LETTERS TO THE EDITOR

DEPOLARIZATION RATIO OF THIRD HARMONIC ELASTIC SCATTERING OF LASER LIGHT IN GASES AND LIQUIDS

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Depolarization of triple-photon elastic scattering of laser light by systems of interacting molecules is studied taking into account fluctuations of molecular munber density as well as translational and orientational fluctuations. The measurement of triple-photon depolarization ratio is feasible and provides a method of direct determination of the anisotropy of nonlinear polarizability at frequency 3ω for axially-symmetric molecules.

Recent laser light-induced third-harmonic generation observations on gases [1], liquids [2] and liquid crystals [3] incite to a quantitative analysis of the third-harmonic scattering hitherto studied in atomic gases and ones consisting of almost-spherical molecules [4].

Similarly as for linear elastic light scattering [5], the depolarization ratios at frequency 3ω are related as follows:

$$D_h^{3\omega}(\vartheta) = \frac{D_v^{3\omega}}{D_v^{3\omega} + (1-D_v^{3\omega})\cos^2\vartheta}, \tag{1}$$

$$D_u^{3\omega}(\vartheta) = \frac{2D_v^{3\omega}}{1+D_v^{3\omega}} + \frac{1-D_v^{3\omega}}{1+D_v^{3\omega}}\cos^2\vartheta, \tag{2}$$

with ϑ — the angle between scattering observation and laser beam incidence; the laser beam can be vertically (v) or horizontally (h) polarized or (u) unpolarized.

In the absence of interference scattering, $D_v^{3\omega}$ does not depend on ϑ, and for an isotropic body we have:

$$D_v^{3\omega} = -\frac{1}{2} + \frac{9 \langle C_{\alpha\gamma\varepsilon\eta}^{3\omega} C_{\alpha\delta\lambda\mu}^{3\omega}\rangle \sigma_{\gamma\delta\varepsilon\eta\lambda\mu}}{2 \langle C_{\alpha\gamma\varepsilon\eta}^{3\omega} C_{\beta\delta\lambda\mu}^{3\omega}\rangle \sigma_{\alpha\beta\gamma\delta\varepsilon\eta\lambda\mu}}, \tag{3}$$

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brackets $\langle \rangle$ denoting statistical averaging, and $\sigma_{\gamma\delta\varepsilon\eta\lambda\mu}$ a tensor consisting of a linear combination of 15 terms of the form $\delta_{\gamma\delta}\delta_{\varepsilon\eta}\delta_{\lambda\mu}$, whereas $\sigma_{\alpha\beta\gamma\delta\varepsilon\eta\lambda\mu}$ consists of 7 terms of the form $\delta_{\alpha\beta}\sigma_{\gamma\delta\varepsilon\eta\lambda\mu}$; $\delta_{\alpha\beta}$ is Kronecker's unit tensor.

The tensor of nonlinear polarizability at frequency 3ω [4] can be written in an approximation for a medium consisting of N molecules as:

$$C^{3\omega}_{\alpha\gamma\varepsilon\eta} = \sum_{p=1}^{N} c^{3\omega(p)}_{\alpha\beta\lambda\mu}\left(\delta_{\beta\gamma} + \frac{\partial F^{(p)}_{\beta}}{\partial E_{\gamma}}\right)\left(\delta_{\lambda\varepsilon} + \frac{\partial F^{(p)}_{\lambda}}{\partial E_{\varepsilon}}\right)\left(\delta_{\mu\eta} + \frac{\partial F^{(p)}_{\mu}}{\partial E_{\eta}}\right), \tag{4}$$

where the third-order polarizability tensor $c^{3\omega(p)}_{\alpha\beta\lambda\mu}$ is for the p-th isolated molecule acted upon by the electric field $F^{(p)}_{\beta}$ due to the other $N-1$ molecules [5].

For condensed atomic substances we have by (1) and (2):

$$D^{3\omega}_v = \frac{3a^2_\omega J_R}{5(1+G_R)[1+0(a^2_\omega)]+36a^2_\omega J_R} ; \tag{5}$$

here, the parameter $G_R = \varrho kT\beta_T - 1$ derives from Smoluchowski's formula for fluctuations of the number density ϱ of molecules (β_T-compressibility coefficient), and J_R accounts for translational fluctuations causing spatial regrouping of atoms mutually distant by r and possessing linear polarizabilities a_ω at frequency ω. With pairwise radial correlations only, one has satisfactorily [5]: [5]: $J_R = 2\varrho\langle r^{-6}\rangle$. J_R can be computed numerically, or determined from the depolarisation ratio of light scattered at fundamental frequency ω [5]:

$$D^\omega_v = \frac{3a^2_\omega J_R}{5(1+G_R)[1+0(a^2_\omega)]+4a^2_\omega J_R} \cdot \tag{6}$$

Eqs (5) and (6) prove that scattered light depolarization in atomic substances is not due to fluctuations of density but rather to spatial redistribution, which is the source of anisotropic light scattering at frequencies ω and 3ω. In the absence of translational fluctuations ($J_R = 0$), the depolarizations (5) and (1) vanish whereas the depolarization (2) reduces to $D^{3\omega}_u = \cos^2\vartheta$, as is the case for linear light scattering.

Depolarization of third-harmonic scattering can also be caused by London dispersional interactions of atoms or molecules, like linear scattering [6].

Taking into account the optical anisotropy of axially-symmetric molecules and their angular correlations, we obtain by (3) and (4) on neglecting spatial redistribution:

$$D^{3\omega}_v = \frac{3(c^{3\omega}_{3333}-c^{3\omega}_{1111})^2(1+J_A)}{20(c^{3\omega}_{3333}+2c^{3\omega}_{1111})^2(1+G_R)+16(c^{3\omega}_{3333}-c^{3\omega}_{1111})^2(1+J_A)} \tag{7}$$

with [5] $J_A = \varrho\langle 3\cos^2\theta-1\rangle/2$ — a parameter describing fluctuations of orientations of molecules with symmetry axes subtending the angle θ. An identical parameter intervenes in the depolarization ratio of linear scattering [5]:

$$D^\omega_v = \frac{3(a^\omega_{33}-a^\omega_{11})^2(1+J_A)}{5(a^\omega_{33}+2a^\omega_{11})^2(1+G_R)+4(a^\omega_{33}-a^\omega_{11})^2(1+J_A)} \tag{8}$$

By Eqs (7) and (8), we derive the relation:

$$\left(\frac{c^{3\omega}_{3333}-c^{3\omega}_{1111}}{c^{3\omega}_{3333}+2c^{3\omega}_{1111}}\right)^2 = 4\left(\frac{a^{\omega}_{33}-a^{\omega}_{11}}{a^{\omega}_{33}+2a^{\omega}_{11}}\right)^2 \frac{(3-4D^{\omega}_v)D^{3\omega}_v}{(3-16D^{3\omega}_v)D^{\omega}_v} , \tag{9}$$

which permits direct determinations of the anisotropy of nonlinear polarizability $(c^{3\omega}_{3333}-c^{3\omega}_{1111})$ of axially-symmetric molecules from measurements of D^{ω}_v and $D^{3\omega}_v$.

In substances consisting of tetrahedral (CH_4, CCl_4) or octahedral (SF_6) molecules, Eqs (3) and (4) yield on neglecting molecular redistributions and angular correlations:

$$D^{3\omega}_v = \frac{10(c^{3\omega}_{3333}-3c^{3\omega}_{1133})^2}{189(c^{3\omega}_{3333}+2c^{3\omega}_{1133})^2(1+G_R)+16(c^{3\omega}_{3333}-3c^{3\omega}_{1133})^2} . \tag{10}$$

For spherical symmetry (atoms in the ground state) $c^{3\omega}_{1111} = c^{3\omega}_{3333} = 3c^{3\omega}_{1133}$, causing the depolarization ratios (7) and (10) to vanish.

For liquid argon at 84.4°K, applying the data of Ref. [5] we compute from Eqs (5) (6) the following values: $D^{\omega}_v = 0.2$, $D^{3\omega}_v = 0.06$, which are accessible to measurement. When D^{ω}_v is known experimentally, the third-harmonic depolarization can be computed from formula $D^{3\omega}_v = 3D^{\omega}_v/(3+32D^{\omega}_v)$ resulting by Eqs (5) and (6).

For liquids consisting of anisotropic molecules, we have by (7)—(9) in satisfactory approximation $D^{3\omega}_v \simeq D^{\omega}_v/4$ on assuming the linear and nonlinear anisotropies equal. For most liquids, this leads to measurable values for $D^{3\omega}_v$. Thus, in CS_2 [5] $D^{\omega}_v = 0.47$, whence $D^{3\omega}_v = 0.12$; in C_6H_6 $D^{\omega}_v = 0.26$, whence $D^{3\omega}_v = 0.065$.

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