EXCITATION OF K^+, Rb^+, *AND* Cs^+ *IONS IN SLOW COLLISIONS WITH INERT GAS ATOMS*

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The excitation functions of the resonance lines of K^+, Rb^+, and Cs^+ ions, which are excited in collisions with inert gas atoms, are measured in the energy range from 12.0 keV to threshold. The excitation of certain resonance lines of the atoms of the gas target were also studied. Thresholds for excitation of the indicated resonance lines are determined for collisions of the following type: K^+ ions with He, Ne, Ar, Kr, and Xe; Rb^+ with He; Cs^+ with He and Ne. Analysis indicates that the thresholds observed in the experiment correspond to the ordinates of the points of intersection of the potential curves pertaining to the ground and excited states of the system of colliding particles. An estimate is made of the values of the abscissae of the points where these potential curves cross. In the simplest cases the shape of the excitation functions is satisfactorily described by the Landau-Zener theory in the two-term approximation. The discrepancies between such a dependence and that observed experimentally for a number of cases of the excitation of individual resonance lines are explained by the influence of other inelastic processes. For the case of three terms, the connection between the cross-sections for the various scattering channels is illustrated by the behavior of the excitation functions of the NeI resonance lines in the vicinity of the threshold for excitation of K II resonance levels in collisions of K^+ ions with Ne atoms.

1. INTRODUCTION

THE emission of the resonance lines of the positive ions K^+, Rb^+, and Cs^+, excited in slow collisions of these ions with the inert gas atoms He, Ne, Ar, Kr, and Xe, were investigated.

An investigation of the processes for excitation of the first resonance levels of atoms and ions is of interest for the theory of atomic collisions; these phenomena apparently can be described with the aid of a fairly simple scheme. As the nuclei of the colliding particles come together, the electron term corresponding to the initial state (when both particles are not excited) successively crosses the electron terms corresponding to the excited states. In this connection first transitions to the terms of the resonance excited states are accomplished, and only subsequently to the other, higher terms. When only two states are considered, the transition probability in the simplest case is described by the Landau-Zener theory.[1,2] When the terms become many, the problem is considerably more complicated, and its solution in general form can be accomplished only under certain assumptions about the type of interaction between the colliding particles.[3] Extraction of the results in such experiments, when the picture of the process is still not very complicated, is therefore of obvious interest for the theory. An investigation of the excitation of the resonance levels is one of such cases.

2. EXPERIMENTAL PROCEDURE

In[4] we described the apparatus for investigating the excitation of K II lines in collisions with He atoms. The present work was done on the same apparatus. Only individual units and the detection scheme were subjected to changes. Sources with surface ionization of the salts of alkali metals were used in order to obtain beams of K^+, Rb^+, and Cs^+ ions. The beam of ions was focused by a system of electrostatic lenses and, passing between the plates of a condenser, intended for modulation of the current, entered into the collision chamber. The current density of the ions was 10^{-7} to 2×10^{-5} A/cm^2. The gas pressure inside the collision chamber was measured by an ionization gauge and was maintained at a level of 10^{-4} to 3×10^{-3} mm Hg. The radiation arising in connection with the excitation of atoms and ions in the collision chamber was analyzed by a vacuum spectrometer with a concave diffraction grating. Light quanta having a definite wavelength were registered by a photoelectric detector located behind the exit slit of the spectrometer. The background (scattered light, field emission from the surface into the detector of quanta, photomultiplier noise) amounted to 5 to 7 pulses/sec at the output of the amplitude discriminator upon turning the ion current off. In order to detect signals whose magnitude is much (50 to 100 times) smaller than this background or comparable with it in magnitude, modulation of the ion beam was used in conjunction with the method of synchronous accumulation in individual counters of the number of pulses for 1) the effect and for 2) the effect mixed with noise. The total charge of the ions passing through the collision chamber was simultaneously measured by integration of the ion current. Automatic normalization of the number of pulses, which is proportional to the effect being studied, per unit charge of the ion beam passing through the collision chamber was realized. The application of such sensitive methods enabled one to detect weak light fluxes in the vacuum ultraviolet region of the spectrum and to study the behavior of atomic and ionic excitation functions near threshold.

3. RESULTS

The excitation functions of the resonance lines K II (λ = 600.7, 607.9, 612.6 Å), Rb II (λ = 697.0, 711.2, 741.4 Å), and Cs II (λ = 808.7, 901.3, 926.7 Å) for collisions of K^+, Rb^+, and Cs^+ ions with He, Ne, Ar, Kr, and Xe atoms were measured for ion energies T from 12.0 keV to threshold. Also the emission of certain resonance lines of the gas atoms was studied (He I, λ = 584.3 Å; Ne I, λ = 735.6, 743.7 Å; Ar I, λ = 1048.2 Å). The "experimental thresholds" observed by us are given in Table I, i.e., those values of the kinetic energy E_0 of the relative motion at which the intensities of the spectral lines under study decrease to values corresponding to ~1% of the noise. In all of the cases investigated the experimentally observed thresholds lie appreciably higher than the corresponding energies (E_{exc}) for the excitation of the spectral lines of an isolated atom or ion. This indicates that the emission of light is a result of excitation of the ion-atom system for internuclear distances corresponding to close approach of the interacting particles. From Table I it is seen that the order of the sequence of threshold energies for each given ion-atom pair is the same as for the excitation energies. An exception is the case of the lines K II, λ = 612.6 Å and Ar I, λ = 1048.2 Å, which are excited in collisions of K^+ ions with Ar atoms. The experimental thresholds for both lines are approximately the same (~140 eV), while the excitation energies of the lines differ by almost a factor of two.

A large part of the measured excitation functions is represented by smooth curves which rapidly increase from threshold to a maximum. The curve for the process of collision of Cs^+ ions with Ne atoms is shown in Fig. 1. This curve is typical of the measured excitation functions. Earlier[4] it was observed by us that the K II lines which are close together in wavelength with λ = 600.7, 607.9, 612.6 Å and which are excited in collisions of K^+ ions with He atoms, have the same dependence of the intensity on the kinetic energy of relative motion. The results of the experiment show that in all other cases studied by us, lines of the ions K^+, Rb^+, Cs^+ which are close together in wavelength or lines of the target atom which are close in wavelength have identical excitation functions for each individual ion-atom pair. As an example the excitation functions of the Rb II lines with λ = 697.0, 711.2, and 741.4 Å, excited in collisions of Rb^+ with He, are given in Fig. 2.

Table I

	K+			Rb+			Cs+		
	λ, Å	E_{exc}, e	E_0, V	λ, Å	E_{exc}, e	E_0, V	λ, Å	E_{exc}, e	E_0, V
He	KII 612,6	20,2	75	RbII 741,4	16,7	81	CsII 926,7	13,4	116
	KII 607,9	20,4	75	RbII 711,2	17,4	84	CsII 901,3	13,7	116
	KII 600,7	20,6	75	RbII 697,0	17,8	89	CsII 808,7	15,3	160
	HeI 584,3	21,2	93						
Ne	KII 600,7	20,6	~430				CsII 926,7	13,4	390
	NeI 743,7	16,7	<300				CsII 901,3	13,7	390
	NeI 735,6	16,8	<300				CsII 808,7	15,3	420
Ar	KII 612,6	20,2	~140						
	KII 607,9	20,4	~140						
	ArI 1048,2	11,8	≤140						
Kr	KII 600,7	20,6	<200						
Xe	KII 607,9	20,4	~430						

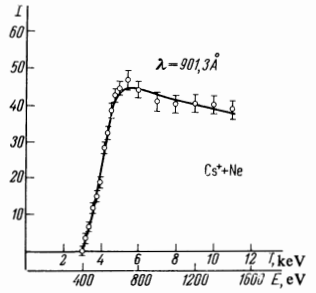

FIG. 1. The excitation function for the Cs II resonance line with λ = 901.3 Å, which is emitted in collisions of Cs^+ ions with Ne atoms. The quantity I is in relative units.

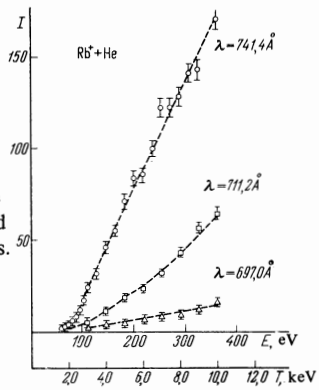

FIG. 2. Excitation functions of the Rb II resonance lines which are emitted in collisions of Rb^+ ions with He atoms.

On the increasing part of the excitation functions of certain lines K II, Rb II, Cs II, excited in collisions of K^+, Rb^+, and Cs^+ ions with He atoms, an abrupt increase in the rate of growth of the excitation function occurs in a narrow region close to the threshold observed in the experiment. An extensive analysis of the behavior of the excitation function for the Cs II line with λ = 926.7 Å in the region near threshold in this case is carried out by us in[5].

The excitation functions of the NeI resonance lines with λ = 735.6, 743.7 Å and of the K II line with λ = 600.7 Å, which are emitted as a result of collisions of K^+ ions with Ne atoms, are shown in Fig. 3. Two maxima are distinctly shown in the excitation functions for the Ne I lines. A comparison of the excitation functions of the lines K II and Ne I permits one to conjecture the presence of correlations between the excitation of resonance levels of the K^+ ion and of the Ne atom in this process. In Sec. 4 we carry out an analysis of this possibility.

An investigation of the spectra of the radiation which appears during collisions of K^+, Rb^+, and Cs^+ ions with inert gas atoms indicates that as the kinetic energy of the relative motion increases (and also with a lowering of the ionization potential of the target gas) the occurrence of an ever-increasing number of processes becomes possible: in the spectra this manifests itself in the appearance of intense lines of the ions of the gas target; thus, if only three K II and one He I line are recorded in the spectrum for the K^+—He pair (for K^+ ions with an energy T = 3.0 keV), then for the K^+ – Xe pair and for the same energy of the K^+ ions many Xe II lines and even some Xe III lines are observed in the spectrum.

It is of interest to note that the ratio of the intensities of the K II lines with λ = 600.7, 607.9, and 612.6 Å

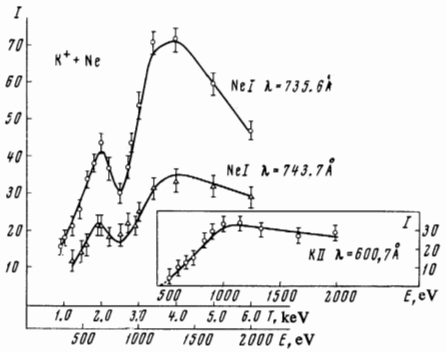

FIG. 3. Excitation functions of the Ne I and K II resonance lines which are emitted in collisions of K^+ ions with Ne atoms.

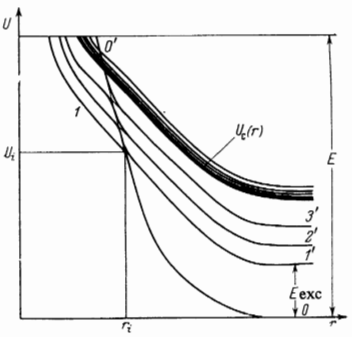

FIG. 4. Hypothetical dependence of the potential energy U of a system of colliding particles on the internuclear distance r. 00′ denotes the ground state term; 11′, 22′, ... are the excited state terms; E_{exc} is the excitation energy; E denotes the kinetic energy of the relative motion U_C (r) is the edge of the continuous spectrum; U_i and r_i denote the coordinates of the points of pseudointersection of the terms 00′, 11′ . . .

changes when these lines are excited in different gases; this ratio amounts, respectively, to 4 : 1 : 1 in He, 2 : 1 : 1.5 in Ne, 1.5 : 1 : 2.5 in Ar, 1 : 1 : 1 in Kr, and 1 : 1.5 : 1 in Xe. Measurements showed that the maximal value of the sum of the intensities of the K II lines with λ = 600.7, 607.9 and 612.6 Å depends on the type of gas target and amounts to, in relative units, 1 in He, 0.15 in Ne, 3.0 in Ar, 3.3 in Kr, and 3.2 in Xe.

4. DISCUSSION OF THE RESULTS

The picture which is realized in collisions of atoms and ions with each other is schematically represented in Fig. 4. As the internuclear distance r decreases, the curve 00′ corresponding to the ground state term for the system of colliding particles successively crosses the curves 11′, 22′, 33′, etc. corresponding to the excited state terms; then perhaps it crosses the edge of the continuous spectrum $U_C(r)$ and reaches a turning point determined by the equation

$$E = U_{00'}(r), \tag{1}$$

where E is the kinetic energy of the relative motion (in the one-dimensional case). At this point a "reflection" occurs, and the system returns along the term 0′0. Similarly, a "reflection" also occurs upon reaching the other turning points determined by the equation E = $U_{ii'}(r)$. At each pseudocrossing 00′—11′, 00′—22′, etc. there is a finite probability that the system either remains on the term 00′ with probability p_i (i = 1, 2, 3, . . .) or else crosses over to the term 1, 2, 3, . . . as r decreases or to . . . 3′, 2′, 1′, respectively, upon return after reflection, with a probability given by

$$q_i = 1 - p_i. \tag{2}$$

When the magnitude of the splitting associated with each pseudocrossing is small in comparison with the distance to the other levels, one can consider each such region separately and in order to determine the transition probabilities one can multiply the appropriate partial probabilities. In[3] it was shown that under well-known conditions the restrictions related to the magnitude of the splitting and to the distance between the levels may be removed; this permits one to extend the Landau-Zener theory to more complicated cases (transitions in the continuous spectrum, the interaction of a large or even infinite number of states, etc.). Such an approach enables one to obtain simple formulas for the transition probability to any state (1′, 2′, 3′, . . .) in those cases when the electronic term 00′ of the ground state interacts with a group of levels corresponding to excited states of the system. If, in the case considered by us, the magnitude of the splitting associated with each pseudocrossing is small in comparison with the distance to the other levels and the turning point is located between the n-th and (n + 1)-th crossing points in the discrete spectrum, then we obtain the following result for the transition probability to the first excited level 1′ of the system:

$$W_{01'} = 2p_1(1-p_1)(1-p_2(1-p_2(1-p_3(1-\ldots-p_n(1-p_n))\ldots), \tag{3}$$

where

$$p_i = \exp\left(-\frac{2\pi V_i^2}{\hbar v_i |\Delta F_i|}\right), \tag{4}$$

V_i is the matrix element connecting the two terms which interact at the i-th intersection, v_i is the relative (radial) velocity of transit of the system through the i-th intersection, and $|\Delta F_i|$ denotes the absolute value of the difference of the forces acting on the system upon crossing the i-th intersection.

If the turning point is located between the first and second intersections, then the probability for the transition 01′ is given by the well-known Landau-Zener formula:

$$W_{01'} = 2p_1(1-p_1). \tag{5}$$

In articles[4,5] we showed that the shape of the excitation functions for the K II lines with λ = 600.7, 607.9, 612.6 Å and for the Cs II line at λ = 926.7 Å, which are excited in collisions of K^+ and Cs^+ ions with He atoms, is satisfactorily described by the Landau-Zener theory over a wide range of energies. The analysis which was carried out[4,5] indicates that the thresholds E_0 observed in these cases (see Table I) have a clear physical meaning—in their value they are close to the ordinate of the point of intersection of the two potential curves 00′ and 11′ (Fig. 4), which correspond to the ground and first excited states of the system. A similar situation is observed in collisions of Rb^+ ions with He and Cs^+ with Ne. In these cases the resonance levels of the ions K^+, Rb^+, Cs^+ are simultaneously also the first excited levels of the system (K^+He, Rb^+He, Cs^+He, Cs^+Ne), where the next (at infinity) excitation levels are appreciably removed from them in energy. Therefore, it is natural that as the colliding atoms and ions approach each other, in these cases the first in-

tersection which leads to excitation of the resonance levels of the ions turns out to be isolated in a rather wide range of the energy E of relative motion. With an increase of the energy the next pseudocrossing points are reached, and the picture of the process is more complex, but the range of energies where the two-term approximation is valid apparently turns out to be rather broad. The identical nature of the behavior of the excitation functions for lines which are close in wavelength enables one to conjecture that these lines are excited during one and the same pseudocrossing but then, with an increase of the internuclear distance r, a distribution takes place over the excitation levels of the individual atoms and ions.

From formula (3) it follows that the energy dependence of the transition probability $W_{01'}$ will undergo changes upon the introduction into effect of each successive pseudocrossing, which must lead to singularities in the curve of cross-section vs. energy in the neighborhood of the threshold for each successive excitation process.

The excitation functions of the resonance lines Ne I and K II, which are radiated in collisions of K^+ ions with Ne atoms, are shown in Fig. 3. It is observed that in this case in the emission spectrum, measured for K^+ ions of energy T = 5.0 keV, only the resonance lines Ne I and K II are excited with any appreciable intensity. This permits one to describe the given process in the three-term approximation: one term (00′) corresponds to the ground state of the K^+ ion and the Ne atom, the next term (11′) is formed when the Ne atom is excited to one of the resonance levels, but the K^+ ion remains in its ground state; the third term (22′) is obtained from the Ne atom in the ground state and the K^+ atom excited to a resonance level. As long as the K^+—Ne system only goes through the region of the first pseudocrossing (00′ – 11′), the probability of excitation of a resonance level of Ne is described by the Landau-Zener formula (5); after reaching the threshold for excitation of the K^+ ion it is described by the formula

$$W_{01'} = 2p_1(1-p_1)(1-p_2(1-p_2)). \tag{6}$$

The cross-section for excitation of the resonance level 1′ is obtained by integration of the expression for the probability $W_{01'}$ over the impact parameter ρ from 0 to the maximum value $R_1 = r_1\sqrt{1-U_1}/E$ (where r_1, U_1 are the coordinates of the first crossing point) according to the formula

$$\begin{aligned}\sigma(E) &= 2\pi\int_0^{R_1} 2p_1(1-p_1)(1-p_2(1-p_2))\,\rho\,d\rho \\ &= \sigma_1(E)-\sigma_2(E)+\sigma_3(E),\end{aligned} \tag{7}$$

where

$$\sigma_1(E) = 2\pi\int_0^{R_1} 2p_1(1-p_1)\,\rho\,d\rho \tag{8}$$

is the cross-section for excitation of the level 1′ in the scheme involving two terms (00′, 11′);

$$\sigma_2(E) = 2\pi\int_0^{R_2} 2p_1p_2(1-p_2)\,\rho\,d\rho$$

is the cross-section for excitation of the level 2′ in the scheme involving three terms (00′, 11′, 22′);

$$\sigma_3(E) = 2\pi\int_0^{R_2} 2p_1^2p_2(1-p_2)\,\rho\,d\rho$$

taken with the opposite sign is the change of the elastic scattering cross section associated with the introduction into effect of a new inelastic channel, namely the excitation of the level 2′. Here

$$R_2 = r_2\sqrt{1-U_2/E} < R_1.$$

It is obvious that $\sigma(E) \equiv \sigma_1(E)$ in the interval (U_1, U_2) of energy E from the threshold U_1 of the first inelastic process to the threshold U_2 of the second. The behavior of the cross-section σ(E) over this interval in principle enables one to determine the probability p_1 as a function of the energy and ordinate of the first crossing point U_1; after this from the experimentally observed dependence $\sigma_2(E)$, one can determine $p_2(E, U_2)$ and predict the dependence of $\sigma_3(E)$, which characterizes the variation in the elastic scattering cross-section. The dependence of W_{01}, on the velocity of crossing of the first intersection,

$$v_1 = \sqrt{\frac{2}{\mu}\left(E-U_1-\left(\frac{\rho}{r_1}\right)^2 E\right)} \tag{9}$$

is shown in Fig. 5 in the approximation of central impact (ρ = 0) and under the assumption that the magnitude of the splitting $V_2 \approx (1/3)V_1$. A comparison of this graph with the excitation functions for the Ne I lines with λ = 735.6, 743.7 Å and for the K II line at λ = 600.7 Å permits one to conjecture that the three-term scheme apparently can satisfactorily approximate the actual situation in this case. For collisions of K^+ ions with Ne, Ar, Kr, or Xe atoms, the first excited terms of the system are produced then when the K^+ ion is in its ground state but the inert gas atom is excited to its resonance level. Since the excitation potential of the K^+ ion is higher than the ionization potential of the atoms Ar, Kr, and Xe, it is natural to assume that the region of pseudo-crossing, leading to an excitation of the K^+ ion, is located beyond the edge of the continuous spectrum, corresponding to ionization of an inert gas atom. With an increase of the kinetic energy of relative motion, ionization and excitation of the ions of the gas target occur. In these cases the actual situation is very complicated; only a measurement of the excitation functions of all the observed lines K II, Ar I, Ar II, . . . , Xe I, Xe II, Xe III, a measurement of the electrons' spectrum and of the energy dependence of the cross-sections for ionization, charge transfer, multiple ionization, etc. would enable one to schematize these problems.

A comparison of the "experimental thresholds" E_0 given in Table I with the excitation potentials for the spectral lines of an isolated atom or ion indicates that excitation of the ion-atom system occurs at internuclear distances corresponding to a close approach of the colliding particles. In this connection, if the pseudo-intersection of the terms corresponding to the ground and excited states occupies a comparatively narrow region of the potential energy, then a rather clearly expressed threshold, equal to the ordinate of the point of intersection, must be observed for the energy. In order to estimate the values of the abscissae of the intersection points which lead to the excitation

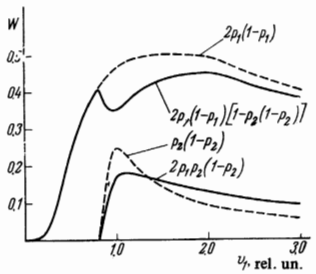

FIG. 5. Dependence of the transition probabilities $W_{01'}$ and $W_{02'}$ on the velocity for the case of three terms.

Table II

	He	Ne	Ar	Kr	Xe
r_0, cm	$6\cdot10^{-9}$	$5.5\cdot10^{-9}$	$10\cdot10^{-9}$	$>10\cdot10^{-9}$	$9\cdot10^{-9}$
r_0^2	1	0.8	~3.0	>3.0	2.3
I_m	1	0.15	3.0	3.3	3.2

of the lines indicated in Table I, we defined an interaction potential for the colliding particles according to the formula

$$U(r)=\frac{Z_1Z_2e^2}{r}\chi\left[(\sqrt{Z_1}+\sqrt{Z_2})^{2/3}\frac{r}{a}\right], \qquad (10)$$

which was proposed by Firsov[6] for the interaction potential of two atoms. Here Z_1 and Z_2 are the nuclear charges, r is the internuclear distance $\chi(x)$ is the Thomas-Fermi screening function,

$$a=\left(\frac{9\pi^2}{128}\right)^{1/3}\frac{\hbar^2}{me^2}=4.68\cdot10^{-9}\text{ cm}.$$

Then those values of the internuclear distances $r = r_0$ were found at which the value of the interaction potential U(r) is equal to the experimentally observed threshold for the excitation of a given line:

$$U(r_0)=E_0.$$

The results of the calculations thus made are shown in Table 2 for the systems which are formed in the collisions of K^+ ions with inert gas atoms.

The values of r_0^2 and the maximal values of the sum of the intensities of the three resonance lines, λ = 600.7, 607.9, and 612.6 Å, of the K^+ ion are given in this Table in relative units. A comparison of these quantities shows that the cross-section σ_{max} is determined not only by the value of the abscissa of the crossing point, leading to the excitation of a given level of the K^+ ion, but also fundamentally depends on the individual properties of the pairs of colliding particles: the relative location and number of the other intersections, which turned out to have an effect on the probability $W_{0n'}$ (and, consequently, on the cross-section) for the excitation of a given level n'.

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[1] L. D. Landau, Sow. Phys. 2, 46 (1932).
[2] C. Zener, Proc. Roy. Soc. (London) A137, 696 (1932).
[3] Yu. N. Demkov and V. I. Osherov, Zh. Eksp. Teor. Fiz. 53, 1589 (1967) [Sov. Phys.-JETP 26, 916 (1968)].
[4] V. B. Matveev, S. V. Bobashev, and V. M. Dukel'skiĭ, Zh. Eksp. Teor. Fiz. 55, 781 (1968) [Sov. Phys.-JETP 28, 404 (1969)].
[5] S. V. Bobashev, V. B. Matveev, and V. A. Ankudinov, ZhETF Pis. Red. 9, 344 (1969) [JETP Lett. 9, 201 (1969)].
[6] O. B. Firsov, Zh. Eksp. Teor. Fiz. 33, 696 (1957) [Sov. Phys.-JETP 6, 534 (1958)].

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