H-atom Relay Reactions in Real Space

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Abstract

Hydrogen bonds are the path through which protons and hydrogen atoms can be transferred between molecules. The relay mechanism, in which H-atom transfer occurs in a sequential fashion along hydrogen bonds, plays an essential role in many functional compounds. Here we use the scanning tunneling microscope (STM) to construct and operate a test-bed for real-space observation of H-atom relay reactions at a single-molecule level. We demonstrate that the transfer of H-atoms along hydrogen-bonded chains assembled on a Cu(110) surface is controllable and reversible, and is triggered by excitation of molecular vibrations induced by inelastic tunneling electrons. The experimental findings are rationalized by ab initio calculations for adsorption geometry, active vibrational modes, and reaction pathway, in order to reach a detailed microscopic picture of the elementary processes.
Assembling nanoscale structures with atomic-scale precision and controlling their functions are key challenges toward molecule-based devices. To this end scanning tunneling microscopy (STM) has made it possible to image, manipulate, and characterize single atoms and molecules on surfaces\textsuperscript{1,2}. Inelastic tunneling electrons from the tip of an STM can be used as a source of energy to induce adsorbate motions such as hopping\textsuperscript{3}, rotation\textsuperscript{4,5}, switching\textsuperscript{6,7}, and desorption\textsuperscript{8}, as well as to initiate chemical reactions such as dissociation\textsuperscript{9,10}, bond formation\textsuperscript{11}, dehydrogenation\textsuperscript{12,13}, and cis-trans conversion\textsuperscript{14}. STM techniques have also been used to study sequential bond dissociation/formation reaction propagating along self-assembled molecular chains\textsuperscript{15}. Here we demonstrate a new class of single-molecule chemistry with the STM involving hydrogen bonds\textsuperscript{16}. By engineering a platform of H-bonded chains assembled on a Cu(110) surface we are able to transfer an H-atom from one end of the chain to the other. The reaction, triggered by excitation of molecular vibrations, is reversible and occurs along the H-bonds in a sequential fashion via the relay mechanism. This class of reaction can be used to transfer single-bit information from one location to another and might provide a way to realize purely mechanical computations, similar to Babbage’s difference engine\textsuperscript{17}, with molecule-based devices.

H-atom/proton transfer through hydrogen bonds plays an essential role in many functional materials such as proton conductors\textsuperscript{18}, organic ferroelectric compounds\textsuperscript{19}, and confined liquids mimicking protein channels\textsuperscript{20}. The relay reaction from one molecular unit to the next is considered to involve coordinated, and often complex, rearrangements within the network, and its study dates back to the idea of ‘structural diffusion’ by Grotthuss two centuries ago to explain the anomalously high mobility of protons in liquid water\textsuperscript{21,22}. Since microscopic characterization of relay reactions is extremely challenging in complex environments, insight has been inferred from computer simulations\textsuperscript{23-25} and spectroscopic techniques\textsuperscript{26-28}. H-atom migration via the relay mechanism was also observed at solid surfaces\textsuperscript{29}, where H-atom/proton dynamics and reactions play crucial roles in, e.g., electrode chemistry and heterogeneous catalysis.

H-bonded chains, represented as H$_2$O-(OH)$_n$ ($n=2-4$), were assembled on Cu(110) using a combination of STM manipulation and controlled dissociation of individual water molecules. As an example, Fig. 1 shows the assembling procedure of H$_2$O-(OH)$_2$. First some water molecules were dissociated into hydroxyl (OH) species and subsequently into atomic oxygen imaged as a round depression on the hollow site (Fig. 1a, right). The chemical identification
of these species is detailed in Supplementary Information. In the next step we manipulated a water molecule, which is imaged as a round protrusion centered on the top site (Fig. 1a left), along the [110] direction to react with the oxygen atom, then yielding the H-bonded hydroxyl dimer, $(\text{OH})_2$ (Fig. 1b, right), as represented by the reaction formula: $\text{H}_2\text{O} + \text{O} \rightarrow (\text{OH})_2$. The produced hydroxyl dimer was identified by vibrational spectroscopy (STM-IETS)\textsuperscript{30} and the possibility of a peroxide molecule was ruled out. Our DFT calculations also show that a peroxide adsorbed on Cu(110) is unstable and spontaneously dissociated into the hydroxyl dimer. Each hydroxyl group is bound in the short-bridge site on adjacent Cu rows and inclined its OH axis along [001] to form stable H bond within the dimer\textsuperscript{30-32}. Finally, a second water molecule was brought to one end of $(\text{OH})_2$, yielding an $\text{H}_2\text{O}-(\text{OH})_2$ chain (Figs. 1d-1f). These reactions occur spontaneously when the reactants come sufficiently close to each other. Longer H-bonded chains were also assembled as described in Supplementary Information.

The structure of the $\text{H}_2\text{O}-(\text{OH})_2$ chain was determined by DFT calculations as shown in Figs. 2a and 2b. The water molecule and hydroxyl groups are bound at short-bridge sites. Figure 2b illustrates how the H bond formed between the water molecule and its neighboring hydroxyl group results in an oxygen atom distance that is slightly shorter than between two short-bridge sites. The corresponding simulated STM image (Fig. 2c) is characterized by a “tadpole”-shaped protrusion with the head and tail appearing over the water molecule and hydroxyl species, respectively, in good agreement with the experimental images. The bright feature in the STM image can thus be assigned to the water molecule in the chain.

A voltage pulse with STM over the water molecule induced the inversion of the image, which corresponds to H-atom transfer as shown in Fig. 2d. Detailed analysis of STM images suggested the binding site of oxygen atoms were not altered during the inversion. This result indicates a mere H-atom relay within the chain, in which intermolecular multiple H-/covalent bond exchange is involved in the process, that moves a water molecule “apparently” from one end of the chain to the other. This relay reaction occurs in a series of H-bonded chains with varying length (Fig. 2d-f), and is reversible and controllable with the STM. It shares some similarities with the reactions observed in self-assembled $\text{CH}_3\text{S-SCH}_3$ aggregates, where S-S bonds were shown to dissociate and form collectively along the chain\textsuperscript{35}. However, our H-bonded chains display different dynamics and allow for production of a new water molecule at the end,
giving rise to the “structural” transfer of a water molecule from one end of the chain to the other.

The H-atom transfer can be directly monitored in the current signal of STM. The inset of Fig. 3a shows the time evolution of tunneling current measured over the water molecule of $\text{H}_2\text{O}-(\text{OH})_2$ with feedback loop open. The high and low current states correspond to the initial and final states of the H-atom transfer, respectively, and the jumps of the current are the moments of the transfer event. The transfer rate can be determined from the distribution of time intervals for each event. Any signature of intermediate states, such as the transition state OH-H$_2$O-OH, was not observed within the time-scale of STM.

To explore the mechanism of the H-atom transfer, the applied bias voltage, tunneling current (gap resistance), and spatial dependence of the transfer rate was investigated for $\text{H}_2\text{O}-(\text{OH})_2$, $\text{D}_2\text{O}-(\text{OD})_2$ and $\text{H}_2\text{O}-(\text{OH})_3$. In Fig. 3a the quantum yield (reaction probability per tunneling electron) of the H-atom transfer is plotted as a function of applied bias voltage. The tip was positioned over the protrusion, i.e., the water molecule, during the measurements. Yields were observable at a range from $10^{-12}$ to $10^{-6}$ per electron within an experimental time scale. For $\text{H}_2\text{O}-(\text{OH})_2$ the yield shows an initial increase around 180 mV, a moderate increase beyond $\sim$220 mV, and a sharp enhancement around 430 mV. For $\text{D}_2\text{O}-(\text{OD})_2$ an isotope effect is observed in which the yield shows an initial increase around 200 mV and a sharp enhancement around 320 mV. The transfer rate shows a linear dependence onto the current at several voltages (Fig. 3b), indicating that the transfer is induced via single-electron processes over the whole bias range. We confirmed that the same results were obtained with the bias polarity inversed, ruling out that the electric field induces the reaction. These results unambiguously suggest that the H-atom transfer is triggered by the vibrational excitation of the adsorbate molecules.

Figure 3c shows the spatial dependence of the transfer yield at $V=243$ and 443 mV, where the yield is plotted as a function of the distance along the H-transfer axis ([001] direction) as indicated in the inset. At both voltages the yield is the largest when the tip is positioned over the water molecule, but at $V=443$ mV it is more broadly distributed over the chain. This indicates that different vibrational modes are involved at these different voltages. The reaction yield was also investigated for $\text{H}_2\text{O}-(\text{OH})_3$ (Fig. 3a, green triangles) and found to be several orders of magnitude smaller than that of $\text{H}_2\text{O}-(\text{OH})_2$.

Here we briefly describe a theory to quantify the relation between the transfer yield and
vibrational excitation (see also Supplementary Information). The yield $Y(V)$ per electron is defined by $Y(V) = R(V)/I(V)$, where $R(V)$ is the transfer rate and $I(V)$ the tunnel current through the adsorbate at an applied voltage $V$. The transfer rate induced by single-electron processes can be expressed as $R(V) = K \Gamma_{\text{int}}(V)$, where $K$ is a prefactor determined by the elementary process and $\Gamma_{\text{int}}$ is the vibrational generation rate$^{33}$. At low temperatures the yield of adsorbate reactions can consequently be written as a sum over contributions from each active vibrational mode$^{34}$

$$Y(V) = \frac{1}{V} \sum_i K_{\text{eff}}^i \int_0^{|eV|} d\omega \rho_{\text{ph}}^i(\omega)(|eV| - h\omega). \quad (1)$$

where all voltage-independent parameters are included in effective prefactors $K_{\text{eff}}^i$ for each mode $i$. Also, $\rho_{\text{ph}}^i(\omega)$ is the vibrational density of states which we assume to be normally distributed around $h\Omega_i$ with a standard deviation $\sigma_{\text{ph}}^i$. This allows us to take into account vibration broadening effects with the parameter $\sigma_{\text{ph}}^i$ including finite temperatures, vibrational relaxation, and anharmonic effects of H bonds. As shown by the solid curves in Fig. 3a, Eq. (1) reproduces the experimental data using the parameters given in the caption. These parameters suggest that three characteristic vibrational modes (free OH/OD stretch, OH*/OD* stretch, and H$_2$O scissors, where H*/D* denotes the shared H/D atom in the H bond) are involved in the relay reaction in the range of voltages where the transfer yield could be observed. The observed onset around 430 [320] mV for H$_2$O-(OH)$_2$ [D$_2$O-(OD)$_2$] can be associated with the free OH [OD] stretch mode. At lower voltages we assign modes centered at 310 meV for H$_2$O-(OH)$_2$ and at 262 meV for D$_2$O-(OD)$_2$ to shared OH*/OD* stretch modes. In the case of H$_2$O-(OH)$_2$ also a third mode around 213 meV is taken into account and associated with the H$_2$O scissors mode. On the other hand, for D$_2$O-(OD)$_2$ the scissors mode is well below the voltage range where the yield is observable. It is noted that the OH*/OD* stretch modes are significantly red-shifted from free OH/OD stretch and also characterized by very large broadenings (38 meV for OH* and 23 meV for OD*). The significant mode softening with respect to the free stretch modes and spectacular enhancement of the width are familiar from IR spectroscopy and known to originate in the strong anharmonic character of a single H bond$^{16}$. Both anharmonicity of the mode potential as well as from a strong coupling to low-energy intermonomer modes affect the detailed features. Furthermore, since anharmonicity is expected to be more pronounced for H than D,
the model parameters for OH*/OD* are also consistent with the largest shift and width in
the case of OH*.

The vibrational mode analysis also explains why the spatial distribution of the transfer
yield (Fig. 3c) is more localized over the water molecule at V=243 mV than at V=443
mV. In the former case only the H$_2$O scissors, which is spatially localized within the chain,
can be excited. In the latter case, however, also the OH*/OH stretch modes of both the
water molecule and hydroxyl groups in the chain can be excited to trigger the transfer,
thus resulting in a broader distribution. We note that the dynamics of our H-bond chain
reactions, which we have clarified to occur by direct vibrational excitation, is fundamentally
different from reactions induced by purely electronic excitations. For instance, the S-S chain
reaction reported in Ref. 15 is consistent with an electronic mechanism where the dissociation
is initiated by temporal attachment of an electron to an antibonding orbital localized on the
S-S bond.

We also investigated the reaction pathway from total energy calculations for the H-atom
transfer reaction (Fig. 4). The initial step is transportation of the shared H-atom to the
center hydroxyl, which is almost barrier-less ($\lesssim$ 0.04 eV). This is in line with the recent
DFT calculations that predicted the H-atom sharing in the water and hydroxyl overlayers is facile due to the quantum nature of the nuclear motion$^{35}$. The subsequent H-bond
cleavage between OH and the center water molecule constitutes the highest barrier of 0.25
eV, in which the displacement of the center water molecule along [001] direction is mainly
involved. The OH, OH* stretch and H$_2$O scissors modes are therefore postulated to couple
to the reaction coordinate for the H-bond cleavage. It is noted that the H-atom transfer was
observed below the bias voltages of 250 mV in the bias voltage dependence (Fig. 3a), where
the tunneling electron should not have enough energy to induce the H-atom transfer via
a merely over-barrier process. We propose that the H-bond cleavage, that mainly involves
rotational motion of the center water molecule, might here proceed via vibrationally-assisted
tunneling$^{36}$ of an entire H$_2$O or D$_2$O molecule through the transition state$^{37}$. The transfer
reaction is therefore completed either via tunneling (at low bias) or over-barrier processes
(at high bias). For the longer chains H$_2$O-(OH)$_{3,4}$, the H-atom transfer reaction occurs in se-
quence and thus the energy dissipation is more significant, giving rise to lower reaction yields
than for H$_2$O-(OH)$_2$. Such energy dissipation plays a crucial role in determining the product,
yield, and pathway in chemical reactions on surfaces. Our results in a well-characterized en-
vironment thus shed new light on the exploration of the fundamental mechanism of H-atom transfer.

We have demonstrated a vibrationally-induced H-atom relay reaction within H-bonded chains assembled on Cu(110) at 6 K using STM. In this reaction H-atom transfer results in the “structural” transfer of a water molecule from one end of the chain to the other without changing the platform of the chain. These artificial H-bonded chains enabled us to study intermolecular reaction processes including multiple H-/covalent bond exchange at a single-molecule limit. Engineering even longer and more sophisticated H-bond systems supported on solid surfaces could provide an opportunity not only to achieve mechanical logic circuits using H-atoms but also to systematically study fundamental steps of the H-atom dynamics in heterogeneous systems. Such systems are conceivable by combining the self-assembling nature of water/hydroxyl complexes with STM manipulation techniques. Our discovery that H-atom transfer along H-bonds is possible directly on metal surfaces suggests that relay reactions may occur more generally at metal-molecule interfaces and therefore in liquids all the way down to the confining surfaces. This is of importance in diverse fields such as nanofluidics and design of hybrid materials for proton conduction.

I. METHODS

A. Experimental

The experiments were performed in an ultra-high vacuum chamber equipped with STM operating at 6 K. The Cu(110) surface was cleaned by repeated cycles of argon ion sputtering and annealing. The surface was exposed to H₂O or D₂O gases at 12 K via a tube doser positioned ~1 cm apart from the sample surface, and the molecules were imaged mainly as isolated monomers after the exposure. By applying $V=2\,V$ and $I=20\,\text{nA}$ to a water molecule, we induced dissociation of a water molecule into hydroxyl. The hydroxyl group was further dissociated by applying $V=0.9\,V$ and $I=10\,\text{nA}$ into atomic oxygen.

We conducted the lateral manipulation of a water molecule by decreasing the tunnel resistance to $\sim 1\,\text{MΩ}$, which brought the tip close to a water molecule, and then the tip was laterally moved at $\sim 0.1\,\text{nm per second}$ in the [110] or [110] direction (along the Cu
row of the substrate) with the feedback maintained. While the manipulation of a water molecule was conducted in a controlled way, that of an isolated hydroxyl group is not feasible. Nevertheless, its complex with water (H₂O-OH) can be moved along the [110] direction by applying ~450 mV (Supplementary Fig. S2). In these ways, we were able to construct hydrogen-bonded complexes of a certain composition and structure.

B. Computational

The atomic structure was determined using Kohn-Sham density functional theory (DFT) with a plane-wave basis and the PBE-GGA exchange correlation functional as detailed in the Supplementary Information. STM images were simulated with the STATE code within the Tersoff-Hamann theory. Phonon modes and harmonic frequencies were calculated by finite differences. The reaction barrier was estimated with the nudged elastic band (NEB) method as implemented in VASP.


We found that the imaginary mode of the transition state corresponds to the rotation-translation of the center water molecule (Figs. S7 and S9), suggesting that the tunneling object has to be the entire molecule.


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III. AUTHOR CONTRIBUTIONS

T.K. and H.O. designed and planned the experiments. T.K. and A.S. measured and analyzed the STM data. I.H. performed the STATE calculations. T.F. performed the VASP calculations. H.O. supervised the project and H.U. provided guidance for the analysis completed by I.H. and T.F. H.O., I.H., T.F., and H.U. discussed the results and wrote the paper.

IV. ADDITIONAL INFORMATION

The authors declare no competing financial interests. Supplementary information accompanies this paper at www.nature.com/naturematerials. Reprints and permission information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to H.O.
FIG. 1. Sequential STM images of the assembly process of the H$_2$O-(OH)$_2$ chain from individual water molecules on Cu(110). The images were recorded in constant current mode at a sample bias voltage of $V$=24 mV and tunneling current of $I$=0.5 nA. (a) A water molecule and two atomic oxygen are imaged as a round protrusion and two depressions, respectively. The white grid lines indicate the lattice of Cu(110). The water molecule was dragged along the [110] direction toward atomic oxygen (dashed arrow). (b) The reactants yield an OH dimer imaged as a semicircular depression. The white dots indicate the short-bridge sites to which oxygen atoms in (OH)$_2$ are bonded. (c) Schematic illustration of the reaction process. The light gray circles represent Cu atoms on the substrate which form “Cu rows” along the [110] direction. STM images of water, oxygen atoms and (OH)$_2$ are also depicted. (d), (e) Subsequently, another water molecule was dragged to the end of (OH)$_2$ (dashed arrow), then yielding an H$_2$O-(OH)$_2$ complex in a chain from. The three dots in (e) depict the nearest short-bridge sites to which oxygen atoms in the complex are bonded. It is noted that the positions of oxygen atoms deviate slightly from the exact short-bridge sites along [001] axis, as shown in the structure optimized by DFT calculations [Fig. 2(a) and (b)]. (f) Schematic illustration of the reaction process of (d) and (e). The image sizes are 20×58 Å$^2$ for (a) and (b), and 20×36 Å$^2$ for (d) and (e).
FIG. 2. Assembled water-hydroxyl chains displaying H-atom transfer reactions. (a) Side view of the H$_2$O-(OH)$_2$ chain optimized by DFT calculations and its counterpart. (b) Top view of (a). (c) STM simulation for (b). (d) Experimental STM images of the H$_2$O-(OH)$_2$ chain and its counterpart superimposed with the lattice of Cu(110) (white lines). The appearance was inverted by the voltage pulse of STM over the protrusion. The inversion was also observed for (e) H$_2$O-(OH)$_3$ and (f) H$_2$O-(OH)$_4$ chains. The dots in (d)-(f) indicate the nearest short-bridge sites binding oxygen atoms in the chains [note that oxygen atom positions deviate from the exact short-bridge sites as shown in (b)]. The inversion of the appearance corresponds to H-atom relay reaction in which a sequential H-atom transfer is included as shown by curved arrows in (a). The images were obtained at $V=24$ mV and $I=0.5$ nA ($18\times29\text{Å}^2$). The range of the height shown in the color scale is from -0.36 to 0.44 Å.
FIG. 3. Yields (rate) of H-atom transfer reactions as a function of voltage, current and position of electron injection. (a) Reaction yields as a function of the applied bias voltage. Data were obtained for H$_2$O-(OH)$_2$ (red circles), D$_2$O-(OD)$_2$ (blue squares), and H$_2$O-(OH)$_3$ (green triangles). The inset shows a typical current trace recorded with the tip fixed over the protrusion for H$_2$O-(OH)$_2$ at $V=213$ mV. The two-state fluctuation indicates the back-and-forth relay reaction in the chain. The red and blue curves are Eq. (1) applied to the H$_2$O-(OH)$_2$ and D$_2$O-(OD)$_2$ data, respectively, with the following parameters: (mode, $\hbar\Omega$/meV, $\sigma_{ph}$/meV, $e^2K_{eff}^{ij}$) = (H$_2$O scissors, 213, 11, 6×10$^{-9}$), (OH$^2_-$ stretch, 310, 38, 18×10$^{-8}$), (OH stretch, 460, 13, 19×10$^{-5}$) and (OD$^2_-$ stretch, 262, 23, 6×10$^{-8}$), (OD stretch, 334, 11, 4×10$^{-6}$). (b) The current dependence of the reaction rates for H$_2$O-(OH)$_2$ (red circles) and D$_2$O-(OD)$_2$ (blue squares) at various voltages. The slopes were estimated to be 0.82±0.03, 0.95±0.02, 0.97±0.04, and 0.93±0.05 for 443, 343, 223 and 210 mV, respectively. The data are presented in logarithmic scale and the slopes are close to unity, indicating single-electron processes in the whole voltage range. (c) Position dependence of the yield along the chain for H$_2$O-(OH)$_2$ at $V=243$ mV (blue circles) and $V=443$ mV (red circles). The position is represented by the distance from the center of the inversion along [001], as shown in the inset with the STM image. While the yield is broadly distributed over the complex at $V=443$ mV, it is more localized at $V=243$ mV above the protrusion (water molecule).
FIG. 4. Calculated potential energy surface for the H-atom relay reaction in an H$_2$O-(OH)$_2$ chain along the [001] direction. The set of images from initial to final states, shown as insets, were determined by the nudged elastic band method (see Supplementary Information). The H-transfer to the center OH is facile ($\lesssim$ 0.04 eV). The transition state (0.25 eV) corresponds to OH-H$_2$O-OH with a broken H bond.