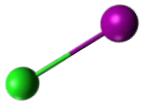
Interactions of matter with intense X-ray pulses

Rebecca Boll, European XFEL
Small Quantum Systems (SQS) Instrument

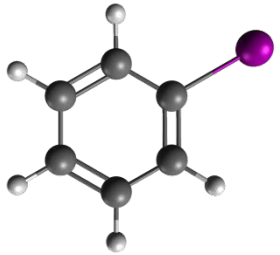
X-ray pulses:

10^{13} photons per pulse
up to 8 mJ per pulse
> 10^{19} W/cm^2
~1 µm focus
0.5 – 9 keV
< 30fs

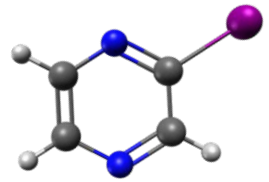
matter: isolated atoms and small molecules
in particular with heavy atoms



ICl

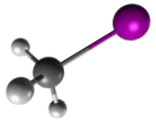


C_6H_5I

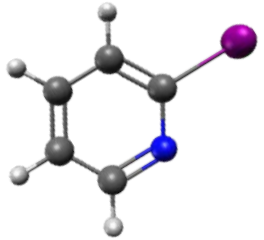


$C_4H_3N_2I$

Xe



CH_3I



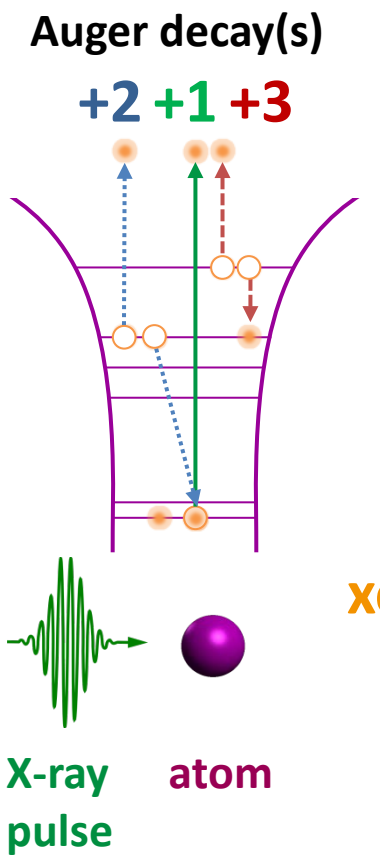
C_5H_4NI

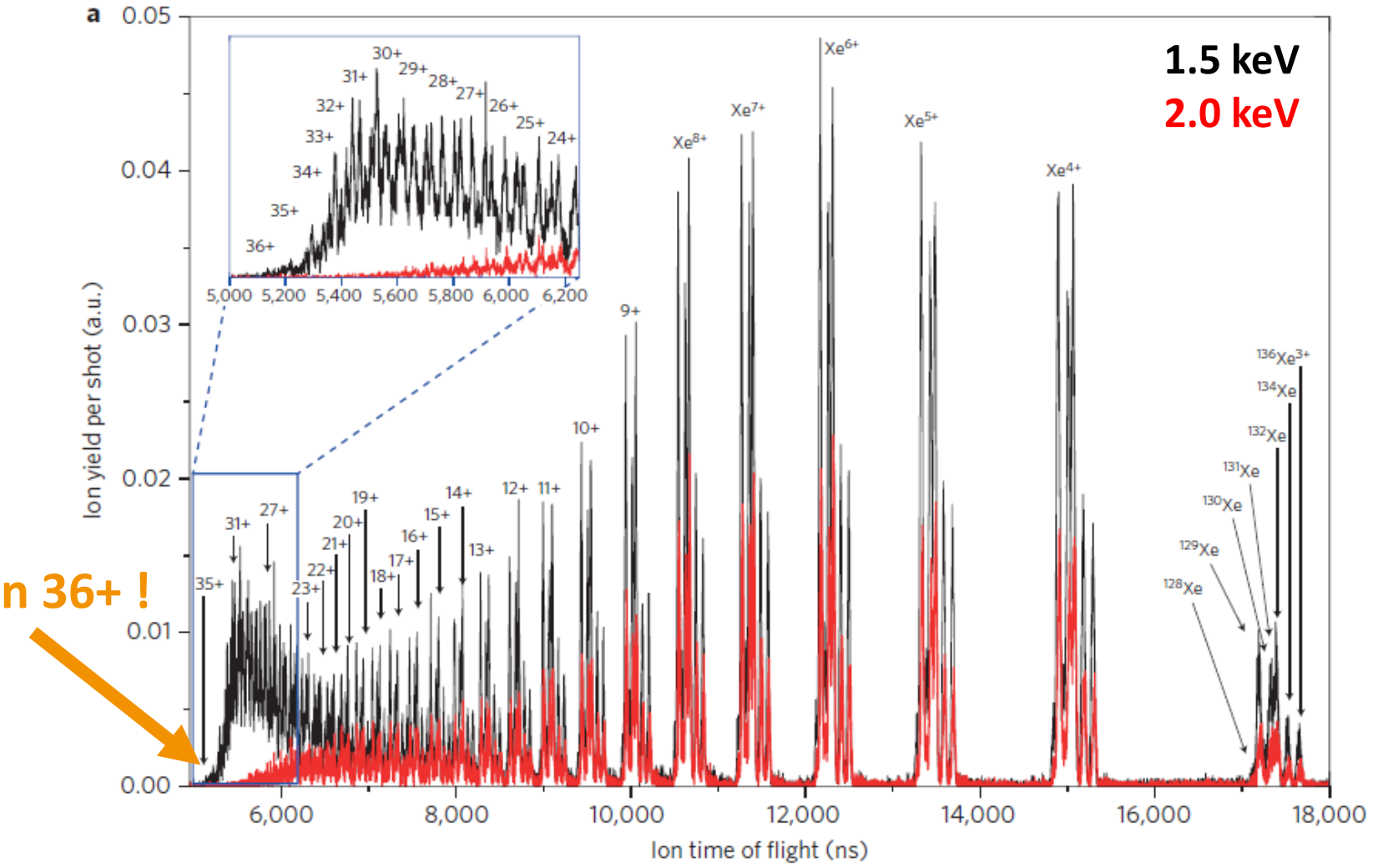
X-ray free-electron lasers offer amazing opportunities for many scientists!

- the development of XFELs enabled new science in various areas
  - most notably for this presentation, it opened the door to non-linear multi-photon effects in the X-ray regime
  - many unknown processes yet to discover, even in the simplest systems
- our goals:
  - understand in detail the atomic response of matter to the very intense pulses
  - study the temporal evolution of photon-matter interaction on the femtosecond timescale
  - make use of the very short X-ray pulse duration in pump-probe experiments
- our experimental tools:
  - ion mass/charge spectra
  - 3d ion momenta measured in coincidence (COLTRIMS)
  - electron spectra and angular distributions
- our theoretical tools: (group of Robin Santra at CFEL, Hamburg)
  - XATOM, XMOLECULE, XMDYN: ab-initio calculations for every electronic configuration of atoms and small molecules during interaction with an XFEL pulse, in combination with classical molecular dynamics for nuclei

Absorption of very intense X-ray pulses in heavy-atoms

- **in atoms: very high charge states through sequence of multiple inner-shell photoabsorptions and Auger decays**





Rudek, Nat. Phot. 6, 858 (2012)

Absorption of very intense X-ray pulses in heavy-atoms

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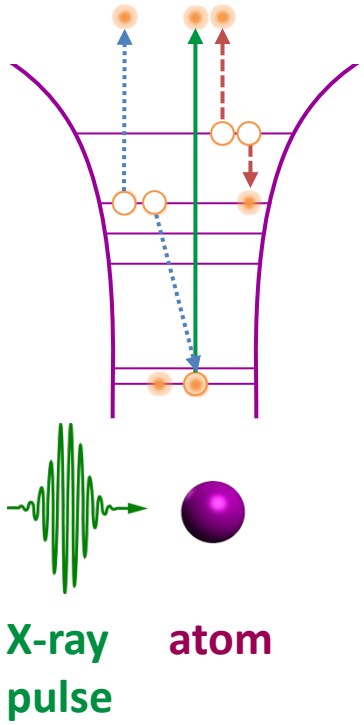
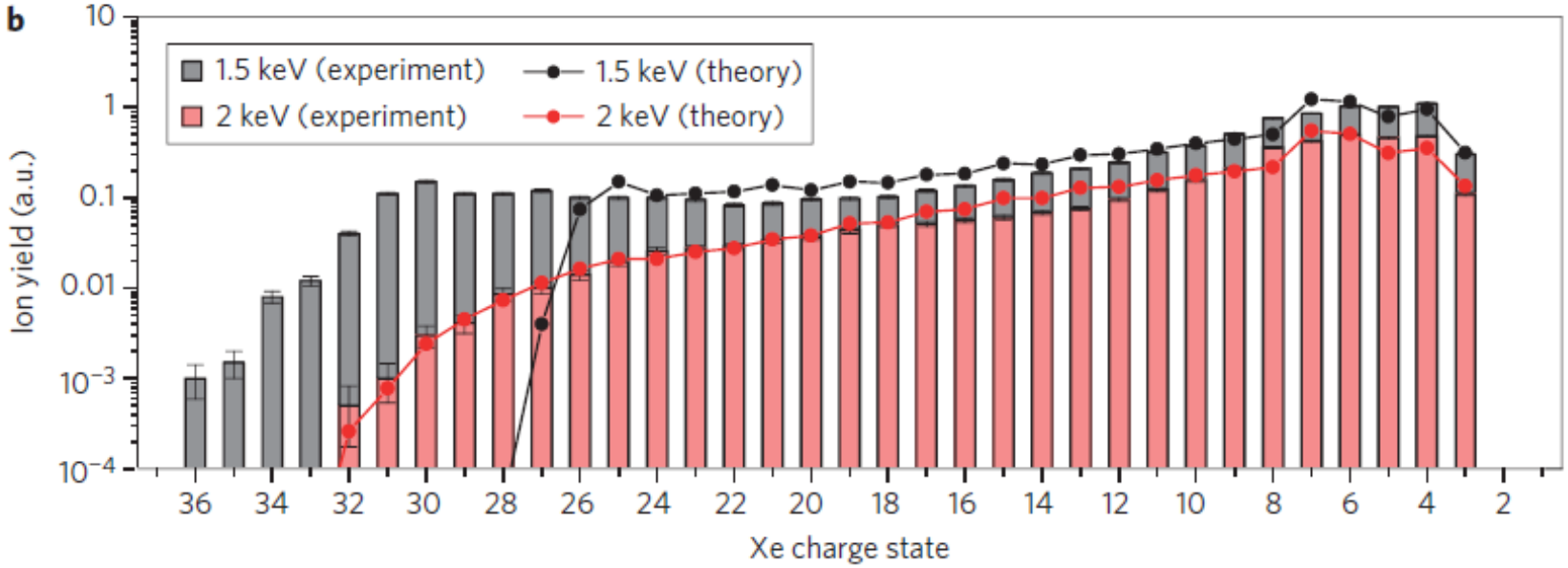
- for certain photon energies, intermediate resonances play an important role



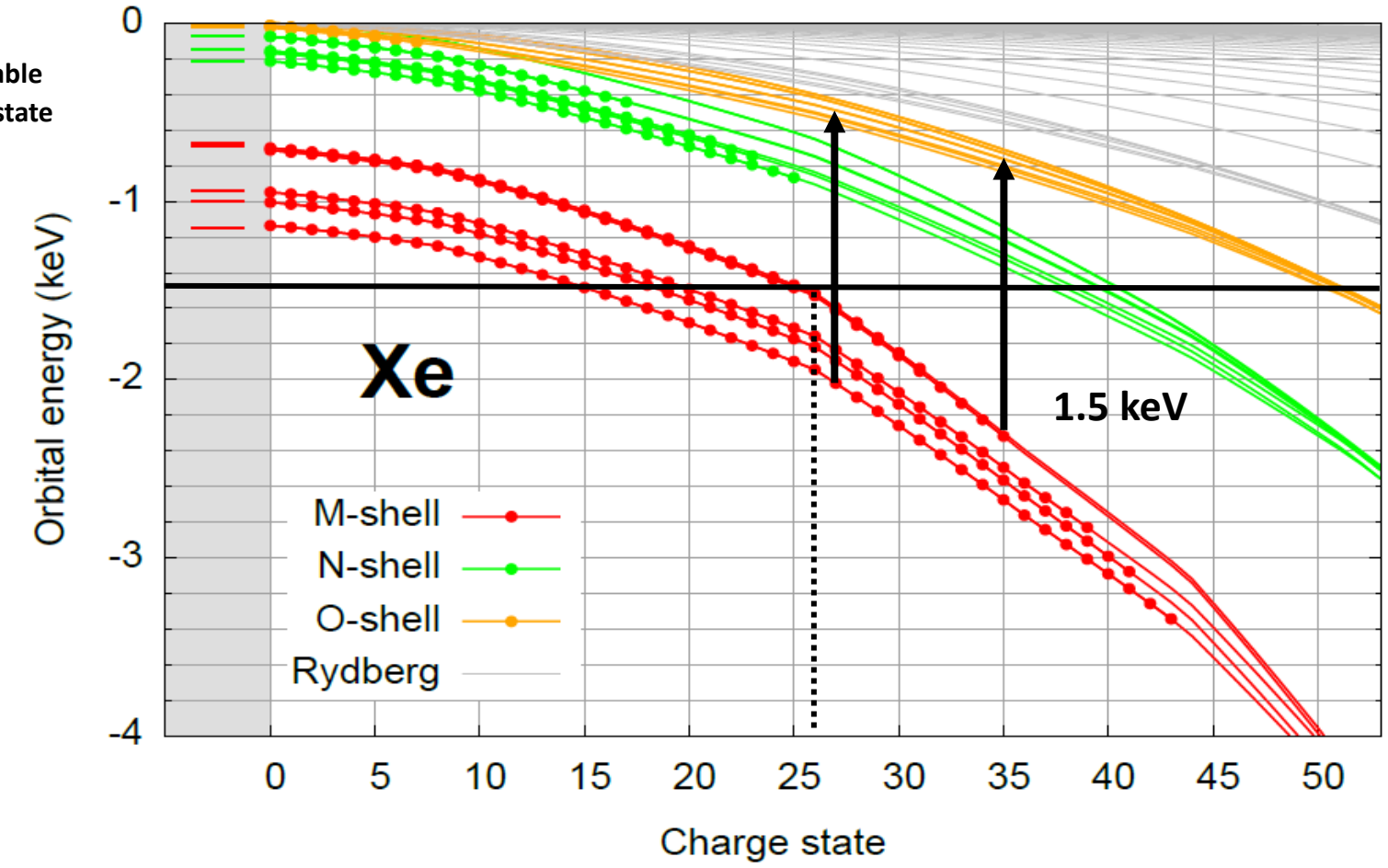
lower photon energy creates higher charge states?!



Rudek, Nat. Phot. 6, 858 (2012)

Resonance-enabled X-ray multiple ionization (REXMI)

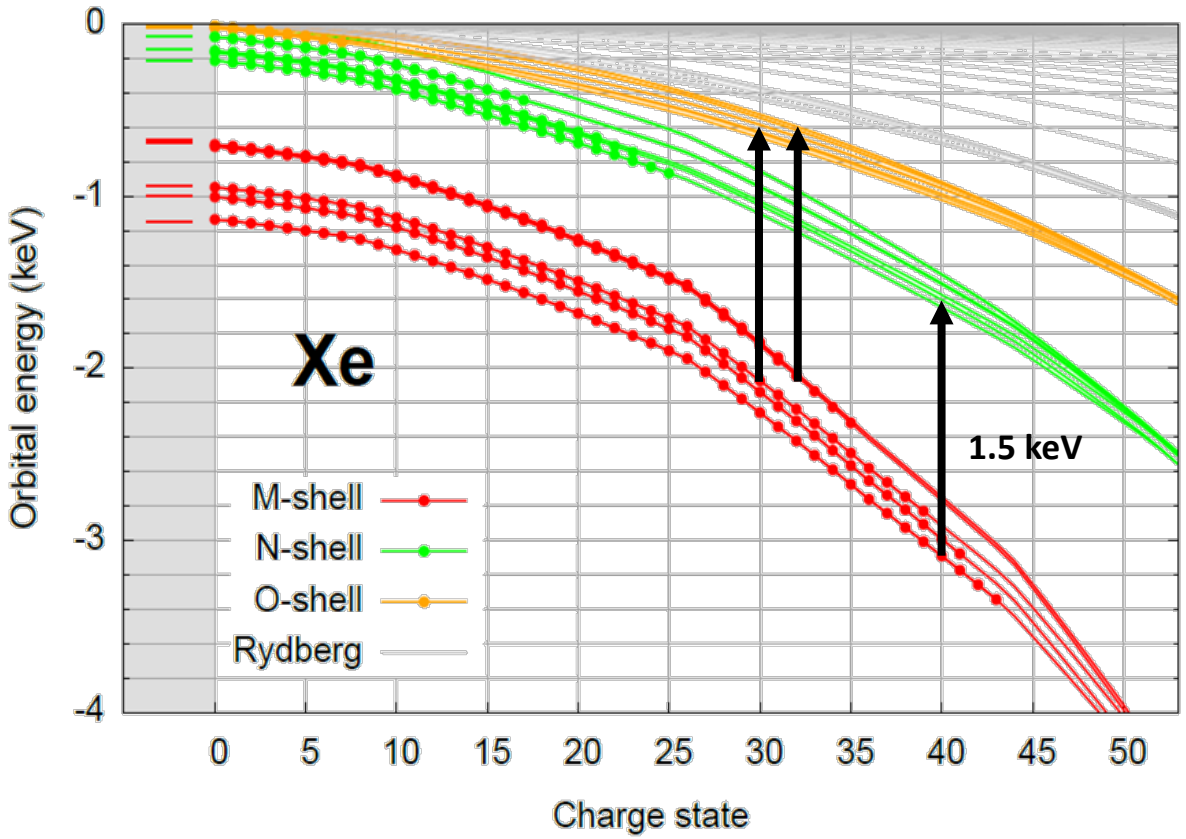
dots represent available electrons in ground state configuration



calculation: Sang-Kil Son

- **electron binding energies shift strongly as a function of charge state**
- **ionization by 1.5 keV photons should stop at Xe^{26+}, however, Xe^{36+} observed!**

Resonance-enabled X-ray multiple ionization (REXMI)



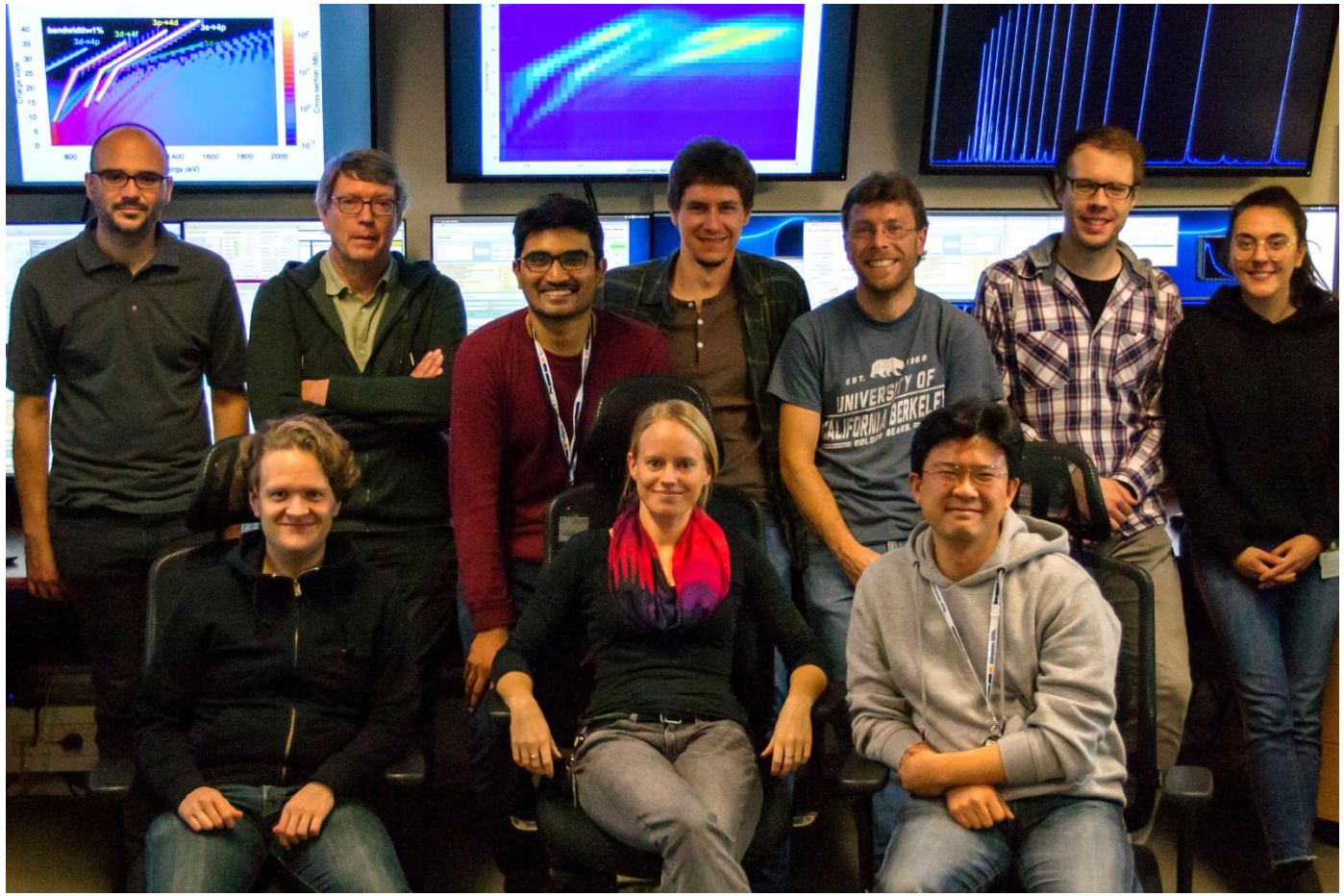
unpublished data, removed for web version.
Thank you for understanding

- resonances strongly depend on the photon energy
- in xenon, a multitude of different resonant excitations can occur
- can we track these resonances experimentally?

European XFEL provides widely tunable photon energy with very high pulse energies in the soft X-ray regime!

Wavelength- and fluence-dependence of xenon ionization

SQS beamtime in October 2019



European XFEL

Thomas Baumann

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Tommaso Mazza

Michael Meyer

Valerija Music

Daniel Rivas

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Svitozar Serkez

Philipp Schmidt

Sergey Usenko

CFEL

Julia Schäfer

Robin Santra

Sang-Kil Son

Kansas State University

Shashank Pathak

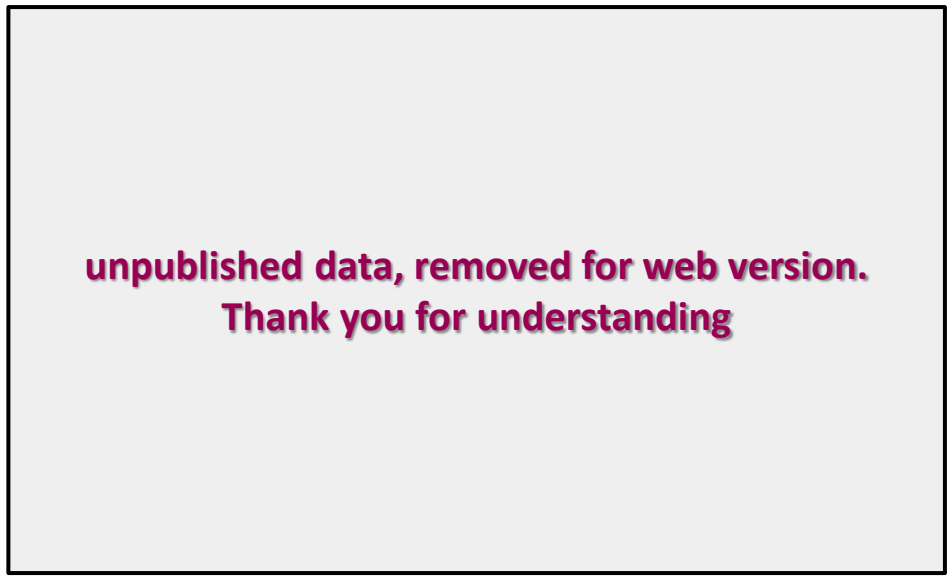
Daniel Rolles

DESY

Benjamin Erk

and the European XFEL machine team!

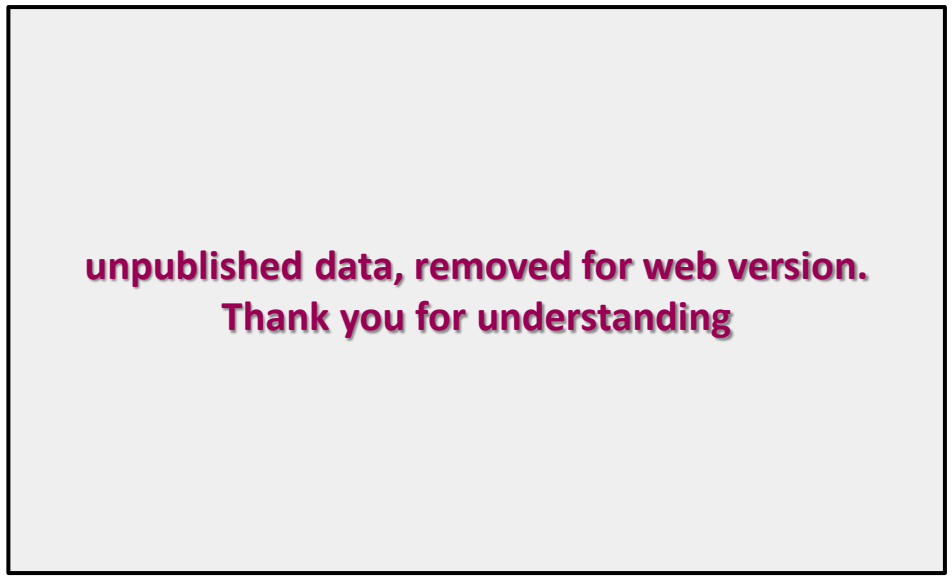
Wavelength-dependence of xenon ionization



- strongly structured features in the xenon charge state spectra as a function of photon energy
- in very good agreement with calculated photoionization cross sections
- provides detailed insight into the electronic structure of highly excited atoms
- how do the resonances depend on the X-ray fluence??

SQS beamtime Son, Boll et al., October 2019

Wavelength- and fluence-dependence of xenon ionization

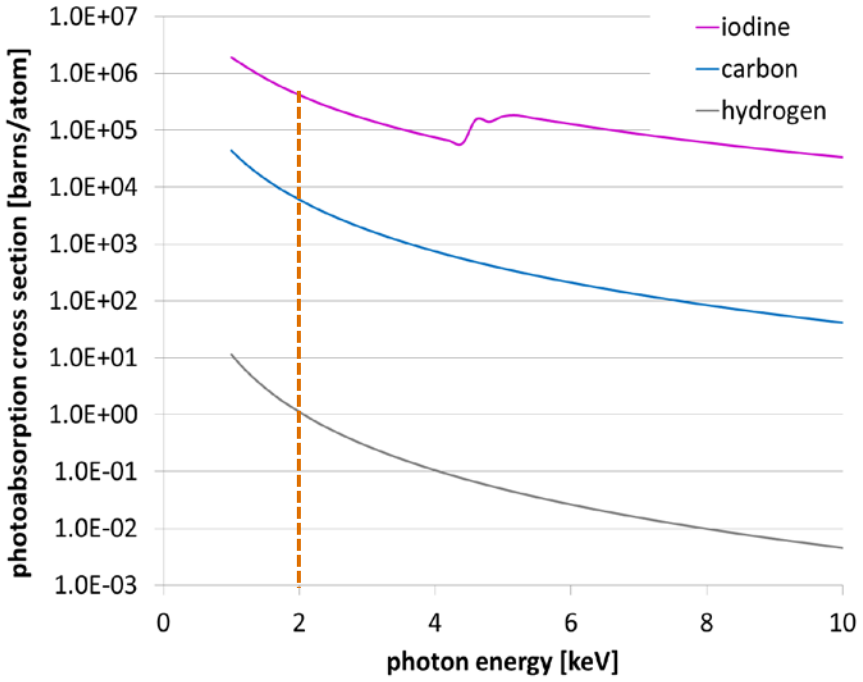


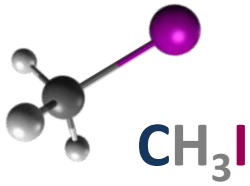
- resonances depend on the fluence, as they result from highly nonlinear effects
- the higher the fluence, the more resonances are accessible
- experimental challenge: keeping the fluence constant throughout the energy scan

SQS beamtime Son, Boll et al., October 2019

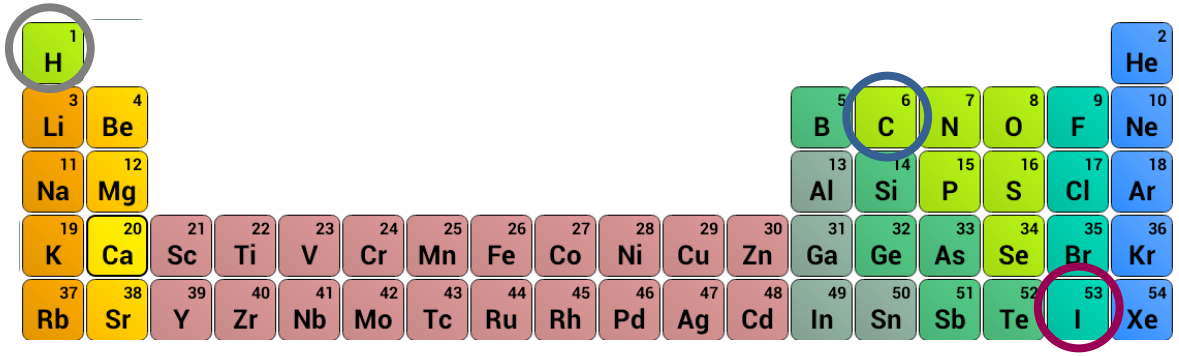
Absorption of very intense X-ray pulses in molecules with heavy atoms

- in atoms: very high charge states through sequence of multiple inner-shell photoabsorptions and Auger decays
- but what happens when a heavy atom is embedded in a molecule???
- exploit element-specificity to localize X-ray absorption at heavy atom





$$\frac{\sigma_I}{\sigma_{CH3}} = \frac{70}{1}$$



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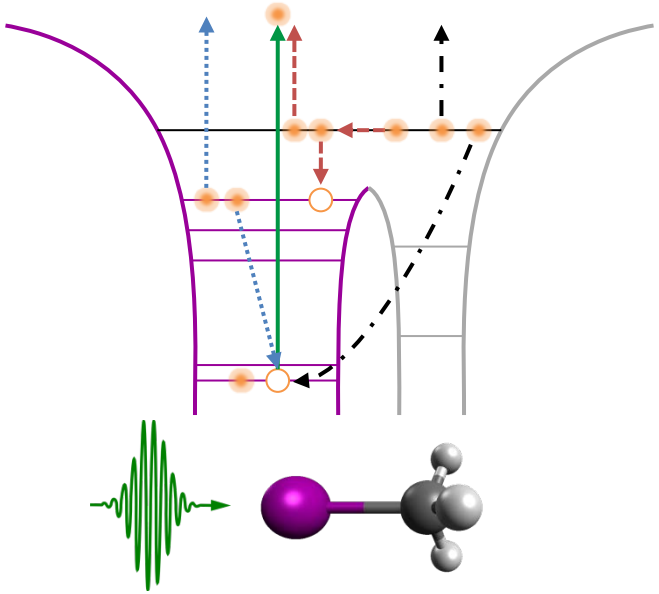
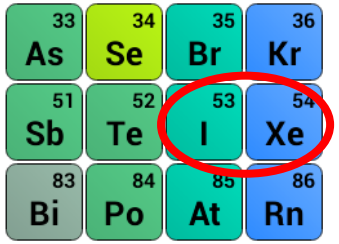
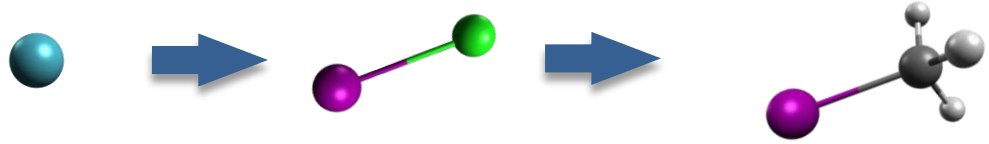
- total molecular charge stays the same, but charge is redistributed to the other atoms

valence electrons delocalized





Xe ICl CH_3I



$Q_{Xe} \approx Q_I + Q_{Cl} \approx Q_I + Q_C + 3Q_H$

$35 \approx 28 + 6 \approx 29 + 4 + 3$

maximum charge states measured

Erk, Phys. Rev. Lett 110, 053003 (2013)
Erk, J. Phys. B 46, 164031 (2013)

Absorption of very intense X-ray pulses in molecules with heavy atoms

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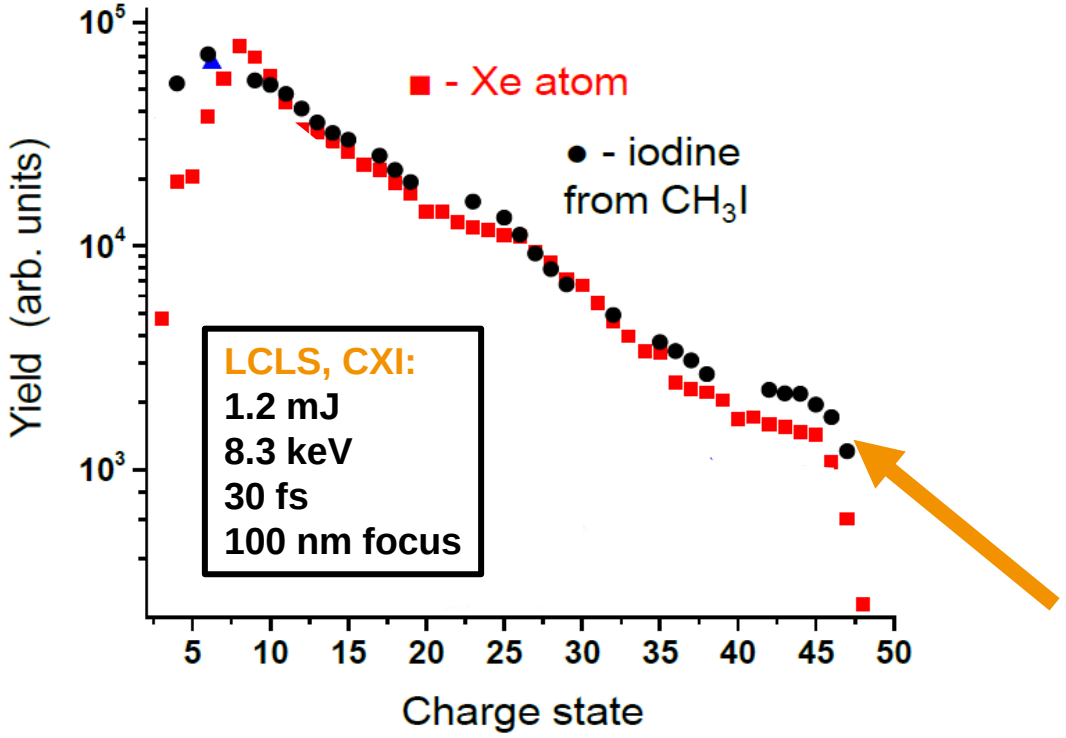
- but what happens when a heavy atom is embedded in a molecule???
- exploit element-specificity to localize X-ray absorption at heavy atom
- total molecular charge stays the same, but charge is redistributed to the other atoms
- ... unless the intensity becomes extremely high!

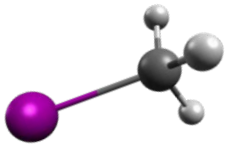


Xe

Q_{Xe}

48

CH_3I



$\approx Q_I + Q_C + 3Q_H$

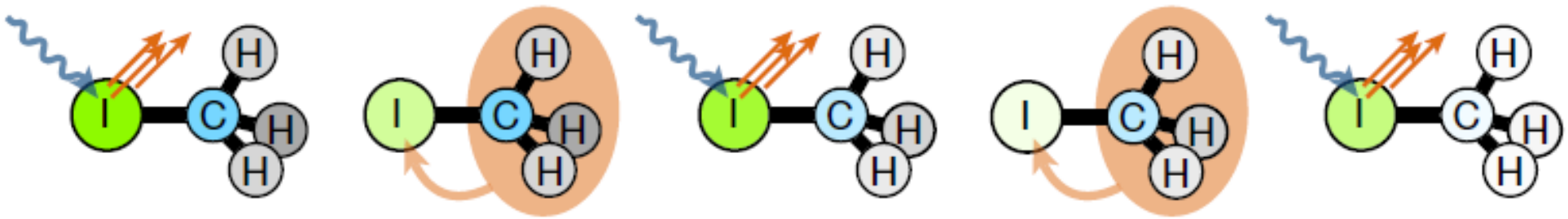
$\not\approx 47 + 4 + 3$

iodine 47+ !

Rudenko, Nature 545, 129 (2017)

Absorption of very intense X-ray pulses in molecules with heavy atoms

- in atoms: very high charge states through sequence of multiple inner-shell photoabsorptions and Auger decays
- but what happens when a heavy atom is embedded in a molecule???
- exploit element-specificity to localize X-ray absorption at heavy atom
- total molecular charge stays the same, but charge is redistributed to the other atoms
- … unless the intensity becomes extremely high!
  - for such extreme intensities, ionization is limited by number of available electrons, not by the photon flux
  - charge-rearrangement-enhanced X-ray ionization of molecules (CREXIM)
  - the larger the molecule, the more ionization?!

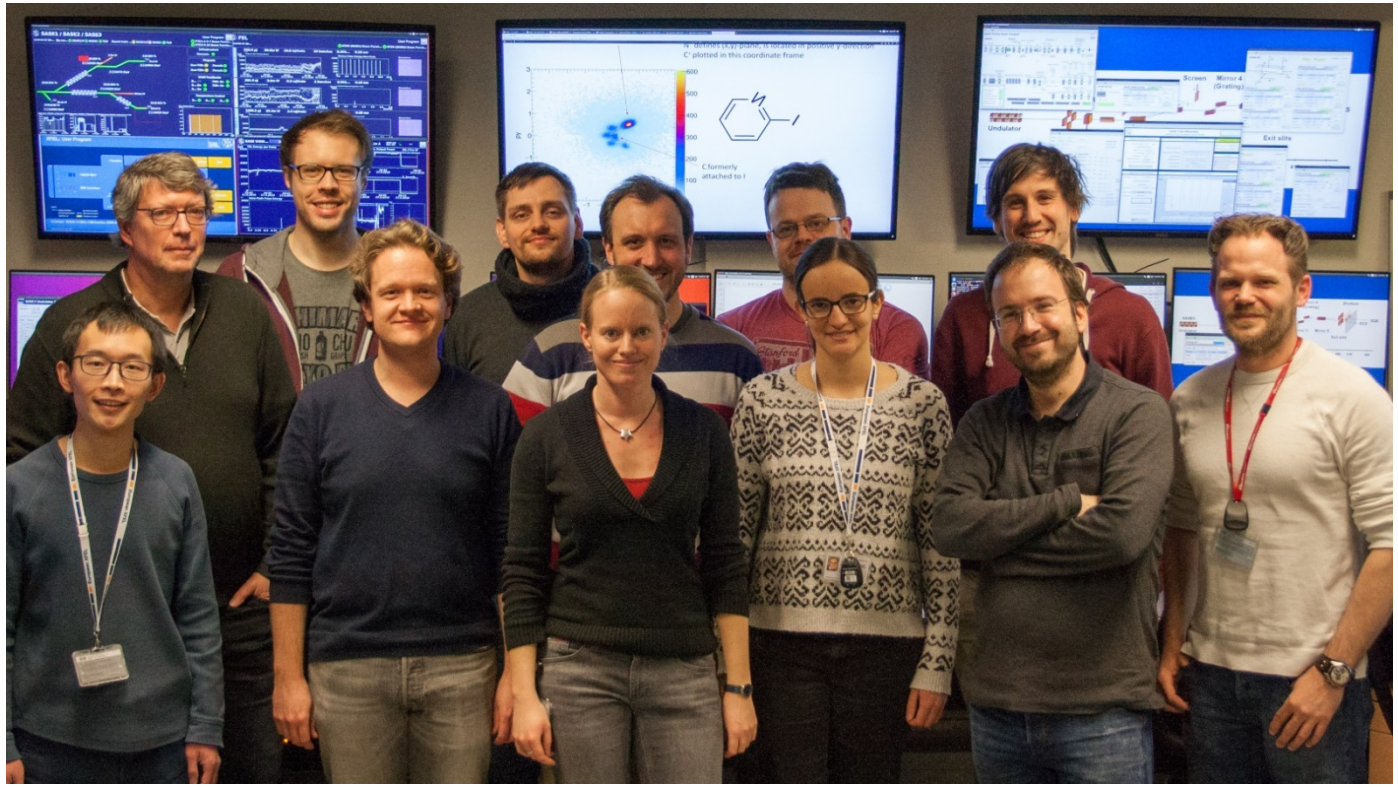


Rudenko, Nature 545, 129 (2017)

Coulomb explosion imaging of ‘large’ molecules with very intense X-ray pulses

SQS beamtime in March 2019 - first block of user beamtimes

reaction microscope built by Dörner group, Uni Frankfurt



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SLAC
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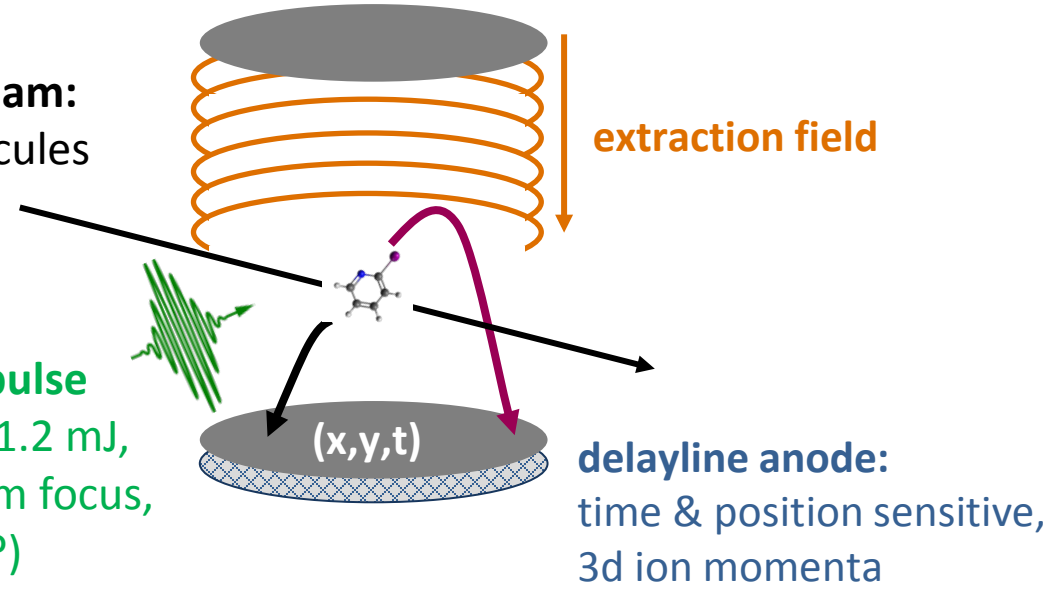
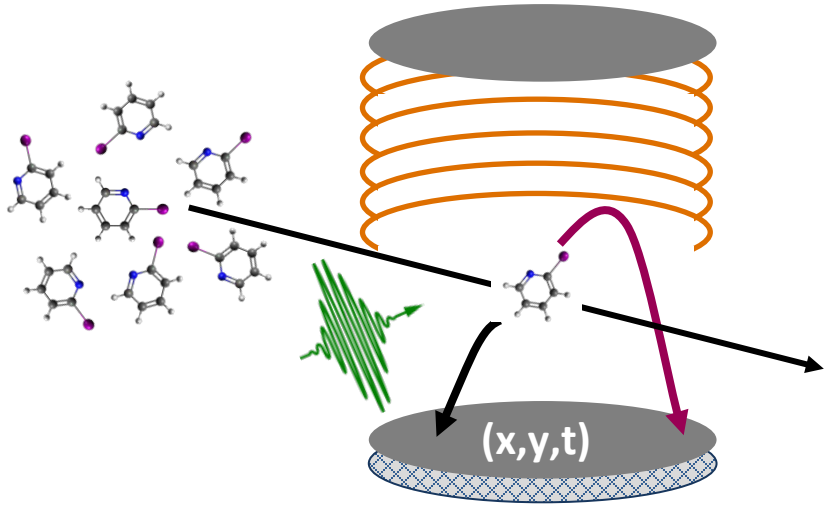
MPI for Medical Research
Lutz Foucar
Ilme Schlichting

Coincident ion momentum imaging

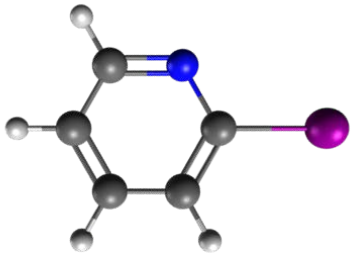


- isolated, gas-phase molecules from supersonic expansion into vacuum
- record time-of-flight spectrum (= mass/charge spectrum) as well as (x,y) position of created ions
- reconstruct 3d momentum
- ion coincidence measurements possible if < 1 molecule hit per pulse

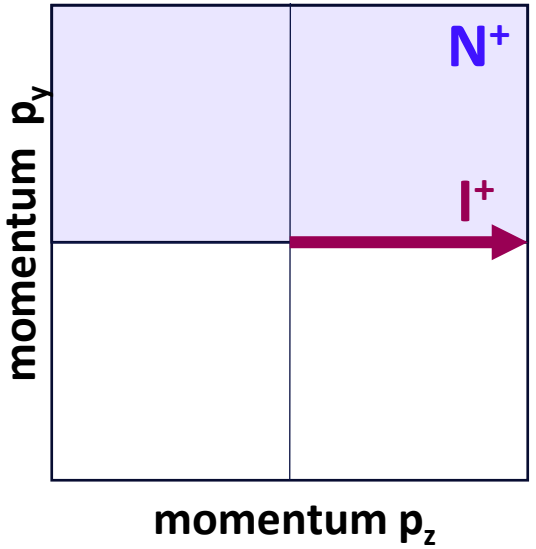
Multi-ion coincidence analysis



2-iodopyridine



C_5H_4NI

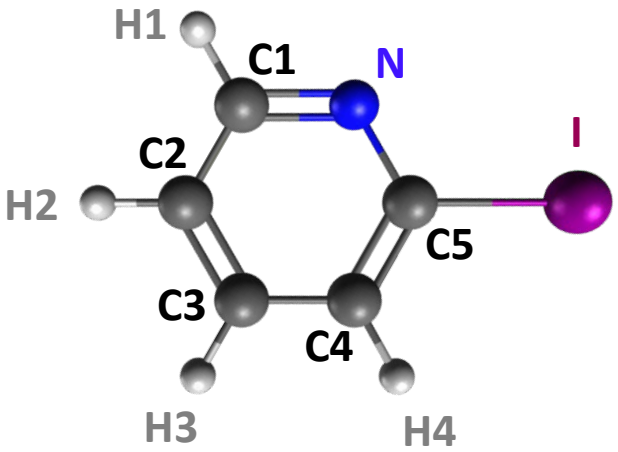


- image the fragmentation following X-ray ionization in the molecular frame
- gas-phase molecules are randomly oriented!
- but: measured 3d ion momenta in coincidence allow to “align” them in the analysis
- create Newton plot of 3 (or more) ions recorded in the same FEL shot
  - make iodine ion point towards $p_x = p_y = 0$, $p_z = 1$
  - make nitrogen ion point towards $p_x = 0$, $p_y > 0$
  - plot momentum of any third particle in this coordinate frame

Complete Coulomb Explosion Imaging

unpublished data, removed for web version.
Thank you for understanding

- molecular structure is very well reflected in measured proton momenta
- hydrogen positions can be identified unambiguously
- no evidence of deformation or rotation before breakup → very fast charging up of the molecules!



SQS beamtime Boll et al., March 2019

Complete Coulomb Explosion Imaging

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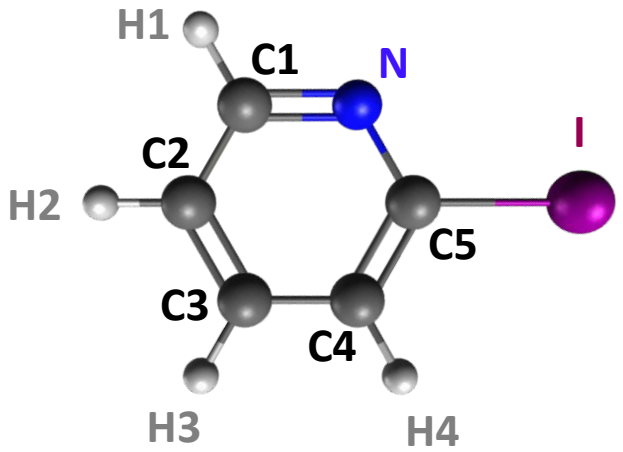
Thank you for understanding

- all carbon positions also clearly distinguishable
- track charge along the ring: differences of mean charge state for the individual carbon positions!
- triple ion coincidence results with good statistics after only ~1-2 hours thanks to high rep. rate



Molecular fingerprints

unpublished data, removed for web version.
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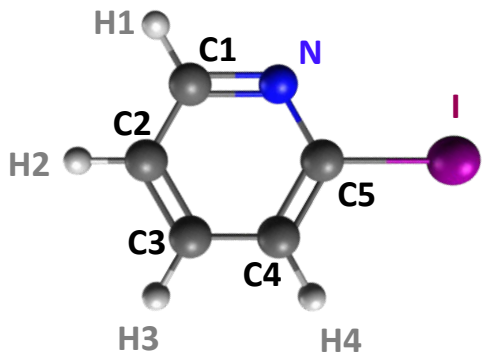
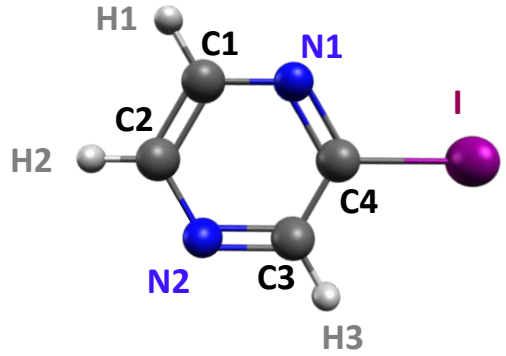


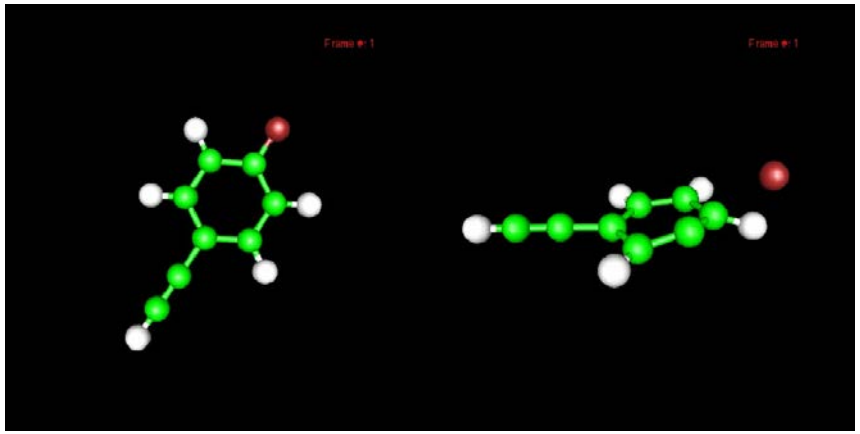
molecular structure can be clearly identified!



these can be the first frames of a molecular movie!

Conclusion and outlook – personal

- **Coulomb explosion induced by femtosecond X-ray pulses is a powerful, complementary imaging technique**
  - yields ‘fingerprints’ of the complete 3d fragmentation of a molecule, including the hydrogen positions
  - ultrafast X-ray and electron diffraction are essentially blind to hydrogen motion, which play a crucial role in many photochemical reactions
  - Coulomb explosion imaging has the potential to achieve superior temporal resolution
- **State-of-the-art theoretical calculations go hand in hand with experiments**
  - can provide detailed insight to experimental XFEL results
  - may trigger new ideas and provide valuable input for experimental parameters of interest



Conclusion and outlook – general/technical

XFEL-based research is (still) focused a lot on the available pulse parameters and experimental techniques

- **shorter pulses – attosecond pulses are already within reach!**
- **'continuous' (non-burst) operation – huge increase in statistics and much easier data handling**
- **two-color X-ray operation – exploit site-specificity of X-rays to localize photoabsorption in extended targets**
- **variable polarization – investigate effects beyond the dipole approximation**
- **advanced X-ray pulse manipulation – seeding, chirp, phase control, ...**

- **advanced in-situ diagnostics of the X-ray pulse parameters are crucial for understanding experimental results**

- **time-resolved FEL experiments benefit a lot from very close collaboration with experienced laser groups**
  - **a majority of the experiments use pump or probe pulses from an external source**
  - **tunable and shorter pump laser pulses allow for more flexibility to investigate ultrafast dynamics**
  - **stable and reliable operation, as well as full support necessary for successful beamtime**

The SQS instrument is available for you as well!

- www.xfel.eu/facility/instruments/sqs
- three dedicated end stations are available at SQS:
  - reaction microscope (REMI)
  - electron, ion, and photon spectroscopy (AQS)
  - clusters and nanoparticles (NQS)
- beam parameters offered for next user run:
  - 500 – 3000 eV (also with mono) freely tunable!!!
  - up to 4000 pulses/sec in 10 Hz burst mode
  - up to 8 mJ pulse energy
  - 25 fs (maybe shorter)
  - ~1 µm focus (installation of bendable KBs next week)
  - synchronized optical lasers are available

the happy SQS team after surviving the first successful user block

next proposal deadline: December 11th

Thank you!
Questions?

Interaction of atoms and molecules with intense X-ray pulses – reading material

Atoms:

- **Sorokin, PRL 99, 213002 (2007)**
  heavy atoms can absorb many XUV photons – 57 XUV photons (93 eV) absorbed in a single xenon atom!
- **Young, Nature 466, 56 (2010)**
  fully stripped neon atoms, intensity-induced X-ray transparency due to hollow atoms with double core holes
- **Rudek, Nat. Phot. 6, 858 (2012); Rudek, PRA 87, 023413 (2013)**
  resonances in highly charged heavy atoms facilitate creation of "forbidden" charge states
- **Rudek, Nat. Comm. 9, 4200 (2018)**
  for ultra-intense (hard) X-rays, relativistic effects become important in heavy atoms

Molecules:

- **Erk, PRL 110, 053003 (2013); Erk, J. Phys. B 46, 164031 (2013)**
  sum of all charges in a molecule is equal to the charge of an atom with the same cross-section
- **Erk, Science 345, 288 (2014)**
  intially localized charge is distributed to neighboring atoms over distances as large as 20 Angstrom
- **Boll, Struct. Dyn. 3, 043207 (2016)**
  temporal evolution of charge rearrangement can be tracked for different molecules and different pump processes
- **Rudenko, Nature 545, 129 (2017)**
  for extreme intensities, ionization of a molecule is enhanced compared to that of an atom with the same cross-section

Theory:

- **XATOM and XMDYN: Jurek, J. Appl. Cryst. 49, 1048 (2016)**
- **XMOLECULE: Hao, Struct. Dyn. 2, 041707 (2015)**