Charge-Transfer Dynamics in Blue Copper Proteins: Experiment and Simulation

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Abstract: Pump-probe and classical dynamics simulation results for electron transfer in blue copper proteins are reported.

Blue copper proteins function as mobile electron carriers in a wide variety of biological systems.[1] In oxidized form, their active sites have a strong ligand-to-metal charge transfer transition between the copper atom and a cysteine sulfur ligand in the region of 595-630 nm.[2] This strong absorption makes blue copper proteins suitable for ultrafast spectroscopic studies of electron transfer in proteins. Elucidation of the electronic and nuclear dynamics of these systems would be useful in understanding the long range electron transfer process of physiological function.

We have used ultrafast pump-probe techniques to examine the charge-transfer dynamics of plastocyanin,[1] a photosynthetic protein, and ceruloplasmin,[3] a protein of vertebrate blood plasma. Figure 1 shows both the wavelength-integrated and wavelength-resolved (detection at 750 nm) signals of plastocyanin pumped and probed with ~16 fs pulses centered around 770 nm. The electronic transition being probed is a $d \rightarrow d$ transition of the copper atom, which borrows intensity from the charge transfer transition. Both signals show rapid decays with superimposed oscillations, corresponding to metal-to-ligand return electron transfer (i.e., decay of ground state bleach with a time constant of ~300 fs) modulated by vibrational coherences coupled to the electronic excitation. A major difference between the two signals is that the amplitudes of the oscillations in the wavelength-integrated signal are much smaller than those of the wavelength-resolved signal. The first point is probably due to the fact that both the pump and probe beams are tuned close to the center of absorption band of the transition, and thus contributions to the oscillatory part of the signal from wavelengths to the red and to the blue of the center frequency are about equal. Since the red-side and blue-side contributions are 180° out of phase with each other,[4] they nearly completely cancel and the integrated signal shows less oscillatory character. The most prominent oscillation in the wavelength-resolved signal has a frequency of ~500 cm^{-1}. This frequency has not been observed in resonance Raman studies of plastocyanin,[5] and therefore cannot represent a ground state mode of the protein. However, the Raman spectra show several vibrations between 350 and 450 cm^{-1}, and the ground and excited state electronic surfaces must be strongly coupled in order to produce the observed rapid return electron transfer. This coupling could make the excited state surface more sharply curved, and thus might effectively increase excited-state frequencies of vibrational modes strongly coupled to the return electron transfer coordinate. Similar results have been obtained for ceruloplasmin.[6]

On the theoretical side, we have developed models for a blue copper active site and a complete plastocyanin protein that can be used in classical simulations. The simulations use the CHARMM molecular mechanics force field modified to incorporate copper atom-protein interactions.[7] The models were tested against resonance Raman data for blue copper proteins[5] and the plastocyanin crystallographic structure.[8] Figure 2 shows the

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Fourier transform of the Cu-$S_{cysteine}$ distance autocorrelation function from an equilibrium simulation of our model blue copper active site. An interesting feature of this spectrum is that it splits the Cu-$S_{cysteine}$ frequency (at about 400 cm^{-1}) into three peaks and a shoulder, which is consistent with resonance Raman spectra.[5] These classical simulations are useful in identifying the nature of nuclear modes coupled to the optical electron transfer.

Finally, because resonant pump-probe experiments monitor the evolution of population in both the ground and excited states, and the dynamics of return electron transfer, classical simulations are inadequate for the interpretation of many aspects of these experiments. To accurately model inherently quantum mechanical processes, quantum dynamics simulations are being undertaken[9] using the spectral density obtained from classical simulations. The dynamics of harmonic nuclear motion coupled to a two-state system will be found using Gaussian bath path averaging,[10] a Feynman path integral method.

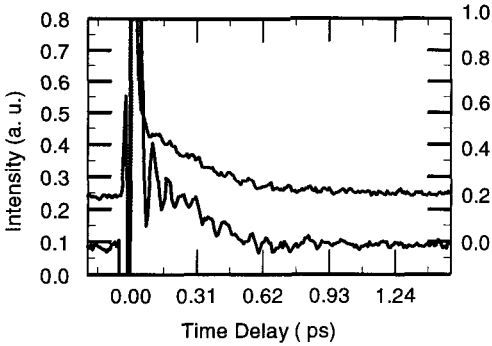

Figure 1. Wavelength-integerated (top) and wavelength-resolved (bottom) (detection at 750 nm) pump-probe signal of plastocyanin. The large amplitude features around the zero of time that go off scale are due to nonresonant absorption by the buffer solution. The traces are offset for clarity.

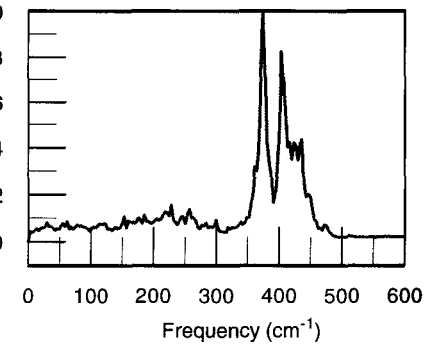

Figure 2. Fourier transform of the Cu-$S_{cysteine}$ distance autocorrelation function in a model blue copper site determined from a classical molecular dynamics simulation. Features around 400 cm^{-1} are the Cu-S strectch mixed with other amino acid motions.

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