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Femtosecond Heterodyne Transient Grating Detection of Conformational Dynamics in the S_0 ($1^1A_g^-$) State of Carotenoids After Nonradiative Decay of the S_2 ($1^1B_u^+$) State[1] JEROME D. ROSCIOLI, SOUMEN GHOSH, MICHAEL M. BISHOP, Michigan State University, AMY M. LAFOUNTAIN, HARRY A. FRANK, University of Connecticut, WARREN F. BECK, Michigan State University — Transient grating spectroscopy was used to study the dynamics of nonradiative decay of the S_1 ($2^1A_g^-$) state in -carotene and peridinin after optical preparation of the S_2) state. The kinetics of the recovery of the absorption and dispersion components of the third-order signal exhibit significantly different time constants. For β-carotene in benzonitrile, the absorption and dispersion recovery time constants are 11.6 and 10.2 ps. For peridinin in methanol, the time constants are 9.9 and 7.4 ps. These results indicate that the initial product of the decay of the S_1 state is a conformationally displaced structure. The decay rate for the S_1 state and the conformational relaxation rate are both slowed in peridinin as the polarity of the solvent decreases; in ethyl acetate, the conformational relaxation time constant is 45 ps, which rules out a dominant contribution from vibrational cooling. These results indicate that the S_1 state develops intramolecular charge transfer character owing to distortions along torsional and out-of-plane coordinates, with a pyramidal structure favored as the most stable conformation. Recovery of the photoselected ground state conformation involves a reverse charge-transfer event followed by relaxation to a planar structure.

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