High-Resolution EXAFS Supports an Open-Core Structure in the Q Intermediate of Methane Monooxygenase

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The fundamental understanding of oxidation of methane to methanol is of key scientific and industrial interest for the development of improved gas-to-liquid fuel conversion technology. Soluble methane monooxygenase (sMMO) employs a diiron active site to activate O_2 and subsequently oxidize methane to methanol. The key catalytic intermediate, **Q**, is a diiron(IV) center, and its structure has eluded researchers for decades. Initially assigned as a bis-mu-oxo 'diamond core,' from a 2.46 Å Fe-Fe distance measure by EXAFS.[1] For the past 20 years, there has been much controversy with regard to this distance parameter, as neither synthetic nor computational models reproduce such a short distance and catalytic model studies do not support a closed core structure. However, the vibration observed in resonance Raman spectra at room temperature in a flowing system are assigned as a characteristic tetra-atomic vibration of the closed core for **Q** generated.[2]

Recently our group has investigated the core structure of **Q** by the technique of Fe Kα High-Energy Resolution Fluorescence Detected (HERFD) X-ray Absorption Near-Edge Structure (XANES) spectroscopy of **Q** compared to various high-valent diiron model complexes. The large pre-edge intensity of **Q** is not supported by a closed core and only rationalized by a diiron core of decreased symmetry with significant covalency contributions core ligands.

As the proposed open and closed core structures possess dramatically different Fe-Fe distances, a reevaluation of the previous EXAFS is now desired to help conclusively determine the core structure. Herein, we have applied Kα HERFD to the EXAFS collection of **Q**, to provide increased spatial resolution and reduce background contributions. HERFD EXAFS of rapid-freeze quench samples of **Q** do not exhibit the short Fe-Fe scatterer of 2.46 Å previously observed. A longer Fe-Fe distance, 3.4 Å, renews the possibility that **Q** is not a closed bis-mu-oxo core but an open mu-oxo with terminal oxo/hydroxo groups. The previous R = 2.46 Å feature is plausibly assigned to background iron contamination (i.e. scattering of iron within the cryostat), whereas the HERFD technique inherently eliminates such background contributions. The HERFD EXAFS of **Q** is best fit modeled with a long diiron distance, more aligned with open core models.

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