Electric-dipole differential hyper-Rayleigh and hyper-Raman scattering of elliptically polarized light

M. Kozierowski
Nonlinear Optics Division, Institute of Physics, A. Mickiewicz University, PL-60-780 Poznań, Grunwaldzka 6, Poland
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The intensities of hyper-Rayleigh and hyper-Raman scatterings are, already in the electric dipole approximation, shown to be different in right- and left-handed elliptically polarized incident light. The existence of this differential scattering requires the third-rank hyperpolarizability tensor b_{ijk} to be complex and j,k symmetric only.

I. GENERAL REMARKS

Initially, hyper-Raman and hyper-Rayleigh scatterings were described on the assumption of full index symmetry in the b_{ijk} tensor.[1,2] This assumption is justified as long as none of the frequencies—incident or scattered—approaches an electronic transition frequency of the molecule. However, in practice, this condition of remoteness from absorption bands is, for the scatterings in question, rather less realistic than that for linear Rayleigh and Raman processes. Hence, the complete description of these nonlinear scatterings demands, in principle, the use of a partly (j,k)-symmetric b_{ijk} tensor;[3] the indices j and k are associated with the same incident frequency. Index unsymmetry in b_{ijk} leads to new selection rules and to the emergence of new purely unsymmetric hyper-Raman lines in the scattered spectrum.[4,5] Purely unsymmetric hyper-Rayleigh also occurs for molecules of the point groups D_4, D_5, and D_6. These scatterings, associated with the unsymmetric irreducible part of weight 2 of b_{ijk}, manifest the phenomenon of inverse polarization[4,5]—an effect comparable with the inverse polarization of antisymmetric Rayleigh and Raman scatterings.

The next step in the generalization of the electric dipole hyper-Rayleigh and hyper-Raman description naturally consists in considering the tensor b_{ijk} as not only unsymmetric but complex as well.[6] This is the procedure we shall adopt here. We shall propose a classical theory of scattering since this will prove sufficient for demonstrating the origin of elliptical differential scattering.

Electric dipole elliptical intensity differential (EDEID) scattering has no counterpart in linear scatterings. The first two letters ED are used to distinguish this effect from CID (circular intensity differential), or generally from EID, which is produced as a result of interference in the scattered field amplitudes arising from electric dipole, magnetic dipole, and electric quadrupole transitions in optically active molecules.[7] As for hyper-Rayleigh and hyper-Raman, CID has been considered in the paper by Andrews and Thirunamachandran.[8] As we shall see further on, EDCID does not exist.

II. THEORY OF SCATTERING

A molecule in a strong electromagnetic wave

$$E_i(\omega,t)=E_i(t)\exp[-i(\omega t-kz)]$$

generally undergoes nonlinear polarization. The latter is a source of new electromagnetic waves of frequencies that are multiples of ω. The processes in question are related to the quadratic in $E_i(\omega,t)$ electric dipole moment induced in the molecule:

$$m_i=\tfrac{1}{2}b_{ijk}E_j(\omega,t)E_k(\omega,t)\ , \tag{1}$$

where the summation convention over a repeated index is implied.

According to the transition polarizability theory of Placzek,[9] extended to the nonlinear case, the tensor b_{ijk} depends on vibrations of nuclei which modulate the scattered amplitudes, and can be expanded in terms of normal coordinates Q_λ of vibration:[1]

$$b_{ijk}=b_{ijk}(Q)=b^0_{ijk}+\sum_\lambda b^\lambda_{ijk}Q_\lambda+\cdots\ . \tag{2}$$

The tensor b^0_{ijk} is responsible for hyper-Rayleigh scattering at the double frequency $\omega_s=2\omega$, whereas hyper-Raman is associated with the derivative b^λ_{ijk} and comprises the Stokes $\omega_s=2\omega-\omega_{Q_\lambda}$ and anti-Stokes $\omega_s=2\omega+\omega_{Q_\lambda}$ frequencies, where ω_{Q_λ} is the frequency corresponding to the vibrational mode λ. The higher terms of the expansion (2) correspond to overtones.

Since the phases of vibrations of different molecules are uncorrelated, the hyper-Raman scattered light is an approximately incoherent sum of scatterings from each of the N molecules. In the case of hyper-Rayleigh this is true in the dilute gas approximation. We shall restrict ourselves to the description of just this incoherent scattering.

The scattered integral intensity tensor $I_{ij}\simeq N\langle \dot m_i \dot m_j^*\rangle_{\Omega,E}$ involves a sixth-order rotational averaging $\langle\ \rangle_\Omega$ of the directional cosines[10] describing the transformation of the tensor components b_{ijk} from the laboratory-fixed frame (Latin indices i,j,k) to the molecule-fixed frame (Greek indices α,β,γ). In general, we have also to perform an averaging $\langle\ \rangle_E$ over the ensemble of the incident field amplitudes E_i if we allow them to fluctuate: $E_i=E_i(t)$—ergodic theorem.

Assume the incident elliptically polarized light propagating along the z direction and having ellipticity ϕ. The elliptic major axis makes an azimuth ψ with the x axis. The scattered light is observed in the $YZ=yz$ plane along the Z axis at an angle θ relative to z. The total intensity scattered at θ is found from $I=I_{ij}X_iX_j+I_{ij}Y_iY_j$, where $\overline{\mathrm{X}}$ and $\overline{\mathrm{Y}}$ are unit vectors along X and Y, respectively.

Finally, after rather cumbersome manipulations, one

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finds:

$$I=\Gamma\{4A+[4B+C(1+\cos^2\theta)]\cos^2(2\phi)+2E(1+\cos^2\theta)+D\cos(2\phi)\cos(2\psi)\sin^2\theta+F\sin(4\phi)\sin(2\psi)\sin^2\theta\}\ , \tag{3}$$

where $\phi>0$ refers to right-handed (+) incident light, while $\phi<0$ (−) to left-handed light in the optical convention. The symbol Γ stands for a scattering factor the exact form of which is redundant here; we mention only that it is proportional to the second-order coherence degree $g^{(2)}$ of the incident light as well as to ω_s^4.

With regard to (3), the elliptical intensity differential ratio[7]

$$\Delta=(I^+-I^-)/(I^++I^-) \tag{4}$$

[where the superscripts (±) following I refer to the incident handedness] takes the form

$$\Delta_\theta=\frac{F|\sin4\phi|\sin(2\psi)\sin^2\theta}{4A+[4B+C(1+\cos^2\theta)]\cos^2(2\phi)+D\cos(2\phi)\cos(2\psi)\sin^2\theta+2E(1+\cos^2\theta)}\ . \tag{5}$$

In particular, for right angled scattering and for $\psi=\pi/4$ and $\phi=\pi/8$ this reads

$$\Delta_{\pi/2}=2F/(8A+4B+C+4E)\ . \tag{6}$$

EDEID manifests some striking properties. Namely, when the axes of the incident polarization ellipse coincide with the axes x and y, Δ tends to zero. The same situation occurs for forward and backward scattering irrespective of ψ. In the case of circular polarization—$\phi=\pm\pi/4$—$\Delta=0$, too.

Generally, Δ can take positive as well as negative values, since the signs of the molecular rotational invariants (and primarily that of the invariant F, fundamental for the effect in question) are not determined. Their form is as follows:

$$\begin{aligned}
A&=11a-6b-5c+4(d+d^*)-6e\ ,\\
B&=-5a+4b+8c-5(d+d^*)+4e\ ,\\
C&=8a-12b-10c+15(d+d^*)-12e\ ,\\
D&=-4a+6b-2c+3(d+d^*)+6e\ ,\\
E&=-6a+9b+4c-6(d+d^*)+9e\ ,\\
F&=\tfrac{7}{2}i(d^*-d)\ ,
\end{aligned} \tag{7}$$

where

$$a=b_{\alpha\beta\gamma}b^*_{\alpha\beta\gamma},\quad b=b_{\alpha\beta\gamma}b^*_{\beta\alpha\gamma},\quad c=b_{\alpha\beta\beta}b^*_{\alpha\gamma\gamma}\ ,$$
$$d=b_{\alpha\beta\beta}b^*_{\gamma\gamma\alpha},\quad e=b_{\beta\beta\alpha}b^*_{\gamma\gamma\alpha}\ .$$

Following the decomposition of the tensor $b_{\alpha\beta\gamma}$ into a symmetric part $b^S_{\alpha\beta\gamma}$ with respect to permutation of all its indices and a residual unsymmetric part $b^U_{\alpha\beta\gamma}$, however, still β,γ symmetric, and using their irreducible weights 1,3 and 1,2, respectively,[5] the parameter F can be represented as

$$F=\frac{21i}{4}(b^{1S}_{\alpha\beta\beta}b^{1U*}_{\alpha\gamma\gamma}-b^{1S*}_{\alpha\beta\beta}b^{1U}_{\alpha\gamma\gamma})\ . \tag{8}$$

So, EDEID is related to interference in the scattered amplitudes coming from the symmetric and unsymmetric irreducible tensors of weight 1.

Under nonresonance conditions, the $b_{\alpha\beta\gamma}$ tensor is complex and simultaneously unsymmetric if the wave functions determining the electric dipole transition moments in $b_{\alpha\beta\gamma}$ are complex as in the case of paramagnetic molecules with degenerate ground electronic level.[11]

Under near-resonance conditions $b_{\alpha\beta\gamma}$ is, by definition, unsymmetric, and becomes complex already owing to the presence of half-width damping factors.[12] Significant enhancement in the magnitude of the scattered intensity is then also expected.

In the case of optically active molecules the magnitude of EDEID should be 10^3 times greater than the differential scattering due to higher-order cross electric dipole and quadrupole and magnetic dipole terms.[8]

[1]S. Kielich, Acta Phys. Polonica **26**, 135 (1964); Physica **30**, 1717 (1964).

[2]S. J. Cyvin, J. E. Rauch, and J. C. Decius, J. Chem. Phys. **43**, 4083 (1965); P. D. Maker, Phys. Rev. A **1**, 923 (1970).

[3]R. B. Bersohn, Y. H. Pao, and H. L. Frisch, J. Chem. Phys. **45**, 3184 (1966).

[4]D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. **68**, 2941 (1978).

[5]K. Altmann and G. Strey, J. Raman Spectrosc. **12**, 1 (1982).

[6]R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Lett. **14**, 681 (1965).

[7]L. D. Barron and A. D. Buckingham, Mol. Phys. **20**, 1111 (1971).

[8]D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. **70**, 1027 (1979).

[9]G. Placzek, in *Handbuch der Radiologie,* edited by E. Marx (Akademische Verlagsgesellschaft, Leipzig, 1934), Vol. 6.

[10]S. Kielich, Acta Phys. Polonica **20**, 433 (1961).

[11]S. Woźniak and R. Zawodny, Acta Phys. Polonica A **61**, 175 (1982).

[12]S. Kielich, in *Progress in Optics,* edited by E. Wolf (North-Holland, Amsterdam, 1983), Vol. XX, p. 155.