Emission spectra of atoms and molecules accelerated by a stationary external field in a gas or a plasma

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Resonance absorption (amplification) spectra of atoms or molecules accelerated by an external field over a length equal to the mean free path are considered. It is shown that the effect of the acceleration on the spectral characteristics of the radiation do not reduce to drift effects. The influence of acceleration is most pronounced for the narrow nonlinear structures arising in saturated-line spectra (nonlinear spectroscopy). Sufficiently large acceleration evokes additional broadening of the structures and an appreciable distortion of their shape as compared with the dispersion shape.

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1. INTRODUCTION

The force-pressure effects due to resonant interaction of atoms or molecules with intense laser radiation can be accompanied by a change in the shapes of the spectral lines. Different aspects of the action of a high-frequency electromagnetic field on the translational motion of atoms (acceleration, recoil effect, spatial localization) have been extensively discussed in the literature (see, e.g., [1–6] and the bibliography therein). Considerable interest attaches also to an investigation of the still-open question of the effect of almost constant acceleration on the spectra of atoms and molecules. The external forces responsible for this acceleration of the emitter can be due to different causes such as electric and magnetic fields in the plasma, the gravitational field, etc.

In problems of this type it is necessary to take into account, besides the change in the particle velocity distribution function[7–11] another very important factor, namely, the dependence of the spectral characteristics of the individual oscillator on the acceleration. The distribution of the radiation energy of an accelerated oscillator over the spectrum is different than of a non-accelerated one. The line contour of such an oscillator does not have a dispersion shape and its parameters (amplitude, shape, width, etc.) depend on the magnitude and direction of the acceleration.

By way of illustration we consider the following simple example: Let an oscillator having a velocity $\mathbf{v}_0$, a natural frequency ω_0, and a corresponding wave vector $\mathbf{k}$ begin to radiate and be simultaneously accelerated at the instant $t=0$. Its oscillations are then subject to the law

$$f(t)\propto \exp[-\Gamma t-i(\omega_0 t-\mathbf{kr}(t))],\quad t>0 \text{ and } f(t)=0,\quad t<0; \tag{1}$$

$$\mathbf{r}(t)=\mathbf{r}_0+\mathbf{v}_0 t+\int_0^t dt'\int_0^{t'}\mathbf{a}(t'')\,dt''.$$

Here Γ is the radiative-damping constant, $\mathbf{r}_0$ is the initial coordinate, and $\mathbf{a}$ is the acceleration. If $\mathbf{v}$ and $\mathbf{a}$ do not depend on the time, then the spectral density $I(\omega)$ of the radiation of frequency ω, corresponding to these oscillations, is determined by the expression

$$I(\omega)\propto\frac{\Gamma}{\pi}\left|\int_{-\infty}^{\infty}f(t)e^{i\omega t}dt\right|^2=\frac{1}{\pi}\operatorname{Re}\int_0^{\infty}\frac{\Gamma\,dt}{\Gamma+i\mathbf{ak}t/2}\exp[-(\Gamma-i\Omega)t-i\mathbf{ak}t^2/2],$$

$$\Omega=\omega-\omega_0-\mathbf{kv}, \tag{2}$$

which coincides with the dispersion curve only in the case of zero acceleration ($\mathbf{a}=0$ or $\mathbf{a}\cdot\mathbf{k}=0$):

$$I(\omega)\propto\frac{1}{\pi}\frac{\Gamma}{\Gamma^2+\Omega^2}. \tag{3}$$

When $\mathbf{a}\cdot\mathbf{k}\neq 0$ and the average frequency shift $\Delta\omega=|\mathbf{a}\cdot\mathbf{k}|/2\Gamma$ during the acceleration time $\tau=1/\Gamma$ is of the order of or larger than Γ, then the line $I(\omega)$ differs quite substantially in shape from a dispersion curve.

The foregoing example gives a qualitative idea of the physical aspect of the effect. In a real system having a discrete level structure it is necessary to take into account the inequality of the lifetimes of the levels and of the polarization in the radiative transition. This circumstance, naturally, complicates the picture, so that the classical scheme employed above is insufficient for the description of such systems.

In this paper we use the method of kinetic equations for the density matrix to investigate resonant interaction of two-level particles with monochromatic radiation with account taken of the effects of the acceleration due to a constant external field. Particular attention is paid to an analysis of situations typical of nonlinear spectroscopy of ultrahigh resolution, where these effects manifest themselves most noticeably.

2. FORMULATION OF PROBLEM AND FUNDAMENTAL EQUATIONS

We consider a gas of two-level particles interacting with a radiation field $\mathbf{E}(\mathbf{r},t)$. The particles execute thermal motion and, furthermore, are accelerated by external forces. The acceleration $\mathbf{a}$ is assumed to be constant and the same for both states of the atom m and n. Collisions with change of velocity are not taken into account. Within the framework of these limitations, the elements of the density matrix $\rho_{ij}(\mathbf{r},\mathbf{v},t)$, describing the ensemble of these particles satisfies the equations

$$(\partial/\partial t+\mathbf{v}\nabla_r+\mathbf{a}\nabla_v+\Gamma_j)\rho_{jj}=q_j\mp 2\operatorname{Re}(iV_{mn}^*\rho_{mn}),\quad j=m,n;$$
$$(\partial/\partial t+\mathbf{v}\nabla_r+\mathbf{a}\nabla_v+\Gamma)\rho_{mn}=iV_{mn}(\rho_{nn}-\rho_{mm}). \tag{4}$$

The interaction with the radiation field is taken into account by the matrix elements V_{mn}; Γ_j and Γ are the level-relaxation and polarization constants; $q_j(\mathbf{r}, \mathbf{v}, t)$ are the excitation functions of the working state. We assume henceforth that the particles are excited with a Maxwellian velocity distribution $F_M(\mathbf{v})$ uniformly in space and in time

$$q_j = Q_j F_M(\mathbf{v}), \quad F_M(\mathbf{v}) = (\sqrt{\pi}\bar{v})^{-3} \exp(-v^2/\bar{v}^2), \quad \bar{v}^2 = 2k_B T/M. \tag{5}$$

Here M and T are the mass and initial temperature of the particles, and k_B is the Boltzmann constant.

The formal difference between (4) and the analogous equations for unaccelerated particles lies in the presence of flux terms $\mathbf{a}\cdot\nabla_\mathbf{v}\rho_{ij}$, which describe the change of ρ_{ij} as the result of the acceleration, the change in the number of particles with given velocity being taken into account by the terms $\mathbf{a}\cdot\nabla_\mathbf{v}\rho_{jj}$, diagonal in the level indices, while the influence of the acceleration on the properties of the spectral line is taken into account by the off-diagonal terms $\mathbf{a}\cdot\nabla_\mathbf{v}\rho_{mn}$.

3. LINEAR THEORY

The analysis of Eqs. (4) becomes much simpler in the case of a weak electromagnetic radiation, when the saturation effects can be neglected. We therefore consider first a purely linear effect in a traveling-wave field

$$\mathbf{E} = \mathrm{Re}[\mathbf{E}_0 \exp(-i\omega t + i\mathbf{kr})], \tag{6}$$

and only then its nonlinear modification. Direct calculation shows that in the linear approximation Eqs. (4) have as their solutions

$$\rho_{jj}^{(0)}(\mathbf{v}) = Q_j \int_0^\infty F_M(\mathbf{v} - \mathbf{a}t) e^{-\Gamma_j t} dt, \quad N_0 = \rho_{mm}^{(0)} - \rho_{nn}^{(0)}, \tag{7}$$

$$\rho_{mn}^{(1)}(\mathbf{r}, \mathbf{v}, t) = -iV_{mn}(\mathbf{r}, t) \int_0^\infty N_0(\mathbf{v} - \mathbf{a}t') \exp\{-(\Gamma - i\Omega')t' + i\mathbf{akt}'^2/2\} dt',$$

$$V_{mn} = Ge^{-i(\Omega t - \mathbf{kr})}, \quad G = \mathbf{E}_0 \mathbf{d}_{mn}/2\hbar, \quad \Omega' = \Omega - \mathbf{kv}. \tag{8}$$

Here $\Omega = \omega - \omega_{mn}$ is the detuning of the radiation frequency $\omega = kc$ relative to the resonant frequency of the working transition ω_{mn}, and d_{mn} is the dipole moment of the transition.

It must be borne in mind that in the case of acceleration the concept of emission spectrum is meaningful only with respect to motion over the entire time axis. A formal reflection of this fact is the time convolution in (8). In the absence of acceleration ($\mathbf{a} = 0$) relations (7) and (8) reduce to the well known results (see, e.g., [12]) for a particle with constant velocity $\mathbf{v}$

$$\rho_{jj}^{(0)}(\mathbf{v}) = N_j F_M(\mathbf{v}), \quad N_j = Q_j/\Gamma_j, \tag{9}$$

$$\rho_{mn}^{(1)}(\mathbf{r}, \mathbf{v}, t) = -iV_{mn}(\mathbf{r}, t) N_0(\mathbf{v}) (\Gamma - i\Omega')^{-1}. \tag{10}$$

After certain simple transformations we can represent the formula for the distribution of the populations in velocity in the form

$$\rho_{jj}^{(0)} = N_j F_M(\mathbf{v}_\perp) F_j(v_\parallel), \tag{11}$$

$$F_j(v_\parallel) = \frac{\bar{v}}{2u_j} \Gamma\left(\frac{1}{2}, z_j\right) e^{z_j^2} F_M(v_\parallel), \quad z_j = \frac{\bar{v}}{2u_j} - \frac{v_\parallel}{\bar{v}}, \quad u_j = \frac{a}{\Gamma_j}$$

$$F_M(\mathbf{v}_\perp) = (\sqrt{\pi}\bar{v})^{-2} \exp(-v_\perp^2/\bar{v}^2),$$

$$F_M(v_\parallel) = (\sqrt{\pi}\bar{v})^{-1} \exp(-v_\parallel^2/\bar{v}^2), \quad v_\parallel = \mathbf{av}/a,$$

where $\Gamma(\frac{1}{2}, z_j)$ is the incomplete Euler Γ function. In this form we have explicitly separated the dependence of the velocity distribution on the velocity component $v_\parallel$ parallel to the acceleration direction. The velocity distribution along the other two projections $\mathbf{v}_\perp$ remains Maxwellian.

The behavior of $F_j(v_\parallel)$, as seen from (11) and from the plots in Fig. 1, is determined by the relation between the thermal velocity $\bar{v}$ and the average increment of the particle velocity $u_j = a/\Gamma_j$ during the lifetime on the level j. The difference between $F_j(v_\parallel)$ and the equilibrium distribution $F_M(v_\parallel)$ consists in the following: The maximum of $F_j(v_\parallel)$ is shifted in the acceleration direction, and the shift depends on a in a nonmonotonic manner. Thus, at small accelerations, when $u_j \ll \bar{v}$, the position of the maximum v_{0j} coincides with u_j, and in the limiting case of large accelerations $u_j/\bar{v} \to \infty$ we have $v_{0j} \to 0$. At small $u_j/\bar{v}$, the distribution of $F_j(v_\parallel)$ is close to equilibrium. To the contrary, if $u_j/\bar{v} \gg 1$, then $F_j(v_\parallel)$ is a strongly asymmetrical function of the velocity. We note that in the calculation of the mean values it is convenient to use the expansion of $F_j(v_\parallel)$ in Chebyshev-Hermite polynomials $H_n(x)$:

$$F_j(v_\parallel) = F_M(v_\parallel) \sum_{n=0}^\infty \left(\frac{a}{\bar{v}\Gamma_j}\right)^n H_n\left(\frac{v_\parallel}{\bar{v}}\right). \tag{12}$$

Taking into account the orthogonality of the polynomials $H_n(x)$ we can, in particular, obtain without difficulty the relations

$$N_j = \int \rho_{jj}^{(0)}(\mathbf{v}) d\mathbf{v} = \frac{Q_j}{\Gamma_j}, \tag{13}$$

$$\mathbf{u}_j = \frac{1}{N_j} \int \mathbf{v}\rho_{jj}^{(0)}(\mathbf{v}) d\mathbf{v} = \frac{\mathbf{a}}{\Gamma_j}, \tag{14}$$

$$d_j^2 = \frac{1}{N_j} \int (\mathbf{v} - \mathbf{u}_j)^2 \rho_{jj}^{(0)}(\mathbf{v}) d\mathbf{v} = \frac{3}{2}\bar{v}^2 + \left(\frac{a}{\Gamma_j}\right)^2. \tag{15}$$

The formula for the dispersion (15) indicates that the width of the distribution $F_j(v_\parallel)$ increases with increasing acceleration. The value of the function $F_j(v_\parallel)$ at the maximum decreases in this case, inasmuch as the area under the $F_j(v_\parallel)$ curve is conserved in accordance with (13).

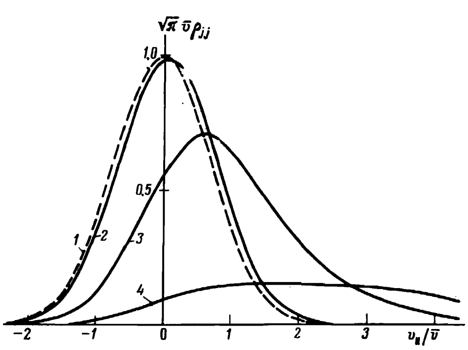

FIG. 1. Distribution function of the populations with respect to velocity without allowance for saturation: curve 1—at $a = 0$; 2—at $a/\Gamma_j\bar{v} = 0.1$; 3—at $a/\Gamma_j\bar{v} = 1$; 4—at $a/\Gamma_j\bar{v} = 10$.

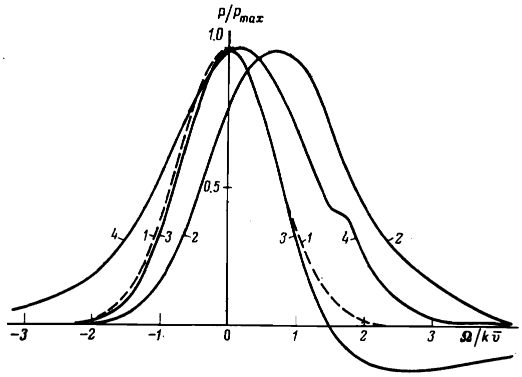

FIG. 2. Shape of spectrum in the linear approximation: curve 1—at $\mathbf{a}\cdot\mathbf{k}=0$; 2—at $\mathbf{a}\cdot\mathbf{k}/\Gamma_j k\bar{v}=1$, $\Gamma_m=\Gamma_n=\Gamma$, $k\bar{v}\gg\Gamma$, $\sqrt{|\mathbf{a}\cdot\mathbf{k}|}$; 3—at $\mathbf{a}\cdot\mathbf{k}/\Gamma_m k\bar{v}=10^{-1}$, $\Gamma_m=10\Gamma_n$, $N_m=N_n$, $k\bar{v}\gg\Gamma$, Γ_j, $\sqrt{|\mathbf{a}\cdot\mathbf{k}|}$; 4—at $\Gamma_j k\bar{v}/2|\mathbf{a}\cdot\mathbf{k}|\gg 1$, $\Gamma/k\bar{v}=4$, $|\mathbf{a}\cdot\mathbf{k}|/\Gamma^2=0.125$.

The effect of acceleration on the velocity distribution function reduces frequently to a particle drift in an external field (see, e.g., [10]). It is evident from (12) and from Fig. 1 that this is permissible only for low energies u_j/v, when $F_j(v_\parallel)\cong F_M(v_\parallel-u_j)$. On the other hand, if $u_j/\bar{v}\gtrsim 1$, then the distribution of the populations in velocity changes in a more complicated manner and the drift concept becomes untenable.

Knowing the solution of Eqs. (4), we trace the frequency dependence of the work performed by the field

$$\mathscr{P}=2\hbar\omega\,\mathrm{Re}\int(i\rho_{mn}V_{nm})\,d\mathbf{v},\tag{16}$$

which is the product of the acceleration by the velocities of the perturbed particles. For emission spectra that are linear in intensity we have

$$\mathscr{P}=2\hbar\omega|G|^2[N_m\bar{Y}_m(\Omega)-N_n\bar{Y}_n(\Omega)],\tag{17}$$

$$Y_j=\mathrm{Re}\int_0^\infty\frac{\Gamma_j}{\Gamma_j+i\mathbf{a}\mathbf{k}t}\exp\left[-\left(\frac{k\bar{v}}{2}\right)^2t^2-i\frac{\mathbf{a}\mathbf{k}}{2}t^2-(\Gamma-i\Omega')t\right]dt.\tag{18}$$

According to (17) and (18), the line shape is determined by the acceleration and by the mutual orientation of the vectors $\mathbf{a}$ and $\mathbf{k}$. The term $i\mathbf{a}\cdot\mathbf{k}t^2/2$ in the argument of the exponential takes into account the change of the radiation phase in accelerated motion, and the resonant factor $(\Gamma_j+i\mathbf{a}\cdot\mathbf{k}t)^{-1}$ is the result of the change of the initial velocity distribution.

If the Doppler broadening is large enough, the spectrum is transformed in such a way that the functions $\bar{Y}_j(\Omega)$ begin to duplicate the form of the distribution of the populations in velocity. This conclusion follows from a comparison of relations (11) with the formula for $\bar{Y}_j(\Omega)$, obtained in the approximation $k\bar{v}\gg\Gamma$, $\sqrt{|\mathbf{a}\cdot\mathbf{k}|}$:

$$\bar{Y}_j(\Omega)=\frac{\sqrt{\pi}}{2\mathbf{k}\mathbf{u}_j}\Gamma\left(\frac{1}{2},\tilde{z}_j\right)\exp\left[\tilde{z}_j^2-\frac{\Omega^2}{(k\bar{v})^2}\right],\qquad \tilde{z}_j=\frac{k\bar{v}}{2\mathbf{k}\mathbf{u}_j}-\frac{\Omega}{k\bar{v}}.\tag{19}$$

If the lifetimes at the levels Γ_j^{-1} are different, then $\bar{Y}_m(\Omega)\neq\bar{Y}_n(\Omega)$, and the function $\mathscr{P}(\Omega)$ can reverse sign, depending on the detuning (Fig. 2). This means that absorption takes place in some sections of the spectrum and amplification at others. The indicated feature makes it possible to amplify coherent radiation even at $N_m-N_n<0$, i.e., in the absence of inversion.

4. NONLINEAR THEORY

We consider now resonant interaction of accelerated particles with high-intensity radiation under conditions when the role of the saturation effect becomes appreciable. For the stationary regime, the general solution of Eqs. (4) can be represented in the form

$$\rho_{jj}(x)=\rho_{jj}^{(0)}\mp\int R_j(x|x')N(x')\,dx',\tag{20}$$

$$\rho_{mn}(x)=i\int f_{mn}(x|x')V_{mn}(x')N(x')\,dx',\tag{21}$$

$$R_j(x|x')=2\,\mathrm{Re}\int f_{jj}(x|x'')V_{mn}^*(x'')f_{mn}(x''|x')V_{mn}(x')\,dx'',\tag{22}$$

where $f_{ij}(x|x')$ is the Green's function of the right-hand sides of (4)

$$f_{ij}(x|x')=\theta(\tau)e^{-\Gamma_{ij}\tau}\delta(\mathbf{v}-\mathbf{v}'-\mathbf{a}\tau)\delta(\mathbf{r}-\mathbf{r}'-\mathbf{v}\tau-\mathbf{a}\tau^2/2),$$
$$\tau=t-t',\qquad\theta(\tau)=\begin{cases}0 & \text{at}\ \tau<0\\ 1 & \text{at}\ \tau>0,\end{cases}\quad\Gamma_{jj}=\Gamma_j,\quad\Gamma_{mn}=\Gamma,\tag{23}$$

and $N(x)$ satisfies the integral equation

$$N(x)=N_0(\mathbf{v})-\int R(x|x')N(x')\,dx'\tag{24}$$

with kernel $R=R_m+R_n$, which depends in a rather complicated manner on the set of variables $x=\{\mathbf{r},\mathbf{v},t\}$. Even in the simplest case of a plane traveling wave it is possible to obtain from these relations some clear results only by numerical methods or with the aid of perturbation theory. When solving (24) below we shall therefore confine ourselves to allowance for only the first corrections due to the presence of a strong field, i.e., we assume

$$N(x)\cong N_0(\mathbf{v})-\int R(x|x')N_0(\mathbf{v}')\,dx'.\tag{25}$$

This corresponds in fact to expanding $N(x)$ in powers of the saturation parameter

$$\varkappa=2|G|^2(\Gamma_m^{-1}+\Gamma_n^{-1})/\Gamma\tag{26}$$

and retaining the terms proportional to $\varkappa$.

Thus, for a plane traveling wave the population difference takes the form

$$N(\mathbf{v})=N_0(\mathbf{v})-\frac{\varkappa\Gamma}{\Gamma_m^{-1}+\Gamma_n^{-1}}\mathrm{Re}\int_0^\infty dt\int_0^\infty dt'N_0(\mathbf{v}-\mathbf{a}(t+t'))$$
$$\times\sum_j\exp\left[-(\Gamma-i\Omega')t+\frac{i\mathbf{a}\mathbf{k}t^2}{2}-(\Gamma_j-i\mathbf{a}\mathbf{k}t)t'\right],\tag{27}$$

where the unsaturated population difference $N_0(\mathbf{v})$ is given by (7). The increment to $N_0(\mathbf{v})$ due to the saturation is described by the integral term, which has the structure of a Bennett "hole"[13] only at $\mathbf{a}\cdot\mathbf{k}=0$.

It was shown above that the width of the distribution of $\rho_{jj}^{(0)}$ in velocity is always larger than or equal to the average thermal velocity $\bar{v}$. Under conditions when the Dopp-

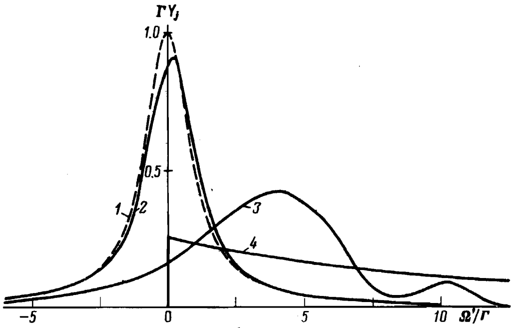

FIG. 3. Plots of the function $Y_j(\Omega')$ at $\mathbf{a}\cdot\mathbf{k}\leq 0$: curve 1—at $\mathbf{a}\cdot\mathbf{k}=0$; 2—at $|\mathbf{a}\cdot\mathbf{k}|/\Gamma\Gamma_j=0.25$; 3—at $|\mathbf{a}\cdot\mathbf{k}|/\Gamma^2=6.25$ ($\Gamma_j=2\Gamma$); 4—at $|\mathbf{a}\cdot\mathbf{k}|/\Gamma\Gamma_j=12.5$ ($\Gamma_j\ll\Gamma$).

ler width exceeds the remaining characteristic widths,

$$k\bar{v}\gg\Gamma_{ij},\ |\mathbf{ak}|/\Gamma_{ij}(i,\ j=m,\ n), \tag{28}$$

we can disregard the influence of acceleration on ρ_{jj} and write approximately in place of (27)

$$N(\mathbf{v})=(N_m-N_n)F_M(\mathbf{v})\left[1-\frac{\varkappa}{\Gamma_m^{-1}+\Gamma_n^{-1}}\sum_{j=m,n}\frac{Y_j(\Omega')}{\Gamma_j}\right], \tag{29}$$

$$Y_j(\Omega')=\operatorname{Re}\int_0^\infty\frac{\Gamma_j}{\Gamma_j-i\mathbf{ak}t}\exp\left[i\frac{\mathbf{ak}}{2}t^2-(\Gamma-i\Omega')t\right]dt, \tag{30}$$

where $Y_j(\Omega')$ determines the contour of the spectral line for particles that had a velocity $\mathbf{v}$ at the initial instant. It is easy to show that the function $\bar{Y}_j(\Omega)$ considered in the preceding section is the result of the convolution

$$\bar{Y}_j(\Omega)=\int F_M(\mathbf{v})Y_j(\Omega')d\mathbf{v}. \tag{31}$$

If $\mathbf{a}\cdot\mathbf{k}=0$, then $Y_0(\Omega')$ assumes the usual dispersion form $Y_j=\Gamma(\Gamma^2+\Omega'^2)^{-1}$. In the general case, however, we have $Y_m(\Omega')\neq Y_n(\Omega')$, since the lifetimes at the levels Γ_m^{-1} and Γ_n^{-1} can be different. Acceleration leads to a redistribution of the intensity over the spectrum without changing its total value

$$\int Y_j(\Omega')d\Omega'=\int\frac{\Gamma\,d\Omega'}{\Gamma^2+\Omega'^2}=\pi. \tag{32}$$

The deformation of the spectrum is expressed, in particular, by the fact that $Y_j(\Omega')$ becomes in the case of acceleration an isometrical function of the detuning $\Omega'=\Omega-\mathbf{k}\cdot\mathbf{v}$:

$$Y_j(-\Omega',\ \mathbf{ak})=Y_j(\Omega',\ -\mathbf{ak}). \tag{33}$$

Plots of the function $Y_j(\Omega')$, calculated for different values of the parameter $|\mathbf{a}\cdot\mathbf{k}|/\Gamma^2$, are given in Fig. 3. At small accelerations, when $|\mathbf{a}\cdot\mathbf{k}|\ll\Gamma^2$, the deviation of $Y_j(\Omega')$ from a dispersion curve is small. In the opposite limiting case $|\mathbf{a}\cdot\mathbf{k}|\gg\Gamma^2$ the changes of the contour of $Y_j(\Omega')$ are quite appreciable: 1) a considerable increase takes place in the effective width of the function $Y_j(\Omega')$ with a simultaneous shift of its maximum, 2) at sufficiently large $|\mathbf{a}\cdot\mathbf{k}|/\Gamma^2$ the function $Y_j(\Omega')$ becomes oscillating. The width of the $Y_j(\Omega')$ contour at $|\mathbf{a}\cdot\mathbf{k}|/\Gamma\gg\Gamma$ agrees in order of magnitude with the Doppler frequency shift $\Delta\omega=|\mathbf{a}\cdot\mathbf{k}|/2\Gamma$, and exceeds greatly the value of Γ. On the other hand, the appearance of oscillations on the plot of $Y_j(\Omega')$ can be attributed to interference between the different spectral components. Indeed, the phases of the radiation at two different instants of time are rigorously correlated, since the velocity of the atom over the mean free path varies in continuous and regular fashion. Consequently, on sections of the spectrum on the order of $\Delta\omega=|\mathbf{a}\cdot\mathbf{k}|2\Gamma$ the radiation will interfere strongly. In this sense, the considered situation is analogous to that which obtains in the diffraction of a plane wave by a transparent screen (Fresnel diffraction[14]).

Formula (29) reflects the fact that the acceleration influences the form of the narrow structures that appear in the velocity distribution of the populations under the influence of a strong field much more noticeably than it does the unsaturated population difference. This effect can manifest itself strongly in the spectral characteristics of the radiation. To illustrate this statement, we consider the spectrum of resonant absorption (or emission) by accelerated particles when the field is represented by a standing wave

$$\mathbf{E}=2\operatorname{Re}(\mathbf{E}_0\cos\mathbf{kr}e^{-i\omega t}), \tag{34}$$

and its work is given in the approximation (28) by the expression

$$\mathscr{P}\propto(N_m-N_n)\exp\left\{-\frac{\Omega^2}{(k\bar{v})^2}\right\}\varkappa\left\{1-\frac{\varkappa}{2}[Y_1(0)+Y_1(\Omega)]\right\}, \tag{35}$$

$$Y_1(\Omega)=\frac{\Gamma}{\Gamma_m^{-1}+\Gamma_n^{-1}}\sum_{j=m,n}\frac{Y_{1j}(\Omega)+Y_{1j}(-\Omega)}{2\Gamma_j},$$
$$Y_{1j}(\Omega)=\operatorname{Re}\int_0^\infty\frac{\Gamma_j\,dt}{\Gamma_j-i\mathbf{ak}t/2}\exp\left[-(\Gamma-i\Omega)t+i\frac{\mathbf{ak}}{4}t^2\right]. \tag{36}$$

It is seen from (35) that in this approximation the contour of the spectral line contains, against the Doppler background, a narrow nonlinear resonance (Fig. 4), which differs in form at $\mathbf{a}\cdot\mathbf{k}=0$ from the usual Lamb dip.[15] Since the nonlinear resonance in the plot of $\mathscr{P}(\Omega)$ is described by arithmetic mean values of the type $[Y_{1j}(\Omega)+Y_{1j}(-\Omega)]/2$, it is symmetrical with respect to the center of the line $\Omega=0$. The function $Y_{1j}(\Omega)$ can be

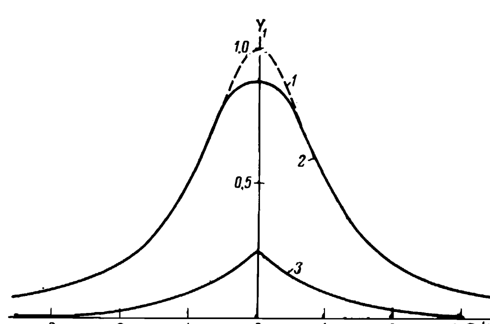

FIG. 4. Form of nonlinear increment to the work of a field represented by a standing wave: curve 1—at $\mathbf{a}\cdot\mathbf{k}=0$, $\lambda=1$; 2—at $|\mathbf{a}\cdot\mathbf{k}|/\Gamma\Gamma_j=0.5$ and $\lambda=1$; 3—at $|\mathbf{a}\cdot\mathbf{k}|/\Gamma\Gamma_n=12.5$ and $\lambda=0.116$ ($\Gamma_n\ll\Gamma_m$).

obtained from $Y_j(\Omega')$ by making the substitutions $\Omega \to \Omega'$ and $\mathbf{a}\cdot\mathbf{k} \to \mathbf{a}\cdot\mathbf{k}/2$. Therefore everything said above concerning the properties of the function $Y_j(\Omega')$ applies automatically to the function $V_{ij}(\Omega)$.

5. REAL OBSERVATION OF ACCELERATION EFFECT

We present estimates that give an idea of the limits of applicability of the developed theory. Without solving the self-consistent problem, we shall show first that the considered effects can be realized, for example, under conditions typical of ionic lasers. Under the influence of the electric field of the discharge in the tube, the ions move along the mean free path with an acceleration whose longitudinal component is $a_\parallel$ [cm/sec²] $\cong 0.96\cdot 10^{12} Z_i E_\parallel/M_i$, where Z_i is the ion charge, M_i is its mass in atomic units, and E is the intensity of the longitudinal electric field in volts per centimeter. For argon-ion lasers, which are the most powerful sources of continuous coherent radiation in the short-wave region of the spectrum,[16] we have[11,17] $M=40$, $Z_i=1$, $E_\parallel \sim 10$ V/cm, $\Gamma\sim 10^8$ sec^{-1}, $k\bar{v}\sim 10^{10}$ sec^{-1} at $\lambda = 2\pi/k = 4880$ Å. If the ion mean free path time is $\tau_f > \Gamma^{-1}$, Γ_j^{-1} (according to the data of[11,17] we have $\tau_f \sim l_f/\bar{v} \sim 10^{-6}$ sec^{-1}, where l_f is the mean free path), then the ion will move during the entire radiation time $\tau = \Gamma^{-}$ with an acceleration $a_\parallel \sim 2.4\times 10^{11}$ cm/sec². Since the Doppler frequency shift is $|\mathbf{a}\cdot\mathbf{k}|/\Gamma \gtrsim 3\times 10^8$ sec$^{-1} \gtrsim \Gamma$, it follows from the inequality that $|\mathbf{a}\cdot\mathbf{k}|/\Gamma \ll k\bar{v}$. Under these conditions the line spectra change little under the influence of the acceleration and we can confine ourselves for the description to a certain modification of the Kagan-Perel' theory.[9] On the other hand, the condition $|\mathbf{a}\cdot\mathbf{k}|/\Gamma \gtrsim \Gamma$ offers evidence of a noticeable change in the shape of the nonlinear spectral structures under the influence of the acceleration. The theory developed in[10] for saturated lines, which reduces all the acceleration effects to a drift, turns out to be unsuitable here.

The formation of excited ions can proceed along different paths: 1) ionization of the atom with simultaneous excitation, and 2) excitation of an ion that had been in the ground state. In the former case it is necessary to take into account the fact that the Debye screening of the charges in the plasma does not set in instantaneously. Our analysis is valid only for sufficiently slow processes, so that the de-excitation time τ should be longer than the screening-formation time τ_p:

$$\tau \gg \tau_p \sim \frac{1}{\nu_p} = (m_e/4\pi e^2 n_e)^{1/2}, \tag{37}$$

where ν_p is the frequency of the Langmuir space-charge oscillations; m_e and n_e are the mass and density of the electrons. The condition (37) is certainly satisfied for an argon laser, where $\tau \sim 10^{-8}$ sec and $n_e \sim 10^{12}$–10^{13} cm^{-3}. In the second case, this condition drops out ($\tau_p = 0$), since the charged particle (ion) existed even before the excitation.

We note that the model assumed by us for the medium does not take into account the change in the velocity of the translational motion of the radiator as a result of the collisions. Such a description is valid if the emission time τ is small in comparison with the characteristic time τ_0 during which the ion loses completely the "memory" of the initial velocity:

$$\tau \ll \tau_0. \tag{38}$$

We bear in mind here the fact that τ_0 is due to elastic processes, inasmuch as inelastic collisions the velocity changes to not manifest themselves. τ_0 can represent several relaxation times. When an excited ion moves in a partially ionized gas, it is convenient to separate two types of collisions that change the velocity: a) collisions with neutral particles, b) collisions with charged particles (Coulomb interaction).

If the ion collides with an atom of its own sort, then the mechanism that makes the largest contribution to the change of the velocity is resonant charge exchange of the ions with simultaneous transfer of excitation. The cross section of this process, $\sigma_{ce} \sim 10^{-14}$–$10^{-15}$ cm², is much larger than the gas kinetic cross section. In each charge-exchange act the velocity of the ion changes by an amount on the order of the average thermal velocity (strong collisions,[18] therefore $\tau_0 \sim 1/\nu_{ce}$, where $\nu_{ce} \sim n_a \sigma_{ce} \bar{u}$ is the effective charge exchange cross section (n_a is the concentration of the neutral atoms and $\bar{u}$ is the relative thermal velocity). Usually the ion temperature in the discharge T_i exceeds somewhat the temperature T of the atoms. For typical values of the parameters ($\Gamma \sim 10^8$ sec^{-1}, $T_i \sim 10^3$ K, $M_i \sim 10$, $\sigma_{ce} \sim 10^{-14}$ cm²) we have

$$\tau/\tau_0 \sim \nu_{ce}/\Gamma \sim n_a\cdot 10^{-17}\ \text{cm}^3, \tag{39}$$

i.e., the collisions with charge exchange can be neglected at an atom concentration $n_a \lesssim 10^{16}$ cm^{-3}.

The main contribution to charged-particle force interaction is made by distant transits, as a result of which the colliding particles are deflected only through small angles with small velocity changes. In the kinetic equation, the Coulomb interaction is taken into account by the Landau collision integral.[19] The deformation introduced into the excited-ion velocity distribution by the Coulomb scattering is characterized by the diffusion tensor $D_{\alpha\beta}(\alpha, \beta = x, y, z)$ and by the dynamic "friction" force F[20]:

$$D_{\alpha\beta} = \sum_s D_{\alpha\beta}^{(s)}, \qquad \mathbf{F} = \sum_s \mathbf{F}^{(s)}, \tag{40}$$

where the index s denotes the source of the charged particles. If the perturbing particles are in local thermodynamic equilibrium, then the components of the diffusion tensor and of the friction force can be determined from the formula

$$D^{(s)} \cong \frac{8\sqrt{\pi}(Zee_s)^2 n_s L_s}{3m_i^2 \bar{v}_s}, \tag{41}$$

$$F^{(s)} \cong \frac{16\sqrt{\pi}(Z_i ee_s)^2 n_s L_s}{3m_s \bar{v}_s^2} \cong \frac{2m_i^2}{m_s \bar{v}_s} D^{(s)}. \tag{42}$$

Here m_i is the mass of the emitting ion; e_s, n_s, m_s, $\bar{v}_s$ are the charge, density, mass, and average thermal velocity of the particles of sort s; L_s is the Coulomb logarithm.[20] The broadening of the velocity distribution during the emission time $\tau = \Gamma^{-1}$ as a result of diffusion can be disregarded if the corresponding diffusion width γ_s satisfies the inequality

$$\gamma_s = \sqrt{\tau D^{(s)}} \ll \Gamma/k. \tag{43}$$

At

$$\tau_0^{(s)} = m_i \bar{v}_s / F^{(s)} \gg \tau \tag{44}$$

we can disregard also the effect of the Coulomb "friction." The last condition is easily obtained with the aid of the approximate equations of motion of the radiated ion

$$\dot{\mathbf{v}} = \mathbf{a} - \eta_s(\mathbf{v} - \mathbf{u}_s), \quad \eta_s = F^{(s)}(m_i - m_s)/m_i^2 \bar{v}_s, \tag{45}$$

(a is the acceleration produced by the external force; $\mathbf{u}_s$ is the average velocity of the perturbed particles); these equations have as their solution

$$\mathbf{v}(t) = \mathbf{v}_0 e^{-\eta_s(t-t_0)} + \frac{\mathbf{a} + \eta_s \mathbf{u}_s}{\eta_s}[1 - e^{-\eta_s(t-t_0)}]. \tag{46}$$

It is seen from (46) that the influence of the "friction" on the spectral characteristics is small at $\eta_s(t - t_0) \sim \eta_s \tau \ll 1$, for in this case $\mathbf{v}(t) = \mathbf{v}_0 + \mathbf{a}(t - t_0)$. The inequality $\eta_s \tau \ll 1$ is directly connected with the condition (44).

In the gas-discharge plasma of an argon laser, the electron temperature T_e is much larger than the ion temperature ($T_e \sim 10^4\,°$K), so that it is the ion-ion collisions ($D^{(i)} \gg D^{(e)}$, $L_i \sim L_e \sim 10$) that are mainly responsible for the diffusion in velocity space. For the values of M_i, T_i, and λ indicated above we have $k\gamma_i/\Gamma \sim \sqrt{n_e} \cdot 10^{-8}$ cm$^{3/2}$, i.e., at an electron density $n_e \lesssim 10^{14}$ cm^{-3} the broadening due to diffusion can be neglected ($k\gamma_i/\Gamma \lesssim 0.1$ at $n_e \lesssim 10^{14}$ cm^{-3}). Under the same conditions ($M_i \sim 10$, $T_i \sim 10^3$ K, $T_e \sim 10^4$ K, $\Gamma \sim 10^8$ sec^{-1}), the influence of the Coulomb "friction" is characterized by the relations

$$\tau/\tau_0^{(i)} \sim n_e \cdot 10^{-14}\ \text{cm}^3, \quad \tau/\tau_0^{(e)} \sim n_e \cdot 10^{-16}\ \text{cm}^3, \tag{47}$$

from which it follows that at $n_e \lesssim 10^{13}$ cm^{-3} (Ar^+ laser) the effects due to the Coulomb scattering are insignificant and the spectral characteristics can be treated within the framework of the model (4). The condition (38) imposes definite requirements on the region of applicability of Eqs. (4), but in the case when this condition is not satisfied, the frequency properties of the radiator still depend on the character of the motion of its inertia center. Of course, from the quantitative point of view this effect manifests itself differently at $\tau \lesssim \tau_0$ than in the absence of collisions (the spectral lines have different forms), but is most important to take into account.

It should be noted that the external electric and magnetic fields act not only on the motion of the inertia center of the radiating particle, but also on the state of the optical electron, causing a splitting of the magnetic sublevels. Allowance for the Stark and Zeeman effects is essential if the frequency splitting Δ of the sublevels is comparable with the widths Γ_j and Γ:

$$\Gamma_j,\ \Gamma \sim \Delta = b_j \mathscr{E}^2/2 \text{ for the Stark effect,}$$
$$\Gamma_j,\ \Gamma \sim \Delta = \mu_0 g_j H/\hbar \text{ for the Zeeman effect } (j = m, n). \tag{48}$$

Here b_j are constants characterizing the displacement of the magnetic sublevels of the state in an external electric field $\mathscr{E}$ while g_j are the Landé factors, which perform the same role in a magnetic field of intensity H. Comparing the inequalities (28) with (48) and recognizing that the motion of the ion in magnetic or electric fields is under the influence of the Lorentz force, we obtain the limits of the values $\mathscr{E}$ and H at which our description remains applicable:

$$\mathscr{E}^3 \ll \frac{4Z_i ek}{b_j^2 m_i}, \quad H \ll \frac{Z_i ek\bar{v}}{\mu_0^2 g_j^2 m_i c}. \tag{49}$$

In the opposite case, the form of the spectrum becomes distorted not only because of acceleration effects, but also as a result of the Stark or Zeeman splitting of the multiplets (see, e.g., [21]).

The influence of the earth's gravitational field may manifest itself in the spectra of the nonlinear absorption in molecular gases of low pressure. Indeed, for $a = 981$ cm/sec^2 and $\lambda = 0.6\ \mu$, we obtain from the general condition of the effect of acceleration on the shape of a nonlinear resonance (28) the approximate inequality $\Gamma \lesssim 10^4$ sec^{-1}. Consequently, in this case the effects due to gravitation are comparable in order of magnitude with the recoil effect[2] and with transit phenomena.[22] Nor is it excluded that the acceleration due to the gravitational field can exert a noticeable influence on the radio emission of interstellar masers.[23] Calculations show that the shapes of narrow nonlinear structures produced in spectra of cosmic OH masers[24] differs from the dispersion shape if $a \gtrsim 10^{-8}$ cm/sec^2 ($\lambda = 18$ cm, $\Gamma \sim 10^{-4}$ sec^{-1}[25]). The acceleration that changes the shape of the nonlinear processes can be negligibly small in this case.

6. CONCLUSION

The main conclusion of our study is that in the investigation of the shapes of the spectra of resonant absorption (amplification) by a medium consisting of accelerated atoms or molecules it is necessary to take into account, besides the changes of the distribution function of the excited particles, also the influence of the acceleration on the relaxation of the dipole moment of the particle. The acceleration manifests itself primarily in the form of the saturated lines, broadening and distorting the contours of the narrow spectral structures in comparison with the dispersion curve (nonlinear spectroscopy). Allowance for the higher orders of perturbation theory in the radiation intensity, while noticeably complicating the analysis, does not lead to a radical qualitative change in the result.

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Collapse of the rotational structure of Raman-scattering spectra in dense media

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A description of the shapes of the Raman-scattering spectra of linear molecules in inert solvents is obtained in mathematically closed form by employing the Keilson–Storer kernel in the integro-differential equations of the theory of pressure broadening. In the case of strong collisions an analytic solution is obtained that describes the transformation of the contour with increasing density. It is shown that in the high-density limit the rotational structure of the spectrum undergoes a collapse during which the intensity is shifted from the sidebands of the *O–Q–S* triplet to the central band, whose width decreases with further growth of density. The narrowing of this band is shown to be a spectral manifestation of the Hubbard relation $\tau_\Theta \tau_J = I/6kT$ (τ_J and τ_Θ are the rotational and orientational relaxation times), a relation reliably confirmed by magnetic resonance experiments.

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1. INTRODUCTION

Raman-scattering (RS) spectra in rarefied gases and liquids differ greatly in shape and in extent. The reserved rotational structure, or at least the less pronounced triplet of *O–Q–S* branches, which is characteristic of gases of moderate density, is transformed in liquids into a single diffuse line, which is much narrower than the width of the rotational band in the gas at comparable temperature.[1–4] Consequently, with increasing density, the structure is not simply smeared out, but is also averaged (collapsed); this gives rise to an over-all narrowing of the spectrum, similar to that observed in NMR and ESR spectra of dense gases and liquids.[5–7] How this takes place, however, has not been investigated so far either theoretically or experimentally. It is only clear that the rotational angular momentum **J** (in units of $\hbar$) is preserved for a long time in a gas, so that all the frequencies $\omega \sim 2J/I \sim 2\bar{\omega} \sim (kT/I)^{1/2}$, are represented in the spectrum, whereas in the liquid the axis of the molecule does not rotate, but executes diffuse motion,[8] and the slower this motion the narrower the spectrum (I is the moment of inertia of the molecule).

Yet it is very important to understand what it is that converts free rotation into Brownian rotation. Do the cohesion forces fix the molecule axis and permit it only rarely to become reoriented,[9–11] or does the reason lie simply in the collisions, which become more frequent with increasing density, and the motion between which is not as free as before. If the rotational diffusion is a consequence of random wandering of the molecule axis, which is forced to overcome energy barriers

