Interatomic Coulombic Decay following Photoionization of the Helium Dimer: Observation of Vibrational Structure

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Using synchrotron radiation we simultaneously ionize and excite one helium atom of a helium dimer (He_2) in a shakeup process. The populated states of the dimer ion [i.e., $He^{*+}(n = 2, 3) - He$] are found to deexcite via interatomic Coulombic decay. This leads to the emission of a second electron from the neutral site and a subsequent Coulomb explosion. In this Letter we present a measurement of the momenta of fragments that are created during this reaction. The electron energy distribution and the kinetic energy release of the two He^+ ions show pronounced oscillations which we attribute to the structure of the vibrational wave function of the dimer ion.

Excited hydrogenlike atoms and ions can deexcite only by emission of a photon. If, however, these excited particles are put into the vicinity of other atoms, the excitation energy can in principle be transferred to the neighbor, where it may lead to emission of an electron. This two-center energy transfer process is known as interatomic Coulombic decay (ICD). It was first predicted by Cederbaum and co-workers for molecular clusters [1]. Today it is well established also experimentally for inner valence excitation of many electron systems such as van der Waals clusters containing Ne, Ar, and Xe (see, e.g., [2–5]) and water clusters [6].

In the present experiment we demonstrate the existence of ICD in the most fundamental system in which it can occur: excited $He^{*+}(n = 2, \ldots)$ with a van der Waals–bound neighboring neutral helium atom. We observe that, different from all the previously considered systems, the energy distribution of the low energy electron emitted via ICD from He-He exhibits an oscillatory structure. Furthermore, the kinetic energy of the ionic fragments (KER) reveals that ICD occurs at interatomic distances up to ≈ 12 a.u. implying that no overlap of the electronic wave function is necessary for ICD to occur.

With a binding energy of only 95 neV, He_2 is the most weakly bound naturally occurring system [7,8]. The delicate interplay of zero point motion and weakness of the He-He van der Waals potential results in an extremely delocalized nuclear wave function (see Fig. 1), which is qualitatively different from all other known clusters: the mean value of the internuclear distance is ≈ 52 Å [8,9], which is off the scale of Fig. 1. The wave function extends from ≈ 5 a.u. to several 100 a.u. Such a delocalized ensemble is an ideal starting point for studies of ICD. The

Coulomb explosion following ICD allows us to watch the decay of this ensemble. Measuring the kinetic energy release (KER) and the direction of the fragments allows us to detect the internuclear distance at which ICD occurred for each individual event.

The experiment was performed at beam line UE112PGM2 at BESSY using the COLTRIMS technique [10–12]. We create helium dimers by expanding He gas through a 5 μm nozzle cooled to 18 K by a continuous flow cryostat. A driving pressure of 1.8 bar and a pressure of 1.2×10^{-4} mbar at the low pressure side of the nozzle yielded a dimer fraction of 1%–2% in the gas beam. This fraction has been determined using diffraction at microstructure gratings as performed in [7]. For the given conditions the fraction of trimers and larger clusters was below 0.2% of the monomers. 10 mm above the nozzle the beam entered a scattering chamber through a 0.3 mm skimmer. The gas beam was intersected with a linearly polarized photon beam in the center of a homogenous electric field region of a COLTRIMS spectrometer. The electric field and a parallel homogenous magnetic field of 10 G guided the electrons and ions towards two microchannel plate detectors (80 mm active diameter) with delay-line position readout [13]. From the measured positions of impact and times-of-flight of ions and electrons their respective momentum vectors and charge to mass ratios are obtained. The back-to-back emission of the two He^+ ions provides a unique signature allowing for an almost perfect suppression of the huge background of ions and electrons from ionization of the monomers. It also allows us to detect possible contaminations resulting from the fragmentation of larger clusters. For all data shown in this Letter we have selected only those events where two He^+ ions are emitted
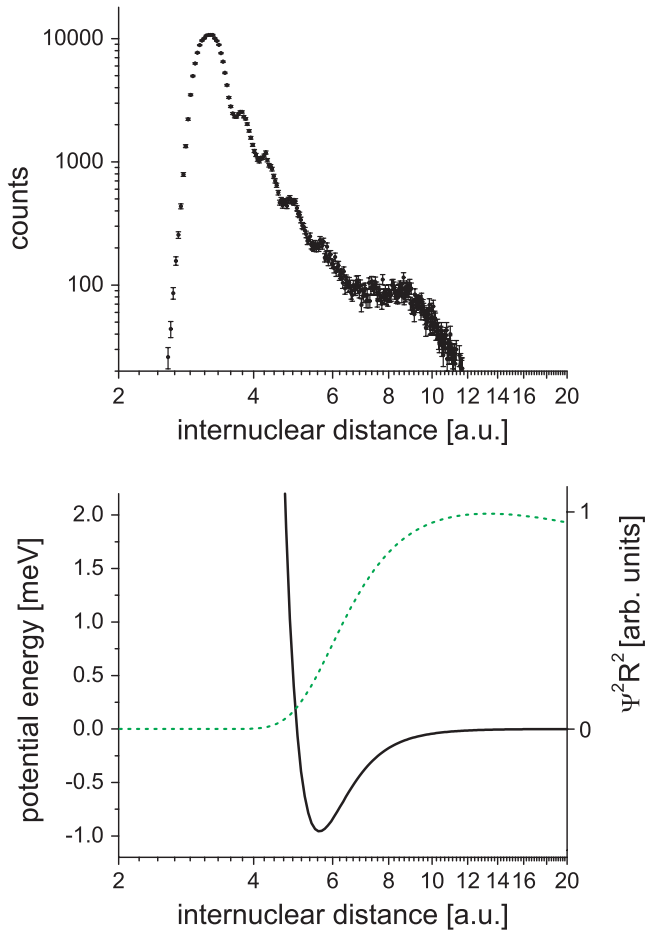
FIG. 1 (color online). Bottom: He dimer potential (left scale) (from [23]). dotted green line in right axis: $\psi^2 R^2$ (from [24]). The expectation value of internuclear distance is 52 Å [8], which is off scale. Upper panel: measured internuclear distance at instant of ICD from $He^{*+}(n=2) - He \rightarrow He^+ + He^+ + e_{ICD}$. Calculated from KER (see Fig. 3) at a photon energy of 68.86 eV using the reflection approximation $R = 1/\text{KER}$.

FIG. 2 (color online). Kinetic energy release of the $He^+ - He^+$ fragments versus the energy of one of the two electrons from photoionization excitation of He_2 at photon energies of 68.86 and 77.86 eV. The arrows indicate the expected position of photoelectron (horizontal line) and the corresponding ICD electron (diagonal lines) for excitation to the intermediate state $He^{*+}(n) - He$.

back to back. At an ion rate of about 10 kHz we observed a rate of about 7 Hz for these He^+ ion pairs. The ion momenta were calibrated using Coulomb explosion of N_2 at 77.86 eV photon energy which leads to a narrow peak at a KER of 10.32 eV [14,15].

Figure 2 shows the energy of one of the detected electrons versus the KER at photon energies of $E_\gamma = 68.68$ and 77.86 eV. The creation of $He^{*+}(n)$ in the excited state of principal quantum number n by photoionization plus simultaneous excitation results in photoelectrons of an energy $E_{\text{ephoto}}(n) = E\gamma - 24.59 \text{ eV} - (54.42 \text{ eV} - 13.6 \text{ eV} \frac{4}{n^2})$ (as depicted by arrows in Fig. 2). In addition to these horizontal lines of the satellite photoelectrons Fig. 2 shows also events along diagonal lines. A diagonal indicates a constant sum of the two quantities plotted on the x and y axis, i.e., a constant sum energy of the electrons and ions observed. These lines are characteristic for ICD [2]:
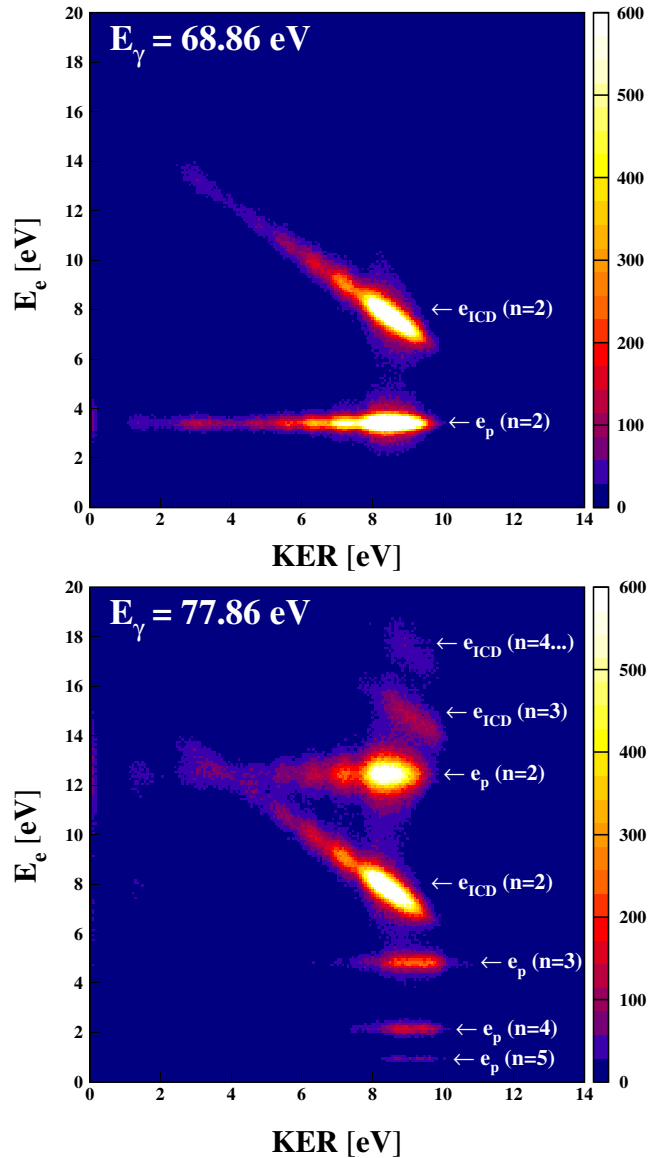
they appear for the case of a decay of an intermediate state with discrete energy that partitions its energy among the kinetic energy of the electron emitted during the decay and the KER of the ions. The positions in energy expected for the decay of $He^{*+}(n) - He \rightarrow He^+(n = 1) - He^+(n = 1) + e^-$ are indicated for the $n = 2, 3, 4$ in Fig. 2. For those events where we detect both electrons in coincidence we have confirmed that each photoelectron is accompanied by its matching ICD electron.

The measured KER for the different n is shown in Figs. 3 and 4. These spectra are generated by projecting only the
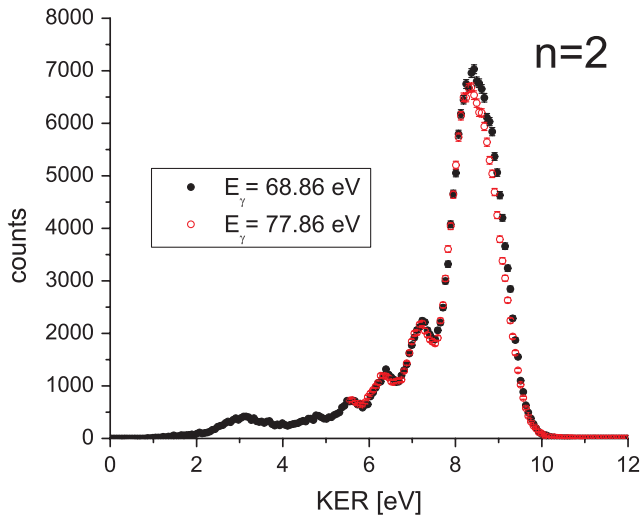
FIG. 3 (color online). Kinetic energy release of the $He^+ - He^+$ fragments for intermediates excited states with principal quantum $n = 2$ [$He^{*+}(n = 2) - He$]. Data are obtained by projecting the respective diagonal line in Fig. 2 onto the KER axis.

events along the respective diagonal lines in Fig. 2 onto the KER axis. Note that for each value of n the ICD electron energy is given by $E_{eICD}(n) = (54.42 - 13.6\frac{4}{n^2}) - 2 \times 24.59 -$ KER. The KER distribution displays a distinct oscillatory structure which looks different for each n state. In the classical reflection approximation [16] the KER of the Coulomb explosion is given by KER $= 1/R$, where R is the internuclear distance at the instant of ICD. We have used this to obtain an estimate of the internuclear distance

at which ICD occurs (top panel in Fig. 1). Clearly this region of internuclear distances is much more confined than the diffuse He_2 ground state. Only about 4% of the ground state of He_2 is in the region 2 a.u. $< R <$ 12 a.u. which we observe for ICD. As we will show below, more than 95% of the excited dimers decay via ICD. We suggest that significant nuclear motion occurs prior to ICD. The $He^{*+}(n = 2, 3, \ldots) -$ He contracts until it reaches the regime where the ICD rates are appreciable.

The ICD rate scales asymptotically like $1/R^6$ [17]. Since this is a monotonic function the observed oscillatory structure can only result from a structure in the R dependence of the nuclear wave function before the decay [18,19]. For $n = 2$ we find 5 minima, suggesting that vibrational wave functions with at least $\nu = 5$ are involved. Since the He_2 potential is much more shallow than the $He^{*+}(n = 2, 3, \ldots) -$ He potential energy curve, the neutral dimer wave function is much more delocalized and its mean internuclear distance is much larger. Hence the vertical transition by the photoionization and excitation of He_2 populates mainly high lying vibrational states of the $He^{*+}(n = 2, 3, \ldots) -$ He. Since the $He^{*+}(n = 2, 3, \ldots) -$ He potential energy curves are attractive at large distances, the vibrational wave packet will start to contract [18,19].

The idea that vibrational structure can become visible in ICD was first suggested in pioneering theoretical work by Santra and co-workers and Moiseyev *et al.* [18,19]. They showed that whether or not a visible oscillatory structure in the KER finally arises depends on the interplay of wave packet dynamics and the R dependent decay rates. For Ne_2 such oscillation appear in calculations only if unrealistic potential energy surfaces are used [20]. The He_2 system
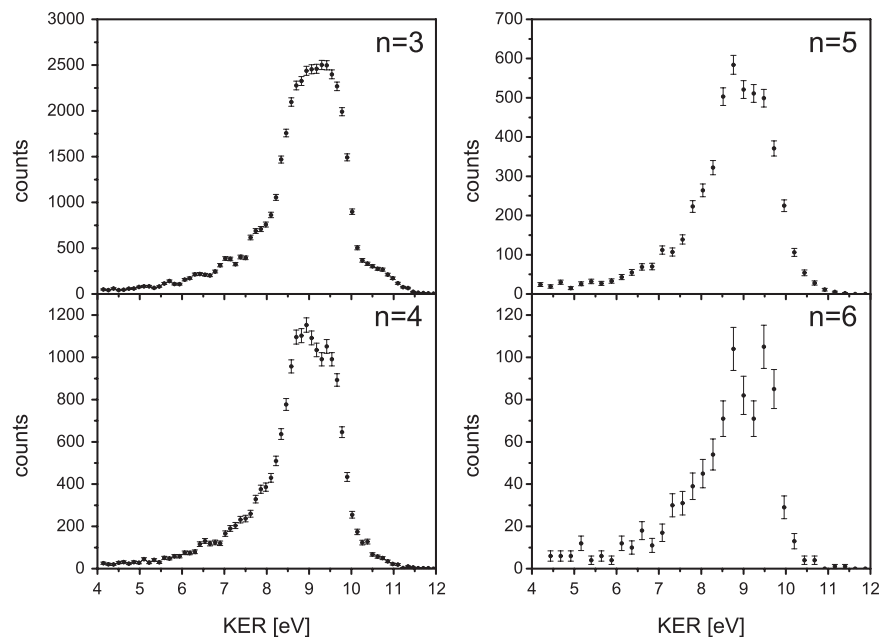

FIG. 4. Distribution of the kinetic energy release for intermediates excited states (n) at a photon energy of 77.86 eV. The principal quantum number n as given in the figure.

studied here is the only system investigated so far which exhibits such structure under real conditions. This is due to the unique delocalization of the neutral ground state which results in the preferred population of the excited states at very large distances. The high contrast of the observed oscillations shows that either preferentially one high lying vibrational state or only a few states where nodes in the wave function coincide are populated.

For all previously studied species the ICD rates were such that, whenever ICD was energetically allowed, it was faster than radiative decay by several orders of magnitude [17]. Because of the $1/R^6$ scaling of the ICD rates, however, this is not true for the large distances in the helium dimer. The lifetime for radiative decay of $He^{*+}(n = 2, l = 1)$ is 99.92 ps [21]. Assuming 85 fs as a typical ICD lifetime at $R = 6$ a.u. [17], ICD and radiative decay rates would become comparable at around $R = 20$ a.u. In addition, the attractive potential of the $He^{*+}(n = 2, 3, \ldots) -$ He at the large distances where it is populated by the vertical transition is very shallow and hence classically the dimer would contract very slowly. It is therefore not clear at all what the overall branching ratio between ICD and radiative decay will be in this system. To get an experimental estimate we have searched for stable He_2^+ ions in our time-of-flight spectrum. In coincidence with photoelectrons from ground state $He^+(n = 1)$ we have found a ratio of He_2^+ to He^+ monomers of about 2% as expected from the dimer fraction in our beam. In coincidence with electrons for $He^{*+}(n = 2)$, however, we did not find any stable He_2^+ in our time-of-flight spectrum above the background. From these numbers we conclude that the ratio of the excited $He^{*+}(n = 2) -$ He decaying radiatively to the bound ground state of He_2^+ to the ones which decay via ICD is <5%. We note that this estimate was gained from an experiment at a photon energy of 65.41 eV which is only 1 meV above the $n = 2$ threshold. This is important since under these conditions the recoil energy of the photoelectron imparted onto the $He^{*+}(n = 2) -$ He is only 68 neV and we can hence safely exclude any significant influence of the recoil effect on the ICD process [22].

In conclusion, we have shown that a single photon leads to two-center double ionization of the helium dimer in a two-step process. First, one site is ionized and excited. This step is followed by ICD. The kinetic energy release shows vibrational oscillatory structure from the intermediate singly charged dimer state. Because of the extreme condition *ab initio* calculations of decay rates and nuclear dynamics are highly challenging. They are currently being performed by the Cederbaum group and will be published separately [25].

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