

# Direct Observation of Ammonia Storage in UiO-66 Incorporating Cu(II) Binding Sites

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**ABSTRACT:** The presence of active sites in metal–organic framework (MOF) materials can control and affect their performance significantly in adsorption and catalysis. However, revealing the interactions between the substrate and active sites in MOFs at atomic precision remains a challenging task. Here, we report the direct observation of binding of NH<sub>3</sub> in a series of UiO-66 materials containing atomically dispersed defects and open Cu(I) and Cu(II) sites. While all MOFs in this series exhibit similar surface areas (1111–1135 m<sup>2</sup> g<sup>-1</sup>), decoration of the –OH site in UiO-66-defect with Cu(II) results in a 43% enhancement of the isothermal uptake of NH<sub>3</sub> at 273 K and 1.0 bar from 11.8 in UiO-66-defect to 16.9 mmol g<sup>-1</sup> in UiO-66-Cu<sup>II</sup>. A 100% enhancement of dynamic adsorption of NH<sub>3</sub> at a concentration level of 630 ppm from 2.07 mmol g<sup>-1</sup> in UiO-66-defect to 4.15 mmol g<sup>-1</sup> in UiO-66-Cu<sup>II</sup> at 298 K is observed. *In situ* neutron powder diffraction, inelastic neutron scattering, and electron paramagnetic resonance, solid-state nuclear magnetic resonance, and infrared spectroscopies, coupled with modeling reveal that the enhanced NH<sub>3</sub> uptake in UiO-66-Cu<sup>II</sup> originates from a {Cu(II)···NH<sub>3</sub>} interaction, with a reversible change in geometry at Cu(II) from near-linear to trigonal coordination. This work represents the first example of structural elucidation of NH<sub>3</sub> binding in MOFs containing open metal sites and will inform the design of new efficient MOF sorbents by targeted control of active sites for NH<sub>3</sub> capture and storage.



## INTRODUCTION

Ammonia (NH<sub>3</sub>) is a major feedstock in the agricultural and chemical industries,<sup>1</sup> but due to its toxic and corrosive nature, storage and transport of NH<sub>3</sub> in large quantities is challenging.<sup>2</sup> It is therefore of great interest to develop efficient sorbent materials that show significant chemical and physical stability and high adsorption capacity for NH<sub>3</sub>. Conventional sorbents, including zeolites,<sup>3</sup> activated carbons,<sup>4</sup> mesoporous silica,<sup>5</sup> and resins,<sup>6</sup> have been studied for NH<sub>3</sub> adsorption, but they show limited capacities and often undergo irreversible structural degradation upon desorption. In addition, fine-tuning and directed chemical manipulation of active sites in these materials at the atomic level can be problematic due to the lack of direct structural insights and limited structural diversity.

Porous metal–organic framework (MOF) materials adopt well-defined structures, are designable, and can show exceptional structural diversity, enabling the control of active sites at atomic precision.<sup>7–10</sup> Structural defects and open metal sites in MOFs are widely considered and used as active sites for binding of guest molecules.<sup>11–18</sup> A variety of MOFs incorporating open metal sites or defects, such as [M<sub>2</sub>(dobpdc)] (dobpdc<sup>4-</sup> = 4,4-dioxidobi-phenyl-3,3-dicarboxylate),<sup>2</sup> Cu<sub>2</sub>Cl<sub>2</sub>(BBTA) [BBTA = 1*H*,5*H*-benzo(1,2-*d*),

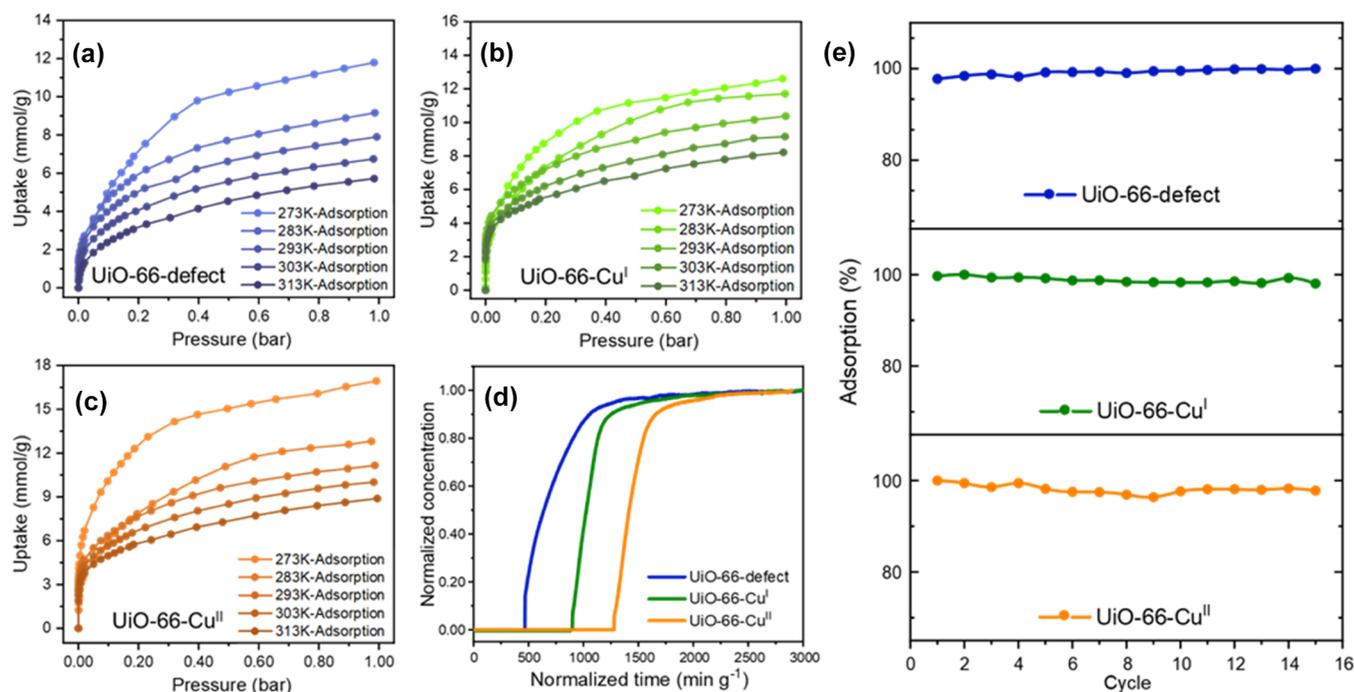
(4,5-*d'*)bistriazole],<sup>19</sup> HKUST-1,<sup>20</sup> and UiO-67,<sup>21</sup> have been reported for NH<sub>3</sub> adsorption. However, it remains highly challenging to identify the precise role of these active sites in binding NH<sub>3</sub> molecules, not least because of the relative invisibility of protons in NH<sub>3</sub> by X-ray diffraction and the complex and rapid host–guest dynamics involved in NH<sub>3</sub> binding. Revealing such insights will enable targeted control of active sites and thus deliver efficient NH<sub>3</sub> stores by design. This will further inform the development of next-generation catalysts for the cracking of NH<sub>3</sub> for portable applications relating to the hydrogen economy.

Here, we report the study of binding domains and dynamics of NH<sub>3</sub> within UiO-66-defect (UiO-66 with a missing carboxylate ligand), UiO-66-Cu<sup>I</sup>, and UiO-66-Cu<sup>II</sup> based upon the direct observation of the location of atomically

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**Figure 1.** Adsorption isotherms for  $\text{NH}_3$  in (a) UiO-66-defect, (b) UiO-66- $\text{Cu}^{\text{I}}$ , and (c) UiO-66- $\text{Cu}^{\text{II}}$  from 273 to 313 K. (d) Breakthrough curves at 298 K of  $\text{NH}_3$  (630 ppm of  $\text{NH}_3$  diluted in He) through a fixed-bed packed with UiO-66-defect, UiO-66- $\text{Cu}^{\text{I}}$ , and UiO-66- $\text{Cu}^{\text{II}}$ . (e) Cycles of pressure-swing sorption of  $\text{NH}_3$  at 298 K between 0 and 0.15 bar in UiO-66-defect, UiO-66- $\text{Cu}^{\text{I}}$ , and UiO-66- $\text{Cu}^{\text{II}}$ .

dispersed active sites and their interactions with  $\text{NH}_3$  molecules. The robustness of the framework in UiO-66 makes it an ideal platform for the study of  $\text{NH}_3$  adsorption, and the incorporation of open Cu(II) sites can provide further strong binding and activation sites. Compared with UiO-66-defect, UiO-66- $\text{Cu}^{\text{II}}$  shows significant enhancement of static (11.8 and 16.9  $\text{mmol g}^{-1}$ , respectively, at 273 K and 1.0 bar) and dynamic (2.07 and 4.15  $\text{mmol g}^{-1}$ , respectively, at 298 K and at 630 ppm concentrations) adsorption of  $\text{NH}_3$ , thus serving as a top-performing  $\text{NH}_3$  sorbent. *In situ* neutron powder diffraction (NPD), inelastic neutron scattering (INS), coupled with density functional theory (DFT) modeling, electron paramagnetic resonance (EPR), solid-state nuclear magnetic resonance (ssNMR), infrared (IR), and ultraviolet–visible (UV–vis) absorption spectroscopies reveal the presence of reversible  $\{\text{Cu}(\text{II})\cdots\text{NH}_3\}$  interactions that underpin the observed high and reversible  $\text{NH}_3$  uptake.

## EXPERIMENTAL SECTION

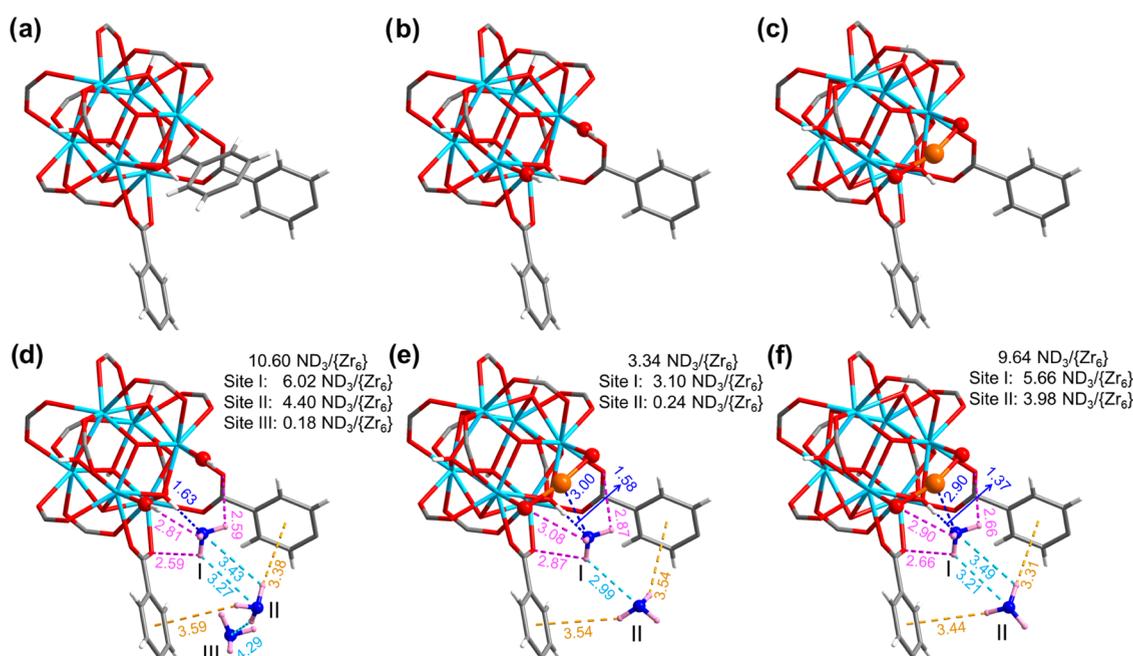
**$\text{NH}_3$  Adsorption Isotherms and Cycling Experiment.** The synthesis and activation of MOF materials have been reported in our previous study<sup>22</sup> and are described in detail in the Supporting Information. Static adsorption isotherms (0–1.0 bar) for  $\text{NH}_3$  were measured on IGA (intelligent gravimetric analyzer, Hidden Isochema, Warrington, U.K.). Desolvated samples of UiO-66-defect, UiO-66- $\text{Cu}^{\text{I}}$ , and UiO-66- $\text{Cu}^{\text{II}}$  were generated *in situ* under dynamic vacuum ( $1 \times 10^{-8}$  mbar) at 393 K for 24 h.  $\text{NH}_3$  (research-grade) was purchased from BOC and used as received. For cycling experiments, the pressure of  $\text{NH}_3$  was increased from vacuum ( $1 \times 10^{-8}$  mbar) to 150 mbar and the uptake was recorded. The pressure was then reduced to regenerate the sample with no assisted heating. This cycling process was repeated for 15 cycles.

**Neutron Powder Diffraction (NPD).** The binding positions of  $\text{ND}_3$  within UiO-66-defect and UiO-66- $\text{Cu}^{\text{II}}$  were determined by NPD experiments at WISH, a long-wavelength powder and single-crystal neutron diffractometer at the ISIS Facility at the Rutherford

Appleton Laboratory (U.K.).<sup>23</sup> Prior to NPD measurements, the sample was activated by heating at 393 K under dynamic vacuum for 16 h, and the desolvated samples were then transferred into cylindrical vanadium sample cells with an indium seal. The samples were further degassed at 373 K under dynamic vacuum to remove the remaining trace guest water molecules. Dosing of  $\text{ND}_3$  was carried out volumetrically at room temperature to ensure that  $\text{ND}_3$  was present in the gas phase when not adsorbed and to ensure sufficient mobility of  $\text{ND}_3$  inside the MOF framework. The temperature during data collection was controlled using a helium (He) cryostat ( $7 \pm 0.2$  K). The quality of the Rietveld refinements has been assured with low goodness-of-fit (Gof) factors, low weighted profile factors ( $R_{\text{wp}}$ ), and well-fitted patterns with reasonable isotropic displacement factors.

**Inelastic Neutron Scattering (INS).** INS experiments were performed at TOSCA neutron spectrometer at the ISIS Facility at the Rutherford Appleton Laboratory (U.K.).<sup>24</sup> Desolvated UiO-66-defect and UiO-66- $\text{Cu}^{\text{II}}$  materials were loaded into cylindrical vanadium sample cells with an indium seal and degassed at 373 K under dynamic vacuum to remove the remaining trace guest water molecules. The temperature during data collection was controlled using a He cryostat ( $7 \pm 0.2$  K). The loading of  $\text{NH}_3$  was performed volumetrically at room temperature, and background spectra of bare MOF samples were subtracted to obtain the difference spectra.

**Solid-State Nuclear Magnetic Resonance (ssNMR) Spectroscopy.** Magic angle spinning (MAS) NMR spectra were recorded using a Bruker 9.4 T (400 MHz  $^1\text{H}$  Larmor frequency) AVANCE III spectrometer equipped with a 4 mm HFX MAS probe. Samples were desolvated and packed into 4 mm o.d. zirconia rotors under inert conditions and sealed with a Kel-F rotor cap. Experiments were carried out at ambient temperature using a MAS frequency of 12 kHz.  $^1\text{H}$ -pulses of 100 kHz and  $^{13}\text{C}$ -pulses of 50 kHz were used, and  $^{13}\text{C}$  spin-locking at  $\sim 50$  kHz was applied for 2 ms, with corresponding ramped (70–100%)  $^1\text{H}$  spin-locking at  $\sim 73$  kHz for CP experiments and with 100 kHz of SPINAL-64<sup>25</sup> heteronuclear  $^1\text{H}$  decoupling throughout signal acquisition. Then, 640–8192 transients were co-added for the CPMAS NMR spectra, depending on the sample.  $^1\text{H}$  Hahn echo spectra used an inter-pulse delay of one rotor period, giving a total echo time of 0.167 ms. For the two-dimensional (2D)  $^1\text{H}$ – $^{13}\text{C}$  FSLG-HETCOR<sup>26</sup> dipolar correlation experiment, 2304



**Figure 2.** Structures of  $\{\text{Zr}_6\}$  clusters in UiO-66 (a) without and (b) with a defect site in terms of a missing ligand and (c) in UiO-66- $\text{Cu}^{\text{II}}$ . Views of the binding sites of  $\text{ND}_3$  in (d) UiO-66-defect and UiO-66- $\text{Cu}^{\text{II}}$  at (e) low and (f) high loadings, respectively. All structures were derived from Rietveld refinements of the NPD data collected at 7 K (C, gray; O, red; Zr, sky blue; Cu, orange; H, white; N, blue; D, pink).

transients were acquired for each of 32 complex  $t_1$  increments and a CP contact time of 0.5 ms was employed.

**Electron Paramagnetic Resonance (EPR) Spectroscopy.** CW EPR spectra were measured with a Bruker EMX 300 EPR spectrometer equipped with a high sensitivity X-band (*ca.* 9.4 GHz) resonator and a liquid He cryostat. The spectra were recorded at a microwave power of 0.0022–2.2 mW, modulation frequency 100 kHz, and modulation amplitude 5 G. Field corrections were applied by measuring relevant EPR standards (Bruker Strong Pitch and DPPH). Pulsed EPR measurements were performed at X-band (*ca.* 9.7 GHz) on a Bruker ElexSys E580 spectrometer. The microwave frequency was measured with a built-in digital counter, and the magnetic field was calibrated using a Bruker strong pitch reference sample.

## RESULTS AND DISCUSSION

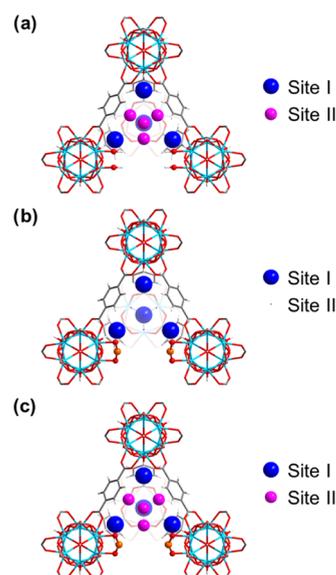
**$\text{NH}_3$  Adsorption Analysis.** Desolvated UiO-66-defect, UiO-66- $\text{Cu}^{\text{I}}$ , and UiO-66- $\text{Cu}^{\text{II}}$  display BET surface areas of 1135, 1111, and 1124  $\text{m}^2 \text{g}^{-1}$ , respectively (Table S1). Thus, the variation of active sites in the pore interior has little impact on the porosity of resultant UiO-66 materials. X-ray absorption fine structure (XAFS) spectroscopy of UiO-66- $\text{Cu}^{\text{II}}$  (Figure S2) shows a lower intensity for the features at a long distance ( $\sim 2.5$  Å) in the Fourier transform of the  $k^2$ -weighted data compared with that for  $\text{CuO}$  as a reference material. This strongly suggests that the  $\text{Cu}(\text{II})$  sites in UiO-66- $\text{Cu}^{\text{II}}$  are atomically dispersed,<sup>22,27</sup> in full agreement with the EPR spectroscopic results, which confirmed the absence of aggregated (long-range magnetically coupled) or binuclear ( $S = 1$ )  $\text{Cu}(\text{II})$  species in UiO-66- $\text{Cu}^{\text{II}}$ .<sup>22</sup> At 273 K and 1.0 bar, UiO-66-defect, UiO-66- $\text{Cu}^{\text{I}}$ , and UiO-66- $\text{Cu}^{\text{II}}$  exhibit  $\text{NH}_3$  uptakes of 11.8, 12.6, and 16.9  $\text{mmol g}^{-1}$  (Figure 1a–c), respectively, comparable with state-of-the-art materials (Table S7). The isotherms display apparent hysteresis loops (Figure S3), indicating the presence of strong host–guest interactions at the binding sites within the two types of cages of the framework (tetrahedral and octahedral cages with diameters of

7 and 9 Å, respectively). UiO-66-defect, UiO-66- $\text{Cu}^{\text{I}}$ , and UiO-66- $\text{Cu}^{\text{II}}$  show high packing density of  $\text{NH}_3$  of 0.52, 0.55, and 0.74  $\text{g cm}^{-3}$ , respectively, demonstrating efficient volumetric storage of  $\text{NH}_3$  (Table S3). It is worth noting that the packing density of UiO-66- $\text{Cu}^{\text{II}}$  is comparable to that of liquid  $\text{NH}_3$  (0.68  $\text{g cm}^{-3}$ ) at 240 K. All three MOFs show high stability toward pressure-swing  $\text{NH}_3$  adsorption with retention of the structure, porosity, and  $\text{NH}_3$  uptakes over at least 15 cycles (Figures 1e, S1, S4, and S6). This is in direct contrast to reported MOFs incorporating four- or five-coordinated open  $\text{Cu}(\text{II})$  sites that lead to irreversible sorption of  $\text{NH}_3$  and structural degradation upon desorption.<sup>19,28–30</sup> Upon desorption under pressure-swing conditions, higher residues of  $\text{NH}_3$  in UiO-66- $\text{Cu}^{\text{I}}$  and UiO-66- $\text{Cu}^{\text{II}}$  (49–67%) were observed compared with UiO-66-defect (27–30%), attributed to the interactions between  $\text{NH}_3$  molecules and  $\text{Cu}$  sites (*vide infra*). The residual  $\text{NH}_3$  in all three systems can be fully released *via* heating, reflecting a relatively strong binding of  $\text{NH}_3$  in these MOFs. The excellent ability of UiO-66-defect, UiO-66- $\text{Cu}^{\text{I}}$ , and UiO-66- $\text{Cu}^{\text{II}}$  to capture  $\text{NH}_3$  at low concentrations (630 ppm) has been confirmed by dynamic breakthrough experiments at 298 K, where the dynamic  $\text{NH}_3$  uptakes were calculated to be 2.07, 3.07, and 4.15  $\text{mmol g}^{-1}$ , respectively (Figure 1d). The introduction of  $\text{Cu}(\text{II})$  sites leads to 100% enhancement of the dynamic  $\text{NH}_3$  adsorption capacity at low concentrations, which is highly desirable for the capture of  $\text{NH}_3$  as a pollutant and/or at low concentrations. With increasing loading of  $\text{NH}_3$ , the isosteric heat of adsorption ( $Q_{\text{st}}$ ) increases, and the adsorption entropy ( $\Delta S$ ) decreases for all three MOFs, indicating the presence of strong intermolecular interactions and ordering of adsorbed  $\text{NH}_3$  molecules in the pore (Figure S5). As expected, UiO-66- $\text{Cu}^{\text{II}}$  shows higher  $Q_{\text{st}}$  than UiO-66-defect and UiO-66- $\text{Cu}^{\text{I}}$  (up to 55, 40, and 35  $\text{kJ mol}^{-1}$ , respectively).

**Determination of the Binding Sites for Adsorbed  $\text{ND}_3$ .** Rietveld refinements of the *in situ* NPD data collected at

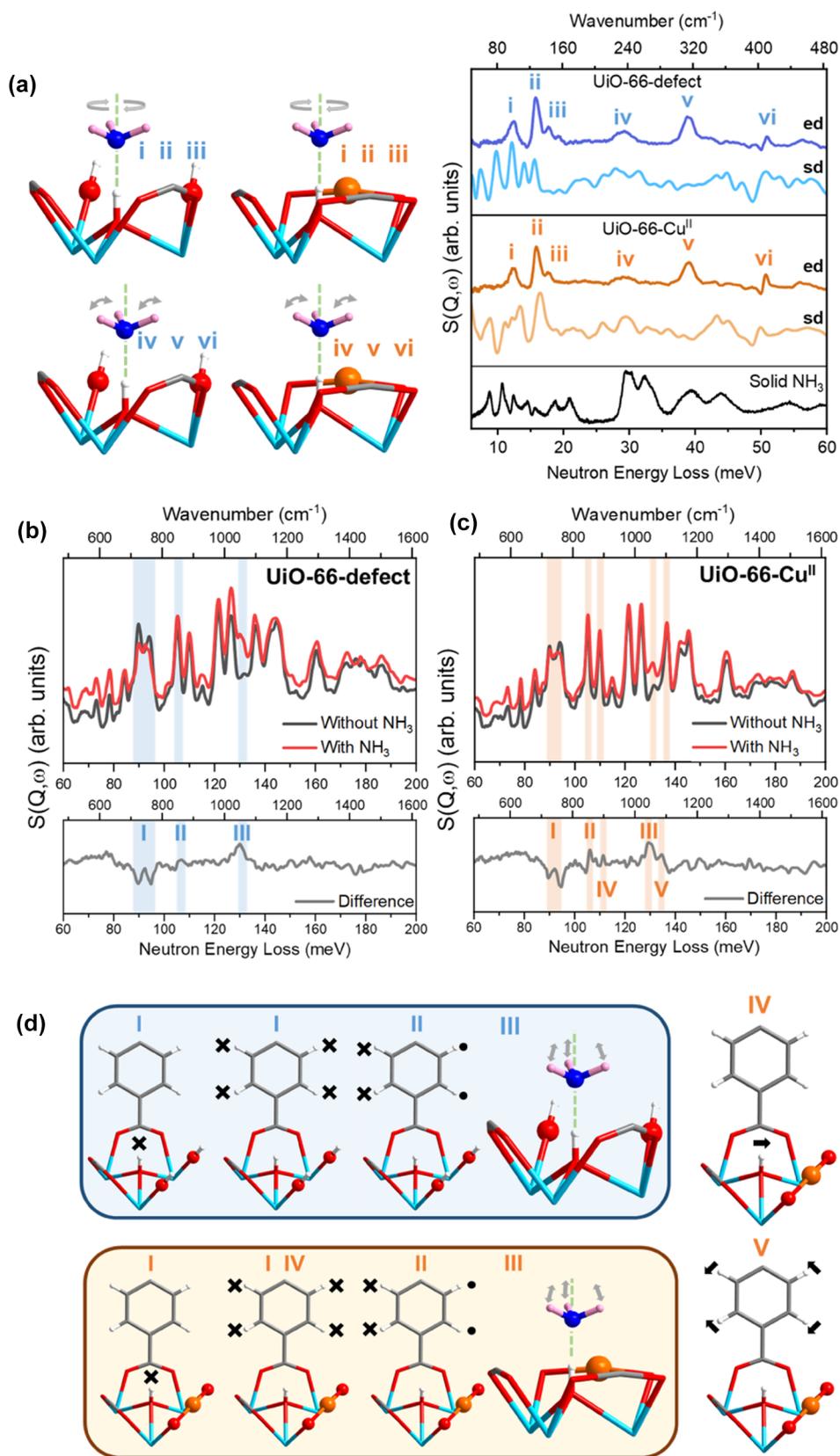
7 K illustrate the binding of  $\text{ND}_3$  to the  $-\text{OH}$  defect site in  $\text{UiO-66-defect-10.6ND}_3$  and to the atomically dispersed  $\text{Cu(II)}$  sites in  $\text{UiO-66-Cu}^{\text{II}}\cdot 3.34\text{ND}_3$  and  $\text{UiO-66-Cu}^{\text{II}}\cdot 9.64\text{ND}_3$ . An additional low loading of  $\text{ND}_3$  was conducted for  $\text{UiO-66-Cu}^{\text{II}}$  to better elucidate the precise role of  $\text{Cu(II)}$  sites in binding  $\text{ND}_3$  at low concentrations. The structures of bare  $\text{UiO-66}$  with and without a defect site are shown in Figures 2b and 2a, respectively. In  $\text{UiO-66-defect-10.6ND}_3$ , three distinct binding sites (I, II, and III) are found (Figures 2d and S14). The primary binding site (Site I) of  $\text{ND}_3$  (occupancy of  $6.02 \text{ ND}_3/\{\text{Zr}_6\}$ ) is anchored by two  $-\text{OH}$  groups at the defect site, forming a series of strong host–guest hydrogen bonds to the  $\mu_3\text{-OH}$  and defect  $-\text{OH}$  groups [ $\text{O}_{\mu_3}\text{-H}\cdots\text{ND}_3 = 1.63(8) \text{ \AA}$ ;  $\text{ND}_3\cdots\text{O}_{\text{defect}}\text{-H} = 2.81(7) \text{ \AA}$ ; and  $\text{ND}_3\cdots\text{O}_{\text{carboxylate}} = 2.59(1) \text{ \AA}$ ]. Compared with the  $\text{ND}_3@ \text{UiO-66}$ ,<sup>21</sup> a stronger hydrogen bond between the defect  $-\text{OH}$  groups and  $\text{ND}_3$  molecules is observed in  $\text{ND}_3@ \text{UiO-66-defect}$  [ $\text{O}_{\mu_3}\text{-H}\cdots\text{ND}_3 = 1.96(1)$  and  $1.63(8) \text{ \AA}$ , respectively], resulting in higher  $\text{NH}_3$  uptake (8.4 and  $11.8 \text{ mmol g}^{-1}$ , respectively). Site II (occupancy of  $4.40 \text{ ND}_3/\{\text{Zr}_6\}$ ) is bound to the framework mainly *via* electrostatic interactions [ $\text{ND}_3\cdots$  aromatic rings =  $3.38(12)\text{--}3.59(29) \text{ \AA}$ ], further supplemented by intermolecular hydrogen bonding between adsorbed  $\text{ND}_3$  molecules [ $\text{ND}_3^{\text{I}}\cdots\text{ND}_3^{\text{II}} = 3.27(1)\text{--}3.43(32) \text{ \AA}$ ]. Site III (occupancy of  $0.18 \text{ ND}_3/\{\text{Zr}_6\}$ ) exhibits no direct interaction with the framework and is stabilized by the interaction with adjacent  $\text{ND}_3$  molecules at Site II through hydrogen bonding [ $\text{ND}_3^{\text{II}}\cdots\text{ND}_3^{\text{III}} = 4.29(13) \text{ \AA}$ ].

The  $\text{Cu(II)}$  ion in  $\text{UiO-66-Cu}^{\text{II}}$  binds to two oxygen centers and shows a near-linear coordination geometry (Figure 2c). The crystal structures for  $\text{UiO-66-Cu}^{\text{II}}\cdot 3.34\text{ND}_3$  and  $\text{UiO-66-Cu}^{\text{II}}\cdot 9.64\text{ND}_3$  determined by NPD both show two binding sites (Figures 2e,f and S15). Site I is anchored simultaneously by the  $\text{Cu(II)}$  site [ $\text{Cu}^{\text{II}}\cdots\text{ND}_3 = 2.90(8)\text{--}3.00(6) \text{ \AA}$ ] and adjacent hydroxyl groups *via* hydrogen bonding [ $\text{O}_{\mu_3}\text{-H}\cdots\text{ND}_3 = 1.37(42)\text{--}1.58(1) \text{ \AA}$ ;  $\text{ND}_3\cdots\text{O}_{\text{defect}} = 2.90(3)\text{--}3.08(2) \text{ \AA}$ ;  $\text{ND}_3\cdots\text{O}_{\text{carboxylate}} = 2.66(3)\text{--}2.87(1) \text{ \AA}$ ]. Site II is stabilized through electrostatic interactions [ $\text{ND}_3\cdots$  aromatic rings =  $3.31(27)\text{--}3.54(39) \text{ \AA}$ ], supplemented by intermolecular hydrogen bonding with surrounding  $\text{ND}_3$  molecules [ $\text{ND}_3^{\text{I}}\cdots\text{ND}_3^{\text{II}} = 2.99(3)\text{--}3.49(59) \text{ \AA}$ ]. At higher  $\text{ND}_3$  loading, the occupancy of  $\text{ND}_3$  molecules at Site I increases by 83% from 3.10 to  $5.66 \text{ ND}_3/\{\text{Zr}_6\}$ . In contrast, the occupancy increases by *ca.* 16 times at Site II from 0.24 to  $3.98 \text{ ND}_3/\{\text{Zr}_6\}$  (Figure 3), unambiguously demonstrating the critical role of unique  $\text{Cu(II)}$  sites in binding  $\text{ND}_3$  at low concentrations, consistent with the ultrahigh dynamic uptake of  $\text{NH}_3$  at low concentrations. The overall binding distances decrease slightly upon increased loading, indicating stronger host–guest interactions between  $\text{ND}_3$  and the framework. Interestingly, hydrogen/deuterium (H/D) site-exchange<sup>31,32</sup> is also observed between the  $\mu_3\text{-OH}$  group and adsorbed  $\text{ND}_3$  molecules in both  $\text{UiO-66-defect}$  and  $\text{UiO-66-Cu}^{\text{II}}$ , suggesting the direct interaction *via* proton exchange between  $\text{ND}_3$  and  $\mu_3\text{-OH}$ . Cooperative  $\{\text{ND}_3\}_\infty$  networks are observed in both systems with intermolecular hydrogen bonds [ $\text{ND}_3\cdots\text{ND}_3 = 2.99(3)\text{--}4.29(13) \text{ \AA}$ ; Figures 3, S14, and S15]. This is reminiscent of the structure of condensed  $\text{ND}_3$  in solid state, and is consistent also with the observed increase in  $Q_{\text{st}}$  with increasing loading of  $\text{NH}_3$  between 3.0 and  $6.7 \text{ mmol g}^{-1}$ . Importantly, this study represents the first example of structural elucidation of  $\text{NH}_3$  binding in MOFs containing open metal sites.

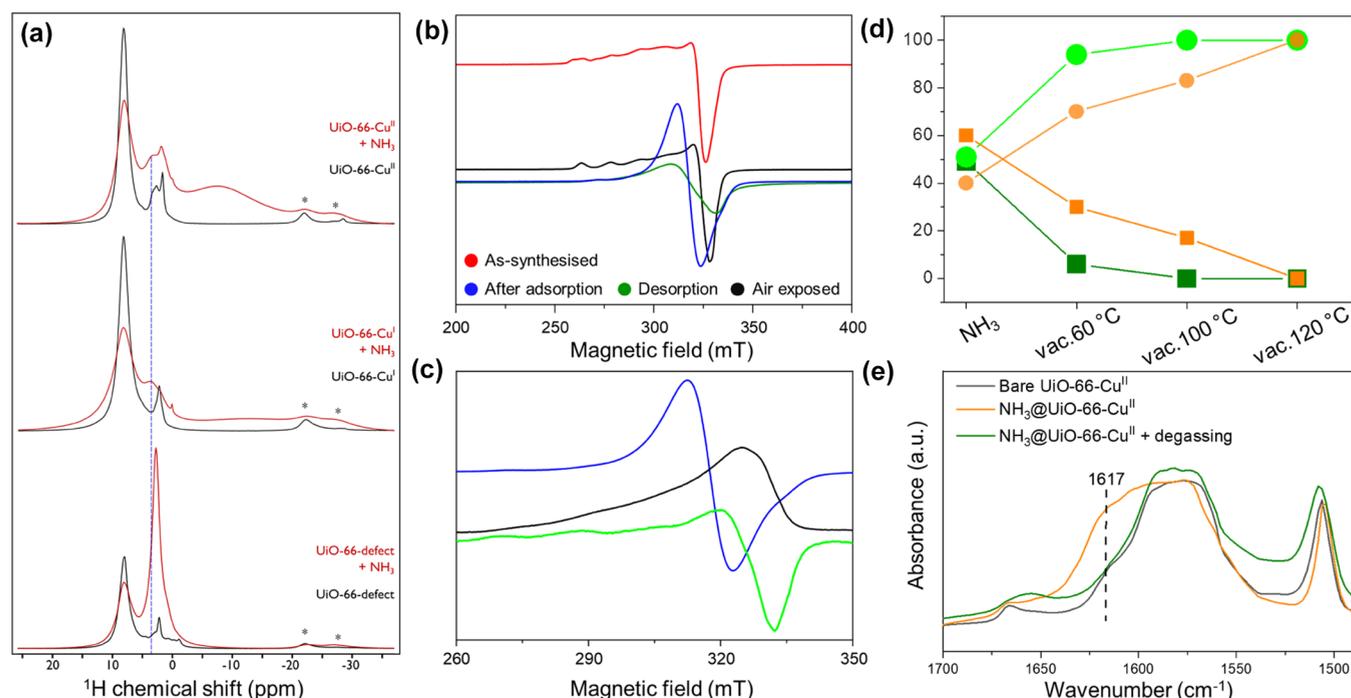


**Figure 3.** Distribution of adsorbed  $\text{ND}_3$  molecules within the tetrahedral cage in (a)  $\text{UiO-66-defect-10.6ND}_3$ , (b)  $\text{UiO-66-Cu}^{\text{II}}\cdot 3.34\text{ND}_3$ , and (c)  $\text{UiO-66-Cu}^{\text{II}}\cdot 9.64\text{ND}_3$  as determined from the refinement of NPD data. The radii of the colored balls of Site I (blue) and Site II (pink) are proportional to their crystallographic occupancies. (a)  $6.02 \text{ ND}_3/\{\text{Zr}_6\}$  for Site I and  $4.40 \text{ ND}_3/\{\text{Zr}_6\}$  for site II; (b)  $3.10 \text{ ND}_3/\{\text{Zr}_6\}$  for Site I and  $0.24 \text{ ND}_3/\{\text{Zr}_6\}$  for Site II; (c)  $5.66 \text{ ND}_3/\{\text{Zr}_6\}$  for Site I and  $3.98 \text{ ND}_3/\{\text{Zr}_6\}$  for Site II.

**Studies of Host–Guest Binding Dynamics.** By combining *in situ* INS and DFT calculations, the vibrational modes of adsorbed  $\text{NH}_3$  molecules and that of the framework host can be deconvoluted and assigned to interpret the rapid dynamics of the system. The experimental and simulated INS spectra showed excellent agreement for bare and  $\text{NH}_3$ -loaded  $\text{UiO-66-defect}$  and bare and  $\text{NH}_3$ -loaded  $\text{UiO-66-Cu}^{\text{II}}$ . By subtracting the spectra of the MOF and sample cell from the  $\text{NH}_3$ -loaded samples, difference INS spectra can be obtained. For the loading of  $2\text{NH}_3$  per  $\{\text{Zr}_6\}$  cluster, the  $\text{NH}_3$  molecules are primarily adsorbed at Site I (Figure 4a). In  $\text{UiO-66-defect}$  and  $\text{UiO-66-Cu}^{\text{II}}$ , librational modes of adsorbed  $\text{NH}_3$  molecules around its  $C_3$  axis are observed at 15.8 and 17.7 meV. The peaks at 29.3, 38.8, and 51.0 meV in  $\text{NH}_3$ -loaded  $\text{UiO-66-defect}$  (29.4, 39.1, and 50.7 meV in  $\text{UiO-66-Cu}^{\text{II}}$ ) correspond to the rocking motions of  $\text{NH}_3$  around the N center. The significant red shift of these peaks compared to solid  $\text{NH}_3$  (librational modes at 29.4–32.3 meV; rocking modes at 39.3–54.4 meV) are attributed to the rotational flexibility of  $\text{NH}_3$  in its adsorbed local environment, in contrast to the  $\text{NH}_3$  molecules in the solid state connected by the three-dimensional hydrogen-bonding network. The peaks (or dips) in the experimental difference INS spectra in the high energy region, mostly corresponding to variations of system dynamics upon  $\text{NH}_3$  binding, are also assigned (Figure 4b–d). Three changes are observed in both  $\text{UiO-66-defect}$  and  $\text{UiO-66-Cu}^{\text{II}}$  systems on loading with  $\text{NH}_3$  corresponding to the following vibrational modes: (I) at 92.3 meV, the  $\mu_3\text{-OH}$  in  $\text{Zr-O-H}$  plane bending and  $\text{H-C}$  out- $C_6$ -plane deformation; (II) at 105 meV, the  $\text{H-C}$  out- $C_6$ -plane deformation; (III) at 130 meV,  $\text{NH}_3$  umbrella motion. For  $\text{UiO-66-Cu}^{\text{II}}$ , two extra changes are observed in the difference spectrum and they correspond to (IV) at 110 meV, the  $\mu_3\text{-OH}$  out of  $\text{Zr-O-H}$  plane bending and  $\text{H-C}$  out- $C_6$ -plane deformation, and (V) at 137 meV, the



**Figure 4.** Views of *in situ* INS spectra, the DFT-calculated spectra, and the corresponding vibrational modes for UiO-66-defect and UiO-66-Cu<sup>II</sup>, before and after NH<sub>3</sub> loading. Difference spectra were obtained by subtraction of the INS spectra of the bare MOF from that for the NH<sub>3</sub>-loaded MOF and are marked as ed (experimental difference spectra) and sd (simulated difference spectra). (a) Comparison of vibrational modes between solid NH<sub>3</sub> at 7 K (8.7–21.0 meV translational modes; 29.4–32.3 meV librational modes; 39.3–54.4 meV rocking modes), and adsorbed NH<sub>3</sub> in the MOF. (b, c) Experimental difference INS spectra for UiO-66-defect and UiO-66-Cu<sup>II</sup> upon NH<sub>3</sub> adsorption in the higher energy range. (d) Selected vibrational modes of UiO-66-defect and UiO-66-Cu<sup>II</sup>.



**Figure 5.** (a)  $^1\text{H}$  DEPTH MAS NMR spectra of bare (black) and  $\text{NH}_3$ -loaded (red) UiO-66-defect (bottom), UiO-66- $\text{Cu}^{\text{I}}$  (middle), and UiO-66- $\text{Cu}^{\text{II}}$  (top). The spectra were recorded at 9.4 T using a MAS frequency of 12 kHz. The dashed vertical blue line highlights the signal from pore-confined  $\text{NH}_3$  in the UiO-66- $\text{Cu}^{\text{I}}$  and UiO-66- $\text{Cu}^{\text{II}}$  samples, and the asterisks denote the position of spinning sidebands. (b) X-band (9.4 GHz) EPR spectra of UiO-66- $\text{Cu}^{\text{II}}$  recorded at 40 K before adsorption of  $\text{NH}_3$  (red, pre-activated solvated form), after adsorption of  $\text{NH}_3$  (blue), desorption of  $\text{NH}_3$  (green), and after exposure to the air for more than 24 h (black). (c) X-band (9.4 GHz) EPR spectra of UiO-66- $\text{Cu}^{\text{II}}$  at 6 K after  $\text{NH}_3$  loading. Blue: CW spectra; black: echo-detected spectra recorded with  $\pi/2 = 16$  ns and  $\tau = 150$  ns; and light green: derivative of echo-detected spectra recorded with  $\pi/2 = 16$  ns and  $\tau = 150$  ns. (d) Relative quantities of the broad (square, orange and deep green) and isolated Cu(II) (circle, light orange and lime green) EPR signals upon degassing  $\text{NH}_3$ @UiO-66- $\text{Cu}^{\text{II}}$  (orange) and  $\text{NH}_3$ @UiO-66- $\text{Cu}^{\text{I}}$  (green) with heating under dynamic vacuum (see SI for details). (e) *In situ* infrared spectra of UiO-66- $\text{Cu}^{\text{II}}$  upon adsorption and desorption of  $\text{NH}_3$ .

H–C in- $\text{C}_6$ -plane bending. The introduction of Cu(II) sites to the structural defects contributes to an increase of the acidity at the  $\mu_3$ -OH moiety with stronger  $\mu_3$ -OH out-of-plane (Zr–O–H) bending in UiO-66- $\text{Cu}^{\text{II}}$  upon  $\text{NH}_3$  adsorption, as evidenced by peak IV. This is in excellent agreement with the shorter distance of O–H $\cdots$  $\text{ND}_3$  hydrogen bonds observed in the NPD study [ $\text{O}_{\mu_3}$ -H $\cdots$  $\text{ND}_3$  of 1.58(1) and 1.63(8) Å in UiO-66- $\text{Cu}^{\text{II}}$  and UiO-66-defect, respectively]. Compared with UiO-66-defect, a slight increase in the intensity of the H–C in- $\text{C}_6$ -plane bending peak is observed in UiO-66- $\text{Cu}^{\text{II}}$  (peak V), which could be related to the shorter distance between  $\text{NH}_3$  and the aromatic ring in this system [ $\text{ND}_3$  $\cdots$ aromatic ring of 3.49(1) Å in UiO-66- $\text{Cu}^{\text{II}}$  and 3.53(1) Å in UiO-66-defect]. Overall, the INS/DFT results afford excellent agreement with the structural models derived from NPD data and new insights into the binding dynamics of  $\text{NH}_3$  in these decorated MOFs.

**Investigation of the Host–Guest Interactions.** *In situ* infrared and ssNMR experiments were carried out to further investigate the interactions of  $\text{NH}_3$  in these porous materials. Upon introduction of  $\text{NH}_3$ , depletion of the O–H stretching bands at 3673 and 3646  $\text{cm}^{-1}$  was observed (Figure S16), consistent with the binding of  $\text{NH}_3$  molecules to  $\mu_3$ -OH and defect –OH sites. Interestingly, an additional band was observed at 1617  $\text{cm}^{-1}$  for  $\text{NH}_3$ -loaded UiO-66- $\text{Cu}^{\text{II}}$  (Figure 5e) assigned to asymmetric vibration of adsorbed  $\text{NH}_3$  molecules on Lewis acid sites [Cu(II) in this case].<sup>33–35</sup> The presence of possible charge transfer between Cu(II) sites and bound  $\text{NH}_3$  molecules has been confirmed by *in situ* UV–vis spectra, which show an additional broad absorption band

centered at around 680 nm in  $\text{NH}_3$ -loaded UiO-66- $\text{Cu}^{\text{II}}$  (Figure S17).<sup>36</sup> The presence of strong binding of  $\text{NH}_3$  to Cu(I) and Cu(II) sites was also confirmed by temperature-programmed desorption of  $\text{NH}_3$  ( $\text{NH}_3$ -TPD) (Figure S18) and  $^1\text{H}$  ssNMR spectroscopy (Figure 5a). The additional TPD peaks at higher temperatures (150–300 °C, Figure S18b) for UiO-66- $\text{Cu}^{\text{I}}$  and UiO-66- $\text{Cu}^{\text{II}}$ , which are not observed in UiO-66-defect, indicate stronger binding of  $\text{NH}_3$  at these Cu sites. In addition, the desorption peaks for UiO-66- $\text{Cu}^{\text{II}}$  appear at higher temperatures compared with those of UiO-66- $\text{Cu}^{\text{I}}$ , suggesting a stronger {Cu(II) $\cdots$  $\text{NH}_3$ } interaction than {Cu(I) $\cdots$  $\text{NH}_3$ }, consistent with the adsorption and breakthrough results. These conclusions are supported further by the corresponding  $^1\text{H}$  magic angle spinning (MAS) NMR spectra of the  $\text{NH}_3$ -loaded materials (Figure 5a). For UiO-66-defect, a large narrow signal from  $\text{NH}_3$  is observed (FWHM  $\sim$  650 Hz, centered at  $\delta\{^1\text{H}\} = 2.8$  ppm), suggesting rapid relative motion of  $\text{NH}_3$  in the pores. For UiO-66- $\text{Cu}^{\text{II}}$  and UiO-66- $\text{Cu}^{\text{I}}$ , this large peak is absent but a broad signal (FWHM  $\sim$  2 kHz, centered at  $\delta\{^1\text{H}\} = 3.7$  ppm) is present that stems from pore-confined  $\text{NH}_3$  (Figure S19). Furthermore, for UiO-66- $\text{Cu}^{\text{I}}$  and UiO-66- $\text{Cu}^{\text{II}}$ , very broad signals are observed at negative chemical shifts (FWHM  $\sim$  7 kHz, centered at  $\delta\{^1\text{H}\} = -7.6$  ppm for UiO-66- $\text{Cu}^{\text{II}}$  and  $\delta\{^1\text{H}\} = -15.0$  ppm for UiO-66- $\text{Cu}^{\text{I}}$ ) corresponding to metal-bound  $\text{NH}_3$ ,<sup>37</sup> again consistent with the infrared and UV–vis spectroscopic studies. One-dimensional (1D)  $^{13}\text{C}$  and 2D  $^1\text{H}$ – $^{13}\text{C}$  dipolar correlation MAS NMR spectra (Figure S19) also indicate a hydrogen-

bonding interaction between  $\text{NH}_3$  molecules and the carboxylate moieties from the organic linkers of the MOFs.

The strong interaction between  $\text{NH}_3$  and Cu(II) site was further elucidated by EPR spectroscopy. UiO-66-Cu<sup>II</sup> in its hydrated form has an X-band continuous wave (CW) EPR spectrum (Figure 5b), with axial (within the resolution of the experiment) spin Hamiltonian parameters [ $g_{x,y} = 2.074$ ,  $g_z = 2.320$ ,  $A_{z(\text{Cu})} = 480$  MHz], typical of isolated Cu(II) ions with a  $d_{x^2-y^2}$  or  $d_{xy}$  ground state and consistent with water coordinated in the  $xy$  plane; the latter is confirmed by HYSCORE measurements.<sup>22</sup> Dehydration of the sample leads to loss of the coordinated water (Figures S20, S21, and S23) and significant intensity loss in the CW EPR spectrum.<sup>22</sup> This phenomenon has been observed in several Cu(II)-doped zeolites [without reduction to Cu(I)], attributed to unusual low-coordinate geometries that can lead to near-degenerate ground states.<sup>38</sup> This is also consistent with the NPD model that suggests a pseudo-linear geometry at the Cu(II) site (Figure 2c) and with the observation that the spectra (CW EPR, HYSCORE) of the solvated system are not restored by exposure to dry  $\text{O}_2$  but are restored by exposure to air *via* the uptake of moisture.

Adsorption of  $\text{NH}_3$  in an activated sample of UiO-66-Cu<sup>II</sup> led to the recovery of the intensity of the signal within the CW EPR spectrum, indicating that the adsorbed  $\text{NH}_3$  interacts with the Cu(II) sites. Two components are observed: (i) an isolated Cu(II) signal with modified parameters [ $g_{x,y} = 2.07$ ,  $g_z = 2.27$ ,  $A_{z(\text{Cu})} = 530$  MHz] and (ii) an unresolved, broad signal at  $g \approx 2.115$  (Figures 5b and S20, and Table S5). Only the former is observed in echo-detected EPR spectroscopy (Figures 5c and S22), demonstrating their different origin and that the species giving rise to the broad signal relaxes quickly. The observed decrease in  $g_z$  and increase in  $A_{z(\text{Cu})}$  (compared to the hydrated form) of the anisotropic component are consistent with a mixed O/N-donor set, and similar changes have been observed in  $\text{NH}_3$  binding in Cu-doped zeolites.<sup>39</sup> The origin of the broad signal is less clear: the lack of resolution and rapid relaxation may indicate exchange interactions between the Cu(II) ions. The nearest possible intra- and inter-node Cu...Cu distances are 4.4 and 5.8 Å, respectively, and an interaction would only need to be a few hundred MHz to affect the CW EPR response significantly. This could be mediated by the hydrogen-bonding network of adsorbed  $\text{NH}_3$  molecules within the tetrahedral cages. Since the defects will be distributed statistically, both coupled and uncoupled spectra could be observed. An alternative explanation for the broad signal would be a fluxional process, which averages the EPR response. However, the spectra are unchanged on cooling to 4 K, which should freeze out any such process. Similar broad, near-isotropic CW EPR signals have been observed on  $\text{NH}_3$  loading on the Cu(II)-MOF, HKUST-1, tentatively attributed to spin-exchange phenomena.<sup>29</sup> In contrast to the HKUST-1 study, where the changes in  $\text{NH}_3$  adsorption were irreversible,<sup>29</sup> the CW EPR and HYSCORE spectra of UiO-66-Cu<sup>II</sup> can be readily regenerated by degassing and exposure to air, confirming excellent stability and reversibility of this system (Figures 5b, S21, and S23). At  $10^{-7}$  mbar at different temperatures, the broad signal is lost first (Figure S20), consistent with preferential loss of  $\text{NH}_3$  molecules at Site II/III, which disrupts the hydrogen-bonding network that facilitates the Cu...Cu interaction.

Similar EPR spectra and behavior are found for UiO-66-Cu<sup>I</sup>, which indicates the presence of a minor amount of Cu(II) ions

along with Cu(I) sites after the reduction. To compare the strength of Cu... $\text{NH}_3$  binding in UiO-66-Cu<sup>II</sup> and UiO-66-Cu<sup>I</sup> materials, the desorption and regeneration processes after  $\text{NH}_3$  adsorption were compared (Figures 5d and S21). The broad isotropic signal is lost more quickly for UiO-66-Cu<sup>I</sup>, demonstrating stronger binding in the UiO-66-Cu<sup>II</sup> system, consistent with the TPD and ssNMR analyses and the isothermal adsorption and breakthrough results.

## CONCLUSIONS

In summary, robust UiO-66 materials incorporating atomically dispersed defects and open Cu(I) and Cu(II) sites show high and reversible  $\text{NH}_3$  adsorption capacities. While the decoration of defects with open Cu(I) and Cu(II) sites exhibits little change to the BET surface area (1111–1135  $\text{m}^2 \text{g}^{-1}$ ), the latter Cu(II) system shows 43 and 100% enhancements in the static and dynamic adsorption of  $\text{NH}_3$ , respectively, compared with UiO-66-defect. This places UiO-66-Cu<sup>II</sup> as one of the state-of-the-art  $\text{NH}_3$  sorbents. The host–guest interactions between the frameworks and adsorbed  $\text{NH}_3$  molecules have been investigated comprehensively at the molecular level. *In situ* NPD, ssNMR, EPR, IR, UV–vis, and INS/DFT studies have established the binding interactions between  $\text{NH}_3$  and defect sites and the critical role of low-coordinate Cu(II) sites in stabilizing  $\text{NH}_3$  molecules has been determined unambiguously. This is distinct from four and five-coordinated Cu(II) sites that lead to irreversible structural degradation upon desorption of  $\text{NH}_3$ . By combining  $\text{NH}_3$ –TPD, *in situ* ssNMR, IR, UV–vis, and EPR experiments, the host–guest interactions have been revealed, and this is accompanied by a reversible change of the unique, near-linear coordination geometry of Cu(II) sites as a function of  $\text{NH}_3$  binding. This is the structural origin of the observed reversible  $\text{NH}_3$  adsorption in this system involving open metal sites. These findings showcase the designed tuning of active sites in MOFs that can result in top-performing  $\text{NH}_3$  adsorption without altering the porosity of a given material. We anticipate that this study will provide key insights into the design and preparation of new efficient sorbents for  $\text{NH}_3$  *via* the full control of active sites with atomic precision.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c00952>.

Additional experimental details, adsorption isotherms, breakthrough experiments, views of crystal structures, XAFS, powder X-ray diffraction (PXRD), NPD, IR, UV–vis,  $\text{NH}_3$ –TPD, EPR, and ssNMR data (Figures S1–S23 and Tables S1–S11) (PDF)

### Accession Codes

CCDC 2124989–2124993 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Rieth, A. J.; Tulchinsky, Y.; Dincă, M. High and Reversible Ammonia Uptake in Mesoporous Azolate Metal–Organic Frameworks with Open Mn, Co, and Ni Sites. *J. Am. Chem. Soc.* **2016**, *138*, 9401–9404.
- (2) Kim, D. W.; Kang, D. W.; Kang, M.; Lee, J.; Choe, J. H.; Chae, Y. S.; Choi, D. S.; Yun, H.; Hong, C. S. High Ammonia Uptake of a Metal–Organic Framework Adsorbent in a Wide Pressure Range. *Angew. Chem., Int. Ed.* **2020**, *59*, 22531–22536.
- (3) Helminen, J.; Helenius, J.; Paatero, E.; Turunen, I. Comparison of Sorbents and Isotherm Models for NH<sub>3</sub>-Gas Separation by Adsorption. *AIChE J.* **2000**, *46*, 1541–1555.
- (4) Zeng, T.; Huang, H.; Kobayashi, N.; Li, J. Performance of an Activated Carbon–Ammonia Adsorption Refrigeration System. *Nat. Resour.* **2017**, *08*, 611–631.
- (5) Furtado, A. M.; Wang, Y.; Glover, T. G.; LeVan, M. D. MCM-41 Impregnated with Active Metal Sites: Synthesis, Characterization, and Ammonia Adsorption. *Microporous Mesoporous Mater.* **2011**, *142*, 730–739.
- (6) Helminen, J.; Helenius, J.; Paatero, E.; Turunen, I. Adsorption Equilibria of Ammonia Gas on Inorganic and Organic Sorbents at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 391–399.
- (7) Chen, Y.; Zhang, X.; Wang, X.; Drout, R. J.; Mian, M. R.; Cao, R.; Ma, K.; Xia, Q.; Li, Z.; Farha, O. K. Insights into the Structure–Activity Relationship in Aerobic Alcohol Oxidation over a Metal–

- Organic-Framework-Supported Molybdenum(VI) Catalyst. *J. Am. Chem. Soc.* **2021**, *143*, 4302–4310.
- (8) Easun, T. L.; Moreau, F.; Yan, Y.; Yang, S.; Schröder, M. Structural and Dynamic Studies of Substrate Binding in Porous Metal–Organic Frameworks. *Chem. Soc. Rev.* **2017**, *46*, 239–274.
- (9) Wei, Y.-S.; Zhang, M.; Zou, R.; Xu, Q. Metal–Organic Framework-Based Catalysts with Single Metal Sites. *Chem. Rev.* **2020**, *120*, 12089–12174.
- (10) Han, X.; Yang, S.; Schröder, M. Porous Metal–Organic Frameworks as Emerging Sorbents for Clean Air. *Nat. Rev. Chem.* **2019**, *3*, 108–118.
- (11) Vikrant, K.; Kumar, V.; Kim, K. H.; Kukkar, D. Metal–Organic Frameworks (MOFs): Potential and Challenges for Capture and Abatement of Ammonia. *J. Mater. Chem. A* **2017**, *5*, 22877–22896.
- (12) Liu, J.; Chen, Z.; Wang, R.; Alayoglu, S.; Islamoglu, T.; Lee, S.; Sheridan, T. R.; Chen, H.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. Zirconium Metal–Organic Frameworks Integrating Chloride Ions for Ammonia Capture and/or Chemical Separation. *ACS Appl. Mater. Interfaces* **2021**, *13*, 22485–22494.
- (13) Fang, Z.; Bueken, B.; De Vos, D. E.; Fischer, R. A. Defect-Engineered Metal–Organic Frameworks. *Angew. Chem., Int. Ed.* **2015**, *54*, 7234–7254.
- (14) Wu, H.; Chua, Y. S.; Krungleviciute, V.; Tyagi, M.; Chen, P.; Yildirim, T.; Zhou, W. Unusual and Highly Tunable Missing-Linker Defects in Zirconium Metal–Organic Framework UiO-66 and Their Important Effects on Gas Adsorption. *J. Am. Chem. Soc.* **2013**, *135*, 10525–10532.
- (15) Taddei, M. When Defects Turn into Virtues: The Curious Case of Zirconium-Based Metal–Organic Frameworks. *Coord. Chem. Rev.* **2017**, *343*, 1–24.
- (16) Rodríguez-Albelo, L. M.; López-Mayra, E.; Hamad, S.; Ruiz-Salvador, A. R.; Calero, S.; Navarro, J. A. R. Selective Sulfur Dioxide Adsorption on Crystal Defect Sites on an Isorecticular Metal Organic Framework Series. *Nat. Commun.* **2017**, *8*, No. 14457.
- (17) Smith, G. L.; Eyley, J. E.; Han, X.; Zhang, X.; Li, J.; Jacques, N. M.; Godfrey, H. G. W.; Argent, S. P.; McCormick McPherson, L. J.; Teat, S. J.; Cheng, Y.; Frogley, M. D.; Cinque, G.; Day, S. J.; Tang, C. C.; Easun, T. L.; Rudic, S.; Ramirez-Cuesta, A. J.; Yang, S.; Schröder, M. Reversible Coordinative Binding and Separation of Sulfur Dioxide in a Robust Metal–Organic Framework with Open Copper Sites. *Nat. Mater.* **2019**, *18*, 1358–1365.
- (18) Bloch, E. D.; Murray, L. J.; Queen, W. L.; Chavan, S.; Maximoff, S. N.; Bigi, J. P.; Krishna, R.; Peterson, V. K.; Grandjean, F.; Long, G. J.; Smit, B.; Bordiga, S.; Brown, C. M.; Long, J. R. Selective Binding of O<sub>2</sub> over N<sub>2</sub> in a Redox–Active Metal–Organic Framework with Open Iron(II) Coordination Sites. *J. Am. Chem. Soc.* **2011**, *133*, 14814–14822.
- (19) Rieth, A. J.; Dincă, M. Controlled Gas Uptake in Metal–Organic Frameworks with Record Ammonia Sorption. *J. Am. Chem. Soc.* **2018**, *140*, 3461–3466.
- (20) Petit, C.; Mendoza, B.; Bandoz, T. J. Reactive Adsorption of Ammonia on Cu-Based MOF/Graphene Composites. *Langmuir* **2010**, *26*, 15302–15309.
- (21) Yoskamtorn, T.; Zhao, P.; Wu, X.; Purchase, K.; Orlandi, F.; Manuel, P.; Taylor, J.; Li, Y.; Day, S.; Ye, L.; Tang, C. C.; Zhao, Y.; Tsang, S. C. E. Responses of Defect-Rich Zr-Based Metal–Organic Frameworks toward NH<sub>3</sub> Adsorption. *J. Am. Chem. Soc.* **2021**, *143*, 3205–3218.
- (22) Ma, Y.; Han, X.; Xu, S.; Wang, Z.; Li, W.; da Silva, I.; Chansai, S.; Lee, D.; Zou, Y.; Nikiel, M.; Manuel, P.; Sheveleva, A. M.; Tuna, F.; McInnes, E. J. L.; Cheng, Y.; Rudić, S.; Ramirez-Cuesta, A. J.; Haigh, S. J.; Hardacre, C.; Schröder, M.; Yang, S. Atomically Dispersed Copper Sites in a Metal–Organic Framework for Reduction of Nitrogen Dioxide. *J. Am. Chem. Soc.* **2021**, *143*, 10977–10985.
- (23) Chapon, L. C.; et al. Wish: The New Powder and Single Crystal Magnetic Diffractometer on the Second Target Station. *Neutron News* **2011**, *22*, 22–25.
- (24) Parker, S. F.; Fernandez-Alonso, F.; Ramirez-Cuesta, A. J.; Tomkinson, J.; Rudic, S.; Pinna, R. S.; Gorini, G.; Castañón, J. F. Recent and Future Developments on TOSCA at ISIS. *J. Phys.: Conf. Ser.* **2014**, *554*, No. 012003.
- (25) Fung, B. M.; Khittrin, A. K.; Ermolaev, K. An Improved Broadband Decoupling Sequence for Liquid Crystals and Solids. *J. Magn. Reson.* **2000**, *142*, 97–101.
- (26) van Rossum, B.-J.; Förster, H.; Groot, H. D. High-Field and High-Speed CP-MAS<sup>13</sup>C NMR Heteronuclear Dipolar-Correlation Spectroscopy of Solids with Frequency-Switched Lee-Goldburg Homonuclear Decoupling. *J. Magn. Reson.* **1997**, *124*, 516–519.
- (27) Abdel-Mageed, A. M.; Rungtaweeworant, B.; Parlinska-Wojtan, M.; Pei, X.; Yaghi, O. M.; Behm, R. J. Highly Active and Stable Single Atom Cu Catalysts Supported by a Metal–Organic Framework. *J. Am. Chem. Soc.* **2019**, *141*, 5201–5210.
- (28) Katz, M. J.; Howarth, A. J.; Moghadam, P. Z.; DeCoste, J. B.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. High Volumetric Uptake of Ammonia Using Cu-MOF-74/Cu-CPO-27. *Dalton Trans.* **2016**, *45*, 4150–4153.
- (29) Borfecchia, E.; Maurelli, S.; Gianolio, D.; Groppo, E.; Chiesa, M.; Bonino, F.; Lamberti, C. Insights into Adsorption of NH<sub>3</sub> on HKUST-1 Metal–Organic Framework: A Multitechnique Approach. *J. Phys. Chem. C* **2012**, *116*, 19839–19850.
- (30) Chen, Y.; Shan, B.; Yang, C.; Yang, J.; Li, J.; Mu, B. Environmentally Friendly Synthesis of Flexible MOFs M(NA)<sub>2</sub> (M = Zn, Co, Cu, Cd) with Large and Regenerable Ammonia Capacity. *J. Mater. Chem. A* **2018**, *6*, 9922–9929.
- (31) Han, X.; Lu, W.; Chen, Y.; da Silva, I.; Li, J.; Lin, L.; Li, W.; Sheveleva, A. M.; Godfrey, H. G. W.; Lu, Z.; Tuna, F.; McInnes, E. J. L.; Cheng, Y.; Daemen, L. L.; McPherson, L. J. M.; Teat, S. J.; Frogley, M. D.; Rudic, S.; Manuel, P.; Ramirez-Cuesta, A. J.; Yang, S.; Schroder, M. High Ammonia Adsorption in MFM-300 Materials: Dynamics and Charge Transfer in Host-Guest Binding. *J. Am. Chem. Soc.* **2021**, *143*, 3153–3161.
- (32) Godfrey, H. G. W.; da Silva, I.; Briggs, L.; Carter, J. H.; Morris, C. G.; Savage, M.; Easun, T. L.; Manuel, P.; Murray, C. A.; Tang, C. C.; Frogley, M. D.; Cinque, G.; Yang, S.; Schröder, M. Ammonia Storage via Reversible Host-Guest Site Exchange in a Robust Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2018**, *57*, 14778–14781.
- (33) Wang, L.; Li, W.; Qi, G. S.; Weng, D. Location and Nature of Cu Species in Cu/SAPO-34 for Selective Catalytic Reduction of NO with NH<sub>3</sub>. *J. Catal.* **2012**, *289*, 21–29.
- (34) Wang, D.; Zhang, L.; Kamasamudram, K.; Epling, W. S. In Situ DRIFTS Study of Selective Catalytic Reduction of NO<sub>x</sub> by NH<sub>3</sub> over Cu-Exchanged SAPO-34. *ACS Catal.* **2013**, *3*, 871–881.
- (35) Hadjiivanov, K. I.; Panayotov, D. A.; Mihaylov, M. Y.; Ivanova, E. Z.; Chakarova, K. K.; Andonova, S. M.; Drenchev, N. L. Power of Infrared and Raman Spectroscopies to Characterize Metal–Organic Frameworks and Investigate Their Interaction with Guest Molecules. *Chem. Rev.* **2021**, *121*, 1286–1424.
- (36) Peng, C.; Chai, L.-Y.; Tang, C.-J.; Min, X.-B.; Song, Y.-X.; Duan, C.-S.; Yu, C. Study on the Mechanism of Copper-ammonia Complex Decomposition in Struvite Formation Process and Enhanced Ammonia and Copper Removal. *J. Environ. Sci.* **2017**, *51*, 222–233.
- (37) Ruiz-Morales, Y.; Schreckenbach, G.; Ziegler, T. Origin of the Hydridic <sup>1</sup>H NMR Chemical Shift in Low-Valent Transition-Metal Hydrides. *Organometallics* **1996**, *15*, 3920–3923.
- (38) Godiksen, A.; Vennestrom, P. N. R.; Rasmussen, S. B.; Mossin, S. Identification and Quantification of Copper Sites in Zeolites by Electron Paramagnetic Resonance Spectroscopy. *Top. Catal.* **2017**, *60*, 13–29.
- (39) Moreno-González, M.; Hueso, B.; Boronat, M.; Blasco, T.; Corma, A. Ammonia-Containing Species Formed in Cu-Chabazite As Per In Situ EPR, Solid-State NMR, and DFT Calculations. *J. Phys. Chem. Lett.* **2015**, *6*, 1011–1017.