

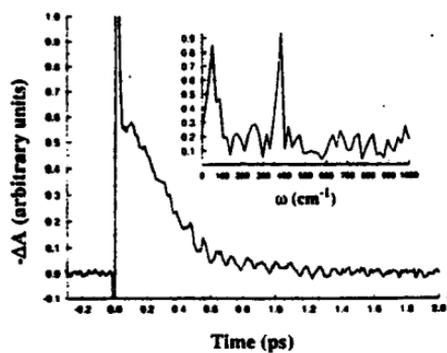
## **QThG10**

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### **Experimental and theoretical study of charge-transfer dynamics in blue copper proteins**

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Blue copper proteins function as mobile electron carriers in a wide variety of biological systems.<sup>1</sup>

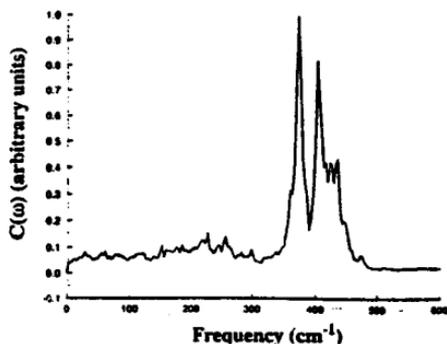


**QThG10** Fig. 1 Wavelength-integrated pump-probe signal of poplar plastocyanin. The large amplitude features around the zero of time that go off scale are due to nonresonant absorption by the buffer solution. The inset shows the Fourier spectrum of the data.

used to examine active site dynamics in three of these charge-transfer proteins: spinach and poplar plastocyanin,<sup>1</sup> two photosynthetic proteins, and ceruloplasmin,<sup>2</sup> a protein of vertebrate blood plasma. Pulses of 16 fs duration from a Ti:sapphire laser centered at 770 nm were used to pump and interrogate electronic and vibrational excitation and relaxation associated with the optically active Cu-S<sub>cysteine</sub> ligand-to-metal charge transfer. Figure 1 shows that the wavelength-integrated pump-probe signal of poplar plastocyanin exhibits a rapid decay with superimposed oscillations. These contributions correspond, respectively, to decay of ground state bleach (with a time constant of ~300 fs, similar to results for spinach plastocyanin and ceruloplasmin) and to modulations of the transition dipole by vibrational coherences of protein modes coupled to the electronic excitation. The most prominent oscillation in this signal has a frequency of ~375 cm<sup>-1</sup>. Wavelength-resolved signals of spinach plastocyanin and ceruloplasmin show a much more intense oscillation at ~500 cm<sup>-1</sup> that is not observed in poplar plastocyanin. By contrast, resonance Raman spectra of these plastocyanins show several vibrations between 350 and 450 cm<sup>-1</sup>, but they show little or no intensity around 500 cm<sup>-1</sup>.<sup>3</sup> This 500 cm<sup>-1</sup> mode may be an excited-state frequency that has been upshifted relative to its ground state analog. The excited state surface must be coupled to the ground state or another electronic state along the nonradiative decay coordinate to show the observed rapid excited state decay.

Classical molecular dynamics simulations have established the nuclear motions associated with photoinduced charge transfer in plastocyanin.<sup>4</sup>

The protein is modeled with use of a molecular mechanics potential; potential parameters for the copper-protein interactions are determined with use of an x-ray crystallographic structure<sup>5</sup> and absorption and resonance Raman spectra.<sup>3</sup> Molecular dynamics simulations yield a variety of information about the ground (oxidized) and a higher-lying optically excited (charge-transfer) state: (1) the free energies of the two states (along the potential difference between them) are quadratic and well into the Marcus inverted region; (2) the two-time autocorrelation function of the difference potential in the ground state and the average of the difference potential following in



**QThG10** Fig. 2 Classical molecular dynamics simulated spectral density of the Cu-S<sub>cysteine</sub> reaction coordinate of poplar plastocyanin. The multiple observed frequencies agree well with resonance Raman results although the amplitudes differ. The spectral structure reflects couplings to other protein modes.

very similar (confirming linear response in this system); their decay indicates that vibrational relaxation occurs in about one picosecond in both states, similar to the decay of the pump-probe oscillations; (3) the vibrations that affect the optical transition can be identified with use of the spectral densities of various internal coordinates; and (4) nuclear motions in the protein are correlated over a distance of more than 20 Å, especially along proposed electron-transport paths. The spectral density of the difference potential correlation function (Fig. 2) is being used in semiclassical simulations of the electron transfer rates for direct comparison with the experimental results of Fig. 1.

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### QThG11

#### Ultrafast protein solvation dynamics in the $\alpha$ subunit of C-phycoerythrin

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We have performed a series of femtosecond transient hole-burning studies with a range of pump wavelengths on the  $\alpha$  subunit of the cyanobacterial light-harvesting protein C-phycoerythrin to understand how the protein matrix controls the excited-state potential surfaces of bound chromophores. The  $\alpha$  subunit contains a single phycoerythrin (open-