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## Nonresonant excitation of atomic fluorescence in alkali-metal vapor

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The mechanism of excitation of atomic fluorescence by radiation having a frequency  $\omega_1$  that differs considerably (by about  $2000\text{ cm}^{-1}$ ) from the atomic-transition frequency  $\omega_0$  is investigated. It is shown that the observed atomic emission is due to direct excitation of atomic electron transitions by nonresonant radiation in particle pair collisions. The process is interpreted in terms of an instantaneous change in the interaction potential of the atoms at the instant of absorption of a light quantum. A nonlinear dependence of the atomic-emission intensity on the exciting-radiation intensity is observed at high intensities of the nonresonant excitation. This dependence is ascribed to saturation effects of the electron-translational colliding atoms in the vicinity of the "intersection-turning" points.

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1. We report here the results of an experimental investigation of atomic fluorescence of alkali-metal vapors excited by laser radiation at a frequency  $\omega_1$  that is not at resonance with the frequency  $\omega_0$  of the atomic transition. The stimulus for this study was the interest in interactions between a radiation field and colliding atoms and of the influence of radiation on the dynamics of particle collision.

It is known that, in the two-level approximation, scattering of light by a system of non-interacting atoms is an elastic process, so that the emission is only at the frequency of the exciting radiation.<sup>[1]</sup> The interaction between the atoms causes the appearance of emission at the frequency  $\omega_0$  of the atomic transition at nonresonant excitation. Without going into details of the character of the collisions, the phenomenon of nonresonant excitation of atomic fluorescence can be described within the framework of the model of phase relaxation of an atomic system.<sup>[2]</sup> With such a description, the trajectories of the colliding atoms are assumed to be given and, as a rule, straight lines, while the action of the collisions reduces only to an instantaneous change of the phase of the state of the excited atom; it is important here that the characteristics of the collisions are assumed to be independent of the parameters of the irradiation field (its frequency and intensity). These approximations are violated at large detunings from resonance  $\omega_1 - \omega_0$ , when the difference between the energies of the incident and scattered photons is of the order of

or larger than the average kinetic energy of the colliding particles. In this case an appreciable change in the particle energy takes place in the active photons scattering by the atoms, and this leads to a noticeable change in the character of their motion. This influence of the radiation on the dynamics of the particle collisions can be interpreted as a result of an instantaneous change in the potential of the interaction between the atoms at the instant when they absorb a light quantum with energy  $\hbar\omega_1$ , a fact that can change not only the magnitude but also the sign of the force of interaction between the atoms. Since the duration of the atom-collision act ( $\sim 10^{-12}$  sec) is incomparably shorter than the lifetime of the optical excitation ( $\sim 10^{-8}$  sec), it follows that the quantum  $\hbar\omega_1$  absorbed at the instant of collision will be emitted in the overwhelming majority of cases by the free atom at the resonant frequency  $\omega_0$ .

Of course, in order for such an elastic process to take place, the electronic energy levels of the incident particles must be displaced at the instant of the collision strongly enough, so that the trajectories of the atoms can no longer be regarded as straight lines, and the process of excitation of the atomic fluorescence at such deviations from resonance should be described by the value of the radiation field quantum (the nonresonance).

Questions concerning the effect of a radiation field on the characteristics of broadening collisions has already



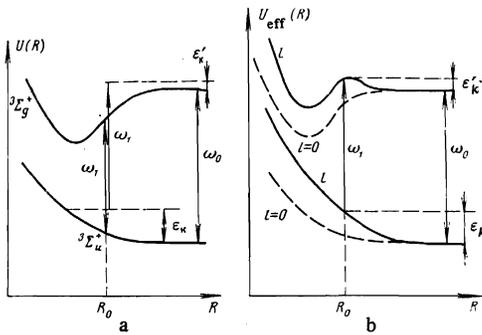


FIG. 5. Scheme of excitations of atomic fluorescence at  $\omega_1 < \omega_0$  for frontal (a) and non-frontal (b) collisions of atoms.

ear dependence). In the region of the transition from the linear dependence to the quadratic dependence (Fig. 4b), the efficiencies of the contributions from the  $Me-Me$  and  $Me-X$  collisions is approximately the same, although the ratio of the metal vapor and buffer concentrations is  $\sim 1:1000$ .

3. The process of nonresonant excitation of atomic lines in pure vapor will be explained here as being due to transitions from a lower repulsion state  ${}^3\Sigma_u$  into the continuum, corresponding to unbound relative motion of the atoms, of the upper  ${}^3\Sigma_g$  state or to  ${}^1\Sigma_g^+ - {}^1\Sigma_u^+$  transitions) for the case when  $\omega_1 < \omega_0$  (Fig. 5), and in the case  $\omega_1 > \omega_0$  to transitions either from the continuum of the lower  ${}^1\Sigma_g$  to the continuum of the upper  ${}^1\Sigma_u$  state, or to transitions  ${}^3\Sigma_u - {}^3\Pi_g$ . The dominant role of the indicated transitions among all others is due to the presence of exact resonances

$$U_1(R_0) + \hbar\omega_1 = U_2(R_0)$$

for these transitions at a certain distance  $R_0$  between the atoms. Here  $U_{1,2}(R)$  are the molecular potentials of the lower and upper excited states, respectively. The value of these resonances for the considered processes is the same as for the points of intersection of the terms in the theory of nonadiabatic Landau-Zener transitions.

The schemes indicated in Fig. 5 for these transitions in the case  $\omega_1 < \omega_0$  corresponded to transitions in frontal collisions of the atoms. The role of non-frontal collisions in these processes is best illustrated with the aid of the effective potential  $U_i^{I,II}(R)$  for the lower (I) and upper (II) states:

$$U_i^{I,II}(R) = U_{i,2}(R) + \hbar^2 l(l+1) / 2\mu R^2,$$

where  $\mu$  is the reduced mass and  $l$  is the orbital quantum number of the colliding atoms. Inasmuch as within the framework of the Born-Oppenheimer approximation there is practically no change in the orbital number  $l$  in the transitions in questions, the location of the resonance points  $R_0$ , determined by the equation

$$U_i^I(R_0) + \hbar\omega_1 = U_i^{II}(R_0),$$

does not depend on  $l$ . However, the values of the energies  $U_i^{I,II}(R_0)$  increase with increasing  $l$ , and starting

with a certain "intersection point"  $l_{min}$ , being located above the dissociation level of the excited state for the case  $\omega_1 < \omega_0$  and of the ground state for  $\omega_1 > \omega_0$ , will simultaneously be also the classical "turning point" for definite values of the kinetic energy  $\epsilon_k$  of the incident atoms

$$\epsilon_k = U_{i_{min}}^I(R_0)$$

for the ground state and

$$\epsilon_k' = U_{i_{min}}^{II}(R_0) - \hbar\omega_0$$

for the excited state.

It is well known<sup>[11]</sup> that the transition probability increases appreciably in the vicinity of such "intersection-turning" points. In the case when the transition probability in the vicinity of these points becomes of the order of unity, one should expect saturation of the atomic fluorescence to set in. This means that the dependence of the emission of the atomic lines should deviate from linear with increasing power density of the exciting radiation.<sup>4)</sup>

4. The effects of saturation of the atomic fluorescence were investigated by us experimentally by exciting Cs, Rb, and K vapors with a neodymium mode-locked laser. The laser pulse duration is measured by the two-photon luminescence procedure and amounted to  $6 \times 10^{-12}$  sec. The maximum radiation-power density was  $\sim 4 \times 10^{11}$  W/cm<sup>2</sup>. The dependence of the emission of the atomic lines on the intensity of the excitation is shown in Fig. 6 in a doubly logarithmic scale. The deviation from linearity manifests itself clearly at powers  $\sim 10^9 - 10^{10}$  W/cm<sup>2</sup> for all alkali metals, and is registered in a sufficiently wide range of variation of the power density. We note that the nonlinear dependence of the atomic-line emission intensity  $S$  on the excitation power density  $I$  is well approximated by the expression  $S \sim I^k$ , where  $k = 0.7 \pm 0.05$ .

We have estimated the power density at which the transition probability near the intersection-turning point is  $W \sim 1$ , by using formula (11)

$$W \approx d^2 E^2 \hbar^{-1/2} (2\mu)^{1/2} (F_e^I F_e^{II})^{-1/2} |F_e^I - F_e^{II}|^{-1/2} \sim 1,$$

where  $E$  is the amplitude of the emission field intensity,  $d$  is the dipole matrix elements of the transition, and  $F_e^{I,II}$  are the interaction forces at the intersection and turning points. Substituting  $d = 3 \cdot 10^{-18}$  cgs esu and  $F_e^I \sim F_e^{II} \sim |F_e^I - F_e^{II}| = D/R_0 = 8 \cdot 10^{-13}$  erg/ $4 \times 10^{-8}$  cm we obtain for the field intensity a value  $E = 10^6$  V/cm, corresponding to a radiation power density  $I \sim 10^9$  W/cm<sup>2</sup>. The latter is of the same order as the experimentally measured value (Fig. 6).

We emphasize that only a small fraction of the particles, having a large kinetic energy on the order of  $\hbar(\omega_1 - \omega_0)$ , can participate in the excitation of the emission of the atomic lines. This fact was verified experimentally by absolute calibration of the sensitivity of the employed installation with the aid of a resonant rubidium

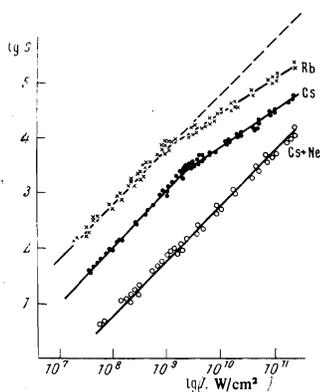


FIG. 6. Dependence of the emission of atomic lines of alkali metals on the excitation power.

lamp of known spectral density; this has made it possible for us to determine the ratio of the number of excited atoms to their total number. At a power density  $4 \times 10^{10}$  W/cm<sup>2</sup>, this ratio was  $10^{-4}$ – $10^{-5}$  for Rb vapor.

5. In addition to the already mentioned measurements, we have investigated the dependence of the intensity of the atomic fluorescence of alkali metals on the excitation power density in an atmosphere of inert gases (Xe, Ne, pressure  $\sim 0.5$  atm). For the Cs–Ne system, this dependence turned out to be linear up to the maximum powers used in the experiment (Fig. 6). This can be attributed to the fact that at the excitation powers realized in the experiment saturation of the transition is possible only in the presence of intersecting lines in the system of the electronic terms, whereas the Cs–Ne system of terms has apparently no intersection points at the investigated wavelengths. On the other hand, the linear character of the dependence of the emission of the Cs atoms in Ne allows us to reject the explanation wherein the observed nonlinearities in the pure alkali-metal vapors are due to multiphoton processes, particularly multiphoton ionization.<sup>5)</sup>

It should be noted that the behavior of the Rb and Rb–Ne systems differs somewhat from that of the remaining systems. This difference manifests itself in the much larger (by 4–5 times) intensity of the emission of the atomic Rb lines in comparison with the Cs vapor, although in the former case the deviation  $\omega_1 - \omega_0$  from resonance is twice as large as in the latter. It manifests itself also in the fact that the deviation from the linear dependence in Rb is observed at the lowest excitation densities. In addition, in the Rb+Ne system there is observed a nonlinear dependence of the emission of the atomic lines, similar to the corresponding dependence in pure vapor. It is possible that these differences in the behavior of the Rb systems are connected with the singularity of the absorption spectrum at the wavelength of the exciting radiation ( $\lambda = 1.06 \mu$ , Fig. 2).

We note in conclusion that a more detailed comparison of the results of the experiments with the model concepts is difficult at present because there is not even a complete stationary theory of non-adiabatic transitions, in which account is taken of the influence of the “intersection–turning” points. We recall that the experimental conditions were essentially nonstationary,<sup>6)</sup> so that we cannot state that the measured power density at

which the transition from the linear dependence to the nonlinear dependence takes place is the minimum value corresponding to the stationary excitation.

Despite the indicated complications in the detailed interpretation of the experimental results, we have enough grounds for stating that the observed nonlinear dependence of the emission of the atomic lines on the excitation power is due to effects of saturation of the electron-translational transitions of the colliding atoms in the vicinity of the “intersection–turning” points.

In addition, it can be regarded as established that there exist atomic–line wings on the short- and long-wave sides at very large ( $\sim 2000$  cm<sup>-1</sup>) distances from the line center. An investigation of such far wings by traditional methods (by using the absorption spectra) is quite difficult both because of the low sensitivity of these methods and, in the case of alkali metals, because of the superposition of the absorption spectra of the molecular and atomic states (Fig. 2). Measurements of the excitation spectra of the atomic lines with the aid of tunable lasers seems to us quite promising for these purposes. On the other hand, the use of lasers uncovers also new possibilities for the study of the influence of the radiation field on the dynamics of the collision of the atoms, namely, the change of the energy of the relative translational motion, the character of the interaction of the colliding particles, and particularly the formation of the molecular state in the radiation field.

<sup>1)</sup>This question is the subject of a paper by Gersten.<sup>[5]</sup> An experimental investigation of the dependence of the dipole matrix elements of the transitions on the internuclear distance by the method of nonresonant excitation of atomic fluorescence in Na vapor was carried out in<sup>[6]</sup>. A critical discussion of the results of that study is given in<sup>[7,8]</sup>.

<sup>2)</sup>A similar dependence of the molecular cross section was observed earlier<sup>[9]</sup> and was attributed to saturation of the transitions in the molecular band.

<sup>3)</sup>We note that these measurements were performed at a power density  $I > 10^9$  W/cm<sup>2</sup>, i. e., in a region where saturation of molecular transitions takes place near the frequency of exciting light. At lower excitation powers, the atomic fluorescence is determined mainly by the transfer of excitation from the molecules to the atoms.<sup>[10]</sup>

<sup>4)</sup>The nonlinear effect connected with saturation of the absorption in the far wing of the atomic line have already been discussed by Lisitsa and Yakovlenko.<sup>[4]</sup>

<sup>5)</sup>Multiphoton ionization of Rb and Cs vapors was observed by us at somewhat higher excitation power densities than indicated in Fig. 6, and was revealed by the appearance of a prolonged recombination emission of a number of atomic lines

<sup>6)</sup>The nonstationary character of the experiment may be due also to the presence of a subpicosecond structure in the laser pulse, which could not be resolved by the employed two-photon luminescence procedure.

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## Atomic collisions in a strong electromagnetic field

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It is shown that the long-range part of the interatomic interaction is significantly altered in a strong electromagnetic field. Instead of the Van der Waals law the asymptotic potential is described by a dipole-dipole  $R^{-3}$  law. The impact line broadening and line shift in a strong nonresonant field are calculated. The possibility of formation of bound states of two atoms in a strong light field is discussed.

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1. The effect of a strong electromagnetic field on the characteristics of inelastic atomic and molecular collisions has been investigated in a number of recent papers.<sup>[1-3]</sup> The main effect studied in these papers is that the energy of the strong field photon cancels the resonance defect of the colliding systems. As a result the inelastic transition probabilities are significantly enhanced.

In the present paper we wish to point out that a strong light field changes also the interaction of colliding atoms at large distances. This affects the characteristics of the elastic scattering and, consequently, the collision width and shift of spectral lines, which can be verified most simply by the following example. Let two different atoms in the  $s$ -state collide in a nonresonant, linearly polarized electromagnetic field  $\mathcal{E}$  of frequency  $\omega$ . Dipole moments  $\alpha_A(\omega)\mathcal{E}_0 \cos\omega t$  and  $\alpha_B(\omega)\mathcal{E}_0 \cos\omega t$  are then induced in the atoms, where  $\alpha_{A,B}$  are the atomic polarizabilities (it is assumed that the atoms are separated from each other by a distance  $R$ , much smaller than the wavelength of light). The long-range part of the atomic interaction, averaged over a period of the field, is obviously

$$U = \frac{\alpha_A \alpha_B \mathcal{E}_0^2}{2R^3} (1 - 3 \cos^2 \theta), \quad (1)$$

where  $\theta$  is the angle between the vectors  $\mathcal{E}_0$  and  $\mathbf{R}$ . Without a field the atomic interaction is caused by Van der Waals forces, i. e.,  $U_0 = c_6 R^{-6}$ . The interaction (1), thus, becomes dominant if  $R > (c_6 / \alpha_A \alpha_B \mathcal{E}_0^2)^{1/2}$ .

We assume that atom  $A$  is in the ground state, and atom  $B$  is excited. For an estimate one can take  $\alpha_A \sim 10$  a.u.,  $\alpha_B \sim 10^2$  a.u., and the constant  $c_6$  can be estimated by the Slater-Kirkwood equation<sup>[4]</sup>:  $c_6 \sim 10^2$  a.u.

In fields  $\mathcal{E}_0 \sim 10^{-2}$  a.u. the interaction (1) exceeds the Van der Waals one at  $R > 10$  a.u.

2. The modified interaction is quite important at significantly lower fields if the field frequency is close to the resonance frequency of one of the atoms (atom  $A$ , for example). We treat this problem in detail. Let the field be in resonance with the transition between the ground and first excited states of atom  $A$ . This atom can be then described by a density matrix for a two-level system, including spontaneous transitions into the ground state. The relation between the duration of atomic flight through the light beam  $T$  and the excited-state lifetime  $1/\gamma$  is an important factor in this case. In real situations the intensity distribution of the field over the cross section of the beam has a characteristic dimension, therefore the duration of field involvement is of the order of the time of flight through the beam. For thermal velocities in a beam of diameter  $\sim 0.1-1$  cm the condition  $\gamma T \gg 1$  can always be assumed to be satisfied. This implies that the two-level system is described only by the induced solution of the equations of motion for the density matrix. As is well-known, this solution is (see, for example,<sup>[5]</sup>)

$$\begin{aligned} \rho_{12} &= -\frac{V}{2} (\rho_{11} - \rho_{22}) \frac{\varepsilon - i\gamma_{12}}{\varepsilon^2 + \gamma_{12}^2} e^{-i\omega t}, \\ \rho_{11} - \rho_{22} &= \frac{\varepsilon^2 + \gamma_{12}^2}{\varepsilon^2 + \gamma_{12}^2 + \gamma_{12} V^2 / \gamma}, \quad \rho_{11} + \rho_{12} = 1. \end{aligned} \quad (2)$$

Here  $v = \mathcal{E}_0 d_A^0$ ,  $d_A^0$  is the transition dipole moment,  $\gamma_{12}$  is the luminescence line width of atom  $A$ , and  $\varepsilon$  is the field frequency, measured from the line center of the atomic transition  $\omega_0$ .

Generally speaking,  $\gamma$  and  $\gamma_{12}$  in Eq. (2) can differ appreciably from each other, since  $\gamma$  contains, besides