Single Photon Double Ionization of the Helium Dimer

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(Received 1 December 2009; published 14 April 2010)

We show that a single photon can ionize the two helium atoms of the helium dimer in a distance up to 10 Å. The energy sharing among the electrons, the angular distributions of the ions and electrons, as well as comparison with electron impact data for helium atoms suggest a knockoff type double ionization process. The Coulomb explosion imaging of He_2 provides a direct view of the nuclear wave function of this by far most extended and most diffuse of all naturally existing molecules.

The helium dimer ($^4He_2$) is an outstanding example of a fragile molecule whose existence was disputed for a long time because of the very weak interaction potential [1] (see black curve in Fig. 1). Unequivocal experimental evidence for $^4He_2$ was first provided in 1994 in diffraction experiments [2] by a nanostructured transmission grating. Subsequently, the average dimer bond length and dimer binding energy could be determined to be 52 Å and 10^{-7} eV (0.9×10^{-3} cm^{-1} or 1.3 mK) [3]. This very large bond length, a factor 100 larger than the hydrogen bond length, goes along with a prediction of very widely delocalized wave function, unseen in any other molecule [4] (see $R^2\Psi_i^2$ function in Fig. 1). It is because of these exotic properties that "as the hydrogen molecule in the past, the helium dimer today became a test case for the development of new computational methods and tools" [5] in quantum chemistry. Despite this fundamental nature of the diffuse helium dimer wave function, it has escaped direct experimental observation until now, as the diffraction grating experiment measures the mean value and not the shape of the wave function itself. Our experiment provides a direct view of this diffuse object.

The large distance between the two helium atoms and the minuscule binding energy make the helium dimer a unique model system to explore electron correlations over large distances. The most sensitive tool for such studies is multiple photoionization. Since photoabsorption is described by a single electron operator the photon energy and angular momentum is best thought of as being initially given to one electron of the atom only. In the absence of electron correlation the ejection of a single electron would be the only possible outcome of the photoabsorption process. Because of the ubiquity of electron correlation, however, the ejection of electron pairs by a single photon is a wide spread phenomenon seen in atoms [6], molecules [7,8], and solids [9]. This two electron process poses at

least two central questions: what is the correlation mechanism by which the photon energy is distributed among the two electrons and over which distance are such correlations active? In the present Letter we report the surprising observation that a single photon can lead to nonsequential ejection of two electrons from two atoms which are separated by many atomic radii and where the overlap of the electronic wave functions is negligible. By measuring the internuclear distance for each ionization event together with the emitted electron pair, we show that as much as
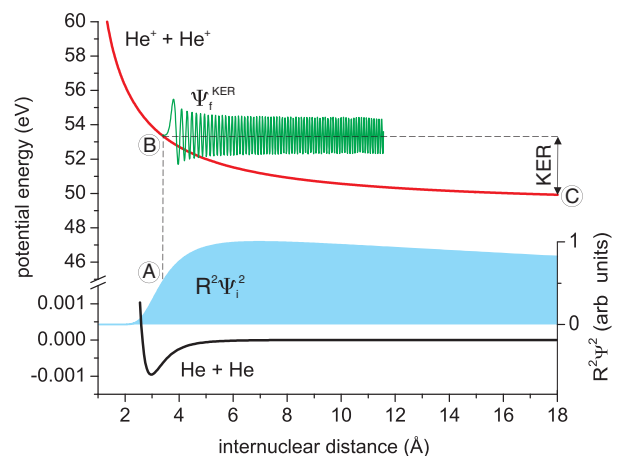

FIG. 1 (color online). The distribution of internuclear distances R [$R^2\Psi_i^2(R)$] of the helium dimer is spread over a range up to several hundred Angstrom (out of scale). Via photoionization a transition from the ground state (lower curve) to the repulsive potential of two He ions (upper curve) is possible (path A to B). In the classical reflection approximation, dissociation (path B to C) leads to a certain kinetic energy release (KER) of the two ions. In a quantum mechanical description the one-to-one relation of R and KER along path A-B-C is replaced by the overlap of $\Psi_i(R)$ with the final state wave function $\Psi_f^{KER}(R)$ for the respective KER.

39.3 eV of energy can be transferred up to a distance of 10 Å. The energy is transferred by a type of "interatomic billiard." Our measured angular distributions suggest that primarily one electron absorbs the energy and is ejected from one of the atoms of the dimer. In some cases it is emitted towards the neighboring atom where it transfers part of its energy to a second electron which is knocked off.

For our experimental investigation we employed COLTRIMS momentum imaging [10–12]. A supersonic jet is crossed with a linearly polarized photon beam inside a spectrometer at beam line UE112PGM2 of the BESSY synchrotron. By means of homogenous electric ($E = 12$ V/cm) and magnetic fields ($B = 10$ G) all charged particles created in the reaction are mapped towards two position and time sensitive detectors [13]. By measuring the positions of impact and the times of flight of all particles in coincidence the vector momentum of each particle is obtained during offline analysis. In order to create helium dimers we have expanded helium gas through a 5 μm nozzle cooled to a temperature of 18 K. A driving pressure of 1.8 bar and a pressure of 1.2×10^{-4} mbar on the low pressure side of the nozzle yielded a dimer fraction of 1%–2 % in the gas beam.

If both He atoms of a dimer are ionized the dimer will undergo Coulomb explosion. In that case both He$^+$ ions are emitted back-to-back with a momentum of same magnitude. This is a clear signature for the breakup of a dimer; thus reactions of trimers and lager clusters can be excluded from the data set. In the absence of electron correlation no He$^+$ − He$^+$ coincidences would be expected. Therefore already the observation of He$^+$ − He$^+$ coincidences proves experimentally the electron correlation that exists between electrons from the two distant atomic centers of the dimer. It is able to transfer at least 24.59 eV of energy (which equals the ionization energy of helium) across the bond length of the dimer.

To unravel the energy transfer mechanisms we now examine how the photon energy is distributed among the two electrons and two ions. Figure 2(a) shows the sum of the energy of both of the He^{1+} ions that were emitted back to back (kinetic energy release KER) versus the energy of one of the electrons measured in coincidence. The ionization potential of the He atom is $E_{i\mathrm{He}} = 24.59$ eV. At a photon energy of $E_{\mathrm{photon}} = 63.86$ eV a total of $E_{\mathrm{photon}} - 2E_{i\mathrm{He}} = 14.68$ eV is left for the four particles to share. The diagonal line in Fig. 2(a) shows this upper bound.

Figure 2(b) shows the energy spectrum of the emitted electrons. Between 0 and 10 eV, the distribution is slightly declining, followed by a steep decay. The first region is similar to the energy sharing of two electron emitted in direct single photon double ionization of a single helium atom [14] or a covalently bound molecule [15], suggesting similar correlation mechanisms to be at work. For the long studied atomic case knockoff and shakeoff are the two well-established mechanisms mediating double electron ejection [16–19]. In the knockoff process the energy is
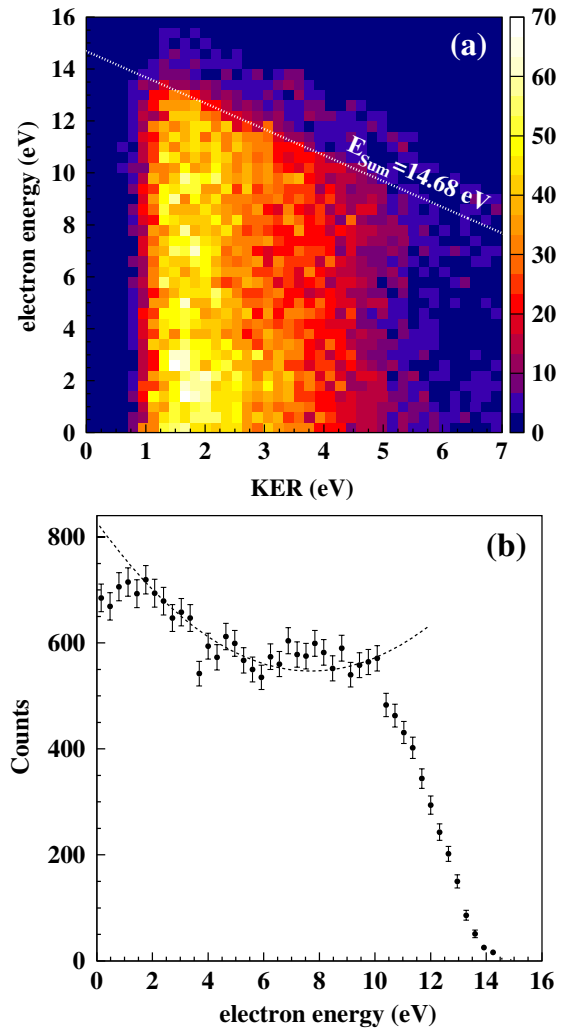

FIG. 2 (color online). Experimental results for double ionization of He$_2$ by one 63.86 eV linearly polarized photon. (a) kinetic energy release (KER) of both fragment ions versus energy of one of the two electrons. The dashed line at a sum energy of 14.68 eV is given by the total available energy. Data points below 1.5 eV KER are affected by decreased detection efficiency. (b) Electron energy spectrum [projection of (a) on vertical axis]. Dashed line: CCC theory, electron impact ionization (e, 2e) of He at 40 eV initial energy [24].

transferred by a binary type collision between the two electrons. For shakeoff the rapid change of the correlated wave function caused by the photoejection of one electron leads to shakeoff of the second electron upon the relaxation of this wave function to the new eigenstates of the altered potential. In the case of a knockoff process, the second ionization step can be considered as the impact of a 39.3 eV electron on a single helium atom (compare [19,20]). This (e, 2e) type process has been examined in multiple experiments (i.e., [21–23]) and is well understood by theory. The dashed line in Fig. 2 shows a convergent close-coupling (CCC) calculation of the single differential cross section, i.e., the electron energy distribution, for an (e, 2e) collision of a free 40 eV electron with a neutral He atom. It agrees

surprisingly well with our measured distribution for photo double ionization of He_2. The edge above 10 eV is due to restricted sum energy. In contrast to an $(e, 2e)$ experiment, the amount of 14.68 eV is not only shared by two electrons, but also by the ions (KER).

The angular distribution of the dimer axis with respect to the photon polarization [Fig. 3(a)] allows us to distinguish between shakeoff and knockoff. Shakeoff is polarization independent resulting in an isotropic distribution of the ionic fragments in the laboratory frame. For the knockoff, however, a simple billiard type scenario suggests that the photoelectron which is launched at one side can hit the second atom only if the dimer axis is oriented along the direction of the primary photoelectron momentum. If that is the case, the angular distribution of the dimer axis should
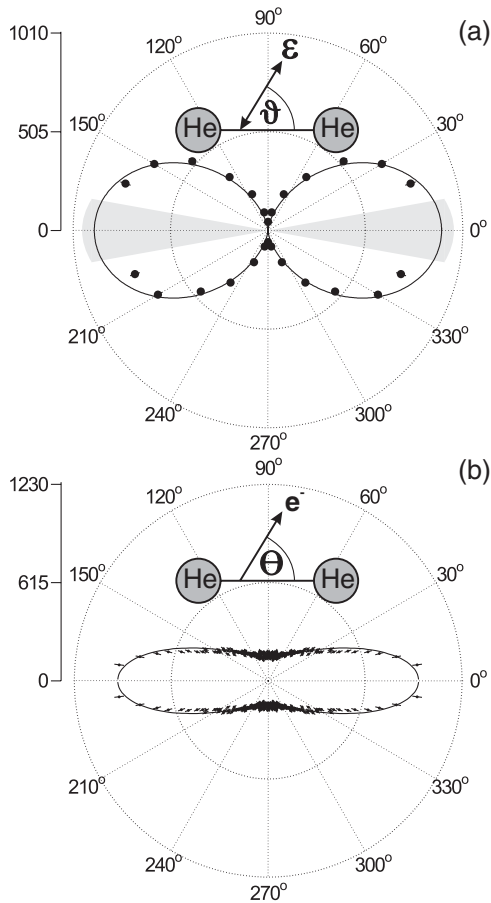

FIG. 3. Upper panel: angle of the dimer axis with respect to the photon polarization ε (horizontal), the black line shows a dipole distribution fitted to the data [$\cos^2(\vartheta)$]. Some data points are missing due to a decreased detection efficiency for certain regions of angles and KERs (gray area). Lower panel: angle between the dimer axis and outgoing electrons integrated over all electron energies. Continuous line: CCC calculation for electron impact ionization $(e, 2e)$ of He at 40 eV initial energy. The calculation is integrated over the secondary electron energies at 1, 4, 7.7, 12.7, and 15 eV from [24]. The theory has been mirrored to account for the indistinguishability of the two centers in the helium dimer.

reflect the angular distribution of the photoelectron of the He monomer. For the case of ionization of an 1s state as in helium this is a dipolar distribution given by $\cos^2(\vartheta)$, where ϑ is the angle between the photoelectron and the polarization axis. The measured experimental angular distribution of the dimer axis [Fig. 3(a)] resembles strikingly that distribution and thus gives a clear evidence for the knockoff process ruling out the shakeoff mechanism.

As we have argued above, the primary photoelectron has to be emitted approximately along the dimer axis to facilitate the knockoff at the neighbor. Thus in the present case the dimer axis is the equivalent to the electron beam axis in the $(e, 2e)$ experiment at an atom. We therefore compare angular distributions of the electron with the dimer axis in the present experiment with the electron angular distribution with respect to the beam axis in the $(e, 2e)$ case [Fig. 3(b)]. As it is not possible to distinguish from which atomic center the photoelectron is emitted, the intensities $I(\theta)$ and $I(180-\theta)$ add. Hence the data of the CCC calculation [24] for the $(e, 2e)$ collision with He has been mirrored accordingly. The theory [line in Fig. 3(b)] is in excellent agreement with the measured distribution.

Our identification of the knockoff mechanism as being responsible for the observed single photon double ionization is hence supported by three independent experimental observables: the energy sharing between the electrons, the angular distribution of the molecular axis and the angular distribution of the electrons with respect to the molecular axis.

We now use this knowledge of the correlation mechanism and the measured coulomb explosion energy to sample the He_2 ground state wave function. This can be done in full quantum version or in a classical mechanics approximation. Within the realm of classical mechanics there is a one-to-one relation of the internuclear distance R of the dimer at the instant of double ionization (labels on top of Fig. 4) to the KER (labels on bottom of Fig. 4). As illustrated by the dashed line in Fig. 1 photon absorption promotes the system from the ground state to the $He^+ +$ He^+ potential (path A to B). Dissociation on this repulsive curve (path B to C) leads to $KER = C/R$ with the proportionality constant $C = 52$ eV/Å. The classical physics reflection approximation [7,25] is successfully used, e.g., in Coulomb explosion imaging in ion beams [26] and strong laser fields [27].

Quantum mechanically the classical relationship $KER = 1/R$ has to be replaced by the overlap of the bound initial state wave function $\Psi_i(R)$ of the dimer with the continuum wave function $\Psi_f^{KER}(R)$ for the respective KER (see Fig. 1). The probability distribution $P(KER)$ is then given by

$$P(\text{KER}) = \left| \int dR \Psi_i(R) \frac{1}{R} \Psi_f^{\text{KER}}(R) \right|^2. \quad (1)$$

Since the second (target) atom can only be ionized if the photoelectron is emitted within a certain solid angle, the knockoff correlation mechanism underlies a classical $1/R^2$
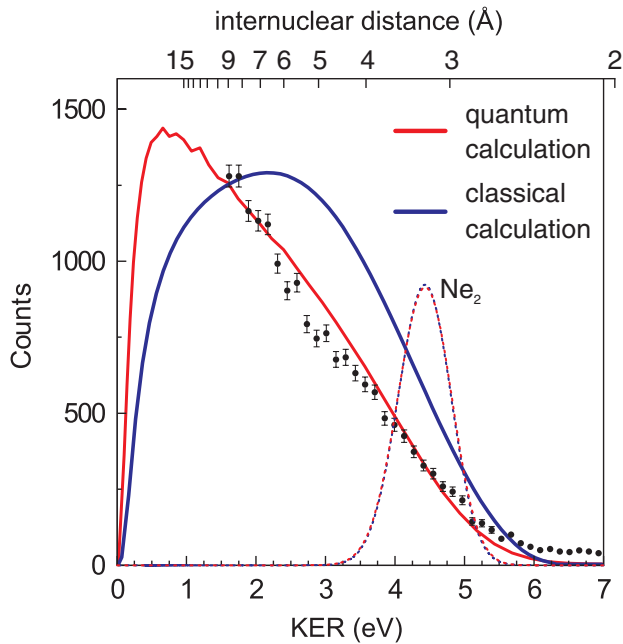
FIG. 4 (color online).   KER distribution. Upper line: classical calculation (reflection approximation, path *A-B-C* in Fig. 1); lower line: quantum calculation. Data points below 1.5 eV are missing due to a decreased detection efficiency in this area. The dotted lines show the two calculations for the neon dimer.

dependency. In the quantum treatment accordingly a geometrical factor $1/R$ has to be inserted to the integral of Eq. (1). Classical and quantum sampling of the ground state wave function are shown by the two continuous lines in Fig. 4. While the classical approximation introduces only a small error when the reflecting potential is very steep and the initial state is confined to a narrow region of R as in covalently bound molecules [7] the extreme dimensions of the helium dimer require the full quantum treatment. The good agreement of the present Coulomb explosion data with the full quantum calculation confirms the unique delocalized character of the He_2 wave function as predicted by theory. Our experiment samples this wave function in the region of approximately 2.5–10 Å. We note that the typical confined Gaussian wave function of all standard ground state molecules and also of all other van der Waals systems would lead to a near Gaussian peak in the KER. For comparison singly photon double ionization of neon dimers leads to a near Gaussian peak as narrow as $\Delta E/E = 0.2$ peaked at 4.4 eV. The differences between classical and quantum calculation is negligible in Ne_2 (see dotted lines in Fig. 4).

In conclusion, we have observed the electron correlation mediated direct ejection of two electrons from two distant sites upon absorption of a single photon. The underlying mechanism of a knockoff type process which has its anal-ogy in double ionization of atoms. For the extreme conditions of the helium dimer the knockoff can be split into a photoionization at one center (the photoelectron gun) followed by an $e, 2e$ collision at the neighbor. This $e, 2e$ collision occurs in the static field of the neighboring coulomb charge, which can be controlled by the internuclear distance. This distance also controls the phase of the photoelectron as it hits the neutral. With very strong external field and phase, two new control parameters are introduced in $e, 2e$. The influence of these parameters escaped observation and also theoretical attention so far. It is related to the rescattering process in a strong laser field, where the intermediate electron is additionally driven by the field.

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