High-frequency susceptibility of a gas of anisotropically polarizable dipole molecules

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(Submitted 12 March 1990; resubmitted 2 November 1990)
Zh. Eksp. Teor. Fiz. **99**, 715–720 (March 1991)

The high-frequency linear and nonlinear susceptibilities of a gas whose molecules are anisotropically polarized by an external field and possess a constant dipole moment are determined quantitatively. The analytic dependence of the susceptibility on the characteristics of the molecule, field strength, and medium are found by using the Kapitza method. Rotation of the molecule is taken into account. The linear and nonlinear inertialess components of the susceptibility, due to jitter of the constant and induced molecular dipoles in the high-frequency field, are determined, as well as the nonlinear inertial component due to angular orientation of the molecules in the high-frequency field.

1. As is known, the χ susceptibility of materials determines the picture of propagation of intense laser radiation in them. The susceptibility connected with the orientations of the constant and induced molecular dipole moments in a constant electric field has been investigated in sufficient detail.[1] The same cannot be said about alternating fields. For example, it is usually assumed that "if a polar molecule is in an alternating electric field then... the orientation of the molecules cannot be established, as a result of which the field does not produce dipole polarization but only the induced polarization."[1] As will be clear from what follows, this assertion requires reconsideration. We shall only note here that it is not taken into account in the theory that, in contrast with the static case, in a high-frequency field the requirement of macro-orientation of the molecules is not essential for the establishment of polarization of the material; further, in the present paper we show that macro-orientation of the molecules occurs also for a system of constant dipoles in a high-frequency field.

We find below, in explicit analytic form, the heretofore unknown linear and nonlinear χ susceptibilities for a nondissipative molecular gas consisting of dipolar diatomic (or linear) anisotropically polarized molecules located in a high-frequency field. In the consideration of induced oscillations of molecular dipoles in high-frequency fields, we use the Kapitza method.[2] In application to diatomic molecules, this method was used in the study of the scattering of electromagnetic waves in a molecular gas, in which the molecules were considered as rigid rotators,[3] and also in the study of the dynamic Stark effect.[4] However, the method has not been used to determine the refractive index of a molecular gas.

In principle, quantum mechanics allows us to determine any parameter of the molecules. This is a very complicated problem and individual for each molecule. Below, we shall assume the following characteristics of the molecule to be known: the linear high-frequency polarizability tensor $\alpha(\omega)$, the dipole moment $\mathbf{p}$ and the tensor of the moment of inertia J. We add to these characteristics of the molecule the parameters of a linearly polarized electric field: the frequency ω, the amplitude E_ω, and also the gas temperature T. The aggregate $\Sigma = \{\alpha(\omega), \mathbf{p}, J, \omega, E_\omega, T\}$ represents the set of parameters entering into the equations of motion of the molecules and into the function of their equilibrium distribution. Consequently, Σ completely determines the equilibrium susceptibility of the molecular gas in the high-frequency field associated with the oscillations of the molecules and their orientation.

Our next problem is to find the $\chi(\Sigma)$ dependence. We note that the macropolarization of the gas amounts to $N(\Sigma)$, where N is the concentration of gas molecules, and the square of the refractive index is $n^2 = 1 + 4\pi N$. We shall limit ourselves below to the case of diatomic and linear molecules. For them, the polarizability tensor, referred to the principal axes x, y, and z with unit vectors $\mathbf{i}, \mathbf{j}, \mathbf{k}$, where the x axis is directed along the axis of the molecule, reduces to two components $\alpha_x = \alpha_z = \alpha \equiv \alpha^{is}$, and the dipole moment $\mathbf{p}$ is directed along the x axis. For these molecules we have $J_x = 0$ and only the moment of inertia J associated with rotation of the molecule about the y and z axes enters into the equations.

2. Let a monochromatic plane-polarized high-frequency electric field act on the molecule:

$$\mathbf{E} = \mathbf{i}'E, \quad E = E_\omega \cos(\omega t). \tag{1}$$

The dipole moment of a molecule in this field can be represented in the form

$$\mathbf{P} = \mathbf{i}\alpha_x E_x + \mathbf{j}\alpha_y E_y + \mathbf{k}\alpha_z E_z + \mathbf{i}p = \alpha^{is}\mathbf{E} + \mathbf{i}(p + \alpha E \cos\theta). \tag{2}$$

Here $\alpha = \alpha_x - \alpha^{is}$ is the orienting linear polarizability,[1] and θ is the angle between the direction of the field and the axis of the molecule, so that $(\mathbf{i}\cdot\mathbf{i}') = \cos\theta$.

The equation of angular motion of the axis of a dipole molecule without account of its polarizability (rigid rotator) was developed in Ref. 3. With account of the polarizability, it takes the following form:

$$\begin{gathered} J\frac{d^2\theta}{dt^2} = -\frac{dU_1(\theta)}{d\theta} - pE_\omega \cos(\omega t)\sin\theta - \frac{\alpha E_\omega{}^2}{4}\cos(2\omega t)\sin 2\theta, \\ J\frac{d\varphi}{dt} = \frac{M_z}{\sin^2\theta}, \\ U_1(\theta) = -\frac{\alpha E_\omega{}^2}{4}\cos^2\theta + \frac{M_z{}^2}{2J\sin^2\theta}. \end{gathered} \tag{3}$$

Here φ is the azimuthal angle, and M_z is the conserved pro-

0038-5646/91/030396-04$03.00

jection of the angular momentum of the molecule in the direction of the field. In gases and vapors, the rotation of the molecules obeys Eq. (3) over times that are shorter than the times between the successive binary collisions of the particles ν^{-1}.

The approximate solutions of the set of Eqs. (3) can be found by the Kapitza method, which is universal for high-frequency effects. Within the framework of this method it is assumed that the solution can be represented in the form $\theta(t) = \theta_0(t) + \xi(\theta_0,t)$, where $\theta_0(t)$ describes a slow, smooth motion along some trajectory, while $\xi(\theta_0,t)$ is a high-frequency oscillation of small amplitude about this trajectory. According to Ref. 2, we obtain the following for θ_0 and ξ:

$$J\frac{d^2\theta_0}{dt^2} = -\frac{dU(\theta_0)}{d\theta_0}, \qquad U(\theta_0) = U_1(\theta_0) + U_2(\theta_0),$$
$$U_2(\theta_0) = -\frac{p^2E_\omega^2}{4J\omega^2}\cos^2\theta_0 + \frac{\alpha^2E_\omega^4}{256J\omega^2}\sin^2 2\theta_0, \tag{4}$$
$$\xi = \frac{pE_\omega}{J\omega^2}\sin\theta_0\cos(\omega t) + \frac{\alpha E_\omega^2}{16J\omega^2}\sin 2\theta_0\cos(2\omega t).$$

As we see, the slow smooth angular motion of the molecular dipole is governed by the potential field $U(\theta_0)$. We note that the orientation of the molecules is manifested in the deviation of their statistical distribution in the high-frequency field from isotropic form. This deviation is governed by the field $U(\theta_0)$ and is connected with the slow smooth angular motion $\theta_0(t)$. The alternating field affects the motion $\theta_0(t)$ through the addition of $U_2(\theta_0)$ to the potential energy (more precisely, to the quasienergy). Further, for the value of the field $E_\omega \ll 8p/\alpha \approx 10^9$ V/cm, we can neglect components $\approx E_\omega{}^4$, and consequently,

$$U(\theta_0) = -a\cos^2\theta_0 + b\sin^{-2}\theta_0,$$
$$a = \frac{E_\omega^2}{4}\left(\alpha + \frac{p^2}{J\omega^2}\right), \qquad b = \frac{M_z^2}{2J}. \tag{5}$$

For $a > 0$ and $a < b$, equilibrium of the axis of the molecule [min $U(\theta_0)$] will occur at $\theta_0^{(1)} = \pi/2$, for $a > 0$ and $a > b$, at $\theta_0^{(2)} = \arcsin^{-1}(b/a)^{1/4}$,[3] only at $b/a \to 0$ we shall have $\theta_0^{(2)} \to 0$. If $a < 0$, then the equilibrium should be observed at $\theta_0^{(3)} = \pi/2$. The linear polarizability and the square of the dipole moment of the molecule enter into U additively, so that even at $\alpha = 0$ there will be orientation of the dipoles. The deviation of the equilibrium distribution from isotropic, is by virtue of (5) symmetric about to the plane perpendicular to E. Consequently, the complete dipole moment of the system is equal to zero in thermodynamic equilibrium, although the distribution of the dipoles is not isotropic. The quadrupole moment of the system is different from zero.

Knowledge of the quantity $U(\theta_0)$ allows us to determine the Boltzmann distribution of the probabilities of orientations of the molecules relative to the direction of the field under conditions of thermodynamic equilibrium. Using (5), we obtain the following for the classical distribution function

$$dw(\theta_0, M_z) = A\exp\left[v^2\cos^2\theta_0 - \frac{M_z^2}{2JkT\sin^2\theta_0}\right]d\theta_0\, dM_z,$$
$$v^2 = \left(\alpha + \frac{p^2}{J\omega^2}\right)\frac{E_\omega^2}{4kT}. \tag{6}$$

Integrating over M_z, we find the equilibrium thermodynamic distribution of the axes of the molecules with respect to the angle θ_0:

$$dw(\theta_0) = \frac{1}{F(v^2)}\exp(v^2\cos^2\theta_0)\sin\theta_0\, d\theta_0,$$
$$F(v^2) = \int_0^\pi \exp(v^2\cos^2\theta_0)\sin\theta_0\, d\theta_0. \tag{7}$$

To determine the susceptibility, the complete dipole moment of the molecule $\mathbf{P}_{E,\theta_0}(t)$ must be averaged over the ensemble, i.e., over the distribution (7):

$$\mathbf{P}_E(t) = \int \mathbf{P}_{E,\theta_0}(t)\, dw(\theta_0),$$

we find next the components that oscillate at the frequency ω, i.e., $\mathbf{P}_{E,\omega} = \chi(\omega,E_\omega)\mathbf{E}$, and also the components that oscillate at frequencies that are multiples of ω. Expanding $\chi(\omega,E_\omega)$ in powers of the field, we obtain the linear and nonlinear components of the susceptibility at the frequency ω.

In the averaging over the dipole moment of the molecule, the components perpendicular to the field direction vanish because of the axial symmetry of the problem. It then suffices to average only the projection of the dipole moment on the direction of the field. This average is then equal to

$$P_{E,\theta} = \alpha^{is}E + (p + \alpha E\cos\theta)\cos\theta. \tag{8}$$

Substituting $\theta = \theta_0 + \xi$, we obtain

$$P_{E,\theta_0}(t) = \sum_{k=0}^{3} a_k\cos(k\omega t),$$
$$a_0 = p\cos\theta_0 - \frac{p\alpha E_\omega^2}{J\omega^2}\sin^2\theta_0\cos\theta_0,$$
$$a_1 = \alpha^{is}E_\omega + \alpha E_\omega\cos^2\theta_0 - \frac{p^2E_\omega}{J\omega^2}\sin^2\theta_0 - \frac{\alpha^2E_\omega^3}{8J\omega^2}\sin^2\theta_0\cos^2\theta_0, \tag{9}$$
$$a_2 = -\frac{9p\alpha E_\omega^2}{8J\omega^2}\sin^2\theta_0\cos\theta_0, \qquad a_3 = -\frac{\alpha^2E_\omega^3}{8J\omega^2}\sin^2\theta_0\cos^2\theta_0.$$

Averaging (9) over the Boltzmann distribution (7), we find the mean value of the dipole moment $P_E(t)$. Components with frequencies 0 and 2ω vanish upon averaging, so that

$$P_E(t) = P_{E,\omega}(t) + P_{E,3\omega}(t),$$
$$P_{E,\omega}(t) = \left[\alpha^{is} - \frac{p^2}{J\omega^2} + \left(\alpha + \frac{p^2}{J\omega^2}\right)\frac{F'}{F} - \frac{\alpha^2E_\omega^2}{8J\omega^2}\frac{F'-F''}{F}\right] \times E_\omega\cos(\omega t), \tag{10}$$
$$P_{E,3\omega}(t) = -\frac{\alpha^2E_\omega^2}{8J\omega^2}\frac{F'-F''}{F}E_\omega\cos(3\omega t).$$

The primes on F correspond to differentiation with respect to v^2. Within the framework of the model used, the resultant formulas are valid up to fields $E_\omega \approx 10^9$ V/cm.

To determine the relative roles of the different components of the susceptibility, we must carry out estimates for them. We use the following molecular characteristics: $\alpha = 10^{-24}$ cm^3, $p = 10^{-18}$ cgs units, $J = 10^{-40}$ g·cm^2 (which corresponds to diatomic molecules containing hydrogen); further, we set $\omega = 10^{15}\ \mathrm{s}^{-1}$ and $T = 300$ K. At $E < 10^8$ V/cm $= 3\cdot 10^5$ cgs units, we obtain $v \ll 1$. Therefore the resultant expressions can be expanded in series in v. For the susceptibility at a frequency ω we obtain finally (with accuracy to E^2)

$$\chi(\omega, E_\omega) = \frac{\alpha_x + 2\alpha^{is}}{3} - \frac{2p^2}{3J\omega^2} - \frac{\alpha^2 E_\omega^2}{60 J\omega^2} + \left(\alpha + \frac{p^2}{J\omega^2}\right)^2 \frac{E_\omega^2}{45kT}. \tag{11}$$

The first term here, which we denote by $\chi_\alpha^{(1)}(\omega)$, is connected with the linear polarizability of the molecule. The second term, denoted by $\chi_p^{(1)}(\omega)$, is the high-frequency linear susceptibility of the molecule due to jitter of the constant dipoles in the high-frequency field. The third term, denoted by $\chi_\alpha^{(3)}(\omega)$, is the nonlinear susceptibility, due to jitter of the induced dipoles in the high-frequency field. All three terms are due only to the high-frequency oscillations of the induced and constant dipole moments of the molecules and are in no way connected with the slow orientation of the molecules. Therefore, they describe the inertialess effects of the response of the medium in the high-frequency field.

The fourth term in (11), which we denote by $\chi_{\alpha,p}^{(3)}$, is the high-frequency nonlinear susceptibility of the molecular gas, due to the anisotropy of the distribution of the directions of the dipole moments of the molecules in the high-frequency field. The macroscopic polarization of the medium associated with $\chi_{\alpha p}^{3}(\omega)$ does not appear instantly with onset of the field, but only after the passage of the time necessary for the establishment of the equilibrium distribution (7). We note that the contribution of the constant dipole moment under the conditions described above is small and the orientational susceptibility is determined basically only by the induced dipole moment. This fact was noted in a study of the scattering of intense light by a molecule.[5] Of course, cases are possible, at small α and ω, in which the effect of the constant dipole moment must also be taken into account. We note that the second, third and fourth terms in (10) are apparently new in the theory.

We now estimate the relative contributions of the different parts of the susceptibility for the values of the problem parameters mentioned above and for $E_\omega = 3\cdot 10^4$ cgs units:

$$\chi_\alpha^{(1)} : \chi_p^{(1)} : \chi_\alpha^{(3)} : \chi_{\alpha,p}^{(3)} = 1 : 10^{-2} : 10^{-7} : 5\cdot 10^{-4}.$$

The main contribution to the linear susceptibility is made by the linear polarizability of the molecule, and to the nonlinear susceptibility by the orienting mechanism.

3. There is interest in comparing the results given above with the known results for the susceptibility of a molecular gas in a constant electric field. In a constant field[1] the term

$$\chi_p^{(1)}(0) = \frac{p^2}{3kT} \gg \chi_\alpha^{(1)}(0) = \frac{\alpha_x(0) + 2\alpha^{is}(0)}{3}$$

usually dominates. In a high-frequency field the situation is reversed, and $\chi_p^{(1)}$ is negative. There is no analog to the quantity $\chi_p^{(3)}$ in a static field. The inertial part of the susceptibility in a static field E_0 is

$$\chi_{\alpha,0}^{(3)}(0) = \frac{2}{45}\frac{\alpha^2 E_0^2}{kT}.$$

Thus, in spite of the differences in the physical picture of orientation of the molecules in the static and high-frequency fields, their orientational susceptibilities have the same functional dependences on the parameters of the problem.

If the asymmetry of the susceptibility of the molecule, i.e., $\alpha = 0$, but $p = 0$, then, according to (10), the high-frequency inertial susceptibility is characterized by the quantity $\chi_{0p}^{(3)}(\omega)$, which amounts to only 10^{-4} of the susceptibility $\chi_{\alpha p}^{(3)}(\omega)$. In the static field,

$$\chi_{0,p}^{(3)}(0) = \frac{p^4 E_0^2}{45(kT)^3}.$$

Therefore, setting $E_0 = 30$ kV/cm and $E_\omega = 10^7$ V/cm for estimates, we obtain $\chi_{0p}^{(3)}(\omega) : \chi_{0p}^{(3)}(0) = -10^{-2}$, i.e., the corresponding susceptibility in a static field is of opposite sign and is significantly greater than the dynamic susceptibility even in relatively weak fields E_0. As we shall see, in contrast with the static case, the case of the dynamic susceptibility associated with the rigid dipole can play a significant role only in the case of weak asymmetry of the polarizability of the molecule. The relative contribution of constant dipoles to the orientational susceptibility is characterized by the parameter $p^2/\alpha J\omega^2$.

Let us now discuss in more detail the limits of applicability for the method developed above. First, a molecular gas is considered in which, in times between two successive binary collisions, the molecular dipole moves only in the field of an external light wave. In order that the Kapitza method be applicable to such motions, satisfaction of the condition $\omega \gg \nu$ is necessary. Second, the condition $\nu \gg \tau_i^{-1}$ should be satisfied, where τ_i is the characteristic time of action of the high-frequency field, which means smallness of change of the field within the time of establishment of the Boltzmann distribution (6). Third, the high-frequency oscillations of the molecular dipoles represent only part of the motion. In addition, there are oscillations about the positions of equilibrium [the minima of the potential energy $U(\theta_0)$]. To be able to apply correctly the Kapitza method it is necessary that the frequency of the high-frequency oscillations significantly exceed the frequency of oscillation of the system about the positions of equilibrium. In weak fields, at $a < b \approx kT/2$, the oscillations are about $\theta_0^{(1)} = \pi/2$ with frequency $\omega_1 \leqslant M_z/J \approx (kT/J)^{1/2} \approx 10^{13}\ \mathrm{s}^{-1}$, and in strong fields at $a > b$ about $\theta_0^{(2)}$ with frequency

$$\omega_2 \approx \left[\frac{2}{J}(\alpha + p^2/J\omega^2)\right]^{1/2} E_\omega \approx 10^8 E_\omega\ \mathrm{s}^{-1}$$

The frequency ω_2 becomes comparable with $\omega \approx 10^{15}\ \mathrm{s}^{-1}$ in fields $E_\omega \approx 10^9$ V/cm. Thus, in a field of intensity less than atomic the oscillations of θ_0 have a frequency less than ω.

4. Use of the Kapitza method turned out to be effective in the investigation of linear and nonlinear susceptibilities. Analytic expressions were obtained for the high-frequency susceptibility of a molecular gas consisting of linear anisotropically polarizable dipole molecules. It was shown that the dynamic susceptibilities, in contrast with the static, are not always governed by the macro-orientations of the molecules. There are linear and nonlinear inertialess components of the susceptibility, due to the jitter of the dipole moments even in isotropic angular distribution of the axes of the molecules. The characters of the orientations of dipole molecules in a constant and in a high-frequency field differ substantially. In a constant field the medium acquires a macroscopic dipole moment, as against a quadrupole moment in a high-frequency field.

As is known[6,7], in the field of a light beam with inhomogeneous distribution of the intensity aver the cross section, a force acts on the free charges that is proportional to the gradient of the intensity, crowding out the charges into the region of minimal interaction of the charge with the field. In the present work it is shown that a similar picture exists also for a free dipole in a light field, except that the crowding-out takes place not over the spatial coordinate but over the angular coordinate.

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Translated by R. T. Beyer