EMSL Research and Capability Development Proposals

Cryogenic NMR and Advanced Electronic Structure Theory as a Unique EMSL Capability for Complex Systems: Application to the Photosynthetic Energy Conversion Systems

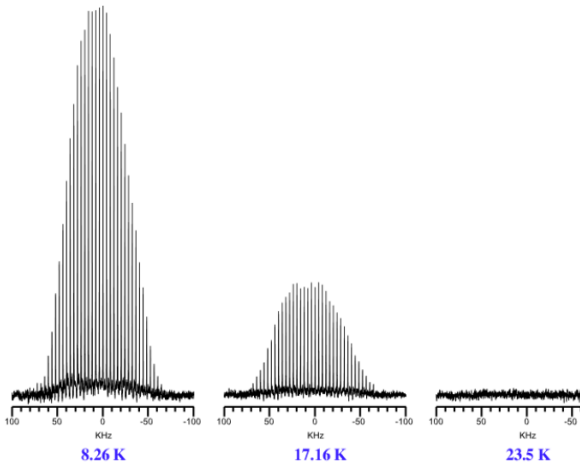
Project start date: April 1, 2010

EMSL Lead Investigator:
Ping Yang
Molecular Science Computing Group, EMSL, PNNL

Co-investigator:
Andrew S. Lipton
Cell Biology & Biochemistry, FCSD, PNNL

Collaborator:
K.V. Lakshmi
Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute

The goal of this proposal is to demonstrate a unique capability to be enabled at EMSL—the integration of leading-edge cryogenic nuclear magnetic resonance (NMR) measurements and advanced electronic structure computations to characterize the structure and dynamics of complex systems. The Oxygen Evolving Complex (OEC) in natural photosynthetic systems continues to offer the single most critical scientific challenge for its importance in life processes and as template for designing artificial energy photoconversion systems. To date, the complete characterization of selected aspects of the structure, physicochemical properties, and oxygen evolution mechanism in the OEC has remained elusive.



Temperature dependence of the on-resonance portion of the ^{55}Mn-NMR spectrum of a Mn(IV,IV) dimer acquired at 9.4 T.

This unique EMSL capability will combine cryogenic solid-state ^{55}Mn-NMR measurements of the OEC and highly electron correlated theories (QM) to bring critical progress toward the definite characterization of the structure of the OEC and mechanism of O_2 formation in the PSII system. Thus far, traditional variants of NMR spectroscopy and density functional theory (DFT) computations have failed to uncover the definitive characterization that will emerge from cryogenic NMR and highly electron-correlated theories applied in concert. The successful application of this unique EMSL capability will clearly demonstrate the combined cryogenic NMR/theory power in providing critical insights and understanding of the structure and function of strongly correlated systems in biosciences and other fields, such as materials for catalysis and magnetic superconductivity.

Our approach will start with the Mn_2(IV,IV), Mn_2(III, IV), and Mn_2(III,III) manganese dimer series and directly compare with experimentally measureable parameters such as electric field gradient (EFG) tensor, electron's *g*-factor, ^{55}Mn hyperfine couplings, etc. Upon complete understanding of these dimer complexes, we will investigate the natural OEC structure in the isolated and purified Photosystem II from spinach and cyanobacteria.

Products and Output

New Capability for EMSL Users

This work will demonstrate the power of the new EMSL capability—the tightly coupled techniques of cutting-edge cryogenic NMR experiments and highly electron correlated theories—to address extreme complex systems in biosciences and energy-related sciences.