Optical and Vibrational Coherence in Bacteriochlorophyll a

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The dynamic nature of a liquid medium causes structural changes to occur on timescales corresponding to the Fourier transform of the far-infrared or Raleigh-wing spectrum of the material. Experiments that are performed on such short timescales are capable of directly capturing the solvent effect on or response to chemical processes. [1] The nonlinear response function description of third-order polarization, $P^{(3)}(t_1,t_2,t_3)$, spectroscopy [2] shows that chromophore optical dephasing is described by the correlation function of the chromophore electronic frequency modulation; this, in turn, depends upon the magnitude of the chromophore transition dipole-bath coupling and the spectral range of bath fluctuations. A comparison of the solvent spectral density obtained from optical Kerr effect studies and the evolution of optical coherence of cyanine dyes has shown that similar bath dynamics are reflected in both measurements. [3]

Optical coherence methods, especially photon echo techniques, have recently been applied to the study of chromophore dephasing in solution.[4-8] These include 2-pulse (2PE), 3-pulse (3PE) and time gated photon echos (TG-PE) that allow variations of coherence and/or population time delays. The TG-PE approach even allows for establishing the temporal profile of the third-order polarization [5b,7] rather than the time-integrated polarization. [3,4,5a,6] Time-gated photon echo signals [7] are obtained via sum-frequency generation of the polarization with a separate gate pulse at time t_{3g} for various values of t_{12} and t_{23} making this a 4-dimensional measurement. Combinations of these different measurements along with nonlinear response function analysis [2,8] can be used to establish the low and high-frequency bath (i.e. solvent) fluctuations that cause evolution of the energy gap correlation function and optical dephasing.

This paper presents the the 3-pulse photon echo response of Bacteriochlorophyll$_a$ (BChla) monomers in pyridine and THF solutions. These measurements reflect the evolution of optical and vibrational coherence of the system along time axes t_{12} and t_{23}, respectively. In particular, optical dephasing is probed by scanning the time delay between the first two pulses (t_{12}), vibrational dephasing is probed while scanning the second delay (t_{23}), and spectral diffusion is detected via the time shift of the photon echo response (scanning t_{12} for various values of t_{23}).

The optical source for the results presented here is a home-built cavity-dumped Kerr lens mode-locked Ti:Sapphire laser of a unique design producing 13fs duration gaussian pulses with 90-100nm spectral bandwidth and 40nJ energies. The sample is contained in a 0.5 mm path length spinning cell and the echo signal is detected in the $k_s=k_3+k_2-k_1$ direction. The system temporal response and the experimental zero-of-time are determined from the nonresonant scattering response of the pure solvent which is detected in the same direction as the resonant photon echo from BChla. The samples included both THF and pyridine solutions of BChla (Sigma, Rb. Sphaeroides). These solvents serve to hexa-coordinate the central Mg atom thereby producing monomeric BChla solutions.

Figure 1 shows the $|P^{(3)}(0,0,t_3)|^2$ "pump-probe scattering" or transient grating response of BChla in THF. **Vibrational coherences** are impulsively driven and detected in the nonlinear optical response; the Fourier absolute magnitude spectrum is shown in the inset. The vibrational frequencies observed in the figure (185, 210, 340, 480, 560, 730, 790, 890, and 1180 cm^{-1}) are in very good agreement with line positions obtained from cw-Raman measurements. [10,11] The time constants for vibrational dephasing are determined to be about 1 ps by singular value decomposition analysis. The vibrational dephasing reflects the force autocorrelation function of the bath projected onto the vibrational modes. Clearly, the timescale for vibrational dephasing is much shorter than the relaxation of the population contribution to the photo-bleach/stimulated emission [12] signal (i.e. dc-offset). Similar results are obtained in pyridine solution. Intense low frequency modes between 100 cm^{-1} and 300 cm^{-1} reported for BChla in the photosynthetic reaction center[11] are weak in the present data. This finding is, however, consistent with the lack of vibrational coherence excitation of BChla in solution obtained with 50 fs pulse excitation and probing. [12]

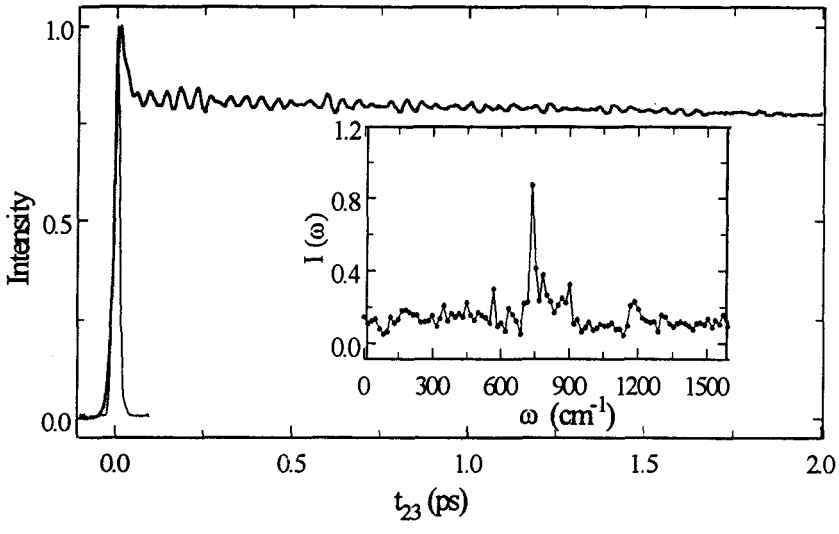

Figure 1. Modulus square four wave mixing response of BChla in THF measured in a Boxcar geometry. Inset: Fourier transform of the time domain data deconvoluted for the finite laser pulse duration. The display is of the absolute magnitude of the FT data, i.e. square-root of the power spectrum. A biexponential decay fit to the time domain data has been subtracted before Fourier transformation.

The $|P^{(3)}(t_1,t_2=t_3)|^2$ **optical coherence** response of BChla in THF is shown in Fig. 2. The echo shape is asymmetric with a significant time-shift (10-12 fs) from the zero-of-time point. The echo shift indicates that the solvent response is not in the homogeneous limit but has an inhomogeneous contribution.[13,14] The prompt decay of the echo signal indicates that homogeneous relaxation is, however, significant; the chromophore coherence decays on a series of timescales reflecting the spectrum of and coupling to the solvent fluctuations. The timescale for **spectral diffusion** is inferred from the evolution of the echo time-shift for increasing t_{23} time delays, $|P^{(3)}(t_1,t_2<t_3)|^2$. These results are shown in figure 3a. The evolution of the optical coherence response in pyridine and THF solutions both show fast and slow contributions to the chromophore spectral diffusion.

Numerical simulations incorporating the solvent polarizability spectral density and the multi-mode aspect of the chromophore response, i.e. intra-chromophore vibrational modes, are capable of faithfully capturing the dynamical responses recorded above. The simulations, using

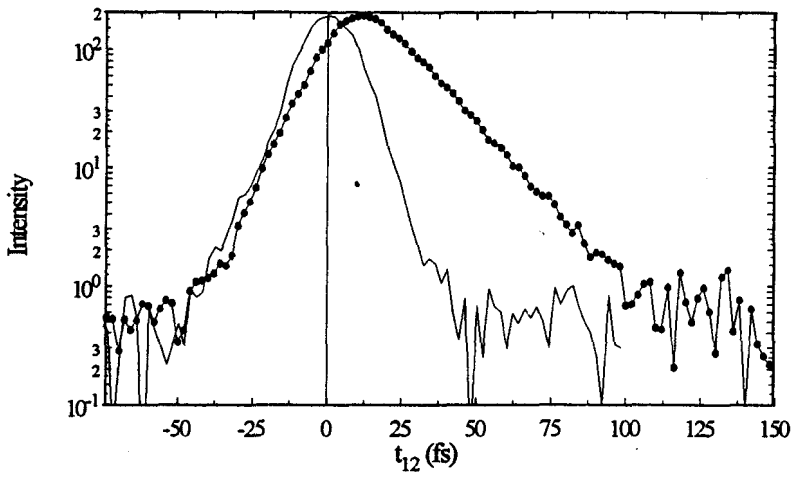

Figure 2. Photon echo response of BChla in pyridine. Solid line + dots: Bchla photon echo signal, line only: pure-solvent (pyridine) 3-beam scattering response. The nonresonant Pyridine response from the pure solvent is at least 5 times smaller than the resonant BChla signal, but is normalized in this representation to show the instrument temporal resolution.

mode displacements from resonance Raman spectra, test both the utility of the pure solvent polarizability response for analysis of short time dynamics as well as the long-time spectral diffusion response. The nonlinear response function simulation peak-shift results are superimposed on the experimental. Good agreement is obtained for early t_{23} time delays up to about 100 fs. The two curves then diverge from each other. The simulation using the measured solvent spectral density does not contain sufficient low frequency amplitude to match the slow change of the experimental peak shift over 5 ps delay (t_{23}). This finding is in agreement with the recent work of Fleming and coworkers on the 3-pulse photon echos of HITCI in ethylene glycol where low frequency terms had to be added to the from a single Brownian oscillator spectral density to reproduce the longer t_{23} spectral diffusion dynamics.[14]

The low frequency spectral density not reflected in the OKE susceptibility/spectral density used here may result from the direct solvent-solute interaction and restricted solvent motions at the solute "interface". These slow solvent bath fluctuations are "inhomogeneous" (static) broadening contributions to the photon echo signal at early t_{23} time delays as shown in fig. 1 (t_{23}=0). Alternatively, other low frequency modes of the chromophore that exhibit an overdamped response may also contribute to the "bath" spectral density. When t_{23} is increased more chromophore intramolecular fluctuations (vibrational coherences) and the lower frequency bath fluctuations contribute to the ernegy gap correlation function. Broadening or bath contributions that were previously static become dynamic and contribute to the "homogeneous" dephasing behavior of the optical coherence.

Figure 3b shows the 3-pulse photon echo peak shift obtained at 9 fs intervals in t_{23}. Here, the peak shift exhibits oscillations over a 1 ps (or more) t_{23} delay. The solid curve through these points is a LPSVD analysis [15] of the time-shift data exhibiting sinusoidal components of 730 and 463 cm^{-1} frequency that are in agreement with the vibrational coherence features seen in the pump-probe scattering data shown in fig. 2. We conclude that chromophore vibrational coherences contribute to the temporal shift of the echo signal and therefore also to the optical coherence dephasing.

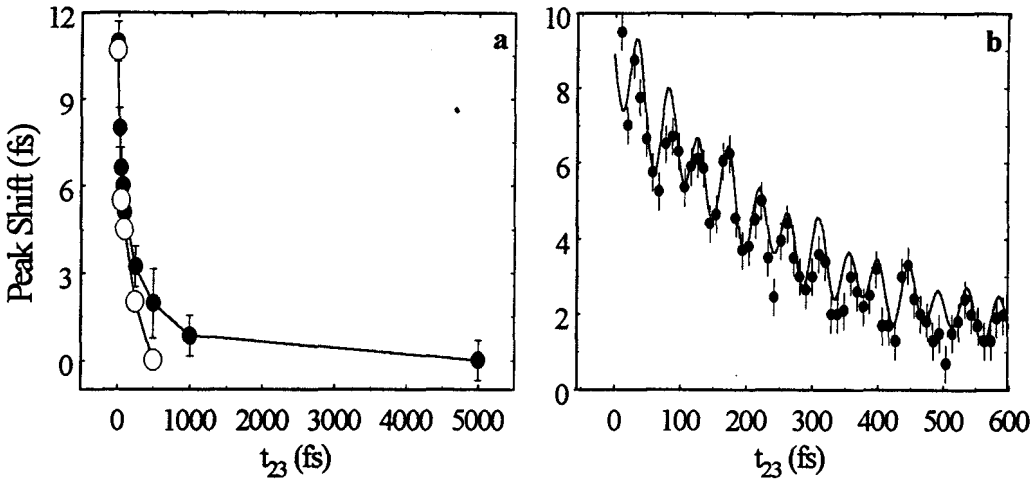

Figure 3. (a) Spectral diffusion dynamics of BChla monomers in pyridine. The solid points and error bars show the experimental echo maxima as a function of t_{23} delay time. The points represent the simulated results based on the solvent polarizability spectral density and multi-mode chromophore response. (b) Spectral diffusion dynamics of BChla monomers in THF observed as a function of t_{23} delay. The experimental echo maxima are shown as points with error bars for t_{23} time steps of 9 fs. The line through the points is a LPSVD fit containing 2 oscillatory components of 730 and 463 cm^{-1}.

Figure 4 shows a comparison between the experimental photon echo signal at t_{23} = 100 fs and the multi-mode spectral density nonlinear response function simulation of the echo signal. The agreement between experiment and simulation is excellent. This result supports the idea that incorporation of seven intra-chromophore modes observed in resonance Raman measurements [11] and displacements [16] along with the measured solvent spectral density well reflects the high frequency fluctuations that contribute to the decay of BChla optical coherence in liquids.

The experimental results presented here indicate that BChla is a useful probe of bath fluctuations in solution and will presumably also serve well in this capacity in the more "glassy" environment inside of proteins. BChla is an important chromophore that is involved in energy and electron transfer processes in photosynthesis. [17, 18] The present results indicate that the vibrational and optical dephasing responses obtained *in vitro* will be helpful in establishing the spectrum of bath fluctuations[19] and the coupling of the chromophore vibrational[20] and electronic coordinates to the protein bath in light harvesting antennas and photosynthetic reaction centers.

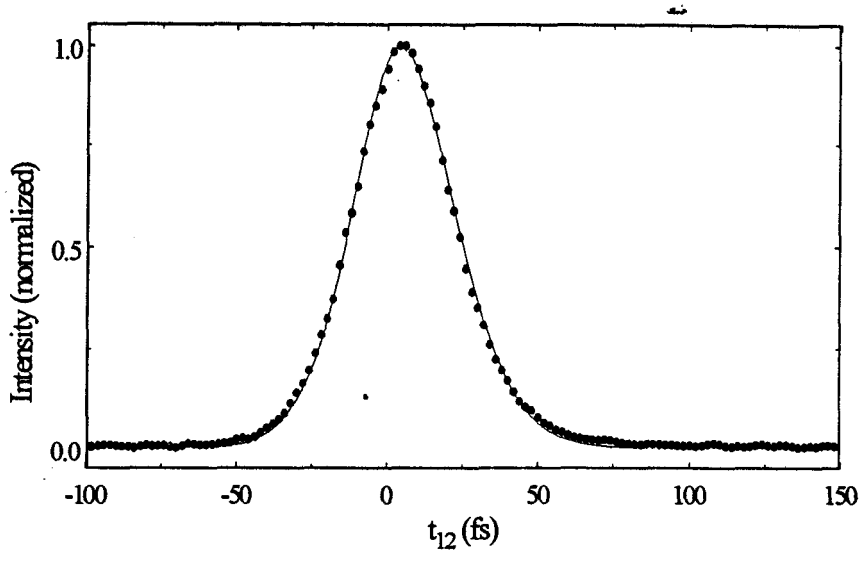

Figure 4. Comparison of 3-pulse photon echo response of BChla in pyridine and simulation using the solvent spectral density approach. The dots are experimental data points for t_{23}=100 fs, while the solid line is the calculated signal for the same t_{23} delay.

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