AFTERGLOW OF THE VUV SPECTRAL LINES OF CESIUM AND RUBIDIUM IN A MIXTURE WITH A NOBLE GAS

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We present in this paper a study of the population decay of resonantly excited energy levels in ions of $Rb^+(5s[1/2]_1, 4d^3P_1)$, $Cs^+(5d[1/2]_1, 6s[3/2]_1, 6s[1/2]_1)$, *and in atoms of* $He(2^1P_1)$, *and* $Ne(3s^1P_1)$ *made using their VUV spectra in a decomposing plasma in the mixtures of* Ne–Cs *and* He–Rb. *The investigations carried out enabled us to derive the rates of helium and neon atomic ion conversion into the molecular ones, resulting from three-particle collisions in* Ne–Cs *and* He–Rb *mixtures. The rates are* $k(Ne) = 0.62(\pm 0.2)\cdot 10^{-31}$ cm^{6}s^{-1} *and* $k(He) = 3.18(\pm 0.8)\cdot 10^{-31}$ cm^{6}s^{-1}, *correspondingly. We also have analyzed the role of nonresonance charge exchange in these mixtures. The total rate constant of the charge exchange in the* He–Rb *mixture has been estimated to be* $\delta = 3.88(\pm 0.9)\cdot 10^{-10}$ cm^{3}s^{-1}. *For the* Ne–Cs *mixture we have obtained the value of the total rate constant of the energy transfer from the particles in metastable states to cesium ions in the nearest resonantly excited states through interaction with low energy electrons* ($\alpha_e = 4.9(\pm 1.6)\cdot 10^{-7}$ cm^{3}s^{-1}). *The value of radiation recombination of* Cs^{++} *was obtained to be equal to* $\alpha_e^{++} = 1.45(\pm 0.3)\cdot 10^{-8}$ cm^{3}s^{-1}.

As known, the charge exchange between the ions of a noble gas, R^+, and atoms, A, may occur, in the electric-discharge plasma, in mixtures of noble gases with easily ionizable atomic components, in two ways:

$$R^+ + A \to R^* + A^+; \quad (1)$$

$$R^+ + A \to R + A^{+*}. \quad (2)$$

In the cases when the production of the excited inert gas atoms by reaction (1) is low probable, because of a large energy deficit, the reaction (2) may become an efficient channel to populate the excited states of an easily ionizable atomic component A^{+*}. This is especially true in the mixtures like Ne–Cs and He–Rb, where Penning ionization can result only in creation of alkali metal ions in the ground energy state. In these cases the reaction (2) is the basic channel of populating the excited energy levels of cesium and rubidium ions during the afterglow. However, the level $Rb^+(5s[3/2]_{1,2})$ may be populated through Penning ionization, but only from the resonantly excited $He(2^1P_1)$ level.

In this paper we present an experimental investigation into the mechanisms of the charge exchange reaction (2) in the mixtures of Ne–Cs and He–Rb that result in populating resonantly excited levels of alkali-metal atoms, which then emit in the VUV region. In so doing we have studied the population decay of resonantly excited energy levels in ions of $Rb^+(5s[1/2]_1, 4d^3P_1)$, $Cs^+(5d[1/2]_1, 6s[3/2]_1, 6s[1/2]_1)$, and in atoms of $He(2^1P_1)$, and $Ne(3s^1P_1)$ using their VUV emission spectra.

The experiments on exciting the atomic mixtures and studying their afterglow have been conducted using the installation described in Ref. 1. The basic instrument of the installation is a DFS–29 spectrograph rebuilt to make up a monochromator operating in the spectral region from 50 to 320 nm. The discharge tube used was made from a glass pipe inside which there were placed a cylinder shaped hollow cathode from a stainless steel grid 25 mm in diameter and 300 mm long and a point anode. The ends of the discharge tube were cooled with circulating water while its central part (150 mm long) heated with a temperature stabilized heating system. The concentration of alkali metals has been being determined based on the discharge tube temperature. Inside the tube we have maintained the thermal tube regime that provides for a uniform and stable distribution of concentration during more than 12 hours. The power supply used provided rectangular shaped highly stabilized current pulses of 5.5 A amplitude and variable, up to 10 μs, pulse length. In a regular operation mode the voltage at the tube was 400 V with the rate of voltage fall off in the trailing edge of $2\cdot 10^9$ V/s. The discharge emission in the VUV region has been being recorded with a FEU–87 PMT operated in photon counting mode. The electronic data acquisition system comprised a pulse shaper, pulse-height discriminator (with a follow-up threshold of the time-to-amplitude converter (TAC)), and a multichannel pulse-

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height analyzer AI–256–6. The whole data acquisition system provided for recording the pulses with the time resolution of 0.8 ns. The afterglow of the VUV spectral lines has been recorded for a 100 μs interval after the discharge current pulse cut off. The data on the afterglow intensity have been processed on a Dell 486SX PC using the least squares method.

The partial pressure of Ne and He was kept, in our experiments, constant at the level of 13 and 10 Torr, respectively. The number density of rubidium and cesium vapor was estimated to be 10^{12} to 10^{14} cm^{-3} based on the discharge tube temperature. To do this we have calibrated the tube following the technique described in Ref. 1, that provides the accuracy of determining the metal vapor concentration about 30%. The number density of electrons in the afterglow region has been determined using the technique[2] of two successive pulses. The time behavior of the VUV line intensity from cesium and rubidium ions exhibits a long afterglow with two distinct phases in its decay (see Fig. 1), namely a rapid fall off and a slow decay during a time that far exceeds the lifetime of their excited states[3] and the relaxation time of fast electrons ($< 10^{-7}$ s) which otherwise could excite these energy levels in the afterglow thus increasing their lifetime. Similar behavior is characteristic of the line intensity of helium (at 58.4 nm) and Ne (at 73.6 nm) emission from the resonance excited states.

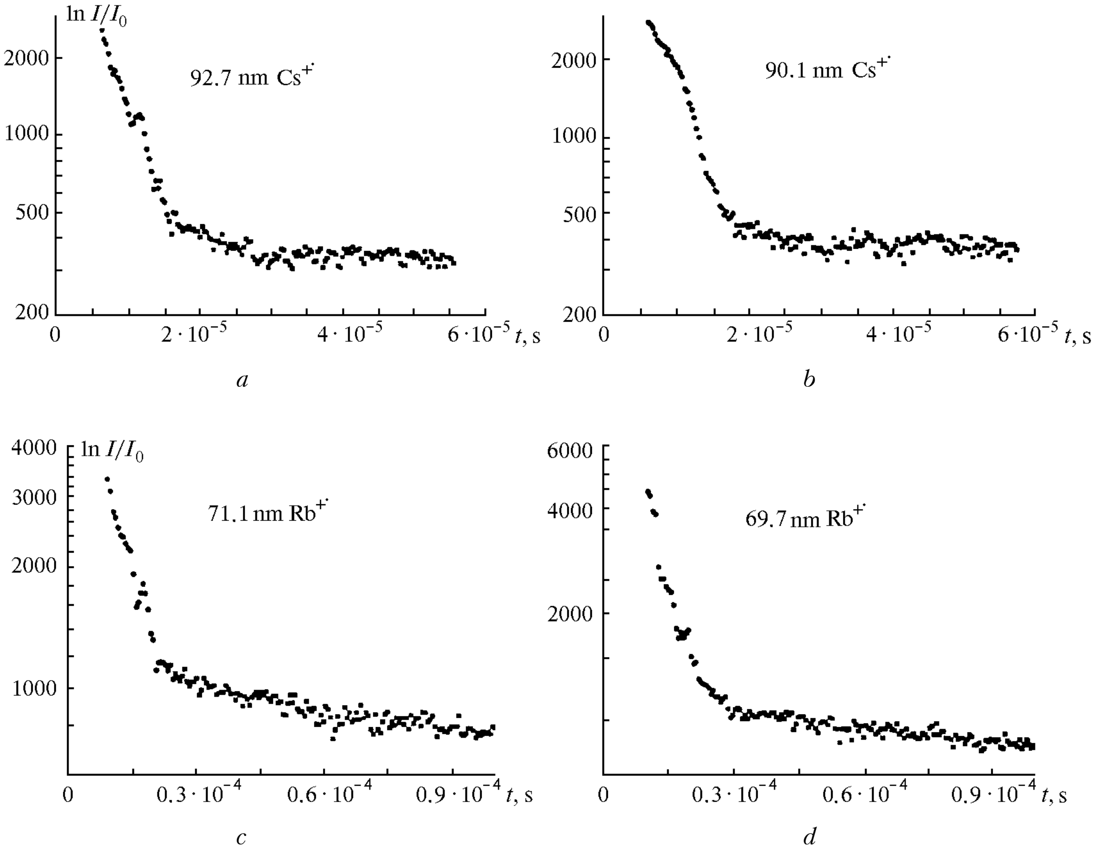


FIG. 1. Time behavior of resonance lines of cesium ion (at 92.7 nm *(a) and* 90.1 nm *(b)) and rubidium ion (at* 71.1 nm *(c) and* 69.7 nm *(d)) in the plasma afterglow in mixtures of* Ne–Cs *and* He–Rb *at cesium vapor number density of* $5\cdot10^{12}$ cm^{-3} *and rubidium density of* $6\cdot10^{13}$ cm^{-3}.

In a Ne–Cs mixture the resonance excited level of atomic neon Ne($3s^1P_1$) that yields the emission line at 73.6 nm wavelength is depopulated at a rate of $1.6(\pm0.3)\cdot10^5$ s^{-1} that is independent of the cesium vapor pressure (see Fig. 2*a*). This corresponds to the lifetime of this energy state under conditions of the emission capture,[4] though the lifetime estimated is a little bit shorter than that calculated by known formula ($\gamma^f = (0.207/\tau)(\lambda/R)^{1/2}$, where τ is the natural lifetime of the resonance level; λ is the wavelength; R is the discharge tube radius. The underestimation of this value in the experiment may occur due to a systematic error in the constant. At the same time it is worth noting that, as was shown in Ref. 5, the assumption on a complete redistribution of the resonance emission frequency may not work at medium pressures (several Torr and lower) thus explaining some possible deviations from the theory.

The processes of plasma de-ionization are much slower and they may provide, during the afterglow, for populating the resonance level of atomic neon, Ne($3s^1P_1$), which then degenerates at the stage of the

73.6 nm line decay. The fall off rate of this line intensity should agree with the total rate of the Ne^+ ion disappearance due to the recombination reactions that mostly yield the creation of molecular ions and the reactions (1) and (2). The charge exchange in the Ne–Cs mixture is very unlikely because of no resonance occurring between them. It is just this circumstance that explains the fact that the fall off rate of the 73.6 nm line intensity in the slow branch of the afterglow decay is also independent of the cesium unimportant regarding the time intervals considered in vapor density (see Fig. 2*b*), being equal to the conversion rate of neon atomic ions into the molecular due to the three-particle collisions (k(Ne) = $= 0.62(\pm 0.2)\cdot 10^{-31}$ cm^6s^{-1}). No data on the rate constant of Penning ionization were available from literature for a resonance excited neon atom($3s^1P_1$) in the Ne–Cs mixture. However, one may state, following Ref. 6 where this constant of Penning ionization has been measured for Ne in metastable states in an Ne–Cs mixture, that this is a much faster process thus being our experiments.

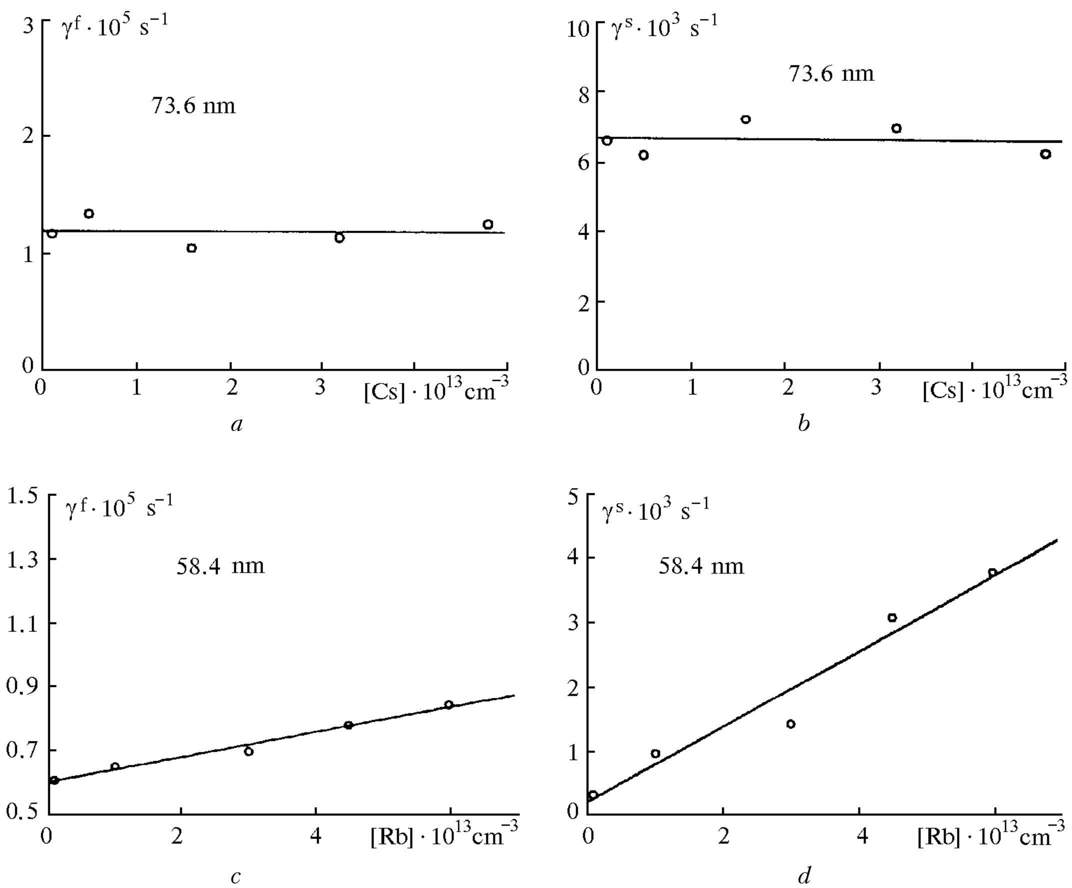


FIG. 2. The rate of the intensity fall off for resonance lines of atomic neon at 73.6 nm *(a and b) and atomic helium at* 58.4 nm *(c and d) at the fast* γ^f *and slow* γ^s *phases of the plasma afterglow in the mixtures of* Ne–Cs *and* He–Rb *as a function of alkali metal concentration.*

Since the probability of populating the cesium ion energy levels due to the charge exchange in the Ne–Cs mixture is low, as mentioned above, the experiments did not reveal any dependence of the VUV cesium spectral line intensities (at 92.7 and 90.1 nm) on the cesium vapor density neither in the fast nor in the slow branches of the afterglow (see Fig. 3).

Thus, the fact of obtaining two different rates of the afterglow decay that are independent of the metal vapor density may only be explained by the collisional populating of the cesium ion energy levels from the nearest metastable states with low energy electrons, whose concentration is quite high during the afterglow (this is discussed below), as well as by the recombination population. During the phase of a rapid decay, for approximately 30 μs, the intensity of resonance lines of cesium ion at 92.7 and 90.1 nm wavelengths fall off at an equal rate $\alpha_e =$ $= 4.9(\pm 1.6)\cdot 10^{-7} cm^3s^{-1}$ (see Fig. 3*a* and *c*). This value corresponds to the total rate of energy transfer from particles, in the nearest metastable states, with the participation of low energy electrons.

Investigations of the electron density time decay in the afterglow of Ne–Cs plasma showed that within the variation of cesium atom concentration occurred the electron density was equal to $n_e = (1.8$ to $2)\cdot 10^{11}\,\mathrm{cm}^{-3}$, being only weakly dependent on the total pressure. The rate constant of the electron removal, determined from the time behavior of the electron density, is $2.8\ (\pm 0.5)\cdot 10^{-8}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ thus showing that there occurs the volume recombination that has a pair nature since it only weakly depends on the electric current.

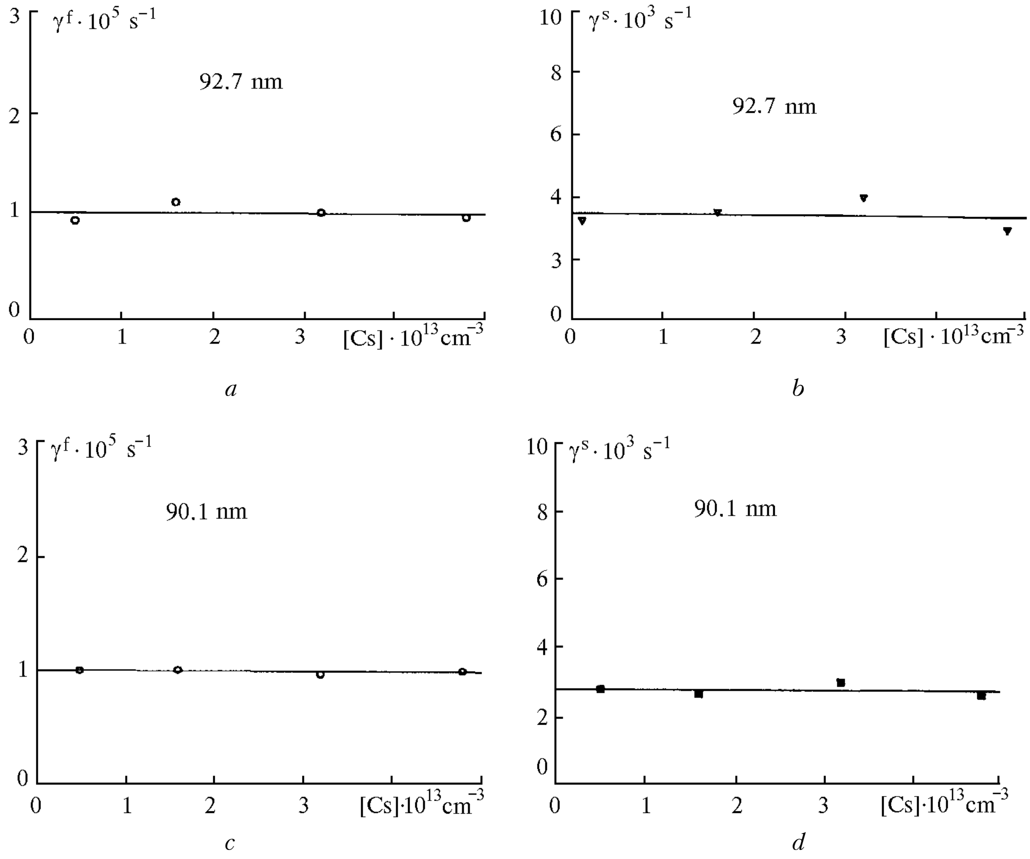


FIG. 3. The rate of the intensity fall off for resonance lines of cesium ions at 92.7 nm *(a and b) and at* 90.1nm *(c and d) at the fast* γ^f *and slow* γ^s *phases of the plasma afterglow in the* Ne–Cs *mixture as a function of cesium concentration.*

The decay rates of cesium ion resonance lines at 92.7 and 90.1 nm wavelengths are, during the slow phase, the same either (see Fig. 3*b* and *d*). This fact is a clear evidence that the source of populating the corresponding energy levels is the same. Under conditions of our experiments this may only be the recombination of one of the long-lived components of the discharge plasma, namely Cs^{++}, that occurs at a rate of $\alpha_e^{++} = 1.45(\pm 0.3)\cdot 10^{-8}\,\mathrm{cm}^3\mathrm{s}^{-1}$. The experiments on studying the ion composition of cesium plasma, carried out earlier,[7] have shown that in a discharge like we have had the ions Cs^+ that are the major source of Cs^{++} ions dominate over Cs_2^+ ions in concentration. At the same time the ions Cs_2^+ dominate at $n_e < 10^{10}\,\mathrm{cm}^{-3}$. According to Ref. 8 the ratio $\mathrm{Cs}_2^+/\mathrm{Cs}^+$ increases with decreasing n_e.

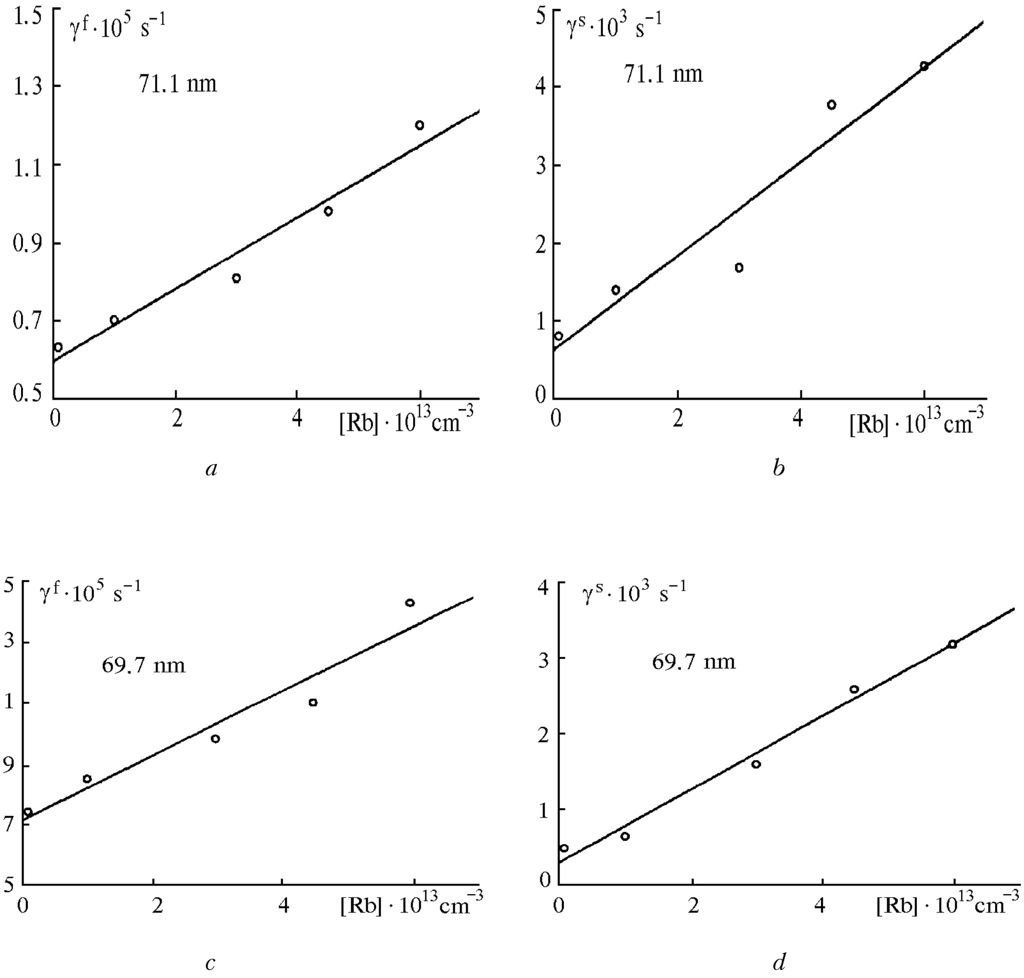
In the mixture of He–Rb we have studied the kinetics of resonance-excited energy level $\mathrm{He}(2^1P_1)$ based on time behavior of the spectral line at 58.4 nm wavelength. The time during which the Penning ionization, that devastates the corresponding energy level, occurs is only several microseconds. Solving the system of kinetic equations (similarly to Ref. 1) has shown that during the phase of a rapid decay the intensity of the resonance line at 58.4 nm should fall off at a rate

$$\gamma^f = k\,[\mathrm{He}]^2 + \delta\,[\mathrm{Rb}], \qquad (3)$$

where the values in square brackets denote the concentration of corresponding components; k is the rate of atomic helium ions conversion into the molecular ones whose concentration, in our experimental conditions, is at least one order of magnitude higher[10] than that of $[\mathrm{Rb}^+]$; δ is the total constant of the charge exchange reactions (1) and (2).

The probability γ^{f} set out in Fig. 2*c* as a function of Rb concentration at the fast afterglow decay stage (during 30 μs) may well be approximated by a linear dependence. The value of the total constant of charge exchange $\delta = 3.88(\pm 0.9)\cdot 10^{-10}$ cm^{3}s^{-1}, determined by the least squares method, well agrees with that found in Ref. 10. The rate of helium atomic ions conversion into the molecular ones in the mixture He–Rb is k(He) = $3.18(\pm 0.8)\cdot 10^{-31}$ cm^{6}s^{-1}. As to the slow decay branch in the afterglow time behavior, it has been studied in Ref. 11 quite thoroughly.

The investigations of the afterglow from the resonance-excited energy levels of rubidium ions, $5s[1/2]_1$ and $4d^3P_1$ emitting the lines at 71.1 and 69.7nm (see Fig. 1*c* and *d*) in the He–Rb mixture have shown that both at the rapid and slow decay stages the intensity of these VUV lines falls off at the same rate since they have the same channels of excitation. At the rapid stage of the afterglow the linear dependence of devastating rate for these levels on the rubidium vapor density (see Fig. 4*a* and *c*) may only be related to the recombination of Rb^{++} ions through the formation of molecular ions at two-particle collisions. The three-particle collisions are more efficient at a higher density of the rubidium atoms. Recombination of the molecular ions due to their dissociation leads to excitation of the resonance energy levels of the rubidium ions. The contribution coming from the charge exchange does not exceed 0.1% of the total cross-section.[10] By linearly fitting the experimental data on the intensity fall off as a function of rubidium vapor density gave the following value for the rate constant of molecular rubidium ion formation due to two-particle collisions $\alpha(\mathrm{Rb}) = 1.0(\pm 0.3)\cdot 10^{-9}$ cm^{3}s^{-1}. The fall off rate of $5s[1/2]_1$ and $4d^3P_1$ levels' population in rubidium ion, at the slow decay stage (Fig. 4*b* and *d*), is the same as that for the helium resonance level He(2^1P_1) population (see Fig. 2*d*). That means that there occurs certain transfer of the excitation from the resonance level of helium atoms, populated due to a slow recombination, to the rubidium ions, as a result of the charge exchange reactions.



a *b*

c *d*

FIG. 4. The rate of the intensity fall off for resonance lines of rubidium ions at 71.1 nm *(a and b)* and at 69.7 nm *(c and d) at the fast* γ^{f} *and slow* γ^{s} *phases of the plasma afterglow in the* He–Rb *mixture as a function of rubidium vapor concentration.*

Thus, the VUV-spectroscopy technique proved to be very convenient in application to studies of the energy re-distribution during the afterglow of plasma in mixtures of noble gases with alkali metals.

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