Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Photochemical carbon-sulfur bond cleavage in thioethers mediated *via* excited state Rydberg-to-valence evolution

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Electronic Supplementary Information

Absorption spectra plus additional quantum chemistry calculations, TRPEI data and analysis.

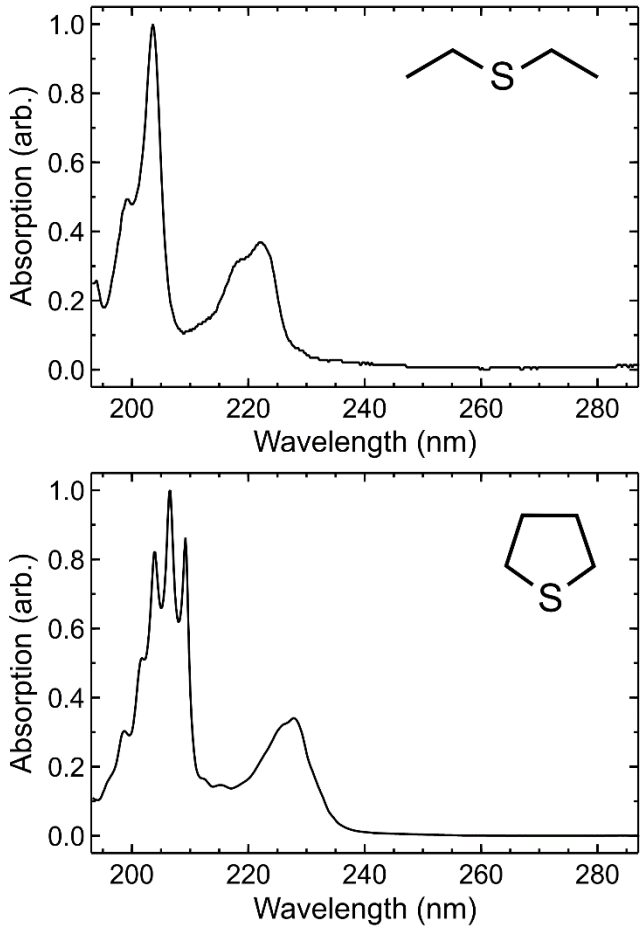


Figure S1: Vapour-phase UV absorption spectra of DES and THT recorded using a commercial benchtop spectrophotometer (Shimadzu UV-2550).

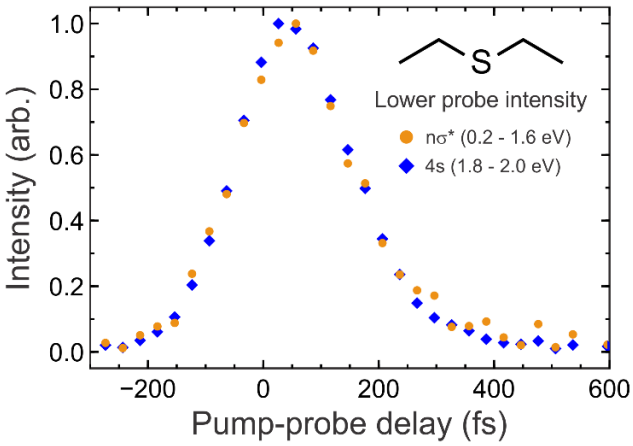


Figure S2: Normalized data points show 200/267 nm pump/probe transient photoelectron signals integrated over energy regions corresponding to 4s and nσ*-type ionization in DES under lower probe intensity conditions. No significant differences in timescale are seen, indicating that any extremely rapid transitory Rydberg-to-valence dynamics are not resolvable given our experimental cross-correlation of 200 ± 10 fs FWHM.

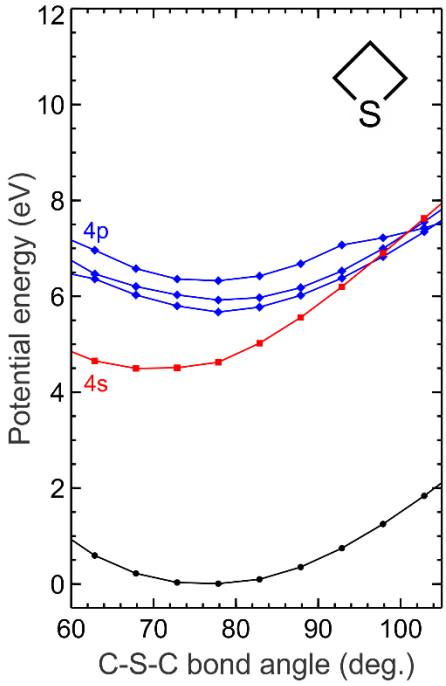


Figure S3: EOM-CCSD potential energy cuts for the S_0, 4s and 4p states of THI along C-S-C bending coordinate. The point of electronic degeneracy between the 4s state and 4p manifold (~15° from the S_0 minimum) is slightly more displaced here than for DES and THT (~6°) but does not appear to significantly reduce internal conversion rates following 200 nm excitation.

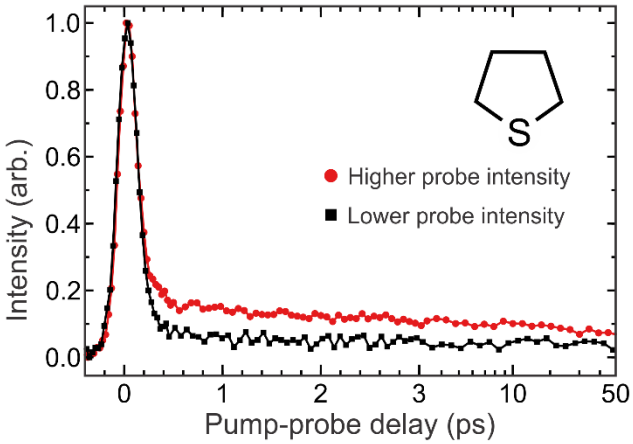


Figure S4: Transient signals from THT under both lower and higher intensity probe conditions when integrating TRPEI signals over all photoelectron kinetic energies following 200/267 nm pump/probe measurements. The enhancement of the long-lived signal extending to 50 ps is clearly seen in the higher probe intensity regime. See Figs. 4 and 7 in the main text for the corresponding energy resolved data.

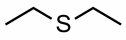
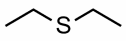
	nσ*	Radical intermediate	4s	4p
 (Higher power)	$\beta_2 = 0.30(1)$ $\beta_4 = 0.03(1)$ $\beta_6 = 0.01(1)$	$\beta_2 = 0.90(4)$ $\beta_4 = 0.19(2)$ $\beta_6 = 0.03(3)$	$\beta_2 = 1.34(4)$ $\beta_4 = 0.28(4)$ $\beta_6 = 0.18(3)$	$\beta_2 = 1.58(4)$ $\beta_4 = 0.44(3)$ $\beta_6 = 0.10(4)$
 (Lower power)	$\beta_2 = 0.33(2)$ $\beta_4 = -0.01(2)$	-	$\beta_2 = 0.94(6)$ $\beta_4 = 0.09(6)$	$\beta_2 = 0.87(3)$ $\beta_4 = 0.18(4)$
 (Higher power)	$\beta_2 = 0.10(1)$ $\beta_4 = -0.09(1)$ $\beta_6 = 0.00(2)$	$\beta_2 = 0.57(2)$ $\beta_4 = -0.04(3)$ $\beta_6 = -0.02(3)$	$\beta_2 = 0.94(2)$ $\beta_4 = 0.10(3)$ $\beta_6 = 0.02(3)$	$\beta_2 = 0.87(1)$ $\beta_4 = 0.17(1)$ $\beta_6 = 0.06(2)$
 (Lower power)	$\beta_2 = 0.18(3)$ $\beta_4 = -0.20(4)$	-	$\beta_2 = 1.22(8)$ $\beta_4 = 0.25(7)$	$\beta_2 = 1.31(6)$ $\beta_4 = 0.34(6)$
 (Higher power)	$\beta_2 = 0.22(2)$ $\beta_4 = -0.03(2)$ $\beta_6 = -0.02(3)$	$\beta_2 = 0.59(2)$ $\beta_4 = -0.01(2)$ $\beta_6 = 0.00(3)$	$\beta_2 = 1.32(2)$ $\beta_4 = 0.29(3)$ $\beta_6 = 0.01(4)$	$\beta_2 = 1.31(2)$ $\beta_4 = 0.27(3)$ $\beta_6 = -0.01(3)$

Table S1: Photoelectron anisotropy parameters obtained for all systems and probe power regimes investigated in this study. Values were obtained from fits to the image data using a time- and energy-integrated form of Eq. 1 given (and discussed) in the main article text. Values in parentheses denote 1σ uncertainties in the final significant figure. Energy integration windows vary slightly between systems but span the individual spectral features assigned to ionization from states exhibiting predominantly 4p, 4s and nσ* character, as well as (for the higher probe intensity scenario) an electronically excited radial fragment (DES) or biradical ring-opened intermediate (THT and THI). See Fig. 7 in the main article text for guidance.