

COOPERATIVE SECOND HARMONIC LASER LIGHT SCATTERING IN LIQUID CYCLOHEXANE, BENZENE AND CARBON DISULPHIDE

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Abstract. Using a Q -switched Nd: glass laser with a high transmission optical system, first measurements of cooperative second harmonic light scattering (SHLS) in liquid cyclohexane, benzene and carbon disulphide were performed. Molecular-statistical theory is extended to show that cooperative SHLS by liquids consisting of centro-symmetric molecules is due to a lowering of their symmetry by the time and space fluctuating electric field of the quadrupoles and hexadecapoles of near neighbouring molecules. Also, the rôle of angular molecular correlations as well as of anisotropy in third-order nonlinear polarisability of the scattering molecules is discussed.

1. Introduction

Second harmonic scattering (SHS) of light by gases [1, 2] and liquids [3, 4] is now an experimental method for the measurement of second-order nonlinear polarisabilities of non-centrosymmetric molecules [5, 6] and of third-order nonlinear polarisabilities of centrosymmetric ones [7]. The process of SHS consists of the following: two photons, of fundamental frequency ω , are incident on a molecule, which scatters elastically a single photon at the doubled frequency 2ω [1, 5] or, inelastically, a photon at frequency $2\omega \pm \omega_M$ [1], where ω_M is a frequency specific to the molecule or medium. Gases give rise to a two-photon scattering which is incoherent [1, 3] and extremely sensitive to the molecular symmetry; this scattering can take place if the molecule does not possess a centre of symmetry. In addition liquids give rise to coherent scattering due to orientational correlations of the molecules [3, 4, 8]. The part played by angular molecular correlations in nonlinear two-photon scattering is similar to the one they fulfill with regard to linear Rayleigh scattering by liquids [9, 10].

Our earlier observations [7] in liquids consisting of centrosymmetric molecules revealed a co-operative double-photon scattering due to fluctuations of electric molecular fields in regions of near-range ordering [4, 11]. This novel scattering permits the determination of third-order molecular polarisability [7] and near neighbourhood structure. In the present paper, we propose a complete theory of this co-operative scattering taking into account, beside radial molecular fields, the angular fields leading additionally to a nonlinear, anisotropic scattering.

In our earlier measurements, we used [7] a ruby laser with the device described in Ref. [12]. Here, with the aim of observing SHS in benzene and CS₂, we had to resort to a *Q*-switched Nd:glass laser and to a modified version of the device [12].

2. Fundamentals of the Theory in Semi-Macroscopic Treatment

Consider, in a continuous isotropic medium of refractive index n_0 , a macroscopic spherical sample of volume V and index n . Let $\mathbf{E}(\mathbf{r}, \omega) = \mathbf{E}(r) \cos \omega t$, denote the electric vector of a light wave oscillating at circular frequency ω at the space point r and propagating from the medium surrounding the sample. Generally, the macroscopic field within the sample, $\mathbf{E}^M(r, \omega)$, will differ from the field $\mathbf{E}(r, \omega)$ existing outside it, and one has:

$$\mathbf{E}^M(r, \omega) = \frac{3n_0^2}{n_\omega^2 + 2n_0^2} \mathbf{E}(r, \omega), \quad (1)$$

n_ω denoting the index of the sample measured at frequency ω . If the surrounding medium is a gas or vacuum, one writes $n_0 = 1$ in Equation (1).

At sufficiently high intensity of the light incident on V , linear scattering at the incident frequency ω (we consider the elastic Rayleigh case only) will be accompanied by various nonlinear scattering processes at the harmonic frequencies $2\omega, 3\omega$, etc. [11]. Considering only SHS of the electric dipole kind in the wave zone, one has the following tensor of intensity scattered at frequency 2ω [4]:

$$I_{ij}^{2\omega} = \frac{1}{2c^4 V} \left\langle \frac{d^2 M_i^{2\omega}}{dt^2} \left(\frac{d^2 M_j^{2\omega}}{dt^2} \right)^* \right\rangle, \quad (2)$$

where the brackets $\langle \rangle$ stand for the appropriate statistical averaging.

The electric dipole moment $M_i^{2\omega}$, induced in V at the frequency 2ω , can be written thus:

$$M_i^{2\omega} = \frac{h_{2\omega}}{4} B_{ijk}^{2\omega} E_j^M(\omega) E_k^M(\omega), \quad (3)$$

with summation extending over the twice occurring indices i and k . In (3), we have introduced the following macroscopic factor:

$$h_{2\omega} = \left(\frac{n_{2\omega}^2 + 2n_0^2}{3n_0^2} \right) \left(\frac{n_\omega^2 + 2n_0^2}{3n_0^2} \right)^2, \quad (4)$$

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

In Equation (3), the third-rank tensor $B_{ijk}^{2\omega} = B_{ijk}(-2\omega, \omega, \omega)$ defines the second-order polarisability of the sample, studied at frequency 2ω , and describes the optical properties and structure of the scattering volume V .

By insertion of the moment (3) into the definition (2) of the intensity tensor of light scattering at frequency 2ω , one obtains:

$$I_{ij}^{2\omega} = \frac{h_{2\omega}^2}{8V} \left(\frac{2\omega}{c} \right)^4 \langle B_{ikm}^{2\omega} B_{jln}^{-2\omega} \rangle I_{kl} I_{mn}, \quad (5)$$

where

$$I_{kl} = E_k(\omega) E_l(-\omega)/2. \quad (6)$$

is the intensity tensor of incident light. For isotropic bodies, one is justified, from the start, in averaging the tensor product $B_{ikm}^{2\omega} B_{jln}^{2\omega}$ of Equation (5) over all possible directions of the electric fields of incident and scattered light with regard to the axes of the co-ordinate system attached to the centre of V . This averaging, in invariant form, is to be found in one of our earlier papers [13], to which we refer when writing the symmetric real part of (5) in the form:

$$I_{ij}^{2\omega} = h_{2\omega}^2 \left(\frac{2\omega}{c} \right)^4 (F_{2\omega} I \delta_{ij} + G_{2\omega} I_{ij}) I, \quad (7)$$

where $I = I_{kk}$ is the total incident intensity, equal to the trace of (6), and δ_{ij} is the Kronecker unit tensor.

In (7), we have introduced the factors $F_{2\omega}$ and $G_{2\omega}$, taking account of the structure and thermodynamical state of the second-harmonically scattering medium:

$$F_{2\omega} = \frac{V^{-1}}{1680} \langle (7\delta_{\alpha\beta}\sigma_{\gamma\delta\epsilon\eta} - \sigma_{\alpha\beta\gamma\delta\epsilon\eta}) B_{\alpha\gamma\epsilon}^{2\omega} B_{\beta\delta\eta}^{-2\omega} \rangle, \quad (8)$$

$$G_{2\omega} = \frac{V^{-1}}{1680} \langle (3\sigma_{\alpha\beta\gamma\delta\epsilon\eta} - 7\delta_{\alpha\beta}\sigma_{\gamma\delta\epsilon\eta}) B_{\alpha\gamma\epsilon}^{2\omega} B_{\beta\delta\eta}^{-2\omega} \rangle \quad (9)$$

with, for brevity, the notation:

$$\begin{aligned} \sigma_{\alpha\beta\gamma\delta} &= \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}, \\ \sigma_{\alpha\beta\gamma\delta\epsilon\eta} &= \delta_{\alpha\beta}\sigma_{\gamma\delta\epsilon\eta} + \delta_{\alpha\gamma}\sigma_{\delta\epsilon\eta\beta} + \delta_{\alpha\delta}\sigma_{\epsilon\eta\beta\gamma} + \delta_{\alpha\epsilon}\sigma_{\eta\beta\gamma\delta} + \delta_{\alpha\eta}\sigma_{\beta\gamma\delta\epsilon}. \end{aligned}$$

The structural factors (8) and (9) are mutually related as follows:

$$K_{2\omega} = F_{2\omega} + G_{2\omega} = \frac{V^{-1}}{840} \langle \sigma_{\alpha\beta\gamma\delta\epsilon\eta} B_{\alpha\gamma\epsilon}^{2\omega} B_{\beta\delta\eta}^{-2\omega} \rangle. \quad (10)$$

Thus, in Equation (7), we have achieved a separation into three parts: (i), that given by (4), which is purely macroscopic, (ii) a semi-macroscopic part defined by the structural factors (8)–(10), and (iii) a part related to the state of polarisation of the intensity tensor (6).

Assume the incident light to propagate along the Y -axis and the SHS light to be analyzed in the X -direction. By using an incident wave linearly-polarized with oscillations in the vertical plane of intensity $I_{zz} = I_v$, one obtains by (7) for the vertical and horizontal components of intensity scattered at 2ω :

$$V_v^{2\omega} = I_{zz}^{2\omega}(I_{zz}) = h_{2\omega}^2 \left(\frac{2\omega}{c} \right)^4 K_{2\omega} I_v^2, \quad (11)$$

$$H_v^{2\omega} = I_{yy}^{2\omega}(I_{zz}) = h_{2\omega}^2 \left(\frac{2\omega}{c} \right)^4 F_{2\omega} I_v^2. \quad (12)$$

Using an incident wave with oscillations in the horizontal plane of intensity $I_{xx} = I_h$, one has from (7) the following relation for the vertical component $V_h = I_{zz}(I_{xx})$ and horizontal component $H_h = I_{yy}(I_{xx})$:

$$V_h^{2\omega} = H_h^{2\omega} = h_{2\omega}^2 \left(\frac{2\omega}{c} \right)^4 F_{2\omega} I_h^2. \quad (13)$$

The depolarisation ratio of the scattered light is, by Equations (11)–(13):

(i) for incident vertically-polarized light:

$$D_v^{2\omega} = \frac{H_v^{2\omega}}{V_v^{2\omega}} = \frac{F_{2\omega}}{K_{2\omega}} = \frac{F_{2\omega}}{F_{2\omega} + G_{2\omega}}, \quad (14)$$

(ii) for incident horizontally-polarized light:

$$D_h^{2\omega} = \frac{V_h^{2\omega}}{H_h^{2\omega}} = 1, \quad (15)$$

(iii) for incident unpolarized light:

$$D_u^{2\omega} = \frac{H_v^{2\omega} + H_h^{2\omega}}{V_v^{2\omega} + V_h^{2\omega}} = \frac{2F_{2\omega}}{F_{2\omega} + K_{2\omega}}. \quad (16)$$

3. Molecular-Statistical Theory for Liquids Consisting of Centrosymmetric Molecules

It is useful to give a discussion of the structural factors (8) and (9) for the case of liquids consisting of atoms and of centrosymmetric molecules. In the absence of electron dispersion and absorption, the second-order nonlinear polarisability tensor $B_{\alpha\beta\gamma}^{2\omega}$ can be considered symmetric in the two last indices β and γ . On this assumption, the factors (8) and (10) become, explicitly:

$$F_{2\omega} = \frac{V^{-1}}{840} \langle 6B_{\alpha\beta\gamma}^{2\omega} B_{\alpha\beta\gamma}^{-2\omega} - 2B_{\alpha\beta\gamma}^{2\omega} B_{\beta\alpha\gamma}^{-2\omega} + 3B_{\alpha\beta\beta}^{2\omega} B_{\alpha\gamma\gamma}^{-2\omega} - 2B_{\alpha\alpha\gamma}^{2\omega} B_{\beta\beta\gamma}^{-2\omega} - B_{\alpha\alpha\beta}^{2\omega} B_{\beta\gamma\gamma}^{-2\omega} - B_{\alpha\beta\beta}^{2\omega} B_{\gamma\gamma\alpha}^{-2\omega} \rangle, \quad (8a)$$

$$K_{2\omega} = \frac{V^{-1}}{840} \langle 2B_{\alpha\beta\gamma}^{2\omega} B_{\alpha\beta\gamma}^{-2\omega} + 4B_{\alpha\beta\gamma}^{2\omega} B_{\beta\alpha\gamma}^{-2\omega} + B_{\alpha\beta\beta}^{2\omega} B_{\alpha\gamma\gamma}^{-2\omega} + 4B_{\alpha\alpha\gamma}^{2\omega} B_{\beta\beta\gamma}^{-2\omega} + 2B_{\alpha\alpha\beta}^{2\omega} B_{\beta\gamma\gamma}^{-2\omega} + 2B_{\alpha\beta\beta}^{2\omega} B_{\gamma\gamma\alpha}^{-2\omega} \rangle. \quad (10a)$$

We assume the volume V to contain N microsystems with the aim of expressing the semi-macroscopic tensor $B_{\alpha\beta\gamma}^{2\omega}$ in terms of molecular and structural quantities.

In a first approximation, we neglect the influence of molecular fields in the medium. One obtains:

$$B_{\alpha\beta\gamma}^{2\omega} = \sum_{p=1}^N b_{\alpha\beta\gamma}^{2\omega} \exp[-i(\Delta\mathbf{k} \cdot \mathbf{r}_p)], \quad (17)$$

where $b_{\alpha\beta\gamma}^{2\omega} = b_{\alpha\beta\gamma}^{(p)}(-2\omega, \omega, \omega)$ is the tensor of second-order nonlinear polarisability of molecule p at \mathbf{r}_p , and $\Delta\mathbf{k} = \mathbf{k}_{2\omega} - 2\mathbf{k}_\omega$, with \mathbf{k}_ω the wave vector of incident light and $\mathbf{k}_{2\omega}$ that of the SHS wave.

Equation (17), inserted into the molecular factors (8)–(10), leads to the results previously discussed [1–5] for SHS by molecules not possessing a centre of symmetry, for which the tensor $b_{\alpha\beta\gamma}^{2\omega}$ presents non-zero tensor elements. In the case of molecules possessing a centre of symmetry, the tensor elements $b_{\alpha\beta\gamma}^{2\omega}$ vanish and, consequently, no SHS can take place in the approximation of Equation (17).

However, higher approximations have to be introduced to account for the time and space fluctuating molecular fields \mathbf{F} , existing in regions of near order. The first non-vanishing term is now of the form:

$$B_{\alpha\beta\gamma}^{2\omega} = \sum_{p=1}^N c_{\alpha\beta\gamma\delta}^{2\omega(p)} F_\delta^{(p)} \exp[-i(\Delta\mathbf{k} \cdot \mathbf{r}_p)], \quad (18)$$

where the fourth rank tensor $c_{\alpha\beta\gamma\delta}^{2\omega(p)} = c_{\alpha\beta\gamma\delta}^{(p)}(-2\omega, \omega, \omega, 0)$ defines the nonlinear polarisability of order 3 of a molecule, acted on by the electric field $\mathbf{F}^{(p)}$ of its neighbours in the medium, in the absence of externally applied fields. This molecular field lowers the molecular symmetry; thus, if the molecule possesses a centre of symmetry in its ground state, the molecular field \mathbf{F} removes it, thus endowing the molecule with the capacity to cause double-photon elastic scattering. But we have moreover to take into consideration that the molecular field not only modifies the symmetry of the molecule by a nonlinear distortion of the latter described by the tensor $c_{\alpha\beta\omega\nu}^{2\omega(p)}$, whose elements are nonzero for all symmetries, including spherical symmetry, but also induces an electric anisotropy in regions of near ordering. In this way, the molecular fluctuational regions, the dimensions of which are small in comparison with the light wavelength λ , do not as a whole possess a centre of symmetry and, accordingly, act as sources of co-operative second harmonic scattering, as expressed by the expansion (18).

To simplify our further calculations, we assume the tensor $c_{\alpha\beta\gamma\delta}^{2\omega}$ to be totally symmetric. The nonzero and mutually independent tensor elements of $c_{\gamma\delta\beta\gamma}^{2\omega}$ are listed in Table I for all point groups [14].

On inserting the tensor (18) into the structural factors (8a) and (10a), we obtain:

$$\begin{aligned} F_{2\omega} &= \frac{V^{1-}}{840} \left\langle \sum_{p=1}^N \sum_{q=1}^N \{4c_{\alpha\beta\gamma\delta}^{2\omega(p)} c_{\alpha\beta\gamma\epsilon}^{2\omega(q)} - c_{\alpha\beta\beta\delta}^{2\omega(p)} c_{\alpha\gamma\gamma\epsilon}^{2\omega(q)}\} \times \right. \\ &\quad \left. \times F_\delta^{(p)} F_\epsilon^{(q)} \exp[i(\Delta\mathbf{k} \cdot \mathbf{r}_{pq})] \right\rangle \\ K_{2\omega} &= \frac{V^{-1}}{280} \left\langle \sum_{p=1}^N \sum_{q=1}^N \{2c_{\alpha\beta\gamma\delta}^{2\omega(p)} c_{\alpha\beta\gamma\epsilon}^{2\omega(q)} + 3c_{\alpha\beta\beta\delta}^{2\omega(p)} c_{\alpha\gamma\gamma\epsilon}^{2\omega(q)}\} \times \right. \\ &\quad \left. \times F_\delta^{(p)} F_\epsilon^{(q)} \exp[i(\Delta\mathbf{k} \cdot \mathbf{r}_{pq})] \right\rangle, \quad (20) \end{aligned}$$

where $\mathbf{r}_{pq} = \mathbf{r}_q - \mathbf{r}_p$ is the vector connecting the centres of the two scattering molecules p and q .

3.1. ISOTROPIC SCATTERING

Let us begin with the case when, in a first approximation, the nonlinear polarisability of the molecules can be assumed as isotropic, permitting us to write:

$$c_{\alpha\beta\gamma\delta}^{2\omega} = \frac{1}{3}c_{2\omega}\sigma_{\alpha\beta\gamma\delta} \quad (21)$$

where

$$c_{2\omega} = c_{\alpha\alpha\beta\beta}^{2\omega}/5 = (c_{3333}^{2\omega} + 2c_{1122}^{2\omega} + 4c_{1133}^{2\omega} + 2c_{1111}^{2\omega})/5 \quad (22)$$

is the mean nonlinear polarisability of a molecule at 2ω .

Inserting (21) into (19) and (20), we get the following relation between molecular isotropic scattering factors:

$$K_{2\omega}^{is} = 9F_{2\omega}^{is} = \frac{c_{2\omega}^2}{24V} \left\langle \sum_{p=1}^N \sum_{q=1}^N \mathbf{F}_p \cdot \mathbf{F}_q \exp[i(\Delta\mathbf{k} \cdot \mathbf{r}_{pq})] \right\rangle \quad (23)$$

since

$$\begin{aligned} c_{\alpha\beta\gamma\delta}^{2\omega} c_{\alpha\beta\gamma\delta}^{2\omega} &= \frac{5}{3}c_{2\omega}^2, \\ c_{\alpha\beta\beta\delta}^{2\omega} c_{\alpha\gamma\gamma\delta}^{2\omega} &= \frac{2}{9}c_{2\omega}^2. \end{aligned}$$

Neglecting internal interference then $\Delta\mathbf{k} \cdot \mathbf{r}_{pq} = 0$ and Equation (23) reduces simply to:

$$K_{2\omega}^{is} = 9F_{2\omega}^{is} = \frac{\varrho}{24} c_{2\omega}^2 \langle F^2 \rangle, \quad (23a)$$

with $\varrho = \frac{N}{V}$, the number density of molecules, and

$$\langle F^2 \rangle = \frac{1}{N} \left\langle \sum_{p=1}^N \sum_{q=1}^N \mathbf{F}_p \cdot \mathbf{F}_q \right\rangle \quad (24)$$

implies the mean square of the molecular electric field, which is in general nonzero in a region of near ordering.

The electric field existing at the centre of molecule p due to the electric charge distribution of the neighbouring $N-1$ molecules is:

$$\mathbf{F}_p = \sum_{\substack{r=1 \\ r \neq p}}^N \mathbf{F}_{pr}, \quad (25)$$

where \mathbf{F}_{pr} denotes the electric field acting on molecule p due to the presence of its neighbour r .

Insertion of (25) into (24) yields in general:

$$\langle F^2 \rangle = \frac{1}{N} \left\langle \sum_{p=1}^N \sum_{q=1}^N \sum_{\substack{r=1 \\ r \neq p}}^N \sum_{\substack{s=1 \\ s \neq q}}^N \mathbf{F}_{pr} \cdot \mathbf{F}_{qs} \right\rangle$$

or, on restricting ourselves in a first approximation to pairwise correlations:

$$\langle F^2 \rangle = \frac{1}{2} \left\langle \sum_{\substack{q=1 \\ q \neq p}}^N (\mathbf{F}_{pq} \cdot \mathbf{F}_{pq} + 2\mathbf{F}_{pq} \cdot \mathbf{F}_{qp} + \mathbf{F}_{qp} \cdot \mathbf{F}_{qp}) \right\rangle. \quad (26)$$

This field can be calculated throughout for molecules of various types of symmetry.

3.1.1.1. *Quadrupolar Molecules*

For centrosymmetric molecules, having symmetry with respect to their 3-axis (vector \mathbf{k}), the electric field at the centre of molecule p due to the permanent electric quadrupole moment Θ_q of molecule q is of the form [13]:

$$\mathbf{F}_{pq} = \frac{3}{2}\Theta_q \{ [5(\mathbf{r}_{pq} \cdot \mathbf{k}_q)^2 - r_{pq}^2] \mathbf{r}_{pq} - 2r_{pq}^2 \mathbf{k}_q (\mathbf{r}_{pq} \cdot \mathbf{k}_q) \} r_{pq}^{-7}. \quad (27)$$

Since, here, $\mathbf{F}_{pq} = -\mathbf{F}_{qp}$, we have by (26) and (27):

$$\langle F^2 \rangle = 3\Theta^2 \left\langle \sum_{\substack{q=1 \\ q \neq p}}^N f_{pq} r_{pq}^{-8} \right\rangle, \quad (28)$$

where we have introduced the following function, describing the angular orientation of molecules p and q :

$$f_{pq} = \frac{3}{8} \{ 5(\cos^2 \theta_p - \cos^2 \theta_q)^2 + 4(\cos^2 \theta_p - 2\cos \theta_p \cos \theta_q \cos \theta_{pq} + \cos^2 \theta_q) \}. \quad (29)$$

Here, $\cos \theta_p = \mathbf{r}_{pq} \cdot \mathbf{k}_p / r_{pq}$ and $\cos \theta_q = \mathbf{r}_{pq} \cdot \mathbf{k}_q / r_{pq}$ are cosines of the angles between the symmetry axes \mathbf{k}_p , \mathbf{k}_q of molecules p , q and the vector \mathbf{r}_{pq} connecting their centres, and $\cos \theta_{pq} = \mathbf{k}_p \cdot \mathbf{k}_q$ is the cosine of the angle between their symmetry axes \mathbf{k}_p and \mathbf{k}_q .

In many cases, Equation (28) is conveniently represented in the form:

$$\langle F^2 \rangle = 3\Theta^2 \frac{\rho}{V} \iint f_{pq} r_{pq}^{-8} g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (28a)$$

where $g^{(2)}(\tau_p, \tau_q)$ stands for the binary correlation function between molecules p and q at configuration τ_p and τ_q .

When it is possible to perform a separation, in the general correlation function $g^{(2)}(\tau_p, \tau_q)$, of a purely radial part $g(r_{pq})$ [9]:

$$g^{(2)}(\tau_p, \tau_q) = g(r_{pq}) G(r_{pq}, \Omega_p, \Omega_q), \quad (30)$$

$G/r_{pq}, \Omega_p, \Omega_q$ is a correlation function dependent also on the molecular orientational variables Ω_p and Ω_q . If correlations of the orientational kind are weak, $G(r_{pq}, \Omega_p, \Omega_q) \rightarrow 1$, and one has:

$$g^{(2)}(\tau_p, \tau_q) \approx g(r_{pq}), \quad (30a)$$

and (28a) becomes:

$$\langle F^2 \rangle = 3\Theta^2 \langle f_{pq} \rangle_{\Omega} \langle r_{pq}^{-8} \rangle = 3\Theta^2 \langle r_{pq}^{-8} \rangle \quad (31)$$

since the molecular orientation function (29), averaged over all possible orientations of molecules p and q with equal probability:

$$\langle f_{pq} \rangle_{\Omega} = \frac{1}{\Omega^2} \iint f_{pq} d\Omega_p d\Omega_q = 1 \quad (32)$$

$$(\Omega = d\Omega_p = d\Omega_q),$$

In Equation (31), we have denoted the mean values:

$$\langle r_{pq}^{-n} \rangle = 4\pi Q \int r_{pq}^{2-n} g(r_{pq}) dr_{pq}, \quad (33)$$

which are accessible to numerical calculation for various radial correlation models [9].

3.1.2. Hexadecapolar Molecules

A further example of the centrosymmetric case is provided by molecules having octahedral symmetry (like SF₆); their lowest permanent nonzero electric moment is the hexadecapole $\Phi = \Phi_{1133}$. The electric field at the centre of molecule p due to the electric hexadecapole Φ_q of molecule q is expressed in the form:

$$\mathbf{F}_{pq} = \Phi_q \{ 3\mathbf{r}_{pq} [5 - 3(\cos^4 \theta_{1q} + \cos^4 \theta_{2q} + \cos^4 \theta_{3q})] + 4r_{pq} (\mathbf{i}_q \cos^3 \theta_{1q} + \mathbf{j}_q \cos^3 \theta_{2q} + \mathbf{k}_q \cos^3 \theta_{3q}) \} r_{pq}^{-7} \quad (34)$$

$\theta_{1q}, \theta_{2q}, \theta_{3q}$ being the angles between \mathbf{r}_{pq} and the unit vectors $\mathbf{i}_q, \mathbf{j}_q, \mathbf{k}_q$ along the principal axes 1, 2, 3 of molecule q .

On inserting the field (34) into Equation (26), and making the assumption of weak orientational correlations, we obtain:

$$\langle F^2 \rangle = \frac{240}{7} \Phi^2 \langle r_{pq}^{-12} \rangle. \quad (35)$$

from which it follows that even very highly symmetric molecules, when undergoing a distortion by the fluctuating molecular fields become, second-harmonic scatterers.

3.2. ANISOTROPIC SCATTERING

With regard to molecules of low symmetry one is not justified in writing a nonlinear polarisability tensor of the form (21). The latter is, in fact, strictly applicable to atoms and to molecules of high e.g. the octahedral symmetry. Anisotropy in the nonlinear polarisability tensor, when properly taken into account, leads additionally to some anisotropic second-harmonic scattering. With regard to the relation (23), the molecular factors (19) and (20) can be expressed as follows:

$$F_{2\omega} = F_{2\omega}^{is} (1 + \delta F_{2\omega}), \quad (36)$$

$$K_{2\omega} = K_{2\omega}^{is} (1 + \delta K_{2\omega}), \quad (37)$$

where

$$\delta F_{2\omega} = \frac{F_{2\omega} - F_{2\omega}^{is}}{F_{2\omega}^{is}}, \quad (38)$$

$$\delta K_{2\omega} = \frac{K_{2\omega} - K_{2\omega}^{is}}{K_{2\omega}^{is}}. \quad (39)$$

are relative variations of the molecular factors due to the anisotropy in nonlinear polarisability.

3.2.1. Axially-Symmetric Molecules

The nonlinear polarisability tensor is, in the present case [1]:

$$c_{\alpha\beta\gamma\delta}^{2\omega(p)} = \frac{1}{3}c_{2\omega}(1 - \kappa_{2\omega})\sigma_{\alpha\beta\gamma\delta} + \frac{1}{2}c_{2\omega}\kappa_{2\omega}(\delta_{\alpha\beta}k_{\gamma}^{(p)}k_{\delta}^{(p)} + \delta_{\alpha\gamma}k_{\beta}^{(p)}k_{\delta}^{(p)} + \delta_{\alpha\delta}k_{\beta}^{(p)}k_{\gamma}^{(p)} + \delta_{\beta\gamma}k_{\alpha}^{(p)}k_{\delta}^{(p)} + \delta_{\beta\delta}k_{\alpha}^{(p)}k_{\gamma}^{(p)} + \delta_{\gamma\delta}k_{\alpha}^{(p)}k_{\beta}^{(p)}), \quad (40)$$

where

$$\kappa_{2\omega} = \frac{c_{3333}^{2\omega} - c_{1111}^{2\omega}}{3c_{2\omega}} = \frac{c_{3333}^{2\omega} - c_{1111}^{2\omega}}{c_{3333}^{2\omega} + 2c_{1111}^{2\omega}} \quad (41)$$

is the anisotropy of nonlinear polarisability of order 3. When deriving formula (40), we assumed for simplicity, in the absence of electronic dispersion:

$$c_{1133}^{2\omega} = \frac{1}{6}(c_{3333}^{2\omega} + c_{1111}^{2\omega}), \quad (42)$$

a condition resulting from studies of DC field second-harmonic generation in liquids [15].

The tensor (40), when inserted into (19) and (20) and on neglecting the term in $\kappa_{2\omega}^2$ leads to:

$$K_{2\omega} = 9F_{2\omega} = K_{2\omega}^{is} + \frac{7Q}{40}c_{2\omega}^2\kappa_{2\omega}\Theta^2 \left\langle \sum_{\substack{q=1 \\ q \neq p}}^N (g_{pq} - f_{pq}) r_{pq}^{-8} \right\rangle, \quad (43)$$

where we have introduced the angular molecular orientation function:

$$g_{pq} = \frac{9}{8} \{ 5(\cos^2\theta_p + \cos^2\theta_q)^2 - 4\cos\theta_p\cos\theta_q\cos\theta_{pq} - 2(\cos^2\theta_p + \cos^2\theta_q)(1 - 2\cos^2\theta_{pq} + 5\cos\theta_p\cos\theta_q\cos\theta_{pq}) \}. \quad (44)$$

If the molecular correlation function $g^{(2)}(\tau_p, \tau_q)$ is independent of orientation, we obtain by unweighted averaging:

$$\langle g_{pq} \rangle_{\Omega} = \langle f_{pq} \rangle_{\Omega} = 1$$

so that the term linear in the anisotropy $\kappa_{2\omega}$ vanishes and leads to the relation:

$$K_{2\omega}^{is} = 9F_{2\omega}^{is} = \frac{Q}{8}c_{2\omega}^2\Theta^2 \langle r_{pq}^{-8} \rangle \quad (45)$$

which holds for isotropic scattering in the absence of angular molecular correlations.

If however, when calculating the molecular factors (19) and (20), one takes into account the next term, proportional to the square of the nonlinear polarisability anisotropy $\kappa_{2\omega}$, one obtains in the absence of angular correlations:

$$F_{2\omega} = F_{2\omega}^{is} + \frac{191Q}{12600}c_{2\omega}^2\kappa_{2\omega}^2\Theta^2 \langle r_{pq}^{-8} \rangle, \quad (46)$$

$$K_{2\omega} = K_{2\omega}^{is} + \frac{89Q}{1400}c_{2\omega}^2\kappa_{2\omega}^2\Theta^2 \langle r_{pq}^{-8} \rangle, \quad (47)$$

where $F_{2\omega}^{is}$ and $K_{2\omega}^{is}$ are defined by the relation (45).

3.2.2. Centro-Symmetric Molecules of Arbitrary Symmetry

We shall consider molecules of arbitrary symmetry whose first nonzero electric moment is the quadrupole, defined by the tensor [16]:

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum_n e_n (3r_{n\alpha}r_{n\beta} - r_n^2 \delta_{\alpha\beta}), \quad (48)$$

where e_n is the n th electric charge of the molecule, and \mathbf{r}_n its radius-vector.

The electric field at the centre of molecule p due to the electric quadrupole of molecule q is, quite generally [16]:

$$F_{\alpha}^{(p)} = \{5r_{pq\alpha}r_{pq\beta}r_{pq\gamma}\Theta_{\beta\gamma}^{(q)} - 2r_{pq\alpha}^2r_{pq\beta}\Theta_{\alpha\beta}^{(q)}\} r_{pq}^{-7}. \quad (49)$$

The above molecular electric field, inserted into the factors (19) and (20), leads in a first approximation, in the absence of direct angular correlations, to:

$$F_{2\omega} = \frac{Q}{308700} \{245(4c_{\alpha\beta\gamma\delta}^{2\omega}c_{\alpha\beta\gamma\delta}^{2\omega} - c_{\alpha\beta\beta\delta}^{2\omega}c_{\alpha\gamma\gamma\delta}^{2\omega})\Theta_{\varepsilon\eta}\Theta_{\varepsilon\eta} - 213c_{\alpha\beta\beta\gamma}^{2\omega}\Theta_{\alpha\gamma}c_{\delta\varepsilon\varepsilon\eta}^{2\omega}\Theta_{\delta\eta}\} \langle r_{pq}^{-8} \rangle, \quad (50)$$

$$K_{2\omega} = \frac{Q}{102900} \{245(2c_{\alpha\beta\gamma\delta}^{2\omega}c_{\alpha\beta\gamma\delta}^{2\omega} + 3c_{\alpha\beta\beta\delta}^{2\omega}c_{\alpha\gamma\gamma\delta}^{2\omega})\Theta_{\varepsilon\eta}\Theta_{\varepsilon\eta} - 621c_{\alpha\beta\beta\gamma}^{2\omega}\Theta_{\alpha\gamma}c_{\delta\varepsilon\varepsilon\eta}^{2\omega}\Theta_{\delta\eta}\} \langle r_{pq}^{-8} \rangle. \quad (51)$$

The tensor elements of $\Theta_{\alpha\beta}$ and $c_{\alpha\beta\gamma\delta}^{2\omega}$ are listed in Tables I and II. On resorting to these Tables, formulae (50) and (51) become immediately applicable to all centro-symmetric molecules.

TABLE I

Tensor elements $c_{\alpha\beta\gamma\delta}^{2\omega}$ of the third-order nonlinear polarizability on the assumption of total symmetricity in the indices $\alpha, \beta, \gamma, \delta$

Point group	Number of non-zero elements	Number of independent elements	Elements of $c_{\alpha\beta\gamma\delta}^{2\omega}$ which are denoted only by their subscripts $\alpha, \beta, \gamma, \delta = 1, 2, 3$
1 (C_i)	81	15	1111; 2222; 3333
$\bar{A}(C_i)$			1122 = 1212 = 1221 = 2211 = 2121 = 2112; = 1133 = 1313 = 1331 = 3311 = 3131 = 3113; 2233 = 2323 = 2332 = 3322 = 3232 = 3223; 1112 = 1121 = 1211 = 2111; 2221 = 2212 = 2122 = 1222; 1333 = 3133 = 3313 = 3331; 2333 = 3233 = 3323 = 3332; 1113 = 1131 = 1311 = 3111; 2223 = 2232 = 2322 = 3222; 1123 = 1213 = 1231 = 1132 = 1312 = 1321 = = 2113 = 2131 = 2311 = 3112 = 3121 = 3211; = 2213 = 2123 = 2132 = 2231 = 2321 = 2312 = = 1223 = 1232 = 1322 = 3221 = 3212 = 3122; = = 1332 = 1323 = 1233 = 2133 = 2313 = 2331 = = 3123 = 3213 = 3231 = 3132 = 3321 = 3312.

Table I (continued)

2 (C_2)	41	9	1111; 2222; 3333;					
m (C_s)			1122 = 1313 = 1221 = 2211 = 2121 = 2112;					
$2/m$ (C_{2h})			1133 = 1212 = 1331 = 3311 = 3131 = 3113;					
			2233 = 2323 = 2332 = 3322 = 3232 = 3223;					
			1112 = 1121 = 1211 = 2111;					
			2221 = 2212 = 2122 = 1222;					
			1332 = 1323 = 1233 = 2133 = 2313 = 2331 =					
			= 3123 = 3213 = 3231 = 3132 = 3321 = 3312,					
222 (D_2)	21	6	1111; 2222; 3333;					
$mm2$ (C_{2v})			1122 = 1212 = 1221 = 2211 = 2121 = 2112;					
mmm (D_{2h})			1133 = 1313 = 1331 = 3311 = 3131 = 3113;					
			2233 = 2323 = 2332 = 3322 = 3232 = 3223.					
4 (C_4)	29	5	3333; 1111 = 2222;					
$\bar{4}$ (S_4)			1122 = 1212 = 1221 = 2211 = 2121 = 2112;					
$4/m$ (C_{4h})			1133 = 1313 = 1331 = 3311 = 3131 = 3113 =					
			= 2233 = 2323 = 2332 = 3322 = 3232 = 3223;					
			1112 = 1121 = 1211 = 2111 =					
			= -2221 = -2212 = -2122 = -1222.					
422 (D_4)	21	4	3333; 1111 = 2222;					
$4mm$ (C_{4v})			1122 = 1212 = 1221 = 2211 = 2121 = 2112;					
$\bar{4}2m$ (D_{2d})			1133 = 1313 = 1331 = 3311 = 3131 = 3113 =					
$4/mmm$ (D_{4h})			= 2233 = 2323 = 2332 = 3322 = 3232 = 3223.					
3 (C_3)	53	5	3333; 1111 = 2222 = 1122 + 1212 + 1221;					
$\bar{3}$ (C_{3i})			1122 = 1212 = 1221 = 2211 = 2121 = 2112;					
			1133 = 1313 = 1331 = 3311 = 3131 = 3113 =					
			2233 = 2323 = 2332 = 3322 = 3232 = 3223;					
			1113 = 1131 = 1311 = 3111 = -2123 = -2231 =					
			= -2321 = -2213 = -2132 = -2312 = -1223 =					
			= -1232 = -1322 = -3122 = -3212 = -3221;					
			2223 = 2232 = 2322 = 3222 = -1213 = -1132 =					
			= -1312 = -1123 = -1231 = -1321 = -2113 =					
			= -2131 = -2311 = -3211 = -3121 = -3112.					
$3m$ (C_{3v})	37	4	3333; 1111 = 2222 = 1122 + 1212 + 1221;					
$\bar{3}m$ (D_{3d})			1122 = 1212 = 1221 = 2211 = 2121 = 2112;					
32 (D_3)			1133 = 1313 = 1331 = 3311 = 3131 = 3113 =					
			= 2233 = 2323 = 2332 = 3322 = 3232 = 3223;					
			2223 = 2232 = 2322 = 3222 = -1213 = -1132 =					
			= -1312 = -1123 = -1231 = -1321 = -2113 =					
			= -2131 = -2311 = -3211 = -3121 = -3112.					
6 (C_6)	19	3	3333; 1111 = 2222 = 1122 + 1212 + 1221;					
$\bar{6}$ (C_{3h})			1122 = 1212 = 1221 = 2211 = 2121 = 2112;					
$6/m$ (C_{6h})			1133 = 1313 = 1331 = 3311 = 3131 = 3113 =					
622 (D_6)			= 2233 = 2323 = 2332 = 3322 = 3232 = 3223;					
$\bar{6}mm$ (C_{6v})								
$6m2$ (D_{3h})								
$6/mmm$ (D_{6h})								
23 (T)	21	2	1111 = 2222 = 3333;					
$m\bar{3}$ (T_h)			1122 = 1212 = 1221 = 2211 = 2121 = 2112 =					
$\bar{4}32$ (O)			= 3311 = 3131 = 3112 = 1133 = 1313 = 1331 =					

Table I (continued)

$\bar{4}3m (T_d)$ $m3m (O_h)$			= 2233 = 2323 = 3223 = 3322 = 3232 = 3223.
$C_{\infty}, C_{\infty v}$ $C_{\infty h}, D_{\infty h}$	19	3	Elements as in the classes of the hexagonal system.
K, K_h Y, Y_h	21	1	Non-zero elements as in the cubic system with the relation 1111 = 1122 + 1212 + 1221.

TABLE II

Nonzero and independent tensor elements of the electric quadrupole moment
 $\Theta_{\alpha\beta}$ for all point groups

Point group	Number of non-zero elements	Number of independent elements	Elements of $\Theta_{\alpha\beta}$ which are denoted by their subscripts $\alpha, \beta = 1, 2, 3$.
C_1, C_i	9	5	11; 22; 33 = -(11 + 22); 12 = 21; 23 = 32; 31 = 13
C_s, C_2, C_{2h}	5	3	11; 22; 12 = 21; 33 = -(11 + 22)
C_{2v}, D_2, D_{2h}	3	2	11; 22; 33 = -(11 + 22)
C_4, S_4, C_{4h} C_{4v}, D_{2d}, D_{4h} D_4, C_3, S_6 C_{3v}, D_3, D_{3d} C_{3h}, C_6, C_{6h} D_{3h}, C_{6v}, D_6 D_{6h}, D_{4d}, C_{5v} C_{5h}, D_{5h}, D_{5d} $D_{6d}, C_{\infty}, C_{\infty v}$ $C_{\infty h}, D_{\infty h}$ T, T_h, T_d $O, O_h, Y,$ Y_h, K, K_h	3 3	1	11 = 22, 33 = -(11 + 22)
	0	0	

In particular, for molecules having symmetry of the point groups C_{6h}, D_{6h} and $D_{\infty h}$, we obtain:

$$F_{2\omega} = F_{2\omega}^{is} + \frac{\rho\Theta^2}{113400} (191\gamma_{2\omega}^2 - 315\gamma_{2\omega}\delta_{2\omega} + 2457\delta_{2\omega}^2) \langle r_{pq}^{-8} \rangle \quad (50a)$$

$$K_{2\omega} = K_{2\omega}^{is} + \frac{\rho\Theta^2}{12600} (89\gamma_{2\omega}^2 + 315\gamma_{2\omega}\delta_{2\omega} - 693\delta_{2\omega}^2) \langle r_{pq}^{-8} \rangle, \quad (51a)$$

where we have introduced the following parameters of nonlinear polarisability anisotropy:

$$\gamma_{2\omega} = \frac{2}{7} (3c_{3333}^{2\omega} - 4c_{1111}^{2\omega} + 3c_{1133}^{2\omega}), \quad (52)$$

$$\delta_{2\omega} = \frac{2}{7} (c_{3333}^{2\omega} - 6c_{1133}^{2\omega} + c_{1111}^{2\omega}). \quad (53)$$

In particular, on assuming the approximation (42), the factors (50a) and (51a) reduce to the form (46) and (47), since the parameters (52) and (53) now become:

$$\gamma_{2\omega} = c_{3333}^{2\omega} - c_{1111}^{2\omega} = 3c_{2\omega}k_{2\omega}, \quad (52a)$$

$$\delta_{2\omega} = 0. \quad (53a)$$

Since the tensor elements of the hexadecapole moment are available for all point groups [16], (19) and (20) may be evaluated for arbitrary hexadecapolar molecules.

4. Applications and Discussion

By (36) and (37), the intensity components of second-harmonic light scattering can be written in the form:

$$V_v^{2\omega} = h_{2\omega}^2 \left(\frac{2\omega}{c} \right)^4 \mathbf{K}_{2\omega}^{is} (1 + \delta \mathbf{K}_{2\omega}) I_v^2, \quad (54)$$

$$H_v^{2\omega} = h_{2\omega}^2 \left(\frac{2\omega}{c} \right)^4 \mathbf{F}_{2\omega}^{is} (1 + \delta \mathbf{F}_{2\omega}) I_v^2, \quad (55)$$

In order to determine numerically the quantities $\delta F_{2\omega}$ and $\delta K_{2\omega}$, defined by (36) and (37), one has to perform measurements of the depolarisation ratio for vertically-polarized and unpolarized incident light:

$$D_v^{2\omega} = \frac{1}{9} \frac{1 + \delta F_{2\omega}}{1 + \delta K_{2\omega}}, \quad (56)$$

$$D_u^{2\omega} = \frac{2(1 + \delta F_{2\omega})}{10 + \delta F_{2\omega} + 9 \delta K_{2\omega}} = \frac{2D_v^{2\omega}}{1 + D_v^{2\omega}}, \quad (57)$$

where the relation (23) is used.

Restricting the theory to the approximation (43), one gets the relation:

$$\delta F_{2\omega} = \delta K_{2\omega} = \frac{63}{40} k_{2\omega} \frac{\left\langle \sum_{q \neq p}^N (q_{pq} - f_{pq}) r_{pq}^{-8} \right\rangle}{\left\langle \sum_{q \neq p}^N f_{pq} r_{pq}^{-8} \right\rangle}. \quad (58)$$

In the above approximation, one has:

$$D_v^{2\omega} = \frac{1}{9} \quad \text{and} \quad D_u^{2\omega} = \frac{1}{3},$$

which is the same as for isotropic scattering.

If correlations of the angular kind are weak i.e. if one can make the approximation (59a) and (51a), one obtains:

$$\delta F_{2\omega} = \frac{1}{1575 c_{2\omega}^2} (191 \gamma_{2\omega}^2 - 31 \cdot 5 \gamma_{2\omega} \delta_{2\omega} + 2457 \delta_{2\omega}^2), \quad (59)$$

$$\delta K_{2\omega} = \frac{1}{1575 c_{2\omega}^2} (89 \gamma_{2\omega}^2 + 315 \gamma_{2\omega} \delta_{2\omega} - 693 \delta_{2\omega}^2). \quad (60)$$

In a previous paper [7]*, with the aim of a simple analysis of the experimental results, we expressed the depolarisation ratio (56) in the form:

$$D_v^{2\omega} = \frac{1}{9} \frac{1 + A_{2\omega}^2}{1 - A_{2\omega}^2}, \quad (61)$$

involving the dimension-less quantity:

$$A_{2\omega}^2 = \frac{\delta F_{2\omega} - \delta K_{2\omega}}{2 + \delta F_{2\omega} + \delta K_{2\omega}}. \quad (62)$$

In cases when $\delta F_{2\omega} < 1$ and $\delta K_{2\omega} < 1$, one has to sufficient approximation:

$$A_{2\omega}^2 \simeq \frac{1}{2} (\delta F_{2\omega} - \delta K_{2\omega}), \quad (62a)$$

The quantity thus defined has the physical meaning of the square of the effective anisotropy of the nonlinear polarisability at frequency 2ω . This is immediately apparent on inserting (59) and (60) into (62a):

$$A_{2\omega}^2 = \frac{17\gamma_{2\omega}^2 - 105\gamma_{2\omega}\delta_{2\omega} + 525\delta_{2\omega}^2}{525c_{2\omega}^2}. \quad (63)$$

Resorting to the approximate relation (42), we reduce the above anisotropy to the previously derived [7] simple form:

$$A_{2\omega}^2 = \frac{51}{175} \left(\frac{\gamma_{2\omega}}{3c_{2\omega}} \right)^2 = \frac{51}{175} \left(\frac{c_{3333}^{2\omega} - c_{1111}^{2\omega}}{c_{3333}^{2\omega} + c_{1111}^{2\omega}} \right)^2 \quad (63a)$$

which is approximately valid for molecules having a centre and axis of symmetry.

In the case of liquids with considerable angular molecular correlations, (63a) has to be replaced by the following formula:

$$A_{2\omega}^2 = \frac{51}{175} \kappa_{2\omega}^2 \frac{\left\langle \sum_{q=p}^N G_{pq} r_{pq}^{-8} \right\rangle}{\left\langle \sum_{q \neq p}^N f_{pq} r_{pq}^{-8} \right\rangle}, \quad (64)$$

where

$$G_{pq} = \frac{5}{6^3} (-3f_{pq} - 4g_{pq} + \frac{10.3}{5} h_{pq}), \quad (65)$$

with

$$\begin{aligned} h_{pq} = & \frac{4.5}{8^2.4} \{ 10 + 25(\cos^2 \theta_p - \cos^2 \theta_q)^2 - 10(\cos^2 \theta_{pq} + \\ & + 7 \cos^2 \theta_p \cos^2 \theta_q + 21 \cos^2 \theta_p \cos^2 \theta_q \cos^2 \theta_{pq} + \\ & + 30 \cos^3 \theta_p \cos^3 \theta_q \cos \theta_{pq}) - \\ & - 4 \cos \theta_p \cos \theta_q \cos \theta_{pq} (2 \cos^2 \theta_{pq} - 31) + \\ & + 2(\cos^2 \theta_p + \cos^2 \theta_q) [40 \cos^2 \theta_p \cos^2 \theta_q - 2 + \\ & + 35(\cos \theta_p \cos \theta_q + \cos \theta_{pq})^2] \}. \end{aligned} \quad (66)$$

* In Ref. [7], the right-hand terms of Equations (2) and (3) should be divided by a factor of 9 and Equation (9) multiplied by

$$[(n^2_{2\omega} + 2)/9]^2 [(n^2_{2\omega} + 2)/3]^4.$$

In the absence of angular correlations $\langle f_{pq} \rangle_\Omega = \langle G_{pq} \rangle_\Omega = 1$, and (64) obviously reduces to (63a).

It should be particularly noted that (it follows from formula (23) a sufficient condition for the occurrence of SHLS in a liquid is the induction of isotropic third-order nonlinear polarisability in its molecules by the electric molecular field existing in the liquid. This is analogous to Voigt's effect, which causes a Kerr effect in atomic substances. The depolarisation ratio of SHLS is then $\frac{1}{3}$. Anisotropy of this nonlinear molecular polarisability will lead to an additional anisotropy of SHLS described by the quantity $\Delta_{2\omega}^2$ which, by Equation (61), raises the depolarisation ratio. A further increase or decrease in $D_v^{2\omega}$ depends on the kind of angular correlation intervenes i.e. on whether we are dealing with a tendency to paratropism or diatropism [17]. From the shape of the angular functions f_{pq} and G_{pq} we conclude that a nearly diatropic structure favours an increase in induced anisotropy for near neighbourhood, whereas a paratropic structure lowers the effective anisotropy causing a vanishing of SHLS. This is quite obvious if one keeps in mind that cooperative SHLS can occur only by way of an anisotropy due to a deviation from centrosymmetry of the molecule and near order region.

From (61) we derive a formula for determining the effective anisotropy of nonlinear polarisability by measuring the depolarisation ratio at frequency 2ω :

$$\Delta_{2\omega}^2 = \frac{9 D_v^{2\omega} - 1}{9 D_v^{2\omega} + 1} = 1 - \frac{2}{9 D_v^{2\omega} + 1}. \quad (67)$$

These considerations thus lead to the result $D_v^{2\omega} \geq \frac{1}{9} \approx 0.11$, in agreement with our earlier [7] and present measurements.

It is interesting to compare conditions when studying nonlinear second-harmonic scattering and linear Rayleigh scattering at frequency ω , for which one has the depolarisation ratios [9]:

$$D_v^\omega = \frac{D_u^\omega}{2 - D_u^\omega} = \frac{3 \Delta_\omega^2}{5 \rho k T \kappa_T + 4 \Delta_\omega^2}, \quad (63)$$

where κ_T is the isothermal compressibility coefficient, and

$$\Delta_\omega^2 = (18 a_\omega^2 N)^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 a_{\alpha\beta}^{(p)} a_{\alpha\beta}^{(q)} - a_{\alpha\alpha}^{(p)} a_{\beta\beta}^{(q)}) \right\rangle \quad (69)$$

is the square of the effective anisotropy of linear polarisability defined by the tensor $a_{\alpha\beta}^\omega$ with $a_\omega = a_{\alpha\alpha}^\omega/3 = (a_{11}^\omega + a_{22}^\omega + a_{33}^\omega)/3$ denoting the mean linear molecular polarisability at ω .

In many cases it is simpler to determine the effective anisotropy (69) directly by measuring the horizontal component [10, 18, 19], given as [9]:

$$H_v^\omega = \frac{3}{5} \rho \left(\frac{\omega}{c} \right)^4 a_\omega^2 \Delta_\omega^2 I_v. \quad (70)$$

5. Experimental Considerations

For an account of our set-up, we refer to earlier papers [12, 7]. As compared to those of the set-up used at Ford Scientific Laboratories [5], the technical characteristics of ours are essentially described in Table III. The chief difference resides in the very considerable transmitted bandwidth imposed by the necessity to employ a very high transmission interference filter. Our set-up moreover gained very high luminosity owing to our choice of a very large effective aperture of the scattered beam and our use of an optical component of large diameter (8–10 cm). This luminosity requirement was imposed by the smallness of the harmonic scattering emitted. We hardly think it possible now to use a monochromator as shown by an attempt made at Ford Scientific Laboratories on a liquid consisting of centro-symmetric molecules [22].

TABLE III
Comparison between our experimental set-up and that of Ford Scientific Laboratories

Technical characteristics	Our set-up	Ford Scientific Laboratories set-up
Pulsed laser wavelength	1.06 μ	0.6942 μ
Mean power	3 – 10 MW	5 MW
Laser pulse rate	1 pulse every 2 min	1 pulse per second
Focusing lens power	+ 10 diopters	+ 6 diopters
Effective aperture of scattered beam	$f/1$	$f/3$
Transmission at the harmonic frequency	0.25	0.12 for the component $H_v^{2\omega}$
Transmitted detection band	500 cm^{-1} ; interference filters used	100 cm^{-1} and then 20 cm^{-1} ; monochromator used

We must also point out that Stimulated Raman Scattering was never observed in our experiments, performed with a multimode laser and a power density at the focus of about 500 MW cm^{-2} . Such powers cannot cause saturation of molecular orientation [15] in the focal zone since the energy of optical orientation of the molecules $\frac{1}{2}(a_{33}^o - a_{11}^o)I$ is less than that of their thermal motion kT . The weak molecular optical reorientation modifies only the anisotropic part of the SHLS intensity components (38) and (39) (and this – but imperceptibly), and has no influence at all on isotropic scattering (23) which in our case plays the chief role.

5.1. RESULTS AND DISCUSSION

Figures 1 and 2 give our experimental results for benzene. Three zones can be distinguished depending on the laser power. Zone (I) relates to SHLS. No parasitical signal is recorded beyond the hyper-Raman effect region ($\pm 3000 \text{ cm}^{-1}$). The sample undergoes no damage, and the relations $V_v^{2\omega} \approx I^2$ and $H_v^{2\omega} \approx I^2$ were satisfactorily verified in spite of the smallness of the $H_v^{2\omega}$ signal (on the average several photoelectrons per laser pulse). A least squares method permitted the determination of the depolarisation ratio and its error. Zone (III) corresponds to breakdown of the dielectric. Signals of

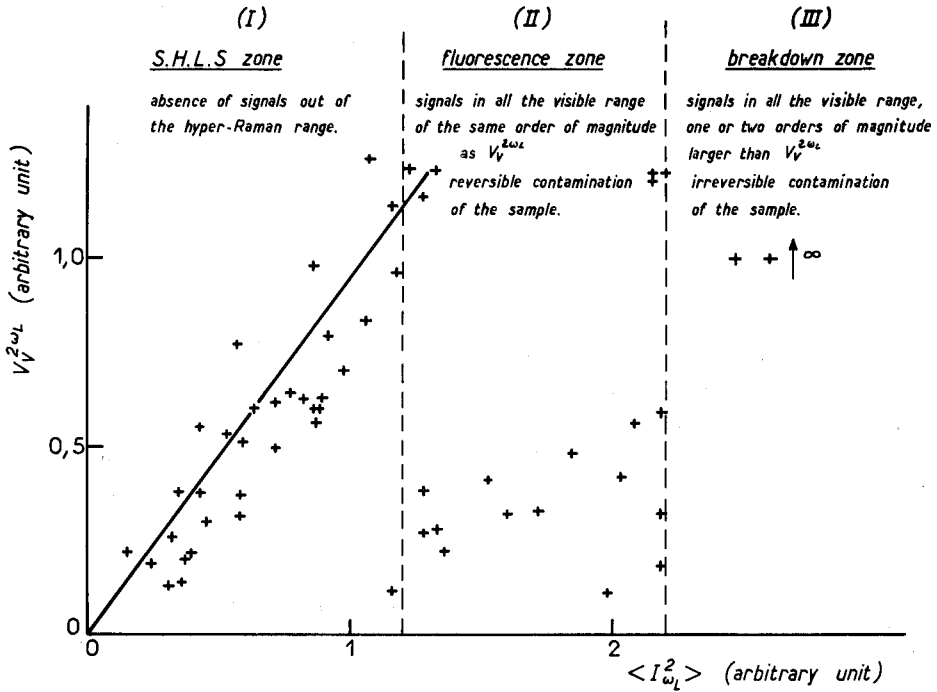


Fig. 1. Dependence of the SHLS intensity $V_v^{2\omega_L}$ on the reference signal $I_{\omega_L}^2$ for benzene. $\lambda_L = 1.06\mu$; $L/2 = 0.53$. Detection bandwidth about 500 cm^{-1} .

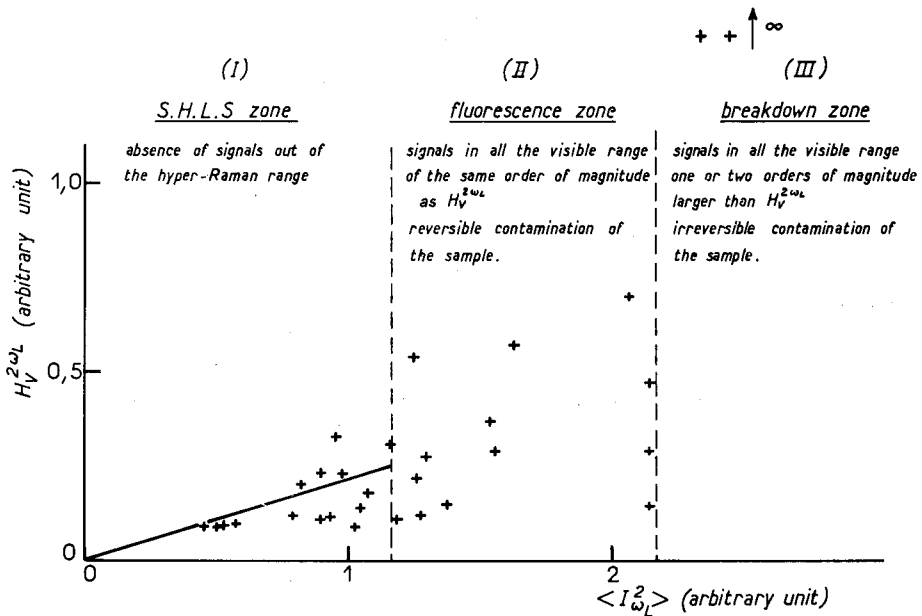


Fig. 2. Dependence of the SHLS intensity $H_v^{2\omega_L}$ on the reference signal $I_{\omega_L}^2$ for benzene. $\lambda_L = 1.06\mu$; $L/2 = 0.53$. Detection bandwidth about 500 cm^{-1} .

very high intensity, saturating our detection devices and uniformly distributed over the entire visible spectrum, were recorded. On inspection, the sample was found to contain impurities, and filtration had to be repeated before the measurements could be continued. The origin of the intermediate zone (II) is not easy to define. Luminous signals of the same order of magnitude as SHLS occur in the visible range having a depolarisation ratio close to unity (nearly total depolarisation). The spectacular decrease in $V_v^{2\omega}$ seems to suggest that the fundamental wave serves as pumping agent for the phenomenon or phenomena observed, before it can ensure the harmonic scattering. However, no irreversible pollution of the sample is observed in this region. Possibly we are dealing here with a pre-breakdown region with luminescent ionisation of several molecules and subsequent recombination. This interpretation is, however, quite speculative. The narrowness of the energy gate permitting the detection and measurement of SHLS is noteworthy.

Our measured depolarisation ratios for cyclohexane, benzene and carbon disulphide are given in Table IV and show increasing divergence from the limiting value $\frac{1}{3}$ for a totally isotropic $c_{ijkl}^{2\omega}$ tensor.

TABLE IV
Experimental results from our SHLS data. $\lambda = 1.06 \mu$, $t = 25^\circ\text{C}$

Liquid	Point group	Number of independent elements		Experimental SHLS depolarization ratio	Calculated effective optical anisotropies		
		Θ_{ij}	$a_{ij\omega}$		Linear	Non-linear	
Cyclohexane	D_{3d}	1	2	$\boxed{c_{ijkl}^{2\omega}}$ $D_v^{2\omega}$	Δ_ω^2	$\Delta_{2\omega}^2$	
Benzene	D_{6h}	1	2	3	0.12 ± 0.04	0.001	
Carbon disulphide	D_{2h}	1	2	3	0.17 ± 0.06	0.032	
					0.21 ± 0.09	0.190	0.04
							0.21
							0.31

It is tempting to attribute these divergences to an increasing anisotropy of the tensor $c_{ijkl}^{2\omega}$. However, the excessively high estimations of the depolarisation ratios can be due to the following two experimental reasons:

(a) The large angular aperture of the harmonic flux detected. The limiting value $D_v^{2\omega} = F_{2\omega} / (F_{2\omega} + G_{2\omega})$ implies an infinitely small angular aperture. The correction for non-zero angular aperture, that is finite body angle Ω , is accessible to calculation. An integration over the body angle Ω has to be performed in the generalized relations derived by one of us [4]:

$$H^{2\omega} \approx (F^{2\omega} + G^{2\omega} \cos^2 \theta \cos^2 \psi)$$

$$V^{2\omega} \approx \{F^{2\omega} + G^{2\omega} (\sin^2 \theta \cdot \cos^2 \varphi - \cos^2 \theta \cdot \sin^2 \varphi \cdot \sin^2 \psi)\},$$

where ψ is the angle between the wave vectors of the incident and scattered waves, θ that between the electric field of the linear polarized incident wave and the mean plane

of observation, and φ that between the wave vector of the scattered wave and the mean scattering plane.

For an incident wave polarized perpendicularly to the mean observation plane, $H_v^{2\omega}$ is always proportional to $F^{2\omega}$, and one obtains for $V_v^{2\omega}$:

$$V_v^{2\omega} \approx \left\{ F^{2\omega} + G^{2\omega} \frac{2\pi}{3} \Omega \left[2 - \frac{1}{\left(1 + \frac{\Omega}{\pi}\right)^{1/2}} - \frac{1}{\left(1 + \frac{\Omega}{\pi}\right)^{3/2}} - \frac{1}{3} \frac{1}{\left(1 + \frac{\Omega}{\pi}\right)^{3/2}} \right] \right\}.$$

This relation is easily shown to lead to the limiting value $V_v^{2\omega} \approx (F_{2\omega} + G_{2\omega})$, for very small Ω . Numerical calculations can be carried out for the aperture $f/1$ of our set-up i.e. for $\Omega/\pi = 0.25$, yielding:

$$V_v^{2\omega} \approx (F^{2\omega} + 0.85G^{2\omega}),$$

$$H_v^{2\omega} \approx F^{2\omega}.$$

Hence, for the case of total isotropy of $c_{ijkl}^{2\omega}$,

$$\frac{F^{2\omega}}{F^{2\omega} + G^{2\omega}} = \frac{1}{2},$$

$$D_v^{2\omega} = \frac{F^{2\omega}}{F^{2\omega} + 0.85G^{2\omega}} \simeq 0.13.$$

Consequently, an overestimation of about 18% can be caused by the large value of our angular aperture. Significantly, earlier results obtained with our set-up, equipped with a ruby laser [7] and having a much smaller aperture (about $f/4$) were not perceptibly affected by this, stemming from the optical system.

(b) The considerable width, (about 500 cm^{-1}) of the band transmitted by our interference filter system, resulting possibly in the detection of some portion of the inelastic hyper-Raman scattering [23, 24]. We have here a fundamental limitation, specific to this kind of study, since it is difficult to considerably reduce the transmitted bandwidth of our detection system without, at the same time, diminishing its luminosity. However an attempt based on the use of special, very high quality filters, is now being made with our set-up. Nevertheless, one should note that:

(i) the hyper-Raman lines which are infra-red inactive for example (A_{1u}^g of cyclohexane; B_{1u} , B_{2u} and E_{2u} of benzene) often correspond to very small frequency shifts (e.g. 300 cm^{-1} in ethane, 60 cm^{-1} in hexafluoroethane [23, 24], which are molecules of the same symmetry group as cyclohexane). Their depolarisation ratio may be calculated from the expression given in Ref. [2], to be 0.66, for a totally polarized incident wave. The experimental values, which range from 0.11 to 0.21, show that the intensities of these lines are certainly small compared to that of the hyper-Rayleigh line.

(ii) The intense hyper-Raman lines which are infra-red active (e.g. A_{2u}^g and E_u of cyclohexane; A_{2u} and E_{1u} of benzene; Σ_u^+ and Π_u of carbon disulphide), and whose calculated depolarisation ratios which are larger than or equal to $\frac{1}{9}$, are completely or nearly completely untransmitted by our filtering system. To assess the order of magnitude of their intensity, we measured the intensities for $V_v^{2\omega-\omega}\nu\text{CH}_2$ and $H_v^{2\omega-\omega}\nu\text{CH}_2$ of the Stokes hyper-Raman line $\nu\text{CH}_2=2900\text{ cm}^{-1}$ of cyclohexane. Relative measured values amounted to:

$$\frac{V_v^{2\omega-\omega}\nu\text{CH}_2}{V_v^{2\omega}} \approx 1; \quad \frac{H_v^{2\omega-\omega}\nu\text{CH}_2}{H_v^{2\omega}} \approx 3.5$$

yielding a depolarisation ratio of $D_v^{2\omega-\omega}\nu\text{CH}_2 \approx 0.4$. The lines corresponding to small differences in frequency and accessible to detection (e.g. the vibration E_u of cyclohexane at 247 cm^{-1}) are virtually unobservable in the usual infra-red spectra. They can presumably be thought to present very low intensities in hyper-Raman and contribute negligibly compared to the hyper-Rayleigh line. This assumption is confirmed by recent experimental work performed with interference filters of 200 cm^{-1} band-width, which have given the same scattered intensities. This is the experimental proof that the scattered intensities have spectral widths less than 200 cm^{-1} and that the hyper-Raman lines give no appreciable contribution.

The measured depolarisation ratios lead to anisotropies $A_{2\omega}^2$ (formula 61) of 0.04, 0.21 and 0.31 for cyclohexane, benzene and carbon disulphide, respectively.

5.2. CONCLUSION

The hyper-Rayleigh effect, studied on liquids consisting of centro-symmetric molecules, should permit the direct measurement of the anisotropy in non-linear third-order molecular polarisability. It should, moreover, provide the first method of direct measurement of the molecular field $\langle F^2 \rangle$ in liquids, and should permit a comparison with the theoretically calculated value [5]. Obviously, the experimental determination of $\langle F^2 \rangle$ requires the measurement not only of the depolarisation ratio $D_v^{2\omega}$ but, also, of the absolute values of the components $V_v^{2\omega}$ and $H_v^{2\omega}$.

Regrettably, the smallness of the scattered fluxes makes its study particularly difficult, and the use of set-ups of very high luminosity involves the complications stated above.

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