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# Ion-core switching in high-lying Rydberg states of XeKr

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【Introduction】 In the previous studies, the Rydberg states of XeRg (Rg = Ne, Ar, Kr) have been investigated in the energy region below 80,000 $cm^{-1}$, where only the Rydberg levels of Xe atom exist, and the interatomic potentials for XeRg and the predissociation dynamics were discussed [1]. However, no information has been clarified so far regarding the highly excited Rydberg state of XeRg in the energy region above 80,000 $cm^{-1}$ and below its ionization threshold, where the Rydberg states of XeRg correlating to both the Rydberg levels of Xe and the Rydberg levels of Rg atoms are closely located energetically, and therefore, the predissociation involving both of the Rydberg series is expected to proceed in a complex manner.

In the present study, the interatomic potentials and predissociation dynamics of the highly excited Rydberg states of XeKr are studied for the first time in the energy region (93,000-97,500 $cm^{-1}$) below the ionization threshold by measuring the optical-optical double resonance (OODR) excitation mass spectra of $^{132}Xe^+$ and $^{84}Kr^+$, produced by the ionization of $Xe^{**}$ and $Kr^{**}$ fragments formed via the predissociation from the high Rydberg states $Xe^{**}Kr$, where the Rydberg states of both Xe and Kr atoms coexist. The evidence of the ion-core switching was identified, i.e. not only (XeKr)** → Xe** + Kr but also (XeKr)** → Xe + Kr** proceeded.

【Experiment】 XeKr was produced by a supersonic expansion of a mixed gas of Xe, Kr, and He into a vacuum chamber through a pulsed valve. The first dye laser ($\omega_1$: 38,967.16 or 38,996.06 $cm^{-1}$) was tuned to the two-photon resonant vibrational levels of $v^*$ =0 ($2\omega_1$=77,934.32 $cm^{-1}$) or $v^*$ =2 ($2\omega_1$= 77,992.12 $cm^{-1}$) of an intermediate electronic excited state of $Xe^*Kr$, correlated to the $Xe^*$ $6p[5/2]_2$ state. The second dye laser ($\omega_2$: 13,000~20,000 $cm^{-1}$) further excited the $Xe^*Kr$ to high-lying Rydberg states $Xe^{**}Kr$ in the energy range 93,200-97,400 $cm^{-1}$. The fragment atoms of both $Xe^{**}$ and $Kr^{**}$ were probed by ionization using $\omega_2$ and $\omega_1$ lasers,

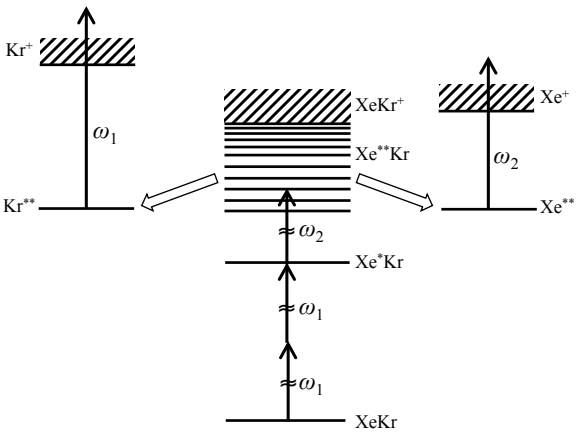


Fig. 1 A schematic diagram of the excitation process of XeKr. The dissociation fragments $Xe^{**}$ and $Kr^{**}$ from the high Rydberg states $Xe^{**}Kr$ are ionized by the laser $\omega_2$ and the laser $\omega_1$, respectively, to produce $Xe^+$ and $Kr^+$ ions.

respectively. The OODR excitation spectra ofboth $^{132}Xe^+$ and $^{84}Kr^+$ are recorded using a time-of-flight mass spectrometer by scanning the wavelength of the second laser (see Fig. 1).

【Result and Discussion】 As a result of the analysis of the OODR spectra, it is assigned that the observed two Rydberg series are correlated to the Xe $n$s[3/2]$_1$ states ($10 \le n \le 28$) and Xe $n$d[7/2]$_3$ states ($8 \le n \le 27$), respectively, and converge to the $Xe^+Kr$ A $^2\Pi_{3/2}$ state. The interatomic potential parameters and the quantum defects of the high Rydberg states are evaluated (not shown). The spectroscopic dissociation energy $D_0^{**}$ of the high Rydberg states for $s$-series shows notable irregularity at $n$ =10 due to a perturbation from Xe$^{**}$ 7s'[1/2]$_1$ state correlating to the Kr ($^1S_0$) + $Xe^+$ ($^2P_{1/2}$) limit (not shown).

In the time-of-flight mass spectra, atomic ions of both $^{132}Xe^+$ and $^{84}Kr^+$, produced by ionizing Xe$^{**}$ and Kr$^{**}$ fragments formed via the predissociation from the high Rydberg states Xe$^{**}$Kr, are identified, showing the evidence of ion-core switching, i.e. both (XeKr)** → Xe** + Kr and (XeKr)** → Xe + Kr** occurs (see Fig. 2). Moreover, it is found that $^{84}Kr^+$ peaks appear in the same energy position as $^{132}Xe^+$ peaks below 96,500 cm$^{-1}$, while $Kr^+$ peaks dominate above 96,500 cm$^{-1}$.

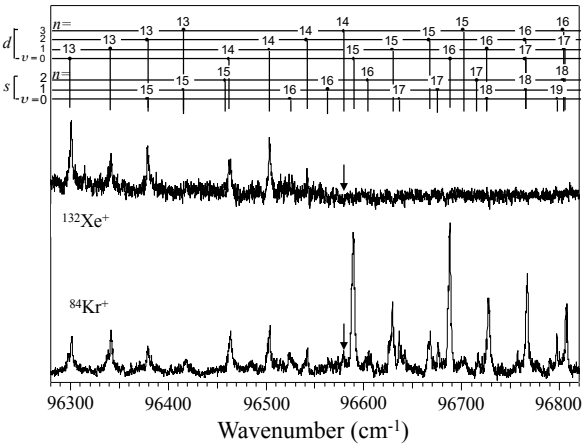


Fig. 2 The OODR mass spectra for $^{132}Xe^+$ and $^{84}Kr^+$ in an energy range 96,280-96,820 cm$^{-1}$ measured when XeKr was excited to $\upsilon^*$ =0 of the intermediate excited state of Xe$^*$Kr. The $^{132}Xe^+$ signal disappears, i.e. the complete ion core switching occurs, at $\upsilon^*$ =3 vibrational level of Xe$^{**}$Kr (96,578.5 cm$^{-1}$) as indicated by an arrow.

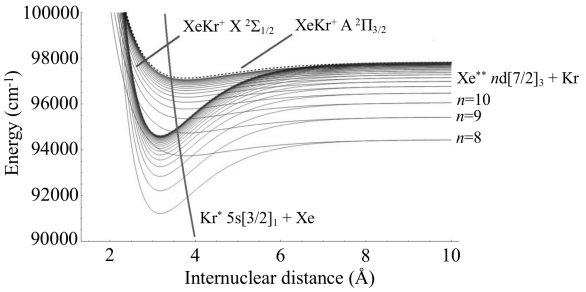


Fig. 3 The calculated potential energy curves (PECs) for Rydberg states of the A $^2\Pi_{3/2}$ ion core and the X $^2\Sigma^+_{1/2}$ ion-core. The PEC correlating to Xe + Kr 5s[3/2]$_1$ most likely intersects the two Rydberg-series around 3.5 Å.

From the analysis of kinetic energy release observed in the mass peak split of the $^nKr^+$ signal in the TOF spectra, it can be concluded that ion core switching occurs because of the interaction between bound potentials of highRydberg states Xe$^{**}$Kr converging to the A $^2\Pi_{3/2}$ state and a repulsive potential of XeKr$^{**}$ correlating to the Xe ($^1S_0$) + Kr$^{**}$ (5s[3/2]$_1$) limit (81,067.3 cm$^{-1}$).

In order to gain insight into the possible non-adiabatic processes being responsible for the ion-core switching process, we carried out theoretical calculations, which show that the observed energy dependence of the ion core switching ratio can be explained by the possible mechanism of population transfer from the high-lying Rydberg states of the A $^2\Pi_{3/2}$ ion core to that of the X $^2\Sigma^+_{1/2}$ ion core (see Fig. 3).

[1] L. Piticco, F. Merkt, Journal of Molecular Spectroscopy **37**, 284 (2013).