POPULATION OF THE QUARTET AUTOIONIZATION LEVELS OF CESIUM AND RUBIDIUM ATOMS IN CHARGE EXCHANGE REACTIONS

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From the analysis of the time decay of VUV lines intensities at 82.4 *and* 109.1 nm *corresponding to radiation transitions from* Rb ($4p^5 5s5p\ ^4S_{3/2}$) *and* Cs ($5p^5 6s5d\ ^4P_{5/2}$) *quasimetastable autoionization levels the rates of the charge transfer reactions of the metastable rubidium and cesium ions on their atoms were measured in mixtures of* He-Rb *and* He-Cs. *They were found to be equal to* $\alpha(\mathrm{Rb}) = 3.76\ (\pm 0.6)\cdot 10^{-11}\ \mathrm{cm}^3/\mathrm{s}$ *and* $\alpha(\mathrm{Cs}) = 9.94\ (\pm 1.5)\cdot 10^{-11}\ \mathrm{cm}^3/\mathrm{s}$, *respectively.*

Experimental investigations of the time behavior of the discharge plasma afterglow in helium-cesium and helium-rubidium mixtures in the VUV spectral region aimed at studying quartet quasimetastable autoionization states of alkali metal atoms is of great importance in the context of the possibility to use these metals for creating VUV lasers (see Ref. 1). The idea is in the fact that charge transfer from a metastable alkali metal ion (A^{+*}) to its neutral atom (A) results in a selective population of the autoionization states of these atoms:

$$A^{+*} + A = A^{**} + A^{+}, \qquad (1)$$

here A^{**} are the quartet quasi-metastable states of the alkali metal atom which has the same parity as the ground state or has excessively high moment of momentum. Thus, the selection rules either on J or parity forbid electrical dipole transitions to the ground state. In this connection decay of the quasi-metastable states occurs to the exited atomic states that makes it possible to use them for creating VUV-lasers in plasma conditions. The reaction of type (1) involving metastable lithium (Li^{+*}) or sodium (Na^{+*}) ions has been studied in Refs. 1–3. The reactions considered, their energy defects, wavelengths of the main radiation transitions and charge transfer cross-sections are listed in Table I.

TABLE I. Formation of the quartet metastable states in the charge transfer reaction (1).

Metastable ion	Donor	Quartet metastable level	Energy defect (cm^{-1})	λ, nm	Cross-section (10^{-15} cm^2)
$Li^{+*}(1s\ 2s)^3\ S_0$	Li $(1s^2\ 2p)^2\ P_{1/2}$	$Li^{**}(1s\ 2p^2)^4\ P_{5/2}$	13930	21.6	1.0 (Ref. 2), 1.2 (Ref. 3)
$Li^{+*}(1s\ 2s)^1\ S_0$	Li $(1s^2\ 2p)^2\ P_{1/2}$	$Li^{**}(1s\ 2s\ 2p)^4\ P_{5/2}$	12985	22.9	–
$Na^{+*}3s\ 3/2\ [3/2]_0$	Na $(2p^6\ 3s)^2\ S_{1/2}$	$Na^{**}(2p^5\ 3p\ 3s)^4\ D_{1/2}$	564	39.8	–
$Na^{+*}3s\ 3/2\ [3/2]_2$	Na $(2p^6\ 3s)^2\ S_{1/2}$	$Na^{**}(2p^5\ 3p\ 3s)^4\ S_{1/2}$	1139	40.5	3.2 (Ref. 2)
$K^{+*}4s\ 3/2\ [3/2]_2$	K $(3p^6\ 4s)^2\ S_{1/2}$	$K^{**}(3p^5\ 4p\ 4s)^4\ S_{3/2}$	1081	67.4	–
$K^{+*}4s\ 3/2\ [3/2]_2$	K $(3p^6\ 4s)^2\ S_{1/2}$	$K^{**}(3p^5\ 4d\ 4s)^4\ P_{5/2}$	2280	72.1	–
$Rb^{+*}5s\ 3/2\ [3/2]_2$	Rb $(4p^6\ 5s)^2\ S_{1/2}$	$Rb^{**}(4p^5\ 5p\ 5s)^4\ S_{3/2}$	614	82.4	1.0 *
$Cs^{+*}6s\ 3/2\ [3/2]_2$	Cs $(5p^6\ 6s)^2\ S_{1/2}$	$Rb^{**}(5p^5\ 5d\ 6s)^4\ P_{5/2}$	1149	109.1	3.2 *

* – results of the present paper.

The technique of direct measurements of the decay of VUV lines' intensities in the discharge plasma afterglow (see Ref. 4) provides for direct information on the elementary processes associated with the population and depopulation of atomic and ion levels. Time behavior of the intensities of resonance levels of rare gas atoms (He at λ = 53.7 and 58.4 nm), alkali metal ions (Rb^+ at λ = 71.1 and 69.7 nm, Cs^+ at λ = 92.7 and 90.1 nm) and radiative decay of the quasi-metastable autoionization states of alkali metal atoms (Rb at λ = 82.4 and 82.2 nm, Cs at λ=109.1, 119.6, and 124.7 nm) (see Fig. 1) were recorded in the wavelength range from 50 to 320 nm at different concentrations of the metal vapor.

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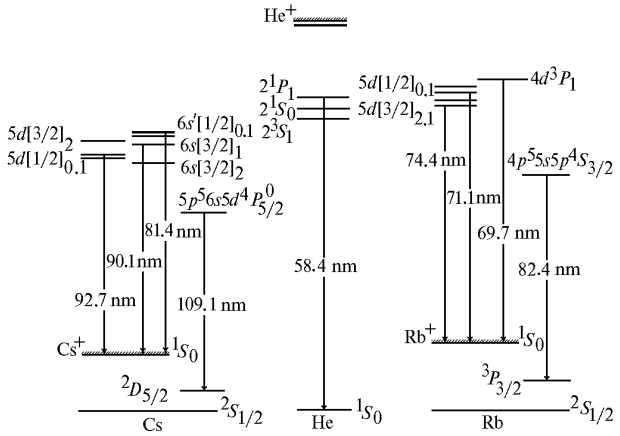

FIG. 1. Diagram of the main levels of He *atom and* Rb *and* Cs *ions.*

The measurements were carried out using a spectrometric system described in details in Ref. 4. The system is based on a DFS–29 spectrometer with the working wavelength range from 50 to 320 nm and inverse linear dispersion of 0.83 nm/mm converted into a monochromator. Glass discharge tube containing mixture of rare gas with a metal vapor has a cylindrical hollow cathode 2.5 cm in diameter and 30 cm in length made from a fine stainless-steel mesh and point shaped anode. The ends of the tube have water cooling while its central section 15 cm in length was heated using special oven equipped with a system for temperature stabilization. The regime of "heat tube" maintaining relatively uniform and stable vapor concentration during more than 12 hours was used. The discharge tube was powered with rectangular stabilized current pulses with a tunable about 1 μs duration and amplitude of 5.5 A. Under operation the 400 V voltage was applied to tube with the decay rate of 2×10^9 V/s. The VUV radiation was detected using a photomultiplier FEU–87 with the window coated with a thin layer of luminophor (sodium salicilate) operated in the photon counting mode. Electronic detecting system of the type "start-stop" includes shaper-discriminator with the watching threshold, time-to-amplitude converter (TAC) and a multichannel analyzer of AI–256–6 type operated in the regime of amplitude analysis with the differential non-linearity of 2%. The system provides detection of pulses with time resolution of 0.8 ns. The linearity of the detecting system was controlled by compiling the pulses statistically independent in time. The intensity of the VUV lines in the afterglow was studied on a time interval up to 100 μs after the current pulse termination. Experimental data were processed using a personal computer DELL–486SX.

Helium pressure of 10 Torr was constant. The density of rubidium and cesium atoms in the range $10^{12} - 10^{13}$ cm^{-3} was determined from the discharge tube temperature for which purpose a preliminary calibration of the tube according to the procedure described in Ref. 4 was performed. Therewith, the error in metal atom concentration determination did not exceed 30%.

Investigation of the time behavior of intensities of the VUV lines at λ = 109.1 and 82.4 nm corresponding to the main radiative transitions from quartet metastable autoionization levels of Rb ($4p^55s5p^4S_{3/2}$) and Cs ($5p^56s5d^4P_{5/2}$) (see Fig. 2) revealed their long afterglow exceeding both the lifetime of these levels and the relaxation time of high-energy (fast) electrons ($<10^{-7}$ s^{-1}) which could excite the levels in the afterglow and extend their relaxation time.

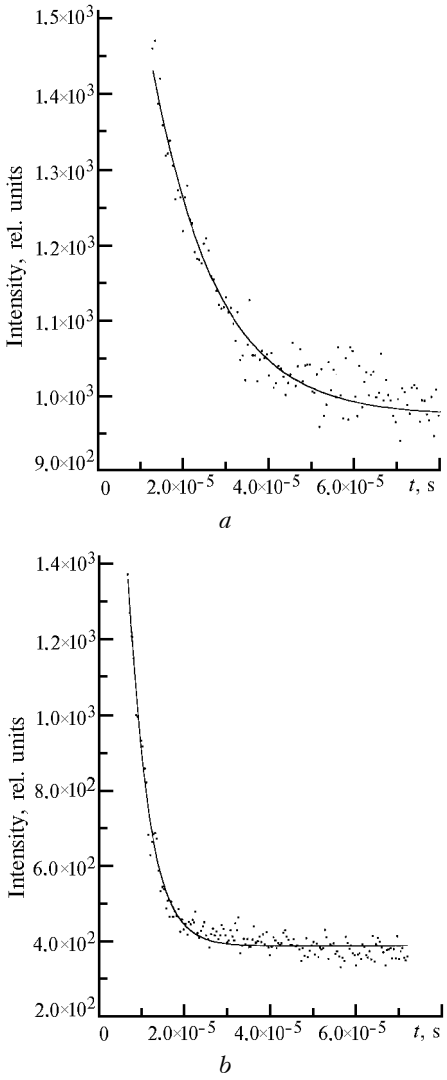

FIG. 2. Intensities of the lines at λ = 109.1 *(a) and* 82.4 nm *(b) versus time in* He-Cs *and* He-Rb *mixtures. Concentrations of* Cs *and* Rb *atoms are* 0.5×10^{-13} cm^{-3} *and* 6×10^{-13} cm^{-3}*, respectively.*

Besides, there are no appropriate helium levels providing collisional transfer of the excitation energy to the quartet quasi-metastable levels of rubidium and cesium. For our experimental conditions we can assume only one possible channel for populating these levels and providing such a long afterglow. It is the reaction of charge transfer from metastable alkali metal ions whose levels are highly populated in low-temperature plasma to the neutral atoms:

$$Rb^{+*}\ (4p^5\ 5s\ [3/2]_2) + Rb\ (4p^6\ 5s^2\ S) =$$
$$= Rb^{**}\ (4p^5\ 5p\ 5s^4\ S_{3/2}) + Rb^{+}\ (4p^6\ {}^1S); \qquad (2)$$

$$Cs^{+*}\ (5p^5\ 6s\ [3/2]_2) + Cs\ (5p^6\ 6s^2\ S) =$$
$$= Cs^{**}\ (5p^5\ 5d\ 6s^4\ P_{5/2}) + Cs^{+}\ (5p^6\ {}^1S). \qquad (3)$$

Metastable states of an alkali metal ion in the discharge plasma are populated not only through the excitation by electron impact and cascade processes, but in the Penning reaction of ionization producing excited ions, as well. Therewith, only resonance excited $He(^1P_1)$ helium atoms and singlet $He(2^1S_0)$ and triplet $He(2^3S_0)$ helium metastable states can be involved in the Penning reaction in helium-rubidium and helium-cesium mixtures. The former two, of the three channels, rapidly decay after the current pulse termination (as our estimation indicates, cascade population in the afterglow can not last over 50 ns and its contribution does not exceed 8%), while the Penning ionization occurs during a relatively long period and produces the main contribution to the population of the metastable levels of the alkali metal ions.

To analyze the experimental results a set of kinetic equations involving equations for populations of metastable and resonance states of helium atoms, alkali metal ions in the ground and metastable states, quartet quasi-metastable states of alkali metal atoms was considered. Reactions of the charge transfer (2), (3), autoionization and radiative decay of the quartet levels, quenching of metastable metal atom by low-energy electron impact (mainly through the resonantly excited ion levels) and formation of the excited molecular ions in the processes of triple collisions, Penning ionization producing ions in ground and excited states, radiation of resonance helium atoms and diffusion losses of particles in metastable states were taken into account. Solution of the set of equations showed that in the afterglow the intensity decay rates of lines at $\lambda = 82.4$ and 109.1 nm are linear functions of the metal vapor concentration

$$\gamma = \gamma_0 + \alpha[M]\ , \qquad (4)$$

where γ_0 is the decay rates of all processes which are independent of metal atom concentration $[M]$, α is the rate of the charge transfer reaction (1). The measured decay rates of the autoionization levels versus alkali metal atom concentrations are shown in Fig. 3. These rates are well described by a linear dependence. Fitting of experimental points according to linear law can give the rate constants of the charge transfer reactions (2), (3) for metastable ions of rubidium and cesium. They are $\alpha(Rb) = 3.76(\pm 0.6)\times 10^{-11}\ cm^3/s$ and $\alpha(Cs) = 9.94(\pm 1.5)\times 10^{11}\ cm^3/s$, respectively. In our previous work (see Ref. 6) the relationship between the line intensity at $\lambda = 109.1$ nm and cesium atom concentration in a DC discharge has been studied. Therewith, mean cross-section of the charge transfer reaction (2) involving metastable cesium ions $\bar{\sigma} = \langle \sigma v_a \rangle / \bar{v}_a$ was measured to be $9(\pm 3)\times 10^{-15}\ cm^2$. Similar measurements for rubidium metastable ions can not be made due to extremely low intensity of the quartet rubidium line at $\lambda = 82.4$ nm. In our experimental conditions at the tube temperature of 600 K the mean charge transfer cross-sections for the metastable cesium and rubidium ions are equal to $\bar{\sigma}(Cs) = 3.2\times 10^{-14}\ cm^2$ and $\bar{\sigma}(Rb) = 1.0\times 10^{-14}\ cm^2$, respectively. The charge transfer cross-section value for cesium ions is somewhat lower than that obtained earlier. This appears to be due to the errors in metal vapor concentration measurements. Besides, no experimental data on some rate constants required for that measurement method are available from literature. The estimate calculations according to the method of the asymptotic theory of collisions within the context of Rosen-Zinger model (see Ref. 7) gave the cross-section value of $3\times 10^{-15}\ cm^2$ at thermal velocity of collisions. It should be noted that measurements of σ in helium-rubidium mixture can not be made since the metastable rubidium ions may, in addition to the excitation process by electron impact, (as it is observed in helium-cesium mixture) only be populated due to collisions with the resonantly excited helium atoms $He(2^1P_1)$ (see Fig. 1) whereas the metastable cesium ions in cesium-helium mixture are populated also from singlet and triplet helium metastables. Besides, the charge transfer cross-section for metastable rubidium ions is lower by a factor of more than tree than that for the metastable cesium ions. This appears to be not enough for efficient population of the autoionization levels of rubidium atoms and can not provide the line intensity required for the current measurements.

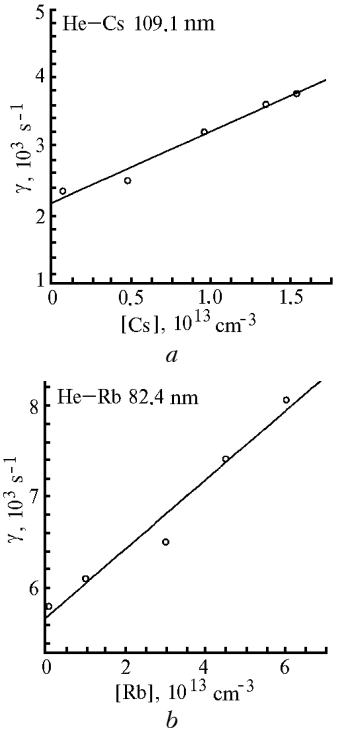

FIG. 3. Decay rates of the intensities of lines at $\lambda = 109.1$ *(a) and* 82.4 nm *(b) in* He-Cs and He-Rb *mixtures versus concentrations of* Cs *and* Rb *atoms.*

Thus, the results obtained demonstrate good efficiency of the application of the methods of VUV–spectroscopy of discharge afterglow to studies of the elementary processes in low-temperature plasma.

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