

Charge transfer to ground-state ions in Ne-Kr mixed clusters producing slow electrons

When X-rays irradiate a light atom, an inner-shell electron is ejected, followed by the emission of one or several Auger electrons of relatively high energy (>200 eV). When X-rays irradiate condensed matter, however, the majority of emitted electrons have low kinetic energy (<20 eV). These slow electrons are traditionally believed to be secondary electrons produced via inelastic scattering of a photoelectron or Auger electrons at the surroundings atoms. In a biological system, a high potency for genotoxic effects has been assigned to these slow electrons [1].

About 20 years ago, new pathways were proposed to produce slow electrons in a loosely bound system. If an ion in the excited state is included in such a system, it may relax to the ground state, emitting an electron from a neighbor. This process is called interatomic/intermolecular Coulombic decay (ICD) [2]. Alternatively, an electron may be transferred from a neighbor to the ion, accompanied by electron emission from another neighbor. This process is called electron-transfer-mediated decay (ETMD) [3]. ETMD has been considered as a minor decay channel since it cannot compete with ICD [3]. It can, however, become a dominant relaxation pathway for configurations in which ICD is energetically forbidden. As an example, Stumpf *et al.* presented *ab initio* calculations for a NeKrKr trimer [4] and showed that ETMD takes place between Ne dications in their ground state and the Kr neighbors (Fig. 1). In this study, we report the experimental identification of this process using Ne-Kr mixed clusters [5].

The experiment was carried out at SPring-8 BL17SU. The photon energies were set to 878 eV and 888 eV, corresponding to 8 eV and 18 eV above the Ne 1s ionization threshold of 870 eV, respectively. A Ne-Kr mixed cluster beam was prepared by expanding a mixed gas through an 80 μm nozzle at a stagnation pressure of 0.6 MPa. The molar mixing ratio of Ne:Kr was 60:1. The temperature of the nozzle was 160 K. The resulting Ne:Kr ratio in the clusters estimated from the experiment was 4:1.

To measure ions and electrons originating from a cluster after a series of events, we used an electron-ion three-dimensional momentum coincidence spectrometer. The spectrometer consisted of two time-of-flight (TOF) spectrometers equipped with delay-line-type position-sensitive detectors. One of them detected ions and the other detected electrons. They faced each other with the crossing point of the X-rays and cluster beams between them. Knowledge of the position and arrival time at the detectors allowed us to extract information about the three-dimensional momentum of each particle.

We expected the production of three singly charged ions (one Ne ion and two Kr ions) and three electrons (photoelectron, Auger electron, and ETMD electron). To search for the target processes, we selected only the events in which we measured these three ions, and identified the photo- and ETMD electrons from electron spectra in coincidence with the events.

Figure 2 shows the TOF spectra of ions. Different

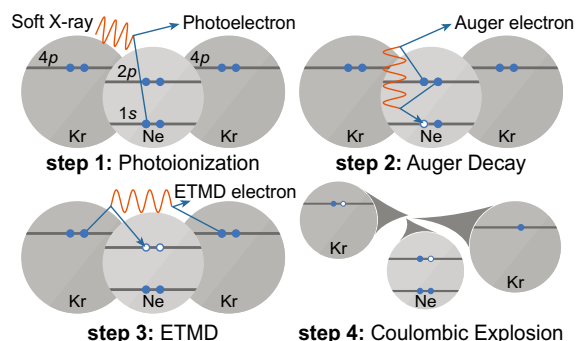


Fig. 1. Schematics of process investigated. First step (photoionization): an ionizing X-ray photon ejects a Ne 1s electron (photoelectron) from a Ne atom in a Ne-Kr mixed cluster. Second step (Auger effect): Auger decay of the resulting Ne ion leads to a dication with two holes in the valence shell and an ejected electron (Auger electron). Third step (ETMD): one of the electrons of a neighboring Kr atom fills one of the Ne valence holes, and one of the valence electrons of another Kr atom is ejected (ETMD electron). Fourth step (Coulomb explosion): the cluster explodes by Coulomb repulsive forces, and releases one singly charged Ne ion and two singly charged Kr ions. Filled blue discs indicate active electrons, and the positive charges are indicated by empty blue circles. [5]

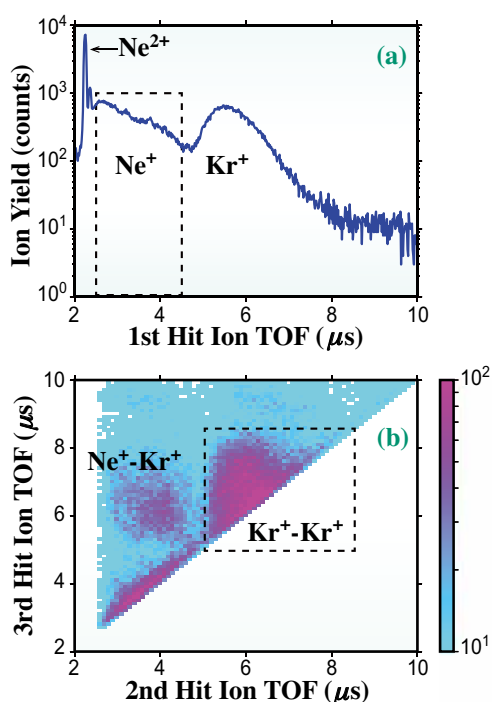


Fig. 2. TOF spectra of ions released from Ne-Kr mixed clusters showing results filtered for events in which three ions were detected in coincidence. The photon energy used was 888 eV. (a) TOF of the first ion arriving at the detector. The region surrounded by a dashed line was used to select events for a Ne monocation. (b) TOFs of the second ion versus the third ion detected in coincidence with the Ne ion as the first ion. The region surrounded by a dashed line was used to select events in which two Kr monocations were detected. The scale bar indicates counts. [5]

mass-to-charge ratios give rise to peaks at different TOF values. The initial velocities of ions broaden the peaks. We expected Ne and Kr monocations to appear around $3.2 \mu\text{s}$ and $6.5 \mu\text{s}$, respectively, and selected only events in which we detected the target three ions.

Figure 3 shows the electron kinetic energy spectra. The regions around 8 eV and 18 eV in Fig. 3(a) correspond to Ne 1s photoelectrons. These regions provide evidence that the ion triples are indeed produced after Ne 1s photoionization. In addition to the photoelectrons, significantly enhanced intensity is seen around 0–5 eV. After subtracting the contributions from photoelectrons (Fig. 3(b)), we can more clearly see that the same low-energy component appears at both photon energies. The intensity of the 0–11 eV electrons, which is the energy corresponding to ETMD, is around 70% of that of the photoelectrons. This implies that a slow electron is almost always emitted from the cluster when a Ne 1s photoionization event occurs at the Ne-Kr interface.

Our results apply to relaxation pathways after

interaction with energetic particles in a broad range of weakly bonded systems, for example, aqueous solutions. We show that non-local autoionization may occur even from states with no or a small amount of electronic excitation energy. Taking these processes into account is very important for understanding the chemical effect of radiation on a microscopic level.

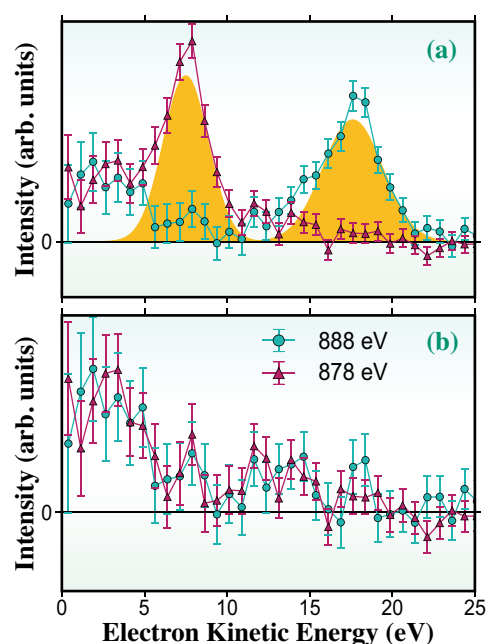


Fig. 3. Electron spectra in coincidence with the target ions. (a) Kinetic energy of electrons detected in coincidence with the ion triple. The two Gaussian functions fitted to the photoelectron peaks are also shown as yellow regions. (b) The same as (a) subtracting the contributions from photoelectrons, fitted by two Gaussian functions. The error bars in (a) and (b) are defined as standard deviations. [5]

Daehyun You^{a,b}, Hironobu Fukuzawa^{a,b} and Kiyoshi Ueda^{a,b,*}

^aInstitute of Multidisciplinary Research for Advanced Materials, Tohoku University
^bRIKEN SPring-8 Center

*Email: kiyoshi.ueda.a2@tohoku.ac.jp

References

- [1] B. Boudaïffa *et al.*: Science **287** (2000) 1658.
- [2] L.S. Cederbaum *et al.*: Phys. Rev. Lett. **79** (1997) 4778.
- [3] J. Zobeley *et al.*: J. Chem. Phys. **115** (2001) 5076.
- [4] V. Stumpf *et al.*: Phys. Rev. Lett. **110** (2013) 258302.
- [5] D. You, H. Fukuzawa, Y. Sakakibara, T. Takanashi, Y. Ito, G.G. Maliyar, K. Motomura, K. Nagaya, T. Nishiyama, K. Asa, Y. Sato, N. Saito, M. Oura, M. Schöffler, G. Kastirke, U. Hergenbahn, V. Stumpf, K. Gokhberg, A.I. Kuleff, L.S. Cederbaum and K. Ueda: Nat. Commun. **8** (2017) 14277.