

Nonlinear Light Scattering by Molecules without a Centre of Inversion

by

S. KIELICH

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Nonlinear polarization of a molecular system

Let us consider a molecular system (a molecule or an assemblage of molecules) acted on by an electrical field $E_1 = \dot{E}_1 \cos \omega_1 t$ oscillating with the frequency ω_1 . As long as the field strength E_1 remains small, the dipole moment P induced in the molecular system is a linear function of E_1 and its α -component in the perturbed ground state g is given as follows [1]:

$$(1) \quad P_\alpha(t) = \frac{1}{2\hbar} \sum_n \left\{ \frac{M_{agn} (M_{ng} \cdot E_1^\pm)}{\omega_{ng} \pm \omega_1} - \frac{(M_{gn} \cdot E_1^\mp) M_{ang}}{\omega_{gn} \mp \omega_1} \right\},$$

where ω_{ng} is the Bohr frequency of the transition $n \rightarrow g$, M_{ng} — the matrix element of the operator of the system's dipole moment related with the transition $n \rightarrow g$ and

$$\frac{E_1^\pm}{\omega_{ng} \pm \omega_1} = \frac{\dot{E}_1 e^{i\omega_1 t}}{\omega_{ng} + \omega_1} + \frac{\dot{E}_1 e^{-i\omega_1 t}}{\omega_{ng} - \omega_1}.$$

If, however, we conceive of our system as subjected to the additional perturbation of another electric field of very great strength $E_2 = \dot{E}_2 \cos \omega_2 t$, the linear relation of Eq. (1) will no longer be adequate but will have to be replaced by the nonlinear expansion [2]

$$(2) \quad P_\alpha(t) = A_{\alpha\beta}^{\omega_1} \dot{E}_{1\beta} \cos \omega_1 t + \frac{1}{2} \{ B_{\alpha\beta\gamma}^{\omega_1 + \omega_2} \cos(\omega_1 + \omega_2) t + \\
 + B_{\alpha\beta\gamma}^{\omega_1 - \omega_2} \cos(\omega_1 - \omega_2) t \} \dot{E}_{1\beta} \dot{E}_{2\gamma} + \frac{1}{8} \{ 2C_{\alpha\beta\gamma\delta}^{\omega_1} \cos \omega_1 t + \\
 + C_{\alpha\beta\gamma\delta}^{\omega_1 + 2\omega_2} \cos(\omega_1 + 2\omega_2) t + C_{\alpha\beta\gamma\delta}^{\omega_1 - 2\omega_2} \cos(\omega_1 - 2\omega_2) t \} \dot{E}_{1\beta} \dot{E}_{2\gamma} \dot{E}_{2\delta} + \dots,$$

whose first term defines the linear polarization of the system by the field E_1 of fundamental frequency ω_1 as given explicitly by the right hand side of Eq. (1) and whose

higher terms account for nonlinear polarization of the molecular system by the very intense electric field E_2 . The first of this latter group is a term consisting of two time-dependent parts with frequencies $\omega_1 + \omega_2$ and $\omega_1 - \omega_2$. Quantum mechanical perturbation calculus yields the part dependent on $\omega_1 + \omega_2$ in the form [2], [3]

$$(3) \quad B_{\alpha\beta\gamma}^{\omega_1+\omega_2} \dot{E}_{1\beta} \dot{E}_{2\gamma} \cos(\omega_1 + \omega_2)t = \frac{1}{2\hbar^2} \sum_{nk} \left\{ M_{agn} \left[\frac{(M_{nk} \cdot E_1^\pm)(M_{kg} \cdot E_2^\pm)}{(\omega_{ng} \pm \omega_1 \pm \omega_2)(\omega_{kg} \pm \omega_2)} + \right. \right. \\ \left. \left. + \frac{(M_{nk} \cdot E_2^\pm)(M_{kg} \cdot E_1^\pm)}{(\omega_{ng} \pm \omega_1 \pm \omega_2)(\omega_{kg} \pm \omega_1)} \right] + M_{ank} \left[\frac{(M_{ng} \cdot E_1^\pm)(M_{kg} \cdot E_2^\pm)}{(\omega_{ng} \mp \omega_1)(\omega_{kg} \pm \omega_2)} + \right. \right. \\ \left. \left. + \frac{(M_{ng} \cdot E_2^\pm)(M_{kg} \cdot E_1^\pm)}{(\omega_{ng} \mp \omega_2)(\omega_{kg} \pm \omega_1)} \right] + M_{ang} \left[\frac{(M_{nk} \cdot E_1^\mp)(M_{kg} \cdot E_2^\mp)}{(\omega_{ng} \pm \omega_1 \pm \omega_2)(\omega_{kg} \pm \omega_2)} + \right. \right. \\ \left. \left. + \frac{(M_{nk} \cdot E_2^\mp)(M_{kg} \cdot E_1^\mp)}{(\omega_{ng} \pm \omega_1 \pm \omega_2)(\omega_{kg} \pm \omega_1)} \right] \right\}.$$

On replacing herein ω_2 by $-\omega_2$ we obtain the part dependent on $\omega_1 - \omega_2$.

The second nonlinear term in the expansion (2) consists of three parts which depend, respectively, on ω_1 , $\omega_1 + 2\omega_2$ and $\omega_1 - 2\omega_2$. Their quantum-mechanical expressions are highly involved and we shall refrain from writing them here [2]. For the case of three electromagnetic waves of frequencies ω_1 , ω_2 and ω_3 , the frequency dependences and symmetry permutation relations of the tensors $B_{\alpha\beta\gamma}^{\omega_1+\omega_2}$ and $C_{\alpha\beta\gamma\delta}^{\omega_1+\omega_2+\omega_3}$ are discussed explicitly in a paper by Armstrong et al [4].

Nonlinear light scattering tensor

We introduce the scattering tensor $I_{\alpha\beta}$ defined as

$$(4) \quad I_{\alpha\beta} = \frac{1}{c_1^4 R_0^2} \langle \overline{P_\alpha P_\beta} \rangle_{E_1, E_2},$$

where c_1 is the velocity of light propagation and R_0 — the distance from the centre of the scattering system to the point of observation of the scattered light; the horizontal straight line — t denotes time-averaging and the brackets $\langle \rangle_{E_1, E_2}$ stand for statistical averaging in the presence of the fields E_1 and E_2 .

By the expansion of Eq. (2), the nonlinear scattering tensor (4) can be expressed in the form

$$(5) \quad I_{\alpha\beta} = I_{\alpha\beta}^{\omega_1} + I_{\alpha\beta}^{\omega_1+\omega_2} + I_{\alpha\beta}^{\omega_1-\omega_2} + I_{\alpha\beta}^{\omega_1+2\omega_2} + I_{\alpha\beta}^{\omega_1-2\omega_2} + \dots,$$

where

$$(6) \quad I_{\alpha\beta}^{\omega_1} = \frac{1}{R_0^2} \left(\frac{\omega_1}{c_1} \right)^4 \left\{ \langle A_{\alpha\gamma}^{\omega_1} A_{\beta\delta}^{\omega_1} \rangle_{E_2} + \frac{1}{4} \langle A_{\alpha\gamma}^{\omega_1} C_{\beta\delta\epsilon\eta}^{\omega_1} + C_{\alpha\gamma\epsilon\eta}^{\omega_1} A_{\beta\delta}^{\omega_1} \rangle_{E_2} \dot{E}_{2\epsilon} \dot{E}_{2\eta} + \right. \\ \left. + \frac{1}{16} \langle C_{\alpha\gamma\epsilon\eta}^{\omega_1} C_{\beta\delta\theta\chi}^{\omega_1} \rangle_{E_2} \dot{E}_{2\epsilon} \dot{E}_{2\eta} \dot{E}_{2\theta} \dot{E}_{2\chi} + \dots \right\} \dot{E}_{1\gamma} \dot{E}_{1\delta} \overline{\cos^2 \omega_1 t}.$$

is the tensor of scattering with the fundamental frequency ω_1 , representing Rayleigh light scattering, which consists of linear scattering (linear in the intensity $I = \frac{1}{2} \dot{E}^2$ of the incident light) and of additional nonlinear scattering due to the intense light beam. The next two tensors in Eq. (5) determine nonlinear scattering with the frequencies $\omega_1 \pm \omega_2$ and are given by

$$(7) \quad I_{\alpha\beta}^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4}{4c_1^4 R_0^2} \langle B_{\alpha\gamma\epsilon}^{\omega_1 \pm \omega_2}, B_{\beta\delta\eta}^{\omega_1 \pm \omega_2} \rangle_{E_2} \dot{E}_{1\gamma} \dot{E}_{1\delta} \dot{E}_{2\epsilon} \dot{E}_{2\eta} \overline{\cos^2(\omega_1 \pm \omega_2) t}.$$

Finally, the last two tensors in (5) are of the form

$$(8) \quad I_{\alpha\beta}^{\omega_1 \pm 2\omega_2} = \frac{(\omega_1 \pm 2\omega_2)^4}{64c_1^4 R_0^2} \langle C_{\alpha\gamma\epsilon\eta}^{\omega_1 \pm 2\omega_2}, C_{\beta\delta\theta\chi}^{\omega_1 \pm 2\omega_2} \rangle_{E_2} \dot{E}_{1\gamma} \dot{E}_{1\delta} \dot{E}_{2\epsilon} \dot{E}_{2\eta} \dot{E}_{2\theta} \dot{E}_{2\chi} \overline{\cos^2(\omega_1 \pm 2\omega_2) t}$$

and determine nonlinear scattering with the frequencies $\omega_1 \pm 2\omega_2$.

If, in particular, the scattering system is optically isotropic we have

$$(9) \quad A_{\alpha\beta} = A\delta_{\alpha\beta}, B_{\alpha\beta\gamma} = 0, \quad C_{\alpha\beta\gamma\delta} = C_{\perp} \delta_{\alpha\beta} \delta_{\gamma\delta} + \frac{1}{2} (C_{\parallel} - C_{\perp}) (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}),$$

and $I_{\alpha\beta}^{\omega_1 \pm \omega_2} = 0$, whereas the tensors $I_{\alpha\beta}^{\omega_1}$ and $I_{\alpha\beta}^{\omega_1 \pm 2\omega_2}$ reduce to

$$(10) \quad I_{\alpha\beta}^{\omega_1} = \frac{1}{2R_0^2} \left(\frac{\omega_1}{c_1} \right)^4 \{ (A^{\omega_1})^2 \dot{E}_{1\alpha} \dot{E}_{1\beta} + \frac{1}{4} A^{\omega_1} [2C_{\perp}^{\omega_1} \dot{E}_{1\alpha} \dot{E}_{1\beta} (\dot{E}_2 \cdot \dot{E}_2) + \\ + (C_{\parallel}^{\omega_1} - C_{\perp}^{\omega_1}) (\dot{E}_{1\alpha} \dot{E}_{2\beta} + \dot{E}_{2\alpha} \dot{E}_{1\beta}) (\dot{E}_1 \cdot \dot{E}_2)] + \frac{1}{16} [(C_{\perp}^{\omega_1})^2 \dot{E}_{1\alpha} \dot{E}_{1\beta} (\dot{E}_2 \cdot \dot{E}_2)^2 + \\ + C_{\perp}^{\omega_1} (C_{\parallel}^{\omega_1} - C_{\perp}^{\omega_1}) (\dot{E}_{1\alpha} \dot{E}_{2\beta} + \dot{E}_{2\alpha} \dot{E}_{1\beta}) (\dot{E}_1 \cdot \dot{E}_2) (\dot{E}_2 \cdot \dot{E}_2) + \\ + (C_{\parallel}^{\omega_1} - C_{\perp}^{\omega_1})^2 \dot{E}_{2\alpha} \dot{E}_{2\beta} (\dot{E}_1 \cdot \dot{E}_2)^2] + \dots \},$$

$$(11) \quad I_{\alpha\beta}^{\omega_1 \pm 2\omega_2} = \frac{(\omega_1 \pm 2\omega_2)^4}{128 c_1^4 R_0^2} \{ (C_{\perp}^{\omega_1 \pm 2\omega_2})^2 \dot{E}_{1\alpha} \dot{E}_{1\beta} (\dot{E}_2 \cdot \dot{E}_2)^2 + \\ + C_{\perp}^{\omega_1 \pm 2\omega_2} (C_{\parallel}^{\omega_1 \pm 2\omega_2} - C_{\perp}^{\omega_1 \pm 2\omega_2}) (\dot{E}_{1\alpha} \dot{E}_{2\beta} + \dot{E}_{2\alpha} \dot{E}_{1\beta}) (\dot{E}_1 \cdot \dot{E}_2) (\dot{E}_2 \cdot \dot{E}_2) + \\ + (C_{\parallel}^{\omega_1 \pm 2\omega_2} - C_{\perp}^{\omega_1 \pm 2\omega_2})^2 \dot{E}_{2\alpha} \dot{E}_{2\beta} (\dot{E}_1 \cdot \dot{E}_2)^2 \},$$

with C_{\parallel} and C_{\perp} denoting nonlinear polarization of the isotropic system at vectors E_1 and E_2 mutually parallel or perpendicular, respectively.

Hence, scattering by an isotropic system is seen to consist of linear and nonlinear Rayleigh scattering and of additional nonlinear scattering with frequencies $\omega_1 \pm 2\omega_2$.

If the scattering system fails to present a centre of inversion, non-zero components of the tensor $B_{\alpha\beta\gamma}$ exist leading to nonlinear scattering with frequencies $\omega_1 \pm \omega_2$, as given by the tensor (7). We now proceed to a discussion of this scattering for several special cases.

Nonlinear scattering by molecules without a centre of inversion

For simplicity, we now assume the incident light beam to be plane polarized and propagating in the direction of the Y -axis, with electric vector E_1 oscillating parallel to the Z -axis. We assume the very intense light beam to be propagating in the same or in any other direction, with the sole restriction its electric vector E_2 shall also oscillate parallel to the Z -axis. If observation of the scattered light takes place along the X -axis, the scattered intensities with oscillations parallel to the Y - and Z -axes are given respectively by

$$(12) \quad I_Y = I_{\alpha\beta} y_\alpha y_\beta \quad \text{and} \quad I_Z = I_{\alpha\beta} z_\alpha z_\beta,$$

where y and z are unit vectors in the Y - and Z -directions of the laboratory system of coordinates XYZ .

If in Eq. (7) quantum statistical averaging is replaced by averaging over all classical orientations of the molecules with respect to the reference system XYZ , we obtain by (12) and with the above assumptions for the scattering system composed of N identical non-interacting molecules

$$(13) \quad I_Y^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4 N}{1680 c_1^4 R_0^2} \langle b_{\alpha\gamma:\varepsilon} b_{\beta\delta:\eta} (7\delta_{\alpha\beta} \sigma_{\gamma\delta\varepsilon\eta} - \sigma_{\alpha\beta\gamma\delta\varepsilon\eta}) \rangle \dot{E}_1^2 \dot{E}_2^2,$$

$$(14) \quad I_Z^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4 N}{840 c_1^4 R_0^2} \langle b_{\alpha\gamma:\varepsilon} b_{\beta\delta:\eta} \sigma_{\alpha\beta\gamma\delta\varepsilon\eta} \rangle \dot{E}_1^2 \dot{E}_2^2,$$

where the following tensors have been introduced:

$$(15) \quad \begin{aligned} \sigma_{\alpha\beta\gamma\delta} &= \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}, \\ \sigma_{\alpha\beta\gamma\delta\varepsilon\eta} &= \delta_{\alpha\beta} \sigma_{\gamma\delta\varepsilon\eta} + \delta_{\alpha\gamma} \sigma_{\delta\varepsilon\eta\beta} + \delta_{\alpha\delta} \sigma_{\varepsilon\eta\beta\gamma} + \delta_{\alpha\varepsilon} \sigma_{\eta\beta\gamma\delta} + \delta_{\alpha\eta} \sigma_{\beta\gamma\delta\varepsilon}, \end{aligned}$$

$\delta_{\alpha\beta}$ being the unit tensor.

For molecules having the symmetry of point group D_2 , the tensor $b_{\alpha\beta:\gamma}$ corresponding to the isolated molecule is of the form *)

$$(16) \quad b_{\alpha\beta:\gamma} = b_{12:3} (i_\alpha j_\beta + j_\alpha i_\beta) k_\gamma + b_{23:1} (j_\alpha k_\beta + k_\alpha j_\beta) i_\gamma + b_{31:2} (k_\alpha i_\beta + i_\alpha k_\beta) j_\gamma,$$

where i, j and k are unit vectors along the axes 1, 2 and 3 of the molecular reference system.

In the case of the symmetry D_{2d} (as exemplified by the $H_2C = C = CH_2$ molecule) $b_{23:1} = b_{31:2} \neq b_{12:3}$, whereas for point group D_4 and D_6 $b_{23:1} = -b_{31:2}$, $b_{12:3} = 0$ and for molecules with the T and T_d symmetry (e.g., CH_4 , CCl_4 , S_nCl_4 etc.) $b_{12:3} = b_{23:1} = b_{31:2} = b_{123}$. In the last case, Eqs. (13) and (14) reduce to the following simpler form:

$$(17) \quad I_Y^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4}{35 c_1^4 R_0^2} N b_{123}^2 \dot{E}_1^2 \dot{E}_2^2, \quad I_Z^{\omega_1 \pm \omega_2} = \frac{3}{2} I_Y^{\omega_1 \pm \omega_2}.$$

*) We assume that the tensor $b_{\alpha\beta\gamma}$ has the same symmetry as the piezoelectric tensor $h_{\alpha\beta\gamma}$ discussed, e.g., in [5].

For point group D_{3h} (e.g., C_3H_6 and $C_6H_3Cl_3$) we have

$$(18) \quad b_{\alpha\beta:\gamma} = b_{11:1} \{(i_\alpha i_\beta - j_\alpha j_\beta) i_\gamma - (i_\alpha j_\beta + j_\alpha i_\beta) j_\gamma\},$$

and Eqs. (13) and (14) yield

$$(19) \quad I_Y^{\omega_1 \pm \omega_2} = \frac{2(\omega_1 \pm \omega_2)^4}{105 c_1^4 R_0^2} b_{111}^2 N E_1^2 E_2^2, \quad I_Z^{\omega_1 \pm \omega_2} = \frac{3}{2} I_Y^{\omega_1 \pm \omega_2}.$$

In the case of group C_{2v} (e.g., H_2O , H_2S , NO_2 , SO_2 , H_2CO , C_6H_5Cl , $C_6H_5NO_2$ etc.),

$$(20) \quad b_{\alpha\beta:\gamma} = (b_{11:3} i_\alpha i_\beta + b_{22:3} j_\alpha j_\beta + b_{33:3} k_\alpha k_\beta) k_\gamma + b_{13:1} (i_\alpha k_\beta + k_\alpha i_\beta) i_\gamma + \\ + b_{23:2} (j_\alpha k_\beta + k_\alpha j_\beta) j_\gamma.$$

For groups C_{4v} (e.g. BrF_5 and JF_5 molecules), C_{6v} and also for $C_{\infty v}$ (e.g., the molecules HCl , HBr , CO , NO , N_2O , HCN , OCS), we have $b_{13:1} = b_{23:2} \neq b_{11:3} = b_{22:3} \neq b_{33:3}$ and

$$(21) \quad b_{\alpha\beta:\gamma} = b_{11:3} (\delta_{\alpha\beta} k_\gamma - k_\alpha k_\beta k_\gamma) + b_{33:3} k_\alpha k_\beta k_\gamma + \\ + b_{13:1} (\delta_{\alpha\gamma} k_\beta + \delta_{\beta\gamma} k_\alpha - 2k_\alpha k_\beta k_\gamma).$$

With the above expressions, Eqs. (13) and (14) lead to the result

$$(22) \quad I_Y^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4 N}{1680 c_1^4 R_0^2} \{3(b_{33:3} + 2b_{13:1})^2 - (b_{33:3} + 2b_{11:3})^2 - \\ - 4(b_{33:3} + 2b_{11:3})(b_{33:3} + 2b_{13:1}) + 2(4b_{33:3}^2 + 13b_{3:11}^2 + 5b_{3:11}^2 + 6b_{11:3} b_{13:1})\} E_1^2 E_2^2,$$

$$(23) \quad I_Z^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4 N}{840 c_1^4 R_0^2} \{(3 b_{33:3} + 2 b_{11:3} + 4 b_{13:1})^2 + \\ + 2(3 b_{33:3}^2 + 2 b_{11:3}^2 + 8 b_{13:1}^2 + 8 b_{13:1} b_{11:3})\} E_1^2 E_2^2.$$

We now proceed to the numerical evaluation of the difference between the total intensity $I = I_Y + I_Z$ scattered in the presence of a very intense light beam and the intensity $I_0 = I_{0Y} + I_{0Z}$ scattered in the absence of such a light beam.

Since tetrahedrally symmetrical molecules possess isotropic polarizability, $a_{\alpha\beta} = a\delta_{\alpha\beta}$, Eqs. (10) and (11) yield for $E_2 = 0$

$$(24) \quad I_{0Y} = 0, \quad I_{0Z} = \frac{1}{2R_0^2} \left(\frac{\omega_1}{c_1}\right)^4 a^2 N E_1^2,$$

and, by (17), the nonlinear variation of I is given by

$$(25) \quad \frac{I - I_0}{I_0} = \frac{1}{7} \left(1 + \frac{\lambda_1}{\lambda_2}\right)^4 \left(\frac{b_{123}}{a}\right)^2 E_2^2.$$

The polarizability of the CCl_4 molecule amounting to $a = 10.5 \times 10^{-24} \text{ cm}^3$, we obtain on assuming $b_{123} = 3 \times 10^{-30} \text{ e.s.u.}$ and $\lambda_1 = 5430 \text{ \AA}$, $\lambda_2 = 6940 \text{ \AA}$ a variation in I of the order of $10^{-13} \dot{E}_2^2$, this being a small quantity which becomes accessible to observation only upward of $\dot{E}_2 = 10^4 \text{ e.s.u.}$

On assuming the tensor $b_{\alpha\beta\gamma}$ to be symmetrical in all indices α, β, γ , we have $b_{11:3} = b_{13:1} = b_{113} \neq b_{333}$ and Eqs. (22), (23) and (24) lead to

$$(26) \quad \frac{I - I_0}{I_0} = \frac{\left(1 + \frac{\lambda_1}{\lambda_2}\right)^4}{210 a^2} \{4 (b_{333} + 2 b_{113})^2 + 5 (b_{333}^2 + 6 b_{113}^2)\} \dot{E}_2^2.$$

We now apply Eq. (26) to chloroform (for which the values of b_{113} and b_{333} are known) although, as a matter of fact, the CHCl_3 molecule possesses symmetry of class C_{3v} with tensor $b_{\alpha\beta:\gamma}$ given as follows:

$$(27) \quad b_{\alpha\beta:\gamma}^{C_{3v}} = b_{\alpha\beta:\gamma}^{C_{4v}} + b_{22:2} \{ (j_\alpha j_\beta - i_\alpha i_\beta) j_\gamma - (i_\alpha j_\beta + j_\alpha i_\beta) i_\gamma \},$$

the tensor $b_{\alpha\beta:\gamma}^{C_{4v}}$ being defined by Eq. (21). With the values [6] $a = 8.23 \times 10^{-24} \text{ cm}^3$, $b_{113} = 12.1 \times 10^{-29} \text{ e.s.u.}$ and $b_{333} = 9.6 \times 10^{-29} \text{ e.s.u.}$, we obtain by Eq. (26) $(I - I_0)/I_0 = 7 \times 10^{-10} \dot{E}_2^2$. Obviously, this result predicts that an intense light beam conveying an electric field strength of 100 e.s.u. shall produce a detectable nonlinear variation in the intensity of the light scattered by chloroform *).

Frequency-dependence of the scattering tensors in the classical case

In certain simpler cases, the dependence of the coefficients a, b and c on the frequencies ω_1 and ω_2 can be obtained easily from classical electron theory. Indeed, for an electron of mass m_i and electric charge e_i bonded to an atom or molecule by a force F_i and undergoing a displacement r_i from its equilibrium position under the influence of the electric fields E_1 and E_2 , the classical equation of motion is of the well-known form

$$(28) \quad m \ddot{r}_i = F_i + e_i (\dot{E}_1 \cos \omega_1 t + \dot{E}_2 \cos \omega_2 t).$$

In the case of an anisotropic and anharmonic oscillator, the α -component of the force F_i is

$$(29) \quad -F_{i\alpha} = \alpha_{i\alpha\beta} r_{i\beta} + \frac{1}{2} \beta_{i\alpha\beta\gamma} r_{i\beta} r_{i\gamma} + \frac{1}{6} \gamma_{i\alpha\beta\gamma\delta} r_{i\beta} r_{i\gamma} r_{i\delta} + \dots,$$

where the first term describes harmonic oscillation and the subsequent terms — anharmonic oscillations.

Assuming for simplicity a one-dimensional oscillator, we derive from the foregoing equations the displacement r_i and thus the dipole moment of the molecule

*) The contribution to I resulting from the effect of optical molecular orientation is calculated in [2] and [7].

$\sum_i e_i r_i$ whose dependence on E_1 and E_2 is of the form of the expansion (2) with the following coefficients:

$$(30) \quad a^{\omega_i} = \sum_i \frac{e_i^2}{m_i(\omega_i^2 - \omega_1^2)}, \quad b^{\omega_1 \pm \omega_i} = \sum_i \frac{e_i^3 \beta_i}{m_i^3(\omega_i^2 - \omega_1^2)(\omega_i^2 - \omega_2^2)[(\omega_i^2 - (\omega_1 \pm \omega_2)^2)]},$$

$$c^{\omega_i} = \sum_i \frac{e_i^4}{m_i^5(\omega_i^2 - \omega_1^2)^2(\omega_i^2 - \omega_2^2)^2} \left\{ \frac{\beta_i^2}{\omega_i^2 - (\omega_1 + \omega_2)^2} + \frac{\beta_i^2}{\omega_i^2 - (\omega_1 - \omega_2)^2} + m_i \gamma_i \right\},$$

$$c^{\omega_1 \pm 2\omega_i} = \sum_i \frac{e_i^4}{m_i^5(\omega_i^2 - \omega_1^2)(\omega_i^2 - \omega_2^2)^2} \left\{ \frac{2\beta_i^2}{[\omega_i^2 - (\omega_1 \pm 2\omega_2)^2]} + m_i \gamma_i \right\},$$

ω_i denoting the eigen-frequency of the charge e_i and β_i and γ_i — its anharmonicity force constants.

In the case of a single electromagnetic wave of frequency ω , we obtain from Eq. (30) the result found by Armstrong et al., [4].

On assuming in Eqs. (10) and (11) that the vectors E_1 and E_2 oscillate in the same direction and on taking into consideration the relations (30) with $\beta_i = 0$ and the fact that $C_{||} = 3C_{\perp} = C$, we have for isotropic molecules *)

$$(31) \quad I_{\alpha\beta}^{\omega_1} = \frac{N}{2R_0^2} \left(\frac{\omega_1}{c_1} \right)^4 \left\{ \frac{\omega_0^2 a^0}{\omega_0^2 - \omega_1^2} + \frac{\omega_0^8 c^0 \dot{E}_2^2}{4(\omega_0^2 - \omega_1^2)^2(\omega_0^2 - \omega_2^2)^2} \right\}^2 \dot{E}_{1\alpha} \dot{E}_{1\beta},$$

$$(32) \quad I_{\alpha\beta}^{\omega_1 \pm 2\omega_i} = \frac{N}{128R_0^2} \left(\frac{\omega_1 \pm 2\omega_2}{c_1} \right)^4 \left\{ \frac{\omega_0^8 c^0 \dot{E}_2^2}{(\omega_0^2 - \omega_1^2)(\omega_0^2 - \omega_2^2)^2[\omega_0^2 - (\omega_1 \pm 2\omega_2)^2]} \right\}^2 \dot{E}_{1\alpha} \dot{E}_{1\beta},$$

where the quantities $a^0 = \sum_i (e_i^2/m_i \omega_0^2)$ and $c^0 = \sum_i (e_i^4 \gamma_i/m_i^4 \omega_0^8)$ are, respectively, the coefficients of linear and nonlinear polarizability at $\omega_1 = \omega_2 = 0$.

In the case of molecules of symmetry D_{3h} , Eqs. (7), (18) and (30) yield for the tensor of light scattering at $\omega_1 \pm \omega_2$

$$(33) \quad I_{\alpha\beta}^{\omega_1 \pm \omega_2} =$$

$$= \frac{N}{105R_0^2} \left(\frac{\omega_1 \pm \omega_2}{c_1} \right)^4 \left\{ \frac{\omega_0^6 b^0 \dot{E}_2}{(\omega_0^2 - \omega_1^2)(\omega_0^2 - \omega_2^2)[\omega_0^2 - (\omega_1 \pm \omega_2)^2]} \right\}^2 (\dot{E}_{1\alpha} \dot{E}_{1\beta} + 2\delta_{\alpha\beta} \dot{E}_1^2),$$

with $b^0 = \sum_i (e_i^3 \beta_i/m_i^3 \omega_0^6)$ denoting the coefficient of nonlinear polarizability of a molecule without a centre of inversion for $\omega_1 = \omega_2 = 0$.

Eq. (33) holds also for molecules of tetrahedral symmetry, when b_0 has to be replaced by $(3/2)^{1/2} b_{123}$.

*) Some amount of error that found its way into the analogous formulas of earlier papers [2], [8] has been eliminated from the above equations.

The results (31)—(33) show that in the neighbourhood of absorption bands very intense nonlinear scattering of light can be expected to occur (nonlinear resonance scattering, the strict treatment of which would require taking into account a damping force $\Gamma_i \dot{r}_i$ in the equation of motion (28)).

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 non-linear polarization of the molecules considered. It is also noteworthy that, by Eqs. (13) and (14), much higher values of $I^{\omega_1+\omega_2}$ can be attained provided an intense light source with frequency ω_2 considerably exceeding the frequency ω_1 of the weak light beam is available.

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Summary

The scattering of light of frequency ω_1 in the presence of another, very intense light beam of frequency ω_2 is considered. It is found that, in the case under consideration, the tensor of the scattered light contains, in addition to the Rayleighian component $I_{\alpha\beta}^{\omega_1}$ with incident light frequency ω_1 , new components $I_{\alpha\beta}^{\omega_1+\omega_2}$, $I_{\alpha\beta}^{\omega_1-\omega_2}$, $I_{\alpha\beta}^{\omega_1+2\omega_2}$ and $I_{\alpha\beta}^{\omega_1-2\omega_2}$, determining nonlinear scattering due to the presence of the intense light beam, as obtained e.g. with a laser. Components with the harmonic frequencies $\omega_1 \pm \omega_2$ are shown to appear only if the scattering gas consists of molecules without a centre of inversion, and are discussed for molecules presenting the point group symmetry C_{2v} , C_{4v} , $C_{\infty v}$, D_{2d} , D_{3h} or T_d . The remaining scattering tensor components with frequencies $\omega_1 \pm 2\omega_2$ exist in the case of molecules of arbitrary symmetry; for the sake of simplicity, they are applied here to a gas of optically isotropic molecules only.

DEPARTMENT OF DIELECTRICS (POZNAŃ), INSTITUTE OF PHYSICS, POLISH ACADEMY OF SCIENCES

(ZAKŁAD DIELEKTRYKÓW (POZNAŃ), INSTYTUT FIZYKI, PAN)

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