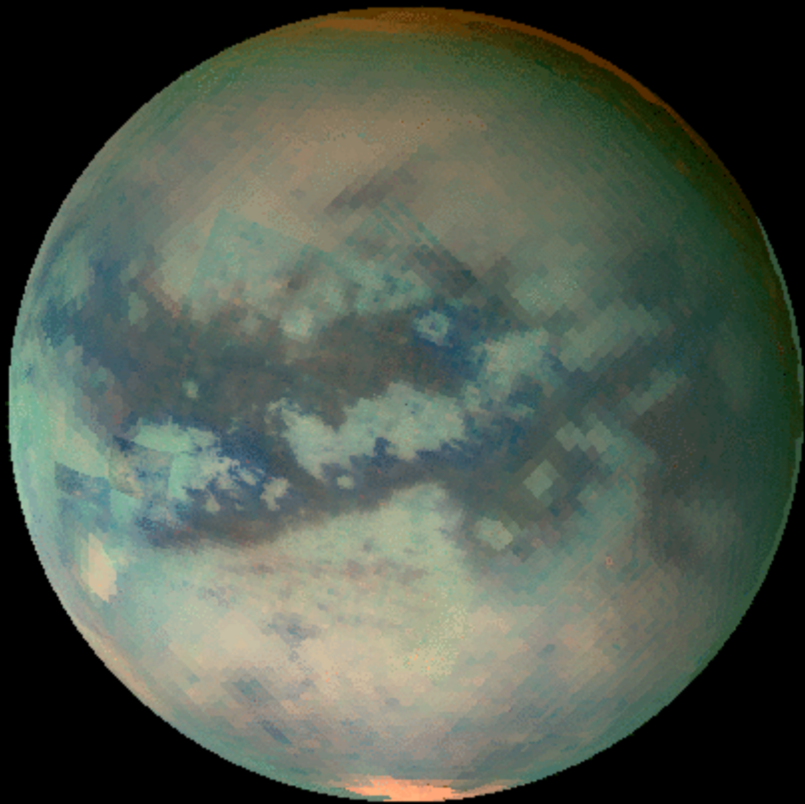
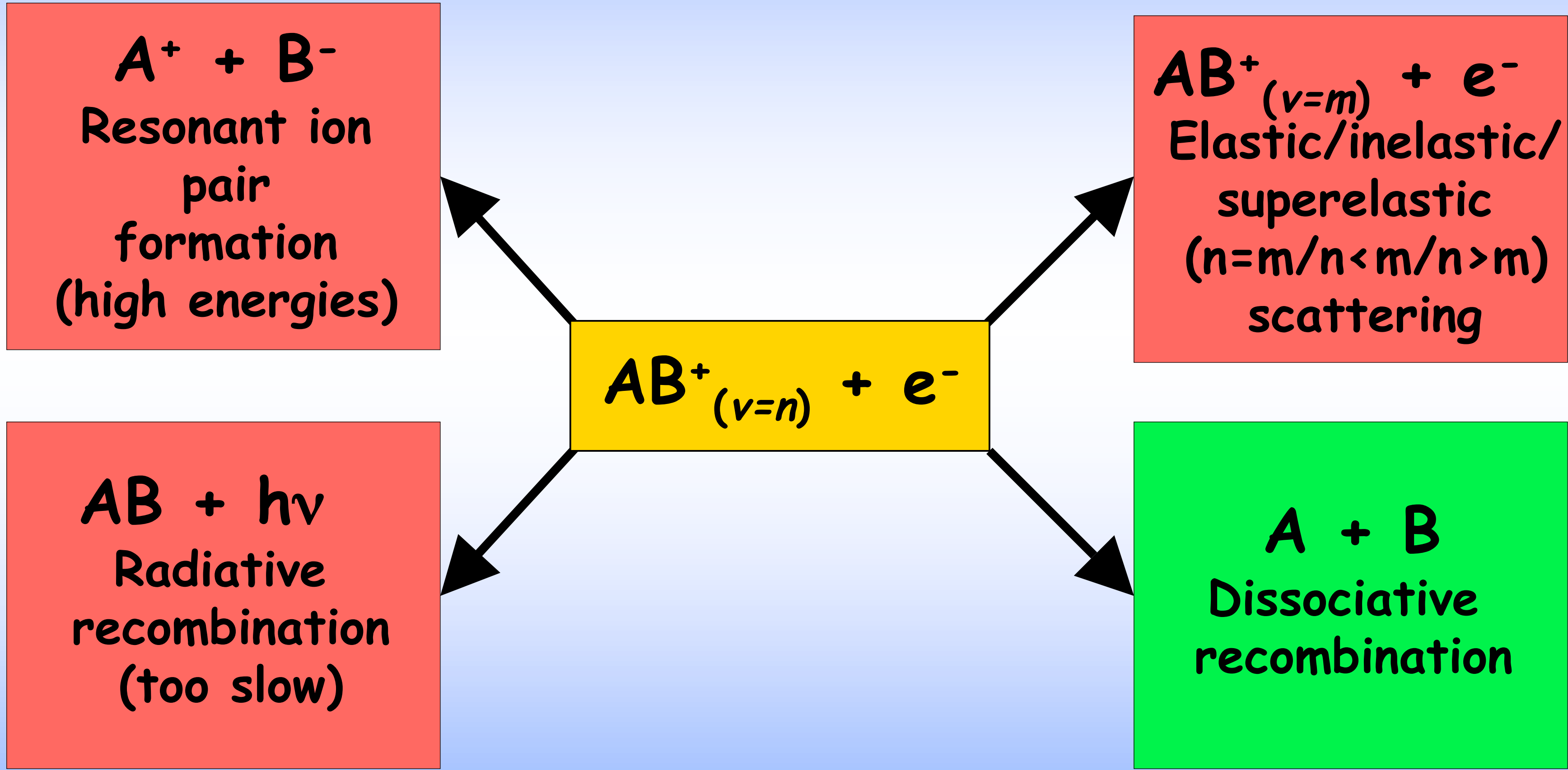
Dissociative recombination reactions

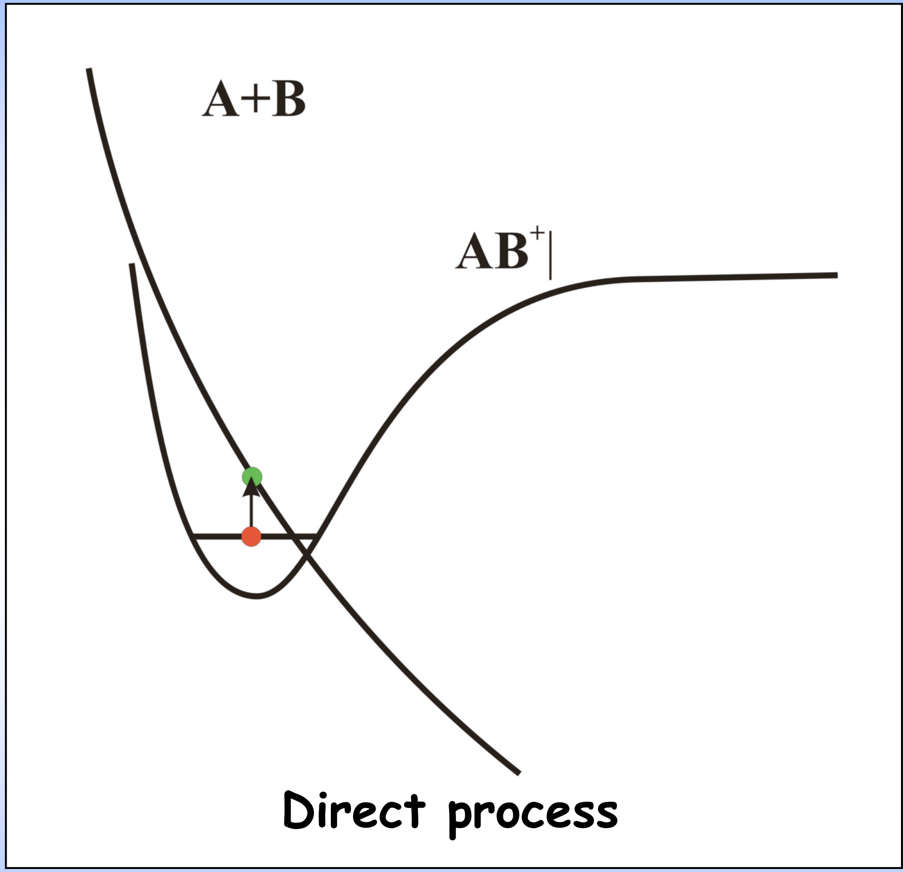


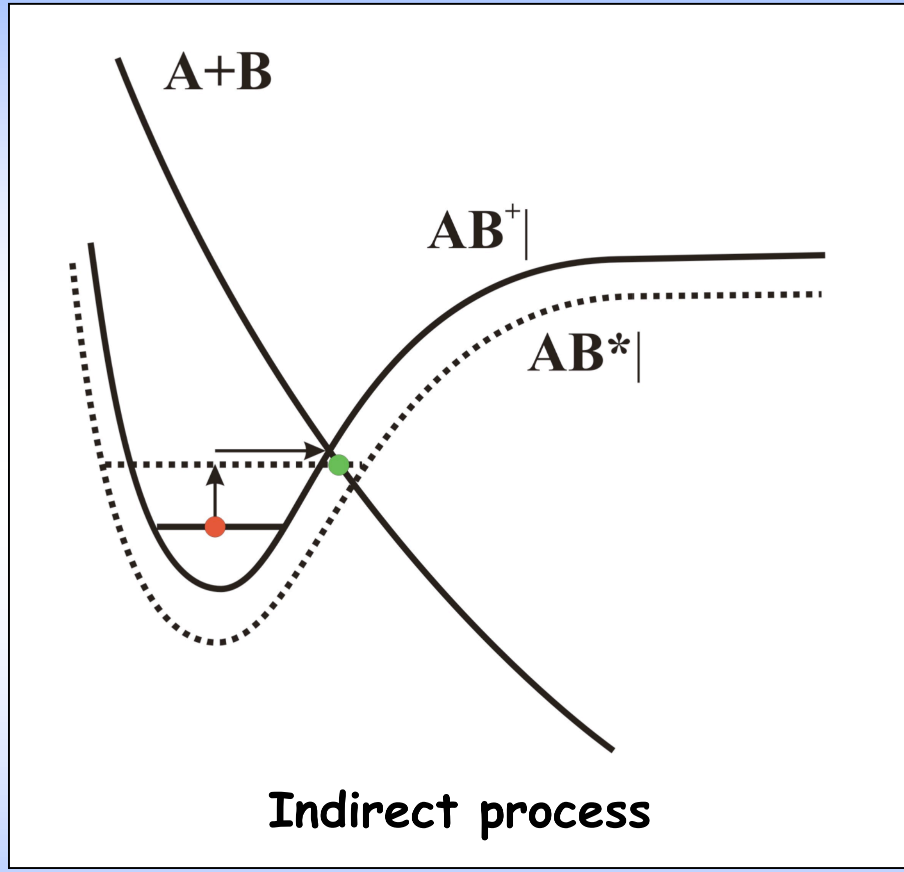
Wolf D. Geppert
ISSI workshop, Bern (CH)
December 2008

Important electron-ion processes



Mechanisms of dissociative recombination (DR)





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

- ★ 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)

$$\begin{aligned}
H_3^+ + C &\rightarrow CH^+ + H_2 \\
CH^+ + H_2 &\rightarrow CH_2^+ + H \\
CH_2^+ + H_2 &\rightarrow CH_3^+ + H \\
CH_3^+ + H_2 &\rightarrow CH_5^+ + h\nu \\
CH_5^+ + e^- &\rightarrow CH_4 + H
\end{aligned}$$

- ★ Competing process for ion-molecule reactions

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

- ★ Sometimes unique destruction pathway for ions (c-$C_3H_3^+$ 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 3×10^{-7} $cm^{-3}s^{-1}$ at 300 K")

→ works fine with small ions HCO^+, N_2H^+

→ DR of larger ions tend to be much faster (often in the range of 2×10^{-7} cm^3s^{-1} at 300 K)

→ Exponential dependence not always $T^{-0.5}$

★ 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:

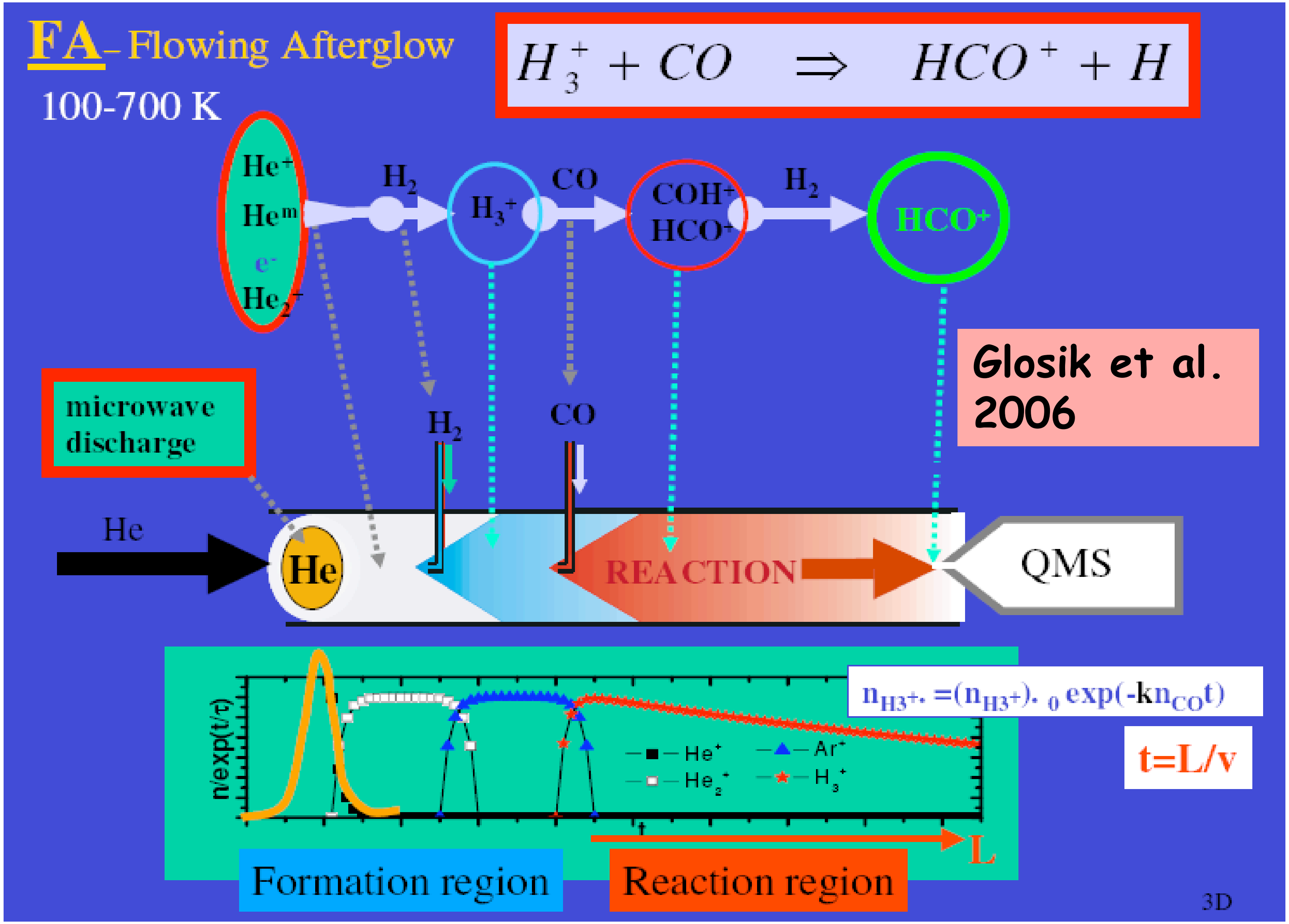
Flowing afterglow methods

- 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 – Flowing Afterglow
100-700 K
$H_3^+ + CO \Rightarrow HCO^+ + H$
He+
Hem
e-
He2+
H2
H3+
CO
COH+
HCO+
H2
HCO+
microwave discharge
H2
CO
He
He
REACTION
QMS
Glosik et al. 2006
n/exp(t/τ)
He+
He2+
Ar+
H3+
$n_{H3^+} = (n_{H3^+})_0 \exp(-k n_{CO} t)$
t=L/v
L
Formation region
Reaction region
3D

FA methods - advantages and disadvantages

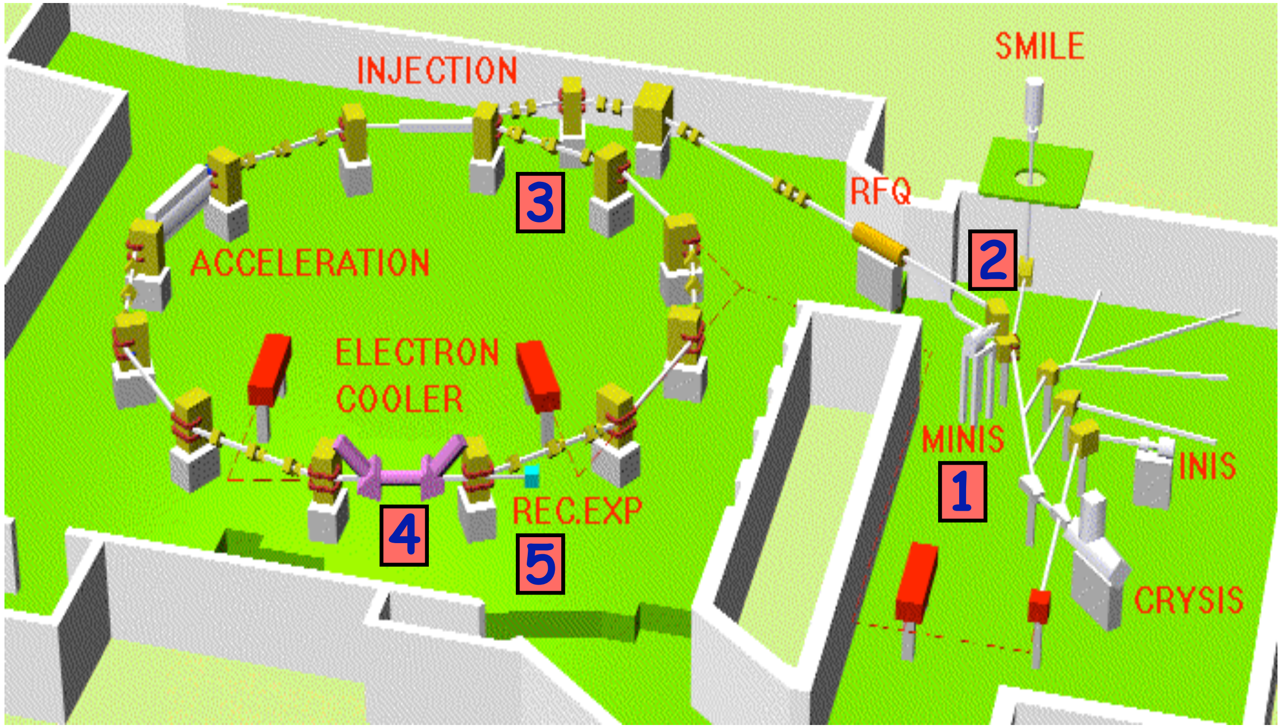
Advantages

- ★ 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 possible)
- ★ Detection of al products difficult
- ★ Intermediates can be deactivated by collisions

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

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
- ★ Ion current measurements difficult (until recently)
- ★ Full branching ratio analysis only for small ions

  High set-up and running costs

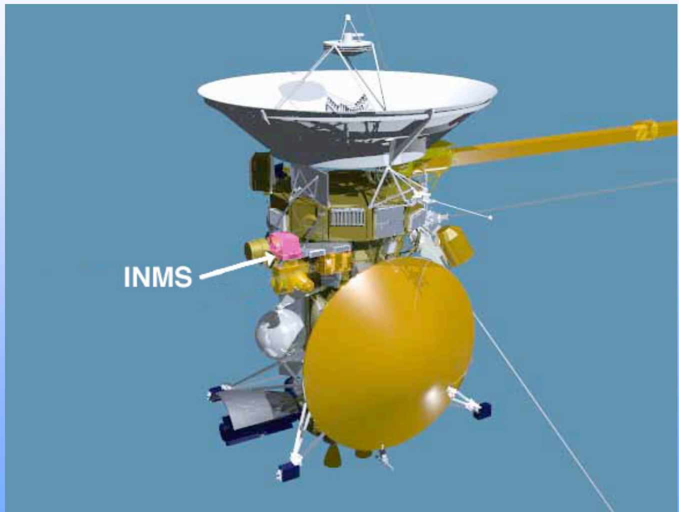
General problems: Ion production

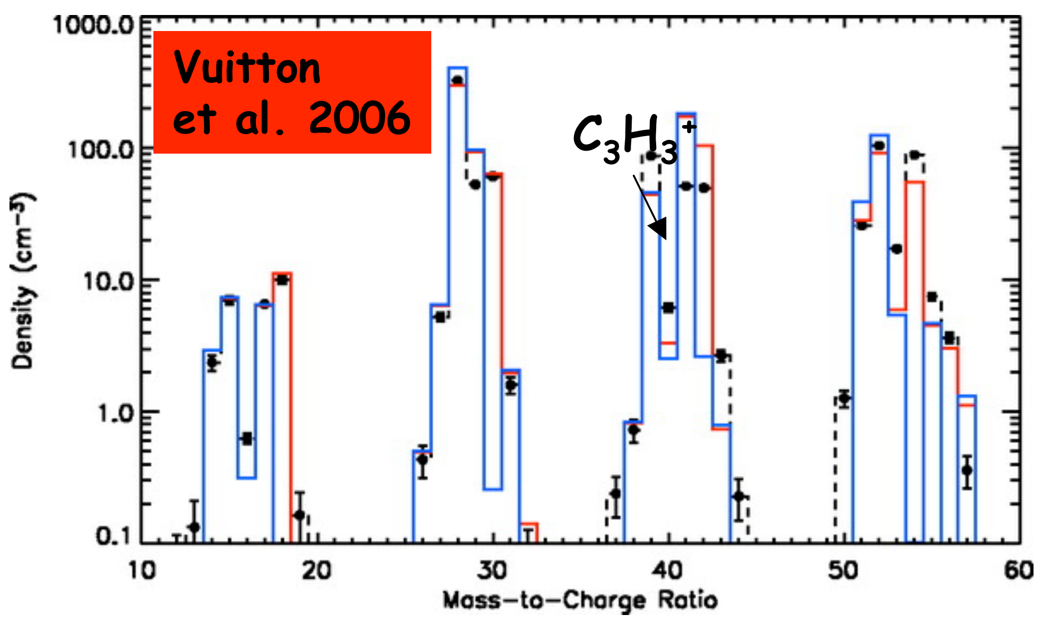
- ★ Mostly by discharge
- ★ Ring methods by hollow-cathode discharge
  → high energies involved (100-400 eV)
- ★ FA mostly by (e. g. by protonation through H_3^+ or charge transfer from e. g. Ar^+)
- ★ Precursors must be easily evaporated
  → but: electrospray ion source
- ★ Isomer ratio affected by precursor choice

General Problems: Different 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^+

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

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

- Especially when CO is ionised

$$H_2 + CO^+ \rightarrow HCO^+ + H \; (\sim 50\ \%)$$
$$ HOC^+ + H \; (\sim 50\ \%)$$

- 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^+ ?

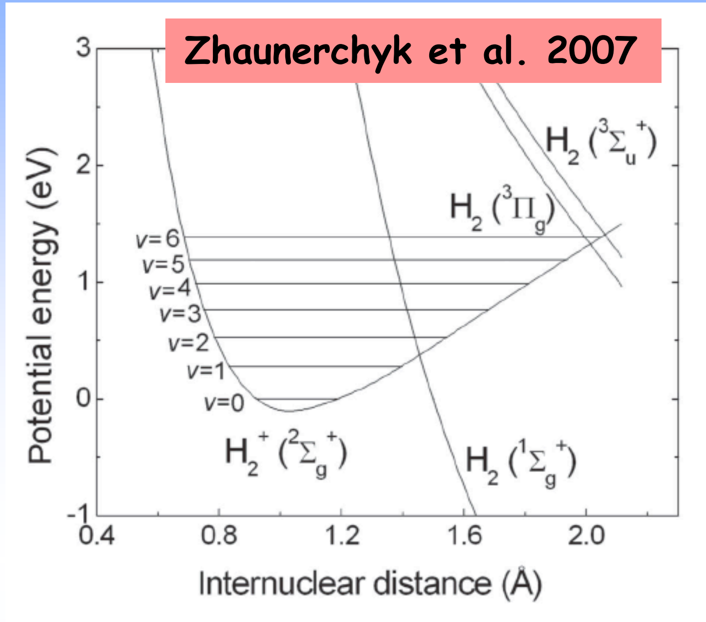
- ★ In DCO^+ excited states vith long lifetime (v_3), not in HCO^+ (Heninger et al. 1999) → CD + O channel opens
- ★ C + OH (C+ OD) channels maybe from HOC+ contaminations

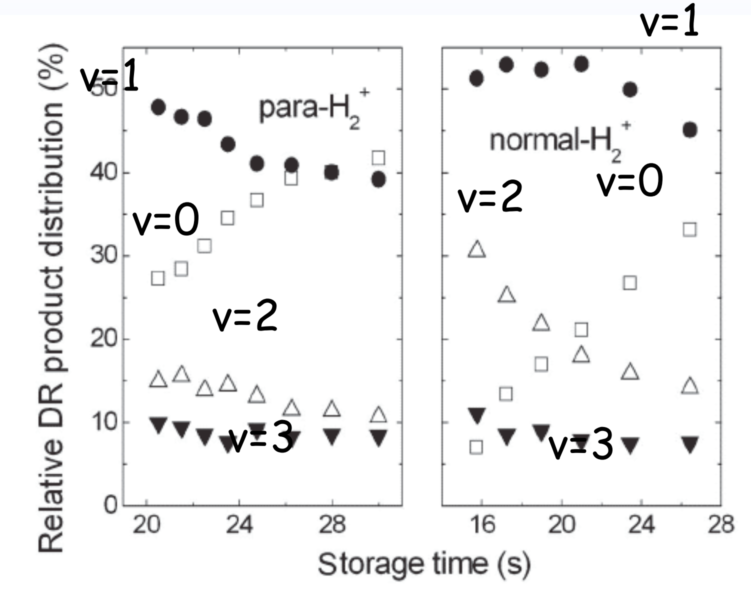
General problem: Excitation in e g. H_2^+

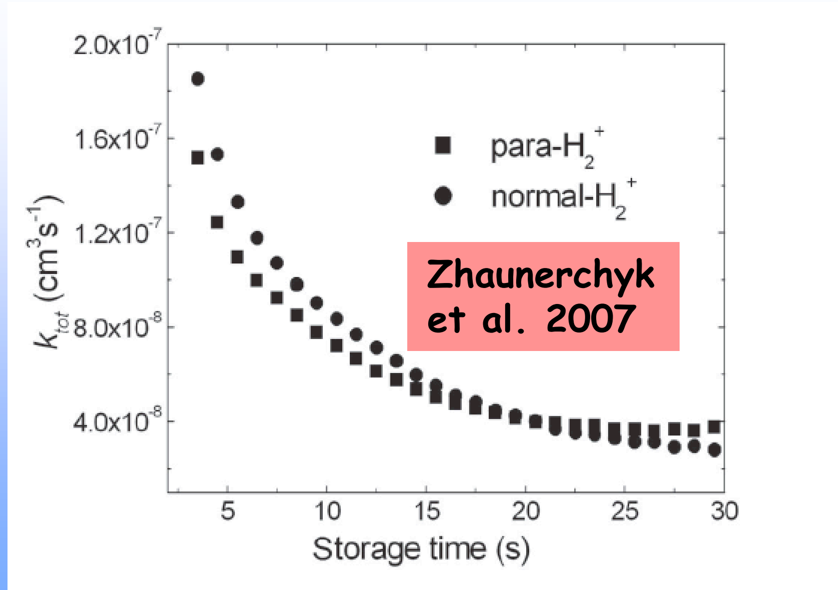
- DR faster for vibrationally excited states of H_2^+
- Opening of direct channel(s) at v>1
- Cool ions by supersonic ion source
- Cooling in ring by superelastic collisions

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

- Imaging allows to gauge v(H_2^+)





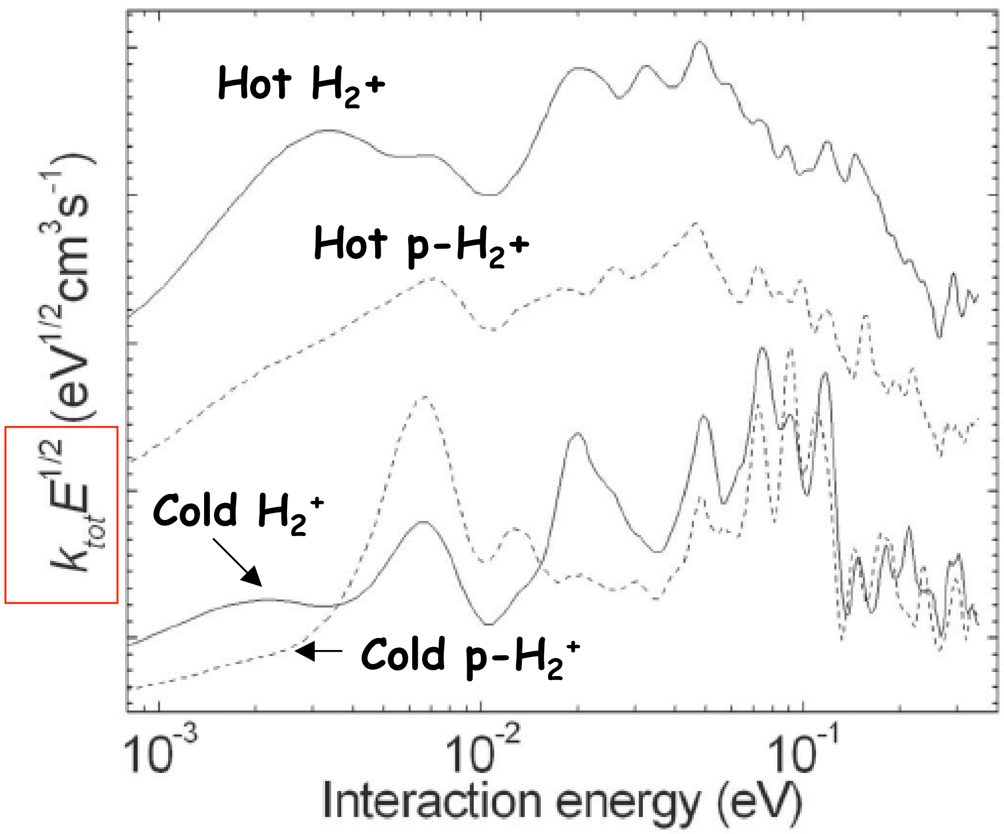


General problems: Nuclear spin and DR

- 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 × $10^{-7} cm^3s^{-1}$	
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

$HCNH^+$

- Major ion in Titan's atmosphere
- DR of $HCNH^+$ could be responsible for HNC/HCN ratio
- Rates: FA: 3.5×10^{-7}
  CRYRING: $2.83 \times 10^{-7}(T/300)^{-0.65}$
- Branching ratios very different

After-glow	$HCNH^+ + e^- \rightarrow$	$HCN/HNC + H$	0.00 -0.68
	$\rightarrow$	$CN + 2H$	0.00 - 0.31
	$\rightarrow$	$CN + H_2$	0.37 -0.69
Storage ring	$HCNH^+ + e^- \rightarrow$	$HCN/HNC + H$	0.68
	$\rightarrow$	$CN + 2H$	0.32
	$\rightarrow$	$CN + H_2$	0.00

★ Different production pathways:

Afterglow: H_3^+ + HCN

Storage ring: CH_3NH_2 + e^-

→ Different isomers (H_2CN^+ or CNH_2^+ could be produced)

★ Flowing afterglow measurements assume slow DR of H_3^+

(probably no consequences since reaction

$$H_3^+ + HCN \rightarrow HCNH^+ + H_2$$ is fast)

★ Collisional desactivation of intermediate HCNH

→ Unlikely to lead to CN + H_2

★ Excited states of $HCNH^+$ in the ring
→ should have same cross section than ground state

★ Such discrepancies also seen in other ions, e. g. D_3S^+

★ Branching ratio HCN + H / HNC + H still unclear
But: theoretical investigations point to a 1:1 ratio

Recommended values:

Branching ratios:

$HCNH^+ + e^-$	→	HCN/HNC	+	H	0.68
	→	CN	+	2H	0.32
	→	CN	+	H_2	0.00

Rate constant: $2.83 \times 10^{-7}(T/300)^{-0.65}$ cm^3s^{-1}

$C_2H_4^+$

- ★ Can easily transfer protons to other hydrocarbons in high density media (planet and satellite atmospheres
- ★ DR could outcompete proton transfer in lower-density objects
- ★ So far only ring experiment (ion probably difficult to form in afterglow)

Branching ratios:

$C_2H_4^+ + e^-$	$\rightarrow$	C_2H_3	$+ H$	0.11
	$\rightarrow$	C_2H_2	$+ H_2$	0.06
	$\rightarrow$	C_2H_2	$+ 2H$	0.66
	$\rightarrow$	C_2H	$+ H + H_2$	0.10
	$\rightarrow$	CH_4	$+ C$	0.01
	$\rightarrow$	CH_3	$+ CH$	0.02
	$\rightarrow$	CH_2	$+ CH_2$	0.04

Rate constant: $5.6 \times 10^{-7}(T/300)^{-0.76}$ cm^3s^{-1}

Values seem reasonable !

$HSiO^+/HOSi^+$

- No measurements available due to

  - lack of suitable precursor
  - existence of 2 isomers, $HOSi^+$ more stable

- Educated guess from isovalent ions difficult,
  HCO^+ and HN_2^+ lose H, HCS^+ breaks C-S bond
  → Equal distribution between H + SiO and HO + Si seems
  good assumption (DR to HSi + O almost thermoneutral)

- No real reason to defect from model values:

Branching ratios:

$HSiO^+ + e^-$	→	H + SiO	0.50
	→	HO + Si	0.50

Rate constant: $3.0 \times 10^{-7}(T/300)^{-0.50}$ $cm^3 s^{-1}$ = 1 Johnsen

H_2CO^+/$HCOH^+$

- The DR of all CH_xO^+ ions have been investigated. Why not CH_2O^+ ?

  → two isomers almost equal in energy

- Possibility to guess ?

- HCO^+ and H_3CO^+ leave their CO-bond intact with DR,
  With more hydrogenated ions (CH_3OH_2) the heavy atom bond is preferentially broken

- Assuming 90 % CO bond retention in CH_2O we consider ejection
  Of two hydrogen atoms to be a major process

- No conclusions about the behaviour of two different isomers possible; for the guesses we consider H_2CO^+

Recommended values:

Branching ratios:

$CH_2O^+ + e^-$	$\rightarrow$	$HCO + H$	0.25
	$\rightarrow$	$HOC + H$	0.05 (rearrangement)
	$\rightarrow$	$CO + 2H$	0.50 (3-body !)
	$\rightarrow$	$CO + H_2$	0.15 (very exoergic)
	$\rightarrow$	$CH + OH$	0.00 (C-O rupture)
	$\rightarrow$	$C + H_2O$	0.00 (rearrangement)
	$\rightarrow$	$CH_2 + O$	0.05 (C-O breakage)

Rate constant: $5.0 \times 10^{-7}(T/300)^{-0.70}$ $cm^3 s^{-1}$

$\rightarrow$ more in line with other CH_xO^+ ions

HC_5NH^+

- ★ Several isomers available, discussion restricted to linear $HCCCCCNH^+$
- ★ No measurements, but following conclusions from HC_3NH^+:
  - around 50 % retention of carbon-nitrogen chain
  - no breakage of multiple bonds
  - 50 % break-up into 2 fragments with 2 resp. 4 heavy atoms
- ★ No three-body channels energetically available

Recommended values:

Branching ratios:

HC_5NH^+ + e-	→	$C_5N + H_2$	0.04 (heavy rearrangement)
	→	HC_5N + H	0.23
	→	C_5NH + H	0.23
	→	HCN + HC_4	0.22
	→	HNC + HC_4	0.22
	→	HC_4N + HC	0.00 (triple bond break)
	→	$HC_3N + HC_2$	0.06 (rearrangement)
	→	$HC_2N + HC_3$	0.00 (triple bond break)
	→	H_2C_5 + N	0.00 (triple bond break)

Rate constant: $2.0 \times 10^{-6}(T/300)^{-0.70}$ cm^3s^{-1}

CNC^+

- No experimental studies available
- No kicking out of central atom in CO_2^+, SO_2^+ and OCS^+
- No three-body channels energetically available
- Rate constants of somewhat alike three-atomic ions around 4.0×10^{-7} cm^{3}s^{-1}

Recommended values:

Branching ratios:

$CNC^+ + e^- \rightarrow$	$CN + C$	0.95
$\rightarrow$	$C_2 + N$	0.05

Rate constant: $4.0 \times 10^{-7}(T/300)^{-0.60}$ cm^{3}s^{-1}

C_4SH^+

- ★ Neither experimental studies nor guesses available
- ★ Data situation too poor to make any guesses

HC_3S^+

- ★ Information available very poor
- ★ No reason to change the guesses in the models (any will do)

HC_4O^+

- ★ Theoretical studies show existence of 5 isomers
- ★ No similar ions studied, guesses very difficult
- ★ No changes from model values suggested

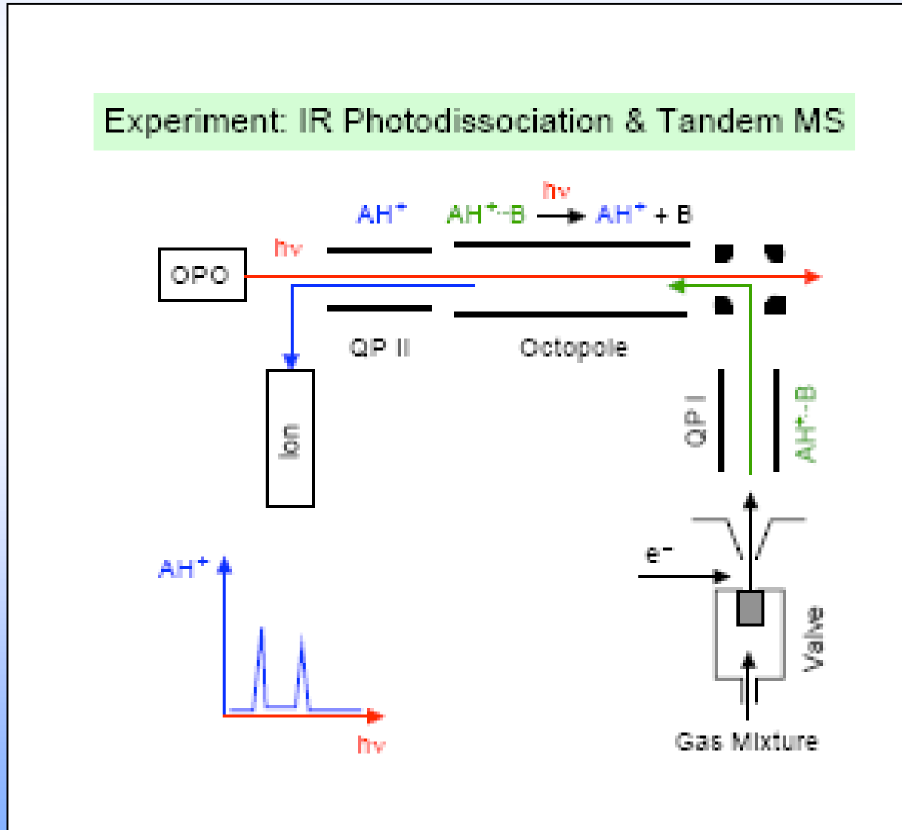
HC_4S^+

- ★ Elusive ion, only one ab initio study (published in Mandarin)
- ★ No founded guesses possible


CAFFE'
HAUSBRANDT

Future chances in DR measurements

- ★ Improvement of ion sources to 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 using a ring with higher rigidity (Lanzhou, China)
- ★ Use of electrospray ion Sources to create ions from badly evaporable precursors



Dopfer and co-workers