

ON NON-LINEAR LIGHT SCATTERING IN GASES

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The present paper deals with non-linear scattering of light in gases, its intensity being given by an equation of the type $I(F) = I_0 + I_2 F^2 + \dots$, wherein I_0 determines the intensity of free light scattering (at $F = 0$) and I_2 accounts for the first perturbation of the scattered light as due to a strong external electric or magnetic field and to the oscillating electric field of the intense incident light beam. It is proved on the example of a gas consisting of axially symmetric molecules that, according to whether F is an external electric field E or magnetic field H , the quantity I_2 is expressed by means of the Kerr constant or Cotton-Mouton constant. In the case of light scattering by a light beam of very great intensity, I_2 is expressed by means of Buckingham's constant. From the equation for $I(F)$, expressions for Rayleigh's ratio S and the depolarization ratio D are derived, discussed for some special cases, and evaluated numerically for several gases.

1. Introduction

A gas whose molecules have to some extent undergone the ordering influence of a strong electric or magnetic field can be generally expected to scatter light otherwise than one whose molecules are free and present random distribution. For the case of a gas of axially symmetric molecules with linear dimensions small as compared to the light wavelength, the problem was considered by Rocard (1928). The effect of a strong electric and magnetic field on the depolarization ratio was recently calculated by Andrews and Buckingham (1960) for the case of a gas possessing molecules of arbitrary symmetry. In addition to the effect of molecular orientation as dealt with previously by Rocard for axially symmetric molecules, Andrews and Buckingham took into account in their theory the effect relating to the hyperpolarizability of the molecules, as produced by the electric or magnetic field. In dense systems, both these effects stand in connection with the angular correlations of the molecules (Kielich 1963).

In the present paper, we shall first calculate the effect of a strong electric or magnetic field on the intensity of the Rayleigh light scattering in gases. We assume for simplicity that the molecules are axially symmetric and that their polarizability is constant. Consequently, we shall not consider the effect of hyperpolarizability (which was computed in an earlier

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paper (Kielich 1961) for the case of spherically symmetric molecules). Such a simplification is justified owing to the molecular hyperpolarizability effect being negligible in the case of anisotropic molecules, as compared with the effect of molecular orientation which plays the essential and decisive rôle. The situation here presents a full analogy with what we encounter in the case of electric or magnetic birefringence, as results from the classical theory of Langevin (1910) and Born (1918). From the equations for the intensity I , formulas for Rayleigh's ratio S and the depolarization ratio D are derived and discussed for several special cases.

As shown by Buckingham (1956), an optically anisotropic molecule undergoes orientation also in the oscillating electric field associated with a light wave, so that the gas becomes birefringent. Hence, a scattering gas illuminated by a very intense light beam should be expected to produce additional, non-linear light scattering as a result of the orientation of its molecules. For this case, an equation accounting for the intensity I is derived in the present paper; this equation is then used for computing S , D and the turbidity τ .

By numerical evaluations, the non-linear variations of S and D are in general insignificant; however, in strongly dipolar vapours or gases, they should be detectable in appropriate experimental conditions. It would be of particular importance to measure the changes in D , since these determine directly the numerical value and the sign of the electric or magnetic anisotropy of the isolated molecule.

2. Intensity of scattered light in the presence of a strong electric field

We consider a system of N identical, noninteracting molecules, and suppose that it is in a strong uniform electric field of strength E . We assume moreover that the wavelength λ of the incident light beam is large with respect to the linear dimensions of the scattering molecules. The intensity of the light scattered by such a system is given as follows:

$$I(E) = \left(\frac{2\pi}{\lambda}\right)^4 \frac{N}{R_0^2} \langle (\mathbf{m} \cdot \mathbf{n})(\mathbf{m} \cdot \mathbf{n})^* \rangle_{\mathbf{E}, E} \quad (1)$$

where \mathbf{m} is the dipole moment induced in the molecule by the oscillating electric field $\vec{C} = \mathbf{A}e^{-2\pi i\nu t}$ associated with the incident light wave, \mathbf{n} — the unit vector describing the vibration of the scattered light transmitted by the Nicol prism at the point of observation separated by a distance R_0 from the origin of the scattering system, and $\mathbf{R}_0 \cdot \mathbf{n} = 0$. The brackets $\langle \quad \rangle_{\mathbf{E}, E}$ denote the statistical average in the presence of the fields \vec{C} and \mathbf{E} , and the asterisk — the complex conjugate.

In the case of axially symmetric molecules, the dipole moment \mathbf{m} can be represented as follows:

$$\mathbf{m} = \alpha \cdot \vec{C} = \alpha \{ (1 - \kappa_a) \mathbf{a} + 3\kappa_a (\mathbf{a} \cdot \mathbf{s}) \mathbf{s} \} \mathbf{A} e^{-2\pi i\nu t}, \quad (2)$$

with the quantities

$$\alpha = \frac{1}{3} (\alpha_{\parallel} + 2\alpha_{\perp}) \quad \text{and} \quad \kappa_a = \frac{\alpha_{\parallel} - \alpha_{\perp}}{3\alpha} \quad (3)$$

denoting the mean optical polarizability and the anisotropy of the optical polarizability of the isolated molecule, respectively; α_{\parallel} is the polarizability along the axis of symmetry and α_{\perp} — the polarizability perpendicular to that axis. The unit vectors \mathbf{s} and \mathbf{a} have the directions of the axis of molecular symmetry and of the amplitude \mathbf{A} of the oscillating electric field \vec{C} , respectively.

On substitution of (2) in Eq. (1), we obtain for an assembly of axially symmetric molecules

$$I(E) = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 N A^2}{R_0^2} \langle (\mathbf{a} \cdot \mathbf{n})^2 + 2\kappa_{\alpha} [3(\mathbf{a} \cdot \mathbf{n})(\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s}) - (\mathbf{a} \cdot \mathbf{n})^2] + \kappa_{\alpha}^2 [9(\mathbf{a} \cdot \mathbf{s})^2 (\mathbf{n} \cdot \mathbf{s})^2 - 6(\mathbf{a} \cdot \mathbf{n})(\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s}) + (\mathbf{a} \cdot \mathbf{n})^2] \rangle_E. \quad (4)$$

Here, the statistical average in the presence of the external electric field E is defined by

$$\langle \Phi \rangle_E = \frac{\int \Phi e^{-\frac{U(\tau, \mathbf{E})}{kT}} d\tau}{\int e^{-\frac{U(\tau, \mathbf{E})}{kT}} d\tau}; \quad (5)$$

$u(\tau, \mathbf{E})$ is the potential energy of the molecule at configuration τ and field strength E , k — Boltzman's constant, and T — the absolute temperature.

For a molecule having the permanent electric dipole moment $\boldsymbol{\mu}$ and electric polarizability tensor $\boldsymbol{\alpha}^e$

$$\begin{aligned} u(\tau, \mathbf{E}) &= u(\tau, 0) - \boldsymbol{\mu} \cdot \mathbf{E} - \frac{1}{2} \mathbf{E} \cdot \boldsymbol{\alpha}^e \cdot \mathbf{E} - \dots \\ &= u(\tau, 0) - \mu(\mathbf{e} \cdot \mathbf{s})E - \frac{1}{2} \alpha^e \{ (1 - \kappa_{\alpha^e}) + 3\kappa_{\alpha^e} (\mathbf{e} \cdot \mathbf{s})^2 \} E^2 - \dots, \end{aligned} \quad (6)$$

where the mean electric polarizability α^e of the isolated molecule and its electric anisotropy κ_{α^e} are defined analogously to (3), and \mathbf{e} is the unit vector in the direction of the applied field \mathbf{E} .

On expanding Eq. (4) in a power series in E and using the energy (6) we obtain, to within the second power of the electric field,

$$I(E) = I_0 + I_2 E^2 + \dots, \quad (7)$$

wherein

$$\begin{aligned} I_0 &= \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 N A^2}{R_0^2} \{ (\mathbf{a} \cdot \mathbf{n})^2 + 2\kappa_{\alpha} [3(\mathbf{a} \cdot \mathbf{n}) \langle (\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s}) \rangle - (\mathbf{a} \cdot \mathbf{n})^2] + \kappa_{\alpha}^2 [9 \langle (\mathbf{a} \cdot \mathbf{s})^2 (\mathbf{n} \cdot \mathbf{s})^2 \rangle - 6(\mathbf{a} \cdot \mathbf{n}) \langle (\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s}) \rangle + (\mathbf{a} \cdot \mathbf{n})^2] \} \end{aligned} \quad (8)$$

is the intensity of the light scattered in the absence of an external electric field ($E = 0$), and

$$\begin{aligned} I_2^e &= \left(\frac{2\pi}{\lambda}\right)^4 \frac{3\alpha^2 \kappa_{\alpha} N A^2}{2R_0^2 kT} \left(3\alpha^e \kappa_{\alpha^e} + \frac{\mu^2}{kT} \right) \{ 2(\mathbf{a} \cdot \mathbf{n}) [\langle (\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s})(\mathbf{e} \cdot \mathbf{s})^2 \rangle - \langle (\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s}) \rangle \langle (\mathbf{e} \cdot \mathbf{s})^2 \rangle] + \kappa_{\alpha} [3 \langle (\mathbf{a} \cdot \mathbf{s})^2 (\mathbf{n} \cdot \mathbf{s})^2 (\mathbf{e} \cdot \mathbf{s})^2 \rangle - \langle (\mathbf{a} \cdot \mathbf{s})^2 (\mathbf{n} \cdot \mathbf{s})^2 \rangle \langle (\mathbf{e} \cdot \mathbf{s})^2 \rangle] - 2(\mathbf{a} \cdot \mathbf{n}) [\langle (\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s})(\mathbf{e} \cdot \mathbf{s})^2 \rangle - \langle (\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s}) \rangle \langle (\mathbf{e} \cdot \mathbf{s})^2 \rangle] \} \end{aligned} \quad (9)$$

is the first non-vanishing contribution determining the influence of a strong electric field on the intensity of the scattered light.

In the absence of external fields, all orientations of the molecule (strictly, of its axis of symmetry \mathbf{s}) are equally probable, so that

$$\begin{aligned}\langle(\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s})\rangle &= \frac{1}{3}(\mathbf{a} \cdot \mathbf{n}), & \langle(\mathbf{e} \cdot \mathbf{s})^2\rangle &= \frac{1}{3}, \\ \langle(\mathbf{a} \cdot \mathbf{s})^2(\mathbf{n} \cdot \mathbf{s})^2\rangle &= \frac{1}{15}[1 + 2(\mathbf{a} \cdot \mathbf{n})^2], \\ \langle(\mathbf{a} \cdot \mathbf{s})(\mathbf{n} \cdot \mathbf{s})(\mathbf{e} \cdot \mathbf{s})^2\rangle &= \frac{1}{15}[(\mathbf{a} \cdot \mathbf{n}) + 2(\mathbf{a} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})], \\ \langle(\mathbf{a} \cdot \mathbf{s})^2(\mathbf{n} \cdot \mathbf{s})^2(\mathbf{e} \cdot \mathbf{s})^2\rangle &= \frac{1}{105}[1 + 2(\mathbf{a} \cdot \mathbf{n})^2 + 2(\mathbf{a} \cdot \mathbf{e})^2 + 2(\mathbf{n} \cdot \mathbf{e})^2 + \\ &+ 8(\mathbf{a} \cdot \mathbf{n})(\mathbf{a} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})].\end{aligned}\quad (10)$$

With respect to the foregoing result for average values at zero external fields, the expressions (8) and (9) become

$$I_0 = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 NA^2}{5R_0^2} \{5(\mathbf{a} \cdot \mathbf{n})^2 + [(\mathbf{a} \cdot \mathbf{n})^2 + 3]\kappa_a^2\}, \quad (11)$$

$$\begin{aligned}I_2^e &= \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 \kappa_a NA^2}{105R_0^2 kT} \left(3\alpha^e \kappa_a^e + \frac{\mu^2}{kT}\right) \{2(7 + 2\kappa_a)[3(\mathbf{a} \cdot \mathbf{n})(\mathbf{a} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e}) - (\mathbf{a} \cdot \mathbf{n})^2] + \\ &+ 3\kappa_a[2(\mathbf{a} \cdot \mathbf{n})^2 + 3(\mathbf{a} \cdot \mathbf{e})^2 + 3(\mathbf{n} \cdot \mathbf{e})^2 - 6(\mathbf{a} \cdot \mathbf{n})(\mathbf{a} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e}) - 2]\}.\end{aligned}\quad (12)$$

The expression (11) for I_0 is analogous to the result derived by Born (1933).

3. The effect of a strong electric field on Rayleigh's ratio

We assume that the reference system $X_1 X_2 X_3$ is attached to the centre of the scattering system, and the system $X'_1 X'_2 X'_3$ — to the point of observation of the scattered light (see, Fig. 1). Consider a primary parallel light beam travelling in the X_2 -direction with unit

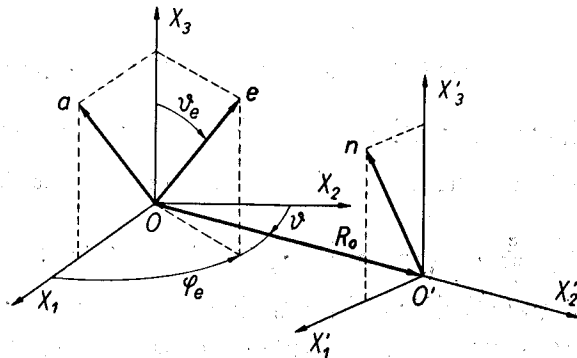


Fig. 1

electric vector \mathbf{a} vibrating in the X_1X_3 — plane. The light scattered is observed in the X_1X_2 - plane (plane of observation) at the angle ϑ with respect to the direction of incidence. In this case the unit vectors \mathbf{a} , \mathbf{n} and \mathbf{e} are given by

$$\begin{aligned}\mathbf{a} &= a_1\mathbf{i}_1 + a_3\mathbf{i}_3, & \mathbf{n} &= n_1\mathbf{i}'_1 + n_3\mathbf{i}'_3, \\ \mathbf{e} &= e_1\mathbf{i}_1 + e_2\mathbf{i}_2 + e_3\mathbf{i}_3,\end{aligned}$$

where $\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3$ and $\mathbf{i}'_1, \mathbf{i}'_2, \mathbf{i}'_3$ are unit vectors in the X_1, X_2, X_3 and X'_1, X'_2, X'_3 directions, respectively. By these equations we have, since $\mathbf{i}_1 \cdot \mathbf{i}'_1 = \mathbf{i}_2 \cdot \mathbf{i}'_2 = \cos \vartheta$,

$$\begin{aligned}\mathbf{a} \cdot \mathbf{n} &= a_3n_3 + a_1n_1 \cos \vartheta, & \mathbf{a} \cdot \mathbf{e} &= a_1e_1 + a_3e_3, \\ \mathbf{n} \cdot \mathbf{a} &= n_3e_3 + n_1(e_1 \cos \vartheta - e_2 \sin \vartheta),\end{aligned}\tag{13}$$

where ϑ is the scattering angle.

In the case when the incident light is unpolarized, and if observation is effected without a Nicol prism, Eqs. (11) and (12) should be averaged over all directions of the unit vectors \mathbf{a} and \mathbf{n} in the planes perpendicular to the propagation direction of the incident and scattered waves, respectively. Since by (13)

$$\begin{aligned}\overline{(\mathbf{a} \cdot \mathbf{n})^2} &= \frac{1}{4}(1 + \cos^2 \vartheta), & \overline{(\mathbf{a} \cdot \mathbf{e})^2} &= \frac{1}{2}(e_1^2 + e_3^2), \\ \overline{(\mathbf{n} \cdot \mathbf{e})^2} &= \frac{1}{2}[e_3^2 + (e_1 \cos \vartheta - e_2 \sin \vartheta)^2], \\ \overline{(\mathbf{a} \cdot \mathbf{n})(\mathbf{a} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})} &= \frac{1}{4}[e_3^2 + (e_1 \cos \vartheta - e_2 \sin \vartheta)e_1 \cos \vartheta],\end{aligned}\tag{14}$$

we obtain from (11) and (12)

$$\begin{aligned}I_0(\vartheta) &= \overline{2I_0} = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 NA^2}{10R_0^2} \{5(1 + \cos^2 \vartheta) + (13 + \cos^2 \vartheta) \kappa_\alpha^2\}, \\ I_2^e(\vartheta) &= \overline{2I_2^e} = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha K_m A^2}{28\pi R_0^2} \{(7 + 2\kappa_\alpha) [(3e_3^2 - 1) + (3e_1^2 - 1) \cos^2 \vartheta - \\ &\quad - 3e_1e_2 \cos \vartheta \sin \vartheta] - 3\kappa_\alpha [(3e_2^2 - 1) \cos^2 \vartheta + 3e_1e_2 \cos \vartheta \sin \vartheta]\},\end{aligned}\tag{16}$$

where in Eq. (16) we introduced the molecular Kerr constant K_m given by the Langevin-Born formula

$$K_m = \frac{4\pi N}{15kT} \alpha \kappa_\alpha \left(3\alpha^e \kappa_{\alpha^e} + \frac{\mu^2}{kT} \right).\tag{17}$$

For a gas consisting of isotropically polarizable molecules, Eqs. (11) and (15) reduce to the well-known Rayleigh formula

$$I_0(\vartheta) = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 NA^2}{2R_0^2} (1 + \cos^2 \vartheta) = \frac{\pi^2(n^2 - 1)^2 V}{2\lambda^4 R_0^2 \rho} (1 + \cos^2 \vartheta) A^2,\tag{18}$$

wherein use was made of the Lorentz-Lorenz formula for the refractive index of a gas:

$$n^2 - 1 = 4\pi \frac{N}{V} \alpha = 4\pi \rho \alpha. \quad (19)$$

Rayleigh's ratio or the scattering ratio for the case when the light scattered by a gas of volume V is observed perpendicularly to the direction of incidence ($\theta = 90^\circ$) is defined as

$$S = \frac{I(90^\circ) R_0^2}{A^2 V}. \quad (20)$$

In the presence of an external electric field this definition and Eqs. (15) and (16) yield

$$S(E) = S_0 + S_2^e E^2 + \dots, \quad (21)$$

Here, S_0 and S_2^e are of the form

$$S_0 = S_0^{\text{is}} \left(1 + \frac{13}{5} \kappa_\alpha^2 \right), \quad (22)$$

$$S_2^e = \frac{S_0^{\text{is}} K_m}{2\pi N \alpha} \left(1 + \frac{2}{7} \kappa_\alpha \right) (3e_3^2 - 1), \quad (23)$$

where

$$S_0^{\text{is}} = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4 \rho} = \frac{1}{2} \left(\frac{2\pi}{\lambda} \right)^4 \alpha^2 \rho \quad (24)$$

is Rayleigh's ratio for isotropically polarizable molecules of a gas.

4. The effect of a strong magnetic field on Rayleigh's ratio

Let us now consider the case of light scattered by a gas in the presence of a strong magnetic field H . The potential energy of a diamagnetic axially symmetric molecule in the field H is given by the equation

$$u(\tau, \mathbf{H}) = u(\tau, 0) - \frac{1}{2} \chi \{ (1 - \kappa_\chi) + 3\kappa_\chi (\mathbf{h} \cdot \mathbf{s})^2 \} H^2 - \dots, \quad (25)$$

where \mathbf{h} is a unit vector having the direction of \mathbf{H} , and

$$\chi = \frac{1}{3} (\chi_{\parallel} + 2\chi_{\perp}), \quad \kappa_\chi = \frac{\chi_{\parallel} - \chi_{\perp}}{3\chi} \quad (26)$$

are the mean magnetic polarizability and the anisotropy of the magnetic polarizability of the isolated molecule, respectively.

If the electric field E of Eqs. (4) and (5) is replaced by the magnetic field H , we obtain analogously to (7), when the energy (25) is used,

$$I(H) = I_0 + I_2^h H^2 + \dots, \quad (27)$$

where I_0 is again given by (11) and I_2^h is of the form

$$I_2^h = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 \chi \kappa_\alpha \kappa_\chi NA^2}{35R_0^2 kT} \{2(7 + 2\kappa_\alpha) [3(\mathbf{a} \cdot \mathbf{n})(\mathbf{a} \cdot \mathbf{h})(\mathbf{n} \cdot \mathbf{h}) - (\mathbf{a} \cdot \mathbf{n})^2] + 3\kappa_\alpha [2(\mathbf{a} \cdot \mathbf{n})^2 + 3(\mathbf{a} \cdot \mathbf{h})^2 + 3(\mathbf{n} \cdot \mathbf{h})^2 - 6(\mathbf{a} \cdot \mathbf{n})(\mathbf{a} \cdot \mathbf{h})(\mathbf{n} \cdot \mathbf{h}) - 2]\}. \quad (28)$$

By the definition of Eq. (20) and with Eq. (27) we obtain

$$S(H) = S_0 + S_2^h H^2 + \dots, \quad (29)$$

where the contribution determining the effect of a strong magnetic field on Rayleigh's ratio is given by

$$S_2^h = \frac{S_0^{\text{is}} C_m}{2\pi N \alpha} \left(1 + \frac{2}{7} \kappa_\alpha\right) (3h_3^2 - 1), \quad (30)$$

with

$$C_m = \frac{4\pi N}{5kT} \alpha \chi \kappa_\alpha \kappa_\chi \quad (31)$$

denoting the molecular Cotton-Mouton constant of a gas, as resulting from the Langevin theory (1910).

5. Nonlinear change of the depolarization ratio

The depolarization ratio is defined as

$$D = \frac{I_{\parallel}}{I_{\perp}}, \quad (32)$$

where I_{\parallel} and I_{\perp} are the intensity of the scattered components vibrating parallel and perpendicularly to the plane of observation, respectively. Substituting the expressions (11), (12) and (13) in Eq. (7) and assuming $n_1 = 1$, $n_3 = 0$ for the I_{\parallel} component and $n_1 = 0$, $n_3 = 1$ for the I_{\perp} component, we obtain by the definition of Eq. (32) for the depolarization ratio in the presence of an external electric field

$$D(E) = D_0 + D_2^e E^2 + \dots, \quad (33)$$

wherein

$$D_0 = \frac{5a_1^2 \cos^2 \vartheta + (3 + a_1^2 \cos^2 \vartheta) \kappa_\alpha^2}{5a_3^2 + (3 + a_3^2) \kappa_\alpha^2} \quad (34)$$

is the depolarization ratio at zero external field and

$$D_2^e = \frac{5K_m}{28\pi N \alpha [5a_3^2 + (3 + a_3^2) \kappa_\alpha^2]} \{2(7 + 2\kappa_\alpha) [3(a_1^2 e_1 + a_1 a_3 e_3) (e_1 \cos^2 \vartheta - e_2 \cos \vartheta \sin \vartheta) - a_1^2 \cos^2 \vartheta] + 3\kappa_\alpha [2(a_1^2 \cos^2 \vartheta - 1) + 3(a_1 e_1 + a_3 e_3)^2 + 3(e_1 \cos \vartheta - e_2 \sin \vartheta)^2 - 6(a_1^2 e_1 + a_1 a_3 e_3) (e_1 \cos^2 \vartheta - e_2 \cos \vartheta \sin \vartheta)] - 2(7 + 2\kappa_\alpha) D_0 [a_3^2 (3e_3^2 - 1) + 3a_1 a_3 e_1 e_3] - 3\kappa_\alpha D_0 [3a_1^2 e_1^2 - (3e_3^2 + 2)(a_3^2 - 1)]\}. \quad (35)$$

If the light scattered is observed at an angle of $\vartheta = 90^\circ$, we obtain from (34) and (35), when the incident light is plane polarized with its electric vector vibrating (i) parallel to the plane of observation ($a_1 = 1$, $a_3 = 0$),

$$D_0 = 1, \quad D_2^e = \frac{15K_m}{28\pi N\alpha\kappa_\alpha} (e_2^2 - e_3^2), \quad (36)$$

and (ii) perpendicular thereto ($a_1 = 0$, $a_3 = 1$),

$$D_0 = \frac{3\kappa_\alpha^2}{5 + 4\kappa_\alpha^2}, \quad (37)$$

$$D_2^e = -\frac{5K_m}{28\pi N\alpha(5 + 4\kappa_\alpha^2)} \{3\kappa_\alpha(3e_1^2 - 1) + 2D_0(7 + 2\kappa_\alpha)(3e_3^2 - 1)\}. \quad (38)$$

For measurements at $\vartheta = 90^\circ$ with an incident unpolarized beam, $\overline{a_1^2} = \overline{a_3^2} = \frac{1}{2}$, $\overline{a_1 a_3} = 0$ and Eqs. (34) and (35) yield

$$D_0 = \frac{6\kappa_\alpha^2}{5 + 7\kappa_\alpha^2}, \quad (39)$$

$$D_2^e = \frac{5K_m}{28\pi N\alpha(5 + 7\kappa_\alpha^2)} \{3\kappa_\alpha(1 + D_0)(3e_2^2 - 1) - 2D_0(7 + 2\kappa_\alpha)(3e_3^2 - 1)\}. \quad (40)$$

Eqs. (37) and (39) are known as the Cabannes-Gans formulas for the depolarization ratios of the light scattered by a gas at $E = 0$. Eqs. (38) and (40), when written in explicite form, are found to be identical with formulas derived by Andrews and Buckingham (1960).

From the foregoing considerations, the simplest expressions for the coefficients,

$$D_0 = \frac{I_0^{\parallel}}{I_0^{\perp}}, \quad D_2^e = \frac{1}{I_0^{\perp}} (I_2^{\parallel} - D_0 I_2^{\perp}), \quad (41)$$

are obtained when the incident light beam is polarized with its electric vector oscillating in a plane parallel to that of observation and when $\vartheta = 90^\circ$. In this case, the change in D due to the effect on the gas of a strong electric field directed arbitrarily is given with respect to Eqs. (33) and (36) by the following simple formula:

$$D(E) - 1 = \frac{15K_m}{28\pi N\alpha\kappa_\alpha} (e_2^2 - e_3^2) E^2. \quad (42)$$

From this formula it is obvious that, if the signs of κ_α and K_m are the same for the scattering gas, the sign of the change in D will depend solely on that of the function (see, Fig. 1)

$$g_e = e_2^2 - e_3^2 = \sin^2 \vartheta_e \sin^2 \varphi_e - \cos^2 \vartheta_e \quad (43)$$

determining the direction of the field E in the system of reference $X_1 X_2 X_3$. In particular, with E lying in the plane $X_2 X_3$ perpendicular to the plane of observation ($\varphi_e = 90^\circ$), we have

$$g_e = \sin^2 \vartheta_e - \cos^2 \vartheta_e = \begin{cases} 1 & \text{for } \vartheta_e = 90^\circ, \\ 0 & \text{for } \vartheta_e = 45^\circ, \\ -1 & \text{for } \vartheta_e = 0^\circ. \end{cases} \quad (44)$$

Consequently, the change in D is negative if E is directed along the X_3 -axis, zero if E acts in the X_2X_3 -plane at an angle of 45° , and positive with E in the direction of propagation of the incident light beam (X_2 -axis).

Since, in a gas consisting of non-interacting molecules, these scatter light independently of one another, we can illustrate the conclusions to be drawn from Eq. (44) by the example of a single molecule. The change in D , which with respect to Eqs. (33), (36) and (41) can be expressed as follows:

$$\Delta D = D(E) - 1 = \frac{1}{I_0^\perp} (I_2^\parallel - I_2^\perp) E^2, \quad (45)$$

will now depend on how the external electric field orients the axis of maximum polarizability of the axially symmetric molecule (or its dipole moment, if present). Clearly, with this axis directed along X_3 , we shall have $I_2^\perp > I_2^\parallel$ and, by (45), the change in D will be negative; conversely, with the molecule's axis directed parallel to the direction of propagation of the light beam, $I_2^\perp < I_2^\parallel$ yielding positive ΔD ; finally, if the axis lies in the X_2X_3 -plane and subtends an angle $\vartheta_e = 45^\circ$ with the X_3 -axis, $I_2^\perp = I_2^\parallel$ and $\Delta D = 0$. The signs of ΔD as discussed above change to the opposite if κ_α and K_m differ in sign for the gas under consideration.

In the presence of an external magnetic field, the formulas for D are derived similarly. We shall restrict ourselves to writing the simplest one, which is the analogon of Eq. (42) and results immediately from (27) and from the definition of Eq. (32):

$$D(H) - 1 = \frac{15C_m}{28\pi N\alpha\kappa_\alpha} (h_2^2 - h_3^2) H^2. \quad (46)$$

On substituting the constant (17) with $\mu = 0$ in Eq. (42), and the constant (31) in Eq. (46), and on assuming that both E and H have the direction of X_3 , we obtain Rocard's formulas¹

$$D(E) - 1 = - \frac{3\alpha^e \kappa_{\alpha^e}}{7kT} E^2 = - \frac{\alpha_{\parallel}^e - \alpha_{\perp}^e}{7kT} E^2, \quad (47)$$

$$D(H) - 1 = - \frac{3\chi \kappa_\chi}{7kT} H^2 = - \frac{\chi_{\parallel} - \chi_{\perp}}{7kT} H^2, \quad (48)$$

which allow to determine immediately the numerical value and the sign of the electric and magnetic anisotropy of an axially-symmetric molecule.

6. Light scattering by an intense light beam

Similarly to Eq. (7), the intensity of the light scattered by a very intense light beam is obtained in the form

$$I(\mathcal{C}) = I_0 + I_2 \widetilde{\mathcal{C}}^2 + \dots, \quad (49)$$

¹ Rocard's paper (1928) contains some insignificant computational errors as a result of which his formulas for D differ from Eqs. (47) and (48) of the present paper by a factor of $4/3$ at the terms in E^2 and H^2 .

where

$$I_2 = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^3 \kappa_\alpha^2 N A^2}{35 R_0^2 k T} \{28(\mathbf{a} \cdot \mathbf{n})^2 + [5(\mathbf{u} \cdot \mathbf{n})^2 + 3] \kappa_\alpha\} \quad (50)$$

with $\widetilde{\mathcal{C}}^2$ denoting the time mean square of \mathcal{C} .

By (14) and (49), Rayleigh's ratio for the light scattered at an angle ϑ is given by

$$S(\mathcal{C}, \vartheta) = S_0(\vartheta) + S_2(\vartheta) \widetilde{\mathcal{C}}^2 + \dots, \quad (51)$$

wherein

$$S_0(\vartheta) = \frac{1}{5} S_0^{\text{is}} \{5(1 + \cos^2 \vartheta) + (13 + \cos^2 \vartheta) \kappa_\alpha^2\}, \quad (52)$$

$$S_2(\vartheta) = \frac{S_0^{\text{is}} B_m}{56\pi N \alpha} \{28(1 + \cos^2 \vartheta) + (17 + 5 \cos^2 \vartheta) \kappa_\alpha\}, \quad (53)$$

with

$$B_m = \frac{4\pi N}{5kT} \alpha^2 \kappa_\alpha^2 \quad (54)$$

being the molecular constant of the optical birefringence or the molecular Buckingham constant of a gas (see Buckingham 1956, Kielich and Piekara 1959).

On integrating Eq. (51) over the surface of the scattering sphere, we obtain for the "turbidity" of a gas

$$\tau(\mathcal{C}) = \int_0^{2\pi} \int_0^\pi S(\mathcal{C}, \vartheta) \sin \vartheta d\vartheta d\varphi = \tau_0 + \tau_2 \widetilde{\mathcal{C}}^2 + \dots, \quad (55)$$

where

$$\tau_0 = \frac{16}{3} \pi S_0^{\text{is}} (1 + 2\kappa_\alpha^2), \quad (56)$$

and

$$\tau_2 = \frac{2}{3} \frac{S_0^{\text{is}} B_m}{N \alpha} (2 + \kappa_\alpha). \quad (57)$$

In this case the depolarization ratio is given as follows:

$$D(\mathcal{C}) = D_0 + D_2 \widetilde{\mathcal{C}}^2 + \dots, \quad (58)$$

where D_0 is given by (34), and

$$D_2 = \frac{5B_m}{28\pi N \alpha [5a_3^2 + (3 + a_3^2) \kappa_\alpha^2]} \{3\kappa_\alpha(1 - D_0) + (28 + 5\kappa_\alpha) (a_1^2 \cos^2 \vartheta - D_0 a_3^2)\}. \quad (59)$$

From Eqs. (34) and (59) we have for the special cases

(i) $a_1 = 1$, $a_3 = 0$,

$$D_0 = \frac{5 \cos^2 \vartheta + (3 + \cos^2 \vartheta) \kappa_\alpha^2}{3\kappa_\alpha^2}, \quad (60)$$

$$D_2 = \frac{5B_m \{3\kappa_\alpha(1 - D_0) + (28 + 5\kappa_\alpha) \cos^2 \vartheta\}}{84\pi N \alpha \kappa_\alpha^2}, \quad (61)$$

(ii) $a_1 = 0, a_3 = 1,$

$$D_0 = \frac{3\kappa_\alpha^2}{5 + 4\kappa_\alpha^2}, \quad (62)$$

$$D_2 = \frac{5B_m\{3\kappa_\alpha - 4(7 + 2\kappa_\alpha)D_0\}}{28\pi N\alpha(5 + 4\kappa_\alpha^2)}, \quad (63)$$

(iii) $\overline{a_1^2} = \overline{a_3^2} = \frac{1}{2},$

$$D_0 = \frac{5 \cos^2 \vartheta + (6 + \cos^2 \vartheta) \kappa_\alpha^2}{5 + 7\kappa_\alpha^2}, \quad (64)$$

$$D_2 = \frac{5B_m\{6\kappa_\alpha(1 - D_0) + (28 + 5\kappa_\alpha)(\cos^2 \vartheta - D_0)\}}{28\pi N\alpha(5 + 7\kappa_\alpha^2)}. \quad (65)$$

If the light scattered is observed perpendicularly to the direction of incidence, Eqs. (60) and (61) reduce to

$$D_0 = 1, \quad D_2 = 0. \quad (66)$$

In this special case, D is seen not to be subject to nonlinear change.

7. Discussion

We shall now proceed to the numerical evaluation of the effect of a strong electric or magnetic field on Rayleigh's ratio and the depolarization ratio of some gases.

Let us represent Eq. (21) in the following form:

$$\frac{S(E) - S_0}{S_0} = \frac{K_m}{2\pi N\alpha} \left(\frac{1 + \frac{2}{7} \kappa_\alpha}{1 + \frac{13}{5} \kappa_\alpha^2} \right) (3e_3^2 - 1) E^2, \quad (67)$$

or, if the anisotropy κ_α of the molecule is very small:

$$\frac{S(E) - S_0}{S_0} = \frac{K_m}{2\pi N\alpha} (3e_3^2 - 1) E^2. \quad (68)$$

For carbon disulphide we have the following data: $\alpha = 8.75 \times 10^{-24} \text{ cm}^3$, $\kappa_\alpha = 0.37$ and, for $t = 20^\circ\text{C}$, $K_m = 427 \times 10^{-12}$; by Eqs. (42) and (67), this yields

$$D(E) - 1 = 37 \times 10^{-12} (e_2^2 - e_3^2) E^2,$$

$$\frac{S(E) - S_0}{S_0} = 13 \times 10^{-12} (3e_3^2 - 1) E^2.$$

For an electric field of intensity $E = 10^3$ e.s.u. and applied along the X_3 -axis ($e_2 = 0$, $e_3 = 1$) we have:

$$D(E) - 1 = -3.7 \times 10^{-5} \quad \text{and} \quad \frac{S(E) - S_0}{S_0} = 2.6 \times 10^{-5}.$$

In the case of nitrobenzene, $\alpha = 12.9 \times 10^{-24} \text{ cm}^3$, $\kappa_\alpha = 0.2$ and $K_m = 11988 \times 10^{-12}$,

so that Eqs. (42) and (67) yield

$$D(E) - 1 = 1380 \times 10^{-12} (e_2^2 - e_3^2) E^2 = -13.8 \times 10^{-4},$$

$$\frac{S(E) - S_0}{S_0} = 222 \times 10^{-12} (3e_3^2 - 1) E^2 = 4.4 \times 10^{-4}.$$

The foregoing evaluations show that in the case of substances such as the vapour of nitrobenzene the changes produced by a strong electric field in both D and S should be accessible to experimental detection. The situation is less favourable in the case of nondipolar gases, the changes in D and S being insignificant, though detectable in appropriate experimental conditions.

Analogously to (67), Eq. (29) can be rewritten as follows:

$$\frac{S(H) - S_0}{S_0} = \frac{C_m}{2\pi N\alpha} \frac{\left(1 + \frac{2}{7} \kappa_\alpha\right)}{\left(1 + \frac{13}{5} \kappa_\alpha^2\right)} (3h_3^2 - 1) H^2, \quad (69)$$

or, in approximation:

$$\frac{S(H) - S_0}{S_0} = \frac{C_m}{2\pi N\alpha} (3h_3^2 - 1) H^2. \quad (70)$$

Substituting herein and in Eq. (46) the data for benzene: $\kappa_\alpha = -0.19$, $\alpha = 10.3 \times 10^{-24} \text{ cm}^3$ and $C_m = 335 \times 10^{-17}$, we obtain

$$D(H) - 1 = -4.7 \times 10^{-17} (h_2^2 - h_3^2) H^2, \quad \frac{S(H) - S_0}{S_0} = 8.4 \times 10^{-17} (3h_3^2 - 1) H^2.$$

Thus, the changes in D and S for benzene, as caused by a magnetic field of the order of 10^5 e.m.u., are of the order of 10^{-6} , which is very close to the theoretical limits of experimental possibilities.

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