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

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Transient X-ray Spectroscopy of Molecules

Huse et al. *JPCL* 2, 880 (2011)
Van Kuiken et al *JPCL* 7, 465 (2016)

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)
Siefermann et al *JPCL* 5, 2735 (2014)

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:


The Thiol-Group

Radical repair reaction:

\[
R-SH + \cdot CRR \rightarrow R-S\cdot + H-CRR
\]

Disulfide formation:

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

The Thiol-Group

Radical repair reaction:

\[
\begin{align*}
R-S-H & \quad + \quad \cdot C-R \\
& \downarrow \quad \downarrow \\
R-S-\cdot & \quad + \quad H-C-R \\
\end{align*}
\]

Thiyl radical

The role of solvent cages:

- In cage radical pair
- In cage recombination
- Diffusive recombination
- Cage escape
- Radical pair survival

Aromatic thiols:

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

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

100 ps

Laser System

storage ring

liquid jet

H₃C
S–S
CH₃

‘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
Sulfur-1s Spectroscopy of Dimethyldisulfide

![Chemical Structure: Dimethyldisulfide]

- Smallest stable Disulfide molecule
  - Solvent cage effects clearly play a role in product formation & relaxation

![Spectroscopic Data]

- In cage radical pair
- In cage recombination
- Diffusive recombination
- Cage escape
- Radical pair survival

M. Ochmann et al., J. Am. Chem. Soc. 2018, 140, 6554
Sulfur-1s Spectroscopy of Dimethyldisulfide

Smallest stable Disulfide molecule
- Solvent cage effects clearly play a role in product formation & relaxation
- Transient S₂ and/or thione formation?
- Formation of polysulfides?

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

M. Ochmann et al., J. Am. Chem. Soc. 2018, 140, 6554
The fs-TRXAS ... show that gas-phase DMDS ... undergoes fast direct dissociation into two CH3S radicals within 120 fs. 

\[ \text{4.6eV pump} \rightarrow \Delta t = 120\text{fs} \rightarrow \text{HHG probe} \]

\[ J. \text{Phys. Chem. Lett. 10, 1382 (2019)} \]
Smallest stable Disulfide molecule

- Solvent cage effects clearly play a role in product formation & relaxation

M. Ochmann et al., J. Am. Chem. Soc. 2018, 140, 6554
Photochemically Generated Thiyl Free Radicals Observed by X-ray Absorption Spectroscopy

Eileen Y. Sneeden,† Mark J. Hackett,‡,§ Julio J. H. Cotelesage,‡ Roger C. Prince, Além 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

H₃C \( \text{S-S} \) CH₃

‘DMDS’
Time-Resolved Sulfur-1s Spectroscopy in Solution

L-Cystine
the L-cysteine dimer
From DMDS to L-Cystine

Absorption Change / arb. u.

Energy eV

2468 2470 2472 2474 2476 2478 2480 2482

Absorption Change / arb. u.

Time Delay / ps

-1 0 1 2 3 4 5

2469.3 eV

Low power

300 fs
From DMDS to L-Cystine

- Ultrafast geminate recombination (little electronic relaxation)
- 2-photon excitation leads to new sulfur species
From DMDS to L-Cystine

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

Absorption Change / arb. u.

Energy eV

2468 2470 2472 2474 2476 2478 2480 2482

Absorption Change / arb. u.

Time Delay / ps

0 10 20 30 40 50 60 70 80 90

2469.3

2474.1

300 fs
Sulfur-Containing Aromatic Systems:

*how do sulfur atoms coupled to aromatic electron systems behave?*
Time-Resolved Sulfur-1s Spectroscopy in Solution
4-Methylthiophenol

SH

\[ \text{hv}_{267 \text{ nm}} \]

\[ \begin{array}{c}
\text{S}^- \\
\text{CH}_3
\end{array} \] + \[ \text{H}^+ \]

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

M. Ochmann et al., J. Am. Chem. Soc. 2017, 139 (13), 4797
Time-Resolved Sulfur-1s Spectroscopy in Solution
Time-Resolved Sulfur-1s Spectroscopy in Solution

Phoenix@SLS: with Chris Milne, Thomas Huthwelker & Majed Chergui
Synthesis and Photochemistry of a New Class of Photocleavable Protein Cross-linking Reagents


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

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