Anomalously Low Barrier for Water Dimer Diffusion on Cu(111)

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Supporting Information

ABSTRACT: A molecular-scale description of water and ice is important in fields as diverse as atmospheric chemistry, astrochemistry, and biology. Despite a detailed understanding of water and ice structures on a multitude of surfaces, relatively little is known about the kinetics of water motion on surfaces. Here, we report a detailed study on the diffusion of water monomers and the formation and diffusion of water dimers through a combination of time-lapse low-temperature scanning tunnelling microscopy experiments and first-principles electronic structure calculations on the atomically flat Cu(111) surface. On the basis of an unprecedented long-time study of individual water monomers and dimers over days, we establish rates and mechanisms of water monomer and dimer diffusion. Interestingly, we find that the monomer and the dimer diffusion barriers are similar, despite the significantly larger adsorption energy of the dimer. This is thus a violation of the rule of thumb that relates diffusion barriers to adsorption energies, an effect that arises because of the directional and flexible hydrogen bond within the dimer. This flexibility during diffusion should also be relevant for larger water clusters and other hydrogen-bonded adsorbates. Our study stresses that a molecular-scale understanding of the initial stages of ice nanocluster formation is not possible on the basis of static structure investigations alone.

KEYWORDS: Diffusion, water, STM, DFT, hydrogen bonds, adsorption energy

In nature, water covers most surfaces. The interaction of water with solid surfaces is thus crucial in several scientific disciplines. In particular, in areas as diverse as environmental science,1-4 solvation science,5 and astrochemistry,6 supported water—ice is of the utmost importance. For this reason, the structure and properties of water and ice have been investigated in depth on a large variety of solid surfaces, including metals, oxides, semiconductors, and carbon nanotubes.7-8 Of these, water at atomically flat surfaces (e.g., Au,9 Pd,10 Cu,11 Ru,12 Pt,13,14 Ni,15 and Ag16) has received considerable attention as a well-defined model system from which a molecular-scale understanding can be obtained. Such work has primarily focused on establishing the structure of metal-supported ice overlayers and nanoclusters. In contrast, the kinetics of water motion on metal surfaces, leading eventually to the formation of such ice structures, has been investigated only scarcely on the single-molecule level.17,18 This is true despite the crucial role that water diffusion plays in the assembly of the water—ice overlayer structures that form. Indeed, recent structure investigations have suggested that the formation of fractal ice structures involves the mobility not only of water monomers but also of small clusters.16,19

In an earlier seminal experiment, it was demonstrated that water dimer diffusion on Pd(111) is, at 40 K, significantly faster than monomer diffusion.17 On this surface, a water dimer consists of one water molecule directly bound via its oxygen lone pair to the metal surface. The second molecule (the hydrogen bond acceptor) sits higher above the surface, and the second molecule thus interacts only scarcely with it. For the motion of the dimer, theory proposed a novel and highly competitive diffusion mechanism at the temperature of the experiment, which includes the exchange of the two molecules in terms of binding and adsorption height.19 This diffusion process can be accelerated as compared to the diffusivity of water monomers by quantum tunneling of the hydrogens within the water molecules at low temperatures. Unfortunately, the much increased diffusivity hindered a systematic temperature-dependent investigation of the dimer motion, and it remains to be explored whether this process is relevant to other surfaces or at higher temperatures. Likewise for dimers consisting of molecules other than water, the increased diffusivity upon dimer formation has so far been

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discussed only on a qualitative level, and the microscopic details of these phenomena are still in question.

In this letter, we report water diffusion, dimer formation, and dimer diffusion on Cu(111). Copper is chosen as a substrate because of its importance as a catalyst for reactions including water. (e.g., in water splitting and water–gas shift reactions), further processes for which the kinetics of water is very important). To reveal the microscopic diffusion mechanism of the monomer and the hydrogen-bonded dimer, we investigate the diffusion of D₂O monomers and dimers on Cu(111) between 23 and 29 K by time-lapse scanning tunneling microscopy (STM). Both species diffuse between on-top sites of the substrate with an almost negligible difference in the diffusion barrier as shown by both experiment and density functional theory (DFT) calculations. Our combined study reveals that despite very different monomer and dimer adsorption energies the diffusion barriers are equivalent because of the role played by the hydrogen bond in the dimer diffusion process. The dominant dimer diffusion mechanism is different from what was previously suggested on Pd(111) and does not require quantum tunneling for rapid dimer diffusion. Thus, fast dimer diffusion should also be valid at higher temperatures, in particular, those relevant to ice and dimer adsorption energies the dimer mechanism is different because of the role played by the hydrogen bond in the gas phase water dimer.

STM measurements were performed with a low-temperature STM under ultrahigh vacuum (UHV) conditions (base pressure \(2 \times 10^{-10}\) mbar). The single-crystal Cu(111) surface was cleaned by several sputtering–annealing cycles: in the initial cycles by sputtering with neon ions at 1.3 keV \(3 \times 10^{-5}\) mbar, 1 to 2 \(\mu\)A, 45 min) and annealing at 900 K for 20 min. The last sputtering was performed at a reduced energy of 650 eV \(3 \times 10^{-5}\) mbar, 0.8 \(\mu\)A, 20 min) followed by a flash to 600 K. This cleaning procedure resulted in a very low concentration of surface impurities of approximately \(4 \times 10^{-5}\) ML. D₂O is purified prior to deposition by several freeze–pump–thaw cycles until no further improvement is observed in the mass spectra of the vapor. The overall purity determined by mass spectrometry in the gas phase was \(98\%\). D₂O was used in this experiment to discriminate it from the residual H₂O during TPD measurements. To obtain water monomers, the water had to be deposited at a temperature at which the molecules are not mobile on the surface. Because conventional liquid-helium-cooled manipulators usually do not reach this temperature regime, the water was dosed in situ with the crystal in the STM. A total coverage of \(6 \times 10^{-5}\) BL (bilayer) was deposited in a sequence of two deposition intervals of 22 and 23 s at a deposition rate of \(8 \times 10^{-4}\) BL/min with the sample below 15 K at all times.

For the diffusion experiments, the temperature of the STM was raised to between 23 and 29 K by passing a current through Zener diodes at its base plate. (For details, see ref 34.) After stabilizing to a temperature change of less than 0.1 K/h, the same spot on the surface was imaged for extended time periods of up to several days at a constant repetition rate of between 60 and 300 s to create a movie. The total number of analyzed STM images was around 3000. In the analysis, consecutive images of a movie were aligned by the positions of immobile surface impurities used as reference points. After alignment, the positions of the molecules were tracked semiautomatically by fitting identical two-dimensional Gaussian profiles to the molecules in all images. The same procedure has been successfully applied in ref 36. Here, the number of analyzed jumps per data point in the Arrhenius plot was between 10 000 at lower temperature and 2000 at higher temperature for the monomers and around 1000 for the dimers in the investigated temperature range. To circumvent the effects of interactions via the surface state on the diffusion process, only molecules with distances larger than 4 nm from any other particle or impurity were considered in the analysis. Details of the analysis procedure and temperature calibration are given in the Supporting Information.

Density functional theory (DFT) calculations were performed using the VASP code, with the optB86b-vdW functional, which accounts for nonlocal van der Waals interactions which are important for this system. A plane-wave cutoff of 600 eV was used. The metal surface was represented using a four-layer-thick slab in a 3 \(\times\) 3 unit cell with a 3 \(\times\) 3 \(\times\) 1 K-point mesh. The vacuum region in the \(Z\) direction between the periodically repeated Cu slabs was 1.4 nm, and dipole corrections along the \(Z\) axis were applied. The climbing image nudged elastic band method was used to obtain the diffusion barriers, with forces optimized to below 0.1 eV/\(\AA\). The top two layers of the metal slab were free to relax in the calculations. Tests with respect to the DFT setup and sensitivity to the exchange-correlation functional are provided in the SI.

Herein, the calculated adsorption energy, \(E_{\text{ads}}\), is defined by

\[
E_{\text{ads}} = |E_{n(H_2O/M)} - E_M - E_{n(H_2O)}|
\]

in which \(n(H_2O)\) is the number of water molecules, \(E_{n(H_2O/M)}\) is the total energy of the \(n(H_2O)\) cluster adsorbed on the metal surface system, \(E_M\) is the total energy of the relaxed bare metal slab, and \(E_{n(H_2O)}\) is the total energy of the relaxed \(n(H_2O)\) cluster in the gas phase. For the adsorption energy of the water dimer, eq 1 implies that this is defined with respect to a gas-phase water dimer.

All reported computed barriers have been corrected for zero-point energy (ZPE) with deuterium masses for the hydrogen and finite size effects. (See the details in the SI.) Specifically, the computed diffusion barriers correspond to the barriers obtained in the \(3 \times 3\) cell plus the finite size correction. As shown in the SI, the finite size correction is the difference in the diffusion barriers between the \(3 \times 3\) and 9 \(\times\) 9 cells obtained on frozen surface slabs. The ZPE of the initial and transition states has been calculated using the finite displacement method within the harmonic approximation. Diffusion prefactors are calculated within the context of classical transition-state theory with the prefactors expressed by

\[
\left(\frac{\Pi \omega_{\text{IS}}}{(2\pi \Pi \omega_{\text{TS}})}\right)
\]

with positive harmonic frequency \(\omega_{\text{IS}}/\omega_{\text{TS}}\) for the initial state/transition state.

We begin by discussing the preparation and formation of adsorbed water monomers. While water forms oligomers on metal surfaces as a result of attractive hydrogen bonds at higher adsorption temperatures, the diffusion of the molecules is suppressed at our deposition temperature below 15 K, leading to well-separated and identical protrusions that are randomly distributed over the surface (Figure la). All protrusions exhibit a full width at half-maximum (fwhm) of \(0.81 \pm 0.02\) nm and an apparent height of \(60 \pm 3\) pm. These values are within the range of values for water monomers reported previously on Cu(111) and on related surfaces such as Au(111) and Ag(111) for similar tunneling parameters. In addition, their uniform size suggests that these single protrusions are indeed single
D$_2$O molecules. This conclusion is confirmed by the diffusion experiments below that rule out any diffusion at the deposition temperature.

Such monomers are adsorbed at on-top sites of Cu(111) (Figure 1d) as calculated before$^{20,28,32}$ and confirmed below by the analysis of diffusion paths. Binding via the highest occupied molecular orbital (HOMO) perpendicular to the plane of the water molecule forces the molecule into an adsorption structure with one of the water molecules (the hydrogen bond acceptor) slightly raised from the molecular plane almost parallel to the surface (Figure 1d).

At elevated temperatures, some of the molecules merge to create dimers, as illustrated in Figure 1. Note that on bilayer-high NaCl(100) islands dimers do not form spontaneously,$^{18}$ while on Ag(111) clusters form at the deposition temperature, inhibiting a kinetics study on these surfaces. The formation of larger oligomers is very rare at the low coverage and low temperature of our measurement.$^{20,30,32}$ The round shape thus reflects the time-averaged positions of this rotating species.

Note that the closest observed distance between two monomers before dimer formation is around three surface lattice distances of Cu(111) ($a_{\text{Cu(111)}} = 0.255$ nm) (i.e. > 0.7 nm). This indicates an attractive interaction between monomers at closer distances.

Having identified monomers and dimers on the surface, we now examine how they diffuse. To make detailed measurements of diffusion rates, we have identified a goldilocks temperature window of 23 to 29 K. Within this temperature window, the motion is fast enough that diffusion is observed on a time scale of hours to days but slow enough that cluster formation is rare. The monomer diffusion is exemplified in the tracking of molecules at 26.7 K in Figure 2. The three encircled molecules in Figure 2a−d are tracked continuously for 20 h. A cutout of the recorded diffusion paths is displayed in Figure 2e. The paths form a hexagonal lattice, reflecting the symmetry of Cu(111). This is confirmed in the diffusion distance histogram (Figure 2f), which displays $\Delta r = \sqrt{\Delta x^2 + \Delta y^2}$ with $\Delta x$ and $\Delta y$ retrieved from all positions of diffusion paths of all molecules in this movie. The fwhm of the first maximum, corresponding to no motion, serves to determine the uncertainty in the position determination. This uncertainty

The round shape of the dimer is in line with DFT calculations, which revealed that the dimer has an asymmetric adsorption structure with one of the water molecules (the hydrogen bond donor) adsorbed at an atop site and the other molecule (the hydrogen bond acceptor) slightly raised from the surface (Figure 1e). This second molecule is nearly free to rotate around the surface-bound molecule even at the low temperature of our measurement.$^{20,30,32}$ The round shape thus reflects the time-averaged positions of this rotating species.

Di$^2$O molecules after preparation (marked by red arrows), with the reference point marked by a white arrow and the z scale in pm. (b) Subsequent image of the region in the red square in panel a after 170 s, with one monomer and one dimer (marked by a green arrow) ($V = 25$ mV, $I = 20$ pA, and $T = 23.1$ K). (c) Apparent height profile of the monomer in red and the dimer in green as marked in panel b. (d, e) Side views of lowest-energy adsorption energy for (d) the monomer and (e) the hydrogen-bonded dimer, with Cu atoms in brown, oxygen atoms in red, and hydrogen atoms in white.

Figure 1. In-situ preparation and dimer formation: (a) Single D$_2$O molecules after preparation (marked by red arrows), with the reference point marked by a white arrow and the z scale in pm. (b) Subsequent image of the region in the red square in panel a after 170 s, with one monomer and one dimer (marked by a green arrow) ($V = 25$ mV, $I = 20$ pA, and $T = 23.1$ K). (c) Apparent height profile of the monomer in red and the dimer in green as marked in panel b. (d, e) Side views of lowest-energy adsorption energy for (d) the monomer and (e) the hydrogen-bonded dimer, with Cu atoms in brown, oxygen atoms in red, and hydrogen atoms in white.

Figure 2. Diffusion of monomers: (a−d) four snapshots from a movie at (a) 0, (b) 5, (c) 10, and (d) 15 h. Three molecules are circled in different colors. (e) Cutout of tracked positions of the monomers (circles) in (a−d), black lines mark close-packed directions of Cu(111) as determined from images with atomic resolution. (f) Diffusion distance histogram for all positions of the movie; numbers and arrows mark characteristic atom distances on Cu(111). Parameters: 25 mV, 20 pA, 26.7 K, $\Delta t = 90$ s, and 853 images in total.
is, at approximately 20 pm, far below the lattice constant of Cu(111). The other maxima clearly correspond to the lattice distances of Cu(111) (indicated by arrows in Figure 2f). A corresponding analysis of the dimer motion reveals the same symmetry and distances (Supporting Information, SI). The observed diffusion maps are consistent with previous DFT calculations, which, as noted earlier, identified the on-top site as the favorable adsorption site for both monomer and dimer. Because the diffusion lattice for monomers and dimers corresponds to Cu(111), the measured diffusion distances are aligned to the nearest on-top positions of Cu(111) for the following analysis.

Before deriving the diffusivity from the recorded data, we ensure that the motion is random. The displacements of monomers and dimers are determined from the recorded movies. We determine mean-square displacements \( \langle \Delta x^2 \rangle \) and \( \langle \Delta y^2 \rangle \) of the diffusion for different time intervals \( \Delta t \) and find the expected linear dependence. The separate diffusivities for \( \Delta x^2 \) and \( \Delta y^2 \) are identical within the error bars (SI). Consequently, we may use the Einstein relation

\[
D = \frac{\langle \Delta r^2 \rangle}{4 \Delta t}
\]

with \( \langle \Delta r^2 \rangle = \langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle \) to determine the diffusivity of the molecules with \( \Delta t \) being the time between two subsequent images.

Our analysis reveals that at the same temperature the diffusivity of monomers and dimers differs by only 1 order of magnitude. In addition, the diffusivities of both monomers and dimers follow Arrhenius behavior within the temperature range examined, as shown in Figure 3. Thus, from the data we extract the energy barrier and diffusion prefactor using

\[
D = D_{0,i} \exp \left( \frac{E_i}{kT} \right)
\]

Here, \( E_i \) is the energy barrier with identifier \( i \) for monomer and dimer, \( T \) is the temperature, and \( k \) is the Boltzmann constant. The prefactor is \( D_{0,i} = a a_{\text{Cu(111)}}^2 \nu_0 \exp \left( \frac{E_i}{k} \right) \), with dimensionality factor \( \alpha = 1.5 \), lattice constant \( a_{\text{Cu(111)}} = 255 \text{ pm} \), fundamental attempt frequency \( \nu_0 \), and change in entropy \( \Delta E_k \). For the linear regression of the data, we resample the experimental data statistically in order to correctly weight the corresponding statistical error of the data (SI). This procedure yields an energy barrier of \( E_{\text{monomer}} = (75 \pm 4) \text{ meV} \) and a diffusivity of \( D_{0,\text{monomer}} = 1.8 \times 10^{-12} \text{ nm}^2/\text{s} \) corresponding to a prefactor of \( \nu_0 \exp \left( \frac{E_{\text{monomer}}}{k} \right) = 1.8 \times 10^{11 \pm 0.7} \text{ Hz} \) for the monomer. For the dimer, the corresponding values are \( E_{\text{dimer}} = (80 \pm 8) \text{ meV} \), \( D_{0,\text{dimer}} = 1.3 \times 10^{-11} \text{ nm}^2/\text{s} \), and \( \nu_0 \exp \left( \frac{E_{\text{dimer}}}{k} \right) = 5.5 \times 10^{11 \pm 1.4} \text{ Hz} \). Thus, we find on Cu(111) that the diffusion barriers for the monomer and the dimer are very similar, with the difference falling within the error bars of the estimates. This is a clear violation of the rule of thumb that predicts a linear dependence of the diffusion energy of atoms and small molecules on several transition-metal surfaces to the corresponding adsorption energy.

To understand why the diffusion barriers for monomers and dimers are so similar, we now turn to DFT for detailed insight into the diffusion mechanisms of each species. The most stable adsorption structures for the monomer and dimer are shown in Figure 4a,b, respectively. The adsorption energy of the monomer is 0.35 eV, and for the dimer it is 0.77 eV (Table 1). In these adsorption structures, both the monomer and the dimer are free to rotate around the surface normal with barriers of <20 meV. Various pathways for water monomer and dimer diffusion were considered with DFT, and the lowest-energy pathways identified are shown in Figure 4. We find that for both species a hopping motion from on-top to an on-top site via a bridge site is preferred. For the monomer, the molecule remains almost parallel to the surface throughout the entire diffusion process (Figure 4a, TS). However, during the hopping motion of the dimer, the lower bound molecule...
changes to an almost upright position in the transition state (Figure 4b, TS). The hydrogen bond to the higher bound molecule is maintained in this upright orientation. However, in the transition state, the barrier for the rotation of the higher bound molecule around the lower bound molecule is increased to 150 meV, effectively suppressing this rotation at our measurement temperature. Following the transition state, the lower bound molecule returns to its almost flat-lying orientation. Note that during the concerted motion of the dimer the two molecules do not move in parallel: the lower bound molecule moves first, while the higher bound molecule simply rotates around its oxygen to maintain the hydrogen bond. Despite the more complex motion, the diffusion barrier of the dimer is, at 89 meV, only slightly larger than that of the monomer, at 86 meV (Table 1). Note that the theoretical values for the diffusion barriers converge slowly with the size of the unit cell, and cell sizes of up to 9 × 9 were considered (S1). At smaller cell sizes, periodic boundary conditions lead to a mutual interaction, reducing the diffusion energy of the monomer but increasing that of the dimer. This trend is consistent with experiments for the monomer, where the attraction between two water molecules becomes significant at an oxygen–oxygen distance of <1 nm (≈ 4αCu(111), Figure 1a,b). These computed barriers of monomer and dimer are in excellent agreement with experiment and are consistent with the fact that the monomer and dimer diffusion barriers are the same within the error of the experimental determinations.

To understand why the dimer diffusion breaks a well-established rule of thumb, we performed a detailed analysis of how the water–water–water interactions change during the diffusion processes. Decompositions such as this are always arbitrary to some extent; however, they can be useful in providing semiquantitative insight. Specifically, we considered the change in the hydrogen bond, $E_{\text{H-bond}}$, specifically, the interactions between the higher bound molecule and the surface, $E_{\text{H-bond}-\text{surf}}$, and between the lower bound molecule and the surface, $E_{\text{H-bond}-\text{surf}}$, upon going from the initial state (IS) to the transition state (TS) of the dimer diffusion process (Table 2). We find that during diffusion the interaction between the higher bound molecule and the surface barely changes ($E_{\text{H-bond}-\text{surf}}$ in Table 2), suggesting that despite this interaction contributing to the dimer adsorption energy it does not contribute to the dimer diffusion barrier. Also, the hydrogen bond interaction at the TS is slightly strengthened compared to the IS, an effect that serves to lower the barrier for dimer diffusion. In contrast, the interaction energy of the lower bound molecule with the surface is halved in the transition state. It is the weakening of this interaction that is the main physical origin of the dimer diffusion barrier, and it is similar to what is found for the water monomer (Table 2). Overall, we see that the dimer diffusion process is intimately related to the directional but flexible hydrogen bond between the two water molecules, and it is this angular flexibility that helps to break the adsorption–diffusion energy rule of thumb.33

We now connect our work to earlier studies to understand why the tunneling-assisted diffusion mechanism, proposed to be responsible for fast dimer diffusion on Pd(111),17 does not influence the water dimer diffusion on Cu(111) despite the adsorption geometry being rather similar. The diffusion process on Pd(111)20 involves a facile rotation of the water dimer in the plane of the surface normal plus an exchange of the donor and acceptor molecules in the hydrogen bond. It is this hydrogen bond donor–acceptor exchange process that is facilitated by proton tunneling. Our calculations reveal that a similar donor–acceptor exchange process is possible on Cu(111). (See Figure S7 in the Supporting Information.) However, on Cu(111) the donor–acceptor exchange process has a barrier of 185 meV. This is more than twice as large as the simple dimer translation barrier of 89 meV on Cu(111). On Pd(111), however, the dimer translation and donor–acceptor exchange barriers are rather similar, within 10 meV of each other. We are currently examining the physical origin of the various energy barriers on Pd, Cu, and several other metal surfaces, and a detailed analysis will be published elsewhere.44

To test whether quantum tunneling influences the diffusivity of the water dimer on Cu(111), we calculated the crossover temperature $T_c = (\hbar a^2)/(2\pi k_B)$ above which the influence of tunneling on the diffusivity is negligible, with the imaginary
frequency \( \omega \), the Boltzmann constant \( k \), and the reduced Planck constant \( \hbar \). From the WKB approximation point of view, assuming the barrier is parabolically topped, \( T_c \) is the temperature where tunneling starts to become favorable compared to over the barrier activation.\(^{45,46}\) From Feynman’s path integral point of view, \( T_c \) is the temperature at which an imaginary time path (which describes quantum statistics) starts to become delocalized around the barrier top. Hence, it is an indication of when tunneling becomes important. These calculations reveal a \( T_c \) of ca. 32 K for the donor–acceptor exchange process. This is so close to the temperature regime examined experimentally that the influence of tunneling is not expected to overturn the large energetic preference for diffusion via the translation mechanism. Note that \( T_c \) for the translation mechanism is, at 12 K, even lower. Calculations thus predict no significant influence of tunneling on the diffusion, and in the temperature range of our experiments, Arrhenius behavior is thus expected, which is in agreement with experiment. Furthermore, the tunneling diffusion of water will clearly be negligible for any of the reactions on Cu(111) mentioned in the introduction under realistic reaction conditions.

Although the experiments were carried out with D\(_2\)O dimers, it is interesting to estimate the importance of tunneling for H\(_2\)O dimers. The \( T_c \) for H\(_2\)O dimers is 44 K. As expected, this is higher than \( T_c \) for the D\(_2\)O dimers. However, given that it remains close to the temperature regime explored in the experiments along with the large difference between the dimer translation and donor–acceptor exchange barriers, it seems unlikely that tunneling will be significant enough to alter the relative rates of H\(_2\)O monomer and H\(_2\)O dimer diffusion on Cu(111). In fact, on the basis of a simple analysis using the WKB approximation on 1D barriers with the same barrier height and \( T_c \) as for the H\(_2\)O donor–acceptor exchange process, we found that even at the lowest experimental temperature, tunneling could not make up for the large barrier difference between donor–acceptor exchange and the translational diffusion barriers on Cu(111).

Our study suggests that the ice structures formed at cryogenic temperature will not differ largely, if formed in the environment on particles in the atmosphere or in astrophysics because tunneling is not important and thus just the time scale of structure formation depends on temperature. Consequently, understanding the kinetics of structure formation enhances our understanding of the interaction of water with surfaces in several disciplines. The flexibility of the bond during diffusion will impact not only the diffusion of the dimers investigated here but also larger clusters, even in the three-dimensional arrangement as present in solvation science, where hydrogen bonds do not necessarily have to be broken during the process of solvation. We hope that our study initiates the study of clusters hydrogen bonded to the fcc(111) surfaces of other elements or to surfaces of different symmetry in the future.

In conclusion, we have developed a molecular-scale picture of monomer and dimer diffusion of D\(_2\)O on Cu(111). On the basis of a major experimental and theoretical effort, diffusion barriers and mechanisms have been measured for both water monomers and dimers. The agreement between the measured and computed barriers is excellent, and both experiment and simulation suggest that the monomer and dimer diffusion barriers are very similar. The fact that the monomer and dimer diffusion barriers are similar despite a substantial difference in monomer and dimer adsorption energies is an apparent contradiction of the linear adsorption–diffusion energy relationship. Analysis reveals that the breakdown of the relationship originates from the crucial role played by the directional and flexible hydrogen bond within the dimer. In particular during the diffusion process, the interaction of the upper water with the surface and the hydrogen bond interaction barely changes. The different degrees of rotational freedom of the monomer and dimer impart a flexibility to their motion, which in general is expected for other hydrogen-bonded oligomers. This is relevant to kinetic models of ice formation as well as the clustering of hydrogen-bonded overlayer structures in general. Indeed, a multitude of rotation–diffusion combinations need to be considered in the future for a proper description of the kinetics of hydrogen-bonded oligomers or, more generally, for systems with bond flexibility and weak adsorbate/substrate interactions. Finally, we note that in the current system at the temperatures considered, tunneling did not play a significant role in altering the relative rates of water monomer and dimer diffusion. However, our comparison to Pd(111) reveals that the importance of tunneling is very much system-dependent, coming down to a delicate balance of the relevant competing diffusion mechanisms. It will be interesting to understand the importance of tunneling in more detail on other substrates and for other adsorbates. We hope that the current study motivates such work in the future from both experimental and theoretical angles.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.9b00392.

Further experimental and theoretical details; experimental diffusion track and histogram of the water dimer on Cu(111); the randomness of the process proven via the Einstein relation for both monomer and dimer motion; tests on the computational setup, the influence of the functional and finite size effects on the results of the DFT calculations explored for the theory; an explanation of the resampling of the diffusivity data for the determination of the energy barrier and prefactor; influence of rotation on the diffusivity; and the most relevant DFT structures (PDF)

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**Notes**

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REFERENCES

(18) Heidorn, S.-C.; Bertram, C.; Cabrera-Sanfeliu, P.; Morgenstern, K. Consecutive Mechanism in the Diffusion of D2O on a NaCl(100) Bilayer. ACS Nano 2015, 9, 3572.


Fang, W.; Pedevilla, P.; Richardson, J.; Li, X.-L.; Michaelides, A. To be published.
