DIELECTRIC CONSTANT OF A GAS NEAR THE QUADRUPOLE TRANSITION FREQUENCY

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The dielectric constant of a gas at the quadrupole transition frequency is determined in the pair collision approximation. The transition between states with momentum 0 (ground state) and 2 (excited state) is considered. The combined effect of collision and Doppler broadening on the line shape is discussed.

THE problem of the absorption line shape in dense gaseous media (the density of atoms n satisfying the condition $n\lambda\!\!\!^{-3} \gg 1$, $\lambda\!\!\!^{-} = c/\omega_0$, where ω_0 is the frequency of the atomic transition under consideration) was recently considered in a number of papers[1-4]. Under these conditions, the line shape is determined by collisions of excited and nonexcited atoms with resonant energy transfer. In the papers mentioned it was assumed that the ground state and the excited levels of the atom are related by an optical dipole transition, and consequently the interaction leading to the resonant transfer of the excitation is the dipole-dipole interaction.

In this paper the dielectric constant of a gas at the quadrupole transition frequency is determined for the case when the momentum of the ground state of the atom is $J_0 = 0$ and the momentum of the atom in the excited state is $J = 2$. In this case the dielectric constant is determined, within certain limitations which will be noted below, by pair collisions of excited and nonexcited atoms with resonant energy transfer due to quadrupole-quadrupole interaction. The energy of this interaction depends on the interatomic distance R like R^{-5}, therefore such an interaction should contribute, in our case, to the collision line width more than the Van der Waals interaction, which is proportional to R^{-6}.

To obtain the dielectric constant we use here the method of temperature-dependent Green's functions, which was used to obtain the optical characteristics of a system in[3] and in a number of other papers[2,5]. In considering the collisions, the pairing condition

$$n\rho_0^3 \ll 1, \tag{1}$$

where ρ_0 is Weisskopf's radius, is assumed to be satisfied, since impact parameters $\rho \sim \rho_0$ are important in collisions with resonance transfer of excitations. In quadrupole-quadrupole interactions (the atomic system of units is used)

$$\rho_0 = Q^{1/2} v^{-1/4}, \tag{2}$$

where Q is the reduced matrix element of the quadrupole moment of the transition, connected with the probability of quadrupole radiation W for the given transition by the relation $Q^2 = 75\,\lambda\!\!\!^{-5}\,W$, and v is the relative velocity of the colliding atoms. It is also assumed that the atomic density satisfies the condition

$$n\lambda\!\!\!^{-3} \gg 1, \tag{3}$$

so that the collision line width is considerably larger than the natural line width of the quadrupole radiation. The population of the excited levels is assumed to be small, i.e., $T \ll \omega_0$.

As shown in[3], when condition (1) is satisfied the retarded two-particle Green's function $K_{nm_0}(\mathbf{p}, \mathbf{k}, \omega)$ of the atomic gas, which determines the polarization operator and by the same token the dielectric constant, satisfies the following integral equation:

$$K_{mm_0}(\mathbf{p}, \mathbf{k}, \omega) = K^0_{mm'}(\mathbf{p}, \mathbf{k}, \omega)\left\{\delta_{m'm_0} - \int d\mathbf{p}'\,\Gamma'_{m'm''}(\mathbf{q}, \mathbf{q}) K_{m''m_0}(\mathbf{p}', \mathbf{k}, \omega)\right\}, \tag{4}$$

and the dielectric constant of the system $\epsilon(\omega)$ is expressed in terms of the two-particle Green's function $K_{nm_0}(\mathbf{p}, \mathbf{k}, \omega)$ in the case under consideration, when quadrupole transitions at the frequency ω_0 are possible, in the following manner:

$$\varepsilon(\omega) = 1 - \frac{\pi}{5} Q^2 k^2 \sum_{mm'} (-1)^m K_{-m} K_{m'} \int d\mathbf{p}\, K_{mm'}(\mathbf{p}, \mathbf{k}, \omega). \tag{5}$$

The reduced matrix element Q of the atomic quadrupole moment between the states characterized by the momenta 0 and 2 is determined as follows:

$$\langle 2m | Q_{2s} | 00 \rangle = \frac{2Q}{\sqrt{5}} \delta_{ms}, \tag{6}$$

where m is the projection of the excited state momentum, and Q_{2S} is the quadrupole moment operator of the atom, written down in form of a second-rank irreducible tensor connected with the ordinary quadrupole moment tensor of the atom:

$$D_{\alpha\beta} = \sum_i (3x_\alpha^i x_\beta^i - r_i^2 \delta_{\alpha\beta})$$

(the summation is over all the electrons of the atom). The normalization of Q_{2S}, like that of all second-rank irreducible spherical tensors used below, is performed so that $D_{ZZ} = Q_{2S}$. The quantity K_m is the second-rank irreducible spherical tensor corresponding to the tensor $k_\alpha k_\beta / k^2 - \frac{1}{3}\delta_{\alpha\beta}$, $k = \omega/c$. The vector q in (4) is given by $\mathbf{q} = \frac{1}{2}(\mathbf{p} - \mathbf{p}')$.

The function $K^0_{mm'}(\mathbf{p}, \mathbf{k}, \omega)$ can be written down in any system of coordinates in the form

$$K^0_{mm'}(\mathbf{p}, \mathbf{k}, \omega) = -n\varphi(\mathbf{p}) \times \tag{7}$$
$$\times \left\{ \frac{\frac{1}{3}\delta_{mm'} + \frac{2}{3}\sqrt{7/2}(22m's|2m)P_s + \frac{1}{3}(-1)^{m'} P_m P_{-m'}}{\omega - \omega_0 - \Sigma_2(\mathbf{p}) - \mathbf{pk}/M} \right.$$
$$+ \frac{\frac{2}{3}\delta_{mm'} - \frac{2}{3}\sqrt{7/2}(22m's|2m)P_s - \frac{1}{3}(-1)^{m'} P_m P_{-m'}}{\omega - \omega_0 - \Sigma_1(\mathbf{p}) - \mathbf{pk}/M}$$
$$\left. + \frac{(-1)^{m'} P_m P_{-m'}}{\omega - \omega_0 - \Sigma_0(\mathbf{p}) - \mathbf{pk}/M} \right\},$$

where $\varphi(\mathbf{p})$ is the Maxwell distribution, $\int d\mathbf{p}\varphi(\mathbf{p}) = 1$, P_m is the irreducible spherical tensor corresponding to the tensor $^3/_2 p_\alpha p_\beta/p^2 - {}^1/_2\delta_{\alpha\beta}$, $(22ms|2m')$ is a Clebsch-Gordan coefficient, and M is the atomic mass.

The mass operators $\Sigma_m = \Sigma_{-m}$ are expressed in terms of the non-exchange four-pole $\Gamma_{mm'}(\mathbf{p}, \mathbf{p}')$, similar to that introduced in[3]. The four-pole $\Gamma_{mm'}(\mathbf{p}, \mathbf{p}')$ in the integral term of Eq. (4) is an exchange one. The four-poles Γ and Γ' play the role of an effective resonance interaction potential of the atoms in the medium, and are expressed in the pair collision approximation in terms of the zero-angle scattering amplitude of two atoms $f_{mm'}(\mathbf{p}, \mathbf{p}')$ at zero angle:

$$\Gamma_{mm'}(\mathbf{p}, \mathbf{p}) = \frac{i}{M}\,\mathrm{Im}\, f_{mm'}(\mathbf{p}, \mathbf{p}),$$
$$\Gamma'_{mm'}(\mathbf{p}, \mathbf{p}) = \frac{1}{M}\,\mathrm{Re}\, f_{mm'}(\mathbf{p}, \mathbf{p}). \tag{8}$$

The non-exchange four-pole Γ describes the interaction of excited and nonexcited atoms, not resulting in excitation transfer from one atom to another, and the exchange one Γ' describes the interaction with nonradiative excitation exchange between the atoms. These expressions for the four-poles Γ and Γ' are valid in the frequency range

$$\omega - \omega_0 \ll Q^2\rho_0^{-5} = Q^{-1/2}v^{5/4} \tag{9}$$

In order to find the scattering amplitude of two atoms we use the quasiclassical method, assuming that the change of the internal states of the atoms (in particular, the change of the momentum projection of the excited atom or the excitation transfer without change of the internal energy) affects weakly the relative motion of the atoms, and this motion can be considered to be along a straight classical trajectory. Such an approximation was used in[3,4,6-8].

The scattering amplitude $f_{mm'}(\mathbf{q}, \mathbf{p})$ of two atoms is

$$f_{mm'}(\mathbf{q}, \mathbf{p}) = M\int d\mathbf{R} e^{-i\mathbf{q}\mathbf{R}} V_{mm'}(\mathbf{R})\Psi_{m'm_0}(\mathbf{R}, \mathbf{p}). \tag{10}$$

The definition (10) differs from the ordinary one by the factor $-1/4\pi$. The matrix elements $V_{mm'}(\mathbf{R})$ are those of the quadrupole-quadrupole interaction operator taken between atomic wave functions and are the first nonvanishing matrix elements generated by expanding the Coulomb interaction potential of two neutral atoms in powers of $1/R$ for the transitions $0 \rightleftarrows 2$. These matrix elements are of the form

$$V_{mm'}(\mathbf{R}) = \frac{Q^2}{R^5}\left(-\frac{7}{15}\delta_{mm'} + \sqrt{\frac{7}{2}}(22ms|2m')Y_s + \frac{21}{4}(-1)^{m'}Y_mY_{-m'}\right), \tag{11}$$

where Y_m is the irreducible spherical tensor corresponding to the tensor $R_\alpha R_\beta/R^2 - {}^1/_3\delta_{\alpha\beta}$. The wave function $\Psi_{mm_0}(\mathbf{R}, \mathbf{p})$ describes the relative motion of atoms with momentum $\mathbf{p}$ and polarization m_0 of the excited atom prior to scattering. If a wave function in the form

$$\Psi_{mm_0}(\mathbf{R}, \mathbf{p}) = e^{i\mathbf{p}\mathbf{R}}S_{mm_0}(\mathbf{R}, \mathbf{p})$$

is looked for, we obtain for the functions S_{mm_0} the equation:

$$iv\nabla S_{mm_0} = V_{mm'}(\mathbf{R})S_{m'm_0}. \tag{12}$$

In deriving Eqs. (12) from Schrödinger's equation we neglected the second derivatives of the functions S_{mm_0}, which can be done if the relative velocity of atoms v satisfies the condition

$$M^{-1/5} \ll v \ll 1. \tag{13}$$

If this condition is satisfied, it can be also assumed that the relative motion of the atoms is along the straight line

formula $$R^2 = \rho^2 + v^2t^2,$$

where ρ is the impact parameter. In this case Eqs. (12) reduce to a system of linear differential equations. Their solution and the calculation of the integrals (10) was performed on an electronic computer and gave the following expression for the zero-angle scattering amplitude:

$$\begin{aligned} f_{mm'}(\mathbf{p}, \mathbf{p}) = {} & i\pi Q\sqrt{{}^1/_2 pM}\{\alpha_2[{}^1/_3\delta_{mm'} + {}^2/_3\sqrt{7/2}(22m's|2m)P_s \\ & + {}^1/_3(-1)^{m'}P_mP_{-m'}] + \alpha_1[{}^2/_3\delta_{mm'} - {}^2/_3\sqrt{7/2}(22m's|2m)\,P_s \\ & - {}^4/_3(-1)^{m'}P_mP_{-m'}] + \alpha_0(-1)^{m'}P_mP_{-m'}. \end{aligned} \tag{14}$$

Here α_2, α_1, and α_0 are constants, obtained by numerical integration of the system (12), and equal

$$\alpha_2 = -2.30 + 0.484i; \quad \alpha_1 = -1.66 - 0.072\,i; \quad \alpha_0 = -1.30 - 0.018\,i. \tag{15}$$

We turn now to Eqs. (4) for the two-particle Green's function of the atoms of the medium. They are too cumbersome to solve in the general case, and therefore we use the four-poles $\Gamma_{mm'}(\mathbf{p}, \mathbf{p})$ and $\Gamma'_{mm'}(\mathbf{p}, \mathbf{p})$, averaged over the direction of the vector $\mathbf{p}$, which we denoted by $\overline{\Gamma}$:

$$\overline{\Gamma}_{mm'}(p) = \frac{1}{4\pi}\int d\Omega\,\Gamma_{mm'}(\mathbf{p}, \mathbf{p}) \tag{16}$$

and similarly for $\Gamma'_{mm'}(\mathbf{p})$. The thus averaged four-poles depend only on the absolute value of $\mathbf{p}$:

$$\overline{\Gamma}_{mm'}(p) = \delta_{mm'}i\pi Q\sqrt{\frac{p}{2M}}\,\alpha',$$
$$\overline{\Gamma}'_{mm'}(p) = -\delta_{mm'}\pi Q\sqrt{\frac{p}{2M}}\,\alpha'', \tag{17}$$

where

$$\alpha' = \mathrm{Re}\,\alpha = \mathrm{Re}\,({}^2/_5\alpha_2 + {}^2/_5\alpha_1 + {}^1/_5\alpha_0) = -1.84,$$
$$\alpha'' = \mathrm{Im}\,\alpha = 0.160.$$

The accuracy of this approximation will be discussed below.

In the general case the mass operator Σ_m is expressed in terms of the non-exchange four-poles $\Gamma_{mm'}$ in the following manner, as shown in[3]:

$$\Sigma_m\delta_{mm'} = in\int d\mathbf{p}'\varphi(\mathbf{p}')\Gamma_{mm'}(\mathbf{q}, \mathbf{q}),$$

where $\mathbf{q} = {}^1/_2(\mathbf{p} - \mathbf{p}')$. The explicit expressions for the mass operator are the following:

$$\begin{aligned} \Sigma_2(p) &= i\sqrt{\pi u}\,nQ(-1.60J_1 - 0.75J_2 + 0.06J_3), \\ \Sigma_1(p) &= i\sqrt{\pi u}\,nQ(-1.98J_1 + 0.54J_2 - 0.22J_3), \\ \Sigma_0(p) &= i\sqrt{\pi u}\,nQ(-2.05J_1 + 0.42J_2 + 0.33J_3), \end{aligned} \tag{18}$$

where $u = (2T/M)^{1/2}$, $x^2 = p^2/2MT$,

$$J_1(x) = \frac{1}{2x}\int_{-\infty}^{\infty}(x-y)\,|x-y|^{1/2}e^{-y^2}dy,$$

$$J_2(x) = \left(1 + \frac{2}{x^2}\right)J_1(x) - \frac{3}{2x^2}\int_{-\infty}^{\infty}|x-y|^{1/2}e^{-y^2}dy,$$

$$J_3(x) = \left(1 - \frac{4}{x^2} - \frac{8}{x^4}\right)J_1(x) - \frac{1}{x^2}\left(1 + \frac{6}{x^2}\right)\int_{-\infty}^{\infty}|x-y|^{1/2}e^{-y^2}dy.$$

When the four-pole $\overline{\Gamma}_{mm'}(p)$ averaged over the directions of the vector **p** is used, the mass operator is independent of the index m:

$$\Sigma_m\delta_{mm'} = \Sigma\delta_{mm'} = \delta_{mm'}i\sqrt{\pi u}\, nQ\alpha' J_1(x). \tag{19}$$

We consider the case when the Doppler width is much smaller than the collision width

$$n\rho_0^2 v \gg \omega_0 v / c, \tag{20}$$

which is valid for the temperature range

$$M(\omega_0/c)^8 \ll T \ll \omega_0.$$

In the denominator of Eq. (7) one can then neglect the terms $\mathbf{p}\cdot\mathbf{k}/M$, which lead to the Doppler broadening, and therefore the Green's function depends only on **p** and ω: $K_{mm'}(\mathbf{p}, \omega)$. The integral equations (4) can be reduced to a system of three equations for the functions $K_0(p, \omega)$, $K_1(p, \omega)$, and $K_2(p, \omega)$, and the angular dependence on the direction of the vector **p** is similar to (7). If the function F(x, s) is introduced in the following manner:

$$\frac{2}{5}K_2(p,\omega)+\frac{2}{5}K_1(p,\omega)+\frac{1}{5}K_0(p,\omega) = -\frac{e^{-x^2}}{(2\pi MT)^{3/2}\sqrt{\pi u}\,Q}F(x,s), \tag{21}$$

where $s = (\omega - \omega_0)/(\pi u)^{1/2}nQ$, we obtain for this function the following equation:

$$F(x,s)(s - i\alpha' J_1(x)) = \\ = 1 - \frac{2}{5}\alpha'' x^{3/2}\int_0^\infty y e^{-y^2}dy\left[\left(1+\frac{y}{x}\right)^{5/2} - \left|1-\frac{y}{x}\right|^{5/2}\right]F(y,s). \tag{22}$$

The dielectric constant (5) can be expressed directly in terms of the solution of Eq. (22):

$$\varepsilon(\omega) = 1 + \frac{16}{45}\frac{Q}{u^{1/2}\chi^2}\chi(s) = 1 + \frac{16}{45}\frac{Q}{u^{1/2}\chi^2}\int_0^\infty x^2 e^{-x^2}F(x,s)\,dx. \tag{23}$$

The solution of Eq. (22) and the calculation of $\chi(s)$ were performed with an electronic computer. The result of the numerical solution is that this function can be approximated with an accuracy of 1% by

$$\chi(s) = \frac{\sqrt{\pi}}{4}(s + 0.170 + i1.98)^{-1}. \tag{24}$$

As well known, under certain conditions the imaginary part of the dielectric constant determines the absorption line shape in a gas. As seen from (23) and (24), in our case and in the frequency range $\omega - \omega_0 \ll Q^{-1/2}v^{5/4}$ the absorption line is described sufficiently accurately by a dispersion distribution, the line shift Δ is

$$\Delta = 0.170\sqrt{\pi u}nQ \tag{25}$$

and the width Γ is larger by about one order of magnitude:

$$\Gamma = 1.98\sqrt{\pi u}nQ. \tag{26}$$

To estimate the accuracy of replacing the four-poles $\Gamma_{mm'}$ and $\Gamma'_{mm'}$ by their averaged values (17), the solution of Eq. (4) was obtained in both cases by the method of successive approximations. The results enable us to conclude that the expression for the dielectric constant $\epsilon(\omega)$, given by Eqs. (23) and (24), is valid within 2% in the gas temperature and density ranges, determined by the inequalities (2), (3), and (20).

Consider now the case corresponding to a transition between excited states, where the lower state has momentum 2 and is related to the ground state of the atom (momentum 0) by a quadrupole transition. The upper state is characterized by a total momentum j and can be related to the lower excited one by a dipole transition, but the transition from it to the ground state is forbidden. Then, if the population of the excited states is small, the integral term of Eq. (4) can be neglected and the dielectric constant can be obtained for any ratio of the Doppler and collision widths. The main contribution to the line broadening is from collisions between atoms in the state with momentum 2 and non-excited atoms.

The dielectric constant is then of the form

$$\varepsilon(\omega) = 1 + \frac{4\pi d_j^2}{(2j+1)k^2}\sum_{\substack{\nu\nu_0\\ mm_0}}(12\nu m|jM)(12\nu_0 m_0|jM)(-1)^\nu k_{-\nu}k_{\nu_0} \\ \times\int d\mathbf{p}\, K^0_{mm_0}(\mathbf{p},\mathbf{k},\omega), \tag{27}$$

where ω_0 is the frequency of the transition $j \to 2$, d_j is the reduced matrix element of the transition $j \to 2$, and the mass operator Σ_m and $K^0_{mm_0}$ are given by Eqs. (18) and (7) with the replacement of n in (7) by $n_2/5$, where n_2 is the density of atoms in states with momentum 2.

If Eq. (19) is used for Σ, which, as noted, gives an error of the order of 2%, the dielectric constant can be written in the form

$$\varepsilon(\omega) = 1 - \frac{4\sqrt{\pi}}{15}\frac{n_2 d_j^2}{ku}\int_{-\infty}^{\infty} x e^{-x^2}dx\left\{\ln[(s+x\delta)^2 + \alpha'^2 J_1^2(x)]\right. \\ \left. + 2i\,\mathrm{arctg}\frac{s+x\delta}{\alpha' J_1(x)}\right\}. \tag{28}$$

Here $\delta = ku/(\pi u)^{1/2}nQ$.

The computer calculations show that in this case the function $J_1(x)$ can also be replaced, accurately within 2%, by the constant $J_1(x_0) = 1.076$, and the line shape is described by the ordinary convolution of Doppler and dispersion distributions:

$$\varepsilon(\omega) = 1 + \frac{4\pi n_2 d_j^2}{15ku}Z(\xi,\eta), \tag{29}$$

where $Z(\xi, \eta)$ are tabulated functions[9]:

$$Z(\xi,\eta) = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{e^{-x^2}dx}{x-\xi-i\eta}, \quad \xi = \frac{\omega-\omega_0}{ku}, \quad \eta = \frac{1{,}98\sqrt{\pi u}\,nQ}{ku}.$$

The foregoing discussion gives grounds for assuming that for any ratio between the Doppler and collision widths the dielectric constant can be represented to the same accuracy by

$$\varepsilon(\omega) = 1 - \frac{16}{45}\frac{Q}{u^{1/2}\chi^2}\frac{1}{\delta}Z(\xi,\eta)\left[1 - \frac{0{,}170}{\delta}Z(\xi,\eta)\right]^{-1} \tag{30}$$

for transitions between the ground and excited states of atoms with momenta 0 and 2, respectively.

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