

REVERSAL RATIO OF DOUBLE-PHOTON SCATTERING BY NONCENTRO-SYMMETRIC MOLECULES

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Received 16 April 1973

We propose that the study of reversal ratios in double-photon scattering (DPhS) offers a new means of direct determination of the anisotropy of nonlinear polarizability in molecules without a centre of symmetry. The fine structure theory of rotational DPhS of circularly polarized light is treated from the viewpoint of angular momentum theory as well as irreducible spherical tensors.

1. Introduction

The theoretical fundamentals of multi-photon elastic and inelastic light scattering [1, 2] along with the earliest observations in liquids with noncentro-symmetric [3, 4] and centro-symmetric [5] molecules have given rise to the modern nonlinear molecular spectroscopy [6, 7]. The present level of laser techniques and highly sensitive methods of photon detection [4] permit the unravelling of fine structure in rotational spectra of double-photon Rayleigh as well as Raman scattering [8–10].

We give an analysis of double-photon scattering (DPhS) by circularly polarized light both classically by cartesian tensors, and by angular momentum theory and irreducible spherical tensors. The former method permits simple calculations of reversal ratios and their relation to the anisotropy of nonlinear polarizability of noncentro-symmetric molecules. The latter permits the fine structure analysis of DPhS spectra due to rotational motion and vibrational–rotational transitions of molecules.

2. Elastic scattering

Consider a molecular gas excited by an intense laser wave with electric field $E(\omega)$ oscillating at the circular frequency ω . The molecular electric dipole moment

induced at doubled frequency 2ω is [1]:

$$m_i^{2\omega} = \frac{1}{4} b_{ijk}^{2\omega} E_j^\omega E_k^\omega, \quad (1)$$

where the third-rank tensor $b_{ijk}^{2\omega}$ defines the second-order nonlinear molecular polarizability, a function of 2ω . In ground states, nonzero tensor elements $b_{ijk}^{2\omega}$ exist only for noncentro-symmetric molecules.

With circularly polarized light propagating along Z , we have for the right sense:

$$E_+^\omega = (E_x^\omega + iE_y^\omega)/\sqrt{2}, \quad (2)$$

whence the induced dipole moments are respectively:

$$m_\pm^{2\omega} = \frac{1}{8} (X_\pm^{2\omega} \mp iY_\pm^{2\omega}) E_+^\omega E_+^\omega / \sqrt{2}. \quad (3)$$

Here, on the assumption of total symmetry of $b_{ijk}^{2\omega}$,

$$X_+^{2\omega} = b_{xxx}^{2\omega} + b_{xyy}^{2\omega}, \quad Y_+^{2\omega} = b_{yyy}^{2\omega} + b_{yxx}^{2\omega}, \quad (4)$$

$$X_-^{2\omega} = b_{xxx}^{2\omega} - 3b_{xyy}^{2\omega}, \quad Y_-^{2\omega} = b_{yyy}^{2\omega} - 3b_{yxx}^{2\omega}. \quad (5)$$

We define the following 2ω scattering intensities for right and left senses:

$$I_\pm^{2\omega} = (N/2c^4) \langle m_\pm^{2\omega} (m_\pm^{2\omega})^* \rangle_\Omega, \quad (6)$$

where $\langle \rangle_\Omega$ denotes averaging over all possible equally

probable orientations Ω of the N molecules. In order to effect the averaging of (6), we transform $b_{ijk}^{2\omega}$ from laboratory ($i, j, k = x, y, z$) to molecular ($\alpha, \beta, \gamma = 1, 2, 3$) coordinates:

$$b_{ijk}^{2\omega} = c_{i\alpha} c_{j\beta} c_{k\gamma} b_{\alpha\beta\gamma}^{2\omega} \quad (7)$$

(directional cosines $c_{i\alpha}$). By (3)–(7), we finally obtain:

$$I_+^{2\omega} = \frac{N}{2100} \left(\frac{2\omega}{c} \right)^4 (14 \alpha_{2\omega}^2 + \beta_{2\omega}^2) I_+^2,$$

$$I_-^{2\omega} = \frac{N}{140} \left(\frac{2\omega}{c} \right)^4 \beta_{2\omega}^2 I_+^2, \quad (8)$$

where we have introduced the following nonlinear, respectively isotropic and anisotropic molecular parameters:

$$\alpha_{2\omega}^2 = b_{\alpha\beta\beta}^{2\omega} b_{\alpha\gamma\gamma}^{2\omega},$$

$$\beta_{2\omega}^2 = \frac{1}{2} (5 b_{\alpha\beta\gamma}^{2\omega} b_{\alpha\beta\gamma}^{2\omega} - 3 b_{\alpha\beta\beta}^{2\omega} b_{\alpha\gamma\gamma}^{2\omega}). \quad (9)$$

By (8), we get the reversal ratio [11] for second-harmonic scattering by a gas of molecules:

$$R_{2\omega} = \frac{I_-^{2\omega}}{I_+^{2\omega}} = \frac{15 \beta_{2\omega}^2}{14 \alpha_{2\omega}^2 + \beta_{2\omega}^2}. \quad (10)$$

In particular for molecular symmetries T_d , D_{3h} and C_{3h} , this yields:

$$\alpha_{2\omega}^2 = 0, \quad \beta_{2\omega}^2 = 15 (b_{123}^{2\omega})^2, \quad (9a)$$

whence $R_{2\omega} = 15$. If, for a given symmetry, the anisotropic parameter vanishes, $\beta_{2\omega} = 0$, then also $R_{2\omega} = 0$. The assumption $\alpha_{2\omega}^2 = \beta_{2\omega}^2$ yields $R_{2\omega} = 1$.

For the molecular symmetries C_{4v} , C_{6v} and $C_{\infty v}$, the nonlinear parameters (9) become [9]:

$$\alpha_{2\omega}^2 = (b_{333}^{2\omega} + 2b_{113}^{2\omega})^2, \quad \beta_{2\omega}^2 = (b_{333}^{2\omega} - 3b_{113}^{2\omega})^2. \quad (9b)$$

Likewise, they can be derived for other molecular symmetries.

3. Rotational fine structure

Consider now a vibrational–rotational transition in the ground electron state giving rise to fine rotational structure of second harmonic scattering.

On denoting by x, y, z the vectors of the cartesian frame X, Y, Z the spherical reference system is defined by spherical vectors of the standard basis:

$$e_{+1} = -\frac{1}{2} i \sqrt{2} (x + iy),$$

$$e_0 = iz,$$

$$e_{-1} = \frac{1}{2} i \sqrt{2} (x - iy). \quad (11)$$

An arbitrary vector $A = xA_x + yA_y + zA_z$ now takes the form

$$A = \sum_q e_q A_{|q|} = \sum_q e_q (-1)^{1-q} A_{-q}, \quad (12)$$

where $q = +1, 0, -1$ and the brackets [] denote a transition to the contrastandard basis.

Starting from the vector components (12) in the spherical basis, we use Clebsch–Gordan coefficients to obtain spherical tensors of successively higher rank in accordance with the formula:

$$T_m^l = \sum_{m_1 m_2} \begin{bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{bmatrix} T_{m_1}^{l_1} T_{m_2}^{l_2}. \quad (13)$$

We assume the phase to be chosen so as to fulfil the relations:

$$T_m^{l*} = (-1)^{l-m} T_{-m}^l. \quad (13a)$$

The above property is unaffected by tensor composition according to (13).

We symmetrize each of the thus described tensors by the genealogical coefficient method [4, 12], obtaining:

$$b_{ijk} = \sum_{lm} c_{ijk}^{lm} B_m^l, \quad (14)$$

Table 1
Coefficients c_{ijk}^{lm}

B_m^l	b_{ijk}									
	b_{000}	b_{+00}	b_{-00}	b_{++0}	b_{--0}	b_{+-0}	b_{+--}	b_{+--}	b_{+++}	b_{---}
B_3^3									1	
B_{-3}^3										1
B_2^3				$1/\sqrt{3}$						
B_{-2}^3					$1/\sqrt{3}$					
B_1^3		$2/\sqrt{15}$					$1/\sqrt{15}$			
B_{-1}^3			$2/\sqrt{15}$					$1/\sqrt{15}$		
B_0^3	$\sqrt{2}/\sqrt{5}$					$1/\sqrt{10}$				
B_1^1		$-1/\sqrt{15}$					$2/\sqrt{15}$			
B_{-1}^1			$-1/\sqrt{15}$					$2/\sqrt{15}$		
B_0^1	$-\sqrt{3}/\sqrt{5}$					$1/\sqrt{15}$				

The transformation coefficients c_{ijk}^{lm} are given in table 1. We define the DPHS intensity tensor [1, 9]:

$$I_{ij}^{\omega_s} = \frac{1}{8} g_I \left(\frac{\omega_s}{c}\right)^4 \frac{N_{vJ\tau}}{2J+1} \times \sum_{MM'} \langle v'J'\tau'M' | b_{i[k][m]}^{\omega_s} | vJ\tau M \rangle \times \langle v'J'\tau'M' | b_{j[l][n]}^{\omega_s} | vJ\tau M \rangle^* I_{kl} I_{mn} \quad (15)$$

$I_{kl} = \frac{1}{2} E_k E_l^*$ is the incident light intensity, $N_{vJ\tau}$ the number of molecules in the initial state, g_I the nuclear statistical weight factor, $\omega_s = 2\omega \pm \omega_m$ the scattered frequency, and ω_m are molecular frequencies. The quantum numbers v define the vibrational state and $JM\tau$ the rotational state. For symmetric top molecules $\tau = K$, and for linear ones moreover $K = 0$.

At incident E_+^{ω} light, we get by (14) and (15) the following right and left circularly polarized scattered light components:

$$I_+^{\omega_s} = \frac{1}{2520} g_I N_{vJK} \left(\frac{\omega_s}{c}\right)^4 (2J'+1) \times \left\{ 28 \binom{J' 1 J}{-K' q K}^2 |\tilde{B}_q^1|^2 + 3 \binom{J' 3 J}{-K r K}^2 |\tilde{B}_r^3|^2 \right\} I_+^2, \\ I_-^{\omega_s} = \frac{1}{56} g_I N_{vJK} \left(\frac{\omega_s}{c}\right)^4 (2J'+1) \binom{J' 3 J}{-K' r K}^2 |\tilde{B}_r^3|^2 I_+^2 \quad (16)$$

The tilde in \tilde{B}_m^l states that the spherical tensor is expressed in coordinates rigidly attached to the molecule. The coefficients $\binom{J_1 J_2 J_3}{M_1 M_2 M_3}$ are Wigner 3j-symbols.

Performing in (16) a summation over all possible quantum transitions $JK \rightarrow J'K'$, we obtain for the total intensity formulas (8), where 2ω has to be replaced by $\omega_s = 2\omega \pm \omega_m$, and the nonlinear parameters in (9) by:

$$\alpha_{\omega_s}^2 = \frac{5}{3} \sum_q |\tilde{B}_q^1|^2, \quad \beta_{\omega_s}^2 = \frac{5}{2} \sum_r |\tilde{B}_r^3|^2 \quad (17)$$

For elastic scattering, these parameters reduce to the form (9) as a result of classical averaging. For inelastic scattering, on the other hand, we have:

$$\sum_q |\tilde{B}_q^l|^2 = \sum_q \left| \left(\frac{\partial B_q^l}{\partial Q_m} \right)_0 \langle v'_m | Q_m | v_m \rangle \right|^2, \quad (17a)$$

where Q_m is a normal coordinate of the m th molecular vibration.

Linear molecules admit transitions with $\Delta J = \pm 1, \pm 3$, and the Wigner coefficients in (16) are simple functions of the quantum number J :

for $\Delta J = +3$:

$$(2J'+1) \binom{J' 3 J}{0 0 0}^2 = \frac{5}{2} \frac{(J+1)(J+2)(J+3)}{(2J+1)(2J+3)(2J+5)},$$

for $\Delta J = +1$:

$$(2J' + 1) \begin{pmatrix} J' & 1 & J \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{J+1}{2J+1},$$

$$(2J' + 1) \begin{pmatrix} J' & 3 & J \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{3}{2} \frac{J(J+1)(J+2)}{(2J-1)(2J+1)(2J+5)}.$$

When considering transitions $\Delta J = -1, -3$, one has to replace J by $J-1$ above.

For T_d -symmetric molecules, with energy independent of the quantum number K , the intensity of the $J \rightarrow J'$ band is obtained after summation over all possible K , with the selection rule $\Delta K = \pm 2$. Eq. (16) yields:

$$I_{-}^{\omega_s} = 15 I_{+}^{\omega_s} = \frac{3}{196} g_I N_{vJ} b_{123}^2 \left(\frac{\omega_s}{c}\right)^4 \frac{2J'+1}{2J+1}. \quad (16a)$$

4. Conclusions

From the above we conclude that the numerical value of the reversal ratio (10) in DPhS lies within the range:

$$0 \leq R_{2\omega} \leq 15, \quad (18)$$

where the lower limit 0 corresponds to weak nonlinear anisotropy ($\beta_{2\omega} \ll \alpha_{2\omega}$) or none at all ($\beta_{2\omega} = 0$) whereas the upper limit 15 is attained in molecules with very large nonlinear anisotropy ($\beta_{2\omega} \gg \alpha_{2\omega}$, or $\alpha_{2\omega} = 0$).

For comparison, in single-photon scattering we have [11]:

$$0 \leq R_{\omega} = 6 \beta_{\omega}^2 / (3 \alpha_{\omega}^2 + \beta_{\omega}^2) \leq 6, \quad (19)$$

with isotropic and anisotropic parameters of the linear polarizability tensor $a_{\alpha\beta}^{\omega}$ in the form:

$$\alpha_{\omega}^2 = a_{\alpha\alpha}^{\omega} a_{\beta\beta}^{\omega}, \quad \beta_{\omega}^2 = \frac{1}{2} (3 a_{\alpha\beta}^{\omega} a_{\alpha\beta}^{\omega} - a_{\alpha\alpha}^{\omega} a_{\beta\beta}^{\omega}). \quad (20)$$

Formula (18), considered against the background of (19), shows that experimental studies of the reversal ratio of DPhS will provide an excellent extension of existing R_{ω} studies. Their advantage over studies based on the depolarisation ratio [1-5, 9]

$$\frac{1}{9} \leq D_{2\omega}^v = \frac{7 \alpha_{2\omega}^2 + 8 \beta_{2\omega}^2}{63 \alpha_{2\omega}^2 + 12 \beta_{2\omega}^2} \leq \frac{2}{3} \quad (21)$$

resides in the fact that the reversal ratio permits the direct determination of the anisotropy of nonlinear molecular polarizability $\beta_{2\omega}$, as is seen from eqs. (8) and (10).

The above-proposed methods can be of use in calculating the ellipticity [13] and angular dependence [14] of nonlinear light scattering.

References

- [1] S. Kielich, *Physica* 30 (1964) 1717; *Acta Phys. Polonica* 26 (1964) 135.
- [2] S.J. Cyvin, J.E. Rauch and J.C. Decius, *J. Chem. Phys.* 43 (1965) 4083.
- [3] R.W. Terhune, P.D. Maker and C.M. Savage, *Phys. Rev. Letters* 14 (1965) 681.
- [4] P.D. Maker, *Phys. Rev.* 1 (1970) 929.
- [5] S. Kielich, J.R. Lalanne and F.B. Martin, *Phys. Rev. Letters* 26 (1971) 1295; *Acta Phys. Polonica* A41 (1972) 479.
- [6] J.F. Verdick, S.H. Peterson, C.M. Savage and P.D. Maker, *Chem. Phys. Letters* 7 (1970) 219.
- [7] D.A. Long and L. Stanton, *Proc. Roy. Soc. (London)* 318A (1970) 441.
- [8] P.D. Maker, in: *Physics of Quantum Electronics* (Mc Graw-Hill, New York, 1966) p. 60.
- [9] T. Bancewicz, Z. Ożgo and S. Kielich, *J. Raman Spectroscopy* 1 (1973), in press.
- [10] F.H.M. Faisal and N.K. Rahman, *Nuovo Cimento* 13B (1973) 114.
- [11] G. Placzek, *Handbuch der Radiologie* (Ed. E. Marx, Akad. Verlagsges., Leipzig, 1934), Vol. 6, part 2, p. 205.
- [12] H.A. Jahn and H. van Wieringen, *Proc. Roy. Soc. (London)* A209 (1951) 502.
- [13] L. Stanton, *Mol. Phys.* 23 (1972) 601; D.A. Long and L. Stanton, *Mol. Phys.* 24 (1972) 57.
- [14] S. Kielich and M. Kozierowski, *Optics Commun.* 4 (1972) 395.