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VUV spectra from the krypton-fluoride ionic excimer

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Abstract. New continuous VUV radiation near 148 nm was observed from $Kr/NF_3/He$ and $Kr/F_2/He$ mixtures under X-ray excitation from a laser-produced plasma. Theoretical and experimental analysis shows that the continuum can be attributed to the transition of the ionic excimer $Kr^{2+}F^-$.

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The generation of short-wavelength laser radiation in the VUV (Vacuum UltraViolet) region below 200 nm is an attractive subject because of its potential applications in many fields such as VUV/XUV laser spectroscopy, laser dissociation, photolithography, and surface science. Intensive efforts have been made to develop lasers at these wavelengths, but only a few kinds of lasers were worked out, such as rare-gas-halide excimer lasers, rare-gas excimer lasers, and the molecular fluorine laser. To extend the laser emission to the shorter-wavelength region, Sauerbrey and Langhoff [1] and Basov et al. [2] proposed the concept of ionic excimers, which have the isoelectronic structure of neutral molecules or excimers, respectively. Since the first proposal in 1985 the existence of more than ten kinds of ionic excimers was verified by experiments, including rare-gas-alkali ionic excimers, rare-gas ionic excimers, and alkali-halide ionic excimers, which yielded radiation between 100–200 nm [3–6]. Recently, optical gain on such a system was reported [7].

The ionic-excimer systems have the advantages of short wavelengths, bound–free transitions, and high gain; so, they are promised to be potential candidates of tunable VUV/XUV laser media [1, 2]. In the present paper, a new kind of ionic excimer, $Kr^{2+}F^-$, which decays by emission near 148 nm, is investigated experimentally for the first time.

1 Theoretical considerations

Rare-gas-halide ionic excimers were first theoretically predicted by Sauerbrey and Langhoff [1]. They employed the analogical method of isoelectronic structure and the Rittner model to calculate the potential curves of ionic excimers. The rare-gas-halide ionic excimer $Rg^{2+}X^-$ is isoelectronic with halide molecules X^+X^-, and may yield radiation with wavelengths shorter than that of halogen molecules. The transition processes can be described as:

$$Rg^{2+}F^- \rightarrow Rg^+F + h\nu$$
$$\rightarrow Rg^+ + F.$$

For the krypton-fluoride ionic excimer $Kr^{2+}F^-$, the transition wavelength was calculated to be 122 nm in [1].

Further calculations were also performed by some of the authors of this paper [8, 9]. In those works, the potential curves and transition parameters were calculated with the aid of the improved Rittner-potential model, which involved parameters revised by an ab initio program (Gaussian 80)

$$V(R) = q_1 q_2 R^{-1} - \frac{1}{2}(q_2^2\alpha_1 + q_1^2\alpha_2)R^{-1} - CR^{-6} + A\exp(-R/\rho),$$

where R is the nuclear distance between ions, q_i the charge of the ion, α the average ionic polarizability, A and ρ repulsive parameters and C the Van der Waals constant.

The calculated potential curves and transition parameters of the ionic excimer $Kr^{2+}F^-$ are shown in Fig. 1 and Table 1.

2 Experiments

Ionic excimers have been studied with ion beams, electron beams and X-rays from Laser-Produced plasmas (LPX) [3–6]. Though ion beams and electron beams are powerful pumping methods for the generation of ionic excimers, LPX is more convenient for spectroscopic purposes.

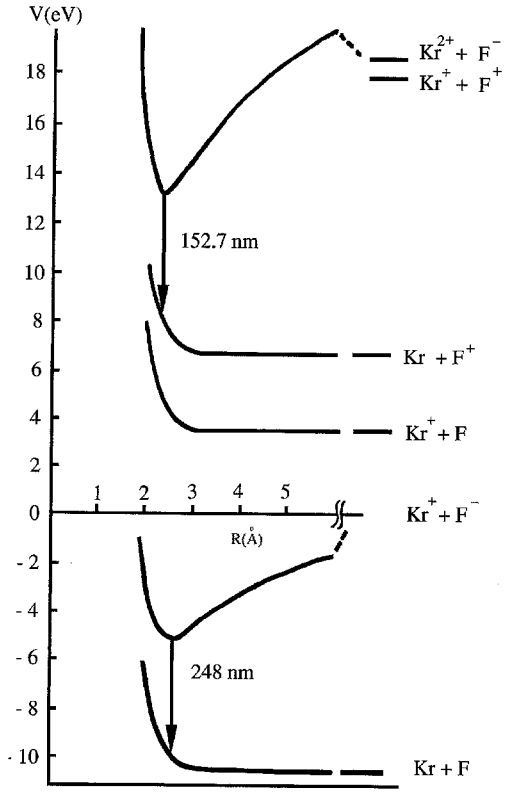

Fig. 1. Potential curves of the Kr/F system

Table 1. Theoretical results of the transition parameters of the ionic excimer $Kr^{2+}F^-$

Wavelength	Band width	Lifetime	Stimulated-emission cross section
152.7 nm	12.1 nm	0.45 ns	2.36×10^{-17} cm^2

Several groups have employed the LPX as an efficient excitation source to get inner-shell-excited atoms or photoionized ions of energies up to 60 eV [10].

The experimental setup is shown in Fig. 2a. A beam from a *Q*-switched Nd: YAG laser was focused onto a Ta target inside a vacuum-sealed chamber. The output beam of the Nd: YAG laser had a divergence of 1 mrad or less. The target was magnetically driven to provide a fresh surface for every shot of the laser and maintain the vacuum-sealed state of the chamber at the same time. A group of lenses without aberrations were employed to get a focusing point of 0.295 mm in diameter on the target. The diameter is calculated assuming a divergence of 1 mrad of the laser beam, which coincides with the measured value. The effective laser energy impinging on the surface of the target is about 500 mJ. Considering a pulse-duration of 15 ns, the power density on the target was about 4.9×10^{10} W/cm^2. The soft X-ray spectra from the laser-produced plasma in the experiments are shown in Fig. 2b. It can be seen that there is strong radiation within 30–70 nm peaking near 55 nm. The LPX pumped the surrounding gas mixtures of $Kr/NF_3/He$ or $Kr/F_2/He$. The fluorescence from the gas mixture was detected by

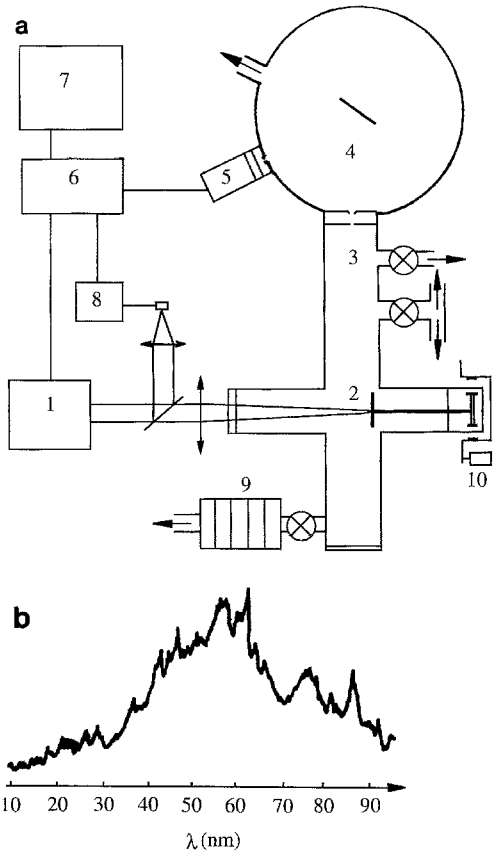

Fig. 2. a Experimental setup (*1.* YAG laser; *2.* Ta target; *3.* LiF window; *4.* monochromator; *5.* scintillator PMT; *6.* boxcar; *7.* recorder; *8.* optical switch; *9.* gas fitters; *10.* motor). **b** Soft X-ray spectrum from laser-produced plasma ($I = 4.9 \times 10^{10}$ W/cm^2)

a PhotoMultiplier Tube (PMT) behind a scintillator through a LiF window and a 0.5 m monochromator (Acton VSN-515). The signal from the PMT was averaged by a boxcar integrator and recorded by a chart recorder. In order to avoid the time drift of the trigger signal from the Nd: YAG laser and get accurate synchronization and time delay between the injected laser and the sampling gate of the boxcar, an optical trigger was used before the incident laser. The pump laser worked at a repetition rate of 5 Hz. The number of shots averaged in the range of 140–155 nm was 2340 at a chart recorder speed of 50 cm/h.

It was found that some radiation from the LPX may disturb the detection of fluorescence from the gas, which is mainly due to recombination radiation from the plasma. Two techniques were employed to exclude the recombination disturbance of the plasma. First, the optical axis of the monochromator-entrance slit was carefully positioned to minimize the recombination radiation of the plasma and maximize the received fluorescence from the gas mixtures. Another method to discriminate against recombination radiation from the plasma was to select the position and width of the sampling gate of the boxcar. The recombination radiation from the Ta plasma usually occurs about 200 ns after the arrival of the laser pulse [3]. So, a 50 ns gate as well as an accurate and adjustable time delay were chosen for the boxcar.

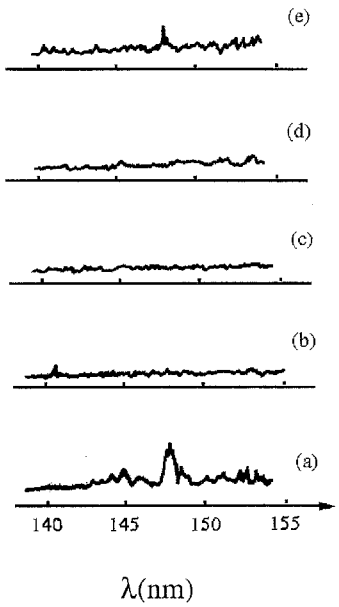

Fig. 3a–e. Emission spectra in mixtures of $Kr/NF_3/He$ under LPX excitation: **(a)** Kr 0.3 kPa/NF_3 0.2 kPa/He 1.4 kPa; **(b)** vacuum; **(c)**He 1.4 kPa/NF_3 0.2 kPa; **(d)** Kr 0.3 kPa; **(e)** Kr 0.3 kPa/NF_3 0.2 kPa/He 1.4 kPa

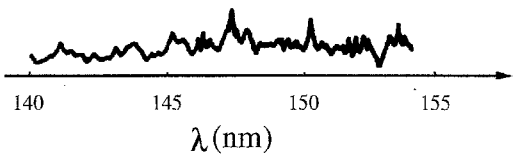

Fig. 4. Emission spectrum in the mixture of Kr 0.7 kPa/F_2 0.1 kPa/He 1.3 kPa

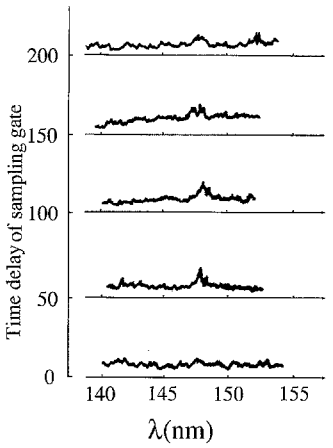

Fig. 5. Time evolution (ns) of radiation from $Kr^{2+}F^-$ under LPX excitation

To ensure that the incident laser is focused exactly onto the surface of the target, adjustment was made for every set of measurements, according to visual inspection through the side-window of the chamber and the detected LPX spectra. The slit width of the monochromator used in the experiments was 250 μm, corresponding to a spectral resolution of 0.4 nm.

In the mixtures of Kr 0.3 kPa/NF_3 0.2 kPa/He 1.4 kPa, emission spectra were obtained under the excitation of LPX, as shown in Fig. 3a. It can be seen that there appeared a continuous spectrum from 142 nm to 150 nm, which peaked near 148 nm. Emission spectra excited by LPX for other conditions such as in vacuum (Fig. 3b), in the mixtures of NF_3 0.2 kPa/He 1.4 kPa(Fig. 3c) and in the rare gas Kr 0.3 kPa (Fig. 3d), were also detected, and the continuous emission near 148 nm was not present. When the chamber was refilled with gas mixtures of Kr 0.3 kPa/NF_3 0.2 kPa/He 1.4 kPa, the continuous emission reappeared, but with less intensity (Fig. 3e), which was caused by the failure of the target. The strong emission near 148 nm appeared again after changing the target. It was also found that there exists a weaker peak near 145 nm. Similar spectra were present in $Kr/NF_3/He$ mixtures of different partial pressures. The measured band width was about 2 nm for the highest peak near 148 nm.

In the mixtures of $Kr/F_2/He$, the continuous emission near 148 nm was also observed. A typical spectrum in mixtures of Kr 0.7 kPa/F_2 0.1 kPa/He 1.3 kPa is shown in Fig. 4. It may be concluded that this continuum is due to the transition of the ionic excimer $Kr^{2+}F^-$, and is in good agreement with the theoretical results in [8, 9].

In order to examine the temporal evolution of the radiation from the ionic excimer $Kr^{2+}F^-$, the sampling gate of the boxcar in the experiment was varied by 50 ns for each step, as shown in Fig. 5. Because the input impedance of the boxcar was chosen as 10 kΩ to increase the signal amplitudes and was not matched to the output impedance of the PMT, the tails of the pulse signals were extended. But the rising edges of the signals, that is, the time sequences of the signals, were changed less. It can be seen from Fig. 5 that the radiation of the ionic excimer $Kr^{2+}F^-$ occurred about after 50 ns, and became stronger near 100 ns, after the arrival of the injected laser pulse, while the recombination radiation from the LPX appeared about 200 ns after the arrival of the laser pulse.

3 Discussion

The ionic excimer $Kr^{2+}F^-$ is isoelectronic with the neutral halogen molecule Br^+F^-. The excited triplet state $D\ ^3\Pi_g$of the heteronuclear halogen Br^+F^- is correlated with ions $Br^+(^3P_2)$ and $F^-(^1S_0)$ in the form of ionic bonding. The lower states correlated to the atoms $Br(^2P^0)$ and $F(^1P^0)$ are $^{1,3}\Sigma^{\pm}$, $^{1,3}\Pi$ and $^{1,3}\Delta$. The transition from $D\ ^3\Pi_g$ to $A\ ^3\Pi_u$ yields radiation near 354 nm. In the case of the ionic excimer $Kr^{2+}F^-$, the positive halogen ion Br^+ in Br^+F^- is substituted by a doubly charged positive ion of the rare gas Kr^{2+}. In analogy with the halogen molecules, the $Kr^{2+}F^-$ excimers will decay through electron-exchange transition to the state of Kr^+F. Because of the much higher ionization energy of the positive ion Kr^+ than that of Br, these transitions may yield photons of higher energy, or radiation at shorter wavelengths.

The wavelength of the radiation observed from the ionic excimer $Kr^{2+}F^-$ is a little shorter than our calculated value of 152.7 nm, although in rather good agreement.

The distortion is mainly due to the calculation error of the polarizabilities of the ions.

The shapes of the spectra of the ionic excimer $Kr^{2+}F^-$ changed a little in the mixtures of $Kr/NF_3/He$ and $Kr/F_2/He$, and at different sampling times, which may be due to different fine structures. These could further reveal the kinetics of the ionic excimers. The peaks of different intensities near 145 nm and 148 nm may come from the transitions between states of different vibrational quantum number, which will be discussed somewhere else.

Considering the relation

$$\sigma \propto 1/\Delta\lambda$$

and the measured band width of 2 nm, which is 6 times less than that calculated, the stimulated cross section may be 6 times larger than the theoretical result, that is to say $\sigma \approx 10^{-16}\,cm^2$. In our experiments, the density of Kr and NF_3 is $4.2 \times 10^{15}\,cm^{-3}$ and $2.4 \times 10^{15}\,cm^{-3}$, respectively. Under the excitation with LPX, the negative ions F^- are produced through the electron attachment of NF_3 or F_2:

$$NF_3 + e \rightarrow NF_2 + F^-,$$

or

$$F_2 + e \rightarrow F + F^-.$$

So, the density of F^- can be of the order of $10^{15}\,cm^{-3}$. The peak photoionization cross sections for Kr and Kr^+ are about $10^{-17}\,cm^2$ and $10^{-19}\,cm^2$, respectively, in the region 30–80 nm. The production of Kr^{2+} by photoionization may be 10^{14}–$10^{15}\,cm^{-3}$. The three-body recombination coefficient can be estimated by [11]

$$\alpha_{RE} = \frac{4}{3}\pi R^3 N \bar{v}_{\pm}\left(\frac{1}{\lambda_+} + \frac{1}{\lambda_-}\right),$$

where $\bar{v}_{\pm}$ is the mean relative speed of positive and negative ions, $\lambda_{\pm}$ the mean free distance of positive and negative ions, and $R = \frac{2}{3}\left|\frac{q_+ q_-}{kT}\right|$, and $q_{\pm}$ are the charges of positive and negative ions. The three- body recombination in the production processes of netrual excimers was estimated to be $10^{-25}\,cm^6\,s^{-1}$ [12]. In the case of ionic excimers, the charges or the R value increases by a factor of 2, and the mean relative speed increases, the mean free distance decreases, so that α_{RE} increases. If we chose the α_{RE} as $10^{-24}\,cm^6\,s^{-1}$, the population inversion of $Kr^{2+}F^-$ from three-body recombination

$$Kr^{2+} + F^- + M \rightarrow Kr^{2+}F^- + M$$

can be of the order of 10^{14}–$10^{15}\,cm^{-3}$, which may yield a gain coefficient of 1–10% cm^{-1} in this case. Stimulated emission may be obtained under appropriate conditions.

In conclusion, the VUV radiation from the ionic excimer $Kr^{2+}F^-$ was observed experimentally for the first time. The results are in good agreement with the formerly calculated ones. Further efforts are being made to obtain more information about this system.

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References

1. R. Sauerbrey, H. Langhoff: IEEEJ. QE-**21**, 179 (1985)
2. N. G. Basov, M. G. Voitik, V. S. Zuev, V. P. Kutakhov: Soviet J. Quantum Electron. **15**, 1455 (1985)
3. S. Kubodera, L. Frey, P. J. Wisoff, R. Sauerbrey: Opt. Lett. **13**, 446 (1988)
4. F. Steigerwald, H. Langhoff, W. Hammer: J. Chem. Phys. **88**, 7376 (1988)
5. P. S. Millar, G. Warwar, P. J. Wisoff, R. Sauerbrey: Appl. Phys. Lett. **55**, 2176 (1989)
6. M. Schumann, H. Langhoff: J. Chem. Phys. **91**, 5440 (1989)
7. Cs. Toth, J. F. Young, R. Sauerbrey: Opt. Lett. **18**, 2120 (1993)
8. Q. Wang, Y. Yao, S. Sun, Z. Ma: 5th Interdisciplinary Laser Science Conf. (ILS-V), Stanford, CA (1989)
9. Q. Wang, Y. Yao, C. Zhou, J. Liu, S. Sun, Z. Ma: High Power Laser Particle Beam **4**, 397 (1993) (in Chinese)
10. R. G. Caro, J. C. Wang, J. F. Young, S. E. Harris: Phys. Rev. A **30**, 1407 (1984)
11. M. R. Flannery, T. P. Yang: Appl. Phys. Lett. **32**, 327 (1978); ibid. p. 356
12. C. K. Rhodes (ed.): *Excimer Lasers*, 2nd edn., Topics Appl. Phys., Vol. 30 (Springer, Berlin, Heidelberg 1984)