Coulomb explosion imaging as structural probe of polyatomic molecules

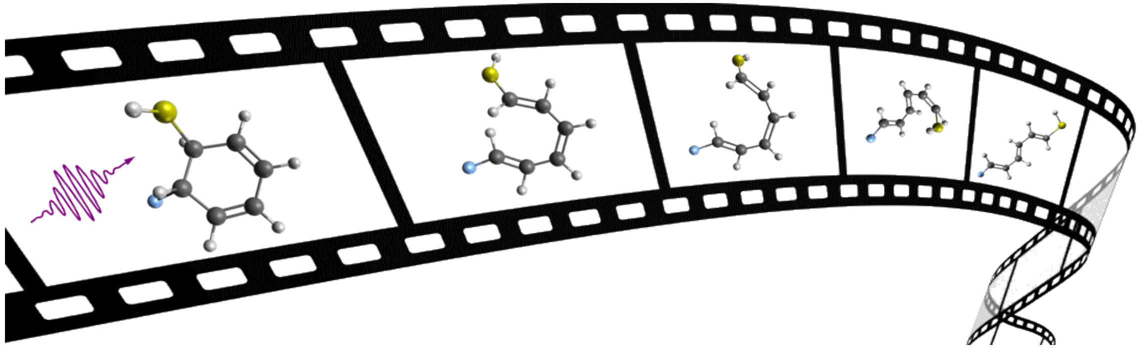
Rebecca Boll

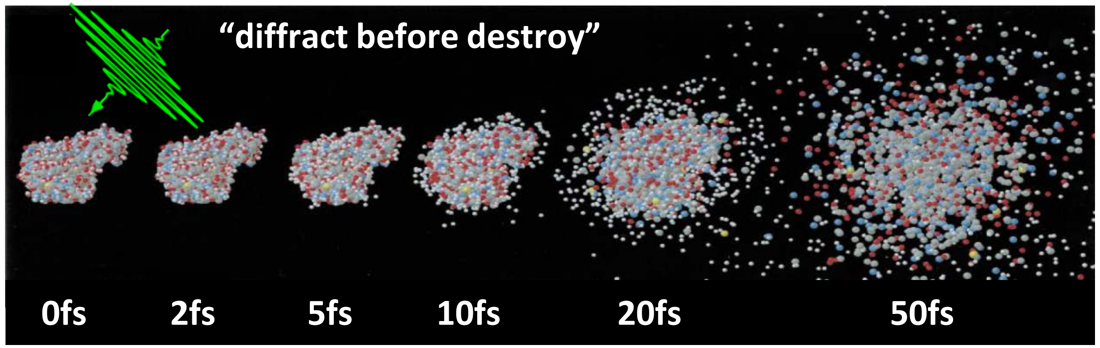
European XFEL

Small Quantum Systems (SQS) Scientific Instrument

European XFEL

'Imaging' of structures at X-ray FELs

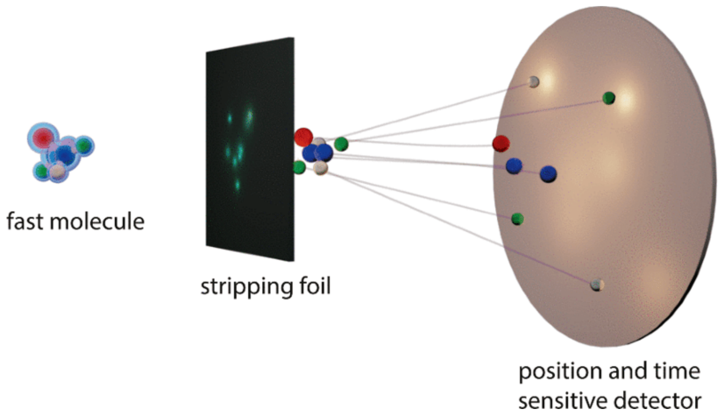


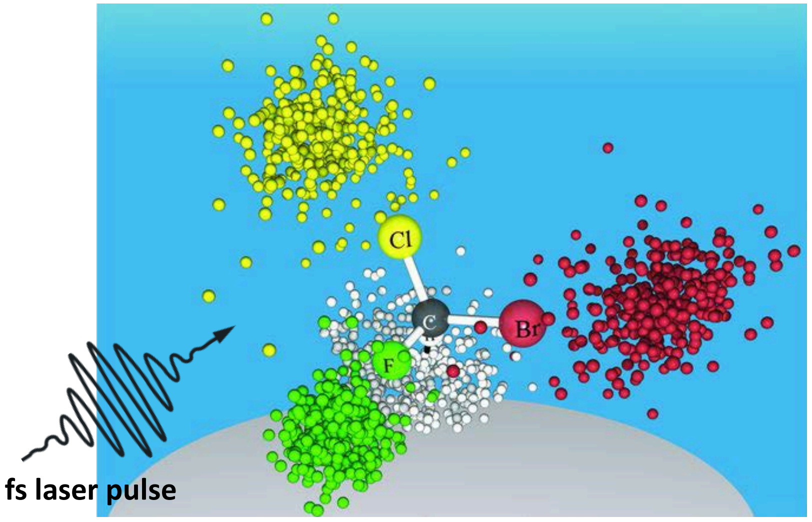


- one key motivation for the development of X-ray FELs was imaging of (dynamic) structure with unprecedented spatial and temporal resolution – recording the famous 'molecular movie'
- but, what does imaging of a structure mean?
  - resolving the overall shape? retrieving the electron density?
  - seeing a particular atom move? obtaining all bond lengths and all bond angles?
- several approaches were successfully demonstrated at FELs, e.g. for tiny crystals, non-reproducible nano-sized objects, molecules in solution and on surfaces, …
  - very challenging to apply on small, gas-phase molecules, and in particular for light atoms such as hydrogens
  - all methods rely, in some form, on the assumption that the 'imaging' takes place before the sample is destroyed

R. Neutze et al., Nature 406, 752 (2000)

Coulomb explosion imaging in a nutshell



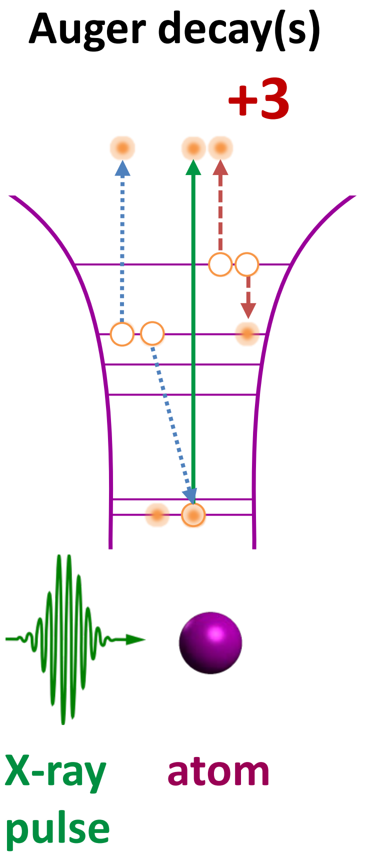


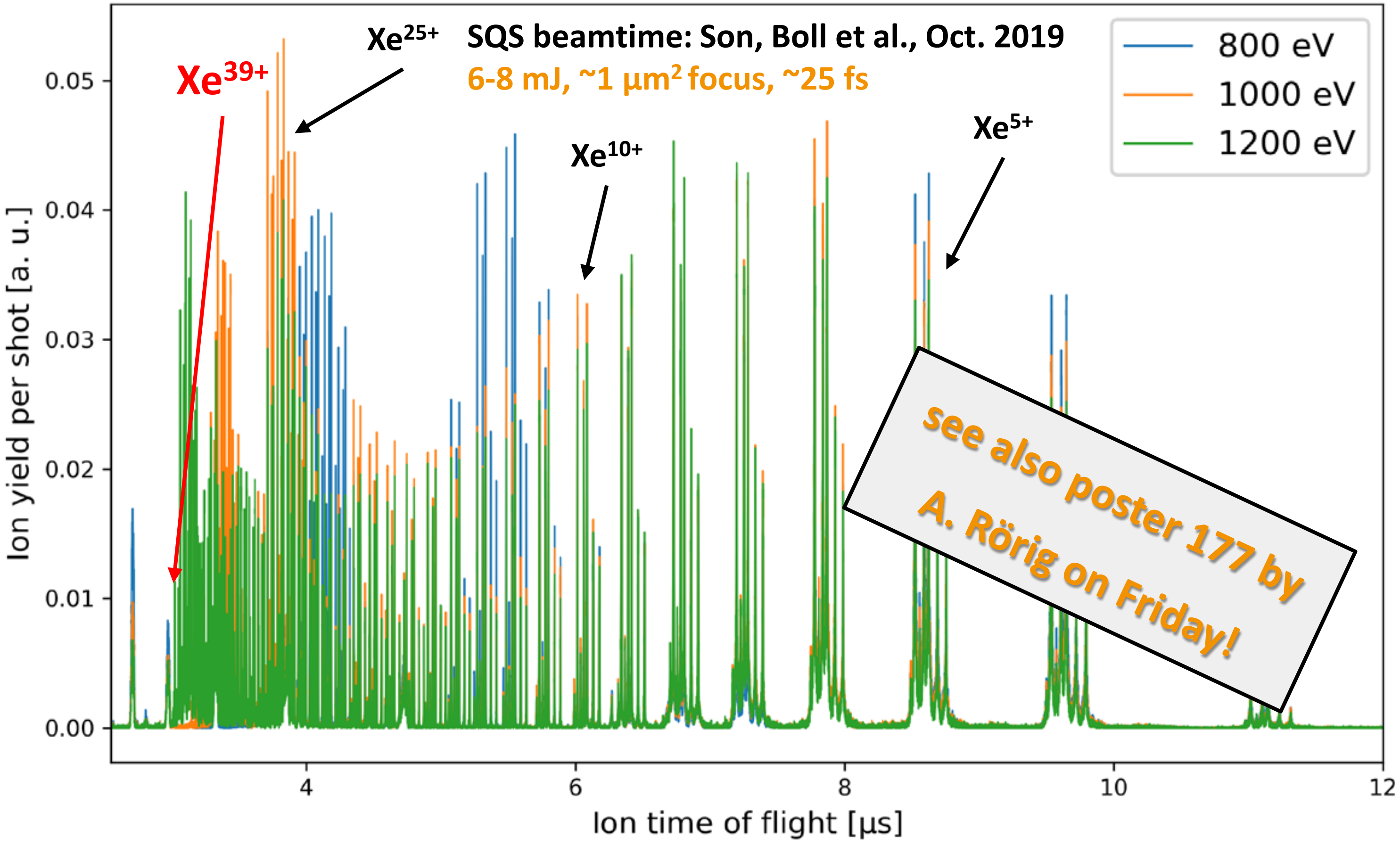
- Coulomb Explosion Imaging (CEI) makes use of the 'destroying'!
- CEI was originally done by shooting ionic molecules through foils, ionizing all atoms during the passage
  - images static structures of small molecules, but unsuitable for dynamics
- photon pulses from lasers or synchrotrons can also ionize!
  - but: larger molecules almost always rotate or fragment before the explosion takes place
  - thus, it was generally thought to be unfeasible to use CEI for imaging larger molecules
- challenge: to put enough charge on a molecule in a short enough time, such that it explodes before it can do anything else
  - instead of diffract-before-destroy, we want to destroy-before-deform!
  - **may a brilliant, short-pulse, high rep. rate XFEL be a solution?**

Vager, Science 244 , 426 (1989)
Herwig, Phys. Rev. A 90, 052503 (2014)
Pitzer, Science 341, 1096 (2013)

A few basics: absorption of very intense X-ray pulses in heavy atoms

- in atoms: very high charge states trough sequence of multiple inner-shell photoabsorptions and Auger decays
- for certain photon energies, intermediate resonances play an important role

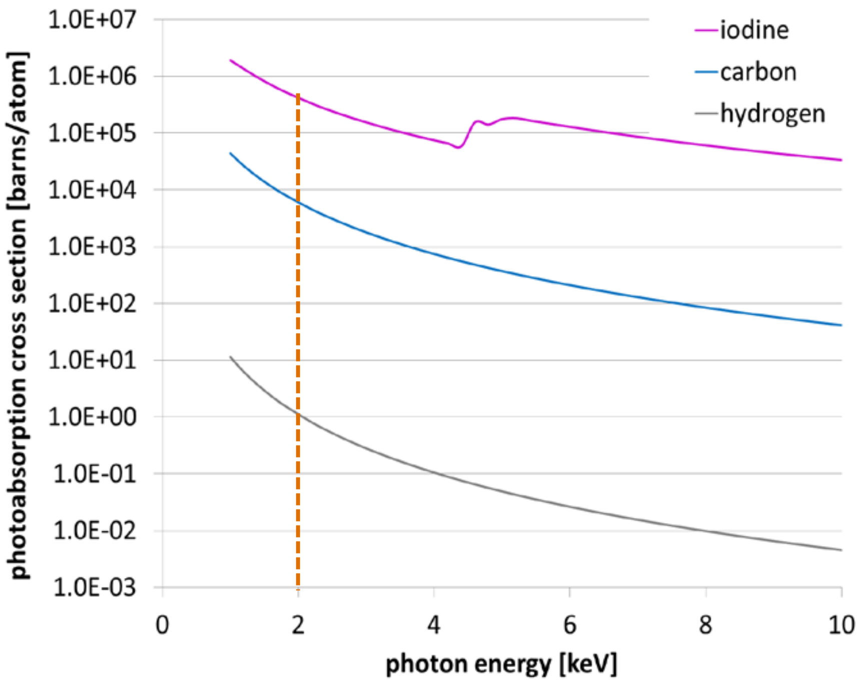


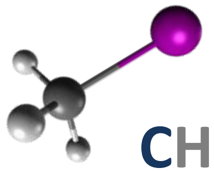


see also:
Rudek, Nat. Phot. 6, 858 (2012)
Rudek, Nat. Comm. 9, 4200 (2018)

A few basics: absorption of very intense X-ray pulses in molecules with heavy atoms

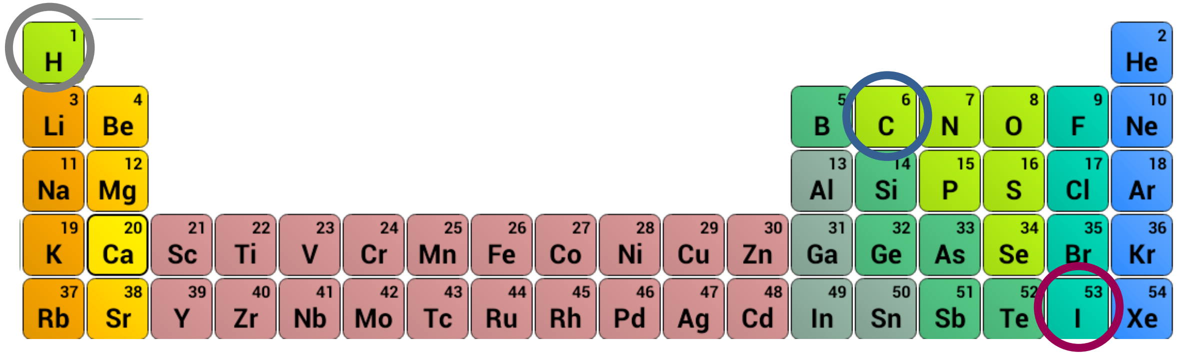
- in atoms: very high charge states trough sequence of multiple inner-shell photoabsorptions and Auger decays
- for certain photon energies, intermediate resonances play an important role
- element-specificity: X-ray absorption is localized at heavy atom – but how do we get Coulomb explosion?!





CH_3I

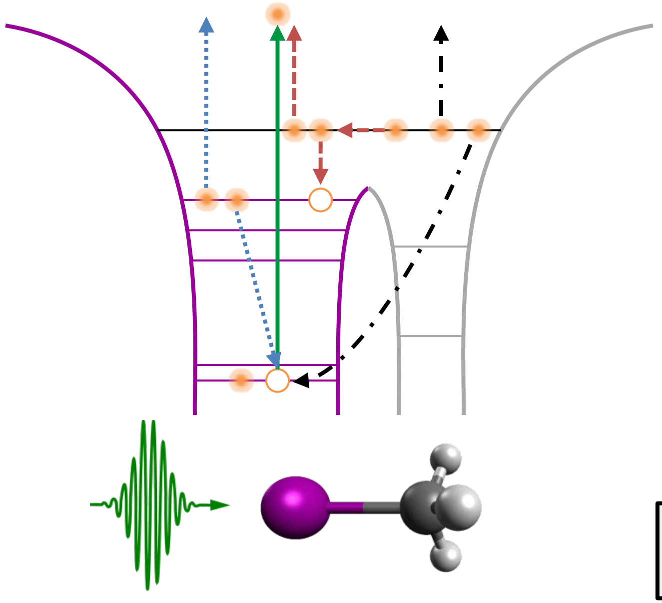
$$\frac{\sigma_I}{\sigma_{CH3}} = \frac{70}{1}$$

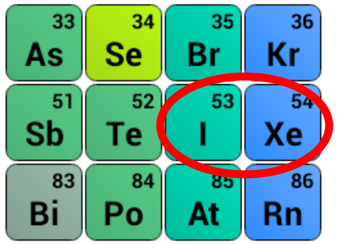


A few basics: absorption of very intense X-ray pulses in molecules with heavy atoms

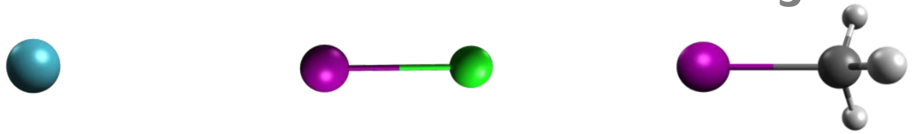
- in atoms: very high charge states trough sequence of multiple inner-shell photoabsorptions and Auger decays
- for certain photon energies, intermediate resonances play an important role
- element-specificity: X-ray absorption is localized at heavy atom – but how do we get Coulomb explosion?!
- in molecules: total molecular charge stays the same, but charge is redistributed to the other atoms

valence electrons delocalized





Xe ICl CH_3I



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

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

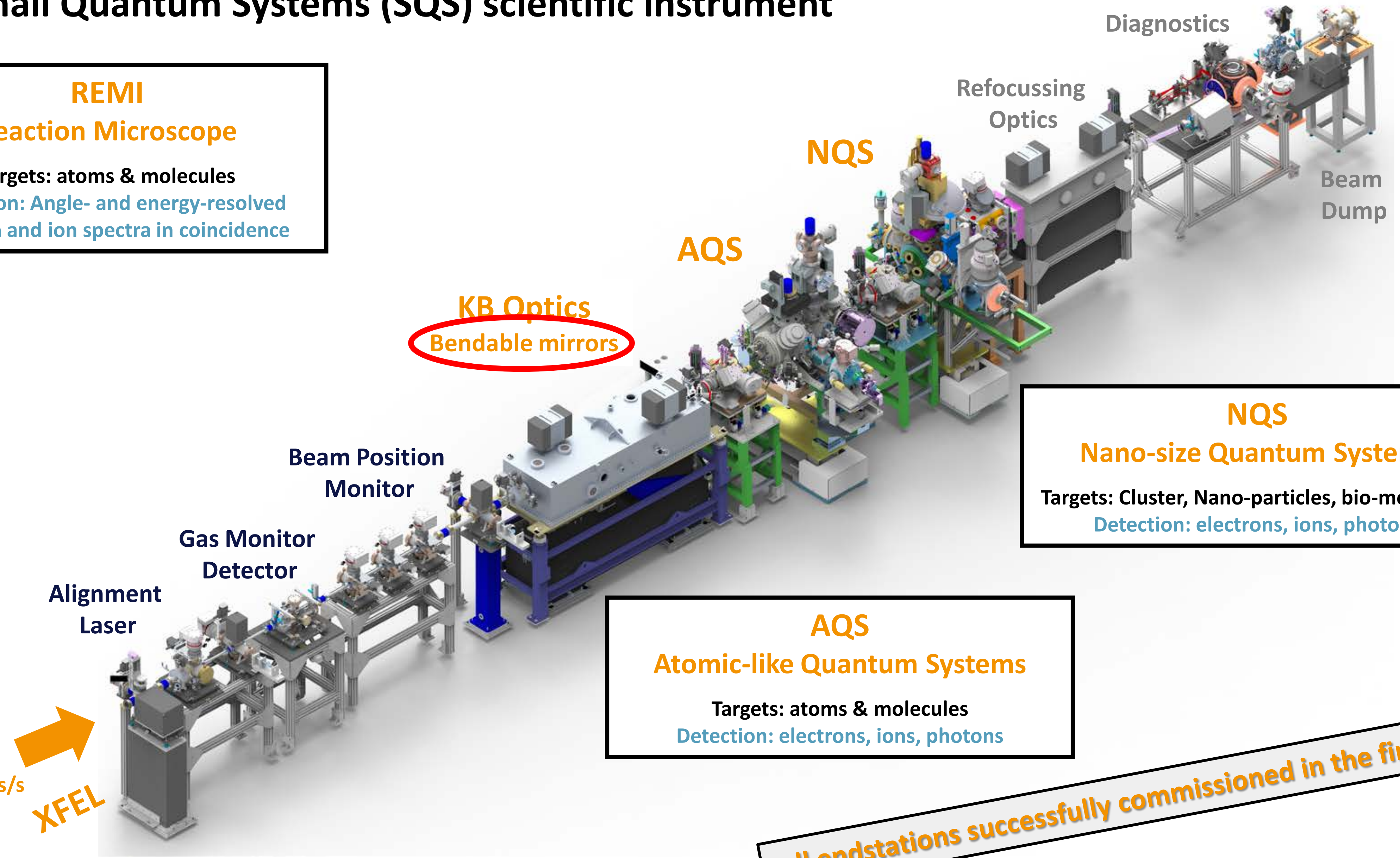
maximum charge states measured

charge can be transferred over distances as large as ~15 Å for I^{20+} !

Erk, Phys. Rev. Lett 110, 053003 (2013)
Erk, J. Phys. B 46, 164031 (2013)
Erk, Science 345, 288 (2014)
Boll, Struct. Dyn. 3, 043207 (2016)

The Small Quantum Systems (SQS) scientific instrument

REMI
Reaction Microscope
Targets: atoms & molecules
Detection: Angle- and energy-resolved electron and ion spectra in coincidence



NQS
Nano-size Quantum Systems
Targets: Cluster, Nano-particles, bio-molecules
Detection: electrons, ions, photons

AQS
Atomic-like Quantum Systems
Targets: atoms & molecules
Detection: electrons, ions, photons

270 – 3000 eV
up to 2000 pulses/s
up to 5 – 8 mJ
~1.2 µm focus

all endstations successfully commissioned in the first user run

The REMI – one year ago

REMI
Reaction Microscope
designed and built by R. Dörner group

January 2019

A huge amount of work of many people…

Goethe University Frankfurt & SQS team

Alexander Achner
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Markus Schöffler
Juliane Siebert
Nico Strenger
Daniel Trabert
Isabel Vela-Perez
Rene Wagner
Miriam Weller
Pawel Ziołkowski

as well as many EuXFEL support groups:

Controls and analysis

Advanced electronics

IT

Vacuum

…

One of the first SQS user beamtimes only two months later

European XFEL
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Christopher Passow
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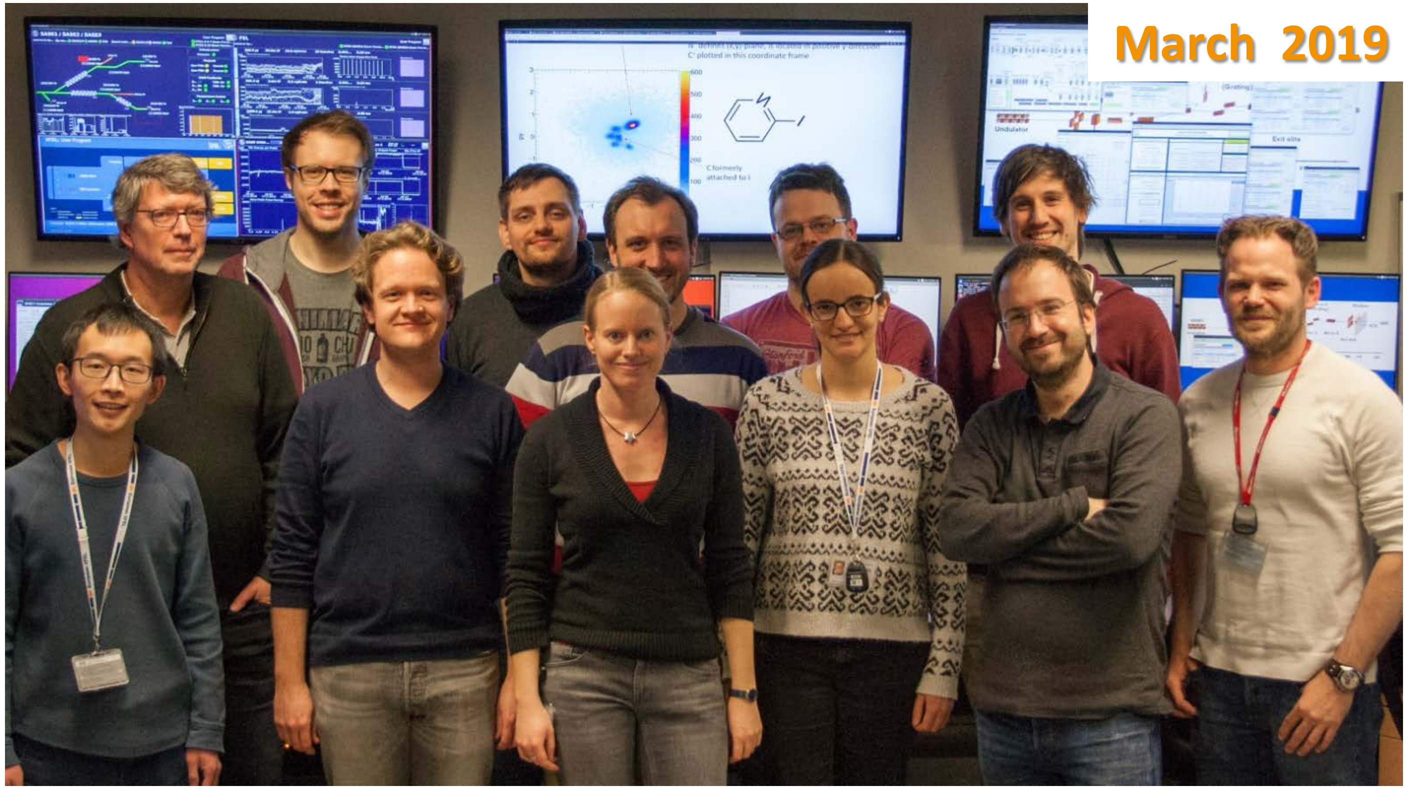
MPI for Nuclear Physics
Severin Meister



March 2019

Kansas State University
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Daniel Rolles
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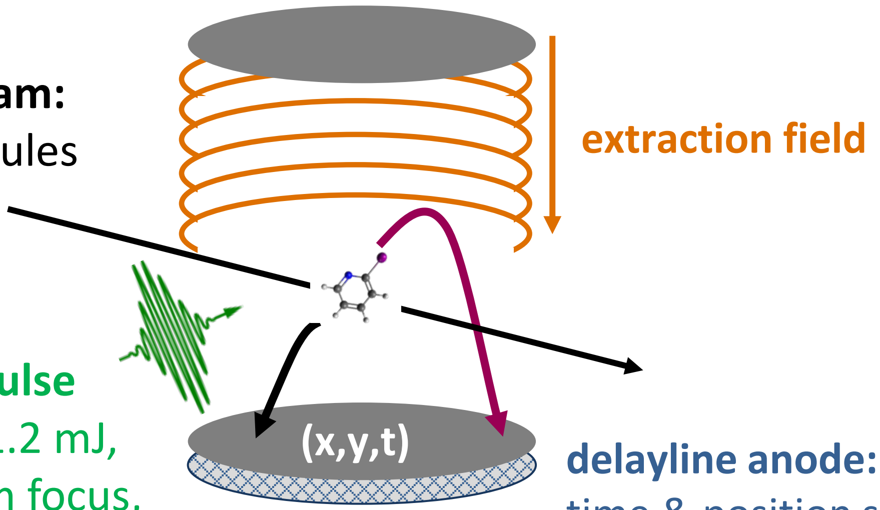
MPI for Medical Research
Lutz Foucar
Ilme Schlichting

SLAC
Peter Walter

Coincident ion momentum imaging with the Reaction Microscope

supersonic beam:
isolated molecules

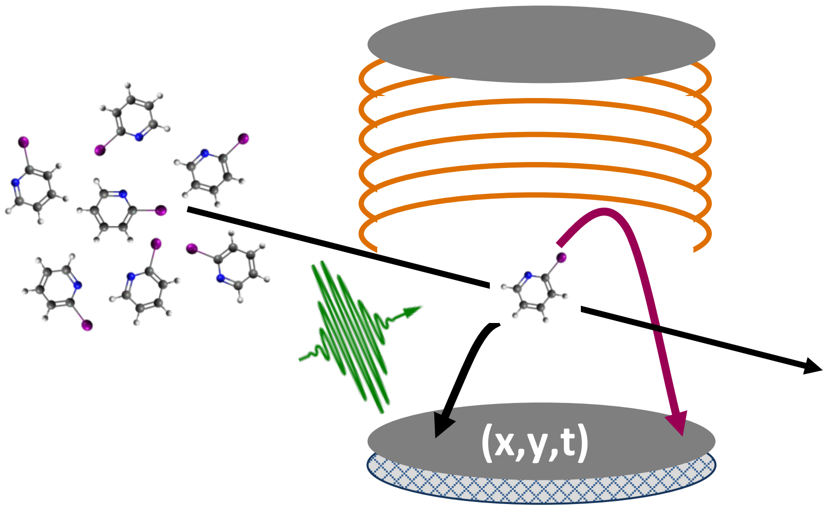


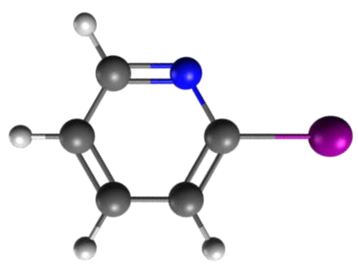
X-ray pulse
2 keV, 1.2 mJ,
~1.2 µm focus,
25 fs (?)

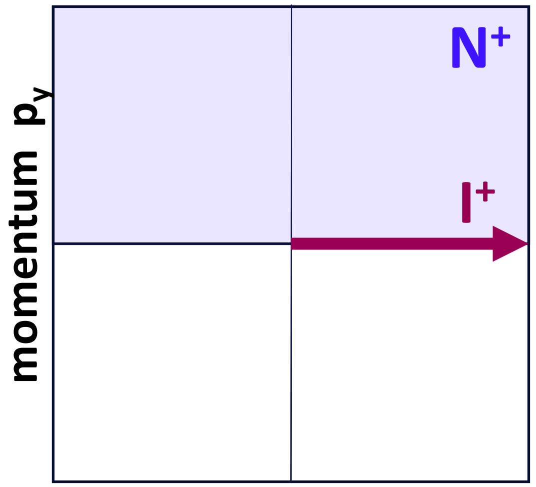
delayline anode:
time & position sensitive,
3d ion momenta

- **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







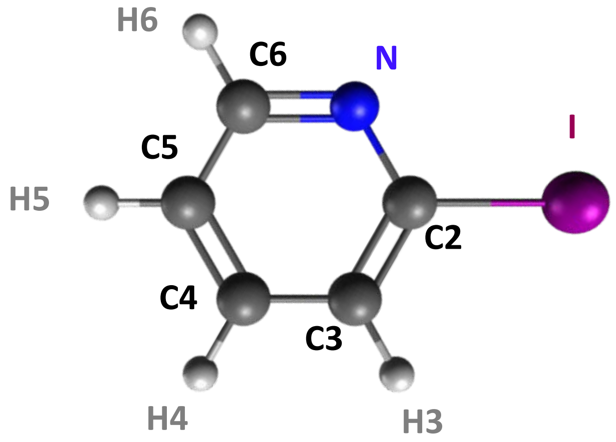
- image the fragmentation following X-ray ionization in the molecular frame
- gas-phase molecules are randomly oriented!
- but: measured 3d ion momenta in coincidence allow to "align" them in the analysis
- create Newton plot of 3 (or more) ions recorded in the same FEL shot
  - make iodine momentum point towards $p_x = p_y = 0$, $p_z = 1$
  - make nitrogen momentum 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!
- positions can be identified unambiguously
- no evidence of deformation or rotation before breakup

→ very fast charging up of the molecules!

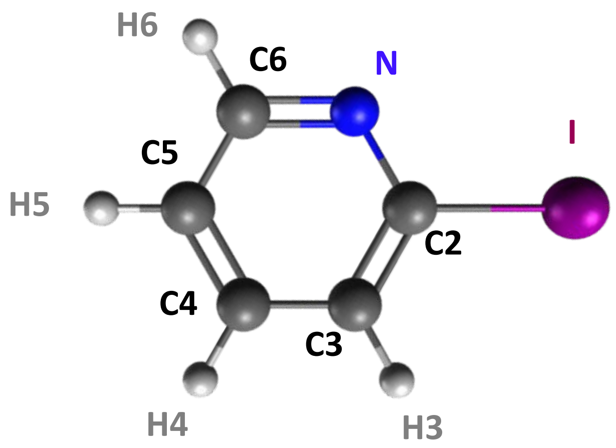


SQS beamtime Boll et al., March 2019

Complete Coulomb Explosion Imaging

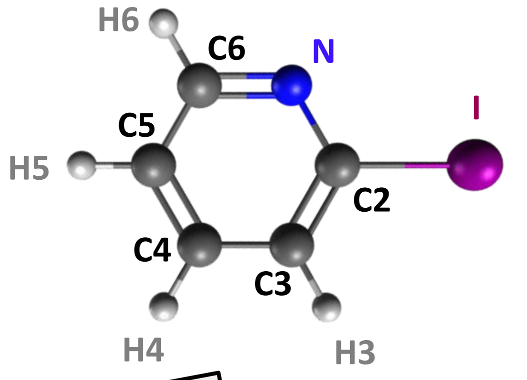
unpublished data, removed for web version.
Thank you for understanding

- all carbon atoms also clearly distinguishable!
- triple ion coincidence results with good statistics after only ~1-2 hours thanks to high rep. rate
  - 250-600 Hz effectively, 183 kHz bunch spacing
- here, 3-fold ion coincidences are sufficient to image the whole molecule with 11 atoms!
  - no need to record all 11 ions in coincidence, as long as all atoms are charged up fast enough!

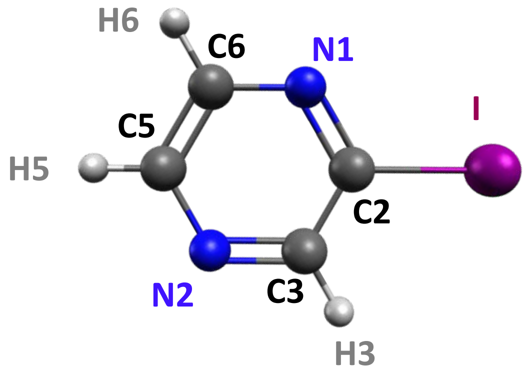


SQS beamtime Boll et al., March 2019

CEI at SQS can serve to record 'fingerprints' of polyatomic molecules with superior quality



these can be the first frames of a 'molecular movie'!



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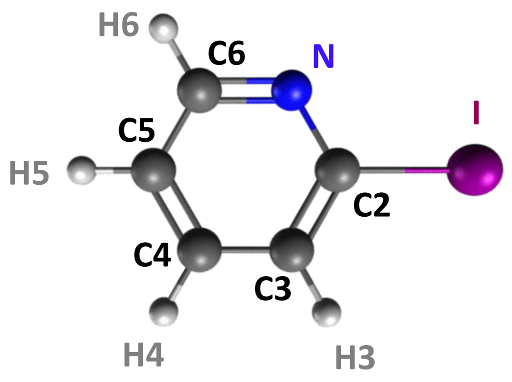
Thank you for understanding

Simulation of CEI using the XMDYN toolkit



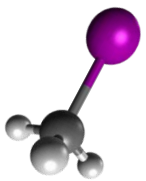
unpublished data, removed for web version.
Thank you for understanding

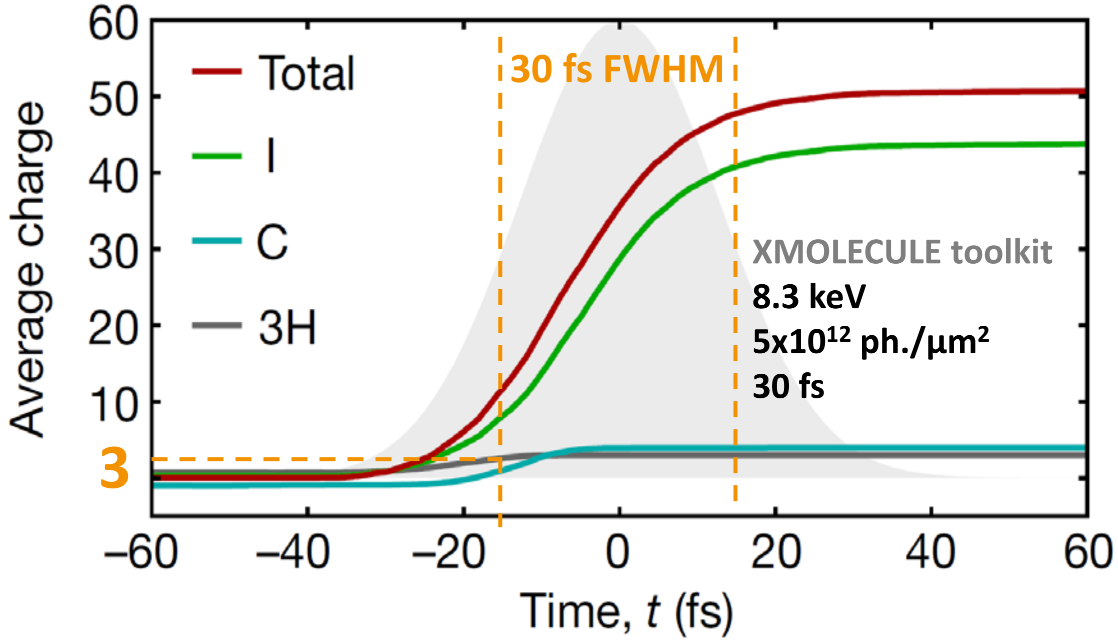
see also poster 191 by J. Schäfer on Friday!

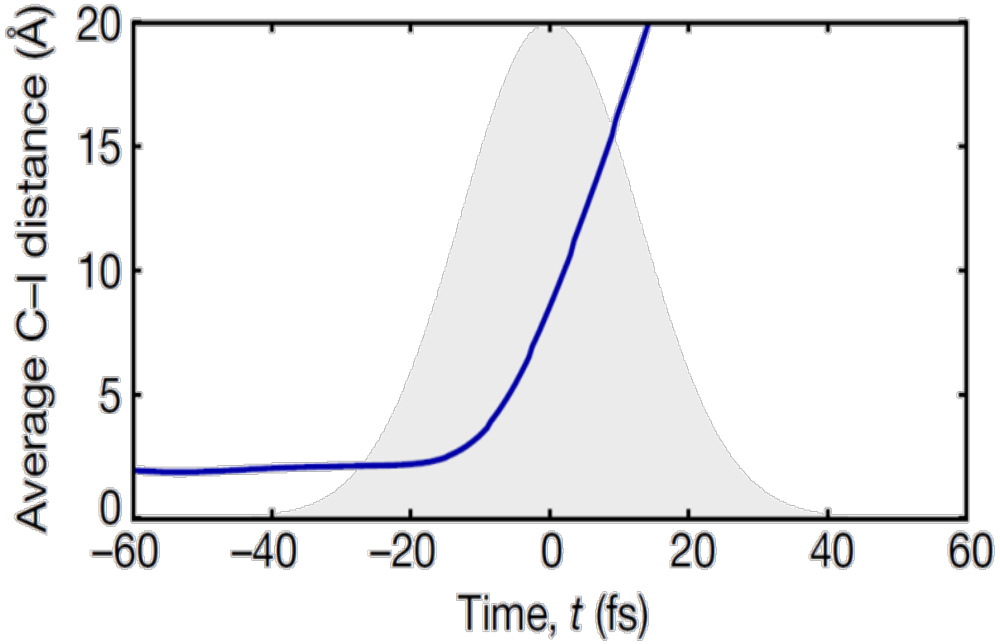
- calculations of carbon and hydrogen momenta using the XMDYN toolkit → R. Santra group, CFEL
  - atomic ab-initio calculations + Monte Carlo + molecular dynamics
- first impression: looks like it works extremely well!
- calculations will enable us to get a deeper insight into the fragmentation and charging-up dynamics
  - where does the charge end up?
  - how fast do the hydrogens fly away?
  - are there different channels contributing?

see also:
Jurek, Son, Ziaja, Santra, J. Appl. Cryst. 49, 1048 (2016)

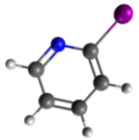
Charge build-up and fragmentation during an X-ray pulse







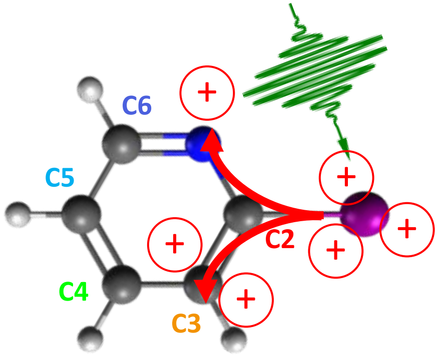
- the ion momenta provide us not only with the structure of the molecule, but also give some insight into the **temporal evolution of molecular fragmentation**
- calculations of time-dependent charge and geometry evolution with XMDYN are currently running

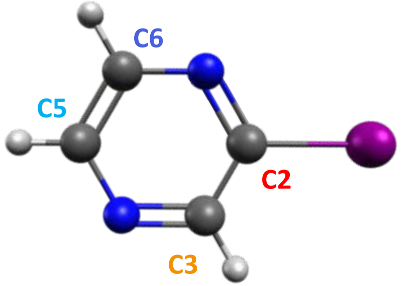


- the measured and calculated proton momenta are unexpectedly low
  - **protons appear to receive charge before the pyridine ring!**

Rudenko, Nature 545, 129 (2017)

Tracing the charge rearrangement along the pyridine ring





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Thank you for understanding

- photoabsorption takes place at iodine – but we can detect where the charge ended up!

- in both molecules and for different I charge states:
  - the C2 atom is more likely to be only singly charged and less likely to be higher charged compared to the other positions!
  - the FAR end of the molecule receives a higher charge, even though the charge originated at the iodine!
  - work in progress, several details still to understand

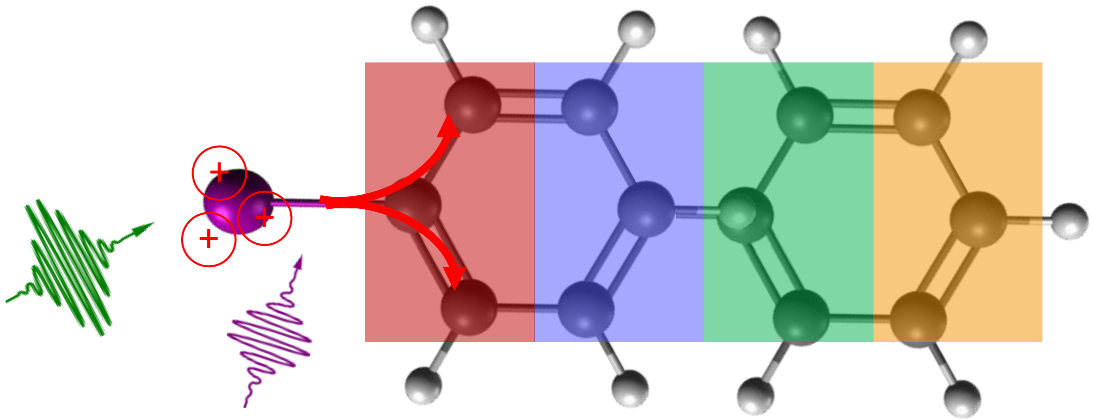
see also:
Hao, Inhester, Son, Santra, Phys. Rev. A 100, 013402 (2019)

Conclusion and Outlook

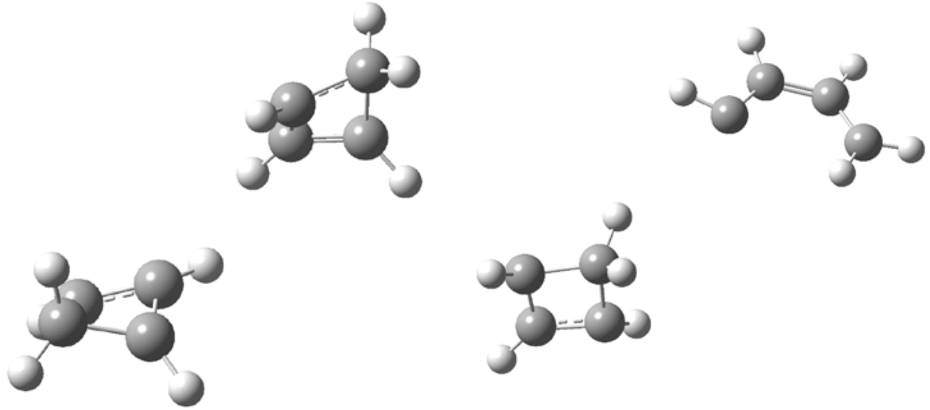
- **Coulomb explosion induced by femtosecond X-ray pulses is a powerful, complementary imaging technique**
  - can yield 'fingerprints' of the complete 3d structure of a molecule, including the hydrogen positions
  - if charge-up is fast enough, few detected ions can contain information about the whole structure

- Coulomb explosion imaging has the potential to achieve superior temporal resolution
  - this opens the door towards various time-resolved studies, including hydrogen motion, which plays a crucial role in many photochemical reactions

distance-dependence of charge transfer



isomerization and hydrogen migration



https://www.ch.imperial.ac.uk/rzepa/blog/?p=11830

The SQS instrument and team is available for you as well!

- three dedicated end stations:
  - reaction microscope (REMI)
  - electron, ion, and photon spectroscopy (AQS)
  - clusters and nanoparticles (NQS)

- current beam parameters:
  - 270 – 3000 eV (also with mono) freely tunable!!!
  - up to 2000 pulses/sec in 10 Hz burst mode
  - up to 5-8 mJ pulse energy
  - 25 fs (possibly shorter)
  - ~1 µm focus (bendable KBs from now on!)
  - synchronized optical lasers

the SQS team is very happy to talk to you!

Thank you! Questions?