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UV-induced cleavage and geminate recombination of the disulfide bond motif followed via ultrafast X-ray absorption spectroscopy

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We investigated photocleavage of the disulfide bond motif in model compounds such as cysteine dimer (L-cystine) by time-resolved X-ray absorption spectroscopy [1,2]. We follow changes in X-ray absorption at the sulfur K-edge (2.5 keV) that appear to be unique to thyil (R-S·) radicals, thereby tracking the fate of the disulfide bond. Ultrafast spectroscopy has revealed homolytic S-S bond cleavage upon ultrafast 267-nm excitation [3], with a dominant yield of geminate recombination in solution within the first picosecond. A minor fraction of the thyil radicals survives at least for microseconds, reminiscent of X-ray induced radical formation [4]. Doubling the ultraviolet excitation energy yields new photoproducts which indicate C-S bond cleavage. Weak relaxation of thyil charge density favors geminate recombination, suggesting at a natural inhibition of radiation from mid-ultraviolet excitation.
[1] M. Ochmann et al., J. Am. Chem. Soc. 139, 4797 (2017)
[2] M. Ochmann et al., J. Am. Chem. Soc. 140, 6554 (2018)
[3] K. Schnorr et al., J. Phys. Chem. Lett. 10, 1382 (2019)
[4] E. Y. Sneeden et al., J. Am. Chem. Soc. 139, 11519 (2017)

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