Ultrafast Polarization Phase Selective (PPS) Studies: Areas of Fundamental Significance to Biochemistry/Biophysics

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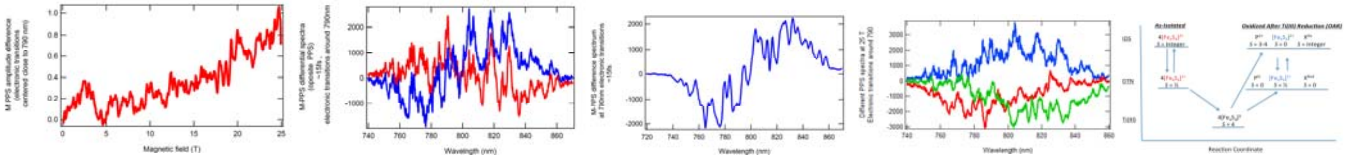
Introduction: Opto-Magnetic (OM) PPS measurements of electron spins signatures in enzymes

In 2014 we published another important scientific breakthrough: measurements of various steps of a newly found controlled non-enzymatic synthesis with the Fe_xS_y enzymes[1] . Earlier, contrary to established models predictions, we found significant novel electron-spin structures in some proteins with Fe_4S_4 clusters during reduction-oxidation processes and proposed new mechanisms of electron transfers with broad relevance to medicine as well as molecular evolution[2]. Our OM PPS modeling and measurements could not only identify radiation signatures (RS)[3] of early spin-electronic events but also identify and image some of the selected electronic trajectories. We expect that combined atto-femto-scale PPS based Spatio-Temporal Electro-Magnetic Processes/structures (STEMP) measurements using recently developed TA, PA, SHG, SFG, HHG and coincidence PPS configurations at LSU, ETH, NHMFL and elsewhere will provide better understanding of relevant correlated electron-spin-nuclear mechanisms.

Experimental

In July 2014, using <20fs pulses and reconfigured 25 T Split-helix magnet at NHMF lab (cell 5) we have developed and tested OM PPS instrumental configurations that could monitor even soft matter systems of our interest. With newly developed precise instruments (PPS-FROG, correlators etc.) we can identify signatures of molecular processes better than 10^{-9} in comparison to similar non-PPS methods. PPS spectra and magnetizations cover the important metal-ligand electron transition range 250-1500nm associated with the effects of the reaction controlling agents (RCA) in complex biophysical processes.

Results and Discussion: 15fs laser pulse, 25T field soft mater PPS system configuration – first results



Figs. 1a-d: Electron transitions in the 800nm range of Fe-S compounds. Fig.1 a: First measured integrated 2-phase difference PPS magnetization curve from 0 to 25 T using ~15fs 800nm centered laser pulse @ 80 MHz. Coherent events are driven in the broadband region. Fig.1 b: Red/blue - opposite PPS at 25 T. OM PPS spectrum can significantly modulate temporal phase and also help selectively resolve different spatio-temporal contributions. Fig. 1 c: Magnetic contribution to 2-phase difference PPS structure at 25 T. Fig. 1 d: Three different PPS spectra at 25 T. Fig 1e:,Our recent PPS high field measurements and models show where we should identify fast electron-spin-nuclear decision making processes that control redox steps in both enzymatic and non-enzymatic Fe-S clusters nonenzymatic synthesis[1].

Conclusions

In July 2014 we have successfully completed the first proof-of-principle OM PPS soft matter measurement using < 20 fs pulses in 25 T magnetic field at NHMFL, and are now preparing work on other biosystems of interest to biochemical/biophysical studies. Many expected and unexpected obstacles were successfully resolved. Based on this experience, we also work on major improvements - including new optical and mechanical parts and system configurations for PPS-STEMP (auto)correlation, pulse tailoring and TA/pump-probe work. Undergraduate and graduate students are actively involved in this project [3-5]. Results of July NHMFL and 2014 LSU work, including preliminary results of TA-pump-probe configuration measurements) are analyzed [7].

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References

[1] Rupnik, K., *et al*., Biochemistry**, 53 (7)** 1108 (2014); [2] Rupnik, K., *et al*., J. Am. Chem. Soc., **134**, 13749-13754 (2012); [3] Rupnik, K. *et all*, DoE projects on PPS RS (1990-1995), [4] Rupnik, K., Proceedings APS March Meeting, Denver CO, (2014); [5] Rupnik, K *et all*., GRC Photoionization - Photo-detachment, (February, 2014); [6] Rupnik, K., GRC Multiphoton Processes (June, 2014) , [7] Rupnik, K. Int. J. Quant. Chem. (invited paper, 2014).