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# Department of Chemistry

## Special Seminar

9:45 a.m. Tuesday, November 22 • 331 Smith Hall



Assistant Professor

### Andrew Moran

Department of Chemistry  
University of North Carolina at Chapel Hill

#### *Probing Ultrafast Dynamics in Photosynthesis and DNA Photoprotection With Nonlinear Spectroscopy*

Research specializes to systems in which these dynamics occur on the femtosecond time scale. The general goal of his experimental work is to understand how interactions between electrons and nuclei control the outcome of photoinduced events.

Website: <http://www.chem.unc.edu/people/faculty/moran/>

#### Abstract

Transport processes and spectroscopic phenomena in light harvesting proteins are intimately connected to the delocalization of electronic states. Decoherence imposed by low-frequency nuclear motion generally suppresses the delocalization of electronic states, whereas the Franck-Condon progressions of high-frequency intramolecular modes underpin a hierarchy of vibronic electrostatic interactions between pigments. We use femtosecond laser spectroscopies to investigate the impact of vibronic couplings on the electronic structures and relaxation mechanisms of two cyanobacterial light harvesting proteins, allophycocyanin (APC) and c-phycocyanin (CPC). Both APC and CPC possess three pairs of pigments (i.e., dimers), which undergo electronic relaxation on the sub-picosecond time scale. Electronic relaxation is approximately 10 times faster in APC than in CPC despite the nearly identical structures of their pigment dimers. We find that electronic relaxation in these closely related proteins is understood on the same footing only in a basis of joint electronic-nuclear states (i.e., vibronic excitons).

Intriguing fundamental physics surround photoinduced relaxation processes in DNA. Internal conversion rapidly (<300fs) deactivates excited electronic states in the DNA bases, thereby suppressing the formation of lesions (e.g., thymine dimers) known to inhibit cellular function. At the instant following internal conversion, the nucleobases are left in "hot" quantum states, wherein a subset of vibrational modes possesses a highly non-equilibrium distribution of excitation quanta (i.e., >4eV in excess energy). Our studies of such non-radiative dynamics in nucleobases and short nucleotides are made possible by our recent extension of specialized laser techniques to the mid-UV spectral range. It will be shown that temperature variation reveals interesting contrasts in the internal conversion and vibrational cooling mechanisms found in adenine and thymine model systems.

Host: Professor Aaron Massari