# Understanding multiply-charged molecular ions through their break-up

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Physical Research Laboratory, Ahmedabad

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# The People

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**From RRCAT**

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# Publications related to this talk

- *Journal of Chemical Physics* **139** 164309 (2013)
- *Review of Scientific Instruments* **84** 073101 (2013)
- *Journal of Physics B* **43** 205204 (2010)
- *Journal of Physics B* **42** 105201 (2009)
- *Physical Review A* **78** 042503 (2008)
- *Journal of Physical Chemistry* **111** 10205–10211 (2007)
- *Journal of Physics B* **40** 13–19 (2007)
- *Physical Review A* **74** 022708 (2006)

# What is experimental atomic and molecular physics?

- Obtaining information about the structure and dynamics of atoms and molecules (neutral and charged) 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!
  - significant technology fallouts: materials science, medical applications etc.
- Experimentally tackle the quantum many-body coulomb problem;
- Standard chemistry different from interaction of single molecules!

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Focus of this talk: multiply charged molecular ions

# Structure of a Molecule

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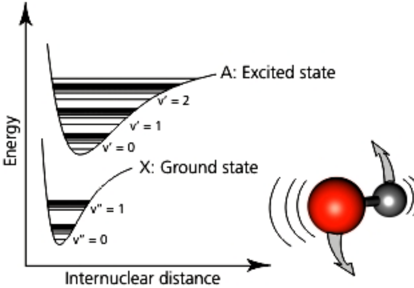
- Large difference in masses of nuclei and electrons permits decoupling of degrees of freedom: rotational, vibrational, electronic
- The net energy of the molecule can be conveniently depicted as a function of the internuclear separation for a given electronic configuration




meV: rotation
sub-eV: vibration
few eV: dissociation/ionisation

# Molecules vs. Molecular ions

- Molecules are stable: usually several stable states
  - energy levels and other static properties are spectroscopically accessible
- Singly charged molecular ions: usually at least one stable state
  - amenable to spectroscopy, but difficulties in having a large ensemble
- Doubly charged molecular ions: often one stable state, or at least a metastable state
  - inaccessible to spectroscopy; rich structure of the PE surfaces
  - *dissociative double ionisation* is particularly interesting
- Higher charged molecular ions : unstable, almost entirely repulsive PE surfaces

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

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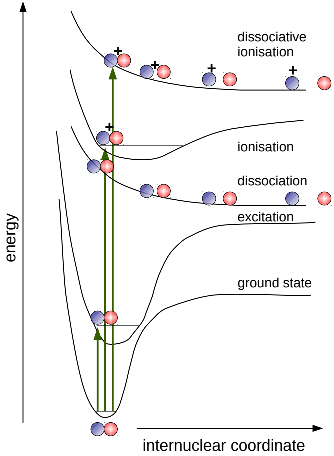
The effect of a perturbation is a change in the mean field seen by the nuclei, causing the nuclei to respond to it

- A perturbation may take a molecule to a high-lying state – leading to dissociative ionisation
- Ionisation and dissociation occur on differing time scales

$$\begin{aligned} AB &\xrightarrow{\gamma, q} AB^{n+} + e^- \quad &[fs] \\ AB^{n+} &\longrightarrow A^{p+} + B^{q+} \quad &[ps] \end{aligned}$$

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



# 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
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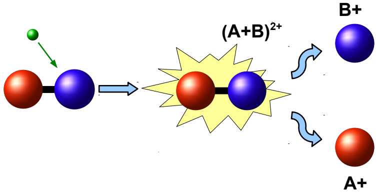
...and study the response

- Detect charged particles or photons, which carry information about the response of the target
  - Ion mass spectrometry
  - Electron energy spectroscopy, angular distributions
  - Photon spectroscopy
- Can combine two or more of the above
- Focus here is on double ionisation and dissociation of molecules

# Molecular ions. . . dissociation dynamics




$$AB \rightarrow AB^{2+} + 2e^{-} \rightarrow A^{+} + B^{+} \; (+\, 2e^{-})$$

fragments give us clues : their kinematic properties are leads to the transient state

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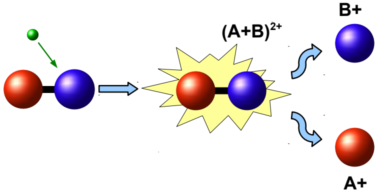


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- for an $N$-body break-up, there are $3N - 4$ free parameters in the momentum space
- $N$-particle continuum: $3N - 4\ (= k)$ free phase space coordinates
- Quantum-mechanically

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

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

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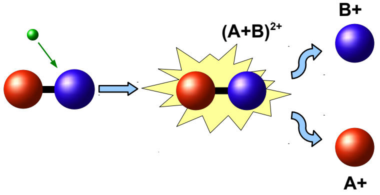


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- Experimental Challenge: detect all fragments and determine all momentum components of each fragment (Kinematically complete measurements)
- No exact solutions to the multi-electron Schrödinger equation
- Measurement of DCS enhances our understanding of the dynamics

# Experimental Strategy

- Create molecular ions by the overlap of a neutral beam and an ionising beam under single collision conditions
- Detect all ions formed in a single collision in coincidence
- Measure the momentum vector of each ion
- Obtain complete correlated kinematic information of all fragments

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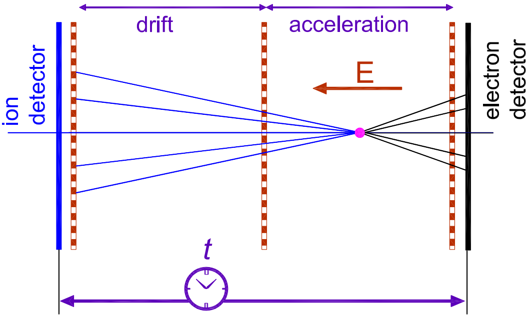
- Obtain complete correlated kinematic information of all fragments
- As perturbing agents our experiments employ
  - electrons [at PRL]
  - soft x-rays [Indus-1]
  - ions [IUAC Delhi]
  - All spectrometers built in-house

# CMI : mass separation and axial momentum components




- Ions (mass $m$, charge $q$) are extracted by a uniform electric field ($\vec{E}$)
- Flight time ($t$) from formation to detection is measured
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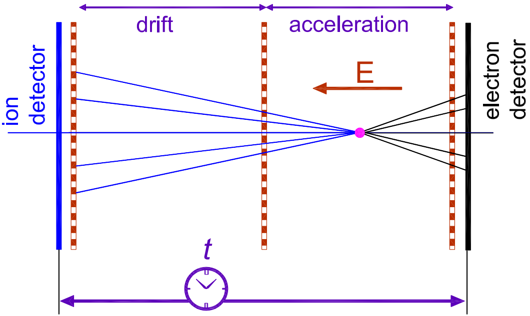


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- If $p_{||} = 0$

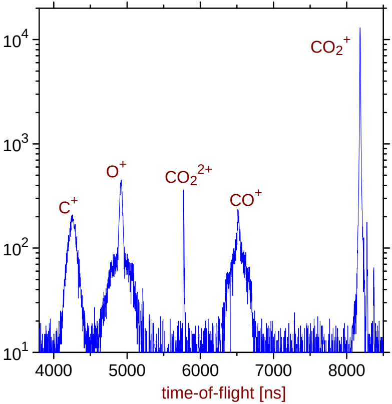
$$t_0 = [8s/E]^{1/2} \, [m/q]^{1/2}$$

- For an ion with arbitrary $\vec{p}$

$$p_{||} \approx (t_0 - t)qE$$

# ToF spectra: a glimpse into dissociation dynamics

$$e^- + CO_2 \rightarrow CO_2^{n+} \rightarrow \text{fragments}$$




What does a ToF spectrum tell us?

- Identification of fragment ion mass/charge and (to some extent) kinetic energy information
- Indication of dissociation pathways (which fragments are formed)
- Glimpse into dissociation mechanisms (sequences, rearrangements etc.)
- To study doubly charged molecular ions, we need to go a step further

# ToF : ion-ion-correlation maps

Double Ionisation/dissociation

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

Concerted dissociation

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

Sequential dissociation

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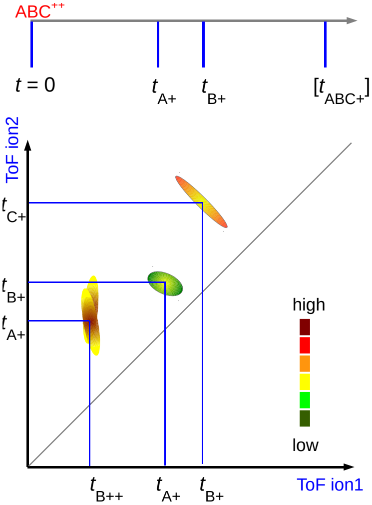


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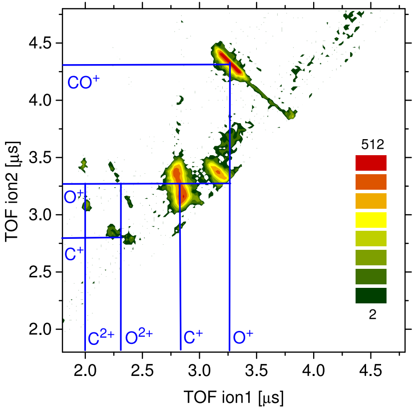
# ToF : ion-ion-correlation maps

Patterns in the map provide insight into fragmentation dynamics

- Position of the island:
  Fragmentation products
- Shape and slope of the island:
  Fragmentation sequence
- Extent of the island:
  Energy release

$CO_2 \rightarrow CO_2^{2+} \rightarrow$ fragments



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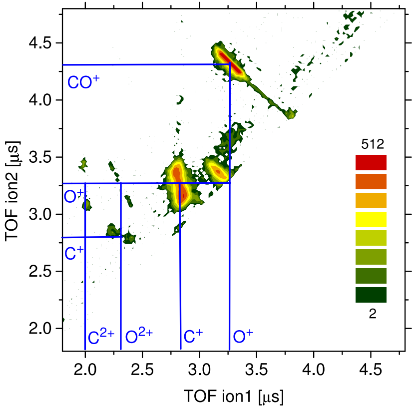
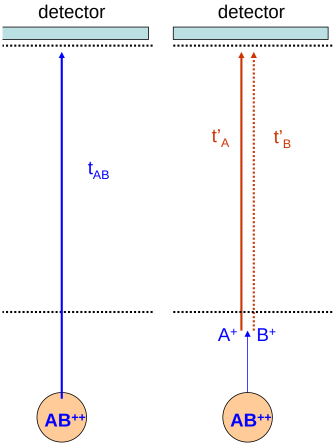



*What's the tail to $CO^+$:$O^+$?*

# Metastable Excited States




- an excited molecular ion in a metastable state may decay into a pair of fragments
- there will be a statistical distribution of the decay time
- under the action of the electric field, the molecular ion will decay at different distances from the detector
- the flight time of the fragments will show up as a tail in ion-ion coincidence map

# Excited State Lifetime

$CO_2^{++} \rightarrow CO^+ + O^+$

- Dissociation is associated with a repulsive PE energy function
- A metastable decay is associated with a finite barrier in the PE function
- This is the case with excited states of $CO_2^{2+}$
  (and a few other species, e.g. $SF_4^{2+}$)
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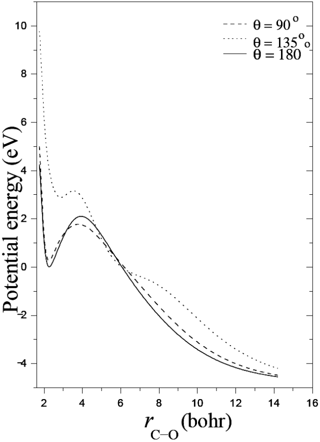
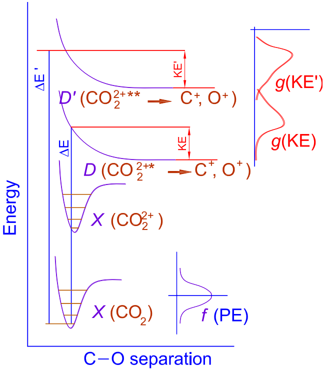


# KER and Excited state energy levels

- KER depends on the overlap of the ground-state with the excited state and the topology of the PES



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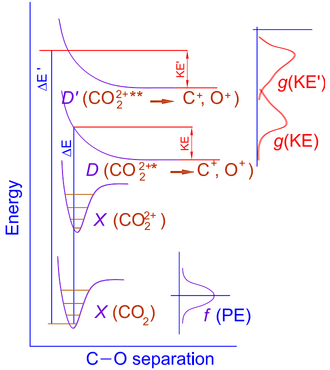


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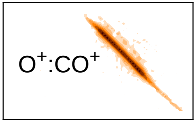


- KER can be derived from the extent of the correlation island (i.e. the the momentum difference of the ion pair)

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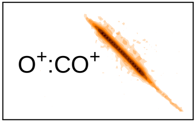


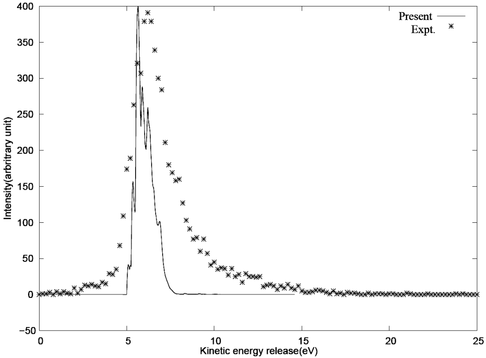


Spectroscopy of excited molecular ion states is effected by mapping KER distribution to excitation functions and calculated of potential energy surfaces

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So far only one component of momentum has been tackled – for complete kinematics we need the remaining momentum components too.

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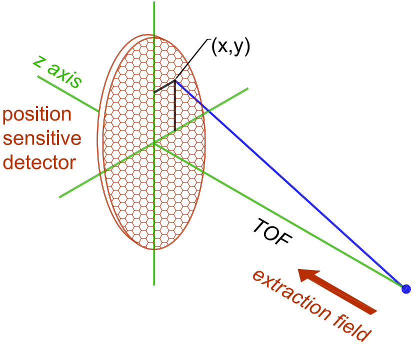


Recall : $p_z \approx (t_0 - t)qE$

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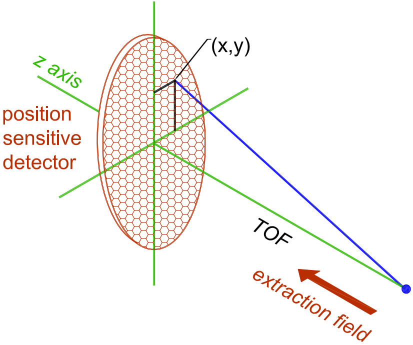


- transverse components of momentum determine the deflection of the particle from the axis
- a large area position resolving detector is required
- if the flight time is known, $(x, y)$ can be easily related to the transverse momenta

$$
\begin{aligned}
p_x &= m(x - x_0)/t \\
p_y &= m(y - y_0)/t
\end{aligned}
$$

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

# CMI : momentum maps

$$\begin{aligned} \mathrm{ABC} &\longrightarrow \mathrm{ABC}^{n+} \quad [+\ ne^-]; \\ \mathrm{ABC}^{n+} &\longrightarrow \mathrm{A}^{n_1+} + \mathrm{B}^{n_2+} + \mathrm{C}^{(n-n_1-n_2)+} \end{aligned}$$

Transform:
$(t, x, y) \mapsto (p_z, p_x, p_y)$
for for all ions from each event

Fragment momenta $\gg$ parent momenta
$\Rightarrow$ lab frame = molecular CM frame

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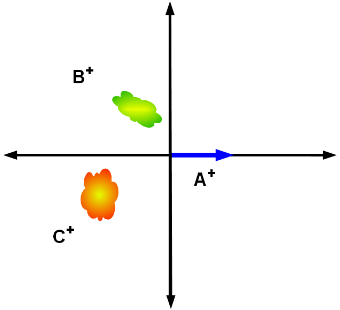
for for all ions from each event

- Derive any desired kinematic parameter from the correlation map
- If one fragment is neutral, its momentum vector can still be derived by applying conservation rules.

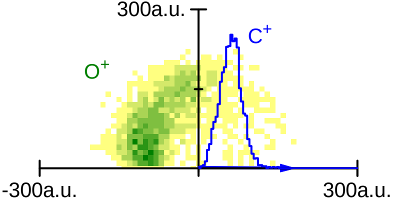
Fragment momenta $\gg$ parent momenta
$\Rightarrow$ lab frame = molecular CM frame



# $CO_2^{2+}$ : 3-body break-ups

- angular distributions in the molecular frame, with $\vec{p}_{ion1}$ as reference

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

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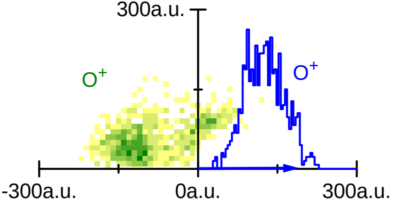
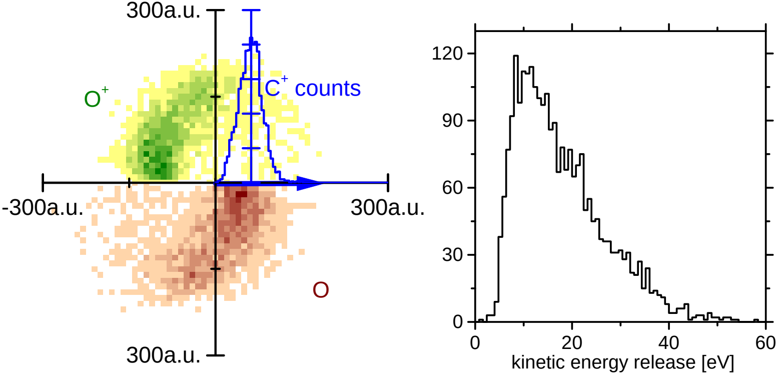



- $\vec{p}_{neut}$ determined from momentum balance in the reaction

# $CO_2^{2+}$ : $C^+$,$O^+$,O break-up




- Most probable $[O–C–O]^{2+}$ bond angle $\approx 155 \pm 8^\circ$
- mean KER $=15.5 \pm 4.1$ eV

# Photo-triple-ionisation of $CO_2$

$$\gamma\ [200\ \text{eV}] + CO_2 \quad \rightarrow \quad CO_2^{3+} \quad \rightarrow \quad C^+ + O^+ + O^+$$

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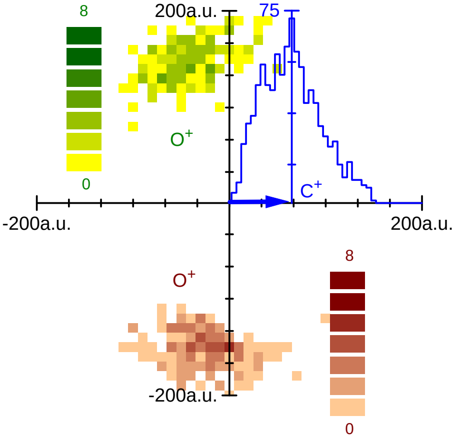

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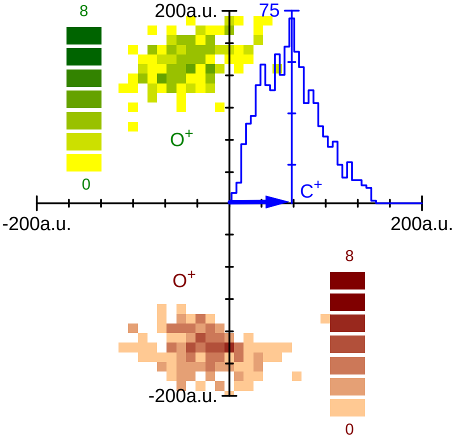


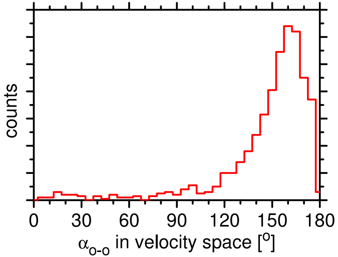


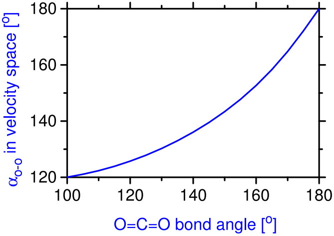

# Back to the PES

$$\gamma\ [200\ \text{eV}] + CO_2 \quad \longrightarrow \quad CO_2^{3+} \quad \longrightarrow \quad \text{fragments}$$

| Experimental branching ratios | | | |
|---|---|---|---|
| $C^{2+}$ | $O^{+}$ | | 0.212 |
| $O^{2+}$ | $C^{+}$ | | 0.142 |
| $O^{2+}$ | $O^{+}$ | | 0.133 |
| $C^{+}$ | $O^{+}$ | $O^{+}$ | 0.517 |

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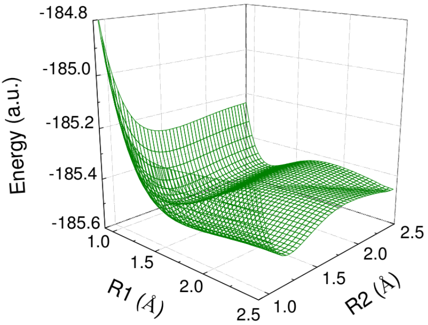
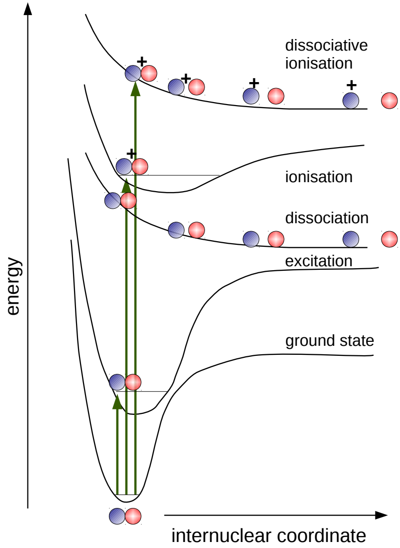



PE surface indicates that asymmetric break-ups are energetically favoured, but this contradicts experiment

# Further: Selectivity in excitation



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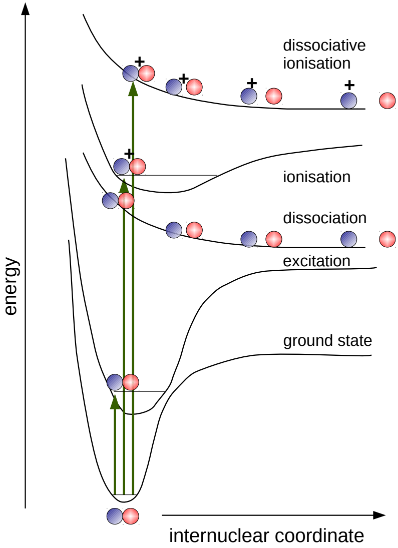
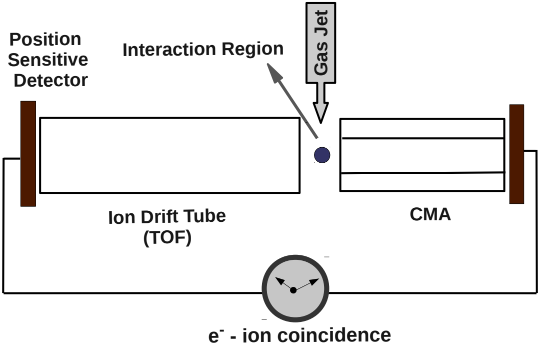



- Dissociation patterns expected to depend on which molecular state is accessed by the excitation
- Can we control or select the excited state that participates in the DI process?
- Such selectivity will bring us closer to the goal of experimentally measuring the fully diferential cross-section to enable a direct comparison with theory
- Selectivity can be brought in by obtaining correlated ion momentum distributions in conjunction with ejected electron energies

# Selectivity in excitation : Technique




- Crossed photon and molecular beams, single collision conditions
- Ion momentum spectrometer augmented with theelectron analyser (CMA)
- Electrons of specific energy, selected by the CMA, start the ion TOF clock

# Selectivity in excitation

- Target: OCS
- Valence electronic configuration $(6\sigma)^2(7\sigma)^2(8\sigma)^2(9\sigma)^2(2\pi)^4(3\pi)^4$
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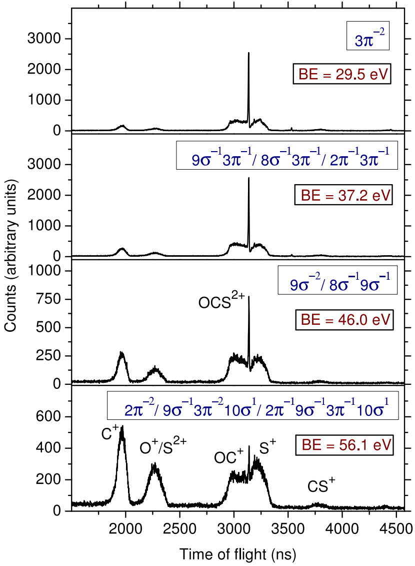
- Ionization to low binding energy states mostly yields stable doubly charged molecular ion
- Fragmentation increases when higher binding energy states are accessed



# Inferences/Summary

We have demonstrated the use of CMI in understanding multiply-charged molecular ions

- determination of the fragmentation sequence of various channels
- measuring the lifetime of metastable states
- estimation of the transient species geometry
- shell-selectivity effects on DI patterns
- Non-coulombic fragmentation of doubly and triply charged molecular ions
- Orientation dependence of fragmentation channels
- Rearrangements in molecular ions leads to formation of new bonds, new species

# What Next?

- Improve on the shell-selectivity – by better electron analysis and a smarter correlation strategy
- Full kinematics – in particular, orientation effects and angular distributions with shell selectivity – still to be explored
  - Higher photon energy, better energy resolution (Synchrotron: Indus-2)
  - Ion impact studies of similar type (MeV class ion accelerator: IUAC)

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- (Re-)building classic experiments that form the bedrock of modern science, for interpretation by undergraduate students