OPTICAL AND VIBRATIONAL COHERENCE STUDIES OF LIQUIDS AND PROTEINS

D.C. Arnett, L.D. Book, L.W. Ungar, H. Hu, G.A. Voth and N.F. Scherer*

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

The ultrafast dynamics of the optically-induced intervalence charge-transfer reaction of the mixed valence dimer[1] $(CN)_5Ru^{II}CNRu^{III}(NH_3)_5$ in various polar solvents will be presented. These results will be used to illustrate the ultrafast vibrational coherence and excitation relaxation dynamics that are observable in femtosecond nonlinear spectroscopy for a system whose electronic relaxation is near barrierless. Furthermore, these studies will be compared and contrasted with optical pump-probe studies of ligand-metal charge-transfer dynamics in proteins.

Blue copper proteins function as mobile electron carriers in biological systems by transfering electrons to and from their "type I" copper active sites liganded to the protein matrix.[2] In oxidized form, these active sites have an optical absorption associated with the ligand-to-metal charge transfer between the copper atom and a cysteine sulfur ligand, which gives the proteins their characterisitic blue color.[3] Elucidation of electronic and nuclear dynamics of these systems requires classical and quantum simulations in conjunction with experiment. The resultant spectral density describing the optically induced charge transfer process may be useful in understanding the long range electron transfer of physiological function.

Wavelength-resolved pump-probe measurements can be used to map out the ultrafast dynamics associated with optically induced inorganic charge transfer reactions.[4] We have experimentally examined the blue copper proteins plastocyanin and ceruloplasmin.[3] The wavelength resolved pump-probe signal of both proteins at 800 nm, using <20 fs pulses centered around 800 nm involves probing a Laporté forbidden $d \rightarrow d$ transition of the type I copper atom, which borrows intensity from the intense ligand-to-metal charge transfer transition. The pump-probe signals show a rapid decay with superimposed oscillations (~400 cm^{-1} frequency), corresponding to metal-to-ligand return electron transfer (i.e., decay of ground state bleach) modulated by vibrational coherences of modes coupled to the electronic excitation. The data indicate that the excited population and ground state bleach has decayed completely by 1 ps. The oscillations are consistent with the frequencies observed in resonance Raman measurements for the $Cu\text{-}S_{cysteine}$ bond.[5],[6]

On the theoretical side, we have developed a model for a generic blue copper active site and a complete plastocyanin protein that can be used in classical molecular dynamics simulations using the CHARMM molecular mechanics force field[7] modified to incorporate copper atom-protein interactions. The model was tested against resonance

Raman data[5],[6] for blue copper proteins and an x-ray crystallographic structure.[8] Simulation of optical excitation is achieved by modeling the potential difference between the ground and excited states as a change in the equilibrium distance between the copper atom and its cysteine sulfur ligand, without changing atomic partial charges.[3],[9] The Figure shows the Fourier transform of the Cu-$S_{cysteine}$ distance autocorrelation function from an equilibrium simulation of our model blue copper active site. The spectrum of the Cu-$S_{cysteine}$ frequency (at about 400 cm^{-1}) is split into three peaks and a shoulder, consistent with resonance Raman spectra.[5],[6] These classical simulations are useful in identifying the frequency, intensity and decay time of nuclear modes coupled to the optical electron transfer.

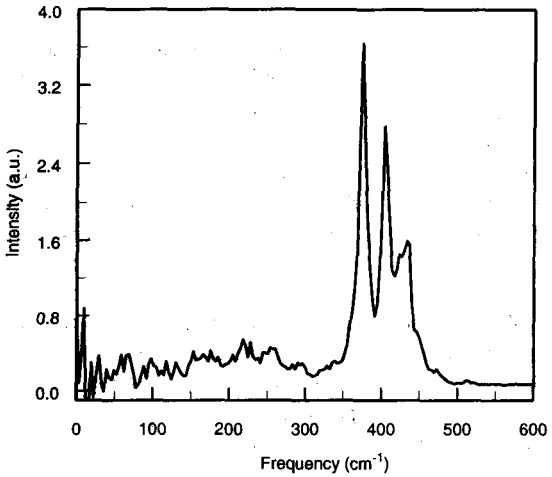

Fig. Fourier transform of the Cu-$S_{cysteine}$ distance autocorrelation function in a model blue copper site determined from a classical molecular dynamics simulation. The intense features around 400 cm^{-1} are Cu-S stretch mixed with other amino acid motions. Amplitude around 250 cm^{-1} reflects weak coupling of Cu to adjacent histidine nitrogens.

1. K. Tominaga, D.A.V. Kliner, A.E. Johnson, N.E. Levinger and P.F, Barbara, *J. Phys. Chem.* **98**, 1228 (1993)
2. R. Langen, I.-J. Chang, J.P. Germanas, J.H. Richards, J.R. Winkler and H.B. Gray, *Science* **268**, 1733 (1995)
3. E.I. Solomon, M.J. Baldwin and M.D. Lowery, *Chem. Rev.* **92**, 521 (1992)
4. D.C. Arnett, P. Vöhringer and N.F. Scherer, *J. Am. Chem. Soc.* **117**, 12262 (1995)
5. W.H. Woodruff, R.B. Dyer and J.R. Schoonover, *Biol. App. Raman Spec.* **3**, 413 (1988)
6. D. Qiu, J.A. Ybe, M.H. Hecht and T.G. Spiro, *J. Am. Chem. Soc.* **117**, 6443 (1995)
7. B.R. Brooks, R.E. Bruccoeri, B.D. Olafson, D.J. States, S. Swaminathan and M. Karplus, *J. Comp. Chem.* **4**, 187 (1983)
8. J.M. Guss and H.C. Freeman, *J. Mol. Biol.* **169**, 521 (1983)
9. S. Larsson, A. Broo and L. Sjölin, *J. Phys. Chem.* **99**, 4860 (1995)