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Vibrational Coherence from the Dipyridine Complex of Bacteriochlorophyll *a*: Intramolecular Modes in the 10−220-cm^{-1} Regime, Intermolecular Solvent Modes, and Relevance to Photosynthesis

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We present the first observations of vibrational coherence in the 10−220-cm^{-1} region from bacteriochlorophyll *a* (BChl) in solution. A distinction can be made for the first time between BChl's intramolecular normal modes and intermolecular modes between BChl and solvent. The results show that the low-frequency vibrations that accompany the initial electron-transfer reaction from the paired-BChl primary electron donor, P, in photosynthetic reaction centers[1] arise predominantly from intramolecular modes of histidine-ligated BChl macrocycles. The results also suggest that polar solvent interactions can significantly perturb the electronic properties of BChl in a manner that might have important functional consequences.

When impulsive (subvibrational period) pump pulses are employed, the stimulated emission and fluorescence signals from P exhibit intensity modulations at several frequencies over the 10−200-cm^{-1} regime that persist as long as the 3-ps time scale for electron transfer to the bacteriopheophytin acceptor, BPh_L.[2] The modulations arise from coherent wave-packet motions (vibrational coherence) on the excited-state potential-energy surface of P, but the nature of the normal modes that contribute to the signal is still debated. Because previous attempts to observe underdamped vibrational coherence from monomeric BChl in solution were unsuccessful,[3] and because changes in the observed modulation frequencies occur in mutants,[4] an assignment to BChl−protein intermolecular modes or to protein-derived modes was suggested.[4,5] Resonance Raman spectra obtained from reaction centers with isotopically labeled cofactors and normal-coordinate analyses suggest, in contrast, that intramolecular BChl modes are involved.[6,7] Several of these modes have an out-of-plane character that would modulate the strong electronic coupling and intramolecular charge-transfer properties of P.[6−8] There is the additional possibility that P exhibits a collective, intrapair mode that does not occur in BChl monomers.[9]

We decided to make a new effort to observe low-frequency vibrational coherence from BChl in solution because of some recent advances in our laboratory that significantly improve the sensitivity and reproducibility of impulsive pump−probe experiments.[10] The dipyridine complex[11] was chosen for an initial study because it affords a monomeric system that is comparable to the histidine-ligated BChl species that occurs in the reaction center.[12] The experimental details, data analysis, and modeling procedures are described fully in the Supporting Information.

Figure 1 shows the 200−7000-fs delay range of the oscillatory portion of the pump−probe signal[13] obtained from BChl in pyridine with excitation of the Q_y transition. Following a relatively intense, rapidly damped feature in the 200−600-fs regime, weaker underdamped cosinusoidal modulations are observed that persist even to the 8-ps delay point. Because the probe wavelength lies just to the blue of the fluorescence spectrum, the modulations arise from overlapping contributions from wave-packet motions on the ground and excited states.[10] The Fourier-magnitude spectrum corresponding to the underdamped modulations is shown in Figure 2. The labeled peaks identify the 12 modulation components over the 11−206-cm^{-1} range that were reproducible in relative intensity and center frequency. The relatively intense 11-cm^{-1} component (3-ps period) exhibits the broadest line shape (damping constant $\gamma = 800$ fs); the higher-frequency components exhibit sharper line shapes ($\gamma =$ 1.2−1.7 ps). Owing to the long damping times, in the range of those observed for intramolecular modes of organic molecules in solution,[10,14] we know that these features arise from intramolecular modes belonging to the BChl−dipyridine complex. Above 30 cm^{-1}, the spectrum strongly resembles the resonance Raman spectra from P or the monomeric species $BChl_L$ or $BChl_M$ in the reaction center[7,15] in having significant peaks at 138 and 183 cm^{-1}, respectively. The spectrum differs from that observed previously in films of BChl[7] in having narrower line shapes and a number of peaks below 120 cm^{-1}. This observation supports the suggestion[7] that the very lowest-frequency components are affected by the nature of the axial ligand to the Mg(II) ion.

In contrast, the rapidly damped ($\gamma = 200$ fs) modulation in the 200−600-fs region arises from an *intermolecular* mode between the BChl molecule and the pyridine solvent molecules. Figure 3 compares the experimental signal with that arising from a distribu-

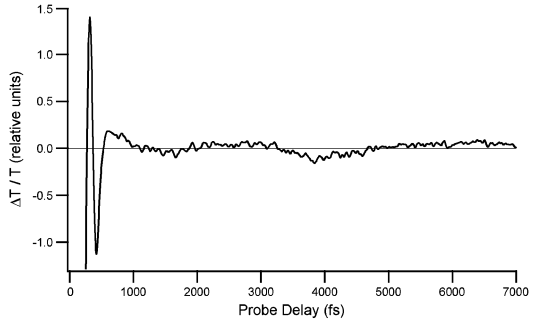

Figure 1. Oscillatory part of the pump−probe signal from BChl in pyridine solvent at room temperature. The full-scale ordinate corresponds to a change in pump-induced transmittance, $\Delta T/T$, of 10^{-5}.

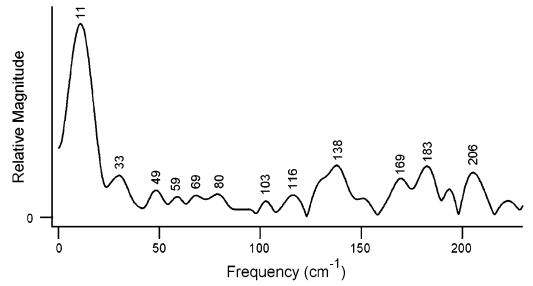

Figure 2. Fourier-magnitude spectrum (with 10-cm^{-1} resolution) obtained from the oscillatory pump−probe signal from BChl in pyridine solvent.

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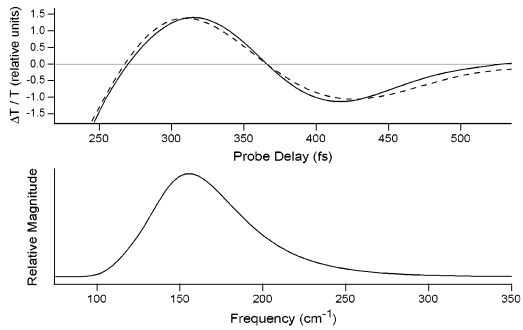

Figure 3. Expanded view of the rapidly damped oscillation from BChl in pyridine solvent (see Figure 1) superimposed with a model (dashed curve) arising from a distribution of mode frequencies, as shown in the bottom panel.

tion of mode frequencies centered at 155 cm^{-1}. Similar broad spectra are observed in *nonresonant* optical Kerr effect (OKE) signals from liquids, which carry modulations arising from librational (hindered reorientational) motions.[16] However, the OKE spectrum from pyridine liquid is observed at a lower frequency, 60 cm^{-1}, with collective modes making a contribution at 15 cm^{-1}.[17] Further, in our experiment, the pyridine OKE signal contributes a background signal that is much weaker than that shown in Figure 1. The *resonant* origin of the present signal requires the involvement of a BChl−pyridine solvent mode that is displaced by the BChl $\pi \rightarrow \pi^*$ transition. The relatively high frequency favors an assignment to a perpendicular hydrogen-bonding interaction like that present in pyrrole,[18] with protons of nonligated pyridines in the first solvent shell attacking the BChl π-electron density.

The intramolecular modes exhibit comparable intensities over the 30−200-cm^{-1} region, but the 11-cm^{-1} mode and the pyridine solvent mode yield much stronger signals. These observations prompt the following conclusions about the role that BChl−protein "solvent" interactions might play in the reaction center:

(1) Owing to its low frequency, the 11-cm^{-1} mode involves motion of a large reduced mass along a coordinate with a weak force constant, such as an out-of-plane distortion of the BChl macrocycle. We suggest that resonance enhancement of this mode involves coupling to the pyridine solvent mode, but it is not obvious why the other low-frequency modes, several of which have some degree of out-of-plane character,[6,7] are not as strongly enhanced. The low-frequency intramolecular modes of BChls in the reaction center might also obtain resonance Raman intensity enhancement by mode-specific and highly directional BChl−protein interactions. In fact, the resonance Raman spectra from $BChl_{L,M}$ and P exhibit distinct low-frequency intensity patterns[6,7,15] that probably arise, at least in part, from the details of the binding sites.

(2) The strength of the signal from the pyridine solvent mode suggests that some of the features of the vibrational coherence from P in mutant reaction center preparations[4] might indeed be explained by the introduction of BChl−protein intermolecular modes. The broad line shape for the pyridine solvent mode arises from the disordered ensemble of solvated BChl structures. In a protein, an *ordered* solvent interaction with BChl would exhibit a *narrow* line shape that might be comparable to those arising from BChl's intramolecular modes.

The observation of polar solvent effects on the resonance Raman intensities from the BChl−dipyridine complex imply that significant changes in the *electronic structure* of the BChl macrocycle should arise from protein-derived solvent perturbations in the reaction center. These interactions might contribute to the protein's control over the reactivity of a BChl site despite not necessarily causing a large change in the geometry. Some larger effects on the resonance Raman spectra and charge-transfer properties of $BChl_L$ and BPh_L owing to an introduction of neighboring *charges* have already been reported.[19]

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Supporting Information Available: Experimental procedures; full pump−probe and solvent-background signals, and details of analysis; tables of BChl mode frequencies, intensities, and damping times; and pyridine solvent mode model parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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