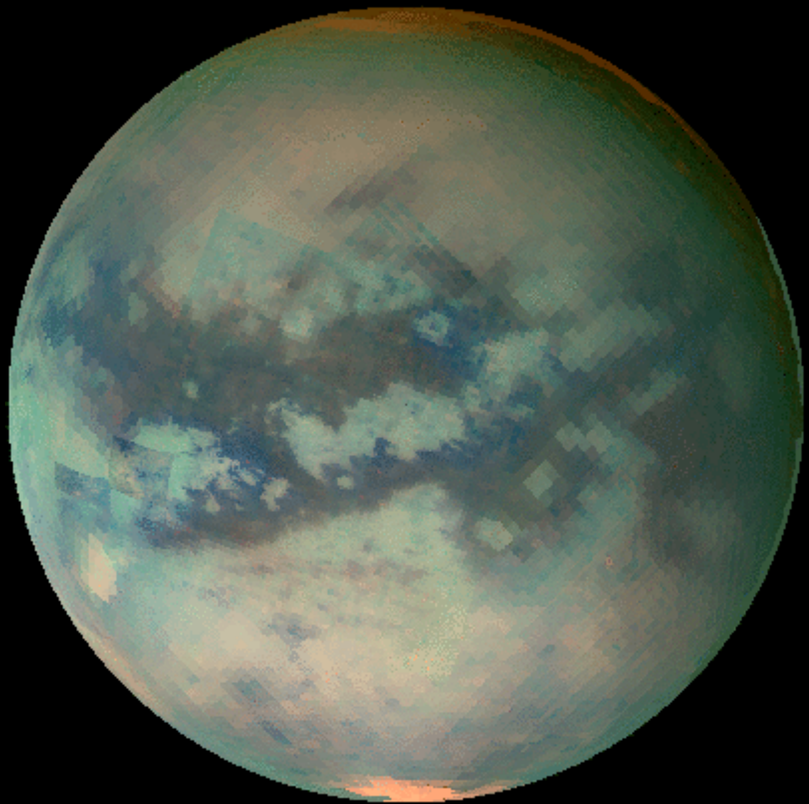
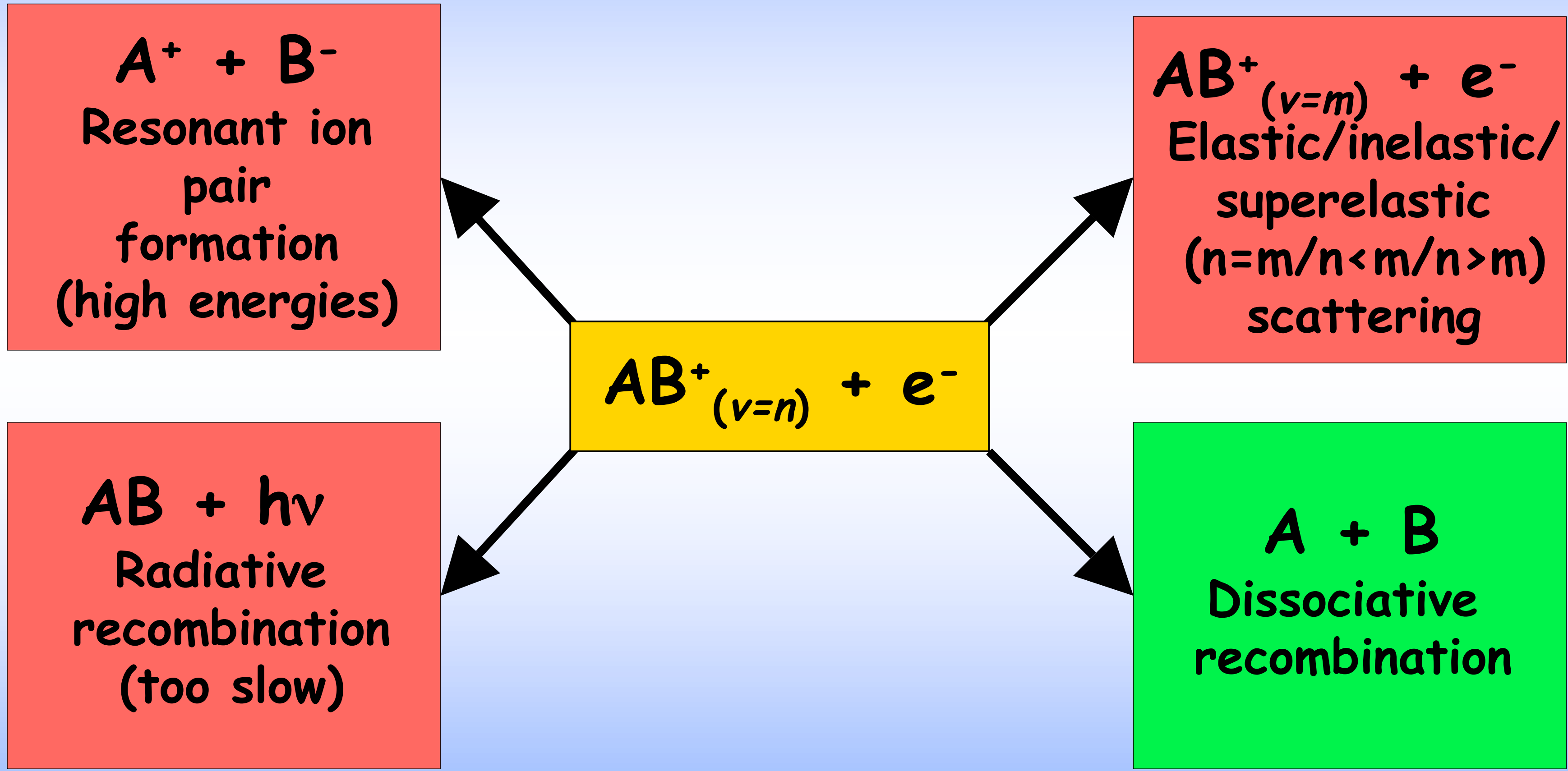
Dissociative recombination reactions

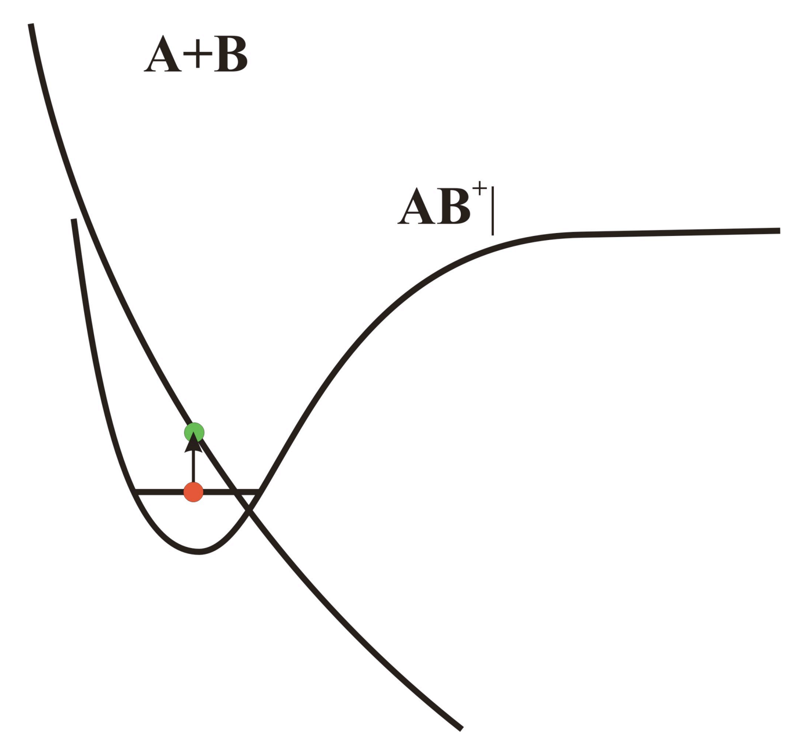


Wolf D. Geppert
ISSI workshop, Bern (CH)
January 2008

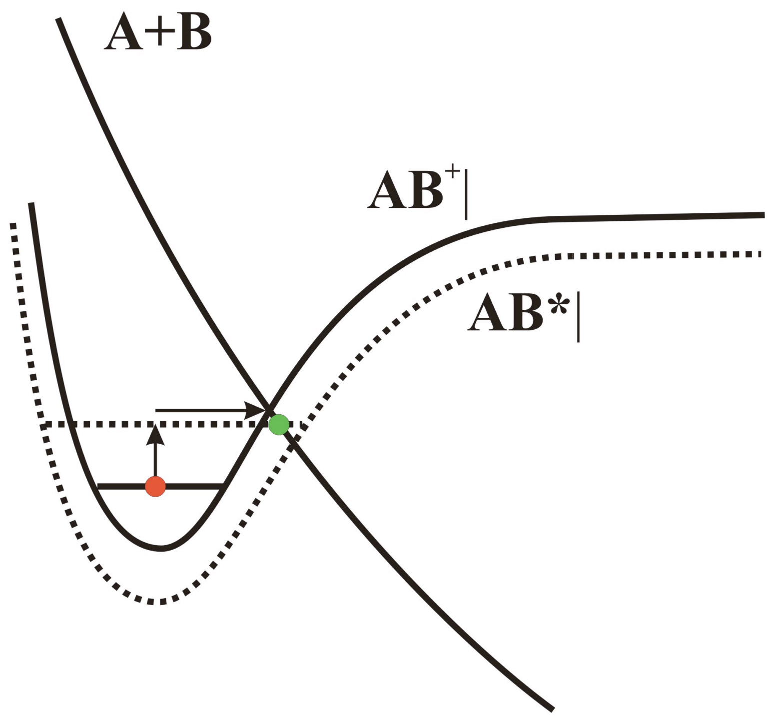
Important electron-ion processes



Mechanisms of dissociative recombination (DR)



Direct process



Indirect process

- ★ rate governed by Coulomb interaction
- ★ cross section $\propto E_{collision}^{-1}$

- ★ interim Rydberg state with certain lifetime
- ★ resonances in σ/E plot possible

Importance of dissociative recombination (DR) in space

★ Major process in molecular clouds, planetary ionospheres and cometary comae

★ final step in synthesis of neutrals (e. g. CH_4)

$$H_3^+ + C \rightarrow CH^+ + H_2$$
$$CH^+ + H_2 \rightarrow CH_2^+ + H$$
$$CH_2^+ + H_2 \rightarrow CH_3^+ + H$$
$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$$
$$CH_5^+ + e^- \rightarrow CH_4 + H$$

★ Competing process for ion-molecule reactions

$$CH^+ + e^- \rightarrow C + H$$

★ Sometimes unique destruction pathway for ions ($c\text{-}C_3H_3^+$ in Titan's ionosphere)

What information is required about DR reactions ?

★ Feasability in the ISM (absence of barrier, two-body process)

→ generally no problem, but: competition with ion-molecule reactions with abundant species (e. g. H_2 in dark clouds)

★ Reaction rate
(R. Johnsen: "always about 2×10^{-7} cm^{-3} at 300 K")

→ works fine with small ions HCO^+, N_2H^+ DR of larger ions much faster

★ Branching ratios
Big problem: unpredictable, counter-intuitive, results from different methods disagree:

CH_5^+ + e^- → CH_4 + H
only 5 % in ring (Semaniak et al.), dominant in afterglow (Adams et al.)

Methods for investigating DR reactions

Two groups:

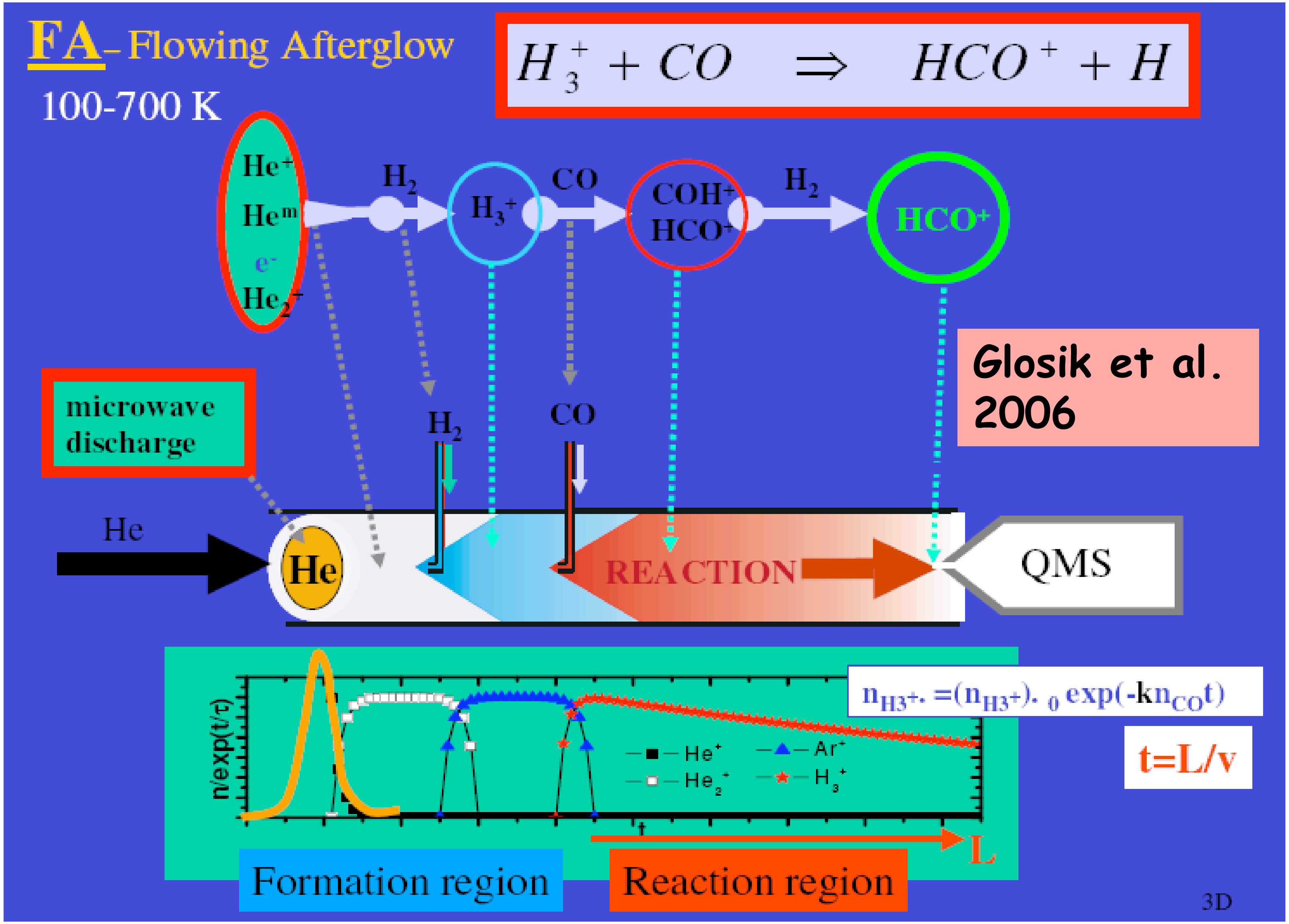
Flowing afterglow methods

- ★ Production of He^+ by microwave discharge
- ★ Ion production by consecutive reactions
- ★ Measurements of ion and electron (Langmuir probe) decay

Storage ring methods

- ★ Ions stored in magnetic or electrostatic ring
- ★ Merged with electron beam

FALP



FA methods - advantages and disadvantages

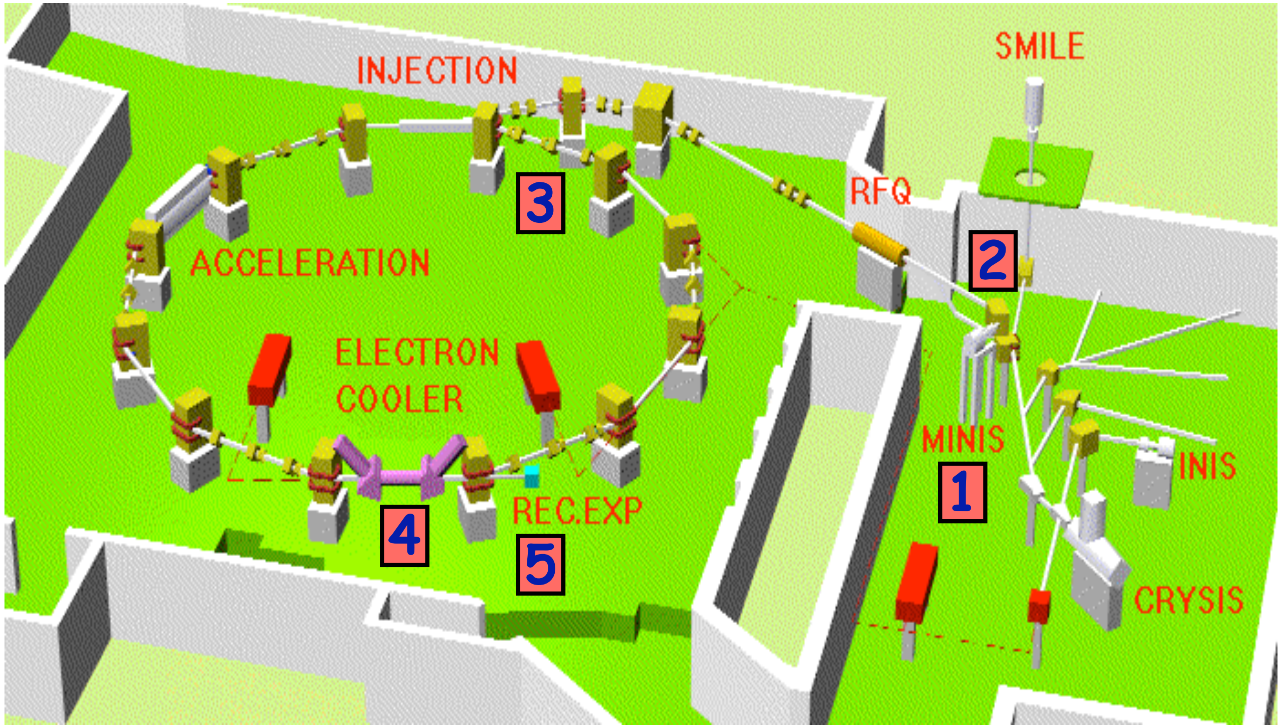
Advantages

- ★ Thermic equilibrium by frequent collisions
- ★ Low running costs

Disadvantages

- ★ Restricted to ions that are easily produced (e. g. by protonation through H_3^+)
- ★ No pure ion beam
- ★ No interstellar conditions (T=100-700K, collisions of intermediates with gas molecules posssible)
- ★ Detection of all products difficult

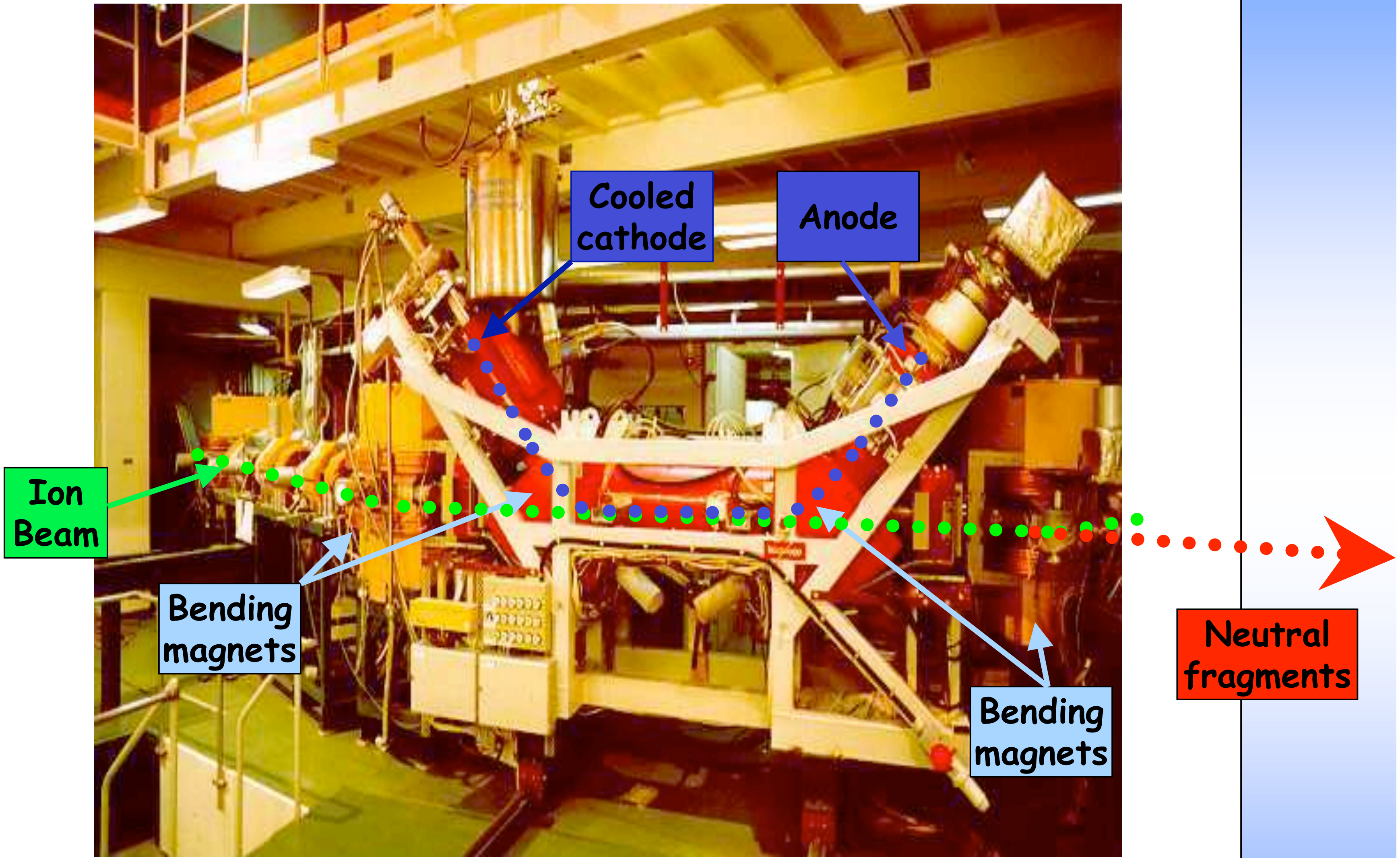
The CRYRING storage ring



Schematic view of CRYRING

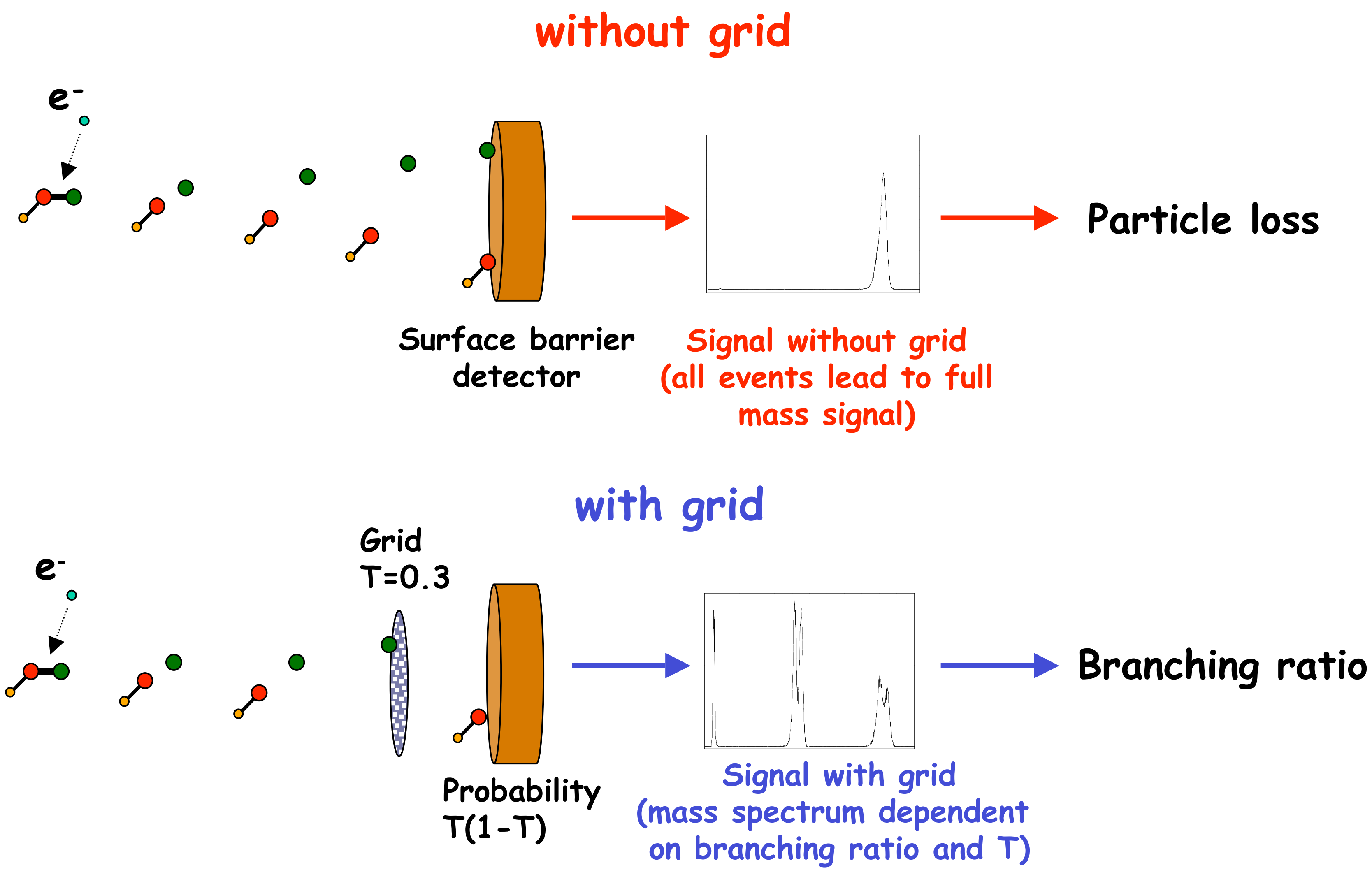
Steps during the experiment

1. Formation of ions in source
2. Mass selection by bending magnet
3. Injection via RFQ and acceleration
4. Merging with electron beam
5. Detection of the neutral products

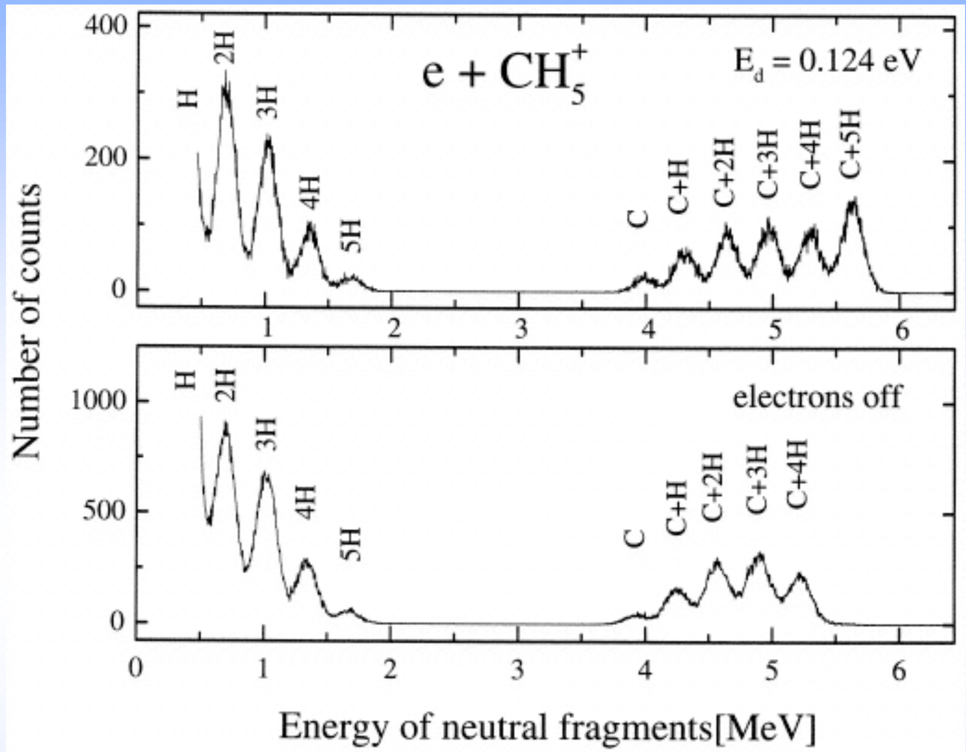


Electron cooler

Grid technique



Branching ratio of CH_5^+



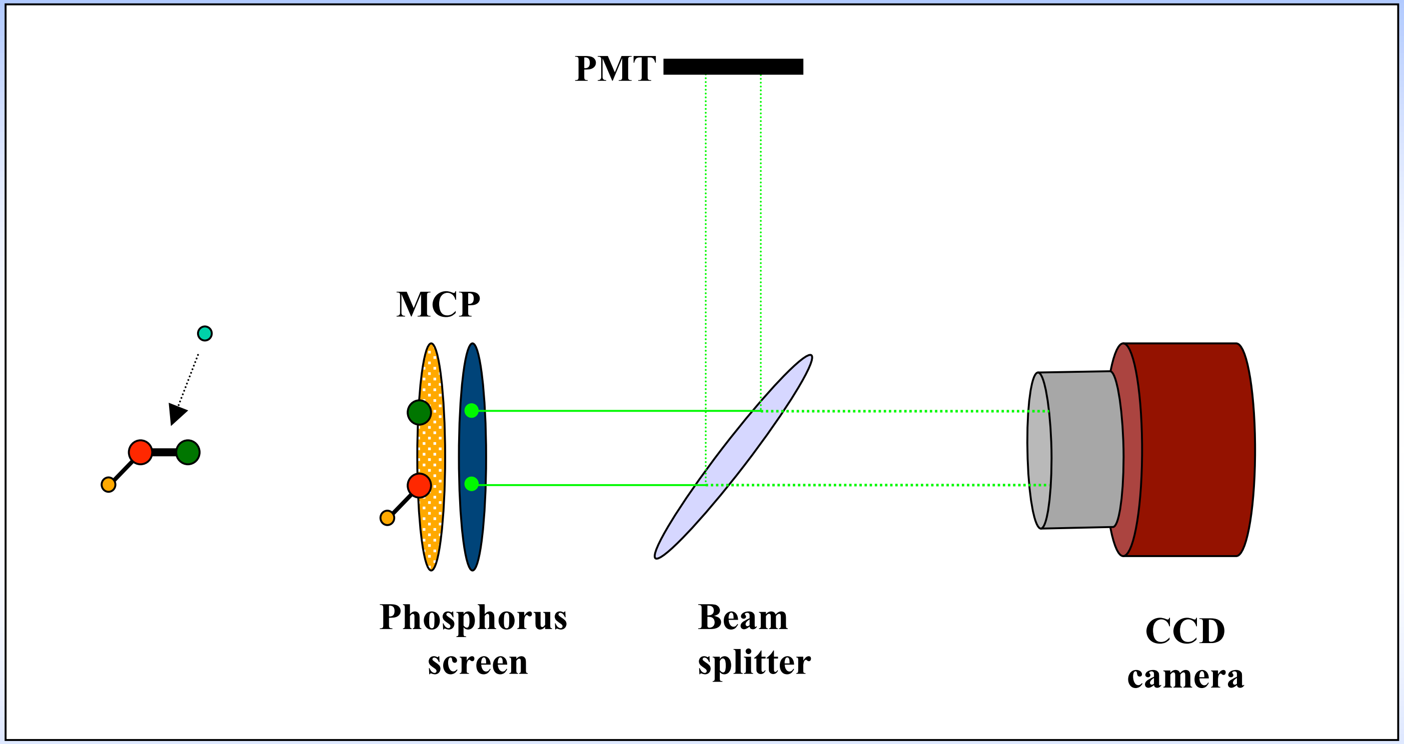
← Signal

← Background with electrons off

CH_5^+ + e^-	→	CH_4	+ H		5 %
	→	CH_3	+ H_2		5 %
	→	CH_3	+ 2H		70 %
	→	CH_2	+ H_2	+ H	17 %
	→	CH	+ H_2	+ H_2	3 %

Disagreement with flowing afterglow (Adams et al.)

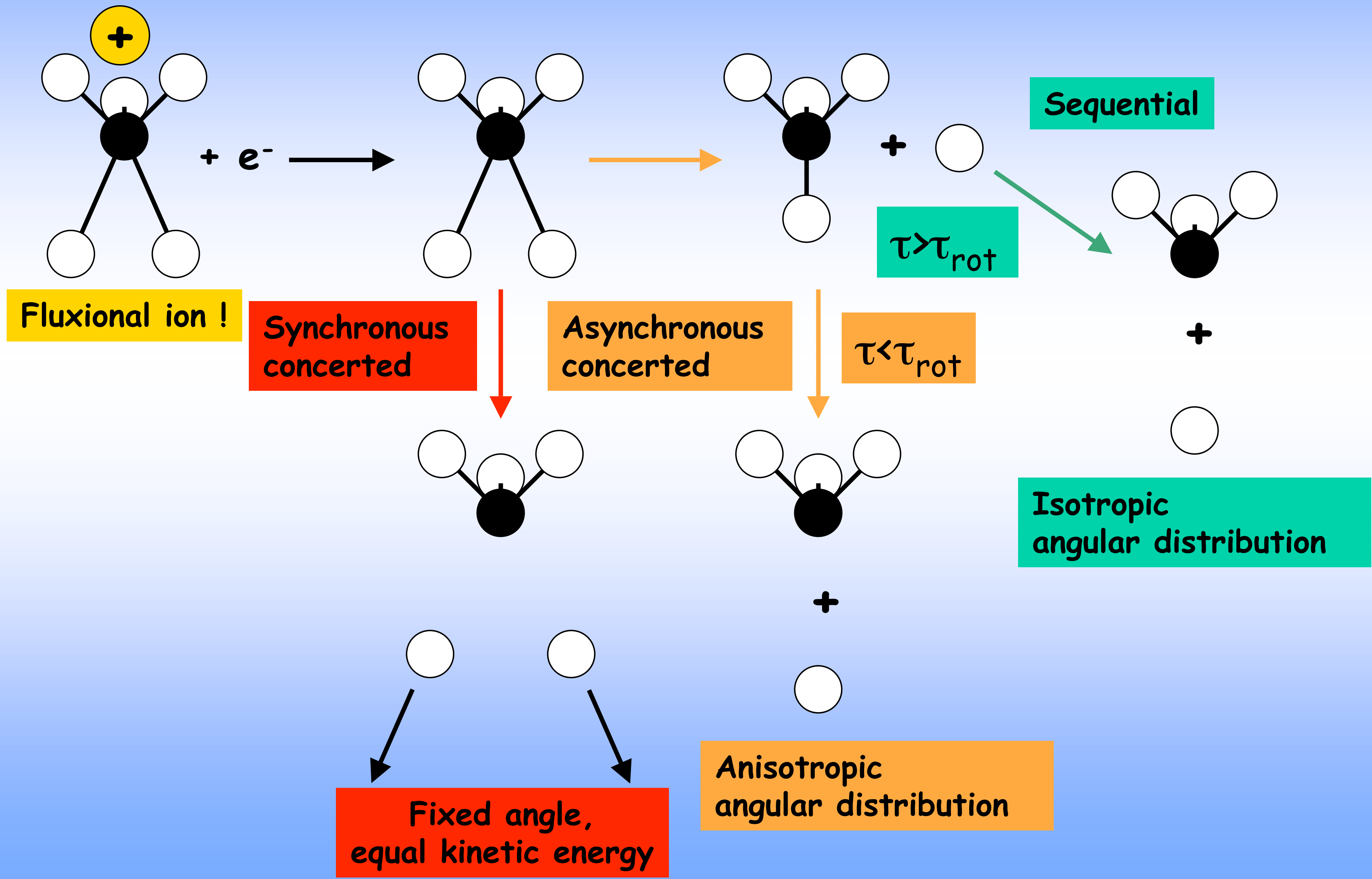
Imaging analysis



★ Yields information about displacement of products (kinetic energy release of products)

→ but not only that !

Synchronous or sequential break-up



Imaging results from DR of CH_5^+

★ Preliminary results suggest a sequential break-up of the CH_5 intermediate:

$$CH_5^+ + e^- \rightarrow CH_4^* + H$$
$$CH_4^* \rightarrow CH_3 + H$$

In presence of buffer gas (FALP):

$$CH_4^* + [M] \rightarrow CH_4 + [M]$$

Desactivation of ecxited CH_4 * → higher yield of CH_4

Three-body processes in DR: H_3^+

$H_3^+ + e^- + He \rightarrow H_2 + H$
$\rightarrow 3H$
$\rightarrow H_3^*$ (long-lived Rydberg)

With high He concentrations H_3^* formation important:

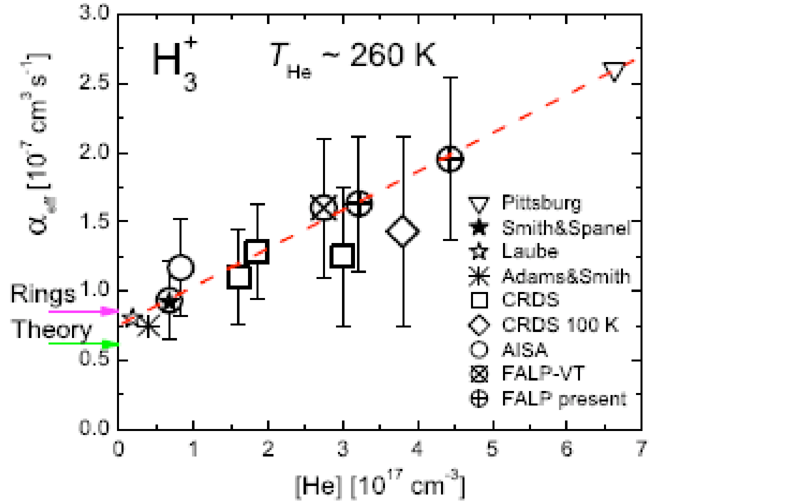
at low H_2 abundance: H_3^* formation competes with DR

at high H_2 abundance: Collisions with H_2 lead to less stable H_3^{**}

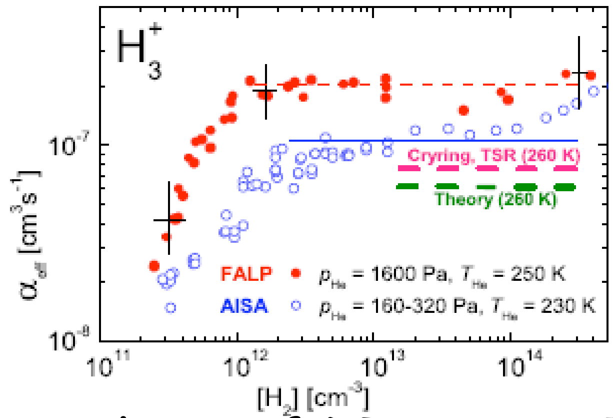
$H_2 + H_3^* \rightarrow H_2 + H_3^{**}$
$H_3^{**} \rightarrow 3H,\ H_2 + H,\ H_3^+$

→ DR rate constant dependent on $[H_2]$

Glosik et al. 2007



Dependence of DR rate on [He]



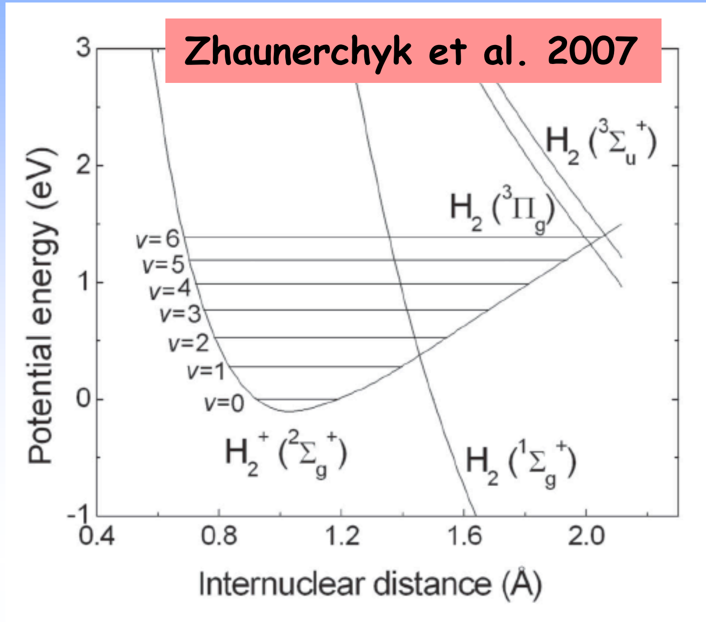
Dependence of DR rate on $[H_2]$

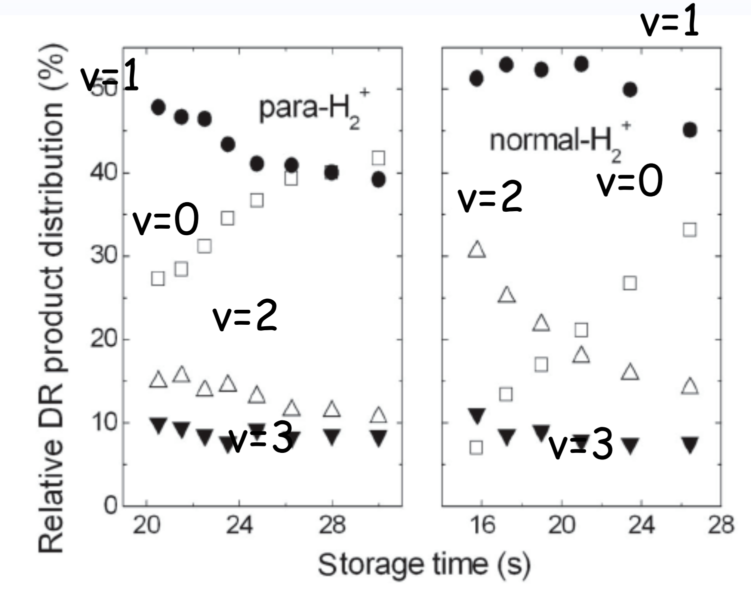
Vibrational excitation and DR: H_2^+

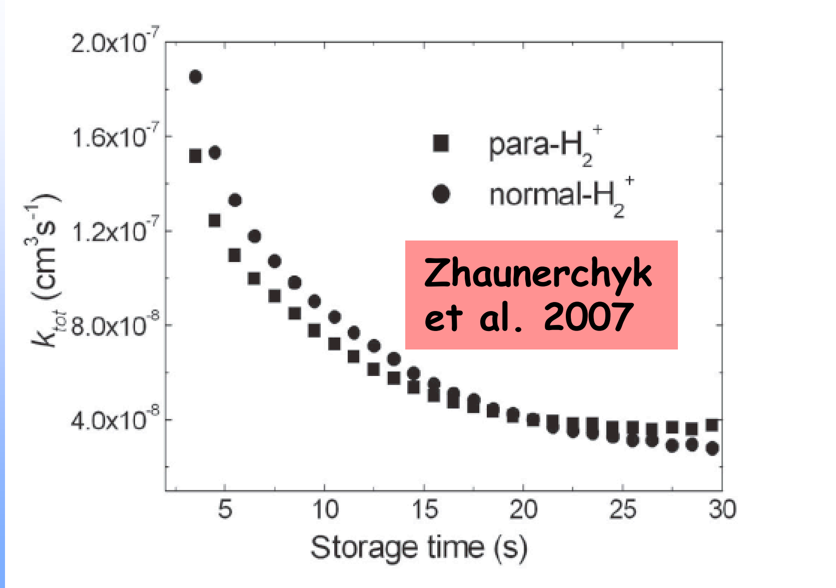
- ★ DR faster for vibrationally excited states of H_2^+
- ★ Opening of direct channel(s) at v>1
- ★ Cooling of ions in supersonic ion source
- ★ Cooling in ring by superelastic collisions

$$H_2^+{}_{(v=n)} + e^- \rightarrow H_2^+{}_{(v<n)} + e^-$$

- ★ Imaging allows to gauge $v(H_2^+)$





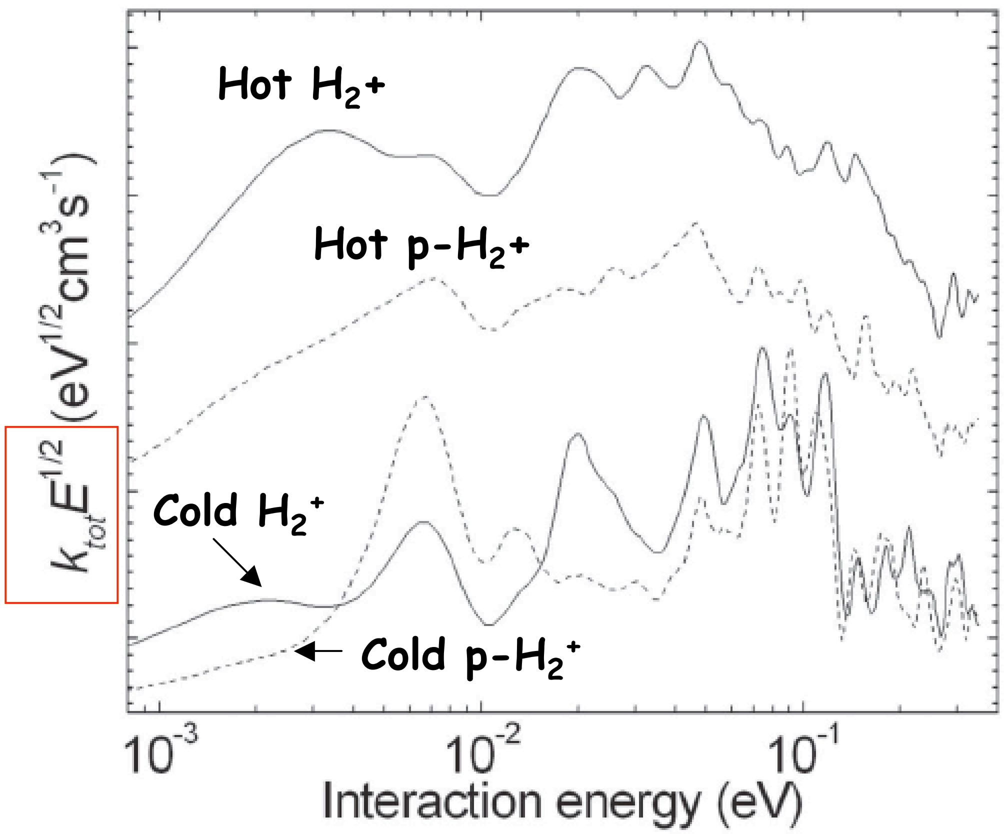


Nuclear spin and DR

- ★ Different rates of DR in ortho/para H_2^+
- ★ Resonances in ortho and para H_2^+
- ★ DR of hot H_2^+ faster
- ★ Resonances different and broader in H_2^+
- ★ Differences observed in H_3^+ (I=1/2, 3/2) also

	Rate constants × $10^{-7} cm^3 s^{-1}$	
v	Normal H_2	Para H_2
0	1.4	2.7
1	11	6.0
2	14	13.6
3	1.6	3.7

DR rate constants of normal and para H_2^+ at different vibrational excitation levels



Rate constants of the DR of hot and cold normal (solid) and para (dashed) H_2^+ (Not to scale)

Zhaunerchyk et al. 2007

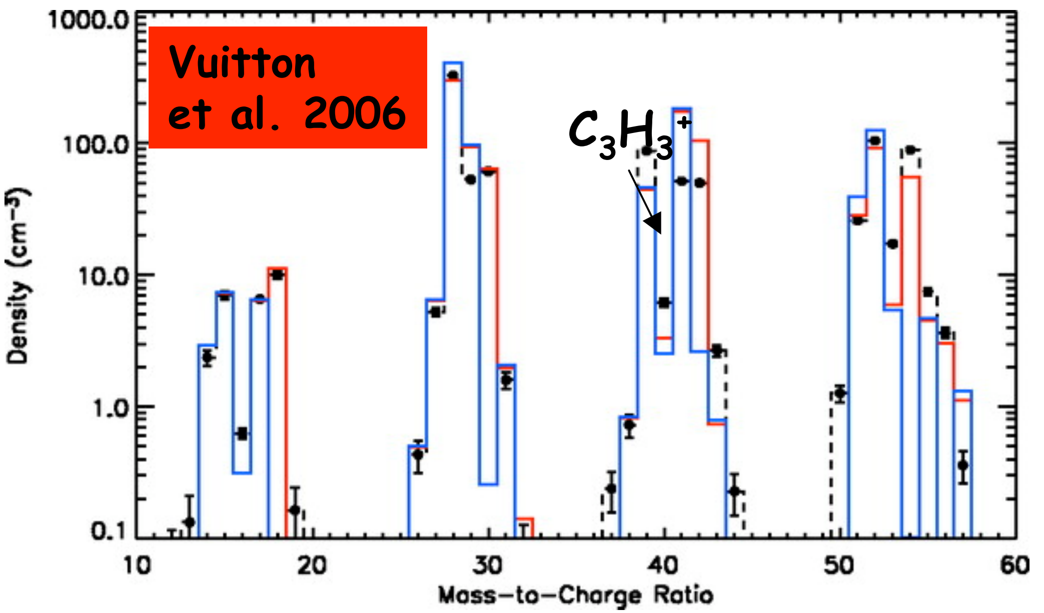
Influence of isomers

★ Many ions detected in cometary comae + planetary ionospheres (Cassini-Huygens mission) by mass spectrometers

★ Question of isomerism arises, e. g. in $C_3H_3^+$ (cyclic and linear form)

★ Linear form undergoes ion neutral reactions, cyclic only DR

$$l\text{-}C_3H_3^+ + C_2H_4 \rightarrow C_5H_7^+$$



INMS spectrum from the T5 flyby of Cassini-Huygens

HCO^+/HOC^+

- ★ Both isomers detected in the interstellar medium
- ★ HCO^+/HOC^+ ratio about 360-6000 in dense clouds (Apponi & Ziurys 1997)
- ★ In FALP and hollow cathode ion sources both isomers formed:

$$H_3^+ + CO \rightarrow HCO^+ + H_2 \quad (98\ \%)$$
$$\qquad\qquad\quad HOC^+ + H_2 \quad (\ 2\ \%)$$

- ★ DR of HCO^+ and HOC^+ have 3 different pathways:

$HCO^+ + e^-$	$\rightarrow$	$H + CO$	$\Delta H = -\ 7.45$ eV
	$\rightarrow$	$HC + O$	$\Delta H = +\ 0.17$ eV
	$\rightarrow$	$HO + C$	$\Delta H = -\ 0.75$ eV

$HOC^+ + e^-$	$\rightarrow$	$H + CO$	$\Delta H = -\ 7.79$ eV
	$\rightarrow$	$HC + O$	$\Delta H = -\ 0.17$ eV
	$\rightarrow$	$HO + C$	$\Delta H = -\ 1.09$ eV

HCO^+/HOC^+

$HCO^+ + e^-$		$DCO^+ + e^-$	
Reaction channel	**Branching ratio**	**Reaction channel**	**Branching ratio**
CO + H	0.92	CO + D	0.88
CH + O	0.01	CD + O	0.06
C + OH	0.07	C + OD	0.06

contribution of excited state

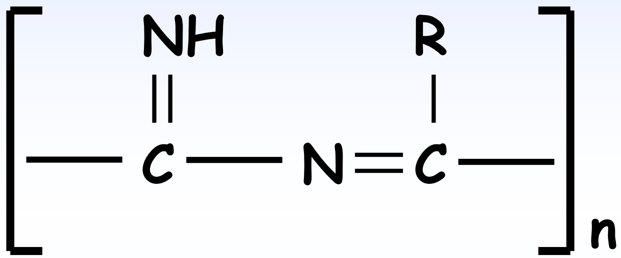
contribution of HOC^+ ?

- **In DCO^+ excited states with long lifetime (v3), not in HCO^+ (Heninger et al. 1999) → CD + O channel opens**
- **C + OH (C+ OD) channels maybe from HOC^+ contaminations**

Heavier systems: Protonated nitriles

- ★ Detected in greater abundances in Titan's ionosphere than thought
- ★ can polymerise (With HCN) to tholines (haze formation)

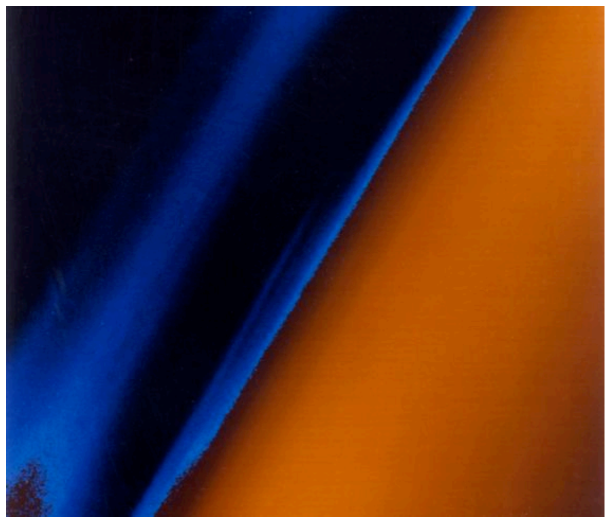
nRCN + nHCN →



Tholins

- ★ very little about ion chemistry of protonated nitriles and other nitrogen-containing ions known
- ★ models still flawed
- ★ identification of ions not unambiguous

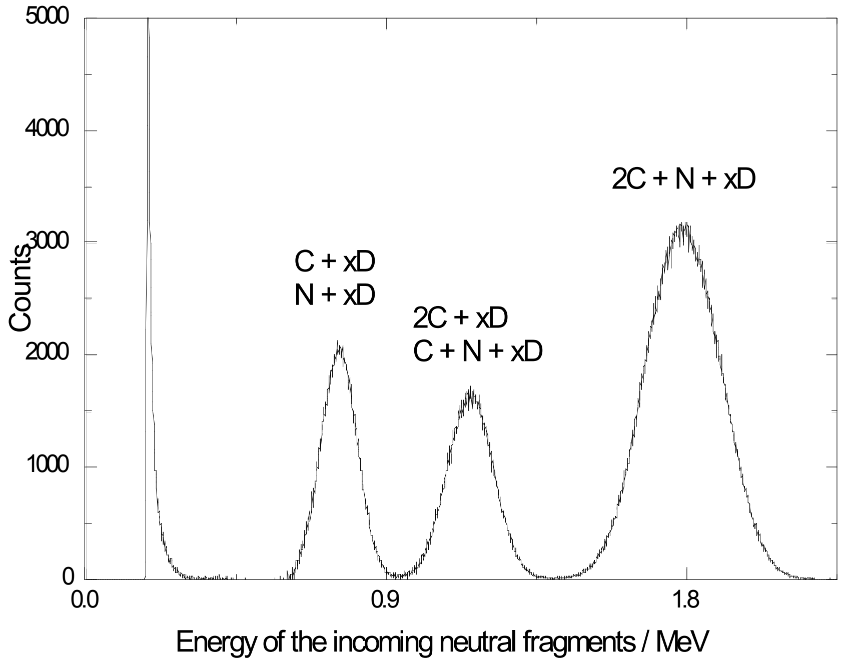
→ more molecular data is needed



Titan's haze seen by Voyager

Protonated acetonitrile (CH_3CNH^+)

- ★ 20 different channels
- ★ Inadequate resolution of peaks separated by single hydrogen (D) mass
- ★ Ring with higher rigidity (B×r) necessary
- ★ In 65 % of cases CCCN chain retained.
- ★ Reaction rate constant $8.1 \times 10^{-7}\ (T/300)^{-0.69}$
- ★ Reaction rate constant $8.1 \times 10^{-7}\ (T/300)^{-0.69}$ (2.5 times higher than in FALP)



DR fragment energy spectrum of CD_3CND^+

Statistical errors in reaction rate Constants measured by ring methods

- ★ Ion current measurement ~10 %
- ★ Background from rest gas collisions (few % at low collision energies)
- ★ Electron energy spread
- ★ Contribution from toroidal regions
- ★ Errors totally around 30 %

Ring methods - advantages and disadvantages

Advantages

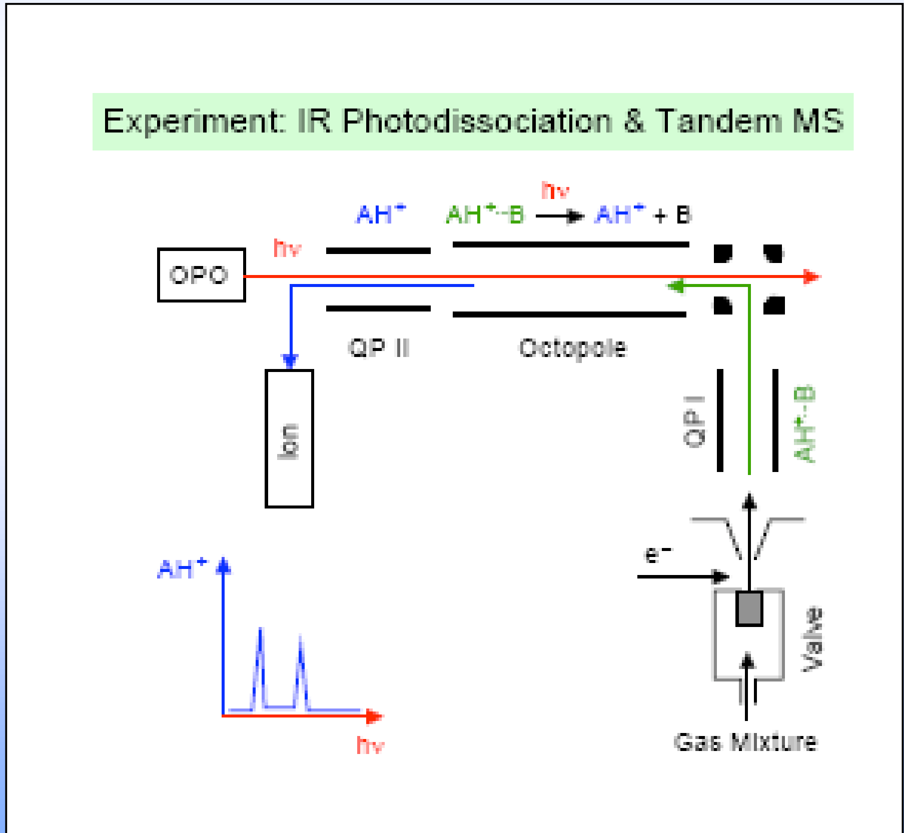
- ★ Mass selection of ions - enables study of more "exotic" species
- ★ Ultrahigh vacuum (10^{-11} mbar), excludes 3-body processes
- ★ Stepless variation of collision energy down to ~2meV
- ★ Identification of all possible reaction pathways (for lighter ions)

Disadvantages

- ★ Restricted to lighter ions (Cryring: M < 100 Dalton)
- ★ Isomers and isobars cannot be separated
- ★ Contributions of long-lived excited states possible
- ★ High set-up and running costs

Future challenges in DR measurements

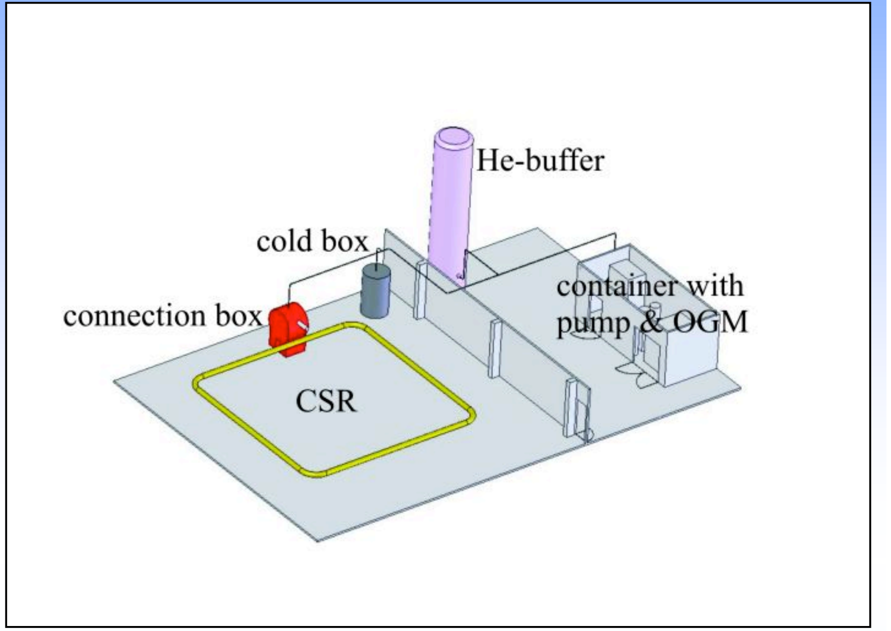
- ★ Perform experiments with rovibrationally cold ions
- ★ Create pure on beams of isomeric species (e.g through cluster dissociation)
- ★ Extend measurements to heavier and more "difficult" ions
- ★ Develop strategies for identi-fying new ions
- ★ Is DR the only important neutralisation process in the ISM and planet atmospheres ?

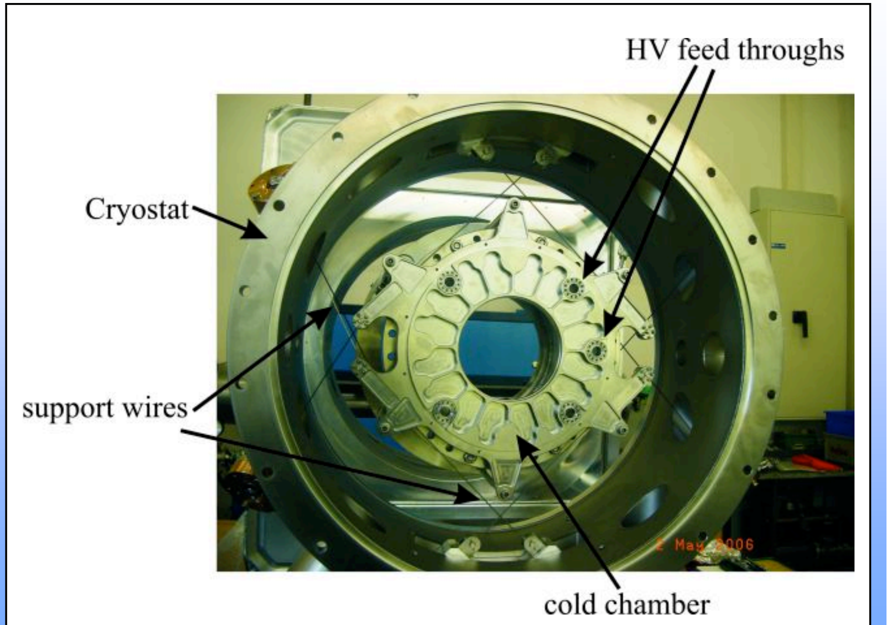


Dopfer and co-workers

Cold storage ring (MPIK,Heidelberg)

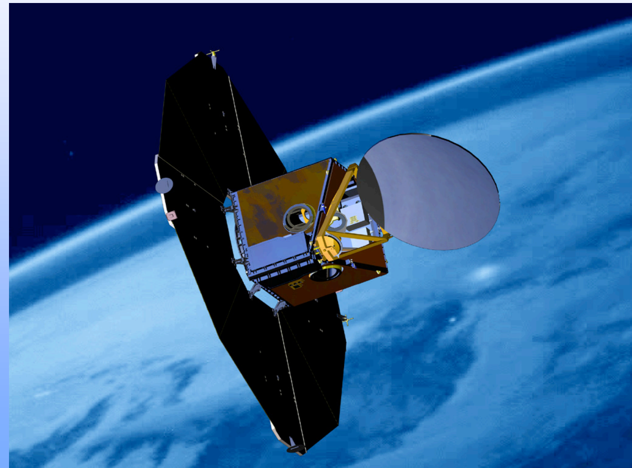
- ★ Electrostatic storage ring
- ★ Cooling down to 2K possible
- ★ Ion energy 20-300 keV/charge (CRYRING 2-96 MeV/charge)
- ★ Electron target with high resolution (500 μeV)
- ★ Detection of products by microcalorimeters
- ★ Commissioning planned 2008





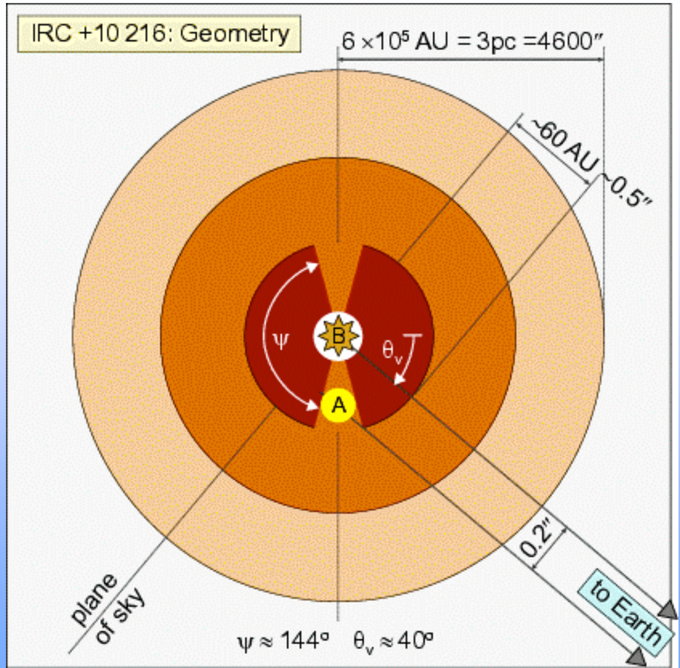
Anions in space

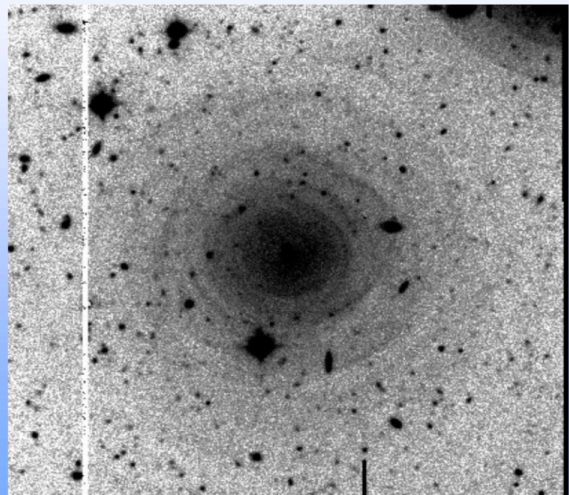
- Negative charge thought mostly to be present in the form of electrons.
- Anions first predicted by Herbst (1981), but detection hampered (lack of spectral, data, receivers, air absorption)
- Tentative detection of HS^- by ODIN in the Orion Molecular Cloud (OMC)

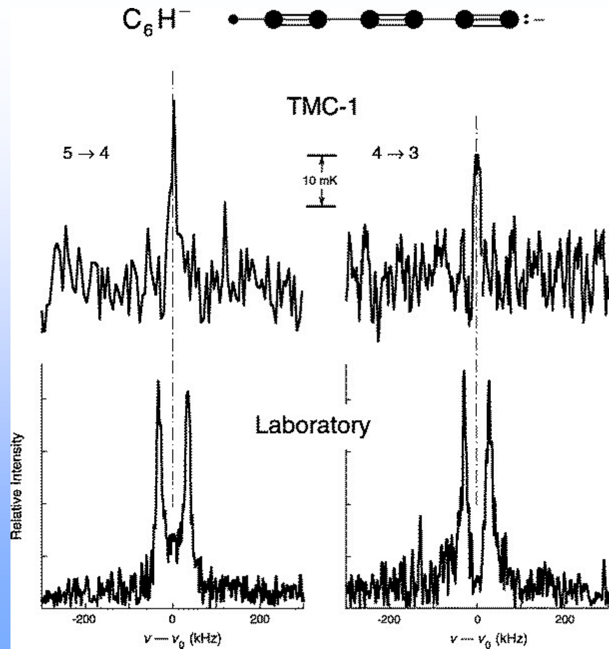


Detection of HC_6^- (Thaddeus & co-workers)

- ★ Detected in IRC+10216 (envelope of high-mass-loss carbon star)
- ★ Also observed in dark cloud TMC-1
- ★ Ratio of HC_6^-/HC_6 ~ 10 %
- ★ Further detected anions: HC_4^-,(L1527), HC_8^- (IRC+10216)



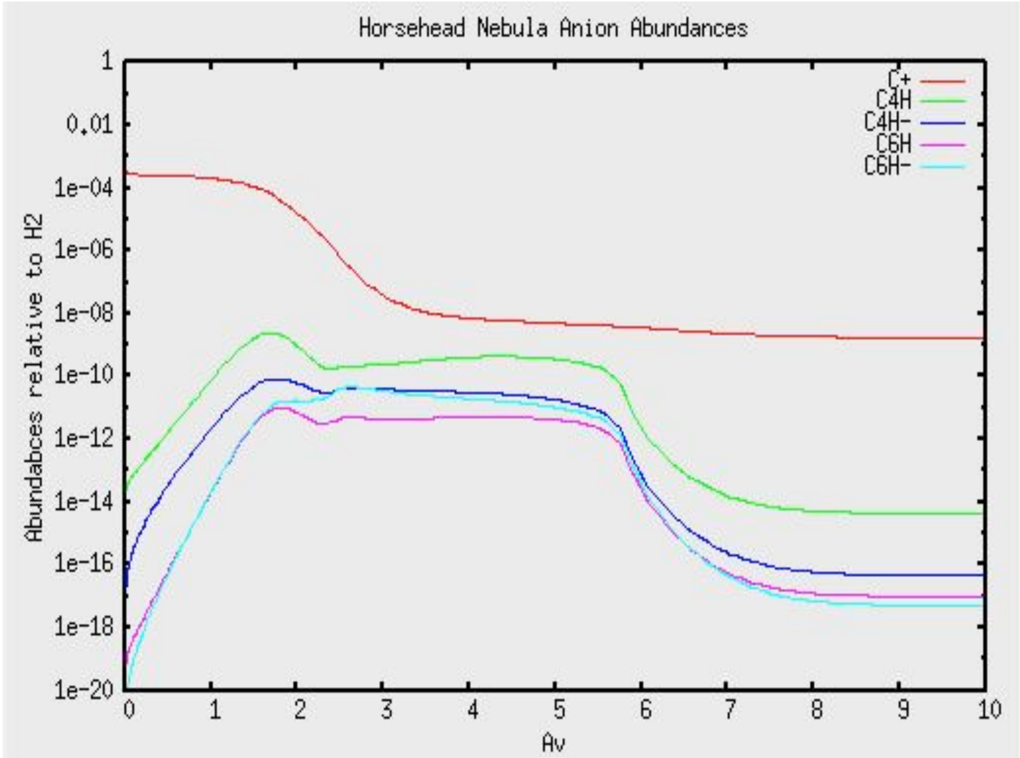




Possible other anion sources: Photon-dominated regions (PDRs)

= strongly irradiated edges of dark clouds

★ Strategy to look at diffuse clouds (high electron abundance) might be wrong



Model by Millar et al. 2007

Anion reactions in space

Associative detachment

$$C_6H^- \;+\; H \;\rightarrow\; C_6H_2 \;+\; e^-$$

probably important in diffuse clouds

Photodetachment

$$C_6H^- \;+\; h\nu \;\rightarrow\; C_6H \;+\; e^-$$

Ion-ion reactions (e. g. mutual neutralisation)

$$C_6H^- + C_2H_2^+ \rightarrow \text{neutral products}$$

Experimental data often lacking !

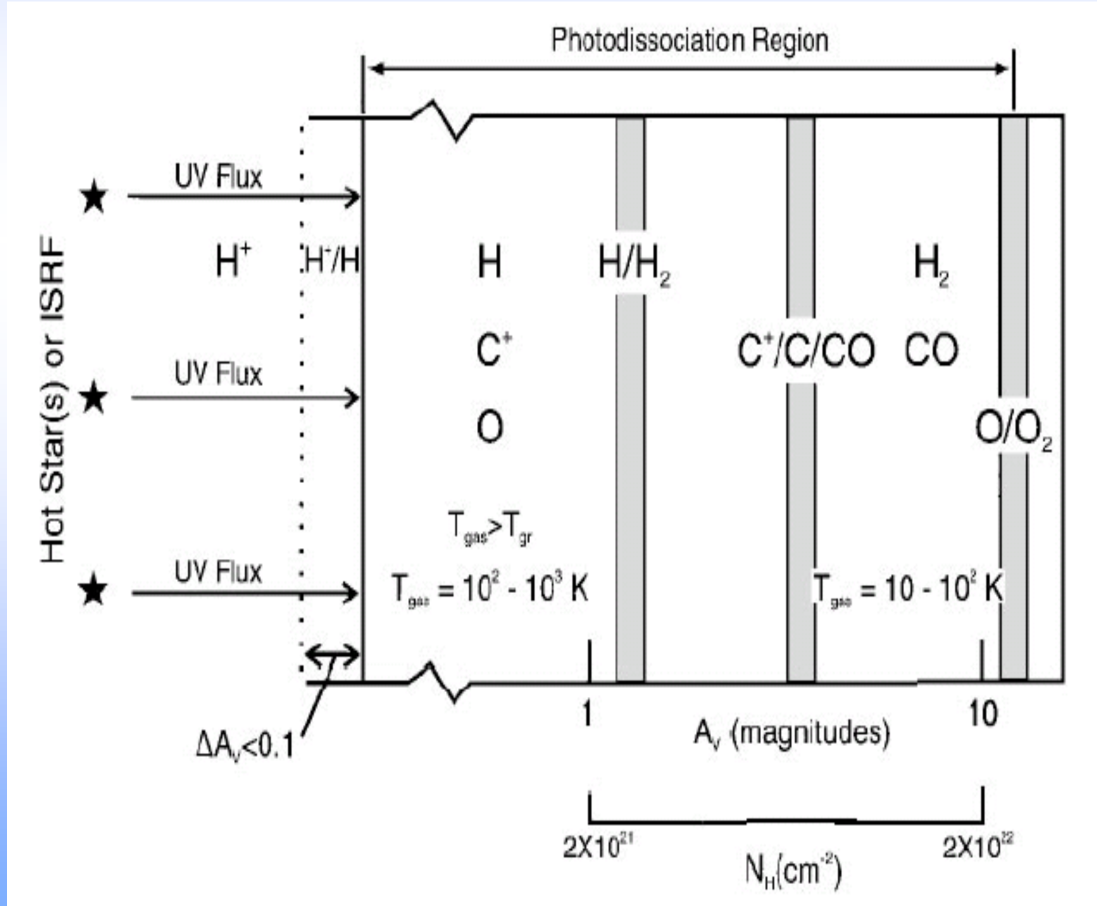
Relative importance of anion reactions

- ★ often dependent on different parameters (density, photon flux) e.g. in photon-dominated regions

- ★ in hot H^+ (HII) zones UV photo-dissociation dominant

- ★ in H region reaction with H

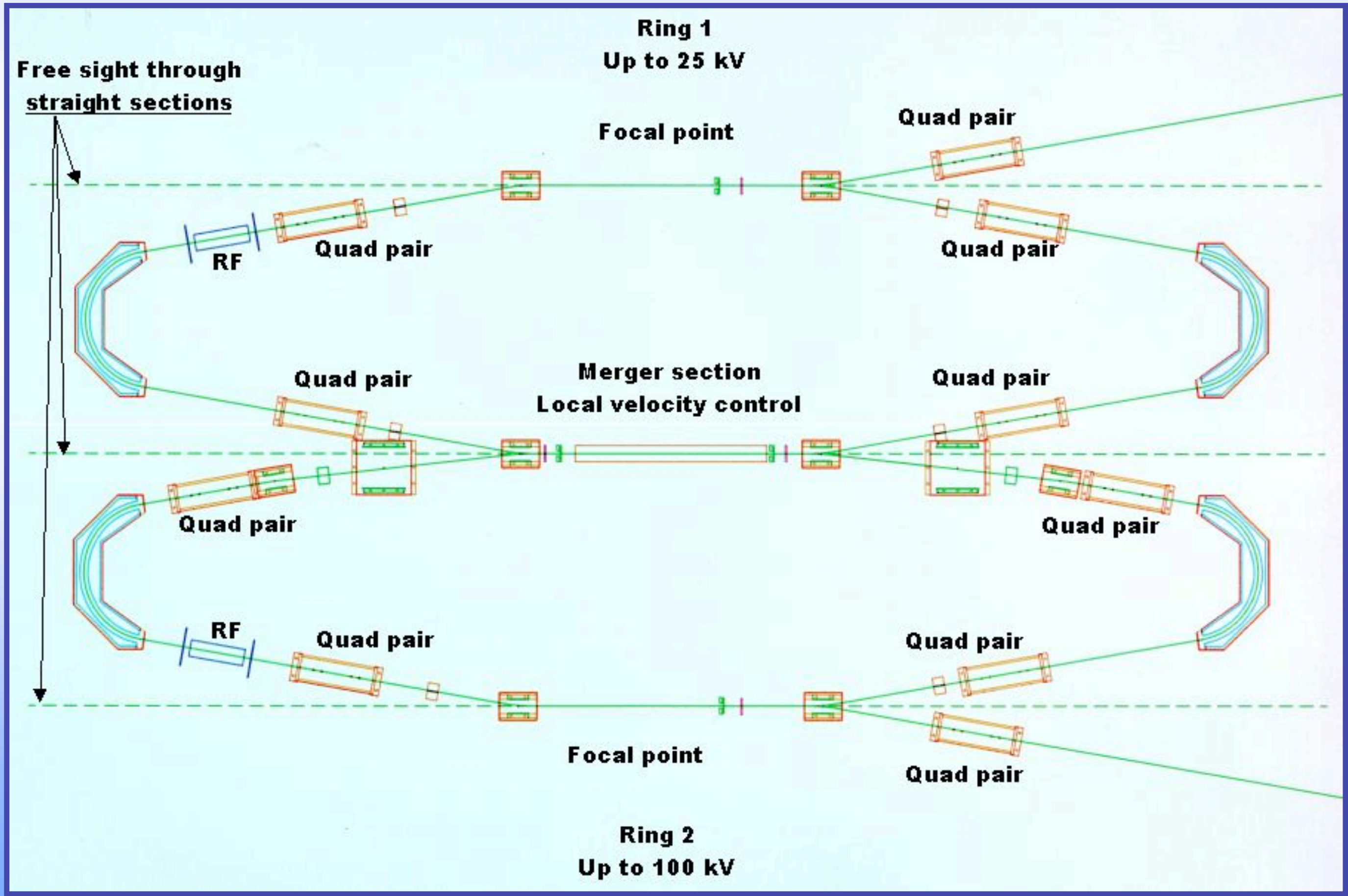
- ★ in darker regions mutual neutralisation



Can we elucidate these processes ?

Associative detachment: Ion traps with H sources (e. g. Chemnitz)

Mutual neutralisation + photodetachment: DESIREE



Conclusions

- ★ Uncertainties in DR reaction not statistic, but systematic
- ★ Main problems:
  - Involvement of excited states
  - Isomerism
  - Influence of nuclear spin
- ★ Many reaction pathways with larger ions
- ★ Anion reactions might play larger role than estimated
- ★ Reliable, up-to date and exhaustive database lacking

Acknowledgments

- My colleagues at Stockholm University: M. Hamberg, E. Vigren, R. D. Thomas, M. Kaminska, M. Larsson …..
- The CRYRING team at Manne Siegbahn Laboratory: A. Källberg, A. Simonsson, A. Paál …...
- EU, Swedish Research Council and Swedish Space Board for funding
- Valentine and the conveners of this workshop

Requirements for a new on-line database on astrochemical reactions

- ★ Exhaustive (not only referring to reactions going into standard models)
- ★ Critical (not only recommeding values, reporting state of discussions, identifying crucial processes)
- ★ Interactive (allowing discussions)
- ★ run by international advisory board
- ★ Up to date
- ★ Funded securely (COST)