Absorption of powerful resonance radiation accompanying collisional line broadening

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This review gives a systematic exposition of the qualitative problems of nonlinear laser resonance spectroscopy, taking into account the effect of the light field on the dynamics of the broadening collision and, correspondingly, on the rate of phase relaxation. The results of experiments, in which these nonlinear optocollisional effects, predicted earlier theoretically, were observed, are presented briefly.

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1. INTRODUCTION

Interaction of resonant optical radiation with a gas and a plasma occurs, for example, during transport of radiation in lines, formation of the light flux in a laser, and propagation of a light pulse from an external source in a resonant amplifying (absorbing) medium. Each of the areas of research listed is very broad and has its own interesting applications and theoretical methods for formulating and analyzing the problems that arise. The common factor is the fact that all these areas make use of the same local characteristics of optical transitions in atomic lines: coefficient of absorption, power absorbed per unit volume, and so on. The frequency dependence of these characteristics (i.e., line profile) is usually determined by collisions, the Doppler effect, and (in laser fields) the radiation intensity.

1. The local characteristics of line profiles were first studied using the theory of broadening of spectral lines,[1-4] which was mainly developed for plasma diagnostics and in connection with the study of radiation transport. In such problems, the effect of the light field on the local line shape can be neglected. This simplification permitted establishing, in a quite detailed manner, the relation between the line profile and the properties of the medium and the "broadening" particles, in particular, it permitted observing the frequencies that are emitted (absorbed) during the free flight time and during a broadening collision.

The development of nonlinear resonance radiation spectroscopy,[5-7] which takes into account the effect of the electromagnetic (EM) field on the optical properties of the medium, began with the appearance of lasers. A theory, based on kinetic equations in which terms describing the transitions under the action of the EM field were not assumed to be small compared to terms that describe relaxation due to collisions, was constructed. Based on this theory, equations describing the saturation of absorbed power density were obtained and the effects of induced transitions on the velocity distribution of emitting (absorbing) particles (hole-burning in the Doppler profile and so on) were examined.

Nevertheless, the already classical theory of absorption of powerful resonance radiation is fundamentally limited by the fact that it does not take into account optical transitions occurring during a collision between an atom and a broadening particle. This is manifested, for example, in the fact that even in the weak-field limit the nonlinear theory does not describe the entire line profile, known from the theory of broadening, and, in addition, a difference arises in the line wings precisely at those frequencies that are absorbed during a collision. It should be noted that this fact was for a long time neglected, since the profound relation between nonlinear spectroscopy and the theory of broadening was not pursued sufficiently completely.

The limitation indicated above is formally a result of the fact that the relaxation constants, describing collisions in kinetic equations,[5-7] are assumed to be independent of the frequency and intensity of the EM field. On the other hand, this dependence can only be obtained

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from a detailed examination of the act of light absorption during a broadening collision.

2. Problems involving absorption of light during a collision in a strong light field were first studied in the theory of radiative collisions.[8] The effects of opticocollisional nonlinearity, related to the effect of a strong field on the dynamics of the optical transition during a collision, were first[9] predicted here. Then, similar effects were studied for broadening collisions as well.[10,11] The theoretical description of absorption of resonance radiation turned out to be more complicated than the theory of radiative collisions. These difficulties are based on the fact that an optical transition in an atom, in resonance with an EM field, can occur both during free flight and during a collision. Even in weak fields, this complicates the analysis of the kinetics of light absorption by the medium, which in general does not reduce to a simple superposition of light absorption acts, as is the case in radiative collisions, where a quantum can be absorbed only while the colliding particles interact. In addition, if the transition is induced by a strong EM field, then the dynamic and kinetic nonlinear effects are mixed in a very complicated manner.[11,12,13]

Nevertheless, based on experience with the theory of broadening and the theory of radiative collisions, the effects indicated above can be separated and given a simple physical description. The foundations of the theory which takes into account the influence of both dynamic and kinetic nonlinear effects on the line shape and which is valid over a comparatively wide frequency range, can already be viewed as formulated. This theory can be called the "nonlinear theory of spectral line broadening."[11] Experiments, in which the predicted opticocollisional nonlinear effects were observed, were recently reported. Of these, the most interesting, apparently, are the experiments by Szöke's group[14,15] and Bonch-Bruevich's group.[16] This review is concerned with an exposition of the foundations of the nonlinear theory of broadening and a discussion of the most interesting of the latest experiments.[1)]

3. The presentation is organized as follows. Section 2 analyzes the absorption of weak radiation based on the usual approximations of the theory of spectral line broadening. However, the analysis presented here differs considerably from the customary form.[1-4,19] It is divided into two stages. First, the dynamics of an optical collision, i.e., a separate act of absorption of a photon during a broadening collision (subsection a in Sec. 2), is analyzed and then, based on this analysis, the transition is made to the kinetic problem, i.e., an analysis of all photon absorption acts in the medium (subsection b in Sec. 2). For pair collisions, this approach is more convenient. It permits using immediately the fact that for frequency detuning much greater than the inverse mean free flight time, light dissipation in the medium can be described as a collection of optical collisions and this makes it possible to obtain the basic results comparatively easily. In addition, this formulation of the theory can be naturally generalized (Sec. 4) to the case of a strong EM field.

In Sec: 3, the simplest nonlinear effect of the kinetic type, saturation of absorption in a two level system, is examined. The analysis does not start from the equations for the density matrix (as is customary[5-7]), but from elementary population balance equations. At the same time, the spectral function, obtained in the theory of broadening (the modified Lorentz equation; Sec. 2), which describes the entire line profile, is used in expressions for the rates of induced transitions. This approach, in spite of its simplicity, permits not only obtaining an expression for the absorbed power, well known in nonlinear spectroscopy, but also extending the results somewhat. Namely, the expression obtained here gives, in the limit of weak fields which do not affect the population, the entire line profile, known from the theory of broadening.

In Secs. 4 and 5, the theory is extended to strong fields, which can affect the dynamics of the optical collisions. The dynamic part of the problem is examined in Sec. 4. The essence of the generalization consists in the transition to a new basis of wave functions for the system "atom + EM field," in which the states of the atom and the field are mixed. The broadening particle causes transitions between these (new) states and it is these transitions that correspond to dissipation of light energy during a collision in a strong EM field. The equations describing optical collisions in a strong EM field are obtained (subsection a in Sec. 4) and the dependence of the optical collision frequency on the characteristics of the EM field (frequency and intensity, subsection b, Sec. 4) is analyzed.

The kinetics of absorption of powerful radiation in a medium taking into account the effect of the EM field on the dynamics of optical collisions are examined in Sec. 5. The nonstationary problem for the case when inelastic relaxation (i.e., collisional and spontaneous radiative transitions between atomic states) can be neglected is analyzed first (subsection a). Then, the stationary problem (the same as in Sec. 3) taking into account inelastic relaxation (subsection b, Sec. 2) is analyzed. The expression obtained for the power absorbed per unit volume can be written in a form that coincides with well-known results.[5-7] However, the collision frequency, which describes the so-called phase relaxation, entering into this expression is a complicated function of both the frequency and intensity of the EM field. The form of this function follows from the analysis in Sec. 4. As the intensity of theEM field increases, the rate of phase relaxation decreases, which leads to the appearance of opticocollisional nonlinear effects. For example, in the static wing of the line, the absorbed power depends nonmonotonically on the EM field intensity.

The opticocollisional nonlinear effects can be qualitatively interpreted as follows. In weak fields, the probability of an optical transition during a collision is proportional to the square of the transition matrix element, i.e., to the light intensity. When this probability is referred to the photon flux density, the cross section

[1)] A more detailed exposition of these problems is contained in Refs. 17 and 18.

for a phototransition, which does not depend on the EM field intensity and which is, in particular, a characteristic of the phase relaxation rate, is obtained. However, in sufficiently strong fields, the probability of a transition during a collision cannot be proportional to the light intensity because it must be less than unity. Therefore, the cross section for a phototransition and the rate of elastic relaxation must decrease with increasing intensity. Determination of the characteristic collision time in general requires a detailed analysis of the dynamic problem (Sec. 4). Here, we point out only that the opticocollisional nonlinearity arises with EM field intensities of 10^5–10^6 V/cm, which corresponds to light intensity of 10^7–10^9 W/cm^2.

Experimental results[14,16] are presented briefly in Sec. 6. Szöke's group,[14] while studying resonance fluorescense of strontium vapor in strong fields ($3.5\cdot10^6 - 3.5\cdot10^7$ W/cm^2), discovered a decrease (by a factor of 7) in the rate of phase relaxation due to collisions between the strontium and the argon buffer gas. Bonch-Bruevich's group intentionally observed the decrease in the absorbed power with increasing laser radiation intensity, as predicted in Ref. 10. The measurements were performed on fluorescense of thallium vapor in argon. The opticocollisional nonlinearity was discovered with light intensities $\approx 10^9$ W/cm^2.

2. WEAK FIELDS

In this section, we examine a situation in which an EM field-induced atomic transition is unlikely during a collision with a broadening particle. In this case, in analysing the act of absorption or emission of a photon during the collision, the field may be assumed to be weak, and this permits finding comparatively simply the optical characteristics of the medium using perturbation theory.

a) Optical collisions

We shall first examine the dynamical problem: an isolated collision between an atom A and a broadening particle B, occurring in a monochromatic EM field with frequency ω, close to the frequency ω_0 of the transition $1 \to 2$ in atom A (Fig. 1). More exactly, we shall examine the following opticocollisional transition:

$$A(1) + B + \hbar\omega \to A(2) + B. \tag{2.1}$$

We shall call a collision during which the transition (2.1) occurs an *optical collision* (OC).

Let the Hamiltonian of the composite (compound) system (field + colliding particle) have the form

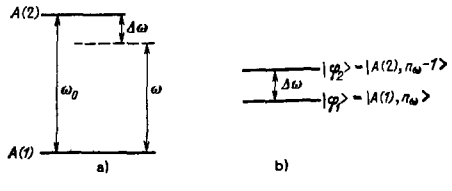

FIG. 1. Term diagram of atom A (a) and of the compound system "atom + EM field" (b).

$$\hat{H} = \hat{H}_A + \hat{H}_{\mathcal{E}} + \hat{V}_{A\mathcal{E}} + V_{AB}(t); \tag{2.2}$$

where $\hat{H}_A$ is the Hamiltonian of the electron shell of A; $\hat{H}_{\mathcal{E}} = \hbar\omega\hat{a}_\omega\hat{a}_\omega^+$ is the Hamiltonian of the free field; $\hat{a}_\omega^+$ and $\hat{a}_\omega$ are creation and annihilation operators for quanta; $\hat{V}_{A\mathcal{E}}$ and $\hat{V}_{AB}$ are operators describing the interaction of atom A with the field and with atom B. The relative motion of A and B is assumed to be classical, so that the kinetic energy operator is omitted in (2.2), while the interaction $\hat{V}_{AB}(t)$ depends explicitly on time.

For now, we will choose the characteristic functions $\varphi_1 = |A(1), n_\omega\rangle$ and $\varphi_2 = |A(2), n_\omega - 1\rangle$ of the Hamiltonian $\hat{H}_0 = \hat{H}_A + \hat{H}_{\mathcal{E}}$ of the noninteracting atom and field as the basis wave functions. For simplicity, we shall assume that the state of the atom is nondegenerate, while the field is classical $n_\omega \gg 1$. In the usual manner (see Ref. 20, p. 173), we obtain equations for the amplitudes a_1 and a_2 of the states φ_1 and φ_2 of the compound system

$$i\dot{a}_1 = U_1(t)\,a_1 + Ve^{i\Delta\omega t}a_2, \qquad i\dot{a}_2 = U_2(t)\,a_2 + Ve^{i\Delta\omega t}a_2, \tag{2.3}$$

where $U_k(t) = \frac{1}{\hbar}\langle\varphi_k|V_{AB}|\varphi_k\rangle$, $(k = 1, 2)$ are the shifts in the atomic terms owing to the A–B interaction; $V = \frac{1}{\hbar}\langle\varphi_1|V_{A\mathcal{E}}|\varphi_2\rangle = d\vec{\mathcal{E}}_0/2\hbar$ is the matrix element of the OC transition; d is the dipole moment matrix element; $\vec{\mathcal{E}}_0$ is the amplitude of the electric field intensity; $\Delta\omega = \omega - \omega_0$ is the frequency detuning. The adiabatic approximation was used in obtaining (2.3), i.e., it was assumed that $\langle\varphi_1|V_{AB}|\varphi_2\rangle = 0$.

We shall assume that the field is weak and we shall use perturbation theory with respect to the transition matrix element of V. Carrying out the transformation $b_k = e_k \exp(i\int_{-\infty}^{t} U_k(t')dt')(k = 1, 2)$, which moves the level shifts into the phase factor, and examining for definiteness absorption $a_1(-\infty) = 1$ and $a_2(\infty) = 0$, we set $b_1(t) = 1$. As a result, we have for the transition probability

$$|a_1(\infty)|^2 = |b_2(\infty)|^2 = V^2\left|\int_{-\infty}^{\infty} dt \exp\{i[\Delta\omega t - \eta(t)]\}\right|^2, \tag{2.4a}$$

where

$$\eta(t) = \int_{-\infty}^{\infty} \Delta U(t')\,dt', \qquad \Delta U = U_2 - U_1, \tag{2.4b}$$

is the increase in the phase of the wave function during a collision.

Equations (2.3) describe the optical transition not only during a collision, but also before and after the A–B interaction. In order to separate out the probability of a transition during a collision, we shall transform (2.4a) using integration by parts (this was first done by Spitzer[21]; compare also Ref. 20, p. 178)

$$|a_2(\infty)|^2 = \left|\frac{Ve^{i[\Delta\omega t - \eta(t)]}}{i\Delta\omega}\Big|_{t\to-\infty}^{t\to\infty} + \frac{V}{\Delta\omega}\int_{-\infty}^{\infty} dt\,\Delta U(t)\,e^{i[\Delta\omega t - \eta(t)]}\right|^2. \tag{2.5a}$$

The first term is proportional to the δ function of the frequency detuning $\Delta\omega$. It describes emission during free flight of infinite duration and vanishes for $\Delta\omega \neq 0$. (The actual width of this function is discussed in subsection b.) The second term in (2.5a) describes light absorption during the collision. Indeed, it vanishes in the absence of the interaction A–B [i.e., for $\Delta U(t) \equiv 0$]. Therefore, we have for the probability of the OC transition

$$w_{OC}=\left|\int_{-\infty}^{\infty} dt\,\frac{V}{\Delta\omega}\,\Delta U(t)\exp\left\{i\left[\Delta\omega t-\int_{-\infty}^{t}\Delta U'(t)\,dt'\right]\right\}\right|^2. \quad (2.5b)$$

Expression (2.5b) is completely analogous to the expression arising in the theory of radiative collisions in the weak-field approximation. The difference lies in the fact that the quantity

$$\tilde{V}(t)=\frac{V}{\Delta\omega}\,\Delta U(t), \quad (2.6)$$

appears as the matrix element of the OC transition, rather than simply $V(t)$ [compare (4.3) in Ref. 8].

We note that expression (2.5b) diverges for $\Delta\omega\to 0$ as $\Delta\omega^{-2}$. This is related to the inapplicability of perturbation theory for $\Delta\omega\lesssim V$ [see (4.1)].

In order to characterize the number of OC transitions and the energy absorbed in them, it is convenient to introduce the cross section of an optical collision

$$\sigma_{OC}=\int_0^{\infty}2\pi\rho\,d\rho\,w_{OC}(\Delta\omega, V, v, \rho), \quad (2.7a)$$

with the help of which the number of OC collisions per unit volume and per unit time is easily determined:

$$K_{OC}(\Delta\omega, V)=k_{OC}(\Delta\omega, V)N_B, \quad (2.7b)$$

where

$$k_{OC}(\Delta\omega, V)=\langle\sigma_{OC}(\Delta\omega, V, v)v\rangle\equiv\int dv f(v)v\sigma_{OC} \quad (2.7c)$$

is the OC reaction rate; ρ is the impact parameter; $f(\mathbf{v})$ is the distribution function for A and B particles over the relative velocities $\mathbf{v}$; and, N_B is the concentration of broadening particles.

It is also convenient to use the following quantity to characterize an OC transition

$$\gamma_{OC}(\Delta\omega)=\frac{\Delta\omega^2}{2V^2}K_{OC}(\Delta\omega, V), \quad (2.8)$$

which does not depend on the field intensity and does not diverge for $\Delta\omega\to 0$ (except for the case of broadening of hydrogen lines by charged particles). Its physical significance will become clear in what follows. Here, we note only that $\gamma_{OC}(\Delta\omega)$ is the inverse time of so-called phase relaxation and characterizes the line width. It is sometimes convenient to use also the "broadening cross section" $\sigma_{br}\equiv(\Delta\omega^2/2V^2)\sigma_{OC}$ whose average magnitude is $\bar{\sigma}_{br}(\Delta\omega)\equiv\gamma_{OC}(\Delta\omega)/v_T N_B$ where v_T is the characteristic thermal velocity.

Since a single photon is absorbed as a result of each OC transition (2.1), we can write for the power absorbed per unit volume due to OC transitions

$$Q_{OC}=\hbar\omega K_{OC}(\Delta\omega, V)(N_1-N_2)=\hbar\omega\frac{2V^2}{\Delta\omega^2}\gamma_{OC}(\Delta\omega)(N_1-N_2), \quad (2.9)$$

where N_1 and N_2 are the populations of states 1 and 2 of atom A.

The profile of the OC line is determined by the dependence of σ_{OC}, k_{OC}, and γ_{OC} on $\Delta\omega$. Analysis of this dependence is completely analogous to the corresponding analysis in Ref. 8 and leads to well-known results,[1-4] which are briefly formulated below (for greater detail, see Ref. 17).

The profile of the OC line is characterized by the *impact* $|\Delta\omega|\ll\Omega_B$ and *quasistatic* $|\Delta\omega|\gg\Omega_B$ regions, where $\Omega_B=v/\rho_B$ is the Weisskopf frequency and ρ_B is the Weisskopf radius, defined as the impact parameter at which the phase shift of the wave function is of the order of unity:

$$\int_{-\infty}^{\infty}\Delta U(\rho_B, v, t)\,dt\sim 1. \quad (2.10a)$$

In what follows, we shall call collisions that shift the phase by unity Weisskopf collisions. They have a cross section $\sigma_B\approx\pi\rho_B^2$ and occur with frequency $\sim\gamma_C=\gamma_{OC}(\Delta\omega=0)\approx\pi\rho_B^2 v_T N_B$ (see below). For a power-law interaction, we have from $\Delta U=c_n/r^n=c_n/(\rho^2+v^2t^2)^{n/2}$, where $r(t)$ is the distance between the nuclei of the colliding atoms,

$$\int_{-\infty}^{\infty}\frac{c_n\,dt}{(\rho^2+v^2t^2)^{n/2}}=\frac{\alpha_n c_n}{v\rho_B^{n-1}}\sim 1,\ \rho_B\equiv\left(\frac{c_n}{v}\right)^{1/(n-1)},\ \alpha_n=\frac{\sqrt{\pi}\,\Gamma((n-1)/2)}{\Gamma(n/2)}, \quad (2.10b)$$

where $\Gamma(x)$ is the gamma function.

In the impact limit ($\Delta\omega\ll\Omega_B$), the integral (2.5b) can be calculated as follows:

$$\sigma_{OC}=\frac{2V^2}{\Delta\omega^2}\sigma_B,\quad \sigma_B\equiv\int_0^{\infty}2\pi\rho\,d\rho\left(1-\cos\int_{-\infty}^{\infty}\Delta U\,dt\right). \quad (2.11)$$

For a power-law interaction, $\sigma_B\approx\pi\rho_B^2$, $\gamma_C\approx\pi\rho_B^2 v_T N_B$ (here, cumbersome factors of the order of unity are omitted; see Ref. 17).

In the quasistatic region ($\Delta\omega\gg\Omega_B$), in the presence of a point of intersection of the levels of the compound system $r_{\Delta\omega}$ (or $t_{\Delta\omega}$), defined by the equality

$$\Delta U(r_{\Delta\omega})=\Delta\omega, \quad (2.12)$$

evaluating the integral (2.5b) by the method of steepest descent gives

$$w_{OC}=2V^2\frac{2\pi}{vF_{\Delta\omega}},\quad \sigma_{OC}=V^2\frac{8\pi^2 r_{\Delta\omega}^2}{vF_{\Delta\omega}},\quad \gamma_{OC}=\frac{4\pi^2 r_{\Delta\omega}^3\Delta\omega^2 N_B}{F_{\Delta\omega}},\quad \text{for}\quad \Delta\omega\Delta U>0,\ \Delta\omega\gg\Omega_B, \quad (2.13)$$

where $F_{\Delta\omega}=\left|d\Delta U/dr\right|_{r=r_{\Delta\omega}}$ is the difference of the slopes of levels of the compound system at the point of intersection. For a power-law interaction,

$$F_{\Delta\omega}=\frac{n}{c_n^{1/n}}\Delta\omega^{(n+1)/n},\quad r_{\Delta\omega}=\left(\frac{c_n}{\Delta\omega}\right)^{1/n},\quad \gamma_{OC}=\frac{4\pi^2}{n}c_n^{2/n}\Delta\omega^{(n-3)/n}N_B. \quad (2.14)$$

We note that when levels cross, the quantities γ_{OC}, k_{OC} and K_{OC} do not depend on the thermal velocity. It is natural to refer to this part of the quasistatic region as the *static* region.

In the absence of level crossing for $\Delta\omega\gg\Omega_B$ (we shall call this region the *adiabatic* region), there is an exponential decrease

$$\delta\propto e^{-\delta},\quad \delta\sim\frac{\Delta\omega r_{\Delta\omega}}{v}. \quad (2.15)$$

Generally speaking, the applicability of perturbation theory in the adiabatic wing requires further analysis.

b) Optical collisions and absorption of radiation during free flight

In analyzing a transition during a collision (OC transition), it was assumed above that the free flight of an

atom before and after a collision is infinite. Actually, as is evident from the preceding analysis, the time of flight with constant phase is limited by the frequency of Weisskopf collisions, i.e., by the quantity $\sim\gamma_c^{-1}$. In this connection, let us substitute into (2.5a) finite limits of integration $t=\pm\gamma_c^{-1}$ instead of $t\to\pm\infty$. In this case, we shall equate the first term on the right side (which was previously neglected for $\Delta\omega\neq 0$) to the second term (describing the OC collision) for $\Delta\omega\sim\gamma_c$. Therefore, in order to neglect radiation during free flight, the following condition must be satisfied:

$$\Delta\omega\gg\gamma_c. \tag{2.16}$$

It is in this frequency detuning range that emission or absorption of light in the gaseous medium can be represented as a collection of isolated OC transitions, characterized by the quantities σ_{OC}, k_{OC}, and γ_{OC}: see (2.7) and (2.8). As is customary in the theory of broadening, we shall call the region of frequencies (2.16) the single-particle region.[3] We note that it would be incorrect to assume that the Weisskopf frequency forms the frequency boundary between the "collisional" and "free-flight" emission, i.e., to associate only the quasistatic region $\Delta\omega\gg\Omega_B$ with emission during a collision. Actually, due to the binary nature of collisions,

$$\rho_B^3 N_B\ll 1 \tag{2.17}$$

the "multiparticle" region $\Delta\omega\ll\gamma_c$ is much smaller than the impact region $\Delta\omega\ll\Omega_B$, since the inverse time between collisions is much less than the inverse collision time,

$$\gamma_c\approx\pi\rho_B^2 v_T N\ll\Omega_B\sim\frac{v}{\rho_B}. \tag{2.18}$$

Thus, the single-particle approximation describes not only the quasistatic wings, $\Delta\omega\gg\Omega_B$, but also the transition between the impact and quasistatic limits $\Delta\omega\sim\Omega_B$ and a large part of the impact region $\gamma_C\ll\Delta\omega\lesssim\Omega_B$, i.e., practically the entire line profile with the exception of the very narrow (but more intense) multiparticle region $\Delta\omega\lesssim\gamma_C$.

In order to find the line profile, valid also in the multiparticle region, it is necessary to follow the absorption of radiation during a time T much longer than the time between Weisskopf collisions $T\gg\gamma_C^{-1}$. Referring the transition probability to the observation time, it is possible to obtain the frequency dependence of the average transition rate, i.e., the line profile. We shall carry out this analysis.

The states of atom A, acted upon by impacts of heavy particles B, are described by the previous equations (2.3), where, however, $U_1(t)$ and $U_2(t)$ give term shifts induced not by a single impact, but by all the impacts (within time T):

$$U_1(t)=\sum_k U_{1k}(t-t_k),\quad U_2(t)=\sum_k U_{2k}(t-t_k), \tag{2.19}$$

where k is an index that characterizes the parameters of the k-th collision. Using the previous reasoning, we arrive at an equation for the probability of a transition $1\to 2$ within the time interval $-T/2\leq t\leq T/2$. The difference from Eq. (2.4a) consists only in replacing the limits of integration $\pm\infty\to\pm T/2$. Dividing the transition probability by T, we obtain the time-averaged transition rate under the action of the EM field, which we shall write in the form

$$K_{em}(\Delta\omega, V)=\frac{1}{T}\left|a_2\left(-\frac{T}{2},\frac{T}{2}\right)\right|^2=2\pi V^2 S(\Delta\omega), \tag{2.20a}$$

where

$$S(\Delta\omega)=\frac{1}{2\pi T}\left|\int_{-T/2}^{T/2} dt\, e^{i\Delta\omega t} f(t)\right|^2, \tag{2.20b}$$

$$f(t)=e^{i\eta t},\quad \eta(t)=\sum_k\int_{-\infty}^{t}\Delta U_k(t'-t_k)\,dt'. \tag{2.20c}$$

The power absorbed per unit volume is determined by the expression

$$Q=\hbar\omega K_{em}(\Delta\omega, V)(N_1-N_2). \tag{2.21}$$

The problem of the theory of broadening consists of determining the explicit form of the spectral function $S(\Delta\omega)$. Of course, in order to study expression (2.20b), in addition to analyzing the dynamics of broadening collisions, static hypotheses are also necessary. Omitting the corresponding static analysis (see Ref. 17), we shall present the final result. In the binary collision approximation, the line profile is given by the expression

$$S(\Delta\omega)=\frac{1}{\pi}\frac{\gamma_{OC}(\Delta\omega)}{(\Delta\omega+\Delta_c)^2+\gamma_c^2},\qquad \gamma_c=\gamma_{OC}(\Delta\omega=0), \tag{2.22}$$

which we shall call, in what follows, the modified Lorentz equation. It was first obtained by V. V. Yakimets[22] using the Green's function method. The important new ingredient here compared to the Lorentz–Weisskopf equation (where it was assumed that $\gamma_{OC}=\gamma_C$) is that the dependence of γ_{OC} on $\Delta\omega$ is taken into account, so that expression (2.22) describes the entire line profile, including multiparticle, impact, and quasistatic regions (Fig. 2). As was later shown by Kogan and Lisitsa,[23] Yakimets' result is contained in the well-known Anderson equation[24] in the binary limit.

The quantity Δ_C is defined by the expression

$$\Delta_c=N_B\int f(v)\,dv\cdot v\int_0^\infty 2\pi\rho\,d\rho\sin\left[\int_{-\infty}^{\infty}\Delta U(t)\,dt\right], \tag{2.23}$$

and Eq. (2.8) is valid for $\gamma_{OC}(\Delta\omega)$.

All the qualitative results discussed above follow from Eqs. (2.22). It is evident that the single-particle

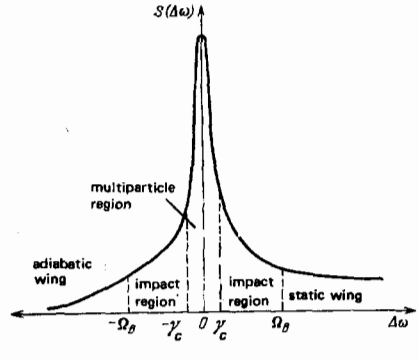

FIG. 2. Qualitative shape of the spectral function, defined by the modified Lorentz equation.

frequency range $\Delta\omega \gg \gamma_C$ (2.16) corresponds to emission during broadening collisions, so that from (2.22) we have

$$S(\Delta\omega \gg \gamma_c) = \frac{1}{\pi}\frac{\gamma_{OC}}{\Delta\omega^2}, \quad K_{em}(\Delta\omega \gg \gamma_c) = K_{OC} = \frac{2V^2}{\Delta\omega^2}\gamma_{OC}. \tag{2.24}$$

In the multiparticle region, $\Delta\omega \leq \gamma_C$, light absorption is already nonlinear with respect to the concentration of broadening particles N_B. We note once again that the multiparticle region is much smaller than the impact region ($\gamma_{OC} \ll \Omega_B$) due to the binary nature of collisions (2.18), while the Weisskopf frequency Ω_B is the characteristic scale of variation of γ_{OC}.

3. SATURATION OF ABSORPTION

We shall examine the simplest nonlinear effect in absorption of resonance radiation, related to the effect of induced transitions on the kinetics of atomic state populations.

We shall limit the analysis to inelastic transitions only between two atomic states 1 and 2. This approximation is possible, for example, for excitation of a resonance transition in metallic vapors, located in an inert gas. We will also assume for simplicity that levels 1 and 2 are degenerate and that the problem is stationary $dN_1/dt = dN_2/dt = 0$. Then, the populations N_1 and N_2 of atom A can be found from the equalities

$$(K_2 + K_{em})N_1 = (K_1 + K_{em})N_2, \quad N_1 + N_2 = N, \tag{3.1a}$$

where K_1 and K_2 are the rates of inelastic transitions $1 \to 2$ and $2 \to 1$ owing to spontaneous emission and electron impacts; K_{em} is defined by expression (2.20); and, $N = \text{const}$ is the total concentration of A atoms. From (3.1), we have

$$N_1 - N_2 = \frac{\Delta N}{1 + [2K_{em}/(K_1+K_2)]} = \frac{\Delta N}{1 + (2\pi V^2 S(\Delta\omega)/\gamma_{ir})}, \tag{3.1b}$$

where $\Delta N = N(K_1 - K_2)/(K_1 + K_2)$ is the difference of populations in the absence of the EM field (which is sometimes referred to as the number of active atoms); $\gamma_{1r} = (K_1 + K_2)/2$ is the average rate of inelastic relaxation of levels. For the absorbed light power, taking into account (2.20), we obtain

$$Q = Q_{sat}\frac{2\pi V^2 S(\Delta\omega)}{\gamma_{ir} + 2\pi V^2 S(\Delta\omega)}, \tag{3.2}$$

where $Q_{sat} = \hbar\omega\gamma_{1r}\Delta N$ is the limiting power which the medium can absorb for given characteristics of inelastic relaxation ($Q \to Q_{sat}$ in the saturation regime, i.e., with $V \to \infty$).

When the line is broadened by elastic collisions with heavy particles, using for the spectral function $S(\Delta\omega)$ expression (2.22), we have

$$Q = Q_{sat}\frac{2V^2}{(\Delta\omega + \Delta_c)^2 + \gamma_c^2 + (2V^2\gamma_{OC}(\Delta\omega)/\gamma_{ir})}. \tag{3.3}$$

This equation generalizes somewhat a well-known result of nonlinear spectroscopy, first obtained by Karplus and Schwinger.[25] Expression (3.3) differs from the well-known results[25,5-7] by the fact that the quantity $\gamma_{OC}(\Delta\omega)$ here, as also in (2.22), is not constant $\gamma_{OC}(0) = \gamma_C$, but is a function of frequency. Therefore, for weak fields ($V \to 0$), expression (3.3), going over into (2.22), describes here the entire collisional profile, and not only the impact region ($\Delta\omega \ll \Omega_B$), as happens in well known results, which contain only γ_C.

We note, however, that due to the validity of (3.3) for the entire range of frequency detuning for weak fields, it by no means follows that it is everywhere valid for strong fields as well, when $2V^2\gamma_{OC}/\gamma_{1r} \sim \Delta\omega^2$. As a more rigorous analysis shows (Secs. 4 and 5), in strong fields, it is, generally speaking, necessary to take into account the effect of the field on the dynamics of a broadening collision. In this case, the quantity γ_{OC} is a function not only of $\Delta\omega$, but also of the field intensity $\mathscr{E}_0$.

The nonlinear dependence of the absorbed power Q on the intensity $I \propto \mathscr{E}_0^2$ of the light interacting with the medium stems from the kinetic effect: the equalization of populations for

$$V^2 \gtrsim V_{cr} = (\Delta\omega^2 + \gamma_c^2)\frac{\gamma_{ir}}{2\gamma_{OC}}. \tag{3.4}$$

Indeed, as follows from (3.1), $N_1 - N_2 \to 0$ for $V^2 \gg V_{cr}^2$. We shall estimate the critical field for $\Delta\omega \ll \gamma_C$:

$$\mathscr{E}_{sat} = \frac{2\hbar}{d}\sqrt{\gamma_c\gamma_{ir}}. \tag{3.5}$$

Assuming, for example, that $\gamma_{1r} \approx 10^8\ s^{-1}$, $\gamma_{OC}/N_B \approx \pi\rho_B^2 v_T \cdot 3\cdot 10^{-14}\ cm^2$, $3\cdot 10^4\ cm/s \approx 10^{-9}\ cm^3\ s^{-1}$, $d \sim 1$ a.u. $\approx 2.5\cdot 10^{-18}\ (erg\cdot cm)^{1/2}$, we have

$$\mathscr{E}_{sat} \approx 10^{-7}\sqrt{N_B(cm^{-3})}\frac{V/cm}{cm} \approx 2\cdot 10^{-17}\sqrt{N_B(cm^{-3})}\ a.u.$$

(the atomic field unit is $\mathscr{E}_{at} = 0.5\cdot 10^{10}$ V/cm). At atmospheric pressure, $N_B \approx 1$ amagats $\approx 3\cdot 10^{19}\ cm^{-3}$, we have $\mathscr{E}_{sat} \approx 0.5\cdot 10^3$ V/cm, which corresponds to light intensity $I_{sat} = c\mathscr{E}_{sat}^2/4\pi \approx 10^3\ N/cm^2$.

We note that the Doppler line profile, obtained using the Maxwell velocity distribution, cannot be substituted into Eq. (3.2) due to the effect of induced and inelastic transitions on the velocity distribution of the emitters.[7]

Summarizing the analysis of the case of weak fields, we point out the following two circumstances. First, finding one of the basic characteristics of the line shape, the phase relaxation rate γ_{OC}, reduces to analyzing Eqs. (2.3), analogous to the equations of the theory of atomic collisions. Second, the phase relaxation rate γ_{OC} even in the weak field limit is not constant, as is usually assumed in nonlinear spectroscopy,[5-7] but depends on $\Delta\omega$. As is evident from (2.8), the phase relaxation rate does not depend on the field intensity for weak fields, when the probability of an OC transition is proportional to light intensity.

4. OPTICAL COLLISIONS IN A STRONG FIELD

In examining the case of strong fields, when the probability of an optical transition in an atom over the time of a broadening collision is not small, it is necessary to generalize somewhat the approach presented above in Secs. 2 and 3. The main point of the generalization is to do away with perturbation theory and, at the same time, to view the atomic states as being mixed together with the state of the EM field.

a) Compound system with strong atom-field coupling

We shall examine an optical collision in the same formulation of the problem as in subsection a of Sec. 2 (see Fig. 1). We are talking about an optical transition occurring during a collision between atom A and a heavy particle B. The transition occurs in a monochromatic EM field with frequency ω, close to the frequency ω_0 of the transition A(1) → A(2). The optical collision (OC) is viewed as an isolated event, during which the atoms interact with one another and with the electromagnetic field. Within the scope of the assumptions made, we can speak about (as in subsection a of Sec. 2) discrete states of the compound system "A + B + $\mathscr{E}$" and, in addition, the transition between these states due to the A–B interaction is the OC transition. The difference in the following analysis lies in the choice of states of the compound system describing the OC transition.

In choosing the states of the compound system, determining dissipation of light energy during a collision, it is necessary to take into account the important fact that the states of atom A and field $\mathscr{E}$, generally speaking, are mixed. Indeed, the field is switched on long before the collision and is not assumed to be weak. Then, even before the collisions, atom A is not in some single state 1 or 2, just as the field $\mathscr{E}$ does not contain a definite number of photons n_ω or $n_{\omega+1}$. The stationary states of the system A + $\mathscr{E}$, taking into account exactly the interaction of the atom and the field, of course, exist, but they correspond to different wave functions. These "other" states correspond to constant energy of the EM field (in the absence of interaction with atom B).[2)] Therefore, transitions precisely between these states are responsible for absorption of light during the A–B interaction.

What was said above is easily taken into account by the formal apparatus of the quantum mechanics of a two-level system. We shall obtain equations that describe the OC transition with strong A–$\mathscr{E}$ coupling. We shall rewrite the previous Hamiltonian (2.2) in the form

$$\hat{H} = \hat{H}_{A\mathscr{E}} + V_{AB}(t), \quad \hat{H}_{A\mathscr{E}} = \hat{H}_A + \hat{H}_{\mathscr{E}} + \hat{V}_{A\mathscr{E}}. \tag{4.1}$$

Since the amplitude of the field $\mathscr{E}_0$ and, correspondingly, the operator $\hat{V}_{A\mathscr{E}}$ are constant, the problem of finding the characteristic functions of the Hamiltonian $\hat{H}_{A\mathscr{E}}$ in the two-level case can be solved exactly (see Ref. 20, p. 171). The characteristic functions of the Hamiltonian

$$\psi_1 = b_1\varphi_1 + b_2\varphi_2, \quad \psi_2 = b_2\varphi_1 - b_1\varphi_2 \tag{4.2a}$$

are expressed in terms of the wave functions of the Hamiltonian $\hat{H}_A + \hat{H}_{\mathscr{E}}$ used in subsection 2.1, $\varphi_1 = |A(1), n_\omega\rangle$ and $\varphi_2 = |A(2), n_\omega - 1\rangle$, not taking into account the A–$\mathscr{E}$ interaction, and in terms of the coefficients

$$b_{1,2} = \frac{1}{\sqrt{2}}\sqrt{1 \pm \frac{\Delta\omega}{\Omega}}, \tag{4.2b}$$

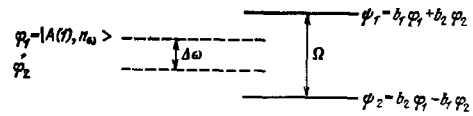

FIG. 3. Levels of the compound system "atom A + EM field" with weak and strong coupling. $\varphi_2 = |A(2), n_\omega - 1\rangle$.

where $\Omega = \Omega\sqrt{\Delta\omega^2 + 4V^2}$ is the hybrid frequency, which is the difference between terms of the compound system A + $\mathscr{E}$ with strong coupling (Fig. 3). The quantity $\Omega = 2V$ for $\Delta\omega = 0$ is usually called the Rabi frequency.

We obtain equations for the amplitudes of the states ψ_1 and ψ_2 from the Schrödinger equation with the Hamiltonian (4.1), similar to (2.3):

$$i\dot{\tilde{a}} = \tilde{U}_1\tilde{a}_1 + \tilde{V}_{12}e^{i\omega t}\tilde{a}_2, \quad i\dot{\tilde{a}}_2 = \tilde{U}_2\tilde{a}_2 + \tilde{V}_{21}e^{-i\omega t}\tilde{a}_1. \tag{4.3}$$

Here, the matrix elements are expressed in terms of the functions ψ_1 and ψ_2. We shall express them in terms of the quantites introduced previously:

$$\left.\begin{aligned} \tilde{U}_1 &= \tfrac{1}{\hbar}(\psi_1|V_{AB}|\psi_1) = b_1^2U_1 + b_2^2U_2, \\ \tilde{U}_2 &= \tfrac{1}{\hbar}(\psi_2|V_{AB}|\psi_2) = b_2^2U_1 + b_1^2U_2, \\ \tilde{V}_{12} = \tilde{V}_{21} &= \tfrac{1}{\hbar}(\psi_1|V_{A\mathscr{E}}|\psi_2) = b_1b_2(U_2 - U_1). \end{aligned}\right\} \tag{4.4}$$

Here and in what follows, in Sec. 5, the quantities corresponding to states of the compound system (matrix elements, populations, and so on) are indicated by a tilde, in order to distinguish them from the analogous quantities for the atom. After the variable substitution $\tilde{b}_k = a_k \exp(i\int_{-\infty}^{t}\tilde{U}_k\,dt)$, taking into account the equalities $b_2^2 - b_1^2 = \Delta\omega/\Omega$ and $b_1b_2 = V/\Omega$, we obtain the system of equations sought that describes the behavior of the amplitudes of the states of the compound system "A + $\mathscr{E}$ + B" taking into account the strong A – $\mathscr{E}$ coupling:

$$\left.\begin{aligned} i\dot{\tilde{b}}_1 &= \tilde{b}_2\Delta U\frac{V}{\Omega}\exp\left\{i\left[\Omega t - \frac{\Delta\omega}{\Omega}\int_{-\infty}^{t}\Delta U(t')\,dt'\right]\right\}, \\ i\dot{\tilde{b}}_2 &= b_1\Delta U\frac{V}{\Omega}\exp\left\{-i\left[\Omega t - \frac{\Delta\omega}{\Omega}\int_{-\infty}^{t}\Delta U(t')\,dt'\right]\right\}. \end{aligned}\right\} \tag{4.5}$$

The system of equations (4.5) in many ways is analogous to the equations describing the radiative collision transitions [see Eqs. (4.2) in Ref. 8], as well as the equations of the theory of atomic collisions in the semiclassical approximation. In contrast to the theory of atomic collisions, Eqs. (4.5) include the parameters not only of particles A and B, but of the EM field as well. Here, the field dependence differs somewhat from that occurring in the theory of radiative collision reactions.

An optical collision is an *inelastic* transition $\psi_1 \rightarrow \psi_2$ in the compound system, but this transition is caused by an *elastic* collision with atom B. The role of the potential causing the OC transition, as is evident from (4.5), is played by the quantity

$$\tilde{V} = \Delta U\frac{V}{\Omega}, \tag{4.6}$$

which for $V \ll \Delta\omega$ goes over into the effective potential (2.6) in the case of a weak field. It is clear from here that the integration by parts (2.5), separating out the term responsible for the OC transition, corresponds to choosing a new basis for the wave functions ψ_1 and ψ_2.

[2)] It may be assumed, generally speaking, that oscillations of the states of the atom A (1), A (2), and the number of photons n_ω, $n_\omega - 1$ occur, but the average energy of the atom and of the field remain unchanged.

We shall assume that before the collision the compound system is located in one of the states ψ_1 or ψ_2, for example, in ψ_1. Then, the initial conditions take the form

$$\tilde{b}_1(-\infty)=1, \quad \tilde{b}_2(-\infty)=0, \tag{4.7}$$

and for the probability of an OC transition, we have $\omega_{OC} = |\tilde{b}_2(\infty)|^2$. The cross section $\sigma_{OC}(\Delta\omega, V, v)$ and the rate of the OC transition $k(\Delta\omega, V)$ are introduced based on previous Eqs. (2.7), where, however, the probability of a transition is found from the new equations (4.5). It is useful to introduce the variable line width (inverse phase relaxation time) γ_{OC} from the equation

$$\gamma_{OC}(\Delta\omega, V)=\frac{\Omega^2}{2V^2}K_{OC}(\Delta\omega, V), \tag{4.8}$$

generalizing (2.8). In contrast to the usual theory of broadening, γ_{OC} in (4.8) depends, generally speaking, not only on frequency, but also on the field intensity.

b) Nature of the frequency and field intensity dependence of OC cross sections

The analysis of the system of equations (4.5), describing an OC transition in an arbitrary field, is in many ways analogous to the analysis of equations describing radiative collisions (see Ref. 8; Sec. 5). In this case, the methods developed in the theory of atomic collisions are widely used. For this reason, without dwelling on the details, we note the main points. We shall present the specific results for the power-law potential $\Delta U = c_n/r^n$.

The nature of the solution (4.5) is determined by the relations between the three quantities: Ω, the splitting between the levels of the compound system; $\Delta U\Delta\omega/\Omega$, the shift of the levels of the compound system; and, $\Delta UV/\Omega$, the matrix elements of the transition in the compound system. The Weisskopf frequency $\Omega_B = v/\rho_B$ at the Weisskopf radius ρ_B plays a fundamental role in this case (see subsection a, Sec. 2).

Perturbation theory with respect to the matrix element $\Delta UV/\Omega$ leads finally (see Ref. 26 for greater detail) to the results of the usual theory of broadening. The applicability of perturbation theory is restricted according by the field intensity by the relations

$$\frac{V^2}{\Delta\omega^2}\ll\begin{cases}1 & \text{for } \Delta\omega\ll\Omega_B,\\ \frac{vF_{\Delta\omega}}{2\pi}=\left(\frac{\Omega_B}{\Delta\omega}\right)^{(n-1)/n} & \text{for } \Delta\omega\gg\Omega_B,\ \Delta U\Delta\omega>0.\end{cases} \tag{4.9}$$

We shall estimate the characteristic magnitude of the Weisskopf field $\mathscr{E}_B=\hbar\Omega_B/d$, for which dynamical nonlinear effects are manifested. Setting $\rho_B\approx 10^{-7}$ cm, d ~ 1 a.u., $v=2\cdot10^4$ cm/s $\approx 10^{-3}$ a.u. we have: $\Omega_B\approx 2\cdot10^{11}$ s$^{-1}\approx 7$ cm^{-1}, $\mathscr{E}_B\approx 3\cdot10^{-6}$ a.u. $\approx 1.5\cdot10^5$ V/cm.

The impact region corresponds to rapid passage. In contrast to the usual theory of broadening, it is determined by the relation

$$\Omega=\sqrt{\Delta\omega^2+4V^2}\ll\Omega_B, \tag{4.10}$$

and, when this relation is satisfied, it is possible to set $\Omega=0$ in the exponents in (4.5). In this case, (4.5) reduces to a differential equation with constant coefficients. As a result, we obtain

$$\sigma_{OC}=\frac{2V^2}{\Omega^2}\sigma_B, \quad \sigma_B=\int 2\pi\rho\,d\rho\left(1-\cos\int_{-\infty}^{\infty}\Delta U\,dt\right). \tag{4.11}$$

Therefore, we have the previous expressions for the quantities γ_{OC} in the impact region (4.10).

The quasistatic region corresponds to slow passage, for which

$$\Omega=\sqrt{\Delta\omega^2+4V^2}\gg\Omega_B. \tag{4.12}$$

Here, as in a weak field, two basic cases arise: a) when the level crossover point $r_{\Delta\omega}$ is such that

$$\Delta U(r_{\Delta\omega})=\Omega^2/\Delta\omega; \tag{4.13}$$

b) when there is no crossover point.

Case a) corresponds to the *static* region. In this region, it is possible to use the Landau–Zener approximation (Ref. 20, p. 402). In this situation, it is valid when the following conditions are satisfied: $\Delta U\Delta\omega/\Omega \gg \Omega_B$ and $\Delta UV/\Omega \ll \Delta U\Delta\omega/\Omega$, which can be rewritten in the form

$$\Delta\omega\gg\Omega_B \qquad (\Delta U\Delta\omega>0). \tag{4.14}$$

For the OC cross section, in this case,

$$\sigma_{OC}=\pi r_{\Delta\omega}^2\bar{w}\,(\mathscr{E}_0^2/\mathscr{E}_{LS}^2), \tag{4.15}$$

where $\mathscr{E}_{LS}=\sqrt{vF_{\Delta\omega}/2\pi d^2}$ is the critical (for this region of values of $\Delta\omega$) field, for which nonlinear effects are manifested [compare (4.9)];

$$\bar{w}(\alpha)=\left\langle 2\int_0^1 dx\,e^{-(\alpha/\sqrt{x})\cos^2\theta_1}\left[1-e^{-(\alpha\sqrt{x})(\cos^2\theta_1-\cos^2\theta_2)}\right]\right\rangle \tag{4.16a}$$

is the probability for passing through both crossover points, the symbol $\langle\ldots\rangle$ indicates averaging over angles θ_1 and θ_2 between the dipole moment and the field intensity at the first and second crossover points, respectively. Expression (4.16a) corresponds to a transition without a change in the magnetic quantum number ($\Delta m = 0$). For transitions with $\Delta m = \pm 1$, the cosines in (4.16a) must be replaced by sines. The limiting expressions for the cross sections have the following form:

$$\sigma_{OC}=\begin{cases}\frac{4}{3}\pi r_{\Delta\omega}^2\alpha, & \alpha\ll 1,\\ \Delta m=0,\\ \frac{4}{3}\frac{\pi r_{\Delta\omega}^2}{\sqrt{\alpha}}, & \alpha\gg 1,\end{cases} \qquad \sigma_{OC}=\begin{cases}\frac{8}{3}\pi r_{\Delta\omega}^2\alpha, & \alpha\ll 1,\\ \Delta m=\pm 1,\\ \frac{8}{3}\pi r_{\Delta\omega}^2\alpha^{-1}, & \alpha\gg 1.\end{cases} \tag{4.16b}$$

Case b) corresponds to the situation, first examined by Stückelberg, when

$$V\gg\Delta\omega,\ \Omega_B. \tag{4.17}$$

In this case, we can write for the OC cross section

$$\sigma_{OC}\propto\left\langle\exp\left[-\left(\frac{\mathscr{E}_0\cos\theta}{\mathscr{E}_w}\right)^2\right]\right\rangle, \quad \mathscr{E}_w=\frac{v^2}{\Delta\omega^{n-1}r}. \tag{4.18}$$

The regions of applicability of the approximations examined above are presented in Fig. 4. The analysis is valid outside a circle with radius $\sim\gamma\approx\pi\rho_B^2 v_T N_B$ (i.e., for $\Omega\gg\gamma_C$), which is shaded in Fig. 4 (for more detail, see below). If, in Fig. 4, we draw the straight line V will determine the line profile for given field V. Note that here we have in mind the line profile corresponding to light absorption only as a result of OC transitions; in order to obtain the line profile corresponding to the total energy absorption, generally speaking, it is necessary to take

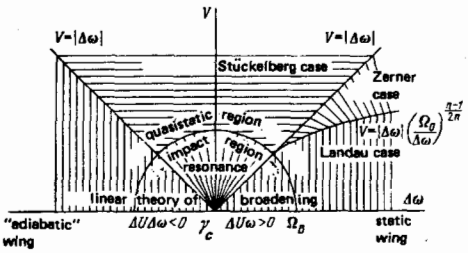

FIG. 4. Complete picture of the physical regions of variation of OC cross sections.

into account kinetic effects. The main property of the OC profile is the decrease in the absorption of light in the presence of nonlinear effects. The enhanced transmission effects, i.e., decrease in absorption due to OC transitions with increasing field, is explained by the fact that the matrix element of the transition causes additional separation of terms of the compound system (see Ref. 8 for greater detail).

5. KINETICS OF ABSORPTION OF POWERFUL RESONANCE RADIATION

In this section, we examine the kinetics of absorption of resonance radiation, when events of light dissipation are not correlated with one another. It turns out that this particular case is most interesting in examining nonlinear opticocollisional effects. In order to obtain the power absorbed per unit volume, it is simply necessary to find the light energy dissipated in each event and to sum these events. The main point in the analysis carried out is that we are examining not the kinetics of atoms, but the kinetics of the compound (atom–EM field) system.

a) Absorption of light in the absence of inelastic transitions

Before going on to more complex aspects of the "nonlinear theory of broadening", we shall illustrate the results presented above using the example of the simplest kinetic problem of absorption of light due to OC transitions in the absence of inelastic relaxation.

It is clear at the outset that the transition between states ψ_1 and ψ_2, in general, does not correspond to absorption of a whole number of photons Δn_ω, just as the states ψ_1 and ψ_2 themselves do not correspond to a definite value of n_ω. For this reason, we shall first obtain an expression for the energy ΔE_{OC}, dissipated per single OC transition. The calculation of the energy dissipated in any transition reduces to finding the average energy of the field in states of the compound system before and after the transition. The state of the compound system is characterized by the wave function

$$\Psi(t)=\tilde{b}_1(t)\,\psi_1+\tilde{b}_2(t)\,\psi_2. \tag{5.1}$$

Therefore, the quantum-mechanical average of the field operator is determined by the equation (see, for example, Ref. 20, p. 60)

$$\langle H_{\mathcal{G}}\rangle_{\Psi}=\sum_{m,m'}\tilde{b}_m\tilde{b}_{m'}\langle\psi_m|H_{\mathcal{G}}|\psi_{m'}\rangle \tag{5.2}$$
$$=|\tilde{b}_1|^2E_1^{\mathcal{G}}+|\tilde{b}_2|^2E_2^{\mathcal{G}}+2\,\mathrm{Re}\,(\tilde{b}_1\tilde{b}_2\langle\psi_1|H_{\mathcal{G}}|\psi_2\rangle),$$

where $E_m^{\mathcal{G}}=\langle\psi_m|H_{\mathcal{G}}|\psi_m\rangle$. In what follows, we shall be interested in expression (5.2), averaged over a statistical ensemble of the compound system with arbitrary initial phases. After such statistical averaging, the third term (5.2) will vanish, and this gives

$$\langle H_{\mathcal{G}}\rangle=|\tilde{b}_1|^2E_1^{\mathcal{G}}+|\tilde{b}_2|^2E_2^{\mathcal{G}}. \tag{5.3}$$

Indeed, averaging over a statistical ensemble assumes summation of expressions (5.2) for all atoms and dividing by the total number of atoms. Since the third term in (5.2) is proportional to $e^{i\eta_k}$, where η_k is the phase of the total wave function of the k-th atom, for a random distribution of phases over atoms, it vanishes.

However, it should be kept in mind that the phases of atoms (and compound systems) are correlated over times of the order of the free-flight time (see subsection b, Sec. 2), which is important for small splitting of the terms of the compound system. In what follows, we shall limit the analysis to the region

$$\Omega=\sqrt{\Delta\omega^2+4V^2}\gg\gamma_c\,, \tag{5.4}$$

which is a natural extension of the single-particle region (2.16). This single-particle condition will then permit representing the dissipation of light as a collection of separate events. We note that dynamic nonlinear effects, as follows from the preceding analysis, are manifested only for $V\gtrsim\Omega_B\gg\gamma_C$. Therefore, the single-particle approximation (5.4) is sufficient to construct a systematic theory. The average energy of the field in the states ψ_1 and ψ_2 is given by the expressions

$$E_1^{\mathcal{G}}=b_1^2\langle\varphi_1|H_{\mathcal{G}}|\varphi_1\rangle+b_2^2\langle\varphi_2|H_{\mathcal{G}}|\varphi_2\rangle=\hbar\omega\,[b_1^2n_\omega+b_2^2(n_\omega-1)]=\hbar\omega(n_\omega-b_2^2),$$
$$E_2^{\mathcal{G}}=b_2^2\langle\varphi_1|H_{\mathcal{G}}|\varphi_1\rangle+b_1^2\langle\varphi_2|H_{\mathcal{G}}|\varphi_2\rangle=\hbar\omega\,[b_2^2n_\omega+b_1^2(n_\omega-1)]=\hbar\omega(n_\omega-b_1^2).$$

Therefore, the energy dissipated in an OC transition equals

$$\Delta E_{OC}=E_{12}^{\mathcal{G}}=E_1^{\mathcal{G}}-E_2^{\mathcal{G}}=\hbar\omega\,(b_1^2-b_2^2)=\hbar\omega\,\frac{\Delta\omega}{\Omega}\,. \tag{5.5}$$

In weak fields, $V\ll\Delta\omega$, naturally, $\Delta E_{OC}=\hbar\omega$.

Under the single-particle conditions (5.4), it is possible to use the concept of the population $\tilde{N}_m$ of the states ψ_m of the compound system. Therefore, for the light power dissipated in a medium due to OC transitions, we have expression (2.9):

$$Q_{OC}=\hbar\omega\,\frac{\Delta\omega}{\Omega}\,K_{OC}\,(\tilde{N}_1-\tilde{N}_2)=\hbar\omega\,\frac{\Delta\omega\Omega}{2V^2}\,\gamma_{OC}\,(\tilde{N}_1-\tilde{N}_2). \tag{5.6}$$

We shall examine the simplest example of the kinetics of light absorption in a medium. For the populations of the compound system $A+\mathcal{G}$, we shall use the balance equations for the closed two-level model

$$\frac{d\tilde{N}_1}{dt}=K_{OC}\tilde{N}_1-K_{OC}\tilde{N}_2,\quad \tilde{N}_1+\tilde{N}_2=N. \tag{5.7}$$

In order to determine the initial conditions, we shall examine the problem of mixing of the states of the atom and of the field. Assume that the field is switched on suddenly at time $t=0$. Assume also that for $t<0$ all atoms are in the ground state A(1). For $t>0$, the wave function of the compound system has the form (Ref. 20, p. 172, 176)

$$\Psi(t)=b_1e^{-i\frac{\Omega t}{2}}\psi_1+b_2e^{i\frac{\Omega t}{2}}\psi_2. \tag{5.8}$$

Therefore, the states of the atoms and of the field are mixed within a time $\sim\Omega^{-1}$, while the characteristic relaxation time of the populations due to OC transitions, as follows from (5.7), is of the order of K_{OC}^{-1}. It follows from the definition of the quantities γ_{OC} and K_{OC} that $\gamma_{OC} > K_{OC}$ and $\gamma_{OC} \leq \gamma_C$ are always satisfied. Thus, in the single-particle approximation, it may be assumed that the states of the field and of the atom are mixed before OC relaxation. Then, in solving Eqs. (5.7), it is necessary to choose the following initial conditions:

$$\tilde{N}_1(0) = b_1^2 N, \quad \tilde{N}_2(0) = b_2^2 N. \tag{5.9}$$

Solution of (5.7), when the quantity K_{OC} does not depend on time, gives

$$\tilde{N}_1(t) = \frac{N}{2}\left(1 + \frac{\Delta\omega}{\Omega} e^{-2K_{OC}t}\right), \quad \tilde{N}_2(t) = \frac{N}{2}\left(1 - \frac{\Delta\omega}{\Omega} e^{-2K_{OC}t}\right). \tag{5.10}$$

For the absorbed power, we have

$$Q_{OC}(t) = \hbar\omega \frac{\Delta\omega^2}{\Omega^2} \frac{N}{2} 2K_{OC} e^{-2K_{OC}t}. \tag{5.11}$$

The total energy, absorbed by the medium due to OC transitions over quite a long time interval $t \gg K_{OC}^{-1}$, equals

$$W_{OC} = \int_0^\infty Q_{OC}\, dt = \hbar\omega \frac{\Delta\omega^2}{\Omega^2} \frac{N}{2}. \tag{5.12}$$

In calculating the total energy absorbed by the medium, in addition to OC transitions, one more dissipation channel related to initial mixing of the states of the atom and of the field must be kept in mind. Indeed, before the interaction is switched on, the energy of the field equals

$$\langle H_{\mathscr{E}}(t<0)\rangle = \hbar\omega n_\omega. \tag{5.13}$$

For $t > 0$, the wave function has the form (5.8), from where we obtain

$$\langle H_{\mathscr{E}}(t>0)\rangle = \hbar\omega\left(n_\omega - \frac{2V^2}{\Omega^2}\right). \tag{5.14}$$

The change in the average energy of the field equals

$$\langle H_{\mathscr{E}}(t<0)\rangle - \langle H_{\mathscr{E}}(t>0)\rangle = \frac{\hbar\omega 2V^2}{\Omega^2}. \tag{5.15}$$

Thus, over a time $t \sim \Omega^{-1}$, the energy

$$W_{on.} = \hbar\omega \frac{4V^2}{\Omega^2} \frac{N}{2}, \tag{5.16}$$

is dissipated and, over a time $t \gg K_{OC}^{-1}$, the energy (5.12) is dissipated in OC transitions. The total energy dissipated simply equals $\hbar\omega N/2$. This result corresponds to equalization of the atomic state populations.

b) Absorption of light taking inelastic relaxation into account

We shall examine the same situation as in Sec. 3, but taking into account the dynamical nonlinear effects. The states of the "atom + field" compound system are characterized by a set of pairwise resonating levels, of which we shall need, in what follows, the following six: $m = 1, 2$; $m_\pm = 1_\pm, 2_\pm$ (Fig. 5). The wave functions ψ_m and $\psi_{m\pm}$, describing these states, are represented as a linear combination of characteristic wave functions φ_m and $\varphi_{m\pm}$ of the Hamiltonian $\hat{H}_A + \hat{H}_{\mathscr{E}}$, similar to (4.2):

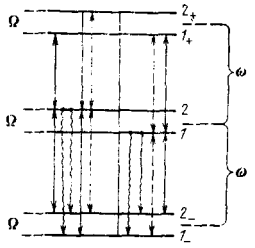

FIG. 5. Energy levels and scheme of inelastic transitions between the states ψ_1, ψ_2, $\psi_{1_\pm}$, $\psi_{2_\pm}$ determined by Eq. (5.3). The continuous arrows indicate collisional transitions; the dashed arrows indicate radiation damping transitions (see Ref. 12, 18); the wavy arrows indicate spontaneous transitions.

$$|\psi_s\rangle = \begin{pmatrix} \psi_{2_+} \\ \psi_{1_+} \\ \psi_2 \\ \psi_1 \\ \psi_{2_-} \\ \psi_{1_-} \end{pmatrix} = \begin{pmatrix} b_2\varphi_{1_+} - b_1\varphi_{2_+} \\ b_1\varphi_{1_+} + b_2\varphi_{2_+} \\ b_2\varphi_1 - b_1\varphi_2 \\ b_1\varphi_1 + b_2\varphi_2 \\ b_2\varphi_{1_-} - b_1\varphi_{2_-} \\ b_1\varphi_{1_-} + b_2\varphi_{2_-} \end{pmatrix}. \tag{5.17}$$

Here, $\varphi_1 = |A(1), n_\omega\rangle$, $\varphi_2 = |A(2), n_\omega - 1\rangle$, $\varphi_{1_\pm} = |A(1), n_\omega \pm 1\rangle$, and $\varphi_{2_\pm} |A(2), n_\omega - 1 \pm 1\rangle$ are wave functions, corresponding to the noninteracting states of the atom and field.

Dissipation of light energy due to elastic collisions is determined by OC transitions, i.e., transitions between the states ψ_1 and ψ_2 of the compound system $A + \mathscr{E}$ (see subsection a, Sec. 4). On the other hand, an inelastic transition of the atom $A(m) \to A(m')$ corresponds to a sudden switching on of the field for atom A, which appears after the transition in the new state m'. As shown in subsection a in Sec. 5, this switching on of the field also leads to dissipation of energy. In addition, an inelastic transition of the atom $A(m) \to A(m')$ is accompanied, generally speaking, by transitions $m \to m'_\pm$, $m'_\pm$ in the compound system $A + \mathscr{E}$ between the states ψ_1, ψ_2 and $\psi_{1_\pm}, \psi_{2_\pm}$. Thus, in order to describe the light energy due to both elastic and inelastic transitions, it is necessary to examine all six states $s = 1_-, 2_-; 1, 2; 1_+, 2_+ = m_-, m, m_+ (m = 1, 2)$ of the compound system, introduced in Eq. (5.17). However, the population of the states ψ_m is not distinguishable from the population of the states $\psi_{m\pm}$ in view of the quasiclassical nature of the field ($n_\omega \gg 1$). Therefore, in the kinetics, it is not necessary to take into account all transitions $s \to s'$, but only transitions from the two states $m = 1, 2$ into the remaining states:

$$m = 1, 2 \to s = m', m'_\pm.$$

In connection with what has been said above, we introduce, following Ref. 12, rectangular (not square) matrices E_{sm} and K_{sm}, giving the energy dissipated in the transition $m \to s$, and the rate (frequency) of the transitions $m \to s$, respectively:

$$\hat{E}^{(\mathscr{E})} = \begin{bmatrix} E_{1_+1} & E_{1_+2} \\ E_{2_+1} & E_{2_+2} \\ 0 & E_{12} \\ E_{21} & 0 \\ E_{2_-1} & E_{2_-2} \\ E_{1_-1} & E_{1_-2} \end{bmatrix}, \quad \hat{K} = \begin{bmatrix} K_{1_+1} & K_{1_+2} \\ K_{2_+1} & K_{2_+2} \\ K_{11} & K_{12} \\ K_{21} & K_{22} \\ K_{2_-1} & K_{2_-2} \\ K_{1_-1} & K_{1_-2} \end{bmatrix}. \tag{5.18}$$

Their specific form is obtained in the Appendix. With the help of the matrices (5.18), it is simple to write

both the equation of balance for the populations and the expression for the light power Q dissipated per unit volume.

In writing down the equations of balance, it is necessary to take into account the fact that the transition $m \to m'_\pm$ is kinetically equivalent to the transition $m \to m'$ in view of the indistinguishability of the states m' and $m'_\pm$. Thus, for the populations $\tilde{N}_m$ of the compound system A + $\mathscr{E}$, we have

$$\frac{d\tilde{N}_m}{dt} = \sum_{m=1,2} \tilde{\tilde{K}}_{mm'} \tilde{N}_{m'}, \qquad m = 1, 2, \tag{5.19}$$

where

$$\tilde{\tilde{K}}_{mm'} = \tilde{K}_{mm'} + \sum_{\pm} \tilde{K}_{m\pm m'}; \tag{5.20}$$

summation with respect to ± indicates summation with respect to $m_\pm$ for fixed m.

The power Q dissipated per unit volume is obtained after multiplying the frequency of each type of transition by the magnitude of the light energy dissipated in this transition and summing over transitions:

$$Q = \sum_{s=1}^{6} \sum_{m=1,2} E_{sm}^{(\mathscr{E})} \tilde{K}_{sm} \tilde{N}_m. \tag{5.21}$$

Within the scope of the simple kinetics presented above, the calculation of Q reduces, as in Sec. 3, to finding the populations $\tilde{N}_m$ from the balance equations (5.19) and substituting them into (5.21).

For the light power density $Q^{(oc)}$ absorbed due to OC transitions (5.6) and for the power $Q^{(ir)} = \sum_{m,m'} \sum_{\pm} E_{m\pm m'}^{(\mathscr{E})} \tilde{K}_{m\pm m'} \tilde{N}_{m'}$ dissipated due to inelastic relaxation, calculations give

$$Q^{(oc)} = Q_{sat} \frac{2V^2}{\Delta\omega^2} \frac{(\Delta\omega/\Omega^2)\gamma_{oc}}{\gamma_{ir} + (2V^2/\Delta\omega^2)(\gamma_{oc} + \gamma_{ir})}, \tag{5.22a}$$

$$Q^{(ir)} = Q_{sat} \cdot \frac{2V^2}{\Delta\omega^2} \frac{[1 - (\Delta\omega^2/\Omega^2)]\gamma_{oc} + \gamma_{ir}}{\gamma_{ir} + (2V^2/\Delta\omega^2)(\gamma_{ir} + \gamma_{oc})}. \tag{5.22b}$$

Here, as in Sec. 3, $Q_{sat} = \hbar\omega\gamma_{ir}\Delta N$ indicates the power absorbed by a two-level system in the saturation regime with given inelastic relaxation, while the quantities entering into (5.21) are written out in the Appendix.

We shall discuss separately inelastic relaxation due to spontaneous radiative transitions.[27] Spontaneous transitions form the following three lines: the principal line at the frequency $\omega_{sp} = \omega$ (i.e., Rayleigh scattering), to which the transitions $1 \to 1-$ and $2 \to 2-$ contribute, as well as two lines accompanying it at frequencies $\omega_{sp} = \omega + \Omega$ (so-called resonance fluorescence) and $\omega_{sp} = \omega - \Omega$ (so-called three-photon scattering), formed by transitions $2 \to 1-$ and $1 \to 2-$, respectively (see Fig. 5). Multiplying the spontaneous transition rate A_{12} by the light energy, dissipated in the corresponding transition, we obtain the following expressions for the power of spontaneous emission of the triplet components

$$Q_{sp} = \hbar\omega A_{12} \times \begin{cases} \frac{1}{4}\left(1 + \frac{\Delta\omega}{\Omega}\right)\tilde{N}_2 \equiv Q_F, & \omega_{sp} = \omega + \Omega, \\ \frac{V^2}{\Omega^2}(\tilde{N}_1 + \tilde{N}_3) \equiv Q_R, & \omega_{sp} = \omega, \\ \frac{1}{4}\left(1 - \frac{\Delta\omega}{\Omega}\right)\tilde{N}_1 \equiv Q_3, & \omega_{sp} = \omega - \Omega. \end{cases} \tag{5.23}$$

Rayleigh scattering Q_R does not depend on collisions. We note that it is most convenient to make measurements, characterizing the interaction of light with the medium, according to the emission of the different triplet components (5.22).

c) Nonlinear effects

The expression for the total absorbed power (5.21) is obtained by summing (5.22a) and (5.22b):

$$Q = Q_{sat} \frac{2V^2(\gamma_{oc} + \gamma_{ir})/\gamma_{ir}}{\Delta\omega^2 + 2V^2(\gamma_{oc} + \gamma_{ir})/\gamma_{ir}}. \tag{5.24}$$

This expression formally coincides with (3.3) to within two unimportant details. First, here, in contrast to (3.3), $\gamma_{oc} + \gamma_{ir}$ enters instead of γ_{oc}, since the inelastic relaxation, in deriving (5.24), was not assumed to be small beforehand compared to elastic relaxation. Second, the term γ_c^2 does not occur in the denominator (5.24). However, this fact is not important for the single-particle region (5.4). Indeed, transforming the denominator (5.24)

$$\Delta\omega^2 + \frac{2V^2(\gamma_{oc} + \gamma_{ir})}{\gamma_{ir}} = \Omega^2 + \frac{2V^2\gamma_{oc}}{\gamma_{ir}}, \tag{5.25}$$

we see that it is large compared to γ_c^2 in the region $\Omega \gg \gamma_c$, for which the analysis carried out is valid.

A much more profound difference is the informal difference between expressions (5.24) and (3.3). The point is that the quantity γ_{oc}, which is a function both of the frequency detuning $\Delta\omega$ and the field V, enters into (5.24). For this reason, expressions (5.24) and (3.3) actually coincide only in the impact region $\Omega \ll \Omega_B$ and for weak fields (see subsection b in Sec. 4, region of applicability of the usual theory of broadening in Fig. 4). We recall that the well-known Karplus-Schwinger expression[25] is valid, in contrast to (3.3), only in the impact region $\Omega \ll \Omega_B$.

The expression for the total power Q is not the only interesting expression; the dependence of the quantities Q_{ir} and Q_{OC} on $\Delta\omega$ and V is also of interest, since they, just as Q, can be directly measured experimentally. The expressions being studied can be represented in the simple form

$$Q = Q_{sat} \frac{u}{u + R}, \qquad \frac{Q_{OC}}{Q} = 1 - R, \tag{5.26}$$

by introducing the dimensionless parameter

$$u = \frac{2V^2}{\Delta\omega}, \qquad R = \frac{\gamma_{ir}}{\gamma_{ir} + \gamma_{oc}}. \tag{5.27}$$

By definition, $R \leq 1$. Therefore, for $2V^2 \gg \Delta\omega^2$, saturation is observed independently of the characteristics of the medium with arbitrary ratio of the contributions of OC transitions and inelastic relaxation; the absorbed power reaches a maximum value $Q = Q_{sat}$ and ceases to depend on the characteristics of the field (we recall that $\Omega \gg \gamma_c + \gamma_{ir}$). When the contribution of optical collisions is large, $\gamma_{oc} \gg \gamma_{ir}$ ("elastic" broadening is large), $R \ll 1$ and saturation begins much earlier, for $2V^2 \gg R\Delta\omega^2$. The quantity R behaves as follows. For small $\Omega < \Omega_B$, under the usual gas kinetic conditions $R \ll 1$, since $\gamma_{oc} \sim \gamma_c \gg \gamma_{ir}$. As Ω increases, the quantity γ_{oc} decreases and, therefore, R increases. The dependences $R(\Delta\omega, V)$ and $Q(\Delta\omega, V)$ can be obtained comparatively simply in each specific case from the results presented in Sec. 4. Here, we shall study in greater de-

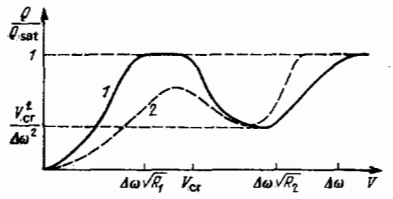

FIG. 6. The dependence of the absorbed light power Q on the field V in the static wing of the line. Curve 1 corresponds to the case $R(V=0)=R_1<V_{cr}^2/\Delta\omega^2$ and curve 2 to the case $R(V=0)=R_2>V_{cr}^2/\Delta\omega^2$.

tail the qualitative form of the dependence of Q on V for values of $\Delta\omega$ corresponding to the static wing (see Fig. 4).

As follows from Sec. 4, for $V<V_{cr}=d\mathscr{E}_B/\hbar$, the quantity γ_{OC} does not depend on V. Let $\gamma_{OC}\ll\gamma_{ir}$ for weak fields. Then, for $V\ll V_{cr}$, $\Delta\omega\sqrt{\gamma_{OC}/\gamma_{ir}}$, the quantity $Q\propto V^2$; for $V\sim\Delta\omega\sqrt{\gamma_{OC}/\gamma_{ir}}$, saturation appears. However, when $V>V_{cr}$, the quantity γ_{OC} drops with increasing V and for this reason saturation disappears. The absorbed power also begins to decrease; the decrease slows down for $\gamma_{OC}(V)\sim\gamma_{ir}$, when $Q\sim Q_{sat}2V_{cr}^2/\Delta\omega^2$. With further increase in V, $Q\propto V^2$ and saturates for $V\sim\Delta\omega$. The case $\gamma_{OC}\sim\gamma_{ir}$, i.e., when for weak fields $R\sim1$, is interesting. In this case, saturation appears only for $V\sim\Delta\omega$ (Fig. 6).

Let us summarize the theoretical analysis.

1. Doppler broadening was not discussed, but it is clear that it can be neglected for $\Omega\gg\gamma_D$, where γ_D is the Doppler width. Thus, the nonlinear theory of broadening, examined here, is limited by the condition

$$\Omega\equiv\sqrt{\Delta\omega^2+4V^2}\gg\gamma_c+\gamma_{ir}+\gamma_D. \tag{5.28}$$

2. An attempt to generalize the well-known result of Karplus-Schwinger[25] to the quasistatic region by averaging with respect to the fixed shifts would be unjustified. Averaging over fixed shifts (see, for example, Ref. 25, p. 369) gives results that differ strongly from (5.27), in the presence of strong fields $V\sim\gamma_C$ or $V\sim\Omega_B$. However, for weak fields, the results of the theory of inhomogeneous broadening (Ref. 25, p. 369) and (5.24) coincide. The point is that the criterion (5.31), used in the present work, is opposite to the assumption that is implicitly contained in the usual approach. Indeed, condition (5.31) indicates, in particular, that we are neglecting inelastic relaxation during OC. Meanwhile, averaging with respect to fixed shifts would correspond to the assumption that the atom has time to relax during the collision process, i.e., the condition inverse to (5.28) is satisfied. For weak fields, this condition, however, is not necessary because of a well-known fact: for the static region, averaging over the impact parameters of the colliding particles is equivalent to averaging over the shifts in the levels of the stationary atoms (compare Ref. 8, p. 266). However, this assertion is valid only for weak fields. If, on the other hand, the field affects the population kinetics or the OC transition itself, then the line shape is not determined by only a shift in the levels.

3. The approach presented above[3),11,12] is based on taking into account systematically the fact that light is absorbed during transitions precisely between the mixed states of the compound system $A+\mathscr{E}$. This complicates the dynamic part of the problem (calculation of the cross sections of OC transitions), but then makes the analysis of the kinetics, in principle, simple and clear. We recall that the most interesting region (where it is possible to observe a new type of nonlinear effect) is analyzed here in contrast to the usual approach[5-7] based on the elementary equations of population balance; there are no fundamental difficulties in making the transition to more complex models as well.

4. Within the scope of the ideas presented above, it is also possible, in principle, to construct a line-shape theory for the triplet components $m\to m'_+$, discussed at the end of subsection c) in Sec. 5. The significant complication of the analysis of the line shape of transitions $m\to m'_+$ in the compound "atom + EM field" system over the theory of broadening of atomic lines presented in Sec. 2 is related to the fact that the pairwise resonating levels 1, 2 and 1_+, 2_+ cannot, generally speaking, be assumed to be isolated during a broadening collision. In other words, the adiabatic approximation is not applicable.

5. Nonlinear effects are manifested most clearly in the static wing (see Figs. 4 and 6) for

$$\sqrt{\frac{vF_{\Delta\omega}}{2\pi}}\ll V\ll\Delta\omega. \tag{5.29}$$

The width of this region increases as $F_{\Delta\omega}$ decreases.

6. EXPERIMENTS

The opticocollisional nonlinear phenomena, described above, are interesting not only in themselves, but also as a new physical effect. In the future, specific practical applications of these phenomena may be discovered. This includes the possibility of studying the characteristics of colliding atoms and the establishment of pulse propagation in a medium with self-induced transparency. However, before discussing such a possibility in detail, it is necessary to discover and investigate these effects experimentally. For now, there are few reports on experiments relating to the problems examined above.[14-16,30-32] In what follows, we shall briefly present the results of two of the more interesting works.[14,16]

a) Investigation of near-resonance scattering of laser radiation

The effects relating to scattering of near-resonance laser radiation accompanying collisional line broadening were studied by Szöke *et al.*[14] They studied a mixture of strontium vapor and argon buffer gas. The dye laser was tuned to the resonant transition $5s^2\,{}^1S_0 \to 5s5p\,{}^1P_1$ ($\lambda_0=460.73$ nm) of the Sr atom (Fig. 7). The argon pressure was varied in the range $P_{Ar}\sim10$–500 Torr and the temperature of the strontium vapor was

[3)] This approach was later used for examining the absorption of light in a medium of identical atoms[28] and in the case of multiparticle broadening.[29]

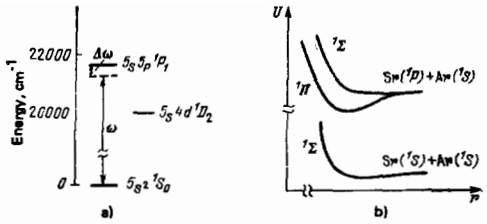

FIG. 7. Simplified energy level diagram of strontium (a) and qualitative form of the terms of the system Sr+Ar (b). The energy of the laser quantum $\hbar\omega$ is close to the energy $\hbar\omega_0$ of the transition $5s^2\,{}^1S_0$–$5s5p\,{}^1P_1$, $\hbar\omega_0 = 21698.482\ \text{cm}^{-1}$ ($\lambda_0 = 460.73$ nm).

about 530 °C, which corresponds to a vapor density $N_{Sr} \sim 10^{14}\ \text{cm}^{-3}$.

Observations were made of the radiation of the triplet components (5.23), whose intensity was studied as a function of frequency and the intensity of the laser, as well as a function of the argon pressure. Investigation of these dependences for weak fields ($I < 1\ \text{MW/cm}^2$) permitted comparing the measured data with the results of the theory of broadening.

As expected from (5.26), Rayleigh scattering varied as $\Delta\omega^{-2}$ (Fig. 8a), while resonance fluorescence, determined by OC transitions, was asymmetrical (Fig. 8b). At the same time, as predicted by theory, for the transition investigated (see Fig. 7b), the static wing lies in the long-wavelength region. The dependence of the broadening cross section $\bar{\sigma}_{br}(\Delta\omega) \equiv \gamma_{OC}(\Delta\omega)/v_T N_{Ar}$ on $\Delta\omega$ was found from the ratio of the resonance fluorescence to the Rayleigh scattering (Fig. 8). For the impact region, in particular, it was found that $\Omega_B \sim 5\ \text{cm}^{-1}$, $\sigma_B \approx 4.4\cdot 10^{-14}\ \text{cm}^2$. The results of the measurements agree qualitatively with theoretical analysis[33] for $C_6(\text{Sr}-\text{Ar}) = 9.8\cdot 10^{-31}\ \text{cm}^6\ \text{s}^{-1} \approx 1.5\cdot 10^3$ a.u. (see Fig. 8).

An analysis of the dependence of the intensities Q_R and Q_F of the triplet components (5.26) on the intensity of the laser field I gave the following results. The Rayleigh scattering Q_R, as expected, saturated for $4V^2 \sim \Delta\omega^2$. However, the dependence of the resonance fluorescence Q_F on I did not fall under the scope of the "usual" theory,[34] which does not take into account the nonlinear dynamic effects, i.e., the dependence of γ_{OC} on V. Then, Carlsten *et al.*,[14] continuing to use the "usual" theory, began to view the γ_{OC} as a free (i.e., adjustable) parameter. Agreement between the experimental and theoretical data was obtained in the parameter range $\Delta\lambda = \pm 0.17$ nm ($\Delta\omega \approx 6\ \text{cm}^{-1}$), $I \approx (0.1\text{–}1)\cdot 3.5\cdot 10^7\ \text{W/cm}^2$: for the "red" side, with $\bar{\sigma}_{br} = 3.2\cdot 10^{-14}\ \text{cm}^2$; for the "blue" side, with $\bar{\sigma}_{br} = 1.8\cdot 10^{-15}\ \text{cm}^2$. These values are, respectively, three and eight times smaller than those obtained in the same experiment[14] with weak fields. The dependence of the resonance fluorescence Q_F on the laser intensity I was also studied for large detunings ($\Delta\omega^2 > 4V^2$), when saturation did not play an important role and the I dependence of Q_R was nearly linear. Good agreement between theoretical and experimental data was obtained in this case only for values of $\bar{\sigma}_{br}$ much less than the values that were obtained in the weak-field limit.

These facts, as well as the fact that the nonlinearity was observed with fields of the order of the critical fields ($\mathscr{E}_0 \sim \mathscr{E}_B$, see subsection b), Sec. 4), provide a basis for assuming that the V dependence of γ_{OC}, related to dynamic effects, was discovered in the experiments carried out by Szöke's group. Carlsten *et al.*,[14] although they paid attention to the dependence of the elementary event on the field intensity predicted in Refs. 9–11, still did not assume that the nonlinear effects that they observed could be related to the nonstationary nature of the problem (for more detail, see Ref. 35). However, in a later analysis,[15] Szöke uniquely relates the observed effects to the influence of the field on the dynamics of the broadening collisions.

b) Observation of nonlinear effects in the line wing

Specific experiments designed to observe nonlinear effects for large frequency detunings $\Delta\omega \gg \Omega_B$ were conducted by A. M. Bonch-Bruevich's group.[16] The Tl+Ar system, whose level diagram is shown in Fig. 9, was investigated. The transition $X_{3/2} - B^2$ was investigated. The choice of this transition stems from the fact that in some frequency range (near $\lambda_0 = 530$ nm), these terms

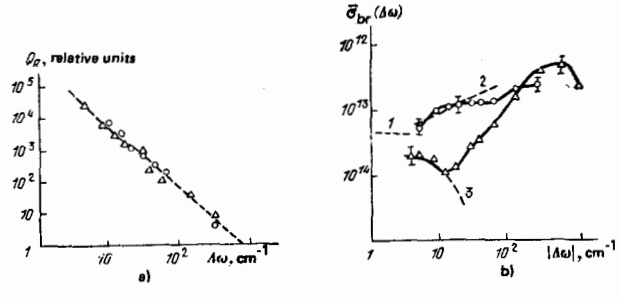

FIG. 8. The dependence on the frequency detuning $\Delta\omega$ of Rayleigh scattering Q_R (a) and resonance fluorescence normalized to it $\bar{\sigma}_{br} = \gamma_{OC}/v_T N_B$ (b). The triangles and circles indicate, respectively, the short-wavelength and long-wavelength parts of the spectrum. The dashed lines indicate the theoretical results: a) shows a $\Delta\omega^{-2}$ dependence and b) shows the theoretical results[33] (1 indicates the impact limit, 2 the static region, 3 the adiabatic region).

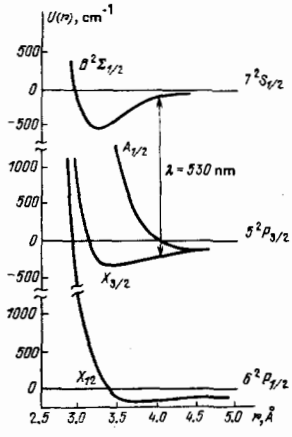

FIG. 9. Term diagram of the system Tl+Ar.

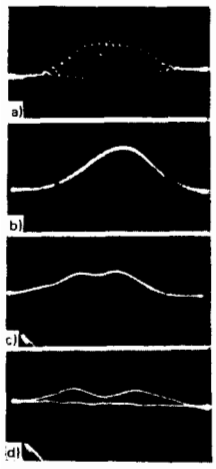

FIG. 10. Oscillograms of the laser pulse (a) and the luminescence pulses for different excitation intensities I (W/cm^2) $=3\cdot10^8$ (b), $2\cdot10^9$ (c), and $8\cdot10^9$ (d).

are practically parallel, while as the difference between the slopes of the terms $F\Delta\omega$ decreases, the region (5.23) with the strongest manifestation of nonlinear effects widens. Near the point of contact of the terms $r_{\Delta\omega}$, the critical field is estimated by the quantity[31,32]

$$V_{cr}=\left(\hbar v^2\frac{d^2\Delta U}{dr^2}\Big|_{r=r_{\Delta\omega}}\right)^{1/3}.$$

In the experiments of Ref. 16 it is the region near the contact of terms that was studied.[4)]

The second harmonic radiation of a neodymium laser, operating in the self-mode-locking regime, served as a source for exciting the Tl+Ar system investigated. The laser pulse consisted of 15 to 18 separate spikes (see Fig. 10a), whose duration was $\Delta t_{sp}=(1-1.5)\cdot10^{-11}$ s. Special attention was directed toward forming a sharp (both in time and space) distribution of the laser field, since various averagings mask the comparatively slow decrease [$\propto \mathscr{E}_0^{-1}\propto 1/\sqrt{I}$; see (4.16)].

The argon pressure $P_{Ar}\sim1$ atm was chosen so that the probability of a broadening collision within the time of passage of the laser pulse ($\Delta t_{las}\sim10^{-10}$ s) was of the order of unity ($\Delta t_{las}\gamma_C\sim1$). In order to have appreciable population of the initial atomic $6P_{3/2}$ level, the vapor cell was heated to a temperature of 830–880 °C and, at the same time, the concentration of atoms was $N_{6P_{3/2}}\approx10^{12}$ cm^{-3}.

The luminescence of thallium atoms in the transitions $7S_{1/2}-6P_{1/2}$ ($\lambda_{sp}=377$ nm) or $7S_{1/2}-6P_{3/2}$ ($\lambda_{sp}=535$ nm) was observed. The measurements of the dependence of the intensity of the integral (over the entire pulse) spontaneous emission in atomic lines on the laser radiation intensity are shown in Fig. 11. The enhanced transmission effect, as can be seen from Fig. 11, is observed for $I\gtrsim10^9$ W/cm^2 ($\mathscr{E}_0\gtrsim10^6$ W/cm).

[4)] Bonch-Bruevich *et al.*[16] refer to the opticocollisional nonlinearity that they observed as a "Landau-Zener" nonlinearity. Since here the levels touch but do not cross, this name, apparently, is not completely satisfactory.

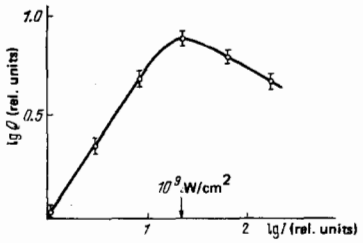

FIG. 11. The dependence of the fluorescence intensity of the thallium line ($7s_{1/2}$–$6p_{1/2}$ transition) on the excitation intensity.

The time-dependence of the luminescence of the atomic lines was also measured (Fig. 10, b–e). At times corresponding to maximum intensity with $I\gtrsim10^9$ W/cm^2, luminescence is observed to decrease. This result can also be viewed as an independent and direct proof of the observation of the phenomenon of enhanced transmission of a medium without it being saturated.

Thus, the effects of opticocollisional nonlinearity, predicted in Refs. 9–11, have been recently confirmed experimentally. Further development of the theory along the following lines is of interest. First, it would be interesting to examine the effect of a strong field on the line shape of the triplet components (5.23). Second, the possibility of the formation of powerful light pulses with steep fronts (high contrast) with the help of the Landau-Zenner type opticocollisional nonlinearity is interesting.

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APPENDIX

We shall calculate the matrix elements $E^{(\mathscr{E})}_{sm}\tilde{K}_{sm}$. The energy of the transition is given by the difference between the average energies of the field, corresponding to the initial and final states of the compound system $E^{(\mathscr{E})}_{sm}=E^{(\mathscr{E})}_c-E^{(\mathscr{E})}_m$. After averaging over arbitrary initial phases of the atoms, the average energy of the states is given by the expressions (compare subsection a, Sec. 5)

$$E^{(\mathscr{E})}_{1\pm}=b^2_1\langle\varphi_{1\pm}|H_{\mathscr{E}}|\varphi_{1\pm}\rangle+b^2_2\langle\varphi_{2\pm}|H_{\mathscr{E}}|\varphi_{2\pm}\rangle,$$
$$E^{(\mathscr{E})}_{2\pm}=b^2_2\langle\varphi_{1\pm}|H_{\mathscr{E}}|\varphi_{1\pm}\rangle+b^2_1\langle\varphi_{2\pm}|H_{\mathscr{E}}|\varphi_{2\pm}\rangle,$$

where $\hat{H}_{\mathscr{E}}$ is the free field operator (see subsection a, Sec. 2), φ_m, $\varphi_{m_\pm}$ are the characteristic functions of the Hamiltonian $\hat{H}_A+\hat{H}_{\mathscr{E}}$, corresponding to different states of atom A(m) and of the field $n_\omega\pm1$, $n_\omega-1\pm1$ [see (5.17)].

The matrix $\tilde{K}_{sm}$ can be obtained from the following considerations.[11] In order to find the transition rates between the given states of the compound system, it is simply necessary to multiply the transition rate between the corresponding states of the atom A by the probabilities, with which these states enter into the states of the compound system being examined. The probability of the presence of an unmixed state is given

by the square of the expansion coefficient: b_1 or b_2 [see (5.17)]. A more careful analysis is carried out in Refs. 12 and 18.

Calculations carried out according to the discussion above give

$$\hat{E}^{(\mathfrak{S})}=\hbar\omega\begin{bmatrix} 1 & 2b_1^2 \\ 2b_2^2 & 1 \\ & & 0 & \frac{\Delta\omega}{\Omega} \\ & & -\frac{\Delta\omega}{\Omega} & 0 \\ -2b_1^2 & & -1 & \\ -1 & & -2b_2^2 & \end{bmatrix}, \quad \hat{K}=\begin{bmatrix} b_1^2b_1^2K_{21} & b_1^2K_{21} & & \\ b_1^2K_{21} & b_2^2b_2^2K_{21} & & \\ -K_{OC} & K_{OC} & & \\ K_{OC} & -K_{OC} & & \\ & & b_2^2K_{12} & b_2^2b_2^2K_{12} \\ & & b_1^2b_2^2K_{12} & b_1^2K_{12} \end{bmatrix}.$$

Using (5.23), we have the following explicit expression for the balance equation (5.19):

$$\frac{d\tilde{N}_1}{dt}=(b_2^2K_{21}+b_1^2K_{12}+K_{OC})\tilde{N}_2-(b_1^2K_{21}+b_2^2K_{12}+K_{OC})\tilde{N}_1,\ \tilde{N}_1+\tilde{N}_2=N.$$

From here, in the stationary case, $d\tilde{N}_m/dt=0$, it follows that

$$\tilde{N}_1=\frac{b_2^2K_{21}+b_1^2K_{12}+K_{OC}}{(1/2)[1+(\Delta\omega^2/\Omega^2)](K_{21}+K_{12})+2K_{OC}},$$
$$\tilde{N}_2=\frac{b_1^2K_{21}+b_2^2K_{12}+K_{OC}}{(1/2)[1+(\Delta\omega^2/\Omega^2)](K_{12}+K_{21})+2K_{OC}}. \qquad (A.1)$$

We note that the transitions $m\to m_\pm$ in the kinetic matrix mutually cancel (only the transitions $m\to m'_\pm$, $m'\neq m$ occur). This is related to the indistinguishability of the states noted above.

Using (A.1), we obtain for the difference of populations the following:

$$\tilde{N}_1-\tilde{N}_2=\frac{(\Delta\omega/\Omega)(K_{21}-K_{12})N}{2K_{OC}+(1/2)[1+(\Delta\omega^2/\Omega^2)](K_{21}+K_{12})}=\frac{(\Delta\omega/\Omega)\Delta N}{(1/2)[1+(\Delta\omega^2/\Omega^2)]+(K_{OC}/\gamma_{1r})},$$

where, as before, $\Delta N=N(K_{21}-K_{12})/(K_{21}+K_{12})$ is the difference of the populations of atomic levels in the absence of the field, $\gamma_{1r}=(K_{21}+K_{12})/2$ is the rate of inleastic relaxation in a two-level system.

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