Excitation function for the spectral lines of Na, K, Rb, and Cs ions in the vacuum ultraviolet

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The excitation of resonance transitions in NaII, KII, RbII, and CsII in the 30–100 nm spectral range has been investigated for the first time between the threshold for the process and 500 eV, using intersecting electron and atomic beams. Analysis of the resulting data and their comparison with theoretical predictions for p ionization show that in the near-threshold region the p-ionization in rubidium and cesium is strongly masked mainly by the excitation of internal s-electrons in the $nsnp^6n'l'n''l''$ states which lead to the additional population of the resonance levels as a result of Auger decays. At the same time, the experimental excitation function for resonance transitions in NaII directly reproduces the p-ionization process.

INTRODUCTION

1. In previous experiments in our laboratory[1] it was established that the single-ionization cross sections of the alkali metals for slow electrons are complicated functions of energy. This is due to the additional contribution to the cross sections of the excitation (followed by self-ionization) of the closed outer shell of these atoms.

Direct experimental investigation of the contribution of inner electrons to the single-ionization process is a difficult task. Only theoretical results are available for the alkali metals.[2,3] On the other hand, when one of the electrons in the filled outer shell (for example, a p-electron) is removed from the atom, the result may be an excited ion, so that the given process, i.e., the contribution to single ionization, can then be investigated spectroscopically by detecting photons emitted during the spontaneous transition of the excited ion to its ground state. However, the radiation emitted in this way lies in the vacuum ultraviolet, and this introduces further difficulties into the design of the experiment.

The aim of this research was to carry out systematic studies of the excitation of resonance states in the ions of sodium, potassium, rubidium, and cesium, which appear during electron-atom collisions.

2. Special apparatus was developed to examine this question. One of the essential differences as compared with the apparatus described earlier[4] was that the atomic-beam technique was used to transport the atoms into the region where they collided with electrons.[1] At the time when the measurements were performed the chief parameters of the apparatus were as follows: density of atoms in the region of beam crossing $\sim 10^{11}$ cm^{-3}, current density in the electron beam not more than 0.01 A.cm^{-2}, and electron energy spread ~2 eV (full width at half height of the distribution curve). The residual gas pressure did not exceed 2×10^{-6} Torr.

Since the radiation emitted as a result of resonance transitions in the ions under investigation occupies a relatively broad spectral region (30—100 nm), a single spectroscopic instrument cannot really be employed. We therefore used two vacuum monochromators designed and built in our laboratory. One of them is a 70-degree monochromator and the other a grazing-incidence monochromator. The former is based on the Seya-Namioka system and incorporates a 0.5-m diffraction grating ruled on aluminum (1200 lines/mm) and coated with a protecting rhodium layer. Most of the radiation in the first order falls in the wavelength region between 42 and 110 nm for a mean reciprocal linear dispersion of ~1.7 nm/mm. The second monochromator is based on a system with a constant angular deviation of 140°. Grazing incidence enabled us to achieve sufficient efficiency between 30 and 50 nm for a mean reciprocal linear dispersion of ~0.9 nm/mm, using a platinum-coated grating (R = 1 m, 600 lines/mm).

The radiation from the excited ions was examined in the direction perpendicular to the plane containing the atomic and electron beams, and after passing through a monochromator was detected by an open secondary-electron multiplier (VÉU-OT-8M or VÉU-1A) capable of counting individual photoelectrons.

RESULTS AND DISCUSSION

1. We have investigated for the first time the spectra of alkali-metal ions in the wavelength region between 30 and 150 nm for different incident electron energies, and have examined the energy dependence of the efficiency of excitation of transitions from resonance states in ions between the threshold and 500 eV. The excitation of KII, RbII, and CsII was investigated, using the apparatus incorporating the 70-degree vacuum monochromator, whilst NaII (and also KII as a control) was investigated with the grazing-incidence monochromator.

The results on the electron excitation of resonance lines in all the above ions are summarized in Fig. 1, and the necessary information on the corresponding transitions is given in Table I. For each element the experimental points have a 90% confidence interval.

Figure 1 shows that the excitation functions for a given ion are similar, independently of the electron configuration to which the uppermost excited level belongs. At the same time, the character of these curves becomes increasingly complicated as one continues toward heavier atoms. Thus, for NaII there is a very slow increase in the excitation function with a broad maximum at about 200 eV, whereas the excitation functions for KII and, especially, for RbII and CsII vary more rapidly above the excitation threshold, reaching a clear maximum at energy as low as two threshold units. This difference in the behavior of the curves can probably be explained by the fact that the relative contribution of different processes to the population of the reso-

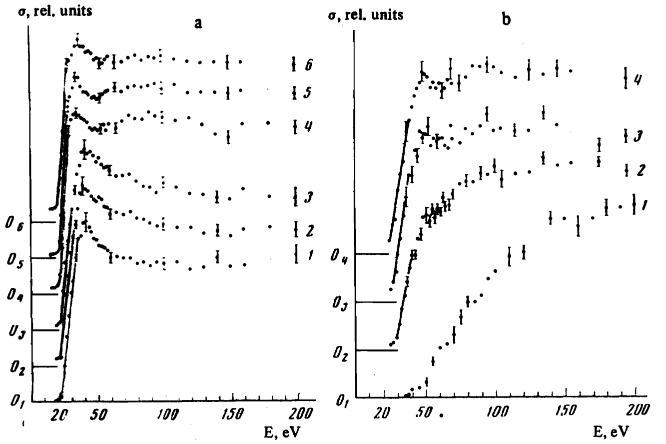

FIG. 1. Energy dependence of resonance-line excitation efficiency: a) RbII (1–λ = 69.7 nm, 2–λ = 74.2 nm, 3–λ = 71.2 nm) and CsII (4–λ = 90.1 nm, 5–λ = 81.4 nm, 6–λ = 92.7 nm); b) NaII (1–λ = 37.2 and λ = 37.6 nm), and KII (2–λ = 60.1 nm, 3–λ = 61.3 nm, 4–λ = 60.8 nm).

TABLE I

Element	Resonance transitions	λ, nm	E_{exc}, eV	E_{max}, eV	σ^{*}_{max}, πa_0^2
Na	$2p^6\,{}^1S_0$—$3s\,[{}^1/_2;\ 1{}^1/_2]_1^0$	37.6 37.2	38.1 38.5	200	0.2
K	$3p^6\,{}^1S_0$—$4s\,[1{}^1/_2]_1^0$	61.3	24.6	50	0.35
	$3p^6\,{}^1S_0$—$4s'\,[{}^1/_2]_1^0$	60.1	25.0	100	0.45
	$3p^6\,{}^1S_0$—$3d\,[{}^1/_2]_1^0$	60.8	24.7	50	—
Rb	$4p^6\,{}^1S_0$—$5s\,[1{}^1/_2]_1^0$	74.2	20.9	40	0.75
	$4p^6\,{}^1S_0$—$5s'\,[{}^1/_2]_1^0$	69,7	22.0	42	0.75
	$4p^6\,{}^1S_0$—$4d\,[1{}^1/_2]_1^0$	71,2	21.6	42	—
Cs	$5p^6\,{}^1S_0$—$6s\,[1{}^1/_2]_1^0$	92.7	17.3	38	1.1
	$5p^6\,{}^1S_0$—$6s'\,[{}^1/_2]_1^0$	81.4	19.1	36	1.1
	$5p^6\,{}^1S_0$—$5d\,[1{}^1/_2]_1^0$	90.1	17.7	36	—

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*The cross sections for these lines are estimated from the calculations in [2] on the assumption that the excitation intensities of all three terms of the $np^S(n + 1)s$ configuration are in the same ratios as their statistical weights. The normalization was carried out at electron energy of 500 eV.

nance levels is appreciably dependent not only on the energy of the bombarding electrons, but also on the atomic number.

2. To analyze the shape of the excitation functions for the resonance lines due to the above ions, let us consider the most important inelastic processes which participate in one way or another in the population of the resonance levels. These processes include the following (cf. level scheme in Fig. 2):

a) Ionization of the atom due to the removal of a p-electron from the outer filled shell (p-ionization):

$$Ans^2np^6(n+1)s+\vec{e}\rightarrow A^{+*}ns^2np^5(n+1)s+2e\rightarrow A^{+}ns^2np^6+2e+h\nu_{\rm res};$$

where A is the normal atom, A^+ and A^{+*} are, respectively, the normal and excited ions, $\vec{e}$ is the bombarding electron prior to collision, n is the principal quantum number of the outer filled shell of the atom, and $\hbar\nu_{res}$ is the energy of the photon emitted as a result of the transition of the ion from one of the two resonance levels to the ground state which is directly observed in our experiment.

b) Radiative decays of states due to ionization with the simultaneous excitation of another electron (i.e., two-electron excitation):

$$Ans^2np^6(n+1)s+\vec{e}\rightarrow A^{+*}ns^2np^5n'l'+2e\rightarrow A^{+*}ns^2np^5(n+1)s+2e+h\nu\rightarrow$$
$$\rightarrow A^{+}ns^2np^6+2e+h\nu_{\rm res},$$

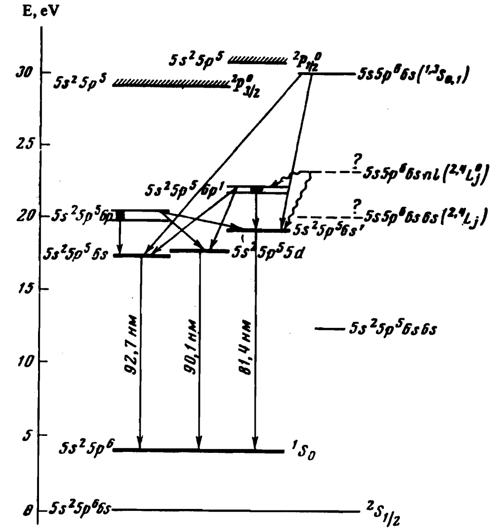

FIG. 2. Energy level scheme for CsI and CsII.

where $\hbar\nu$ is the photon emitted as a result of the transition of the ion from the upper excited states to the resonance states (these transitions can also be cascade transitions).

c) Radiationless decay of discrete self-ionization states of the atom due to the excitation of an s-electron from the filled outer shell:

$$Ans^2np^6(n+1)s+\vec{e}\rightarrow A^{*}nsnp^6(n+1)sn'l'+e\rightarrow A^{+*}ns^2np^5n'l'+e+\tilde{e}\rightarrow$$
$$\rightarrow A^{+*}ns^2np^5(n+1)s+e+\tilde{e}+h\nu\rightarrow A^{+}ns^2np^6+e+\tilde{e}+h\nu_{\rm res},$$

where $\tilde{e}$ is an Auger electron.

d) Radiative cascade due to the removal of an s-electron from the filled outer shell (s-ionization):

$$Ans^2np^6(n+1)s+e\rightarrow A^{+*}nsnp^6(n+1)s+2e\rightarrow$$
$$\rightarrow A^{+*}ns^2np^5(n+1)s+2e+h\nu_{\rm ux}\rightarrow A^{+}ns^2np^6+2e+h\nu_{\rm res},$$

where $h\nu_{ux}$ is the ultrasoft x-ray emission due to the rearrangement of the outer filled shell.

3. To elucidate the relative importance of each of the above processes, let us consider Fig. 3 which shows the excitation function for the resonance transitions in the elements which we have investigated. The vertical lines in this figure show (a) thresholds for the p-ionization process, (b) minimum level energies from which radiative cascades are possible, (c) thresholds for the formation of doubly ionized particles and (d) thresholds for s-ionization. The numerical values for these threshold energies are given in Table II.

It is clear from Fig. 3 and Table II that the s-ionization threshold for sodium lies much higher than the energy for the formation of the double ion. Its discrete self-ionization levels (due to the excitation of $2s2p^63snl$ states tending to the $2s2p^63s$ limit) will therefore lie above the threshold for double ionization. Hence it is clear that the decay of these states in sodium can proceed effectively to the ground state of the double ion. At the same time, for heavy elements, and particularly for cesium, the corresponding thresholds are close, and the analogous self-ionization states lie mainly below the double ionization thresholds. Hence they can decay to different discrete states of the single ion, leading to an increase in the populations of both the resonance and higher-lying levels [cf. process (c) and the level scheme in Fig. 2].

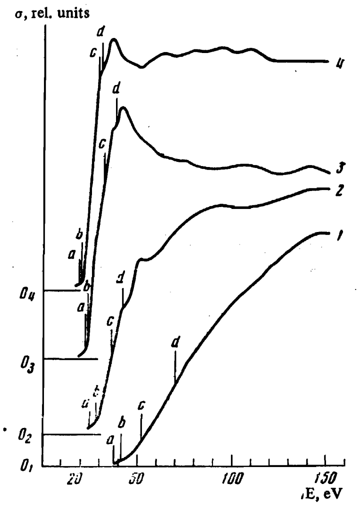

FIG. 3. Excitation functions for the resonance transitions $np^6\ {}^1S_0 - np^5(n+1)s'[1/2]_1^0$ in: 1—NaII (n = 2), 2—KII (n = 3), 3—RbII (n = 4), 4—CsII (n = 5).

TABLE II

Element	p-ionization threshold, eV [8]	Minimum energy for the excitation of radiative cascades, eV [8]	Double-ionization threshold, eV [8]	s-ionization threshold, eV		
				[2]	[9]	[10]
Na	38.1 38.5	41.5	52,4 52.6	70	—	66
K	24.7 25.0	27.6	36.1 36.4	41	52	37
Rb	20.9 22.0	23.3	31.7 32.7	38	45	32
Cs	17.3 19.1	19.8	29.0 30.7	30	36	25

It was shown in[5,6] that the excitation of the self-ionization $5s^25p^5n'l'n''l''$ states in the cesium atom has a well defined energy dependence at the threshold. In all probability, a similar energy dependence occurs also for the excitation of the $5s5p^6n'l'n''l''$ states in cesium. This may explain the rapid rise of the function for CsII (and also KII and RbII) near the threshold. Thus, only the excitation function for NaII reproduces the p-ionization process. For heavier elements, this process is strongly masked by the contribution due to the excitation of inner s-electrons in an interval of two threshold units. The structure (though not well defined) of the excitation functions for these elements at higher energies can be explained in a similar way by the excitation of still deeper lying electrons.

4. As regards process (d), it follows from the theoretical calculations reported in[2] for the alkali metals, and also from the recent experimental work[4] on the excitation of inert gases by electron impact, that the efficiency of the s-ionization process for such objects is relatively low. However, our own studies of the emission spectra show that the transitions

$$ns^2np^5(n+1)s(^1,\ ^3P_j^0) - nsnp^6(n+1)s(^1,\ ^3S_j)$$

have low probabilities in alkali metals. It is probable that the decay of these highly excited states proceeds effectively to the ground state of the double ion. Hence the s-ionization process cannot have an important influence on the excitation functions for the above transitions.

5. We now consider process (b) and estimate the importance of cascade transitions in the population of resonance levels. The excitation cross sections for the strongest potassium and cesium ion lines in the visible were investigated in[7]. We have used these data to analyze the contribution of cascade transitions to the populations of levels belonging to the $np^5(n+1)s$ and np^5nd configurations, which has in fact been found to be substantial. It may therefore be supposed that the similarity between the energy dependence of the excitation of states belonging to the np^5nd and $np^5(n+1)s$ configurations in KII, RbII, and CsII is largely due to the cascade transitions.

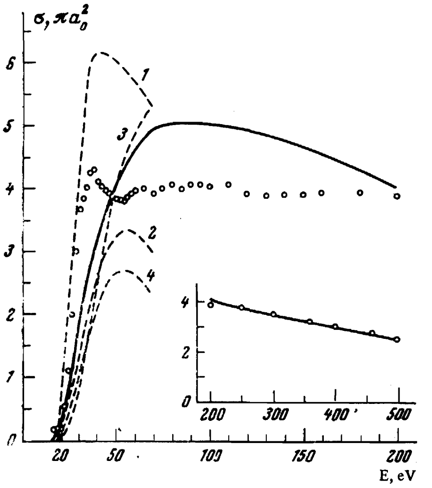

FIG. 4. Comparison of calculations on the 5p-ionization of cesium with experimental data. Solid curve—calculation in [2], open circles-experimental excitation function for the $5p^6\ {}^1S_0 - 5p^56s\ [1/2;\ 1\tfrac{1}{2}]_1^0$ transitions in CsII normalized to the results in [2], broken curve—calculations from [3]: 1—Born approximation, 2—distorted wave approximation, 3—spherical wave method, 4—variant 3 with allowance for the distortion of the incident wave.

6. We must now compare our results on the energy dependence of the excitation of the resonance $5p^6\ {}^1S_0 - 5p^56s\,[\tfrac{1}{2};\ 1\tfrac{1}{2}]_1^0$ transitions in cesium with the theoretical calculations reported by Omidvar[2] and by Liepin'sh and Rabik[3] (see Fig. 4). The experimental curve is normalized to Omidvar's result at 500 eV.[1)] It is clear from the figure that the theoretical cross section for 5p-ionization and its energy dependence are very dependent on the choice of the wave functions and the method of calculation. It is therefore very difficult to decide which particular method of calculation is to be preferred. However, the more rapid variation observed experimentally immediately after the excitation threshold, and the presence of a well-defined experimental maximum seems to us to show once again that the excitation of the s-electron has an important effect on the p-ionization of the heavy alkali metals.

We note in conclusion that the spectroscopic method of investigating the excitation of atoms by electron impact, in which the emission in the vacuum ultraviolet is recorded, yields valuable information on the ionization of closed electron shells and the mechanism of rearrangement in these shells.

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[1)] The last column in Table I gives the cross sections at the maximum of the excitation functions for the resonance transitions obtained by normalization to the theoretical results. [2]

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