

THE PHOTOCHEMICAL FUNNEL OF 1,2-DITHIANE REVEALED BY NON-ADIABATIC SURFACE-HOPPING GAS-PHASE DYNAMICS

C. D. Rankine,^{1*} J. P. F. Nunes,¹ M. S. Robinson,² P. D. Lane,³ D. A. Wann¹

¹ University of York, Heslington, York, UK, YO10 5DD

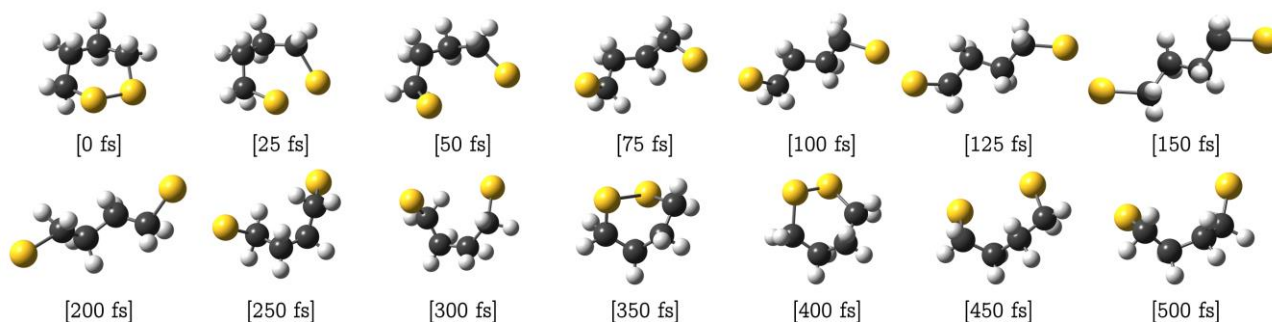
² University of Nebraska-Lincoln, Lincoln, Nebraska, USA, NE 68588

³ Heriot-Watt University, Riccarton, Edinburgh, UK, EH14 4AS

* Corresponding Author: cr684@york.ac.uk

A sulfur-sulfur bond (or disulfide bridge) spanning two cysteine residues is a ubiquitous structural motif in the natural world. It ought to come as a surprise that this structural motif survived the punishing conditions of primordial Earth; what early experiments have taught us of aliphatic disulfides is that the sulfur-sulfur motif is innately unstable to heat and to illumination by light in the near-UV. This appears at odds with the tendency of nature to select for structural motifs of remarkable resilience to (rather than to invest in the energetically-costly repair of) photodamage. It transpires that an elegant ultrafast photochemical funnel^[1] is at work in these systems. The S_1 and S_0 states couple *via* a conical intersection (CI) along one of the degrees of freedom that is activated upon electronic excitation to the S_1 state; the same degree of freedom is relied upon to funnel the system towards certain visitation of the CI and mediate safe, non-radiative return to the S_0 state.^{[2],[3]}

1,2-dithiane, the simplest cyclic disulfide, is studied computationally using an SA3-CASSCF(10,8)/CASPT2 approach coupled with on-the-fly non-adiabatic surface-hopping gas-phase dynamics to unravel the nature of the photochemical funnel as our group pushes on towards our first gas-phase ultrafast electron diffraction experiment. An ultrafast “*Newton’s Cradle*”-type molecular motion is revealed that activates instantaneously upon absorption of light in the near-UV and encourages 1,2-dithiane to make many periodic passes of the CI, challenging the contemporary understanding of the photochemical funnel in this system.



References:

- (1) C. E. Crespo-Hernandez, B. Cohen and B. Kohler, *Nature*, **2005**, 436, 1141-1144.
- (2) A. B. Stephansen, R. Y. Brogaard, T. S. Kuhlman, L. B. Klein, J. B. Christensen and T. I. Sølling, *J. Am. Chem. Soc.*, **2012**, 134, 20279-20281.
- (3) A. B. Stephansen, M. A. B. Larsen, L. B. Klein and T. I. Sølling, *Chem. Phys.*, **2014**, 442, 77-80.