

The article is published in Nature Physics and currently available on the Nature Physics preprint server:

<http://www.nature.com/nphys/journal/vaop/ncurrent/full/nphys1498.html>

Nature Physics (2010) 10.1038/NPHYS1498

Ultrafast Energy Transfer between Water Molecules

T. Jahnke^{1,*}, H. Sann¹, T. Havermeier¹, K. Kreidi¹, C. Stuck¹, M. Meckel¹, M. Schöffler², N. Neumann¹, R. Wallauer¹, S. Voss¹, A. Czasch¹, O. Jagutzki¹, A. Malakzadeh¹, F. Afaneh³, Th. Weber², H. Schmidt-Böcking¹, and R. Dörner¹

¹ *Institut für Kernphysik, University of Frankfurt,
Max-von-Laue-Str. 1, D-60438 Frankfurt Germany*

² *Lawrence Berkeley National Laboratory, Berkeley California 94720*

³ *Physics Department, Science Faculty,
The Hashemite University, Zarqa 13133, Jordan*

(Dated: October 27, 2009)

*Electronic address: jahnke@atom.uni-frankfurt.de

At the transition from the gas to the liquid phase of water a wealth of new phenomena emerge, which are absent for isolated H_2O molecules. Many of those are important for the existence of life, for astrophysics and atmospheric science. In particular the response to electronic excitation changes completely as more degrees of freedom become available. Here we report on the direct observation of an ultrafast transfer of energy across the hydrogen bridge in $(\text{H}_2\text{O})_2$ (a so called water dimer). This intermolecular Coulombic decay leads to an ejection of a low energy electron from the molecular neighbor of the initially excited molecule. We observe that this decay is faster than the proton transfer which is usually a prominent pathway in case of electronic excitation of small water clusters and leads to dissociation of the water dimer into two H_2O^+ ions. As electrons of low energy (~ 0.7 eV to 20 eV) have been recently found to efficiently breakup DNA-constituents [1, 2] the observed decay channel might contribute as a source for electrons that can cause radiation damage in biological matter.

The water molecule is, as a triatomic molecule, still rather simple in structure and its geometry is well known. In contrast to that, the interplay of compounds of water molecules or other atoms and molecules with water, for example in a solution, is very rich and far from being fully understood. Already at the very onset of condensation when two water molecules are combined to the *water dimer* a new dimension of complexity arises: electronic excitation of this complex spawns nuclear dynamics leading to fragmentation into a protonated fragment (i.e. H_3O^+) and an OH group [3, 4]. For this fragmentation first a proton migrates from one of the molecules to its neighbor, usually along a distance that is larger than the bond lengths found in the water molecule itself. Such fragmentation dynamics are characteristic for larger cluster, as well [5]. Typical mass spectra of fragments of water droplets show a breakup into protonated cluster fragments $(\text{H}_2\text{O})_n\text{H}^+$ of different size and into OH groups. A reason for this is the absence of direct transitions within the Franck-Condon region to breakup channels that do not involve proton migration [6–8]. Furthermore the migration itself is highly efficient and occurs on a timescale of < 60 fs [9].

The response of condensed water to electronic excitation has far reaching consequences for biological systems. Radiation damage to cells naturally depends sensitively on the routes by which energy deposited into the cells is finally distributed and which fragmentation and deexcitation pathways are favored. During the last years experiments have shown that the constituents of DNA are highly vulnerable to low energy electrons [1]. The latter studies

revealed, that not only the primary ionization by high energetic particles or photons causes the damage but especially low energy electrons efficiently breakup bio-molecules [2].

In the present letter we report on the observation that inner valence ionized water dimers fragment completely contrary to the standard scenario sketched above. They relax ultrafast and directly, without a preceding migration of protons. Their deexcitation is observed to go along with the emission of a low energetic electron that has - depending on the states involved - an energy < 10 eV. That energy range coincides with the energy range relevant for radiation damage. The relaxation occurs via an Intermolecular Coulombic Decay (ICD), a process first predicted by Cederbaum and coworkers 12 years ago [10]. ICD occurs when the excited particle is only loosely attached to neighboring particles by e.g. Van-der-Waals forces or hydrogen bonding. In such a scenario an intermolecular decay involving the emission of an electron from a *neighboring partner* of the initially excited particle may become *the* dominant channel for deexcitation. ICD is an highly efficient ionization mechanism and happens for species investigated so far on time scales < 100 fs. Other intermolecular or interatomic ionization mechanisms, as for example electron impact ionization after photo ionization, are typically one order of magnitude less probable. It occurs after ionization of an appropriate atomic shell (i.e. an inner valence shell) [11–13], after excitation [14–16], and especially as a terminal step after Auger decay [17–19] and therefore after ionization of the cluster compound with high energetic particles or photons. Most recently the main characteristic of ICD, ionization of nearest neighbor molecules by energy transfer, was also seen in the core hole relaxation of OH^- dissolved in water [20]. In all cases except the last one, the electron being emitted as a result of ICD is of low energy. Since ICD happens at some step of a possible reaction chain it is nearly independent of the energy of the initially ionizing particle. Therefore, ICD is an efficient and general mechanism for converting high energetic radiation into low energetic free electrons.

Providing experimental evidence that this decay occurs in water clusters is not straight forward, even if it is the dominant decay channel. Its main feature is a low energy electron being emitted from a different site than the originally excited one. In larger clusters inelastic electron scattering usually leads to a photo electron spectrum with kinetic energies down to zero energy masking possible ICD electrons. To avoid this problem we investigate the water dimer instead of larger droplets. This has the advantage that all charged particles that are created during the process can be measured in coincidence and in addition the

system is small enough to allow for theoretical modeling of all steps of the process in the future. Model calculations for the primary ICD step in water dimers for a fixed geometry have already been reported [21].

We trigger the process by removing an inner valence electron from one of the water molecules of the dimer. After ICD occurred a second electron is emitted and the second water molecule of the dimer becomes charged (See Fig. 1 (b,c)). By measuring the mass, charge, direction and energy of both ions and both electrons we obtain a complete picture of the reaction. Firstly, we can check for momentum conservation and thus show that the particles originate from the same event of ionization and that the two water ions initially formed a water dimer. From the mass spectrum we can tag which of the bonds broke and identify potential proton migration. From the energy of the ions we can deduce the internuclear distance of the two ions at the time the Coulomb explosion was triggered. That internuclear distance can be compared to the values for the ground state of the dimer found in the literature, already giving a first hint on the time scale of the decay dynamics and therefore on the efficiency of ICD in the competition with other processes. The emitted electrons provide a fingerprint of the decay process: we expect a photo electron within a certain energy range, determined by the photon energy and the binding energy of the ionized orbital, and a low energetic ICD electron.

The experiment was performed at the Berlin synchrotron BESSY II at beamline U125-2/SGM as described in the experimental methods section.

During offline analysis in a first step the breakup channel of the dimer was identified: after emission of two electrons the dimer will fragment into two singly charged ions in a Coulomb explosion. The two ions are emitted back-to-back with momenta of equal magnitude but opposite direction. Since the time-of-flight depends on the momentum and the mass of the particle, the back-to-back emission leads to a line structure in the time correlation map of both particles shown in Figure 2. Different masses correspond to different lines and an asymmetric breakup into fragments of unequal masses appears as a V-shaped structure. The dashed lines indicate the locus of events for fragmentation after proton migration ($\text{H}_3\text{O}^+ + \text{OH}^+$) and the solid line that of direct fragmentation without proton rearrangement ($\text{H}_2\text{O}^+ + \text{H}_2\text{O}^+$). We do not find indications of proton migration thus proving that the decay leading to the emission of two electrons is so fast, that the water dimer explodes by Coulomb repulsion before there is time for a proton to change its position.

To unveil the mechanisms by which the photon energy dumped at one site is transferred across the dimer we now investigate the ion and electron energies. Fig. 3(a) shows the measured sum of the kinetic energies of the two H_2O^+ ions (kinetic energy release, KER). At large internuclear distances the intermolecular potential drops with $1/R$ given by the Coulomb repulsion between the two charged centers at the internuclear distance R . Therefore the intermolecular distance at the instant of ejection of the second electron can be obtained from the measured KER [28]. A KER of 4.9 eV corresponds to $R = 2.9 \text{ \AA}$. This value nicely corresponds to typical distances of the two molecules of the water dimer in its ground state [21] as shown by the red circle in Figure 1(a). The measured electron energy spectrum (Fig. 3(b)) clearly shows apart from the photo electron distribution a great amount of electrons with low energies as expected for the ICD process.

Finally, Fig. 4 depicts the energy of the two electrons measured in coincidence. Firstly, it shows energy conservation: for the case of inner valence ionization and a photon energy of $h\nu = 43 \text{ eV}$ the maximum sum energy of the two electrons can be approx. 14.5 eV depending on the orbitals involved in the decay and the KER. Apart from that, two sharp features linking an electron of nearly zero energy to a broad distribution of higher energies are visible. A comparison to calculated binding energies (Fig. 4 (top), adapted from [21]) shows that the distribution from approx. 4 eV to 13 eV corresponds to a photo electron leaving the singly charged water dimer ion in a single inner valence hole state. These photo electrons are accompanied by a second, low energetic electron from the IC decay. The electrons at zero energy show this most prominently, but as for the manifold of involved states other combinations of photo electrons and ICD electrons with a sum energy $< 14.5 \text{ eV}$ occur, as well, just as Fig. 4 reveals. The calculated spectrum in Fig. 4 shows narrow lines for the photo electron spectrum since it corresponds to a fixed geometry of the dimer, neglecting the decay width and, more importantly, the distribution of angles and internuclear distances in the ground and excited state. Including those would lead to widely overlapping, broadened lines in a measured electron energy spectrum.

Our work unveils the presence of an intermolecular decay in loosely bound matter. Similar findings were just recently observed by Mucke and coworkers [30]. The elaboration of the role of this mechanism in radiation damage of biological systems in high detail is beyond the scope of this experiment. However, that role could be explored in future investigations: with our setup any species that can be prepared as a molecular beam can be examined.

Experiments similar to those described in [2] are thinkable. Instead of employing an electron gun as a donor for electrons the experiment can be performed using an aqueous solution of the target species. In that case the complete pathway of the damage can be examined: from the fragments occurring after the reaction being triggered by photo ionization it can be deduced which electron attached to the DNA constituent. That way the significance of intermolecular decays to radiation damage can be directly investigated and separated from other sources of damage.

Acknowledgments

We would like to thank the staff at BESSY, especially H. Pfau and G. Reichardt, for extraordinary support during the beamtime. Many discussions on ICD with L. Cederbaum and his group are gratefully acknowledged. This work was supported by the DFG and BESSY GmbH.

I. EXPERIMENTAL METHODS

The experiment was performed at the Berlin synchrotron BESSY II at beamline U125-2/SGM in single bunch operation using COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS) [22–24]. A photon beam with an energy of $h\nu = 43$ eV was crossed with a preheated supersonic jet consisting of water vapor. We achieved a sufficiently dense target with a reasonable fraction of condensed water molecules by heating the nozzle, the gas line and the water reservoir to a temperature of 110°C, 110°C and 95°C respectively. Under these conditions the stagnation pressure of the vapor was 0.8 bar, leading to a dimer fraction of $> 1\%$, while the production of larger clusters was still suppressed: a trimer fraction of less than one tenth of the dimers was deduced from mass spectroscopy measurements. A COLTRIMS analyzer consisting of two multi channel plate detectors with delayline position readout [25] was used to perform the coincident measurement of all reaction products. In brief, a homogenous electric field guides electrons and ions to two opposing position and time sensitive detectors. By measuring the time-of-flight and the position of impact for each particle their vector momentum after the photo reaction are obtained. The information is recorded as raw timing as a listmode dataset. From that momenta are calculated in an offline

analysis where, furthermore, constraints (e.g. by checking for momentum conservation for each photo ionization event recorded) can be applied to the dataset reducing the background. A superimposed homogenous magnetic field confines the electrons to the spectrometer volume. With values of $E = 9.6$ V/cm for the homogenous electric and $B = 7$ Gauss for the magnetic extraction field electrons with an energy up to 12 eV and ions with an energy up to 8 eV can be detected within 4π emission solid angle. The electron arm of the analyzer employed McLaren-time focussing [29] and a hexagonal delayline anode (Roentdek HEX-80, see <http://www.roentdek.com> for details on the detectors) was used in order to reduce the deadtime of the electron detector enabling the coincident measurement of the two electrons.

II. AUTHOR CONTRIBUTIONS

Experiment design and setup(T.J., T.H., K.K., H.S., O.J.), beamtime(T.J., H.S., T.H., K.K., C.S., M.M., M.S., N.N., R.W., S.V., F.A.), data analysis(T.J.), interpretation of data(T.J., R.D., T.W., A.M., H.S.B.), manuscript preparation(T.J., R.D., T.W., M.S., A.C.). Correspondence should be addressed to - T.J.

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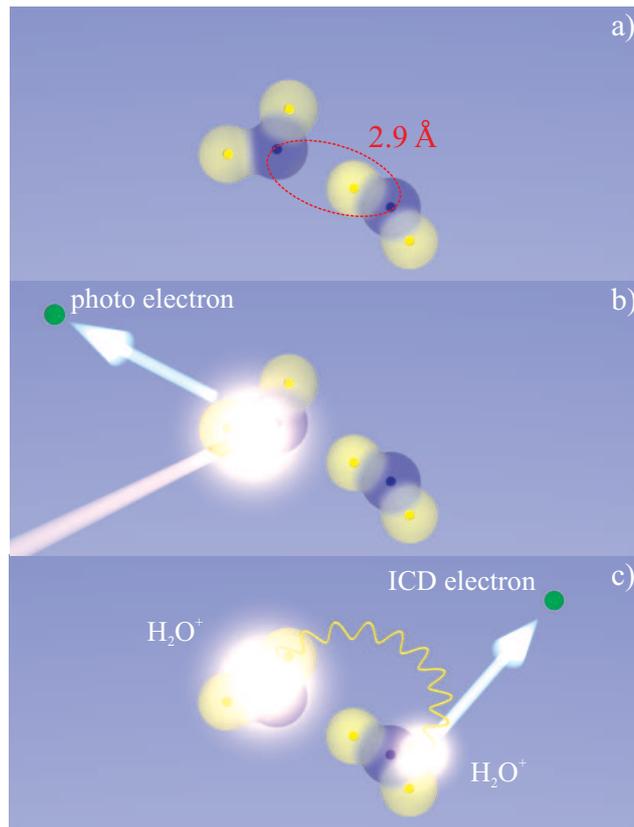


FIG. 1: Investigated species and process. (a) Geometry of the water dimer (adapted from [21]). The red circle shows an internuclear distance of 2.9Å with a corresponding kinetic energy release of 4.9 eV after the photo reaction. (b) and (c) depict the process observed in this experiment: (b) an electron from the inner valence shell of one of the molecules of the dimer is ejected by absorption of a photon. (c) the energy released by deexcitation at this site is transferred to the *neighboring* site from where a second, low energy electron is emitted.

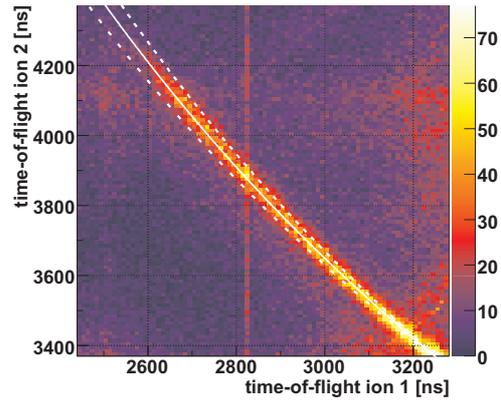


FIG. 2: Correlation of the times-of-flight of the two measured ions. The distribution reveals the decay of the dimer into $\text{H}_2\text{O}^+ + \text{H}_2\text{O}^+$ (full white line). The V-shaped dashed white line shows the expected position of events for the breakup after proton migration, i.e. into $\text{H}_3\text{O}^+ + \text{OH}^+$.

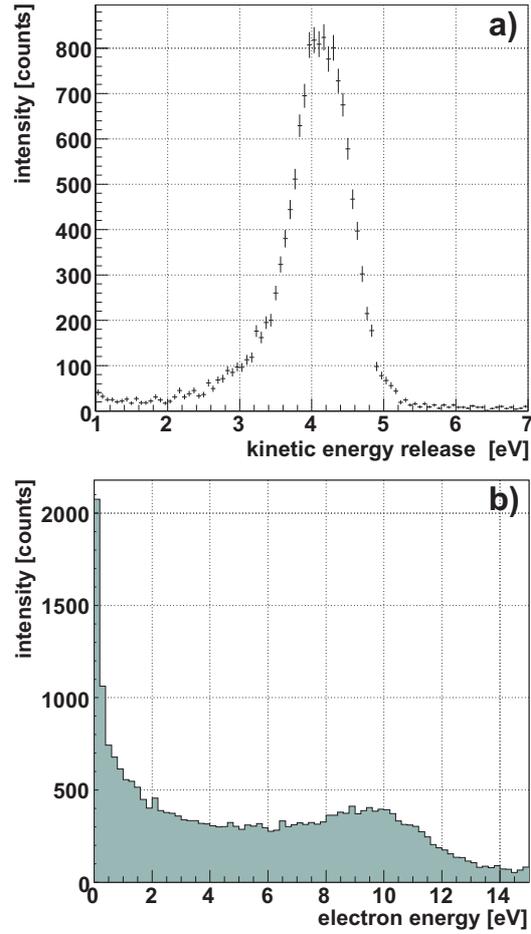


FIG. 3: Energies of the particles measured in the experiment. (a) Measured kinetic energy release of the ions after breakup of the dimer into $\text{H}_2\text{O}^+/\text{H}_2\text{O}^+$. An energy of 4.9 eV corresponds to an internuclear distance of 2.9\AA as indicated in Figure 1(a). The error bars correspond to the statistical error. (b) Measured electron kinetic energy for breakup of the dimer into $\text{H}_2\text{O}^+/\text{H}_2\text{O}^+$.

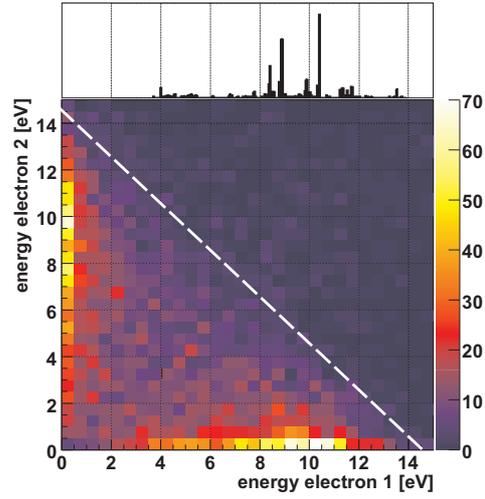


FIG. 4: Energy correlation found for the two electrons measured in coincidence. Bottom: Experimental energy distribution of the two electrons measured in coincidence. Top: calculated energies and probabilities for $(\text{H}_2\text{O})_2$ inner valence photo ionization at a photon energy of 43 eV adapted from [21].