SLAC-PUB-13828

Low-Dimensional Water on Ru(0001); Model System for X-ray Absorption Spectroscopy Studies of Liquid Water

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ABSTRACT

We present an x-ray absorption spectroscopy results for fully broken to a complete H-bond network of water molecules on Ru(0001) by varying the morphology from isolated water molecules via two-dimensional clusters to a fully covered 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 (-NH_2) 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. The results give further evidence for the interpretation of the various spectral features of liquid water and for the general applicability of x-ray absorption spectroscopy to analyze H-bonded systems.

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Work supported in part by US Department of Energy contract DE-AC02-76SF00515.

The properties of water are determined by the versatile 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 anomalies[1-4]. In its condensed ice Ih phase each water molecule is coordinated with 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) study[5] proposed that the dominant species in water, denoted 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 (XES) data on water[6] show the presence of two rather distinct different local H-bond configurations, a picture which is also supported by the previous x-ray absorption spectroscopy (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 experimental 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. Adsorption of water on well-defined surfaces provides a platform for growing 2D 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 hexagonal geometry of ice, *e.g.*, the ice Ih(0001) surface. Here we present an XAS study of small water clusters adsorbed on Ru(0001). Our primary goal is to provide information about the effect of H-bond symmetry on the x-ray absorption spectrum based on experimental data alone.

The STM and XAS experiments were performed on two different ultra-high vacuum (UHV) instruments. For STM, the experimental set-up 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 512x512 image pixels. The gray scale is chosen such that bright corresponds to the tip being farther away and dark closer to the surface.

The XAS experiments were performed at the elliptically polarized undulator beamline 11.0.2 of the Advanced Light Source (ALS) in Berkeley. The XAS spectra were recorded with a total energy resolution of about 0.1 eV. X-ray and electron damage effects [9-11] were negligible as a result of minimizing the photo-generated and inelastically scattered electrons down to a total of ~0.03 e^-/water molecule[9] by scanning the sample rapidly.

In both experimental set-ups, clean, well-ordered Ru(0001) surfaces with impurities below 0.2 % of a monolayer (ML) were prepared in UHV by cycles of noble gas (Ar, Ne) ion bombardment, and annealing at 1100-1300 K. The water was ultra-pure grade and purified by pumping over the ice and by freeze-thaw cycles. Water vapor was admitted into the chambers and adsorbed on the samples at temperatures below 40 K.

Fig. 1 shows STM images of water on Ru at different coverages deposited at 37 K. At low coverage we only observe isolated water molecules (fig. 1, Left) seen as a single protrusion similar to previously observed for water on Pd(111)[12]. When we increase the coverage clusters are formed with the water molecules forming small hexagonal clusters (fig. 1, Middle and Right). Infrared absorption spectroscopy (IRAS) at this intermediate coverage shows no intensity in the OH stretch region[11]. Based on the surface selection rule for IRAS, where only vibrational modes perpendicular to the surface are dipole active, 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 in a non-donor (ND) single acceptor configuration at the edges which are mobile and thereby 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, either bonded through the oxygen atom with the molecular plane near-parallel to the surface, as in the low coverage regime, or bonding through one OH group pointing towards the surface[9, 11, 13].

Fig. 2 shows O K-edge 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, 14, 15]. The liquid water spectrum shows a strong pre-edge peak at 535 eV, a main-edge peak at 537.5 eV, and a post-edge 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 post-edge 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 intensity of the post-edge will be nearly twice as large compared with the SD configurations. Heating the liquid results in further loss of post-edge intensity, coupled with a concomitant increase in the pre-edge and main-edge region [5]. In this sense part of the intensity of the post-edge is transferred to the pre-edge and main-edge upon breaking one donor bond forming SD from DD configurations.

The alignment of the H-bond network along the two-dimensional surface and the directionality of the photon E-vector, allows us to study the effect of H-bond asymmetry along the direction parallel to the surface. Fig 3 shows the experimental O1s 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 ice[16] and gas-phase water[15], with guide lines for the energy positions of the molecular gas-phase orbitals $4a_1$ (534 eV) and $2b_2$ (536 eV) as well as for the strong post-edge in ice (540.5 eV).

In the low-coverage phase corresponding to monomer water we see spectral features associated with the gas-phase molecular orbitals that are broadened due to the coupling to the conduction band of the metal. We note that there is no H-bonding and consequently no distinct post-edge feature in the spectrum. As the coverage increases with formation of hexagonal clusters, the effect of H-bonding can be seen in the x-ray absorption spectrum. From an H-bonding perspective the water molecules in the clusters have a high asymmetry with one donor H-bond broken. We note that two features emerge as a function of coverage. First, we see significant intensity in the post-edge region above 540 eV, which was not present for the monomers. Second, a new feature emerges at energy intermediate of the gas-phase $4a_1$ and $2b_2$ peaks.

As the coverage increases, inter-cluster 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 hydrogen-bonds with other water clusters (see fig. 1). This is reflected in the spectrum as an increase (and sharpening) of the post-edge feature, along with a decrease of the pre-edge state. Upon completion of the monolayer, the post-edge becomes even more intense whereas the pre-edge diminishes and almost disappears and the spectrum gains a strong resemblance with the spectrum of bulk ice.

It is clear from the spectra in Fig. 3 that the pre-edge can indeed be associated with water species in asymmetric H-bonding configuration, whereas the post-edge can be associated with the presence of H-bonds in either asymmetric or symmetric species. In a simple picture the spectra from these surface adsorbed species reflect the spectral characteristics from the three different aggregation forms of water: low coverage with no H-bonds corresponds to gas phase, intermediate coverage with asymmetrical H-bond donor situation gives rise to a pre-edge feature similar to the liquid spectrum while finally the monolayer coverage where all donating H-bonds parallel to the surface are saturated gives rise to a dominating strong post-edge and significant reduced pre-edge spectral features nearly identical to what is seen in ice.

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[5,14]. Through resonant Auger and XES measurements [6, 17, 18] it has indeed been verified that excitation into the pre-edge leads to an extremely localized state whereas excitation into the post-edge leads to a delocalization process along the H-bonding network on an attosecond timescale. Let us now take a closer look at this localization using another molecular system with a functional group that is also locally in C_{2v} symmetry, namely the NH_2 group in glycine.

In Fig. 4 we show symmetry-resolved XAS spectra of the amino group in deprotonated glycine (glycinate) on Cu(110) taken from[19, 20]. The Cu(110) surface has two-fold 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[19, 21, 22]. The formation of H-bonds between the carboxylic and amino functional groups on neighboring molecules gives rise to an ordered (3x2)*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 3 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 one, and we can get a very direct connection between geometrical symmetry and x-ray absorption transition amplitudes by orienting the E-vector along either of the two N-H groups. Fig. 4 directly demonstrates the excited state localization on the two N-H groups due to lowering of the symmetry resulting from the asymmetrical H-bonding. We observe the corresponding pre-edge and main-edge features in the spectrum with the E-vector along the free N-H and the post-edge feature along the H-bonded N-H. This also gives further evidence that the pre-edge and main-edge spectral features are associated to broken or weak H-bonds and the post-edge to H-bonds.

In conclusion, we have shown an XAS study of 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 study the effect of the H-bond environment in the XAS spectrum along the direction of the hydrogen-donating OH groups. Specifically, the excitation of single-donor molecules, 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 monomers. Upon completion of the H-bond network, the intensity of this pre-edge feature is suppressed, and a strong post-edge feature is observed, associated with states along localized 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.

This work was supported by the National Science Foundation (US) CHE-0809324 and CHE-0431425 and the Swedish Research Council. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL), a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The STM work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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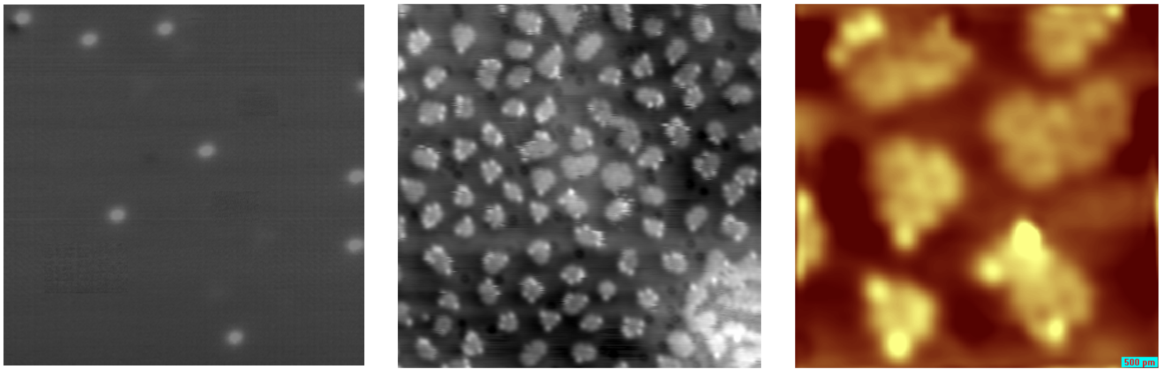

Fig. 1 Left: 10 × 10 nm^2 STM image of isolated water molecules (bright spots) on Ru(0001); Middle: 17.5 × 17.5 nm^2 showing clusters of water molecules forming hexamers and clusters of a few hexamers. Right: enlarged view (5 × 5 nm^2) showing the honeycomb structure of the clusters. Images acquired at T = 50 K. Scanning conditions: 170 mV, 0.7 nA.

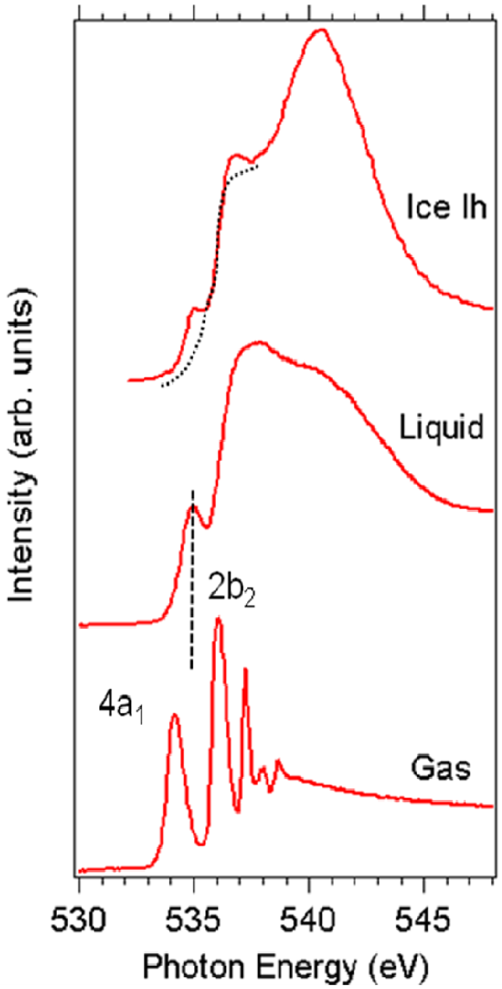

Fig. 2 XAS spectra of water in the gas phase, liquid and ice[5, 15, 16]. The intensity above the dotted line in the ice spectrum is related to small amount of beam damage, defects at grain boundaries and the surface.

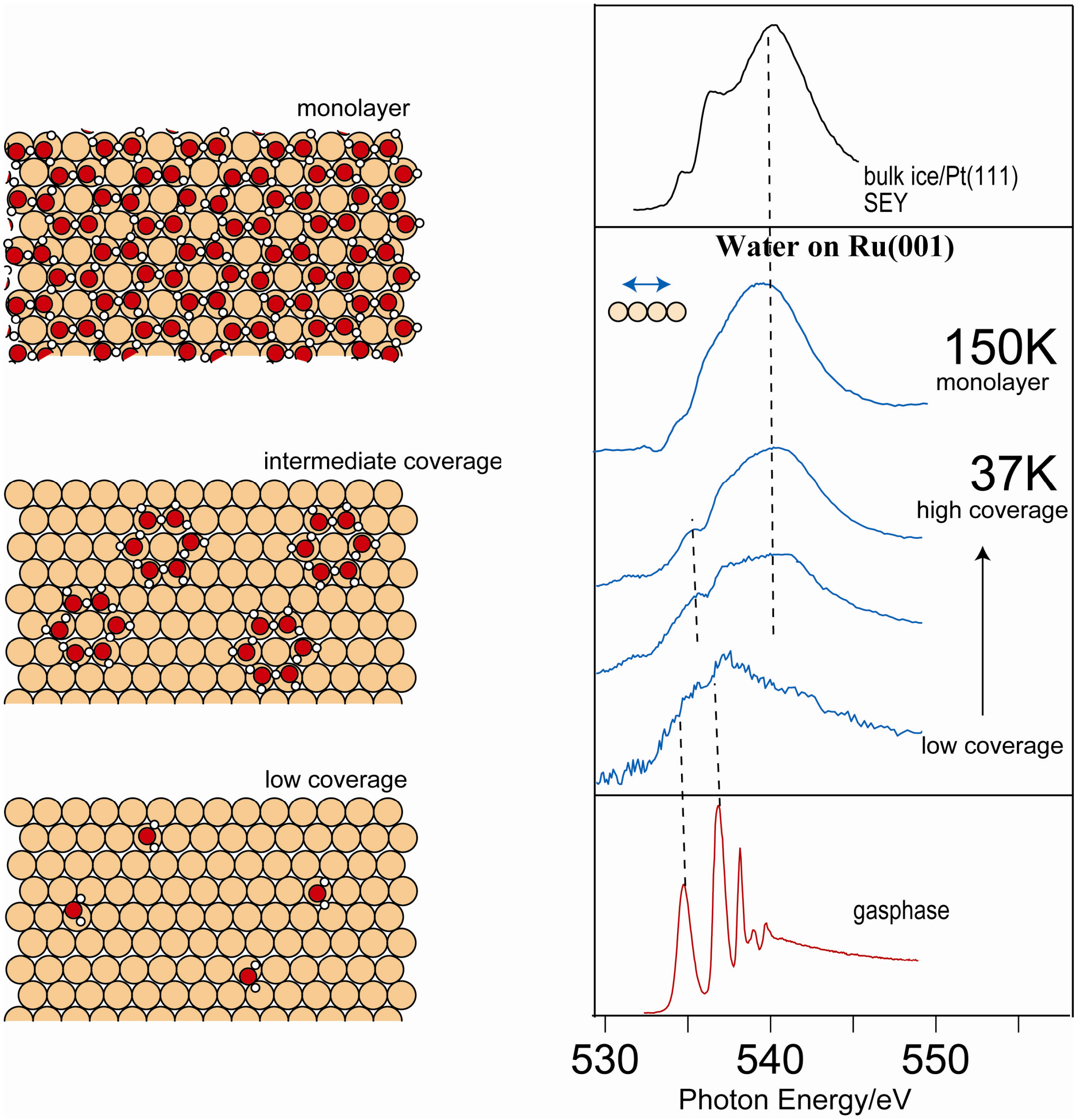

Fig. 3 (left) Proposed structure of water at various coverages on Ru(0001) from low coverage with individual water molecules, intermediate coverage where small clusters are formed with asymmetrical H-bonding at edges and complete monolayer where nearly all H-bonds are saturated in the plane parallel 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 also annealed to 150 K. Spectra of gas phase and ice[5, 15, 16] are shown as comparison.

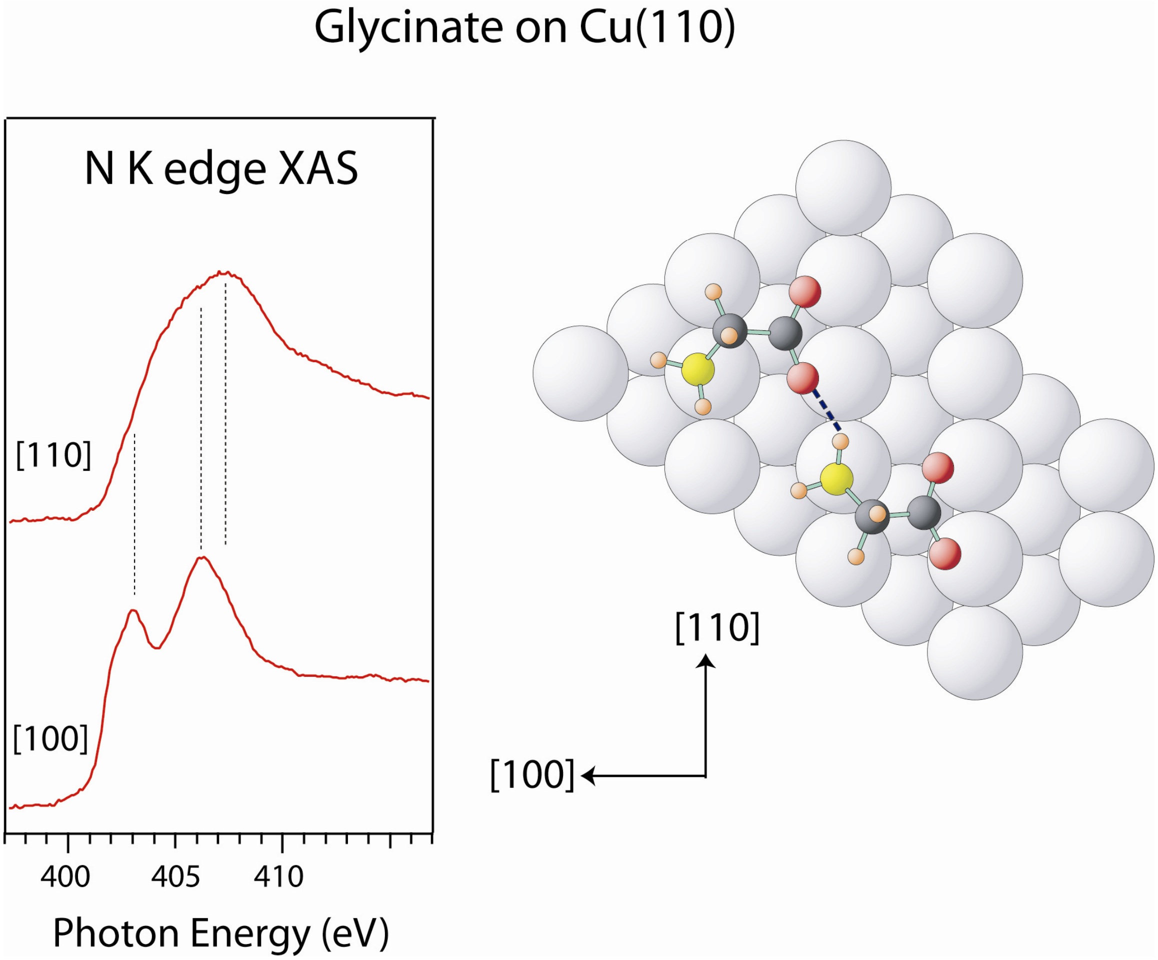

Fig. 4 (left) N K edge XAS spectra of glycinate on Cu(110) with the E-vector in plane and either in the [100] or the [110] directions[19]. The pre-edge and main-edge spectral features are observed at 403 eV and 406 eV, respectively, in the spectrum with the E-vector aligned with the [100] direction whereas the post-edge is observed at 407 eV in the spectrum in the [110] direction. (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.