BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences math., astr.
et phys. — Vol. XI, No. 4, 1963

THEORETICAL PHYSICS

Non-linear Optical Effects in Gases. I. Classical Calculation for Spherical Molecules

by

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Presented by A. PIEKARA on February 9, 1963

Introduction

According to the electron theory evolved by Lorentz [1], an atom can be regarded as an isotropic oscillator. Voigt [2] showed that such an atom when placed in a strong d.c. electric field behaves like an anisotropic oscillator whose frequency of oscillations parallel to the field vector is three times that of the oscillations perpendicular to the field. These variations in eigenfrequencies of the oscillator are proportional to the square of the electric field strength and give rise to optical birefringence in the gas, which now presents an assembly of such anisotropic oscillators. The birefringence, generally, is insignificant; however, it can become anomalously large for light of a frequency near an absorption line.

According to Buckingham [3], an atom or spherical molecule should also become optically anisotropic when in the oscillating electric field of a light wave. The intensity of the latter being large enough, the gas can produce optical birefringence even if no d.c. electric field be present. Similarly, in the electric field of an intense light beam, non-linear variations of the dielectric permittivity can appear, as shown by Piekara and the present author [4], [5]. Finally, in addition to the usual Rayleigh scattering [6], the interaction of atoms or spherical molecules with an intense light beam can give rise to non-linear light scattering as considered recently by the present author [7]. As yet, of all the non-linear effects mentioned above, only the one predicted by Voigt has been observed in rarefied sodium vapour in the vicinity of the D line [8]. At present, there is hope of observing the other three non-linear optical effects, as devices exist ("lasers") making possible to produce light beams of very great intensity.

In the relations derived by Buckingham and by Piekara and the present author, account had not been taken explicitly of the dependence of the non-linear optical effects on the frequency of the light wave. It is the aim of the present paper to give a discussion of the dispersion of the non-linear optical effects on the basis of Lorentz's classical electron theory (a treatment based on quantum mechanical perturbation theory is the subject of Part II of this investigation). The author feels justified in dealing with these effects on the classical as distinct from the quantum level, since, indeed, the classical theory of dispersion of the refractive index is in satisfactory agreement with the experimental data. The formulas derived in the course of the present investigation allow to determine with accuracy in what conditions the effects under consideration should be expected to achieve anomalously high values.

Foundations of the theory

We shall consider a gas of volume V containing N like atoms or spherical molecules. Let two plane polarized electromagnetic waves of oscillation frequencies ω_1 and ω_2, respectively, $\omega_1 \neq \omega_2$, be incident on the volume V. We assume the electric field strength $\boldsymbol{E}_1 = \boldsymbol{E}_{01}\, e^{i\omega_1 t}$ conveyed by the wave of frequency ω_1 to be small and assign to it the role of measuring field, whereas that of the other wave, $\boldsymbol{E}_2 = \boldsymbol{E}_{02}\, e^{i\omega_2 t}$, suffices for producing non-linear polarisation of the gas. In the case under consideration, the dipole moment induced in a spherical molecule can be expressed by means of the vector equation (here, let $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$ have the same direction)

$$\boldsymbol{m} = \left\{ a(\omega_1) + \frac{1}{2}\gamma(\omega_1, \omega_2) E_2^2 + \ldots \right\} \boldsymbol{E}_1 , \tag{1}$$

where $a(\omega_1)$ denotes the isotropic polarizability of the molecule dependent on the oscillation frequency ω_1 and accounting for the linear effect produced by the weak measuring field $\boldsymbol{E}_1$. The non-linear polarizability of the molecule due to the square of the intense polarizing field $\boldsymbol{E}_2$ is determined by the hyperpolarizability coefficient $\gamma(\omega_1, \omega_2)$, which depends on the oscillation frequencies ω_1 and ω_2 of the two electric fields.

The dependence of $a(\omega_1)$ and $\gamma(\omega_1, \omega_2)$ on ω_1 and ω_2 in explicit form can be obtained quite easily from Lorentz's classical electron theory [1]. Let the i-th electric charge e_i of a molecule of mass m_i undergo the displacement $\boldsymbol{r}_i$ with respect to its equilibrum position as a result of the oscillating electric fields $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$; its equation of motion can now be written as follows:

$$m_i \ddot{\boldsymbol{r}}_i + m_i \beta_i \dot{\boldsymbol{r}}_i + (k_i - c_i r_i^2)\boldsymbol{r}_i = e_i(\boldsymbol{E}_{01}\, e^{i\omega_1 t} + \boldsymbol{E}_{02}\, e^{i\omega_2 t}) , \tag{2}$$

where k_i and c_i are the coefficients of the elastic forces tying e_i to its equilibrum position, k_i being the coefficient of harmonicity and c_i — that of anharmonicity of the oscillations. In Eq. (2) the term $m_i \beta_i \dot{\boldsymbol{r}}_i$ accounts for damping of the oscillations of the charges, where β_i is called the damping constant.

Let $\omega_i = (k_i/m_i)^{1/2}$ denote the eigenfrequency of the charge e_i; the solution of (2) is now of the form

$$\boldsymbol{r}_i = \frac{e_i \boldsymbol{E}_{01}\, e^{i\omega_1 t}}{m_i(\omega_i^2 - \omega_1^2 + i\beta_i\omega_1)} + \frac{e_i \boldsymbol{E}_{02}\, e^{i\omega_2 t}}{m_i(\omega_i^2 - \omega_2^2 + i\beta_i\omega_2)} + \tag{3}$$

$$+ \frac{3c_i e_i^3 \boldsymbol{E}_{01}\, e^{i\omega_1 t} E_{02}^2\, e^{i2\omega_2 t}}{m_i^4(\omega_i^2 - \omega_1^2 + i\beta_i\omega_1)(\omega_i^2 - \omega_2^2 + i\beta_i\omega_2)^2\,[\omega_i^2 - (\omega_1 + 2\omega_2)^2 + i\beta(\omega_1 + 2\omega_2)]} .$$

With regard to the definition of the dipole moment of the molecule, $\boldsymbol{m} = \sum_i e_i \boldsymbol{r}_i$, we have from Eqs. (1) and (3)

$$\alpha(\omega_1) = \mathrm{Re} \sum_i \frac{e_i^2}{m_i(\omega_i^2 - \omega_1^2 + i\beta_i \omega_1)}, \tag{4}$$

$$\gamma(\omega_1, \omega_2) = \tag{5}$$

$$= \mathrm{Re} \sum_i \frac{6c_i e_i^4}{m_i^4(\omega_i^2 - \omega_1^2 + i\beta_i\omega_1)(\omega_i^2 - \omega_2^2 + i\beta_i\omega_2)^2 [\omega_i^2 - (\omega_1 + 2\omega_2)^2 + i\beta_i(\omega_1 + 2\omega_2)]}.$$

Thus, in addition to the fundamental harmonic oscillations of frequencies ω_1 and ω_2, oscillations of the third harmonic occur with the frequency $\omega_1 + 2\omega_2$.

Now, if the molecular oscillator possesses the only oscillatory eigenfrequency ω_0, the foregoing formulas yield

$$\alpha(\omega_1) = \alpha(0) \frac{\omega_0^2}{\omega_0^2 - \omega_1^2}, \quad \alpha(0) = \sum_i \frac{e_i^2}{m_i \omega_0^2}, \tag{6}$$

$$\gamma(\omega_1, \omega_2) = \gamma(0) \frac{\omega_0^8}{(\omega_0^2 - \omega_1^2)(\omega_0^2 - \omega_2^2)^2 [\omega_0^2 - (\omega_1 + 2\omega_2)^2]}, \tag{7}$$

$$\gamma(0) = 6 \sum_i \frac{c_i e_i^4}{m_i^4 \omega_0^8},$$

where for simplicity we have omitted the terms with damping β_i, and $\alpha(0)$ and $\gamma(0)$ are the polarizability and hyperpolarizability of the molecule at $\omega_1 = \omega_2 = 0$, respectively.

For the case of oscillations of the vectors $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$ directed variously along unit vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$, Eq. (1) has to be replaced by

$$\boldsymbol{m} = \{\alpha(\omega_1)\boldsymbol{e}_1 + \frac{1}{6}\gamma(\omega_1, \omega_2)\, [\boldsymbol{e}_1 + 2(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2)\boldsymbol{e}_2] E_2^2 + \dots\} E_1. \tag{8}$$

Non-linear variation of the dynamical electric permittivity

The relation between the electric permittivity ε of a gas and the mean value of the projection of the dipole moment on the direction of the measuring field, $\langle \boldsymbol{m} \cdot \boldsymbol{e}_1 \rangle_{E_1, E_2}$ in the presence of the fields E_1 and E_2, is given by the well known equation

$$(\varepsilon - 1) E_1 = 4\pi\varrho \langle \boldsymbol{m} \cdot \boldsymbol{e}_1 \rangle_{E_1 E_2}, \tag{9}$$

where $\varrho = N/V$ is the number density of the molecules. On substituting herein Eq. (8), the following expression is obtained for the dynamical electric permittivity:

$$\varepsilon - 1 = 4\pi\varrho \left\{\alpha(\omega_1) + \frac{1}{6}\gamma(\omega_1, \omega_2)\, [1 + 2(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2)^2] \widetilde{E_2^2} + \dots\right\}, \tag{10}$$

the wave-line ($\sim$) denoting the time average.

Eq. (10) leads to the following expression:

$$\Delta\varepsilon = \frac{2\pi}{3}\varrho\gamma(\omega_1,\omega_2)\,[1+2(\boldsymbol{e}_1\cdot\boldsymbol{e}_2)^2]\,\widetilde{E_2^2} \tag{11}$$

for the change in the electric permittivity of the gas, as due to the strong electric field of an electromagnetic wave incident thereon.

If the measuring electric field E_1 varies but very slowly with respect to the rapid oscillations of the polarizing field E_2 (of e.g. optical frequency) or if $\omega_1 \to 0$, Eq. (11) with respect to (7) reduces to (we put $\omega_2 = \omega$, and $\widetilde{E_2^2} = (1/2)\,E_0^2$ with E_0 denoting the amplitude of the wave)

$$\Delta\varepsilon = \frac{1}{3}\pi\varrho\frac{\omega_0^6\gamma(0)}{(\omega_0^2-\omega^2)^2(\omega_0^2-4\omega^2)}\,[1+2(\boldsymbol{e}_1\cdot\boldsymbol{e}_2)^2]\,E_0^2. \tag{12}$$

This formula determines electric saturation as produced in the gas by an intense light beam — an effect previously discussed by Piekara and the present author [4], [5] for light of a frequency very remote from absorption bands. For the case of parallel vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ the quantity $\Delta\varepsilon_{||}$ is largest, whereas if $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are mutually perpendicular $\Delta\varepsilon_{\perp}$ is one third of $\Delta\varepsilon_{||}$.

Optical birefringence

Let us assume the measuring electromagnetic wave to propagate in the direction of the Y-axis; computation from (10) of the dynamical electric permittivity in the directions of the axes X and Z now leads to the expression

$$\varepsilon_z-\varepsilon_x = \frac{4\pi}{3}\varrho\gamma(\omega_1,\omega_2)\,[(\boldsymbol{k}\cdot\boldsymbol{e}_2)^2-(\boldsymbol{i}\cdot\boldsymbol{e}_2)^2]\,\widetilde{E_2^2} \tag{13}$$

determining the birefringence produced in the gas by the strong oscillating electric field $\boldsymbol{E}_2$ ($\boldsymbol{i}$ and $\boldsymbol{k}$ are unit vectors in the directions of the axes X and Z of the laboratory reference system, respectively). Eq. (13) shows that the value and sign of the optical birefringence depends on the direction of oscillations of the electric vector $\boldsymbol{E}_2$. In particular, with $\boldsymbol{E}_2$ oscillating in the direction of the Z-axis ($\boldsymbol{e}_2 = \boldsymbol{k}$), we have by Eqs. (13) and (7):

$$\varepsilon_z-\varepsilon_x = \frac{4\pi}{3}\varrho\frac{\omega_0^8\gamma(0)\widetilde{E_2^2}}{(\omega_0^2-\omega_1^2)(\omega_0^2-\omega_2^2)^2\,[\omega_0^2-(\omega_1+2\omega_2)^2]}. \tag{14}$$

It should be noted that, if the wave $\boldsymbol{E}_2$ is non-polarized and propagates in the direction of Y, birefringence vanishes in accordance with Eq. (13), or is equal to $\pm 1/2$ of the amount given by Eq. (14) according to whether the wave $\boldsymbol{E}_2$ propagates in the direction of Z or of X.

If the frequencies ω_1 and ω_2 are equal or differ but little, Eq. (14) reduces to

$$\varepsilon_z-\varepsilon_x = \frac{2\pi}{3}\varrho\frac{\omega_0^8\gamma(0)E_0^2}{(\omega_0^2-\omega^2)^3(\omega_0^2-9\omega^2)}. \tag{15}$$

At optical frequencies, this formula describes dispersion of the effect predicted by Buckingham [3].

Eq. (14) is also applicable if E_2 is an electrostatic field ($\omega_2 = 0$), yielding the relation

$$(16) \qquad \varepsilon_z - \varepsilon_x = \frac{4\pi}{3} \varrho \frac{\omega_0^4 \gamma(0)}{(\omega_0^2 - \omega^2)^2} E^2,$$

which accounts for Voigt's effect [2].

Non-linear light scattering

Let us assume c_1 to be the propagation velocity of the electromagnetic wave of frequency ω_1. With the wave $E_2 = E_{02}\, e^{i\omega_2 t}$ simultaneously incident on the gas, the intensity of the wave scattered by the latter, as observed at a distance R_0 from the origin of XYZ, is given by the formula

$$(17) \qquad I_n = \frac{N}{c_1^4 R_0^2} \langle (\ddot{\boldsymbol{m}} \cdot \boldsymbol{n})^2 \rangle_{E_1, E_2},$$

wherein the unit vector $\boldsymbol{n}$ determines the direction of oscillation of the electric vector in the scattered wave.

With respect to Eq. (8), the intensity I_n is obtained as follows from (17) on retaining the terms in α^2 and $\alpha\gamma$ (higher order terms are discussed in [7]):

$$(18) \qquad I_n = \frac{N}{R_0^2} \left(\frac{\omega_1}{c_1}\right)^4 \{\alpha^2(\omega_1)(\boldsymbol{e}_1 \cdot \boldsymbol{n})^2 \widetilde{E_1^2} + \\ + \frac{1}{3} \alpha(\omega_1) \gamma(\omega_1, \omega_2) \left[1 + 2\frac{\omega_2}{\omega_1}\right]^2 [(\boldsymbol{e}_1 \cdot \boldsymbol{n})^2 + 2(\boldsymbol{e}_1 \cdot \boldsymbol{n})(\boldsymbol{e}_2 \cdot \boldsymbol{n})(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2)] \widetilde{E_1^2 E_2^2}\},$$

where $\alpha(\omega_1)$ and $\gamma(\omega_1, \omega_2)$ are given by (4) and (5) or by (6) and (7).

In considering scattering produced by a single, extremely intense light beam of frequency ω, the intensity I_n is given by

$$(19) \qquad I_n = \frac{1}{2} \frac{N}{R_0^2} \left(\frac{\omega}{c}\right)^4 \left\{\alpha^2(\omega) + \frac{9}{4} \alpha(\omega) \gamma(\omega) E_0^2\right\} (\boldsymbol{e} \cdot \boldsymbol{n})^2 E_0^2;$$

by (6) and (7), this can be rewritten thus

$$(20) \qquad I_n = \frac{1}{2} \frac{N}{R_0^2} \left(\frac{\omega}{c}\right)^4 \left\{\frac{\omega_0^4 \alpha^2(0)}{(\omega_0^2 - \omega^2)^2} + \\ + \frac{9\omega_0^{10} \alpha(0) \gamma(0)}{4(\omega_0^2 - \omega^2)^4 (\omega_0^2 - 9\omega^2)} E_0^2 + \ldots\right\} (\boldsymbol{e} \cdot \boldsymbol{n})^2 E_0^2.$$

The above formula accounts for both the usual Rayleigh scattering [6] and the additional non-linear scattering [7] in its dependence on the incident light frequency ω.

Discussion

We introduce the following functions of the oscillation frequency ω:

$$f_4 = \frac{\omega_0^4}{(\omega_0^2 - \omega^2)^2}, \qquad f_6 = \frac{\omega_0^6}{(\omega_0^2 - \omega^2)^2 (\omega_0^2 - 4\omega^2)}, \tag{21}$$

$$f_8 = \frac{\omega_0^8}{(\omega_0^2 - \omega^2)^3 (\omega_0^2 - 9\omega^2)}, \qquad f_{10} = \frac{\omega_0^{10}}{(\omega_0^2 - \omega^2)^4 (\omega_0^2 - 9\omega^2)}. \tag{22}$$

The function f_4 describes the dispersion of Voigt's effect (Eq. (16)) and of Rayleigh's scattering (the term linear in the incident light intensity $I_0 = 1/2\, E_0^2$ in Eq. (20)). The functions f_6, f_8 and f_{10} describe, respectively, dispersion of electro-optical saturation (Eq. (12)), dispersion of optical birefringence (Eq. (15)), and dispersion of non-linear light scattering (the second term in Eq. (20)). Hence, Voigt's effect and linear Rayleigh scattering are seen to present but one absorption line for $\omega_0 = \omega$, as in the case of dispersion of refraction, given by the function

$$f_2 = \frac{\omega_0^2}{\omega_0^2 - \omega^2}. \tag{23}$$

The other three optical effects, in addition to this absorption line, exhibit yet another line: electro-optical saturation at $\omega_0 = 2\omega$, whereas optical birefringence and non-linear scattering at $\omega_0 = 3\omega$.

We see from Eqs. (21) and (22) that in the neighbourhood of the resonance line all effects under consideration can exhibit very high values. This suggests that the gases and the experimental conditions should be matched in such a way as to provide for maximal values of the effects investigated. Obviously, quite near the resonance line, their values may differ as a result of forces, not considered here, damping the oscillations of the electric charges (see Eqs. (3)—(5)).

For simple gases, the hyperpolarizability can at the most amount to $\gamma(0) = 3 \times 10^{-36}$ e.s.u., so that Eqs. (12) and (15) now yield

$$\Delta\varepsilon_{\parallel}\, V = \pi N \gamma(0) f_6 E_0^2 = 6 \times 10^{-12} f_6 E_0^2, \tag{24}$$

$$(\varepsilon_z - \varepsilon_x)\, V = \frac{2\pi}{3} N \gamma(0) f_8 E_0^2 = 4 \times 10^{-12} f_8 E_0^2, \tag{25}$$

with N denoting Avogadro's number and V — the molar volume of the gas. Now, with a ruby laser producing radiation with an electric field strength of the order of 3×10^4 V/cm $= 10^2$ e.s.u., Eqs. (24) and (25) yield for a simple gas in normal conditions

$$\Delta\varepsilon_{\parallel} \simeq 10^{-12} f_6, \qquad \varepsilon_z - \varepsilon_x \simeq 10^{-12} f_8.$$

From the above evaluations, it will be inferred that in these conditions the effect of light on the dielectric permittivity of a gas ($\Delta\varepsilon$) should not be accessible to observation. On the other hand, there are good chances of observing optical birefringence ($\varepsilon_z - \varepsilon_x$), as measurements of Kerr's effect in gases have been known to detect variations in the refractive index of the order of 10^{-12}. Moreover, since the optical birefringence as evaluated above can increase by a factor of at least $f_8 = \pm 100$ in the neighbourhood of the absorption line, it should be conveniently accessible to measurement.

In the case of a liquid consisting of spherical molecules, we obtain instead of (24) and (25) the following formulas, if the Lorentz [1] local field is used,

$$\Delta\varepsilon_{\parallel} = \pi\varrho\gamma(0) f_6 \left(\frac{\varepsilon+2}{3}\right)^4 E_0^2, \tag{26}$$

$$\varepsilon_z - \varepsilon_x = \frac{2\pi}{3}\varrho\gamma(0) f_8 \left(\frac{\varepsilon+2}{3}\right)^4 E_0^2. \tag{27}$$

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