

## Experimental Evidence for Interatomic Coulombic Decay in Ne Clusters

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Electron spectra of photoexcited Ne clusters are shown to display a signal at low kinetic energies that is neither present in the Ne monomer nor at photon energies below the inner-valence  $2s$  threshold. These findings are strong evidence for the existence of interatomic Coulombic decays (ICD), a mechanism that was recently predicted theoretically [Phys. Rev. Lett. **79**, 4778 (1997)]. In ICD, an inner-valence hole state in a weakly bonded system can undergo ultrafast relaxation due to energy transfer to a neighboring atom, followed by electron emission from this neighboring site.

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The nonradiative decay of a core hole vacancy in an excited atom by electron emission is a well known process in spectroscopy, commonly denoted as Auger decay. Traditionally, it is assumed that in extended aggregates—molecules or bulk matter—electrons only at the excited site actively take part in the decay and that the environment of the initially excited atom only modifies the Auger energy spectrum via its influence on the energy levels [1–3]. In contrast to that, for weakly bound aggregates, such as van der Waals clusters and hydrogen bonded systems, a radiationless decay mechanism has been predicted, which is possible *only* by electron emission from *neighboring* sites of the vacancy [4–6]. The final states populated in this so-called “interatomic Coulombic decay” (ICD) thus have two positive charges distributed at two different atoms of the system [7]. This lowers their total energy by shielding the Coulomb repulsion of the final state holes. For a lot of systems, it is just this shift in final state energy which makes the decay energetically possible. Where present, ICD should be an ultrafast relaxation pathway, which proceeds on time scales of 1–100 fs. It is therefore expected that it dominates over competing channels, like radiative decay or relaxation involving the nuclear dynamics.

Although recently an indirect indication of the relevance of interatomic transitions in the core vacancy decay of molecules has been found [8], an experimental verification of the effect is missing. The major reason for this is probably the low kinetic energy of the electrons emitted by ICD, which is typically a few eV. The unambiguous identification of these electrons would be the only distinct proof for the process. However, the region close to zero kinetic energy in the electron spectrum of a bulk material exposed to vacuum ultraviolet radiation is dominated by inelastically scattered photoelectrons from the valence band. The same is true for clusters, but due to the limited spatial dimensions of the system short range effects like

ICD make a relatively higher contribution to the signal close to zero kinetic energy.

In this Letter we present direct experimental evidence for ICD in the photoexcited electron spectra of small Ne clusters.

In the following, we first introduce the ICD mechanism in some detail. Excited electronic states can decay in two ways, namely, radiatively by emission of a fluorescence photon or nonradiatively by the ejection of an electron. Moreover, a part of the electronic energy can be used to initiate nuclear dynamics, such as conformation changes or dissociation. Roughly, it depends on the energy of the initial vacancy as to which of the mechanisms will be most likely. For excitation energies below the keV regime electronic decay mechanisms typically will dominate if they are energetically possible. To be more specific, we now turn to the inner-valence ( $2s$ ) hole states of first row elements, such as O, F, and Ne. In the isolated atom, these states have a lower energy than the first dicationic state of the respective atom and therefore will decay by fluorescence. In molecules for example CO, again the largest part of the band of states resulting from inner-valence ionization is located below the appearance energy of the doubly charged molecule. The decay will therefore proceed by dissociation, followed by atomic Auger decay [9], or by fluorescence. We now consider systems which are not covalently bound, but condense by van der Waals interactions. Ne clusters constitute one example. Here, due to the larger interatomic distance doubly charged states can be constructed, in which the two vacancies are distributed among neighboring atoms at a larger distance than in an isolated molecule. Consequently, the Coulomb repulsion between them, and thus the total state energy, will be reduced. It has been shown by extensive Green's function calculations for a number of van der Waals and hydrogen bonded systems that the level structure turns out such that this reduction in energy is sufficient to

render inner-valence hole states unstable towards decay into doubly charged cations with distributed vacancies [4–6]. The physical picture behind the IC decay of these states is fairly clear [5,10]: The initial inner-valence hole is filled by an outer-valence electron from the same site. The energy released by this transition is consumed to eject another outer-valence electron from a neighboring site. Preferentially, nearest neighbor sites are emptied by the ICD. The process therefore is mediated by ultrafast *energy transfer*. Transitions in which the inner-valence hole is filled by an electron from a neighboring site (*charge transfer*) can also be considered [11], but seem to be of lesser importance in homoatomic clusters. For Ne clusters, this relationship is sketched in Fig. 1. Contrary to conventional autoionization or Auger processes, decays of these  $2s^{-1}$  states are facilitated only by the assistance of the chemical environment surrounding the initially excited site.

The experiments have been carried out at the undulator beam line U125/1-PGM of the synchrotron radiation source BESSY II (Berlin, Germany). A beam of free clusters was produced by expanding Ne gas through a  $200\ \mu\text{m}$  nozzle with a half opening angle of  $15^\circ$ . The nozzle was cooled with LHe. The expansion chamber and the main vacuum chamber were separated by a conical skimmer. Electrons were detected by a hemispherical spectrometer (Scienta ES-200) mounted perpendicular to the light propagation axis, and under  $54.7^\circ$  relative to the electric field vector of the synchrotron radiation.

Electron spectra of two different Ne cluster sizes were measured at photon energies below and above the Ne  $2s$

threshold. A nozzle temperature of 40 K and a Ne stagnation gas pressure of 100 mbar led according to Ref. [12] to a mean cluster size of  $\langle N \rangle = 30$ , whereas a nozzle temperature of 38 K and a Ne stagnation gas pressure of 150 mbar led to  $\langle N \rangle = 70$ . Pressures in the expansion chamber and the main chamber then were at  $1.3 \times 10^{-3}$  and  $2.3 \times 10^{-6}$  mbar.

The transmission function of the analyzer was checked by comparing measured intensities of the Ne  $2s$  photo line to literature data [13] and was found to substantially decrease for kinetic energies below 0.5 eV, with the lowest energy detectable at 0.38 eV. However, no quantitative correction was attempted.

Figure 2 shows electron spectra of Ne clusters of an average size of  $\langle N \rangle = 70$  atoms per cluster. The spectrum at 40 eV is the only one shown below the Ne  $2s$  threshold. At photon energies above the threshold the sharp, atomic Ne  $2s$  photoelectron line can be identified. The presence of this line is due to uncondensed Ne atoms in the beam. The cluster to monomer intensity ratio, as derived from the  $2p$  photo line (not displayed), was around 1, with a time dependent variation of less than 20%. In addition to the  $2s$  monomer line there is a twofold structure at lower binding energies, characteristic of the photoelectron signal of Ne clusters. The splitting of the line is due to differences in the binding energy of Ne atoms at surface and bulk sites of the cluster.

In the region below 3 eV kinetic energy in all spectra a gradual increase of the signal can be seen. This might partly be caused by electrons inelastically scattered on apparatus parts, or on other clusters inside the beam. The spectrum recorded at 40 eV photon energy can also be influenced by the onset of satellites due to  $2p$  cluster photoionization plus creation of an excitonic state [14]. However, a much more significant modulation, with its maximum at about 1.2 eV kinetic energy, is present in this region at photon energies above the  $2s$  photoionization threshold. This part of the signal disappears when the conditions for cluster formation in the beam are no longer met. In contrast to the features produced by direct photoionization, the position of this modulation does not change with photon energy. Moreover, its shape is very similar for the spectra taken at 51.5 and 58 eV. In the spectrum taken at 49.5 eV photon energy, also the  $2s$  photoelectron lines fall within this region of kinetic energies. However, comparing their shape, especially the valley between monomer and cluster peak, with the spectrum taken at 51.5 eV, it seems to be very plausible that another contribution similar to the features observed in the two former spectra is also underlying the  $2s$  lines in the 49.5 eV spectrum. Altogether, from these facts it seems to be very unlikely that the modulation in the low kinetic energy signal that we observe above the Ne  $2s$  threshold is caused by secondary electrons. We therefore attribute this part of the signal to ICD processes taking place in the Ne clusters after  $2s$  photoionization.

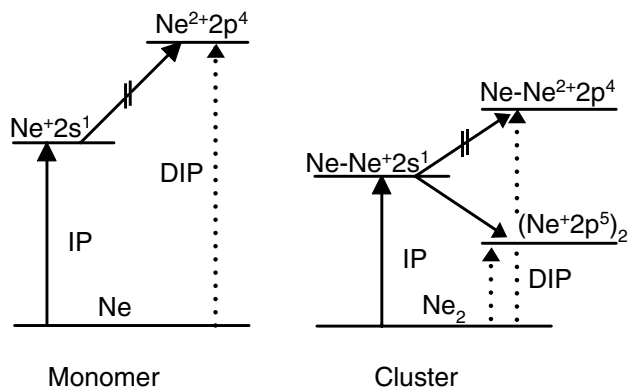


FIG. 1. Sketch of the important energy levels in Ne and  $\text{Ne}_2$ . In Ne, a  $2s$  vacancy cannot decay by an Auger process, because the transition from  $\text{Ne}^+ 2s^1 2p^6$  to the final state  $\text{Ne}^{2+} 2s^2 2p^4$  by electron emission would consume energy (left panel). For a Ne cluster the situation is different. In this case a  $2s$  vacancy can relax from  $\text{Ne}^+ 2s^1 2p^6$  to  $(\text{Ne}^+ 2s^2 2p^5)_2$  by ICD. So, in the final state the two  $\text{Ne}^+ 2s^2 2p^5$  sites in the cluster will have a significantly lower Coulomb repulsion than  $\text{Ne}^{2+}$ . Subsequently, the cluster will fragment by Coulomb explosion. The ionization potential (IP) and the double ionization potential (DIP) are given in the figure.

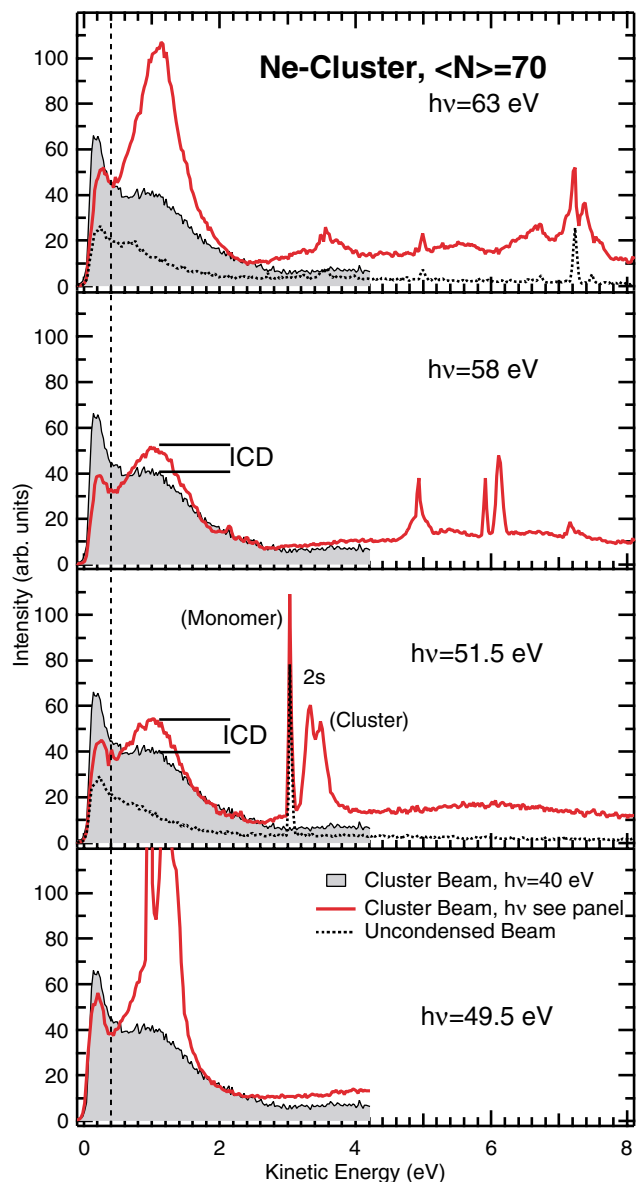


FIG. 2 (color online). Photon excited electron spectra of Ne clusters with an average size of  $\langle N \rangle = 70$  atoms. The spectra depicted by thick solid lines are taken at different photon energies above the Ne  $2s$  threshold. For comparison, in every panel a spectrum recorded below the  $2s$  threshold is shown (shaded region). At 51.5 and 63 eV, we also show the spectrum obtained with a Ne beam at temperatures slightly higher than the onset of condensation (thin, dotted lines). All spectra were measured as one series and have been normalized by the photocurrent of the last refocusing mirror of the beam line. The signal at kinetic energies below 0.4 eV (left of vertical, dashed line) contains contributions of unphysical, scattered electrons.

The spectrum taken at 63 eV photon energy differs from the aforementioned three spectra by an even higher signal in the region between 0.8 and 2 eV kinetic energy. Here, the photon energy is sufficient for photo double ionization of a single site within the cluster. The energy

for this process has been calculated as 60.9 eV for  $\text{Ne}_2$  and slightly lower for  $\text{Ne}_3$  [5]. For atomic Ne, 62.53 eV were found experimentally [15]. A photon energy of 63 eV therefore is sufficient to yield two photoelectrons, each with a kinetic energy below 2 eV, which might cause the enhancement of the 1.2 eV electron peak.

The spectra at photon energies of 58 and 63 eV exhibit further discrete structures around 4–8 eV kinetic energy. These can partly be identified as photoelectron lines of the Ne  $2p$  correlation satellites excited in the atomic fraction of the beam. The spectrum at 63 eV we can also compare to the signal obtained from an uncondensed beam. This reveals evidence for additional, weak satellitelike lines present only in the spectrum of the cluster beam, the study of which, however, cannot be discussed further here.

The spectra of the smaller clusters of  $\langle N \rangle = 30$  (not displayed) after subtraction of an atomic background do as well show an enhancement of the intensity in the region around 1–2 eV, but less prominently than in Fig. 2. This can be explained by the larger fraction of uncondensed monomers in the supersonic beam at these conditions of the expansion source. Of course, the monomers contribute to the background of inelastically scattered electrons, but not to ICD.

In contrast to Ne, the energy levels in Ar clusters do not allow ICD of the  $3s$  vacancy. (We have determined IPs of 28.7 and 28.4 eV for surface and bulk  $3s$  electrons, respectively, while the DIP is at 32 eV or higher, dependent on cluster size [16].) In an independent experiment under similar conditions as delineated before, we have recorded the low kinetic energy signal of Ar and Ne spectra to compare. Similar number densities of the gas targets were chosen. The photon energy was set below the threshold of photo double ionization for a single Ne site (see above). Results are shown in Fig. 3. Inspection of the region below 2 eV kinetic energy in the Ar spectrum does not reveal the presence of any pronounced features. In our opinion, this adds further evidence to our interpretation of the enhanced low kinetic energy intensity observed from Ne clusters. The full results of these additional measurements will be reported elsewhere.

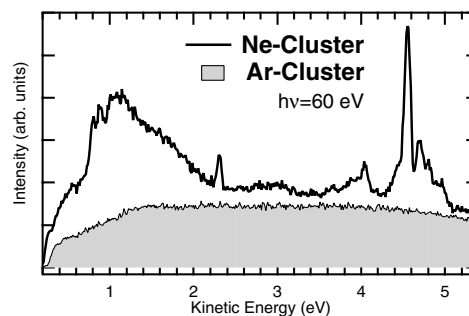


FIG. 3. Low kinetic energy electron spectra of Ne (solid line) and Ar (shaded region) clusters, normalized as in Fig. 2.

The lifetime broadening due to ICD therefore has been found to strongly depend on the number of neighboring atoms. For the central atom of a  $\text{Ne}_{13}$  aggregate, it has been calculated as 200 meV, corresponding to a lifetime of the inner-valence hole of only 3.3 fs. In this configuration, the atom is fully surrounded by nearest neighbors. Therefore, results for even larger clusters should be in a similar range. For Ne atoms in surface sites, a lifetime of 10 fs has been estimated [17]. The broadening of the ICD structure due to the underlying doubly charged states can be estimated as 0.75 eV for the central atom in a  $\text{Ne}_{13}$  configuration [17,18]. For the decay of surface atoms, a lesser number of different states is important; on the other hand, here the ICD line might be broadened due to the effect of the subsequent Coulomb explosion of the system [5]. Additional broadening of the observed electron lines in our experiment, as compared to the calculation, can be expected, since our cluster beam contains a distribution of different cluster sizes and since we cannot distinguish ICD electrons emitted from different sites within the cluster. The observed width of the feature assigned to ICD in our experiment qualitatively agrees with the combined effect of these line broadening mechanisms.

ICD can be compared with other recent findings, which have questioned the strictly local picture of autoionizing transitions. In spectra of MnO and other bulk metal oxides, a weak but significant amplification of the O 1s photoelectron line was found by tuning the photon energy to a resonant core excitation of manganese [19]. This effect was explained by taking into account Coulomb transition matrix elements, in which the resonantly created Mn core hole is filled by a local electron, and energy is transferred to a neighboring oxygen site to eject a 1s electron. Since this process competes with other, purely local decay channels, its relative importance is in the percent range at most. The local model of Auger decay was also questioned in a recent study of the lifetime broadening of molecular inner-shell photoelectron lines, which reflect the Auger transition strengths integrated over all final states. Significant differences of the experimental results to calculations within the one-center approximation have been found [8].

As the result of an IC decay, a weakly bound aggregate with two positive charges at different sites is formed. Thus, very shortly after the initial excitation a Coulomb explosion of the final state will follow. For van der Waals clusters, this channel will fragment the cluster much faster than the usually considered mechanism by hole localization into a more strongly bound oligomer inside the cluster and subsequent fragmentation of the cluster by the excess energy release [20]. The ICD mechanism may also have important implications for proposed experiments on condensed matter with ultrashort x-ray pulses, e.g., from a free electron laser. Since the energy dissipation by ICD occurs on a very short time scale, it may

foreclose the currently often assumed tunneling mechanisms for interatomic charge equilibration [21].

In conclusion, we have collected experimental evidence for the radiationless decay of inner-valence ionized states in Ne clusters. This process can proceed only by active participation of an electron pertaining to a second site in the cluster, for example, a neighboring atom. Our results are consistent with theoretical predictions for a nonlocal decay mode of vacancies in a huge variety of weakly bonded systems, which has been termed interatomic Coulombic decay.

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