Vacuum ultraviolet transitions from rare-gas alkali ionic excimers $(XeRb)^+$ and $(KrRb)^+$ by electron beam excitation

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Vacuum UV fluorescences from ionic rare-gas alkali excimer molecules were observed by electron beam excitation. A gas mixture of xenon or krypton with a hot vapor of rubidium was excited to obtain a diffuse emission band centered at 164 nm from $(XeRb)^+$ and 133 nm from $(KrRb)^+$ molecular ions. The observed emission bands are assigned to the $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ transition of $(XeRb)^+$ and $(KrRb)^+$, respectively.

Recently ionic excimer molecules were proposed as possible vacuum ultraviolet (VUV) laser species.[1,2] Subsequently the production of such species by charged-particle excitation and direct photo-ionization using soft x-rays from a laser-produced plasma was reported.[3–10] Recently, the *ab initio* calculations for the alkali-halide ionic excimer and the rare-gas alkali ionic excimer molecules have also been reported.[11,12]

In potential laser applications, high excited-state densities are necessary; this should be feasible by electron beam pumping.[13] In this letter, as a preliminary step towards the development of a rare-gas alkali ionic excimer laser, we report the observation of the emission spectra from electron beam pumped $(XeRb)^+$ at 164 nm and $(KrRb)^+$ at 133 nm.

The apparatus used in this work, as shown in Fig. 1, is similar to that described previously.[14] The electron beam supplied by a modified[15] Febetron 706 had a peak current of 4.5 kA, a beam diameter of 1.8 cm, a pulse width of 3 ns (full width at half maximum), and an electron particle energy of 500 keV. The electron beam, which is confined by an externally applied 1.5 kG axial magnetic field (nonuniformity less than 2 %), was passed through the anode foil and a drifting chamber of 15 cm length filled with low-pressure helium, and entered into a hot Rb vapor cell longitudinally, which was separated from the drifting section by a Kapton foil. The cell had a diameter of 4.5 cm, a total length of 100 cm, and an active length of 55 cm determined by the distance of the cooling coils in where the alkali metal was liquefied and transferred back to the cell. The fluorescence from the active zone of the oven cell was collected by a 10 cm focal length LiF lens and focused onto the entrance slit of a 0.2 m VUV spectrometer. The spectrum was analyzed with a spectrum multichannel analyzer (SMA) composed of a model IRY-512 detector (Princeton Instrument Inc.) which was in combination with a sodium salicylate scintillator and an optical imaging system. The spectral resolution of the SMA system was 0.12 nm/channel, which used a 1200 groves/mm grating. In most experiments the total emission of one shot was registered by gating the SMA with 0.5 μs.

To initiate the experiments, the cell was loaded with about 10 g of Rb under as argon atmosphere, after evacuation to 10^{-4} Torr, filled with xenon or krypton, and an Ar/Xe or Ar/Kr mixture. The vapor pressure of Rb was varied from 1 to 20 Torr by varying the temperature from 300 to 430 °C. The densities of the alkali vapors were estimated from vapor pressure curves[16] and the cell temperature.

Figure 2(a) shows a VUV emission spectrum observed by the electron beam excitation of an Xe/Rb vapor mixture. The xenon pressure was 100 Torr and the cell temperature was 390 °C, corresponding to an Rb vapor pressure of 10 Torr. An approximate continuum structure was observed, which was attributed to the $(XeRb)^+$ ionic excimer fluorescence in the previous study.[6] The spectrum exhibits one 4-nm-wide peak entered at 164 nm and a weak feature from 160 to 150 nm, which agrees approximately with the position of the spectral features observed in Refs. 6 and 7. Measurements also included the 170 nm region where Xe_2^* excimer emission was expected. In this region, the Xe_2^* emission was observed at room temperate and small rubidium pressures. For Xe pressures below 100 Torr and for alkali pressures above 4 Torr, the Xe_2^* signal is completely quenched by the presence of alkali vapor.

The measured VUV spectrum from the electron beam excited $(KrRb)^+$ is shown in Fig. 2(b). The krypton pressure was 100 Torr and the Rb vapor pressure was 8 Torr. The spectrum exhibits a main peak centered at 133 nm, which is slightly shorter than the position of the spectrum observed in ion beam excitation.[6] In addition, the weak Kr_2^* emission band at 145 nm was also present at low alkali pressures.

The VUV emission of the $(XeRb)^+$ or $(KrRb)^+$ was also observed when argon or helium was used as the buffer gas, but its intensity decreased with increasing the helium or argon pressure within the pressure region used in the present experiment, especially for the helium buffer gas. In fact, the strongest emission was observed in mixtures of xenon and krypton with Rb vapor without buffer gases. The main features of the observed spectrum did not change under different conditions except that the spectra showed some variations at higher temperatures due to the self-absorption of the Rb vapor or rare-gas-Rb molecules.

In order to show a comparison of the experimental results with the theory, we calculated Franck–Condon factors for the $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ transition of the $(XeRb)^+$ and $(KrRb)^+$. In the calculations, the *ab initio* potentials of the rare-gas potassium[17] have been used with a modifica-

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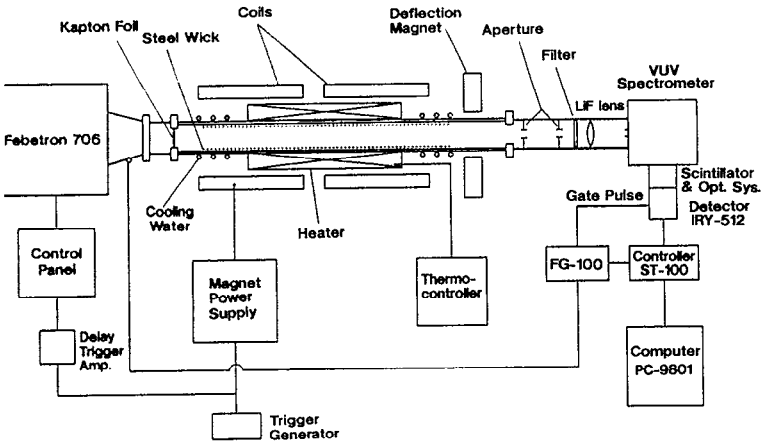

FIG. 1. Schematic diagram of the experimental apparatus.

tion of the transition energy by 0.164 eV,[18] to take into account the difference in the ionization potential of Rb and K. The result shows that emissions are almost due to the transitions to the larger internuclear separation region of the ground $1^1\Sigma^+$ state where the potential curve is nearly flat, especially for the lower vibrational levels of the $2^1\Sigma^+$ state. Figures 3(a) and 3(b) show simulated spectra of the $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ emissions of the $(XeRb)^+$ and $(KrRb)^+$ by taking into account the lower ten vibrational levels of the upper state. The population distribution of the vibrational states was assumed to be nonthermal and a linear surprisal distribution[19] was used. It was clearly exhibited that the $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ transition has a main peak at 166 nm with a blue-shaded quasi-continuous feature for $(XeRb)^+$ and a similar continuum centered at 137 nm for $(KrRb)^+$. They are in good agreement with the observed results in spectral shapes. The difference in transition wavelength for $(KrRb)^+$ is due to an approximate potential and an underestimation of the $Kr(^1S)$–$Kr^+(^2P)$ ionization energy in the *ab initio* calculation.[17]

By comparing Figs. 2(a) and 2(b) with Figs. 3(a) and 3(b), the observed 164 and 133 nm bands can be assigned to the $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ transition of $(XeRb)^+$ and $(KrRb)^+$ molecular ions, respectively. One can see that the observed fluorescence spectra in Fig. 2 should consist of many transitions originating from various vibrational levels of the $2^1\Sigma^+$ state, because of a nonselective excitation by the electron beam.

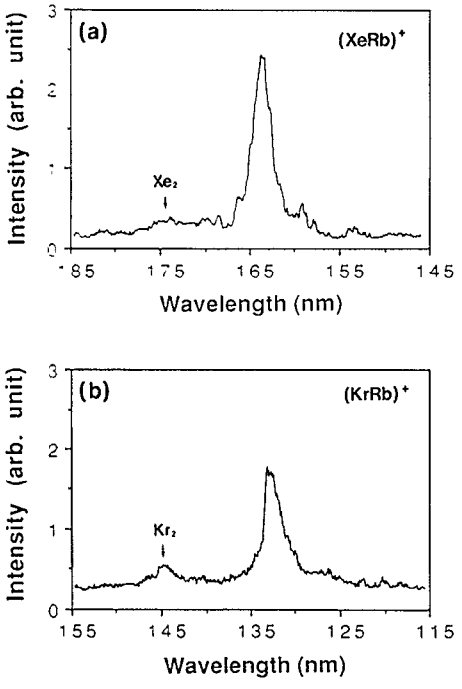

FIG. 2. (a) Emission spectrum in the spectral region from 145 to 185 nm for electron beam excited Xe/Rb mixture. The cell temperature: 390 °C and the xenon gas pressure: 100 Torr. (b) Emission spectrum in the spectral region from 115 to 155 nm for electron beam excited Kr/Rb vapor mixture. The cell temperature: 375 °C and the krypton gas pressure: 100 Torr.

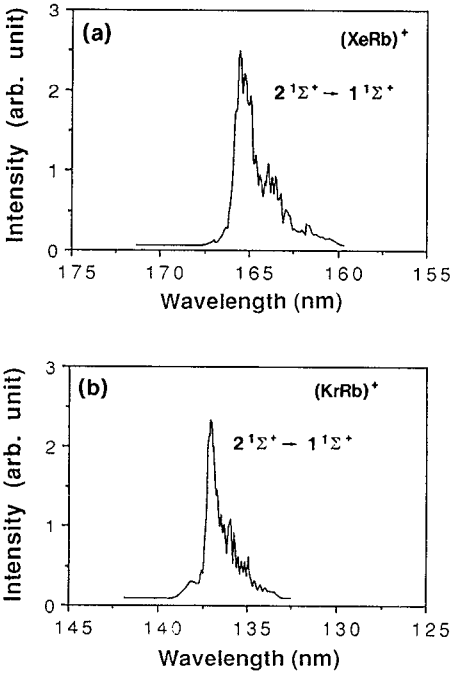

FIG. 3. Simulated spectra for the $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ transition of (a) $(XeRb)^+$ and (b) $(KrRb)^+$ by using the potential curves given in Ref. 17 with the modification of the transition energy, and assumed a linear surprisal distribution in Ref. 19.

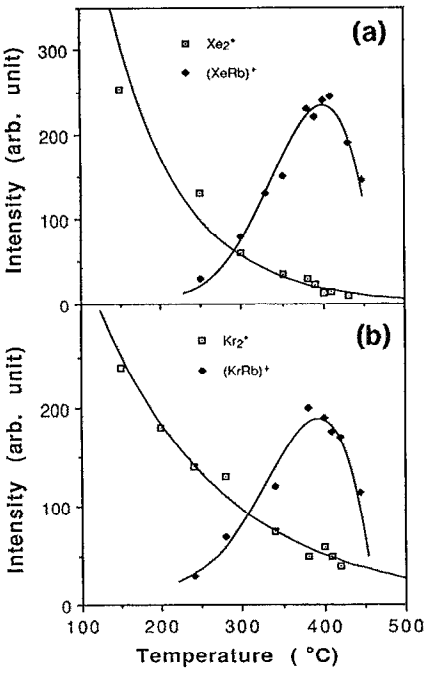

FIG. 4. Observed temperature dependencies of the fluorescences of (a) $(XeRb)^+$ and (b) $(KrRb)^+$ ionic quasiexcimers.

Figure 4 shows temperature dependencies of the intensities of (a) 164 nm band of $(XeRb)^+$ and (b) 133 nm band of $(KrRb)^+$ observed in the range of 300–450 °C (corresponding to the Rb vapor pressure of 1–20 Torr). VUV emissions were not present at the lower temperatures. The maximal intensities of the fluorescences were observed at 400 °C for $(XeRb)^+$ and 380 °C for $(KrRb)^+$, which correspond to about 10 and 8 Torr of Rb vapor pressures, respectively. On increase in the Rb density caused an increase in the absorption of the radiation by the Rb vapor and the fluorescence intensity decreases with increase of Rb pressure. From Figs. 4(a) and 4(b) one can see that the higher population density is yielded, and this can be qualitatively supported by the observation that the $(XeRb)^+$ and $(KrRb)^+$ fluorescence signals are comparable to the Xe_2^* and Kr_2^* signals in the unheated cell under the same pumping conditions.

The formation and radiative decay of $(XeRb)^+$ and $(KrRb)^+$ molecules are expected to proceed by the following reactions:

$$Rg + e \rightarrow Rg^+ + 2e, \tag{1}$$

$$Rg^+ + \mathrm{Rb} + M \rightarrow Rg^+\mathrm{Rb} + M, \tag{2}$$

$$Rg^+\mathrm{Rb} \rightarrow Rg + \mathrm{Rb}^+ + h\nu, \tag{3}$$

where Rg is Xe or Kr and M is either Xe and Rb or Kr and Rb. The formation process (2) of the ionic molecules is more effective than the corresponding process in mixtures of rare gases with halogens or oxygen. This conclusion is drawn from the identity of the electronic structures of the rare-gas ions and halogen atoms which interact very rapidly with alkali metals. It is also supported by the recent *ab initio* calculation for the electronic states of the rare-gas-alkali molecules.[12,17]

The reaction[20] of the ionic molecules Rg_2^+ with alkali atoms, $Rg_2^+ + A \rightarrow Rg^+A + Rg$, which is an analog of the "harpoon" reaction between alkali metals and halogens, is expected to be unlikely because the depth of the potential well of Rg^+A is not greater than that of Rg_2^+.[11,12,17]

For the three-body formation rates of Ne^+Na and Xe^+Cs which are analogous to reaction (2), the rate coefficients in the range of $5\times10^{-28}\sim5\times10^{-29}$ cm^6 s^{-1} are proposed in Refs. 20 and 21. Our estimates for the formation rate coefficient of Rg^+Rb are consistent with the lower limit of this range. This yields a formation rate for Rg^+Rb of the order of 10^{21} cm^{-3} s^{-1} in the present experiment. This value should be further increased with increasing the rare-gas pressure and input energy of electron beam.

In conclusion, the emissions of the rare-gas alkali ionic excimer species produced through reactive kinetics have been observed by electron beam excitation. Judging from the results of the recent *ab initio* calculation,[17] the observed diffuse emissions centered at 164 and 133 nm can be assigned to the $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ transition of $(XeRb)^+$ and $(KrRb)^+$ ions, respectively.

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