Ultrafast probes of the first events in photosynthesis: Pump probe anisotropy studies of the photosynthetic reaction center

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Although much work has focused on the dynamics prior to and during charge separation
cally excited special pair (P', where P is the special pair ground state) and its influence on energy and electron transfer. In this report we present "two color" wavelength-resolved pump-probe anisotropy measurements of the photosynthetic reaction center (RC) of Rhodobacter Sphaeroides at room temperature. The major Q absorption bands are collectively excited using short (13-18 fs) pulses with a broad spectral range, or individually excited with longer, spectrally narrowed pulses, which overlap with the transition(s) of interest. A broadband probe records the response of the system with respect to wavelength, time, and polarization. The resulting "two color" pump probe anisotropy transients yield detailed experimental descriptions of the dynamics prior to charge separation, particularly energy transfer from B to P.

Four distinct contributions to the wavelength resolved anisotropy measurements are observed: ground state bleach and stimulated emission components from B and P, excited state absorption from P, and a newly identified narrow bleach/stimulated emission band at 825 nm, identified as P'. This latter spectroscopic feature appears immediately after exclusive excitation of P and yields anisotropy values consistent with a transition dipole moment rotated 70° from the P-P transition moment, in agreement with low temperature results for P' but the absorption wavelength is significantly higher (825 nm versus 810 nm at low temperature).

The wavelength resolved magic angle transient observed after excitation of B is shown in Fig. 1. This three-dimensional plot clearly shows the rapid decay of B and the subsequent rise of P following energy transfer. The three-dimensional data are analyzed using experimentally determined spectra and anisotropy values for B, P, and P'. A satisfactory fit to data is obtained with a model wherein energy transfer from the B to P occurs by a two step mechanism, with P' serving as the intermediate. The results of this kinetic analysis are shown in Fig. 2. The resulting time constants for this reaction center chromophore cannot be ignored.

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QThG8

Solvation effects on stimulated librational scattering

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Low-frequency (1 to 70 cm⁻¹) stimulated Stokes (i.e., red-shifted) scattering of polarizable molecules such as carbon disulfide has been observed in liquid-filled hollow core fibers and microdroplets. Such geometries provide long interaction pathlengths for the buildups of nonlinear optical processes. This