Interatomic Coulombic Decay from Auger Final States in Argon Dimer

It is well known that an isolated atom in an inner-shell excited state decays through a cascade of radiative and/or Auger transitions. As a result, photons and electrons are emitted at specific energies to the atom. Many analytical methods, such as electron spectroscopy, are based on this fact and used nowadays as key techniques in many studies including those at SPring-8. Then, what will happen when other atoms exist in the vicinity of the excited atom? Generally, it is considered that the neighboring atoms merely distort or shift the energy spectrum. However, recent theoretical [1] and experimental [2-4] studies demonstrated that the excited atom can decay through a new mechanism called interatomic Coulombic decay (ICD). In the ICD, the excited atom can decay through the transfer of its excitation energy to the neighboring atom and an ICD electron is emitted. Although we report here a result for the argon dimer in Auger final states as a simplified example, the ICD can be expected to occur after Auger decay in any systems including biomolecules in water. It is worth noting that DNA is damaged not only by primary energetic radiations (X-, γ- and β-rays) but also, perhaps more efficiently, by an electron at energy lower than 20 eV [5] and that the energy of the ICD electron is generally low (<10 eV).

Experiments were carried out at the soft X-ray photochemistry beamline **BL27SU** with an operation mode of 6/42 filling + 25 bunch. Argon dimers were produced through the expansion of cooled argon gas (130 K and 1.3 bar) via an aperture of 50 μm diameter [4]. The dimers produced were irradiated using monochromatized soft X-rays at 257 eV, i.e., about 10 eV above the 2*p* ionization threshold of the atomic argon. The electrons and ions produced were accelerated toward position-sensitive detectors, which are installed face to face. We measured the time-of-flights (TOFs) and detection positions of all charged particles (except energetic Auger electrons) in coincidence, and determined the 3-dimensional momenta of all charged particles emitted upon ionization and subsequent fragmentation. Each detector can detect up to six electrons/ions for one ionization event.

Figure 1 shows the TOF spectrum derived with the ion-ion coincidence mode. The x and y coordinates correspond to the TOFs of the first and second ions. Two curved lines show the (A):Ar^++Ar^+ and (B):Ar^++Ar^{2+} coincidences because the Ar^+ and Ar^{2+} ions with zero kinetic energy result in the TOFs of 5.1 and 3.5 μs, respectively. In fact, the atomic ions have large initial kinetic energies owing to a mutual Coulombic repulsion and the dimer has a random orientation with respect to the spectrometer axis. As a result, the coincidence TOF spectra have significantly broad distributions, as shown in Fig. 1.

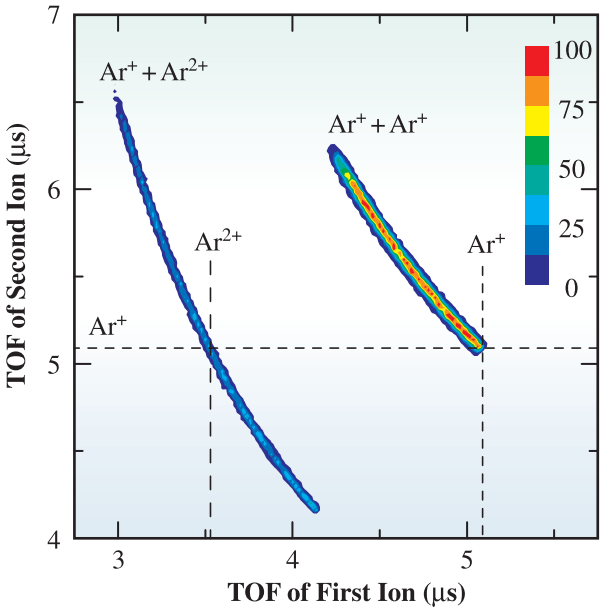

Fig. 1. Time-of-flights (TOFs) of ions from argon dimers. The dashed lines show the TOFs of ions with zero kinetic energy.

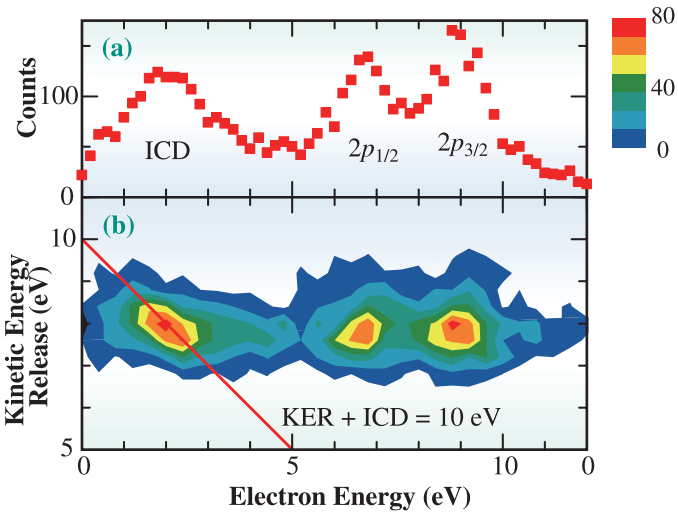

Fig. 2. **(a)** Electron spectrum of argon dimers. **(b)** Correlation between electron energy and kinetic energy release by fragment argon ions.

By limiting the gate on Ar^{+}+Ar^{2+} coincidence signals, we determined events in which the dimer dissociates into an Ar^{+}+Ar^{2+} ion pair and obtained the electron energy spectrum (see Fig. 2(a)). The two peaks at 6.5 and 8.7 eV correspond to photoelectrons from the Ar2$p_{1/2}$ and 2$p_{3/2}$ inner shells, and the peak at 2 eV originates from the ICD electrons, as described below. Figure 2(b) shows the correlation between the electron energy and the kinetic energy release (KER) by the Ar^{+}+Ar^{2+} pair. The photoelectron peaks have almost no correlation with the KER, while the ICD peak tilts with a slope of -1, suggesting that the sum of the ICD electron energy and KER is constant (~10 eV). It was also confirmed that the ICD electron energy is independent of the photon energy, while the two photoelectron peaks shift according to the photon energy.

Figure 3 shows the energy levels relevant to ICD emission. Most of the $2p^{-1}$ states in the photoionized dimer decay to $nl^{-1}nl'^{-1}$ states (n = 3) via conventional Auger transitions, forming Ar^{2+}+Ar Auger final states, i.e., the dimer consisting of a doubly charged ion and a neutral atom. These Auger final states cannot decay further through electron emission if the atomic Ar^{2+} ion is isolated because the triple ionization threshold (84.13 eV) is above these states. However, the decay becomes possible if an ICD electron can be emitted from the neighboring Ar atom. If we consider the ionization of the outermost electron from an Ar atom (15.76 eV), the sum of the Ar^{2+} and Ar^{+} energies at the dissociation limit are about 10 eV below $Ar^{2+}(3p^{-3}3d)$ Auger final states. The Coulombic repulsion energy between Ar^{2+} and Ar^{+} is about 8 eV at a nuclear distance of 3.8 Å (i.e., the equilibrium bond distance of a neutral dimer). Thus, the $Ar^{2+}(3p^{-3}3d)$+Ar of the Auger final states and $Ar^{2+}(3p^{-2})$ + $Ar^{+}(3p^{-1})$ at distances ~3.8 Å provide an energy of ~2 eV to the ICD electron emitted from the neighboring Ar atom.

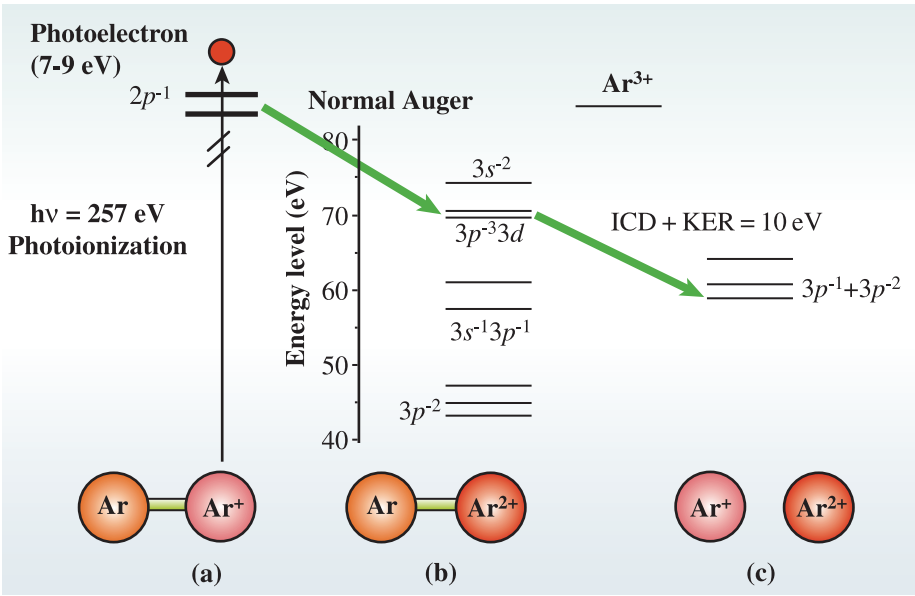

Fig. 3. Energy levels relevant to ICD electron emission.

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