Tracing the active atomic sites in photochemistry with soft X-ray resonant inelastic X-ray scattering

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Session: "Time-Domain Spectroscopy"

IXS2019
Stony Brook University, New York, USA, June 23 – 27, 2019

Why time resolved RIXS?

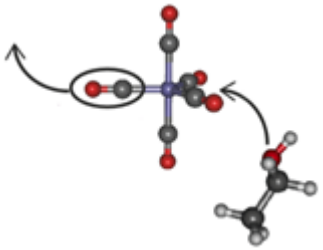
Governing Principles of Matter and Functionality:

- Driven states of matter, emergence, control, efficient switching
- Limiting steps that control rate and selectivity in chemistry
- Convert and store energy

Time scales in chemistry span from the ultrafast to every day life

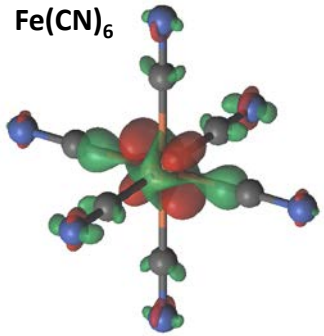
catalysis

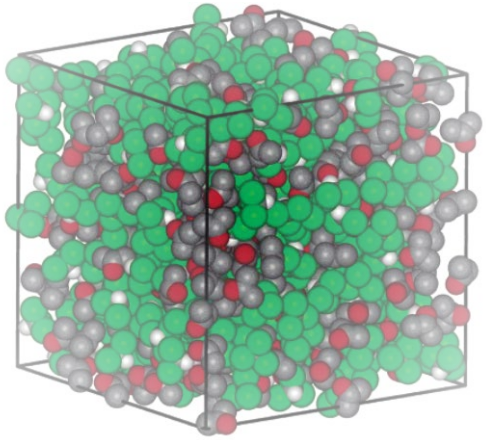
$Fe(CO)_5$



electro chemistry

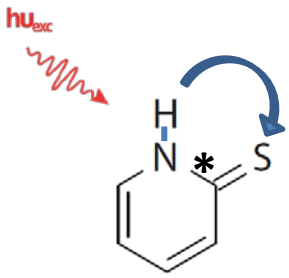
$Fe(CN)_6$





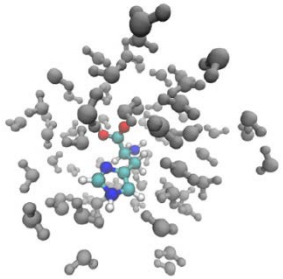
photoprotection

tautomerization 2MP



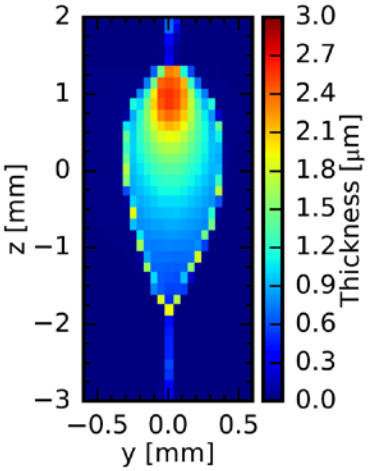
large amplitude

bio-relevant: Histidin

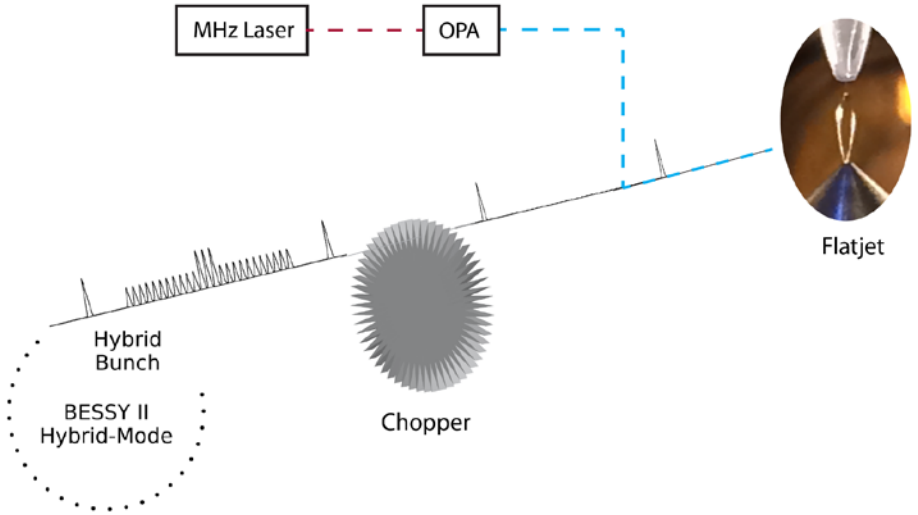


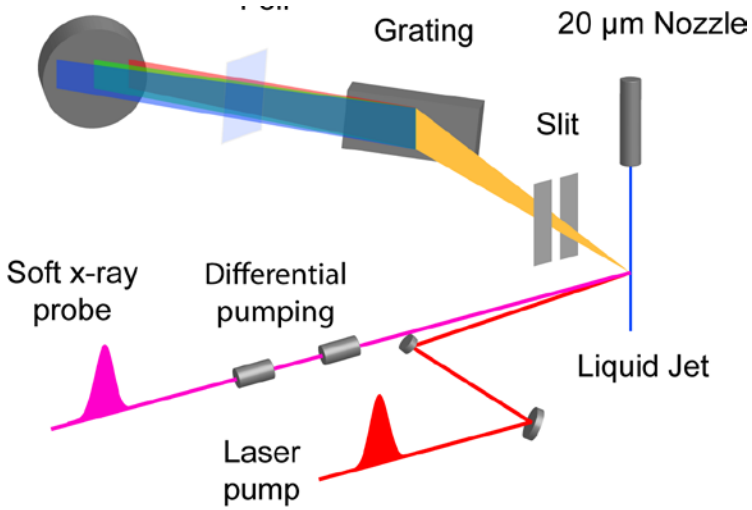
Time scales in chemistry span from the ultrafast to every day life

✓ In vacuum liquid jet technology



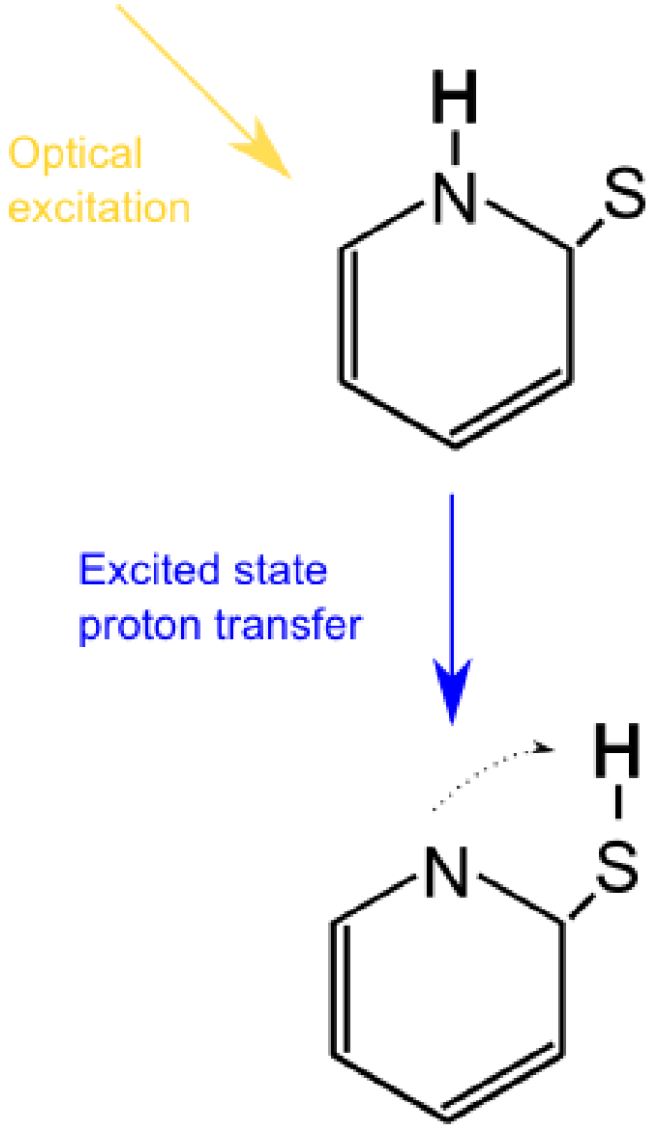
✓ ps at BESSY II and fs at FELs





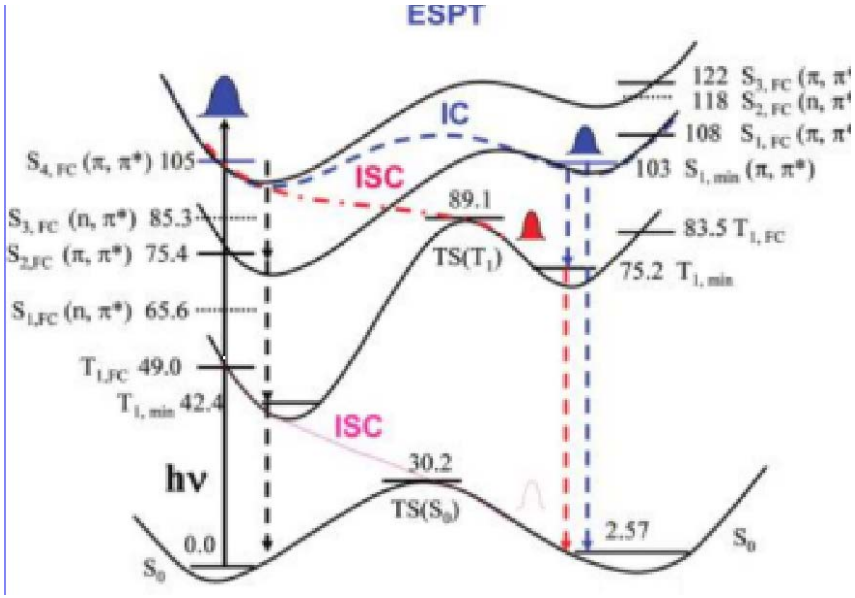
✓ RAS-SCF theory Odelius (Stockholm)

Excited State Proton Transfer (ESPT) is important process in Photoprotection



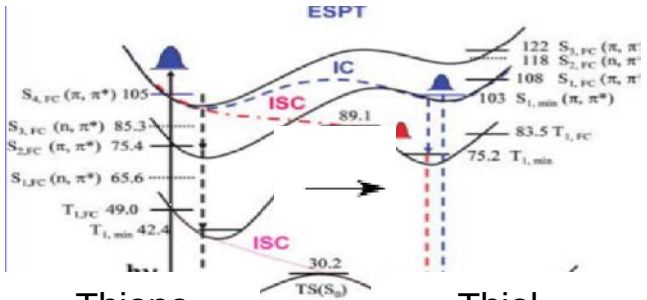
With soft X-ray spectroscopy adress involved atomic sites

ESPT in the thione – thiol system
2-Thiopyridone (2-TP)/2-Mercaptopyridine (2-MP)



- Proposed pathway

  Du et al., J. Phys. Chem. B, 2011 115 (25), 8266-8277
  M. Ross, et al. Ultrafast Phenomena XIX. Springer International Publishing, 2015. 403-406.
- Start with N-site deprotonation



Thione
2-TP

Thiol
2-MP

OR ?

2-TP
(protonated)

2-TP⁻
(anion, deprotonated)

Acknowledgments

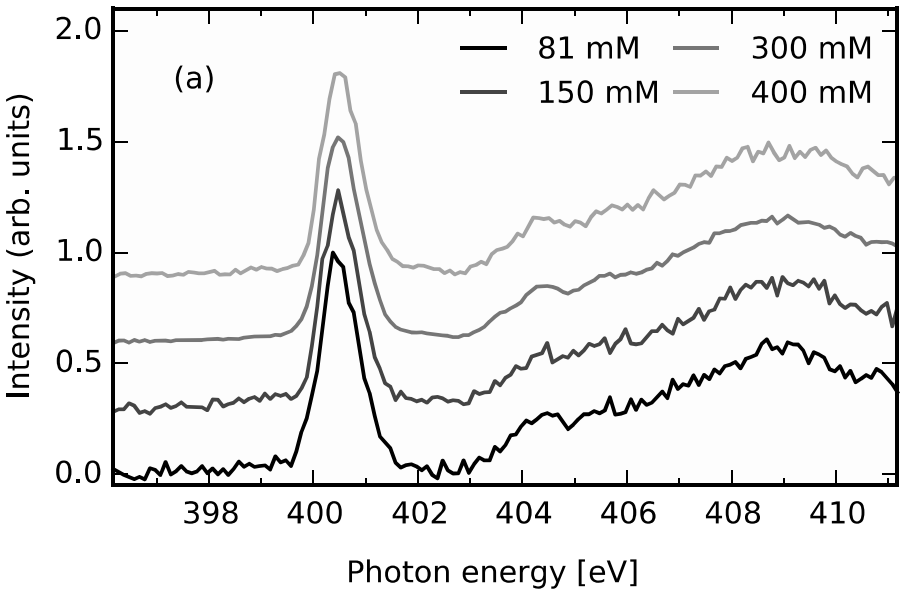
Ultrafast Independent N− H and N− C Bond Deformation Investigated with Resonant Inelastic X-Ray Scattering,
S. Eckert, J. Norell, P. S. Miedema, M. Beye, M. Fondell, W. Quevedo, B. Kennedy, M. Hantschmann, A. Pietzsch, B. E. Van Kuiken, Matthew Ross, M.P. Minitti, S. P. Moeller, W. F. Schlotter, M. Khalil, M. Odelius, and A. Föhlisch
Angewandte Chemie International Edition 56 (22), 6088-6092 (2017)

Molecular structures and protonation state of 2-Mercaptopyridine in aqueous solution
S. Eckert, P. S. Miedema, W. Quevedo, B. O'Cinneide, M. Fondell, M. Beye, A. Pietzsch, M. Ross, M. Khalil, and A. Föhlisch
Chemical Physics Letters 647, 103–106 (2016)

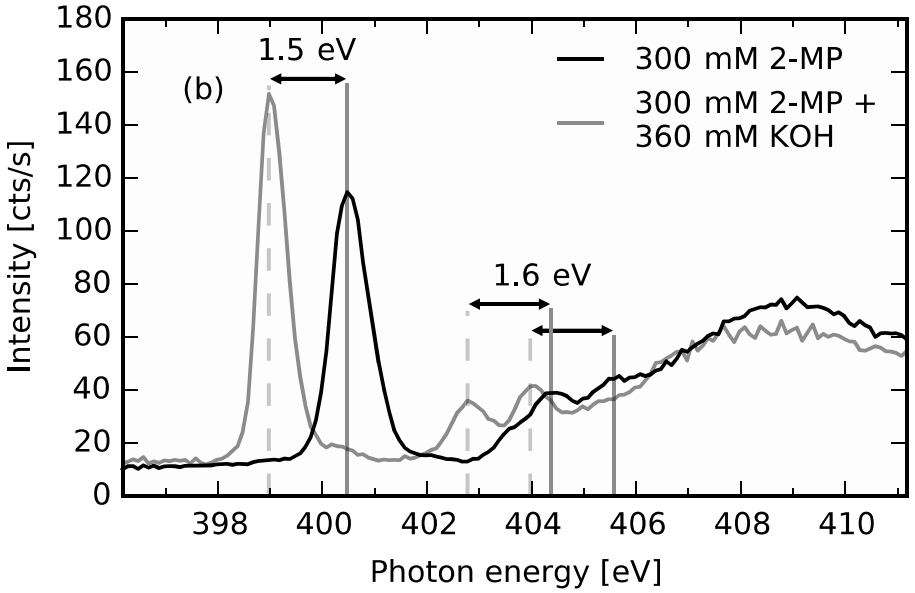
T1 Population as the Driver of Excited-State Proton-Transfer in 2-Thiopyridone,
S. Eckert, J. Norell, R. M. Jay, M. Fondell, R. Mitzner, M. Odelius, A. Föhlisch.
Chemistry – A European Journal
https://doi.org/10.1002/chem.201804166 (2018)

Protonation and Deprotonation as a function of k = [2-TP]/[KOH]

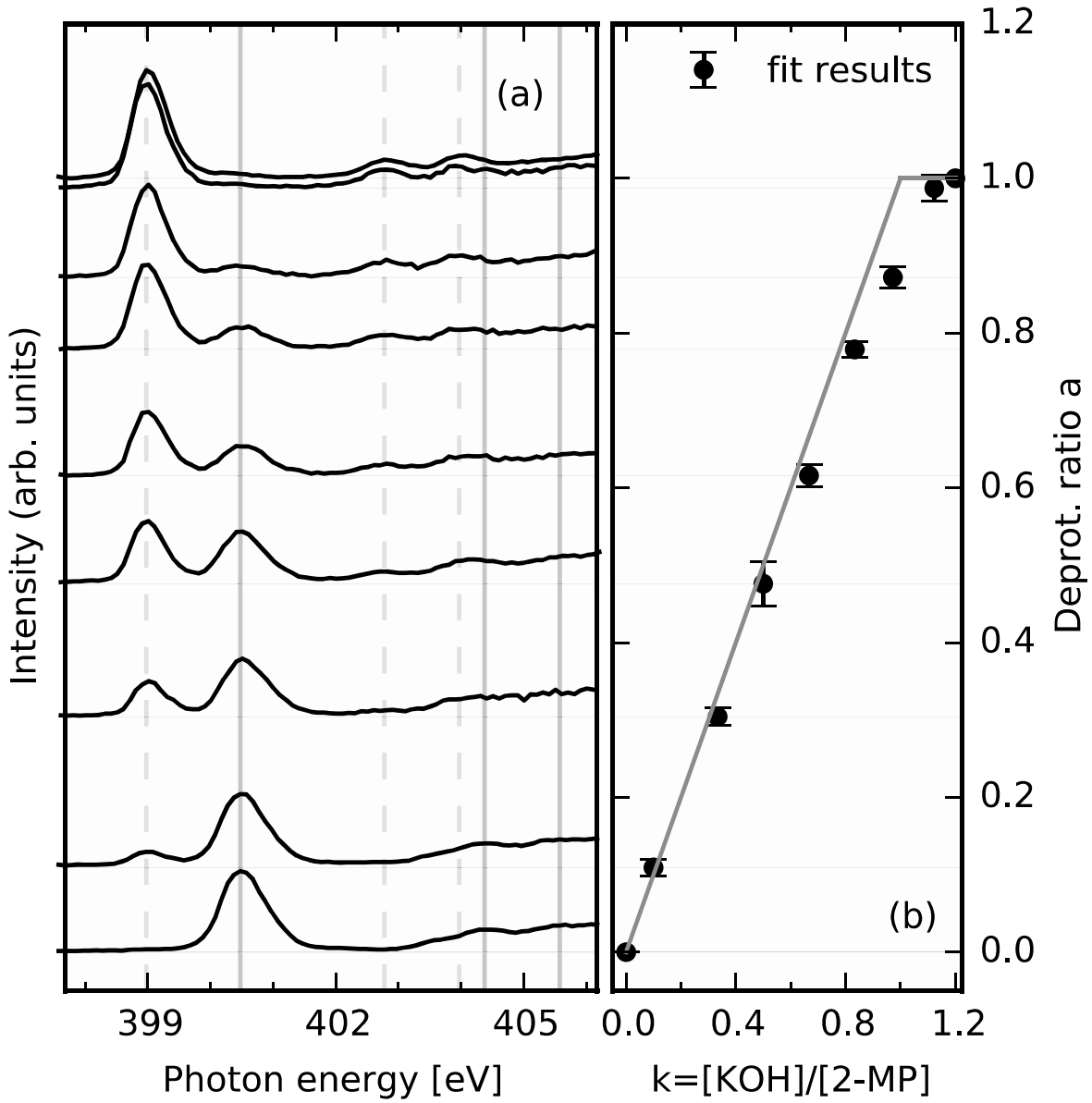
2-TP in pure water as a function of concentration



2-TP in pure water [2-TP] = 300 mM
vs.
alkaline aqueous solution
[2-TP] = 300 mM, [KOH] = 360 mM.

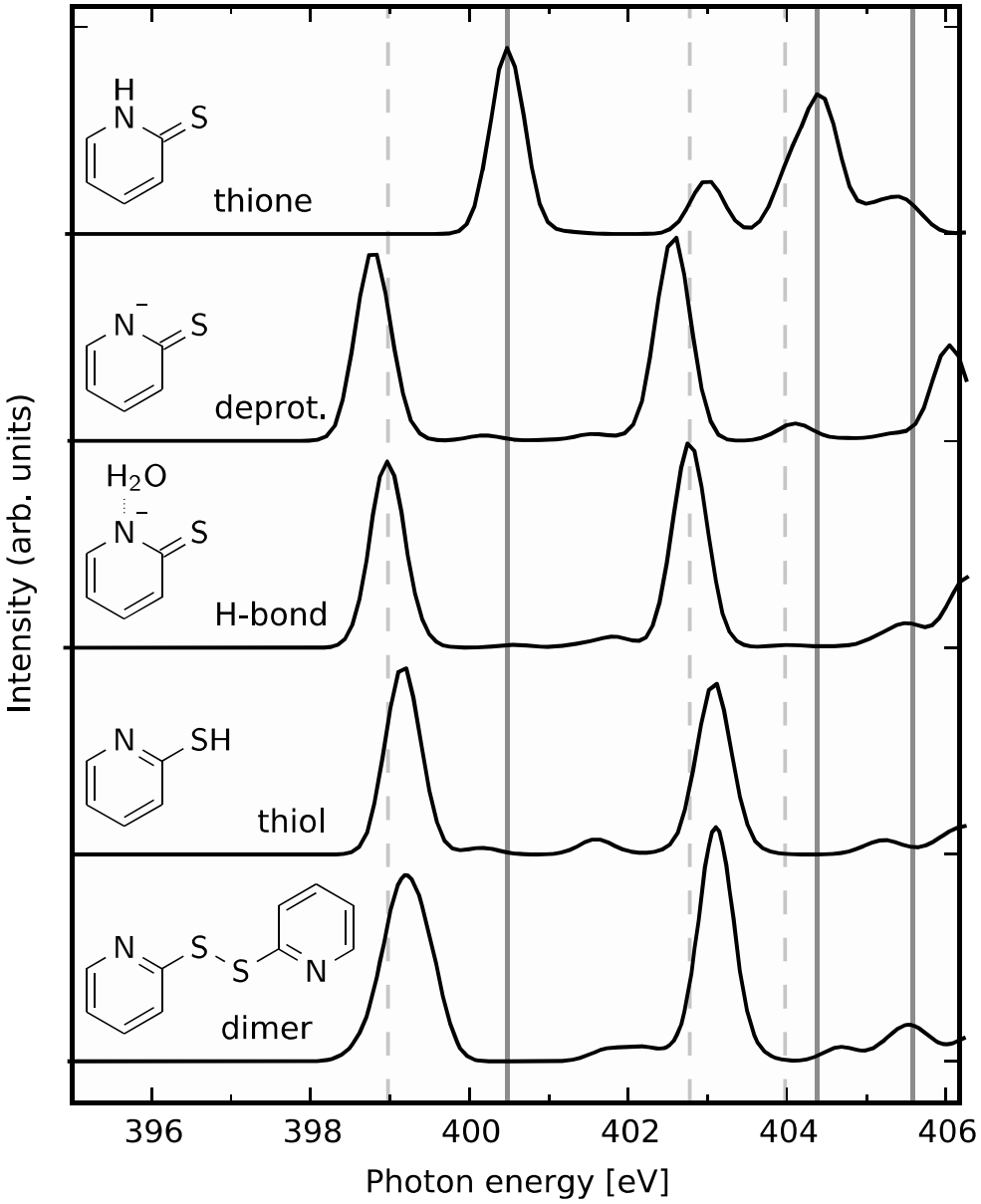


Protonation and Deprotonation as a function of k = [2-TP]/[KOH]

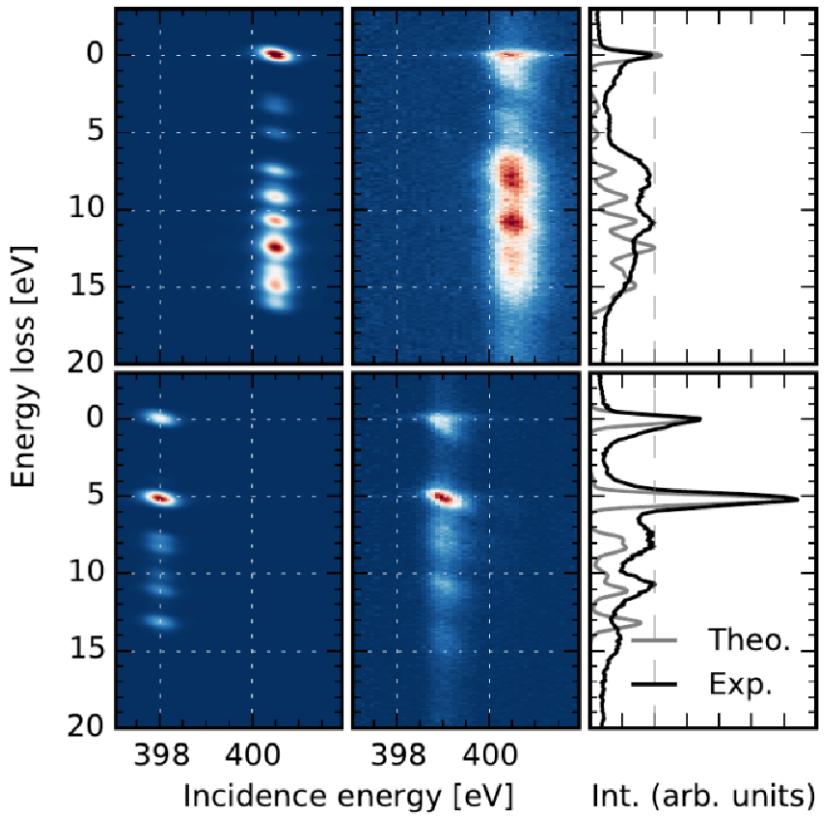


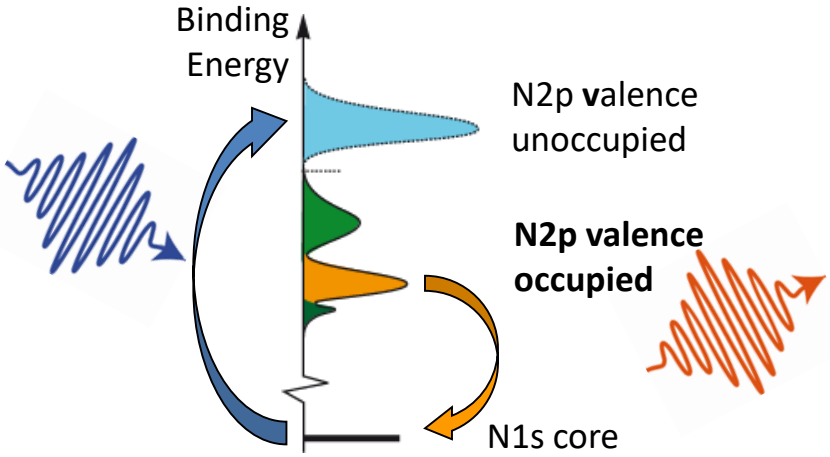
linear dependence: kinetic model of direct coordination 2-TP to OH^-

TD-DFT computation of Near Edge X-ray Absorption Fine Structure of the N K-edge of 2-TP/2-MP in different (de)-protonation states

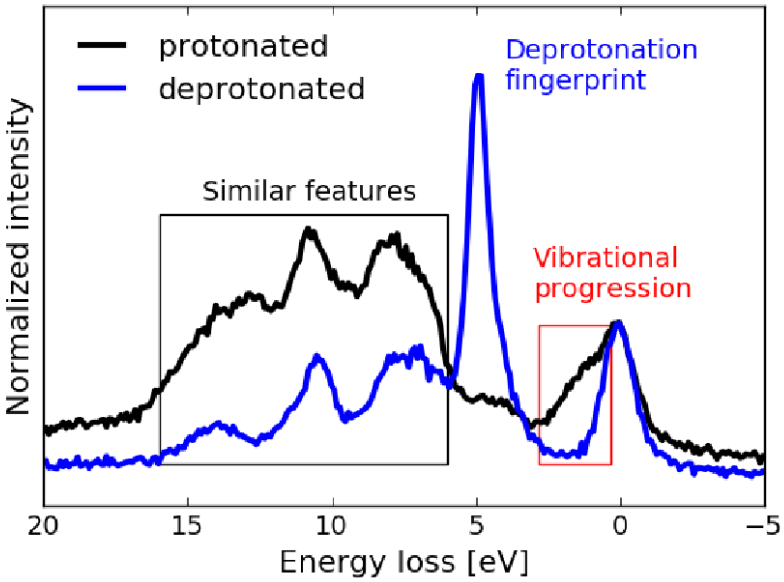


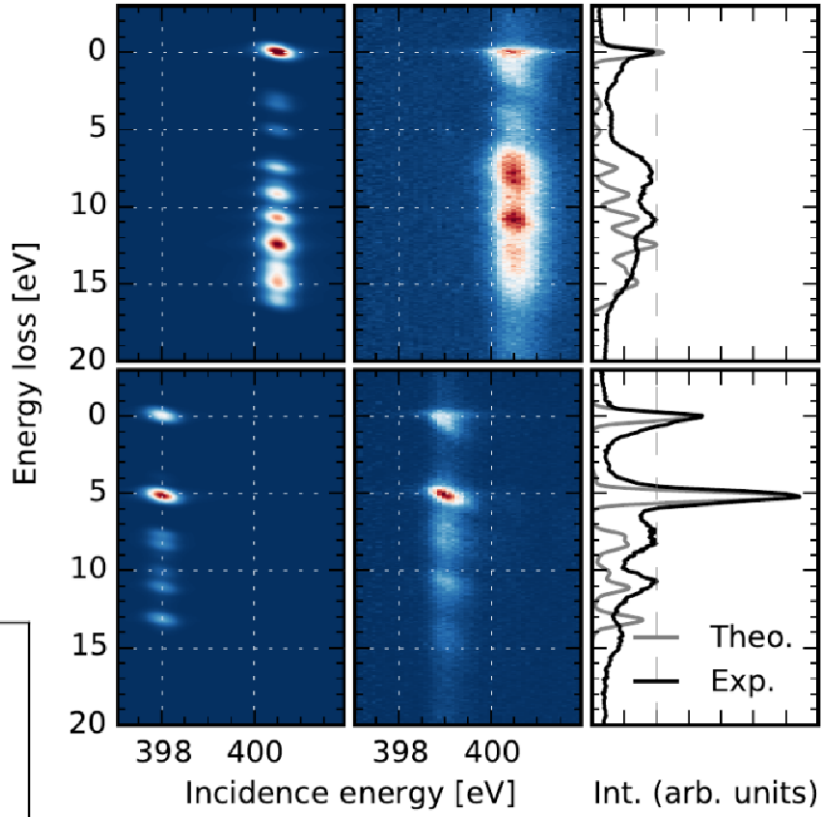
N 1s Resonant Inelastic X-ray Scattering Signatures of Protonated and Deprotonation States

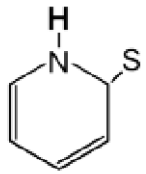




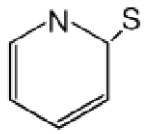
What do we see?







2-TP
(protonated)



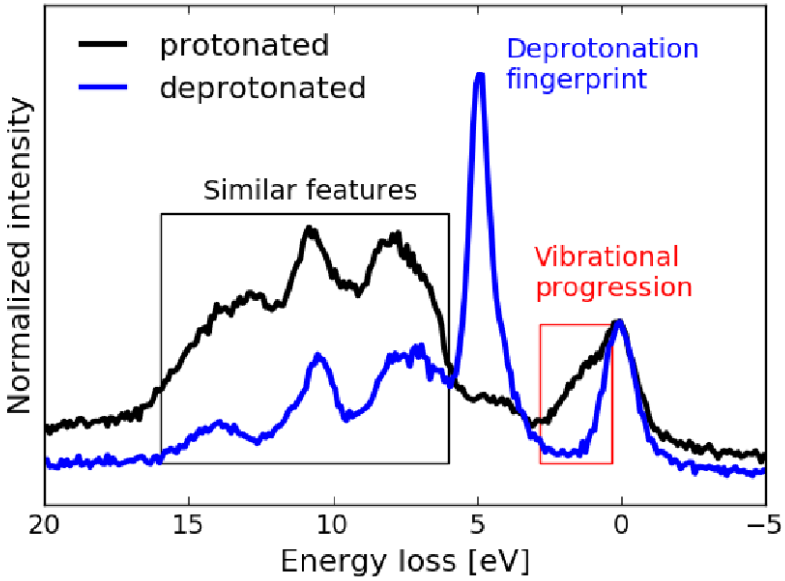
2-TP $^{-}$
(deprotonated)

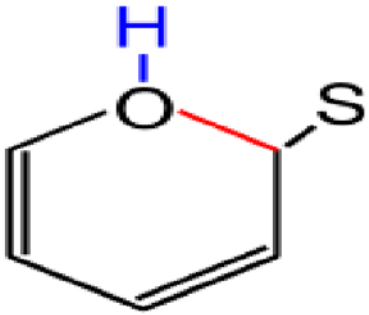
What do we see?

Equivalent core approximation of X-ray spectroscopy:

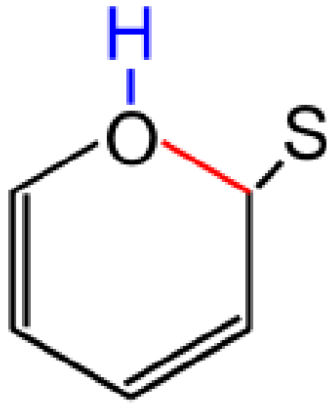
Core excited N is chemically equivalent to Oxygen

BUT: Which Bond is excited? N-H or N-C ?



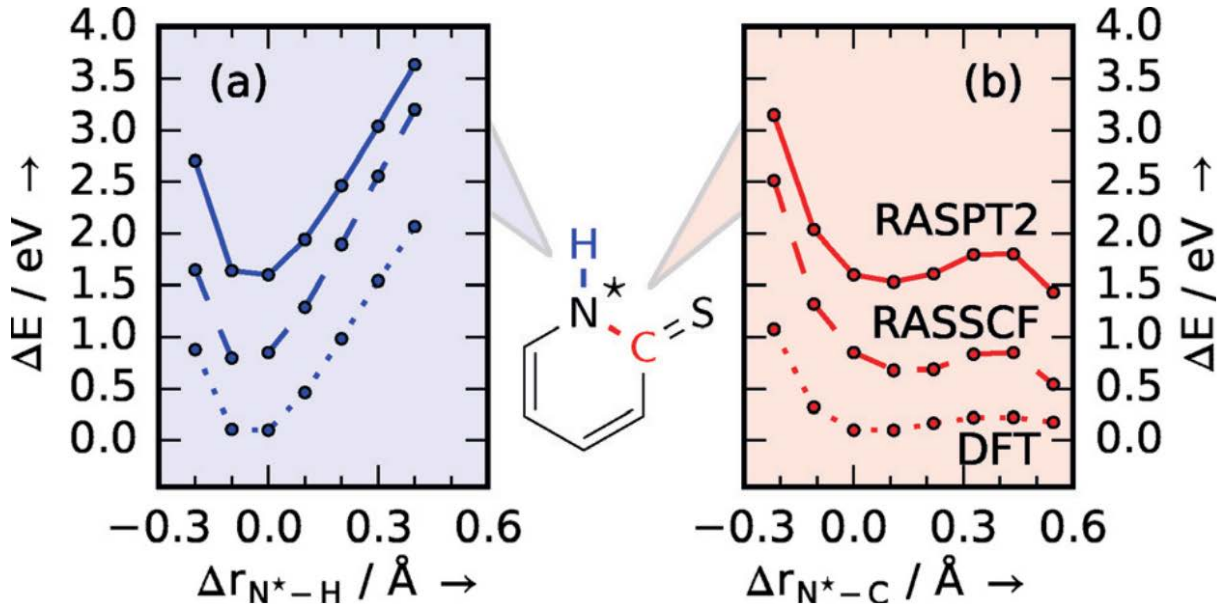


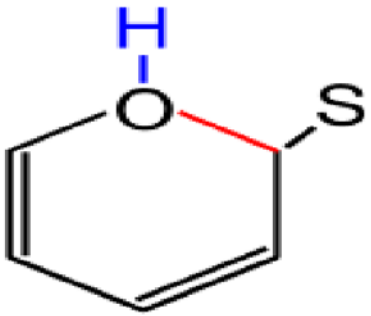
2-TP (deprotonated)



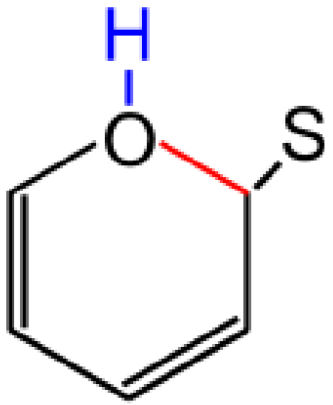
2-TP

N1s core excited state dynamics in different models



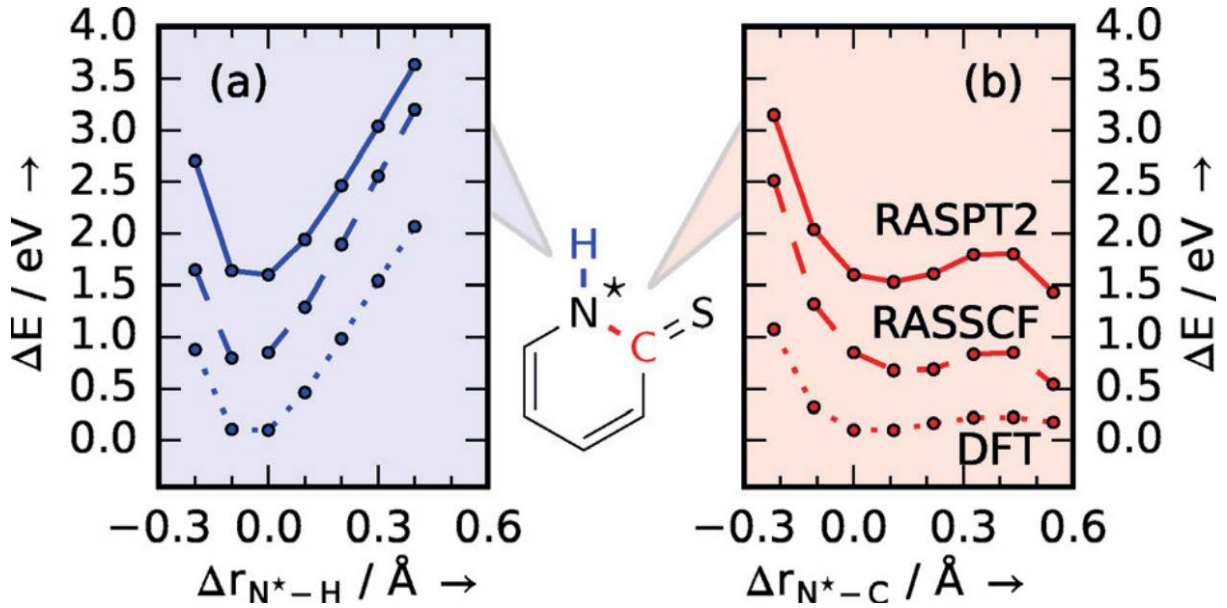


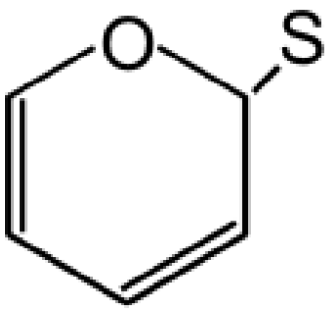
2-TP (deprotonated)



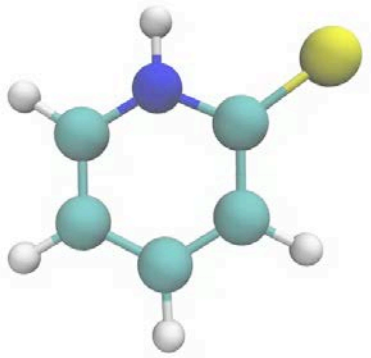
2-TP

Dynamics during 4 fs N1s core hole life (scattering duration) time!

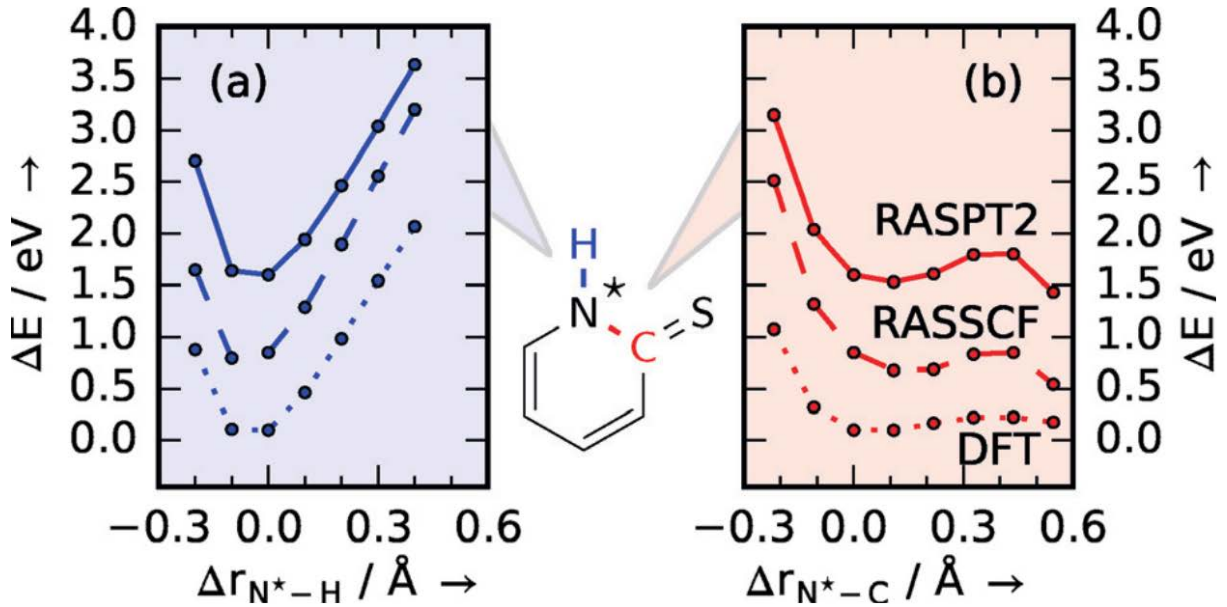


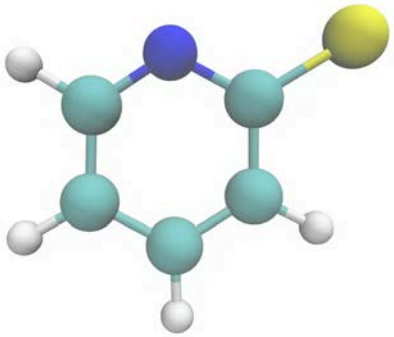


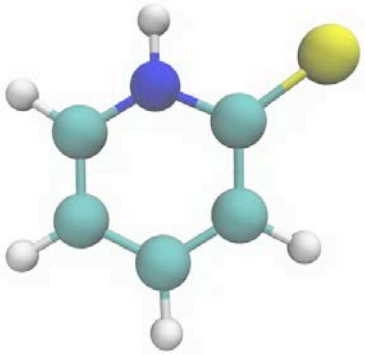
2-TP (deprotonated)



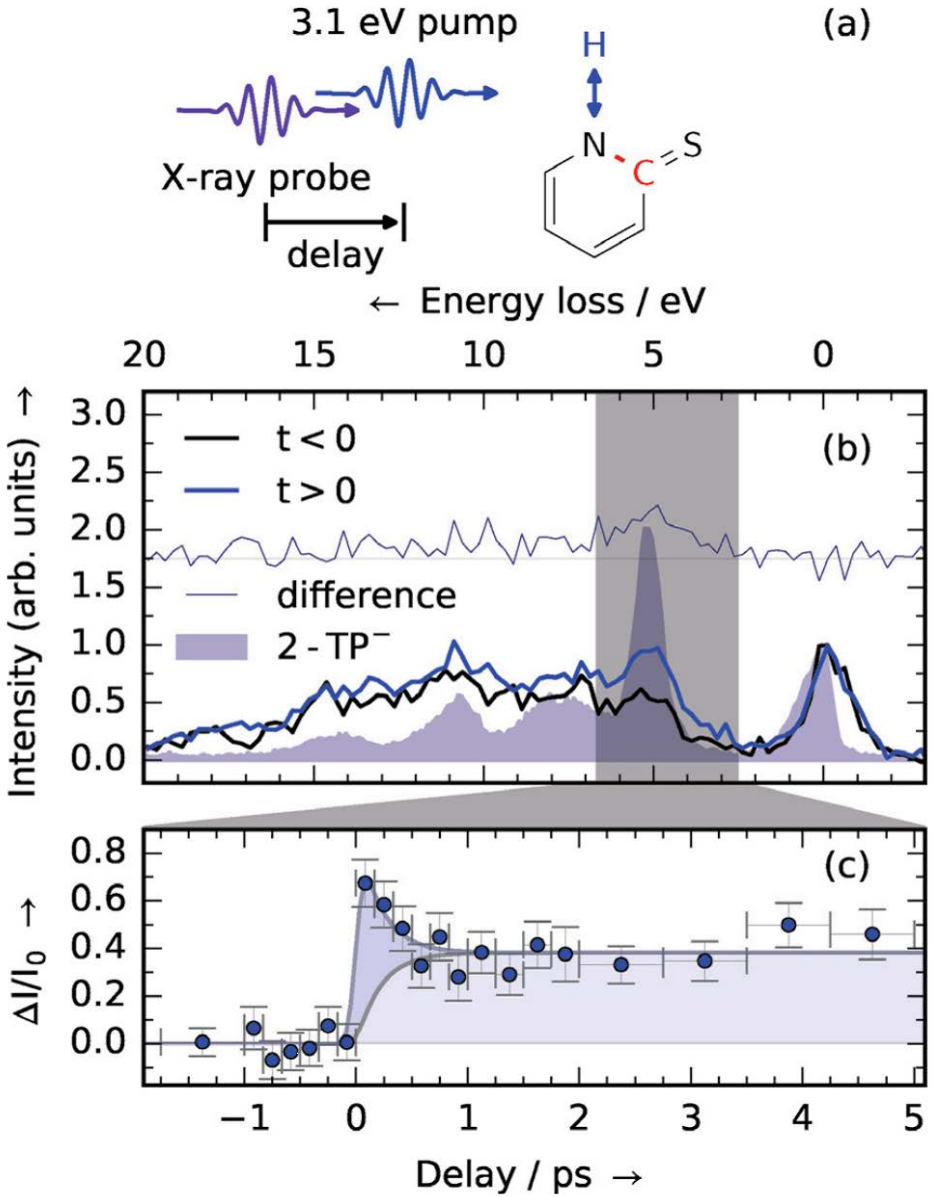
Dynamics during 4 fs N1s core hole life (scattering duration) time!



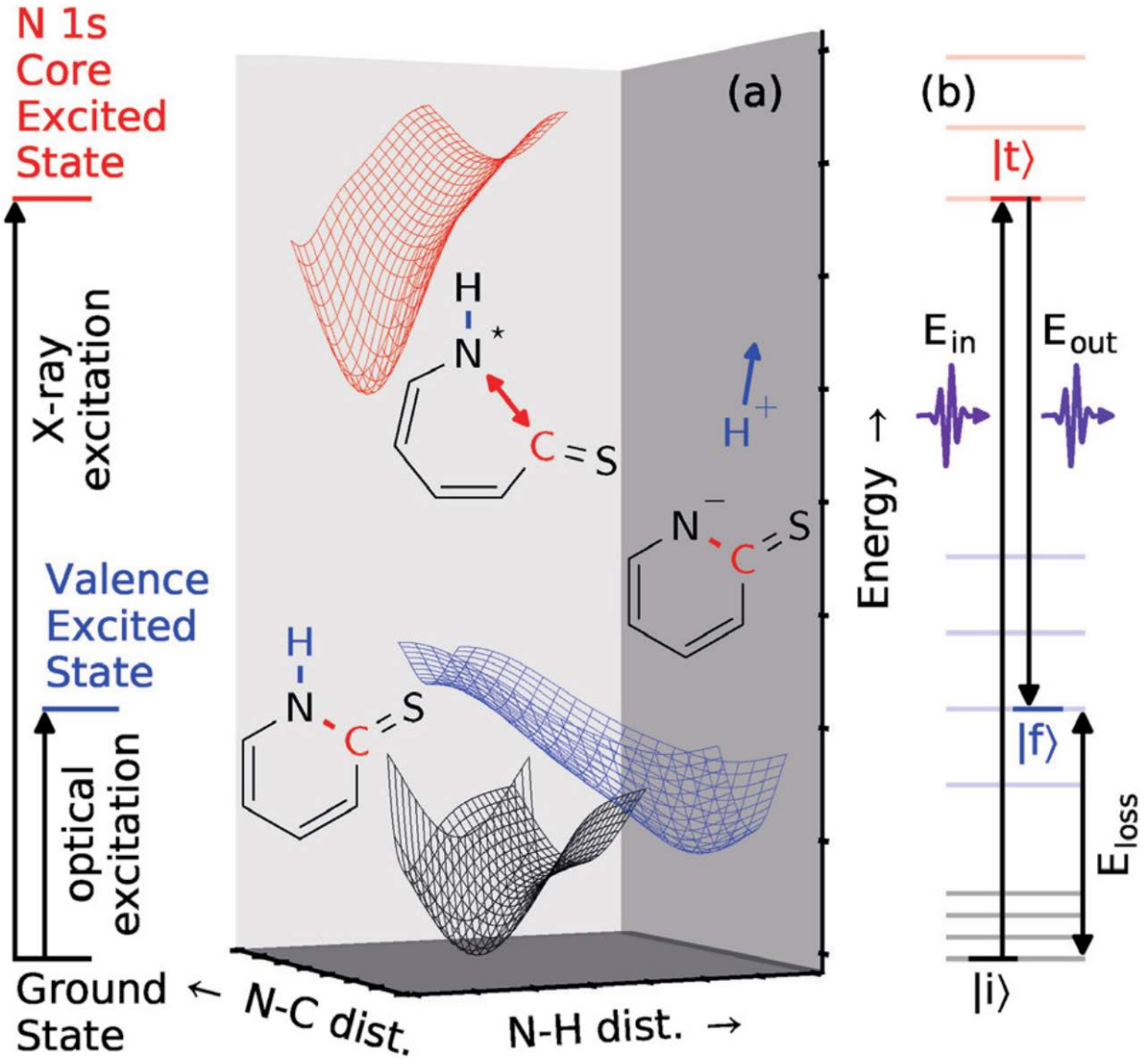




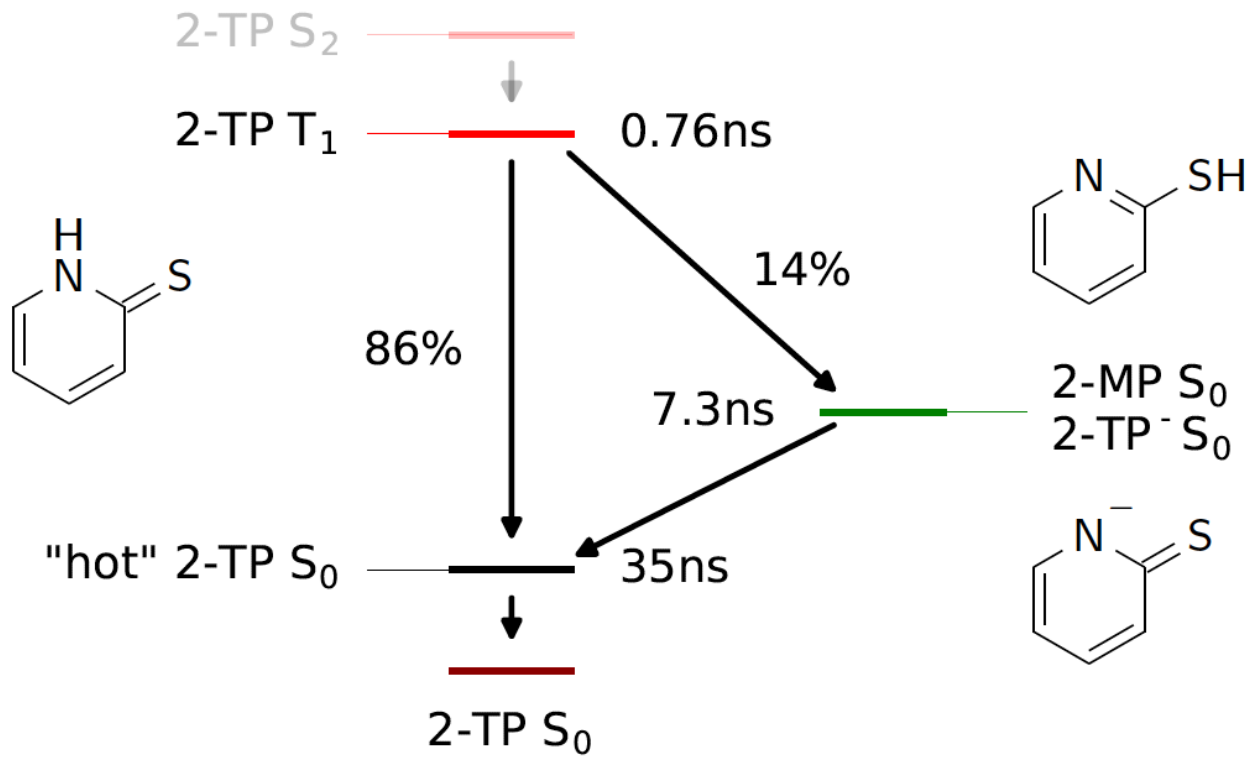
Now photoinduced deprotonation probed with femtosecond time resolved RIXS at the Nitrogen atoms of 2- MP (aq)



Optical excitation drives N-H coordinate, X-ray excitation the N-C coordinate



T1 Population as the Driver of Excited-State Proton-Transfer in 2-Thiopyridone



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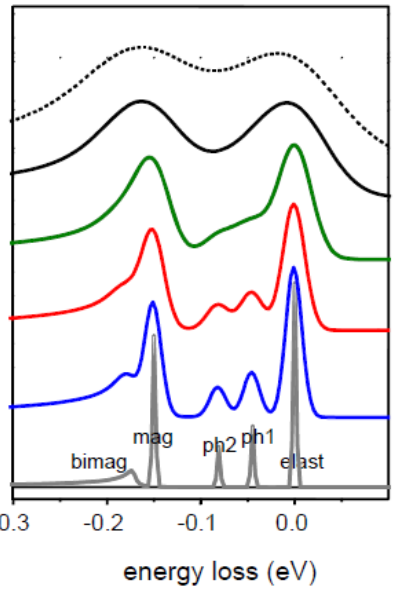
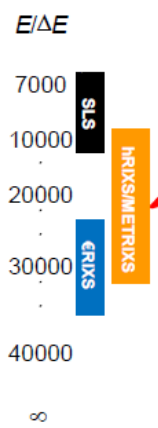
S. Eckert, et al *Angewandte Chemie International Edition* 56 (22), 6088-6092 (2017)

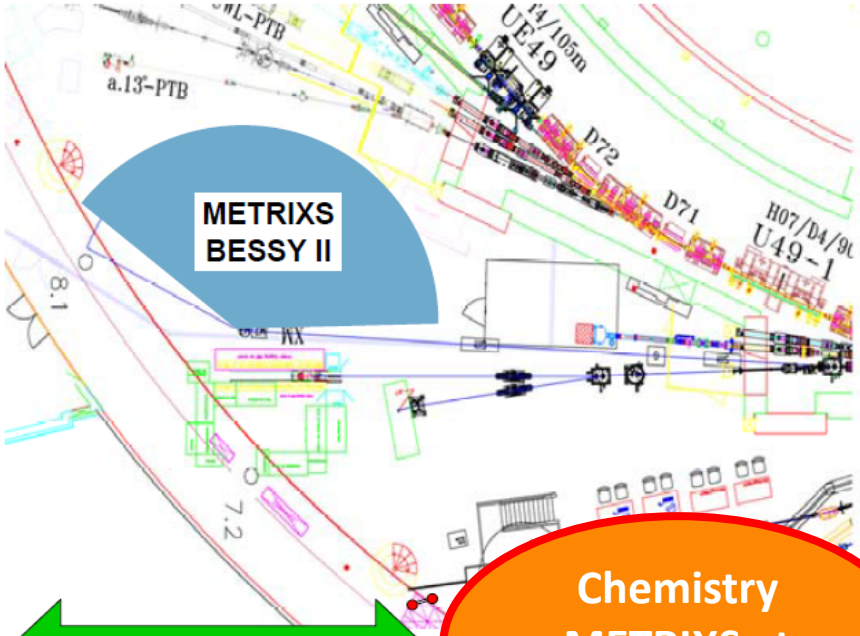
Molecular structures and protonation state of 2-Mercaptopyridine in aqueous solution
S. Eckert et al. *Chemical Physics Letters* 647, 103–106 (2016)

Static and Dynamics at the transform limit





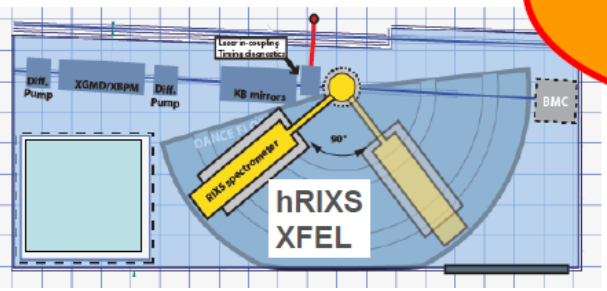
Δ t (fs) @ 1 keV	Δ t (fs) @ 300 eV
41	137
82	273
123	410



femtosecond timescale: hRIXS @ XFEL

Chemistry METRIXS at BESSY II

A. Pietzsch, F. Senf, K. Bauer, A.F.



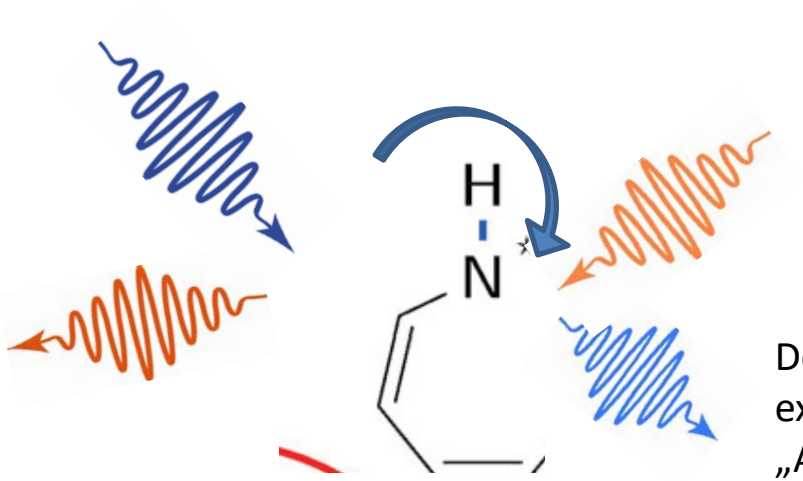
Helmholtz international users consortia at XFEL
S. Neppl, F. Senf, A. F. (Potsdam, ERC),
T. Laarmann, S. Techert (DESY), G. Ghiringhelli, Y. Peng (Milano),
A. Scherz, J. Schlappa, (B. van Kuiken), S. Molodtsov (XFEL)
S. Huotari, E.Kukk (FIRI Det II)

Solid State PEAXIS at BESSY II

K. Fritsch, K. Lieutenant, K. Habicht

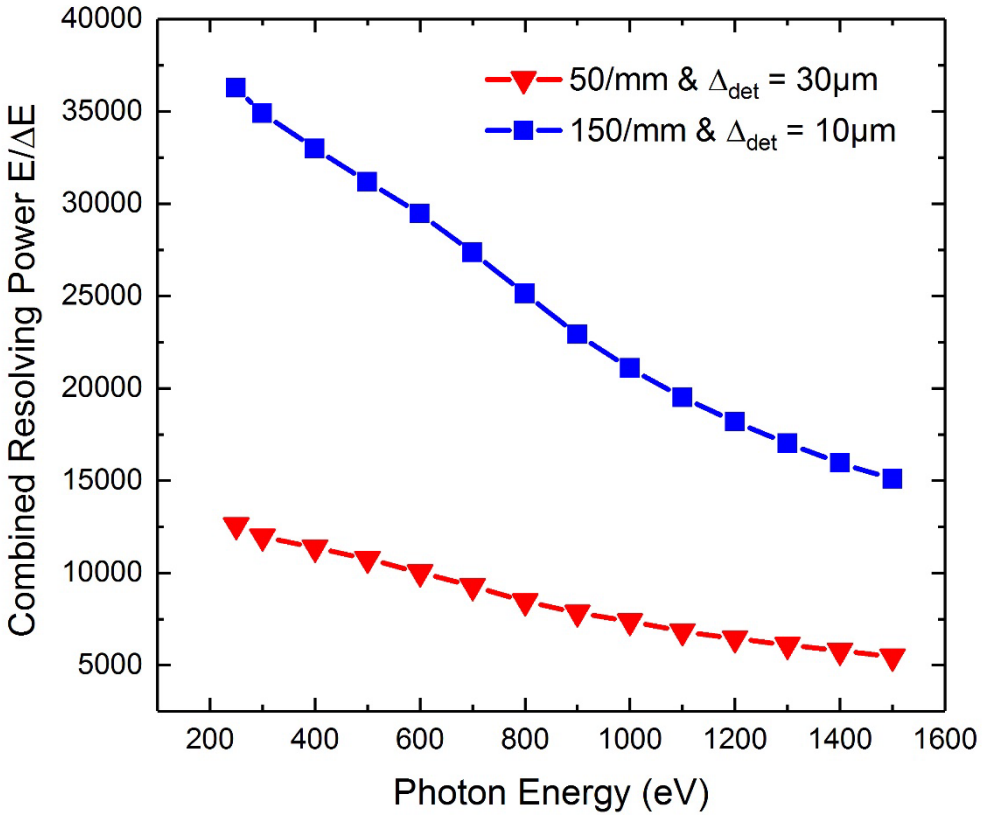
Multi centre dynamics between atomic moities
Non-linear soft X-ray spectroscopy: 4 wave mixing

Create at one site
excitation through a
„Stokes“ RIXS process



Detect at another site
excitation through a
„Anti-Stokes“ RIXS process

Projected Day-1 Operation



Δ_{source} = 5 μm
$\Delta_{slope\text{-}error}$ = 0.1 μrad

- **Baseline mono operation: 50 l/mm grating**
- **MCP/DLD spatial resolution: 30 μm**
- **Single pulse discrimination (MCP/DLD) for pump-probe experiments**

Conclusion

- Optical excitation drives N-H bond breaking in 2-Mercaptopyridine
- Nitrogen K-edge excitation streches N-C bond (which came to us as a surprise!)
- T1 Population as the Driver of Excited-State Proton-Transfer in 2-Thiopyridone (Rate Model derived)
- Upcoming ideal photochemistry and driven states of matter capabilities through hRIXS Infrastructure at European XFEL, matched by METRIXS and PEAXIS at BESSY II

Thank You