Quantitative Prediction of the K-edge XANES of Hydrated Transition Metal ions

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I. Background: Solvated transition metal ions in aqueous environment play an important role in many reactions occurring in chemical and biological systems as well as in industrial applications. The local solvation structure of these transition metal ions plays an important role in the underlying reaction dynamics at the active sites. In addition to biological systems, the aqueous phase chemistry of metal ions play a critical role in geochemistry, biochemistry, energy storage, electrocatalysis, and environmental chemistry. Experimentally, X-ray absorption fine structure (XAFS) spectroscopy that directly probe the local solvation structure around a specific metal center are ideal. X-ray absorption fine structure (XAFS) spectroscopy is a powerful experimental technique for local structural determination. Here, X-ray absorption spectra of metal ion K-edge have been studied both experimentally and computationally to explore local solvation structure of hydrated V^{2+}, V^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions.
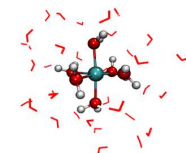

Figure 1. Transition metal ion in presence of water

II. Structures: All solutions in this study were prepared using weakly complexing ions (e.g. ClO_4^-) such that water is the only ligand coordinating all the metal ions, allowing us to study the impact of subtle orbital changes on the coordination structure in detail. To obtain good agreement between experimental and computed spectra, it is essential to have very accurate computed structures. Figure 2 shows excellent agreement between experimental and computed metal-oxygen bond distances.
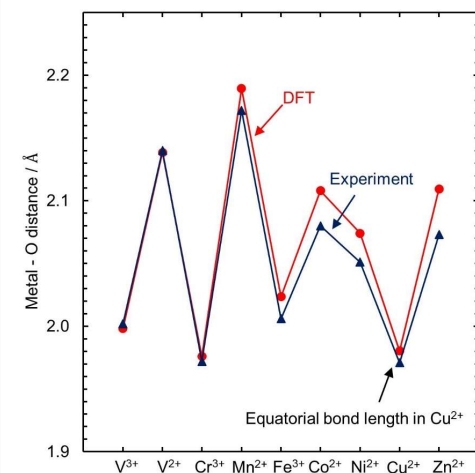

Figure 2. Metal-oxygen bond distances from density functional theory (DFT/PBE0) and experiment. Values from experiment are calculated from fitting EXAFS spectra. Values from theory are from this work. For Cu^{2+}, Metal-O distance corresponds to only equatorial bonds.
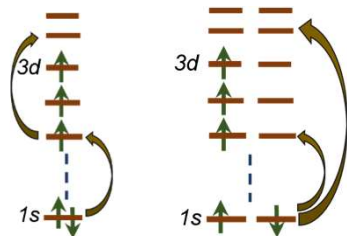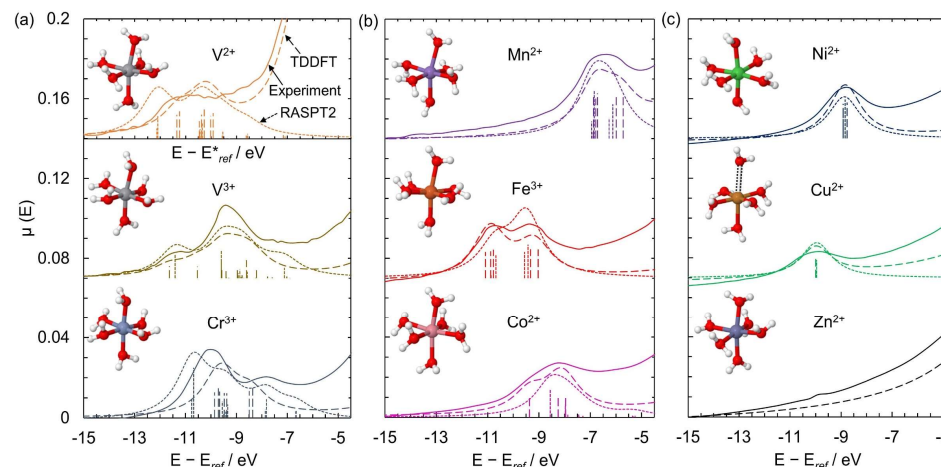

Figure 3. Experimental and computational 1s-3d pre-edge spectra for the series of aqueous ions, (a) V^{2+}, V^{3+}, and Cr^{3+}; (b) Mn^{2+}, Fe^{3+}, and Co^{2+}; (c) Ni^{2+}, Cu^{2+}, and Zn^{2+}.

III. Experimental vs Computational Spectra: Time dependent density functional theory (TDDFT) calculations provide accurate results for spectra that are dominated by single excitations, while significant improvements were obtained with restricted active space second order perturbation theory (RASPT2) calculations that correctly distinguish between singly and doubly excited states, where relevant (V^{2+}, V^{3+} and Cr^{3+}), with quantitative accuracy compared with experiment (Figure 3).

Figure 4. Nature of double excitations vs single excitations contributing to NXAFS in V^{2+}, V^{3+} and Cr^{3+} ions.

IV. Importance of Double Excitations: Multireference calculations show that double excitations play important role in the near edge XAFS (NXAFS) of V^{2+}, V^{3+} and Cr^{3+} ions. These doubly excited configurations involve an excitation of a β electron from the 1s orbital to a singly occupied $3d$ orbital and excitation of an α electron from an occupied $3d$ orbital to an unoccupied 3d orbital (Figure 4).

V. Concluding Remarks: In summary, we have presented a comprehensive study of the pre-edge XANES of the first-row transition metal ion series in water and make careful comparisons between experimental and computed spectra. Since water is used as the common ligand to solvate all the ions, this series represents a powerful benchmark to test the predictive ability of theory compared with experiment. We have shown that computational methods can accurately predict solvated structure of the ions and NXAFS for first row transition metal ions.

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