Vibrational-orientational polarization of molecular gases in a two-frequency optical field

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The vibrational-orientational polarization, linear or cubic in the field, of a molecular gas in a bichromatic optical field is analyzed for the cases of collinear and orthogonal electric vector configurations. This polarization is also analyzed for a gas in the field of elliptically polarized light. Analytic expressions are derived for the vibrational-orientational polarizations of a molecular gas at the fundamental, multiple, and sum and difference frequencies, which depend on the parameters of the molecules, the field, and the medium. The nonlinear polarization at the frequency of one of the incident waves depends on both the intensity of this wave (the self-polarization) and the intensity of the other wave (the induced polarization). The self- and induced cubic orientational susceptibilities are on the same order of magnitude. There is no orientational cubic polarization at multiple frequencies or at sum and difference frequencies. The vibrational cubic self-susceptibilities at the fundamental frequencies are usually smaller than the induced susceptibilities. The latter increase rapidly with decreasing difference between the frequencies of the incident waves. This increase is also found for the cubic susceptibilities at certain sum and difference frequencies.

Various factors can cause nonlinear polarization of a molecular gas in an optical field. One is a change in the number density of molecules caused by the optical field (ponderomotive and thermal effects). Another is the excitation of the molecules by the light and thus a change in their polarization characteristics. A third is an electronic nonlinearity due to an anharmonic response of the electron cloud of the molecule to the alternating field. Finally, there are stimulated vibrations of the constant and induced dipole moments of the molecules with respect to their average orientation and changes in the angular distribution of these average orientations in the field of the light wave.

The mechanism of a vibrational-orientational optical polarization of a molecular gas was discussed in Refs. 1 and 2. The orientational polarization arises from a deviation of the angular distribution of the average directions (the average is over the oscillations) of the axes of the molecules from isotropy. The linear and nonlinear vibrational polarizations in an optical field arise from a high-frequency stimulated oscillation of the axes of the molecules and occur even when the distribution of the average molecular orientations is isotropic.

In Ref. 1 we studied the vibrational-orientational polarization of a molecule gas in the case in which the external field is a linearly polarized monochromatic plane wave. The polarization of the medium during the simultaneous application of a monochromatic wave and a constant electric field was studied in Ref. 2.

In the present paper we wish to determine the vibrational-orientational polarization of a nonabsorbing molecular gas of diatomic or linear molecules in the vibrational ground state in the field of two monochromatic waves at frequencies ω_1,ω_2 with wave vectors k_1,k_2, which are directed along the z axis. We consider the case in which the oscillation planes (an oscillation plane is defined by the vectors **E** and **k**) are parallel and also the case in which they are perpendicular. We derive the vibrational-orientational polarization of a gas in the field of an elliptically polarized wave.

1. Let us examine the polarization of the medium when the oscillation planes of two monochromatic waves with amplitudes E_1 and E_2 oriented along the x axis are coincident:

$$\mathbf{E}=\mathbf{i}_x[E_1\cos(\omega_1 t-k_1 z)+E_2\cos(\omega_2 t-k_2 z)].$$

We will be discussing the polarization in a volume Δv in which the number of molecules is large enough that we can take statistical averages, but is small in comparison with[2] $\lambda_{1,2}^3(\lambda_{1,2}=2\pi c\omega_{1,2}^{-1})$. We can ignore the changes in the spatial phases $k_{1,2}z$ within Δv, and we can examine the behavior of the gas in a field

$$\mathbf{E}=\mathbf{i}_x(E_1\cos\omega_1 t+E_2\cos\omega_2 t). \tag{1}$$

If the initial oscillation phases $\delta_{1,2}$ are not zero, as in Ref. 1, they appear in time-dependent factors for their polarization, in which $\omega_{1,2}t$ should be replaced by $\omega_{1,2}t+\delta_{1,2}$.

In the coordinate system fixed in a diatomic or linear molecule (a rigid rotator) the molecule is characterized by the linear dynamic polarizability $\alpha_\omega^{(1)}=\alpha_\omega^{(2)}=\alpha_\omega^{is}$; $\alpha_\omega^{(3)}$ and the principal axes of (a) the ellipsoids of revolution and (b) the moments of inertia $J_1=J_2=J$; $J_3=0$. The index 3 corresponds to the direction parallel to the axis of the molecule, along which the constant dipole moment p (if it exists) is also oriented. The "orienting"[3] polarizabilities α_1 and α_2 are $\alpha_{1,2}=\alpha_{\omega_{1,2}}^{(3)}-\alpha_{\omega_{1,2}}^{is}$. We wish to stress that nonlinear components of the electronic polarizability are not being discussed here.

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The properties of the medium, i.e., of the molecular gas, are characterized by the temperature T (in kelvins) and the number density N (number per cubic centimeter).

Using these characteristics of the field, the molecules, and the medium, we will determine the vibrational-orientational polarization of the gas to within terms cubic in the field.

Since the gas is isotropic, the polarization vector is directed along the field E. It is thus sufficient to consider only that component of the dipole moment which is along the polar (x) axis:

$$p_E = p\cos\theta + (\alpha_1^{is} + \alpha_1\cos^2\theta)E_1\cos\omega_1 t + (\alpha_2^{is} + \alpha_2\cos^2\theta)E_2\cos\omega_2 t. \qquad (2)$$

Here θ is the angle between the field and the dipole moment p. The polarization vector $\mathbf{p}_E$ is

$$\mathbf{p}_E = \mathbf{i}_x N\bar{p}_E = N\mathbf{i}_x \int p_E dw(\theta), \qquad (3)$$

where $dw(\theta)$ characterizes the distribution of the axes of the molecules with respect to the angle θ in the external field. Assuming that the gas is in thermodynamic equilibrium, we use a Gibbs canonical distribution[4] to determine $dw(\theta)$:

$$dw(p_i,q_i) = Ae^{-H/kT}dp_i dq_i. \qquad (4)$$

Here H is a Hamiltonian, i.e., the total energy of a molecule in the field E. The Hamiltonian H contains the kinetic energy of rotation, $T_r(p_i,q_i)$ ($q_i = \theta,\varphi$ are the polar and azimuthal angles; $p_i = M_\theta, M_\varphi$ are the corresponding angular momenta), and $U(q_i,t)$, the potential energy of the dipole in the field E:

$$T_r = \frac{M_\theta^2}{2J} + \frac{M_\varphi^2}{2J\sin^2\theta}, \quad U(q_i,t) = U_0(q_i) + F(q_i,t),$$

$$U_0(q_i) = U_0(\theta), \quad F(q_i,t) = F(\theta,t),$$

$$U_0(\theta) = -(\alpha_1 E_1^2 + \alpha_2 E_2^2)\frac{\cos^2\theta}{4},$$

$$\begin{aligned} F(\theta,t) = {} & -p(E_1\cos\omega_1 t + E_2\cos\omega_2 t)\cos\theta \\ & -\frac{\cos^2\theta}{4}(\alpha_1 E_1^2\cos 2\omega_1 t + \alpha_2 E_2^2\cos 2\omega_2 t) \\ & -\frac{(\alpha_1+\alpha_2)E_1E_2\cos^2\theta}{4}[\cos(\omega_1+\omega_2) \\ & \times t + \cos(\omega_1-\omega_2)t], \end{aligned} \qquad (5)$$

$$H(p_i,q_i,t) = H_0(p_i,\theta) + F(\theta,t), \quad H_0 = T_r + U_0(\theta).$$

Since H depends on the time, the question of the quasiequilibrium distribution of axes of molecules with respect to the angle θ in the alternating external field is decided by the period of the driving force, $\tau = 2\pi\omega^{-1}$. If $\tau \gg \tau_p$ holds, where the right side is the time scale of the relaxation of the system to an equilibrium distribution, then at any instant the distribution is approximately the equilibrium distribution corresponding to the energy at the same instant. If $\tau \ll \tau_p$ holds, which is the condition that usually prevails during polarization in an optical field, the total energy should be averaged over the period of the high-frequency forced oscillations, and the average value $\bar{H}$ should be used in the distribution function[3] with respect to average angles.

The time dependence of the function H, which is related to the quantity $F(\theta,t)$, stems from not only the factors $\propto\cos\omega_i t$ in the terms of Eq. (5) but also the amplitudes of these terms, which depend on the time through the time dependence of the angle $\theta(t)$. The motion of the axis of a molecule is characterized by oscillations of two types. First, there are the forced high-frequency oscillations at the frequencies $\Omega = \omega_1, \omega_2, 2\omega_1, 2\omega_2, \omega_1+\omega_2$, $\Delta\omega = |\omega_1 - \omega_2|$. Second, there are the low-frequency motions of the axis of the molecule at a frequency ω_0, which are due to the time-independent part of the Hamiltonian, H_0.

In this paper we assume $\omega_0 \ll \Omega$. In this situation we should use the approximate method[5] with which the name of P. L. Kapitsa is linked. In this method one assumes $\theta = \theta_0 + \xi$, where θ_0 describes low-frequency motions with a frequency ω_0 (i.e., θ_0 is the value of the angle θ averaged over the period of the high-frequency oscillations), and $\xi \ll 1$ are forced high-frequency oscillations at frequencies Ω. The exact solution of the equation of motion of the molecule in the bichromatic field is

$$\begin{aligned} & J\ddot{\theta} = -\frac{\partial H_0}{\partial\theta} + \sum_{\omega_i=\Omega} f\omega_i(\theta)\cos\omega_i t, \\ & f_{\omega_{1,2}} = -pE_{1,2}\sin\theta, \\ & f_{2\omega_{1,2}} = -\frac{\alpha_{1,2}E_{1,2}^2}{4}\sin 2\theta, \\ & f_{\omega_i\pm\omega_2} = -\frac{\alpha_1+\alpha_2}{4}E_1E_2\sin 2\theta. \end{aligned} \qquad (6)$$

In the method we are using, this equation splits in two. The first equation is for ξ; its solution is

$$\xi = -\frac{1}{J}\sum_{\omega_i=\Omega}\frac{f\omega_i}{\omega_i^2}\cos\omega_i t. \qquad (7)$$

The other equation is for θ_0; its solution is

$$\begin{aligned} J\ddot{\theta}_0 & = -\frac{\partial H_0}{\partial\theta_0} + \overline{\xi\frac{\partial}{\partial\theta_0}\sum_{\omega_i=\Omega} f_{\omega_i}\cos\omega_i t} \\ & = -\frac{\partial}{\partial\theta_0}\left[H_0 - \frac{p^2}{4J}\left(\frac{E_1^2}{\omega_1^2} + \frac{E_2^2}{\omega_2^2}\right)\cos^2\theta_0\right] - \frac{\partial\Phi(E^4)}{\partial\theta_0}. \end{aligned} \qquad (8)$$

The bar over the summation means an average over the period of the high-frequency oscillations. The function $\Phi(E^4)$ is

$$\Phi(E^4) = \frac{\sin^2 2\theta_0}{16J}\left[\frac{\alpha_1^2 E_1^4}{16\omega_1^2} + \frac{\alpha_2 E_2^4}{16\omega_2^2} + 2\frac{(\alpha_1+\alpha_2)^2(\omega_1^2+\omega_2^2)}{(\Delta\omega)^2(\omega_1+\omega_2)^2}E_1^2E_2^2\right]. \qquad (9)$$

Since the analysis is being restricted to the nonlinearity which is cubic in the field, the quantity $\partial\Phi(E^4)/\partial\theta_0$ drops out, and we have

$$J\ddot{\theta}_0=-\frac{\partial\bar{H}(\theta_0)}{\partial\theta_0},\quad \bar{H}(\theta_0)=T_r+U_{eff}(\theta_0),$$

$$U_{eff}(\theta_0)=-(\alpha_{1e}E_1^2+\alpha_{2e}E_2^2)\,\frac{\cos^2\theta_0}{4},\tag{10}$$

$$\alpha_{1e,2e}=\alpha_{1,2}+\frac{p^2}{J\omega_{1,2}^2}.$$

To analyze the polarization we do not need to look for solutions of Eqs. (8) or (10); it is sufficient to determine simply $\bar{H}(\theta_0)$, the Hamiltonian averaged over the high-frequency oscillations.

Using $\bar{H}(\theta_0)$ in a Gibbs distribution,[4] and integrating it over the angular momenta and the coordinate φ, we find the distribution of the axes of the molecules with respect to the angle θ_0:

$$dw(\theta_0)=Ae^{-U_{eff}/kT}\sin\theta_0 d\theta_0.\tag{11}$$

Assuming $|U_{eff}/kT|\ll 1$, we find, to within terms cubic in the field,

$$dw(\theta_0)=\frac{1}{2}\left[1+\frac{1}{4kT}(\alpha_{1e}E_1^2+\alpha_{2e}E_2^2)\right.$$
$$\left.\times\left(\cos^2\theta_0-\frac{1}{3}\right)\right]\sin\theta_0 d\theta_0.\tag{12}$$

To average p_E over the orientations of the molecular axes, we should determine the amplitudes of the high-frequency components of p_E as a function of θ_0. Since we have

$$p_E(\theta,t)=p_E(\theta_0,t)+\xi\left(\frac{\partial p_E}{\partial\theta}\right)_{\theta=\theta_0},\tag{13}$$

we find the following result by differentiating p_E in (2) and using Eq. (7) for ξ:

$$p_E(\theta,t)=\sum_{\omega_i=\Omega_1}p_E^{\omega_i}(\theta_0)\cos\omega_i t,$$
$$\Omega=\begin{cases}0,\omega_1,\omega_2,2\omega_1,2\omega_2,\omega_1+\omega_2,\Delta\omega\\3\omega_1,3\omega_2,|2\omega_2\pm\omega_1|,|2\omega_1\pm\omega_2|\end{cases},\tag{14}$$

where

$$p_E^0=p\cos\theta_0-\frac{p}{2}\left(\frac{\alpha_1E_1^2}{J\omega_1^2}+\frac{\alpha_2E_2^2}{J\omega_2^2}\right)\sin\theta_0\sin 2\theta_0,$$

$$p_E^{\omega_1}=\left[\alpha_1^{is}-\frac{p^2}{J\omega_1^2}+\alpha_{1e}\cos^2\theta_0-\frac{\alpha_1^2E_1^2}{32J\omega_1^2}\sin^2 2\theta_0\right.$$
$$\left.-\frac{\alpha_2(\alpha_1+\alpha_2)}{4J(\Delta\omega)}\frac{(\omega_1^2+\omega_2^2)}{(\omega_1+\omega_2)^2}E_2^2\sin^2 2\theta_0\right]E_1,$$

$$p_E^{\omega_2}=\left[\alpha_2^{is}-\frac{p^2}{J\omega_2^2}+\alpha_{2e}\cos^2\theta_0-\frac{\alpha_2^2E_2^2}{32J\omega_2^2}\sin^2 2\theta_0\right.$$
$$\left.-\frac{\alpha_1(\alpha_1+\alpha_2)}{4J(\Delta\omega)^2}\frac{(\omega_1^2+\omega_2^2)}{(\omega_1+\omega_2)^2}E_1^2\sin^2 2\theta_0\right]E_2,$$

$$p_E^{2\omega_1}=-\frac{9}{8}\frac{p\alpha_1E_1^2}{J\omega_1^2}\sin^2\theta_0\cos\theta,$$

$$p_E^{2\omega_2}=-\frac{9}{8}\frac{p\alpha_2E_2^2}{J\omega_2^2}\sin^2\theta_0\cos\theta_0,\tag{15}$$

$$p_E^{\omega_1\pm\omega_2}=\frac{pE_1E_2}{J}\left[\frac{\alpha_1}{\omega_2^2}+\frac{\alpha_2}{\omega_1^2}+\frac{\alpha_1+\alpha_2}{2(\omega_1\pm\omega_2)^2}\right]\sin^2\theta_0\cos\theta_0,$$

$$p_E^{3\omega_1}=-\frac{\alpha_1^2E_1^3}{32J\omega_1^2}\sin^2 2\theta_0,\quad p_E^{3\omega_2}=-\frac{\alpha_2^2E_2^3}{32J\omega_2^2}\sin^2 2\theta_0,$$

$$p_E^{2\omega_2\pm\omega_1}=-\frac{\alpha_2E_1E_2^2}{32J}\left[\frac{\alpha_1}{\omega_2^2}+4\frac{\alpha_1+\alpha_2}{(\omega_1\pm\omega_2)^2}\right]\sin^2 2\theta_0,$$

$$p_E^{2\omega_1\pm\omega_2}=-\frac{\alpha_1E_1^2E_2}{32J}\left[\frac{\alpha_2}{\omega_1^2}+4\frac{\alpha_1+\alpha_2}{(\omega_1\pm\omega_2)^2}\right]\sin^2 2\theta_0.$$

Taking an average of (14) in accordance with (3) over the equilibrium in (12), we find the average molecular polarization:

$$\overline{p_E(t)}=\sum_{\omega_i=\Omega_2}\overline{p_E^{\omega_i}}\cos\omega_i t,$$
$$\Omega_2=\begin{cases}\omega_1,\omega_2,3\omega_1,3\omega_2\\|\omega_1\pm 2\omega_2|,\ |2\omega_1\pm\omega_2|\end{cases}.\tag{16}$$

For the amplitudes of the monochromatic components we find (here and below, we use either the first index or the second in the case of a double index)

$$\overline{p_E^{\omega_{1,2}}}=\left[\bar{\alpha}_{1,2}-\frac{2}{3}\frac{p^2}{J\omega_{1,2}^2}+\left(\frac{\alpha_{1e,2e}^2}{45kT}-\frac{\alpha_1^2}{60J\omega_{1,2}^2}\right)E_{1,2}^2\right.$$
$$+\left(\frac{\alpha_{1e}\alpha_{2e}}{45kT}-\frac{2}{15}\frac{\alpha_{2,1}(\alpha_1+\alpha_2)}{J(\Delta\omega)^2}\right.$$
$$\left.\left.\times\frac{(\omega_1^2+\omega_2^2)}{(\omega_1+\omega_2)^2}\right)E_{2,1}^2\right]E_{1,2},$$
$$\overline{p_E^{3\omega_{1,2}}}=-\frac{\alpha_{1,2}^2E_{1,2}^3}{60J\omega_{1,2}^2},\tag{17}$$
$$\overline{p^{2\omega_{2,1}\pm\omega_{1,2}}}=-\frac{\alpha_{2,1}E_{1,2}E_{2,1}^2}{60J}\left[\frac{\alpha_{1,2}}{\omega_{2,1}^2}+4\frac{\alpha_1+\alpha_2}{(\omega_1\pm\omega_2)^2}\right].$$

Here $\bar{\alpha}_{1,2}=\alpha_{1,2}^{is}+\alpha_{1,2}/3$ is the average polarizability of a molecule in the case in which the axes have an isotropic distribution.

The "even" frequencies $2\omega_1,2\omega_2,\omega_1\pm\omega_2$ are thus missing from the polarization of the gas. The reason is the axial symmetry of the problem. We are left with simply the "odd" frequencies in the set Ω_2.

Here and below, unless we stipulate otherwise, we assume the following values in the estimates:

$$\alpha_{1,2}=10^{-24}\ \text{cm}^3;\quad p=10^{-18}\ \text{cgs};\quad J=10^{-40}\ \text{g}\cdot\text{cm}^2,\tag{A}$$

$T=300$ K; $\omega_{1,2}\cong 10^{15}$ s^{-1}.

The quantity J corresponds to diatomic molecules which contain hydrogen. With the parameter values in (A), the condition $|U_{eff}/kT|\ll 1$, which leads to Eq. (12), holds for $E\ll 10^8$ V/cm.

We would like to know whether the conditions for the applicability of our method hold for $E\ll 10^8$ V/cm. These conditions are $\xi\ll 1$ and $\Omega\gg\omega_0$, where ω_0 characterizes the low-frequency motions of the axis of a molecule. Since ω_1 and ω_2 can take on nearly equal values, the most stringent requirement associated with the condition $\xi\ll 1$ stems from the driving-force term in (7), which oscillates at a frequency $\Delta\omega$. We should estimate the minimum permissible values of $\Delta\omega$ according to our method.

Since low-frequency motions of rotating molecules occur at frequencies $\omega_r\sim\sqrt{kT/J}\sim 10^{13}$ s^{-1}, while for nonrotating molecules the oscillations in the field U_{eff} occur at frequencies $\omega_0\sim\sqrt{(dE^2/2J)E}$ (for $E\ll 10^8$ V/cm and $\omega_0\ll 10^{13}$ s^{-1}), the requirements on Ω are $\Omega\gg\omega_r\sim 10^{13}$ s^{-1}. In the estimates below we assume that the lowest frequencies for which our method is valid are $\omega_1,\omega_2,\Delta\omega\sim 10^{14}$ s^{-1}. We believe that a deviation from this condition in the low-frequency direction (to $\sim 3\omega_r$) is completely permissible. We recommend experimental measurements of the polarization of a molecular gas at frequencies up to $\sim\omega_r$. In particular, such measurements would be of assistance in determining the behavior of the vibrational nonlinearity and in distinguishing it from an electronic nonlinearity.

The contribution of the dipole moment $p^2/J\omega_{1,2}^2$ to the effective nonlinear polarizability $\alpha_{1e,2e}$ [see (10)] is comparable to the contribution of the linear polarizability $\alpha_{1,2}$ at $\omega_{1,2}=10^{14}$ s^{-1}.

We consider the polarization amplitude $\overline{p_E^{\omega_1}}$. Introducing the susceptibility χ, we write this amplitude as follows:

$$\overline{p_E^{\omega_1}}=(\chi_1^{(1)}+\chi_{11}^{(3)}E_1^2+\chi_{12}^{(3)}E_2^2)E_1,\quad \chi_1^{(1)}=\bar{\alpha}_1-\frac{2}{3}\frac{p^2}{J\omega_1^2},$$

$$\chi_{11}^{(3)}=\chi_{11}^{(3)o}+\chi_{11}^{(3)v},\quad \chi_{11}^{(3)o}=\frac{\alpha_{1e}^2}{45kT},\quad \chi_{11}^{(3)v}=-\frac{\alpha_1^2}{60J\omega_1^2},$$

$$\chi_{12}^{(3)}=\chi_{12}^{(3)o}+\chi_{12}^{(3)v},\quad \chi_{12}^{(3)o}=\frac{\alpha_{1e}\alpha_{2e}}{45kT},$$

$$\chi_{12}^{(3)v}=-\frac{2}{15}\frac{\alpha_2(\alpha_1+\alpha_2)}{J(\Delta\omega)^2}\frac{(\omega_1^2+\omega_2^2)}{(\omega_1+\omega_2)^2}.$$

The linear dynamic susceptibility is seen to consist of an average electronic component $\sim 10^{24}$ cm^3 and a negative vibrational component $-2p^2/3J\omega_1^2$. We see that the linear dynamic susceptibility consists of an average electronic component $\sim 10^{-24}$ cm^3 and a negative vibrational component $-2p^2/3J\omega_1^2$. For the parameter values in (A) the latter is $\sim 10^{-26}$ cm^3, but in the far-IR region, $\omega_1\sim 10^{14}$ s^{-1}, it is $\sim 10^{-24}$ cm^3, and it is comparable in magnitude to the electronic component. Consequently, the linear susceptibility may be affected not only through the frequency dependence of $\bar{\alpha}_1$ but also through the vibrational component.

The nonlinear polarization has a component $\propto E_1^2$. This is a self-polarization, and its corresponding susceptibility is $\chi_{11}^{(3)}$. The other component of the polarization, $\propto E_2^2$, is induced by the wave at the frequency ω_2. The corresponding susceptibility is $\chi_{12}^{(3)}$. The refractive index of the gas at the frequency ω_1, i.e., $n(\omega_1,E_1,E_2)$, has a vibrational-orientational component $\Delta n=2\pi N[n(\omega_1,0,0)]^{-1}\times(\chi_{11}^{(3)}E_1^2+\chi_{12}^{(3)}E_2^2)$.

On the other hand, the nonlinear susceptibilities can be classified on the basis of their physical origin.

First, there is the orientational inertial polarization $\sim T^{-1}$. It is very small while the light is acting on the gas, $t\ll\tau_p$. The orientational susceptibilities are positive at $t\gtrsim\tau_p$, equal to $\chi_{11}^{(3)o}$ and $\chi_{12}^{(3)o}$. The self-polarizations and the induced orientational polarizations are comparable in magnitude at $\alpha_{1e}E_1^2\approx d_{2e}E_2^2$. This result was to be expected, since the particular factor responsible for the corresponding orientational asymmetry is irrelevant to the polarization at any frequency. For the parameter values in (A), the dynamic orientational susceptibility is $\sim 5\cdot 10^{-37}$ cgs/molecule.

Second, there is the instantaneous vibrational polarization, independent of the temperature and unrelated to the asymmetry of the distribution of molecular axes. For this polarization, the susceptibilities $\chi_{11}^{(3)v}$ and $\chi_{12}^{(3)v}$ are negative. If we have $\Delta\omega\sim\omega_1,\omega_2$, the self-susceptibility is an order of magnitude smaller than the induced susceptibility, i.e., we have $\chi_{11}^{(3)v}\sim 0{,}1\chi_{12}^{(3)v}$. For the parameter values in (A) we have $\chi_{12}^{(3)v}\sim 10^{-39}$ cgs/molecule. With decreasing $\Delta\omega$, the induced susceptibility increases $\propto(\Delta\omega)^{-2}$. If $\Delta\omega\simeq 10^{14}$ s^{-1} holds, we have $\chi_{12}^{(3)v}\sim 10^{-37}$ cgs/molecule, and the induced vibrational susceptibility moves closer to the orientational susceptibility.

For comparison, we can derive a crude estimate of the nonlinear electronic susceptibility: $\chi^{(3)e}\sim d/E_a^2\sim 10^{-37}$ cgs/molecule ($E_a\sim 10^9$ V/cm is the strength of the atomic field). The estimates thus lead to the relations $\chi^{(3)o}>\chi^{(3)e}>\chi^{(3)v}$. This is of course a crude estimate, and the particular features of the individual molecules will play an important role.

Everything that we have said about the polarization $\overline{p_E^{\omega_1}}$ can be extended to $\overline{p_E^{\omega_e}}$, with the corresponding changes in indices from 1,2 to 2,1.

The polarization in (17) at the frequencies $3\omega_1$, $3\omega_2$, $2\omega_2\pm\omega_1$, and $2\omega_1\pm\omega_2$ is due exclusively to the vibrational mechanism; there is no orientational effect. At $\Delta\omega\sim\omega_1\sim\omega_2$, the cubic vibrational susceptibility is small at all frequencies: $\sim(10^{-2}\text{–}10^{-1})\alpha^2/J\omega^2\sim 10^{-(39\text{–}40)}$ cgs/molecule.

A case of particular interest is the vibrational polarization for approximately equal frequencies ω_1 and ω_2 ($\Delta\omega\ll\omega_1,\omega_2$). In this case the polarization spectrum consists of two quartets, one near ω_1 and the other near $3\omega_1$. Within a quartet, the polarization frequencies are spaced at a uniform distance $\Delta\omega$.

The first quartet consists of two doublets with frequencies ω_1, $\omega_1+2\Delta\omega$ and ω_2, $\omega_2-2\Delta\omega$. The negative vibrational susceptibilities of all four lines are approximately equal at $\approx 0{,}1\alpha_1^2/J(\Delta\omega)^2$. For the parameter values in (A) and for $\Delta\omega=10^{14}$ s^{-1}, these susceptibilities are $\sim 10^{-37}$ cgs/molecule. The polarization intensity of the first doublet is $\sim E_1\cdot E_2^2$, and that of the second $\sim E_1^2\cdot E_2$.

The second spectral quartet of polarizations, with frequencies $3\omega_1+j\Delta\omega$ ($j=0,1,2,3$) has vibrational susceptibilities smaller by a factor $\sim\omega_1^2/(\Delta\omega)^2$ than those in the first quartet. For the outer frequencies, $j=0$ and 3, the susceptibility is smaller by a factor of 3 than that for the inner frequencies, $j=1$ and 2.

2. Let us examine the polarization of a molecular gas in the field of two monochromatic waves whose oscillation planes are perpendicular:

$$\mathbf{E}=\mathbf{i}_x E_1\cos\omega_1 t+\mathbf{i}_y E_2\cos\omega_2 t, \tag{18}$$

where $\mathbf{i}_x$ and $\mathbf{i}_y$ are unit vectors along the x and y axes.

The cosines of the angles made by the constant dipole moment of the molecule with the x and y axes are $\cos\theta$ and $\sin\theta\cos\varphi$. The x and y projections of the total dipole moment of the molecule are

$$\begin{aligned} p_x&=p\cos\theta+(\alpha_1^{is}+\alpha_1\cos^2\theta)E_1\cos\omega_1 t\\ &\quad+\alpha_2E_2\sin\theta\cos\theta\cos\varphi\cos\omega_2 t,\\ p_y&=p\cos\theta\cos\varphi+\alpha_1E_1\sin\theta\cos\theta\cos\varphi\cos\omega_1 t\\ &\quad+(\alpha_2^{is}+\alpha_2\sin^2\theta\cos^2\varphi)E_2\cos\omega_2 t. \end{aligned} \tag{19}$$

In the case of collinear fields, the polarization of the gas is parallel to the field because of the cylindrical symmetry of the system; this symmetry makes the problem one-dimensional. When the fields are perpendicular, the system loses its cylindrical symmetry, and the problem becomes two-dimensional. This circumstance complicates the necessary calculations, of course. There is no point in reproducing them here in detail. We will simply draw a schematic picture of them and present the final result.

In the method used above, we set $\theta=\theta_0+\xi_\theta$ and $\varphi=\varphi_0+\xi_\varphi$, where $\xi_\theta,\xi_\varphi\ll 1$ are small high-frequency shifts. Let us find the functions $\xi_{\theta,\varphi}(\theta_0,\varphi_0,t)$. Taking an average of the Hamiltonian over the high-frequency oscillations, we find the following expression, accurate to within terms cubic in the field, for the effective potential energy of the "slow" motion, as in Ref. 10:

$$V_{eff}=-\tfrac{1}{4}(\alpha_{1e}E_1^2\cos^2\theta_0+\alpha_{2e}E_2^2\sin^2\theta_0\cos^2\varphi_0). \tag{20}$$

The function V_{eff} determines the thermodynamic-equilibrium distribution of the axes of the molecules with respect to the angles θ_0, φ_0, as in (11) for collinear fields.

Using the values ξ_θ and ξ_φ in (19), we find the x and y projections of the dipole moment of the molecule: $p_{x,y}=\Sigma_{\omega_i=\Omega}p_{x,y}^{\omega_i}\cos\omega_i t$. Averaging p_x over the equilibrium distribution, we find

$$\begin{aligned} \overline{p_x^{\omega_1}}&=E_1\left[\chi_1^{(1)}+\frac{\alpha_{1e}^2E_1^2}{45kT}-\frac{\alpha_1E_1^2}{60J\omega_1^2}-\frac{\alpha_{1e}\alpha_{2e}E_2^2}{90kT}\right.\\ &\quad\left.-\frac{\alpha_2(\alpha_1+\alpha_2)(\omega_1^2+\omega_2^2)E_2^2}{10J(\Delta\omega)^2(\omega_1+\omega_2)^2}\right], \end{aligned} \tag{21}$$

$$\overline{p_x^{\omega_1\pm2\omega_2}}=\frac{\alpha_2E_1E_2^2}{120J}\left[\frac{\alpha_1}{\omega_2^2}-6\frac{\alpha_1+\alpha_2}{(\omega_1\pm\omega_2)^2}\right],$$

$$\overline{p_x^{3\omega_1}}=-\frac{\alpha_1^2E_1^3}{60J\omega_1^2}.$$

We find the y projections of the polarization by changing the indices in Eqs. (21): $x\rightarrow y$, $1\rightarrow 2$, $2\rightarrow 1$.

Of the 13 frequencies Ω_1 at which the dipole moment of an individual molecule oscillates, only four are associated with a polarization after an average is taken over the equilibrium thermodynamic distribution in the molecular gas. This comment applies to both the polarization of the gas along the x axis and that along the y axis. This large difference in the numbers of frequencies characteristic of the oscillations of the dipole moment of an individual molecule and of the polarization of the gas (the dipole moment per unit volume) stems from the high symmetry of V_{eff}, for which all the coordinate planes are mirror-symmetry planes.

The vibrational nonlinear polarization at the frequency ω_1 [under the condition $\alpha_2(\alpha_1+\alpha_2)>0$] increases in the presence of a second wave of frequency ω_2 (and vice versa), as in the case of collinear fields.

In contrast with the case of identically polarized waves, the two terms which determine the orientational cubic nonlinearity in $\overline{p_x^{\omega_1}}$ and $\overline{p_y^{\omega_2}}$ and which are proportional to E_1^2 and E_2^2 differ in sign and thus weaken the orientational effect. If $2^{\pm1}\alpha_{1e}E_1^2=\alpha_{2e}E_2^2$ holds, then there is no orientational polarizability in $\overline{p_x^{\omega_1}}$ in the case of the plus sign, while in the case of the minus sign there is no orientational polarizability in $\overline{p_y^{\omega_2}}$. By varying the field amplitudes E_1 and E_2 we can thus suppress the orientational nonlinear polarization along either the x axis or the y axis. For the vibrational polarization at the frequencies $2\omega_2\pm\omega_1$, $2\omega_1\pm\omega_2$ the situation is similar. According to (21), any of them can be suppressed through an appropriate choice of the frequencies ω_1 and ω_2.

The results for approximately equal frequencies ($\Delta\omega\ll\omega_1,\omega_2$) are reminiscent of those derived above for collinear fields. The differences are as follows: In the first quartet, the polarizations with frequencies ω_2 and $\omega_2-2\Delta\omega$ are oriented along the y axis, rather than along the x axis; in the second quartet, the susceptibilities $\approx\alpha_1^2/60J\omega^2$ are identical at all frequencies, and the polarization at the frequencies $3\omega_2$ and $3\omega_2-2\Delta\omega$ is oriented along the y axis.

3. Let us examine the polarization of a gas in an elliptically polarized wave. The method which was used in Ref. 5 is based on a separation of high- and low-frequency oscillations. The polarization of the gas in an elliptical wave thus cannot be found from the results for waves of different frequencies with mutually perpendicular polarizations by taking the limit $\Delta\omega\rightarrow 0$ and by changing the initial phase. Formally, this procedure leads to a divergence of the vibrational polarization in (21). We should bear in mind that in the limit $\Delta\omega\rightarrow 0$ the corresponding oscillation

changes from high-frequency to low-frequency; this point requires a separate study.

Using a method similar to that outlined above for examining the polarization of a thermodynamic-equilibrium molecular gas in the field of an elliptically polarized wave

$$\mathbf{E}=\mathbf{i}_x E_1 \cos \omega_1 t+\mathbf{i}_y E_2 \sin \omega_1 t, \tag{22}$$

we find the following expressions for the linear and cubic vibrational-orientational polarizations:

$$\begin{aligned}\bar{p}_x=&\left[\bar{\alpha}_1-\frac{2}{3}\frac{p^2}{J\omega_1^2}+\frac{\alpha_{1e}^2(E_1^2-E_2^2/2)}{45kT}-\frac{\alpha_1^2(E_1^2+E_2^2/4)}{60J\omega_1^2}\right]\\ &\times E_1 \cos \omega_1 t-\frac{\alpha_1^2(E_1^2+3E_2^2/4)}{60J\omega_1^2} E_1 \cos 3\omega_1 t,\\ \bar{p}_y=&\left[\bar{\alpha}_1-\frac{2}{3}\frac{p^2}{J\omega_1^2}+\frac{\alpha_{1e}^2(E_2^2-E_1^2/2)}{45kT}-\frac{\alpha_1^2(E_2^2+E_1^2/4)}{60J\omega_1^2}\right]\\ &\times E_2 \sin \omega_1 t+\frac{\alpha_1^2(E_2^2+3E_1^2/4)}{60J\omega_1^2} E_2 \sin 3\omega_1 t.\end{aligned} \tag{23}$$

For the elliptically polarized wave (22), the electric vector E rotates in a definite direction. We would naturally expect that the tips of all the polarization vectors (linear and nonlinear) in a macroscopically isotropic gas would, in tracing out the ellipse, rotate in the same direction. However, this is not the case.

According to (23), the vectors of the linear, vibrational cubic, and orientational (for $0.5<E_1^2/E_2^2<2$) polarizations rotate in the same direction as the E vector of the light field.

The vectors of the cubic orientational polarization (for $E_1^2/E_2^2<0.5$ and $E_1^2/E_2^2>2$) and the vibrational polarization at the tripled frequency, on the other hand, rotate opposite the rotation of the light field, in contrast with our expectations. According to (23), with $E_1^2/E_1^2=2^{\pm 1}$ the orientational cubic polarization degenerates from elliptical to linear, directed along either the x axis (in the case of the plus sign) or the y axis (the minus sign).

In summary, this paper has continued the theoretical study, begun in Ref. 1, of how certain factors which have previously been ignored in the theory affect the optical polarization of molecular gases. These factors are the orientational effect which stems from the constant dipole moments of the molecule in the alternating field and the forced high-frequency vibrations of the axes of these molecules. We have derived analytic expressions for the vibrational-orientational polarization for the case in which two monochromatic waves differing in frequency are applied to a molecular gas. We have studied the polarization effect of these waves on each other; this effect is particularly large when the incident waves are approximately equal in frequency. The nonlinear polarization at one frequency depends most strongly on the strength of the field at the other frequency.

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