Rapid water diffusion at cryogenic temperatures through an inchworm-like mechanism

Wei Fang,†‡ Kastur M. Meyer auf der Heide,¶ Christopher Zaum,§ Angelos Michaelides,*∥† and Karina Morgenstern*¶

†Thomas Young Centre, London Centre for Nanotechnology, and Department of Physics and Astronomy, University College London, London WC1E 6BT, UK
‡Laboratory of Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland
¶Ruhr-Universität Bochum, Lehrstuhl für physikalische Chemie I, Universitätsstr. 150, D-44801 Bochum, Germany
§Leibniz Universität Hannover, Institut für Festkörperphysik, Appelstr. 2, D-30167 Hannover, Germany
∥Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

E-mail: am452@cam.ac.uk; karina.morgenstern@rub.de

Abstract

Water diffusion across the surfaces of materials is of importance to disparate processes such as water purification, ice formation, and more. Despite reports of rapid water diffusion on surfaces the molecular-level details of such processes remain unclear. Here, with scanning tunneling microscopy, we observe structural rearrangements and diffusion of water trimers at unexpectedly low temperatures (<10 K) on a copper surface; temperatures at which water monomers or other clusters do not diffuse. Density
functional theory calculations reveal a facile trimer diffusion process involving transformations between elongated and almost cyclic conformers in an inchworm-like manner. These subtle intermolecular reorientations maintain an optimal balance of hydrogen-bonding and water-surface interactions throughout the process. This work shows that the diffusion of hydrogen-bonded clusters can occur at exceedingly low temperatures without the need for hydrogen bond breakage or exchange; findings that will influence Ostwald ripening of ice nanoclusters and hydrogen bonded clusters in general.

**Keywords:** water, oligomers, diffusion, hydrogen-bonding

**Introduction**

The operation of desalination membranes or magnesium-air batteries, the formation of clouds or the fracture of rocks by ice, skiing, skating or the impact of raindrops on glass – these and countless other everyday technological and scientific processes involve the motion of water molecules across the surfaces of inorganic materials. This broad importance has motivated a large body of work aimed at the understanding of interfacial water. At the fundamental molecular-level much of this work has focused on the structure and dynamics of interfacial and confined water.\(^\text{1-5}\) However, despite this large body of work – from which we have learned a great deal about the fundamental nature of water at interfaces – understanding of how water moves across surfaces remains incomplete. This applies to both the flow of liquid water and the motion of individual water molecules or clusters. Whether it is water flowing through a nanoscale channel or individual water clusters diffusing across a surface, the motion depends on a balance of water-water and water-surface interactions. However, understanding these interactions in detail remains a challenge.

However, by examining well-defined atomically precise surfaces at cryogenic temperatures it is possible to track the motion of individual water molecules and water clusters. In particular, with scanning tunneling microscopy (STM), detailed and fascinating results for water motion on the surfaces of metals and oxides have been obtained (see e.g. refs.\(^\text{4,6-8}\)).
Notably, in a seminal contribution from Salmeron and co-workers, it was shown that on a Pd surface water dimers diffuse more rapidly than water monomers. This result was surprising because of the larger mass of the dimer and also the stronger interaction strength of the dimer with the surface; often diffusion barriers of adsorbates on surfaces are proportional to the strength of the adsorption bond.

These observations have been explained with the help of density functional theory (DFT) and a mechanism for rapid dimer motion involving a tunneling assisted hydrogen bond exchange process. Subsequent studies on other metal surfaces showed that on Cu(111) monomers and dimers have similar diffusion rates, whereas on Ag(111), monomers are the faster species. What happens beyond the dimer remains largely unexplored, although clusters larger than the dimer also diffused rapidly in the Pd experiments, and water clusters of unknown size have been shown to be involved in the formation of ice.

In this article we go down to 5 K where almost all adsorbate motion is frozen out to explore in detail the motion of water clusters on a surface. Through a combination of painstaking time-lapsed STM and DFT we find that of the species on the Cu(111) surface studied, water trimers have the highest mobility: changing conformation and diffusing at temperatures as low as ca. 6 K. Notably, frequent changes between elongated and compact trimer structures promote, together with facile rotation of the elongated form, rapid trimer diffusion; diffusion which exceeds that of water monomers and all other adsorbed water clusters observed on the surface. In contrast to the case of rapid dimer motion on Pd, the rapid motion of the trimer is achieved through delicate changes of internal structure and does not require the (tunneling assisted) donor acceptor (DA) exchange of hydrogen bonds.

Materials and Methods

Our STM measurements were performed under ultrahigh vacuum (UHV) conditions with a variable low-temperature STM, calibrated to sub-Kelvin precision between 5 K and 50 K.
The Cu(111) surface was cleaned by repeated cycles of sputtering (Ne⁺, 4 to 5 · 10⁻⁵ mbar, 1 to 2 µA, 1.3 keV, 40 min) and annealing (873 K, 8 min). Water (D₂O) of milli-Q quality is filled into a glass tube that is connected via a leak valve to a vacuum chamber that is separated from the preparation chamber by a gate-through valve. After purification through several freeze-pump-thaw cycles, a pressure of 1.5 · 10⁻⁷ mbar is established in the molecule deposition chamber via a leak valve from the room temperature water vapor in the glass tube. The sample is either exposed for 45 s at 15 K or for 6.4 s at 81 K. In the former case, the sample resides within the cold shields surrounding the STM, reducing the deposition rate to around 10⁻³ BL/min leading to a coverage around 6 · 10⁻⁴ BL (bilayer, corresponding to a buckled monolayer at a density of two water molecules per three Cu surface atoms). In the latter case, it is on a nitrogen-cooled manipulator close to the water inlet, where the effective pressure at the sample is around 10⁻⁹ mbar, yielding a coverage of around 5 · 10⁻³ BL. At 15 K monomers are immobile, while at 81 K, these and other oligomers are mobile on Cu(111), but rearrangements of water molecules within amorphous water structures is inhibited. Dynamical changes are investigated in time-lapsed series between 5 K and 12 K as detailed in.

The density-functional theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP) with the optB88-vdW functional. A plane-wave cutoff of 500 eV was used. The metal surfaces were represented using a slab with 4 layers of Cu in a 5×4 unit cell with a 3×3×1 K-point mesh. A vacuum of at least 1.4 nm was placed above each surface. The climbing image nudged elastic band (CI-NEB) method was used to obtain the potential energy barriers and minimum energy pathways. The force convergence criteria for the geometry optimizations and CI-NEB calculations was 0.01 eV/Å. Since surface relaxation effects during the diffusion processes are small, the substrate atoms were fixed at the relaxed clean surface geometry during optimizations while the water molecules were fully relaxed. These computational settings are consistent with those used in our recent studies on related systems. We present in the supporting information (SI) sections S.VII and

4
Results and discussion

We begin by demonstrating the high mobility of water trimers on Cu(111) compared to water monomers and dimers. Fig. 1a displays an STM image of water monomers (M) and a water dimer (D) on Cu(111). As shown before, both species image as bright circular protrusions, with the dimer having a slightly larger diameter. The adsorption geometry of each species has been characterized before and is shown as insets in Fig. 1a. Monomers adsorb at atop sites of Cu(111). In the dimer, one of the molecules (the hydrogen bond donor, \(d\)) adsorbs in a similar atop site configuration, while the other molecule (the hydrogen bond acceptor, \(a\)) interacts weakly with the substrate and rotates easily around the surface-bound molecule. It is because of this facile rotation that the dimer also images as a circular protrusion, but with a larger diameter than the monomer.

![Figure 1](image_url)

Figure 1: Water monomer and dimer adsorption and trimer formation. (a) 3D view of an STM image showing two monomers (M) and a dimer (D) along with the calculated structures; \(d\) and \(a\) mark the water molecules in the dimer acting as hydrogen bond donor and acceptor, respectively. (b to d) Time sequence of STM images showing a monomer and dimer approaching (panels b to c) and subsequently disappearing from view once a mobile trimer forms (panel d). A false color-scale from blue to red is used and the following imaging conditions were employed: 24 K, 25 mV, 20 pA.

The diffusion barriers of the monomer and dimer were previously determined to be 75 (± 4) meV and 80 (± 8) meV, respectively, from time-lapsed STM diffusivity studies. From
DFT calculations these barriers were predicted to be 86 and 89 meV (including harmonic zero point energy (ZPE) corrections) for the monomer and dimer, respectively, and thus close to the experimental values. DFT also showed that the most favorable process for both monomer and dimer diffusion was a simple hopping process from atop to atop sites (see SI section S.X). At 24 K and on the timescale of the measurements shown in Fig. 1 both species diffuse across Cu(111). In the sequence of images shown in panels (b) to (d) a monomer and dimer approach each other and merge to form a new species; a trimer which immediately disappears from view and is absent from the region of the surface imaged in panel (e) (see supplementary movie). Thus, trimer diffusion is considerably more facile than monomer and dimer diffusion, implying a lower diffusion barrier for the trimer than the two other species.

In order to deepen understanding of the trimer and the diffusion process we carried out STM measurements at different coverages and temperatures and used DFT to aid the interpretation. Fig. 2 shows the surface at a lower temperature of 5 K and at a slightly higher water coverage, where clusters of up to approx. 10 molecules are observed. As noted earlier, the smallest round protrusions are monomers and the next largest protrusions dimers. Monomers and dimers are centro-symmetric, in contrast to the next largest protrusions which are the focus of the current study. These slightly larger clusters are either circular (referred to as pseudo-cyclic, PC) or elongated (E). The circular protrusions are, at a half-width of 1 nm, around ten percent broader than the round protrusions of the dimers. In addition, each exhibits a small off-center protrusion of greater apparent height. Similarly, also each elongated protrusion exhibits a small protrusion of greater apparent height (Fig. 2a,b). The long axes of the elongated protrusions roughly follow the ⟨112⟩ directions of Cu(111) (Fig. 2b).

To learn more about the structures of the trimers we did a set of DFT calculations for adsorbed water trimers, taking into consideration adsorbed trimers with different hydrogen-bonding arrangements. From this we concluded that the elongated structure is a trimer with a wide internal angle (Fig. 2b), whereas the circular trimer is a pseudo-cyclic structure (Fig.
Figure 2: Water oligomers on Cu(111). (a) STM image with various species indicated: Pseudo-cyclic trimers marked by circles (T$_{pc}$); Elongated trimers marked by ellipses (T$_e$); for reference a monomer (M) and; a dimer (D) are also shown. The imaging conditions were: 5.2 K, 65 mV, 24 pA. (b - c) Lowest-energy configurations of the elongated trimer (T$_e$, panel b) and the pseudo-cyclic trimer (T$_{pc}$, panel c) shown from top and side views. The labels $a$ and $d$ mark water molecules acting as hydrogen-bond acceptors and donors, respectively.

The elongated trimer structure shown in Fig. 2b is the lowest energy adsorbed trimer structure identified. (See the SI section S.III for other metastable trimer structures, including a structure only 10 meV less stable with a different chirality.) The adsorption energy of the trimer is 1.0 eV, relative to a gas phase trimer. This is larger than the equivalent adsorption energies of the water dimer (0.68 eV) and water monomer (0.32 eV). As with the monomer and dimer, water molecules are located at atop sites with one molecule acting as a hydrogen bond donor ($d$), one as a hydrogen bond acceptor ($a$), and the central molecule acting as both an acceptor and donor ($ad$). The pseudo-cyclic structure is only 31 meV less stable than the lowest energy elongated structure. In this structure the water molecules are again at atop sites and we refer to it as pseudo-cyclic because the water-water distances within the trimer ring are not equal and one water sits higher above the surface than the other two. Indeed, using a standard definition of hydrogen-bonding,$^{23}$ we conclude that there are just two hydrogen-bonds in the PC structure and we label the molecules accordingly as $d$, $a$, and $ad$ in Fig. 2b. We discuss in the SI section S.VI that this finding is not very sensitive to the choice of H-bond definition. Note that the pseudo-cyclic structure is 51 meV more stable
than its cyclic counterpart despite having one H-bond less, because there is less geometric deformation (strain) in the case of the pseudo-cyclic cluster. In both the elongated and pseudo-cyclic trimers the \( a \) molecule has its hydrogen bonds pointing towards the surface and sits higher above the surface than the other molecules, giving rise to the protrusion of larger apparent height in the STM images. The two lowest energy trimers thus reflect the symmetry of the two experimentally observed structures.

Figure 3: Rotation and interconversion between water trimers at 5-7 K. (a) Time series showing two elongated trimers (T\(_e\)) reorientating between different rotational configurations. (b) Time series showing the conversion from a T\(_e\) trimer to a T\(_{pc}\) (pseudo-cyclic) trimer and back again to a T\(_e\) trimer. The series in (a) was recorded at 7 K, with the following tunneling conditions: 65 mV, 24 pA. The series in (b) was recorded at 5.1 K (first image) to 5.8 K (two later images), with the following tunneling conditions: 65 mV, 24 pA. The times indicated in (a) and (b) are in h:min:s.

To probe the dynamics of the trimer we varied the temperature in the 5 to 10 K temperature regime and imaged the surface for extended time periods. Interestingly we find that upon very slightly increasing the temperature (by less than 1.0 degree) motion of the water trimers is observed. Specifically, the elongated trimer interconverts between different configurations. This is seen by imaging a pair of adsorbed trimers for almost 8 hours at
7 K (Fig. 3a and SI for a movie). After this time, the trimer on the left is in a different orientation at the same chirality, while the trimer on the right is in the same orientation but with different chirality, with the brighter protrusion changing its position upwards on the image with respect to the less bright one. The surface symmetry of an fcc(111) surface facilitates six rotamers of each of the two enantiomers for the elongated trimer; there should thus exist twelve different forms. As shown in the SI section S.II all twelve forms have indeed been imaged. In addition to the rotation process we also see interconversion between the elongated and pseudo-cyclic trimer structures. The elongated trimers in Fig. 3b are static for more than an hour at 5.1 K. Upon raising the temperature to 5.8 K, the one at the lower left converts into a pseudo-cyclic trimer after approximately 90 minutes and back to an elongated trimer approximately 2 minutes later. Thus, an interconversion between the elongated and pseudo-cyclic trimer is possible starting at temperatures as low as around 6 K. The greater abundance of elongated trimers and the short lifetime of the pseudo-cyclic trimers are in line with the calculated higher stability of the elongated trimer.

Having identified the most stable trimers and seen that the trimers are mobile and can interconvert we now use DFT to examine mechanisms for diffusion and exchange between the different conformers. We began by computing the barrier for the most stable trimer to translate across the surface through a straightforward hopping mechanism. The lowest energy pathway for this process has a barrier of 118 meV (see the SI section S.V for details of the mechanism). This barrier is larger than the barriers for the monomer and dimer, which as noted earlier are approximately 75 - 90 meV, from both experiment and DFT calculations. Given that water dimer motion through a H-bond exchange mechanism is possible on surfaces, we explored various trimer diffusion processes in which H-bonds are broken and reformed. These calculations revealed that for the trimer on Cu(111) all H-bond exchange processes considered had relatively high barriers of ≥300 meV (SI section S.IV). Thus H-bond exchange processes do not explain the motion observed.

However, analysis of the various trimer structures and their interconversion mechanisms
Table 1: DFT computed activation energy barriers for the key processes discussed in the text. Specifically, the following processes are considered: The overall inchworm diffusion process shown in Fig. 4; A simple trimer translation process; Rotation of the T_e trimer; Transition from the T_e trimer to the T_{pc} trimer. Barriers are reported using the “standard” computational set-up (as described in the methods section) and “corrected” to take into account zero point energy, surface relaxation, and finite size effects, as detailed in SI section S.VII.

|                      | Inchworm | T_e translation | T_e rotation | T_e to T_{pc} |
|----------------------|----------|-----------------|--------------|---------------|
| “Standard” Barrier (meV) | 82       | 118             | 35           | 31            |
| “Corrected” Barrier (meV) | 75       | 108             | 33           | 43            |

offers important insights. The transition from the elongated to the pseudo-cyclic structure occurs simply through a rotational motion in which the a molecule moves across a bridge site (Fig. 4(a)). The H-bond between the ad and a molecules is retained during this process and as a consequence the ad molecule rotates by ca. 60°, while the position of the d molecule is hardly affected. Following this the pseudo-cyclic structure can further convert into a C_3-symmetric cyclic trimer (Fig. 4(a), middle). If from this symmetric position the roles of the original a, ad, and d molecules exchange (e.g. d becomes ad, ad becomes a, and a becomes d) then when the trimer relaxes back to an elongated structure it will have moved by one surface atom. Subsequently the ad and d waters in the trimer can rotate about the d water thus completing the full diffusion process (Fig. 4(c)). Thus the overall process involves an elongated trimer, converting to a cyclic trimer via the pseudo-cyclic trimer, which converts back to a different pseudo-cyclic trimer, which then opens to a different elongated trimer (Fig. 4(a)). The overall barrier for this process is approx. 80 meV (Fig. 4(a) and Table I); a barrier that is lower than the monomer, dimer, or any of the other trimer diffusion barriers identified when all barriers are computed with a consistent set of computational settings. Because the overall process involves contraction and expansion in a manner similar to inchworm propulsion, we refer to the mechanism as “inchworm”-like diffusion.

It remains to be seen whether facile water timer diffusion can occur on transition metal surfaces in general or it is unique to Cu. We have shown that the barrier of the inchworm trimer diffusion mechanism mainly depends on the energy of the cyclic trimer T_c relative to
Figure 4: A mechanism for facile water trimer motion. (a) Top and side view of the inchworm mechanism. (b) Minimum energy pathway characterized using the intrinsic reaction coordinate\textsuperscript{29} for the inchworm diffusion mechanism of the water trimer. (c) T\textsubscript{e} rotation process that completes the inchworm diffusion process.

\(T\textsubscript{e}\). Therefore, as a first step towards understanding trimer diffusion on other metal surfaces, we computed the energies of \(T\textsubscript{c}\) and \(T\textsubscript{e}\) on the (111) surfaces of Ag, Pd, Pt, and Rh. The results show that on Pd, Pt, and Rh, the energy differences between \(T\textsubscript{c}\) and \(T\textsubscript{e}\) are 75 meV, 115 meV, and 84 meV respectively, which is smaller than the monomer and dimer diffusion barriers computed on these surfaces (with the same functional) in our previous work.\textsuperscript{13} This suggests that the trimer could be more mobile than the dimer and the monomer on these metal surfaces as well. On Ag, the most stable conformer is \(T\textsubscript{pc}\), indicating that water trimers on this surface are different.

Before concluding, we briefly discuss the quantitative agreement between experiment and simulation in terms of energetics; an issue of broad interest to diffusion at surfaces. The inchworm mechanism rationalizes the experimental observations and the predicted DFT barrier of \textit{ca.} 80 meV is lower than the diffusion barriers for either the monomer or dimer. However, the barrier is higher than expected for a thermally activated process to occur at \(<10\) K at
the rates observed experimentally. To address this issue we first explored the sensitivity of the various diffusion barriers to the basic computational settings (unit cell size, surface relaxation) as well as the inclusion of ZPE effects. These results are shown in Table I where it can be seen that the “standard” and subsequent “corrected” barriers never differ by much (2-12 meV). In addition, tests with different DFT exchange-correlation functionals show that altering the functional does not lead to significant changes in the observed behavior (SI section S.VIII). Previous calculations have shown that nuclear tunneling can, for certain systems, play an important role in water cluster diffusion.\textsuperscript{12,13,30} However, a preliminary analysis shows that despite evidence of significant tunneling (including oxygen tunneling) in this process, these effects alone are insufficient to explain the low temperature mobility of the water trimers (SI section S.IX). Another effect that seems more likely to be relevant is the influence of the electric field from the STM tip. Tip effects are known to have an influence on adsorbate diffusion in general, including water diffusion.\textsuperscript{31–33} In fact, recently it has been shown for water monomer diffusion on metals that applying a constant chemical potential for the electrons yields lower barriers and better quantitative agreement with experiments.\textsuperscript{32} and large bias induced water molecule reorientation can be visualized by STM.\textsuperscript{34} Indeed, through careful examination of the STM time series obtained for the water trimers we do see some evidence that the electric field from the tip could play a role. Simulations (reported in SI section S.X) also reveal that an electric field can alter the barrier for the inchworm process; albeit to a minimal extent small (< 10 meV). However, going beyond this and quantifying the influence of the tip with STM through e.g. temperature dependent measurements of the trimer diffusion process is highly challenging because the temperature difference between no observable motion and facile rotation plus diffusion is a mere 6 K. In addition, it is not clear how the contributions of the individual processes could be deconvoluted experimentally. However, independent of a possible influence of the electric field on the extent of trimer motion, the direct comparison to the simultaneously imaged monomers and dimers is qualitatively consistent with the smaller trimer barrier deduced theoretically.
Overall more work is required to fully resolve this issue and obtaining quantitative agreement for diffusion at surfaces remains a general challenge for future research.

**Conclusion**

In conclusion, we have demonstrated that water trimers show a much richer and faster kinetics than water monomers and other water clusters on Cu(111). We have revealed that the interconversion between different configurations aided by a facile rotation leads to a center-of-mass motion far below the temperature at which monomers and dimers are observed to diffuse. The overall interaction strength of the trimer with the surface is greater than that of either the monomer or dimer. Thus we have found another example of how the delicate balance of hydrogen bonding and water-surface interactions can enable more strongly bound adsorbates to diffuse more rapidly than weakly bound adsorbates.\(^5\) In addition, in contrast to the water dimer, the motion of trimers occurs without the need for hydrogen bond exchange.

Water cluster motion at the temperatures considered here demonstrates that the growth of extended ice structures may be easier than previously expected. Moreover, kinetic models for ice growth on surfaces should take growth through trimer and other water cluster building blocks into consideration. Indeed since the proportion of trimers on the surface will vary with temperature and depend on the mobility of monomers and dimers from which they form, fascinating growth kinetics is to be expected. Beyond ice, it would be interesting to explore if the exceptionally facile interconversion between different hydrogen bonded structures seen here on Cu(111) might go some way to explaining rapid water flow under nano-confinement.\(^5\) Finally, it is worth considering if the large angular flexibility of hydrogen bonded systems in general could be exploited to facilitate rapid motion of other types of hydrogen bonded clusters across the surfaces of materials.
ASSOCIATED CONTENT

The Supporting Information is available free of charge at https://pubs.acs.org/

- STM experiment footage.
- Additional experimental and computational results.

Acknowledgments

This work was supported by the Research Training group 'Confinement-controlled Chemistry', which is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - GRK2376 / 331085229 and by the DFG under Germany’s Excellence Strategy - EXC-2033 - Projektnummer 390677874 RESOLV. We are grateful to the Materials Chemistry Consortium (funded by EPSRC (EP/L000202)) and to the UK Materials and Molecular Modelling Hub (funded by EPSRC (EP/P020194/1 and EP/T022213/1)) for computational resources.

Author contributions

K.M. and A.M. conceived and supervised the project. K.M., M.adH., and C.Z. performed the experiments and K.M. analyzed the experimental data. W.F. carried out the simulations and W.F. and A.M. analyzed the simulation data. A.M., K.M., and W.F. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

References

(1) Henderson, M. A. The interaction of water with solid surfaces: fundamental aspects revisited. Surf. Sci. Rep. 2002, 46, 1–308.
(2) Carrasco, J.; Hodgson, A.; Michaelides, A. A Molecular Perspective of Water at Metal Interfaces. Nat. Mater. 2012, 11, 667–674.

(3) Björneholm, O.; Hansen, M. H.; Hodgson, A.; Liu, L.-M.; Limmer, D. T.; Michaelides, A.; Pedevilla, P.; Rossmeisl, J.; Shen, H.; Tocci, G.; Tyrode, E.; Walz, M.-M.; Werner, J.; Bluhm, H. Water at Interfaces. Chem. Rev. 2016, 116, 7698–7726.

(4) Maier, S.; Salmeron, M. How Does Water Wet a Surface? Acc. Chem. Res. 2015, 48, 2783–2790.

(5) Siria, A.; Bocquet, M.-L.; Bocquet, L. New avenues for the large-scale harvesting of blue energy. Nat. Rev. Chem. 2017, 1, 0091–1–9.

(6) Mitsui, T.; Rose, M. K.; Fomin, E.; Ogletree, D. F.; Salmeron, M. Water Diffusion and Clustering on Pd(111). Science 2002, 297, 1850–1852.

(7) Meyer, B.; Rabaa, H.; Marx, D. Water adsorption on ZnO(1010): from single molecules to partially dissociated monolayers. Phys. Chem. Chem. Phys. 2006, 8, 1513–1520.

(8) Kebede, G. G.; Spångberg, D.; Mitev, P. D.; Broqvist, P.; Hermansson, K. Comparing van der Waals DFT methods for water on NaCl(001) and MgO(001). J. Chem. Phys. 2017, 146, 064703–1–13.

(9) Nilekar, A. U.; Greeley, J.; Mavrikakis, M. A. Simple Rule of Thumb for Diffusion on Transition-Metal Surfaces. Angew. Chem. Int. Ed. 2006, 45, 7046.

(10) Seebauer, E. G.; Allen, C. E. Estimating surface diffusion coefficients. Prog. Surf. Sci. 1995, 49, 265–330.

(11) Yildirim, H.; Sankaranarayanan, S. K.; Greeley, J. P. Periodic Trends in Adsorption and Activation Energies for Heterometallic Diffusion on (100) Transition Metal Surfaces. J. Phys. Chem. C 2012, 116, 22469–22475.
(12) Ranea, V. A.; Michaelides, A.; Ramirez, R.; de Andres, P. L.; Verges, J. A.; King, D. A. Water Dimer Diffusion on Pd(111) Assisted by an H-Bond Donor-Acceptor Tunneling Exchange. Phys. Rev. Lett. 2004, 92, 136104.

(13) Fang, W.; Chen, J.; Pedevilla, P.; Li, X.-Z.; Richardson, J. O.; Michaelides, A. Origins of fast diffusion of water dimers on surfaces. Nat. Comm. 2020, 11, 1689.

(14) Bertram, C.; Fang, W.; Pedevilla, P.; Michaelides, A.; Morgenstern, K. Anomalously Low Barrier for Water Dimer Diffusion on Cu(111). Nano Lett. 2019, 19, 3049–3056.

(15) Heidorn, S.; Bertram, C.; Morgenstern, K. Low-Temperature Growth of Amorphous Water Ice on Ag(111). J. Phys. Chem. C 2018, 122, 15304–15310.

(16) Heidorn, S.; Bertram, C.; Morgenstern, K. The Fractal Dimension of Ice on the Nanoscale. Chem. Phys. Lett. 2016, 665, 1–5.

(17) Zaum, C.; Bertram, C.; Meyer auf der Heide, K.; Mehlhorn, M.; Morgenstern, K. Temperature Calibration for Diffusion Experiments to Sub-Kelvin Precision. Rev. Sci. Instr. 2016, 87, 053902.

(18) Bertram, C.; Morgenstern, K.; Pedevilla, P.; Michaelides, A. Anomalously Low Barrier for Water Dimer Diffusion on Cu(111). Nano Lett. 2019, 19, 3049–3056.

(19) Mehlhorn, M.; Morgenstern, K. Faceting during the Transformation of Amorphous to Crystalline Ice. Phys. Rev. Lett. 2007, 99, 246101.

(20) Morgenstern, K.; Braun, K.-F.; Rieder, K.-H. Direct Imaging of Cu Dimer Formation, Motion, and Interaction with Cu Atoms on Ag(111). Phys. Rev. Lett. 2014, 93, 056102.

(21) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 1996, 54, 11169–11186.

(22) Klimeš, J.; Bowler, D. R.; Michaelides, A. Chemical accuracy for the van der Waals density functional. J. Phys. Condens. Matter 2010, 22, 022201–1–5.
(23) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. 2000, 113, 9901–9904.

(24) Michaelides, A.; Morgenstern, K. Ice Nanoclusters at Hydrophobic Metal Surfaces. Nat. Mater. 2007, 6, 597–601.

(25) Meng, S.; Wang, E.-G.; Gao, S. Water Adsorption on Metal Surfaces: A General Picture from Density Functional Theory Studies, Phys. Rev. B 2004, 69, 195404.

(26) Carrasco, J.; Michaelides, A.; Scheffler, M. Insight from first principles into the nature of the bonding between water molecules and 4d metal surfaces. J. Chem. Phys. 2009, 130, 184707–1–13.

(27) Poissier, A.; Ganeshan, S.; Fernandez-Serra, M. V. The role of hydrogen bonding in water-metal interactions. Phys. Chem. Chem. Phys. 2011, 13, 3375–3384.

(28) Luzar, A.; Chandler, D. Hydrogen-bond kinetics in liquid water. Nature 1996, 379, 55–57.

(29) Fukui, K. The path of chemical reactions - the IRC approach. Acc. Chem. Res. 1981, 14, 363–368.

(30) Guo, J.; Li, X.-Z.; Peng, J.; Wang, E.-G.; Jiang, Y. Atomic-scale investigation of nuclear quantum effects of surface water: Experiments and theory. Prog. Surf. Sci. 2017, 92, 203–239.

(31) Gawronski, H.; Carrasco, J.; Michaelides, A.; Morgenstern, K. Manipulation and Control of Hydrogen Bond Dynamics in Absorbed Ice Nanoclusters. Phys. Rev. Lett. 2008, 101, 136102.

(32) Hagiwara, S.; Hu, C.; Nishihara, S.; Otani, M. Bias-dependent diffusion of a H₂O
molecule on metal surfaces by the first-principles method under the grand-canonical ensemble. *Phys. Rev. Materials* **2021**, *5*, 065001.

(33) Kumagai, T. Direct observation and control of hydrogen-bond dynamics using low-temperature scanning tunneling microscopy. *Prog. Surf. Sci*. **2015**, *90*, 239–291.

(34) Mehlhorn, M.; Schnur, S.; Groß, A.; Morgenstern, K. Molecular-scale Imaging of Water Near Charged Surfaces. *ChemElectroChem* **2014**, *2*, 431–435.
Supplementary Information:
Rapid water diffusion at cryogenic temperatures through an
inchworm-like mechanism

Wei Fang,1,2 Kastur M. Meyer auf der Heide,3 Christopher
Zaum,4 Angelos Michaelides,5,1,* and Karina Morgenstern3,†

1 Thomas Young Centre, London Centre for Nanotechnology,
and Department of Physics and Astronomy,
University College London, London WC1E 6BT, UK
2 Laboratory of Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland
3 Ruhr-Universität Bochum, Lehrstuhl für physikalische Chemie I,
Universitätsstr. 150, D-44801 Bochum, Germany
4 Leibniz Universität Hannover, Institut für Festkörperphysik,
Appelstr. 2, D-30167 Hannover, Germany
5 Yusuf Hamied Department of Chemistry, University of Cambridge,
Lensfield Road, Cambridge CB2 1EW, UK
In the supplementary information we provide additional experimental and simulation results. The contents are organised in the following order:

- I. Oligomers imaged with scanning tunnelling microscopy (STM) at enhanced contrast
- II. Rotamers of the elongated water trimer imaged with STM
- III. Water trimer adsorption conformers predicted using density functional theory (DFT)
- IV. Transition between water trimer conformers
- V. Translational diffusion pathway of the water trimer
- VI. Characterization of hydrogen bonds in the water trimer during the transition from elongated to cyclic trimer structures
- VII. Harmonic zero-point energy (ZPE) corrections, finite size corrections, and surface relaxation effects on the water trimer diffusion barriers
- VIII. Functional dependence of the water trimer diffusion barriers
- IX. Quantum tunneling contributions to the inchworm diffusion mechanism at low temperature
- X. Water monomer and dimer diffusion on metal (111) surface
FIG. 1. Identification of trimers, 8.8 K, M: monomer, D: dimer, T: elongated trimer, Tc: circular trimer, STM images of same region of surface imaged by (a) conventional tip, 82 mV, 41 pA (b) modified tip, Laplace-filtered STM image, 82 mV, 35 pA.

The assignment of structures to trimers in the main manuscript is further corroborated by imaging them by a modified tip that is sharpened by an incidentally picked-up water molecule (Fig. 1). By this tip, the number of molecules in both, the elongated and circular protrusions is visualized, particularly well visible after a Laplace filtering (Fig. 1b). While monomers are still imaged as single protrusions (Fig. 1b, M), the images of the dimers (D) feature a sixfold symmetry by this tip, reflecting the six equivalent positions of the rotating upper molecule [1]. Note that this hexagonal structure is distinctly different from the hexagonally symmetric image of a hexamer by a metallic tip [2]. In particular, the distance between the protrusions differs. Here it is, at 0.45 nm, around only half the one of the hexamer in [2].

The objects of this study, the circular and the elongated trimers, consist indeed of three protrusions; one is brighter than the other two. The distances between the protrusions of the circular trimer (Tc in Fig. 1b) are, at 0.42, 0.44, and 0.46 nm, rather similar, but larger than the interatomic distance of Cu(111) of 0.255 nm. For the elongated trimer (Te in Fig. 1b), the two outer molecules lead to well-separated protrusions, while the inner molecule is rather visible as an extended increase in apparent height. Also in this case, the distance between the two outer protrusions, is, at (0.67 ± 0.01) nm, considerably larger than the expected $\sqrt{3}$ distance of the Cu(111) surface of 0.44 nm. Such image distortion is, however, typical for
flexible molecular tips [3–6]. Regardless of these distortions, the number of imaged molecules corroborates our assignment of the elongated and circular protrusions with brighter corners to the elongated and circular trimers, respectively.

S.II. POSSIBLE ROTAMERS AND ENANTIOMERS OF ASYMMETRIC ELONGATED TRIMER

FIG. 2. Different forms of two elongated trimers with schematics superimposed to scale on the right trimer and displayed next to the STM images enlarged by a factor of two. The circles mark the molecules with larger height above the surface according to calculation. The six-way cross marks the ⟨110⟩ directions of Cu(111) as determined from images with atomic resolution.

The surface symmetry of an FCC(111) surface facilitates six rotamers of each of the two enantiomers for the elongated AD trimer; there should thus exist twelve different forms. Indeed, twelve different forms are observable for one trimer in course of 8 hours during which its motion was recorded at 7 K (Fig. 2). The possible rotamers of the two enantiomers fit thereby perfectly to the STM images.

S.III. WATER TRIMER ADSORPTION GEOMETRIES ON Cu(111) PREDICTED BY DFT

The six most stable water trimer conformers found in our DFT calculations are shown in Fig. 3. Among them, the most stable conformer is the elongated trimer (Tₑ), and the relative energy of the other conformers with respect to Tₑ are given in Table I. Tₑ₋₂ has not
been observed in the experiment perhaps because it requires the water monomer to approach the donor water in the dimer, which is unlikely to happen as water dimers on the surface rapidly rotate about the donor water.

FIG. 3. Water trimer adsorption geometries found on Cu(111). $T_e$: elongated water trimer, $T_{e-2}$: form 2 of the elongated water trimer, $T_{e-s}$: elongated water trimer conformer with $C_s$ symmetry, $T_c$: cyclic water trimer, $T_{pc}$: pseudo-cyclic water trimer, $T_{tri}$: triangular water trimer.

| Geometry | Relative energy wrt $T_e$ (meV) | harmonic ZPE corrected (meV) |
|----------|---------------------------------|-----------------------------|
| $T_{e-2}$ | 10                              | 13                          |
| $T_{e-s}$ | 20                              | 9                           |
| $T_c$    | 82                              | 82                          |
| $T_{pc}$ | 31                              | 41                          |
| $T_{tri}$ | 96                              | -                           |

TABLE I. Relative energies of the water trimer conformers found with respect to the most stable conformer ($T_e$). The geometry of all the trimers are shown in Fig. 3. The harmonic zero point energy (ZPE) corrected values are also presented.
S.IV. SWITCHING BETWEEN DIFFERENT CONFORMERS OF THE WATER TRIMER

The water trimer can switch between different conformers on the surface.

- Switching between $T_e$ and $T_{e-2}$ can happen through “wagging” of the donor (d) water. DFT calculations show that this process has a potential energy barrier of 61 meV.

- Switching between $T_e$ and $T_{e-s}$ can happen via a donor-acceptor exchange mechanism as shown in Fig. 4. The water trimer can effectively diffuse on the surface via this process, similar to the water dimer waltz diffusion mechanism [1, 7]. However, this process has a relatively high energy barrier of 300 meV for the water trimer on Cu(111), making it unfavorable compared to the other diffusion mechanisms. This is because the donor-acceptor exchange barrier is already relatively high for the water dimer on this surface (186 meV [7]), and that the H-bond strength (which correlates positively to this barrier [7]) is stronger in the trimer than in the dimer (as indicated by the O-O distance, which is 2.75 Å for the dimer and 2.7 Å for the trimer).

- Switching between $T_e$ and $T_c$ via $T_{pc}$ has been extensively discussed in the main text.

- Switching between $T_{e-2}$ and $T_{e-s}$ via $T_{tri}$. Note that the trimer cannot effectively diffuse on the surface via this mechanism, because the d water does not change in the process.

FIG. 4. Geometry of the donor-acceptor exchange process of the elongated water trimer on Cu(111). The second geometry is the transition state.

S.V. TRANSLATIONAL DIFFUSION PATHWAY OF THE WATER TRIMER

The water trimer ($T_e$) translational diffusion pathway is shown in Fig. 5. In a step-wise manner, the d water molecule first moves to the bridge, then followed by the translation of
the entire water trimer water, similar to the water dimer translational diffusion mechanism [7, 8].

FIG. 5. Geometry of the donor-acceptor exchange process of the elongated water trimer on Cu(111).

S.VI. CHARACTERIZATION OF H-BONDS IN THE WATER TRIMER DURING THE TRANSITION FROM ELONGATED TO CYCLIC TRIMER

To understand the stability of T_{pc} and T_{c}, we show the O-O distance $d_{OO}$ and the H-bond bending angle change during the transition from T_{e} to T_{c} (Fig. 6). One can see that two H-bonds in T_{e} bend and become less stable during the process, while a third H-bond forms and stabilizes the cluster.

FIG. 6. Change of the O-O distance and bending angles during the transition from T_{e} to T_{c} via T_{pc}. The H-bond length is characterized by the O-O distance $d_{OO}$ and the bending angle is defined as $\alpha = \angle O_{D} - O_{A} - H_{D}$, where $O_{D}$ ($O_{A}$) is the O of the donor (acceptor) water, and $H_{D}$ is the H on the donor water that forms an acute angle with the $O_{D}-O_{A}$ direction. The light grey points are the other geometries along the NEB path. The solid black line marks the H-bond definition from Ref. 9.
We have also considered other geometrical H-bond characterization methods used for water. We find that 3 other definitions [10–12] also found that there are two H-bonds in $T_{pc}$ and three H-bonds in $T_c$, in agreement with the definition from Ref. 9. We note that there is a definition that has a stricter limit on the H-bond bending angle [13] predicts that only one H-bond in $T_{pc}$ qualifies as a H-bond and that $T_c$ has no H-bonds.

S.VII. CORRECTIONS TO THE POTENTIAL ENERGY BARRIER

First we consider ZPE effects in the harmonic approximation. This correction is computed by taking the difference of the harmonic ZPE of the transition state and the reactant (Table II). We note that anharmonic ZPE effects could also be important, but due to the extremely low temperature in the experiment, such effects are very difficult to simulate.

Then we corrected for the finite size effects. We computed the energy barriers with the unit cell extended to a $10\times8$ supercell (with a $3\times3\times1$ k-point mesh), with the geometries fixed at the optimized geometries obtained in a $5\times4$ unit cell. The corrections are obtained by taking the difference between the barriers in the large and small unit cell.

Next we considered the effects of flexible surface vs frozen surface. We reoptimized the adsorption geometries and transition state geometries with the first layer of the substrate flexible in the optimization. The surface relaxation correction is defined as the barrier difference computed with a frozen surface and a flexible surface.

Finally, we have also performed calculations with applied electric fields of $\pm 0.05$ eV/Å. The geometries of the $T_e$ and $T_c$ have been re-optimized with the presence of the electric field. We found that the barrier for the inchworm diffusion mechanism changes from 82 meV to 89 meV (74 meV) for an electric field of $+0.05$ eV/Å ($-0.05$ eV/Å).

S.VIII. EXAMINATION OF DFT FUNCTIONAL DEPENDENCE

Next we investigate the impact of the choice of DFT functional on the results. We tested 3 other functionals (including a meta-GGA functional) that accounts for the van der Waals interactions: optB86b-vdW [15], PBE-D3 [16, 17], and TPSS-D3 [17, 18]. The results are compared in Table III. Although the choice of DFT functional has a quantitative impact on the barriers (suggesting that it is difficult to obtain quantitatively accurate results for this
Specifically, the following processes are considered: The inchworm diffusion process shown in Fig. 4 of the main text; A simple trimer translation process; Rotation of the $T_e$ trimer; Transition from the $T_e$ trimer to the $T_{pc}$ trimer. The harmonic ZPE correction, and finite size correction (the difference between the barrier computed in a large $10 \times 8$ unit cell and in a $5 \times 4$ unit cell), surface relaxation correction (the difference between the barrier computed with the first layer of substrate atoms fixed and optimized). Barriers are reported using the “standard” computational set-up (as described in the methods section of the main text) and “corrected” to take into account all the corrections above.

| DFT functional       | Inchworm $T_e$ to $T_{pc}$ | $T_e$ translation | $T_e$ to $T_{pc}$ |
|----------------------|-----------------------------|------------------|-------------------|
| optB88-vdW [14]      | 82                          | 118              | 35                |
| optB86b-vdW [15]     | 94                          | 126              | 10                |
| PBE-D3 [16, 17]      | 129                         | 134              | 10                |
| TPSS-D3 [17, 18]     | 124                         | 134              | 8                 |

TABLE III. DFT functional dependence of the potential energy barriers of the following processes: inchworm diffusion, transition to $T_{pc}$, and trimer translation. The functional dependence of the energy difference between $T_{e2}$ and $T_e$ are also given. All units are in meV. The geometries are re-optimized for every functional.
Finally we consider quantum tunneling effects in the inchworm diffusion mechanism at low temperatures. As shown in the main text, the minimal energy pathway for this process features a so-called broad-top barrier. This is also supported by the fact that vibrational analysis of $T_c$ shows no imaginary mode. Upon estimating the crossover temperature from classical over-the-barrier hopping to quantum tunneling (using the definition designed for broad-top barriers [19]), we obtain a value of 16 K. Therefore we expect tunneling to play a role below 16 K. To obtain an idea of the tunneling pathway, we preformed ring-polymer instanton [20–22] optimizations at a temperature below the crossover temperature (10 K). Due to the complexity of the pathway and the exceedingly low temperature, instanton theory calculations become extremely challenging and we have so far only obtained preliminary insights (Fig. 7). Nevertheless, the results of the instanton calculations indicate that there is some heavy atom tunneling (of the oxygen atoms) and that this likely enhances water trimer diffusion at low temperatures.

![Image of instanton at 10 K with 34 ring-polymer beads, with total force optimized to below 0.8 eV/Å.](image)

FIG. 7. Geometry of the instanton at 10 K with 34 ring-polymer beads, with total force optimized to below 0.8 eV/Å.

To estimate the tunneling contributions to the trimer diffusion rate, we resort to using the minimal energy pathway as a 1 dimensional model for this process and the WKB approximation [23], which is more crude and approximate but feasible for this system. We predict that tunneling increases the rate by 20 fold at 15 K, and by 8 orders of magnitude at 10 K. This means that tunneling (of the heavy oxygen atoms) does indeed contribute to increasing the diffusivity of the water trimer at low temperatures. However, tunneling alone is not enough to bridge the gap between experimental observation and theory as the rate for the inchworm diffusion is still too low to be observed at these temperatures ($< 1E-10$ s$^{-1}$) even after accounting for tunneling effects. A full study of the importance of quantum
nuclear effects is beyond the scope of the current article.

S.X. WATER MONOMER AND DIMER DIFFUSION ON METAL (111) SURFACE

FIG. 8. Top view of the water monomer translation, dimer translation, and dimer donor-acceptor (DA) exchange diffusion pathways on transition metal (111) surfaces.
[1] V. A. Ranea, A. Michaelides, R. Ramirez, P. L. de Andres, J. A. Verges, and D. A. King, “Water dimer diffusion on Pd(111) assisted by an h-bond donor-acceptor tunneling exchange,” Phys. Rev. Lett. 92, 136104 (2004).

[2] A. Michaelides and K. Morgenstern, “Ice nanoclusters at hydrophobic metal surfaces,” Nat. Mater. 6, 597–601 (2007).

[3] P. Hapala, G. Kichin, C. Wagner, F.S. Tautz, R. Temirov, and P. Jelinek, “mechanism of high-resolution stm/afm imaging with functionalized tips,” Phys. Rev. B 90, 085421 (2014).

[4] N. Moll, B. Schuler, S. Kawai, F. Xu, L. Peng, A. Orita, J. Otera, A. Curioni, M. Neu, J. Repp, G. Meyer, and L. Gross, “Image distortions of a partially fluorinated hydrocarbon molecule in atomic force microscopy with carbon monoxide terminated tips,” Nano Lett. 14, 6127–6131 (2014).

[5] M. Emmrich, F. Huber, F. Pielmeier, J. Welker, T. Hofmann, M. Schneiderbauer, D. Meuer, S. Polesya, S. Mankovsky, D. Ködderitzsch, H. Ebert, and F.J. Giessibl, “Subatomic resolution force microscopy reveals internal structure and adsorption sites of small iron clusters,” Science 348, 308–311 (2015).

[6] C.-S. Guo, X. Xin, M.A. Van Hove, X. Ren, and Y. Zhao, “Origin of the contrast interpreted as intermolecular and intramolecular bonds in atomic force microscopy images,” J. Phys. Chem. 119, 14195–14200 (2015).

[7] Wei Fang, Ji Chen, Philipp Pedevilla, Xin-Zheng Li, Jeremy O Richardson, and Angelos Michaelides, “Origins of fast diffusion of water dimers on surfaces,” Nat. Comm. 11, 1689 (2020).

[8] C. Bertram, K. Morgenstern, P. Pedevilla, and A. Michaelides, “Anomalously low barrier for water dimer diffusion on Cu(111),” Nano Lett. 19, 3049–3056 (2019).

[9] A. Luzar and D. Chandler, “Hydrogen-bond kinetics in liquid water,” Nature 379, 55–57 (1996).

[10] Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. Å. NÄslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, L. G. M. Pettersson, and A. Nilsson, “The
structure of the first coordination shell in liquid water," Science 304, 995–999 (2004).

[11] Teodora Todorova, Ari P. Seitsonen, J Åkerfalk Hutter, I-Feng W. Kuo, and Christopher J. Mundy, “Molecular dynamics simulation of liquid water: Hybrid density functionals,” J. Phys. Chem. B 110, 3685–3691 (2006).

[12] Alenka Luzar, “Resolving the hydrogen bond dynamics conundrum,” J. Chem. Phys. 113, 10663–10675 (2000).

[13] I-Feng W. Kuo and Christopher J. Mundy, “An ab initio molecular dynamics study of the aqueous liquid-vapor interface,” Science 303, 658–660 (2004).

[14] J. Klimeš, David R Bowler, and Angelos Michaelides, “Chemical accuracy for the van der Waals density functional,” J. Phys. Condens. Matter 22, 022201–1–5 (2010).

[15] J. Klimeš, David R. Bowler, and Angelos Michaelides, “Van der Waals density functionals applied to solids,” Phys. Rev. B 83, 195131 (2011).

[16] John P. Perdew, Kieron Burke, and Matthias Ernzerhof, “Generalized gradient approximation made simple,” Phys. Rev. Lett. 77, 3865–3868 (1996).

[17] Stefan Grimme, Stephan Ehrlich, and Lars Goerigk, “Effect of the damping function in dispersion corrected density functional theory,” J. Comput. Chem. 32, 1456–1465 (2011).

[18] Jianmin Tao, John P. Perdew, Viktor N. Staroverov, and Gustavo E. Scuseria, “Climbing the density functional ladder: Nonempirical meta–generalized gradient approximation designed for molecules and solids,” Phys. Rev. Lett. 91, 146401 (2003).

[19] Wei Fang, Jeremy O. Richardson, Ji Chen, Xin-Zheng Li, and Angelos Michaelides, “Simultaneous deep tunneling and classical hopping for hydrogen diffusion on metals,” Phys. Rev. Lett. 119, 126001 (2017).

[20] Stefan Andersson, Gunnar Nyman, Andri Arnaldsson, Uwe Manthe, and Hannes Jónsson, “Comparison of quantum dynamics and quantum transition state theory estimates of the H + CH₄ reaction rate,” J. Phys. Chem. A 113, 4468–4478 (2009).

[21] Jeremy O. Richardson, “Ring-polymer instanton theory,” Int. Rev. Phys. Chem. 37, 171–216 (2018).

[22] Johannes Kästner, “Theory and simulation of atom tunneling in chemical reactions,” WIREs: Comput. Mol. Sci. 4, 158–168 (2014).

[23] R. P. Bell, Tunnel Effect in Chemistry (Chapman & Hall, 1980).
Graphical TOC Entry