Ion–molecule Collisions

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Outline

- Outline of an atomic/molecular physics experiment
- Basics of collisions and molecular structure
- Some aspects of molecular collision dynamics
- Types of collision investigations

What is experimental atomic and molecular physics?

- information about the structure and dynamics of atoms and molecules by spectroscopy, collisions
- Why study these processes?
  - they are of relevance to atmospheric and stellar, even biological processes
  - atomic and molecular processes occur all around us – everywhere!
- experimentally tackle the quantum many-body coulomb problem;
- significant overlap with other branches: astrophysics physics, materials science, earth and atmospheric science, chemistry, medical applications etc.
- Standard chemistry different from interaction of single molecules!

How do we do it?

Perturb atoms or molecules (targets) using charged particles or photons

- Photon interaction
  - energy selective
    ($E = \hbar\omega$)
  - angular momentum selective
    ($\Delta L = 1$)

- Charged particle interaction
  - a range of energy and momentum transfers
  - no angular momentum selection rules

How do we do it?

. . . and study the response

- Detect charged particles or photons, which carry information about the response of the target
  - Ion mass spectrometry (m/q)
  - Electron energy spectroscopy, angular distributions
  - Photon spectroscopy

- Can combine two or more of the above

Focus here is on Ion–Molecule collisions

Scattering Basics

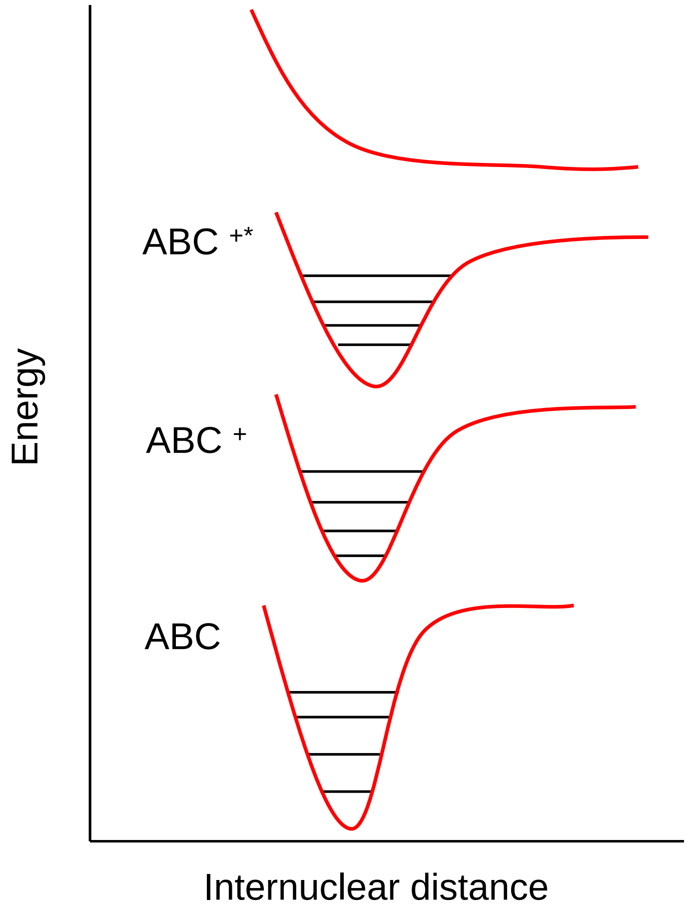
- A beam of particles (ions) crosses a collection of target particles (molecules) in vacuum.
- Usually single collision conditions are maintained
- Coulomb interaction with electrons in the molecules changes the path of the ions (ion–nucleus interaction neglected)
- Perturbed molecule responds leading to rearrangement of electrons and nuclei
- The response is detected in the form of
  –photon emission (fluorescence)
  –electron emission (ionisation)
  –charged or neutral atom or radical emission (dissociation or ionisation)
- Target–projectile roles may be reversed (i.e. the projectile may be the object of investigation and target may be the probe or vice versa)

Perturbation of a Molecule

A molecule may be thought of as a collection of nuclei moving in the mean field of electrons, with overall charge neutrality

- Large difference in masses of nuclei and electrons permits decoupling of degrees of freedom (rotation, vibration, electronic)

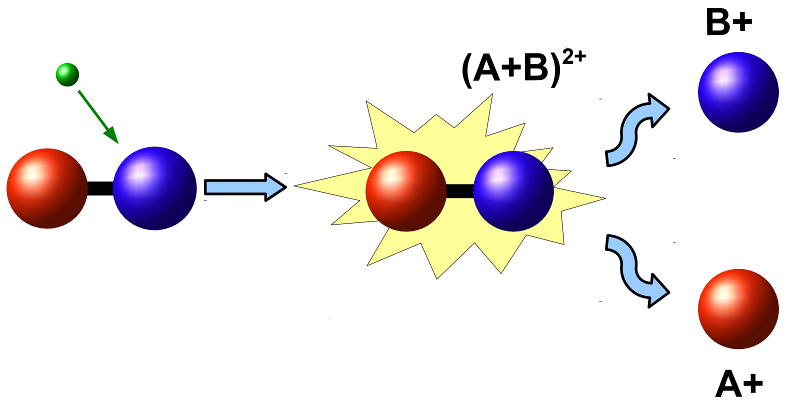
- Can be perturbed by a charged particle or photon
  meV: rotation
  sub-eV: vibration
  few eV: dissociation/ionisation



Collision Regimes

- Fast ions
  - Large velocities
  - Short interaction times
  - Vertical transitions
  - Frozen molecule
- Slow ions
  - Low velocities
  - Long interaction times
  - Electron clouds can adjust
  - Chemistry

Dissociative Ionisation



- The effect of ionisation is a change in the mean field seen by the nuclei, causing the nuclei to respond to it

- An excited molecule may dissociate producing charged and neutral fragments

- Ionisation and dissociation occur on differing time scales

$$AB + \gamma \longrightarrow (AB^{n+})^* + e^- \quad [\sim \text{ fs}]$$
$$(AB^{n+})^* \longrightarrow A^{p+} + B^{q+} \quad (n = p + q) \quad [\sim \text{ ps}]$$

- Dissociation patterns expected to depend on the type of electronic excitation

- Fragments carry information about the excited molecular ion state

Dissociative ionisation example: CO_2

Ionisation followed by dissociation of the molecular ion

Ionisation

$$CO_2 \rightarrow CO_2^{2+} + 2e^-$$

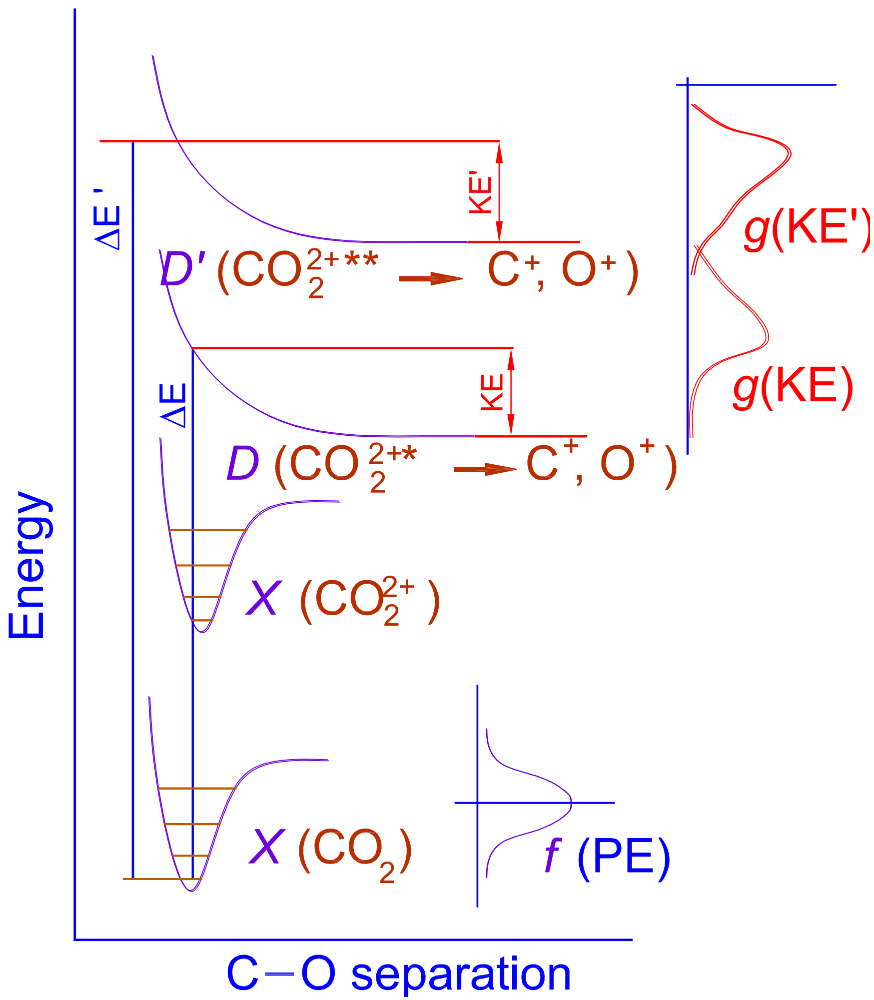
Concerted fragmentation

$$\begin{aligned}
CO_2^{2+} &\rightarrow O^+ + CO^+ \\
CO_2^{2+} &\rightarrow C^+ + O^+ + O \\
CO_2^{2+} &\rightarrow C + O^+ + O^+
\end{aligned}$$

Sequential fragmentation

$$\begin{aligned}
CO_2^{2+} \rightarrow CO^{2+} + O &\rightarrow C^+ + O^+ + O \\
CO_2^{2+} \rightarrow CO^+ + O^+ &\rightarrow C^+ + O + O^+
\end{aligned}$$

Energy diagram of dissociative ionisation



- Kinetic Energy released depends on
  - the participating excited state
  - the overlap of the ground-state with the excited state
- Also to be taken into account
  - fragmentation sequence
  - metastability
  - explosion geometry

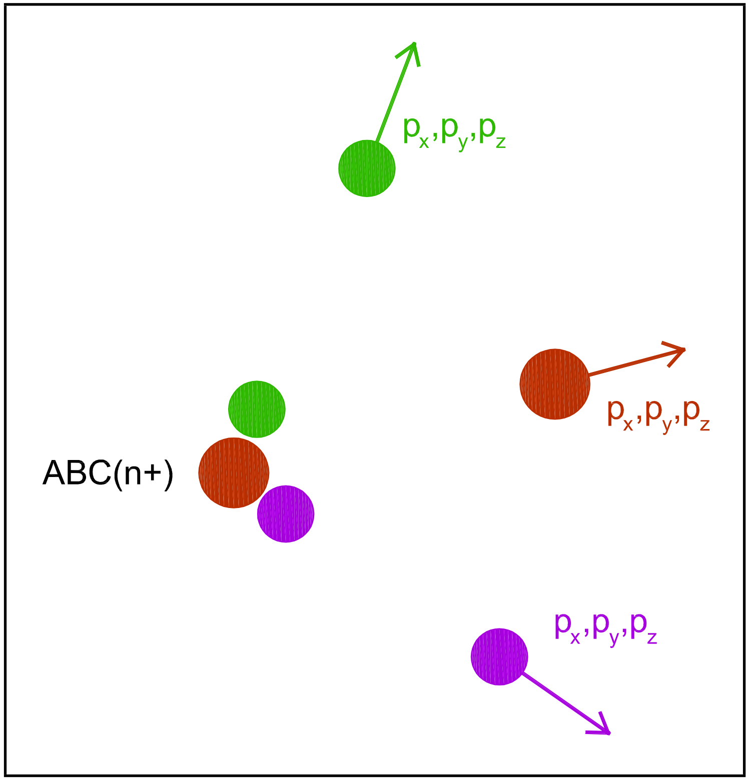
Molecular ions. . . dissociation dynamics

$$\mathrm{ABC} \rightarrow \mathrm{ABC}^{n+} \rightarrow \mathrm{A}^{p+} + \mathrm{B}^{q+} + \mathrm{C}^{(n-p-q)+}$$

- fragments give us clues : their kinematic properties are the leads
- for an N-body break-up, there are $3N-4$ free parameters in the momentum space
- N-particle continuum: $3N - 4\ (= k)$ free phase space coordinates
- Quantum-mechanically

$$T_{fi} = \langle f | \frac{q}{|b - \vec{v}_p\, t|} | i \rangle$$

$$|T_{fi}|^2 \Leftrightarrow d^k\sigma / dq_1 \ldots dq_k$$



Need kinematically complete measurements

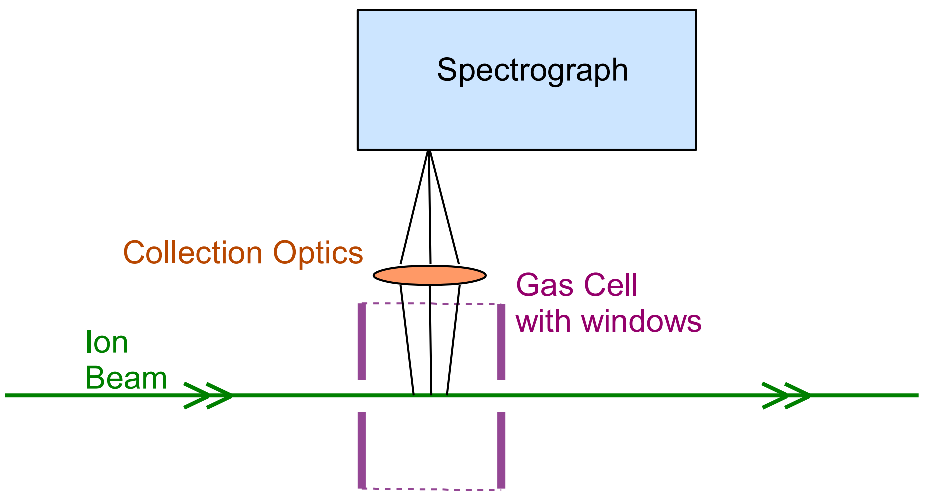
i.e. determine all momentum components of all fragments

Types of Collision Spectrometry

- Collision-induced fluorescence
- Translational Energy Spectrometry
- Time-of-flight Spectrometry
- Ion Momentum Imaging
- Complete Kinematics : electron & ion coincidence mapping

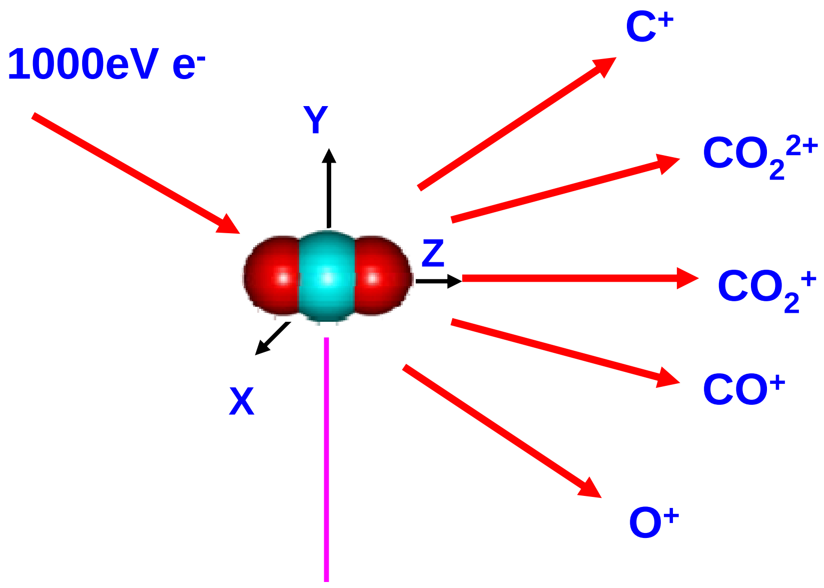
Collision-induced fluorescence

- Targets in the form of a cell (gas or liquid)
- limited to UV-VIS-IR wavelengths
- Targets not dense (to carry out collisions) so count rates low
- Not easy to get angular distributions and wavelength dispersion simultaneously.



Charged particle Spectrometry

- More "efficient" than photons, ability to count single particles
- Low number density OK
- Charged particles can be manipulated easily, while also dispersing them in velocity, mass etc, and deriving angular distributions



Translational Energy Spectroscopy

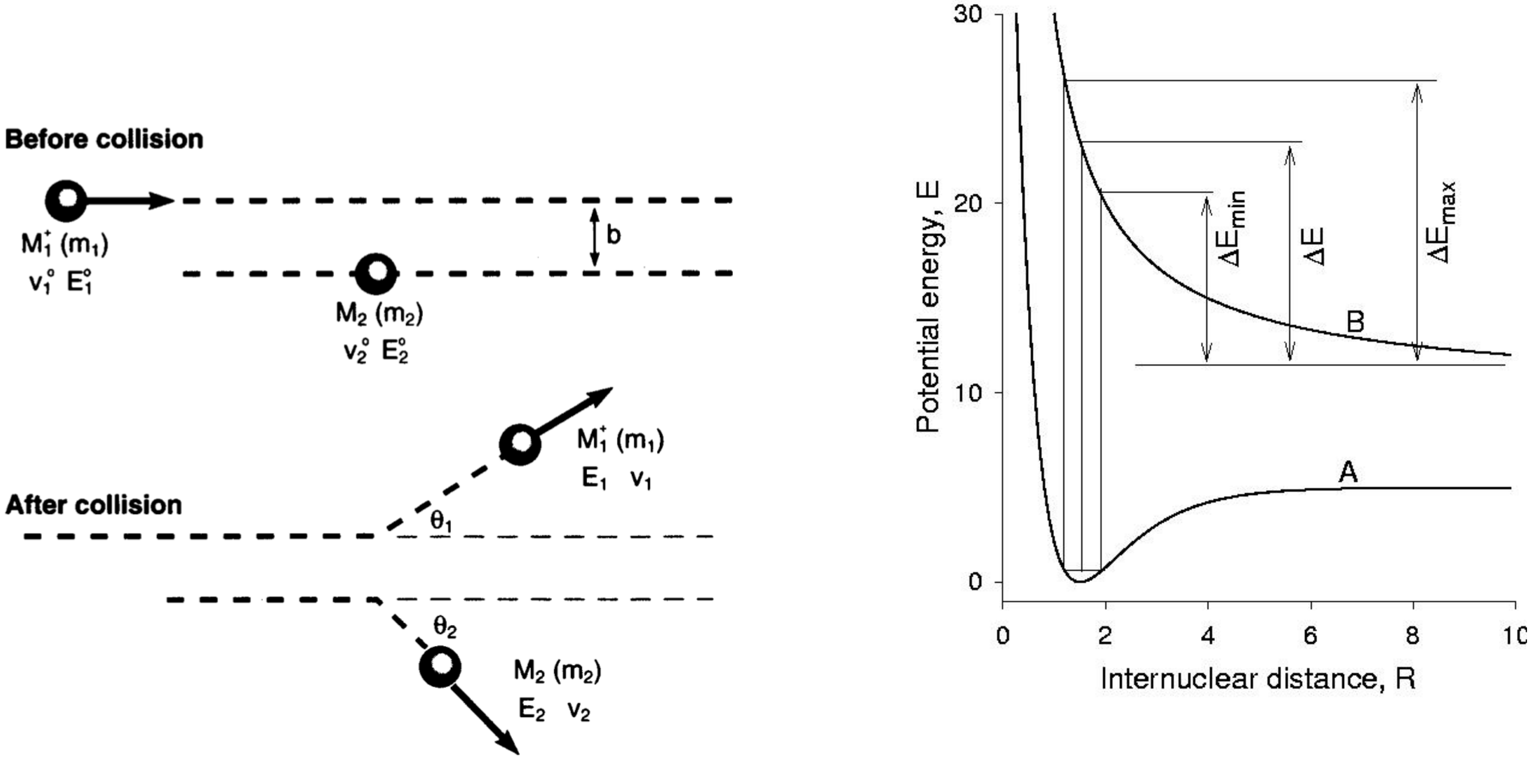
Technique

- A fast ion (a few keV in energy) is made to collide with a neutral target gas.
- Energy and angular deflection of scattered ion is measured.

Insights

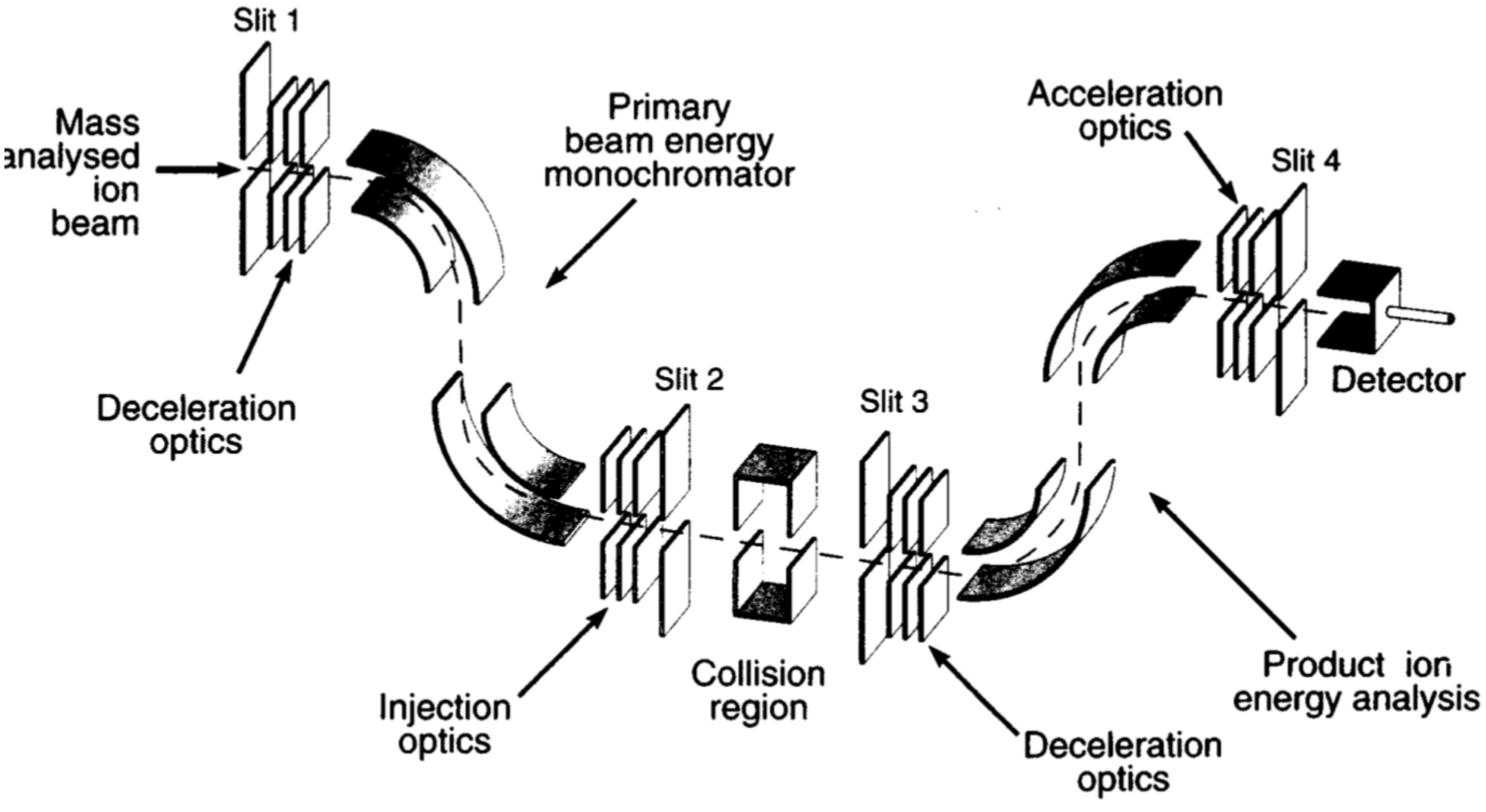
- the states of the participating species
- dynamics of the collision
- lifetimes of species
- collision cross-sections state populations

Translational Energy Spectroscopy



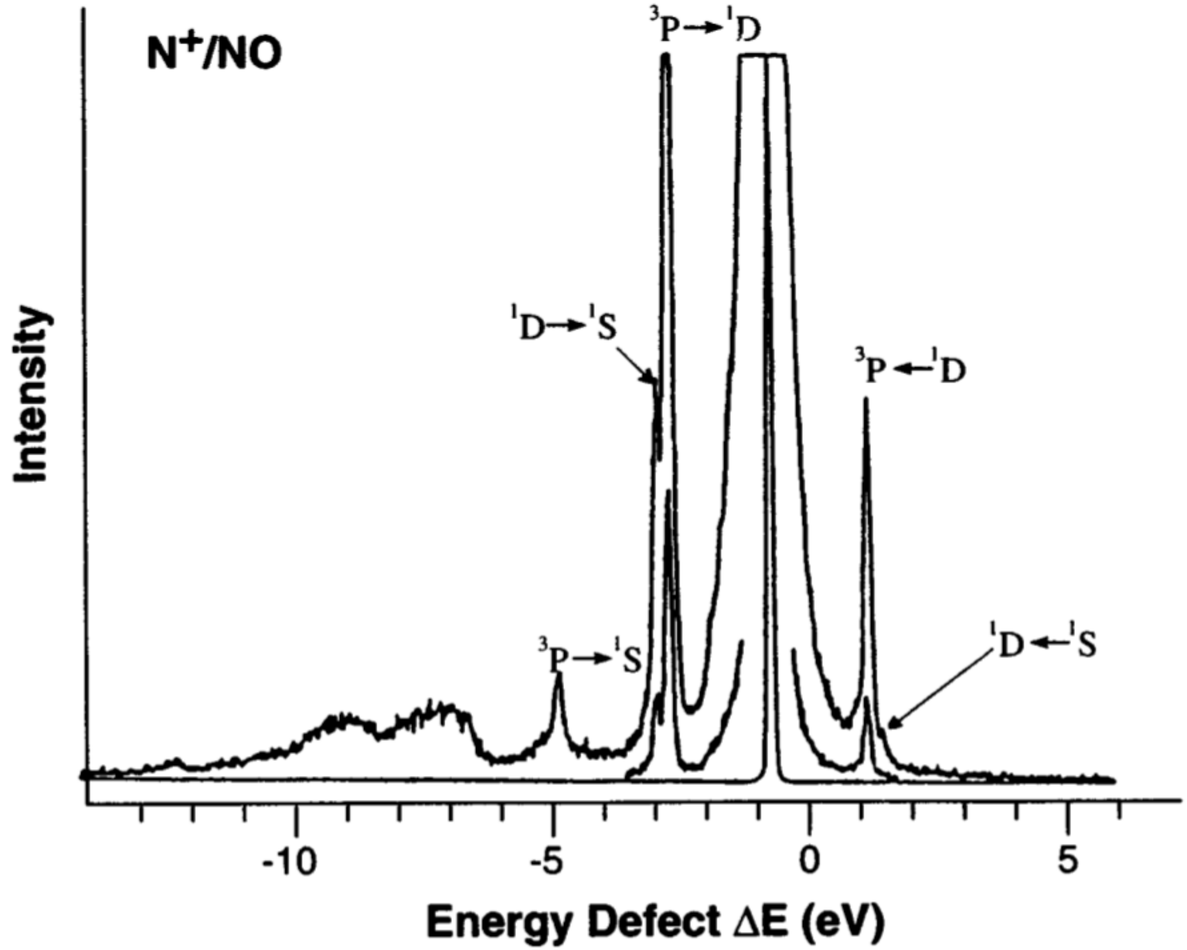
Binary collision between a fast ion and a neutral target

Translational Energy Spectroscopy



Arrangement of a high resolution energy loss spectrometer

Translational Energy Spectroscopy



TES spectrum of N_2^+ colliding with NO, at 3000 eV collision energy.

Motivation for other techniques

Limitations of TES

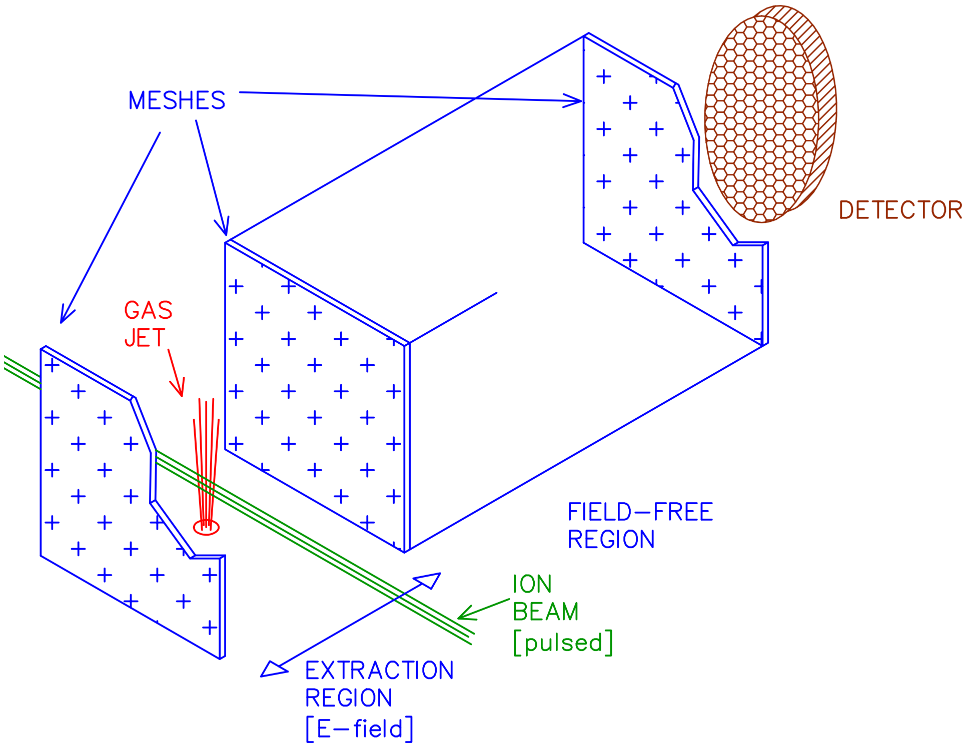
- Not very useful for dissociating species
- Low efficiency
- Large Equipment

Advantages of TOF

- Compact, simple apparatus
- Ability to collect multiple fragments

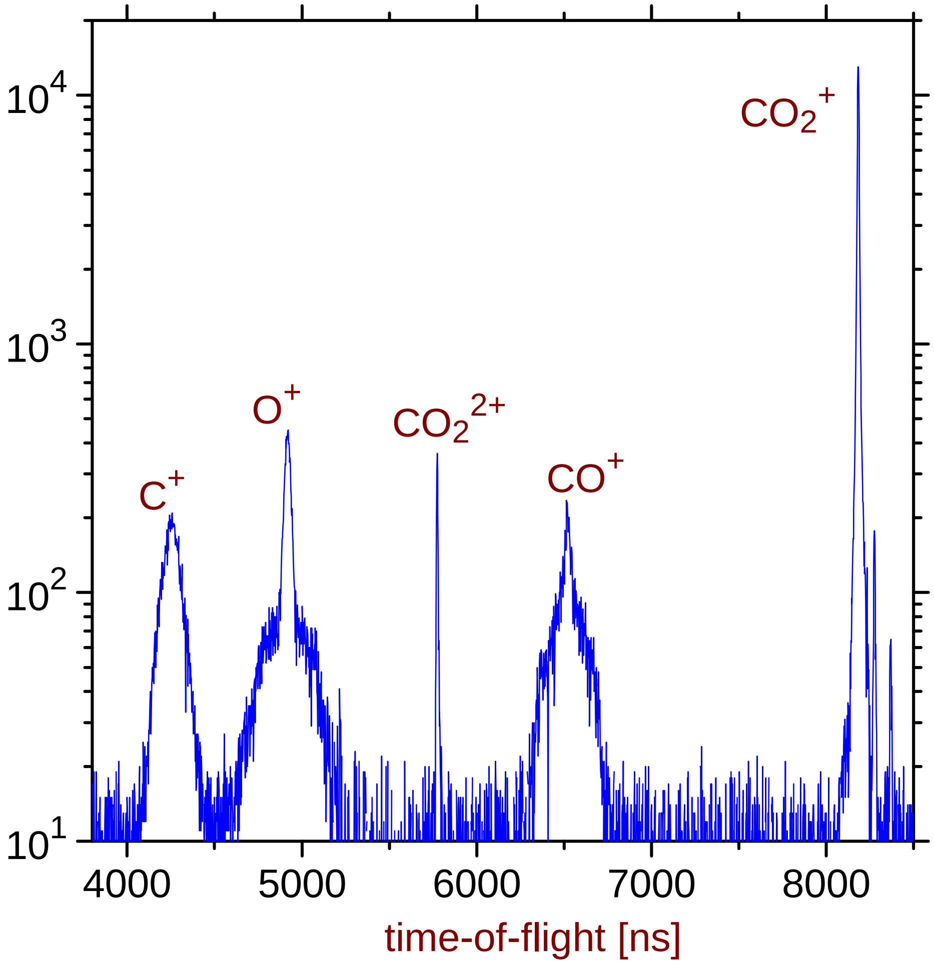
Time-of-Flight Mass Spectrometry : Technique

- A crossed molecular beam and ion beam arrangement
- Electric field to extract ions and transport them to a detector
- Event trigger
  - Pulsed ion beam
  - Pulsed extraction field
  - Ejected electron detection using separate detector
- Time-of-Flight to the detector measured w.r.t. the event trigger
- A fast response detector to record successive ion arrivals

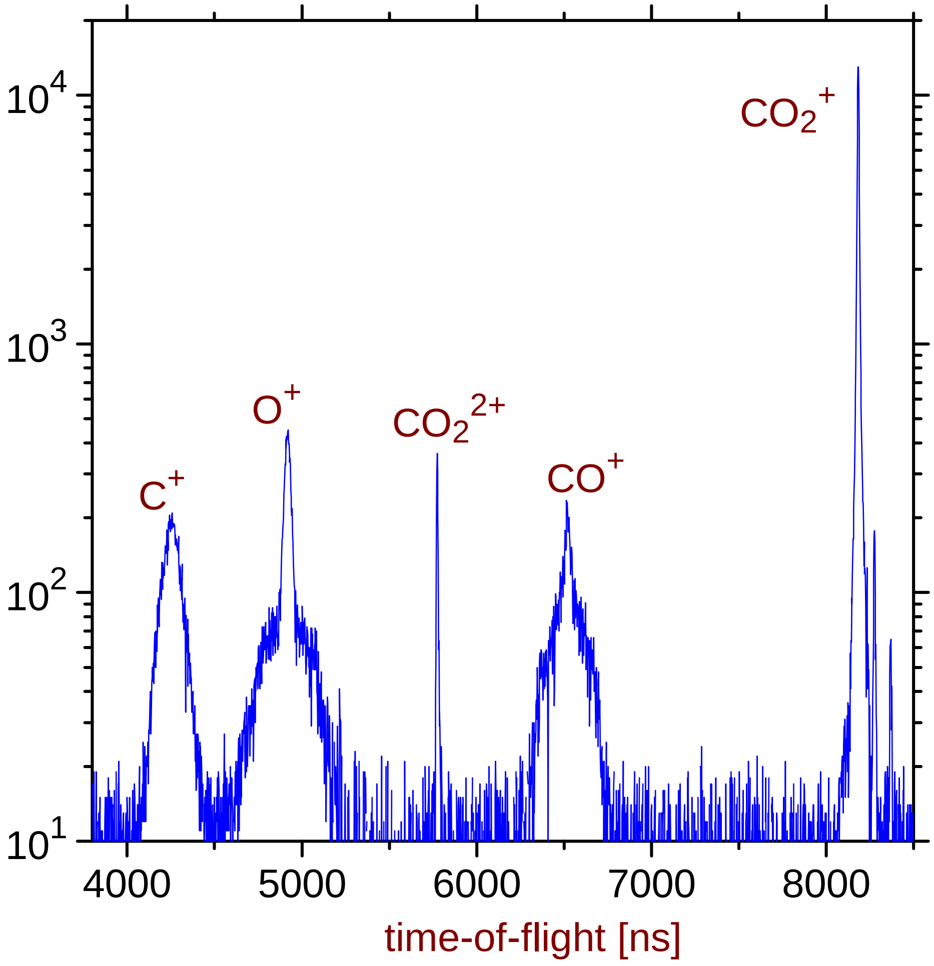


$$TOF \propto \sqrt{\frac{m}{q}}$$

TOF: sample spectrum

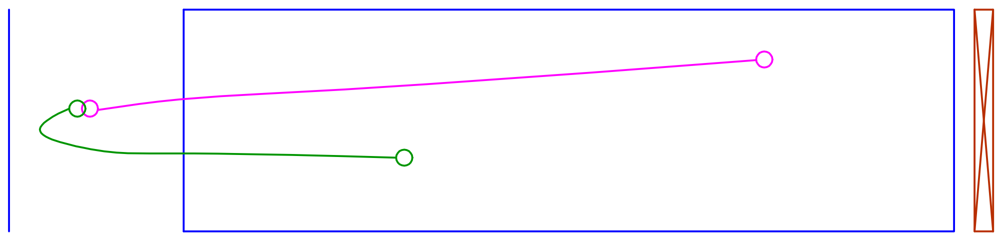


TOF: insights into dissociation dynamics



- Gives fragment ion mass and (to some extent) kinetic energy information
- Determination of dissociation pathways (which fragments are formed)
- Glimpse into dissociation mechanisms (sequences, rearrangements etc.)

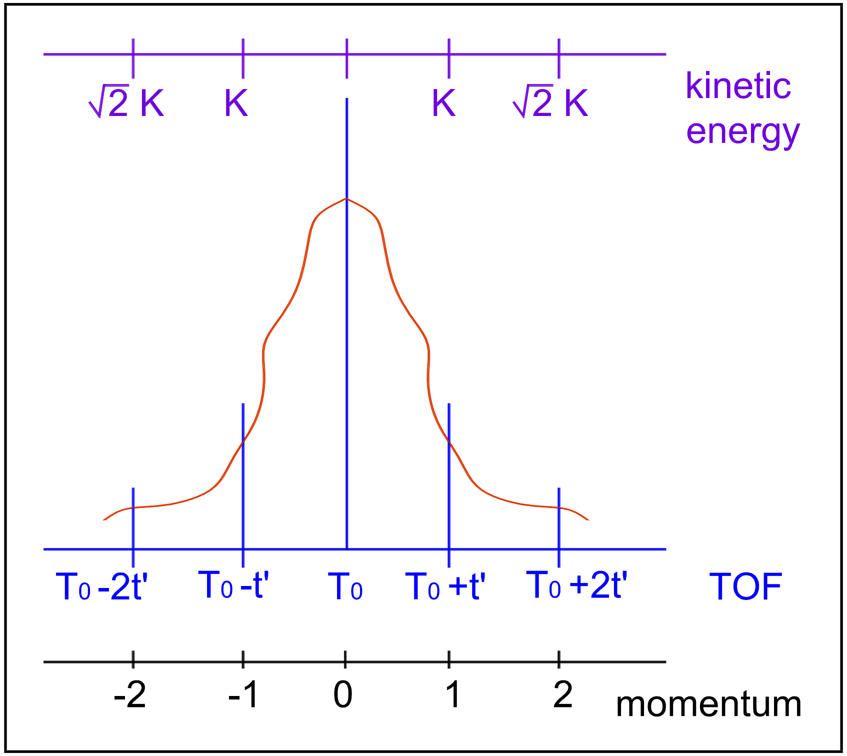
TOF : kinetic energy information



- In general, $t \equiv t(m, q, p_{||}, \vec{E}, s, d)$
- *Assuming equipartition*, KE of every ion can be *estimated*:

$$p_{||} \approx (t - T_0)qE$$

$$KE \equiv 3p_{||}^2/2m$$

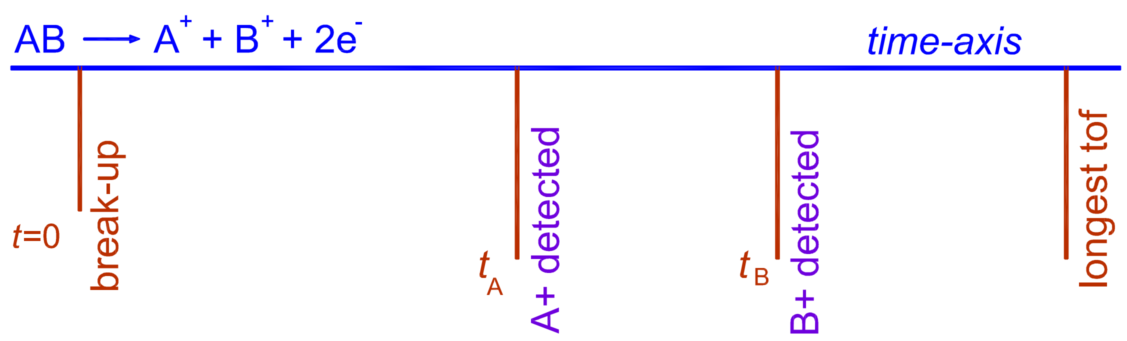


TOF : multi-ion-coincidence

- Record all ions arising from one event

$$\mathrm{ABC} \rightarrow \mathrm{ABC}^{2+} \quad [+2e^{-}] \rightarrow \mathrm{A}+ + \mathrm{B}^{+} + \mathrm{C}$$

- TOF techniques allow recording in a sequence



- Create correlation map
  - for each ion from each event, record $t_1, t_2 \ldots$
  - repeat for several events – list mode
  - Sort the correlated time pairs and look for patterns

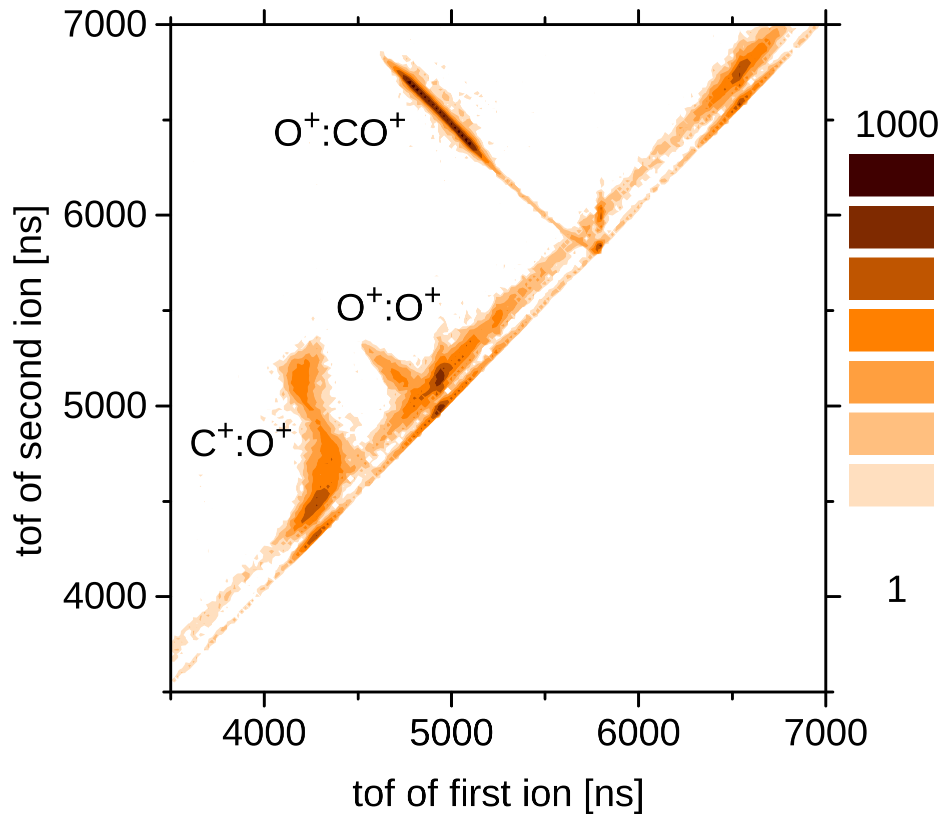
TOF : ion-ion-correlation maps

Fragmentation Pathways

- Detect ion pairs from a break-up
- Plot a correlation map of the pairs
- Patterns in the map:

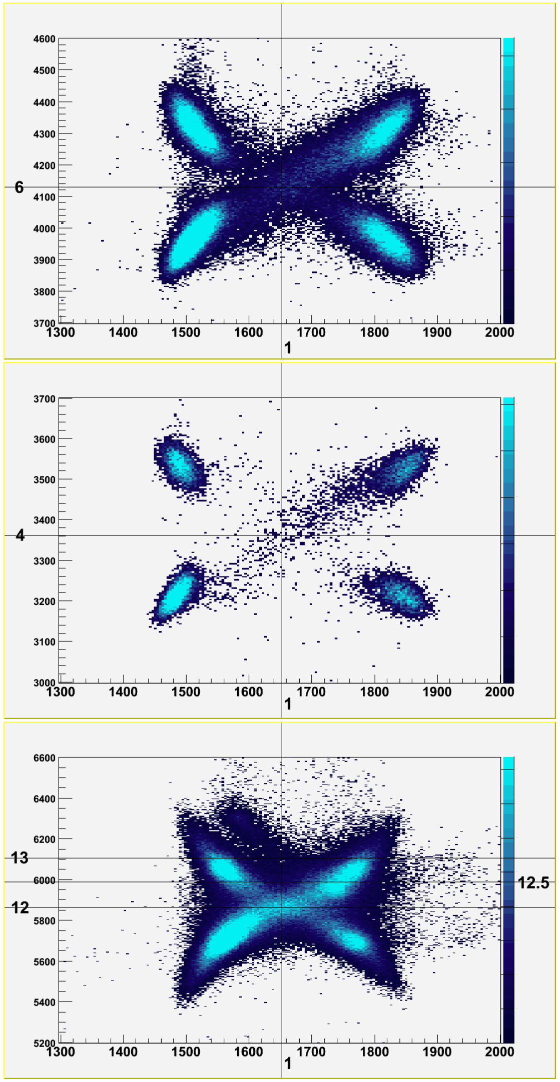
$$\text{slope} = -\frac{p_{2||}}{p_{1||}} \cdot \frac{q_1}{q_2}$$

Size of blob ≡ Kinetic Energy release
Shape of the blob ⇒ fragmentation sequence



ion-ion correlation map of CO_2 fragments

TOF : ion-ion-correlation



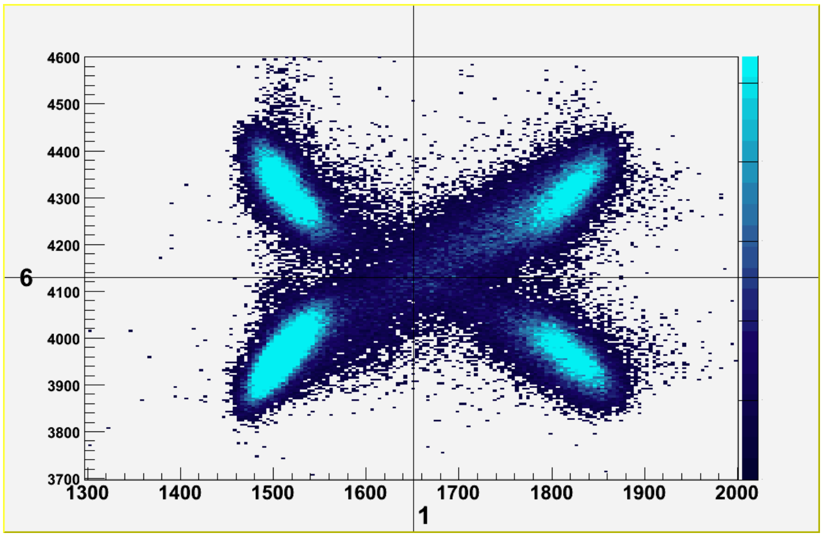
Acetylene molecule under ion impact:

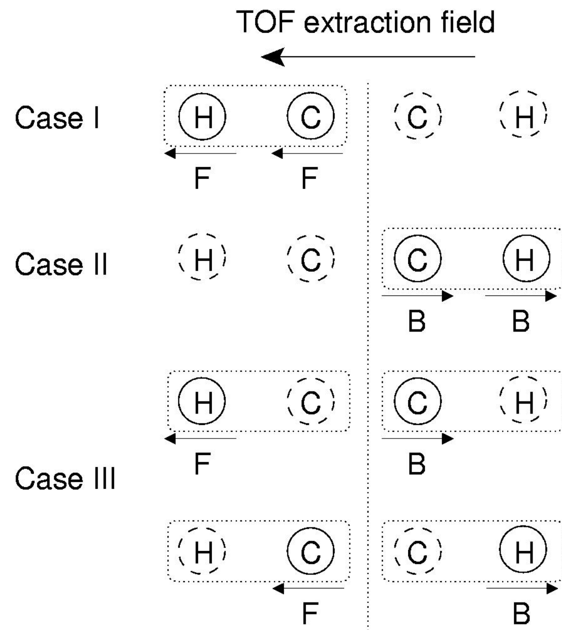
$Ar^{8+} + C_2H_2 \rightarrow C^{2+} + H^+ + X$

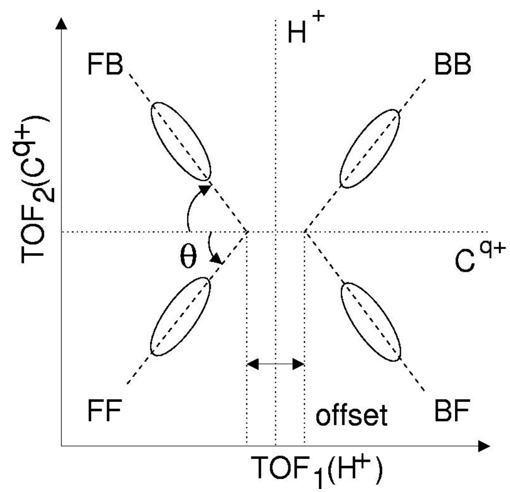
$Ar^{8+} + C_2H_2 \rightarrow C^{3+} + H^+ + X$

$Ar^{8+} + C_2H_2 \rightarrow C^{+} + H^+ + X$

TOF : ion-ion-correlation







Shapes and orientation of the blobs (islands) can be analysed for dissociation kinematics to reveal the internal motion of the molecular ion!

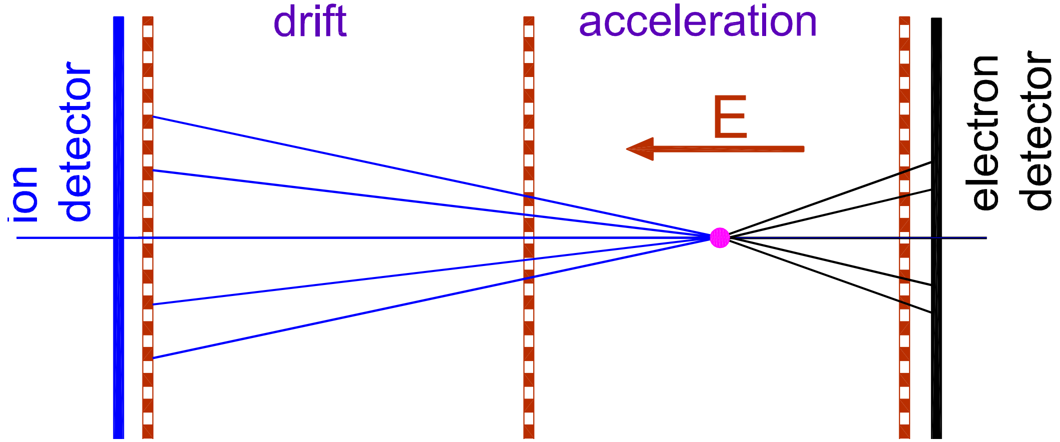
TOF : motivation for Coincidence Momentum Imaging

Do we have complete information about the fragmentation dynamics
(from TOF-TOF correlation maps)?

No! We have incomplete kinetic energy information, no angular information – need full momentum information.

Coincidence Momentum Imaging : axial components

Ions (mass m, charge q) are extracted by a uniform electric field ($\vec{E}$)



- Flight time (t) from formation to detection is measured
  - start: pulsed ion source or electron detection
  - stop: ion detection
- To nullify spatial spread influence

$$\ell(\text{drift}) = 2 \times \ell(\text{acceleration})$$

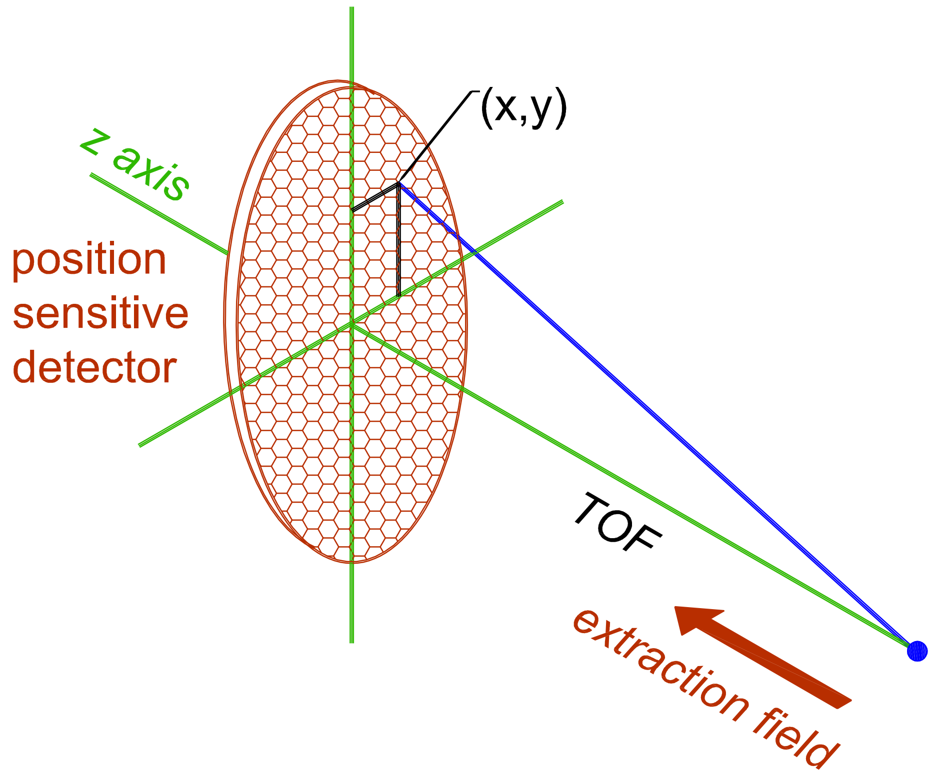
- For $p_z = 0$

$$t_0 = [8s/E]^{1/2} [m/q]^{1/2}$$

- For an arbitrary ion

$$p_z \approx (t_0 - t)qE$$

Coincidence Momentum Imaging : Transverse components



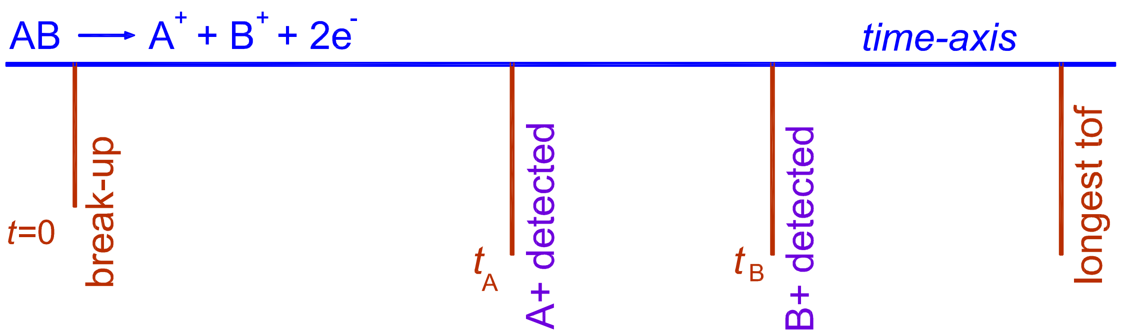
- transverse components of momentum determine the deflection of the particle from the axis
- a large area position resolving detector is required
- if the flight time is known, (x, y) can be easily related to the transverse momenta

$$p_x = m(x - x_0)/t$$
$$p_y = m(y - y_0)/t$$

CMI : multi-ion-coincidence

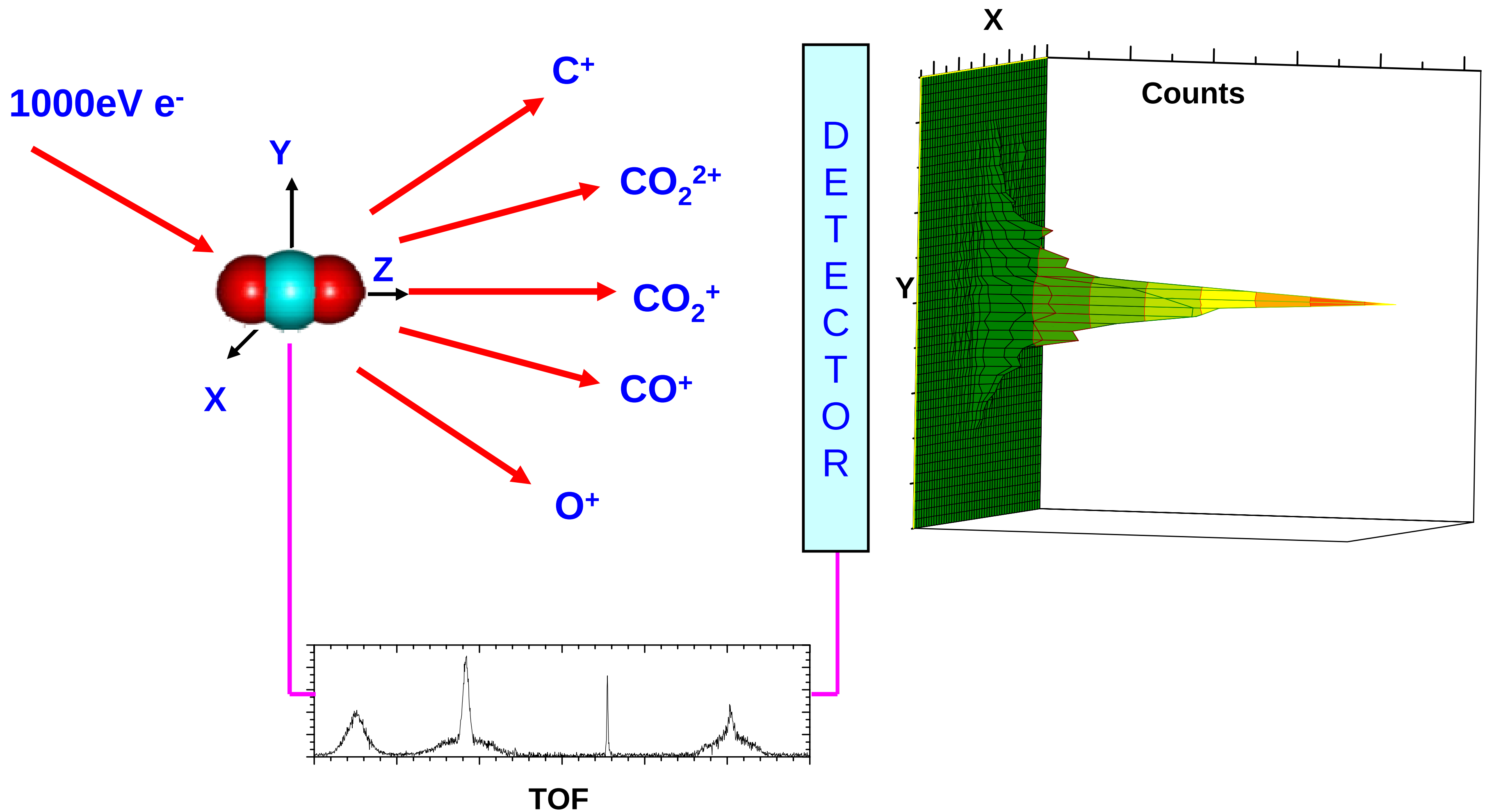
- Record all ions arising from one event

$$ABC \rightarrow ABC^{n+}[+ne^-] \rightarrow A^{n_1+} + B^{n_2+} + C^{(n-n_1-n_2)+}$$



- Create correlated momentum map
  - for each ion from each event, record (t_i, x_i, y_i)
  - repeat for several events – list mode
  - transform $(t, x, y) \Longrightarrow (p_z, p_x, p_y)$ for all ions from each fragmentation

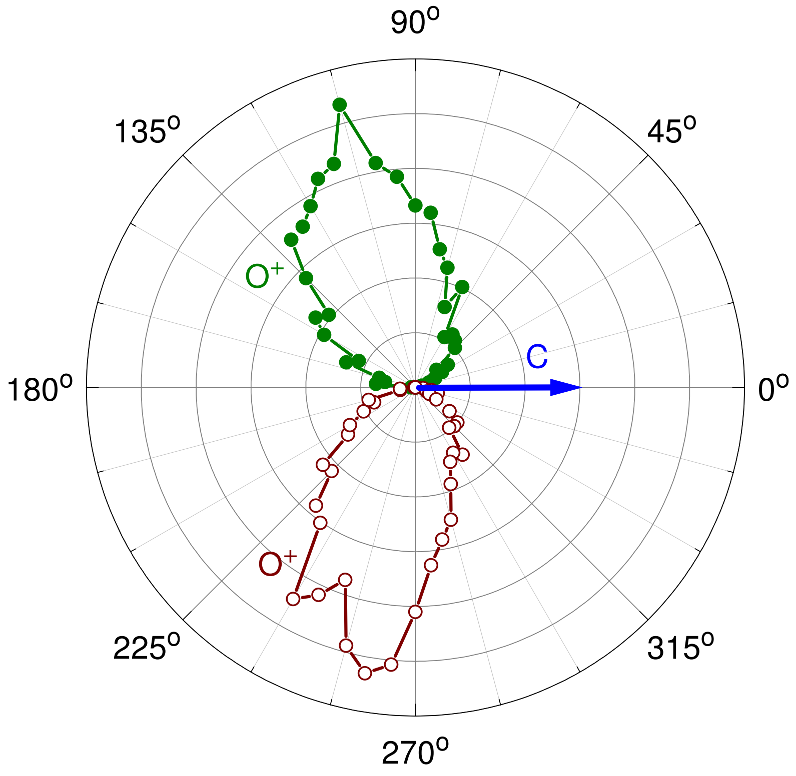
CMI : complete momentum map



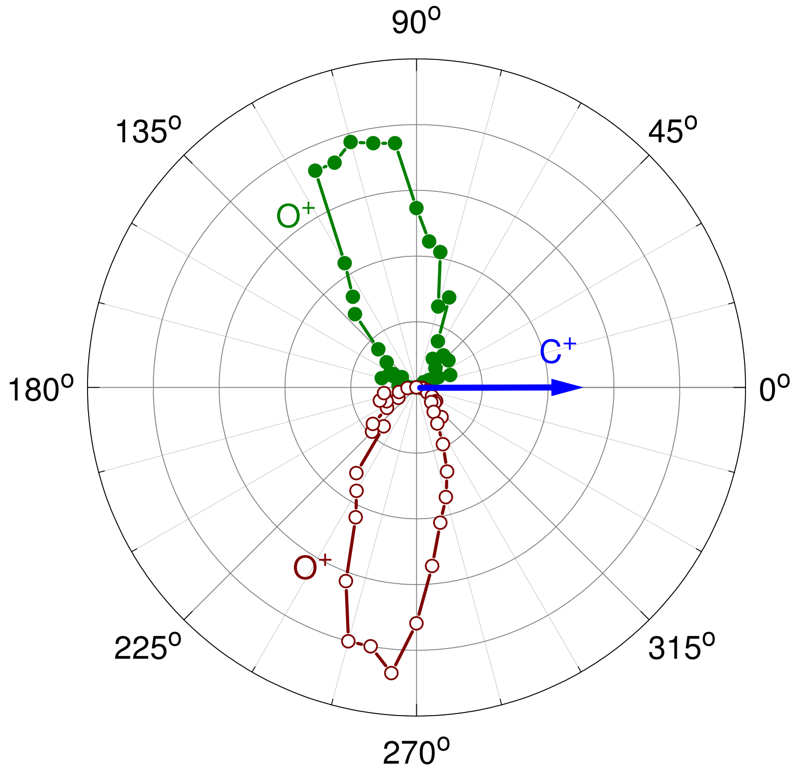
Position and TOF are simultaneously recorded and stored as a list of *x*, *y*, *t* triplets

CO_2 : angular distribution of fragment ions

$CO_2^{2+} \rightarrow C + O^+ + O^+$



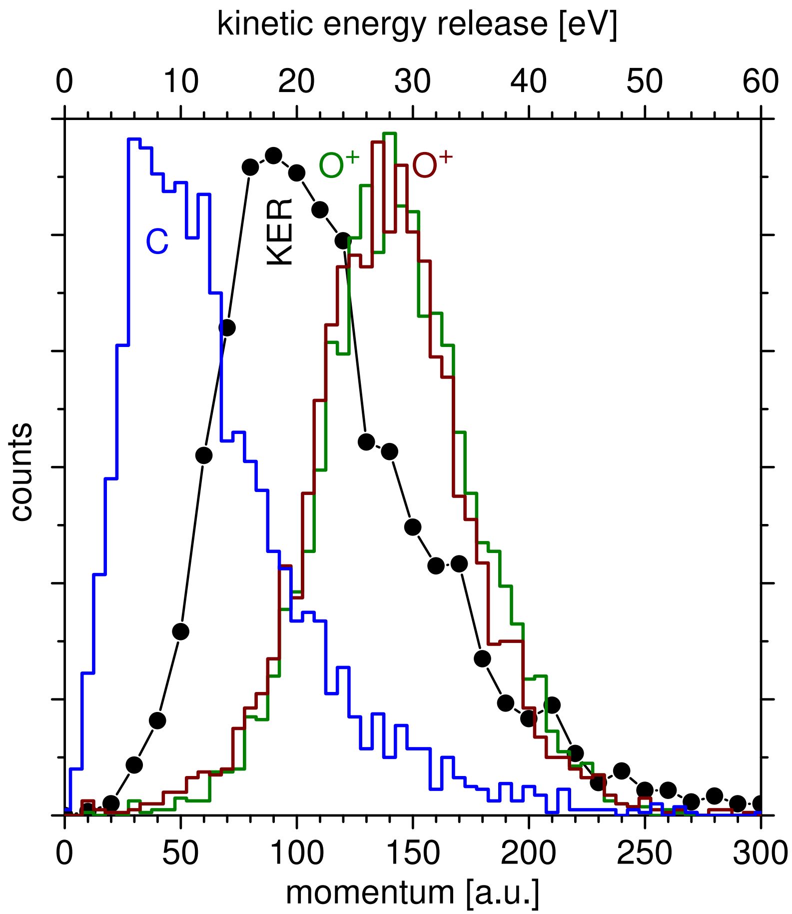
$CO_2^{3+} \rightarrow C^+ + O^+ + O^+$



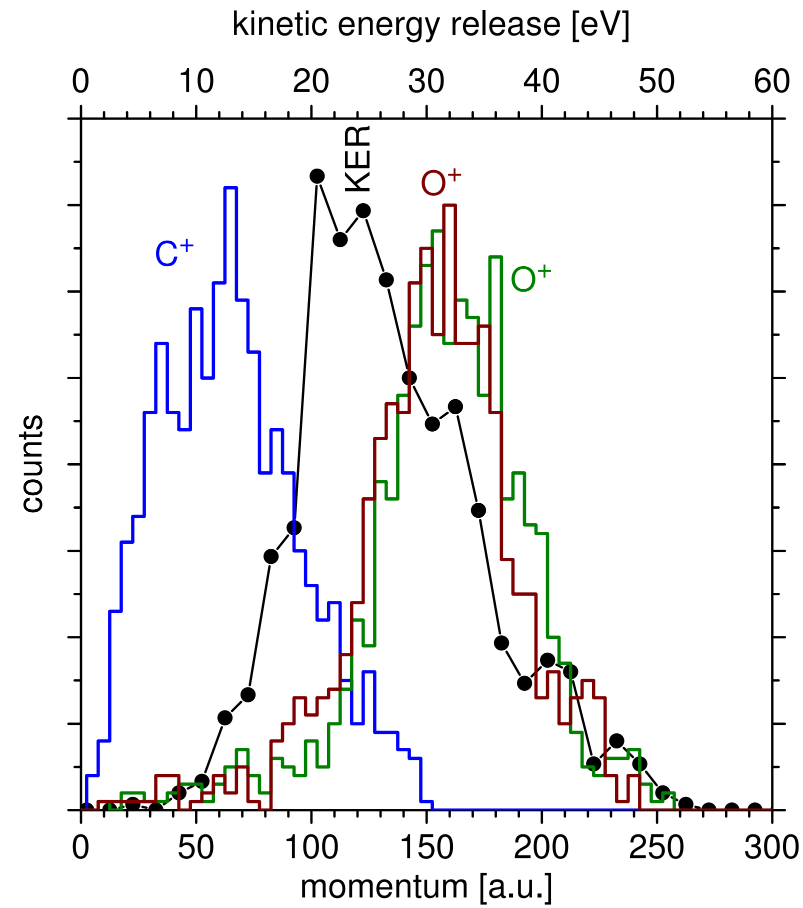
Deviation from linear structure?

CO_2 : kinetic energy distribution of fragment ions

$$CO_2^{2+} \rightarrow C + O^+ + O^+$$



$$CO_2^{3+} \rightarrow C^+ + O^+ + O^+$$



Non-coulombic fragmentation

CMI : insights

We can discern from such maps

- Angular distribution of fragments in the molecular reference frame
- Bond angle at the instant of formation
- Kinetic Energy Release distribution

Coincidence Momentum Imaging

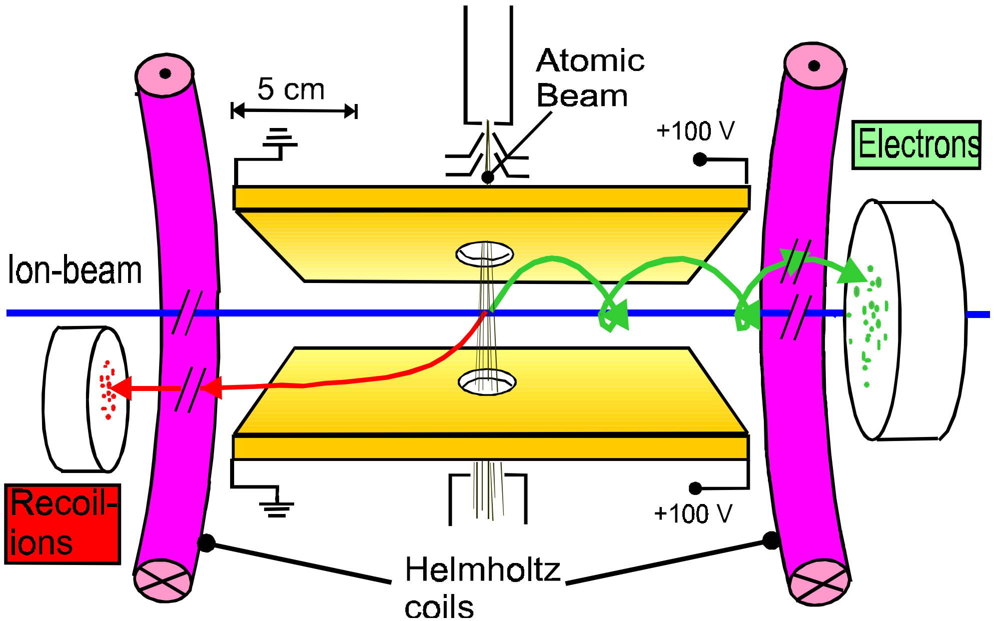
Do we now have complete information about the fragmentation dynamics
(From coincidence momentum imaging)?

No! We have ignored the electrons!!

Still far away from tackling the quantum-mechanical coulomb many-body problem

Dissociative Ionisation : the complete picture

Detection and identification of all the ionic fragments along with the electrons emitted in the process:



- Electron energy and dissociation fragments are detected in coincidence
- Momentum vectors are determined by TOF/imaging methods
- Need short pulse ion beams
- Need (very) fast detectors and electronics

Summary

- Several techniques exist for investigting ion molecule collisions
- Deep insights can be had into dissociative ionisation by looking into ion channels
- Some handle on structure and dynamics of molecular ions from collision studies
- Plenty of scope for further investigations – "complete experiments"