

Ammonia Adsorption and Co-adsorption with Water in HKUST-1: Spectroscopic Evidence for Cooperative Interactions

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Abstract. Ammonia interactions and competition with water at the interface of nanoporous metal organic framework thin films of HKUST-1 (Cu_3Btc , Btc=1,3,5-benzenedicarboxylate) are investigated with Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS). In the absence of water, ammonia adsorption at the Cu^{2+} metal center weakens the metal-linker bond of the framework. In the presence of water, due to the higher binding energy (adsorption strength) of ammonia compared to water, ammonia replaces water at the unsaturated Cu^{2+} metal centers. The water molecules remaining in the pores are stabilized by hydrogen bonding to ammonia. Hydrogen bonding between the water and ammonia strengthens the metal-ammonia interaction due to cooperative interactions. Cooperative interactions result in a reduction in the metal center oxidation state facilitating linker replacement by other species explaining the previously reported structure degradation.

1. Introduction.

Metal Organic Frameworks (MOFs) are attractive in areas related to gas separation and storage, gas sensing, catalysis, air purification, and removal of toxic gases.¹⁻¹⁰ MOFs are porous materials composed of metal centers, or nodes, connected with organic components to form three-dimensional ordered networks. MOFs exhibit large surface areas, high porosity, and structural tunability by varying the attached linkers and metal nodes to modify the pore chemistry.^{11,12} Removal of toxic gases, such as ammonia, by MOFs has been a focus of recent research.⁷ HKUST-1 (Cu_3BTC_2) with the open Cu^{2+} metal sites has been investigated for the removal of ammonia, nitric oxide, and CO_2 .¹³⁻¹⁶ Ammonia uptake in HKUST-1 exceeds that of porous carbon.¹³⁻¹⁵ However, the degradation associated with the presence of moisture renders HKUST-1 unsuitable for practical applications.¹³⁻¹⁷ Therefore, probing co-adsorption of gases in MOFs with open metal center such as HKUST-1 is important. Previous work characterizing water and ammonia exposure of HKUST-1 were performed ex-situ after exposure to high concentrations of water and ammonia. Post exposure characterization indicated degradation with ammonium ions reacting with the linker, while the copper metal center was hydroxylated.¹³⁻¹⁷ Ex-situ characterization provides useful information, however interactions during initial co-adsorption at low pressures can only be revealed through in-situ characterization. Probing interactions during co-adsorption of guests is fundamentally important because it simulates conditions similar to those experienced in practical applications, for example during gas separation. Probing adsorptive interactions in-situ with chemical specificity can reveal mechanisms not observed by adsorption isotherms alone.¹⁸⁻²⁴ Therefore, an in-situ study of the co-adsorption is critical for revealing adsorbate-metal center and adsorbate-adsorbate interactions. Here, competitive

interactions of water and ammonia are interrogated by the APXPS technique at low relative humidity and partial pressure of ammonia to investigate interactions leading to degradation.

In this work, we report evidence for cooperative interactions between ammonia and water with the Cu^{2+} metal centers of HKUST-1 caused by hydrogen bonding of water with ammonia. The ammonia- Cu^{2+} interaction strength is increased leading to the degradation of the framework observed in previous work.¹³

2. Materials and Methods.

Thin film synthesis. HKUST-1 thin films (40 layers, ~100 nm) were synthesized using the Layer-by-Layer liquid phase epitaxy method on a hydroxylated SiO_2 coated quartz crystal microbalance (QCM) substrate following published methods.²⁵⁻²⁷ The SiO_2 coated QCM substrates (QCM crystals with SiO_2 coatings were purchased from Biolin Scientific) were cleaned by dipping them into a 2 % sodium dodecyl sulfate followed by deionized water rinse with a final step of UV ozone exposure for 10 minutes. The UV ozone exposure creates hydroxyl groups on the surface. The film deposition was performed by flowing a 0.2 millimolar ethanolic solution of copper acetate over the functionalized substrate followed by a solvent rinse (ethanol), then flowing a 1 millimolar ethanolic solution of trimesic acid, followed by another solvent rinse, for a total of 40 layers (~100 nm). Deposition temperature was kept at 22 °C and the mass deposition per layer was monitored by the QCM technique. Layer thickness is calculated from the density and deposited mass. The X-ray diffraction pattern of a 40 layer HKUST-1 thin film is shown in Figure S1 of supporting information.

Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS). Synchrotron X-ray spectroscopy measurements in the presence of a gas were performed at the Advanced Light

Source (ALS) beamline 11.0.2. The experimental setup is described in detail in a paper by Ogletree *et al.* and a review by Bluhm *et al.*^{28,29} HKUST-1 thin film samples were heated in-situ overnight at a temperature of 110 °C in ultra-high vacuum (UHV) using a resistive button heater. A photon energy of 490 eV is used for C 1s core electrons, 600 eV for the N1s core electrons, 735 eV for O1s, and 1140 eV for Cu 2p; these photon energies result in electrons escaping with energies of 200 eV, providing similar sample probe depths. An additional set of data for each element was collected at 735 eV and used for calibration of binding energy shifts. Cu NEXAFS spectra were collected in partial electron yield mode with a kinetic energy of 750 eV and a kinetic energy bandwidth of 50 eV. The amount of adsorbed gas per copper was calculated from the integrated areas of the photoelectron peaks. The integrated peak area was normalized by the sensitivity factors of the different elements and the photon flux, measured using a calibrated photo diode.³⁰ Reduction of the metal center oxidation state and framework degradation due to X-ray exposure was previously observed and can be clearly identified in HKUST-1 NEXAFS spectra.¹⁸ To prevent sample degradation, measurements were performed at different sample positions.¹⁸ The uncertainties in the Cu¹⁺ percentages are less than 5 %, and in the ratios $\sim\pm 4$ % of the values. Uncertainties are determined by varying the fitting parameters, i.e. changing the background slope and limits of the peaks fitting area. The time for dosing the gas into the chamber followed by data acquisition precludes detailed kinetic studies. Performing measurements at lower temperatures would allow higher loadings (higher intensity) to be achieved and possible extraction of kinetic and thermodynamic information. However, kinetic studies may be limited to relatively slow processes due to the time required for data acquisition (~20-30 seconds) and time for gas dosing (~15 seconds) . The integrated areas of the peaks were measured at initial dosing after 1 minute and after 4 minutes and no change is observed. To

ensure equilibrium, we waited 10 minutes after gas dosing for measurements reported here. Thus, the combined instrumental (beamline + spectrometer) resolution varies from 0.32 eV at 490 eV to 0.43 eV at 1140 eV incident photon energy.

3. Results and discussion.

3.1 NH₃ interactions in HKUST-1.

To determine the spectroscopic signature of the adsorbed ammonia, ammonia interactions with HKUST-1 were studied as a function of ammonia uptake by X-ray Photoelectron Spectroscopy (XPS) and NEXAFS. These experiments were performed prior to studying the co-adsorption of ammonia and water in HKUST-1.

Spectroscopic signature and loading of ammonia from APXPS. The left panel of Figure 1 shows the N1s photoelectron spectra of HKUST-1 as a function of ammonia pressure. At the lowest ammonia pressures (a loading of $< \sim 0.8 \text{ NH}_3:\text{Cu}^{2+}$), the N1s peak at 400.6 eV is attributed to physisorbed ammonia at the Cu²⁺ sites. Changes in color due to adsorption at the Cu²⁺ site have been reported as a result of ammonia adsorbed in HKUST-1 binding to the unsaturated metal centers via Lewis-acid base interactions.³¹ With increasing ammonia pressures ($> 10^{-5}$ Torr) the N1s peak shifts by -0.3 eV. This decrease in binding energy with increasing ammonia uptake indicates a slight weakening of the ammonia-Cu²⁺ interaction (less electron donation from ammonia to the metal). This shift does not result from sample charging because different peaks shift differently. A decrease in the heat of adsorption of ammonia with increasing ammonia loading has been attributed to ammonia-ammonia interactions on neighboring Cu²⁺ sites.¹⁶ Intermolecular interactions were previously observed by vibrational spectroscopy and result in a

shift of the vibrational frequency of the adsorbed molecules.³² The right panel of Figure 1 shows the number of ammonia molecules per copper (calculated from the ratios of integrated areas of the N1s and Cu 2p photoelectron peaks) as a function of ammonia pressure at equilibrium. At a pressure of 0.025 Torr a plateau is reached that corresponds to an occupation of $\sim 2.8 \pm 0.2$ NH₃ per Cu²⁺, a value higher than previously reported (~ 1.5 NH₃:Cu²⁺).^{13,16}

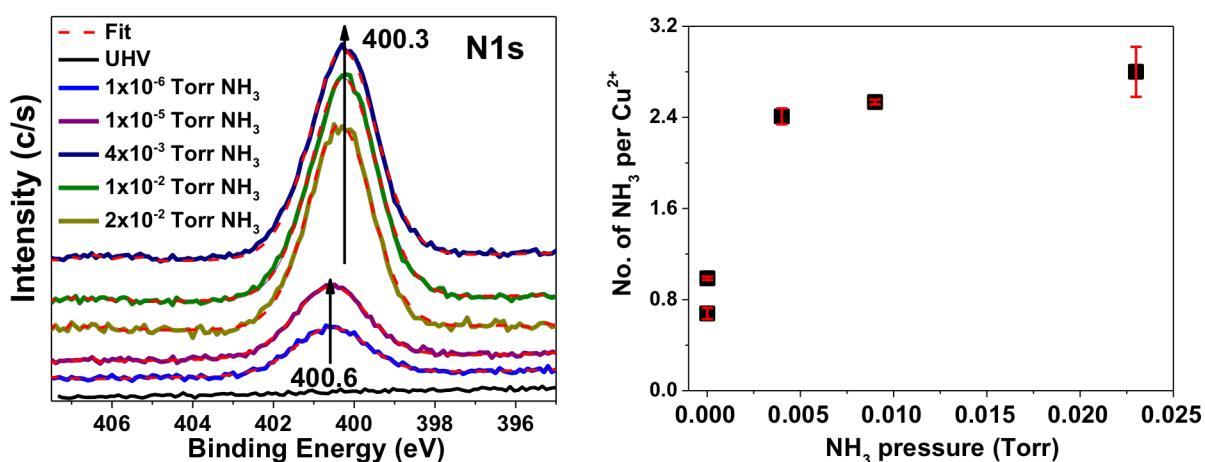


Figure 1. Left: N1s photoelectron spectra as a function of ammonia pressure. With increasing NH₃ loading a slight decrease (-0.3 eV) in the N1s peak binding energy occurs. Right: number of ammonia molecules per copper as a function of ammonia pressure. N 1s and Cu 2p photoelectron spectra are collected at 600 eV and 1140 eV photon energies, respectively, and the amount adsorbed is calculated from the integrated peak areas measured at equilibrium. The amount of ammonia adsorbed increases rapidly and plateaus at ~ 0.025 Torr at $\sim 2.8 \pm 0.2$ NH₃ per Cu²⁺. Equilibrium was reached at each pressure and measurements are performed 10 minutes after gas introduction.

XPS is surface sensitive (inelastic mean free path of electrons is $\sim 1-2$ nm under the conditions used in these experiments and probe depth is 3-6 nm) and specifically provides information about the gas-porous material interface and chemical interactions. Hence, these measurements differ from adsorption isotherms that average over the entire sample and lack chemical specificity. The amount of adsorbed ammonia per copper at a pressure of 10^{-5} Torr, $< \sim 0.8 \pm 0.1$

$\text{NH}_3:\text{Cu}^{2+}$, (calculated from the N1s peak integrated area) indicates occupation of nearly all metal sites with a saturation of $\sim 2.8 \text{ NH}_3:\text{Cu}^{2+}$ at 0.023 Torr. Compared to bulk powder MOF measurements, the metal center saturation occurs at a lower ammonia pressure.¹⁵ The higher ammonia adsorption for the 40 layer film indicates a higher local loading at the HKUST-1 thin film surface. The 40 layer HKUST-1 film is oriented in the [222] crystallographic direction with the tetrahedral small pores ($\sim 5 \text{ \AA}$) aligned parallel to the surface (figure S1).¹⁸ Adsorption of one ammonia molecule (gas kinetic diameter of 3.57 \AA) in these constricted pores could facilitate ammonia-ammonia interactions and result in higher local loading. Moreover, constriction of the pores interconnecting the small tetrahedral pockets to the larger cavities would enhance the adsorbate interaction with the framework walls providing additional adsorption sites. These observations are consistent with a higher loading at the MOF peripheries that occur due to the presence of local minima for adsorption.^{32,33}

Changes of the copper-ligand bond with ammonia adsorption. To examine changes in the metal-linker bonding and the unsaturated metal center oxidation state, NEXAFS spectra of the Cu L3-edge are recorded before and after ammonia exposure. Figure 2 shows NEXAFS Cu L3-edge spectra under UHV (black solid line) and at 0.01 Torr ammonia (brown dashed line), where the loading is $\sim 2.5 \text{ NH}_3:\text{Cu}^{2+}$. The NEXAFS spectra are normalized to the pre-edge intensity. The Cu^{2+} L3 peak at 931.4 eV arises from the electric dipole-allowed 2p-3d transition and the Cu^{1+} L3 peak arises from $2p^6 3d^{10}$ to $2p^5 3d^{10} 4s^1$ transition.^{34,35}

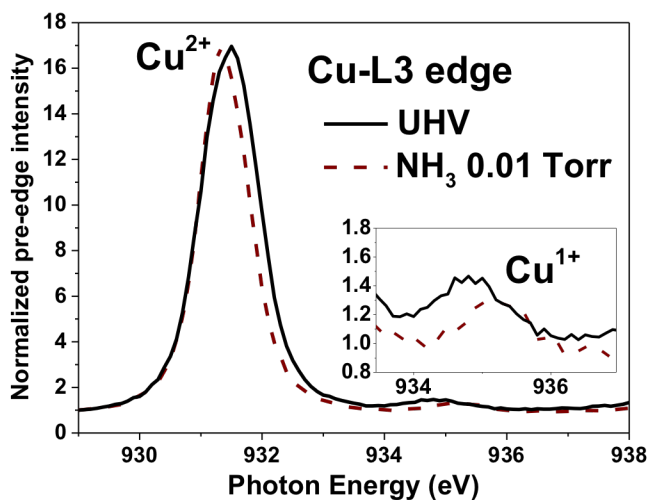


Figure 2. Cu L3-edge NEXAFS spectra under ultra high vacuum (UHV) (solid line) and under 0.01 Torr ammonia (dashed spectrum), slight shifts in the Cu^{2+} and Cu^{1+} peaks (discussed in the text) are observed. Inset: Cu^{1+} peak.

Using the Cu 2p photoelectron spectra, the Cu^{1+} percentage calculated from the peak intensities is $\sim 3.5\%$ Cu^{1+} (Figure S2 (top) of supporting information). This value is consistent with our previous studies on pristine thin films.³⁶ Cu^{1+} defects in the thin films are attributed to missing linkers and partially coordinated linkers to the copper dimers.^{18,36,37} A -0.2 eV shift in the L3 Cu^{2+} peak position indicates a decrease in ligand field splitting and a weakening of the ligand-metal bond due to the interaction with ammonia.³⁸ The L3 Cu^{2+} peak position is a measure of the 2p-3d transitions in the metal. The ligand field splitting occurs due to hybridization of the 2p orbitals of the oxygen and the 3d orbitals of the metal causing a splitting in the energy of the metal's 3d orbitals. If the metal-ligand bond weakens this would alter the hybridization of the p and d orbitals of the copper and the ligand's 2p oxygen (decrease in the metal orbital filling). Therefore, a decrease in the L3 Cu^{2+} peak position indicates a decrease in the energy required for the 2p-3d transition in the metal. This effect is caused by the decrease in 3d metal orbitals

splitting (ligand field splitting) a result of the weaker hybridization of the oxygen p orbitals with 3d orbitals of the copper. Hydrogen bonding between the ammonia molecules on neighboring sites and the ligand may contribute to the weakening of the Cu-O bond and stabilization of the second ammonia. The peak linewidth also decreases by 0.2 eV. The L3 peak of the Cu¹⁺ (inset of right panel of Figure 2) shifts towards higher photon energy with adsorption of NH₃ at the Cu¹⁺ defects indicating a change in 4s orbitals. Indeed, interaction of ammonia with materials having Cu¹⁺ was previously observed by infrared photo-dissociation spectroscopy to be electrostatic in nature, which is enhanced by hybridization of the 4s and 3d orbitals of the Cu¹⁺.³⁹

3.2 Co-adsorption of NH₃ and H₂O in HKUST-1 film.

Spectroscopic signature of NH₃ and water co-adsorbed in HKUST-1. Co-adsorption of water and ammonia in HKUST-1 was investigated by exposing an activated (sample heated at 110 °C in vacuum to remove residual solvent) thin film to water vapor and introducing ammonia thereafter. The left panel of Figure 3 shows O1s photoelectron spectra of HKUST-1 under UHV (top spectrum), at 0.26 Torr H₂O (middle spectrum), and after addition of 0.03 Torr NH₃ (bottom spectrum). The main O1s peak at 532 eV is assigned to the C-O bond of the Btc linker. The O1s peak at 533.7 eV, which only appears in the presence of H₂O, is assigned to physisorbed H₂O at the Cu²⁺ metal sites. Note that upon the addition of water vapor or ammonia, the signal intensity decreases due to scattering of electrons by the gas phase water.⁴⁰ The water uptake at 0.26 Torr H₂O corresponds to 1.4 H₂O:Cu²⁺. This loading indicates the presence of a second water molecule that is hydrogen bonded to the primary water molecule adsorbed at Cu²⁺ (three water molecules per Cu-Cu dimer). With addition of 0.03 Torr NH₃ a +0.6 eV shift in the O1s peak position of adsorbed water is observed (bottom left panel, Figure 3) indicating a change in the interaction of adsorbed water in HKUST-1. Previously, high binding energy O1s peak positions,

observed beyond a monolayer of water adsorption, were attributed to water hydrogen bonding with other water molecules.⁴¹ Therefore, the 534.3 eV peak in the O1s spectrum indicates hydrogen bonding of the remaining water to ammonia adsorbed at the Cu²⁺ metal center. The N1s photoelectron spectrum at 0.26 Torr H₂O and with the subsequent addition of 0.03 Torr NH₃ is shown in the right panel of Figure 3. The N1s peak at 400.3 eV is assigned to NH₃ adsorbed at Cu²⁺ with a loading of 1.4 ± 0.05 NH₃:Cu²⁺ at an ammonia partial pressure of 0.03 Torr and water vapor pressure of 0.26 Torr. This is a significant decrease in loading compared to that measured in the absence of water (2.8 NH₃:Cu at 0.025 Torr NH₃, see right panel Figure 1) suggesting adsorption of water replacing the second shell ammonia molecules in the larger cages. Comparison of Figure 1 (left) and Figure 3 (right) shows that the shoulder at 401.8 eV in the N1s photoelectron spectrum only occurs when both water and ammonia are present. This higher binding energy peak position indicates a stronger donation of the non-bonding lone pair electron to the metal due to hydrogen bonding with water. This is consistent with a simplistic initial state model where binding energy peak positions are related to how strongly electrons are bound to the nucleus. Removal of an electron from the nitrogen results in a stronger attraction of the remaining electrons to the nucleus, therefore increasing its binding energy.¹⁸ Changes in the copper metal center due to electron donation from the ammonia to the copper are discussed in the next section.

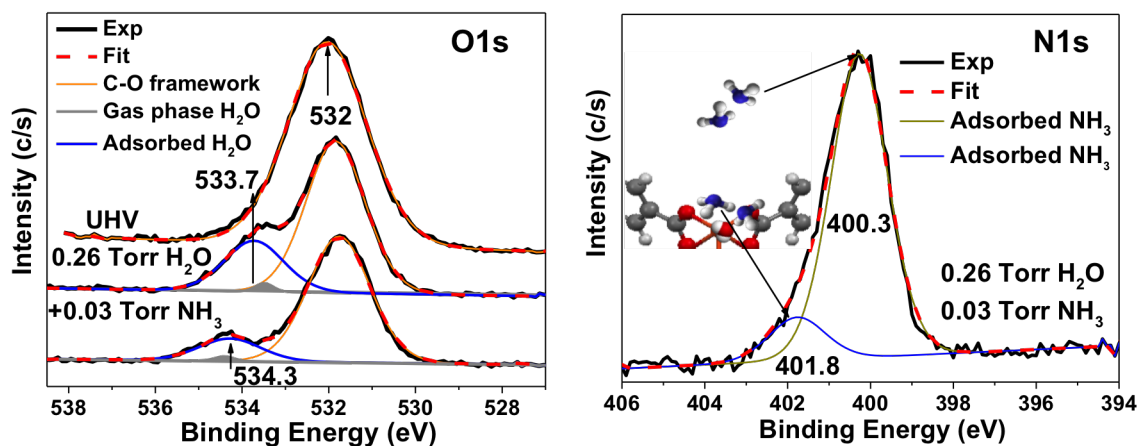


Figure 3. Left: O1s photoelectron spectra under UHV (top), 0.26 Torr H₂O (middle), and after addition of 0.03 Torr ammonia (bottom). Right: N1s photoelectron spectra in the presence of 0.26 Torr H₂O and 0.03 Torr NH₃. The inset is a schematic illustrating the peak assignments. The N1s peak at 401.8 eV appears only in the presence of water. Water gas phase peaks (grey peaks) shift differently with varying measurement position on the sample due to the inequivalent charging of the gas molecules at the sample surface.

At a water vapor pressure of 0.26 Torr, at equilibrium the amount of adsorbed ammonia and water molecules per copper as a function of ammonia vapor pressure are summarized in Figure 4. The amount of adsorbed water (calculated from the ratios of integrated areas of the O1s and Cu 2p photoelectron peaks) drops from 1.4 H₂O:Cu²⁺ to 0.32 H₂O:Cu²⁺ with addition of 0.1 Torr NH₃, indicating replacement of water by ammonia. Ammonia is expected to replace water because of the higher binding energy of ammonia to the Cu²⁺ (~82 kJ/mol) compared to H₂O (~42 kJ/mol).^{16,42} Approximately 22 ± 4 % of the initial water remains adsorbed in HKUST-1 at 0.1 Torr of ammonia. This is most likely due to stabilization of adsorbed water by hydrogen bonding with ammonia in the larger pores that can fit both adsorbed molecules. The amount of ammonia at the higher binding energy position (401.8 eV) corresponds to ~0.12 NH₃:Cu²⁺ (1 ammonia molecule for every 4 copper dimers).

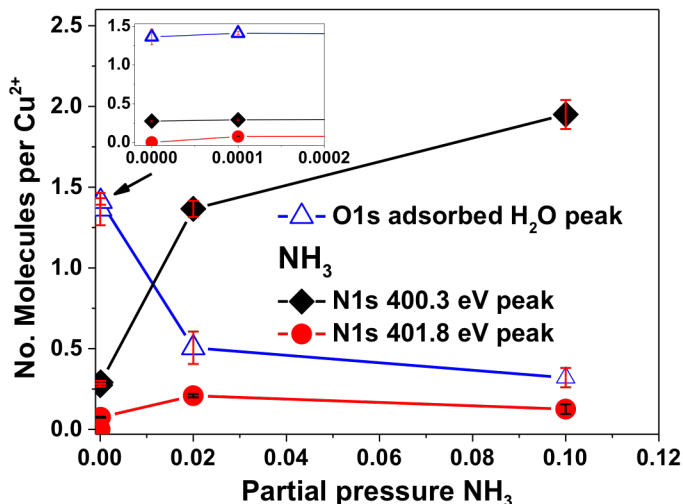


Figure 4. Calculated number of adsorbed water molecules from the O1s (open triangles), and ammonia N1s peaks at 400.3 eV (black diamonds) and 401.8 eV (red circles) in the presence of 0.26 Torr of water vapor as a function of ammonia vapor pressure starting from a pressure of 10^{-4} Torr ammonia. As ammonia pressure increases, the pre-adsorbed H₂O decreases. Measurements are performed after 10 minutes. Inset: Zoom of data points in the low pressure region.

Changes in ammonia-metal interaction with co-adsorption of water—cooperative interactions.

To probe the metal center during co-adsorption of ammonia and water, NEXAFS spectra are recorded before and after exposure to water and ammonia. Figure 5 shows Cu L3-edge NEXAFS spectra under UHV (black line), after addition of 0.26 Torr H₂O (blue dashed line) and addition of 0.01 Torr NH₃ (brown squares). The Cu²⁺ peak shifts by -0.2 eV with exposure to water, similar to what was observed for ammonia (Figure 2, Figure S3) due to an interaction of the lone pair of electrons on the oxygen of the water with the Cu²⁺ in a Lewis-base interaction.

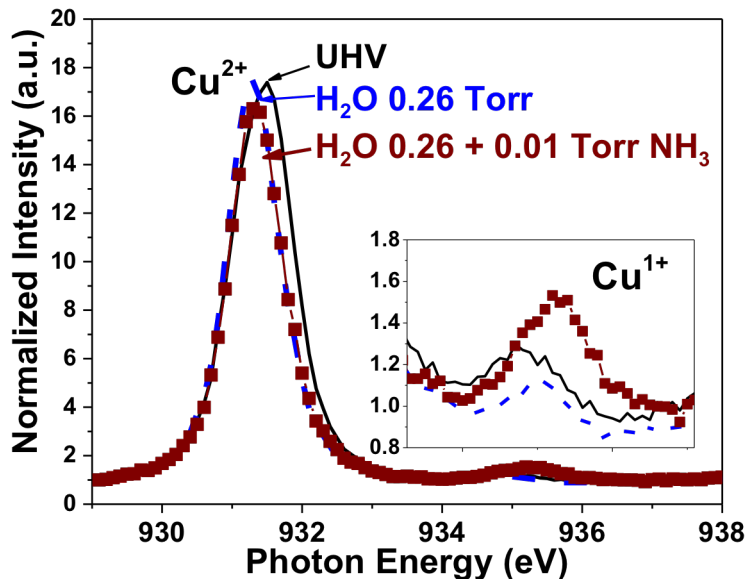


Figure 5. Cu L3-edge NEXAFS spectra of HKUST-1 under ultra high vacuum (UHV) (black line) and after exposure to 0.26 Torr water (blue dashed line). The inset shows the Cu^{1+} peak. A -0.2 eV shift in the Cu^{2+} L3 peak position is observed in the presence of water. An increase in the Cu^{1+} peak area is observed in the presence of both water and ammonia.

As shown in Figure S3, Cu^{2+} L3-edge spectra measured with only water or only NH_3 overlap with one another and are all shifted to lower photon energies than UHV conditions (see Figure 2). In the presence of both water and ammonia, the Cu^{1+} peak is more intense than if only water or only ammonia are present (Figure S3). From the integrated peak areas, the amount of Cu^{1+} from the Cu 2p spectra is $\sim 6\%$ at 0.01 Torr water and 0.26 Torr NH_3 . Reduction of the metal center oxidation state indicates that the ammonia adsorbed at the Cu^{2+} acts as a stronger electron donor in the presence of water than in its absence. The change in ammonia interaction with the metal center stems from hydrogen bonding of water and ammonia which polarizes the ammonia molecule and strengthens its electron donation character, an effect referred to as cooperative hydrogen bonding.^{43,44} Cooperative hydrogen bonding was previously observed to affect interactions of water bound to metal surfaces.^{43,44}

3.3 Cooperative effect of ammonia-ammonia and ammonia-water hydrogen bonding interactions.

In this section, we compare the interaction of water with pre-adsorbed ammonia in HKUST-1 at loadings of ~ 1 $\text{NH}_3:\text{Cu}^{2+}$ and ~ 2 $\text{NH}_3:\text{Cu}^{2+}$. The objective is to elucidate the influence of ammonia pre-loading on water incorporation and its effect on the ammonia interaction with the Cu^{2+} .

Initial loading of ~ 1 $\text{NH}_3:\text{Cu}^{2+}$. The left panel of Figure 6 shows N1s photoelectron spectra at 10^{-4} Torr ammonia (top spectrum) and after exposure to an additional 0.1 Torr water (bottom spectrum). The ammonia loading of 10^{-4} Torr corresponds to 0.94 $\text{NH}_3:\text{Cu}^{2+}$. The right panel of Figure 6 summarizes the number of ammonia and water molecules adsorbed per Cu^{2+} as the partial pressure of water is increased at equilibrium. When 0.1 Torr of water is introduced (corresponding to a loading of 0.35 $\text{H}_2\text{O}:\text{Cu}^{2+}$ (O1s peak, not shown)), the N1s peak at 400.3 eV decreases and a second N1s peak at 401.8 eV appears, (Figure 6 left panel). With the addition of water the integrated areas of the N1s peaks correspond to loadings of 0.77 $\text{NH}_3:\text{Cu}^{2+}$ and 0.11 $\text{NH}_3:\text{Cu}^{2+}$, respectively (Figure 6 right). Up to ~ 6 % of the adsorbed ammonia is replaced by water (~ 0.94 $\text{NH}_3:\text{Cu}^{2+}$ initial loading decreases to 0.88 $\text{NH}_3:\text{Cu}^{2+}$ after addition of water). This is due to the water increased chemical potential at these pressures as shown by Watanabe *et al.* allowing replacement of the ammonia adsorbed at the Cu^{2+} .⁴² Approximately 12 % of the remaining ammonia molecules (0.11 of the total remaining 0.88 $\text{NH}_3:\text{Cu}^{2+}$) are hydrogen bonded to water adsorbed at the Cu^{2+} and participate in cooperative interactions (401.8 eV N1s peak). The next section will contrast the influence of twice the amount of pre-adsorbed ammonia on promoting water incorporation.

Initial loading of $\sim 2 \text{ NH}_3:\text{Cu}^{2+}$. Figure 7 summarizes the changes in the number of adsorbed molecules starting with $\sim 2.2 \text{ NH}_3:\text{Cu}^{2+}$ as a function of partial pressure of water. Data are plotted for N1s (400.3 eV (black diamonds) and 401.8 eV (red circles)) and the O1s peak of adsorbed water at 534.3 eV (blue open triangles). The percentage of Cu^{1+} (brown squares) is also calculated and increases with water exposure. The slight change in copper oxidation state is caused by an increased donation of electrons from the ammonia to the Cu^{2+} in the presence of water (see section 3.2). After $\sim 0.05 \text{ Torr H}_2\text{O}$ is added with an initial ammonia loading of $2 \text{ NH}_3:\text{Cu}^{2+}$ ($\sim 0.7 \text{ H}_2\text{O}:\text{Cu}^{2+}$ and $\sim 1.94 \text{ NH}_3:\text{Cu}^{2+}$) the intensity of the N1s and O1s peaks are relatively independent of the water vapor pressure. Approximately 12 % of the total ammonia (a decrease from $\sim 2.2 \text{ NH}_3:\text{Cu}^{2+}$ to $\sim 1.94 \text{ NH}_3:\text{Cu}^{2+}$) is replaced by water at lower binding energy sites (second shell of ammonia). This corresponds to twice as much ammonia replaced by water

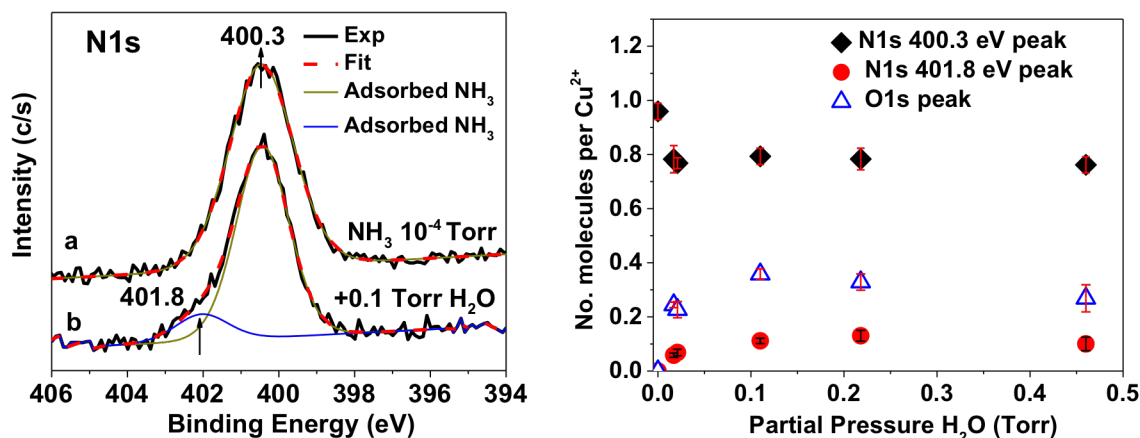


Figure 6. Left: N1s photoelectron spectra at 10^{-4} Torr ammonia without water vapor (spectrum a) and after addition of 0.1 Torr water vapor (spectrum b). The peak at 401.8 eV only appears when both NH_3 and H_2O are present. Right: Number of molecules of NH_3 (N1s peaks at 400.3 eV (diamonds), and 401.8 eV (circles)) and H_2O (O1s peak of adsorbed water at 534.3 eV (triangles)) adsorbed in HKUST-1 as a function of H_2O partial pressure at equilibrium. With the initial addition of water, the adsorbed ammonia decreases due to replacement of adsorbed ammonia (at the second shell) by water. Equilibrium is reached at each pressure by waiting 10 minutes after introducing the gas.

compared to the lower ammonia loading conditions. Replacement of the second ammonia is

expected because the primary ammonia has a higher binding energy to the Cu^{2+} than water. Cooperative interactions of hydrogen bonded water and the primary ammonia adsorbed at the Cu^{2+} (401.8 eV N1s peak) result in an increased donation of the non-bonding lone pair electrons of the ammonia to the metal (change in the metal center oxidation state (Figure 5, 7)). The reduced Cu^{1+} increases to $\sim 10\%$ with increasing water loading.

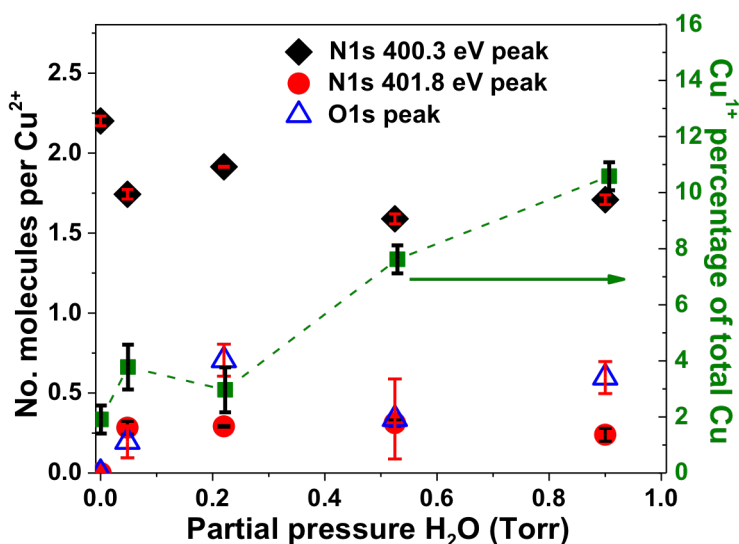


Figure 7. Number of molecules adsorbed as a function of H_2O partial pressure at equilibrium. Values are calculated from the integrated photoelectron peak areas of N1s (400.3 eV (diamonds) and 401.8 eV (circles)) and the O1s peak of adsorbed water at 534.3 eV (triangles). In the absence of H_2O , the highest NH_3 loading was $\sim 2.2 \pm 0.05 \text{ NH}_3:\text{Cu}^{2+}$. The squares represent the calculated percentage of Cu^{1+} as a function of water vapor pressure.

Comparison of the two initial ammonia loading conditions. At similar water vapor pressures both the area of the 401.8 eV N1s peak ($\sim 0.24 \text{ NH}_3:\text{Cu}^{2+}$) and the amount of adsorbed water ($\sim 0.6 \text{ H}_2\text{O}:\text{Cu}^{2+}$) are a factor of two larger at a loading of $2 \text{ NH}_3:\text{Cu}^{2+}$ than for $1 \text{ NH}_3:\text{Cu}^{2+}$.

This higher water uptake and the integrated area of the N1s 401.8 eV at 2 NH₃:Cu²⁺ suggest an enhancement of water incorporation (due to hydrogen bonding to pre-adsorbed ammonia) within the pores. Cooperative hydrogen bonding were previously observed to enhance adsorption of ammonia in porous organic polymers.⁴⁵ Adsorption of 2 NH₃ molecules per copper promotes hydrogen bonding between the ammonia molecules. Ammonia-ammonia hydrogen bonding makes the second adsorbed ammonia a better proton donor, facilitating hydrogen bonding to water. In the presence of water, and due to hydrogen bonding polarization of the ammonia molecules, an increased electron donation of the primary ammonia to the Cu²⁺ occurs (in a similar fashion to interactions resulting from directly interacting water with primary ammonia).

Two potential sites for water hydrogen bonding to ammonia are schematically shown in Figure 8. Figure 8 is a visualization of the different adsorption sites present and is not a result of simulations. Water can bind directly to the primary ammonia by replacing the second adsorbed ammonia (second shell ammonia), or water can interact with the secondary adsorbed ammonia molecules. Water adsorption at these two sites could explain the higher 401.8 eV peak area and water incorporation at 2 NH₃:Cu²⁺ compared to lower ammonia loading conditions. The results presented here indicate the need for further theoretical investigations of water and ammonia cooperative interactions in HKUST-1 and their influence on framework degradation. Previous theoretical calculations have focused on adsorption energies of ammonia and water to Cu²⁺ and thermal degradation of HKUST-1. For example, Watanabe *et al.* have calculated the binding energy of different molecules such as NO, H₂O, NH₃, CO, C₂H₂ and H₂S and found that pyridine and ammonia have the highest binding energy. Adsorption of ammonia was observed to cause a ~4.2 % volume contraction of the structure and a decrease in the Cu-O bond by ~1.9 %. Even though a pair of ammonia molecules adsorbed at the metal center has a higher binding energy

than water, it was found that a significant amount of water binds due to the large water chemical potential at high partial pressures (10^{-3} - 10^{-2} Torr).⁴² Huang *et al.* reported molecular dynamic simulations of the framework thermal stability and found that HKUST-1 structure is stable up to 565 K. Above 800 K decomposition of HKUST-1 was observed to produce CO, O₂, CO₂, glassy carbon, and 1,3,5-benzenetricarboxylate.⁴⁶

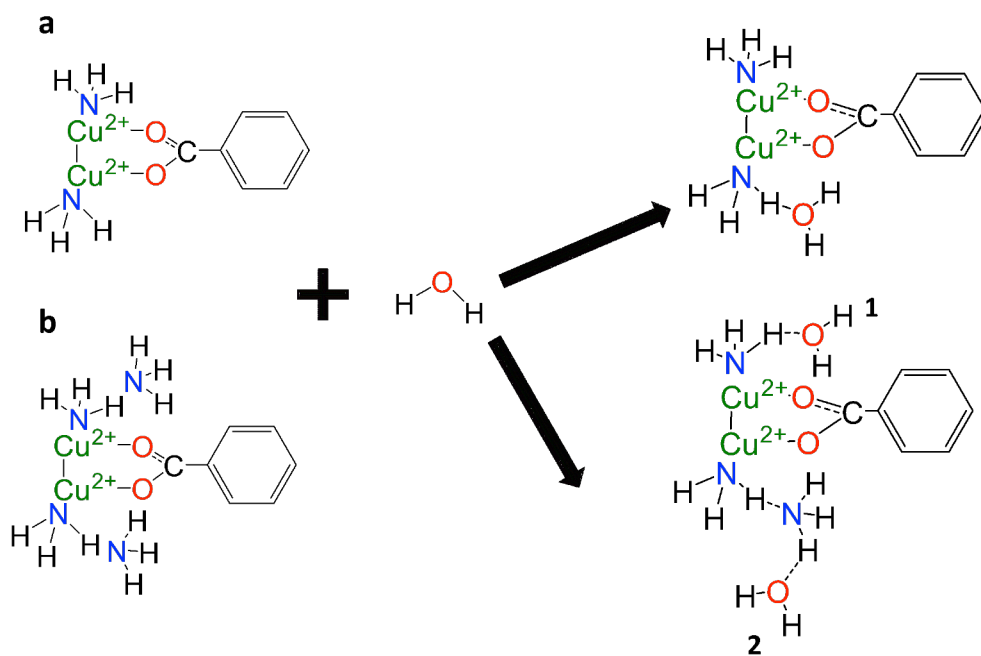


Figure 8. Schematic representation visualizing possible cooperative interactions between water, ammonia, and Cu²⁺ in HKUST 1 for loadings of a: 1NH₃:Cu²⁺ and b: 2NH₃:Cu²⁺. These schematics illustrate possible hydrogen bonding interactions. In case b, two potential adsorption sites for water are present that could produce the cooperative interactions measured in this work.

Implications of ammonia-water cooperative interactions. Results presented here for low loading conditions show that water residing in the pores may strengthen the ammonia-copper interactions compared to dry conditions. The stronger ammonia-copper interaction was observed to reduce the copper oxidation state (Cu²⁺ accepting one of the lone paired electrons (Figure 5)). Cu¹⁺ usually forms lower coordination number compounds.^{37,47} Moreover, hydrogen bonding of

ammonia molecules at the higher loadings $> 1 \text{ NH}_3:\text{Cu}^{2+}$ promotes hydrogen bonding and incorporation of water. Therefore, replacement of the linker by other molecules such as water is possible, leading to framework degradation at higher relative humidity and ammonia loadings previously observed by Peterson *et al.*¹³

4. Conclusions.

NEXAFS and XPS measurements show that ammonia adsorbs at both Cu^{1+} and Cu^{2+} in HKUST-1. Adsorption on the Cu^{2+} unsaturated metal center weakens the metal-linker bond. The ammonia adsorbs to the Cu^{2+} through Lewis-base interactions, while for Cu^{1+} the interaction is electrostatic in nature and is possible due to 4s and 3d orbital hybridization. For a hydrated film ammonia replaces pre-adsorbed water at the unsaturated metal centers due to its higher binding energy. However, $\sim 20\%$ of the pre-adsorbed water remains in the pores due to hydrogen bonding between water and ammonia.

Evidence for cooperative interactions between hydrogen-bonded water to ammonia, which is adsorbed at the Cu^{2+} , are observed. These cooperative interactions result in the increased strength of the ammonia- Cu^{2+} interaction compared to ammonia adsorbed under dry conditions. Two situations exist depending on ammonia loading, one where water hydrogen bonds to a single ammonia molecule (low ammonia loading), and/or participation of two ammonia molecules and water in the hydrogen bond. Ammonia-ammonia hydrogen bonding is observed to enhance water co-adsorption. The presence of water in the pores and the cooperative effect, detected spectroscopically, can explain framework degradation observed in previous work occurring at higher pressures.^{13,17}

ASSOCIATED CONTENT

Supporting Information. Supporting information provided for x-ray diffraction of a 40 layer HKUST-1 film, Cu2p photoelectron spectra, and Cu L3-edge spectra in the presence of only water, only ammonia, and in the presence of both. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The broad scope of the experiments was conceived by N.N., M.K.G., and S.R.L. Experiments were performed by N.N. and K.F. under the guidance of H.B., N.N. conceived of the specific experiments performed here, analyzed the data (with guidance from H.B.) and wrote the manuscript. M.K.G., S.R.L., and H.B. all provided feedback and contributed to the manuscript preparation.

Acknowledgement

M. K. G., H. B., and beamline 11.0.2 at the Advanced Light Source (AL) are supported through the Condensed Phase and Interfacial Molecular Science Program of DOE. N. N. and S. R. L. were supported by the Office of the Secretary of Defense National Security Science and Engineering Faculty Fellowship. K. F. was supported by The German Academic Exchange Service (DAAD). The ALS is supported by the U.S. Department of Energy, Office of Science,

Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division at Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231. The authors thank Dr. Martin Kunz and Dr. Kei Nakamura at the ALS micro diffraction facility on beamline 12.3.2.

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Cooperative interactions between hydrogen bonded water and ammonia with Cu^{2+} are observed spectroscopically to increase ammonia electron donation to the Cu^{2+} .

