

Detecting ultrafast interatomic electronic processes in media by fluorescence

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Interatomic Coulombic Decay (ICD), a radiationless transition in weakly bonded systems, such as solutes or van-der-Waals bound aggregates, is an effective source for electrons of low kinetic energy. So far, the ICD processes could only be probed in ultra-high vacuum by using electron and/or ion spectroscopy. Here we show that resonant ICD processes can also be detected by measuring the subsequently emitted characteristic fluorescence radiation, which makes their study in dense media possible.

ICD is an energy transfer mechanism that occurs inside a chemical environment between excited atoms and their atomic neighbors [1]. As a result of the energy transfer, electrons of low kinetic energy are created [2]. As these electrons are known to be genotoxic, it was suggested that ICD might contribute to radiation damage [3] and could be employed in novel cancer treatment scenarios [4,5]. So far, the emitted charged particles were used to detect ICD [2]. This is, however, not possible in dense – especially biological - media [6]. Here we employ the detection of fluorescence light to verify the occurrence of ICD in a model system. This novel approach is the only known method for tracing ICD in dense matter. Thus, it holds great promise for exploring the role of this efficient energy transfer mechanism in biological systems.

The present experiments were performed for the prototype Ne-clusters, for which it is known that resonant excitation of an inner valence electron triggers ICD [7]. The process is sketched in Fig. 1. An incoming photon resonantly excites an inner-valence (2s) electron of atom A (a). This electronic excitation is known to relax via two competing pathways: (i) by autoionization of the same atom A leading to the emission of fast electrons (kinetic energy between 23 and 27 eV); and, alternatively, (ii) via the resonant ICD which gives rise to the emission of slow electrons (kinetic energy between 0 and 10 eV) from Atom B (b). Both processes are ultrafast and completely suppress the resonant fluorescence of the initially excited state. If the first pathway takes place, the relaxation process ends. This is not the case in the second pathway which is described in Fig. 1. Importantly, ICD becomes the dominant relaxation pathway when the cluster size grows [8]. In ICD, a valence electron of atom A fills the hole in the inner-valence shell. The energy gained is ultrafast transferred to a valence electron of a neighboring atom B, leading to its release (b). As can be seen in Fig. 1, due to the presence of the excited electron, a part of the excess energy is still stored in atom A where one electron remains excited. This excess energy is not sufficient to further ionize the system and is released by the emission of a photon (c), which is used here to identify the preceding ICD.

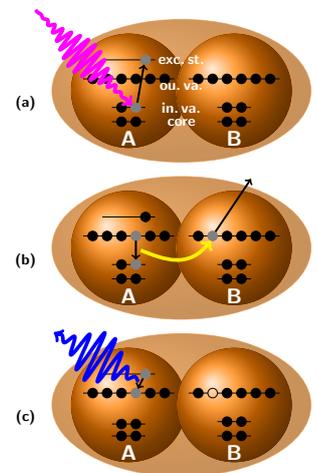


Figure 1: Schematic of fluorescence following ICD after resonant excitation in Ne-clusters.

References

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