

Abstract Submitted
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Excited State Vibrational Dynamics of a Porphyrin Molecule Measured with Multidimensional Pump-Degenerate Four-Wave Mixing Spectroscopy¹ BAXTER ABRAHAM, JESUS NIETO-PESCADOR, LARS GUNDLACH, Univ of Delaware — Knowledge of the excited state relaxation mechanisms of porphyrin molecules is necessary for understanding the underlying photochemical processes of many biological and artificial light harvesting systems. The complex electronic structure of these molecules has given rise to several conflicting relaxation models. We employ pump-degenerate four-wave mixing spectroscopy to provide further insight into the ultrafast dynamics. An actinic pump pulse precedes a three pulse probing sequence which produces a spatially independent pulse induced by polarization changes in the excited state. Recording the intensity of the generated pulse over the course of increasing pump delays produces a time-varying signal that is Fourier transformed to observe time-dependent frequency spectra. Measurements on a porphyrin archetype reveal new information on the vibrational dynamics of the excited state. Raman active features are monitored after photoexcitation, and amplitude and energy changes are observed. Peaks attributed to the chromophore are in phase with each other and out of phase with solvation shell vibrations. Measured frequency upshifts are consistent with relaxation in an anharmonic potential energy surface. These results elucidate the role of vibrational cooling versus optically dark states.

¹Department of Energy

Baxter Abraham
Univ of Delaware

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