Absorption of radiation in collisions of alkali-metal atoms

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The cross section for photon absorption in collisions of alkali-metal atoms is calculated. This process is connected with a transition between electronic levels of the quasimolecule made up of the atoms. Its mechanism, which is due to the formation of quasibound states of the colliding atoms, is considered. An expression is obtained for the coefficient of absorption of gas or vapor as a result of this process as a function of the frequency of the absorbed photon. Actual calculations are carried out for the collisions of alkali-metal atoms that result in the formation of resonantly excited atoms and electron-excited molecules. The measurement of the absorption coefficient of gas, vapor, or plasma as a result of absorption of the radiation in the collisions of atoms can become a convenient method for the determination of the potential curves of the quasimolecules.

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We consider in this paper the absorption of photons in collisions between atoms. We calculated the absorption coefficients for alkali-metal atomic collisions of the type

$$A + B + \hbar\omega \;{\nearrow\, A + B^* \atop \searrow\, AB^*} \tag{1}$$

These calculations were motivated by experiments of A. M. Bonch-Bruevich *et al.*[1] on the absorption of resonant radiation in rubidium and cesium vapor.

The investigated process is a phototransition from one term of the quasimolecule produced when the atoms collide to another term. A general approach to the determination of the characteristics of processes of this kind was developed in the classical papers of Jablonski,[2] Kramers and ter Haar,[3] and Bates.[4] This approach was subsequently extended to include a large circle of problems in the theory of radiative transitions and collisions. A fairly complete investigation was made of the quenching of the metastable state of an atom in collisions with gas particles.[5–8] This process reduces essentially to the fact that the quasimolecule made up of the metastable atom and its collision partner has a small dipole moment of the transition between the metastable and ground states, which depends on the distance between the nuclei. A photon is therefore emitted in the collision process and this leads to the destruction of the metastable state. Photon emission and absorption take place in similar fashion on forbidden vibrational-rotational transitions of molecules.[9–11] The vibrational-rotational spectra of homonuclear diatomic molecules H_2, O_2, and others, induced by collisions with gas particles, have by now been investigated quite fully.

The dependence of the cross section of a process of the type (1) on the frequency of the absorbed or emitted photon was investigated theoretically[12–14] and experimentally.[12,15–19]. In these experiments we considered phototransitions far from the resonant lines of rubidium and cesium, which take place in inert gases with vapors of these metals as additives. These transitions occur at instants when the alkali-metal and inert-gas atoms collide, and their investigation has made it possible to determine the potential curves of quasimolecules made up of rubidium and cesium atoms and inert-gas atoms.

Gudzenko, Yakovlenko, and Lisitsa[20,21] investigated one of the channels of the process (1), corresponding to the change in the states of both atoms as a result of the collision at an absorbed-photon energy close to the energy difference between the isolated atoms. In this case, which should be regarded as a limit, the collision cross section is determined by the interaction of the atoms at large distances between them in comparison with their dimensions. For this reason it does not contain information on the potential curves of the colliding particles.

In this paper we consider from a unified point of view both channels of the process (1). In addition to the "direct" mechanism of the reaction,[12–14] account is taken also of another mechanism due to the formation of quasibound states in the system of colliding atoms. It is shown that this additional mechanism plays an important role when the absorbed-radiation power is not too high.

1. The expression for the cross section of the process (1) depends on the shape of the potential curves of the interacting atoms in both channels of the transition. The most characteristic are two physical situations. One corresponds to repulsion of the atoms in the lower state, and the other to attraction of the atoms (Fig. 1). We shall assume that the nuclei move in accordance with classical laws, while the electronic and nuclear degrees of freedom are separated. This enables us to obtain a simple resonance condition. Namely, the photon is absorbed only at a distance between nuclei such that its energy coincides with the difference between the electron energies of the quasimolecule in the transition states.

On the basis of this condition, we calculate the cross section for photon absorption in collisions between the atoms. By definition, the cross section of a collision with absorption of a photon in a unit frequency interval is equal to

$$\sigma(\omega) = \frac{g}{g_A g_P} \int_{\rho_{min}}^{\rho_{max}} 2\pi\rho \, d\rho \int_{-\infty}^{\infty} W(t) \, dt. \tag{2}$$
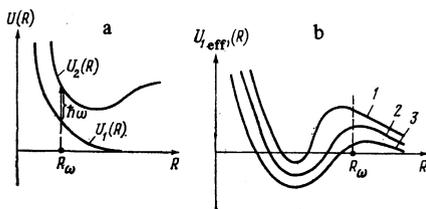
FIG. 1. Potential curves of electronic terms of quasimolecules. a) Illustration of the process (1) for a repulsive form of the potential curve of the lower electronic term; $U_1(R)$ and $U_2(R)$ are the potential curves of the lower and upper electronic terms, R is the distance between nuclei, $\hbar\omega$ is the energy of the absorbed photon, and R_ω is the internuclear distance corresponding to the resonance condition. b) Family of plots of the effective interaction potential of atoms in the lower state of the transition; the electronic term has a "well." Curve 1—$\rho(R_\omega)$ <ρ_{capt}, curve 2—$\rho(R_\omega)$=ρ_{capt}, curve 3—$\rho(R_\omega)$>ρ_{capt}, where $\rho(R_\omega)$ is the impact parameter of a collision in which the closest-approach distance of the atoms is equal to R_ω, and ρ_{capt} is the impact parameter of the capture.

Here g_1, g_B, and g_A are the statistical weights of the lower electronic terms and of the free atoms, i.e., $g_1/g_A g_B$ is the probability that the colliding atoms turn out to be on the considered branch of the lower potential curve, ρ is the impact parameter of the collision, and $W(t)$ is the probability of radiative transition per unit time with absorption of a photon in a unit frequency interval. The values ρ_{max} and ρ_{min} are determined by the shapes of the potential curves.

According to the laws of classical mechanics we have

$$dt = \frac{dR}{v[1-\rho^2/R^2-U_1(R)/\varepsilon]^{1/2}}, \tag{3}$$

where ε and v are the relative energy and velocity of the collisions, R is the internuclear distance, and $U_1(R)$ is the potential curve of the lower electronic term. The probability $W(R)$ will be represented as the product of the flux of photons of a given frequency j_ω by the absorption cross section, which is equal to[22,23]

$$\sigma_{abs} = \frac{\pi^2 c^2}{\omega^2 \tau} \frac{g_2}{g_1} a_\omega.$$

Here c is the speed of light, g_2 is the statistical weight of the upper electronic term, τ is the lifetime of the upper state relative to spontaneous emission with transition to the lower state, and the function a_ω characterizes the shape of the spectral line, i.e., $a_\omega d\omega$ is the probability that photons with frequencies in the interval from ω to $\omega+d\omega$ are produced in spontaneous de-excitation of the upper state. In our case, by virtue of the resonant character of the process, we have for the transition, at a distance R between the nuclei,

$$a_\omega = \delta(\omega-\omega(R)),$$

where $\hbar\omega(R)$ is the difference between the electronic energies of the states of the quasimolecule transition. We thus obtain for the probability of photon absorption per unit time at an internuclear distance R the expression

$$W(R) = \frac{\pi^2 c^2}{\omega^2 \tau(R)} \frac{g_2}{g_1} j_\omega \delta(\omega-\omega(R)). \tag{4}$$

The time of the spontaneous emission is determined by the relation[22,23]

$$\frac{1}{\tau} = \frac{4\omega^3}{3\hbar c^3} g_1 d^2(R), \tag{5}$$

where ω is the frequency of the emitted photon and $d(R)$ is the matrix element of the dipole-moment operator for the considered electronic transition. Taking into account the obtained expressions, we transform formula (2) into

$$\sigma(\omega) = \frac{g_1 g_2}{g_A g_B} \frac{16\pi^3 \omega}{3c\Delta F(R_\omega)} j_\omega \int_{\rho_{min}}^{\rho_{max}} \rho \, d\rho \frac{d^2(R_\omega)}{v[1-\rho^2/R_\omega^2-U_1(R_\omega)/\varepsilon]^{1/2}}. \tag{6}$$

The distance R_ω is introduced on the basis of the relation

$$\hbar\omega = U_2(R_\omega) - U_1(R_\omega). \tag{7}$$

so that at an internuclear distance R_ω resonance takes place for a photon with energy $\hbar\omega$ ($U_2(R)$ is the potential curve of the upper electronic term). The quantity

$$\Delta F(R_\omega) = \left| \frac{d}{dR}(U_2(R)-U_1(R)) \right|_{R=R_\omega} \right|$$

is the difference of the slopes of the potential curves of the upper and lower terms at the point R_ω. It appears in (6) as a result of integration of $\delta(\omega-\omega(R))$ with respect to dR.

If the interaction of the colliding atoms corresponds to repulsion (Fig. 1a), then the internuclear distance R_ω is reached at collision impact parameters

$$0 < \rho < R_\omega[1-U_1(R_\omega)/\varepsilon]^{1/2}. \tag{8}$$

Integrating in (6) and using the given values of ρ_{min} and ρ_{max}, we obtain for the cross section of atom collision with absorption of a photon in a unit frequency interval

$$\sigma(\omega) = \frac{g_1 g_2}{g_A g_B} \frac{16\pi^3 \omega d^2(R_\omega) R_\omega^2}{3cv\Delta F(R_\omega)} \left[1 - \frac{U_1(R_\omega)}{\varepsilon}\right]^{1/2}. \tag{9}$$

With the aid of this relation we determine the rate constants of the process

$$\alpha(\omega) = \frac{\langle v\sigma(\omega)\rangle}{j_\omega} = \frac{g_1 g_2}{g_A g_B} \frac{16\pi^3 \omega d^2(R_\omega) R_\omega^2}{3c\Delta F(R_\omega)} \exp\left\{-\frac{U_1(R_\omega)}{T}\right\}. \tag{10}$$

The angle brackets denote here averaging over the particle velocities. The particle velocity distribution function was assumed to be Maxwellian, and the limits of the integration with respect to energy were $U_1(R_\omega)$ and ∞. If relation (7) is satisfied for several values of R_ω, then it is necessary to sum in (10) over all these values.

The illustrated derivation of formulas (9) and (10) constitutes a modification of the Kramers–ter Haar–Bates approach.[3,4] Formula (10) can also be obtained[12-14] on the basis of the results of the Jablonski theory.[2]

The quantity $\alpha(\omega)$ is a characteristic of the elementary process and does not depend on either the gas density or the radiation intensity. Let us connect this quantity

with the macroscopic parameters that determine the absorption of the radiation. The rate of formation of the excited states of the quasimolecules, or the number of absorbed photons per unit volume and per unit time, is determined by the balance equation

$$\frac{dN_{A,B}}{dt} = -N_A N_B \int \alpha(\omega) j_\omega \, d\omega, \tag{11}$$

where N_A and N_B are the particle densities. The coefficient of absorption by the gas medium as a result of the considered process is

$$k_\omega = \alpha(\omega) N_A N_B. \tag{12}$$

If the absorbed radiation is monochromatic, then the right-hand side of (11) contains the quantity $-N_A N_B \alpha(\omega) j$, where j is the photon current, i.e., the number of photons passing per unit area in a unit time.

2. Consider the case when the lower electron term has a "well." The effective interaction potential of the colliding atoms, with allowance for the centrifugal energy, is equal to $U_{1\,\mathrm{eff}} = U_1(R) + \varepsilon \rho^2 / R^2$. It follows therefore that for certain collision impact parameters there exists a potential barrier that exceeds the collision energy. We consider next two limiting cases, depending on whether transitions of the particles under the barrier do or do not occur.

We turn to Fig. 1b, which shows a family of curves for the effective potential of the interaction at different impact parameters of the collision. It follows from this figure that the situation differs significantly, depending on whether the point R_ω, corresponding to the resonance condition, lies to the right or to the left of the potential barrier. In the former case, the radiative transitions take place in exactly the same manner as for the repulsion shape of the curve $U_1(R)$. In the second case, the barrier prevents the atoms from approaching each other to a distance $R \sim R_\omega$ if its height exceeds the collision energy. At this collision energy the atoms can reach the classical region of motion on the left of the barrier only by transitions below the barrier into quasibound states. We shall assume that the number of produced quasibound states is large, and neglect their decay in collisions with the gas particles. Two limiting cases are then realized.

In the first, the intensity of the electromagnetic field of the radiation is low and dynamic equilibrium, wherein atoms are situated on both sides of the barriers, can be established during the time of the radiative transition. Thus, the action of the barrier can be neglected and the integration over the impact parameter in formula (6) can be carried out between the limits indicated in formula (8). We arrive in this case again at expression (9) for the cross section of the collision with absorption of a photon. Averaging the constant of this process with a Maxwellian distribution in the relative-motion energies, we obtain

$$\alpha(\omega) = \frac{g_1 g_2}{g_A g_B} \frac{16\pi^3 \omega d^2(R_\omega) R_\omega^2}{3c\Delta F(R_\omega)} \frac{2}{\sqrt{\pi}} \int_0^\infty \left[x - \frac{U_1(R_\omega)}{T} \right]^{1/2} e^{-x} dx, \tag{13}$$
$$U_1(R_\omega) < 0,$$

where $x = \varepsilon / T$ and the integration over the energies, in contrast to the case of the repulsion curve $U_1(R)$, is between the limits 0 and ∞.

In the other limiting case, when the intensity of the electromagnetic field is high, the radiative transitions from the quasibound states to the upper electronic term occur rapidly in comparison with the decay of these states as a result of tunneling under the barrier. The formation of quasibound states in the atom-collision process can therefore be neglected. As follows from Fig. 1b, the condition that the R_ω point lie to the left of the barrier takes the form

$$\rho(R_\omega) > \rho_{\mathrm{capt}}(\varepsilon), \tag{14}$$

where $\rho_{\mathrm{capt}}(\varepsilon)$ is the capture impact parameter[1] and

$$\rho(R_\omega) = R_\omega [1 - U_1(R_\omega)/\varepsilon]^{1/2}$$

is the impact parameter of a collision in which the shortest-approach distance of the atoms is equal to R_ω. In this case the impact parameter in formula (6) is concentrated in the interval

$$0 < \rho < \rho_{\mathrm{capt}}(\varepsilon)$$

and the cross section of a collision with absorption of a photon turns out to be

$$\sigma(\omega) = \frac{g_1 g_2}{g_A g_B} \frac{16\pi^3 \omega d^2(R_\omega) R_\omega^2 j_\omega}{3cv\Delta F(R_\omega)}$$
$$\times \left(\left[1 - \frac{U_1(R_\omega)}{\varepsilon} \right]^{1/2} - \left[1 - \frac{\rho_{\mathrm{capt}}^2(\varepsilon)}{R_\omega^2} - \frac{U_1(R_\omega)}{\varepsilon} \right]^{1/2} \right). \tag{15}$$

If the inverse of relation (14) is satisfied, then integration over the impact parameter in (6) must be carried out between the limits 0 and $R_\omega[1 - U_1(R_\omega)/\varepsilon]^{1/2}$. This yields formula (9) for the collision cross section. The constant of the process (1) in the limit of high intensities of the electromagnetic field of the radiation, averaged with a Maxwellian collision-velocity distribution function, is

$$\alpha(\omega) = \frac{g_1 g_2}{g_A g_B} \frac{16\pi^3 \omega d^2(R_\omega) R_\omega^2}{3cv\Delta F(R_\omega)} \frac{2}{\sqrt{\pi}}$$
$$\times \left\{ \int_0^\infty \left[x - \frac{U_1(R_\omega)}{T} \right]^{1/2} e^{-x} dx - \int_0^{\varepsilon_0/T} \left[x - \frac{x\rho_{\mathrm{capt}}^2(x)}{R_\omega^2} - \frac{U_1(R_\omega)}{T} \right]^{1/2} e^{-x} dx \right\} \tag{16}$$
$$U_1(R_\omega) < 0.$$

where ε_0 is determined from the equation $R_\omega[1 - U_1(R_\omega)/\varepsilon]^{1/2} = \rho_{\mathrm{capt}}(\varepsilon)$ and is equal to the height of the potential barrier in the case when its "hump" is located at the point R_ω.

The condition that the time of the radiative transition from the quasibound states to the upper electronic terms be small in comparison with their lifetime relative to the tunneling below the barrier is conveniently represented in the form

$$\sigma_{\mathrm{ph}} \tau j \gg 1. \tag{17}$$

Here $j = cE^2/4\pi\hbar\omega$ is the current of the absorbed-radiation photons, σ_{ph} is the photoabsorption cross section, and τ is the lifetime of the quasibound states relative to

spontaneous decay via tunneling below the barrier. If this condition is satisfied, formula (16) is valid. If the electromagnetic field intensity is low and the inverse relation holds, then formula (13), which takes into account the formation of quasibound states of the colliding atoms, is valid.

The entire preceding analysis was based on the classical approach, which can be used if the difference between the potential-curve slopes at the resonance point $\Delta F(R_\omega)$ is large enough. A quantum-mechanical analysis by the method developed in[24] yields a criterion for the validity of the classical approach:

$$\left(\frac{T\hbar^2}{\mu}\right)^{1/6}\frac{[\Delta F'(R_\omega)]^{1/3}}{\Delta F(R_\omega)}\ll 1, \tag{18}$$

where

$$\Delta F'(R)=\left|\frac{d^2}{dR^2}(U_2(R)-U_1(R))\right|,$$

and μ is the reduced mass of the atoms. In the opposite limiting case, the rate constant of the process (1), averaged with a Maxwellian velocity distribution function of the colliding atoms, turns out to be

$$\alpha(\omega)=\frac{g_1 g_2}{g_A g_B}\frac{16(2\pi)^{1/2}}{3B(^2/_3;^2/_3)}\left(\frac{3\hbar}{\Delta F'(R_\omega)}\right)^{2/3}\left(\frac{\mu}{T}\right)^{1/6}$$

$$\times\frac{\pi^2\omega d^2(R_\omega)R_\omega^2}{\hbar c}\frac{1}{\Gamma(^1/_3)}\int_{\max(0,U_1(R_\omega)/T)}^{\infty}\left(x-\frac{U_1(R_\omega)}{T}\right)^{1/3}e^{-x}dx, \tag{19}$$

$$\sigma_{ph}\tau j\ll 1;$$

$$\alpha(\omega)=\frac{16(2\pi)^{1/2}}{3B(^2/_3;^2/_3)}\frac{g_1 g_2}{g_A g_B}\left(\frac{3\hbar}{\Delta F'(R_\omega)}\right)^{2/3}\left(\frac{\mu}{T}\right)^{1/6}\frac{\pi^2\omega d^2(R_\omega)R_\omega^2}{\hbar c} \tag{20}$$

$$\times\frac{1}{\Gamma(^1/_3)}\left\{\int_0^{\infty}\left(x-\frac{U_1(R_\omega)}{T}\right)^{1/3}e^{-x}dx-\int_0^{\varepsilon_0/T}\left(x-\frac{U_1(R_\omega)}{T}-\frac{x\rho_{capt}^2(x)}{R_\omega^2}\right)^{1/3}e^{-x}dx\right.$$

$$\sigma_{ph}\tau j\gg 1,\quad U_1(R_\omega)<0.$$

Formulas (16) and (20), which were obtained in the limit of high electromagnetic-field intensities and therefore do not take into account the formation of quasibound states of the colliding atoms, were derived earlier in[13,14] where the mechanism of the process (1) with participation of quasibound states was not considered at all. A quantum mechanical calculation makes it possible to generalize the results presented here to include the case when there are no resonance points R_ω. Then $\alpha(\omega)$ decreases exponentially as we advance into the "nonclassical" frequency region. The corresponding expressions for the constant of the "direct" mechanism of the process (1), which is described here by formula (19), were obtained in[13,14] and can be modified for formula (20). We shall not write them out here because of their complexity.

3. We proceed now to an analysis of the singularities of the process in question. The transition from formula (13) to (16) with increasing intensity of the absorbed radiation characterizes the nonlinear dependence of the absorption coefficient of the gas medium on the electromagnetic field intensity. However, by virtue of the strong dependence of the time of the below-barrier transitions on the particle energy and on the height of the

barrier, the transition from formula (13) to (16) proceeds smoothly enough with increasing field intensity. In particular, in the case of process (1) with participation of sodium stoms, this transition proceeds as the radiation flux varies in the interval from 10^4 to 10^9 W/cm^2, and in the case of potassium—in the interval from 10^4 to 10^8 W/cm^2. For this reason, the nonlinearity of the absorption coefficient as a function of the intensity of the absorbed radiation is relatively weak.

Let us discuss the appearance of nonlinear effects[2], which was considered in part in[1]. The electromagnetic field of the radiation effectively splits the energy levels by an amount[25] Ed, where d is the matrix element of the dipole-moment operator and E is the intensity of the electromagnetic field of the radiation. Our analysis is valid in the limit of low field intensities, when this splitting is small in comparison with the energy indeterminacy due to the process itself. Let us estimate the latter quantity. It is of the order of $\Delta F\Delta R$, where ΔR is the width of the transition region. Far from the turning point we have $\Delta R\sim\hbar v/Ed$ (v is the collision velocity and $\hbar/Ed$ is the characteristic time of the radiative transition). This yields the following estimate for the parameter region in which the results are valid:

$$Ed\ll(\hbar v\Delta F)^{1/2}. \tag{21}$$

If the radiative transition takes place near a turning point, where the atom velocity is close to zero, then the nonlinear processes begin at lower electromagnetic field intensities.[11] Near a turning point, the width of the transition region, as follows from the Schrödinger equation that describes the relative motion of the particles, is $\Delta R\sim(\hbar^2 F/\mu\Delta F^2)^{1/2}$,[25] where μ is the reduced mass of the particles. This leads to the following condition for the linearity of the process in accordance with this mechanism:

$$Ed\ll(\hbar^4 F_1 F_2\Delta F/\mu^2)^{1/4}. \tag{22}$$

$\alpha\cdot 10^{37}$,cm^5
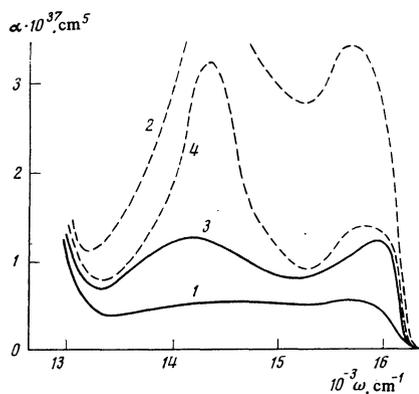
FIG. 2. Dependence of the rate constants of the reaction $K+K+\hbar\omega\to K+K$ (transition $X^1\Sigma_g^+\to B^1\Pi_u$) on the frequency of the absorbed photon: curves: 1—plot of $\alpha(\omega)$ without allowance for the below-barrier transitions at $T=300$ K, 2—plot of $\alpha(\omega)$ with allowance for below-barrier transitions at $T=300$ K, 3—plot of $\alpha(\omega)$ without allowance for the below-barrier transitions at $T=2000$ K, 4—plot of $\alpha(\omega)$ with allowance for the below-barrier transitions at $T=2000$ K.
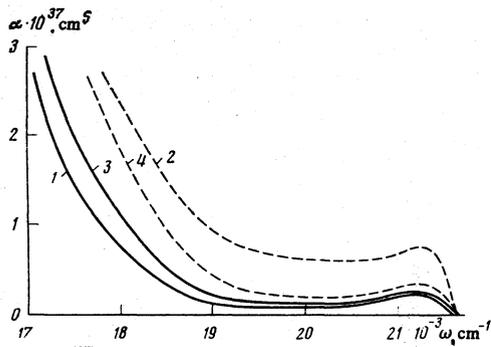
FIG. 3. The same as in Fig. 2, but for the reaction Na + Na + $\hbar\omega \to$ Na + Na (transition $X\,^1\Sigma_g^+ \to B\,^1\Pi_u$).

FIG. 5. The same as in Fig. 2, but for the reaction Na + Na + $\hbar\omega \to$ Na + Na (transition $X\,^1\Sigma_g^+ \to A\,^1\Sigma_u^+$).

In concrete cases of the process (1) with participation of sodium atoms (phototransitions $X^1\Sigma_g^+ \to B^1\Pi_u$ and $X^1\Sigma_g^+ \to A^1\Sigma_u^+$) these conditions yield respectively for the frequencies 17 500–21 000 and 12 000–18 500 cm^{-1}

$$j = cE^2/4\pi \sim 8\cdot 10^{10}-10^{10}\ \text{W/cm}^2, \quad j \sim 4\cdot 10^{10}-5\cdot 10^{9}\ \text{W/cm}^2.$$

In the case of the phototransition $X^1\Sigma_g^+ \to B^1\Pi_u$ in the frequency region 13 000–16 000 cm^{-1} and collisions of potassium atoms we have

$$j \sim 8\cdot 10^{9}-10^{9}\ \text{W/cm}^2.$$

Conditions similar to (21) and (22) can be easily obtained also at $\Delta F = 0$. The values of the radiation flux at which the nonlinearity sets in will be in this case half as large.

We call attention to one more singularity of the considered process, which takes place when the radiative transition proceeds from quasibound states of the lower term to discrete levels of the upper term (quasibound or bound). In this case the absorption coefficient, as a function of the frequency, should have a resonant structure. In the considered concrete cases, the conditions necessary for the appearance of resonances in the cross section were satisfied. However, owing to the large number of levels in the upper and lower states, the resonance picture turned out to be smeared out, and the absorption coefficient did not have an oscillatory structure.

ture. Nonetheless, under other conditions (in the presence of a narrow and deep well in the potential curves), a resonance structure can be observed in the absorption coefficient.

4. We present the results of actual calculations. Figures 2–7 show plots of $\alpha(\omega)$ for the reactions

a) $K(4S) + K(4S) + \hbar\omega \to K_2(B^1\Pi_u) \to K(4S) + K(4P),$

b) $Na(3S) + Na(3S) + \hbar\omega \to Na_2(B^1\Pi_u) \to Na(3S) + Na(3P),$

c) $Na(3S) + Na(3S) + \hbar\omega \to Na_2(A^1\Sigma_u^+) \to Na(3S) + Na(3P),$

d) $Na(3S) + Na(3S) + \hbar\omega \Big\langle \begin{array}{l} Na_2^*(A^1\Sigma_u^+) \\[6pt] Na_2(A^1\Sigma_u^+) \to Na(3S) + Na(3P) \end{array}$

e) $Rb(5S) + Rb(5S) + \hbar\omega \to Rb_2(B^1\Pi_u) \to Rb(5S) + Rb(5P),$

f) $Cs(6S + Cs(6S) + \hbar\omega \to Cs_2(B^1\Pi_u) \to Cs(6S) + Cs(6P),$

obtained with the aid of formulas (10), (13), (15), (19), and (20). The calculation results have shown that for the phototransitions $X^1\Sigma_g^+ \to B^1\Pi_u$ no electronically-excited molecules Na_2^*, K_2^*, Rb_2^* and Cs_2^* can be produced in the considered frequency region. The electronic-term potential curves used in the calculations were taken from[26-31]. The values of the dipole moments $d(R)$ were reconstructed on the basis of the experimental data on the radiative lifetimes of the excited electronic states of the molecules.[32,33]

The rate constant $\alpha(\omega)$ near the resonant frequency ω_0 was obtained under the assumption that the interac-

FIG. 4. The same as in Fig. 2, but for the reaction

Na + Na + $\hbar\omega \Big\langle \begin{array}{l} Na_2^* \\ Na + Na \end{array}$ (transition $X\,^1\Sigma_g^+ \to A\,^1\Sigma_u^+$).
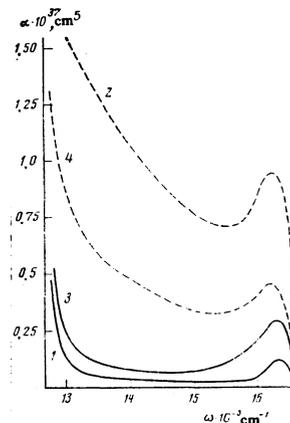
FIG. 6. The same as in Fig. 2, but for the reaction Rb + Rb + $\hbar\omega$ $\to$ Rb + Rb (transition $X\,^1\Sigma_g^+$ $\to B\,^1\Pi_u$).

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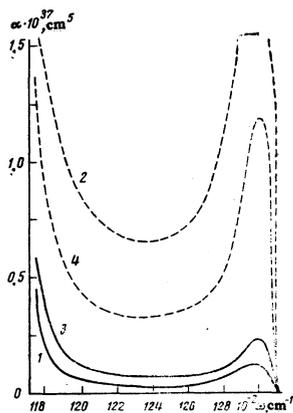
FIG. 7. The same as in Fig. 2, but for the reaction $Cs + Cs + \hbar\omega \rightarrow Cs + Cs$ (transition $X^1\Sigma_g^+ \rightarrow B^1\Pi_u$).

tion of the excited atom with the atom in the ground state is resonant ($U_2(R) \sim d^2/R^3$, d is the dipole moment of the transition of the atom) and greatly exceeds the interaction of the atoms in the ground state in the region of those internuclear transitions which make the main contribution to the result. For this case $\alpha(\omega)$ was determined from the relation

$$\alpha(\omega) = \frac{32}{9} \frac{\pi^3}{(\omega-\omega_0)^2} \frac{g_1}{g_A g_B} \frac{d^4\omega}{\hbar^2 c}. \qquad (23)$$

As seen from Fig. 2, the contribution of the below-barrier transitions to the room-temperature absorption coefficient of the gas is two–five times larger than the contribution due to elastic scattering. With increasing temperature, the formation of quasibound states plays an ever decreasing role. At $T = 2000\,K$ the values of $\alpha(\omega)$ for the investigated reactions, obtained with and without allowance for the below-barrier transitions, differ by at most 1.5–2 times.

The accuracy with which the rate constant of the process (1) can be calculated on the basis of the derived formulas depends on the accuracy with which the potential curves of the electronic terms are known. In our case, for reactions in which Na and K atoms participate, it amounts to 30–50%. On the other hand, the values of $\alpha(\omega)$ for Rb and Cs are correct only as to order of magnitude.

It follows from the results that at a photon current $j \approx 10^{23}$ cm^{-2}sec^{-1}, i.e., at a radiation power ~ 0.3 MW/cm^2, the rate of the considered reactions is $\alpha j \approx 10^{-13} - 10^{-14}$ cm^3/sec. This points to a significant role of the absorption of the radiation in collisions of atomic particles in a strong electromagnetic field. The investigated process is of interest, however, not only at high absorbed-radiation powers. In our opinion, the most interesting practical result of an experimental investigation of the reaction (1) is the determination of the potential curves of the colliding particles. This calculation shows that the absorption coefficient is very sensitive to the numerical characteristics of the potential curves. It follows therefore that the measurement of the absorption coefficient with a limited accuracy makes it possible to obtain sufficiently good information on the potential curves. One more singularity of this process is

connected with the fact that in the presence of several potential curves in the upper or lower channel of the transition we can separate parameters of one of them, confining ourselves to a frequency interval in which transitions with participation of only this state manifest themselves.

All this indicates that the accomplishments of modern laser technology provide us with a convenient tool for the reconstruction of the potential curves of electronic terms.

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[1] At collision impact parameters smaller than $\rho_{capt}(\varepsilon)$, the collision energy is larger than the height of the centrifugal barrier, and the closest approach distance of the atoms corresponds to the repulsion potential.

[2] The nonlinear effects are characterized by a dependence of the absorption on the electromagnetic field intensity.

[3] In the case of Rb and Cs, the value of $d(R)$ was obtained from the dipole moment of the resonant transition of the isolated atom. This is justified by the results obtained with Na and K, where this approach and calculation, using data on the radiative lifetimes of the electronically excited molecules lead to identical results.

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Dynamic and stochastic oscillations of soliton lattices

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The dynamics of lattices (one-dimensional sequences) of solitons is investigated. It is shown that in the stable case the soliton motion is described by the Toda lattice equation. Approximate periodic and conditionally periodic solutions are constructed, corresponding to envelope waves for the initial sequence of the solitons. In the case of an unstable lattice made up of oscillating solitons, stochastization of the motion in the system was experimentally observed. It is shown that the effect is due to a nontrivial interaction of the oscillating solitons.

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It was shown that in a preceding paper that the interaction of solitary nonlinear waves—solitons—having close energies (velocities) is approximately described by the equations for classical particles. The same paper, with two solitons as an example, dealt with the possible types of their interaction, which are determined to a considerable degree by the character of the field far from the maxima. In this paper we regard solitons as classical particles and investigate the dynamics of larger ensembles of solitons, particularly infinite sequences (one-dimensional lattices) of solitons with nearly equal parameters. This approach makes it possible to solve the problem of the stability of the stationary soliton lattices (periodic waves) and to obtain, in the stable case, a system of nonstationary solutions corresponding to modulation waves propagating along the lattice. We indicate in this connection that recently Its and Matveev, and also Dubrovin and Novikov, [2] have obtained for the Korteweg–de Vries (KdV) equation exact solutions that are periodic and conditionally periodic analogs of multisoliton solutions (see the paper of Dubrovin et al. [3] concerning similar solutions for the Toda lattice equation). In all probability the solutions obtained below belong to this class. At the same time, these approximate solutions are more universal in the sense that they are valid for equations which cannot be integrated exactly.

A most interesting problem is that of the evolution of the wave motion in this case of an unstable soliton lattice. The presented results of experiments with lattices made up of oscillating solitons show that instability can lead to complicated, including stochastic, motions in the system. We note that at the present time there are several known examples of nonlinear conservative systems in which stochastization evolved from regular initial conditions (see, e.g., [4,5]). The distinguishing feature of the process observed by us is that the stochastization takes place in a traveling wave. It is important also that in this case the wave motion takes the form of a random sequence of pulses that are close in their parameters to oscillating solitons, and thus constitute an example of a strong wave turbulence.

THEORY

In the description of modulated nonlinear waves it is customary to use some variant of an averaging method. [6,7] A shortcoming of this approach is that in the first-order approximation one obtains for the parameters (amplitudes, frequencies, wave numbers) of the initial waves a system of equations of the hydrodynamic type, which leads in the general case to the appearance of physically inadmissible discontinuities, and consequently to the need for taking into account higher-order