Atomic and Molecular Physics with XFELs I

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1. Why do atomic and molecular physics with XFELs

- Atoms and molecules are the fundamental building blocks of matter
- X-rays allow structural and electronic state resolved measurements and permit excited state dynamics to be followed
- Gas phase systems (i.e. atoms, molecules & clusters) can open to study channels obscured in condensed phase and allow individual molecules to be studied (e.g. through coincidence methods)
- Fundamentals of electronic dynamics (e.g. charge migration, Auger decay, ICD, exciton dynamics) and electron-nuclear coupling (e.g. charge transfer, vibronic coupling, quantum dynamics at conical intersections, coupling to environment) can be studied in these systems with full experimental resolution and tractable theory
- Clusters & droplets give systematic access to the development of intramolecular interactions (e.g. solvation effects etc.)

1. In molecules and condensed matter the spacings between atomic nuclei are ~ 0.1- 0.2 nm
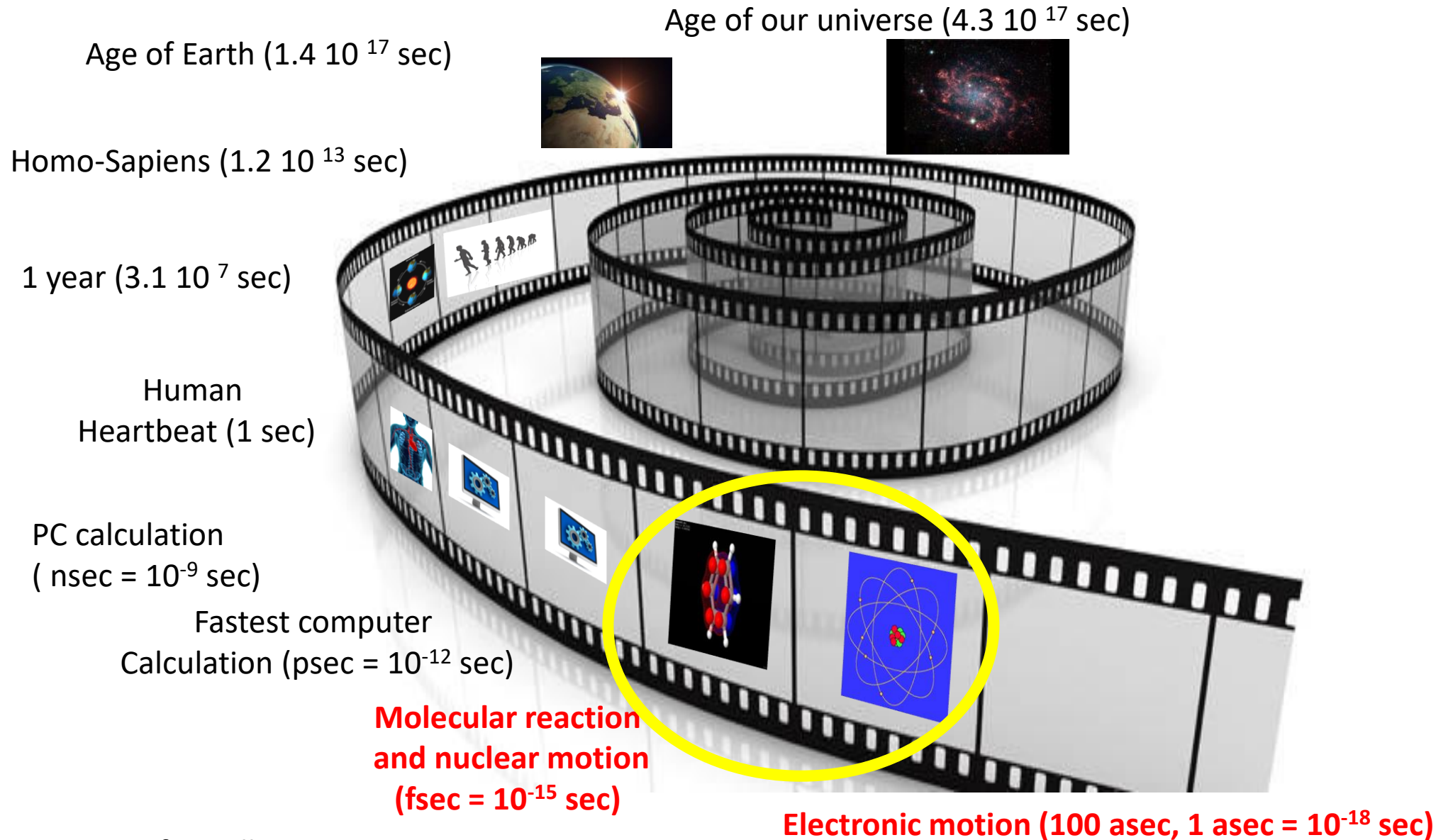

Benzene Molecular Orbitals

0.14 nm
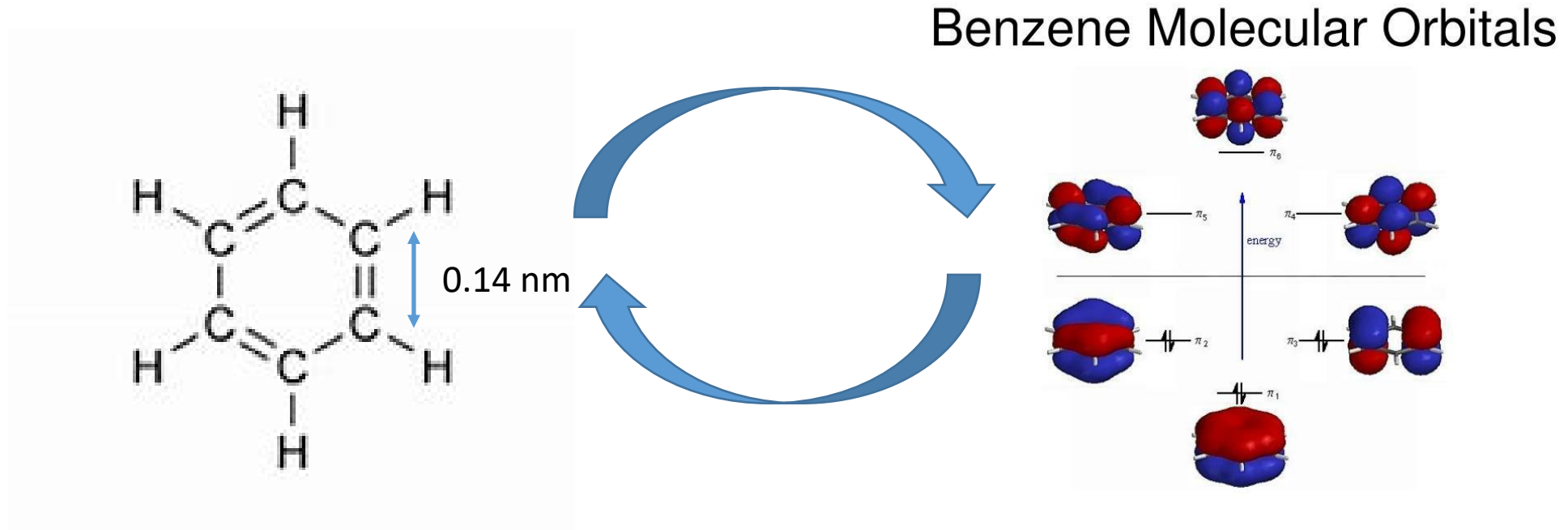
Arrangement of atomic nuclei in a benzene molecule

Electrons arranged in this structure according to the rules of quantum mechanics which ultimately determines the arrangement of atomic nuclei

In nature these structures are NOT static - there is constant internal motion and the possibility of fast rearrangement of atomic nuclei and electron e.g. in a chemical reaction, either thermally driven or triggered by photon or electronic interactions

1. Time scales

Age of our universe ($4.3 \cdot 10^{17}$ sec)

Age of Earth ($1.4 \cdot 10^{17}$ sec)

Homo-Sapiens ($1.2 \cdot 10^{13}$ sec)

1 year ($3.1 \cdot 10^{7}$ sec)

Human Heartbeat (1 sec)

PC calculation (nsec = 10^{-9} sec)

Fastest computer Calculation (psec = 10^{-12} sec)

Molecular reaction and nuclear motion (fsec = 10^{-15} sec)

Electronic motion (100 asec, 1 asec = 10^{-18} sec)

Courtesy of Amelle Zair

1. Structure and dynamics in matter

Consider a material system
e.g. this metal-ligand complex
- a largish molecule

The atoms are arranged in
a specific geometry
with a bond angle and length
that can be defined for each pair/
group of atoms in the structure

This is the *structure* of the matter
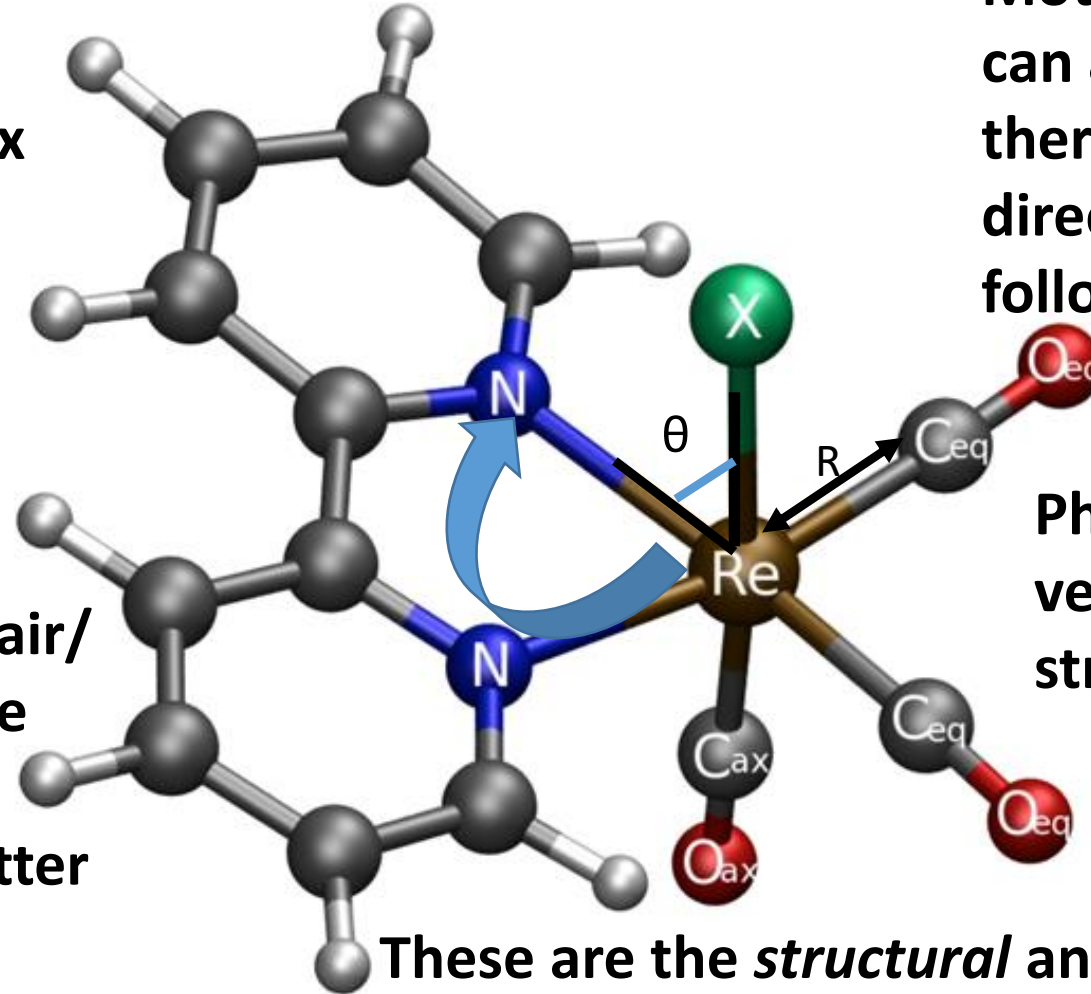
Motion of the structure
can also occur: through
thermal fluctuations or
directed changes e.g.
following photo-excitation

Photo-excitation can drive
very rapid electron and
structural motion

These are the *structural* and *electronic dynamics*
of the system that underpin chemical and physical
changes

1. Rotational motion in a molecule

$$E_R = \frac{L^2}{2I}$$

For a rigid rotor rotational energy E_R depends upon the rotational constant B_o and the angular momentum J of the rotational state:

$$E_R = B_o J(J+1)$$
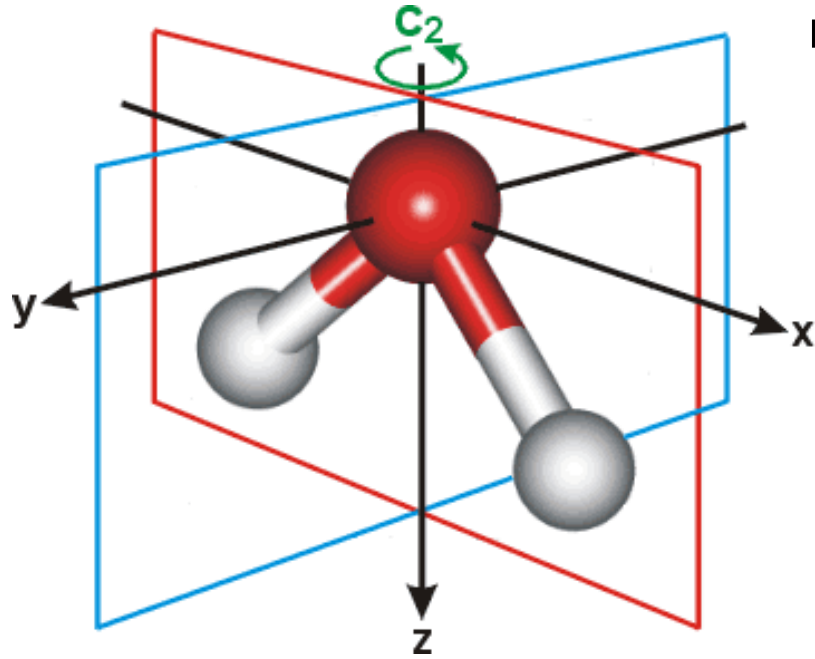
$$B_o = \frac{\hbar^2}{2\mu R_0^2}$$

$$T_{rot} = \frac{h}{2B_0}$$

The rotational period varies from ~100fs for a light molecule to many picoseconds for large molecules.

# 1. Vibrational and nuclear motion in a molecule

Modes of Vibration of Molecules

Symmetric stretching

Asymmetric stretching

Bending

Rotating
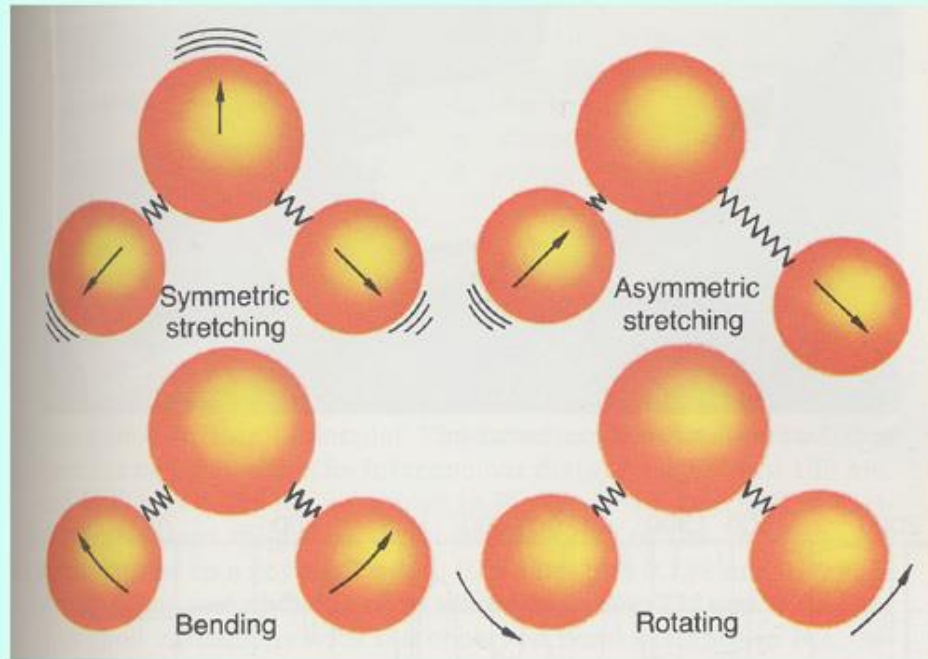
$$E_n = (n + \frac{1}{2})\hbar\omega$$

The vibrational states and energies are approximately those of a quantum harmonic oscillator…

Each mode oscillates (vibrates) with a characteristic frequency, corresponding to vibrational periods of 8 fs (H_2) to pico-seconds for very weakly bound molecules.

1. Electronic motion in a molecule

excitation

charge migration

(a)

$t = 0$ fs

$t = 0.25$ fs

$t = 0.5$ fs

$t = 0.75$ fs
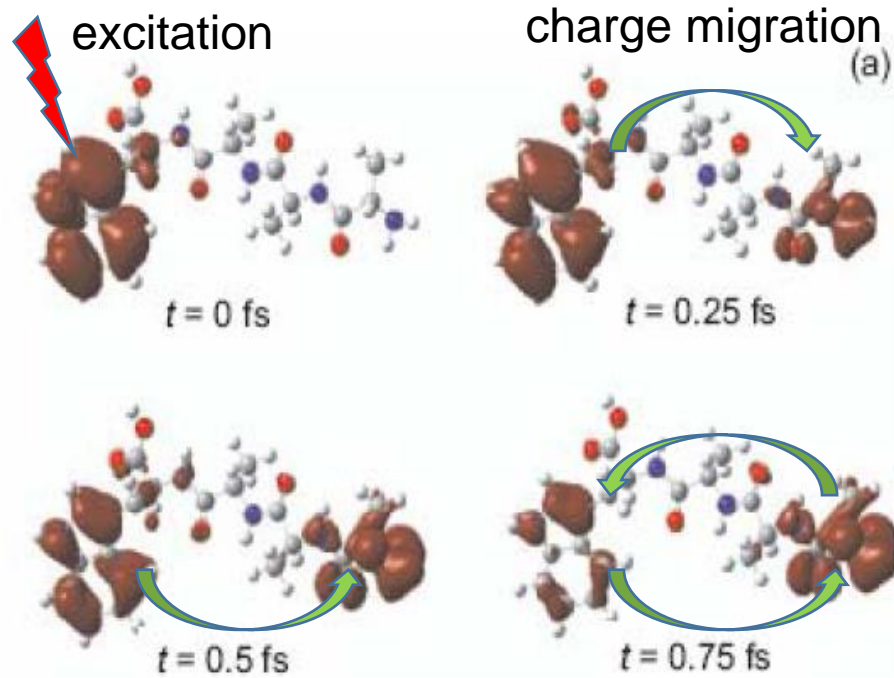
Calculated electron dynamics in a dipeptide

Electron Orbit in Bohr Model

$T_{orbit} \approx 150$ *as* for H ground state

Motion on timescales of 0.01 fs- 10 fs

In a chemical reaction or physical change all three types of motion: electronic, vibrational & rotational will occur in a highly correlated fashion

1. Science driver for ultrafast X-rays is real-time access to the processes and fluctuations in matter down to the quantum scale
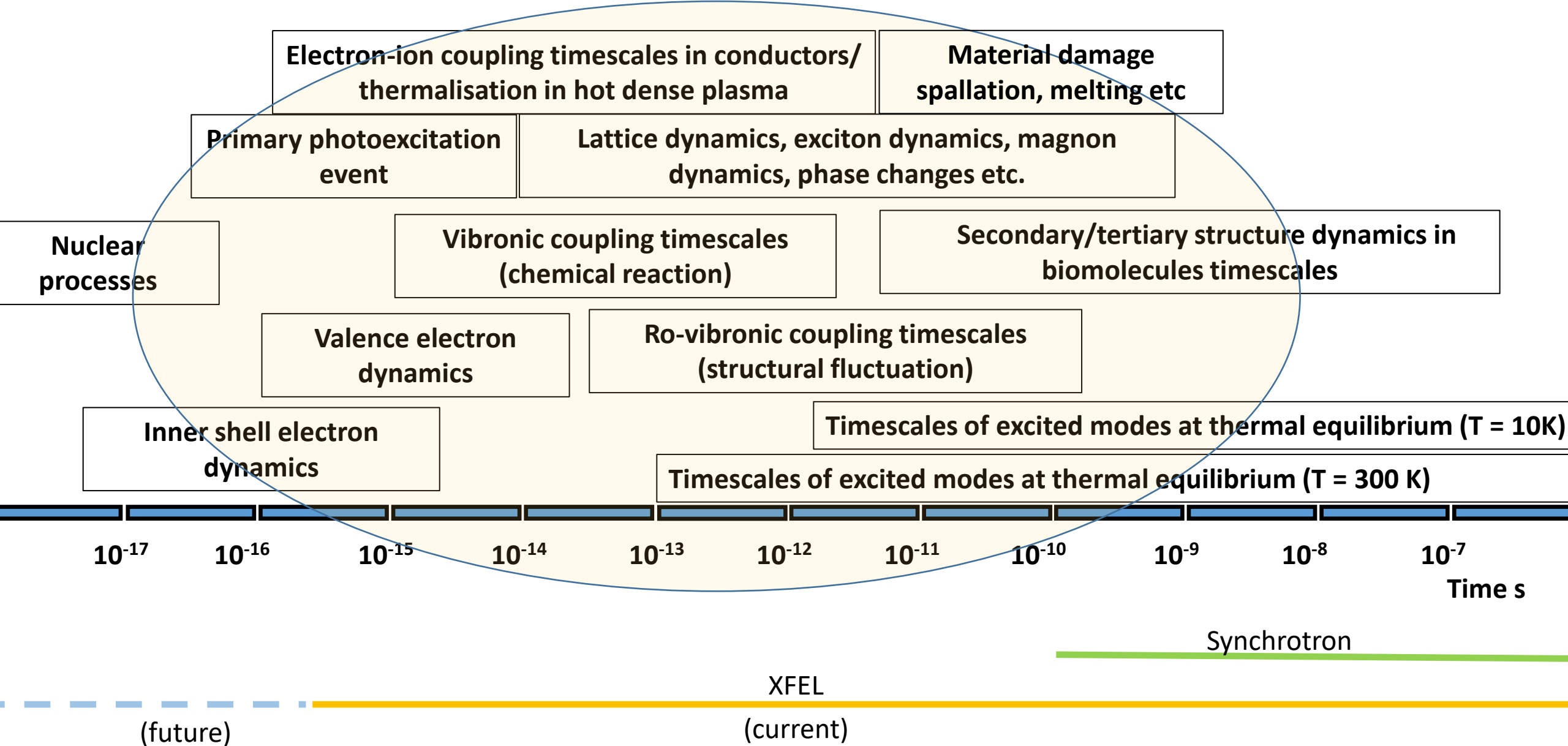
1. Why are the ultrafast dynamics of electronically excited systems so important to us ?

Life-on earth, and increasingly our sustainable technologies, are powered by solar driven electronic excitation.

This provides a timely impetus for the science, along with the needs of chemical, materials, communications, detector and computing technologies

Ultrafast X-rays give us access to the $< 10^{-10}$ m *spatial* and $< 10^{-15}$ s *temporal* scales needed to fully track and understand the electronic excitation driven dynamics in matter.
They give access to fundamental decoherence times in molecules and materials that will advance our understanding in key areas of science

2. X-ray probing of the nanoscale *structure* of matter using scattering

X-Ray Diffraction

$$\Delta k = k_0 - k_S \qquad I(\Delta k)$$

k_0

k_S

X-Ray Beam
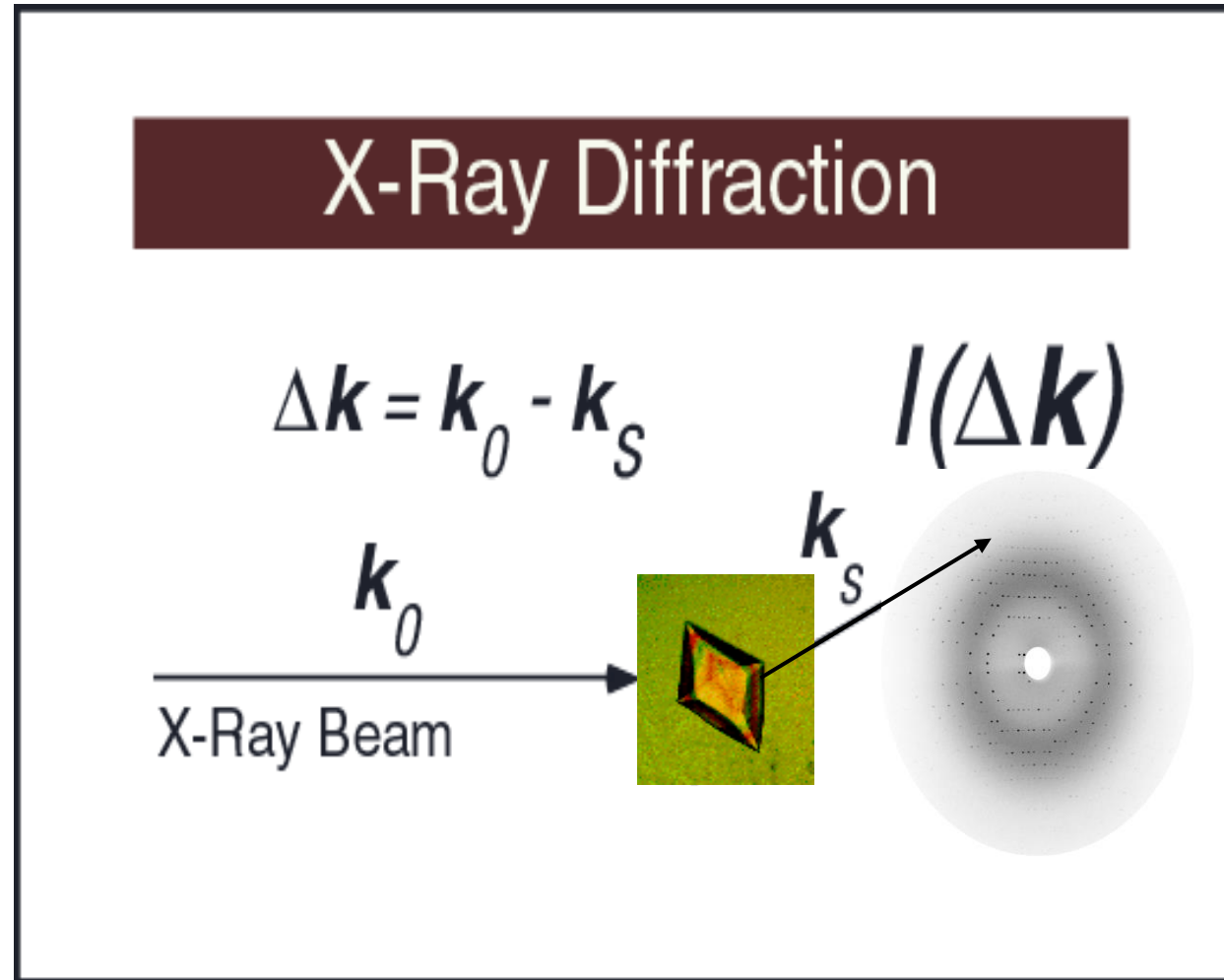
Structure from Thomson/Compton scattering of x-rays by electrons located at atomic sites. In crystal coherent amplification for scattering satisfying the Bragg condition, even non-crystalline systems will yield a characteristic scattering pattern that permits structural retrieval

2. X-ray probing of the nanoscale *structure* of matter using X-ray spectroscopy

X-ray Spectroscopy

X-ray Absorption

$\hbar\omega_{fluorescence}$

X-ray Fluorescence

SAMPLE

I_0 electrons

I_T

d

inner shell – valence or free state transitions

Auger decay

$$I_T = I_0 e^{-\mu \cdot d}$$

$$\mu \approx \frac{\rho \cdot Z^4}{A \cdot E_{x-ray}^3}$$
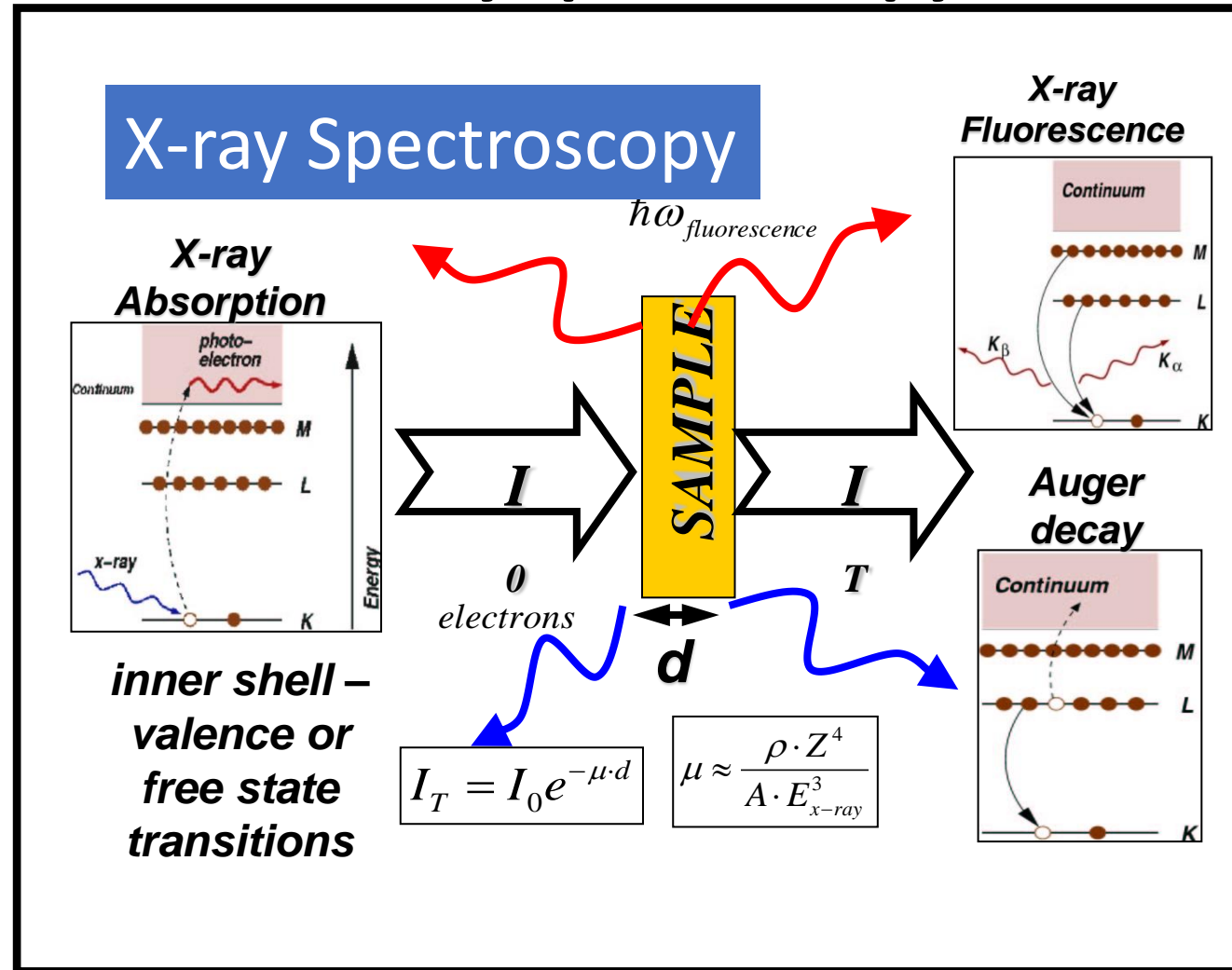
Characteristic core/ core-valence electronic transitions provide chemical/site specific information of electronic structure and occupations

2. X-ray probing of the dynamics of matter using charged particle fragments: photoelectron, Auger electrons & ions

valence XPS

core XPS
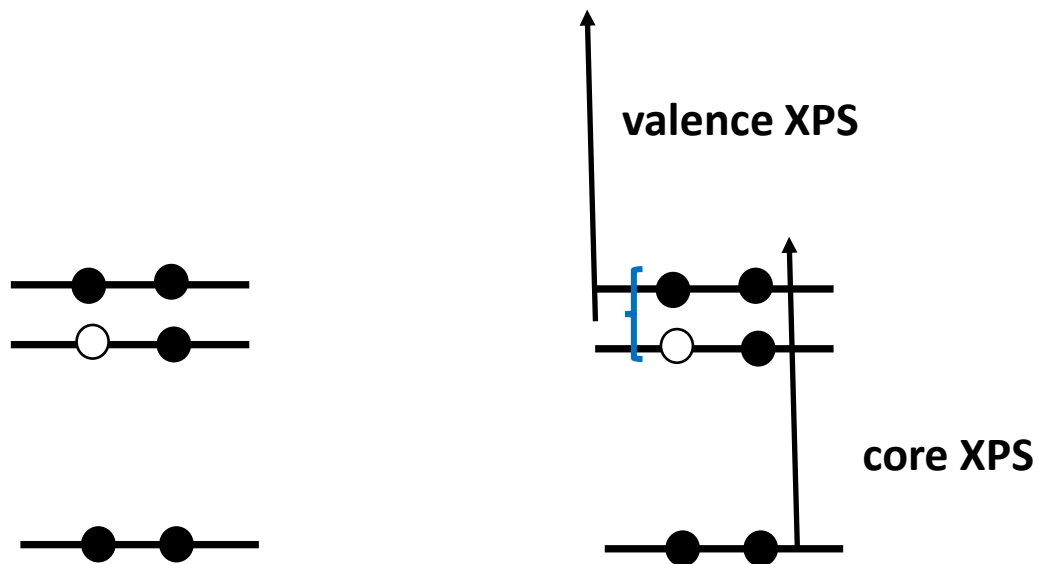
Characteristic core/ core-valence photo-electronic spectrum provides site specific information of electronic state. Additional information from electron angular distribution and Auger electrons

**Coulomb explosion provides information on instantaneous structure.
Electron- ion positions in coincidence permit full reconstruction of event**
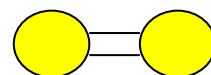
Bonding and other electrons stripped by x-ray ionisation, leading to multi-electron dissociative ionisation (MEDI)

e⁻   + +   e⁻

e⁻
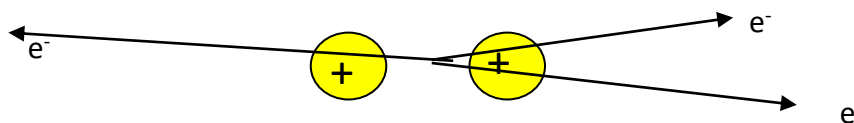
Coulomb potential energy released as kinetic energy

+   +
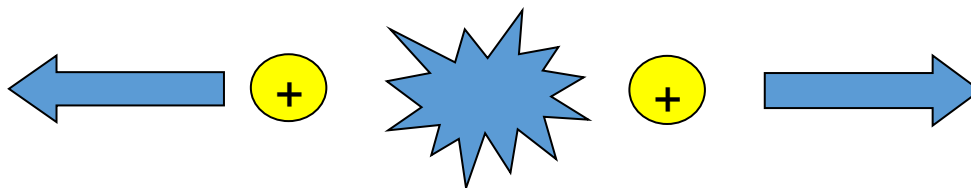
Direction of release gives alignment state of molecule (at least for simple molecules)

2. X-ray photon sources for probing femtosecond to attosecond dynamics using time-resolved spectroscopy

High harmonic generation - HHG

- **Isolated attosecond pulse (IAP) duration < 200 as**

- **Photon energy to 100 eV with 800 nm drives and to > 500 eV with longer wavelength**

- **$> 10^8$ (25 eV) - $< 10^3$ (500 eV) photons/pulse**

- **Excellent coherence and synchronisation**

X-ray free electron laser - XFEL

- **Pulses few fs to < 0.5 fs**

- **Photon energy to > 10 keV**

- **$>10^{11}$ photons/pulse**

- **Synchronisation to external lasers > 10 fs**

- **Two colour**

1 2 3

Tunnel ionisation   Acceleration   X-ray Light Emission

Incoherent emission: electrons randomly phased

Coherent emission: electrons bunched at radiation wavelength
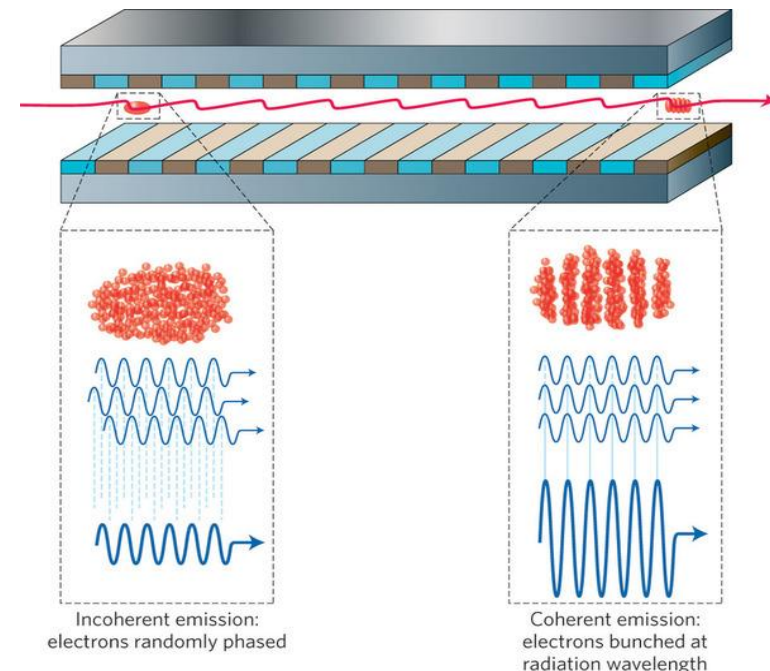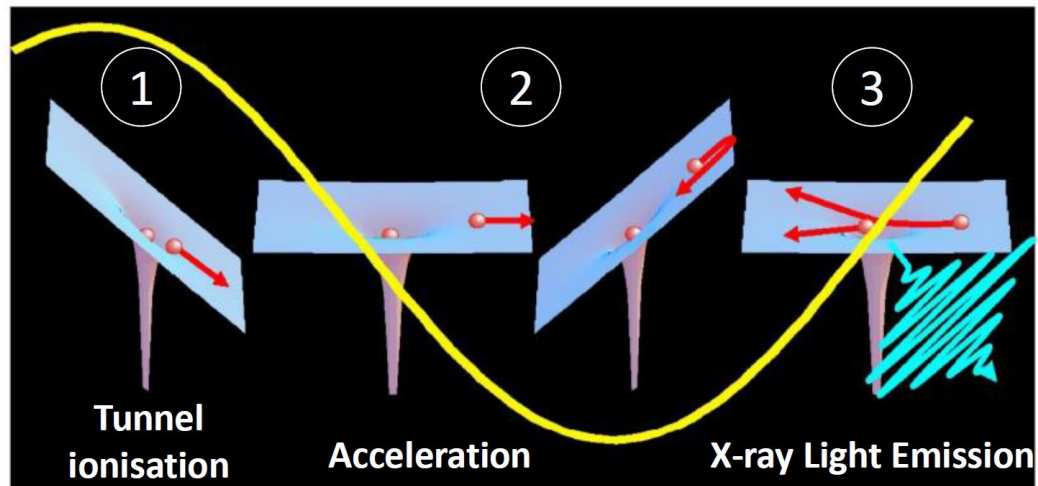
2. Time-resolved X-ray measurements by the pump-probe methodology
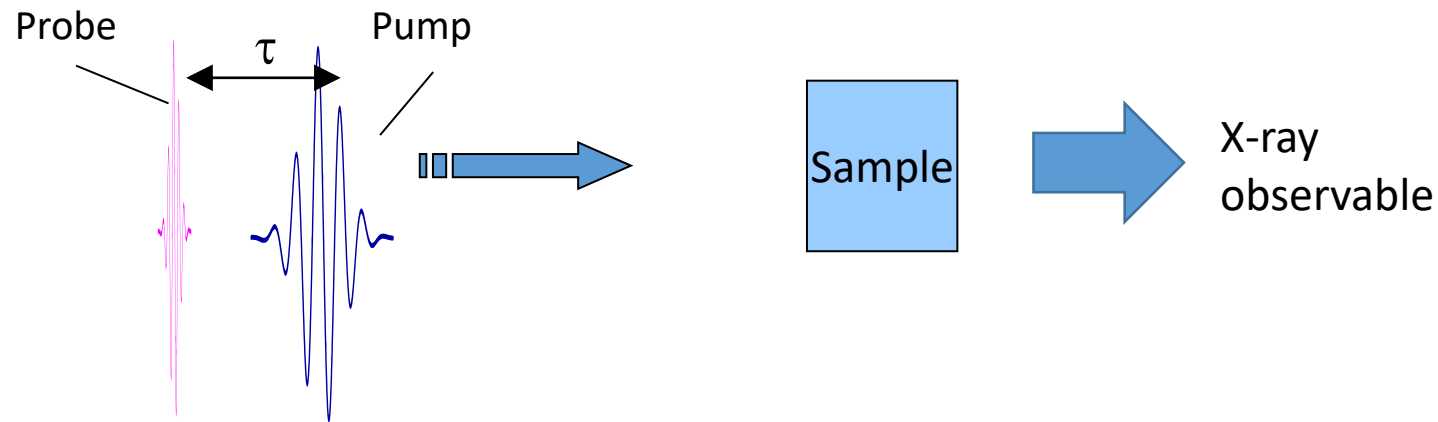
In a pump-probe measurement the sample is excited/activated by a pump pulse and probed after a controllable delay τ through observation of a suitable observable. As τ is varied the dynamics can be mapped

Pump (X-ray to THz) – activates the sample:
e.g. Sudden heating, injection of hot electrons, electronic state photoexcitation/photoionisation, excitation of vibrational/phonon or rotational modes etc.

Probe (X-ray) – interrogates the sample after delay time τ by generating a suitable observable:
e.g. X-ray scattering/diffraction, resonant inelastic X-ray scattering (RIXS), X-ray spectroscopy (absorption (XAS) and emission (XES), X-ray photoelectron spectroscopy (XPS) etc.)

2. Pump – probe measurements with incisive X-ray probes

X-ray scattering

X-ray spectroscopy

Capture time evolution: **Structure**   **Electronic states**   **Spin states**
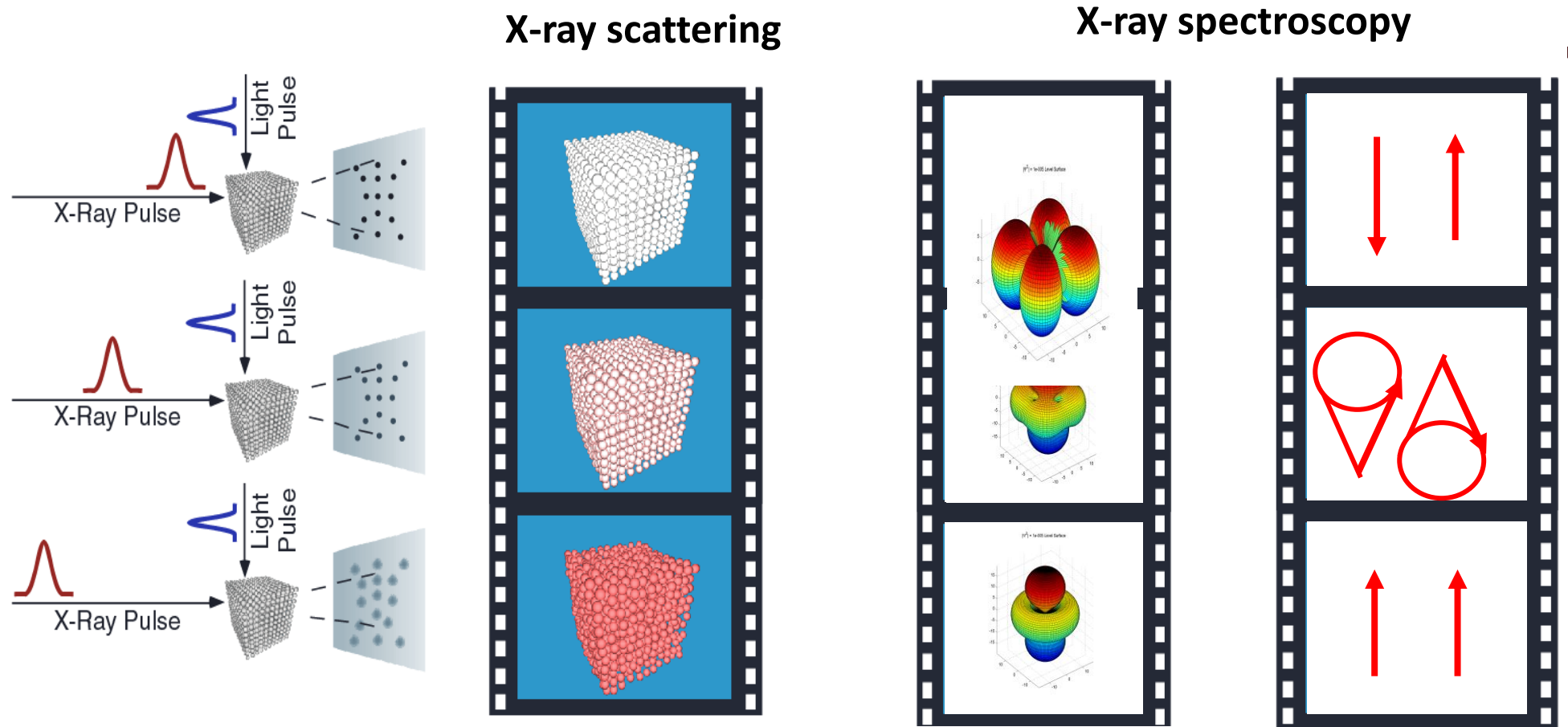
2. X-ray spectroscopies and allied x-ray photoelectron spectroscopies are examples of incisive X-ray probes
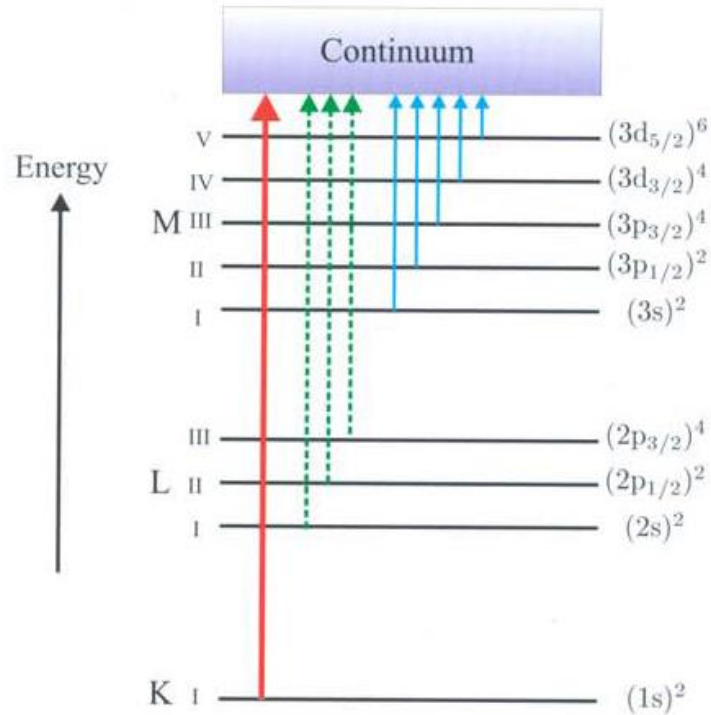
Summary of the nomenclature of the absorption edges of the elements. The electronic shells are labelled $(nl_j)^{2j+1}$ where n is the principal quantum number, l is the orbital momentum and j is the total angular momentum. (2j+1) is the multiplicity.
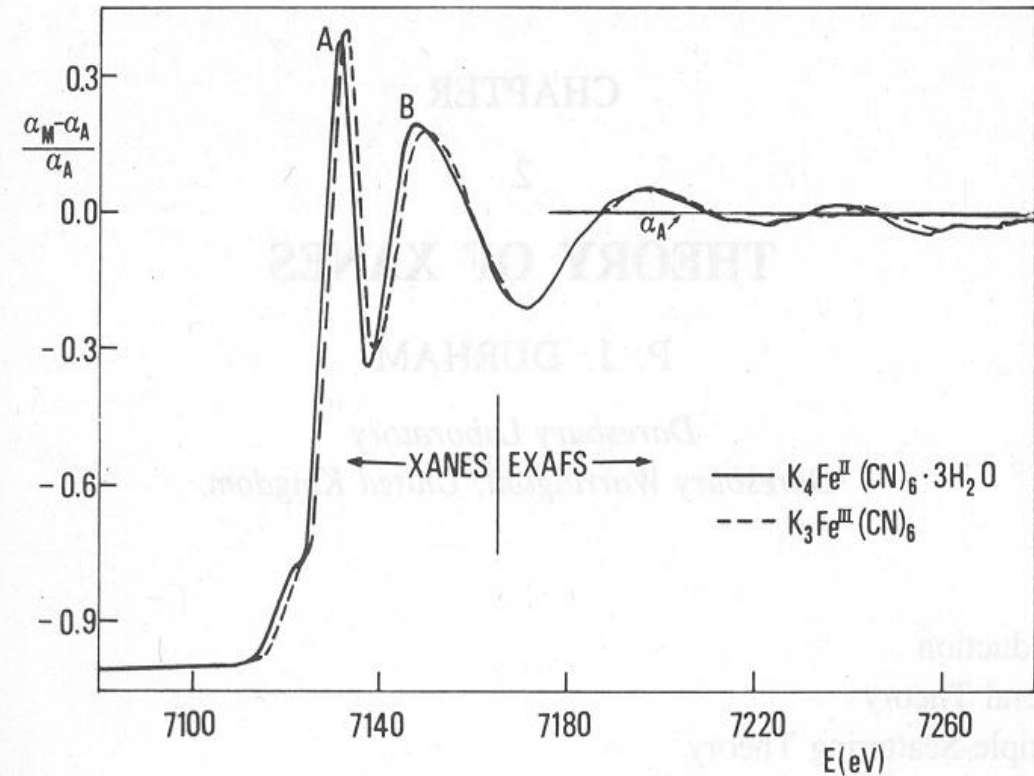
XANES: X-ray Absorption Near Edge Structure

EXAFS: Extended X-ray Absorption Fine Structure

2. Access to x-ray K, L and M edges vital to spectroscopic measurements with element/site specificity

2. Attosecond supercontinuum pulses from HHG covering 150 – 600 eV

CEP Scan at z=33710

CEP Scan at z=32875
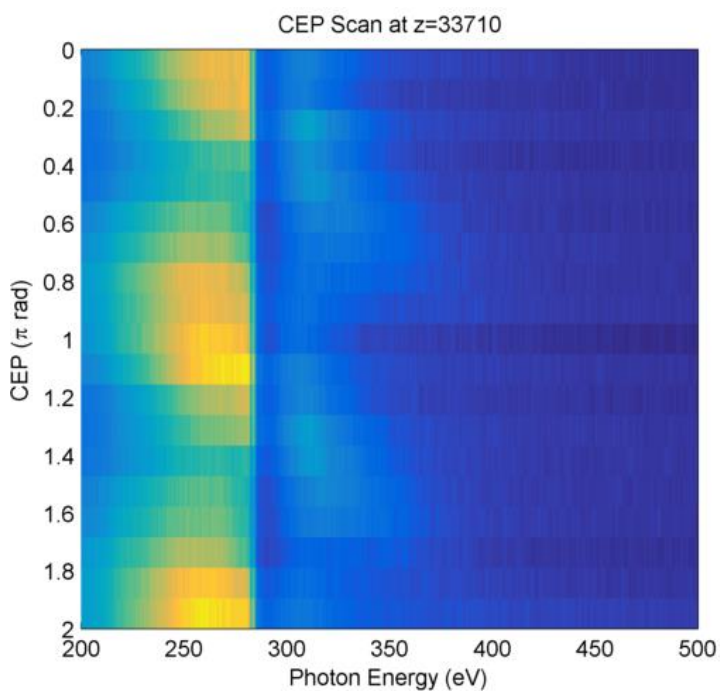
Using a few-cycle 1.8 μm pulses CEP stable pulses & by changing gas species, pressure, and focus position, an isolated sub-femtosecond pulse can be generated centred at photon energies from 150 – 600 eV
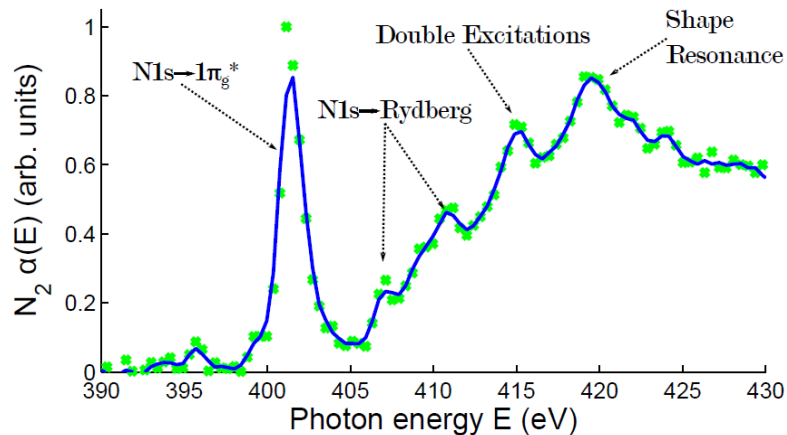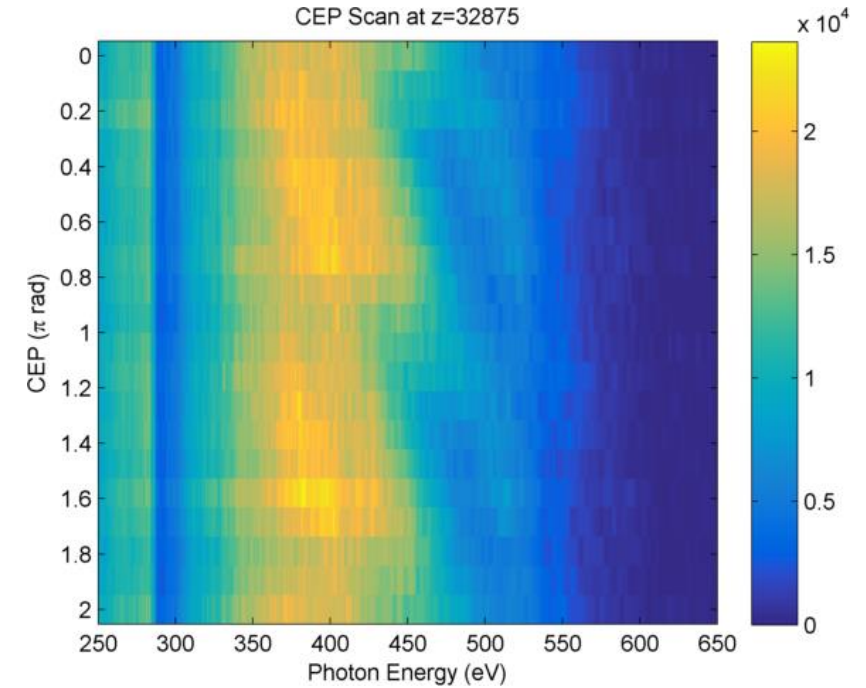
Top left: 200-350eV
Top right: 280-350 eV
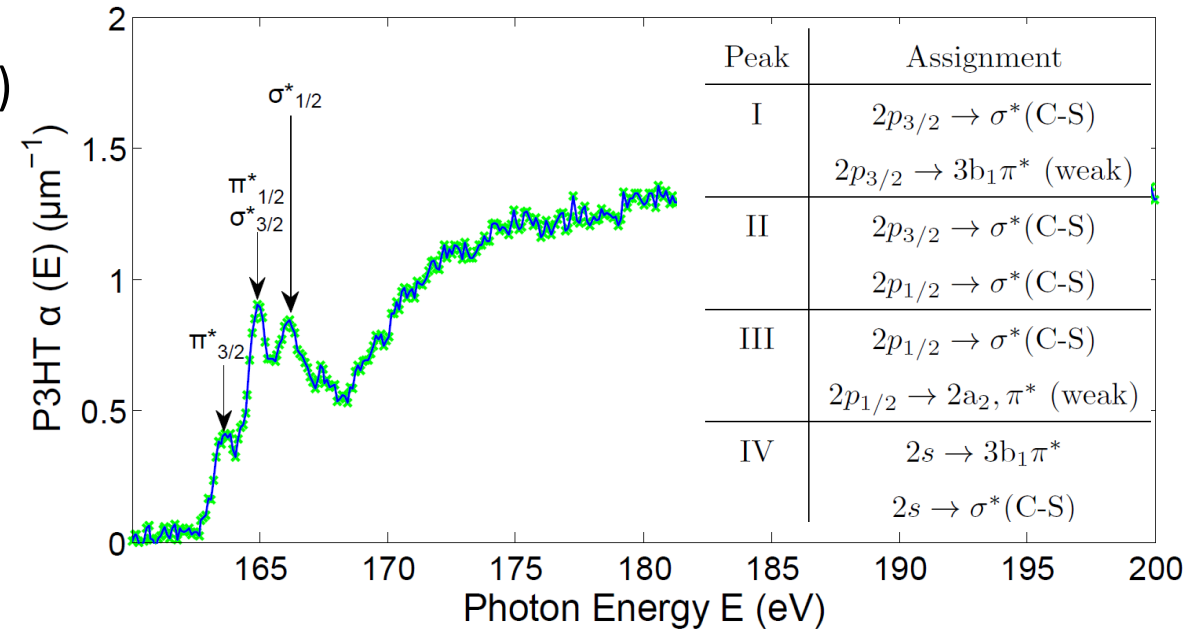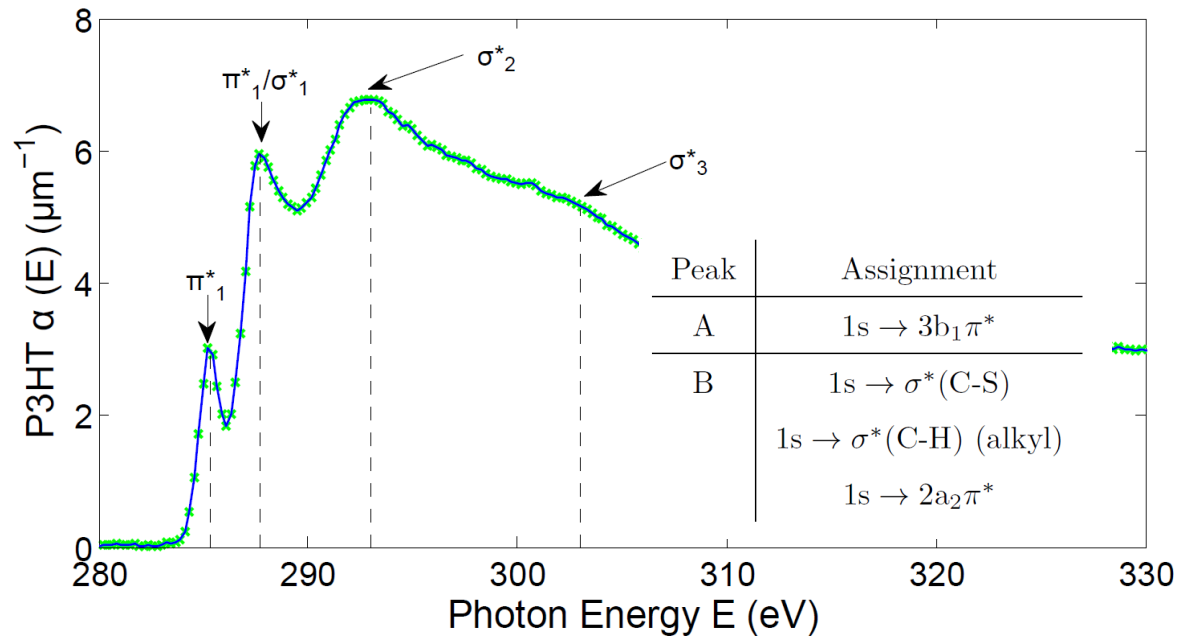Bottom left: 350-450 eV
Bottom right: 500-600eV
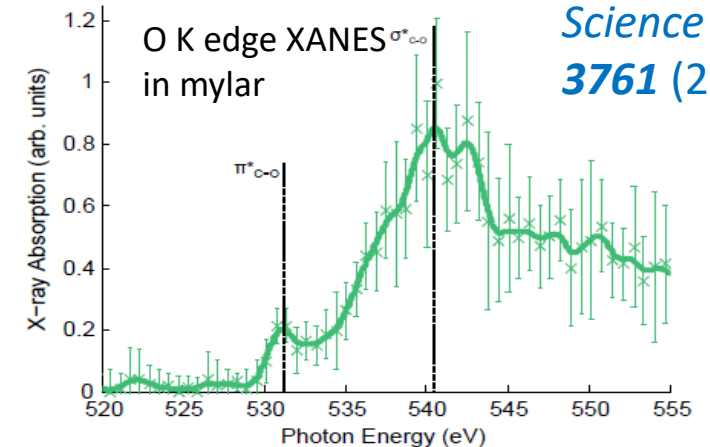
A.Johnson et al *Science Advances **4**, **3761*** (2018)

O K edge XANES in mylar

$CH_2(CH_2)_4CH_3$

For time-resolved SXR absorption we fabricate free standing P3HT* (polythiophene) polymer films of ~100 nm thickness using spin coating methods.

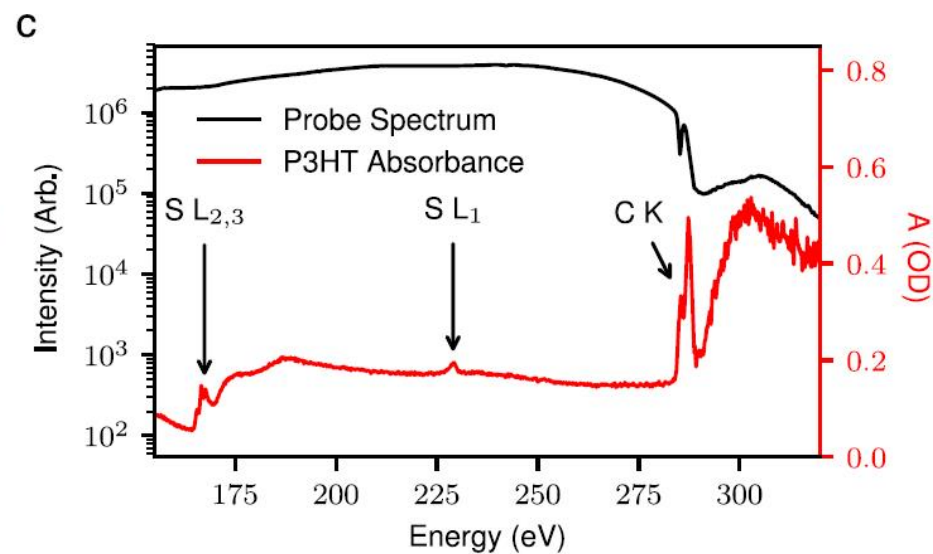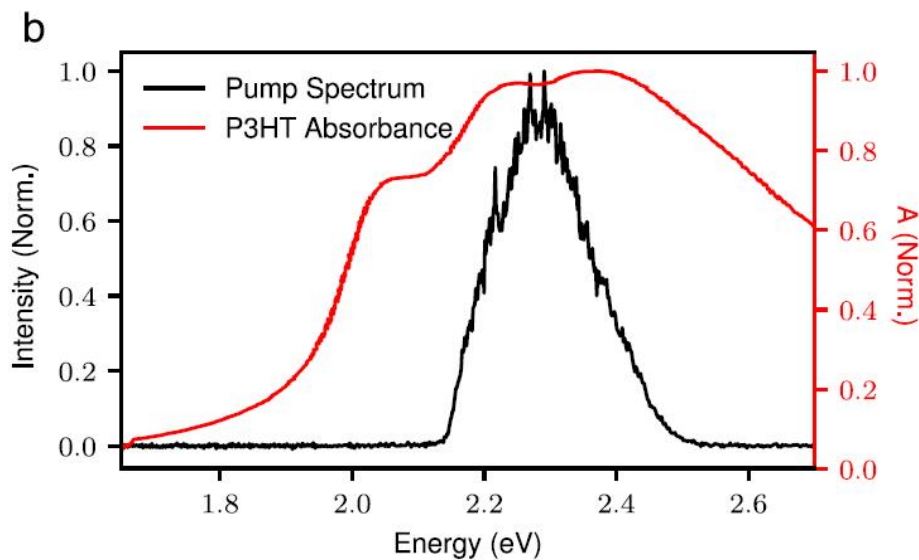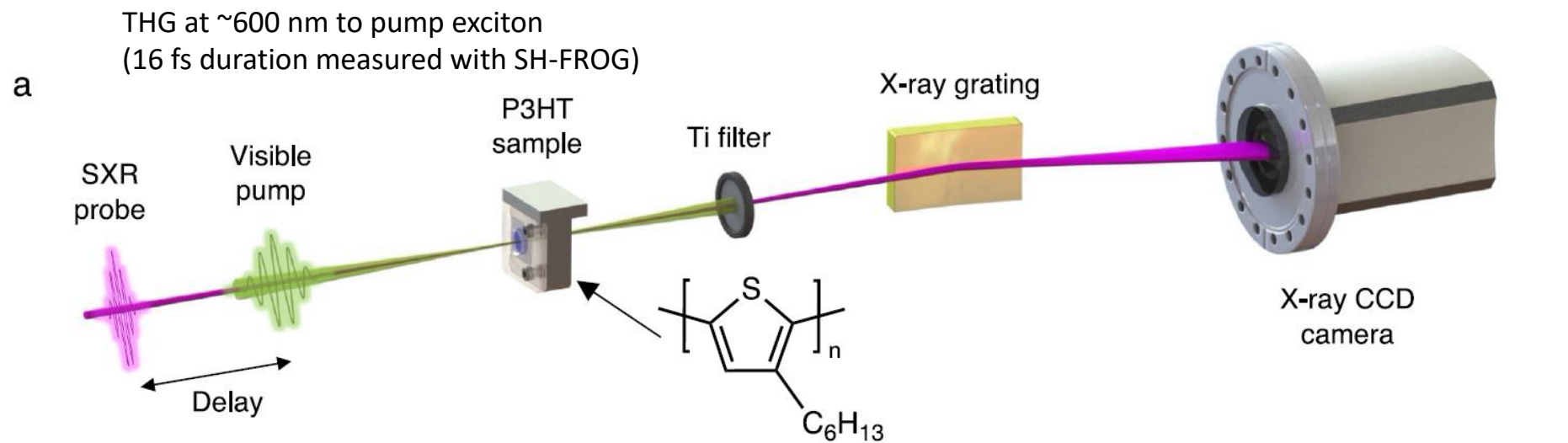*Base material for important class of polymer optoelectronic materials*

Peak	Assignment
I	$2p_{3/2} \rightarrow \sigma^*(\text{C-S})$
	$2p_{3/2} \rightarrow 3b_1\pi^*$ (weak)
II	$2p_{3/2} \rightarrow \sigma^*(\text{C-S})$
	$2p_{1/2} \rightarrow \sigma^*(\text{C-S})$
III	$2p_{1/2} \rightarrow \sigma^*(\text{C-S})$
	$2p_{1/2} \rightarrow 2a_2, \pi^*$ (weak)
IV	$2s \rightarrow 3b_1\pi^*$
	$2s \rightarrow \sigma^*(\text{C-S})$

Peak	Assignment
A	$1s \rightarrow 3b_1\pi^*$
B	$1s \rightarrow \sigma^*(\text{C-S})$
	$1s \rightarrow \sigma^*(\text{C-H})$ (alkyl)
	$1s \rightarrow 2a_2\pi^*$

A. Johnson et al, Structural Dynamics, 3, 062603 (2016)

XANES at S L edge and C K edge measured in P3HT films with HHG from our source (likely close to an IAP).
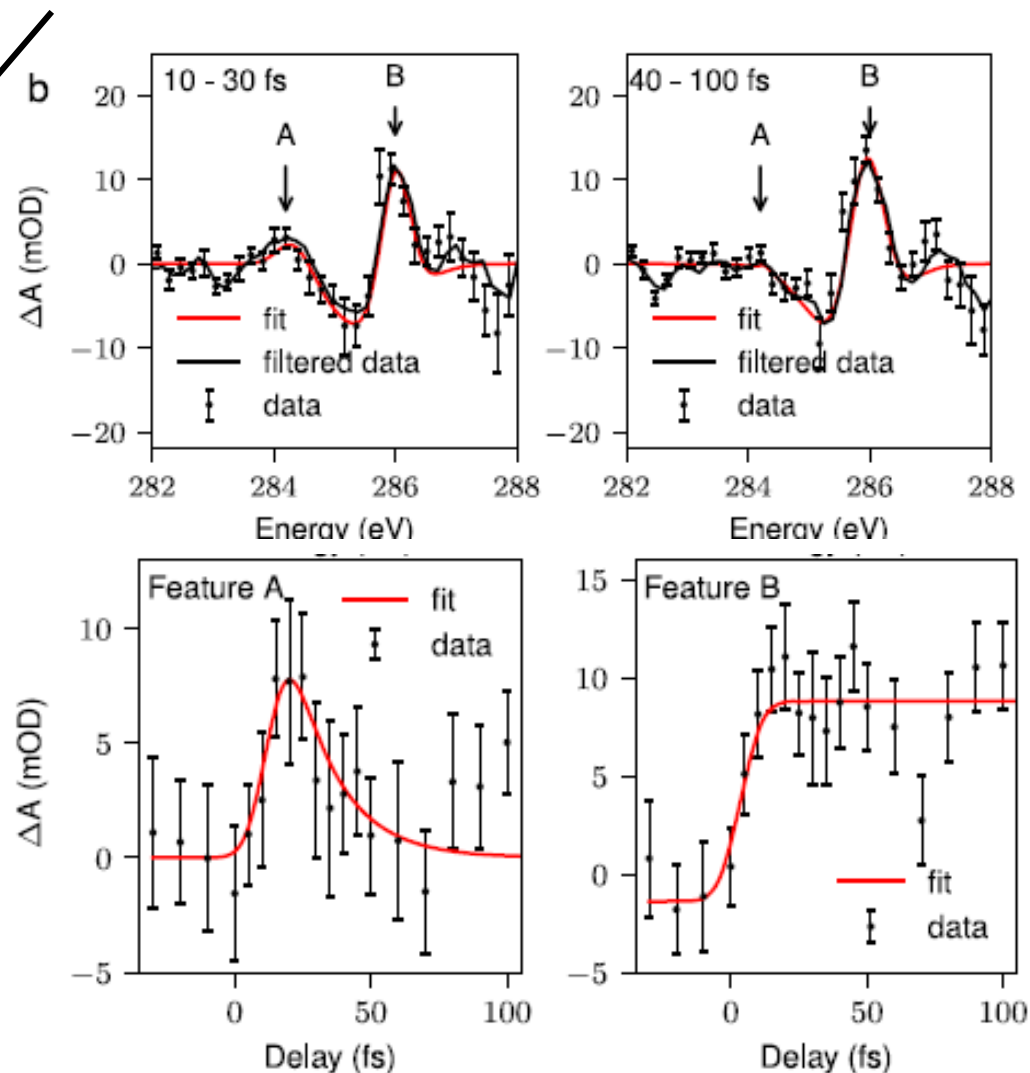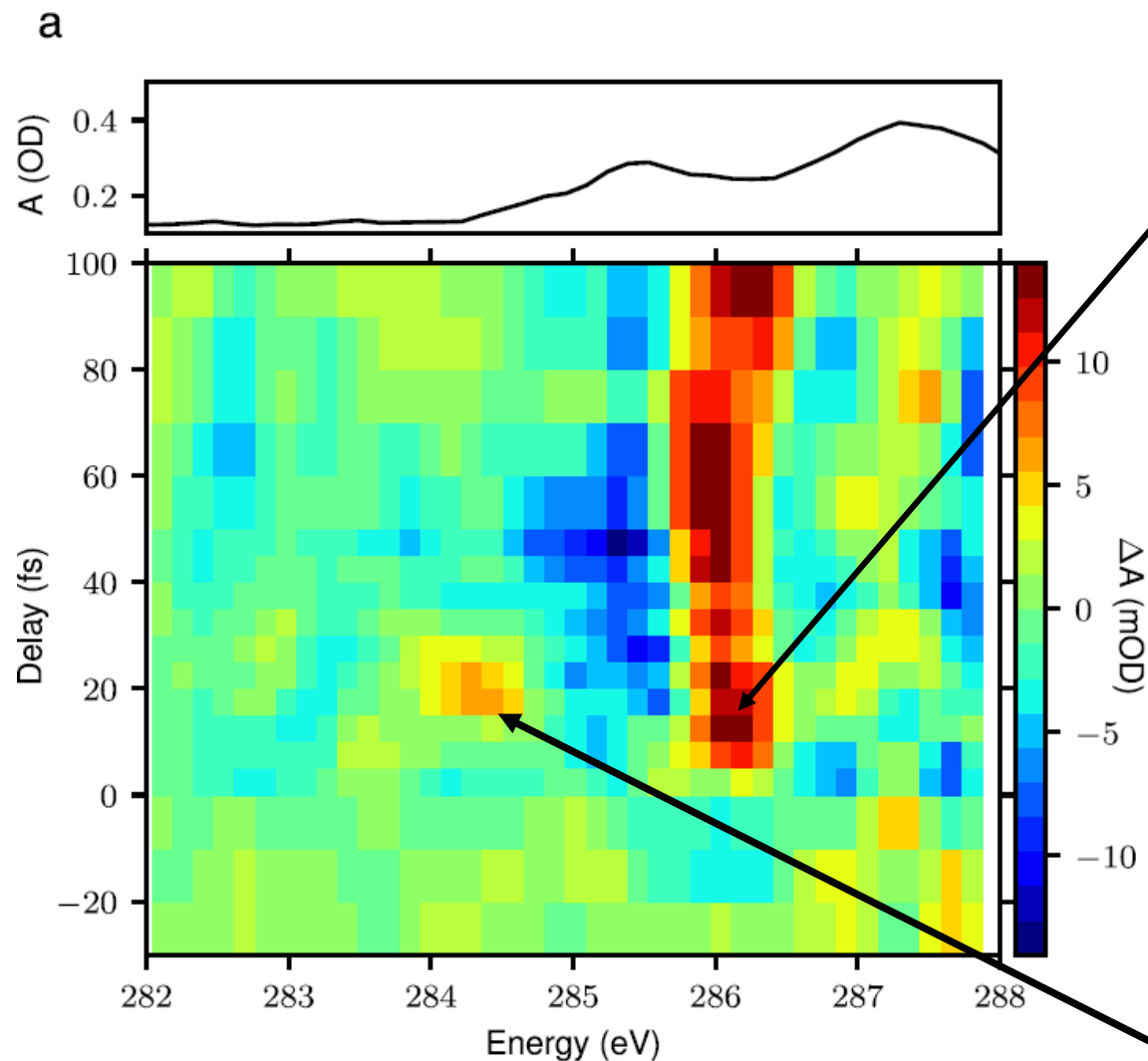
2. Time-resolved HHG based XAS in organic semiconductor P3HT

Dougie Garratt, David Wood, Lukas Miseikis, Esben Larsen, Mary Matthews, Artem Bakulin, Tom Penfold, JPM

B. Edge shift following exciton creation

A. Transient feature – pre-edge absorption associated with exciton delocalised across neighbouring chains

2. X-ray transient absorption signal provides a direct probe of the initial delocalisation and cooling of the hot exciton formed by the pump

XAS spectra simulated with TDDFT by Tom Penfold (Newcastle)

Garratt, D., Misiekis, L., Wood, D. *et al.* Direct observation of ultrafast exciton localization in an organic semiconductor with soft X-ray transient absorption spectroscopy. *Nat Commun* **13,** 3414 (2022). https://doi.org/10.1038/s41467-022-31008-w
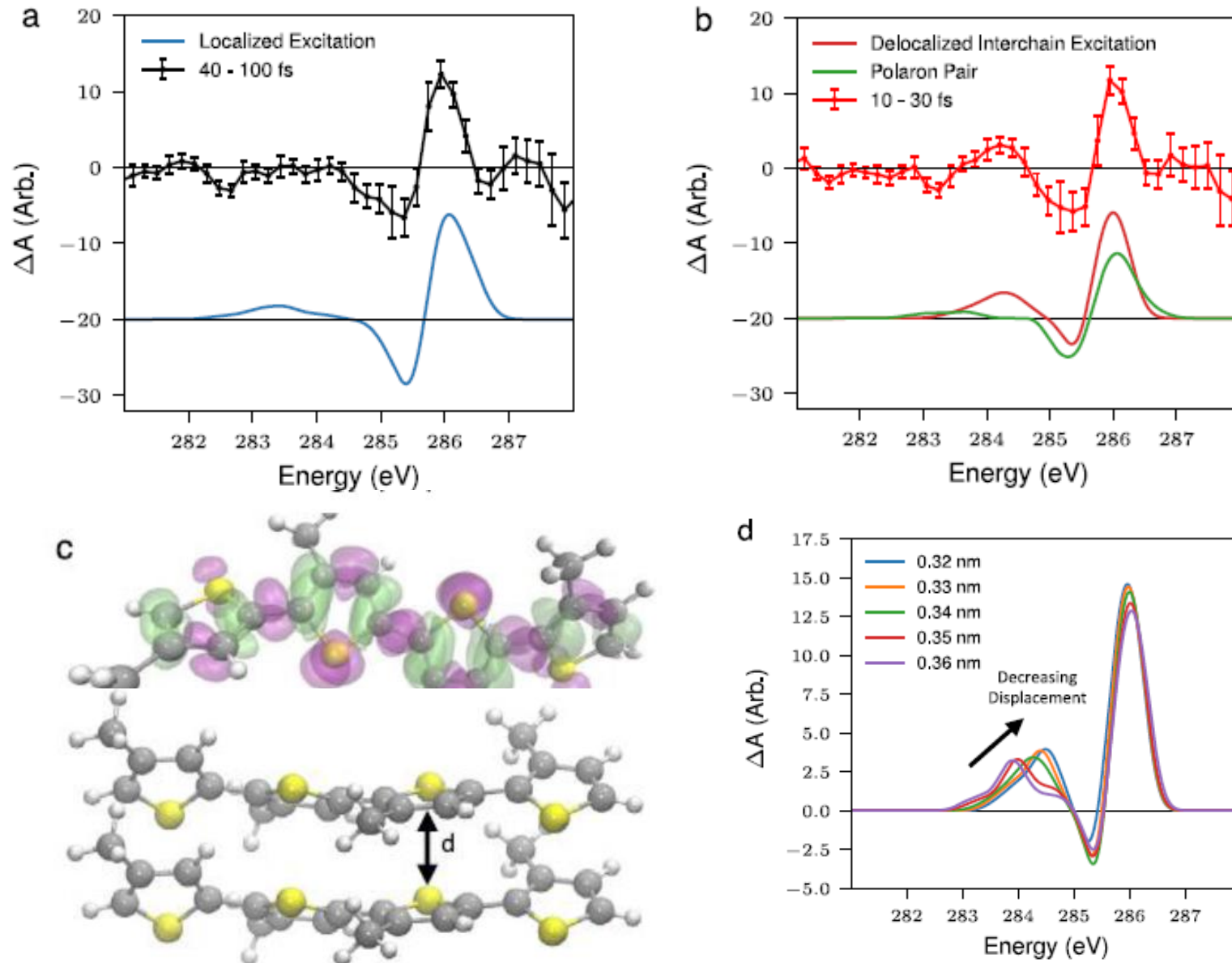
2. Charge fragment methods: Photoelectron spectroscopy, Auger spectroscopy and fragmentation patterns

- Cold targets and helium droplets and cluster sources (from supersonic nozzles)
- Warm targets from ovens (effusive beams) or techniques for larger molecules (e.g. electrospray)
- Access to all particle fragments in gas phase systems, often with high efficiency enabling covariance or coincidence reconstruction of fragment correlations (ion-ion, ion-electron or electron-electron)
- Time-of-flight (TOF) ion (charge/mass fragment analysis & kinetic energy release) and electron spectrometers (for photoelectron and Auger spectrum)
- Angular distribution of ions and electrons – from an array of TOFs or VMI
- Full momentum reconstruction and coincidence of all fragments (COLTRIMs)

2. Cooling of rotational states of molecules is achieved by supersonic expansion of gas through a nozzle into vacuum

pulsed valve

gas jet

cooled gas

Added skimmers to collimate molecular beam
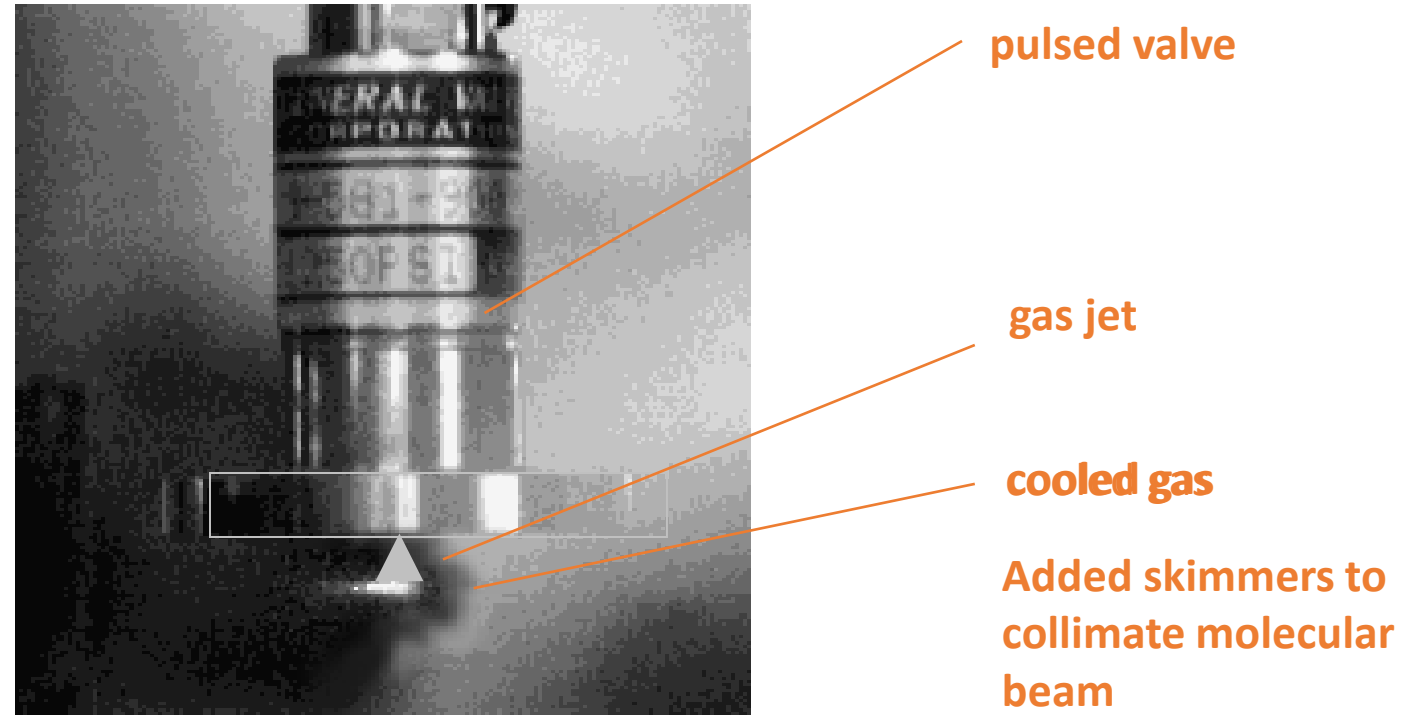
When the gas expands supersonically into a vacuum it cools rapidly with collisions causing the translational cooling to couple to rotational cooling.

Nozzle diameter d is typically 100 – 500 microns and experiments are performed at a scaled distance x/d: x/d = 5 - 100
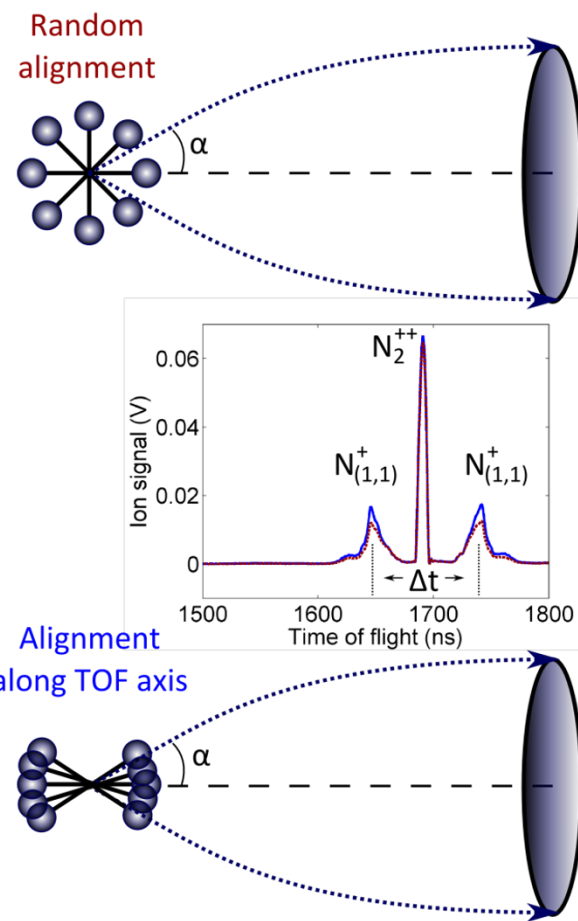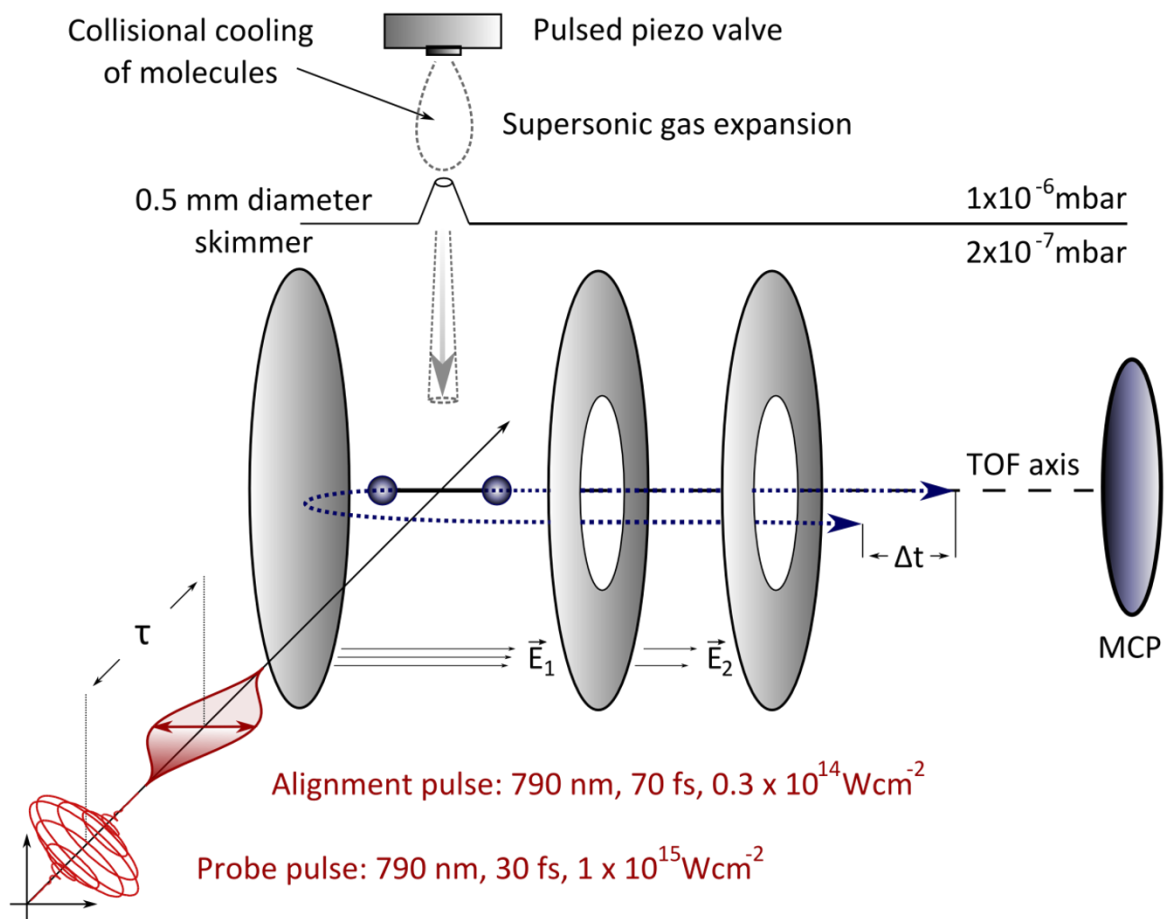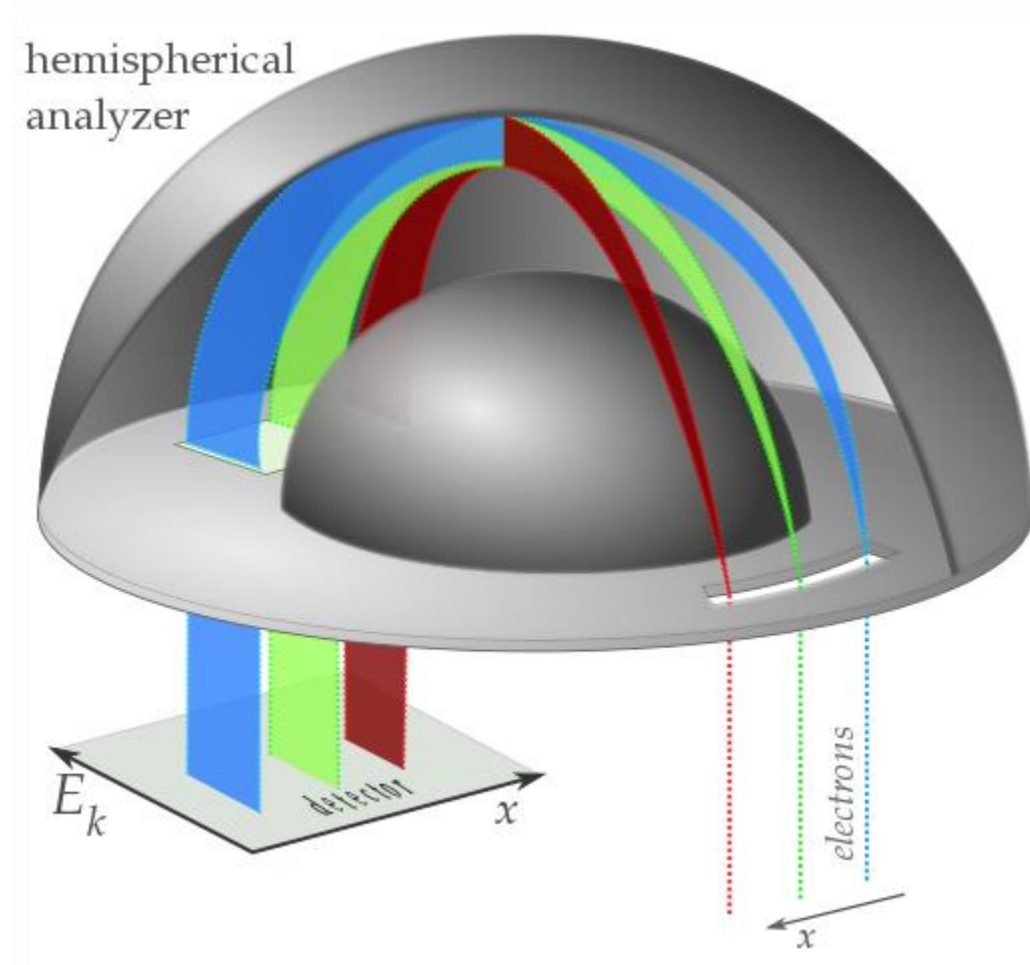
2. Electron/Ion TOFs are widely used, high collection efficiency with high energy resolution achieved using the magnetic bottle configuration
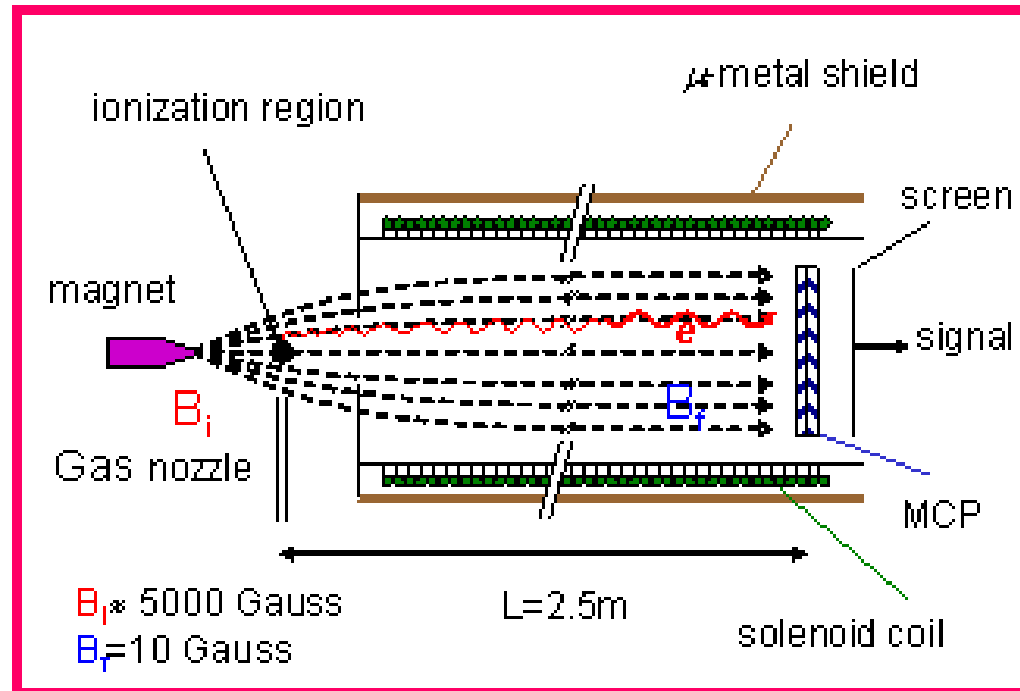
P. Kruit and F. H. Read, J. Phys. E 16, 313 (1983)

J. H. D. Eland et al, Phys. Rev. Lett. 90, 053003 (2003)

2. Other widely used electron spectrometer options are the hemispherical analyzers that can preserve some angular resolution

Velocity map imaging (VMI) is widely used to retain angular distribution information from ions and electrons by projection on a 2D plane
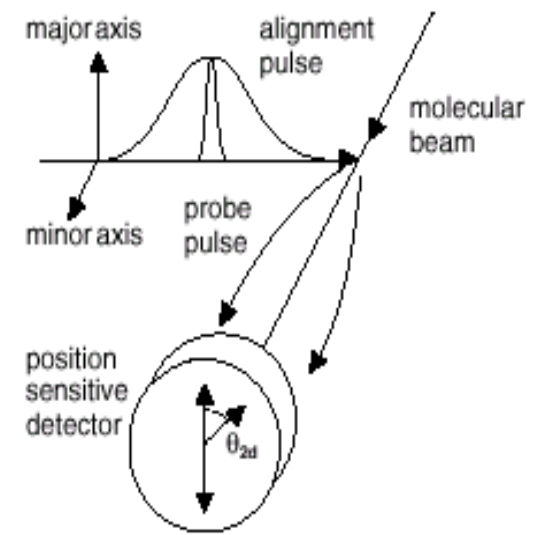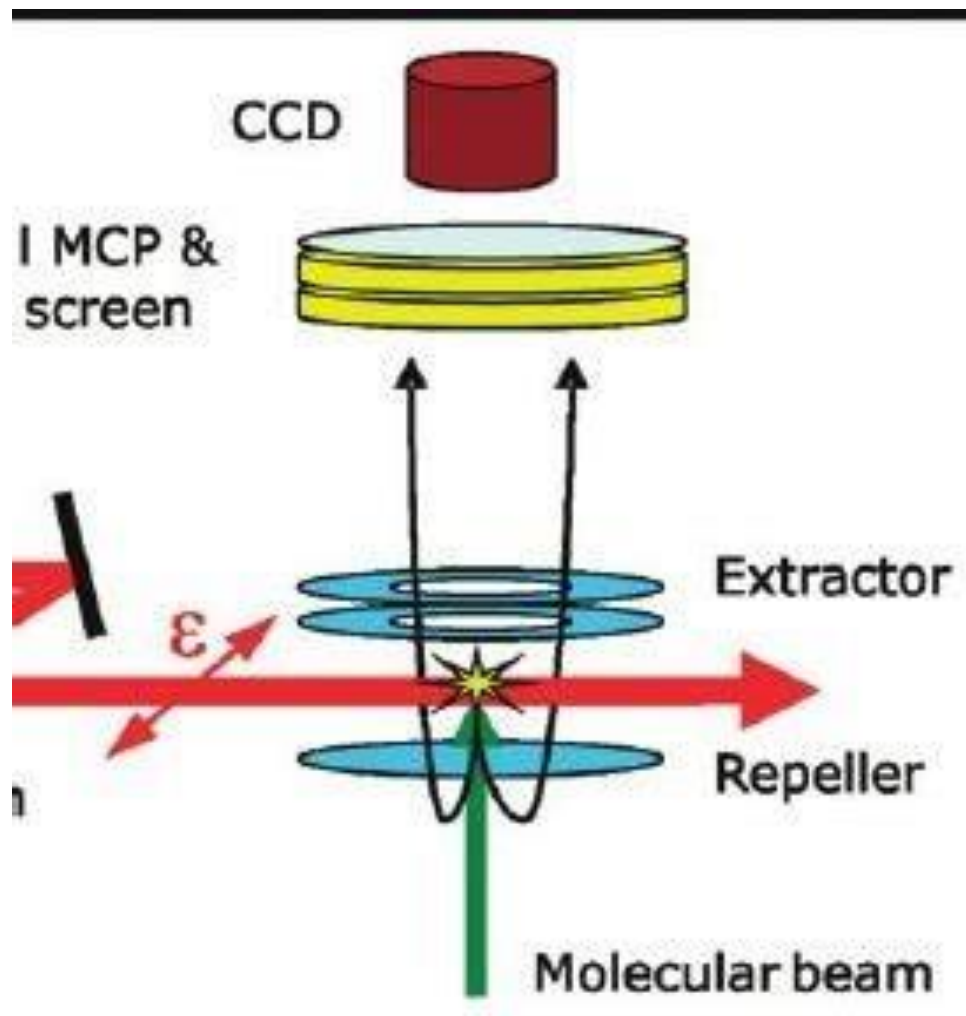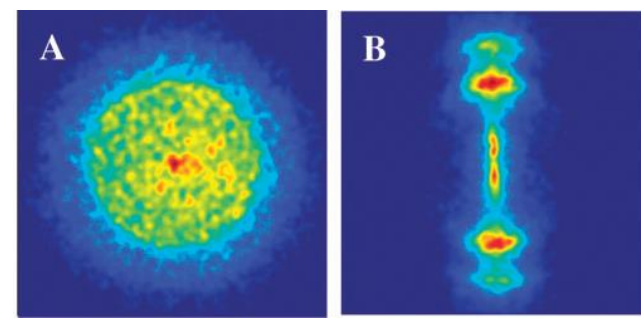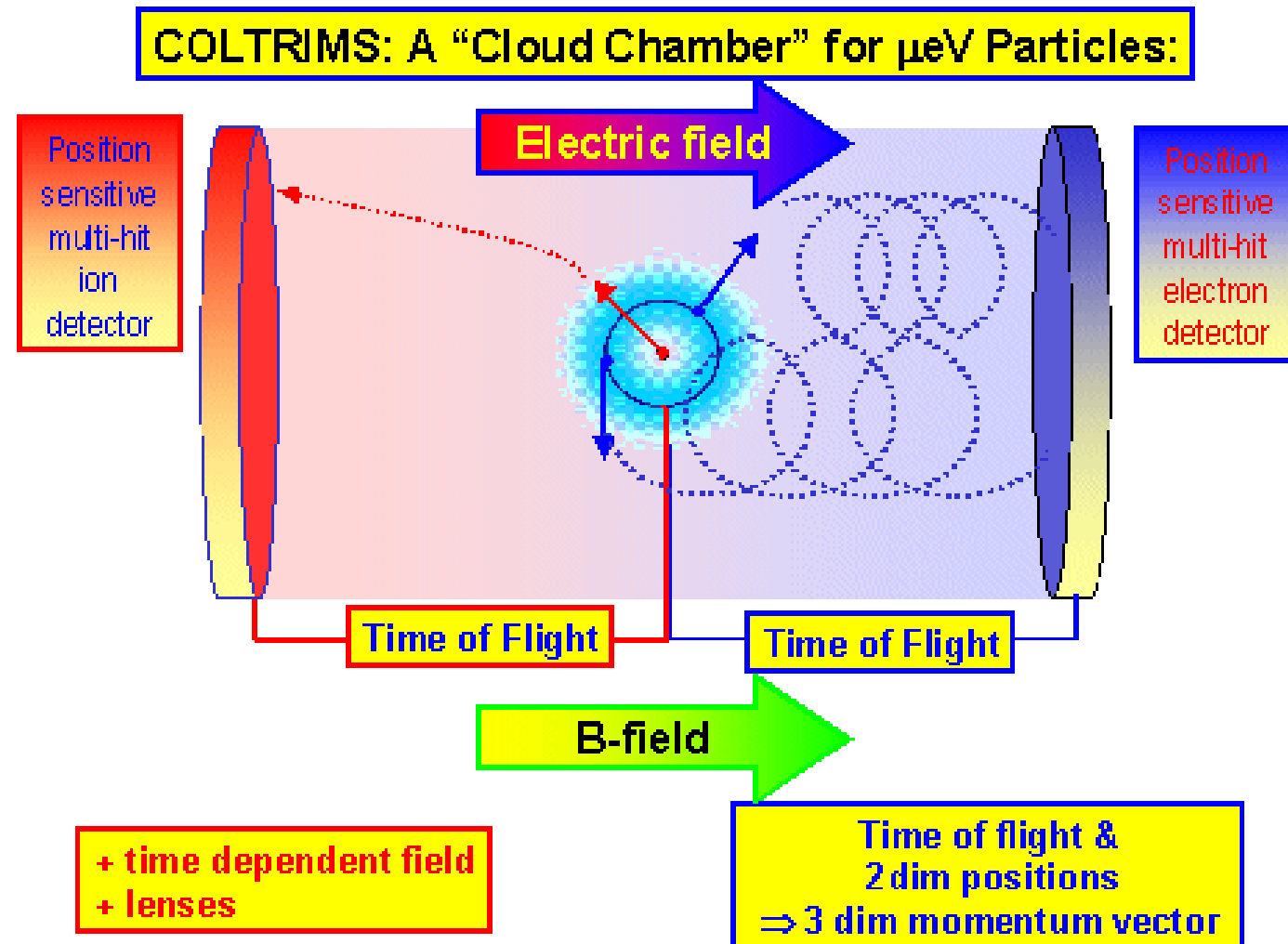

FIG. 3. Schematic overview of the apparatus. The major axis of the YAG polarization is parallel to the detector surface and the minor axis is parallel to the molecular beam.

2. Full 3D fragment distribution of both electrons and ions can be preserved in a COLTRIMs (COLd Target Recoil Ion Momentum system)

COLTRIMS: A "Cloud Chamber" for µeV Particles:

Position sensitive multi-hit ion detector

Electric field

Position sensitive multi-hit electron detector

Time of Flight

Time of Flight

B-field

+ time dependent field
+ lenses

Time of flight &
2 dim positions
⇒ 3 dim momentum vector

2. Upgraded end-stations are being built for high rep-rate attosecond capability at LCLS – operational from 2023

Variable Kirkpatrick-Baez focus mirrors to achieve high intensity

High resolution electron spectrometers, ion velocity mapping VMI, and coaxial electron VMI + single shot spectral monitor

COLTRIMS – Momentum microscope for coincidence detection
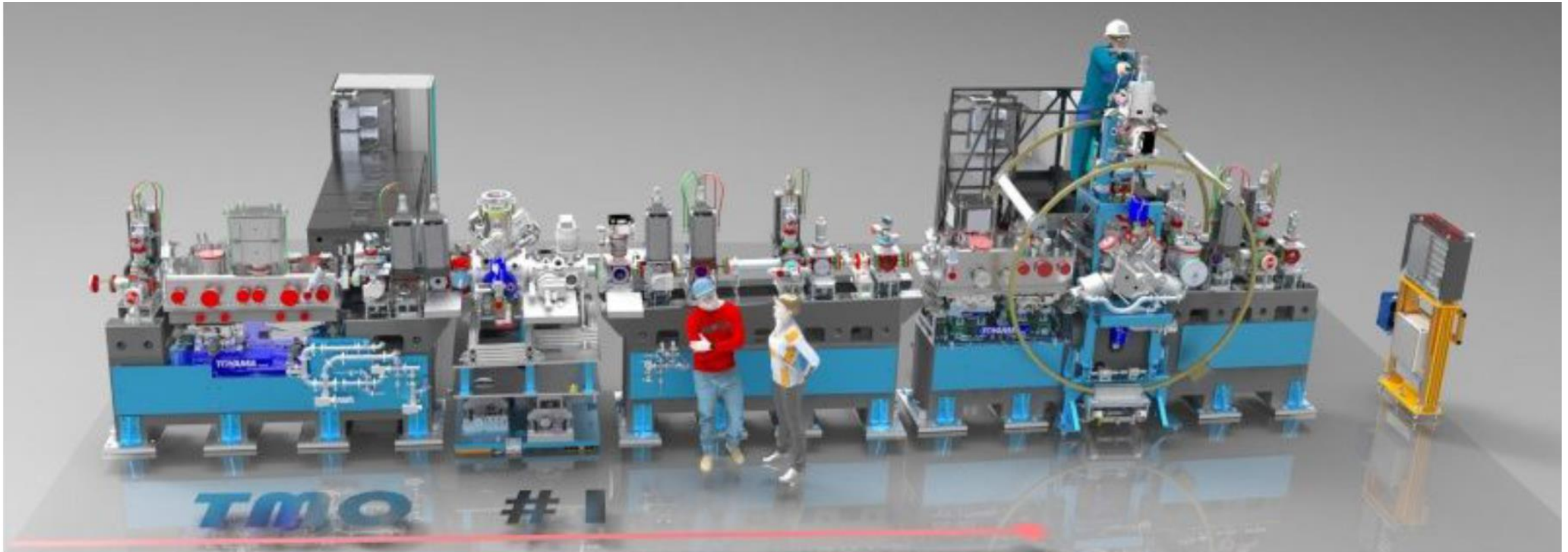
End of part I

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