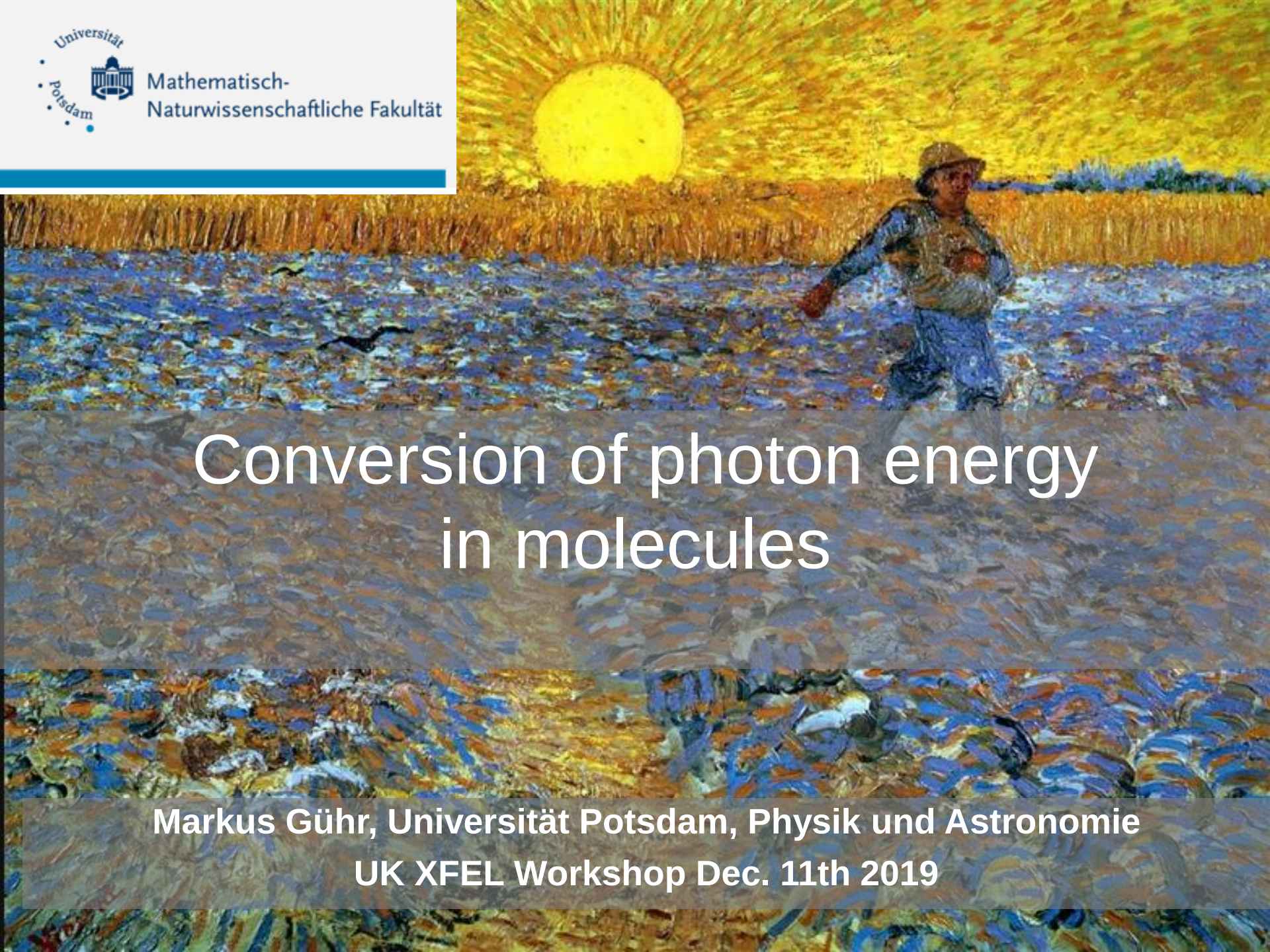


Universität Potsdam

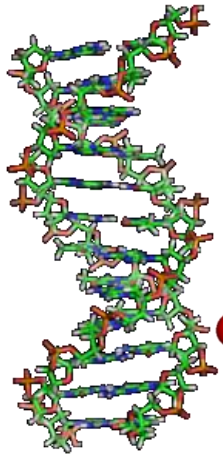
Mathematisch-Naturwissenschaftliche Fakultät

Conversion of photon energy in molecules

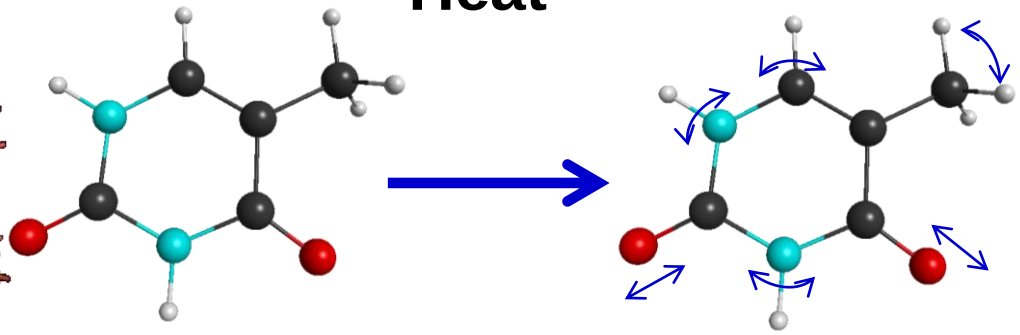
Markus Gühr, Universität Potsdam, Physik und Astronomie

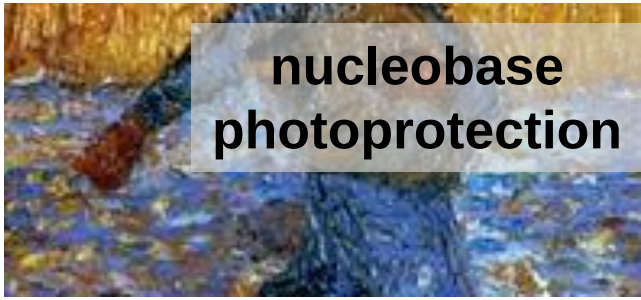
UK XFEL Workshop Dec. 11th 2019

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

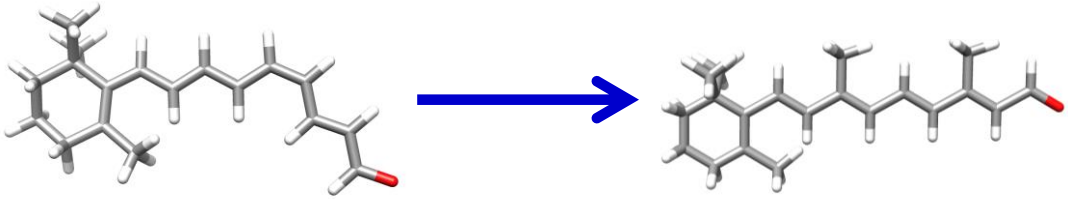


Heat



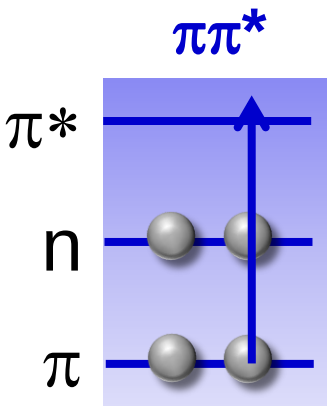


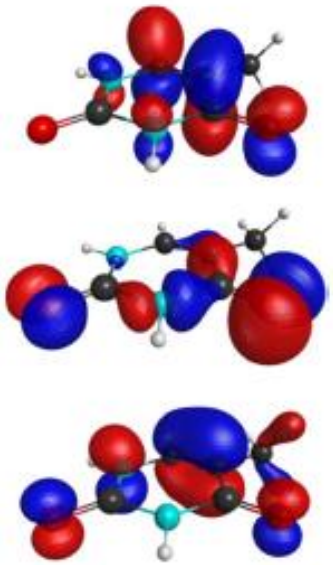
Chemical bond change

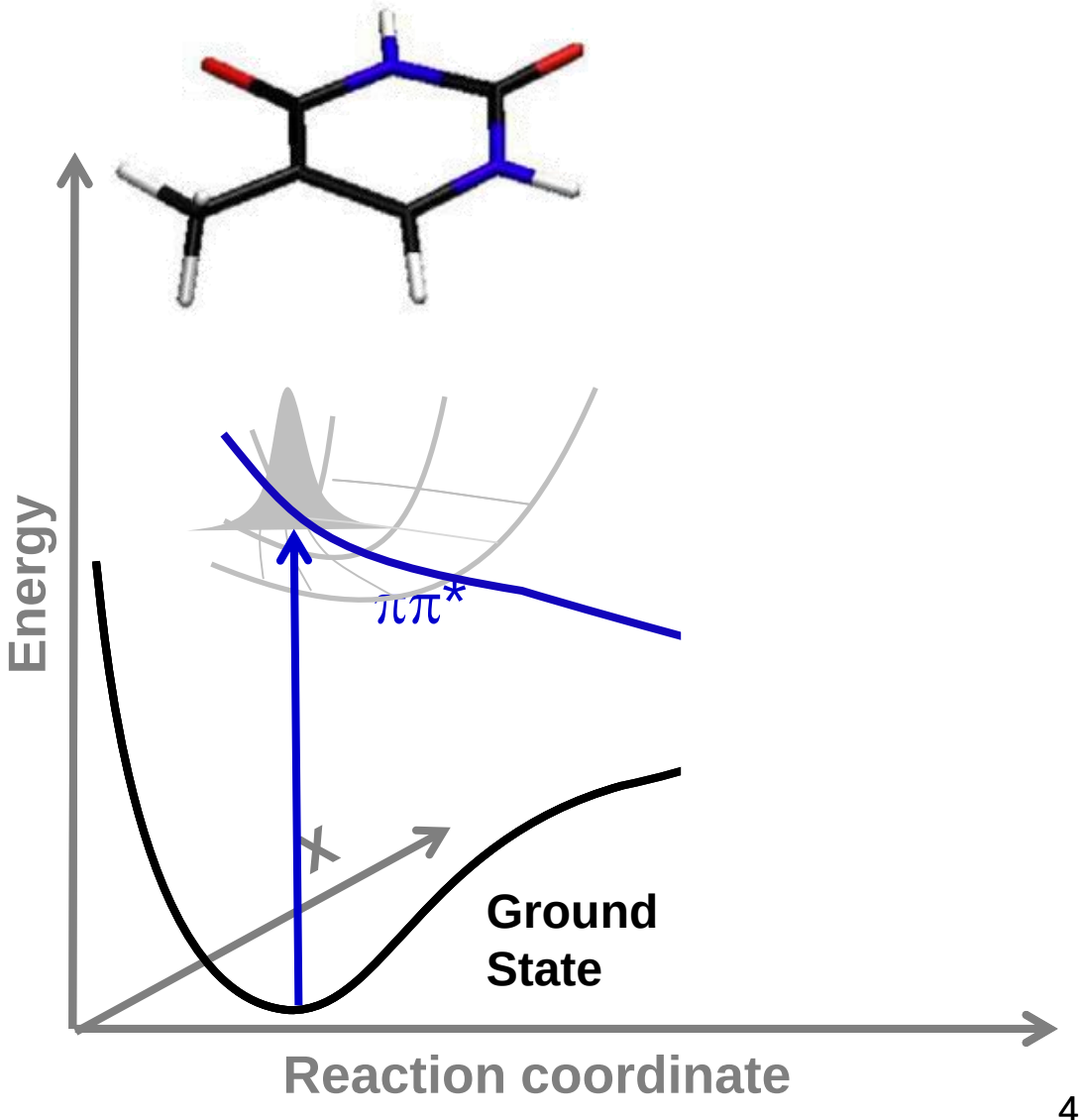


A short introduction to photon-electron-nuclear coupling

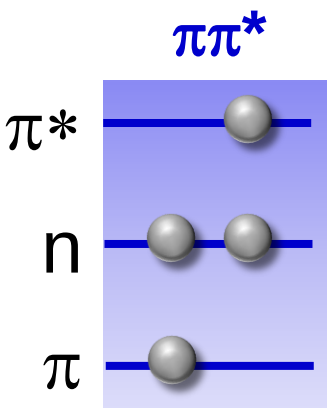
Light excitation couples to electrons.

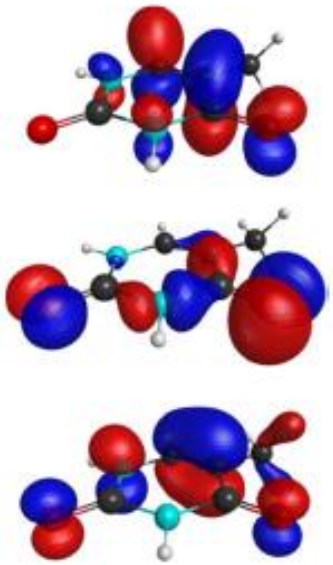


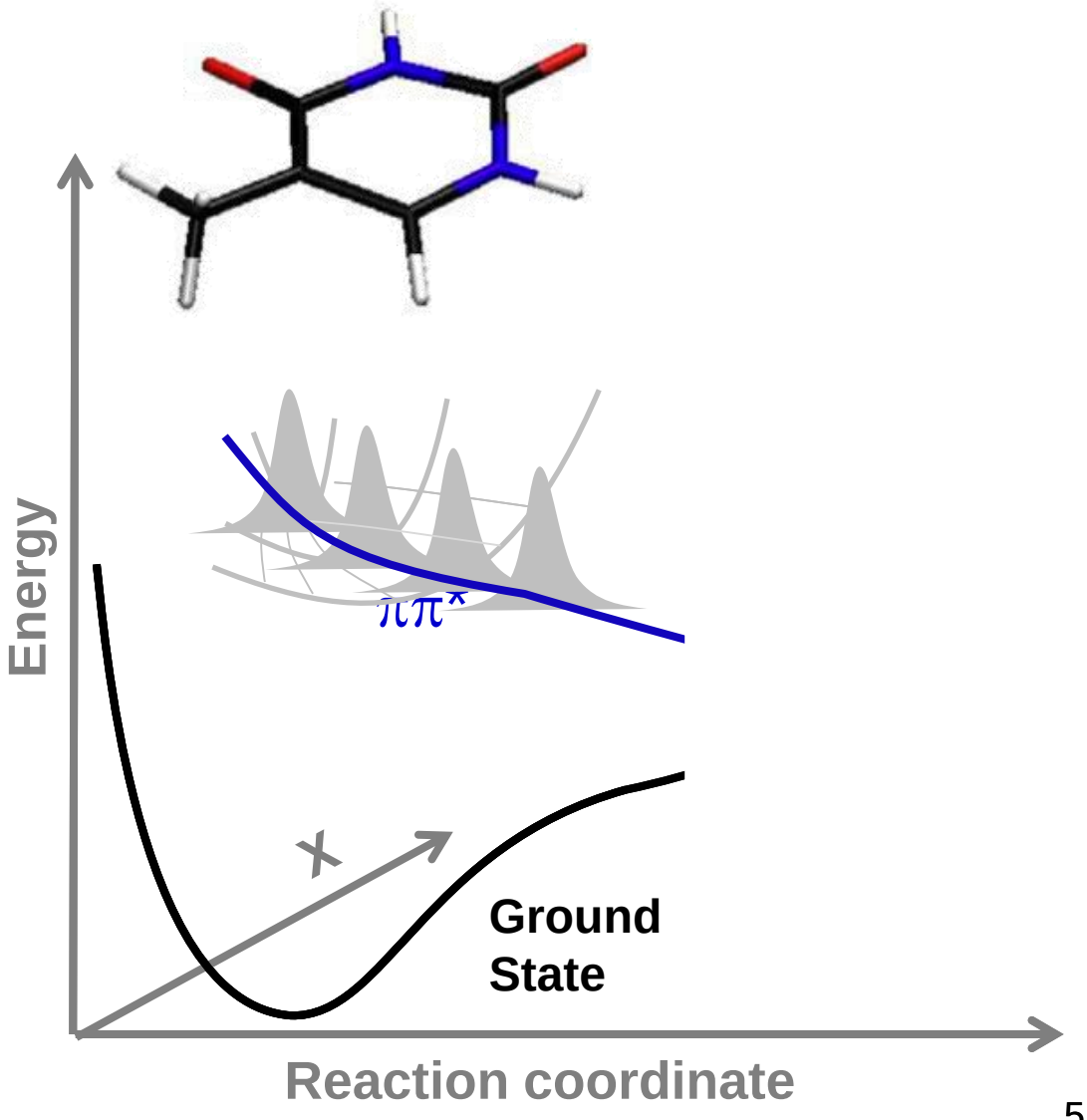




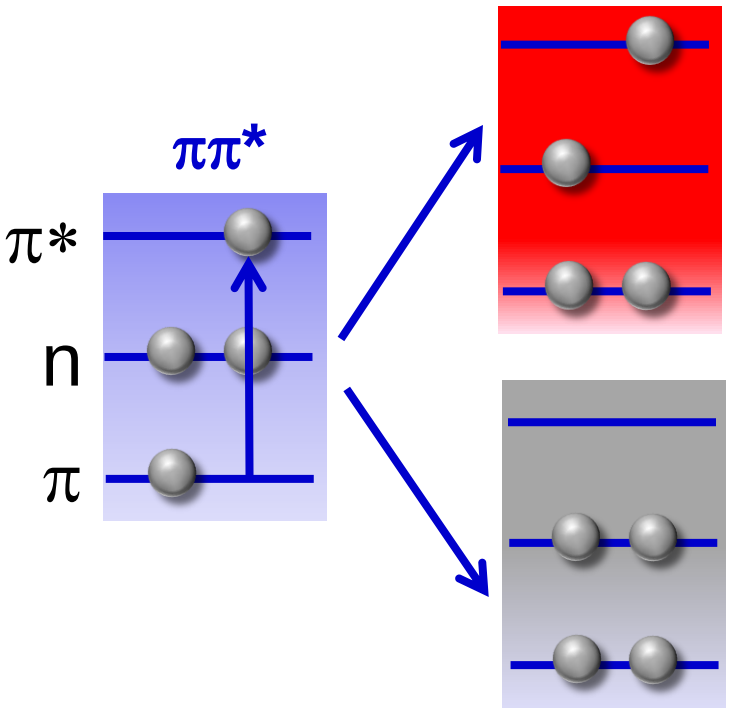
Electrons couple to nuclei.

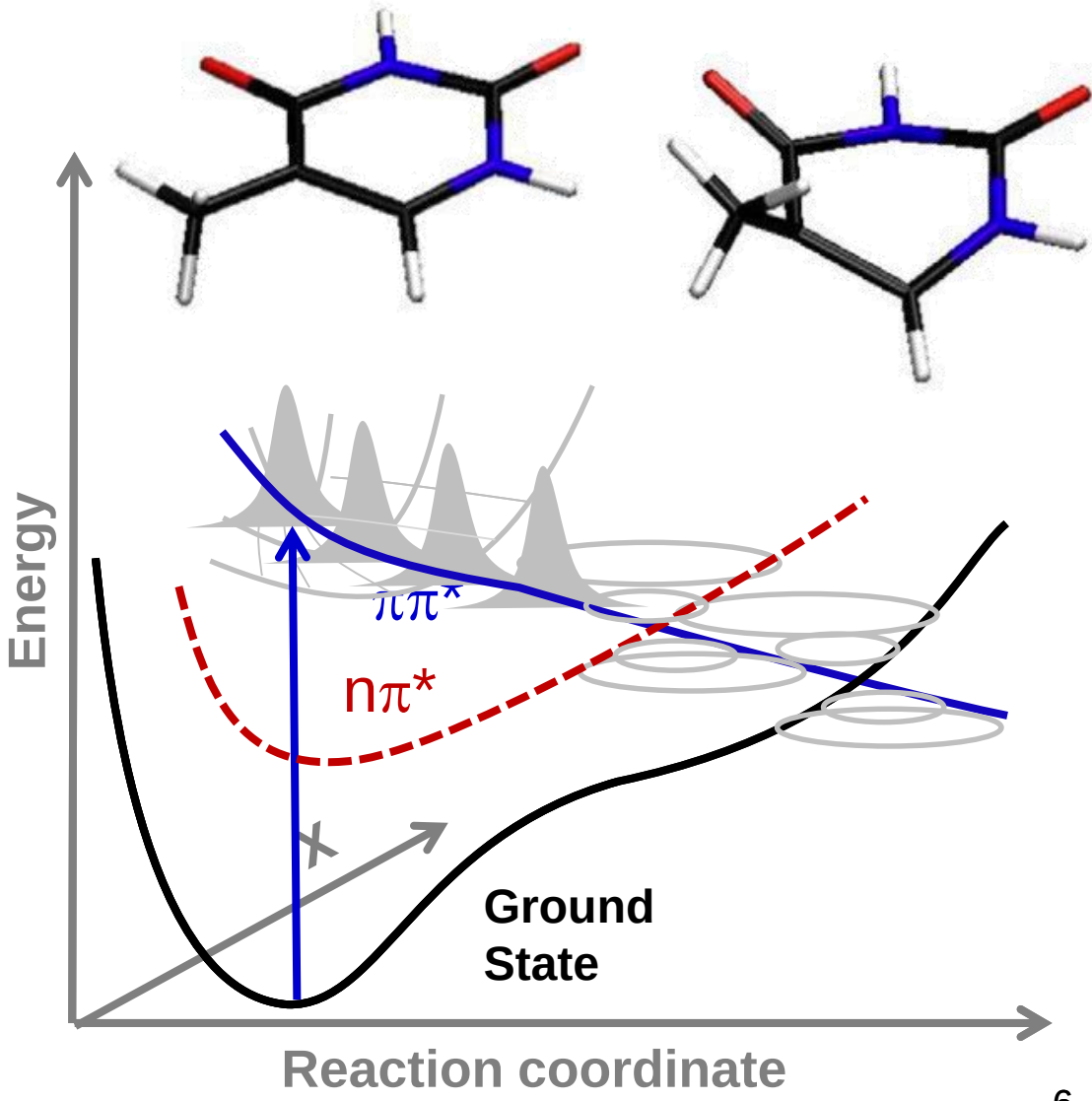




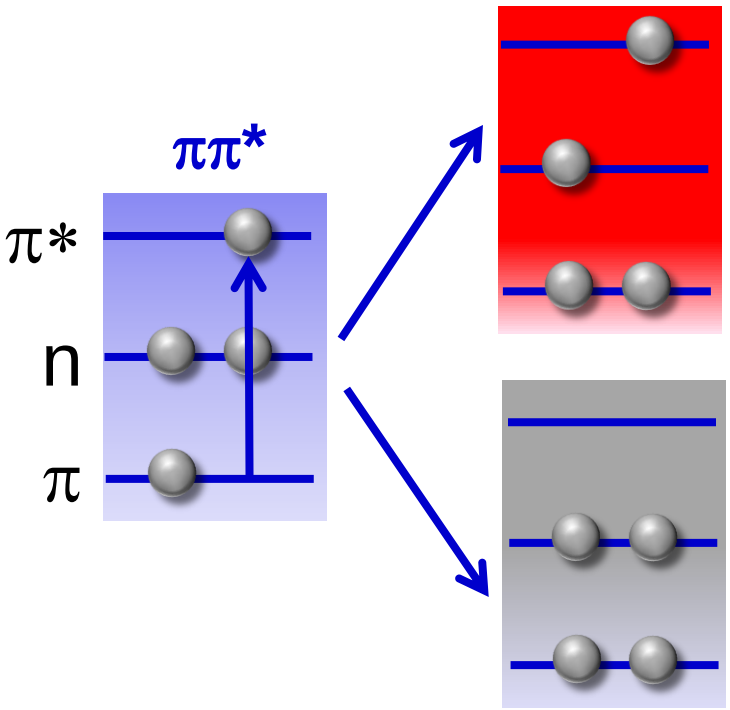


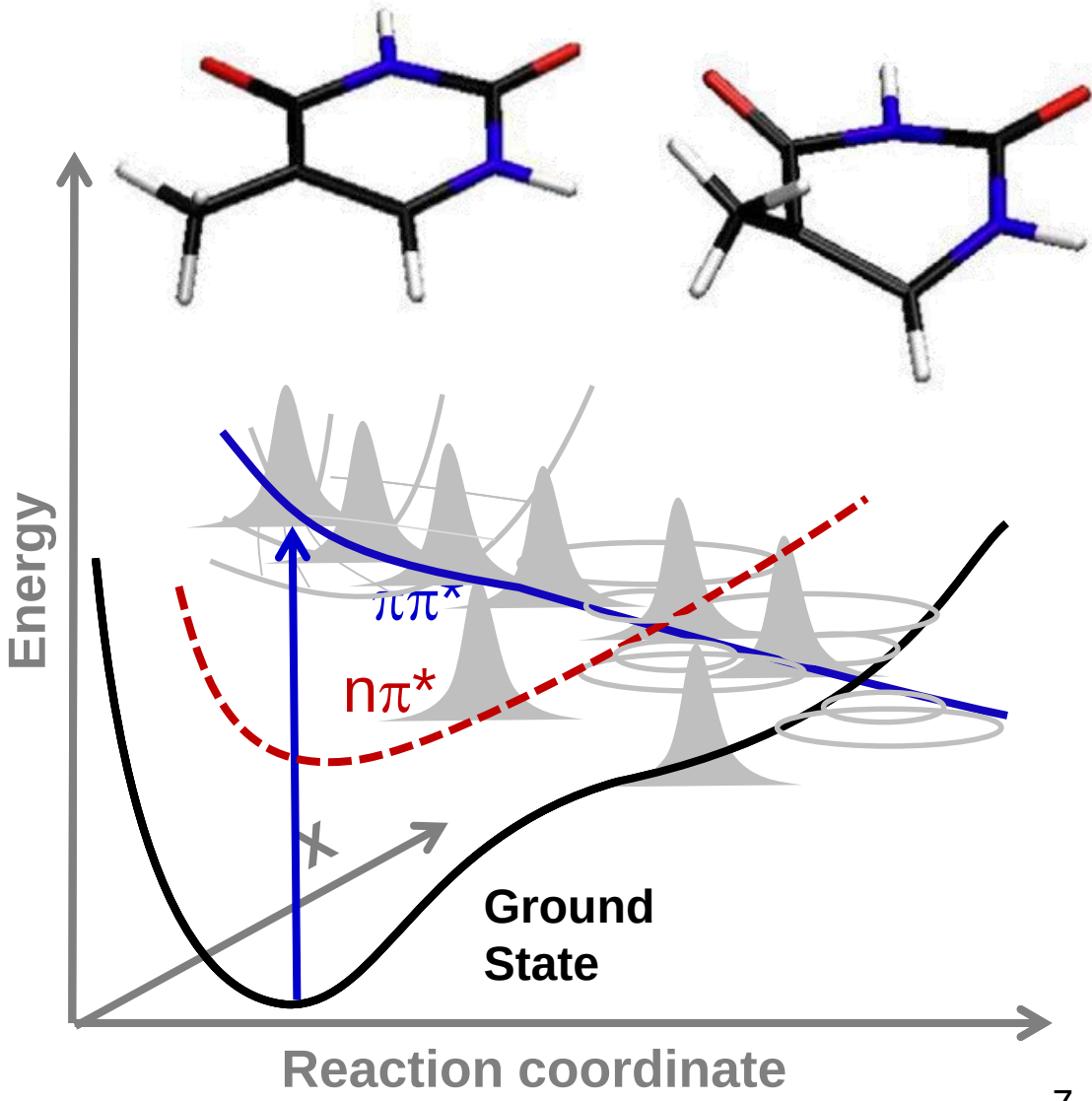
Nuclei couple to electrons.





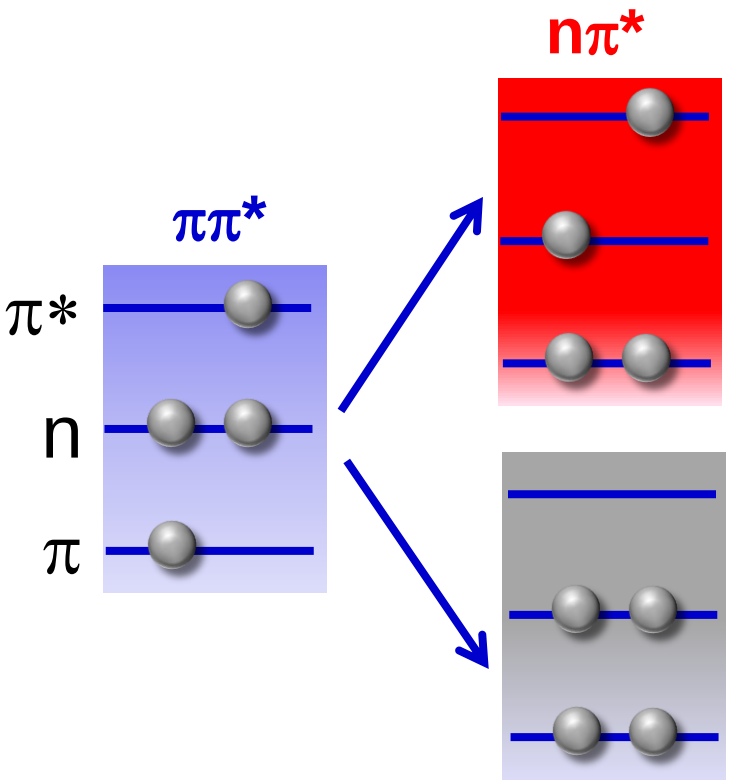
Nuclei couple to electrons.



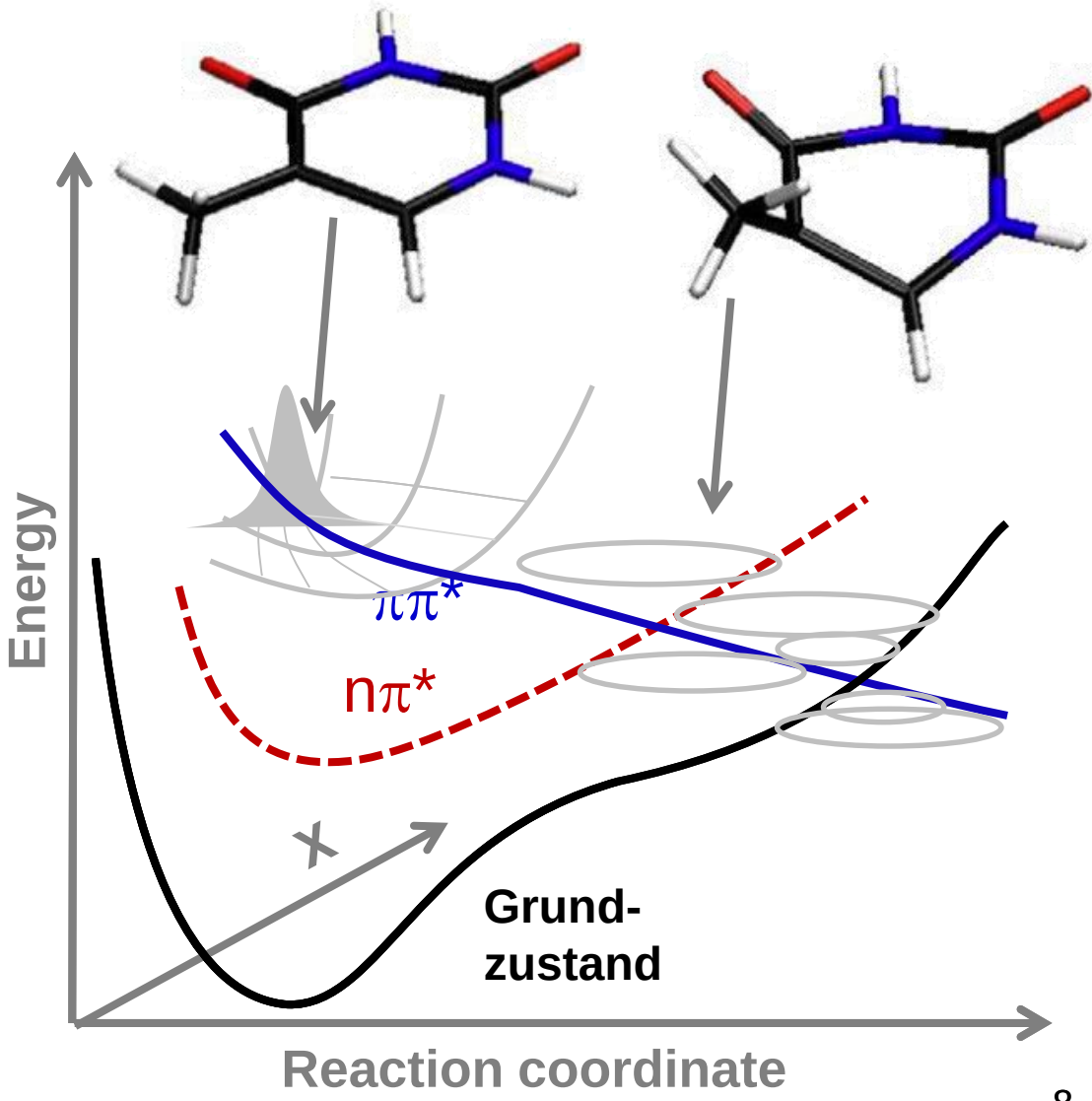


Two sides of the problem:

Electronic structure

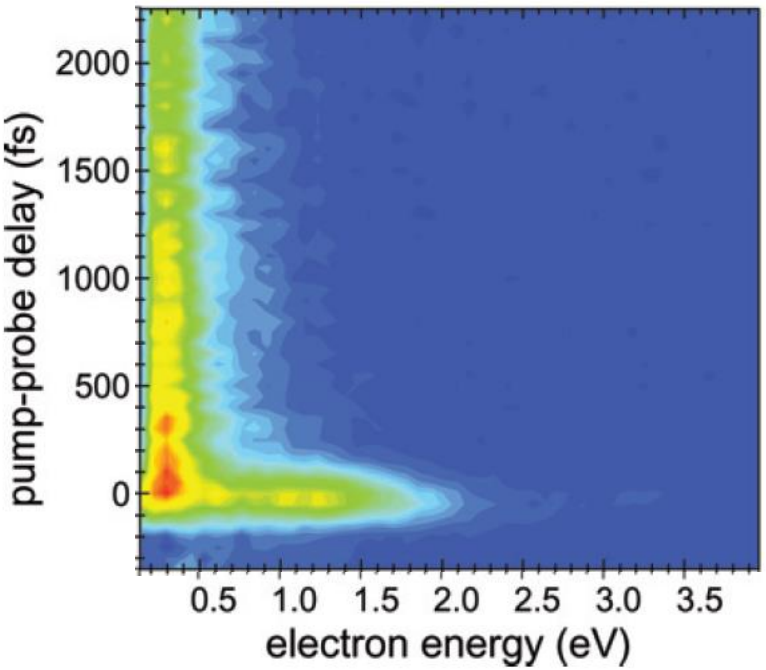


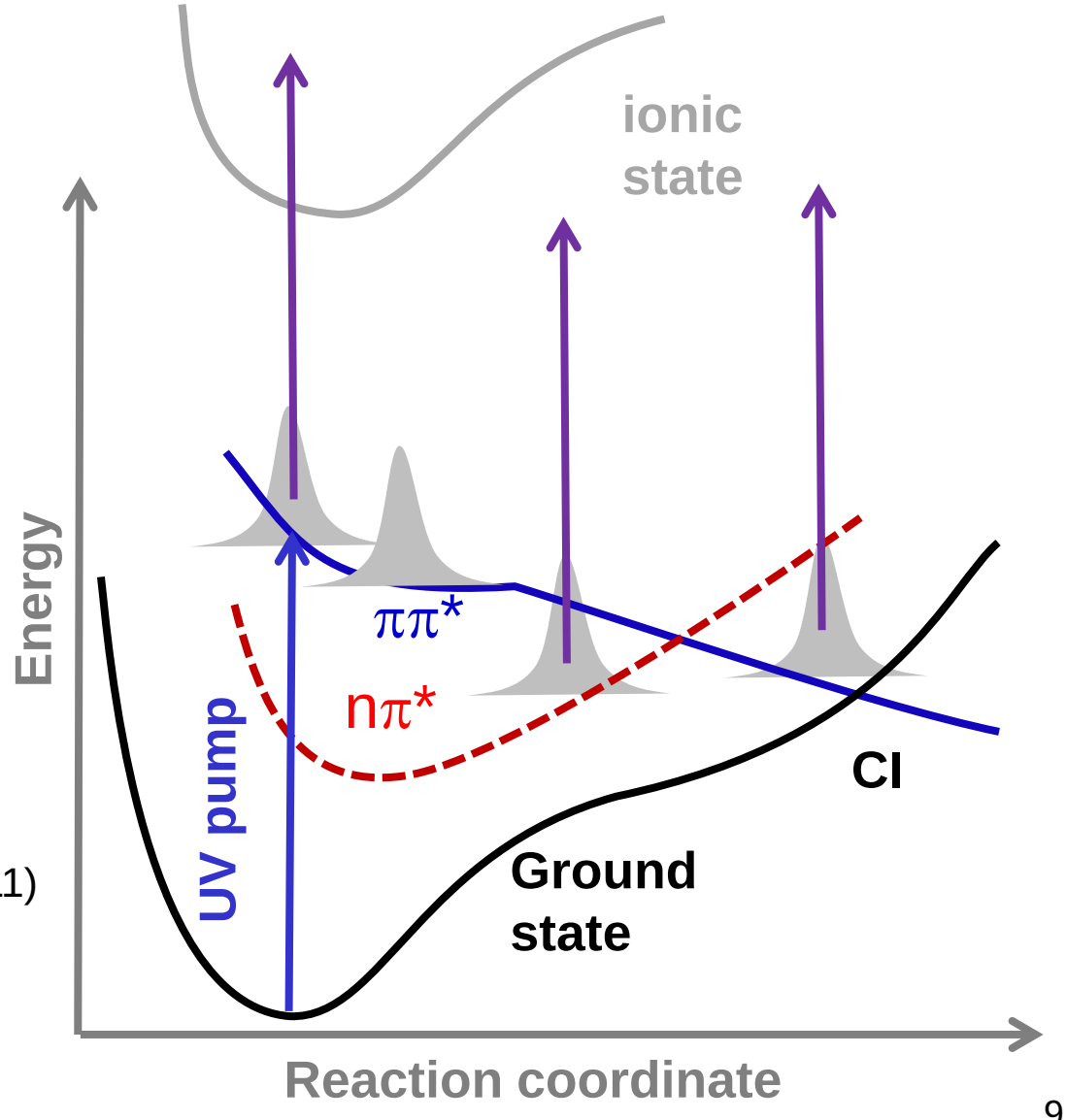
Nuclear geometry



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.





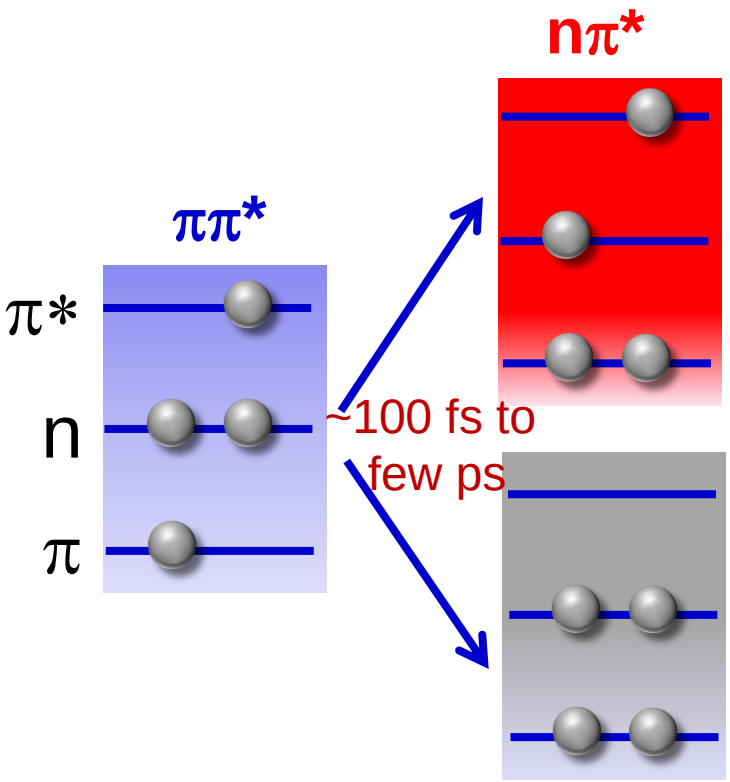
Ullrich et al. PCCP **6**, 2796 (2004)
Barbatti and Ullrich, PCCP **13**,15492 (2011)

Stolow, Weinacht, Newmark, Leone**...**

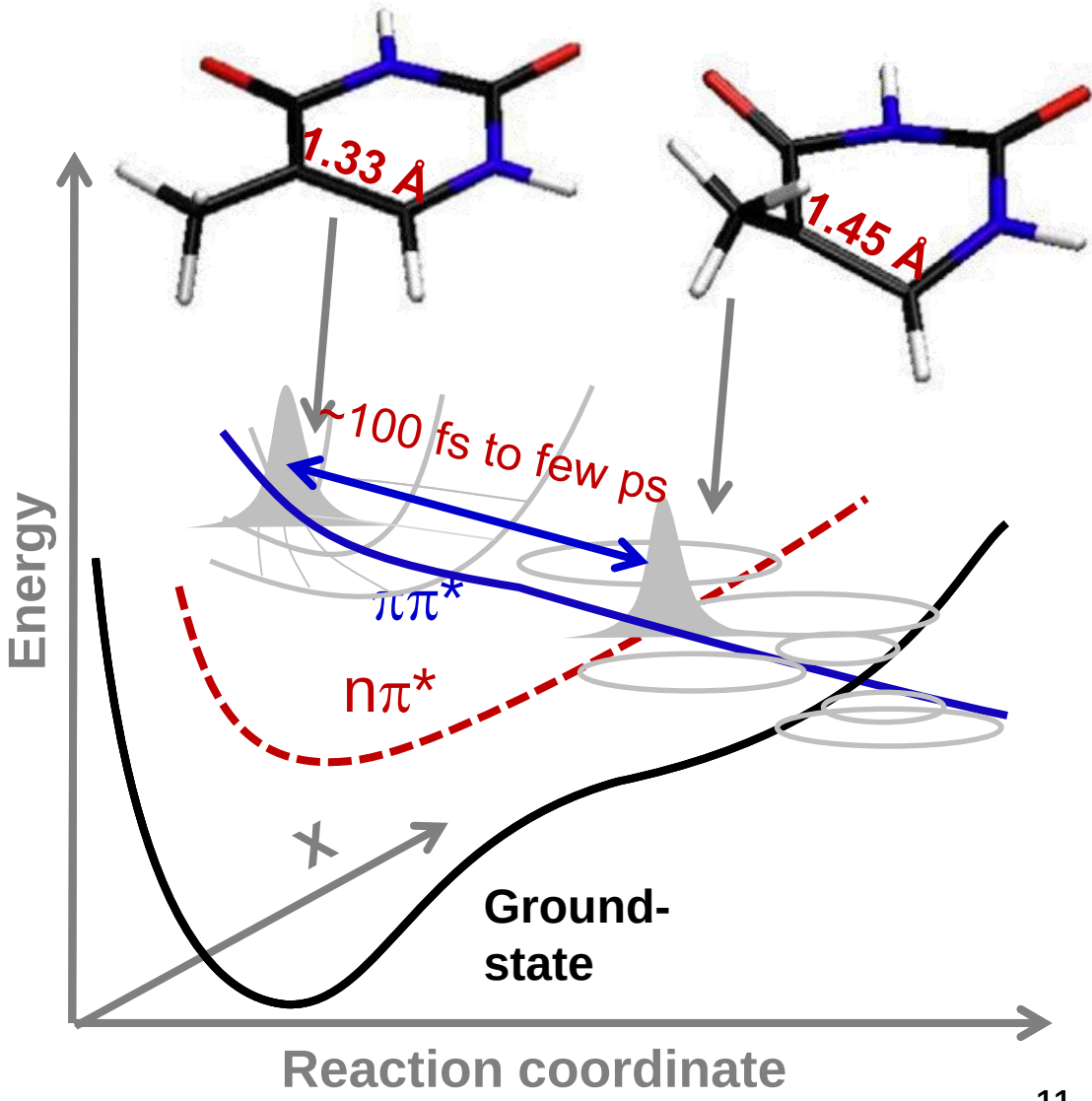
Can x-ray probing help to get an additional view on the process?

Is there a chance in the x-ray domain?

X-ray spectroscopy

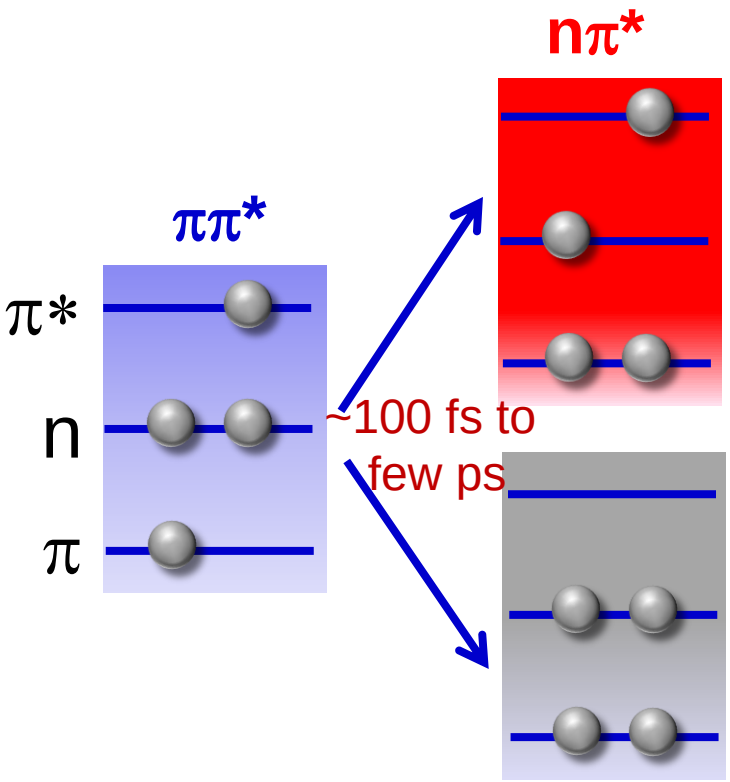


X-ray diffraction

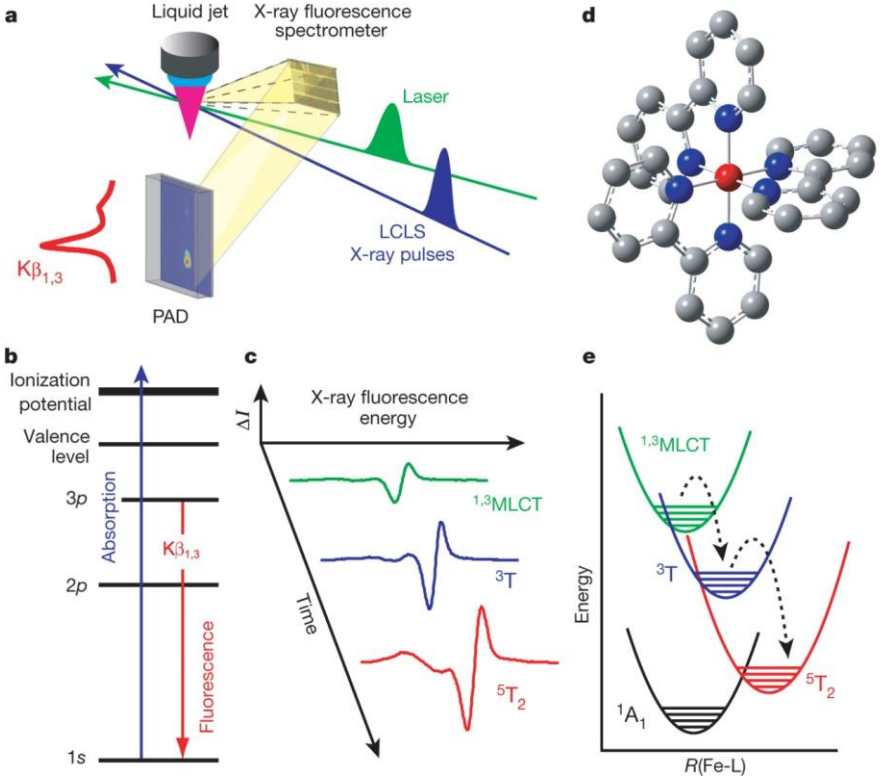


Element and site specific probing:

Electronic structure



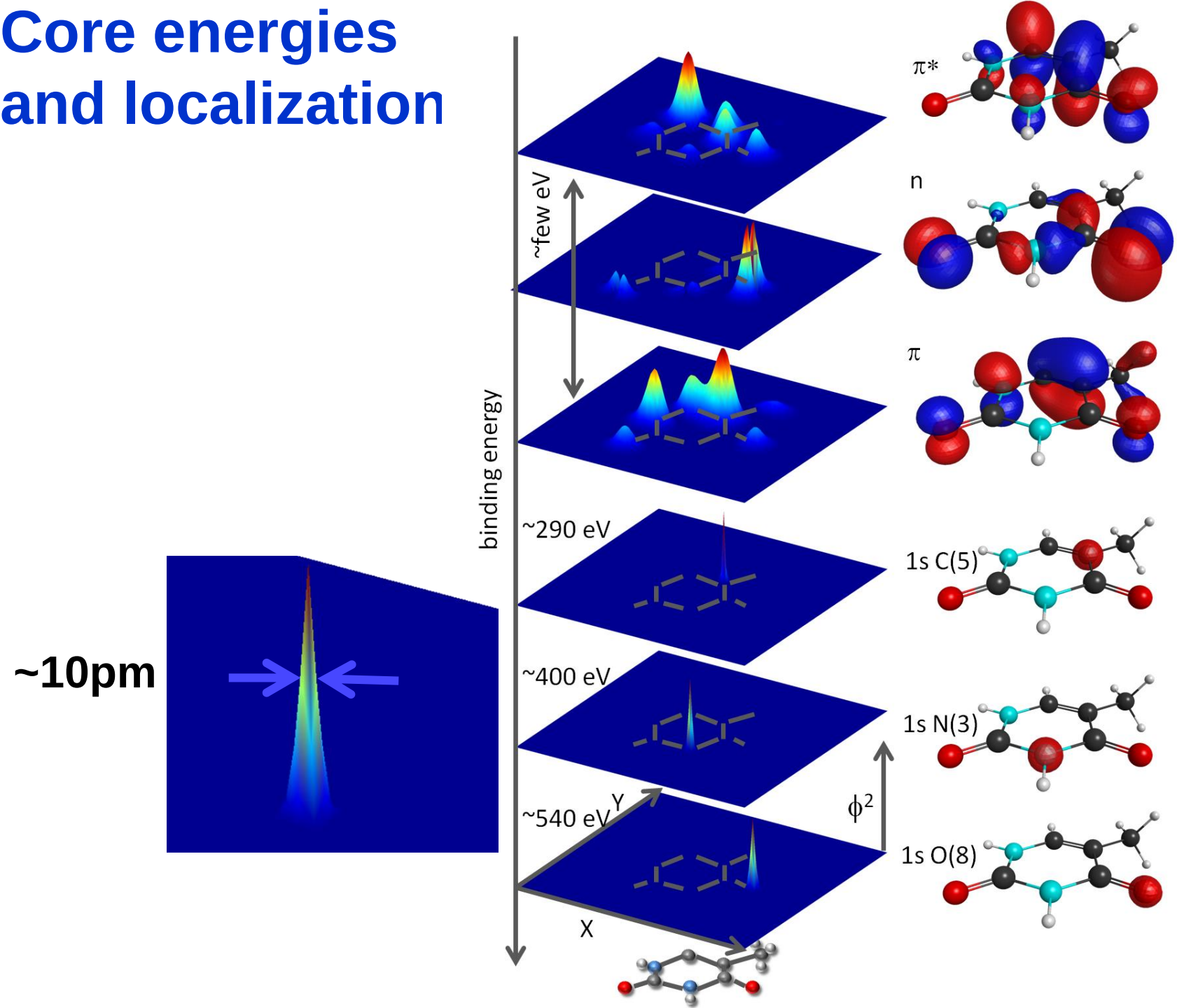
TR Hard X-ray spectroscopy: Metals



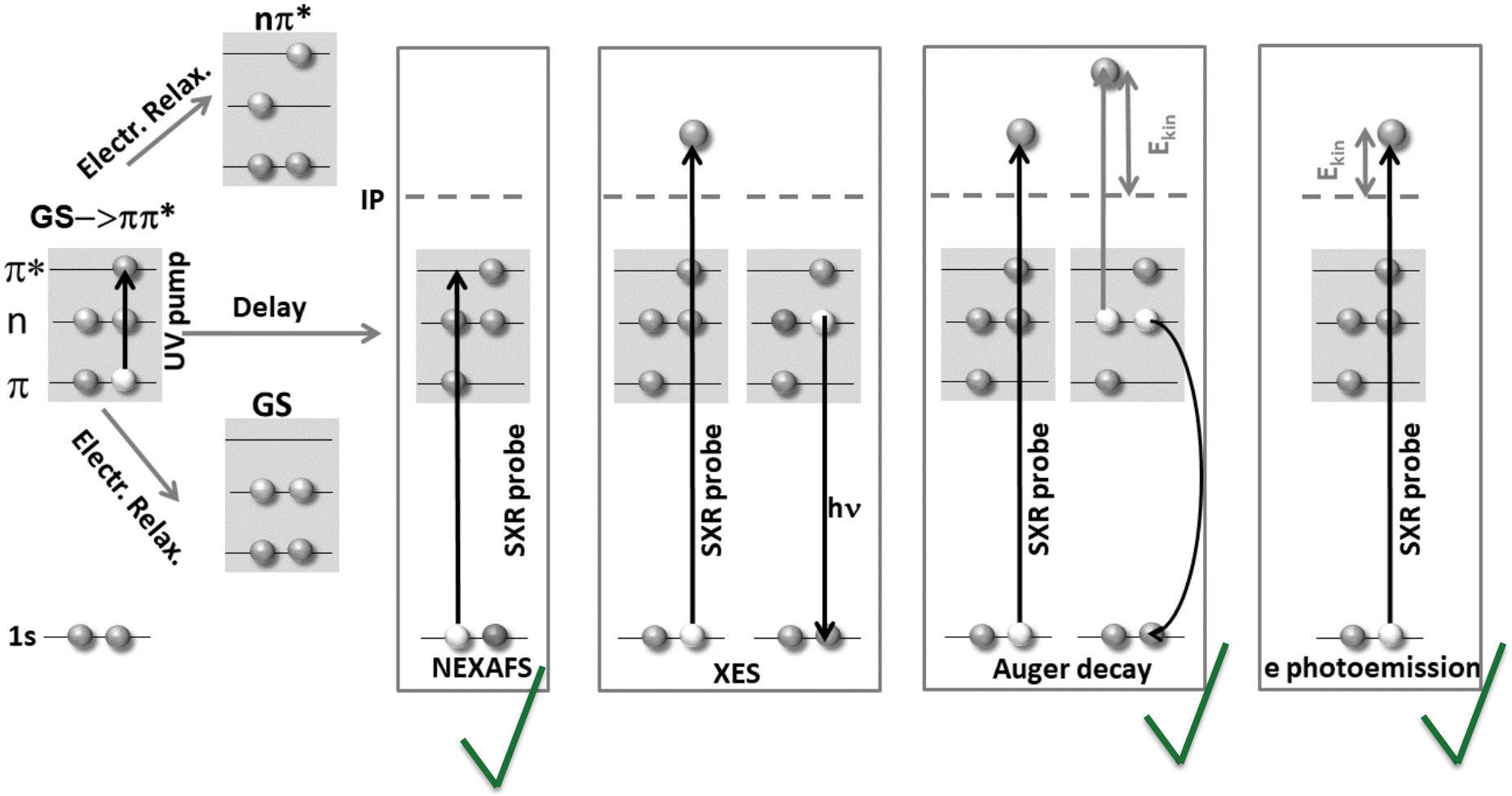
TR Soft X-ray spectroscopy: Access to all organic molecules via C, N, O edges!

Bressler et al., Science 323, 5913 (2009)
Milne, Penfold, Chergui Coord. Chem. Rev. 277 44 (2014)
Zhang *et al.*, Nature 509, 345 (2014)

Core energies and localization

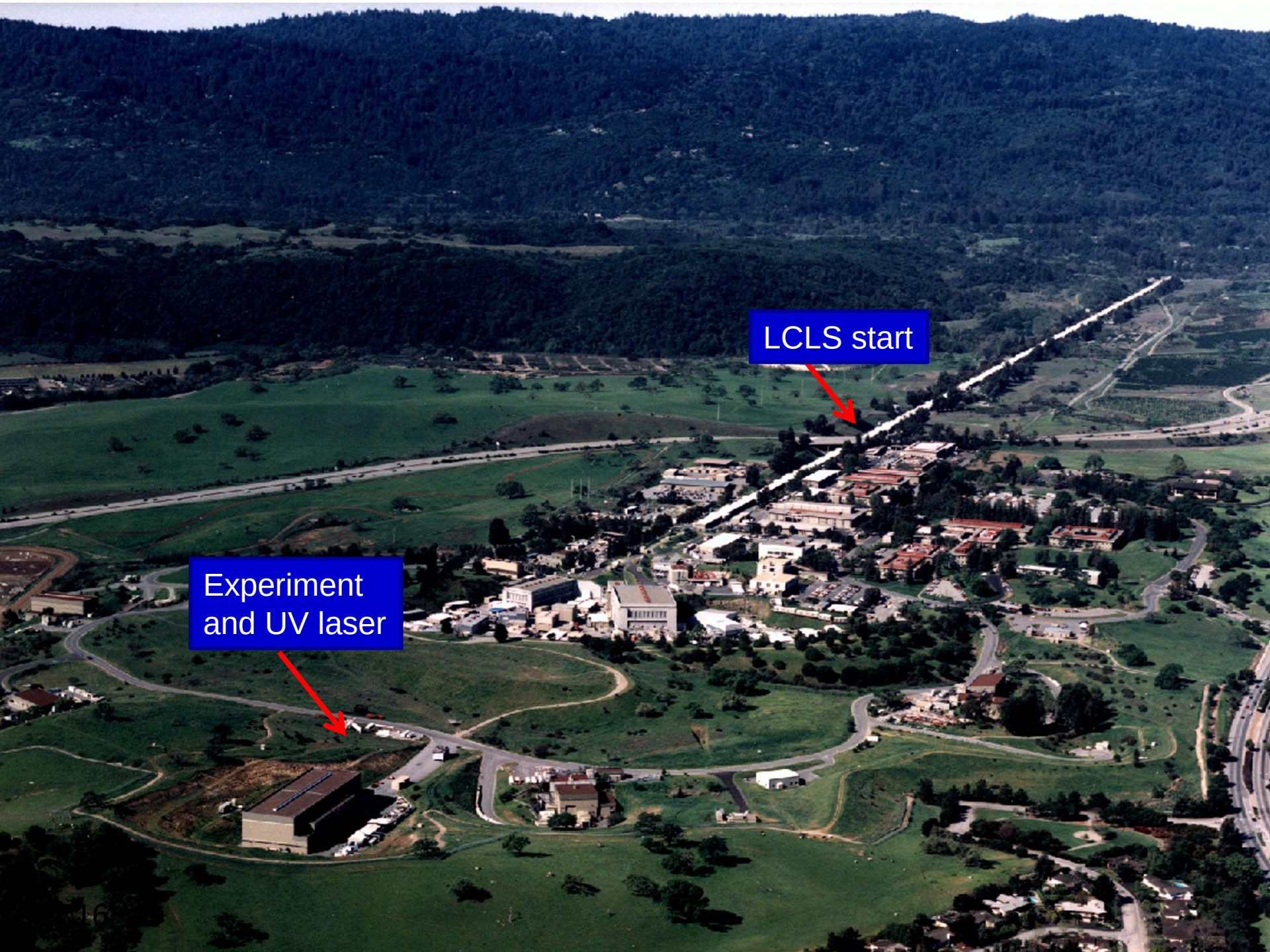


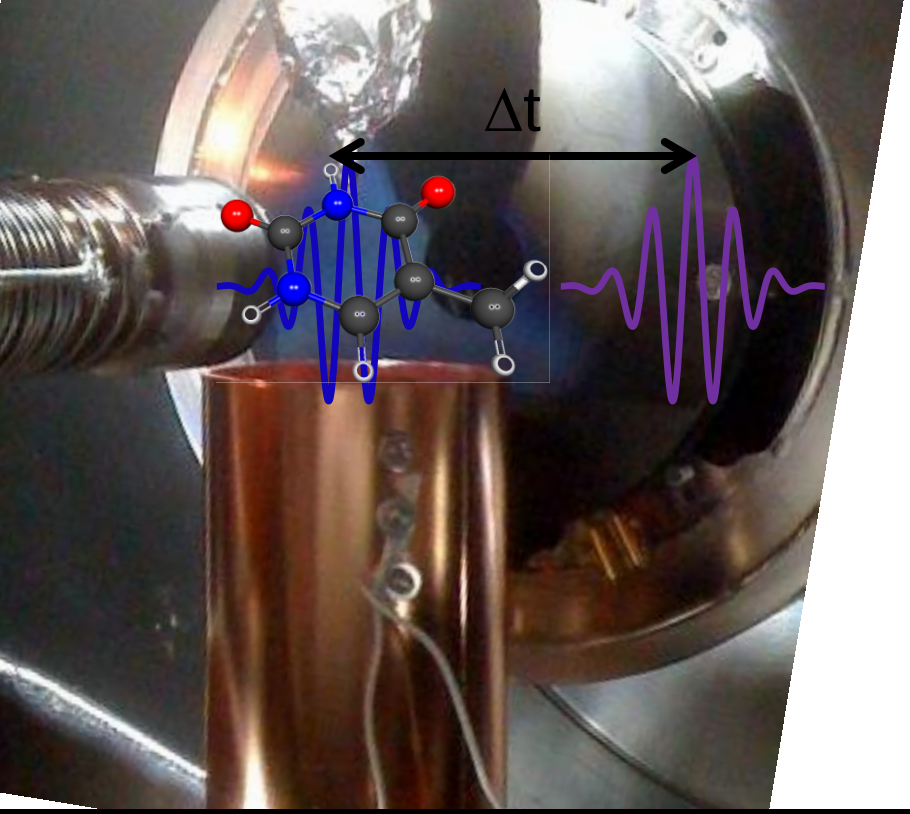
Different probe methods

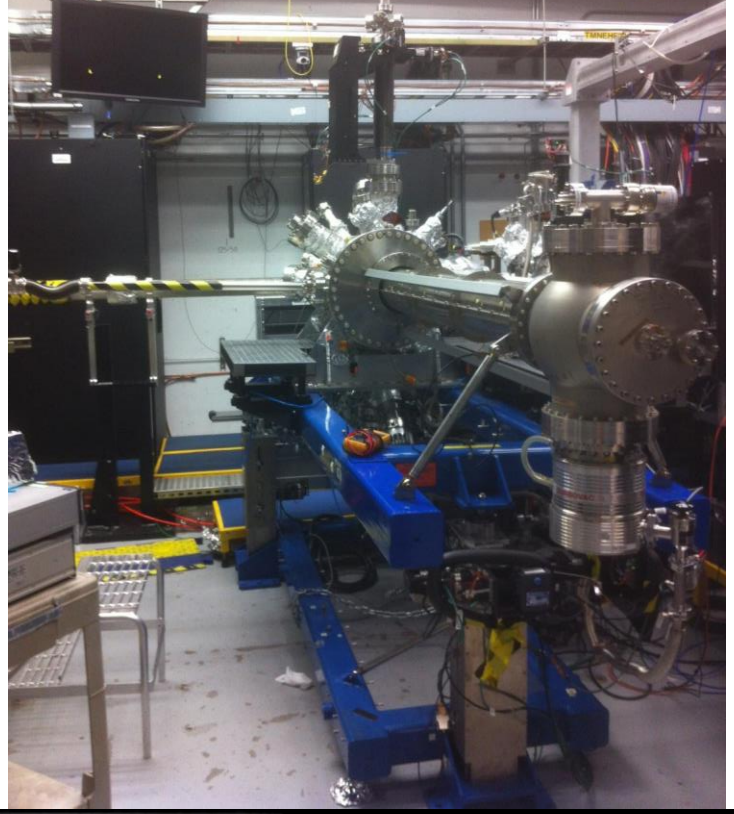


M. Gühr
in: Ultrafast Dynamics Driven by Intense Light Pulses,
eds.: M. Kitzler S. Graefe (Springer, Heidelberg, 2016)

Resonant probing of photoexcited dynamics


LCLS start
Experiment
and UV laser



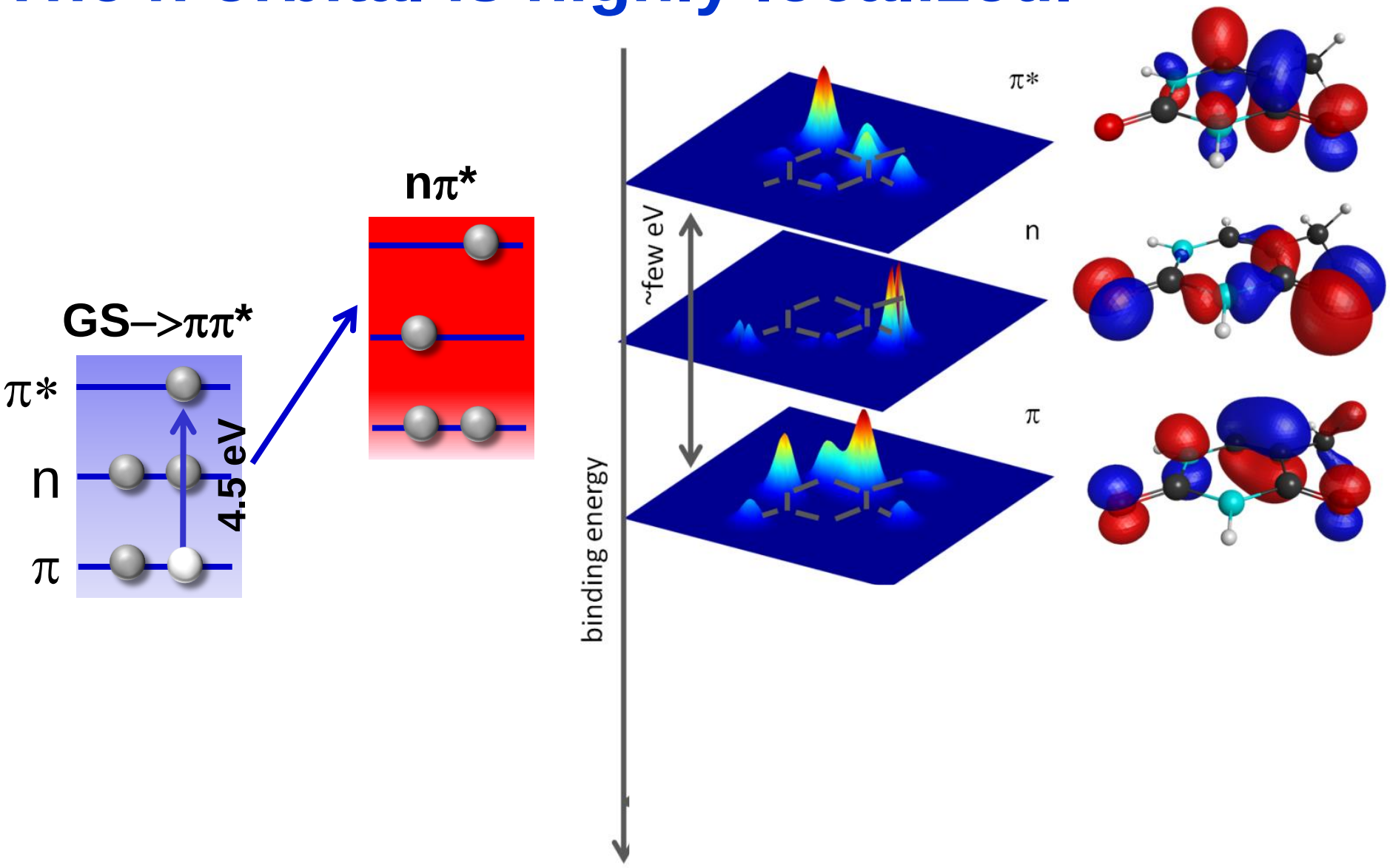


Focusing Optics

Monochromator
0.5 eV FWHM

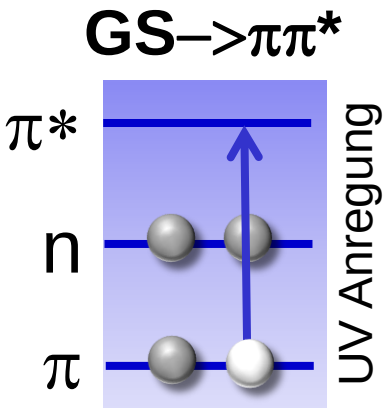
Spectral jitter - filtering by monochromator
Temporal jitter – single shot pulse correlator

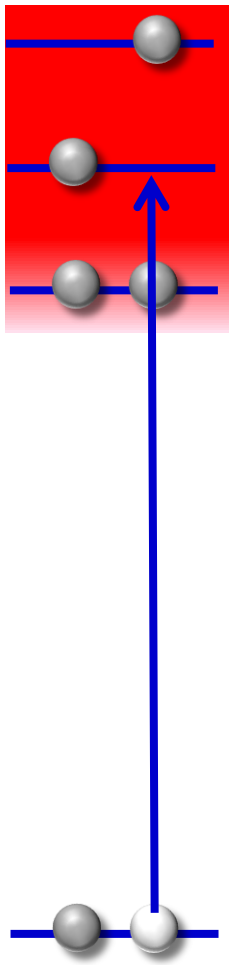
The n orbital is highly localized.

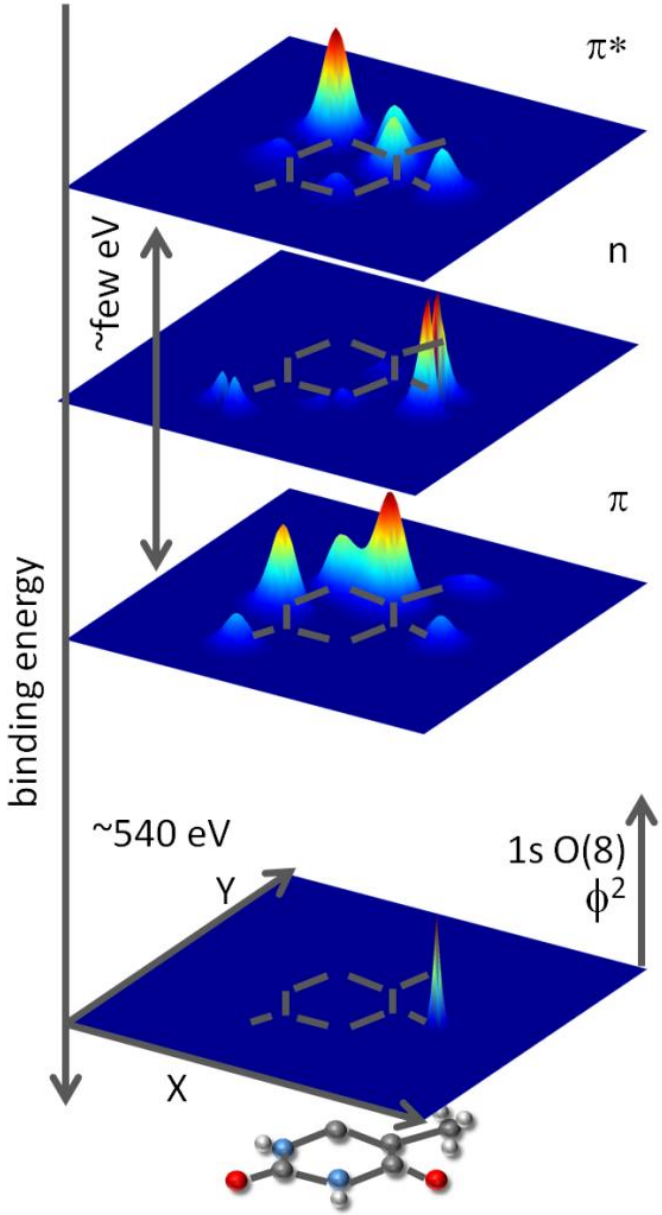


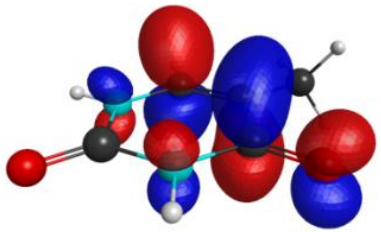
Previous work: McFarland *et al.*, Nature Comm. **5**, 4235 (2014)

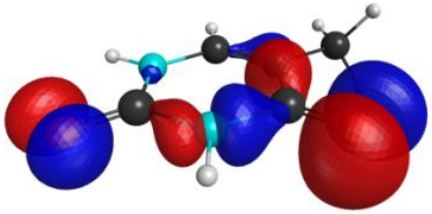
The1s to n absorption is strong.

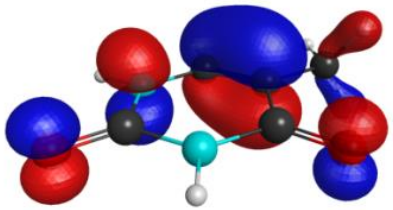


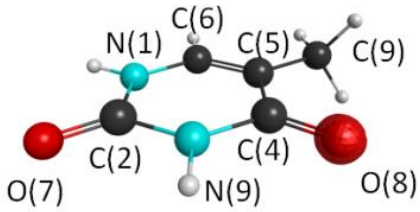




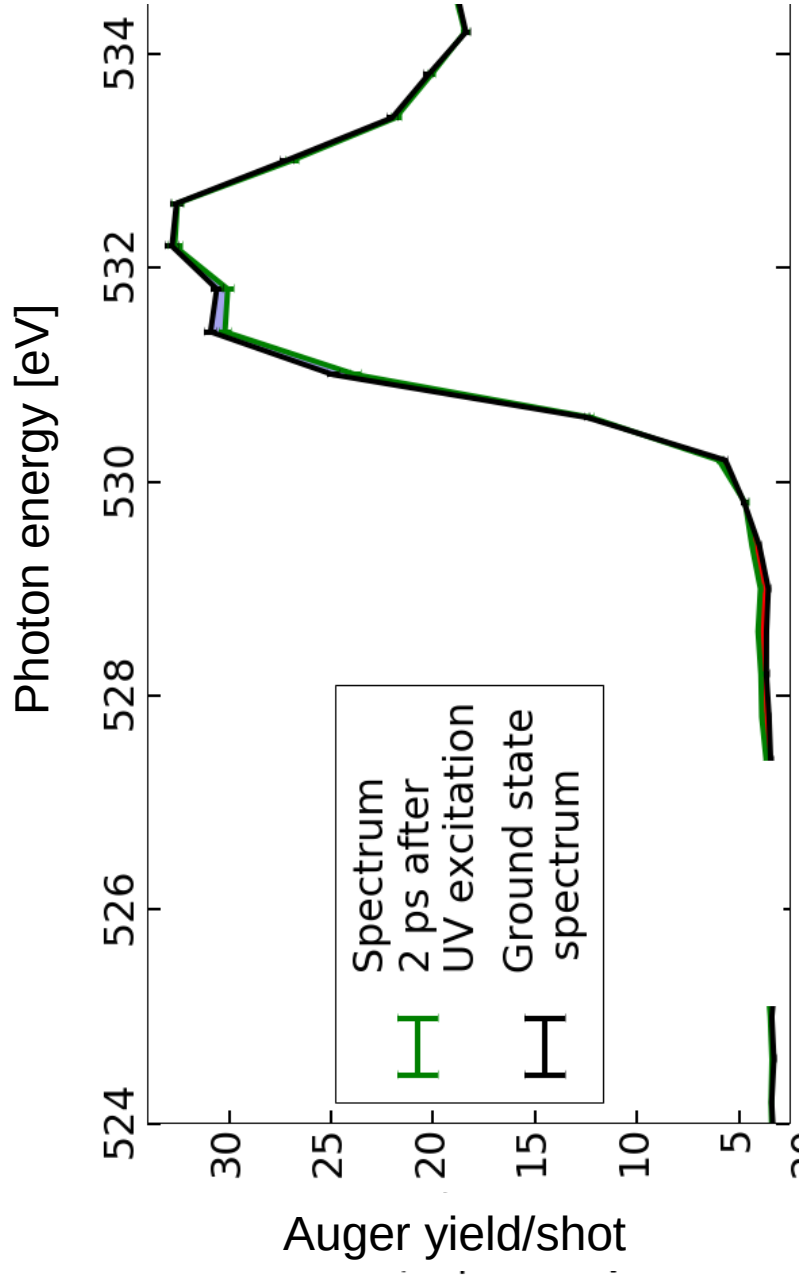


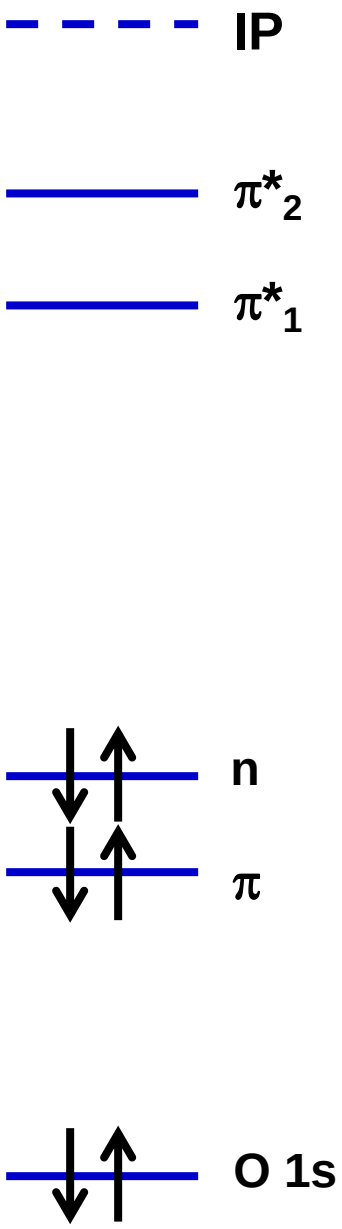


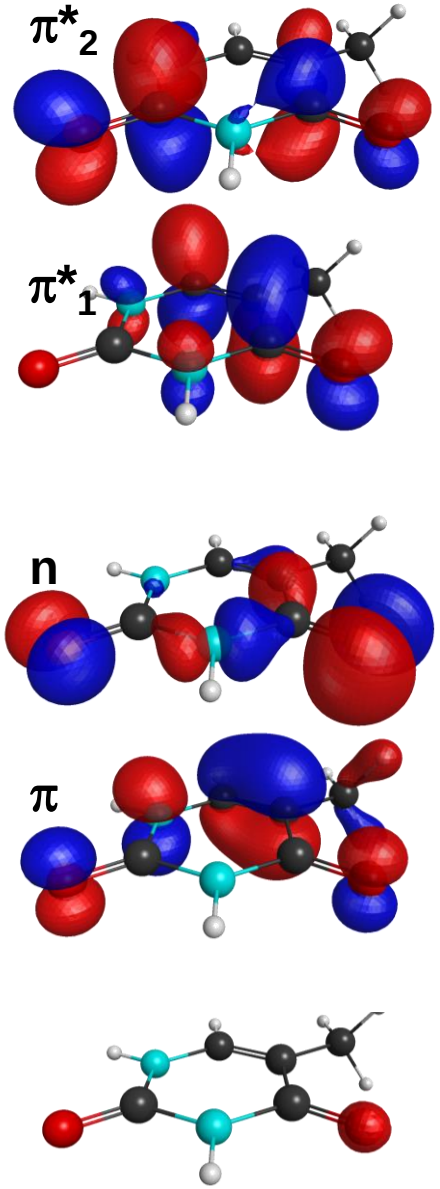




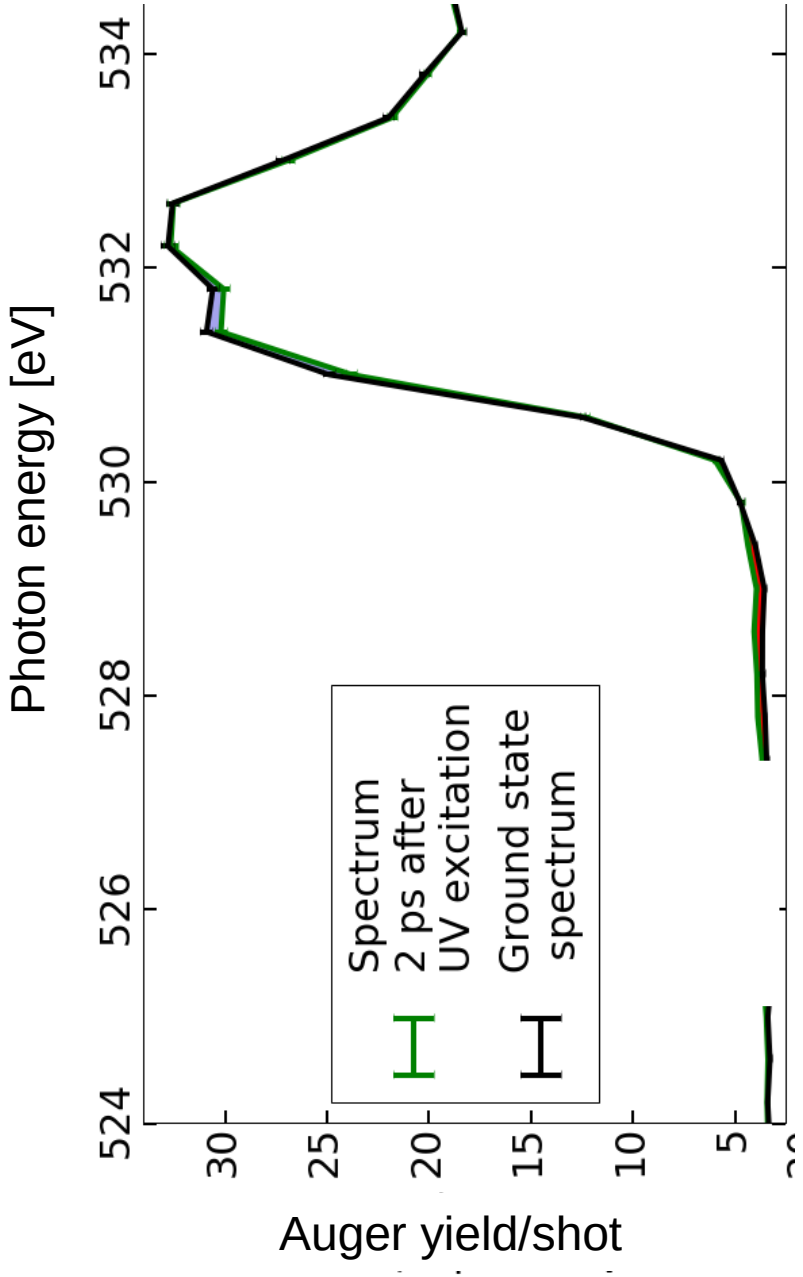
NEXAFS shows resonances

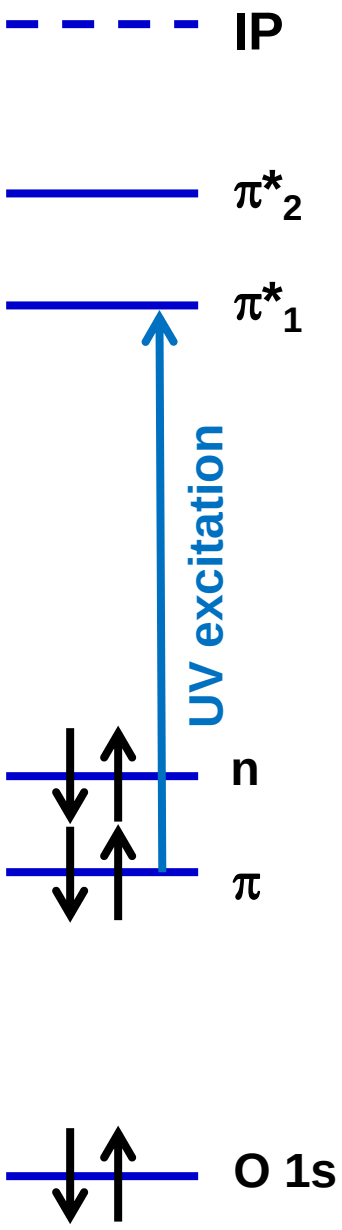


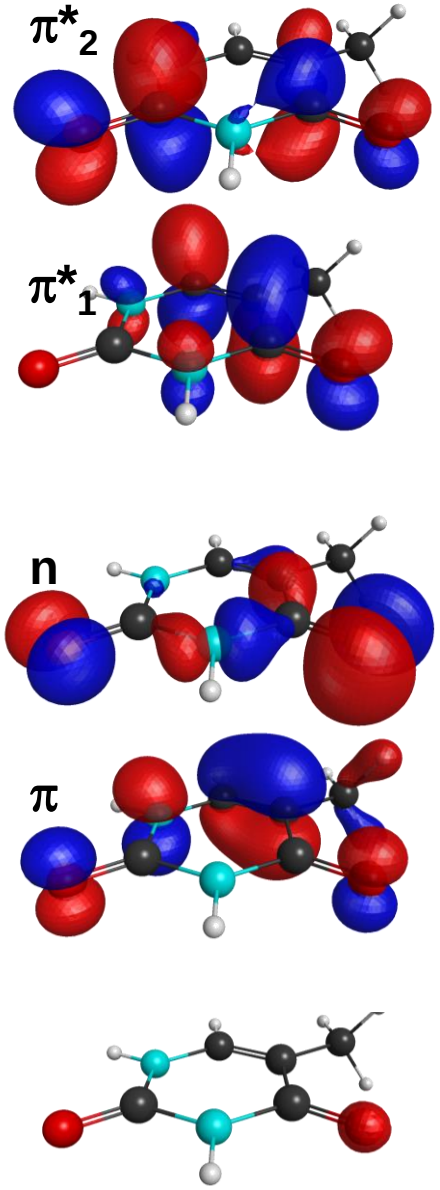




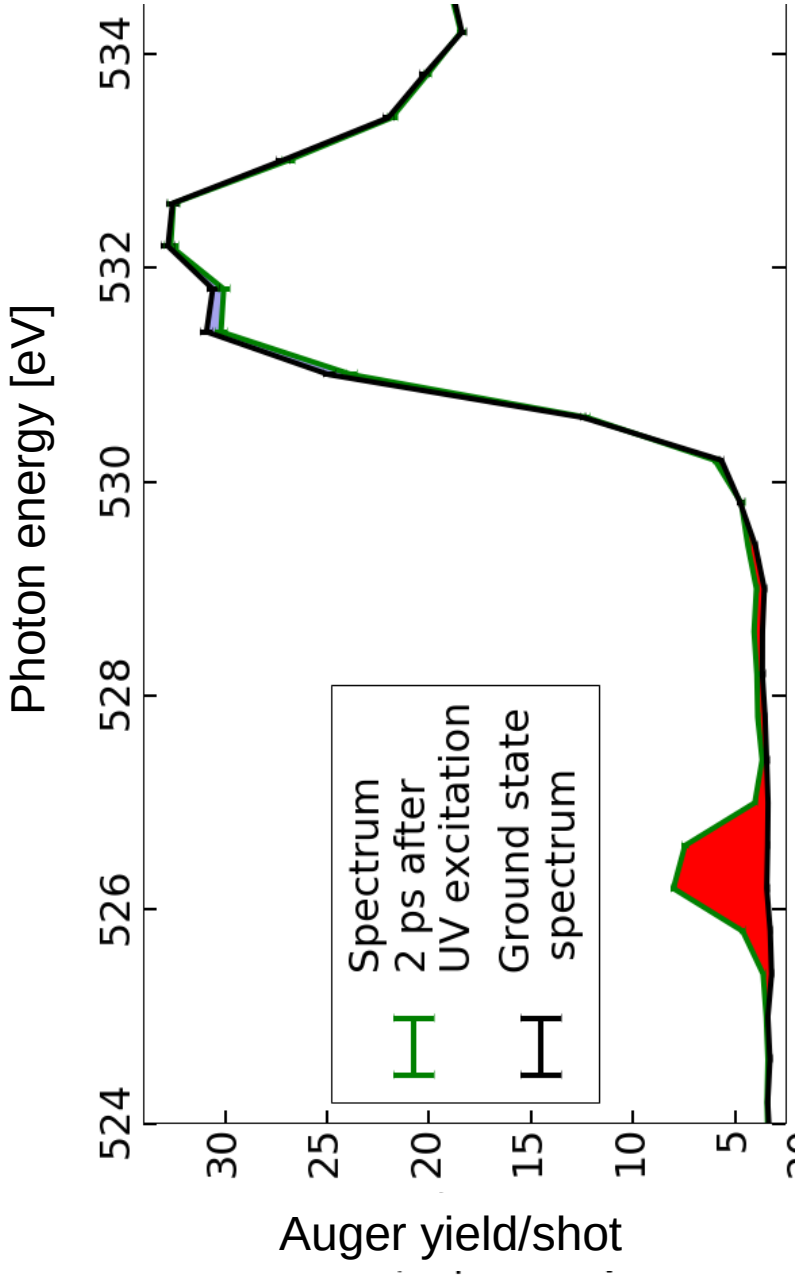
NEXAFS shows resonances

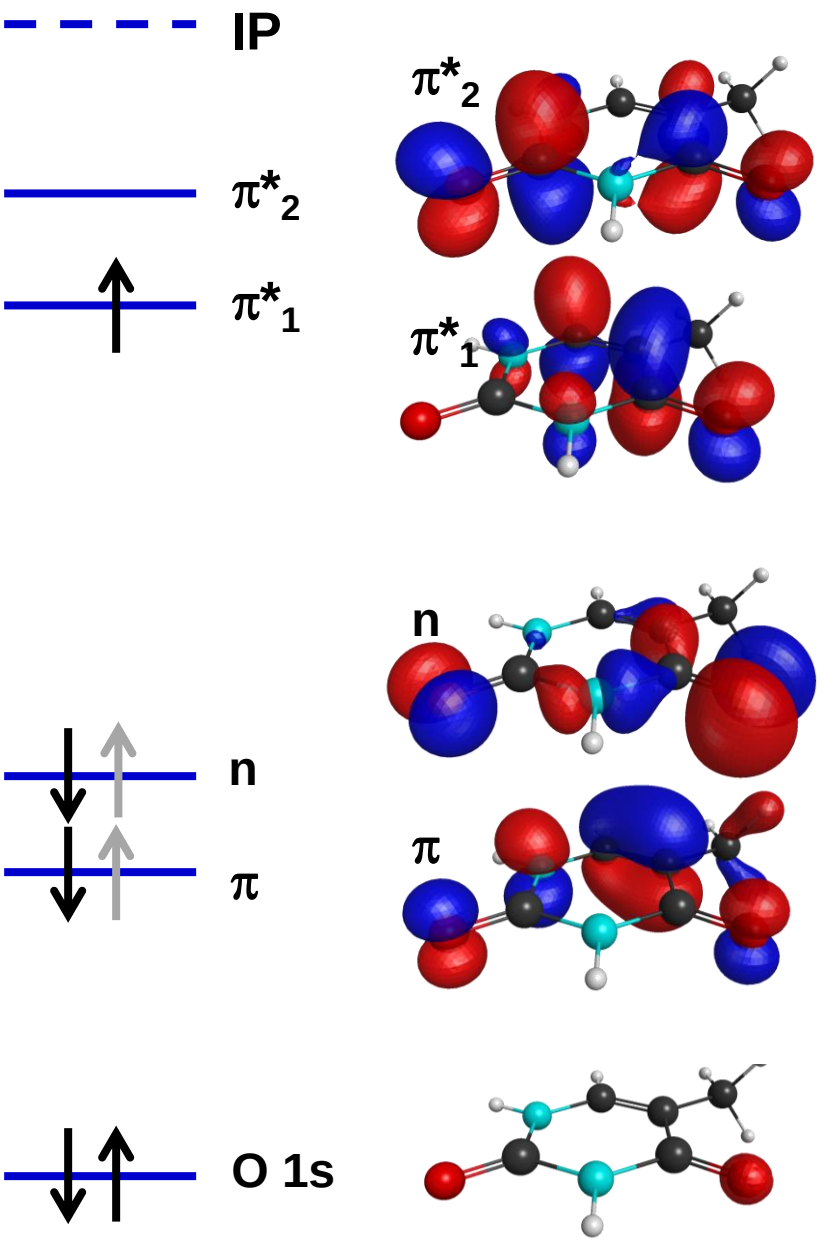


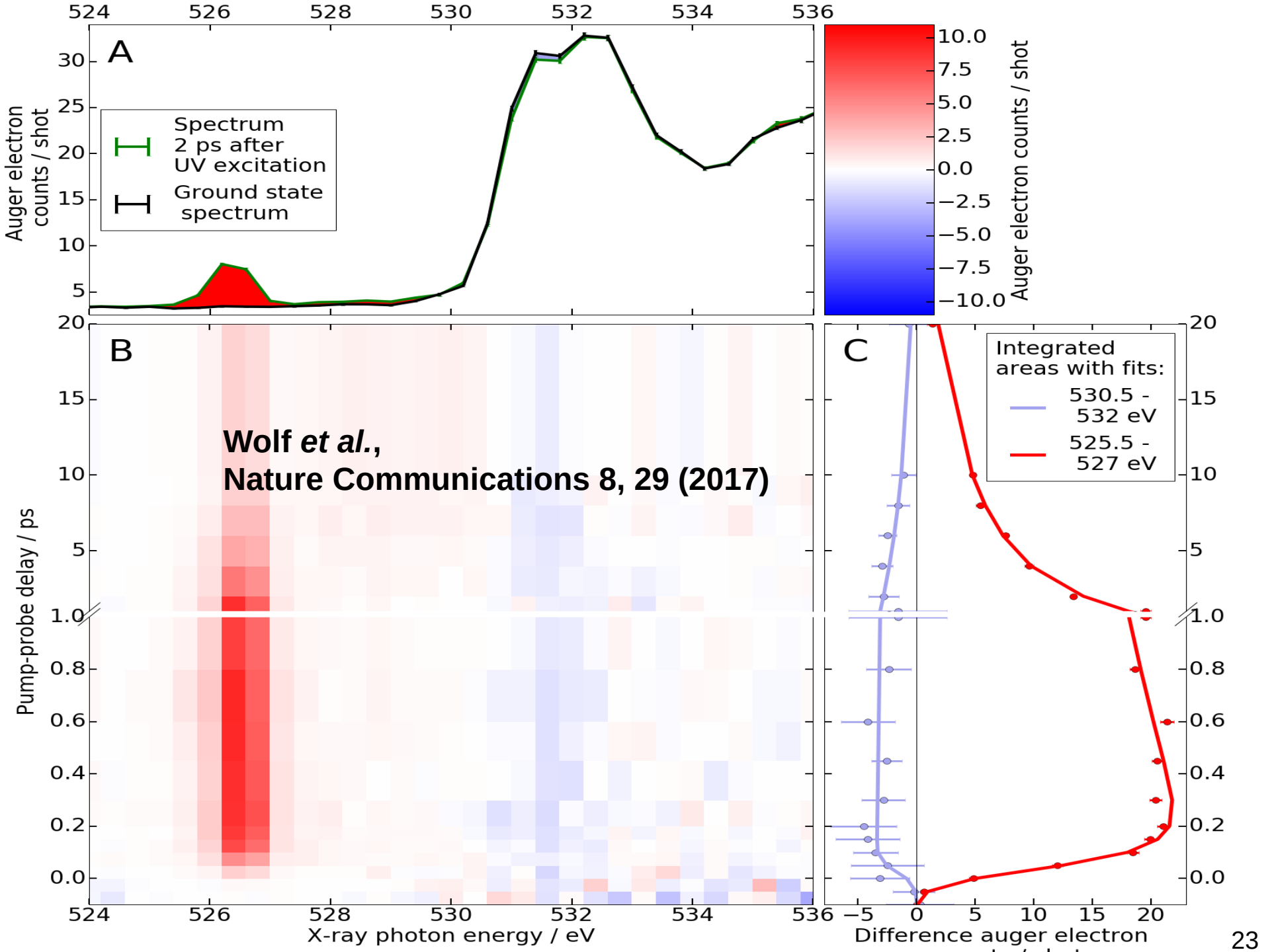


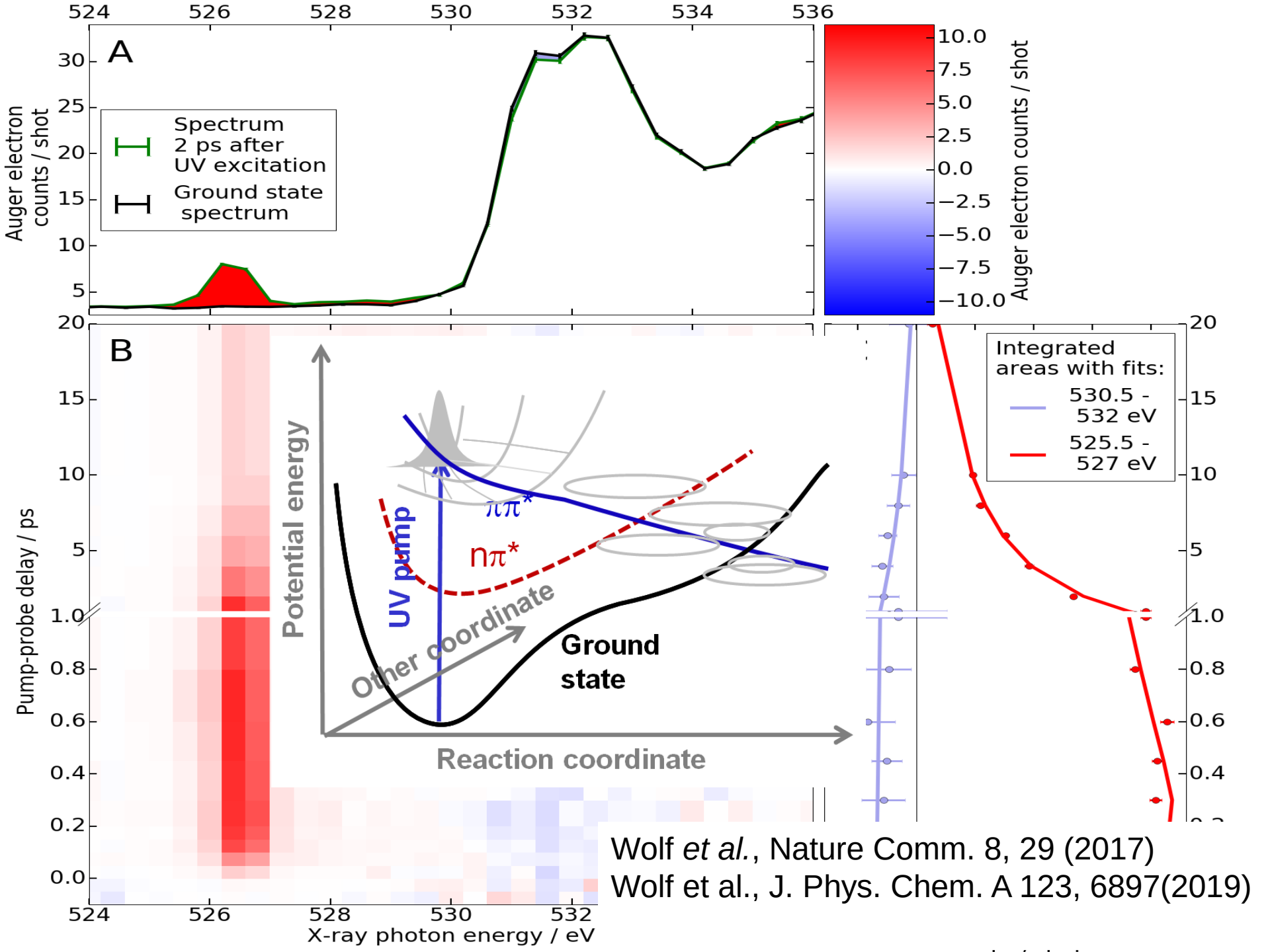


NEXAFS shows resonances

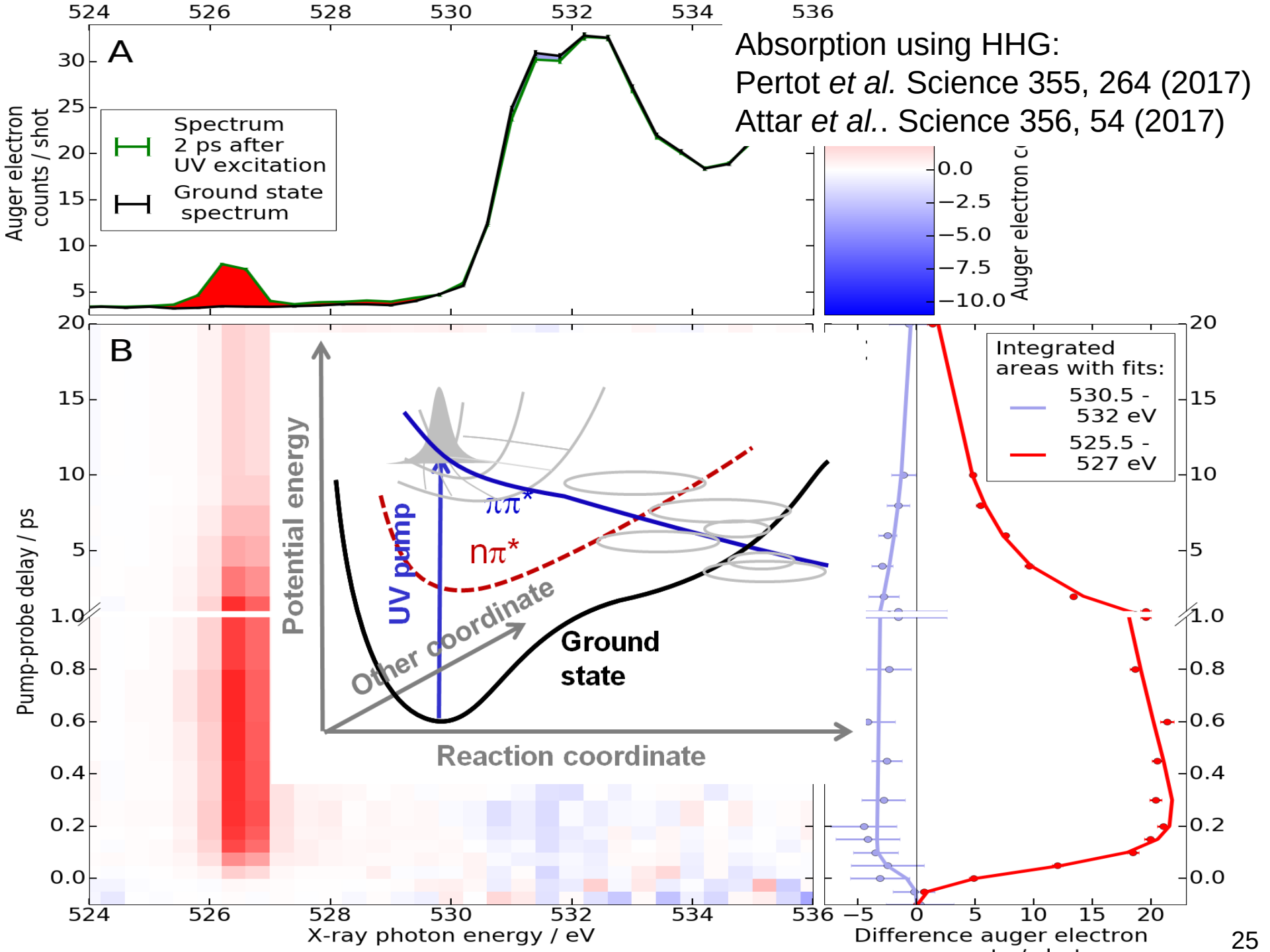




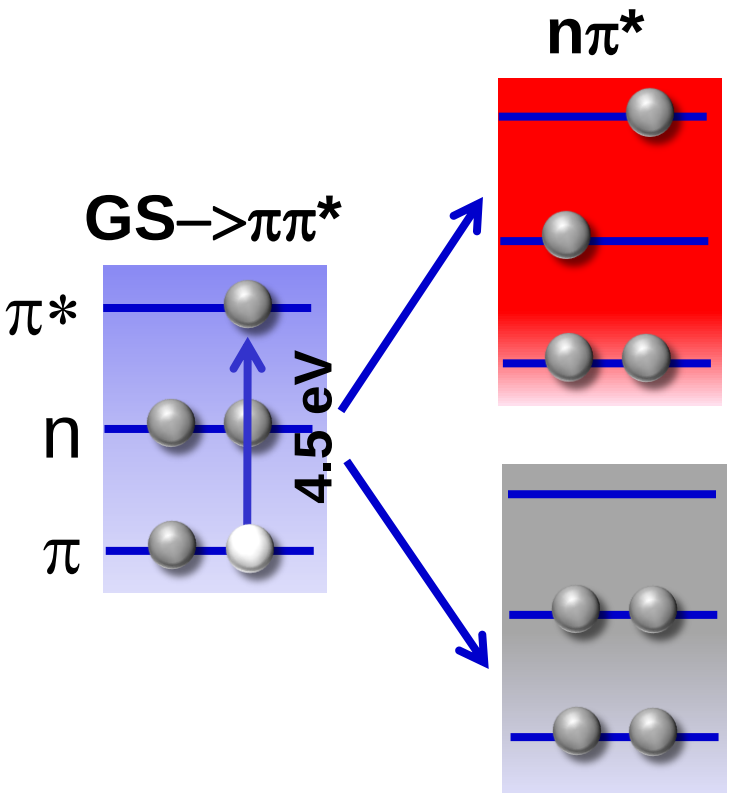

A
Spectrum
2 ps after
UV excitation
Ground state
spectrum
Auger electron
counts / shot
Auger electron counts / shot
B
Wolf *et al.*,
Nature Communications 8, 29 (2017)
Pump-probe delay / ps
X-ray photon energy / eV
C
Integrated
areas with fits:
530.5 -
532 eV
525.5 -
527 eV
Difference auger electron

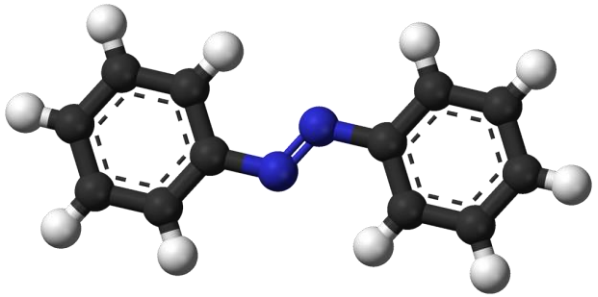


Wolf *et al.*, Nature Comm. 8, 29 (2017)
Wolf et al., J. Phys. Chem. A 123, 6897(2019)

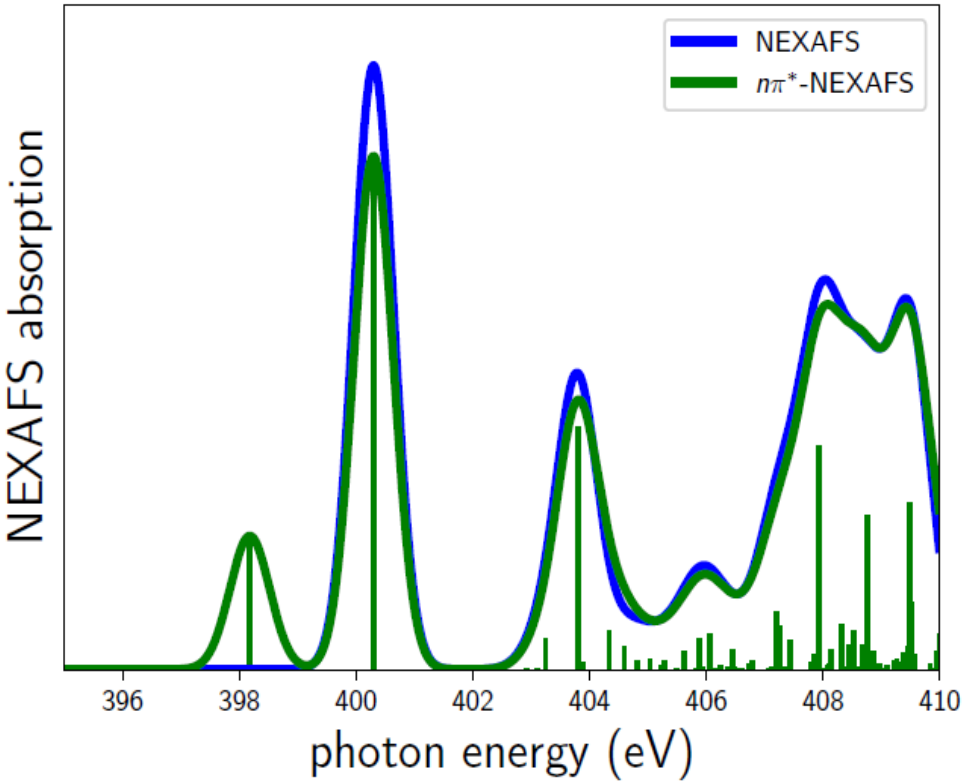

Absorption using HHG:
Pertot et al. Science 355, 264 (2017)
Attar et al.. Science 356, 54 (2017)
A
Auger electron counts / shot
Spectrum 2 ps after UV excitation
Ground state spectrum
B
Pump-probe delay / ps
X-ray photon energy / eV
Potential energy
UV pump
ππ*
nπ*
Other coordinate
Ground state
Reaction coordinate
Integrated areas with fits:
530.5 - 532 eV
525.5 - 527 eV
Difference auger electron

*The nπ** relaxation is a universal process.





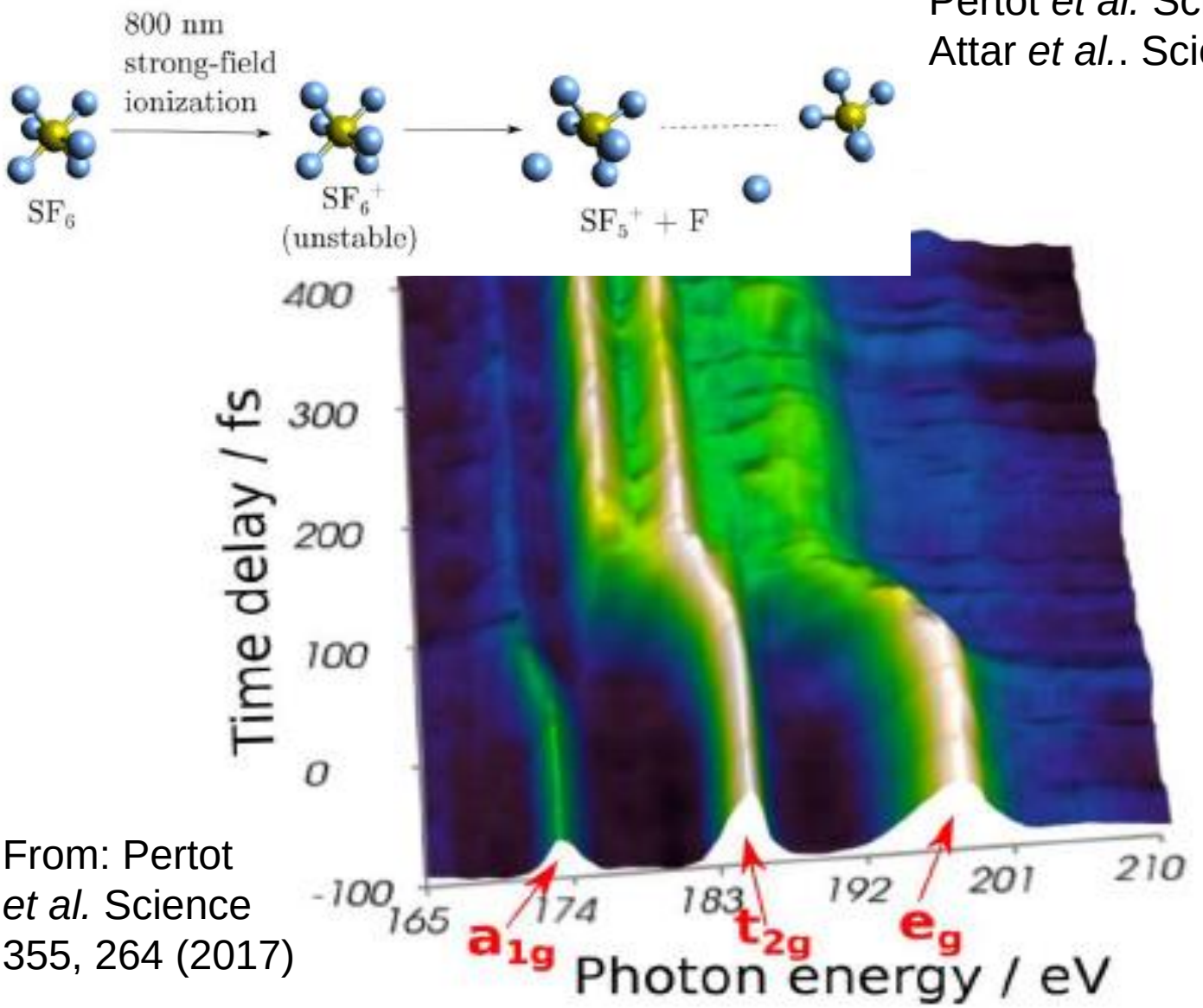
(b) $n \rightarrow \pi^*$



Ehlert, Gühr, Saalfrank
J. Chem. Phys. 149, 144112 (2018)

Using HHG continua for transient absorption

Absorption using HHG:
Pertot *et al.* Science 355, 264 (2017)
Attar *et al.*. Science 356, 54 (2017)



From: Pertot *et al.* Science 355, 264 (2017)

Photoelectron probing of photoexcited dynamics

Ultrafast relaxation of photoinduced triplet generators: thio-nucleobases

Thionucleobase collaboration

FLASH:
Stefan Düsterer
Bastian Manschwetus
Skirmantas Alisauskas

Gothenburg:
Raimund Feifel
Richard Squibb
Mans Wallner

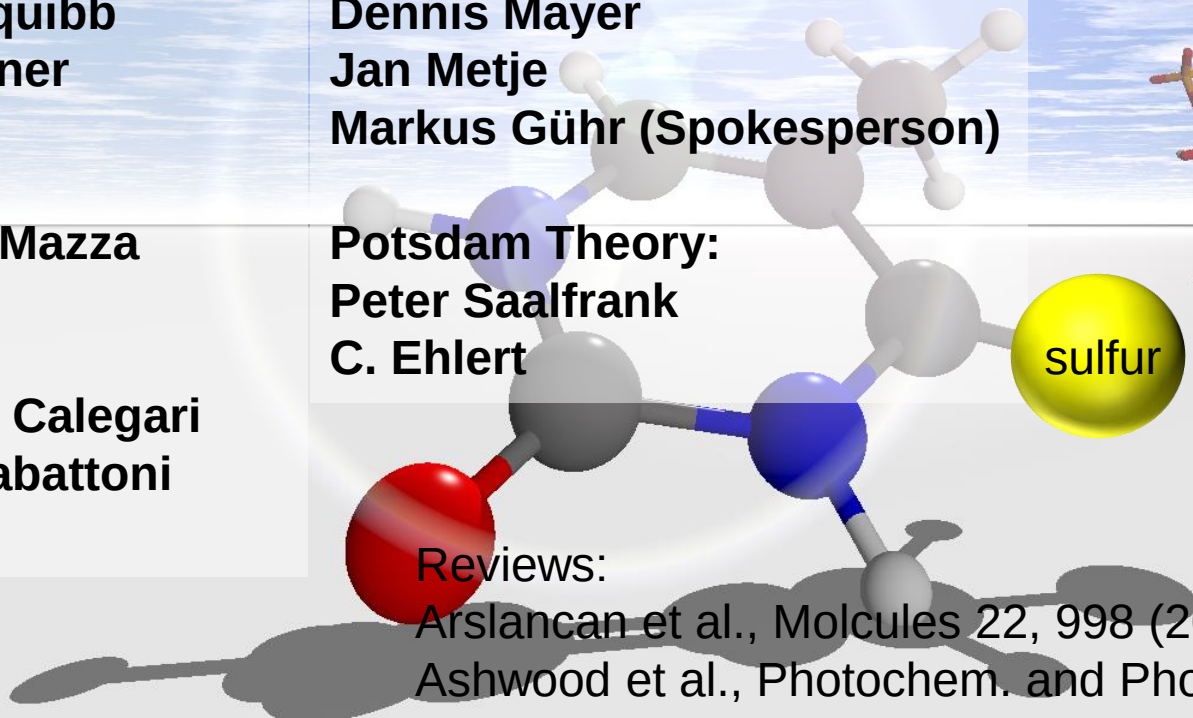
XFEL:
Tommaso Mazza

CFEL:
Francesca Calegari
Andrea Trabattoni

SLAC:
Thomas Wolf

Potsdam:
Matthew Robinson
Fabiano Lever
Mario Niebuhr
Dennis Mayer
Jan Metje
Markus Gühr (Spokesperson)

Potsdam Theory:
Peter Saalfrank
C. Ehlert



Reviews:
Arslancan et al., Molcules 22, 998 (2017)
Ashwood et al., Photochem. and Photobiol. 95, 33 (2019)

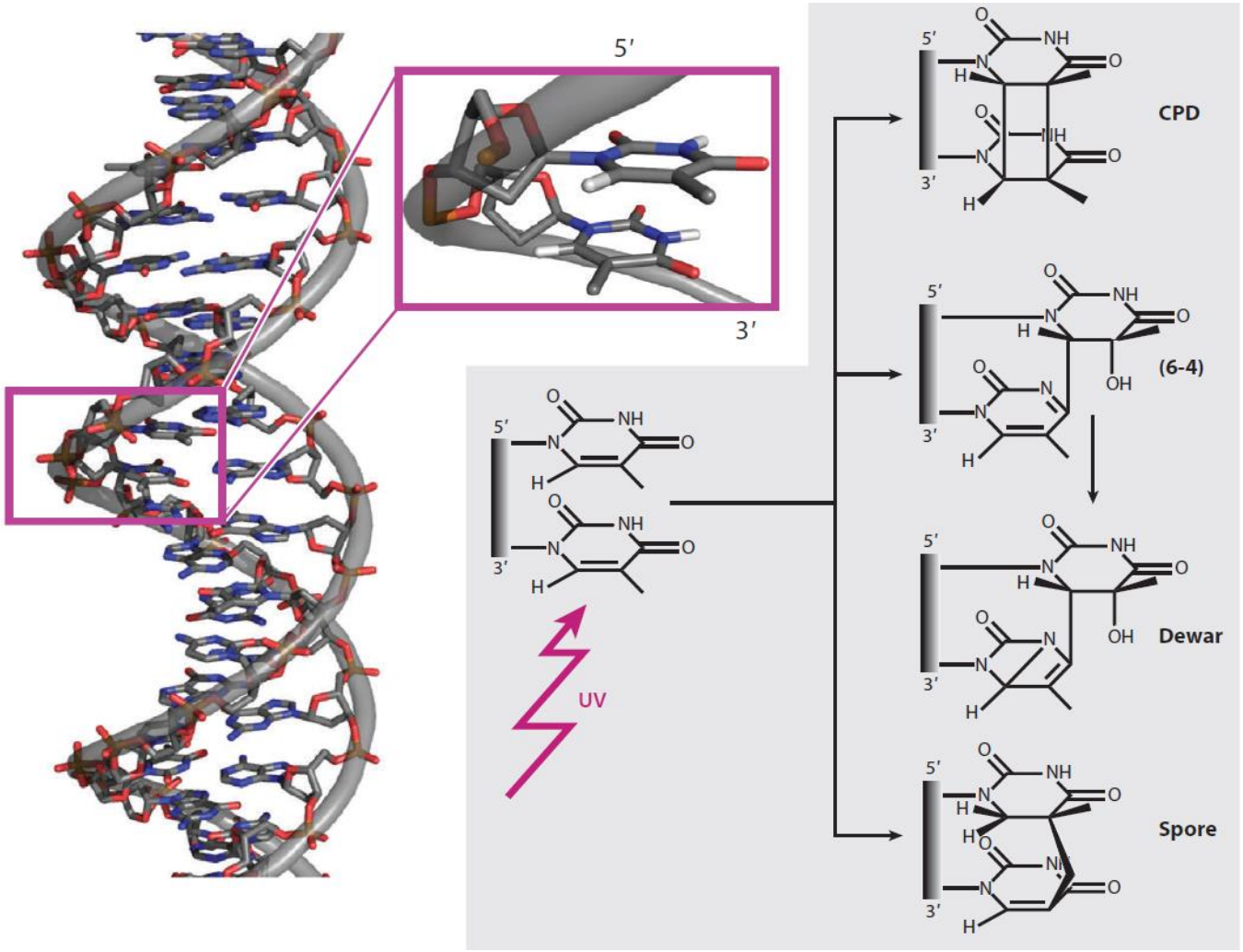
You can use that instrument a FLASH

Potsdam, FLASH Feb. 21st 2019

Difference photoelectron spectra indicate a UV induced shift.

Future directions:

Dilute samples
Example: DNA lesions



Schreier, W.J., P. Gilch, and W. Zinth, *Early events of DNA photodamage.* Annu Rev Phys Chem, 2015. **66**: p. 497-519.

Kneuttinger, A.C., et al., *Formation and Direct Repair of UV-induced Dimeric DNA Pyrimidine Lesions.* Photochem Photobiol, 2014. **90**(1): p. 1-14.

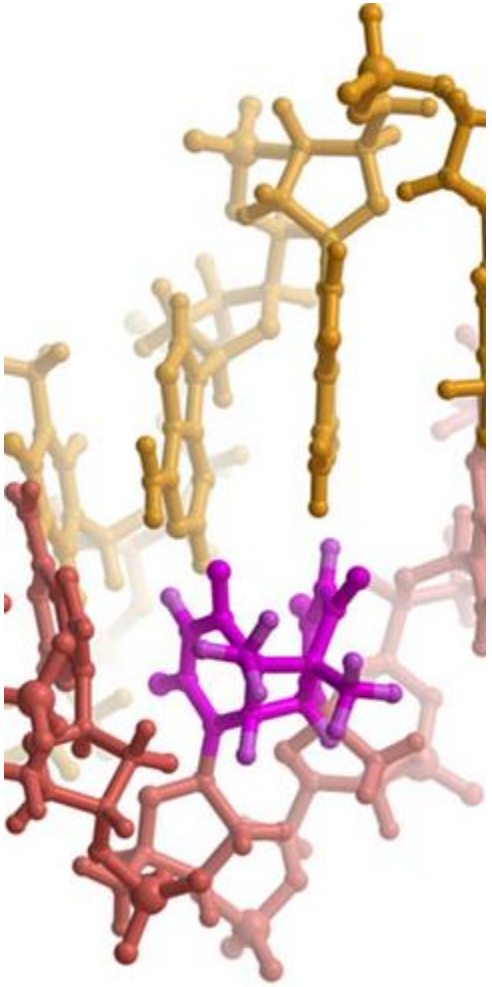
Dilute samples
Example: DNA lesions

Challenge:
- ‚see' UV induced features in large background from environment

- ‚Gas phase' might circumvent some of the problems

- First experiments Th. Schlathölter and group (Groningen) with ion trap technology at FLASH

- Demanding on average flux

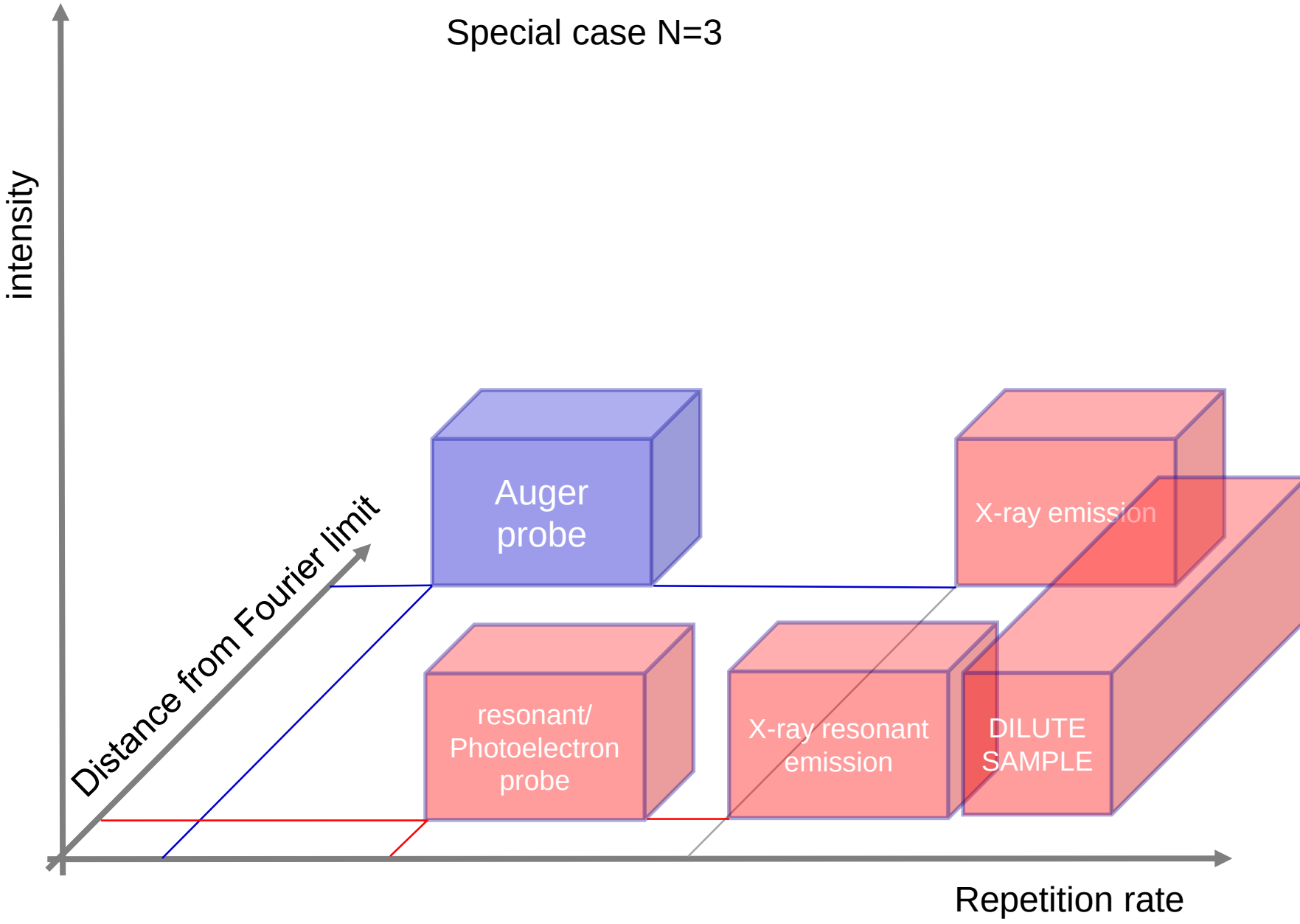


Cyclopyrimidine dimer induced by UV irradiation in DNA (source: http://pdb101.rcsb.org/motm/91)

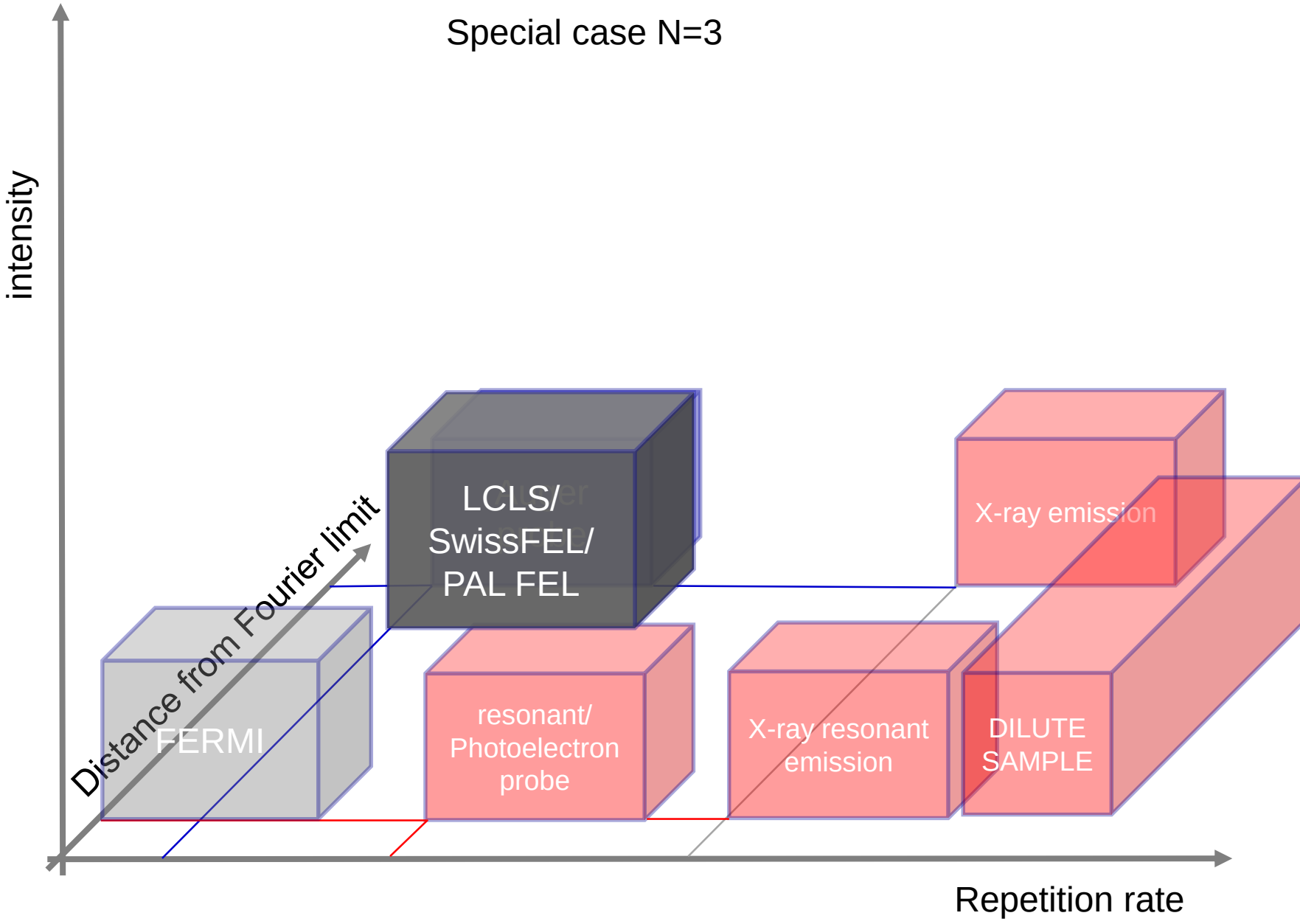
Alternatives are P edge spectra
Czapla-Masztafiak et al., Biophys. J. 110, 1304 (2016)

N-dimensional FEL parameter space

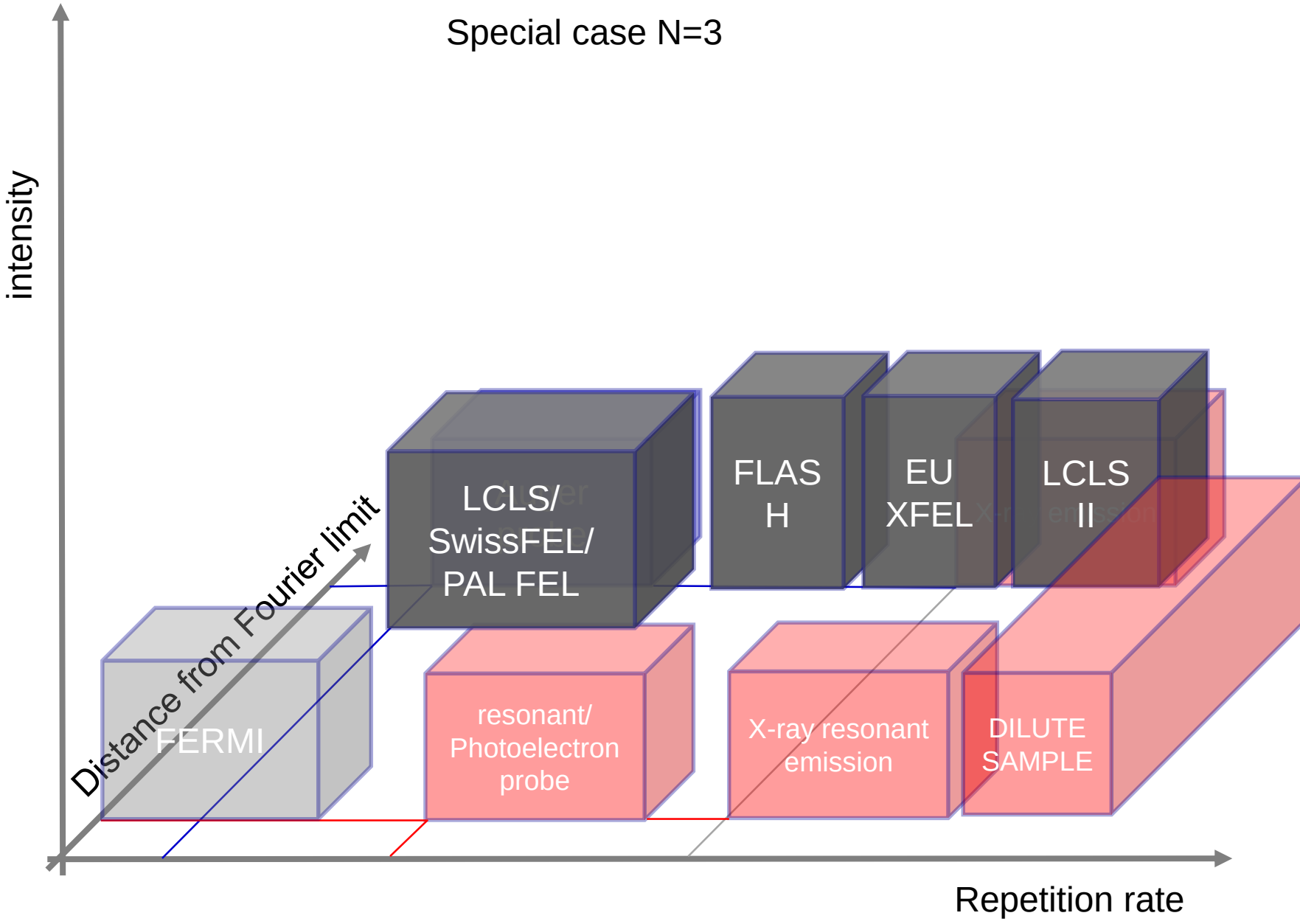
N-dimensonal FEL parameter space



N-dimensonal FEL parameter space



N-dimensonal FEL parameter space

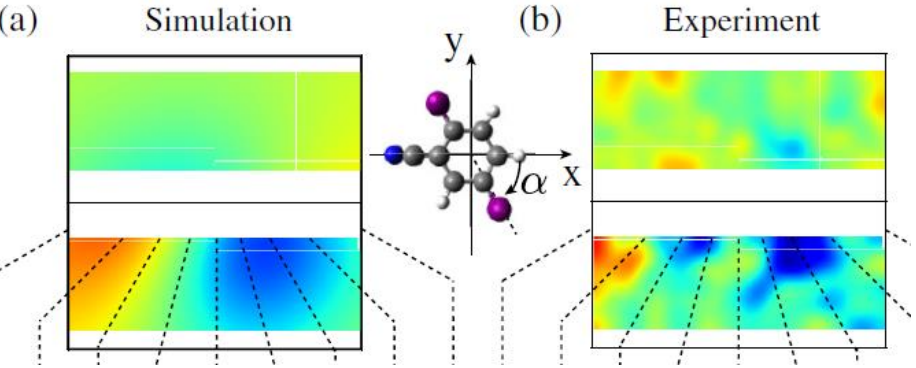


Time resolved diffraction techniques

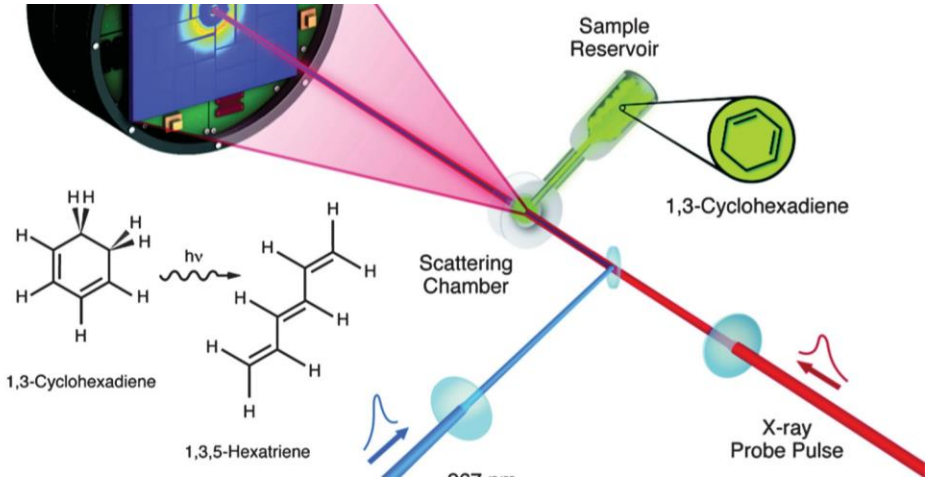
X-rays

Spatial resolution: above 1 Å

Temporal resolution: below 100 fs



Küpper *et al.*, PRL 112, 083002 (2014)

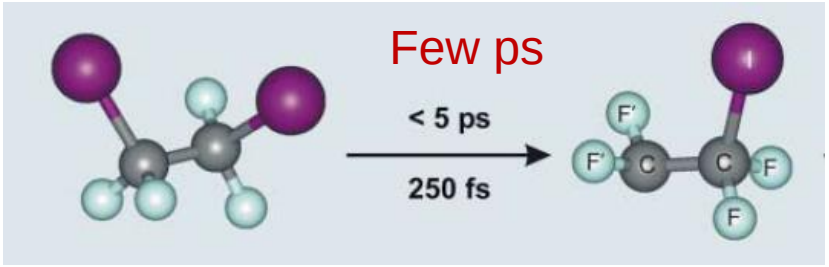


Minitti *et al.*, PRL 114, 255501 (2015)

Electrons

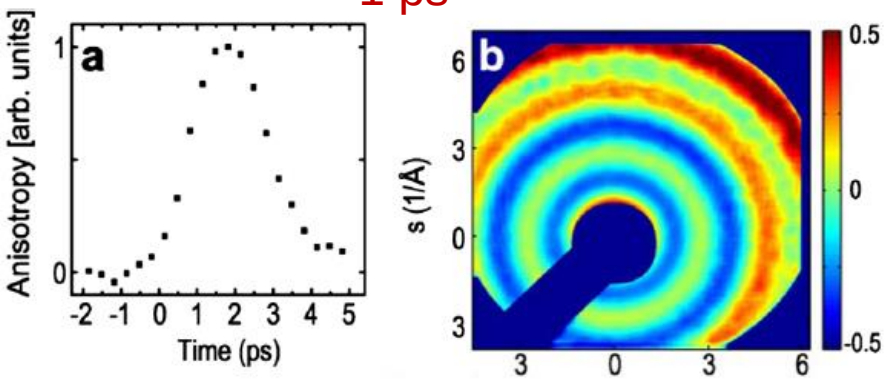
Spatial resolution: below 1 Å

Temporal resolution: hard to obtain



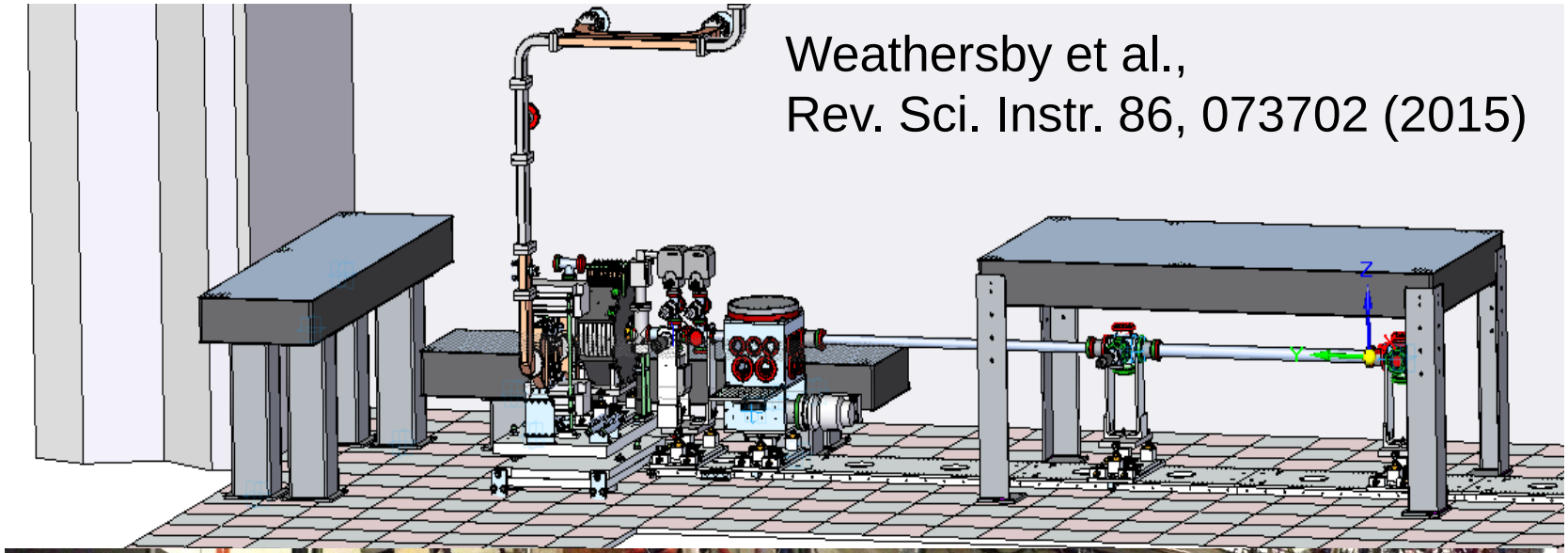
Zewail, Weber, Miller

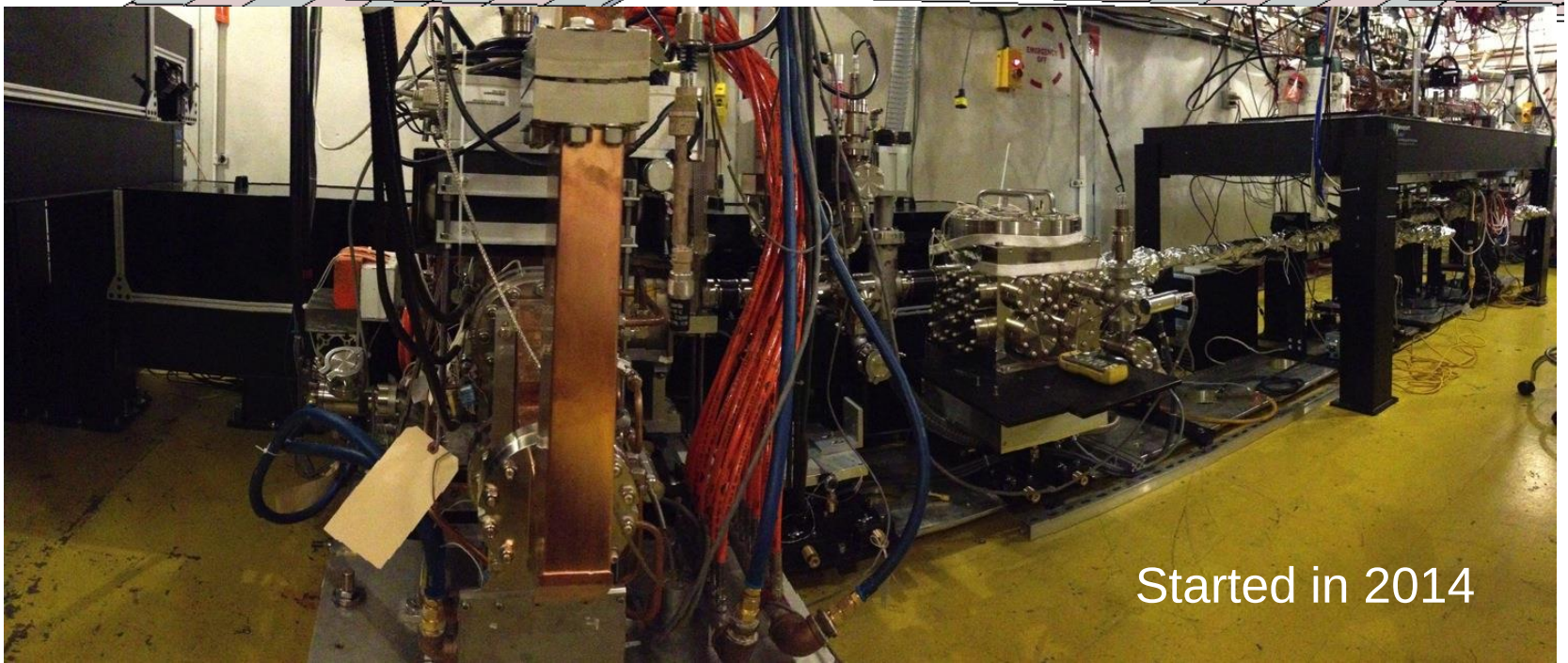
1 ps



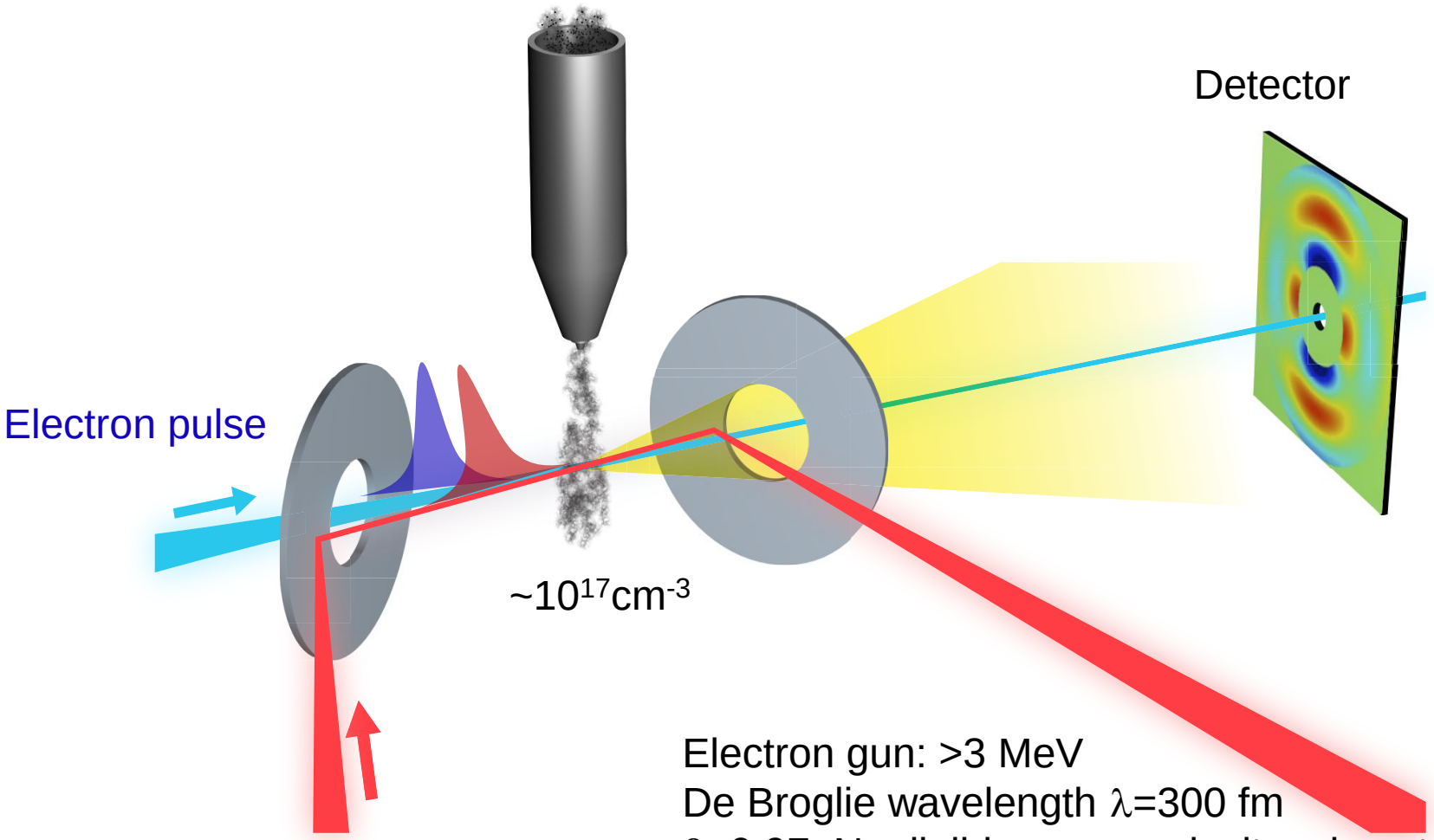
Hensey et al. PRL 13, 133203 (2012)

Relativistic electron gun at SLAC





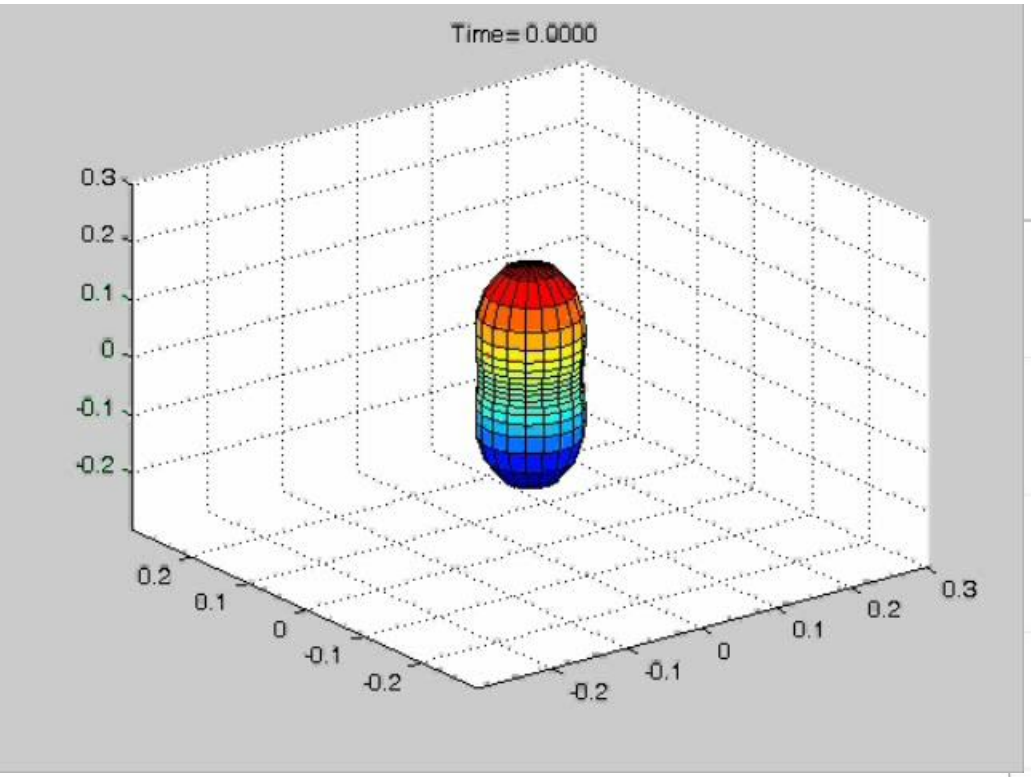
Interaction region: match velocities

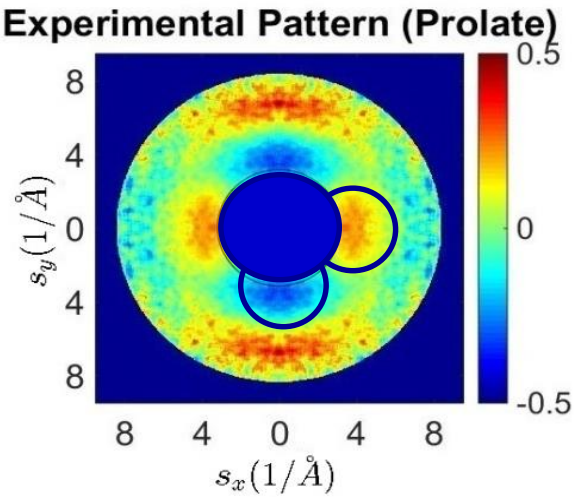


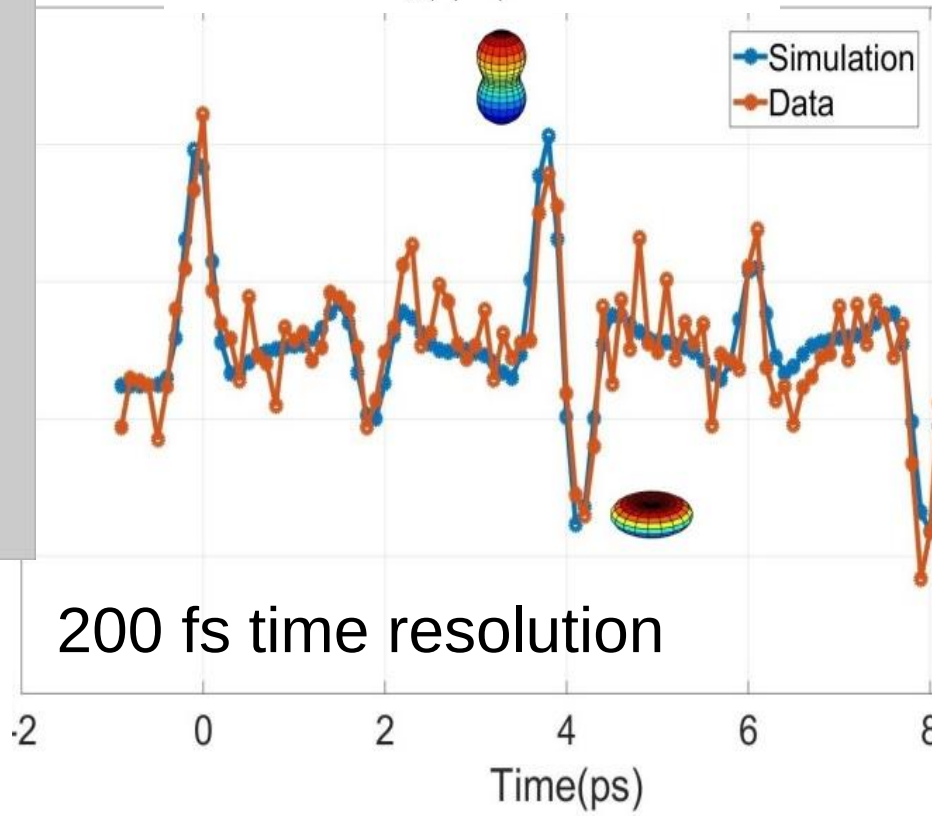
Electron gun: >3 MeV
De Broglie wavelength λ=300 fm
β=0.97, Negligible group velocity mismatch
10^5 Electrons per pulse

Weatherby et al.
Rev. Sci. Instr. **86**, 073702 (2015)

Revivals in diffraction





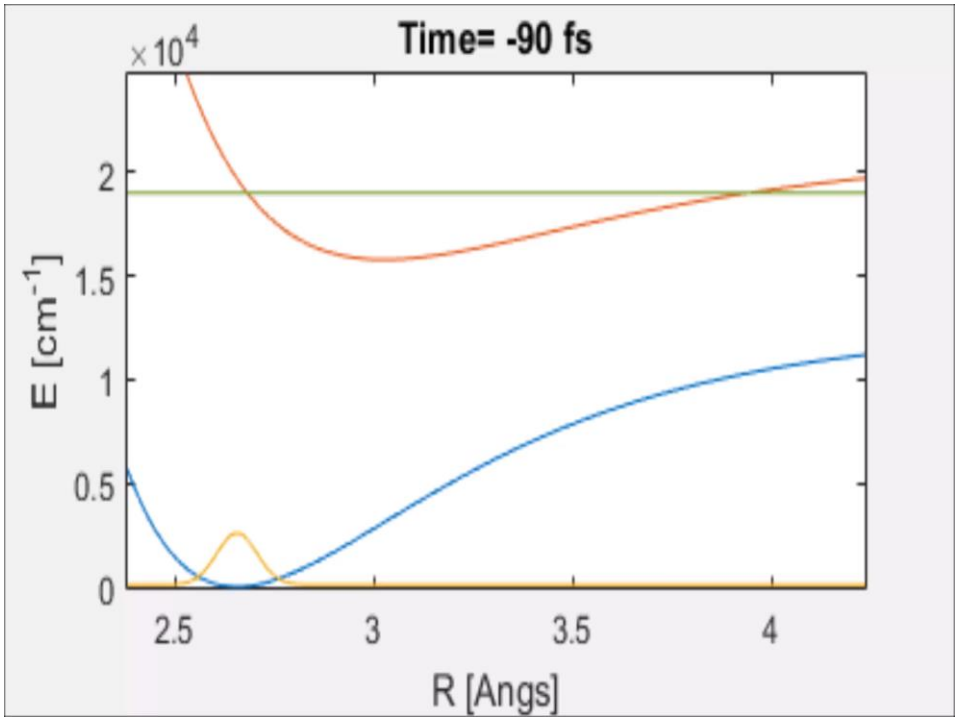


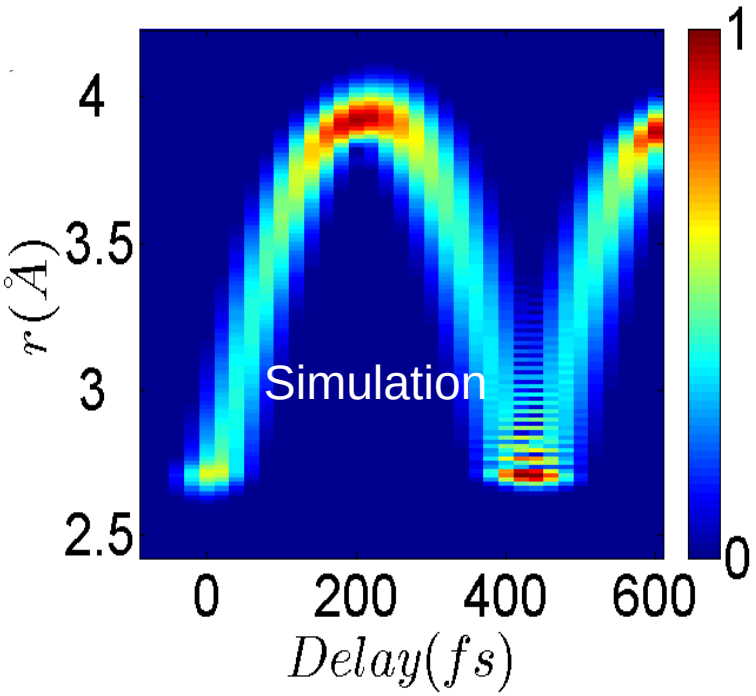
200 fs time resolution

Yang, Gühr, Vecchione *et al.*,
Nature Comm. 7, 11232 (2016)

UED on Vibrational Wavepackets

Wavepaket propagation

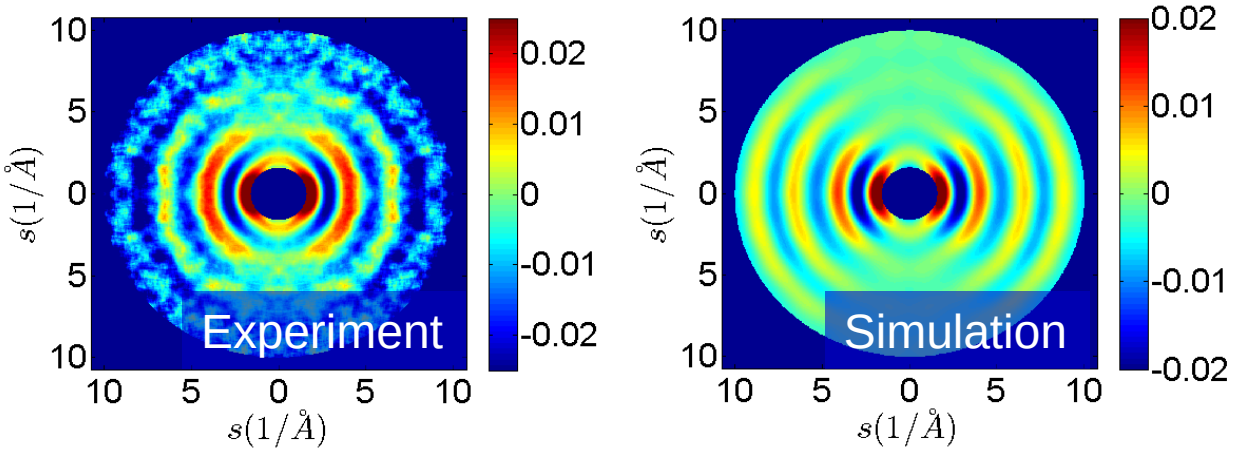


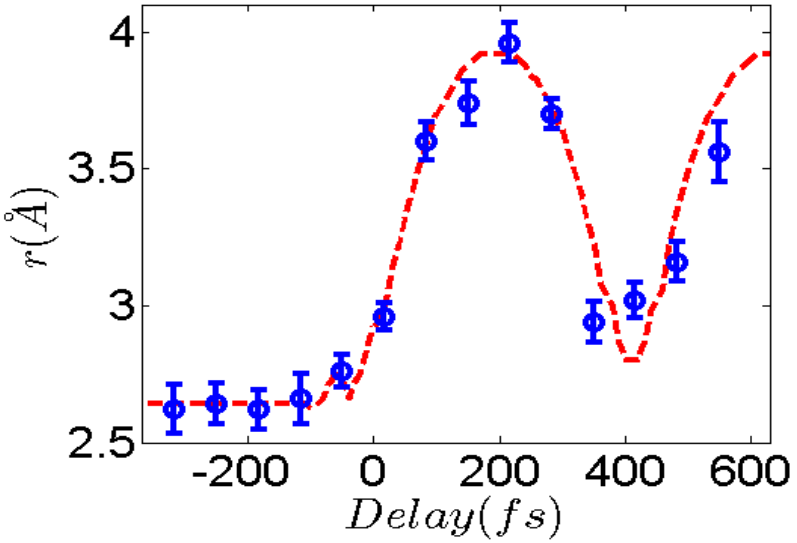


Excitation at maximal absorption of the B ($^3\Pi_{u0}$) state of I_2
Iodine is heavy (scatters a lot) and slow

Simulation with split operator method
(see Tannor, Introduction to quantum mechanics, University Science books)

UED on Vibrational Wavepackets



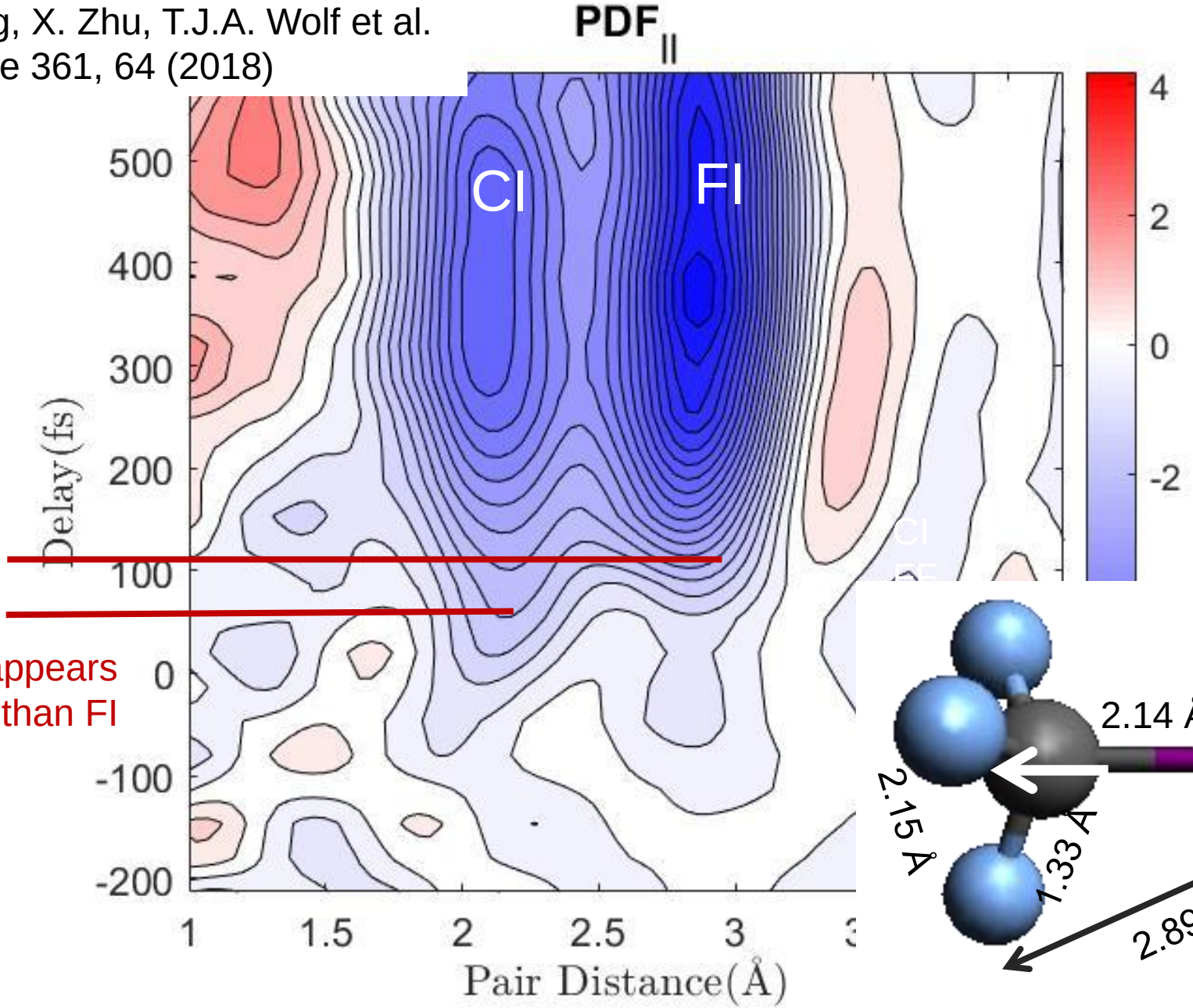


- resolution 0.7 Å
- error bar (~0.1 Å) is less than resolution, Now even better

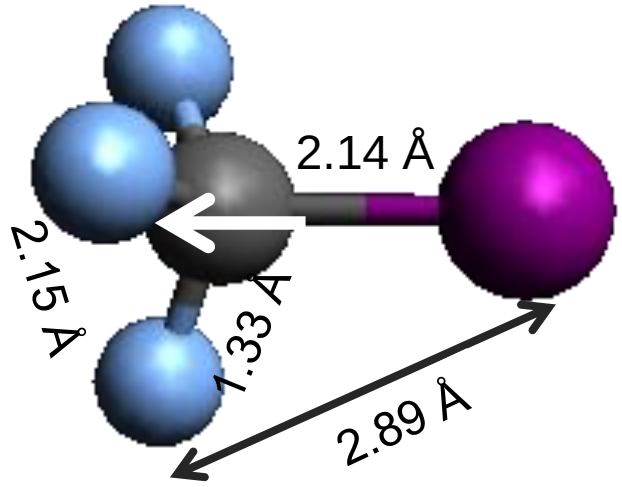
J. Yang, M. Gühr, X. Shen, R. Li et al.
PRL **117**, 153002 (2016)

The CI bond bleaches earler than the FI bond

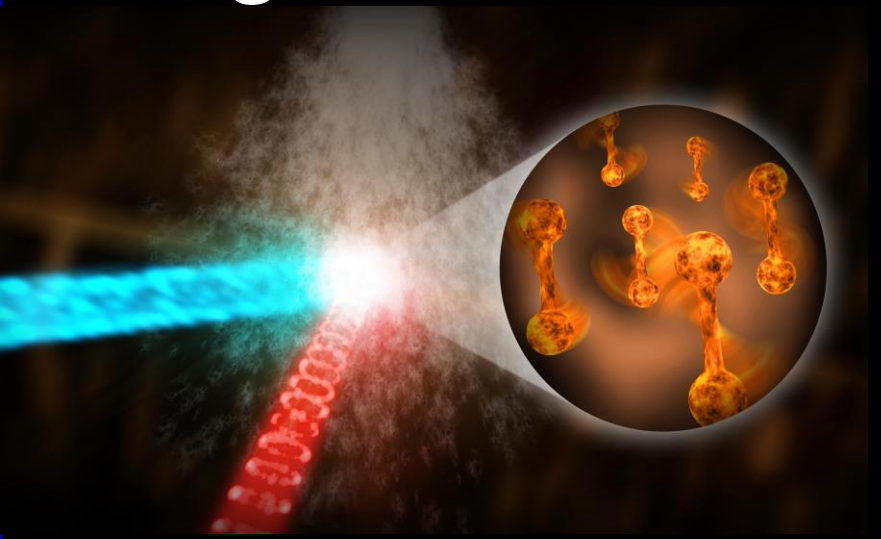
J. Yang, X. Zhu, T.J.A. Wolf et al.
Science 361, 64 (2018)

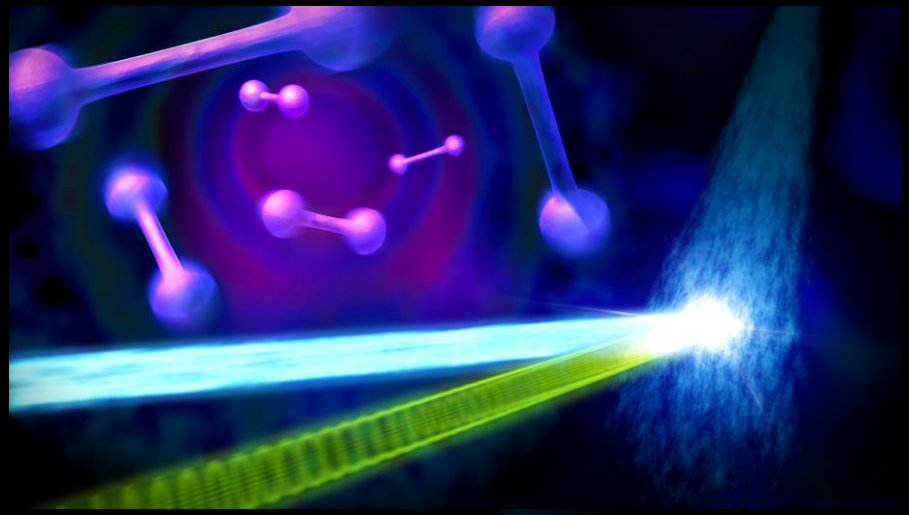


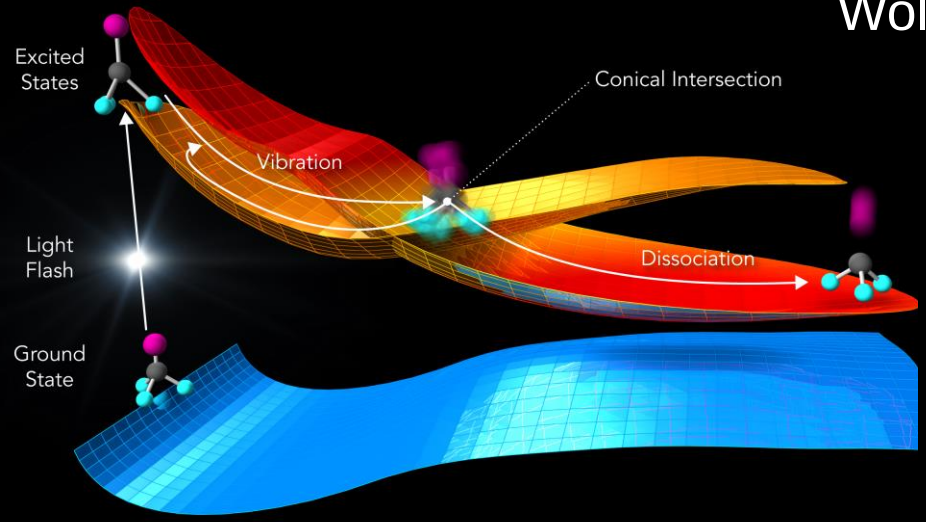
CI disappears earlier than FI



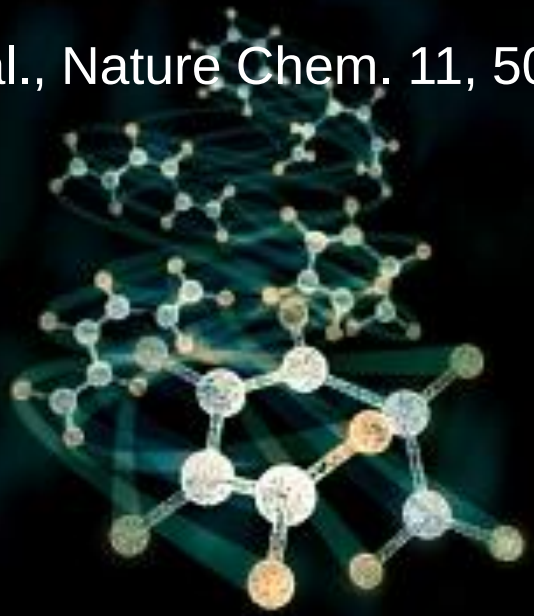
Past success with relatively large bond changes

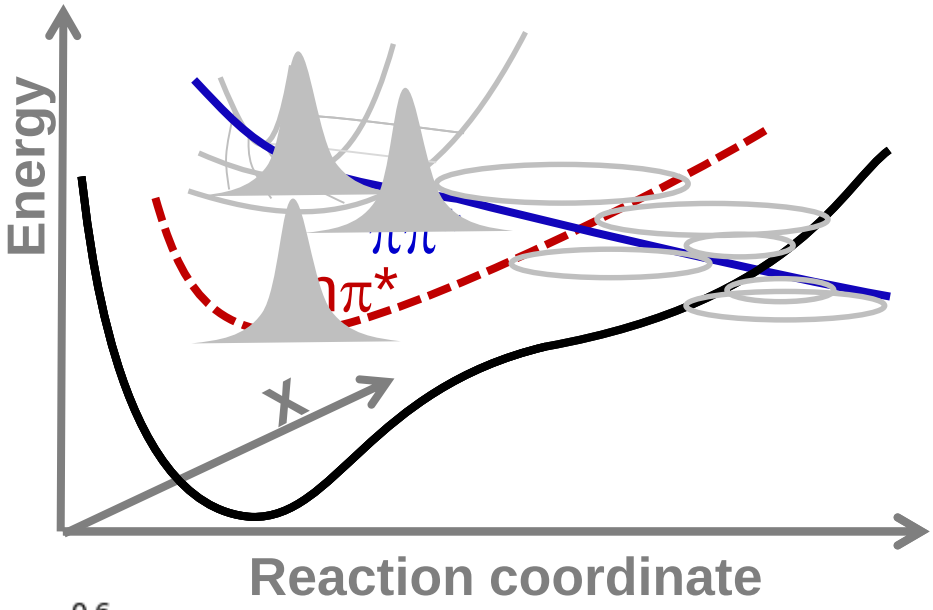


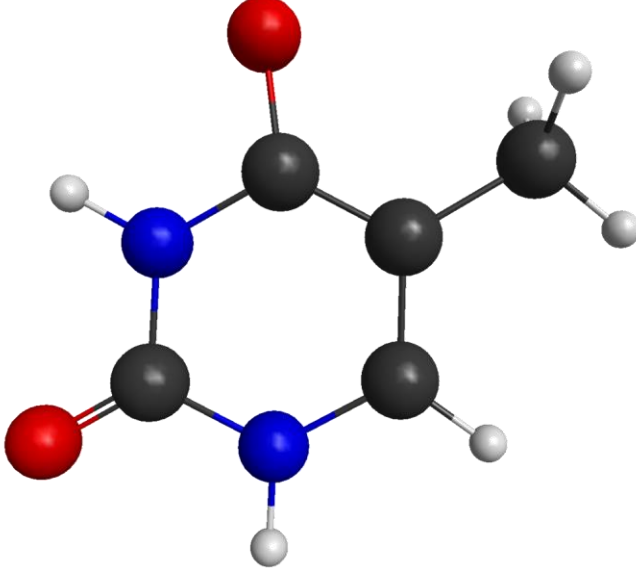


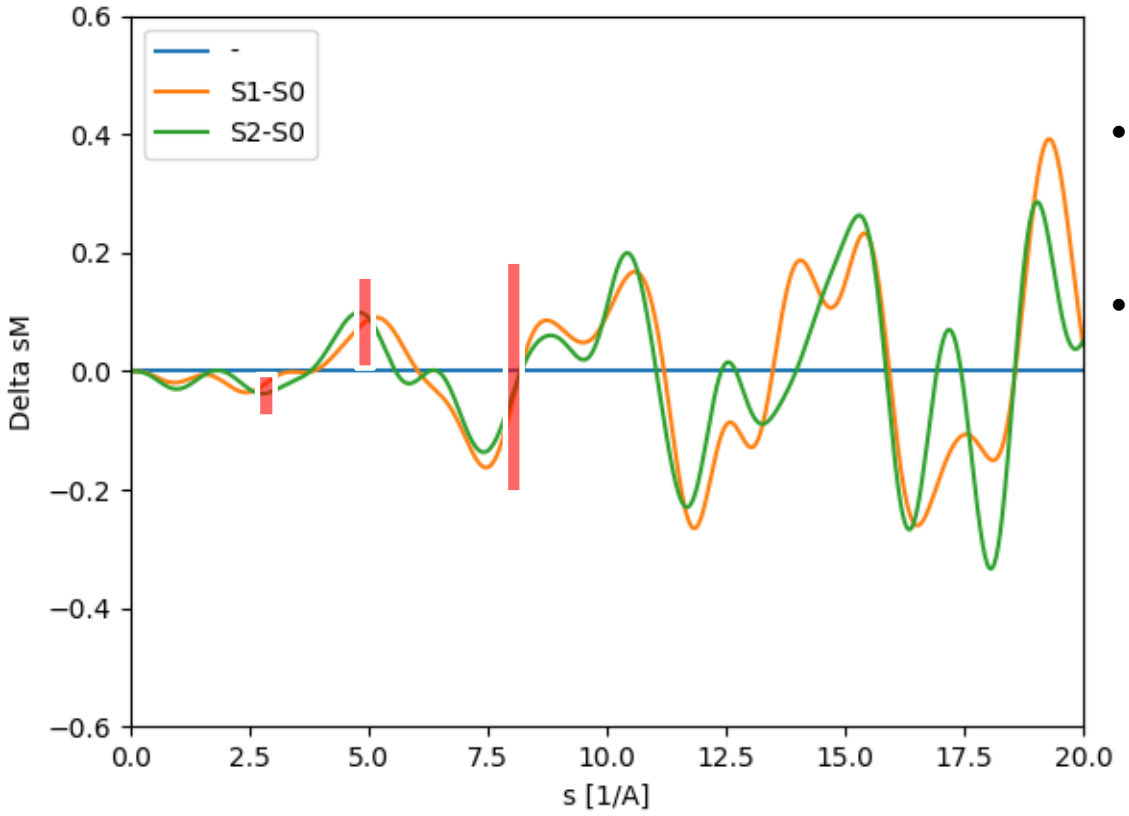


Wolf et al., Nature Chem. 11, 504 (2019)



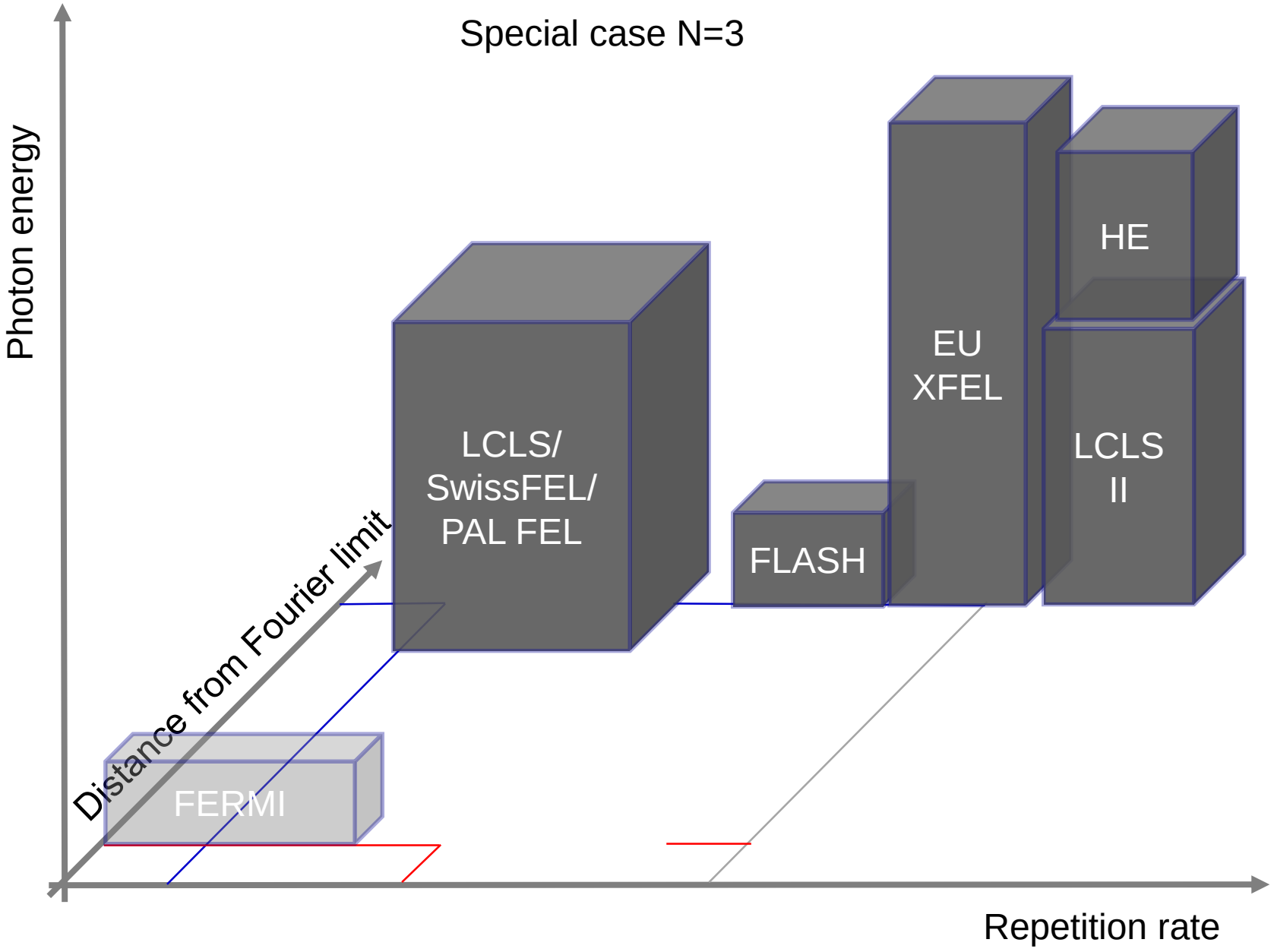






- ΔsM for thymine with error bars from CHD in red
- *Additional effect not accounted for here: wavepacket broadening* (Kirrander and Weber, Appl. Sci. 7, 534 (2017)

N-dimensonal FEL parameter space



Acknowledgements

FEL

SLAC
T. Wolf
J. Cryan
C. Bostedt
A. Natan
S. Moeller
G. Coslovic
T. Martinez
P. Bucksbaum
K. Gaffney

Connecticut
N. Berrah
R. Obaid

Uppsala
R. Squibb
R. Feifel

Trieste
O. Plekan
S. Coriani

Trondheim
R. H. Myhre
H. Koch

Trieste
O. Plekan

Hamburg
T. Mazza
F. Callegari
A. Trabattoni

UED

SLAC
J. Yang
T. Wolf
X. Zhu
R. Li
Z. Li
X. Shen
T. Veccione
S. Weatherby
Ch. Yoneda
Q. Zheng
K. Jobe
J. Cryan
R. Coffee
K. Hegaze
T. Martinez
X. Wang

Lincoln
J. Yang
M. Robinson
P. Nunes
K. Wilkin
M. Centurion

Potsdam: D. Mayer, F. Lever, M. Niebuhr, M. Robinson, J. Metje, A. Heuer, MG C. Ehlert, P. Saalfrank