BULLETIN DE LA SOCIÉTÉ DES AMIS
DES SCIENCES ET DES LETTRES DE POZNAŃ
Série B – Livraison XXII – 1970/71
Nadbitka

# MOLECULAR CORRELATION EFFECT ON THIRD-HARMONIC LIGHT SCATTERING

by

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*(Présenté à la séance du 13 Mars 1970)*

Summary. Third-harmonic light scattering by dense isotropic media is studied. Semi-macroscopically, a formula for the third-harmonic intensity component in the **n** direction is derived:

$$I_n^{3\omega}=\frac{I^3}{2880}\left(\frac{3\omega}{c}\right)^4\left\{3F_{\text{anis}}^{3\omega}+(20F_{\text{is}}^{3\omega}+13G_{\text{anis}}^{3\omega})(\mathbf{n}\cdot\mathbf{e})^2\right\},$$

where $F_{\text{is}}^{3\omega}$, $F_{\text{anis}}^{3\omega}$ and $G_{\text{anis}}^{3\omega}$ are isotropic and anisotropic parts of the scattered light discussed on a molecular-statistical basis involving orientational and radial molecular correlations. With molecular spatial redistribution and dispersional interactions taken into consideration, it is shown that isotropically polarizable molecules can depolarize the scattered light.

## 1. INTRODUCTION

Recent measurements by Ward and New [1] on optical third-harmonic generation in gases by a focussed laser beam incite us to work out a complete theory of third-harmonic light scattering. Attention has already been given to the problem for the case of gases consisting of atoms, isotropic molecules [2], or anisotropic molecules [3]. Here, we shall discuss the role played in third-harmonic scattering by the molecular correlations active in sufficiently dense media such as real gases and liquids. A similar discussion is available for second-harmonic scattering, by a statistical and semi-macroscopic method [4, 5], and shows the total intensity $I^{2\omega}$ scattered at frequency $2\omega$ to be separable into an incoherent part $I_{\text{incoh}}^{2\omega}$ accounting for scattering by isolated molecules [2] and a coherent part $I_{\text{coh}}^{2\omega}$ due to cooperative scattering of neighbouring molecules whose positions and orientations are correlated [5].

We shall propose a general theory of third-harmonic scattering by dense media in a semi-macroscopic approach separating the total scattered intensity $I^{3\omega}$ into an isotropic part $I_{\text{is}}^{3\omega}$ dependent on radial correlations and translational fluctuations only and an anisotropic part $I_{\text{anis}}^{3\omega}$ dependent in general on angular correlations and translational-orientational fluctuations. Some simpler models of isotropically polarizable molecules as wel as axially symmetric anisotropically polarisable molecules, when the intervening parameters of radial correlations $G_R$ and of angular correlations $J_A$ are the same as in linea scattering of light at the fundamental frequency $\omega$ [6], will be discussed. Also, formula will be derived for the depolarization ratios, and numerical evaluations of the order of magnitude of the effects will be made. It is shown that especially large third-harmoni scattering can be expected from solutions of macromolecules and colloid particles.

## 2. FORMAL THEORY

Consider a dense isotropic medium of scattering volume $V$ with $N$ molecules, o which a plane polarized laser beam with electric vector $\mathbf{E}^{\omega}(t)=\mathbf{E}_0\cos\omega t$ oscillating a frequency $\omega$ is incident. If the incident intensity is sufficiently large, it will induce a non-linear dipole moment $\mathbf{M}$ in the medium:

$$M_\alpha=\sum_{k=1}^{\infty}\frac{1}{k\,!}A_{\alpha\alpha_1\ldots\alpha_k}E_{\alpha_1}^{\omega}\ldots E_{\alpha_k}^{\omega}. \qquad (1$$

Excluding from our considerations dispersion and absorption, the $k$-harmonic component of the dipole moment induced by $\mathbf{E}^{\omega}$ can be written as follows:

$$M_\alpha^{(k\omega)}=\frac{1}{k\,!\,2^{k-1}}A_{\alpha\alpha_1\ldots\alpha_k}^{k\omega}E_{0\alpha_1}\ldots E_{0\alpha_k}\cos k\omega t. \qquad (2$$

$A_{\alpha\alpha_1\ldots\alpha_k}^{k\omega}$ is the optical polarizability tensor of rank $k+1$. We have neglected in (2) smal contributions from higher-order tensors.

From (2), we see that in the medium there can appear radiation at the fundamental frequency $\omega$, radiation with harmonic frequencies $2\omega$, $3\omega$, and higher.

Generally, for the wave zone, on the assumption that the incident wavelength $\lambda$ i large as compared with intermolecular distances, the $k$-harmonic scattered light component in the $\mathbf{n}$ direction is described by the following expression [2]:

$$I_n^{k\omega}=\frac{1}{Vc^4}\int\left\langle\frac{d^2M_\alpha^{(k\omega)}}{dt^2}\frac{d^2M_\beta^{(k\omega)}}{dt^2}\right\rangle_t n_\alpha n_\beta f(\tau,I)\,d\tau, \qquad (3)$$

where the unit vector $\mathbf{n}$ denotes an arbitrarily chosen direction of electric oscillations in the scattered light, the symbol $\langle\ \rangle_t$ stands for averageing over the time, $c$ is the light velocity and $I=E_0^2/2$ the incident beam intensity; $f(\tau, I)$ is a statistical distribution given by the Maxwell-Boltzmann function

$$f(\tau,I)=\frac{\exp\{-\beta U(\tau,I)\}}{\int\exp\{-\beta U(\tau,I)\}\,d\tau} \qquad (4$$

with $\beta=1/kT$, and $U(\tau, I)$ is the total potential energy of the system at configuration $\tau$ in the presence of the laser beam $I$.

On expanding the right hand side of (4) in a power series in $\beta U < 1$, we obtain

$$f(\tau, I) = f(\tau, 0) + \sum_{i=1}^{\infty} f^{(i)}(\tau, I), \tag{5}$$

where

$$f(\tau, 0) = \frac{\exp\{-\beta U(\tau, 0)\}}{\int \exp\{-\beta U(\tau, 0)\}\, d\tau} \tag{6}$$

is the distribution function in the absence of the beam $I$, and $f^{(i)}(\tau, I)$ are $i$-th order distribution functions in the presence of $I$.

Restricting (5) to the first term only, eq. (3) with regard to (2) for $k=3$ on substituting $A^{3\omega}_{\alpha\alpha_1\alpha_2\alpha_3} = C^{3\omega}_{\alpha\beta\gamma\delta}$ and averageing over the time, takes the form:

$$I_n^{3\omega} = \frac{I^3}{144V} \left(\frac{3\omega}{c}\right)^4 \int C^{3\omega}_{\alpha\gamma\varepsilon\lambda} C^{3\omega}_{\beta\delta\eta\tau} n_\alpha n_\beta e_\gamma e_\delta e_\varepsilon e_\eta e_\lambda e_\tau f(\tau, 0)\, d\tau, \tag{7}$$

where we have introduced $e_\alpha$ as the direction of oscillations of the electric vector component $E_\alpha$ in the incident light.

In the absence of the laser beam, all directions of the vectors **e** and **n** with respect to laboratory axes $XYZ$ (the frame is rigidly attached to the scattering centre) are equally possible. The mean isotropic value of the product of unit vector components $\langle n_\alpha n_\beta e_\gamma e_\delta e_\varepsilon e_\eta e_\lambda e_\tau \rangle_\Omega$ is derived in [3], where it is also generally shown that (for $r=2k$, $k \geqslant 2$)

$$\langle n_{\alpha_1} n_{\alpha_2} e_{\alpha_3} \dots e_{\alpha_r} \rangle_\Omega = \frac{1}{2(2k+1)!!} \{[2k+1][1-(\mathbf{n}\cdot\mathbf{e})^2]\, \delta_{\alpha_1\alpha_2} \sigma_{\alpha_3 \dots \alpha_r} + \\ + [3(\mathbf{n}\cdot\mathbf{e})^2 - 1]\, \sigma_{\alpha_1\alpha_2\alpha_3 \dots \alpha_r}\} \tag{8}$$

with the tensor

$$\sigma_{\alpha_1\alpha_2\alpha_3 \dots \alpha_r} = \delta_{\alpha_1\alpha_2} \sigma_{\alpha_3 \dots \alpha_r} + \delta_{\alpha_1\alpha_3} \sigma_{\alpha_2\alpha_4 \dots \alpha_r} + \delta_{\alpha_1\alpha_{r-1}} \sigma_{\alpha_2\alpha_3 \dots \alpha_{r-2}\alpha_r} + \delta_{\alpha_1\alpha_r} \sigma_{\alpha_2\alpha_3 \dots \alpha_{r-1}}. \tag{9}$$

Taking in (8) $k=4$ and inserting in (7), we find:

$$I_n^{3\omega} = I^{3\omega}_{n\,\mathrm{is}} + I^{3\omega}_{n\,\mathrm{anis}} \tag{10}$$

and

$$I^{3\omega}_{n\,\mathrm{is}} = \frac{I^3}{144} \left(\frac{3\omega}{c}\right)^4 F^{3\omega}_{\mathrm{is}} (\mathbf{n}\cdot\mathbf{e})^2, \tag{11}$$

$$I^{3\omega}_{n\,\mathrm{anis}} = \frac{I^3}{2880} \left(\frac{3\omega}{c}\right)^4 \{3F^{3\omega}_{\mathrm{anis}} + 13G^{3\omega}_{\mathrm{anis}} (\mathbf{n}\cdot\mathbf{e})^2\},$$

where the quantities

$$F^{3\omega}_{\mathrm{is}} = \frac{1}{225V} \sigma_{\alpha\gamma\varepsilon\lambda} \sigma_{\beta\delta\eta\tau} \langle C^{3\omega}_{\alpha\gamma\varepsilon\lambda} C^{3\omega}_{\beta\delta\eta\tau} \rangle,$$

$$F^{3\omega}_{\mathrm{anis}} = \frac{2}{567V} \{9\delta_{\alpha\beta} \sigma_{\gamma\delta\varepsilon\eta\lambda\tau} - \sigma_{\alpha\beta\gamma\delta\varepsilon\eta\lambda\tau}\} \langle C^{3\omega}_{\alpha\gamma\varepsilon\lambda} C^{3\omega}_{\beta\delta\eta\tau} \rangle, \tag{12}$$

$$G^{3\omega}_{\mathrm{anis}} = \frac{2}{4095V} \{5\sigma_{\alpha\beta\gamma\delta\varepsilon\eta\lambda\tau} - 15\delta_{\alpha\beta} \sigma_{\gamma\delta\varepsilon\eta\lambda\tau} - 14\sigma_{\alpha\gamma\varepsilon\lambda} \sigma_{\beta\delta\eta\tau}\} \langle C^{3\omega}_{\alpha\gamma\varepsilon\lambda} C^{3\omega}_{\beta\delta\eta\tau} \rangle$$

define respectively isotropic and anisotropic third-harmonic light scattering. The symbol $\langle\ \ \rangle$ in (12) stands for statistical averageing over molecular interactions with the distribution function (6).

We assume in general that the tensor $C^{3\omega}_{\alpha\beta\gamma\delta}$ is symmetric in the last three indices $\beta$, $\gamma$, $\delta$.

Hence (12), with regard to (9), takes the form:

$$F^{3\omega}_{\mathrm{is}}=\frac{1}{25V}\langle C^{3\omega}_{\alpha\alpha\gamma\gamma}C^{3\omega}_{\beta\beta\delta\delta}\rangle,$$

$$F^{3\omega}_{\mathrm{anis}}=\frac{2}{189V}\langle 16C^{3\omega}_{\alpha\beta\gamma\delta}C^{3\omega}_{\alpha\beta\gamma\delta}-6C^{3\omega}_{\alpha\beta\gamma\delta}C^{3\omega}_{\beta\alpha\gamma\delta}+24C^{3\omega}_{\alpha\beta\gamma\gamma}C^{3\omega}_{\alpha\beta\delta\delta}-3C^{3\omega}_{\alpha\beta\gamma\gamma}C^{3\omega}_{\beta\alpha\delta\delta}-6C^{3\omega}_{\alpha\beta\gamma\gamma}C^{3\omega}_{\delta\delta\alpha\beta}-$$
$$-6C^{3\omega}_{\alpha\alpha\gamma\delta}C^{3\omega}_{\gamma\delta\beta\beta}-6C^{3\omega}_{\alpha\alpha\gamma\delta}C^{3\omega}_{\beta\beta\gamma\delta}-3C^{3\omega}_{\alpha\alpha\gamma\gamma}C^{3\omega}_{\beta\beta\delta\delta}\rangle,$$

$$G^{3\omega}_{\mathrm{anis}}=\frac{2}{1365V}\langle -20C^{3\omega}_{\alpha\beta\gamma\delta}C^{3\omega}_{\alpha\beta\gamma\delta}+30C^{3\omega}_{\alpha\beta\gamma\delta}C^{3\omega}_{\beta\alpha\gamma\delta}-30C^{3\omega}_{\alpha\beta\gamma\gamma}C^{3\omega}_{\alpha\beta\delta\delta}+15C^{3\omega}_{\alpha\beta\gamma\gamma}C^{3\omega}_{\beta\alpha\delta\delta}+ \tag{13}$$
$$+30C^{3\omega}_{\alpha\beta\gamma\gamma}C^{3\omega}_{\delta\delta\alpha\beta}+30C^{3\omega}_{\alpha\alpha\gamma\delta}C^{3\omega}_{\gamma\delta\beta\beta}+30C^{3\omega}_{\alpha\alpha\gamma\delta}C^{3\omega}_{\beta\beta\gamma\delta}-27C^{3\omega}_{\alpha\alpha\gamma\gamma}C^{3\omega}_{\beta\beta\delta\delta}\rangle.$$

Let the incident wave propagate in the $Y$-direction and observation be in the $XY$-plane at an angle $\vartheta$ to $Y$. When the incident beam oscillates in the plane vertical to $XY$, the horizontal and vertical components of the scattered light are:

$$\begin{aligned}{}^{v}I^{3\omega}_{h}&=H^{3\omega}_{v}=\frac{I^{3}}{960}\left(\frac{3\omega}{c}\right)^{4}F^{3\omega}_{\mathrm{anis}},\\ {}^{v}I^{3\omega}_{v}&=V^{3\omega}_{v}=\frac{I^{3}}{2880}\left(\frac{3\omega}{c}\right)^{4}(20F^{3\omega}_{\mathrm{is}}+3F^{3\omega}_{\mathrm{anis}}+13G^{3\omega}_{\mathrm{anis}}),\end{aligned}\tag{14}$$

where the upper left-hand index at $I^{3\omega}$ denotes the polarization of the incident light.

Along similar lines we get

$$\begin{aligned}{}^{h}I^{3\omega}_{h}&=H^{3\omega}_{h}=\frac{I^{3}}{2880}\left(\frac{3\omega}{c}\right)^{4}\{3F^{3\omega}_{\mathrm{anis}}+(20F^{3\omega}_{\mathrm{is}}+13G^{3\omega}_{\mathrm{anis}})\cos^{2}\vartheta\},\\ {}^{h}I^{3\omega}_{v}&=V^{3\omega}_{h}=\frac{I^{3}}{960}\left(\frac{3\omega}{c}\right)^{4}F^{3\omega}_{\mathrm{anis}}.\end{aligned}\tag{15}$$

We see that in the case of third-harmonic light scattering Krishnan's reciprocity relation $H^{3\omega}_{v}=V^{3\omega}_{h}$ still holds.

For unpolarized incident light we obtain:

$$\begin{aligned}{}^{u}I^{3\omega}_{h}&=H^{3\omega}_{u}=H^{3\omega}_{v}+H^{3\omega}_{h}=\frac{I^{3}}{2880}\left(\frac{3\omega}{c}\right)^{4}\{6F^{3\omega}_{\mathrm{anis}}+(20F^{3\omega}_{is}+13G^{3\omega}_{\mathrm{anis}})\cos^{2}\vartheta\},\\ {}^{u}I^{3\omega}_{v}&=V^{3\omega}_{u}=V^{3\omega}_{v}+V^{3\omega}_{h}=\frac{I^{3}}{2880}\left(\frac{3\omega}{c}\right)^{4}(20F^{3\omega}_{\mathrm{is}}+6F^{3\omega}_{\mathrm{anis}}+13G^{3\omega}_{\mathrm{anis}}).\end{aligned}\tag{16}$$

By (14 - 16), the depolarization ratios for the three polarizations of the incident light beam are:

$$D_v^{3\omega}=\frac{H_v^{3\omega}}{V_v^{3\omega}}=\frac{3F_{\text{anis}}^{3\omega}}{20F_{\text{is}}^{3\omega}+3F_{\text{anis}}^{3\omega}+13G_{\text{anis}}^{3\omega}}, \tag{17}$$

$$D_h^{3\omega}(\vartheta)=\frac{V_h^{3\omega}}{H_h^{3\omega}}=\frac{3F_{\text{anis}}^{3\omega}}{3F_{\text{anis}}^{3\omega}+(20F_{\text{is}}^{3\omega}+13G_{\text{anis}}^{3\omega})\cos^2\vartheta}, \tag{18}$$

$$D_u^{3\omega}(\vartheta)=\frac{H_u^{3\omega}}{V_u^{3\omega}}=\frac{6F_{\text{anis}}^{3\omega}+(20F_{\text{is}}^{3\omega}+13G_{\text{anis}}^{3\omega})\cos^2\vartheta}{20F_{\text{is}}^{3\omega}+6F_{\text{anis}}^{3\omega}+13G_{\text{anis}}^{3\omega}}. \tag{19}$$

When observation is carried out along the $X$-axis ($\vartheta=90°$) we have by eqs (18 - 19):

$$D_h^{3\omega}=1, \quad D_u^{3\omega}=\frac{6F_{\text{anis}}^{3\omega}}{20F_{\text{is}}^{3\omega}+6F_{\text{anis}}^{3\omega}+13G_{\text{anis}}^{3\omega}}. \tag{20}$$

Hence by analogy to linear scattering we obtain the following relations:

$$\begin{gathered}
D_h^{3\omega}(\vartheta)=\frac{D_v^{3\omega}}{D_v^{3\omega}+(1-D_v^{3\omega})\cos^2\vartheta}, \\
D_u^{3\omega}(\vartheta)=D_u^{3\omega}\left(1+\frac{1-D_u^{3\omega}}{D_u^{3\omega}}\cos^2\vartheta\right)=\frac{1}{1+D_v^{3\omega}}\{2D_v^{3\omega}+(1-D_v^{3\omega})\cos^2\vartheta\}, \\
D_u^{3\omega}=\frac{2D_v^{3\omega}}{1+D_v^{3\omega}}.
\end{gathered} \tag{21}$$

## 3. MOLECULAR-STATISTICAL THEORY

For our further discussion, it is convenient to relate the tensor $C_{\alpha\beta\gamma\delta}^{3\omega}$ characterizing the medium to the hyperpolarizability tensor of the molecule $c_{\alpha\beta\gamma\delta}^{3\omega}$.

We have, with satisfactory accuracy, in the absence of molecular fields,

$$C_{\alpha\beta\gamma\delta}^{3\omega}=\sum_{p=1}^{N}c_{\alpha\beta\gamma\delta}^{3\omega(p)}. \tag{22}$$

In this approximation, we can consider the tensor $C_{\alpha\beta\gamma\delta}^{3\omega}$ as totally symmetric. This is true for inactive molecules beyond dispersion and absorption.

Then eqs. (13) transform to:

$$\begin{aligned}
F_{\text{is}}^{3\omega}&=\frac{1}{25V}\langle C_{\alpha\alpha\gamma\gamma}^{3\omega}C_{\beta\beta\delta\delta}^{3\omega}\rangle, \\
F_{\text{anis}}^{3\omega}&=\frac{2}{189V}\langle 10C_{\alpha\beta\gamma\delta}^{3\omega}C_{\alpha\beta\gamma\delta}^{3\omega}+3C_{\alpha\beta\gamma\gamma}^{3\omega}C_{\alpha\beta\delta\delta}^{3\omega}-3C_{\alpha\alpha\gamma\gamma}^{3\omega}C_{\beta\beta\delta\delta}^{3\omega}\rangle, \\
G_{\text{anis}}^{3\omega}&=\frac{2}{1365V}\langle 10C_{\alpha\beta\gamma\delta}^{3\omega}C_{\alpha\beta\gamma\delta}^{3\omega}+75C_{\alpha\beta\gamma\gamma}^{3\omega}C_{\alpha\beta\delta\delta}^{3\omega}-27C_{\alpha\alpha\gamma\gamma}^{3\omega}C_{\beta\beta\delta\delta}^{3\omega}\rangle.
\end{aligned} \tag{23}$$

We first proceed to consider the general case of arbitrarily symmetric molecules, for which by (22) we have, to within pairwise correlations,

$$
\begin{aligned}
F_{\text{is}}^{3\omega} &= \frac{\rho}{25} c_{\alpha\alpha\gamma\gamma}^{3\omega} c_{\beta\beta\delta\delta}^{3\omega} (1+G_R), \\
F_{\text{anis}}^{3\omega} &= \frac{2\rho}{189} \{ 10 c_{\alpha\beta\gamma\delta}^{3\omega} c_{\alpha\beta\gamma\delta}^{3\omega} + 3 c_{\alpha\beta\gamma\gamma}^{3\omega} c_{\alpha\beta\delta\delta}^{3\omega} - 3 c_{\alpha\alpha\gamma\gamma}^{3\omega} c_{\beta\beta\delta\delta}^{3\omega} + \\
&\quad + \frac{\rho}{V} \iint [ 10 c_{\alpha\beta\gamma\delta}^{3\omega(p)} c_{\alpha\beta\gamma\delta}^{3\omega(q)} + 3 c_{\alpha\beta\gamma\gamma}^{3\omega(p)} c_{\alpha\beta\delta\delta}^{3\omega(q)} - 3 c_{\alpha\alpha\gamma\gamma}^{3\omega(p)} c_{\beta\beta\delta\delta}^{3\omega(q)} ] g^{(2)}(\tau_p, \tau_q)\, d\tau_p\, d\tau_q \}, \qquad (24) \\
G_{\text{anis}}^{3\omega} &= \frac{2\rho}{1365} \Big\{ 10 c_{\alpha\beta\gamma\delta}^{3\omega} c_{\alpha\beta\gamma\delta}^{3\omega} + 75 c_{\alpha\beta\gamma\gamma}^{3\omega} c_{\alpha\beta\delta\delta}^{3\omega} - 27 c_{\alpha\alpha\gamma\gamma}^{3\omega} c_{\beta\beta\delta\delta}^{3\omega} + \\
&\quad + \frac{\rho}{V} \iint [ 10 c_{\alpha\beta\gamma\delta}^{3\omega(p)} c_{\alpha\beta\gamma\delta}^{3\omega(q)} + 75 c_{\alpha\beta\gamma\gamma}^{3\omega(p)} c_{\alpha\beta\delta\delta}^{3\omega(q)} - 27 c_{\alpha\alpha\gamma\gamma}^{3\omega(p)} c_{\beta\beta\delta\delta}^{3\omega(q)} ] g^{(2)}(\tau_p, \tau_q)\, d\tau_p\, d\tau_q \Big\},
\end{aligned}
$$

wherein $\rho = N/V$ is the number density of molecules. The integral parameters describe angular pairwise correlations of molecules, irrespective of their symmetry class (excluding isotropically polarizable molecules).

Furthermore, we have the parameter [6]

$$G_R = \frac{\rho}{V} \iint [g^{(2)}(\tau_p, \tau_q) - g^{(1)}(\tau_p) g^{(1)}(\tau_q)]\, d\tau_p\, d\tau_q \qquad (25)$$

determining molecular correlations of the radial kind. $g^{(1)}(\tau_p)$, $g^{(2)}(\tau_p, \tau_q)$ denote one- and two-molecule correlation functions respectively and $\tau_p$, $\tau_q$ are variables defining the positions and orientations of molecules $p$ and $q$.

The factor $1+G_R$ can be represented in the thermodynamical form due to Smoluchowski [7] and Einstein [8] in their theory of linear light scattering

$$1+G_R = \rho k T \beta_T. \qquad (26)$$

($\beta_T$ is the isothermal compressibility coefficient).

In the absence of molecular interactions, the angular correlation parameters always vanish and $\rho k T \beta_T$ tends to unity.

Our considerations have hitherto been of an entirely general nature and can now be particularized for various molecules.

a. Isotropic – polarizable molecules. For isotropic molecules, the hyperpolarizability tensor $c_{\alpha\beta\gamma\delta}^{2\omega}$ can be written as follows:

$$c_{\alpha\beta\gamma\delta}^{3\omega} = \frac{1}{3} c_{3\omega} \sigma_{\alpha\beta\gamma\delta}, \qquad (27)$$

where, according to (9),

$$\sigma_{\alpha\beta\gamma\delta} = \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma},$$

and $c_{3\omega} = c_{\alpha\alpha\beta\beta}^{3\omega}/5$ is the mean hyperpolarizability.

From (24) with (26), we get

$$F^{3\omega}_{\text{is}}=c^2_{3\omega}\rho^2kT\beta_T, \quad F^{3\omega}_{\text{anis}}=G^{3\omega}_{\text{anis}}=0, \tag{28}$$

and the depolarization ratios (17 - 19) become:

$$D^{3\omega}_v=D^{3\omega}_h=0, \quad D^{3\omega}_u(\vartheta)=\cos^2\vartheta. \tag{29}$$

In this approximation, when the incident beam is plane polarized, atoms or isotropic molecules do not depolarize the scattered light. For unpolarized incident light, the depolarization of third-harmonic scattered light is just the same as that of linearly scattered light: $D^{3\omega}_u(\vartheta)=D^{\omega}_u(\vartheta)$ [6].

b. Anisotropically polarizable molecules. For such molecules possessing the axial symmetry e. g. about their 3-axis we have in the absence of nonlinear dispersion [9]:

$$c^{3\omega}_{\alpha\beta\gamma\delta}=\tfrac{1}{3}c_{3\omega}\{\sigma_{\alpha\beta\gamma\delta}+\tfrac{1}{2}\kappa_c[3(\delta_{\alpha\beta}k_\gamma k_\delta+\delta_{\alpha\gamma}k_\beta k_\delta+ \\ +\delta_{\alpha\delta}k_\beta k_\gamma+\delta_{\beta\gamma}k_\alpha k_\delta+\delta_{\beta\delta}k_\alpha k_\gamma+\delta_{\gamma\delta}k_\alpha k_\beta)-2\sigma_{\alpha\beta\gamma\delta}]\}, \tag{30}$$

where $k_\alpha$ is the $\alpha$ – component of a unit vector along the axis of symmetry of the molecule, and the quantities

$$c_{3\omega}=\frac{c^{3\omega}_{3333}+2c^{3\omega}_{1111}}{3}, \quad \kappa_c=\frac{c^{3\omega}_{3333}-c^{3\omega}_{1111}}{3c_{3\omega}}$$

define respectively the mean optical hyperpolarizability and its anisotropy.

By (30), eqs. (24) take the form

$$F^{3\omega}_{\text{is}}=c^2_{3\omega}\rho^2kT\beta_T, \\ F^{3\omega}_{\text{anis}}=G^{3\omega}_{\text{anis}}=c^2_{3\omega}\kappa^2_c\rho(1+J_A), \tag{31}$$

with [6]

$$J_A=\frac{\rho}{2V}\iint[3\cos^2\theta_{pq}-1]\,g^{(2)}(\tau_p,\tau_q)\,d\tau_p\,d\tau_q \tag{32}$$

denoting the angular correlations parameter of the axially symmetric molecules. $\theta_{pq}$ is the angle between the symmetry axes of molecules $p$ and $q$.

The parameter $J_A$ given by (32) is well-known from the theories of linear light scattering and optical birefringence of liquids the molecules of which are axially symmetric [6, 10].

In general, the parameter $J_A$ can take positive and negative values. This means that the assemblages of interacting molecules can enhance or weaken the scattered light intensity (e. g. for $C_6H_6$ molecules, the parameter estimated from linear scattering and birefringence data is: $J_A=-(0.18\div0.5)$ [11]). The depolarization ratios (17 - 19) are, in this case

$$D^{3\omega}_v=\frac{3\kappa^2_c(1+J_A)}{20\rho kT\beta_T+16\kappa^2_c(1+J_A)}, \tag{33}$$

$$D_h^{3\omega}(\vartheta)=\frac{3\kappa_c^2(1+J_A)}{3\kappa_c^2(1+J_A)+[20\rho kT\beta_T+13\kappa_c^2(1+J_A)]\cos^2\vartheta}, \tag{34}$$

$$D_u^{3\omega}(\vartheta)=\frac{6\kappa_c^2(1+J_A)+[20\rho kT\beta_T+13\kappa_c^2(1+J_A)]\cos^2\vartheta}{20\rho kT\beta_T+19\kappa_c^2(1+J_A)}. \tag{35}$$

In the absence of angular molecular interactions, the parameter $J_A$ vanishes. Indeed, e. g. in rarefied gases, the scattering molecules can assume all possible configurations with identical probability. In this case $g^{(2)}(\tau_p, \tau_q)=\Omega^{-2}$, $\Omega=\int d\omega_p=\int d\omega_q$, and we have

$$J_A=\frac{N}{2\Omega^2}\iint[3\cos^2\theta_{pq}-1]\,d\omega_p\,d\omega_q=0, \tag{36}$$

where $\omega_p$ and $\omega_q$ are variables determining the orientation of molecules $p$ and $q$.

Thus, eqs. (31) reduce to

$$F_{\text{is}}^{3\omega}=\rho c_{3\omega}^2, \qquad F_{\text{anis}}^{3\omega}=G_{\text{anis}}^{3\omega}=\rho c_{3\omega}^2\kappa_c^2, \tag{37}$$

and the depolarization ratios become

$$D_v^{3\omega}=\frac{3\kappa_c^2}{20+16\kappa_c^2}, \tag{38}$$

$$D_h^{3\omega}(\vartheta)=\frac{3\kappa_c^2}{3\kappa_c^2+(20+13\kappa_c^2)\cos^2\vartheta}, \tag{39}$$

$$D_u^{3\omega}(\vartheta)=\frac{6\kappa_c^2+(20+13\kappa_c^2)\cos^2\vartheta}{20+19\kappa_c^2}. \tag{40}$$

It is of much interest here to draw attention to the likeness between the depolarization ratio (33) and $D_v^{\omega}$ – the depolarization ratio of linearly scattered light:

$$D_v^{\omega}=\frac{3\kappa_a^2(1+J_A)}{5\rho kT\beta_T+4\kappa_a^2(1+J_A)} \tag{41}$$

($\kappa_a$ denoting the anisotropy of linear polarizability of the axially symmetric molecules).

We easily find the simple relation:

$$\kappa_c^2=4\frac{D_v^{3\omega}}{D_v^{\omega}}\left(\frac{3-4D_v^{\omega}}{3-16D_v^{3\omega}}\right)\kappa_a^2. \tag{42}$$

One can determine $\kappa_c$ directly (knowing $\kappa_a$) from experiments by measurements of depolarization ratios of third-harmonic and linearly scattered light only. The last formula circumvents the difficulties of evaluating the parameter $J_A$ from other experimental data.

With the aim of more exact calculations, we shall now consider the effect of molecular spatial redistribution [6, 12] on third-harmonic light scattering in dense media.

By Eq. (1),

$$C_{\alpha\beta\gamma\delta}^{3\omega}=\left(\frac{\partial^3 M_\alpha^{3\omega}}{\partial E_\beta^{\omega}\,\partial E_\gamma^{\omega}\,\partial E_\delta^{\omega}}\right)_0. \tag{43}$$

Also $\mathbf{M}=\sum_{p=1}^{N}\mathbf{m}^{(p)}$, where $\mathbf{m}^{(p)}$ is the electric dipole moment of the $p$-th molecule immersed in the medium and in general subjected to the laser field $\mathbf{E}^{\omega}$ and a molecular field $\mathbf{F}$ [6].

Eq. (43) now becomes:

$$C^{3\omega}_{\alpha\beta\gamma\delta}=\sum_{p=1}^{N}\left(\frac{\partial^3 m_{\alpha}^{3\omega(p)}}{\partial E^{\omega}_{\beta}\,\partial E^{\omega}_{\gamma}\,\partial E^{\omega}_{\delta}}\right)_0. \tag{44}$$

The dipole moment induced in the $p$-th molecule at frequency $3\omega$ is:

$$m_{\alpha}^{3\omega(p)}=\tfrac{1}{6}c^{3\omega(p)}_{\alpha\beta\gamma\delta}(E^{\omega}_{\beta}+F^{(p)}_{\beta})(E^{\omega}_{\gamma}+F^{(p)}_{\gamma})(E^{\omega}_{\delta}+F^{(p)}_{\delta})+\dots. \tag{45}$$

$\mathbf{F}^{(p)}$ is the molecular field additionally acting on the $p$-th molecule due to the $N$-1 molecules in the presence of $\mathbf{E}^{\omega}$. This field can be accounted for by Kirkwood's method [12].

In a linear approximation, we write [6]:

$$F^{(p)}_{\alpha}=F^{(p)}_{0\alpha}-\sum_{\substack{q=1\\ q\neq p}}^{N}T^{(pq)}_{\alpha\beta}a^{\omega(q)}_{\beta\gamma}E^{\omega}_{\gamma}+\sum_{\substack{q=1\\ q\neq p}}^{N}\sum_{\substack{r=1\\ r\neq q}}^{N}T^{(pq)}_{\alpha\beta}a^{\omega(q)}_{\beta\gamma}T^{(qr)}_{\gamma\delta}a^{\omega(r)}_{\delta\varepsilon}E^{\omega}_{\varepsilon}-\dots \tag{46}$$

with $F^{(p)}_{0\alpha}$ denoting the $\alpha$-component of the molecular field acting on the $p$-th molecule in the absence of the laser beam, and

$$T^{(pq)}_{\alpha\beta}=-r^{-5}_{pq}(3r_{pq\alpha}r_{pq\beta}-r^{2}_{pq}\delta_{\alpha\beta}) \tag{47}$$

the dipole-dipole interaction tensor of molecules $p$ and $q$ (distant by $r_{pq}$) which is non-zero for $p\neq q$ and equal to zero for $p=q$. $a^{\omega(p)}_{\alpha\beta}$ is the linear polarizability tensor of the $p$-th molecule.

Neglecting higher-order hyperpolarizabilities in the expansion (45), we have with regard to (44):

$$C^{3\omega}_{\alpha\beta\gamma\delta}=\sum_{p=1}^{N}c^{3\omega\, p)}_{\alpha\varepsilon\eta\lambda}\left(\delta_{\varepsilon\beta}+\frac{\partial F^{(p)}_{\varepsilon}}{\partial E^{\omega}_{\beta}}\right)\left(\delta_{\eta\gamma}+\frac{\partial F^{(p)}_{\eta}}{\partial E^{\omega}_{\gamma}}\right)\left(\delta_{\lambda\delta}+\frac{\partial F^{(p)}_{\lambda}}{\partial E^{\omega}_{\delta}}\right). \tag{48}$$

From the above expansion we see that the tensor $C^{3\omega}_{\alpha\beta\gamma\delta}$ is symmetric in the indices $\beta$, $\gamma$, $\delta$ only, but that $c^{3\omega}_{\alpha\beta\gamma\delta}$ is still totally symmetric.

a. Isotropically polarizable molecules. On inserting (48) in (11), we get for such molecules by (27) with satisfactory accuracy:

$$\begin{aligned}F^{3\omega}_{\mathrm{is}}=\frac{1}{15V}\Big\langle\sum_{p=1}^{N}\sum_{q=1}^{N}c^{3\omega}_{p}c^{3\omega}_{q}\Big\{15+15\left(\frac{\partial F^{(p)}_{\alpha}}{\partial E^{\omega}_{\alpha}}+\frac{\partial F^{(q)}_{\alpha}}{\partial E^{\omega}_{\alpha}}\right)+9\left(\frac{\partial F^{(p)}_{\alpha}}{\partial E^{\omega}_{\beta}}\,\frac{\partial F^{(p)}_{\alpha}}{\partial E^{\omega}_{\beta}}+\frac{\partial F^{(q)}_{\alpha}}{\partial E^{\omega}_{\beta}}\,\frac{\partial F^{(q)}_{\alpha}}{\partial E^{\omega}_{\beta}}\right)+\\ +2\left(\frac{\partial F^{(p)}_{\alpha}}{\partial E^{\omega}_{\alpha}}\,\frac{\partial F^{(p)}_{\beta}}{\partial E^{\omega}_{\beta}}+\frac{\partial F^{(q)}_{\alpha}}{\partial E^{\omega}_{\alpha}}\,\frac{\partial F^{(q)}_{\beta}}{\partial E^{\omega}_{\beta}}\right)+15\,\frac{\partial F^{(p)}_{\alpha}}{\partial E^{\omega}_{\alpha}}\,\frac{\partial F^{(q)}_{\beta}}{\partial E^{\omega}_{\beta}}\Big\}\Big\rangle,\\ F^{3\omega}_{\mathrm{anis}}=\frac{13}{33}G^{3\omega}_{\mathrm{anis}}=\frac{2}{9V}\Big\langle\sum_{p=1}^{N}\sum_{q=1}^{N}c^{3\omega}_{p}c^{3\omega}_{q}\Big\{3\,\frac{\partial F^{(p)}_{\alpha}}{\partial E^{\omega}_{\beta}}\,\frac{\partial F^{(r)}_{\alpha}}{\partial E^{\omega}_{\beta}}-\frac{\partial F^{(p)}_{\alpha}}{\partial E^{\omega}_{\alpha}}\,\frac{\partial F^{(q)}_{\beta}}{\partial E^{\omega}_{\beta}}\Big\}\Big\rangle.\end{aligned} \tag{49}$$

Putting in (46) $a_{\alpha\beta}^{\omega}=a_{\omega}\delta_{\alpha\beta}$ (where $a_{\omega}=a_{\alpha\alpha}^{\omega}/3$ is the mean linear polarizability), inserting in (49), and restricting calculations to pairwise interactions only, we obtain to within $a_{\omega}^2$ the result:

$$\begin{aligned} F_{\mathrm{is}}^{3\omega}&=c_{3\omega}^2\rho^2kT\beta_T[1+0(a_{\omega}^2)], \\ F_{\mathrm{anis}}^{3\omega}&=\frac{13}{33}G_{\mathrm{anis}}^{3\omega}=4\rho a_{\omega}^2c_{3\omega}^2J_R^{(6)}+\dots, \end{aligned} \tag{50}$$

where $0(a_{\omega}^2)$, calculated with the assumption that fluctuations of the density are independent of translational fluctuations, is:

$$0(a_{\omega}^2)\simeq\frac{96}{5\rho kT\beta_T}a_{\omega}^2J_R^{(6)}+\dots. \tag{51}$$

$J_R^{(6)}$ denotes the radial correlation parameter [10]:

$$J_R^{(6)}=2\langle r_{pq}^{-6}\rangle=8\pi\rho\int r_{pq}^{-4}g(r_{pq})\,dr_{pq}. \tag{52}$$

Generally, numerical calculations of $\langle r_{pq}^{-n}\rangle$ for $n\geqslant 4$ can be performed in Kirkwood's approximation [12], yielding [13]:

$$\langle r_{pq}^{-n}\rangle=\frac{4\pi\rho}{n-3}\left(\frac{\pi}{6v}\right)^{\frac{n-3}{3}}, \tag{53}$$

where $v$ is the volume of the molecule.

From (50), it results that there can appear an insignificant depolarization of third-harmonic scattered light even if the scattering medium consists of isotropic molecules:

$$D_v^{3\omega}=\frac{3a_{\omega}^2J_R^{(6}}{5\rho kT\beta_T[1+0(a_{\omega}^2)]+36a_{\omega}^2J_R^{(6)}}. \tag{54}$$

This is a direct consequence of the fact that the assemblages of interacting atoms or isotropic molecules behave as optically anisotropic elements which then cause anisotropic light scattering. The depolarization ratio is moreover temperature-dependent since $J_R^{(6)}=J_R^{(6)}(T)$.

b. Anisotropically polarizable molecules. By (A.1 - A.3) (see Appendix), Eq. (30), and taking for axially symmetric molecules $a_{\alpha\beta}^{\omega}=a_{\omega}\delta_{\alpha\beta}+a_{\omega}\kappa_a(3k_{\alpha}k_{\beta}-\delta_{\alpha\beta})$, where $a_{\omega}=\frac{a_{33}^{\omega}+2a_{11}^{\omega}}{3}$ is the mean polarizability and $\kappa_a=\frac{a_{33}^{\omega}-a_{11}^{\omega}}{3a_{\omega}}$ its anisotropy, we obtain:

$$\begin{aligned} F_{\mathrm{is}}^{3\omega}&=c_{3\omega}^2\rho^2kT\beta_T[1+0(a_{\omega}^2)], \\ F_{\mathrm{anis}}^{3\omega}&=c_{3\omega}^2\rho\left[\kappa_c^2(1+J_A)+4a_{\omega}^2J_R^{(6)}(1+\dots)\right], \\ G_{\mathrm{anis}}^{3\omega}&=c_{3\omega}^2\rho\left[\kappa_c^2(1+J_A)+\tfrac{132}{13}a_{\omega}^2J_R^{(6)}(1\quad\dots)\right], \end{aligned} \tag{55}$$

where we have neglected in terms with $J_R^{(6)}$ small contributions from the anisotropies $\kappa_a$ and $\kappa_c$.

Thus, the depolarization ratio $D_v^{3\omega}$ can be written in this approximation as:

$$D_v^{3\omega}=\tfrac{1}{4}\cdot\frac{3\left[\kappa_c^2(1+J_A)+4a_{\omega}^2J_R^{(6)}\right]}{5\rho kT\beta_T[1+0(a_{\omega}^2)]+4\left[\kappa_c^2(1+J_A)+9a_{\omega}^2J_R^{(6)}\right]}. \tag{56}$$

It is important, moreover, that we can evaluate the parameter $J_R^{(6)}$ not only by theoretical approximation (53) but also from depolarization ratios of linearly scattered light or electric, magnetic and optical birefringence data [6, 10, 13] and from molecular polarization or refraction [12].

In condensed media, the molecules polarize one another by way of their intrinsic microscopic fields $\mathbf{F}_0$, even though no external field may be acting on the medium.

Considering in (45) higher-order polarizabilities, by (44) we additionally obtain:

$$C_{\alpha\beta\gamma\delta}^{3\omega}=\sum_{p=1}^{N}\left(c_{\alpha\beta\gamma\delta}^{3\omega(p)}+d_{\alpha\beta\gamma\delta\varepsilon}^{3\omega(p)}F_{0\varepsilon}^{(p)}+\tfrac{1}{2}e_{\alpha\beta\gamma\delta\varepsilon\eta}^{3\omega(p)}F_{0\varepsilon}^{(p)}F_{0\eta}^{(p)}+\dots\right). \tag{57}$$

If the molecule possesses a centre of inversion, all components of the hyperpolarizability tensor $d_{\alpha\beta\gamma\delta\varepsilon}$ vanish and so does the first contribution due to the linear field $\mathbf{F}_0$ in this case.

Therefore for centrosymmetric molecules, we have:

$$C_{\alpha\beta\gamma\delta}^{3\omega}=\sum_{p=1}^{N}\left(c_{\alpha\beta\gamma\delta}^{3\omega(p)}+\tfrac{1}{2}e_{\alpha\beta\gamma\delta\varepsilon\eta}^{3\omega(p)}\mathbf{F}_{0\varepsilon}^{(p)}\mathbf{F}_{0\eta}^{(p)}\right), \tag{58}$$

where $\mathbf{F}_0^{(p)}=\sum_{q\neq p}\mathbf{F}_0^{(pq)}$ is the electric field induced at the centre of the $p$-th molecule by all the other molecules of the medium and related with London's dispersion forces.

The tensor $e_{\alpha\beta\gamma\delta\varepsilon\eta}$ for spherical symmetry can be written as follows [14]:

$$e_{\alpha\beta\gamma\delta\varepsilon\eta}^{3\omega}=\tfrac{1}{7}e_{3\omega}\sigma_{\alpha\beta\gamma\delta\varepsilon\eta} \tag{59}$$

with $e_{3\omega}$ denoting a mean hyperpolarizability of the fifth order.

Inserting (59) into (58), we have by (27), from (23), for the anisotropic parts:

$$F_{\text{anis}}^{3\omega}=G_{\text{anis}}^{3\omega}=\frac{2}{49V}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N}e_p^{3\omega}e_q^{3\omega}\left\{3\left(F_{0\alpha}^{(p)}F_{0\beta}^{(p)}\right)\left(F_{0\alpha}^{(q)}F_{0\beta}^{(q)}\right)-\left(F_{0\alpha}^{(p)}F_{0\alpha}^{(p)}\right)\left(F_{0\beta}^{(q)}F_{0\beta}^{(q)}\right)\right\}\right\rangle. \tag{60}$$

We further have for two atoms interacting with London's dispersion forces [15]:

$$a_p^{\omega}F_{0\alpha}^{(pq)}F_{0\beta}^{(pq)}=a_q^{\omega}F_{0\alpha}^{(qp)}F_{0\beta}^{(qp)}=\frac{h}{4}\frac{\nu_p\nu_q}{\nu_p+\nu_q}\,a_p^{\omega}a_q^{\omega}r_{pq}^{-8}\left(3r_{pq\alpha}r_{pq\beta}+r_{pq}^2\delta_{\alpha\beta}\right), \tag{61}$$

$h\nu_p$ and $h\nu_q$ being energies characteristic of the atoms $p$ and $q$, respectively.

Assuming that $\nu_p=\nu_q$, one obtains from (60) for pairwise atomic interactions

$$F_{\text{anis}}^{3\omega}=G_{\text{anis}}^{3\omega}=\frac{9\rho}{392}a_{\omega}^2e_{3\omega}^2(h\nu)^2\langle r_{pq}^{-12}\rangle, \tag{62}$$

where $\langle r_{pq}^{-12}\rangle$ is determined by (53) for $n=12$.

From (62), we see that in this case atoms interacting with London dispersional forces also depolarize the third-harmonic scattered light, like in linear scattering [16].

All in all, the depolarization of third-harmonic light scattered by atoms or isotropic molecules arises from two mechanisms: firstly molecular redistribution (54) and, second, molecular interactions with forces of the dispersional kind.

## 4. DISCUSSION

We shall now perform some simple numerical evaluations, which will reveal the order of magnitude of the various above-considered effects of molecular interaction.

Let us begin by the effect of spatial molecular redistribution on the component $V_v^{3\omega}$ (14) of light scattered by isotropically polarizable molecules.

The intensity ratio $k_1$ calculated from (50) and (28) is:

$$k_1 = 1 + \frac{96 a_\omega^2 J_R^{(6)}}{5 \rho k T \beta_T} .$$

In argon at 84,4°K, $J_R^{(6)} = 8.4 \cdot 10^{45}$ cm$^{-6}$, $\rho = 21.3 \cdot 10^{21}$ cm$^{-3}$, $\beta_T = 204 \cdot 10^{-12}$ e. s. u. whereas $a_\omega = 1.63 \cdot 10^{-24}$ cm$^3$, whence we get $k_1 \simeq 10.5$. This leads to conclude directly that radial interactions yield a contribution which raises the scattered component $V_v^{3\omega}$ by 950 per cent.

This contribution moreover causes a modification in the scattering of light by atoms and isotropic molecules. In fact, an anisotropic component appears. Let us compare, for such scatterers, the effects of molecular redistribution and of dispersional interactions by calculating the ratio of components $H_v^{3\omega}$ (14) given by eqs. (62) and (50):

$$k_2 = \frac{9 (h\nu)^2}{1568} \left( \frac{e_{3\omega}}{c_{3\omega}} \right)^2 \frac{\langle r_{pq}^{-12} \rangle}{J_R^{(6)}} .$$

With regard to (53) at $n=6$, $n=12$ and $\rho v = 0.6$, this expression goes over into:

$$k_2 \simeq 2.9 \cdot 10^{-5} (\pi \rho h \nu)^2 \left( \frac{e_{3\omega}}{c_{3\omega}} \right)^2 .$$

Taking the values $\rho \simeq 10^{22}$ cm$^{-3}$, $h\nu \simeq 10^{-11}$ e. s. u., $c_{3\omega} \simeq 10^{-36}$ e. s. u., $e_{3\omega} \simeq 10^{-48}$ e. s. u., which are typical for liquids, we obtain $k_2 \simeq 10^{-6}$. Thus, translational fluctuations are a decisive factor in the production of an anisotropic component in light scattering by atoms and isotropic molecules.

Similarly, we shall discuss the problem for anisotropic molecules having the axial symmetry.

By eqs. (55) and (31), we obtain for the component $H_v^{3\omega}$ (14) the ratio:

$$k_3 = 1 + \frac{4 a_\omega^2 J_R^{(6)}}{\kappa_c^2 (1 + J_A)} .$$

Let us moreover assume that $\kappa_c = \kappa_a$. For benzene molecules, we have in particular: $a_\omega = 10.32 \cdot 10^{-24}$ cm$^3$, $\kappa_a^2 = 3.58 \cdot 10^{-2}$, $J_A = -0{,}25$ [11] and $\rho = 6.74 \cdot 10^{21}$ cm$^{-3}$. These data, by (52 - 53) at $\rho v = 0{,}6$ yield $J_R^{(6)} = 1.56 \cdot 10^{44}$ cm $^{-6}$. As a result, we get $k_3 \simeq 2.3$. Thus, the effect of molecular redistribution raises the anisotropic component by 130 per cent.

Taking moreover $\beta_T = 95 \cdot 10^{-12}$ e.s.u., we calculate from (56) $D_v^{3\omega} \simeq 0{,}08$, whereas the depolarization calculated from (42) for $\kappa_c = \kappa_a$ is $D_v^{3\omega} = \frac{1}{4} D_v^{\omega} = 0{,}07$ ($D_v^{\omega} = 0.266$ [17]). These values are by one order of magnitude larger than the value obtained in the „gas approximation" [3].

Let us consider the values of the ratio of the component $H_v^{3\omega}$ of third-harmonically scattered light and the component $H_v^{\omega}$ of light linearly scattered by axially symmetric molecules. This will give us an answer as to whether the phenomenon is accessible to observation.

Quite generally, we have:

$$\frac{H_v^{3\omega}}{H_v^{\omega}} = \frac{9c_{3\omega}^2\{\kappa_c^2(1+J_A)+4a_\omega^2 J_R^{(6)}\}}{64a_\omega^2\{\kappa_a^2(1+J_A)+a_\omega^2 J_R^{(6)}\}} I^2 .$$

Hence, for weakly anisotropic molecules, we obtain:

$$\frac{H_v^{3\omega}}{H_v^{\omega}} \simeq \frac{9}{16}\left(\frac{c_{3\omega}}{a_\omega}\right)^2 I^2 .$$

In chloroform, $c\,(-\omega, \omega, -\omega, \omega) = \frac{1}{3}c(-3\omega, \omega, \omega, \omega) = 5\cdot 10^{-36}$ e.s.u. [10], $a_\omega = 8.32 \times \times 10^{-24}$ cm$^3$, and we obtain $H_v^{3\omega}/H_v^{\omega} \simeq 2\cdot 10^{-24}\ I^2$.

For strongly anisotropic molecules, we resort to the general formula for $\frac{H_v^{3\omega}}{H_v^{\omega}}$.

In nitrobenzene, $c_{3\omega} = 25.5\cdot 10^{-35}$ e.s.u. [10], $a_\omega = 12.92\cdot 10^{-24}$ cm$^3$, $\kappa_c^2 = \kappa_a^2 = 0.05$, $J_A = 1.25$ [18], $J_R^{(6)} = 1.26\cdot 10^{44}$ cm$^{-6}$, leading to the result: $H_v^{3\omega}/H_v^{\omega} \simeq 10^{-22} I^2$.

An especially strong effect of third-harmonic light scattering should take place in solutions of macromolecules.

The order of magnitude of the nonlinear polarizability can be determined from Kerr's effect; on assuming that the effect due to nonlinear polarizability $c(-\omega, \omega, 0, 0) = \frac{1}{12}c_{3\omega}$ constitutes 1 per cent of the effect of orientation of anisotropic molecules $(a_\omega \kappa_a)^2/kT$, we can write:

$$c_\omega = \frac{(a_\omega \kappa_a)^2}{5kT} 10^{-2} = \frac{(a_{33}^\omega - a_{11}^\omega)^2}{45kT} 10^{-2} .$$

For the macromolecules of fibrinogen we have $a_{33}^\omega - a_{11}^\omega = 1.2\cdot 10^{-17}$ cm$^3$, for collagen $3.10^{-15}$ cm$^3$, for TMV (tobacco mosaic virus) $3.3\cdot 10^{-14}$ cm$^3$, and for DNA $1.4\cdot 10^{-15}$ cm$^3$ (references data for 20°C [19]).

With these data, we obtain the following results: fibrinogen $c_{3\omega} = 9.5\cdot 10^{-23}$ e.s.u., collagen $5.3\cdot 10^{-19}$ e.s.u., TMV $7.2\cdot 10^{-17}$ e.s.u., DNA $1.2\cdot 10^{-19}$ e.s.u.

On neglecting both angular and radial correlations, we get from the general formula for anisotropic molecules:

$$\frac{H_v^{3\omega}}{H_v^{\omega}} \simeq \frac{9}{64}\left(\frac{c_{3\omega}}{a_\omega}\right)^2 I^2 .$$

One can assume $a_\omega$ of order $10^{-15}$ cm$^3$ for collagen and DNA, $10^{-16}$ cm$^3$ for fibrinogen, and $10^{-13}$ cm$^3$ for TMV.

These data yield ratios of $H_v^{3\omega}/H_v^{\omega} \simeq 7\cdot 10^{-8} I^2$ for TMV, $\simeq 4\cdot 10^{-8} I^2$ for collagen, $\simeq 10^{-9} I^2$ for DNA, and $\simeq 10^{-13} I^2$ for fibrinogen.

The present theory is easily extended to the case of inelastic frequency-broadened third-harmonic scattering, taking into account also the collision-induced light scattering recently studied in linear scattering [20]. Also, spectral width can be included, as done recently by Maker [21] for the case of elastic second-harmonic light scattering.

## APPENDIX

We shall now discuss molecular redistribution in the case of arbitrarily symmetri molecules.

Inserting (46) in (48) and restricting calculations to pairwise interactions only, w obtain from (13) to within $a_\omega^2$:

$$F_{\mathrm{is}}^{3\omega}=\frac{\rho^2 kT\beta_T}{25}\left\{c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega}+25\cdot 0(a_\omega^2)\right\}, \qquad (A.1$$

where $0(a_\omega^2)$ calculated with the assumption that density fluctuations are independent o translational fluctuations is:

$$\begin{aligned}0(a_\omega^2)\simeq\frac{J_R^{(6)}}{2500\rho kT\beta_T}\big[&3(21c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\delta}^{3\omega}+85c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega})a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega}+(39c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\delta}^{3\omega}-58c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega})+\\&+a_{\varepsilon\varepsilon}^{\omega}a_{\eta\eta}^{\omega}+478c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\varepsilon}^{3\omega}a_{\varepsilon\delta}^{\omega}a_{\eta\eta}^{\omega}+63c_{\alpha\alpha\gamma\varepsilon}^{3\omega}c_{\beta\beta\delta\eta}^{3\omega}a_{\varepsilon\gamma}^{\omega}a_{\eta\delta}^{\omega}\big]+\ldots,\end{aligned}$$

$$\begin{aligned}F_{\mathrm{anis}}^{3\omega}=\frac{2\rho}{189}\Big\{&10c_{\alpha\beta\gamma\delta}^{3\omega}c_{\alpha\beta\gamma\delta}^{3\omega}+3c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\delta}^{3\omega}-3c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega}+\\&+\frac{\rho}{V}\iint(10c_{\alpha\beta\gamma\delta}^{3\omega(p)}c_{\alpha\beta\gamma\delta}^{3\omega(q)}+3c_{\alpha\beta\gamma\gamma}^{3\omega(p)}c_{\alpha\beta\delta\delta}^{3\omega(q)}-3c_{\alpha\alpha\gamma\gamma}^{3\omega(p)}c_{\beta\beta\delta\delta}^{3\omega(q)})g^{(2)}(\tau_p,\tau_q)\,d\tau_p\,d\tau_q+\\&+\frac{J_R^{(6)}}{700}\big[7(3326c_{\alpha\beta\gamma\delta}^{3\omega}c_{\alpha\beta\gamma\delta}^{3\omega}+303c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\delta}^{3\omega}-601c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega})a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega}+\\&+(-1554c_{\alpha\beta\gamma\delta}^{3\omega}c_{\alpha\beta\gamma\delta}^{3\omega}+2163c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\delta}^{3\omega}+2048c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega})a_{\varepsilon\varepsilon}^{\omega}a_{\eta\eta}^{\omega}+\\&+2(7000c_{\alpha\beta\gamma\delta}^{3\omega}c_{\alpha\beta\gamma\varepsilon}^{3\omega}+4200c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\varepsilon}^{3\omega}-5717c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\varepsilon}^{3\omega})a_{\varepsilon\delta}^{\omega}a_{\eta\eta}^{\omega}+\\&+112(5c_{\beta\varepsilon\eta\delta}^{3\omega}a_{\varepsilon\beta}^{\omega}+c_{\beta\beta\delta\varepsilon}^{3\omega}a_{\varepsilon\eta}^{\omega})c_{\alpha\alpha\gamma\gamma}^{3\omega}a_{\eta\delta}^{\omega}-4200c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\varepsilon\delta\delta}^{3\omega}a_{\varepsilon\beta}^{\omega}a_{\eta\eta}^{\omega}+\\&+6021c_{\alpha\alpha\gamma\varepsilon}^{3\omega}c_{\beta\beta\delta\eta}^{3\omega}a_{\varepsilon\gamma}^{\omega}a_{\eta\delta}^{\omega}\big]\Big\}+\ldots,\end{aligned}\qquad (A.2$$

$$\begin{aligned}G_{\mathrm{anis}}^{3\omega}=\frac{2\rho}{1365}\Big\{&10c_{\alpha\beta\gamma\delta}^{3\omega}c_{\alpha\beta\gamma\delta}^{3\omega}+75c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\delta}^{3\omega}-27c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega}+\\&+\frac{\rho}{V}\iint(10c_{\alpha\beta\gamma\delta}^{3\omega(p)}c_{\alpha\beta\gamma\delta}^{3\omega(p)}+75c_{\alpha\beta\gamma\gamma}^{3\omega(p)}c_{\alpha\beta\delta\delta}^{3\omega(p)}-27c_{\alpha\alpha\gamma\gamma}^{3\omega(qr}c_{\beta\beta\delta\delta}^{3\omega(q)})g^{(2)}(\tau_p,\tau_q)\,d\tau_p\,d\tau_q+\\&+\frac{J_R^{(6)}}{700}\big[7(2930c_{\alpha\beta\gamma\delta}^{3\omega}c_{\alpha\beta\gamma\delta}^{3\omega}+11679c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\delta}^{3\omega}-5785c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega})a_{\varepsilon\eta}^{\omega}a_{\varepsilon\eta}^{\omega}+\\&+(-1470c_{\alpha\beta\gamma\delta}^{3\omega}c_{\alpha\beta\gamma\delta}^{3\omega}-4641c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\delta}^{3\omega}+18092c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\delta}^{3\omega})a_{\varepsilon\varepsilon}^{\omega}a_{\eta\eta}^{\omega}+\\&+2(7000c_{\alpha\beta\gamma\delta}^{3\omega}c_{\alpha\beta\gamma\varepsilon}^{3\omega}+21000c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\beta\delta\varepsilon}^{3\omega}-28481c_{\alpha\alpha\gamma\gamma}^{3\omega}c_{\beta\beta\delta\varepsilon}^{3\omega})a_{\varepsilon\delta}^{\omega}a_{\eta\eta}^{\omega}+\\&+560(c_{\beta\varepsilon\eta\delta}^{3\omega}a_{\varepsilon\beta}^{\omega}+101c_{\beta\beta\delta\varepsilon}^{3\omega}a_{\varepsilon\eta}^{\omega})c_{\alpha\alpha\gamma\gamma}^{3\omega}a_{\eta\delta}^{\omega}+63000c_{\alpha\beta\gamma\gamma}^{3\omega}c_{\alpha\varepsilon\delta\delta}^{3\omega}a_{\varepsilon\beta}^{\omega}a_{\eta\eta}^{\omega}+\\&+75573c_{\alpha\alpha\gamma\varepsilon}^{3\omega}c_{\beta\beta\delta\eta}^{3\omega}a_{\varepsilon\gamma}^{\omega}a_{\eta\delta}^{\omega}\big]\Big\}+\ldots,\end{aligned}\qquad (A.3$$

where, for simplicity of the final results, we have performed in quadratic brackets an averageing over all possible molecular orientations. We have to average the products of four and six directional cosines. The general result of this procedure is given in [22].

The Eqs (A.1 - A.3) are quite general and can be particularized for molecules of any kind.

From (A.1 - A.3) by (27) and $a^{\omega}_{\alpha\beta} = a_{\omega}\delta_{\alpha\beta}$, we can also obtain the result (51) for isotropic molecules.

## REFERENCES

1. Ward J. F., New G. H. C., Phys. Rev. **185**, 57 (1969). – 2. Kielich S., Bull. Acad. Polon. Sci. Sér. Sci. Math. Astron. Phys., **12**, 53 (1964); Physica, **30**, 1717 (1964); Acta Phys. Polonica, **26**, 135 (1964). – 3. Kozierowski M., Bulletin de la Société des Amis des Sciences et des Lettres de Poznań, Série B, **22**, 5 (1970/71). – 4. Kielich S., Bulletin de la Société des Amis des Sciences et des Lettres de Poznań, Série B, **17**, 43 (1962/63); Acta Phys. Polonica, **33**, 89 (1968). – 5. Bersohn R., Yoh-han Pao, Frisch H. L., J. Chem. Phys., **45**, 3184 (1966); Weinberg D. L., J. Chem. Phys., **47**, 1307 (1967). – 6. Kielich S., Acta Phys. Polonica, **19**, 149, 573 (1960); J. Chem. Phys., **46**, 4090 (1967). – 7. Smoluchowski M., Bull. Acad. Crac. p. 1057 (1907). – 8. Einstein A., Ann. Physik, **33**, 1275 (1910). – 9. Kielich S., Acta Phys. Polonica, **25**, 85 (1964). – 10. Kielich S., Acta Phys. Polonica, **30**, 683 (1966); Proc. Phys. Soc., **90**, 847 (1967). – 11. Lalanne J. R., J. Physique **30**, 643 (1969). – 12. Yvon J., Compt. Rend. **202**, 35 (1936); Kirkwood J. G., J. Chem. Phys. **4**, 592 (1936). – 13. Kielich S., Chem. Phys. Letters **2**, 112 (1968); IEEE- J. Quantum Electronics, **QE-4**, 744 (1968). – 14. Kielich S., Bulletin de la Société des Amis des Sciences et des Lettres de Poznań, Série B **16**, 69 (1960/61). – 15. Kielich S., Acta Phys. Polonica, **22**, 65, 477 (1962). – 16. Kielich S., Acta Phys. Polonica, **33**, 63 (1968). – 17. Goumou D. J., Mackor E. L., Hijmans J., Trans. Faraday Soc. **60**, 1539, 2244 (1964). – 18. Kielich S., Surma M., Poznań Soc. Friends Sci., Math. and Natural Sci. **11** 153 (1962). – 19. Kielich S., Acta Phys. Polonica, **A 37**, 447 (1970). – 20. Levine H. B., Birnbaum G., Phys. Rev. Letters **20**, 439 (1968); McTaque J. P., Birnbaum G., Phys. Rev. Letters, **21**, 661 (1968); Mc Taque J. P., Fleury P. A., Du Pré D. B., Phys. Rev. **188**, 303 (1969). – 21. Maker P. D., Phys. Rev. A **1**, 923 (1970). – 22. Kielich S., Acta Phys. Polonica, **20**, 433 (1961).

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