Ion reactions as pathways to complex molecules in space and atmospheres

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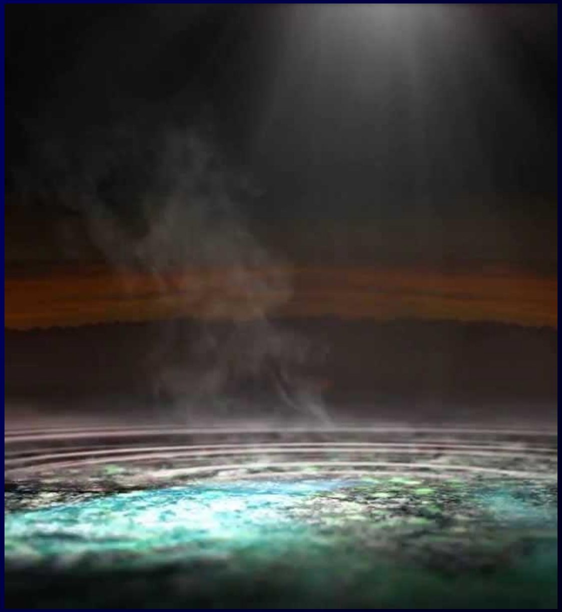
Complex organic molecules

How do they come to Earth?

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

Protoplanetär skiva

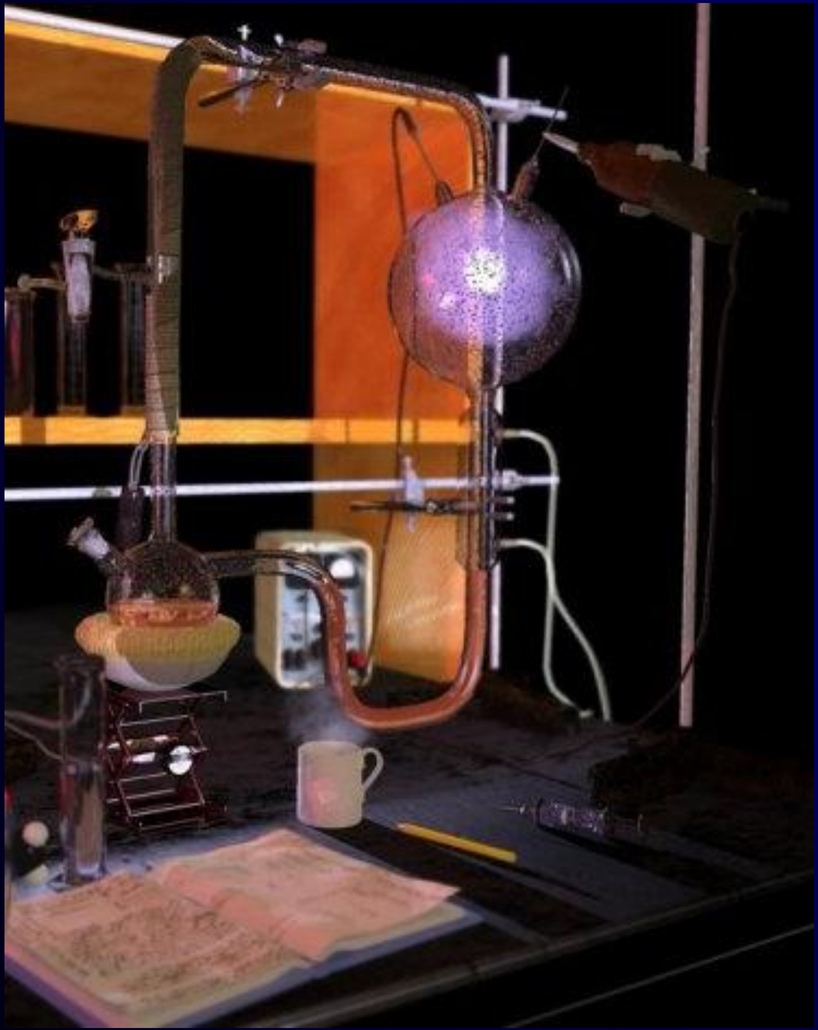
Comet Hale-Bopp

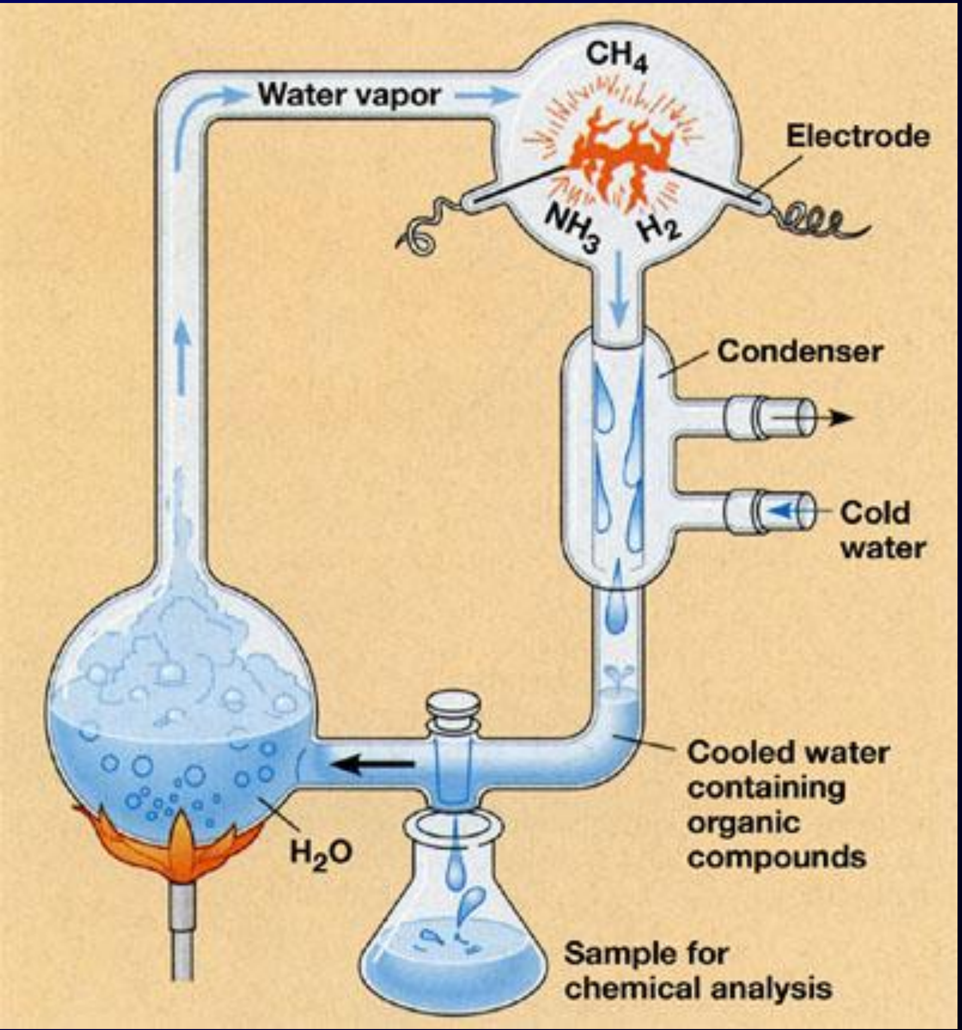


Primeval soup

Urey-Miller experiment

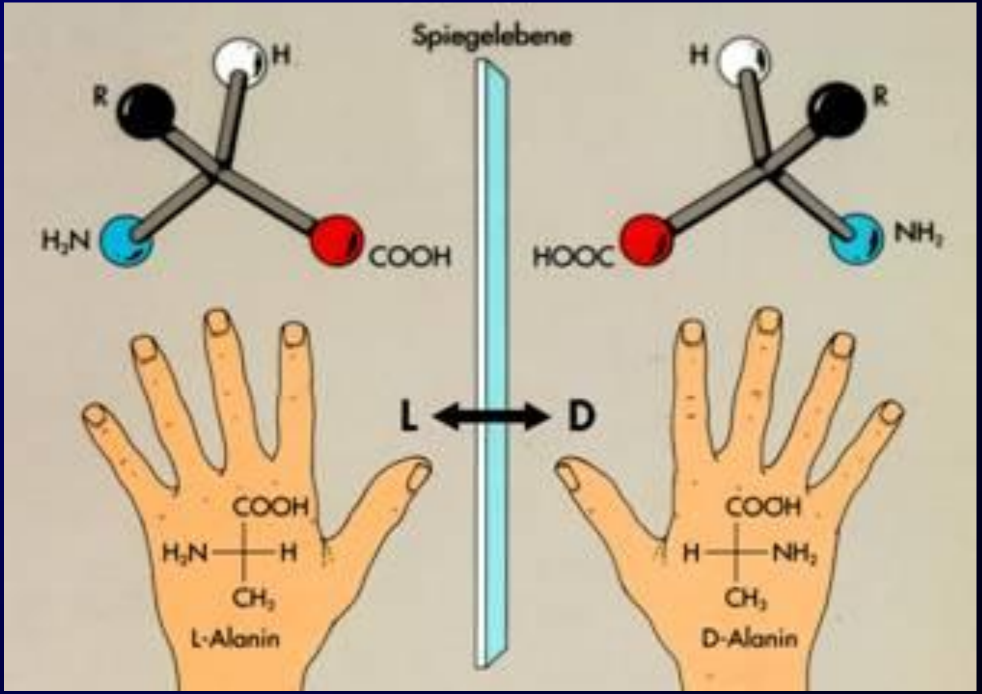
- Gas mixture resembling Jupiter's atmosphere CH_4, NH_3, H_2
- Elektrical discharge, formation of aminoacids and nucleobases





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)

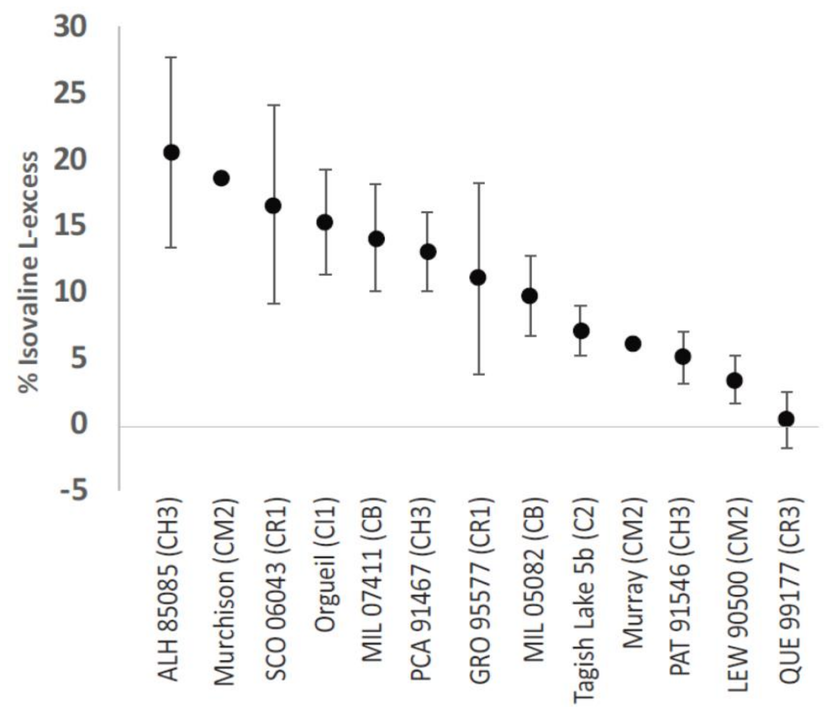


Biomolecules from space?

- 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

Murchison



Isovaline Enantiomeric excess

Where and how are they formed?

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

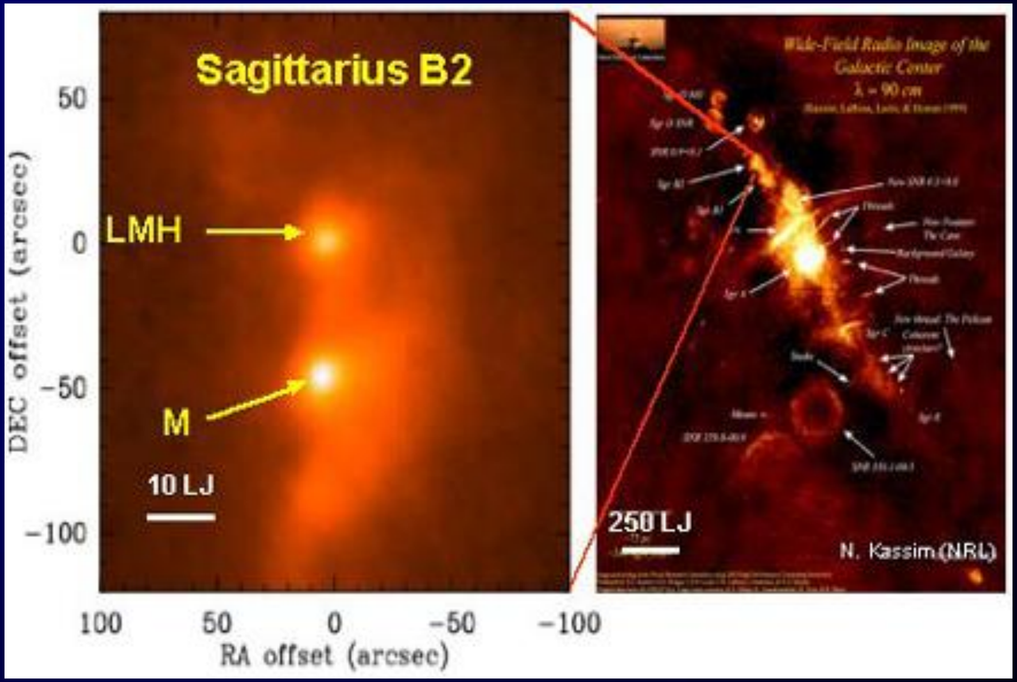
- Aminoacetonitrile in "Large Molecule Heimat" in Sagittarius B at the galactic centre (Belloche et al. 2008)

- 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



Important interstellar and ionospheric ion processes

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

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

Ion-electron reactions

for molecules as good as exclusively dissociative recombination

$$HeH^+ \quad + \quad e^- \quad \rightarrow He \quad + \quad H$$

Ion-ion reactions

mutual neutralisation

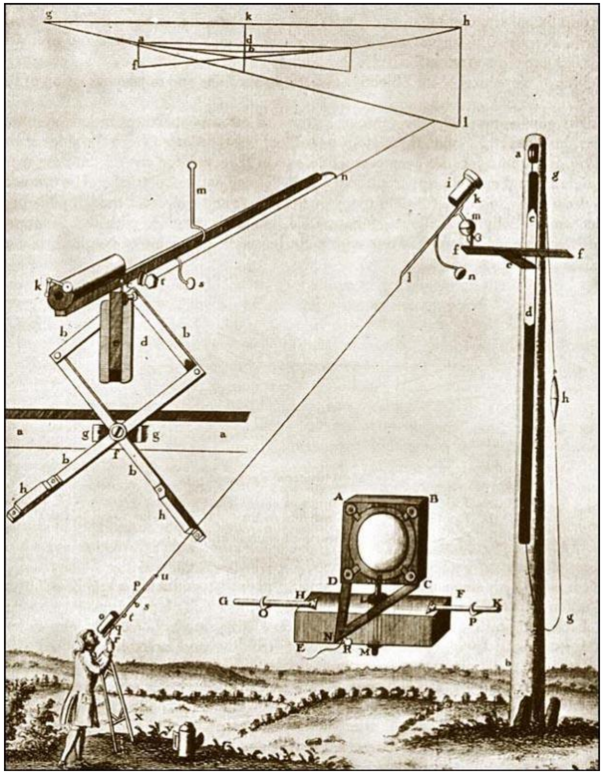
$$C^+ \quad + \quad C_4H^- \quad \rightarrow CH \quad + \quad C_4$$

Reactions in ionospheres

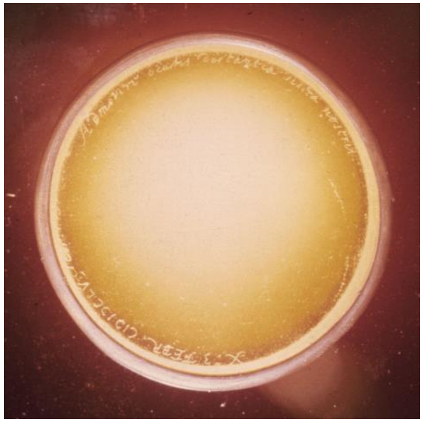
- Ionic reactions common in higher layers of ionospheres
- Similar to interstellar conditions: low densities and temperatures
- Chemistry bears resemblances to interstellar one

Titan

- discovered by Christiaan Huygens 1655
- one of Saturn's >80 confirmed satellites

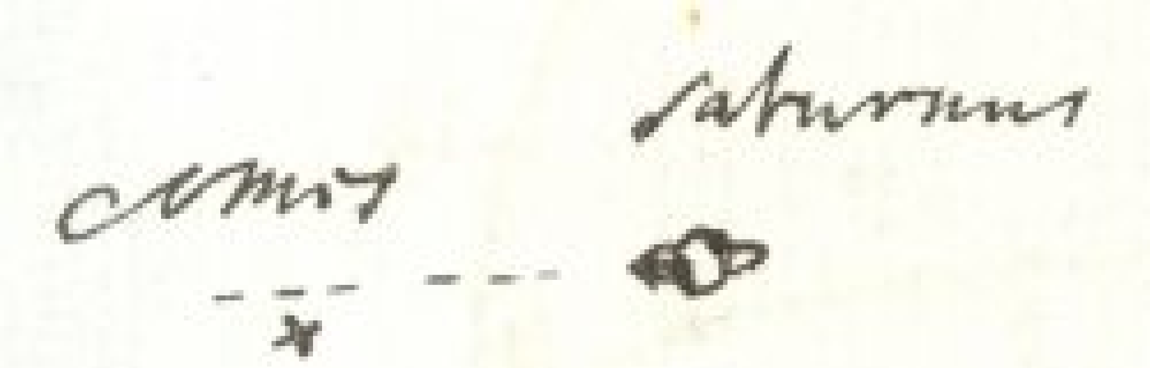


Telescope constructed by Huygens



Lens used by Huygens

Christiaan Huygens (1629-1695)



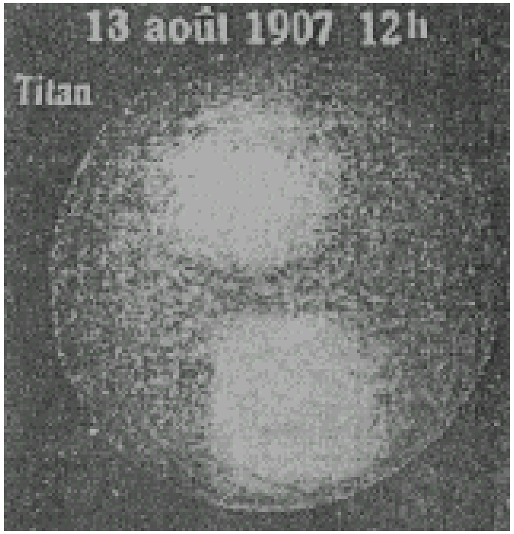
"De Saturni luna observatio nova"

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
7. Jupiter III
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

Generation of radicals and ions in Titan's ionosphere

Magnetospheric electrons

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

Long-lived excited state

$CH_4 + e^- \rightarrow CH_3^+ + H + 2e^-$

$CH_4 + e^- \rightarrow CH_4^+ + 2e^-$

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

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

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

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

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

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

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

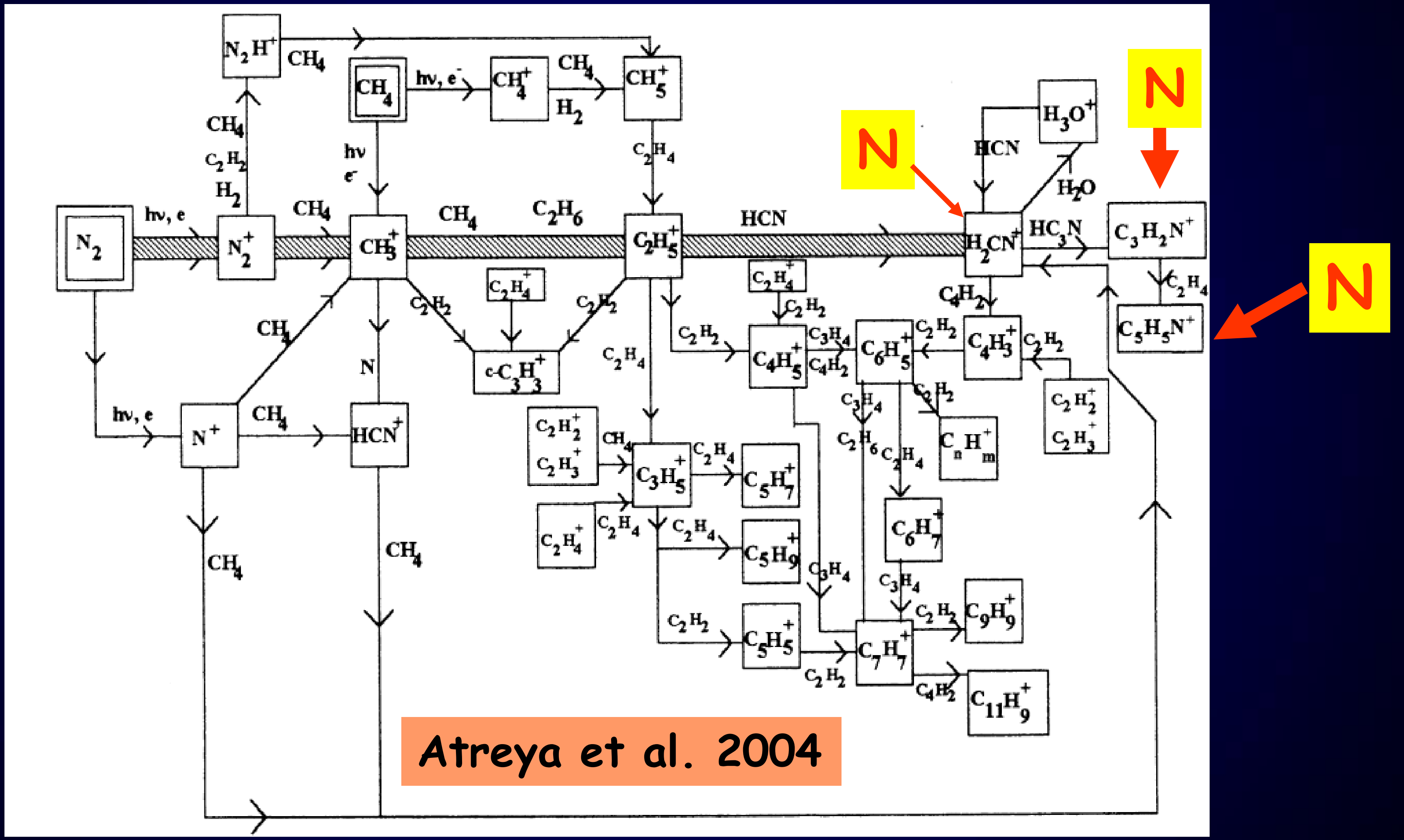
Radical-neutral reactions

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

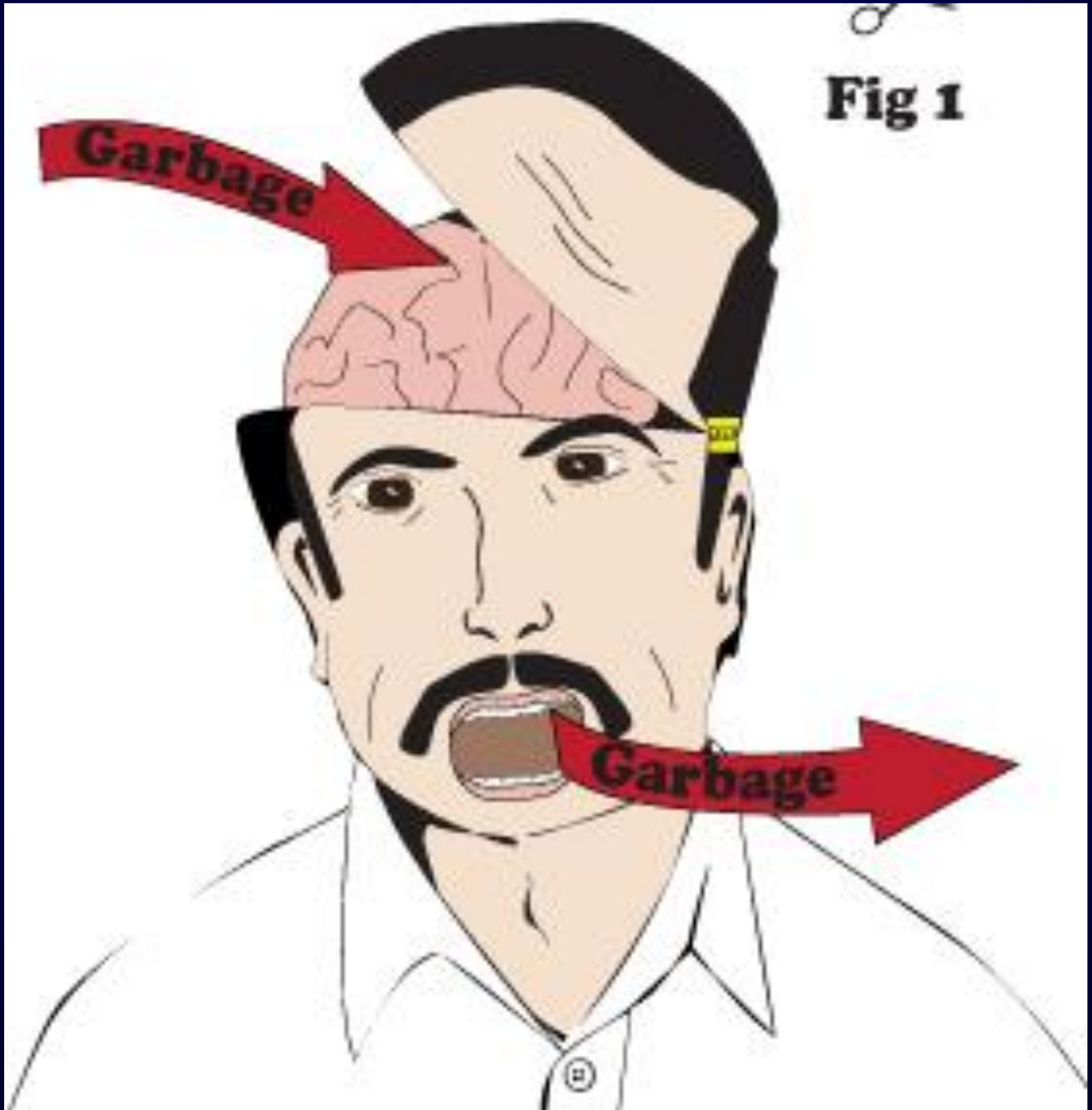
Rate constants and product branching ratios often unknown !

Models of Titan's ionosphere

Old models: mostly protonated hydrocarbons formed



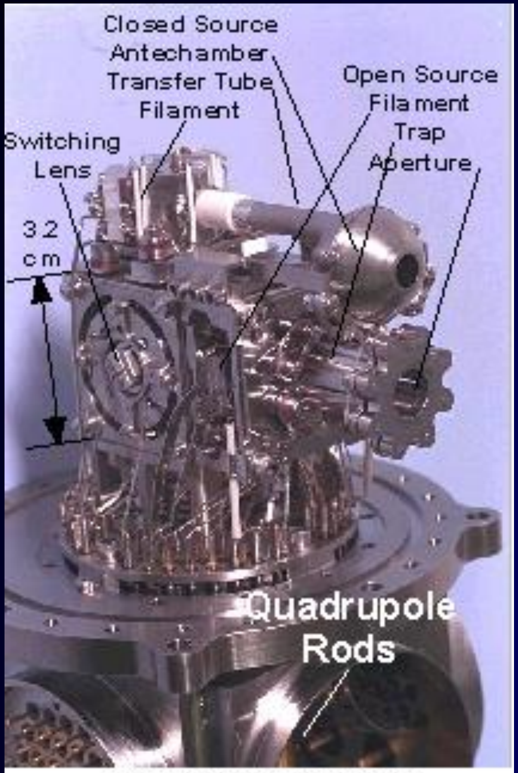
GIGO principle for models of Titan's ionosphere



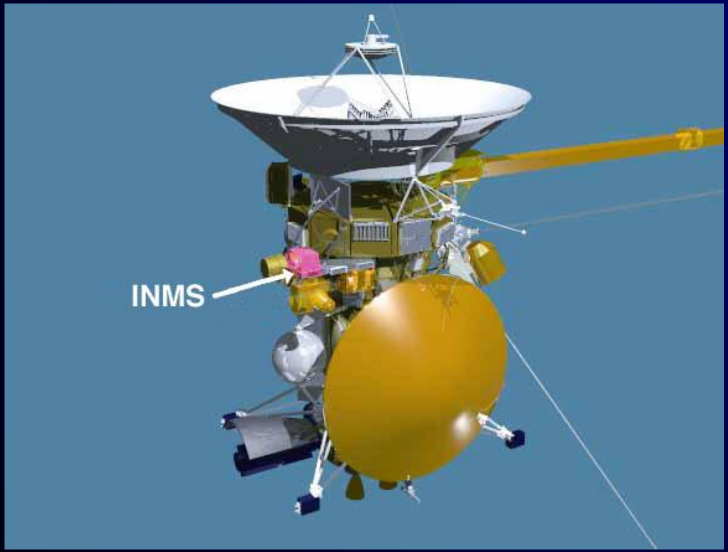
Ion-Neutral Mass Spectrometer (INMS) on board of Cassini

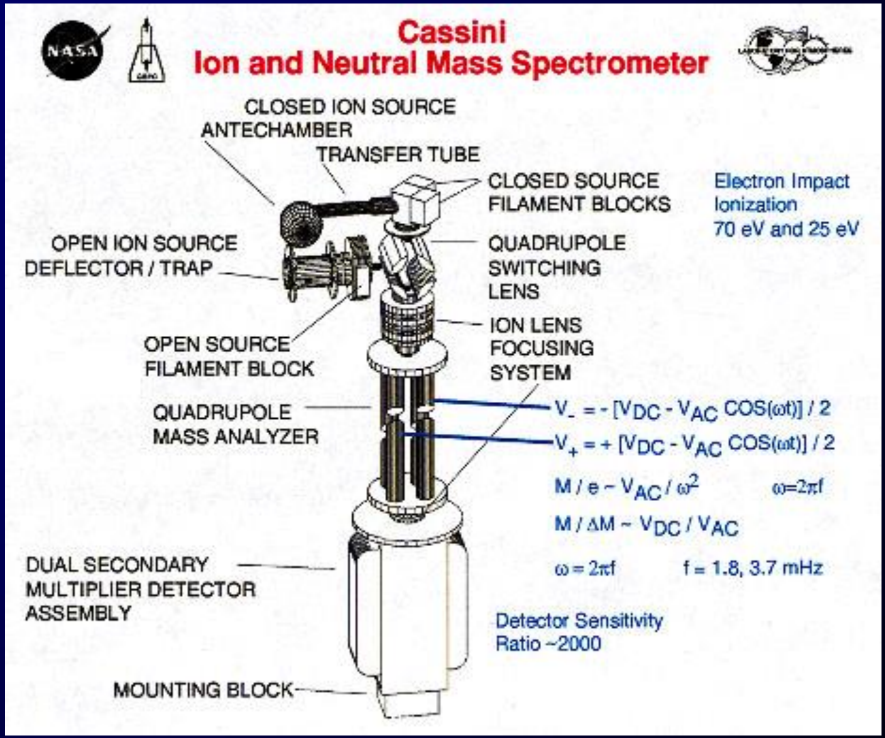
2 operating modes:

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

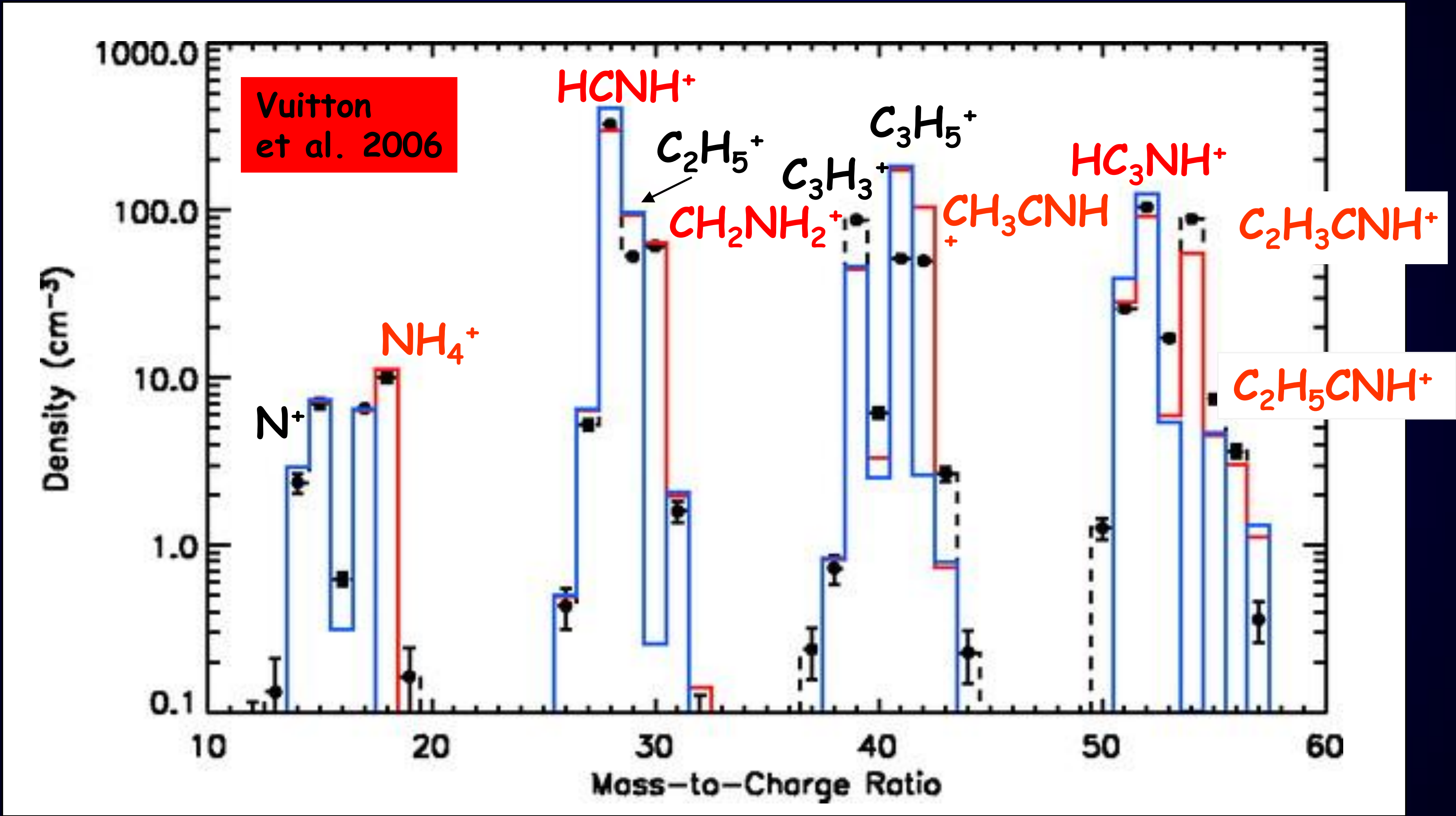


Dual inlet gas/ion source





INMS results in open mode



Blue line = fit without including new ions

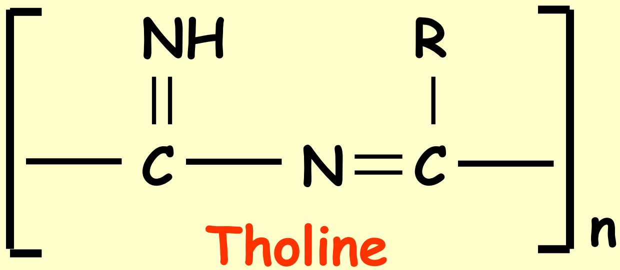
Red line = fit including N-species, black dots data from Cassini

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 →



Tholine

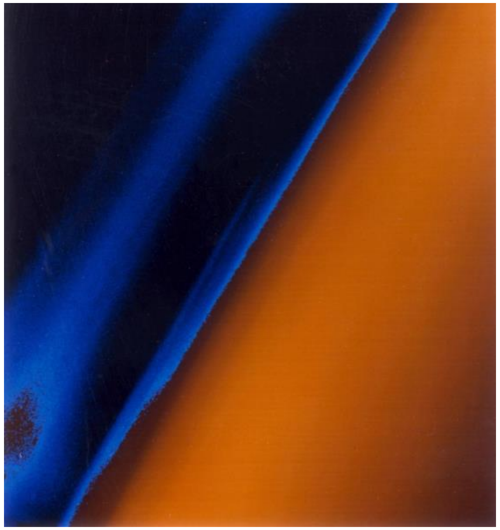
- ★ Chemically inert: Destroyed mainly by protonation and dissociative recombination

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

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

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

- ★ Possible exception: CH_2CN+

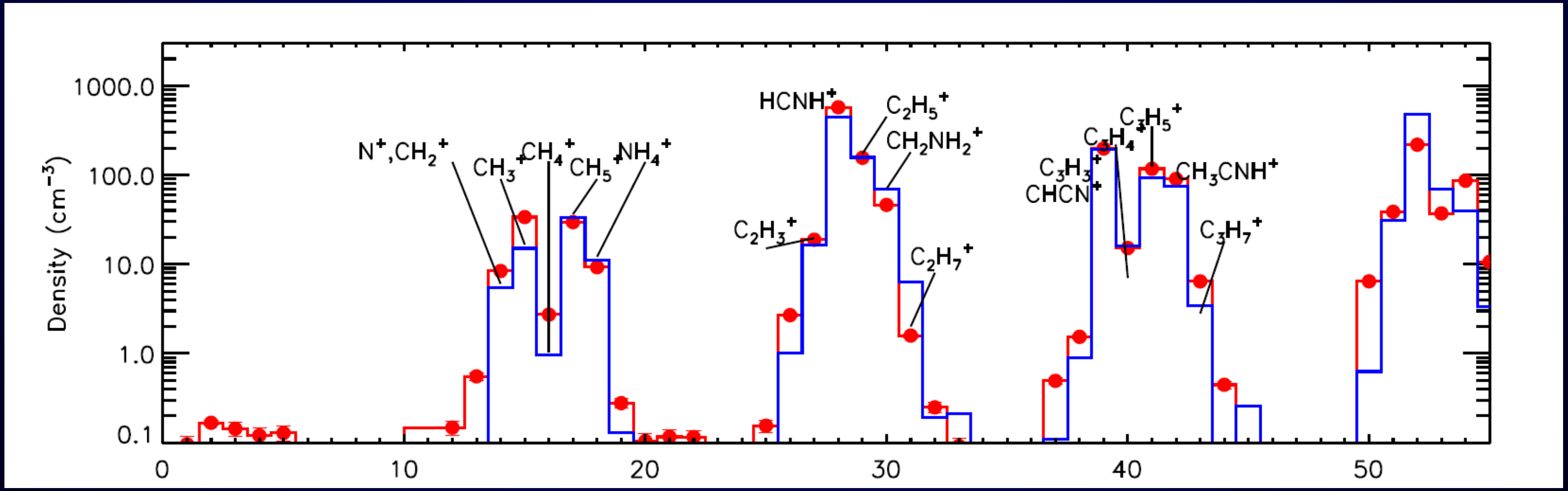


Titan's haze layer

Tholine from the lab

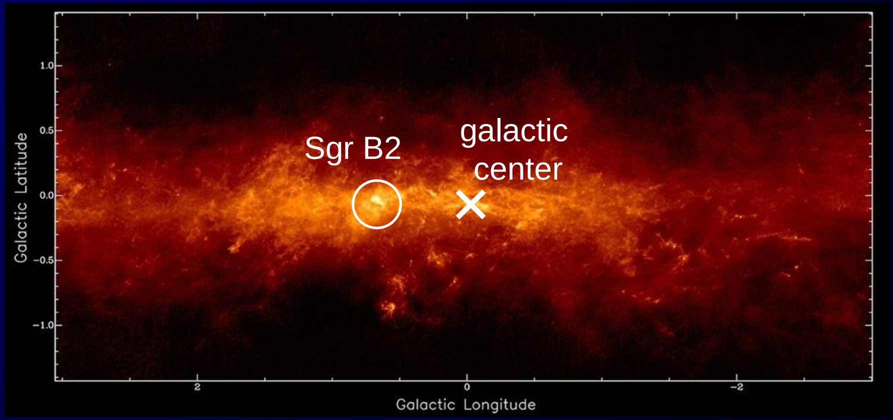
CH_2CN^+ - a possible reactive cyano intermediate to build larger molecules

- 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)

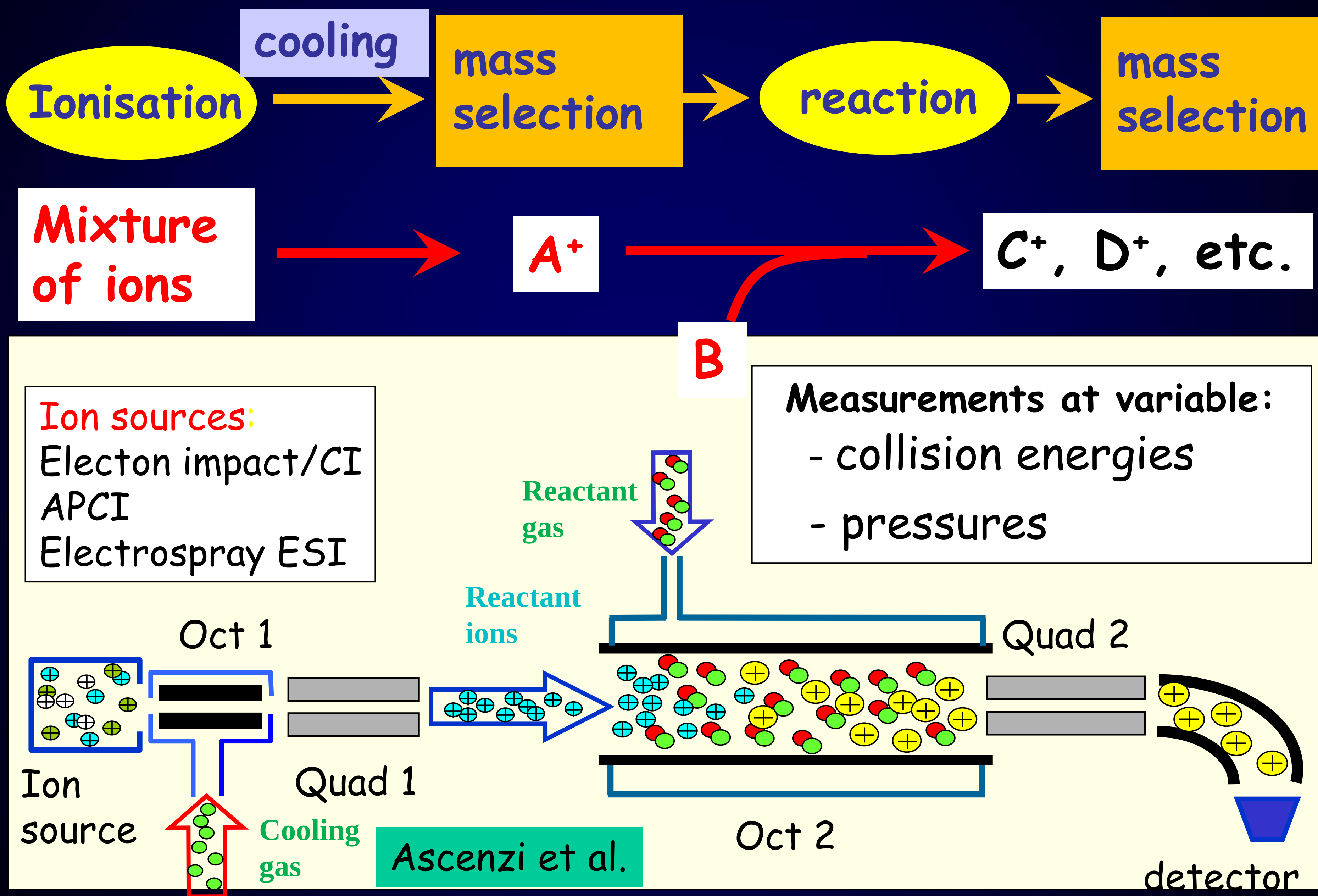


Nitriles in the interstellar medium

- 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



Formation of ions

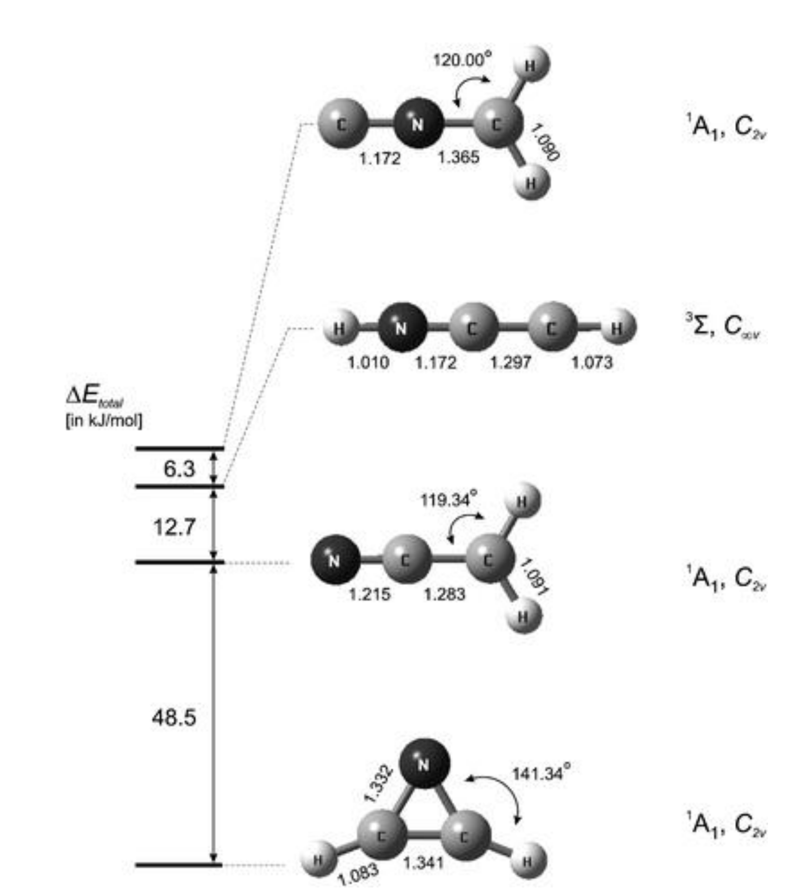
★ Electron impact ionisation of chloroacetonitrile ($ClCH_2CN$)

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

★ 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 sreen of astrochemists: (HCO^+/HOC^+, HCN/HNC)

- Increasing molecular complexity augnments 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^+

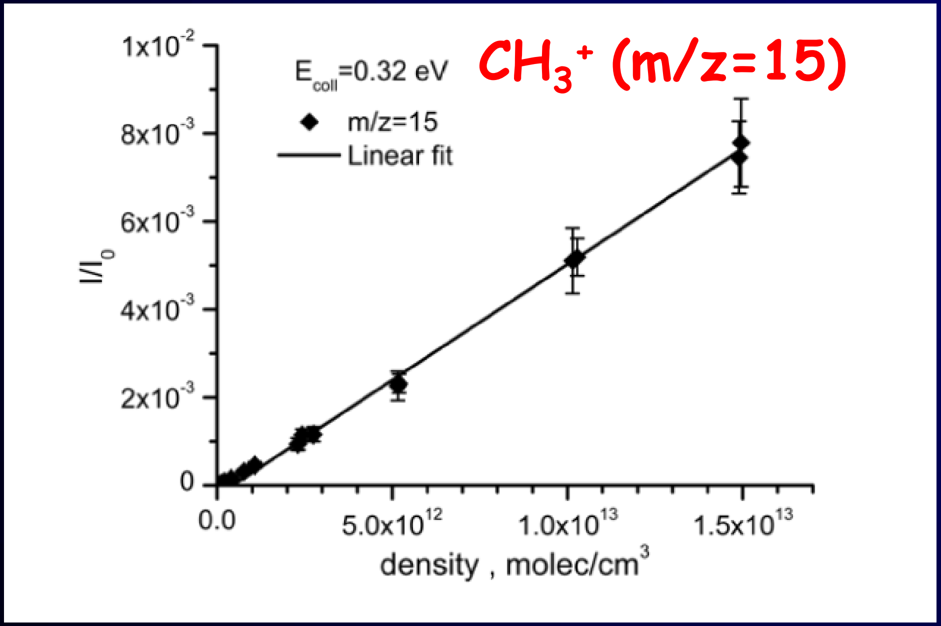
- Electron impact ionosation of $ClCH_2CN$ leads to CH_2CN+

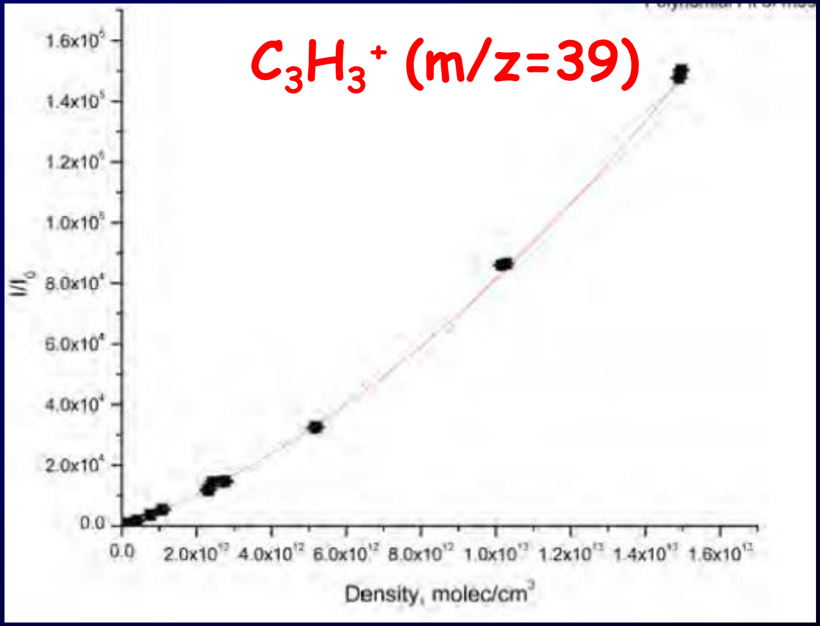
- Photodissiociative ionosation using synchrotron radiation of CH_3CN at lower energies delivers azirine$^+$ cation

Pressure dependence

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

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

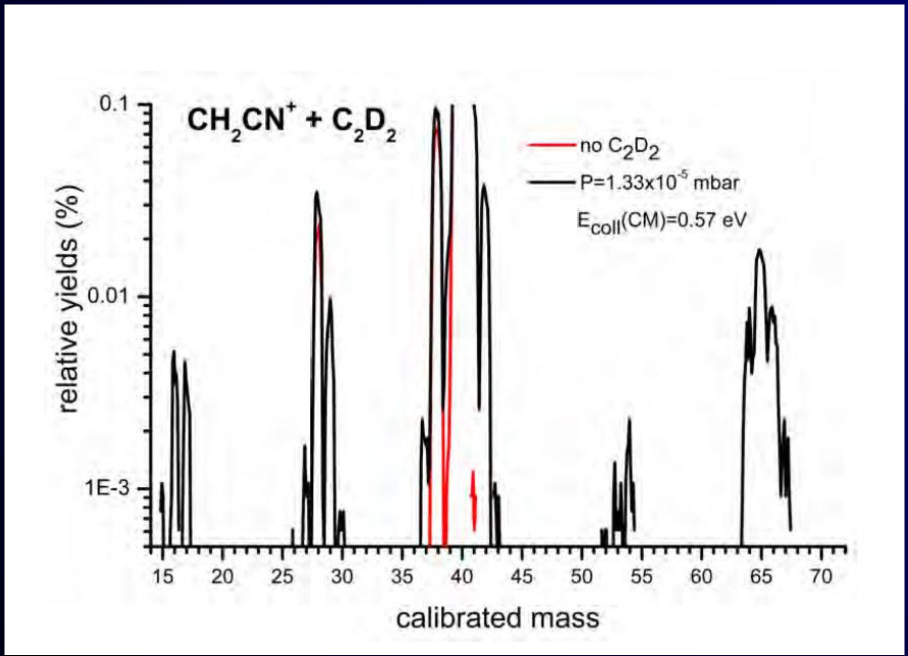


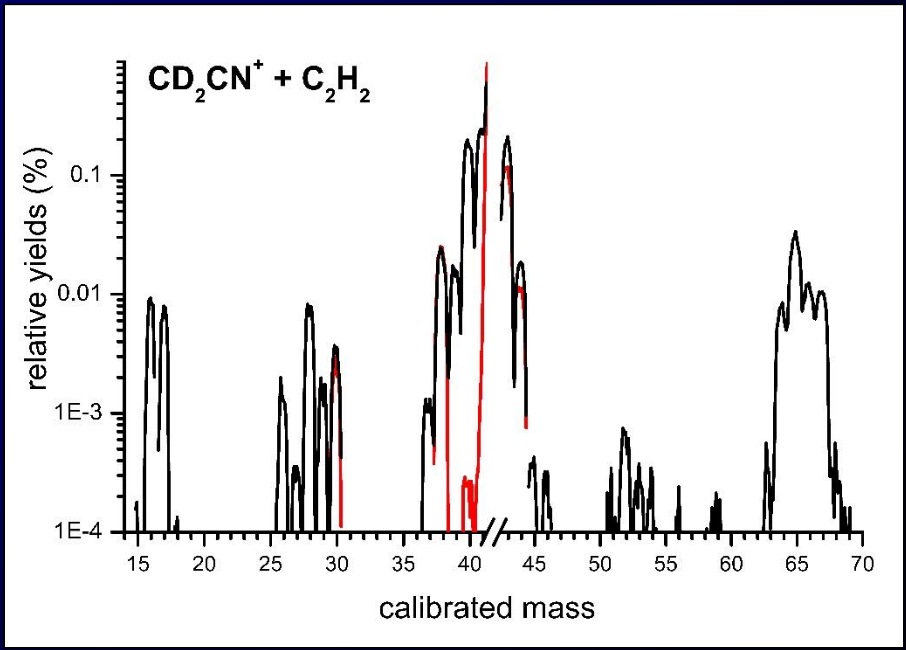


Use of deuterated isotopomers

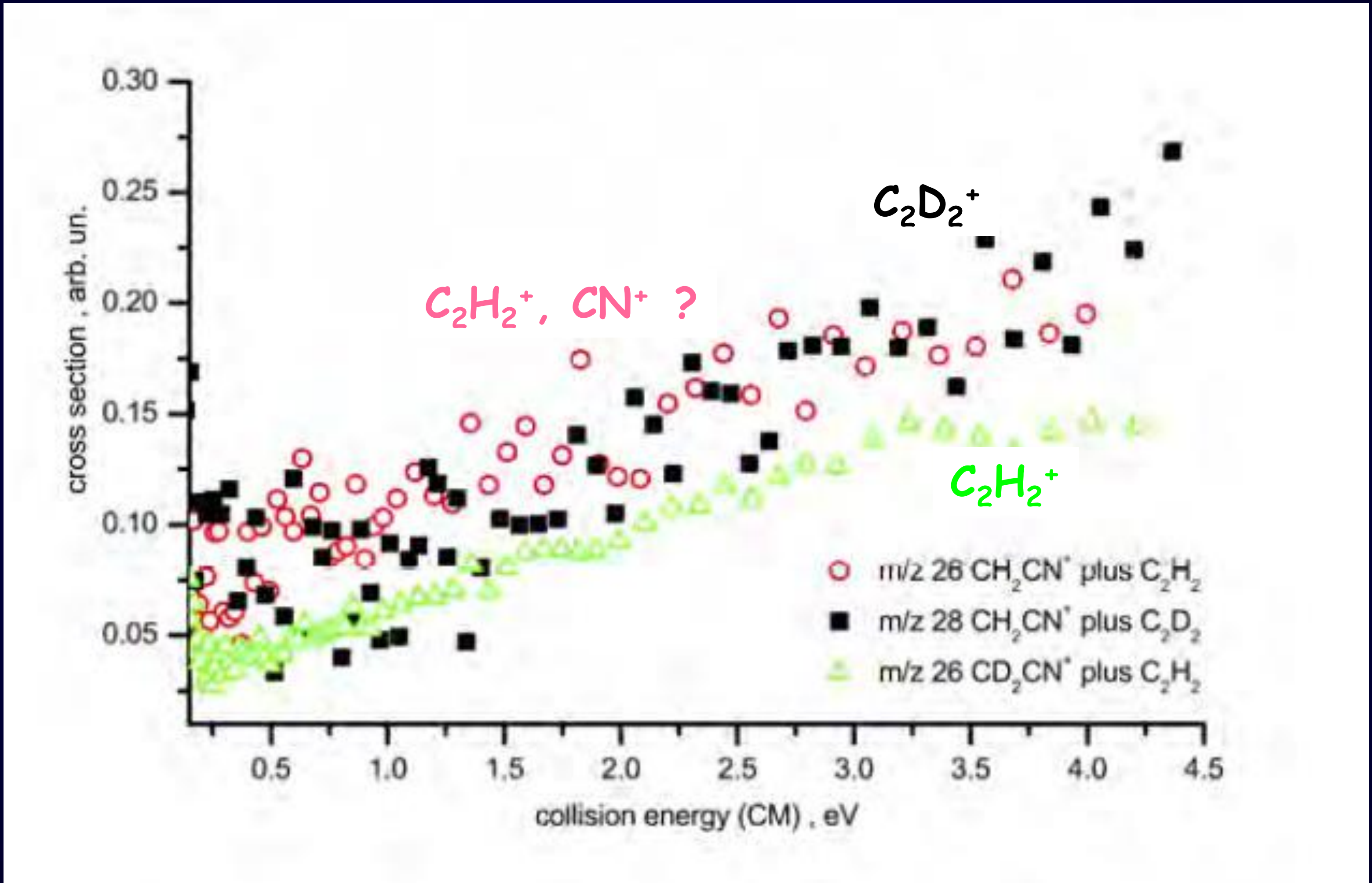
★ Use of deuterated isotopomers to
  - distinguish between channels leading to similar masses
  - identify main product pathways and their thermodynamics

★ 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

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

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

$\rightarrow C_2H_3 + HCCN^+$

$\rightarrow H_2 + H_2C_4N^+$

$\rightarrow C_2H_4 + CCN^+$

$\rightarrow C_2H_3 + HCNH^+$

$\rightarrow C_2H_3^+ + HCNH$

$\rightarrow C_2H_3 + HCNH^+$

$\rightarrow CH_3^+ + HCCCN$

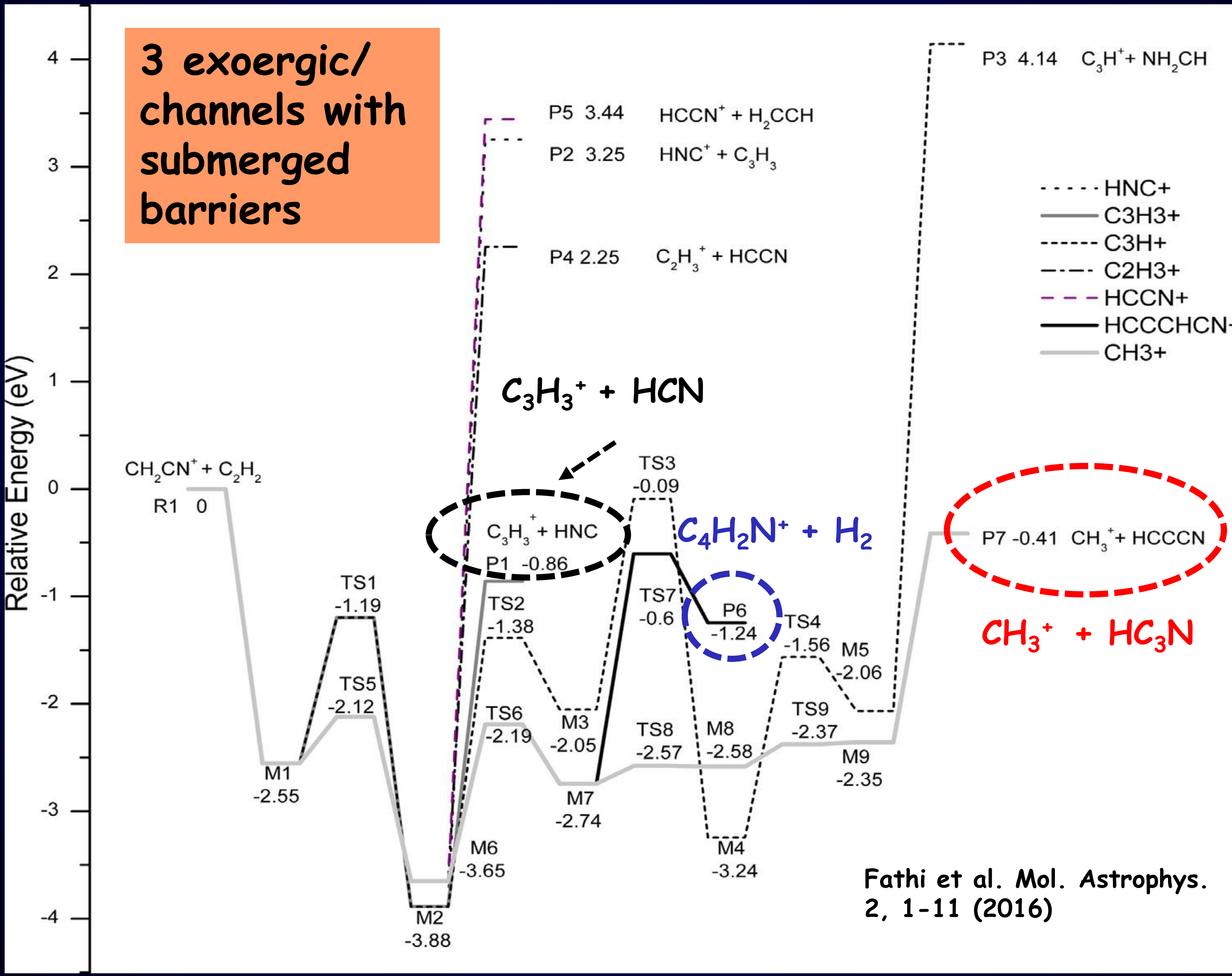
$\rightarrow CH_3 + HCCCN^+$

$\rightarrow C_2H_2 + H_2C_2N^+$

$\rightarrow C_2H + H_3C_2N^+$

$\rightarrow C_3H^+ + H_3CN^+$

Potential surface of $CH_2CN^+ + C_2H_2$



Fathi et al. Mol. Astrophys. 2, 1-11 (2016)

Possible exoergic barrierless reactions

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

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

$\rightarrow C_2H_3 + HCCN^+$

$\rightarrow H_2 + H_2C_4N^+$

$\rightarrow C_2H_4 + CCN^+$

$\rightarrow C_2H_3 + HCNH^+$

$\rightarrow C_2H_3^+ + HCNH$

$\rightarrow C_2H_3 + HCNH^+$

$\rightarrow CH_3^+ + HCCCN$

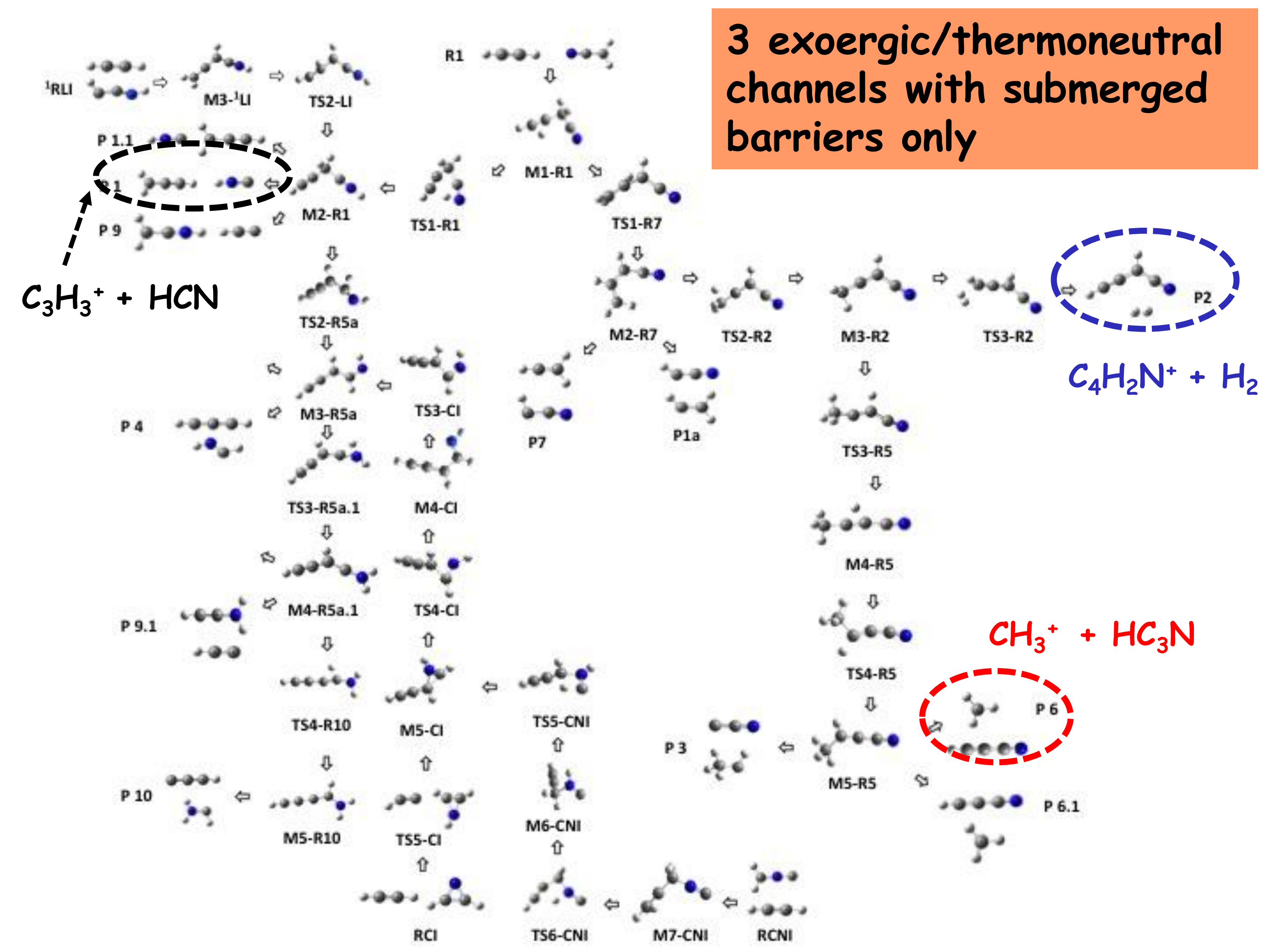
$\rightarrow CH_3 + HCCCN^+$

$\rightarrow C_2H_2 + H_2C_2N^+$

$\rightarrow C_2H + H_3C_2N^+$

$\rightarrow C_3H^+ + H_3CN^+$

Flow chart with exoergic product pathways



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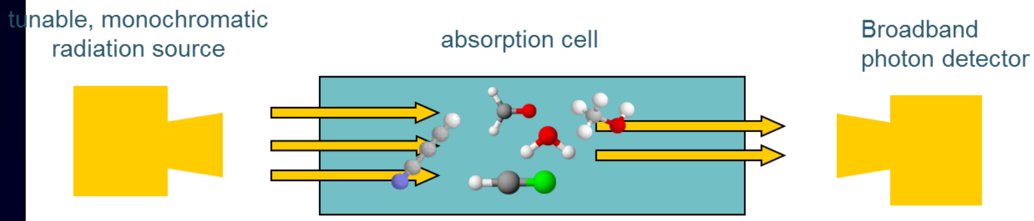
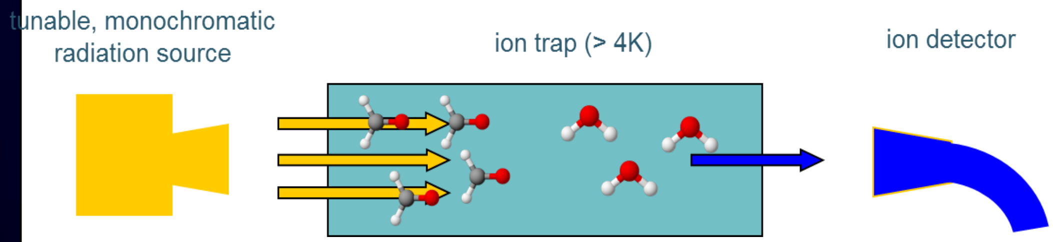
Spectroscopy of ions in traps (Brünken et al.)

Typical absorption experiment



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

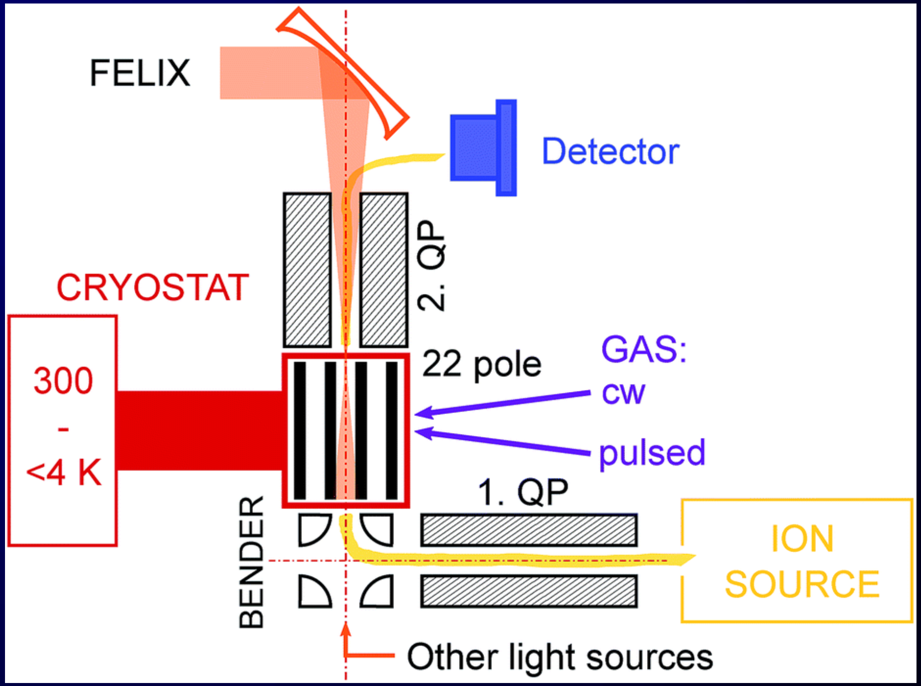
Action Spectroscopy in Cryogenic Ion Traps



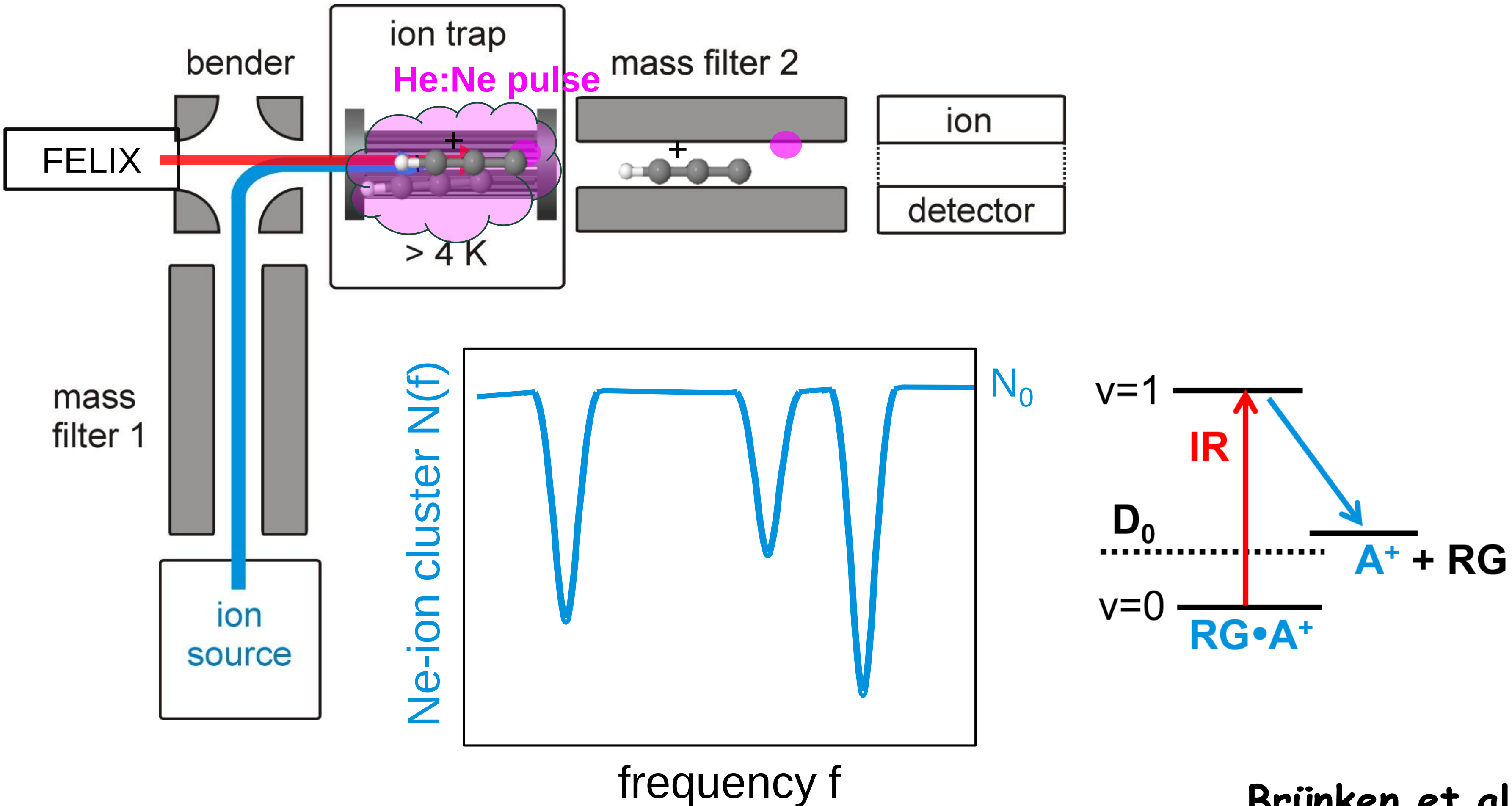
- **sensitive** (only few 1000 ions)
- **mass selection**
- **isolation** of reactive ions
- **low ion temperatures**
  → less congested spectra
  → higher S/N & accuracy
- **long interaction times**

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.

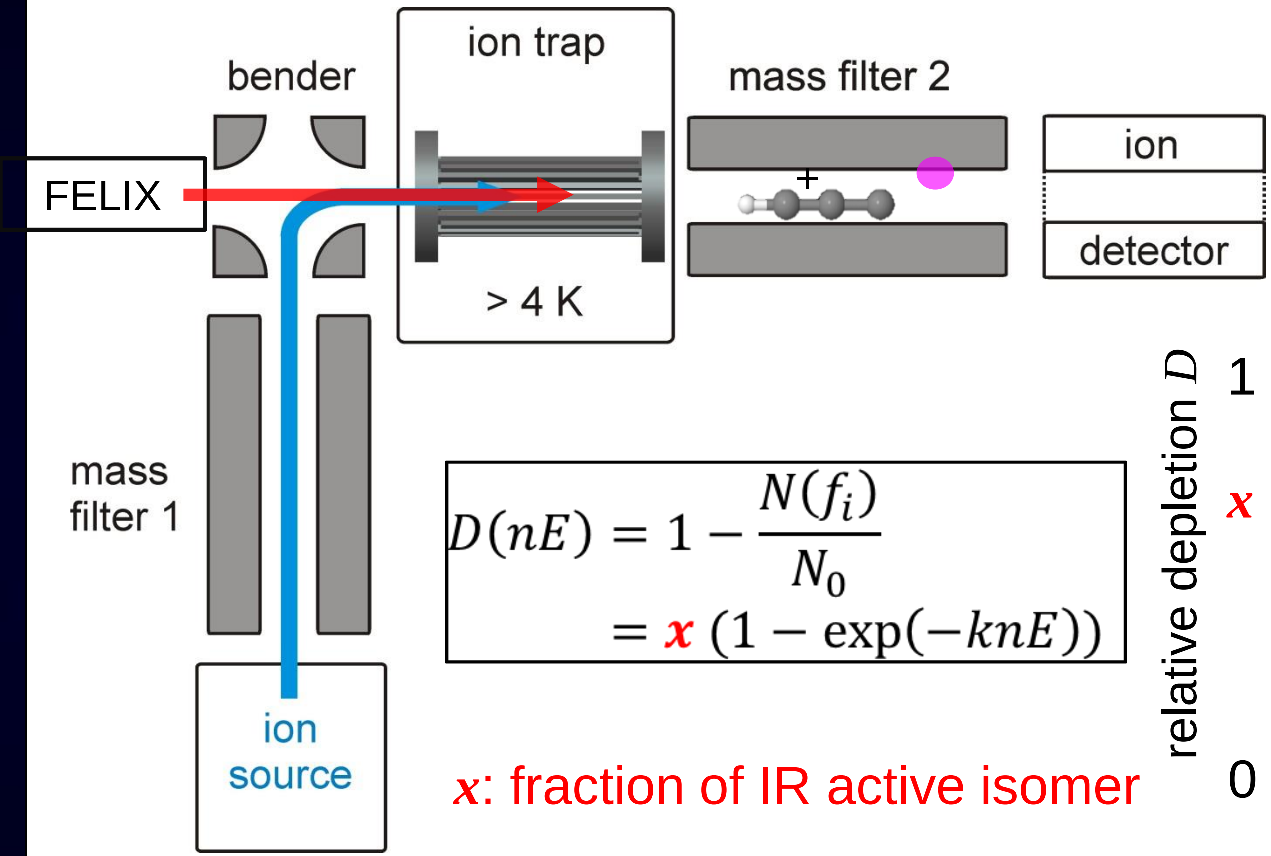
IRPD - weakly bound messenger infrared predissociation

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*

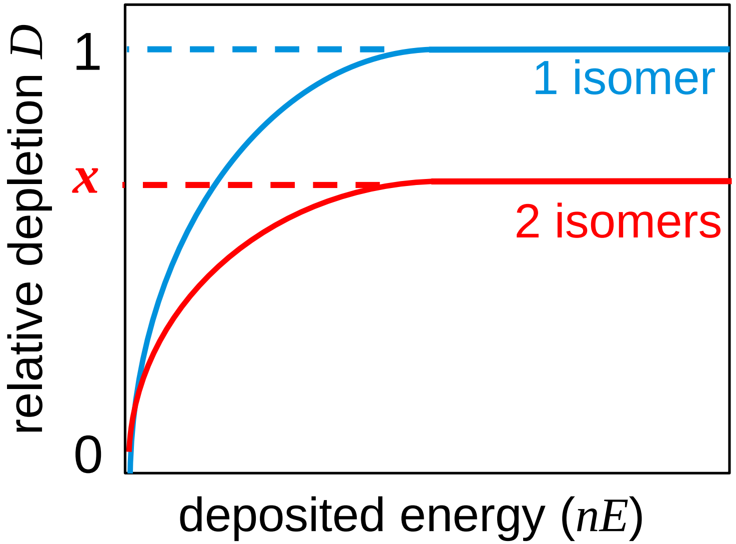
Infrared predissociation depletion spectroscopy

Brünken et al.



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

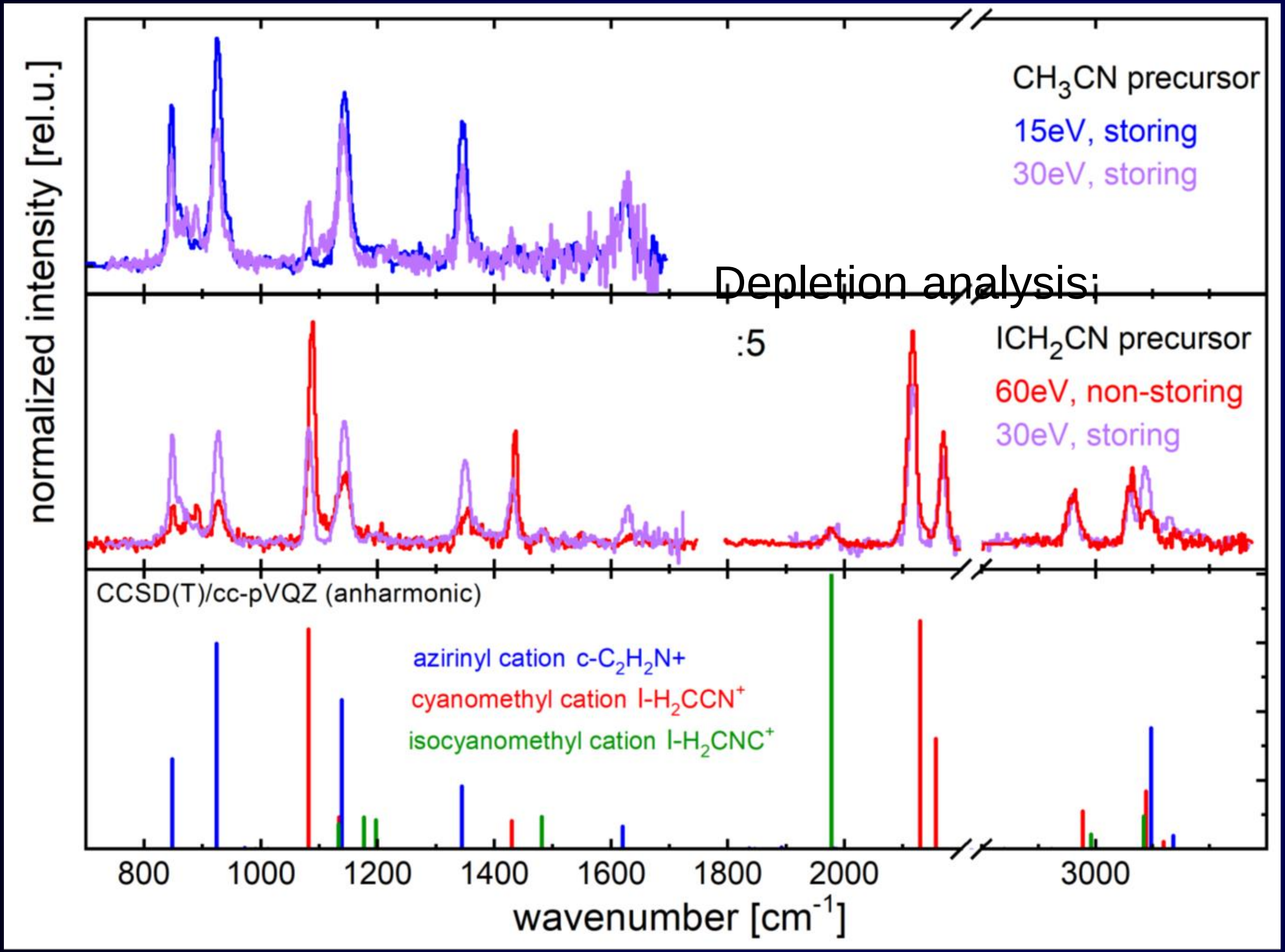
x: fraction of IR active isomer



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)

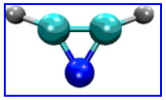
Results for CH_2CN^+

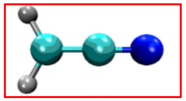


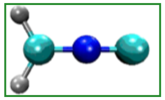
Depletion analysis:

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

$c\text{-}CHCHN^+$	$l\text{-}H_2CCN^+$
% 35(5)	**63(3)** %
% 50(3)	40(2) %







Brünken et al.

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

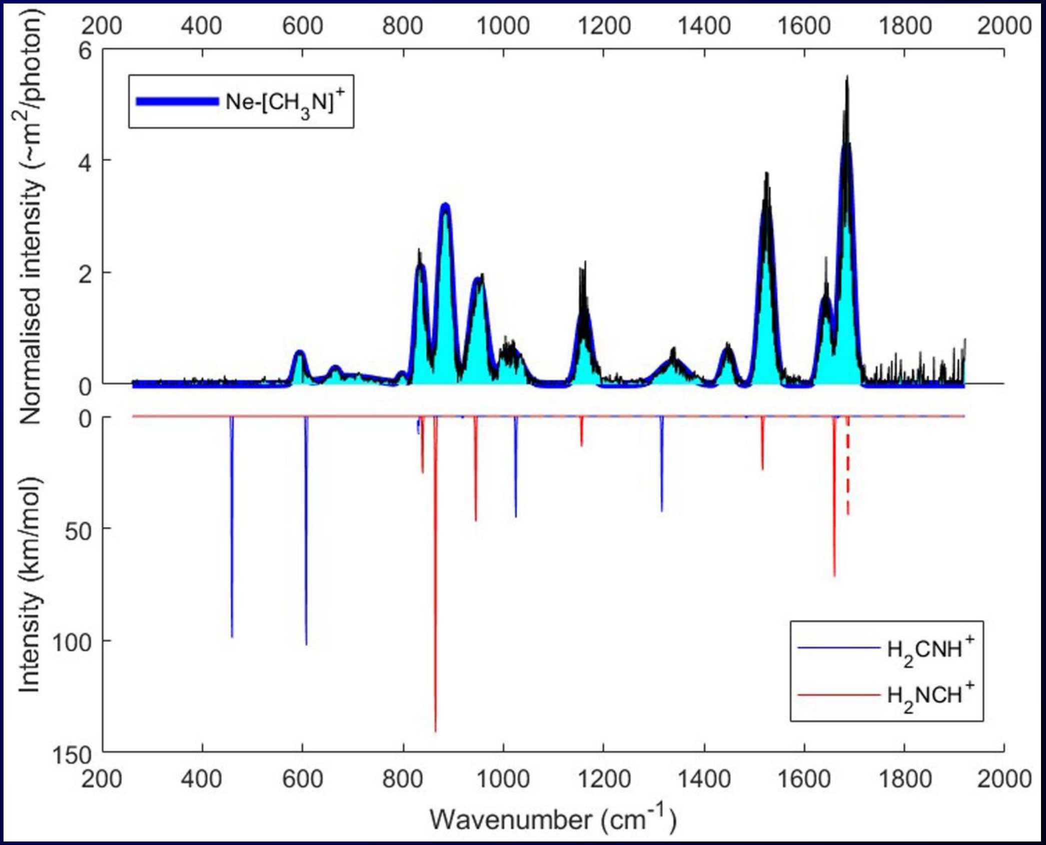
→ m/z=64 detected by INMS (not predicted in hydro-carbon models)

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

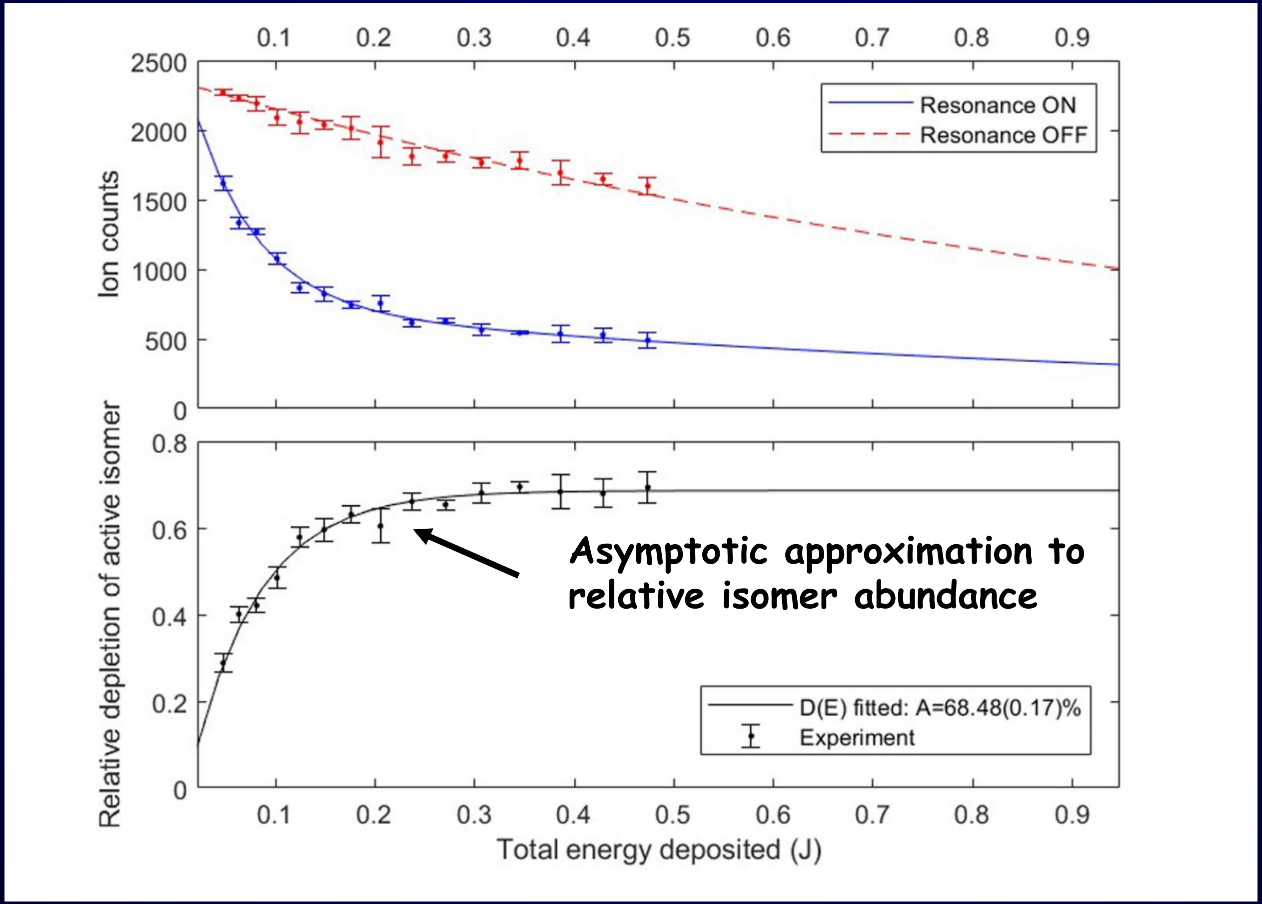
CH_2NH^+ and $HCNH_2^+$

- Another type of reactive carbon-nitrogen compounds
- Vibrational modes measured with IRPD and assigned with ab initio calculations at the CCSD(T)/ANO0 level
- Isotope ratio with electron impact ionisation (33 eV) 70:30 in favour of $HCNH_2^+$
- $HCNH_2^+$ also lower in energy by 4.2 kcal/mol.



Infrared predissociation spectroscopy

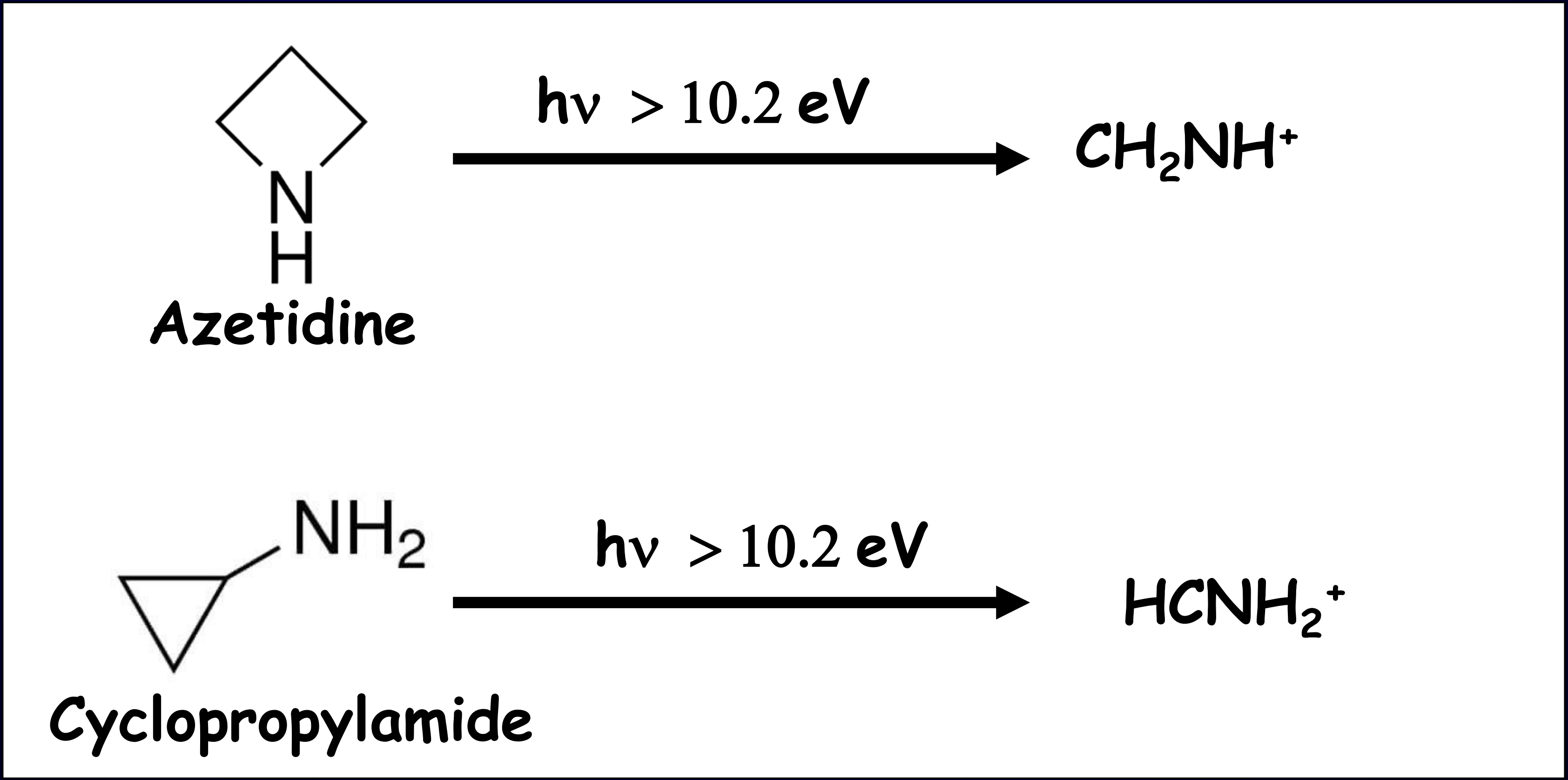
- At resonance of a particular isomer ion signal loss due to resonant infrared predissociation of cluster



$X^+ \cdot Ne + h\nu \rightarrow X^+ + Ne$

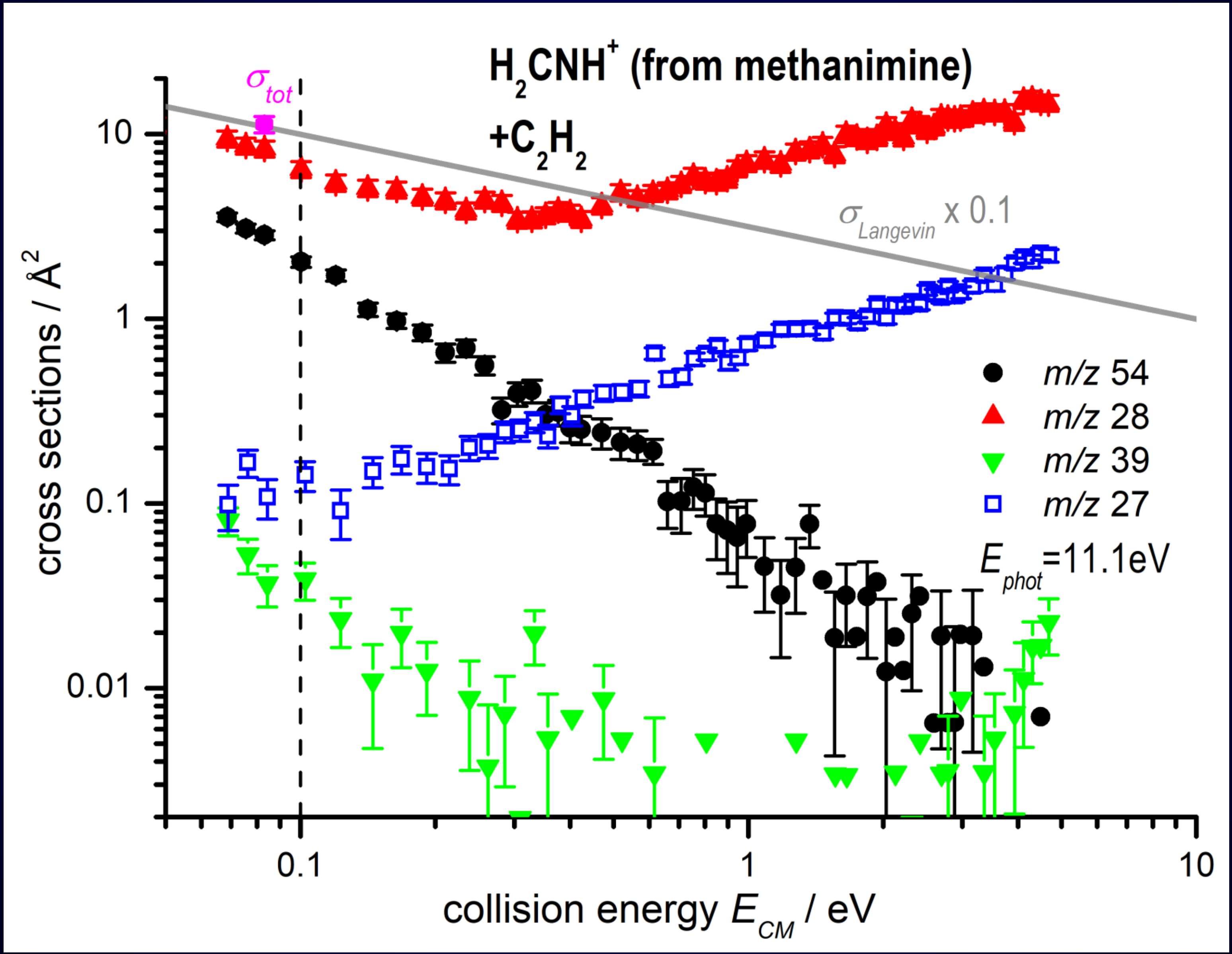
Reactions of CH_2NH^+ and $HCNH_2^+$

- Selective generation of isomers possible with dissociative photoionisation by apt precursor substances.

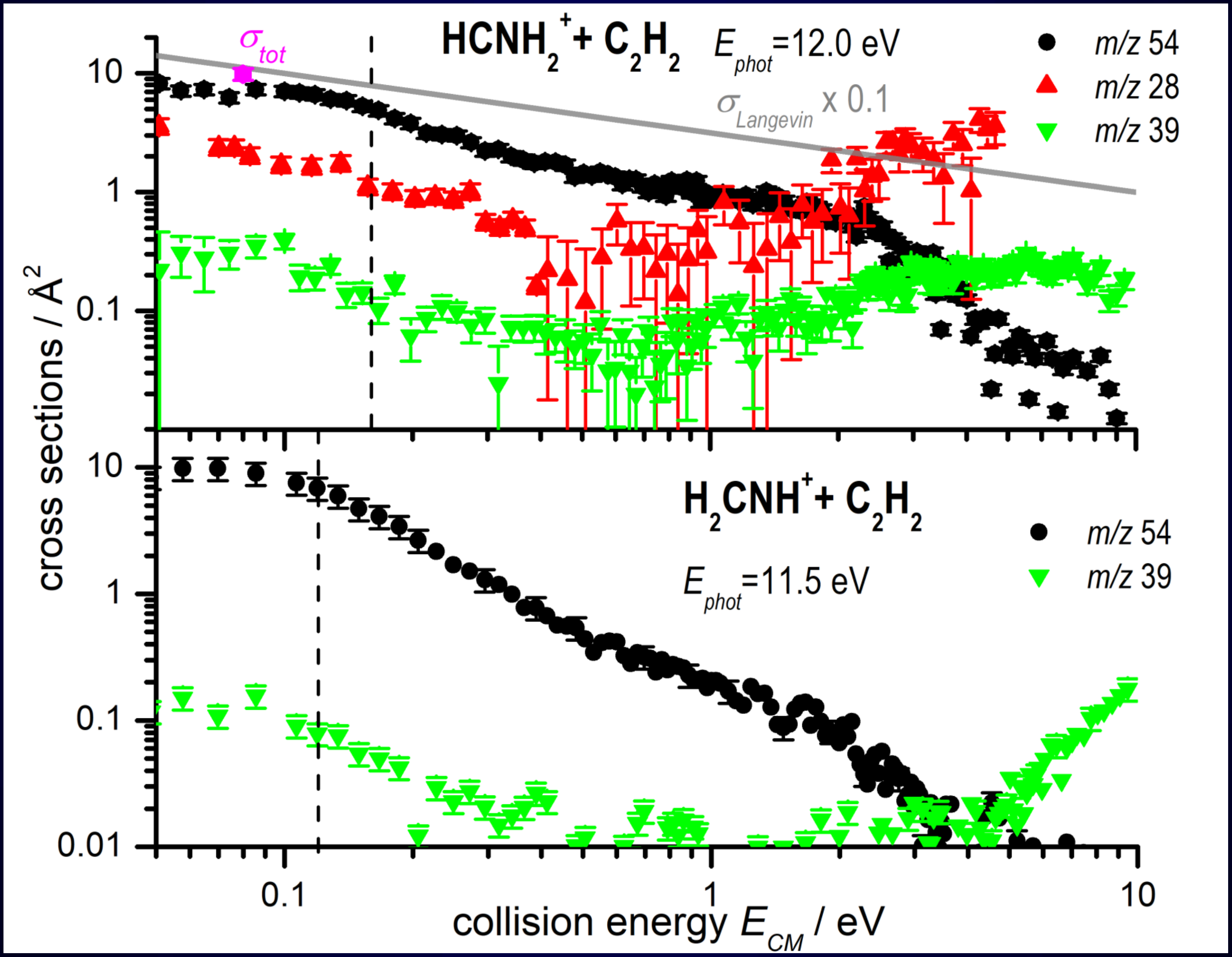


Contamination due to $C_2H_5^+$ and $^{13}CCH_4^+$ an issue

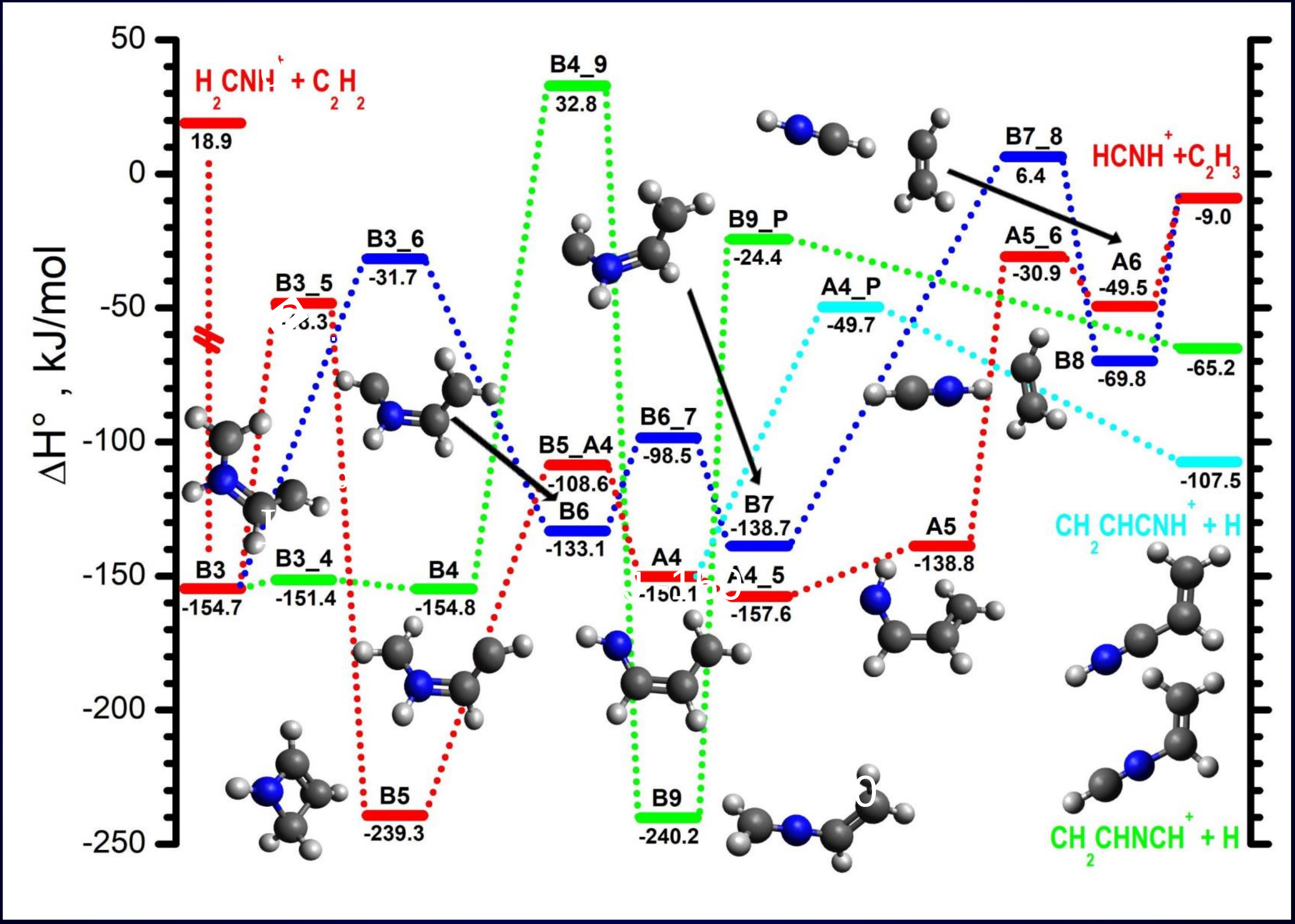
Collisional energy dependence of $CH_2NH^+ + C_2H_2$



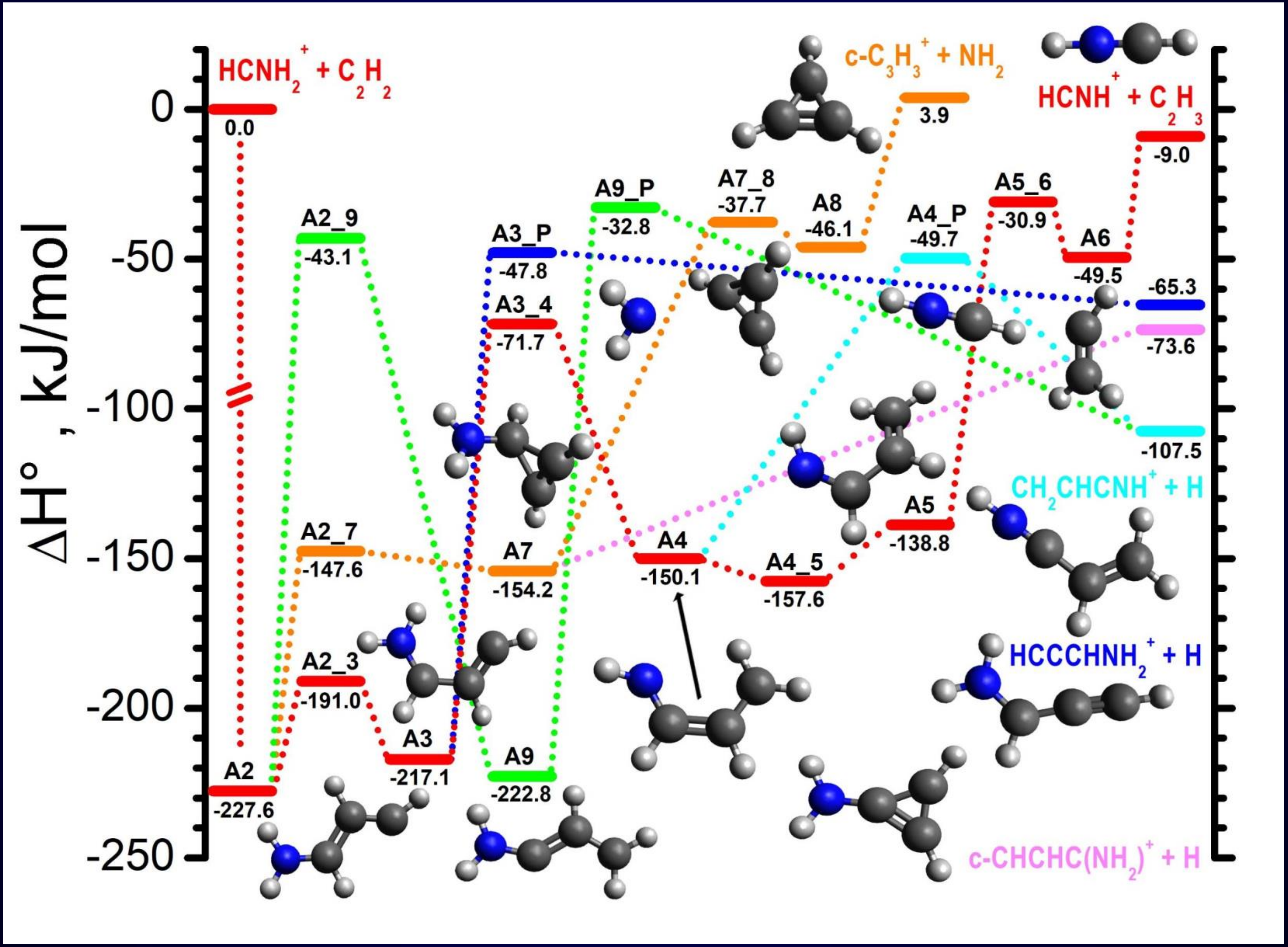
Collisional energy dependence of $HCNH_2^+ + C_2H_2$



Collisional energy dependence of $CH_2NH^+ + C_2H_2$



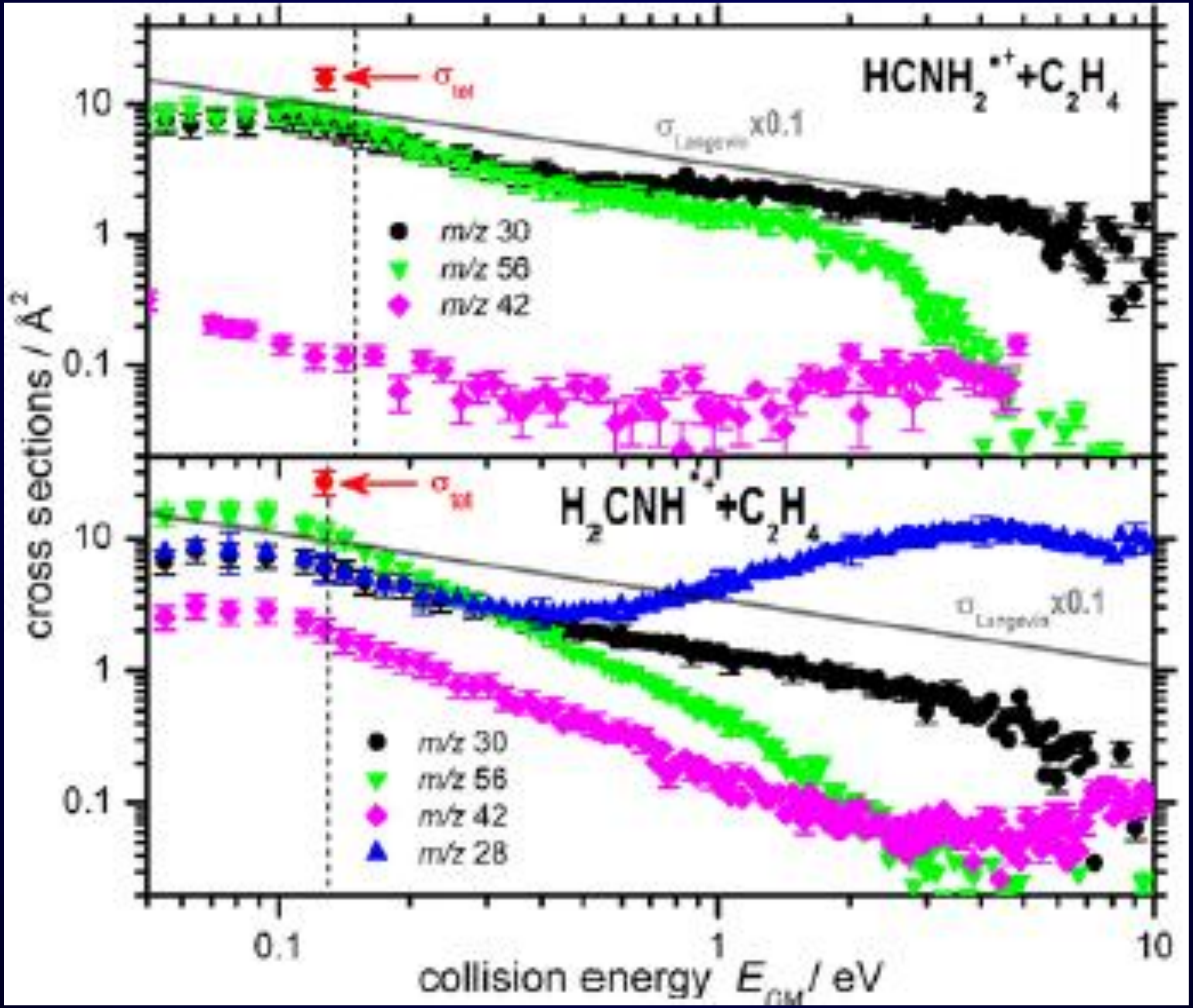
Collisional energy dependence of $HCNH_2^+ + C_2H_2$

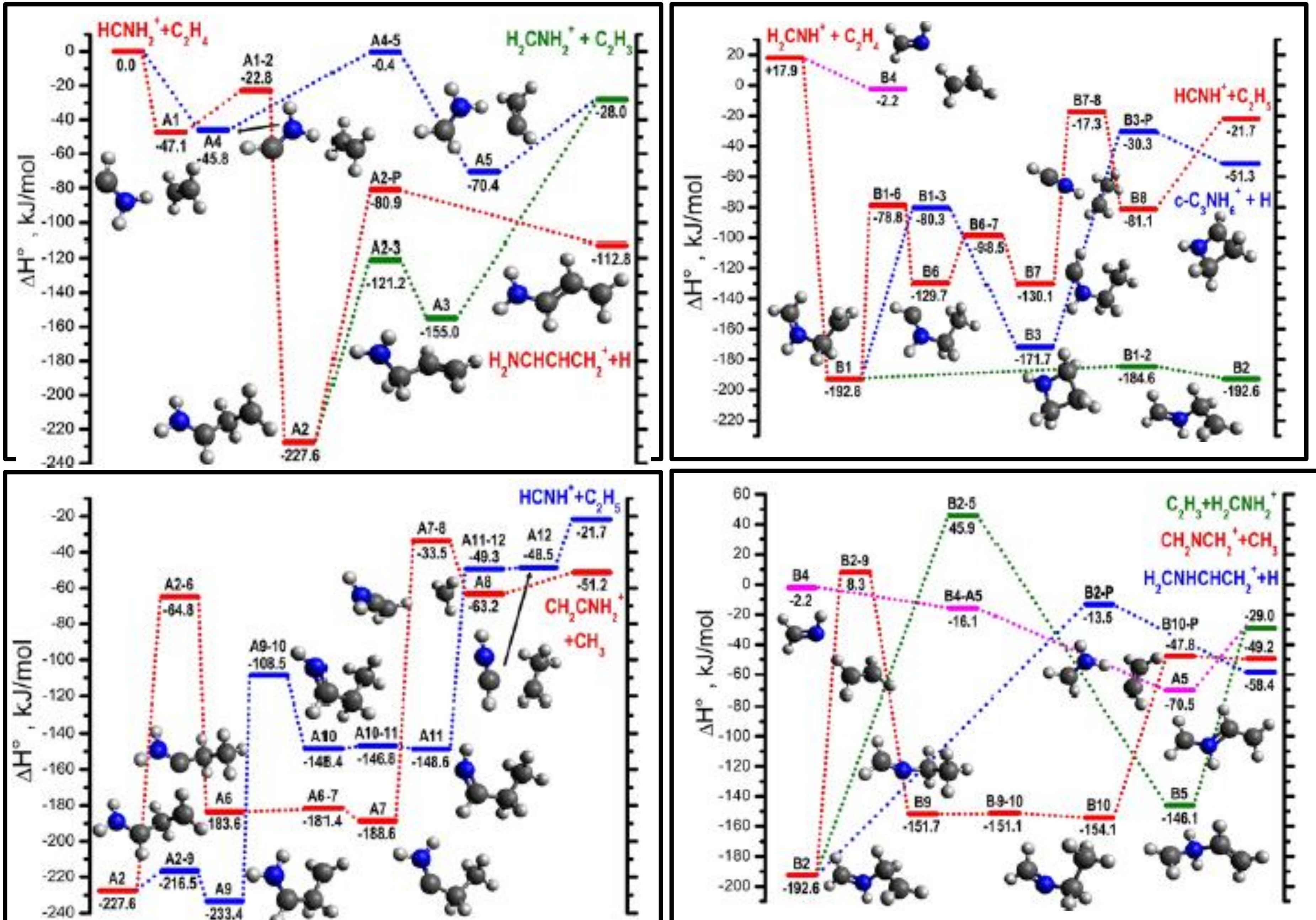


Conclusions from $HCNH_2^+$/ CH_2NH^+ + C_2H_2

- 3 main ionic products: $C_3H_4N^+$ (dominant sat low relative translational energies), C_3H_3+ and $HCNH^+$ (only for $HCNH_2^+$)
- Formation of heavier $C_3H_4N^+$ ions can be explained by reactions exhibiting only submerged barriers.
- Smaller contribution of almost thermoneutral $C_3H_3^+$ - (complicated pathway for CH_2NH^+)
- HCNH+ dominates at higher energies (fragmentation of primary products?)
- Minute contribution of $C_2H_3^+$ (proton transfer, fragmentation of $HCNH^+$)

Collisional energy dependence of $CH_2NH^+/HCNH_2^+ + C_2H_4$





HCNH$_2^+$+C$_2$H$_4$
H$_2$CNH$_2^+$ + C$_2$H$_3$
0.0
A1
-47.1
A4
-45.8
A1-2
-22.8
A4-5
-0.4
A5
-70.4
-28.0
A2-P
-80.9
-112.8
A2-3
-121.2
A3
-155.0
H$_2$NCHCHCH$_2^+$+H
A2
-227.6
ΔH°, kJ/mol
H$_2$CNH$^+$ + C$_2$H$_4$
+17.9
B4
-2.2
HCNH$^+$+C$_2$H$_5$
B7-8
-17.3
B3-P
-30.3
-21.7
-51.3
B8
-81.1
c-C$_3$NH$_6^+$ + H
B1-6
-78.8
B1-3
-80.3
B6-7
-98.5
B6
-129.7
B7
-130.1
B3
-171.7
B1-2
-184.6
B1
-192.8
B2
-192.6
HCNH$^+$+C$_2$H$_5$
A7-8
-33.5
A11-12
-49.3
A12
-48.5
-21.7
A8
-63.2
-51.2
A2-6
-64.8
CH$_2$CNH$_2^+$
+CH$_3$
A9-10
-108.5
A10
-148.4
A10-11
-146.8
A11
-148.6
A6
183.6
A6-7
-181.4
A7
-188.6
A2-9
-216.5
A9
-233.4
C$_2$H$_3$+H$_2$CNH$_2^+$
CH$_2$NCH$_2^+$+CH$_3$
H$_2$CNHCHCH$_2^+$+H
B2-5
45.9
B2-9
8.3
B4-A5
-16.1
B2-P
-13.5
B10-P
-47.8
-29.0
-49.2
-58.4
A5
-70.5
B5
-146.1
B9
-151.7
B9-10
-151.1
B10
-154.1

Conclusions from $HCNH_2^+$/ CH_2NH^+ + C_2H_4

- 3 main ionic products: $H_2CNH_2^+$, $C_3H_6N^+$ (dominant at low relative translational energies) and $HCNH^+$ (only for H_2CNH^+)

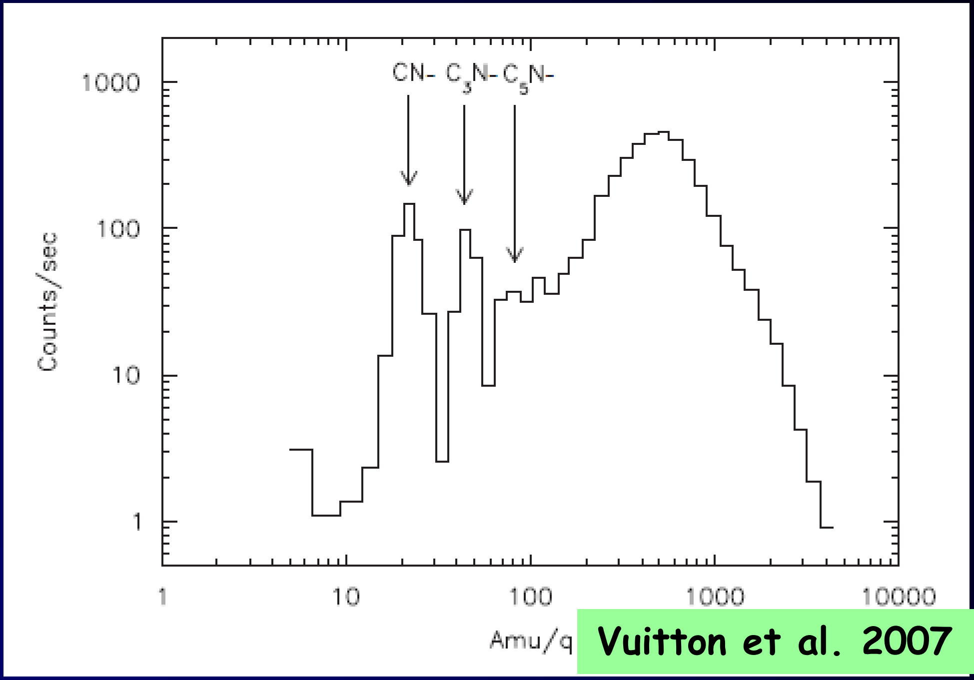
- Formation of heavier $C_3H_6N^+$ ions can be explained by reactions exhibiting only submerged barriers.

- Smaller contribution of $CH_2NCH_2^+$ - (methyl radical elimination), barrierless for $HCNH_2^+$.

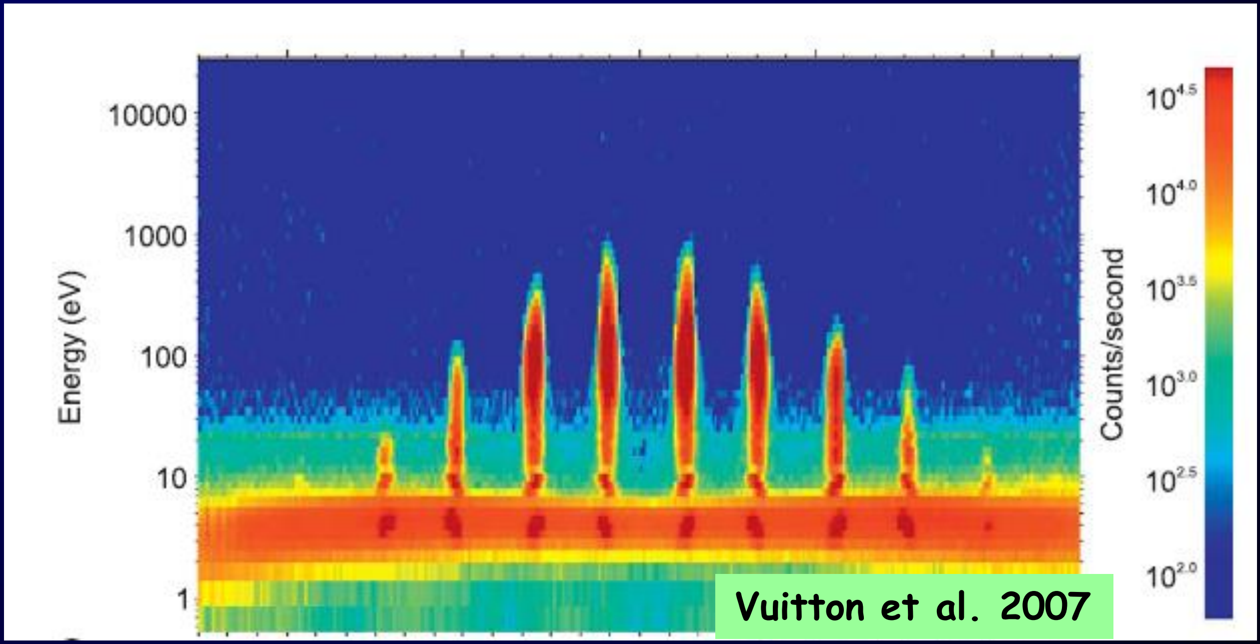
- $HCNH^+$ dominates at higher energies for H_2CNH^+ fragmentation of adduct favoured or collisional induced dissociation of parent, threshold at 1.3 eV)

Heavy anions

- Anions with large mass detected by CAPS Cassini Plasma Spectrometer
- Also lighter cyano anions found (CN^-, C_3N^-, C_5N^-)
- Nature of larger ions fairly unknown
- Could play sub-stantial role in aerosol formation



Vuitton et al. 2007

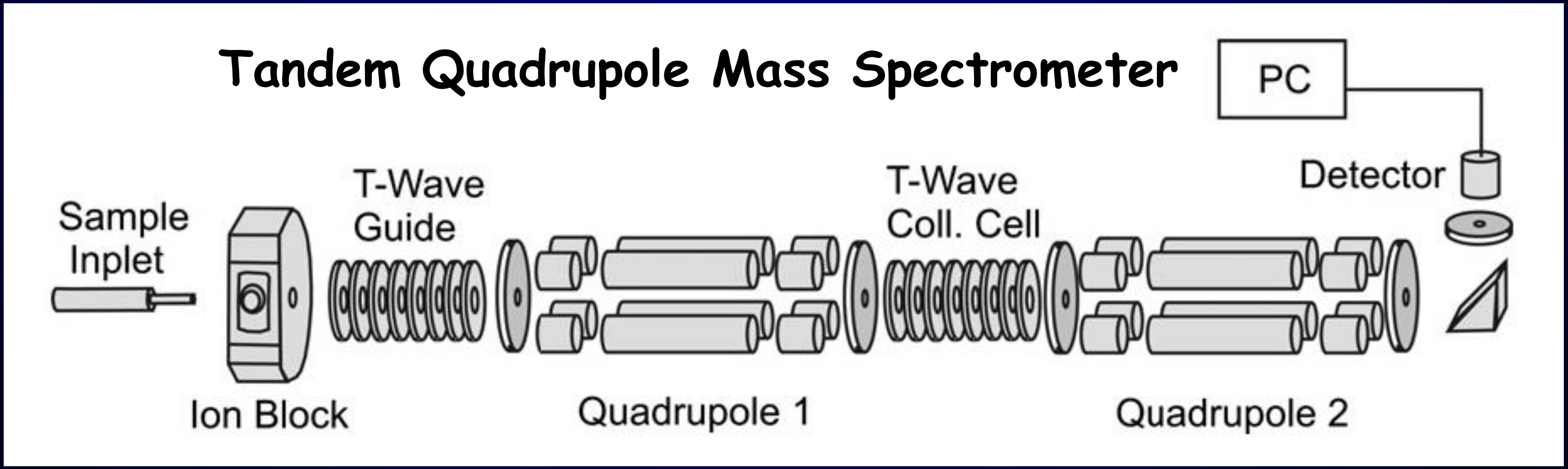


Vuitton et al. 2007

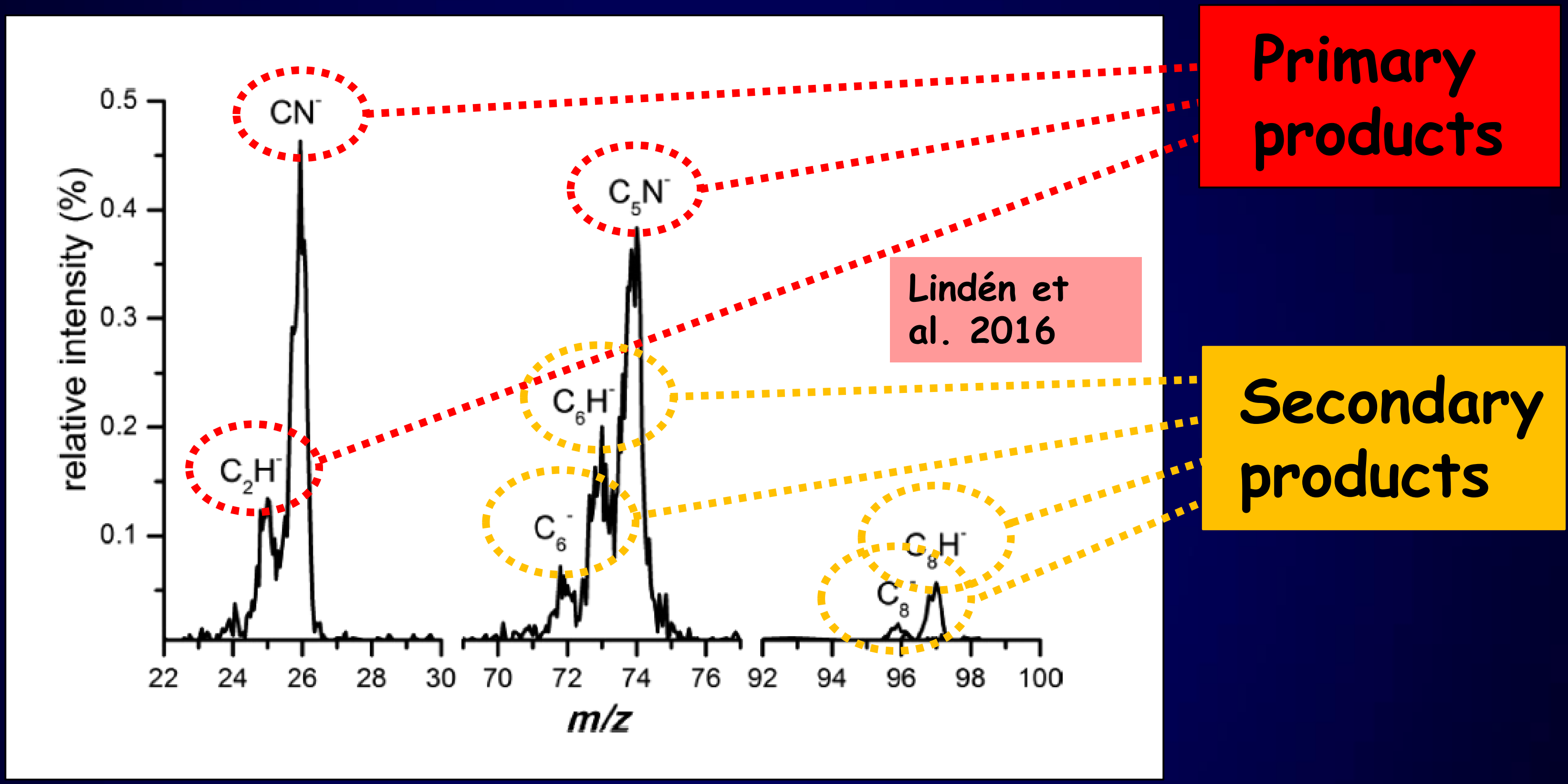
Investigation of the C_3N^- + C_2H_2 reaction

★ **3 different guided ion beam apparatuses:**

- Triple Quadrupole Mass Spectrometer (Trento
- Tandem Quadrupole Mass Spectrometer (Prague)
- "CERISES" Guided Ion Beam Apparatus (Paris)

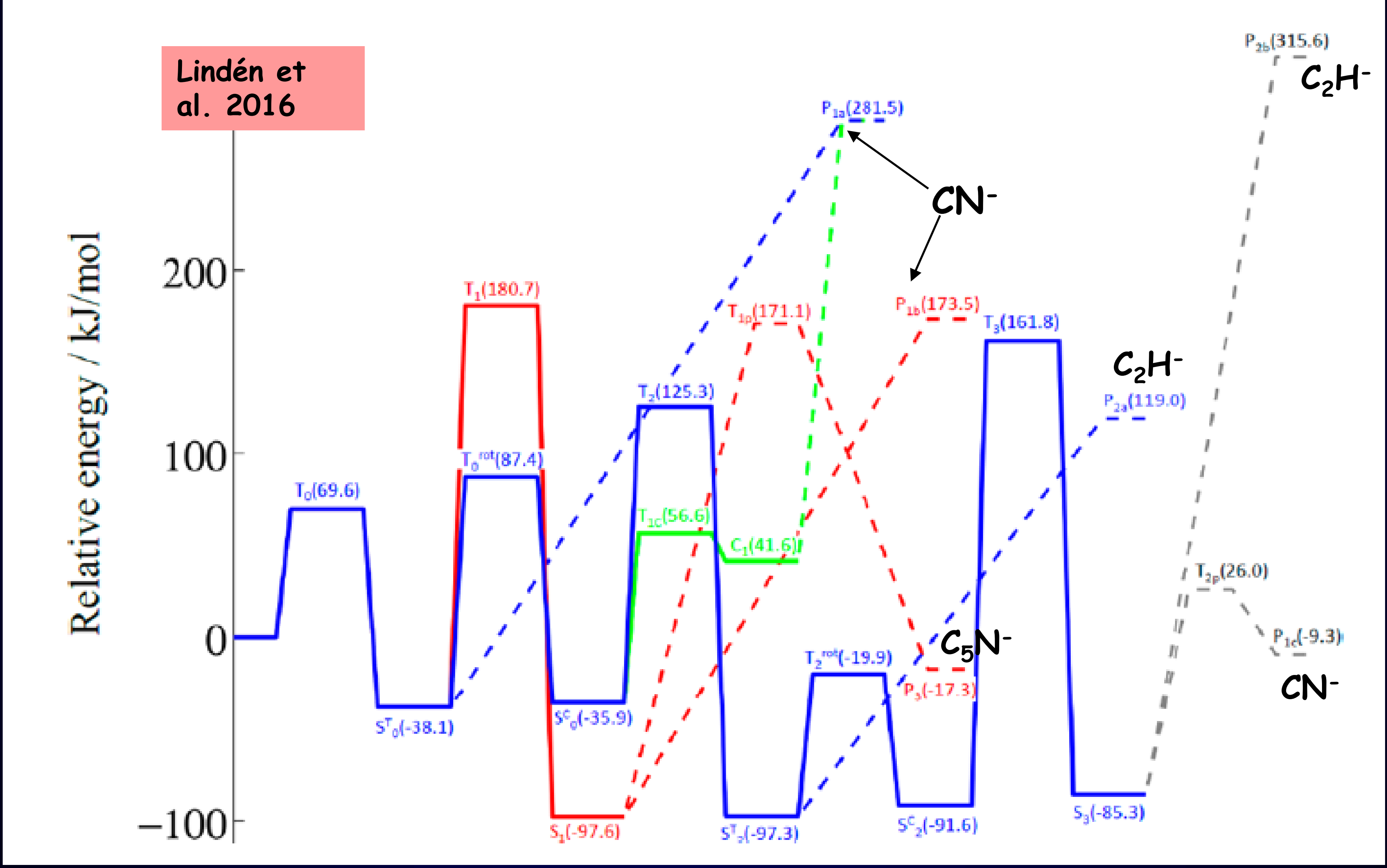


C_3N^- + C_2H_2: Observed products



$$C_3N^- + C_2H_2 \rightarrow H_2 + C_5N^-$$
$$\rightarrow CN^- + HCCCH$$
$$\rightarrow C_2H^- + HCCCN$$

Reaction pathways



Reaction pathways

Primary pathways:

$C_3N^- + C_2H_2 \rightarrow C_5H^- + H_2$

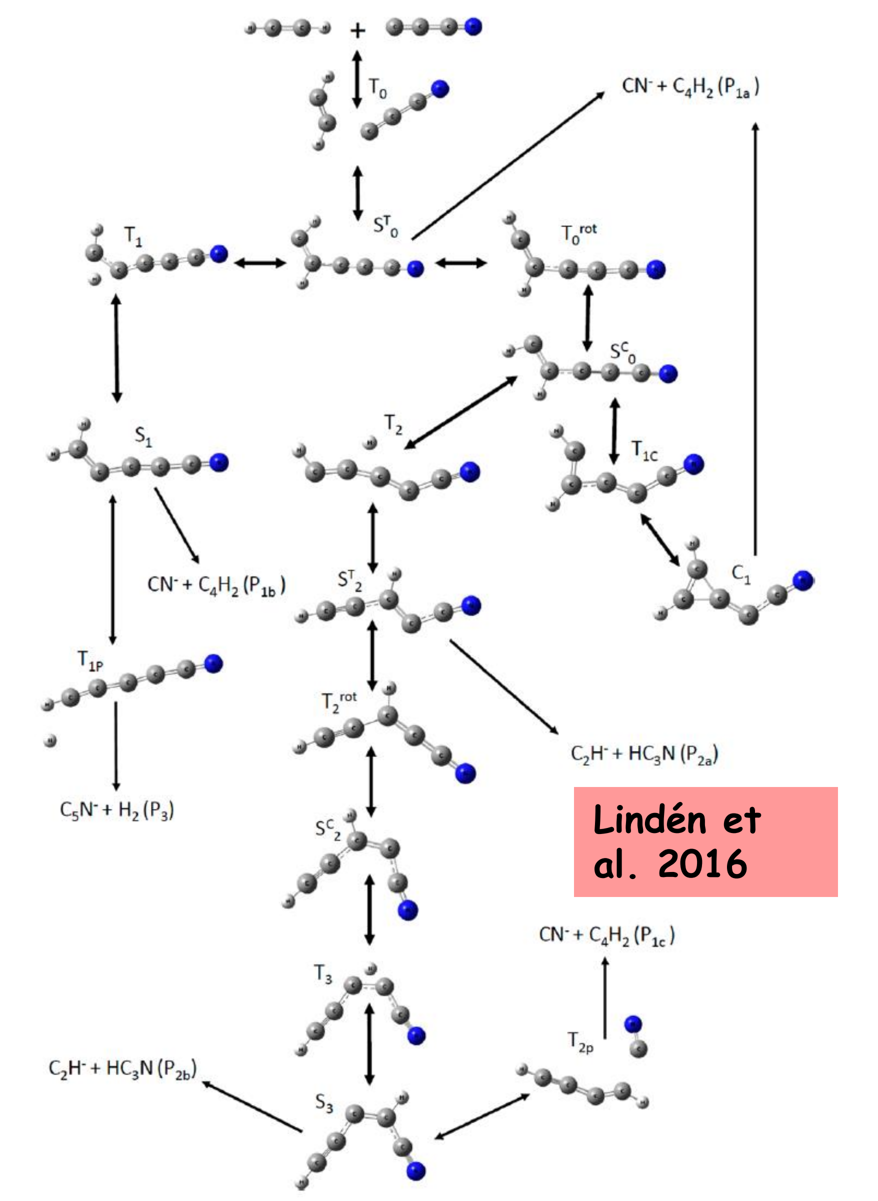
$C_3N^- + C_2H_2 \rightarrow C_4H_2 + CN^-$

Other processes:

$C_3N^- + C_2H_2 \rightarrow C_2H^- + HC_3N$
(proton transfer)

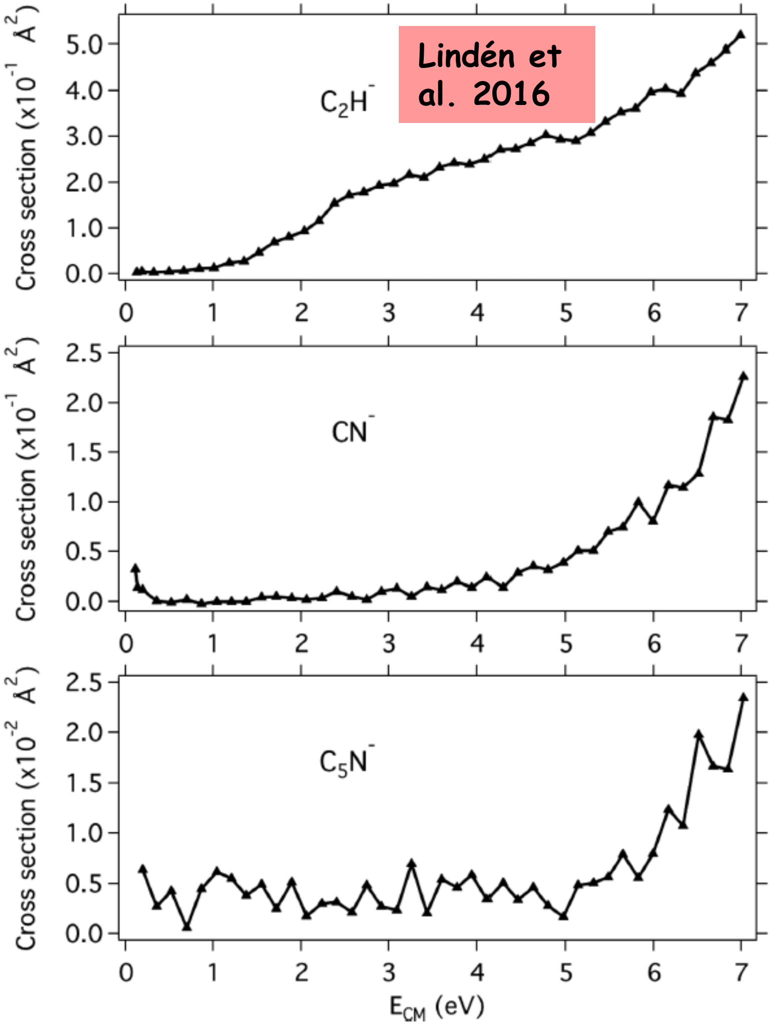
$C_3N^- + C_2H_2 \rightarrow C_2 + C_2H_2 + CN^-$
(collision induced dissociation)

★ Production of C_2H^- and C_5N^- favoured

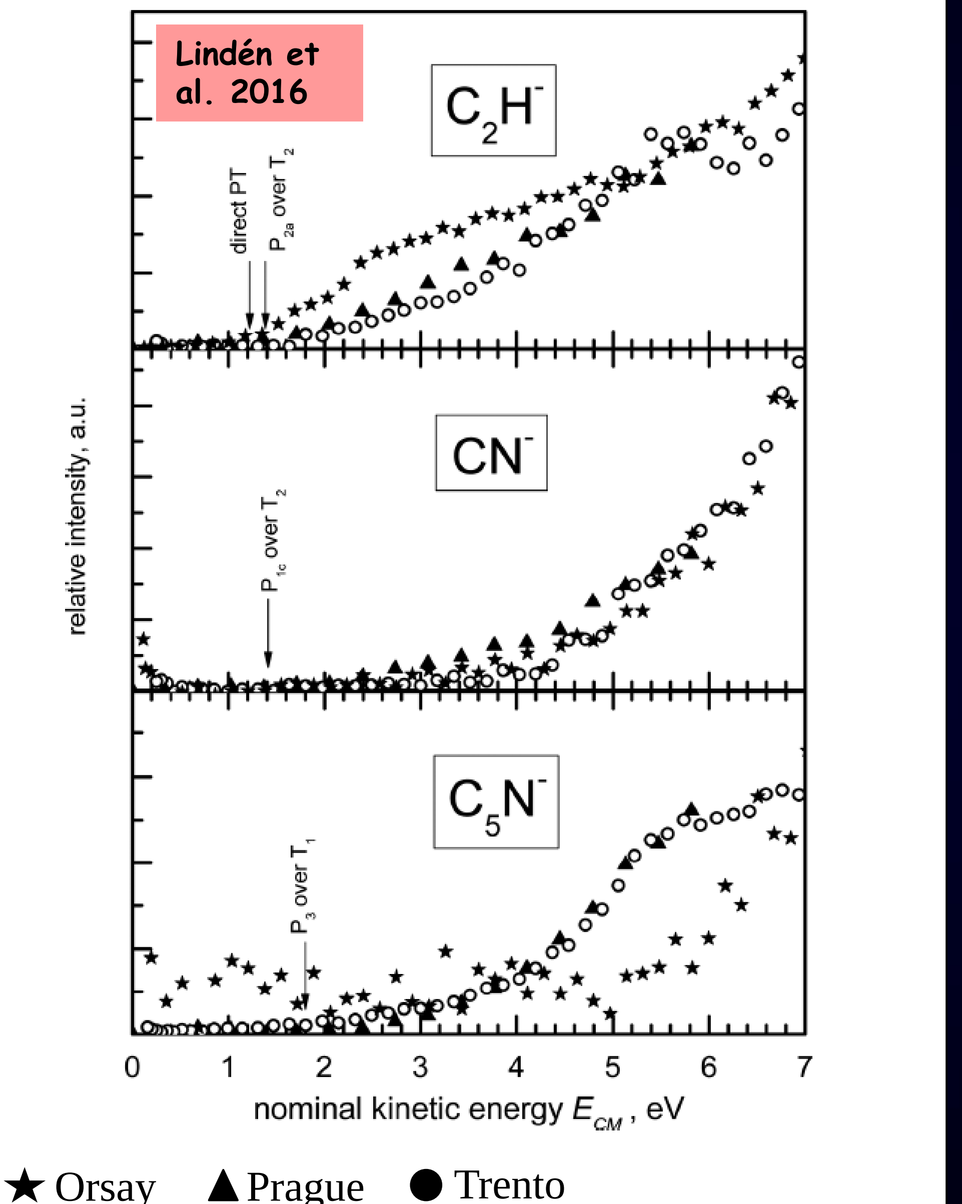


Lindén et al. 2016

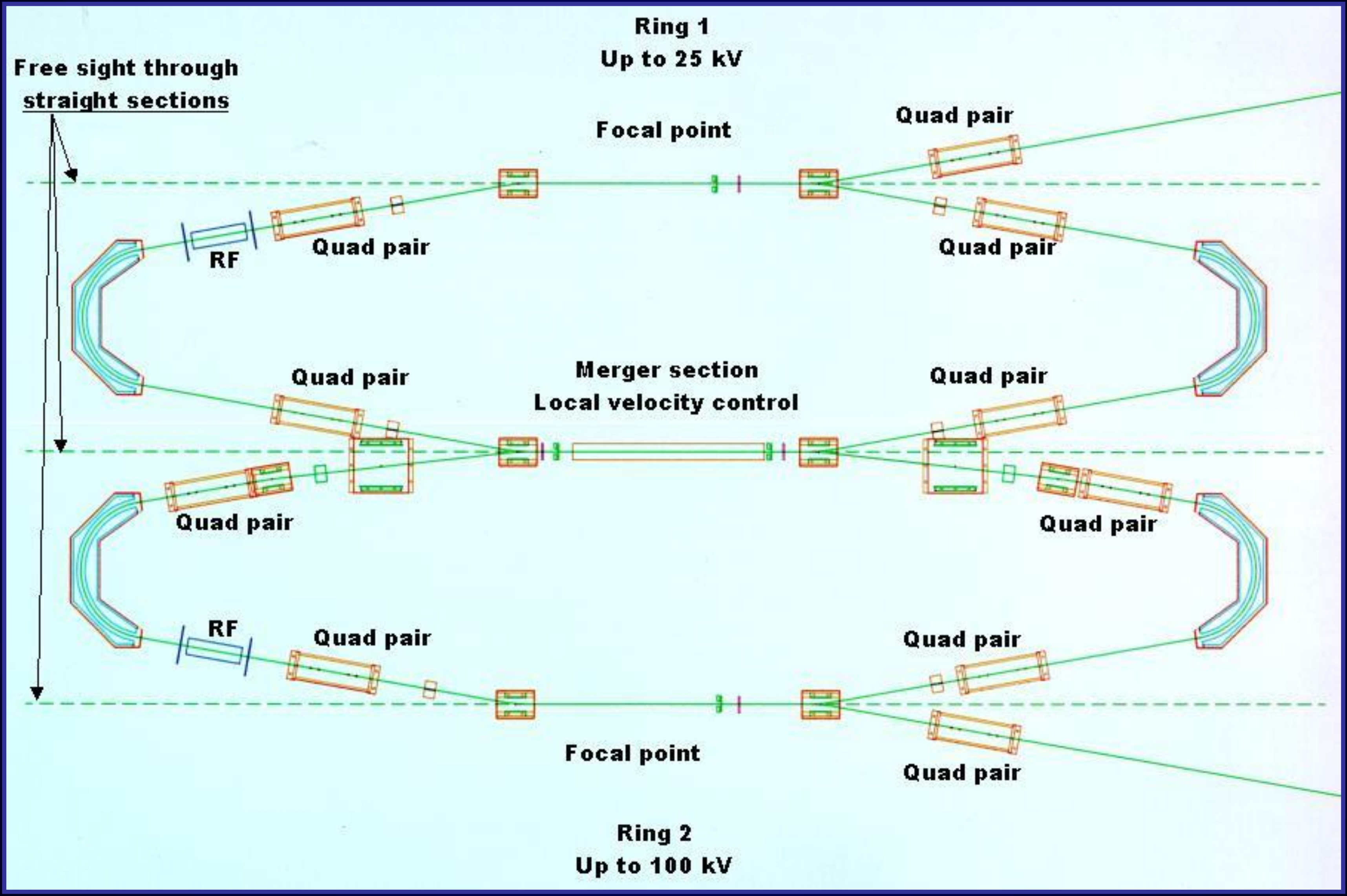
Reaction pathways



Absolute cross sections of product formation (Orsay)



DESIREE

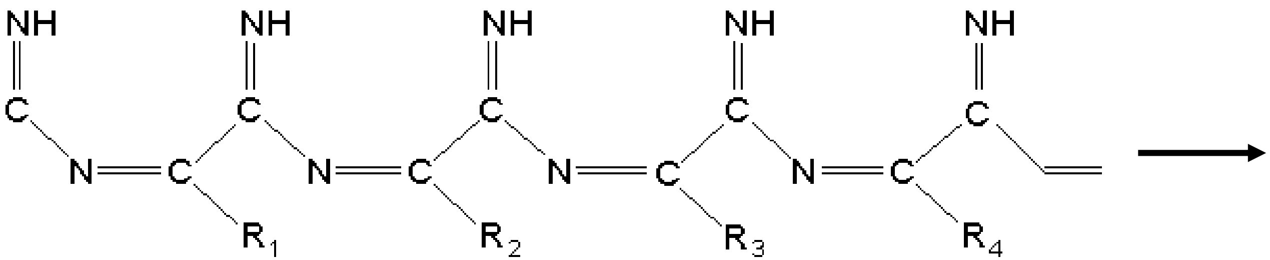

Ring 1
Up to 25 kV
Free sight through
straight sections
Focal point
Quad pair
RF
Quad pair
Quad pair
Merger section
Local velocity control
Quad pair
Quad pair
Quad pair
Quad pair
RF
Quad pair
Quad pair
Focal point
Quad pair
Ring 2
Up to 100 kV

Conclusions (Anions)

- Anion reactions have great impact on the chemistry of planetary ionospheres, interstellar clouds and circumstellar envelopes
- Chain elongation of through reaction of C_2H_2 + C_3N^- inefficient at low temperatures
- Molecular data on many anion reactions still lacking.
- New experimental facilities (electrostatic storage rings, magnetoelectodynamic traps, ion traps) will enable research into these processes.

Relevance for Earth

- In Urey-Miller experiment amino acids formed in liquid
- Also tholines generated
- Amino acids and nucleobases formed from water
- Possible process on Early Earth?
- Happening on exoplanets?



nucleobases, Amino acids

Conclusions

- Reactions of CH_2CN^+ with acetylenehas several barrierless reaction pathways and can lead to larger nitrogen-containing entities
- 1-Cyano-2-propynyl cation could act as template for build-up of larger entities
- Reactions of $HCNH_2^+$/ CH_2NH^+ lead to larger ions under hydrogen atom elimination (amongst other products)
- Infrared photodissociation allows distinction between different isomers of ions
- Isomerism an issue even for small ions – photoionisation through synchrotron radiation can lead to selected isomeric species