

DEPOLARIZATION AND ANGULAR DEPENDENCES OF n -HARMONIC SCATTERED LIGHT IN STATISTICALLY INHOMOGENEOUS MEDIA

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A semi-classical theory of multi-harmonic scattering of intense light on individual molecules, as well as on statistical fluctuations of molecular fields in near ordering areas of isotropic bodies, is proposed. Vertical and horizontal intensity components and depolarisation ratios of n -harmonics are discussed as functions of the scattering angle, and relations between them are derived. The even harmonics are shown to be sensitive to molecular symmetry (natural, or induced by molecular field fluctuations) whereas odd harmonics can be scattered from any substances, molecular or atomic.

1. INTRODUCTION

Up to now, second-harmonic light scattering has been observed in liquids and gases consisting of molecules without a centre of symmetry [1] as well as in liquids with correlating centrosymmetric molecules [2]. Previous to those experiments, one of us [3] proposed the quantum-mechanical fundamentals of Rayleigh and Raman second-harmonic scattering which, in gases, is strongly dependent on the symmetry of the individual molecule [3, 4] and, in liquids, depends on molecular correlations [5-8]. The studies in question are of great importance to nonlinear molecular spectroscopy of both the Rayleigh and Raman kinds [9] and provide much valuable information, that is not available from the study of other nonlinear optical phenomena [10]. Third-harmonic light scattering, though considered theoretically [3], has as yet not been observed in molecular substances; it should prove accessible to observation in macromolecular substances [11], or in molecular ones in fluctuations near the critical point [8], and probably also in liquid crystals [12] and in crystals with defects [13], where scattering from phonons [7] has to be taken into account. It thus appears useful to continue studying higher-harmonic light scattering [14].

2. ELASTIC SCATTERING INTENSITY TENSOR

Consider solely elastic scattering in a dipole approximation, which is justifiable provided the linear dimensions of the scattering centers are small compared with the incident light wavelength $\lambda = 2\pi c/\omega$. The tensor of total scattered light intensity is [14]:

$$I_{ij}^S = I_{ij}^{\omega} + I_{ij}^{2\omega} + I_{ij}^{3\omega} + \dots = \sum_{n=1}^{\infty} I_{ij}^{n\omega}, \quad (1)$$

where the real and symmetric part of the tensor $I_{ij}^{n\omega}$ of n -harmonic scattered light is

$$I_{ij}^{n\omega} = \frac{2^{1-2n}}{V(n!)^2} \left(\frac{n\omega}{c}\right)^4 \langle A_{ii_1 \dots i_n}^{n\omega} A_{jj_1 \dots j_n}^{-n\omega} E_{i_1}^0 E_{j_1}^0 \dots E_{i_n}^0 E_{j_n}^0 \rangle. \quad (2)$$

Here, $A_{ii_1 \dots i_n}^{n\omega}$ is a tensor of rank $n+1$, determining n th order optical polarisability induced in a volume V of the medium scattering at frequency $n\omega$ by the n th power of the electric field $E^\omega = E^0 \cos \omega t$ of incident light with amplitude E^0 . The symbol $\langle \rangle$ stands for suitable statistical averaging.

For isotropic bodies, it is necessary in (2) to average tensors over all possible directions of the electric vector. This procedure was solved generally [15] for $n = 1$ (tensor of rank 4) and $n = 2$ (tensor of rank 6) but becomes immensely intricate from $n = 3$ upwards. However, the problem simplifies if, in (2), instead of averaging the product of polarizability tensors one averages products of unit vectors \mathbf{e} in the direction of the vector \mathbf{E} . In this case, the general result is [16]:

$$\langle c_{i\alpha} c_{j\beta} e_{i_1} e_{j_1} \dots e_{i_n} e_{j_n} \rangle_0 = \frac{1}{2(2n+3)!!} \{ (2n+3) (\delta_{ij} - e_i e_j) \delta_{\alpha\beta} \sigma_{i_1 j_1} \dots i_n j_n + (3e_i e_j - \delta_{ij}) \sigma_{\alpha\beta i_1 j_1} \dots i_n j_n \}, \tag{3}$$

where $c_{i\alpha}$ is the cosine of the angle between the laboratory i axis and the α axis of a mobile frame attached to a given point of the scattering volume. The tensor $\sigma_{\alpha\beta i_1 j_1} \dots i_n j_n$ is a $(2n+1)$ -fold combination of the type $\delta_{\alpha\beta} \sigma_{i_1 j_1} \dots i_n j_n$, and $\sigma_{i_1 j_1} \dots i_n j_n$ is a $(2n-1)$ -fold combination of the type $\delta_{i_1 j_1} \sigma_{i_2 j_2} \dots i_n j_n$, etc., with $\delta_{\alpha\beta}$ denoting Kronecker's unit tensor.

By (3), we have for the intensity of n -harmonic scattering [14]:

$$I_{ij}^{n\omega} = \left(\frac{n\omega}{c}\right)^4 \{ F_{n\omega} I \delta_{ij} + G_{n\omega} I_{ij} \} I^{n-1}, \tag{4}$$

where $I_{ij} = E_i^0 E_j^0 / 2$ is the intensity tensor of the incident laser light and $I = I_{ii}$ its total intensity.

The factors in (4) account for the optical properties, molecular structure and thermodynamical state of the scattering medium:

$$F_{n\omega} = V^{-1} \langle A_{\alpha i_1 \dots i_n}^{n\omega} A_{\beta j_1 \dots j_n}^{-n\omega} f_{\alpha\beta i_1 j_1 \dots i_n j_n} \rangle, \\ G_{n\omega} = V^{-1} \langle A_{\alpha i_1 \dots i_n}^{n\omega} A_{\beta j_1 \dots j_n}^{-n\omega} g_{\alpha\beta i_1 j_1 \dots i_n j_n} \rangle, \tag{5}$$

where we have introduced the tensors:

$$f_{\alpha\beta i_1 j_1 \dots i_n j_n} = C_n \{ (2n+3) \delta_{\alpha\beta} \sigma_{i_1 j_1} \dots i_n j_n - \sigma_{\alpha\beta i_1 j_1} \dots i_n j_n \}, \\ g_{\alpha\beta i_1 j_1 \dots i_n j_n} = C_n \{ 3\sigma_{\alpha\beta i_1 j_1} \dots i_n j_n - (2n+3) \delta_{\alpha\beta} \sigma_{i_1 j_1} \dots i_n j_n \}, \tag{6}$$

with $C_n^{-1} = 2^n (n!)^2 (2n+3)!!$.

The scattering factors in the semi-macroscopic form (5) can be discussed on the microscopic scale if we express the n th order polarizability tensor of the volume V containing N molecules as follows:

$$A_{\alpha i_1 \dots i_n}^{n\omega} = \sum_{p=1}^N \{ a_{\alpha i_1 \dots i_n}^{n\omega(p)} + b_{\alpha i_1 \dots i_n, \gamma}^{n\omega(p)} F_{\gamma}^{(p)} + \frac{1}{2} c_{\alpha i_1 \dots i_n, \gamma\delta}^{n\omega(p)} F_{\gamma}^{(p)} F_{\delta}^{(p)} + \dots \} \exp[i(\Delta\mathbf{k}_n \cdot \mathbf{r}_p)], \tag{7}$$

where $\Delta\mathbf{k}_n = \mathbf{k}_n - n\mathbf{k}_f$, with \mathbf{k}_n denoting the wave vector of the scattered n -harmonic wave, \mathbf{k}_f that of the incident wave of fundamental frequency ω , and \mathbf{r}_p the radius vector of a scattering molecule p .

In (7), $a_{\alpha i_1 \dots i_n}^{n\omega(p)}$ is the n th order polarizability tensor (of rank $n+1$) of the p th molecule immersed in the medium; the next $(n+2)$ -rank tensor $b_{\alpha i_1 \dots i_n, \gamma}^{n\omega(p)}$ determines the $(n+1)$ -order polarizability induced in the p th molecule by the molecular electric field $F_{\gamma}^{(p)}$ of the other $N-1$ molecules of the medium. Similarly, the $(n+3)$ -rank tensor $c_{\alpha i_1 \dots i_n, \gamma\delta}^{n\omega(p)}$ determines the $(n+2)$ -order polarizability induced by the square of the molecular field. The expansion (7) can, in general, also contain contributions from statistical translational fluctuations of the molecules. Generally, the molecular field $F^{(p)}$ fluctuating in time and space can lower the symmetry of the molecule (e.g., by destroying its centre of symmetry), or can induce a local anisotropy in areas of near neighbourhood thus giving rise to cooperative scattering [2, 6].

In rarefied substances, when statistical fluctuations are absent, even-harmonic scattering (i.e., with $n = 2, 4 \dots$) can stem solely from molecules not possessing a centre of symmetry in their ground state. With respect to odd harmonics ($n = 1, 3 \dots$), the molecular symmetry is not decisive, since such scatterings can be caused by centres (scatterers) having spherical symmetry (e.g., atoms in their ground state). If however, a medium consisting of centrosymmetric molecules exhibits fluctuational molecular fields, then with regard to the second term of (7) it will give rise to cooperative scatterings of even harmonics too, and this has in fact been observed quite recently in the case of the second harmonic [2]. Consequently, eqs. (5) - (7) permit particularly for $n = 2$, formulas to be obtained for the above considered second-harmonic scatterings from gases [3, 4] and liquids [5, 6] consisting of molecules without a centre of symmetry, as well as liquids consisting of centrosymmetric molecules [2, 6]. Similarly, for $n = 3$ one obtains formulas for third-harmonic scattering from gases [3, 16] and liquids [11].

3. DEPOLARISATION RATIOS AND ANGULAR DEPENDENCE

Assume the incident light wave to propagate along the Y axis and the electric vector E to oscillate in the XZ plane at an angle ψ to the XY plane. The XYZ frame, with unit base x, y, z is fixed at the centre of the scattering volume. The scattered light is observed in the frame $X'Y'Z'$ (units x', y', z') in the plane $X'Y' \parallel XY$ along the X' axis, which subtends an angle θ with the Y axis (θ is the scattering angle, i.e., the angle of observation).

We thus have [6]:

$$\begin{aligned} \tilde{e}_x &= x \cos \psi + z \sin \psi, \\ y' &= -x \cos \theta + y \sin \theta, \\ z' &= z. \end{aligned} \tag{8}$$

We obtain the scattered light components with oscillations horizontal (H) and vertical (V) to the observation plane from (4) in accordance with the definition:

$$H^{n\omega} = I_{ij}^{n\omega} y'_i y'_j, \quad V^{n\omega} = I_{ij}^{n\omega} z'_i z'_j.$$

Hence we find:

$$H^{n\omega}(\psi, \theta) = \left(\frac{n\omega}{c}\right)^4 \{F_{n\omega} + G_{n\omega} \cos^2 \psi \cos^2 \theta\} I^n, \quad V^{n\omega}(\psi) = \left(\frac{n\omega}{c}\right)^4 \{F_{n\omega} + G_{n\omega} \sin^2 \psi\} I^n. \tag{9}$$

For $\psi = 90^\circ$ and $\psi = 0^\circ$ we obtain, respectively, vertical and horizontal polarisation of the incident light (which we denote by subscripts v and h), and from (9) it results that:

$$\begin{aligned} H_v^{n\omega} &= \left(\frac{n\omega}{c}\right)^4 F_{n\omega} I_v^n, & V_v^{n\omega} &= \left(\frac{n\omega}{c}\right)^4 \{F_{n\omega} + G_{n\omega}\} I_v^n, \\ H_h^{n\omega} &= \left(\frac{n\omega}{c}\right)^4 \{F_{n\omega} + G_{n\omega} \cos^2 \theta\} I_h^n, & V_h^{n\omega} &= \left(\frac{n\omega}{c}\right)^4 F_{n\omega} I_h^n. \end{aligned} \tag{10}$$

At perpendicular observation Krishnan's relation $V_h^{n\omega}/I_h^n = H_v^{n\omega}/I_v^n = H_h^{n\omega}(90^\circ)/I_h^n$ is thus fulfilled for any n -harmonically scattered light.

For unpolarized incident light, we have to average expressions (9) over all values of the angle ψ ; with respect to (10), we obtain:

$$H_u^{n\omega}(\theta) = \frac{1}{2} \{H_v^{n\omega} + H_h^{n\omega}(\theta)\}, \quad V_u^{n\omega} = \frac{1}{2} \{V_v^{n\omega} + V_h^{n\omega}\}. \tag{11}$$

By (10) and (11), we obtain for the respective depolarisation ratios:

$$D_v^{n\omega} = \frac{H_v^{n\omega}}{V_v^{n\omega}} = \frac{F_{n\omega}}{F_{n\omega} + G_{n\omega}}, \quad D_h^{n\omega}(\theta) = \frac{V_h^{n\omega}}{H_h^{n\omega}} = \frac{F_{n\omega}}{F_{n\omega} + G_{n\omega} \cos^2 \theta}, \quad D_u^{n\omega}(\theta) = \frac{H_u^{n\omega}}{V_u^{n\omega}} = \frac{2F_{n\omega} + G_{n\omega} \cos^2 \theta}{2F_{n\omega} + G_{n\omega}}, \tag{12}$$

and one easily notes that for arbitrary harmonic scattering the following simple relations are fulfilled:

$$D_h^{n\omega}(\theta) = \frac{D_v^{n\omega}}{D_v^{n\omega} + (1 - D_v^{n\omega}) \cos^2 \theta},$$

$$D_u^{n\omega}(\theta) = \frac{1}{1 + D_v^{n\omega}} \{2D_v^{n\omega} + (1 - D_v^{n\omega}) \cos^2 \theta\} = D_u^{n\omega} \left\{1 + \frac{1 - D_u^{n\omega}}{D_u^{n\omega}} \cos^2 \theta\right\}, \quad (13)$$

where

$$D_u^{n\omega} = D_u^{n\omega}(90^\circ) = 2D_v^{n\omega} / (1 + D_v^{n\omega}). \quad (14)$$

Furthermore it turns out that, for certain groups of molecular symmetries, simple relations can exist between the depolarisation ratios of n and $n+2$ harmonically scattered light, similar to those already derived for linear and third-harmonic scattering [11].

We see that investigations of n -harmonic light scattering in conjunction with other nonlinear optical phenomena [10, 17] allow insight to be gained into the statistical structure of matter and to study the influence on it of the statistics of electromagnetic fields [18].

REFERENCES

- [1] R. W. Terhune, P. D. Maker and C. M. Savage, Phys. Rev. Letters 14 (1965) 681; P. D. Maker, Phys. Rev. 1 (1970) 923.
- [2] S. Kielich, J. R. Lalanne and F. B. Martin, Phys. Rev. Letters 26 (1971) 1295.
- [3] S. Kielich, Physica 30 (1964) 1717; Acta Phys. Polon. 26 (1964) 135.
- [4] S. J. Cyvin, J. E. Rauch and J. C. Decius, J. Chem. Phys. 43 (1965) 4083.
- [5] R. Bershon, Y. H. Pao and H. L. Frisch, J. Chem. Phys. 45 (1966) 3184; D. L. Weinberg, J. Chem. Phys. 47 (1967) 1307.
- [6] S. Kielich, Acta Phys. Polon. 33 (1968) 89; IEEE J. Quantum Electron. QE4 (1968) 744.
- [7] V. L. Strizhevsky and V. M. Klimenko, Zh. Eksperim. i Teor. Fiz. 53 (1967) 244; V. L. Strizhevsky and V. V. Obuhovsky, Zh. Eksperim. i Teor. Fiz. 58 (1970) 929; S. S. Jha and J. W. F. Woo, Nuovo Cimento 2B (1971) 167.
- [8] I. Freund and I. Kopf, Phys. Rev. Letters 24 (1970) 1017.
- [9] J. F. Verdick, S. H. Peterson, C. M. Savage and P. D. Maker, Chem. Phys. Letters 7 (1970) 219; S. H. Peterson, Ph. D. Thesis, University of Michigan (1971).
- [10] S. Kielich, Opto-Electron. 2 (1970) 125 and references therein.
- [11] S. Kielich and M. Kozierowski, Acta Phys. Polon. A38 (1970) 271; Bull. Soc. Amis Sci. Lettres Poznań B22 (1970/71) 16.
- [12] L. S. Goldberg and J. M. Schnur, Appl. Phys. Letters 14 (1969) 306; Radio Electronic Engineer 39 (1970) 279.
- [13] H. Rabin, Proc. Intern. Conf. Technol. at New Delhi, India (1969) p. 167.
- [14] S. Kielich, Chem. Phys. Letters 1 (1967) 441; Acta Phys. Polon. 33 (1968) 141.
- [15] S. Kielich, Acta Phys. Polon. 20 (1961) 433.
- [16] M. Kozierowski, Bull. Soc. Amis Sci. Lettres Poznań B22 (1970/71) 5.
- [17] S. A. Akhmanov and A. S. Chirkin, Izv. V. U. Z. Radiofiz. 13 (1970) 787.
- [18] J. Ducuing and N. Bloembergen, Phys. Rev. 133A (1964) 1493; L. Mandel and E. Wolf, Rev. Mod. Phys. 37 (1965) 231.