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

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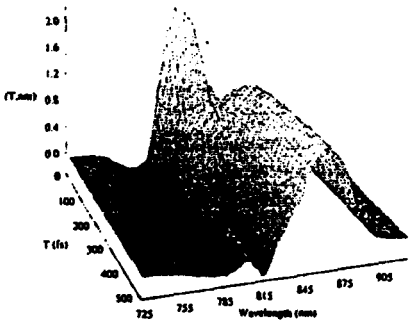
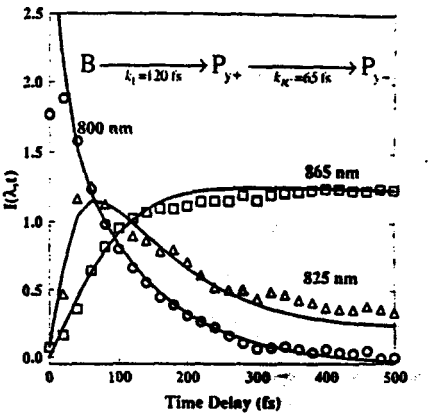
Although much work has focused on the dynamics prior to and during charge separation



QThG7 Fig. 1 Entire temporal and spectral response following excitation of the accessory bacteriochlorophyll. Here a positive signal indicates a transient bleach, while a negative signal indicates a transient absorption. The surface plot shows the rapid decay of a bleach at 800 nm resulting from B, and a corresponding buildup of bleach at 860 nm from P_{y-}.



QThG7 Fig. 2 Kinetic fits to the wavelength-resolved magic angle pump probe spectra obtained after excitation at 800 nm. The model consists of a two-step energy transfer mechanism, $B \rightarrow P_{y+} \rightarrow P_{y-}$, where the two steps occur with 120 fs and 65 fs time constants, respectively, and the spectra for each species is experimentally determined. Experimental data (symbols) and the calculated fits (solid curves) are shown for 800, 825, and 865 nm.

cally excited special pair (P_{y+}, where P is the special pair ground state) and its influence on energy and electron transfer.[2,3] In this report we present "two color" wavelength-resolved pump-probe anisotropy measurements[4] of the photosynthetic reaction center (RC) of Rhodobacter Sphaeroides at room temperature. The major Q_y 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 Py+. This latter spectroscopic feature appears immediately after exclusive excitation of P_{y-} and yields anisotropy values consistent with a transition dipole moment rotated 70° from the P-P_{y-}* transition moment, in agreement with low temperature results for P_{y+}[5,6]—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_{y-}* following energy transfer. The three-dimensional data are analyzed using experimentally determined spectra and anisotropy values for B, P_{y+}, and P_{y-}. A satisfactory fit to data is obtained with a model wherein energy transfer from the B to P_{y-} occurs by a two step mechanism, with P_{y+} serving as the intermediate. The results of this kinetic analysis are shown in Fig. 2. The resulting time constants for the

tion of P_{y+}. These time constants are substantially different than those reported by Jonas *et al.*[2] The fast time constants for energy transfer imply substantial electronic overlap between B and P_{y+}. Therefore a supermolecular picture of the reaction center chromophores cannot be ignored.[6]

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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 buildup of nonlinear optical processes. The