

INFLUENCE OF A STRONG OPTICAL ELECTRIC FIELD ON THE MOLECULAR SCATTERING OF LIGHT

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Synopsis

Quantum-mechanical formalism is used to show that under the effect of the electric field of an intense light beam e.g. from a laser, of frequency ω_2 , acting on the medium, scattered light can contain – in addition to Raman scattering with the fundamental frequency ω_1 augmented or diminished by the transition frequencies ω_{kl} – some slight nonlinear and noncoherent scattering. If the molecules have no centre of inversion (e.g. one presenting symmetry of the point groups D_{3h} , C_{3v} , $C_{\infty v}$, T_d , etc.), this latter additional light scattering occurs with frequencies $\omega_1 \pm \omega_2 \pm \omega_{kl}$. For molecules having a centre of inversion, one obtains only very weak scattering with frequencies $\omega_1 \pm 2\omega_2 \pm \omega_{kl}$. The numerical discussion is restricted to the classical case only, when it is possible to make a simple estimation of how the degree of depolarization of light scattered in gases varies under the effect of the intense optical electric field.

Introduction. Investigation, experimental and theoretical, of various nonlinear optical effects allows among other things to gain better insight into the behaviour of atoms and molecules in electric fields of an intensity unattainable but several years ago and now accessible to experimenters with light beams from a laser. This explains the increasingly great interest on the part of physicists in the nonlinear interactions of matter with light from lasers. Recently the subject has been dealt with theoretically by several authors, of whom we shall quote Armstrong *e.a.*¹⁾, as well as Franken and Ward²⁾, who also give a review of the results relating to nonlinear optical phenomena and optical-harmonics generation up to August 1962.

Nonlinear interaction between atoms or molecules and an optical electric field is apparent specifically in the effect of light scattering in the presence of the very strong electric field of another light beam incident on the scattering medium. The possibility of intense light (e.g. from a laser) influencing the Rayleigh scattering of light in gases has already been discussed for some special cases, namely for gases consisting of isotropic nonlinearly polarizable molecules³⁾, for gases possessing axially symmetric and linearly polarizable molecules⁴⁾ and for gases of nonlinearly polarizable molecules without a centre of inversion⁵⁾. In this note we shall present in brief a formal, quantum-mechanical, extension of the above problem to embrace

both coherent and noncoherent light scattering in gases. Also, the depolarization ratio of the scattered light is discussed on a classical level for certain simpler cases.

Light scattering tensor for the transition $k \rightarrow l$. We consider a scattering system subjected to the optical electric field $2\mathbf{E}_1 = \mathbf{E}_1^+ e^{i\omega_1 t} + \mathbf{E}_1^- e^{-i\omega_1 t}$ of small intensity and frequency ω_1 and another optical electric field $2\mathbf{E}_2 = \mathbf{E}_2^+ e^{i\omega_2 t} + \mathbf{E}_2^- e^{-i\omega_2 t}$ of very great strength, and frequency ω_2 . Let \mathbf{P}_{kl} be the electric dipole moment induced in the scattering system by the electric field \mathbf{E}_1 in the presence of the strong electric field \mathbf{E}_2 ; as the system goes over from quantum state k to quantum state l , the $\alpha\beta$ -component of the tensor of scattered light is defined as

$$I_{\alpha\beta}^{kl} = \overline{\langle \mathbf{P}_{\alpha kl} \mathbf{P}_{\beta lk} \rangle_{E_1, E_2, -t}} \quad (1)$$

where the brackets stand for the statistical average in the presence of the electric fields E_1 and E_2 and $-t$ denotes time averaging.

Since, in the case considered here, the induced dipole moment \mathbf{P}_{kl} is linear in \mathbf{E}_1 and nonlinear in \mathbf{E}_2 , the scattering tensor of (1) can be expressed as follows, if $\omega_1 \neq \omega_2 \neq 0$,

$$I_{\alpha\beta}^{kl} = I_{\alpha\beta}^{\omega_{kl} \pm \omega_1} + I_{\alpha\beta}^{\omega_{kl} \pm \omega_1 \pm \omega_2} + I_{\alpha\beta}^{\omega_{kl} \pm \omega_1 \pm 2\omega_2} + \dots, \quad (2)$$

where

$$I_{\alpha\beta}^{\omega_{kl} \pm \omega_1} = \frac{1}{2}(\omega_{kl} \pm \omega_1)^4 \langle A_{\alpha\gamma}^{kl}(\pm \omega_1) A_{\beta\delta}^{kl}(\mp \omega_1) \rangle_{E_2} E_{1\gamma}^{\pm} E_{1\delta}^{\mp} \quad (3)$$

determines the normal Raman scattering discussed e.g. in the monograph of Bhagavantam ⁶). The explicit form of the linear polarizability tensor of the scattering system $A_{\alpha\beta}^{kl}$ results immediately from the well known Kramers-Heisenberg theory ⁷).

The subsequent scattering tensors in eq. (2) are of the form

$$I_{\alpha\beta}^{\omega_{kl} \pm \omega_1 \pm \omega_2} = \frac{1}{8}(\omega_{kl} \pm \omega_1 \pm \omega_2)^4 \cdot \langle B_{\alpha\gamma\epsilon}^{kl}(\pm \omega_1, \pm \omega_2) B_{\beta\delta\eta}^{kl}(\mp \omega_1, \mp \omega_2) \rangle_{E_2} E_{1\gamma}^{\pm} E_{1\delta}^{\mp} E_{2\epsilon}^{\pm} E_{2\eta}^{\mp}, \quad (4)$$

$$I_{\alpha\beta}^{\omega_{kl} \pm \omega_1 \pm 2\omega_2} = \frac{1}{128}(\omega_{kl} \pm \omega_1 \pm 2\omega_2)^4 \cdot \langle C_{\alpha\gamma\epsilon\eta}^{kl}(\pm \omega_1, \pm 2\omega_2) C_{\beta\delta\theta\chi}^{kl}(\mp \omega_1, \mp 2\omega_2) \rangle_{E_2} E_{1\gamma}^{\pm} E_{1\delta}^{\mp} E_{2\epsilon}^{\pm} E_{2\eta}^{\mp} E_{2\theta}^{\pm} E_{2\chi}^{\mp} \quad (5)$$

and determine the influence of the strong optical electric field \mathbf{E}_2 on noncoherent light scattering.

The tensors $B_{\alpha\beta\gamma}^{kl}$ and $C_{\alpha\beta\gamma\delta}^{kl}$ characterizing the nonlinear polarization of the scattering system due to a strong optical electric field \mathbf{E}_2 and their quantum mechanical expressions can be obtained by Dirac's perturbation method up to the third-order approximation. Since the explicit expressions of $B_{kl}^{\alpha\beta\gamma}$ and $C_{\alpha\beta\gamma\delta}^{kl}$ are highly involved, we shall refrain from writing them here. For

the case of coherent scattering the explicit quantum mechanical calculations are performed by Armstrong *e.a.*¹⁾ for the general case of two or three light waves and by Franken and Ward²⁾ for certain special cases (see also refs. 5 and 8).

It is seen from the foregoing expressions that the strong optical field of frequency ω_2 enforces additional (with regard to normal Raman scattering) noncoherent scattering of light with the new frequencies $\omega_{kl} \pm \omega_1 \pm \omega_2$, $\omega_{kl} \pm \omega_1 \pm 2\omega_2$, $\omega_{kl} \pm \omega_1 \mp \omega_2$, The fundamental oscillations of frequencies $\pm \omega_1$ and the transition frequencies ω_{kl} are increased or diminished in the nonlinearly scattered light by the amounts ω_2 and $2\omega_2$ in various combinations. The scattering tensors with harmonic frequencies $\omega_1 \pm \omega_2$ appear only for molecules without a centre of inversion, whereas tensors with frequencies $\omega_1 \pm 2\omega_2$ exist in all other cases of molecules of arbitrary symmetry, including optically isotropic molecules.

Depolarization ratio in the classical case. For the sake of simplicity we now apply the scattering tensor of eq. (2) to the evaluation of the depolarization ratio in the purely classical case, i.e. when the quantum system reverts to its ground-state $g = k = l$. To this purpose, we go over from the tensors $A_{\alpha\beta}^{kl}$, $B_{\alpha\beta\gamma}^{kl}$, and $C_{\alpha\beta\gamma\delta}^{kl}$ to the tensors $a_{\alpha\beta}$, $b_{\alpha\beta\gamma}$ and $c_{\alpha\beta\gamma\delta}$ related with the molecular coordinate system and characterizing the classical properties of the isolated scattering molecules. In this case the quantum statistical averaging in eqs. (3)–(5) can be replaced by averaging over all classical orientations of the scattering molecules with respect to the reference system XYZ .

Let the primary light beam propagate in the Y axis direction with its electric vector \mathbf{E}_1 oscillating in the XZ plane at an angle ψ to the plane of observation (XY plane) in which the scattered light is observed at the angle ϑ with respect to the direction of incidence (Y axis). We also assume for simplicity that the electric vector \mathbf{E}_2 of the strong field oscillates perpendicularly to the plane of observation. Since the depolarization ratio is defined as the ratio of the $I_y = I_{\alpha\beta\gamma\alpha\gamma\beta}$ and $I_z = I_{\alpha\beta\gamma\alpha z\beta}$ scattered intensity components oscillating in the directions of \mathbf{y} and \mathbf{z} , respectively, we obtain by eqs. (3) and (5) and with the above assumptions for the scattering system of N non interacting and isotropically polarizable molecules

$$\frac{D^\pm - D_0}{D_0} = -\frac{1}{64} \left(\frac{\omega_1 \pm 2\omega_2}{\omega_1} \right)^4 \left(\frac{c_{\parallel}^2 - c_{\perp}^2}{a^2} \right) \overset{\circ}{E}_{2z}^4 \quad (6)$$

Here, a is the mean linear polarizability of the isolated molecule and c_{\parallel} and c_{\perp} are its nonlinear polarizabilities for \mathbf{E}_1 and \mathbf{E}_2 directed mutually parallel or perpendicular, respectively, and $D_0 = \cos^2 \psi \cos^2 \vartheta / \sin^2 \psi$ denoting the depolarization ratio of the scattered light in the absence of a strong electric field ($E_2 = 0$).

From eq. (6) we see that in the case of scattering by nonlinearly polarizable

isotropic molecules the change in depolarization ratio due to the strong optical electric field is proportional only to E_{2z}^4 and its value is then very small, since the ratios of $c_{||}/a$ and c_{\perp}/a are in the best case of order 10^{-12} .

For molecules having the symmetry of point group D_2 the nonlinear change in D is of the form

$$D^{\pm} - D_0 = \frac{(\omega_1 \pm \omega_2)^4 (b_{123}^2 + b_{231}^2 + b_{312}^2) \dot{E}_{2z}^2}{84\omega_1^4 a^2 [5 \sin^2 \psi + (3 + \sin^2 \psi) \kappa_a^2]} \cdot \{(2 + \sin^2 \psi) (3 - 4D_0) - 1 + 3 \cos^2 \psi \cos^2 \vartheta\}, \quad (7)$$

with

$$D_0 = \frac{5 \cos^2 \psi \cos^2 \vartheta + (3 + \cos^2 \psi \cos^2 \vartheta) \kappa_a^2}{5 \sin^2 \psi + (3 + \sin^2 \psi) \kappa_a^2}, \quad (8)$$

where $\kappa_a^2 = \{(a_{11} - a_{22})^2 + (a_{22} - a_{33})^2 + (a_{33} - a_{11})^2\}/18a^2$ describes the anisotropy of linear polarizability of the isolated molecule.

From the above expressions we obtain for $a_{11} = a_{22} \neq a_{33}$ and $b_{231} = b_{312} \neq b_{123}$ formulas for the point group D_{2d} (e.g. $\text{H}_2\text{C} = \text{C} = \text{CH}_2$ molecule); however, on replacing in eq. (7) $b_{123}^2 + b_{231}^2 + b_{312}^2$ by $2b_{111}^2$ we have an expression that holds for molecules of the point group D_{3h} (e.g., BCl_3 , C_3H_6 and $\text{C}_6\text{H}_3\text{Cl}_3$).

If, in particular, the molecules possess the tetrahedral symmetry of point group T_d , $\kappa_a = 0$ and $b_{123} = b_{231} = b_{312}$, and eq. (7) assumes the simpler form

$$D^{\pm} - D_0 = \frac{(\omega_1 \pm \omega_2)^4}{140\omega_1^4} \left(\frac{b_{123}}{a} \right)^2 (13 - 17 \cos^2 \vartheta) \dot{E}_{2z}^2, \quad (9)$$

in the case when the incident light is unpolarized and for which $D_0 = \cos^2 \vartheta$.

We now proceed to the discussion for molecules possessing symmetry of point group C_{3v} (e.g. NH_3 , CHCl_3 etc.). For simplicity we shall assume that the incident light is polarized with the electric vector \mathbf{E}_1 oscillating in the plane of observation ($\psi = 0$) and the scattered light is observed at an angle of $\vartheta = 90^\circ$. It is readily seen from eq. (8) that in this case $D_0 = 1$ and in the presence of the strong optical electric field we have by eqs. (3) and (4),

$$D^{\pm} - 1 = - \frac{(\omega_1 \pm \omega_2)^4}{252\omega_1^4 a^2 \kappa_a^2} \cdot \{2(b_{333} - b_{113})^2 + 6b_{222}^2 + 3b_{131}(5b_{131} + 2b_{333} - 2b_{113})\} \dot{E}_{2z}^2. \quad (10)$$

On putting herein $b_{222} = 0$, we have an expression that holds for molecules of the point groups C_{4v} ($B\gamma F_5$, JF_5), C_{6v} , as well as $C_{\infty v}$ (e.g. CH , OCS , and the like). This result for $b_{222} = 0$ and $b_{131} = 0$ reduces to

$$D^{\pm} - 1 = - \frac{(\omega_1 \pm \omega_2)^4}{14\omega_1^4} \left(\frac{b_{\kappa b}}{a\kappa_a} \right)^2 \dot{E}_{2z}^2. \quad (11)$$

where $\kappa_b = (b_{333} - b_{113}) / (b_{333} + 2b_{113}) = (b_{333} - b_{113}) / 3b$ determines the anisotropy of nonlinear polarizability of an axially symmetric molecule without centre of inversion.

We shall now evaluate the order of magnitude of the change in D for chloroform for which we have the following data ⁹⁾: $a = 8.23 \times 10^{-24} \text{ cm}^3$, $\kappa_a = -0.094$, $b = 11.3 \times 10^{-29} \text{ e.s.u.}$, $\kappa_b = -0.074$. Thus, we obtain from (11)

$$D^{\pm} - 1 = -8.2 \times 10^{-12} \left(\frac{\omega_1 \pm \omega_2}{\omega_1} \right)^4 \dot{E}_{2z}^2. \quad (12)$$

At $\dot{E}_{2z} = 100 \text{ e.s.u.}$ and $\omega_2/\omega_1 = 0.8$ (corresponding to wavelengths of $\lambda_1 = 5430 \text{ \AA}$ and $\lambda_2 = 6940 \text{ \AA}$) the nonlinear change in depolarization ratio amounts to $D - 1 = -86 \times 10^{-8} \sim -10^{-6}$, whereas for $\dot{E}_{2z} = 10^3 \text{ e.s.u.}$ it is of the order of 10^{-4} and, consequently, is accessible to observation.

For carbon tetrachloride $a = 10.5 \times 10^{-24} \text{ cm}^3$, whence we obtain by eq. (9) for $\vartheta = 90$ on assuming $b_{123} = 10 \times 10^{-30} \text{ e.s.u.}$ (the value of b_{123} is not known for the CCl_4 molecule) a variation in D of the order of $10^{-12} \dot{E}_{2z}^2$, this being a small quantity which becomes accessible to observation only upward of $\dot{E}_{2z} = 10^3 \text{ e.s.u.}$

The discussion for other experimental conditions can be performed as already done elsewhere (see refs. 4, 5 and 8).

The above considerations prove that investigation of the effect of an intense light beam (e.g. as emitted by a laser) on the scattering of light by substances consisting of molecules without a centre of inversion will allow to make conclusions concerning the nonlinear polarization of the molecules.

APPENDIX

We shall give here an explicit and short evaluation of the depolarization ratio of nonlinear light scattering for the classical case. Up to second harmonic scattering we have by eq. (2) for $k = l$, in the coordinate system of observation of the scattered light at an angle ϑ from the direction of the incident beam,

$$D^{\pm} = D_0 + \frac{1}{I_z^{\omega_1}} \{ I_y^{\omega_1 \pm \omega_2} - D_0 I_z^{\omega_1 \pm \omega_2} \}, \quad (\text{A. 1})$$

where $D_0 = I_y^{\omega_1} / I_z^{\omega_1}$ is the depolarization ratio when the strong optical field is absent.

The scattered intensity components $I_y^{\omega_1}$, $I_z^{\omega_1}$, $I_y^{\omega_1 \pm \omega_2}$ and $I_z^{\omega_1 \pm \omega_2}$ can be evaluated directly from eqs. (3) and (4) for $k = l$. We have performed these calculations here for the case when the distribution (orientation) of the mole-

cules of the scattering substance is quite random, as in a gas. In this case, the fourth and sixth powers of the products of transformation coefficients between the polarizability tensor components $a_{\alpha\beta}$ and $b_{\alpha\beta\gamma}$ given, on the one hand, in the system attached rigidly to the molecule and, on the other, in the laboratory system, can be averaged classically over all possible orientations of the molecules. We obtain finally for the experimental conditions formulated in the third section of this paper,

$$I_y^{\omega_1} = \frac{\omega_1^4}{60} \langle a_{\alpha\gamma} a_{\beta\delta} \rangle \{ 2\delta_{\alpha\beta} \delta_{\gamma\delta} (2 - \cos^2 \psi \cos^2 \vartheta) + (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) (3 \cos^2 \psi \cos^2 \vartheta - 1) \} \dot{E}_1^2, \quad (\text{A. 2})$$

$$I_z^{\omega_1} = \frac{\omega_1^4}{60} \langle a_{\alpha\gamma} a_{\beta\delta} \rangle \{ 2\delta_{\alpha\beta} \delta_{\gamma\delta} (2 - \sin^2 \psi) + (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) (3 \sin^2 \psi - 1) \} \dot{E}_1^2, \quad (\text{A. 3})$$

$$I_y^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4}{1680} \langle b_{\alpha\gamma\epsilon} b_{\beta\delta\eta} \rangle \{ 2\delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\eta} (3 + 5 \cos^2 \psi \sin^2 \vartheta) + \delta_{\alpha\beta} (\delta_{\gamma\epsilon} \delta_{\delta\eta} + \delta_{\gamma\eta} \delta_{\delta\epsilon}) (6 - 4 \cos^2 \psi \sin^2 \vartheta - 7 \cos^2 \psi) - \delta_{\gamma\delta} (\delta_{\alpha\epsilon} \delta_{\beta\eta} + \delta_{\alpha\eta} \delta_{\beta\epsilon}) (1 + 4 \cos^2 \psi \sin^2 \vartheta) - \delta_{\epsilon\eta} (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) (1 + 11 \cos^2 \psi \sin^2 \vartheta - 7 \cos^2 \psi) + [\delta_{\alpha\gamma} (\delta_{\beta\epsilon} \delta_{\delta\eta} + \delta_{\beta\eta} \delta_{\delta\epsilon}) + \delta_{\alpha\delta} (\delta_{\beta\epsilon} \delta_{\gamma\eta} + \delta_{\beta\eta} \delta_{\gamma\epsilon}) + \delta_{\alpha\epsilon} (\delta_{\beta\gamma} \delta_{\delta\eta} + \delta_{\gamma\eta} \delta_{\beta\delta}) + \delta_{\alpha\eta} (\delta_{\beta\gamma} \delta_{\delta\epsilon} + \delta_{\gamma\epsilon} \delta_{\beta\delta}) \} (3 \cos^2 \psi \sin^2 \vartheta - 1) \} \dot{E}_1^2 \dot{E}_{2z}^2, \quad (\text{A. 4})$$

$$I_z^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4}{1680} \langle b_{\alpha\gamma\epsilon} b_{\beta\delta\eta} \rangle \{ 2\delta_{\gamma\delta} (\delta_{\alpha\beta} \delta_{\epsilon\eta} + \delta_{\alpha\epsilon} \delta_{\beta\eta} + \delta_{\alpha\eta} \delta_{\beta\epsilon}) (3 - 2 \sin^2 \psi) + [\delta_{\alpha\beta} (\delta_{\gamma\epsilon} \delta_{\delta\eta} + \delta_{\gamma\eta} \delta_{\delta\epsilon}) + \delta_{\epsilon\eta} (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) + \delta_{\alpha\gamma} (\delta_{\beta\epsilon} \delta_{\delta\eta} + \delta_{\beta\eta} \delta_{\delta\epsilon}) + \delta_{\alpha\delta} (\delta_{\beta\epsilon} \delta_{\gamma\eta} + \delta_{\beta\eta} \delta_{\gamma\epsilon}) + \delta_{\alpha\epsilon} (\delta_{\beta\gamma} \delta_{\delta\eta} + \delta_{\gamma\eta} \delta_{\beta\delta}) + \delta_{\alpha\eta} (\delta_{\beta\gamma} \delta_{\delta\epsilon} + \delta_{\gamma\epsilon} \delta_{\beta\delta}) \} (3 \sin^2 \psi - 1) \} \dot{E}_1^2 \dot{E}_{2z}^2, \quad (\text{A. 5})$$

where $\delta_{\alpha\beta}$ is a unit tensor whose components are unity for $\alpha = \beta$ and zero for $\alpha \neq \beta$.

From the foregoing results, the simplest expression for D is obtained when the incident light beam is polarized with its electric vector oscillating in a plane parallel to that of observation ($\psi = 0^\circ$) and when observation is perpendicular to the direction of the incident beam ($\vartheta = 90^\circ$). In this case $D_0 = 1$, and the nonlinear change in D , due to the effect of the strong optical electric field directed along the z -axis, is given by the simple formula

$$D^\pm - 1 = \frac{I_y^{\omega_1 \pm \omega_2} - I_z^{\omega_1 \pm \omega_2}}{I_z^{\omega_1}}, \quad (\text{A. 6})$$

or, in explicit form,

$$D^{\pm-1} = \frac{(\omega_1 \pm \omega_2)^4}{504\omega_1^4} \frac{\langle b_{\alpha\gamma\epsilon} b_{\beta\delta\eta} \rangle}{a^2 \kappa_a^2} \{ 10\delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\epsilon\eta} - 4\delta_{\alpha\beta}(\delta_{\gamma\epsilon}\delta_{\delta\eta} + \delta_{\gamma\eta}\delta_{\delta\epsilon}) - \\ - 11\delta_{\gamma\delta}(\delta_{\alpha\epsilon}\delta_{\beta\eta} + \delta_{\alpha\eta}\delta_{\beta\epsilon}) - 4\delta_{\epsilon\eta}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) + 3[\delta_{\alpha\gamma}(\delta_{\beta\epsilon}\delta_{\delta\eta} + \delta_{\beta\eta}\delta_{\delta\epsilon}) + \\ + \delta_{\alpha\delta}(\delta_{\beta\epsilon}\delta_{\gamma\eta} + \delta_{\beta\eta}\delta_{\gamma\epsilon}) + \delta_{\alpha\epsilon}(\delta_{\beta\gamma}\delta_{\delta\eta} + \delta_{\gamma\eta}\delta_{\beta\delta}) + \\ + \delta_{\alpha\eta}(\delta_{\beta\gamma}\delta_{\delta\epsilon} + \delta_{\gamma\epsilon}\delta_{\beta\delta}) \} E_{2z}^2, \quad (\text{A. 7})$$

where we have denoted

$$\kappa_a^2 = \langle a_{\alpha\gamma} a_{\beta\delta} \rangle (4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}) / 18a^2.$$

For the symmetry of the point group D_2 we have the following nonzero elements of the tensor $b_{\alpha\beta\gamma}$:

$$b_{\alpha\beta\gamma} = b_{123}(i_\alpha j_\beta + j_\alpha i_\beta) k_\gamma + b_{231}(j_\alpha k_\beta + k_\alpha j_\beta) i_\gamma + b_{312}(k_\alpha i_\beta + i_\alpha k_\beta) j_\gamma, \quad (\text{A. 8})$$

and we obtain from (A. 7) the result

$$D^{\pm-1} = - \frac{(\omega_1 \pm \omega_2)^4}{84\omega_1^4} \left(\frac{b_{123}^2 + b_{231}^2 + b_{312}^2}{a^2 \kappa_a^2} \right) E_{2z}^2, \quad (\text{A. 9})$$

which is identical with eq. (7) for $\psi = 0^\circ$ and $\vartheta = 90^\circ$; in eq. (A. 8), \mathbf{i} , \mathbf{j} and \mathbf{k} are the unit vectors of the molecular coordinate system.

In the case of molecules possessing symmetry of the point group C_{3v} ,

$$b_{\alpha\beta\gamma} = b_{113}(\delta_{\alpha\beta} k_\gamma - k_\alpha k_\beta k_\gamma) + b_{131}(\delta_{\alpha\gamma} k_\beta + \delta_{\beta\gamma} k_\alpha - 2k_\alpha k_\beta k_\gamma) + \\ + b_{222}\{(i_\alpha j_\beta - i_\alpha i_\beta) j_\gamma - (i_\alpha j_\beta + i_\beta j_\alpha) i_\gamma\} + b_{333} k_\alpha k_\beta k_\gamma, \quad (\text{A. 10})$$

and from eq. (A. 7) we find immediately the formula (10).

Note added in the press on April 22, 1964. At the First Polish Conference on Radiospectroscopy and Quantum Electronics held at Poznań, Poland from April 13–15, 1964, the author, owing to the kindness of Dr. Bakos and Dr. Csillag from Budapest, gained knowledge of the result of Professor Neugebauer on two-quantum scattering processes. At the same time they gave him a copy of Professor Neugebauer's paper published in Acta Phys. Hung. **14** (1962) 77, containing the first discussion of the experimental possibility of observing light scattering on molecules with double frequency 2ν as previously predicted theoretically. The result there is analogous to that derived i.a. in papers 5 and 8 for molecules without a centre of inversion and is a special case of eqs. (3) and (4) of this paper for $\omega_{kl} = 0$ and $\omega_1 = \omega_2 = 2\nu$.

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