Chemical Sensitivity of Valence-to-Core X-ray Emission Spectroscopy Due to the Ligand and the Oxidation State: A Computational Study on Cu-SSZ-13 with Multiple H₂O and NH₃ Adsorption

Renqin Zhang,✉† Hui Li,✉‡,∥ and Jean-Sabin McEwen✉∗,†,‡,§,♠

†The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, ‡Department of Physics and Astronomy, and §Department of Chemistry, Washington State University, Pullman, Washington 99164, United States
∥College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan, China 030024

Supporting Information

ABSTRACT: Valence-to-core X-ray emission spectroscopy (vtc-XES) is a powerful experimental tool that can overcome the sensitivity limitations of X-ray absorption near edge structure (XANES) measurements with regard to ligand identification. To further elucidate the sensitivity of this experimental technique, the corresponding emission spectrum of a Cu cation when exchanged within a chabazite structure (Cu-SSZ-13) was calculated from first principles. By comparing vtc-XES spectra of H₂O and NH₃ adsorbed on Cu⁺ (or Cu²⁺) cations, we find a blue shift for the kβ′ emission line from a Cu-O to a Cu–N ligation. In addition, the adsorption of NH₃ results in a stronger kβ₂,5 emission line intensity than the corresponding one for H₂O. Therefore, one can discriminate the adsorption of H₂O or NH₃ by the different vtc-XES emission lines of Cu–O and Cu–N. By scanning the vtc-XES of multiple H₂O and NH₃ adsorbed Cu-SSZ-13 structures, we find a shift in the energy of the kβ′ line between H₂O and NH₃ adsorbed conformations, which increases by increasing the population of Cu–ligand bonds for both the Cu⁺ and Cu²⁺ cations. By analyzing the partial density of states (PDOS) for these structures, the kβ′ emission line results from a N 2s to Cu 1s transition, while the kβ₂,5 emission line is generated from the transition going from a mixed N 2p and Cu 3d and 4p state to a Cu 1s core hole, where the Cu 4p state plays a key role in this transition. Further PDOS analysis shows the chemical sensitivity of vtc-XES, since the ligand environment is intrinsically determined by the different potential binding energies of ligand 2s states. Finally, we compare our computed XES results to the measured XES of several reference compounds, which seem to suggest a different assignment than what was suggested in the literature. As such, the vtc-XES spectrum is a complementary tool to XANES and is well-suited for uncovering the state of the active site and the nearest neighbor environment of Cu ions in Cu-SSZ-13 during the selective catalytic reduction of NO or, more generally, of metal ions in a working catalyst.

1. INTRODUCTION

A number of reports on copper-exchanged SSZ-13 (Cu-SSZ-13) claim that it is more active and selective toward the formation of N₂ in the selective catalytic reduction (SCR) of NO with NH₃ as compared to Cu-ZSM-5 and Cu-beta.1 Also, it was found that Cu-SSZ-13 is more hydrothermally stable than the Cu-Y, Cu-ZSM-5, and Cu-beta zeolites and that this is likely due to the smaller cavity dimensions that make up the CHA structure.2 The spectroscopic properties3−5 of Cu-SSZ-13 have attracted significant attention due to their potential for uncovering chemical bonding and electronic structure relationships as well as the mechanism of SCR on Cu cations,6,7 which could further support the design of new catalysts.

X-ray absorption spectroscopy (XAS) is a versatile tool that is sensitive to the oxidation state and the local structure of the probed atoms.8 Cu K-edge X-ray absorption near edge structure (XANES) spectra have been widely used to determine the oxidation state and local structure of Cu cations in different species.6,7,9,10 However, as pointed out by Bauer,11 an XAS analysis suffers from a lack of sensitivity to the ligands that coordinate to the metal ions. This difficulty of ligand identification gives rise to a serious hindrance in our ability to uncover the underlying mechanism in the SCR of NO with NH₃ with regard the role of each gaseous component in the reaction and the structure of principal intermediate species. This limitation could be overcome by using valence-to-core X-ray emission spectroscopy (vtc-XES), which is used for the characterization of the valence electronic levels.12−14 Under standard SCR conditions, the XANES spectra of the Cu cations are found to be independent of the Si/Al ratio, although the Cu-complexes are Cu²⁺(NH₃)₄ and [Cu³⁺(OH⁻)]⁺(NH₃), for low and high Si/Al ratios, respectively.6 XANES cannot distinguish the species of Cu²⁺(NH₃)₄ and [Cu³⁺(OH⁻)]⁺(NH₃). Using vtc-XES, it is possible to...
distinguish oxygen or nitrogen ligation of the Cu active sites. This technique provides more information concerning the valence electron orbitals near the Fermi level, which are formed by the interaction between the metal and ligand orbitals. Consequently, vtc-XES is highly sensitive to the ligands and provides complementary information to an XAS analysis. For example, it was found that the temperature strongly influences the local structures of Cu cations during SCR by combining XANES and XES techniques. The aforementioned analysis concluded that low-temperature SCR is characterized by balanced populations of \( \text{Cu}^{2+} / \text{Cu}^{4+} \) sites and dominated by mobile \( \text{NH}_3 \)-solvated Cu-species, while the largely dominant Cu-species are framework-coordinated \( \text{Cu}^{3+} \) sites under high-temperature SCR.

Thanks to the development of density functional theory (DFT) and more powerful computational resources, vtc-XES spectra can be modeled, providing further insights into spectroscopic properties at the atomic and electronic level. Grunwaldt and co-workers studied the vtc-XES of Cu-SSZ-13 under different conditions and found different feature peaks in vtc-XES spectra for Cu-SSZ-13 samples with and without \( \text{NH}_3 \) in the feed. The difference is attributed to a N atom in the coordination sphere of Cu cations. Computational vtc-XES based on DFT calculations of cluster models with and without \( \text{NH}_3 \) confirmed this experimental finding. However, further analysis at an electronic level is missing. Lamberti and co-workers also employed several techniques combined with a computational analysis of vtc-XES to find that the dominant structural components of Cu-SSZ-13 upon \( \text{O}_2 \) and He-activation are \( [\text{CuOH}]^+ \) and bare \( \text{Cu}^+ \) cations, respectively. Computational spectroscopic studies are advantageous due to their ability to aid theoretical interpretations of experimental results and, to some extent, suggest new hypotheses that can be verified by additional experiments.

As part of our continuing efforts toward understanding the spectroscopic properties of Cu-SSZ-13, we studied vtc-XES of the Cu cations in Cu-SSZ-13 under different conditions. We employed Cu-SSZ-13 models with periodic boundary conditions and excited a 1s core electron to generate vtc-XES spectra. In this contribution, we will investigate the sensitivity of vtc-XES to ligation, population of adsorbed molecules, and oxidation state for Cu cations in Cu-SSZ-13. We will present our insight into our ability to identify ligand environments of Cu cations using vtc-XES by performing a density of state (DOS) analysis when the 1s core electron is excited. The use of DFT surely represents a significant step forward toward a more robust spectroscopic interpretation.

2. COMPUTATIONAL DETAILS

DFT calculations for the energetics were performed with the Vienna Ab initio Simulation Package (VASP). The projector augmented-wave (PAW) method and the generalized-gradient approximation (GGA), using the PW91 functional, were employed for the treatment of the electron-ion interactions and the exchange-correlation effects, respectively. With PAW potentials, VASP combines the accuracy of all-electron methods with the computational efficiency of plane-wave approaches. The total energy convergence threshold was set to \( 10^{-6} \) eV, and the geometries were considered to be fully relaxed when the forces were less than 0.01 eV/Å. A 400 eV plane-wave cutoff and a single \( \Gamma \)-point sampling of the Brillouin zone were used for the optimization calculations. A rhombohedral unit cell of SSZ-13 was used in this study.

More detailed information about the structure of the rhombohedral unit cell can be found in our previous work. The \( \text{Cu}^{2+} / \text{Cu}^{4+} \) redox reaction plays an important role in the mechanism of the SCR reaction on Cu-SSZ-13. In the rhombohedral unit cell, charge deficiencies are generated upon replacement of Si atoms by Al atoms. Up to two Si atoms can be substituted by Al atoms within our system, which can result in sites containing one or two charge deficiencies. Cu cations are then used to compensate such insufficiencies, which determine their formal oxidation states, which can be +1 or +2. The corresponding Cu-SSZ-13 zeolites are denoted as ZCu (1Al) and Z_2Cu (2Al), which represent Cu-SSZ-13 with high and low Si/Al ratios, respectively. Cu\(^{2+}\) cations in Z_2Cu could be reduced and the new charge deficiency compensated by an H\(^+\) cation. The corresponding conformation is labeled as HZ_2Cu. For a ZCu sample, a Cu\(^+\) cation could be oxidized to Cu\(^{2+}\) by forming \([\text{Cu}^{2+}(\text{OH}^-)]^+\), denoted as ZCuOH.

The aforementioned method and He-activation are \([\text{Cu}^{2+}(\text{OH}^-)]^+\) conformation has been reported via a number of different techniques. The Cu\(^{2+} / \text{Cu}^{4+} \) redox reaction happens in 1Al and 2Al samples via ZCu \( \Leftrightarrow \) ZCuOH and HZ_2Cu \( \Leftrightarrow \) Z_2Cu, respectively. Paolucci et al. demonstrated that 1Al and 2Al samples exhibit similar turnover rates, apparent activation energies, and apparent reaction orders under standard SCR conditions. The local structures of the Cu cation for ZCu, HZ_2Cu, Z_2Cu, and ZCuOH configurations are shown in Figure 1. In this contribution, the vtc-XES of Cu cations in ZCu, HZ_2Cu, Z_2Cu, and ZCuOH when bonded to multiple \( \text{NH}_3 \) and \( \text{H}_2\text{O} \) with the molecular number ranging from 1 to 6, are generated through DFT calculations. Optimized structures of multiple \( \text{NH}_3 \) and \( \text{H}_2\text{O} \) (\( n = 1-6 \)) adsorbed on Cu-SSZ-13 are shown in Figure S1 of the Supporting Information. Each conformation is denoted as \text{molecule}_n\_Cu-SSZ-13. For example, \text{NH}_3\_1\_ZCu is for one \( \text{NH}_3 \) adsorbed within the ZCu conformation.

The calculations of the vtc-XES spectra, the corresponding projected density of states (PDOS) analyses, and the orbital calculations for Cu cations in Cu-SSZ-13 were performed using the CASTEP code. Ultrasoft pseudopotentials were generated...
on the fly,34 where one electron was excited from the 1s core level when performing core–hole calculations. Energy cutoffs of 550 eV and k-point grids of \((5 \times 5 \times 5)\) were used. Spectral broadening due to instrumental smearing was employed using the Gaussian method, using a value of 0.6 eV, and lifetime broadening was applied with a value of 1.55 eV.34 In order to obtain accurate PDOS for Cu, N, and O, \(\text{O}_{\text{Ofw}}\)–Cu–\(\text{N}\)–NH\(_3\) conformations, as shown in Figure 2b, the DOS of the excited state.4,5,35 As a result, we will be comparing the PDOS in the final (excited) state to analyze our computed vtc-XES spectra.

3. RESULTS AND DISCUSSIONS

3.1. Limitation of the XANES. Under reducing conditions, the Cu K-edge XANES of Cu-SSZ-13 samples have a feature peak around 8983 eV.6,7,13,14,20,36−39 This strong peak is recognized as a fingerprint of a Cu\(^{\text{+}}\) cation with a linear configuration (unpublished results). Recent experimental results assigned this linear configuration to either \(\text{O}_{\text{Ofw}}\)–Cu\(^{\text{+}}\)–\(\text{NH}_3\) or \(\text{H}_2\text{N–Cu}^{\text{+}}\)–\(\text{NH}_3\) configurations in the NH\(_3\)_1_ZCu and NH\(_3\)_2_ZCu conformations, respectively,6,7,13,14 where \(\text{O}_{\text{Ofw}}\) is a framework O atom of the zeolite. Our calculations also show that one or two \(\text{NH}_3\) adsorbed on a Cu\(^{\text{+}}\) cation in ZCu or H\(_3\)N\(^{-}\)Cu configurations in the NH\(_3\)_1_ZCu and NH\(_3\)_2_ZCu conformations, both of which are shown in Figure S1 of the Supporting Information. However, upon examination of the Cu K-edge XANES for these NH\(_3\)_1_ZCu and NH\(_3\)_2_ZCu conformations, as shown in Figure 2b, the line between H\(_2\)O\(_1\)_HZ2Cu and NH\(_3\)_1_HZ2Cu is 1.5 eV, which is larger than that between H\(_2\)O\(_1\)_HZ2Cu and NH\(_3\)_1_ZCu. Second, NH\(_3\)_1_ZCu has a stronger \(\beta\) emission line about 0.9 eV for the \(\beta\) peak in the XES as compared to the \(\alpha\) peaks. The shifts are 1.7 and 1.8 eV for of \(\beta_{\text{k}}\) and \(\beta_{\text{k}}\,\text{O}_{\text{OH}}\), respectively. When comparing the \(\text{O}_{\text{OH}}\) and O ligands, as shown in Figure 3b, the difference between the Cu cations in the H\(_2\)O\(_4\)_Z2Cu and H\(_2\)O\(_4\)_ZCuOH conformations consists of one O and one \(\text{NH}_3\) ligands (4 O vs 3 O and 1 OOH). It turns out that the additional O ligand also has shifts of 1.3 and 0.8 eV for the \(\beta\) and \(\beta_{\text{k}}\text{O}_{\text{OH}}\) emission lines. However, here we focus on the identification of O in H\(_2\)O and N in NH\(_3\). The same conclusion can be reached for another type of Cu\(^{\text{+}}\) cation of O in H\(_2\)O and N in NH\(_3\). Therefore, in the following results, we will not further examine the effect of \(\text{O}_{\text{OH}}\) and \(\text{O}_{\text{OH}}\) on the XES when comparing our XES results with either O- or N-bound Cu ligands.

In order to further identify the ligand environments through vtc-XES, two structural models, H\(_2\)O\(_1\)_ZCu and NH\(_3\)_1_ZCu, were chosen for further analysis. They both have a Cu\(^{\text{+}}\) cation with a linear configuration, as shown in the inset of Figure 4. The only difference between these two structures is the Cu–O and Cu–N bond, where the O and N atoms are from an adsorbed H\(_2\)O and NH\(_3\) molecule, respectively. Their corresponding vtc-XES results are shown in Figure 4. The two emission lines in the vtc-XES, noted as \(\beta_{\text{k}}\) and \(\beta_{\text{k}}\,\text{O}_{\text{OH}}\), are related to the nature of the ligands coordinated to the metal centers.11,12,18 This is clearly shown in the differences of the vtc-XES plots for the H\(_2\)O\(_1\)_ZCu and NH\(_3\)_1_ZCu conformations. First, one can see a blue shift of about 0.9 eV for the \(\beta_{\text{k}}\) lines, where the \(\beta_{\text{k}}\) emission energy of the Cu cation in NH\(_3\)_1_ZCu is higher than that in H\(_2\)O\(_1\)_ZCu. Second, \(\beta_{\text{k}}\text{O}_{\text{OH}}\,\text{ZCu}\) has a stronger \(\beta_{\text{k}}\text{O}_{\text{OH}}\) emission line than H\(_2\)O\(_1\)_ZCu. As a result, one can distinguish between the adsorption of H\(_2\)O or NH\(_3\) by the different vtc-XES emission lines of Cu–O and Cu–N. It also supports previous reports regarding the ability of vtc-XES to identify different ligands that are bonded to the Cu cations.11,13

The same conclusion can be reached for another type of Cu\(^{\text{+}}\) cation environment in the H\(_2\)O\(_1\)_HZ2Cu and NH\(_3\)_1_HZ2Cu2Al site conformations, as shown in Figure S2 of the Supporting Information. The energy shift of the \(\beta_{\text{k}}\) line between H\(_2\)O\(_1\)_HZ2Cu and NH\(_3\)_1_HZ2Cu is 1.5 eV, which is larger than that between H\(_2\)O\(_1\)_ZCu and NH\(_3\)_1_ZCu. This implies that the presence of a Bronsted...
acid site could enhance the $k^\beta$ line energy shift between Cu–O and Cu–N ligation.

Moving forward to the Cu$^{2+}$ cations in Cu-SSZ-13, the H$_2$O$_{1}$Z$_2$Cu and NH$_3$$_1$Z$_2$Cu conformations with two Al sites were taken into consideration. Their structures are displayed as an inset to Figure 5. Cu$^{2+}$ cations in H$_2$O$_{1}$Z$_2$Cu and NH$_3$$_1$Z$_2$Cu conformations have a coordination number of 4, which includes three framework O atoms and one O or N atom from adsorbed molecules. The only structural difference between H$_2$O$_{1}$Z$_2$Cu and NH$_3$$_1$Z$_2$Cu is the Cu–O or Cu–N bond. Similar with the difference of vtc-XES plots among H$_2$O$_{1}$ZCu and NH$_3$$_1$ZCu (shown in Figure 4), Cu$^{2+}$ cations in H$_2$O$_{1}$Z$_2$Cu and NH$_3$$_1$Z$_2$Cu have a blue shift of about 0.7 eV for the $k^\beta$ lines and a stronger $k^\beta_{2,5}$ intensity for the NH$_3$$_1$Z$_2$Cu conformation presented in Figure 5. This result again confirms the ability to identify ligands for Cu cations through use of vtc-XES. However, for Cu$^{2+}$ cations in the H$_2$O$_{1}$ZCuOH and NH$_3$$_1$ZCuOH conformations with one Al in the chabazite framework, the energy difference of the $k^\beta$ lines is very small (0.1 eV), which is shown in Figure S3 of the Supporting Information. This suggests that the formation of [Cu$^{2+}$-(OH$^-$)]$^+$ species weakens the difference between the Cu–O and Cu–N ligation.

Overall, for both Cu$^+$ and Cu$^{2+}$ cations in the Cu-SSZ-13 structure, the discrimination of the ligands containing O and N atoms can be revealed from the $k^\beta$ and $k^\beta_{2,5}$ lines in vtc-XES spectra. Note that in the above structures, the $k^\beta$ shift energy between H$_2$O$_{1}$Z$_2$Cu and NH$_3$$_1$Z$_2$Cu is only considered when a single Cu–O or Cu–N bond is varied. As such, a natural question that arises is whether the number of Cu–O or Cu–N bonds affects the energy shift of the $k^\beta$ line in the corresponding emission spectra. To address this concern, we constructed structures with the same population of Cu–O and Cu–N bonds to model multiple H$_2$O and NH$_3$ adsorption on Cu-SSZ-13. Note that the population of Cu–O or Cu–N bonds does not include the contribution from framework

Figure 3. XES comparison for different types of O ligands: (a) O$_{fw}$ vs O and (b) O$_{OH}$ vs O. The structures of Z$_2$Cu, H$_2$O$_4$Z$_2$Cu, and H$_2$O$_4$ZCuOH are shown at the bottom.

Figure 4. Computational vtc-XES of Cu cations in the H$_2$O$_{1}$ZCu and NH$_3$$_1$ZCu conformations. Two emission lines, $k^\beta$ and $k^\beta_{2,5}$, are presented. The inset displays structures of the H$_2$O$_{1}$ZCu and NH$_3$$_1$ZCu conformations.

Figure 5. Computational vtc-XES of Cu cations in H$_2$O$_{1}$Z$_2$Cu and NH$_3$$_1$Z$_2$Cu. Two emission lines, $k^\beta$ and $k^\beta_{2,5}$, are presented. The inset displays the H$_2$O$_{1}$Z$_2$Cu and NH$_3$$_1$Z$_2$Cu structures.
oxygen atoms (population number ≠ coordination number). The population numbers for all structures studied in this work are shown in Figure S1 of the Supporting Information. For a Cu⁺ cation, using ZCu for an example, H₂O₁₂ZCu and NH₃₁₁ZCu have a single Cu—O or Cu—N bond (N_population = 1), respectively, while the H₂O₆₂ZCu and NH₃₂ZCu conformations have N_population = 2 and the H₂O₄₂ZCu and NH₃₃ZCu conformations have N_population = 3 (note that not all molecules absorb to the Cu cation). For Cu²⁺ cations, now using Z₃Cu as an example, the H₂O₁₂Z₂Cu and NH₃₂Z₂Cu conformations have N_population = 1, while the H₂O₂₂Z₃Cu and NH₃₂₃Z₃Cu conformations have N_population = 2 and the H₂O₄₄Z₅Cu and NH₃₄₄Z₅Cu conformations have N_population = 4. These structures can be found in Figure S1 of the Supporting Information. The kβ″ line energy shift between the H₂O and NH₃ adsorbed species as a function of N_population is shown in Figure 6. We find that the energy shift of the kβ″ line between H₂O and NH₃ adsorbed Cu-SSZ-13 as a function of N_population of H₂O and NH₃ for (a) a Cu⁺ cation in ZCu and (b) a Cu²⁺ cation in Z₂Cu. The corresponding relative fractions of N_population with respect to the total coordination number (CN) of Cu cations are shown at the top of the figure as N_population/CN.

Figure 6. Energy shift of the kβ″ line between H₂O and NH₃ adsorbed Cu-SSZ-13 as a function of N_population of H₂O and NH₃ for (a) a Cu⁺ cation in ZCu and (b) a Cu²⁺ cation in Z₂Cu. The corresponding relative fractions of N_population with respect to the total coordination number (CN) of Cu cations are shown at the top of the figure as N_population/CN.

the kβ″ line between H₂O and NH₃ adsorbed Cu-SSZ-13 increases with increasing N_population for both the Cu⁺ and Cu²⁺ cations. Similar trends are also found for HZ₂Cu and ZCuOH conformations, which are shown in Figure S4 of the Supporting Information. As for the energy shift trend of the kβ″ line, we also consider the relative fraction of N_population of N and O with respect to the total number of bonds in the first coordination sphere of the Cu cation (i.e., the Cu cation coordination number), as shown in Figure 6.

3.3. Characterization of vtc-XES by Varying the Cu Oxidation State. On the basis of the results from the previous section, it is clear that vtc-XES has the ability to identify different ligand environments. In the discussion up to now, we fixed the oxidation state of Cu as either Cu⁺ or Cu²⁺ and computed the XES while varying the ligand environment. As is well-known from the XANES literature, one expects a higher edge position due to the higher binding energy of electrons when the exchanged cation is in a higher oxidation state. However, we recently have shown that this relationship is more complex (unpublished results). On the other hand, it is also important to understand the relationship between the emission line energies in vtc-XES and the oxidation state of the metal exchanged ion. Figure 7 shows the simulated kβ″ and kβ₂,₅ lines of vtc-XES spectra of Cu cations that have the same ligand environment when its oxidation state is varied. We find that the location of both kβ″ and kβ₂,₅ lines shifts slightly as the oxidation state of Cu shifts from Cu⁺ to Cu²⁺, although the intensity of the kβ″ and kβ₂,₅ lines changes significantly. This result is consistent with the experimental results reported by Borfecchia et al. where He-activated and O₂-activated samples (representing Cu⁺ and Cu²⁺, respectively) have same location of the kβ″ line.

3.4. PDOS Analysis and Chemical Sensitivity of the Ligand for vtc-XES. To investigate in detail the origins of the valence-to-core kβ″ and kβ₂,₅ lines, PDOS and orbital calculations are employed using the final state wave function, where a core hole is created in the exchanged Cu cation. For simplicity, the NH₃₂₂Z₅Cu structure was analyzed due to its linear, symmetric N—Cu—N configuration, as shown in Figure S1 of the Supporting Information. The calculated Cu vtc-XES and corresponding PDOS for the Cu and N atoms are presented in Figure 8. We find that the emission energy of the kβ″ line correlates very well with the N 2s peak position around 8960 eV. The orbital distribution also clearly shows that the N 2s orbitals mainly contribute to the kβ″ emission line at 8960 eV. This shows that the kβ″ emission line arises from a transition from the N 2s electron to the Cu 1s core hole. This statement not only applies to Cu⁺ but also to other metal...
centers. In other words, the emission energy of the kβ mixing line is determined by the binding energy of the ligand 2s orbital.

For the kβ_{2,5} emission line, we find that the emission energy correlures well to a mixture of N 2p and Cu 3d and 4p states in the 8973 eV energy range. Compared to the 8971 eV energy range, where vtc-XES does not have an emission line but has a large Cu 3d character, the 8973 eV energy range is mainly due to contributions from the Cu 4p state. This means that the Cu 4p state plays a key role in generating the kβ_{2,5} emission line. However, for Cu cations, the Cu 4p state is supposed to be distributed above the Fermi level. We can rationalize that the appearance of the Cu 4p state below the Fermi level originates from an orbital mixing with the Cu 3d state. As displayed in Figure 8b, the orbital distribution also clearly shows that the Cu and N atoms both contribute to the states around 8973 eV. Therefore, we conclude that the kβ_{2,5} emission line is generated from the transition that mixes the N 2p and Cu 3d and 4p states to the Cu 1s core hole, where the Cu 4p state plays a key role in this transition.

On the basis of the above analysis, it is clear that the kβ’ emission line is generated by a ligand 2s to Cu 1s transition. To understand the chemical sensitivity of vtc-XES on the bonding of the Cu ligand, we plot the PDOS of the N 2s and O 2s for the H2O_1_ZCu and NH3_1_ZCu in Figure 9. In order to interpret the ability of vtc-XES to identify the bonding ligand environment (shown in Figure 3), we compare the PDOS of different ligands have different 2s state binding energies. It is clear that the chemical sensitivity of the vtc-XES is due to the ligand environment and is intrinsically determined by the different binding energies of the ligand 2s state. Note that the interpretation of the kβ_{2,5} emission line is more complex than that of the kβ’ emission line. Further studies are needed to understand the kβ_{2,5} emission line at an electronic level.

3.5. Feedback to Experimental Results. We compared our computational vtc-XES results with the experimental data that is available in the literature. As shown in Figure 10a, the blue, gray, and red vtc-XES spectra are assigned to the ZCuOH, H2O_6_Z2Cu, and NH3_2_ZCu structures. The corresponding computational vtc-XES spectra are shown in Figure 10b. We find that the computational vtc-XES spectra for ZCuOH and H2O_6_Z2Cu are in good agreement with the experimental ones. However, the computational vtc-XES results of NH3_2_ZCu show totally different emission lines, including the intensity and locations with respect to that of ZCuOH and H2O_6_Z2Cu conformations. The assignment of NH3_2_ZCu was made by concluding that a Cu^{2+} cation in a Cu-SSZ-13 sample could be reduced to Cu^{+} in the presence of NO and NH3. We reconsider this assignment and propose that the Cu^{2+} cation was probably not completely reduced to a Cu^{+} cation when exposed to NO and NH3, where the [Cu(NH3)_4]^{2+} could be formed. In Figure 10c, the computational vtc-XES spectra of ZCuOH, H2O_6_Z2Cu, and NH3_4_Z2Cu conformations are plotted, which are consistent with the experimental results in Figure 10a. This suggests that the reduction of Cu^{2+} when exposed to NO and NH3 is perhaps more complex than originally suggested in the literature.

The assignment of a Cu^{+} cation was originally made in the literature because of the large peak around 8984 eV that was observed experimentally in the XANES when Cu-SSZ-13 is exposed to NO and NH3. Additionally, it was also reported that the exposure of oxidized Cu-SSZ-13 to NO + NH3 at 200 °C results in a Cu^{+} species, since a drastic abatement of the EPR signal was observed. Further evidence of a Cu^{+} species arises from the absence of a pre-edge peak deriving from a 1s to 3d transition and by comparing the similar XANES and EXAFS features when Cu-SSZ-13 is exposed to NO + NH3 to those of a reference [Cu(NH3)4]^{2+} compound in the solution phase. However, the comparison between the computational and experimental XES suggests a different assignment on Cu-SSZ-13 when exposed to NO and NH3, as shown in Figure 10a–c. As such, a natural question that arises is whether the XANES spectra of a Cu^{+} cation bonded to two NH3 is similar to a Cu^{2+} cation bonded to four NH3 have peaks that are located in the same photon energy range. In Figure 10d, we compare the XANES spectra of these two conformations. Figure 10d shows that [Cu(NH3)_2]^{2+} has a peak with a strong intensity around 8984 eV, while [Cu(NH3)_4]^{2+} has a peak with a weak intensity in the same photon energy range. As such, both species could contribute to the peak around 8984 eV.
Finally, it is also interesting to note that the intensity of the 8984 eV peak is much greater than of the 8994 eV peak in the NH3_2_ZCu conformation, which is not in agreement with the experimental observations where, depending on the reaction conditions, the intensity of the 8984 eV peak is found to be similar or smaller than that of the 8994 eV peak.7,13 We also note, as discussed in our previous work,4 that the computed XANES in Figure 10d also differs from that of the experimental [Cu(NH3)4]2+ reference compound when put in an aqueous solution, since the presence of water significantly affects the computed XANES spectrum by shifting the photon energy of the white line to higher computed values as well as affecting its peak shape. As such, we do not expect the XANES spectra as shown in Figure 10d to be identical to what was found in the literature for the experimental [Cu(NH3)4]2+ reference compounds,38 which will both surely interact with water when put in an aqueous solution. In sum, these results suggest an open question that would need to be revisited with regard to the interpretation of the XANES features, for which the appearance of a [Cu(NH3)2]+ species in the corresponding SCR reaction mechanism has been proposed in the literature for Cu-SSZ-13.15,40

4. CONCLUSIONS

In this study, the chemical sensitivity of vtc-XES due to the ligand environment and the oxidation state of the metal exchanged ion was investigated using DFT calculations. It is found that the vtc-XES can overcome the ligand identification limitation of XANES. By comparing vtc-XES of H2O_1_ZCu and NH3_1_ZCu conformations, we found the kβ″ line shifted by about 0.9 eV, meaning that the kβ″ emission energy of a Cu cation in NH3_1_ZCu is higher than that in H2O_1_ZCu. In addition, NH3_1_ZCu has a kβ_2,5 line of stronger intensity than that of the H2O_1_ZCu conformation. Therefore, one can discriminate the adsorption of H2O or NH3 due to the different vtc-XES emission lines resulting from Cu−O and Cu−N bonds. In addition, the presence of a Brønsted acid site could enhance the kβ″ line energy shift between Cu−O and Cu−N ligation for a Cu cation. Similar conclusions are also obtained for Cu2+ cations and the formation of [Cu2+(OH−)]+ species, which weakens the difference between Cu−O and Cu−N ligation. When examining the vtc-XES of multiple H2O and NH3 adsorbed Cu-SSZ-13 structures, it is found that the shifts of the kβ″ energy line between H2O and NH3 adsorbed Cu-SSZ-13 increases when increasing the population of Cu−ligand bonds for both Cu+ and Cu2+ cations. The effect of oxidation state on vtc-XES was also studied. We concluded that the variation of the oxidation state slightly changes the peak positions of emission lines while the corresponding intensity changes significantly. By performing a PDOS analysis, the kβ″ emission line is generated by the N 2s to Cu 1s transition, while the kβ_2,5 emission line is generated from a transition going from a mixed N 2p and Cu 3d and 4p state to the Cu 1s core hole, where the Cu 4p state plays a key role in this transition.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b04309.

Optimized structures of multiple NH3 and H2O (n = 1–6) adsorbed on Cu-SSZ-13 (ZCu, HZ2Cu, Z2Cu, and
ZCuOH), computational vtc-XES of Cu ions in HZCu and ZCuOH, and the shift energy of the k/f line as a function of N\textsubscript{population} for a Cu\textsuperscript{+} cation in HZCu and a Cu\textsuperscript{3+} cation in ZCuOH (PDF)

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: js.mc ewen@wsu.edu.*

**ORCID**

Renqin Zhang: 0000-0002-4489-2050
Hui Li: 0000-0002-3203-6686
Jean-Sabin McEwen: 0000-0003-0931-4869

**Author Contributions**

R.Z. and H.L. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Science Foundation GOALI program under contract No. CBET-1258717. A portion of the computer time for the computational work was spent on EMSL, a national scientific user facility sponsored by the Department of Energy’s Office of Biological and Environmental Research and located at PNNL. PNNL is a multiprogram national laboratory operated for the US DOE by Battelle. H.L. acknowledges the financial support of the National Natural Science Foundation of China (grant No. 11404235) and also the support of the Program for the Top Young Academic Leaders of Higher Learning Institutions of Shanxi. We thank Mr. Kyle Groden, Dr. Janos Sznayi, and Dr. Feng Gao for their useful suggestions and comments. We also thank Prof. Fabio Ribeiro for the experimental XANES data and Prof. Borfecchia for the experimental XES results.

**REFERENCES**


