CHEMICAL PHYSICS LETTERS 1 (1967) 441-442. NORTH-HOLLAND PUBLISHING COMPANY, AMSTERDAM

MULTI-HARMONIC MOLECULAR LIGHT SCATTERING IN LIQUIDS

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Received 12 November 1967

A theory of multi-harmonic scattering processes in isotropic media acted on by strong laser beams is presented. Some simple examples illustrate the role of molecular symmetries and correlations in agreement with the experimental results on second-harmonic scattering.

The first successful observations of molecular second-harmonic light scattering in liquids by Terhune, Maker and Savage [1] incite to a continuation of work on this type of scattering and to extend investigation to higher-order e.g. third-harmonic scattering.

From the quantum-mechanical viewpoint, second-harmonic elastic scattering is a process involving three photons, as two photons of the beam incident on the molecule and one photon with doubled frequency 2ω is scattered [1-3]. Detailed analysis shows [1-5] that second-harmonic scattering is more highly sensitive to molecular symmetry than linear Rayleigh scattering. In condensed media, second-harmonic scattering depends strongly on the various pairwise and triple correlations [6-8], owing to which it can occur even in substances consisting of centrosymmetric molecules.

It is our aim to propose a formal theory of multi-harmonic light scattering in isotropic bodies acted on by strong laser beams. Here, we consider only dipole elastic light scattering with intensity given by the tensor [2]

$$I_{\sigma\tau}^{S} = \langle \frac{d^2 P_\sigma}{dt^2} \frac{d^2 P_\tau^*}{dt^2} \rangle . \qquad (1)$$

$P_\sigma(t)$ is the component of the dipole moment induced in the medium by the electric field $E(t) = E_0 e^{i\omega t}$ of the incident light wave of frequency ω, and the brackets $\langle\ \rangle$ denote statistical averageing.

Considering solely the harmonic part of the induced moment, we can write

$$P_\sigma(t) = \sum_{n=1}^{\infty} A_{\sigma\sigma_1 \dots \sigma_n}^{n\omega} E_{0\sigma_1} \dots E_{0\sigma_n} e^{in\omega t} , \qquad (2)$$

where $A_{\sigma \dots \sigma_n}^{n\omega}$ is the tensor of dipole polarizability of order n, dependent on the n-harmonic frequencies.

By eqs. (1) and (2) we have

$$I_{\sigma\tau}^{S} = I_{\sigma\tau}^{\omega} + I_{\sigma\tau}^{2\omega} + I_{\sigma\tau}^{3\omega} + \dots = \sum_{n=1}^{\infty} I_{\sigma\tau}^{n\omega} \qquad (3)$$

with the intensity tensor of n-harmonic scattering

$$I_{\sigma\tau}^{n\omega} = \qquad (4)$$

$$= (n\omega)^4 \langle A_{\sigma\sigma_1 \dots \sigma_n}^{n\omega} A_{\tau\tau_1 \dots \tau_n}^{-n\omega} \rangle I_{\sigma_1\tau_1} \dots I_{\sigma_n\tau_n} ,$$

whereas $I_{\sigma\tau} = E_{0\sigma} E_{0\tau}^*$ is the intensity tensor of the incident light.

In the special case of a gas or liquid (consisting of N molecules), eq. (4), on averaging over all possible orientations of the molecules, becomes

$$I_{\sigma\tau}^{n\omega} = (n\omega)^4 (F_{n\omega} I \delta_{\sigma\tau} + G_{n\omega} I_{\sigma\tau}) I^{n-1} , \qquad (5)$$

where $I = I_{\nu\nu} = I_{xx} + I_{yy} + I_{zz}$ is the total incident light intensity.

The factors $E_{n\omega}$ and $G_{n\omega}$ account for the optical properties, structure and thermodynamical state of the medium and are of the form

$$\begin{aligned} F_{n\omega} &= N a_{\alpha\alpha_1 \dots \alpha_n}^{n\omega} a_{\beta\beta_1 \dots \beta_n}^{-n\omega} f_{\alpha\beta \dots \alpha_n\beta_n} ; \\ G_{n\omega} &= N a_{\alpha\alpha_1 \dots \alpha_n}^{n\omega} a_{\beta\beta_1 \dots \beta_n}^{-n\omega} g_{\alpha\beta \dots \alpha_n\beta_n} , \end{aligned} \qquad (6)$$

where $a_{\alpha \dots \alpha_n}^{n\omega}$ is the n-th order polarizability tensor of the isolated molecule, and $f_{\alpha\beta \dots \alpha_n\beta_n}$ and $g_{\alpha\beta \dots \alpha_n\beta_n}$ are tensors of molecular correlations.

From eq. (5), the degree of depolarisation of n-harmonic scattering is given as

$$D_{n\omega} = \frac{F_{n\omega}}{F_{n\omega} + G_{n\omega}}. \qquad (7)$$

Eqs. (5)-(7) are applicable to second-, third- and multi-harmonic scattering processes, as determined by the type of symmetry of the molecules and by the mutual molecular correlations.

For CCl_4, measurements by Terhune et al. [1] yielded a value of $D_{2\omega}$ of about $\frac{1}{3}$, whereas the theoretical value calculated without intermolecular interactions was [1, 2] $D_{2\omega} = \frac{2}{3}$. Now, if one takes into consideration correlations causing molecular redistribution [9], eq. (7) leads to $D_{2\omega}$ in the form

$$D_{2\omega} = \tfrac{2}{3}\{1 - \tfrac{168}{5}\pi\rho a^2 \int r^{-4}\, g(r)\, \mathrm{d}r - \mathrm{O}(a^2, \rho^2)\}, \qquad (8)$$

where a is the mean polarizability, ρ the density and $g(r)$ the radial distribution function of molecules distant by r. We see that eq. (8) lowers the $\frac{2}{3}$-value in accordance with experiment [1].

Eq. (7) applied to molecules without a center of inversion yields with satisfactory accuracy $D_{2\omega}^{\mathrm{theor}} = \frac{19}{123} \simeq 0.15$. The measurements yielded [1]:

$$D_{2\omega}^{\mathrm{exp}} \simeq \begin{cases} 0.10 & \text{for} \quad CH_3CN; \\ 0.12 & \text{for} \quad H_2O. \end{cases}$$

A discussion of eq. (7) taking into account the effect of molecular fields in liquids [6, 9] leads to non-zero values of $D_{2\omega}$ amounting to about $\frac{1}{9}$ even if the liquid consists of molecules possessing a center of inversion (point groups C_{6h}, D_{6h}, $D_{\infty h}$). As yet, no observations of second-harmonic scattering in liquids with centro-symmetric molecules are available.

These and other examples prove that a full treatment of second-harmonic scattering in liquids involves considering various molecular correlations of the radial or angular type [9].

At the most, eq. (5) yields a ratio of $I^{3\omega}/I^{\omega} \simeq$ $\simeq 10^{-22} I^2$ for molecular substances. The detection of so small a change in intensity due to third-harmonic scattering would be possible only in experiments using a focussed laser beam of intensity $I \simeq 10^8$ esu.

Simple evaluations show that existing laser techniques are adequate for detecting not only the hitherto studied second-harmonic but also third-harmonic scattering processes, particularly near resonance where large nonlinear variations of $I^{3\omega}$ are to be expected. Extensive studies of multi-harmonic scattering can provide better insight into the electromagnetic structure, nonlinear properties and correlations of atoms and molecules in condensed phases than was hitherto possible by linear molecular optics.

The foregoing considerations can be extended to general nonelastic processes with n photons of frequencies $\omega_1, \omega_2 \ldots \omega_n$ incident on the molecule, which if making a transition from quantum state k to l frequency ω_{kl}, scatters a photon with frequency

$$\omega = \sum_{i=1}^{n} \omega_i \pm \omega_{kl}.$$

The theoretical treatment of such processes requires quantum-mechanical methods yielding explicit dependences of the molecular polarizability tensors on the harmonic frequency in the entire frequency range including absorption regions [10].

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