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MULTI-PHOTON SPECTROSCOPY OF CORRELATED ATOMS AND MOLECULES

1. INTRODUCTION

It is our aim to review concisely the results achieved in recent years in the spectroscopy of multi-photon spontaneous Rayleigh and Raman light scattering processes [1-3,21].

The usual spectroscopy of absorption [4] and scattering [5] in gases has long become a source of valuable information concerning the structure of the atoms and molecules as well as the processes accompanying their collisions at sufficiently high densities (pressure broadening). Among others, of late, light scattering spectroscopy in dilute systems has increasingly been used to probe density fluctuations of a wavelength λ comparable to the mean free path between collisions — a region where hydrodynamics ($l \ll \lambda$) is no longer applicable and where one has to have recourse to various statistical-kinetic methods ($l \gg \lambda$). The theories of single-photon and double-photon spectroscopy are by now so far advanced as to permit the description of various finer effects of the broadening of atomic and molecular spectra [3-6].

It appears that the time has come for an adequate theoretical formulation of three- and multi-photon spectroscopy. The earliest attempts at a stochastic approach bore on molecular hyper-Rayleigh [1] and hyper-Raman [7,8] spectroscopy without taking into account the role of molecular correlations [3,9]. It was only after cooperative three-photon scattering had been discovered [10] that the need to include the coherent scattering, due to various radial and angular intermolecular correlations in liquids [11] and atomic-molecular correlations in mixtures [12], became apparent. The three-photon process in atomic systems consists in incoherent scattering on electric quadrupole and magnetic dipole transitions [13,14] and coherent scattering on triple atomic correlations [12,14]. Since the methods of intensity correlation spectroscopy permit the obtaining of separation times of the order of 10^{-9} s, when applied to the study of multi-

photon scattering processes they provide information on the translational motions of atoms and molecules as well as on the rotational motions of molecules sufficiently large to present relaxation times longer than 10^{-9} s [15]. Rapid molecular rotations (in the $10^8 - 10^{12}$ Hz range), giving rise to relatively broad lines in the scattered light, are studied applying filter techniques (e.g. a $10^{10} - 10^{14}$ Hz grating monochromator or $10^6 - 10^{11}$ Hz Fabry-Pérot interferometer). Thus, by combining photon correlation and interferometric techniques in spectral studies of scattered light, one can measure the relaxation times of various individual and collective processes in a wide range, from 10 down to 10^{-14} s. Plausibly, the recently perfected multichannel spectrometer technique [16] permits the investigation of slow and rapid stochastic molecular motions by the method of multi-photon spontaneous scattering observation.

2. STOCHASTIC THEORY

In this paper, we shall discuss the theory of multi-photon spontaneous scattering spectra in a stochastic approach, consisting in the calculation of the (first-order) time correlation tensor of the field of light, scattered by a system of N interacting atoms or molecules:

$$\left\langle \sum_{p=1}^N \sum_{q=1}^N \ddot{z}_i(t_p + \tau, \tau_p) \ddot{z}_j(t_q, \tau_q)^* \right\rangle \quad (1)$$

where $t_p = t - |\vec{R} - \vec{r}_p|/c$, with \vec{R} — the vector of scattered light observation and \vec{r}_p the radius vector of the p -th scattering centre.

Z_i is the Hertz vector component, involving in general electric and magnetic multipole moments, linear as well nonlinear [13,14]. In a statistically inhomogeneous medium, $Z_i(t, \tau)$ is dependent both on the t -time variations characterizing the response of the scatterer to a short pulse of the electromagnetic field of radiation and on the τ -time variations characterizing the scattering centres or regions of correlated scatterers (e.g. times related with thermal fluctuations [17]).

One can write:

$$Z_i(t, \tau) = Z_i(t, 0) + \delta Z_i(t, \tau) \quad (2)$$

where $Z_i(t, 0)$ describes the individual electromagnetic properties of a microscopic scattering centre, whereas $\delta Z_i(t, \tau)$ moreover describes the variations in Hertz vector due to collisions and interactions between a given scatterer and others surrounding it, or due to collective processes (e.g. spatial redistribution of correlated atoms or molecules) or fluctuational processes (e.g. molecular field fluctuations). (a) Taking into account but the first term of the Hertz vector (2) in our analysis of the correlation tensor (1) we obtain the commonly applied approximation of multi-photon atomic (molecular) spectroscopy. Namely, in the well known manner, by applying Van Hove's distribution function:

$$G(\vec{r}, t) = G_S(\vec{r}_p^t, \vec{r}_p^0) + G_C(\vec{r}_p^t, \vec{r}_q^0) \quad (3)$$

we decompose the tensor (1) into an incoherent ($p=q$) and a coherent ($p \neq q$) part [3,9]. In this way, assuming e.g. the Vineyard approximation [11] for the other-correlation function $G_C(\vec{r}_p^t, \vec{r}_q^0)$, we come to the conclusion that both incoherent and coherent scattering convey information regarding atomic and molecular motions such as is conveyed by the analytic form of the self-correlation function $G_S(\vec{r}_p^t, \vec{r}_p^0)$. Usually, the function G_S is determined from the equation of free diffusion: then, with regard to the circumstance that (in the electric dipole approximation) the correlation tensor (1) depends on the time and space variations by way of the factor

$$\exp \{-i n \omega_0 t - i(\vec{k}_n - n \vec{k}_0)(\vec{r}_p^t - \vec{r}_q^0)\},$$

the n -th scattered harmonic spectrum is obtained as a Lorentzian line.

(b) In some cases, the first term of (2) is absent or negligibly small compared to the second term, thus in second-harmonic scattering by atoms and centrosymmetric molecules when $Z_1(2\omega, 0) = 0$ for the electric dipole transition, as well as in usual scattering, when $Z_1(\omega, 0)$ is isotropic for atoms and the experimentally observed depolarisation of light scattered by inert gases is due to polarizability anisotropy of colliding atoms [18]. In atomic liquids, a similar effect is caused by molecular redistribution [3].

Quite generally, the field time correlation tensor of light, scattered on time-fluctuations (as distinct from Smoluchowski scattering on fluctuations in number density of atoms or molecules alone) is:

$$\left\langle \sum_{p=1}^N \sum_{q=1}^N \delta \ddot{Z}_1(t_p + T, \tau_p) \delta \ddot{Z}_1(t_q, \tau_q) \right\rangle \quad (4)$$

Above, the vector $\delta Z(t, \tau)$ is stochastic in the time-argument τ [17]. From the aforesaid, this correlation tensor describes coherent scattering on pairwise, triple, etc. atomic and molecular correlations only. Consequently, here, in addition to the binary correlation function in Eq. (3), also the ternary, quaternary and higher time-correlation functions have to be available [3].

The distribution function of N molecules in the phase space point Γ_N and at the moment of time t fulfils the well known Liouville equation of motion in operator form:

$$i \frac{\partial f^{(N)}(\Gamma_N, t)}{\partial t} = L f^{(N)}(\Gamma_N, t), \quad (5)$$

where in general the Liouville operator L contains the N -molecule interaction Hamiltonian:

$$H_N = \sum_{p=1}^N u_p + \frac{1}{2} \sum_{p \neq q}^N u_{pq} + \frac{1}{6} \sum_{p, q, r}^N u_{pqr} + \quad (6)$$

On introducing the reduced distribution function of s molecules ($s \ll N$)

$$f^{(s)}(\Gamma_s, t) = \frac{N!}{(N-s)!} \int f^{(N)}(\Gamma_N, t) d\Gamma_{N-s} \quad (7)$$

we get, by (5) and (6), the hierarchical Bogolyubov - Born - Kirkwood - Yvon equation, extended to many-body interaction. However, it is hardly feasible to solve (7) for the function $f^{(s)}$ at $s > 2$ analytically without assuming Kirkwood's superposition approximation. This convinces us of the relevance of whatever information regarding the functions $f^{(3)}(\Gamma_3, t)$, $f^{(4)}(\Gamma_4, t), \dots$ can be gleaned from a study of the correlation tensor (4) for cooperative triple- and more-photon scattering from stochastic assemblages of three, four and more atoms or centrosymmetric molecules [10-12].

Theoretically, there is still the possibility of a direct analysis of the correlation tensor (4) by the Mori memory-function formalism [19]. However, even for very simple models of interacting atoms, this fails to yield explicit analytic solutions. In spite of the considerable progress made in recent years [20], it is to be regretted that no effective method leading simply and explicitly to the form of the distribution function (7) has as yet been evolved within the framework of the statistical mechanics of non-equilibrium processes. In this situation, nothing remains but to introduce, in replacement of (7), the following configurational time-correlation functions of s particles:

$$g^{(s)}(\vec{r}_s, t) = \frac{N!}{(N-s)!} \int f^{(N)}(\Gamma_N, t) d\vec{r}_N d\vec{r}_{N-n}, \quad (8)$$

accessible to determination (at least qualitatively) from experimental studies of the correlation tensor (4), written out successively for pairwise, triple, and higher stochastic clusters of atoms and molecules.

Under well defined assumptions one can decompose the correlation tensor into two factors, corresponding to two distinct time scales for t and τ and then consider separately the correlation functions of molecular electric field fluctuations:

$$\langle \Delta \vec{F}(\vec{r}_p, \tau) \cdot \Delta \vec{F}(\vec{r}_q, 0)^* \rangle \quad (9)$$

In general, the electric field existing in molecule p at the point \vec{r}_p engendered by the electric charges of molecule s in the point $\vec{r}_s = \vec{r}_p + \vec{r}_{ps}$ is related with the dyadic Green function

$$\vec{G}(\vec{r}_{pq}, \omega) = [\nabla_p \nabla_s - (\frac{\omega}{c})^2 \vec{U}] r_{ps}^{-1} \exp [i (\frac{\omega}{c}) r_{ps}],$$

where \vec{U} is the unit dyadic vector.

At small distances ($\omega_r \ll c$), the total electric field in the point \vec{r}_p is due to the successive multipoles $\vec{M}^{(k)}(\vec{r}_s, \tau)$ of the surrounding $N-1$ molecules [3,13]:

$$\bar{F}(\vec{r}_p, \tau) = \sum_{s \neq p}^N \sum_{k=1}^{\infty} (-1)^k \frac{2^k k!}{(2k)!} \nabla^{k-1} \bar{T}(\vec{r}_{ps}) (\vec{r}_{ps}) [k] \bar{M}^{(k)}(\vec{r}_s, \tau) \quad (10)$$

with $\bar{T}(\vec{r}_{ps}) = \nabla_p \nabla_s r_{ps}^{-1}$ - the interaction tensor between molecules p and s .

In particular, the molecular field fluctuation correlation function (9) accounts for three-photon cooperative scattering on centrosymmetric molecules having quadrupole ($k=2$) or hexadecapole ($k=4$) moments, [10]. Thus, this is at present the only possibility of a direct experimental determination of the function (9), which plays an important role in other molecular-stochastic processes as well [3,10]. Obviously, also other mechanisms intervene involving collisional-distortional effects, quadrupole transitions, etc. [14].

(c) Beside the two above-discussed cases of scattering on individual molecules and on stochastic fluctuations, one still has to consider mixed scattering, which we obtain by insertion of Eq. (2) into (1). This type of scattering generally is non-zero and of relevance for achieving quantitative agreement between theory and experiment [3], as well as in the case of mixtures [12]. Under special assumptions, mixed scattering can be made to vanish.

3. CONCLUSIONS

It is obvious from the preceding considerations that highly important information concerning many-body time correlation functions are to be obtained from the spectra of multi-photon coherent scattering on fluctuating media and ones of interacting atoms or molecules. Raman multi-photon spectroscopy is chiefly related with incoherent scattering and thus provides information essentially on the time self-correlation function [21]. Abundant novel information can be expected from studies of stimulated multi-photon Raman scattering processes; hitherto, such observations have been performed by stimulated hyper-Raman scattering on metal vapours [22,23]. Similarly, observations of stimulated Mandelshtam-Brillouin harmonics component scatterings are to be expected [24].

Eq. (1) describes the first-order scattering field correlation tensor $G_{ij}^{(1)}(t, \tau)$, accessible by heterodyne spectroscopy [25]. In self-beat spectroscopy, one measures (using a correlator or spectrum analyzer [25]) the second-order scattering intensity correlation tensor $G_{ijkl}^{(2)}(t, \tau)$ which, in our case, is defined as:

$$\langle \sum_{pqrs}^N \bar{z}_i(t_p, \tau_p) \bar{z}_j(t_q, \tau_q)^* \bar{z}_k(t_r + T, \tau_r) \bar{z}_l(t_s + T, \tau_s)^* \rangle \quad (11)$$

This tensor has been discussed in detail for two-photon [26] as well as generally multi-photon scattering [15] by statistically independent

anisotropic microsystems. The analysis can be extended to strongly correlated atomic and molecular many-body clusters with the aim of elucidating their evolution in time. The time-evolution of the two-parameter correlation tensors (1) and (11) can be calculated simply by having recourse to Mori's [19] projection operator formalism.

Obviously, the complete theoretical analysis of the time-correlation tensors (1) and (11) and higher-order ones requires the consideration of the statistical and quantal properties of the radiation field itself [27-29]. However, when proceeding along this path, one comes up against the very striking problem of whether and to what degree multi-photon (spontaneous and stimulated) scattering is sensitive to the purely quantal effect of photon anticorrelation (antibunching) which, as shown quite recently, can occur in the generation of the second [30, 31] and higher harmonics of coherent light [32].

Primarily, it was our aim to draw attention to the need for a consistent microscopic theory of multi-photon scattering processes formulated on the basis of electrodynamics and stochastic mechanics [20,29] and ensuring satisfactory conformity with experiment both in the hydrodynamical and kinetic regions. The formal methods of time-dependent statistical mechanics [19] have now attained a high level of development, many of them having evolved from work on the theory of lasers and other synergetical processes [20, 29]. But this, by far, does not mean that we be able to apply these methods automatically for quantitative calculations, the results of which obviously depend on the concrete microscopic model adopted for the dynamical structure of the liquid. For example, a problem as yet not solved to the end concerns the expressing of the s -particle time-correlation function (8) in terms of the corresponding equilibrium correlation functions $g^{(s)}(\vec{r}_s)$. It is in fact well known that the Vineyard convolution approximation for G_c in Eq. (3) and G_s determined from the free diffusion equation fails to yield Brillouin-Mandel'shtam components in the scattered spectrum. The range of applicability of this approximation is thus rather strongly restricted (nonetheless, it is used often [11] for a lack of more satisfactory analytical relations). In spite of these difficulties, existing stochastic methods are, in fact, adequate for interrelating the microscopic processes and parameters with the macroscopic quantities measured experimentally. In order to check the validity of the information on the correlation functions thus obtained within the framework of multi-photon spectroscopy, one can operate a comparison with the corresponding relations derived from other nonlinear phenomena of molecular optics [3, 27] or studies of neutron scattering [33], leading to information on Van Hove type functions. Theoretically, at least, there is the possibility of determining the s -particle correlation functions (8) directly by using, in experiment, s heterodyne spectrometers simultaneously to detect the intensity correlation function $G^{(s)}(t)$ of the s -th order. In particular, for systems of like atoms, coherent s -photon scattering will occur only if s atoms interact with one another simultaneously.

It is finally worth reminding that, whereas studies of integral multi-photon scattering lead to information concerning the nonlinear polarizabilities of atoms and molecules as well as their interactions (equilibrium correlation functions)[31], spectral studies of multi-photon scattering phenomena will provide abundant novel information regarding the motions of individual atoms and molecules as well as the dynamics of various collective motions and processes in dense fluids. Hence, the outlooks of multi-photon inter-atomic and inter-molecular spectroscopy are brilliant and eminently promising [21, 34-36].

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