Abstract Submitted
for the MAR16 Meeting of
The American Physical Society

Femtosecond Heterodyne Transient Grating Studies of Nonradiative Decay of the S_2 ($1^1B_u{}^+$) State of Peridinin: Detection and Spectroscopic Assignment of an S_x Intermediate State[1] SOUMEN GHOSH, MICHAEL M. BISHOP, JEROME D. ROSCIOLI, Michigan State University, AMY M. LAFOUNTAIN, HARRY A. FRANK, University of Connecticut, WARREN F. BECK, Michigan State University — Femtosecond heterodyne transient grating spectroscopy was employed to investigate the nonradiative relaxation dynamics of peridinin from the S_2 state to the S_1 ($2^1A_g{}^-$) state in methanol. A global target analysis indicates that S_2 decays in 12 fs to populate an intermediate state, S_x. The absorption and dispersion components of the transient grating signal exhibit a response that is very similar to that of β-carotene in benzonitrile solution. Numerical simulation of the experimental data indicates that the excited state absorption transition from S_x has a larger oscillator strength than that of S_1, which rules out an assignment of S_x to a vibrationally excited S_1 state. The lifetime of S_x is found to be strongly dependent on the polar solvation timescale. This result indicates that nonradiative decay from S_x to S_1 involves large-amplitude torsional motions and a concomitant formation of intramolecular charge transfer character. The present work provides the first evidence that peridinin has an ultrashort S_2 lifetime owing to the onset of torsional motions and shows that the S_x acts as an active state for excitation energy transfer to chlorophyll in light-harvesting proteins.

[1]Work supported by the Photosynthetic Systems program of U.S. Department of Energy under Award Number DE-SC0010847.

Warren Beck
Michigan State Univ

Date submitted: 06 Nov 2015 Electronic form version 1.4