

Non-linear Optical Effects in Gases. II. Quantum-Mechanical Calculation

by

S. KIELICH

Presented by A. PIEKARA on February 9, 1963

Introduction

In the course of 1962, a number of papers appeared on the generation by lasers of higher radiation harmonics and on the theory of various non-linear optical effects related to such radiation and able to appear in different systems (see, e.g. [1]—[5]).

The present part of our investigation is intended to give a concise account of the formal theory of two non-linear optical effects that predictably can be produced in certain conditions by a periodic field of high frequency and very great intensity. The one consists in the effect of dynamical (optical) birefringence of the medium, whereas the other — in the non-linear depolarisation of Rayleigh scattering.

Our theory is based on the calculation of the oscillating dipole moment induced in a given molecular system by a periodically varying electric field E_1 of low intensity and of frequency ω_1 in the presence of another field E_2 of very great intensity and of frequency ω_2 . Use is made of Dirac's quantum-mechanical perturbation calculus, to the third approximation inclusively. The first approximation determines the linear polarisation of the system due to the field E_1 , while the second and third account for its non-linear polarization as produced additionally by the strong field E_2 . In an isotropic medium such as a gas or liquid, the presence of the non-linear effect is due not only to the direct influence of the strong field E_2 on the dipole moment of an atom or molecule (hyperpolarizability effect), but, moreover, to statistical orientation of the induced dipoles in the effective field E_2 . In some cases the latter effect can by far exceed that of hyperpolarizability. A formula for the degree of depolarization, to be derived here for the latter case, yields directly the sign and value of the optical anisotropy of an axially symmetric molecule.

Calculation of the oscillating dipole moment

Consider a molecular system subjected to two macroscopic electric fields $E_1(t)$ and $E_2(t)$ varying periodically with frequencies ω_1 and ω_2 (conveyed by two electromagnetic waves). The total Hamiltonian of the system is

$$(1) \quad H = H_0 + H' + H'',$$

where H_0 is the Hamiltonian of the non-perturbed system (at zero external fields, $E_1 = E_2 = 0$), and

$$(2) \quad H' = -\frac{1}{2}(\mathbf{M} \cdot \mathbf{E}_1^+ + \mathbf{M} \cdot \mathbf{E}_1^-), \quad H'' = -\frac{1}{2}(\mathbf{M} \cdot \mathbf{E}_2^+ + \mathbf{M} \cdot \mathbf{E}_2^-)$$

are the Hamiltonians of the perturbed system. The negligible interaction between the magnetic fields and the molecular system is not taken into account. In Eqs. (2), for brevity, we use the notation

$$(3) \quad \mathbf{E}_1^\pm = \mathbf{E}_{01}^\pm e^{\pm i\omega_1 t}, \quad \mathbf{E}_2^\pm = \mathbf{E}_{02}^\pm e^{\pm i\omega_2 t},$$

where \mathbf{E}_{01}^\pm and \mathbf{E}_{02}^\pm are arbitrary vectors with, generally, complex components. The operator of the system's electric dipole moment is given by

$$(4) \quad \mathbf{M} = \sum_i e_i \mathbf{r}_i,$$

where e_i is the elementary charge and \mathbf{r}_i —its radius vector; summation in (4) extends over all charges of the system.

Assume the system, previous to applying the fields \mathbf{E}_1 and \mathbf{E}_2 , to have occupied one of its energy levels W_g . We assume this as the ground state and denote the eigenfunction corresponding thereto by $\Psi_g^{(0)}(\mathbf{r}, 0)$. The state of the system in the presence of the fields $\mathbf{E}_1(t)$ and $\mathbf{E}_2(t)$ is given by the wave function $\Psi_g(\mathbf{r}, t)$, which has to fulfil Schrödinger's equation. Our problem consists in calculating the electric dipole moment $\mathbf{P}(t)$ induced in the system by the oscillating field $\mathbf{E}_1(t)$ in the presence of the strong field $\mathbf{E}_2(t)$. The quantum-mechanical mean value of the α -component of $\mathbf{P}(t)$, for the state given by Ψ_g , is

$$(5) \quad P_{\alpha g g} = \int \Psi_g^* P_\alpha \Psi_g dt.$$

We shall calculate this mean value by Dirac's perturbation method for non-degenerate and non-stationary states to within the third approximation. Accordingly, we proceed to expand the wave function of the perturbed system in the state g , as follows:

$$(6) \quad \Psi_g(t) = \sum_n \{a_n^{(0)} + a_n^{(1)} + a_n^{(2)} + a_n^{(3)} + \dots\} \Psi_n^{(0)} e^{-i\omega_n t};$$

here $a_n^{(0)} = \delta_{ng}$, while the remaining coefficients $a_n^{(1)}$, $a_n^{(2)}$, ..., $a_n^{(s+1)}$ are functions of the time and can be calculated from the set of differential equations

$$(7) \quad i\hbar \dot{a}_n^{(s+1)} = \sum_k (H'_{nk} + H''_{nk}) a_k^{(s)} e^{i\omega_{nk} t}, \quad s = 0, 1, 2, 3, \dots$$

The Bohr frequencies have been denoted

$$(8) \quad \omega_n = W_n/\hbar, \quad \omega_{nk} = \omega_n - \omega_k = (W_n - W_k)/\hbar,$$

and the matrix elements of the perturbations

$$(9) \quad H'_{nk} = \int \Psi_n^{(0)*} H' \Psi_k^{(0)} d\tau, \quad H''_{nk} = \int \Psi_n^{(0)*} H'' \Psi_k^{(0)} d\tau.$$

On putting the integration constants equal to zero in calculating the coefficients $a_n^{(s+1)}$ from Eq. (7) (indeed, we are interested solely in the terms linear in E_1 and in the ones proportional to products of E_1 and E_2 or E_2^2), we have

$$\begin{aligned}
 a_n^{(1)} &= \frac{1}{2\hbar} \left\{ \frac{(M_{ng} \cdot E_1^\pm)}{\omega_{ng} \pm \omega_1} + \frac{(M_{ng} \cdot E_2^\pm)}{\omega_{ng} \pm \omega_2} \right\} e^{i\omega_{ng} t}, \\
 a_n^{(2)} &= \frac{1}{4\hbar^2} \sum_k \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)} + \frac{(M_{nk} \cdot E_1^\pm)(M_{kg} \cdot E_2^\mp)}{(\omega_{ng} \pm \omega_1 \mp \omega_2)(\omega_{kg} \mp \omega_2)} + \right. \\
 &\quad + \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)} + \frac{(M_{nk} \cdot E_2^\pm)(M_{kg} \cdot E_1^\mp)}{(\omega_{ng} \mp \omega_1 \pm \omega_2)(\omega_{kg} \mp \omega_1)} + \\
 &\quad \left. + \frac{(M_{nk} \cdot E_2^\pm)(M_{kg} \cdot E_2^\pm)}{(\omega_{ng} \pm 2\omega_2)(\omega_{kg} \pm \omega_2)} + \frac{(M_{nk} \cdot E_2^\pm)(M_{kg} \cdot E_2^\mp)}{\omega_{ng}(\omega_{kg} \mp \omega_2)} \right\} e^{i\omega_{ng} t}, \\
 a_n^{(3)} &= \frac{1}{8\hbar^3} \sum_{kl} \left\{ \frac{(M_{nk} \cdot E_1^\pm)(M_{kl} \cdot E_2^\pm)(M_{lg} \cdot E_2^\pm)}{(\omega_{ng} \pm \omega_1 \pm 2\omega_2)(\omega_{kg} \pm 2\omega_2)(\omega_{lg} \pm \omega_2)} + \right. \\
 (10) \quad &\quad + \frac{(M_{nk} \cdot E_1^\pm)(M_{kl} \cdot E_2^\pm)(M_{lg} \cdot E_2^\mp)}{(\omega_{ng} \pm \omega_1)\omega_{kg}(\omega_{lg} \mp \omega_2)} + \frac{(M_{nk} \cdot E_1^\mp)(M_{kl} \cdot E_2^\pm)(M_{lg} \cdot E_2^\mp)}{(\omega_{ng} \mp \omega_1)\omega_{kg}(\omega_{lg} \mp \omega_2)} + \\
 &\quad + \frac{(M_{nk} \cdot E_1^\mp)(M_{kl} \cdot E_2^\pm)(M_{lg} \cdot E_2^\pm)}{(\omega_{ng} \mp \omega_1 \pm \omega_2)(\omega_{kg} \pm 2\omega_2)(\omega_{lg} \pm \omega_2)} + \\
 &\quad + \frac{(M_{nk} \cdot E_2^\pm)(M_{kl} \cdot E_1^\pm)(M_{lg} \cdot E_2^\pm)}{(\omega_{ng} \pm \omega_1 \pm 2\omega_2)(\omega_{kg} \pm \omega_1 \pm \omega_2)(\omega_{lg} \pm \omega_2)} + \\
 &\quad + \frac{(M_{nk} \cdot E_2^\pm)(M_{kl} \cdot E_1^\pm)(M_{lg} \cdot E_2^\mp)}{(\omega_{ng} \pm \omega_1)(\omega_{kg} \pm \omega_1 \mp \omega_2)(\omega_{lg} \mp \omega_2)} + \\
 &\quad + \frac{(M_{nk} \cdot E_2^\mp)(M_{kl} \cdot E_1^\pm)(M_{lg} \cdot E_2^\mp)}{(\omega_{ng} \pm \omega_1 \mp 2\omega_2)(\omega_{kg} \pm \omega_1 \mp \omega_2)(\omega_{lg} \mp \omega_2)} + \\
 &\quad + \frac{(M_{nk} \cdot E_2^\mp)(M_{kl} \cdot E_1^\pm)(M_{lg} \cdot E_2^\pm)}{(\omega_n \pm \omega_1)(\omega_{kg} \pm \omega_1 \pm \omega_2)(\omega_{lg} \pm \omega_2)} + \\
 &\quad + \frac{(M_{nk} \cdot E_2^\pm)(M_{kl} \cdot E_2^\pm)(M_{lg} \cdot E_1^\pm)}{(\omega_{ng} \pm \omega_1 \pm 2\omega_2)(\omega_{kg} \pm \omega_1 \pm \omega_2)(\omega_{lg} \pm \omega_1)} + \\
 &\quad + \frac{(M_{nk} \cdot E_2^\pm)(M_{kl} \cdot E_2^\pm)(M_{lg} \cdot E_1^\mp)}{(\omega_{ng} \mp \omega_1 \pm 2\omega_2)(\omega_{kg} \mp \omega_1 \pm \omega_2)(\omega_{lg} \mp \omega_1)} + \\
 &\quad \left. + \frac{(M_{nk} \cdot E_2^\mp)(M_{kl} \cdot E_2^\pm)(M_{lg} \cdot E_1^\mp)}{(\omega_{ng} \mp \omega_1)(\omega_{kg} \pm \omega_1 \pm \omega_2)(\omega_{lg} \pm \omega_1)} \right\} e^{i\omega_{ng} t}.
 \end{aligned}$$

In the above expressions, M_{nk} is a matrix element of the electric moment vector (4) defined as in (9); moreover, for brevity, use has been made of the notation

$$\frac{E_1^\pm}{\omega_{ng} \pm \omega_1} = \frac{E_1^+}{\omega_{ng} + \omega_1} + \frac{E_1^-}{\omega_{ng} - \omega_1}, \text{ etc.}$$

From the definition of Eq. (5) and the expansion (6), with the coefficients (10), we obtain the required expansion of the induced dipole moment of the system, thus

$$(11) \quad P_{\alpha\beta} = \{A_{\alpha\beta}^{gg}(\omega_1) + B_{\alpha\beta\gamma}^{gg}(\omega_1, \omega_2) E_{2\gamma} + \frac{1}{2} C_{\alpha\beta\gamma\delta}^{gg}(\omega_1, \omega_2) E_{2\gamma} E_{2\delta} + \dots\} E_{1\beta},$$

where the first term is given by

$$(12) \quad A_{\alpha\beta}^{gg}(\omega_1) E_{1\beta} = \sum_{nk} \{ \delta_{ng} a_k^{(1)} + a_n^{(1)*} \delta_{kg} \} M_{ank} e^{i\omega_{nk} t} = \\ = \frac{1}{2\hbar} \sum_n \left\{ \frac{M_{\alpha gn} M_{\beta ng} E_{1\beta}}{\omega_{ng} \pm \omega_1} - \frac{E_{1\beta}^{\mp} M_{\beta gn} M_{\alpha ng}}{\omega_{gn} \mp \omega_1} \right\}.$$

The polarizability tensor $A_{\alpha\beta}$ of the system, as defined by the foregoing expression, characterizes the linear effect produced by the weak oscillating electric field $E_1 = E_{01}(\cos \omega_1 t + \varphi_1)$. A similar tensor appears in the quantum theory of dispersion due to Kramers [6].

The remaining two terms of the expansion (11) are given by

$$(13) \quad B_{\alpha\beta\gamma}^{gg}(\omega_1, \omega_2) E_{1\beta} E_{2\gamma} = \sum_{nk} \{ \delta_{ng} a_k^{(2)} + a_n^{(1)*} a_k^{(1)} + a_n^{(2)*} \delta_{kg} \} M_{ank} e^{i\omega_{nk} t}$$

$$(14) \quad C_{\alpha\beta\gamma\delta}^{gg}(\omega_1, \omega_2) E_{1\beta} E_{2\gamma} E_{2\delta} = \\ = 2 \sum_{nk} \{ \delta_{ng} a_k^{(3)} + a_n^{(1)*} a_k^{(2)} + a_n^{(2)*} a_k^{(1)} + a_n^{(3)*} \delta_{kg} \} M_{ank} e^{i\omega_{nk} t}.$$

The tensors $B_{\alpha\beta\gamma}$ and $C_{\alpha\beta\gamma\delta}$ defined thereby account for the non-linear effect produced by the additional interaction of the molecular system and the strong electric field $E_2 = E_{02}(\cos \omega_2 t + \varphi_2)$ and are termed the hyperpolarizability tensors of the system. On substituting into (13) and (14) the coefficients $a_n^{(1)}$, $a_n^{(2)}$ and $a_n^{(3)}$ defined by (10) and on effecting the necessary operations, we retain on the right hand side only terms proportional to $E_1 E_2$ and $E_1 E_2^2$, respectively. The results thus obtained consist of a large number of terms and cannot be conveniently presented here in an explicit form; the way they depend on the frequencies ω_1 and ω_2 is clearly seen from the form of the coefficients (10) (similar expressions for three frequencies ω_1 , ω_2 and ω_3 are given explicitly in [2]).

Dynamical birefringence

The tensor of the dynamical electric permittivity of an anisotropic system of volume V is given by the equation

$$(15) \quad (\epsilon_{\sigma\tau} - \delta_{\sigma\tau}) V = 4\pi \left\langle \frac{\partial P_\sigma}{\partial E_{1\tau}} \right\rangle_{E_1},$$

where the symbol $\langle \rangle_{E_1}$ stands for the statistical mean value in the presence of the strong fields E_2 , whilst σ and τ are indices labelling the components along the axes of the laboratory coordinate system XYZ .

On substituting the expansion of (11) in Eq. (15), we have

$$(16) \quad (\epsilon_{\sigma\tau} - \delta_{\sigma\tau}) V = 4\pi \langle A_{\sigma\tau}(\omega_1) + B_{\sigma\tau\nu}(\omega_1, \omega_2) E_{2\nu} + \frac{1}{2} C_{\sigma\tau\nu\rho}(\omega_1, \omega_2) E_{2\nu} E_{2\rho} + \dots \rangle_{E_1}.$$

In particular, we now proceed to discuss this equation for a molecular system possessing a centre of inversion, for which $B_{\sigma\tau\nu} = 0$. Indeed, if we consider that, by statistical mechanics,

$$(17) \quad \langle \Phi \rangle_{E_1} = \frac{\sum_g \Phi_{gg} \exp \left\{ -\frac{1}{kT} \left(Wg - \frac{1}{2} A_{\alpha\beta}^{gg}(\omega_2) \overline{E_{2\alpha} E_{2\beta}} - \dots \right) \right\}}{\sum_g \exp \left\{ -\frac{1}{kT} \left(Wg - \frac{1}{2} A_{\alpha\beta}^{gg}(\omega_2) \overline{E_{2\alpha} E_{2\beta}} - \dots \right) \right\}},$$

we obtain the dynamical birefringence, by Eq. (16), as follows:

$$(18) \quad (\epsilon_{zz} - \epsilon_{xx}) V = 2\pi \left\langle \left\{ C_{\alpha\beta\gamma\delta}(\omega_1, \omega_2) + \frac{1}{kT} A_{\alpha\beta}(\omega_1) A_{\gamma\delta}(\omega_2) \right\} (k_\alpha k_\beta - i_\alpha i_\beta) e_{2\gamma} e_{2\delta} \right\rangle \overline{E_2^2};$$

here, i and k are unit vectors along the axes X and Z of the laboratory system, respectively (the electro-magnetic wave with vector E_1 propagates in the Y -direction), and e_2 is the unit vector in the direction of the field E_2 . The brackets $\langle \rangle$ without lower index denote the mean statistical value for the non-perturbed system as resulting from Eq. (17) for $E_2 = 0$. The tensor $A_{\gamma\delta}(\omega_2)$ accounts for the polarizability of the system due to the electric field E_2 ; its form results from (12) on replacing therein ω_1 by ω_2 .

If isotropic averaging of $(i_\alpha i_\beta - k_\alpha k_\beta) e_{2\gamma} e_{2\delta}$ can be carried out first independently of statistical averaging, Eq. (18) yields

$$(19) \quad (\epsilon_{zz} - \epsilon_{xx}) V = \frac{\pi}{15} [(k \cdot e_2)^2 - (i \cdot e_2)^2] \{ \langle 3C_{\alpha\beta\alpha\beta}(\omega_1, \omega_2) + 3C_{\alpha\beta\beta\alpha}(\omega_1, \omega_2) - 2C_{\alpha\alpha\beta\beta}(\omega_1, \omega_2) \rangle + \frac{1}{kT} \langle 3A_{\alpha\beta}(\omega_1) A_{\alpha\beta}(\omega_2) + 3A_{\alpha\beta}(\omega_1) A_{\beta\alpha}(\omega_2) - 2A_{\alpha\alpha}(\omega_1) A_{\beta\beta}(\omega_2) \rangle \} \overline{E_2^2}.$$

If, in particular, the system consists of N non-interacting atoms or molecules possessing the spherical symmetry, Eq. (19) reduces to

$$(20) \quad (\varepsilon_{zz} - \varepsilon_{xx}) V = 2\pi N \sum_g P_g \{ \gamma_{\parallel}^{gg}(\omega_1, \omega_2) - \gamma_{\perp}^{gg}(\omega_1, \omega_2) \} \tilde{E}_2^2;$$

herein, γ_{\parallel} and γ_{\perp} are the hyperpolarizabilities of the isolated atom or molecule for E_1 and E_2 directed mutually parallel or perpendicularly (the matrix elements γ_{\parallel}^{gg} and γ_{\perp}^{gg} can be computed from Eq. (14)), whereas P_g is the probability of the system being in the state of energy W_g . Moreover, in passing from Eq. (19) to (20), the assumption was made that the electric vector E_2 oscillates parallel to the Z -axis.

For the case of anisotropic non-interacting molecules, on dropping the term relating to hyperpolarizability in (19), we have

$$(21) \quad (\varepsilon_{zz} - \varepsilon_{xx}) V = \frac{2\pi N}{15kT} \sum_g P_g \{ 3\alpha_{\alpha\beta}^{gg}(\omega_1) \alpha_{\alpha\beta}^{gg}(\omega_2) - \alpha_{\alpha\alpha}^{gg}(\omega_1) \alpha_{\beta\beta}^{gg}(\omega_2) \} \tilde{E}_2^2.$$

Here, by (12), the tensors $\alpha_{\alpha\beta}^{gg}(\omega_1)$ and $\alpha_{\alpha\beta}^{gg}(\omega_2)$ of the dynamical polarizability of the molecule are determined as follows ($s = 1$ or 2):

$$(22) \quad \alpha_{\alpha\beta}^{gg}(\omega_s) = \frac{2}{\hbar} \sum_n \frac{\omega_{ng}}{\omega_{ng}^2 - \omega_s^2} m_{\alpha gn} m_{\beta ng},$$

with m_{gn} denoting a matrix element of the dipole moment of the isolated molecule.

On going over to the purely classical case and assuming the frequencies ω_1 and ω_2 to be far remote from the absorption band, Eqs. (20) and (21) yield formulas already derived by Buckingham [7].

Non-linear depolarization of Rayleigh scattering

We now proceed to calculate the depolarization of the scattered electromagnetic wave of frequency ω_1 when another wave of frequency ω_2 is incident on the scattering system. The intensity component of the scattered wave with oscillations given by the unit vector n , at a point distant by R_0 from the origin, is now

$$(23) \quad I_n = \frac{1}{c_1^4 R_0^2} \langle \ddot{P}_{\sigma} \ddot{P}_{\tau} n_{\sigma} n_{\tau} \rangle_{E_1, E_2}.$$

If the incident wave of intensity I_{01} and velocity c_1 propagates in the Y -direction and observation takes place in that of the X -axis, the degree of depolarization is given by the ratio of the I_y and I_z components and, by (11), (17) and (23), assumes the form

$$(24) \quad D = D_0 + \frac{1}{I_z^{(0)}} \{ I_y^{(2)} - D_0 I_z^{(2)} \} \tilde{E}_2^2,$$

where $D_0 = I_y^{(0)}/I_z^{(0)}$ is the degree of depolarization of the scattered wave E_1 when no other wave is present ($E_2 = 0$). The respective components should be computed from the following expressions, putting therein $n = j$ or $n = k$:

$$(25) \quad I_n^{(0)} = \frac{I_{01}}{R_0^2} \left(\frac{\omega_1}{c_1} \right)^4 \langle A_{\sigma\tau}(\omega_1) A_{\nu\varrho}^*(\omega_2) n_{\sigma} e_{1\tau} n_{\nu} e_{1\varrho} \rangle,$$

$$(26) \quad I_n^{(2)} = \frac{I_{01}}{2c_1^4 R_0^2} \left\langle \left\{ \left[\omega_1^2 (\omega_1 + 2\omega_2)^2 (A_{\sigma\tau}(\omega_1) C_{\nu\varrho\lambda\mu}^*(\omega_1, \omega_2) + C_{\sigma\tau\lambda\mu}(\omega_1, \omega_2) A_{\nu\varrho}^*(\omega_1)) + 2(\omega_1 + \omega_2)^4 B_{\sigma\tau\lambda}(\omega_1, \omega_2) B_{\nu\varrho\mu}^*(\omega_1, \omega_2) \right] e_{2\lambda} e_{2\mu} + \frac{\omega_1^4}{kT} A_{\sigma\tau}(\omega_1) A_{\nu\varrho}^*(\omega_1) [A_{\lambda\mu}(\omega_2) e_{2\lambda} e_{2\mu} - \langle A_{\lambda\mu}(\omega_2) e_{2\lambda} e_{2\mu} \rangle] \right\} n_\sigma e_{1\tau} n_\nu e_{1\varrho} \right\rangle.$$

$I_n^{(0)}$ determines non-perturbed Rayleigh scattering and $I_n^{(2)}$ — the additional non-linear scattering due to the perturbing effect of the second, high intensity electromagnetic wave E_2 .

If, in particular, the vector E_1 of the first, plane polarized wave oscillates in the direction of the X -axis ($e_1 = i$), we have $D_0 = 1$ and Eq. (24) becomes

$$(27) \quad D - 1 = \frac{G_{\text{anis}}}{F_{\text{anis}}} [(e_2 \cdot j)^2 - (e_2 \cdot k)^2] \overline{E_2^2}.$$

The quantities F_{anis} and G_{anis} are obtained directly from Eqs. (25) and (26) by isotropic averaging over all possible directions of the unit vector n , e_1 and e_2 as follows:

$$(28) \quad F_{\text{anis}} = \frac{1}{2} \langle A_{\sigma\tau}(\omega_1) A_{\nu\varrho}^*(\omega_2) (4\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\varrho} \delta_{\tau\nu} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \rangle,$$

$$(29) \quad G_{\text{anis}} = \frac{1}{28} \left\langle \left\{ \left(1 + 2 \frac{\omega_2^2}{\omega_1} \right)^2 [A_{\sigma\tau}(\omega_1) C_{\nu\varrho\lambda\mu}^*(\omega_1, \omega_2) + C_{\sigma\tau\lambda\mu}(\omega_1, \omega_2) A_{\nu\varrho}^*(\omega_1)] + 2 \left(1 + \frac{\omega_2^2}{\omega_1} \right)^4 B_{\sigma\tau\lambda}(\omega_1, \omega_2) B_{\nu\varrho\mu}^*(\omega_1, \omega_2) + \frac{1}{kT} A_{\sigma\tau}(\omega_1) A_{\nu\varrho}^*(\omega_1) A_{\lambda\mu}(\omega_2) \right\} \times \right. \\ \left. \times \left\{ 4\delta_{\sigma\nu} (\delta_{\tau\lambda} \delta_{\varrho\mu} + \delta_{\tau\mu} \delta_{\lambda\varrho}) + 4\delta_{\lambda\mu} (\delta_{\sigma\tau} \delta_{\nu\varrho} + \delta_{\sigma\varrho} \delta_{\tau\nu}) - 10\delta_{\sigma\nu} \delta_{\tau\varrho} \delta_{\lambda\mu} + 11\delta_{\tau\varrho} (\delta_{\sigma\lambda} \delta_{\nu\mu} + \delta_{\sigma\mu} \delta_{\nu\lambda}) + 3 [\delta_{\sigma\tau} (\delta_{\nu\lambda} \delta_{\varrho\mu} + \delta_{\nu\mu} \delta_{\lambda\varrho}) + \delta_{\sigma\varrho} (\delta_{\nu\lambda} \delta_{\tau\mu} + \delta_{\nu\mu} \delta_{\tau\lambda}) + \delta_{\sigma\lambda} (\delta_{\tau\nu} \delta_{\varrho\mu} + \delta_{\nu\varrho} \delta_{\tau\mu}) + \delta_{\sigma\mu} (\delta_{\tau\nu} \delta_{\varrho\lambda} + \delta_{\nu\varrho} \delta_{\tau\lambda}) \right] \right\} \right\rangle.$$

From Eq. (27), the non-linear variation in D produced by the polarized electromagnetic wave of frequency ω_2 is seen to be positive or negative according to whether the vector E_2 oscillates in the direction of Y or Z . In the case of E_2 oscillating parallel to X , we have $D = 1$ meaning that the degree of depolarization undergoes no non-linear variation. Also, Eq. (27) can be applied in the case when E_2 is conveyed by a non-polarized wave; now, however, the factor $[(e_2 \cdot j)^2 - (e_2 \cdot k)^2]$ has to be averaged over all possible directions of the vector e_2 in the plane perpendicular to the direction of propagation of the wave.

For the case of a gas consisting of N axially-symmetric molecules, Eqs. (28) and (29) reduce to (neglecting the terms accounting for hyperpolarizability)

$$(30) \quad F_{\text{anis}} = N \sum_g P_g \{ \alpha_{\parallel}^{gg}(\omega_1) - \alpha_{\perp}^{gg}(\omega_1) \}^2,$$

$$(31) \quad G_{\text{anis}} = \frac{N}{7kT} \sum_g P_g \{ \alpha_{\parallel}^{gg}(\omega_1) - \alpha_{\perp}^{gg}(\omega_1) \}^2 \{ \alpha_{\parallel}^{gg}(\omega_2) - \alpha_{\perp}^{gg}(\omega_2) \},$$

with a_{\parallel} and a_{\perp} denoting, respectively, the polarizabilities in the directions parallel and perpendicular to the symmetry axis of the molecule.

If, in particular, the gas molecules are all in one ground state, by (30) and (31) Eq. (27) reduces to the simple form

$$(32) \quad D - 1 = \frac{a_{\parallel}(\omega_2) - a_{\perp}(\omega_2)}{7kT} [(e_2 \cdot j)^2 - (e_2 \cdot k)^2] \overline{E_2^2}.$$

The formula derived above allows to determine easily the sign and value of the anisotropy of polarizability of the axially symmetric molecule. It is analogous to Rocard's [8] formula for the static case, when $\omega_2 \rightarrow 0$ (cf., moreover, [9]).

Finally, the preceding considerations can be generalized directly to the case of non-linear Raman scattering. For this purpose, utilizing the function (6) with coefficients (10), we have to calculate the electric moment $P_{ng}(t)$ induced in the quantum system as the latter goes over from state n to state g owing to the effect of the two incident electromagnetic waves of frequencies ω_1 and ω_2 , respectively. In the case of molecules presenting no centre of inversion (e.g. tetrahedral CH_4 or CCl_4 molecules), in addition to the usual Raman scattering with frequencies $\omega_{ng} \pm \omega_1$, additional non-linear scattering appears with combinations of the frequencies $\omega_{ng} \pm \omega_1 \pm \omega_2$ and $\omega_{ng} \pm \omega_1 \mp \omega_2$. In the case of molecules possessing a centre of inversion, non-linear scattering appears with combinations of the frequencies $\omega_{ng} \pm \omega_1$ and the frequencies $\omega_{ng} \pm \omega_1 \pm 2\omega_2$, $\omega_{ng} \pm \omega_1 \mp 2\omega_2$, etc. This problem will be discussed in full detail separately.

The author wishes to thank Professor A. Piekara for his encouragement in undertaking the present investigation and for his helpful discussions.

DEPARTMENT OF DIELECTRICS (POZNAŃ), INSTITUTE OF PHYSICS, POLISH ACADEMY OF SCIENCES
(ZAKŁAD DIELEKTRYKÓW (POZNAŃ), INSTYTUT FIZYKI, PAN)

REFERENCES

- [1] R. Braunstein, *Phys. Rev.*, **125** (1962), 475.
- [2] J. A. Armstrong, N. Bloembergen, J. Ducuing and P. S. Pershan, *Phys. Rev.*, **127** (1962), 1918.
- [3] D. A. Kleinman, *Phys. Rev.*, **126** (1962), 1977.
- [4] R. Loudon, *Proc. Phys. Soc. London*, **80** (1962), 952.
- [5] Yoh-Han Pao, *J. Opt. Soc. Amer.*, **52** (1962), 871.
- [6] H. A. Kramers, *Nature*, **113** (1924), 673; **114** (1924), 310.
- [7] A. D. Buckingham, *Proc. Phys. Soc. London*, **B 69** (1956), 344.
- [8] Y. Rocard, *Ann. de Phys.*, **10** (1928), 472.
- [9] S. Kielich, *Acta Phys. Polon.* **23** (1963), 321.