



Friday, December 1st, 2017 – 2:00 pm
CFEL Seminar room III, EG 080 (Bldg. 99)

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Ultrafast Multidimensional Spectroscopy of Molecules with x-ray pulses and Quantum Light in Microcavities

Multidimensional spectroscopy uses sequences of optical pulses to study dynamical processes in complex molecules through correlation plots involving several time delay periods. Extensions of these techniques to the x-ray regime will be discussed. Ultrafast nonlinear x-ray spectroscopy is made possible by newly developed free electron laser and high harmonic generation sources. The attosecond duration of X-ray pulses and the atomic selectivity of core X-ray excitations offer a uniquely high spatial and temporal resolution. Stimulated Raman detection of an X-ray probe may be used to monitor the phase and dynamics of nonequilibrium valence electronic state wavepackets created by e.g. photoexcitation, photoionization and Auger processes. Novel ultrafast X ray probes for strongly coupled electron-nuclear dynamics, techniques based on a coherent stimulated Raman process that employs a composite femtosecond/ attosecond X-ray pulse to directly detect the electronic coherences (rather than populations), and new imaging techniques based on x-ray diffraction from electronic coherence will be presented.

Nonlinear optical signals induced by quantized light fields and entangled photon pairs are presented. Conventional nonlinear spectroscopy uses classical light to detect matter properties through the variation of its response with frequencies or time delays. Quantum light opens up new avenues for spectroscopy by utilizing parameters of the quantum state of light as novel control knobs and through the variation of photon statistics by coupling to matter.

Entangled-photon pairs are not subjected to the classical Fourier limitations on the joint temporal and spectral resolution. Strong coupling of molecules to the vacuum field of micro cavities can modify the potential energy surfaces thereby manipulating the photophysical and photochemical reaction pathways. Crossings of electronic potential surfaces in nuclear configuration space, known as conical intersections, determine the rates and outcomes of virtually all photochemical molecular processes. Strong coupling of molecules to the quantum vacuum field of micro cavities that can be used to manipulate their photophysical and photochemical reaction pathways and polariton relaxation in photosynthetic antennae are demonstrated.

- [1] J. Biggs, D. Healton, Y. Zhang, and S. Mukamel. "Multidimensional Attosecond Resonant X-ray Spectroscopy of Molecules; Lessons from the Optical Regime", *Ann Rev Phys Chem*, 64, 101-127 (2013).
- [2] Markus Kowalewski, Kochise Bennett, and Shaul Mukamel. "Monitoring Nonadiabatic Avoided Crossing Dynamics in Molecules by Ultrafast X-Ray Diffraction", *Structural Dynamics*, 4,054101 (2017)
- [3] Konstantin E. Dorfman, Frank Schlawin, and Shaul Mukamel. "Nonlinear optical signals and spectroscopy with quantum light", *Rev. Mod. Phys.* 88, 045008 (2016)
- [4] "Monitoring polaritons dynamics in the LHCII photosynthetic antenna in a microcavity by two-photon coincidence counting", Zhedong Zhang, Prasoon Saurabh, Konstantin E. Dorfman, Arunangshu Debnath, and Shaul Mukamel. *J. Chem. Phys* (submitted, 2017)
- [5] Markus Kowalewski, Kochise Bennett, and Shaul Mukamel. "Cavity femtochemistry; Manipulating nonadiabatic dynamic avoided crossings", *J. Phys. Chem. Lett*, 2016, 7, 2050-2054

Host: Dwayne Miller

