

Slow Interatomic Coulombic Decay of Multiply Excited Neon Clusters

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Ne clusters (~ 5000 atoms) were resonantly excited ($2p \rightarrow 3s$) by intense free electron laser (FEL) radiation at FERMI. Such multiply excited clusters can decay nonradiatively via energy exchange between at least two neighboring excited atoms. Benefiting from the precise tunability and narrow bandwidth of seeded FEL radiation, specific sites of the Ne clusters were probed. We found that the relaxation of cluster surface atoms proceeds via a sequence of interatomic or intermolecular Coulombic decay (ICD) processes while ICD of bulk atoms is additionally affected by the surrounding excited medium via inelastic electron scattering. For both cases, cluster excitations relax to atomic states prior to ICD, showing that this kind of ICD is rather slow (picosecond range). Controlling the average number of excitations per cluster via the FEL intensity allows a coarse tuning of the ICD rate.

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When an electronically excited atom (or molecule; we will ignore the distinction from here on) that can decay only radiatively if alone, is placed close to other atoms, a new more efficient nonradiative relaxation pathway may be opened. The electronically excited atom may relax by transferring its energy to ionize a neighboring atom. Such an electronic decay was first predicted by Cederbaum, Zobeley, and Tarantelli in 1997 and called interatomic or intermolecular Coulombic decay (ICD) [1]. Since then, ICD has been extensively investigated experimentally and theoretically in a variety of loosely bound systems (for recent reviews, see Refs. [2–4]). ICD was first observed in Ne clusters [5–7] and later identified as a source of low-energy electrons in water [8,9]. Noting that low-energy electrons cause genotoxic effects [10], it was argued that ICD is relevant to radiation damage in biosystems [8,9].

To initiate ICD, the electronically excited atom may be produced by various processes such as inner valence ionization [5–9], inner valence excitation [11–14], shakeup satellites [15–17], and after normal Auger decay [18–20]. It was demonstrated that the energy of ICD electrons can be controlled in ICD cascades following resonant (spectator) Auger decay [21–23]. Since the site- and energy-selected electrons can be produced via resonant-Auger-induced ICD, this ICD scheme may be beneficial for applications in radiation therapy [24,25].

A completely different excitation mechanism triggering ICD was proposed by Kuleff *et al.* in 2010 [26], benefiting from the advent of extreme ultraviolet free electron lasers (EUVFELs) that can generate ultrashort, intense, and tunable photon energy light pulses [27–29]. When a cluster is exposed to such pulses with the photon energy tuned to a resonance below the ionization threshold, a multiply

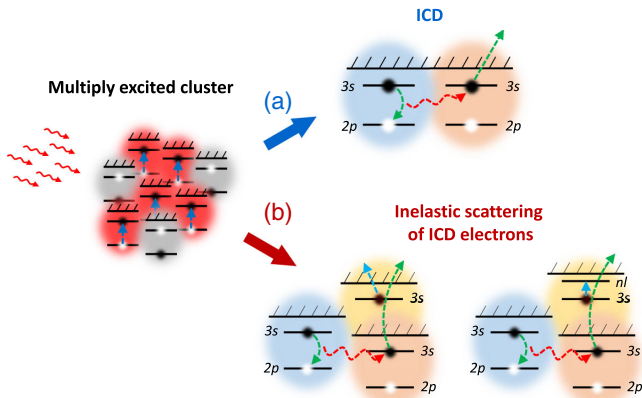


FIG. 1. Schematic representation of interatomic Coulombic decay scenarios (a) when only few atoms are excited in the cluster and (b) in the multiply excited cluster.

excited state is formed. This state can decay nonradiatively via energy exchange between at least two excited atoms [Fig. 1(a)]. Such a decay process belongs to the class of ICD and was shown theoretically to be the dominant ionization mechanism in comparison with two-photon ionization of individual atoms in the cluster [26].

Stimulated by the work of Kuleff *et al.* [26] and following the measurement of ionic fragmentation upon $2p \rightarrow 3d$ multiple excitation (20.26 eV) of Ne clusters [30], Yase *et al.* [31] investigated the EUV-FEL-induced electron emission from Ne clusters at SCSS (SPring-8 Compact SASE Source test accelerator, Japan) [28]. However, in the FEL intensity range they used ($\geq 3 \times 10^{13}$ W/cm²), no ICD processes could be identified. Later, by reducing the FEL intensity ($\leq 5 \times 10^{11}$ W/cm²), Nagaya *et al.* [32] discovered that $3d$ states mostly decay to $3s$ states ionizing another $3d$ excited atom. This process quenches the direct ICD, which involves recombination of the $3d$ electron with a $2p$ hole. This new process was termed intra-Rydberg ICD and may be followed by subsequent ICD between $3s$ states. In a study of multiply excited He clusters, Ovcharenko *et al.* [33] found that ICD, in which the $2p$ electron recombines with the $1s$ hole, can be very efficiently quenched by collective autoionization (CAI) [34] involving at least three excited atoms.

In the present Letter, we have clearly identified ICD emission following multiple excitation of Ne clusters. For this purpose we investigated the lowest electron excitation $2p \rightarrow 3s$ of both surface and bulk atoms of the cluster. Surface $2p \rightarrow 3s$ excitation provides a clean ICD pathway and the electron emission spectra allow the identification of all the relaxation steps; ICD relaxation of bulk atoms is additionally affected by the inelastic electron scattering from other excited atoms. Coulomb blockade sets an upper limit to the attainable concentration of excited states, thus a lower limit to the ICD lifetime, which allows cluster excitations to relax to atomic states prior to ICD.

The specific sites (surface and bulk) of a Ne cluster can be probed selectively due to their slightly different resonance energies. According to the absorption spectra of Ne clusters ($N = 2200$) [35] and solid Ne [36], the $2p \rightarrow 3s$ resonance energy is lower by 0.5 eV for surface atoms than for bulk atoms. The present experiment became possible with the advent of the coherent seeded EUV-FEL light available only at FERMI [29], which was specifically configured for the desired spectral range. Its precise tunability and narrow bandwidth are essential to selectively probe the specific sites of the Ne cluster excitations.

The experiment was performed at the Low Density Matter beam line [37]. FEL pulses with photon energies $h\nu = 17.12$ and 17.65 eV with bandwidth of 90 meV (FWHM) were used to populate surface and bulk $2p \rightarrow 3s$ excitations, respectively. The beam was focused to 30 μm FWHM spot size with an estimated pulse duration of 100 fs. The pulse energy was varied in the range 1–82 μJ and measured on a shot-by-shot basis with further corrections due to transport optics losses [37,38]. Ne clusters were produced by adiabatic expansion of Ne gas at 10 bar stagnation pressure through a commercial pulsed valve (Parker model 9, convergent-to-cylindrical nozzle with flat aperture of 250 μm diam) at a temperature of 60 K. According to the well-known Hagen scaling law [39] these clusters contain on average 5000 atoms. The projections of three-dimensional electron emission were recorded using a velocity map imaging (VMI) spectrometer. The electron momentum distribution was then reconstructed using the pBASEX algorithm [40].

The ionization potential (IP) of Ne clusters ($N = 5000$) was estimated at several photon energies (26–40 eV) above the $2p$ ionization threshold. Besides the broadening of cluster photolines, no energy shift was observed compared to bare atoms within the spectrometer energy resolution (0.6 eV at 13 eV kinetic energy). Thus all binding energies were derived from the atomic IP, 21.6 eV. Previous photoionization experiments on Ne clusters ($N = 100$ –1100) reported a slight decrease of the $2s$ binding energy, by a few hundred meV [7,41].

The electron emission spectra (normalized by FEL intensity) following multiple excitations of Ne clusters are presented in Figs. 2(a) and 2(b). The electron spectra show rather rich structure although the photon energies are set below the direct ionization threshold.

Figure 2(a) corresponds to the $2p \rightarrow 3s$ excitation of the surface atoms. The small peak at 12.64 eV which is marked with a vertical dashed line corresponds mostly to ionization of the uncondensed atomic beam by the FEL 2nd harmonic ($2 \times 17.12 - 21.6 = 12.64$ eV). Indeed, due to the lasing mechanism of FELs, the light pulse always contains a small fraction (up to a few percent) of 2nd and 3rd harmonics. The main peak at 11.5 eV is assigned to ICD of two $2p$ excited atoms as illustrated in Fig. 1(a). A clear shift of about -1.1 eV indicates that resonantly excited cluster

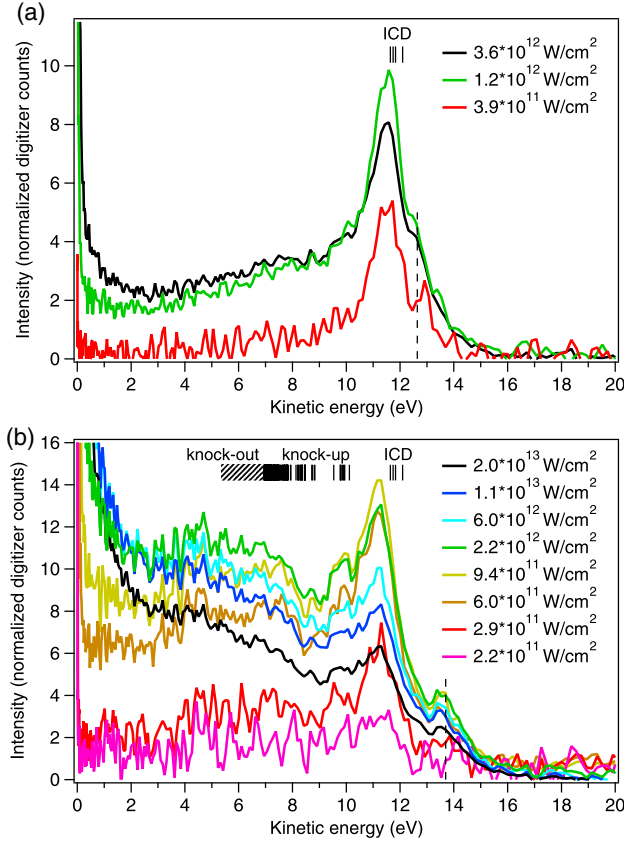


FIG. 2. FEL intensity normalized electron emission spectra of Ne clusters ($N = 5000$) measured for (a) surface and (b) bulk $2p \rightarrow 3s$ excitations at $h\nu = 17.12$ and 17.65 eV, respectively. Spectra were recorded at different FEL intensities as indicated. The vertical dashed lines indicate the electron kinetic energy ($2 \times h\nu - \text{IP}$) when uncondensed Ne atoms or clusters are ionized by FEL 2nd harmonic radiation. Labels on top of the spectra indicate ICD electron energy after the excited cluster atoms relaxed to atomic $3s$ states as well as ICD electron energy losses via inelastic scattering on other $3s$ excited atoms, promoting them to higher Rydberg states (knock-up) as well as to the continuum (knock-out) (Ne energy levels from NIST ASD [42]).

surface atoms ($E_{2p \rightarrow 3s}^{\text{surface}} = 17.12$ eV) relax to atomic states which are lower in excitation energy ($E_{2p \rightarrow 3s}^{\text{atom}} \approx 16.7$ eV average energy of the $2p^5 3s$ configuration) and thus result in $2 \times 16.7 - 21.6 = 11.8$ eV ICD kinetic energy [marked on top of the spectra in Fig. 2(a)]. This assignment also implies that the lifetime of cluster relaxation to atomic states is smaller than the ICD lifetime. Previously, extensive information has been obtained on the formation of atomic self-trapped excitons (*a*-STE), in particular, the $n = 1$ exciton excitation in solid Ne relaxes to *a*-STE with characteristic time of about 1 ps at the temperature of 60 K according to the scaling law [43]. More recently, cluster relaxation to atomic states was observed in He nanodroplets during Penning ionization [44].

Since at the current FEL intensities many atoms are excited within a single cluster, the broadening, asymmetry,

and additional shift of the peak at 11.5 eV results from the overlap of several ICD peaks. Each of the subsequent ICD electrons is downshifted in energy due to the developing Coulomb field, and the electron spectrum shows a plateau declining towards lower kinetic energies. This plateau is very similar to the plateau observed in the photoionization of Ar clusters at FLASH FEL [45], where it was explained by sequential electron emission from the same cluster, each progressively shifted to lower kinetic energy due to cluster charge buildup [45,46]. Both sequential atomic photoionization in the developing cluster Coulomb potential as well as ionization heating are responsible for the structure of the plateau. The fact that a clear peak, rather than a pure step function, is observed in the electron spectrum stems from the FEL volume effect. Clusters in the wings of the FEL focal spot are weakly excited and thus give rise to very few ICD events: those contribute to the main peak, not to the plateau.

An average shift after each ionization event can be estimated using the Coulomb potential $-e^2/4\pi\epsilon_0 r$. In a Ne cluster of 5000 atoms, corresponding to a diameter of 6 nm, the average distance between any two atoms on the cluster surface is $\langle r \rangle = 3.8$ nm which gives a value of -0.38 eV for the energy shift between two ionization events. This estimate leads to ionization frustration after about 30 ICD events from the same cluster and eventually nanoplasma formation. The characteristic thermal emission can be seen in the electron spectra at low kinetic energies as an exponential distribution [Fig. 2(a)], which becomes prominent at FEL intensities above 10^{12} W/m². One can also note the strong contribution of extremely low kinetic energy electrons (< 30 meV). This indicates the presence of high-lying Rydberg states that are formed during nanoplasma expansion and then ionized by the static electric field of the VMI spectrometer [47].

Another contribution to the shift of the ICD peak is the increased IP of the multiply excited cluster in comparison with a cluster in the ground state. *Ab initio* calculations (using the algebraic diagrammatic construction scheme [48]) of the IP of a Ne atom in the presence of a neighbor $3s$ excited Ne atom have shown a significant change of the IP as a function of the internuclear separation. While for somewhat larger separation (~ 7 Å) the IP is slightly lowered, reflecting the stronger bonding due to the large polarization of the electronically excited atom, for short distances an increase of up to 1.7 eV (for the Ne dimer equilibrium internuclear separation of 3.1 Å) is found, which is due to the repulsion between the ionic cores.

Let us finally note that the presence of many excited atoms within a cluster sets an upper limit to their abundance, by shifting the energy of the transition out of resonance (Coulomb blockade). By comparison with the $3s$ doubly excited Ne dimer [49] we can assume that an excited atom blocks all nearest neighbors, setting the excitation abundance limit to $\approx 8\%$ of the atoms in the

cluster. The same reasoning sets a lower limit to the ICD lifetime: according to the interatomic distance dependence of ICD rate ($\propto 1/R^6$) [50], and after carrying the summation over all pairs of atoms in a cluster while taking into account that one excited atom blocks its 12 nearest neighbors and an overall 8% excitation abundance, we can scale the *ab initio* calculated ICD lifetime of 200 fs in the $\text{Ne}^*(3s) - \text{Ne}^*(3s)$ dimer [49] to a bigger cluster. The limit to the ICD lifetime in a multiply excited cluster is then 1 ps.

Turning our attention to the $2p \rightarrow 3s$ excitation of the bulk atoms, one can notice that although the resonant photon energy is higher by 0.5 eV with respect to surface excitation, the position of the ICD peak did not change substantially [Fig. 2(b)]. This additionally suggests that the excited bulk atoms also relax to atomic states prior to undergoing ICD. The striking difference between surface and bulk excitation is the broad hump between 2 and 10 eV in the latter electron spectra. It is assigned to the inelastic scattering of ICD electrons by other excited atoms in the cluster. The outgoing ICD electron can either ionize another excited atom (knock-out) or promote it to higher Rydberg state (knock-up) [see Fig. 1(b)]. The corresponding energy losses are marked in Fig. 2(b). The experimental spectra allow us to resolve a small feature around 10 eV, which is attributed to ICD electron energy loss due to $3s \rightarrow 3p$ excitation. The energy losses due to higher excitations form a broad structure which evolves into a continuum where both the ICD electron and knock-out electron share the remaining energy of 7 eV.

The importance of inelastic scattering effects was already discussed for multiple excitation of He clusters [33] as well as for the $2p$ photoionization of Ne clusters [11,41,51]. Inelastic electron scattering becomes a very important process during the relaxation of the multiply excited cluster interior. Let us now estimate the probability of such a process based on atomic data. The electron impact cross section for the $3s \rightarrow 3p$ transition is ≈ 2000 Mb at 12 eV electron energy, whereas for excitation from the ground state its peak value is < 1 Mb [52]. Assuming that 8% of atoms in the Ne cluster ($N = 5000$) are excited, one obtains a mean free path of 1.4 nm. Thus, it is very probable that ICD electrons lose 1.4 eV on $3s \rightarrow 3p$ excitation while escaping a 6 nm diameter cluster, and thus resulting in a small peak at 10 eV. The high cross section for ionization of $3s$ states by electron impact (≈ 500 Mb [53]) is responsible for the broad structure below 7 eV in Fig. 2(b). As in the case of cluster surface excitation, all features in the electron emission spectra are additionally affected by the cluster charge buildup.

To summarize, we have studied the relaxation processes in Ne clusters following multiple valence excitations by intense FEL pulses. Benefiting from the precise tunability and narrow photon bandwidth of the FERMI FEL, specific sites of the cluster were probed selectively. The interatomic Coulombic decay processes of such multiply

excited clusters have been identified unambiguously. The $2p \rightarrow 3s$ excitation of cluster surface atoms is followed by a clear sequence of ICD processes involving pairs of excited atoms. The ICD following $2p \rightarrow 3s$ excitation of cluster interior atoms is additionally affected by the intracluster inelastic scattering of emitted ICD electrons from excited atoms, promoting them to the higher Rydberg states or to the continuum. For both surface and bulk excitations, the cluster atoms relax to atomic states prior to ICD, indicating its long lifetime (\sim ps) in comparison to ICD following photoionization, which is usually very fast (of the order of 10 fs). The lifetime of the ICD state is very sensitive to the environment, in particular, to the distance between the neighbors. The long lifetime of the presently observed ICD stems from the distances between the two adjacent excited states. Generally it is rather difficult to control the distance between the atoms in the cluster: in this case the Coulomb blockade sets a convenient limit; this observation furthermore suggests that we can control the ICD rate by the laser intensity since it controls the number of excited states in the cluster. The controllable relaxation mechanism of multiply excited Ne clusters reported in this Letter is expected to be a very general phenomenon occurring in any weakly bound systems exposed to intense resonant light.

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