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Non-Adiabatic Mechanism for Photosynthetic Energy Transfer and All-Optical Determination of Concentration using Femtosecond Lasers

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Understanding the fundamental physics of light-harvesting in both, natural and artificial systems is key for the development of efficient light-harvesting technologies. My thesis addresses the following topics, i.) the mechanism underlying the remarkably efficient electronic energy transfer in natural light harvesting antennas, ii.) a femtosecond time-resolved photonumeric technique to quantitatively characterize transient chemical species. This talk will concentrate on the first project, while briefly touching the key ideas of the second project. Light harvesting antennas use a set of closely spaced pigment molecules held in a controlled relative geometry by a protein. It is shown that in certain antenna proteins the excited state electronic energy gaps between the pigments are resonant with a quantum of pigment vibrational energy. With such a vibrational-electronic resonance, anti-correlated motions between the pigments lead to a strong coupling between the electronic and nuclear motions, that is, breakdown of the Born-Oppenheimer approximation, over a wide range of pigment vibrational motions. It is shown that the 2D spectroscopic signatures of the resulting unavoidable nested non-adiabatic energy funnel on the excited states of photosynthetic antennas are consistent with all the reported 2D signatures of long-lived coherent oscillations, including the ones that are not explained by prior models of excited state electronic energy transfer. Extensions that account for both resonant and near-resonant pigment vibrations suggest that photosynthetic energy transfer presents a novel design in which electronic energy transfer proceeds non-adiabatically through clusters of vibrations with frequencies distributed around electronic energy gaps. I will also briefly talk about our experiments demonstrating quantitative time-resolved measurement of *absolute* number of excited state molecules. Based on these measurements, an all-optical technique that simultaneously determines concentration and extinction coefficient of an unknown sample is presented. Unlike prior analytical techniques, any requirements such as sample isolation, physical handling or in situ calibrant are eliminated allowing possible extensions towards characterizing transient chemical species.