbf{n} \cdot \mathbf{e})^2 + 3(\mathbf{p} \cdot \mathbf{e})^2 - 5(\mathbf{n} \cdot \mathbf{e})^2 (\mathbf{p} \cdot \mathbf{e})^2 - 4(\mathbf{n} \cdot \mathbf{p})(\mathbf{n} \cdot \mathbf{e})(\mathbf{p} \cdot \mathbf{e})] \delta_{kl} \sigma_{ijmnop} \\ & + 9 [-3 + 2(\mathbf{n} \cdot \mathbf{p})^2 + 3(\mathbf{n} \cdot \mathbf{e})^2 + 7(\mathbf{p} \cdot \mathbf{e})^2 - 5(\mathbf{n} \cdot \mathbf{e})^2 (\mathbf{p} \cdot \mathbf{e})^2 - 4(\mathbf{n} \cdot \mathbf{p})(\mathbf{n} \cdot \mathbf{e})(\mathbf{p} \cdot \mathbf{e})] \delta_{ij} \sigma_{klmnop} \\ & + [1 + 2(\mathbf{n} \cdot \mathbf{p})^2 - 5(\mathbf{n} \cdot \mathbf{e})^2 - 5(\mathbf{p} \cdot \mathbf{e})^2 + 35(\mathbf{n} \cdot \mathbf{e})^2 (\mathbf{p} \cdot \mathbf{e})^2 + \\ & - 20(\mathbf{n} \cdot \mathbf{p})(\mathbf{n} \cdot \mathbf{e})(\mathbf{p} \cdot \mathbf{e})] \sigma_{ijklmnop} + 9 [1 - 2(\mathbf{n} \cdot \mathbf{p})^2 - (\mathbf{n} \cdot \mathbf{e})^2 - (\mathbf{p} \cdot \mathbf{e})^2 + \\ & - 5(\mathbf{n} \cdot \mathbf{e})^2 (\mathbf{p} \cdot \mathbf{e})^2 + 8(\mathbf{n} \cdot \mathbf{p})(\mathbf{n} \cdot \mathbf{e})(\mathbf{p} \cdot \mathbf{e})] [\delta_{ik} \sigma_{jlmnop} + \delta_{il} \sigma_{jkmnop} + \\ & + \delta_{jk} \sigma_{ilmnop} + \delta_{jl} \sigma_{ikmnop}] \}. \end{aligned} \quad (\text{A.2})$$

The preceding result can easily be checked by putting $\mathbf{p} = \mathbf{e}$. The result obtained in this way coincides with the earlier [15] result of $\langle n_i n_j e_k e_l e_m e_n e_o e_p \rangle_\Omega$ for third-harmonic dipole scattering.

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