

Excited State Structural Dynamics Probed with Time-Resolved Sulfur K-edge X-ray Absorption Spectroscopy

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Abstract: Time-Resolved X-ray absorption spectroscopy at the sulfur K-edge (~ 2.4 keV) is used to monitor structural dynamics following excited state proton transfer in an organosulfur molecule. The timescales of electronic structural relaxation are solvent dependent.

OCIS codes: (300.6560) Spectroscopy, x-ray; (320.5390) Picosecond phenomena

1. Introduction

Many biological and chemical systems rely on the transfer of protons between bonding sites. In some cases this transfer occurs as excited state proton transfer (ESPT) after a molecule or protein has been promoted to an excited state.[1] Much of the work to study ESPT using optical methods utilizes broad, overlapping visible absorptions which lack spatial resolution. Ultrafast time-resolved X-ray absorption (XA) is unique in its ability to measure chemical dynamics in solution with atomic specificity by probing excitations from highly localized core-level electrons. In recent years, time-resolved XA spectroscopy has been demonstrated to study photoexcited structural dynamics in disordered media.[21] We present, for the first time, to the best of our knowledge, transient XA spectroscopy at the S K-edge. The molecule of interest is 2-thiopyridon (2TP, C_5H_5NS). After photo-excitation, the proton, bonded initially to nitrogen in the 2TP form, undergoes ESPT to bond with sulfur in the 2MP (2-mercaptopyridine) form (see Fig 1a). By probing the S K-edge in this system we are able to monitor the proton transfer process with site specificity and we measure how the solvent modulates the excited state dynamics. Our experiments open up the possibility of performing transient S K-edge experiments as a sensitive probe of the covalency of metal-sulfur bonds in small molecules and metalloproteins.[2]

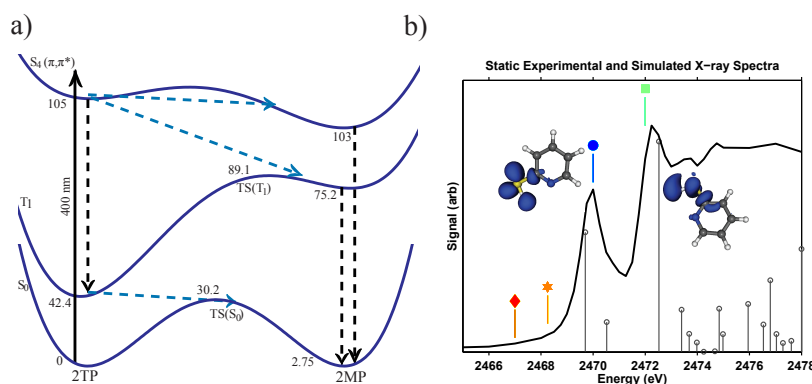


Fig. 1. (a) Energy level diagram of transitions in the 2TP to 2MP photoisomerization. (b) DFT predicted energy levels of 2TP (grey stems, scaled 2.3%) compared to measured static x-ray absorption in acetonitrile. Symbols and sticks indicate energy of time traces shown in fig. 2b. Inset orbital densities represent the orbital occupation of the excited core electron to following X-ray excitation at the lowest energy near-edge absorption,

2. Transient Sulfur K-edge spectroscopy

Experiments on the sulfur K-edge of 2TP after photo excitation at 400 nm were performed at BL 6.0.1 at the advance Light Source using monochromated (~ 2 eV width) 70 ps camshaft-driven X-ray pulses with $\sim 10^4$ photons/pulse using a previously described set-up.[3] The transient XA experiments were performed in transmission mode with a 0.75 M solution of 2TP in acetonitrile in a 50 μ m thick free flowing jet housed in a He atmosphere. In polar solutions the 2TP species, with the proton bonded to nitrogen dominates and is thought to be excited to the fourth excited singlet, $S_4(\pi, \pi^*)$ upon irradiation by near UV light.[4] Subsequent decay is thought to proceed through the first excited triplet, T_1 . This is diagrammed in Figure 1a. Figure 1b shows the measured

differential absorption spectra of the sulfur K-edge of 2TP in acetonitrile solution. The simulated spectra agree qualitatively with the observed experimental peak positions and amplitudes of near-edge transitions at the sulfur K-edge. We assign the peak at 2470 eV to a $1s \rightarrow \sigma_1^*$ transition and the peak at 2472 eV to a $1s \rightarrow \sigma_2^*$ transition in 2TP.

Figure 2a shows the differential pump probe spectra at S K-edge for several delay times. We observe bleaches at the strongest edge features seen in fig. 1b, as well as new transient absorption features at lower energies. Figure 2b shows pump-probe time traces for several X-ray probe energies. The initial rise/decay for most of the energies can be fit to 70 ± 10 ps, which is consistent with the time resolution of synchrotron based X-ray pulses. The traces in Figure 2b show longer dynamics on timescales of 0.8 ns for the 2467 eV feature and 3.4-3.8 ns for the other spectral features. The mechanisms for these longer timescale dynamics are still under investigation; however, it is clear that there are multiple timescales accompanying ESPT in 2TP dissolved in acetonitrile.

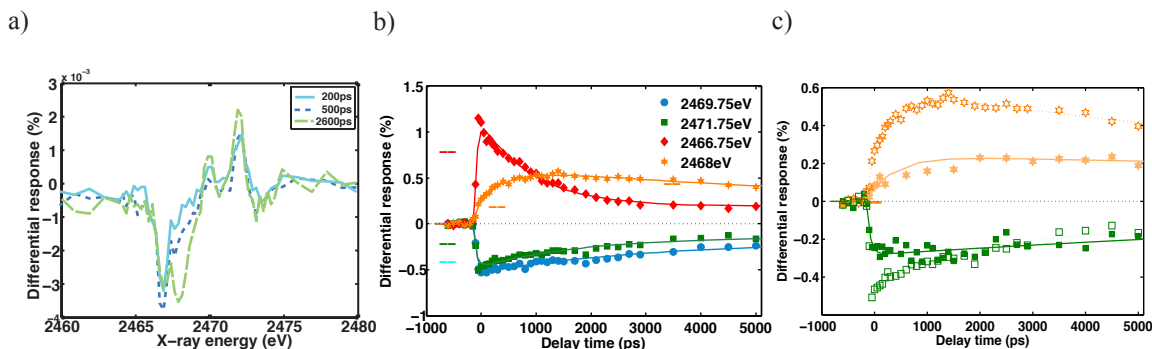


Fig. 2. (a) Experimental (black lines) absorption as detected by fluorescence intensity and sulfur K-edge modes predicted by simulation (grey stems, scaled by 2.3%) of the 2TP isomer. Colored lines and symbols indicate energies used in pump-probe traces. (b) Pump probe traces for several X-ray energies demonstrating multiple time scales, with most initial responses too fast to resolve with 70 ps X-ray pulses. (c) Comparison of 2472 eV and 2468 eV time traces for acetonitrile (empty symbols and dashed lines) and water (solid symbols and lines).

Figure 2c compares the transient sulfur K-edge XA spectroscopy of 2TP dissolved in acetonitrile and water. As in the acetonitrile, the 2470 eV and 2472 eV ground state bleaches recover at the same rates, but slow by from 1.9 ns to 19 ns in water. The dynamics of the excited state feature at 2468 eV also slows by an order of magnitude from 7 ns to 68 ns. These slower responses may be due to increased interaction with water compared with acetonitrile which would increase the time required for the proton to settle into the excited T_1 state of 2MP after proton transfer.

3. Summary

In summary, our data shows detailed changes to the electronic structure on the picosecond time-scale to an organosulfur compound engaged in ESPT using atomic site specific x-ray probes at the sulfur K-edge. We demonstrate the viability of transient S K-edge XA spectroscopy to probe proton transfer and other redox processes in solution with microscopic details.

References

- [1] R. Du, C. Liu, Y. Zhao, K. Pie, H. Wang, X. Zheng, M. Li, J. Xue, D.L. Phillips, "Resonance Raman Spectroscopic and Theoretical Investigation of the Excited State Proton Transfer Reaction Dynamics of 2-Thiopyridone," *J. Phys. Chem. B* 115, 8266-8277 (2011)
- [2] C.J. Mine; M. Chergui "Time-resolved X-ray absorption spectroscopy," *Spectroscopy Europe* 24, 16 (2012)
- [3] B. Van Kuiken, M. Valiev, S. Daifuku, C. Bannan, M. Strader, H. Cho, N. Huse, R.W. Schoenlein, N. Govind, M. Khalil "Simulating Ru L3-edge X-ray absorption spectroscopy with time-dependent density functional theory: model complexes and electron localization in mixed valence metal dimers," *J. Phys. Chem. A* 117 4444-54 (2013)
- [4] E. I. Solomon, B. Hedman, K. O. Hodgson, A. Dey, and R. K. Szilagy, *Coordination Chemistry Reviews* 249, 97 (2005).