

Intermolecular decay mechanisms in helium nanodroplets

A. C. LaForge^{*1}, M. Shcherbinin[‡], F. Stienkemeier^{*}, R. Richter[†], M. Mudrich[‡]

^{*} Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

[†] Elettra-Sincrotrone Trieste, Basovizza, 34149 Trieste, Italy

[‡] Department of Physics and Astronomy, Aarhus University, 8000 Aarhus, Denmark

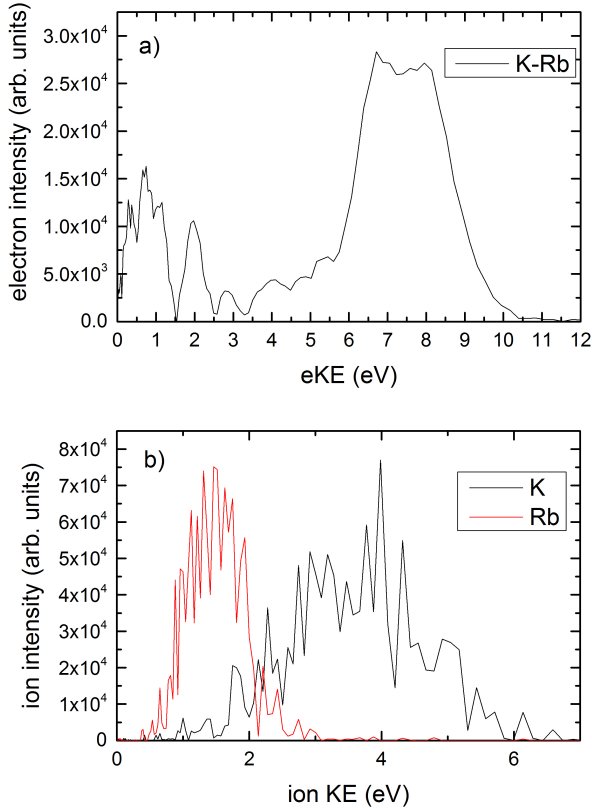


Figure 1. a) electron kinetic energy distributions correlated to K^+-Rb^+ ion-ion coincidences (black line). b) ion kinetic energy distributions correlated to K^+-Rb^+ ion-ion coincidences for K (black line) and Rb (red line). The photon energy is 21.6 eV. The droplet size is 50 000 He atoms.

As opposed to molecular systems where electron dynamics proceed only through intramolecular processes, weakly bound complexes create an environment in which locally excited electrons can additionally interact with neighboring molecules leading to new intermolecular decay mechanisms. Intermolecular Coulombic decay (ICD) [1] is a particularly interesting decay mechanism which occurs when local electronic decay is energetically forbidden. ICD offers a new, ultrafast decay path, typically on the femtosecond timescale, where energy is exchanged with a neighboring atom leading to its ionization. Since its discovery, ICD has been observed in a wide variety of weakly-bound systems from He dimers to biological

systems such as water clusters [2]. Electron transfer mediated decay (ETMD) [3] is an additional intermolecular decay mechanism where charge transfer releases energy leading to ionization of surrounding molecules. Although generally considered a weaker decay, ETMD, however, has gained new interest as it was predicted and shown to occur from the ionic ground state where ICD is not allowed [4, 5].

Here, we present a systematic study of intermolecular decay mechanisms of mixed alkali dimers (K-Na, K-Rb, Na-Rb) in He nanodroplets using synchrotron radiation. By coincidence imaging techniques, we can fully characterize and energetically resolve the different decay paths with mass-correlated photoelectron/ion spectra. In particular, we observed a new decay mechanism where the alkali dimer was doubly-ionized by the excited He atom. The process is similar to that observed by Buchta et al. [6] where the energy of an excited He atom is transferred to the neighboring atom leading to ionization. Here, we show the process can *even* lead to *double ionization* of the dimer followed by Coulomb explosion. The photoelectron spectrum (Fig. 1a) shows the characteristic U-shaped distribution similar to single photon double ionization [7] while the photoion spectrum (Fig. 1b) shows the energetic ionic fragments from Coulomb explosion. In addition, we observed electron transfer mediated decay [4, 5] between alkali dimers and He ions. By varying the attached dimers, we can gain a better understanding of the interaction strength depending on the internuclear distance and the role of nuclear dynamics in the process.

References

- [1] L. S. Cederbaum *et al.* 1997 *Phys. Rev. Lett.* **79** 4778
- [2] T. Jahnke 2015 *J. Phys. B: At., Mol. Opt. Phys.* **48** 082001
- [3] J. Zobeley *et al.* 2001 *J. Chem. Phys.* **115** 5076
- [4] V. Stumpf *et al.* 2014 *Phys. Rev. Lett.* **112** 193001
- [5] A. C. LaForge *et al.* 2016 *Phys. Rev. Lett.* **116** 193001
- [6] D. Buchta *et al.* 2013 *J. Phys. Chem. A* **117** 4394
- [7] R. Wehlitz *et al.* 1991 *Phys. Rev. Lett.* **67** 3764

¹E-mail: aaron.laforge@physik.uni-freiburg.de