



Experiment title: Characterization of the Iron-Oxygen Bond in Compound I and Compound II Heme Intermediates Using $K\alpha$ -RIXS

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CH-4587

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Report:

The measurements performed under the previous proposal focused on Compound I and Compound II heme intermediates. Compound I and Compound II refer to $Fe^{IV}=O$ heme intermediates, where the former is a $S=3/2$ system due to a porphyrin cation radical ferromagnetically coupled to the iron. We started with a non-heme $Fe^{IV}=O$ system, $Fe^{IV}N4Py$; this system was characterized by us using various optical methods, allowing for easier interpretation of the RIXS spectrum. Comparison with the Compound II spectrum will reveal the effect that the heme ligand has on the reactive frontier molecular orbitals (FMOs) in these complexes. Finally, we also measured the RIXS spectrum of Compound I, with the goal of determining how having the porphyrin radical affects the $Fe=O$ bond and therefore affects reactivity in these systems. In order to get satisfactory data quality for these systems, multiple RIXS planes were averaged together across multiple sample batches. Furthermore, since these high-valent systems are susceptible to photoreduction, the X-ray attenuation and integration times were carefully chosen for each sample to ensure that the spectra are not affected by photodegraded product. Since multiple sample spots are used throughout the experiment, a set of concentration scans are performed following collection of the RIXS plane, moving the incident energy past the Fe K-edge and collecting the X-ray emission again for each point, allowing for a spot-to-spot RIXS intensity correction. Following the concentration correction, the data is normalized using the post edge with a similar method to that used in K-edge XAS. Finally, the incident and transfer energies are both calibrated using the $t2g$ peak present in iron ferricyanide, which has been analyzed by us previously using a valence bond configuration interaction (VBCI) approach.¹

The full Fe $K\alpha$ -RIXS plane for $Fe^{IV}N4Py$, Compound I, and Compound II are shown in Fig. 1-3, respectively. Also displayed are the constant emission energy (CEE) cut, which yield a high energy resolution K-edge spectrum, and the constant incident energy (CIE) cut, which yields an L-edge XAS-like spectrum. The Compound II RIXS plane exhibits a weaker pre-edge region than the N4Py or Compound I samples; this intensity difference is due to protonation of the oxo-group, which increases the centrosymmetry of this system and reduces 4p-3d orbital mixing. Cytochrome P450, unlike many other heme systems, exhibits a protonated oxo-group, which should exhibit a RIXS spectral signature similar to that obtained for our Compound II model. The average CIE cut for this system appears to be more featured than that observed for the other samples, possibly due to 3d-4p mixing not being the dominant intensity mechanism in this system.

The Compound I has a stronger pre-edge intensity in the CEE relative to the Compound II sample, consistent with a loss in centrosymmetry due to the short Fe=O bond length. Similar to N4Py, the Compound I CEE cut has a broad pre-edge peak due to contributions from multiple peaks (fitting not shown). The N4Py CEE cut exhibits an additional weak transition at lower energy (~7111.8 eV), but it is not clear if this peak is present in the Compound I CEE. The Compound I average CIE cut is broad and featureless, similar to that of N4Py; the N4Py does exhibit a weak shoulder at ~707 eV which is not readily apparent in the Compound I sample. The RIXS data will be simulated using a VBCI approach, which has proven capable of modelling Fe L-edge XAS and K α -RIXS spectra. This will allow us to extract the differential orbital covalency and determine how the porphyrin ring, the protonation of the oxo-group in Compound II, and the porphyrin radical in Compound I, affect the various frontier molecular orbitals in ferryl-oxo heme intermediates.

References:

- 1) Lundberg, M.; Kroll, T.; DeBeer, S.; Bergmann, U.; Wilson, S. A.; Glatzel, P.; Nordlund, D.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* 2013, 135, 17121.

