

## Evolution of Interatomic Coulombic Decay in the Time Domain

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During the past 15 years a novel decay mechanism of excited atoms has been discovered and investigated. This so-called interatomic Coulombic decay (ICD) involves the chemical environment of the electronically excited atom: the excitation energy is transferred (in many cases over long distances) to a neighbor of the initially excited particle usually ionizing that neighbor. It turned out that ICD is a very common decay route in nature as it occurs across van der Waals and hydrogen bonds. The time evolution of ICD is predicted to be highly complex, as its efficiency strongly depends on the distance of the atoms involved and this distance typically changes during the decay. Here we present the first direct measurement of the temporal evolution of ICD using a novel experimental approach.

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In 1997 Cederbaum and co-workers realized that the presence of loosely bound atomic or molecular neighbors opens a new relaxation pathway to an electronically excited atom or molecule. In the decay mechanism they proposed—termed intermolecular Coulombic decay (ICD)—the excited particle relaxes efficiently by transferring its excitation energy to a neighboring atom or molecule [1]. As a consequence, the atom or molecule receiving the energy emits an electron of low kinetic energy. The occurrence of ICD was proven in experiments in the mid 2000s by means of electron spectroscopy [2] and multicoincidence techniques [3]. Since that time a wealth of experimental and theoretical studies have shown that ICD is a rather common decay path in nature, as it occurs almost everywhere in loosely bound matter. It has been proven to occur after a manifold of initial excitation schemes [4–8]. ICD has also been observed in many systems as rare gas clusters [9], even on surfaces [10] and small water droplets [11,12]. The latter suggested that ICD might play a role in radiation damage of living tissue [13], as it creates low energy electrons, which are known to be genotoxic [14,15]. More recently that scenario was reversed as it was suggested to employ ICD in the treatment of tagged malignant cells [16]. Apart from these potential applications, the elementary process of ICD is under investigation, as the decay is predicted to have a highly complex temporal behavior. The efficiency and thus the decay times of ICD depend strongly on the size of the system, i.e., the number of neighboring particles and the distance between them and the excited particle. Even for model systems consisting of only two atoms the temporal evolution of the decay is nontrivial and predicted theoretically to exhibit exciting physics [17]: as ICD happens on a time scale that is fast compared to relaxation via photon

emission, but comparable to the typical times of nuclear motion, the dynamics of the decay are complicated and so far only theoretically explored [18,19]. Examining the temporal evolution of ICD in an experiment is therefore one of the grand challenges in ultrafast science. Here we present an experimental study resolving ICD in a helium dimer ( $\text{He}_2$ ) in the time domain.

The helium dimer is known to be the most weakly bound ground state system in the Universe [20] with a binding energy of only 95 neV and a bond length that extends from about 5 Å over its mean value of 52 Å into the macroscopic regime of a few hundred angstroms. Nonetheless, even in this extended system ICD occurs transferring about 40 eV of energy from one helium atom to its neighbor. While initially ICD was investigated after innervalence ionization, in the case of helium simultaneous photoionization and excitation was used to produce an intermediate ionic dimer state that is able to undergo intermolecular Coulombic decay (ICD) [21]. A multicoincidence measurement yielded not only the proof of the existence of ICD even in a system as extended as the helium dimer, but for the first time showed the occurrence of nodal structures in the measured energy distributions [22]. Previously expected for the neon dimer [18], these occur as the vibrational wave function of the excited intermediate dimer state is mapped onto the repulsive final state after ICD visualizing directly the wave nature of the vibrating nuclei. A sketch of the process and the involved potential energy curves is shown in Fig. 1. A key feature of ICD in  $\text{He}_2$  is the long distance over which the energy transfer takes place. Consequently, the decay times here are very long in comparison to that of other systems, allowing for the vibrational structure to form in the excited state. We observe this time evolution by making use of a new experimental

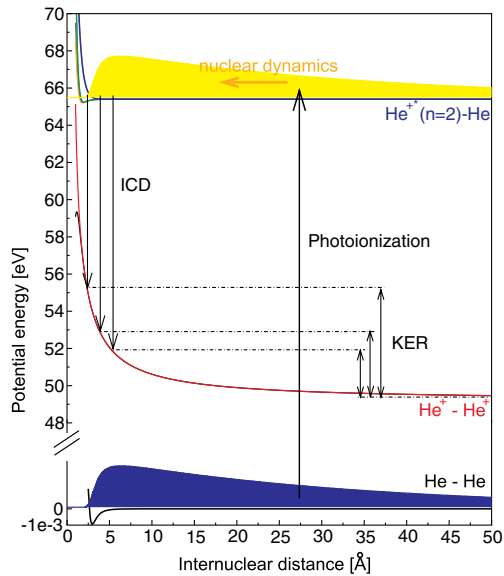


FIG. 1 (color online). Sketch of the potential energy diagram of the states involved in the process. The ground state, which is only bound by 95 neV, is photoionized and excited. Because the mean internuclear distance of the excited state is much smaller than that of the ground state, nuclear motion sets in: the vibrational wave packet starts to evolve on the potential energy curves of the excited states. During that time, ICD happens, mapping the evolving vibrational wave packet to the repulsive  $\text{He}^+/\text{He}^+$  final states. By measuring the kinetic energy release (KER) information on the internuclear distance (i.e., the distribution of the wave packet) at the instant of the decay is obtained.

technique, which maps time to kinetic energy of an emitted electron. Such a mapping of time to energy is typically employed in attosecond science by streaking of electrons with a time varying external field [23]. In our case the time-dependent field is created by the decaying system itself and the photoelectron, which we launch in the pump step, acts as the probe particle, which experiences the streaking.

Even though it is rarely stressed in literature, the mapping of decay time to photoelectron energy naturally occurs whenever a decay produces a secondary electron, which is significantly faster than the photoelectron [24–26]. The change of the kinetic energy of the emitted particles is known as postcollision interaction (PCI) [27]. So far, PCI has been studied in great detail after Auger decay [28]. As the Auger electron is emitted in the decay, the charge of the remaining ion changes. Accordingly, an emerging photoelectron starts to leave a singly ionized atom, but as the decay happens, the photoelectron is suddenly exposed to the Coulomb force of a doubly charged ion. This results in lowering the energy of the emerging photoelectron and increasing the kinetic energy of the Auger electron. The energy shift of the photoelectron wave packet depends on the time the Auger electron needs to emerge from the ion. Therefore, as the shift of the electron energy can be measured, a way to access the time domain of an electronic decay in an experiment arises.

In the present case we therefore used cold target recoil ion momentum spectroscopy [29–31] to measure the energy of the photoelectron carrying the time information and the fragment ions on which we observe the time evolution of ICD in coincidence. The experimental setup was similar to that described in [21]. In order to convert the measured shift in energy of the photoelectron into a decay time, we used a simple classical model. In a simulation an electron of a kinetic energy of 140 meV is launched. The ICD electron (with a kinetic energy of 10 eV) is launched after a delay time  $t_{\text{ICD}}$ . As the ICD electron reaches the photoelectron the distance the photoelectron traveled  $R_p$  is obtained. The energy difference between a Coulomb potential of charge two and a Coulomb potential of charge one at  $R_p$  is the amount of energy the electron is decelerated. This simplest model already shows a strong non-linear behavior for the dependency of the emission time of the second electron and the energy shift the first electron experiences as shown in Fig. 3(a) for different initial (i.e., unshifted) energies of the photoelectron. Apart from being a fully classical model, it furthermore neglects effects that occur due to the different emission angles of the two electrons. However, this effect is known to be strong only for a small region of almost equal emission directions [32]. Furthermore, it turns out that the minimum time that can be investigated depends on the initial energy of the photoelectron. This is due to the fact that electrons that exhibit a severe shift are recaptured into the ion. Choosing an unperturbed energy of 140 meV for the photoelectron yields a minimum accessible decay time of 50 fs within our simple model. In the experiment this was implemented by employing a linearly polarized photon of an energy of 65.536 eV from beam line UE112-PGM-1 at BESSY.

In the present case the temporal evolution of the kinetic energy release (KER) is investigated. The KER is the energy that the two nuclei gain after dissociating in a Coulomb explosion as ICD occurred. The KER closely corresponds to the internuclear distance of the two atoms of the dimer, at the instant they were ionized: within the so-called reflection approximation [33] the Coulomb interaction yields (in atomic units) the following simple relation:  $\text{KER} = 1/R$ . The results from the theoretical investigation shown in Fig. 2, left, depict the KER for different times at which ICD happened. At short times a first peak at lower kinetic energies occurs. This can be understood classically: As the internuclear distance of  $\text{He}_2$  in the ground state is much larger than in the excited state, the decay starts to evolve at larger internuclear distances, i.e., smaller KERs. After some time the main peak at high KERs builds up as the dimer contracts towards the mean internuclear distance of the excited ionic state. As this happens, the probability for ICD increases (which is proportional to  $1/R^6$  at large distances [34]), as Fig. 2 reveals. At longest times finally the vibrational features form, yielding the distribution, which is known from the non-time-resolved

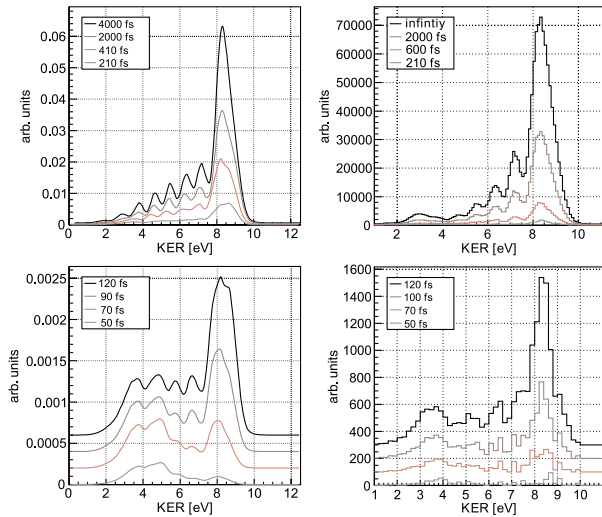


FIG. 2 (color online). Left: Theoretical predictions of the time evolution of the kinetic energy release for different decay times. Bottom to top: KER for a time integrated from 0 fs to 50, 70, 90, 110, 210, 410, 2000, and to 4000 fs. Right: Measured KER distributions for different decay times.

investigation [21,22]. The time-resolved KER spectra, shown in Fig. 2, were computed using the approach reported in [35]. The electronic structure input data used for these computations are presented and discussed in [36].

In Fig. 3(b) the experimental results are depicted. The top panel shows the correlation of the measured KER and the kinetic energy of the electrons. As expected, the electron spectrum consists of a photoelectron line at an energy of approximately 140 meV that is streaked towards lower electron energies. The plot reveals the expected behavior: at lowest photoelectron energies (which correspond to shortest ICD times), mainly low KERs occur. As the electron energy increases, the main peak at a KER of about

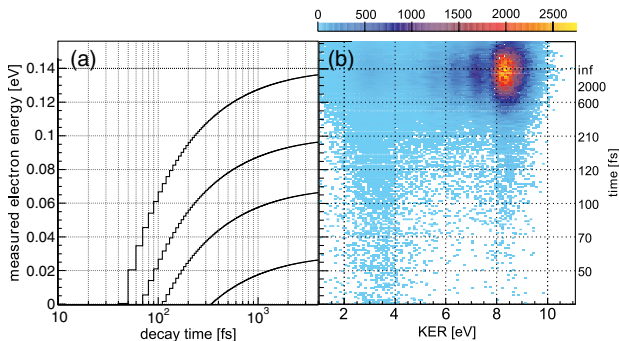


FIG. 3 (color online). (a) Dependence of the shift in electron energy and the decay time obtained from our classical model. The plot depicts on the y axis the energy a measured electron will have if the decay happens after a certain time (shown on the x axis). The behavior is plotted for different initial photoelectron energies. From bottom to top: 30, 70, 100, 140 meV. (b) Electron energies and kinetic energy releases measured in coincidence.

8.5 eV builds up. For even later times the vibrational structures form. The two right-hand panels of Fig. 2 show the KER for different slices in the electron energy for direct comparison with the theoretical results. In Fig. 4 the depopulation of the excited state that undergoes ICD is shown yielding the integrated temporal behavior of the decay. In this plot the contributions of excited states that decay radiatively are omitted by normalizing the initial population of the remaining excited states (i.e., those that decay by ICD) to one. The decay is nonexponential as both theory and experiment reveal: for shortest decay times the decay rates are small as typical internuclear distances are large. As the dimer contracts during later decay times, the rates increase and keep showing the nonexponential behavior that is determined by nuclear motion. The error bars on the experimental data were extracted by converting the experimental electron energy resolution (which scales linearly in energy) to an error in the decay time using our classical PCI model. As suggested by Fig. 3(a), these error bars are (especially at longer decay times) strongly asymmetric, as the conversion is strongly nonlinear. The differences observed between the theoretical description of ICD in the time domain and the experiment are assumed to be attributed to the accuracy of the decay rates entering the nuclear dynamics simulation as discussed in [19].

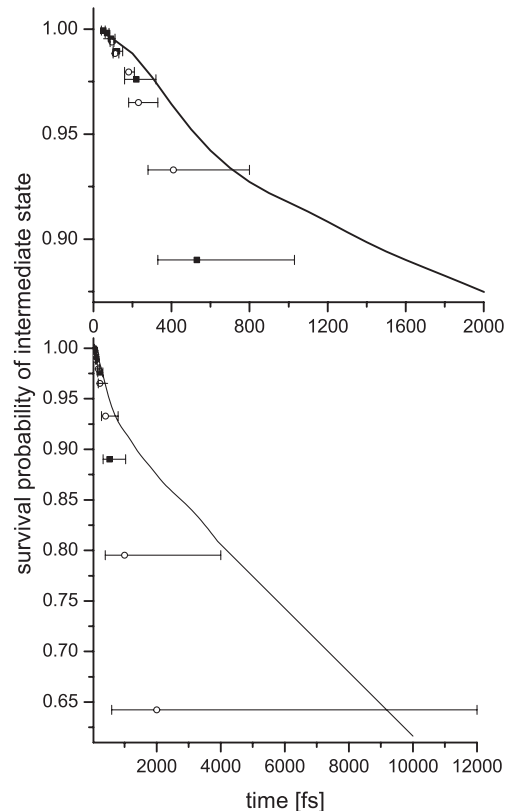


FIG. 4. Temporal behavior of the survival probability of the intermediate excited state prior to ICD for two different time ranges. Contributions that undergo radiative decay are neglected.

In conclusion, we have added a new powerful streaking approach to the toolbox of ultrafast science and applied it to visualize the time dependence of an interatomic decay process. The results directly show the evolution of the vibrational wave packet of a helium dimer during the decay and thus give insight into the complex behavior of ICD in the time domain. The measurement approach presented here can be used to investigate other processes and systems in the time domain as well. Experiments investigating the evolution of a hole created inside an atom or molecule and, for example, the hopping of core holes in molecules [37] could be traced in time in the future using the same approach.

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*Note added.*—Very recently the extraction of the decay time of ICD in Ne<sub>2</sub> assuming an exponential decay behavior has been achieved in an impressive time-resolved experiment by Schnorr *et al.* [38].

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