

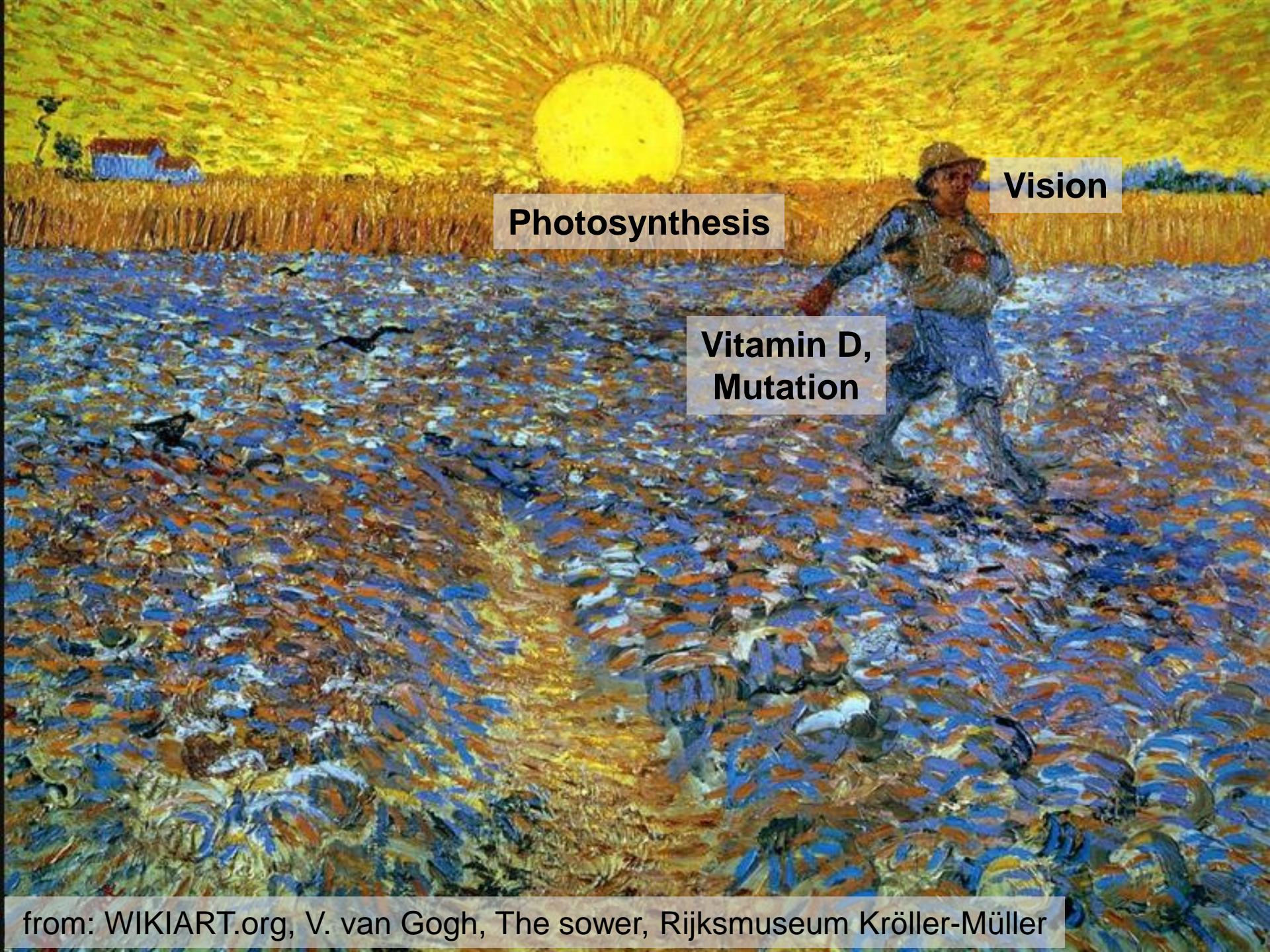


Investigations of molecular photoenergy conversion using ultrashort x-ray pulses

EuPRAXIA@SPARC_LAB user workshop 2021

Markus Gühr, Universität Potsdam, Physik und Astronomie



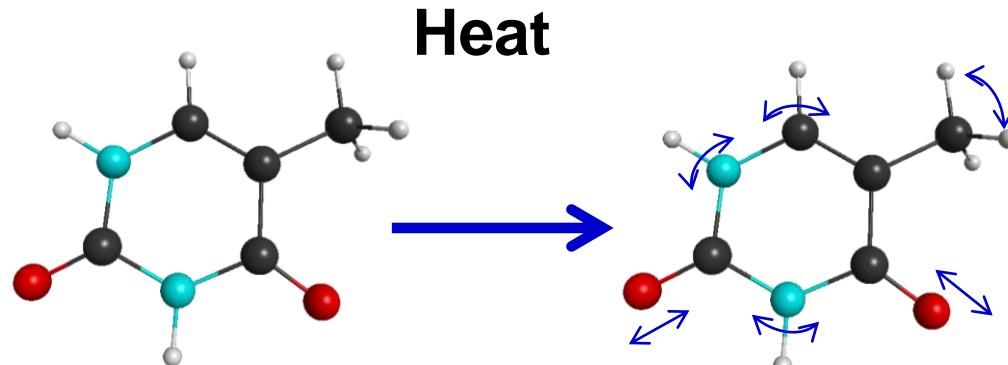


Photosynthesis

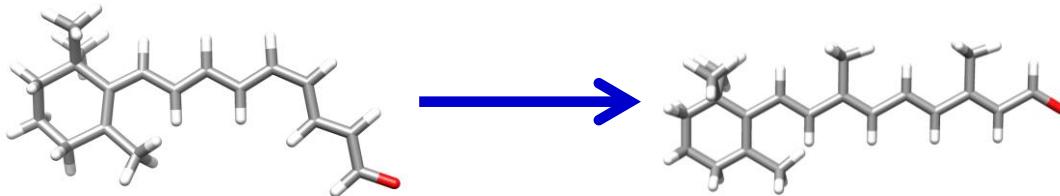
Vision

**Vitamin D,
Mutation**

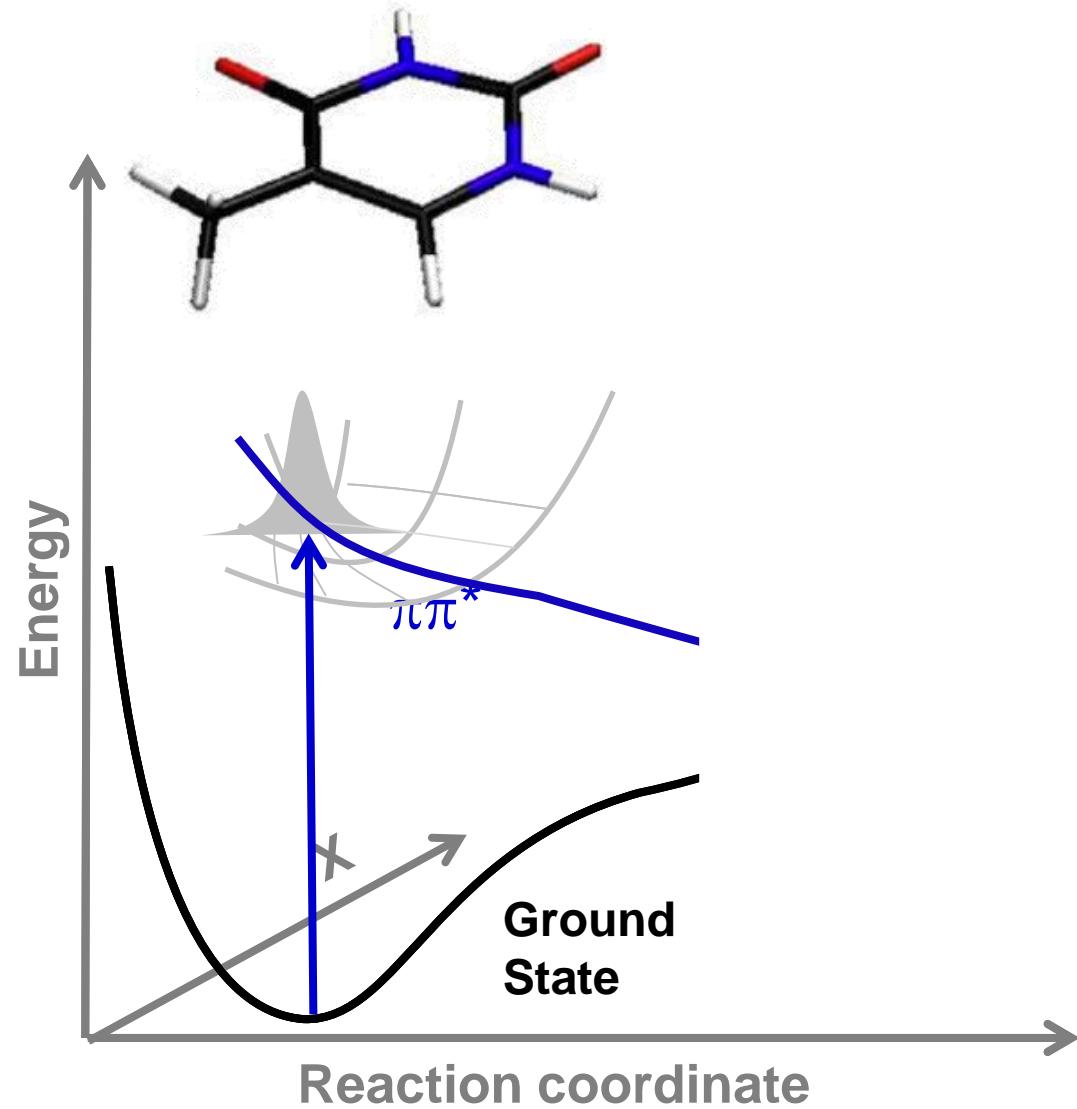
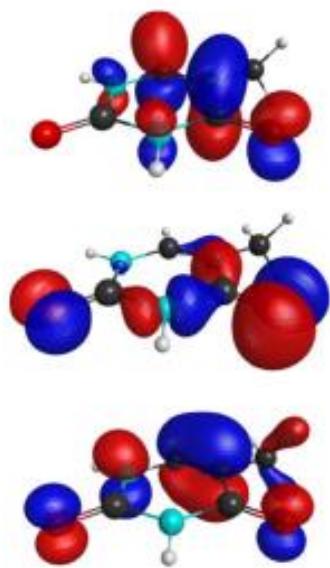
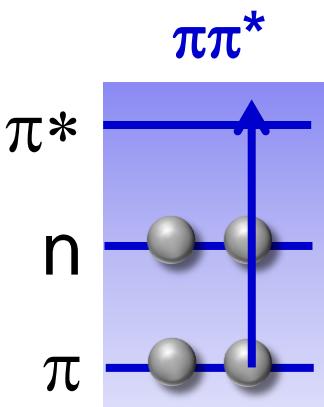
Transformation of light energy to other energies occur (ultra)fast.



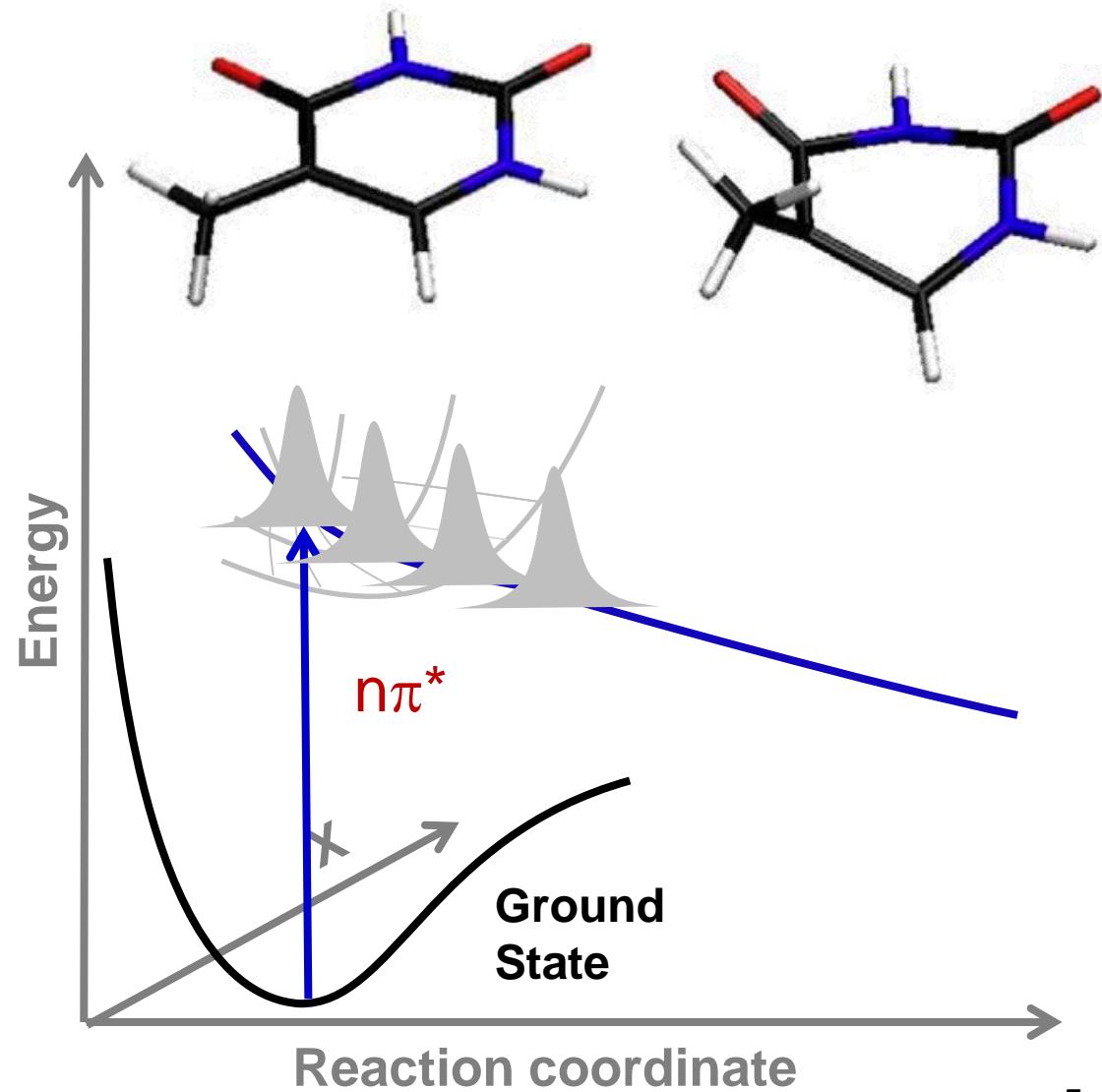
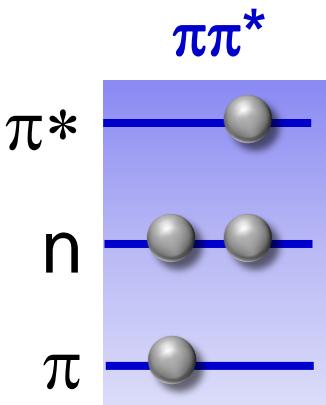
Chemical bond change



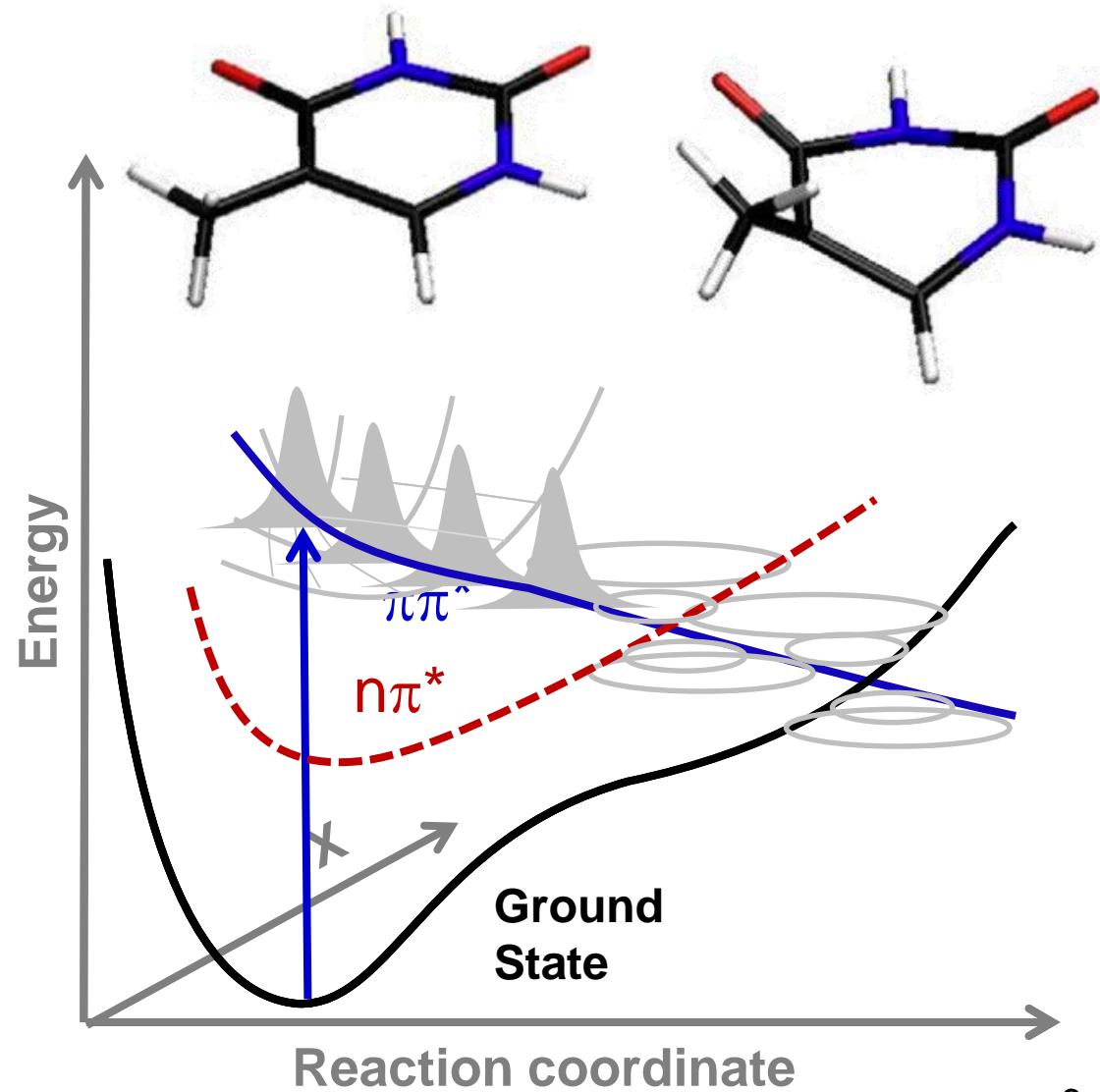
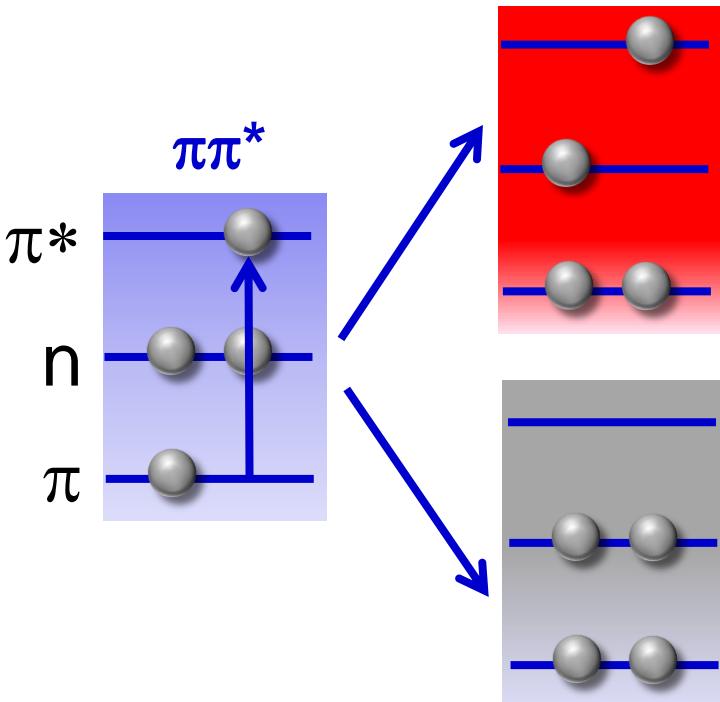
Light excitation couples to electrons.



Electrons couple to nuclei.

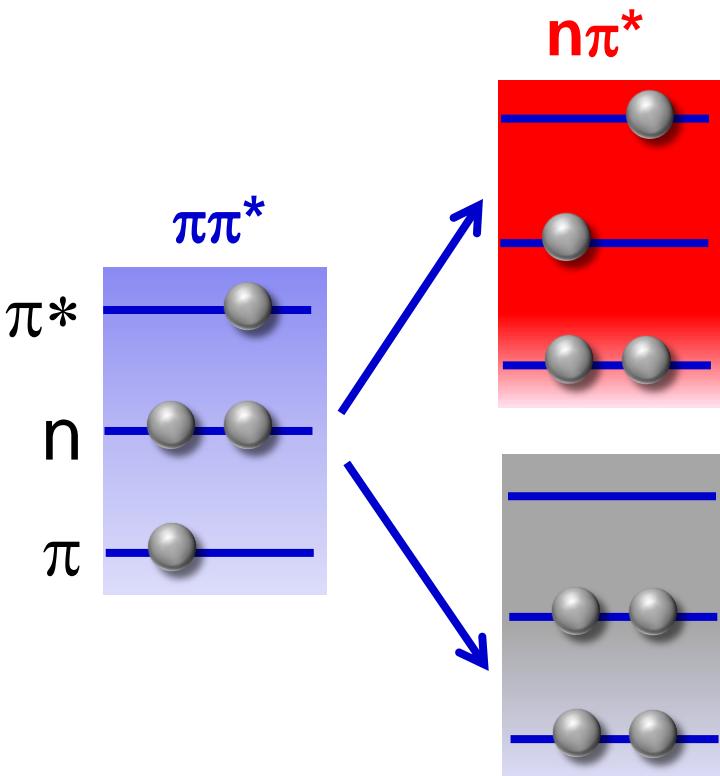


Nuclei couple to electrons.

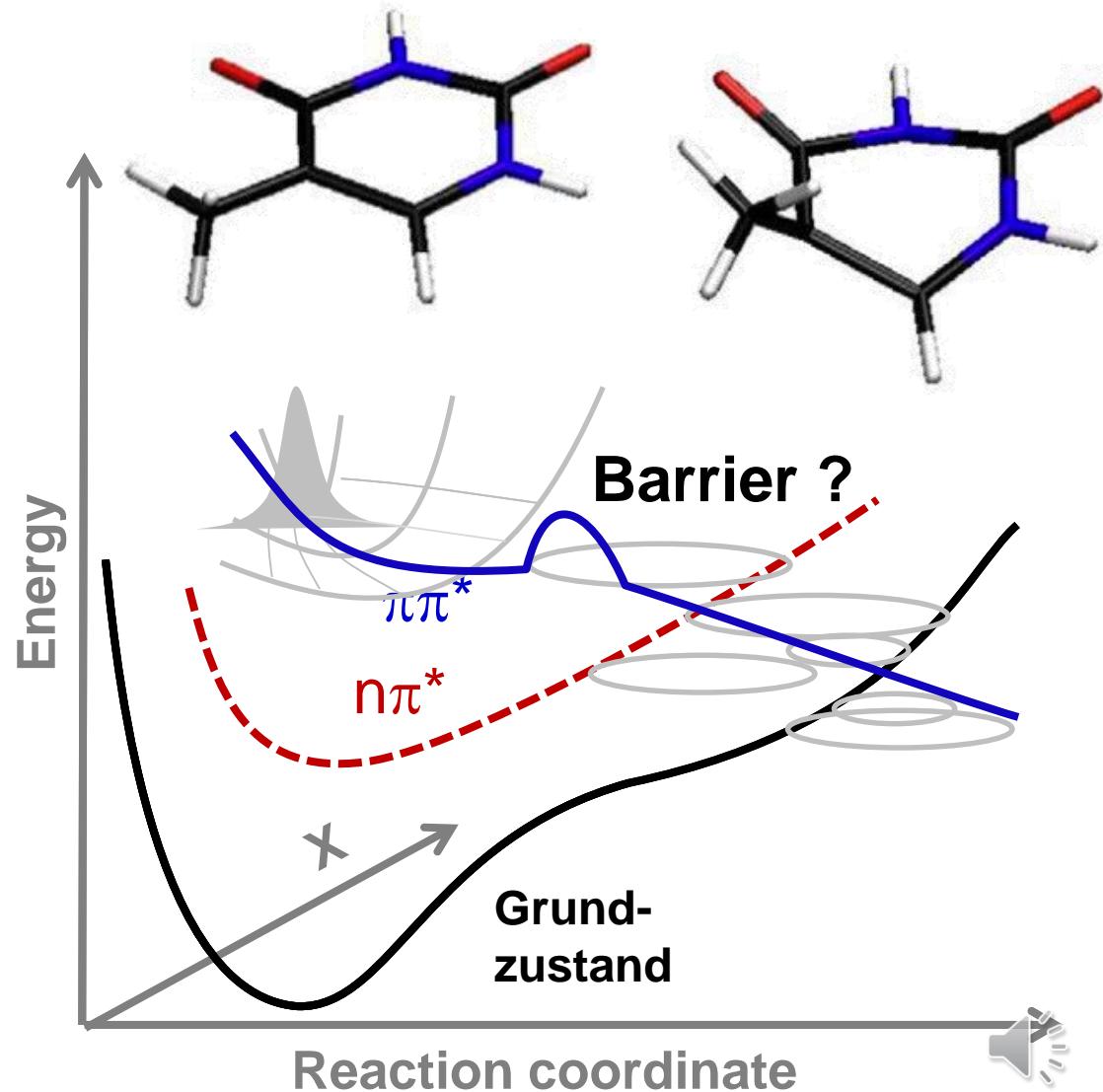


Two sides of the problem:

Electronic structure

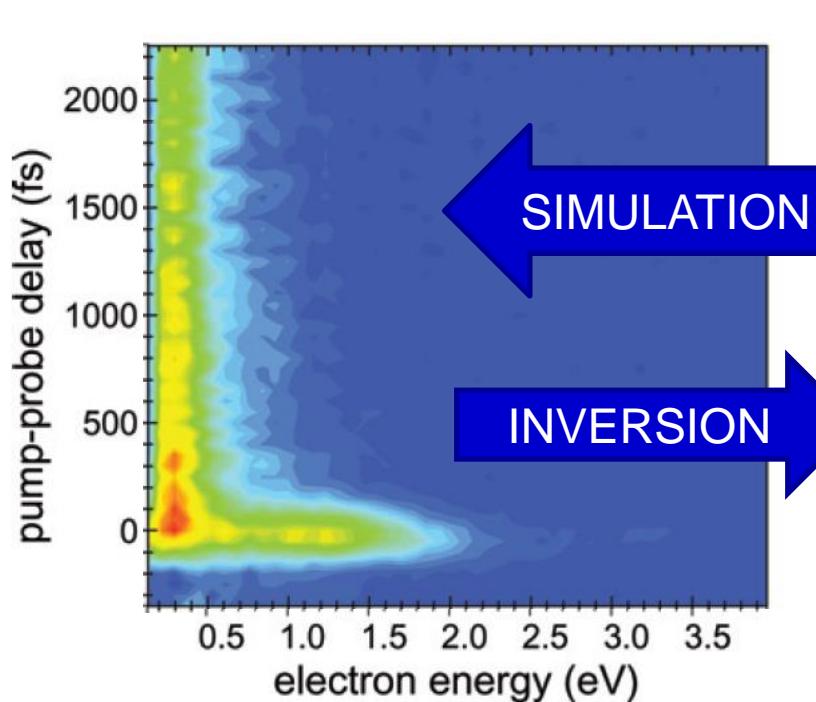


Nuclear geometry



Asturiol et al.,
J. Phys. Chem. A, 113, 10211 (2009)
Hudock et al.,
J. Phys. Chem. A, 111, 85 (2007)

Many observables depend on both.



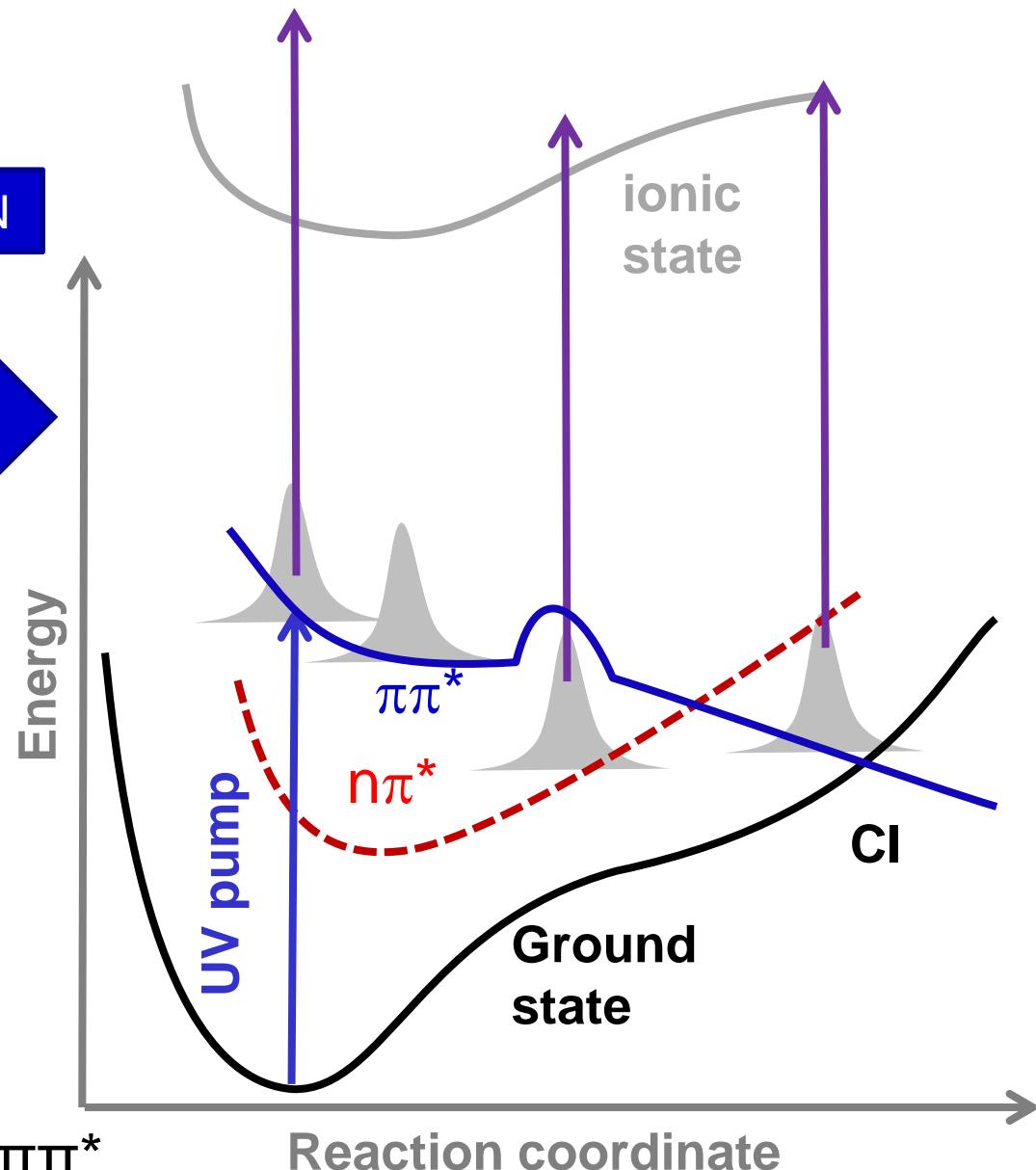
Ullrich et al. PCCP **6**, 2796 (2004)

Asturiol et al.,

J. Phys. Chem. A, **113**, 10211 (2009)

Hudock et al.,

J. Phys. Chem. A, **111**, 85 (2007)



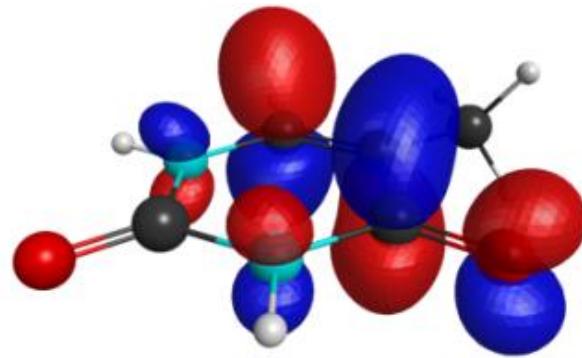
Few picosecond lifetime of $\pi\pi^*$

The more *different* observables, the easier it is to find something out about a molecule.

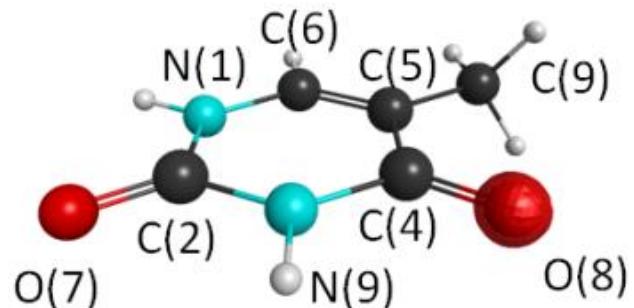


From the book cover of:
'Gödel, Escher, Bach' by R. Hofstadter
20th anniversary edition, Perseus Books 1999

Valence electrons

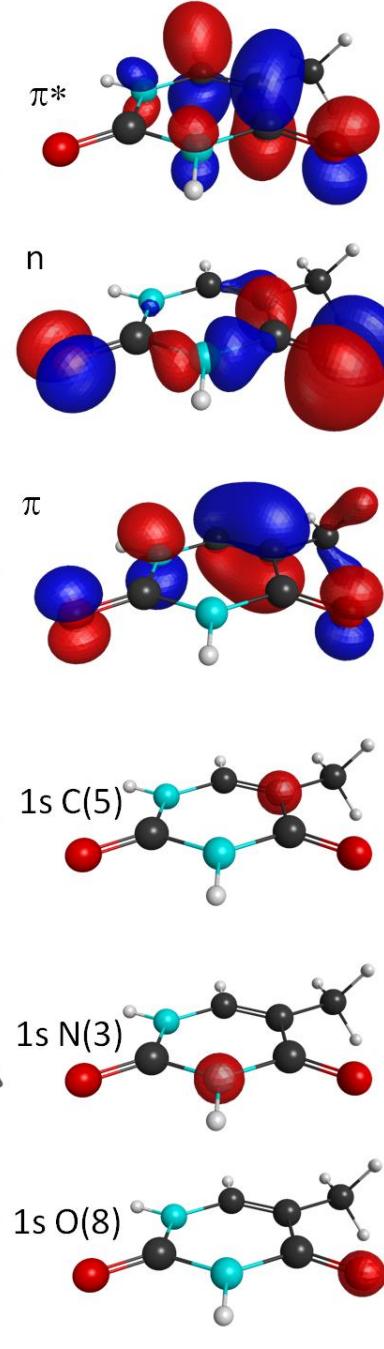
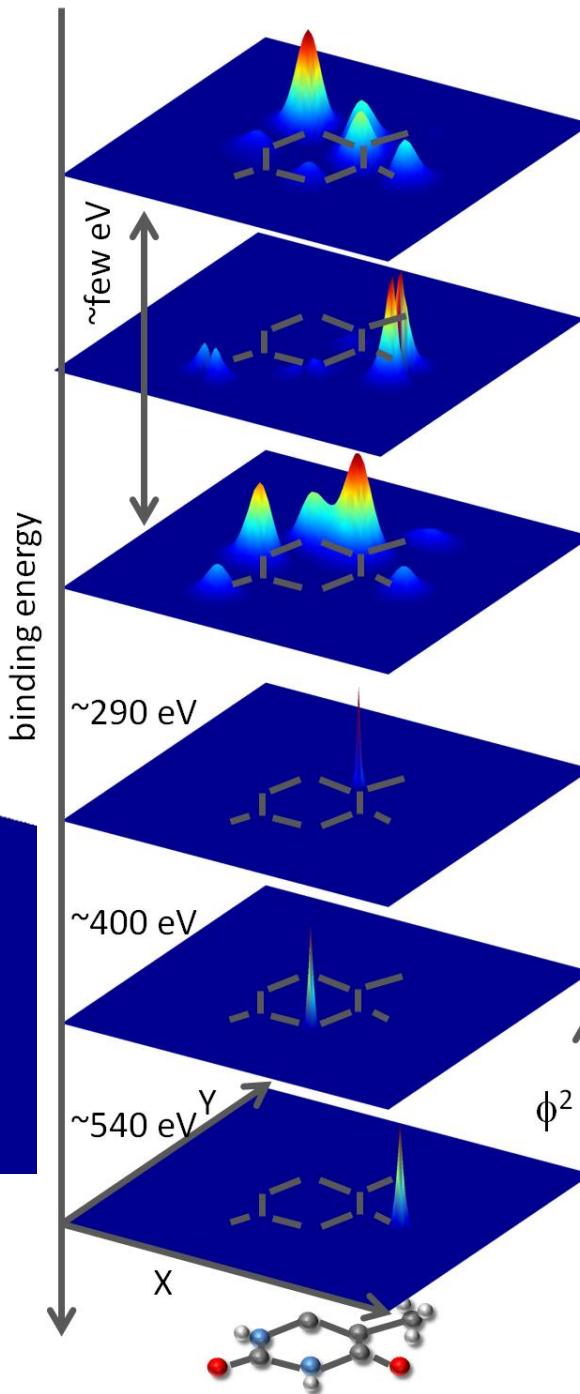
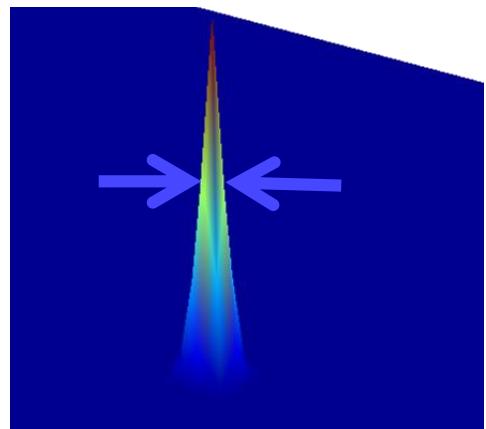


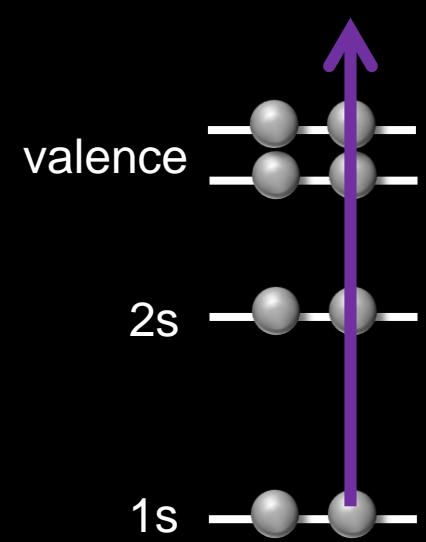
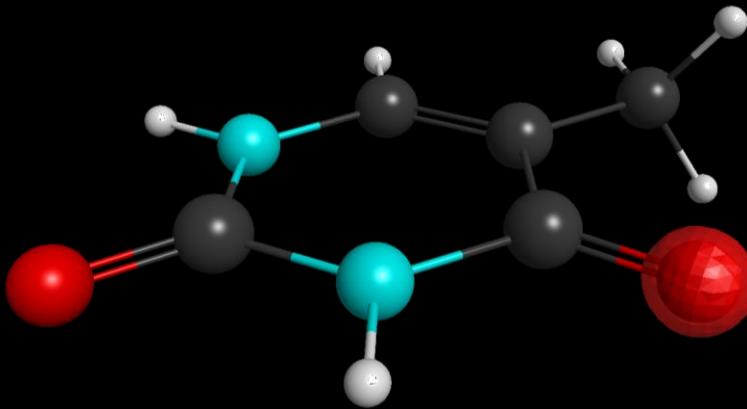
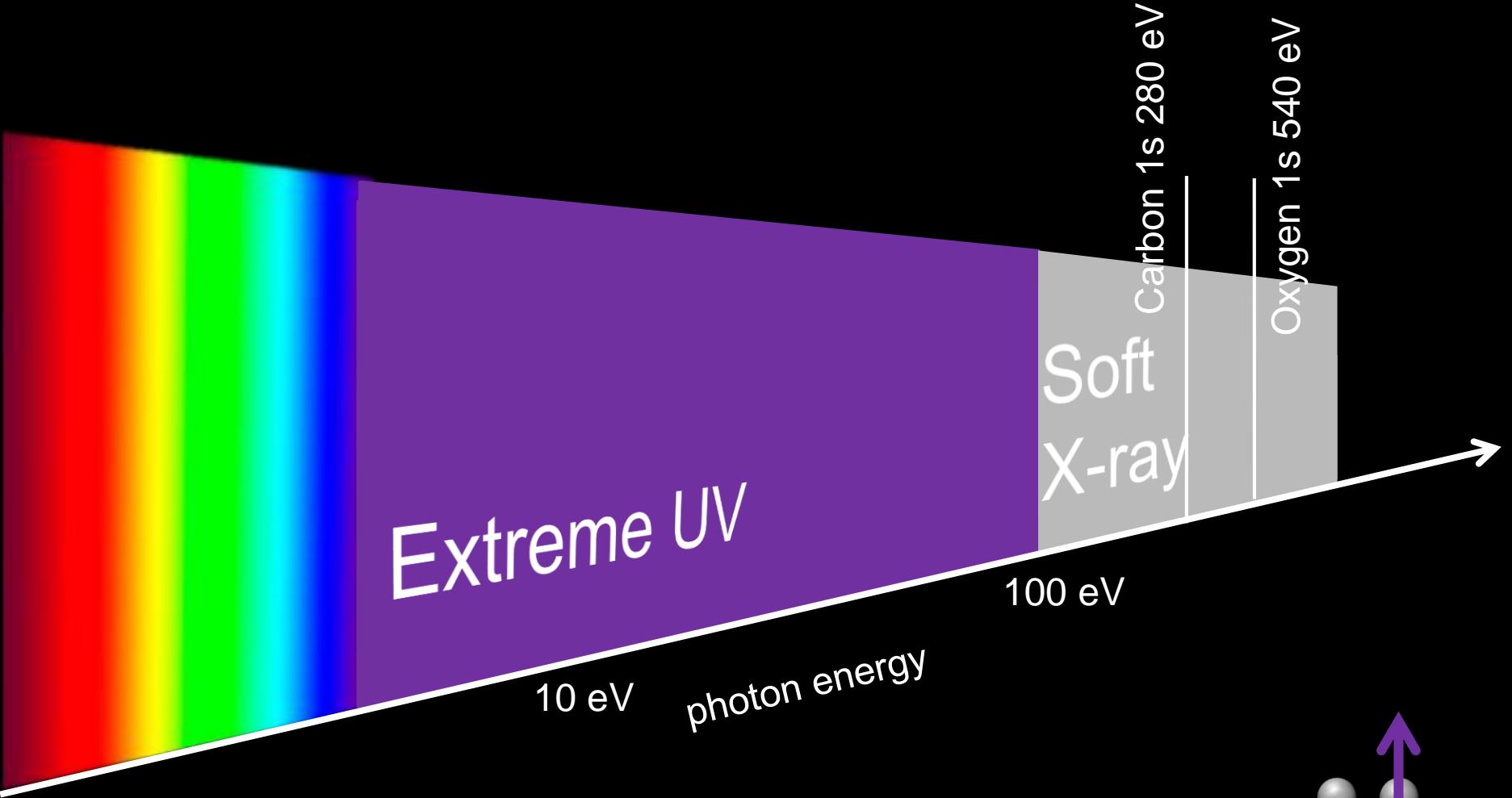
Core electrons



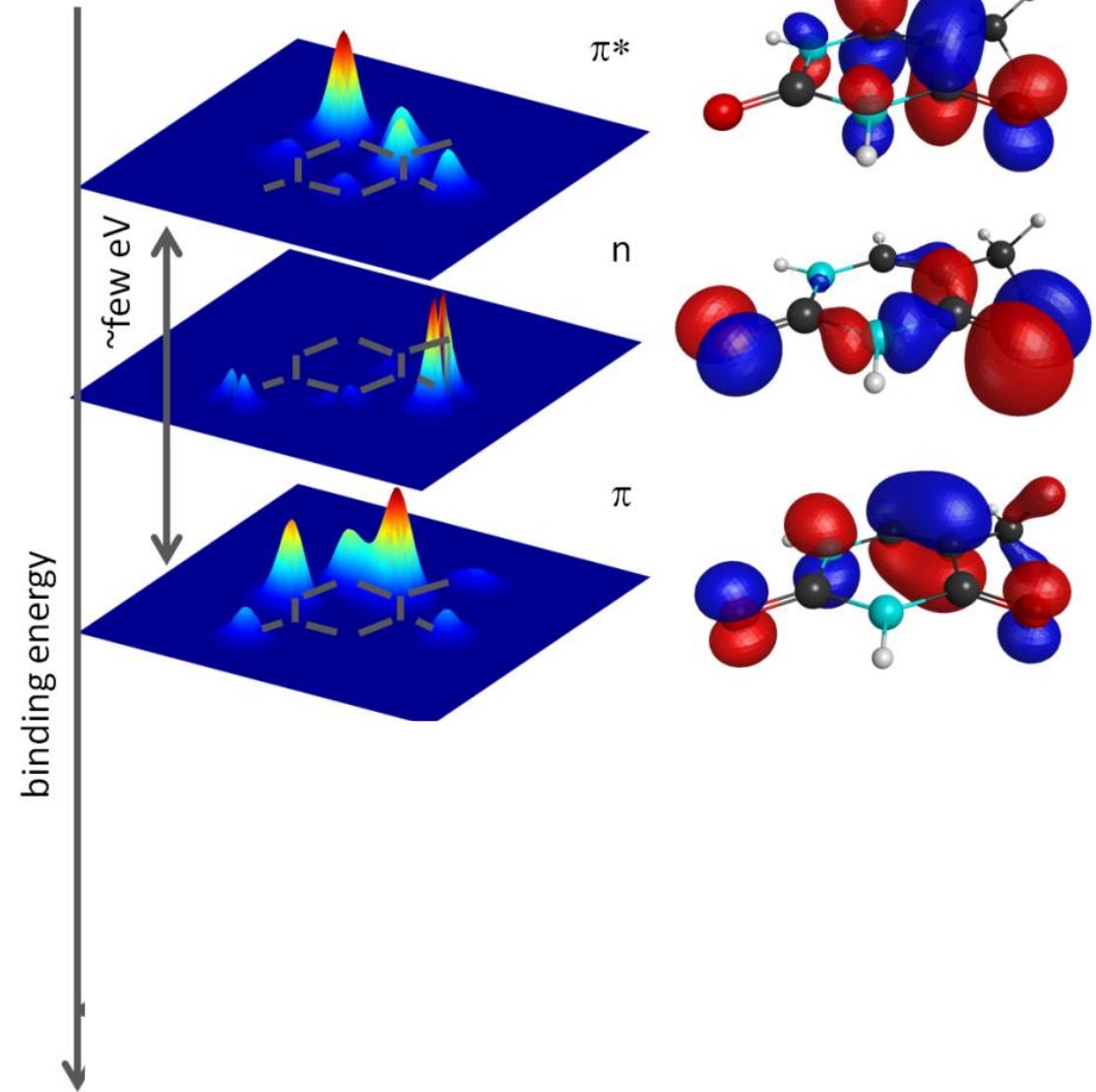
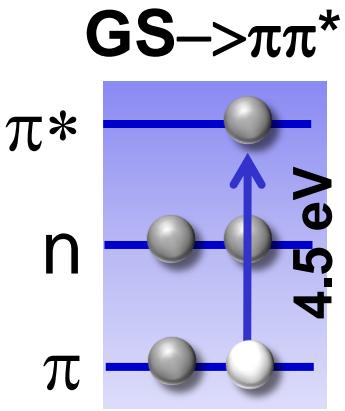
Core energies and localization

$\sim 10\text{pm}$



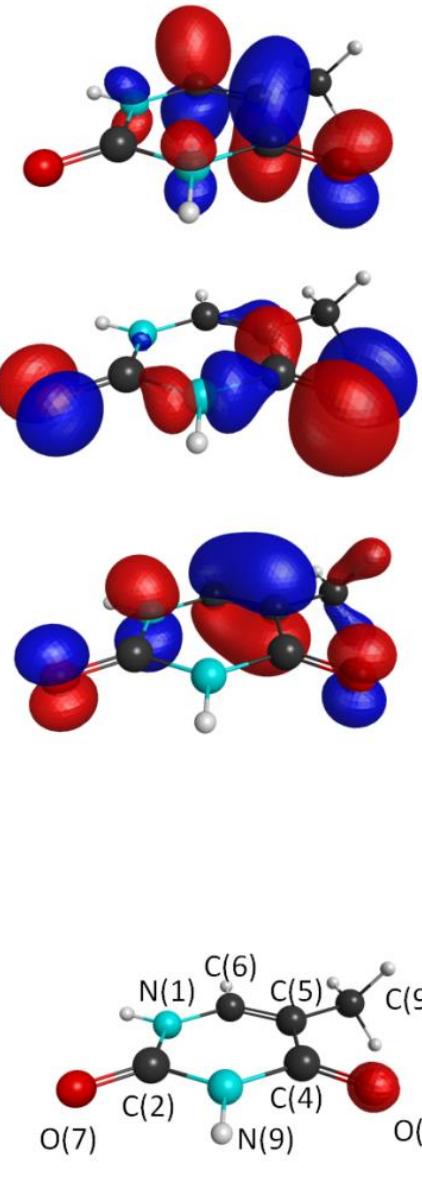
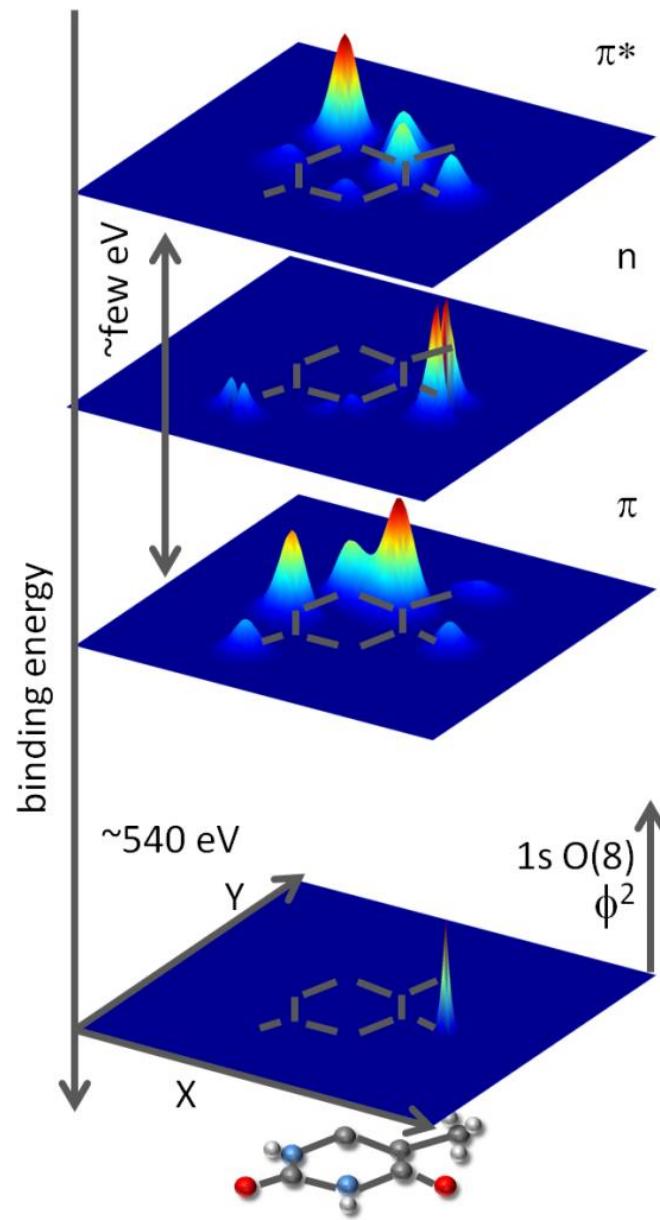
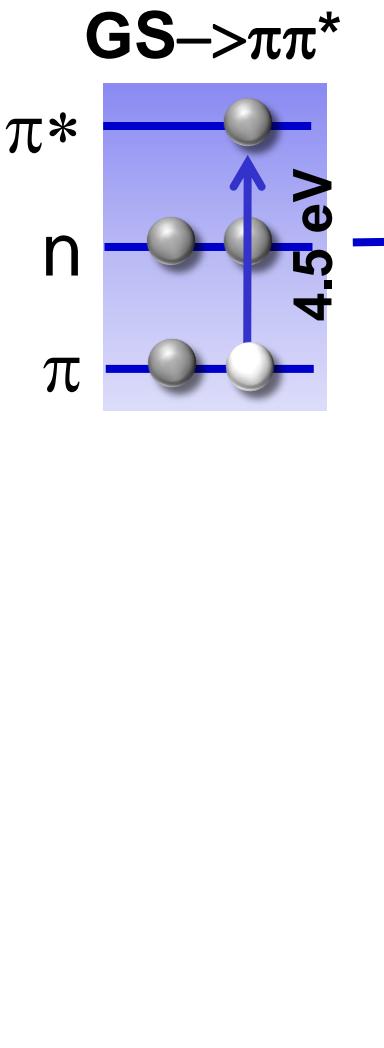


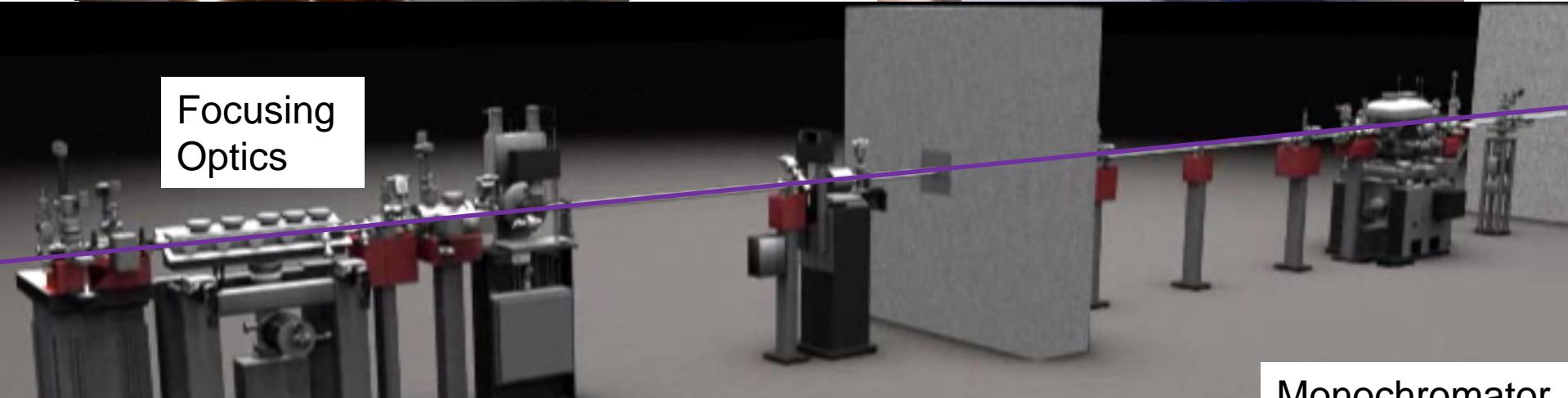
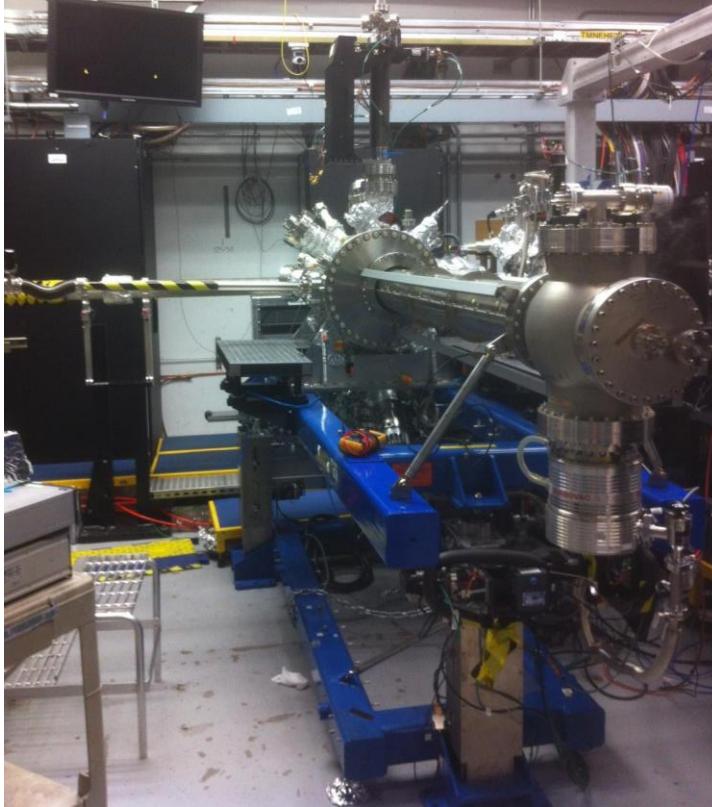
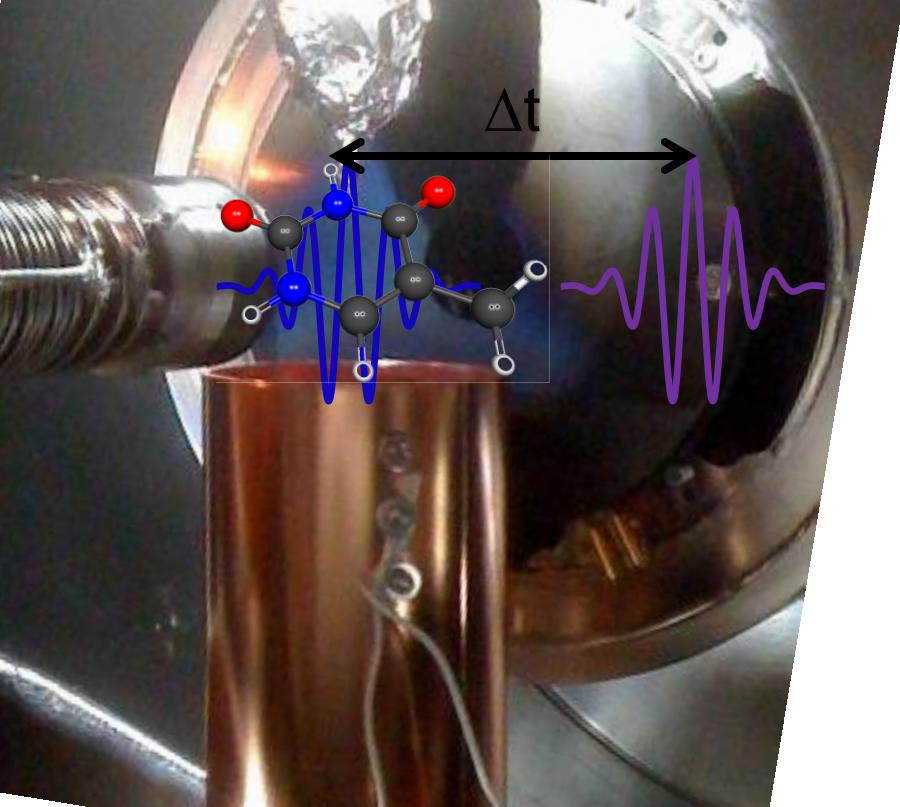
Advantages of TR-XAS



Previous work: McFarland *et al.*, Nature Comm. 5, 4235 (2014)

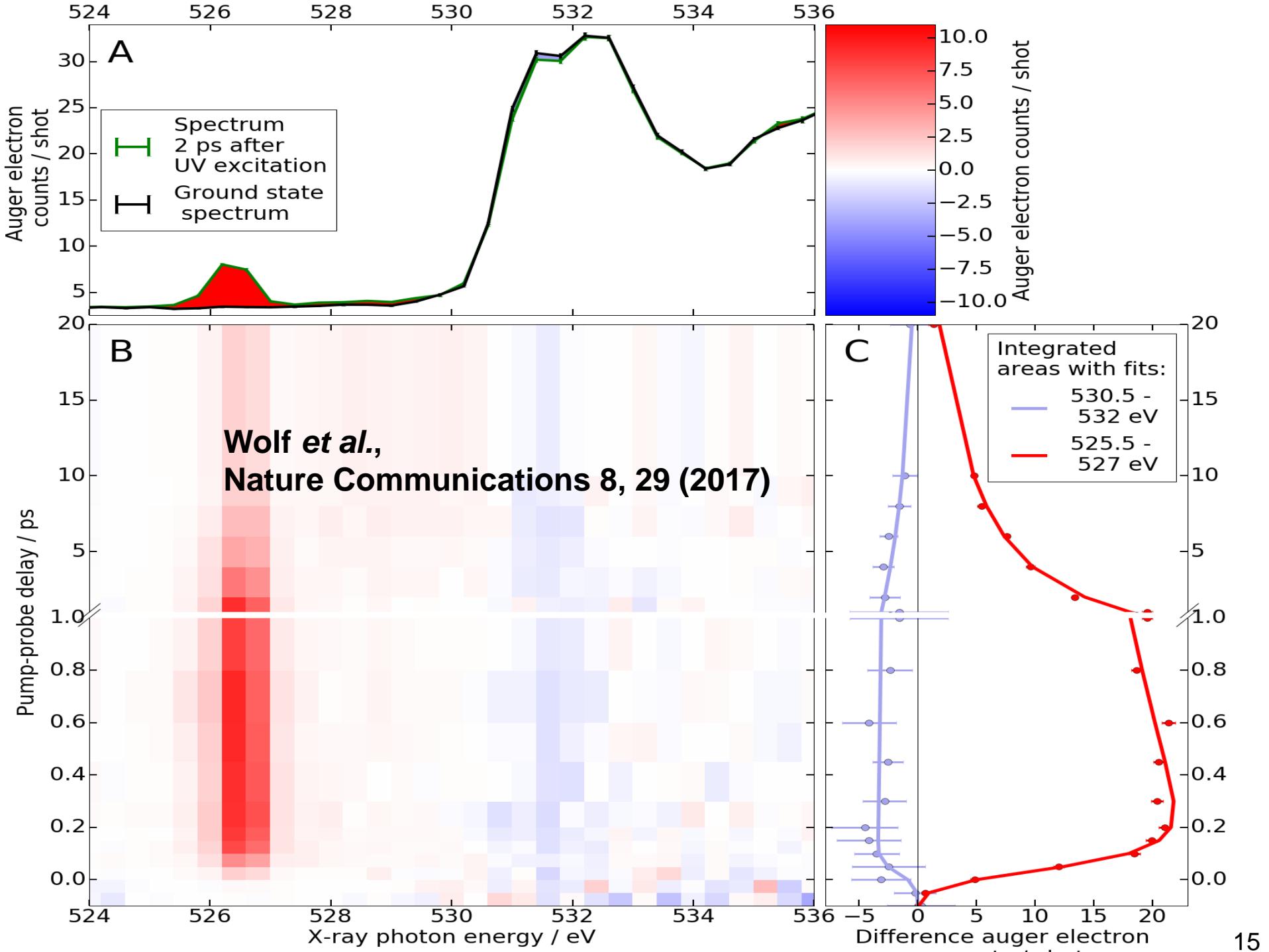
The 1s to n absorption is strong.

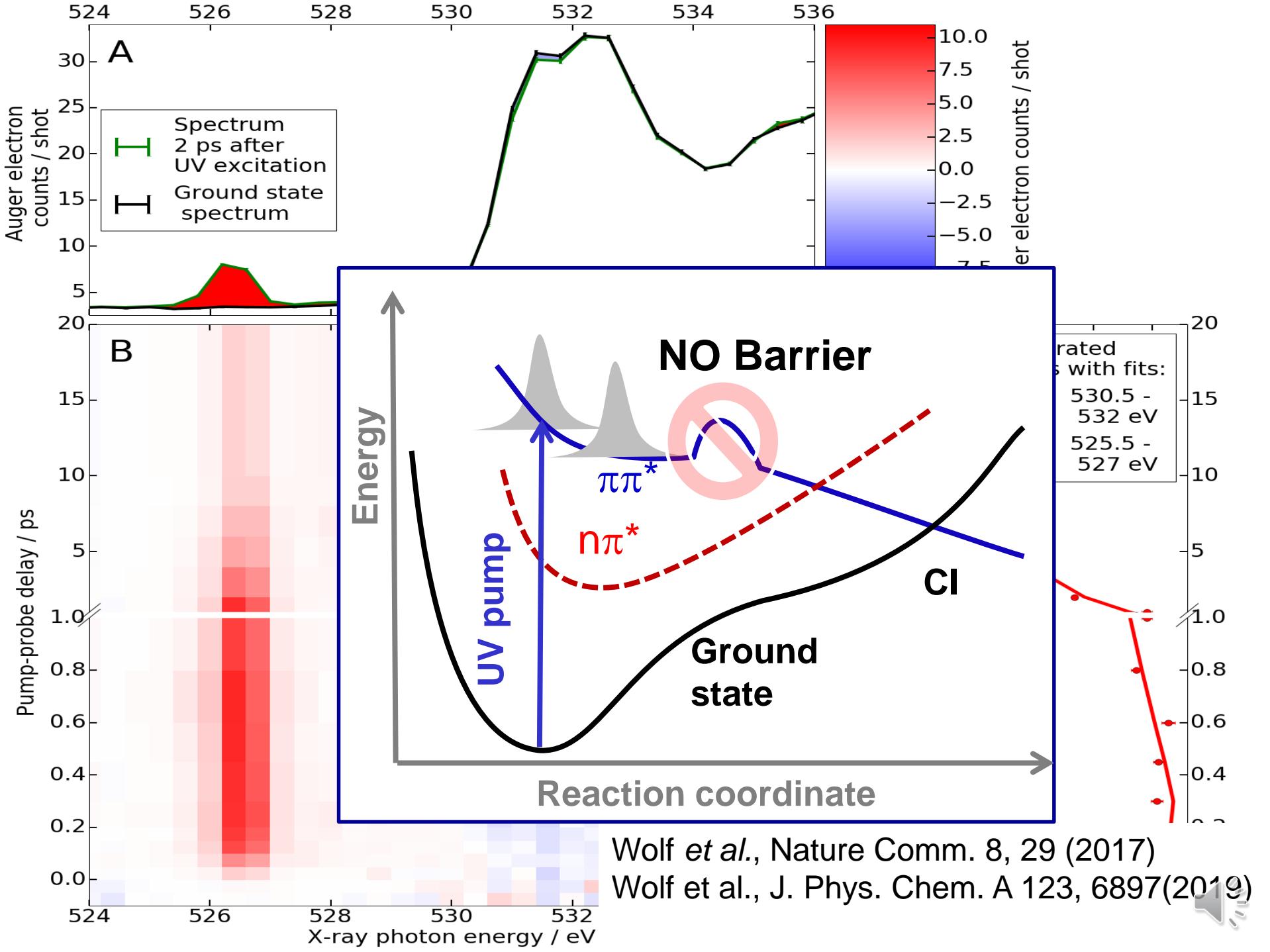




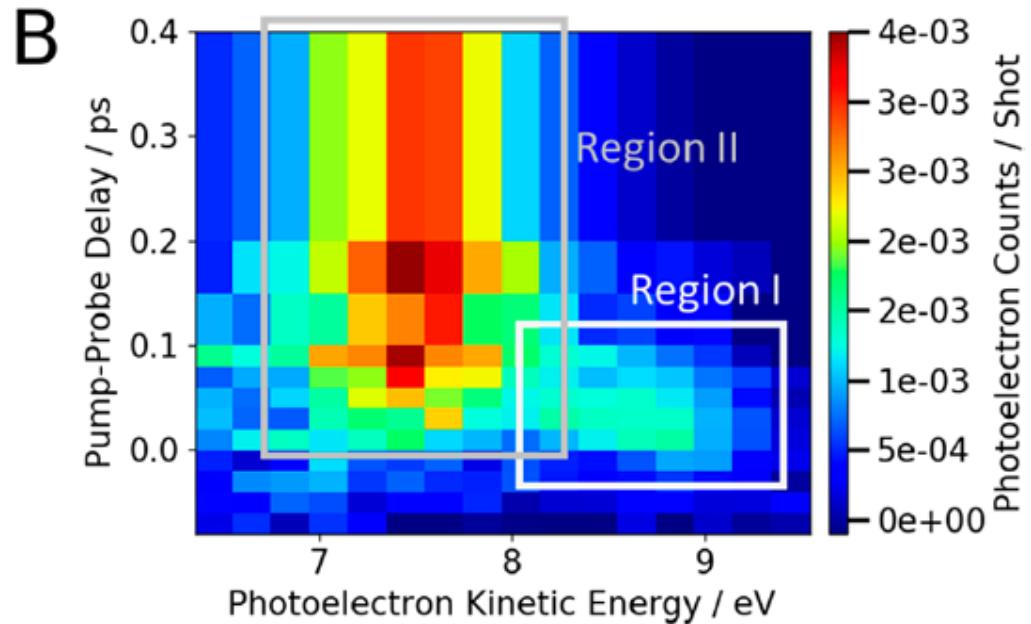
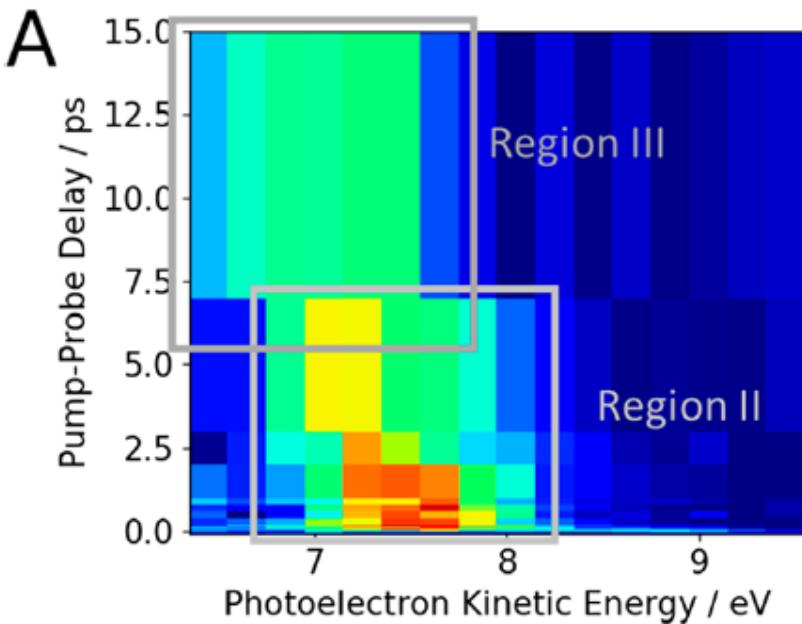
Spectral jitter - filtering by monochromator
Temporal jitter – single shot pulse correlator

Monochromator
0.5 eV FWHM



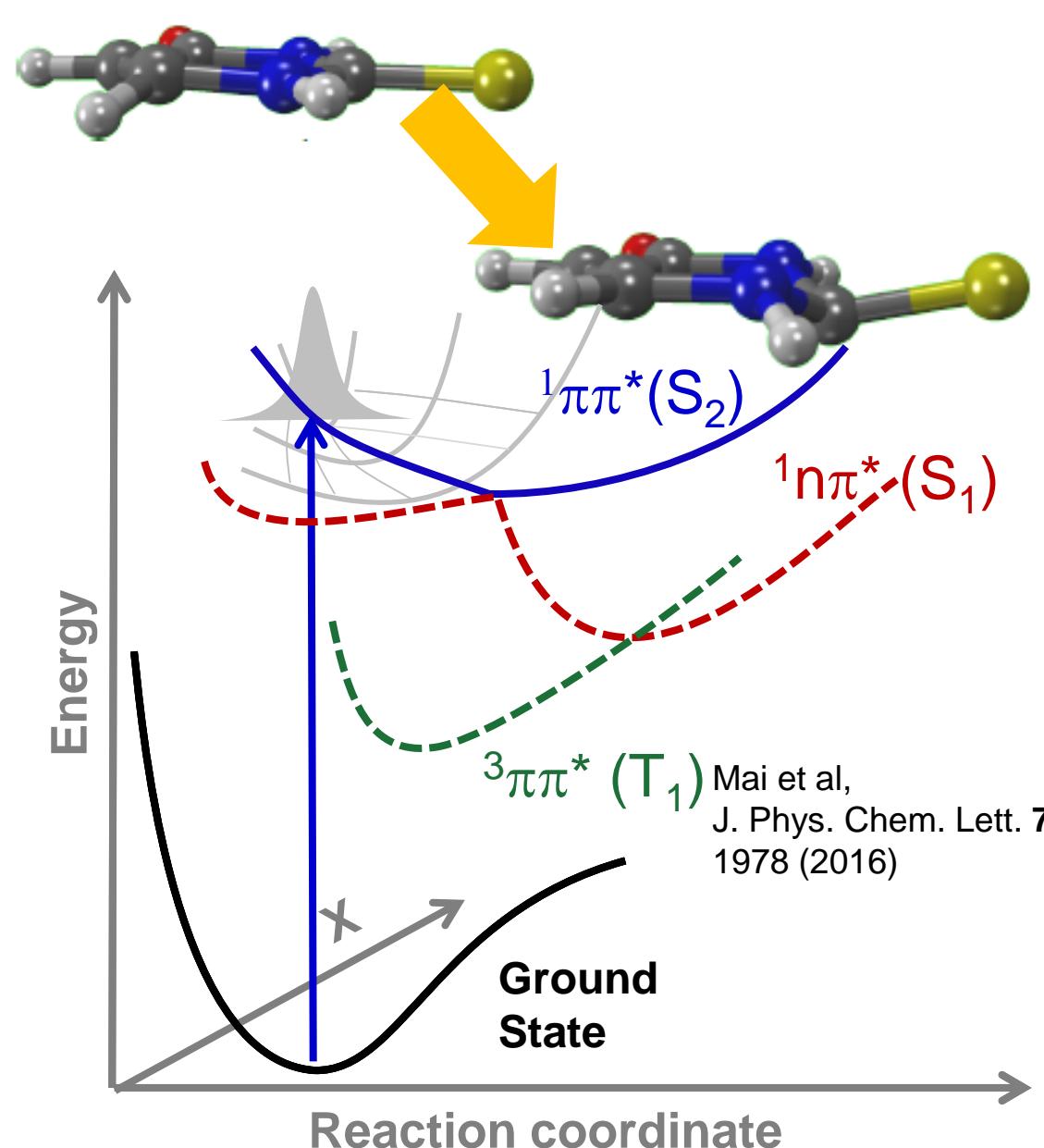
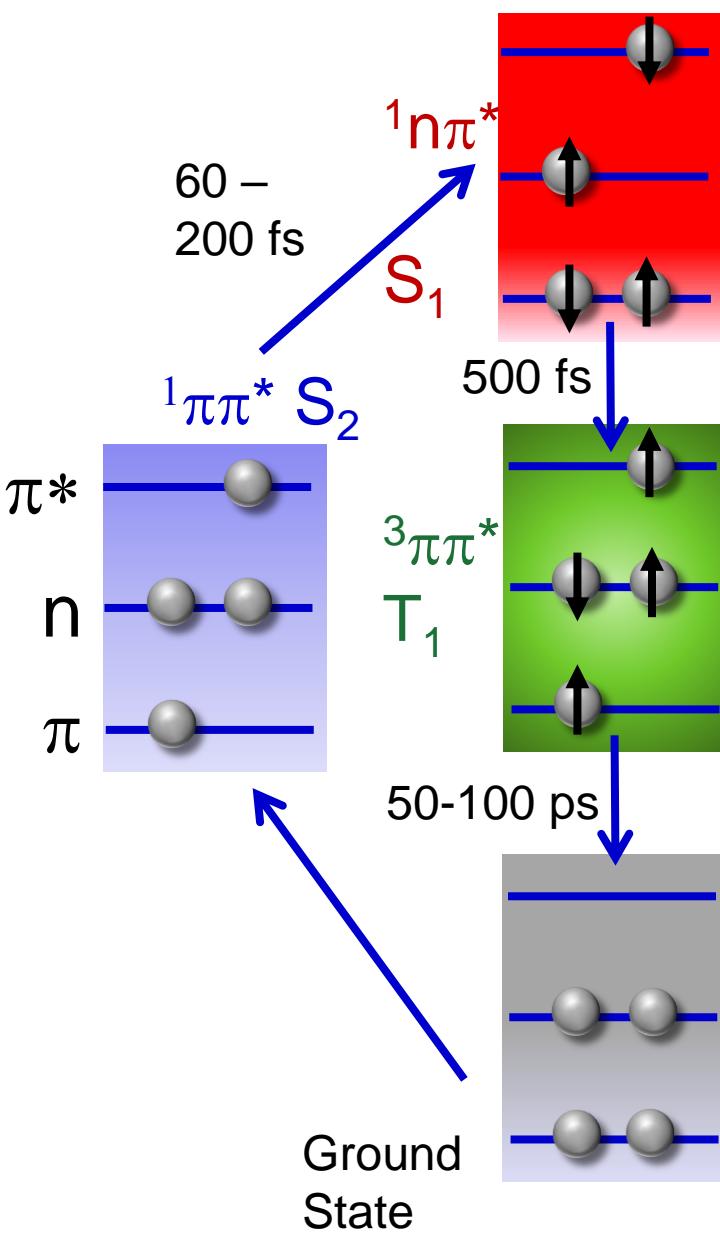


VUV probing of Nucleobase dynamics



**14 eV probe pulses from high harmonic source
Region III is attributed to triplet states**

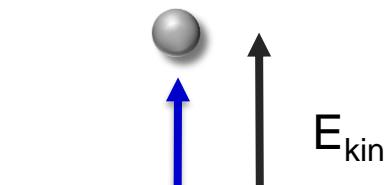
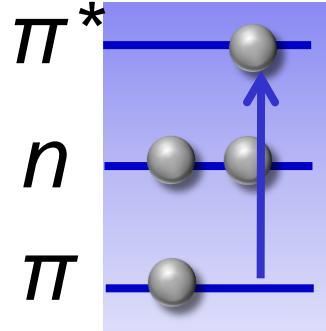
Nuclei couple to electrons and their spin.



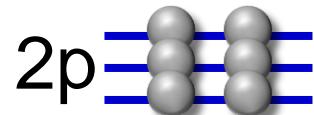
Mai et al,
J. Phys. Chem. Lett. 7,
1978 (2016)

Advantages of XPS

$\text{GS} \rightarrow \pi\pi^*$

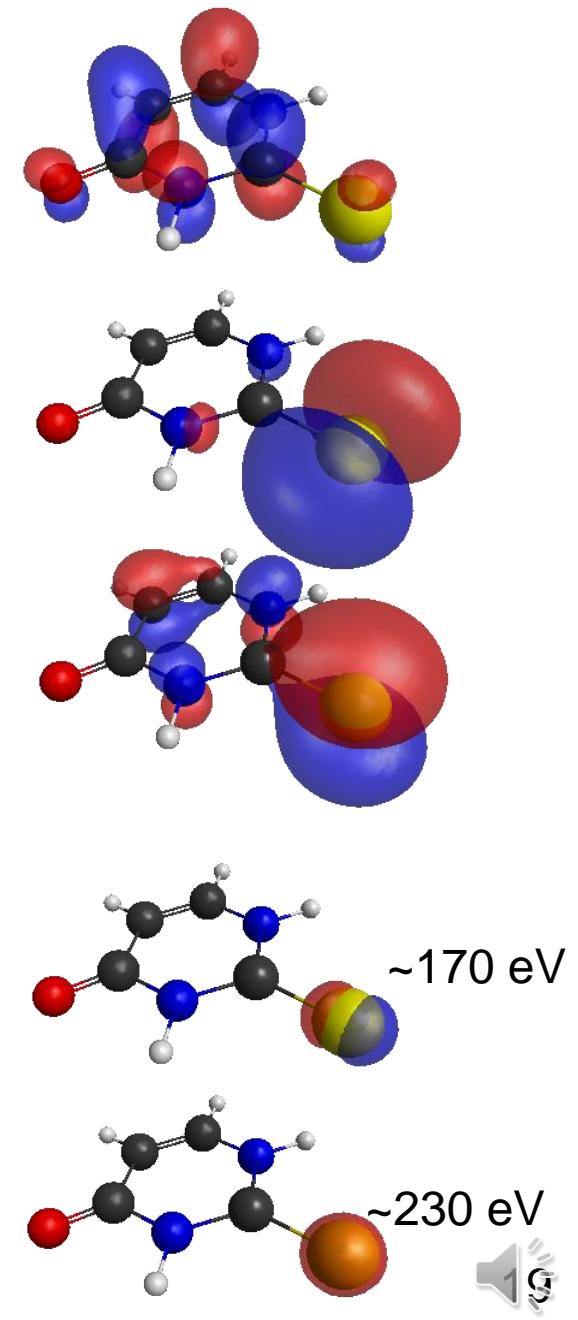


DELAY

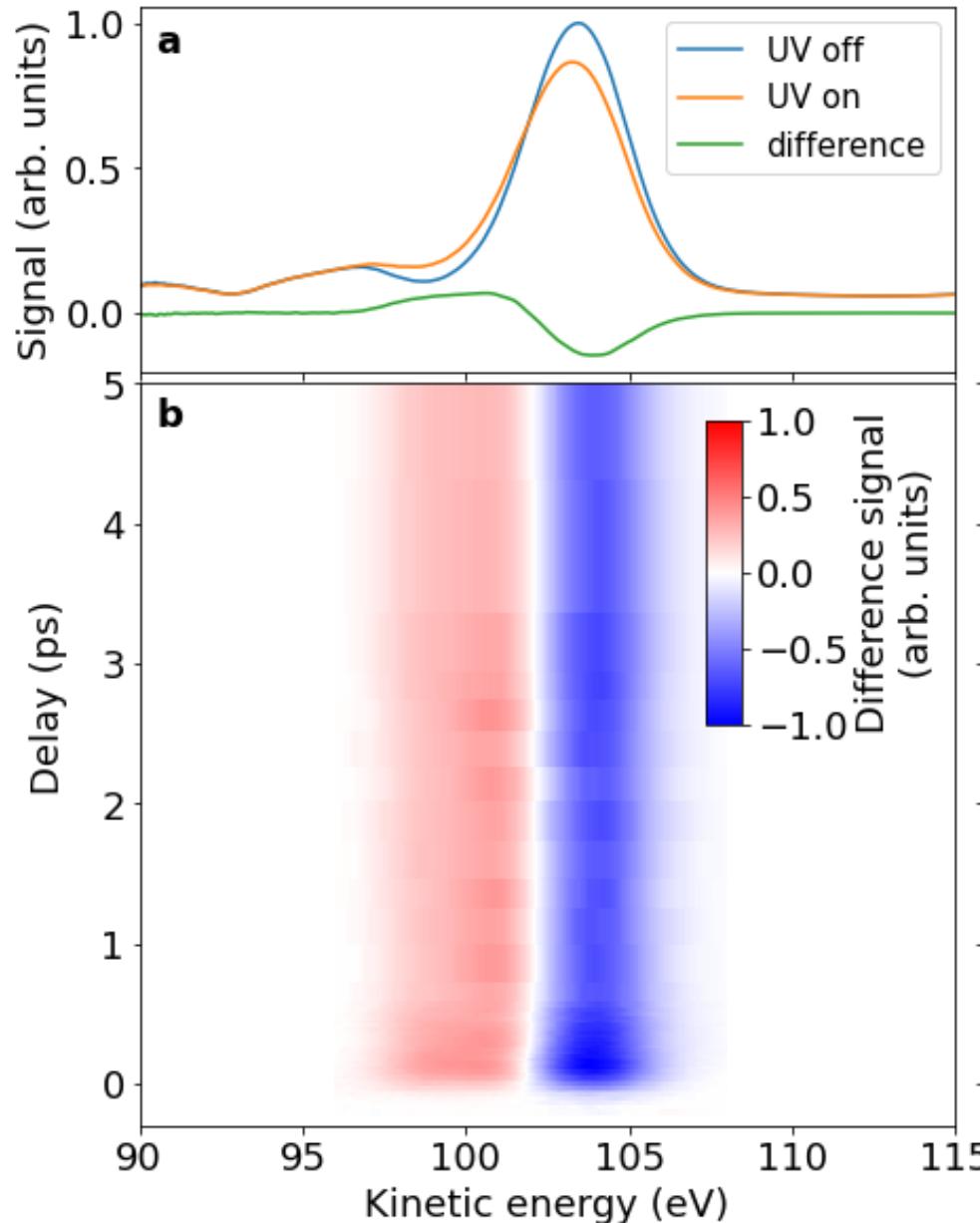


UV pump

X-ray probe

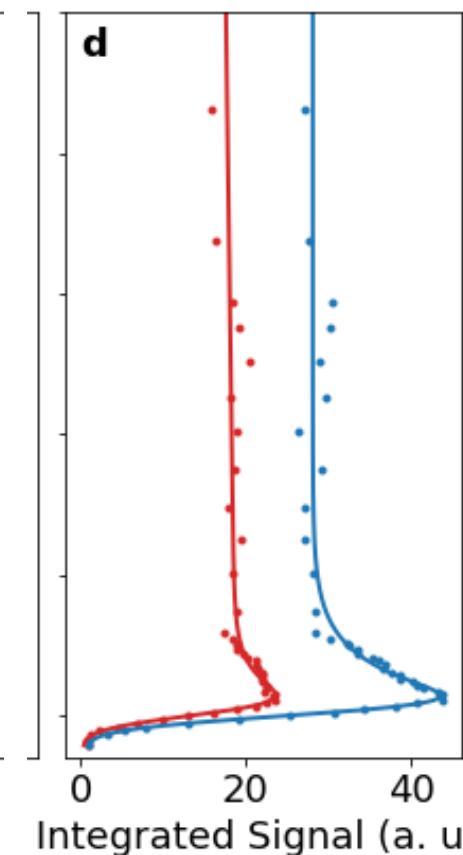


Ground state relaxation within 200 fs

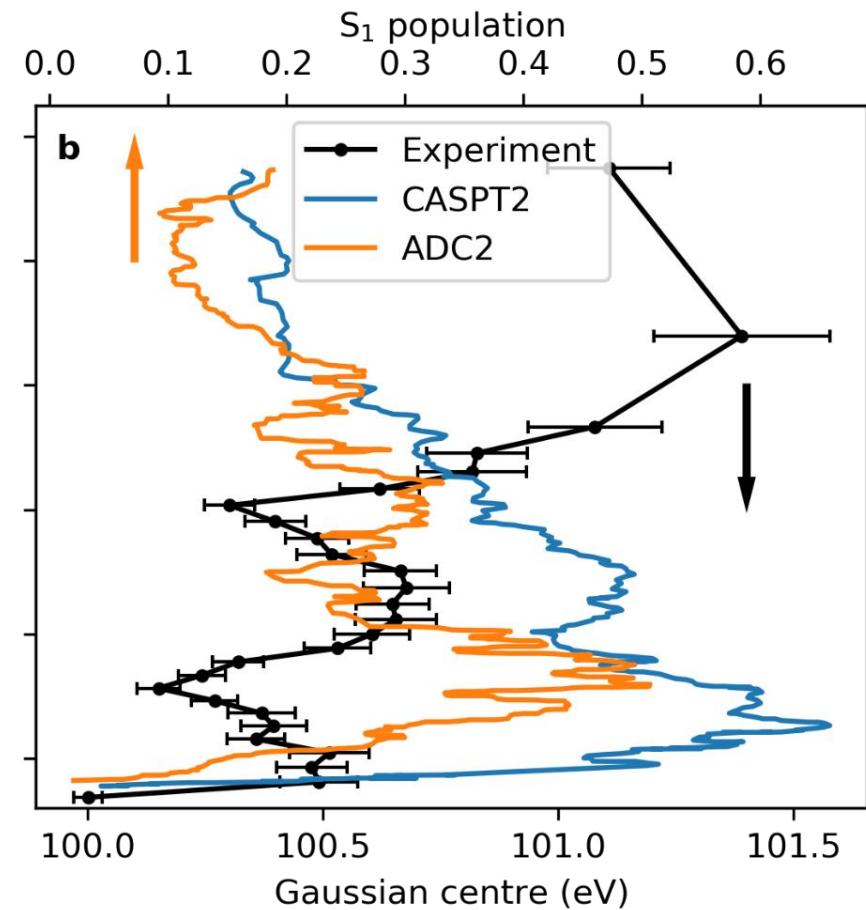
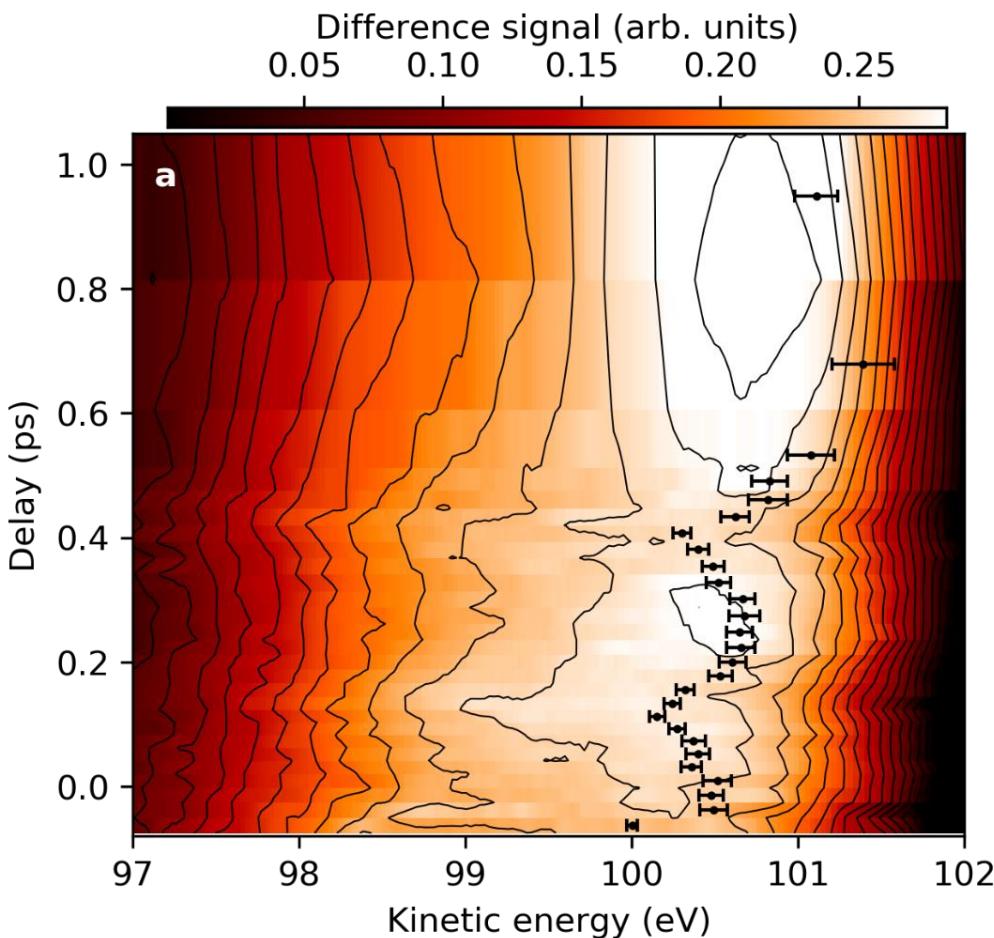


Mayer *et al.*, [arXiv:2102.13431](https://arxiv.org/abs/2102.13431) (2021)
Lever *et al.*, J. Phys. B. **54**, 014002 (2021)

In strong contrast to other results with no ultrafast ground state relaxation



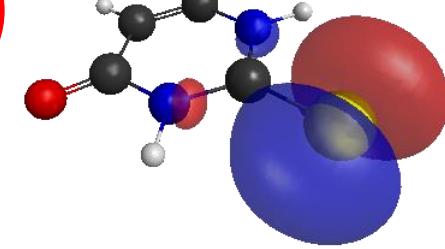
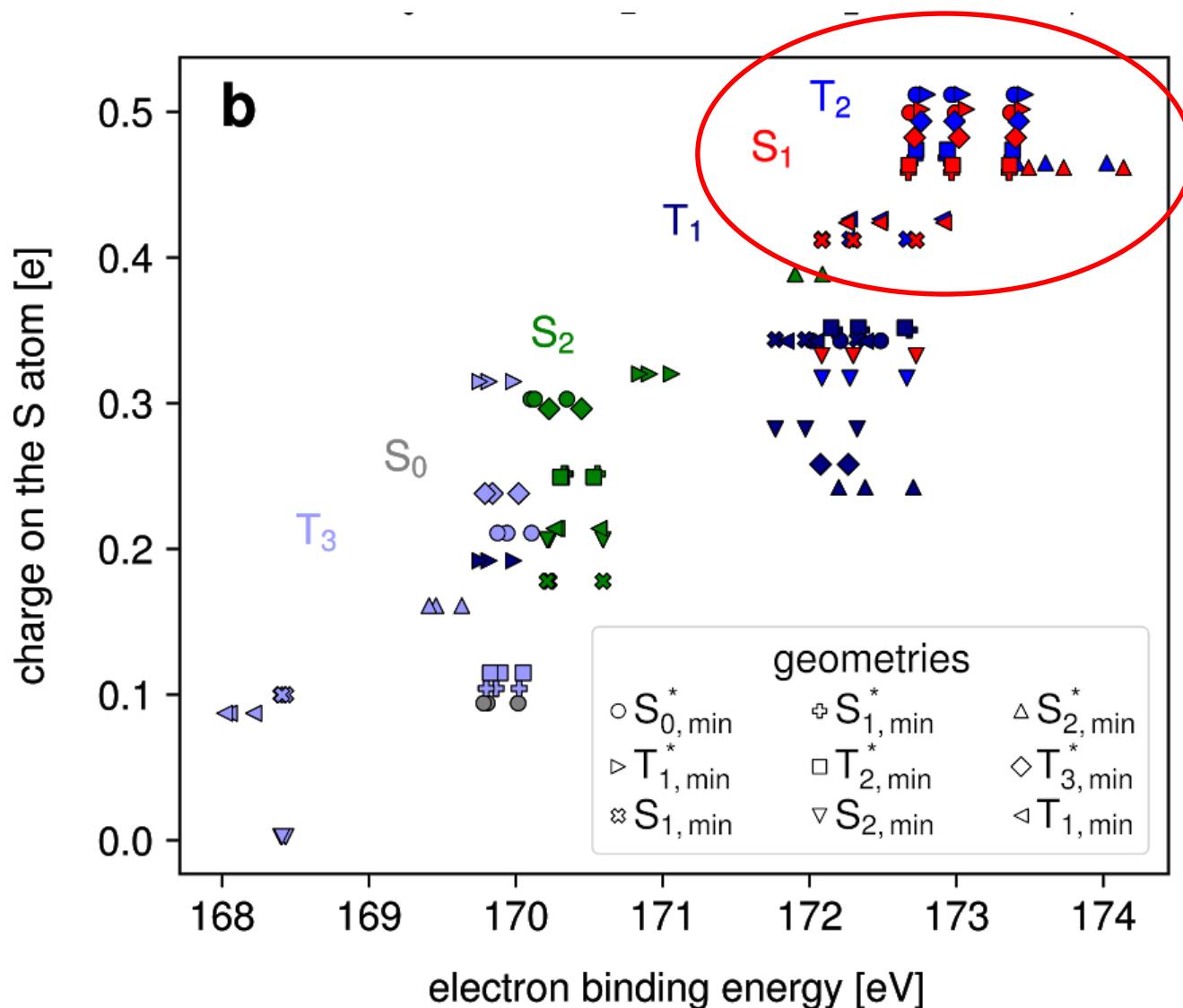
Coherent electronic dynamics in 2-tUra



Mayer, Lever, Picconi ...MG
[arXiv:2102.13431](https://arxiv.org/abs/2102.13431)

Simulations:
Mai, Marquetand, González,
J. Phys. Chem. Lett. **7**, 1978–1983 (2016)
Mai *et al.* J. Chem. Phys. **147**, 184109 (2017)

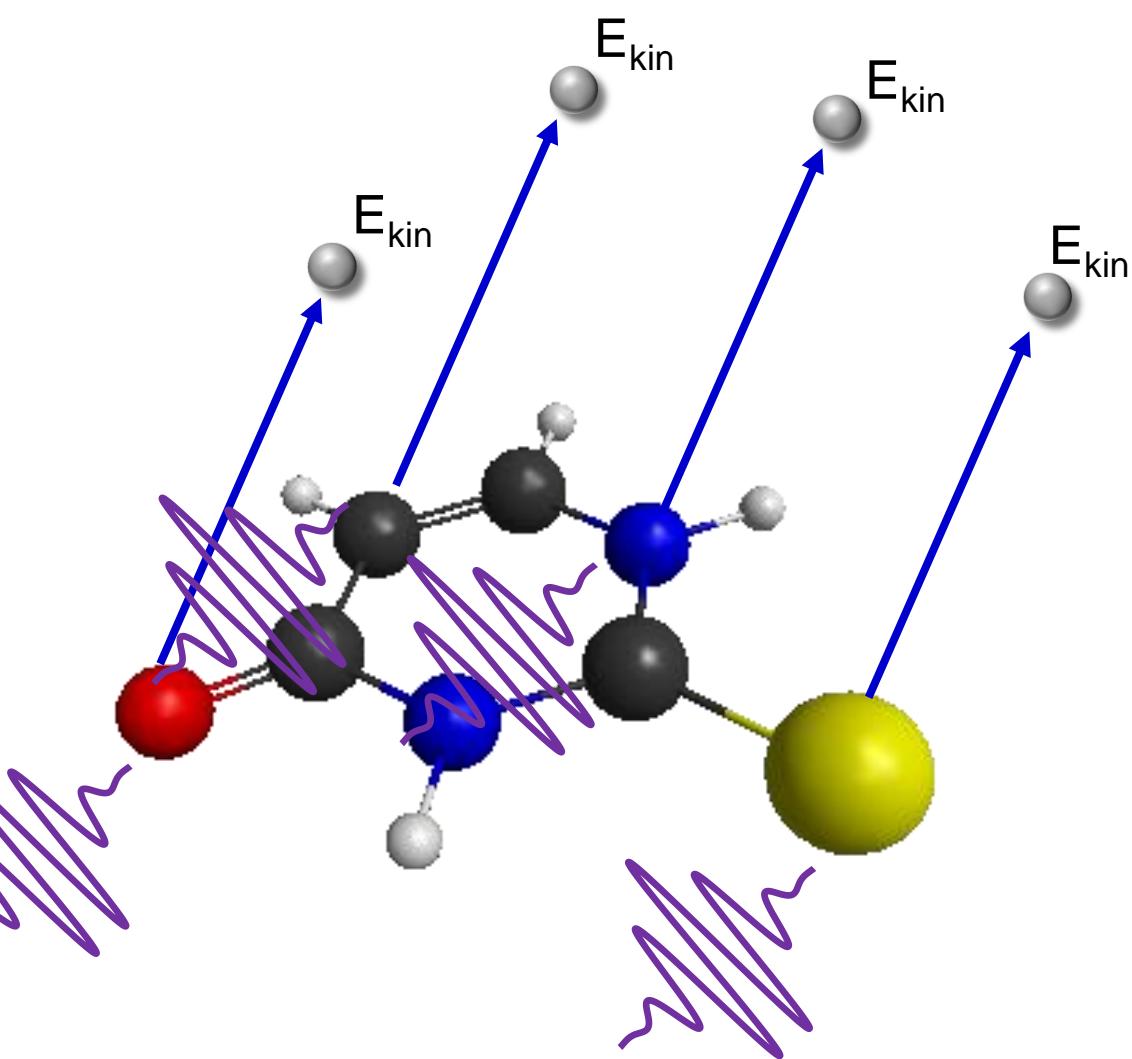
The electronic state determines most of the binding energy change



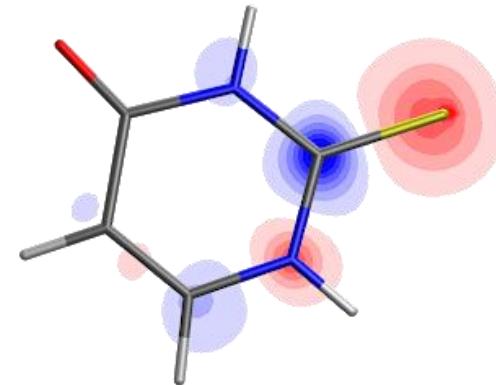
Mayer, Lever, Picconi ...MG
[arXiv:2102.13431](https://arxiv.org/abs/2102.13431)

Challenge for the near future: Deduce valence charge changes at many sites

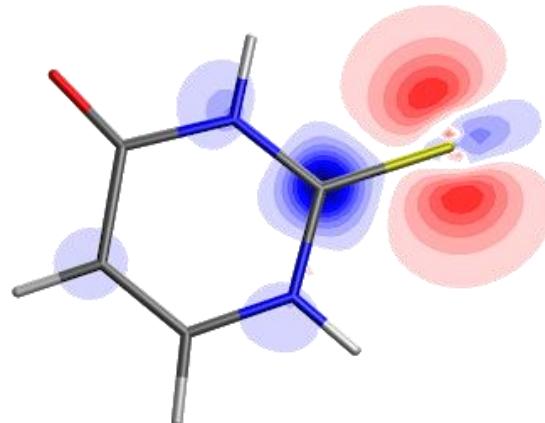
Charge density change

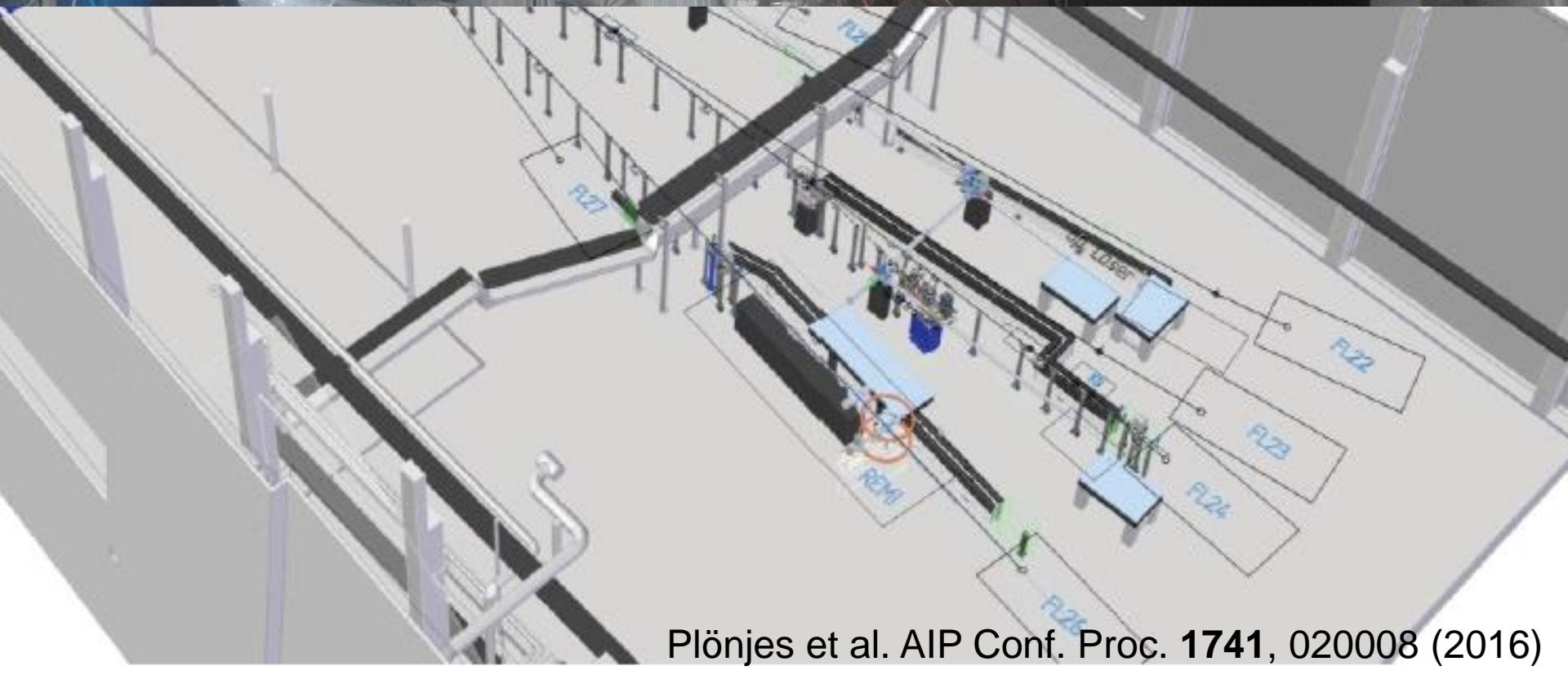
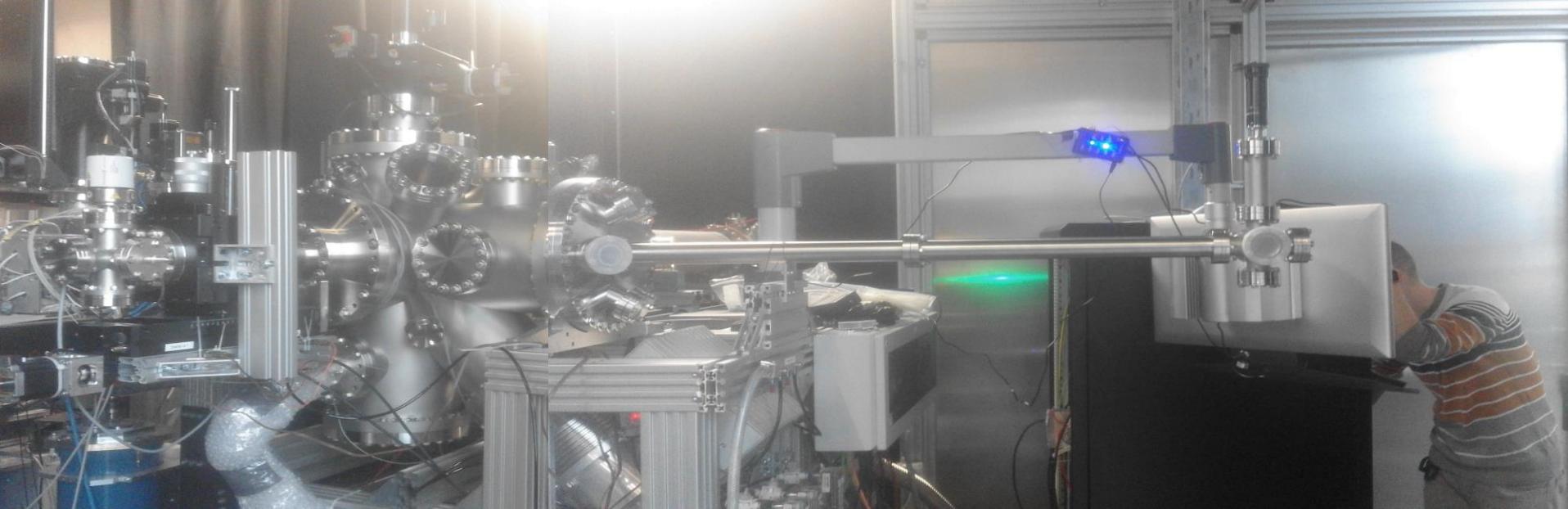


$\pi\pi^*$

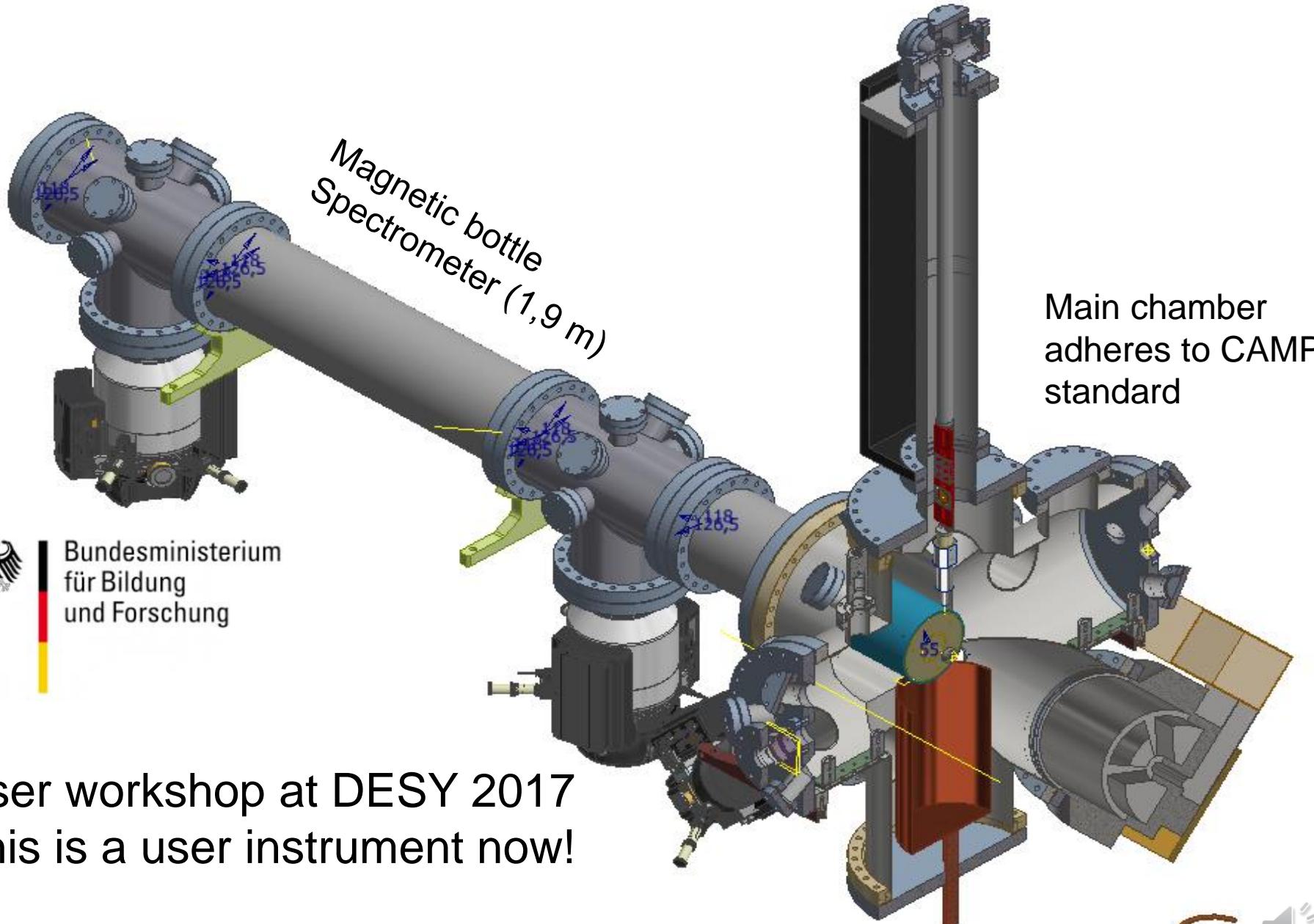


$n\pi^*$





URSA-PQ Instrument at FLASH

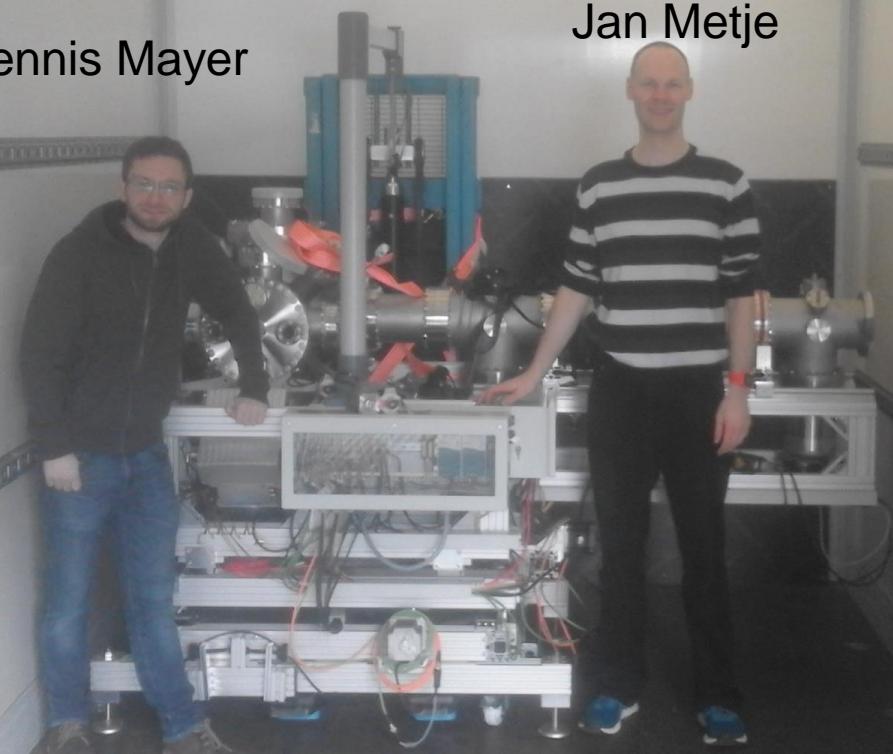


User workshop at DESY 2017
This is a user instrument now!

You can use that instrument a FLASH

Dennis Mayer

Jan Metje



Potsdam, FLASH Feb. 21st 2019

Thionucleobase collaboration 2019



FLASH:

Stefan Düsterer
Bastian Manschwetus
Skirmantas Alisauskas
Marion Kuhlmann

Gothenburg:

Raimund Feifel
Richard Squibb
Mans Wallner

XFEL:

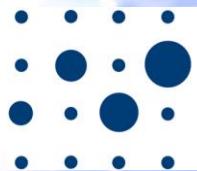
Tommaso Mazza

CFEL:

Francesca Calegari
Andrea Trabattoni

SLAC:

Thomas Wolf



VolkswagenStiftung

Potsdam Experiment:

Fabiano Lever
Dennis Mayer
Jan Metje
Mario Niebuhr
Matthew Robinson
Markus Gühr

DFG

Deutsche
Forschungsgemeinschaft

Potsdam Theory:

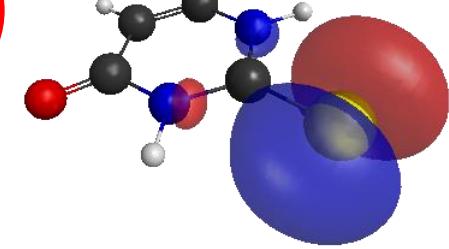
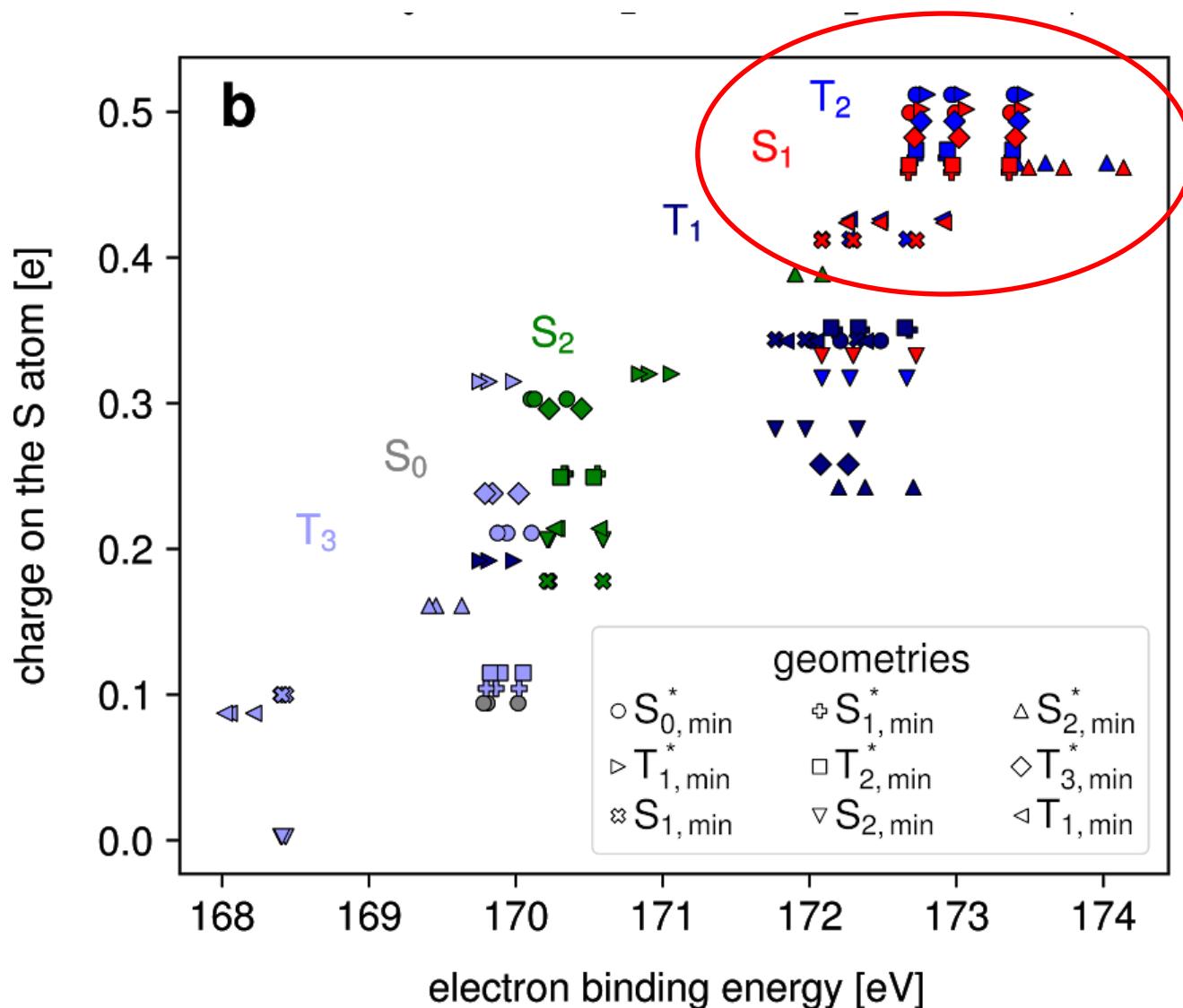
David Picconi
Peter Saalfrank
Christopher Ehlert



Bundesministerium
für Bildung
und Forschung



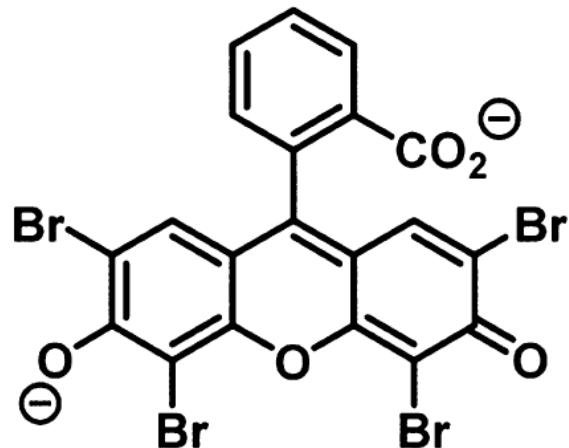
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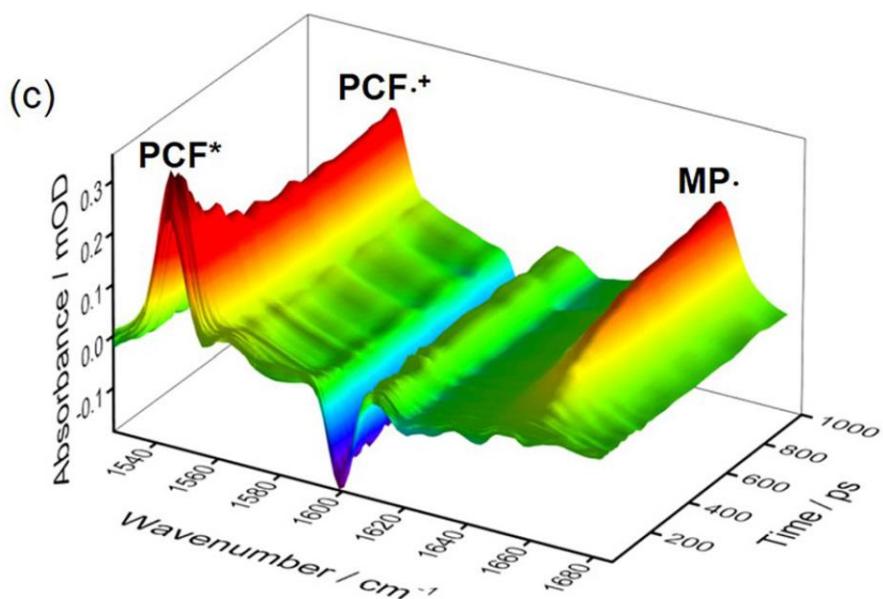
Photoredox catalysis – new opportunities

Photoredox catalysis for aromatic substitutions



Majek, Jacobi von Wangelin,
Acc. Chem. Res. 49, 2316 (2016)

Organocatalyzed atom-transfer

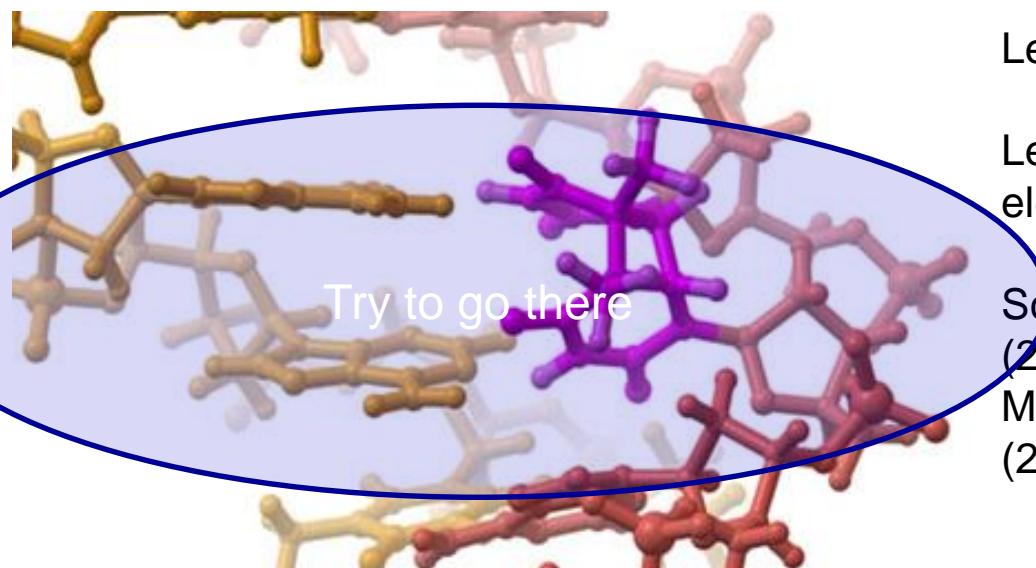
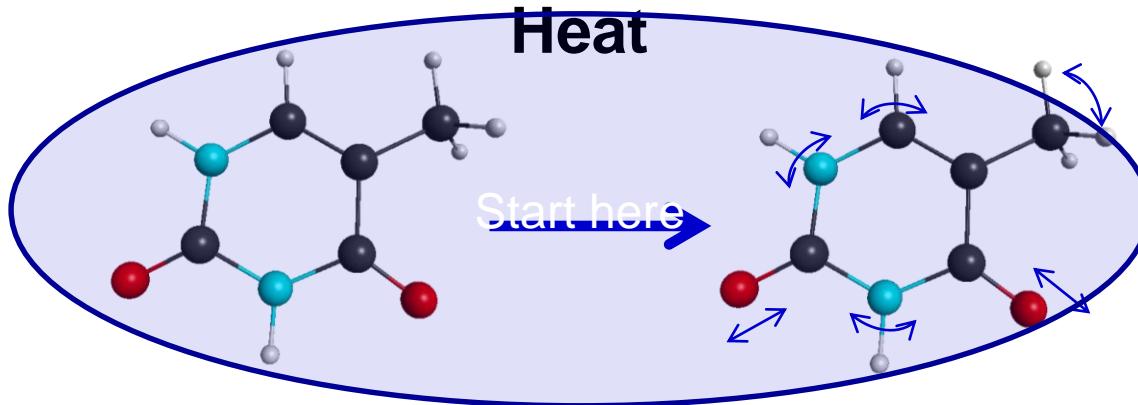


Orr-Ewing, Struct. Dyn. 6, 010901 (2019)

'Further advances in transient spectroscopy, for example, using emerging techniques such as **ultrafast X-ray absorption spectroscopy**, ... may offer additional dynamical insights...'

All these outcomes will go some considerable way to **bridging the divide between the structural dynamics and synthetic organic chemistry communities.**'

The machinery of life is complex.



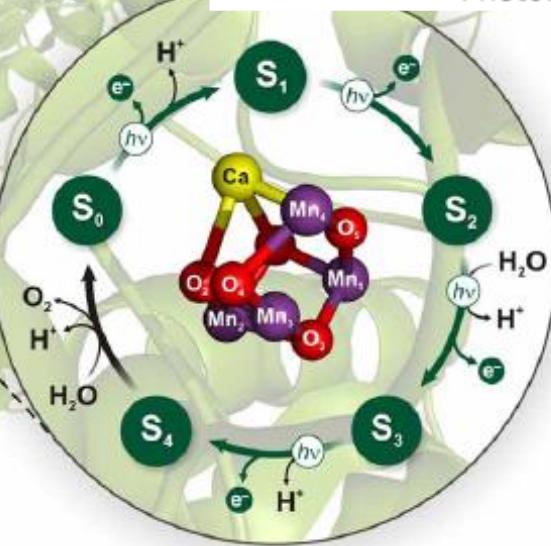
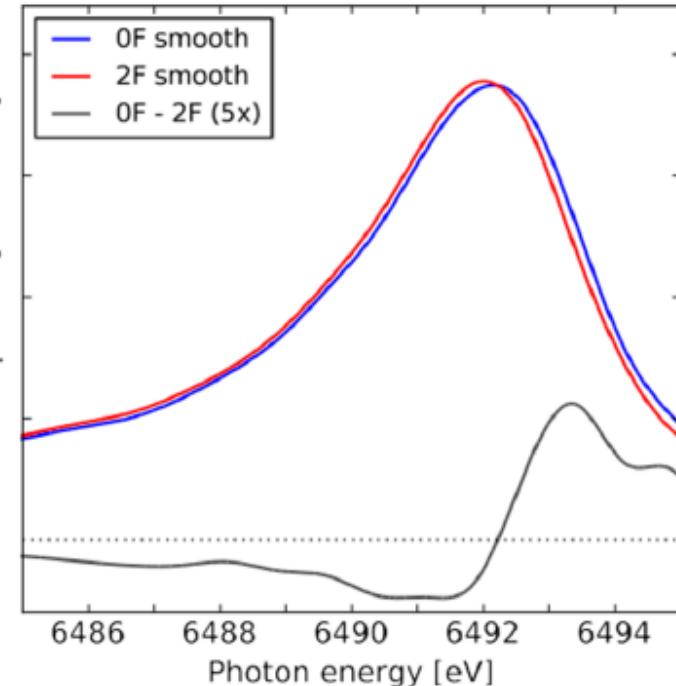
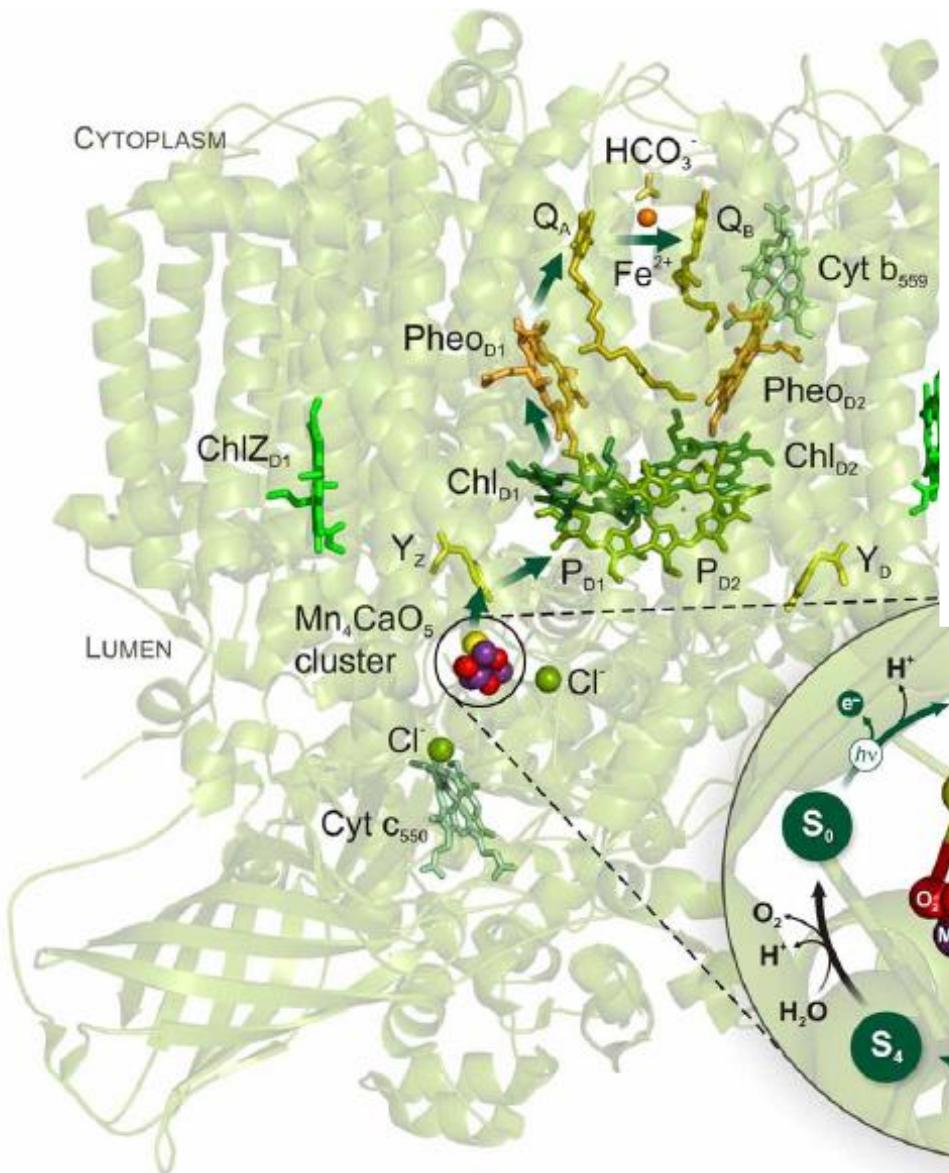
Less than 1% probability for lesion formation

Lesion formation competes with ultrafast electronic relaxation

Schreier *et al.*, Ann. Rev. Phys. Chem. **66**, 497 (2015)

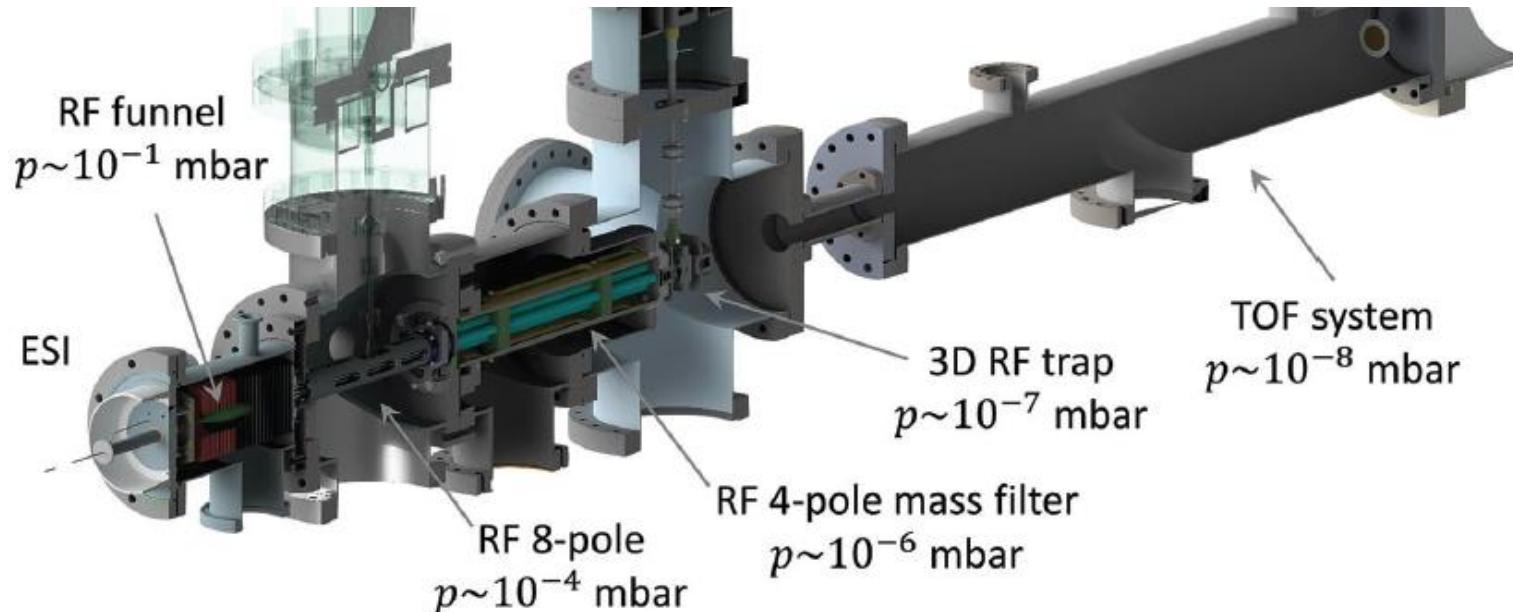
Middleton *et al.*, Ann. Rev. Phys. Chem. **60**, 217 (2009)

Getting at complexity with x-rays



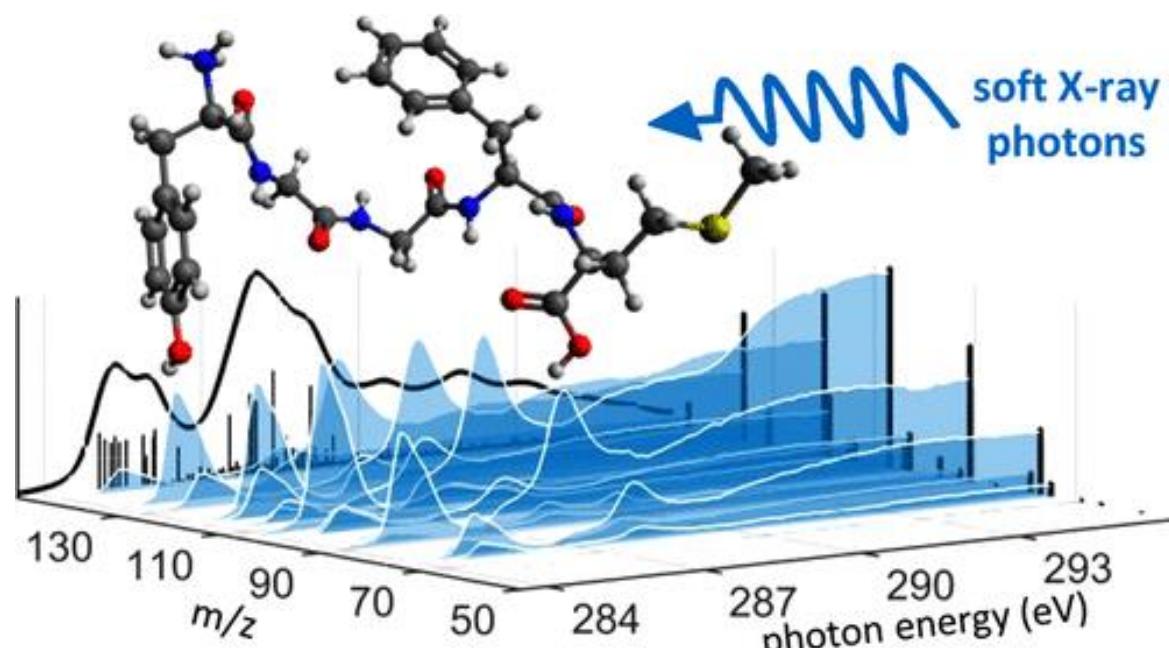
Fransson et al.,
Biochemistry 57,
4629 (2018)

Electrospray sources and ion waveguides



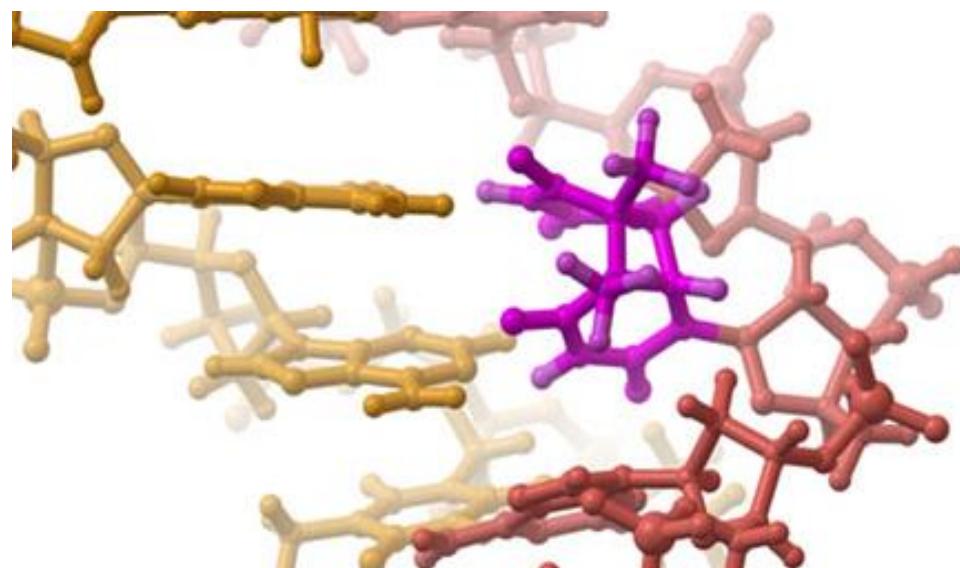
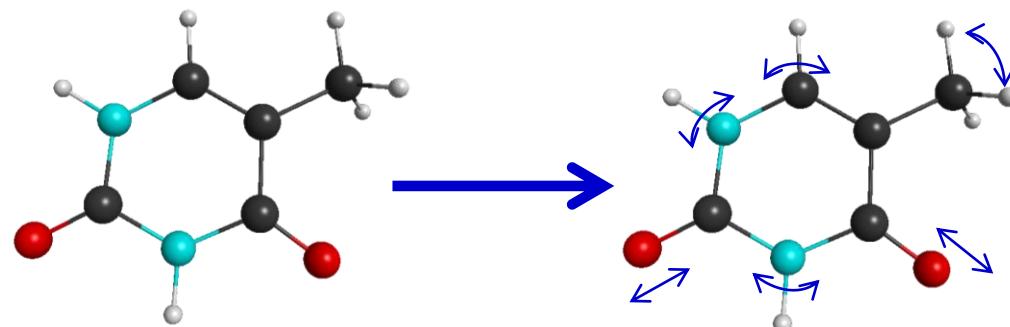
Rapacioli...Schlathölter
PCCP **20**, 22427 (2005)

Ion yield related
related to site of
ionization



Dörner...Bari., J. Am. Soc. Mass Spectrom **32**, 670 (2021)

The machinery of life is complex.



Cyclopyrimidine dimer induced by UV irradiation in DNA
(source: <http://pdb101.rcsb.org/motm/91>)