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## The production kinetics for rare gas alkali ions

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In a recent paper it was shown that rare gas ions form bound molecular states which decay by emission of radiation in the VUV. They are potential candidates as storage media for VUV lasers. In the present investigation the ions  $Kr^+K$ ,  $Kr^+Cs$ ,  $Xe^+K$ , and  $Xe^+Cs$  are produced by electron beam excitation of suitable gas mixtures with He as buffer gas. Studies of the reaction kinetics were performed for  $Kr^+K$ . The rate constant for the reaction  $Kr^+ + K + He$  was determined to be  $2.8 \times 10^{-30}$  cm<sup>3</sup> s<sup>-1</sup>.  $Kr^+K$  is strongly quenched by plasma electrons and by reaction with Kr. The fluorescence yield at intense excitation was determined to be about  $5 \times 10^{-2}$  VUV quanta per He<sup>+</sup> ion.

### INTRODUCTION

In a recent paper<sup>1</sup> it was demonstrated that diatomic molecular ions  $Rg^+A$  are formed by combining rare gas ions with alkali atoms. These ions decay by emission of VUV radiation into the weakly bound state  $RgA^+$ . The formation and the decay of Xe<sup>+</sup>Rb was also observed by Millar *et al.*<sup>2</sup> Since the  $Rg^+A$  ions are promising candidates as storage media for VUV lasers, it seems to be of interest to study their formation kinetics. In the present paper KrK<sup>+</sup>, XeK<sup>+</sup>, KrCs<sup>+</sup>, and XeCs<sup>+</sup>, which decay by emission of radiation at 135.5, 167.1, 132.5, and 159.9 nm, respectively, were investigated. Since it turned out that the relevant reaction paths proceed quite similar, only the reactions leading to KrK<sup>+</sup> were studied in detail.

## **EXPERIMENTS**

In the previous experiments the  $Rg^+A$  ions were produced by exciting a Rg/A mixture using a continuous-wave (cw) beam of 3.6 MeV Ar ions. Since in potential laser applications an intense excitation is necessary, the present experiments were performed by pulsed excitation using an electron beam of about 500 A/cm<sup>2</sup> and 1.75 MeV.

The basic experimental set up has been described previously.<sup>3</sup> The electron beam was supplied by a modified Febetron 705. After transversing a titanium foil the electron beam passed the cylindrical reaction cell longitudinally. A magnetic guiding field kept the beam radius to be at 0.5 cm. The beam energy per pulse amounted to about 30 J. The pulses had a width of 30 ns. In order to avoid radiation damage of the exit window a transverse magnetic field was placed at the end of the cell. By this, the length of the excited zone was defined to be L = 45 cm.

The reaction cell was filled with a few mbar of the rare gas and several bar of a buffer gas. A glass ampoule containing the alkali to be investigated was broken under vacuum outside of the reaction cell, the metal was liquified and transferred into the cell. The experiments were performed at a temperature which corresponds to a vapor pressure of several mbar of the alkali. The front ends of the cell were equipped with water cooled baffles in order to avoid condensation of the alkali at the titanium foil and at the MgF<sub>2</sub> window attached at the opposite end. At typical buffer gas pressures of several bar the length of the vapor zone was determined for potassium by probing with the 404.4 nm light supplied by a dye laser. From the cross section of absorption for the 404.4 nm transition  $(4s \rightarrow 5p)$  an effective length of the vapor zone of l = 15 cm resulted. The relation between vapor density and temperature is well known for potassium. From measurements of the temperature distribution in the cell the vapor density distribution was evaluated. The resulting l agreed with the result of the absorption measurement. Since l is small compared to L, a considerable contribution of the fluorescence (Rg<sub>2</sub><sup>\*</sup>) originated from zones with pure Rg/buffer gas mixtures.

The emitted light was passed through a 0.5 m Seya Namioka VUV spectrograph. In the focal plane a Na-salicylate film served as a converter for the VUV light. The visible light was transferred by a lens system into an optical multichannel analyser (OSMA). In most experiments the total light output of one shot was registered by gating the OSMA with a 1  $\mu$ s pulse. In order to investigate the time dependence the width of the gating pulse was reduced to 36 ns and delayed with respect to the exciting pulse between 0 and 1000 ns.

### RESULTS

Figures 1(a)-1(d) show typical spectra obtained for the rare gases Kr or Xe mixed with K or Cs vapor. The buffer gas was 2 bar of helium. Due to the gate width of 1  $\mu$ s the spectra correspond to time integrated intensities. The broad continuum centered at 146 nm with Kr donor and at 172 nm with Xe donor are caused by the decay of Kr<sup>2</sup> and Xe<sup>2</sup>, respectively, while the narrow bands are attributed to the decay of Kr<sup>+</sup>K, Xe<sup>+</sup>K, Kr<sup>+</sup>Cs, and Xe<sup>+</sup>Cs, respectively. The wavelengths of these transitions agree with the results of the previous investigations<sup>1</sup> except for Xe<sup>+</sup>Cs, where the present experiment yields a slightly higher wavelength of  $\lambda = 132.5$  nm for the line center. The gas mixtures chosen to obtain Figs. 1(a)-1(d) were optimized to give the highest Rg<sup>+</sup>A fluorescence in comparison to the Rg<sup>2</sup> fluorescence.

Figure 2 shows the result of a shot with the narrow gate and a delay of 70 ns. The comparison with Fig. 1(a) indicates that build up and decay of  $Rg^+A$  are fast with respect to  $Rg_2^*$ . The time dependence was investigated in more detail for  $Kr^+K$  in different gas mixtures. A typical result is shown

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FIG. 1. Spectra of the time integrated radiation emitted after electron excitation of helium (2 bar) with admixtures of Rg and A of several mbar. The narrow band at wavelength  $\lambda$  is attributed to the decay of Rg<sup>+</sup>A, the broad continuum to the decay of Rg<sup>\*</sup>. (a) Kr<sup>+</sup>K,  $\lambda = 135.5$  nm, 28 mbar Kr, 11 mbar K; (b) Xe<sup>+</sup>K,  $\lambda = 167.1$  nm, 5 mbar Xe, 8 mbar K; (c) Kr<sup>+</sup>Cs,  $\lambda = 132.5$  nm, 28 mbar Kr, 16 mbar Cs; (c) Xe<sup>+</sup>Cs,  $\lambda = 159.9$  nm, 5 mbar Xe, 16 mbar Cs. While Rg<sup>+</sup>A can only be formed in the vapor zone, the continua are excited also in the cooled section of the cell.

in Fig. 3. The time for the buildup of the fluorescence is independent of the gas pressure and corresponds to the rise time of the exciting pulse, while the decay times were determined to be between 50 and 170 ns. They turned out to be inversely proportional to the He and K pressure. The  $Kr_2^*$  fluorescence appears later due to the slow formation rate for the  $Kr_2^*$  excimer.

Figure 4 shows the relative yield of the  $Kr^+K$  fluorescence by varying the K, Kr, and He pressures. For comparison the yield for  $Kr_2^*$  is also indicated. Intense fluorescence from  $Kr^+K$  is obtained only for small K- and Kr- admixtures to the buffer gas. The cross section for absorption by the potassium donor is  $3.5 \times 10^{-19}$  cm<sup>2.4</sup> The correction of the intensities for the vapor densities used in the experiments is small. For the data in Fig. 4(c) it has been taken into account. A further correction arises from the variation of the vapor density in the cell. In the analysis of the data in Fig. 4(c) this has been considered.



FIG. 2. Spectrum of  $Kr^+K$  obtained under the same conditions as Fig. 1(a) but gating the OSMA 70 ns after the electron beam excitation pulse for 36 ns. The comparison with Fig. 1(a) indicates that the  $Kr^+K$  population decays much faster than the  $Kr_2^*$  population.



FIG. 3. Relative intensities of the radiation from  $Kr^+K$  and  $Kr_2^*$  vs delay time, indicating the fast rise and decay time of  $Kr^+K$ . The data were obtained for 4 bar He, 56 mbar Kr, and 8 mbar K at a gate width of 36 ns.

Above 1 bar, the dependence of the fluorescence yield on the buffer gas is about linear. Since also the energy deposition of the electron beam increases almost linearly with the buffer gas pressure the result indicates that the  $Kr^+K$  yield



FIG. 4. Relative intensity of the radiation emitted in the decay of Kr<sup>+</sup>K and Kr<sub>2</sub><sup>\*</sup> vs (a) He pressure,  $p_{\rm k} = 4$  mbar,  $p_{\rm Kr} = 8$  mbar; (b) Kr pressure,  $p_{\rm He} = 2$  bar,  $p_{\rm K} = 3.7$  mbar; (c) K pressure,  $p_{\rm He} = 2$  bar,  $p_{\rm Kr} = 5.4$  mbar.

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FIG. 5. Kinetic scheme proposed for the reactions leading to  $Kr^+K$ . The reactions and their rate constants are listed in Table I.

should rise with higher input power. Varying the pumping density at constant pressure the intensity of the  $Kr_2^*$  continuum and of the  $Kr^+K$  radiation increased almost proportional with the pumping power. This indicates that quenching of the fluorescence by plasma electrons plays an unimportant role. As an other possibility to increase the input power Ne and Ar as buffer gas were investigated. For argon  $Kr^+K$  was hardly observable. For neon the yield per deposited pumping energy decreased by a factor of 10 compared to helium as buffer gas.

The intensity of the  $Kr_2^*$  radiation increases quadratically with Kr and He pressure. Since only part of the cell contains the K donor, the behavior reflects mainly the kinetics of He/Kr mixtures. The same dependence is observed in experiments with the cell at low temperatures where no K vapor was present.

In order to estimate the absolute fluorescence yield a deuterium lamp with a  $MgF_2$  window was placed in front of the spectrograph at the position of the cell. Adopting the calibration curve published by Key and Preston<sup>5</sup> for this

type of lamp an absolute calibration of the set up is performed with an uncertainty of about a factor of 2. Under best conditions a fluorescence energy of 400  $\mu$ J/cm<sup>3</sup> per shot is emitted by Kr<sup>+</sup>K. Comparing this result with the energy deposited by the electron beam in He<sup>6</sup> indicates that only about 0.05 135.5 nm quanta are emitted per one created He<sup>+</sup> ion.

The cw data indicated appreciable self-absorption of the fluorescence due to the lower weakly bound state  $KrK^+$ . In the present experiment self-absorption would have shown up in the time dependent spectra (Fig. 2) when taken at large delay times. However, no effect was observed. Thus, self-absorption can be ruled out as reason for the low fluorescence yield.

#### DISCUSSION

In order to reproduce the experimental data the reaction scheme for  $Kr^+K$  shown in Fig. 5 is proposed. The corresponding rate constants are listed in Table I. The He<sup>+</sup> ions produced by the exciting electron beam form He<sub>2</sub><sup>+</sup> in a termolecular reaction in typically 10 ns. Due to the small admixtures of Kr and K reactions with He<sup>+</sup> play a minor role unless the He pressure is below 1 bar.

 $He_2^+$  may react with Kr or K in a change transfer reaction to the ionic ground states, while reactions to excited ionic states are energetically forbidden. For  $He_2^+ + Kr$  the rate constant was determined to be  $k_4 = 2 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> by Bohme *et al.*<sup>7</sup> at T = 200 K. More efficient is the termolecular reaction  $He_2^+ + Kr + He$ , which has been investigated by Collins and Lee.<sup>8</sup> Similar results have been obtained for the corresponding reactions with He and Ar or Xe.<sup>9</sup> These rate constants predict a fast transfer to Kr<sup>+</sup> for the present conditions. A too small Kr admixture causes dissociative recombinations of  $He_2^+$  by plasma electrons or a quenching of  $He_2^+$  by K( + He). The latter reaction is responsible for the decreasing fluorescence efficiency with rising K density [Fig. 4(c)], while quenching by plasma electrons plays only a minor role for the present conditions.

The rate limiting step observed by the decay time  $\tau$  of

TABLE I. Important rate constants for the formation of Kr<sup>+</sup>K in excited He/Kr/K mixtures.

No.	Reaction	Rate constant	Reference
k <sub>i</sub>	$He^+ + 2He \rightarrow He_2^+ + He$	$1 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$	15
$k_2$	$He^+ + K \rightarrow quench$	$1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$	16
$k_3$	$He_2^+ + K(+M) \rightarrow K^+ + 2He(+M)$	$0.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$	This expt.
-	$(He_2^+ + Kr \rightarrow Kr^+ + 2He)$	$2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	7
$k_4$	$He_2^+ + Kr + He \rightarrow Kr^+ + 3He$	$1.7 \times 10^{-29} \text{ cm}^{6} \text{ s}^{-1}$	8 and 9
k,	$Kr^+ + Kr + He \rightarrow Kr_2^+ + He$	$6 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$	17
k <sub>6</sub>	$Kr^+ + K + He \rightarrow Kr^+K + He$	$2.8 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$	This expt.
$k_{7}$	$Kr^+ + 2e \rightarrow Kr^+ + e$	6×10 <sup>-20</sup> ×(0.025/	•
		$Te)^4 cm^6 s^{-1}$	13ª
$k_8$	$\mathbf{Kr^{+}K} + \mathbf{Kr} \begin{cases} \rightarrow \mathbf{Kr_{2}^{+}} + \mathbf{K} \\ \rightarrow \mathbf{Kr_{2}^{*}} + \mathbf{K}^{+} \end{cases}$	$1 \times 10^{-18} \times A_{\rm eff}  {\rm cm}^3$	This expt.
k <sub>9</sub>	$Kr^+K + e \rightarrow quench$	$3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$	14 <sup>6</sup>

\* Value for He<sup>+</sup>.

=

<sup>b</sup>Estimated from  $Kr_2^+ + e$ .

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the fluorescence must be one of the following steps.  $Kr^+$  has to be the precursor of  $Kr^+K$ . The reactions of  $Kr^+$  to  $Kr_2^+$ via the Kr + He reaction is too slow to account for the observed decay time  $\tau$ . Therefore, the rate limiting step is attributed to  $Kr^+ + K +$  He or  $Kr^+ + K +$  Kr. Due to the large He/Kr ratios used in the present experiments the first reaction dominates. Because of the rather long lifetime of  $Kr^+$  quenching by plasma electrons with average density [e] have also be considered. Hence,  $\tau^{-1} = k_6$  $\times [K] \times [He] + k_7 \times [e]^2$  is assumed.

If the reaction scheme in Fig. 5 is accepted, the shape of the yield curves in Figs. 4(b) and 4(c) are determined by the reactions 3, 6, and 7. The experimental values for the lifetime and the yield curves are reproduced, if the rate constants are chosen to be  $k_3 = 0.9 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>,  $k_6 = 2.8 \times 10^{-30}$ cm<sup>6</sup> s<sup>-1</sup>, and  $k_7 \times [e]^2 = 1.8 \times 10^6$  s<sup>-1</sup>. The fit for the data of Fig. 4(b) improves, if the reaction Kr<sup>+</sup>K + Kr is taken into account choosing  $k_8 = 1 \times 10^{-18} \times A_{\text{eff}} \cdot A_{\text{eff}}$  is the effective transition probability for the decay of Kr<sup>+</sup>K by emission of radiation and by quenching due to plasma electrons.

Although the value for  $k_6$  is considerably larger than the one for the corresponding reaction with Kr ( $k_5$  in Table I), the value is below the limiting rate constant assuming a spiraling capture of K by Kr<sup>+</sup> (Langevin value) as has been estimated by Basov *et al.*<sup>10</sup> The reaction may lead to several final Kr/K states (Kr<sup>+</sup>K, KrK<sup>+</sup>, Kr + K<sup>+</sup>), however the reaction to Kr<sup>+</sup>K is expected to be the most efficient, because it has the smallest reaction energy. Quenching of Kr<sup>+</sup> by K<sub>2</sub>, which is contained in the potassium vapor<sup>11</sup> to about 2%, could also contribute. The formation of Rg<sup>+</sup>A is energetically possible for some Rg/A combinations (e.g., Rg<sup>+</sup>Cs). Since the yield was found to be not different from cases, where the reactions are energetically forbidden (e.g., Rg<sup>+</sup>Na), the reaction seems to be not important.

If Ne or Ar are used as a buffer gas, the reaction of  $Kr^+$ proceeds via the intermediate states  $(KrNe)^+$  or  $(KrAr)^+$ , respectively, to  $Kr_2^+$ . Since the corresponding rates are much larger than the reactions with He as buffer gas and also because  $(HeKr)^+$  is unstable,<sup>12</sup> the yield of  $Kr^+K$  is reduced, when Ne or Ar are used as buffer gas in spite of the larger power input.

The density of the plasma electrons in pure He at the present conditions had been investigated previously.<sup>6</sup> For 0.5-4 bar an almost pressure independent value of  $[e] \approx 10^{15}$  cm<sup>-3</sup> resulted at the end of the excitation pulse. With the quenching constant of  $k_7 \approx 2 \times 10^{-24}$  cm<sup>3</sup> s<sup>-1</sup> for Kr<sup>+13</sup> a quenching rate of  $k_7 \times [e]^2 \approx 2 \times 10^6$  s<sup>-1</sup> may be expected in very good agreement with the result from the analysis of the yield curves.

Presumably  $Kr^+K$  is destroyed by the dissociative re-

combination with a rate constant comparable to those for  $Kr_2^+$  or other similar ions. Adopting for the dissociative recombination of  $Kr^+K$  the rate constant for  $Kr_2^+$ ,  $k = 3 \times 10^{-7}$  cm<sup>3</sup> s<sup>-1</sup>,<sup>14</sup> the inverse lifetime of  $Kr^+K$  is estimated to be  $A_{eff} \ge 3 \times 10^8$  s<sup>-1</sup>. This value is compatible with the lower limit obtainable from the rise time of the  $Kr^+K$ fluorescence. Also the resulting rate constant for the quenching of  $Kr^+K$  by Kr of  $k_8 \approx 3 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> corresponds to the value expected from the Langevin formula.

The rather low fluorescence yield for the  $Kr_2^*$  radiation in the present experiment is due to the slow formation rate of  $Kr_2^*$ . The precursor  $Kr^*$  is mainly destroyed by the plasma electrons. Raising the Kr and He density leads to a substantial increase of the fluorescence yield as has been observed.

Inspecting the reaction scheme given in Fig. 5 indicates that the low fluorescence yield for  $Kr^+K$  is mainly caused by the high density of the plasma electrons which leads to a high rate for recombination of  $Kr^+K$  and its precursors. The observed yield is reproduced quantitatively by the assumed reaction scheme.

Concluding, the  $Rg^+A$  ions are suitable as storage media for lasers. However, they are easily destroyed by dissociative recombination. Therefore the excitation density has to be low in order to avoid quenching by plasma electrons.

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