

POLARIZATION STATE AND ANGULAR DEPENDENCE
OF NONLINEAR MOLECULAR LIGHT SCATTERING
DERIVED BY RACAHA ALGEBRA

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Synopsis

Methods of Racah algebra are applied to describe quantitatively second-harmonic light scattering for arbitrary polarization of incident and scattered photons and arbitrary conditions of observation. The general formula derived for the intensity tensor of second-harmonic scattering is applied to calculate the angular dependence of depolarization ratios and reversal ratios. The measurement of these quantities will help to determine numerically the tensor elements of second-order nonlinear polarizability for non-centrosymmetric molecules in the ground state.

1. *Introduction.* Hitherto, in nonlinear light-scattering work^{1,2}), experimenters measured the vertical and horizontal components at observation perpendicular to the incident beam. It would appear that there is an urgent need for nonlinear scattering-intensity measurements *vs.* the angle of observation and for measurements of the reversal ratio³) in addition to the depolarization ratio.

The angular dependence of elastic harmonic scattering has previously been analyzed theoretically by simple classical methods^{4,5}). In this paper, it is our aim to describe the problem by the method of Racah algebra^{6,7}). This permits us to express advantageously the intensity tensor of scattered light in a form valid for arbitrary states of polarization (*e.g.* linear, circular, elliptic) of the incident and scattered photons and thus permits the calculation of measurable quantities, like active cross sections, depolarization ratios, reversal ratios, and so forth. The methods of Racah algebra, moreover, permit the quantitative description of inelastic higher-harmonic scattering and the study of its spectral fine structure (in particular rotational)⁸⁻¹⁰). For obvious reasons of simplicity, we shall consider here only second-harmonic scattering by the individual non-centrosymmetric molecules of an optically transparent gas.

2. *Theory.* It is our aim to find the intensity of nonlinearly scattered light for arbitrary angles of observation and diverse states of polarization of the incident beam. Three systems of reference will be used: (i) the system of laboratory coordinates XYZ , related to the incident beam in such a manner that the Z axis points in the direction of its propagation; (ii) the system of laboratory coordinates $\bar{X}\bar{Y}\bar{Z}$, in which the \bar{Z} axis points in the direction of observation of the scattered light; and (iii) the molecular coordinate system xyz rigidly attached to the scattering molecule.

The mutual orientation of these reference systems will be described in terms of Euler angles, after ref. 6; that of the system $\bar{X}\bar{Y}\bar{Z}$ with respect to XYZ will be given by angles $\Omega = \alpha, \beta, \gamma$, and that of the molecular system xyz with respect to XYZ by angles $\Omega_m = \alpha_m, \beta_m, \gamma_m$.

The properties of the elastically scattered light are inherent in the scattering tensor⁴):

$$I_{ij} = (N/4\pi c^3) \langle \ddot{m}_i(t) \ddot{m}_j(t) \rangle_{\Omega_m, t}, \quad (1)$$

where the symbol $\langle \rangle_{\Omega_m, t}$ stands for the appropriate time and statistical-orientational averaging, m_i is the i th component of the electric-dipole moment induced in the molecule by a field of strength $E(t) = E_0 \cos \omega t$ and N is the number of molecules of the sample. At high light intensity the induced moment is nonlinear in the field strength and can be expanded in a series of harmonic contributions¹¹):

$$m_i(t) = a_{ij}^{\omega} E_{0j} \cos \omega t + \frac{1}{4} b_{ijk}^{2\omega} E_{0j} E_{0k} \cos 2\omega t + \frac{1}{24} c_{ijkl}^{3\omega} E_{0j} E_{0k} E_{0l} \cos 3\omega t + \dots, \quad (2)$$

where a_{ij}^{ω} is the tensor of linear molecular polarizability at the fundamental vibration frequency ω ; $b_{ijk}^{2\omega}$ is the tensor of nonlinear polarizability of the second order at the second-harmonic frequency 2ω ; and $c_{ijkl}^{3\omega}$ is the tensor of third-order nonlinear polarizability at the third-harmonic frequency 3ω .

Second-harmonic scattering is related to the second term of the expansion (2) and depends on the third-rank tensor $b_{ijk}^{2\omega}$ with nonzero elements for molecules without a centre of symmetry only when in the ground state¹⁰). We shall not consider third-harmonic scattering⁵), given by the tensor $c_{ijkl}^{3\omega}$ with nonvanishing elements in all molecular symmetries^{12,13}).

Our method of calculating the intensity (1) will rely on Racah algebra and we have to express all tensorial quantities by spherical tensors. For the dipole-moment vector $\mathbf{m} (m_x, m_y, m_z)$ we have:

$$M_1^1 = -\frac{i}{\sqrt{2}} (m_x + im_y), \quad M_{-1}^1 = \frac{i}{\sqrt{2}} (m_x - im_y), \quad M_0^1 = im_z. \quad (3)$$

The inverse transformation is found easily; we write it as follows:

$$m_i = \sum_m C_i^m M_m^1. \tag{4}$$

For the scattering tensor I_{ij} , calculated with respect to the system of reference $\bar{X}\bar{Y}\bar{Z}$, we have:

$$I_{ij} = \frac{N}{4\pi c^3} \left\langle \sum_{mn} C_i^m C_j^{n*} \ddot{M}_m^1 \ddot{M}_n^{1*} \right\rangle_{\Omega_m, t}; \tag{5}$$

this, upon transformation, becomes:

$$I_{ij} = (N/4\pi c^3) \left\langle \sum_{mn} \sum_{m'n'} C_i^m C_j^{n*} \dot{M}_m^1 \dot{M}_{n'}^{1*} D_{m'm}^1(\Omega) D_{n'n}^1(\Omega)^* \right\rangle_{\Omega_m, t}, \tag{6}$$

where the $D_{m'm}^1(\Omega)$ are Wigner functions.

In our study of second-harmonic scattering, we shall consider only that part of the dipole moment (2):

$$m_i^{2\omega}(t) = \frac{1}{4} b_{ijk}^{2\omega} E_{0j} E_{0k} \cos 2\omega t,$$

which, expressed in spherical tensors, takes the form⁸⁾:

$$M_{m'}^1(2\omega) = \frac{1}{4} \sum_{lpa} (-1)^{r+a} \begin{pmatrix} p & l & 1 \\ -q & -r & m' \end{pmatrix} B_q^{(l,p)} E_r^l \cos 2\omega t \left(-\sqrt{2p+1} \right). \tag{7}$$

Above, $B_q^{(l,p)}$ is the spherical tensor of nonlinear polarizability and E_r^l the spherical tensor arising from the second-rank cartesian tensor $E_{ij} = E_{0i} E_{0j}$.

On assuming that the nonlinear polarizability tensor is totally symmetric and on denoting it by B_q^p , we obtain the relation:

$$B_q^{(l,p)} = A_p^l B_q^p, \tag{8}$$

where the A_p^l are coefficients of fractional parentage amounting to: $A_1^0 = \frac{2}{3}$, $A_1^2 = (5/9)^{\frac{1}{2}}$, $A_3^2 = 1$. Averaging over all possible orientations of the molecules in space is performed in accordance with the formula:

$$\langle B_q^p B_v^{u*} \rangle_{\Omega_m} = [1/(2p+1)] \delta_{pv} \delta_{qv} \sum_{q'} |\tilde{B}_{q'}^p|^2. \tag{9}$$

The tilde denotes that the quantity is defined in the molecular reference system xyz . For brevity, we write the molecular parameter $\sum_{q'} |\tilde{B}_{q'}^p|^2$ as $\tilde{B}_p^{2\omega}$. Next, using

the equality⁶⁾:

$$D_{m' m}^{j_1 j_2 j} D_{n' n}^{j_1 j_2 j} = \sum_j (2j + 1) \begin{pmatrix} j_1 j_2 j \\ m' n' -k' \end{pmatrix} \begin{pmatrix} j_1 j_2 j \\ m n -k \end{pmatrix} D_{-k', -k}^{j*}, \quad (10)$$

and carrying out the summation over m', n', q and time-averaging, we finally obtain from eq. (6) for second-harmonic scattering:

$$I_{\alpha\beta}^{2\omega} = \frac{cN}{128\pi} \left(\frac{2\omega}{c} \right)^4 \sum_{\substack{mnrw \\ pjlt}} (-1)^{w+n+k+k'+j+p} \tilde{B}_p^{2\omega} |A_p^l|^2 C_\alpha^m C_\beta^{n*} \\ \times (2j + 1) \begin{pmatrix} 1 & 1 & j \\ m & n & -k \end{pmatrix} \begin{pmatrix} l & t & j \\ r & w & -k' \end{pmatrix} \begin{Bmatrix} l & 1 & p \\ 1 & t & j \end{Bmatrix} D_{k'k}^j(\Omega) E_r^l E_w^{t*}. \quad (11)$$

Above, parentheses and braces denote, respectively, $3j$ and $6j$ symbols^{6,7)}.

3. *Depolarization ratio and reversal ratio.* The general scattered-light intensity formula (11) derived above will now be written out in explicit form for three particular cases: 1) for that of incident light linearly polarized along X ; 2) along Y ; and 3) for right-circularly polarized incident light.

For linearly polarized light, the scattering-tensor elements take the values:

$$I_{XX}^{2\omega} \begin{pmatrix} X \\ Y \end{pmatrix} = \frac{\pi N}{1890c} \left(\frac{2\omega}{c} \right)^4 \\ \times I_0^2 [77\tilde{B}_1^{2\omega} + 42\tilde{B}_3^{2\omega} + (28\tilde{B}_1^{2\omega} + 3\tilde{B}_3^{2\omega}) (\phi_{-0} \mp 3\phi_{-2})], \quad (12a)$$

$$I_{YY}^{2\omega} \begin{pmatrix} X \\ Y \end{pmatrix} = \frac{\pi N}{1890c} \left(\frac{2\omega}{c} \right)^4 \\ \times I_0^2 [77\tilde{B}_1^{2\omega} + 42\tilde{B}_3^{2\omega} + (28\tilde{B}_1^{2\omega} + 3\tilde{B}_3^{2\omega}) (\phi_{+0} \mp 3\phi_{+2})], \quad (12b)$$

where $I_0 = (c/8\pi) E_0^2$ is the incident-light intensity. The upper sign refers to the experimental situation when light of intensity I_0 is polarized parallel to X . The lower sign refers to polarization parallel to Y .

The angular distribution functions are of the form:

$$\phi_{-0} = 1 + 3 \cos^2 \alpha (\cos^2 \beta - 1), \\ \phi_{+0} = 1 + 3 \sin^2 \alpha (\cos^2 \beta - 1), \quad (13) \\ \phi_{\mp 2} = \frac{1}{2} (1 - \cos^2 \beta) \cos 2\alpha \\ \mp \frac{1}{2} [(1 + \cos^2 \beta) \cos 2\alpha \cos 2\gamma - 2 \cos \beta \sin 2\alpha \sin 2\gamma].$$

In particular, if $\alpha = \gamma = 0$, they simplify to:

$$\phi_{+0} = \phi_{+2} = 1, \quad \phi_{-0} = (3 \cos^2 \beta - 2), \quad \phi_{-2} = -\cos^2 \beta, \quad (14)$$

leading to the following values of the tensor elements $I_{ij}^{2\omega}$:

$$\begin{aligned} I_{XX}^{2\omega}(X) &= (\pi N/630c) (2\omega/c)^4 \\ &\quad \times I_0^2 [7\tilde{B}_1^{2\omega} + 12\tilde{B}_3^{2\omega} + (56\tilde{B}_1^{2\omega} + 6\tilde{B}_3^{2\omega}) \cos^2 \beta], \\ I_{YY}^{2\omega}(X) &= I_{XX}^{2\omega}(Y) = (\pi N/630c) (2\omega/c)^4 I_0^2 (7\tilde{B}_1^{2\omega} + 12\tilde{B}_3^{2\omega}), \\ I_{YY}^{2\omega}(Y) &= (\pi N/70c) (2\omega/c)^4 I_0^2 (7\tilde{B}_1^{2\omega} + 2\tilde{B}_3^{2\omega}). \end{aligned} \quad (15)$$

For incident right-circularly polarized light (+) of the intensity $I_+ = (c/8\pi) E_+^2$, we have:

$$\begin{aligned} I_{\pm\pm}^{2\omega}(+) &= \frac{\pi N}{1260c} \left(\frac{2\omega}{c} \right)^4 I_+^2 [14\tilde{B}_1^{2\omega} (1 \pm 2 \cos \beta + \cos^2 \beta) \\ &\quad + 3\tilde{B}_3^{2\omega} (13 \mp 14 \cos \beta + 3 \cos^2 \beta)]. \end{aligned} \quad (16)$$

Knowledge of the tensor elements of second-harmonic light scattering permits the calculation of two experimentally highly significant parameters, namely the depolarization ratio $D^{2\omega}$ and reversal ratio $R^{2\omega}$, defined as follows⁵:

$$D_X^{2\omega} = \frac{I_{YY}^{2\omega}(X)}{I_{XX}^{2\omega}(X)}, \quad D_Y^{2\omega} = \frac{I_{XX}^{2\omega}(Y)}{I_{YY}^{2\omega}(Y)}, \quad R^{2\omega} = \frac{I_{+-}^{2\omega}(+)}{I_{++}^{2\omega}(+)}. \quad (17)$$

From eqs. (15) it can be seen that $D_X^{2\omega}$ does not depend on the angle β and amounts to⁹):

$$D_Y^{2\omega} = \frac{1}{9} \frac{7\tilde{B}_1^{2\omega} + 12\tilde{B}_3^{2\omega}}{7\tilde{B}_1^{2\omega} + 2\tilde{B}_3^{2\omega}}; \quad (18)$$

whereas $D_X^{2\omega}$ is the following function of β :

$$D_X^{2\omega}(\beta) = \frac{7\tilde{B}_1^{2\omega} + 12\tilde{B}_3^{2\omega}}{7\tilde{B}_1^{2\omega} + 12\tilde{B}_3^{2\omega} + (56\tilde{B}_1^{2\omega} + 6\tilde{B}_3^{2\omega}) \cos^2 \beta}. \quad (19)$$

The reversal ratio $R^{2\omega}$ in general always depends only on β , and according to (16) amounts to:

$$R^{2\omega}(\beta) = \frac{14\tilde{B}_1^{2\omega} (1 - \cos \beta)^2 + 3\tilde{B}_3^{2\omega} (13 + 14 \cos \beta + 3 \cos^2 \beta)}{14\tilde{B}_1^{2\omega} (1 + \cos \beta)^2 + 3\tilde{B}_3^{2\omega} (13 - 14 \cos \beta + 3 \cos^2 \beta)}. \quad (20)$$

For $\beta = \frac{1}{2}\pi$, one has the equality $D_X^2(\frac{1}{2}\pi) = R^{2\omega}(\frac{1}{2}\pi) = 1$. For $\beta = 0$, the reversal ratio $R^{2\omega}(0)$ takes the value^{3,5)}:

$$R^{2\omega}(0) = \frac{45\tilde{B}_3^{2\omega}}{3\tilde{B}_3^{2\omega} + 28\tilde{B}_1^{2\omega}}, \quad \text{whereas} \quad D_X^{2\omega}(0) = D_Y^{2\omega}. \quad (21)$$

From eqs. (18) and (19), we derive the following relation:

$$D_Y^{2\omega} = \frac{R^{2\omega}(0) + 1}{R^{2\omega}(0) + 9}. \quad (22)$$

4. *Applications and conclusions.* According to eqs. (18)–(21), the measurement of the depolarization ratio and reversal ratio of second-harmonic light scattering permits us to determine the two molecular parameters $\tilde{B}_1^{2\omega}$ and $\tilde{B}_3^{2\omega}$ which, in the case of symmetric scattering, are expressed as follows by the nonlinear polarizability tensor $b_{\alpha\beta\gamma}^{2\omega}$ ³⁾:

$$\tilde{B}_1^{2\omega} = \frac{3}{2}\alpha_{2\omega}^2, \quad \tilde{B}_3^{2\omega} = \frac{2}{3}\beta_{2\omega}^2, \quad (23)$$

where the quantities¹⁴⁾

$$\alpha_{2\omega}^2 = b_{\alpha\beta\beta}^{2\omega} b_{\alpha\gamma\gamma}^{2\omega}, \quad (24)$$

$$\beta_{2\omega}^2 = \frac{1}{2}(5b_{\alpha\beta\gamma}^{2\omega} b_{\alpha\beta\gamma}^{2\omega} - 3b_{\alpha\beta\beta}^{2\omega} b_{\alpha\gamma\gamma}^{2\omega}), \quad (25)$$

define, respectively, isotropic and anisotropic second-harmonic light scattering.

For linear molecules (point group $C_{\infty v}$), we get by (24) and (25) the parameters:

$$\alpha_{2\omega} = b_{333}^{2\omega} + 2b_{113}^{2\omega}, \quad (24a)$$

$$\beta_{2\omega} = b_{333}^{2\omega} - 3b_{113}^{2\omega}, \quad (25a)$$

defining, respectively, isotropic and anisotropic nonlinear electric polarizability of axially symmetric molecules.

It is of interest to consider separately the case of tetrahedral molecules (point groups T and T_d), for which:

$$\alpha_{2\omega}^2 = 0, \quad (24b)$$

$$\beta_{2\omega}^2 = 15(b_{123}^{2\omega})^2, \quad (25b)$$

so that the reversal ratio reduces to the form:

$$R_{\text{anis}}^{2\omega}(\beta) = \frac{13 + 14 \cos \beta + 3 \cos^2 \beta}{13 - 14 \cos \beta + 3 \cos^2 \beta}, \quad (26)$$

defining anisotropic light scattering only. In particular, if observation is performed at the scattering angle $\beta = 0^\circ$, eq. (26) yields the maximal value of the reversal ratio, namely

$$R_{\text{anis}}^{2\omega}(0) = 15. \quad (26a)$$

If anisotropic scattering is absent, $\tilde{B}_3^{2\omega} = 0$, eq. (20) yields for isotropic second-harmonic scattering:

$$R_{\text{is}}^{2\omega}(\beta) = \left(\frac{1 - \cos \beta}{1 + \cos \beta} \right)^2 = \text{tg}^4 \frac{\beta}{2}. \quad (20a)$$

This result coincides with the one for usual scattering at the fundamental frequency ω^6 .

Similarly, for purely isotropic scattering ($\tilde{B}_3^{2\omega} = 0$) the depolarization ratios of second-harmonic scattering (18) and (19) become:

$$D_Y^{2\omega} = \frac{1}{9}, \quad (18a)$$

$$D_X^{2\omega}(\beta) = 1/(1 + 8 \cos^2 \beta), \quad (19a)$$

whereas for purely anisotropic scattering ($\tilde{B}_1^{2\omega} = 0$):

$$D_Y^{2\omega} = \frac{2}{3}, \quad (18b)$$

$$D_X^{2\omega}(\beta) = 2/(2 + \cos^2 \beta). \quad (19b)$$

One is hence easily convinced that complete measurements of the angular dependence of second-harmonic scattering will provide supplementary information concerning the elements of the nonlinear polarizability tensor $b_{\alpha\beta\gamma}^{2\omega}$ of non-centrosymmetric molecules.

In addition to the intensity scattered into an arbitrarily chosen direction of observation, the method based on angular-momentum theory and spherical tensors discloses naturally the rotational structure of the spectrum^{9,10}. For linear as well as symmetric top molecules, we can thus find the intensity of a rotational line. This is related to a transition of the molecule from the state JK to the state $J'K'$ in the act of light scattering at frequency $2\omega \pm \omega_{\text{rot}}$ by replacing the parameter

$\tilde{B}_p^{2\omega}$ by the expression $\bar{\tilde{B}}_p$, which amounts to¹⁵⁾:

$$\bar{\tilde{B}}_p = (2J + 1) \begin{pmatrix} J' & p & J \\ -K' & q' & K \end{pmatrix}^2 |\tilde{B}_{q'}^p|^2, \quad (27)$$

and on replacing N by N_{JK} (the number of molecules in the initial state JK). The parameters $|B_q^p|^2$, which are functions of the cartesian elements of the nonlinear polarizability tensor $b_{\alpha\beta\gamma}^{2\omega}$, are to be found in refs. 9 and 10.

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