

## SPECTRA OF MULTIPLE-PHOTON RAMAN SCATTERING IN MOLECULAR FLUIDS \*

S. KIELICH, M. KOZIEROWSKI and Z. OŹGO

*Nonlinear Optics Division, Institute of Physics, A. Mickiewicz University, 60-780 Poznań, Poland*

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A general formula is derived for the spectral intensity distribution of inelastic multiple-photon scattered light in the model of free rotational and translational diffusion for motions of molecules. The method of spherical tensors is used, permitting to specify those of the reorientational relaxation times  $\tau_{JM}$  which intervene in the process of multiple-photon scattering, related with a given type of molecular vibrations.

### 1. Introduction

The quantum-mechanical fundamentals of the theory of double- and triple-photon Raman scattering [1,2] as well as the selection rules for these novel nonlinear spontaneous scattering processes [3,4] are by now well established. Raman double-photon scattering (RDPS), apparent in the earliest experiment by Terhune et al. [5], has been observed in gases [6], liquids [7], and crystals [8,9], and Raman triple-photon scattering (RTPS) in diamond [8].

Maker [10] first studied the spectral width of elastic double-photon scattering of liquids interpreting their spectra on the approximate model of self-diffusional brownian motion of the molecules. The model has been applied by Alexiewicz et al. [11] to the description of RDPS spectra.

In this paper, we propose a spectral theory of Raman multiple-photon scattering in molecular fluids on the basis of previous quantum-mechanical results [12]. To achieve generality, we have recourse to the methods of angular momentum and irreducible spherical tensors already applied with success to the analysis of double- [10,11,13] and triple-photon [14,15] scattering. Here, the term "Raman scattering of order  $n$ " refers to processes where  $n$  photons of frequency  $\omega_0$  are incident on a molecule which performs a quantal transition at frequency  $\omega_\nu$  and scatters a photon with frequency  $\omega_n = n\omega_0 \pm \omega_\nu$ .

### 2. General theory

Consider a medium composed of  $N$  molecules, the  $p$ th having the position  $r_i^p$  and orientation  $\Omega_i^p$  at time  $t$ . Intense laser light with electric vector  $E(r, t) = E \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega_0 t)\}$ , incident on the medium, leads quite generally to light scattering of the  $n$ th order defined by the intensity tensor [12,16]:

$$I_{ij}^n(\tau) = (8\pi c^3)^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N (d^2 m_{pi}^n(t)/dt^2) (d^2 m_{qj}^n(t+\tau)/dt^2)^* \exp\{-i\Delta\mathbf{k} \cdot (\mathbf{r}_i^p - \mathbf{r}_{i+\tau}^q)\} \right\rangle, \quad (1)$$

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with  $\Delta k = k_n - nk$ , whereas  $k_n$  is the wave vector of scattered light, and the symbol  $\langle \rangle$  denotes appropriate averaging over molecular orientations, positions and vibrations with time-dependent distribution function.

The dipole moment of  $n$ th order  $m_{pi}^n(t)$ , induced in molecule  $p$ , is of the form:

$$m_{pi}^n(t) = (2^{n-1}n!)^{-1} A_{ii_1 \dots i_n}^n(\Omega_i^p, Q_i^p) E_{i_1} \dots E_{i_n} \exp(-in\omega_0 t). \quad (2)$$

$A_{ii_1 \dots i_n}^n(\Omega_i^p, Q_i^p)$  is a tensor of rank  $n + 1$  defining the  $n$ th order nonlinear polarizability of the  $p$ th molecule and dependent on its orientational and vibrational variables  $\Omega_i^p$  and  $Q_i^p$ .

We express the cartesian components of the dipole moment vector,  $m_{pi}^n(t)$ , in terms of spherical components  $m_{p\alpha}^n(t)$ :

$$m_{pi}^n(t) = \sum_{\alpha} c_i^{\alpha} m_{p\alpha}^n(t). \quad (3)$$

$c_i^{\alpha}$  are elements of the transformation matrix. The spherical components of the dipole moment can be written as follows:

$$m_{p\alpha}^n(t) = (2^{n-1}n!)^{-1} \sum_{\substack{lk \\ \lambda\kappa}} (-1)^{l+k+\alpha} (2l+1)^{1/2} \begin{pmatrix} l & k & 1 \\ \lambda & \kappa & -\alpha \end{pmatrix} A_{\lambda}^{n(l)}(\Omega_i^p, Q_i^p) E_{\kappa}^{(k)} \exp(-in\omega_0 t), \quad (4)$$

where  $\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$  is a Wigner  $3j$  symbol,  $A_{\lambda}^{n(l)}$  the spherical tensor of rank  $l$  of nonlinear molecular polarizability, and  $E_{\kappa}^{(k)}$  a spherical tensor of rank  $k$  representing the  $n$ th rank cartesian tensor with the elements  $E_{i_1} E_{i_2} \dots E_{i_n}$ . The cartesian tensors are assumed as completely symmetric with respect to permutation of indices. For completely symmetric tensors,  $l$  takes successive values only from the interval  $[0, n + 1]$ : even (odd) for odd (even)  $n$ , whereas  $k$  takes values from  $[0, n]$  of the same parity as  $n$ .

The polarizability tensors  $A_{\lambda}^{n(l)}$  can be expressed in a simple manner in terms of the polarizability tensors  $a_{\lambda}^{n(l)}$ , defined in a system of coordinates attached to the molecule:

$$A_{\lambda}^{n(l)}(\Omega_i^p, Q_i^p) = \sum_{\lambda'} a_{\lambda'}^{n(l)}(Q_i^p) D_{\lambda'\lambda}^l(\Omega_i^p), \quad (5)$$

where  $D_{\lambda'\lambda}^l(\Omega_i^p)$  is the Wigner function describing the orientation in space of the molecule with respect to the laboratory coordinate system.

We resolve the intensity tensor (1) into an incoherent part, arising from scattering by an individual molecule ( $p = q$ ) and a coherent part, due to scattering by correlated molecules ( $p \neq q$ ). Since the normal vibrations of the molecules are statistically independent, only the incoherent part plays a role in processes of inelastic scattering.

Thus, we perform the averaging of (1) with a statistical distribution function fulfilling the diffusion equation for free rotation and translation of the molecules. When expanding the nonlinear polarizability tensors in a Taylor series, we restrict ourselves to terms linear in  $Q^{\nu}$ . Finally, for symmetrical and spherical top molecules, we obtain the scattering tensor in the form of a superposition of terms with well-defined reorientation relaxation times  $\tau_{JM}$  related with the order  $J$  of the spherical nonlinear polarizability tensor:

$$I_{ij}^{n,\pm\nu}(\tau) = \sum_{JM} I_{ij}^{n,\pm\nu}(\tau=0, JM) C_{\nu}(\tau) \exp\{i[n\omega_0 \pm \omega_{\nu} - \tau_{JM}^{-1} - (\Delta k)^2 D_T] \tau\}, \quad (6)$$

where

$$I_{ij}^{n,\pm\nu}(\tau=0, JM) = F_{\pm} N(n\omega_0 \pm \omega_{\nu})^4 (8\pi c^3)^{-1} (2^{n-1}n!)^{-2} \sum_{\substack{k_1 k_2 f \varphi_1 \varphi_2 \\ \kappa_1 \kappa_2 \alpha_1 \alpha_2}} c_i^{\alpha_1} c_j^{\alpha_2*} (-1)^{J+f+\kappa_1+\alpha_1} (2f+1) \\ \times \begin{pmatrix} k_1 & k_2 & f \\ \kappa_1 & -\kappa_2 & -\varphi_1 \end{pmatrix} \begin{pmatrix} 1 & 1 & f \\ \alpha_1 & -\alpha_2 & -\varphi_2 \end{pmatrix} \left\{ \begin{matrix} 1 & 1 & f \\ k_1 & k_2 & J \end{matrix} \right\} |a_{\nu, M}^{n(J)}|^2 \langle |Q_i^{\nu}|^2 \rangle_{\text{vib}} E_{\kappa_1}^{(k_1)} E_{\kappa_2}^{(k_2)*} D_{\varphi_1 \varphi_2}^f(\Omega_s) \quad (7)$$

is the integral intensity corresponding to the order  $J$  of the spherical nonlinear polarizability tensor under considera-

tion. The symbol  $\{\cdot\cdot\cdot\}$  stands for a Wigner  $6j$  symbol, and  $a_{\nu,M}^{n(J)}$  is the first derivative of the tensor with respect to the normal coordinate of vibration  $Q^\nu$ , taken at the point of equilibrium of the atoms in the molecule. The Wigner function  $D_{\varphi_1\varphi_2}^f(\Omega_s)$  describes the angular distribution of scattered radiation, with  $\Omega_s$  denoting the mutual orientation of the two laboratory reference systems, connected with the incident and scattered light.  $D_T$  is the coefficient of translational diffusion. The factor  $F_\pm$  introduced in (7) ensures the correct ratio of Stokes-scattered (-) and anti-Stokes-scattered (+) intensities resulting from the principle of detailed equilibrium at scattering and stating that:

$$F_+ = \exp(-\hbar\omega_\nu/kT) F_- . \quad (8)$$

$C_\nu(\tau)$  is the normalized vibrational autocorrelation function, of the form:

$$C_\nu(\tau) = \langle Q_t^\nu Q_{t+\tau}^\nu \rangle_{\text{vib}} / \langle |Q_t^\nu|^2 \rangle_{\text{vib}} . \quad (9)$$

### 3. Discussion

The influence of translational motions, occurring on a slow time scale, can be studied by having recourse to optical mixing technique [17]. The heterodyne technique measures the real part of the scattered light intensity (6) whereas the homodyne technique measures the second-order intensity correlation tensor [16]. Traditional spectroscopy, determining the intensity distribution as a function of frequency, is appropriate for the study of fast processes of molecular relaxation (reorientational motions) contributing measurably to spectral line broadening.

The spectral line shape of scattered light is given by the Fourier transform of (6). On neglecting the contribution from translational motion, we have:

$$I_{ij}^{n,\pm\nu}(\omega) = \sum_{JM} I_{ij}^{n,\pm\nu}(\tau=0, JM) \int_{-\infty}^{\infty} \frac{1}{\pi} \frac{\tau_{JM}^{-1}}{(n\omega_0 \pm \omega_\nu - \omega - \omega')^2 + \tau_{JM}^{-2}} C_\nu(\omega') d\omega' , \quad (10)$$

where  $C_\nu(\omega')$  is the Fourier transform of the vibration autocorrelation function (9). It describes the natural vibrational line shape due to damping of the molecular vibrations, and is accessible to determination i.e. from absorption measurements in IR. For odd  $n$  and completely symmetric vibrations the scattered light contains an isotropic intensity component, related with the zeroth-order spherical tensor ( $J=0$ ) of nonlinear polarizability independent of processes of molecular reorientation.

The separation of the isotropic part moreover permits the determination of the function  $C_\nu(\omega')$ . Generally, this involves the necessity of having recourse to different states of polarisation of the incident light wave and of performing analyses of the angular distribution of scattered radiation. In particular, for usual Raman scattering, the isotropic part can be separated simply by carrying out measurements of the horizontal component  $I_{\parallel}^{1,\pm\nu}(\omega)$  and vertical component  $I_{\perp}^{1,\pm\nu}(\omega)$  (referred to the plane of observation) applying incident light polarized linearly and vertically to the plane of observation. The two components are then independent of the scattering angle, and one has quite generally:

$$I_{is}^{1,\pm\nu}(\omega) = I_{\parallel}^{1,\pm\nu}(\omega) - \frac{4}{3} I_{\perp}^{1,\pm\nu}(\omega) . \quad (11)$$

With regard to scattering at the frequencies  $3\omega \pm \omega_\nu$ , one can apply the same, linear incident light polarisation and, additionally, circular polarisation:

$$I_{is}^{3,\pm\nu}(\omega) = I_{\parallel}^{3,\pm\nu}(\omega) - \frac{16}{15} [I_{\perp}^{3,\pm\nu}(\omega) + 2I_{+}^{3,\pm\nu}(\omega)] , \quad (12)$$

$I_{+}^{3,\pm\nu}$  denoting the component scattered head-on, circularly polarized with sensity the same as the circularly polarized incident light. For spherical top molecules  $4I_{+}^{3,\pm\nu}(\omega) = I_{\perp}^{3,\pm\nu}(\omega)$ , whereas for linear ones  $I_{+}^{3,\pm\nu}(\omega) = 2I_{\perp}^{3,\pm\nu}(\omega)$ , so that from (12) one obtains, respectively:

$$I_{is}^{3,\pm\nu}(\omega) = I_{\parallel}^{3,\pm\nu}(\omega) - \frac{8}{5} I_{\perp}^{3,\pm\nu}(\omega), \quad (13)$$

$$I_{is}^{3,\pm\nu}(\omega) = I_{\parallel}^{3,\pm\nu}(\omega) - \frac{16}{3} I_{\perp}^{3,\pm\nu}(\omega). \quad (14)$$

Spectral line shape investigation leads to the reorientation relaxation times. The well known transformation properties of spherical tensors with respect to the irreducible representations of the point groups make it possible to pinpoint quite generally those of the relaxation times  $\tau_{JM}$  which intervene in a scattering process related with a given type of molecular vibration [18, 19]. For example, in the case of the  $C_{3v}$  group,  $J$  takes an arbitrary value for each irreducible representation (still  $J \leq n + 1$ ), but  $M$  is restricted as follows:

$$A_1 \quad |M| \bmod(+6) = 0, 3;$$

$$A_2 \quad |M| \bmod(+6) = 3, 6;$$

$$E \quad |M| \bmod(+6) = 1, 2, 4, 5.$$

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