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## Preference towards five-coordination in Ti silicalite-1 upon molecular adsorption

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*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/130491> since 2018-01-18T13:44:52Z

*Published version:*

DOI:10.1002/cphc.201200893

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# CHEMPHYSICHEM

## Supporting Information

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### **Preference towards Five-Coordination in Ti Silicalite-1 upon Molecular Adsorption**

Erik Gallo,<sup>[a, b, c]</sup> Francesca Bonino,<sup>[b]</sup> Janine C. Swarbrick,<sup>[a]</sup> Taras Petrenko,<sup>[d]</sup>  
Andrea Piovano,<sup>[e]</sup> Silvia Bordiga,<sup>[b]</sup> Diego Gianolio,<sup>[b, f]</sup> Elena Groppo,<sup>[b]</sup> Frank Neese,<sup>[d]</sup>  
Carlo Lamberti,<sup>\*[b]</sup> and Pieter Glatzel<sup>\*[a]</sup>

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## Supporting Information

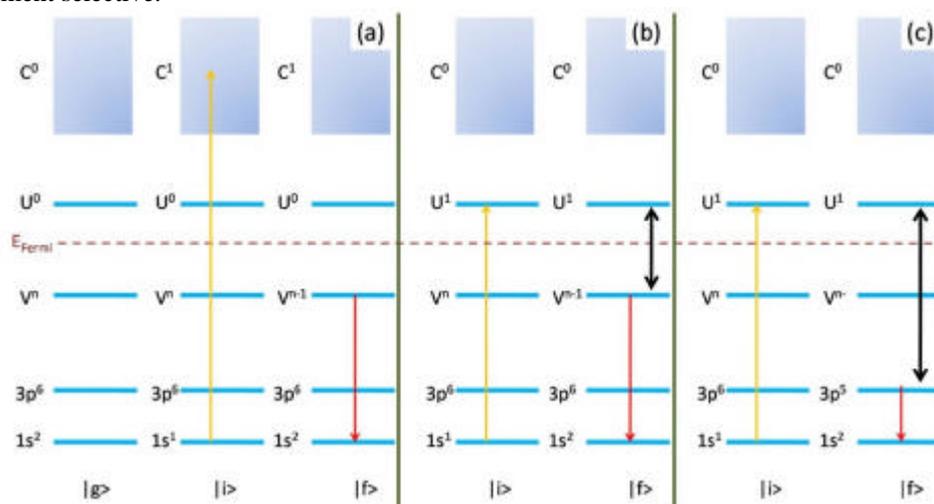
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### SI1. X-ray emission and absorption spectroscopy

The transition of a metal 3p electron to a metal 1s hole (core-to-core or ctc-XES) gives rise to the K $\beta$  main lines historically referred to as K $\beta_{1,3}$  and K $\beta'$  that are sensitive to the metal oxidation- and spin-state.<sup>[1]</sup> The transition of a valence electron to the metal 1s hole gives rise to the valence-to-core (vtc)-XES that is responsive to the type, distance and number of metal ligands as well as to the metal oxidation and spin-state.<sup>[1-14]</sup> The vtc-XES can be divided in two regions: K $\beta''$  and K $\beta_{2,5}$ . The first is mainly linked to transitions involving s type atomic orbital of the metal ligands while the second is primarily due to 3d-3,4p metal and ligand p orbital mixing.<sup>[2, 3, 5]</sup> The K $\beta_{2,5}$  feature is particularly sensitive to changes in the valence orbitals of the system under investigation. It has been shown that a theoretical interpretation using ground state density functional theory (DFT) calculation adopting the one-electron approximation is effective.<sup>[13, 15]</sup> In the one electron approximation, the basic steps of vtc-XES can be described using Scheme SI 1a: (1) a core electron is excited above the Fermi energy ( $E_{\text{Fermi}}$ ) by an incident photon producing an intermediate state  $|i\rangle$  with a core hole that subsequently decays into a final state  $|f\rangle$ .<sup>[6, 7, 13]</sup> The energy distribution of the unoccupied states just above  $E_{\text{Fermi}}$  (lowest unoccupied molecular orbitals, LUMOs) shows distinct features as this region is dominated by bound states while towards higher energies the features become broad reflecting a continuous distribution. Transitions into bound states are referred to as resonant (r) excitations. We distinguish furthermore between decays of the intermediate state where the 1s hole is filled by a valence electron (rvtc-XES) or by another core (c) electron (rctc-XES), see Scheme 1b,c. In case of resonant excitation it is helpful to define the energy transfer  $E_T$  as the difference between incident and emitted energy. This energy that remains in the sample can be interpreted as a net transition of the system. For rvtc-XES the net excitation can be as low as few eV corresponding to the range of optical spectroscopy with the difference that rvtc-XES is element selective.



Scheme SI1. Simplified representation, using a one electron picture, of: (a) the vtc-XES; (b) the rvtc-XES; and (c) rctc-XES processes. The ground state  $|g\rangle$  is given only for vtc-XES.  $V^n$  indicates the number ( $n$ ) of electrons in the valence molecular orbitals (V) just below the Fermi Energy ( $E_{\text{Fermi}}$ ).  $U$  indicates the unoccupied molecular orbitals just above  $E_{\text{Fermi}}$  and  $C$  the

continuum excitations. The yellow arrow represents the transition of the Ti 1s electron due to the adsorption of an incoming photon to reach the intermediate state  $|i\rangle$ . The red arrow indicates the decay of an electron from higher level to the core hole with final state  $|f\rangle$ . The energy transfer ( $E_T$ ) is indicated with a black arrow.

## SI2. Valence MOs for $\text{Ti}(\text{OH})_6$ and $\text{Ti}(\text{OH})_4$ models

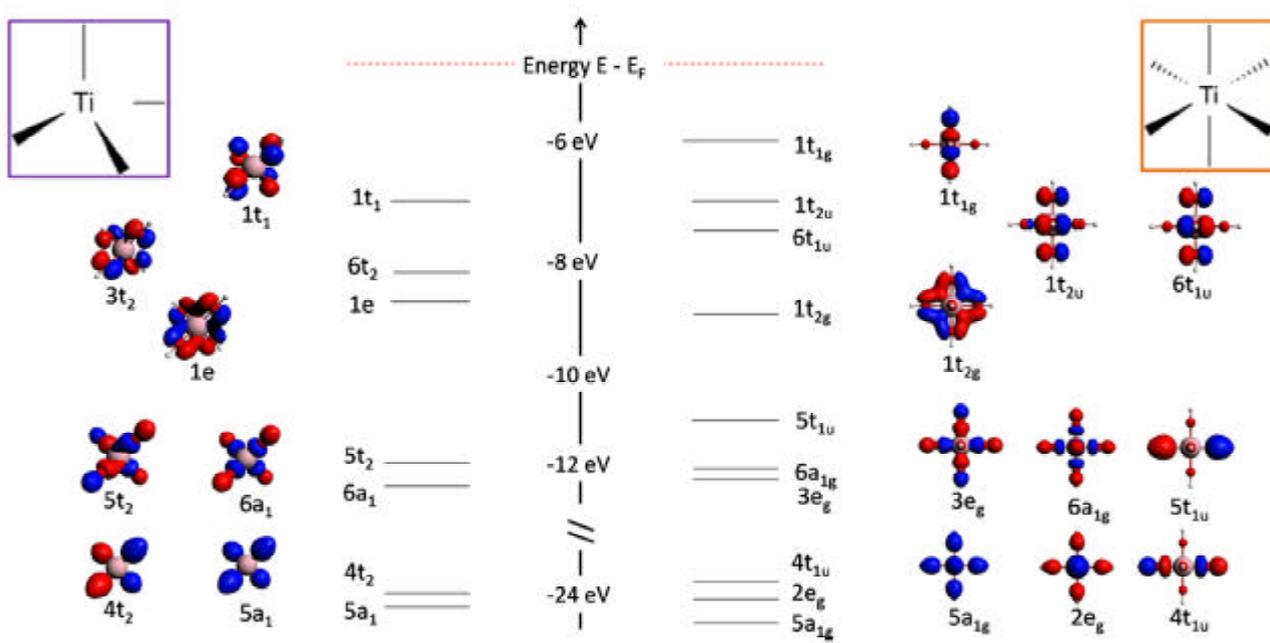
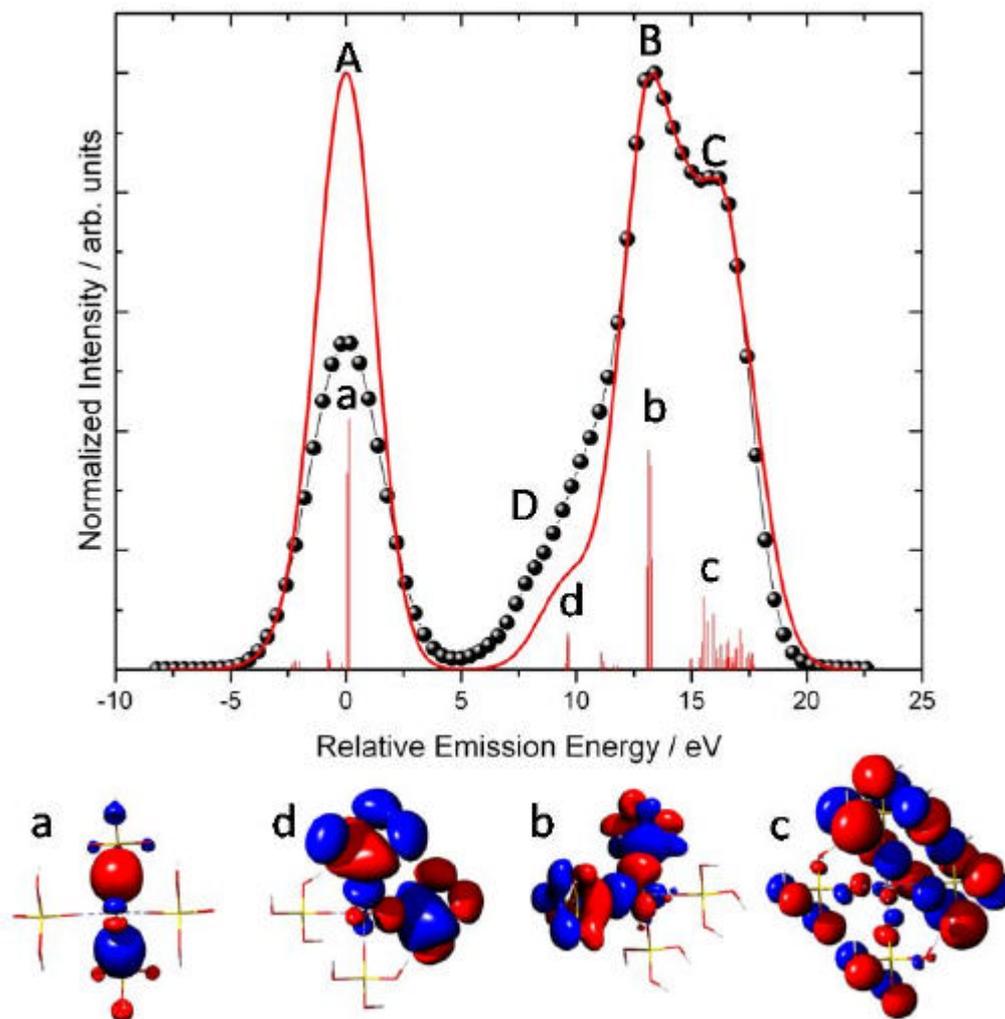


Figure SI1. Valence molecular orbitals for  $\text{Ti}(\text{OH})_4$  and  $\text{Ti}(\text{OH})_6$  symmetry.

In Figure 2, we report the vtc-XES spectra of two simple models with tetrahedral ( $\text{Ti}(\text{OH})_4$ ) and octahedral ( $\text{Ti}(\text{OH})_6$ ) symmetry. The vtc-XES of  $\text{Ti}(\text{OH})_6$  consists of two main peaks that involve molecular orbitals (MOs) with  $t_{1u}$ -symmetry:  $4t_{1u}$  and  $5t_{1u}$  (cf. Figure 2b and Figure SI1). The  $4t_{1u}$ - and the  $5t_{1u}$ -MOs have strong O(2s) and O(2p) atomic character, respectively. We point out that MOs which have the correct ungerade symmetry (in  $O_h$ ) but small (e.g.  $6t_{1u}$ ) or zero (e.g.  $1t_{2u}$ ) Ti p-character (i.e. orbital moment  $l=1$  with respect to Ti centre) do not significantly contribute to the spectra (cf. Figure 2 and Figure SI1). The vtc-XES of  $\text{Ti}(\text{OH})_4$  is composed of three peaks. Each peak is associated with MOs with  $t_2$ -symmetry and thus Ti p-character. We observe that the absence of inversion symmetry and thus possibility for  $pd$ -mixing in  $T_d$  symmetry increases the number of observed transitions in the  $\text{KB}_{2,5}$  region of vtc-XES.

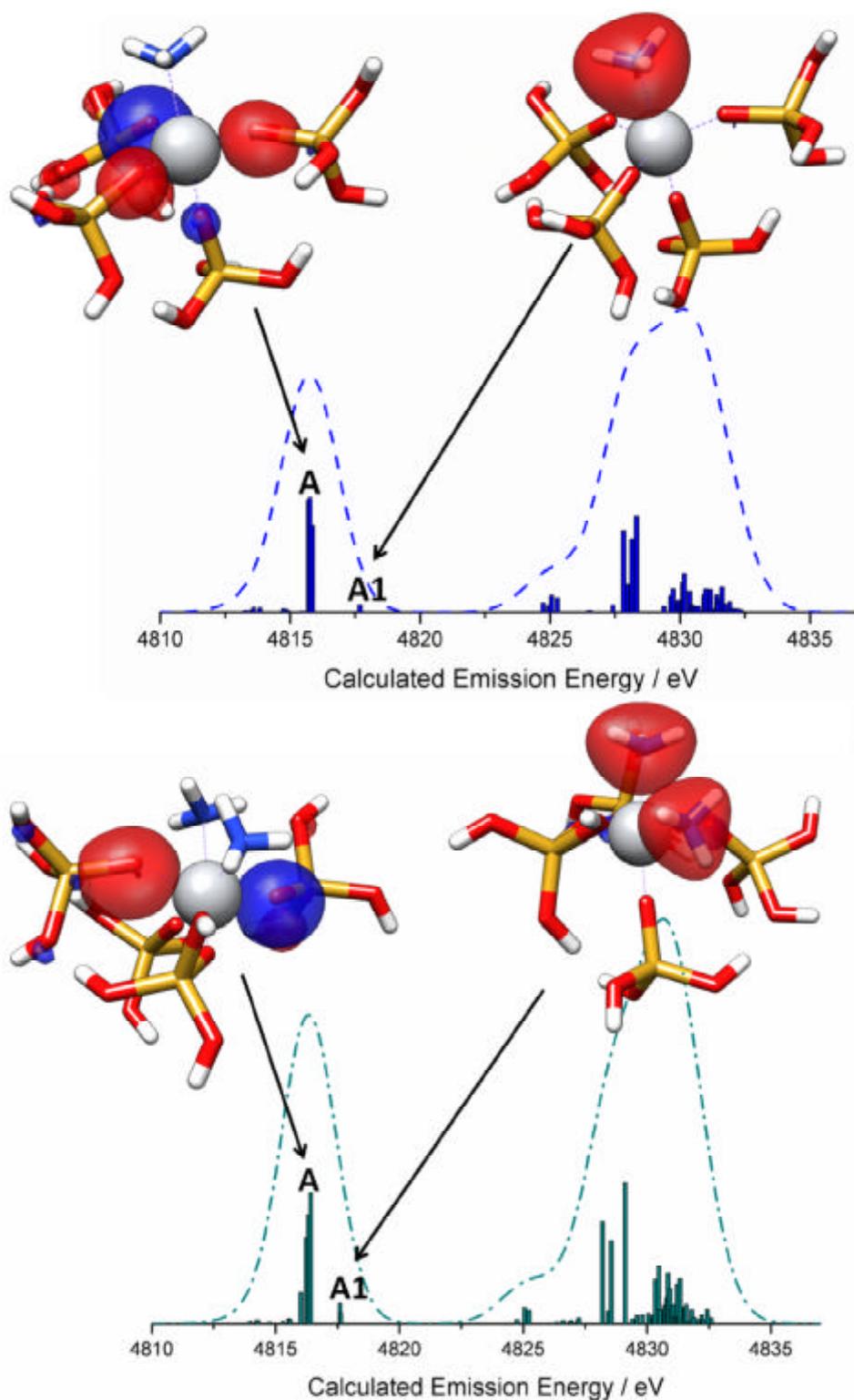
### SI3. Analysis of the MOs involved in the vtc-XES transitions of TS-1/act



**Figure SI2.** Experimental (black circles) and theoretical (red line) vtc-XES spectra of TS-1/act. Four main features identified and labelled as A, D, B and C that represent families of transitions (sticks): for each family, the MO related to the most intense one is reported and labeled with a, d, b and c.

Figure SI2 shows a comparison of the calculated vtc-XES with the experimental data for TS-1/act. In contrast to Figure 2a the cluster that is used for the calculations now contains atoms including the 3<sup>rd</sup> coordination sphere of Ti.<sup>[16]</sup> The analysis of the MOs (see Figure SI2) reveals that the main contributions to the  $K\beta''$  are due to degenerate MOs (a, see Figure 3) with strong O(2s) atomic character. The  $K\beta_{2,5}$  is affected by three groups of MOs labelled d, b and c. The d-MOs have strong Si(3s) and O third shell (2p) atomic character, the b-MOs present strong O first shell (2p) atomic character and only slight contribution from higher shell atoms while the c-MOs have both first shell and third shell O(2p) atomic contributions. The reader is referred to Ref.<sup>[16]</sup> for further details.

**SI4. How the vtc-XES transitions change upon molecular adsorption: the case of TS-1/NH<sub>3</sub>**



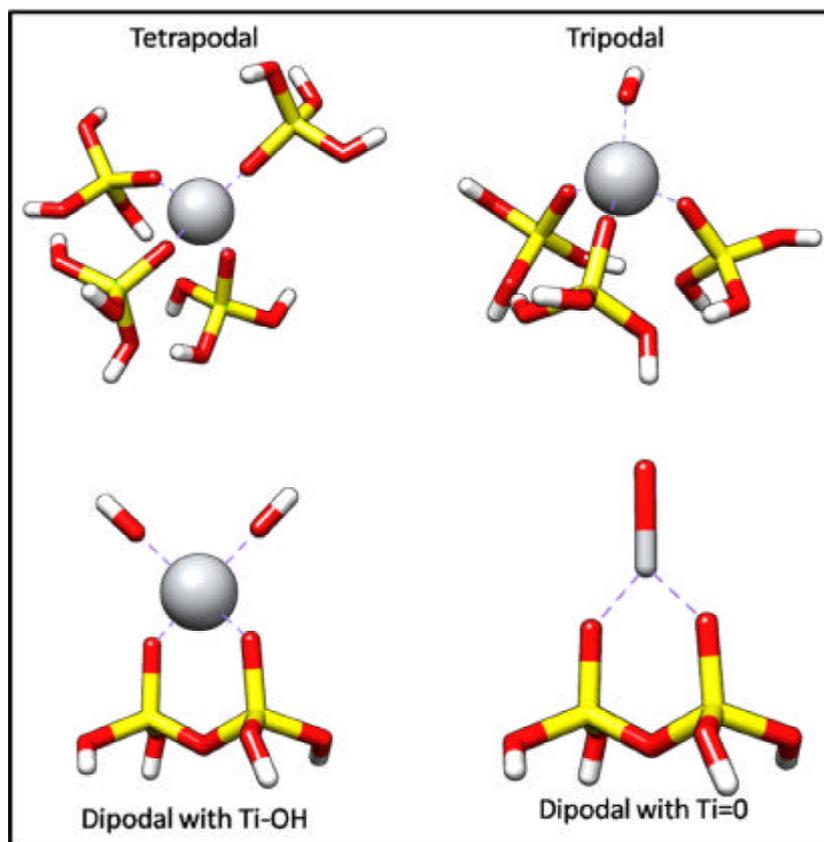
**Figure SI3.** vtc-XES of two simplified clusters (see SI7) of TS-1 with one (top) and two (bottom) molecules of ammonia adsorbed. The MOs that affect the  $K\beta''$  are also reported. The colour code is gray for Ti, red for O, blue for N and yellow for Si.

Figure SI3 reports the calculated TS-1/NH<sub>3</sub> vtc-XES spectra using small clusters<sup>[16-20]</sup>. We mimic the adsorption of ammonia on the Ti centres with one (top) and two (bottom) molecules of NH<sub>3</sub>. The adsorption of ammonia removes the degeneracy of the a-MOs (cf. Figure SI2) and introduces new transitions (a1, see Figure SI3) at higher energy. Such transitions are linked to MOs with strong N(2s) character. As expected the most important modifications arise in the valence band, *i.e.* in the  $K\beta_{2,5}$

region. The degeneracy of the b-MOs is removed (*cf.* Figure SI2) and a deep modification of the computed transitions occurs. The overall effect in case of two adsorbed ammonia molecules is a concentration of spectral intensity at excitation energies above 4830 eV resulting in a sharper  $K\beta_{2,5}$  feature.

## SI5. Calculation of valence to core XES spectra of the models proposed by Gleeson et. al.

Gleeson and coworker performed an EXAFS study to determine the structure of the active site in TS-1. They assumed four possible models<sup>[21]</sup> that are presented in Figure SI4.



**Figure SI4.** Models proposed by Gleeson and coworkers. The colour code is gray for Ti, red for O, yellow for Si and white for H.

Using the models of Figure SI4 we computed the vtc-XES spectra presented in Figure SI5. We observe that vtc-XES can distinguish between these models and confirm that the Ti site in TS-1/act is tetrapodal.<sup>[16, 21]</sup>

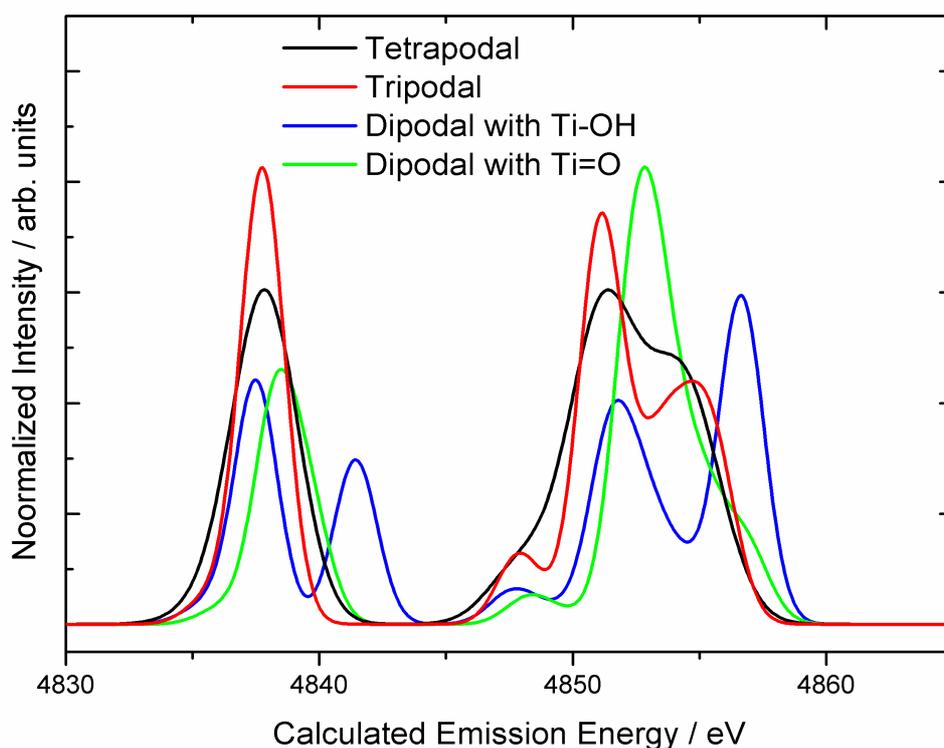


Figure S15. vtc-XES spectra of the proposed models in Figure S14.

## SI6. Implementation of the resonant valence to core transitions in ORCA

The ORCA code implements a one electron approach for the calculation of the resonant valence to core transitions. The resonant valence to core cross section can be written based on the inelastic cross section that is proportional to the modulus square of the polarizability tensor  $\alpha_{\gamma,\gamma'}$  that is defined as follow:

$$\sum_F \sum_V \left( \frac{\langle F | m | V \rangle \langle V | m | I \rangle}{\omega_{VI} - \Omega - i\frac{\Gamma}{2}} + \frac{\langle F | m | V \rangle \langle V | m | I \rangle}{\omega_{VF} - \omega - i\frac{\Gamma}{2}} \right)$$

where F, V and I represent the full electron final, intermediate and ground states, respectively, while  $\omega_{VI}$  and  $\omega_{VF}$  are the difference in energy between the states.  $\Omega$  and  $\omega$  are respectively the energy of the incident and emitted photon while  $\Gamma$  is a parameter describing the core hole life time. The program implements the Kohn-Sham procedure which is linked to the Kohn-Sham determinant that is built from the computed one electron molecular orbitals. We indicate with i, j and k (a,b and c) the occupied (unoccupied) molecular and with  $\epsilon_i, \epsilon_j, \dots$  the corresponding energies. We can write I as

$$I = |i \dots j \dots n\rangle$$

If the 1s core orbital is indicated with i, the unoccupied 3d orbital with a and one general valence molecular orbital with j we may write the intermediate and finale state as follow

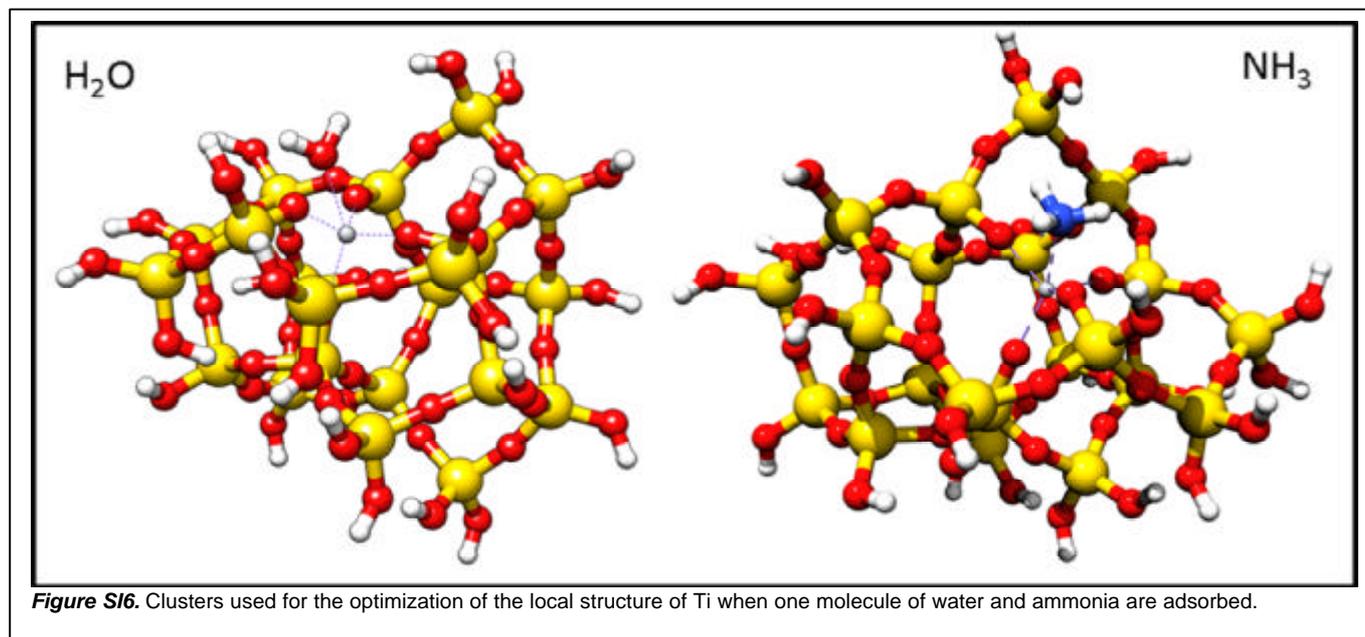
$$V = |a \dots j \dots n\rangle$$

$$F = |a \dots i \dots n\rangle$$

Then we approximate the differences between the full electron states  $\omega_{VI}$  and  $\omega_{VF}$  with respectively  $\epsilon_a - \epsilon_i$  and  $\epsilon_j - \epsilon_i$ . Substituting in the previous equation for the polarizability tensor we obtained a simplified one electron form for the resonant valence to core cross section.

## SI7. Clusters used for the vtc-XES calculation reported in Figure 1.

The clusters reported in Figure SI6 have been optimized, then cut and saturated (with H atoms) to include atoms up to the third shell for the calculation of TS-1/H<sub>2</sub>O and TS-1/NH<sub>3</sub> vtc-XES (see main text). As shown in Ref.<sup>16</sup> the vtc-XES calculation are sensitive to the cluster size. However, the use of three shells of atoms around Ti has been shown to be sufficient for TS-1.



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