THEORY OF LIGHT SCATTERING BY NONLINEAR DEFORMABLE SPHERICAL MOLECULES OF A GAS

by

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S u m m a r y. In this paper Rayleigh's classic theory is extended for the case of scattering of light by nonlinear deformable spherical gas molecules. The nonlinear molecule deformation is caused by a strong static electric or magnetic field, or by the electric field of a strong light beam. A general formula for the scattered light is given, and the depolarization ratio and Rayleigh coefficient are obtained therefrom. The formulas are used for some special cases and can be applied in order to describe the hyperpolarizability of spherical gas molecules.

1. INTRODUCTION

The theory of light scattering by gases consisting of spherical molecules small compared to the wave length is due to Lord R a y-l e i g h [1]. In the present paper Rayleigh's theory will be extended to the case when the scattering spherical molecules are deformed by a strong electric or magnetic field.

In absence of an external electric or magnetic field, the spherical molecules polarize themselves under the influence of the weak electric field of the incident light equally in all directions (isotropic polarization). Their polarizability is a scalar (a) and we have to do with Rayleigh classic scattering. If, however, the scattering gas is placed in a strong electric field E, then its molecules experience in addition a nonlinear polarization which is different for the two directions: parallel and perpendicular to the direction of the field E. Depending on whether the external electric field E is parallel or perpendicular to the light vector, the molecule has the following total optic polarizability:

$$\pi_{\parallel} = a + \frac{1}{2}\gamma_{\parallel}E^2 + \frac{1}{24}\varepsilon_{\parallel}E^4 + \ldots , \qquad (1.1)$$

$$\pi_\perp = a + \frac{1}{2}\gamma_\perp E^2 + \frac{1}{24}\varepsilon_\perp E^4 + \ldots \qquad (1.2)$$

The coefficients $\gamma_\parallel$, $\varepsilon_\parallel$ and $\gamma_\perp$, $\varepsilon_\perp$ describe the electro–optic nonlinear deformation of the spherical molecule in the direction parallel and perpendicular to the direction of the applied electric field E, respectively. One can call them the electro–optic deformability of the molecule, or simply its hyperpolarizability. The hypothesis of square deformation of the molecule was already used by V o i g t [2] in order to explain the electric birefringence of atomic gases.

On the basis of equations (1.1) and (1.2), a general formula for the scattered light in the case under consideration is developed out of which formulas for the depolarization ratio D and Rayleigh ratio S are obtained. Measurements of D and S when possible, enable us to calculate in a direct way the numerical values of the hyperpolarizability γ and ε for the spherical molecules under investigation. The order of magnitude of the above effects is close to the limits of present measuring possibilities. Therefore, the problem under consideration is, as yet, only of theoretical significance.

2. INTENSITY OF SCATTERED LIGHT

Let us consider a gaseous system consisting of N identical molecules. In the presence of an external static electric field E the intensity of the light scattered by the gas is [3]:

$$I_n(E) = \left(\frac{2\pi}{\lambda}\right)^4 \frac{NI_0}{R_0^2} \langle \pi_{\alpha\beta}\,\pi_{\gamma\delta}\,n_\alpha\,a_\beta\,n_\gamma\,a_\delta \rangle_E, \qquad (2.1)$$

where I_0 denotes the intensity of the incident light and R_0 is the distance between the point of observation and the centre of the scattering system. $\mathbf{n} = (n_1, n_2, n_3)$ is the unit vector perpendicular to the direction of observation $(\mathbf{R}_0 \cdot \mathbf{n} = 0)$ and describing the direction of vibration transmitted by the Nicol prism, and $\mathbf{a} = (a_1, a_2, a_3)$ — a unit vector having the direction of the electric field of the incident light wave of amplitude $\mathbf{A} = \mathbf{a}\,A$. The bracket $\langle\ \rangle_E$ denotes the average statistical value in the presence of the electric field E:

$$\langle \Phi \rangle_E = \frac{\int \Phi(\tau, \mathbf{E}) \exp\left\{-\dfrac{u(\tau, \mathbf{E})}{kT}\right\} d\tau}{\int \exp\left\{-\dfrac{u(\tau, \mathbf{E})}{kT}\right\} d\tau}, \qquad (2.2)$$

where integrations are over all molecular configurations τ; k is Boltzmann's constant, and T — the absolute temperature.

The total potential energy, $u(\tau, \mathbf{E})$, and the optical polarizability tensor, $\pi_{\alpha\beta}(\tau, \mathbf{E})$, of a molecule in an external electric field $\mathbf{E}$ are given by:

$$u(\tau, \mathbf{E}) = u(\tau, 0) - \mu_\alpha E_\alpha - \frac{1}{2} a_{\alpha\beta} E_\alpha E_\beta - \frac{1}{6} b_{\alpha\beta\gamma} E_\alpha E_\beta E_\gamma - \frac{1}{24} c_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta - \ldots, \quad (2.3)$$

$$\pi_{\alpha\beta}(\tau, \mathbf{E}) = a_{\alpha\beta} + \beta_{\alpha\beta:\gamma} E_\gamma + \frac{1}{2} \gamma_{\alpha\beta:\gamma\delta} E_\gamma E_\delta + \frac{1}{6} \delta_{\alpha\beta:\gamma\delta\varepsilon} E_\gamma E_\delta E_\varepsilon +$$

$$+ \frac{1}{24} \varepsilon_{\alpha\beta:\gamma\delta\varepsilon\eta} E_\gamma E_\delta E_\varepsilon E_\eta + \ldots, \quad (2.4)$$

where μ_α is the permanent dipole moment of an isolated molecule, and $a_{\alpha\beta}$ and $a_{\alpha\beta}$ — its electric and optic polarizability tensors, whereas $b_{\alpha\beta\gamma}$, $c_{\alpha\beta\gamma\delta}$ and $\beta_{\alpha\beta:\gamma}$, $\gamma_{\alpha\beta:\gamma\delta}$, $\delta_{\alpha\beta:\gamma\delta\varepsilon}$, $\varepsilon_{\alpha\beta:\gamma\delta\varepsilon\eta}$ are the electro-electric and electro-optic hyperpolarizability tensors, respectively.

If the isolated molecule possesses the spherical symmetry, all odd order tensor elements vanish:

$$\mu_\alpha = b_{\alpha\beta\gamma} = \beta_{\alpha\beta:\gamma} = \delta_{\alpha\beta:\gamma\delta\varepsilon} = 0, \quad (2.5)$$

whereas those of even order reduce to isotropic tensors given by the following relationships:

$$a_{\alpha\beta} = a\delta_{\alpha\beta}, \qquad c_{\alpha\beta\gamma\delta} = \frac{1}{3} c \left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} \right),$$

$$a_{\alpha\beta} = a\delta_{\alpha\beta}, \qquad \gamma_{\alpha\beta:\gamma\delta} = \gamma_\perp \delta_{\alpha\beta}\delta_{\gamma\delta} + \frac{1}{2}(\gamma_{\parallel} - \gamma_\perp)(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}),$$

$$\varepsilon_{\alpha\beta:\gamma\delta\varepsilon\eta} = \frac{1}{3} \varepsilon_\perp \delta_{\alpha\beta} \left(\delta_{\gamma\delta}\delta_{\varepsilon\eta} + \delta_{\gamma\varepsilon}\delta_{\delta\eta} + \delta_{\gamma\eta}\delta_{\delta\varepsilon} \right) + \frac{1}{12}(\varepsilon_{\parallel} - \varepsilon_\perp)\{\delta_{\alpha\gamma}(\delta_{\beta\delta}\delta_{\varepsilon\eta} + \delta_{\beta\varepsilon}\delta_{\delta\eta} + \delta_{\beta\eta}\delta_{\delta\varepsilon}) +$$

$$+ \delta_{\alpha\delta}(\delta_{\beta\gamma}\delta_{\varepsilon\eta} + \delta_{\beta\varepsilon}\delta_{\gamma\eta} + \delta_{\beta\eta}\delta_{\gamma\varepsilon}) + \delta_{\alpha\varepsilon}(\delta_{\beta\gamma}\delta_{\delta\eta} + \delta_{\beta\delta}\delta_{\gamma\eta} + \delta_{\beta\eta}\delta_{\gamma\delta}) +$$

$$+ \delta_{\alpha\eta}(\delta_{\beta\gamma}\delta_{\delta\varepsilon} + \delta_{\beta\delta}\delta_{\gamma\varepsilon} + \delta_{\beta\varepsilon}\delta_{\gamma\delta})\}, \quad (2.6)$$

with

$$\delta_{\alpha\beta} = \begin{cases} 1 \text{ for } \alpha = \beta, \\ 0 \text{ for } \alpha \neq \beta. \end{cases}$$

Here, the scalar quantities

$$a = \frac{1}{3} a_{\alpha\alpha}, \qquad a = \frac{1}{3} a_{\alpha\alpha}, \qquad c = \frac{1}{5} c_{\alpha\alpha\beta\beta} \quad (2.7)$$

are the mean optic and electric polarizability of the molecule and its mean electro-electric hyperpolarizability, respectively.

If the electronic vibration frequencies of the molecule parallel and perpendicular to the electric field E are set equal, then we have for the mean hyperpolarizabilities:

$$\gamma = \gamma_{||} = 3\gamma_{\perp} = \frac{1}{5}\,\gamma_{aa\beta\beta}\,,$$

$$\varepsilon = \varepsilon_{||} = 5\varepsilon_{\perp} = \frac{1}{7}\,\varepsilon_{aa\beta\beta\gamma\gamma}\,. \qquad (2.8)$$

By (2.5) and (2.6), the expansions (2.3) and (2.4) may be rewritten in the form:

$$u\,(\tau, \mathbf{E}) = u\,(\tau, 0) - \frac{1}{2}\,aE^2 - \frac{1}{24}\,cE^4 - \dots, \qquad (2.9)$$

$$\pi_{a\beta}(\tau, \mathbf{E}) = a\delta_{a\beta} + \frac{1}{2}\,[\gamma_{\perp}\delta_{a\beta} + (\gamma_{||} - \gamma_{\perp})e_a e_\beta]\,E^2 +$$

$$+ \frac{1}{24}\,[\varepsilon_{\perp}\delta_{a\beta} + (\varepsilon_{||} - \varepsilon_{\perp})\,e_a e_\beta]\,E^4 + \dots, \qquad (2.10)$$

wherein $\mathbf{e} = (e_1, e_2, e_3)$ is a unit vector in the direction of the static electric field $\mathbf{E} = \mathbf{e}\,E$.

For the total optical polarizability of the molecule in the presence of an external electric field, we can get from eq. (2.10) the following formula:

$$\pi_{a\beta}n_a a_\beta = a\,(\mathbf{n}\cdot\mathbf{a}) + \frac{1}{2}\,[\gamma_{\perp}\,(\mathbf{n}\cdot\mathbf{a}) + (\gamma_{||} - \gamma_{\perp})\,(\mathbf{n}\cdot\mathbf{e})\,(\mathbf{a}\cdot\mathbf{e})]\,E^2 +$$

$$+ \frac{1}{24}\,[\varepsilon_{\perp}\,(\mathbf{n}\cdot\mathbf{a}) + (\varepsilon_{||} - \varepsilon_{\perp})\,(\mathbf{n}\cdot\mathbf{e})\,(\mathbf{a}\cdot\mathbf{e})]\,E^4 + \dots \qquad (2.11)$$

If, in particular, the unit vectors $\mathbf{n}$, $\mathbf{a}$ and $\mathbf{e}$ are parallel, i. e. $\mathbf{n}\cdot\mathbf{a} = \mathbf{n}\cdot\mathbf{e} = \mathbf{a}\cdot\mathbf{e} = 1$, eq. (2.11) reduces to (1.1); when the vectors $\mathbf{n} = \mathbf{a}$ are perpendicular to $\mathbf{e}$ ($\mathbf{n}\cdot\mathbf{a} = 1$, $\mathbf{n}\cdot\mathbf{e} = \mathbf{a}\cdot\mathbf{e} = 0$), eq. (2.11) yields (1.2).

Substituting (2.9) and (2.11) in (2.1), the fundamental equation for $I_n(E)$ may be written as follows:

$$I_n(E) = \left(\frac{2\pi}{\lambda}\right)^4 \frac{NI_0}{R_0^2}\left\{a^2(\mathbf{n}\cdot\mathbf{a})^2 + a\,[\gamma_{\perp}\,(\mathbf{n}\cdot\mathbf{a})^2 + \right.$$

$$+ (\gamma_{||} - \gamma_{\perp})(\mathbf{n}\cdot\mathbf{a})(\mathbf{n}\cdot\mathbf{e})(\mathbf{a}\cdot\mathbf{e})]\,E^2 + \frac{1}{4}\,[\gamma_{\perp}^2\,(\mathbf{n}\cdot\mathbf{a})^2 +$$

$$+ 2\gamma_{\perp}(\gamma_{||} - \gamma_{\perp})(\mathbf{n}\cdot\mathbf{a})(\mathbf{n}\cdot\mathbf{e})(\mathbf{a}\cdot\mathbf{e}) + (\gamma_{||} - \gamma_{\perp})^2(\mathbf{n}\cdot\mathbf{e})^2(\mathbf{a}\cdot\mathbf{e})^2]\,E^4 +$$

$$\left. + \frac{1}{12}\,a[\varepsilon_{\perp}\,(\mathbf{n}\cdot\mathbf{a})^2 + (\varepsilon_{||} - \varepsilon_{\perp})(\mathbf{n}\cdot\mathbf{a})(\mathbf{n}\cdot\mathbf{e})(\mathbf{a}\cdot\mathbf{e})]\,E^4 + \dots\right\}. \qquad (2.12)$$

Eq. (2.12) determines the general form of the classical theory of light scattering by spherical molecules nonlinear deformable in a strong static electric field E.

3. DEPOLARIZATION RATIO OF SCATTERED LIGHT

The depolarization ratio of the light scattered is defined as follows:

$$D = \frac{I_{\shortparallel}}{I_{\perp}}, \tag{3.1}$$

where $I_{\shortparallel}$ is the intensity of the scattered component vibrating in the plane of observation ($X_1 X_2$ — plane, see fig.1), and $I_{\perp}$ is the perpendicular component ("Rayleigh component").
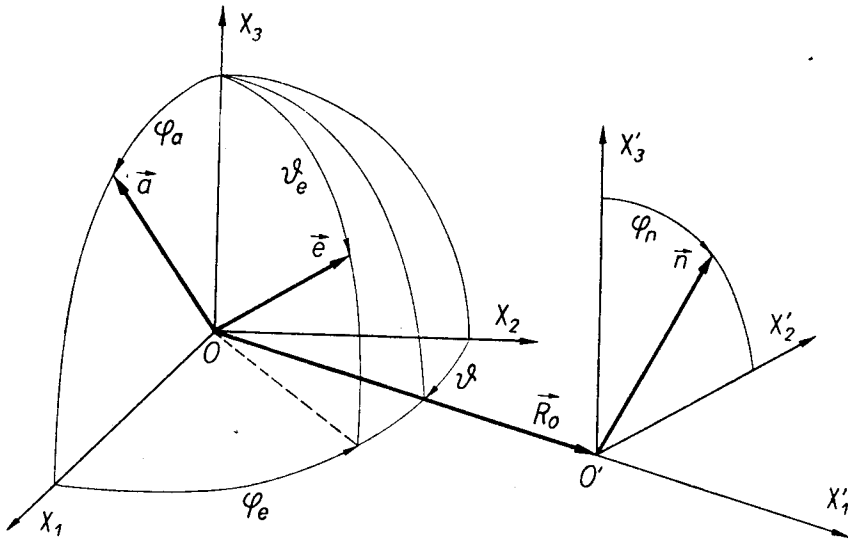

Fig. 1. A primary parallel light beam is travelling in the X_2 — direction with unit electric vector **a** vibrating in the $X_1 X_3$ — plane at an angle φ_a to the X_3 — direction. The light scattered is observed in the $X_1 X_2$ — plane (plane of observation) at the angle ϑ with respect to the direction of incidence. **e** denotes a unit vector describing the direction of the applied electric field **E**

According to eq. (2.12), D must be an even function of E:

$$D(E) = D_0 + D_2 E^2 + D_4 E^4 + \dots, \tag{3.2}$$

where

$$D_0 = \left(\frac{J_{\shortparallel}}{J_{\perp}}\right)_{E=0} \tag{3.3}$$

is the depolarization ratio when the light is scattered in absence of an external field $(E=0)$, and

$$D_2 = \frac{1}{2} \left\{ \frac{d^2 D}{dE^2} \right\}_{E=0} = \frac{1}{2} \left\{ \frac{1}{J_\perp} \left(\frac{d^2 J_\parallel}{dE^2} - D_0 \frac{d^2 J_\perp}{dE^2} \right) \right\}_{E=0} ,$$

$$D_4 = \frac{1}{24} \left\{ \frac{d^4 D}{dE^4} \right\}_{E=0} = \frac{1}{24} \left\{ \frac{1}{J_\perp} \left(\frac{d^4 J_\parallel}{dE^4} - D_0 \frac{d^4 J_\perp}{dE^4} \right) - 12 \frac{D_2}{J_\perp} \frac{d^2 J_\perp}{dE^2} \right\}_{E=0} , \quad (3.4)$$

are contributions determining the influence of a strong electric field on the depolarization ratio.

The unit vectors, **a**, **n** and **e** are given by the equations (see fig. 1.):

$$\mathbf{a} = a_1 \mathbf{i}_1 + a_3 \mathbf{i}_3 \ , \quad \mathbf{n} = n_2 \mathbf{i}'_2 + n_3 \mathbf{i}'_3 \ ,$$

$$\mathbf{e} = e_1 \mathbf{i}_1 + e_2 \mathbf{i}_2 + e_3 \mathbf{i}_3 \ , \quad (3.5)$$

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, and:

$$a_1 = \sin \varphi_a \ , \quad a_3 = \cos \varphi_a \ , \quad n_2 = \sin \varphi_n \ , \quad n_3 = \cos \varphi_n \ ,$$

$$e_1 = \sin \vartheta_e \cos \varphi_e \ , \quad e_2 = \sin \vartheta_e \sin \varphi_e \ , \quad e_3 = \cos \vartheta_e \ , \quad (3.6)$$

By (3.5), we have:

$$\mathbf{a} \cdot \mathbf{n} = -a_1 n_2 \cos \vartheta + a_3 n_3 \ ,$$

$$\mathbf{a} \cdot \mathbf{e} = a_1 e_1 + a_3 e_3 \ ,$$

$$\mathbf{e} \cdot \mathbf{n} = -(e_1 \cos \vartheta - e_2 \sin \vartheta) n_2 + e_3 n_3 \ , \quad (3.7)$$

where ϑ is the scattering angle.

Substituting the expressions (3.7) in eq. (2.12) and assuming $n_2 = 1$, $n_3 = 0$ for the $I_\parallel$ component, and $n_2 = 0$, $n_3 = 1$ for the $I_\perp$ component, we obtain for the expansion coefficients D_0, D_2 and D_4 defined by (3.3) and (3.4):

$$D_0 = \frac{a_1^2}{a_3^2} \cos^2 \vartheta \ , \quad (3.8)$$

$$D_2 = \frac{1}{a a_3^2} \left\{ \gamma_\perp (a_1^2 \cos^2 \vartheta - D_0 a_3^2) + (\gamma_\parallel - \gamma_\perp) [(a_1^2 e_1 + a_1 a_3 e_3) (e_1 \cos \vartheta - e_2 \sin \vartheta) \cos \vartheta - \right.$$

$$\left. - D_0 (a_1 a_3 e_1 + a_3^2 e_3) e_3] \right\} , \quad (3.9)$$

$$D_4 = \frac{1}{12 a^2 a_3^2} \left\{ (3 \gamma_\perp^2 + a \varepsilon_\perp) (a_1^2 \cos^2 \vartheta - D_0 a_3^2) + \right.$$

$$+ [6 \gamma_\perp (\gamma_\parallel - \gamma_\perp) + a(\varepsilon_\parallel - \varepsilon_\perp)] [(a_1^2 e_1 + a_1 a_3 e_3) (e_1 \cos \vartheta - $$

$$- e_2 \sin \vartheta) \cos \vartheta - D_0 (a_1 a_3 e_1 + a_3^2 e_3) e_3] +$$

$$+ 3 (\gamma_{||} - \gamma_{\perp})^2 (a_1 e_1 + a_3 e_3)^2 [(e_1 \cos \vartheta - e_2 \sin \vartheta)^2 - D_0 e_3^2] -$$

$$- 12 a D_2 [\gamma_{\perp} a_3^2 + (\gamma_{||} - \gamma_{\perp})(a_1 a_3 e_1 + a_3^2 e_3) e_3] \Big\} . \tag{3.10}$$

We shall now proceed to apply the foregoing formulas to some special cases:

(i) If the incident light is plane polarized with its electric vector parallel to the X_3 — direction, i. e., $a_1 = 0$ and $a_3 = 1$, we have:

$$D_0 = 0, \quad D_2 = 0,$$

$$D_4 = \frac{1}{4} \left(\frac{\gamma_{||} - \gamma_{\perp}}{a} \right)^2 (e_1 \cos \vartheta - e_2 \sin \vartheta)^2 e_3^2 . \tag{3.11}$$

When observation of the scattered light is carried out at the angle $\vartheta = 90°$, the expression (3.11) reduces to:

$$D_4 = \frac{1}{4} \left(\frac{\gamma_{||} - \gamma_{\perp}}{a} \right)^2 \cos^2 \vartheta_e \sin^2 \vartheta_e \sin^2 \varphi_e . \tag{3.12}$$

(ii) For unpolarized incident light, $\overline{a_1^2} = \overline{a_3^2} = \frac{1}{2}$, $\overline{a_1 a_3} = 0$, and eqs. (3.8), (3.9) and (3.10) yield:

$$D_0 = \cos^2 \vartheta ,$$

$$D_2 = - \left(\frac{\gamma_{||} - \gamma_{\perp}}{a} \right) [(e_3^2 - e_1^2) \cos^2 \vartheta + e_1 e_2 \cos \vartheta \sin \vartheta] ,$$

$$D_4 = \frac{1}{12} \Big\{ \left[6 \left(\frac{\gamma_{\perp}}{a} \right) \left(\frac{\gamma_{||} - \gamma_{\perp}}{a} \right) - \left(\frac{\varepsilon_{||} - \varepsilon_{\perp}}{a} \right) \right] [(e_3^2 - e_1^2) \cos^2 \vartheta + e_1 e_2 \cos \vartheta \sin \vartheta] +$$

$$+ 3 \left(\frac{\gamma_{||} - \gamma_{\perp}}{a} \right)^2 [(e_1^2 + e_3^2)(e_1 \cos \vartheta - e_2 \sin \vartheta)^2 +$$

$$+ (3 e_3^2 - 5 e_1^2) e_3^2 \cos^2 \vartheta + 4 e_1 e_2 e_3^2 \cos \vartheta \sin \vartheta] \Big\} . \tag{3.13}$$

If the electric field E is perpendicular to the plane of observation ($e_1 = e_2 = 0$, $e_3 = 1$), eqs. (3.13) reduce to

$$D_0 = \cos^2 \vartheta , \quad D_2 = - \left(\frac{\gamma_{||} - \gamma_{\perp}}{a} \right) \cos^2 \vartheta ,$$

$$D_4 = \frac{1}{12} \Big\{ 9 \left(\frac{\gamma_{||} - \gamma_{\perp}}{a} \right)^2 + 6 \left(\frac{\gamma_{\perp}}{a} \right) \left(\frac{\gamma_{||} - \gamma_{\perp}}{a} \right) - \left(\frac{\varepsilon_{||} - \varepsilon_{\perp}}{a} \right) \Big\} \cos^2 \vartheta . \tag{3.14}$$

4. RAYLEIGH'S RATIO

For a gas of volume V Rayleigh's ratio is defined as

$$S = \frac{\overline{I}_n}{I_0} \frac{R_0^2}{V}, \qquad 4.1)$$

where $\overline{I}_n$ is the value of I_n given by eq. (2.12), 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 wave, respectively. Namely, by (3.7) we have:

$$\overline{(\mathbf{n} \cdot \mathbf{a})^2} = \frac{1}{2}(1 + \cos^2 \vartheta),$$

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

$$\overline{(\mathbf{n} \cdot \mathbf{e})^2 (\mathbf{a} \cdot \mathbf{e})^2} = \frac{1}{2}(e_1^2 + e_3^2)[e_3^2 + (e_1 \cos \vartheta - e_2 \sin \vartheta)^2]. \qquad (4.2)$$

By definition (4.1), with eqs. (2.12) and (4.2), the following result for Rayleigh's ratio in the presence of an external electric field is obtained:

$$S(E) = S_0 + S_2 E^2 + S_4 E^4 + \ldots, \qquad (4.3)$$

where

$$S_0 = \frac{1}{2}\left(\frac{2\pi}{\lambda}\right)^4 a^2 \varrho \,(1 + \cos^2 \vartheta) = \frac{\pi^2 (n^2 - 1)^2}{2\,\lambda^4 \varrho}(1 + \cos^2 \vartheta) \qquad (4.4)$$

is the well-known Rayleigh formula for the light scattered by a gas in the absence of an external electric field; n is the refractive index of the gas and $\varrho = N/V$ — the number density of molecules. The coefficients S_2 and S_4 have the form:

$$S_2 = \frac{S_0}{1 + \cos^2 \vartheta}\left\{\left(\frac{\gamma_\perp}{a}\right)(1 + \cos^2 \vartheta) + \left(\frac{\gamma_\parallel - \gamma_\perp}{a}\right)[(e_1 \cos \vartheta - e_2 \sin \vartheta) e_1 \cos \vartheta + e_3^2]\right\},$$

$$S_4 = \frac{S_0}{12(1 + \cos^2 \vartheta)}\left\{\left[3\left(\frac{\gamma_\perp}{a}\right)^2 + \left(\frac{\varepsilon_\perp}{a}\right)\right](1 + \cos^2 \vartheta) + \left[6\left(\frac{\gamma_\perp}{a}\right)\left(\frac{\gamma_\parallel - \gamma_\perp}{a}\right) + \right.\right.$$

$$\left. + \left(\frac{\varepsilon_\parallel - \varepsilon_\perp}{a}\right)\right][(e_1 \cos \vartheta - e_2 \sin \vartheta) e_1 \cos \vartheta + e_3^2] +$$

$$+ 3\left(\frac{\gamma_\parallel - \gamma_\perp}{a}\right)^2 [(e_1 \cos \vartheta - e_2 \sin \vartheta)^2 + e_3^2](e_1^2 + e_3^2)\right\}. \qquad (4.5)$$

If the scattered light is observed perpendicularly to the direction of incidence ($\vartheta = 90°$), eqs. (4.4) and (4.5) yield:

$$S_0^{90} = \frac{\pi^2 (n^2-1)^2}{2\,\lambda^4 \varrho},\qquad(4.6)$$

$$S_2^{90} = S_0^{90}\left\{\left(\frac{\gamma_\perp}{a}\right) + \left(\frac{\gamma_{||}-\gamma_\perp}{a}\right)e_3^2\right\},$$

$$S_4^{90} = \frac{1}{12}S_0^{90}\left\{3\left(\frac{\gamma_\perp}{a}\right)^2 + \left(\frac{\varepsilon_\perp}{a}\right) + \left[6\left(\frac{\gamma_\perp}{a}\right)\left(\frac{\gamma_{||}-\gamma_\perp}{a}\right) + \left(\frac{\varepsilon_{||}-\varepsilon_\perp}{a}\right)\right]e_3^2 + \right.$$

$$\left. + 3\left(\frac{\gamma_{||}-\gamma_\perp}{a}\right)^2 (e_1^2+e_3^2)(e_2^2+e_3^2)\right\}.\qquad(4.7)$$

For the light intensity scattered at the angle ϑ, when the electric vector E is parallel to the X_3 — direction ($e_1 = e_2 = 0$, $e_3 = 1$), (4.5) becomes

$$S_2 = \frac{S_0}{1+\cos^2\vartheta}\left\{\left(\frac{\gamma_{||}}{a}\right) + \left(\frac{\gamma_\perp}{a}\right)\cos^2\vartheta\right\},$$

$$S_4 = \frac{S_0}{12(1+\cos^2\vartheta)}\left\{3\left(\frac{\gamma_{||}}{a}\right)^2 + 3\left(\frac{\gamma_\perp}{a}\right)^2\cos^2\vartheta + \left(\frac{\varepsilon_{||}}{a}\right) + \left(\frac{\varepsilon_\perp}{a}\right)\cos^2\vartheta\right\}.\qquad(4.8)$$

5. ELECTRIC BIREFRINGENCE

By definition of the Kerr constant of a gas,

$$K = \frac{n_{||}-n_\perp}{n}\,\frac{1}{E^2} = \frac{2\pi (n^2+2)^2}{9n^2}\,\varrho\left(\frac{\pi_{||}-\pi_\perp}{E^2}\right),\qquad(5.1)$$

and eqs. (1.1) and (1.2), we obtain the expansion:

$$K = K_0 + K_2 E^2 + \ldots \qquad(5.2)$$

Here [4]

$$K_0 = \frac{2\pi (n^2+2)^2}{9n^2}\,\varrho \lim_{E\to 0}\left\{\frac{\pi_{||}-\pi_\perp}{E^2}\right\} = \frac{\pi(n^2+2)^2}{9n^2}\,\varrho\,(\gamma_{||}-\gamma_\perp)\qquad(5.3)$$

is the usual Kerr constant determining Voigt's deformational effect, whereas

$$K_2 = \frac{1}{2}\left\{\frac{d^2K}{dE^2}\right\}_{E=0} = \frac{\pi (n^2+2)^2}{108n^2}\,\varrho\,(\varepsilon_{||}-\varepsilon_\perp)\qquad(5.4)$$

characterizes the influence of the strong electric field on the Kerr constant.

From these formulas it is seen that the Kerr constant K of a gas, the Rayleigh ratio S, and the depolarization ratio D, for light scattering

in the presence of an external electric field, are expressed in terms of the same molecular quantities γ and ε.

6. LIGHT SCATTERING IN THE PRESENCE OF A STRONG MAGNETIC FIELD

All theoretical considerations presented in the foregoing sections can be transferred automatically to the case of light scattering in the presence of a strong magnetic field H. Optic polarizability of the molecules is then described by an equation similar to equation (2.11):

$$\pi_{\alpha\beta},(\tau,\mathbf{H})\ n_a a_{\beta} = \alpha\,(\mathbf{n}\cdot\mathbf{a}) + \frac{1}{2}\left[\eta_{\perp}\,(\mathbf{n}\cdot\mathbf{a}) + (\eta_{\shortparallel}-\eta_{\perp})\,(\mathbf{n}\cdot\mathbf{h})\,(\mathbf{a}\cdot\mathbf{h})\right]H^2 +$$

$$+\frac{1}{24}\left[\Phi_{\perp}\,(\mathbf{n}\cdot\mathbf{a}) + (\Phi_{\shortparallel}-\Phi_{\perp})\,(\mathbf{n}\cdot\mathbf{h})(\mathbf{a}\cdot\mathbf{h})\right]H^4 + \ldots \qquad (6.1)$$

Here $\eta_{\shortparallel}$, $\Phi_{\shortparallel}$ and $\eta_{\perp}$, $\Phi_{\perp}$ are the magneto–optic hyperpolarizabilities determining the changes of optic polarizability of the molecule, caused by a magnetic field in the direction parallel and perpendicular to this field, respectively; $\mathbf{h}$ denotes a unit vector describing the direction of the applied magnetic field $\mathbf{H}$.

One can see that in order to get formulas for I_n, D or S, in the presence of a magnetic field, it is sufficient to start from eq. (2.12), replacing the hyperpolarizabilities $\gamma_{\shortparallel}, \gamma_{\perp}, \varepsilon_{\shortparallel}$ and $\varepsilon_{\perp}$ by $\eta_{\shortparallel}, \eta_{\perp}$, $\Phi_{\shortparallel}$ and $\Phi_{\perp}$, and the field E by $-H$.

7. INFLUENCE OF A STRONG LIGHT BEAM ON RAYLEIGH'S RATIO

If the intensity of the incident light is high enough, the oscillating electric field can be considered as a nonlinear deformation factor of a spherical molecule. In this case the Rayleigh ratio is defined by the following expansion

$$S = S_0 + S_2 A^2 + S_4 A^4 + \ldots, \qquad (7.1)$$

where A is the amplitude of the light electric vector. S_0 is described by (4.4), and the coefficients S_2 and S_4 are given by:

$$S_2 = \frac{3}{4}\left(\frac{\gamma}{\alpha}\right)S_0,$$

$$S_4 = \frac{5}{96}\left\{3\left(\frac{\gamma}{\alpha}\right)^2 + \left(\frac{\varepsilon}{\alpha}\right)\right\}S_0, \qquad (7.2)$$

where γ and ε are the optic hyperpolarizabilities of the molecule.

One can also consider the case of two mutually independent light beams, one of which has small intensity, and the other — high intensity; the electric field of the second beam causes a nonlinear deformation of the molecules of the scattering gas. Let us suppose, as before, that the first light beam is unpolarized propagating in the X_2 — direction, whereas the second beam, propagating in the X_3 — direction is plane polarized with its electric vector parallel to the X_1 — axis. In this case one can obtain again equation (7.1); except that the coefficients S_2 and S_4 are expressed in the following way:

$$S_2 = \frac{S_0}{2(1 + \cos^2 \vartheta)} \left\{ \left(\frac{\gamma_\perp}{a} \right) + \left(\frac{\gamma_{||}}{a} \right) \cos^2 \vartheta \right\},$$

$$S_4 = \frac{S_0}{32(1 + \cos^2 \vartheta)} \left\{ 3 \left(\frac{\gamma_\perp}{a} \right)^2 + 3 \left(\frac{\gamma_{||}}{a} \right)^2 \cos^2 \vartheta + \left(\frac{\varepsilon_\perp}{a} \right) + \left(\frac{\varepsilon_{||}}{a} \right) \cos^2 \vartheta \right\}. \qquad (7.3)$$

If both light beams are unpolarized and propagate in the X_2 — direction, then the coefficients S_2 and S_4 in the expansion (7.1) are given by:

$$S_2 = \frac{1}{4} \left(\frac{\gamma_{||} + \gamma_\perp}{a} \right) S_0,$$

$$S_4 = \frac{1}{64} \left\{ 3 \left(\frac{\gamma_{||}^2 + \gamma_\perp^2}{a^2} \right) + \left(\frac{\varepsilon_{||} + \varepsilon_\perp}{a} \right) \right\} S_0. \qquad (7.4)$$

8. DISCUSSION

Let us draw attention to an interesting fact arising from formulas (4.7). Namely, if the electric field E is applied along the X_3 — axis, then we can get

$$S_2^{90} = \left(\frac{\gamma_{||}}{a} \right) S_0^{90},$$

$$S_4^{90} = \frac{1}{12} \left\{ 3 \left(\frac{\gamma_{||}}{a} \right)^2 + \left(\frac{\varepsilon_{||}}{a} \right) \right\} S_0^{90}. \qquad (8.1)$$

When the electric field E is applied perpendicularly to the X_3 — direction formulas (4.7) yield

$$S_2^{90} = \left(\frac{\gamma_\perp}{a} \right) S_0^{90},$$

$$S_4^{90} = \frac{1}{12} \left\{ 3 \left(\frac{\gamma_\perp}{a} \right)^2 + \left(\frac{\varepsilon_\perp}{a} \right) \right\} S_0^{90}. \qquad (8.2)$$

We can see that measurements of the ratios S_2/S_0 and S_4/S_0 for the cases when the direction of E is parallel or perpendicular to the X_3 — axis gives directly the values of the deformation of a spherical molecule in these directions, i. e., numerical values of $\gamma_\parallel$, $\varepsilon_\parallel$ and $\gamma_\perp$ and $\varepsilon_\perp$, respectively. This circumstance has a very important meaning, because we cannot get this on the basis of measurements of the electric birefringence alone, which, as follows from formulas (5.3) and (5.4), allow only to describe the difference of these hyperpolarizabilities, i. e., $\gamma_\parallel - \gamma_\perp$ and $\varepsilon_\parallel - \varepsilon_\perp$.

Substituting the coefficients (3.14) in the expansion (3.2), and assuming, for simplicity, that the condition (2.8) is satisfied, we obtain

$$D(E) = \left\{ 1 - \frac{2}{3}\left(\frac{\gamma}{a}\right)E^2 + \left[\frac{4}{9}\left(\frac{\gamma}{a}\right)^2 - \frac{1}{15}\left(\frac{\varepsilon}{a}\right)\right]E^4 + \ldots \right\}\cos^2\vartheta . \qquad (8.3)$$

For the CCl_4 molecule we have the following data: $a = 10.5 \cdot 10^{-24}$ cm^3 and $\gamma = 6.5 \cdot 10^{-36}$ e. s. u. (see [5]), then formula (8.3), to the accuracy of E^2, yields:

$$D(E) = \left\{ 1 - 0.4 \cdot 10^{-12}E^2 \right\}\cos^2\vartheta .$$

Thus, for an electric field of high intensity, $E = 2 \cdot 10^3$ e. s. u. and we can expect, in the best case, a change of $D(E)$ to be of the order of 10^{-6}, which is very close to the theoretical limits of experimental possibilities.   •

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