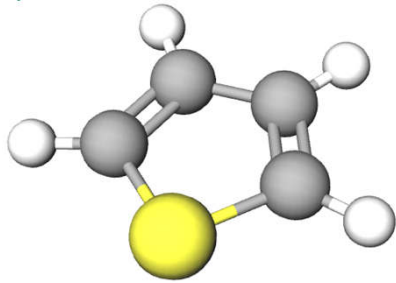




Coulomb explosion of highly charged small quantum systems – simple or not so simple?

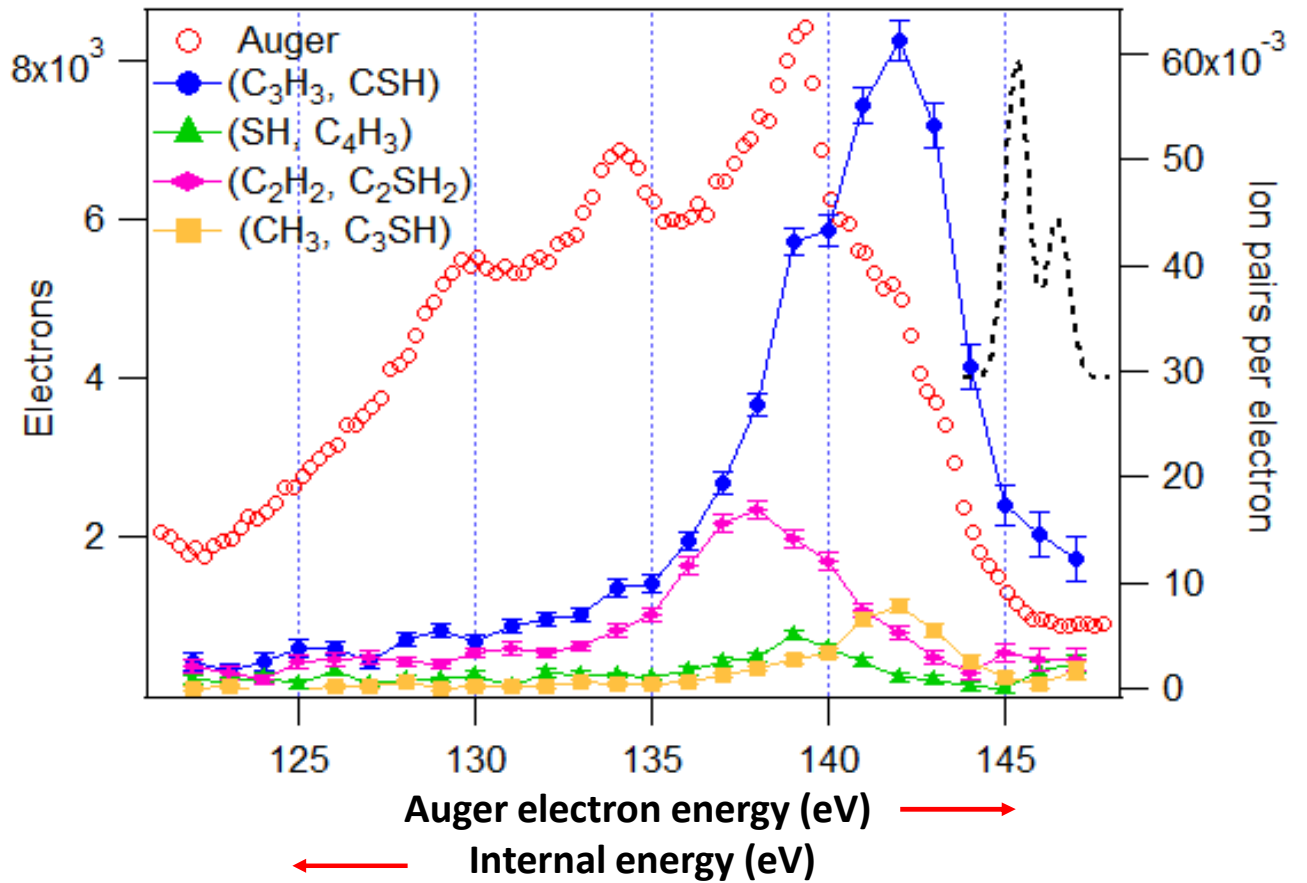
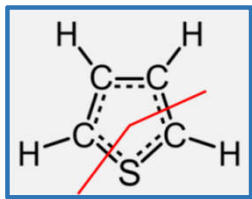
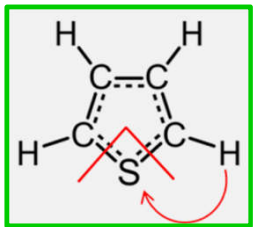
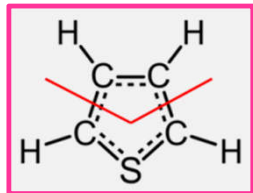
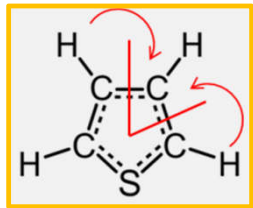
Edwin Kukk
University of Turku
Finland

Dissociation and internal energy



PEPIPICO experiment at synchrotron (MAX-lab)

$Q_{tot}=+2$



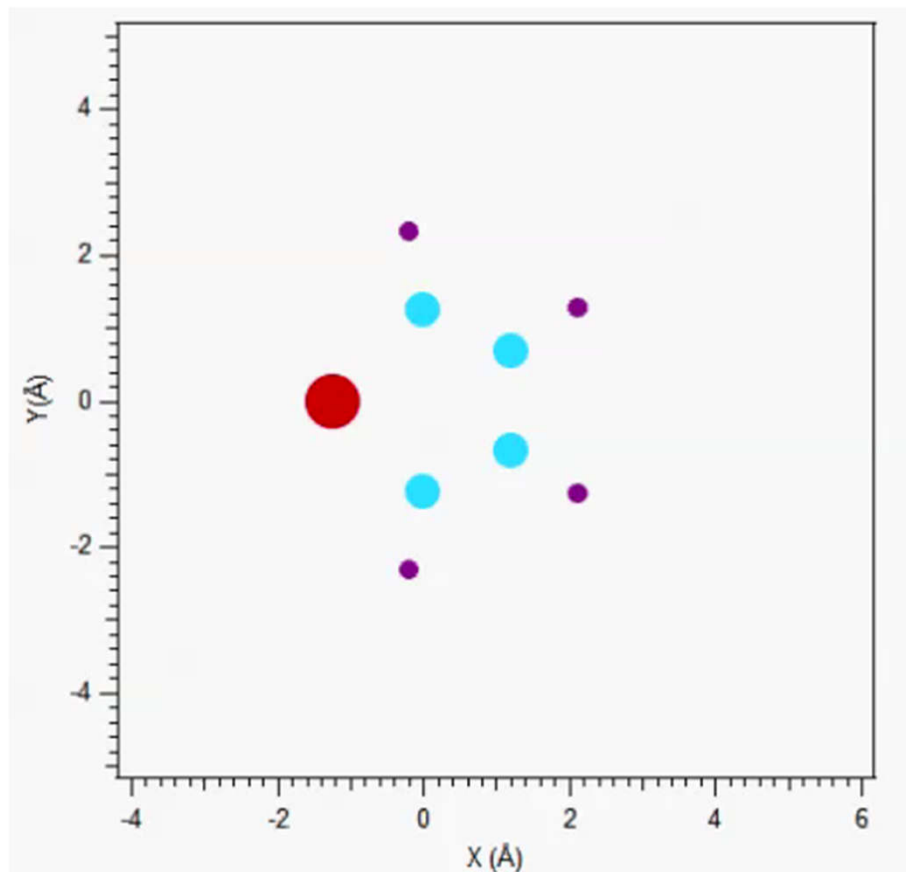
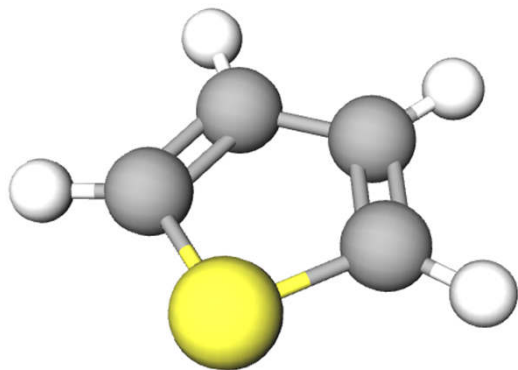
E. Kukk *et al.*, "Internal energy dependence in x-ray-induced molecular fragmentation: An experimental and theoretical study of thiophene," *Physical Review A*, vol. 91, no. 4, p. 43417, (2015).

Coulomb explosion -- simple...?

$\tau=35$ fs

Thiophene

$Q_{\text{tot}}=+9$

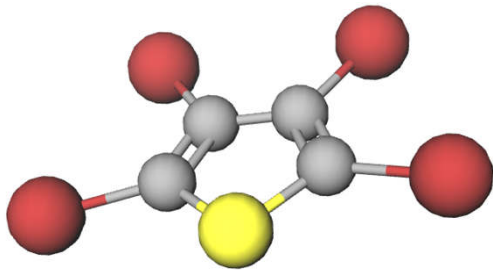


...or not so simple -- Coulomb implosion

$\tau=40$ fs

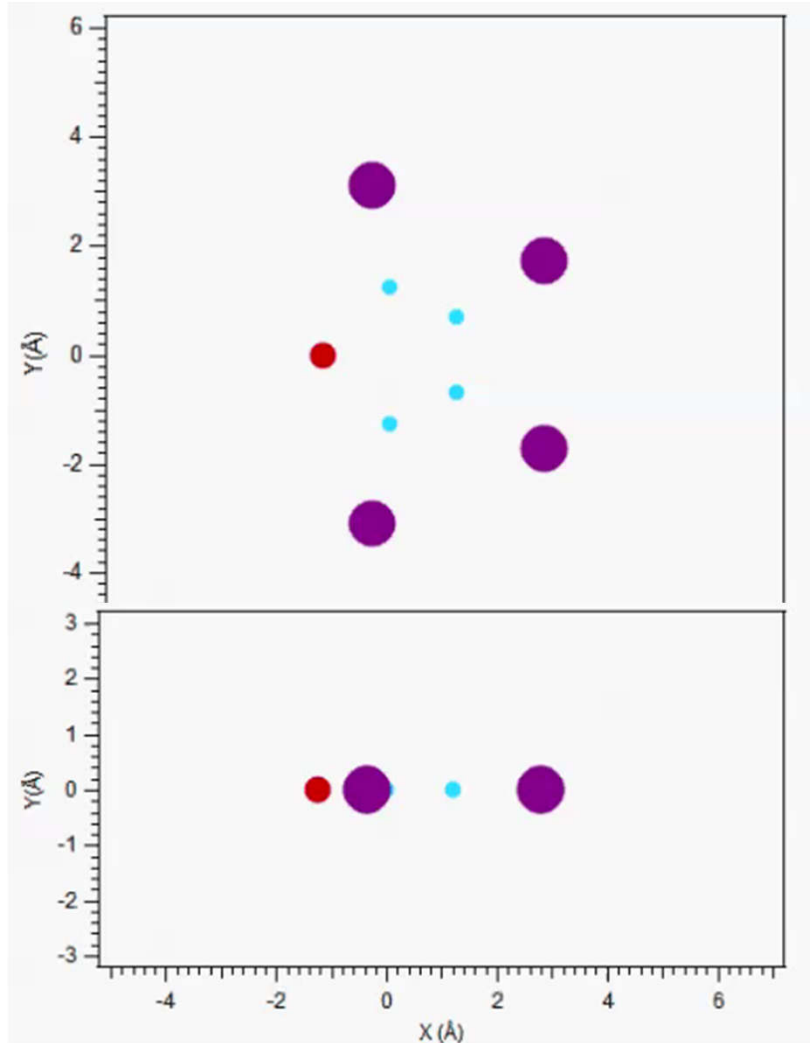
Tetrabromothiophene

$Q_{\text{tot}}=+13$



Coulomb energy 350 eV

Vibrational energy 0.8 eV

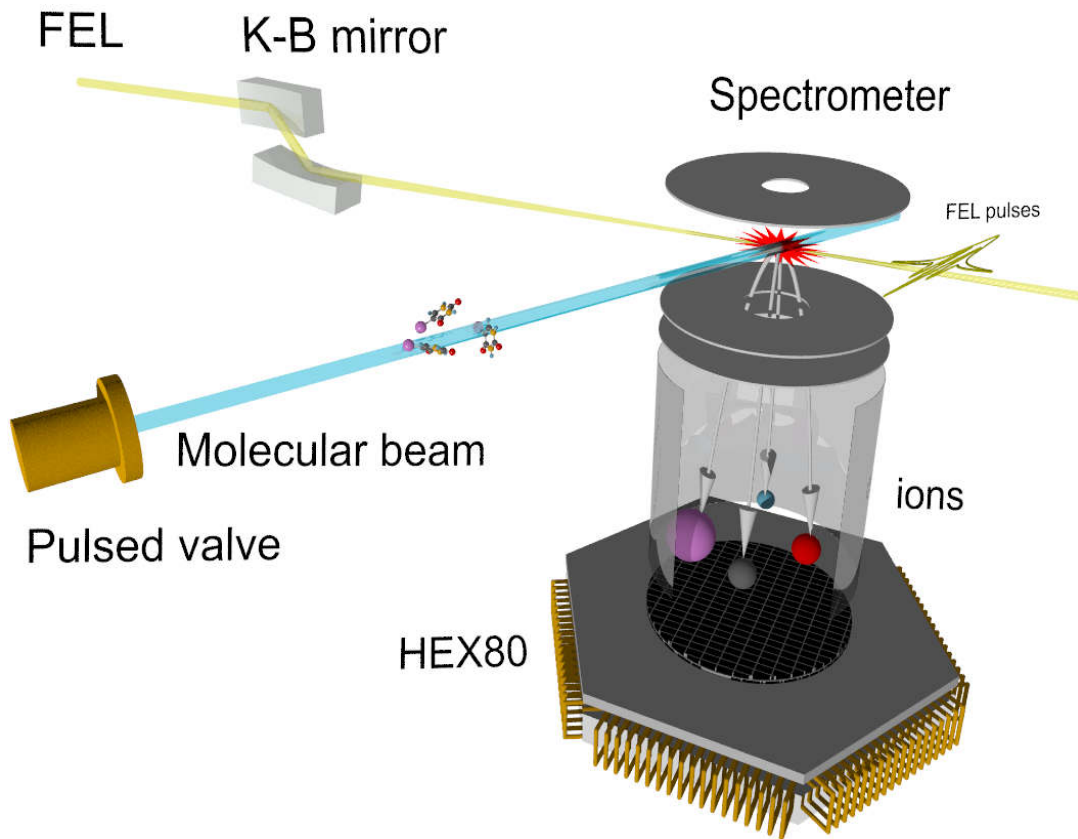


Coulomb implosion trajectories are very sensitive to:

- **Vibrational motion**
- **Internal energy**
- **Charge buildup and dynamics**

E. Kukk *et al.*,
Phys.Rev. A **99**, 023411, (2019).

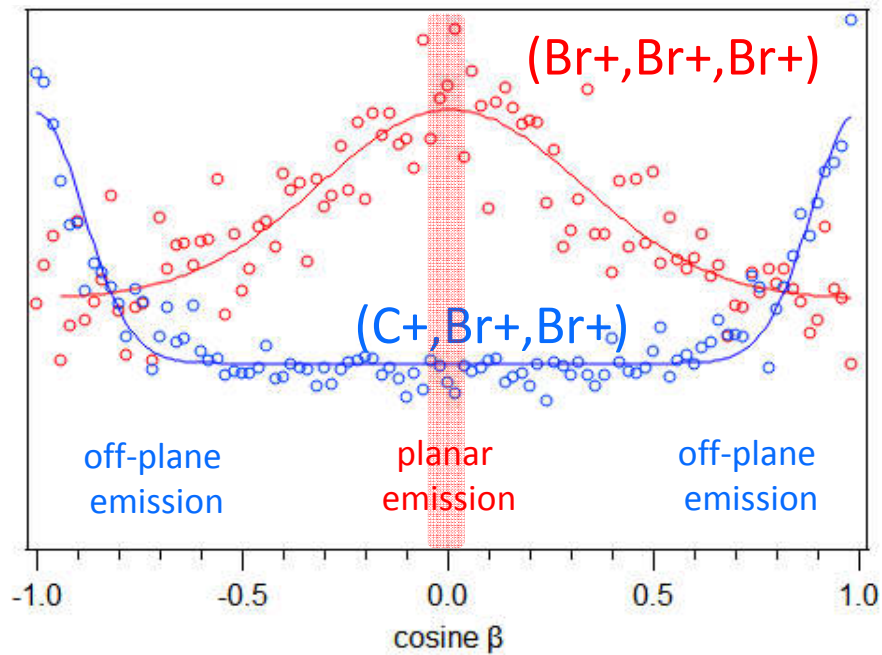
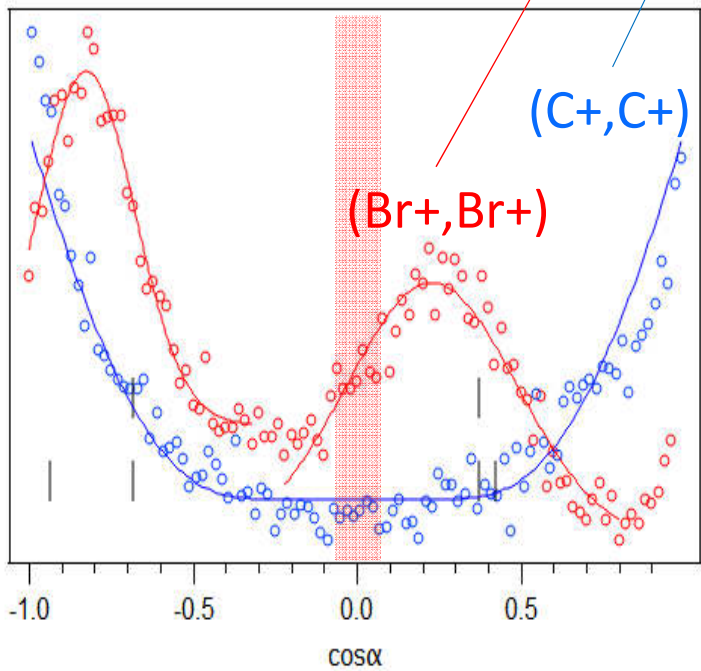
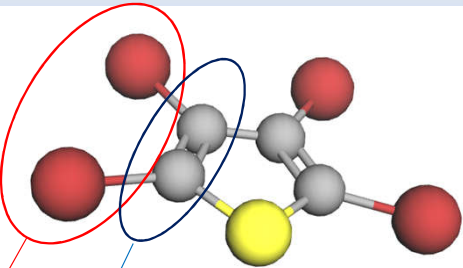
Coulomb explosion dynamics experiments at SACLA



Momentum imaging
multiparticle ion
coincidence TOF
spectroscopy

H. Fukuzawa, K. Nagaya, and K. Ueda, *Nuclear Instruments and Methods in Physics Research Section A: vol. 907, p. 106, (2018).*
 E. Kukk, K. Motomura, H. Fukuzawa, K. Nagaya, and K. Ueda, *Applied Sciences*, vol. 7, no. 6, p. 531, (2017).
 K. Motomura *et al.*, *The Journal of Physical Chemistry Letters*, vol. 6, no. 15, pp. 2944–2949, (2015).

Coulomb explosion dynamics experiments at SACLA

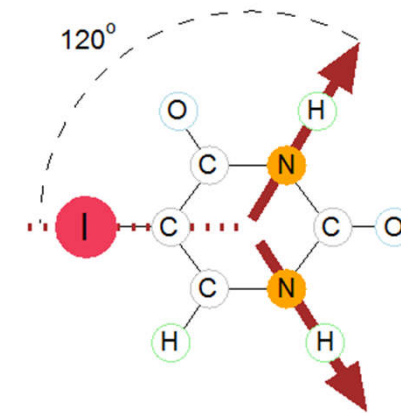
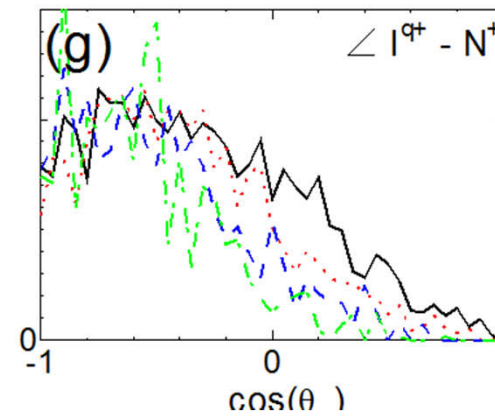
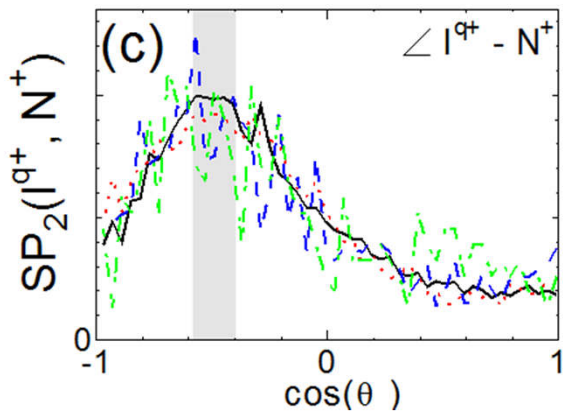
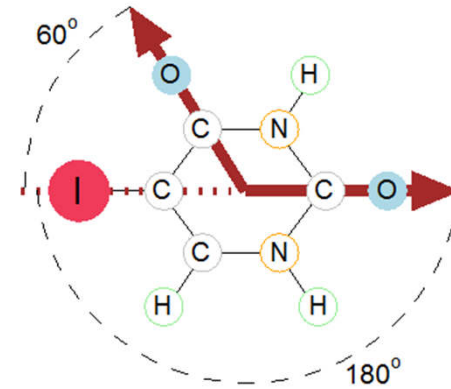
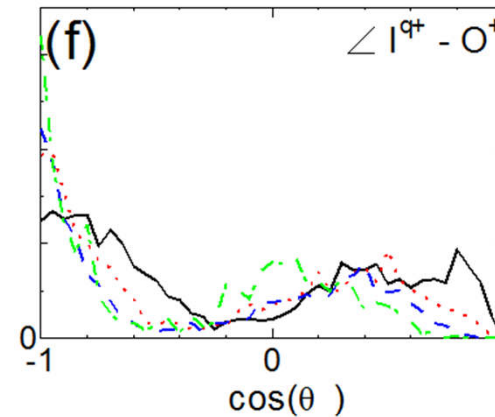
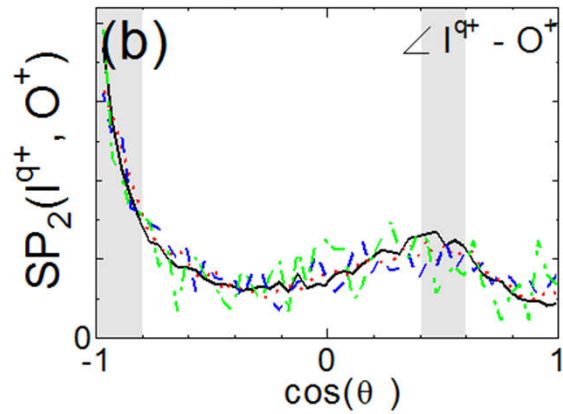


E. Kukkk *et al.*, *Phys.Rev. A* **99**, 023411, (2019).

Molecular dynamics experiments at SACLA: iodouracil

Experiment

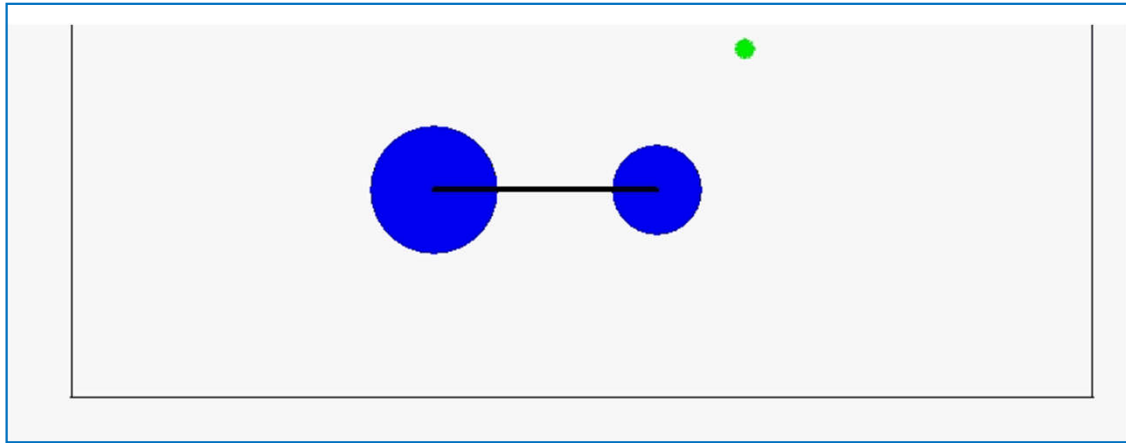
Simulation



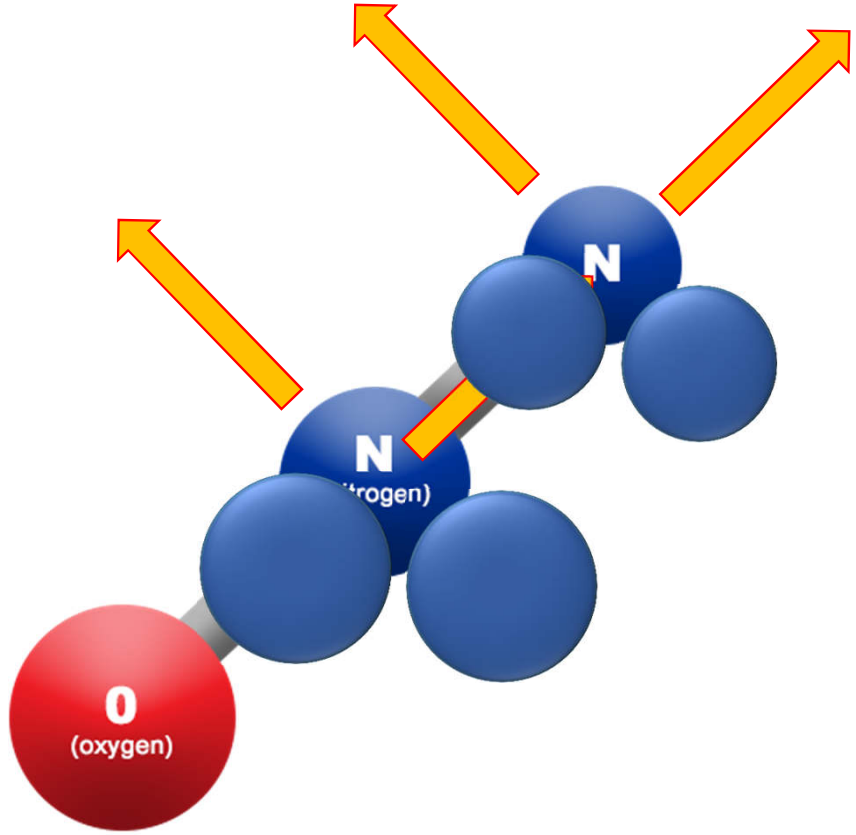
K. Nagaya *et al.*, "Ultrafast Dynamics of a Nucleobase Analogue Illuminated by a Short Intense X-ray Free Electron Laser Pulse" *Physical Review X* **6**, 21035 (2016).

Steering molecular dynamics by recoil

Photoelectron recoil



The fate of recoil energy



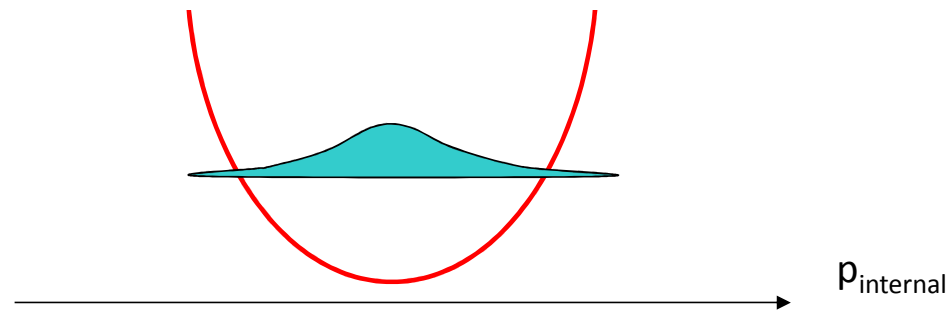
Recoil deposits energy into:

Depending on ionization site and molecular-frame emission angle.

Photoelectron recoil quantum mechanically

We can study the process in momentum space.

Recoil momentum Δp displaces the nuclear wavefunction in momentum space.

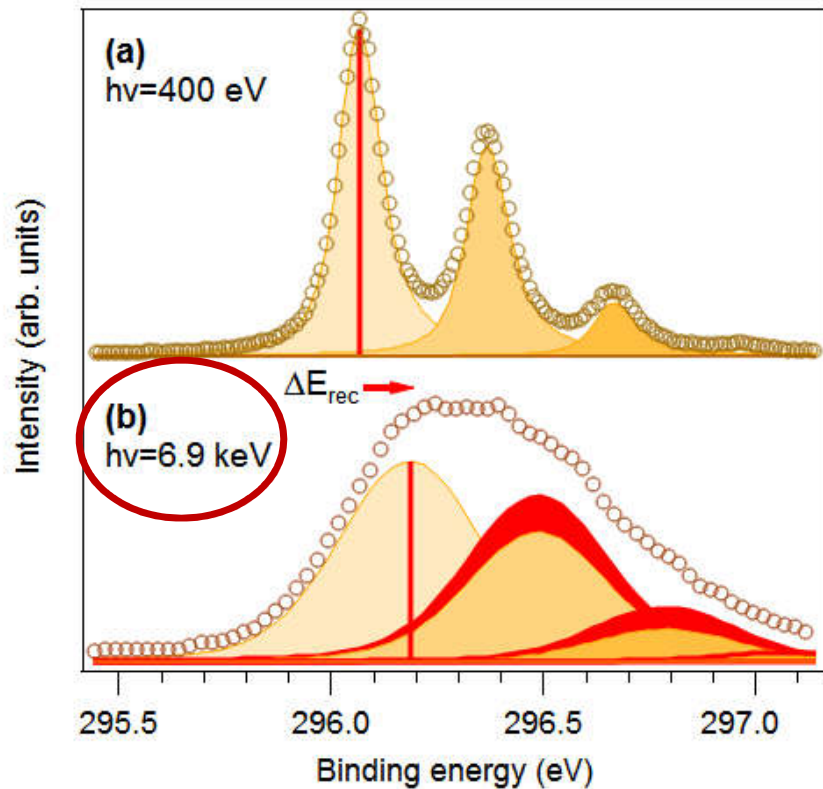


Old wavefunction \rightarrow linear combination of new eigenfunctions.
Excitation probabilities by "Franck-Condon factors":

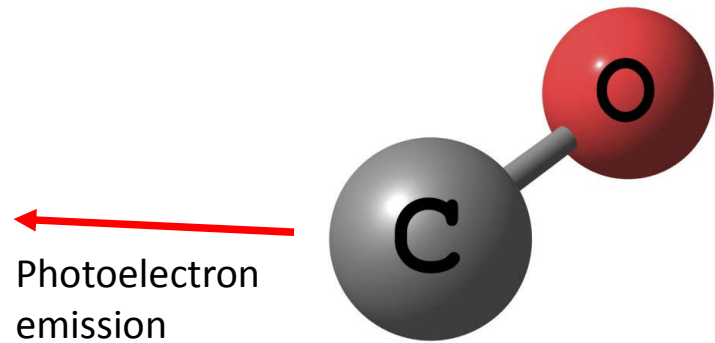
$$p_{i \rightarrow f} = \langle \Psi_f(p) | \Psi_i(p + \Delta p) \rangle^2$$

With soft x-rays typical recoil excitation $E_{\text{rec}} < \omega_{\text{vib}}$

Photoelectron recoil as seen in electron spectrum



GALAXIES tender x-ray beamline, SOLEIL
C 1s photoemission



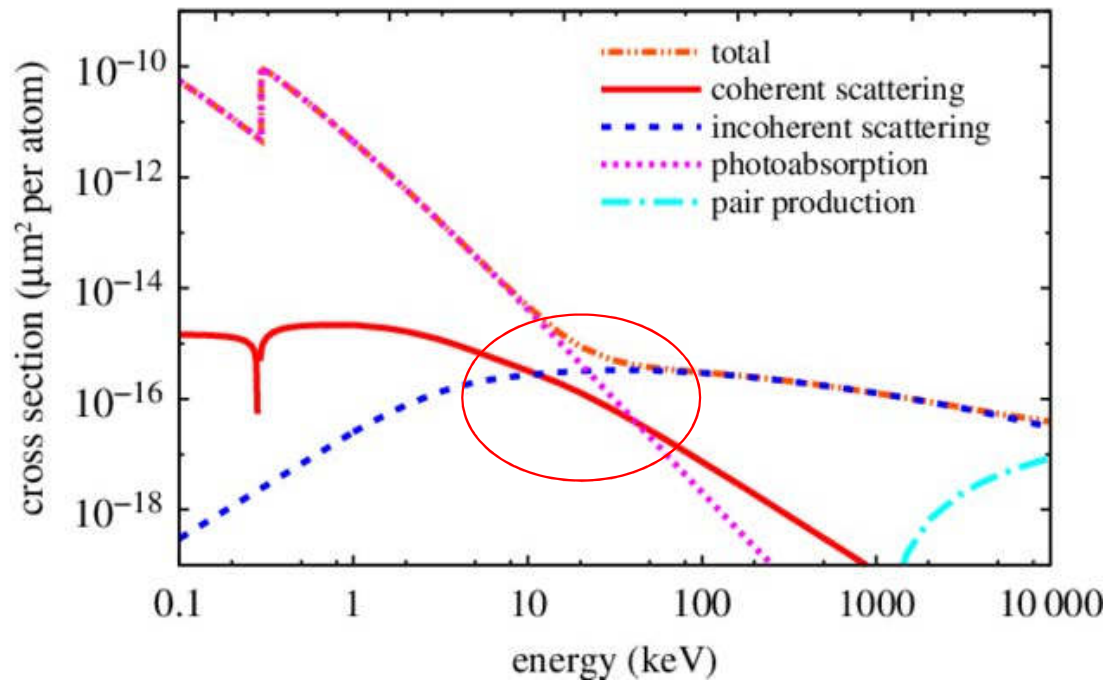
Domcke, W. & Cederbaum, L. S. Electronic recoil effects in high-energy photoelectron spectroscopy.

Journal of Electron Spectroscopy and Related Phenomena **13**, 161–173 (1978).

T.D. Thomas *et al.*, J. Chem. Phys. **133**, 174312 (2010).

E. Kukk *et al.*, Phys. Rev. Lett. **121**, 73002 (2018).

Photoemission vs. Compton scattering



PHILOSOPHICAL
 TRANSACTIONS
 OF
 THE ROYAL
 SOCIETY **B**

Diffraction before destruction

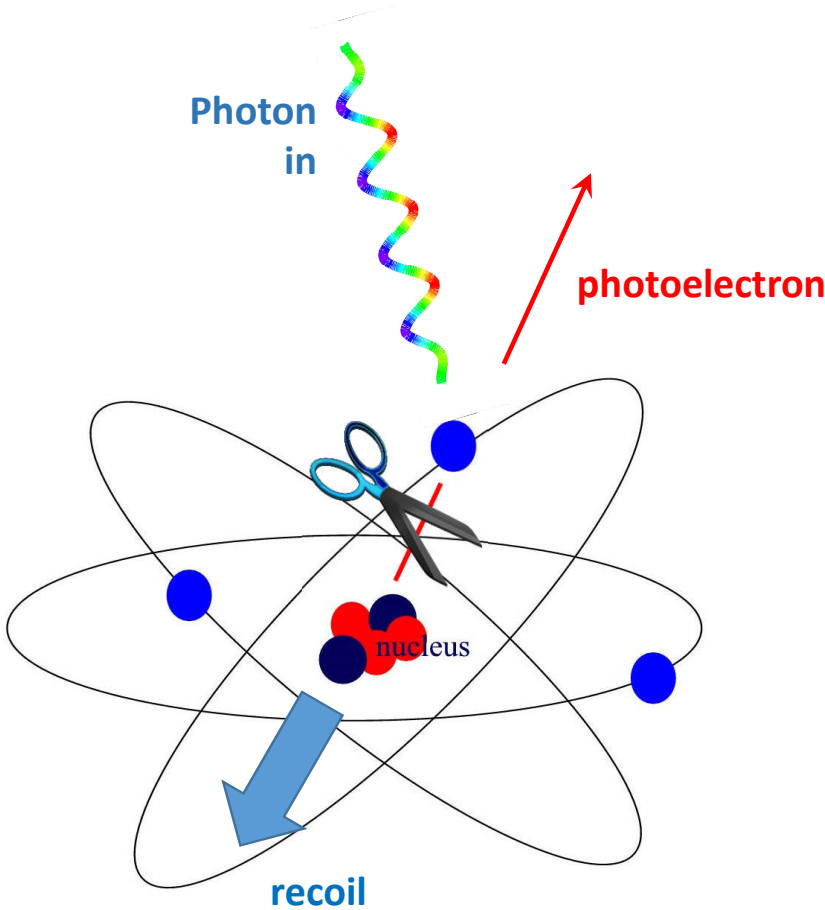
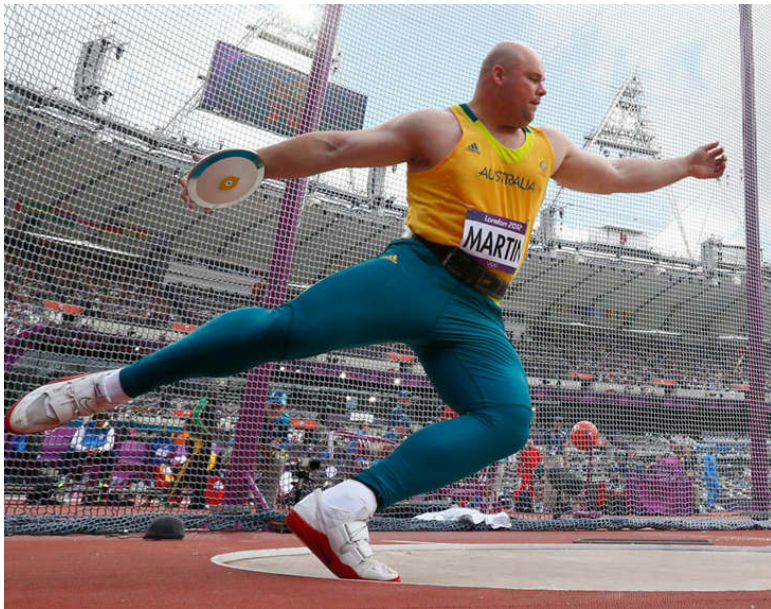
Henry N. Chapman^{1,2,3}, Carl Caleman^{1,4} and Nicusor Timneanu^{4,5}

¹Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany

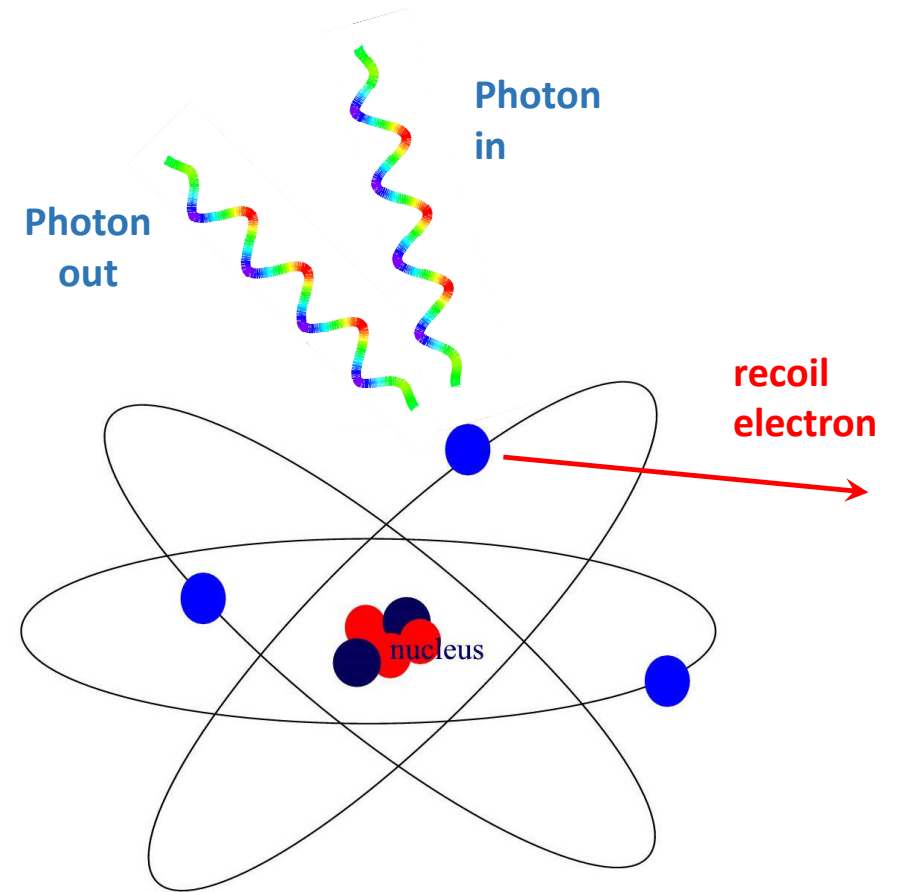
²Department of Physics, University of Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

³Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany

Recoil in photoemission



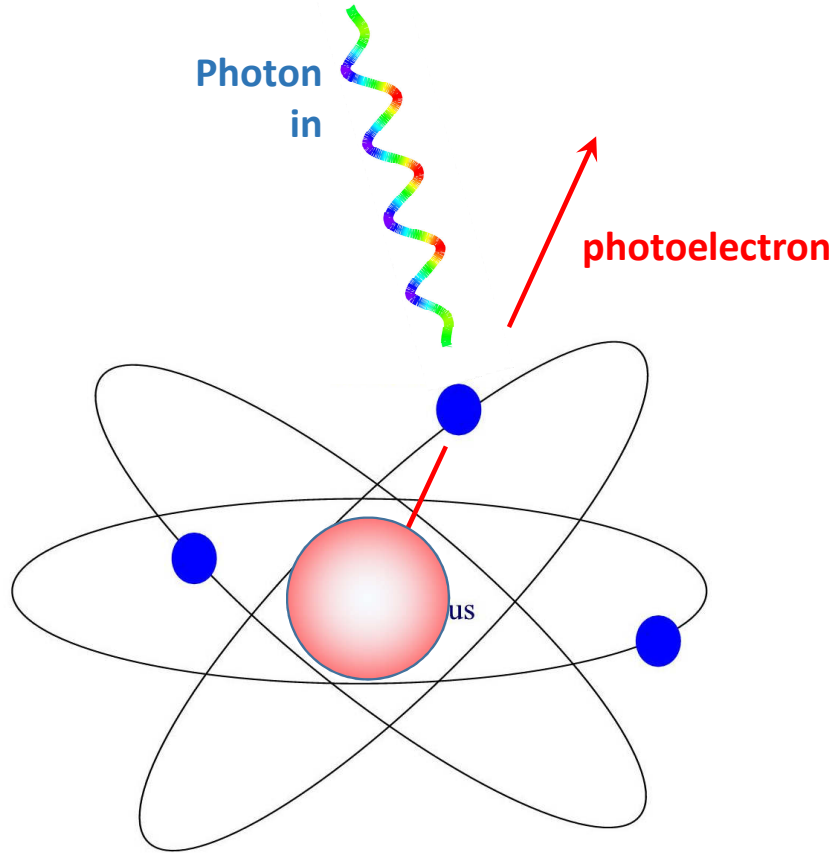
Compton scattering



Spielberger, L. *et al.* Separation of Photoabsorption and Compton Scattering Contributions to He Single and Double Ionization. *Physical Review Letters* **74**, 4615–4618 (1995).

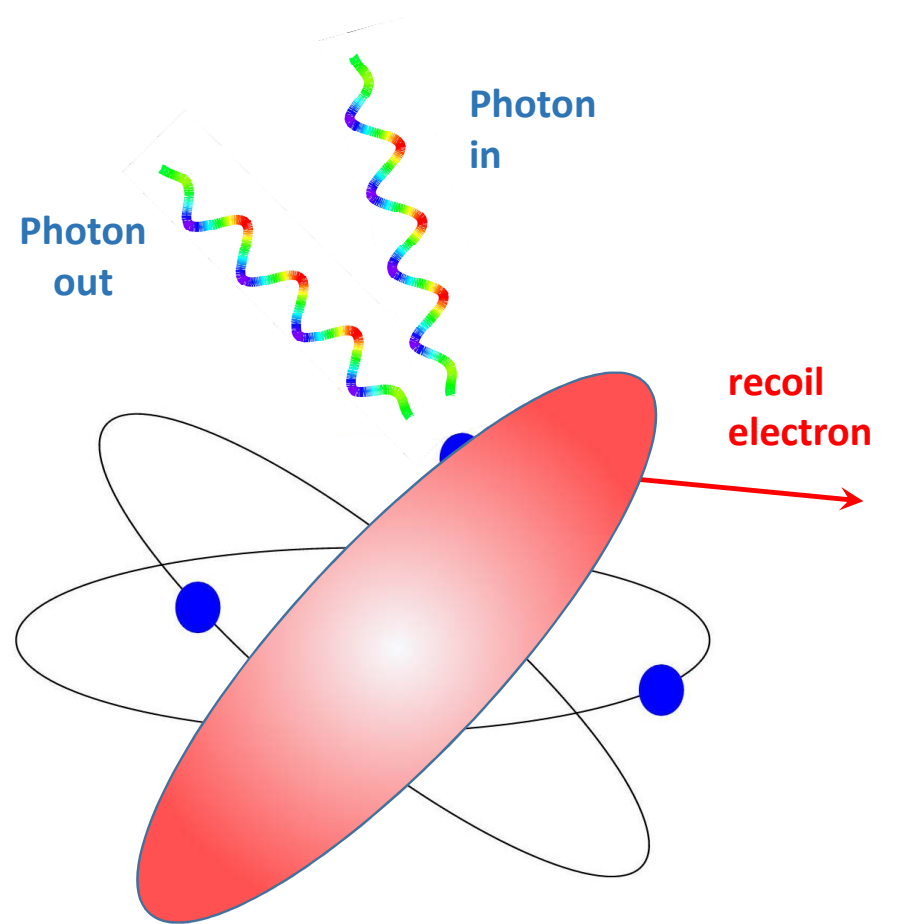
Recoil: photoemission vs. Compton scattering

Photoemission



High photon energy: Electron orbital regions close to nuclei

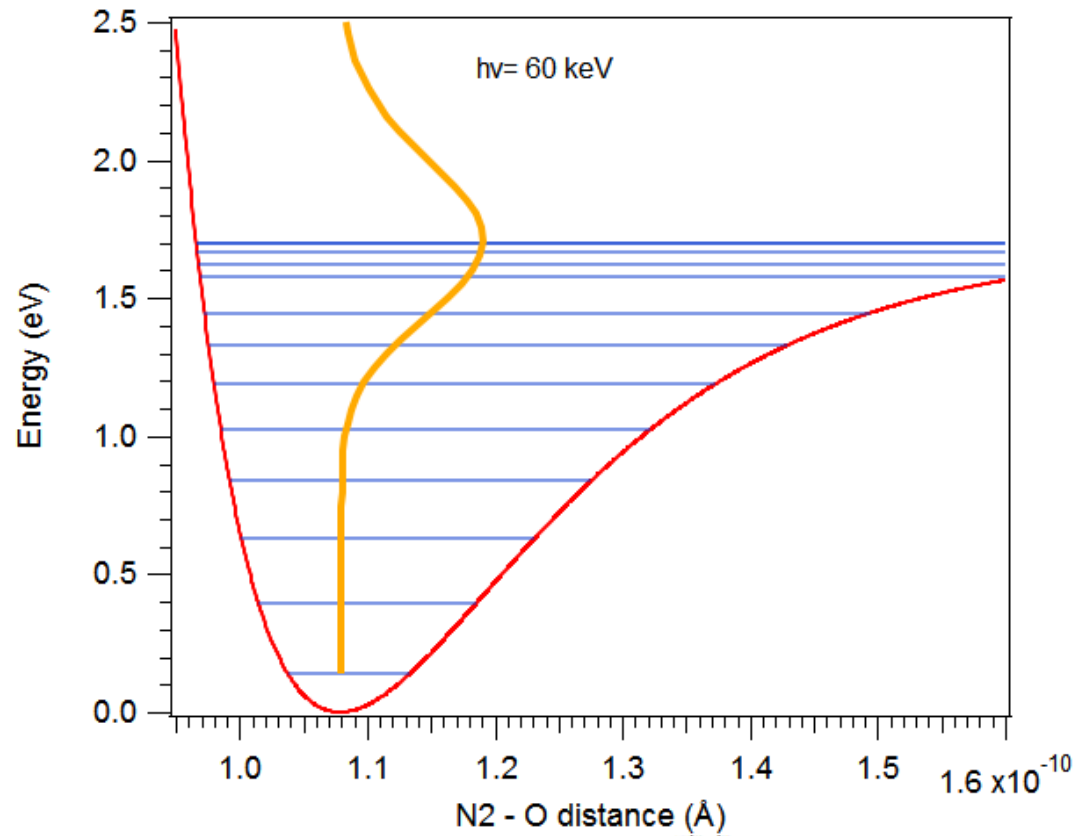
Compton



Entire electron orbital

Recoil at high energy

hν (keV)	E _{rec} (eV)
7	0.19
20	0.53
40	1.07
60	1.60



Dibeler, Vernon H., James A. Walker, and Susan K. Liston. "Mass Spectrometric Study of Photoionization. VII. Nitrogen Dioxide and Nitrous Oxide." *J. Res. Natl. Bur. Stand., Sect. A* 71 (1967): 371-378.

Single photon absorption

Recoil momenta

Instantaneous

Defined by normal modes and MFPAD

Electron orbitals near nuclei
(momenta defined by photoelectron)

Coulomb-repulsion momenta

Slow build-up

Defined by molecular geometry and
potential surfaces

Electron orbital momentum mapping

Multiphoton absorption

(in light elements, feasible only with tender x-rays?)

Combination with previous recoil

Charge build-up and spread time-
dependence

Two-colour experiments

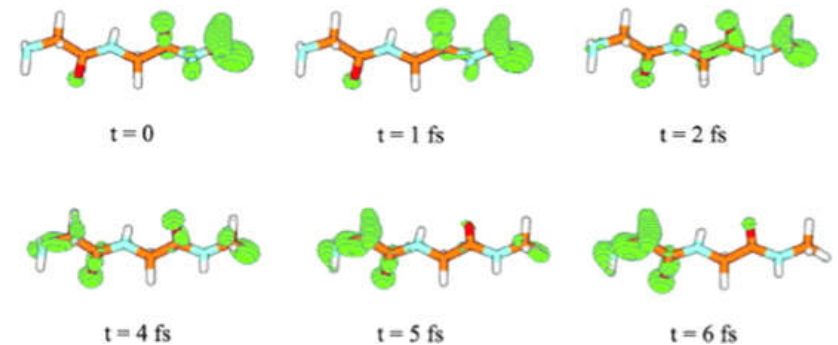
High-energy recoil pump to initiate (and tune) the molecular dynamics

or

Low-energy spectroscopic probe
High-energy probe to test the nuclear wavepacket by adding second recoil momentum


Pump (soft x-ray, UV) to initiate charge fluctuations, bound molecular dynamics

High-energy probe (recoil, Compton)
(Recoil sensitive to core hole locations)



Belshaw, L. et al., *The Journal of Physical Chemistry Letters* **3**, (2012).

Academy of Finland funded *Finnish Contribution to EuXFEL*: two-colour insert to SASE3, 1st phase ready by 2021



Summary

- High-energy FEL pulses ($\sim 10\text{-}50\text{keV}$) can initiate molecular dynamics in unique and selective ways.
- Multi-recoil and pump-probe (two-colour XFEL, UV-XFEL) schemes to follow charge localization (especially core holes) and nuclear wavepacket development.
- Mapping the full landscape of the molecular dynamics: multi-particle coincidence measurements, high rep-rates!, flexible P&P schemes.

Academy of Finland funded *Finnish Contribution to EuXFEL*: two-colour insert to SASE3, 1st phase ready by 2021



Acknowledgements

Materials Science Group

Ueda Lab

Berrah Group

Marc Simon et al.

Galaxies beamline

Funding: the Academy of Finland

University of Turku, Finland

Tohoku University, Japan

University of Connecticut, USA

Sorbonne, France

SOLEIL, france

Thank you for your attention!

Recoil energy in C 1s photoemission from CF₄

Recoil energy of the emitter (C) atom, immediately after electron emission,

$$E_r = \frac{m_e}{M_c} E_{kin}$$

electron mass
electron energy
emitter mass

For Al K_a radiation $E_{kin} \approx 1200$ eV,

$$E_r = 54 \text{ meV}$$

The momentum conservation also requires that the translational energy of the whole molecule after recoil,

$$E_M = \frac{m_e}{M} E_{kin}$$

electron mass
electron energy
molecular mass

$$E_M = 8 \text{ meV}$$

$$E_r - E_M = 46 \text{ meV}$$

vibrational
excitations

Recoil effects predicted theoretically by Domcke and Cederbaum in 1978.