Formation of biomolecule precursors in solar and extrasolar planets

Wolf D. Geppert
SRS meeting
Stockholm, March 2010

Basic building stones of biomolecules

- ★ Amino acids
- ★ Carbohydrates
- ★ Nucleobases
- ★ Fatty acids

How were they formed ?

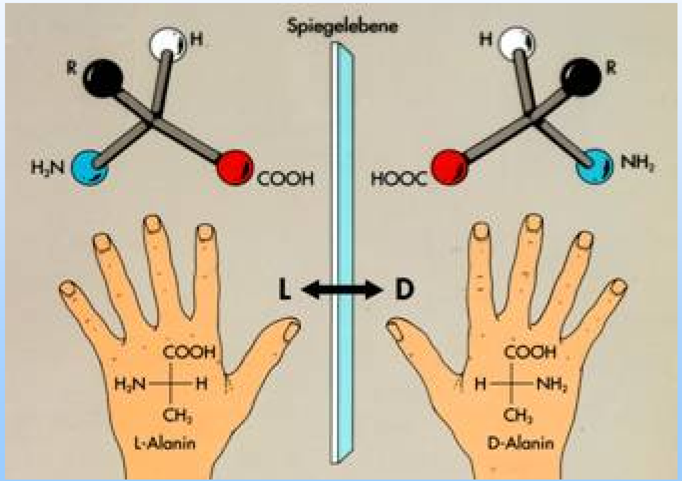
Urey-Miller experiment

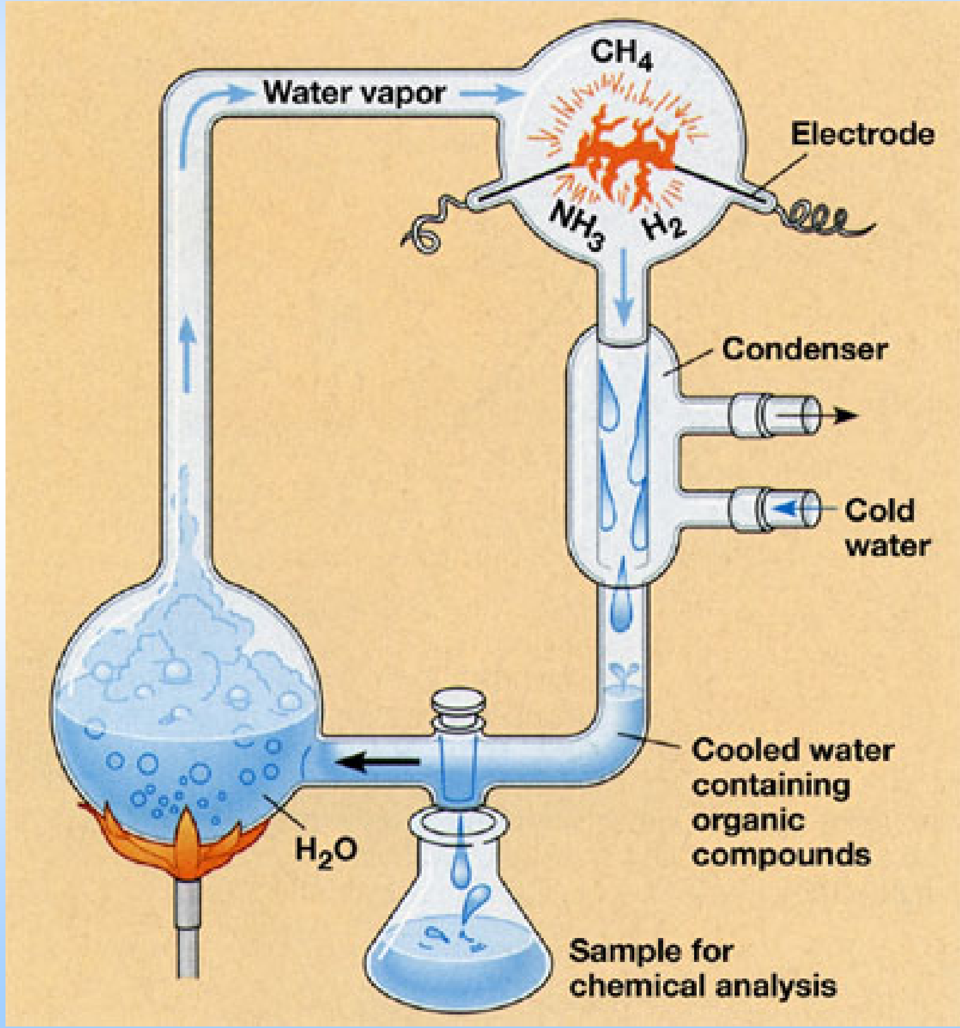
★ Formation of biomolecules in primeval soup under an atmosphere containing CH_4, NH_3, H_2

Problems:

optically active compounds produced as racemates

synthesis of biomolecules severely hampered by presence of O_2.





Biomolecules from space ?

- ★ Several amino acids found in the Murchison meteorite
- ★ enantiomeric excess (L-form) detected

Problem:
survival of biomolecules through star-forming phase doubtful (Ehrenfreund, 2006)
But: Precursors might survive ?

Where were biomolecule precursors formed ?

Delivery from space ?

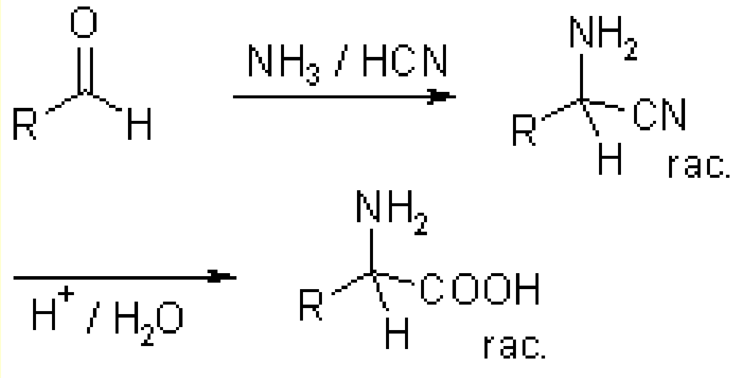
Atmospheric reactions on early Earth ?

Fragment of Murchison metorite

Murchison

Stable biomolecule precursors

Nitriles (R-CN)



★ Involved in the Strecker synthesis of amino acids

★ higher UV stabilty than corresponding acids (Bernstein et al. 2004)

★ more than 10 nitriles detected in the ISM

★ largest interstellar molecules are nitriles ($HC_{11}N$)

Alcohols (R-OH)

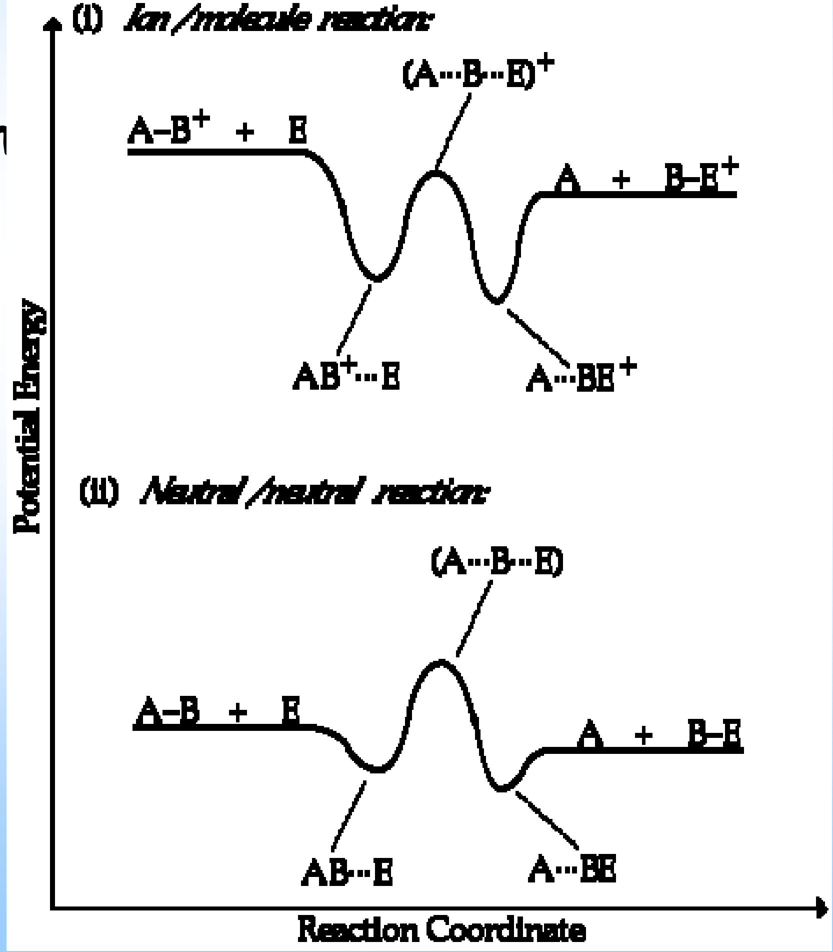
★ Can form carbohydrates by reaction with HCO of 10 longer

$$CH_3OH + HCO \rightarrow HOCH_2CHO + H$$

★ UV stable

Atmosphere of early Earth

- Probably nitrogen-methane dominated atmosphere
- Biomolecule precursors delivered Earth by impactors or synthesised in situ
- extensive UV-induced chemistry in ionosphere
- In ionospheres (low temperatures, low pressure) barrier-less two-body reactions favoured.
- Many radical and ion-induced reactions fulfil these criteria

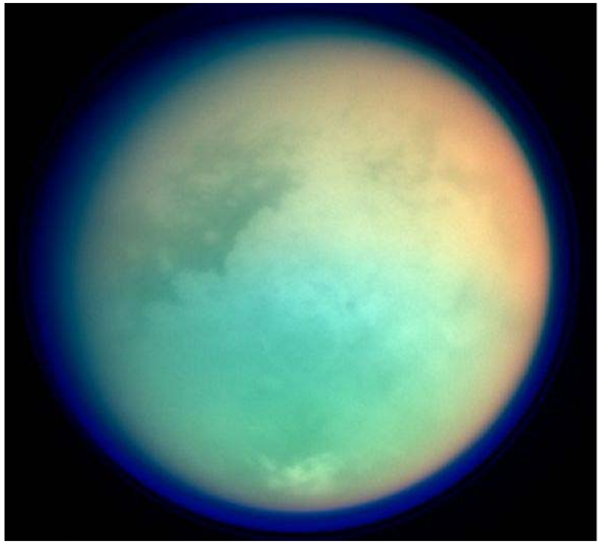


Can we study the chemistry of early Earth's Ionosphere ?

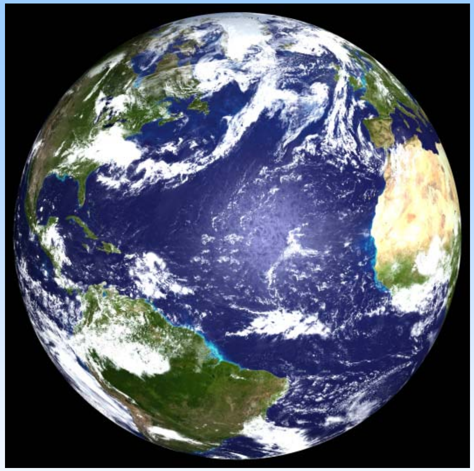
Titan's atmosphere

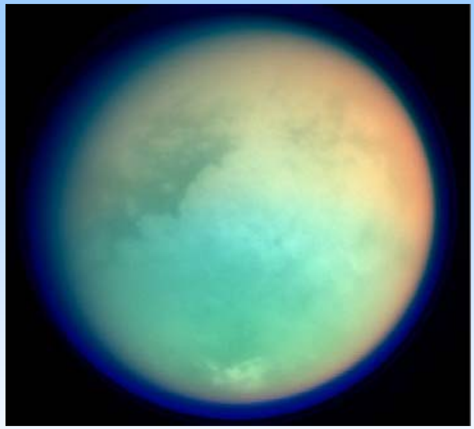
- ★ 147 kPa surface pressure
- ★ 94 % N_2, 6 % CH_4 + Ar
- ★ could resemble atmosphere of early Earth
- ★ Traces of hydrocarbons and nitrogen compounds
- ★ mixing extending to higher altitudes

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



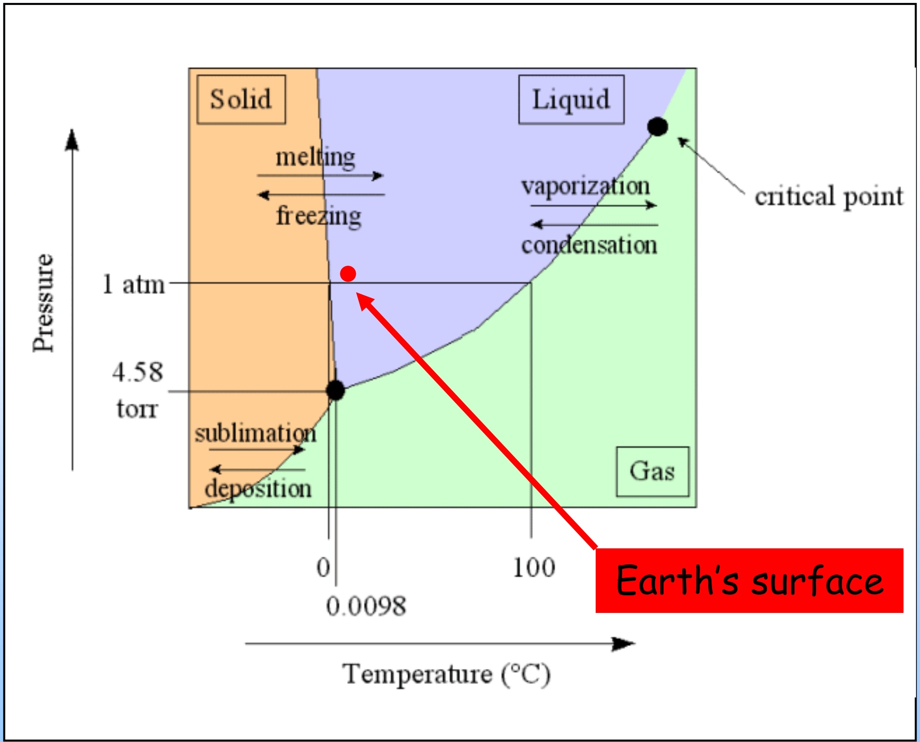
IR (above) and visible (below) picture of Titan

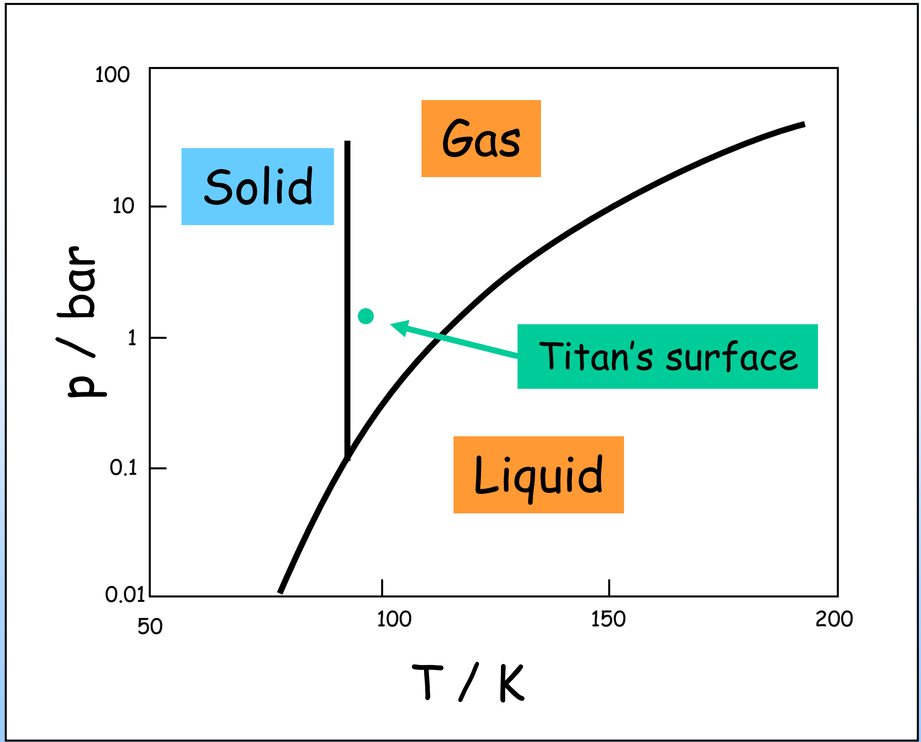




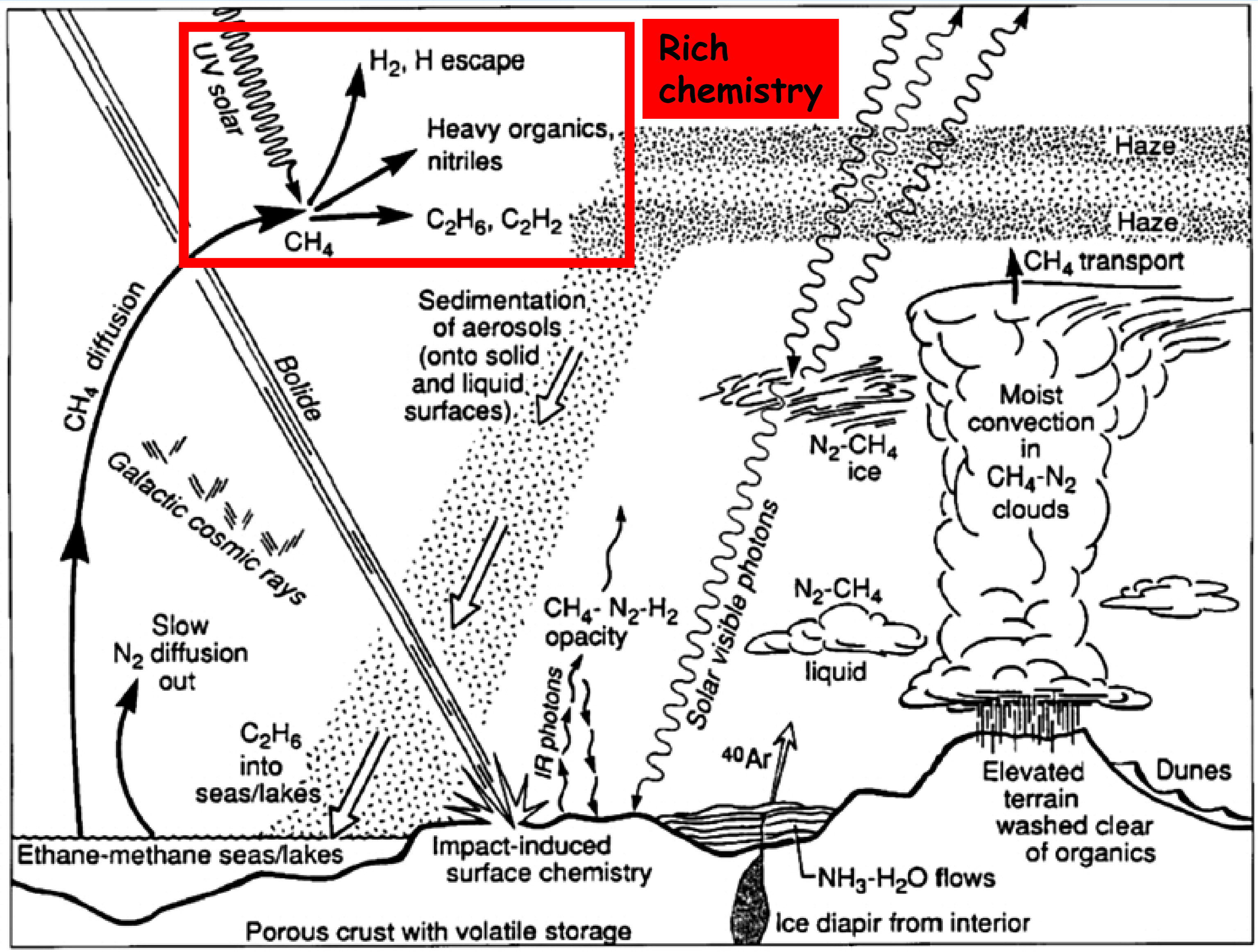
T near triple point of water !

T near triple point of methane !





Methane cycle on Titan



Chemical processes in ionospheres

★ absence of barrier requested & no third body processes

Ion-neutral reactions (e. g. radiative association, proton transfer)

$$A^+ + B \rightarrow AB^+ + h\nu$$

Ion-electron reactions

for molecules as good as exclusively dissociative recombination

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

Ion-ion reactions

mutual neutralisation

$$A^+ + B^- \rightarrow C + D$$

Radical-neutral reactions

$$A^\cdot + B \rightarrow \text{products}$$

Generation of radicals and ions in Titan's ionosphere

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

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:

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

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

Radical-neutral reactions

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

Rate constants and product branching ratios often unknown !

Models of ion reactions inTitan'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**

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

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

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

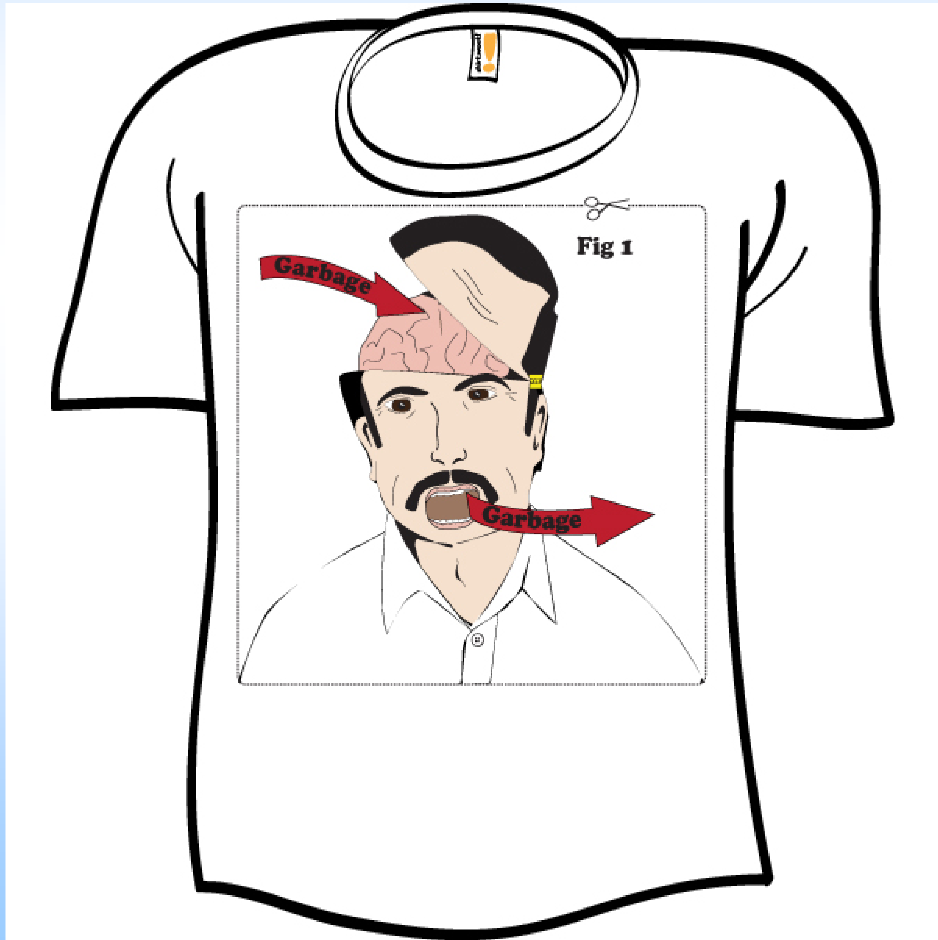
$N_n^+ + e^- \rightarrow$ products

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
Φ = transfer branching ratio
σ_n = ionisation cross section
α_i = dissociative recomb. rate constant
k = Transfer rate constant

Problems with models

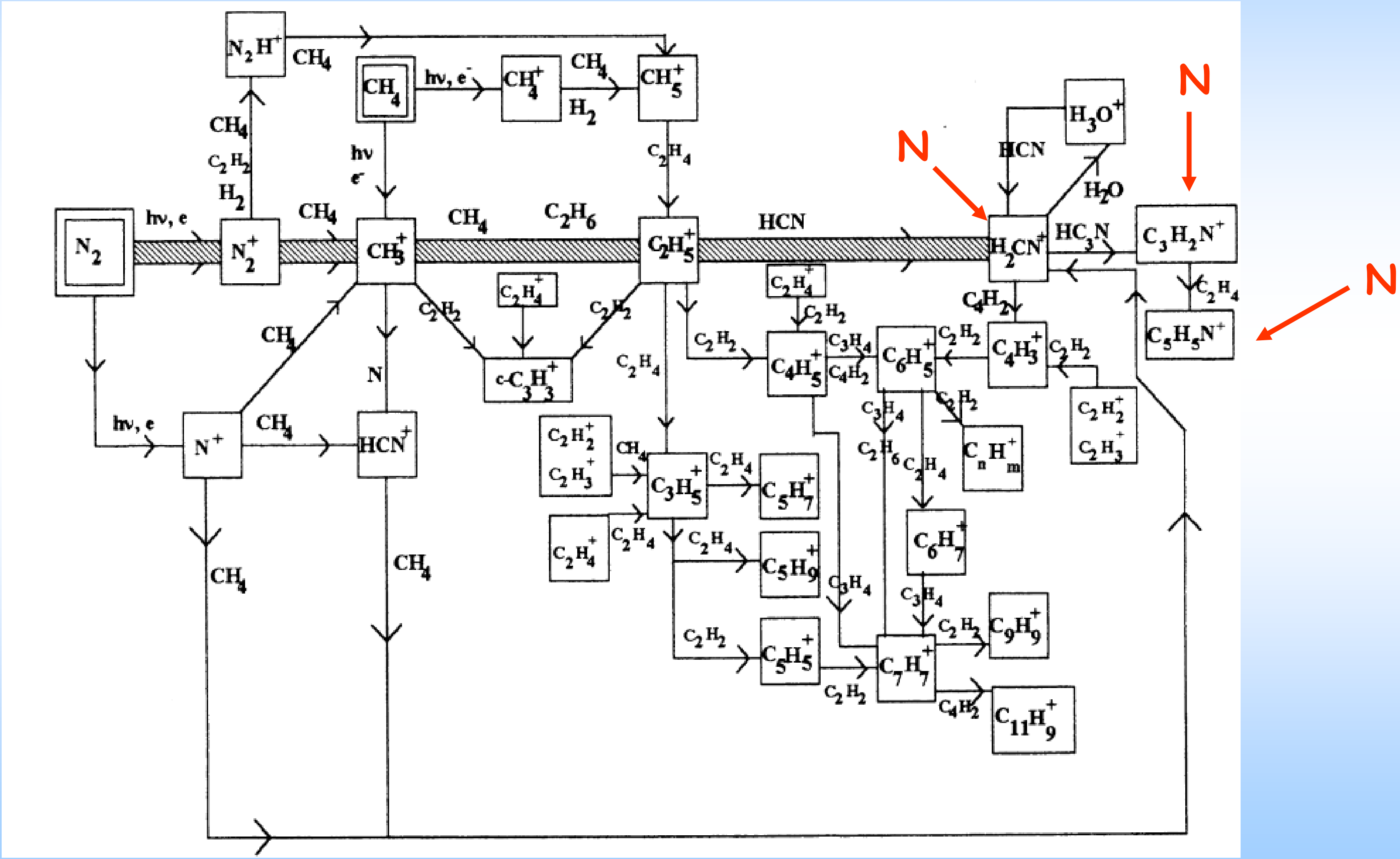
- ★ often separated, uncoupled models for ion and neutral chemistry

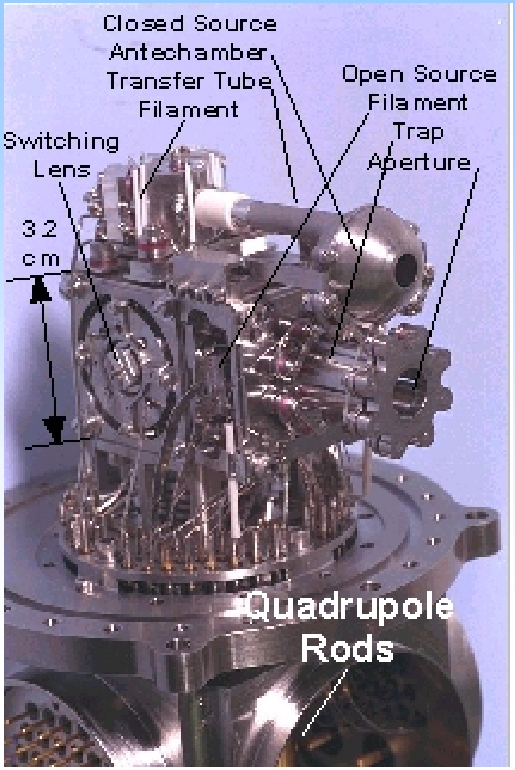
- ★ necessary data on reactions often lacking



Models of Titan's ionosphere

Old models: mostly protonated hydrocarbons formed



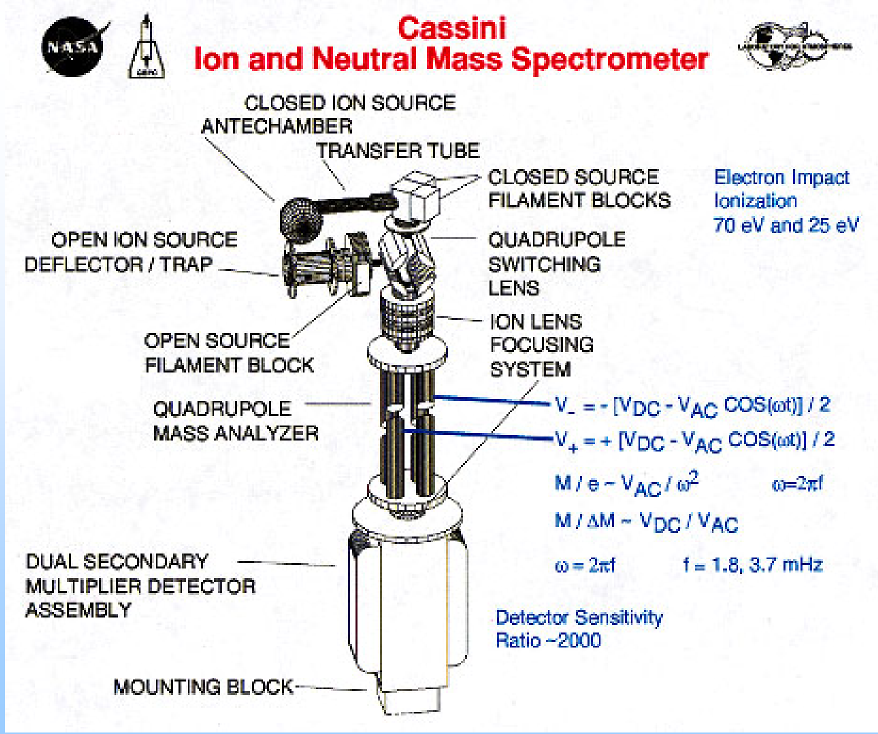


Dual inlet gas/ion source

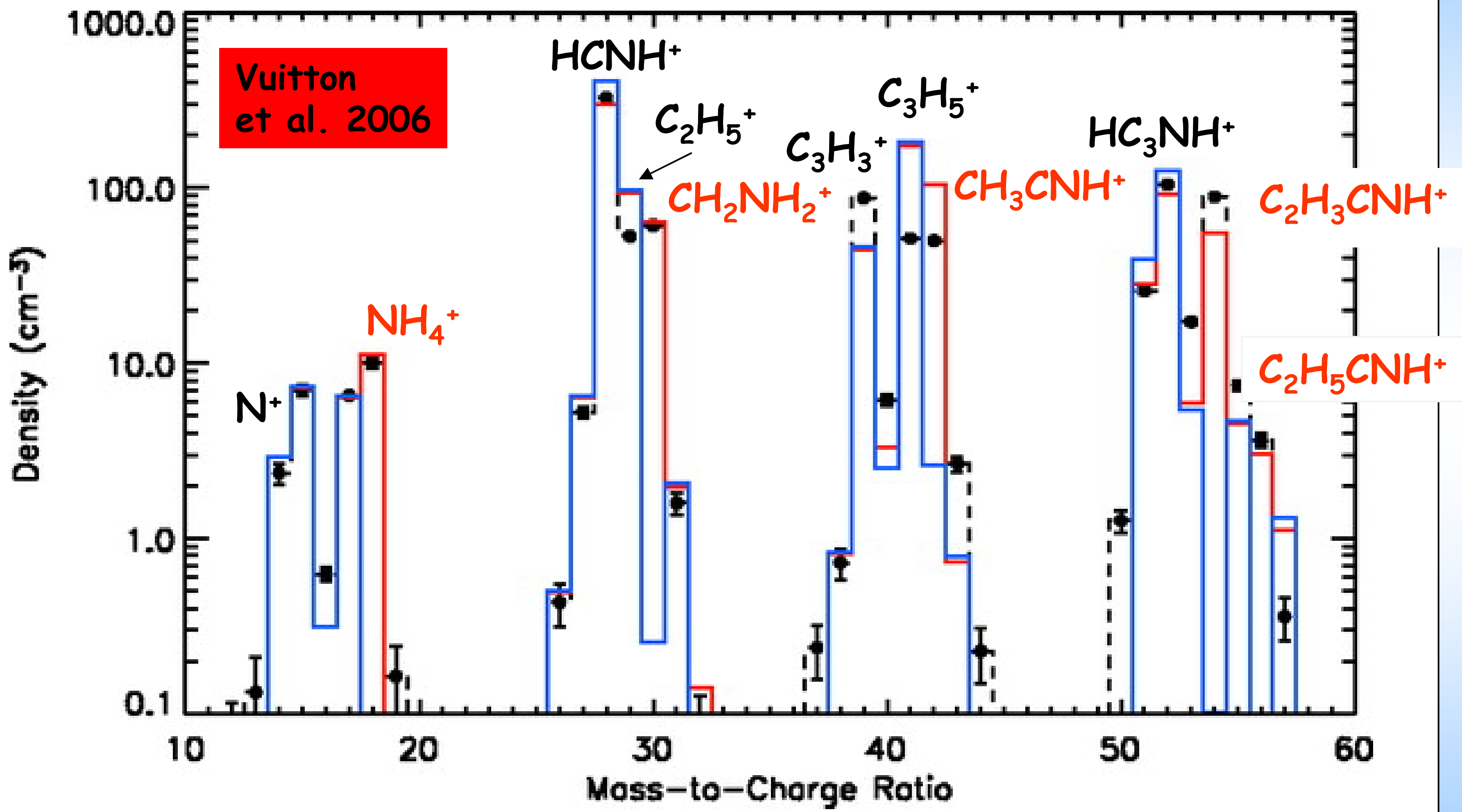
Ion-Neutral Mass Spectrometer (INMS) on board of Cassini

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

Nitrile formation: Acetonitrile (CH_3CN)

2 pathways of synthesis conceivable:

1.

$$C_2H_4 + N(^2D) \rightarrow CH_3CN + H + \text{other products}$$

Abundance of $N(^2D)$ unclear

★ Problem: Only 0.8 % CH_3CN production (Balucani et al. 2004)
But: other products can isomerise to CH_3CN

2.

$$CH_3^+ + HCN \rightarrow CH_3CNH^+$$

$$CH_3CNH^+ + e^- \rightarrow CH_3CN + H$$

Product branching ratio ?

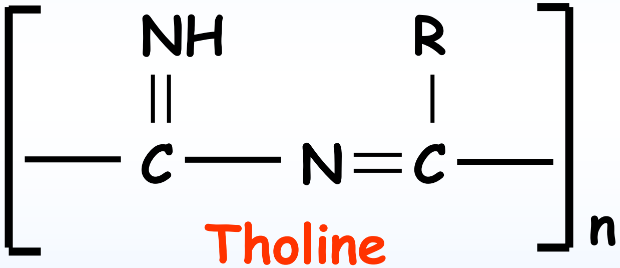
★ So far not included in models of planetary atmospheres

Nitriles 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

- Destroyed by sequence protonation – dissociative recombination ?

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

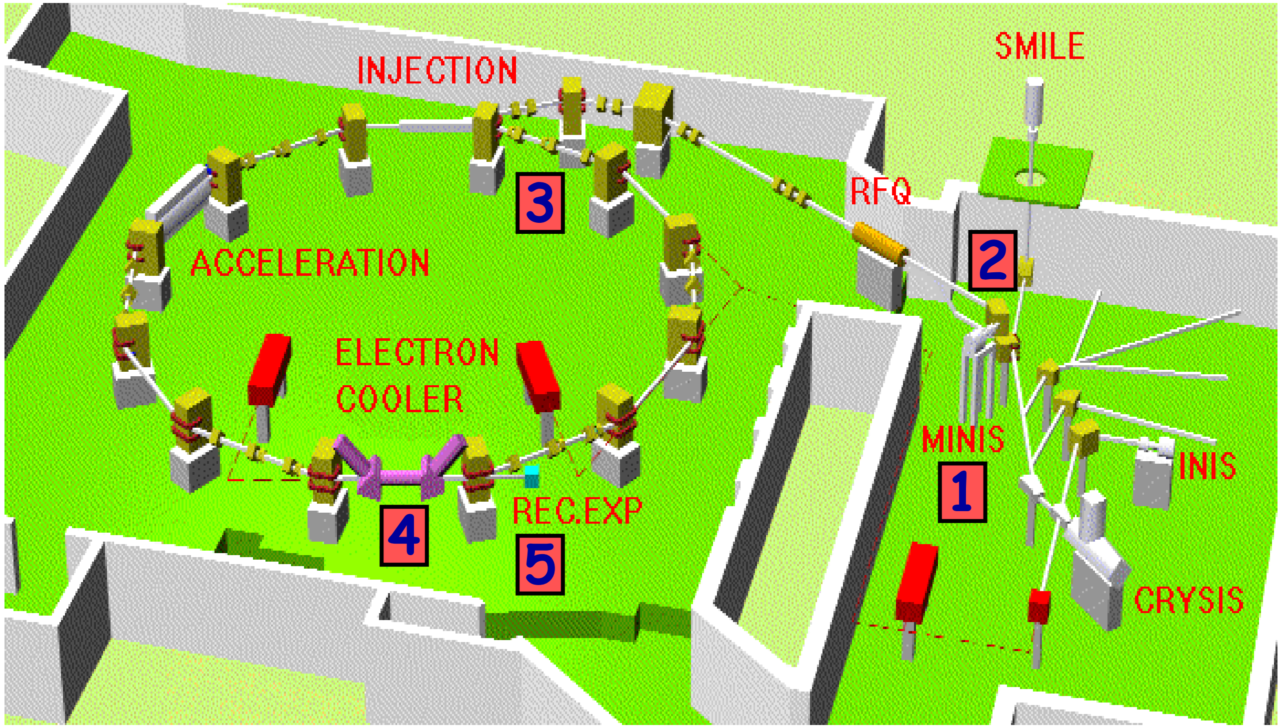
$RCNH^+ + e^- \rightarrow RCN + H$

$\rightarrow$ other products ?

Titan's haze layer

Tholine from the lab

The CRYRING storage ring



Schematic view of CRYRING

Steps during the experiment

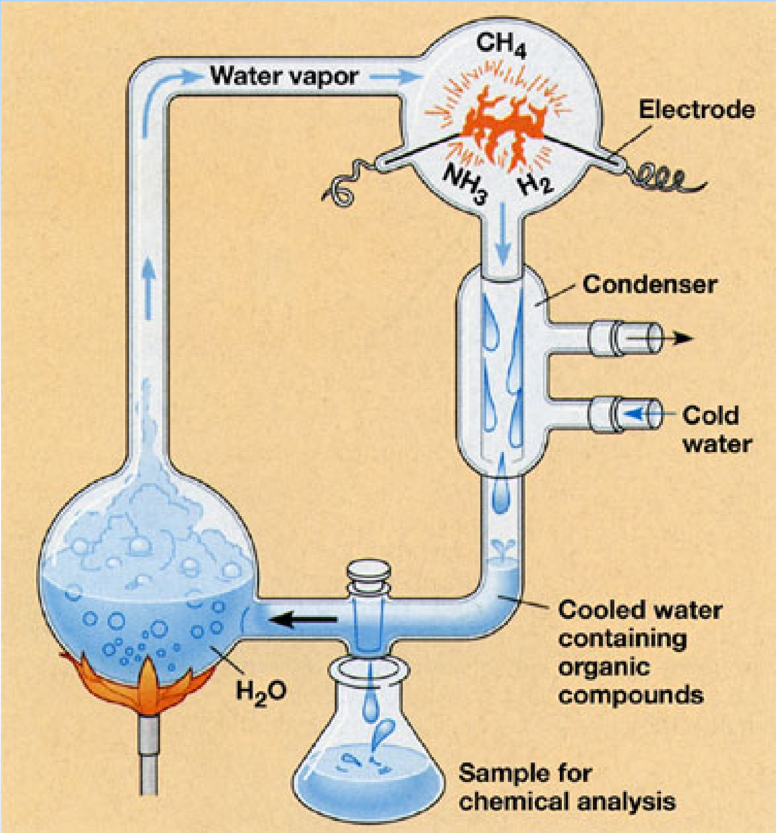
1. Formation of ions in source
2. Mass selection by bending magnet
3. Injection via RFQ and acceleration
4. Merging with electron beam
5. Detection of the neutral products

Dissociative recombination of protonated nitriles

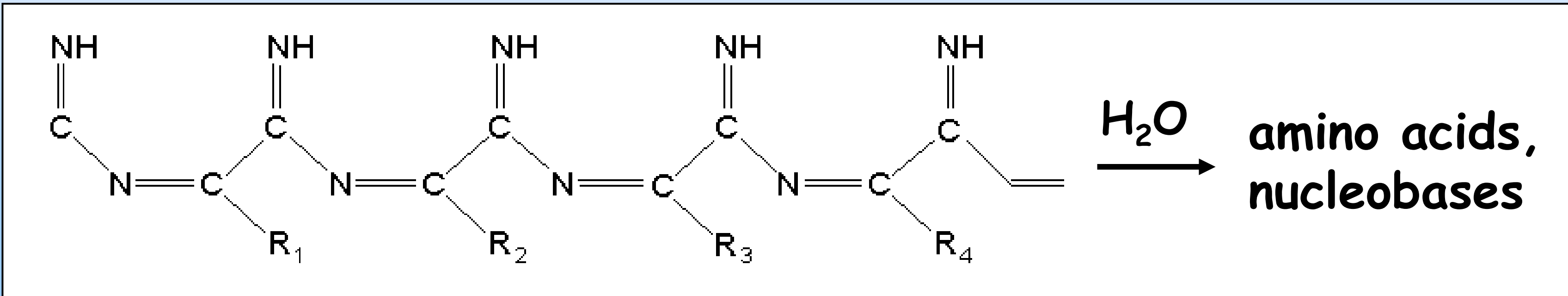
Ion	Rate constant / $cm^3 s^{-1}$	Probability of retention of carbon-nitrogen chain	Probability of break-up of one C-C or C-N bond
CH_3CNH^+	$8.1 \times 10^{-7} (T/300)^{-0.69}$	65 %	35 %
$C_2H_3CNH^+$	$1.8 \times 10^{-6} (T/300)^{-0.80}$	50 %	50%
$HCCCNH^+$	$1.5 \times 10^{-6} (T/300)^{-0.58}$	28 %	72 %

- ★ In $C_2H_3CNH^+$ and C_2H_3CNH+ mostly central C-C bond broken
- ★ Dissociative recombinations of protonated nitriles partly Recycles nitriles lost through protonation.
- ★ Other reactive fragments also formed.
- ★ Reactions possibly important for exoplanets and early Earth

Conclusions on early Earth's atmosphere

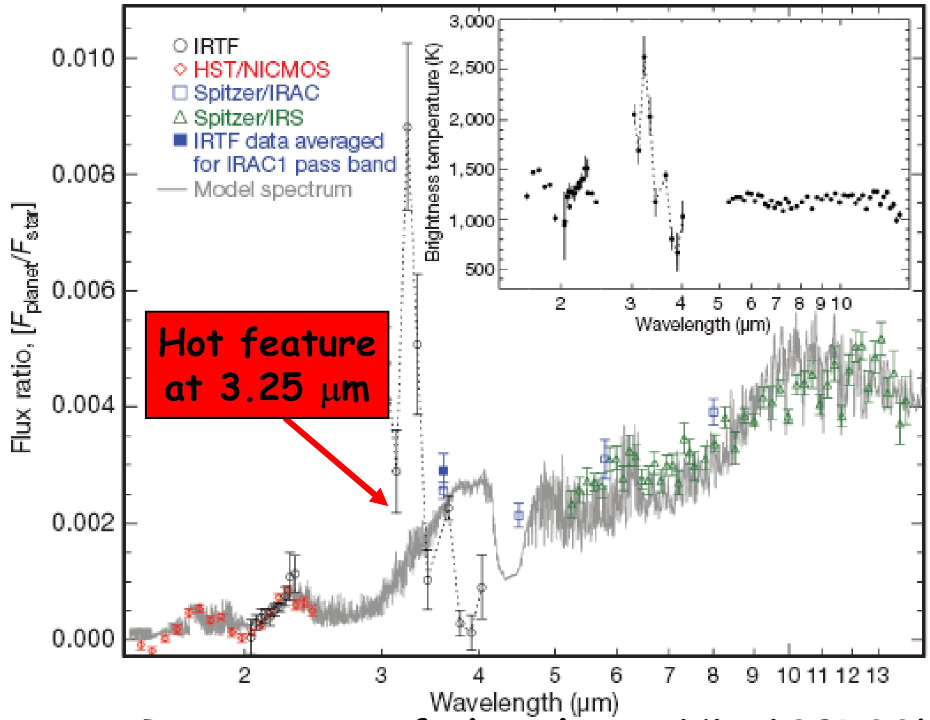


- ★ In Urey-Miller experiment amino acids formed in liquid
- ★ tholines also generated
- ★ lead to amino acids upon hydrolysis
- ★ feasible process on early Earth ?
- ★ happening on exoplanet ?



Atmospheres of exoplanets

- ★ CH_4 CO_2, CO and H_2O detected in Jupiter-like exoplanets.
- ★ In HD189733b "hot" methane (non-LTE) identified
- ★ No info on N_2-content
- ★ similar chemistry to early Earth/Titan possible



IR -spectra of the planet HD 189733b (Swain et al. 2010)

Acknowledgments

★ My colleagues at Stockholm University: M. Hamberg, E. Vigren, R. D. Thomas, M. Kaminska, M. Larsson …...

★ CRYRING team at Manne Siegbahn Laboratory: A. Källberg, A. Simonsson, A. Paál …....

★ SRS for invitation