Experimental Observation of Interatomic Coulombic Decay in Neon Dimers

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(Received 6 May 2004; published 13 October 2004)

Recently Cederbaum *et al.* [Phys. Rev. Lett. **79**, 4778 (1997)] predicted a new decay channel of excited atoms and molecules termed interatomic Coulombic decay (ICD). In ICD the deexcitation energy is transferred via virtual photon exchange to a *neighboring* atom, which releases it by electron emission. We report on an experimental observation of ICD in $2s$ ionized neon dimers. The process is unambiguously identified by detecting the energy of two Ne^{1+} fragments and the ICD electron in coincidence, yielding a clean, background free experimental spectral distribution of the ICD electrons.

DOI: 10.1103/PhysRevLett.93.163401 PACS numbers: 36.40.Mr, 33.80.Eh, 34.30.+h, 82.33.Fg

Electronically excited states of atoms, ions, and molecules are of key importance for many technical applications. They also played and still play a major role in the development of quantum theory. This is because the spectral lines of photons emitted from excited atoms, ions, and molecules have been used ever since their discovery as a fingerprint of the particle's electronic structure. Electronically excited matter is found, for example, in stellar plasmas or fluorescence tubes. In 1925 Auger [1] discovered that, in competition with the emission of these characteristic photons, excited atoms can release their energy by emission of one of their electrons. Here, one electron from a higher electronic level fills the hole in a more tightly bound orbital, while the excess energy leads to emission of a second electron. The properties of Auger and fluorescence decay are mainly determined by the atom or molecule which has been initially excited. Interaction with the environment is known to cause distortions such as broadening of spectral lines, but was for a long time not expected to principally alter the decay routes. In a pioneering theoretical work Cederbaum and co-workers have shown that this textbook perspective is not the full story [2]. Their calculations predict that if the excited atom or molecule is put in close neighborhood of other particles, a fundamentally new decay mechanism, interatomic Coulombic decay (ICD) may emerge. The excited species can transfer its energy in an extremely efficient way to a *neighboring* particle which then releases that energy by emission of one of its own outer shell electrons. ICD is different from the Auger decay since first the electron does not emerge from the excited particle, but from its neighbor and second this emission is not mediated by the overlap of the participating wave functions but rather by an energy transfer via a virtual photon.

A reason why this fundamental effect has not been discovered along with Auger and radiative decay is that ICD electrons are of low energy, in the order of a few eV, and emerge from weakly bonded systems, such as van der Waals clusters or hydrogen bonded liquids. In these systems, plenty of slow secondary electrons are produced by inelastic scattering within the ionized species, which experimentally mask the ICD electrons, thus leaving this decay mechanism concealed. A surplus of electrons with kinetic energy of 0.8–2 eV at photon energies above the neon $2s$ ionization threshold has recently been reported in an experiment on large neon clusters [3]. This has been interpreted as an evidence for the existence of ICD.

A clean prototype system for which the signature of ICD has been calculated and which we chose for our investigation is the neon dimer (Ne_2) [4]. In this exotic but exhilarating species two neon atoms are bound by the van der Waals force with an energy of 2 meV at an internuclear distance of 3.4 Å [5], which is 6 times larger than the radius of the hydrogen atom. In neon the $1s$, $2s$, and $2p$ shells are filled. If an electron is removed from the $2s$ shell, in a single, isolated neon atom Auger decay is energetically prohibited: The energy gained by the transition of a $2p$ electron to the $2s$ vacancy, 26.84 eV, is not sufficient to enable another $2p$ electron to escape from the *singly charged* neon ion. In contrast to that, ICD is energetically allowed, since the amount of energy is sufficient to emit a $2p$ electron from a *neighboring* neutral neon atom.

The ICD process in the neon dimer, and the sequence of events which allowed its separation from the background of secondary electrons in the present experiment is shown in Fig. 1. At first a $2s$ electron from a Ne_2 is removed by absorption of a photon [Fig. 1(a)]. After that the $Ne_2^{1+}(2s^{-1})$ dimer cation undergoes IC decay [Fig. 1(b)], leading to a second free electron and two adjacent singly charged Ne^{1+} ions repelling each other. Consequently, the ions are emitted back-to-back with a kinetic energy release (KER) corresponding to the internuclear distance at the instant of the ICD [Fig. 1(c)]. Taking the $2s$ ionization energy in a cluster as 48.5 eV [4,6], the energy difference to a state consisting of two atomic Ne^{1+} $2p^{-1}$ ions at asymptotic distance is $48.48 - 2 \times 21.66$ eV $= 5.16$ eV.

This amount of energy will be distributed to the kinetic energy of the ICD electron and the KER of the Ne^{1+} ion pair. Therefore a unique fingerprint of ICD is the coincident three particle detection of two ions, which are emitted back-to-back, and one electron, with the further constraint that the sum of all kinetic energies has to add up to a constant. Therefore measuring the three particles' energy sharing and the back-to-back emission of the two Ne^{1+} ions reveals the existence of ICD.

The experiment has been performed at beam line U125/1-PGM of the BESSY synchrotron radiation facility in Berlin in single bunch operation using the COLTRIMS (cold target recoil ion momentum spectroscopy) technique [7–9]. The neon dimers have been produced by expanding neon gas at room temperature through a 30 μm diameter nozzle at a stagnation pressure of 25 bar. The dimer fraction in the beam has been measured by means of time-of-flight mass spectrometry after $2p$ photoionization to be at least 0.5%. For the experiment a photon energy of 58.8 eV, sufficient for ionization of the $2p$ and $2s$ levels but below the double ionization potential of atomic neon has been chosen [10]. Ions and electrons created in the interaction volume are guided by a combination of parallel electric and magnetic fields (5.5 V/cm and 6.9 Gauss, respectively) towards two

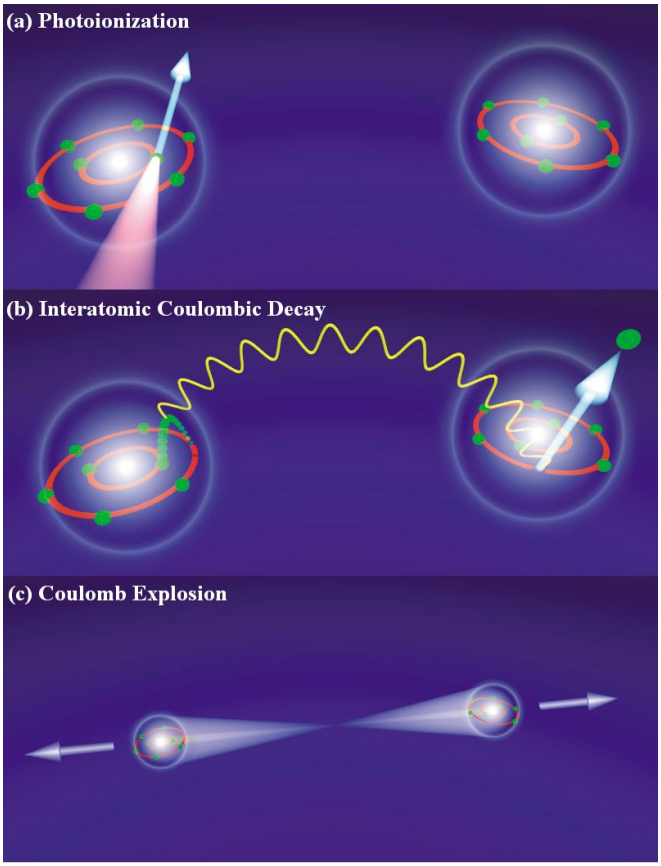

FIG. 1 (color online). Sequence of events observed in the present experiment. (a) Creation of a $2s$ hole in a neon dimer by photoionization; (b) successive interatomic Coulombic decay: the $2s$ hole is filled by a $2p$ electron, the excess energy is transferred to the neighboring neon atom causing the ejection of one of its $2p$ electrons; (c) back-to-back emission of the fragments after Coulomb explosion of the Ne dimer.

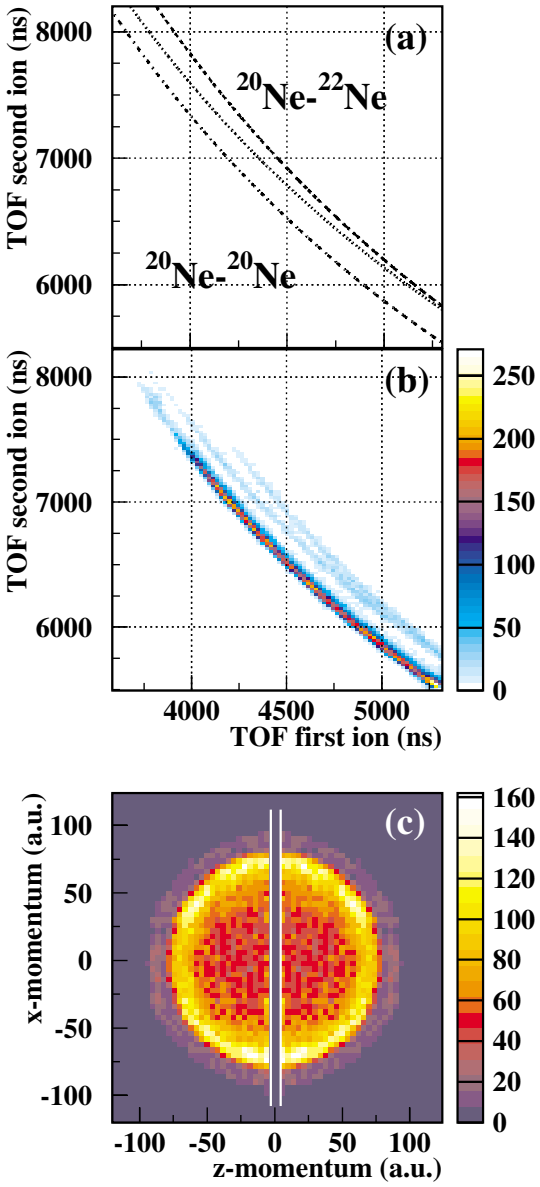

FIG. 2 (color online). (a) simulated relation of the time-of-flight of two 20 Ne 1+ ions (left) and a pair of $^{20}Ne^{1+}$, $^{22}Ne^{1+}$ ions (v-shaped structure) being emitted back-to-back with equal momentum after Coulomb explosion taking into account the spectrometer's geometry; (b) measured time-of-flight relation; (c) measured ion momenta parallel to the spectrometer's axis and perpendicular to that axis. The gap in the distribution at 0 a.u. is a result of the coincidence's dead time and background suppression.

position and time sensitive channel plate detectors. The guiding fields and geometry of the spectrometer yield a 4π acceptance solid angle for electrons with an energy of up to 12 eV and Ne^{1+} ions up to 4 eV. For each event, in which two ions and at least one electron were detected, the positions and times-of-flight of all particles have been recorded for offline data analysis. From these data all three components of the momentum vector of each particle are obtained.

Figure 2(b) shows the time-of-flight (TOF) distribution of two successively detected ions. The TOF for a $^{20}Ne^{1+}$ ion starting with zero momentum in the interaction volume is 5.8 μs. Ions starting with some momentum towards the ion detector have a shorter TOF, those starting in the opposite direction are turned by the electric field and hit the detector after a longer flight time. Back-to-back emission with equal but oppositely directed momenta results in a unique relationship between the TsOF of the two Ne^{1+} ions [9]. The calculated locus of this type of events for $^{20}Ne^{1+} - {}^{20}Ne^{1+}$ and the isotopic $^{20}Ne^{1+} - {}^{22}Ne^{1+}$ is shown in Fig. 2(a). Both predicted structures are clearly seen in the experimental distribution [Fig. 2(b)]. The relative intensity of the two different dimer channels reflects the fact, that neon gas with the natural ratio of the two isotopes (90.5% ^{20}Ne, 9.2% ^{22}Ne) has been used. In addition to the TOF information the position of impact on the detector is registered for each hit. Ions with vanishing momentum hit the center of the detector, while ions of 4 eV energy and a initial direction that is perpendicular to the spectrometer's axis reach the detector's edge. From the TOF and the position of impact the ions' three initial momentum components can be derived [see Fig. 2(c), showing the momentum in the direction of the spectrometer axis versus one perpendicular component]. Clearly, the detected Ne^{1+} ions are located on a sphere in momentum space. The high momenta and the back-to-back emission of the ions furthermore allow an almost complete suppression of the huge amount of background ions originating from the ionization of monomers. These monomer ions have a very low energy (1.1 meV, corresponding to 1.7 atomic units (a.u.) of momentum, since their momentum results only from the recoil of the emitted photoelectron). If by chance two of those ions are produced within a short period of time, they form a random-coincidence event that is located in the center of Fig. 2(c) and is rejected.

The coincidentally measured ion momenta serve a double purpose: the back-to-back fragmentation identifies the dimer ionization and the localization of one positive charge per neon atom, and second the KER is obtained and can be related to the simultaneously measured electron energy. This relation is shown in Fig. 3(a) and is the key result of our experiment. The two prominent structures both result from 2*s* photoionization followed by ICD. As the photon energy during the

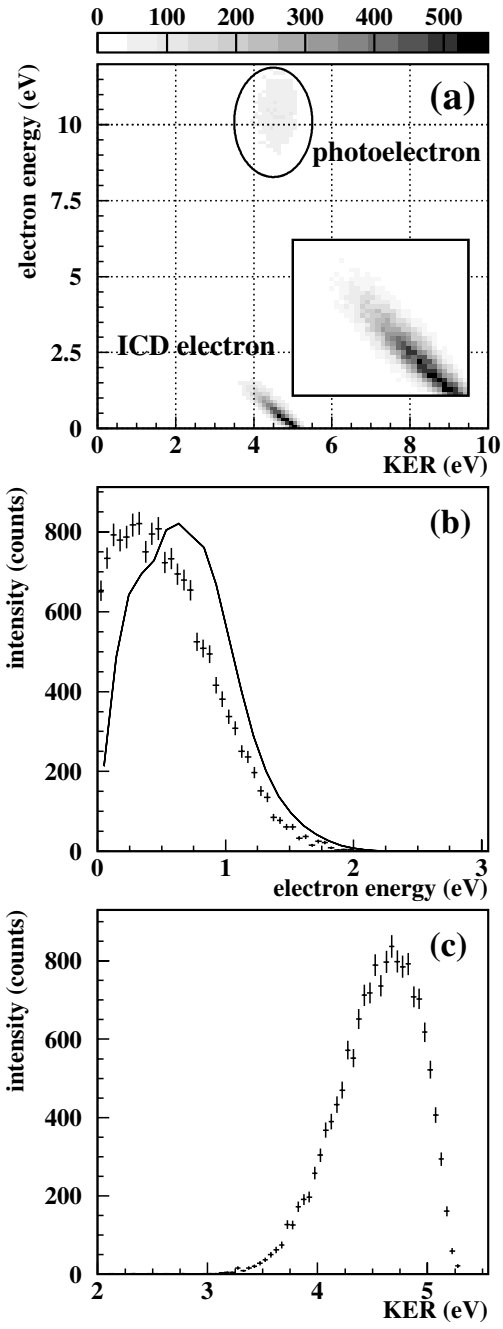

FIG. 3. (a) Kinetic energy release (KER) of the ionic neon fragments in relation to the measured energy of one detected electron with a zoomed view of the ICD electron's region (inset), (b) ICD electron energy distribution, solid line: recent theoretical calculations [12]. (c) Kinetic energy release distribution from ICD.

experiment was set to 10 eV above the Ne-2*s* ionization threshold (58.8 eV), events located at a KER of 3.3 to 5.5 eV and an electron energy of ~10 eV are cases where the 2*s* photoelectron is detected together with the Coulomb exploding doubly charged dimer. The accompanying ICD electron is not detected in those events. The

second feature, the narrow diagonal line, shows events where the ICD electron is detected. For ICD the sum of KER and ICD electron energy is a constant resulting in that diagonal when one is plotted vs the other. Our measured sum energy is 5.1 eV which is, considering the experimental energy resolution, in good agreement with value obtained from [4]. The narrow distribution of the sum energy shows that these events are created in a two-step process, where first a $2s$ hole is created by the emission of a photoelectron. Successively, and without significant exchange of energy with the photoelectron, the intermediate $Ne_2^{1+}(2s^{-1})$ decays by emitting the electron which is observed. Since two singly charged Ne^{1+} ions are created, the decay is indeed "interatomic," the ICD electron is emitted from the formerly neutral side of the dimer.

While the diagonal structure proves the existence of ICD, the distribution of events along the diagonal, corresponding to the electron energy and KER distribution, elucidates the dynamics of the phenomenon [11]. It allows us to investigate the underlying potential energy surfaces of the $Ne_2(2s)^{-1}$ ($2^2\Sigma_g^+$ and $2^2\Sigma_u^+$) and the (Ne^{1+}, Ne^{1+}) systems. The measured ICD electron spectrum [Fig. 3(b)] is in good agreement with most recent theoretical estimates [12].

In conclusion, we have shown that even weak interactions with a chemical environment may qualitatively alter the deexcitation pathways of electronically excited atoms or molecules. The unambiguous experimental proof of this predicted process, named ICD, was possible by the use of a modern multiparticle coincidence imaging technique. The details of the electron energy distribution are an extremely sensitive probe for the decay rates and potential energy surfaces [11]. Even though previously unseen, ICD is expected to be a very general deexcitation channel of weakly bound matter, such as hydrogen bonded systems. Most of the very common hydrogen or van der Waals bonded systems, most prominently liquid water [2], will often release excitation energy via this decay channel. Low energetic electrons produced in an aqueous environment have recently been demonstrated to be responsible for much of biological radiation damage [13,14]. More generally, ICD is a route for charge dissipation without assistance of the nuclear dynamics, a finding whose consequences for chemistry have yet to be explored.

The experimental work was supported by BESSY, DFG. The experiment was inspired by a discussion with L. Cederbaum. We are grateful for very fruitful discussions with S. Scheit, H. D. Meyer, V. Averbukh, and R. Santra and for the permission to include their calculated electron spectrum prior to publication. We acknowledge the advice on the cluster preparation from Th. Möller. We would like to thank G. Reichardt and the staff at BESSY for the support during the beam time.

Note added.—Very recently, the lifetime of IC-decaying neon clusters of larger size has been measured [15].

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