SECOND-ORDER CORRELATION TENSOR OF
n-HARMONICALLY SCATTERED LIGHT INTENSITY*

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General formulas are derived for the time dependence of the second-order correlation tensor of the intensity of n-harmonically elastically scattered light in the model of free translational and rotational diffusion for motions of statistically independent particles.

1. Introduction

Multi-photon scattering processes set off by intense laser beams are of a universal nature, since their occurrence is independent of synchronisation conditions. Hence they accompany to a higher or lesser degree numerous nonlinear optical processes, among others those of harmonics generation. Since Terhune, Maker and Savage's first experiment [1], in which they observed second-harmonic scattering (SHS) by non-centrosymmetric molecules, SHS has been detected from correlated centrosymmetric molecules in regions of short-range order [2], from critical regions in order—disorder transitions [3,4], and in ferroelectric domains [5,6]. Recently, double- and triple-photon scattering from diamond has been reported [7].

These and other [8] recent experimental achievements stimulate to continue work on the theory of multi-photon light scattering from statistically inhomogeneous media [9]. Primarily, the progress in spectral techniques [10] calls for a transition from integral scattering studies to a spectral approach to nonlinear scattering processes. The first experimental and theoretical steps in this field have been taken by Maker [11] with regard to SHS in liquids. Lately, a spectral treatment of three- [12] and multi-harmonic [13] scattering has been outlined.

In this communication, we propose a spectral stochastical analysis of the second-order correlation tensor $G^{(2)}(t)$ of the intensity of n-harmonically scattered light.

General studies of the processes under consideration for the integral intensity of scattered light $G^{(1)}(0)$ have been performed [9]. Measurements of the time-evolution of the tensor $G^{(2)}(t)$ and its spectral density $G^{(2)}(\omega)$ can become a new method, revealing the finer details of translational—rotational molecular motion and molecular interaction. Detection of changes in $G^{(2)}(t)$ due to "rapid" rotational motions of molecules is possible if the respective relaxation times exceed the resolution time of the electronic recording device. A situation like this can occur when dealing with scattering by large molecules, macromolecules, colloid particles, etc., which leads to an increase in scattered intensity owing to the large polarizabilities of such microsystems [14].

2. Fundamentals of the theory

We consider a system of N non-interacting particles. This is the case of dilute solutions of macromolecules. We

also neglect solute—solvent interaction.

In the wave zone at a distance R from the centre of the scattering sample the correlation tensor $G_{ijkl}^{(2)}(t)$ for the steady-state process is given as [15]:

$$^{n\omega}G_{ijkl}^{(2)}(t) = k_{n\omega}^8 R^{-4} \langle M_i^{n\omega}(0) M_j^{*n\omega}(0) M_k^{n\omega}(t) M_1^{*n\omega}(t) \rangle, \tag{1}$$

with $k_{n\omega} = (n\omega/c)^4$ = the wavevector value of the n-harmonically scattered light, and $\boldsymbol{M}^{n\omega}(t)$ is the n-harmonic component of the electric dipole moment induced in the medium by an intense laser light beam $\boldsymbol{E}_L(r, t) = \boldsymbol{E}_L e \times \exp\{-i(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})\}$ [9]:

$$M_i^{n\omega}(t) = \frac{E_L^n}{2^{n-1}n!} \sum_{p=1}^{N} a_{ii_1\ldots i_n}^{n\omega}(\Omega_t^{(p)}) e_{i_1} \ldots e_{i_n} \exp\{-i(n\omega t + \Delta\boldsymbol{k}\cdot\boldsymbol{r}_t^{(p)})\}. \tag{2}$$

$a_{ii_1\ldots i_n}^{n\omega}(\Omega_t^{(p)})$ is the cartesian tensor of rank $n+1$ of the nth order polarizability of a scatterer having position $\boldsymbol{r}_t^{(p)}$, and orientation given by the set of Euler angles $\Omega_t^{(p)}$ at the moment of time t. Beyond electron absorption bands the tensor is in fact completely symmetric with regard to permutations of indices. The vector $\Delta\boldsymbol{k} = \boldsymbol{k}_{n\omega} - n\boldsymbol{k}_0$ has the absolute value $|\Delta\boldsymbol{k}| = 2(n\omega/c)\sin(\frac{1}{2}\vartheta)$, with ϑ = the scattering angle. $\langle\ldots\rangle$ stands for statistically averaging over ensembles of random positions and orientations of the particles and over states of the electric field of the incident light, assumed as coherent.

For statistically independent particles, the definition (1) becomes:

$$^{n\omega}G_{ijkl}^{(2)}(t) = [^{n\omega}G_{ij}^{(1)}(0)\,^{n\omega}G_{kl}^{(1)}(0) + ^{n\omega}G_{il}^{(1)}(t)\,^{n\omega}G_{jk}^{*(1)}(t)] (1 - N^{-1}) + ^{n\omega}S_{ijkl}^{(2)}(t), \tag{3}$$

where $^{n\omega}G_{ij}^{(1)}(t)$ is the tensor of the first-order correlation of the n-harmonically scattered light electric field. For $t = 0$, it goes over into our earlier integral intensity formulas [9]. The correlation tensor $^{n\omega}S_{ijkl}^{(2)}(t)$, accounting for the effect of self-scattering and proportional to N only, represents together with the factor in square brackets multiplied by N^{-1}, the non-gaussian correction.

Generally, the time-evolution of (3) is determined by the translational—rotational molecular motions. It can be determined by specifying a model of these motions, in particular by the free diffusion model.

The problem of rotational diffusion can be solved simply in the irreducible spherical tensor representation. The solution is further simplified by assuming the scatterer to have mechanical symmetry of the spherical top or symmetric top. For particles of asymmetric top it is not possible to give the general form of the probability distribution function of molecular orientations for arbitrary angular momentum values.

The unit vector e of the polarization state of the incident light ($e \cdot e^* = 1$) can also be transformed to the spherical reference system. We refrain from effecting this here, without loss of generality. If the laser beam is linearly polarized, it is even more convenient to use the cartesian basis. However, in order to describe arbitrary light polarizations and angular dependences of the scattered light, it is convenient to apply Racah algebra [16].

We assume the light incident along z' and linearly polarized along the axis x' of the laboratory system, rigidly attached to the centre of the scattering volume. The scattered nth harmonic is observed at an angle ϑ in the plane $yz = y'z'$ along the z-axis of the xyz coordinate system. For rigid molecules we obtain:

$$^{n\omega}G_{ij}^{(1)}(t) = C_{n\omega} \sum_{JKM} \frac{1}{2J+1} c_{i,nx}^{JK} c_{j,nx}^{*JK} |^{n\omega}\tilde{a}_M^J|^2 g(t) \exp\{i n\omega - \tau_{JM}^{-1})t\}, \tag{4}$$

where $^{n\omega}\tilde{a}_M^J$ is the Mth component of the Jth rank spherical tensor of the n-order polarizability in the molecular reference system attached to the principal axes of the microsystem. The

$$c_{i,nx}^{JK} = c_{i\underbrace{x\cdots x}_{n}}^{JK}$$

are coefficients of the transformation from cartesian to spherical laboratory coordinates. Generally, on the as-

sumed complete symmetry of the polarizability tensors $^{n\omega}\tilde{a}_M^J$, the numbers J are: even, from the interval $[0, n+1]$, for odd n; and odd, from $[1, n+1]$, for even n.

τ_{JM} is the rotational relaxation time which, for axial particles, is:

$$\tau_{JM}^{-1} = J(J+1)D_1 + M^2(D_3 - D_1). \tag{5}$$

In the spherical top approximation $D_3 = D_1$. By $g(t)$ we denote the translational part of the correlation tensors:

$$g(t) = \exp\{-(\Delta k)^2 D_T t\}, \tag{6}$$

with D_T is the translational diffusion coefficient, and Δk defined above. The coefficient $C_{n\omega}$ is of the form:

$$C_{n\omega} = (2^{n-1} n!)^{-2} N k_{n\omega}^4 \langle E_L^2 \rangle^n. \tag{7}$$

The non-gaussian correction is:

$$^{n\omega}S_{ijkl}^{(2)}(t) = N^{-1} C_{n\omega}^2 \sum_{\substack{J_1 J_2 J_3 J_4 J \\ K_1 K_2 K_3 K_4 K \\ M_1 M_2 M_3 M_4 M}} (-1)^{K_2 + K_4 - K - M_2 - M_4 + M} (2J+1) c_{i,nx}^{J_1 K_1} c_{j,nx}^{*J_2 K_2} c_{k,nx}^{J_3 K_3} c_{l,nx}^{*J_4 K_4}$$

$$\times \, ^{n\omega}\tilde{a}_{M_1}^{J_1} \, ^{n\omega}\tilde{a}_{M_2}^{*J_2} \, ^{n\omega}\tilde{a}_{M_3}^{J_3} \, ^{n\omega}\tilde{a}_{M_4}^{*J_4} \begin{pmatrix} J_1 & J_2 & J \\ M_1 & -M_2 & -M \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J \\ K_1 & -K_2 & -K \end{pmatrix} \begin{pmatrix} J_3 & J_4 & J \\ M_3 & -M_4 & M \end{pmatrix} \begin{pmatrix} J_3 & J_4 & J \\ K_3 & -K_4 & K \end{pmatrix} \exp\{-t/\tau_{JK}\}. \tag{8}$$

The parentheses ($\vdots$) are Wigner $3j$-symbols.

Eqs. (4) and (8) are at the present stage directly applicable if $n = 1, 2, 3$. For these n, the coefficients $c_{i,nx}^{JK}$ and the polarizability tensor elements $^{n\omega}\tilde{a}_M^J$ have been tabulated [11,12,17].

3. Applications and discussion

In the approximation of non-interacting particles eqs. (4) and (8) vanish for even n-harmonics for microsystems having a centre of inversion in the ground state, since the polarizability tensor elements $^{n\omega}\tilde{a}_M^J$ then vanish.

As in ref. [15], the general notion of second-order depolarization of n-harmonically scattered light can be introduced. We shall not consider this here for the sake of brevity.

Eqs. (3), (4) and (8) show that studies of the time-evolution of the tensor $G^{(2)}(t)$ and its spectral density $G^{(2)}(\omega)$ are a source of data on the higher-order rotational relaxation times, intervening in the theories of other nonlinear optical effects as well [18].

Finally, let us apply eqs. (4) and (8) to SHS, in the simplest case of spherical top particles with tetrahedral symmetry. Here, only a single independent spherical tensor element, $^{2\omega}\tilde{a}_2^3 = ^{2\omega}\tilde{a}_{-2}^3$, exists, directly related to the cartesian tensor element $\sqrt{3}b_{123}^{2\omega} = ^{2\omega}\tilde{a}_2^3$ [11]. From (3) we calculate but 2 of the 8 non-zero tensor elements: the polarized one, $G_{xxxx}^{(2)}(t)$, and the depolarized one, $G_{yyyy}^{(2)}(t)$:

$$G_{xxxx}^{(2)}(t) = \tfrac{144}{1225} C_{2\omega}^2 (b_{123}^{2\omega})^4 \{1 + \exp(-2t/\tau_3) g^2(t) + N^{-1}[-\exp(-2t/\tau_3) g^2(t) + \tfrac{84}{121}\exp(-t/\tau_4) + \tfrac{800}{1573}\exp(-t/\tau_6)]$$

$$G_{yyyy}^{(2)}(t) = \tfrac{64}{1225} C_{2\omega}^2 (b_{123}^{2\omega})^4$$
$$\times \{1 + \exp(-2t/\tau_3) g^2(t) + N^{-1}[-\exp(-2t/\tau_3) g^2(t) + \tfrac{49}{121}\exp(-t/\tau_4) + \tfrac{870}{1573}\exp(-t/\tau_6)]\}. \tag{9}$$

Thus, the non-gaussian correction involves higher relaxation times which will be accessible to measurement at sufficiently small N. Likewise, the general formulas (3), (4) and (8) can be applied to calculate the other correlation tensor elements and to solve cases of other molecular symmetry.

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