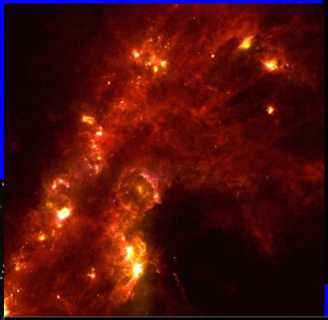
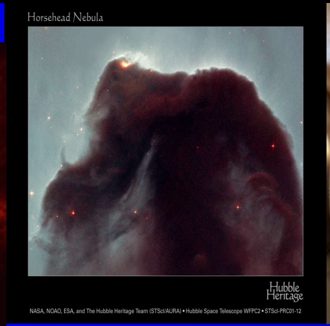
Merged-beams Tools for the Study of Ultra-cold Reactions.

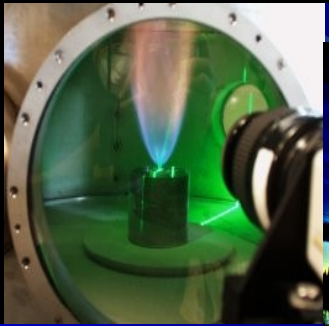
Rich D. Thomas

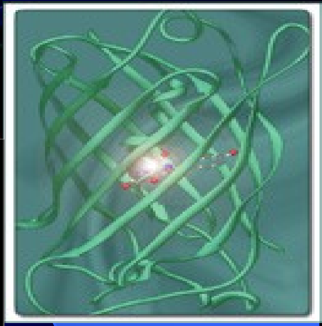
Department of Physics, Stockholm University

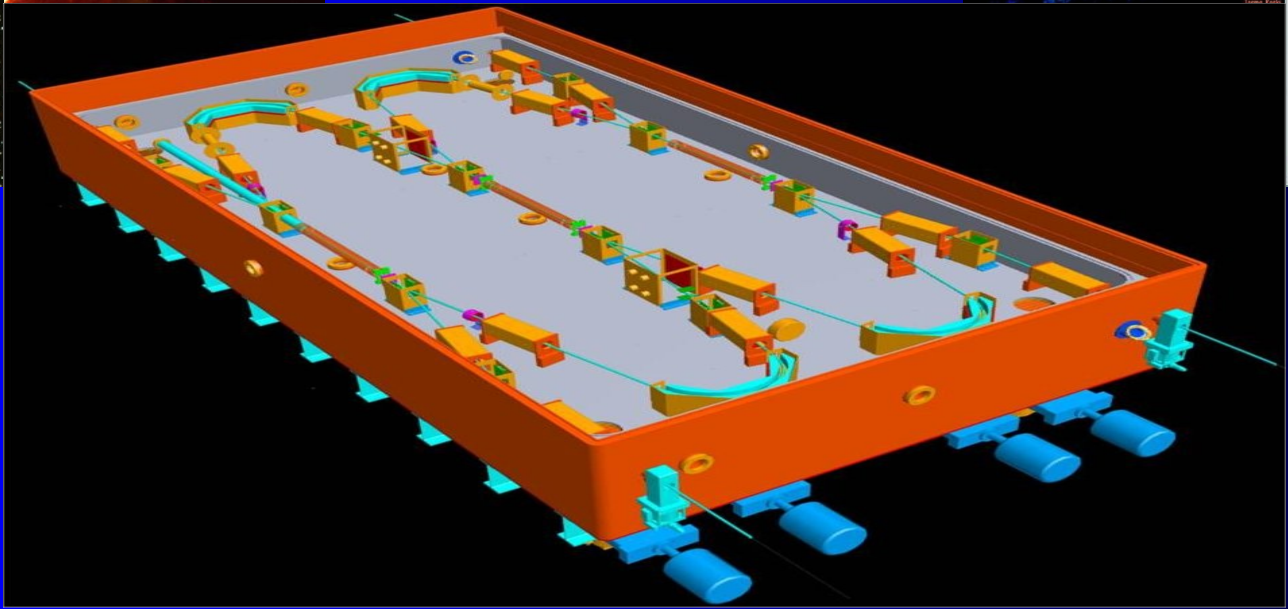
FYSIKUM











11th March 2011, 3rd DITANET workshop, Stockholm, Sweden

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Introduction	**Molecules. Why Molecules ?** **What do these molecules do ?** **Why is that important?**
Molecular-reaction illustration	**Dissociative Recombination**
Ion Storage Rings I	**CRYRING:** **The techniques, example results, and what we learn**
Ion Storage Rings II	**Magnetic vs Electrostatic Storage: Limitations and advantages**
DESIREE	**What is it?**
What can we do that is different and important	**Unique opportunities and possibilities**
The Future	**Where are we with DESIREE?**

Introduction: Molecules. Why Molecules

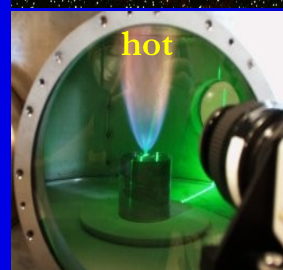
Molecules are present in many environments, from …

How can molecules …
- form clouds ?
- probe temperature?
- effect isotopic abundance?

to

How do they influence …
- Protein folding and structure?
- Radiation induced cell damage?
- DNA fragmentation?
- Drug efficiency?

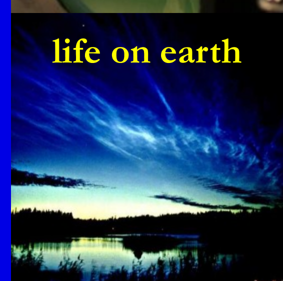
How can molecules …
- Raise combustion efficiency?
- Make combustion cleaner?
- Influence nuclear fusion?



to

How are molecules …
- created?
- destroyed?

How are they involved in …
- ice formation?
- aurorae?
- pollution?



to

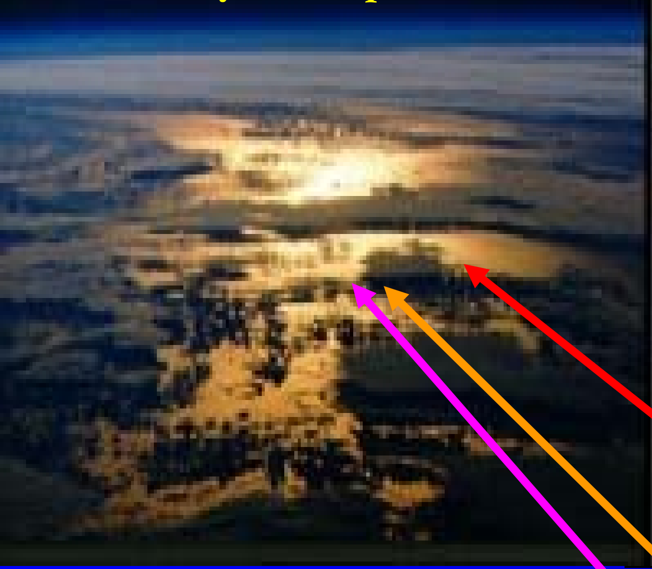
Molecules and philosophy …
- How do molecules determine life?
- Are amino acids in space?
- Molecules arriving on comets and meteorites?

Knowledge on how molecules interact and react is vital to understanding these environments.

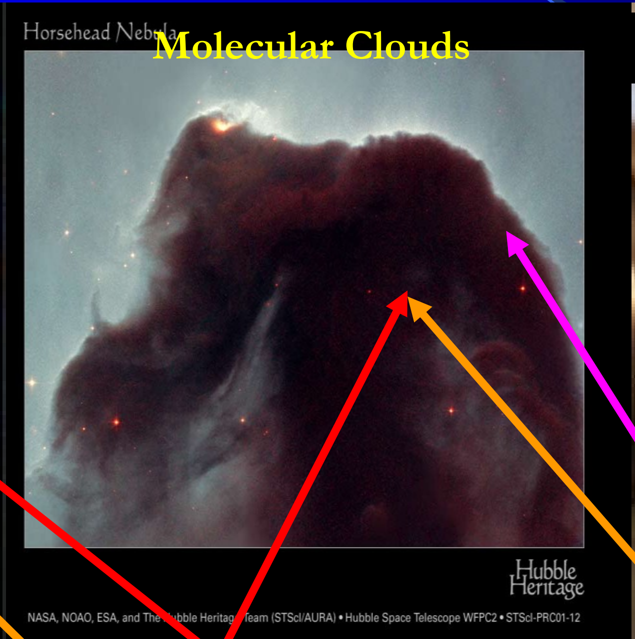
Introduction

What about these environments – a few examples

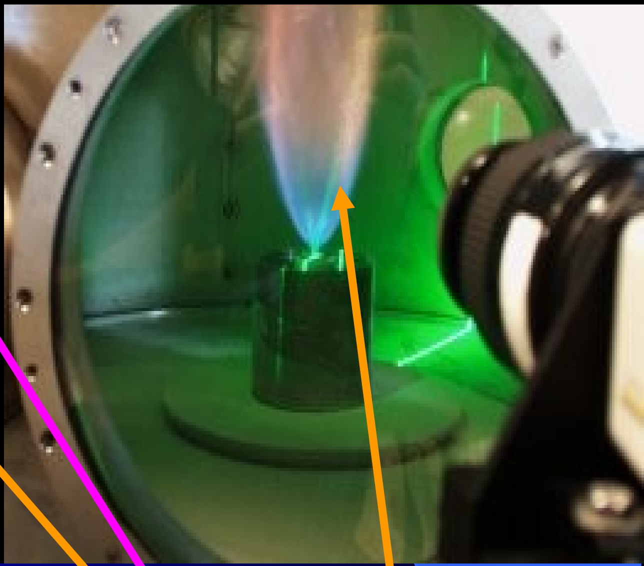
Planetary Atmospheres



Molecular Clouds



Combustion & Flames



Low density: Binary reactions only

High Level of Ionisation: Stellar Radiation, Cosmic Rays & Heat

Low temperature: Barrierless reactions; ion-neutral & e^--ion

Introduction: Reactions

GAS PHASE ION REACTIONS

Types Of Reaction

- Electron-Neutral
  - **Non Dissociative Attachment**
  - **Dissociative Electron Attachment**
- Electron-Ion
  - **Resonant Ion-Pair Formation**
  - **Excitation**
  - **Ionization**
  - **Dissociative Recombination**
- Ion-Ion
  - **Associative Attachment**
  - **Charge/ Ion Exchange**
  - **Neutralisation**
- Ion-Neutral
  - **Charge Transfer**
  - **Dissociative Charge Transfer**
  - **Ion-Atom Exchange**
  - **Association**

Laboratory Techniques

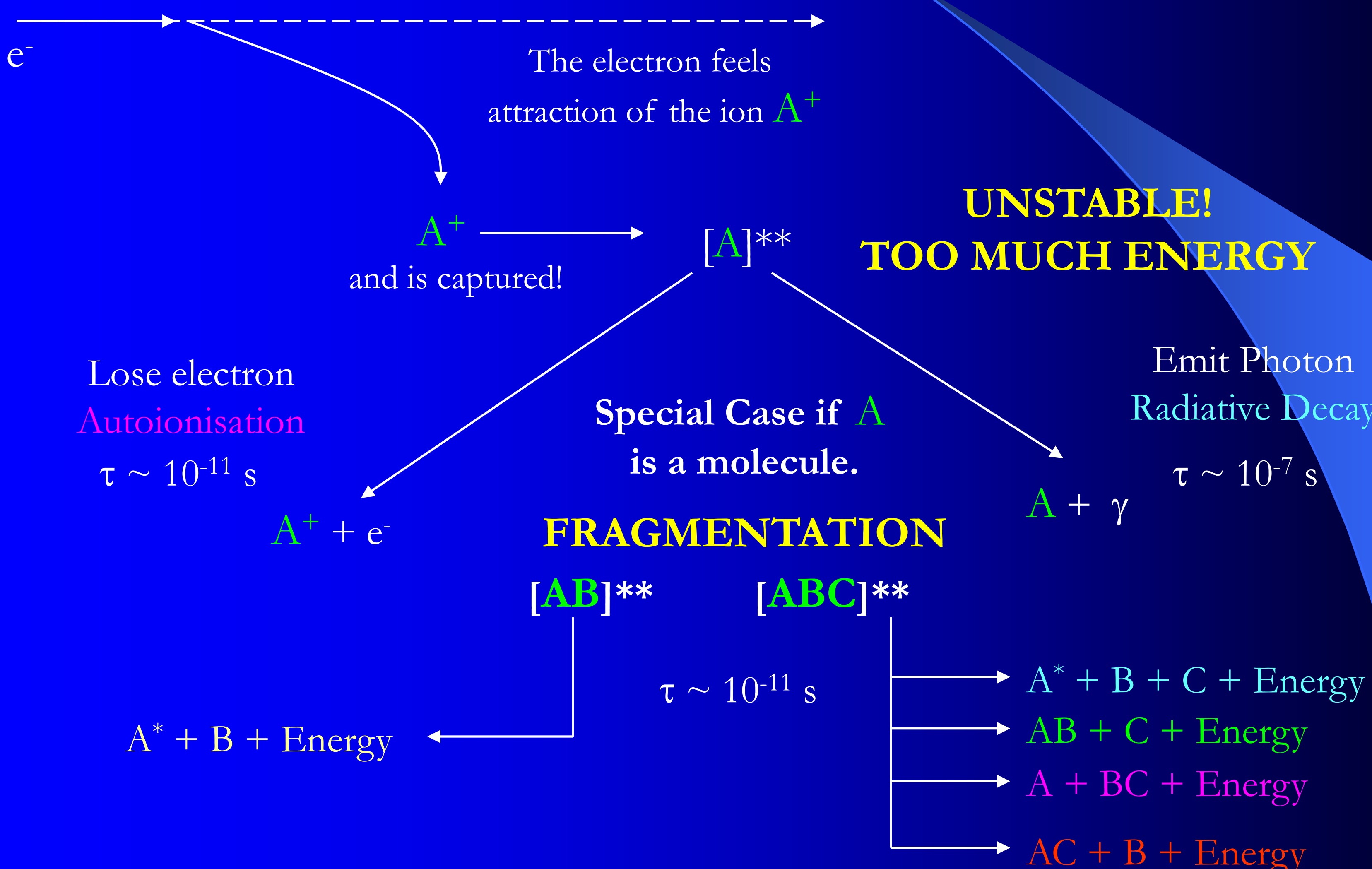
Important process of ionisation balance and production of reactive radicals in these regions:

Reactions of molecular cations with electrons or anions

Dissociative Recombination & Mutual Neutralisation

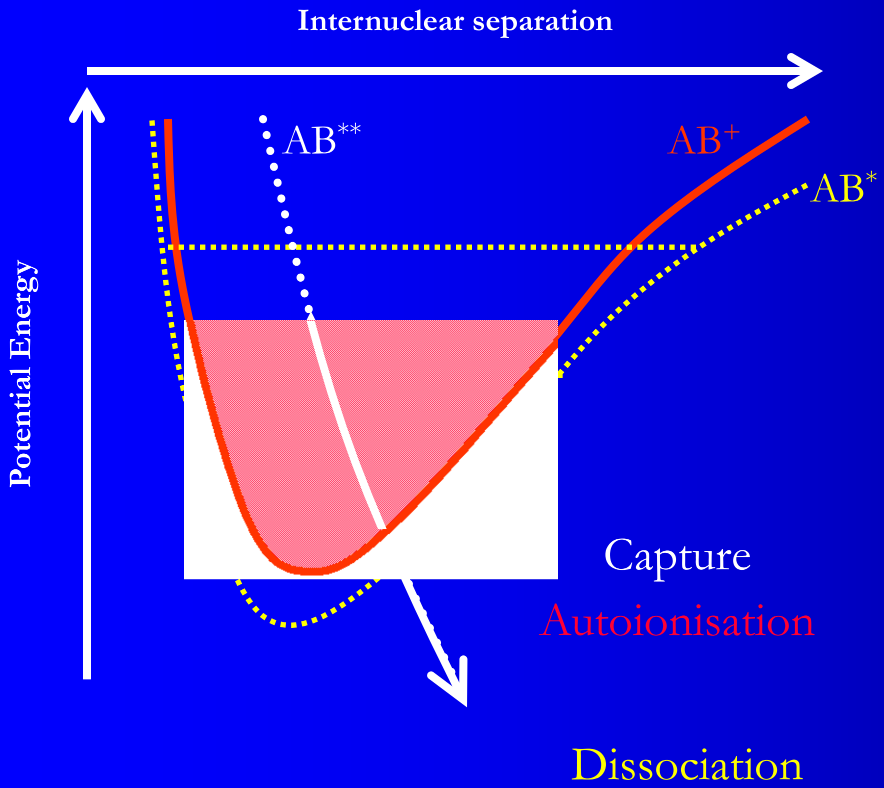
Dissociative Recombination:

What is it - I?

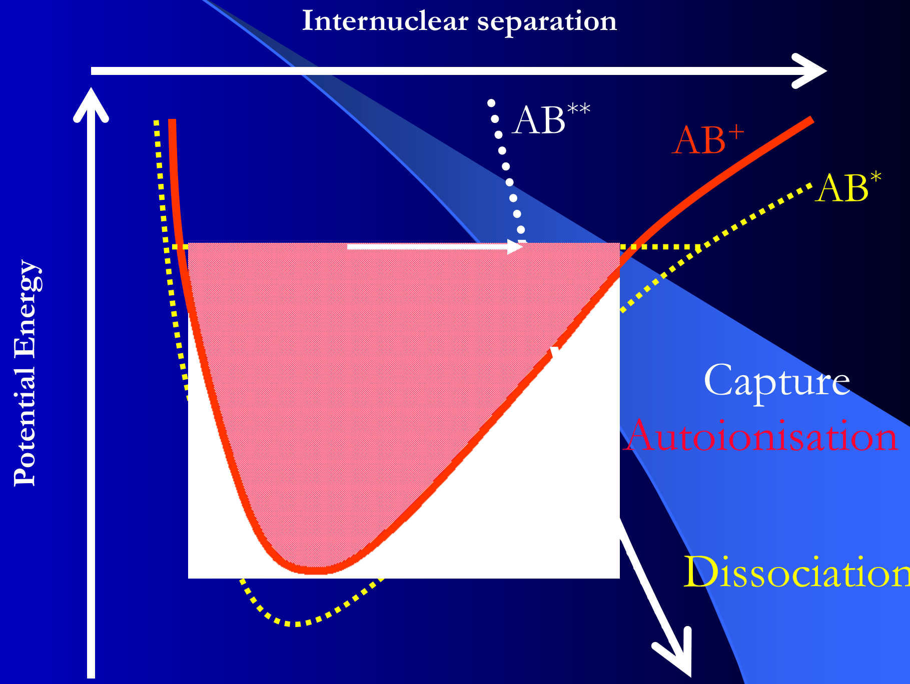


Dissociative Recombination:

What is it - II?



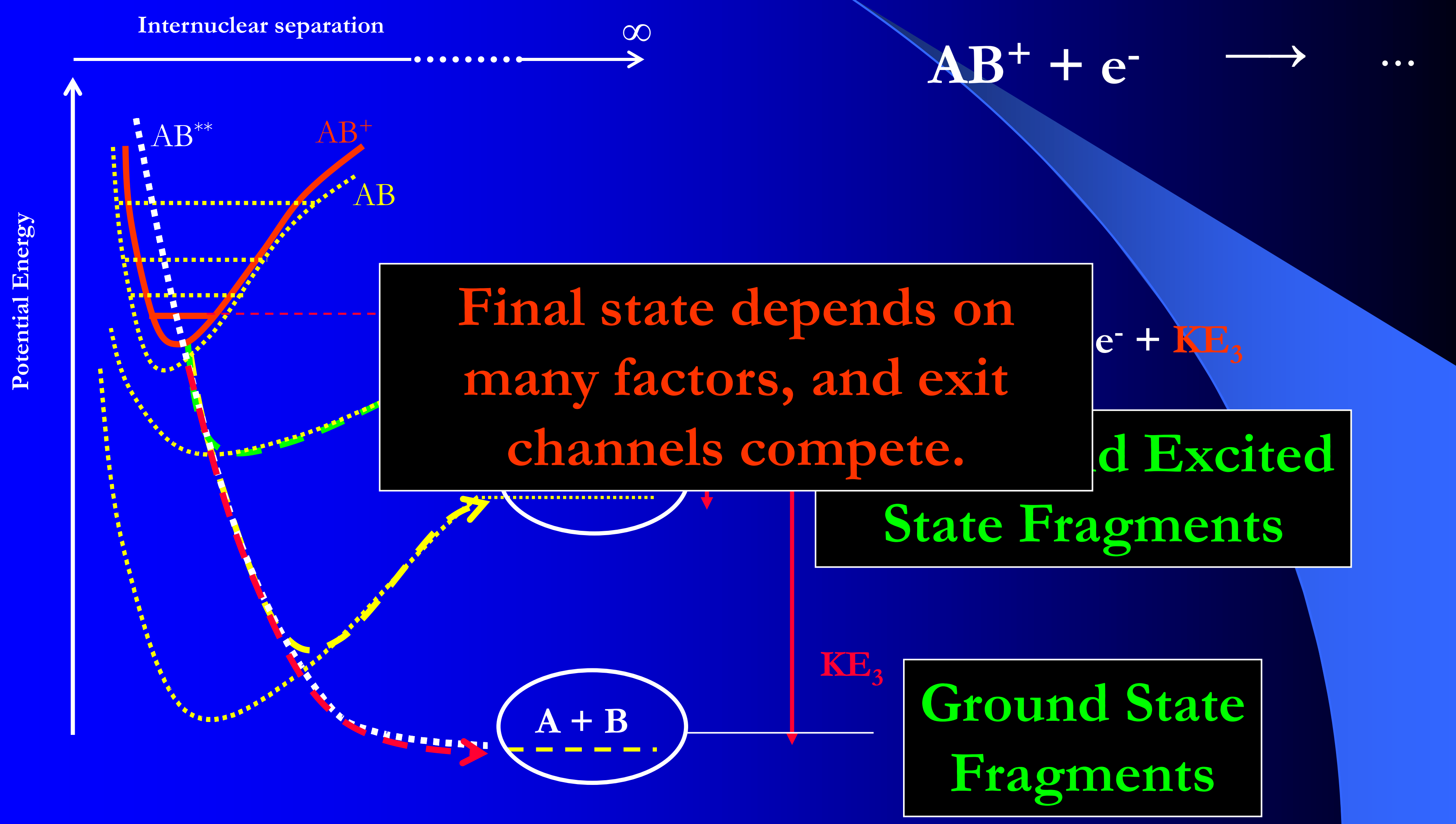
Direct Mechanism



Indirect Mechanism

Dissociative Recombination:

What is it - III?



What are the most instructive **Techniques**?

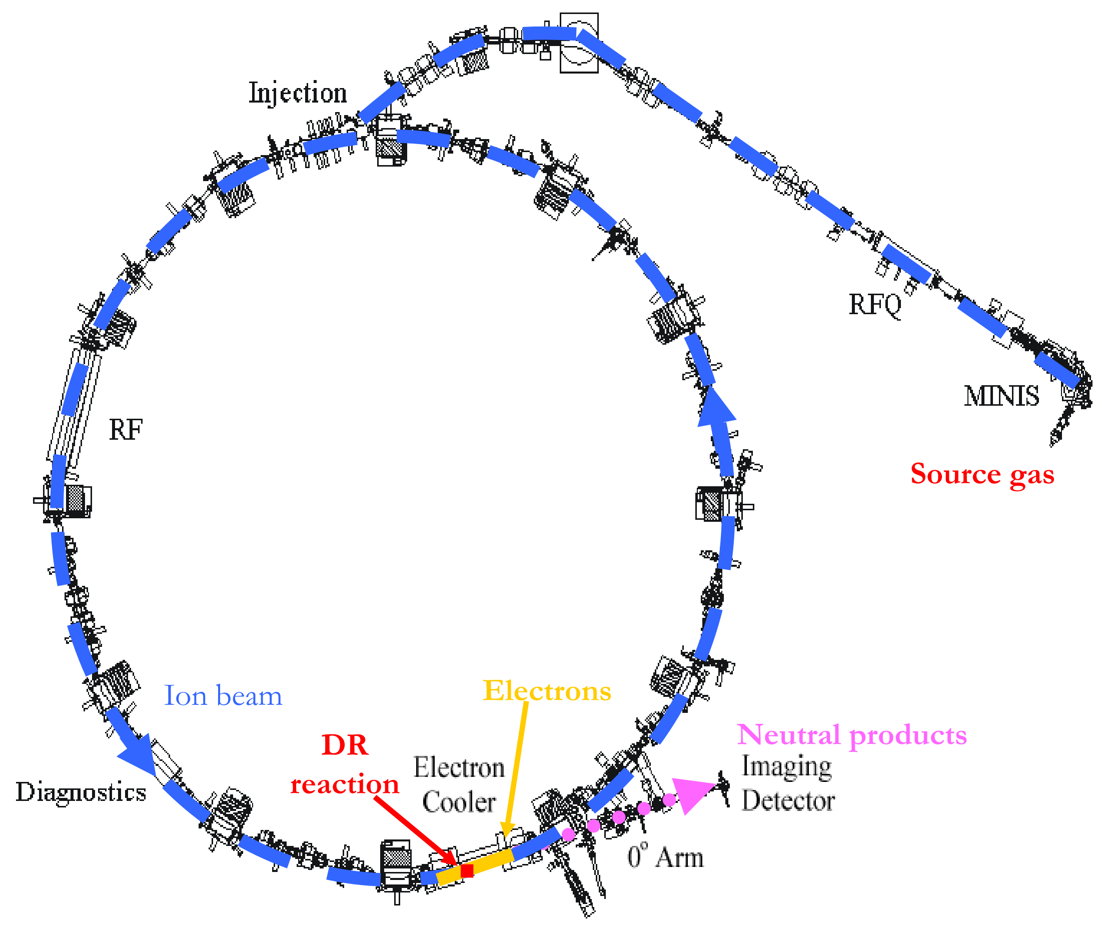
Experimental Requirements

- High Beam Energy + Good Vacuum → Low Background
- High Energy → Low c.m. energy
- Multi-pass → Good Data Rate

Ion Storage Ring

Ion Storage Rings I

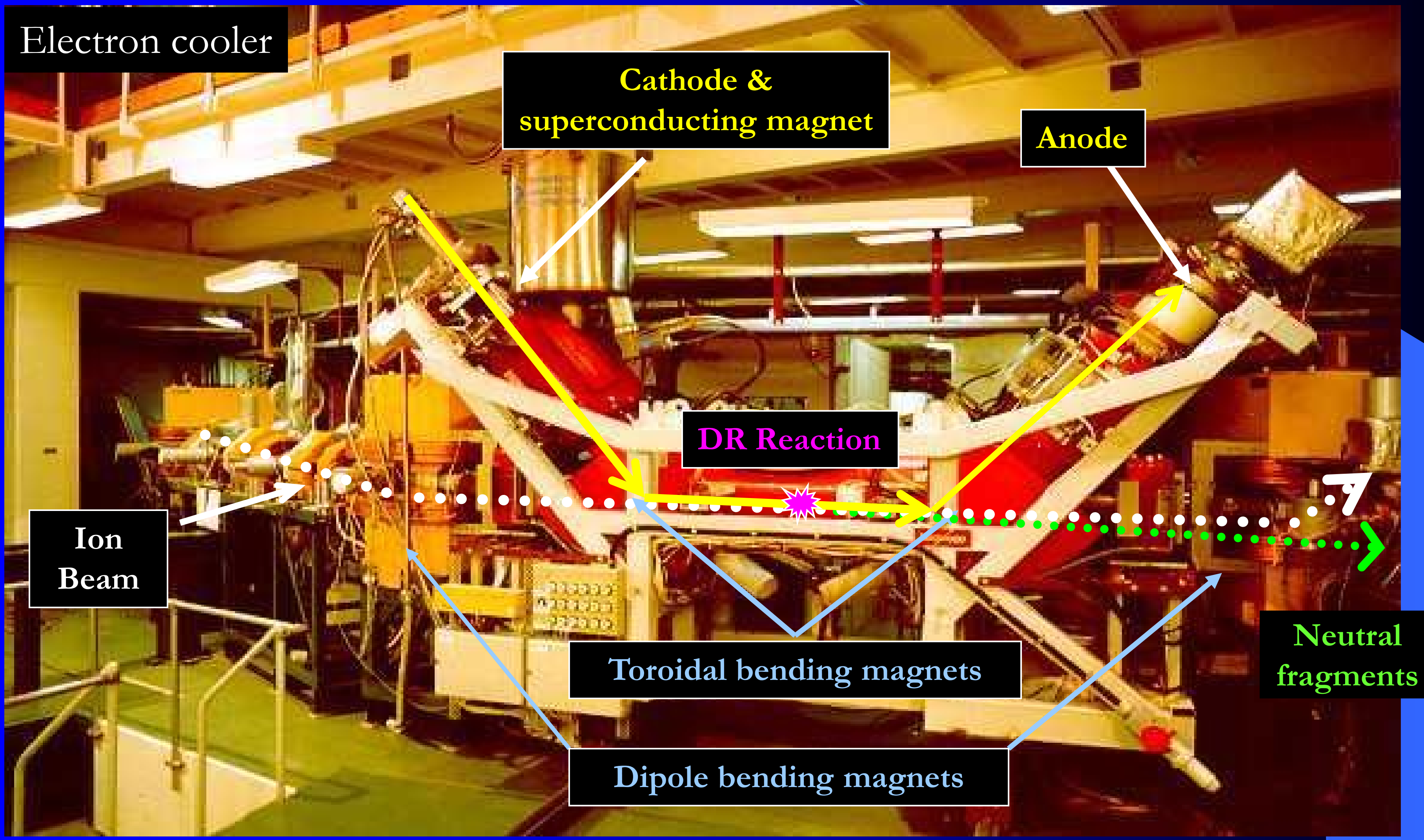
CRYRING



Movie

Ion Storage Rings I

The Techniques



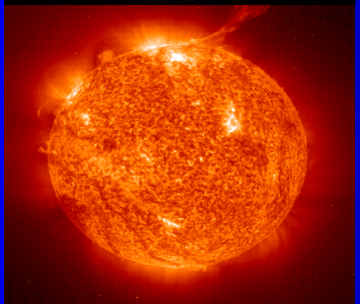
What do we want to **Learn? – In Pictures!**

How fast

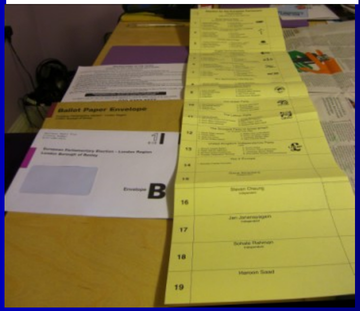
How violent

How complex

How predictable



1 + 1 = 2



Ion Storage Rings I

The **Techniques**

XYZ$^+$ beam

e$^-$ beam

Neutrals

XYZ$^+$

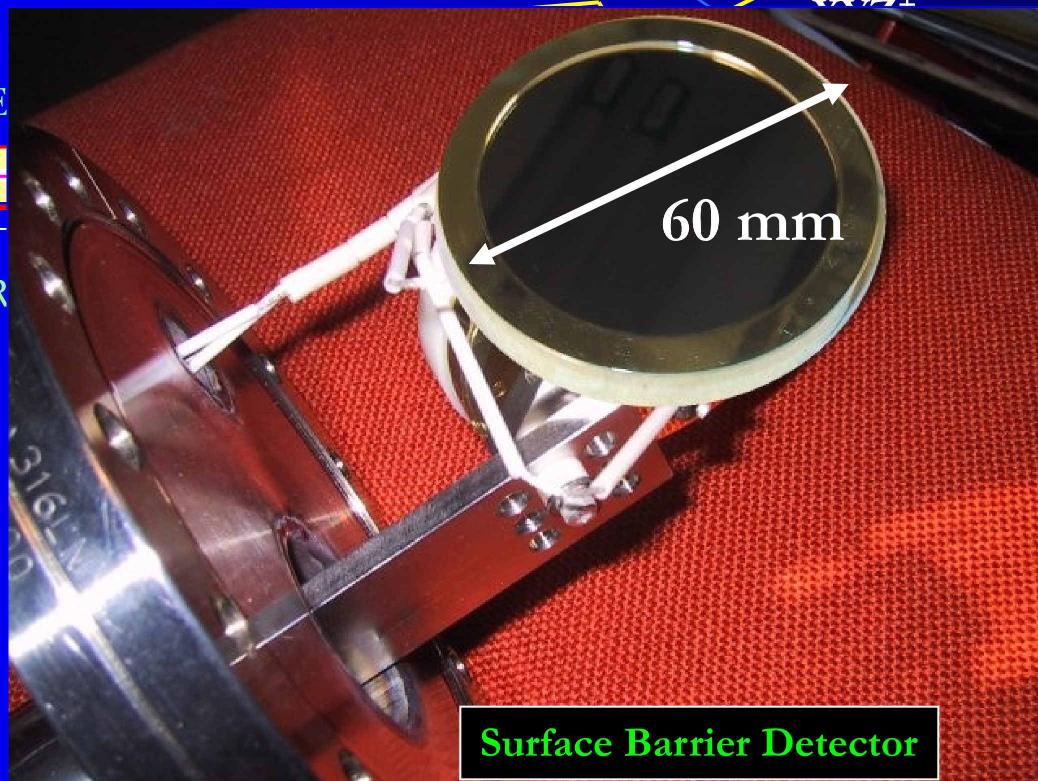
E

R

n Arm

Grid Detectors

, XZ …



Surface Barrier Detector

Info loss-

all events lead to full mass signal

Branching ratio

spectrum dependent on branching ratio and T

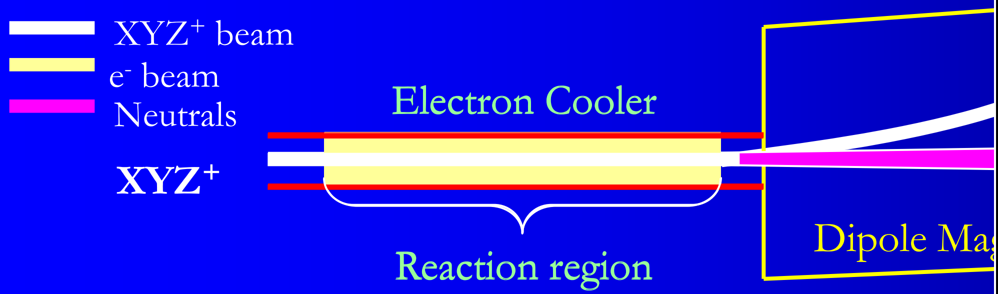
Mass/Energy sensitive detection

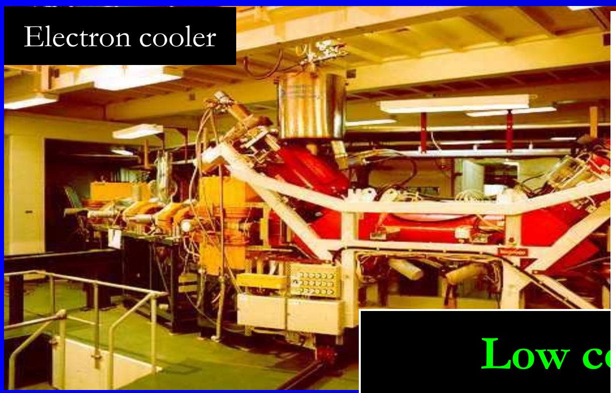
Probability

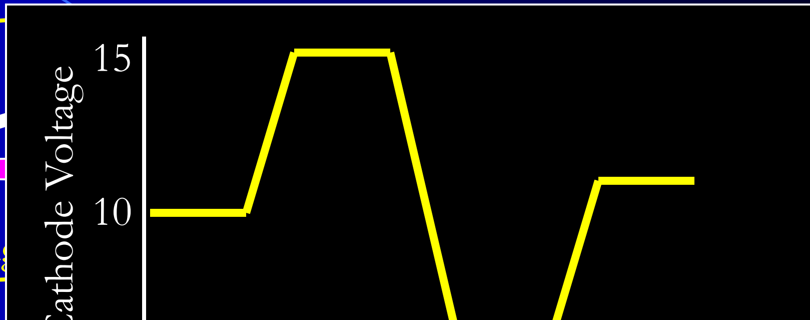
T(1-T)

Ion Storage Rings I

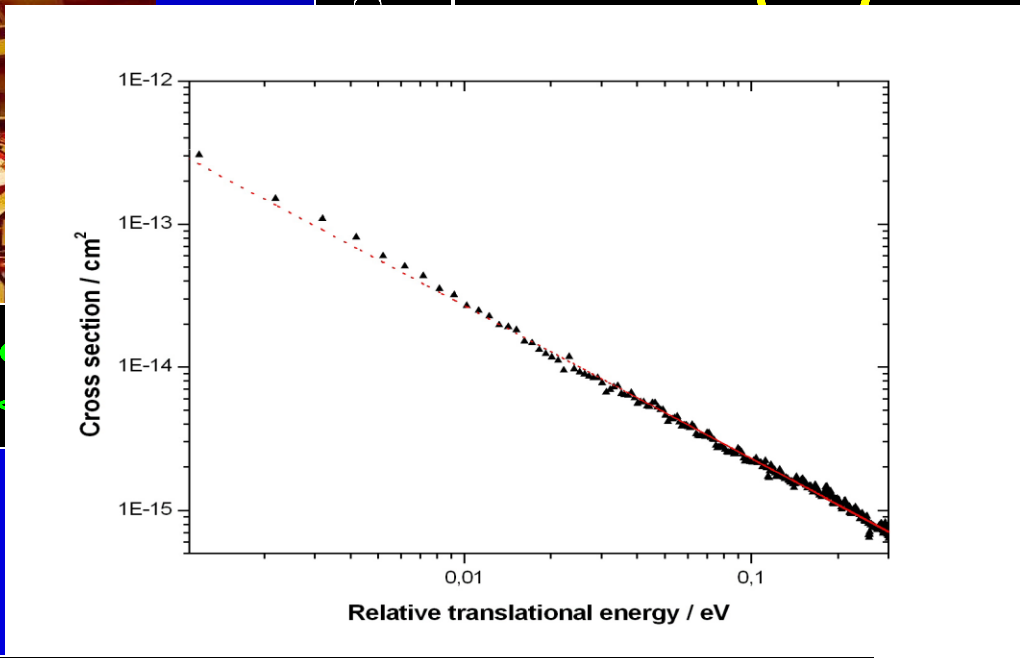
The **Techniques**







Low c
energies <

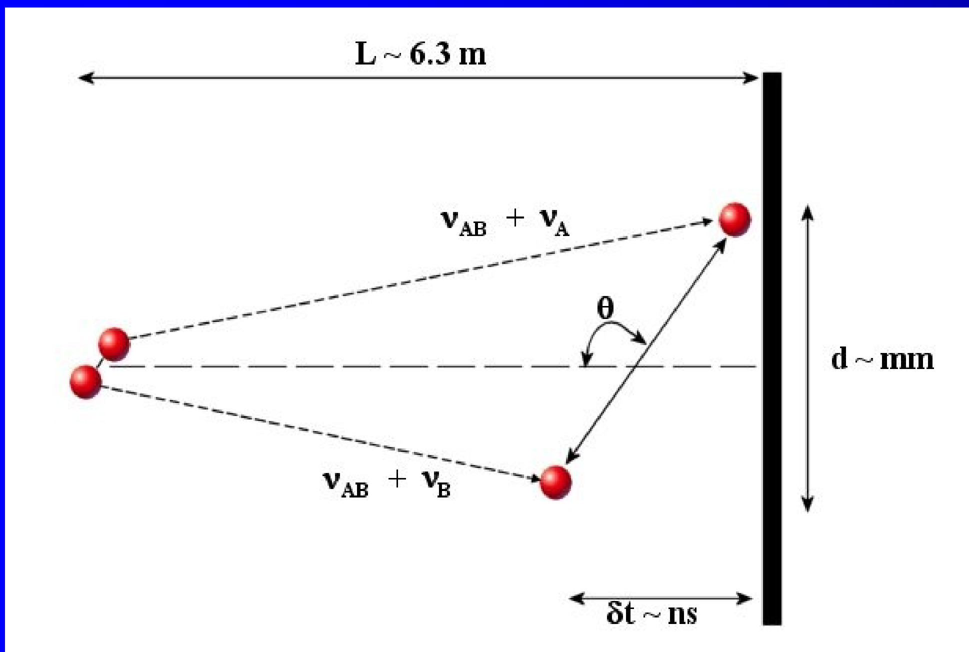


Collision energy-dependence

Ion Storage Rings I

The Techniques

Imaging



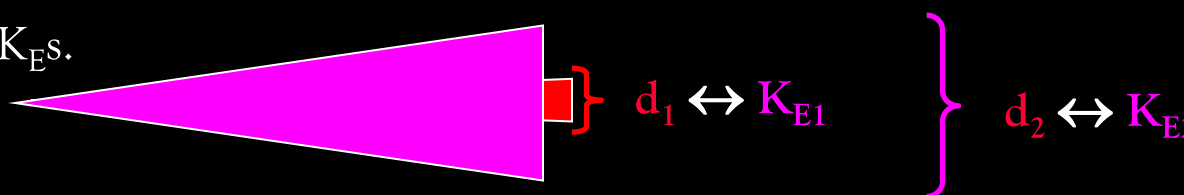
Reaction energy, K_E
Ion beam energy, B_E

$$d \;\alpha\; L \sqrt{\frac{K_E}{B_E}}$$

For standard conditions:
$K_E/B_E \approx 10^{-3}$, $L \approx 1.5$ m
$d \approx 10$ mm

Different channels have different K_Es.

∴ Different d

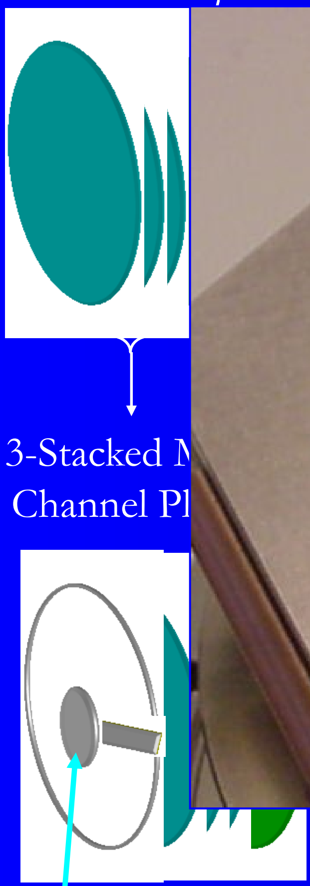


Position sensitive detection

Ion Storage Rings I

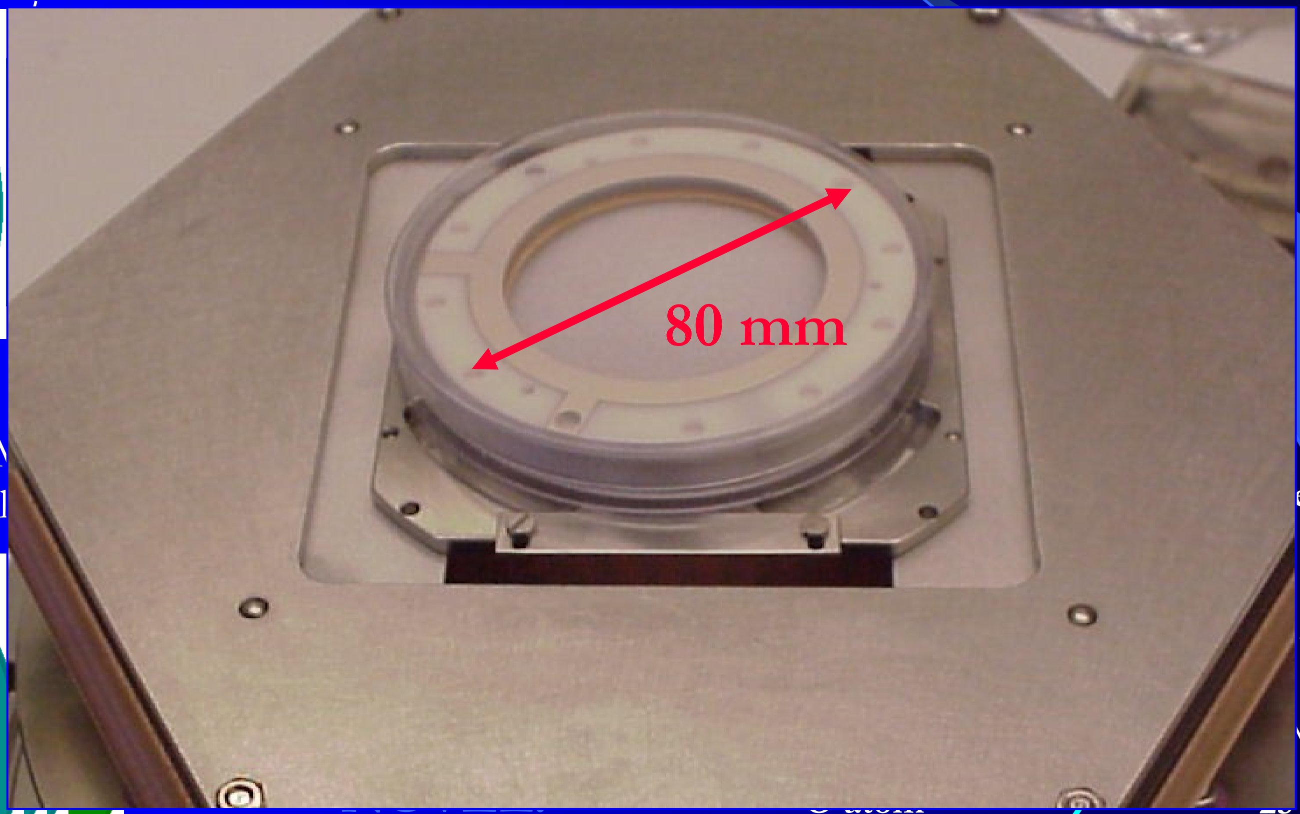
The **Techniques**

Phosphor Screen



3-Stacked M

Channel Pl



ed

Slowed

keV/A

A thin foil was placed in-front of the MCP.

Movie

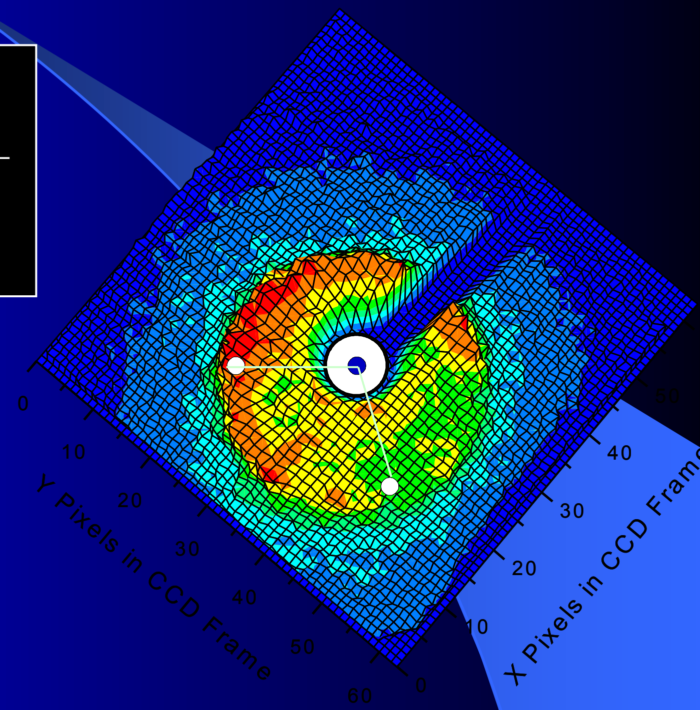
Ion Storage Rings I

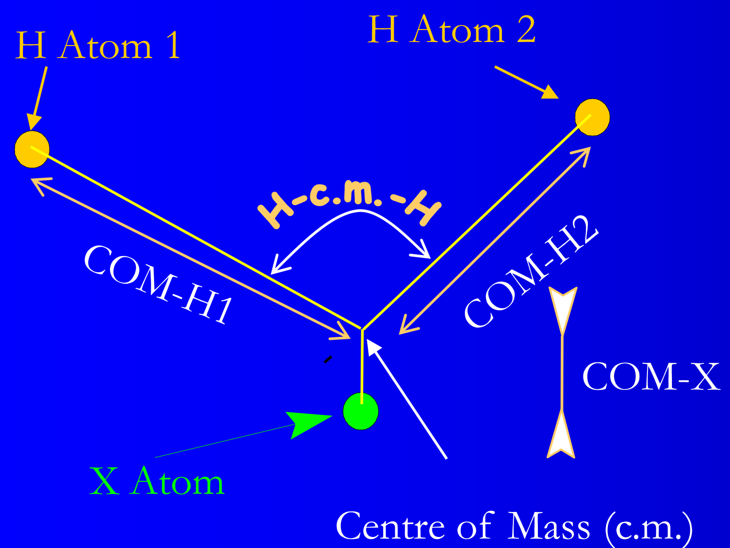
The **Techniques**

XH_2^+: Heavy X atom, light h atoms

H: Take most energy, large r & sensitive to internal excitation of the heavy atom.

BH_2^+, CH_2^+
OH_2^+, NH_2^+
SD_2^+, PD_2^+



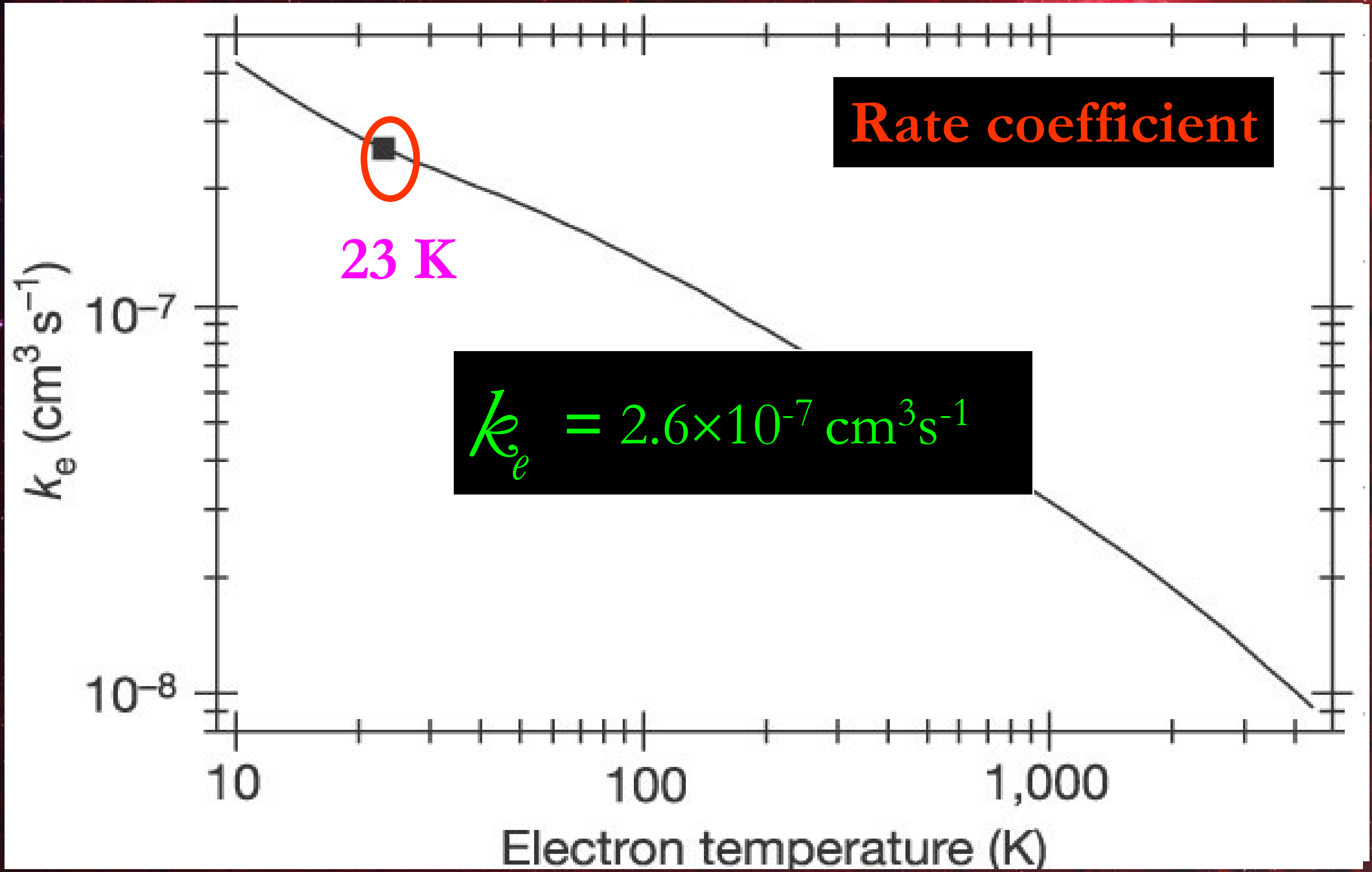


KER

∠ H-c.m.-H **E(H)**

Ion Storage Rings I

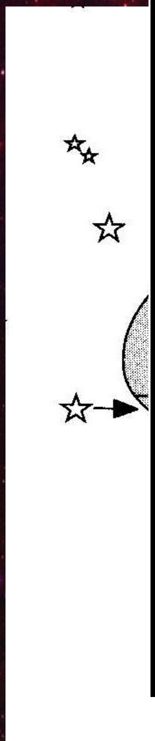
Example Results and What we Learn



… in diffuse interstellar clouds

Ion Storage Rings I

Example Results and What we Learn



Cosmic ionization rate

H_3^+ column density

H_2^+ column density

Length of cl

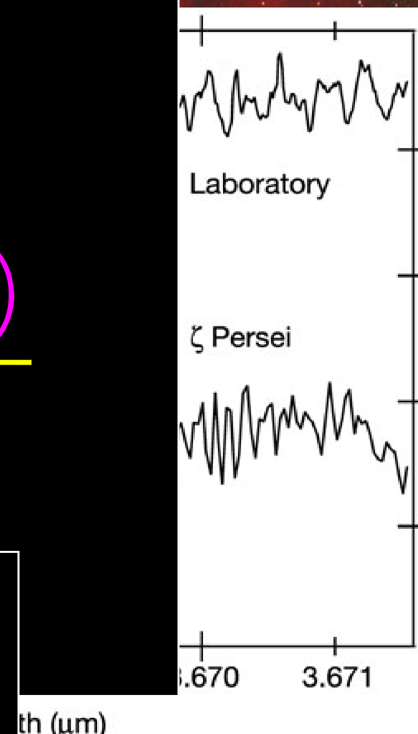
DR

$N(e)$

$$LV = 8{,}000 \text{ cm s}^{-1}$$

$$L = 2.1 \text{ pc}$$

$$\therefore \zeta = 1.2 \times 10^{-15} \text{ s}$$



Cosmic ray ionization rate …

40x higher than previously assumed

Ion Storage Rings I

Example Results and What we Learn

In the ionosphere:

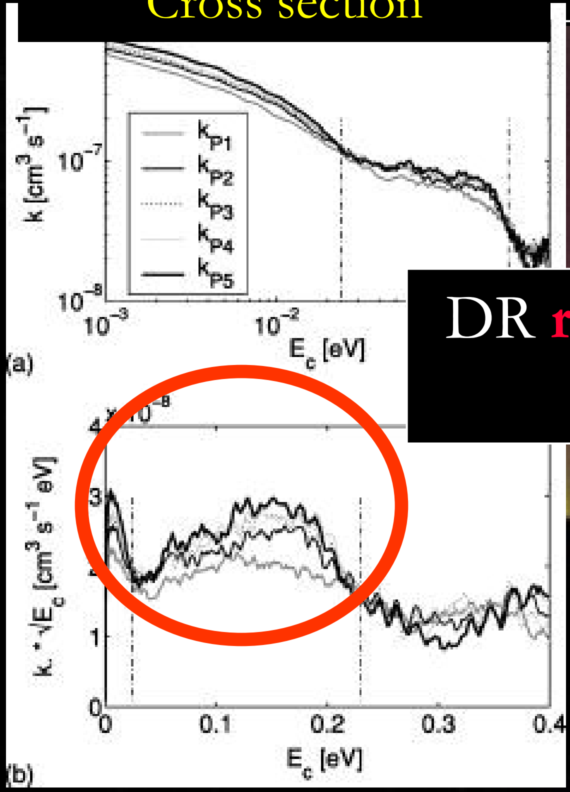
O_2^+ +

DR is only source of $O(^1S)$ in the nighttime F- region

$O(^1D) + O$ ✓

$O(^1S) + O$ ✓

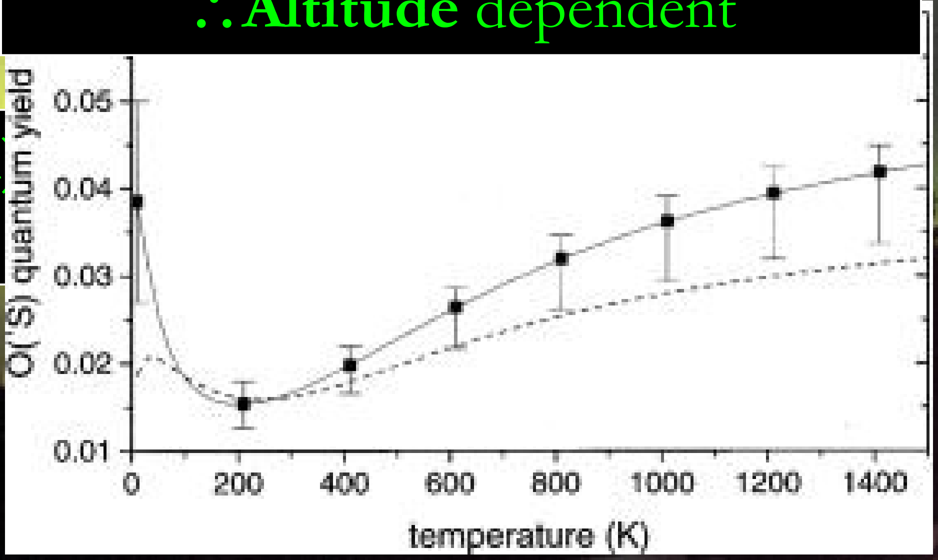
Cross section



DR rate is $O_2^+(v,n,l)$ dependent

$O(^1S)$ yield is T-dependent

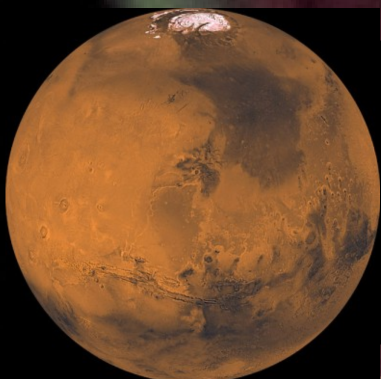
∴ Altitude dependent



… in planetary atmospheres

Ion Storage Rings I

Example Results and What we Learn



In the atmosphere:

$^{14}N^{15}N^{+}$

^{15}N

m(^{1}

∴ v

$^{14}N^{15}N^{+} + e^{-} \rightarrow$

3.44 eV ✓

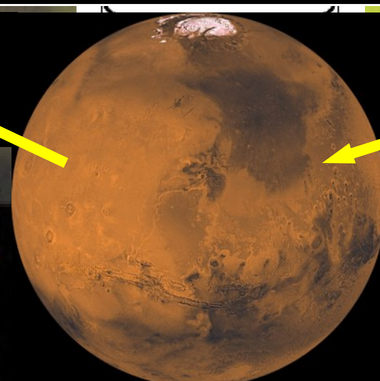
3.44 eV

1.78 ^{14}N

1.66 ^{15}N

DR leads to isotope fractionation

^{14}N escape



trapped ^{15}N

… in planetary atmospheres

Ion Storage Rings I

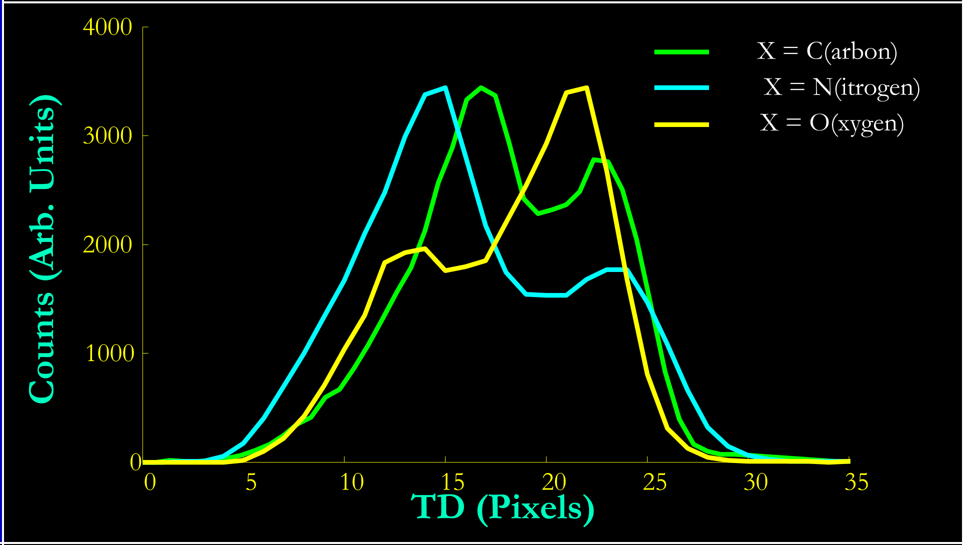
Example Results and What we Learn

$OH_2^+ + e^- \rightarrow O(^3P)/O(^1D)$

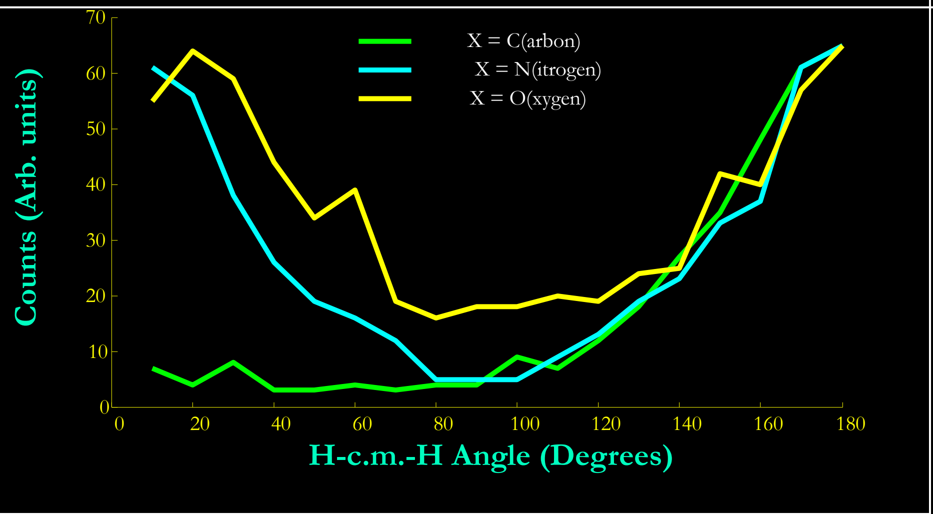
$NH_2^+ + e^- \rightarrow N(^4S)/N(^2D)/N(^2P)$

$CH_2^+ + e^- \rightarrow C(^3P)/C(^1D)$

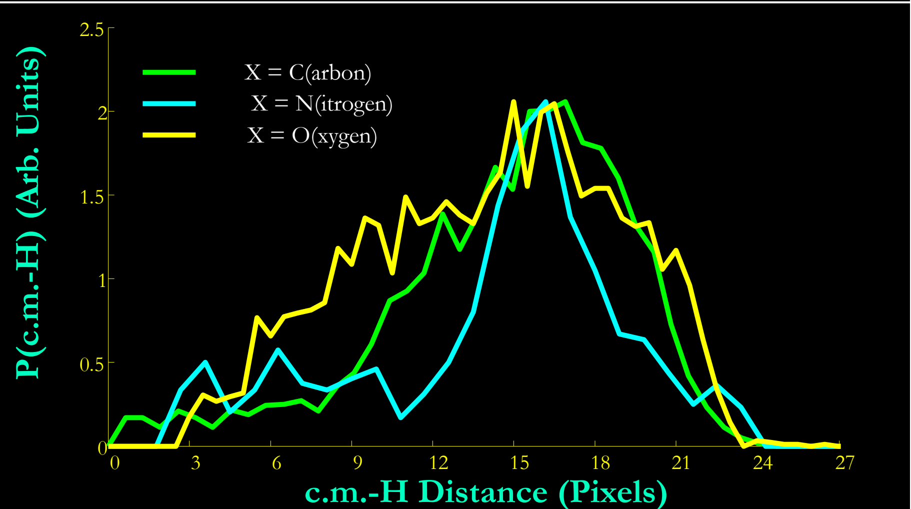
Ground/Excited state competition



Molecular Geometry on break-up



Fragment energy distribution



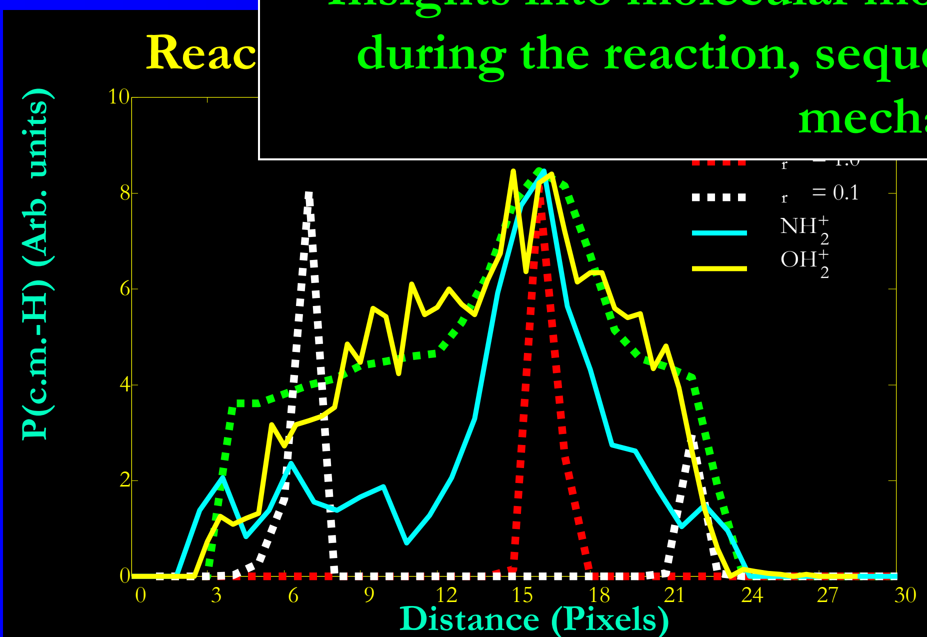
Ion Storage Rings I

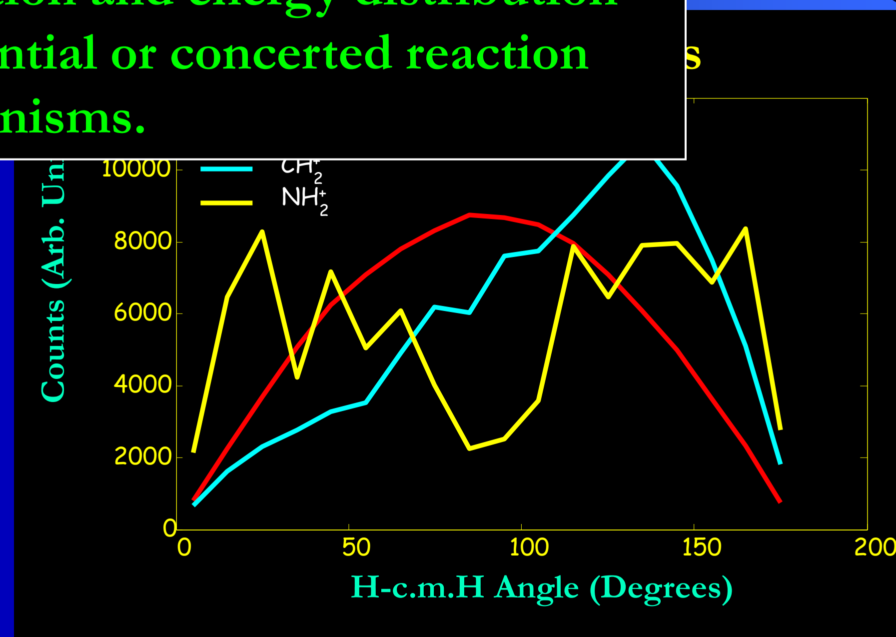
Example Results and What we Learn

State populations

Ion	Ground eV	First eV	Ratio
CH_2	$C(^3P)$ 2.45	$C(^1D)$ 1.24	1.0:1.0
NH_2	$N(^4S)$ 3.94	$N(^2D)$ 1.56	1.1:1.0
OH_2	$O(^3P)$	$O(^1D)$	3.5:1.0

Insights into molecular motion and energy distribution during the reaction, sequential or concerted reaction mechanisms.





Conclusions - I

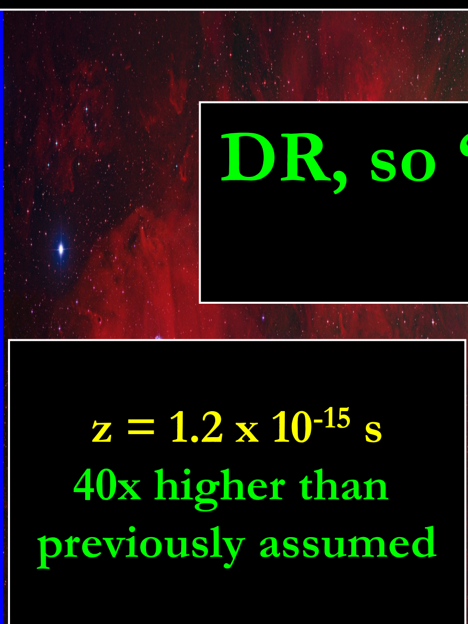
Molecules are present in many environments

The presence of ions and electrons plays a huge role

Dissociative Recombination is a critical mechanism

Ion Storage Rings are a perfect tool for studying DR

DR of H_3^+



$z = 1.2 \times 10^{-15}$ s
40x higher than previously assumed

DR of N_2^+,O_2^+…

Excited, radiating products

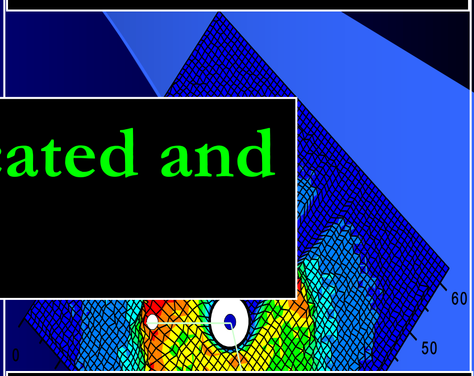
Isotope fractionation

Combustion & Flames

Excited, reactive products

Improved air-breating engines

Polyatomics



Extremely violent

Large system differences

DR, so "simple", is extremely complicated and still needs to be understood.

Ion Storage Rings: Magnetic vs Electrostatic

For magnetic storage:
CRYRING, TSR, ASTRID, TARN II

$$BE \propto \left(\frac{B \cdot \rho \cdot q}{m} \right)^2$$

q=1

B • ρ=1.44 Tm

For 0-eV collisions (DR)

m_{max} ~ 100 amu

DR @ CSR (Lanzhou) (increase B·ρ)

Can study small, astrophysically and atmospherically important systems …

H_3^+, H_2^+
H_2O^+
CH^+
O_2^+, NO^+
…

For electrostatic storage:
ELISA, DESIREE, CSR

$$BE \propto E_{acc} \cdot q$$

"No" mass limit for the ions that can be stored

DR @ CSR (Heidelberg) (still similar m_{max})

We can now study large biologically important systems … but not DR

amino acids
peptides, proteins
chromophores
DNA fragments
Nanoparticles
…

Formation of H_2

Cooling of Gas in Primordial Galaxies

$k_2 << k_1$

Destruction of H^- ?

Photodissociaiton

eutralisation

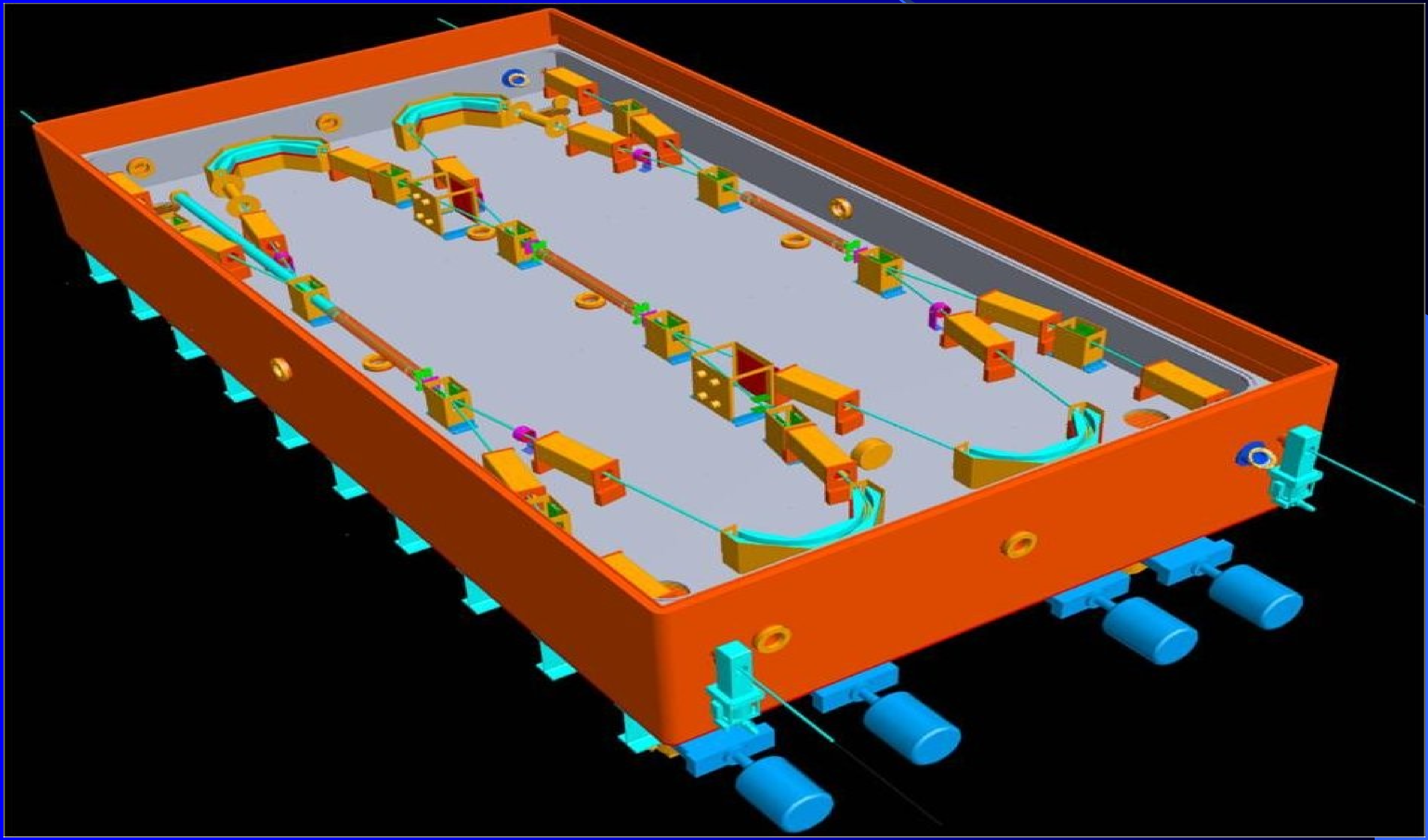
Most Fundamental Reaction
desires
Accurate Measurement

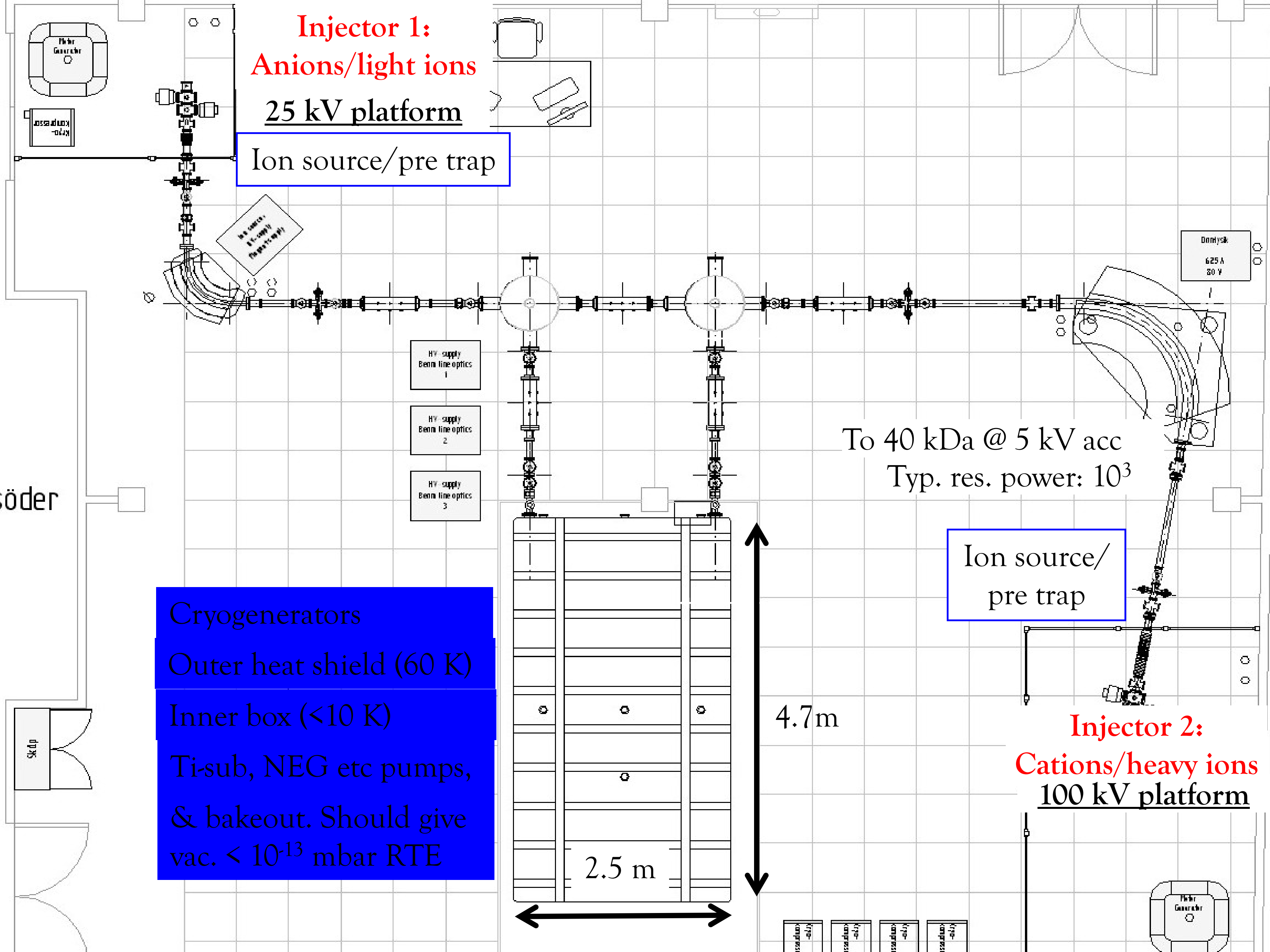
Savin: Recent re … or low T factor 3-4 uncertainty in MN

… in the primordial universe

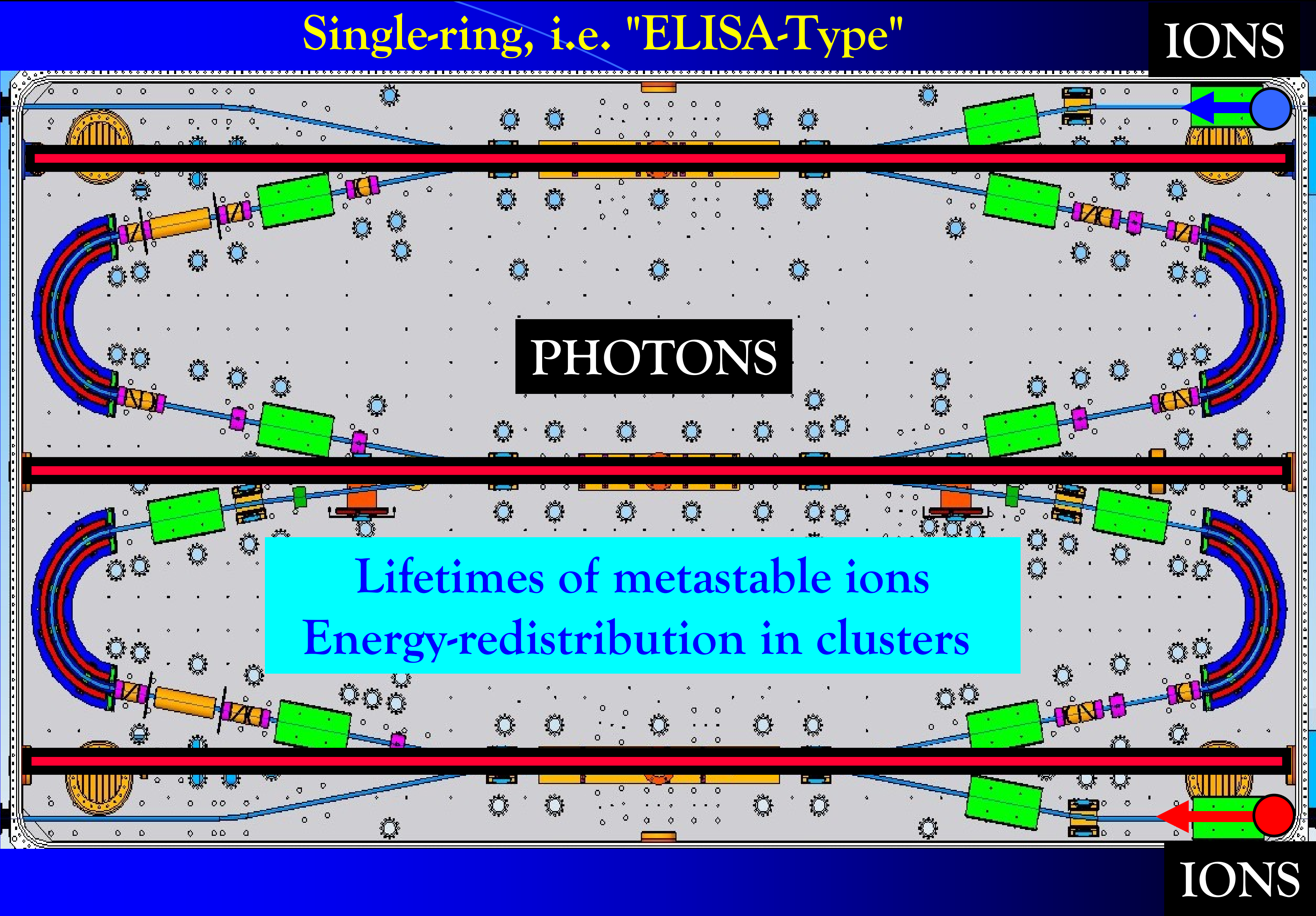
Ion Storage Rings II

Double ElectroStatic Ion Ring ExperimEnt: DESIREE



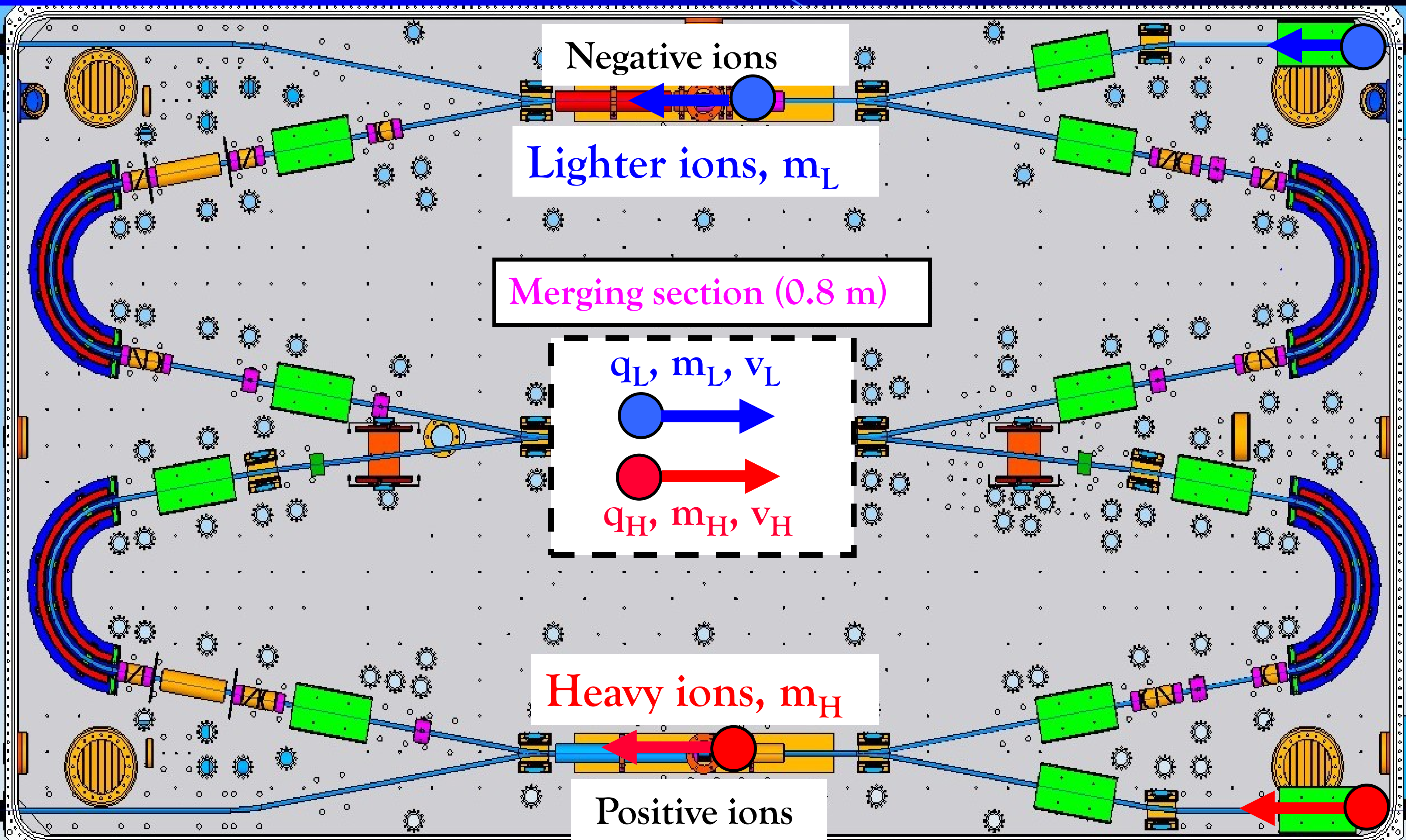

Injector 1:
Anions/light ions
25 kV platform
Ion source/pre trap
HV-supply
Beam line optics
1
HV-supply
Beam line optics
2
HV-supply
Beam line optics
3
To 40 kDa @ 5 kV acc
Typ. res. power: 10^3
Ion source/
pre trap
Cryogenerators
Outer heat shield (60 K)
Inner box (<10 K)
Ti-sub, NEG etc pumps,
& bakeout. Should give
vac. < 10^-13 mbar RTE
4.7m
2.5 m
Injector 2:
Cations/heavy ions
100 kV platform
söder

Single-ring, i.e. "ELISA-Type"



Ion Storage Rings II

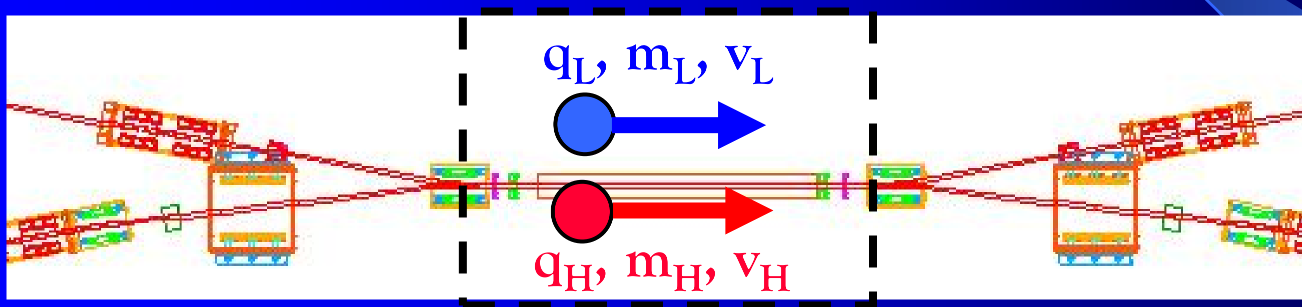
Double ElectroStatic Ion Ring ExperimEnt: DESIREE



Ion Storage Rings II

Double ElectroStatic Ion Ring ExperimEnt: DESIREE

The Merging section – Controlling the collision energy



$$T_L = \frac{m_L v_L^2}{2}$$

$$T_H = \frac{m_H v_H^2}{2}$$

The velocity of the centre-of-mass, $v = \frac{m_H}{m_H + m_L} v_H + \frac{m_L}{m_H + m_L} v_L$

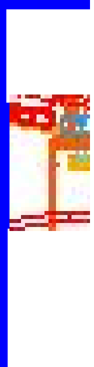
Collision energy available in the center-of-mass, $T_{CM} = \frac{m_H m_L}{m_H + m_L} \left[\sqrt{\frac{T_H}{m_H}} - \sqrt{\frac{T_L}{m_L}} \right]^2$

Ion Storage Rings II

Double ElectroStatic Ion Ring ExperimEnt: DESIREE

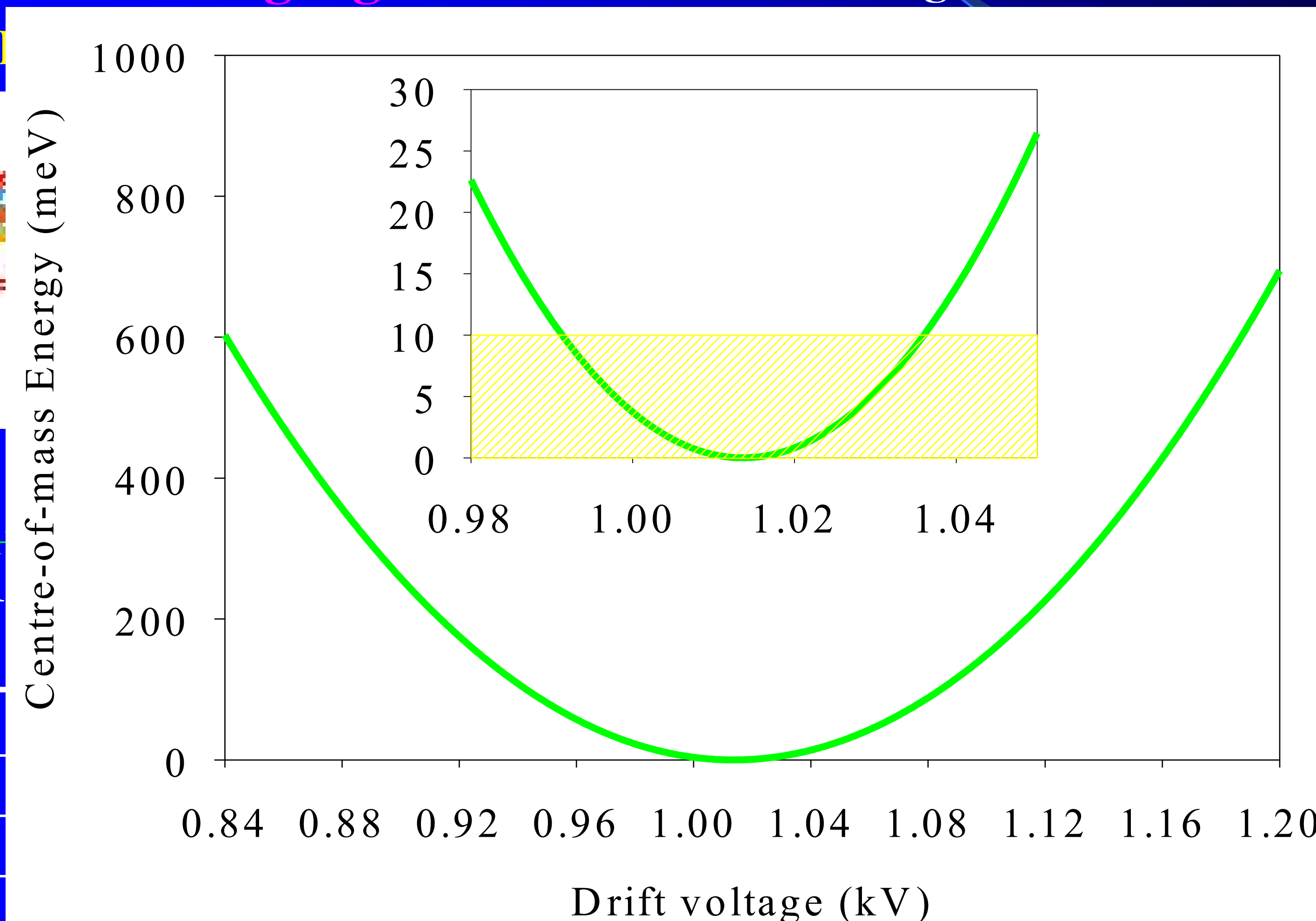
The Merging section – Controlling the collision energy

ection:



$q_L U_{tune}$

$q_H U_{tune}$



For m_H … = 0 for

q_H = +1 … T_H - T_L)/2)

	V)
	3
	3
	6

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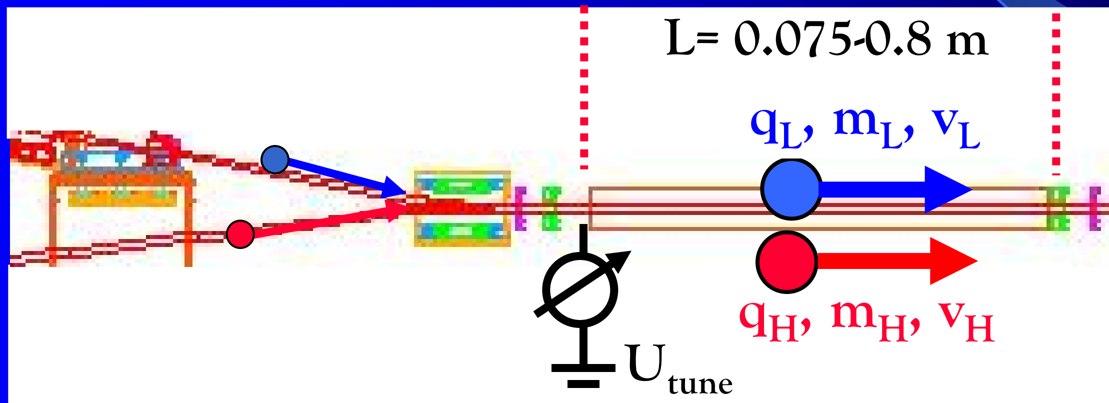
Double ElectroStatic Ion Ring ExperimEnt: DESIREE

The Merging section –

Calculating possible reaction rates, i.e. is something worth doing?



The rate of, e.g., MN in the merging section of length L is given by:

$$\text{Rate} = \frac{I_H I_L}{e^2} \frac{v_{rel}}{v_H v_L} \frac{L\sigma}{A_{max}}$$

I_H, I_L: ion currents. Largest beam x-section area, A_{max}

$\sigma = \sigma(T'_{CM})$

Assuming again
$m_H = m_L$,
$q_H = +1, q_L = -1$:

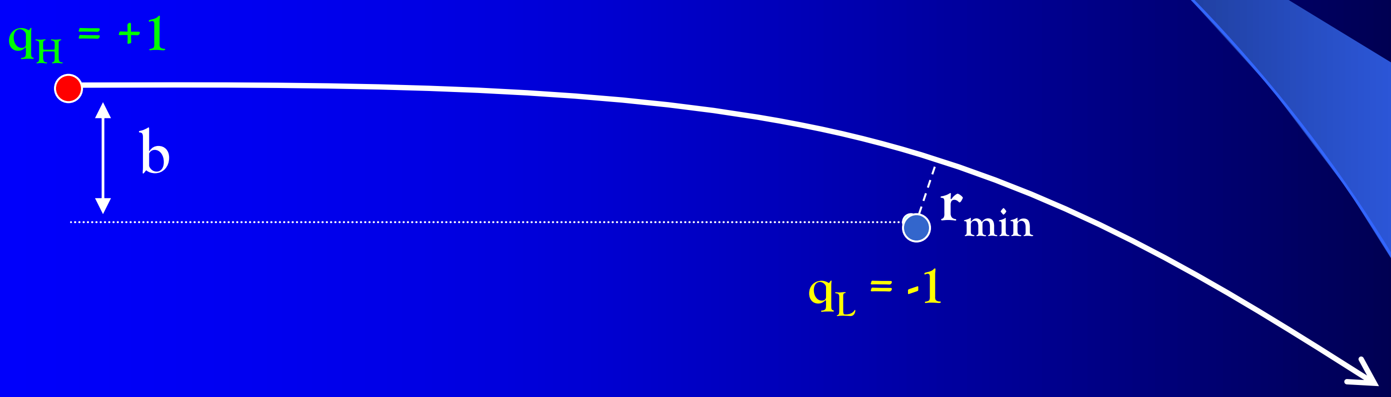
$$\text{Rate} = \frac{I_H I_L}{e^2} \sqrt{\frac{m_L T'_{CM}}{(T_H - U_{tune})(T_L + U_{tune})}} \frac{L\sigma(T'_{CM})}{A_{max}}$$

Ion Storage Rings II

Double ElectroStatic Ion Ring ExperimEnt: DESIREE

The Merging section – Cross sections

The E-dependence for the electron capture cross section, $\sigma = \sigma(T_{CM})$, ...



...depends on the relationship between the distance of closest approach, $\mathbf{r_{min}}$, and the impact parameter **b**:

$$r_{min} = b \frac{[T'_{CM}(eV)\, b/13.6]}{1 + \sqrt{1 + [\,T'_{CM}(eV)\, b/13.6\,]^2}}$$

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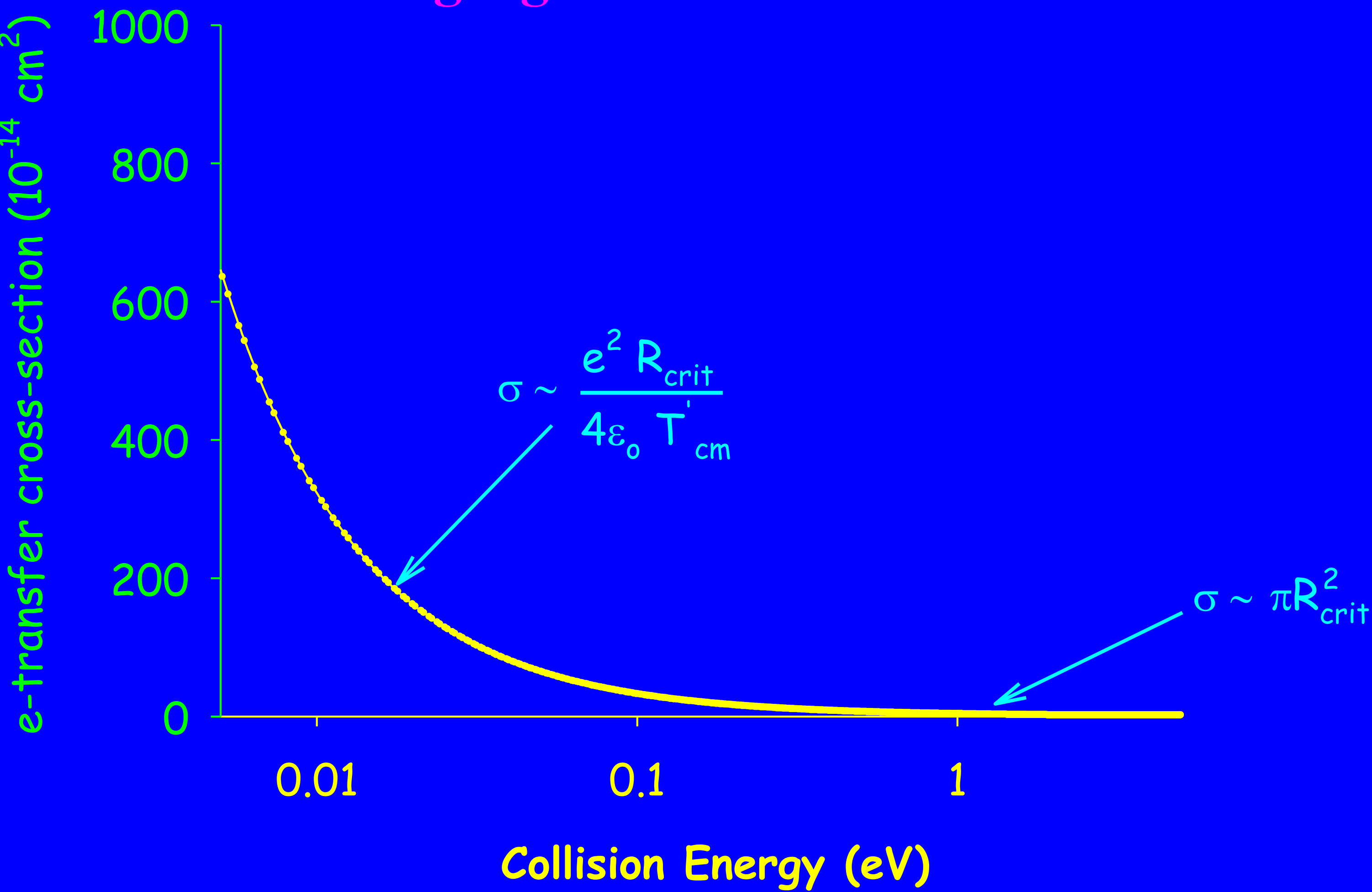
Double ElectroStatic Ion Ring ExperimEnt: DESIREE

The Merging section – Cross sections



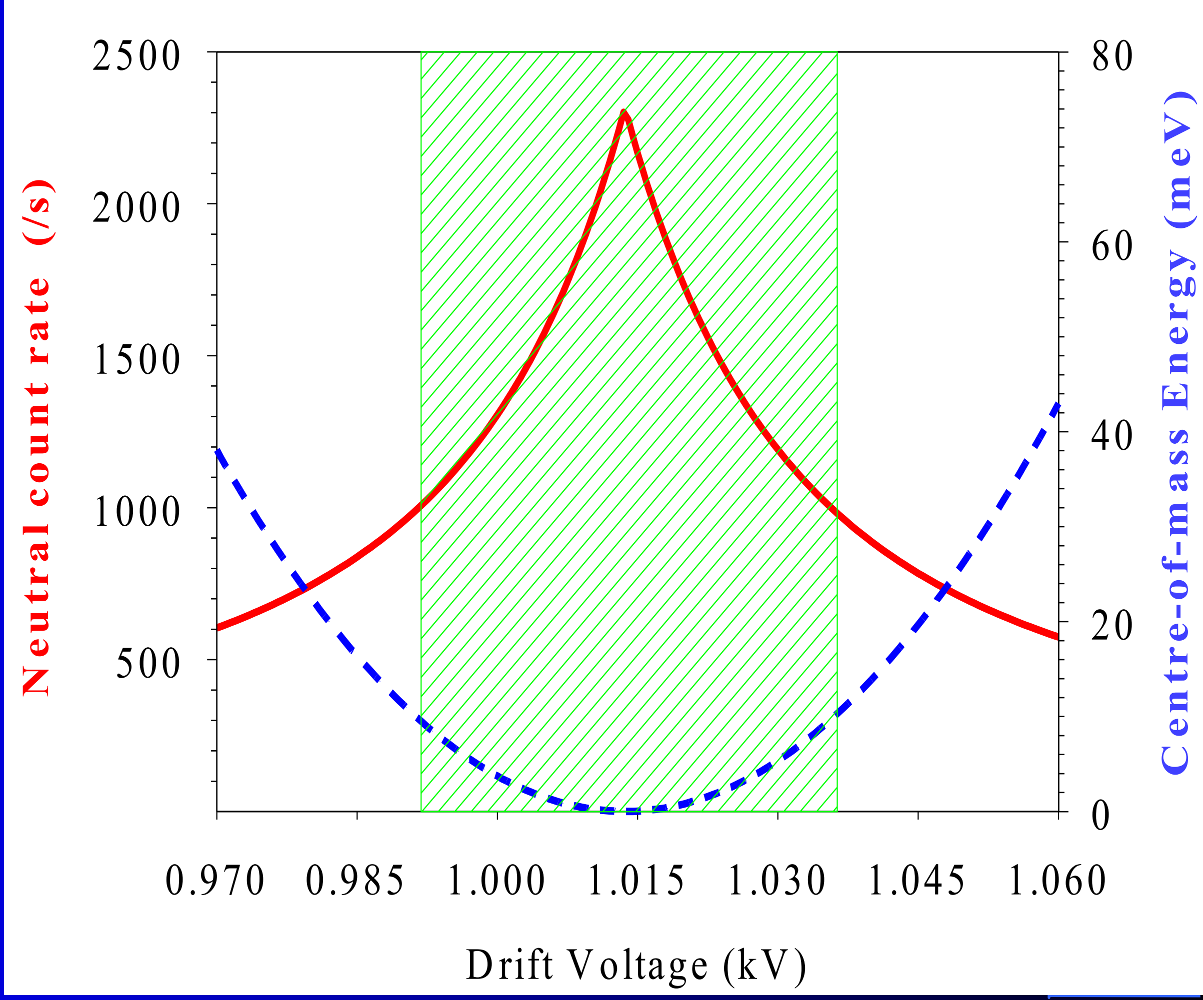
Ion Storage Rings II

Double ElectroStatic Ion Ring ExperimEnt: DESIREE

The Merging section – Count rates

$$\text{Rate} = \frac{I_H I_L}{e^2} \frac{v_{rel}}{v_H v_L} \frac{L\sigma}{A_{max}}$$

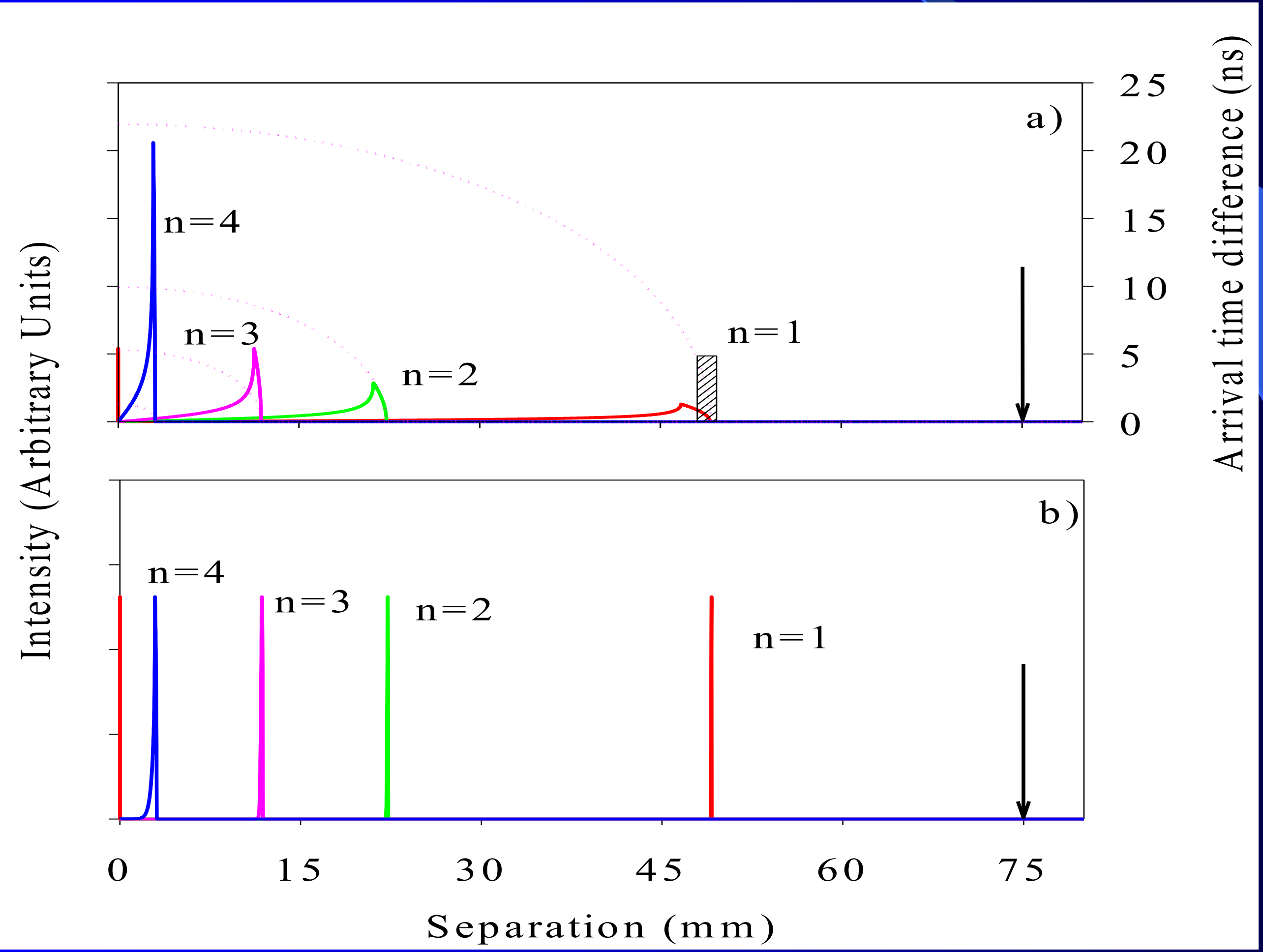
$I_H = I_L = 500$ nA,
$m_H = H^+$, $m_L = H^-$,
$T_H = 26$ keV, $T_L = 24$ keV,
$A_{max} = 2\ cm^2$, $L = 7.5$ cm,
$R_{crit} = 35\ a_o$



Ion Storage Rings II

Double ElectroStatic Ion Ring ExperimEnt: DESIREE

The Merging section – Imaging, and using arrival times



What Can We Do That Is Different?

- Mutual Neutralisation:

$$O_2^+ + O_2^- \rightarrow 4O$$

$\Delta H = \approx$-1.3 eV

Multiple bond breaking?

$$H^+ + H^- \rightarrow H + H$$

ΔH = -11.33 eV

1 elect.-excited product?

First experiment

$$C_{60}^+ + C_{60}^- \rightarrow C_{60} + C_{60}$$

$\Delta H = \approx$-5 eV

Stay as buckyballs?

- Two-step reactions driven by EA:

$$Br^- + F^+ \rightarrow Br^+ + F^-$$

	$\Delta_f H$ (eV)	IE (eV)	EA (eV)
F	0.823	17.42	3.40
Br	1.159	11.81	3.36

$2e^-$

$[^-Br \ldots F^+]$

ΔH = -5.63 eV

- Charge Exchange/Transfer:

$$H^+ + D^- \rightarrow H^- + D^+$$

Background free!

$$C_{60}^+ + C_{60}^- \rightarrow C_{120}$$

Molecular Fusion!

- Investigate thresholds and reactive collisions:

$$Na^+ + PO_3^- \rightarrow Na + PO_2 + O \quad \Delta H = \approx +0.4 \text{ eV}$$

$$Na^+ + PO_3^- \rightarrow Na + PO + O_2 \quad \Delta H = \approx +0.8 \text{ eV}$$

vs

$$Na^+ + PO_3^- \rightarrow NaO + PO_2 \quad \Delta H = \approx -2.4 \text{ eV}$$

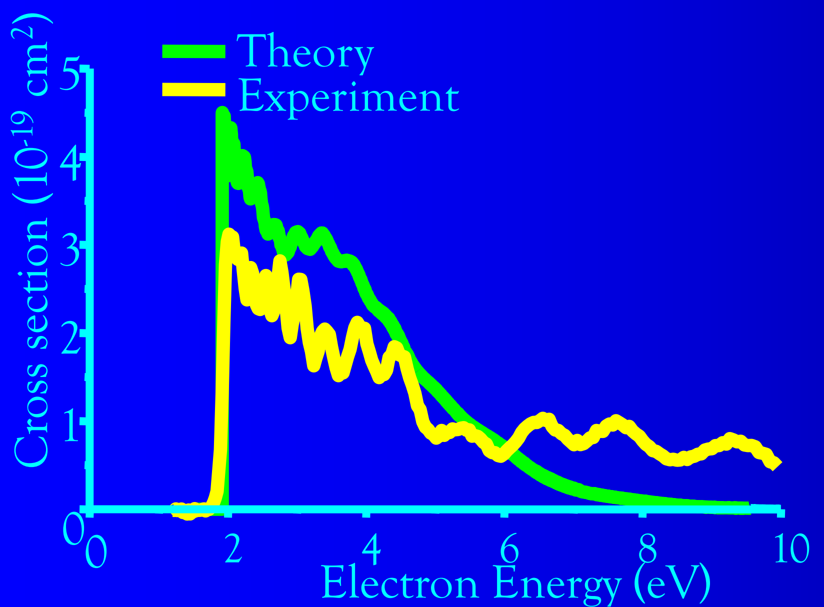
What Can We Do That Is Different?

CRYRING/TSR

Resonant Ion-Pair Formation

$$AB^+ + e^- \rightarrow A^+ + B^-$$

$$HD^+ + e^- \rightarrow H^+ + D^-$$



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Associative Attachment

$$A^+ + B^- \rightarrow AB^+ + e^-$$

$$H^+ + D^- \rightarrow HD^+ + e^-$$

?

"Run the theory backwards"?

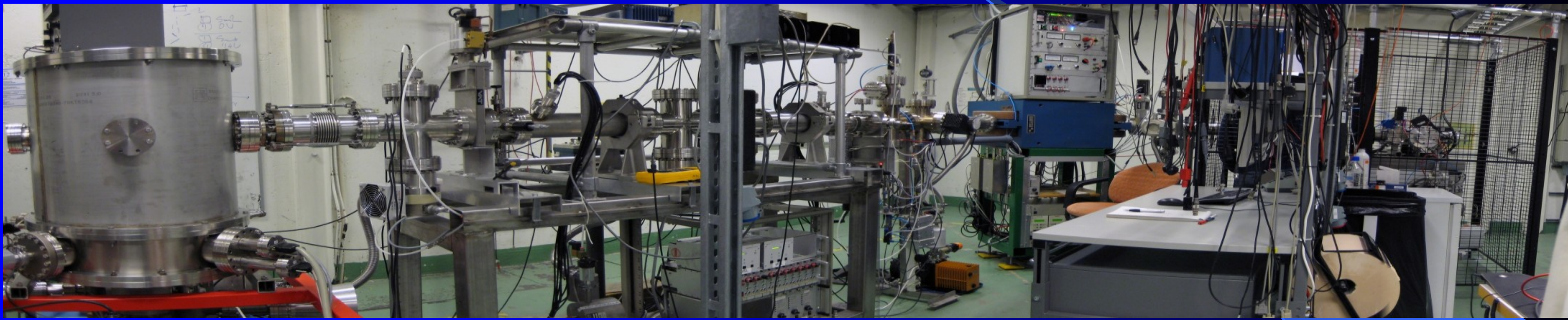
- Should we expect to see resonance in AB^+ production?
- Initial state dependencies

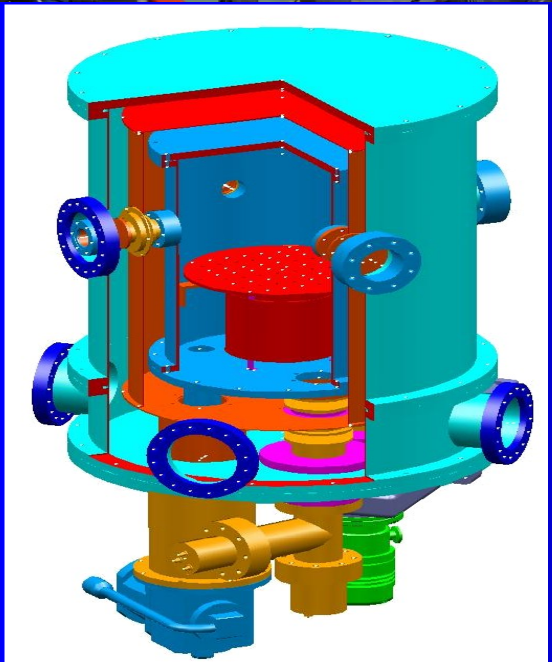
DESIREE

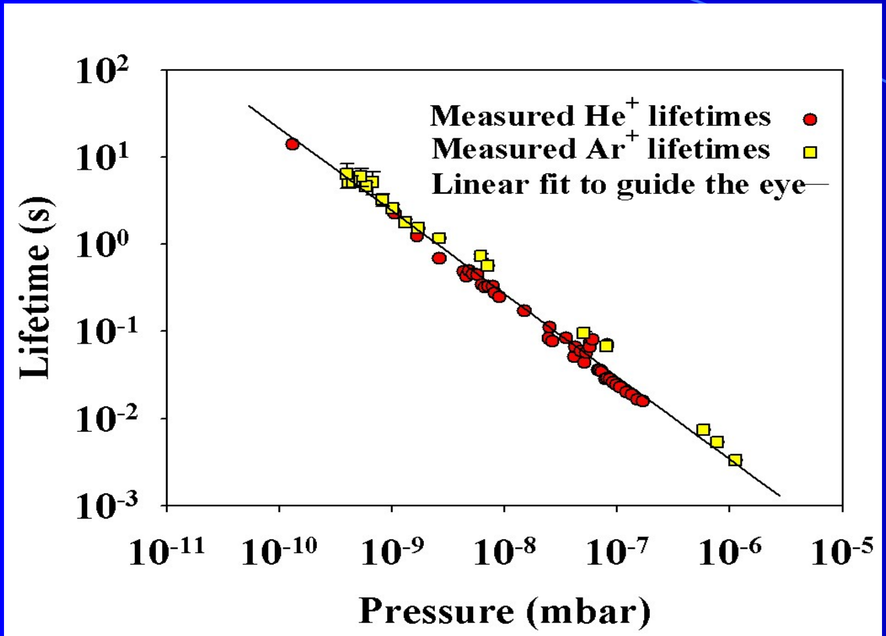
For Testing of

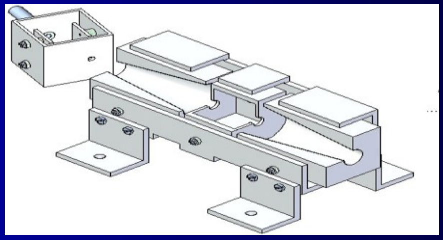
- Cryogenerators
- Feedthroughs
- Detectors
- Bake-out
- Laser Ports

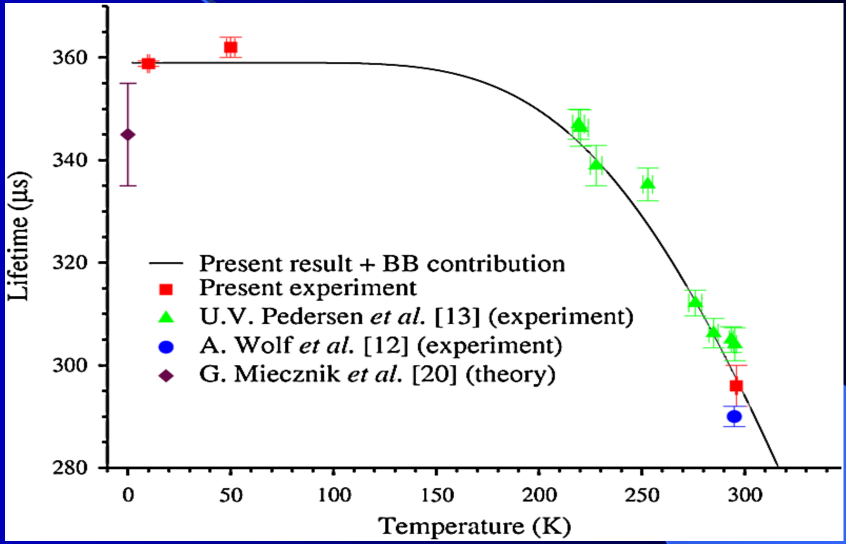
A test cryostat was built for ion-trap experiments.











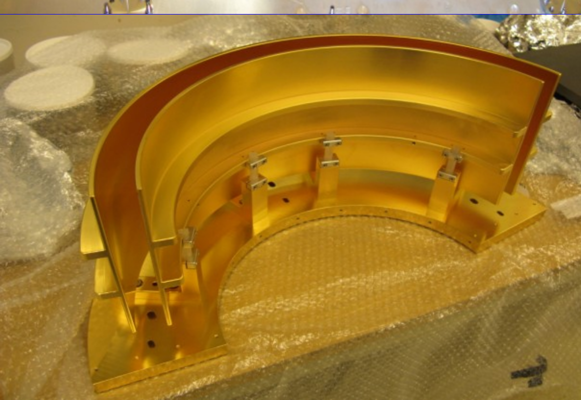
Publications from testing

S. Rosén *et al.*, Rev. Sci. Instrum. **78**, 113301 (2007)
P. Reinhed *et al.*, Phys. Rev. Lett 103, 213002 (2009)
P. Reinhed *et al*, NIM A 621, 83 (2010)

Complete DESIREE technical paper

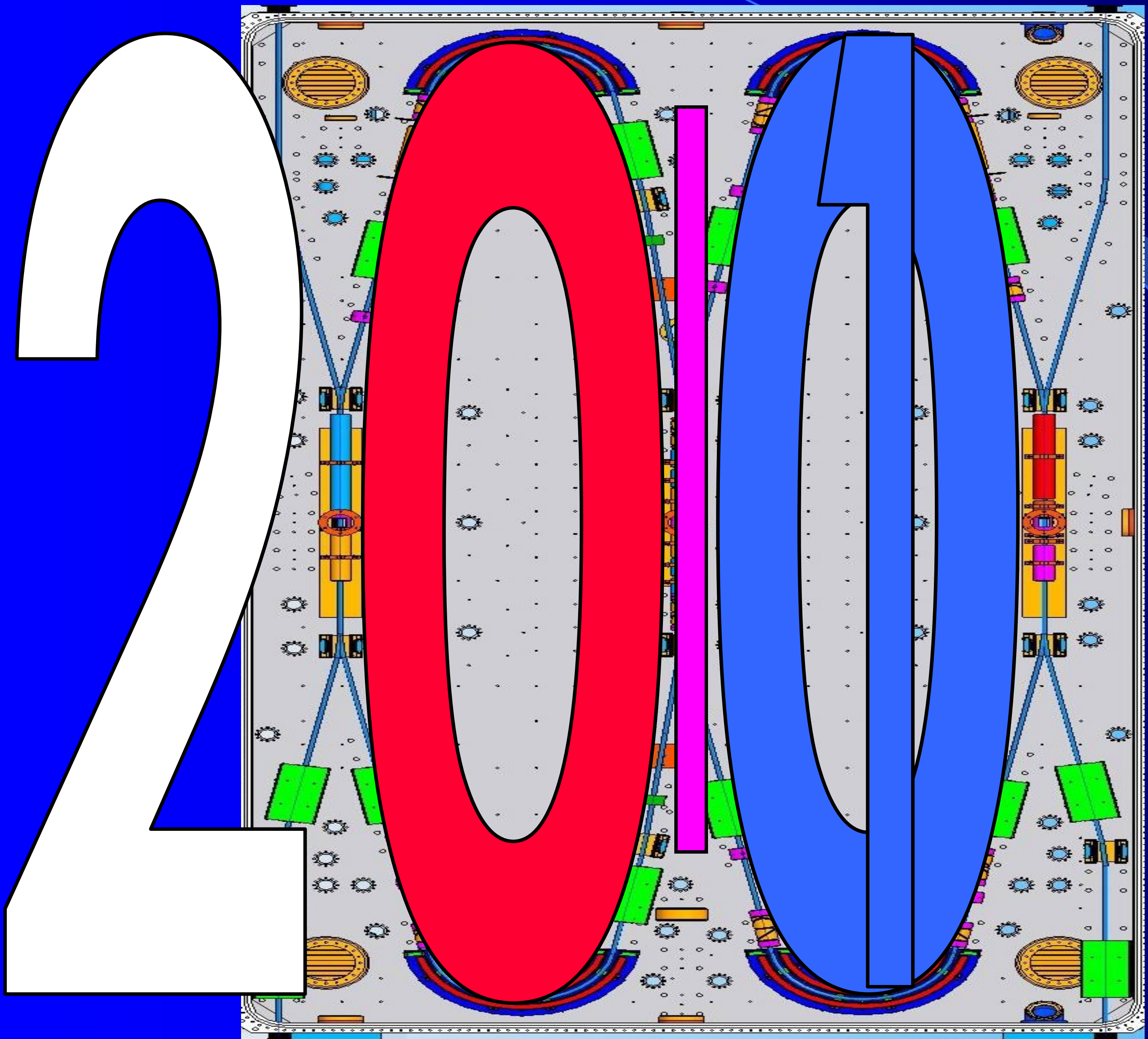
R. D. Thomas *et al.*, submitted to Rev. Sci. Instrum. Feb. 2011

Merged-beams Tools for the Study of Ultra-cold Reactions.



OK, just one magnet

First stored ions in ...



Thanks for your attention