Chemical dynamics of organic disulfides probed via ultrafast X-ray spectroscopy

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Condensed Phase Dynamics Group

Institute for Nanostructure & Solid State Physics

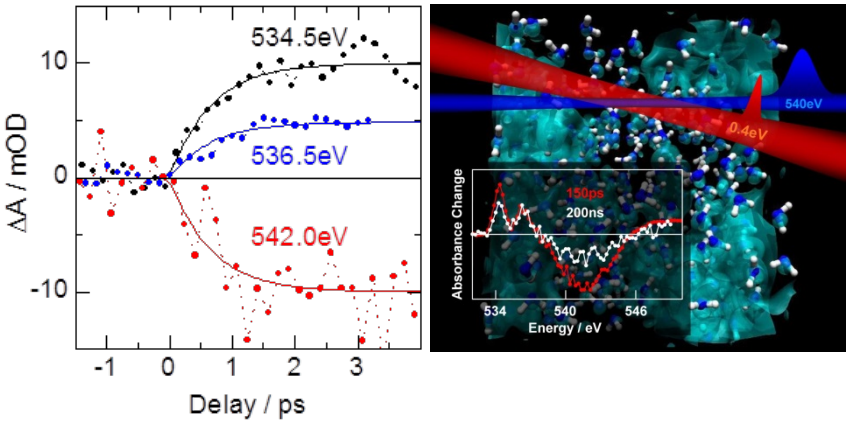
Physics Department, University of Hamburg

UK XFEL workshop, Newcastle 2019

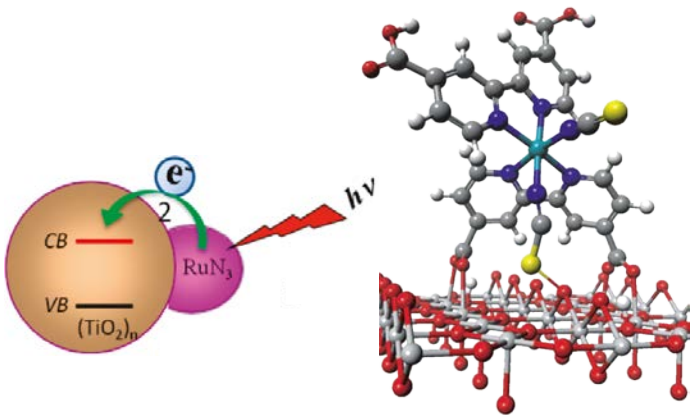
11. December 2019

Courtesy: hammeskrause architekten

Transient X-ray Spectroscopy of Molecules

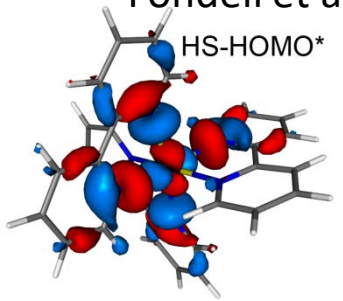


*Huse et al. PCCP **11**, 3951 ('09)*
*Wen et al. JCP **131**, 234505 ('09)*

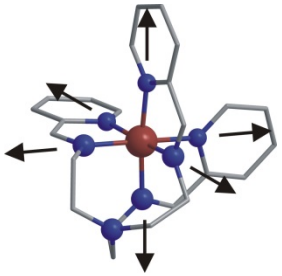


Van Kuiken et al *JPCL* **3**, 1695 (2012)
Van Kuiken et al *JPCA* **117**, 4444 (2013)
Gilbert et al. *PCCP* **15** (2013)
Siefermann et al *JPCL* **5**, 2735 (2014)

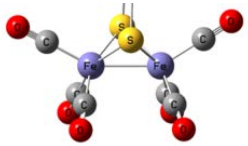
Huse et al. *JACS 132*, 6809 (2010)
Huse et al. *JPCL* **2**, 880 (2011)
Cho et al. *Faraday Discuss* **157** (2012)
Hong et al. *Acc. Chem. Res.* **48**, 2957 (2015)
Van Kuiken et al *JPCL* **7**, 465 (2016)
Fondell et al. *Struct. Dyn.* **4**, 054902 (2017)

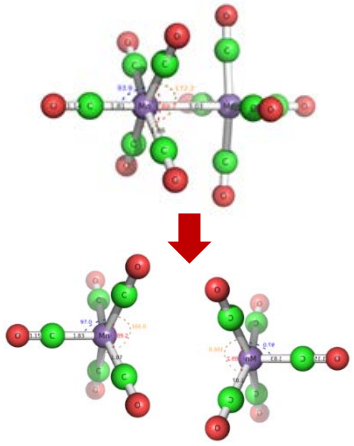


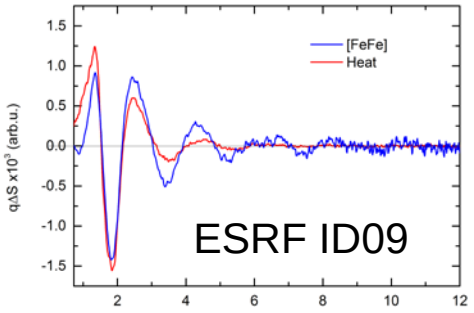
$^1A_{1g} \rightarrow {}^5T_{2g}$



Understanding active sites of Hydrogenase co-factors





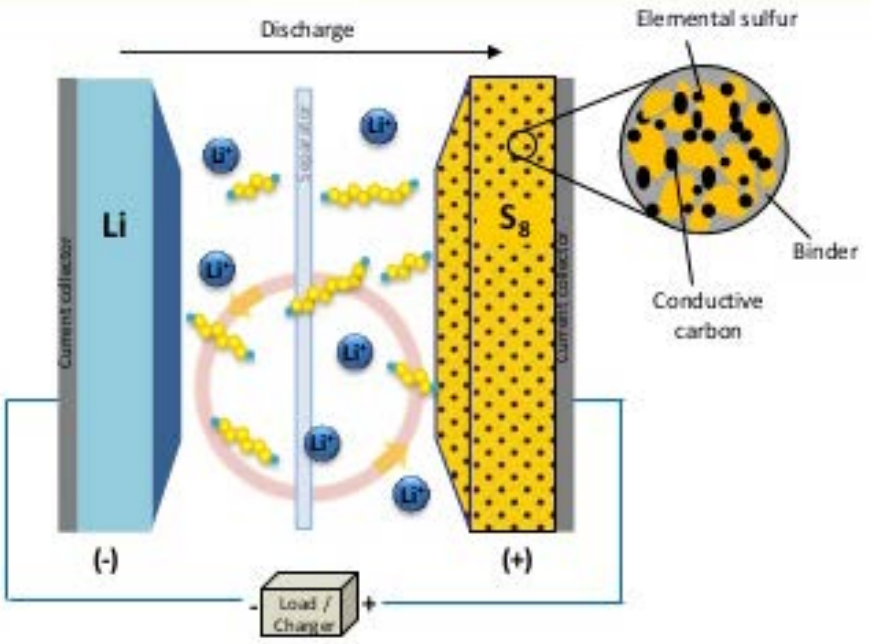


Cho et al. *IC* **55**, 5895 (2016) & Ma et al. In preparation
Cordones et al. *Nat. Comm.* **9**, 1989 (2018)

Motivation

Sulfur has high significance in materials & chemical sciences

Polymers, nanoparticles, battery material, molecular electronic devices



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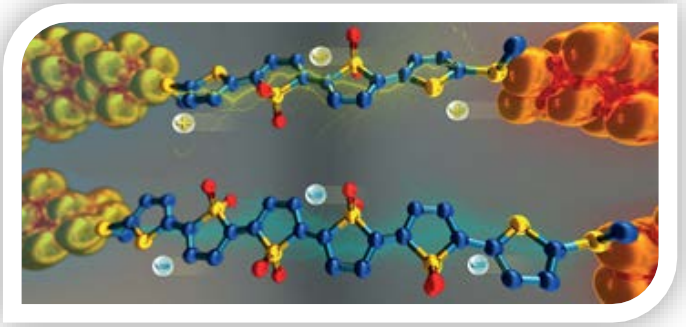


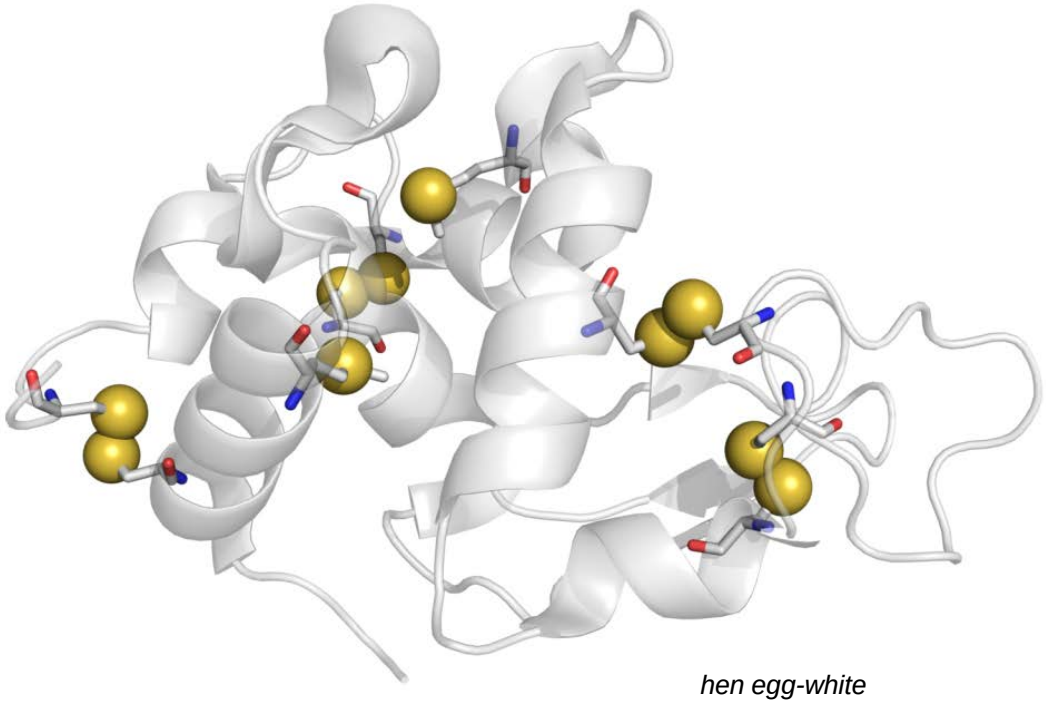
*Dell et al., Nature Chemistry **2015**, 7, 209–214*

*David et al., Scientific Reports **2015**, 5, 9792*

Motivation

High biological relevance

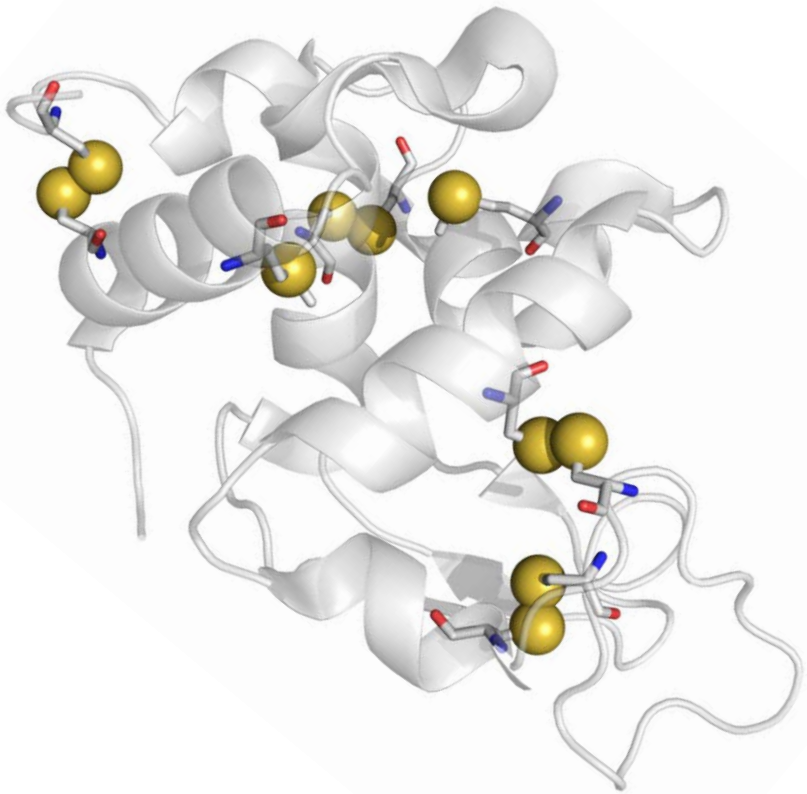
Thiol groups, thiolates and disulfide bridges in proteins



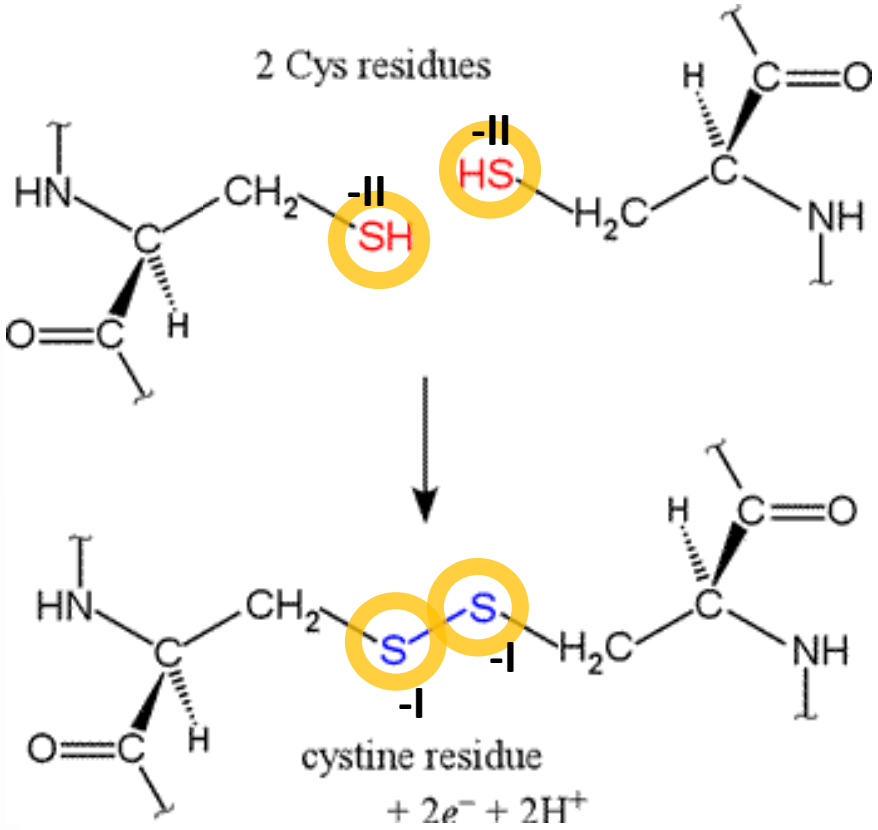
hen egg-white lysozyme

The Thiol-Group

Tertiary structure element:



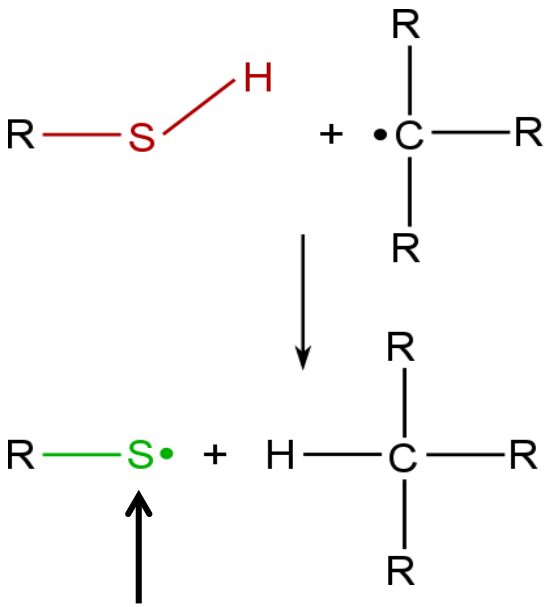
Disulfide formation:



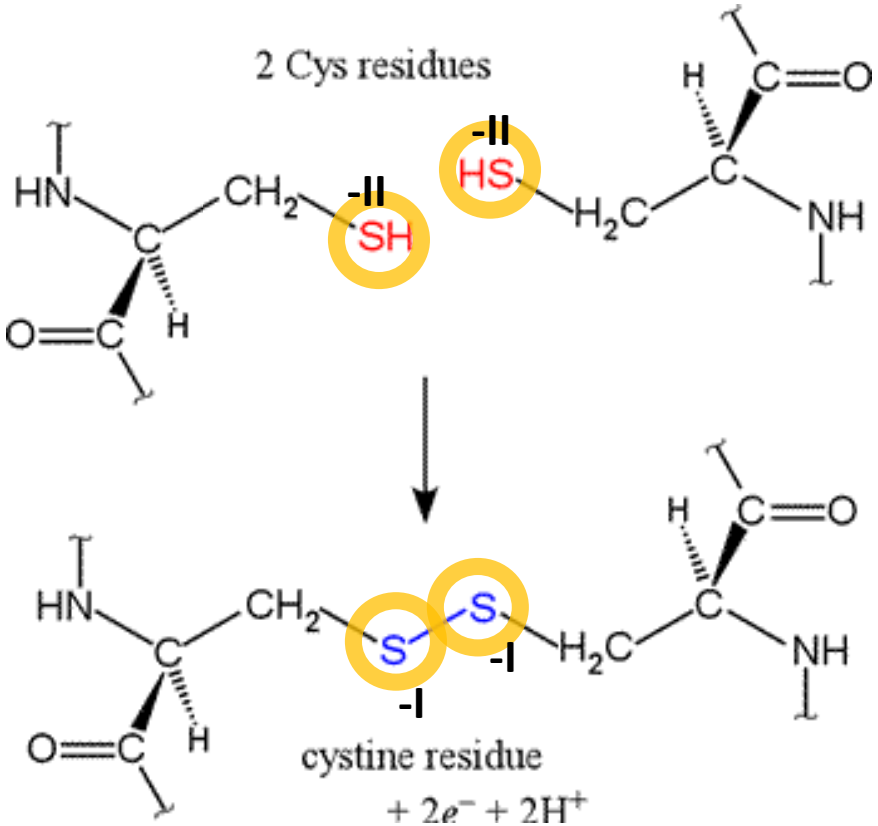
Schöneich. *Methods Enzymol.*, **1995**, 251, 45.
http://biology-forums.com/definitions/index.php/Disulfide_bond

The Thiol-Group

Radical repair reaction:



Disulfide formation:



Aromatic thiols:

- Higher nucleophilicity
- Higher reactivity towards disulfides
- Thiophenol increases protein folding/unfolding rates

Schöneich. *Methods Enzymol.*, **1995**, 251, 45.

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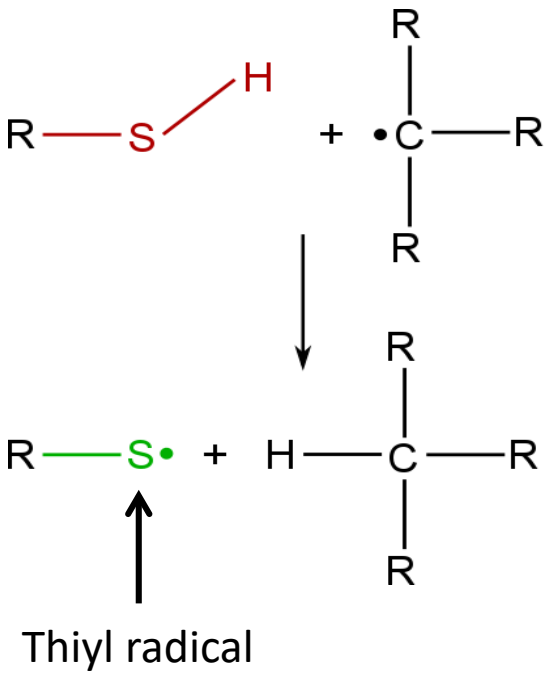
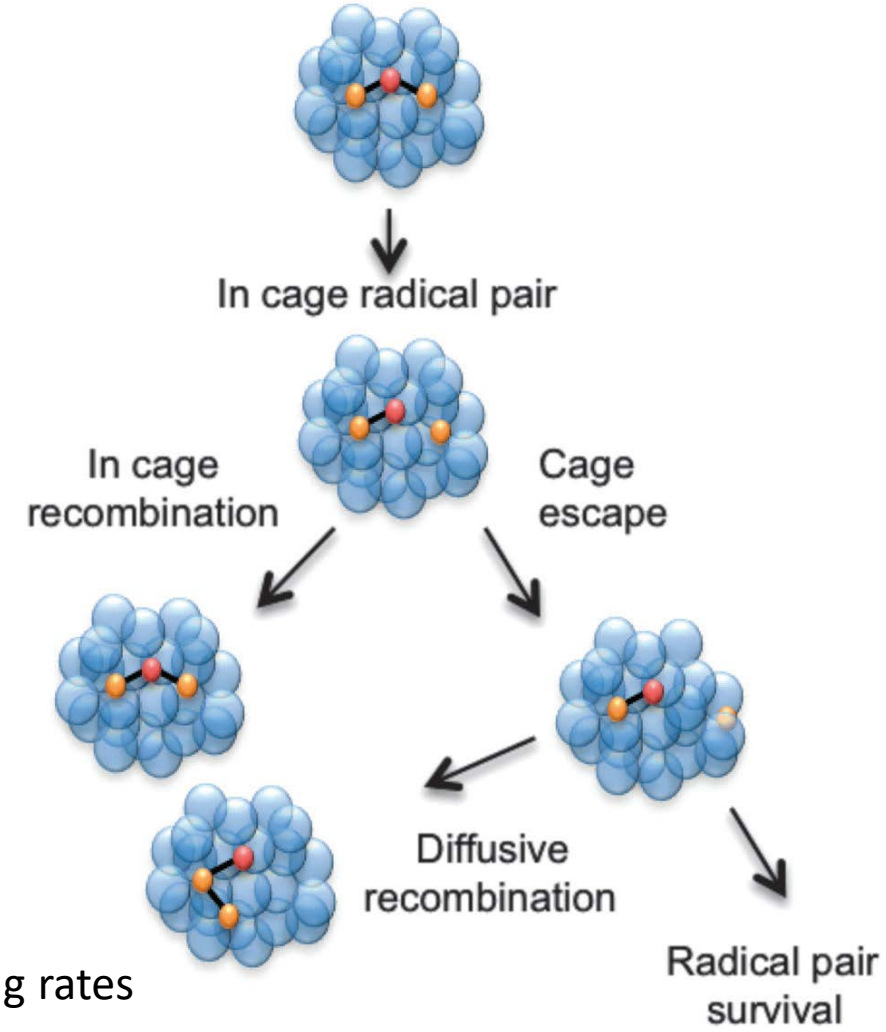
The Thiol-Group

Radical repair reaction:



The role of solvent cages:



Aromatic thiols:

- Higher nucleophilicity
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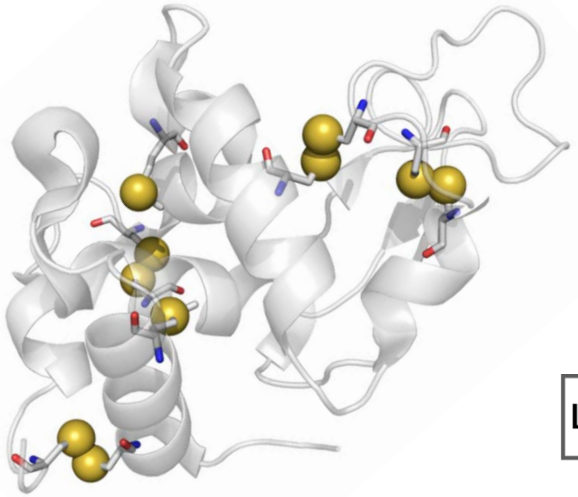
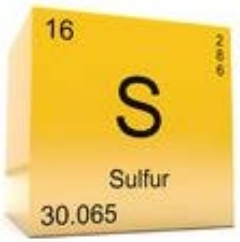
*S. J. Harris et al., PCCP **15**, 6567 (2013)*

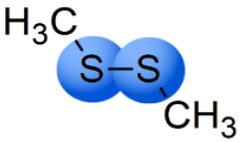
Disulfide Chemistry in Solution:

how does a sulfur-sulfur bond in solvated organic molecules break?

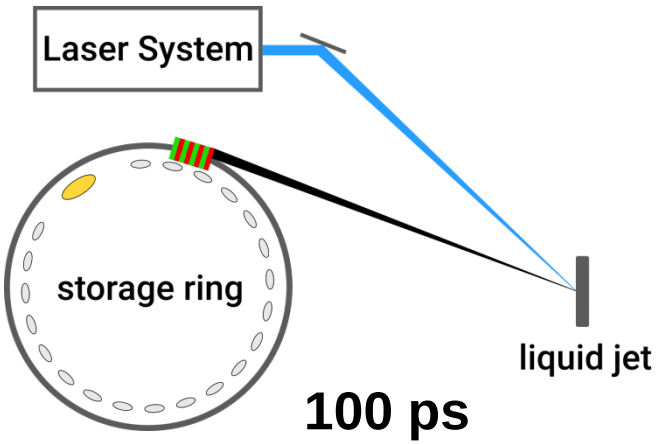
Time-Resolved Sulfur-1s Spectroscopy in Solution



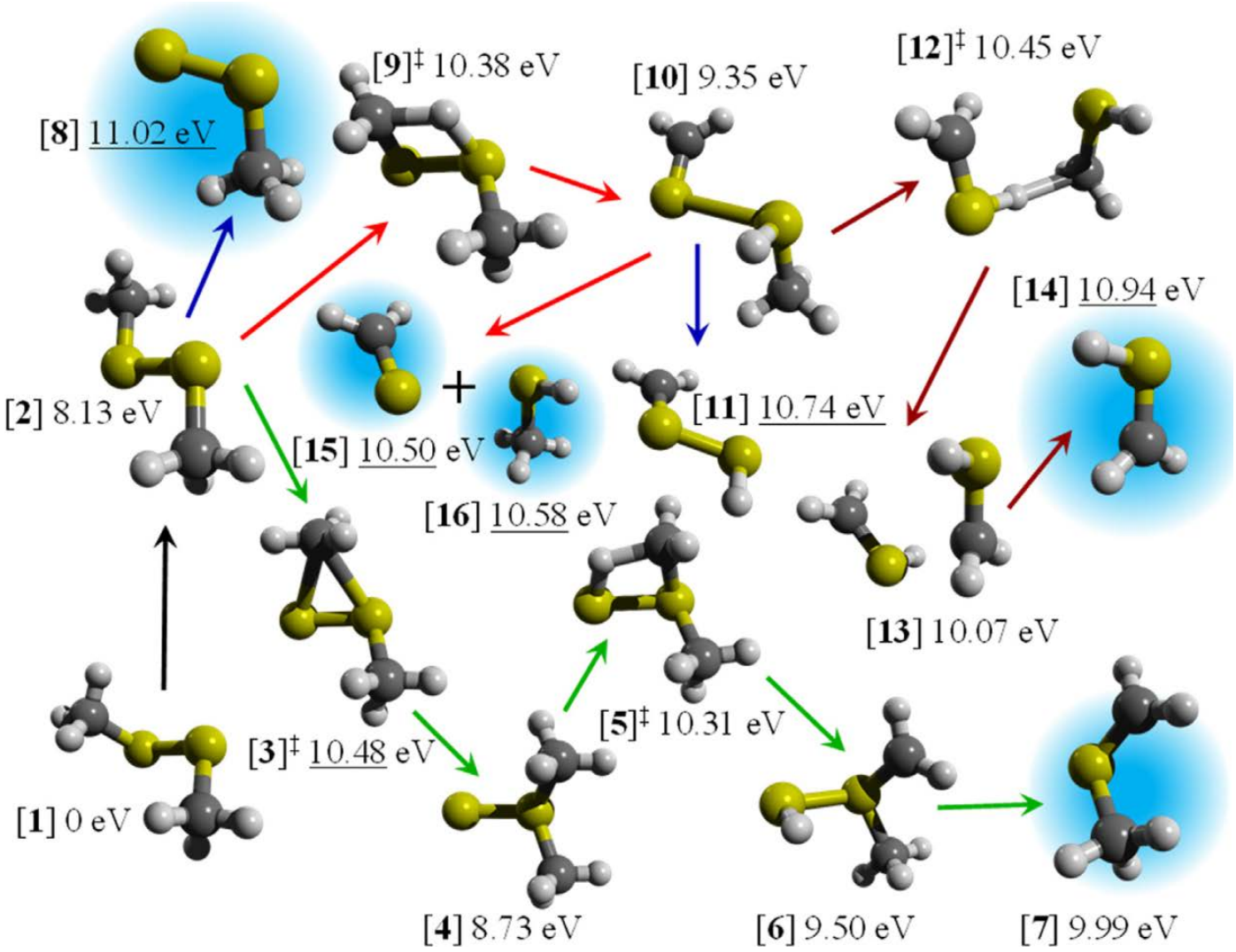




‘DMDS’

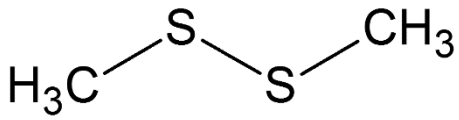


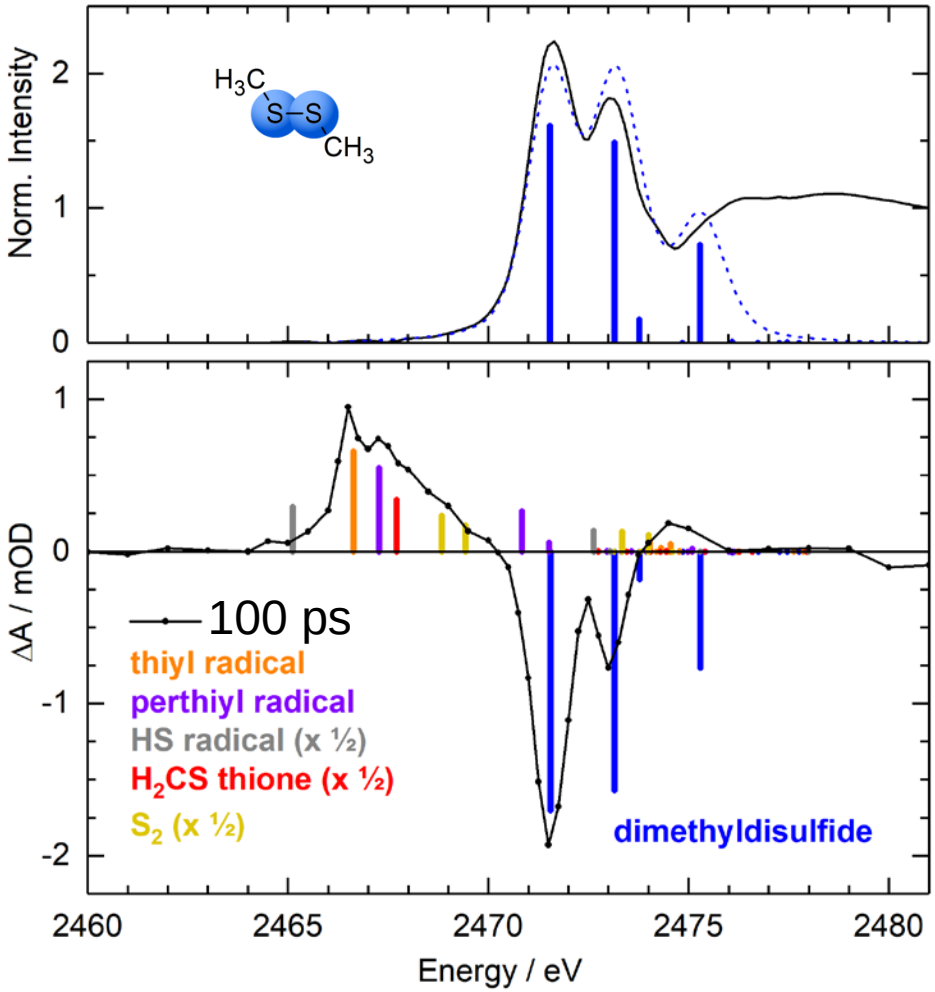
Energetics of DMDS variants



*S. Borkar et al., JESRP **196**, 165 (2014)*

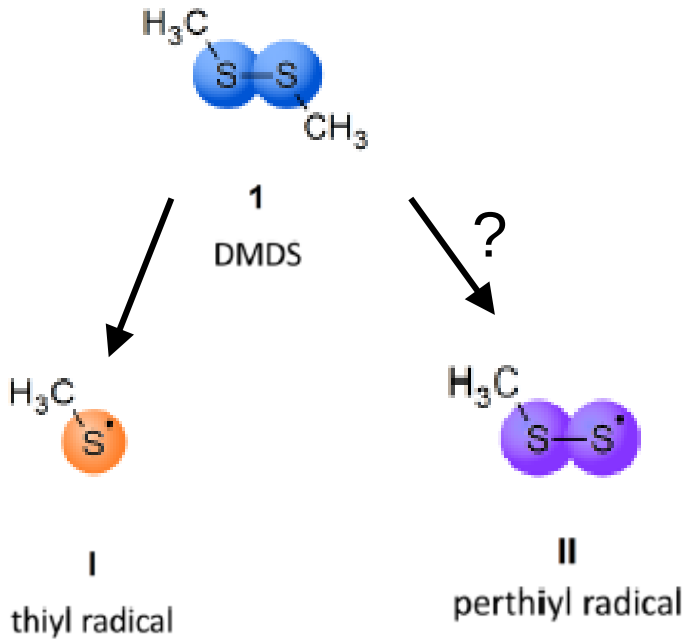
Sulfur-1s Spectroscopy of Dimethyldisulfide





Smallest stable Disulfide molecule

- *Found in atmospheric and interstellar chemistry*
- *Contains basic photochemistry of disulfides*
- *Complex reaction pathways reported in many time-resolved studies*



M. Ochmann *et al., J. Am. Chem. Soc.* **2018**, 140, 6554

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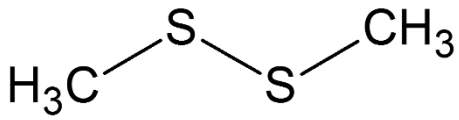

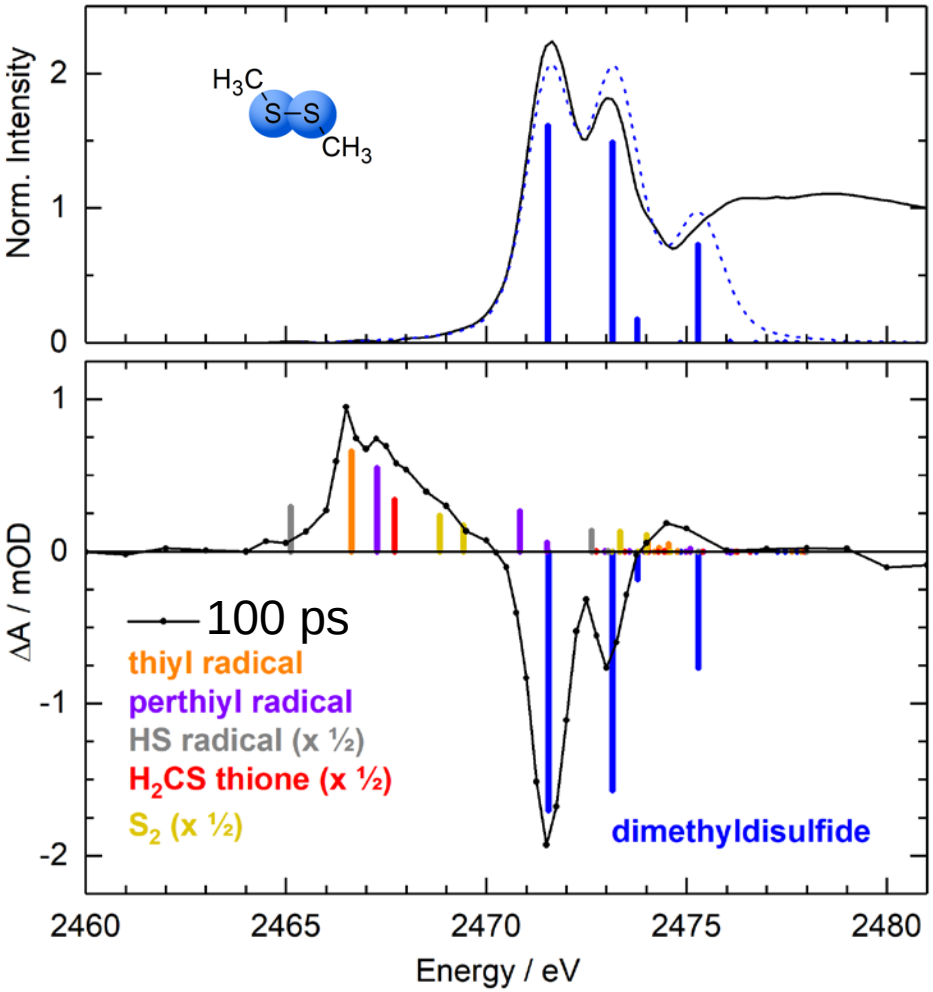

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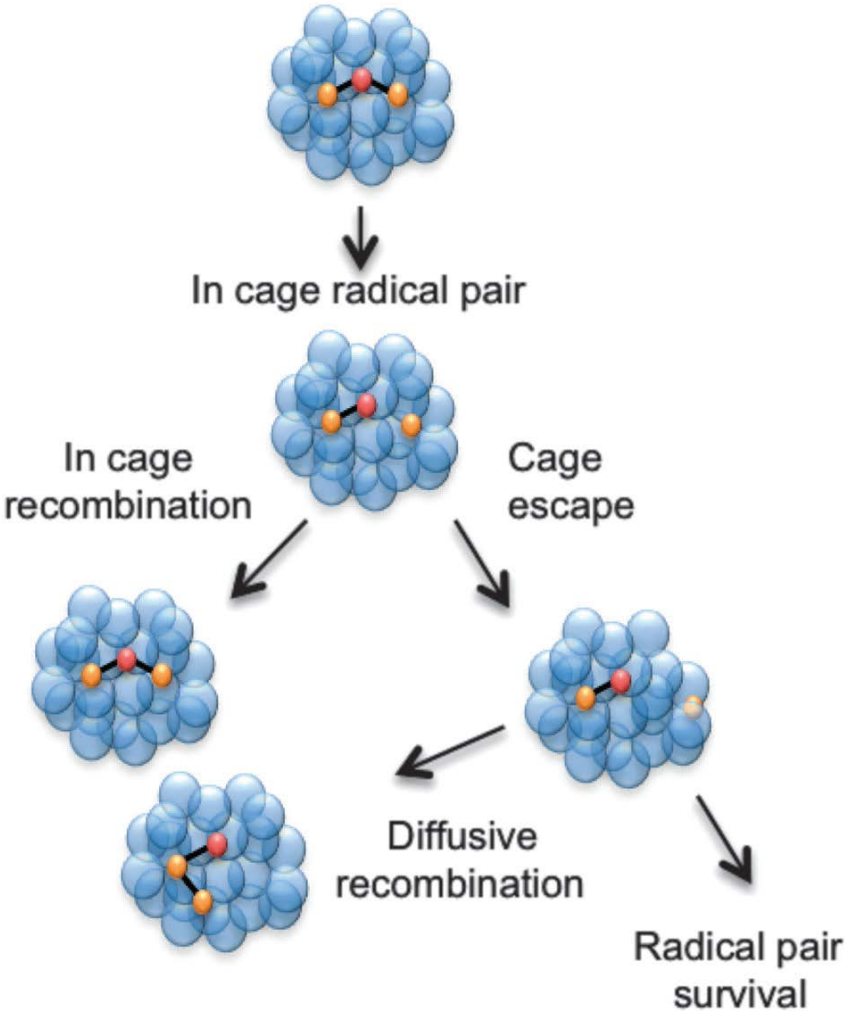

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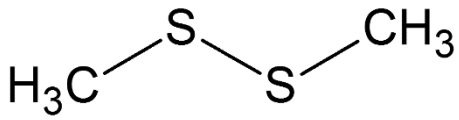
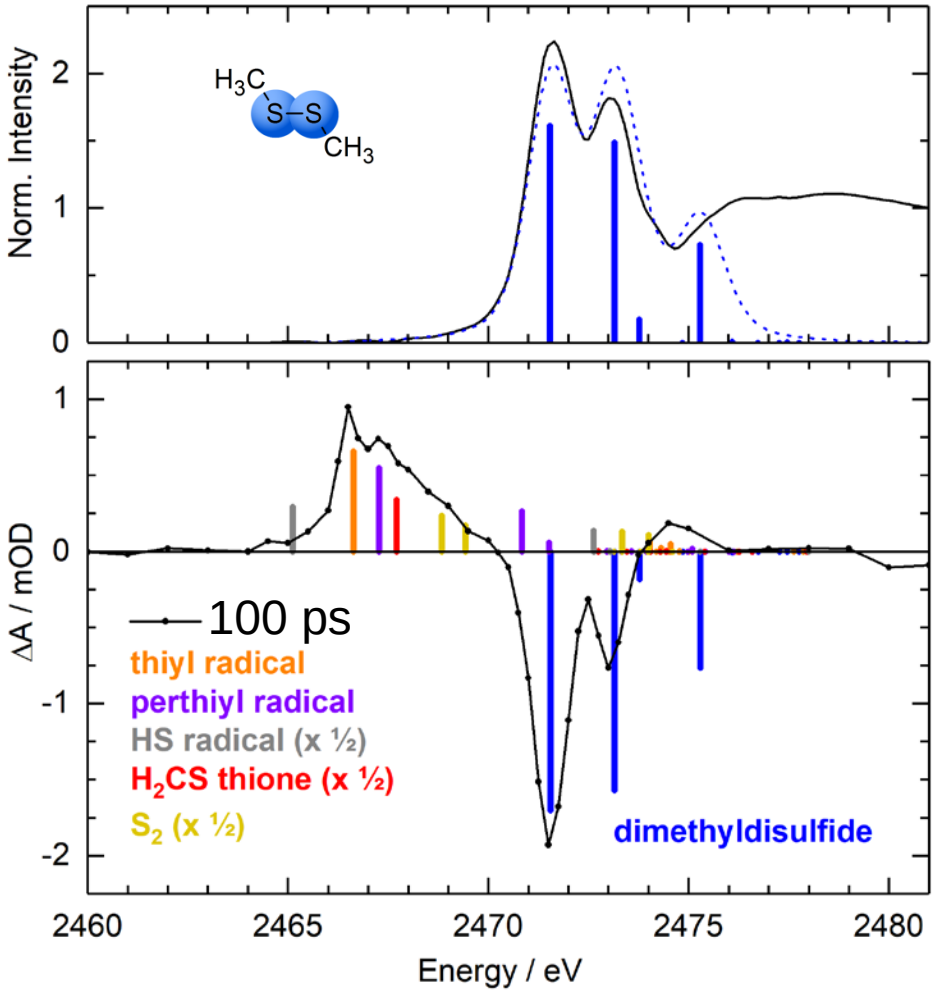
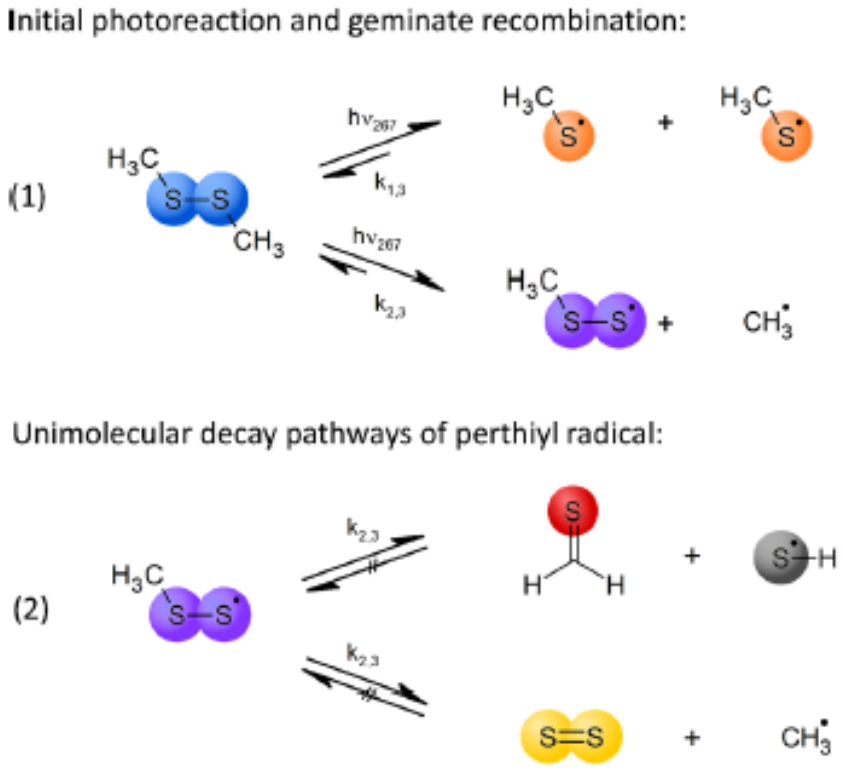




Smallest stable Disulfide molecule

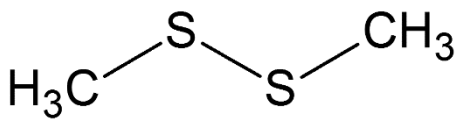
- *Solvent cage effects clearly play a role in product formation & relaxation*
- *Transient S_2 and/or thione formation?*
- *Formation of polysulfides?*



Delay / ns

M. Ochmann *et al., J. Am. Chem. Soc.* **2018**, 140, 6554

Sulfur-1s Spectroscopy of Dimethyldisulfide



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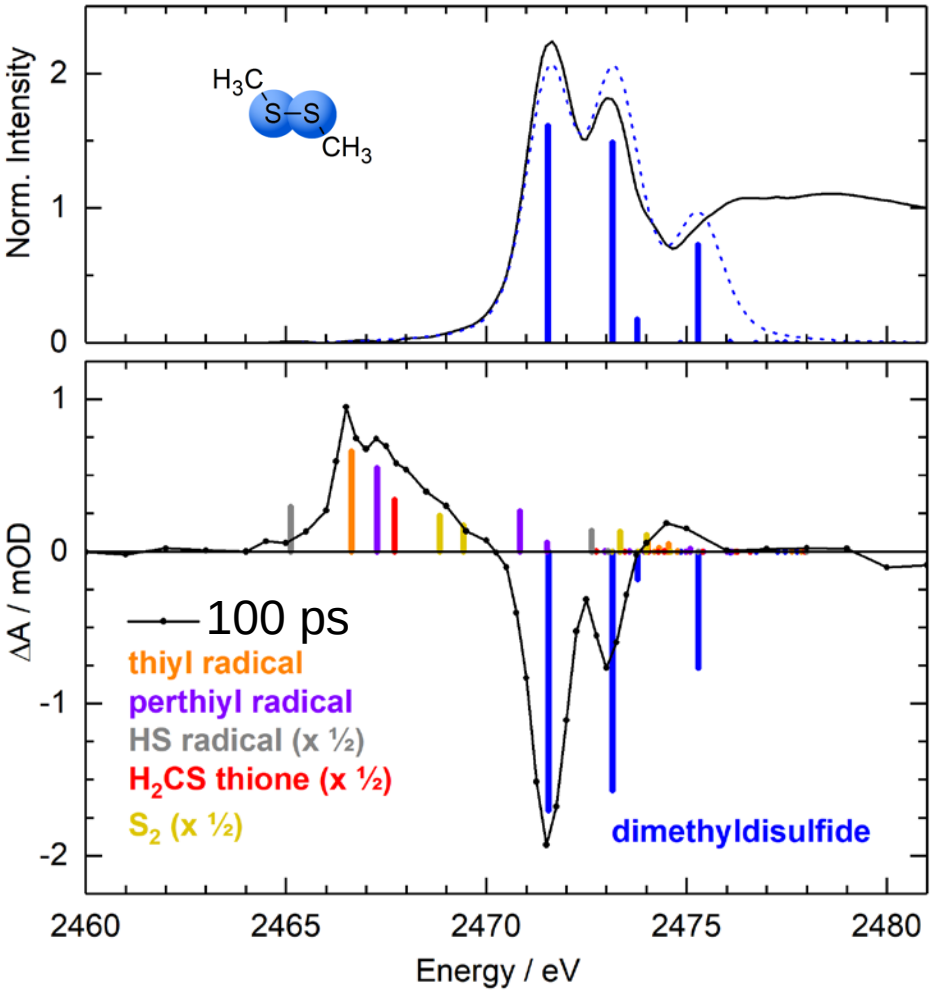
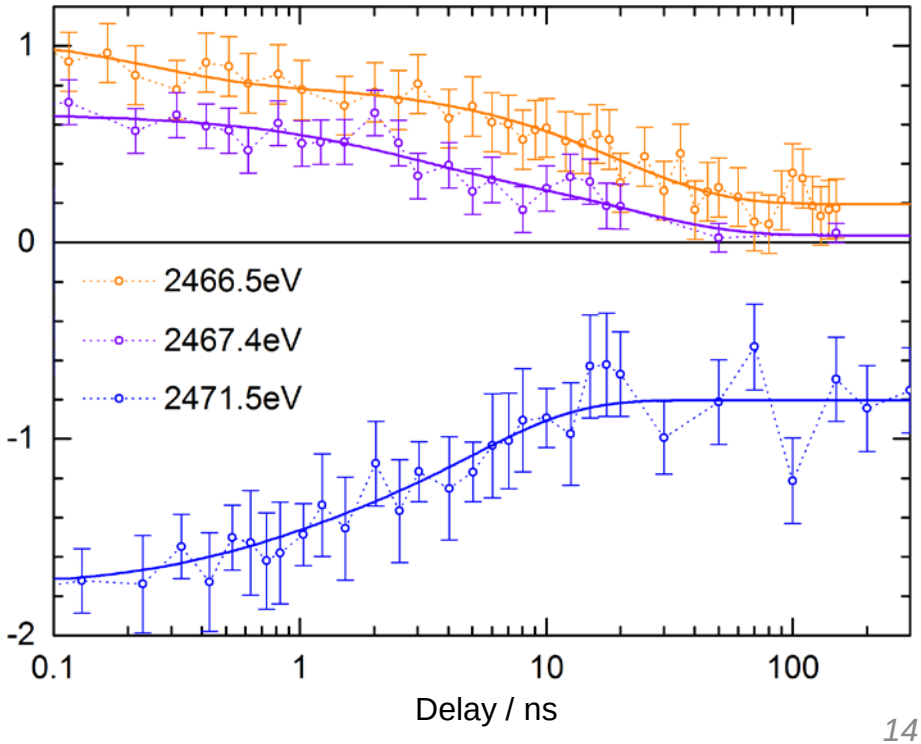




M. Ochmann *et al., J. Am. Chem. Soc.* **2018**, 140, 6554

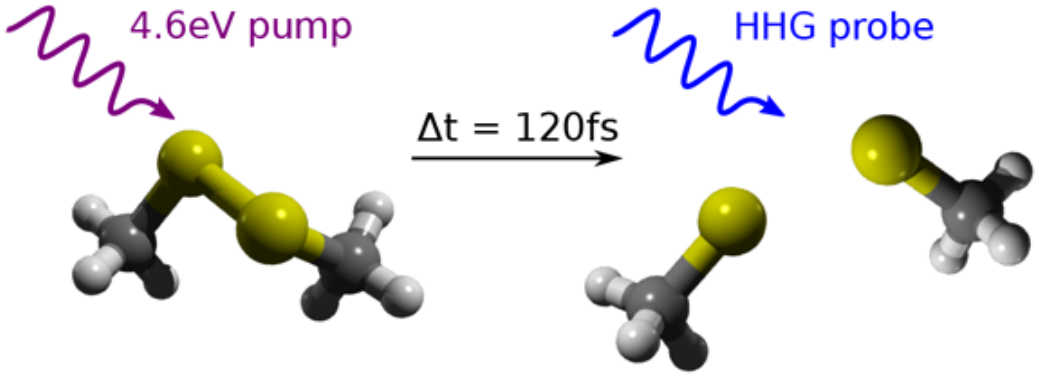
Sulfur-2p Spectroscopy of Dimethyldisulfide

Tracing the 267 nm-Induced Radical Formation in Dimethyl Disulfide Using Time-Resolved X-ray Absorption Spectroscopy

Kirsten Schnorr,[*,†,‡] Aditi Bhattacherjee,[†,‡] Katherine J. Oosterbaan,[†,‡] Mickaël G. Delcey,[†,‡] Zheyue Yang,[†,‡] Tian Xue,[†,‡] Andrew R. Attar,[†,‡] Adam S. Chatterley,[†,‡] Martin Head-Gordon,[†,‡] Stephen R. Leone,[†,‡,¶] and Oliver Gessner[*,‡]

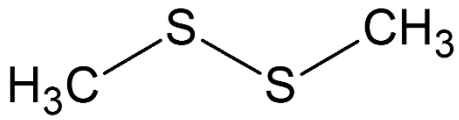
[†]Department of Chemistry, University of California, Berkeley, California 94720, United States
[‡]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
[¶]Department of Physics, University of California, Berkeley, California 94720, United States

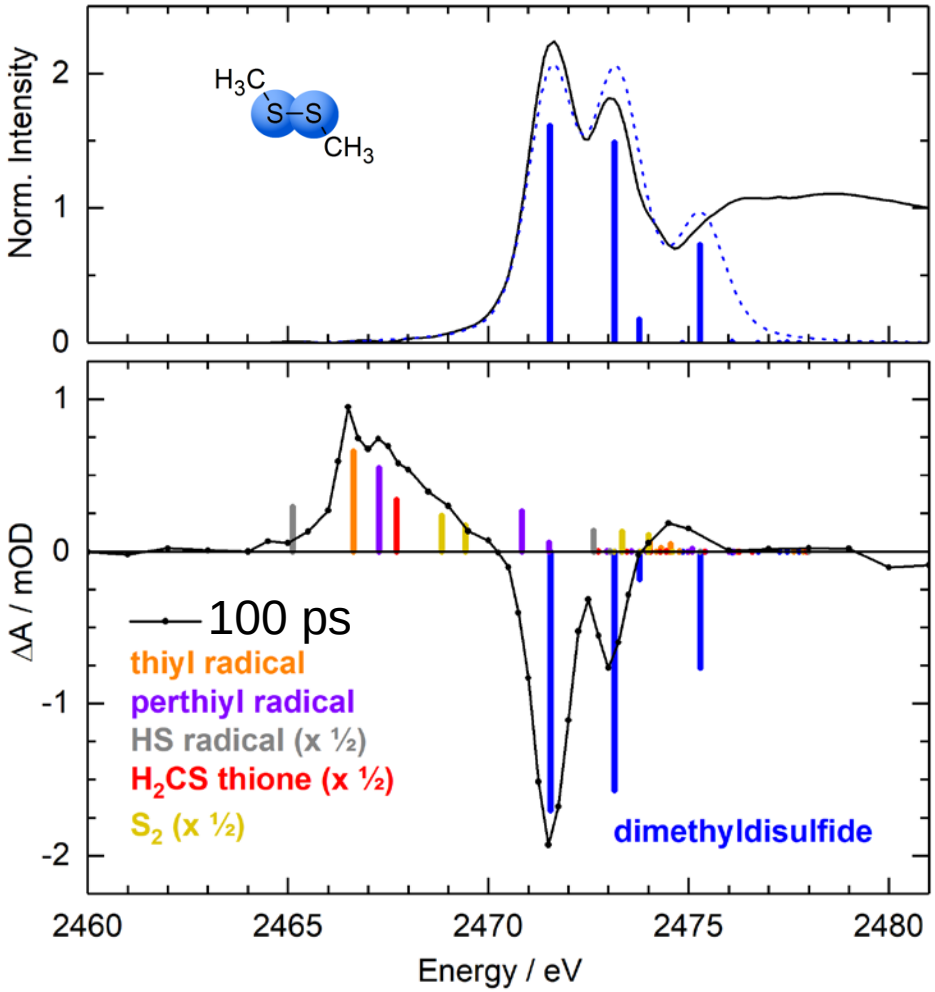
The fs-TRXAS … show that gas-phase DMDS … undergoes fast direct dissociation into two CH3S radicals within 120 fs



J. Phys. Chem. Lett. **10**, 1382 (2019)

Sulfur-1s Spectroscopy of Dimethyldisulfide





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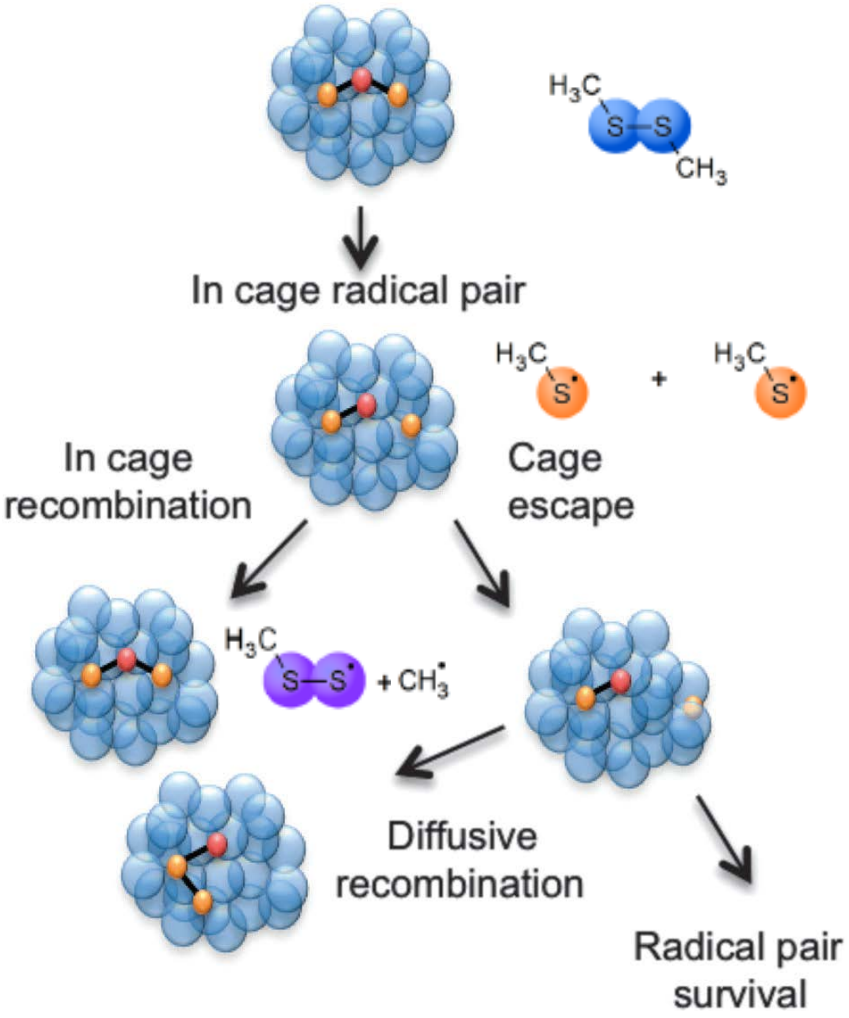
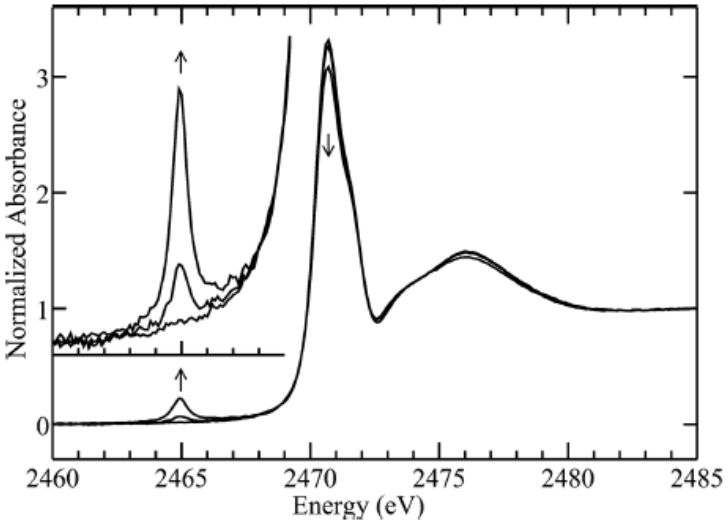
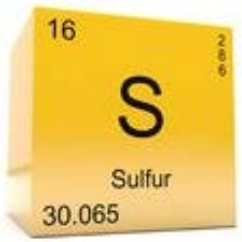
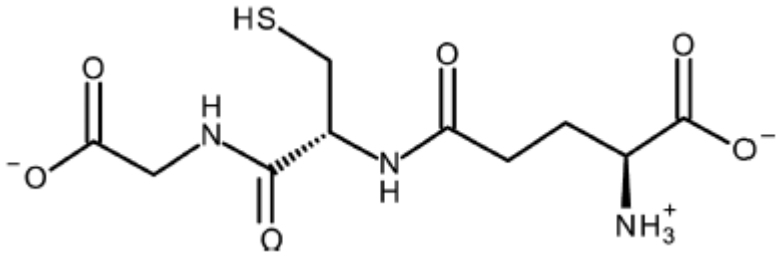


M. Ochmann *et al., J. Am. Chem. Soc.* **2018**, 140, 6554

Time-Resolved Sulfur-1s Spectroscopy in Solution





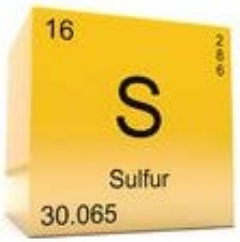


Photochemically Generated Thiyl Free Radicals Observed by X-ray Absorption Spectroscopy

Eileen Y. Sneeden,[†] Mark J. Hackett,[‡,§] Julien J. H. Cotelesage,[‡] Roger C. Prince,[⊥] Monica Barney,[⊗] Kei Goto,[∥] Eric Block,[▽] Ingrid J. Pickering,[‡,¶] and Graham N. George[*,‡,¶]

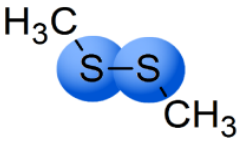
J. Am. Chem. Soc. 2017, 139, 11519

Time-Resolved Sulfur-1s Spectroscopy in Solution



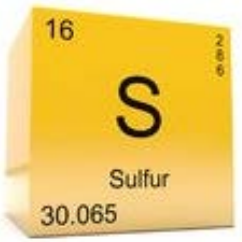
PAL

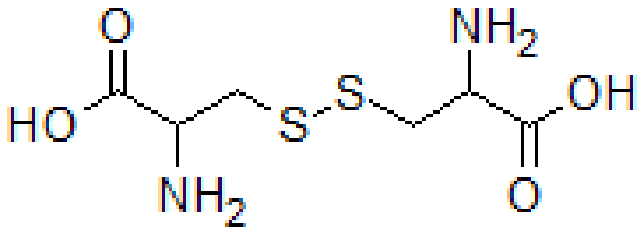
POHANG ACCELERATOR LABORATORY



‘DMDS’

Time-Resolved Sulfur-1s Spectroscopy in Solution

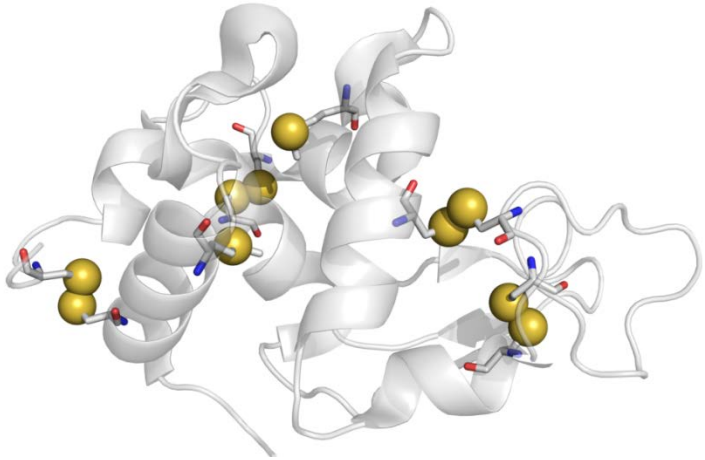


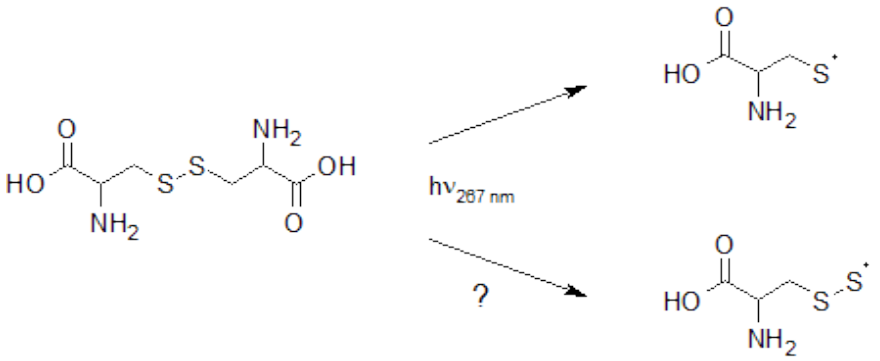


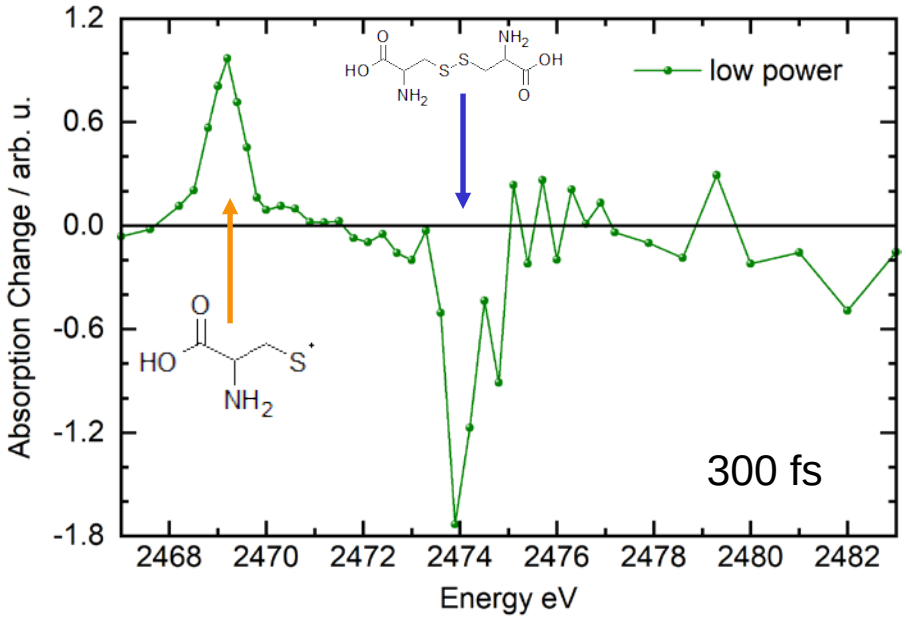
L-Cystine
the L-cysteine dimer

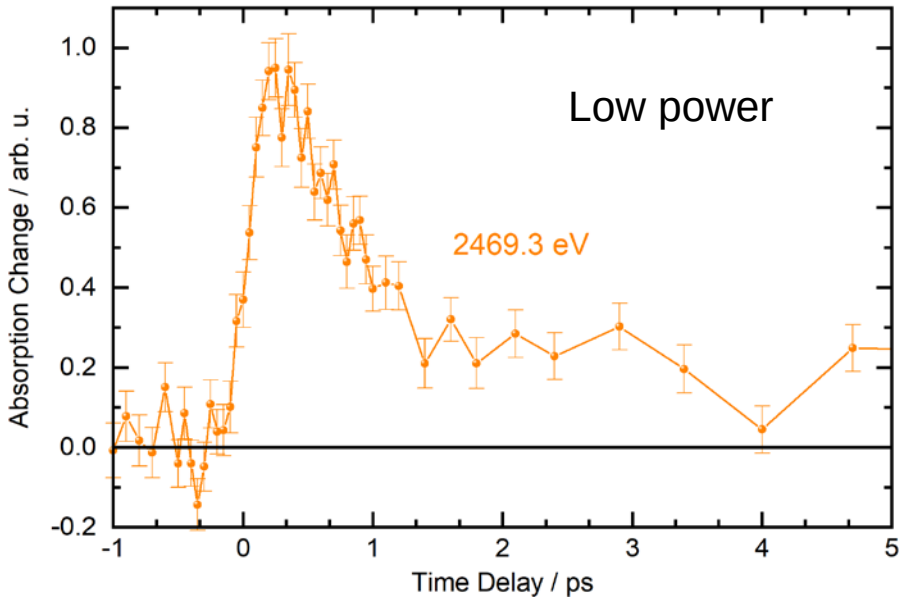
POHANG ACCELERATOR LABORATORY

From DMDS to L-Cystine

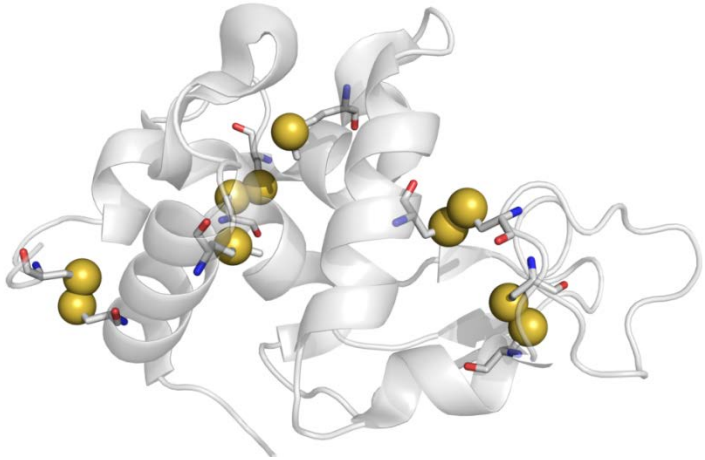


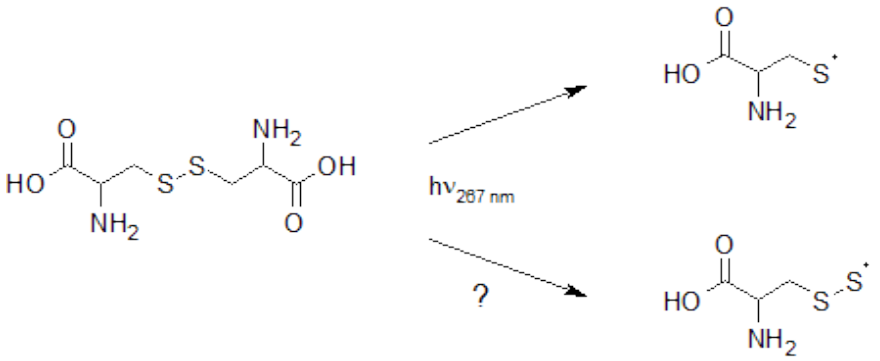




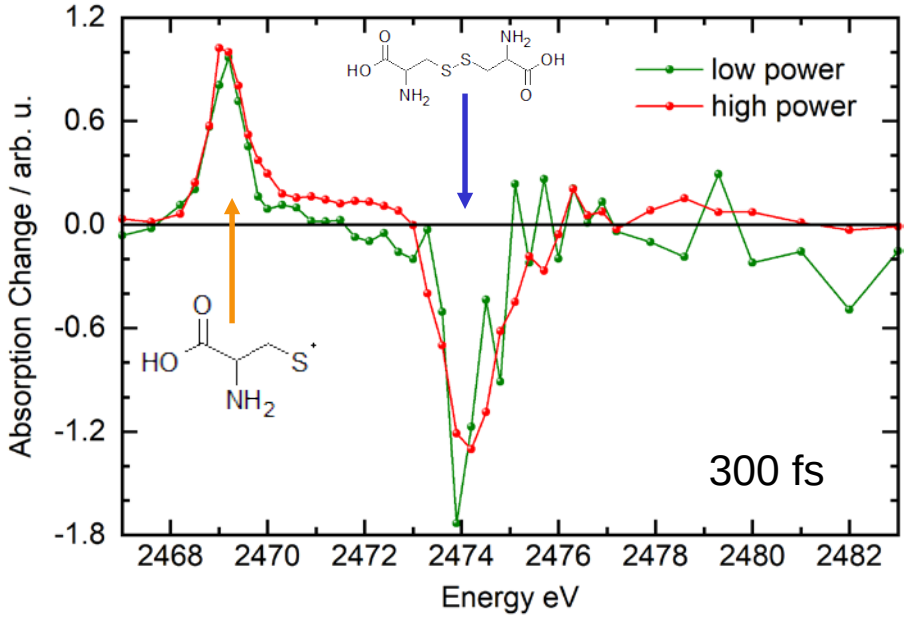


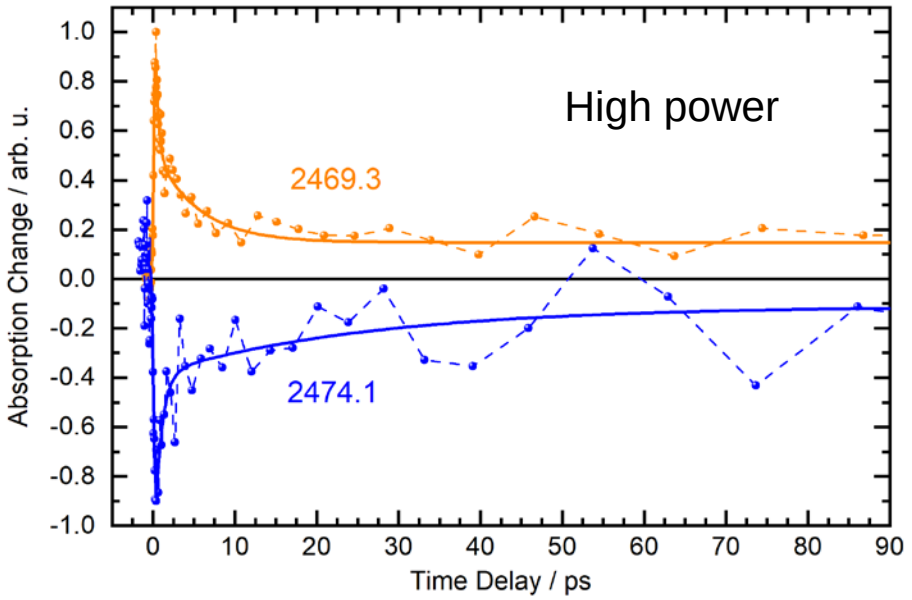
From DMDS to L-Cystine



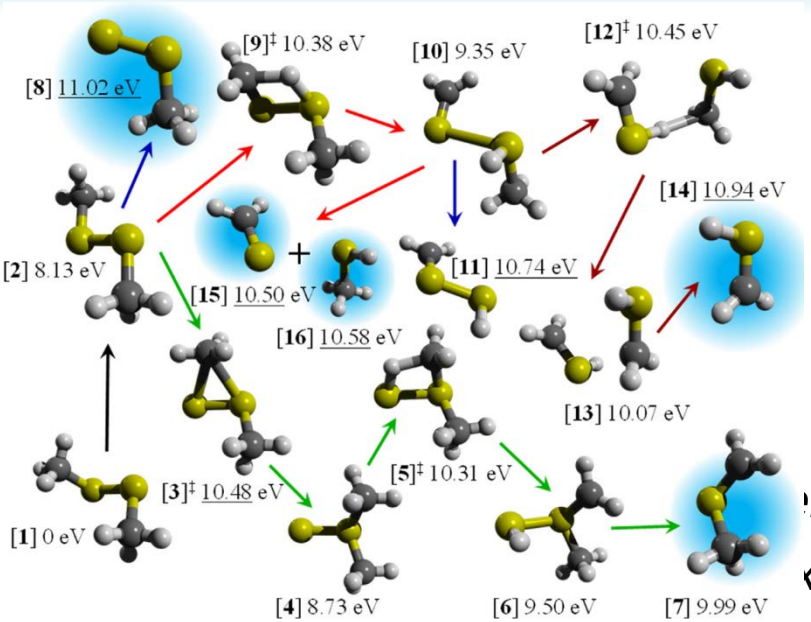


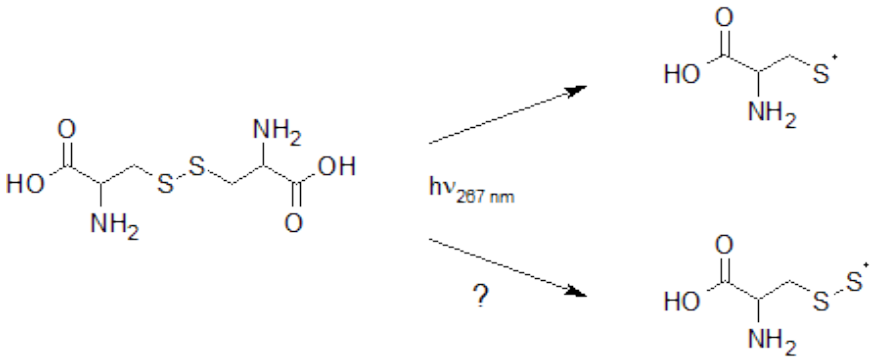
- *Ultrafast geminate recombination (little electronic relaxation)*
- *2-photon excitation leads to new sulfur species*





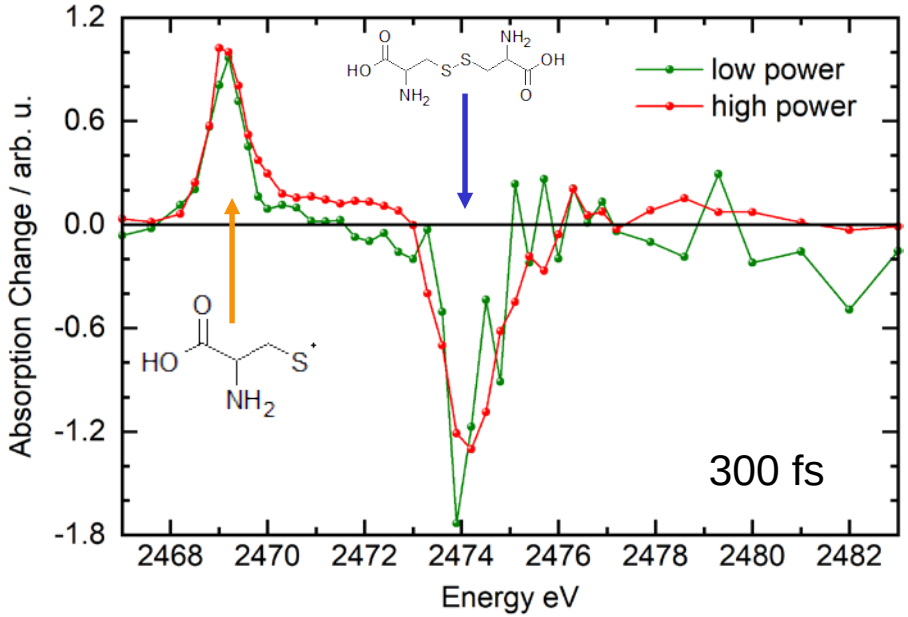
From DMDS to L-Cystine

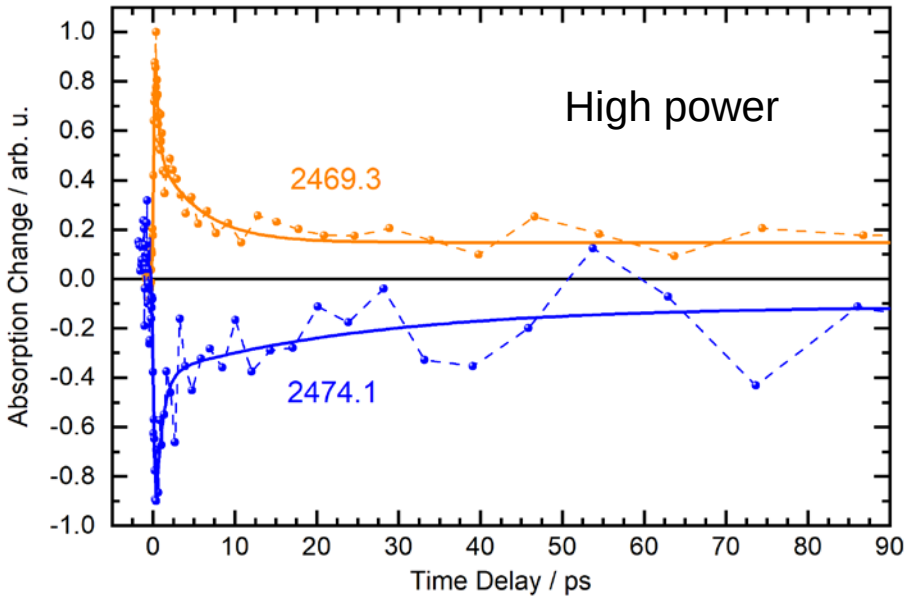




…minate recombination (little electronic relaxation)

…xcitation leads to new sulfur species

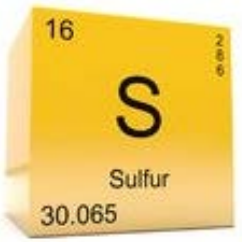


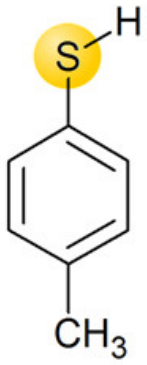


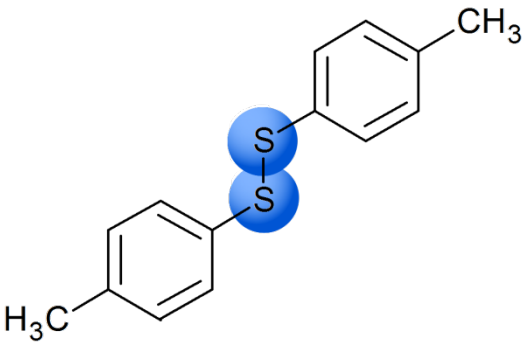
Sulfur-Containing Aromatic Systems:

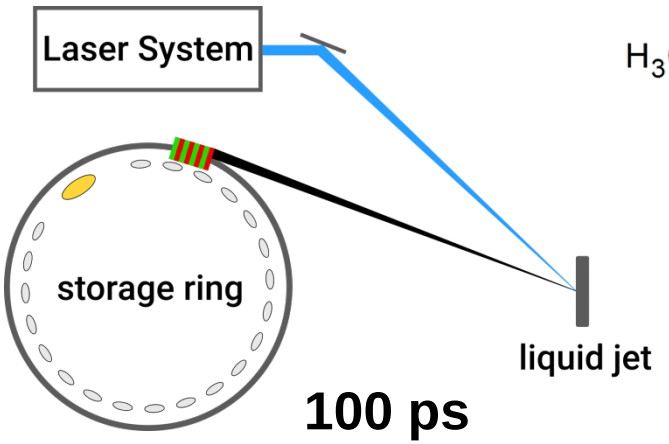
how do sulfur atoms coupled to aromatic electron systems behave?

Time-Resolved Sulfur-1s Spectroscopy in Solution

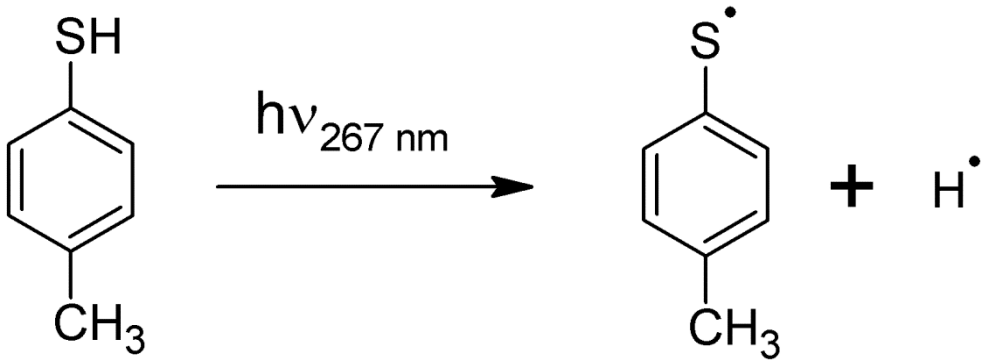


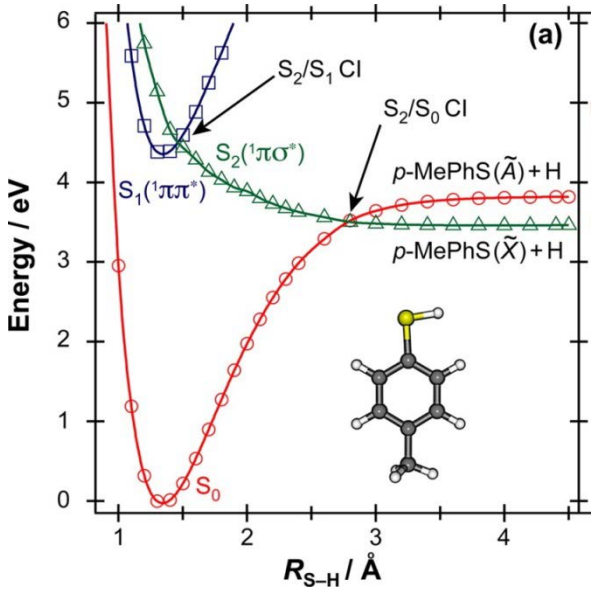


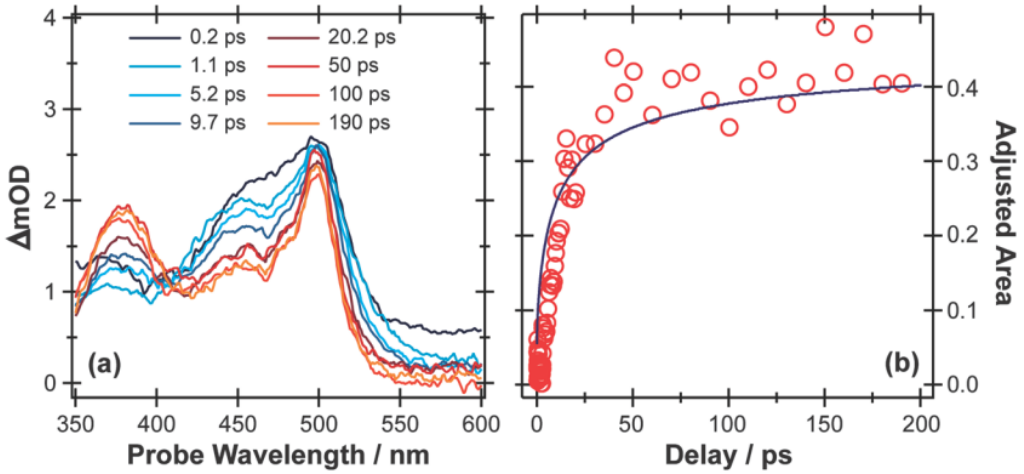


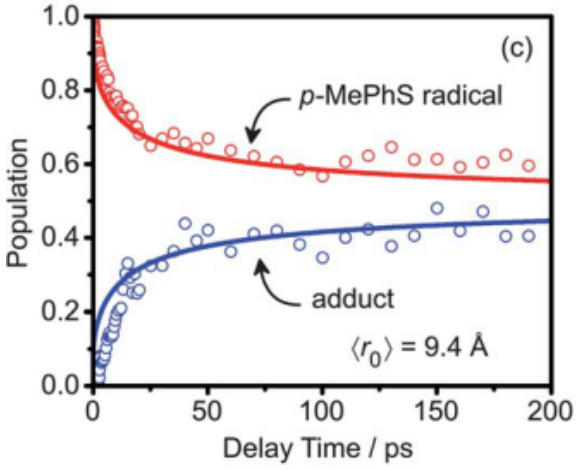


4-Methylthiophenol









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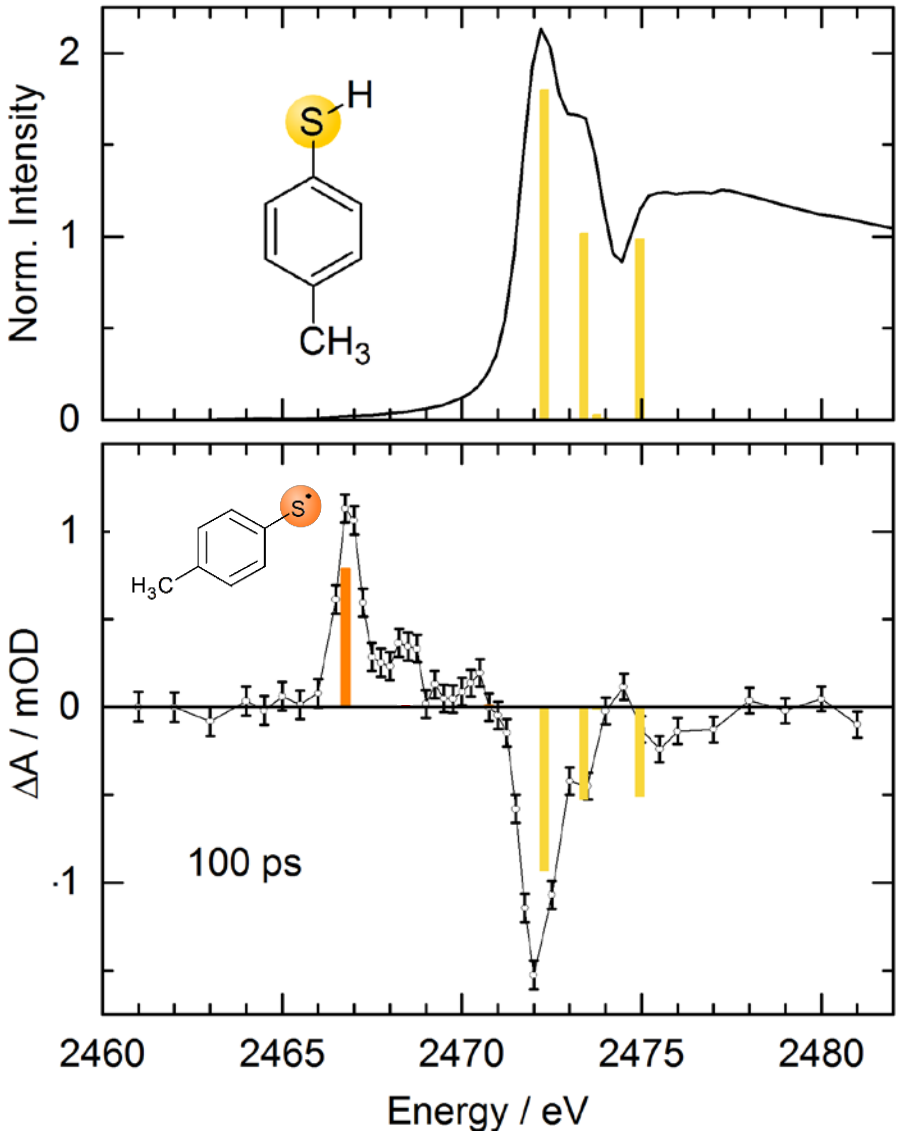
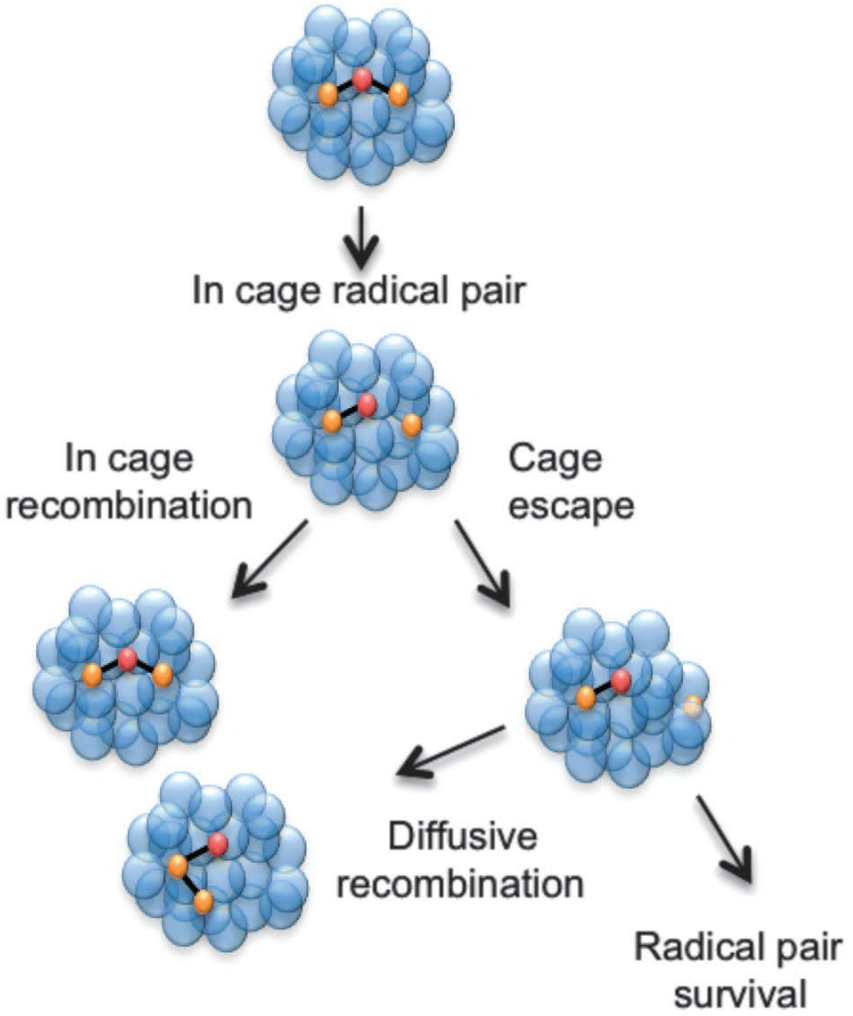
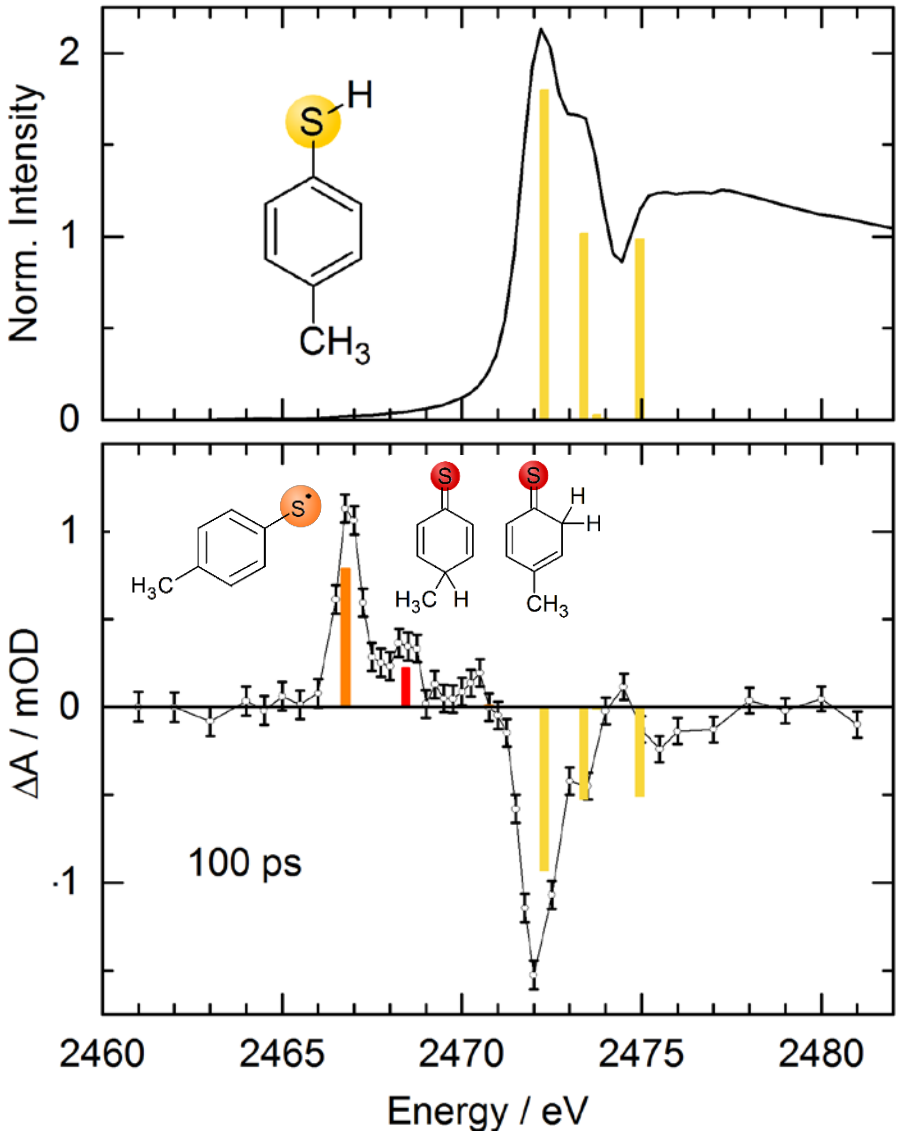
Sulfur-1s Spectroscopy of 4-MTP

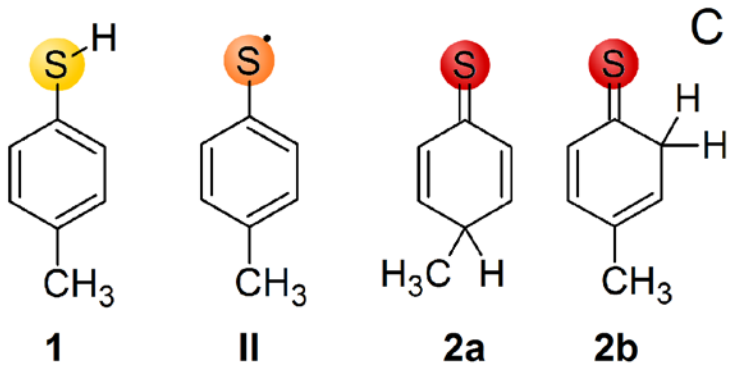




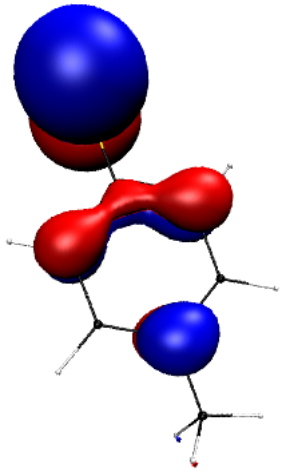
M. Ochmann *et al., J. Am. Chem. Soc.* **2017**, 139 (13), 4797

Sulfur-1s Spectroscopy of 4-MTP





Regioselectivity of hydrogen attachment results from valence orbital symmetry



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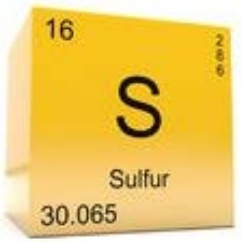
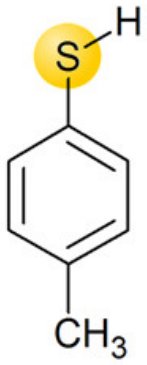
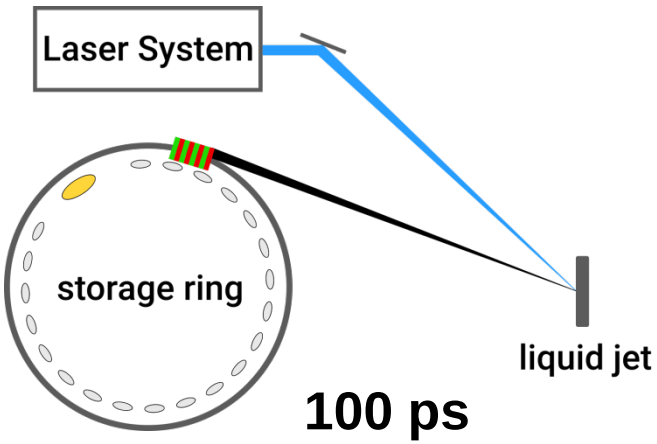
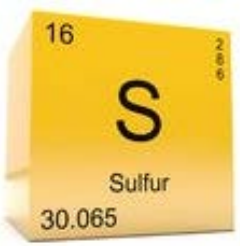
Time-Resolved Sulfur-1s Spectroscopy in Solution

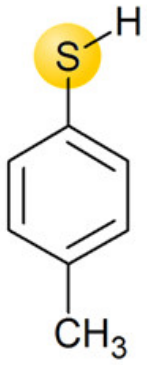


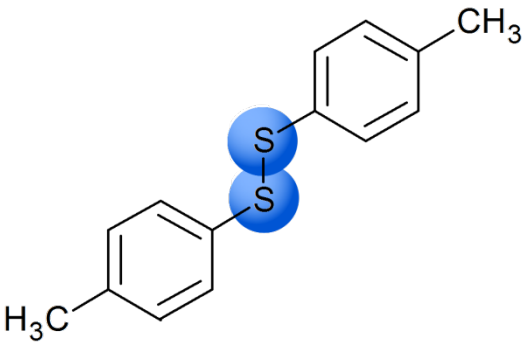


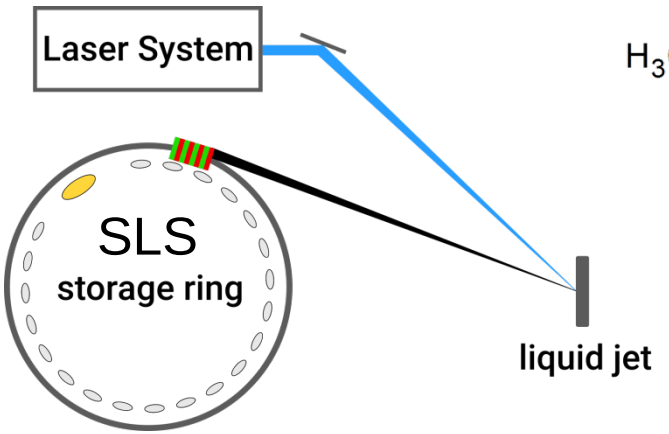


Time-Resolved Sulfur-1s Spectroscopy in Solution









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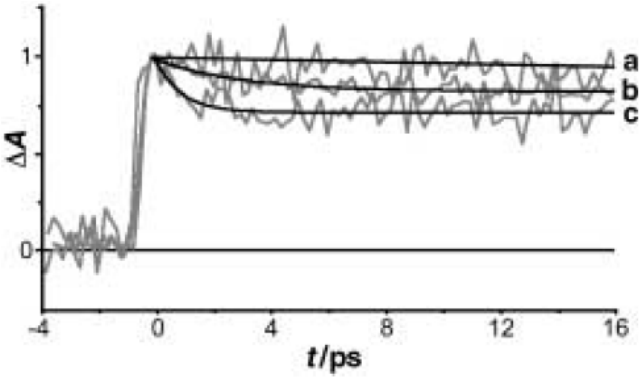
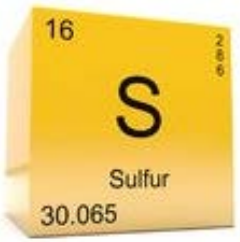
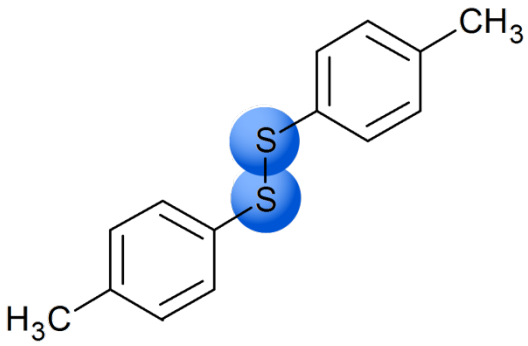
Time-Resolved Sulfur-1s Spectroscopy in Solution





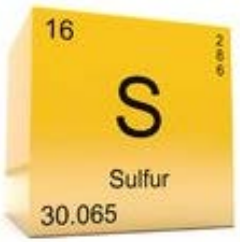


Synthesis and Photochemistry of a New Class of Photocleavable Protein Cross-linking Reagents

Lilia Milanesi,[a] Gavin D. Reid,[b] Godfrey S. Beddard,[b] Christopher A. Hunter,*[a] and Jonathan P. Waltho[c]

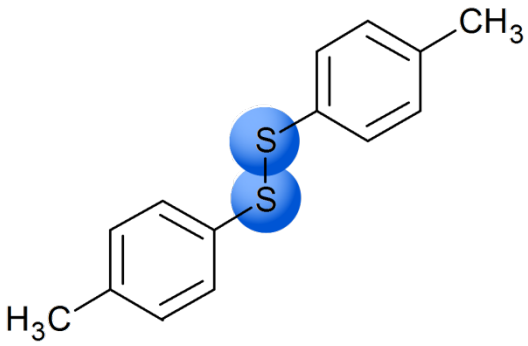
Chem. Eur. J. 2004, 10, 1705

Time-Resolved Sulfur-1s Spectroscopy in Solution

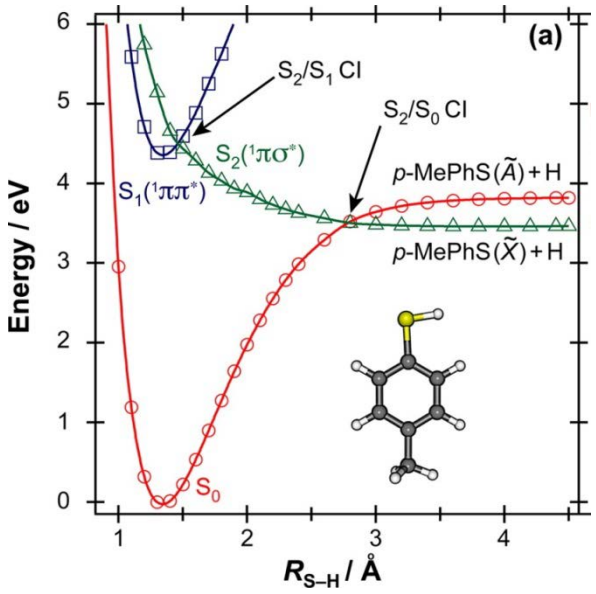


PAL

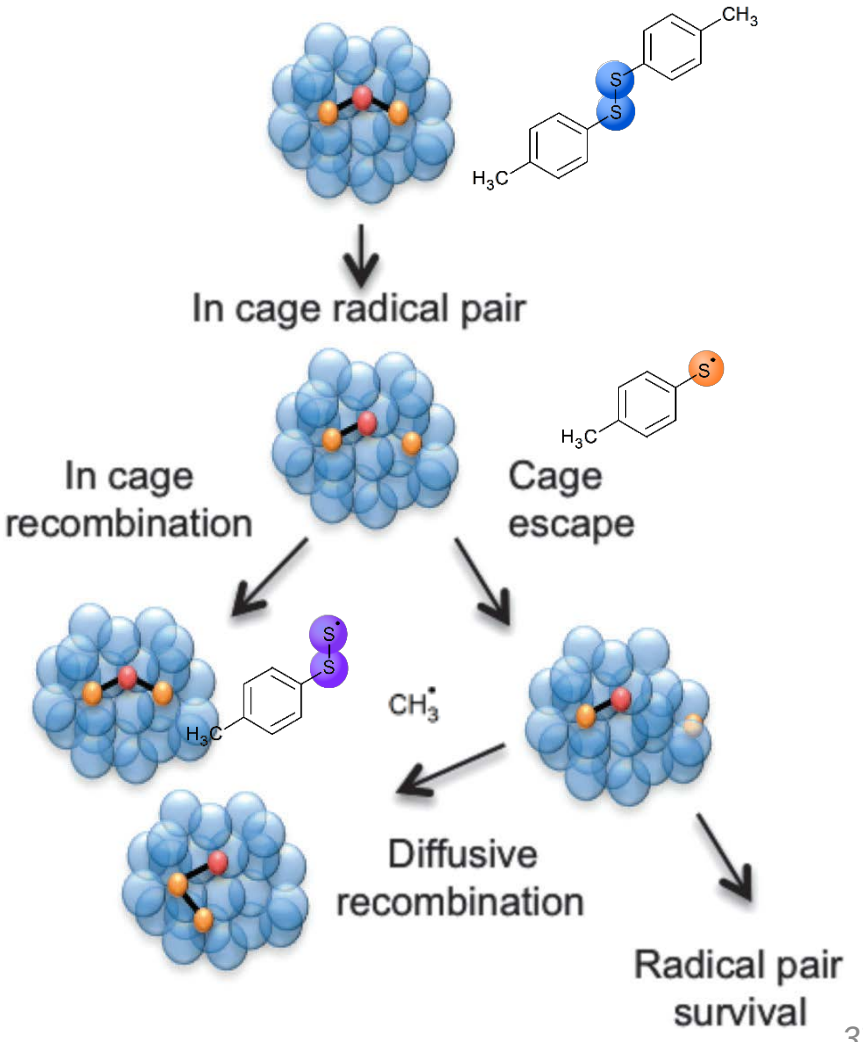
POHANG ACCELERATOR LABORATORY



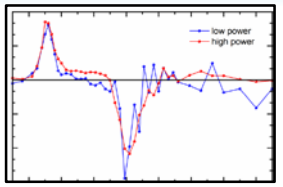
Time-Resolved Sulfur-1s Spectroscopy in Solution

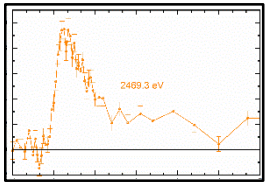


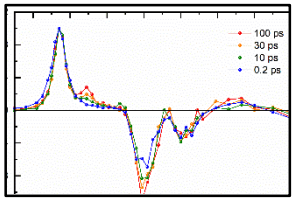
- Unaltered spectra up to TW/cm²
- Biphasic rise of primary radical
- Slow geminate recombination
- Secondary product manifests



Conclusions and Thanks







- Aliphatic disulfides exhibit high degree of ultrafast geminate recombination
- New reaction pathways exist for excitation into higher electronic states
- Geminate recombination in aromatic disulfides is strongly suppressed, possibly due to efficient relaxation of the radical charge density
- Aromatic electron systems appear to channel higher excitations into the energetically lowest reaction pathway

Many Thanks

***Miguel Ochmann**, **Abid Hussain**, **Oriol Vendrell**, **Nils Huse**,*
Niko Höppel, Anke Puchert, Kateryna Kusyak

***Tae Kyu Kim**, **Bob Schoenlein**, Amy Cordones-Hahn, Kiryong Hong,*
Hana Cho, Jae Hyuk Lee, Rory Ma

***Chris Milne**, **Majed Chergui**, **Thomas Huthwelker**, Dominik Kinschel,*
James Budarz, Jochen Rittmann, Gediminas Galinas, Jon Marangos

***The PAL-XFEL team** for a great support and exciting results*

DOE MPG FHH