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Structure and energetics of hydrogen-bonded networks of methanol on close packed transition metal surfaces

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Methanol is a versatile chemical feedstock, fuel source, and energy storage material. Many reactions involving methanol are catalyzed by transition metal surfaces, on which hydrogen-bonded methanol overlayers form. As with water, the structure of these overlayers is expected to depend on a delicate balance of hydrogen bonding and adsorbate-substrate bonding. In contrast to water, however, relatively little is known about the structures methanol overlayers form and how these vary from one substrate to another. To address this issue, herein we analyze the hydrogen bonded networks that methanol forms as a function of coverage on three catalytically important surfaces, Au(111), Cu(111), and Pt(111), using a combination of scanning tunneling microscopy and density functional theory. We investigate the effect of intermolecular interactions, surface coverage, and adsorption energies on molecular assembly and compare the results to more widely studied water networks on the same surfaces. Two main factors are shown to direct the structure of methanol on the surfaces studied: the surface coverage and the competition between the methanol-methanol and methanol-surface interactions. Additionally, we report a new chiral form of buckled hexamer formed by surface bound methanol that maximizes the interactions between methanol monomers by sacrificing interactions with the surface. These results serve as a direct comparison of interaction strength, assembly, and chirality of methanol networks on Au(111), Cu(111), and Pt(111) which are catalytically relevant for methanol oxidation, steam reforming, and direct methanol fuel cells. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4882863]

I. INTRODUCTION

Methanol and water are ubiquitous molecules in chemistry, and the study of their interaction with surfaces is essential for a full understanding of their reactivity. Elucidating the binding and assembly of these molecules at surfaces has relevance to a number of fields, such as electrochemistry, environmental chemistry, fluid transport, and heterogeneous catalysis.1, 4 It is also a source of general insight into molecular self-assembly at interfaces and the fundamental nature of interfacial hydrogen bonds.

Hydrogen-bonded networks of water on surfaces have been well studied,3–21 and scanning tunneling microscopy (STM) coupled with density functional theory (DFT) has been particularly useful in determining the structure and stability of the assemblies.22–26 Previous experimental work in ultra-high vacuum (UHV) conditions and at cryogenic temperatures showed that water forms networks of various sizes, from dimers to oligomers, on metal surfaces.19 The water hexamer is a particularly important structure, as it is considered the smallest building block of ice.27 Water hexamers consist of six water monomers arranged in a ring where each monomer accepts and donates a hydrogen bond. This ring can be arranged in either a buckled or a planar manner.5 Each monomer in the planar arrangement binds at the same height above the surface, while the monomers in the buckled hexamer are arranged at two discrete heights reminiscent of the buckling found in the basal plane of ice. Theoretical predictions of relative water hexamer stability on specific surfaces have been reported; however, the experimental images do not always match the predicted lowest-energy structure. While the buckled arrangement is predicted to be more stable on Cu(111), hexamers on this surface appear planar in STM images.19 Limitations with STM imaging may produce this apparent contradiction. It has been proposed that the electric field from the STM tip reorients the water molecules into a planar arrangement during the scan or the planar hexamer image is a dynamic average of many structures over the time-scale of the STM scan.9,19, 28 The buckled hexamer of water has been imaged with STM on a hexagonal boron nitride nanomesh on Rh(111),29 where it is postulated that every second water monomer is bound weakly to an underlying nitrogen atom through a hydrogen bond.30 Planar water hexamers have been investigated on Ru(0001) by low-energy electron diffraction, reflection adsorption IR spectroscopy and DFT, where it was found that Ru-water...
interactions dominate over hydrogen bonds resulting in planar hexamers. \(^{31}\)

In contrast to the abundant work regarding adsorbed water, the adsorption of intact methanol has only recently begun to be investigated. \(^{32–35}\) Under UHV conditions, methanol molecules adsorb on metal surfaces through the oxygen atom and can form two hydrogen bonds to other methanols via the hydroxyl group. The resulting hydrogen-bonding between monomers drives the assembly of chains and hexamers. \(^{33–35}\) At near monolayer coverages on Au(111) and Cu(111), methanol forms chains, which consist of hydrogen-bonded molecules that are linearly arranged in the \(\sqrt{3}\) directions, resulting in ordered domains across the whole surface. At lower coverages methanol forms cyclic hexamers reminiscent of water hexamers. In contrast to water, the chiral footprint of the adsorbed methanol hexamers is apparent in STM imaging. \(^{33}\) Chiral planar methanol hexamers have been observed on both Au(111) and Cu(111), while buckled surface-bound methanol hexamers have not been reported. \(^{33,34}\)

The relative stabilities of the various hydrogen-bonded overlayers are dictated by the interplay of attractive molecule-molecule interactions, binding to the surface and surface coverage induced crowding/repulsion. It has been established for water that the formation of either buckled or planar hexamers is directed by competition between molecule-molecule and molecule-surface interactions that maximizes the binding energy per monomer. \(^{5}\) The buckled hexamer produces a reduced interaction with the surface for half of the molecules in favor of increased interactions between molecules, while the planar structures optimize the interaction between all molecules and the surface while sacrificing the ideal molecule-molecule hydrogen bonding. \(^{19}\) The corresponding investigation for buckled and planar methanol hexamers has not been performed. The lack of work in this area is because to date buckled methanol hexamers have not been observed on surfaces. Previous work on methanol on Au(111) and Cu(111) has investigated hydrogen bonded chains and planar hexamers and showed that the population distribution is dependent on surface coverage; the chain networks pack methanol monomers more efficiently at higher coverages, while hexamers are more stable at low coverages. These networks relate to the structures of solid and liquid methanol, in which the solid phase has been shown to consist of very long hydrogen-bonded chains of methanol \(^{36}\) and the liquid phase is proposed to be the dominated by hexamers. \(^{37}\) Methanol hydrogen bonded network formation on more reactive surfaces, such as Pt(111), has not been investigated.

To investigate the interplay of binding energy and surface coverage on network formation at the surface of close-packed transition metals, we have been engaged in joint STM and DFT studies of methanol adsorbed at various coverages on various transition metal surfaces. Here, we report results for methanol on Au(111), Cu(111), and Pt(111) using a functional that accounts for van der Waals (vdW) interactions. These metals are important in catalysts for the oxidation and steam reforming of methanol, in direct methanol fuel cells, and as templates for self-assembly. \(^{38–41}\) Additionally, we provide new theoretical results for water hexamers, which to the best of our knowledge, are the first vdW-inclusive calculations of water hexamers adsorbed on close-packed transition metal surfaces, and we compare these results to previous experimental results for water and methanol hexamers. We report a new chiral buckled methanol hexamer on Cu(111) and Pt(111), which exists alongside the planar hexamers allowing us to study the STM tip induced inter-conversion of these structures. Our analysis presents insight into the interaction, assembly, energetics, and chirality of methanol as a function of coverage at the surface of catalytically relevant metals.

II. EXPERIMENTAL

All experiments were performed with Omicron Nano-Technology variable-temperature (VT) or low-temperature (LT) ultra-high vacuum scanning tunneling microscopes. Data were recorded with Veeco and Omicon etched W tips, as well as mechanically cut 85:15 Pt-Ir and chemically etched Ni tips. The Ni tips were electro-chemically etched using a 2 M KCl solution. \(^{42}\) All tips were washed in methanol before being introduced to the UHV system. Once in vacuum the tips were conditioned by applying voltage pulses while scanning a clean surface. For methanol deposition 99.8+-% ultrapure HPLC grade methanol from Alfa Aesar was used, with further purification via freeze–pump–thaw cycles. The Au(111), Cu(111), and Pt(111) crystals were prepared with standard Ar\(^+\) sputter (1.5 keV, 12 \(\mu\)A) and anneal (1000 K) cycles. The base pressure in the VT-STM setup, before cooling the STM stage with liquid helium via a flow cryostat, was \(<10^{-10}\) mbar. Pre-cooling the STM before the sample was loaded decreased the pressure in the STM chamber \(<5 \times 10^{-11}\) mbar. Annealing experiments were performed \textit{in situ} in the VT-STM chamber with the STM tip held several mm away from the surface. For LT experiments, the crystal was transferred in less than 5 min in vacuum \(<10^{-10}\) mbar to the pre-cooled STM stage after cleaning. The sample cooled from room temperature to 5 K in \(\sim\)40 min. Methanol was deposited directly onto the 30 K (VT) or 5 K (LT) surface via a collimated molecular doser. Precise heating to progressively higher temperatures induced partial desorption, rearrangement, and hence structural changes in the methanol overlayer. The samples were then cooled to cryogenic temperatures for imaging. The selection of heating temperatures was guided by temperature programmed desorption experiments on Au(111), Cu(111), and Pt(111), which quantify the desorption temperatures of multilayer and monolayers of methanol from each surface. \(^{33–45}\) In all of the STM scanning conditions, the voltage refers to the sample bias. Typical STM gap conditions for imaging methanol were between \(\pm 1.0\) V and 2–10 pA.

III. THEORETICAL METHODS

DFT calculations within the periodic supercell approach as implemented in the Vienna \textit{ab initio} simulation package (VASP) were performed. \(^{46}\) The optB88-vdW functional \(^{37}\) was used throughout. This is a modified version of the non-local vdW-density functional of Dion \textit{et al.} \(^{38}\) which has been implemented in VASP by Klimes \textit{et al.} \(^{49}\) and which shows
improved accuracy for a wide variety of systems.\textsuperscript{50-53} The inner electrons were replaced by projector augmented wave (PAW) potentials\textsuperscript{54} whereas the valence states were expanded in plane-waves with a cut-off energy of 500 eV. Adsorption calculations of monomers and hexamers of both water and methanol were carried out considering (6 x 6) metal slabs cut along the (111) direction consisting of 3 atomic layers thickness and separated by 18 Å of vacuum. Tests on a smaller (5 x 5) unit cell show that the adsorption energy of MeOH hexamers on Pt(111) is only 10 meV less than on a (6 x 6) unit cell; this suggests that a (6 x 6) unit cell is sufficiently large to avoid spurious lateral adsorbate-adsorbate interactions.

In the case of adsorbed chains, a (7√3 x √3) unit cell was used. The metal atoms in the bottom layer were fixed to the bulk optB88-vdW optimal positions (a_{Cu} = 3.623 Å, a_{Au} = 4.158 Å, and a_{Pt} = 3.978 Å), whereas all other atoms (in the substrate and adsorbates) were allowed to relax. A relaxed but otherwise unreconstructed (111) surface was used for all substrates, including Au. We used a Monkhorst-Pack \textbf{k}-points grid of 2 x 2 x 1 and 1 x 7 x 1 for the (6 x 6) and (7√3 x √3) unit cells, respectively. A dipole correction along the direction perpendicular to the metal surface was applied, and geometry optimizations were performed with a residual force threshold of 0.025 eV/Å. STM images were simulated using the Tersoff-Hamann approach,\textsuperscript{55} with a voltage of -100 mV and at a height of ~6 Å above the metal surface.

Adsorption energies per molecule were computed as follows:

\[ E_{ads} = \frac{E[m/M] - E[M] - nE[m]}{n}, \]

where \( E[m/M] \) is the total energy of the adsorbed \( n \) methanol or water adstructure, \( E[M] \) is the total energy of the relaxed bare metal slab, and \( E[m] \) is the total energy of an isolated gas phase methanol or water molecule. Favorable (exothermic) adsorption corresponds, therefore, to negative adsorption energy.

In order to analyze the role of molecule-molecule and molecule-metal interactions on adsorption, we have decomposed \( E_{ads} \) into these two contributions. We define the molecule-molecule contribution (essentially H-bonding interactions within the adsorbed molecules) to \( E_{ads} \) as

\[ E^{MM}_{ads} = \frac{nE[\hat{m}] - nE[m]}{n}, \]

where \( E[\hat{m}] \) is the total energy of the methanol or water adstructure in the absence of the metal substrate, but with all the atoms fixed in the geometries they adopt in the adsorption structure. The methanol-metal or water-metal contribution, \( E^{MM}_{ads} \), is simply taken as the difference between \( E_{ads} \) and \( E^{MM}_{ads} \). This particular energy decomposition scheme follows the widely adopted approach used to aid understanding of hydrogen bonded water adlayers on metal surfaces.\textsuperscript{56}

\section{IV. RESULTS AND DISCUSSION}

In the following we report results from STM and DFT for methanol on the (111) surfaces of Au, Cu, and Pt. First, we present results at near monolayer coverage (Sec. IV A), then submonolayer (Sec. IV B), and then low coverages (Sec. IV C). This allows us to establish a qualitative “phase diagram” for adsorbed methanol on the three surfaces considered. At low coverage we also discuss results from additional STM measurements in which interconversions of various structures on Cu(111) were performed, including interconversions of the novel buckled chiral hexamer we report here for the first time. We follow these results in Section V with a DFT-based analysis of the relative importance of hydrogen bonding and adsorbate-substrate bonding in determining the methanol adsorption structures formed, and compare this to what we find for water adsorption on the same surfaces.

\subsection{A. Near monolayer coverage of methanol}

Initial experiments focused on monolayer coverages of methanol on Au(111), Cu(111), and Pt(111). Between zero and a complete monolayer, a number of methanol structures are observed, which are outlined in Fig. 1. Monolayers and submonolayer amounts of methanol were prepared in the following manner. Multilayers of methanol were deposited onto the sample, followed by heating to the temperature indicated in the respective figure (Figs. 2-4). This heating step desorbed the excess methanol leaving the desired surface coverage. The samples were subsequently cooled to 30 K before imaging. At near monolayer coverages methanol forms long chains composed of many hundreds of molecules, in which each monomer is hydrogen bonded to two neighbors (Fig. 1 A1). Overall, the methanol chains are observed to run along the √3-axis of the underlying surface (Fig. 2), with Au(111) being a special case as the local herringbone reconstruction

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figure1.png}
  \caption{Rows 1 and 2 show top and side-views of DFT optimized methanol structures on a close-packed (111) metal surface. Row 3 shows the corresponding simulated STM images of these structures on the Cu(111) surface (tip height \( \approx 6 \) Å, \( V = -100 \) mV). The yellow hexagonal mesh in the third row indicates the underlying Cu lattice. Row 4 shows actual STM data of methanol on Cu(111) acquired at 5 K (–100 mV 100 pA. Scale bar = 1 nm). Column A reports data for an extended chain structure, B for a planar hexamer, and C and D for two types of buckled hexamer. The buckled hexamer C was not observed experimentally by STM and so panel C4 is blank.}
\end{figure}
leads to a compression of two of the three $\sqrt{3}$ axes of that surface (0.48 nm versus 0.50 nm). On Au(111) the methanol chains orient along these compressed axes in order to maximize the molecule-molecule interactions, and form domains comprised of pairs of chains with a unit cell of 11 $\times$ $\sqrt{3}$. On Cu(111), methanol also forms double chains, where a staggering in the sets of chains results in Peierls-like distortion and a unit cell of 6 $\times$ $\sqrt{3}$. While short chains are observed on Pt(111), large-scale ordering is not evident.

Turning now to DFT, our calculations predict that the methanol chains which form at high coverages have a similar structure on the three metals studied (Fig. 1(a)). Within the chains, individual methanol monomers bind at atop sites of the underlying atomic lattice through one of the lone pair of electrons on the oxygen atom and are hydrogen bonded to two neighbors in a zigzag fashion, resulting in a chain running in a $\sqrt{3}$ direction of the substrate lattice. Our DFT calculations predict that the adsorption energy per methanol in the chain structure is $-726$ meV on Au(111), $-745$ meV on Cu(111), and $-844$ meV on Pt(111) (see also Table 1). These adsorption energies are $\sim 100–200$ meV/methanol larger than the adsorption energies of the isolated methanol monomers, indicating that the chains are stable with respect to breaking up into individual adsorbed methanol molecules. The O-O spacing may be expected to follow the metal-metal nearest neighbor distances, which in our DFT calculations are: 0.295 nm for Au, 0.259 nm for Cu, and 0.281 nm for Pt. However, our DFT calculations show a compression of the O-O spacing of the linear chains on Au(111) (0.277 nm) and Pt(111) (0.271–0.274 nm), while the spacing is slightly expanded on Cu(111) (0.261 nm). The O-O-O angle on Pt(111) (126.5°) is likewise between that of Au(111) (132.5°) and Cu(111) (113.9°), with the larger angle producing a “straighter chain.”

B. Submonolayer coverages of methanol

Further experiments investigated submonolayer coverages of methanol. The samples were prepared by annealing methanol multilayers to temperatures corresponding to partial desorption of the monolayer and then cooled to 30 K for imaging (Fig. 3). Desorption was evident by a reduction in surface coverage and the increased spacing between methanol chains. On Au(111), meandering closed loops comprised of chains running predominately in the compressed $\sqrt{3}$ directions are observed. On Cu(111), double chains are formed with a unit cell of $7\sqrt{3}$ $\times$ $\sqrt{3}$. The linear nature of the chains on both Au(111) and Cu(111) is evident. In contrast, methanol on Pt(111) displays a more disordered network, where both isolated hexamers and short winding chains are present (Fig. 3(c)). Repulsive interactions between the methanol structures are evident on each surface, as the size of the gaps between chains increases with decreasing coverage.

The structure of the methanol networks depends on the substrate and there is a notable lack of long range ordering on Pt(111) compared to Au(111) and Cu(111). A tempting explanation for this is dehydrogenation of methanol by the reactive Pt(111) surface, which would lead to an absence of available O-H groups and no opportunity for hydrogen bonding and hence a lack of driving force for network formation. However, it has previously been shown that methanol adsorbs and desorbs reversibly from the terraces of Pt(111), with only trace amounts of methanol dehydrogenating at step edges. Additionally, the short chain and hexamer structures of methanol we observe on Pt(111) are consistent with both the hydrogen-bonded structures predicted by DFT, and those observed on Au(111) and Cu(111). These results demonstrate that dehydration of the methanol by a reactive Pt(111) surface is not the cause of the lack of long range ordered networks. Instead, we propose two potential mechanisms that contribute to this effect: the lower diffusion rate of methanol...
on Pt(111) and the lower total relative energy of the chains compared to the monomer. The barrier to diffusion of methanol on Pt(111) is expected to be higher than that on Au(111) or Cu(111) since methanol monomers bind more strongly to Pt(111) (−733 meV per methanol) than to Au(111) (−436 meV per methanol) or Cu(111) (−554 meV per methanol). This would result in a reduced diffusion rate of methanol on Pt(111) which hinders the ability of the system to sample all possible microstates and obtain the global lowest-energy structure. Additionally, the driving force to form chains is significantly lower on Pt(111) than either Au(111) or Cu(111). DFT calculations show that upon forming adsorbed chains methanol monomers are stabilized by 290, 190, and 110 meV per methanol on Au(111), Cu(111), and Pt(111), respectively. (This stabilization energy is simply the difference in adsorption energy between methanol adsorbed as monomers and adsorbed in chains.) The lower stabilizing effect on Pt(111) results in a decreased driving force to form long range ordered structures. This, along with the slower methanol diffusion expected on Pt, most likely explains the lack of long range ordering of hydrogen-bonded methanol chains on Pt(111).

### C. Low coverage methanol: Hexamers and short chains and STM induced interconversions

In the next set of experiments, the samples were heated to a temperature required to induce near total desorption of methanol then cooled to 30 or 5 K prior to imaging (Fig. 4). The methanol remaining on the surface formed hydrogen-bonded hexamers that were highly dispersed on the surface as seen in Fig. 4. The high degree of dispersion indicates a repulsive interaction between the hexamers. As we discuss in more detail below, the hexamers consist of six methanol monomers arranged in a cyclic manner, in which each monomer donates and accepts one hydrogen bond. The hexamer geometry allows each methanol molecule within the cluster to bind at atop positions of the underlying substrate. The hydrogen-bonded network has either a counterclockwise or a clockwise rotation, resulting in two surface-bound enantiomers of the hexamers. Planar hexamers are observed on Au(111), Cu(111), and Pt(111), and a second form is observed simultaneously on Cu(111) and Pt(111). The STM image of this second form resembles the buckled form of water predicted by DFT and observed on the hexagonal boron nitride nanomesh on Rh(111).29

Samples with coexisting planar and buckled methanol hexamers were observed on Cu(111) and Pt(111) and offered a unique opportunity to interrogate their structure and interconversion which has been impossible for water to date. On Cu(111), buckled and planar hexamers and short chains were prepared by adsorption of a small amount (0.2 Langmuir) of methanol on a clean Cu(111) surface at 5 K, followed by annealing to 20 K and cooling to 5 K (Fig. 5). On Pt(111), they were prepared by dosing multilayers of methanol, heating to 200 K, and cooling to 30 K (Fig. 4(c) and inset of same). Isolated methanol hexamers are observed on Pt(111) (Fig. 4(c)) alongside chains, and separation between the two features indicates repulsive interactions between them.

By combining our STM measurements with DFT calculations we have been able to determine the structures of the various hexamers. The DFT calculations were performed on a number of hexamer structures including buckled and planar forms. The most stable structures resulting from these calculations are shown in Fig. 1. The previously discussed planar structure (Fig. 1(b)) and one of the buckled hexamer models (Fig. 1(d)) produce simulated STM images that are consistent with the experimental data. One of the buckled hexamers (Fig. 1(c)) was simulated by DFT but not observed experimentally. In the planar hexamer, the methyl groups are arranged coplanar to the surface. Each methanol binds to an atop site of the substrate and the methanol-methanol hydrogen bond distance between neighboring molecules is equivalent. The structure of both types of buckled hexamers differs from the planar hexamer in a number of ways. First, in the buckled hexamers there are two alternating types of methanol molecules, arranged so that their methyl groups are either coplanar or perpendicular to the surface. The coplanar methanols are ~0.7–0.9 Å closer to the surface than the methanols that have the methyl groups directed away from the surface. Second, in the buckled hexamers binding to the surface is principally through the oxygen atoms of the three lower methanol molecules, whereas in the planar hexamer binding occurs through all six methanols. The third key

### TABLE I. Adsorption energies (in meV/molecule) of methanol and water hexamers and extended chains on Au(111), Cu(111), and Pt(111). The molecule-molecule (H-bonding, $E_{\text{HB}}$) and molecule-metal ($E_{\text{MM}}$) contributions to the total adsorption energy ($E_{\text{ads}}$) are also provided. See the text for precise definitions of each of these terms.

<table>
<thead>
<tr>
<th></th>
<th>Au(111)</th>
<th>Cu(111)</th>
<th>Pt(111)</th>
</tr>
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<tr>
<td></td>
<td>$E_{\text{ads}}$</td>
<td>$E_{\text{HB}}$</td>
<td>$E_{\text{MM}}$</td>
</tr>
<tr>
<td>Methanol</td>
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</tr>
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<td>−436</td>
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<tr>
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<td>−362</td>
<td>−364</td>
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<tr>
<td>Planar hexamer</td>
<td>−726</td>
<td>−368</td>
<td>−358</td>
</tr>
<tr>
<td>Buckled hexamer</td>
<td>−657</td>
<td>−388</td>
<td>−269</td>
</tr>
<tr>
<td>Buckled hexamer</td>
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<td>−383</td>
<td>−255</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monomer</td>
<td>−276</td>
<td>0</td>
<td>−276</td>
</tr>
<tr>
<td>Planar hexamer</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Buckled hexamer</td>
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<td>−214</td>
</tr>
<tr>
<td>Extended chain</td>
<td>−541</td>
<td>−307</td>
<td>−234</td>
</tr>
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difference is that in the buckled hexamers the methanol-methanol separations within the hexamer (measured, e.g., through the O-O separation between neighboring methanols) are not equivalent and alternate around the ring. As we discuss below the extent of the alteration in O-O distances varies from one substrate to the next from as little as 0.05 Å on Au to 0.18 Å on Pt. A similar alteration in O-O distances has been reported before for buckled water hexamers. Comparing the two types of buckled hexamers, buckled hexamer C (Fig. 1(c)) has each methanol molecule close to an atop site (i.e., similar sites to the planar hexamer), whereas in the second buckled hexamer (Fig. 1(d)) the methanols are close to bridge sites. As a result the center of mass of buckled hexamer C is located above an atop site, whereas for hexamer D it is above a threefold hollow site. We think this difference in binding position on the surface is relevant to why only one type of buckled hexamer is observed experimentally, as we discuss below.

The adsorption energies of the various hexamers on each metal surface are summarized in Table I. Binding methanol monomers together in a hexamer stabilizes the monomers and results in an increase in the adsorption energy (compare $E_{ads}$ of monomers and hexamers in Table I). On all surfaces the planar hexamers are more stable than the buckled hexamers by ~60–90 meV/methanol. STM imaging supports this conclusion, as we observe that the planar hexamers remain on the surface after all other structures have desorbed (Fig. 4). In order to rationalize the greater stability of the planar configurations, we decomposed the total adsorption energy into hydrogen bonding between methanol molecules ($E_{HB}^{mol}$) and the binding of individual methanol molecules to the metal surface ($E_{ads}^{mM}$) as given by Eq. (2). This reveals that the planar hexamers offer the best trade-off between the methanol-methanol and methanol-metal interactions, leading to the strongest overall binding. While the buckled hexamer results in an increased methanol-methanol component compared to planar hexamers, the decrease in the methanol-metal interaction is more significant, leading to an overall decrease in stability. On Pt(111), the molecule-metal contribution dominates the binding of both the planar and buckled hexamers, which is in line with the behavior expected of more reactive surfaces. Interestingly, our DFT calculations indicate that unlike the O-O spacings of the chain, the O-O spacing of the planar hexamers is almost identical regardless of the metal substrate: 0.265 nm on Au(111), 0.265 nm on Cu(111), and 0.268 on Pt(111). In our DFT calculations the corresponding metal-metal nearest neighbor distances are: 0.295 nm for Au, 0.259 nm for Cu, and 0.281 nm for Pt. The fact that the H-bond lengths remain relatively unaltered when changing the substrate suggests that methanol-metal interactions are a weaker function of total energy than the methanol-methanol interactions when balancing these two contributions to the overall stability of the cluster.

Each lobe of the planar hexamers appears identically in STM and DFT simulated images resulting in $C_g$ symmetry. For the buckled hexamers, the relative arrangement of perpendicular and parallel methyl groups image as brighter and darker lobes, respectively, and give rise to the appearance of two interlocking triangles. The resulting buckled hexamers exhibit $C_3$ symmetry. By measuring the rotation of the brighter lobes relative to the close packed direction of the underlying atomic lattice, we have determined that only one of the buckled hexamers predicted by theory is present on the surface (Fig. 1(d)). STM line scans show the relative heights of the features corresponding to the perpendicular vs. planar methyl groups on opposite sides of the hexamer (Fig. 6(a)).

The methanol hexamers are comprised of homochiral surface-bound methanol monomers that assemble into a structure which is itself rotated from the high symmetry substrate directions and hence is chiral. As supported by our DFT calculations, reflective symmetry dictated by the direction of the hydrogen-bonding network gives rise to two surface-bound enantiomers. The chirality of both planar and buckled hexamers is apparent in both STM data and DFT calculations as a rotation of the hexamers as a whole from the close packed substrate directions. The planar hexamers on Cu(111) are rotated ±5° depending on chirality. DFT predicts a rotation of ±3.7° for the buckled hexamer which is in good agreement with the value of 3.8 ± 0.7° measured by STM (Fig. 6(b)). Rotation of the buckled hexamer in the plane of the surface gives rise to structures where the apex of the brighter triangle of lobes corresponding to the perpendicular methyl groups points either up or down in the STM images.
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The presence or absence of specific hydrogen bonded networks allows us to speculate on the barriers to conversions between them. The coexistence of the planar hexamer, which is centered around an atop site (Fig. 1(b)), and the buckled hexamer, which is centered at a threefold site (Fig. 1(d)), implies that the observed buckled hexamer is a trapped metastable structure with a barrier to conversion to the planar hexamer. Additionally, the absence of the buckled hexamer centered at an atop site (Fig. 1(c)) suggests a small barrier or non-activated process to conversion between this type of buckled hexamer and the more stable planar hexamer. The conversion from the buckled hexamer centered at a three-fold hollow site (Fig. 1(d)) to the planar hexamer requires movement (diffusion) of the hexamer as a whole from being centered at a three-fold hollow surface site to an atop site, together with the movement and rotation of three methanol monomers towards the surface. In contrast, the conversion from the buckled hexamer centered at the atop site (Fig. 1(c)) to planar hexamer (Fig. 1(b)) does not require movement to a new binding site, as both are centered at atop sites. The fact that one buckled hexamer has to change adsorption sites is, therefore, a likely source of this barrier between the buckled (Fig. 1(d)) and planar (Fig. 1(b)) hexamers. The buckled hexamer (Fig. 1(c)) can be considered a short-lived metastable structure that rapidly rearranges into the more energetically favorable planar hexamer through an almost barrierless process.

Low temperature (5 K) STM allowed us to investigate the interconversion of these different types and chiralities of methanol structures as shown in Fig. 5. The stability and re-ordering of the structures on Cu(111) was investigated by rastering the STM tip over the surface at perturbative conditions (400 mV, 100 pA) between non-perturbative observation scans. A number of conformational changes of the hydrogen-bonded methanol networks were observed, as outlined in Figure 5. Chirality inversions of both the buckled and planar hexamer were also seen (yellow arrows, Fig. 5). The buckled hexamer has a unique conformational interconversion, analogous to the ring-flip in cyclohexane, which results in the upward pointing methyl groups pointing down and vice versa (green arrows, Fig. 5). This ring-flip results in an apparent rotation of the triangles relative to the substrate lattice. The green/yellow diagonal arrows represent interconversions, where both a chirality and ring-flip occur. Rearrangement and breaking of the hydrogen-bonds can occur, allowing the buckled hexamer to form a six-membered chain, and the six-membered chain and planar hexamers to be interconverted (gray arrows). The formation of a buckled hexamer from either a planar hexamer or chain was not observed; this implies that the buckled hexamer is less stable than either the planar hexamer or chain, which is supported by our theoretical calculations, in which chains and planar hexamers, respectively, are 76 and 58 meV per methanol more energetically favorable than the buckled hexamer (Fig. 1(d)), see Table I.

V. COMPARISON OF WATER AND METHANOL NETWORKS

Finally, before concluding, it is interesting to compare what we find for methanol adsorption with what is known about water. First, like methanol, water has been observed to form clusters (including hexamers) and chains when adsorbed on several metals. However, water also forms two-dimensional overlayer structures, such as on Pt(111) where an extended overlayer built from hexagons, pentagons, and heptagons has been observed. We found no evidence for any two-dimensional hydrogen bonded overlayers of methanol on Pt(111) or on either of the two other surfaces considered here. Given that solid methanol is built from methanol chains the absence of ordered two-dimensional hydrogen bonded methanol structures is not unexpected.

If we focus now on comparing the methanol and water hexamer structures adopted on the different metals we find that this depends on a balance between molecule-molecule and molecule-metal interactions. For methanol, the molecule-metal interactions play the dominant role. In contrast, with water, preserving a strong hydrogen bond network prevails over forming water-metal bonds since the water-metal interaction is weaker than the methanol-metal interaction (Table I). Our STM and theoretical analysis indicate that
planar methanol hexamers are more stable on each metal studied (Table I). Additionally, our theoretical work indicates that planar water hexamers are preferred on reactive metals such as Pt(111) (Table I), while buckled hexamers are preferred on less reactive metals, which is in agreement with previous experimental and theoretical results.29,31 To date, buckled and planar water hexamers have not been observed in coexistence in the same experiment. Conversely, our STM analysis shows buckled and planar methanol hexamers simultaneously on Cu(111) and Pt(111), which has allowed for the analysis of interconversions between these hydrogen bonded structures that has not yet been possible for water systems.

Let us focus now on the buckling in the water and methanol hexamers. Interestingly, when we look at the structure of both the buckled methanol and water hexamers we find that in addition to the buckling there is an alteration in the O-O distances, with a set of relatively short O-O distances and a set of relatively long O-O distances (Table II). This “kekulé-like” alteration in O-O distances has been predicted before for water, but is observed here for methanol with DFT for the first time. The alterations in O-O distances arise from a competition between specific lone pair orbitals of water and methanol that are involved in bonding with the surface and in accepting hydrogen bonds.53 The result is a buckled structure that can be viewed as a hexamer built from three weakly interacting dimers. When we compare the extent of the alteration in O-O distances we find that this is actually related to how strongly the molecules bond to the surface. We show this in Fig. 7 where we plot the extent of the alteration in O-O distances (ΔO-O) as a function of monomer adsorption energy for both water and methanol. Clearly as the strength of the interaction increases, so too does the asymmetry in the hexamer.

**VI. CONCLUSION**

We have investigated coverage-dependent networks of methanol from near monolayer to extremely low coverage on Au(111), Cu(111), and Pt(111) with STM and DFT, showing coverage and surface dependence on the networks formed. In particular, the stronger adsorbate-substrate binding of Pt(111) hinders the formation of long range ordered methanol networks. A new structure formed by surface-bound methanol on Cu(111) and Pt(111), which we assign, through STM imaging and DFT calculations, as a buckled hexamer of hydrogen-bonded methanol molecules has been identified. The chirality of these structures is expressed in a rotational effect which allows us to assign enantiomers. This structure is similar to the buckled water hexamers that are hypothesized to exist on less reactive metals. We observe buckled and planar methanol hexamers simultaneously on two separate metals, and using DFT we determine that the planar methanol hexamer is preferred on all investigated surfaces, as it produces the optimal balance between hydrogen bonding and the more dominant methanol-metal interactions. In order to compare methanol and water hexamer adsorption we did the first set of vdw-inclusive calculations of adsorbed water hexamers. This revealed that for the water hexamers, hydrogen bonding interactions generally play a larger role, and drive the formation of buckled hexamers, and only on more reactive metals is the molecule-metal interaction large enough to force a preference for planar hexamers. These results serve as a cross comparison of

**TABLE II. Adsorption geometries (in Å) of methanol and water buckled hexamers on Au(111), Cu(111), and Pt(111). The six d_{O,M} heights are defined as the distance between the O atom of each monomer within the hexamer and its corresponding nearest metal atom in the surface layer. The six nearest-neighbor O-O distances (ΔO-O) alternate between two characteristic values as discussed in the text and the difference between them is also provided (ΔΔO-O).**

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<tr>
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<th>Au(111)</th>
<th>Cu(111)</th>
<th>Pt(111)</th>
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<td>d_{O,O}</td>
<td>ΔO-O</td>
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![Fig. 7. Alteration in O-O distances within buckled hexamers (ΔO-O) and monomer adsorption energy (E_ads) for both water and methanol on Au(111), Cu(111), and Pt(111).](image-url)
the interaction strength, assembly, and chirality of hydrogen bond networks on catalytically relevant close packed metal surfaces.

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