

Investigating Cu(II) solvation through resonant Valence-to-core X-ray Emission Spectroscopy

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Ionic hydration is one of the most attractive subjects to chemists, especially to those who are interested in reactions occurring in aqueous solutions. The structure of transition metal aqua ions has been the universal benchmark against which all other transition metal sites are referenced. Cu(II) ions are present in many biological systems and play a fundamental role in different vital processes, but, surprisingly, the structure of the simplest complex, that of Cu(II) in an aqueous solution, is a matter of ongoing debate. It has long been described as a Jahn-Teller distorted six-coordinated Cu–O octahedron. However, although there is a general agreement concerning the stable presence of four equatorial water ligands, which exhibit a uniform Cu–O distance of about 1.96 Å, there are several difficulties in detecting the number and even presence of the axial water ligands. In particular, neither X-ray or neutron diffraction nor X-ray absorption spectroscopy have provided an unambiguous probe of the loosely bound axial water molecules. In a first investigation, it has been proposed that the Cu(II) aqua ion adopts a fivefold coordination fluctuating between both a regular square pyramid and a regular trigonal bipyramid configuration, while a recent XANES study points out two equally populated 6- and 5-fold hydration conformations [1-2].

In the last decade, X-ray Emission Spectroscopy has been successfully applied to study ionic hydration. For instance, non-resonant Valence-to-core X-ray Emission Spectroscopy (Vtc-XES) was employed to determine the character of chemical bonding and to identify ligands for the solvated Mn(II) ion in water and for a series of Mn coordination complexes [3]. On the other hand, Resonant Vtc-XES experiments have been performed mostly in the solid phase, to investigate inorganic compounds such as transition-metal oxides, magnetoresistance manganites, Fe compounds and proteins [4].

In this work, Resonant Vtc-XES spectra were recorded at the Cu K-edge for water, methanol and acetonitrile solutions containing Cu(II) salts.

In order to gain insights on the local Cu(II) solvation geometry, a series of selected model geometries were then used to theoretically calculate the associated Resonant Vtc-XES spectra using the density-functional theory approach implemented in the OCEAN package [5]. The combination of Resonant Vtc-XES with theoretical tools will allow to carefully evaluate and describe the hydration geometry of Cu(II).

References

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