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

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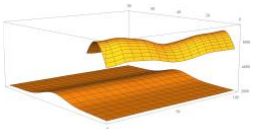
Introduction Our February 2017 UFPPS measurements using >15fs pulses and up to 25 T magnetic fields provide information about previously unseen *in situ* correlated electron-spin-hole (ESH) dynamics. PPS methods at these scales also aim to image some of the ESH trajectories[1,3]. As shown in our publications, Opto-magnetic (OM) PPS measurements can identify electronic processes where other methods cannot, including[2] : (1) a recent scientific breakthrough in Fe_xS_y enzymes study, where we observed various steps of a newly found controlled non-enzymatic synthesis, (2) a study of redox processes in enzymes, where we found novel ES structures and were also able to propose new mechanisms of electron transfers with broad relevance to medicine as well as molecular evolution[2]. In 2016/17 we measured[2]: (1) enzymatic TO in Av1, (2) ES dynamics during radical SAM activity, (3) ES signatures during P-protein synthesis, and (4) nanoparticles assisted enzyme activation. The ongoing collaborative research at LSU, ETH, NHMFL, and other USA institutions continues.

Experimental In February 2017 we continued development of new instrumental configurations using 50fs to 15fs pulses and 25 T field from newly reconfigured Split-helix magnet in cell 5 NHMFL. We tested optics for CEP stabilized 7fs lasers. We measured ultrafast better than 10^{-9} sensitive multi-spectral domain PPS spectra (HG, SFG and cross-correlation configurations). We encountered problems with lasers (Coherent) and some enzyme preparations, all of which took some time to resolve them. *In the fall 2017 we prepared material for new UF-parallel-magnetic-field system, but that work is now moved to 2018.* Instead, at LSU we developed and applied new multi-beam SFG, cross correlation and Spectral Imaging (SI) techniques. All these methods will be available to NHMFL users.

Results and Discussion In February 2017 at NHMFL, we acquired large data sets from measured broadband ultrafast multidimensional (frequency, field, PPS etc.) ES molecular spectra and CCD images. Data show some familiar OM features, but with new different sub-structures, and indicate novel time-domain signatures in soft matter systems of our interest. We also measured new enzymes/proteins and metal-radicals compounds and some of their time-dependent biological reactions. We started UFPPS *in vitro* measurements with new Nanoparticle-enzyme Based Hybrids (NEBH). These nanoparticles of different sizes, shapes and with different required electron energies could provide spatially and temporally controlled EMF-driven ESH separations and transfers to desired molecular locations. In December 2017 we prepared materials for *in vivo* tests of medical interest.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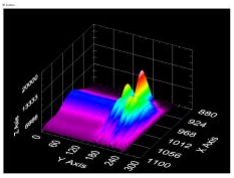
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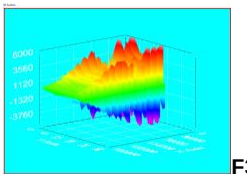
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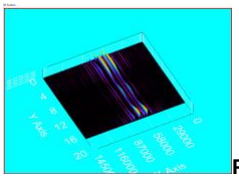
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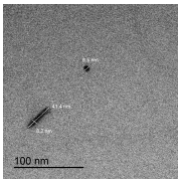

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Fig. 1: measured broad band PPS spectral regions 267, 400, 800 nm using ~15fs oscillator- this SFG based OM PPS analysis clearly shows polarization dependences; **Fig. 2:** new PPS cross-correlation technique captures temporal components -it could provide most information when in CEP controlled measurements; **Fig 3.:** shows difference between ~1T field on and off –Fe ESH; Fig. 4: Large PPS data sets form Spectral Imaging (SI); **Fig 5**: TEM images of new nanostructures for Nanoparticle-enzyme Based Hybrids (NEBH).

Conclusions New results complement our previous PPS studies and indicate feasibility of significantly better measurement techniques at molecular-electronic level. This new science requires understanding of attomechanics based on UF spatio-temporally resolved electro-magnetic (STEM) processes and structures in molecular systems, a novel and very different research objective. Our goal now is to better integrate UF technology into biophysical enzyme studies. Additional magnet time will be used to expand instrumentation, methods and to complete data sets.

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