Vibrational-rotational optical polarization of molecular gases in a constant electric field

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We report a theoretical study of the vibrational-rotational polarization of a molecular gas in parallel and crossed constant electric and alternating high-frequency electromagnetic fields. We obtain formulae for the polarization of the gas at the frequencies 0, ω, 2ω, and 3ω which make it possible to estimate the contribution of this mechanism to optical rectification, the nonlinear variation of the refractive index of the medium at the carrier frequency, and the generation of second and third harmonics.

The optical properties of a medium are determined by the way its polarization $P(E)$, i.e., the dipole moment per unit volume, depends on the electric field strength E. For $E \ll E_a$ ($E_a \sim 10^9$ V/cm is the strength of the atomic field) the polarization can be written in the form

$$P(E) = \sum_{i=1}^{\infty} \chi^{(i)} E^i, \tag{1}$$

where the $\chi^{(i)}$ are the susceptibilities of the appropriate orders. In weak fields it is sufficient to restrict oneself to the terms linear in E. With the appearance of strong radiation sources nonlinear effects $\sim E^i$ ($i \geqslant 2$) start to play an important role.

Nonlinear polarization of a molecular gas has many causes. These are the electron nonlinearity and electrostriction, as well as various thermal effects.[1] In the present paper we consider theoretically only the nonlinearity with $i \leqslant 3$ which is connected with the oscillations and rotations of the constant and linearly induced dipole moments of the molecules in the field.

The way the rotational susceptibility depends on the characteristics of the molecules, the field, and the medium for molecular gases in a static field was found at the beginning of this century (Langevin, Debye). The vibrational-rotational susceptibilities in a field of a plane-polarized monochromatic light wave of frequency ω were determined in Ref. 2. In that case the dipole moment of a separate molecule oscillates with frequencies which are multiples of ω and, in particular, with twice the frequency. However, the polarization of the gas has no component at the frequency 2ω. The doubled frequency drops out of the polarization owing to the symmetry of the distribution of the molecular axes relative to the field E and the $\theta = \pi/2$ plane (θ is the angle between the field and the molecular axis). To generate the doubled frequency one must diminish the symmetry of the distribution of the molecule axes. This can be realized by using together with the field of the wave also a constant field $\mathbf{E}_0$. Experiments carried out in such a field by Mayer *et al.*[3,4] made it possible to determine the mean nonlinear second- and third-order polarizations at the frequency 2ω.[3] One of the aims of the present paper is to get a theoretical estimate of the contribution of the vibrational-rotational mechanism to the generation of the second harmonic.

1. Let the electric field acting on a molecule be a superposition of a static field $\mathbf{E}$ and an alternating field $\mathbf{E}_\omega$ of a monochromatic wave. We consider the case when these fields are collinear:

$$\mathbf{E} = \mathbf{i}_E (E_0 + E_\omega \cos \omega t). \tag{2}$$

We have dropped here the spatial part of the phase of the monochromatic wave. This is permissible when the statistical averaging over the angle θ is carried out for molecules concentrated in a volume $v \ll \lambda^3$ ($\lambda = 2\pi c \omega^{-1}$). Assuming that 10^3 molecules are sufficient for a statistical average one finds easily that for $T = 300$ K and $\lambda = 10^{-4}$ cm we can use Eq. (2) for pressures larger than 20 mm Hg.

We shall consider symmetric-top molecules in the vibrational ground state. For those the principal moments of inertia are equal to $J_1 = J_2 = J$ and J_3. In the particular case of a rigid rotator (diatomic and linear molecules) we have $J_3 = 0$. In a frame of reference fixed to the molecule the linear polarizability of the molecule is characterized by an ellipsoid of revolution with semiaxes $\alpha_1(\omega) = \alpha_2(\omega) = \alpha_\omega^{is}$ and $\alpha_3(\omega)$ while $\alpha_3(\omega)$ and the constant dipole moment of the molecule $\mathbf{p}$ (if there is one) are along the axis of the top. The "orienting polarizability"[4] determining together with p the moment of the forces exerted on the molecule by the electric field will be equal to $\alpha_\omega = \alpha_3(\omega) - \alpha_\omega^{is}$. We consider the case of polarization in a nonabsorbing medium. In the present paper we shall not be concerned with the electron nonlinearity connected with the internal molecular degrees of freedom and we shall only consider the linear component of its polarizability.

Owing to the isotropy of the gas, the polarization vector is directed along the field. The components of the molecular dipoles perpendicular to the field drop out on averaging. The polarization P will be equal to

$$P = N \int p_E(\theta) \, dw(\theta) = N \overline{p_E}, \tag{3}$$

where

$$p_E(\theta) = p \cos \theta + (\alpha_0 E_0 + \alpha_\omega E_\omega \cos \omega t) \cos^2 \theta + \alpha_0^{is} E_0 + \alpha_\omega^{is} E_\omega \cos \omega t, \tag{4}$$

N is the number of molecules per unit volume, $p_E(\theta)$ is the component of the (constant and induced) molecular dipole moment along the field, and $dw(\theta)$ is the θ-distribution of the molecular axes.

In order to determine $dw(\theta)$ we must find the Hamiltonian $H(p_i, q_i, t)$, i.e., the total energy of the molecule in the field E. It consists of the rotational kinetic energy $T(p_i, q_i)$

($q_i = \theta, \varphi, \psi$ are the Euler angles and $p_i = M_\theta, M_\varphi, M_\psi$ the corresponding angular momenta) and the potential energy $U(q_i, t)$ of the constant and induced dipoles in the field E:

$$H(p_i, q_i, t) = T(p_i, q_i) + U(q_i, t),$$
$$T(p_i, q_i) = M_\theta^2/2J + (M_\varphi - M_\psi \cos\theta)^2/2J \sin^2\theta + M_\psi^2/2J_3,$$
$$U(q_i, t) = U_0(q_i) + F(q_i, t),$$

$$U_0(q_i) = -pE_0\cos\theta - \left(\frac{\alpha_\omega E_\omega^2}{4} + \frac{\alpha_0 E_0^2}{2}\right)\cos^2\theta,$$

$$F(q_i, t) = -\left(pF_\omega\cos\theta + \frac{\alpha_0 + \alpha_\omega}{2}E_0E_\omega\cos^2\theta\right)\cos\omega t$$
$$- \frac{\alpha_\omega E_\omega^2}{4}\cos^2\theta\cos 2\omega t.$$

It is convenient to write down the Hamiltonian, splitting off the time dependence as a separate term:

$$H(p_i, q_i, t) = H_0(p_i, q_i) + F(q_i, t),$$
$$H_0(p_i, q_i) = T(p_i, q_i) + U_0(q_i). \tag{6}$$

The Hamiltonian equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

give for the motion of the molecular axis with respect to the angle θ the equation

$$J\ddot\theta = -\frac{\partial H_0}{\partial\theta} + f_\omega(\theta)\cos\omega t + f_{2\omega}(\theta)\cos 2\omega t, \tag{7}$$

where

$$f_\omega(\theta) = -[pE_\omega\sin\theta + (\alpha_0 + \alpha_\omega)E_0E_\omega\sin\theta\cos\theta],$$
$$f_{2\omega}(\theta) = -\frac{\alpha_\omega E_\omega^2}{2}\sin\theta\cos\theta.$$

Since H depends on the time the solution of the problem of the equilibrium θ-distribution of the molecular axes in an alternating external field is found to depend on the length of the period $\tau = 2\pi\omega^{-1}$ of the applied field. If τ is longer than the time τ_r of relaxation of the system to its equilibrium distribution, the distribution is at any moment close to the equilibrium distribution corresponding to the energy at that time. If τ is appreciably smaller than τ_r, as is the case for polarization in the field of a light wave, one must average the total energy over the period of the high-frequency applied waves and use the averaged value $\overline{H}$ in the distribution function.[4]

In the case considered the time-dependence of the Hamiltonian (6) is connected with the term $F(q_i, t) \equiv F(\theta, t)$. If we averaged over the explicit time-dependence of $F(\theta, t)$ we would obtain $\overline{F(\theta, t)} = 0$. Such an averaging in a monochromatic field leads in particular, to the incorrect conclusion that no linear polarization is caused by the constant molecular dipole moment.[2] When averaging the energy we must take into account the time dependence of the angle θ and this leads to $\overline{F(\theta, t)} \neq 0$.

For determination of $\theta(t)$ a simple and elegant approximate method[5] which bears P. L. Kapitza's name is used. In this method one puts $\theta = \theta_0 + \xi$, where ξ describes the high-frequency small-amplitude forced oscillations around the quasi-equilibrium position θ_0 and the quantity θ_0 itself changes slowly with a characteristic time τ_θ such that $\tau_\theta \gg \tau$.

In our case Eq. (7) splits in this method into two equations: one for ξ with the solution

$$\xi = -\frac{f_\omega(\theta_0)}{J\omega^2}\cos\omega t - \frac{f_{2\omega}(\theta_0)}{4J\omega^2}\cos 2\omega t \tag{8}$$

and another for θ_0:

$$J\ddot\theta_0 = -\frac{\partial\overline{H}(\theta_0)}{\partial\theta_0}, \quad \overline{H}(\theta_0) = H_0 + \frac{f_\omega^2(\theta_0)}{4J\omega^2} + \frac{f_{2\omega}^2(\theta_0)}{16J\omega^2} = T + U_{eff}, \tag{9}$$

$$U_{eff} = -pE_0\cos\theta_0 - \left[\frac{(\alpha_\omega + p^2/J\omega^2)E_\omega^2}{4} + \frac{\alpha_0 E_0^2}{2}\right]\cos^2\theta_0$$
$$+ \frac{p(\alpha_0 + \alpha_\omega)E_0E_\omega^2}{2J\omega^2}\sin^2\theta_0\cos\theta_0$$
$$+ \frac{E_\omega^2}{4J\omega^2}\left[(\alpha_0 + \alpha_\omega)^2 E_0^2 + \frac{\alpha_\omega^2 E_\omega^2}{16}\right]\sin^2\theta_0\cos^2\theta_0.$$

$\overline{H}(\theta_0)$ is the total energy of the molecule averaged over a period of the high-frequency oscillations. The correction to H_0 is the average kinetic energy of the oscillatory motion.[5] As we are not interested in higher than cubic terms in the susceptibility, we can neglect the last terms which are $\propto E^4$ in Eq. (9) for U_{eff}.

To determine the probability for the different orientations in the angle θ_0 of the molecular axes we use a canonical Gibbs distribution:[6]

$$dw(p_i, q_i) = A\exp[-H(p_i, q_i)/kT]dp_idq_i. \tag{10}$$

We obtain the probability distribution over the angle θ_0 by integrating (10) over all variables ($m_\theta, M_\varphi, M_\psi, \varphi, \psi$) but θ_0. Only the rotational kinetic energy of the molecule $T(p_i, q_i)$ depends on the p_i. The functional form of this function is determined by the spatial distribution of the molecular mass. The rotational properties of the molecules correspond either to a rigid rotator, or to a symmetric top, or to an asymmetric top. In all these cases we have

$$\int\exp[-T(p_i, q_i)/kT]dM_\theta dM_\varphi dM_\psi = A_1\sin\theta_0 \tag{11}$$

and hence

$$dw(\theta_0, \varphi, \psi) = A_2\exp[-U_{eff}(\theta_0)/kT]\sin\theta_0 d\theta_0 d\varphi d\psi,$$
$$dw(\theta_0) = A_3\exp[-U_{eff}(\theta_0)/kT]\sin\theta_0 d\theta_0. \tag{12}$$

Here the A_i ($i = 1, 2, 3$) are constants independent of the angular coordinates.

Since we are not interested in terms higher than cubic in the susceptibility we must expand $\exp(-U_{eff}/kT)$ in a series up to terms $\sim E^3$. This will be valid for $U_{eff}/kT \ll 1$. Here and in what follows we shall use for estimates the following values of the parameters:

$$\alpha_{0,\omega} = 10^{-24}\text{ cm}^3, \quad p = 10^{-18}\text{ CGS},$$
$$J = 10^{-40}\text{ g}\cdot\text{cm}^2, \quad \omega = 10^{15}\text{ s}^{-1}, \quad T = 300\text{ K}. \tag{13}$$

The magnitude of E_0 is bounded from above by the field breakdown strength E_0^p (under normal conditions $E_0^p = 3\times 10^4$ V/cm). There are no such rigorous restrictions on the magnitude of E_ω. The requirement $U_{eff}/kT \ll 1$ thus leads according to (9) to $E_\omega \ll 10^8$ V/cm. Expanding the probability $dw(\theta_0)/d\theta_0$ in a series in the field we find

$$\frac{dw(\theta_0)}{d\theta_0} = \frac{1}{2}\left(1 - \frac{a}{3}\right)(1 + b\cos\theta_0 + a\cos^2\theta_0 + c\cos^3\theta_0)\sin\theta_0 d\theta_0, \tag{14}$$

where

$$a = \frac{(\alpha_\omega + p^2/J\omega^2)E_\omega^2}{4kT} + \frac{(\alpha_0 + p^2/kT)E_0^2}{2kT},$$

$$b = \frac{pE_0}{kT}\left[1 - \frac{(\alpha_0 + \alpha_\omega)E_\omega^2}{2J\omega^2}\right],$$

$$c = \frac{pE_0}{kT}\left\{\frac{E_\omega^2}{4kT}\left[\alpha_\omega + \frac{p^2}{J\omega^2}\right.\right.$$
$$\left.\left. + 2(\alpha_0 + \alpha_\omega)\frac{kT}{J\omega^2}\right] + \frac{E_0^2}{2kT}\left(\alpha_0 + \frac{p^2}{3kT}\right)\right\}.$$

To determine the polarization (3) we must write p_E as a function of θ_0. Since $E \ll E_a$ for $\xi \ll 1$, the component of the dipole moment along the field (4) will, if we use (8), have the form

$$p_E(\theta) = p_E(\theta_0) + \xi\frac{\partial p_E(\theta_0)}{\partial\theta_0} = \sum_{j=0}^{3} p_E^{j\omega}\cos j\omega t, \qquad (15)$$

where

$$p_E^0 = p\cos\theta_0 + \alpha_0^{is}E_0 + \alpha_0 E_0\cos^2\theta_0$$
$$-\frac{p\alpha_\omega E_\omega^2}{J\omega^2}\sin^2\theta_0\cos\theta_0 - \frac{\alpha_\omega(\alpha_0 + \alpha_\omega)E_0 E_\omega^2}{J\omega^2}\sin^2\theta_0\cos^2\theta_0,$$

$$p_E^\omega = \left\{\alpha_\omega^{is} + \alpha_\omega\cos^2\theta_0 - \frac{p^2}{J\omega^2}\sin^2\theta_0\right.$$
$$-\frac{p(\alpha_E + 3\alpha_0)E_0}{J\omega^2}\sin^2\theta_0\cos\theta_0$$
$$\left. - \left[\frac{2\alpha_0(\alpha_0 + \alpha_\omega)E_0^2}{J\omega^2} + \frac{\alpha_\omega^2 E_\omega^2}{8J\omega^2}\right]\sin^2\theta_0\cos^2\theta_0\right\}E_\omega,$$

$$p_E^{2\omega} = -\left[\frac{9}{8}\frac{p\alpha_\omega E_\omega^2}{J\omega^2}\sin^2\theta_0\cos\theta_0\right.$$
$$\left. + \frac{\alpha_\omega E_\omega^2 E_0}{J\omega^2}\left(\alpha_\omega + \frac{5}{4}\alpha_0\right)\sin^2\theta_0\cos^2\theta_0\right],$$

$$p_E^{3\omega} = -\frac{\alpha_\omega^2 E_\omega^3}{8J\omega^2}\sin^2\theta_0\cos^2\theta_0.$$

(16)

Averaging over the angular distribution (14) we find the average value

$$\overline{p_E} = \sum_{j=0}^{3}\overline{p_E^{j\omega}}\cos j\omega t,$$

i.e., the polarization per molecule:

$$\overline{p_E^0} = E_0\left\{\alpha_0^{is} + \frac{\alpha_0}{3} + \frac{p^2}{3kT} + \left[2\alpha_0^2 + \frac{4\alpha_0 p^2}{kT} - \left(\frac{p^2}{kT}\right)^2\right]\frac{E_0^2}{45kT}\right.$$
$$+ \left(\alpha_\omega + \frac{p^2}{J\omega^2}\right)\left(\alpha_0 + \frac{p^2}{kT}\right)\frac{E_\omega^2}{45kT}$$
$$\left. - \frac{2}{15}\frac{\alpha_\omega E_\omega^2}{J\omega^2}\left[\alpha_0 + \alpha_\omega + \frac{p^2}{2kT}\left(3 + \frac{\alpha_0}{\alpha_\omega}\right)\right]\right\},$$

$$\overline{p_E^\omega} = E_\omega\left\{\alpha_\omega^{is} + \frac{\alpha_\omega}{3} - \frac{2p^2}{3J\omega^2} + \left(\alpha_\omega + \frac{p^2}{J\omega^2}\right)^2\frac{E_\omega^2}{45kT}\right.$$
$$- \frac{\alpha_\omega E_\omega^2}{60J\omega^2} + 2\left(\alpha_\omega + \frac{p^2}{J\omega^2}\right)\left(\alpha_0 + \frac{p^2}{kT}\right)\frac{E_0^2}{45kT}$$
$$\left. - \frac{4}{15}\frac{\alpha_0 E_0^2}{J\omega^2}\left[\alpha_0 + \alpha_\omega + \frac{p^2}{2kT}\left(3 + \frac{\alpha_\omega}{\alpha_0}\right)\right]\right\},$$

$$\overline{p_E^{2\omega}} = -\frac{\alpha_\omega E_\omega^2}{6J\omega^2}\left(\alpha_0 + 0.8\alpha_\omega + 0.9\frac{p^2}{kT}\right)E_0,$$

$$\overline{p_E^{3\omega}} = -\frac{\alpha_\omega^2 E_\omega^3}{60J\omega^2}.$$

(17)

The first four terms in the curly brackets in the formula for $\overline{p_E^0}$ correspond to the polarization in a static field. The last two terms characterize the effect of the alternating field on the static polarization (optical rectification[4]) and the first of these makes the largest contribution in the case of the parameter values (13). Comparing it with the purely static nonlinear polarization (the fourth term) we find that their ratio is

$$\gamma_p \sim \frac{\alpha_\omega kT}{p^2}\frac{E_\omega^2}{E_0^2}, \qquad p\neq 0.$$
$$\gamma_a = E_\omega^2/E_0^2, \qquad p = 0.$$

Since E_0 is bounded from above by the value E_0^p while E_w can be considerably larger than E_0^p the static nonlinear polarization is in a strong alternating field determined by E_w,[4] rather than by E_0. For instance, when $E_0 = E_0^p$ and $E_w = 10^7$ V/cm we get $\gamma_p \sim 4\times10^3$, $\gamma_a \sim 10^5$.

The nonlinear polarization with frequency ω in strong alternating fields is $E_\omega \gg E_0$, close to what happens when there is no constant field.[2] The relative extra nonlinear contribution is proportional to E_0^2/E^2 and is $\ll 1$.

In the approximation used, the vibrational-rotational polarization at the doubled frequency is caused by the anisotropic molecular polarizability; it vanishes when $\alpha_\omega = 0$. For $p = 0$ the nonlinear polarization at the frequency 2ω does not need an anisotropy of the orientation of the axes; it occurs for an isotropic distribution. for $p\neq 0$ and $p^2/kT > \alpha_0, \alpha_\omega$ the polarizability at the frequency 2ω is determined by the field E_0 induced by the asymmetry of the θ_0-distribution of the axes of the oscillating molecules.

The polarization at the frequency 3ω is independent of E_0; it is the same as in the case of a monochromatic driving force[2] for $E_0 = 0$. In the approximation used the generation at the triple frequency occurs for an isotropic distribution of the axes. It is independent of the presence of a constant dipole moment and is determined solely by the magnitude of the anisotropy of the linear polarizability α_ω.

We note that according to (13) we have

$$\frac{p^2}{J\omega^2} < \alpha_\omega \sim \alpha_0 < \frac{p^2}{kT}.$$

The contribution of a monochromatic wave to the nonlinear polarization is thus caused basically by the directive polarizability α_ω and the effect of the constant dipole moment p dominates in the contribution of the static field.

Equation (17) contains essentially two results: firstly, the polarization when there is a thermodynamic equilibrium distribution and, secondly, the polarization obtained formally from (17) as $T\to\infty$ which corresponds to an isotropic distribution existing up to the switching on of the field. After a fast (but adiabatic) switching on of the field the transition from an isotropic to a thermodynamic equilibrium distribution proceeds during a time τ_r. Assuming that one needs for the relaxation several molecular collisions, which under normal conditions have a frequency of $\sim 10^{11}$ s^{-1}, we find $\tau_r \sim 10^{-11}$–10^{-10} s.

2. All we have said so far referred to the case when static and the alternating fields are collinear. One should consider the polarization also when the fields are at right angles to one another. Let the alternating field be directed along the x-axis (unit vector $\mathbf{i}_x$) and the constant field along the y-axis (unit vector $\mathbf{i}_y$):

$$\mathbf{E} = \mathbf{i}_x E_\omega \cos \omega t + \mathbf{i}_y E_0. \qquad (18)$$

A procedure similar to the one carried out for collinear fields, involving the use of Kapitza's method to average the energy, leads after cumbersome calculations to the following results for the polarization:

$$\overline{p_y^0} = E_0 \left\{ \alpha_0^{ix} + \frac{\alpha_0}{3} + \frac{p^2}{3kT} + \left[2\alpha_0^2 + \frac{4\alpha_0 p^2}{kT} - \frac{p^4}{(kT)^2} \right] \frac{E_0^2}{45kT} \right.$$
$$- \left(\alpha_0 + \frac{p^2}{kT} \right) \left(\alpha_\omega + \frac{p^2}{J\omega^2} \right) \frac{E_\omega^2}{90kT}$$
$$\left. - \left[\alpha_0 + \alpha_\omega + \frac{p^2}{2kT} \left(3 + \frac{\alpha_0}{\alpha_\omega} \right) \right] \frac{\alpha_\omega E_\omega^2}{10J\omega^2} \right\}.$$

$$\overline{p_x^\omega} = E_\omega \left\{ \alpha_\omega^{ix} + \frac{\alpha_\omega}{3} - \frac{2}{3} \frac{p^2}{J\omega^2} + \left(\alpha_\omega + \frac{p^2}{J\omega^2} \right)^2 \frac{E_\omega^2}{45kT} \right.$$
$$- \frac{\alpha_\omega^2 E_\omega^2}{60J\omega^2} - \left(\alpha_0 + \frac{p^2}{kT} \right) \left(\alpha_\omega + \frac{p^2}{J\omega^2} \right) \frac{E_0^2}{45kT}$$
$$\left. - \frac{\alpha_\omega E_0^2}{5J\omega^2} \left[\alpha_0 + \alpha_\omega + \frac{p^2}{2kT} \left(3 + \frac{\alpha_\omega}{\alpha_0} \right) \right] \right\}, \qquad (19)$$

$$\overline{p_y^{2\omega}} = - \frac{\alpha_\omega (\alpha_0 + 1{,}2\alpha_\omega + 1{,}1 p^2/kT)}{12J\omega^2} E_0 E_\omega^2 = \chi_{2\omega} E_0 E_\omega^2.$$

$$\overline{p_x^{3\omega}} = - \frac{\alpha_\omega^2 E_\omega^3}{60J\omega^2}, \qquad \overline{p_x^0} = \overline{p_y^\omega} = \overline{p_x^{2\omega}} = \overline{p_y^{3\omega}} = 0.$$

We shall compare the polarizations in the cases 1 and 2.

The dependence of the static polarizations p_E^0 and p_y^0 on the constant field E_0 is the same in the cases 1 and 2, but the dependence on the alternating field E_ω (optical recitification[4]) is different. The dependence of the polarizations on the frequency ω, i.e., the dependence of $\overline{p_E^\omega}$ and $\overline{p_x^\omega}$ on the alternating field E_ω is the same in the cases 1 and 2, but the dependence on the static field E_0 is different. The difference between the cases 1 and 2 occurs only in the effect on the polarization at one frequency by a field with another frequency.

As to the vibrational-rotational susceptibility $\chi_{2\omega}$ it is, according to (17) and (19), with the parameter values of (13), equal to $\sim 10^{-38}$ cgs units/molecule for molecules with a dipole and $\sim 10^{-39}$ cgs units/molecule for molecules without a dipole. On the other hand, measurements[3,4] give values of $\chi_{exp}^{2\omega} \sim 10^{-35}\text{--}10^{-37}$ cgs units/molecule. The main contribution to the second harmonic generation therefore does not come from the vibrational-rotational mechanism.

According to Refs. 3 and 4 the electron susceptibility of a molecular gas at the doubled frequency $\chi^{2\omega}$ consists of a part caused by the third-order susceptibility $\sim \chi^{(3)}$ [see (1)] and an electron rotational part which depends on the temperature and is connected with the second-order susceptibility $\sim (p/kT)\chi^{(2)}$.

To estimate $\chi^{(2)}$ and $\chi^{(3)}$ we note that the series (1) for the electron polarizability is essentially an expansion in the parameter $E/E_a \ll 1$ so that[7] $\chi^{(i)} \propto E_a^{-i}$. Putting $\chi^{(1)} = \alpha$, we get the estimates $\chi^{(2)} \sim \alpha/E_a \sim 3 \times 10^{-31}$ cgs units/molecule and $\chi^{(3)} \sim \alpha/E_a^2 \sim 10^{-37}$ cgs units/molecule. Since we have $p/kT \sim 3 \cdot 10^{-5}$ cgs units, a rough estimate of the electron susceptibility will be $\chi^{2\omega} \sim 10^{-35}\text{--}10^{-37}$ cgs units/molecule. This is close to the experimental results. We can thus assume that the main contribution to the second-harmonic generation comes from the electron nonlinearity.

The polarizations at the triple frequency are the same in the cases 1 and 2.

In conclusion we note that we have extended in the present paper the theoretical study, started in Ref. 2, of the effect of factors previously neglected in the theory on the optical polarization of molecular gases. These factors are: a directional effect caused by the constant molecular dipole moments in an alternating field and the induced high-frequency oscillations of their axes. We considered the case of polarization when we have simultaneous action of a constant and an alternating field. We obtained analytical formulae which made it possible to estimate the magnitude of the polarization of molecular gases caused by the vibrational-rotational mechanism at the frequencies ω, 2ω, and 3ω.

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