



Exploring molecular dynamics with ultrashort X-ray pulses

ELI Summer School

Szeged

04.09.2024

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and Physikalische Chemie, Universität Hamburg

The background of the slide is a reproduction of the painting 'The Sower' by Vincent van Gogh. It depicts a golden sun in a bright sky over a field of wheat, with a body of water in the foreground reflecting the light. The painting is characterized by its vibrant colors and visible brushstrokes.

Conference on ultrafast imaging of matter 2024 At DESY in Hamburg

For for further information and registration use:
<https://indico.desy.de/event/43918/>

Rhodopsin



PDB 1F88

Vision

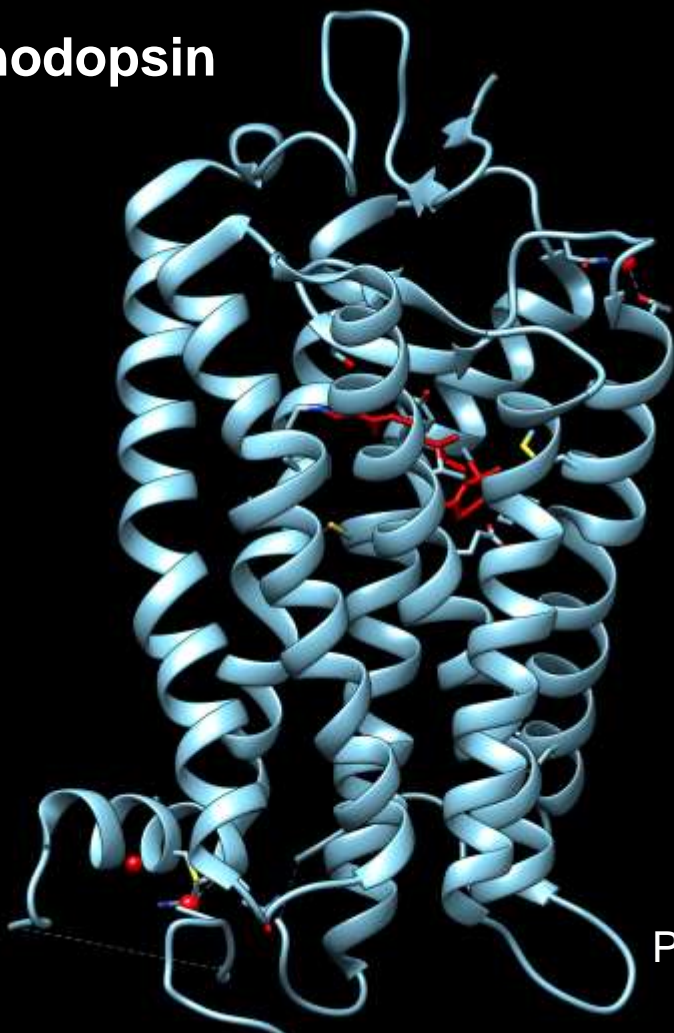
**Chromophore
Retinal**



Femtosecond changes in the structure

X-ray femtosecond pulses are needed

Rhodopsin



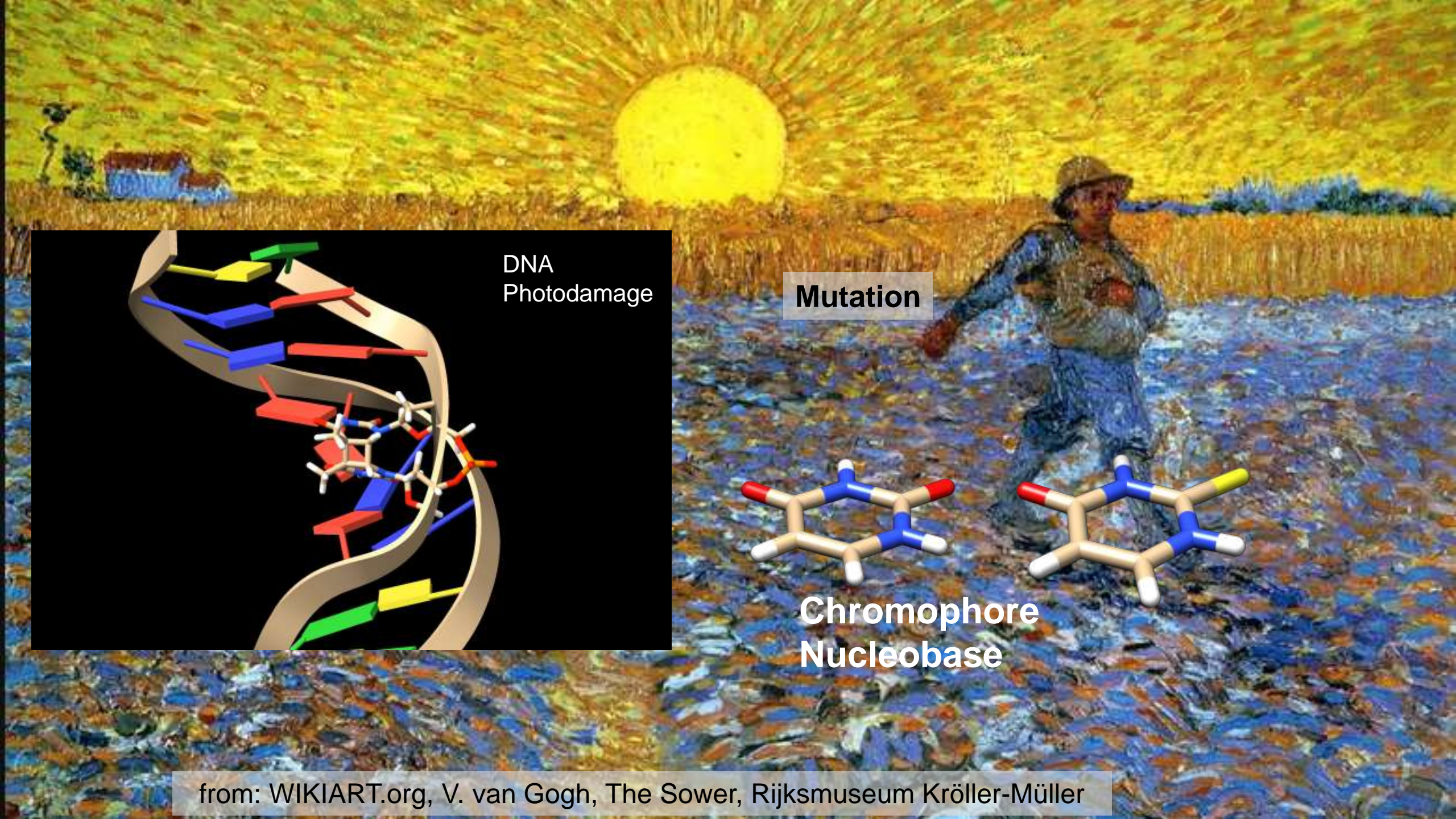
PDB 1F88

Vision

**Chromophore
Retinal**



from: WIKIART.org, V. van Gogh, The Sower, Rijksmuseum Kröller-Müller



DNA
Photodamage

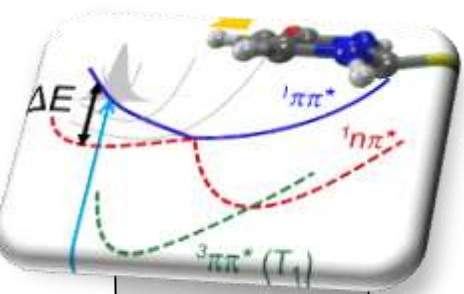
Mutation

Chromophore
Nucleobase

from: WIKIART.org, V. van Gogh, The Sower, Rijksmuseum Kröller-Müller

Outline

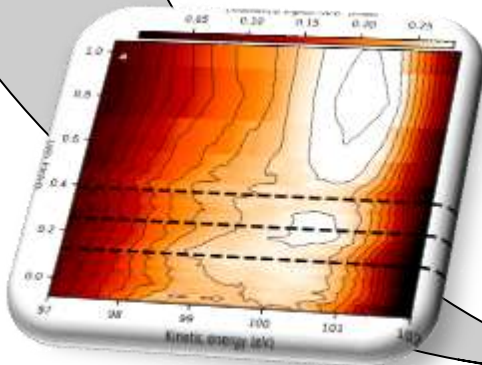
**Molecular
Photoenergy
Conversion**



**X-ray
Probing**



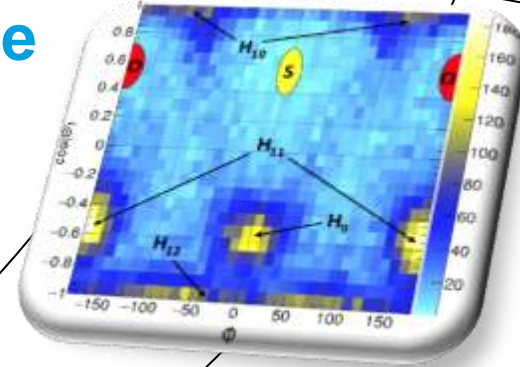
**Electronic
Movie**



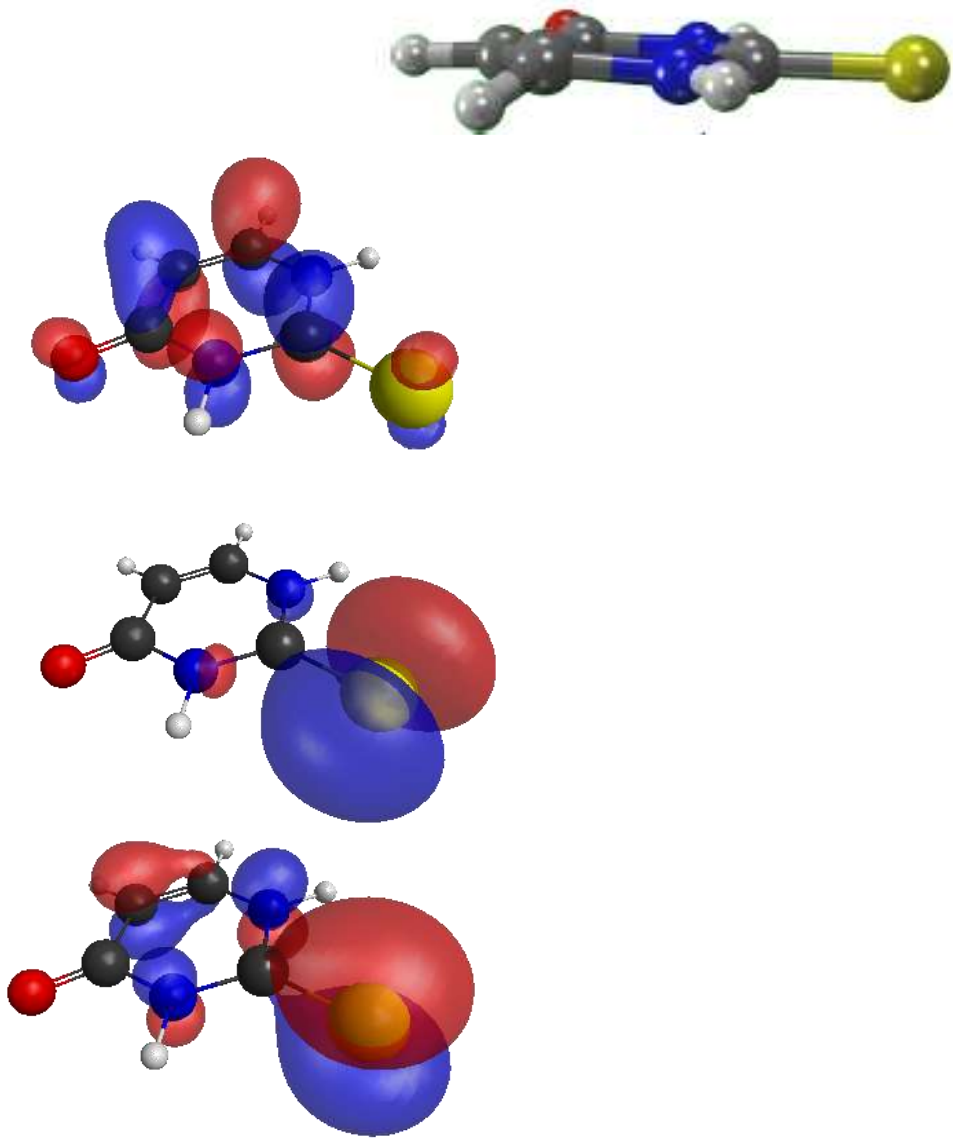
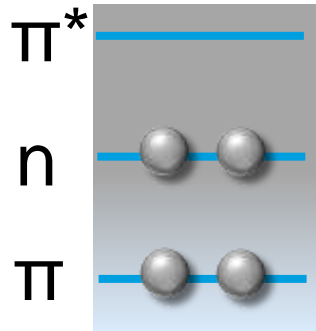
**Experimental
Setting**



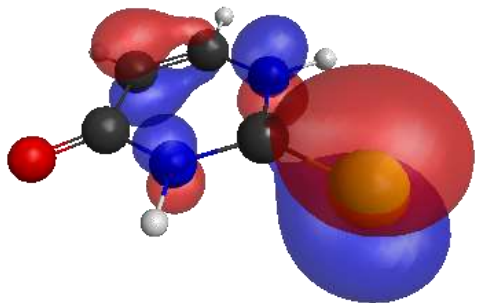
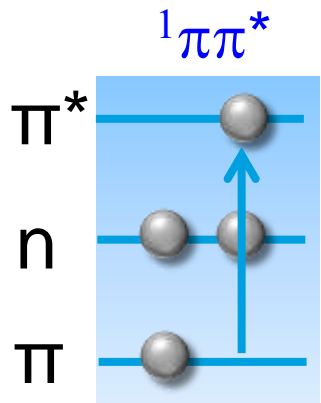
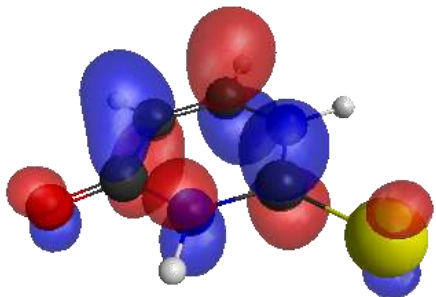
**Geometry
Movie**



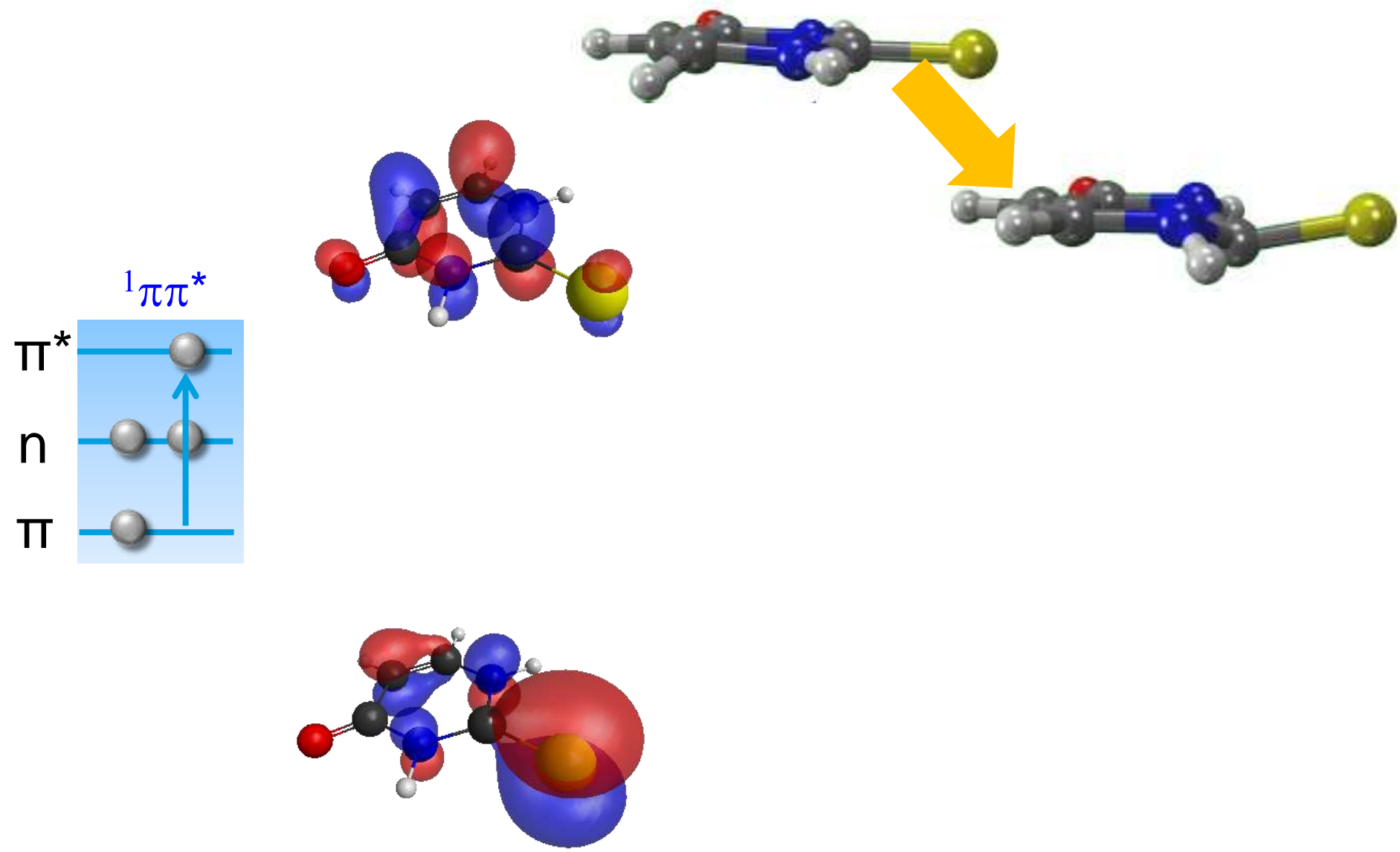
Light couples to electrons



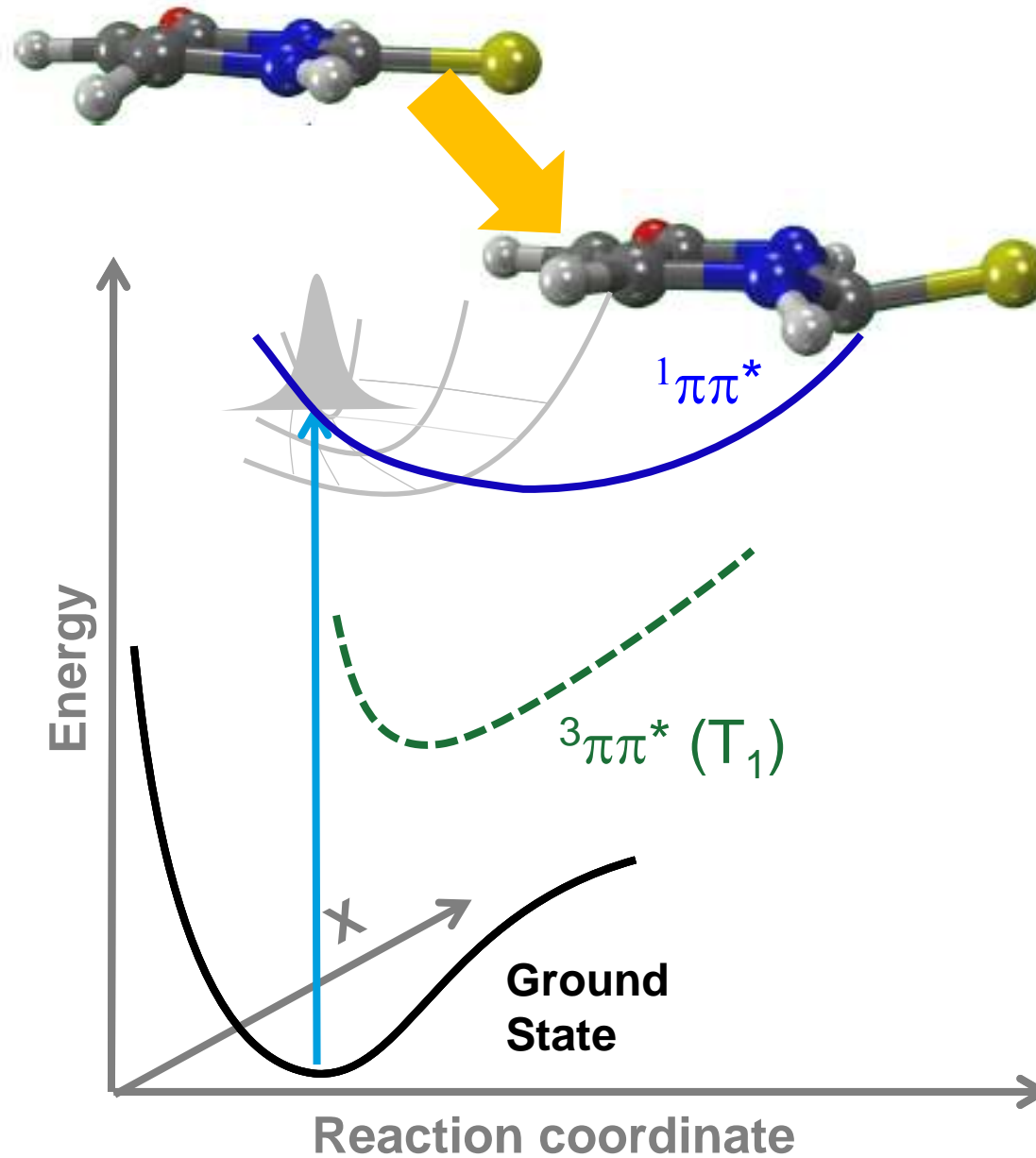
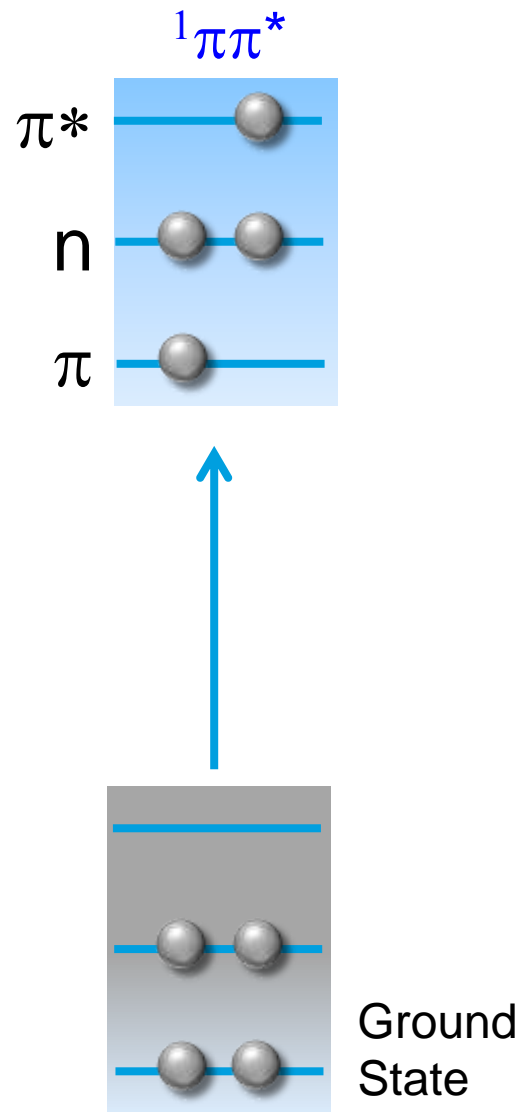
Light couples to electrons



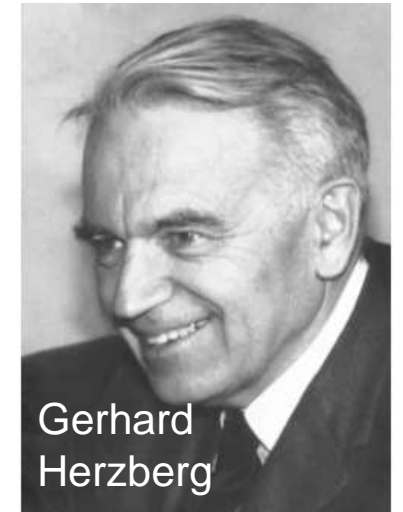
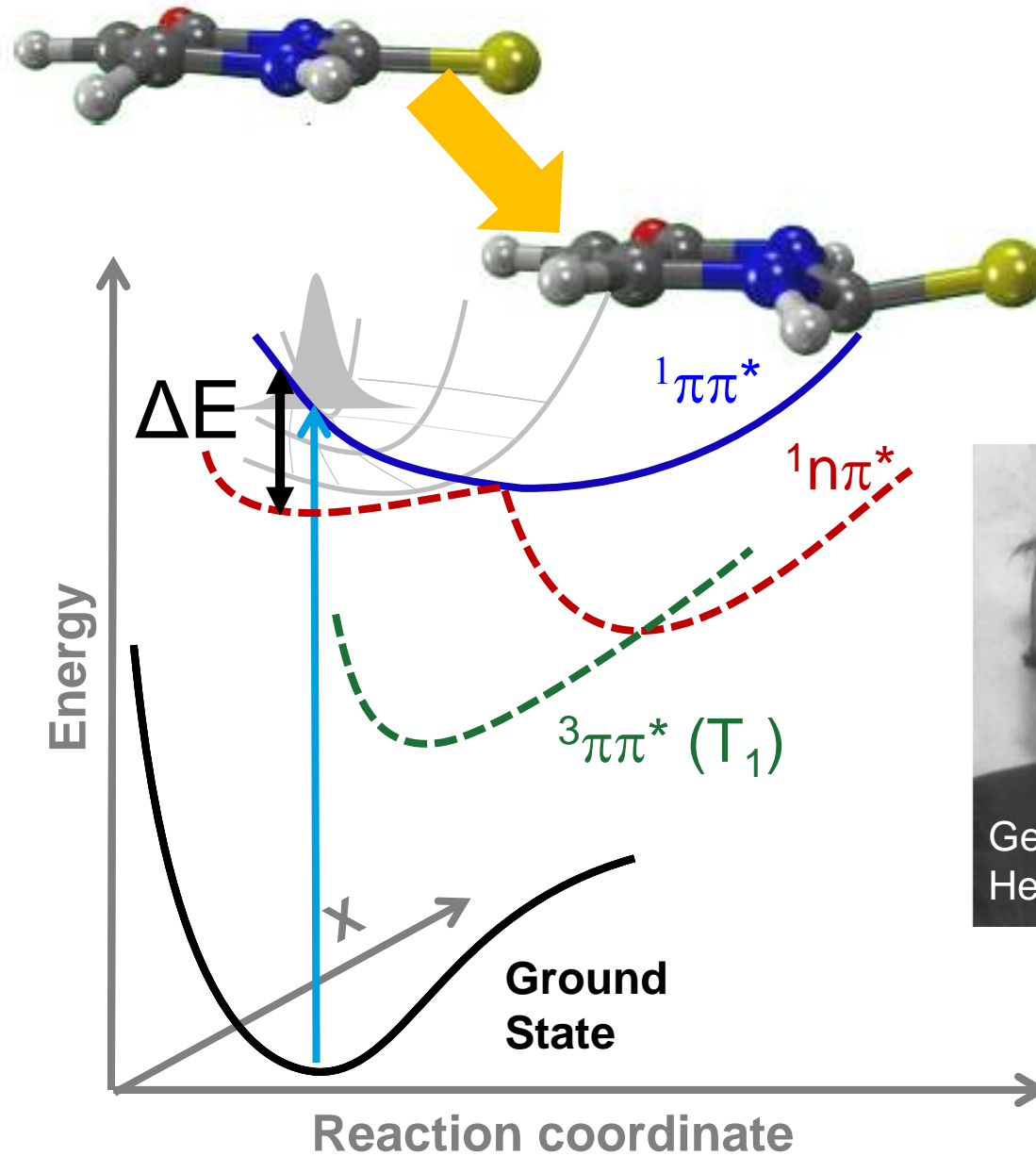
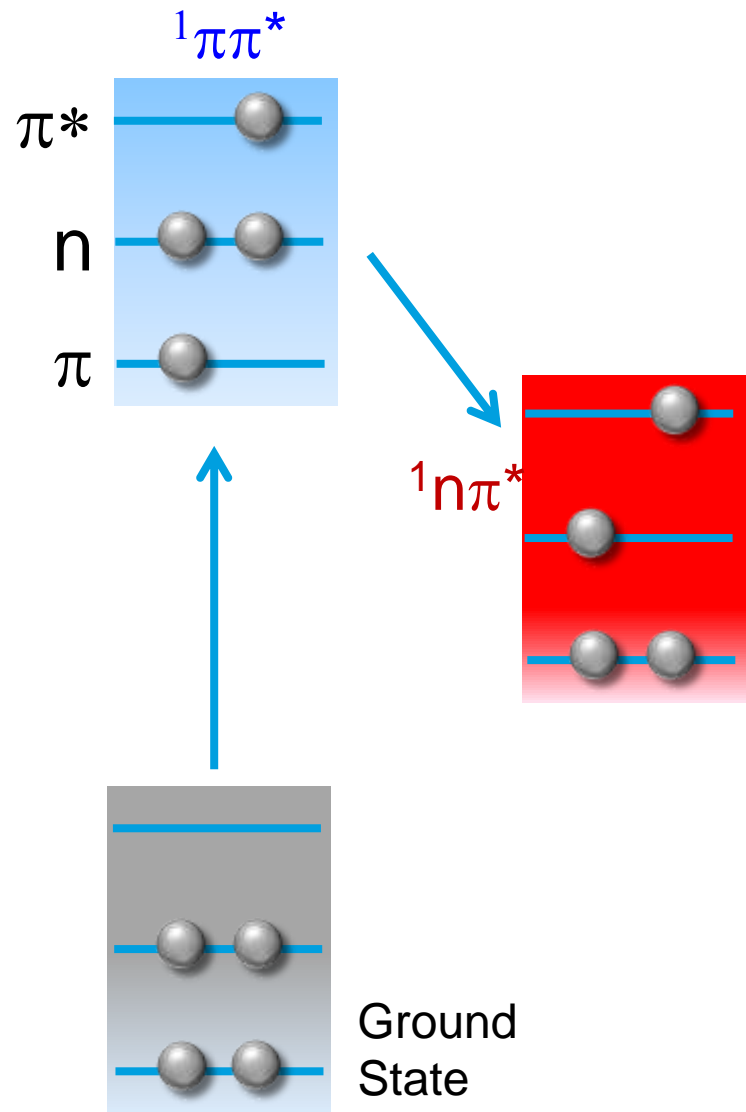
Electrons couple to nuclei



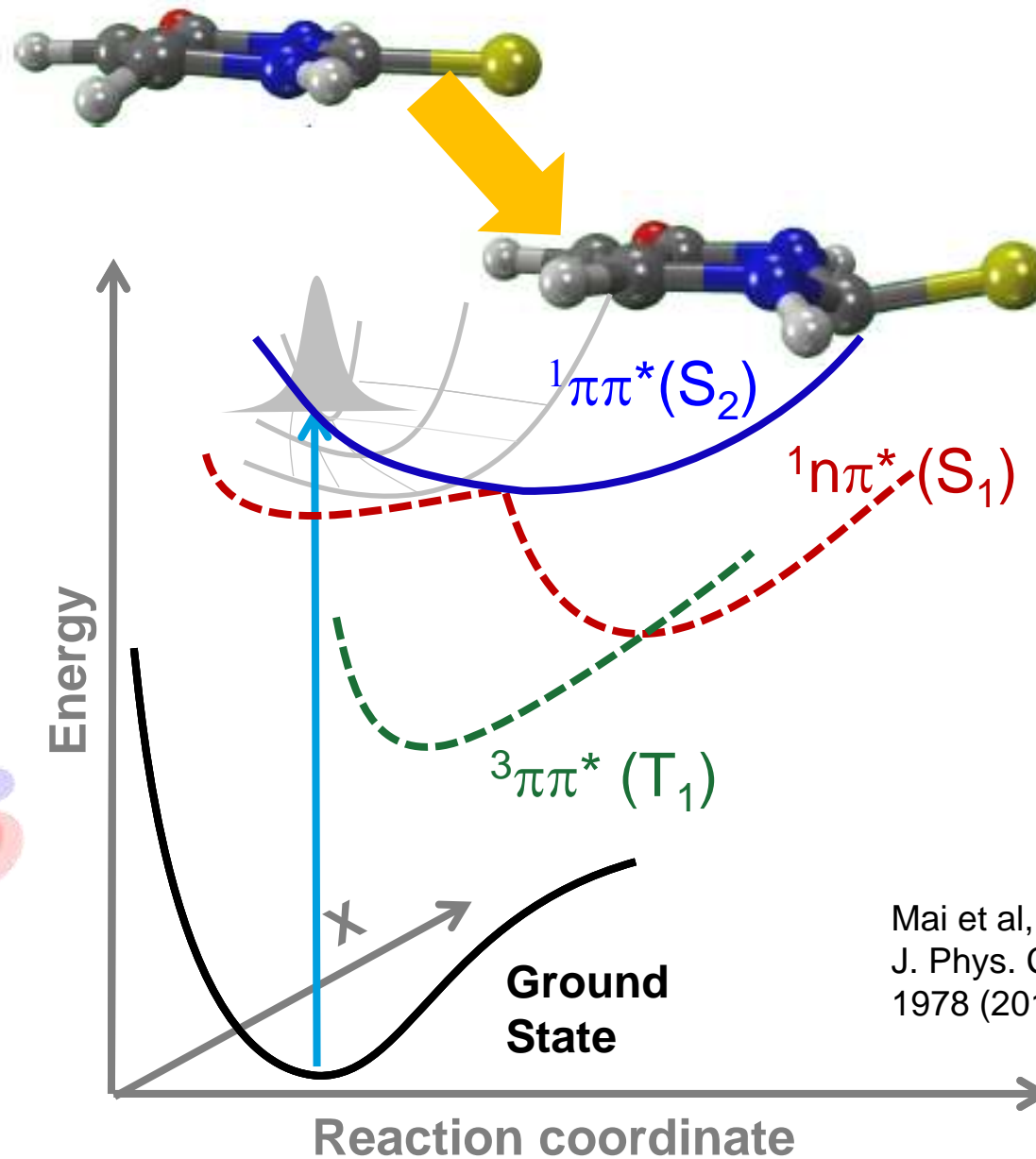
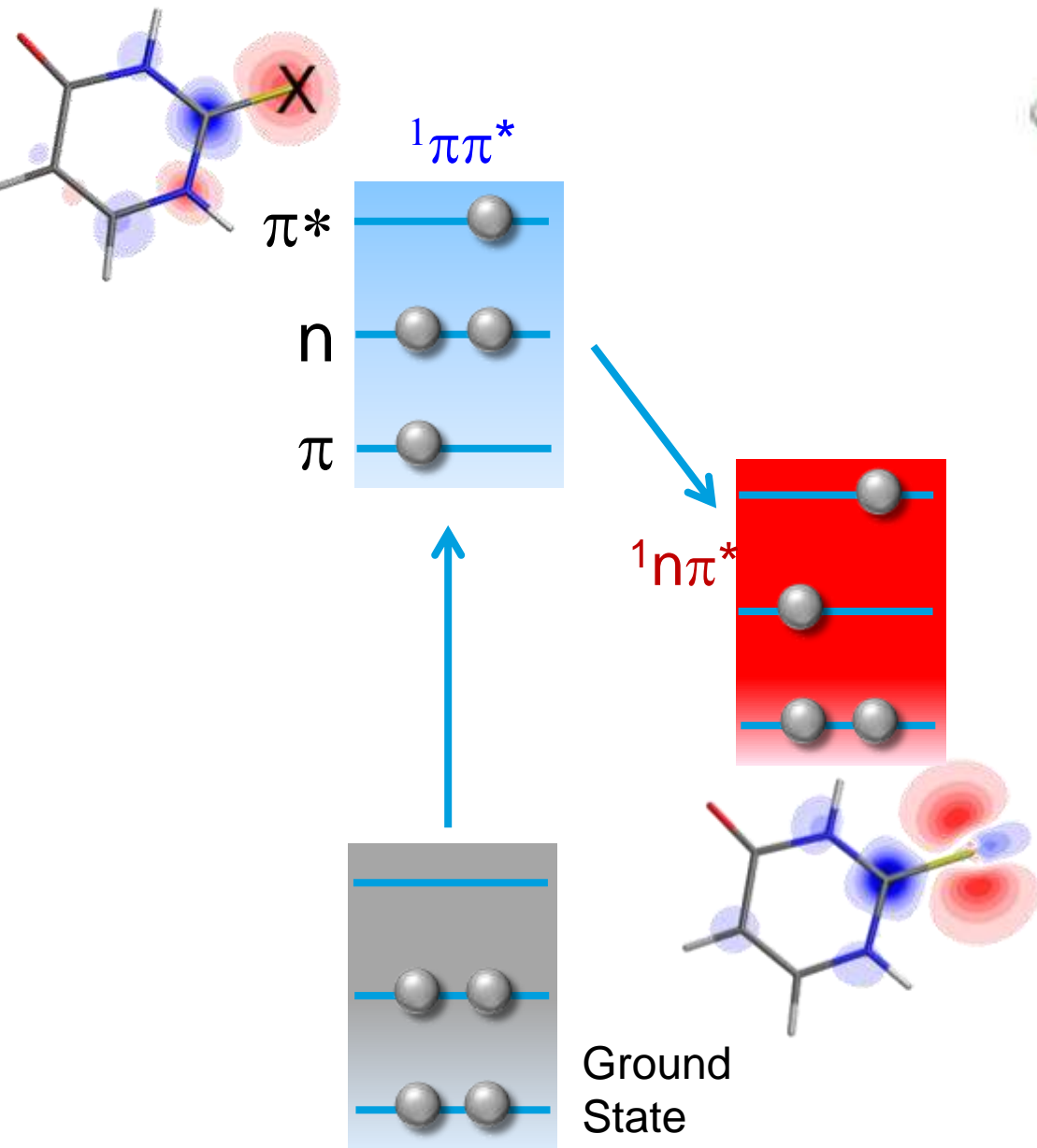
Electrons couple to nuclei



Nuclei couple to electrons



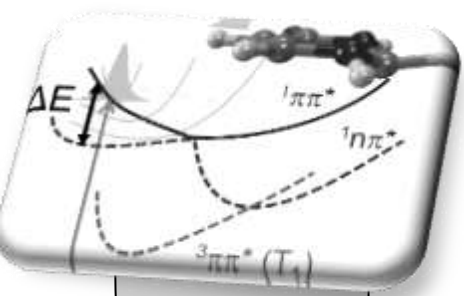
Nuclei couple to electrons and their spin



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

Outline

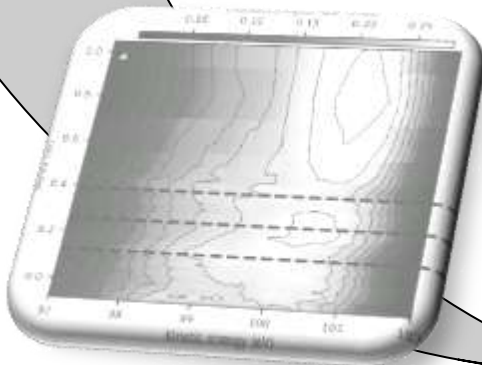
**Molecular
Photoenergy
Conversion**



**X-ray
Probing**



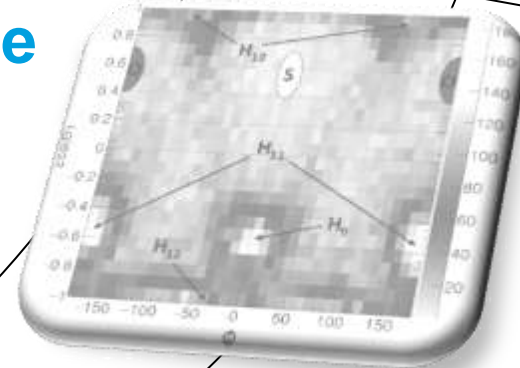
**Electronic
Movie**



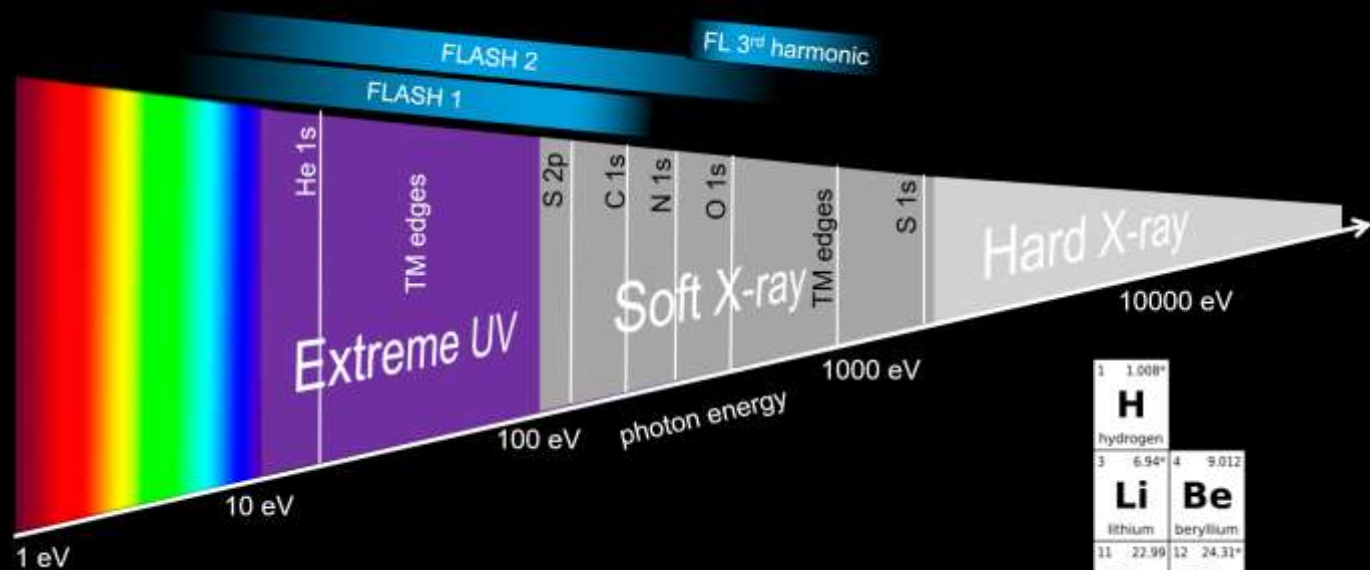
**Experimental
Setting**



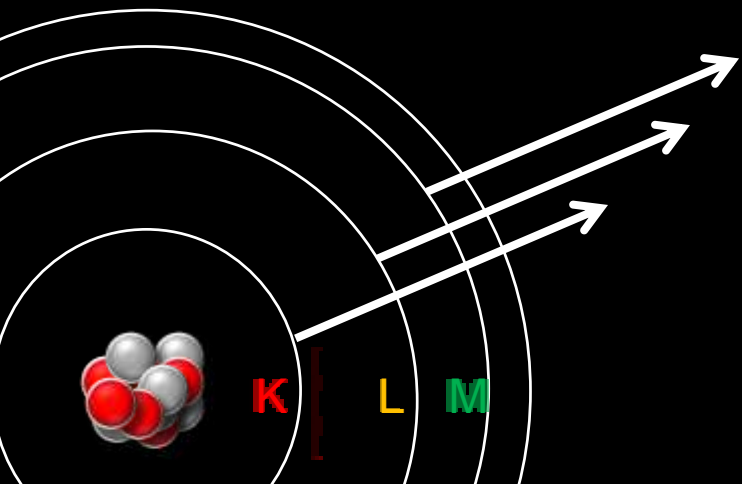
**Geometry
Movie**



X-rays allow element and site specific electronic probing

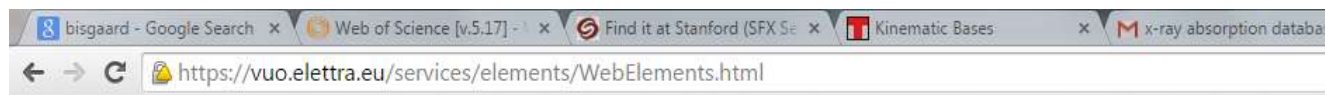


| | | | | | | | | | | | | | | | | | | | | | | | |
|-----------------------|------------------------|----------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|---------------------------|--------------------------|--------------------------|-----------------------|------------------------|------------------------|--------------------------|-------------------------|------------------------|----------------------|------------------------|----------------------|------------------------|--------------------|-----------------------|--------------------|
| 1 1.008* | | | | | | | | | | | | | | | | | 2 4.003 | | | | | | |
| H hydrogen | | | | | | | | | | | | | | | | | He helium | | | | | | |
| 3 6.94* | 4 9.012 | | | | | | | | | | | | | | | | | 5 10.81* | 6 12.01* | 7 14.01* | 8 16.00* | 9 19.00 | 10 20.18 |
| Li lithium | Be beryllium | | | | | | | | | | | | | | | | | B boron | C carbon | N nitrogen | O oxygen | F fluorine | Ne neon |
| 11 22.99 | 12 24.31* | | | | | | | | | | | | | | | | | 13 26.98 | 14 28.09* | 15 30.97 | 16 32.06* | 17 35.45* | 18 39.95 |
| Na sodium | Mg magnesium | | | | | | | | | | | | | | | | | Al aluminium | Si silicon | P phosphorus | S sulfur | Cl chlorine | Ar argon |
| 19 39.10 | 20 40.08 | 21 44.96 | 22 47.87 | 23 50.94 | 24 52.00 | 25 54.94 | 26 55.85 | 27 58.93 | 28 58.69 | 29 63.55 | 30 65.38* | 31 69.72 | 32 72.63 | 33 74.92 | 34 78.97* | 35 79.90* | 36 83.80 | | | | | | |
| K potassium | Ca calcium | Sc scandium | Ti titanium | V vanadium | Cr chromium | Mn manganese | Fe iron | Co cobalt | Ni nickel | Cu copper | Zn zinc | Ga gallium | Ge germanium | As arsenic | Se selenium | Br bromine | Kr krypton | | | | | | |
| 37 85.47 | 38 87.62 | 39 88.91 | 40 91.22 | 41 92.91 | 42 95.95* | 43 [98] | 44 101.1 | 45 102.9 | 46 106.4 | 47 107.9 | 48 112.4 | 49 114.8 | 50 118.7 | 51 121.8 | 52 127.6 | 53 126.9 | 54 131.3 | | | | | | |
| Rb rubidium | Sr strontium | Y yttrium | Zr zirconium | Nb niobium | Mo molybdenum | Tc technetium | Ru ruthenium | Rh rhodium | Pd palladium | Ag silver | Cd cadmium | In indium | Sn tin | Sb antimony | Te tellurium | I iodine | Xe xenon | | | | | | |
| 55 132.9 | 56 137.3 | 72 178.5 | 73 180.9 | 74 183.8 | 75 186.2 | 76 190.2 | 77 193.2 | 78 195.1 | 79 197.0 | 80 200.6 | 81 204.4* | 82 207.2 | 83 209.0 | 84 [209] | 85 [210] | 86 [222] | | | | | | | |
| Cs caesium | Ba barium | Hf hafnium | Ta tantalum | W tungsten | Re rhenium | Os osmium | Ir iridium | Pt platinum | Au gold | Hg mercury | Tl thallium | Pb lead | Bi bismuth | Po polonium | At astatine | Rn radon | | | | | | | |
| 87 [223] | 88 [226] | 104 [267] | 105 [268] | 106 [269] | 107 [270] | 108 [277] | 109 [278] | 110 [281] | 111 [282] | 112 [285] | 113 [286] | 114 [289] | 115 [290] | 116 [293] | 117 [294] | 118 [294] | | | | | | | |
| Fr francium | Ra radium | Rf rutherfordium | Db dubnium | Sg seaborgium | Bh bohrium | Hs hassium | Mt meitnerium | Ds darmstadtium | Rg roentgenium | Cn copernicium | Nh nihonium | Fl flerovium | Mc moscovium | Lv livermorium | Ts tennessine | Og oganesson | | | | | | | |



| | | | | | | | | | | | | | | |
|------------------------|----------------------|---------------------------|------------------------|-------------------------|------------------------|------------------------|-------------------------|------------------------|--------------------------|--------------------------|----------------------|--------------------------|------------------------|-------------------------|
| 57 138.9 | 58 140.1 | 59 140.9 | 60 144.2 | 61 [145] | 62 150.4 | 63 152.0 | 64 157.3 | 65 158.9 | 66 162.5 | 67 164.9 | 68 167.3 | 69 168.9 | 70 173.0 | 71 175.0 |
| La lanthanum | Ce cerium | Pr praseodymium | Nd neodymium | Pm promethium | Sm samarium | Eu europium | Gd gadolinium | Tb terbium | Dy dysprosium | Ho holmium | Er erbium | Tm thulium | Yb ytterbium | Lu lutetium |
| 89 [227] | 90 232.0 | 91 231.0 | 92 238.0 | 93 [237] | 94 [244] | 95 [243] | 96 [247] | 97 [247] | 98 [251] | 99 [252] | 100 [257] | 101 [258] | 102 [259] | 103 [266] |
| Ac actinium | Th thorium | Pa protactinium | U uranium | Np neptunium | Pu plutonium | Am americium | Cm curium | Bk berkelium | Cf californium | Es einsteinium | Fm fermium | Md mendelevium | No nobelium | Lr lawrencium |

X-ray data – useful help

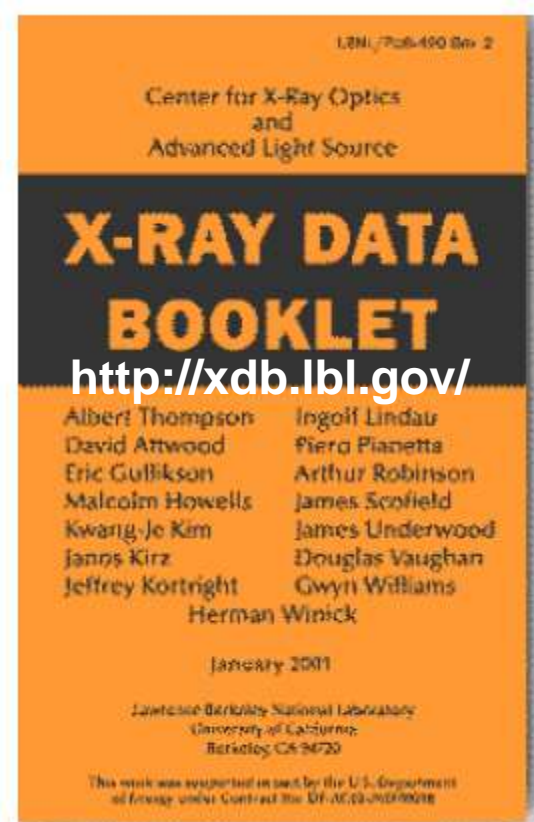


Cross-Sections and Asymmetry Parameters

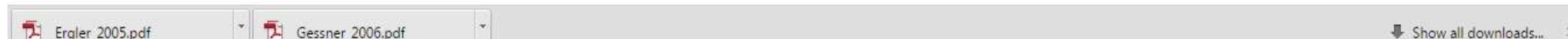
This periodic table interface was developed to easily access the calculated atomic cross sections for photoionization and the related asymmetry parameters. *Calculation of Photoionization Cross-Sections and Asymmetry Parameters*, Gordon and Breach Science Publishers, Langhorne, PE (USA), 1993 *Data Tables*, 32, 1-155 (1985). The data shown here are those calculated in the dipole length approximation.

This is a beta version: [comments](#) are welcome.

| Group | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | | | | | | |
|-------------|----------|----------|--------------|-----------|-----------|-----------|-----------|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| | 1A | 2A | 3B | 4B | 5B | 6B | 7B | 8B | | | 1B | 2B | | | | | | |
| Period | | | | | | | | | | | | | | | | | | |
| 1 | 1 H | | | | | | | | | | | | | | | | | |
| 2 | 3 Li | 4 Be | | | | | | | | | | | | | | | | |
| 3 | 11 Na | 12 Mg | | | | | | | | | | | | | | | | |
| 4 | 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | | | | | | |
| 5 | 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | | | | | | |
| 6 | 55 Cs | 56 Ba | * 71 Lu | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 7 | 87 Fr | 88 Ra | ** 103 Lr | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Uun | 111 Uuu | 112 Uub | 113 Uut | 114 Uuq | 115 Uup | 116 Uuh | 117 Uus | 118 Uuo |
| lanthanides | | | * 57 La | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | | |
| actinides | | | ** 89 Ac | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | | |

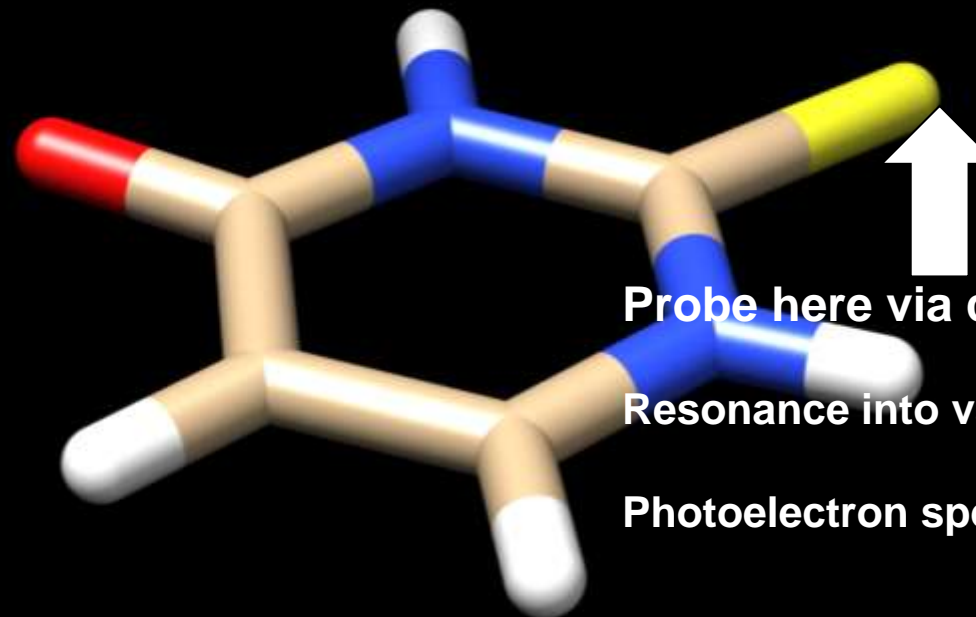
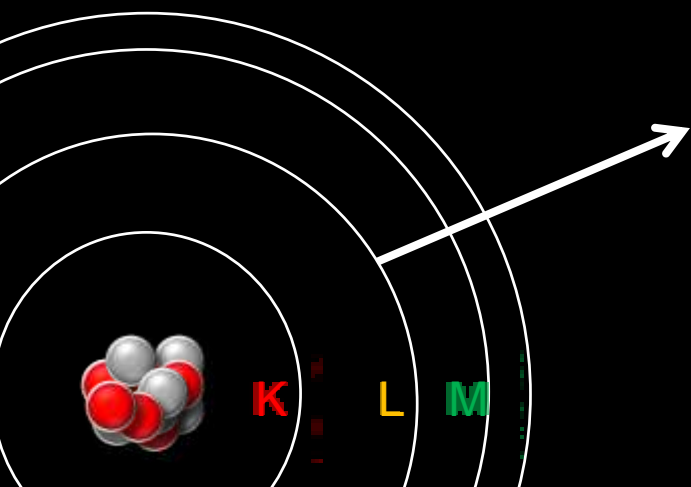
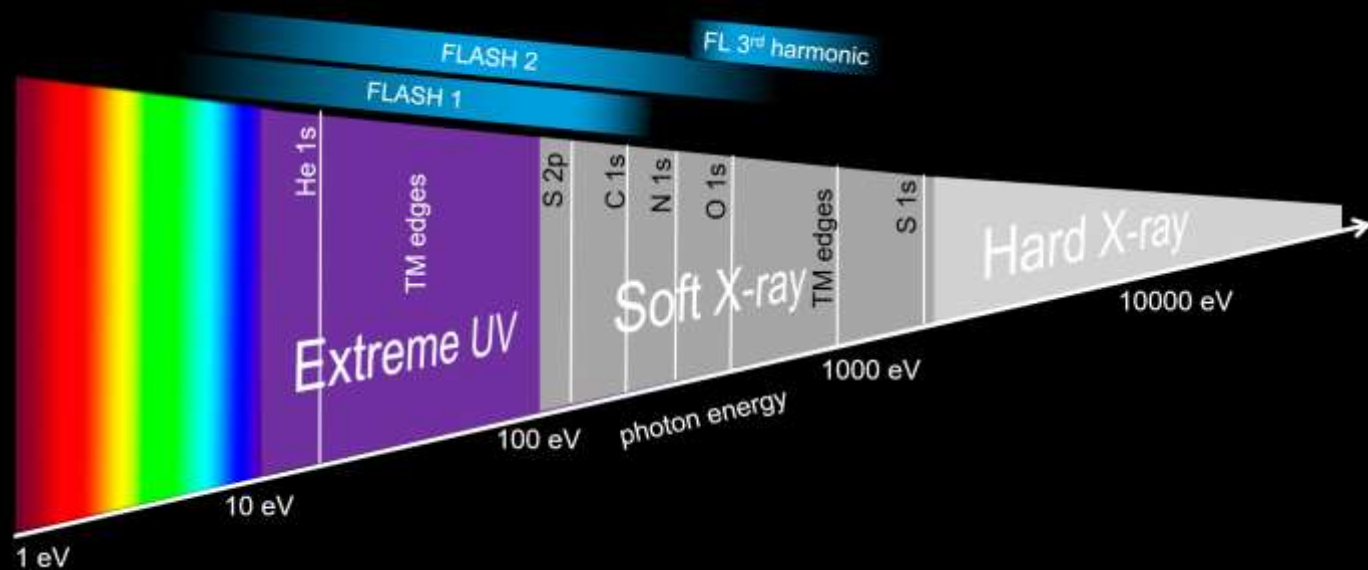


<http://xdb.lbl.gov/>



<https://vuo.elettra.eu/services/elements/WebElements.html>

X-rays allow element and site specific electronic probing

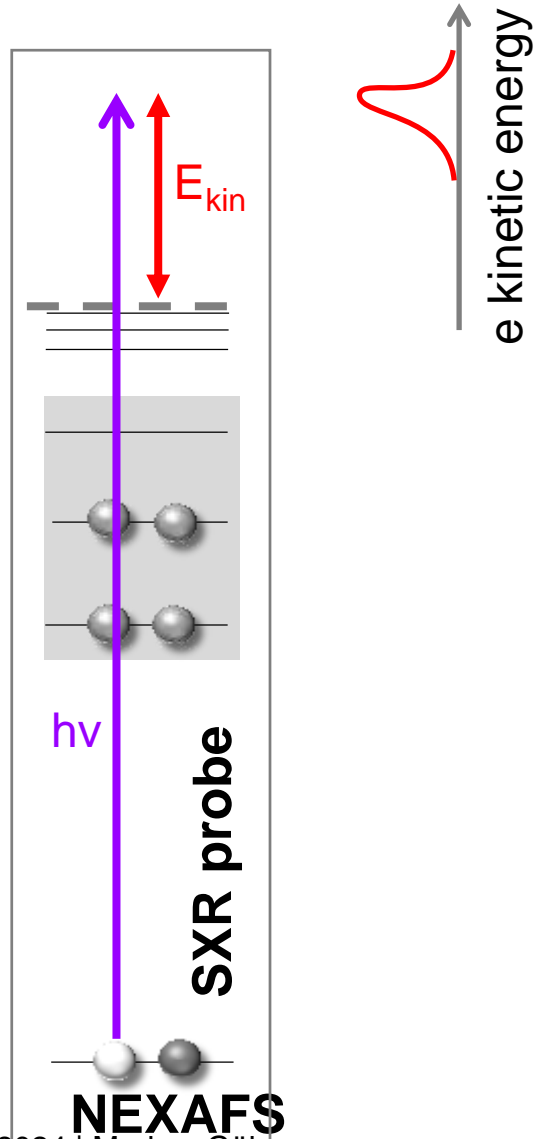


Probe here via core ionization

Resonance into valence states

Photoelectron spectroscopy

X-ray photoemission (XPS)



Kinetic energy = photon energy - binding energy



A. Einstein

Bern, den 17. März 1905.

A deeper look: Site selectivity - chemical shift

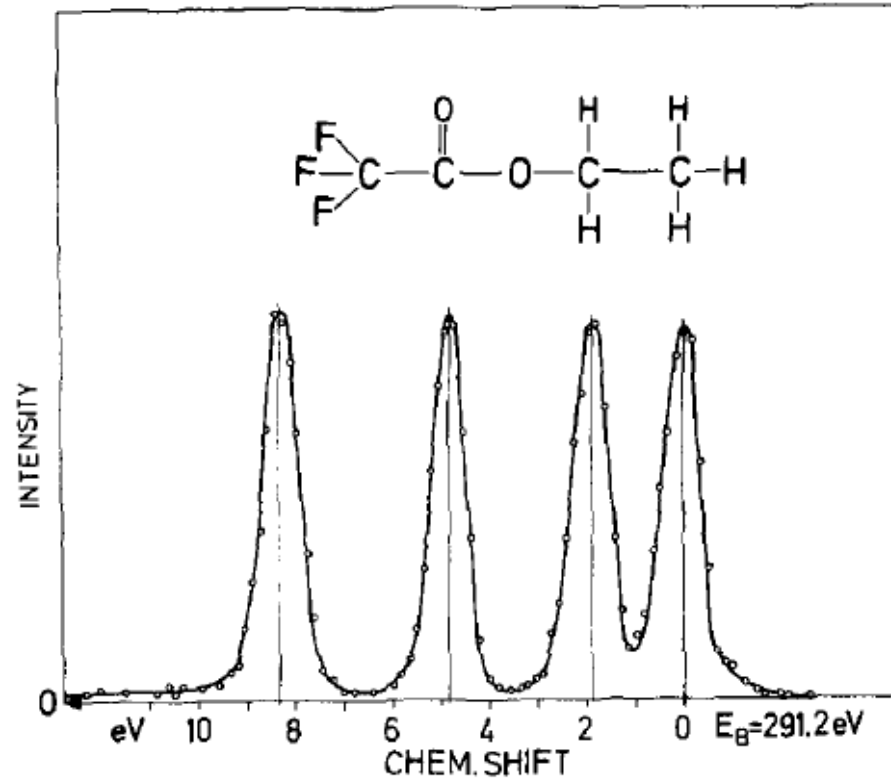
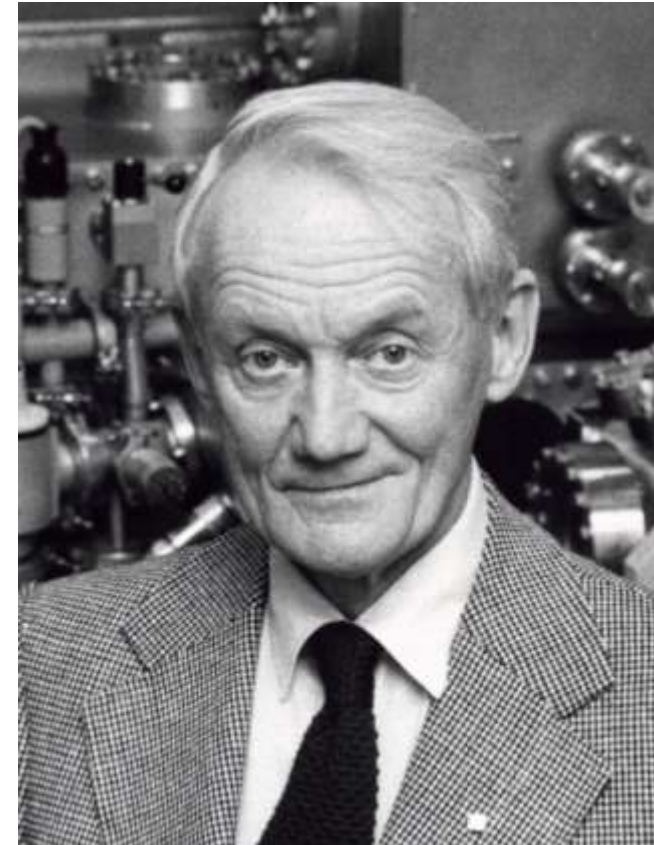


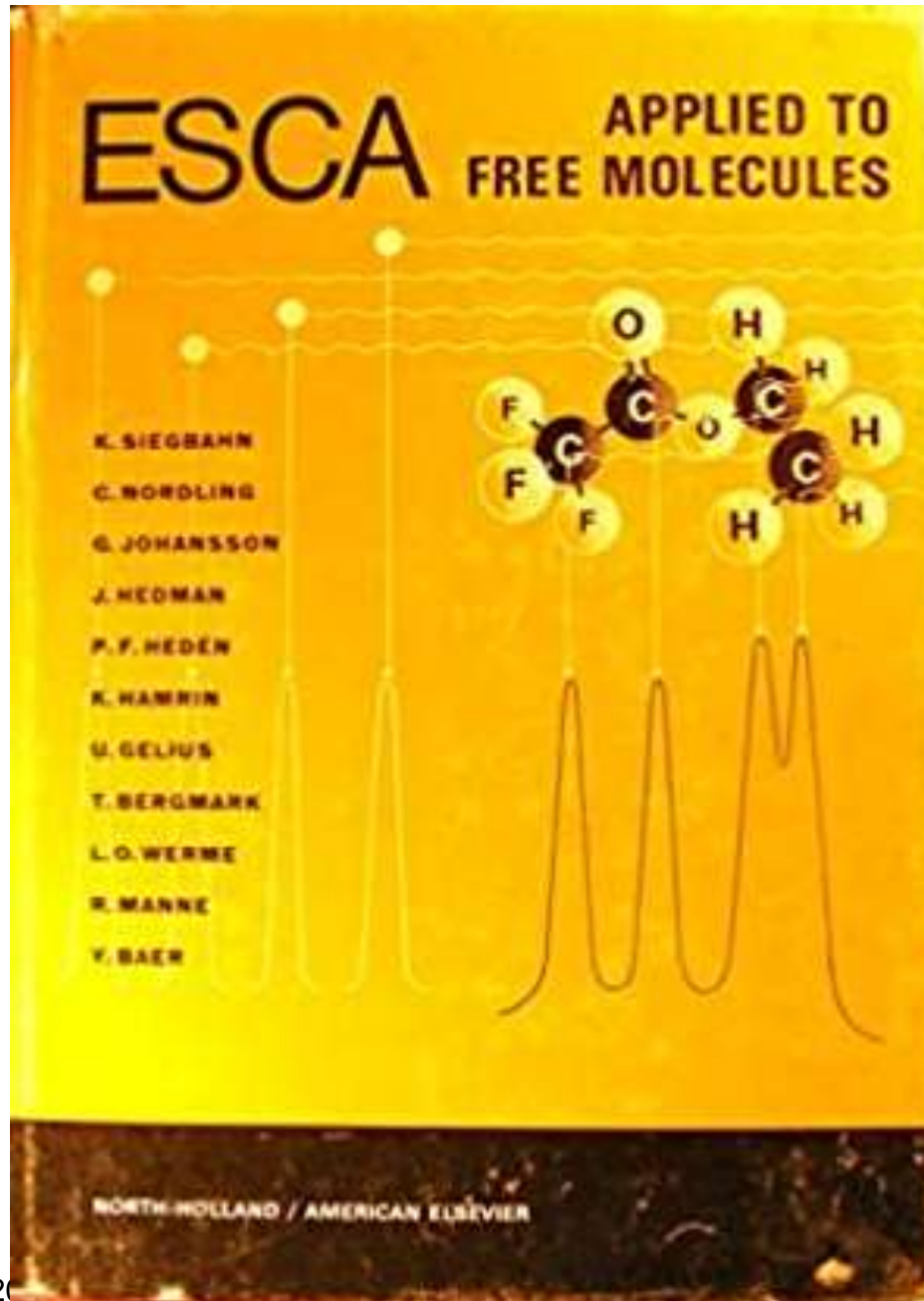
Figure 18. The carbon 1s electron lines in ethyl trifluoroacetate.



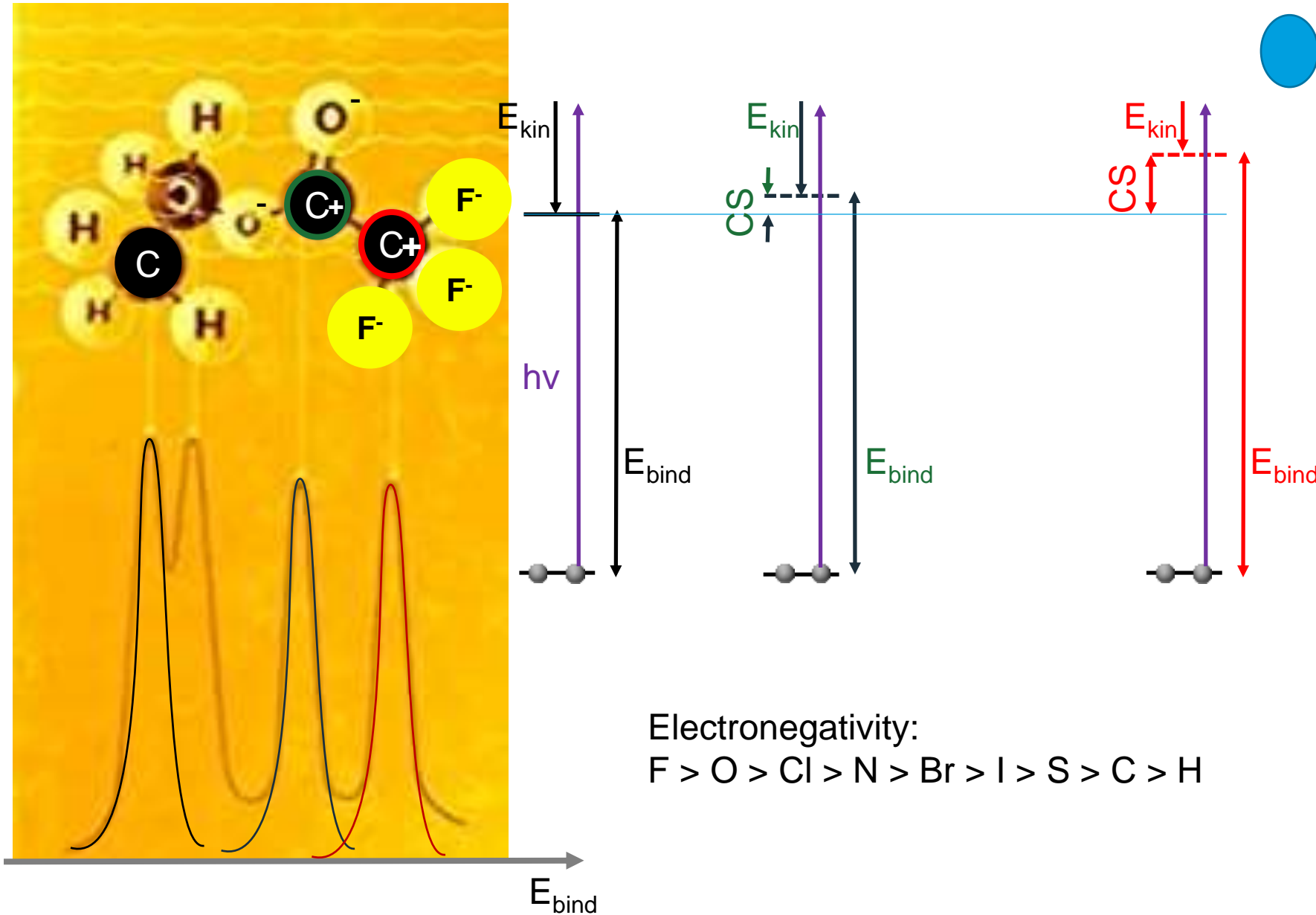
K. Siegbahn

Gelius *et al*, J. Electr. Spectr. Rel. Phen. **2**, 405 (1974)

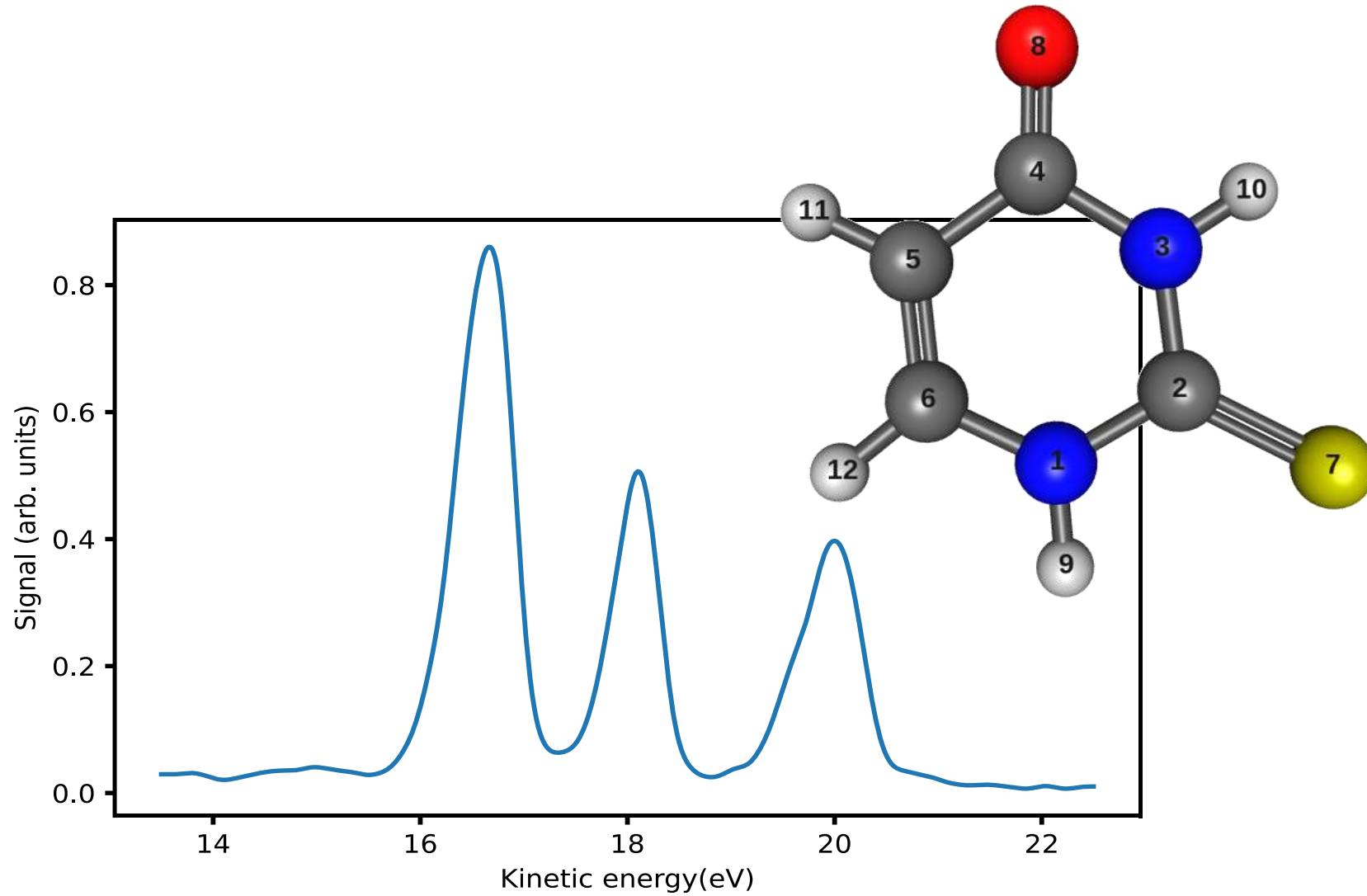
Chemical shift and local charge



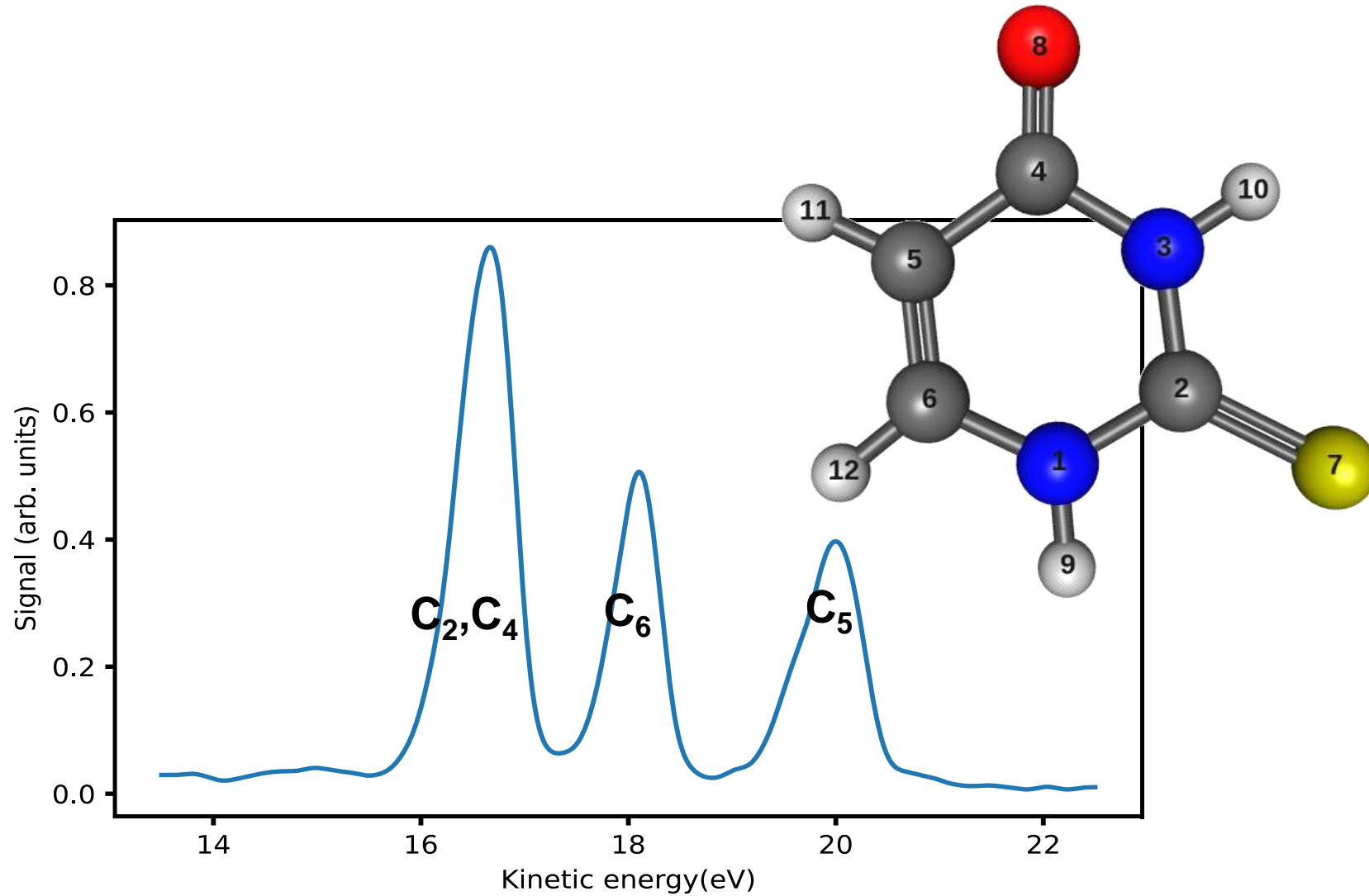
Chemical shift and local charge



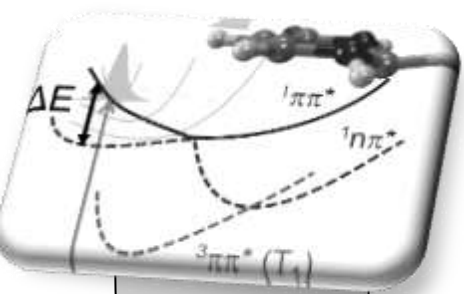
Site sensitivity – chemical shift



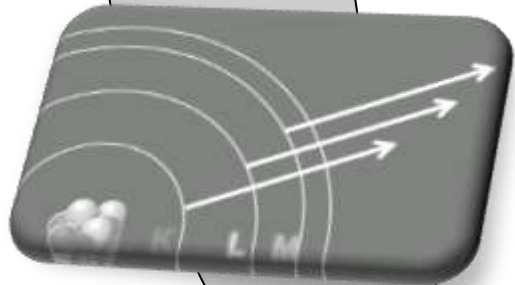
Site sensitivity – chemical shift



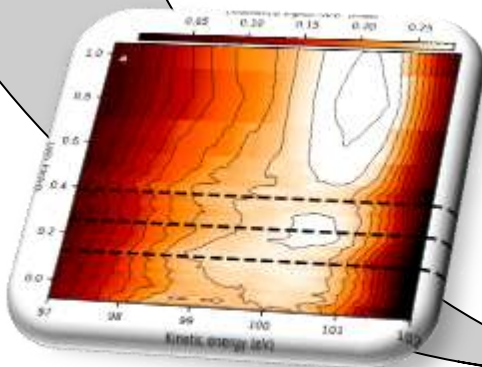
Outline



**Molecular
Photoenergy
Conversion**



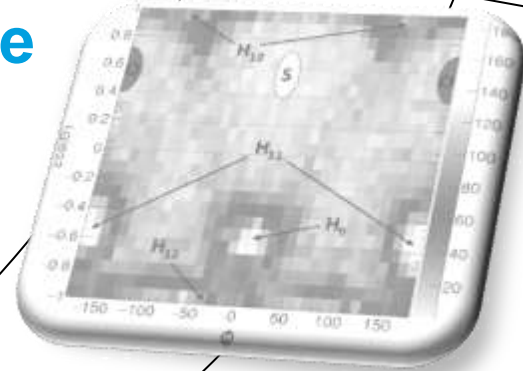
**X-ray
Probing**



**Electronic
Movie**

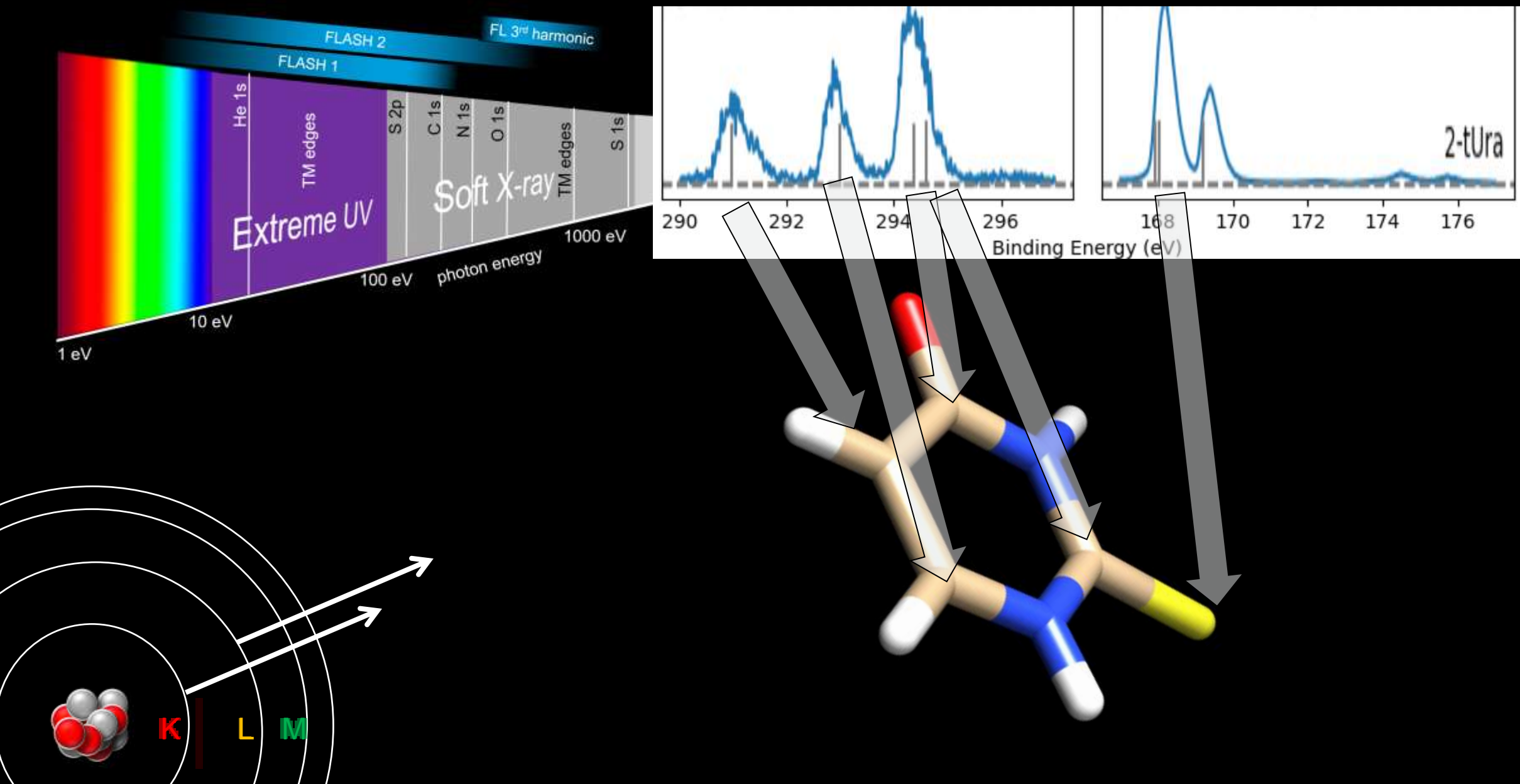


**Experimental
Setting**

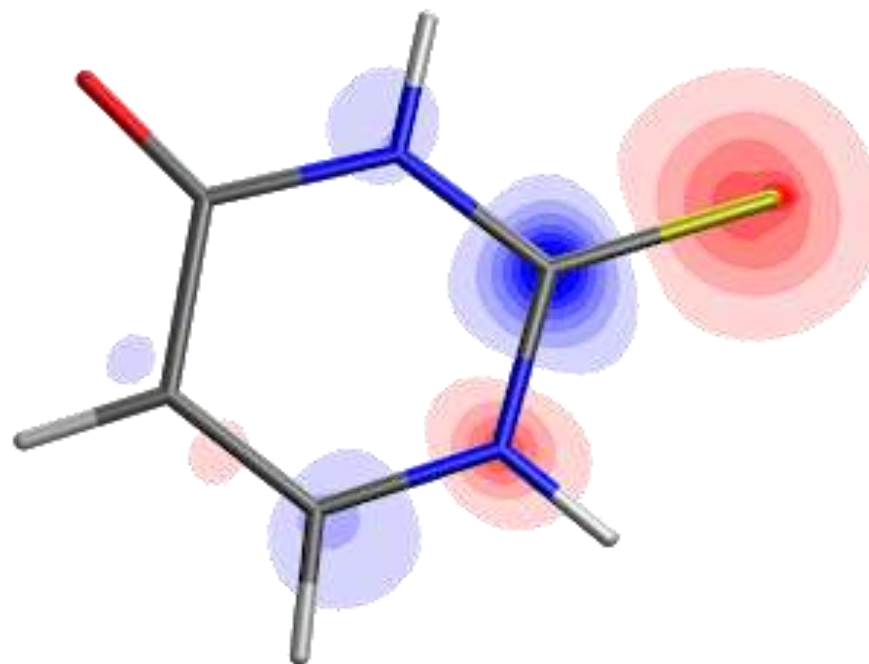
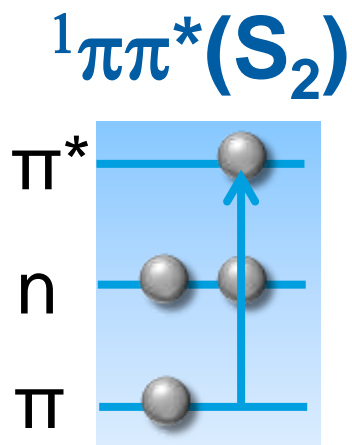
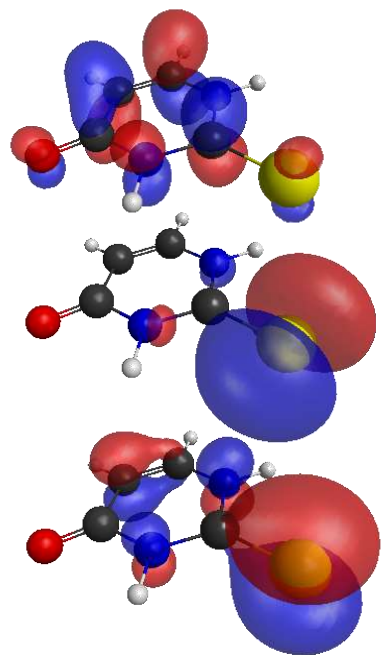


**Geometry
Movie**

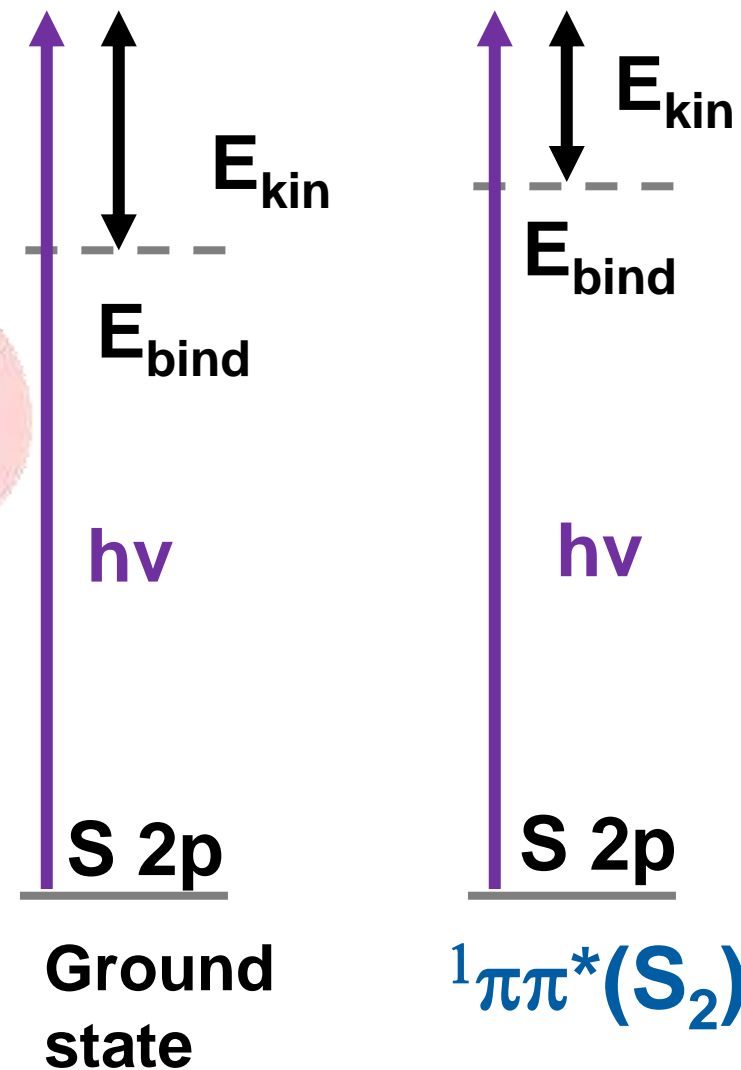
FLASH allows element and site specific electronic probing



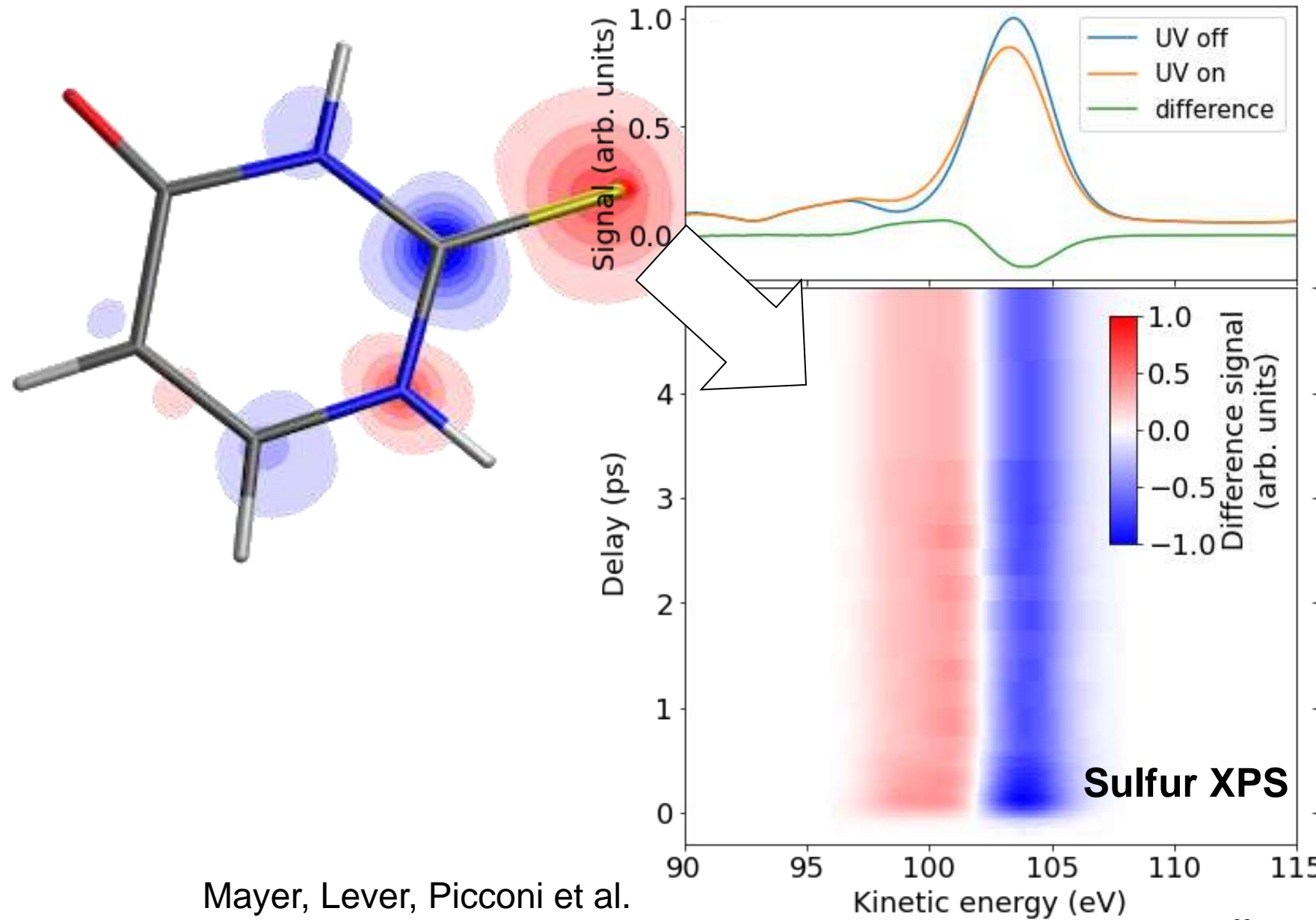
The electronic molecular movie



Charge difference plot

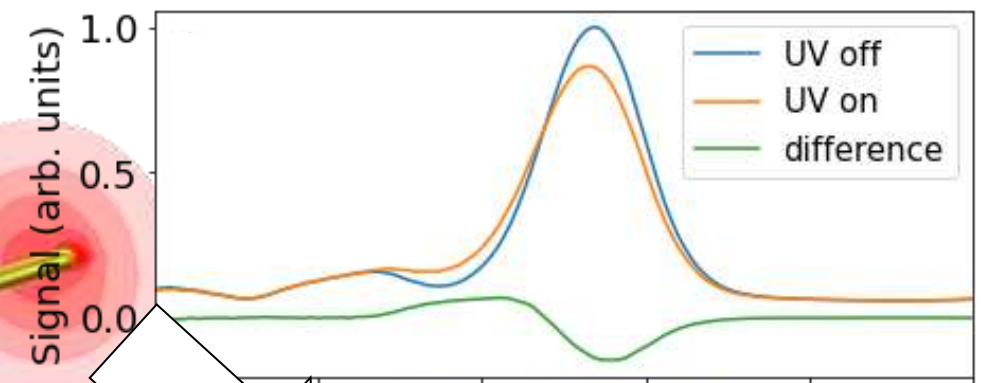
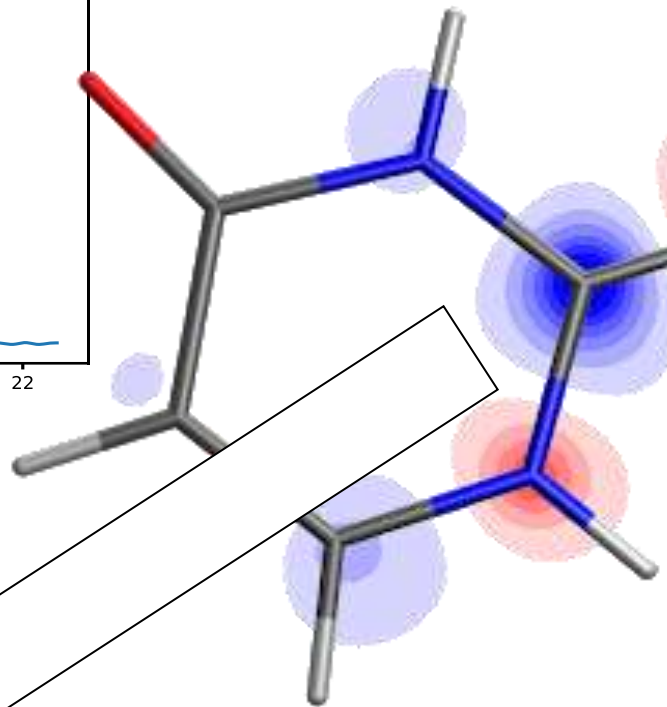
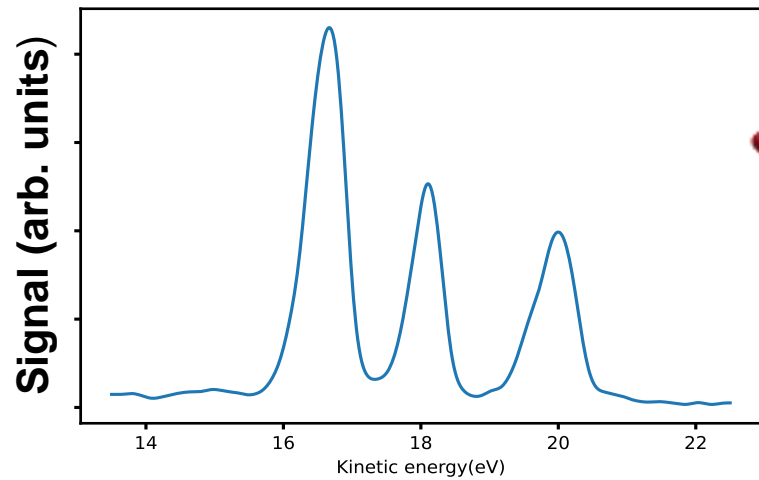


The electronic molecular movie

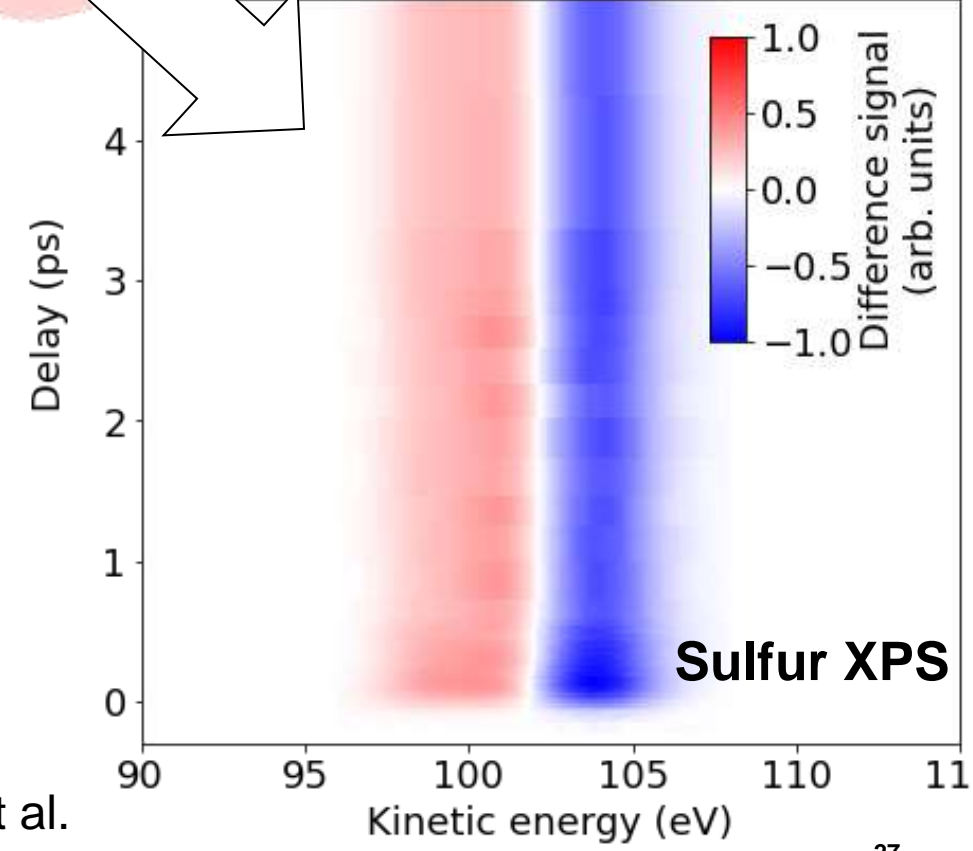


Mayer, Lever, Picconi et al.
Nature Comm. **13**, 198 (2022)

The electronic molecular movie



unpublished



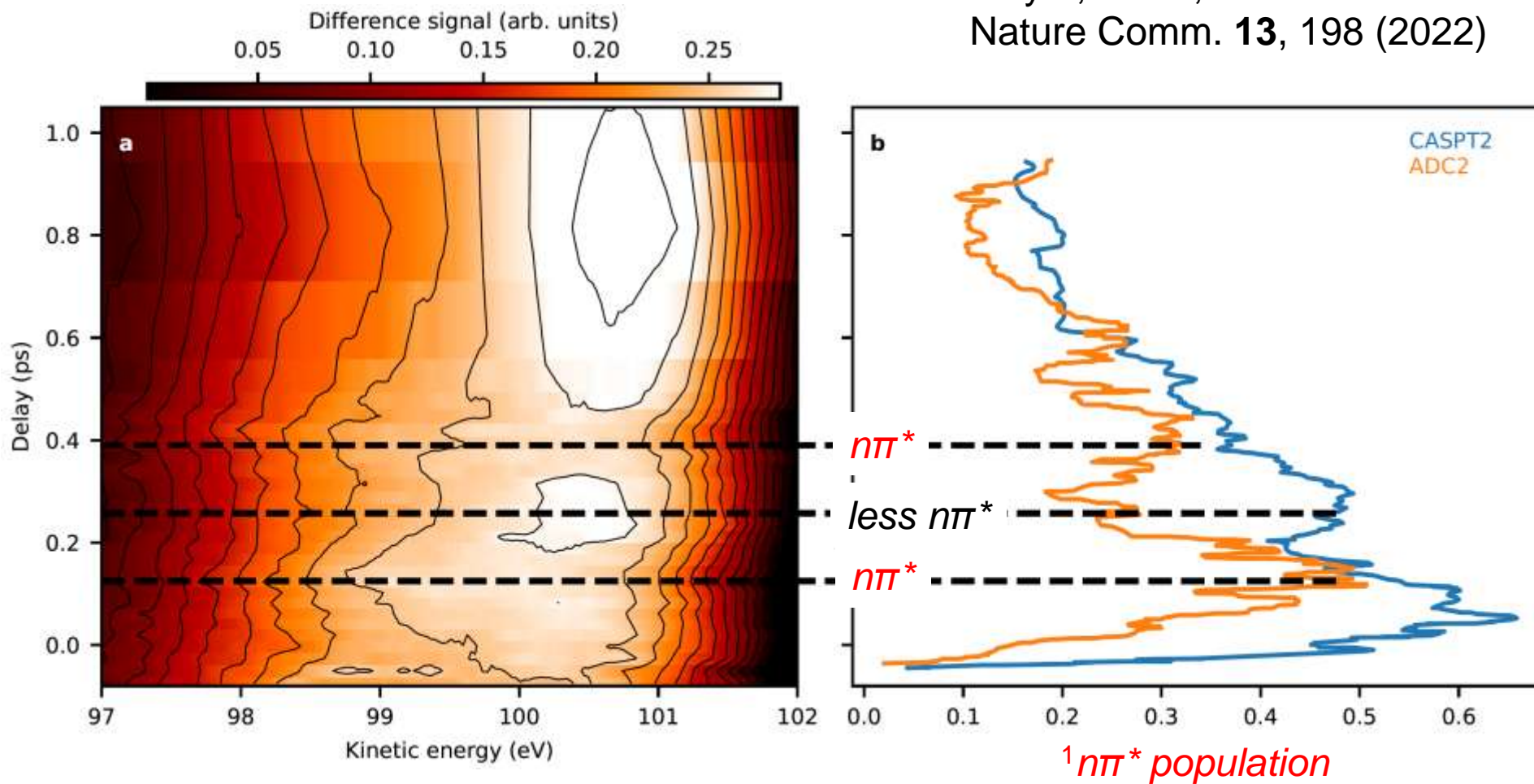
Carbon XPS

Sulfur XPS

Mayer, Lever, Picconi et al.
Nature Comm. **13**, 198 (2022)

Oscillations exhibit coherent molecular dynamics

Mayer, Lever, Picconi et al.
Nature Comm. **13**, 198 (2022)

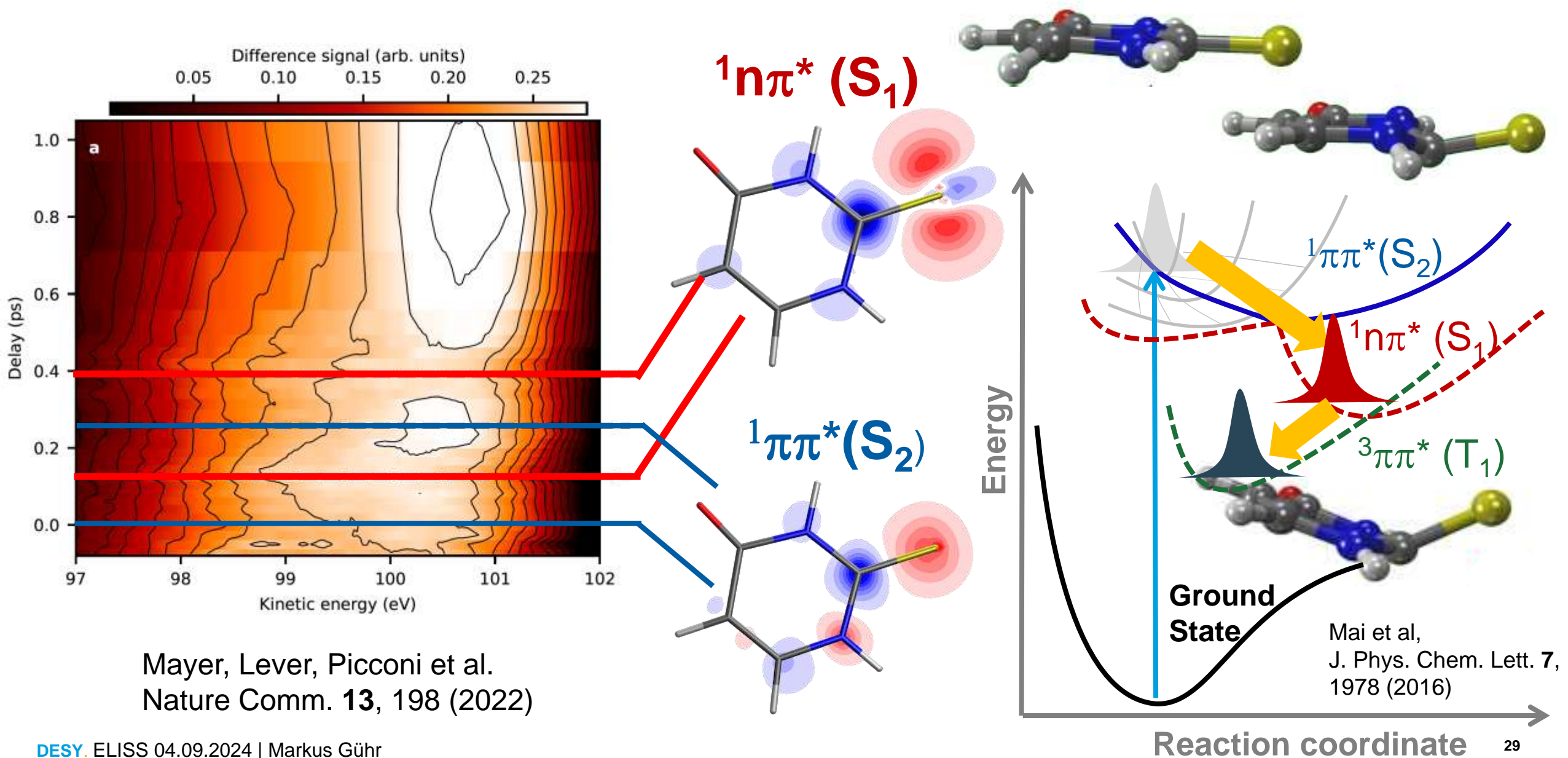


Simulations:

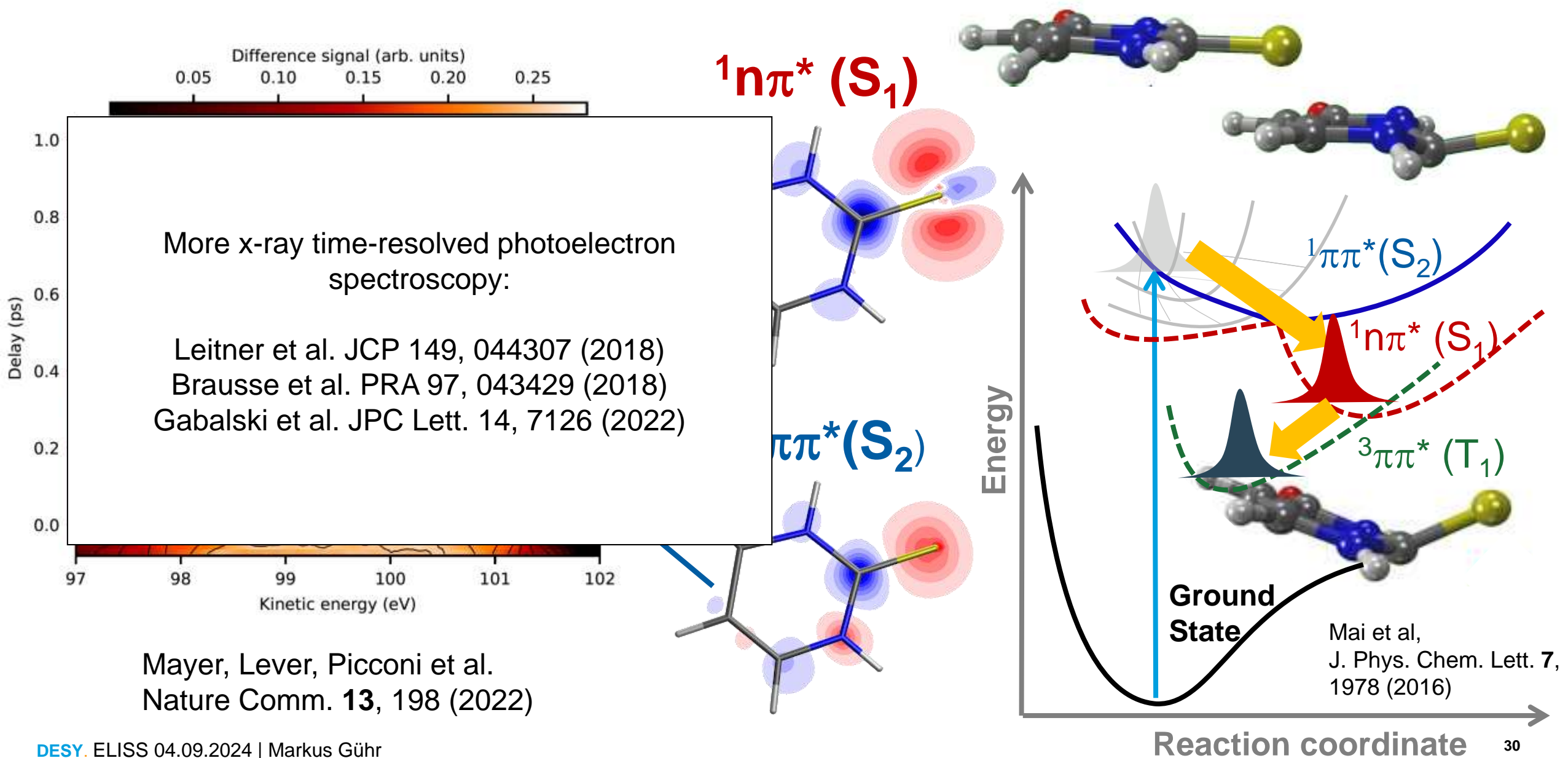
Mai, Marquetand, González, J. Phys. Chem. Lett. **7**, 1978–1983 (2016)

Mai et al. J. Chem. Phys. **147**, 184109 (2017)

Coupling of electrons and nuclei determines photochemistry



Coupling of electrons and nuclei determines photochemistry



Mayer, Lever, Picconi et al.
Nature Comm. **13**, 198 (2022)

DESY

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Mans Wallner

UCL:

Rebecca Ingle

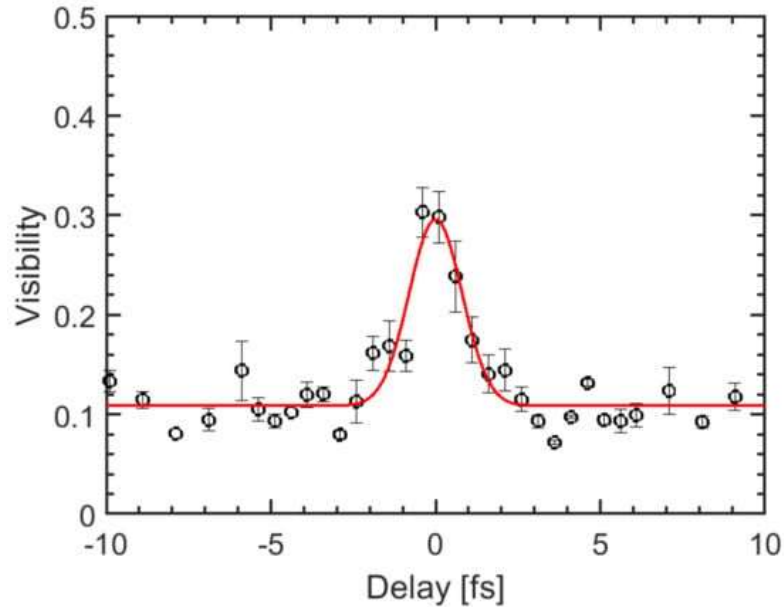
SOLEIL:

John Bozek
Christophe Nicolas

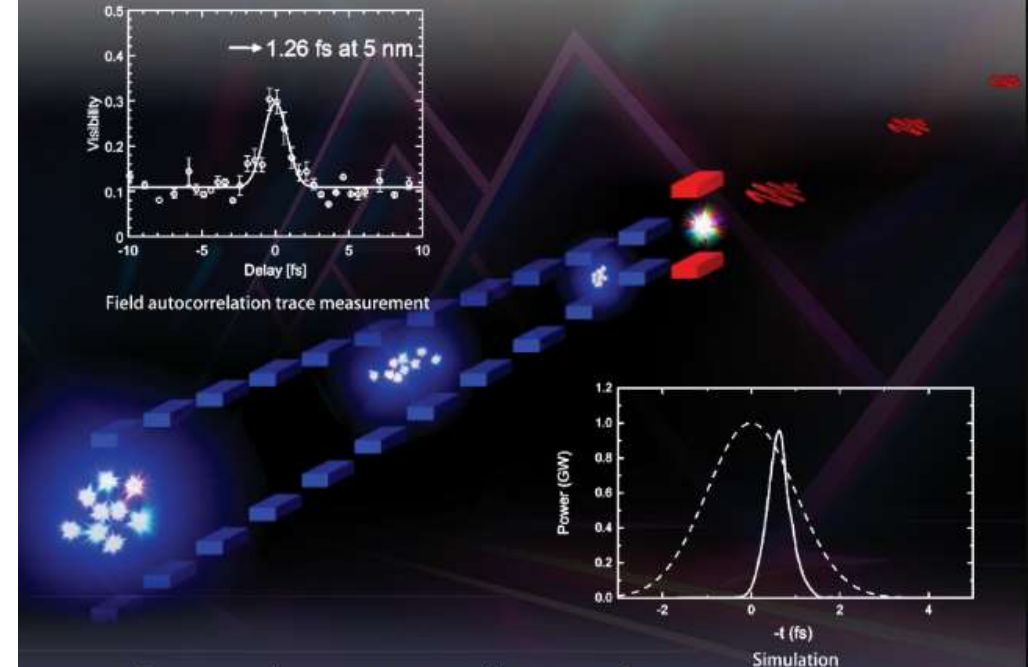


Dennis Mayer, Fabiano Lever, David Picconi et al.
Nature Comm. **13**, 198 (2022)

1.26 fs pulse duration



- Correlation using the split-and-delay setup at FLASH 2 delivers **1.26 fs** pulse length at **5 nm** wavelength
- Collaboration of FLASH with University of Münster



Open Access Communication

Generation of Ultrashort Pulses in XUV and X-ray FELs via an Excessive Reverse Undulator Taper

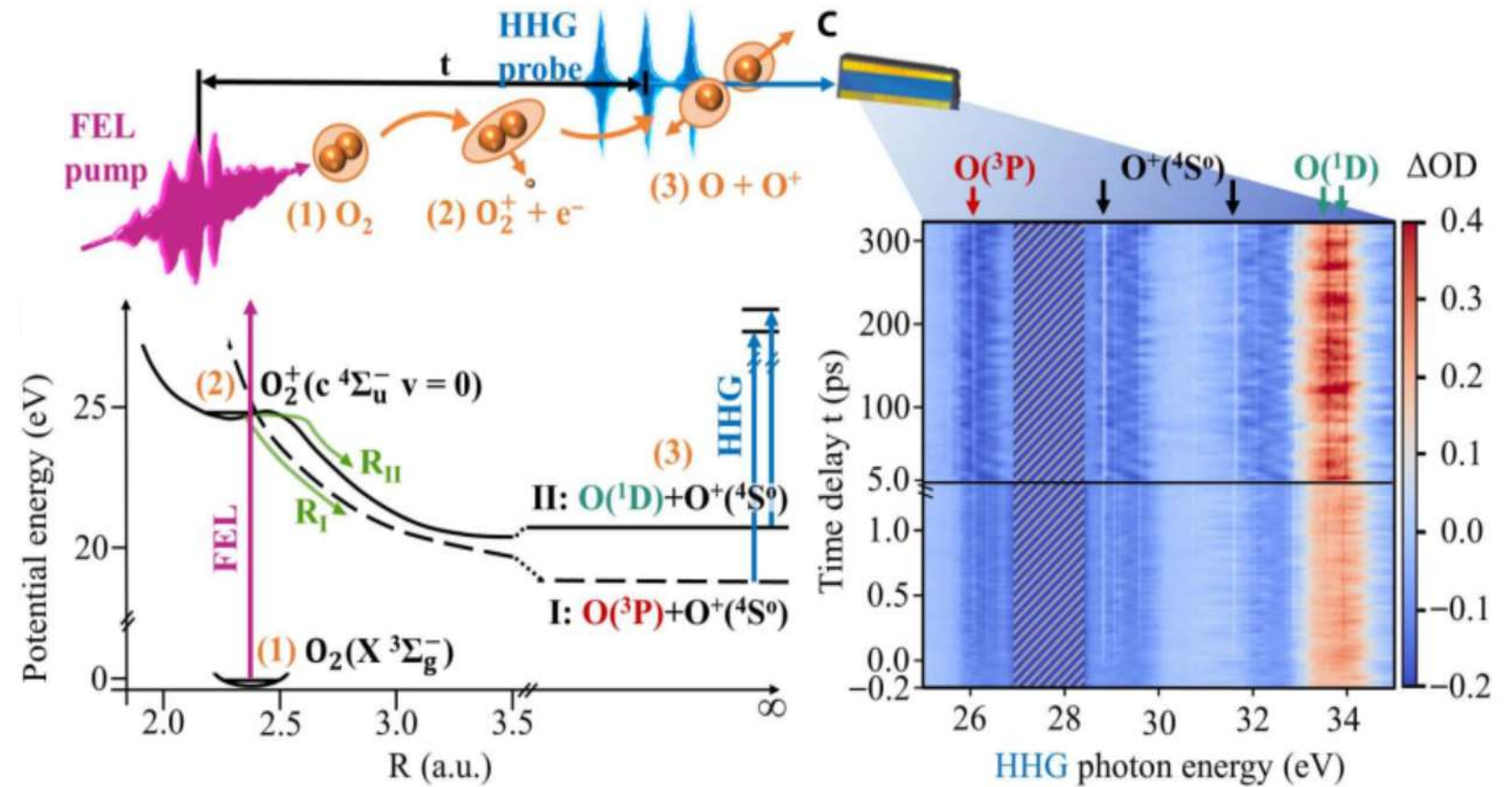
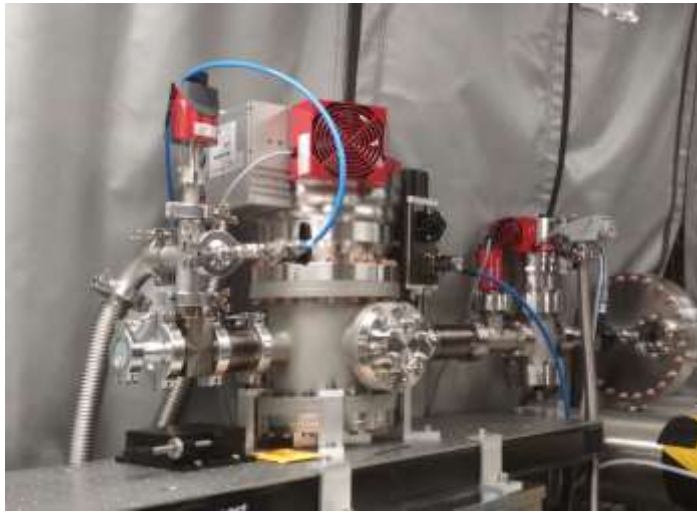
by [Evgeny Schneidmiller](#)^{1,*}, [Matthias Dreimann](#)², [Marion Kuhlmann](#)¹,
[Juliane Rönsch-Schulenburg](#)¹ and [Helmut Zacharias](#)²

Volume 10 · Issue 6 | June 2023

Schneidmiller et al., Photonics 10, 653 (2023)

FLASH AMO science

Broadband EUV probing



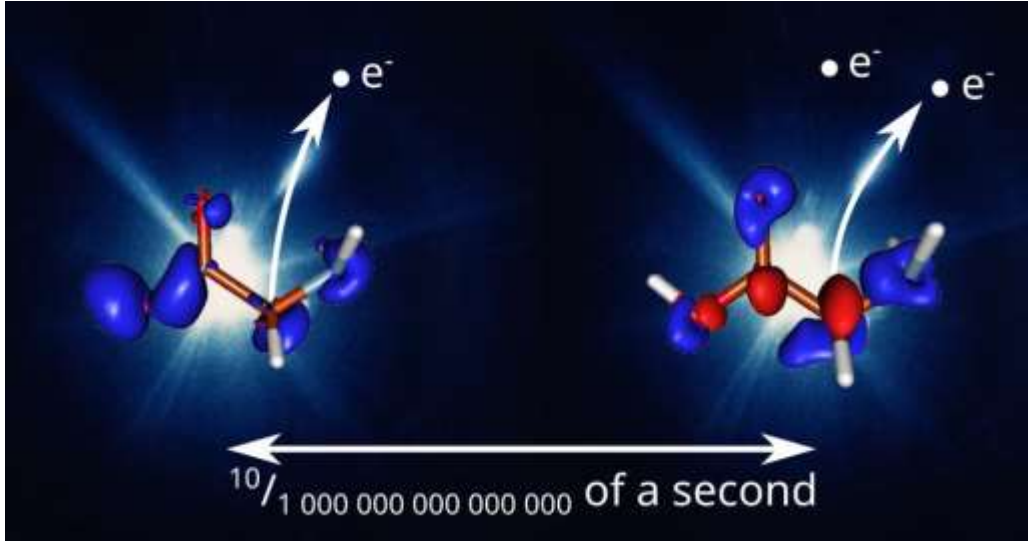
Courtesy: Christina Papadopoulou

ErUm funded in collaboration
with Uni Hannover

Magunia et al., Sci. Adv. **9**, eadk1482 (2023)

FLASH Science

Electronic dynamics in glycine

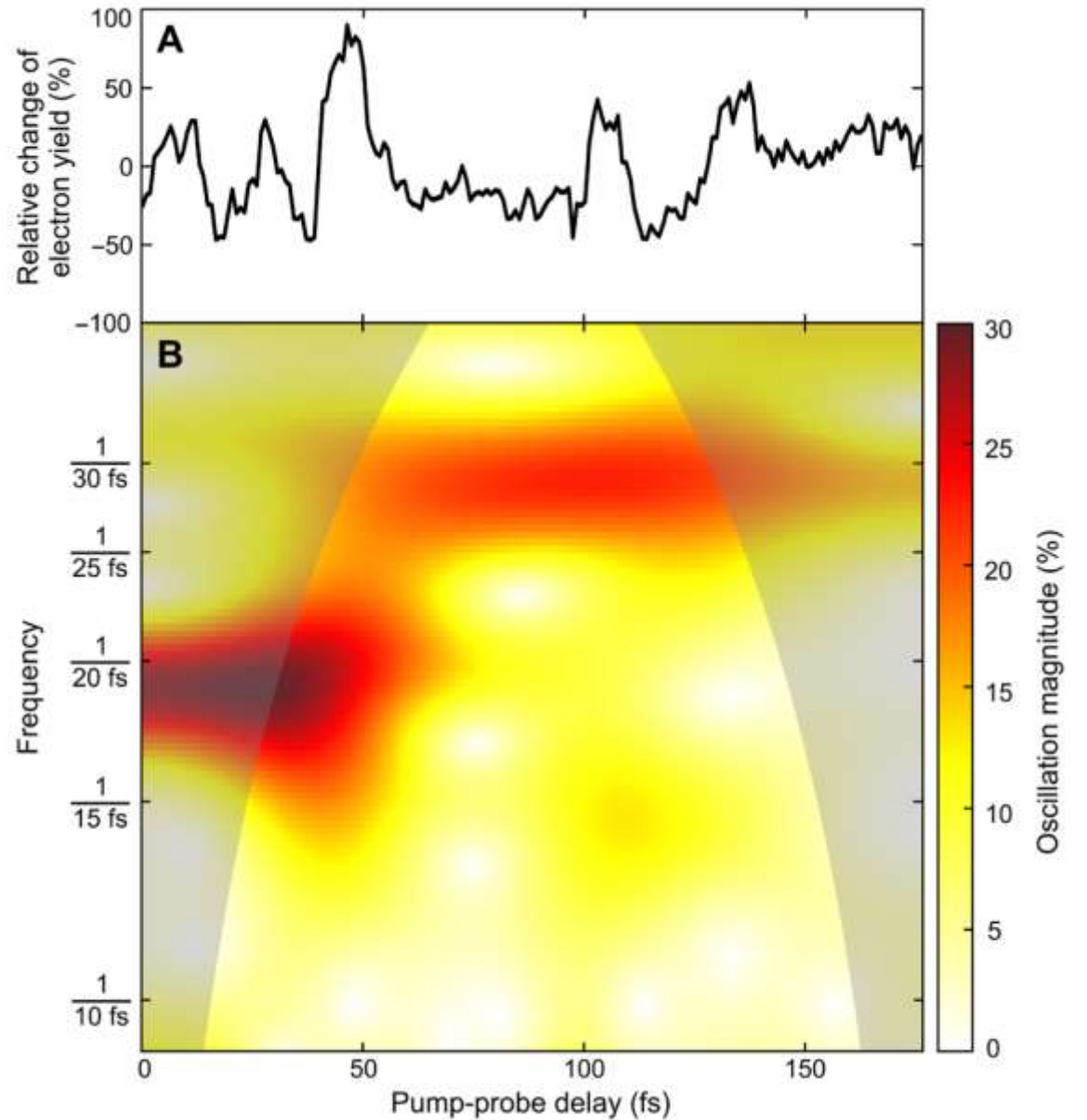


D. Schwickert, ..., J. Marangos, T. Laarmann, Science Advances, 2022

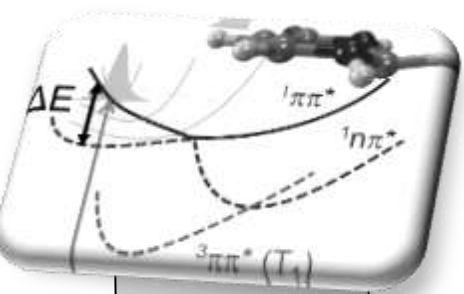
X-ray pump probe study on an amino acid

Excitation pulse leaves molecule in an electronic superposition

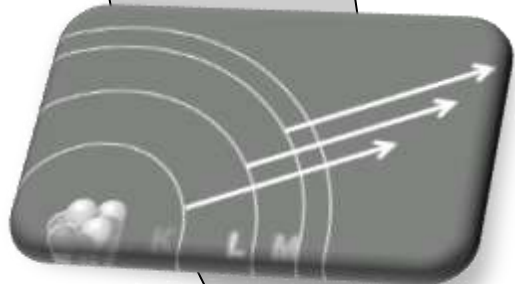
Local probing at C K-edge shows the charge migration and its coupling to nuclear vibrations



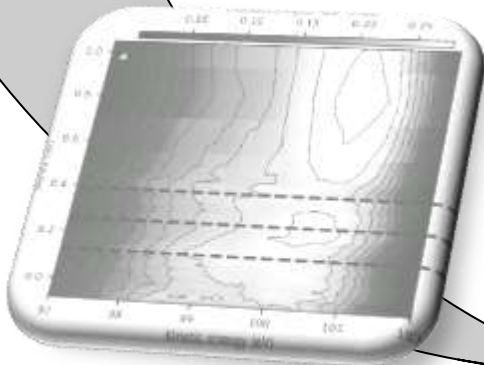
Outline



**Molecular
Photoenergy
Conversion**



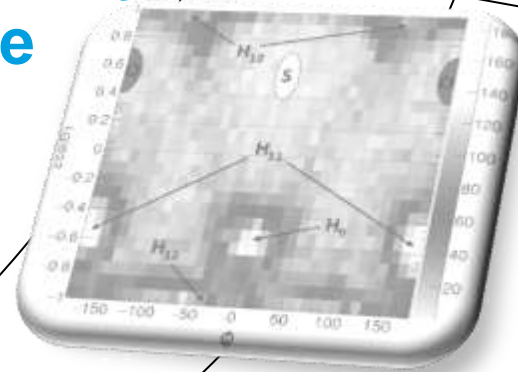
**X-ray
Probing**



**Electronic
Movie**



**Experimental
Setting**

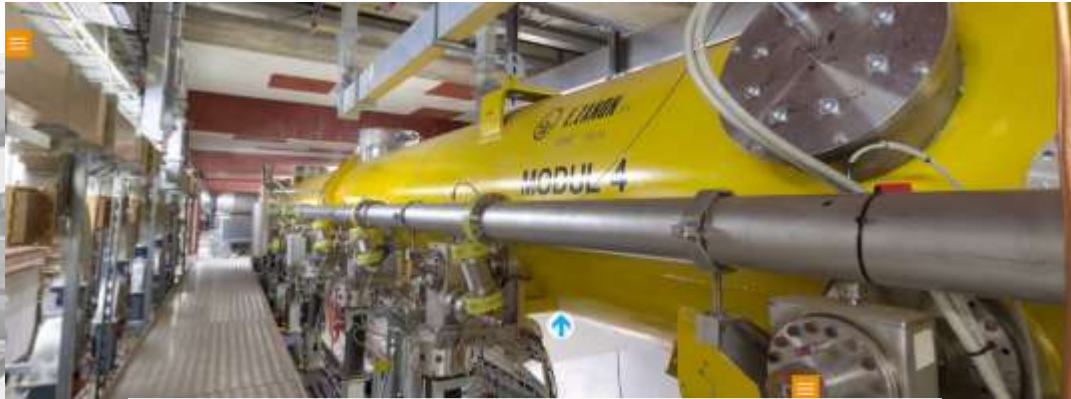


**Geometry
Movie**

Free electron laser FLASH at DESY in Hamburg



FLASH

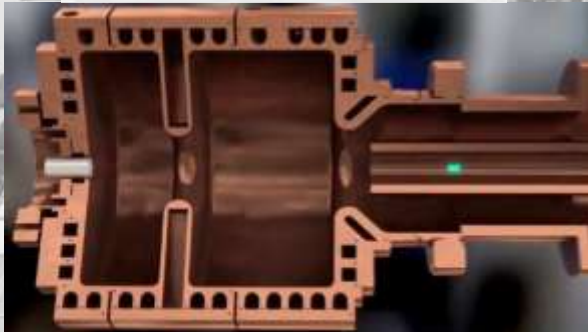


Superconducting accelerator

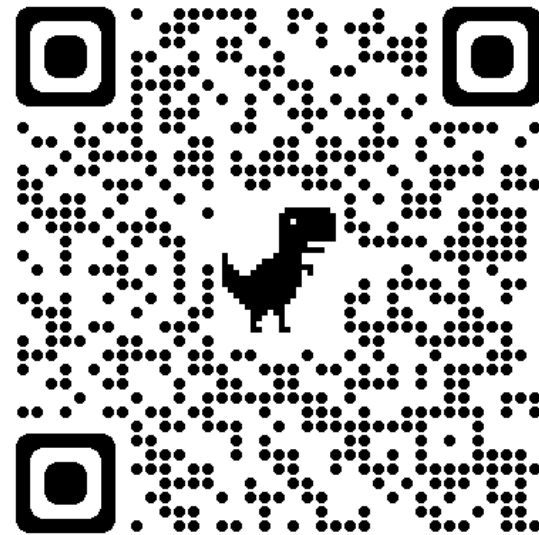


Undulator

Electron source

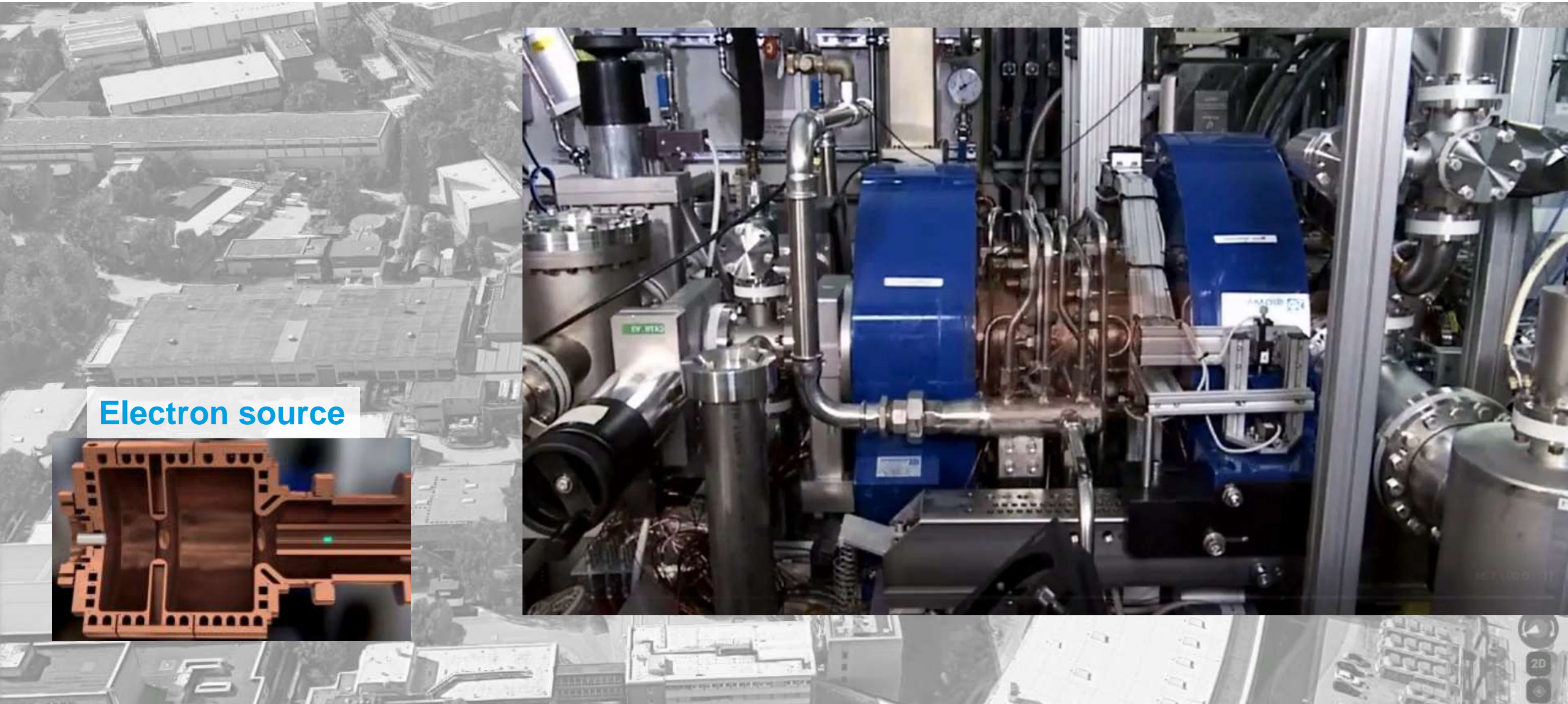


Photon diagnostics and instruments



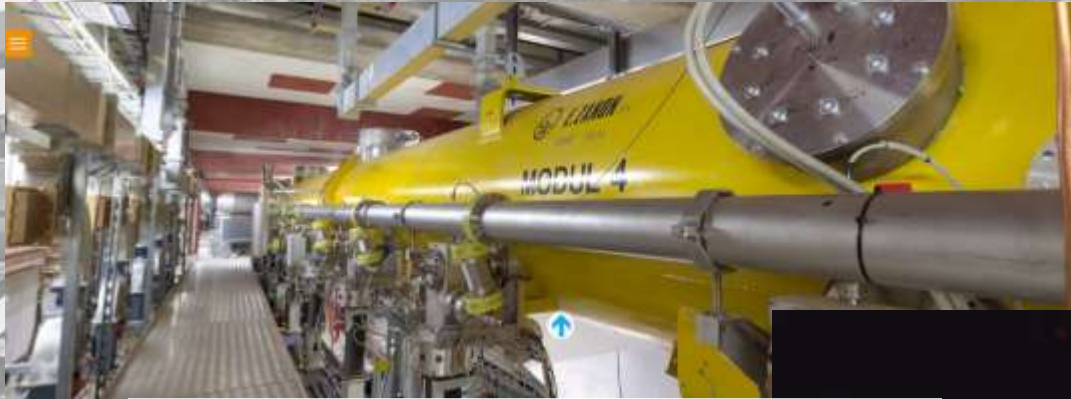
https://vtour.desy.de/desytour/index_de.html#node5

Working principle of a Free Electron Laser



Electron source

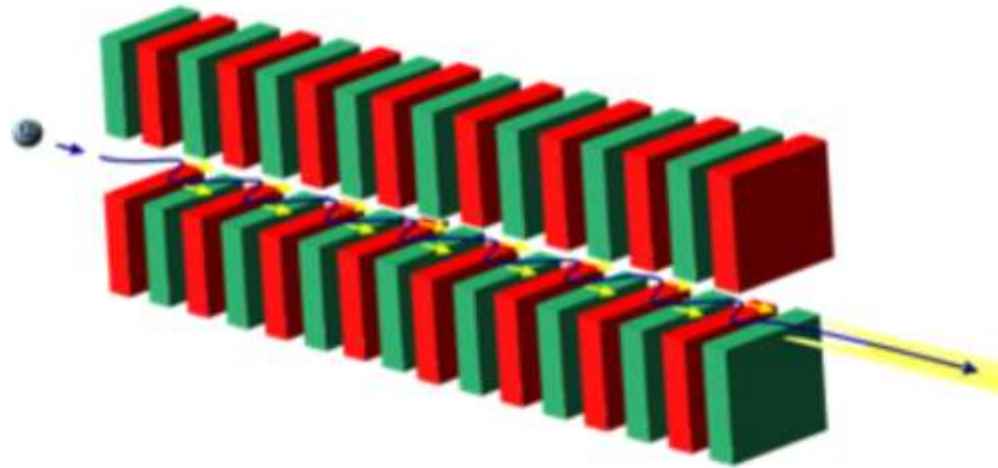
Working principle of a Free Electron Laser



Superconducting accelerator



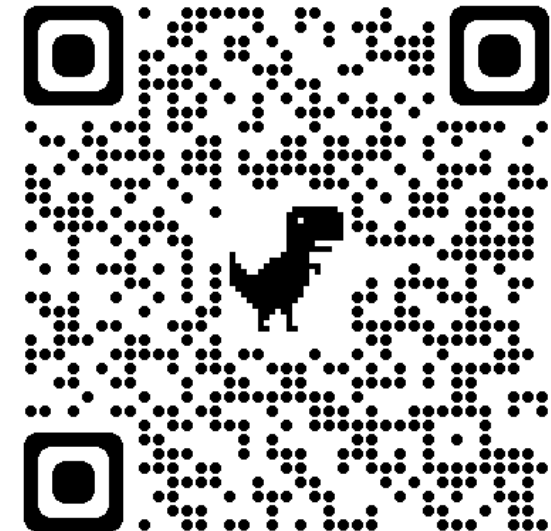
Working principle of a Free Electron Laser



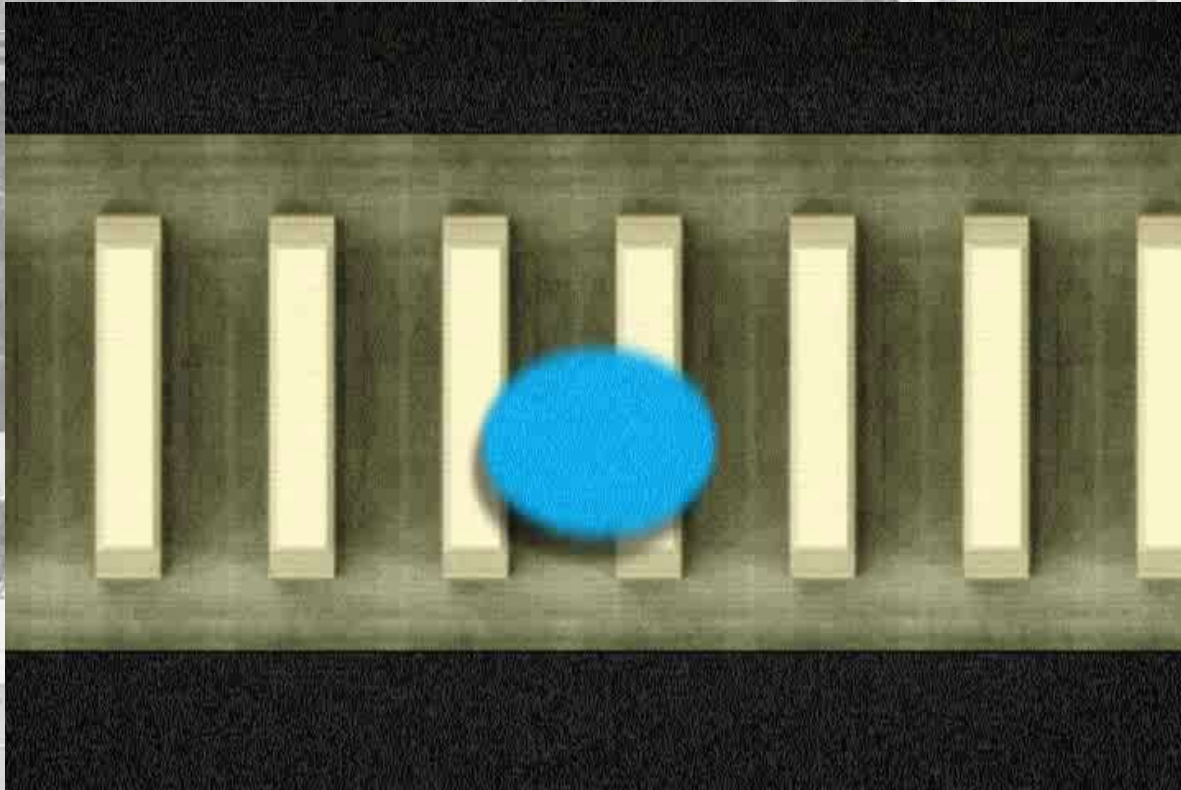
<https://science.hzbblog.de/what-is-an-undulator>



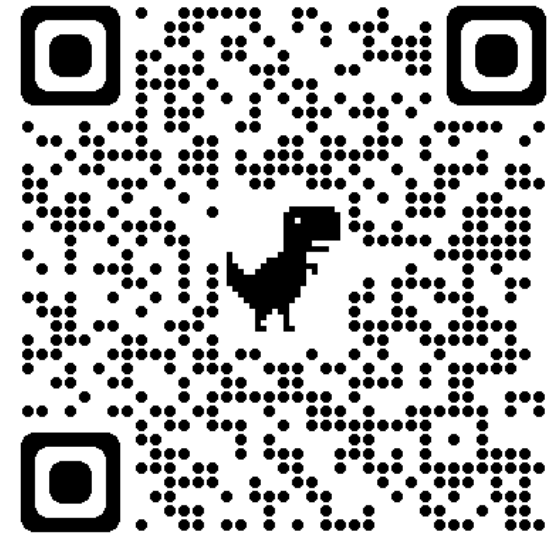
Undulator



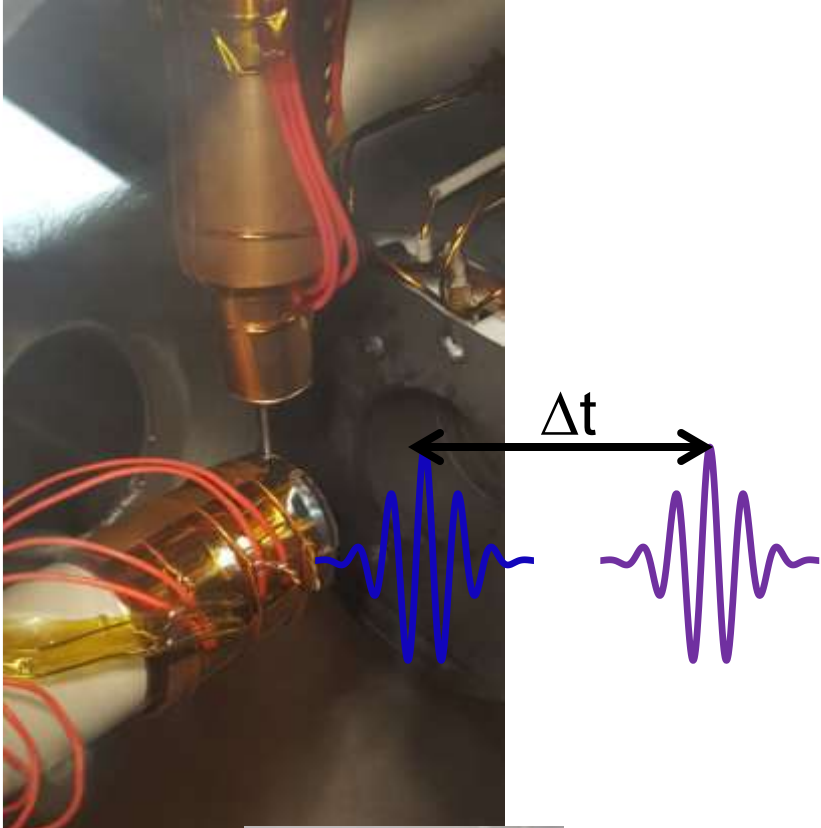
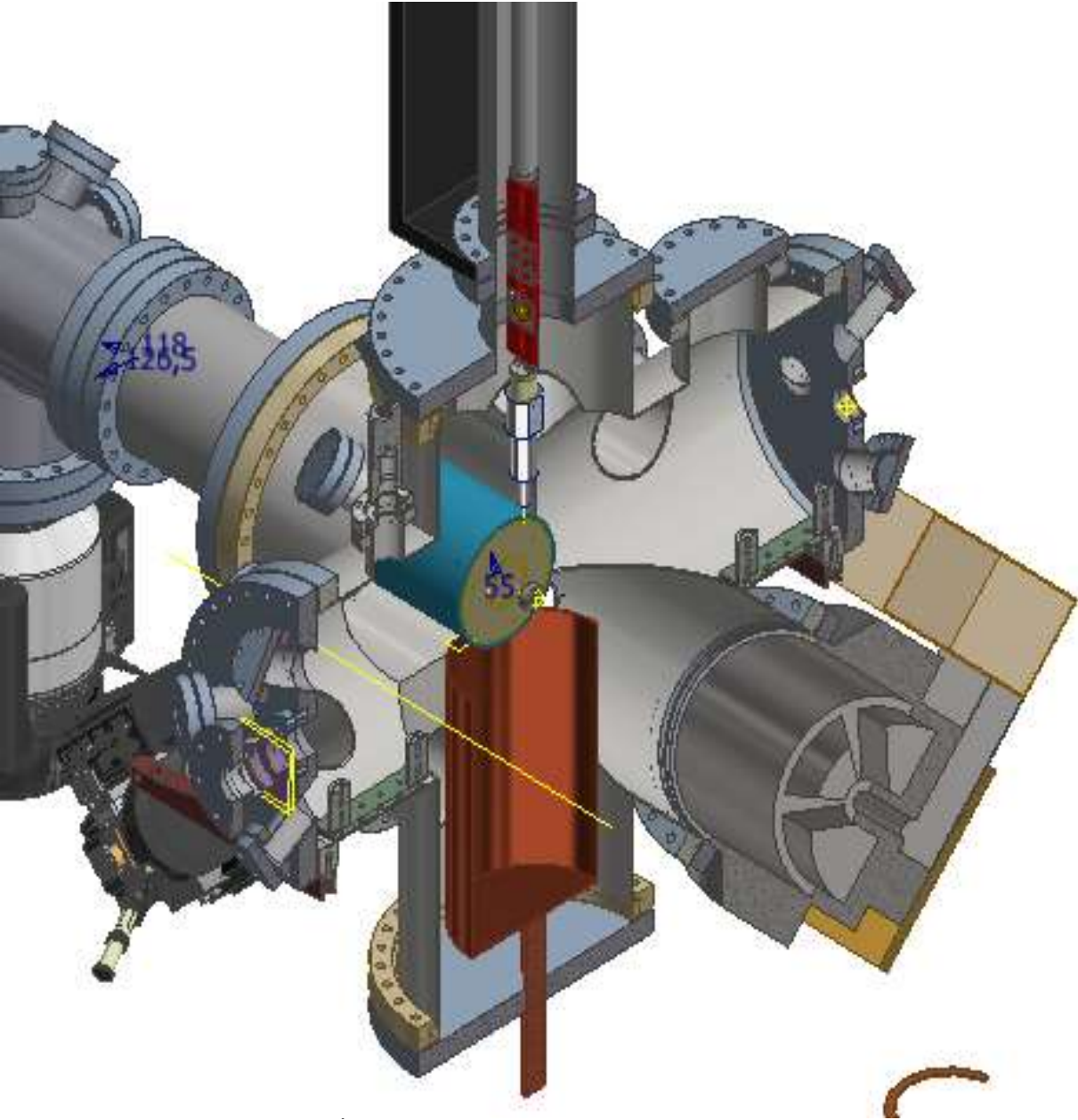
Working principle of a Free Electron Laser



Undulator



Experiment in the URSA instrument at FLASH



Dennis Mayer

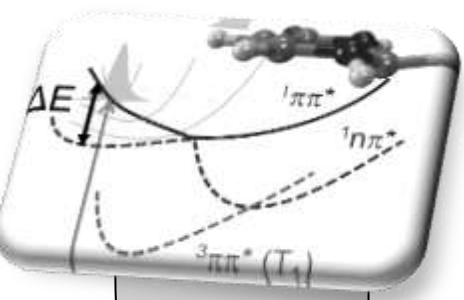


Fabiano Lever

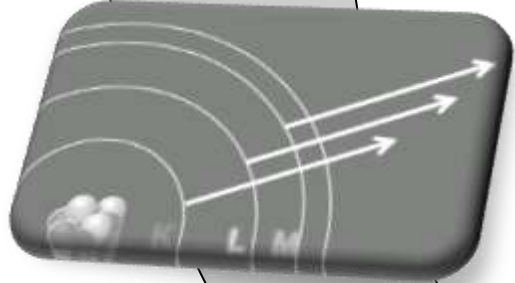


Jan Metje

Outline

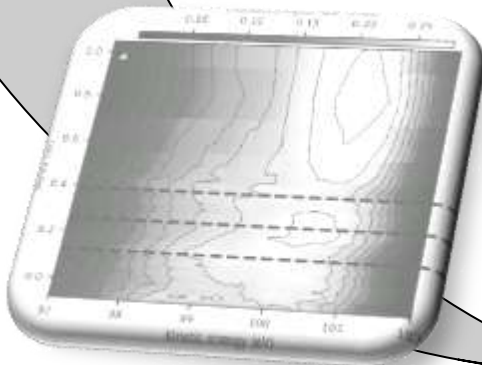


**Molecular
Photoenergy
Conversion**



**X-ray
Probing**

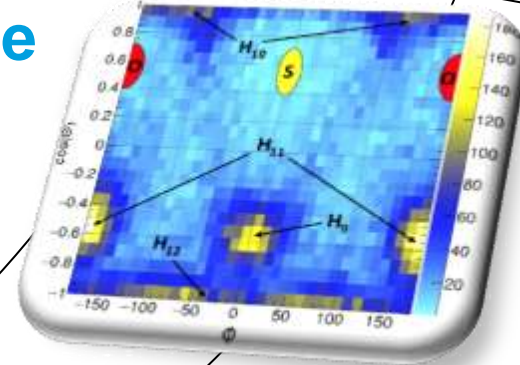
**Electronic
Movie**



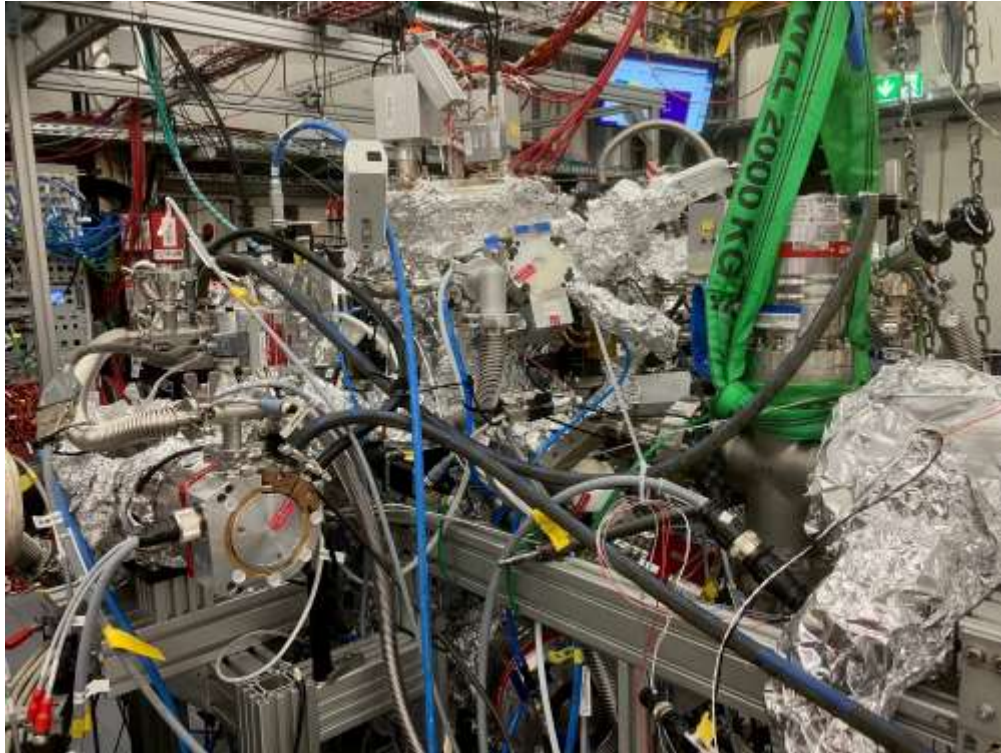
**Experimental
Setting**



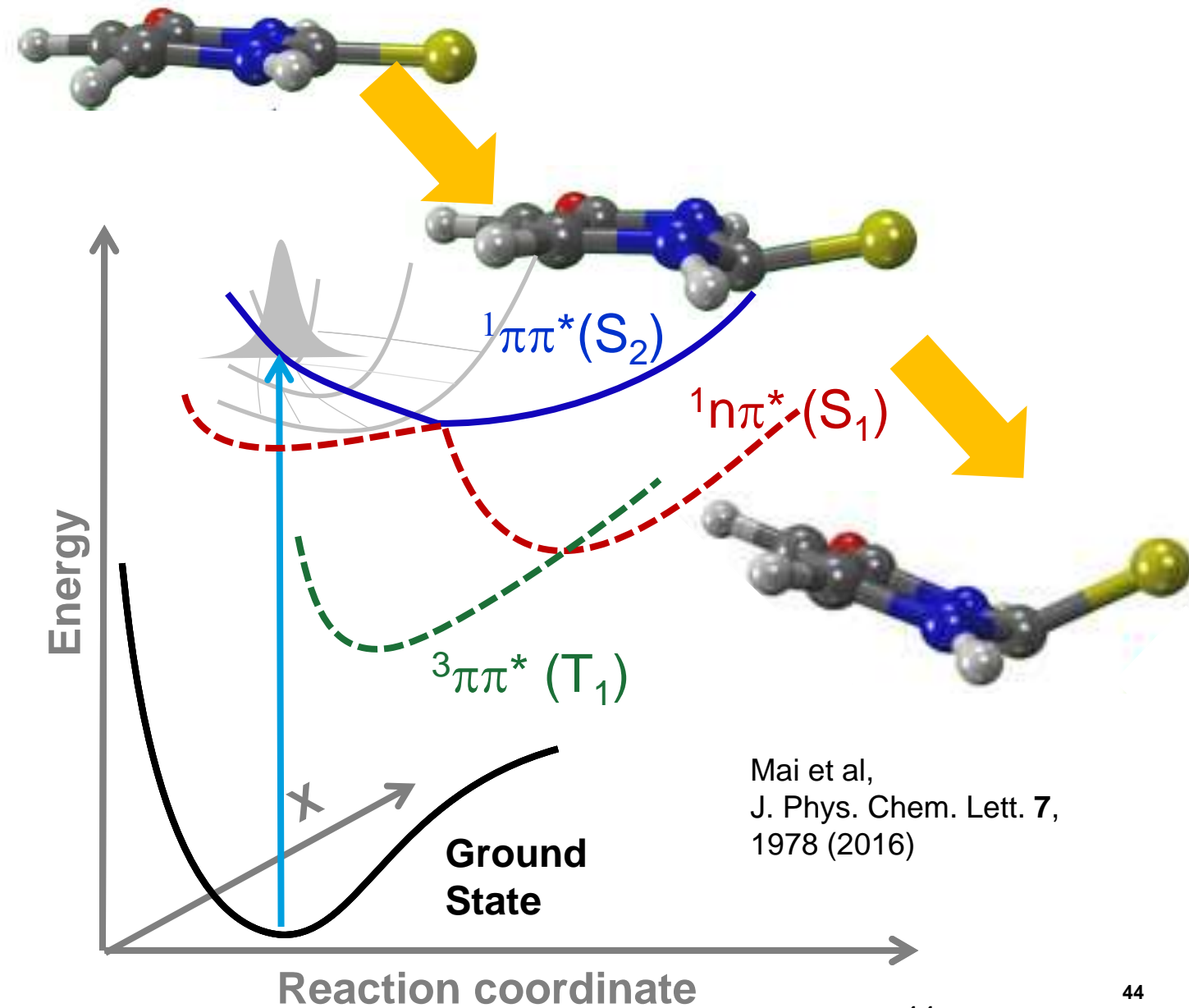
**Geometry
Movie**



Looking at the same dynamics via nuclear geometry



R. Boll,T. Jahnke, Nat. Phys. **18** 423 (2022)



DESY

**Ulrike Frühling
Markus Ilchen
Atia Tul Noor
Florian Trinter
Fabiano Lever
Dennis Mayer
Markus Gühr**

Oxford

Maria-Elena Castellani

INRS Montreal

Heide Ibrahim

UCL

Rebecca Ingle

Uni Frankfurt

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Europea XFEL

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Kansas State

**Surjendu Bhattacharyya
Keyu Chen
Artem Rudenko
Daniel Rolles**



Rebecca Boll
EU XFEL



Heide Ibrahim
INRS Montreal



Till Jahnke
MPK Heidelberg

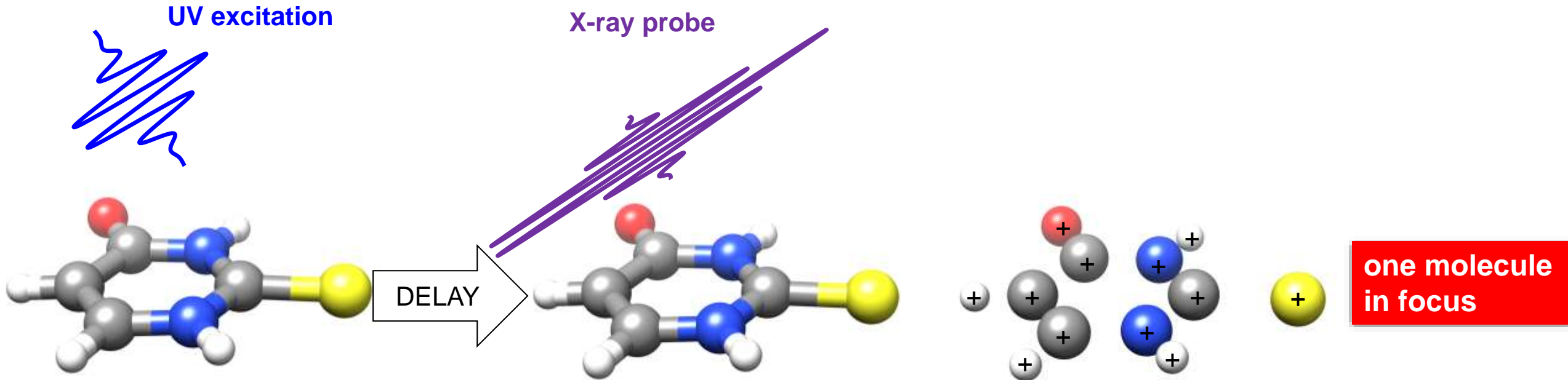


Sebastian Mai
Uni Wien

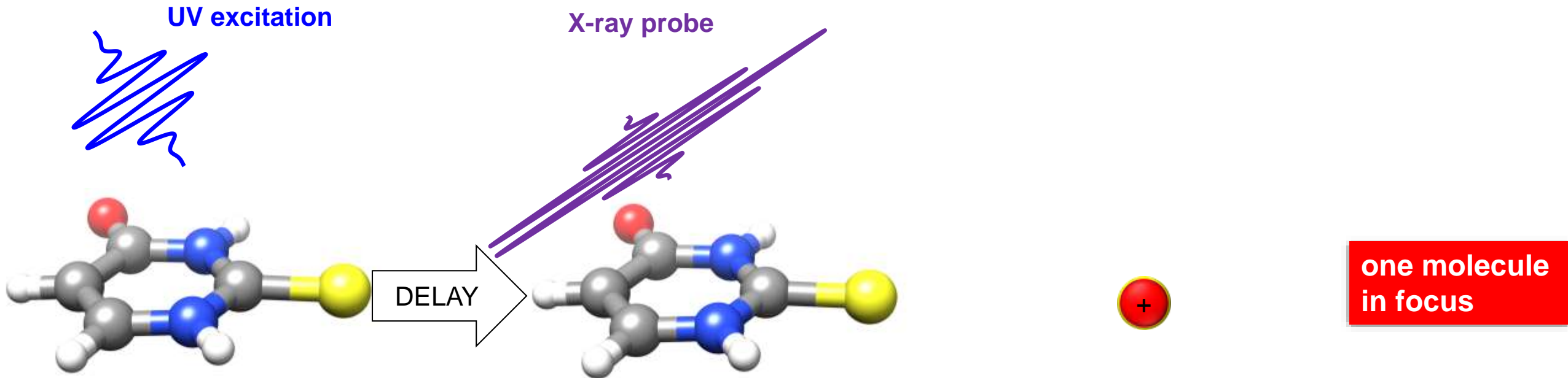
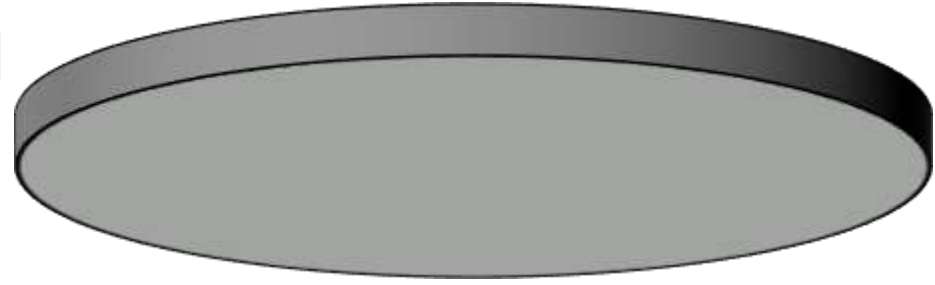
Coulomb Explosion Imaging



For more information on x-ray Coulomb Explosion Imaging:
Boll et al., Nature Phys. 18, 423 (2022)

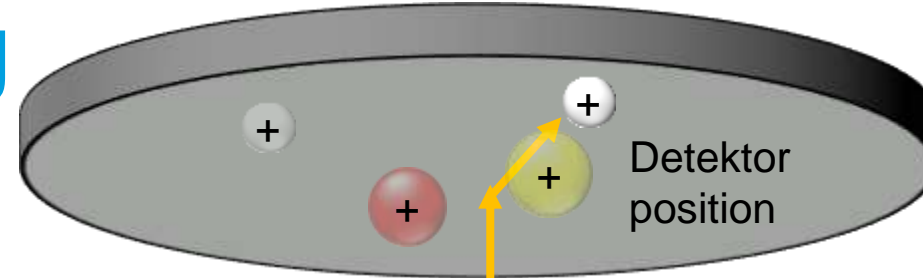
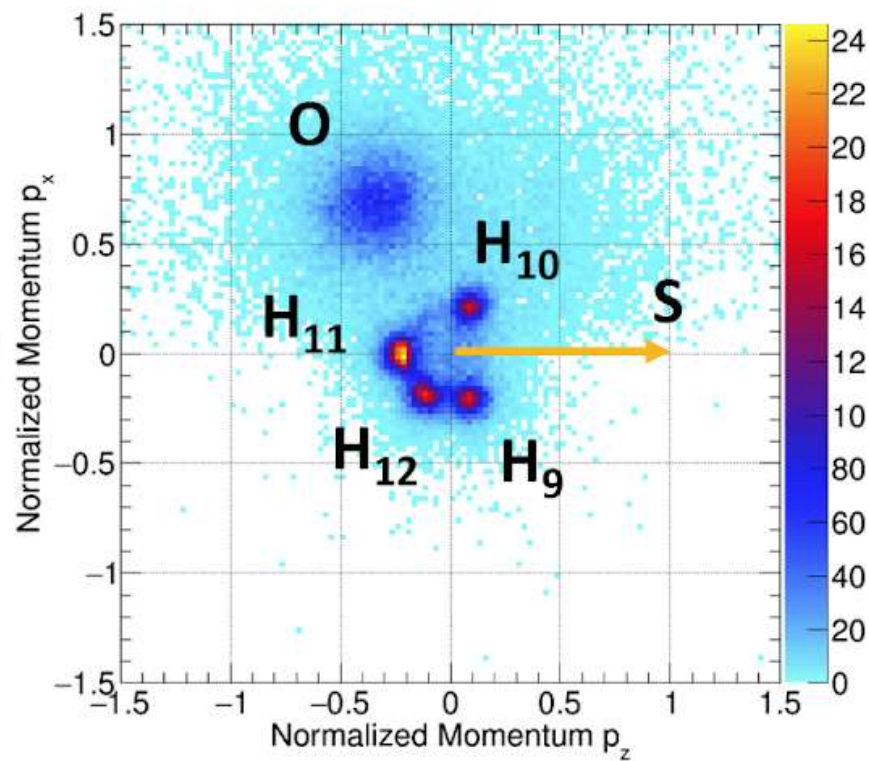
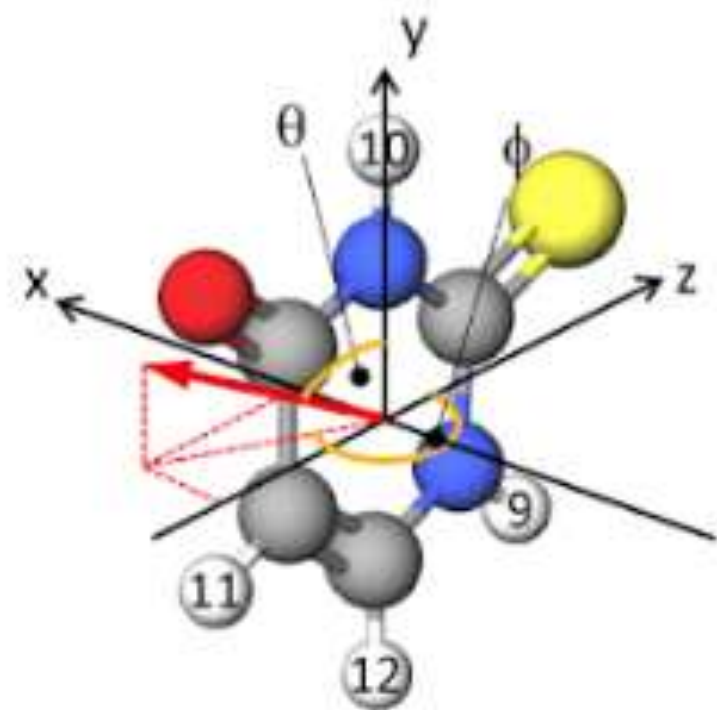


Coulomb Explosion Imaging



Coulomb Explosion Imaging

Courtesy
Till Jahnke



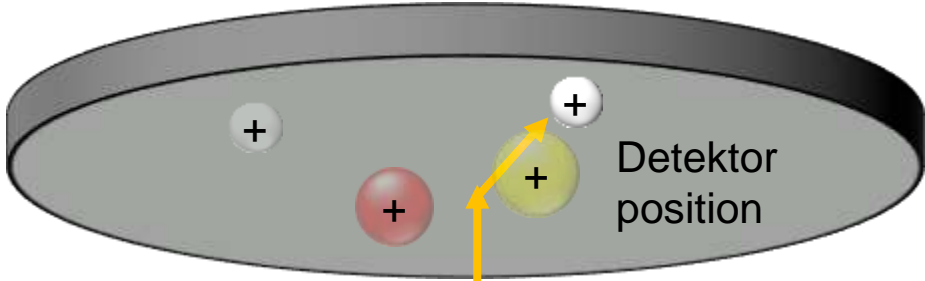
Time of flight

Reconstruction
of 3D momentum

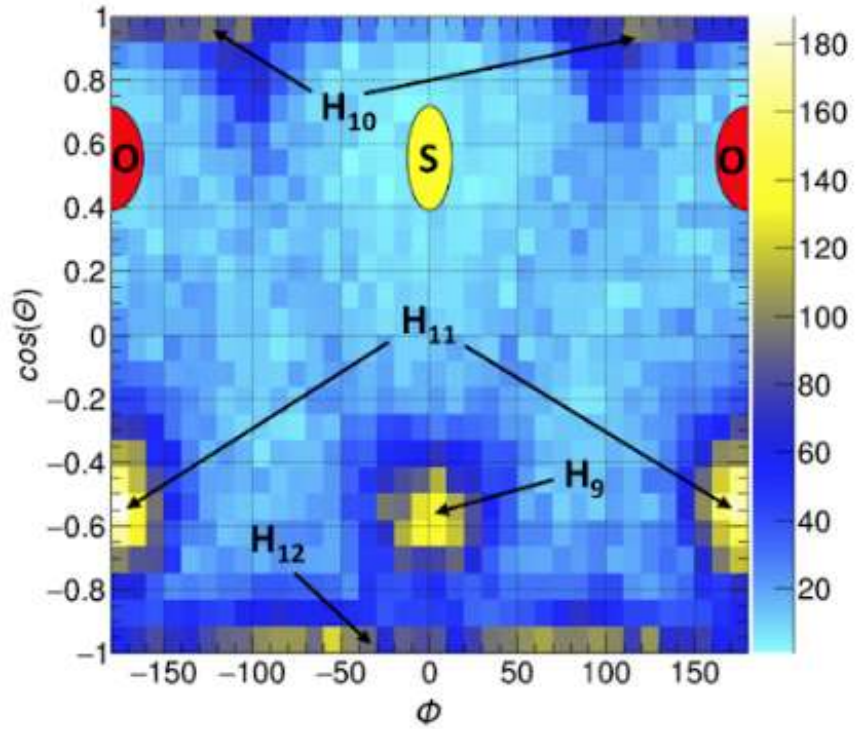
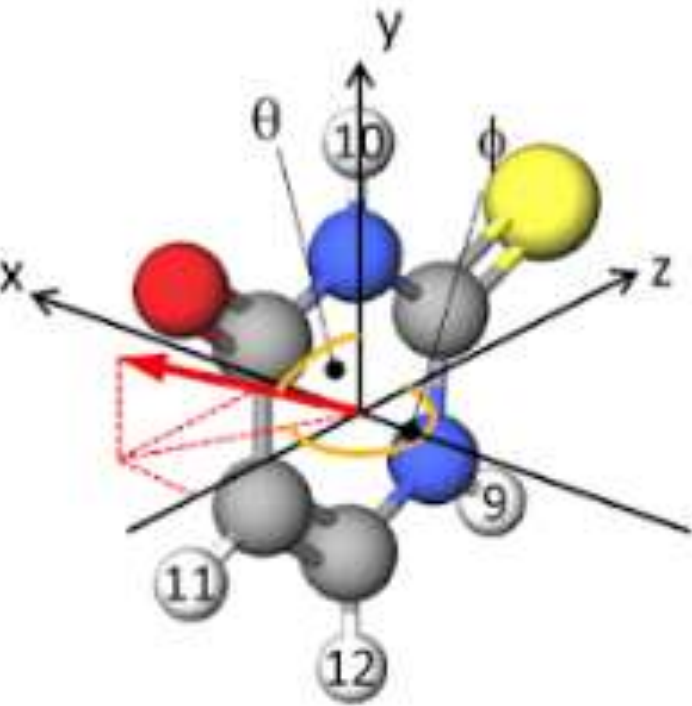


**one molecule
in focus**

Coulomb Explosion Imaging



Courtesy
Till Jahnke



Time of flight

Reconstruction
of 3D momentum

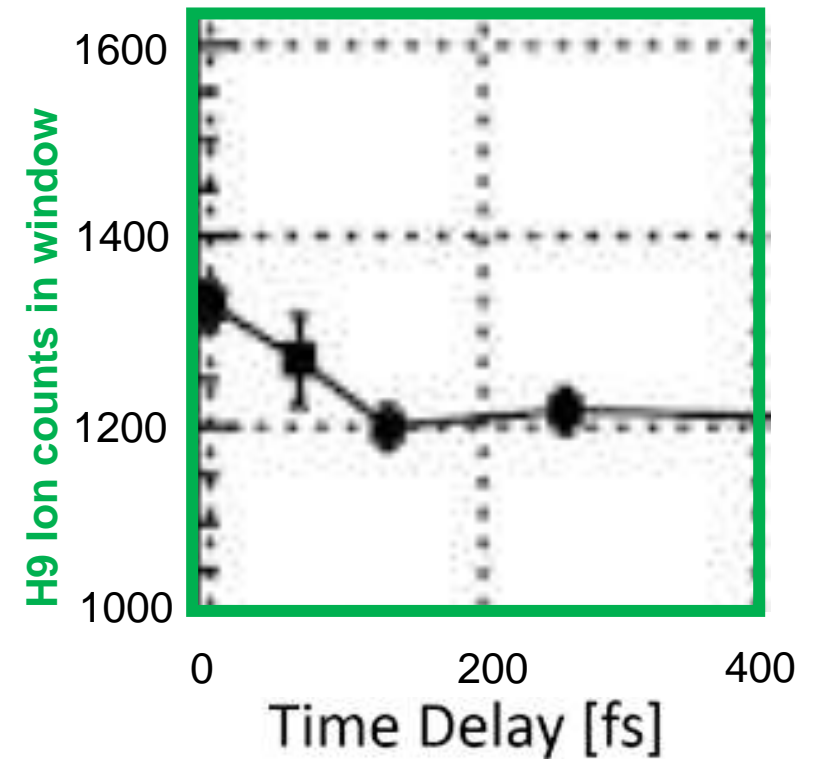
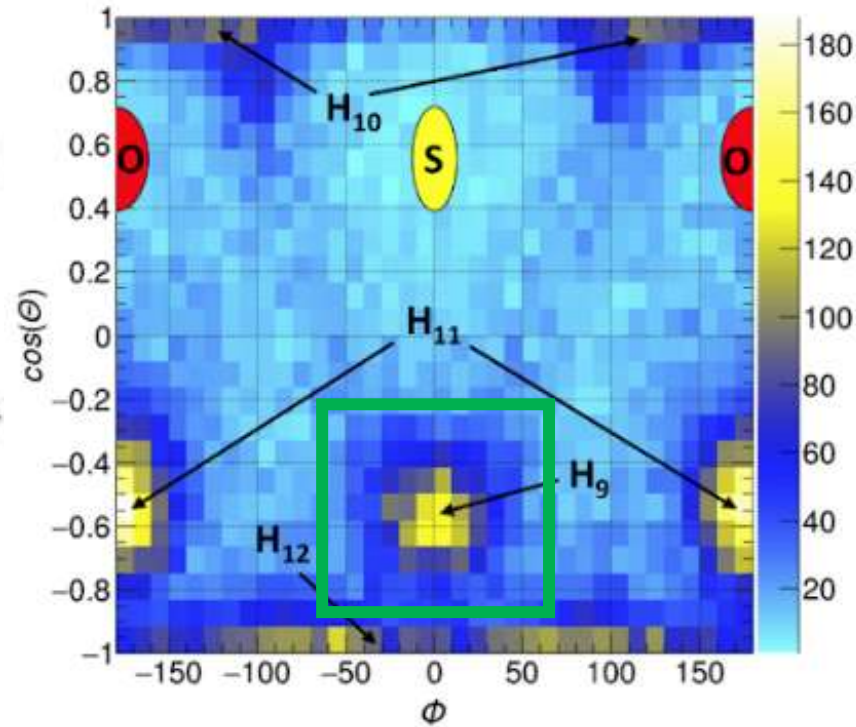
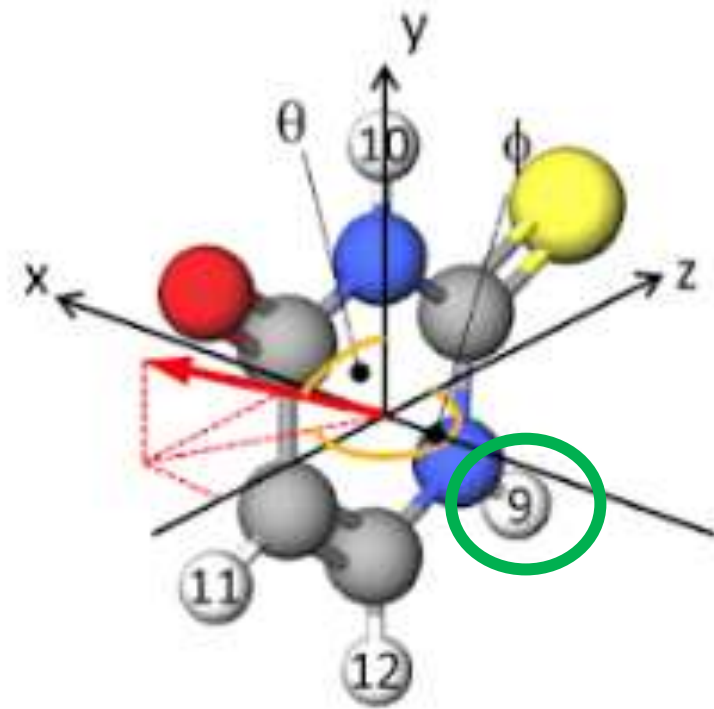
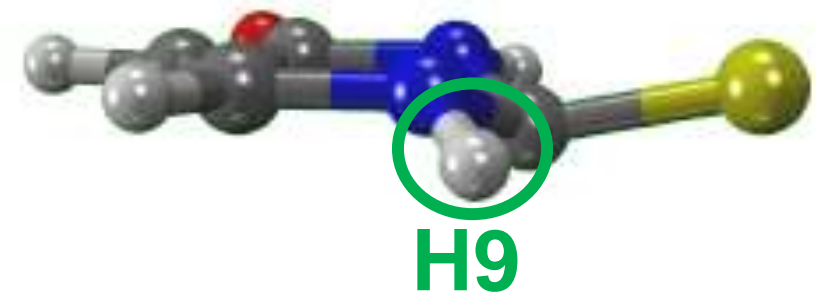


**one molecule
in focus**

Jahnke et al. <https://arxiv.org/pdf/2405.15367> (2024)

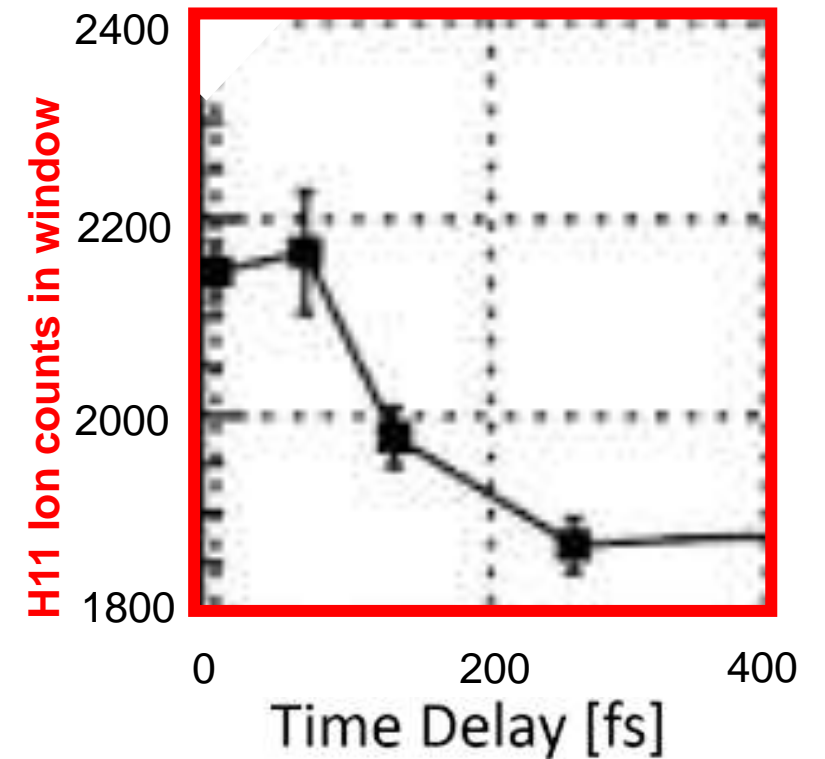
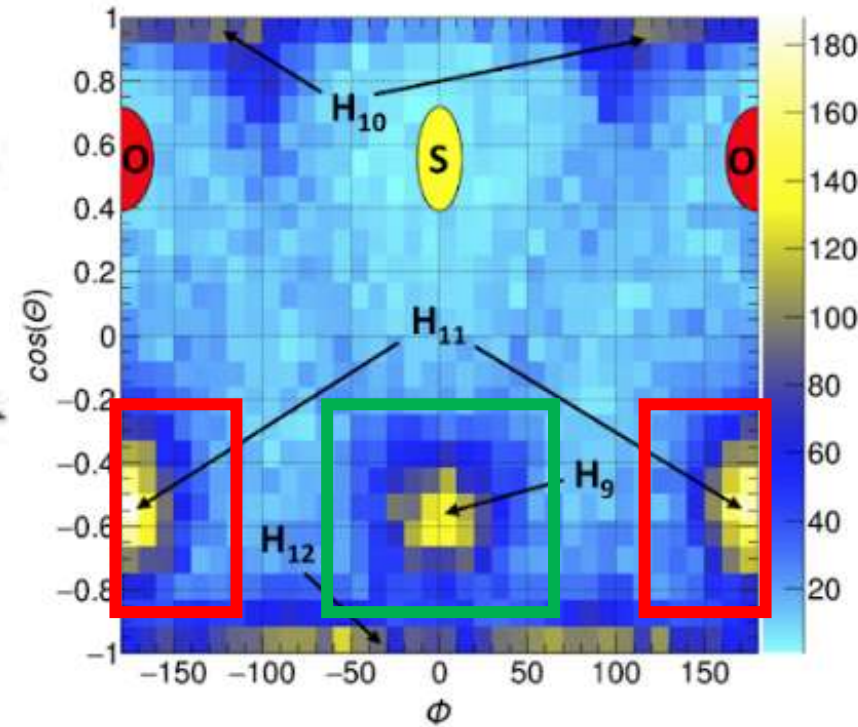
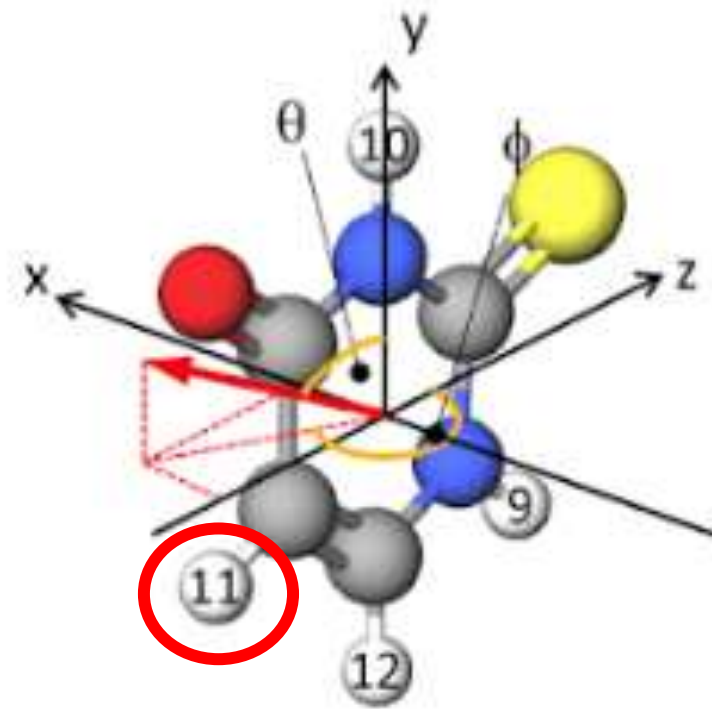
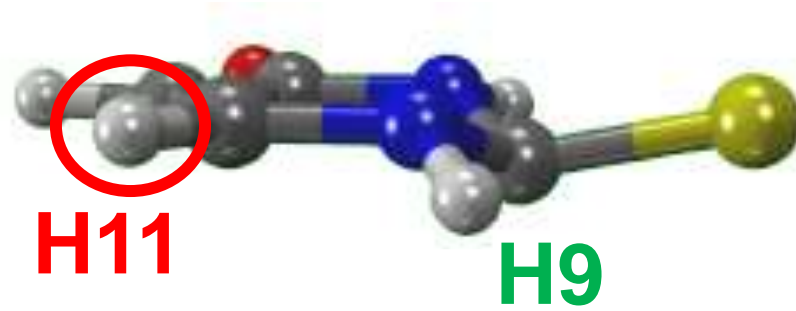
First the ring is puckering to go through the conical intersection...

Courtesy
Till Jahnke

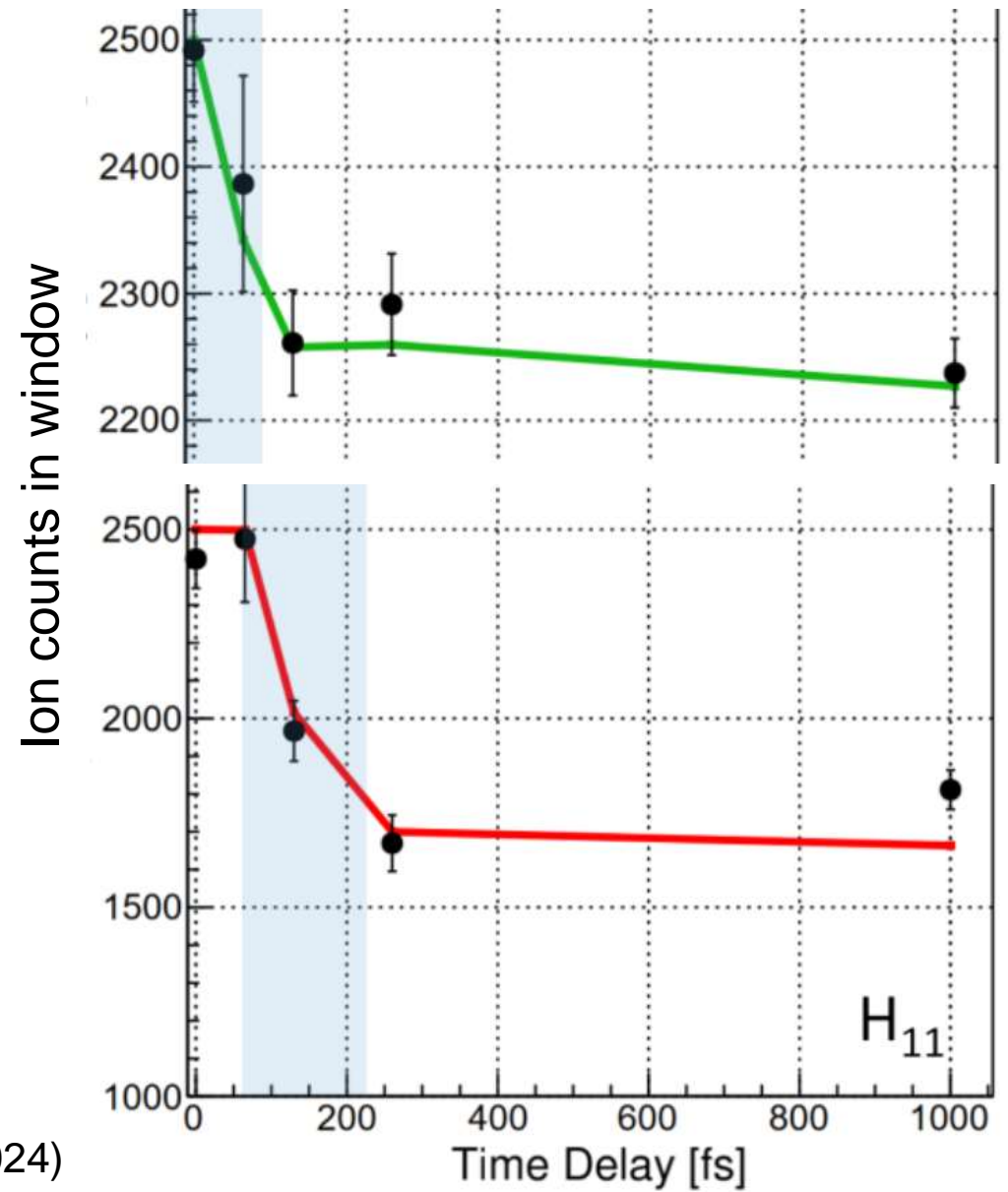
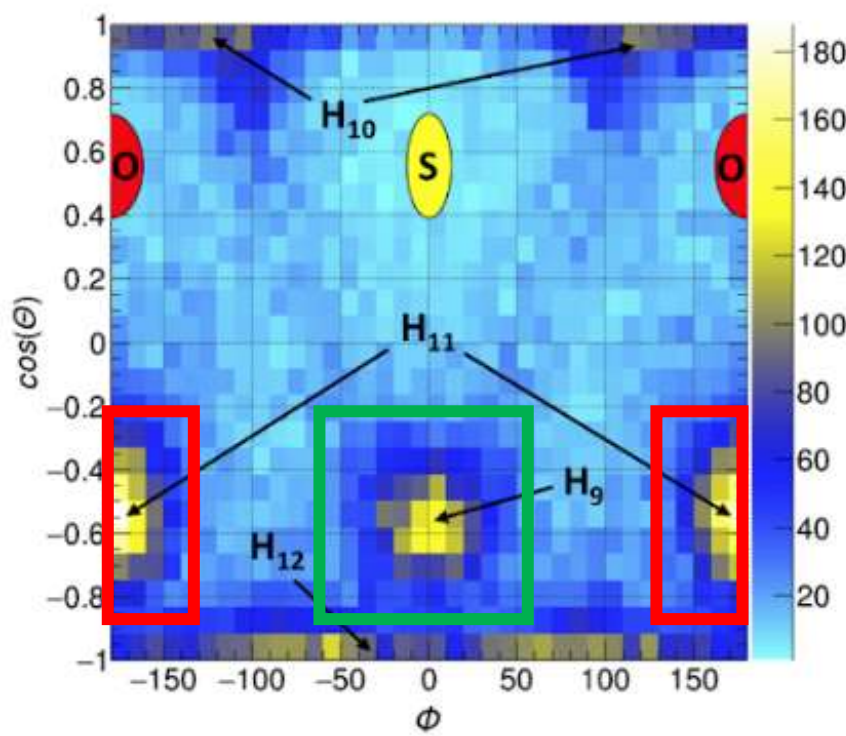
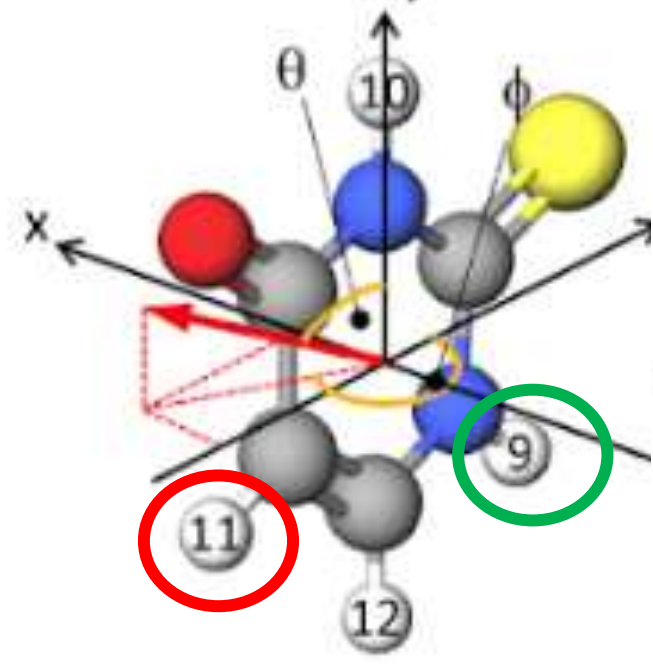
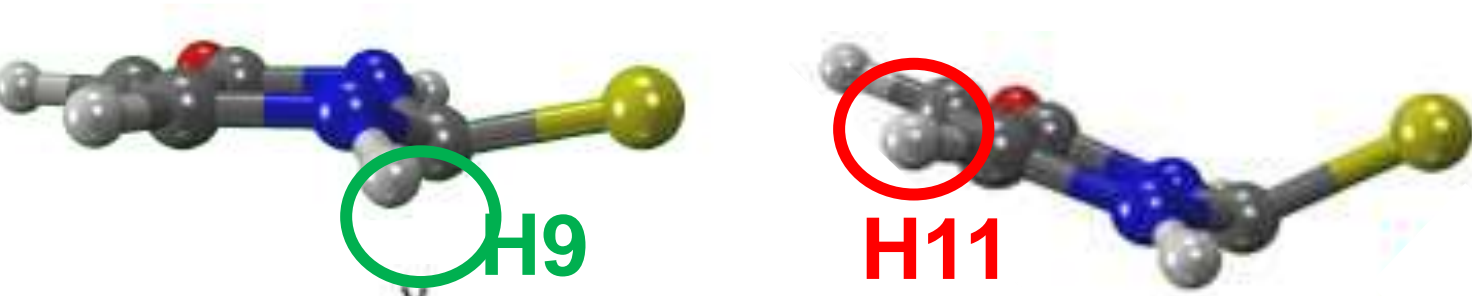


....then the sulfur points up with a delay of 60 fs

Courtesy
Till Jahnke

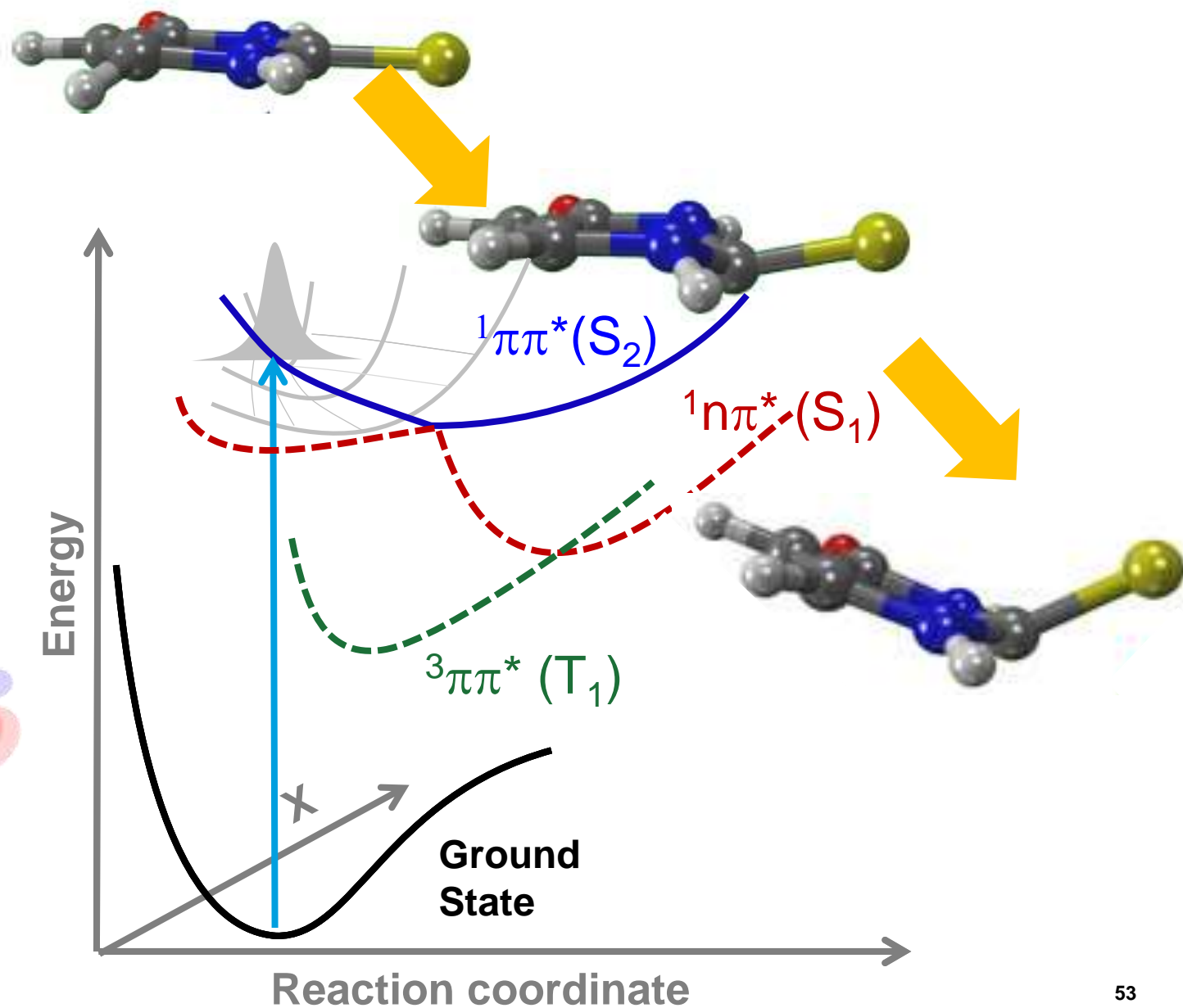
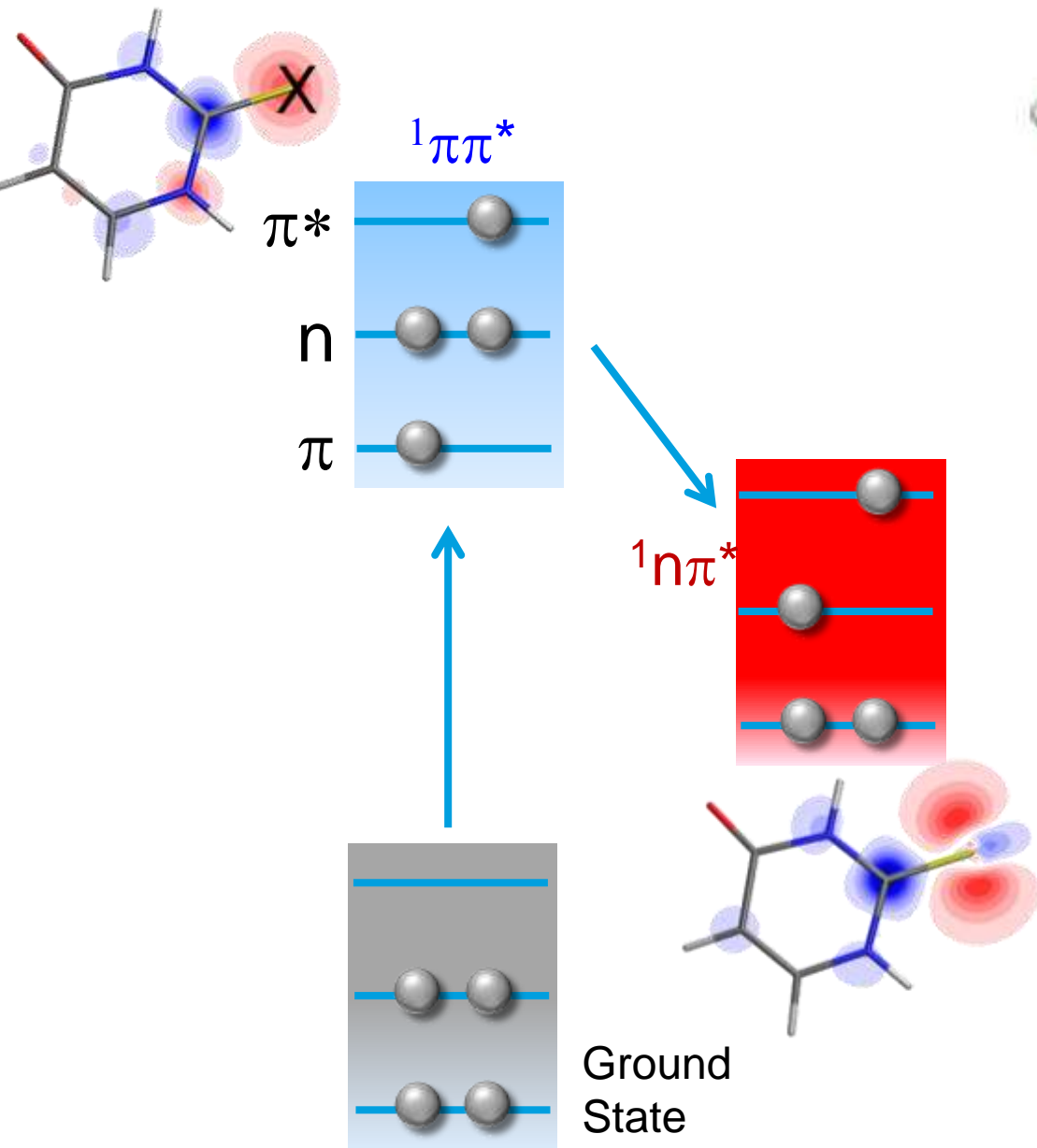


Imaging deplanarization with CEI



Jahnke et al. <https://arxiv.org/pdf/2405.15367> (2024)

Nuclei couple to electrons and their spin



Further reading

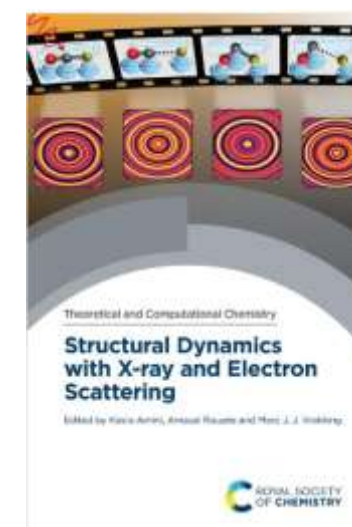
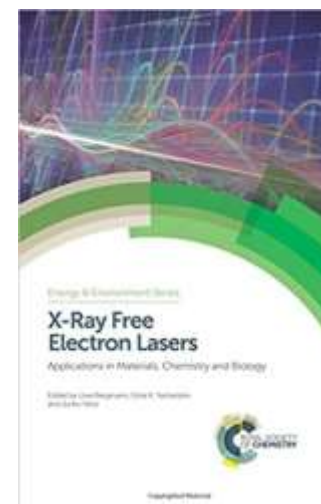
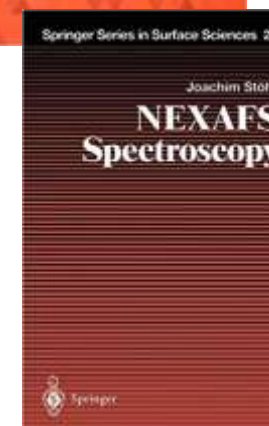
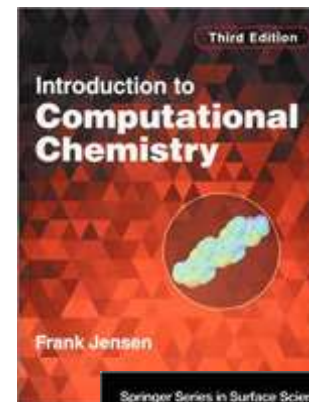
Basics: Coupled electronic and nuclear dynamics in molecules

- Jensen, Introduction to Computational Chemistry, 3rd edition, Wiley (2017)

X-ray matter interaction

- Stöhr, NEXAFS, Springer (1992)
- Santra, PhD tutorial J. Phys. B: At. Mol. Opt. Phys. **42** (2009) 023001 (16pp)

- Wolf, Gühr in X-ray free electron lasers, editors: Bergmann, Yachandra, Yano
- Gühr in Structural Dynamics with X-ray and Electron scattering, editors: Amini, Rouzee, Vrakking
- D. Mayer, F. Lever, and M. Gühr, Photochemistry and Photobiology 100, 275 (2024)



Thanks to the team at FLASH



Thanks for your attention!