

## Characterization of a Genuine $S=1/2$ Fe(V) Complex

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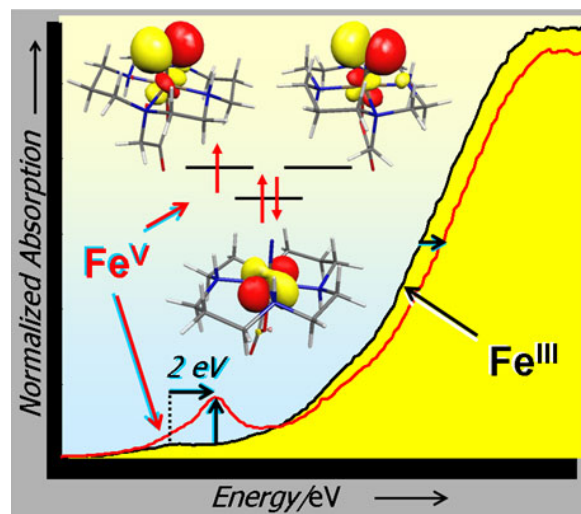
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High-valent Fe(IV) and Fe(V) intermediates are invoked in the catalytic mechanisms of both heme and non-heme iron enzymes.<sup>[1,2]</sup> Over the last several years, many Fe(IV)-oxo complexes have been synthesized and spectroscopically characterized, providing important markers for the characterization of Fe(IV) species.<sup>[3]</sup> In contrast, much less is known about Fe(V) species.

Recently, Frank Neese, Karl Wieghardt and co-workers have examined an Fe(V)-nitrido complex, which is generated by photolysis of an Fe(III)-azide precursor.<sup>[4]</sup> Mössbauer parameters for the Fe-nitrido complex are consistent with the an Fe(V) oxidation state assignment. However, further experimental data were needed to corroborate this result. For this reason, Fe K-edge X-ray Absorption (XAS) spectroscopy was used, in conjunction with electronic structure calculations, to obtain further insight into the Fe(V) complex.

The Fe K-edge is sensitive to changes in the effective nuclear charge on the metal, showing an  $\sim 1$  eV increase in the edge per oxidation state. Comparison of the Fe(V)-nitrido complex to the Fe(III) precursor shows an  $\sim 2$  eV shift, consistent with the formulation of this complex as an Fe(V) species. The appearance of the pre-edge feature at 7114.2 eV (using a reference calibration point of 7111.2 eV for the first inflection point of an Fe foil) is  $\sim 1$  eV higher than that of reported Fe(IV) species and provides an important reference for future XAS characterization of Fe(V). In addition, there is a dramatic increase in pre-edge intensity, consistent with the formation of a much shorter Fe-N bond in the nitrido species. EXAFS data were used to determine the first shell distances for the Fe(III) precursor and the Fe(V)-nitrido complex. It was found that the Fe(V) complex contained a short 1.60 Å Fe-N component, which was not present in the precursor.

Density functional theory (DFT) calculations on the Fe(V) species were carried out, allowing for either a doublet ( $S=1/2$ ) or quartet ( $S=3/2$ ) ground state. As the Fe(V) species is  $d^3$  and isoelectronic with Cr(III) and Mn(IV), an  $S=3/2$  ground state would be expected. Surprisingly, the results favor an unprecedented doublet ground state. In addition, the calculations show a rather large difference in the short Fe-N bond distance, giving optimized Fe-N bond distances of 1.61 Å and 1.74 Å for the doublet and quartet states, respectively.



Fe K-edge XAS spectra of the Fe(III)-azide precursor (black) and the Fe(V)-nitrido complex (red)

Hence the computational results, coupled with the EXAFS analysis, support a doublet ground state in the Fe(V) species.

The combined experimental and computational results provide strong evidence for the formulation of the Fe-nitrido complex as a genuine  $S=1/2$  Fe(V) complex. This study also provides important experimental markers for the characterization of other Fe(V) species, including high-valent iron intermediates within protein systems .

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**References:**

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