Abstract Submitted
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Torsional Dynamics, Intramolecular Charge Transfer, and Solvent Friction in the S_2 ($1^1B_u^+$) Excited State of Peridinin: A Mechanism for Enhanced Mid-Visible Light Harvesting in the Peridinin–Chlorophyll *a* Protein[1] WARREN BECK, JEROME ROSCIOLI, SOUMEN GHOSH, MICHAEL BISHOP, Michigan State University, AMY LAFOUNTAIN, HARRY FRANK, University of Connecticut — The structural mechanism that allows peridinin to provide one of the highest quantum efficiencies for excitation energy transfer to chlorophyll (Chl) *a* acceptors in the peridinin–chlorophyll *a* protein (PCP) from dinoflagellates involves an order-of-magnitude slowing of the S_2 ($1^1B_u^+$) $\rightarrow S_1$ ($2^1A_g^-$) nonradiative decay pathway compared to carotenoids lacking carbonyl substitution. Using femtosecond transient grating spectroscopy with heterodyne detection, we have determined for the first time that the decay of an intermediate state termed S_x, which we assign to a twisted form of the S_2 state, is substantially slowed by solvent friction in peridinin due to its intramolecular charge transfer (ICT) character. The S_x intermediate exhibits a long enough lifetime to serve as an efficient excitation energy transfer donor to Chl *a* in PCP. The possibility that the Franck–Condon S_2 state also transfers excitation via quantum coherent mechanisms is being considered currently using broadband two-dimensional electronic spectroscopy.

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