Ion-core switching in Rydberg series of XeKr

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ABSTRACT

We investigate spectroscopic and dynamical properties of XeKr in the high Rydberg states by optical-optical double resonance (OODR) mass spectroscopy. We excite XeKr in the electronic ground state by the first laser pulse (256.6 and 256.4 nm) via two-photon absorption to the vibrational levels of $\upsilon^*=0$ (77,934.32 cm^{-1}) and $\upsilon^*=2$ (77,992.12 cm^{-1}) of an intermediate electronic excited state Xe*Kr correlating to Xe* 6p[5/2]$_2$ and excite Xe*Kr by the second laser pulse (500-770 nm) via one-photon absorption to the high Rydberg states Xe**Kr in the energy range of 93,200-97,400 cm^{-1}, converging to the first excited state A $^2\Pi_{3/2}$ of XeKr$^+$ correlating to the Kr ($^1S_0$) + Xe$^+$ ($^2P_{3/2}$) limit. In the time-of-flight mass spectra, atomic ions ^{132}Xe$^+$ and ^{84}Kr$^+$ produced by the ionization of Xe** and Kr** fragments formed via the predissociation of Xe**Kr are identified, showing the evidence of the ion-core switching, i.e. Kr** is produced in the course of the predissociation of Xe**Kr. By monitoring either ^{132}Xe$^+$ or ^{84}Kr$^+$, we scan the wavelength of the second laser in the corresponding energy range of 93,200-97,400 cm^{-1}, and identified the two Rydberg series of Xe**Kr, that is, Xe**(nd[7/2]$_3$)Kr ($8 \le n \le 27$) and Xe**(ns[3/2]$_1$)Kr ($10 \le n \le 28$), converging to the A $^2\Pi_{3/2}$ state of XeKr$^+$. From the OODR spectra, we determine the interatomic potential parameters and the quantum defects of the high Rydberg states, and show that the spectroscopic dissociation energies D_0^{**} of the high Rydberg states for s-series exhibit a notable irregularity at n=10 originating from the perturbation from Xe** 7s'[1/2]$_1$ state correlating to the Kr ($^1S_0$) + Xe$^+$ ($^2P_{1/2}$) limit. From the analysis of the kinetic energy release determined from the split peak of the ^{n}Kr$^+$ (n = 80, 82, 83, 84, and 86) signal in the TOF spectra, we conclude that the ion core switching occurs because of the interaction between bound potentials of the high Rydberg states of Xe**Kr converging to the A $^2\Pi_{3/2}$ state of XeKr$^+$ and the repulsive potential of XeKr** correlating to the Xe ($^1S_0$) + Kr** (5s[3/2]$_1$) limit. Moreover, we find that ^{84}Kr$^+$ peaks appear at the same energy positions as ^{132}Xe$^+$ peaks in the energy region below 96,500 cm^{-1}, while Kr$^+$ peaks dominate above 96,500 cm^{-1}. We interpret this variation of the branching ratio in the ion core switching in terms of the population transfer from the bound potentials of the high Rydberg states Xe**Kr converging to the A $^2\Pi_{3/2}$ state of XeKr$^+$ to those converging to the electronic ground X $^2\Sigma^+_{1/2}$ state of XeKr$^+$.

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1. INTRODUCTION

The highly excited Rydberg-states of homonuclear [@-@] and heteronuclear [@-@] rare gas dimers have been extensively studied in the past few decades spectroscopically and their interatomic potential energy curves (PECs) have been determined. The spectroscopic measurements have also revealed complex perturbation among the Rydberg state potentials, resulting in irregular level spacings [@-@], and the predissociation, resulting in the broadening of the spectral peaks[@-@] as well as in the formation of a rare gas atom in the Rydberg states [@-@].

Among the rare gas dimers, heteronuclear gas dimers such as XeKr is noteworthy.

Determination of the excited interatomic potentials of rare gas dimers contributes to our understanding of the chemical and physical processes occurring in rare gas electrical discharges and plasmas.

The earliest VUV absorption spectra of the homonuclear rare-gas dimer Xe_2 were measured by Freeman [1] and by Castex [2,3]. In the case of Xe_2, the spectroscopic parameters of the *ungerade* excited states, responsible for the emission in the Xe_2 excimer laser, correlating to 6s-[4], 6p,5d-[5] Rydberg levels of Xe atom have been investigated. The *gerade* Xe_2 excited states, correlating to 6s-[6,7], 6p-[6,7,8,9,10], 5d-[7,8,9,11,12,13,14], *n*f-(*n*=4-6)[15,16] Rydberg levels of Xe atom, have been also studied, providing information on the spectroscopic parameters and the symmetries of the corresponding potential energy curves (PECs). For example, complex predissociation mechanisms and perturbations in the 5d-manifold have been investigated using a velocity map imaging [14].

On the other hand, the earliest VUV absorption spectrum of the heteronuclear rare-gas dimer were measured by Castex [17] and by Freemam [18]. The first detailed spectroscopic analyses of excited states were accomplished later by Tsuchizawa [19], who resolved the vibrational band systems of jet-cooled XeRg (Rg = Ne, Ar, Kr) near Xe 6s[1/2] by exciting single-photon transitions with a tunable VUV laser generated by four-wave mixing in a nonlinear medium. Up to now, in the case of heterogeneous rare gas dimers XeRg (Rg=Ne, Ar and Kr), Rydberg states correlating to 6s-[20 , 21], 6s'-[19, 22 , 23 , 24], 6p-[24,25,26,27,28,29,30,31,32], and 5d-[27,30] Rydberg levels of Xe atom have been intensively studied. For example, in Rydberg states of XeRg correlating to the Xe $6s[3/2]_1$ level, an exchange interaction between a Rydberg electron and its ion core causes an unstabilization of an interatomic potential state and distorts its interatomic potential from that of its ion core [20,21]. In Rydberg states of XeAr correlating to the Xe 6s'$[1/2]_1$ level, a nonadiabatic interaction between Rydberg states causes an avoided crossing between their interatomic potentials [19,23]. The excited states of XeKr molecules in the range of Xe^* 6p$[5/2]_{2,3}$ have been investigated by measuring $^{m}Xe^{n}Kr^+$ and atomic ions $^{m}Xe^+$ and $^{n}Kr^+$ to extract precise data regarding excited states of XeKr molecules [31]. Recently, the rotationally resolved electronic spectra of the $C0^+$, $D1 \leftarrow X0^+$ transitions of KrXe have been studied to investigate structural and interaction parameters of $C0^+$ and D1 states by resonance-enhanced (1 + 1') two-photon ionization spectroscopy [24]. The predissociation dynamics affected by an interaction between the Rydberg states of XeAr has been studied with a tunable vacuum ultraviolet (VUV) laser [23], where the mass-resolved resonantly enhanced two photon ionization (RE2PI) excitation spectra of the $C1 \leftarrow X0^+$ band of XeAr in the energy region near the atomic transition of Xe 6s'$[1/2]_1 \leftarrow {}^1S_0$ were measured by monitoring the parent $^{132}Xe^{40}Ar^+$ ions and the fragment $^{132}Xe^+$ ions. From the analysis of the rotational structures of the $C1 \leftarrow X0^+$ vibronic bands, the existence of the two dissociation pathways from the C1 state was identified as the homogeneous predissociation and the heterogeneous predissociation. The avoided crossing between the potential curves of the C1 state and the repulsive same symmetry state results in the irregular vibrational quantum number dependence of the vibrational energy spacing and the rotational constants.

However, to the best of our knowledge all the preceding studies on Rydberg states of XeRg (Rg=Ne, Ar, Kr) have been conducted in an energy region below 80**,**000 cm^{-1}**,** where only the Rydberg levels of Xe atom exist**,** and the interatomic potentials for XeRg [19,20,21,22,24,25,26,27,28,29,30,32] and the predissociation dynamics [23, 31] were reported in detail. The predissociation channel in the Rydberg state of the XeRg in this energy region produces the excited state of the Xe atom and the ground state of the Rg atom [23,27,28,29,31]. No information has been so far clarified regarding the highly excited Rydberg state of the XeRg molecule in an energy region above 80**,**000 cm^{-1} and below its ionization threshold**,** where the atomic Rydberg-states of both rare gas components can be found. In such a highly-excited energy region, different PECs dissociating to different excited atoms can coexist and cross each other. Such PEC crossings might lead to predissociaton pathways, in which the molecule starts from a Rydberg-state with an ion-core corresponding to one of the rare gas atoms being ionized, but ends up dissociating through a Rydberg-states with an ion-core corresponding to the other rare gas atom being ionized. We call such a process ion-core switching.

In the present study, the interatomic potentials and predissociation dynamics of the highly excited Rydberg state of the XeKr molecules 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 ionizing Xe^{**} and Kr^{**} fragments formed via the predissociation from the high Rydberg states $Xe^{**}Kr$, where the Rydberg states of both the Xe and Kr atoms coexist. From the analysis of the OODR excitation mass spectra, the evidence of the ion-core switching, *i.e.*, Kr^{**} fragment production via the predissociation from the high Rydberg states $Xe^{**}Kr$, was identified. The interatomic potentials of the highly excited *d*- and *s*-Rydberg states of the XeKr molecule and the A $^2\Pi_{3/2}$ state of the $XeKr^+$ ion, to which observed Rydberg states converge, were evaluated.

II. Experiment

The experimental setup consists of a vacuum chamber, a pulsed molecular beam source to generate the jet-cooled XeKr molecules, a high-resolution reflectron mass spectrometer, and tunable UV (ω_1) and visible (ω_2) pulsed laser light sources [23]. A schematic diagram of the optical-optical double resonance (OODR) excitation process of XeKr is shown in Fig. l. XeKr molecules were produced by the supersonic expansion of a mixed gas of Xe, Kr, and He (Xe : Kr : He = 1 : 9 : 90) into the vacuum chamber through a pulsed valve (General Valve) with an orifice diameter of 0.2 mm. The molecular beam was skimmed and collimated by a skimmer (ϕ3 mm) located at 40 mm downstream from the pulsed valve. The background pressure in the vacuum chamber was maintained at $\sim 5\times10^{-5}$ Torr at a stagnation pressure of 5-8 atm.

The frequency doubled output (ω_1 : 38,967.16 or 38,996.06 cm^{-1}) of the first dye laser (Lambda Physik Scanmate), pumped by a Nd:YAG laser (Coherent Infinity 40-100), was tuned to the two-photon resonant vibrational levels of $\upsilon^*=0$ ($2\omega_1=77{,}934.32$ cm^{-1}) or $\upsilon^*=2$ ($2\omega_1=77{,}992.12$ cm^{-1}) of an intermediate electronic excited state of Xe^*Kr, correlated to the Xe^* $6p[5/2]_2$ state [29]. The output (ω_2 : 13,000~20,000 cm^{-1}) of the second dye laser (Lambda Physik FL3002) pumped by a XeCl excimer laser (Lambda Physik LPX205i) further excited the Xe^*Kr to high Rydberg states $Xe^{**}Kr$ in the energy range 93,200-97,400 cm^{-1}. The two lasers, ω_1 and ω_2, were counter propagated coaxially in opposite direction and perpendicular to the molecular beam, and focused by a *f*=300 mm lens and a *f*=800 mm lens, respectively. Temporal and spatial overlaps among the two lasers and the molecular beam operated at 10 Hz were secured at the laser-molecule interaction point during the measurements. Frequency calibration of the ω_2 laser was achieved by recording the optogalvanic spectrum of Ne in a Fe/Ne hollow cathode lamp. The frequency resolution of the ω_2 laser was estimated to be 0.30 cm^{-1}.

The fragment atoms of both Xe^{**} and Kr^{**} produced by the predissociation via the high Rydberg states $Xe^{**}Kr$ were probed by ionization using ω_2 and ω_1 lasers, respectively (see Fig. 1). The produced ions were extracted by a repeller into a high-resolution reflectron time-of-flight (TOF) mass spectrometer with a mass resolution of $m/\Delta M\sim1{,}100$ (Comstok RTOF201) and detected by two microchannel plate (MCP) detectors connected to a current preamplifier (Princeton Applied Research 115).

Figure 2(a) shows the typical TOF mass spectrum obtained when molecules were excited to the energy level of 96,687.6 cm^{-1}, which is later assigned to the $\upsilon^{**}=0$ vibrational level of the Xe**Kr correlating to Xe** 16d[7/2]$_3$. The ^{m}Xe^{+} (*m*=124 (<1 %), 126 (<1 %), 128 (1.9 %), 129 (26.4 %), 130 (4.1 %), 131 (21.2 %), 132 (26.9 %), 134 (10.4 %), 136 (8.9 %)) and ^{n}Kr^{+} (*n*=78 (< 1 %), 80 (2.3 %), 82 (11.6 %), 83 (11.5 %), 84 (57.0 %), 86 (17.3 %)) along with the isotopologues for the parent ^{m}Xe^{n}Kr^{+} were resolved from each other. In this study, to restrain the isotopic spectral congestion to a minimum, the OODR excitation mass spectra were obtained by monitoring the yields of the most abundant two fragment ions ^{132}Xe^{+} and ^{84}Kr^{+}, and the parent ion ^{m}Xe^{n}Kr^{+} with $m+n=216$, 15.3 % of which corresponds to ^{132}Xe^{84}Kr^{+}, by using a boxcar averager/gated integrator (Stanford Research Systems SR250). For the ^{n}Kr^{+} signals, the mass peak splittings due to a kinetic energy release (KER) during the dissociation event are clearly seen in Fig. 2(b) as will be discussed later in Section III-6..

III. Results and Discussion

1. Overall spectral features

Figures 3 and 4 show, respectively, the OODR excitation mass spectra of XeKr when XeKr was excited to $\upsilon^{*}=0$ ($2\omega_1$=77934.32 cm^{-1}) and $\upsilon^{*}=2$ ($2\omega_1$=77992.12 cm^{-1}) of the intermediate excited state of Xe*Kr correlating to the Xe* 6p[5/2]$_2$ level, while scanning the wavelength of the ω_2 laser in the energy range of 93,500-97,470 cm^{-1}. The top, middle, and bottom spectra were those obtained by monitoring ^{132}Xe^{+}, ^{84}Kr^{+}, and ^{m}Xe^{n}Kr^{+} with $m+n=216$, respectively. In these spectra, two series of vibrational progressions, the stronger and the weaker series, are commonly recognized at the same wavenumber positions. As will be assigned in the section III-3, the stronger and the weaker series belong to the *d*- and the *s*-Rydberg series of molecule XeKr, respectively. In the spectra obtained by monitoring the yields of parent ions ^{m}Xe^{n}Kr^{+} with $m+n=216$, intensity dips appear at the same wavenumber positions as those of fragment ions of ^{132}Xe^{+} and ^{84}Kr^{+}, which are produced by ionizing ^{132}Xe** and ^{84}Kr** fragments produced via the predissociation from the high Rydberg states ^{132}Xe^{**84}Kr. The excitation spectrum measured by monitoring ^{84}Kr^{+} exhibits the same vibrational progression pattern as that obtained by monitoring the ^{132}Xe^{+} signal. As the energy increases, the ^{132}Xe^{+} signal decreases and finally disappears, while the ^{84}Kr^{+} signal dominates at the energies above 96,500 cm^{-1}. As will be discussed later, this result originates from crossings of potential energy curves, which trigger the ion-core switching in the high Rydberg states Xe**Kr.

The intervals between the groups of vibrational peaks become smaller in the higher energy region and finally converge at around 97,300 cm^{-1}, just below the ionization energy of Xe^{+} $^{2}P_{3/2}$ (97,834 cm^{-1}). This observation is consistent with the level energies of molecular Rydberg states given by

$$E_R^{\upsilon^{**}}(n) = E_{ion}^{\upsilon^+} - \frac{R}{(n-\delta_l)} \tag{1}$$

where $E_R^{\upsilon^{**}}(n)$, $E_{ion}^{\upsilon^+}$, R, and δ_l are the vibrational energy of the molecular Rydberg state with a principal quantum number n and a vibrational quantum number υ^{**}, the vibrational energy of the molecular ion core state with a vibrational quantum number υ^+ to which the molecular Rydberg state converges, the Rydberg constant, and a quantum defect of a Rydberg series with an orbital angular momentum quantum number l, respectively. The term values of all the vibrational peaks are given in Tables I and II for the *d*- and the *s*-Rydberg series, respectively. In the energy region investigated, the XeKr$^+$ ion core has two electronic states, X $^2\Sigma^+_{1/2}$ and A $^2\Pi_{3/2}$, with equilibrium internuclear distances of 3.177 Å and 3.742 Å [24], respectively. Considering the Frank-Condon overlap between these ion-core states and the intermediate state of Xe*Kr correlating to the Xe* 6p[5/2]$_2$ level and having r_e^* =3.95(3) Å [29], we conclude that the Rydberg series observed in this study converge to the A $^2\Pi_{3/2}$ ion core.

2. Assignment of vibrational quantum numbers

The assignment of a vibrational quantum number υ^{**} and the equilibrium internuclear distance r_e^{**} of high Rydberg states were determined by using the Franck-Condon principle and by assuming that the shape of the interatomic potentials are represented by the Morse potential. The observed Franck-Condon patterns reflect the overlap of vibrational wave functions between the intermediated state and the high Rydberg state. The potential parameters for the intermediate state Xe*Kr correlating to the Xe* 6p[5/2]$_2$ level have been already reported as ω_e^* =31.597(73)cm^{-1}, $\omega_e x_e^*$ =0.901(18) cm^{-1}, and r_e^* =3.95(3) Å [29], where ω_e^* and $\omega_e x_e^*$ are the frequency of the harmonic vibration and the anharmonicity constant, respectively. The reported potential parameters of the ion core state XeKr$^+$ A $^2\Pi_{3/2}$ of ω_e^+ =40.72(29) cm^{-1} and $\omega_e x_e^+$ =0.893(40) cm^{-1} [33] were employed for the high Rydberg states Xe**Kr, assuming that the potential shape of the high Rydberg states are almost identical to that for the ion core state [34]. The intensity pattern of the transitions from the υ^* =0 or υ^* =2 of the Xe*Kr to the vibrational levels υ^{**} of the Xe**Kr was evaluated and compared to the experiments by changing the r_e^{**} of the Xe**Kr. Figures 5(a)-5(d) show the best-fit results of the Franck-Condon simulations for the 15*d*- and 10*s*- states as a typical example, respectively. The simulated pattern shows a fairly good agreement with that of the experiment. The results were obtained when the r_e^{**} for the 15*d*- and 10*s*- states are adjusted to 3.79(1) and 3.79(5) Å, respectively, which gives the assignment of υ^{**} = 0-6. Similar Franck-Condon simulations were performed for other high Rydberg states and the results are shown in Appendices 1(a)-1(d). The assignment of a vibrational quantum number for all the high Rydberg states is shown in Tables I and II for the *d*- and the *s*-Rydberg series, respectively.

3. Assignments of *n* and *l* for the high Rydberg series

The assignment of a principle quantum number *n* and an orbital angular momentum quantum number *l* of the two molecular Rydberg series are performed. Figure 6 shows the OODR excitation mass spectrum of high Rydberg ^{132}Xe atom measured by exciting ^{132}Xe to the intermediate state ^{132}Xe* 6p[5/2]$_2$ ($2\omega_1$ =78,120.303 cm^{-1}) and scanning the wavelength of the ω_2 laser in an energy range 96,800-98,000 cm^{-1}, while monitoring the ^{132}Xe^{+}. In the spectrum, two Rydberg series, the stronger and the weaker series, are recognized. As shown in Tables III and IV, the term values for the stronger and weaker series are found to be almost the same as those reported for the Xe** *n*d[7/2]$_3$ series [35,36,37] and the Xe** *n*s[3/2]$_1$ [35,36,37,38] series, respectively. Therefore, it is concluded that the stronger and weaker molecular Rydberg series correlate to the Xe** *n*d[7/2]$_3$ series ($8 \le n \le 27$) and the Xe** *n*s[3/2]$_1$ series ($10 \le n \le 28$), respectively.

The validity of the assignment is supported by the quantum defect of each series. Based on the assignment of *n* and *l* for the two molecular Rydberg series, the vibrational energy $E_{ion}^{\upsilon^+}$ of XeKr^{+} A $^2\Pi_{3/2}$ and the quantum defect δ_l are calculated using the equation (1) by a least-squares fitting using the observed vibrational level energies of the high Rydberg molecular state $E_{Ry}^{\upsilon^{**}}(n)$ with the associated principal quantum number *n* ($n \ge 15$). The quantum defects for the Xe** *n*d[7/2]$_3$ and Xe** *n*s[3/2]$_1$ series are calculated to be δ_d=2.44 and δ_s=4.00, respectively. These are in good agreement with the reported values of δ_d=2.45(1) [37] and δ_s=3.99(1) [37,38]. Moreover, as shown in Table V, the vibrational energies $E_{ion}^{\upsilon^+}$ of XeKr^{+} A $^2\Pi_{3/2}$ calculated for the Xe *n*s[3/2]$_1$ (υ^+=0-2) and Xe *n*d[7/2]$_3$ (υ^+=0-5) series agree with the reported values [24,39,40].

4. Potential parameters of highly excited Rydberg states

Figures 7(a) and 7(b) show the Birge-Sponer plot [41] for the 15*d*- and the 10*s*- states as a typical example, respectively, where the differences between the adjacent vibrational energy levels

$$\Delta G_{\upsilon^{**}+1/2} = \omega_e^{**} - 2\omega_e x_e^{**}(\upsilon^{**}+1) \qquad (2)$$

were plotted against υ^{**}+1/2. As shown in Fig. 7(a), the linear decrease in $\Delta G_{\upsilon^{**}+1/2}$ is observed for the 15*d*-state. Similar linear decrease was observed for the other *nd*-series with $8 \le n \le 25$ as shown in Appendix 2(a), which demonstrates that the potentials for the stronger series can be well approximated by the Morse potential. On the other hand, as shown in Fig. 7(b), for the 10*s*-state, there is no linear dependence between $\Delta G_{\upsilon^{**}+1/2}$ and υ^{**}+1/2. Similar trend was observed for the other *ns*-series with $10 \le n \le 25$ as shown in Appendix 2(b), which demonstrates that the potentials for the *s*-series are distorted. The distortion can be attributed to perturbations from other potentials correlating to Xe (*n*-4)f[3/2], (*n*-4)f[5/2], (*n*-4)f[7/2], and (n-4)f[9/2] states, which are located closely to each Xe ns$[3/2]_1$ state by 17.6 and 1.8 cm^{-1} for n = 10 and 20, respectively [35]. Therefore, potential parameters ω_e^{**} and $\omega_e x_e^{**}$ can be calculated by the least-squares fitting only for the d-Rydberg series and are shown in Tables I and VI.

The dissociation energy D_0^{**} measured from $\upsilon^{**}=0$ level represented by the relation,

$$D_0^{**}(\mathrm{Xe^{**}Kr}) = D_0(\mathrm{XeKr}) + E(\mathrm{Xe^{**}}) - E_{00}(\mathrm{Xe^{**}Kr}) \qquad (3)$$

is shown in Tables VI and VII for the d- and the s-Rydberg series, respectively, where $D_0(\mathrm{XeKr}) = 150.5$ cm^{-1} is the dissociation energy from $\upsilon''=0$ for the electronic ground state of XeKr calculated using a potential function based on experimental information by Bobetic et al. [42], $E(\mathrm{Xe^{**}})$ is the energy level of Xe** to which the vibrational progression under consideration correlates [35,36,37,38], and $E_{00}(\mathrm{Xe^{**}Kr})$ is the energy between the $\upsilon''=0$ level of the electronic ground state and the $\upsilon^{**}=0$ level of the high Rydberg state obtained in this study.

5. Irregularity in potential parameters

In Fig. 8(a), the D_0^{**} dissociation energies measured from $\upsilon^{**}=0$ level for the d- and s-Rydberg states of XeKr** are plotted as a function of the effective quantum number $n_{\mathrm{eff}} = n - \delta_l$. The D_0^{**} for $n_{\mathrm{eff}} \leq 13$ increases as n_{eff} increases, while it becomes constant for $n_{\mathrm{eff}} \geq 13$. This result shows that for $n_{\mathrm{eff}} \geq 13$ the interatomic potentials of the d- and the s-series can be regarded as identical to that of the ion core Xe$^+$Kr A $^2\Pi_{3/2}$, *i.e.*, the high Rydberg molecular state can be described as a simple structure of a Rydberg electron originated from Xe atom having an orbital around the Xe$^+$Kr ion core. On the other hand, for $n_{\mathrm{eff}} \leq 13$ such a Rydberg character becomes less important. The potential parameters for Xe$^+$Kr A $^2\Pi_{3/2}$ are determined as ω_e (Xe$^+$Kr)=42.0(1) cm^{-1}, $\omega_e x_e$ (Xe$^+$Kr)=0.72(2) cm^{-1}, D_0^+ =700.6(5) cm^{-1}, and r_e^+ =3.79(1) Å by averaging over $16 \leq n \leq 25$ for the d-series. As shown in Table VI, these values are consistent with the previous reports [24,25,26,33,39,40,43,44], confirming that the assumption in Section III-2 that the potential shape of the high Rydberg states are almost identical to that for the ion core state is correct.

Concerning the irregularity at $n_{\mathrm{eff}} \approx 7.0$, correlating to the Xe 11s$[3/2]_1$ state, in the D_0^{**} dependence on the n_{eff} for the s-Rydberg series, it can be explained by the fact that the energy level of Xe 11s$[3/2]_1$ state (95,591.0 cm^{-1}) is perturbed by the nearby Xe 7s'$[1/2]_1$ state (95,800.6 cm^{-1}) converging to the Xe$^+$ $^2P_{1/2}$ state (108,370.8 cm^{-1}) (see Fig. 8(b)). In fact, the quantum defect δ_s=4.005, calculated from the data in ref [39], for the Xe 11s$[3/2]_1$ state is found slightly larger than δ_s=3.994 for the other ns$[3/2]_1$-Rydberg states (see Fig. 8(c)). This difference in δ_s corresponds to the lowering of the energy level of the Xe 11s$[3/2]_1$ state by 9 cm^{-1} from the original position, which matches well with the observed energy shift in the D_0^{**} of 10 cm^{-1}. Therefore, it is concluded that the irregularity in the D_0^{**} for the s-Rydberg series at $n_{\mathrm{eff}} \approx 7.0$

is caused by the shift in the correlating Xe atomic energy level due to the perturbation from the Xe 7s'[1/2]$_1$ Rydberg state.

6. Mechanism of the Ion-Core Switching

As shown in Figs. 3 and 4, Xe^+ and Kr^+ signals are commonly recognized at the same wavenumber positions. This result comes from the fact that not only Xe^{**}, but also Kr^{**} are produced from dissociation processes of $Xe^{**}Kr$, since the excited states of both Xe^{**} and Kr^{**} atoms coexist in the energy region. This observation indicates that the high molecular Rydberg states $Xe^{**}Kr$ have two predissociation pathways as

(1) producing the excited state of the Xe^{**} atom and the ground state of the Kr atom, and

(2) producing the excited state of the Kr^{**} atom and the ground state of the Xe atom.

The latter predissociation process includes the ion-core switching process from the (Xe^+ + e^-) + Kr to the Xe + (Kr^+ + e^-). Figure 9 shows the ion-core switching branching ratio R_{Kr+} for each high Rydberg state as a function of excitation energy, defined as $R_{Kr+}=I_{Kr+}/(I_{Kr+} + I_{Xe+})$, where I_{Xe+} and I_{Kr+} represent peak areas in the mass spectra for Xe^+ and Kr^+ signals, respectively. In the energy region below 95,000 cm^{-1}, the Kr^+ ions are produced with R_{Kr+}=0.3-0.7. In the energy region of 95,000-96,000 cm^{-1}, the less Kr^+ ions are produced with R_{Kr+}<0.1. As the energy increases from 96,000 cm^{-1}, however, the R_{Kr+} rapidly increases and only the Kr^+ ions are produced, *i.e.*, R_{Kr+}=1.0, above 96,500 cm^{-1}.

As shown in Fig. 10, even after the complete ion core switching (*i.e.* R_{Kr+}=1.0), the discrete vibrational progression patterns for the high Rydberg $Xe^{**}Kr$ molecule continues to be observed. Figure 10 also shows the energy position where the Xe^+ signal disappears. The complete ion core switching, *i.e.*, the cutoff of the Xe^+ production, occurs at υ^{**}=3 vibrational level of $Xe^{**}Kr$ (96,578.5 cm^{-1}) correlating to Xe^{**} 14d[7/2]$_3$.

The dissociating energy level of Kr^{**} atom can be identified from the mass peak split of $^nKr^+$ signal in the TOF spectra as observed in Fig. 2(b), where the $^nKr^+$ mass peaks split due to a large kinetic energy release (KER) during the dissociation event. From the difference in TOF (Δt) of the mass peaks splitting, the kinetic energy released during the dissociation event is estimated by calculating the turn round time (Δt) in the acceleration region as,

$$\Delta t = \frac{4 m_{\mathrm{Kr}} \upsilon_0}{1.929 E} \tag{4}$$

where m_{Kr}, υ_0, and E are the mass of Kr^+, the initial velocity of Kr^+, and the electric field in the acceleration region, respectively [45]. By employing Δt=0.156 μs ($^{80}Kr^+$), 0.154 μs ($^{82}Kr^+$), 0.154 μs ($^{83}Kr^+$), 0.155 μs ($^{84}Kr^+$), 0.155 μs ($^{86}Kr^+$), E=184.3672 V/cm, and the mass of the counter part Xe of 131.3882 considering the isomer ratio, the KER is estimated as 15,530±200 cm^{-1}. Since initially the XeKr was excited to the $\upsilon^{**}=0$ vibrational level (96,687.6 cm^{-1}) of the $\mathrm{Xe}^{**}\mathrm{Kr}$ correlating to Xe^{**} $16\mathrm{d}[7/2]_3$ + Kr by the OODR process, the energy level of the dissociation limit should be around 81,157 ± 200 cm^{-1}. Energetically, the Xe + Kr^{**} $5\mathrm{s}[3/2]_1$ limit (81,067.3 (=80,916.8+150.5) cm^{-1}) is the most plausible candidate for the dissociating pathway (see Fig. 11). The dissociation pathway (2) occurs, because a repulsive part of the interatomic potentials of the XeKr^{**} molecule correlating to the Rydberg state of the Kr^{**} atom is crossed with a bound potential correlating to the Rydberg state of the Xe^{**} atom.

The energy dependence of the $R_{\mathrm{Kr+}}$ and the cutoff of the Xe^{+} production at 96,578.5 cm^{-1} can be explained by considering interactions with other electronic states as follows: The repulsive potential energy curve (PEC) correlating to the Xe + Kr^{**} $5\mathrm{s}[3/2]_1$ limit (81,067.3 cm^{-1}) is expected to be very steep in the energy range above 93,200 cm^{-1}, where the ion core switching occurs. Since the PECs for high Rydberg states of the A $^2\Pi_{3/2}$ ion core could be nearly identical, the observed energy dependence of $R_{\mathrm{Kr+}}$ should originate from interactions with other electronic states. A possible candidate is the *nd*-Rydberg-series converging to the X $^2\Sigma^+_{1/2}$ ion-core as shown in Fig. 12(a).

Due to a large number of PEC crossings and the high density of states, population from the high Rydberg state of the A $^2\Pi_{3/2}$ ion core can be transferred to the Rydberg state of the X $^2\Sigma^+_{1/2}$ ion-core, if the respective vibrational eigenstates have the same energy within the energy uncertainty determined by the lifetime of the high Rydberg state of the A $^2\Pi_{3/2}$ ion-core and the respective vibrational wavefunctions are overlapped. The possibility of the Rydberg-series of the X $^2\Sigma^+_{1/2}$ ion-core being populated from a given measured Rydberg-state of the A $^2\Pi_{3/2}$ ion-core can be estimated by summing up the square overlaps with all possible vibronic states of the Rydberg series of the X $^2\Sigma^+_{1/2}$ ion-core, which lie within the energy uncertainty range of the measured state. The total effect is obtained by weighting this sum of the overlaps with the Frank-Condon factor of the measured state with respect to the vibrational state located on the intermediate electronic state, from which it was populated in the experiment. The quantity described above can be expressed as

$$I^{\mu}_{\Delta E}(n,\upsilon)=\sum_{\substack{n',\upsilon' \\ \left|E^{\mathrm{X}\,^2\Sigma^+_{1/2}}_{n',\upsilon'}-E^{\mathrm{A}\,^2\Pi_{3/2}}_{n,\upsilon}\right|<\Delta E}}\left|\left\langle n'd_{\mathrm{X}\,^2\Sigma^+_{1/2}},\upsilon'\middle|nd_{\mathrm{A}\,^2\Pi_{3/2}},\upsilon\right\rangle\right|^2\left|\left\langle nd_{\mathrm{A}\,^2\Pi_{3/2}},\upsilon\middle|\mathrm{Kr+Xe\ 6p[5/2]_2},\mu\right\rangle\right|^2 \tag{5}$$

where $\left|nd_{\mathrm{A}\,^2\Pi_{3/2}},\upsilon\right\rangle$ is the υth vibrational state on the *nd*-Rydberg PEC of the A $^2\Pi_{3/2}$ ion-core having energy $E^{\mathrm{A}\,^2\Pi_{3/2}}_{n,\upsilon}$, $\left|n'd_{\mathrm{X}\,^2\Sigma^+_{1/2}},\upsilon'\right\rangle$ is the υ'th vibrational state on the *n′d*-Rydberg PEC of the X $^2\Sigma^+_{1/2}$ ion-core having energy $E^{\mathrm{X}\,^2\Sigma^+_{1/2}}_{n'\upsilon'}$, $\left|\mathrm{Kr+Xe\ 6p[5/2]_2},\mu\right\rangle$ is the μth vibrational state on the intermediate electronic state to Kr + Xe^{*} $6\mathrm{p}[5/2]_2$, and ΔE is the energy uncertainty. In the calculations, ΔE was chosen to be

10 cm^{-1}, similar to the approximate width of the spectral lines observed. Numerical tests with $\Delta E = 5$ cm^{-1} and $\Delta E = 20$ cm^{-1} showed that our results are not sensitive to the exact value of ΔE.

For computing the quantities of equation (5), the potential energy curves (PECs) of the n=8, 9, 10, … , 25 Rydberg-states of the A $^2\Pi_{3/2}$ ion-core, correlating to Kr + Xe* nd[7/2]$_3$ were represented as Morse-functions with the potential parameters set to the ones obtained for the A $^2\Pi_{3/2}$ ion-core state, and with an overall energy shift applied to match the experimentally determined dissociation asymptotes. The PECs for the n=8, 9, 10, … , 25 Rydberg-states of the X ion-core state were obtained in a similar way, but using the Morse-parameters of the X ion-core state taken from Ref. [24]. Furthermore, to simulate the presence of additional Rydberg-states in the X ion-core manifold, additional Morse-potentials representing the n=26, 27, 28, … , *nmax* Rydberg-states were also included (using energy shifts with respect to the ion-core state set to follow the n^{-2} pattern of the energy asymptotes), where *nmax* was chosen to be 35. The qualitative features of the simulation results showed to be insensitive to the further increase of nmax. The intermediate PEC correlating to Kr + Xe* 6p[5/2]$_2$ was also represented as a Morse-potential, its parameters taken from Ref. [27]. For computing the vibrational energies and wavefunctions supported by the different PECs, the matrix representations of the corresponding 1-D vibrational Hamiltonians were constructed using 160 Fourier-DVR basis functions obtained from box-normalized plane wave functions with the transformation method [46], with the DVR grid points lying equidistantly in the internuclear distance range of 0-16 bohr. The eigenpairs computed by diagonalizing the Hamiltonian matrices are converged with respect to the basis set size and the employed coordinate range (eigenvalues are converged to within 0.1 cm^{-1}, thus to much better extent than the accuracy of the PECs).

The computed quantities of equation (5) are presented in Fig. 13. Assuming that the Rydberg series of the X $^2\Sigma^+_{1/2}$ ion-core produce Xe$^+$ due to predissociation leading to the Xe** + Kr limit, while the Rydberg series of the A $^2\Pi_{3/2}$ ion-core mainly produce Kr$^+$ due to population transfer to the PEC correlating to the Xe + Kr** 5s[3/2]$_1$ limit, and that the PEC correlating to the Xe + Kr** 5s[3/2]$_1$ limit intersects the two Rydberg series around 3.5 Å as shown in Fig. 12(b), the energy dependence of the quantity defined in the equation (5) semi-quantitatively explains the energy dependence of $R_{\mathrm{Kr+}}$ and the cutoff of the Xe$^+$ production observed in Fig. 9 as follows: The total overlap with X $^2\Sigma^+_{1/2}$ ion core states (quantity of equation (5)) decreases below 94,800 cm^{-1}, because the Rydberg states of the X $^2\Sigma^+_{1/2}$ ion core appear less frequently as the energy decreases, therefore, there are less corresponding vibrational states to be found within the "energy windows" where overlaps are taken into account, which could give $R_{\mathrm{Kr+}}$ = 0.3-0.7 below 95,000 cm^{-1} in Fig. 9. Between 94,800 cm^{-1} and 96,200 cm^{-1}, the Rydberg states on the X $^2\Sigma^+_{1/2}$ ion core are located much more densely, and their highly excited vibrational states can overlap with the vibrational states of the Rydberg states on the A $^2\Pi_{3/2}$ ion core, which could give the lower $R_{\mathrm{Kr+}} < 0.1$ in this energy region. Above 96,200 cm^{-1}, the non-oscillatory parts of the highly excited vibrational states on the Rydberg states of the X $^2\Sigma^+_{1/2}$ ion core are shifted to larger internuclear distances, and their overlap with the vibrational states on the Rydberg states of the A $^2\Pi_{3/2}$ ion core decreases rapidly with the increase of energy, which could finally give $R_{\mathrm{Kr+}} = 1.0$.

As discussed previously, from the KER of the observed Kr$^+$ ions, it can be concluded, that they originate from the PEC correlating to the Xe + Kr** 5s[3/2]$_1$limit, however, the situation for the Xe$^+$ ions is more complicated. Considering the lower KER (~2,300 cm^{-1}) of the observed Xe$^+$ ions, there are 60 candidate states as predissociation products (Xe** *n*s[3/2]$_j$ (*n*=9,10; j=1 or 2), Xe** *n*p[K]$_j$ (*n*=8,9; K=3/2, 5/2; j=K-1/2 or K+1/2), Xe** *n*d[K]$_j$ (*n*=7,8; K=3/2, 5/2, 7/2; j=K-1/2 or K+1/2), Xe** *n*f[K]$_j$ (*n*=5,6; K=3/2, 5/2, 7/2, 9/2; j=K-1/2 or K+1/2), Xe** 5g[K]$_j$ (K=3/2, 5/2, 7/2, 9/2, 11/2; j=K-1/2 or K+1/2), and Xe** 5d'[K]$_j$ (K=3/2, 5/2; j=K-1/2 or K+1/2)) located around 91,500~95,000 cm^{-1}, which could produce more than 200 repulsive and bound state PECs that could cross at the inner wall of the Rydberg-state PEC.

Finally, we address the question of the possible mechanisms responsible for the predissociation of the high-lying Rydberg-states converging to the X $^2\Sigma^+_{1/2}$ or A $^2\Pi_{3/2}$ ionic states. The three most likely mechanisms are population transfer to lower lying electronic states via [47,48]

1) non-adiabatic couplings near the crossing(s) of the Rydberg-state PEC at the inner wall with a lower lying repulsive state PEC(s) or a lower lying bound state PEC(s),
2) coupling between angular momentum of Rydberg electron and molecular rotation,
3) spin-orbit coupling.

All three possibilities require the vibrational wavefunctions of the respective coupled electronic states to overlap. The possibility of mechanism 2 could be small, because the energy spacing between rotational energy levels (~0.1 cm^{-1}) for XeKr is much smaller than that between the Rydberg states. The magnitude of mechanism 3 is also likely to be small for Rydberg-states with large principal quantum number *n*, due to the strong decrease of the spin-orbit coupling with increasing electron-core distance [49]. Therefore, mechanism 1 seems to be most plausible. For a more quantitative argument, the non-adiabatic couplings between the different electronic states should be computed and taken into account in the equation (5).

IV. CONCLUSIONS

The OODR excitation mass spectra of the high Rydberg states of the XeKr molecule in the energy region of 93,000-97,500 cm^{-1} below the first ionization threshold, where the Rydberg states of both the Xe and Kr atoms coexist, were measured by monitoring the fragment ions of both ^{132}Xe$^+$ and ^{84}Kr$^+$ with a reflectron TOF mass analyzer. 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 Xe^+Kr A $^2\Pi_{3/2}$ state. The potential parameters for the *d*-series and those for the A $^2\Pi_{3/2}$ state of Xe^+Kr are determined as ω_e =42.0(1) cm^{-1}, $\omega_e x_e$ =0.72(2) cm^{-1}, D_0 =700.6(5) cm^{-1}, and r_e =3 .79(1) Å. It is found that the potentials for the *s*-series are distorted because of the perturbations from other potentials correlating to Xe *n*f[5/2], *n*f[7/2], and *n*f[9/2] states, which are closely located to each Xe *n*s$[3/2]_1$ state within 10 cm^{-1}. The D_0 plot against n^* shows that (i) the interatomic potential of the Rydberg state of XeKr converges to the ion core, Xe^+Kr at n^*=10 for both *s*- and *d*-Rydberg series, and (ii) the observed decrease in the D_0 at the 11s-Rydberg state of XeKr is caused by the perturbation from Xe 7s'$[1/2]_1$ state.

The observation of the ionized fragments of both Xe^+ and Kr^+ in the same energy positions shows that two predissociation processes producing both the Xe^{**} and Kr^{**} fragments compete in the high Rydberg states $Xe^{**}Kr$, and that the ion core of high Rydberg molecule switches from (Xe^+Kr + e^-) to ($XeKr^+$ + e^-). From the analysis of kinetic energy release (KER) observed in the mass spectrum of $^nKr^+$, it is found that the Kr 5s$[3/2]_1$ state (80,916.8 cm^{-1}) is the most plausible candidate for the dissociating Rydberg state. The ion core switching occurs due to interaction between the bound potentials of high Rydberg states $Xe^{**}Kr$ of the A $^2\Pi_{3/2}$ ion core and a repulsive potential of $XeKr^{**}$ associated with the Xe + Kr^{**} 5s$[3/2]_1$ limit. The complete ion core switching occurs at υ^* =3 vibrational level of $Xe^{**}Kr$ (96,578.5 cm^{-1}) correlating to Xe^{**} 14d$[7/2]_3$. The observed energy dependence of ion core switching ratio can be explained from the population transfer from the bound potentials of high Rydberg states of the A $^2\Pi_{3/2}$ ion core to that of the X $^2\Sigma^+_{1/2}$ ion-core. This scenario is supported by the model calculations summing up the square overlaps between all possible vibronic *n*d-Rydberg states of the X $^2\Sigma^+_{1/2}$ ion core and the measured Rydberg state of the A $^2\Pi_{3/2}$ ion core, weighted with the Frank-Condon factor of the measured state with respect to the vibrational state located on the intermediate electronic state of Xe^*Kr correlating to Xe^* 6p$[5/2]_2$, from which it was populated in the experiment.

Acknowledgement:

TABLE CAPTIONS

Table I:

Vibrational levels, potential parameters, and quantum defects of high Rydberg states of XeKr molecule, correlating to Xe *n*d$[7/2]_3$ ($8 \le n \le 27$) states.

Table II:

Vibrational levels, potential parameters, and quantum defects of high Rydberg states of XeKr molecule, correlating to Xe ns$[3/2]_1$ ($10 \leq n \leq 28$) states.

Table III:

Energy levels and quantum defects for high Rydberg states of Xe atom, correlating to Xe ns$[3/2]_1$ ($18 \leq n \leq 25$) states.

Table IV:

Energy levels and quantum defects for high Rydberg states of Xe atom, correlating to Xe nd$[7/2]_3$ ($13 \leq n \leq 25$) states.

Table V:

Vibrational energy levels $E_{ion}^{\upsilon^+}$ of XeKr$^+$ B $^2\Pi_{3/2}$ calculated for Xe ns$[3/2]_1$ (υ^+=0-2) and Xe nd$[7/2]_3$ (υ^+=0-5) series.

Table VI:

Potential parameters for high Rydberg states of XeKr molecule, correlating to Xe nd$[7/2]_3$ ($8 \leq n \leq 27$) states.

Table VII:

Potential parameters for high Rydberg states of XeKr molecule, correlating to Xe ns$[3/2]_1$ ($10 \leq n \leq 28$) states.

FIGURE CAPTIONS

Figure 1:

A schematic diagram of the excitation process of XeKr. The XeKr molecule was excited to the intermediate Rydberg state Xe*Kr correlated with the Xe* 6p[5/2]$_2$ atom by the two photon excitation of the W_1 laser light. The second W_2 laser light further excites the molecule to the high Rydberg states of the Xe**Kr. The dissociation fragments Xe** and Kr** from the high Rydberg states are ionized by the W_1 laser and the W_2 laser, respectively, to produce Xe$^+$ and Kr$^+$ ions.

Figure 2:

(a) The TOF mass spectrum recorded by exciting XeKr to the U^{**} =0 level of the high Rydberg molecular state, correlating to Xe** 16d[7/2]$_3$ state. The mass resolution was estimated to be m/ Δ m=1,100 from the XeKr$^+$ spectra. (b) The TOF mass spectrum for the Kr$^+$. The split of the mass peaks due to the large kinetic energy release during the predissociation process is clearly observabed.

Figure 3:

The OODR mass spectra measured when XeKr was excited to U^* =0 (2 W_1 =77934.32 cm^{-1}) of the intermediate excited state of Xe*Kr correlating to Xe* 6p[5/2]$_2$, while scanning the wavelength of the W_2 laser in an energy range (a) 93,500-94,500 cm^{-1}, (b) 94,500-95,500 cm^{-1}, (c) 95,500-96,500 cm^{-1}, and (d) 96,500-97,420 cm^{-1}. The top, middle, and bottom were obtained by monitoring the fragment ions ^{132}Xe$^+$ and ^{84}Kr$^+$, and the parent ions ^{132}Xe^{84}Kr$^+$, respectively.

Figure 4:

The OODR mass spectra measured when XeKr was excited to U^* =2 (2 W_1 =77992.12 cm^{-1}) of the intermediate excited state of Xe*Kr correlating to Xe* 6p[5/2]$_2$, while scanning the wavelength of the W_2 laser in an energy range (a) 93,500-94,500 cm^{-1}, (b) 94,500-95,500 cm^{-1}, (c) 95,500-96,500 cm^{-1}, and (d) 96,500-97,470 cm^{-1}. The top, middle, and bottom were obtained by monitoring the fragment ions ^{132}Xe$^+$ and ^{84}Kr$^+$, and the parent ions ^{132}Xe^{84}Kr$^+$, respectively.

Figure 5:

The observed signal intensities and the simulated best-fit FC factors for (a) the 10s-Rydberg state via the U^* =0 intermediate state, (b) the 10s-Rydberg state via the U^* =2 intermediate state, (c) the 15d-Rydberg state via the U^* =0 intermediate state, and (d) the 15d-Rydberg state via the U^* =0 intermediate state. The observed signal intensities are the sum of both the Xe$^+$ and Kr$^+$ signal intensities. Morse parameters are assumed for the10s- and 15d-Rydberg states, and the intermediated state.

Figure 6:

The OODR excitation dip spectrum measured by exciting Xe to the intermediate state Xe* 6p[5/2]$_2$ (2 w_1 =78120.303 cm^{-1}) and scanning the wavelength of the w_2 laser in an energy range 96,800-98,000 cm^{-1}, while monitoring the ^{132}Xe$^+$. The fluctuation in the base line is due to long term drift of the laser intensities and the temporal and special overlap among the two lasers and the molecular beam.

Figure 7:

The Birge-Sponer plot for (a) the 10s- and (b) the 15d-Rydberg states as a typical example.

Figure 8:

(a) The dissociation energy D_0 of the s- and the d-Rydberg series of the XeKr molecule plotted against the effective quantum number n_{eff}. The abrupt fa11 of the dissociation energy of the s-Rydberg state at n* =7.0 are caused by the interaction between the 11s[3/2]$_1$ Rydberg state and the 7s'[1/2]$_1$ Rydberg state of the Xe atom. (b) Excited energy levels of Xe atom around the Xe 11s[3/2]$_1$ Rydberg state (95,591.0 cm^{-1}), which is perturbed by the nearby Xe 7s'[1/2]$_1$ state (95,800.6 cm^{-1}). (c) The quantum defects for the Xe ns[3/2]$_1$ state d_s plotted against the effective quantum number n_{eff} calculated from the data in ref [27].

Figure 9:

The ion core switching branching ratio $R_{\mathrm{Kr+}}$, defined as $I_{\mathrm{Kr+}}/(I_{\mathrm{Kr+}} + I_{\mathrm{Xe+}})$, as a function of excitation energy.

Figure 10:

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 u^* =0 of the intermediate excited state of Xe*Kr, while scanning the wavelength of the w_2 laser in an energy range 96,280-96,820 cm^{-1}. The Xe$^+$ signal disappears, i.e. the complete ion core switching occurs, at u^* =3 vibrational level of Xe**Kr (96,578.5 cm^{-1}) as indicated by an arrow.

Figure 11:

A schematic diagram of the ion core switching process of XeKr in high Rydberg states. From the analysis of kinetic energy release (KER) in the predissociation process, the Kr 5s[3/2]$_1$ state (80,916.8 cm^{-1}) is the most plausible candidate for dissociating Rydberg level (see details in the text).

Figure 12:

(a) Calculated potential energy curves (PECs) for Rydberg states of the A $^2\Pi_{3/2}$ ion core and the X $^2S^+_{1/2}$ ion-core. The PECs correlating to Kr 5s[3/2]1 + Xe and to Xe 6p[5/2]2 + Kr are also shown. (b) The PECs correlating to Xe + Kr* 5s$[3/2]_1$ intersects the two Rydberg-series around 3.5 Å.

Figure 13:

Computed quantities of Eq. (6) as a function of energy in the cases when XeKr was excited to (a) u^* =0 and (b) u^* =2 of the intermediate excited state of Xe*Kr correlating to Xe* 6p$[5/2]_2$. The position where the Xe$^+$ signal disappears, i.e. the complete ion core switching occurs is indicated by an arrow.

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