Fe L-edge XAS Definition of the Differences between Heme and Non-heme Fe Site Electronic Structures

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Fe porphyrin compounds form the basis for electron transfer in a number of biological systems. In the redox cycles of the cytochromes both the Fe(II) and Fe(III) oxidation states are of functional significance. The delocalization of the Fe d-orbitals into the porphyrin ring and its effect on the redox chemistry of these systems has been difficult to study spectroscopically because of the dominant porphyrin π to π^* transitions. Recently, we have developed a methodology that allows for the interpretation of the multiplet structure of Fe L-edges in terms of differential orbital covalency (i.e. differences in delocalization of the different d orbitals) using a valence bond configuration interaction (VBCI) model.[‡] Applied to heme systems, this methodology allows experimental study of the delocalization of the Fe d-orbitals into the porphyrin ring. The technique has been applied to a number of other systems that will also be discussed.

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