ON THREE-PHOTON LIGHT SCATTERING IN ATOMIC FLUIDS

By S. Kielich

Department of Molecular Physics, A. Mickiewicz University, Poznań*

(Received January 19, 1967)

The occurrence of three-photon light scattering in atomic fluids is discussed classically, and shown to be related only with the nonlinear polarization of atoms induced by a strong optical field in the presence of (i) an external DC electric field, (ii) an optical field gradient or (iii) microscopic electric fields existing between the atoms of highly condensed fluids. Numerical evaluations prove the feasibility of detecting three-photon scattering in liquefied argon when using an intense laser beam.

1. Introduction

Theoretical work on three-photon light scattering [1, 2] started in the 1930s but has progressed recently [3—6] owing to laser techniques, which permitted the observation of nonlinear scattering in several organic liquids [7] and gases [8] thus paving the way for further theoretical and experimental studies of the nonlinear optical properties of molecules and for new nonlinear Rayleigh and Raman spectrocopies [5—10] providing insight into the finer details of molecular structure.

2. Scattering by molecules without a centre of inversion

Consider a gas of N molecules without centre of inversion on which two light waves with electric vectors $\boldsymbol{E}^{\omega_1} = \boldsymbol{E}_1^0 e^{i\omega_1 t}$ and $\boldsymbol{E}^{\omega_2} = \boldsymbol{E}_2^0 e^{i\omega_2 t}$ are incident; in addition to the usual linear Rayleigh scattering with frequency ω_1 given by the intensity tensor

$$I_{\alpha\beta}^{\omega_1} = \omega_1^4 N \langle a_{\alpha\gamma}^{\omega_1} a_{\beta\delta}^{\omega_1} \rangle I_{1\gamma\delta}, \tag{1}$$

we now have nonlinear light scattering with frequency $\omega_1+\omega_2$ given by the intensity tensor [6]

$$I_{\alpha\beta}^{\omega_1+\omega_2} = \frac{1}{2}(\omega_1+\omega_2)^4 N \langle b_{\alpha\gamma\varepsilon}^{\omega_1+\omega_2} b_{\beta\delta\eta}^{\omega_1+\omega_2} \rangle I_{1\gamma\delta} I_{2\varepsilon\eta}, \tag{2}$$

---

* Address: Uniwersytet im. A. Mickiewicza, Katedra Fizyki Molekularnej, Poznań, ul. Grunwaldzka 6, Polska.

where $a_{\alpha\beta}$ and $b_{\alpha\beta\gamma}$ are the tensors of linear and nonlinear polarizabibities of the molecule, $I_{1\gamma\delta} = \frac{1}{2} E_\gamma^{\omega_1} E_\delta^{-\omega_1}$ and $I_{2\varepsilon\eta} = \frac{1}{2} E_\varepsilon^{\omega_2} E_\eta^{-\omega_2}$ the intensities of the incident beams, whereas the symbol $\langle \ \rangle$ stands for appropriate statistical averageing.

The three-photon scattering (2) has been discussed in detail in earlier papers [4, 6] for a number of molecules having the point group symmetries D_{2d}, D_{3h}, C_{3v}, C_{4v}, C_{6v}, $C_{\infty v}$ and T_d and observed by Terhune *et al.* [7] in a number of liquids (H_2O, CCl_4, CH_3CN) and by Maker [8] in methane pressurized to 100 atmospheres. A full discussion of the symmetry properties of the second-order polarizability tensor $b_{\alpha\beta\gamma}$ has also been given by Cyvin *et al.* [9].

For atoms or molecules with a centre of inversion, the three-photon scattering of Eq. (2) does not occur in this approximation of the theory. In the next, scattering with frequencies $\omega_1+2\omega_2$ or $\omega_1\pm\omega_2\mp\omega_3$ appears [4, 6], involving four photons. This very weak third-order scattering takes place irrespective of a centre of symmetry, and thus in atoms also [6].

3. *Nonlinear scattering by atoms*

It is our aim here to show that in certain conditions three-photon scattering can occur also in the case of atomic substances. We shall consider 3 cases:

(i) If in addition to the optical fields $\boldsymbol{E}^{\omega_1}$ and $\boldsymbol{E}^{\omega_2}$ the atoms is acted on by a *DC* electric field $\boldsymbol{E}^{DC}$, it gains a dipole moment

$$m_\alpha = a_{\alpha\beta}^{\omega_1} E_\beta^{\omega_1} + c_{\alpha\beta\gamma\delta}^{\omega_1+\omega_2} E_\beta^{\omega_1} E_\gamma^{\omega_2} E_\delta^{DC} + \ldots \tag{3}$$

leading to three-photon scattering as follows:

$$I_{\alpha\beta}^{\omega_1+\omega_2} = \frac{1}{2}(\omega_1+\omega_2)^4 N \langle c_{\alpha\gamma\varepsilon\vartheta}^{\omega_1+\omega_2} c_{\beta\delta\eta\chi}^{\omega_1+\omega_2} \rangle I_{1\gamma\delta} I_{2\varepsilon\eta} E_\vartheta^{DC} E_\chi^{DC}. \tag{4}$$

The above nonlinear scattering is related with the induction of nonlinear third-order polarization in the atom as given by the tensor $c_{\alpha\beta\gamma\delta}$ which, for spherical symmetry, can be written thus [6]:

$$c_{\alpha\beta\gamma\delta} = c_{1133}\,\delta_{\alpha\beta}\delta_{\gamma\delta} + \frac{1}{2}(c_{3333}-c_{1133})(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}). \tag{5}$$

Considering that for atoms with regard to (1) linear scattering is given by $I_{\alpha\beta}^{\omega_1} = \omega_1^4 a^2 N I_{1\alpha\beta}$, we obtain the component of (4) in the z-direction as

$$I_{zz}^{2\omega}/I_{zz}^{\omega} = 8\left(\frac{c}{a}\right)^2 I_{zz} E_{DC}^2 \tag{6}$$

assuming for simplicity a single incident beam ($\omega_1 = \omega_2 = \omega$), with electric vector oscillating along the Z-axis. Here, a and c denote respectively the mean linear and nonlinear polarizability of the atom. For argon, $a = 1.63\times10^{-24}$ cm^3 and [11] $c = 0.7\times10^{-36}$ esu, and the ratio of three-photon and two-photon scattering is $\sim 1.6\times10^{-24}\, I_{zz}E_{DC}^2$. It is to be regretted that as yet measuring techniques are unable to detect this very weak effect of nonlinear scattering.

(ii) We proceed to the case when a gradient of one of the optical fields *e. g.* $\boldsymbol{E}^{\omega_2}$ induces a quadrupole moment $\boldsymbol{Q}$ in the atom and when the total dipole moment induced by the field $\boldsymbol{E}^{\omega_1}$ is, in the present approximation,

$$m_\alpha = a^{\omega_1}_{\alpha\beta} E^{\omega_1}_\beta + \frac{1}{3} Q^{\omega_1+\omega_2}_{\alpha\beta\gamma\delta} E^{\omega_1}_\beta \nabla_\gamma E^{\omega_2}_\delta + \dots \tag{7}$$

The nonlinear scattering involved by the tensor of $\boldsymbol{Q}$ is [12]

$$I_{\omega_1+\omega_2} = \frac{1}{18} (\omega_1+\omega_2)^4 N \langle Q^{\omega_1+\omega_2}_{\alpha\gamma\varepsilon\vartheta} Q^{\omega_1+\omega_2}_{\beta\delta\eta\chi} \rangle I_{1\gamma\delta} I_{2\varepsilon\eta} k_{2\vartheta} k_{2\chi}, \tag{8}$$

where $k_{2\vartheta}$ is the component of the wave vector attached to the field $\boldsymbol{E}$. For atoms, we have [13]

$$Q_{\alpha\beta\gamma\delta} = \frac{1}{4} Q(3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}), \tag{9}$$

whence by (8) we obtain for a single light wave

$$I^{2\omega}_{\alpha\beta} = \frac{1}{32} (2\omega)^4 N Q^2 k_\alpha k_\beta I_{\gamma\delta} I_{\gamma\delta}. \tag{10}$$

For argon [14] $Q = -1 \times 10^{-38}$ esu and Eq. (10) yields the relative nonlinear scattering as $18 \times 10^{-30}\, I k^2$ which, as one sees, is again extremely little even if an intense beam of very short wavelength is used.

(iii) The preceding considerations dealt with scattering by the individual atoms of a rarefied gas. We shall now consider a substance whose atoms interact by way of electric fields $\boldsymbol{F}$ contributing towards their nonlinear polarization jointly with the fields $\boldsymbol{E}^{\omega_1}$ and $\boldsymbol{E}^{\omega_2}$. In the above approximation, we again have the expansion (3) on replacing the external *DC* field $\boldsymbol{E}^{DC}$ in the nonlinear term by the interatomic field $\boldsymbol{F}$. In place of (4), we now get

$$I^{\omega_1+\omega_2}_{\alpha\beta} = \frac{1}{2} (\omega_1+\omega_2)^4 \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} c^{\omega_1+\omega_2}_{i\alpha\gamma\varepsilon\vartheta} c^{\omega_1+\omega_2}_{j\beta\delta\eta\chi} F_{i\vartheta} F_{j\chi} \right\rangle I_{1\gamma\delta} I_{2\varepsilon\eta}, \tag{11}$$

where $\boldsymbol{F}_i$ is the electric field induced at the centre of the i-th atom by all other atoms of the medium. Assuming it to be related with London's dispersion forces, we have by (11) in a satisfactory approximation

$$I^{2\omega}_{zz}/I^{\omega}_{zz} = 2 \left(\frac{c}{a}\right)^2 h\nu a \frac{\mathcal{J}_R}{\gamma_R} I_{zz}, \tag{12}$$

where $h\nu$ in the characteristic energy of the atom, and [15—17]

$$\gamma_R = 1 + 4\pi\varrho \int_0^\infty \{g(r)-1\}\, r^2 dr = \varrho k T \beta_T, \tag{13}$$

$$\mathcal{J}_R = 8\pi\varrho \int_0^\infty r^{-6} g(r) r^2 dr \tag{14}$$

are parameters of radial correlations between atoms distant by $\boldsymbol{r}$ which involve the radial function $g(r)$; ϱ is the number density and β_T — isothermal compressibility.

For argon $h\nu = 17.5$ eV and in the liquid state at $T = 84.25$°K we have $\gamma_R = 0.042$, $\mathcal{J}_R = 8.4\times 10^{45}$ cm^{-6} (values calculated from Refs [16, 17]), whence Eq. (12) yields $I^{2\omega}_{zz}/I^{\omega}_{zz} = 2.4\times 10^{-12}\, I_{zz}$. Thus, in liquefied argon, three-photon scattering should be accessible to observation using a laser beam of intensity 10^5—10^6 esu.

4. *Conclusions*

In this context, it would be highly desirable to extend measurements of linear Rayleigh scattering in simple gases [18] to nonlinear scattering from the liquefied gases using strong lasers. Since in the cases (i) and (ii) three-photon scattering in rarefied atomic gases is extremely weak, it ought rather to be searched for near resonance lines, when nonlinear resonance scattering can attain correspondingly larger values, as is the case for linear resonance scattering.

Since, in the linear approximation, isolated atoms in the ground state do not produce depolarisation of the scattered light, it may be preferable to concentrate the experiments on the depolarisation induced in the gas by intense light. By (4), (8) or (11), such depolarisation will occur only if the atoms undergo nonlinear optical deformation [6, 13]. The simple classical considerations of this Note can be extended to the quantal case of nonlinear Raman scattering [6, 12].

REFERENCES

[1] J. Blaton, *Z. Physik*, **69**, 835 (1931).
[2] P. Güttinger, *Helv. Phys. Acta*, **5**, 237 (1932).
[3] T. Neugebauer, *Acta Phys. Hungar.*, **16**, 217, 227 (1963).
[4] S. Kielich, *Bull. Acad. Polon. Sci, Ser. Sci. Math., Astron. Phys.*, **11**, 201 (1963); **12**, 53 (19 64).
[5] Li-Yin-Yuan, *Acta Phys. Sinica*, **20**, 164 (1964).
[6] S. Kielich, *Physica*, **30**, 1717 (1964); *Acta Phys. Polon.*, **25**, 85 (1964); **26**, 135 (1964).
[7] R. Terhune, P. Maker and C. Savage, *Phys. Rev. Letters*, **14**, 681 (1965).
[8] P. D. Maker, *Physics of Quantum Electronics*, p. 60 Mc Graw-Hill Book Company, Inc., New York 1966.
[9] S. J. Cyvin, J. E. Rauch, and J. C. Decius, *J. Chem. Phys.*, **43**, 4083 (1965).
[10] C. A. Akhmanov and D. N. Klishko, *Zh. Eksper. Teor. Fiz.,Letters*. **2**, 171 (1965).
[11] A. D. Buckingham and J. A. Pople, *Proc. Phys. Soc.*, *A***68**, 905 (1965).
[12] S. Kielich, *Proc. Phys. Soc.*, **86**, 709 (1965).
[13] S. Kielich, *Physica*, **29**, 938 (1963).
[14] A. D. Buckingham, *J. Chem. Phys.*, **30**, 1580 (1959).
[15] F. Zernike and J. A. Prins, *Z. Phys.*, **41**, 184 (1927).
[16] A. D. Buckingham and M. J. Stephen, *Trans. Faraday Soc.*, **53**, 884 (1957).
[17] S. Kielich, *Acta Phys. Polon.*, **22**, 299 (1962).
[18] L. Slama, *These*, C. E. N. Saclay, 1963; T. V. George, L. Goldstein, L. Slama and M. Yokoyama, *Phys. Rev.*, **137**, *A*369 (1965).