ASTROCHEMISTRY

FROM THE BIG BANG TO LIFE

Global Astrochemistry Lecture Series (GALS) 2024

LABORATORY ASTROCHEMISTRY. GAS-PHASE PROCESSES

Wolf Geppert. *Stockholm University, Sweden*

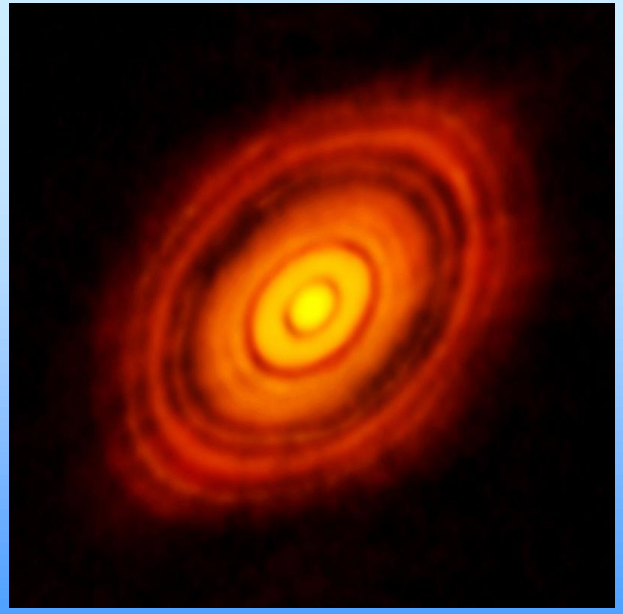
29.02.2024 | 15:00 - 17:00 CET

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY
NanoSpace
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Complex organic molecules

How do they come to Earth?

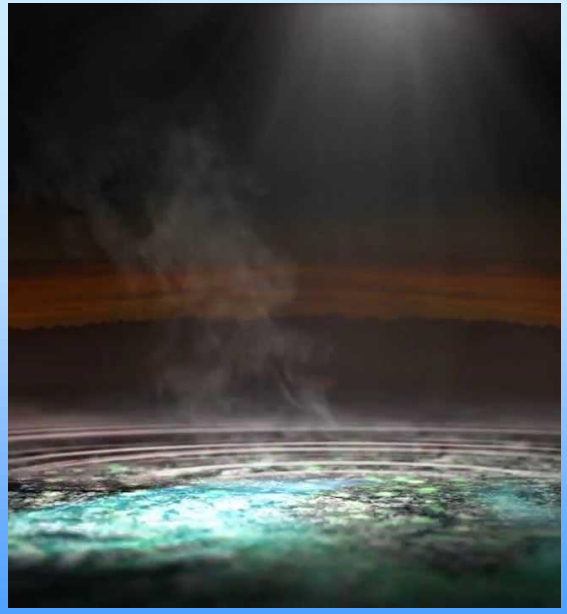
- Accretion under the formation of the solar system
- Delivery trough asteroid-, meteorite- and comet impacts
- Formation on Earth (primeval soup and/or atmosphere)



Protoplanetary disk



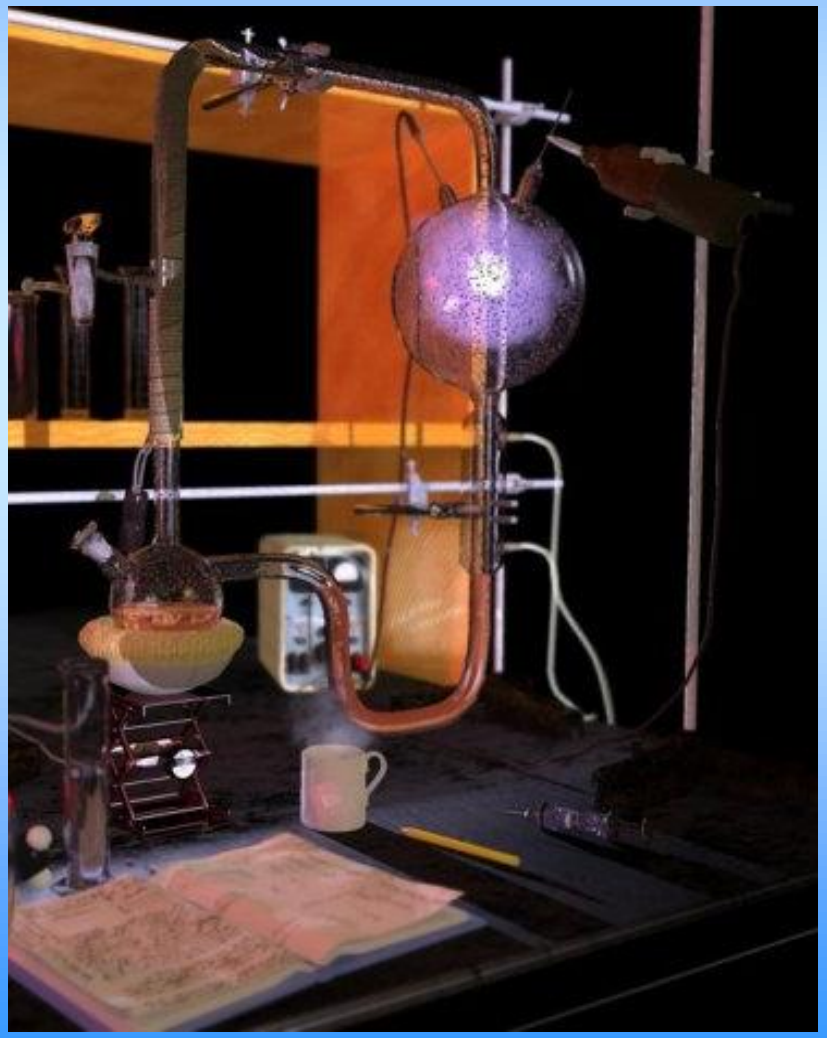
Comet Hale-Bopp

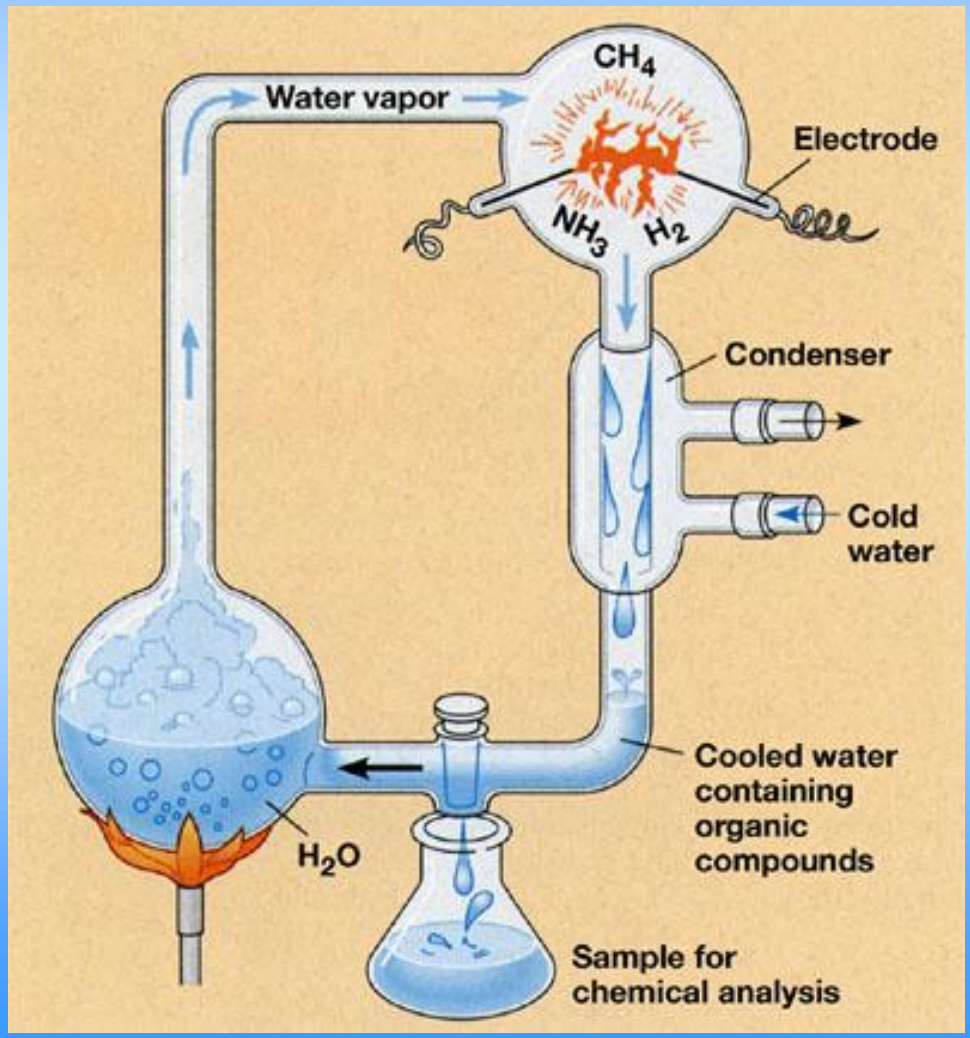


Primeval soup

Urey-Miller experiment

- ★ Gas mixture resembling Jupiter's atmosphere CH_4, NH_3, H_2
- ★ Electrical discharge, formation of aminoacids and nucleobases





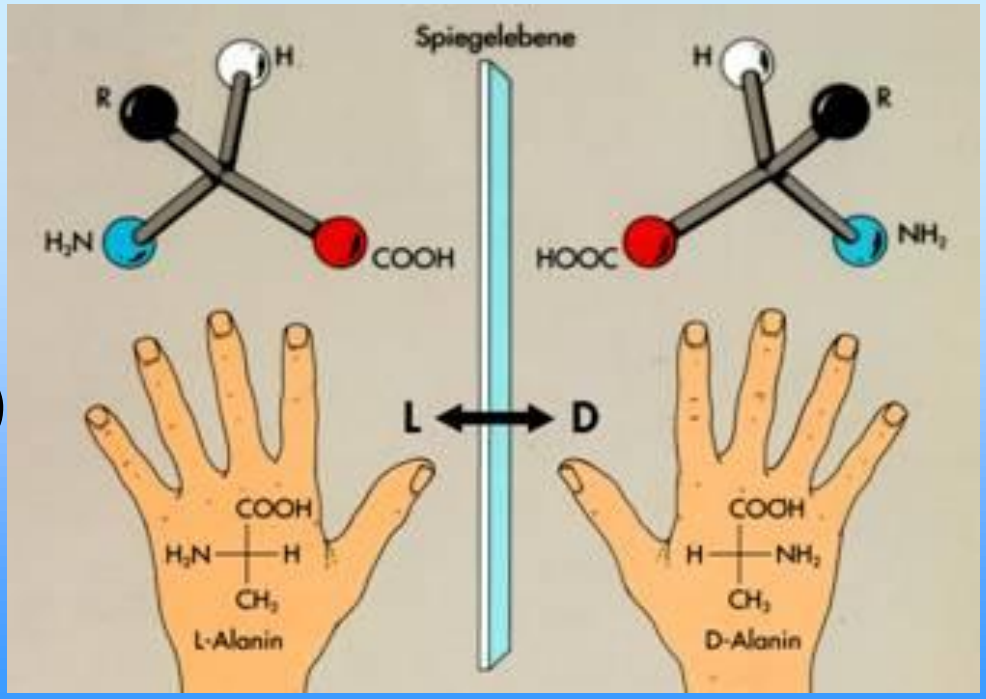
Problems with Urey-Miller experiment

★ Almost all amino acids exist in 2 distinctive forms (L- and D-form)

★ In Urey-Miller-experiment **equal** amounts of both forms are produced, life uses only **one** form

★ How did this homo-chirality emerge

★ Synthesis of bio-molecules is impeded by traces of oxygen (O_2)



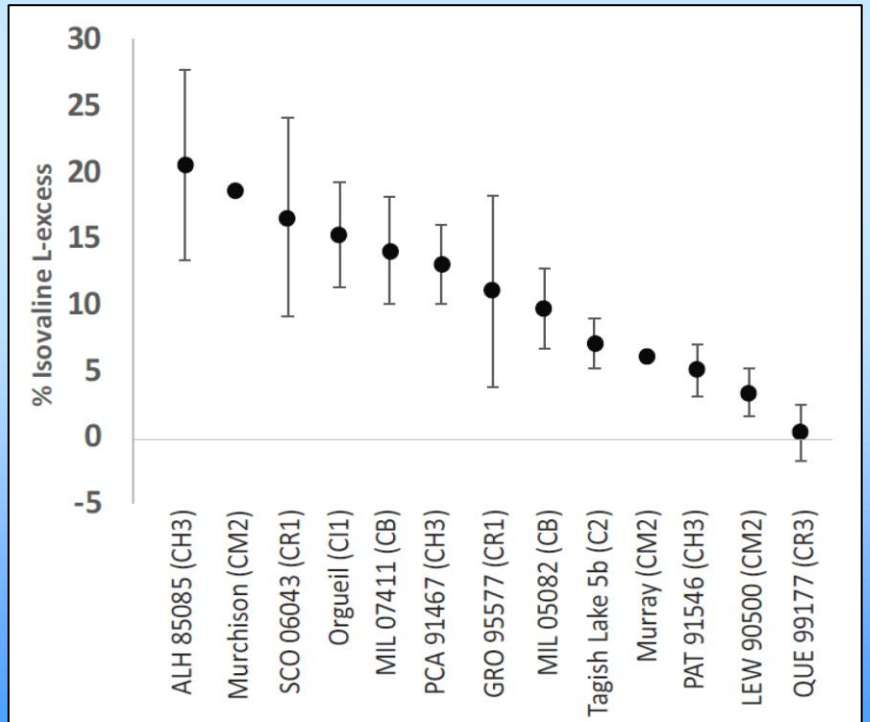
Biomolecules from space?

- Some amino acids found in Murchison- and other meteorites
- Excess of the "correct" L-form present (also with amino acids not used by life)



Meteorite fragment

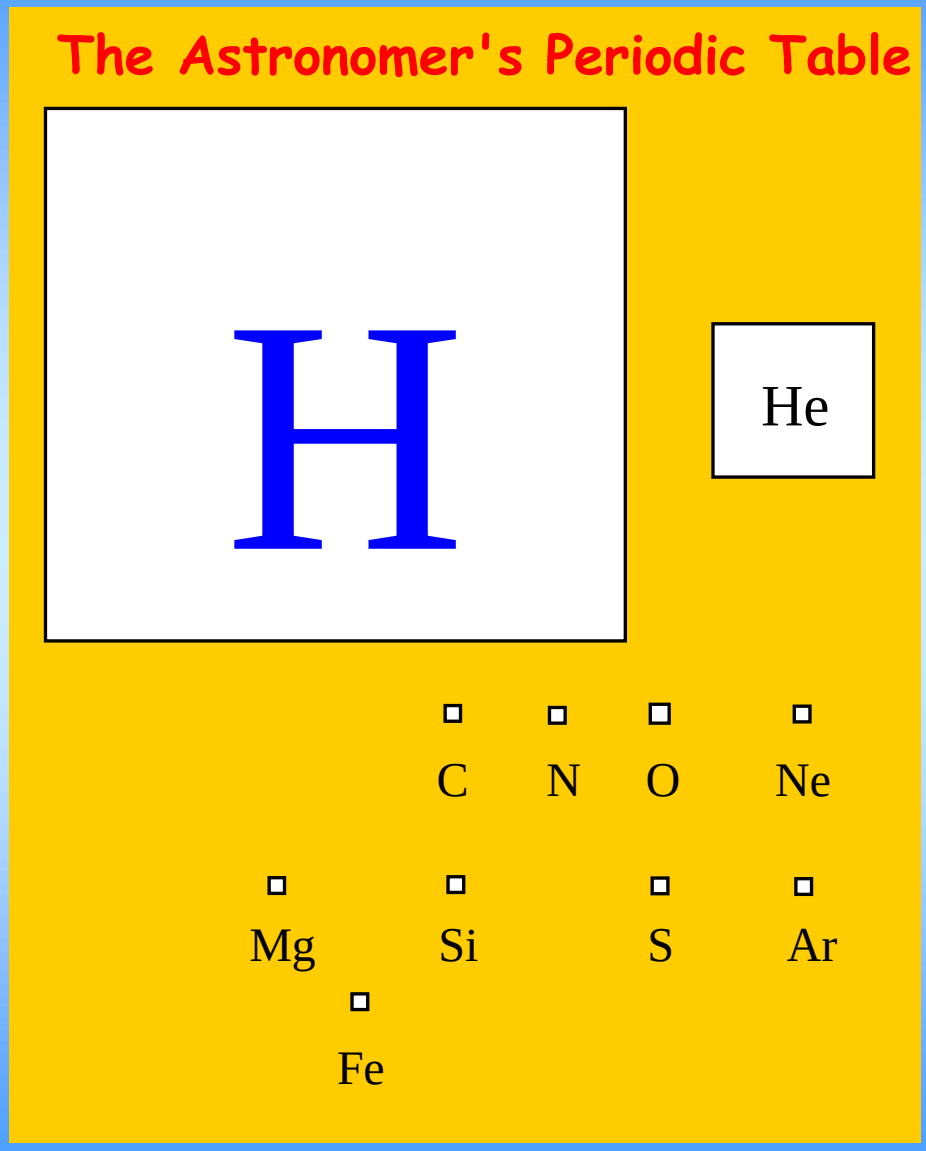




Isovaline Enantiomeric excess

Where and how are they formed?

Abundance of elements in the ISM



Cosmic Abundance of some elements

Element	Abundance (relative)
hydrogen (H)	1.000.000
helium	80.147
oxygen	739
carbon	445
neon	138
nitrogen	91
magnesium	40
Silcon	37
Sulfur	19

Space – an odd place for chemistry?

- Very low temperatures
- Very low particle density in the interstellar medium (0.0001 – 1000000 particles per cm^3)
- Simple atom-atom reactions fail:

$$N + N \not\rightarrow N_2$$

- UV-radiation from stars destroy the reaction products
- Arthur Eddington: "No conceivable way that molecules could exist in abundance in space"



Arthur Eddington (1888-1944)

Interstellar and circumstellar neutral molecules

2 atoms		3 atoms		4 atoms		5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 + atoms	
AlCl	NS	AlNC	HCP	CH_3	HNCS	CH_4	c-H_2C_3O	C_2H_4O	CH_3CC_2CN	CH_3C_4H	$(CH_3)_2CO$	C_9H_8
AlF	NaCl	AlOH	HCS	l-C_3H	NH_3	CH_3O	HNCHCN	CH_3C_2H	HC_3H_2CN	CH_3OCH_3	$(CH_2OH)_2$	$C_{10}H_7CN$
AlO	O_2	C_3	HNO	c-C_3H	HSCN	c-C_3H_2	C_2H_4	H_3CNH_2	$H_2COHCHO$	CH_3CH_2CN	CH_3CH_2CHO	$C_{10}H_7CN$
C_2	PN	C_2H	HSC	C_3N	SiC_3	l-H_2C_3	CH_3CN	CH_2CHCN	$(CHOH)_2$	CH_3CONH_2	CH_3OCH_2OH	$C_{11}H_{12}N_2O_2$
CH	PO	CCN	KCN	C_3O	HMgNC	H_2CCN	CH_3NC	HCCCHNH	$HCOOCH_3$	CH_3CH_2OH	CH_3C_5N	C_{60}
CN	SH	C_2O	MgCN	C_3S	HNO_2	H_2C_2O	CH_3OH	H_2CHCOH	CH_3COOH	C_8H	CH_3CHCH_2O	
CO	SO	C_2S	MgNC	C_2H_2		H_2CNH	CH_3SH	C_6H	H_2C_6	HC_7N	$NH_2CH_2CH_2OH$	C_{70}
CP	SiC	C_2P	NH_2	H_2CN		HNCNH	l-H_2C_4	HC_4CN	CH_2CHCHO	CH_3CHCH_2	HC_8CN	
CS	SiN	CO_2	N_2O	H_2NC		C_4H	$HCONH_2$	HC_4NC	CH_2CCHCN	CH_3CH_2SH	C_2H_5OCHO	
FeO	SiO	CaNC	NaCN	H_2CO		HC_3N	HOCOOH	HC_5O	CH_3CHNH	CH_3NHCHO	CH_3COOCH_3	
H_2	SiS	FeCN	NaOH	H_2CS		HCC-NC	C_5H	CH_3CHO	$C_2H_3NH_2$		CH_3C_6H	
HCl	TiO	H_2C	OCS	HCCN		HCOOH	C_5N	CH_3NCO	C_7H		C_6H_6	
HF		H_2O	O_3	HCCO		NH_2CN	HC_2CHO	$HOCH_2CN$	NH_2CH_2CN		C_3H_7CN	
HO		HO_2	SO_2	HCNO		NH_2OH	HC_4N		$(NH_2)_2CO$		$(CH_3)_2CHCN$	
KCl		H_2S	c-SiC_2	HOCN		HC(O)CN	CH_2CNH				C_6H_5CN	
NH		HCN	SiCSi	CNCN		C_5	C_5S				$HC_{10}CN$	
N_2		HNC	SiCN	HOOH		SiC_4						
NO		HCO	SiNC	HNCO		SiH_4						
			TiO_2	HNCN								

★ Roughly 300 molecules detected in space

Interstellar and circumstellar ions

2 atoms		3 atoms	4 atoms	5 atoms	6 atoms	8 atoms	10 + atoms
ArH^+	OH^+	HOC^+	CH_3^+	NH_4^+	HC_3NH+	C_8H^-	C_{60}^+
CH^+	NO^+	H_2N^+	$l\text{-}C_3H^+$	H_2COH^+	C_6H-		
CN^+	MgH^+	HCS^+	C_3N^-	C_4H^-			
CO^+	SH^+	HCO^+	H_3O^+	$NCCNH^+$			
CN^-	SO^+	H_2O^+	H_2CN^+	$C5N^-$			
HeH^+		H_2Cl^+	$HCNH^+$				
HCl^+		H_3^+	$HOCO^+$				

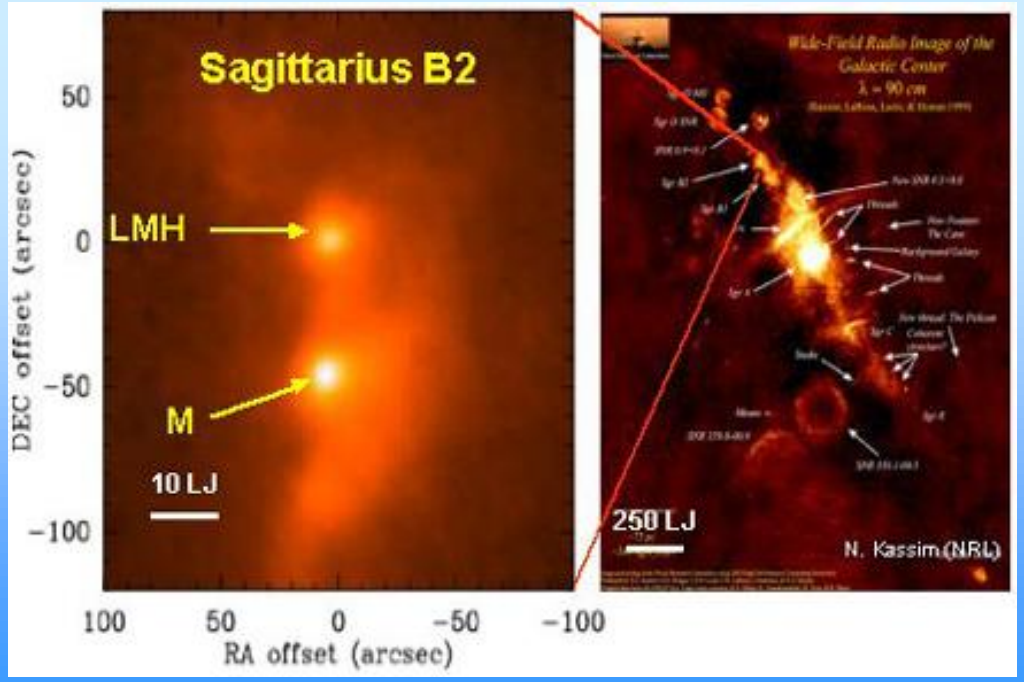
- ★ Mostly cations detected
- ★ Ion abundances in astronomic objects often smaller than the one of corresponding neutrals
- ★ Spectroscopic data often lacking

Observed complex molecules

- Aminoacetonitrile in "Large Molecule Heimat" in Sagittarius B at the galactic centre (Belloche et al. 2008)
- Can react with water to form glycine

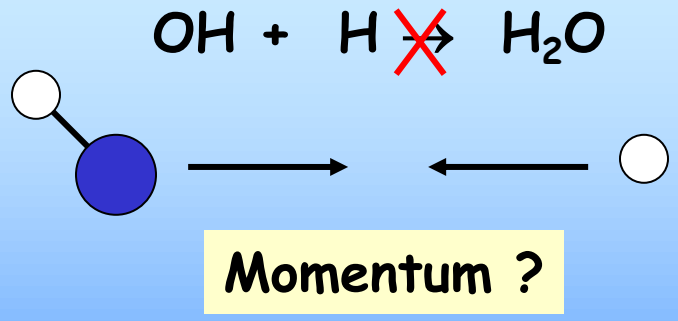
$$H_2NCH_2CN + 2H_2O \rightarrow H_2NCH_2COOH + NH_3$$

- Glycol aldehyde (simple carbohydrate) observed in the same place (Hollis 2000)
- More and more to be expected due to high-performance telescopes



Requirements for chemical reactions in the interstellar medium

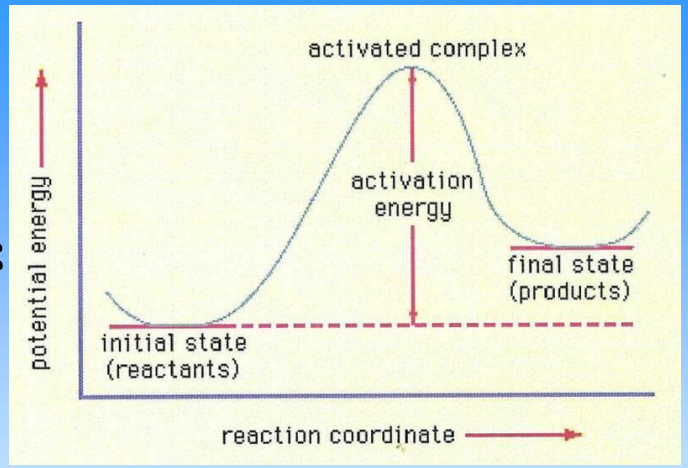
- ★ absence of barrier requested (very low temperatures)
- ★ no three-body processes
- ★ no 2 + 1 processes leading to single processes (molecules must conserve momentum)



- ★ Grain surfaces can take momentum of reactions (can take up momentum and energies from reactive processes)

Temperature behaviour of chemical reactions

★ In case of barrier Arrhenius behaviour:



$$A + B \rightarrow C$$

$$d[C]/dt = k\,[A][B]$$

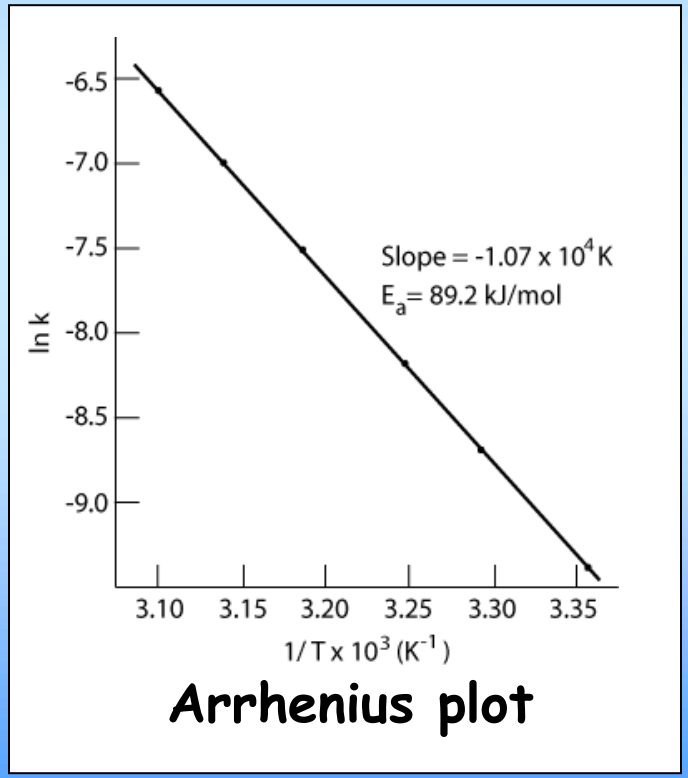
$$k(T) = A \exp\left(\frac{-E_A}{k_B T}\right)$$



Svante Arrhenius

k = rate constant
A = reaction constant
E_A = activation energy
k_B = Boltzmann constant

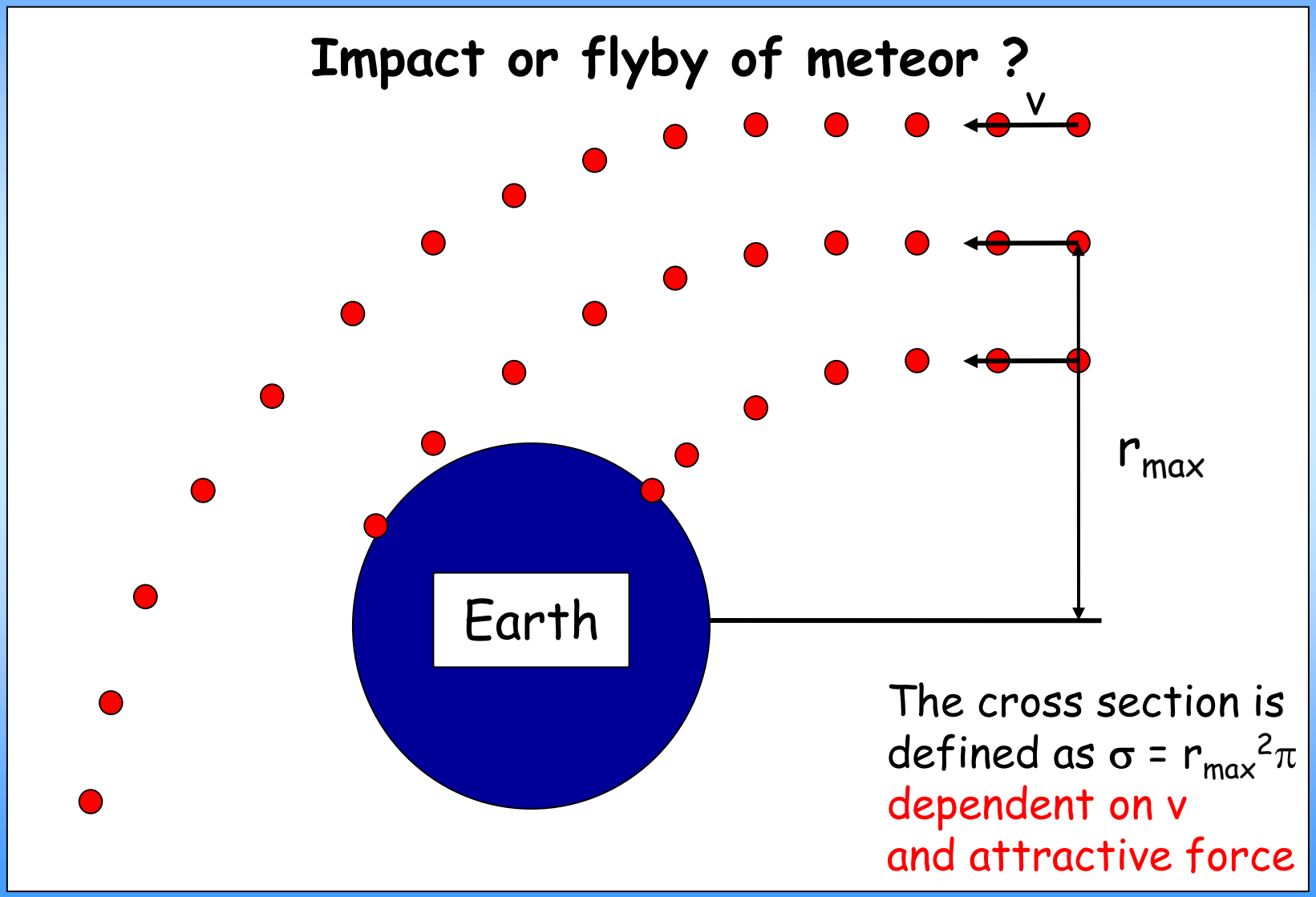
With low T: k =low



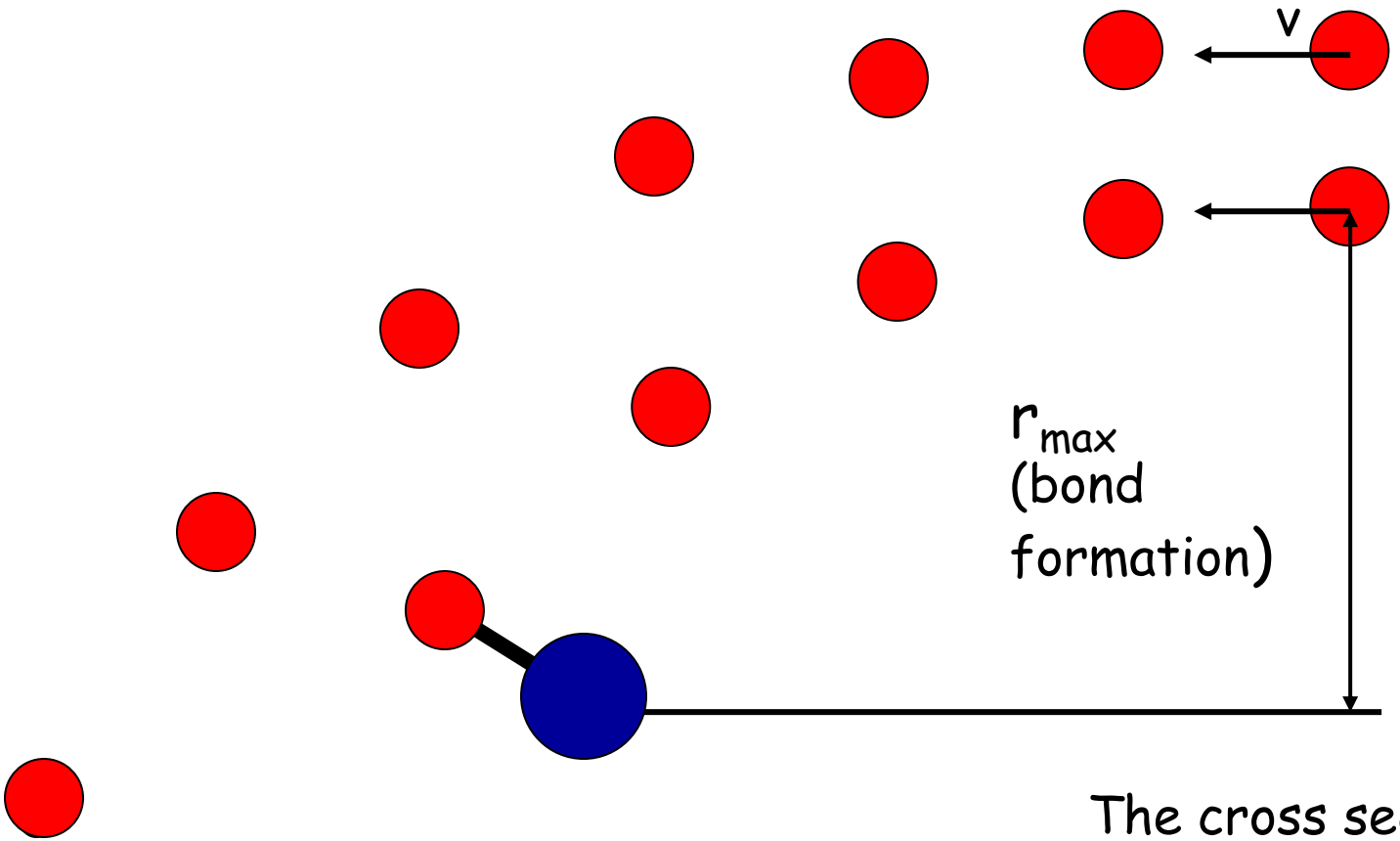
Arrhenius plot

In case of absence of barriers ?

In barrierless reactions every collision leads to reaction if particles pass within a certain maximum distance (dependent on velocity)



With chemical reaction



The cross section is defined as $\sigma = r_{max}^2 \pi$
dependent on v (E_{kin}) and potential curve

Reaction with barrier
(Arrhenius equation)

$$k(T) = A \exp\left(\frac{-E_A}{k_B T}\right)$$

Barrierless processes
(Langevin equation)

$$k(T) = AT^{-\alpha} \qquad \alpha \approx 0.5$$

In tables often constants α, β ,γ listed:

$$k(T) = \alpha\left(\frac{T}{300}\right)^{\beta} \exp\left(\frac{-\gamma}{T}\right)$$

With β = 0 Arrhenius behaviour
With γ = 0 Langevin behaviour

Important reactions in the ISM

Neutral-neutral reactions between closed shell molecules ?

- Relatively high activation energy - not feasible at low temperatures !

Neutral-radical and radical-radical reactions

- Often no activation barrier, feasible down to very low temperatures.

Ion-electron, ion-ion and ion-neutral reactions

- mostly no activation energy.

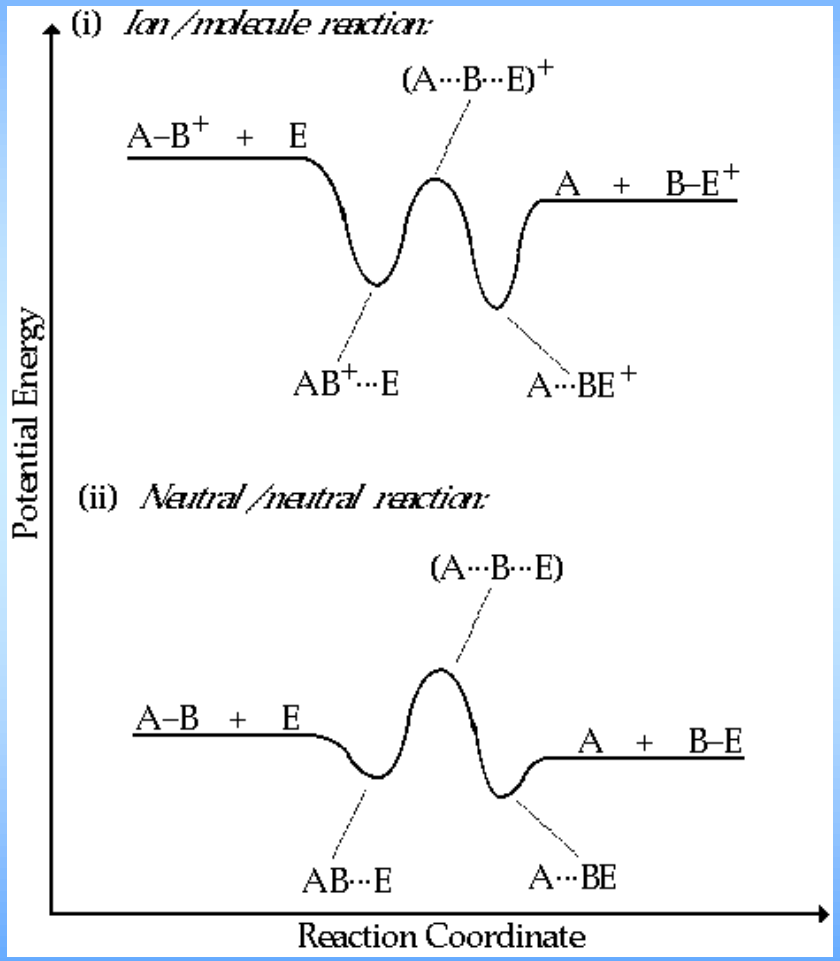
Ion-molecule vs. neutral-neutral reactions (Millar, 2006)

Ion-neutral reactions

- Activation energy barriers rare if process is exothermic
- mostly inversely dependent on 1/T or temperature independent
- feasible at very low T

Neutral-neutral reactions

- Often have activation energy barriers (Exception: Radicals and atoms)
- Arrhenius dependency on temperature



Important interstellar ion processes

Ion - neutral reactions (e. g. radiative association)

$$H_3^+ + C \rightarrow CH^+ + H_2$$

Ion-electron reactions

for molecules as good as exclusively dissociative recombination

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

Ion-ion reactions

mutual neutralisation

$$C^+ + C_4H^- \rightarrow CH + C_4$$

Ion chemistry in dark clouds (Millar, 2006)

Time-scales for reaction for molecular ion M^+

- $10^9/n(H_2)$ for fast reaction with H_2
- $10^6/n(e^-)$ for fast dissociative recombination with e^-
- $10^9/n(X)$ for fast reaction with X

Since $n(e) \sim 10^{-8}/n(H_2)$, dissociative recombination is unimportant for ions which react with H_2 with $k > 10^{-13}$ cm^3 s^{-1};

Reactions with X are only important if the ion does not react, or reacts very slowly, with H_2.

Rich chemistry possible, but we have to have ions to begin with

Chemistry in dark clouds - How does it start ?

$$H_2 + cr \rightarrow H_2^+$$

Cosmic ionisation rate (ζ) = 10^{-17} s-1 in dark clouds

$$H_2 + H_2^+ \rightarrow H_3^+ + H$$

$k = 2 \times 10^{-9}$ $cm^3 s^{-1}$
(Theard & Huntress, 1974)

Cosmic rays:

87 % protons (H^+)

12 % α particles (He^{2+})

Rest: γ rays, myons, electrons



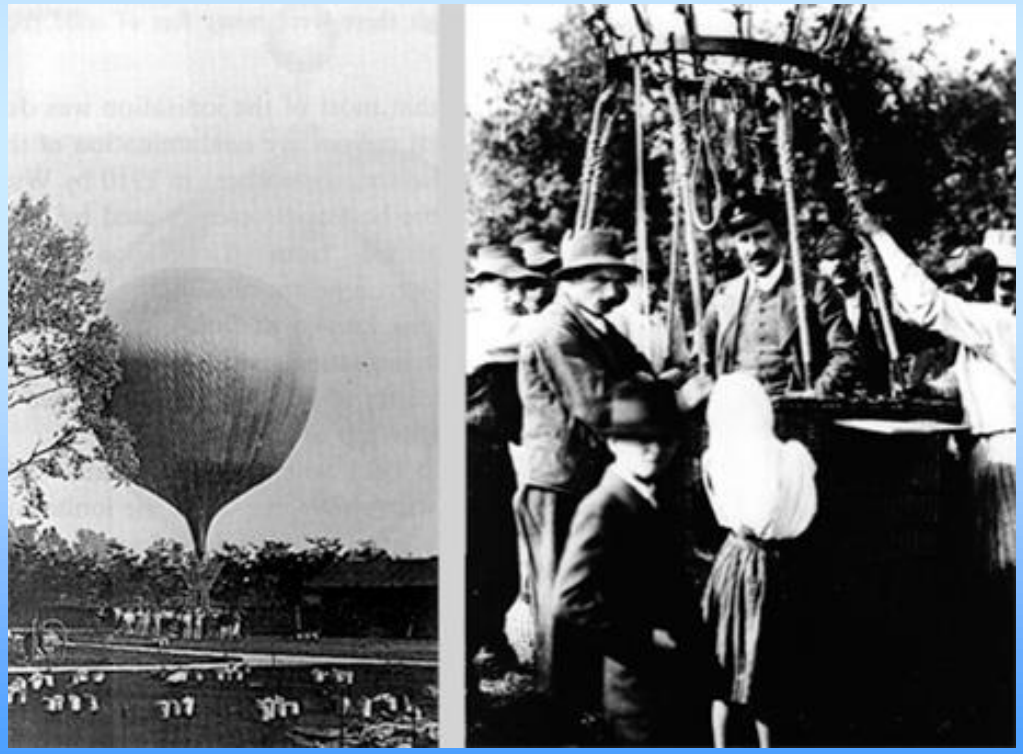
Viktor Franz Hess

Cosmic Radiation

- Existence of ionising radiation on Earth was known (thought to emerge from Earth´s radio activity or the sun)

- Increases with height (cannot emerge from Earth)

- Not mitigated by solar eclipse (no solar source)



Ballongflyg av Viktor Franz Hess från Aspern (Wien)

Ion chemistry in dark clouds
How does it proceed ?

Succession of ion-neutral reactions and dissociative recombination leading to the wanted molecule (XH_2) is often invoked

$$H_3^+ + X \rightarrow XH^+ + H_2$$

$$XH^+ + H_2 \rightarrow XH_2^+ + H$$

$$XH_2^+ + H_2 \rightarrow XH_3^+ + H$$

$$XH_3^+ + e^- \rightarrow XH_2 + H$$

Formation of water in dark clouds

$$H_3^+ + O \rightarrow OH^+ + H_2$$

$k = 8.4 \times 10^{-10}\ cm^3 s^{-1}$ (Milligan & McEwan, 2000)

$$H_2^+ + O \rightarrow OH^+ + H$$ (less important)

Successive hydrogen addition:

$$OH^+ + H_2 \rightarrow H_2O^+ + H$$

$k = 1.1 \times 10^{-9}\ cm^3 s^{-1}$ (Jones, Birkinshaw & Twiddy, 1981)

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H$$

$k = 5.9 \times 10^{-9}$ cm3s-1 (Anicich et al, 1974)

Protonation by other ions possible, but less important

Dissociative recombination:

$H_3O^+ + e^- \rightarrow$

H_2O	+	H		(25 %)
OH	+	$2H$		(60 %)
OH	+	H_2		(14 %)
OH	+	H_2	+ H	(1 %)

(Jensen et al., 2000)

$OH + H_2 \rightarrow H_2O + H$

possesses activation barrier
$\rightarrow$ inefficient at 10K

OH reacts otherwise:

$OH + O \rightarrow O_2 + H$

$OH + C \rightarrow CO + H$

Also: Grain surface formation of water:

$$O + H \rightarrow OH$$
$$OH + H \rightarrow H_2O$$

H_2O from grains can then be photodesorbed

But: In cold clouds water abundances much (up to a factor of 1000) lower than predicted by models

In diffuse clouds and outflows agreement better.

Formation of methane (CH_4) in dark clouds

H_3^+ is the starter

$$H_3^+ + C \rightarrow CH^+ + H_2$$

Successive hydrogen addition:

$$CH^+ + H_2 \rightarrow CH_2^+ + H$$

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H$$

$$CH_3^+ + H_2 \not\rightarrow CH_4^+ + H$$ (endoergic !)

But: radiative association

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$$

$$k = 1 \times 10^{-13}\ cm^3 s^{-1}$$

Finally: dissociative recombination

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

No efficient methane formation in the gas phase !

Way out : proton transfer

$$CH_5^+ + CO \rightarrow HCO^+ + CH_4$$

Why does methane matter ?

Build-up of hydrocarbon chains !

C insertion:

$$C + CH_4 \rightarrow C_2H_3 + H$$

$$C^+ + CH_4 \rightarrow C_2H_2^+ + H_2$$

C insertion:

$$C + C_mH_n \rightarrow C_{m+1}H_{n-1}^+ + H$$

$$C + C_mH_n^+ \rightarrow C_{m+1}H_{n-1}^+ + H$$

$$C^+ + C_mH_n \rightarrow C_{m+1}H_{n-1}^+ + H$$

Carbon chains can elongate by binary reactions:

$C_2H + C_2H_2^+ \rightarrow C_4H_2^+ + H$

$C_2H_2 + C_2H_2^+ \rightarrow C_4H_2^+ + H_2$

$\rightarrow C_4H_3^+ + H$

$C_2H + C_2H_2 \rightarrow C_4H_2 + H$

$CN + C_2H_2 \rightarrow HC_3N + H$

Iteratively, this reactions lead to long carbon chains with little H-saturation.

detected in dark clouds !

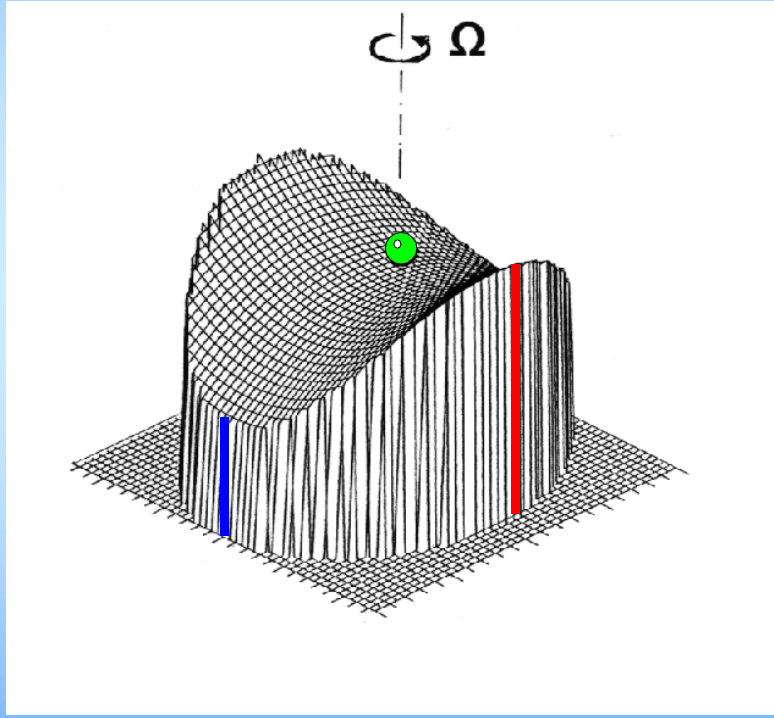
Especially interesting:

$C + C_2H_2 \rightarrow C_3H + H$

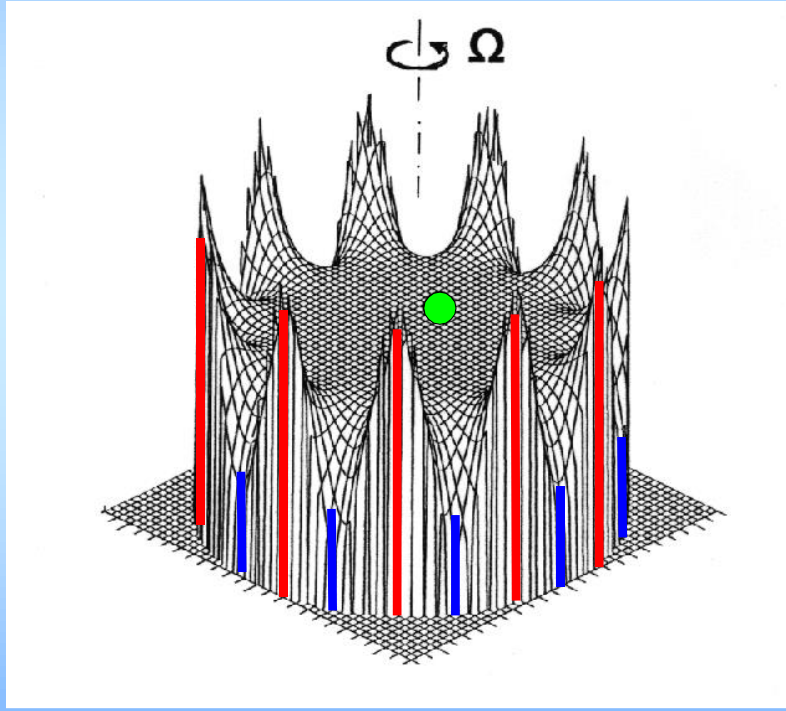
Two isomers, one cyclic, one linear

At low relativ kinetic energy, preferential forming of c-C_3H

Investigationg Ion-Neutral reactions: Radiofrequency Ion Traps

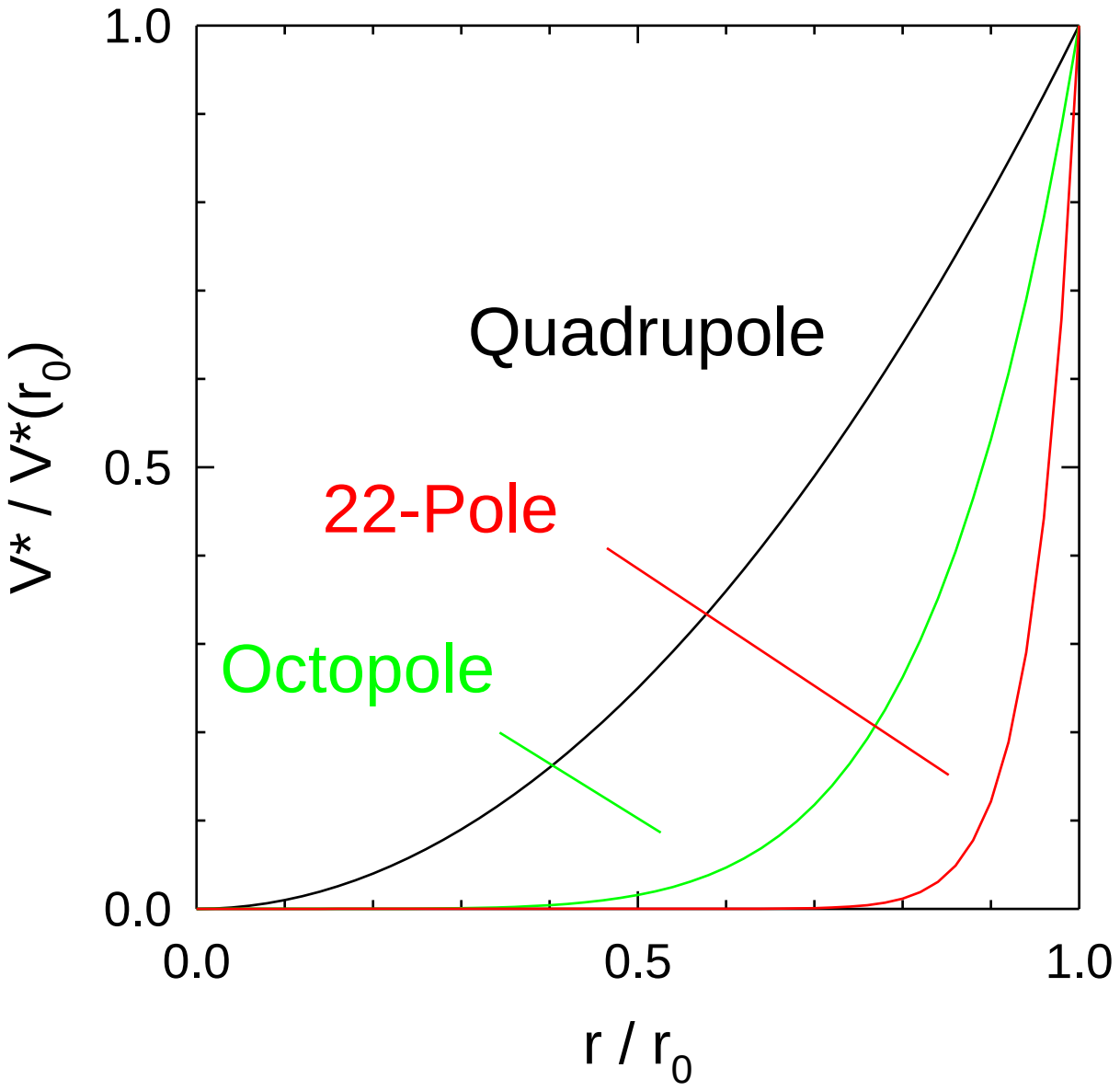


Quadrupole

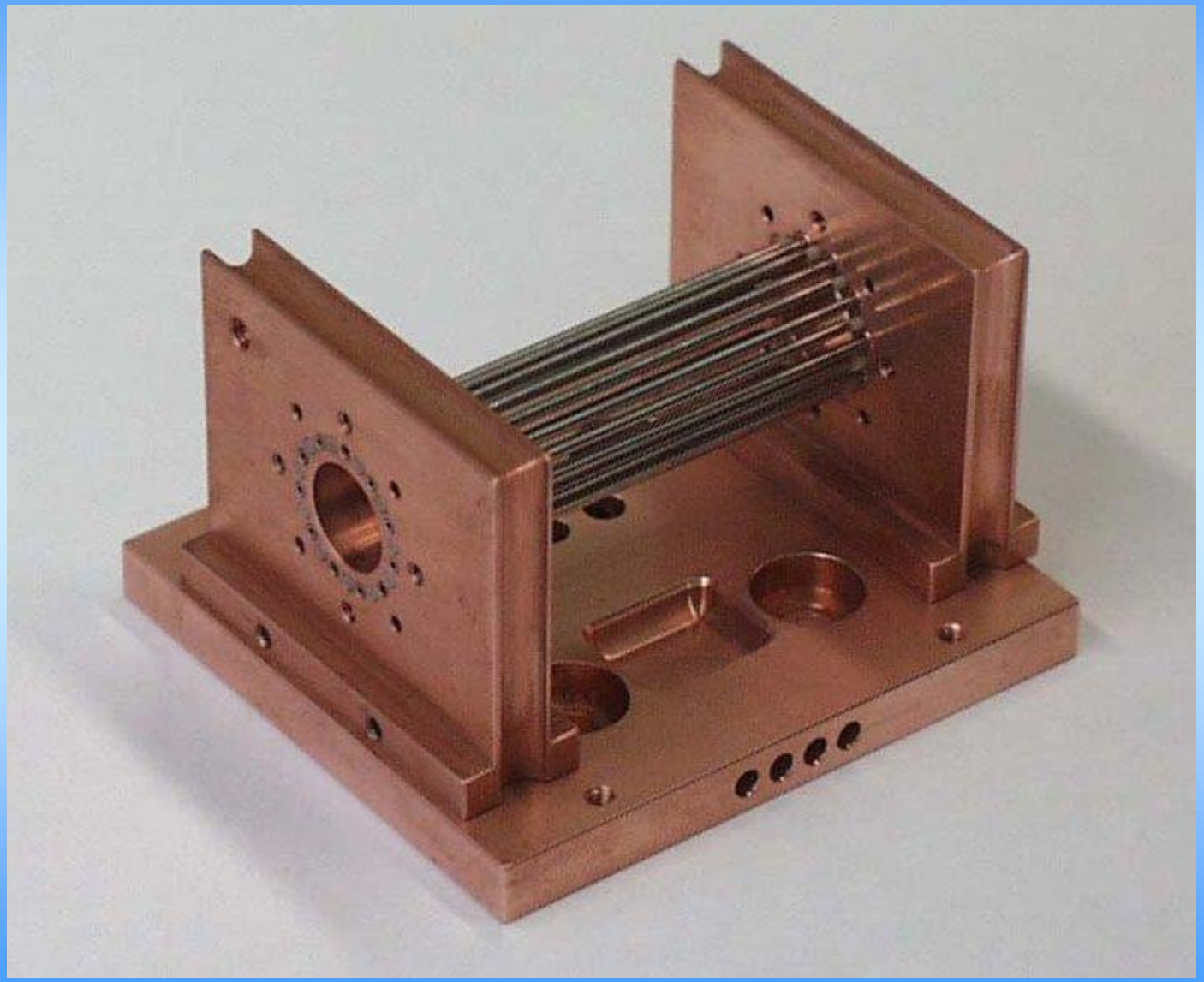


22-Pole

Effective Potential

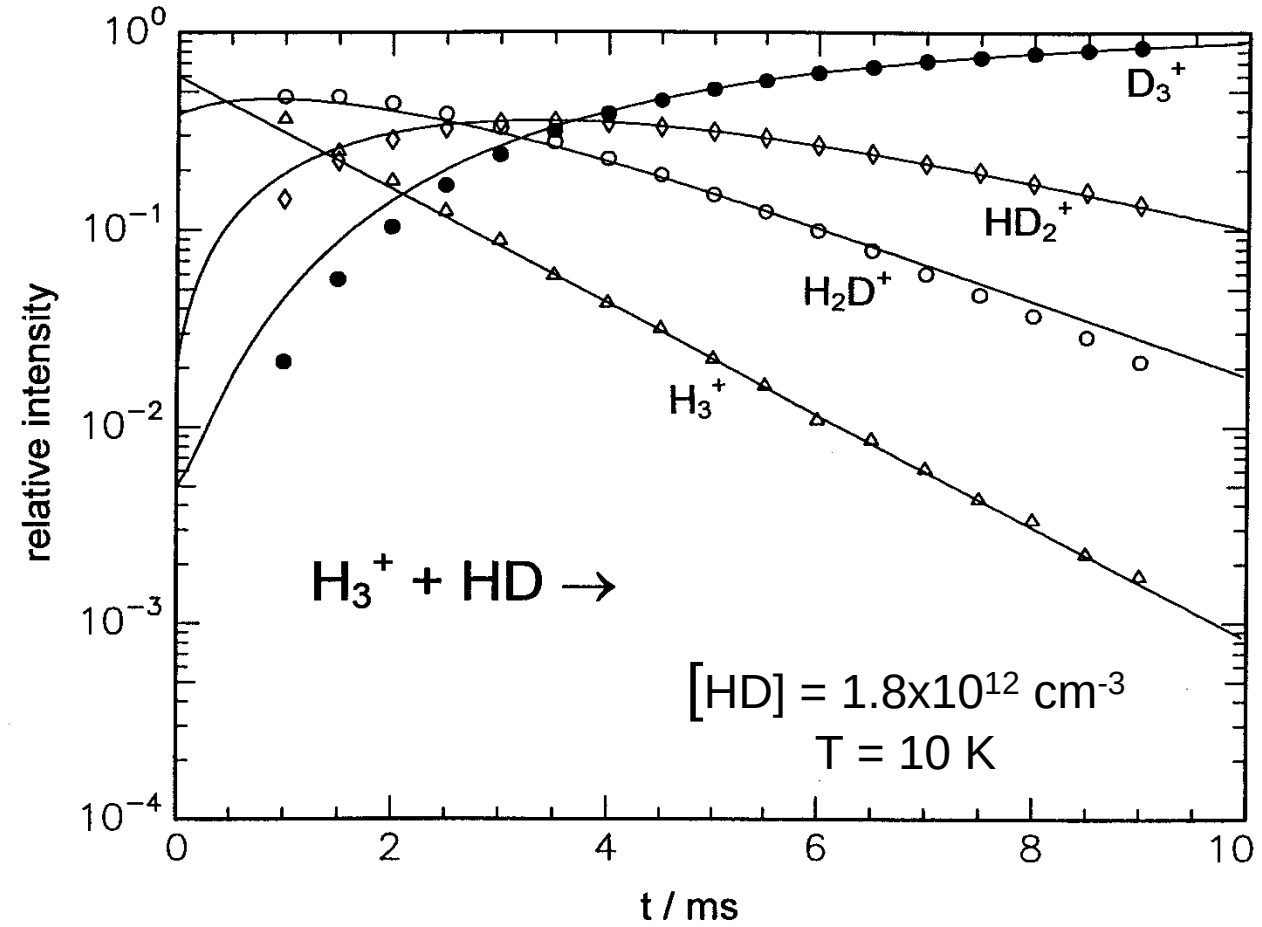


Low Temperature 22 Pole Ion Trap

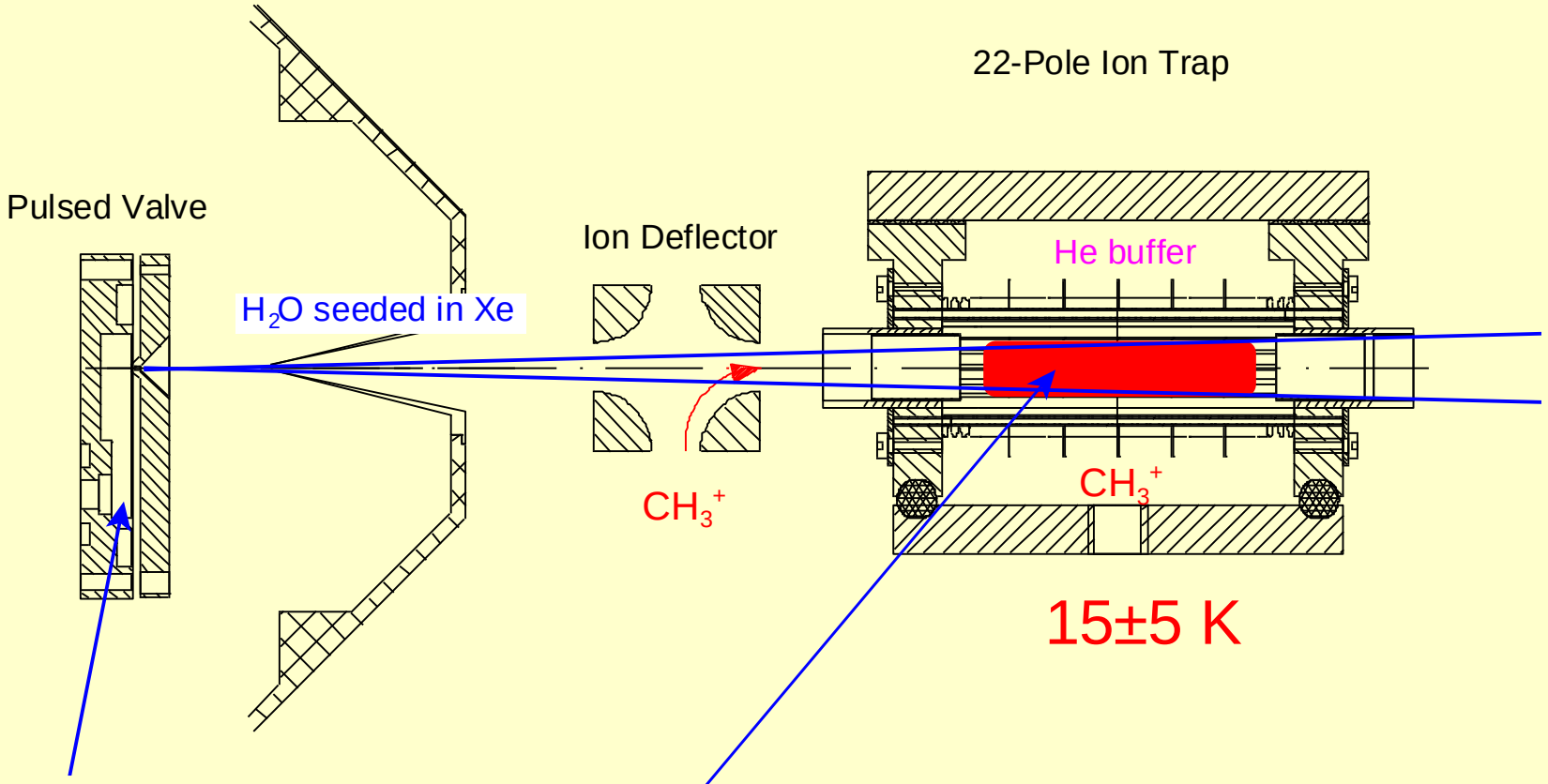


Deuteration of H_3^+

$$H_3^+ \xrightarrow[k_1]{HD} H_2D^+ \xrightarrow[k_2]{HD} D_2H^+ \xrightarrow[k_3]{HD} D_3^+$$



Experimental Setup



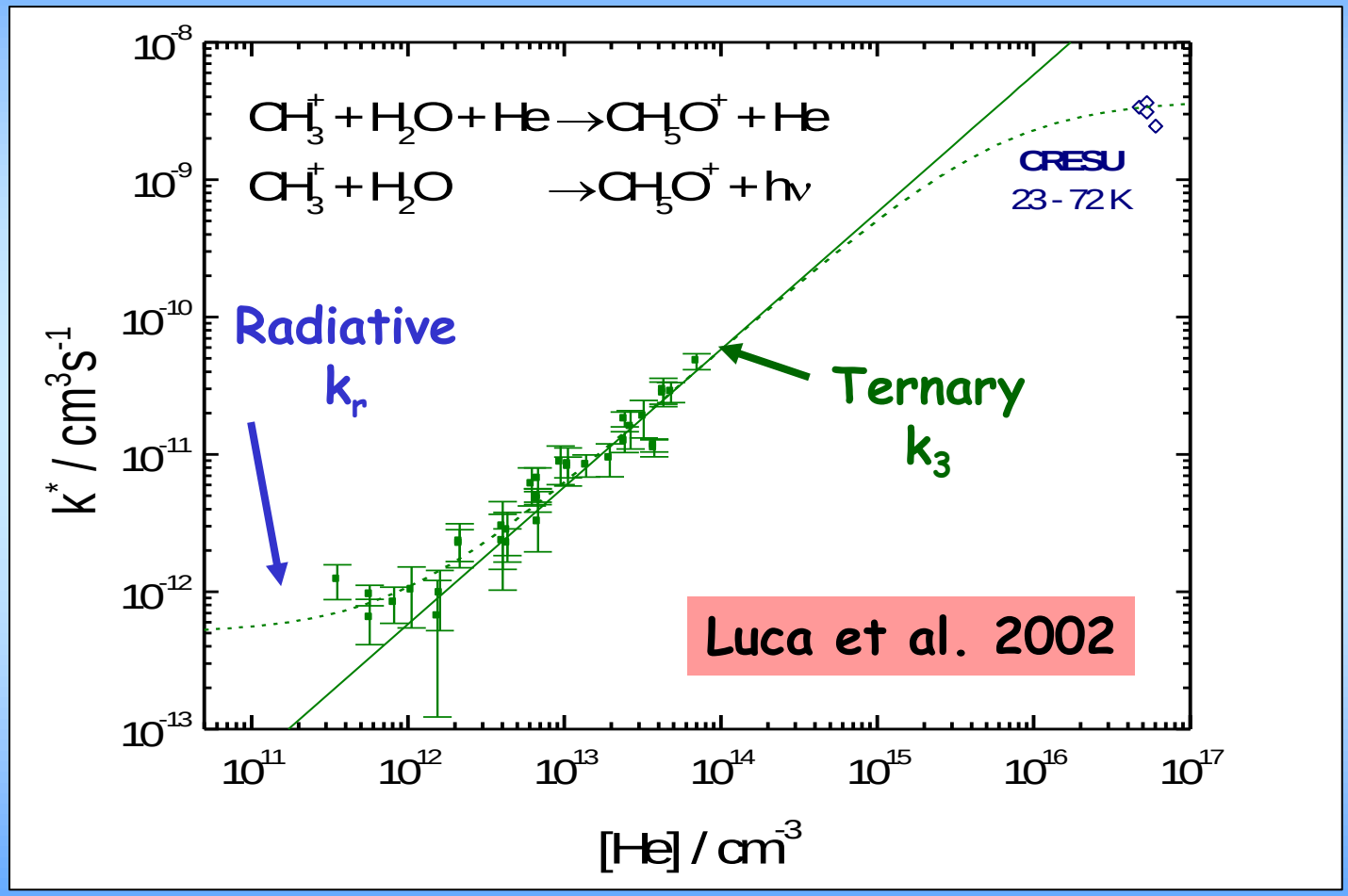
Stagnation pressure: 365 mbar
H_2O partial pressure: 26mbar at 295 K
H_2O 7%
Xe 93 %

Instantaneouce densities:
$[H_2O] = 7 \cdot 10^8$ cm^{-3}
$[Xe] = 1 \cdot 10^{10}$ cm^{-3}

Effective temperature
$T_{eff} = 50 \pm 30$ K

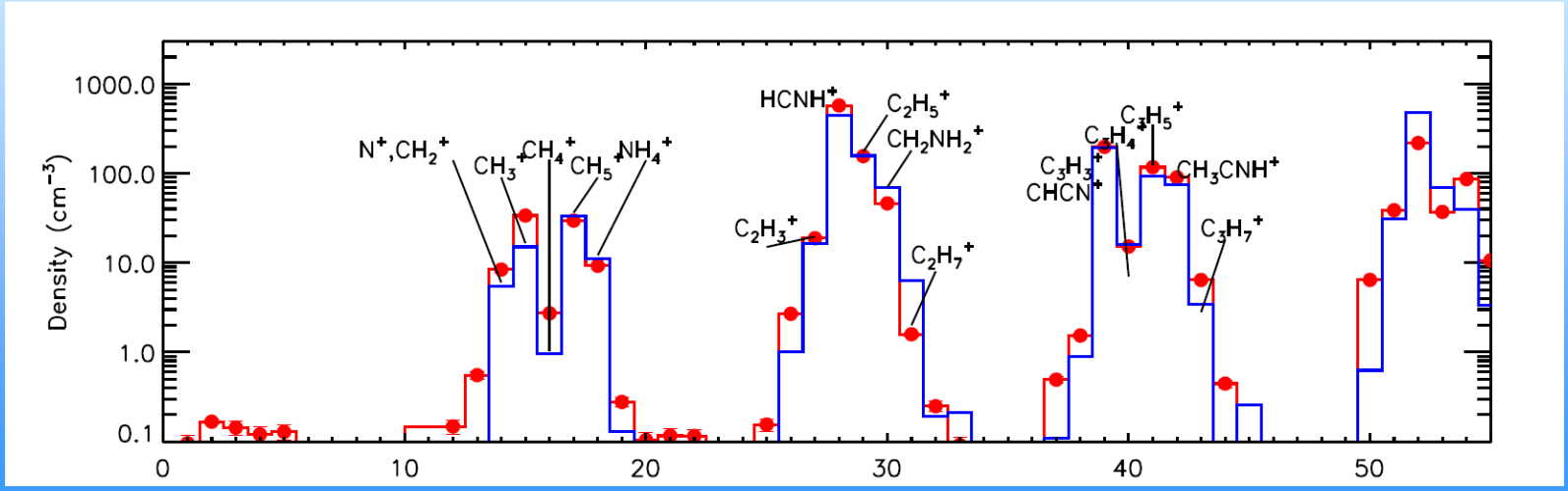
$CH_3^+ + H_2O$

★ two processes - radiative and ternary



CH_2CN^+ - a possible reactive cyano intermediate to build larger molecules

- Mass 40 detected with INMS – most likely $C_2H_2N^+$
- Model calculations predict a density 13 cm^{-3} at the peak of Titans ionosphere (1125 km). (Vuitton et al. 2018)
- In previous models without N compounds underestimated
- Could be reactive with unsaturated hydrocarbons and form templates for larger molecules (tholines)

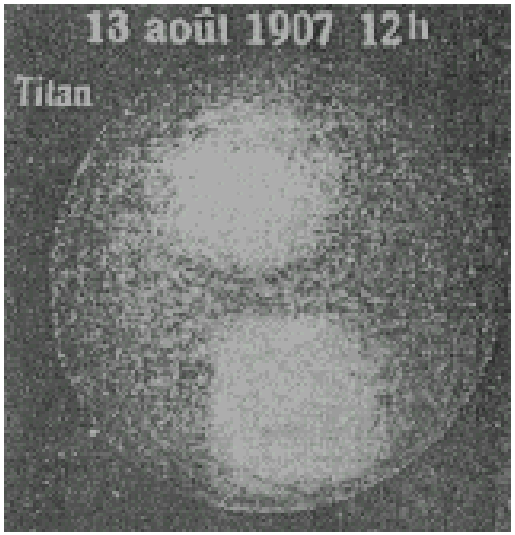


A moon with an atmosphere ?

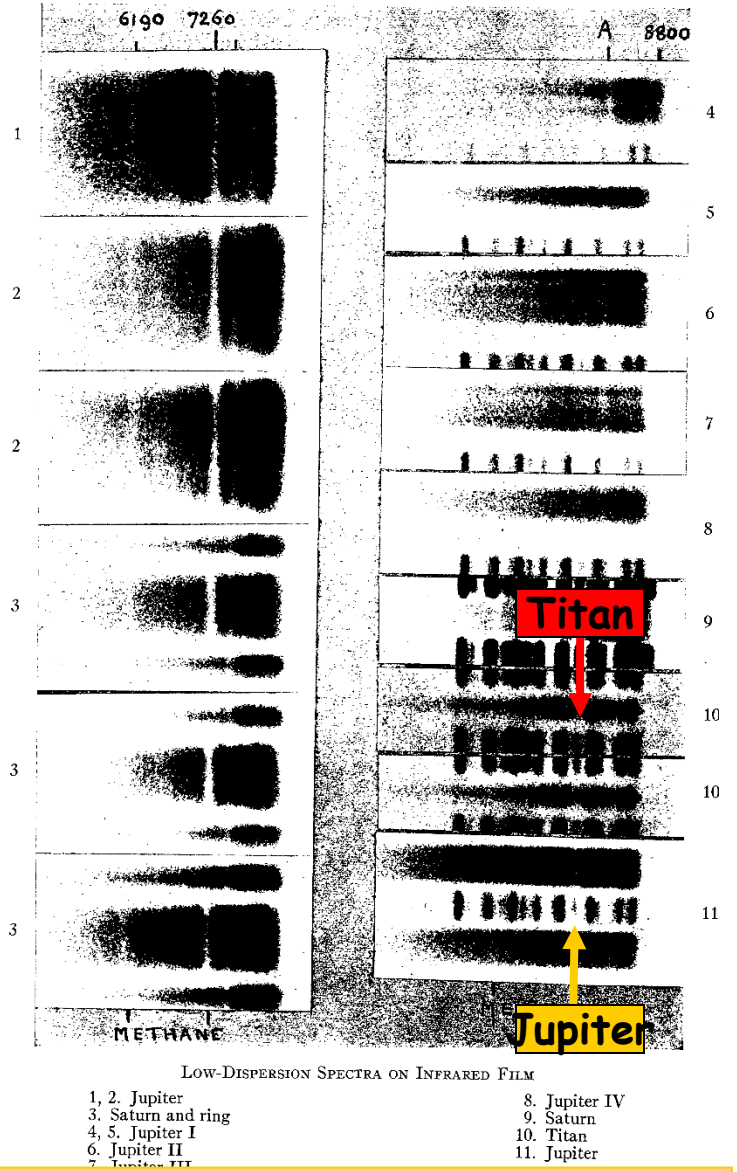
- ★ edge darkening of Titan pointing to an atmosphere first claimed by Josep Comas Solà
- ★ methane discovered in its atmosphere by Kuiper 1944



Josep Comas Solá



Drawing by Solà (1907)



Low-Dispersion Spectra on Infrared Film

1, 2. Jupiter
3. Saturn and ring
4, 5. Jupiter I
6. Jupiter II
8. Jupiter IV
9. Saturn
10. Titan
11. Jupiter

Observation of the 726 nm methane line on Titan (Kuiper 1944)

Titan's atmosphere

- 147 kPa surface pressure
- 94 % N_2, 6 % CH_4 + Ar
- could resemble atmosphere of early Earth
- Traces of hydrocarbons and nitrogen compounds
- mixing extending to higher altitudes

	Titan	Earth
Dominant molecule	N_2	N_2
Tropopause	35 km	8-18 km
Homopause	1195 km	85 km



Dixit et ignotas animum dimittit in artes

"Omnia possideat, non possidet ardua Minos"

Generation of radicals and ions in Titan's ionosphere

Magnetospheric electrons

$N_2 + e^- \rightarrow N(^2D) + N(^4S) + e^-$

Long-lived excited state

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

$CH_4 + e^- \rightarrow CH_4^+ + e^-$

CH_4^+ easily donates protons:

$CH_4 + CH_4^+ \rightarrow CH_5^+ + CH_3$

UV photons

$N_2 + h\nu \rightarrow N(^4S) + N^+ + e^-$

$\rightarrow N(^2D) + N^+ + e^-$

$\rightarrow N_2^+ + e^-$

$\rightarrow N(^2D) + N(^4S)$

$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$ (7%)

$\rightarrow {}^3CH_2 + 2H$ (59%)

$\rightarrow CH + H_2 + H$ (7%)

$\rightarrow CH_3 + H$ (29%)

Lavvas et al. 2008, Yung et al. 1984

Further build-up of more complex substances

Ion-neutral reactions followed by dissociative recombination

$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$

$C_2H_5^+ + e^- \rightarrow C_2H_4 + H$ (12 % of events)

$\rightarrow$ other products

$C_2H_5^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_4$

$C_3H_5^+ + e^- \rightarrow C_3H_4 + H$

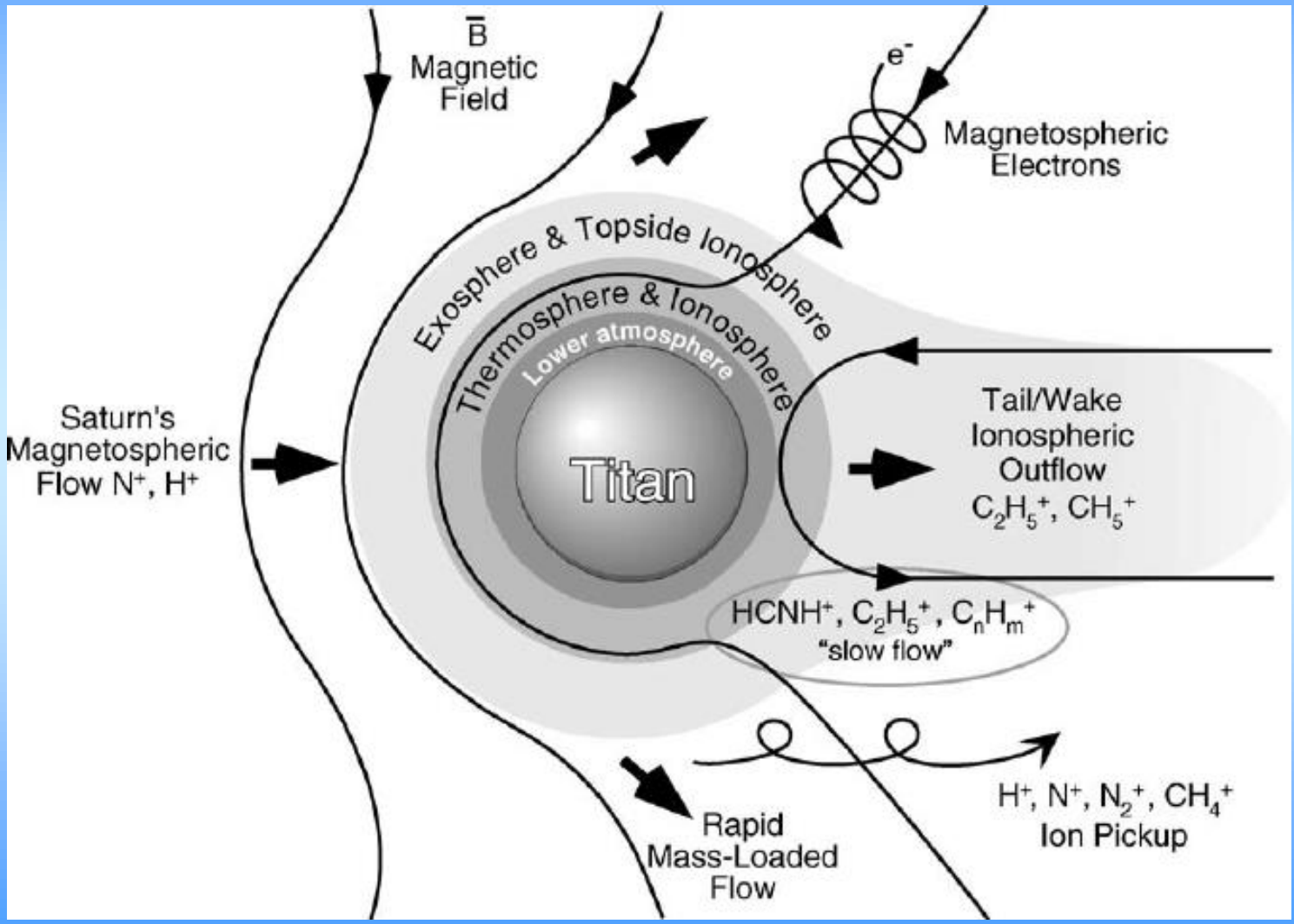
$\rightarrow$ other products

Radical-neutral reactions

$N(^2D) + C_2H_4 \rightarrow CH_3CN + H$

Rate constants and product branching ratios often unknown !

Magnetospheric electrons in Titan's ionosphere



Models of ion reactions in Titan's ionosphere

Equilibrium between production and decay

$$\frac{dN_i}{dt} = P_i - L_i N_i$$

Ionisation rate

Transfer rate

$$P_i = \sum_n \sigma_n N_n + \sum_{i'n} k_{i'n} \Phi_{i'n} N_{i'} N_n$$

Dissociative recomb. rate

Transfer rate

$$L_i = \alpha_i N_e N_i + \sum_{i'n} k_{in} N_i N_n$$

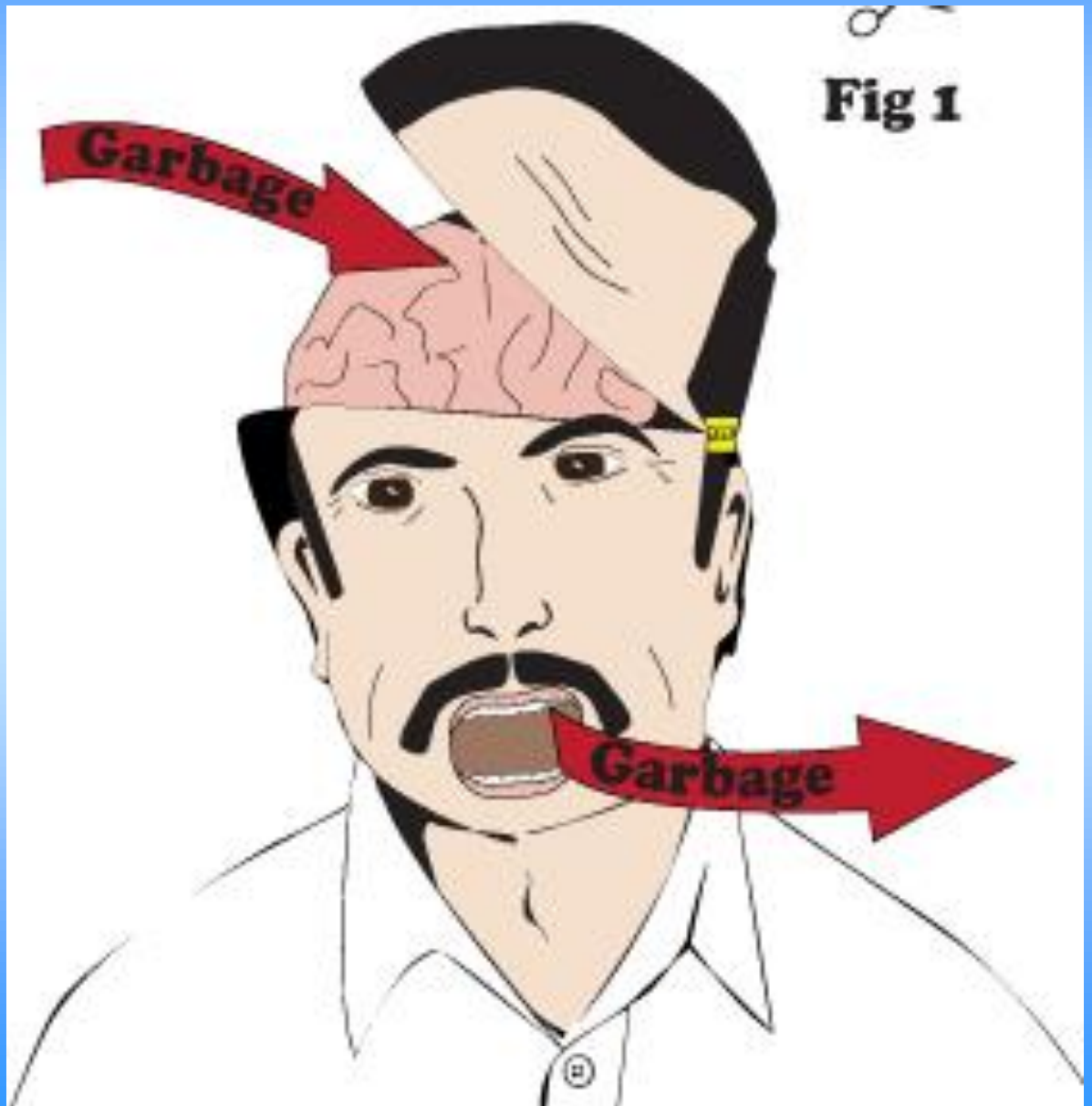
$N_n + h\nu \rightarrow N_n^+ + e^-$

$N_{i'}^+ + N_n \rightarrow N_n^+ + N_{i'}$

$N_n^+ + e^- \rightarrow$ products

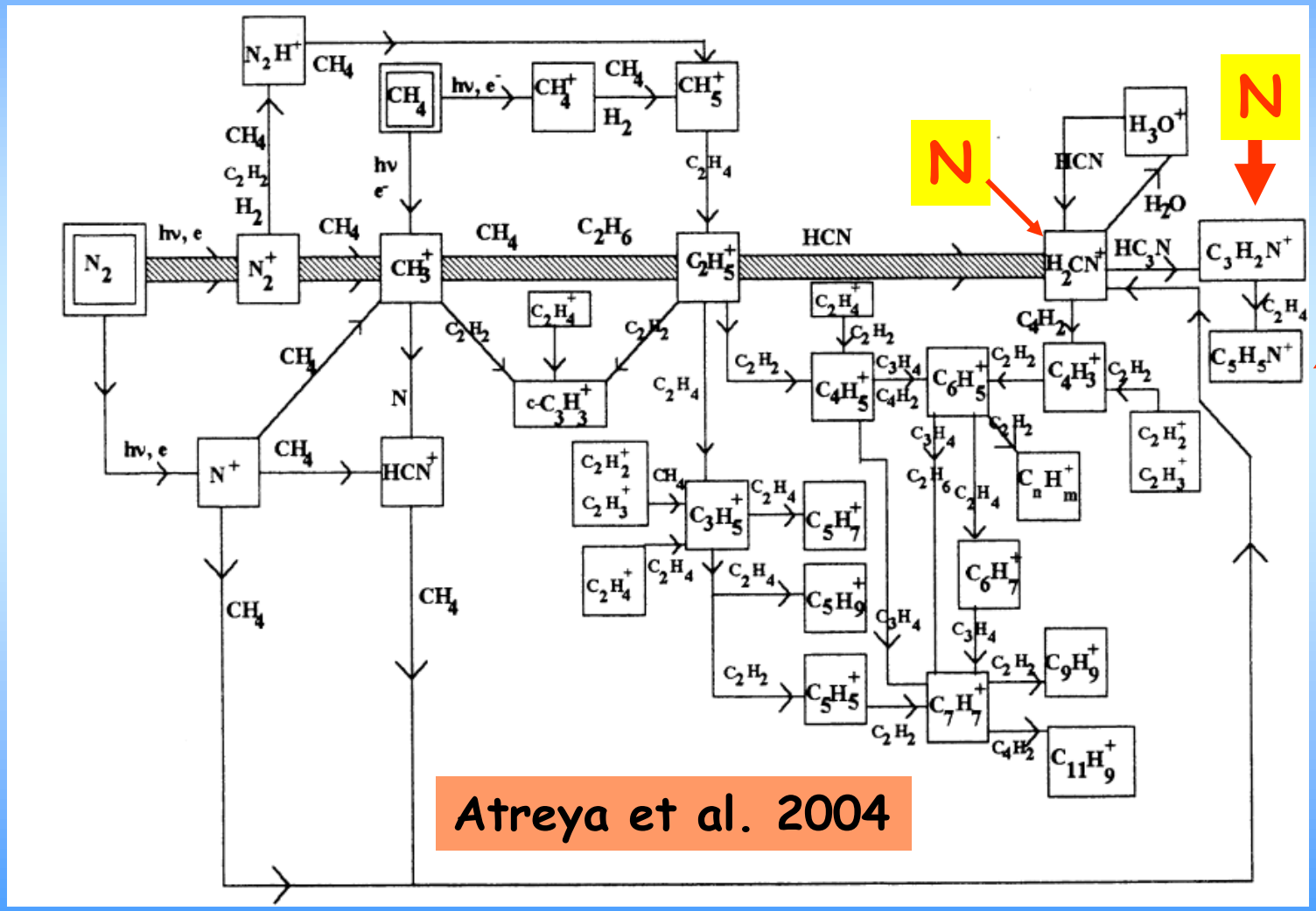
P_i = production rate
L_i = loss rate
N_i = number of ions i
$N_{i'}$ = number of other ions i'
N_i = number of neutrals
N_e = number of electrons
σ_n = ionisation cross section
α_i = dissociative recomb. rate constant
k = Transfer rate constant

GIGO principle for models of Titan's ionosphere

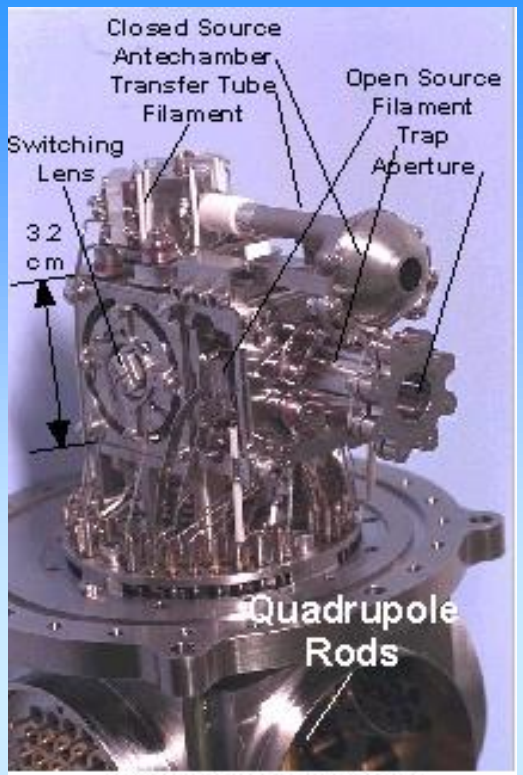


Models of Titan's ionosphere

Old models: mostly protonated hydrocarbons formed



Ion-Neutral Mass Spectrometer (INMS) on board of Cassini

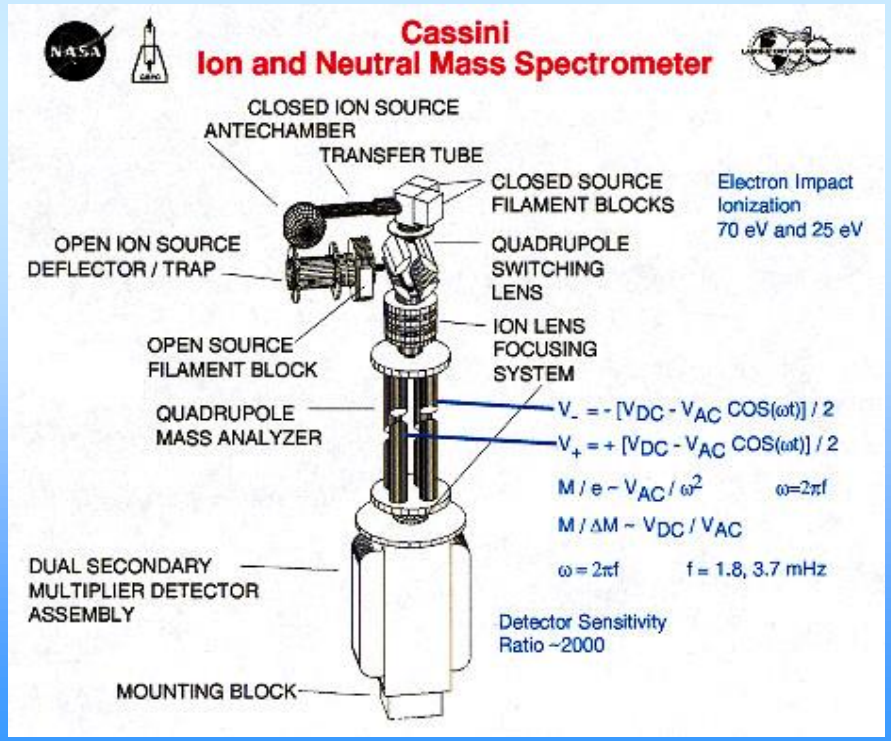


Dual inlet gas/ion source

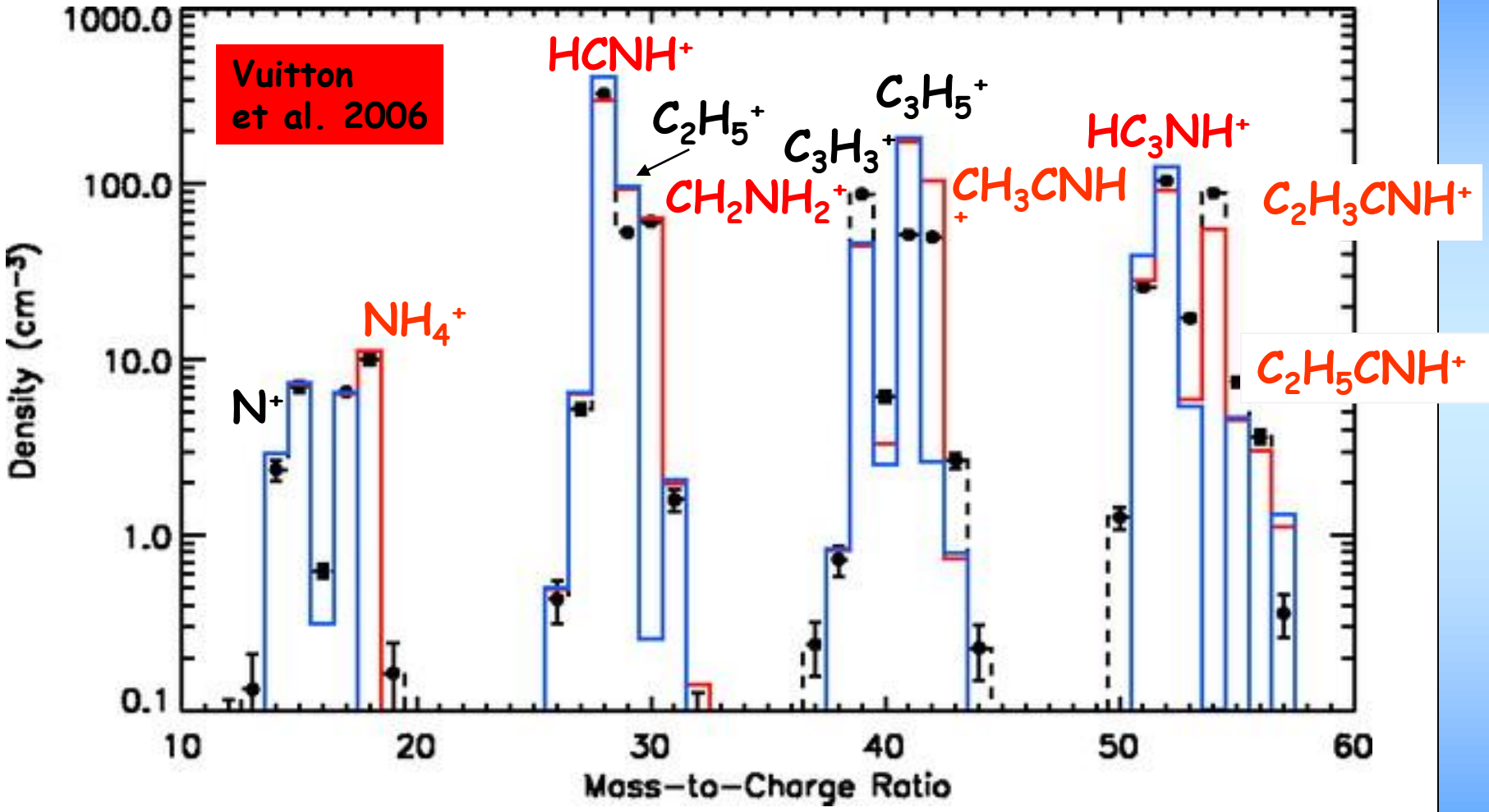
2 operating modes:

a) open source mode for ions
b) closed source for neutrals





INMS results in open mode



Blue line = fit without including new ions

Red line = fit including new species, black dots data from Cassini

Nitriles (RC≡N) in atmospheres

★ Rich nitrile chemistry in N_2/CH_4 atmospheres, first step to biomolecules

★ can polymerise (e. g. with HCN) to tholines (aerosol and haze formation):

$$nRCN + nHCN \rightarrow \left[\text{—} C(=NH) \text{—} N{=}C(R) \text{—} \right]_n$$

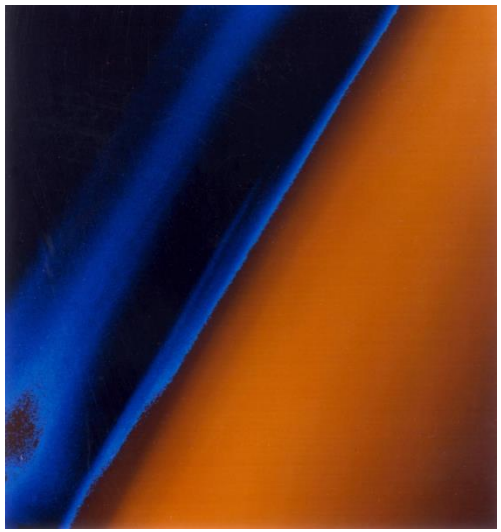
Tholine

★ **Chemically inert:** Destroyed mainly by protonation and dissociative recombination

$$RCN + C_2H_5^+ \rightarrow RCNH^+ + C_2H_4$$

$$RCNH^+ + e^- \rightarrow RCN + H$$

$$\rightarrow \text{other products}$$



Titan's haze layer

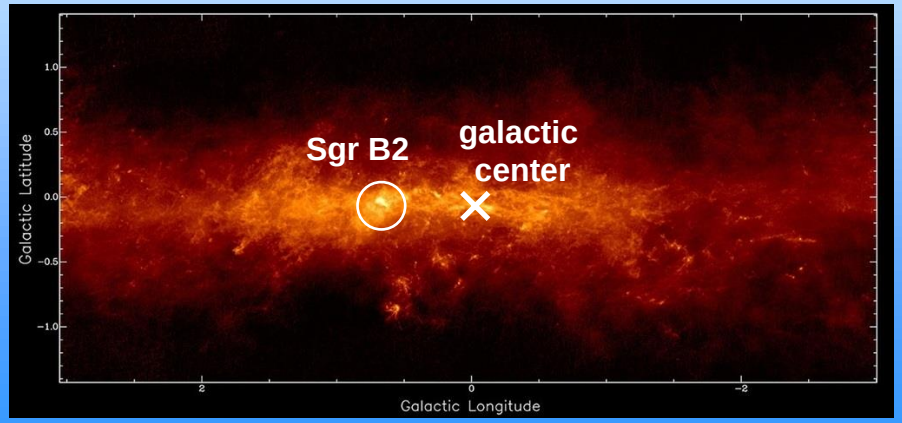


Tholine from the lab

Nitriles in the interstellar medium

- ★ CH_3CN Methyl cyanide – Solomon 1971
- ★ CH_3NC Methyl isocyanide – Cernicharo 1988H2CCN
- ★ CH_2CN Cyanomethyl radical – Irvine 1988
- ★ HCCN cyanomethylene radical – Guelin 1991





Guided ion beam mass spectrometer

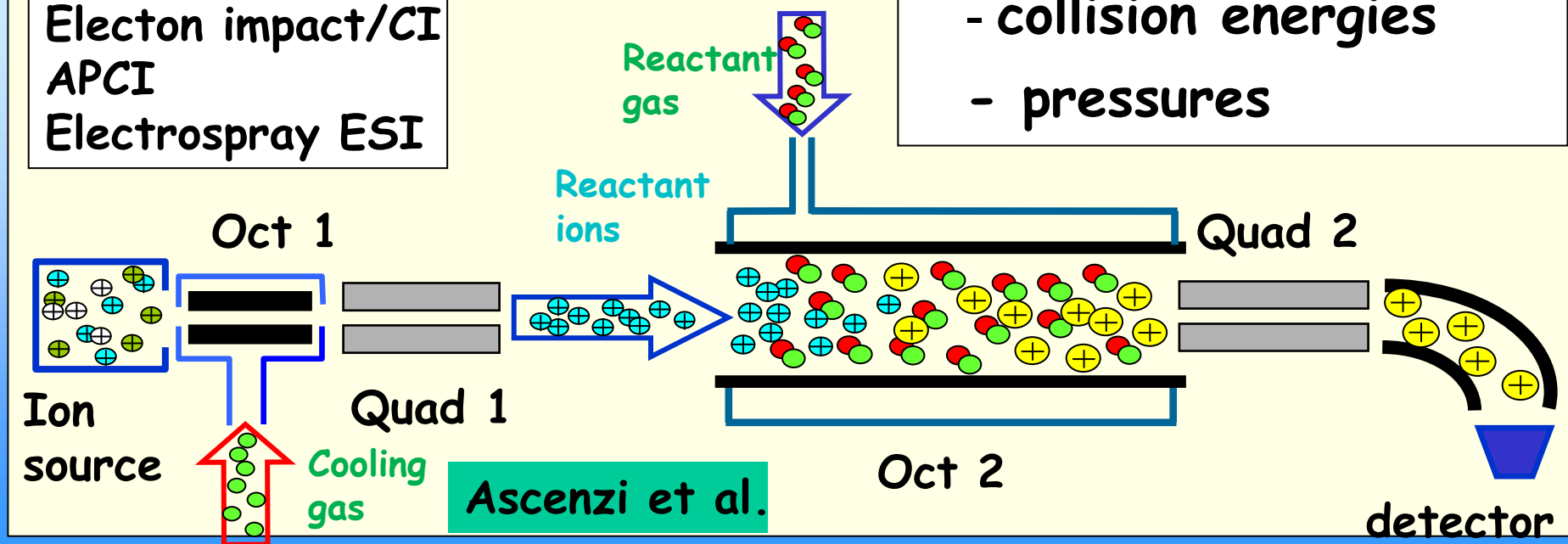
Ionisation → cooling → mass selection → reaction → mass selection

Mixture of ions → A^+ → C^+, D^+, etc.

B

Ion sources:
Electon impact/CI
APCI
Electrospray ESI

Measurements at variable:
- collision energies
- pressures



Ascenzi et al.

Formation of ions

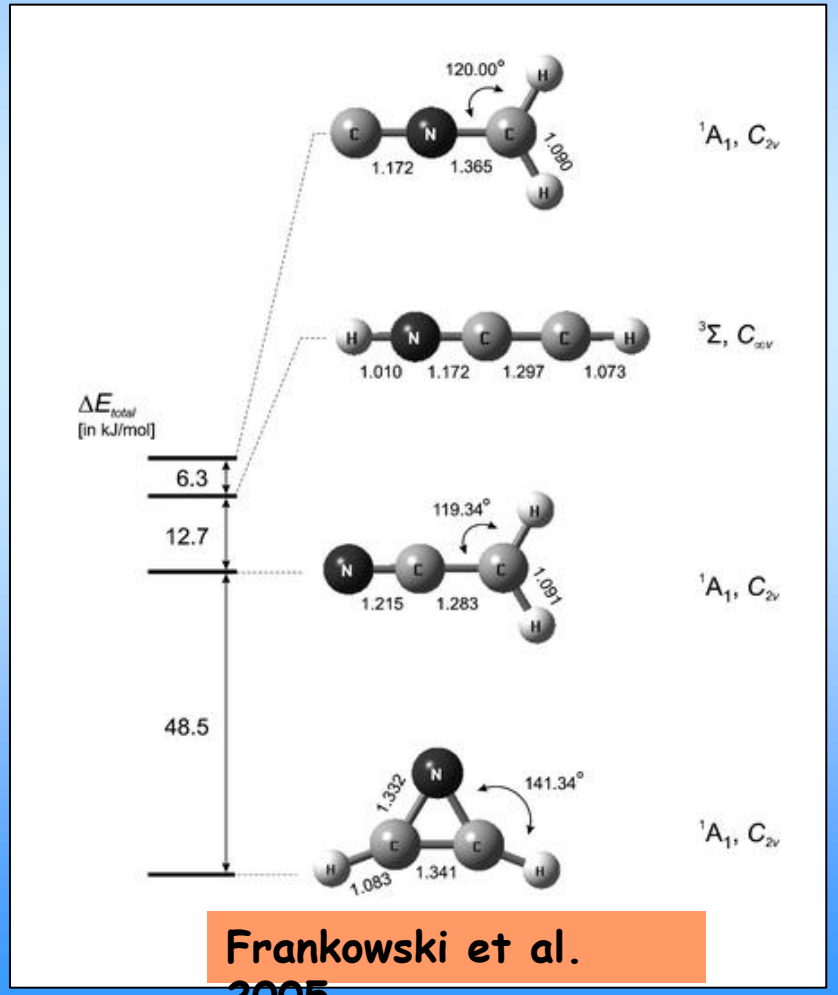
★ Electron impact ionisation of chloroacetonitrile ($ClCH_2CN$)

$$ClCH_2CN \rightarrow CH_2CN^+ + Cl^-$$

★ Formation of 4 isomers possible:

-Cyclic $^1C_2H_2N^+$
-Linear $^1CH_2CN^+$
-Linear $^3HCCNH^+$
-Linear $^1CH_2NC^+$

★ Theoretical calculations disagree about energetic order of two highest-energy isomers



Frankowski et al. 2005

Isomers in interstellar and ionospheric chemistry

- ★ Long on the radar screen of astrochemists: (HCO^+/HOC^+, HCN/HNC)
- ★ Increasing molecular complexity augments number of possible isomers
- ★ Even rotamers can function as distinctive species in low-temperature environments (different radiofrequency spectra)

Selective production of isomeric ions

★ Selection of apt precursor molecules can lead to different isomers

- Electron impact ionisation of CH_3CN leads to cyclic azirine$^+$ cation and CH_2CN^+

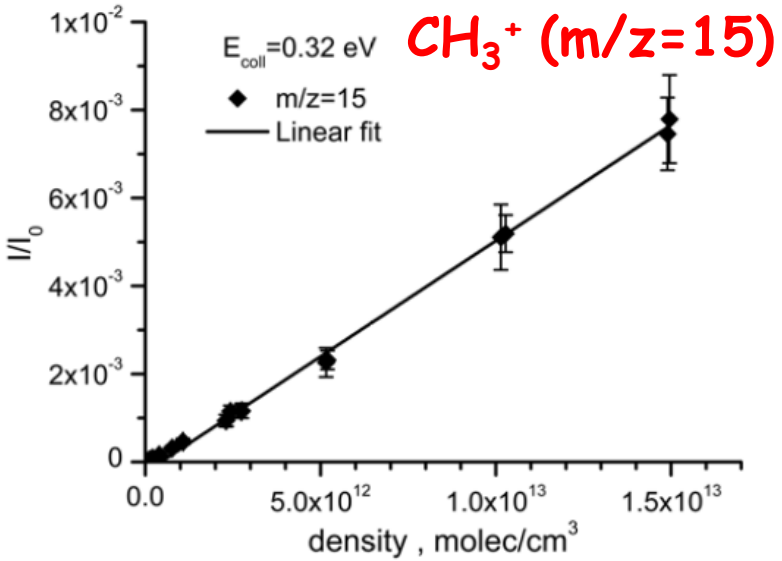
- Electron impact ionosation of $ClCH_2CN$ leads to CH_2CN+

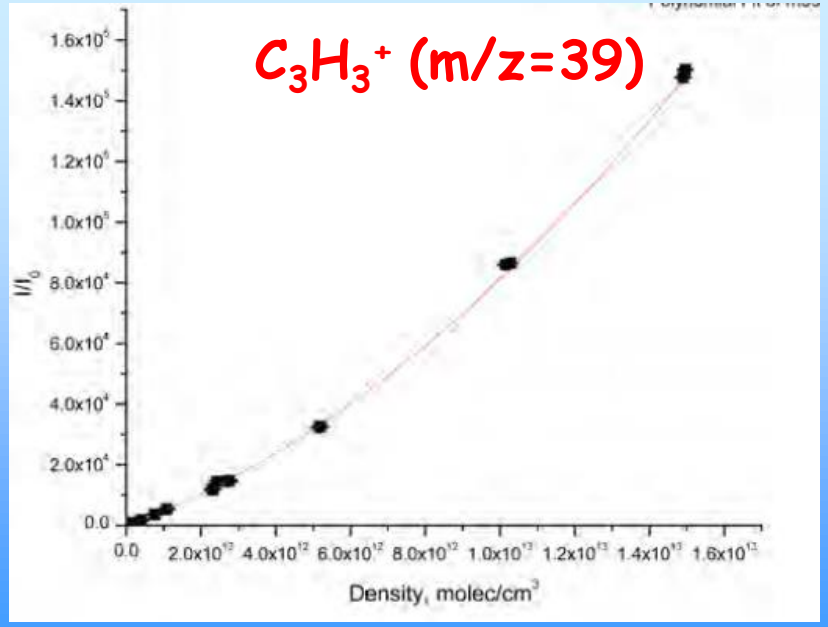
- Photodissiociative ionosation using synchrotron radiation of CH_3CN at lower energies delivers azirine$^+$ cation

Pressure dependence

$CH_2CN^+ + C_2H_2 \rightarrow CH_3^+ + HC_3N$ (primary) $\rightarrow$ Linear

$CH_3^+ + C_2H_2 \rightarrow C_3H_3^+ + H_2$ (secondary) $\rightarrow$ Quadratic (linear part at low pressure)

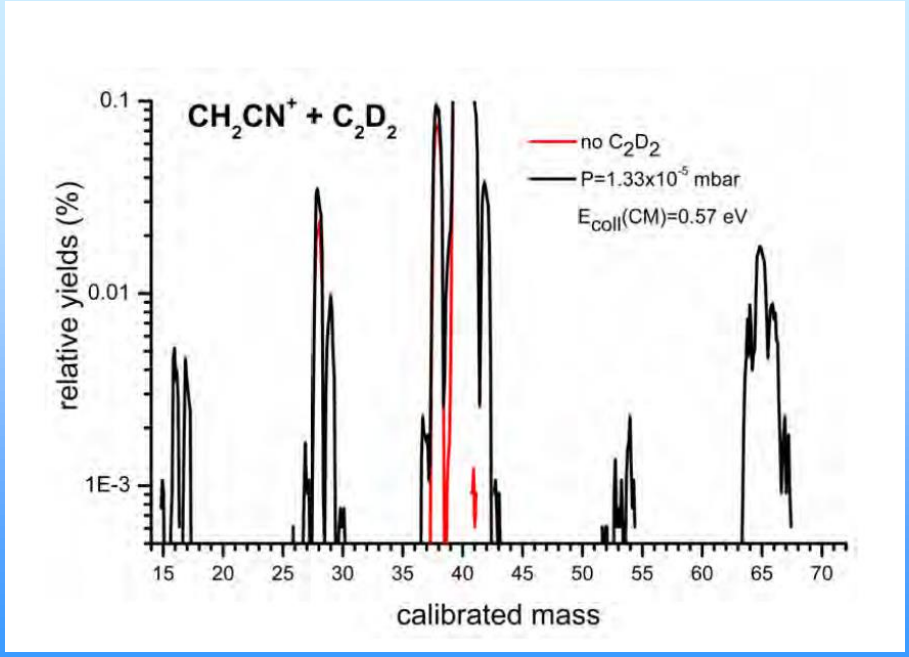


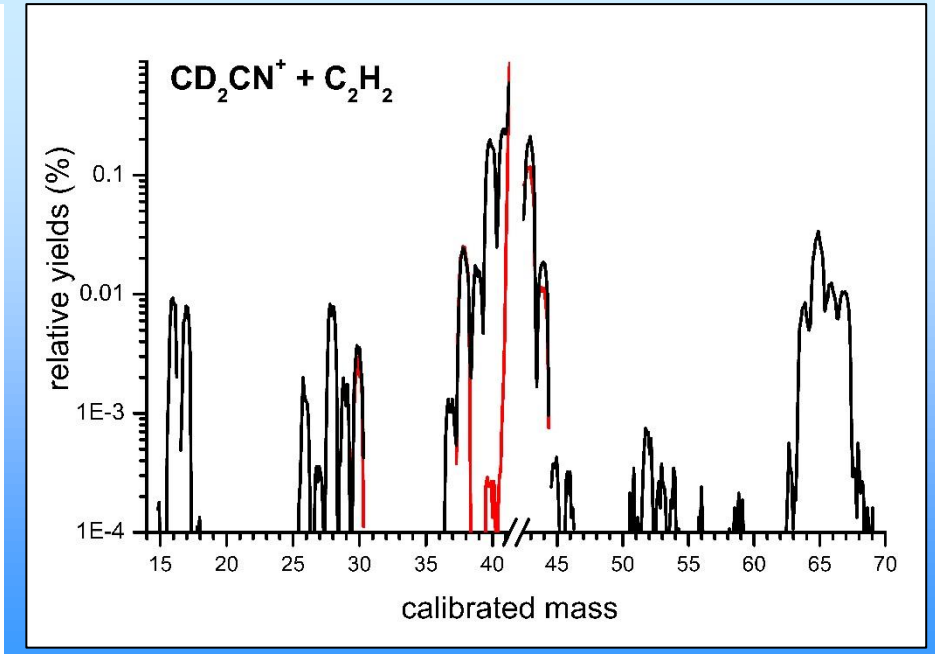


Use of deuterated isotopomers

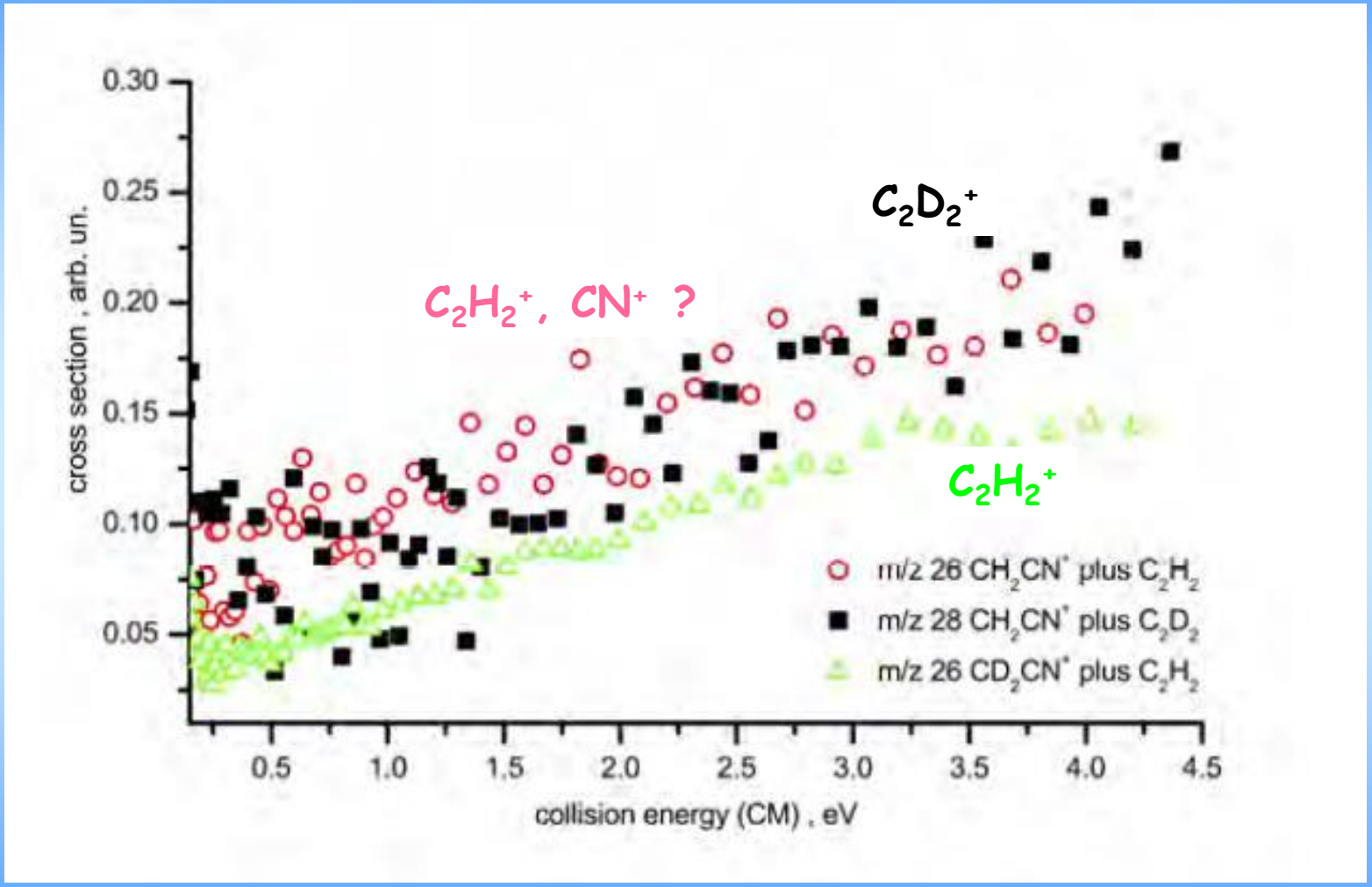
- Use of deuterated isotopomers to
  - distinguish between channels leading to similar masses
  - identify main product pathways and their thermodynamics

- Both $CH_2CN^+ + C_2D_2$ and $CD_2CN^+ + C_2H_2$ studies done





Isotopomer studies



→ $C_2H_2^+$ produced by charge transfer, CN^+ production not dominating

Possible reactions

$CH_2CN^+ + C_2H_2 \rightarrow C_3H_3^+ + HCN/HNC$

$\rightarrow C_3H_3 + HCN^+/HNC^+$

$\rightarrow C_2H_3 + HCCN^+$

$\rightarrow H_2 + H_2C_4N^+$

$\rightarrow C_2H_4 + CCN^+$

$\rightarrow C_2H_3 + HCNH^+$

$\rightarrow C_2H_3^+ + HCNH$

$\rightarrow C_2H_3 + HCNH^+$

$\rightarrow CH_3^+ + HCCCN$

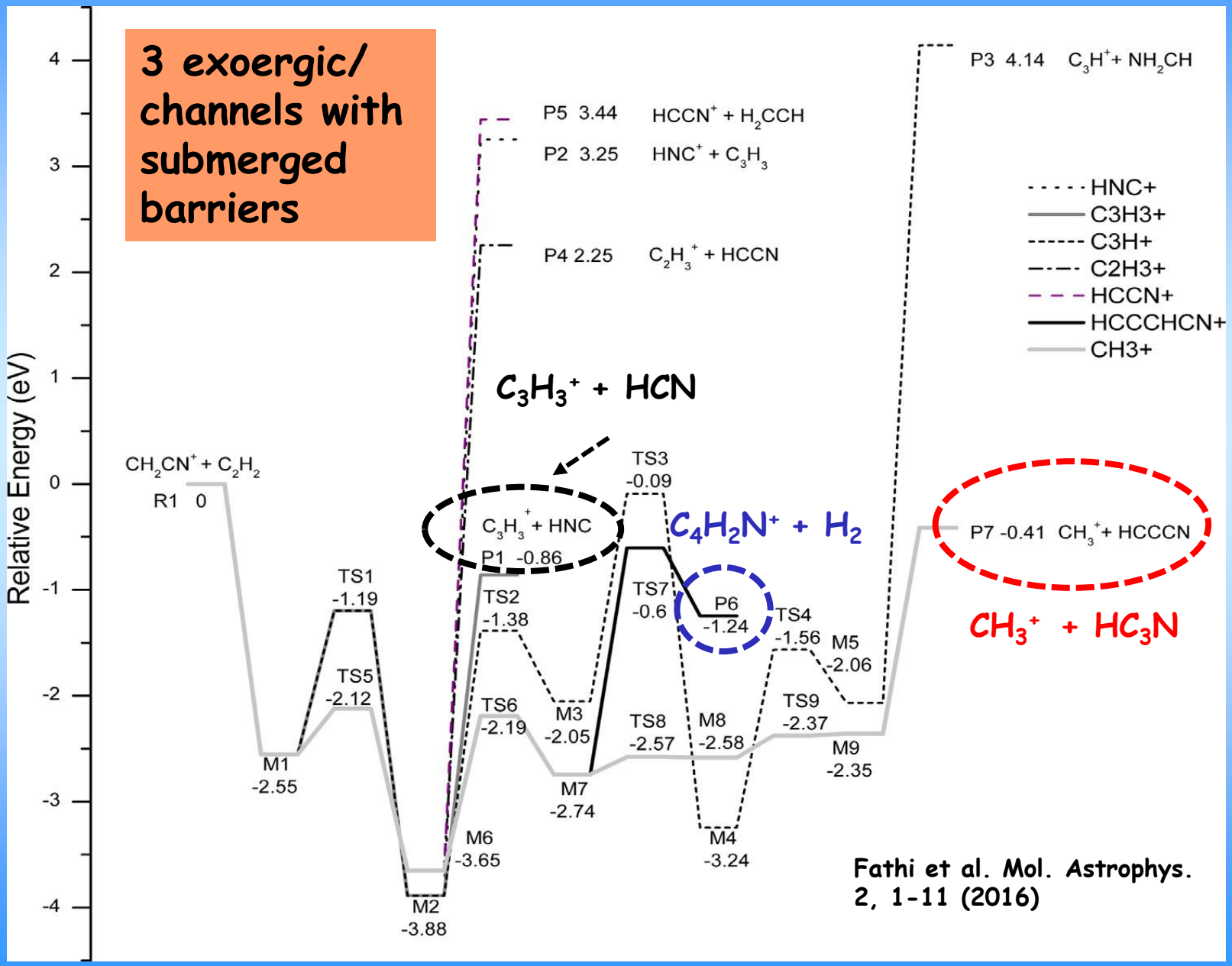
$\rightarrow CH_3 + HCCCN^+$

$\rightarrow C_2H_2 + H_2C_2N^+$

$\rightarrow C_2H + H_3C_2N^+$

$\rightarrow C_3H^+ + H_3CN^+$

Potential surface of $CH_2CN^+ + C_2H_2$



Possible exoergic barrierless reactions

$CH_2CN^+ + C_2H_2 \rightarrow C_3H_3^+ + HCN/HNC$

$\rightarrow C_3H_3 + HCN^+/HNC^+$

$\rightarrow C_2H_3 + HCCN^+$

$\rightarrow H_2 + H_2C_4N^+$

$\rightarrow C_2H_4 + CCN^+$

$\rightarrow C_2H_3 + HCNH^+$

$\rightarrow C_2H_3^+ + HCNH$

$\rightarrow C_2H_3 + HCNH^+$

$\rightarrow CH_3^+ + HCCCN$

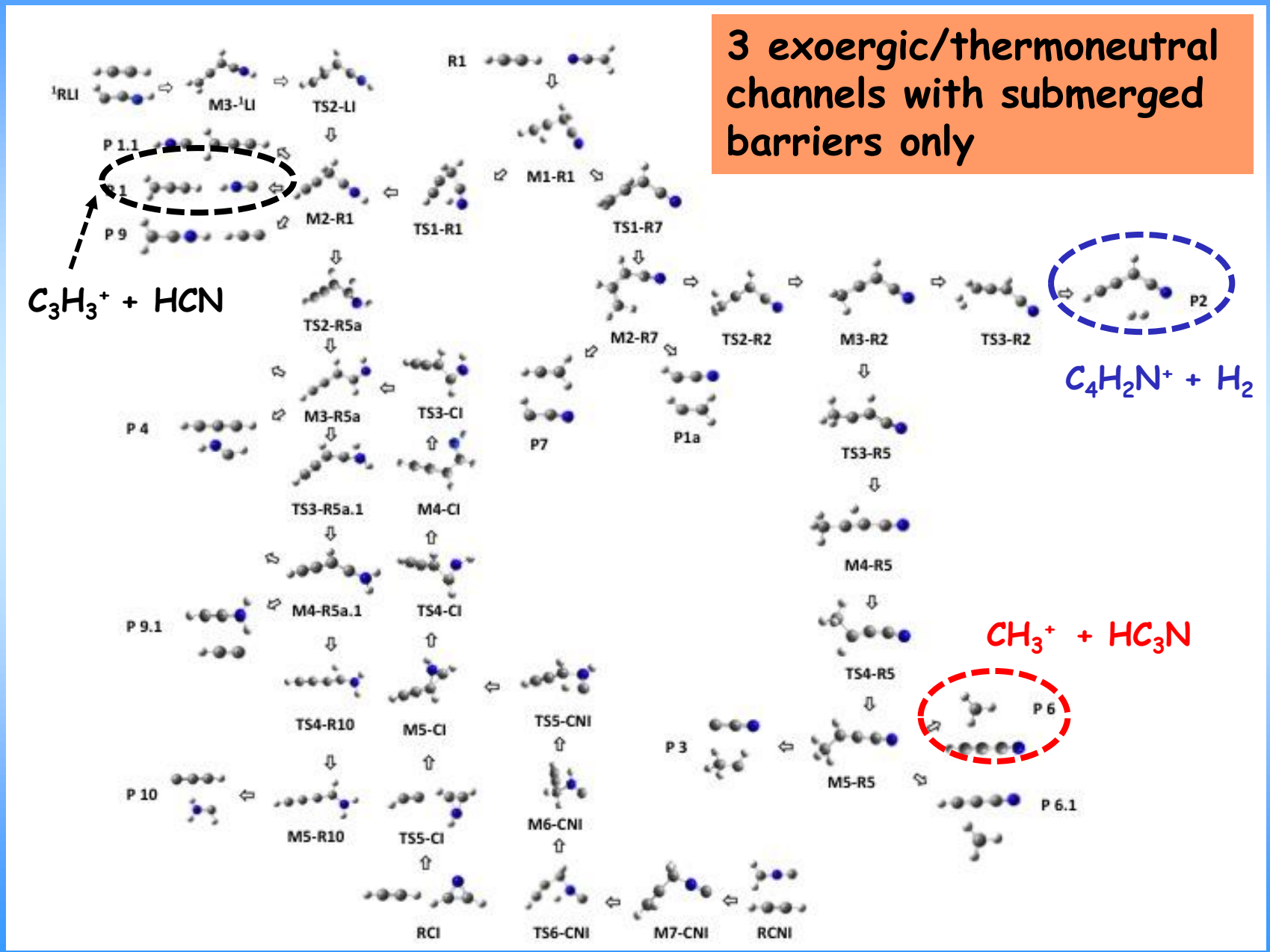
$\rightarrow CH_3 + HCCCN^+$

$\rightarrow C_2H_2 + H_2C_2N^+$

$\rightarrow C_2H + H_3C_2N^+$

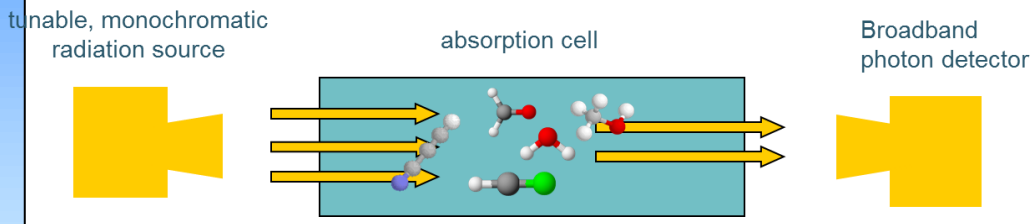
$\rightarrow C_3H^+ + H_3CN^+$

Flow chart with exoergic product pathways



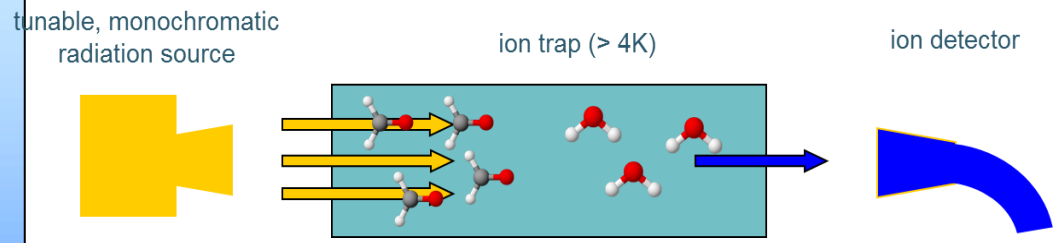
Spectroscopy of ions in traps (Brünken et al.)

Typical absorption experiment



- high number densities necessary
  → difficult for reactive ions
- line contamination

Action Spectroscopy in Cryogenic Ion Traps



- sensitive (only few 1000 ions)
- mass selection
- isolation of reactive ions
- low ion temperatures
  → less congested spectra
  → higher S/N & accuracy
- long interaction times

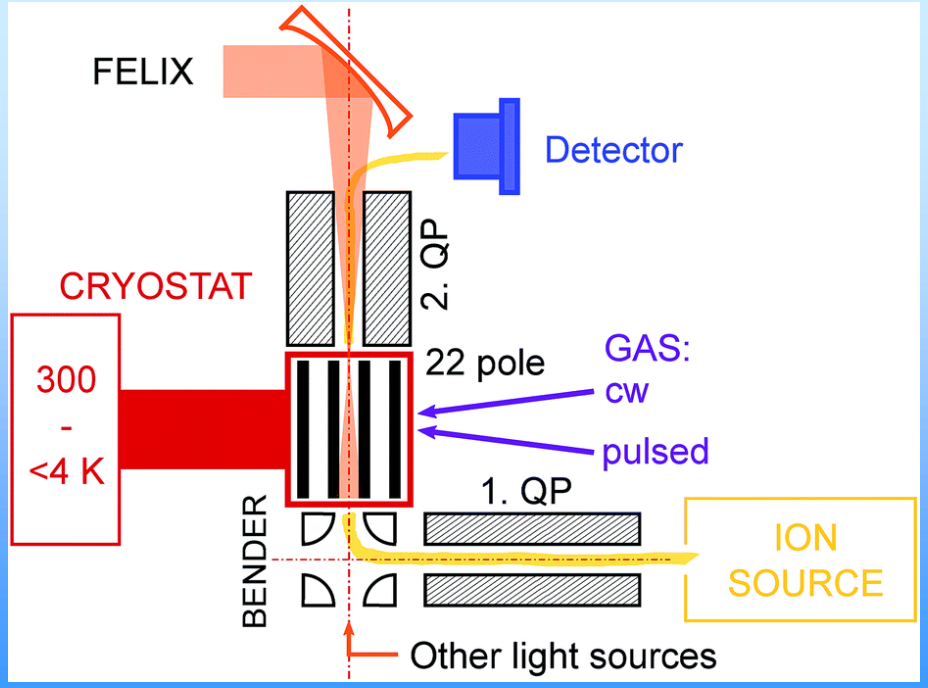
Infrared predissociation spectroscopy (IRPD)

★ Tagging of molecular ion with noble gas (Ne)

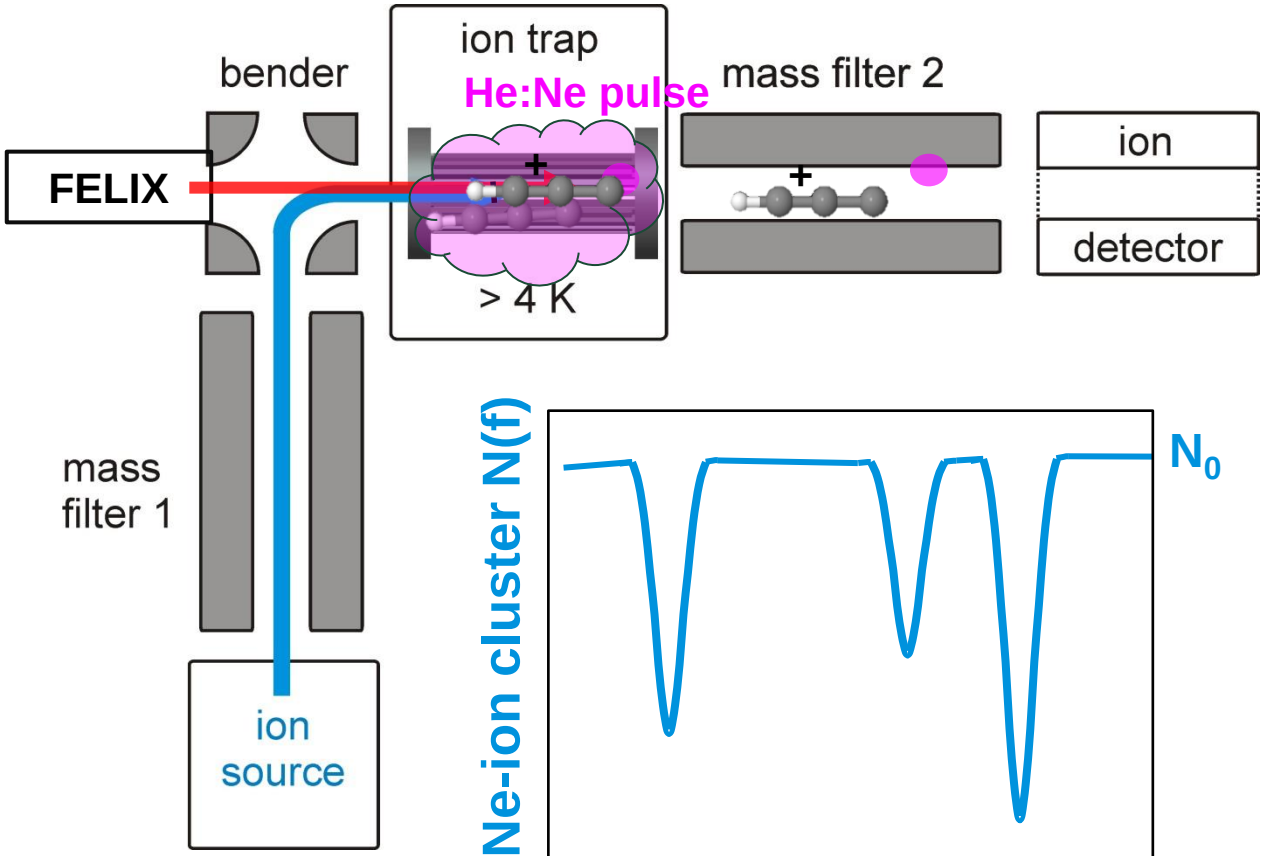
★ Irradiated with laser: Resonance with vibrational mode of ion leads to cluster destruction
→ loss of ion signal of cluster

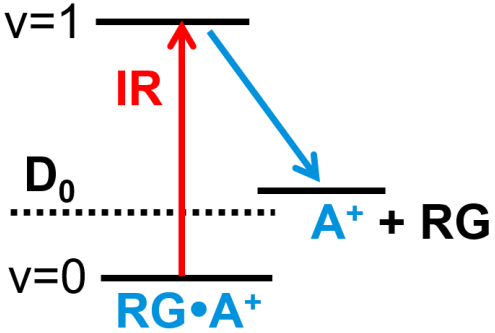
★ Identity of ions and their relative abundance can be established

★ Comparison of assignment of vibrational lies with ab initio calculations



Infrared predissociation spectroscopy (IRPD)





Brünken et al.

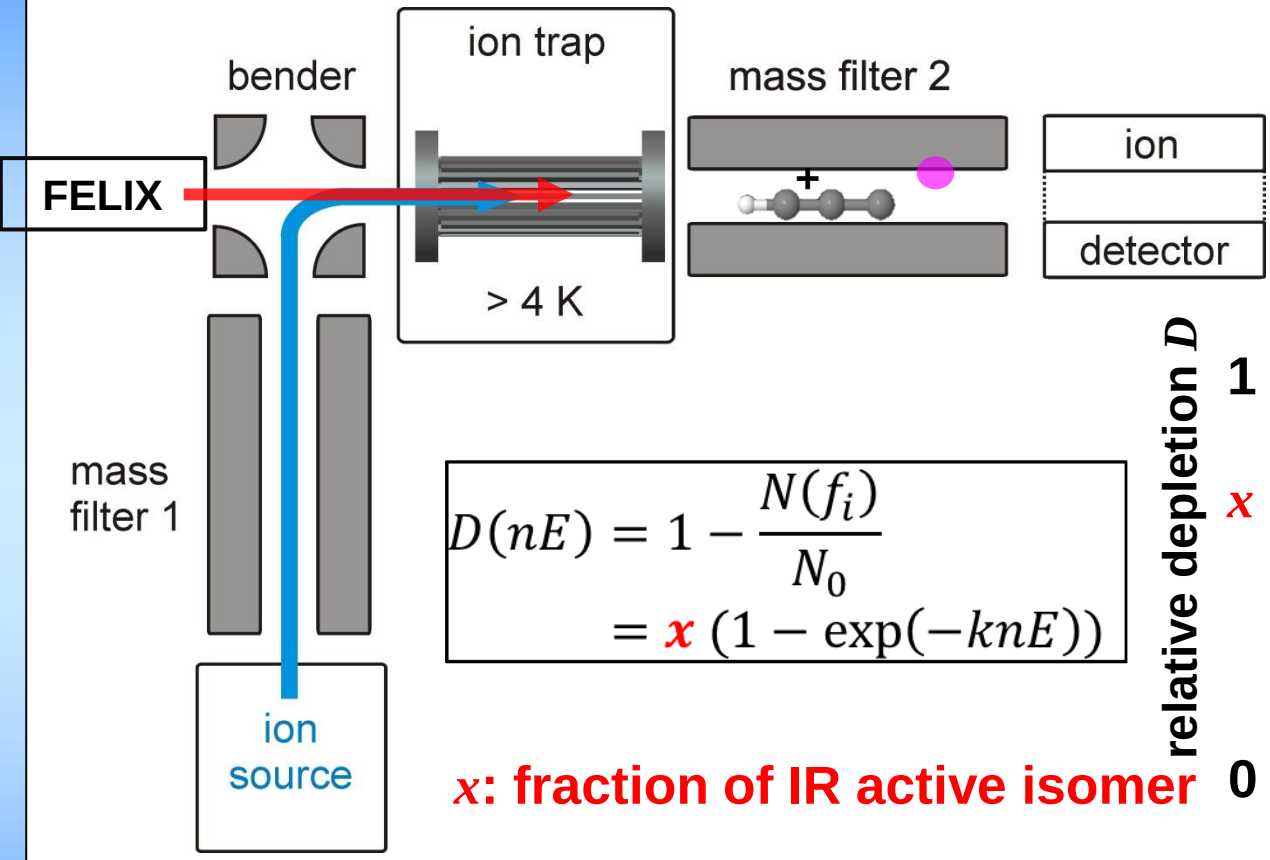
IRPD - weakly bound messenger infrared predissociation

Y.T. Lee, M. Duncan, M. A Johnson, K. Asmis, O. Dopfer, J. Roithova, …

See also: *Schwarz & Asmis, Chem. Eur. J. 2019, 25, 1 – 16*

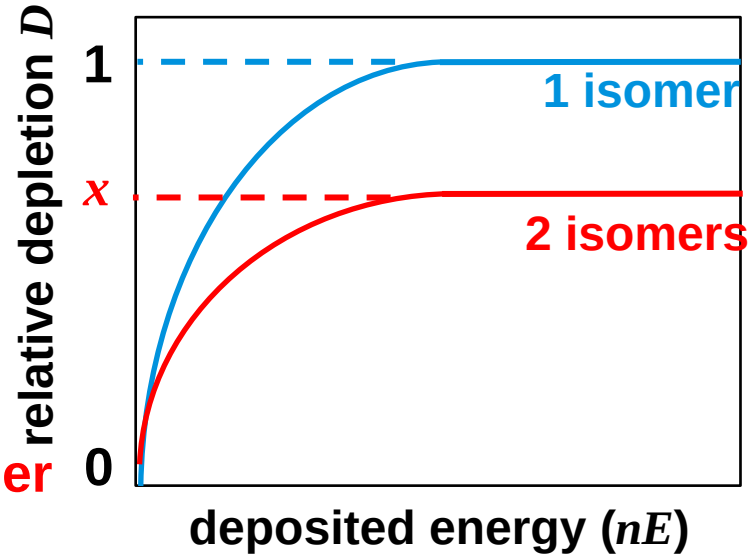
Infrared predissociation depletion spectroscopy

Brünken et al.



$$D(nE) = 1 - \frac{N(f_i)}{N_0} = x\,(1 - \exp(-knE))$$

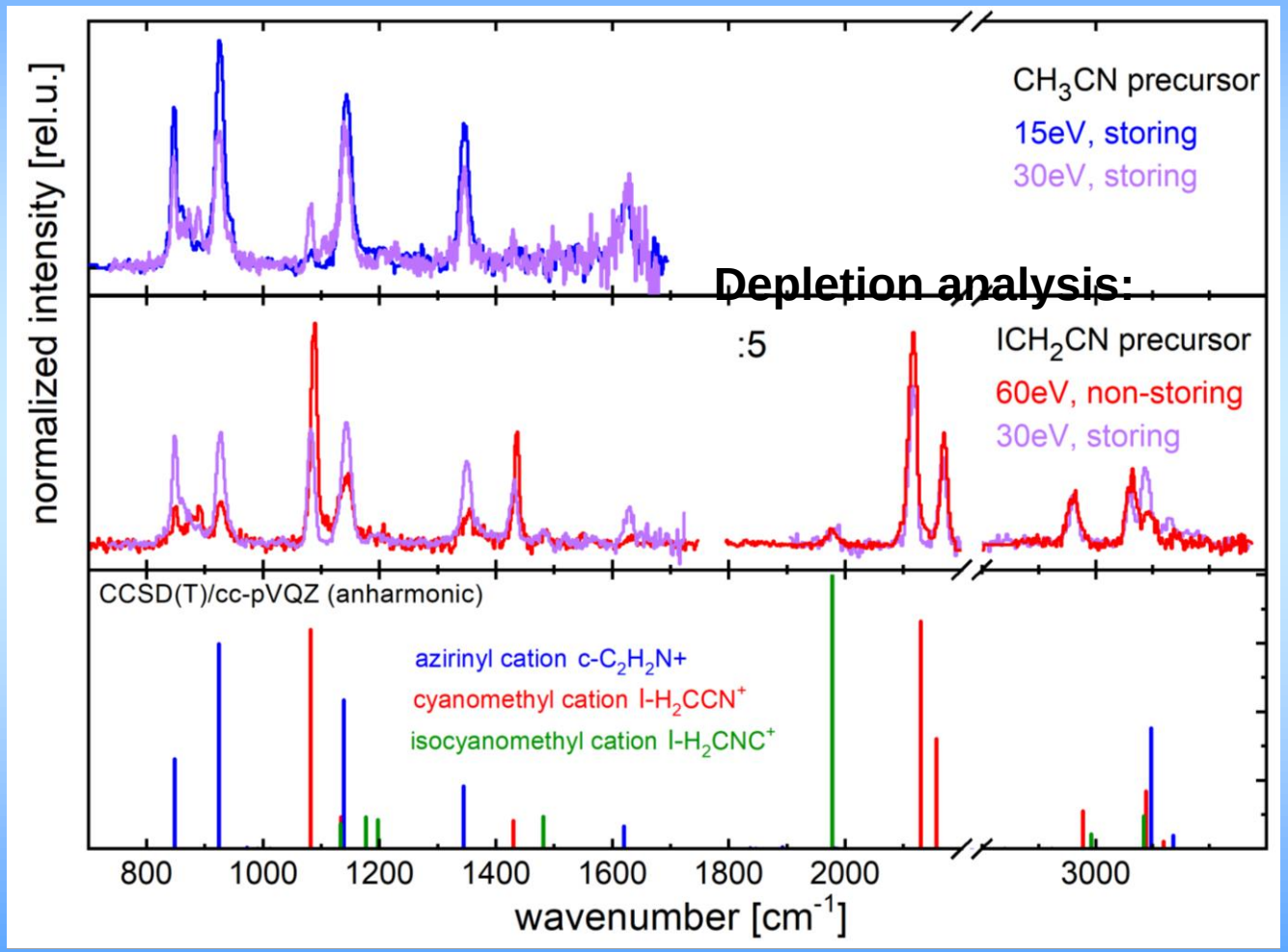
x: fraction of IR active isomer



n: number of FEL pulses
E: energy per pulse

See: *Prell et al., J. Am. Chem. Soc. 132 (2010)*
Jasik et al., J. Phys. Chem. A 119 (2015)
Jusko et al., ChemPhysChem 23 (2018)

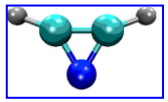
Results for CH_2CN^+

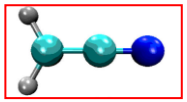


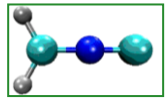
Depletion analysis:

c-CHCHN$^+$	l-H_2CCN$^+$
95(5) %	
55(5) %	30(10)%

c-CHCHN$^+$	l-H_2CCN$^+$
% 35(5)	63(3) %
% 50(3)	40(2) %







Brünken et al.

Conclusions (CH_2CN^+)

- ★ Reactions of CH_2CN^+ with acetylene can lead to larger nitrogen-containing entities.
- ★ Several barrierless reaction pathways for CH2CN+, Cyc-$C_2NH_2^+$ only leads to $C_2H_3^+$.
- ★ 1-Cyano-2-propynyl cation could act as template for build-up of larger entities
- ★ Isomerism a problem – photoionisation through synchrotron radiation can lead to selected isomeric species
- ★ Hot species probably present – ion trap and VUV photoionisation studies envisaged and partly performed

Implication for Titan's atmosphere

$CH_2CN^+ + C_2H_2 \rightarrow C_3H_3^+ + HNC$

→ Not particularly relevant, many routes to $C_3H_3^+$

$CH_2CN^+ + C_2H_2 \rightarrow CH_3^+ + HCCCN$

→ Small contribution to HCCCN formation possible

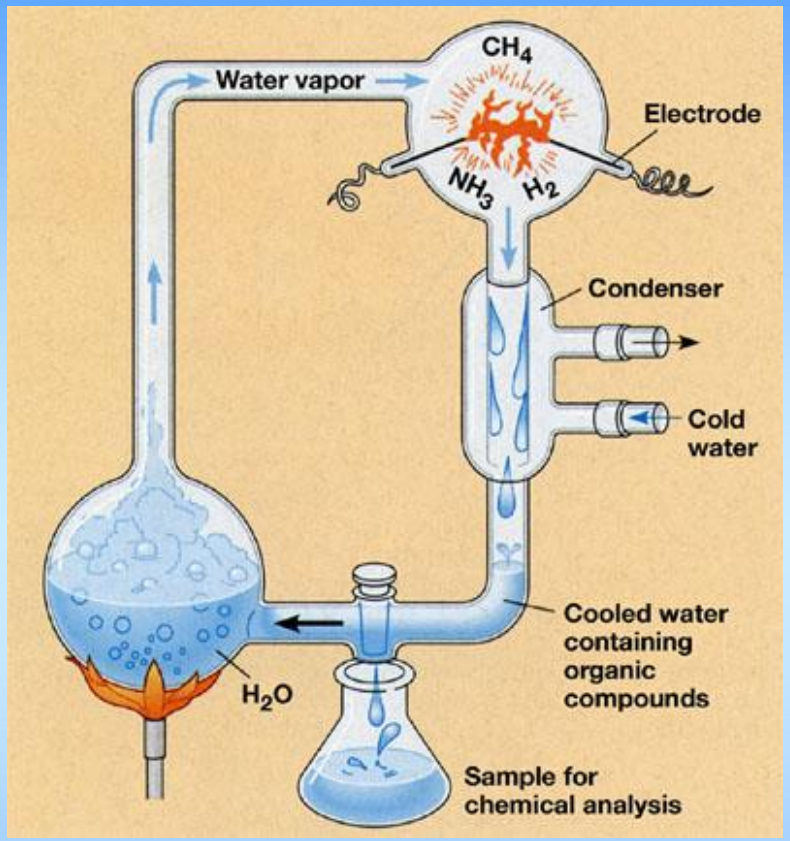
$CH_2CN^+ + C_2H_2 \rightarrow H_2C_4N^+ + H_2$

→Leads to 1-Cyano 2-propynyl ion ($HCCC(H)CN^+$)

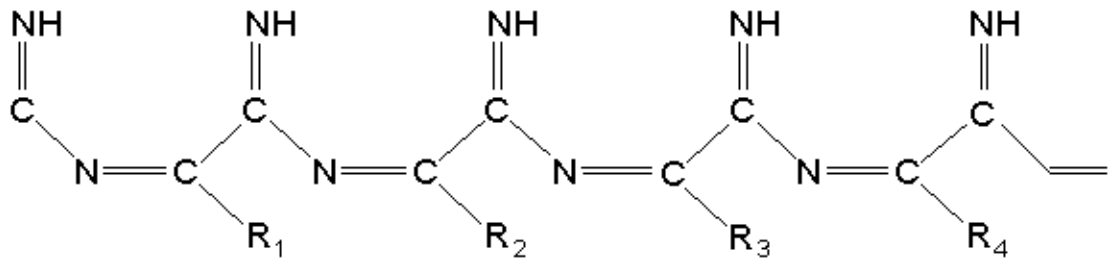
→can function as template to build heavier ions

→m/z=64 detected by INMS (not predicted in hydro-carbon models)

Relevance for atmospheres

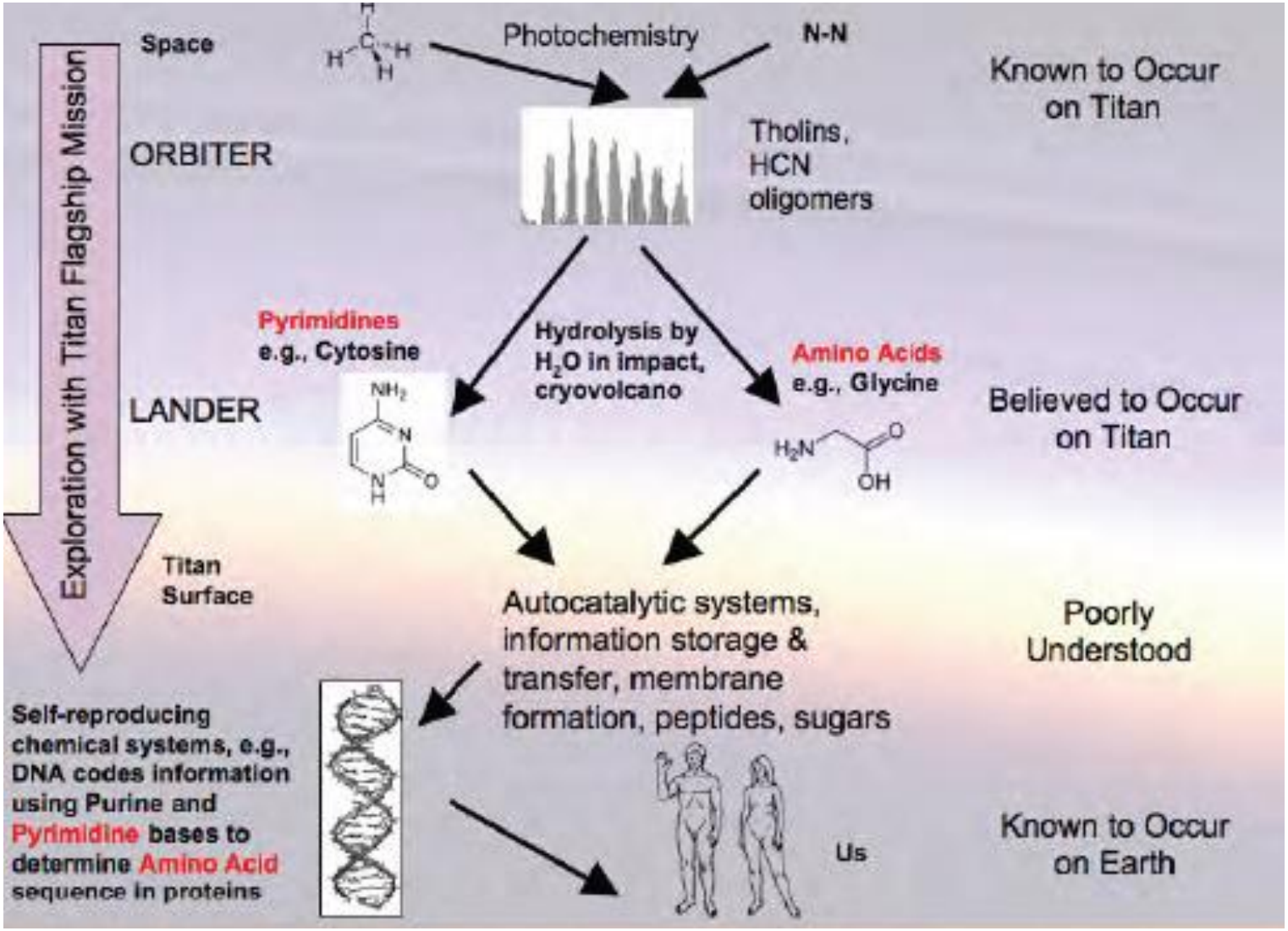


- ★ In Urey-Miller experiment amino acids formed in liquid
- ★ tholines also generated
- ★ lead to amino acids upon hydrolysis
- ★ feasible process on other celestial bodies?
- ★ happening on exoplanet ?

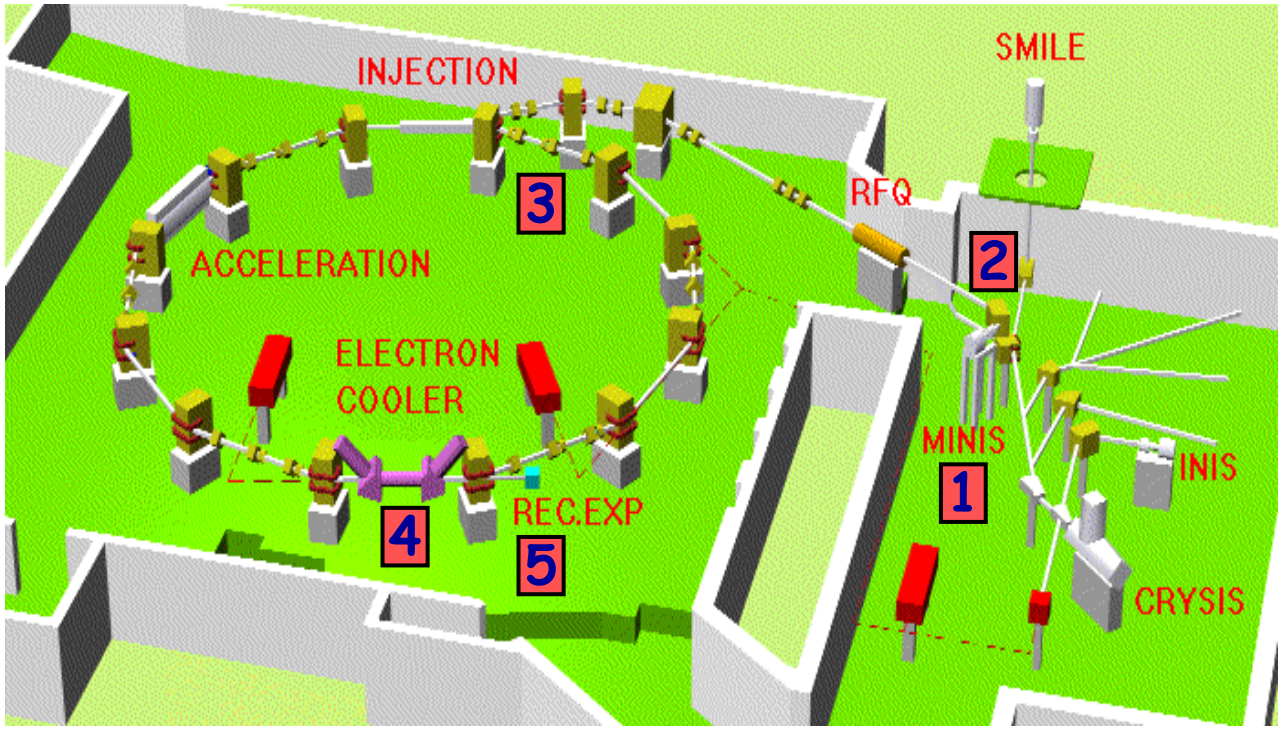


H_2O → amino acids, nucleobases

How could it go on ?



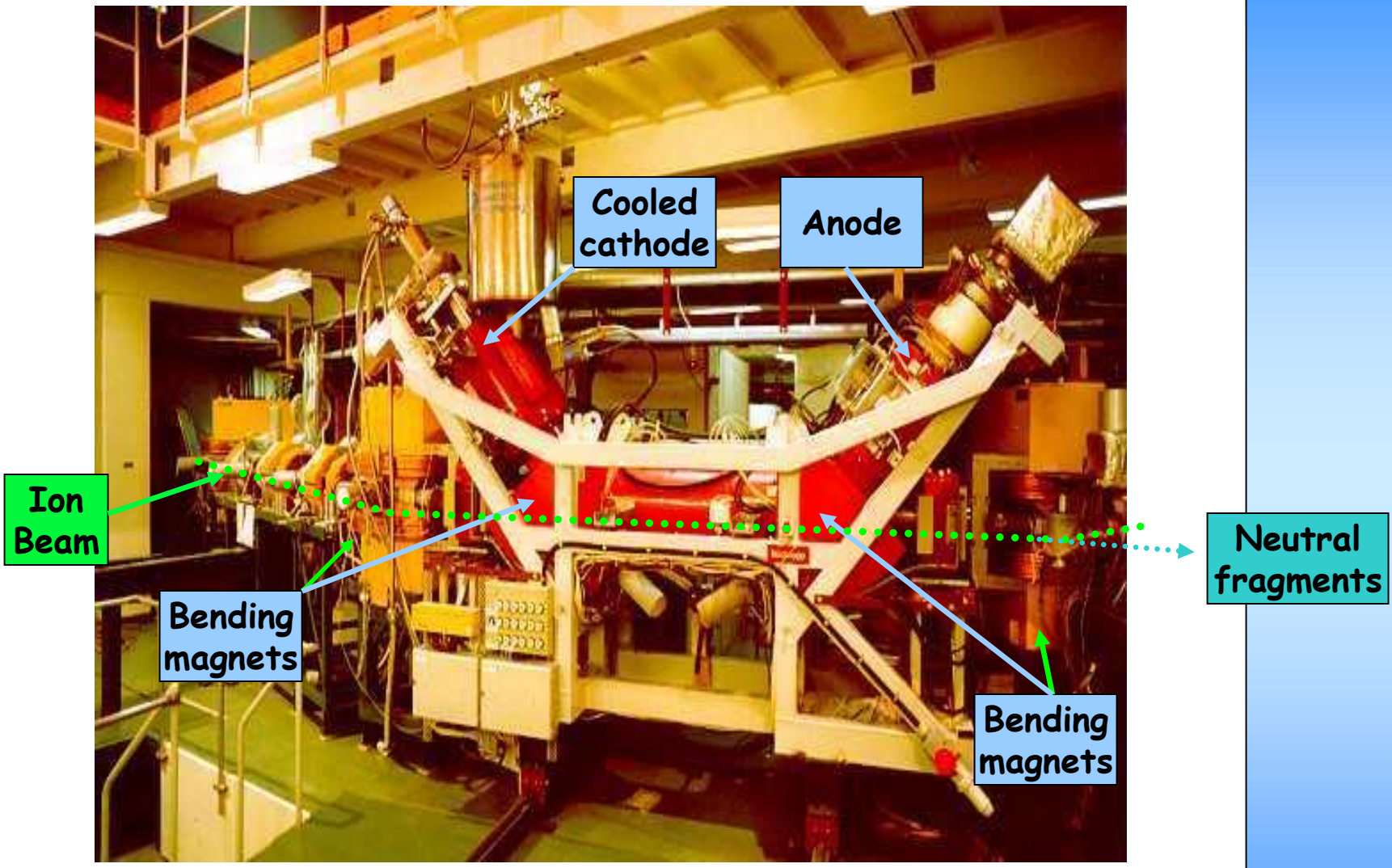
Ion-electron reaction in storage rings



Schematic view of CRYRING

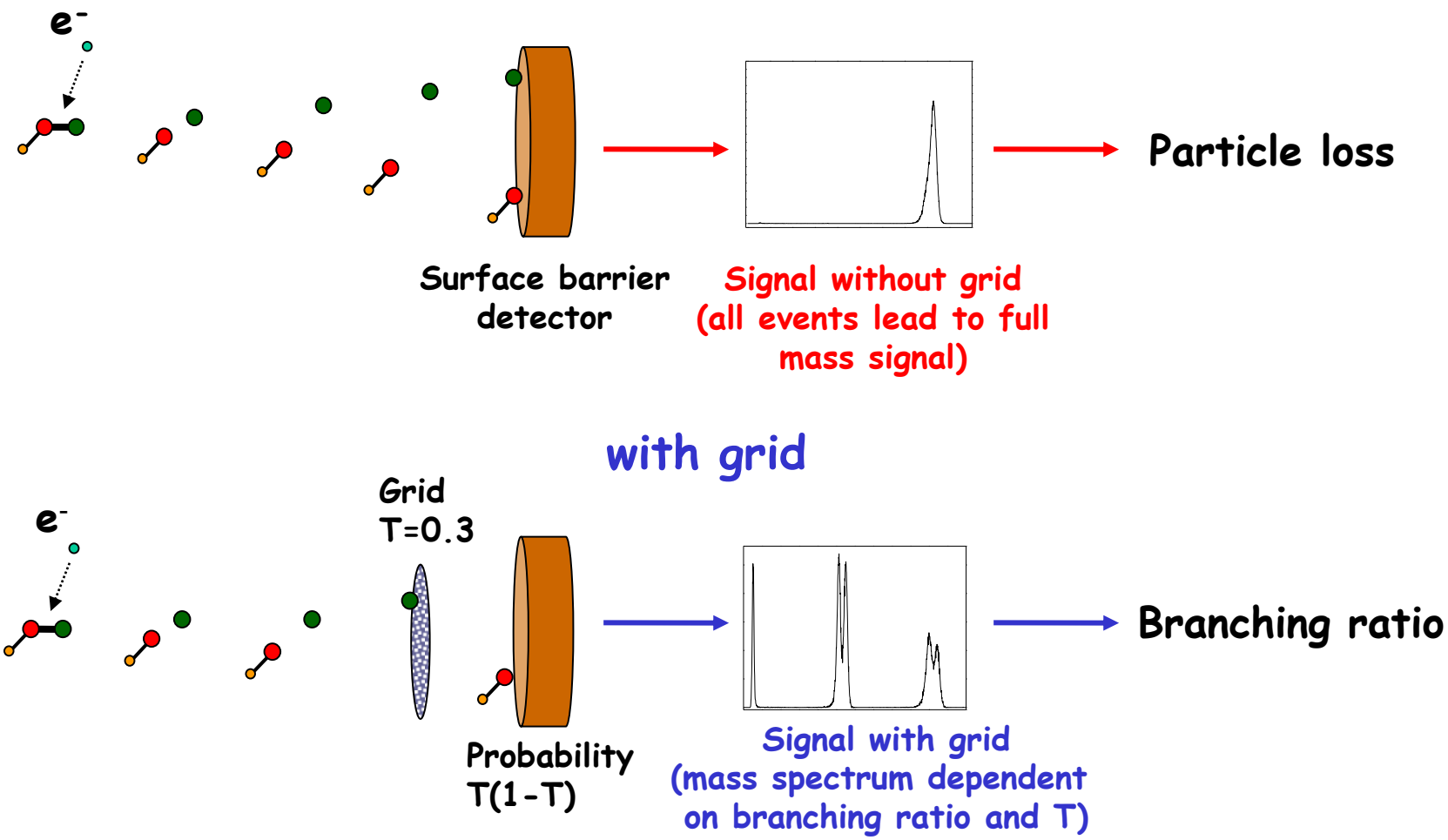
Steps during the experiment

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

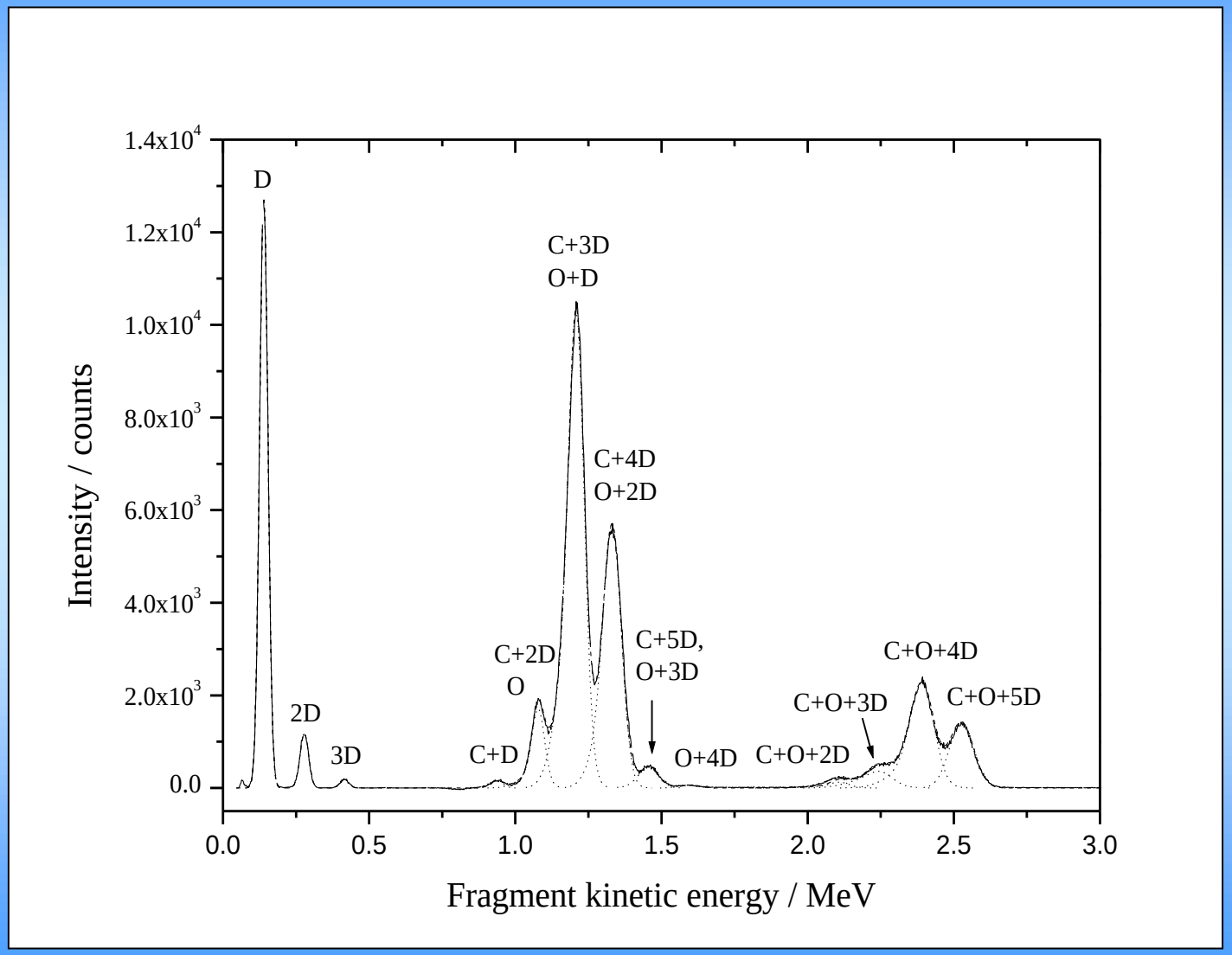


Electron cooler

Grid technique



Fragment energy spectrum

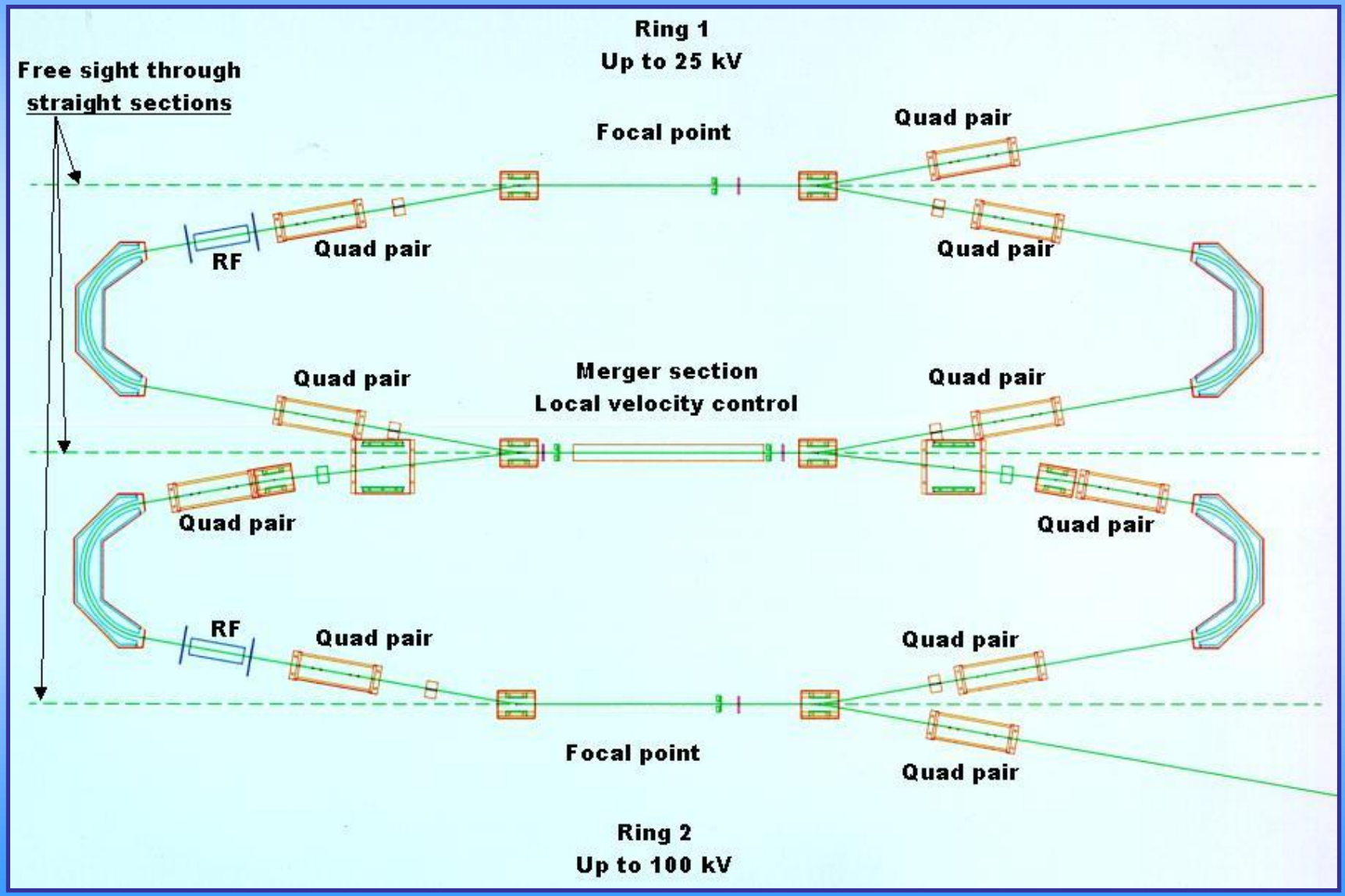


Branching ratios of the DR of $CD_3OD_2^+$ and $CH_3OH_2^+$

Reaction pathway	Branching ratio
$CD_3OD + D$	0.06
$CD_3 + D_2O$ ($CD_4 + OD$)	0.11
$CD_3O + D_2$	0.05
$CD_3 + OD + D$	0.59
$CD_2 + D_2O + D$ ($CD_4 + O + D$)	0.16
$CD + D_2O + D_2$	0.01
$CD_3O + 2D$	0.00
$CD_2O + D_2 + D$	0.02
$CD_2O + 3D$	0.00

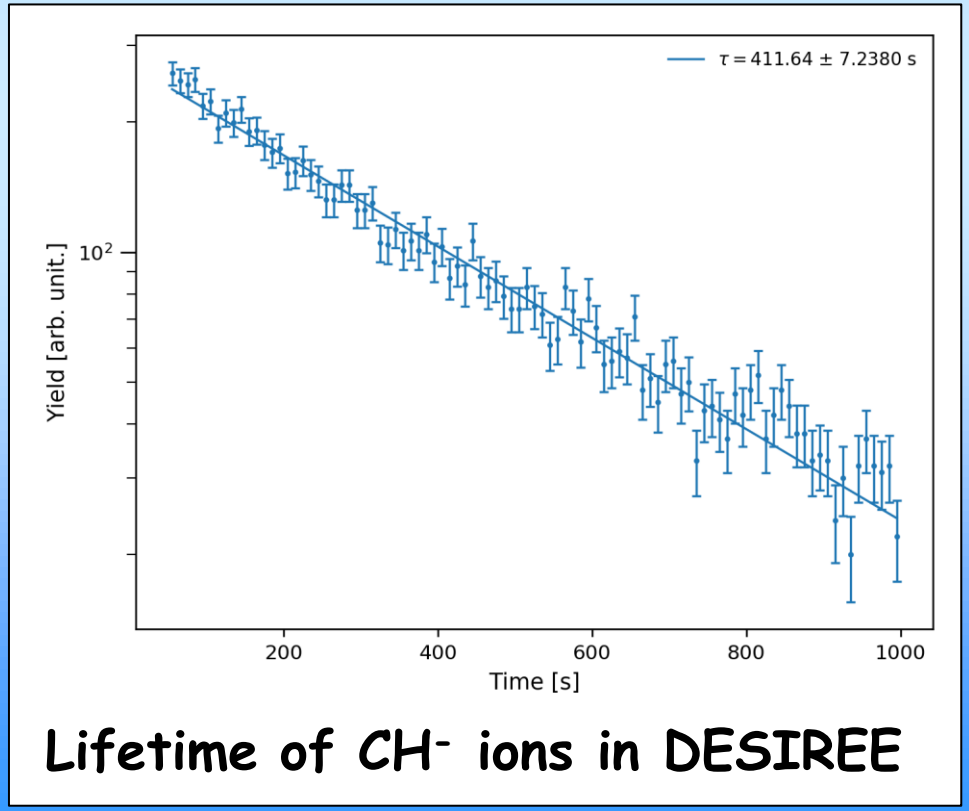
Reaction pathway	Branching ratio
$CH_3OH + H$	0.03
$CH_3 + H_2O$	0.09
$CH_4 + OH$	0.00
$CH_3O + H_2$	0.07
$CH_3 + OH + H$	0.51
$CH_2 + H_2O + H$	0.21
$CH_4 + O + H$	0.00
$CH + H_2O + H_2$	0.00
$CH_3O + 2H$	0.00
$CH_2O + H_2 + H$	0.09
$CH_2O + 3H$	0.00

Ion-ion reactions: DESIREE



Advantages of DESIREE

- Easy ion production by different sources (discharge, electrospray)
- Efficient cooling down to several K
- Very low rest gas pressures → long lifetimes of ions, can be several 100s and more
- Efficient detection of neutral products
- Lifetime measurements by repeatedly probing the stored ion beam through photodetachment by laser pulses



Lifetime of CH^- ions in DESIREE

Neutral-neutral reactions: Measurements in condensed phase

+ High density of probe species

+ Thermal equilibrium with environment

- Third body processes important

- Radicals and most ions rapidly destroyed in most environments.

- Conditions largely irrelevant for interstellar medium.

Measurement of kinetics: Adiabatic expansion

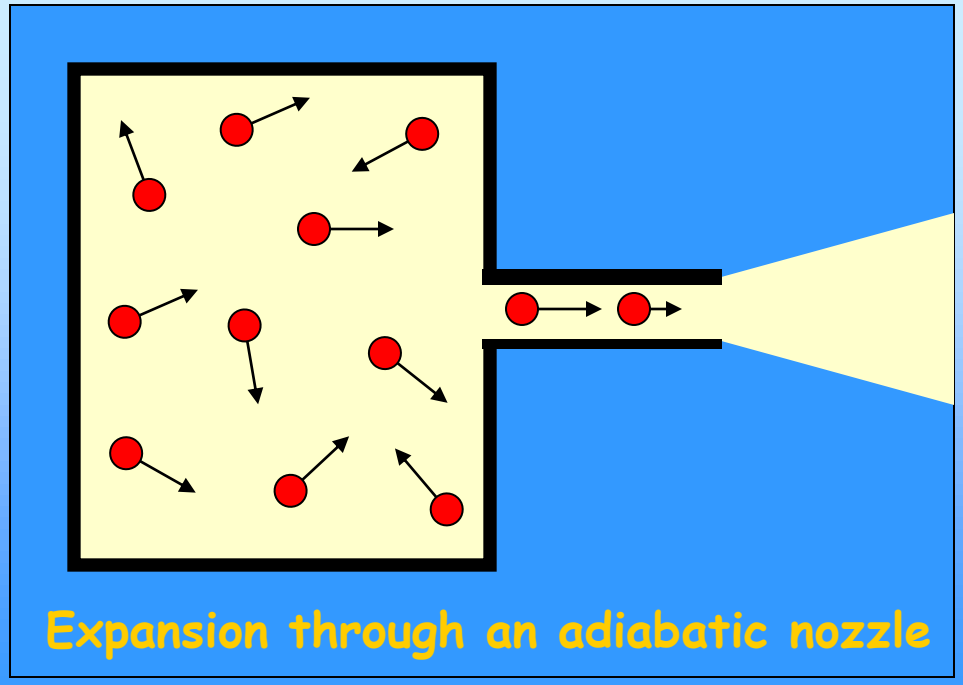
- Expansion through nozzle into vacuum

- No heat transfer from gas to environment → adiabatic process

- In real (imperfect) gases cooling with expansion (intermolecular forces)

- Particles with low transversal and high longitudinal cooling

- Additionally, longitudinal (in direction of expansion) uniforming of velocity through collisions in the orifice.

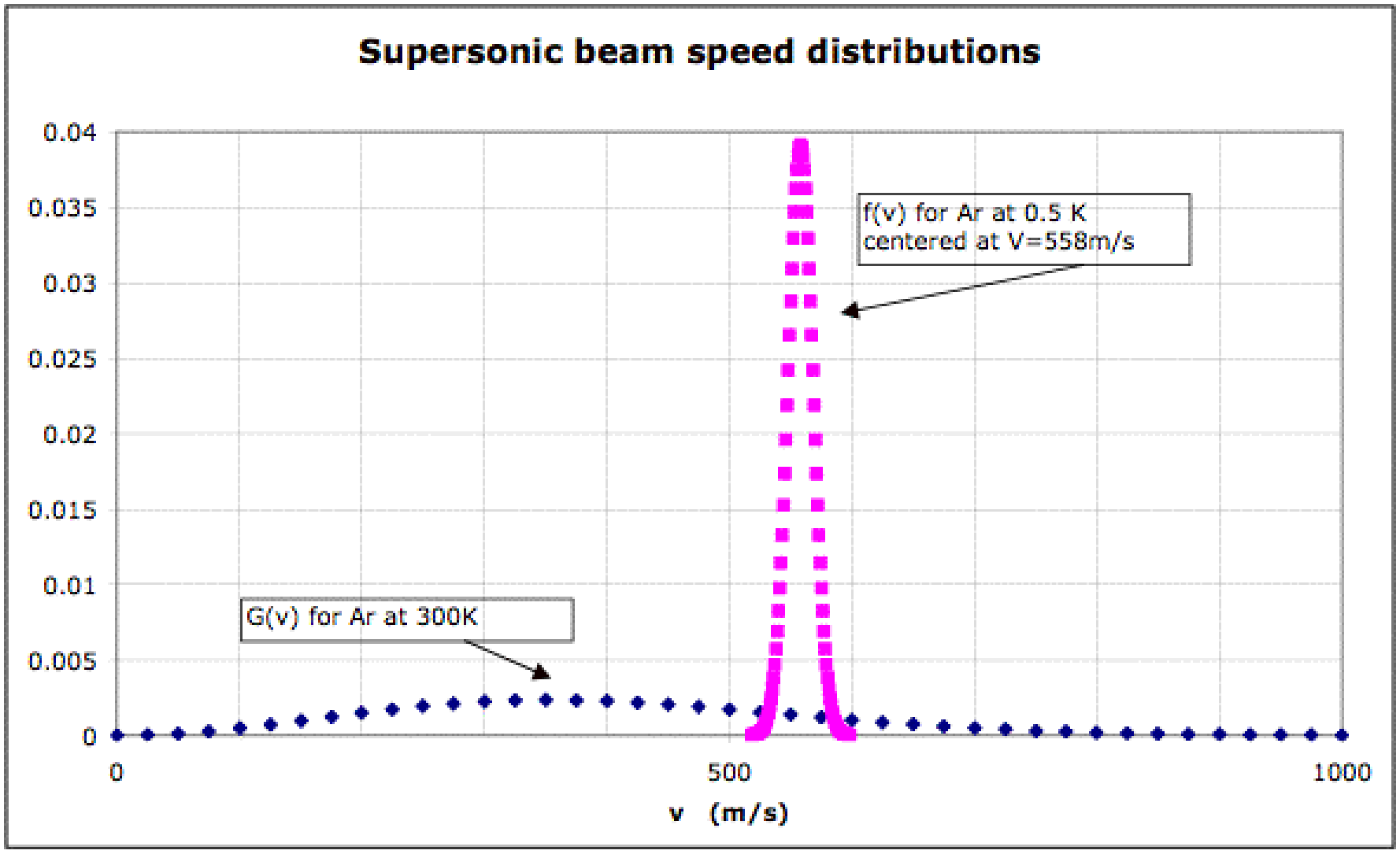


Expansion through an adiabatic nozzle



Cloud formation through adiabatic cooling

Non-supersonic and supersonic velocity distribution



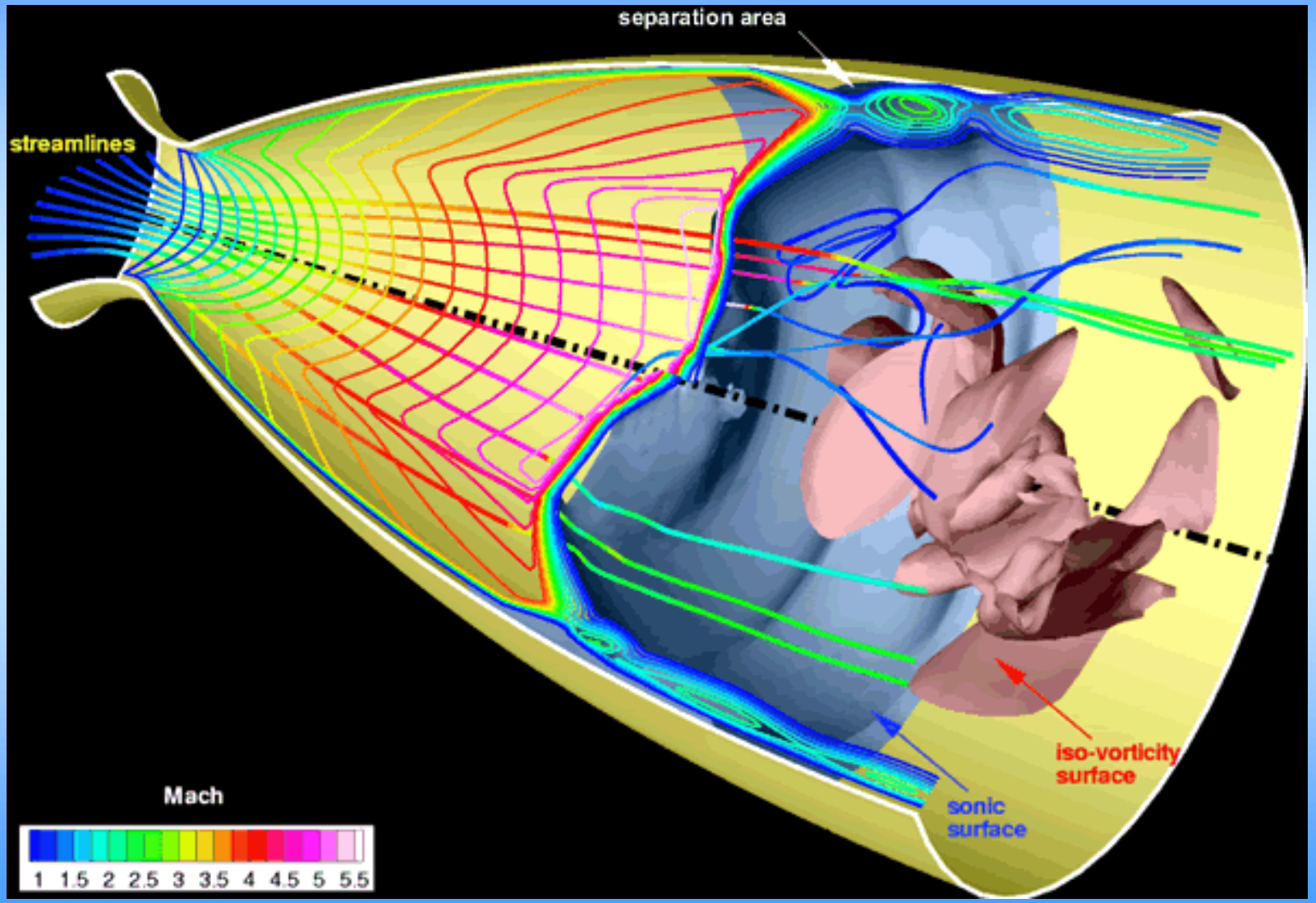
Energy in supersonic beams

Translational energy: continuum of energies, cooling through collisions very efficient.
T (translation) = several K

Rotational energy: energy quanta, cooling through collisions fairly efficient. T (rotation) = 30-90 K

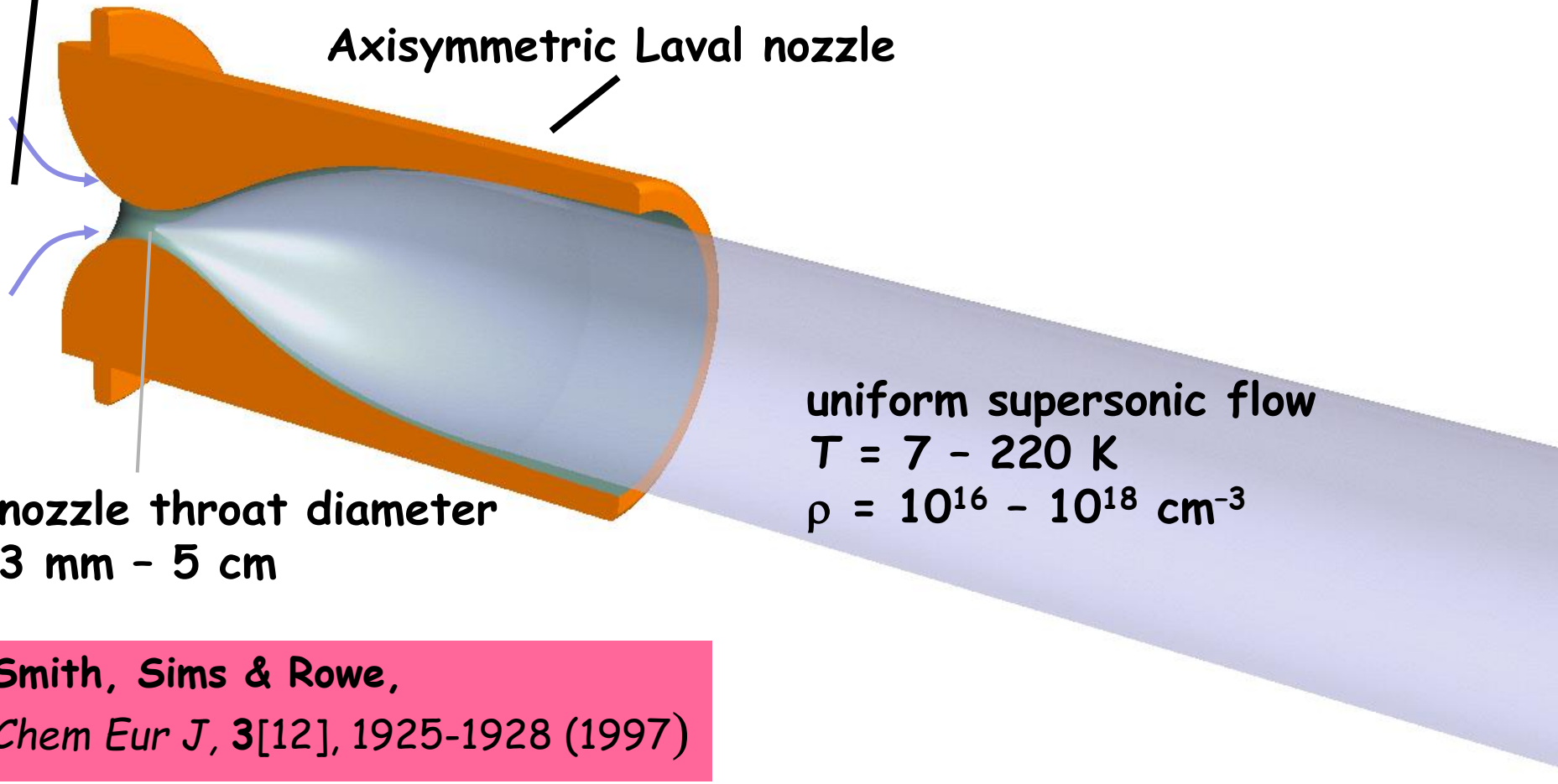
Vibrational energy: energy quanta, cooling through collisions very inefficient.
T (vibration) > 100 K

Supersonic velocities



50-100 l/min carrier gas (He, Ar) + reagent + precursor

chamber pressure 0.1 – 0.25 mbar
max pumping speed ~ 30000 $m^3\ h^{-1}$



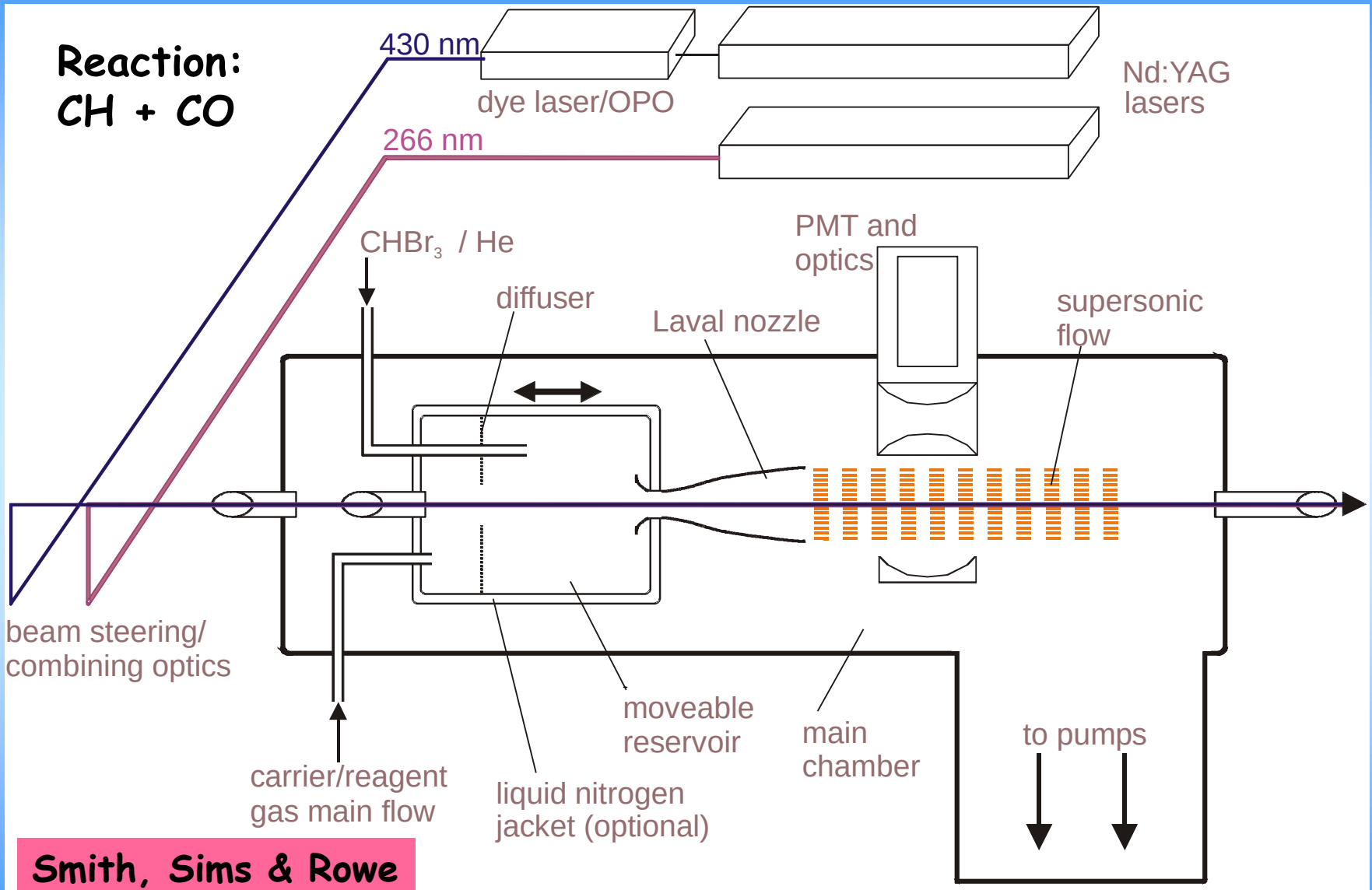
Smith, Sims & Rowe,
Chem Eur J, **3**[12], 1925-1928 (1997)

Laval nozzle and isentropic flow

CRESU technique

- French acronym for Cinétique de Réaction en Ecoulement Supersonique Uniforme.
- ultra-low temperature environment in thermal equilibrium, temperatures 7 - 200 K dependent on nozzle
- supersonic uniform (Mach no, temperature and density) flow
- ultra-cold wall-less reaction vessel
- cooling rapid without condensation
- very strong pumps and loads of gases needed
- different nozzle for each temperature

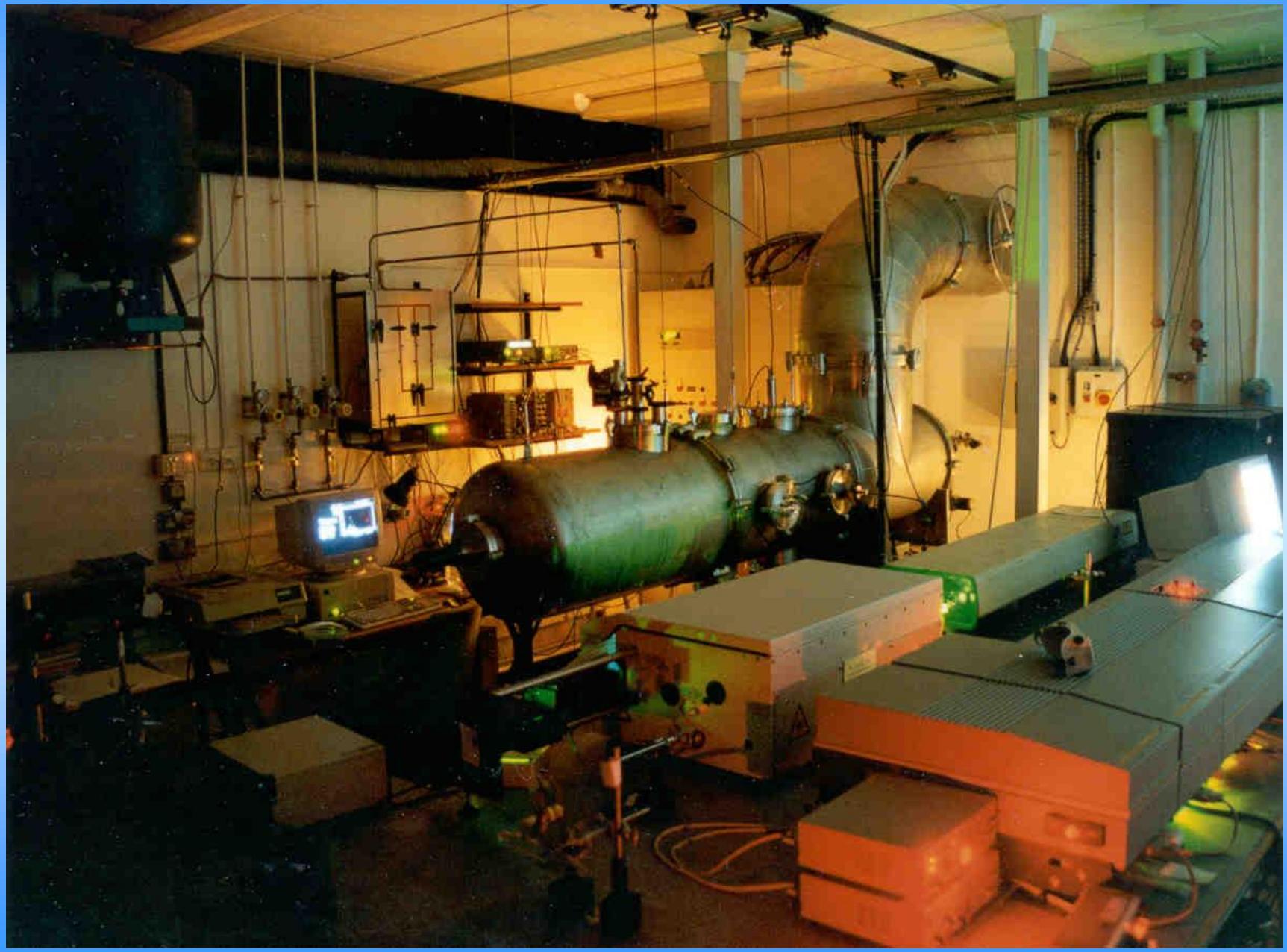
Schematic of the CRESU apparatus



Smith, Sims & Rowe

Schematic diagram of combined PLP-LIF / CRESU apparatus

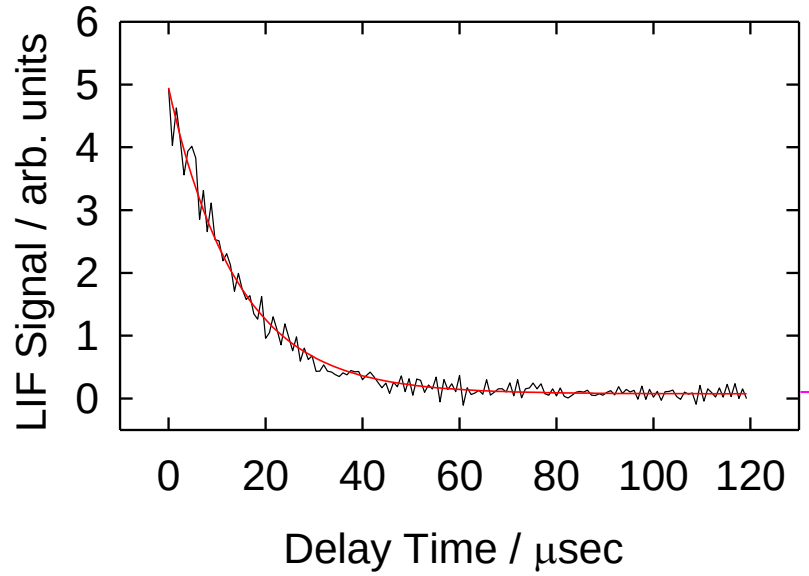
CRESU apparatus

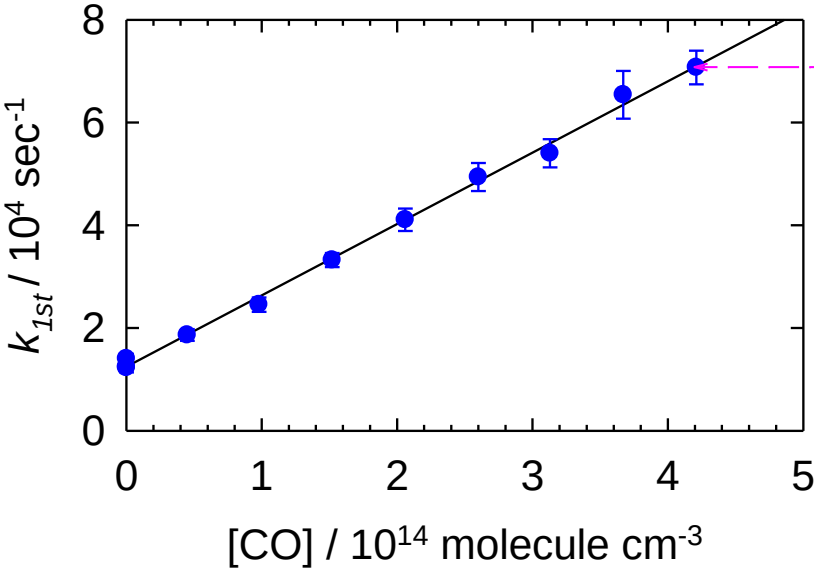


Vacuum pumps (16 000 ls^{-1})





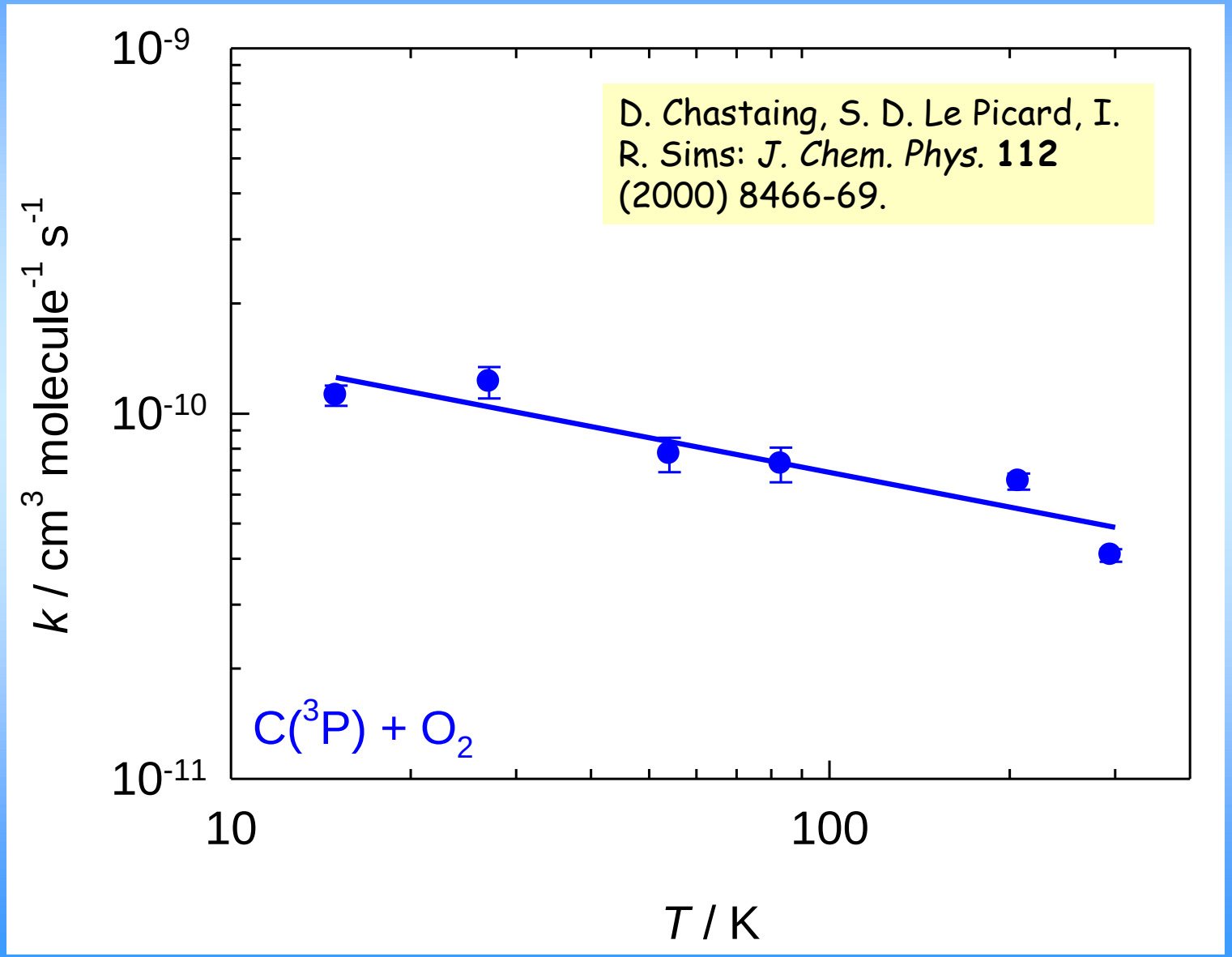




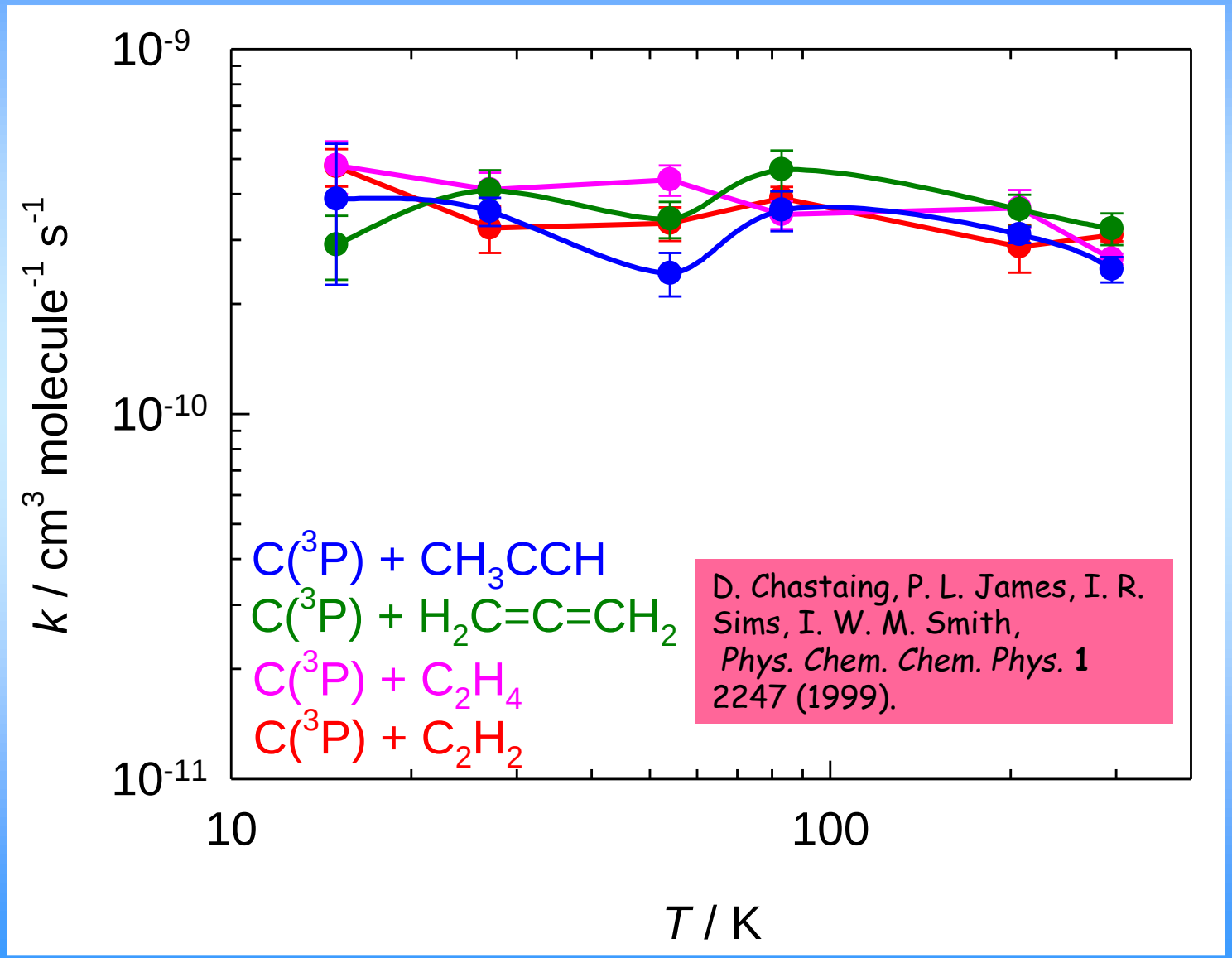
First-order decay of LIF signal from CH(v=1) in the presence of 4.2 × 10^{14} molecule cm^{-3} of CO at 44 K in Ar, fitted to a single exponential decay

Pseudo-first order decay constants for CH(v=1) at 44 K in Ar plotted against the concentration of CO.

$C + O_2 \rightarrow CO + O$



Reactions of carbon(^{3}P) with hydrocarbons



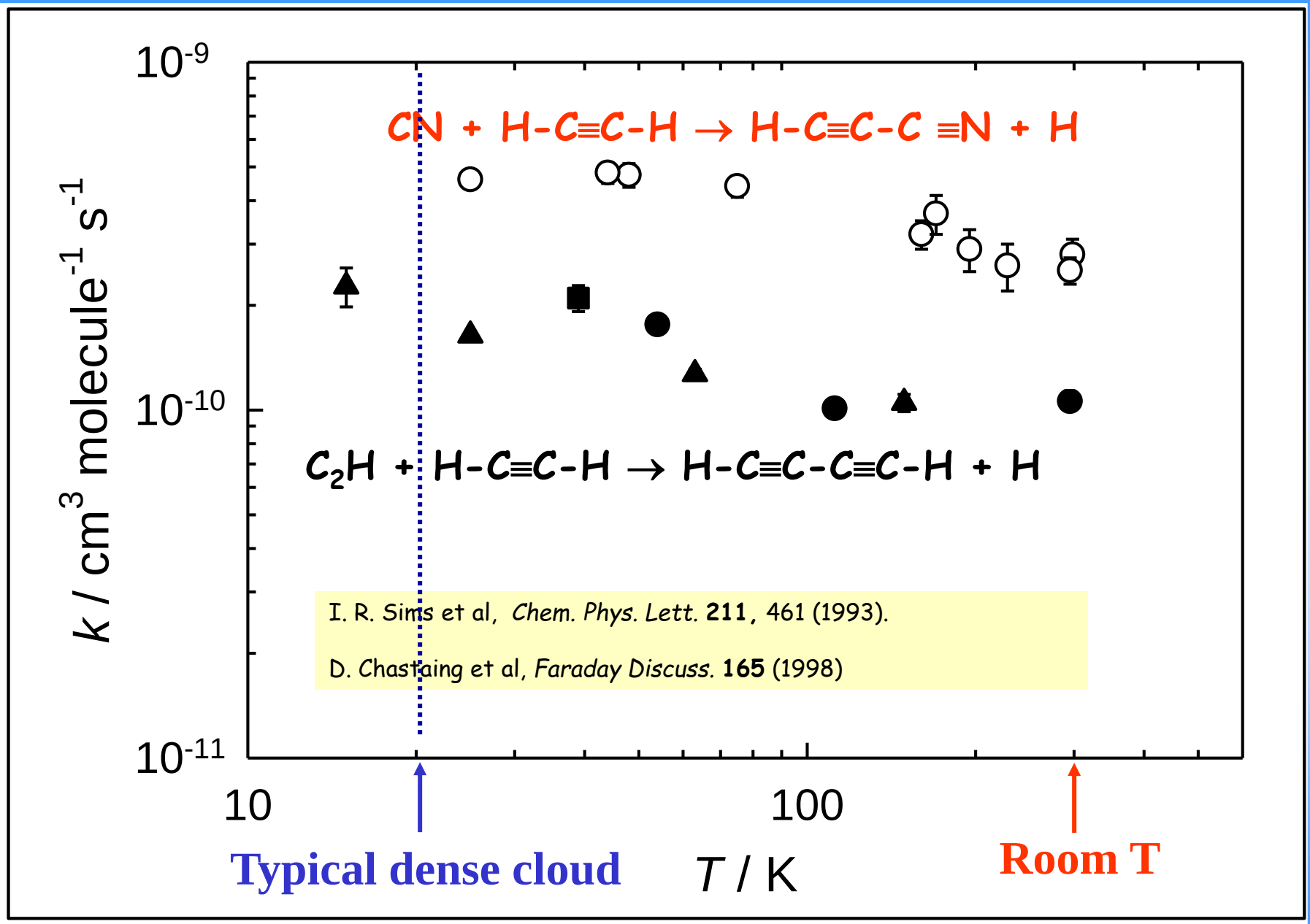
Formation of cyanopolyynes

- Cyanopolyynes ($HC_{2x}CN$) are important intermediates in building large carbon chains.

- Can be formed as follows:

$$HC_{2x}H + CN \rightarrow HC_{2x}CN + H$$

- Reaction $HC_{2x}H + C_2H \rightarrow HC_{2x+2}H + H$ very fast at low T CN isoelectronic with C_2H.


CN + H-C≡C-H → H-C≡C-C ≡N + H
C2H + H-C≡C-H → H-C≡C-C≡C-H + H
k / cm3 molecule-1 s-1
10-9
10-10
10-11
10
100
T / K
Typical dense cloud
Room T
I. R. Sims et al, Chem. Phys. Lett. 211, 461 (1993).
D. Chastaing et al, Faraday Discuss. 165 (1998)

Conclusions

- ★ Ion and radical reactions have great impact on the chemistryof planetary ionospheres, interstellar clouds and circumstellar envelopes
- ★ Many different formation and destruction processes of ions exist
- ★ More and more complex molecules detected in space: ion- and radical induced reactions may play an important role in their formation
- ★ Molecular data on many ion reactions still lacking.
- ★ New experimental facilities (supersonic beams and flows, electrostatic storage rings, magnetoelectodynamic traps, ion traps) will enable research into these processes.