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# Exchange interaction in Kr 3d excitations of small krypton clusters

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ABSTRACT

X-ray absorption spectra of small krypton clusters with average size of ~15 atoms were measured with $Kr_2^+$ ion yields at the Kr $3d_{5/2}$ and $3d_{3/2}$ region. The second lowest Rydberg transition $3d^{-1}6p$ is redshifted from the corresponding atomic transition, and shows an asymmetric broad shoulder feature. This characteristic feature is attributable to some surface sites with different coordination numbers such as corner, edge and face as previously observed in the Kr 3d photoexcitation and photoelectron spectra. Diffuse Rydberg states are influenced predominantly with induced polarization of the surrounding atoms. On the other hand, the lowest transition $3d^{-1}5p$ is blueshifted, and shows a rather narrow peak. The blueshift arises from short-range repulsive interaction, that is, exchange interaction of the Rydberg electron with the surrounding atoms. The larger coordination number of the nearest neighbor atoms increases both the exchange (blueshift) and induced polarization (redshift) effects. In the higher Rydberg state, the blueshift effect is drastically reduced but the redshift effect is most dominant. Cancelation of these two effects can be expected in the lowest Rydberg transition. The present experimental analysis enables us to discuss the site-dependent and state-dependent exchange interaction.



## 1. Introduction

Clusters are intermediate states between isolated atoms and bulk solids, and have properties of both surface and bulk, dependent on their sizes. Inner-shell spectroscopic approaches such as X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) are promising methods to investigate local, or site-selected, electronic structures of clusters, especially weakly bound van der Waals rare gas clusters such as Kr [1–5], Ar [5–11], Ar/Kr [12], Ne [13–15], and Xe [5,16]. Large rare gas clusters show both bulk and surface features in XAS [1,3,4,6,7,9,10,13] and in XPS [5,7–9,11,12,14–16]. Rare gas solids also show small surface features in addition to the bulk band in XAS [17,18]. Positively charged states created in clusters and solids by inner-shell ionization are stabilized by induced polarization (induction effect) of the surrounding atoms [8,11] and even non-polar molecules [19,20]. The ionization energy in XPS corresponds to the ionization threshold where the Rydberg series is converged in XAS. The ionization energy or threshold is redshifted by the induction interaction when the coordination number increases from atom to surface and from surface to bulk and when the cluster size is increased [7,8,14]. Inner-shell excitations to higher Rydberg states show rather large redshift [4,19], which is explained by their convergence to the ionization threshold.

On the other hand, low-lying valence and Rydberg states of clusters do not always show the redshift. Core-to-valence excited states of non-polar $N_2$ and benzene clusters show very small energy shifts [20,21], which is recently detectable by using high resolution soft X-ray undulator beamlines. Some lowest core-to-Rydberg excited states of clusters and solids do not show any redshift but blueshift from the atomic ones: Kr $3d^{-1}5p$ [1,3,4], Ar $2p^{-1}4s$ [6,7,9,10,17,18], Ne $1s^{-1}3p$ [13], and $N_2$ $1s^{-1}3s/3p$ [19]. The blueshift in the lowest Rydberg states of clusters indicates that the exchange interaction between the Rydberg electron and the surrounding atoms/molecules is stronger than the induced polarization interaction. Because the exchange interaction occurs only in the short range (namely, overlapping region of the two wavefunctions) and is predominantly dependent on the coordination number of nearest neighbor atoms, the blueshift effect due to the exchange repulsion in the lowest core-to-Rydberg excited state can be larger than the redshift effect due to induced polarization interaction in clusters. The exchange interaction is given by orthogonalization of the Rydberg orbital with the wave functions of surrounding atoms/molecules, with an additional node created at the surrounding atoms/molecules in the Rydberg orbital and with the Rydberg electron confined within a cage composed of the nearest neighbors [19]. The confinement of the core-excited orbital is also discussed for Ar $2p^{-1}4s$ in the surface and bulk Ar [22]. The smaller 'cage' size causes the larger exchange interaction, namely, larger blueshift. On

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the other hand, the higher and more diffuse Rydberg state beyond the first coordination shell reduces such exchange repulsion [18,19].

Small rare gas clusters with only a few bulk sites (typical average size: $N < 50$ atoms) can show different surface sites as previously observed in XAS for Kr $3d^{-1}5p$ [1] and XPS for Kr $3d^{-1}$ [2,12]. The Rydberg electrons in these surface sites have different exchange and induced polarization interactions with the surrounding atoms of different coordination numbers. In the present work, to reveal surface site-dependent and state-dependent exchange and polarization effects in detail, we analyze Kr $3d_{5/2}$ and $3d_{3/2}$ XAS spectra of small Kr clusters ($\langle N\rangle \sim 15$ atoms). The site-dependent Rydberg transitions in the small Kr clusters are discussed in comparison with those in Kr atoms and in larger Kr clusters ($\langle N\rangle = 4700$ atoms) [4].

## 2. Experimental

The present experiments were performed using an in-vacuum soft X-ray undulator beamline BL3U [23] at the storage ring UVSOR-II. Kr clusters were produced by the same procedure as in the previous work [2]. The average size $\langle N\rangle$ of the Kr clusters was evaluated to be ~15 by comparing with the published data [1,2]. In order to get higher photon fluxes in the XAS measurement, the photon energy band path was set to be about 60 meV at $h\nu = 90$ eV.

It is known that the atomic/molecular dimer ion formation is proportional to the photoabsorption of small atomic/molecular clusters [1,6,21]. To get X-ray absorption spectra of small Kr clusters by $Kr_2^+$ ion yields, we developed a compact Wiley–McLaren type TOF mass spectrometer [24]. Positively charged Kr ions emitted from Kr clusters after X-ray absorption were triggered by a pulsed voltage apparatus, secondly accelerated and traveled in a drift tube, and collected by a micro-channel plate detector. Fig. 1 shows a TOF mass spectrum of Kr clusters by using a digital phosphor oscilloscope. Most Kr clusters are decomposed after photoabsorption, and emit $Kr_2^+$ dimer ions. The amount of clusters is much smaller than that of isolated atoms in the present experimental condition [2]; that is, in Fig. 1, the $Kr^+$ ions from isolated Kr atoms are dominantly observed with $Kr^{2+}$ and $Kr^{3+}$ ions produced by multiple ionization. To obtain Kr $3d_{5/2}$ and $3d_{3/2}$ XAS spectra of small Kr clusters, the intensity of $Kr_2^+$ dimer ions was extracted from the total signals as a function of photon energy [1] by combination of a delay-pulse generator and a constant-fraction discriminator. The $Kr^+$ ion yields were also measured at the same time to obtain atomic Kr 3d XAS spectra, which were used to calibrate the photon energy. The repetition rate of the pulsed trigger was 10 kHz, and the duration time at each photon energy was 3 s.

Kr 3d XPS spectra of small Kr clusters were also measured by using a hemispherical electron energy analyzer (SCIENTA SES-200 combined with the lens and control system MBS A-1) with the pass energy of 100 eV. The photon energy was set to be 140 eV with the energy resolution of 70 meV. The Kr 3d binding energies of the atomic transitions were calibrated by using 93.8 eV (Kr $3d_{5/2}$) and 95.0 eV (Kr $3d_{3/2}$) [2].

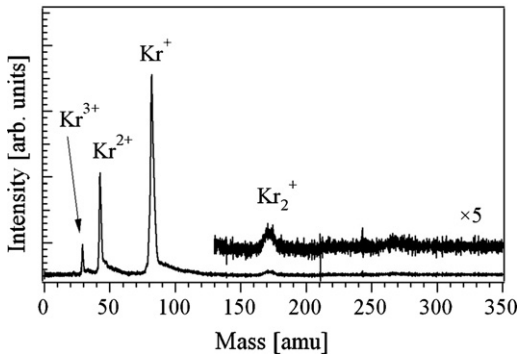


**Fig. 1.** A time-of-flight mass spectrum obtained at $h\nu = 90$ eV for Kr clusters with average size of ~15 atoms, which contain dominant contributions from Kr atoms. $Kr_2^+$ dimer ions are mainly formed by photoabsorption of Kr clusters.

## 3. Results and discussion

### 3.1. Exchange interaction of Rydberg electrons

Fig. 2 shows Kr 3d XAS spectra of Kr dimers and clusters with average sizes $\langle N\rangle \sim 15$ based on $Kr_2^+$ dimer ion yields. Atomic Kr 3d XAS spectra based on $Kr^+$ ion yields are also shown. The observed peak energies are summarized in Table 1, showing the average energies over the site-dependent features (*vide infra*) in the small cluster. The dimer contributions have already been discussed in detail in the previous work [1]. In the present work, the cluster peaks are discussed in comparison with the atomic peaks. In addition, Table 1 shows comparative results for large Kr clusters ($\langle N\rangle \sim 4700$) with distinct surface and bulk sites, measured by Tchaplyguine et al. [4].

In comparison with the atomic lowest Rydberg transitions $3d_{5/2}{}^{-1}5p$ and $3d_{3/2}{}^{-1}5p$, the corresponding cluster peaks are found to be blueshifted by 0.14 eV. These cluster peaks contain different surface-site components as will be shown later in Table 2. The 0.14 eV blueshift of $3d^{-1}5p$ in the small clusters is almost the same as 0.13–0.14 eV blueshift in the surface site of the large cluster. On the other hand, the 0.34 eV redshift of $3d^{-1}6p$ in the small clusters is smaller than 0.45 eV redshift in the surface site of the large cluster. In comparison with the atomic Kr $3d_{5/2}$ and $3d_{3/2}$ ionization thresholds 93.80 and 95.04 eV, the ionization energies of the small Kr clusters are redshifted by 0.54–0.56 eV (as later shown in Fig. 3), and the ionization energies of the surface (bulk) site of the large Kr clusters are redshifted by about 0.77–0.80 eV (1.07–1.10 eV) [4]. It is reasonable considering the larger clusters have the more face and bulk sites than the smaller clusters [2] and long-range electrostatic interaction due to induced polarization of surrounding atoms beyond the nearest neighbor coordination.

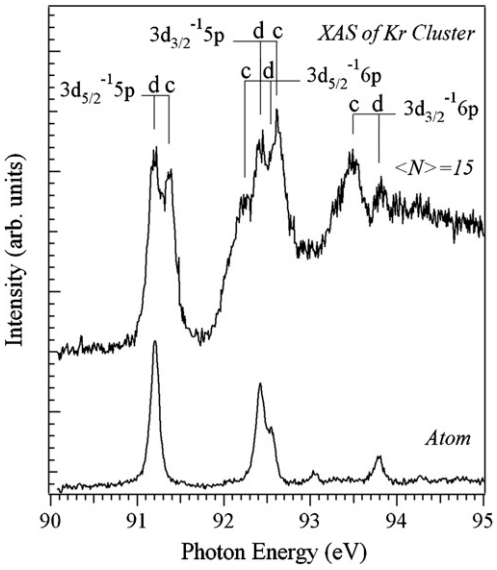


**Fig. 2.** Kr $3d_{5/2}$ and $3d_{3/2}$ XAS spectra of Kr atoms and Kr clusters (average size $\langle N\rangle \sim 15$) measured by $Kr^+$ and $Kr_2^+$ ion yields, respectively. Peak assignments of observed Rydberg transitions are shown, where 'd' and 'c' denote dimer and cluster (surface) peaks. The energies are summarized in Table 1.