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ELECTRONIC AND VIBRATIONAL COHERENCE IN PHOTOSYNTHETIC COFACTORS: COMPARISON OF SOLUTIONS AND PROTEINS

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The interaction between photosynthetic cofactors and the surrounding bath or protein environment is addressed *via* experimental measurements of the optical coherence responses from bacteriochlorophyll$_a$ (Bchl$_a$) chromophores within the photosynthetic reaction center (RC) of *Rhodobacter sphaeroides* and solutions of Bchl$_a$ monomers in THF and pyridine. The results indicate that both the spectrum of fluctuations and chromophore bath coupling strengths vary between solutions and protein. In particular, the protein environment yields faster dephasing, faster spectral diffusion, and significantly more inhomogeneity than solutions.

Keywords: Photosynthesis; optical coherence; vibrational coherence; photon echoes

Optical coherence, or photon echo measurements can be used to determine the correlation function of the chromophore transition frequency, M(t), that, in turn, reflects the magnitude of the chromophore-bath coupling and the spectral range of bath fluctua-

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tions [1]. Recently, two groups have suggested that the three pulse photon echo peak shift measurement (3PEPS) reflects the time scales and characteristics of the correlation function M(t) and the related spectral density $C(\omega)$ [2, 3]. The results of 3PEPS, as well as two pulse photon echoes (2PE) [4, 5], transient grating (TG), and pump probe measurements (PP) are reported and used to interrogate the bacteriochlorophyll$_a$ (Bchl$_a$)-bath interactions both in solution and the native protein environment.

The 3PEPS results, as shown in Figure 1, indicate that *spectral diffusion in the reaction center RC is significantly faster than in solution.* The data are fit *via* a singular value decomposition (SVD) method to a series of exponentially damped cosines (of both zero and finite frequencies). Oscillations are evident in the 3PE peak shifts, resulting from impulsively prepared vibrational coherences ($100-1000\,cm^{-1}$), that primarily correspond to Bchla monomer modes. The best fit SVD analysis of the 3PEPS of Bchl$_a$ in THF solution requires 6 oscillatory

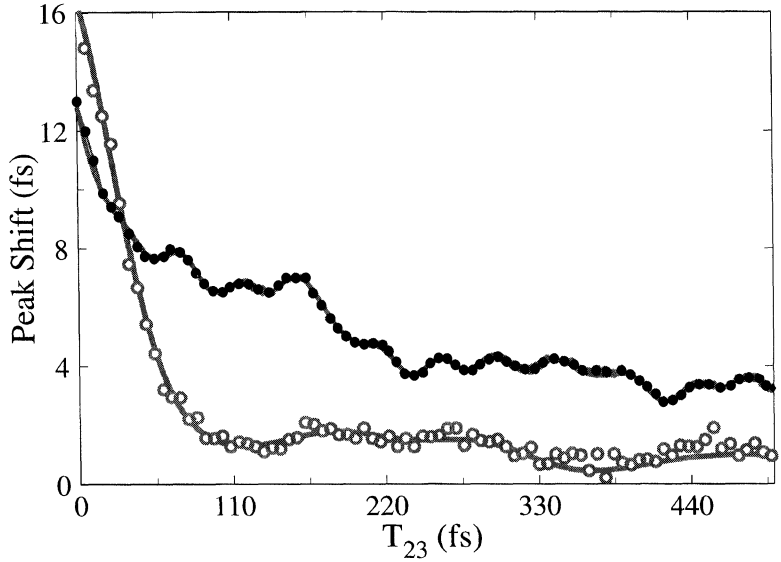

FIGURE 1 Three pulse photon echo peak shift values *vs* T_{23} time delay. Bchl$_a$ in THF solution (solid points), special pair ($P-P^*$) of bacterial reaction center protein (open points). Solid lines are the result of SVD analysis of the data (see text).

components with frequencies of 187 to 912 cm^{-1} in addition to 3 exponential decays (100 fs, 940 fs, and 6 ps). The special pair results, however, are fit with only 3 oscillatory components 140 – 300 cm^{-1} and 2 exponentials (30 fs and $\gg$ 10 ps). All of the 3PEPS responses collected in the protein environment have significant residual (*i.e.*, non zero) peak shift values for long T_{23} delays, indicating that "static" conformations of the protein still exist on the 20 ps time scale at room temperature.

The photon echo signals are simulated using the nonlinear response function formalism employing a multi-mode spectral density that accounts for chromophore-protein interactions and intra-chromophore dynamics [6]. The optical coherence measurements indicate that both the spectrum and amplitude of fluctuations show a dramatic dependence on the environment surrounding the $Bchl_a$ cofactor. The spectrum of fluctuations, as taken directly from the 3PEPS measurements, and scaled by the root mean squared fluctuation amplitude, $< \Delta\omega^2 >^{1/2}$, are shown in Figure 2 for $Bchl_a$ in THF and for the special pair optical transition (P – P*) of the reaction center.

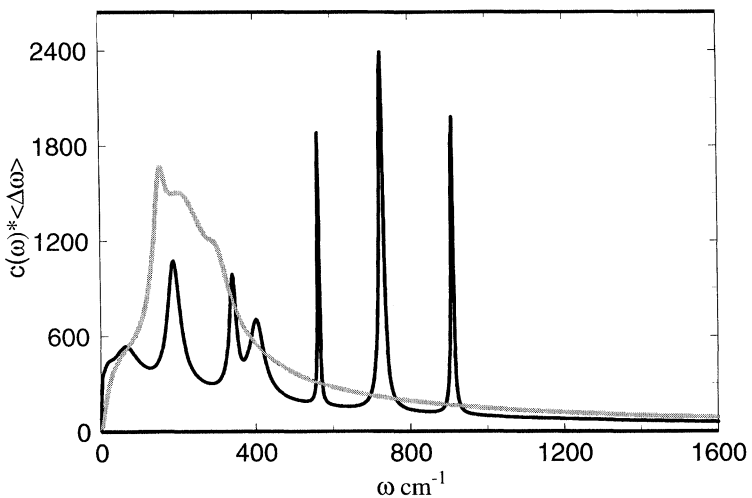

FIGURE 2 Weighted spectral density of energy gap fluctuations. $Bchl_a$ in THF solution (solid dark line), special pair of Bchl's in the bacterial reaction center (light solid line). The spectra are weighted by the coupling strength necessary to fit the respective absorption spectra (not shown).

In contrast to previous results for dye molecules in solution [2, 6, 7], the spectrum of fluctuations measured for $Bchl_a$ in solutions of THF or pyridine deviate strongly from the optical Kerr effect polarizability spectral density of the pure liquid. This result indicates that strong interactions with the nearest (few) solvation shell(s), particularly the two axially "ligated" solvent molecules coordinating the Mg atom, "control" the optical dephasing of this chromophore.

Hole burning results for photosynthetic cofactors indicate that the Bchl's are typically coupled to a distribution of low frequency acoustic phonons. The strength of the coupling depends greatly on the biological function of the cofactor; weak coupling of cofactors in light harvesting antennae is contrasted by extremely strong coupling in the reaction center [8]. This trend is also observed in the spectra obtained *via* the present 3PEPS measurements. In addition, the width of the bath spectra is significantly broader for the reaction center than for B820 dimers isolated from LH-1 [9], or the spectra obtained for antenna units of LH2 [10].

In conclusion, correlation functions of chromophore energy gap fluctuations obtained from various photon echo experiments and analyzed *via* simulation give valuable insight into the function of the reaction center. Nonlinear response function analysis of the experiments yield coupling strengths, vibrational displacements, and electronic/vibrational dephasing times.

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