TIME RESOLVED ENTHALPY AND VOLUME CHANGES ASSOCIATED WITH INTER-MOLECULAR ELECTRON TRANSFER BETWEEN AN ANIONIC FREE-BASE PORPHYRIN AND CYTOCHROME C. William A. Maza, Randy W. Larsen, Department of Chemistry, University of South Florida, 4202 E Fowler Ave CHE 205A, Tampa, FL, 33620.

We report results from photoacoustic calorimetry experiments yielding molar enthalpy and volume changes for photoinduced ET between Uroporphyrin (UroP) and cytochrome C (Cc). Fits to the photoacoustic traces of UroP in the presence of Cc show two resolvable phases in addition to the initial prompt (τ< 20ns) phase: a 200ns (20°C) phase which is attributed to triplet ET and a 2.8μs (20°C) phase attributed to thermal back ET with corresponding enthalpy changes of -33 kcal/mol and 45 kcal/mol respectively. The two phases are accompanied by a fast volume contraction of ~7 mL/mol and slow expansion of ~9 mL/mol. These results are consistent with a model in which protein conformational changes (i.e. contraction of the protein) upon reduction of the heme isolates the active site from the bulk solvent environment, thereby imposing a large reorganizational energy (λ ~ 26 kcal/mol) barrier required for back electron transfer.