Neutralization of Multiply Charged Ground-State Ions by Collective Electron Transfer from an Environment

Lutz Marder,[1,*] Catmarna Küstner-Wetekam,[1] Nils Kiefer,[1] Johannes Viehmann,[1] Niklas Golchert,[1] Emilia Heikura,[1] Florian Trinter,[2] Denis Cubaynes,[3] Jérôme Palaudoux,[4] Francis Penent,[4] Arno Ehresmann,[1,†] Lorenz S. Cederbaum,[5] Přemysl Kolorenč,[6] and Andreas Hans[1,‡]

[1]*Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany*
[2]*Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*
[3]*Institut des Sciences Moléculaires d'Orsay, CNRS, Bâtiment 520, Université Paris-Saclay, 91405 Orsay-Cedex, France*
[4]*Laboratoire de Chimie Physique - Matière et Rayonnement, Sorbonne Université, CNRS, LCP-MR, 75005 Paris Cedex 05, France*
[5]*Theoretische Chemie, Physikalisch-Chemisches Institut, Heidelberg University, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany*
[6]*Faculty of Mathematics and Physics, Institute of Theoretical Physics, Charles University, V Holešovičkách 2, 180 00 Prague, Czech Republic*

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Highly charged cations are omnipresent species after the interaction of high-energy or high-intensity light with matter. When embedded in environments, the mechanism and outcome of the redistribution of the cation's charge are crucial for the further fate of the whole system. Generally, ground-state cations can decay by charge transfer, proceeding radiatively, through nuclear dynamics, or by electron-transfer-mediated decay (ETMD). ETMD causes electron emission from a remote neighbor and appears ubiquitous in loosely bound systems. It remained unclear how multiply charged ions decay if conventional ETMD channels are closed. Here, we show that a yet undiscovered variant of ETMD is possible, where multiple electrons are collectively transferred. Explicitly, we observe ETMD in which two electrons from two distinct neighbors (partially) neutralize a multiply charged ion, and an electron from a fourth site is emitted. According to the established nomenclature, we suggest naming the process ETMD(4).

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The deposition of a large amount of energy in an atom or molecule typically leads to its multiple ionization, often caused by a cascade of secondary processes until the ground state of the ion is reached [1–6]. During the last decades, it became clear that a highly charged ion, although it may be in its ground state, can be (partially) neutralized by electron transfer from surrounding atoms or molecules if it is embedded in an environment. Such processes are of utmost importance in radiation biology because, e.g., multiply charged biomolecule ions, produced as a result of their interaction with x-rays, will dissociate due to Coulomb repulsion [7,8]. While this introduces severe harm to biological matter, neutralization and charge redistribution may ultimately reduce the final damaging dose. In general, interatomic and intermolecular energy and charge transfer processes have been studied extensively in recent years, and by now, it is well established that they occur universally in dense matter [9–11].

Although individual isolated ground-state ions cannot decay any further, in an environment the total energy of the system can be further reduced by charge delocalization. For the final fate of the system as a whole, it is of fundamental importance by which mechanisms the charge delocalization proceeds. In that context, theoretical and experimental work so far focused on the transfer of a single electron to singly or doubly charged cations [12]. Here, (partial) neutralization by electron transfer can proceed radiatively (radiative charge transfer, RCT) [13–16], through nuclear dynamics [17], or through autoionization by electron-transfer-mediated decay (ETMD) [10,18]. In ETMD, the ion is partially or fully neutralized by electron transfer from the environment, and another electron is emitted, either from the same site where the transferred electron originated [ETMD (2)] or from a third site [ETMD(3)]. Variants of ETMD have been observed and discussed in numerous investigations for van der Waals clusters [19–21], in droplets [22], and in aqueous solutions [23–25].

*Contact author: lutz.marder@uni-kassel.de
†Contact author: ehresmann@physik.uni-kassel.de
‡Contact author: hans@physik.uni-kassel.de

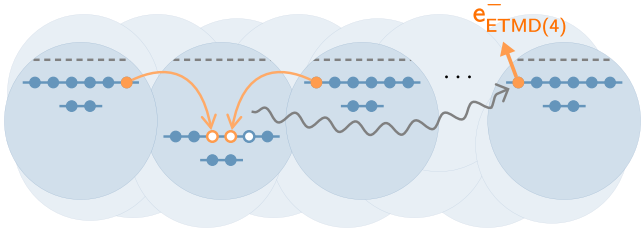

FIG. 1. Sketch of the double-electron-transfer-mediated decay process, ETMD(4), in a homogeneous rare-gas cluster. The initial state in this example is a triply charged ground-state ion in an environment of neutral atoms of the same species. Two electrons are transferred simultaneously from different neighboring atoms, and the total energy difference is carried over to a fourth site—possibly at a larger distance—via a virtual photon, ionizing it. Depicted are only valence orbitals relative to the ionization threshold (dashed line); deeper shells have been omitted for clarity.

In the present Letter, we demonstrate that if ETMD(2) and ETMD(3) are energetically impossible, the charge of a highly charged ion can nevertheless efficiently be delocalized by a collective simultaneous transfer of several electrons from different atoms, resulting in ionization of yet another atom. We combine theoretical estimates of the decay widths of such processes with the experimental investigation of two different prototype systems. Without loss of generality, we will first focus on the combined transfer of two electrons from two different sites. The mechanism is illustrated in Fig. 1 for the exemplary case of a homogeneous rare-gas cluster with a triply charged ion as the initial state. Here, the energy released by the transfer of two electrons is transferred to an additional site, which thereby emits an electron. According to the established nomenclature, we suggest naming this process ETMD(4), since four different sites are involved.

ETMD(4) can be described as

$$X_{N-1}X^{q+} \longrightarrow X_{N-4}X^{(q-2)+}(X^{+})_3 + e^{-}_{\mathrm{ETMD}(4)} \qquad (1)$$

in a cluster composed of N atoms of species X including a q-fold charged cation. All participating sites are assumed to end up in their local ground states. In general, homogeneous and heterogeneous environments can be considered, i.e., not all X have to be of the same species.

As a first exemplary prototype system, we consider the decay of $Ar^{2+}\ (3p^{-2})$ ions in a heterogeneous cluster composed of N Ar and M Kr atoms. Equation (1) can now be specified to

$$\mathrm{Ar}_{N-1}\mathrm{Ar}^{2+}\mathrm{Kr}_M \longrightarrow \mathrm{Ar}_N\mathrm{Kr}_{M-3}(\mathrm{Kr}^{+})_3 + e^{-}_{\mathrm{ETMD}(4)}. \qquad (2)$$

The energetics of the initial $Ar^{2+}\ (3p^{-2})$ and possible final states are sketched in the potential energy curve (PEC) diagram in Fig. 2. The figure shows estimated PECs for the relevant charge-transfer processes which are candidates for the decay of the $\mathrm{Ar}_{N-1}\mathrm{Ar}^{2+}\ (3p^{-2})\mathrm{Kr}_M$ dicationic ground state. For the calculation of the PECs, we used experimentally determined values for the asymptotic ionization potentials of the respective atoms and pairwise Coulomb energies between the resulting ions after the charge transfer. Note that due to polarization screening, the ionization potentials are somewhat shifted to lower energies in the clusters compared to the atomic values [26,27]. The varied parameter R is the internuclear distance at which the decay is considered to take place. For ETMD, only the distance between the atom emitting the (ETMD) electron and the closest ion was varied. The other distances (i.e., for electron transfers) remained constant at their equilibrium values. Since the process considered is expected to be faster than typical nuclear dynamics and charge transfers are unlikely at larger distances, the equilibrium distance from the neutral dimer R_{eq} is a sensible choice for the distances at which the electrons are exchanged. For details on the computation and generation of this diagram, see Supplemental Material [28].

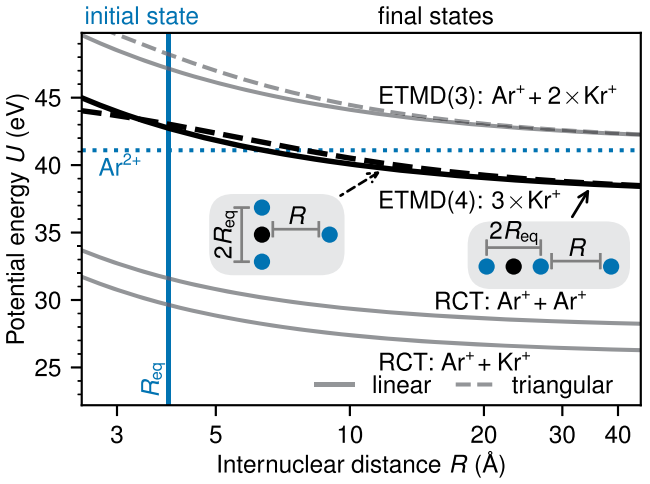

FIG. 2. Potential energy curves for charge-transfer processes of $Ar^{2+}\ (3p^{-2})$ in $\mathrm{Ar}_N\mathrm{Kr}_M$ clusters. The potential energy is calculated as a function of the internuclear distance R for ETMD(3) and ETMD(4) channels, and two kinds of RCT channels (Ar–Ar and Ar–Kr). The considered linear and triangular geometries are depicted in the shaded insets for the ETMD(4) process, where the black and blue circles represent the Ar ion and Kr atoms, respectively. The initial-state potential energy (blue dotted line) was determined experimentally. The equilibrium distance R_{eq} in the neutral Ar–Kr dimer of 3.92 Å [29] is indicated as a blue solid vertical line. Only ionic ground states are considered here. For details on the computation see the text and Supplemental Material [28].

The energy of the initial doubly charged $\mathrm{Ar}_{N-1}\mathrm{Ar}^{2+}\ (3p^{-2})\mathrm{Kr}_M$ state is indicated in Fig. 2 by a horizontal line (blue dotted), which is typically valid at internuclear distances greater than the equilibrium distance [30]; it was determined from the experimental cluster

Auger electron spectrum. Both RCT channels with Ar or Kr neighbors of the dication are energetically allowed, Ar–Ar lying a bit above Ar–Kr in energy due to the difference in ionization potentials between Ar and Kr. Two curves are shown for the ETMD(3) process: for a triangular geometry (dashed line) and a linear geometry (solid line), the latter is energetically slightly favored. Evidently, ETMD(3) is energetically impossible due to the high Coulomb energy introduced by two directly neighboring ions and the required ionization energy for the third atom.

The ETMD(4) curves were calculated for two similar geometries, a linear and a triangular arrangement, as depicted in the insets in Fig. 2.

In contrast to ETMD(3), which is energetically closed, the ETMD(4) channel is operative. This can be attributed mainly to the full neutralization of the Ar^{2+} center ion by its two atomic Kr neighbors. The resulting singly charged Kr ions are then located at $2R_{eq}$, effectively halving the respective Coulomb energy. The ionization-energy difference between Ar and Kr further increases the energy available for the ionization of the fourth atom. These effects shift the PEC such that the process becomes viable at an internuclear distance of around 8 Å, which approximately corresponds to $2R_{eq}$ [29]; i.e., it may happen with the next-nearest neighbor atom. It is a well-known characteristic of clusters that, mainly due to size-distribution effects, all states exhibit a significant broadening in their potential energies [31]. As a consequence, the depicted states are also somewhat broadened, which favors a crossing of the initial-state $Ar_{N-1}Ar^{2+}(3p^{-2})\,Kr_M$ PEC and the ETMD(4) final-state PEC at even shorter R.

To estimate whether the decay rate of an ETMD(4) process is competitive with RCT, we have used the Fano-ADC method [32] to estimate the ETMD(4) width in the Kr_3Ar tetramer. The calculations were conducted using a T-shape arrangement with the Kr_2Ar trimer in equilibrium linear geometry and the third Kr atom at a distance R perpendicular to the trimer; more details on the calculations can be found in Supplemental Material [28], and the results are shown in Fig. 3.

The calculated lifetime presented in Fig. 3 follows the trend expected for a dipole transition between the Kr_2Ar trimer and the Kr atom, $\tau = \alpha R^6$ with $\alpha = 5.0 \times 10^{-5}$ Å^{-6} ns. For $R = 2R_{eq} = 7.84$ Å corresponding to the second shell in the cluster, the predicted lifetime is $\tau_{tetramer} \approx 12$ ns. Assuming the combinatorics of M_1 and M_2 Kr atoms in the first and second coordination shells, respectively, the ETMD(4) lifetime of the $Ar^{2+}(3p^{-2}\,{}^1S)$ state in a large icosahedral cluster (where $M_1 = 12$ and $M_2 = 42$ [33]) can be as short as $\tau_{cluster} = \tau_{tetramer}/(M_2 \cdot \binom{M_1}{2}) = 4$ ps. However, this is probably somewhat overestimating the rate, as not all combinations of Kr atoms in the first and second coordination shells will form an energetically open ETMD(4) channel.

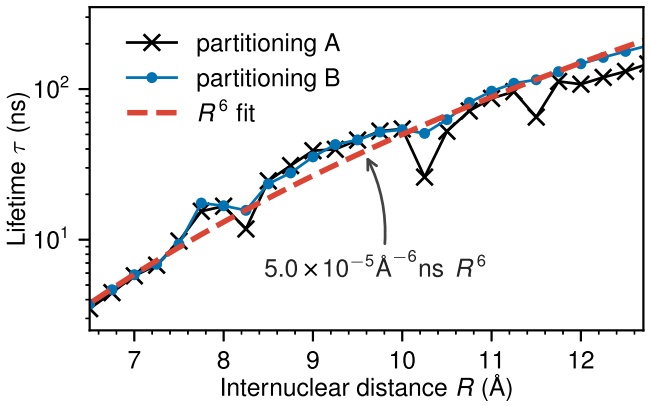

FIG. 3. Calculated ETMD(4) lifetime for the $Kr_3Ar^{2+}(3p^{-2}\,{}^1S)$ tetramer as a function of the distance R between the Kr_2Ar trimer in linear equilibrium geometry and a distant Kr atom. The black and blue curves with crosses and dots were obtained using two different partitionings of the configuration space into the continuum and boundlike subspaces, see Supplemental Material for details [28]. The variations of the calculated curves around the fitted R^6 trend are below the accuracy of the method.

In RCT in Ar clusters, an electron is transferred from a neutral neighboring atom to the doubly charged ground-state ion, and the energy difference is emitted as an ultraviolet (UV) photon in the range between 6.6 and 10.7 eV [34]. The lifetime of radiative decay by RCT has been experimentally determined in homogeneous Ar clusters to be about 5 ns [35]. It is thus safe to conclude that the ETMD(4) lifetime will be at least two orders of magnitude shorter.

Validating our hypothesis that the $Ar^{2+}(3p^{-2})$ state decays via ETMD(4) in heterogeneous clusters of Ar and Kr, we performed an experiment similar to those in Refs. [34,35], but added Kr to the Ar cluster sample. The experimental setup consists of a magnetic-bottle-type electron spectrometer and a photon detector with a collecting-mirror assembly to increase the solid angle, whose photocathode enables the detection of UV photons, and the clusters are produced via supersonic coexpansion. A Kr:Ar mixing ratio of 1:10 for the gas mixture was used to produce the clusters. Note that this does by no means reflect the final composition of the clusters [36,37]. Details of the setup are described in Supplemental Material [28] and in Refs. [17,34].

We investigated both homogeneous Ar clusters and heterogeneous ArKr clusters, where adding Kr was observed to alter the emission pattern of the sample strongly. A photon energy of 265 eV was chosen to efficiently populate $Ar^{2+}(3p^{-2})$ states via photoionization of Ar $2p$ orbitals and subsequent *LMM* Auger decay. The competition between RCT and ETMD(4) was monitored by coincident detection of electrons and photons. The target consists partly of clusters and partly of uncondensed atoms, and in principle it is not trivial to separate atomic from

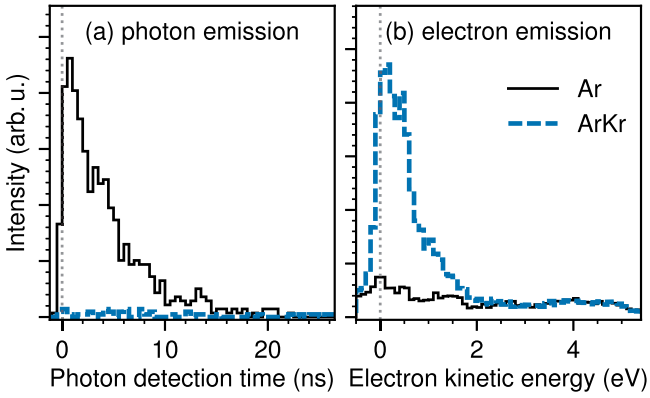

FIG. 4. Competition of (a) UV photon and (b) slow electron emission in homogeneous Ar and heterogeneous ArKr clusters. The data show the third particle (UV photon or electron) detected in coincidence with the photoelectron and Auger electron populating the $Ar^{2+}(3p^{-2})$ state following initial $2p$ photoionization and a subsequent *LMM* Auger decay. In homogeneous Ar clusters (black solid lines), a significant yield of UV photons is observed, but barely any emission of slow electrons. The opposite is the case for heterogeneous ArKr clusters (blue dashed lines). Dotted vertical lines indicate the zero position.

cluster signal. However, the atomic contribution can be neglected in our case since from atoms neither RCT photons nor ETMD electrons can be expected.

To investigate the decay of the $Ar^{2+}(3p^{-2})$ dicationic ground state, we filter the datasets for the first two arriving particles to be the $2p$ photoelectron with kinetic energies around 16 eV [38] and the following fast *LMM* Auger electron with kinetic energies slightly above 200 eV [39]. In Fig. 4, we compare the subsequent emission of UV photons and slow electrons as third particles from homogeneous Ar clusters and heterogeneous ArKr clusters. To allow a comparison between the measurements, all spectra have been normalized to the respective *LMM* Auger intensity, i.e., the population of the initial $Ar^{2+}(3p^{-2})$ state. The Ar cluster case (solid black lines) shows the expected behavior and serves as a reference: the state decays by RCT and a significant yield of UV photons is observed [Fig. 4(a)]. An exponential fit (not shown) to the photon detection time yields a lifetime of (4.5 ± 0.2) ns for this process, which is reasonably consistent with the literature value of about 5 ns [35]. In heterogeneous ArKr clusters (blue dashed lines), no significant RCT emission was detected at all.

Considering the emission of a possible third electron [Fig. 4(b)], the measurements show the opposite behavior. In homogeneous Ar clusters, only a small number of slow electrons is observed. This is a typical phenomenon in electron spectra of dense media, and these electrons may mainly originate from scattering effects [40]. In contrast, in ArKr clusters, a distinct feature peaking at 0 eV kinetic energy and rapidly decreasing is detected. We conclude that following the population of $Ar^{2+}(3p^{-2})$, the RCT channel is efficiently quenched by adding Kr to the system due to the opening of a faster autoionization process. Since ETMD(3) is energetically closed, the only remaining option is a collective electron transfer process such as ETMD(4). The maximum of the electron spectrum at zero kinetic energy strongly supports the estimate that ETMD(4) opens at somewhat larger distances than R_{eq}.

Although the quenching of the UV photon emission in Fig. 4(a) is quite a striking observation, the electron spectra in Fig. 4(b) have to be handled with care due to the normalization process. The normalization with respect to the number of photoelectron–Auger electron coincidences is prone to uncertainties because of the different target compositions, i.e., the condensation ratio and mean cluster size may be different upon the addition of Kr. Therefore, it is an intriguing question whether ETMD(4) can also be observed in *homogeneous* clusters. We chose homogeneous Kr clusters, for which triply charged ground-state ions can be reliably produced experimentally (see Refs. [41,42]), and which provide a similar scenario as the ArKr case discussed above. An analogous discussion leads to the same conclusion that ETMD(3) is energetically closed for the $Kr^{3+}(4p^{-3})$ state and only RCT is competing with ETMD(4), which may in fact already be operable with the nearest neighbors. Computational details and the resulting PECs are presented in Supplemental Material (Fig. S1) [28].

An experiment on homogeneous Kr was conducted with a similar electron-photon multicoincidence setup as before, but with a different electron spectrometer providing higher energy resolution (for details, see Supplemental Material [28]). Following the formation of $Kr^{+}(3p^{-1})$ core-hole states through photoionization with an exciting-photon energy of 350 eV, the predominant (over 60% [42]) first relaxation step is Coster-Kronig (CK) decay into $Kr^{2+}(3d^{-1}4p^{-1})$. This CK final state relaxes further via a secondary Auger decay, leaving the atom in a triply charged state with three valence holes ($4p^{-3}$, $4s^{-1}4p^{-2}$, $4s^{-2}4p^{-1}$, or $4p^{-4}nl$) [42]. Although investigating the formation and follow-up decay processes of these states in clusters is an interesting topic of its own, here we focus on the $Kr^{3+}(4p^{-3})$ tricationic ground state.

Figure 5 shows the results of measurements with Kr clusters (solid black line) and atoms as a reference (blue dotted line). The data has been filtered for coincidence events involving three or four electrons, the fastest three with kinetic energies within the literature values of the respective transitions leading to the $Kr^{3+}(4p^{-3})$ state [42], where each emitted electron naturally increases the charge state of the ion. This increase in charge state is accompanied by a characteristic kinetic-energy shift of the Auger electrons in clusters due to so-called polarization screening [26]. In the monomer case, the decay cascade from photoelectron over Coster-Kronig electron to secondary Auger electron evidently ends in the triply charged

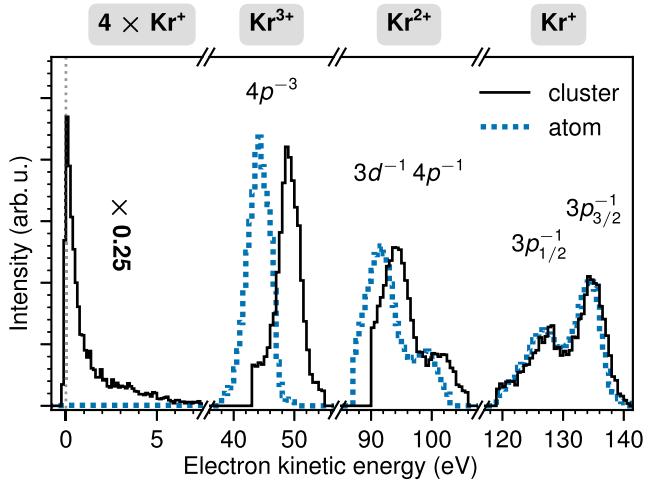

FIG. 5. Emission of slow electrons from Kr^{3+} in pure Kr clusters. Following the photoionization with an exciting-photon energy of 350 eV, the $Kr^{+}(3p^{-1})$ core-hole states relax, and Coster-Kronig decay into $Kr^{2+}(3d^{-1}4p^{-1})$ is the most prominent feature (kinetic-energy range ca. 85 eV to 105 eV). This state can undergo Auger decay into the $Kr^{3+}(4p^{-3})$ tricationic ground state (kinetic-energy range ca. 40 eV to 55 eV). In clusters (black solid line), the final step in the cascade is ETMD(4), leading to the emission of a slow electron (scaled down by a factor of 4 in the figure) and charge distribution into a non-local $(Kr^{+})_4$ final state. In monomers (blue dotted line), the ionic Kr^{3+} ground state cannot decay further. A dotted vertical line indicates the zero position.

ground state; a fourth electron was rarely detected. The situation is vastly different in clusters, where we recorded a high amount of slow (<2 eV) fourth electrons as the final step of the cascade, similar to the ArKr clusters case peaking at zero kinetic energy, though here extending to around 6 eV. Events with only three coincidentally measured electrons have been found to originate predominantly from uncondensed Kr atoms and have therefore been discarded in the cluster spectrum. No significant number of photons was detected in coincidence with the electrons leading to a population of the $Kr^{3+}(4p^{-3})$ state.

We conclude that ETMD(4) is operable in homogeneous Kr clusters after the population of the local tricationic ground state. From the two independent coincidence experiments presented that combine multiple electron and photon detection, we provide strong evidence that ETMD(4) occurs in two different prototype systems. Theoretical estimates on the lifetime support the interpretation of the experimental data, i.e., that ETMD(4) is dominant over the only accessible competitor, namely radiative decay. We motivate the additional detection of ion fragments after the final Coulomb explosion, which will yield further valuable information and characterization for the identification of the relaxation mechanisms involved, and in particular, on the geometry of the participating atoms.

As a final remark, we would like to point out that collective electron-transfer relaxation mechanisms like ETMD(4) might be general candidates for the decay of multiply charged (ground-state) ions in dense media, i.e., a common final step in the decay cascades initiated by deep inner-shell or multi-photon excitation or ionization. In particular, the neutralization of even more than two charges by simultaneous transfer of more than two electrons is a natural assumption following the present work. The transfer of multiple electrons from a single donor site, possibly accompanied by electron emission from the donor itself, is also conceivable. We suggest that the generality of collective ETMD should be subject to further theoretical and experimental studies.

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Data availability—The data that support the findings of this Letter are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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