

# Experimental and Theoretical High Energy Resolution X-Ray Absorption Spectroscopy

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## Introduction:

Copper containing enzymes are a prominent example for bio catalysts that enable electron transfer. Understanding complexes like these is of great interest for catalytic applications. Two very important factors are the geometry and electronic structure, which strongly depend on the oxidation state of the metal. Exact knowledge of involved mechanisms is essential for understanding these compounds. High Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy (HERFD-XAS) provides information about local geometry and the local spin state, by reflecting the details of the lowest unoccupied states.<sup>[1]</sup> In this study we investigated a Cu(I) complex in the gas and in the crystalline phase as well as a single complex in water solution.

## Methods:

High Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy (HERFD-XAS) was used in conjunction with different computational approaches. The fact that x-ray absorption spectroscopy is independent of the state of aggregation is important to study the complexes in their natural environment (e.g. soluted in water). The HERFD-XANES approach was used instead of the conventional XANES because of the higher resolution.

Calculations were carried out with the CP2K program suite.<sup>[2]</sup> A combination of Ab initio molecular dynamics (AIMD) and DFT calculated XAS spectra was used. The computational approach involved an expansion of the Kohn-Sham orbitals in Gaussians while the electron density was described by a plane wave approach.

## Results and Discussion:

The experimental spectrum shows no prepeak as expected for Cu(I) ( $d^{10}$ ) but several features in the edge which were already discussed elsewhere.<sup>[3]</sup> This study mainly focused on approaches for calculating these spectra with periodic boundary conditions and in solution. The agreement is good for each individual approach but several distinct differences will be shown. One example for these differences is the intensity ratio of the features to one another. This intensity depends in some cases on the approach and clearly shows the influence of the kind of underlying transition (e.g. charge transfer).

## Conclusion:

We show that this computational approach is in good agreement with the experimental spectra up to high energies. This is often a shortcoming for other approaches because of the highly delocalized electron density for the high energy transitions.

It will also become clear that the most expensive and generally most valid approach might not always give the best results.

**References:** [1] A. J. Atkins, C. R. Jacob, M. Bauer, *Chem. Eur. J.* **2012**, *18*, 7021-7025, [2] J. Hutter, M. Iannuzzi, F. Schiffmann, J. Vandevonede, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014**, *4*, 15–25, [3] N. J. Vollmers, P. Müller, M. Bauer et. al., *Inorg. Chem.* **2016**, *55*, 11694-11706