Polarization Phase Selective (PPS) Studies of Biosystems: New Split-Florida Helix Magnet (SFHM) Configurations

K. Rupnik (LSU, Chemistry)

Introduction

High field (>10T) Opto-Magnetic (OM) Variable Temperature (VT, 1 to 300 K) PPS studies of Reaction Control Agents (RCA) in complex molecules of biomedical interest using new SFHM continued in 2013. After successfully completing first fs-scale setup, we move now to shorter timescales which brings proteins research to new challenges. We recently made several important scientific breakthroughs in these areas[1]: (1) from a study of reduction-oxidation processes in enzymes we found significant novel spin structures in some proteins with Fe_4S_4 clusters, (2) were able to propose new mechanisms of electron transfer and (3) in 2013 we also looked at their role in various steps of enzyme and non-enzyme synthesis. Our results had impact in various fields from the design of single molecule-magnets to our understanding of molecular evolution. We are currently testing improved fs configurations developed for the bio-samples measured at the SFHM.

Experimental

The September 2012 and May 2013 experiments were done in Cell 5 on our OM-PPS configuration at SFHM. Most of the PPS work was focused on the 350-1100nm, but now we can cover VUV and NIR. SFHM measurements on bio-samples require very specific novel sample embedding and heat removal techniques: we introduced prototype of new more sensitive detector/electronic configurations and new holding cell, one with reflective path for low fs measurements. We also made new cross- and autocorrelations instruments with fs resolution, prepared sub 25fs optics tests, tested new pump-probe, SHG, SFG systems and prepare plans for possible HHG work. Our OM-PPS experimental work was always focused on better all-photonic Spatio-Temporal EM Structure (STEM) measurements for imaging and interaction mechanisms

Results and Discussion

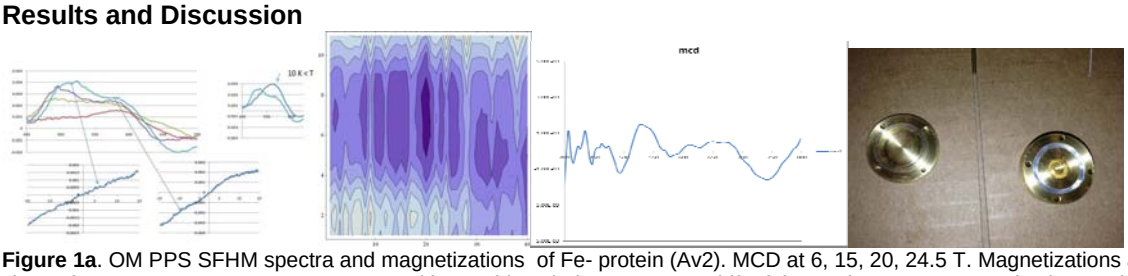

Figure 1a. OM PPS SFHM spectra and magnetizations of Fe- protein (Av2). MCD at 6, 15, 20, 24.5 T. Magnetizations at 580 and 520nm are shown from -24.5 to 24.5 T. Temperature with sapphire windows ~10K. A shift of the peak at 520->580nm is observed at higher temperatures. High are very different from what we observed in low fields**. Fig 1b** Our PPS method is a multidimensional technique that acquires not only spatial, temporal, and various spectral data but also internal phases – PPS improves the STEM resolution. With high OM fields we also modify temporal phase and have obtained much higher selectivity which resulted in new information about enzymatic structures. Results indicate also the presence of oscillatory structures in fs region where our models predict new coupling between different RCAs **Fig. 1c**. New results from one of Fe3S4 systems. **Fig 1d**. New sample holders.

Conclusions

After successfully completing first OM-PPS-SFHM measurements we are preparing for sub 50fs domain. Many technical obstacles were successfully resolved. Our observations question interpretations of previously proposed electron spin structure models and mechanisms and indicate possible new controlling mechanisms through highly selective coupled channels that combine specific redox and photonic RCA[2]. Of major importance now will be ultrafast measurements (10-100fs) of highly correlated electron spin and vibrational coupling, which require our newly developed sample presentation and embedding techniques. It was suggested that such OM PPS technology will provide significant improvement to the present MRI-like technologies in biology and medicine.

Acknowledgements

NHMFL Award number 227000-520-022742, LSU R&E and students support funds, IAS, NSF Magneto-optics materials and education project (2012-2015), NSF Cooperative Agreement No. DMR-1157490, the State of Florida, and the U.S. Department of Energy.

References:

[1] K. Rupnik et al. (submitted), Rupnik, K, *et al*., J. Am. Chem. Soc., **134**, 13749-13754 (2012), Rupnik, K. *et al*., J. Am. Chem. Soc., **133**, 6871-6873 (2011);
[2]K. Rupnik, Proceedings HPC-LSU Conference 2013, K. Rupnik, Proceedings ISTCP, 2013, K Rupnik, GRC Quantum Control, 2013, K. Rupnik, Int.. J. Quant. Chem. (invited paper, 2014).