Polyatomic systems at high x-ray intensity

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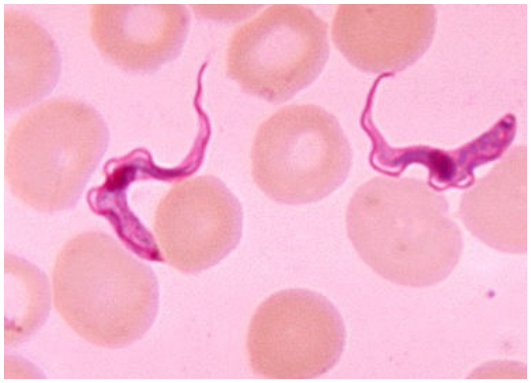
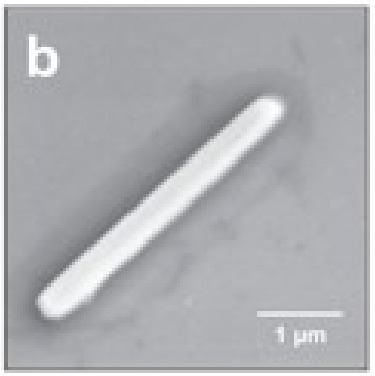
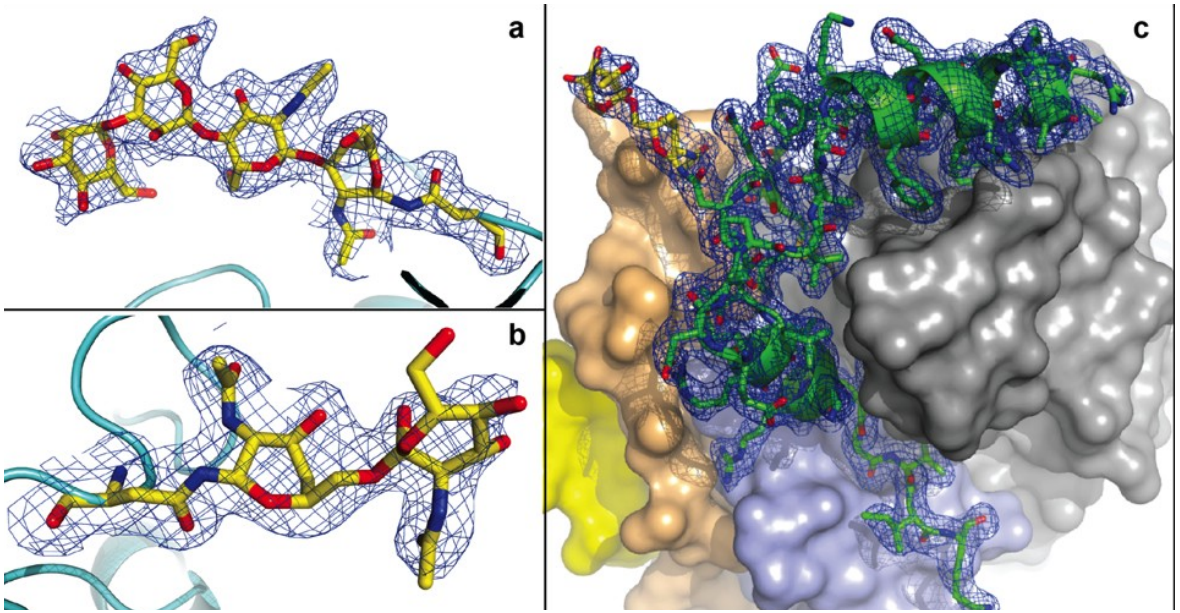
Serial femtosecond crystallography using an x-ray free-electron laser (Henry Chapman *et al.*)





The parasite Trypanosoma brucei causes African sleeping sickness, which is lethal and infects 50,000 people a year.

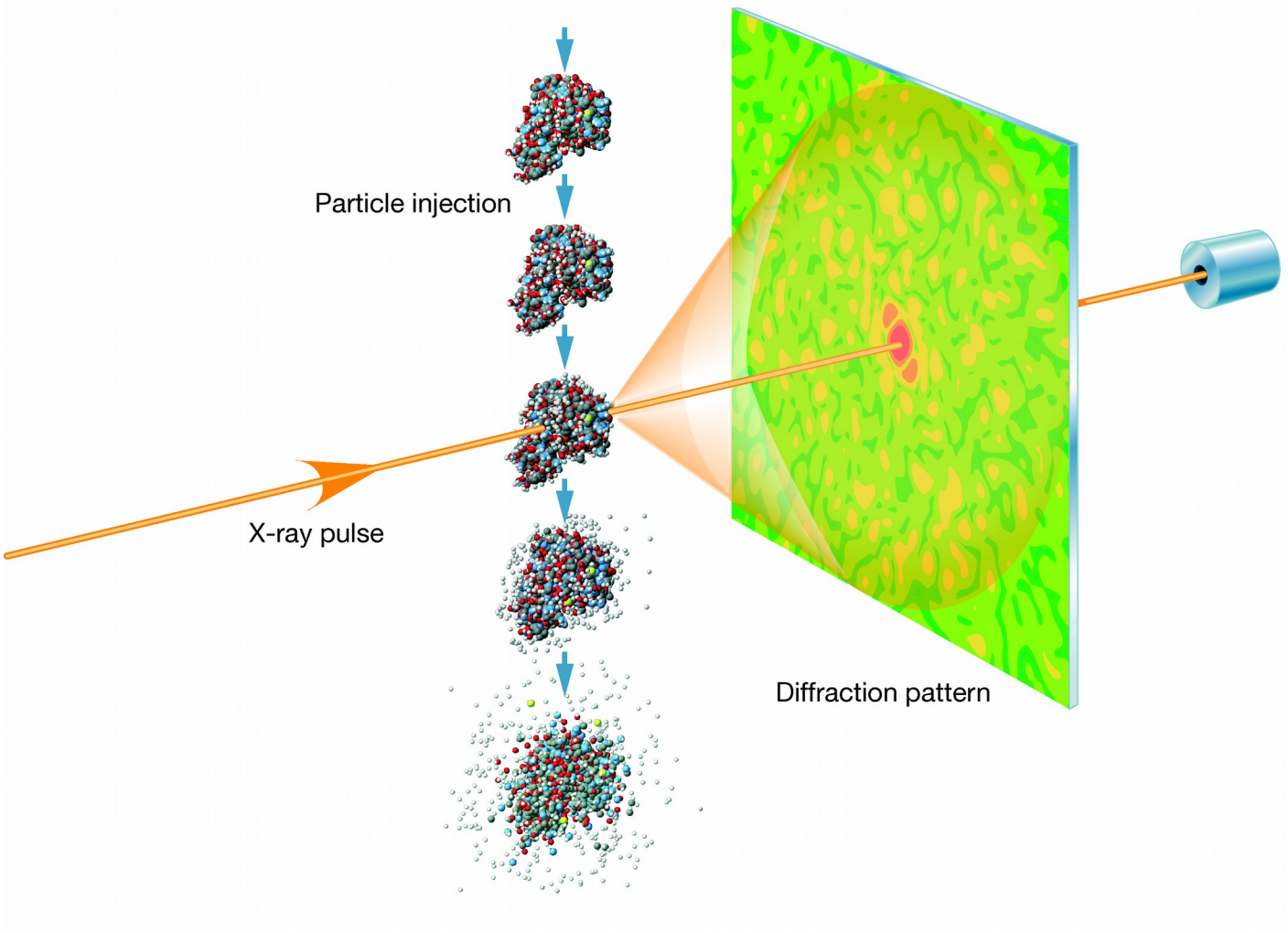


Microcrystals of the enzyme Cathepsin B from the parasite, formed by in vivo crystallisation, were too small for synchrotron studies.

The structure shows the natural inhibition of the enzyme, giving clues for drug discovery.

L. Redecke *et al.*, Science **339**, 227 (2013).

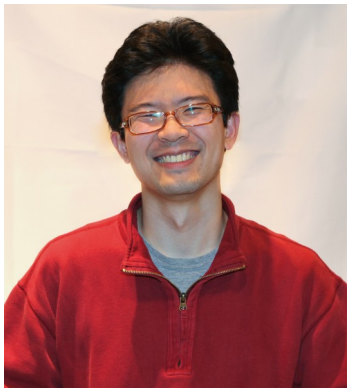
Single-shot structure determination of biomolecules



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

XMDYN

Zoltan Jurek



Sang-Kil Son

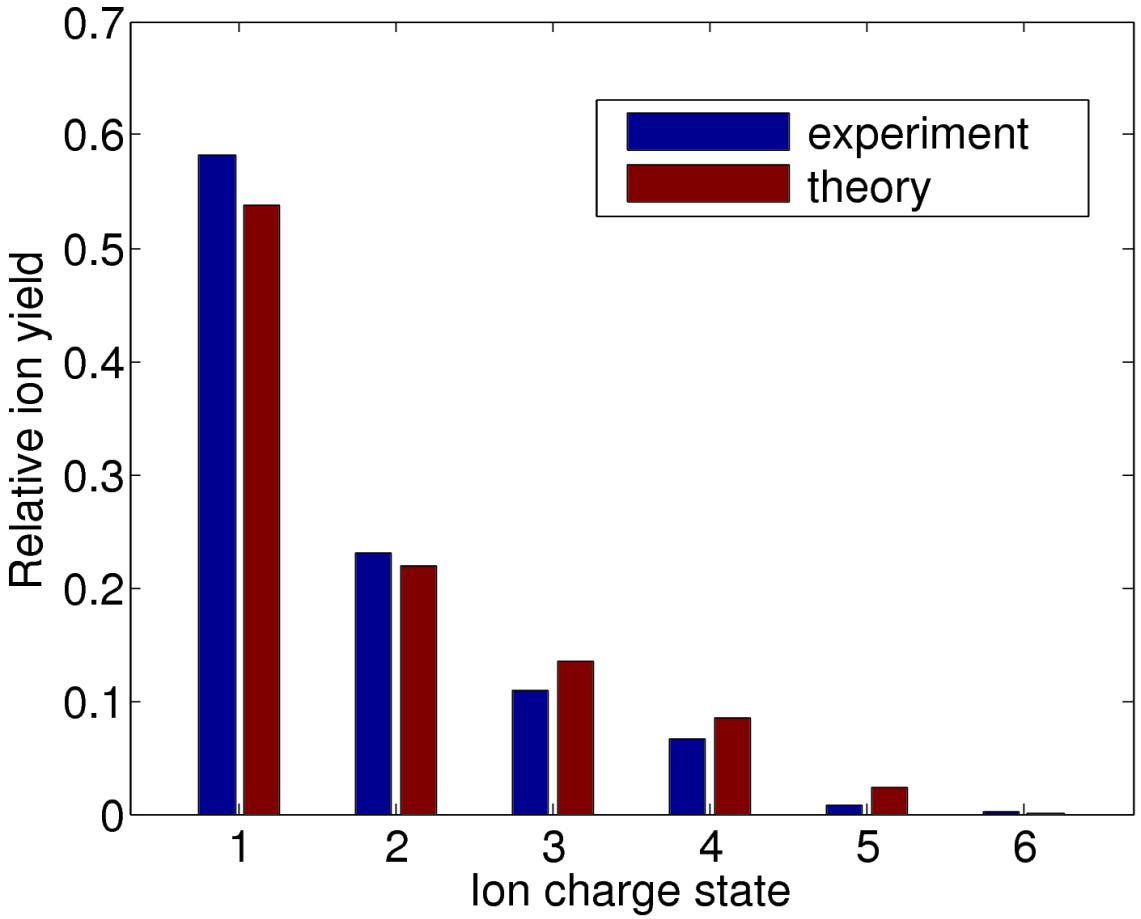
→ ab-initio calculation of atomic parameters (subshell photoionization cross sections, electronic decay rates, x-ray scattering cross sections) for arbitrary electronic configurations →uses XATOM

→ description of electronic population dynamics via Monte Carlo

→ classical molecular dynamics for nuclei and ionized electrons

C_{60} @ LCLS (Nora Berrah *et al.*)

> **Atomic ions** – experimental and volume integrated theoretical **yields**



Pulse:

30 fs

485 eV, 0.345 mJ,

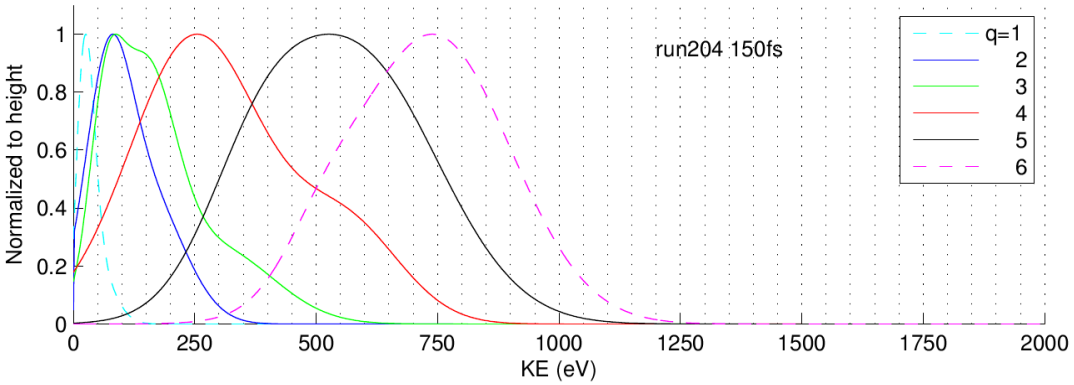
focus = $(1.4\ \mu m)^2$

B. F. Murphy *et al.*, Nature Commun. **5**, 4281 (2014).

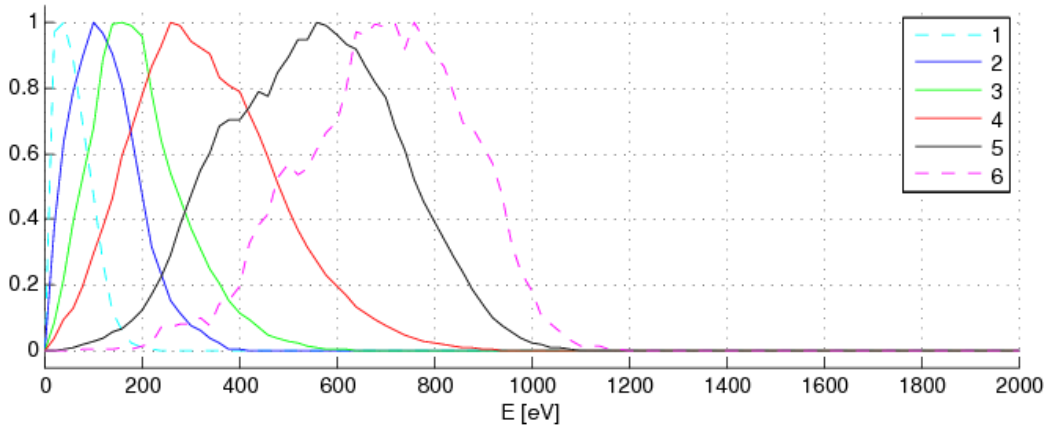
C_{60} @ LCLS (Nora Berrah *et al.*)

> Atomic ions – kinetic energy spectra

Pulse: 90 fs,
485 eV, 0.91 mJ,
focus = (1.4µm)^2



– Experiment



– Theory

no parameter fitting!

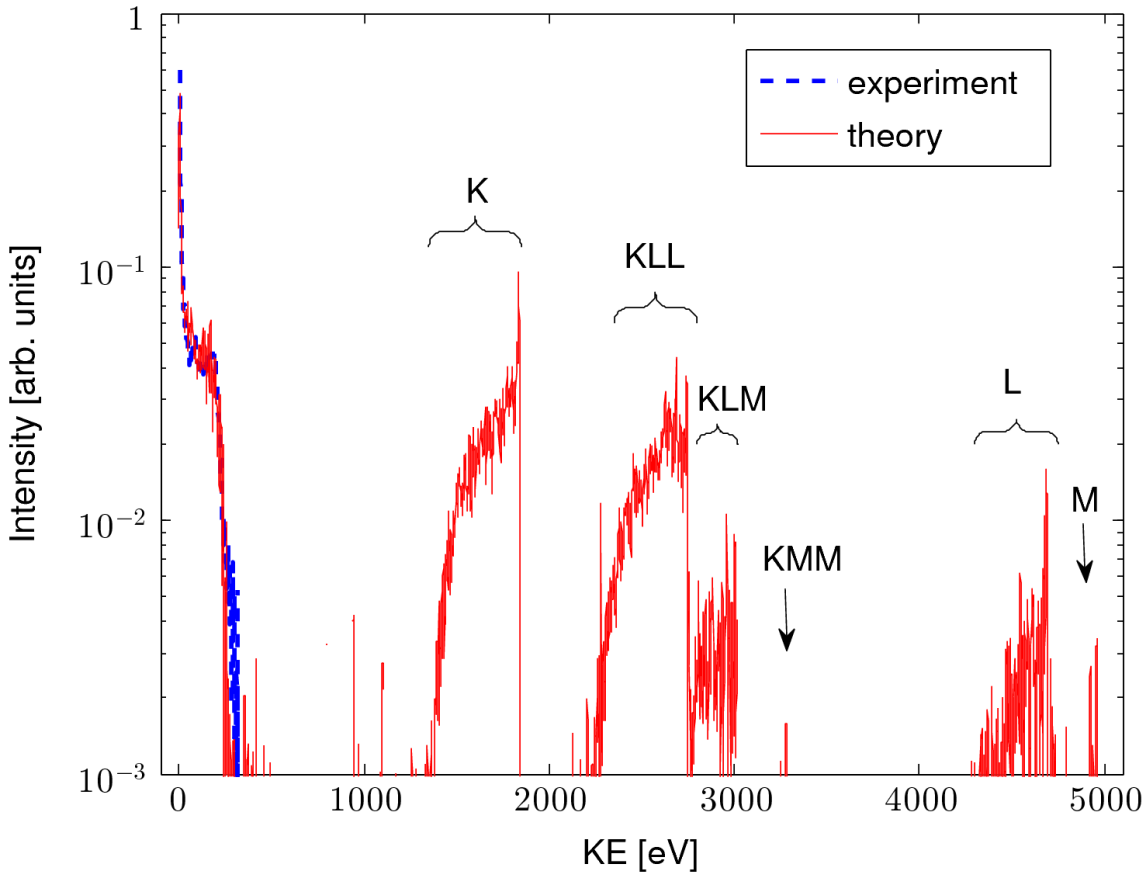
B. F. Murphy *et al.*, Nature Commun. **5**, 4281 (2014).

Argon clusters @ SACLA (Kiyoshi Ueda *et al.*)

> Theoretical and experimental electron kinetic energy spectra,

5 keV, 30 fs

N=1000 atoms



– Experiment

– Theory

no parameter fitting!

T. Tachibana *et al.*, Scientific Reports **5**, 10977 (2015).

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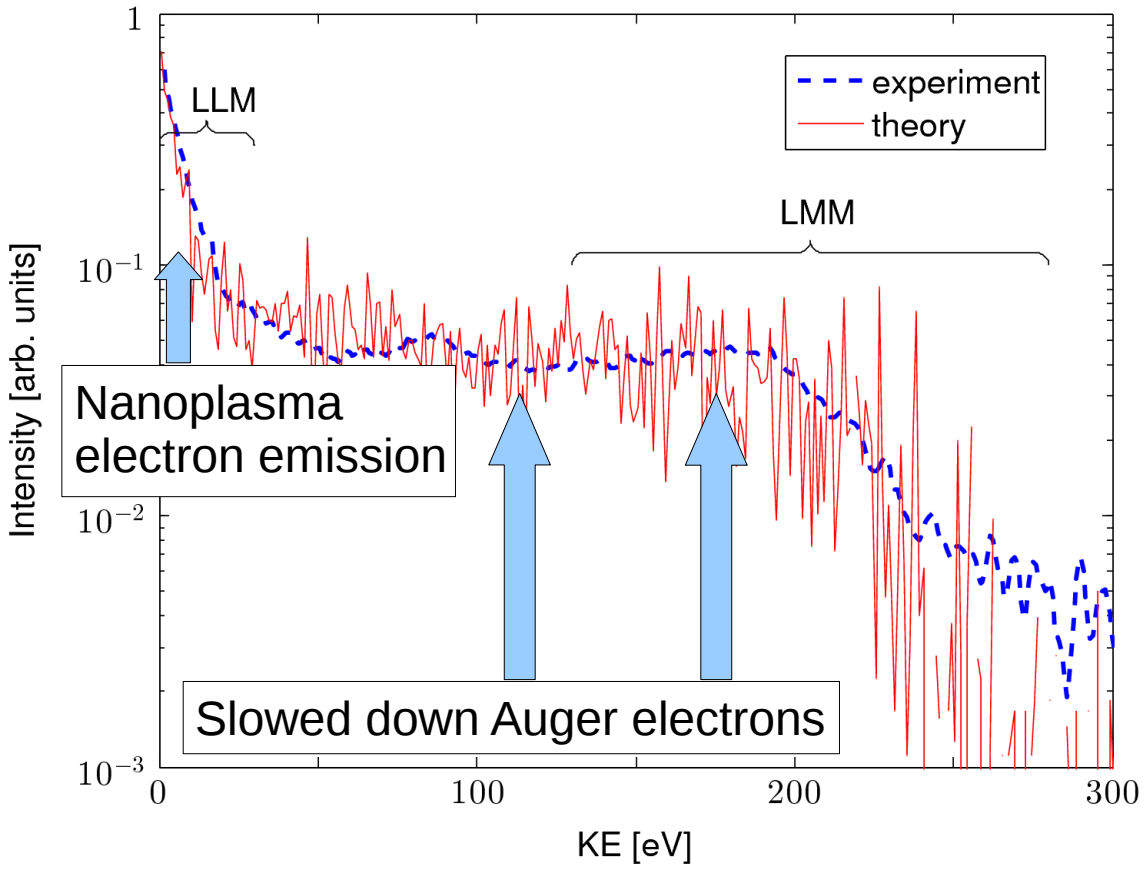


– Experiment

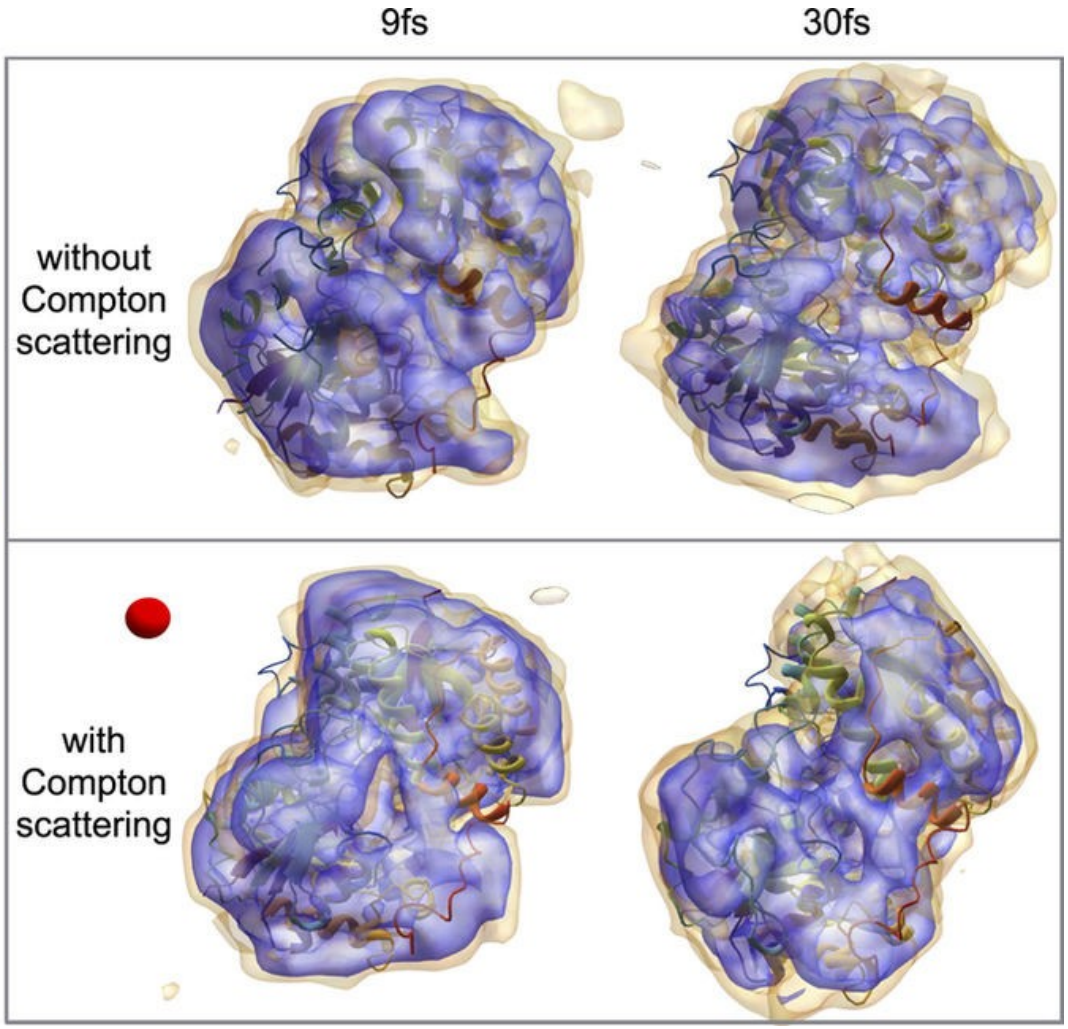
– Theory

no parameter fitting!

T. Tachibana *et al.*, Scientific Reports **5**, 10977 (2015).

XMDYN is part of a start-to-end simulation framework for single-particle imaging at the European XFEL

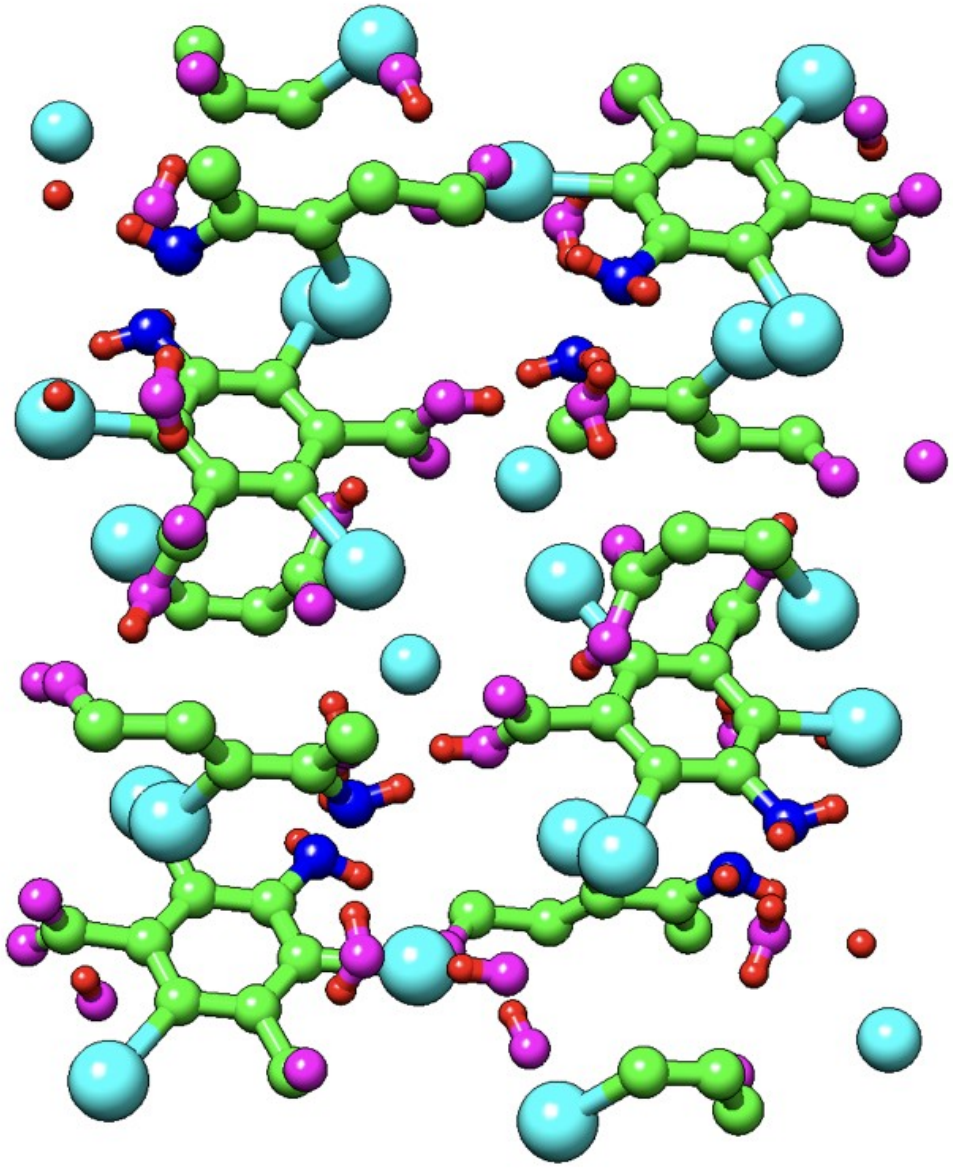
Red reference sphere has a diameter of 7 Å



nitrogenase iron protein

C. H. Yoon *et al.*, Sci. Rep. **6**, 24791 (2016).
C. Fortmann-Grote *et al.*, IUCrJ **4**, 560 (2017).

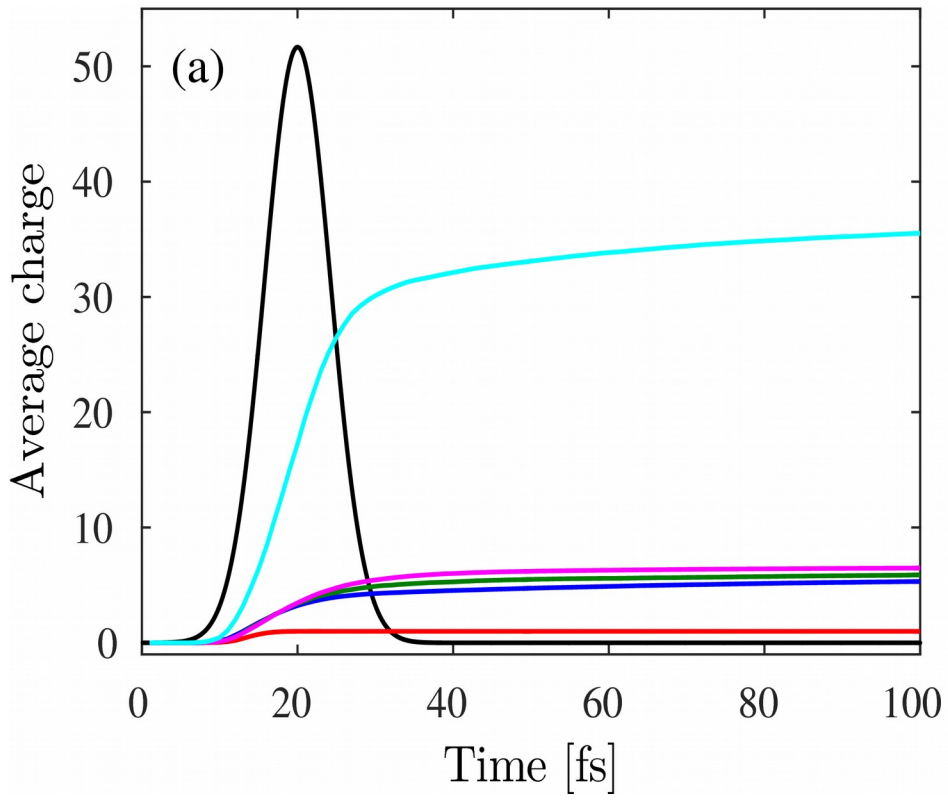
XMDYN using periodic boundary conditions



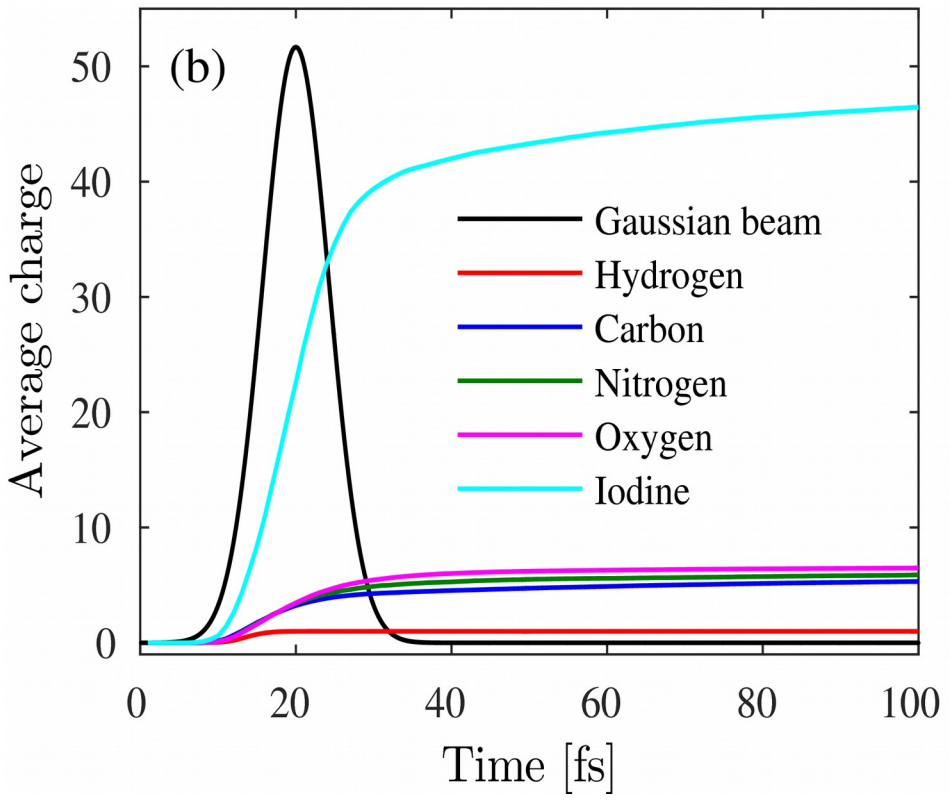
I3C crystal
(5-amino-2,4,6-triiodo-isophthalic acid, $C_8H_4I_3NO_4$)

Ionization dynamics in I3C crystal (photon energy 9.7 keV)

5×10^{12} photons/μm^2

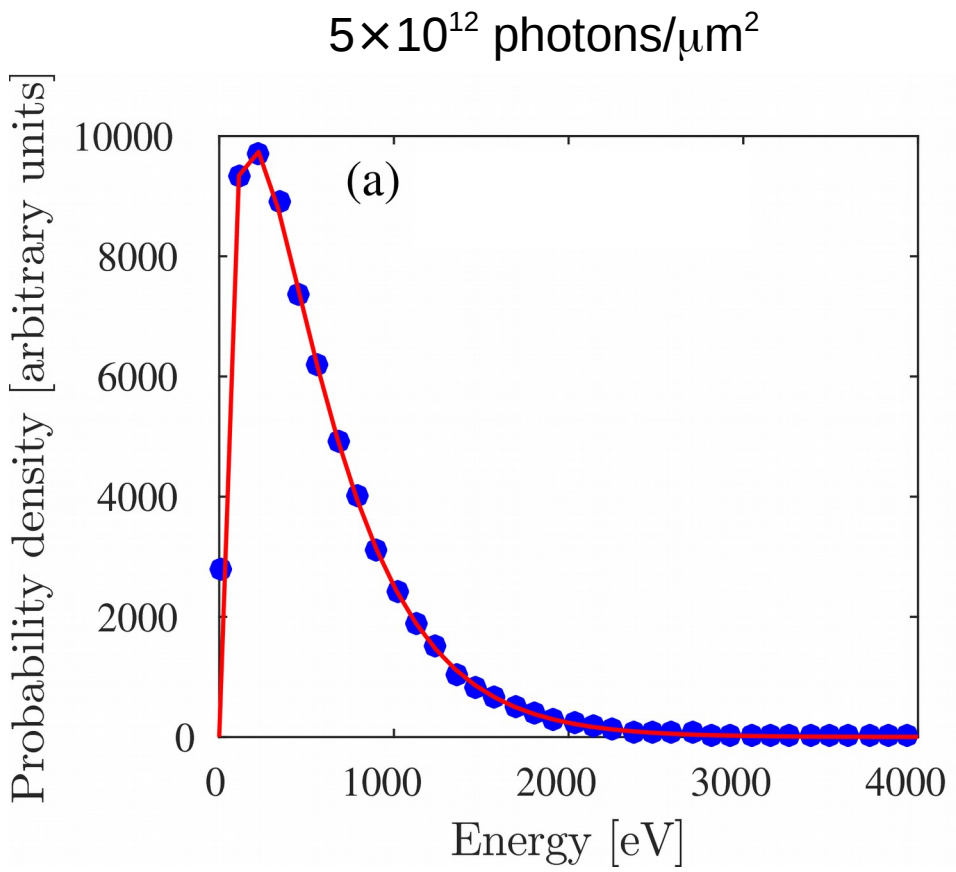


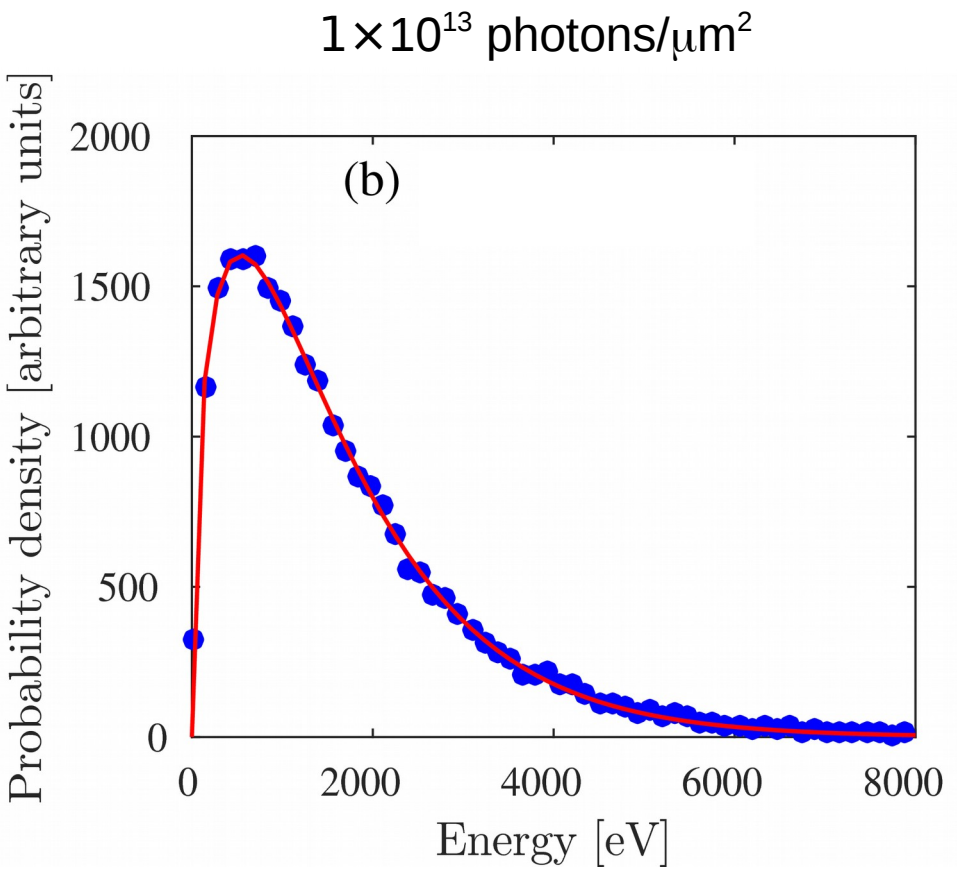
1×10^{13} photons/μm^2



M. M. Abdullah *et al.*, Phys. Rev. E **96**, 023205 (2017).

Electron thermalization in I3C crystal (250 fs after a 9.7-keV x-ray pulse)





M. M. Abdullah *et al.*, Phys. Rev. E **96**, 023205 (2017).

Limitations

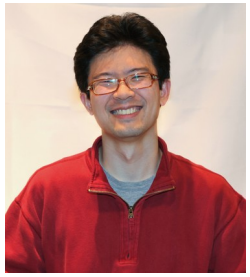
- no rigorous treatment of electronic structure of highly excited, polyatomic systems
- no first-principles treatment of chemical bonds; uses force fields, which are optimized only for the neutral ground state
- no first-principles treatment of influence of molecular environment on decay processes
- no first-principles treatment of charge transfer
- no first-principles treatment of electron impact ionization in molecular environment

XMOLECULE

Yajiang Hao

Ludger Inhester

Kota Hanasaki



Sang-Kil Son

- An ab-initio electronic-structure approach dedicated to ionization dynamics of molecules
- Self-consistent-field calculation for every electronic configuration formed during interaction with intense XFEL pulse
- Demonstration of a new ionization enhancement mechanism

Molecular multiple-hole state calculation

- Hartree-Fock-Slater method

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_X(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

- MO represented by linear combination of AO: $\psi_i(\mathbf{r}) = \sum_\mu C_{\mu i}\phi_\mu(\mathbf{r})$
- Matrix eigenvalue problem: $\mathbf{HC} = \mathbf{SCE}$

$$H_{\mu\nu} = \int d^3r\, \phi_\mu(\mathbf{r})\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\phi_\nu(\mathbf{r}), \quad S_{\mu\nu} = \int d^3r\, \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})$$

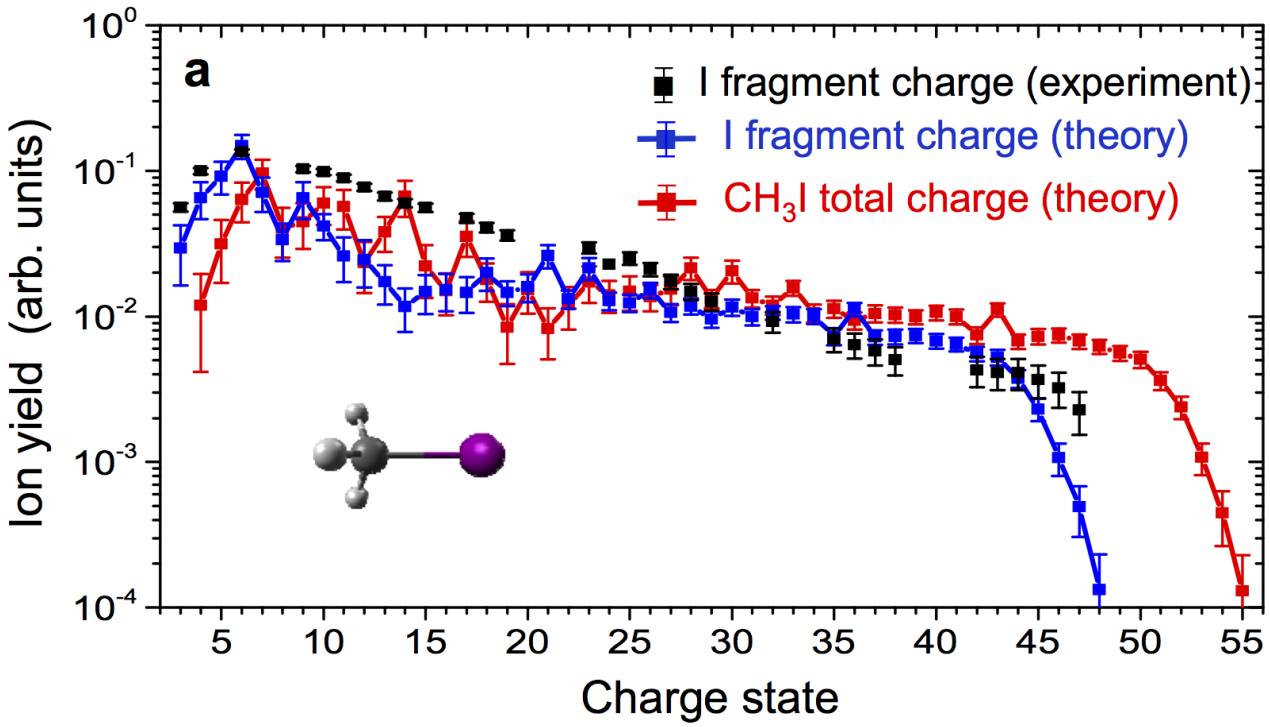
- AO: numerical solutions of corresponding atomic core-hole states

$$\phi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\varphi)$$ calculated using XATOM

- Various numerical techniques employed
  - Multicenter integration on a molecular grid built from atomic grids
  - Multicenter expansion and multipole expansion in direct Coulomb interaction
  - Maximum overlap method to prevent variational collapse

Y. Hao *et al.*, Structural Dynamics **2**, 041707 (2015).

The highest charge states ever produced using light!



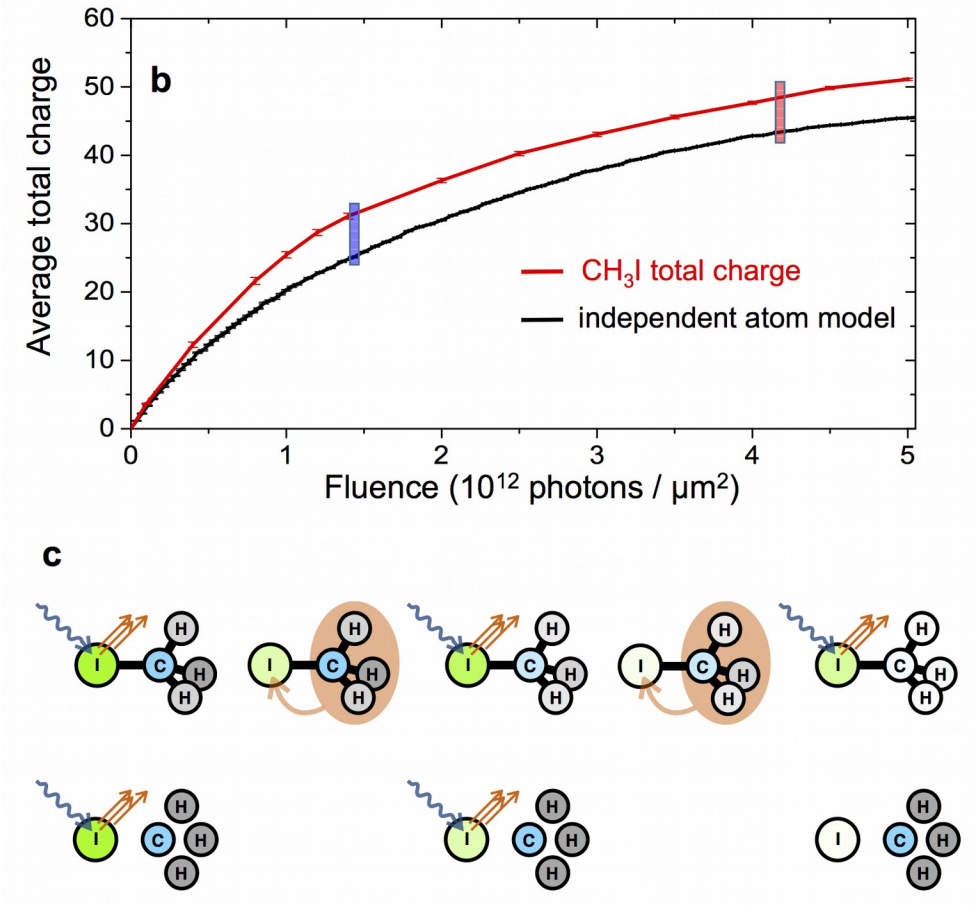
Photon energy: 8.3 keV

X-ray peak intensity:
> 10^{19} W/cm^2

Experimental data taken by Artem Rudenko, Daniel Rolles, and collaborators

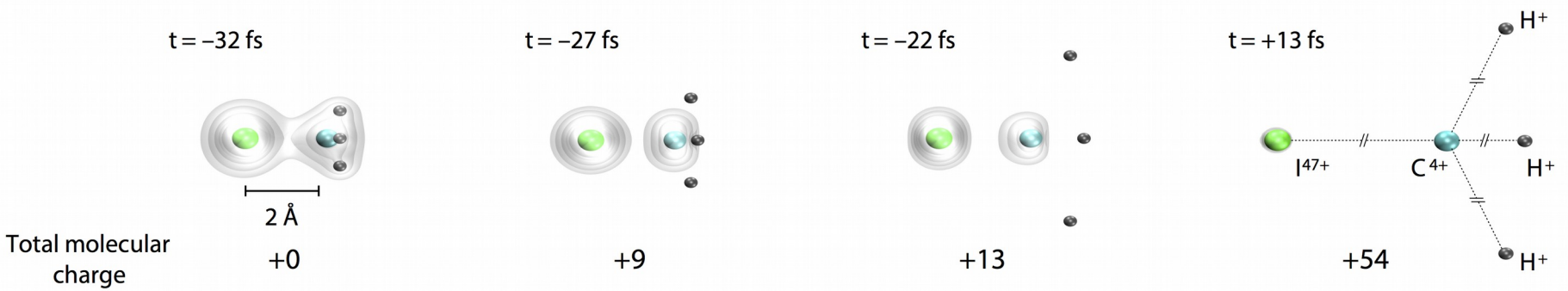
A. Rudenko *et al.*, Nature **546**, 129 (2017).

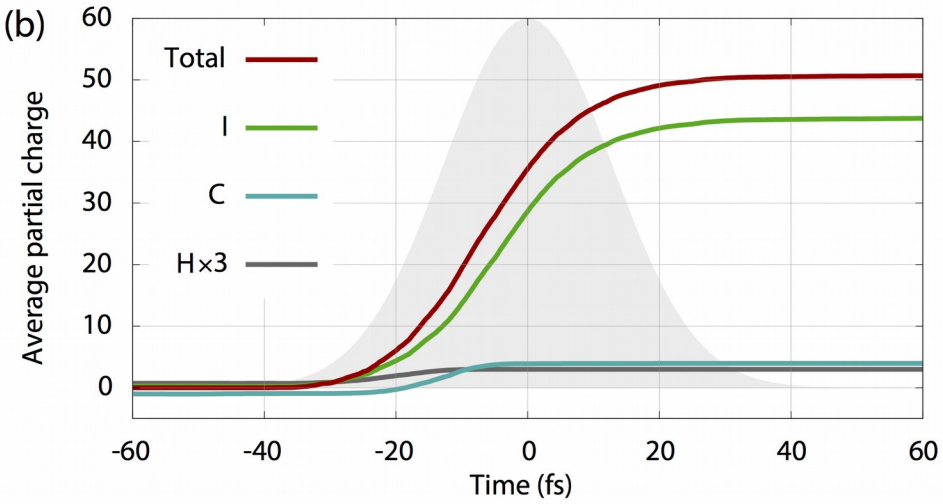
New ionization enhancement mechanism (molecular effect!)

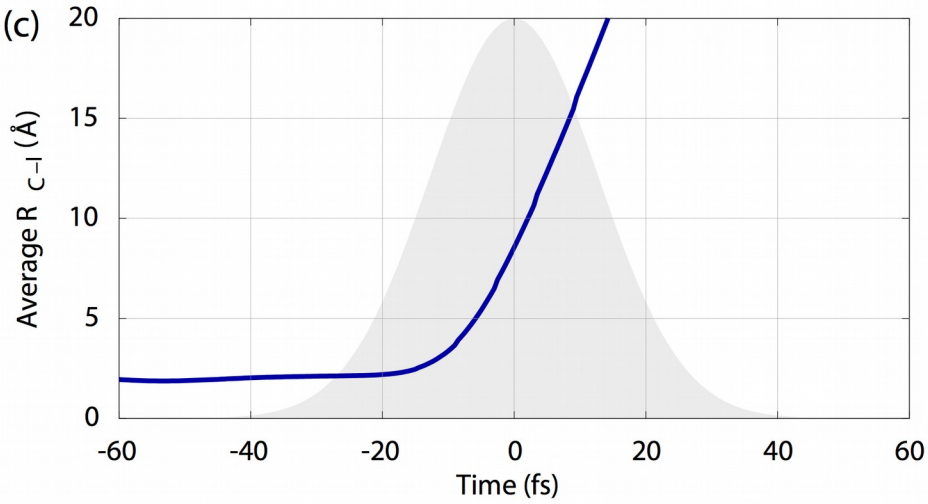


A. Rudenko *et al.*, Nature **546**, 129 (2017).

Time-resolved ionization dynamics (theory)

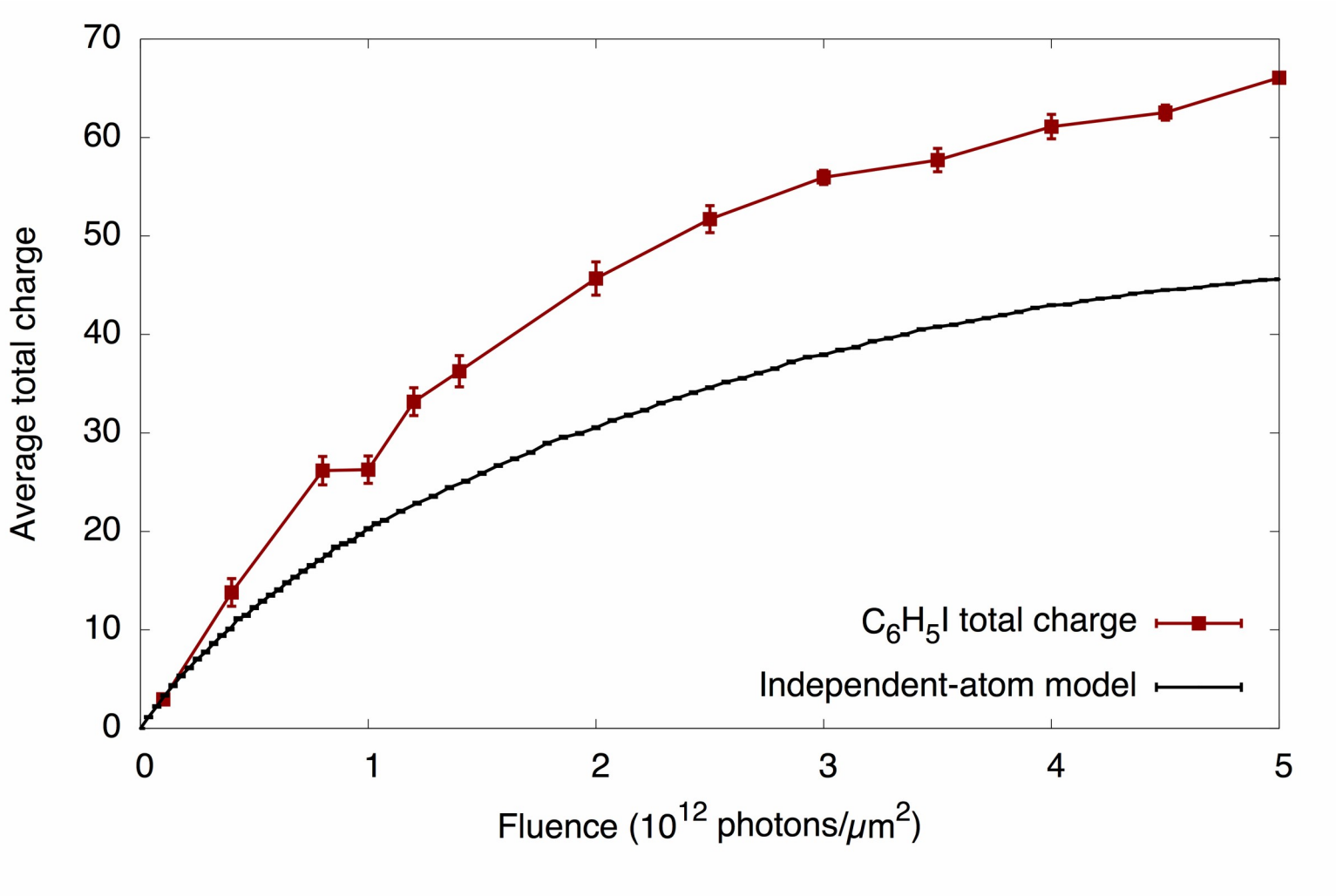






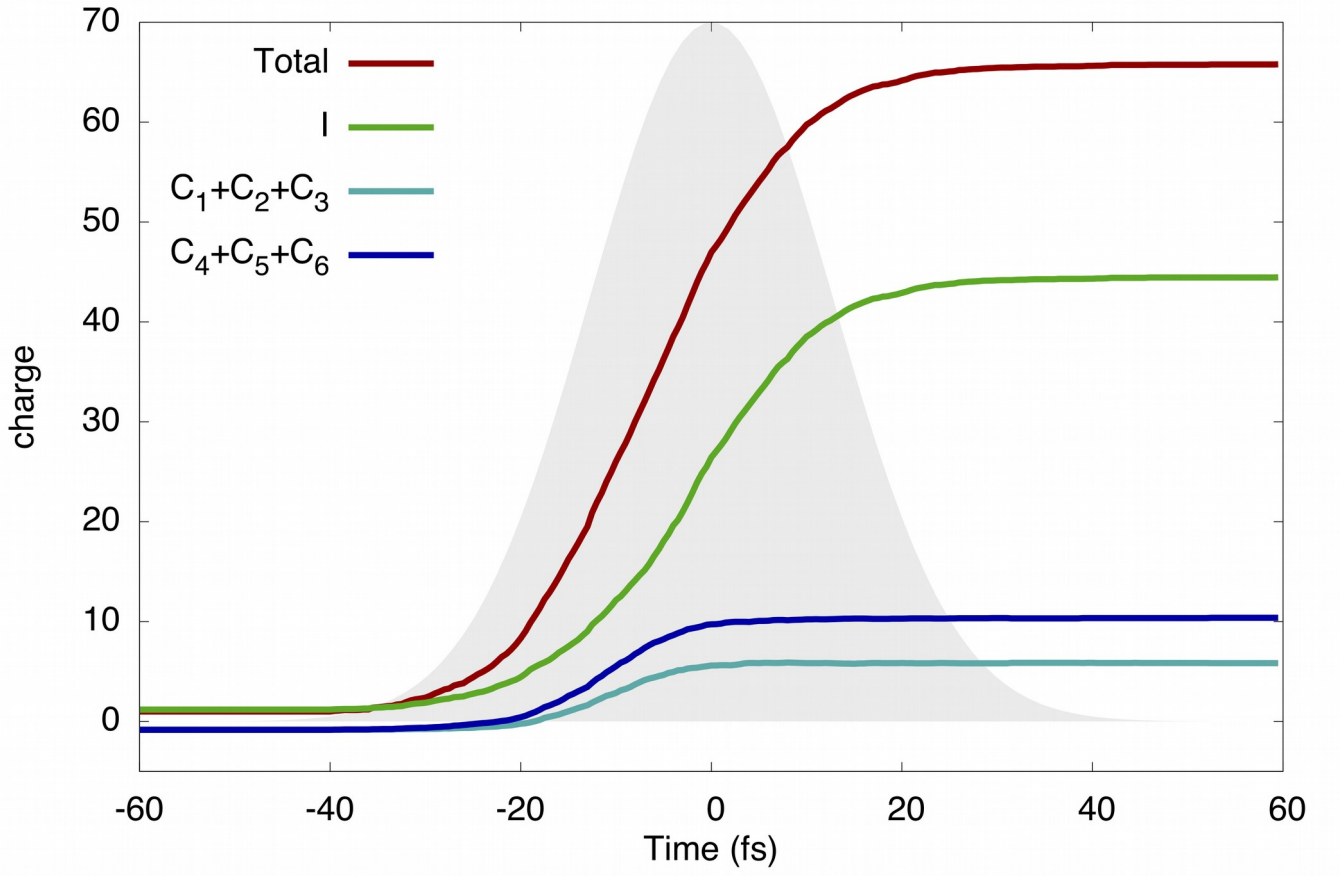
A. Rudenko *et al.*, Nature **546**, 129 (2017).

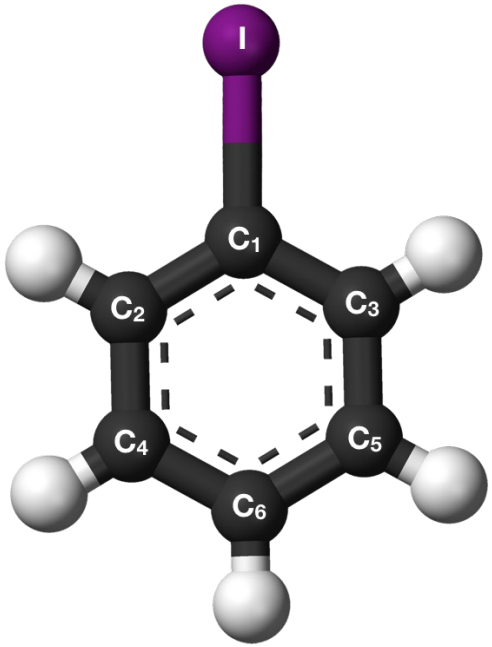
Iodobenzene (photon energy 8.3 keV)



Y. Hao *et al.*, Phys. Rev. A **100**, 013402 (2019).

Ionization dynamics in iodobenzene (photon energy 8.3 keV, fluence 5×10^{12} photons/μm^2)





Y. Hao *et al.*, Phys. Rev. A **100**, 013402 (2019).

Conclusions I

- Single-shot x-ray imaging of single particles (macromolecules, viruses, ...) requires x-ray intensities that are so high that electronic radiation damage during the x-ray pulse becomes important.

- In order to quantitatively describe the associated radiation damage, dedicated software has been, and is being, developed: XATOM, XMDYN, and XMOLECULE.

- Sub-fs charge transfer underlies a new ionization enhancement mechanism at high x-ray intensity.

- Calculations on iodomethane and iodobenzene demonstrate that the ionization enhancement increases with the number of light atoms.

http://www.desy.de/~xraypac