LETTERS TO THE EDITOR

HIGHER-ORDER ELASTIC SCATTERING OF LASER LIGHT

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A formal theory predicting various higher-order scattering processes in dense isotropic media transmitting a strong laser beam is proposed.

Dipolar light scattering of intensity tensor [1]

$$I_{ij}^{S} = \langle \ddot{P}_i \ddot{P}_j^* \rangle \tag{1}$$

is considered. The brackets denote classical or quantal statistical averaging and P_i the i-component of the dipole moment optically induced in the isotropic medium. At incidence of a strong light beam (intensity I, frequency ω) linear as well as higher-order scatterings occur, whence (1) can be expanded in a series

$$I_{ij}^{S} = \sum_{n=1}^{\infty} I_{ij}^{(n)}, \tag{2}$$

where the tensor

$$I_{ij}^{(n)} = \sum_{k=1}^{n} (k\omega)^4 \left(F_n^{k\omega} I \delta_{ij} + G_n^{k\omega} I_{ij}\right) I^{n-1} \tag{3}$$

defines n-th order elastic scattering. $F_n^{k\omega}$ and $G_n^{k\omega}$ are factors characterizing the isolated molecule optically and the scattering medium structurally and thermodynamically, and are in general implicite functions of the harmonic frequencies ω, 2ω, ..., $k\omega$. For $k = n$, the tensor (3) defines n-harmonic scattering, which can be resolved from amongst the other nonlinear scattering effects ($k < n$) in experiments bearing not only on frequency-depend-

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ence but also on temperature-dependence, since $F_n^{n\omega}$ and $G_n^{n\omega}$ depend to a much lesser extent on temperature than is the case for $F_n^{k\omega}$ and $G_n^{k\omega}$; $2 \leqslant k < n$.

The tensor (3), which defines many-quantum processes involving generally $n+1$ photons, splits into a part independent of polarization of the incident intensity I and a part depending on its polarisation as given by the intensity tensor I_{ij}. In this respect, (3) represents the general expression for the angular dependence of nonlinear light scattering observation.

In particular, for first-order scattering we get by (3)

$$I_{ij}^{(1)} = \omega^4 \left(F_1^{\omega} I \delta_{ij} + G_1^{\omega} I_{ij}\right), \tag{4}$$

the well-known formula for linear Rayleigh scattering with ground frequency ω. F_1^{ω} and G_1^{ω} depend on the linear optical properties of the atoms or molecules and on their various correlations in dense media [2].

For second-order scattering, (3) yields

$$I_{ij}^{(2)} = \omega^4 \left(F_2^{\omega} I \delta_{ij} + G_2^{\omega} I_{ij}\right) I + (2\omega)^4 \left(F_2^{2\omega} I \delta_{ij} + G_2^{2\omega} I_{ij}\right) I. \tag{5}$$

In general, this points to nonlinear scattering both at ground frequency ω and at second harmonic frequency 2ω, as observed experimentally by Terhune *et al* [3]. Their respective microscopic mechanisms in gases are quite different: the one depends essentially on optical orientation of anisotropic linearly polarizable molecules [4], whereas the second harmonic process is due directly to second-order nonlinear polarisation, which can occur only in molecules in the ground state without a centre of inversion [1], [3], [5]. Condensed media involve considerable dependence on a variety of radial or angular pairwise and triple molecular correlations [4], [6], [7], which can give rise to scattering even in substances with centro-symmetric molecules. Detailed statistical-molecular analysis of $F_2^{2\omega}$ and $G_2^{2\omega}$ shows moreover that second harmonic scattering is more sensitive to molecular symmetry and statistical structure of the medium than is linear Rayleigh scattering (4).

By (3), the third-order scattering intensity tensor is

$$I_{ij}^{(3)} = \omega^4 \left(F_3^{\omega} I \delta_{ij} + G_3^{\omega} I_{ij}\right) I^2 + (2\omega)^4 \left(F_3^{2\omega} I \delta_{ij} + G_3^{2\omega} I_{ij}\right) I^2 + + (3\omega)^4 \left(F_3^{3\omega} I \delta_{ij} + G_3^{3\omega} I_{ij}\right) I^2 \tag{6}$$

involving generally three different processes. Those with frequencies ω and 3ω depend more weakly on the molecular symmetry than does second harmonic scattering; it is essential that they can result from isolated atoms or isotropic molecules by nonlinear third-order polarisation [1]. However, the light intensity is less affected by third-order than by second-order scattering processes. Indeed, $I^{(2)}/I^{(1)}$ is of the order of $(10^{-11}-10^{-12})\, I$ and is at present accessible to measurement by laser techniques [3]. But $I^{(3)}/I^{(1)} \sim (10^{-22}-10^{-24}) I^2$ would only be detectable experimentally with laser beam intensities above 10^8 esu *i. e.* at near-threshold conditions for multiphoton photoionization.

Similarly (3) enables to calculate scattering processes of orders higher than the third. Their probabilities are extremely small, since $I^{(n+1)}/I^{(1)} \sim (10^{-11}-10^{-12})^n I^n$. From quantum-mechanical considerations [1], [8], it should be possible to detect these many-photon processes near resonance regions, where nonlinear variations of the tensor (3) are considerable. Obviously, extensive studies of higher-order scattering processes will provide better insight into the fine electro-magnetic structure of atoms and molecules, their nonlinear properties and correlations in dense media than was hitherto possible in linear molecular optics.

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