

Sensitivity of x-ray absorption spectroscopy to hydrogen bond topologyD. Nordlund,¹ H. Ogasawara,^{1,2} K. J. Andersson,^{1,3} M. Tatar khanov,⁴ M. Salmerón,^{4,5}
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We demonstrate the sensitivity of x-ray absorption spectroscopy to hydrogen bonding using as experimental model system water on Ru(0001). We stepwise go from fully broken to complete H-bond network by varying the morphology from isolated monomers via two-dimensional clusters to a saturated monolayer as probed by scanning tunneling microscopy. The sensitivity of x-ray absorption to the symmetry of H bonding is further elucidated for the amino (-NH₂) group in glycine adsorbed on Cu(110) where the *E* vector is parallel either to the NH donating an H bond or to the non-H-bonded NH. We show that the pre-edge in the x-ray absorption spectrum is associated with an asymmetric hydrogen-bonding situation while the postedge is directly associated with hydrogen bond formation. The results give further evidence for the much debated interpretation of the various spectral features of liquid water and demonstrate the general applicability of x-ray absorption spectroscopy to analyze H-bonded systems.

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I. INTRODUCTION

The properties of water are determined by the flexible nature of the hydrogen bond (H-bond) network formed among water molecules, giving rise to a very complex phase diagram and a large number of anomalous properties.¹⁻⁴ In its condensed ice Ih phase each water molecule is coordinated by four others in a near-tetrahedral arrangement forming an ordered crystal structure. In the liquid phase the most common picture of the H-bond network is as a distribution of H-bonded species with continuous distortions in a near-tetrahedral arrangement. A recent x-ray absorption spectroscopy (XAS) and x-ray Raman-scattering (XRS) study⁵ proposed that the dominating species in water, denoted as single donor (SD), corresponds to molecules in an asymmetrical H-bonding situation, where one of the donating H bonds is significantly weakened whereas the other is kept nearly intact. Furthermore, recent x-ray emission spectroscopy data on water⁶ show the presence of two rather distinct different local H-bond configurations, a picture which is also supported by the previous XAS study.⁵ However, there has been an intense debate regarding the interpretation and impact of the x-ray spectroscopy results (see Ref. 6 for a detailed discussion).

To settle some of the controversies surrounding the interpretation of the XAS/XRS water spectrum and the underlying scientific question regarding the structure of liquid water, it is imperative to experimentally establish how the x-ray spectrum of water changes in different well-defined H-bonding geometries other than ice and gas phase. This approach has been most successful in studies of small free water clusters using various vibrational spectroscopies.⁷ Due to the directionality of the hydrogen bond and the fact that x rays produced as synchrotron radiation can be linearly polarized, it is particularly advantageous to study the H-bond environment in lower dimensions where the x-ray *E* vector can be aligned to selectively probe the in-plane H-bond in-

teractions. Adsorption of water on well-defined surfaces provides a platform for growing two-dimensional hydrogen bond structures and offers many established surface-science techniques for structural characterization. In particular, close-packed metal surfaces such as Pt(111) and Ru(0001) have hexagonal geometries that are closely matched to the basal plane of ice Ih. Here we present an XAS study of small water clusters adsorbed on Ru(0001). Our primary goal is to provide information about the effects of H-bond coordination on the x-ray absorption spectrum based on experimental data alone.

II. SYSTEMS AND METHODS

The scanning tunnel microscopy (STM) and XAS experiments were performed on two different ultrahigh-vacuum (UHV) instruments. For STM, the experimental setup consists of a homemade, variable temperature STM that has been described in detail previously.⁸ The STM has a modified scanner enclosed in a copper shield clamped to the sample stage so that tip and sample are at the same temperature. In the STM images a gray or color scale is used to represent tip heights at each of the 512 × 512 image pixels. The gray scale is chosen such that bright corresponds to the tip being farther away and dark closer to the surface.

In both experimental setups, clean, well-ordered Ru(0001) surfaces with impurities below 0.2% of a monolayer (ML), as verified by low-energy electron diffraction and x-ray photoelectron spectroscopy (XPS) or STM, were prepared in UHV by cycles of noble gas (Ar, Ne) ion bombardment and annealing at 1100–1300 K. The water was ultrapure grade and purified by pumping over the ice and by freeze-thaw cycles. Water vapor was adsorbed on the samples at temperatures below 40 K in order to prepare the low-coverage phases.

The XAS experiments were performed at the elliptically polarized undulator beamline 11.0.2 of the Advanced Light

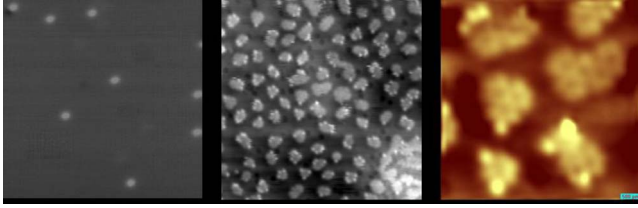


FIG. 1. (Color online) Left: $10 \times 10 \text{ nm}^2$ STM image of isolated water monomers (bright spots) on Ru(0001); middle: $17.5 \times 17.5 \text{ nm}^2$ showing clusters of water molecules forming hexamers and clusters of a few hexamers. Right: enlarged view ($5 \times 5 \text{ nm}^2$) showing the honeycomb structure of the clusters. Images acquired at $T=50 \text{ K}$. Scanning conditions: 170 mV and 0.7 nA.

Source (ALS) in Berkeley, USA. The XAS spectra were recorded with a total-energy resolution of about 0.1 eV. All phases were prepared and measured at 37 K except for the monolayer which was annealed at 150 K, and measured at 100 K, to ensure a fully relaxed H-bond network.^{9–11} Dissociation of water on Ru(0001) is kinetically hindered in the temperature range employed here but may be induced by x-ray and electron damage effects.^{9–11} By scanning the sample rapidly, resulting in only ~ 0.03 photon-generated e^- /water molecule,⁹ beam damage was negligible (hydroxyl $\leq 4\%$ of total coverage) as determined by XPS and XAS (out-of-plane).

The details of the symmetry-resolved XAS spectra of the amino group in deprotonated glycine (glycinate) on Cu(110) can be found in Ref. 12.

III. RESULTS

A. Topology observed by STM

Figure 1 shows STM images of water on Ru at different coverages deposited at 37 K. At low coverage we only observe isolated water monomers (Fig. 1, left) seen as a single protrusion similar to previously observed for water on Pd(111).¹³ When we increase the coverage, small hexagonal water clusters are formed (Fig. 1, middle and right), similar to what is observed on other substrates.^{13,14} Infrared absorption spectroscopy (IRAS) at this intermediate coverage shows no intensity in the OH stretch region.¹¹ Based on the surface selection rule, where only vibrational modes perpendicular to the surface are observed in IRAS, this shows that the molecular plane is parallel to the surface. The unique situation is that at the edges of the clusters each water molecule has a free OH group. In some cases we also observe water molecules at the edges in a nondonor (ND) single acceptor configuration as in Ref. 13 which are extremely mobile and thus weakly bonded. Most of the edges have SD species and this corresponds to an asymmetrical situation with one strong and one missing donor H bond. The size of the clusters increases with increasing coverage until a two-dimensional overlayer develops where we have two types of water molecules, bonding to the metal either through the oxygen atom with the molecular plane near parallel to the surface, as in the low-coverage regime, or through one OH group pointing toward the surface.^{9,11,15}

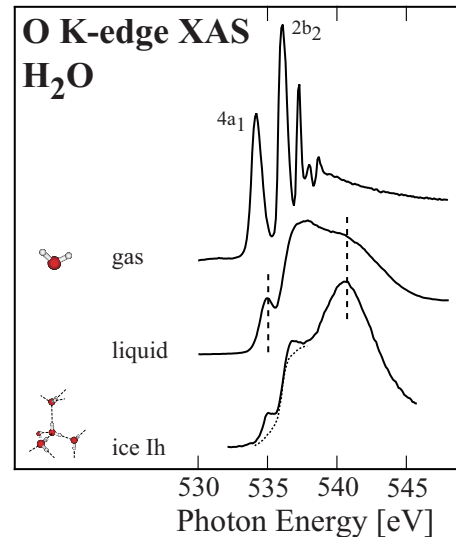


FIG. 2. (Color online) XAS spectra of water in the gas, liquid, and ice phases (Refs. 5, 16, and 17). The intensity above the dotted line in the ice spectrum is related to a small amount of beam damage, defects at grain boundaries, and the surface.

B. H-bond topology observed in XAS

Figure 2 shows O *K*-edge XAS spectra of water in its three aggregation states indicating that the electronic transitions in the condensed forms are significantly different from those in the gas phase.^{5,16,18} The liquid water spectrum shows a strong pre-edge peak at 535 eV, a main-edge peak at 537.5 eV, and a postedge peak around 541 eV.⁵ The suggested interpretation in Wernet *et al.*⁵ is the following: the weakly coordinated OH in molecules with asymmetric donating H bonds gives rise to the strong pre-edge and main-edge features observed for liquid water as well as for the ice surface while the more strongly H-bonded OH contributes to the postedge peak.⁵ In tetrahedral configurations, as in ice, both OH groups are coordinated with neighboring water molecules giving rise to double-donor (DD) species. Thereby the contribution to the intensity at the postedge from a DD species will be nearly twice that from an SD configuration. Heating the liquid results in further loss of postedge intensity, coupled with a concomitant increase in the pre-edge and main-edge regions.⁵ In this sense part of the intensity of the postedge is transferred to the pre-edge and main-edge upon breaking one donor bond forming SD from DD configurations.

The spectral features in liquid water can be further elucidated using water on Ru(0001) as model system. The alignment near parallel to the surface allows us to selectively study the H-bond network by aligning the linearly polarized photon *E* vector along this direction; the water-metal interaction is mainly in the vertical direction and affects the spectra only indirectly.¹⁵ Figure 3 shows the experimental O *1s* XAS spectra from low-coverage water up to a completed monolayer with the *E* vector of the exciting photon in plane. For comparison, we show the x-ray absorption spectrum from hexagonal ice¹⁷ and gas-phase water,¹⁶ with guide lines for the energy positions of the broadened molecular gas-

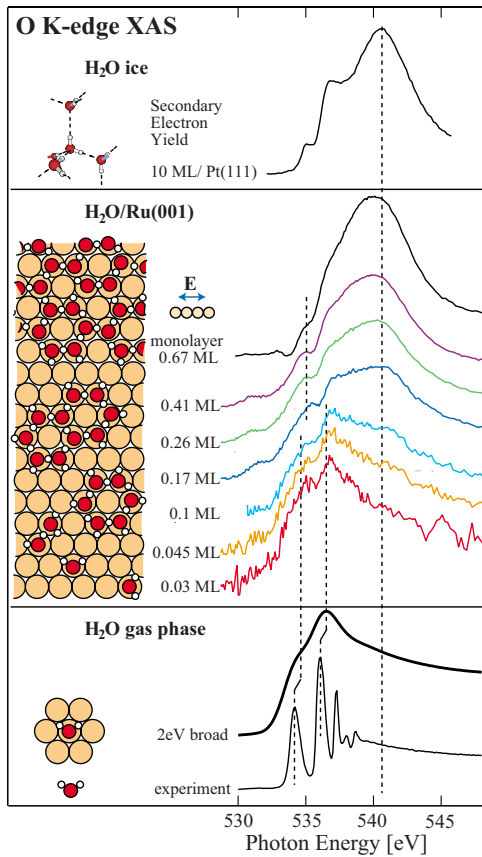


FIG. 3. (Color online) (Left) Schematic illustrations of STM observations for water at various coverages on Ru(0001) from low coverage with individual water molecules, intermediate coverage where small clusters are formed with asymmetrical H bonding at edges and the complete monolayer where nearly all H bonds are saturated in the plane parallel to the surface. (Right) XAS spectra measured with the E vector in plane with respect to the surface of water adsorbed on Ru(0001) at different coverages deposited and measured at 37 K except for the monolayer coverage which was annealed to 150 K and measured at 100 K. Spectra of gas and ice phases (Refs. 5, 16, and 17) are shown as comparison.

phase orbitals $4a_1$ and $2b_2$ as well as for the strong postedge in ice (540.5 eV).

In the low-coverage phases (<0.1 ML), corresponding to mobile¹³ monomer water and low-membered clusters, a comparison with the gas-phase spectrum broadened by 2 eV indicates spectral features associated with the gas-phase molecular orbitals also for the molecules at the surface. The spectrum becomes broadened and shifted in energy due to variations in local geometry and coupling to the conduction band of the metal. There is no distinct postedge feature in the spectrum and most of the intensity is at lower energy similar to the gas phase. As the coverage increases STM shows (Fig. 1, middle and right) formation of isolated immobile hexagonal clusters and we can see the effects of H bonding in the x-ray absorption spectra. From an H-bonding perspective, the water molecules in the clusters have a high asymmetry with one strong donor H bond and one OH group pointing along the in-plane direction away from the cluster. We see significant intensity in the postedge region above 540 eV,

which was not present for the low coverage. We also note that a rather well-defined pre-edge peak emerges at an energy intermediate of the gas-phase $4a_1$ and $2b_2$ peaks.

As the coverage increases, intercluster bonding increases and, as a result, we should see the effect of increased H bonding, and decreased asymmetry as more of the non-H-bonded donor sides form H bonds with other water clusters (see Fig. 1). This is reflected in the spectrum as an increase (and sharpening) in the postedge feature, along with a decrease in the pre-edge state. Upon completion of the monolayer, the postedge becomes even more intense whereas the pre-edge diminishes and almost disappears compared to the dominating postedge; the spectrum gains a strong resemblance with the spectrum of bulk ice.

It is clear from the spectra in Fig. 3 that the postedge can be associated with the presence of H bonds in either asymmetric or symmetric species. In the free water molecule, the $4a_1$ and $1b_2$ orbitals are delocalized on both OH groups in the water molecule due to the C_{2v} symmetry. It has been suggested from theoretical calculations that the appearance of the pre-edge feature for asymmetrical H-bonded species is a result of a localization of the OH antibonding orbital onto the free or weakly donating OH group.^{5,18} Through resonant Auger measurements^{19,20} it has indeed been verified that excitation into the pre-edge leads to an extremely localized state whereas excitation into the postedge leads to a delocalization process along the H-bonding network on an attosecond time scale. We address the geometrical symmetry of this localized state as seen through XAS using another molecular system with a functional group that is also locally in C_{2v} symmetry, namely, the NH_2 group in glycine.

C. H-bond asymmetry

In Fig. 4 we show symmetry-resolved XAS spectra of the amino group in deprotonated glycine (glycinate) on Cu(110), taken from Ref. 12. Theoretical simulations and associated interpretation of the full adsorbate system have been reported by Nyberg *et al.*²¹ The Cu(110) surface has twofold symmetry with the surface Cu atoms oriented into rows. The glycine molecular skeleton bridges over two Cu rows on the surface in order to bond through both the carboxylic and amino functional groups.^{12,22,23} The formation of H bonds between the carboxylic and amino functional groups on neighboring molecules gives rise to an ordered $(3 \times 2)pg$ overlayer on the Cu(110) surface with one of the amino hydrogens H bonded and the other not. This leads to an asymmetrical H-bonding situation in the NH_2 group with one strong donating bond whereas the other hydrogen atom is not involved in any H bonds as shown in Fig. 4. The highly oriented system means that we have three directions defined for the p components, p_x , p_y , and p_z , respectively. Here, the alignment of the E vector relative to the rows in the open Cu(110) surface reduces the dimensionality to 1, and we can get a very direct connection between geometrical symmetry and x-ray absorption transition amplitudes by selectively orienting the E vector along either of the two N-H groups. Figure 4 directly demonstrates the excited-state localization on the free N-H group due to lowering of the symmetry resulting from the

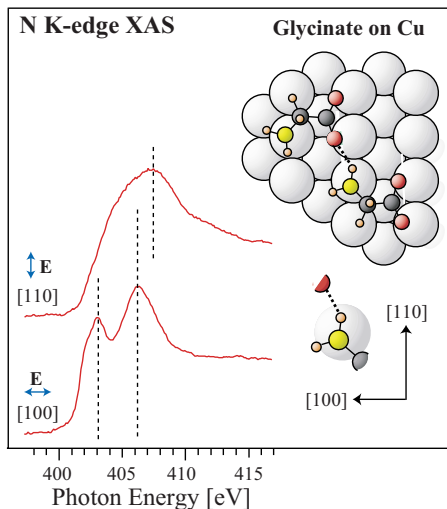


FIG. 4. (Color online) (Right) Structural model of the adsorption geometry of glycinate on Cu(110) where the amino group in the lower molecule has two N-H where one donates an H bond to the carboxylate group on a neighboring molecule and the other is non-H-bonded. (Left) N *K*-edge XAS spectra of glycinate on Cu(110) with the *E* vector in plane and either in the [100] or the [110] directions (Ref. 12). The pre-edge and main-edge spectral features are observed at 403 and 406 eV, respectively, in the spectrum with the *E* vector aligned with the [100] direction whereas the postedge feature is observed at 407 eV in the spectrum in the [110] direction.

asymmetrical H bonding. Similar to asymmetrically H-bonded water we observe pre-edge and main-edge features in the spectrum with the *E* vector along the free N-H while the postedge feature is observed with the *E* vector along the H-bonded N-H.

IV. CONCLUSION

In conclusion, we have demonstrated the unique sensitivity of XAS to H-bonding topology by using low-dimensional

water on Ru(0001), from monomers to a complete monolayer. The alignment of the hydrogen bonds along the surface plane allows us to selectively study the effect of the H-bond environment in the XAS spectrum along the direction of the hydrogen-donating OH groups. Specifically, excitation of single-donor molecules on the surface, where an H bond has been broken on the H-donating side, shows strong spectral features in the low-energy part of the spectrum which are different in energy relative to the gas phase. Upon completion of the H-bond network, the intensity of this pre-edge feature is suppressed, and a strong postedge feature is observed, associated with hydrogen bonds. The effect on the XAS profile due to broken symmetry and the subsequent localization of the excited-state wave function is furthermore demonstrated for the oriented amino group in glycine adsorbed on Cu(110) where the *E* vector can be oriented parallel to either the H-bonded or non-H-bonded NH. This study settles some of the controversies surrounding the interpretation of the XAS/XRS results and the underlying scientific question (the local structure of liquid water), by further establishing the connection between spectral features in x-ray absorption of water and the symmetry of the local hydrogen bond environment.

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