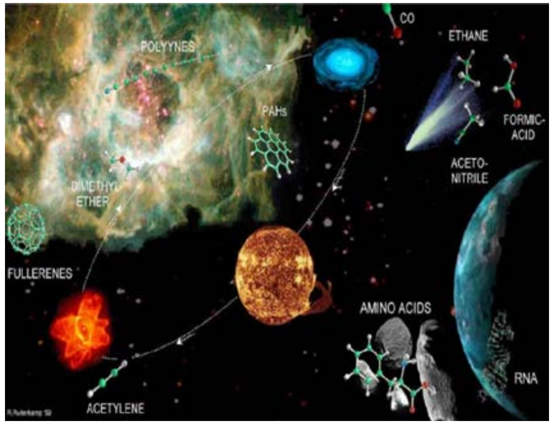

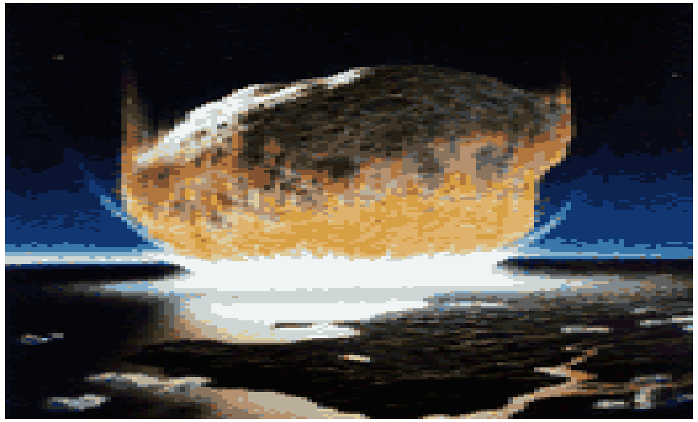

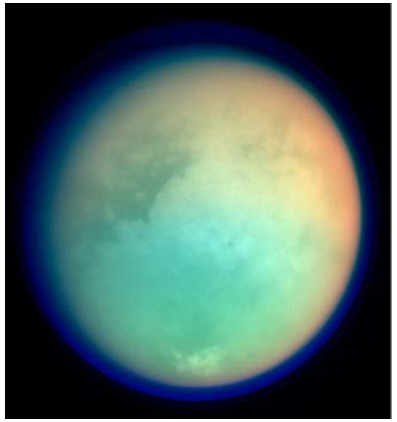

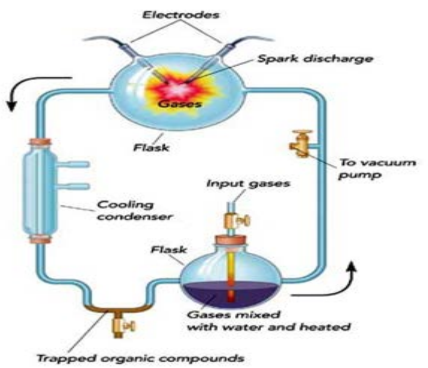

Understanding the Molecular Complexity of Astrochemistry
Laboratory synthesis of prebiotic species

europlanet

Nigel J Mason
The Open University

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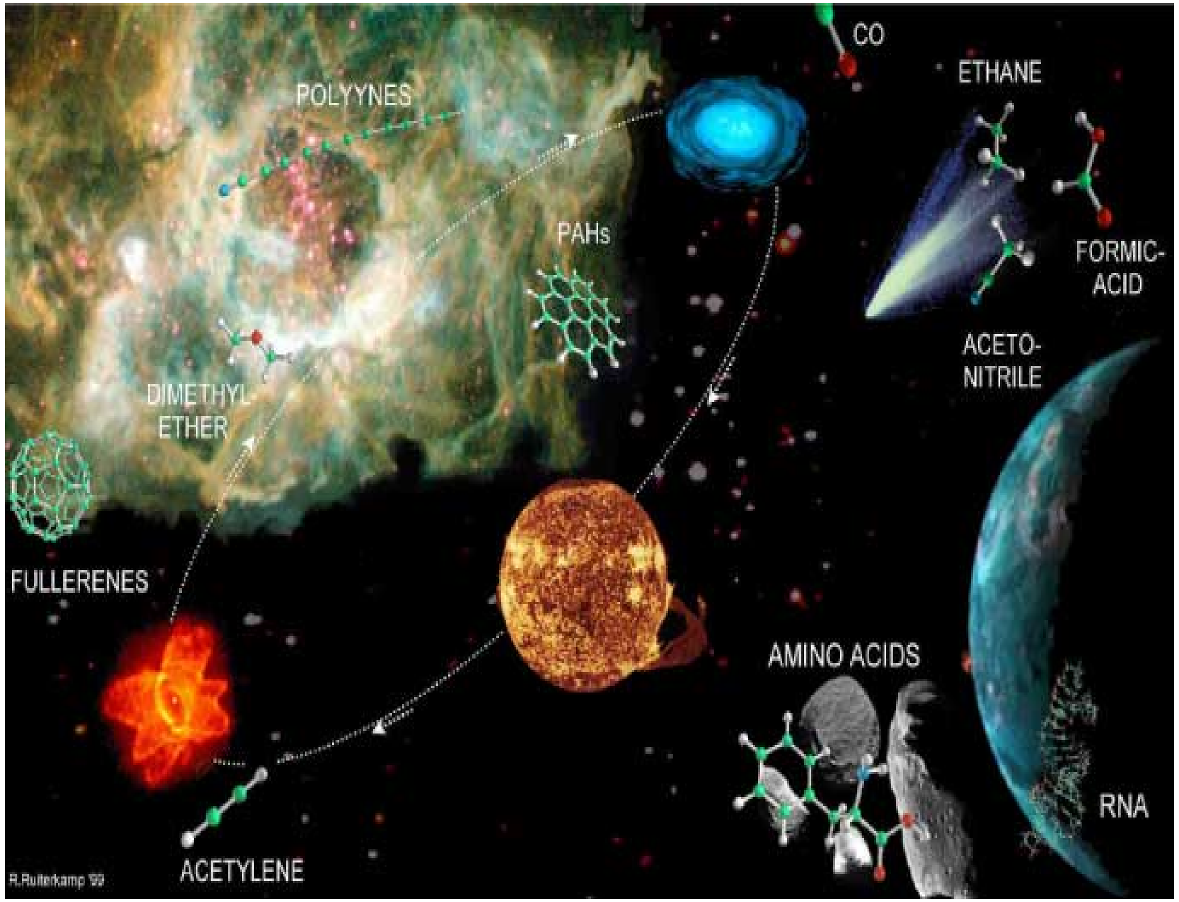
Core Questions for Astrochemistry & Astrobiology

- Where are the building blocks of life synthesised ? ISM or on planet?
- Are the conditions for such synthesis common/universal ?
- European Astrobiology Roadmap. Published 2016



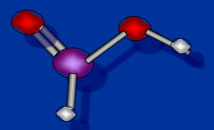
Outline

- **Ice studies**
- Introduction – summary of previous talks
- Laboratory studies - Methodology
- Electron induced chemistry - some conclusions

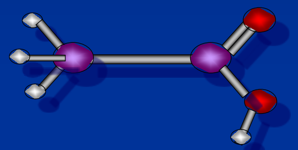
- Atmospheric Chemistry
- Urey Miller synthesis
- Plasma studies – ion chemistry

>140 Interstellar and Circumstellar Molecules

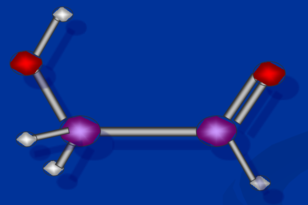
2	3	4	5	6	7	8	9	10	11
H_2	C_3	c-C_3H	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N?	HC_9N
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	
AlCl	C_2O	C_3N	C_4Si	C_2H_4	CH_3C2H	CH_3COOH	$(CH_3)_2O$	NH_2CH_2COOH ?	12
C_2	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH		C_6H_6
CH	CH_2	C_3S	c-C_3H_2	CH_3NC	NH_2CH_3	H_2C_6	HC_7N		
CH^+	HCN	C_2H_2	CH_2CN	CH_3OH	$HCOCH_3$	CH_2OHCHO	C_8H		13+
CN	HCO	CH_2D+ ?	CH_4	CH_3SH	c-C_2H_4O				$HC_{11}N$
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	CH_2CHOH				PAHs
CO^+	HCS+	HCNH+	HC_2NC	HC_2CHO					$C60^+$
CP	HOC+	HNCO	HCOOH	NH_2CHO					
CSi	H_2O	HNCS	H_2CHN	C_5N					
HCl	H_2S	HOCO+	H_2C_2O						
KCl	HNC	H_2CO	H_2NCN						
NH	HNO	H2CN	HNC_3						
NO	MgCN	H_2CS	SiH_4						
NS	MgNC	H_3O^+	H_2COH^+						
NaCl	N_2H+	NH_3							
OH	N_2O	SiC_3							
PN	NaCN								
SO	OCS								
SO+	SO_2								
SiN	c-SiC2								
SiO	CO_2								
SiS	NH_2								
CS	H_3^+								
HF	SiCN								
SH	AlNC								
FeO									



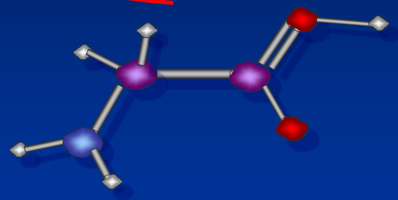
Formic Acid



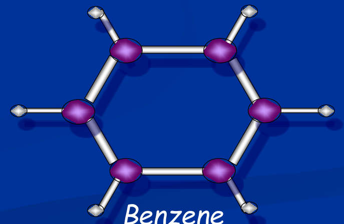
Acetic Acid



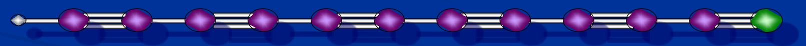
Glycolaldehyde



Glycine ?



Benzene



Cyanopolyynes

National Radio Astronomy Observatory

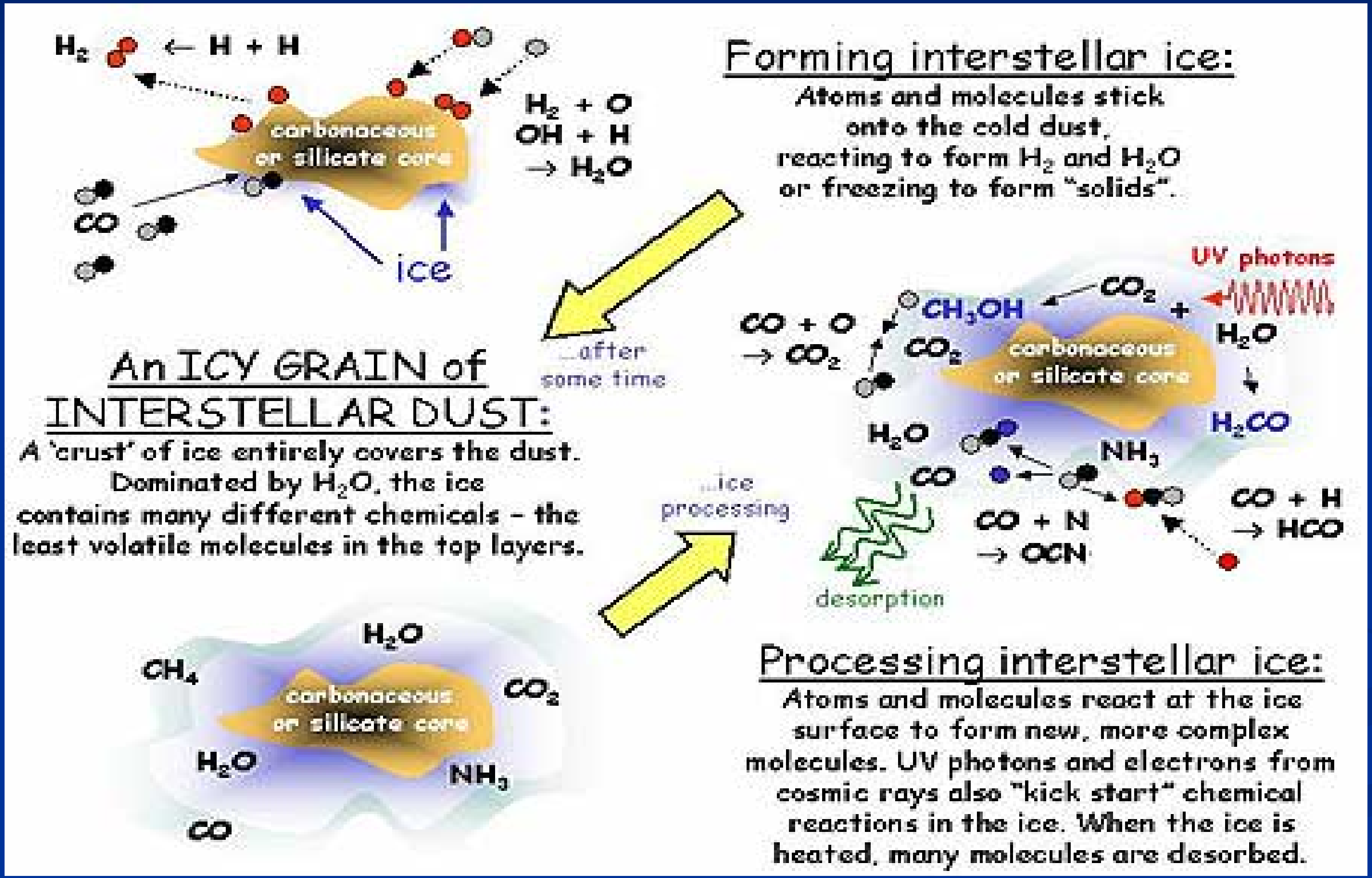
http://www.cv.nrao.edu/~awootten/allmols.html

Astrochemistry

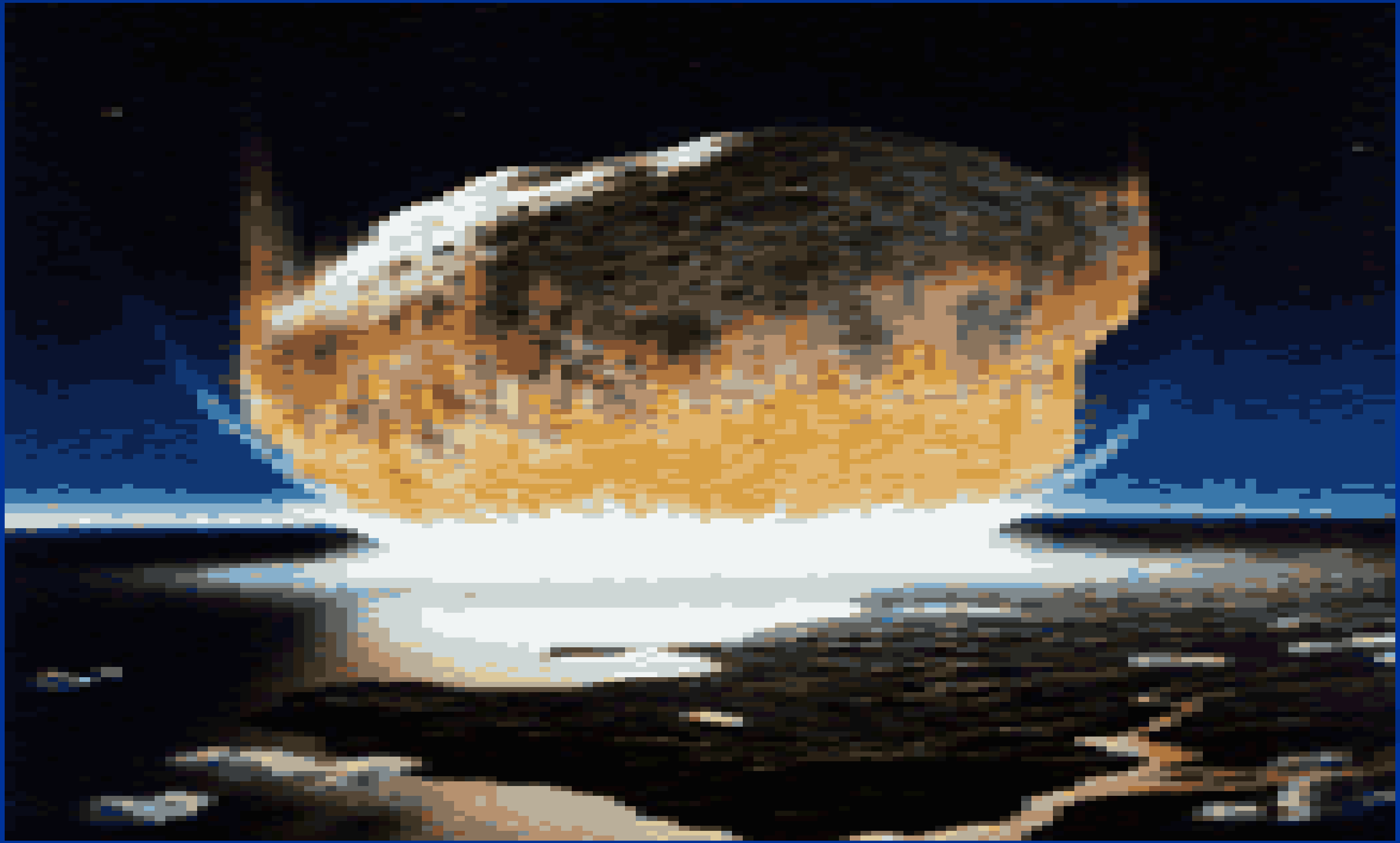
- How is such rich inventory of molecules created?

We have a dusty grain picture

Molecular synthesis on dust grains

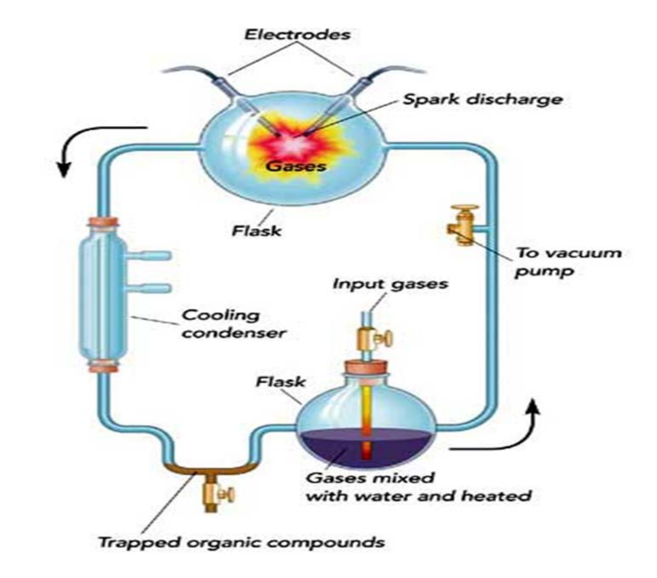


Building products delivered to planets



But ….

- Remember reactions can occur in gas phase
- First molecules had to be formed without dust (no stars)
- **And molecules of life may be synthesised in planetary atmospheres**



Ion –molecule reactions

Ion-Molecule reactions are a typical example of a reaction that do not require energy input

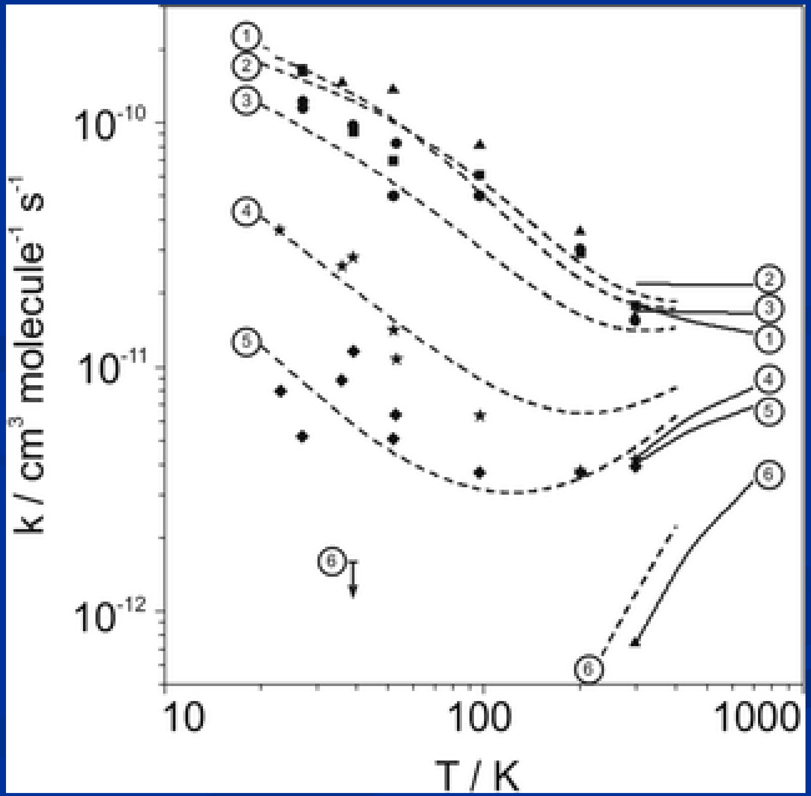
e.g.

$NH_3^+ + H_2 \rightarrow NH_4^+ + H$

$Ar^+ + H_2 \rightarrow ArH^+ + H$

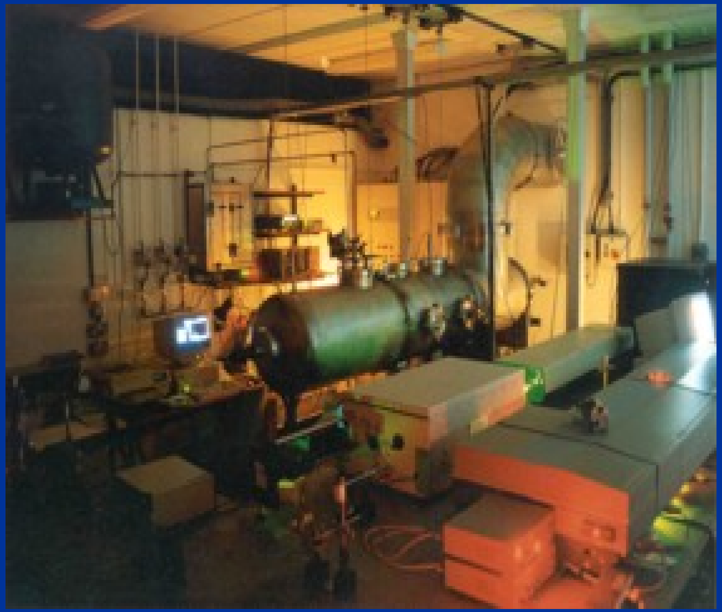
$He^+ + H_2 \rightarrow He + H^+ + H$

$H_2^- + H \rightarrow H + H_2 + e-$



Ion molecule studies

CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) to study neutral-neutral reactions and energy transfer processes in the gas phase down to temperatures as low as ~10 K. (Rennes)



But lets go back to dust …

Gas phase experiments can not explain all the chemistry in the ISM

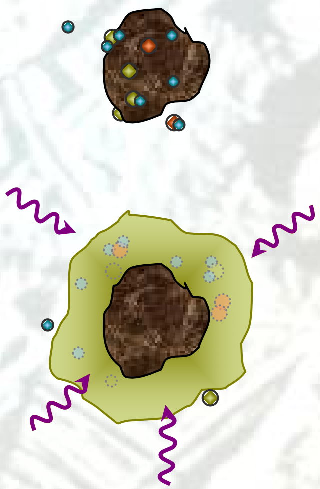
E.g. the formation of H_2 …. the most common molecule in the ISM can not be formed in the gas phase in quantities required

Instead it is formed by reactions on the surface of little dust grains …

Chemistry on Dust grains

- **Some of these grains are covered with an icy mantle formed by freezing out of atoms/molecules from the gas phase**

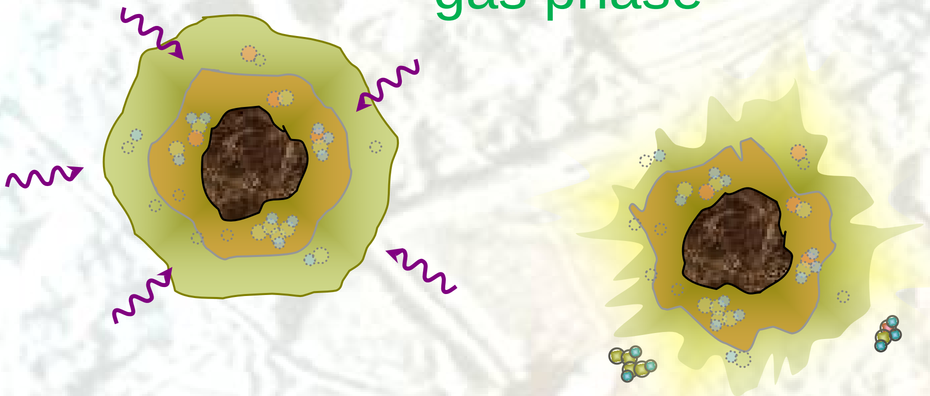
- **Hence we need to explore ice chemistry !**



•The ices in the mantle are bombarded with cosmic rays, Ions, solar UV, electrons.

•Chemistry occurs making molecules.

•Desorption back to gas phase



How to make the ISM in the lab ?

- **We need to mimic the conditions of the ISM as accurately as we can**

We need

- **Mimic of dust grain surfaces**
- **ISM Is COLD**
- **ISM is empty**
- **To mimic radiation sources**

- **Plus we need methodology to probe results !**

Making nothing !!

- Space is empty
- More empty than we can reproduce in the laboratory
  - **Typically experiments that explore such astrochemistry iare performed at pressures of P~10^{-8} - 10^{-10} mbar**
    - **Still > a million times higher than ISM!**
- But why is this a problem ??

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Making nothing

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- Even at P~10^{-8} - 10^{-10} mbar there is enough residual gas to freeze out on your sample and form a contamination layer !!
- Thus during your experiment you are depositing molecules from vacuum
- Most common contaminants are WATER, CO/CO_2 and hydrocarbons –all molecules you may want to explore and can play role in chemistry
- Best vacuum after bake our remove water and dry pumps reduce hydrocarbon content
- Distinguish background CO/CO_2 by using ^{13}C $_{as}$ target carbon (just more expensive)
- It is expensive making nothing and time consuming !!!

Getting (really) cold

- **How do make surface cold --- 10K ??**
- **Use coolant**
- **LN_2 takes you to 77K**
- **Liquid helium (4K) but not 100% efficient – IR radiation from walls of chamber heat your sample**
- **Liquid helium is expensive (more than whisky per litre !) world shortage So recycle it**

Dust grain mimics

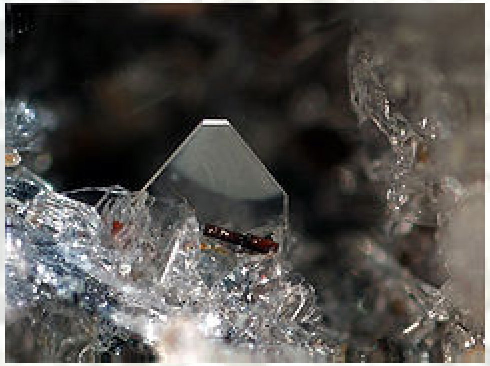
- What are they made of ?

- Carbon ?
- Silicates

One good substrate is

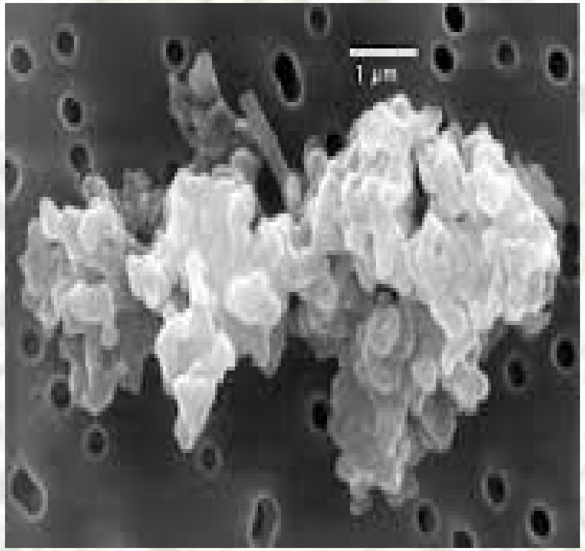
- Olivine $(Mg,Fe)_2SiO_4$.

- But is non conducting



Dust Grain mimics

- **But the grains are small .... micron or nano scale !!**
- **To date experiments have used bulk samples Cm in size (few, VERY FEW exceptions)**
- **Is chemistry and ice morphology same on micron/nano surface as on bulk ?**
- **How does struture effect diffusion? Desorption ? etc**



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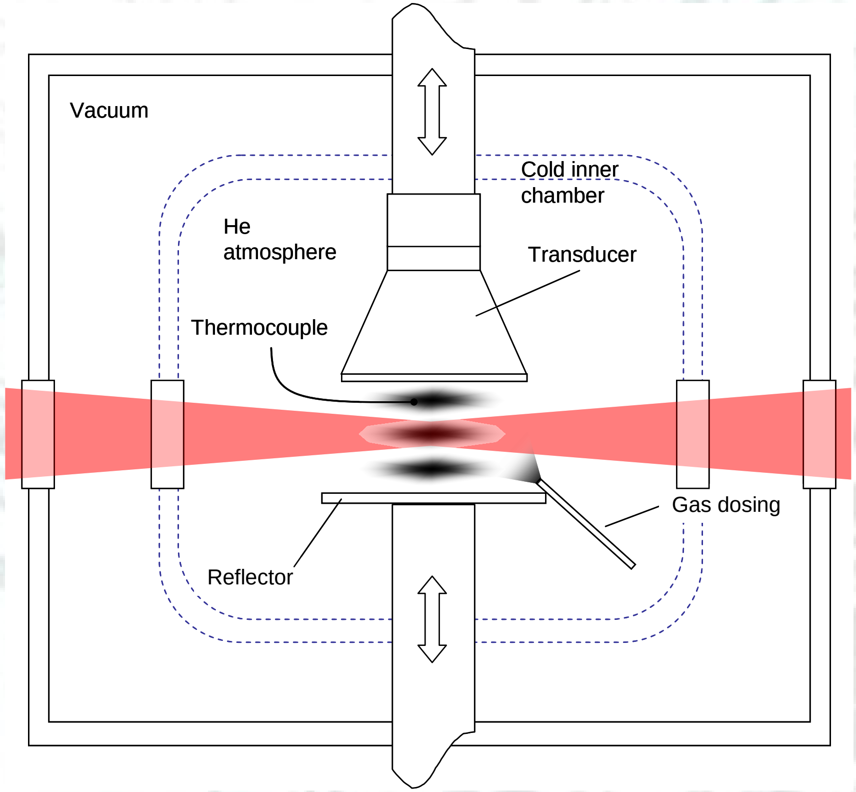
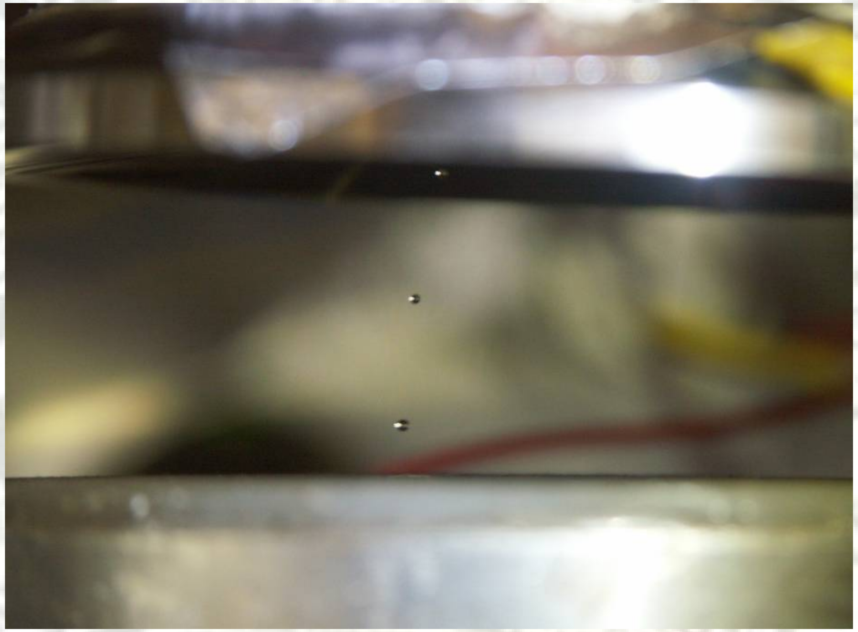
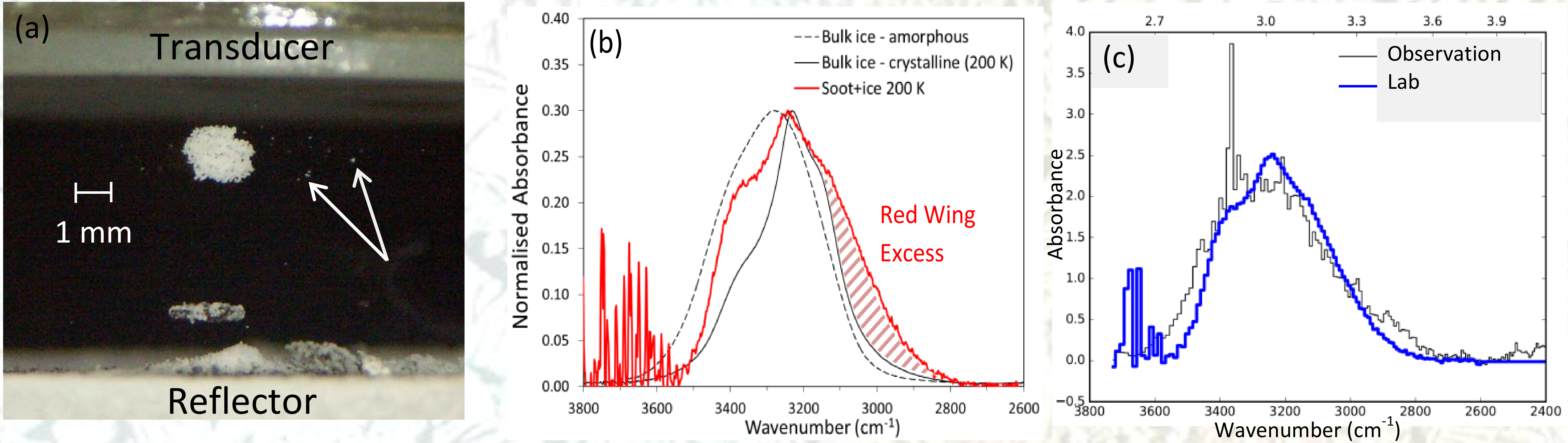
Ultrasonic dust trap





- **IR of water ice on carbon dust in a levitatation trap**
- **Spectra match water ice specta recorded by AKARI in star forming region.**



What about time ?

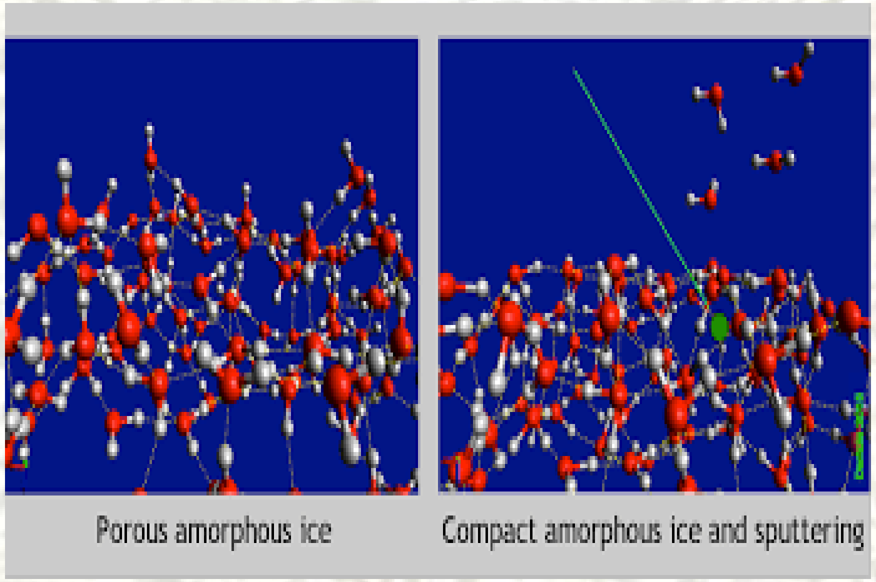
- In space events take time

- 1 molecule absorbed a day/week/month !
- 1 collision every few years !

- **Yet in lab we speed it up !**

- Are ices formed so slowly in space same morphology as ices formed in lab ?
- Do collisions scale with fluence - can we replicate synthesis in lab via fluence ?

- ***We have to assume time is not important is this true ?***
- ***This requires modelling of molecule by molecule ice film growth***



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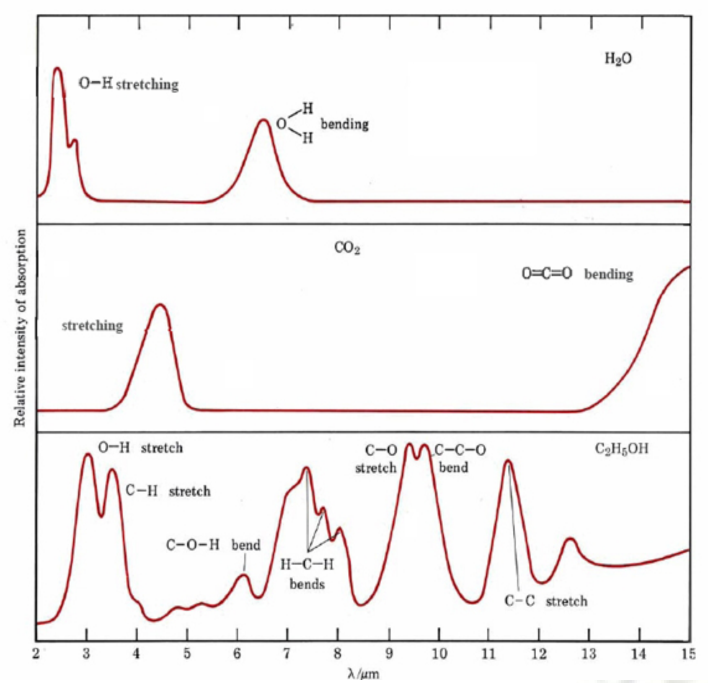
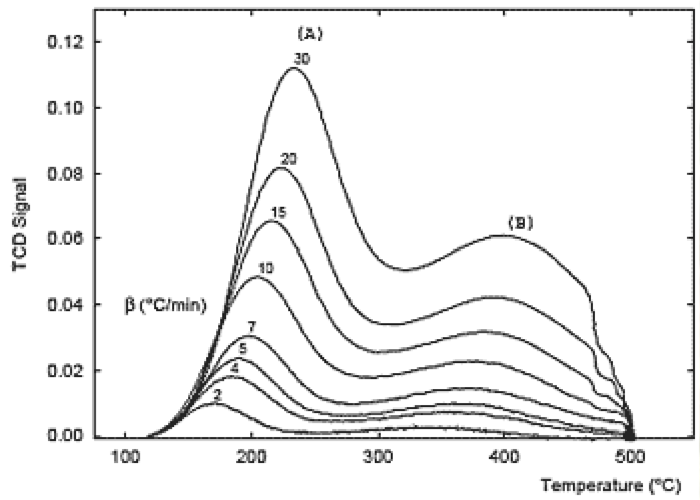
How do we monitor chemistry ?

- **Spectroscopy** --
InfraRed (via FTIR or Raman)
or Ultraviolet



- If we desorb from surface may use Mass spectrometry

- TPD Temperature Programmed Desorption)



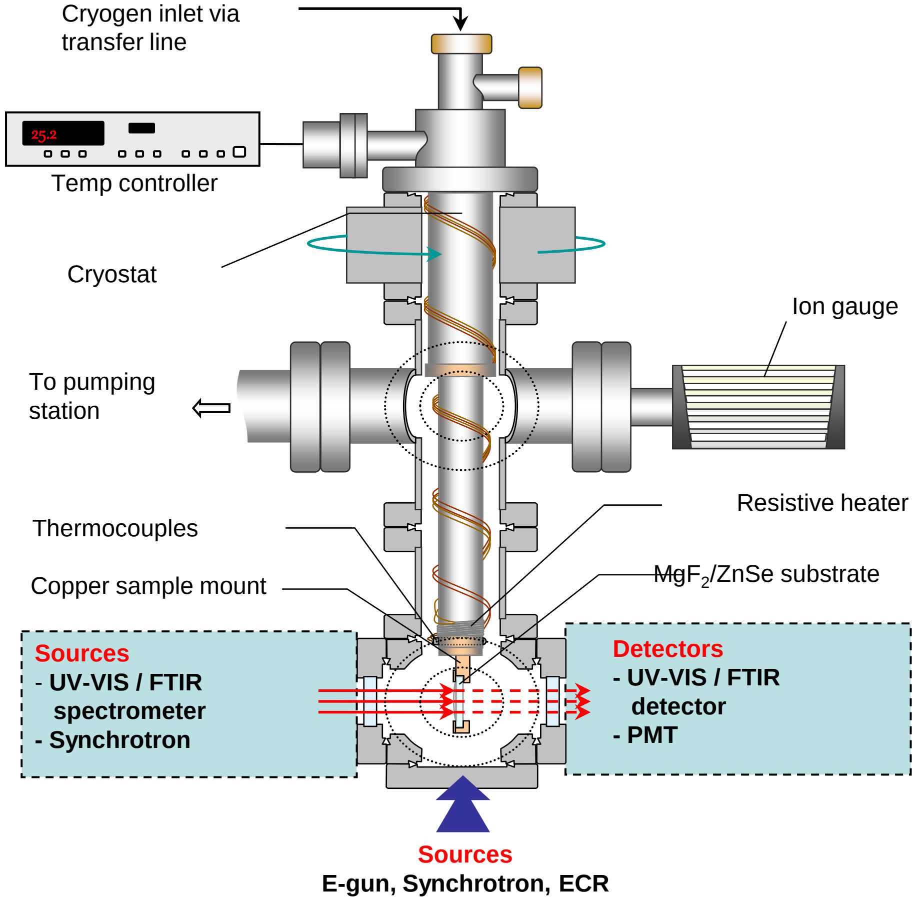
Experimental Programme at the OU

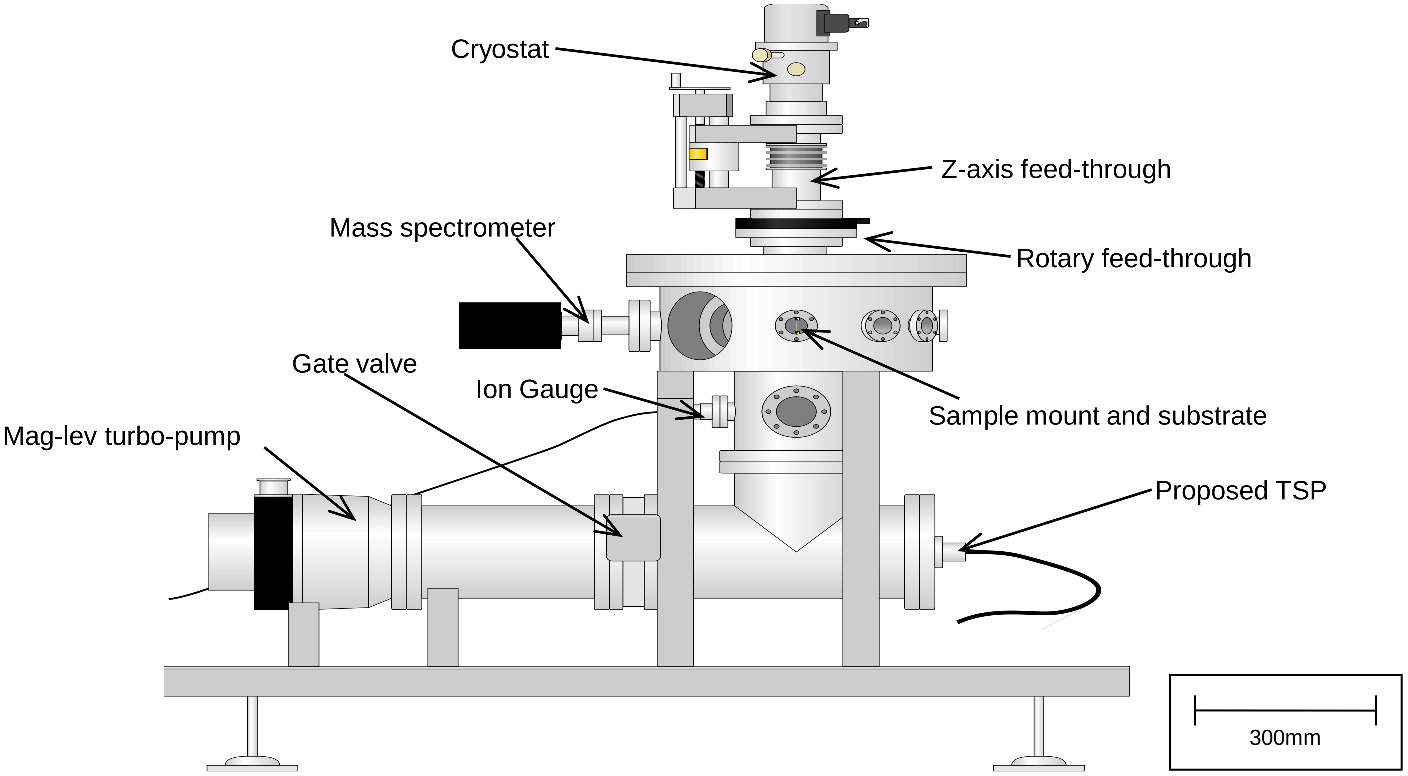
OU Portable System:

- Transmission UV & FTIR Spectroscopy and Processing
- Designed to be transported to central facilities → Synchrotrons, RAL, QUB

OU Static System:

- TPD, RAIRS and Processing
- Molecular synthesis with electrons and photons → E-gun, UV lamp





Energetic Sources

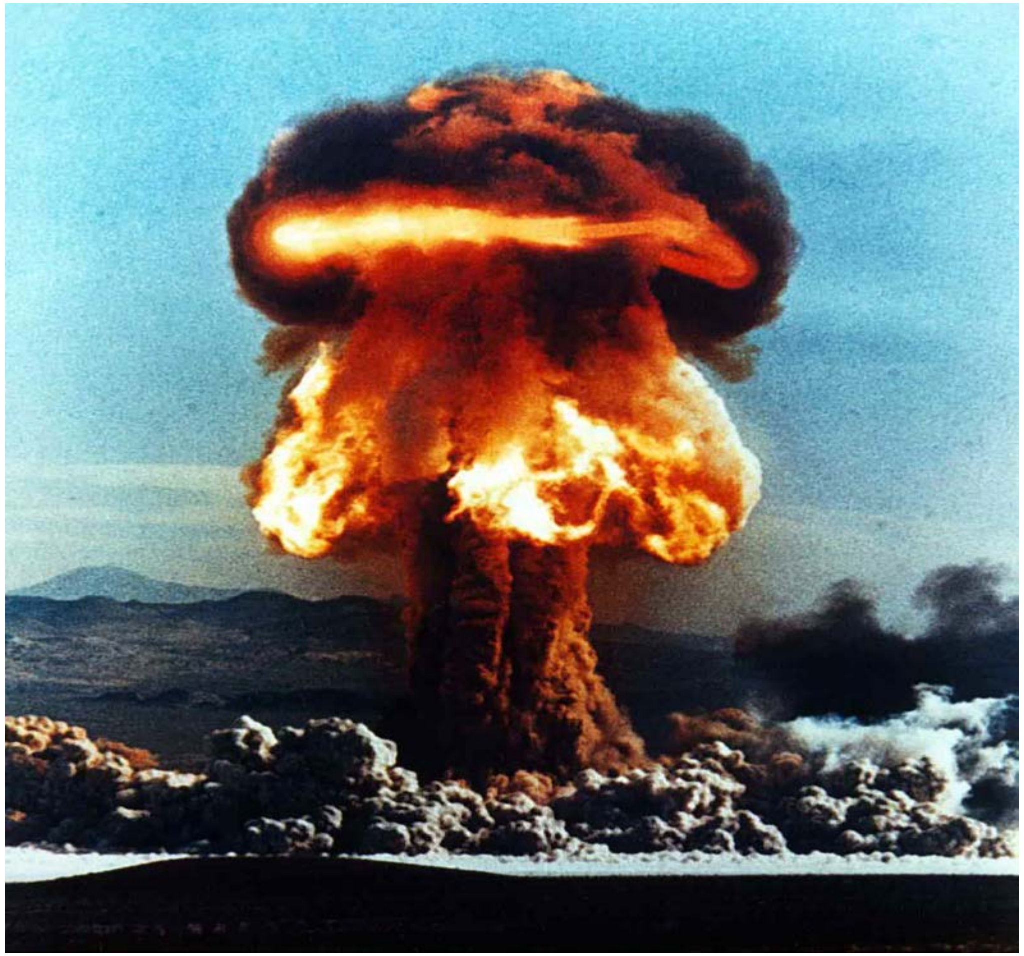
- **VUV light**
- **Ion beams**
- **Electron beams**

Experimental studies of chemical processing of astrochemical ices

First we need to find a mimic of star light !

Stars are fuelled by nuclear reactions

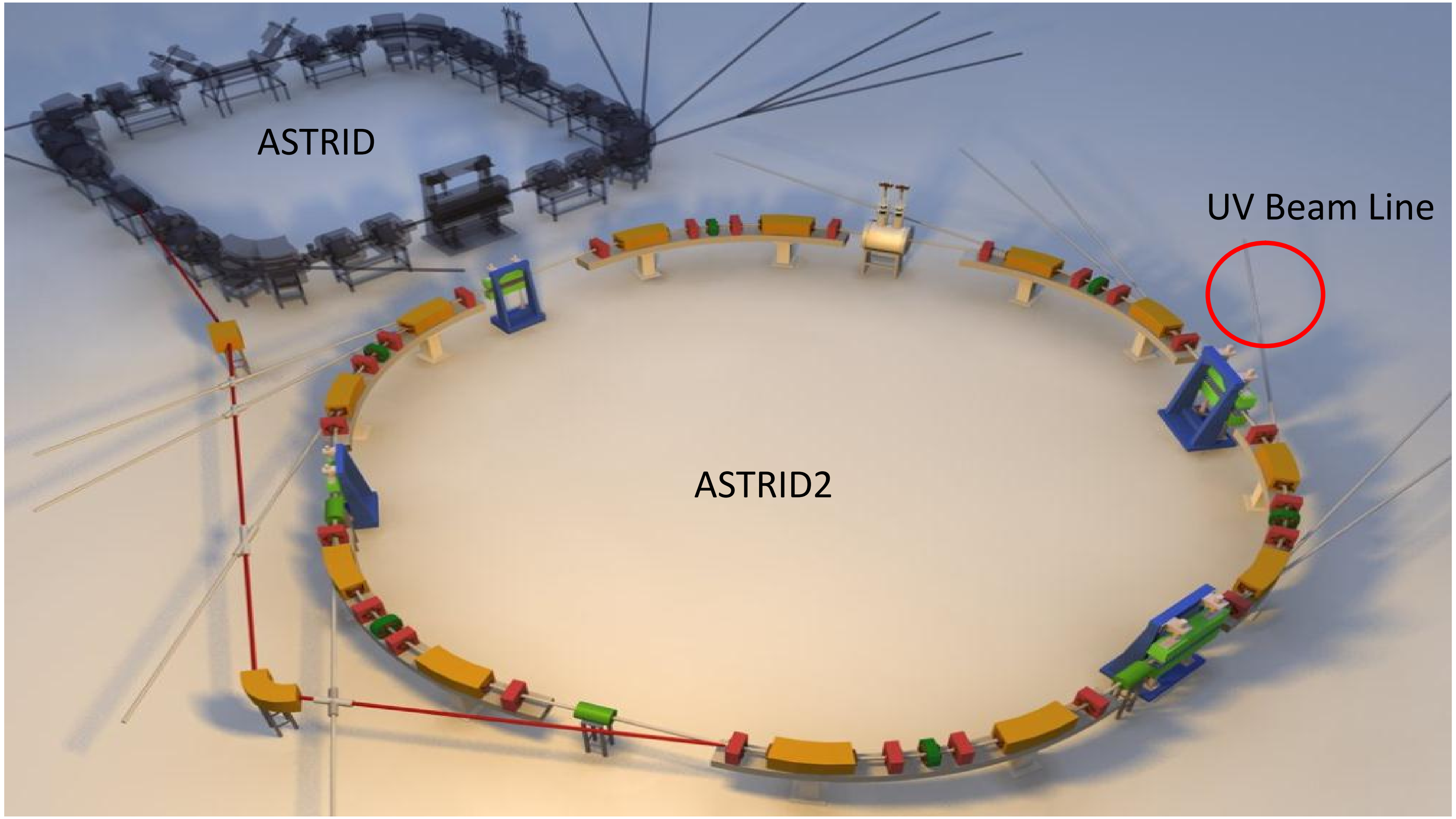
We can't use these in a laboratory



ASTRID2

"The Ultimate Synchrotron Radiation Source"

ISA- Institute for Storage Ring Facilities,
Department of Physics and Astronomy, University of Aarhus



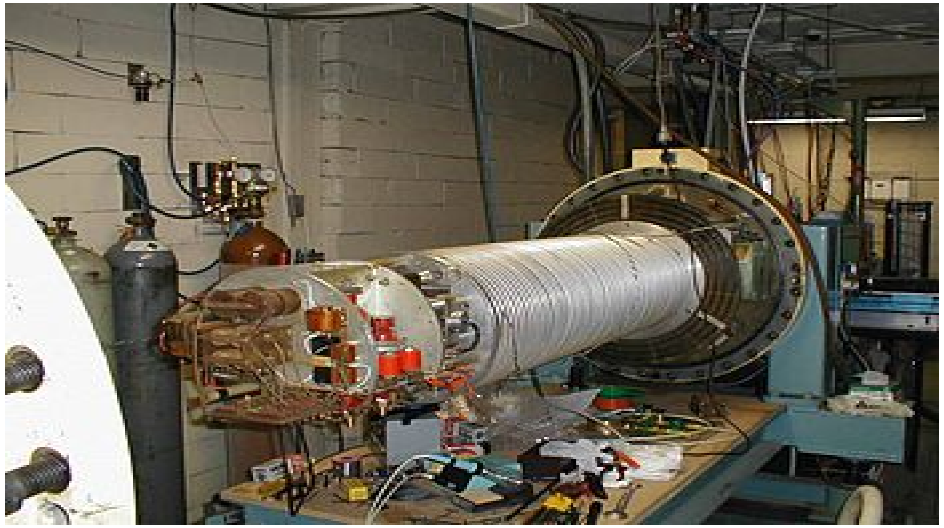
Energy = 580 MeV
Circumference = 45.7 m
Lifetime = Infinite (top-up)

How do we study Cosmic Ray (CR) induced chemistry ?

To study CR chemistry we need to;

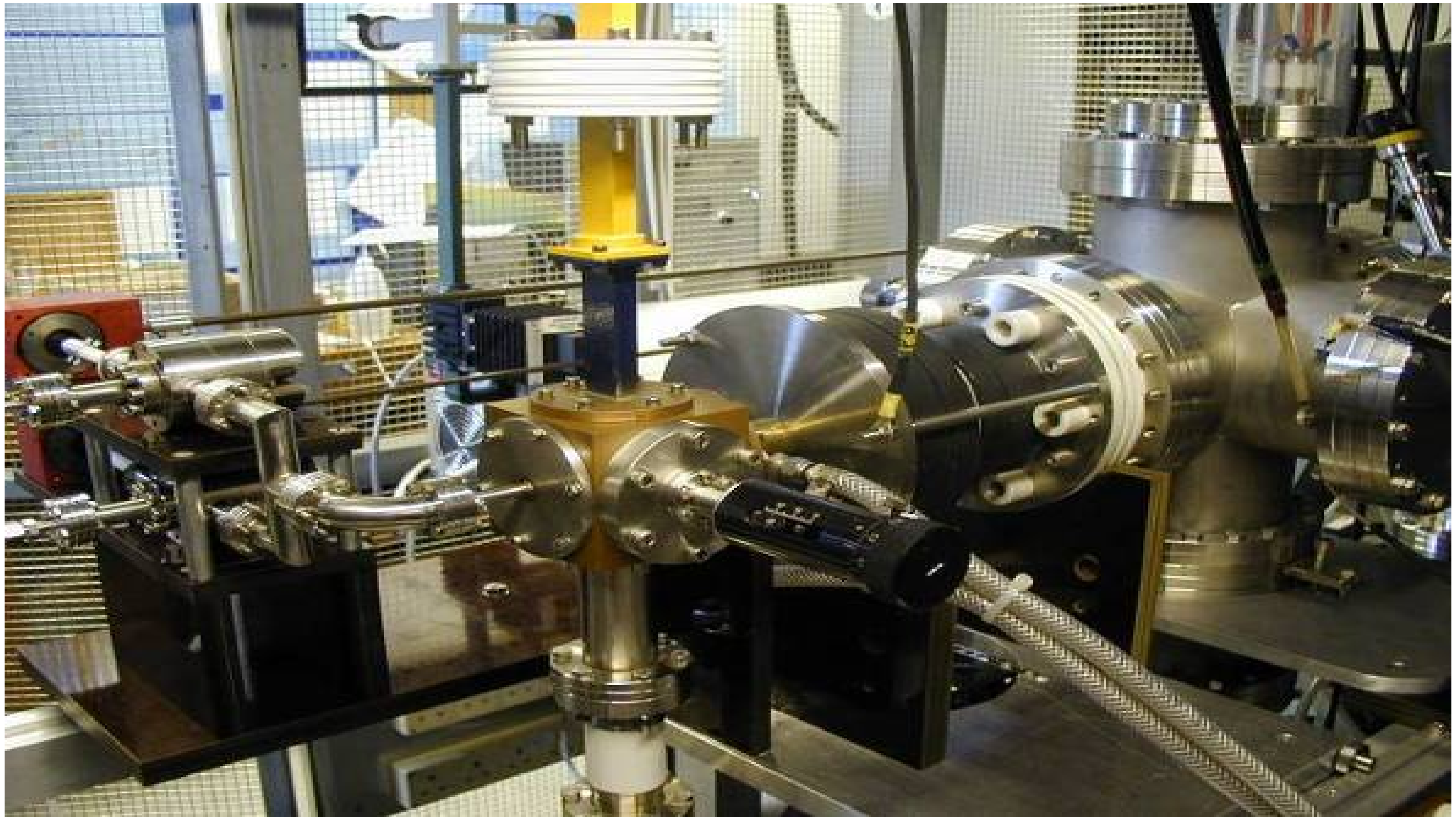
1. **Produce beams of CRs – protons, alpha particles and electrons**
2. **Accelerate CRs to high energies**

Use particle accelerators - Van der Graf Accelerators



Modern version ECRIS Ion source

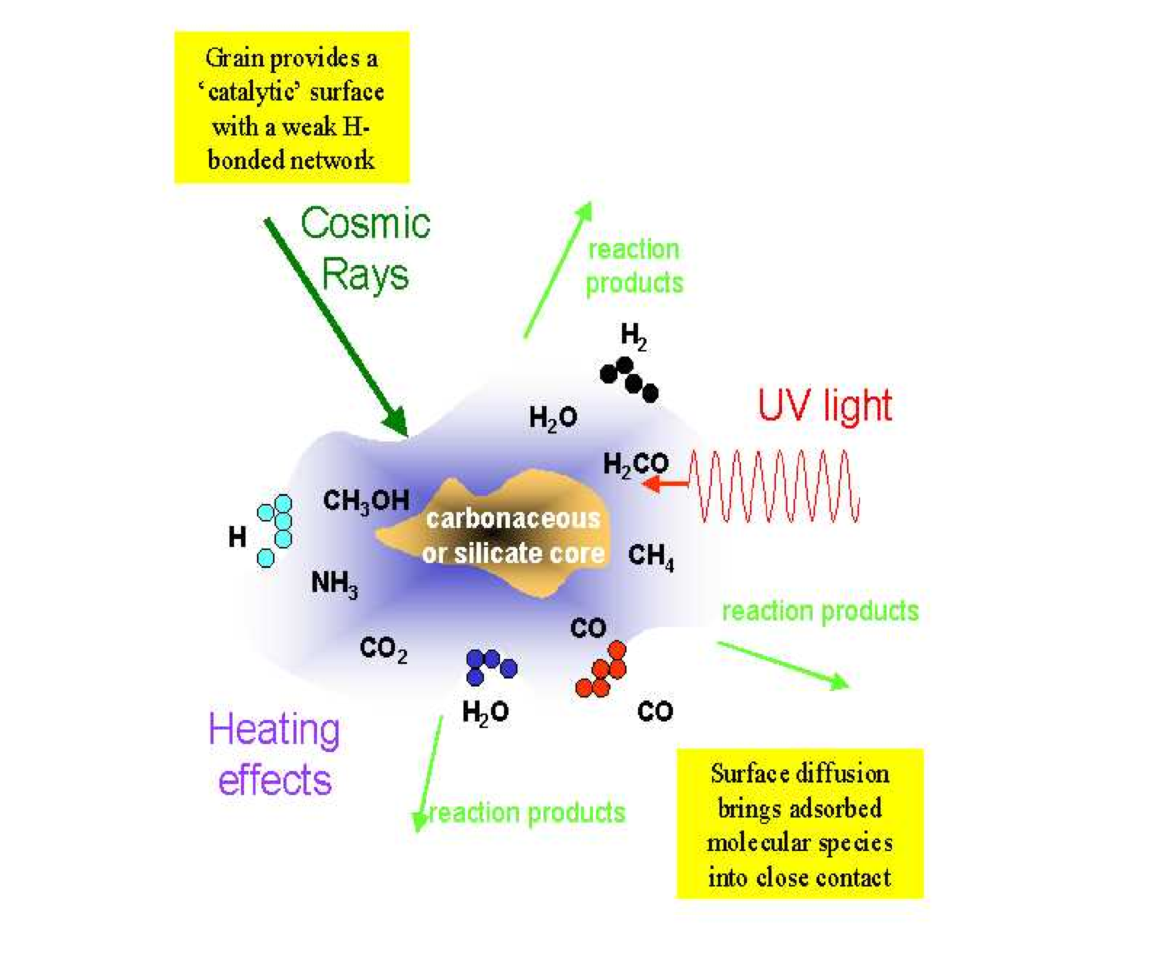
9.0 – 10.5 GHz Electron Cyclotron Resonance Ion Source at Belfast



Role of electrons ?

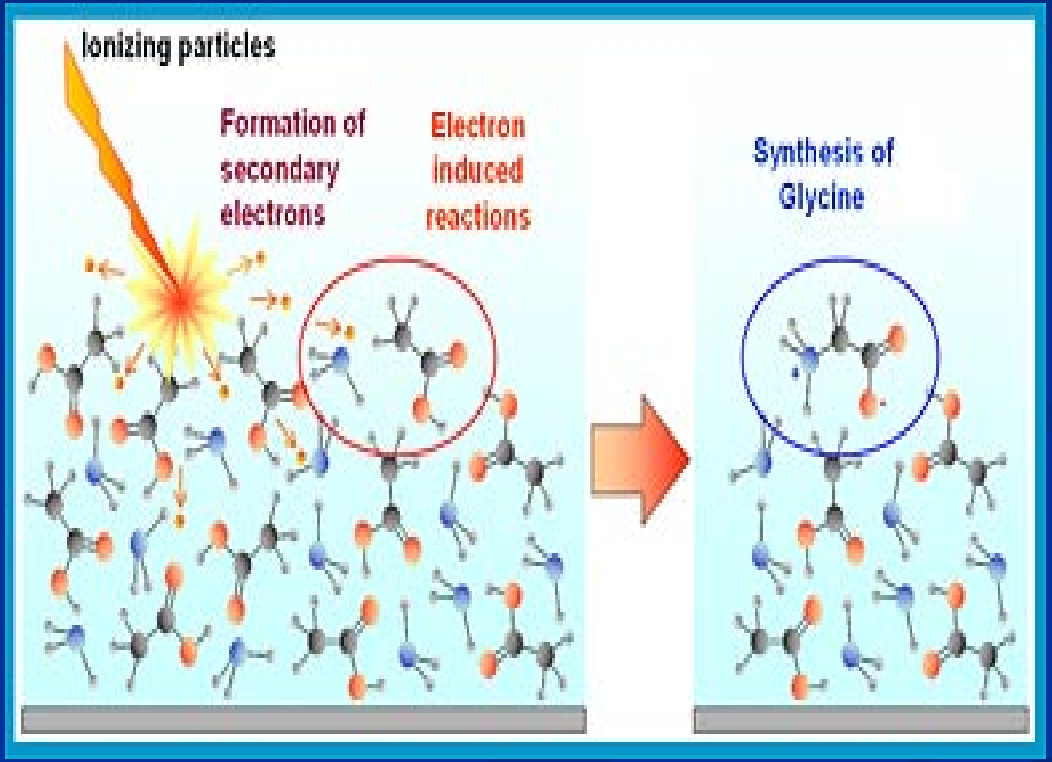
- To date most processing studies have explored UV irradiation - ok for diffuse clouds but dense clouds ?

- UV and cosmic rays induce secondary electrons



Cosmic rays as secondary electron source

- Major product of cosmic rays are Secondary electrons and they can induce chemistry
- Indeed one CR may produce an avalanche of 10^4 electrons whose energy vary from close to CR energy to thermal energy.

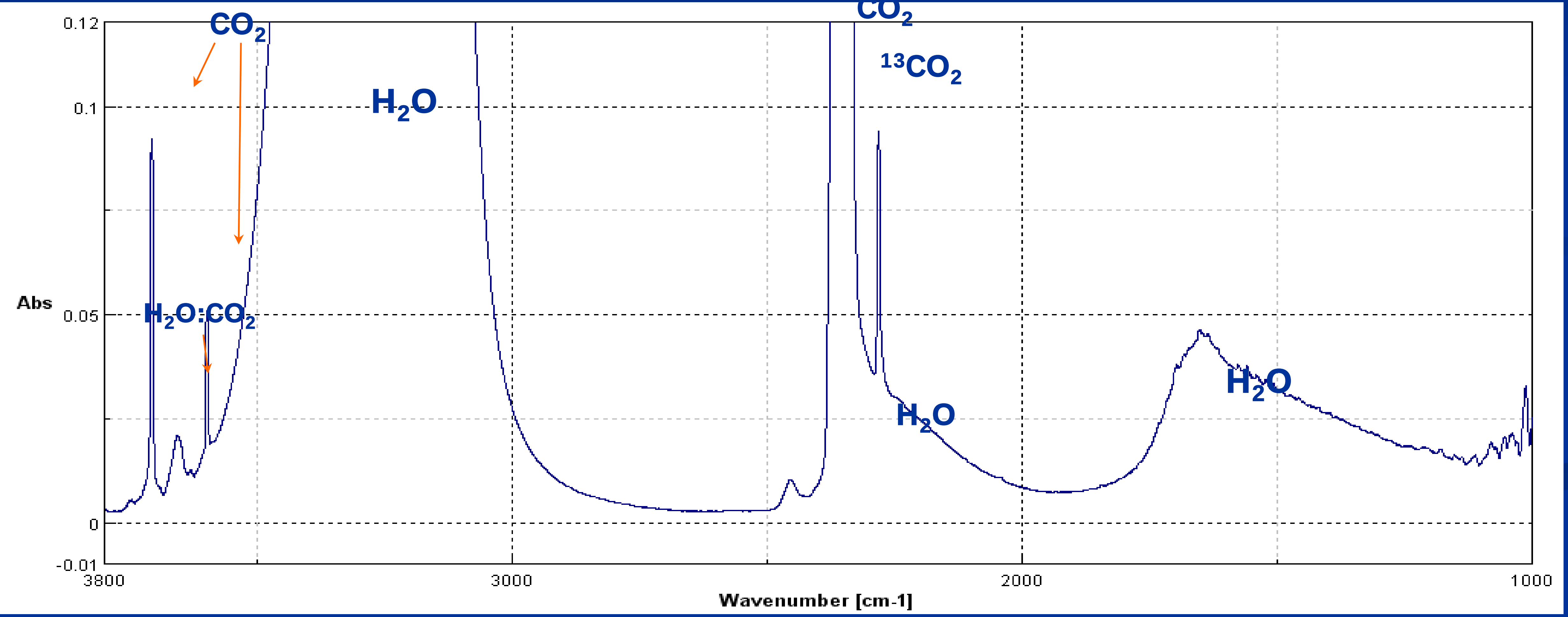


So what do we know ?

- Experiments are exploring synthesis routes.

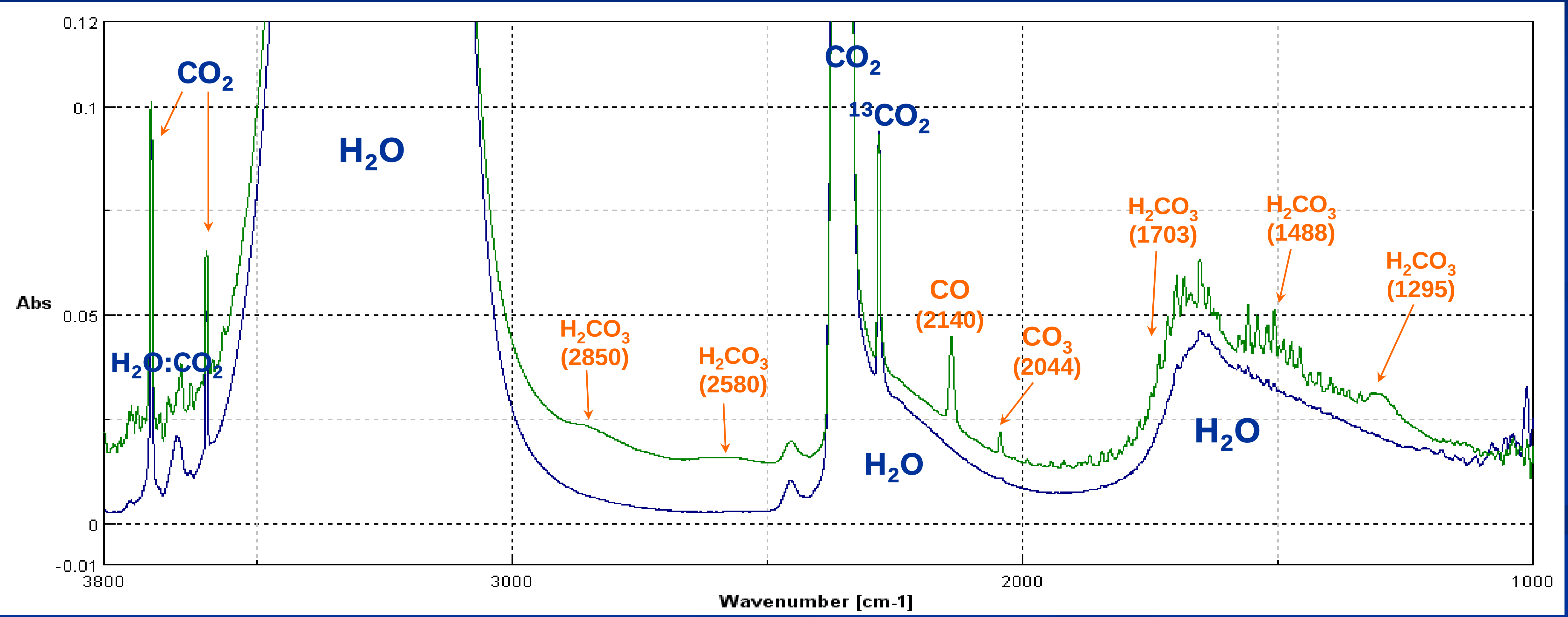
Irradiation of H_2O:CO_2 ice

Before irradiation

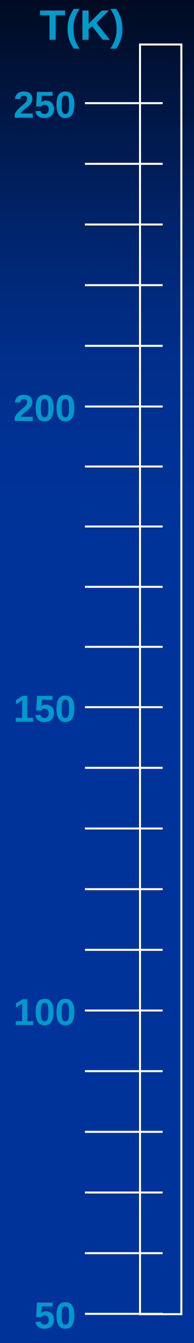


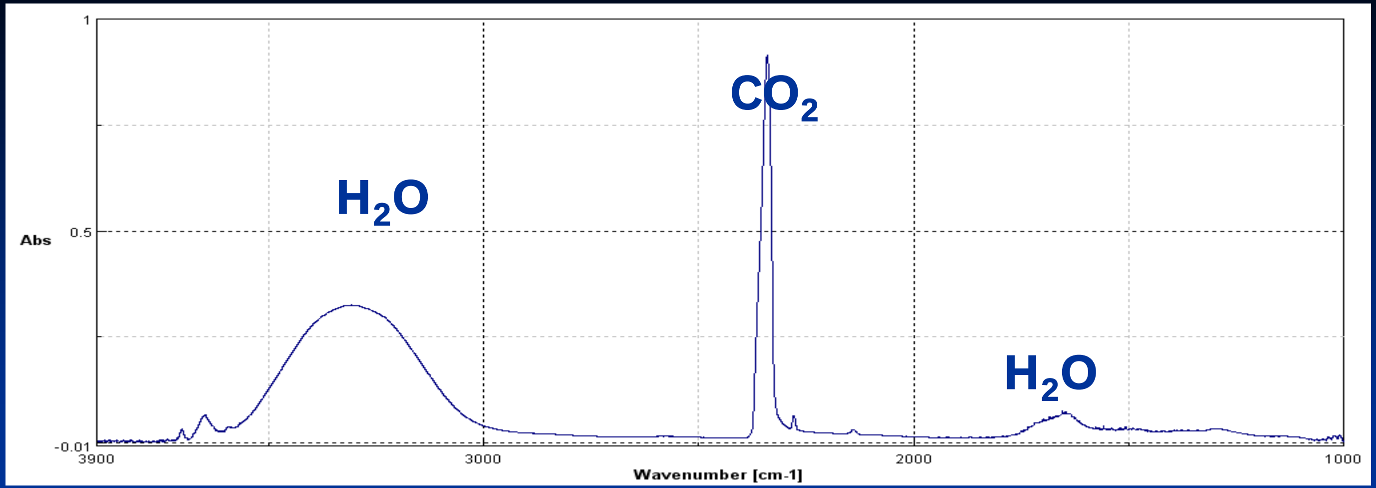
Irradiation of $H_2O:CO_2$ ice

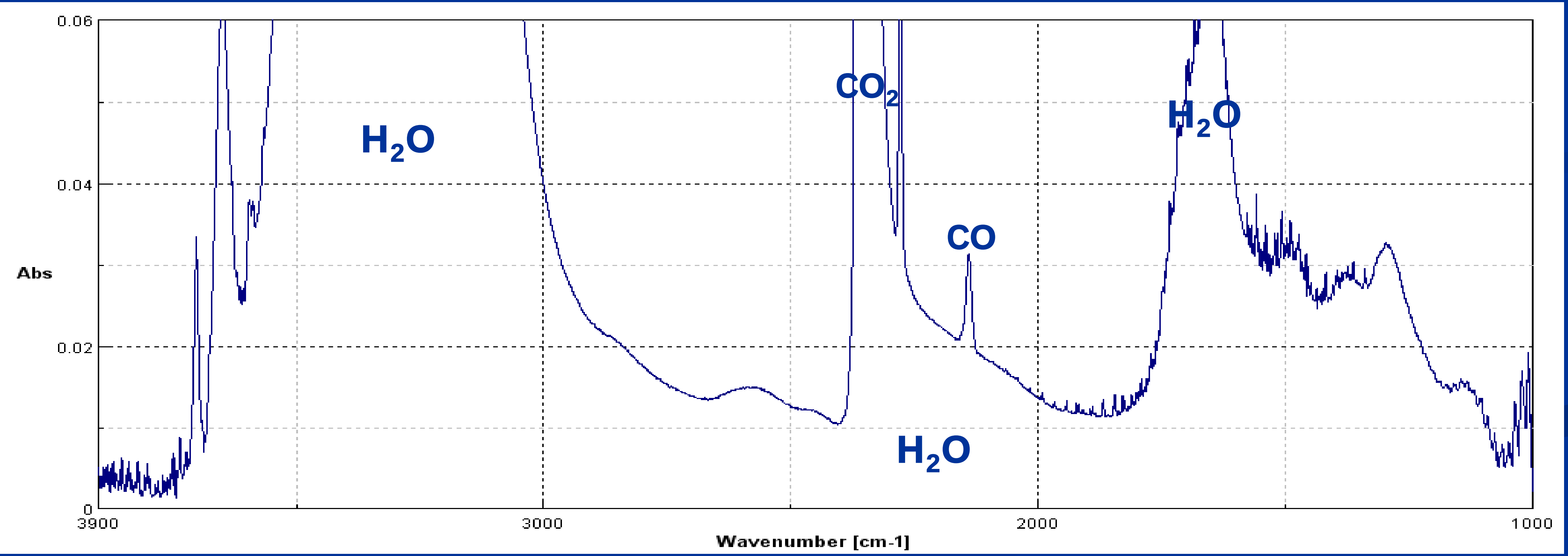
After irradiation for 1 hour

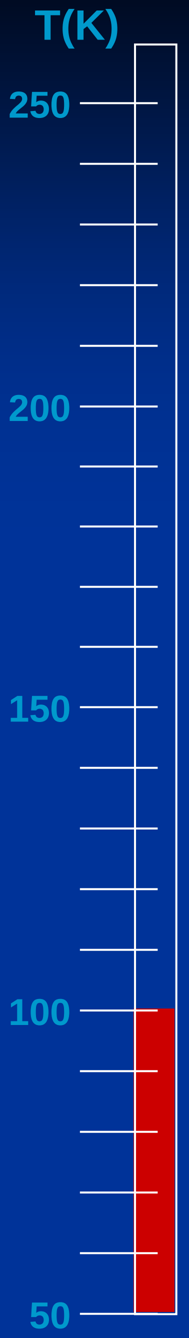


Warm-up +Irradiation of $H_2O:CO_2$ ice

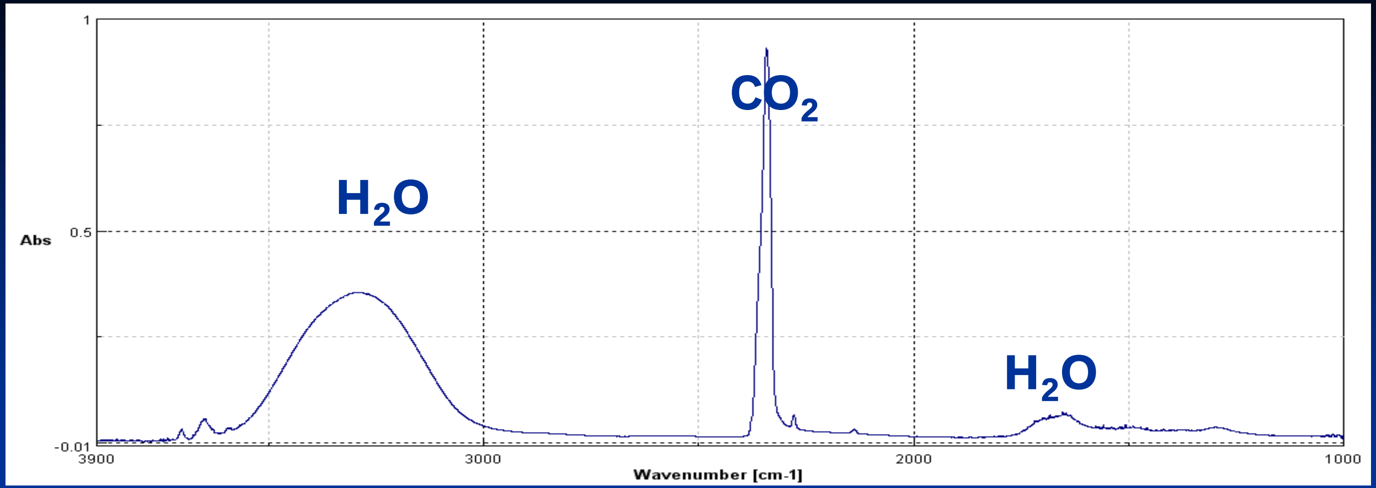


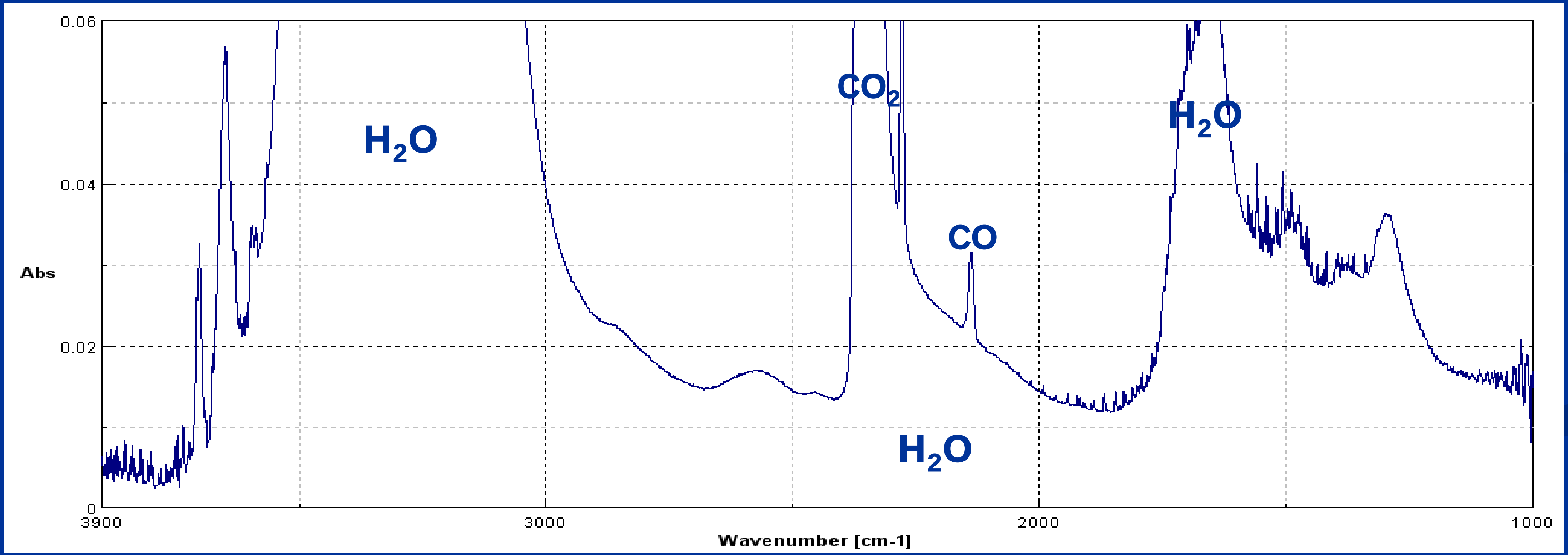






Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice





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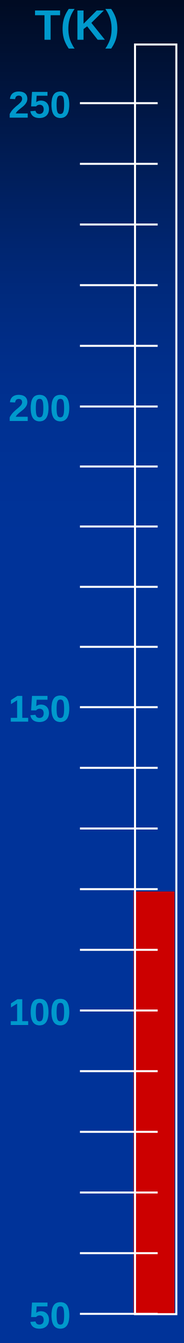

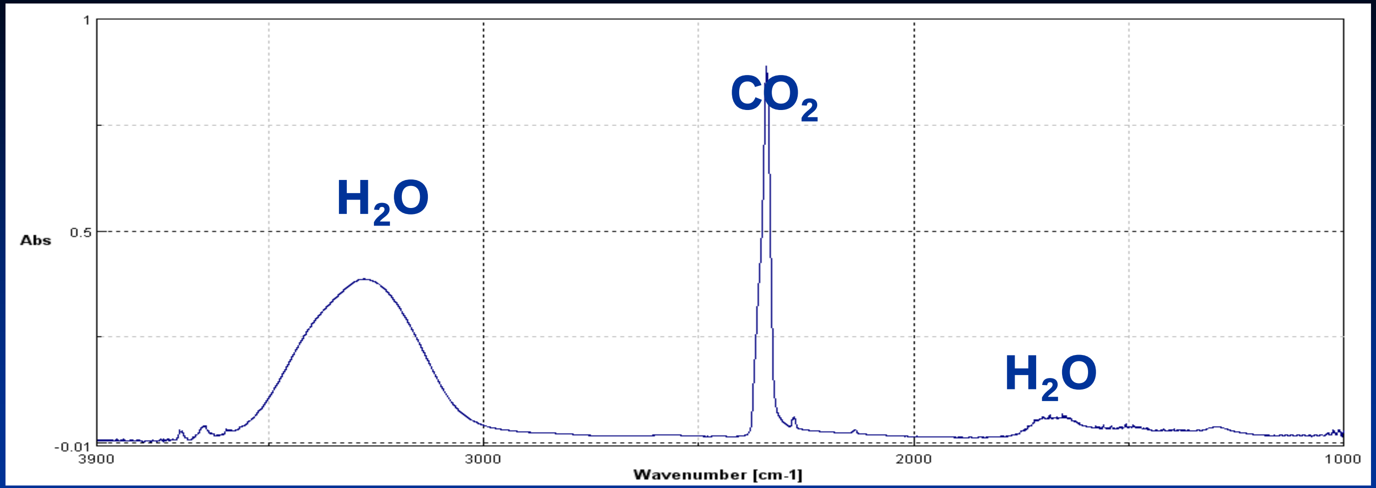

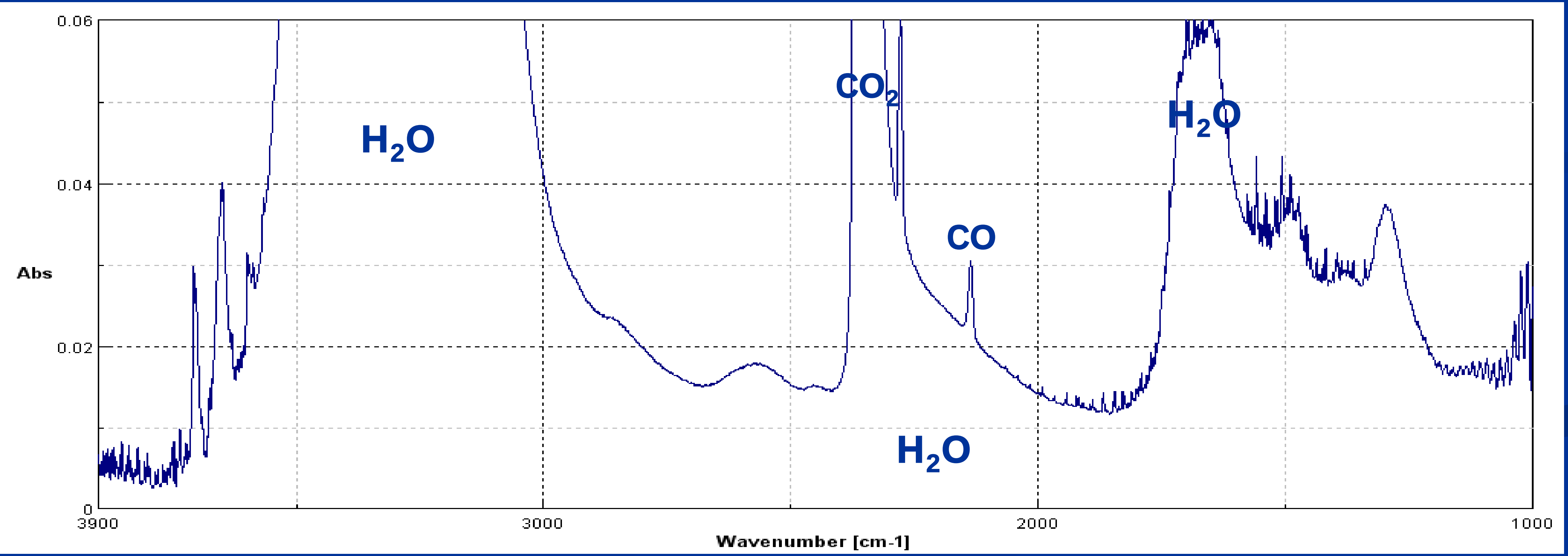

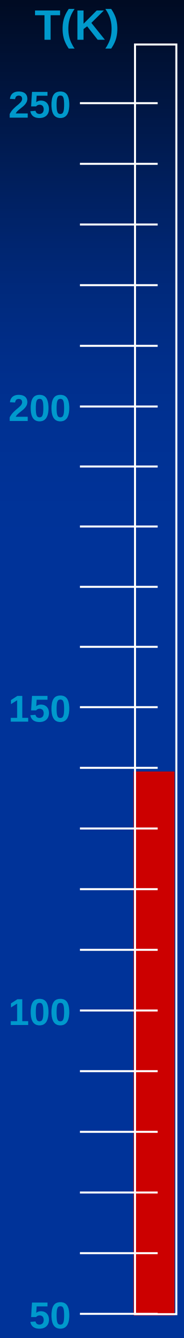

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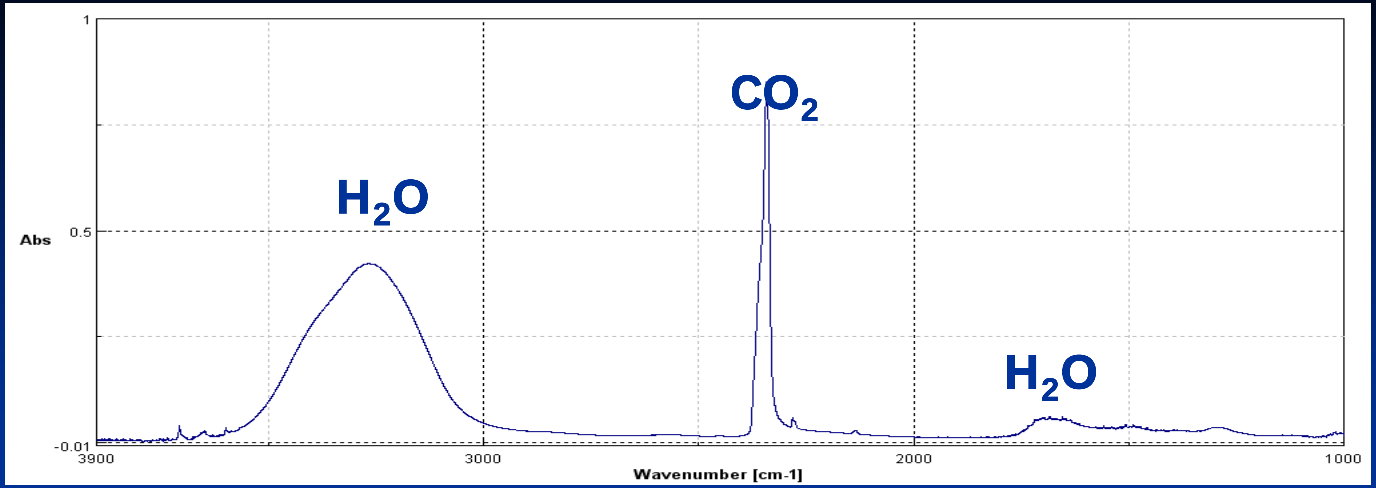
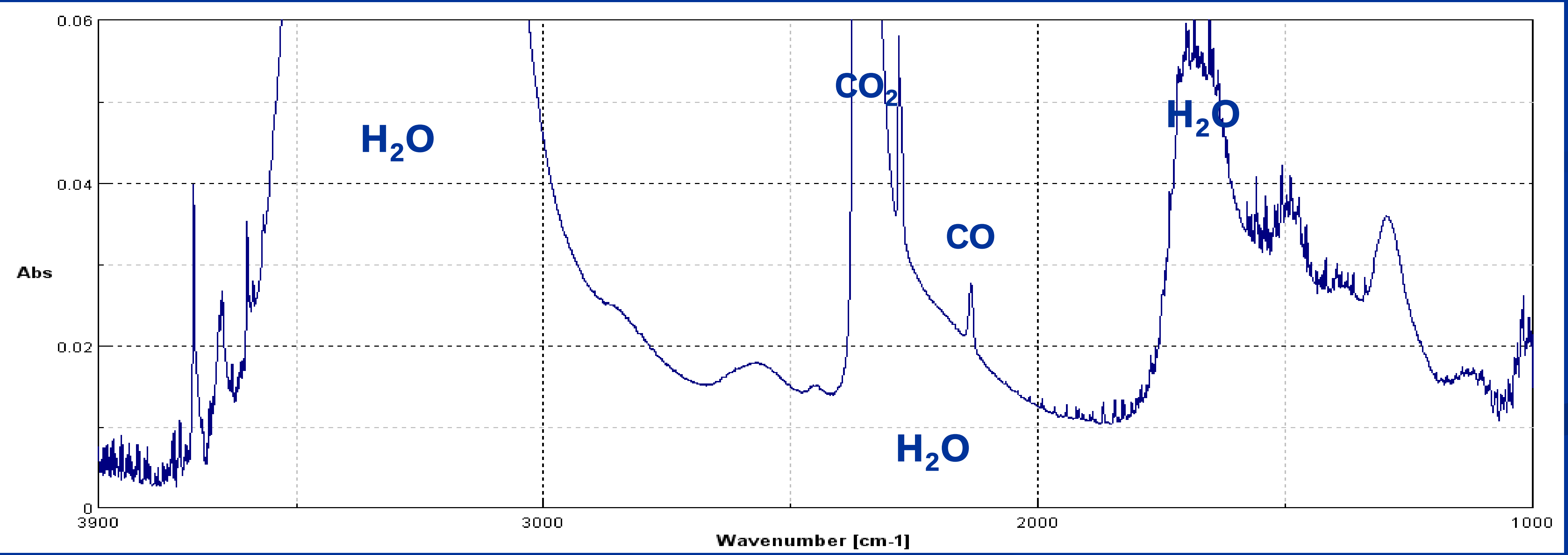
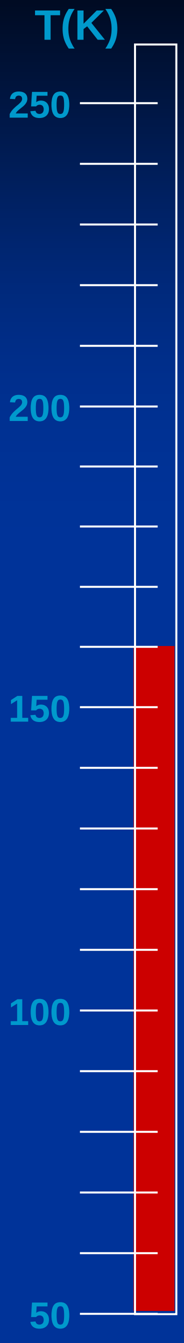
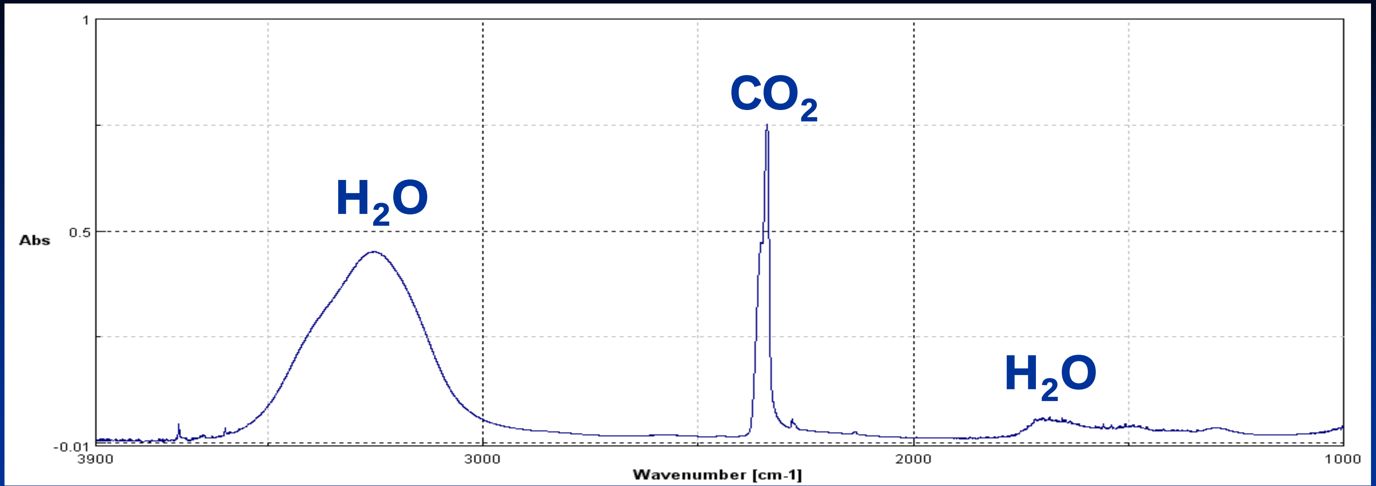
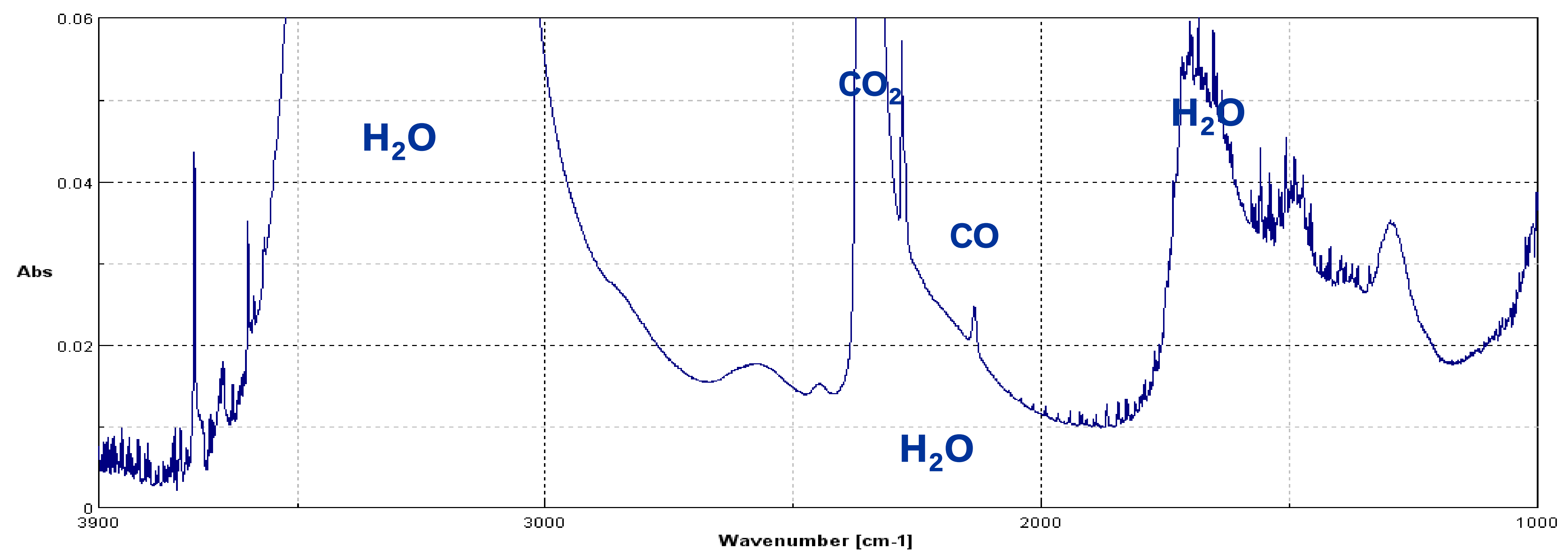




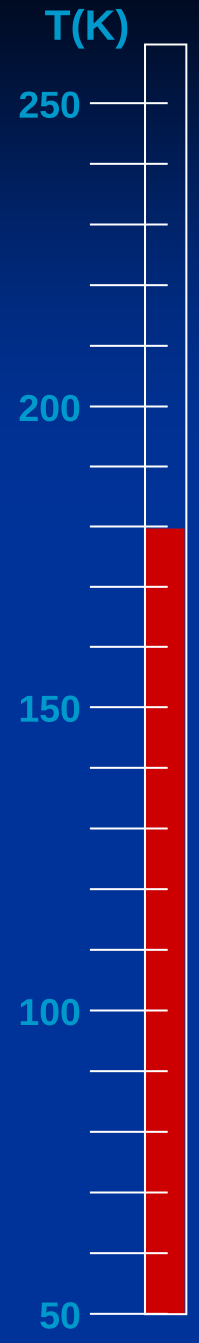


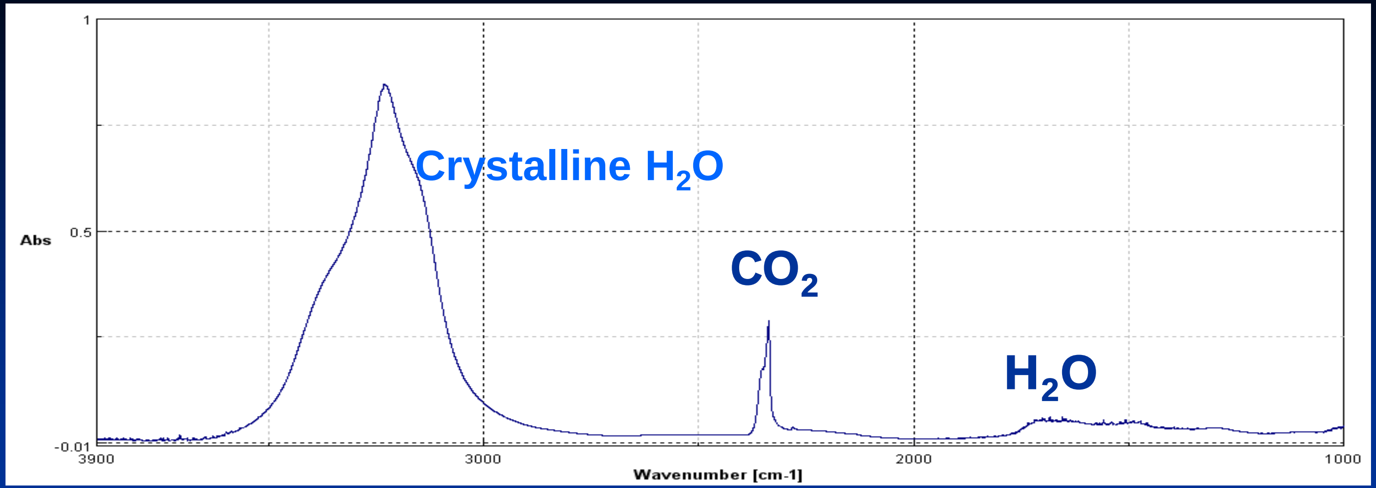
Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice

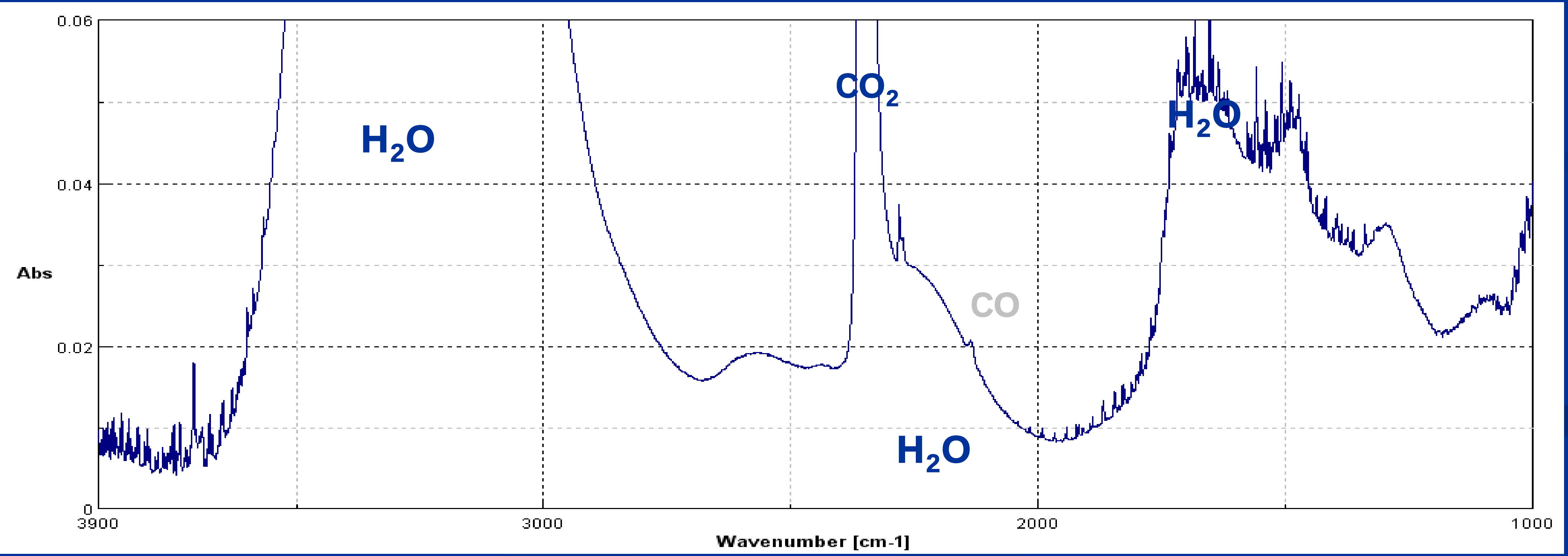




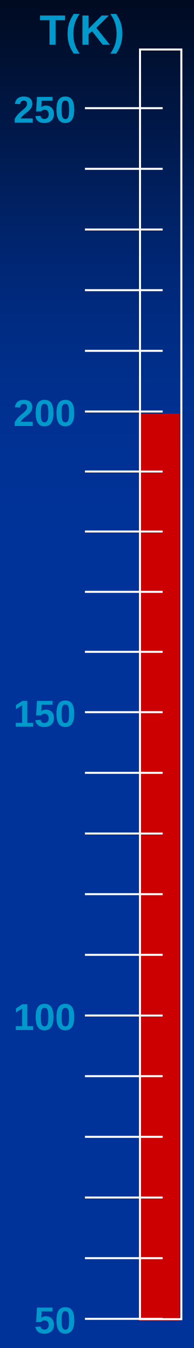
Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice

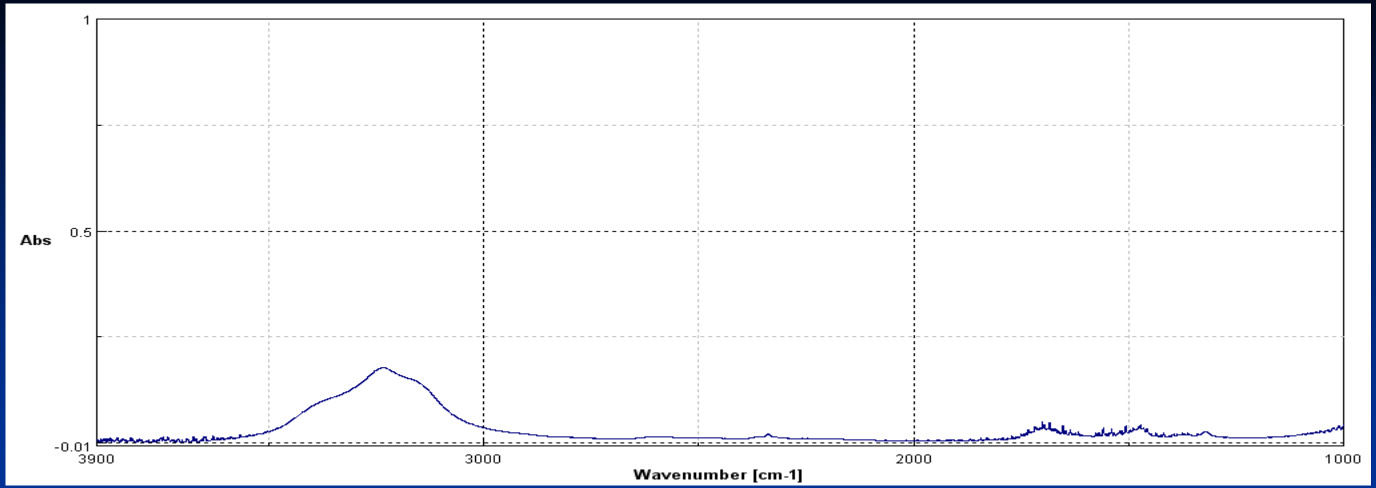


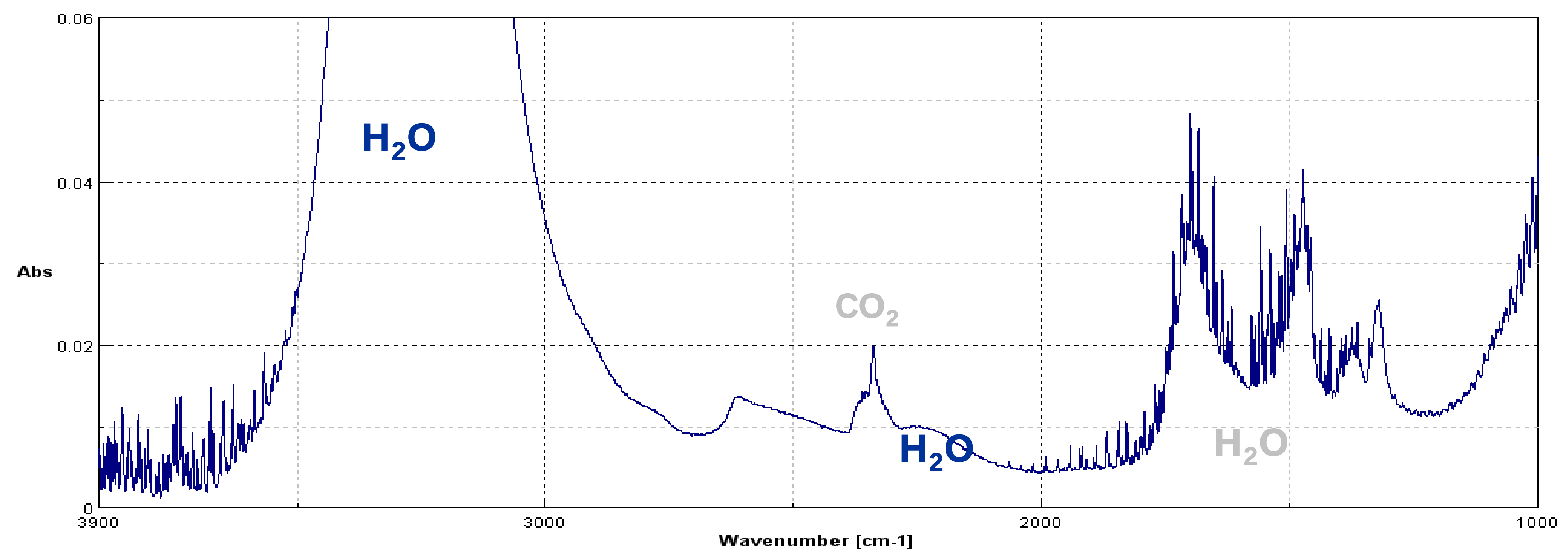


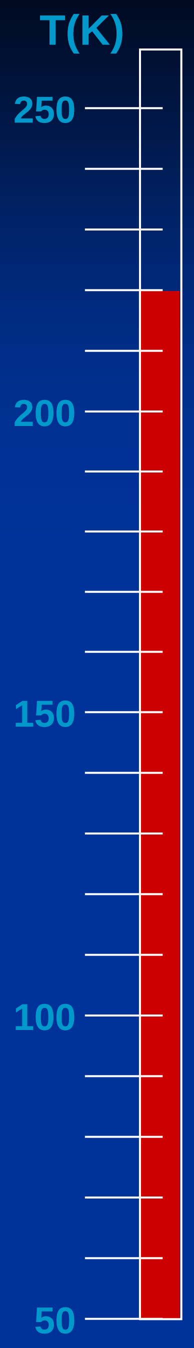


Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice

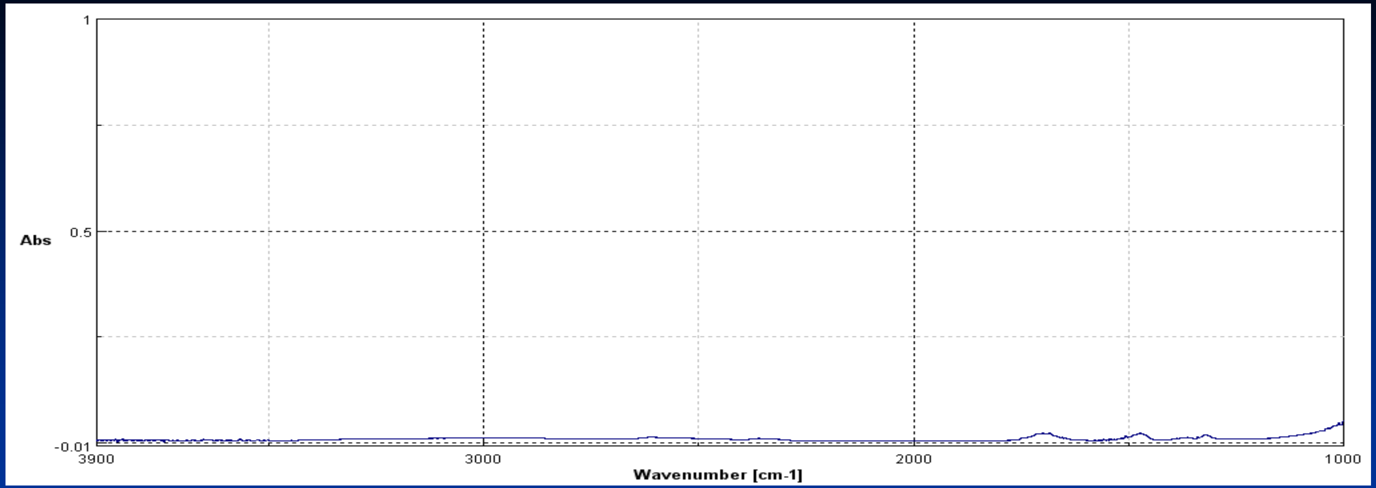


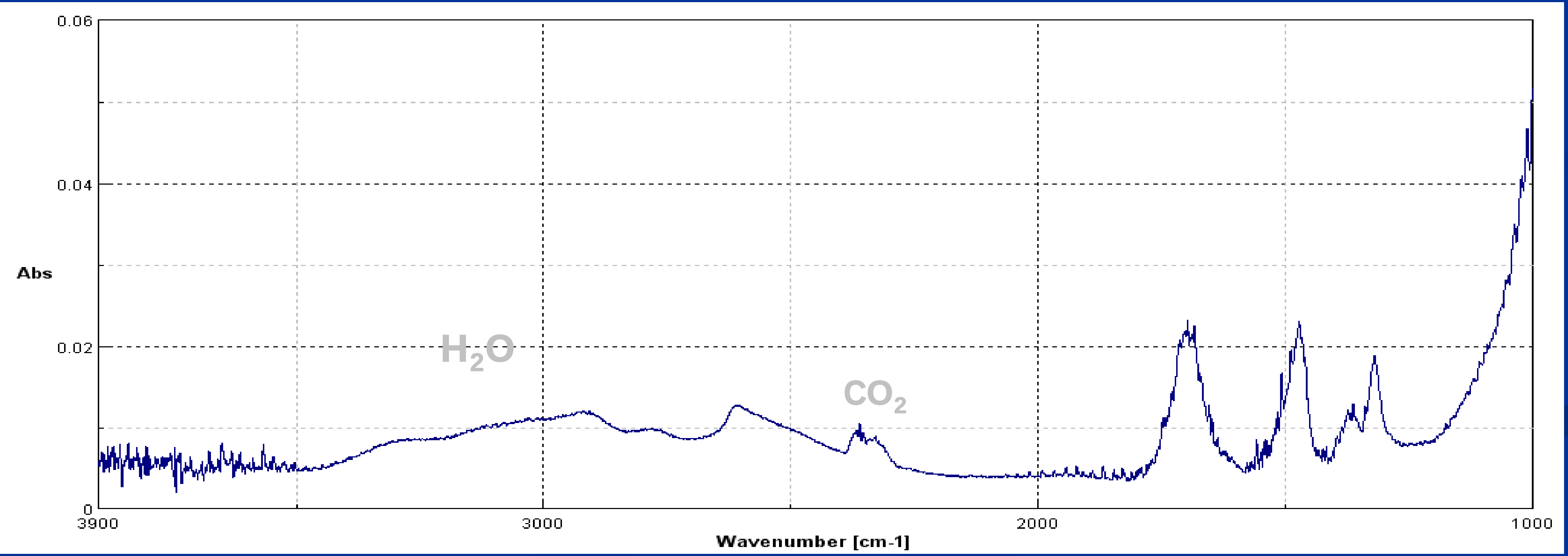


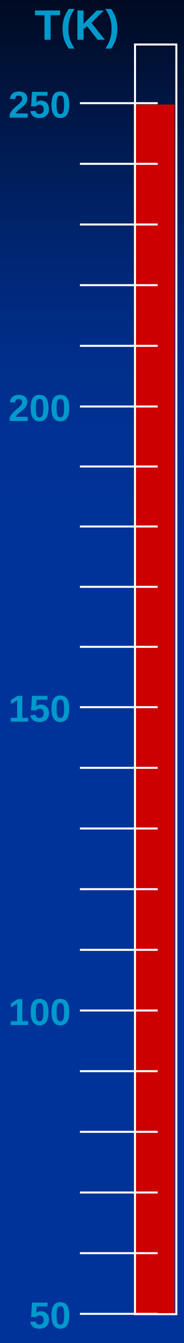




Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice

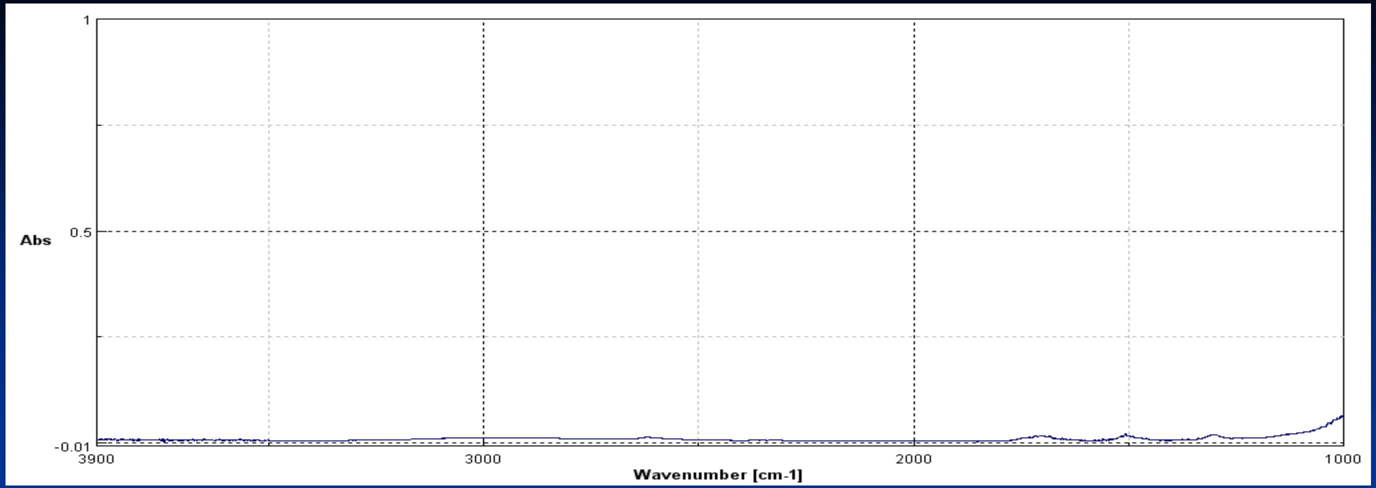


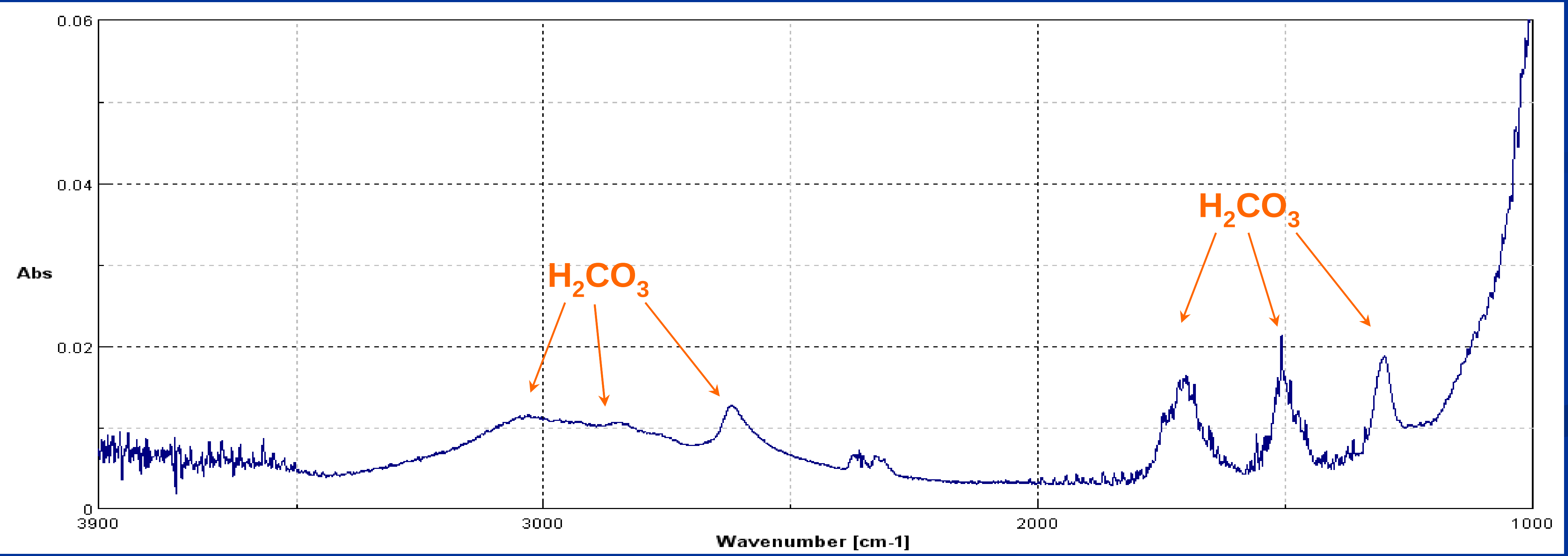




Warm-up after Irradiation of H_2O:CO_2 ice

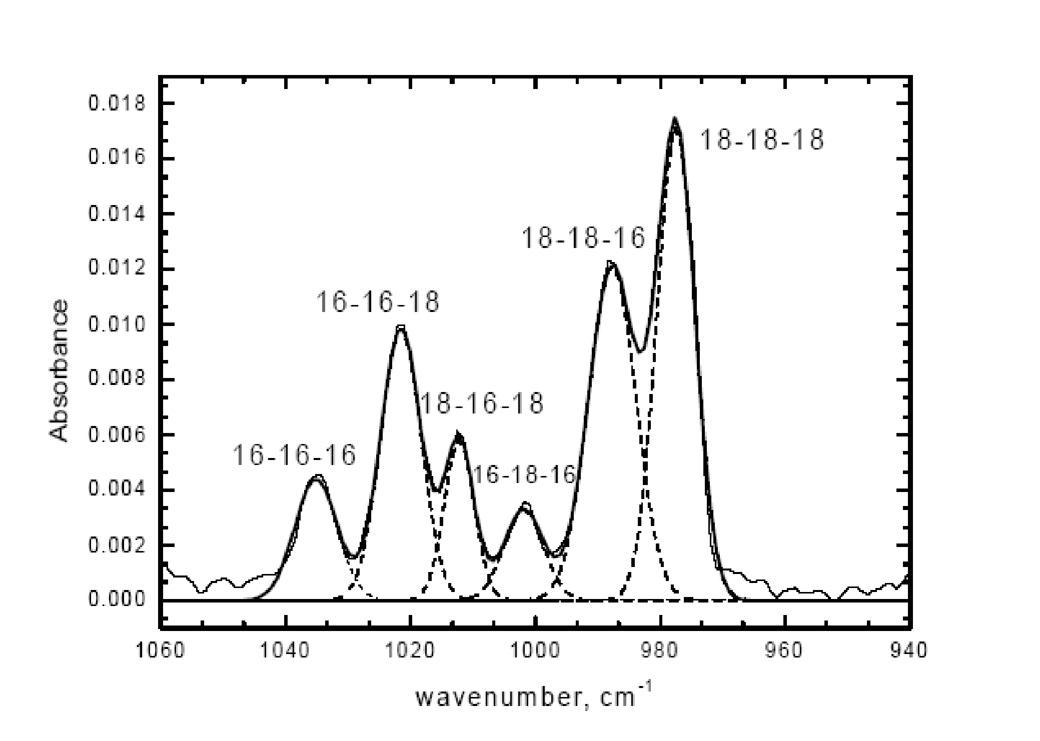
This is Martian ice cap





Electron Induced Chemistry

- Give some examples of how electrons irradiating ice can induce synthesis.



‘Simple’ single ices are not simple !

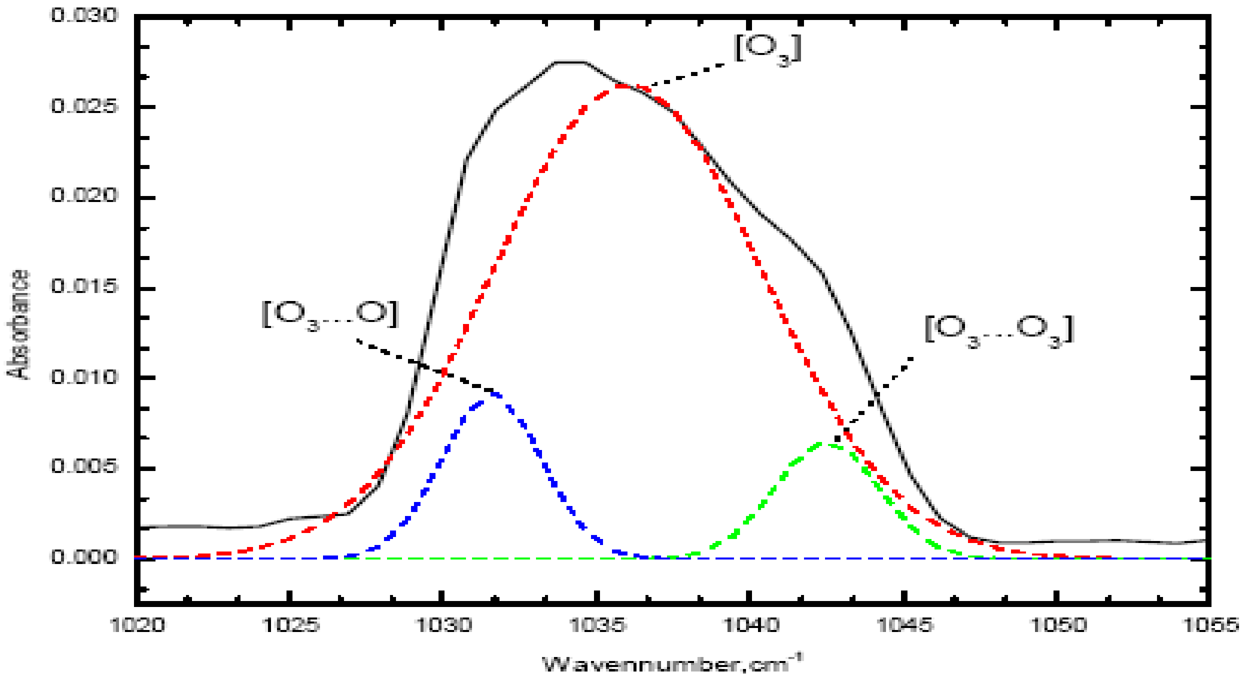
- **Oxygen → to ozone**
- Methanol ice → CO and CO_2 H_2CO and ‘complex’

Mechanisms for electron induced astrochemistry

The Open University

Look at irradiation of pure ices of oxygen

Ozone formation



Ozone monomer synthesis

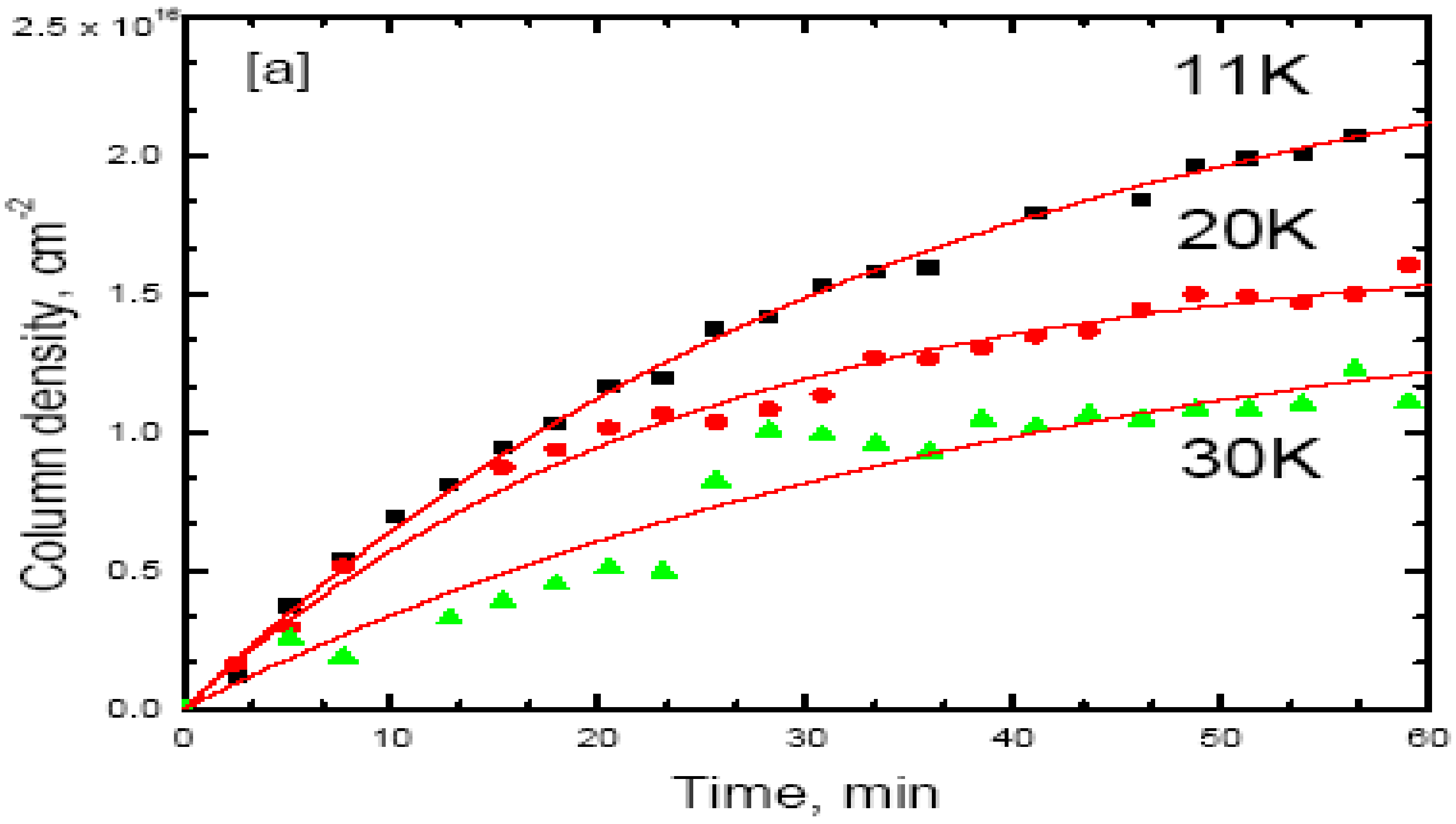
- Inter cluster chemistry !

$$(O_2 \ldots O_2) \rightarrow (O_2 \ldots O \ldots O) \rightarrow (O_3 \ldots O)$$

Ozone monomer synthesis

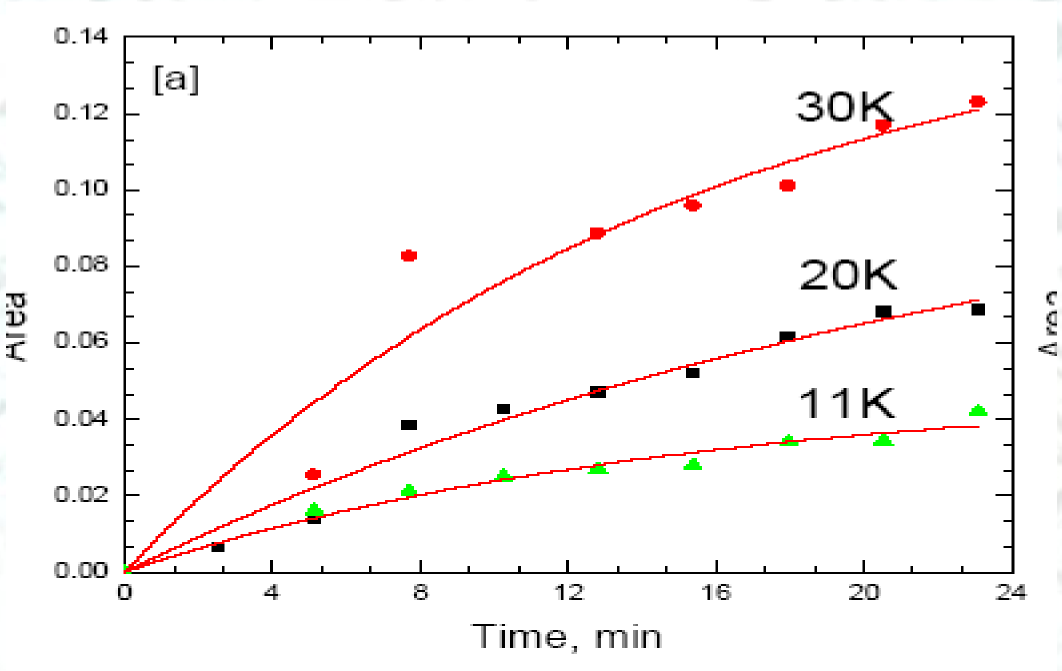
Temperature dependence ;

- **Yield largest at lowest Temperature**

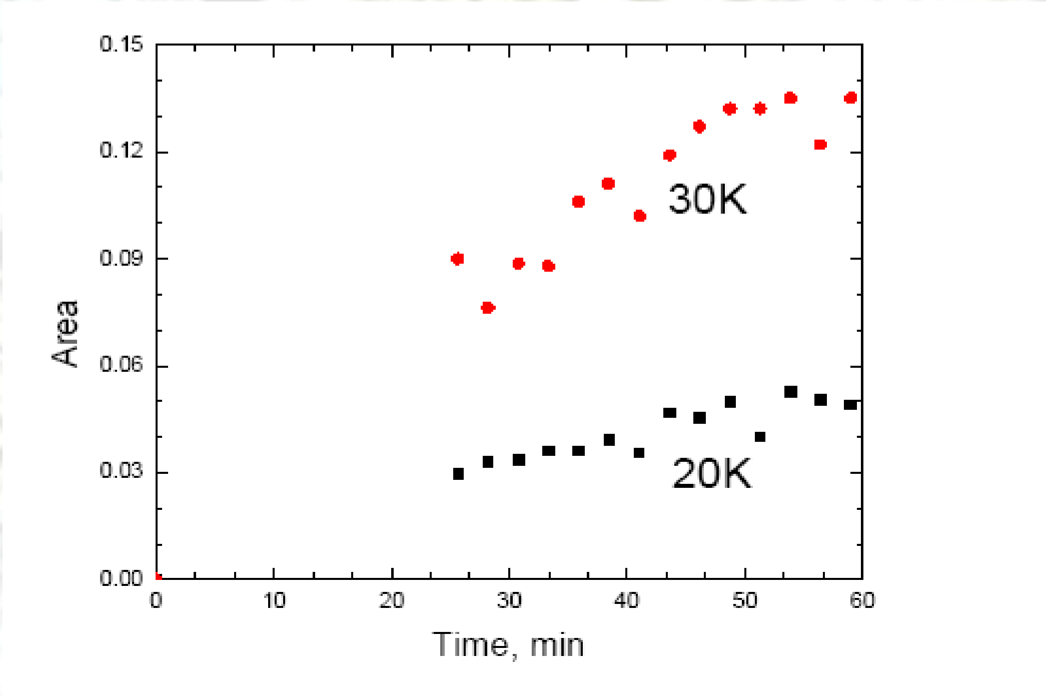


Ozone complexes

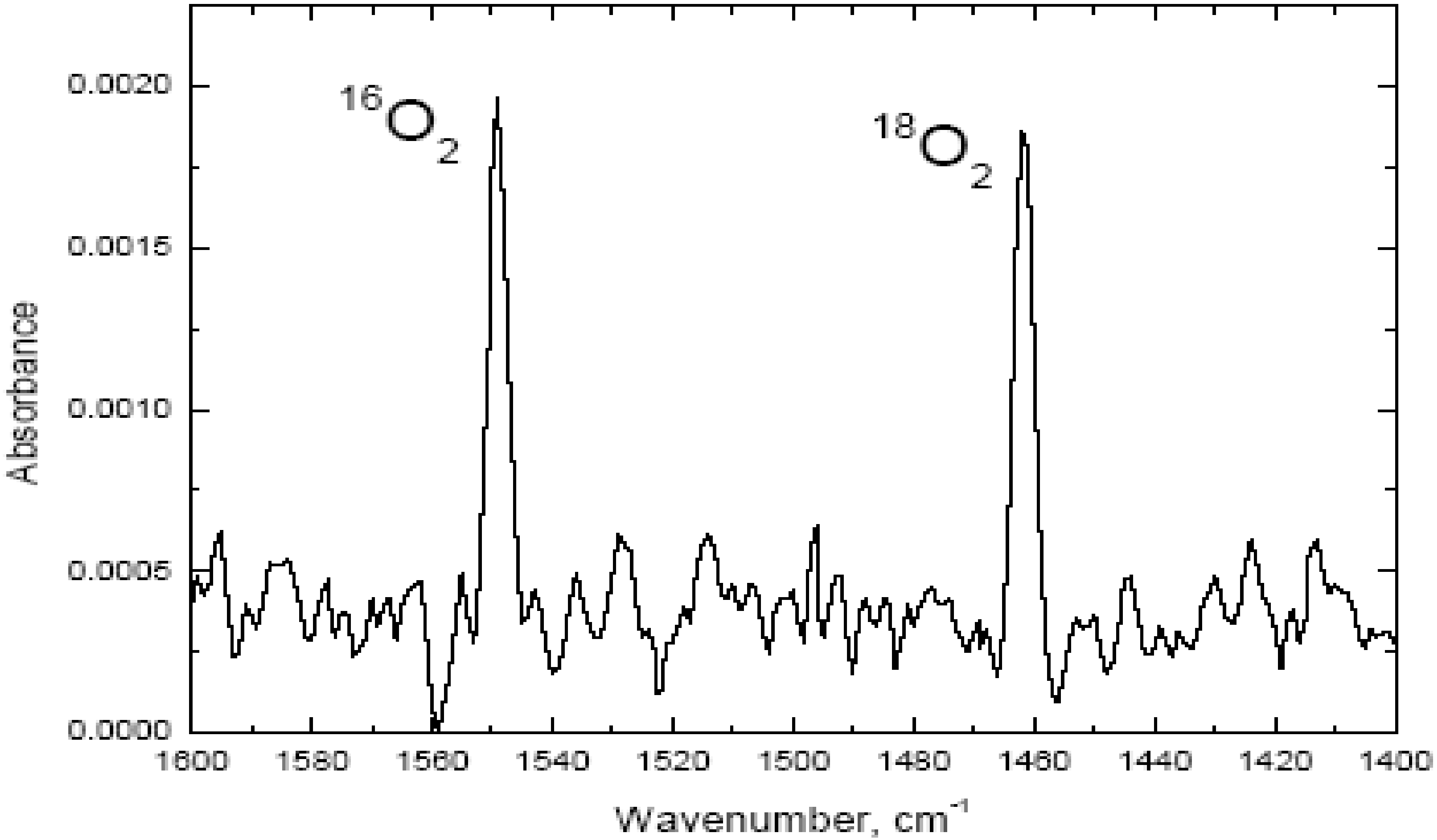
- O_3 - O



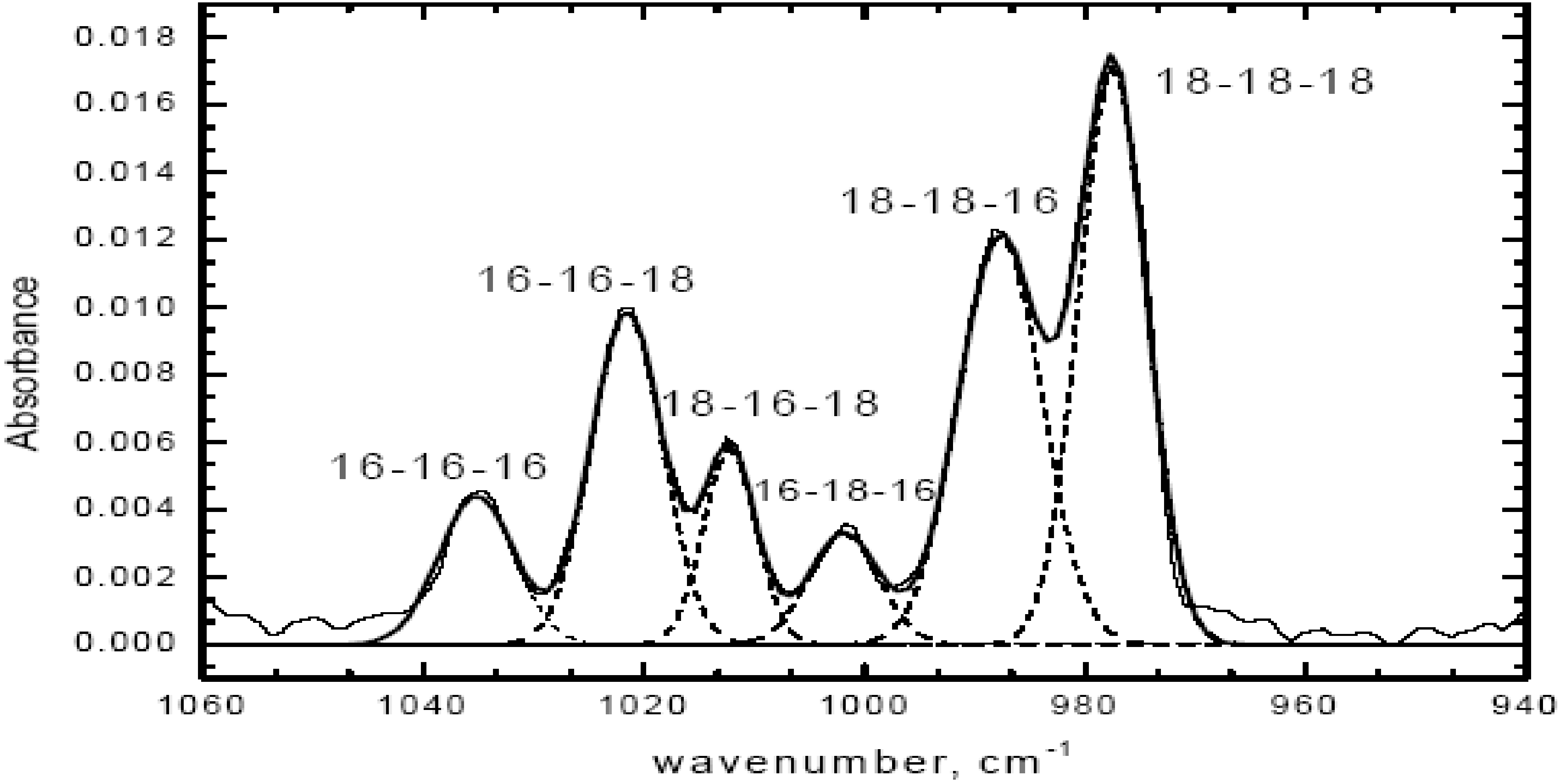
O_3 - O_3



Co-deposit two isomers



Formation of isotopomers (11K)

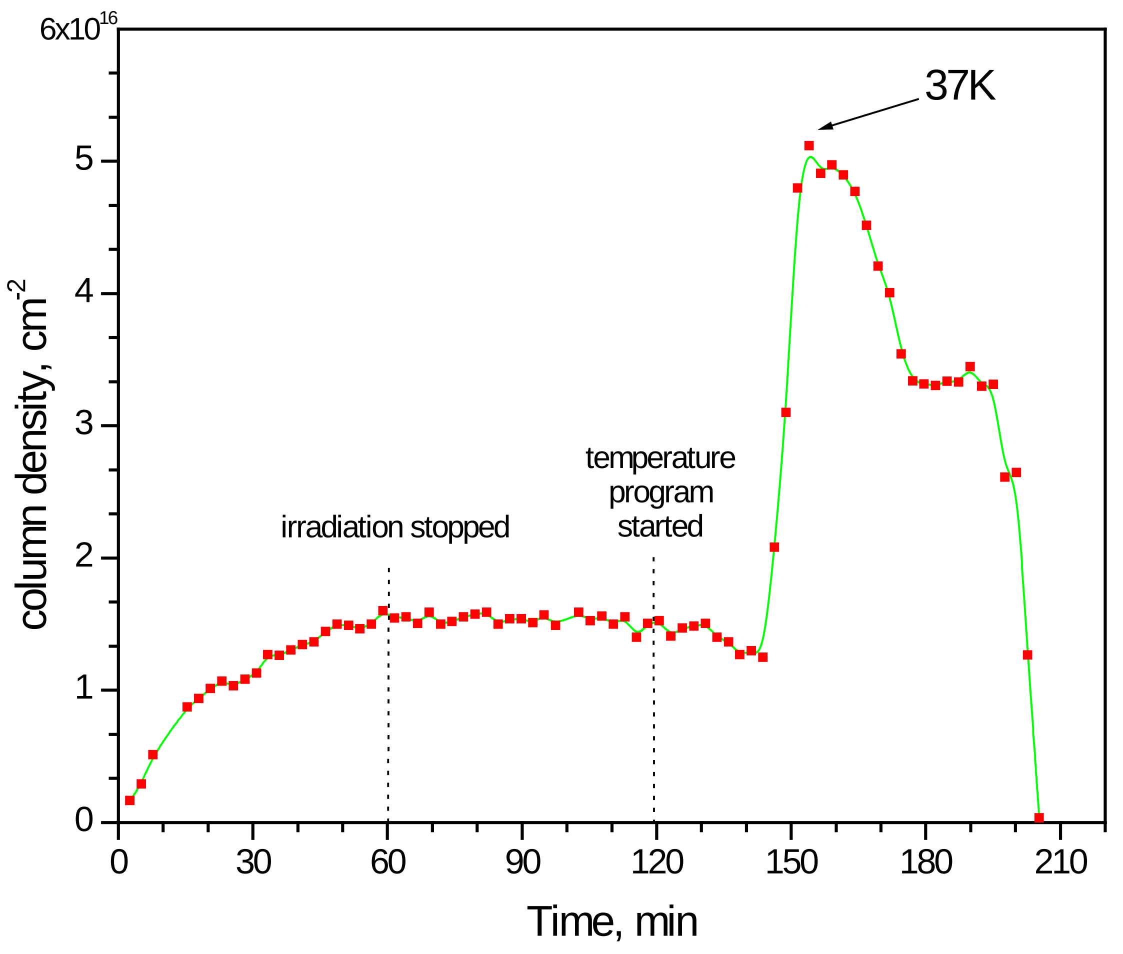


Desorption

The Open University

Mass spectrometric detection of species but

- Heating can induce synthesis eg ozone formation in O_2 ice
- Molecules can fragment upon desorption – mass fragment may not be parent species



So can we go on to make building blocks of life ?

- How to create an amino acid ?
- How to create a sugar in space ?

- Synthesis in the ice mantles ?

Formation of ethylene glycol in pure methanol ice

$HOH_2C\text{-}CH_2OH$

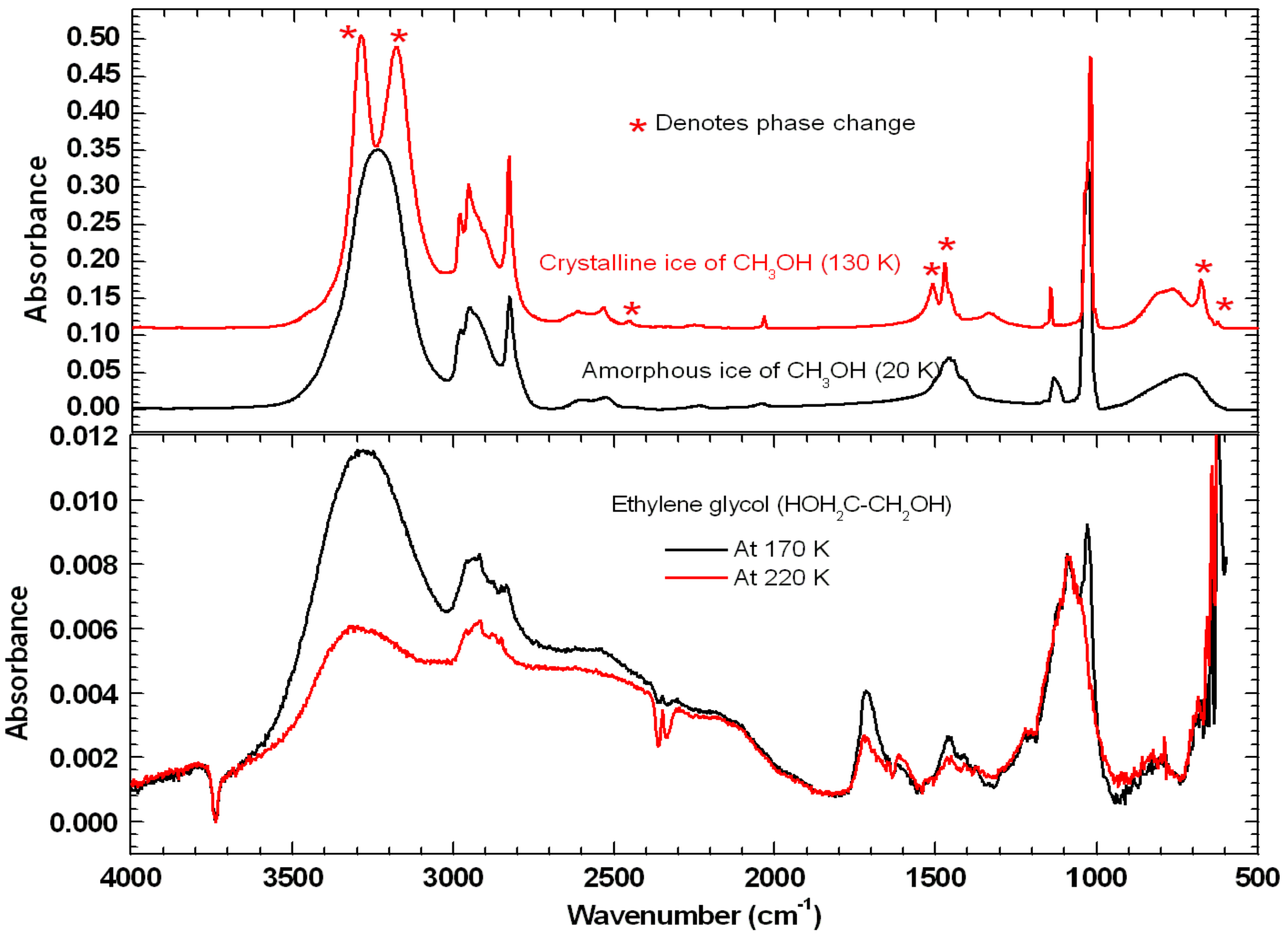


Fig. 6-3: Ethylene glycol was observed after irradiation of pure CH_3OH with 1 keV e^- at 30 K and then annealing process

Formation of methyl formate CH_3OHCO

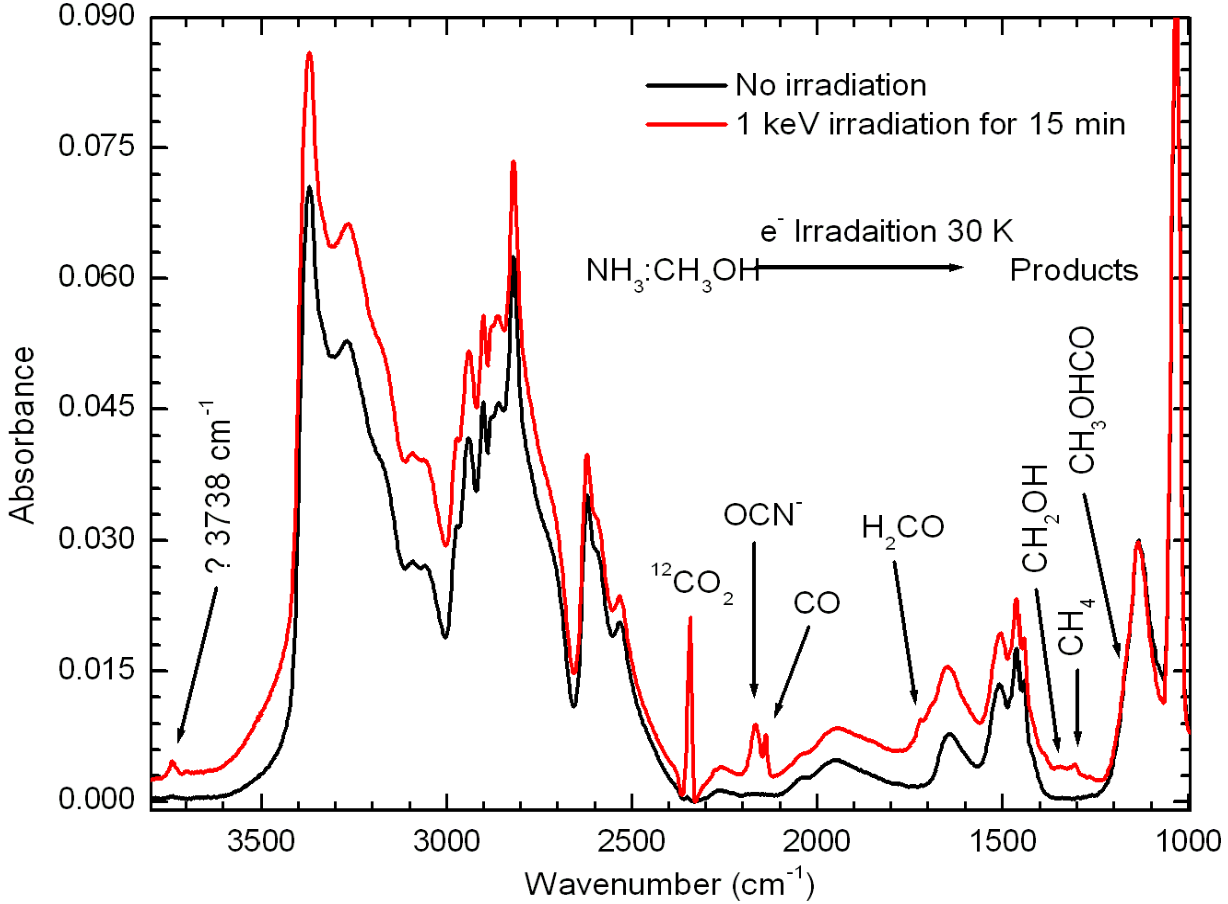


Fig. 6-9: Irradiation of 1:1 binary mixture of NH_3:CH_3OH with 1 keV e^- at 30 K

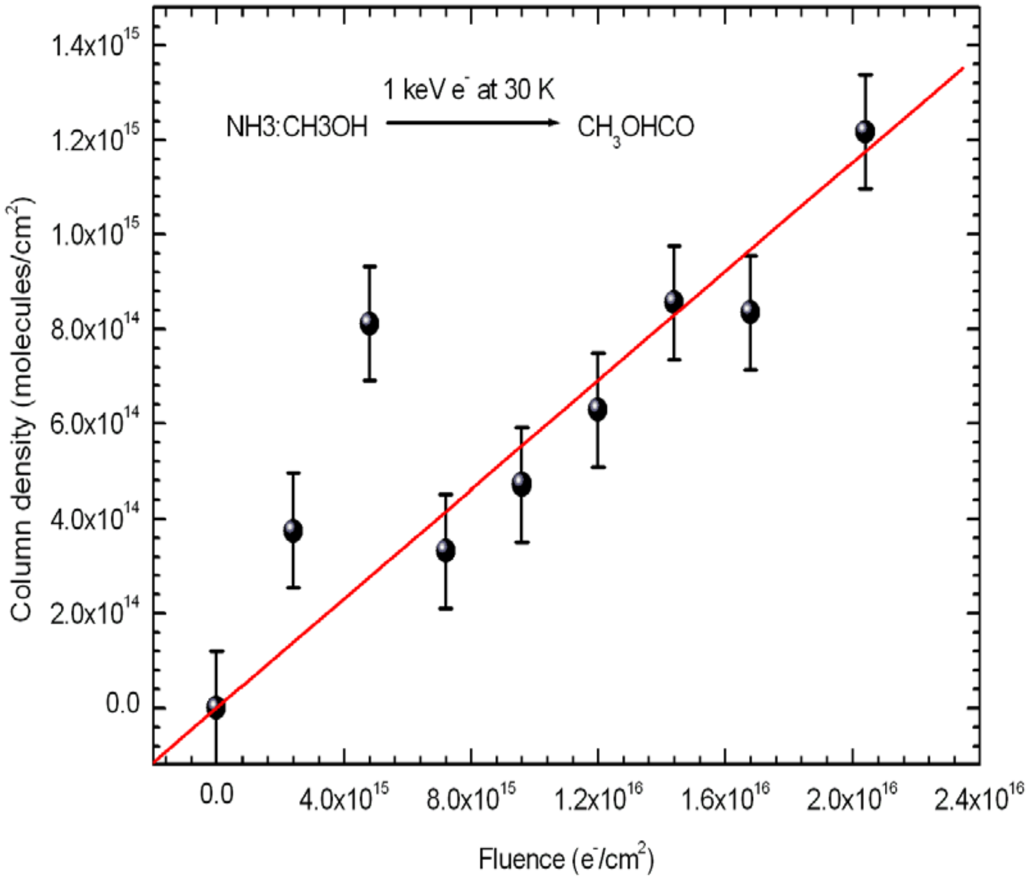


Fig 6-14: Formation of CH_3OHCO during the irradiation of binary mixture NH_3:CH_3OH with 1 keV e^- at 30 K

Create exotic compounds – Ammonium carbamate

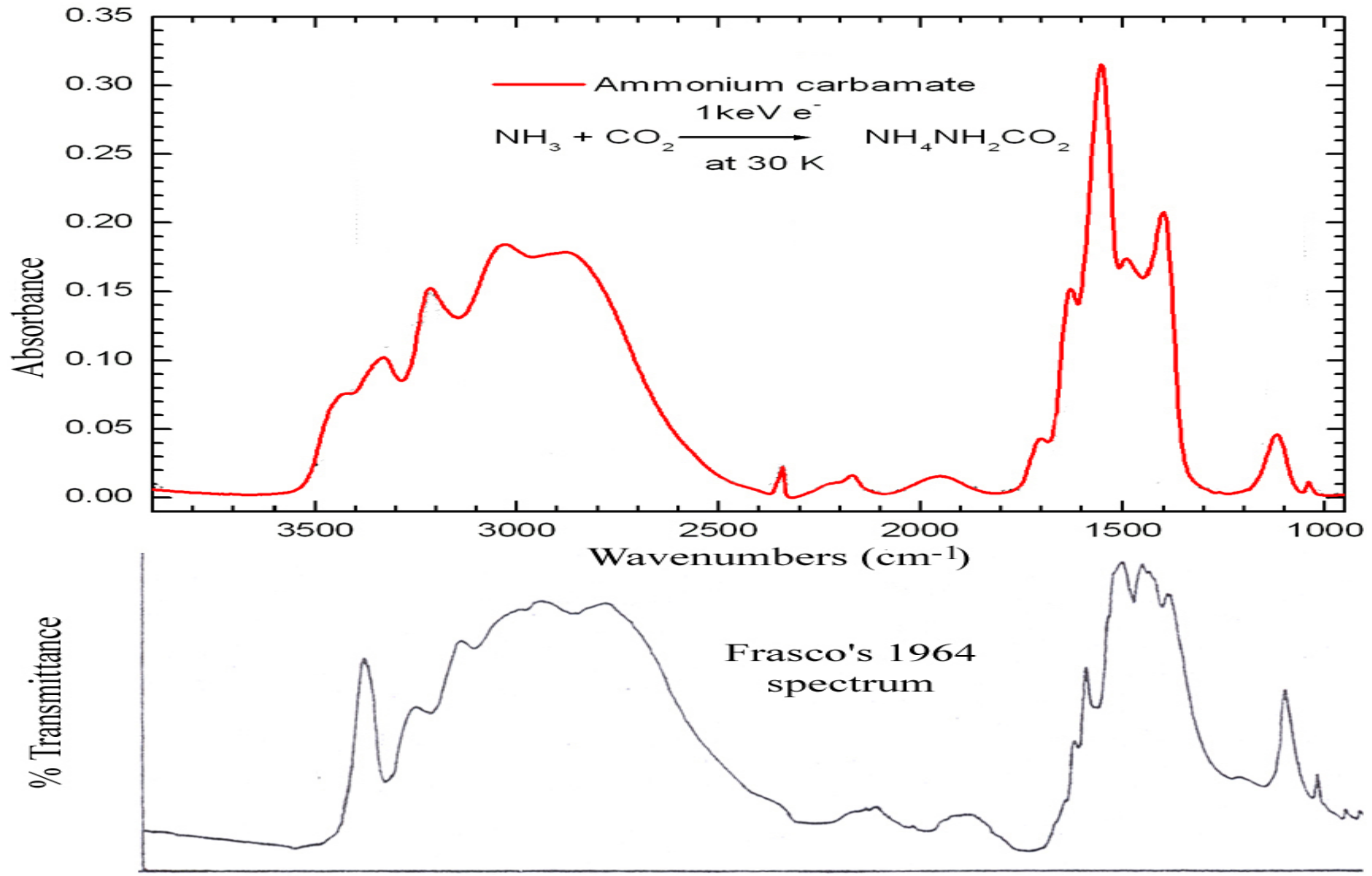


Fig. 5-5: IR spectra of $NH_3:CO_2$ (1:1), (a) post-irradiation (58 min) and after warm-up (220 - 270 K); and (b) comparing Frasco's actual 1964 experimental spectrum at 248 K

Formation of formamide $HCONH_2$ from irradiation of ammonia/methanol ice

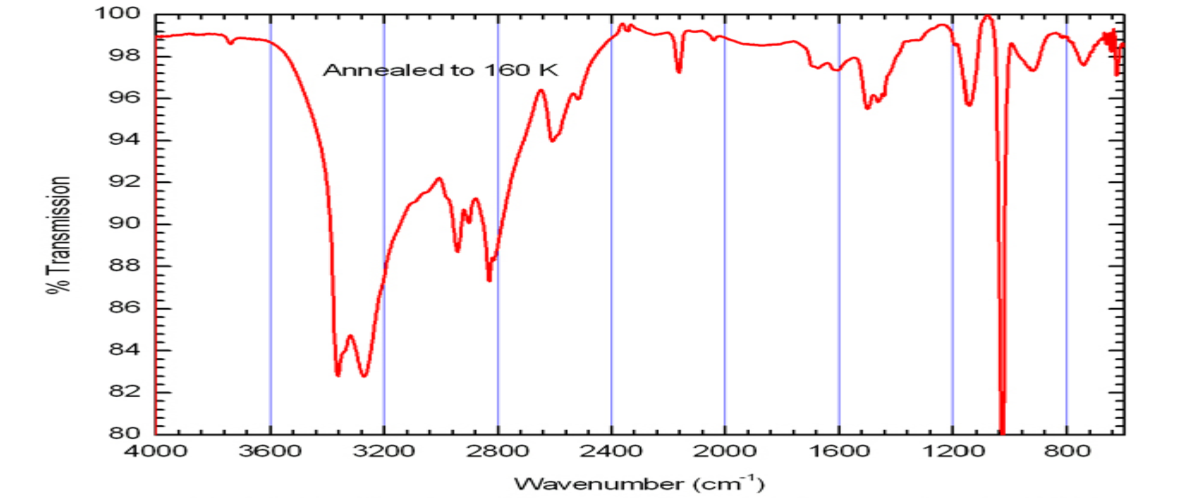


Fig. F6-16a: Spectrum of formamide formed during annealing to 160 K of irradiated ice of 1:1 binary mixture of NH_3:CH_3OH with 1 keV e^- at 30 K

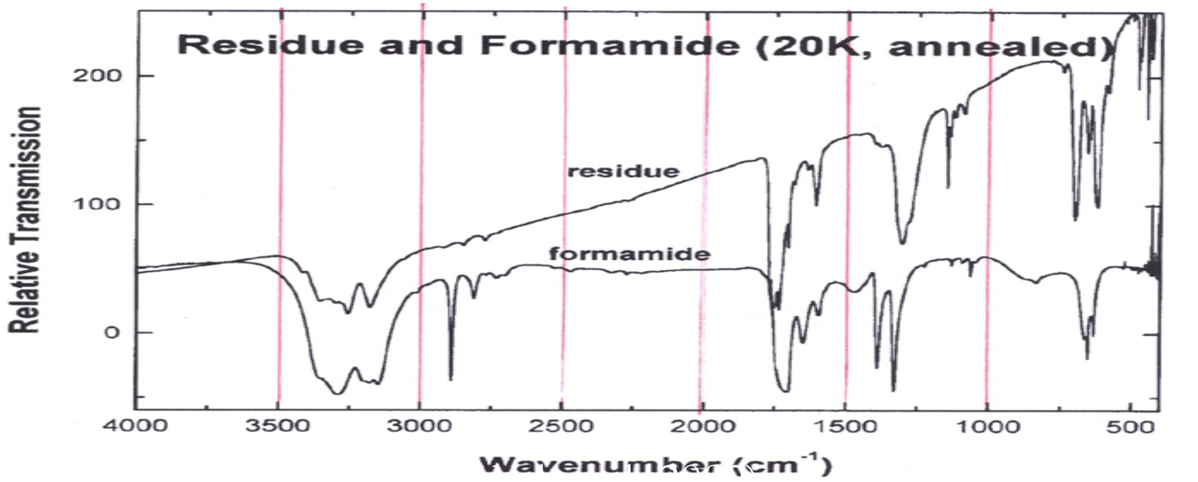


Fig. 6-16b. Comparison of infrared spectra of residue with formamide. Both deposits have been anealed (to 165 K) and recooled to 20 K to produce crystaline structure

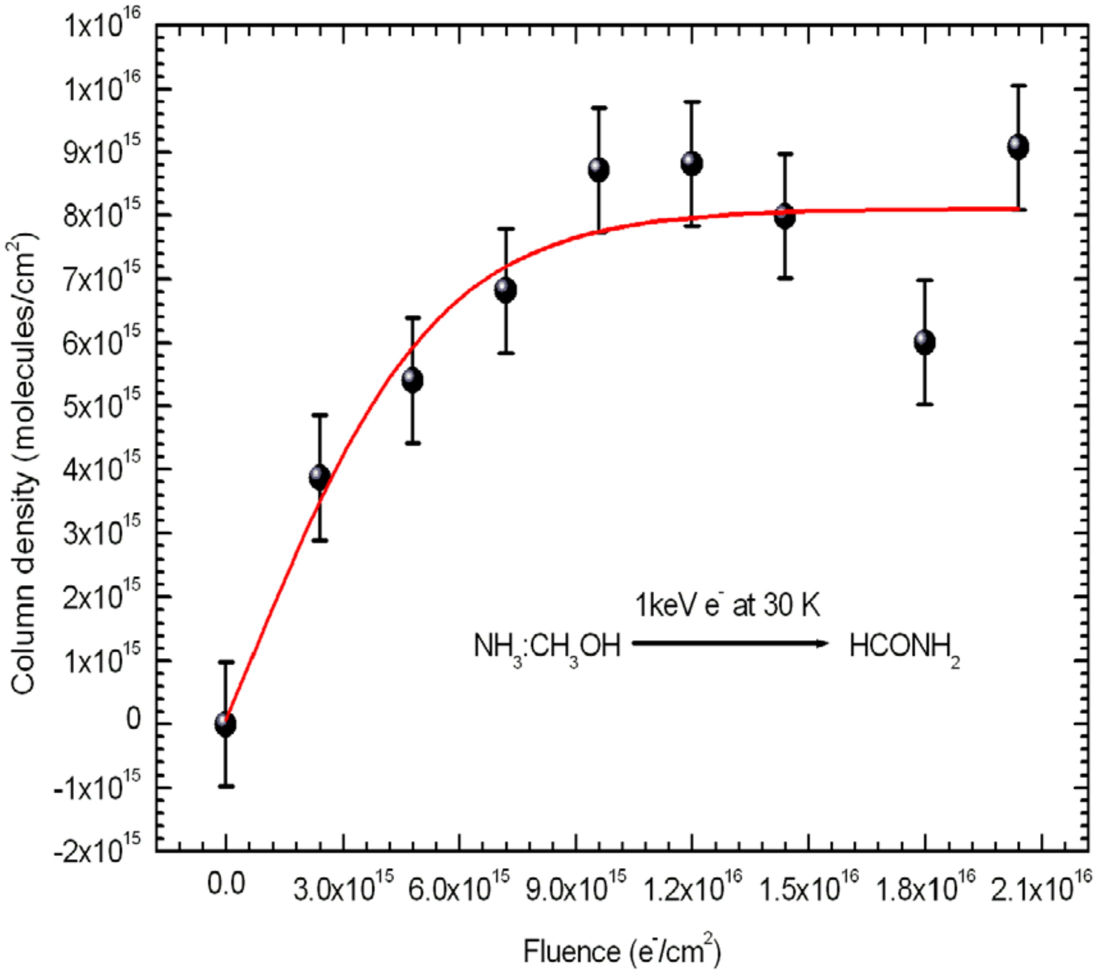


Fig. 6-15: Formation of $HCONH_2$ during the irradiation of 1:1 bianry mixture of NH_3:CH_3OH with 1 keV at 30 K

Irradiation of methylammine and carbon dioxide ice makes glycine simple amino acid

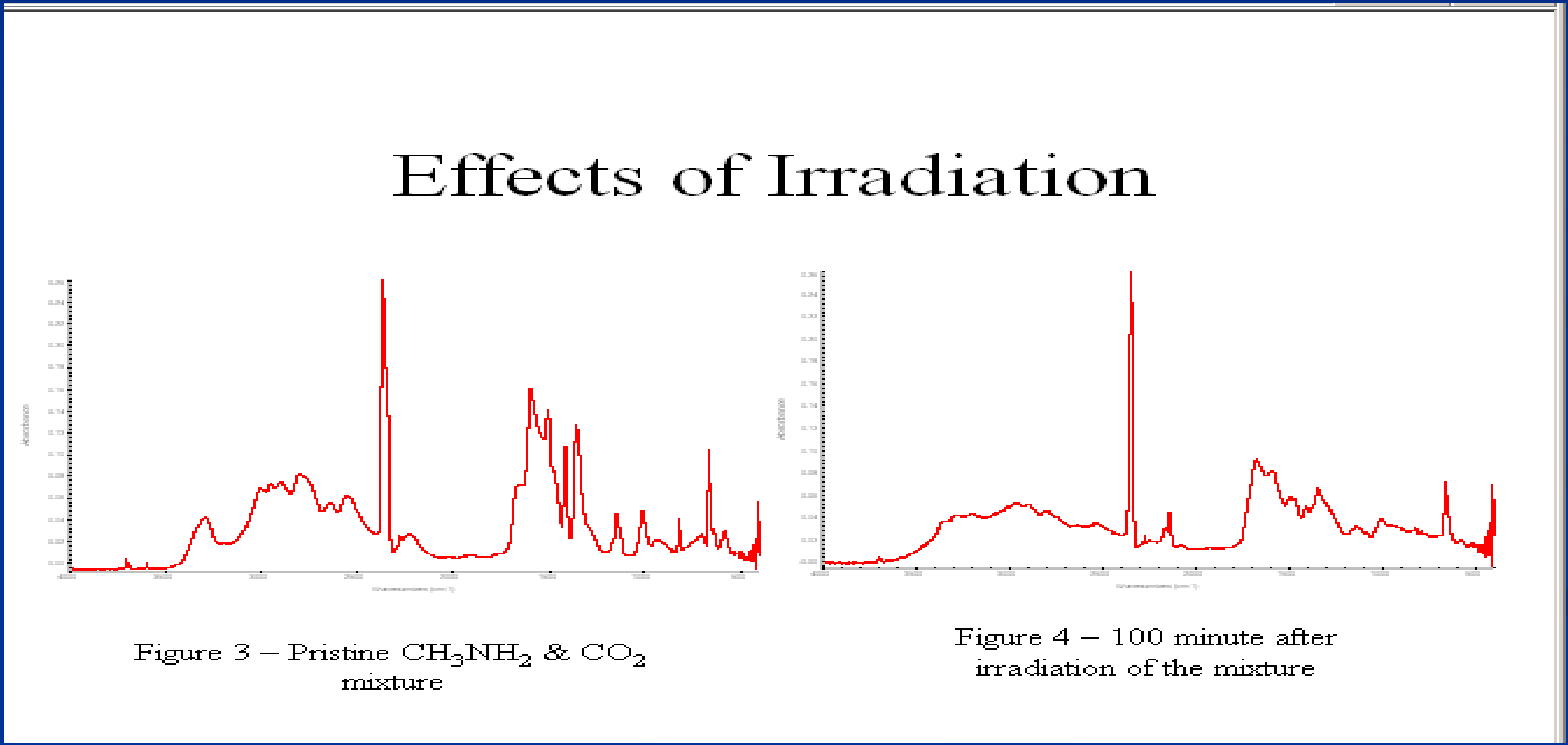


Figure 3 – Pristine CH_3NH_2 & CO_2 mixture

Figure 4 – 100 minute after irradiation of the mixture

Electron Induced Chemistry - summary

- Experiments reveal;
- Electron irradiation is efficient at molecular synthesis (>UV per event ?)
- Can make complex molecules from simple ‘ingredients’
- Low energy electrons (< photo dissociation energy) meV to 10eV can induce chemistry (via dissociative electron attachment == anion chemisty_so no barriers

Electron induced chemistry

- Can make larger molecules e.g. methyl formate; ethylene glycol; ammonium carbamate; glycine; all from simple Methanol/ammonia ices

- Strong Temperature and morphology dependence

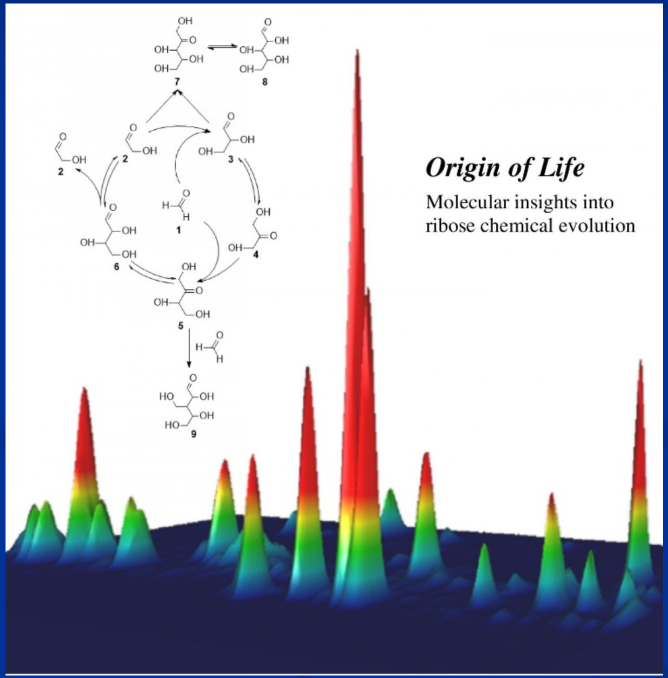
- *Does it play a role in ISM Chemistry Question to answer?*

So big question ?

- How large are the molecules you can synthesize ?

- Can make sugar and amino acids
- RIBOSE (Meinert et al Science 352, pp. 208-212 (2016)

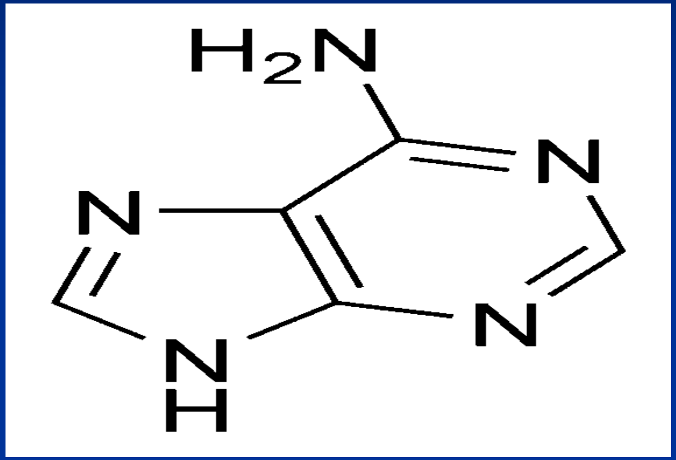
- How do you make the real 'building blocks of life' ? The nuclear bases?

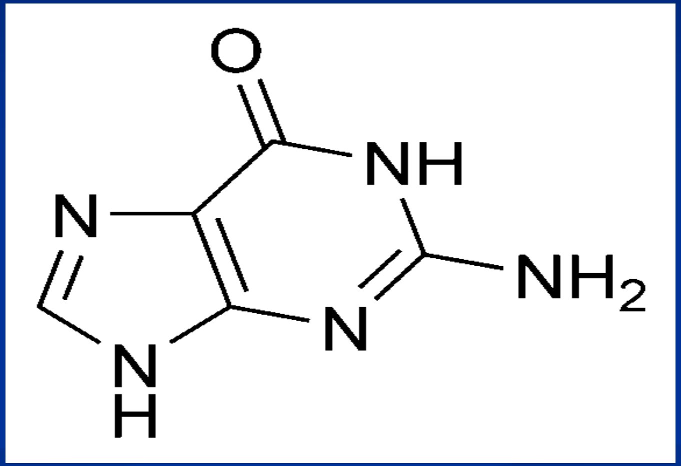


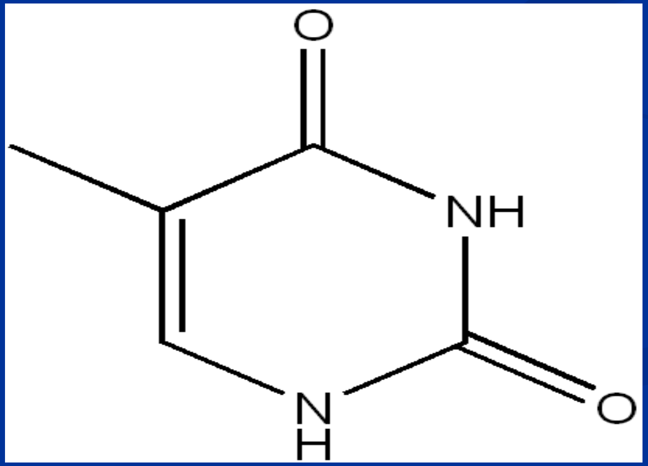
Nucleobases

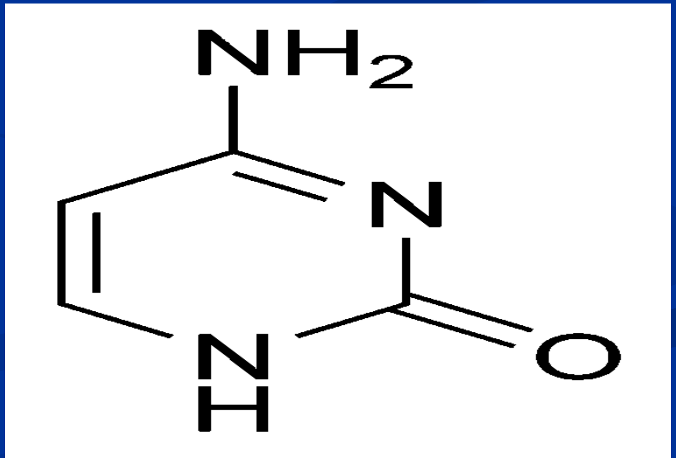
- Adenine
- Guanine
- Thymine
- Cytosine

- Paired in DNA
- AT
- CG

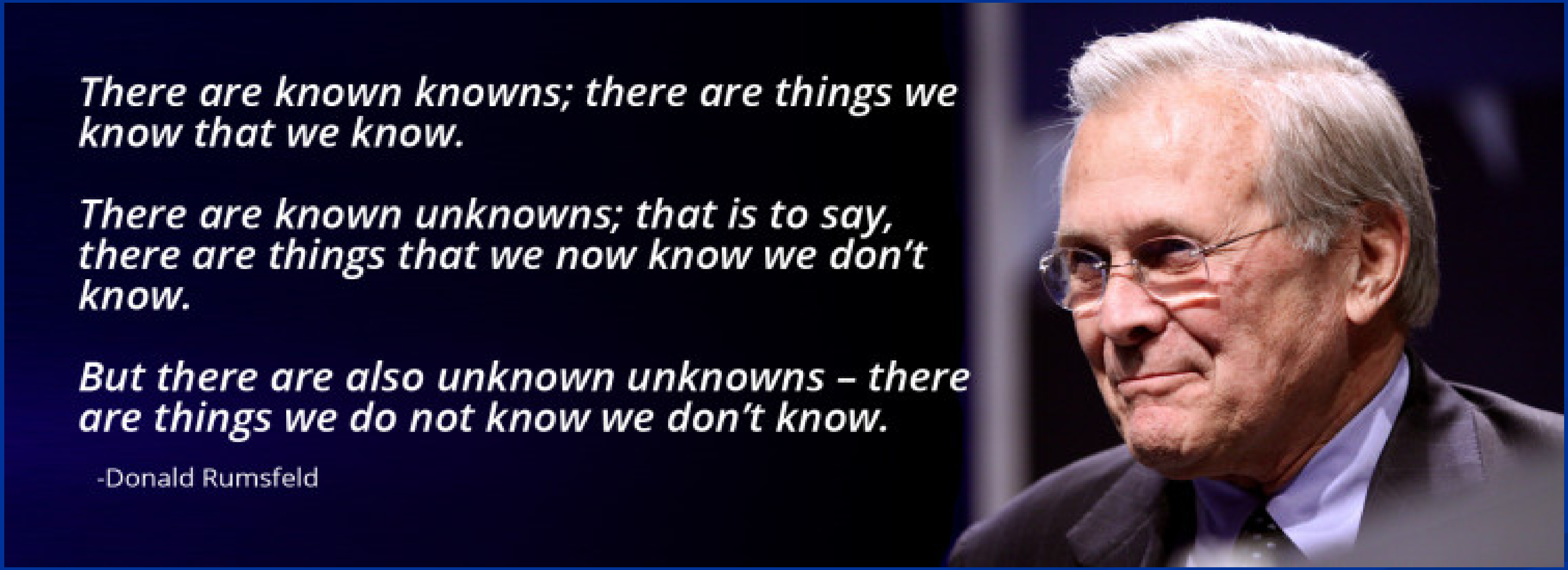




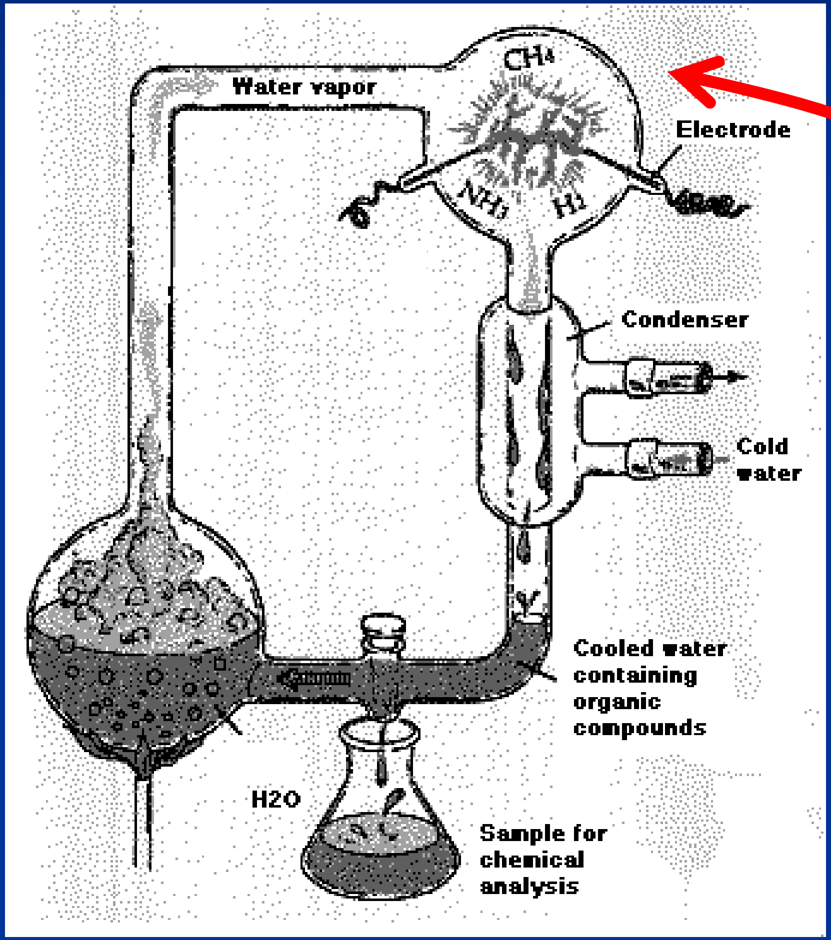




but there is still much to do /learn

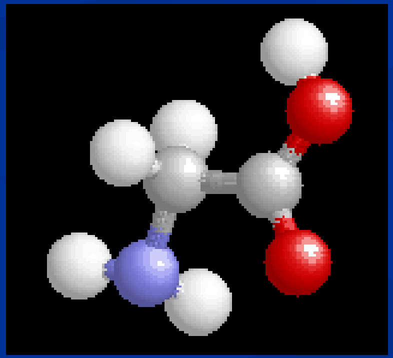


Route 2 to molecular synthesis;
Form on the planet
The UREY MILLER Experiment



$CH_4 + NH_3 + H_2$

+ energy

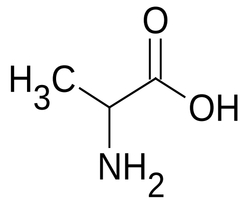


Glycine

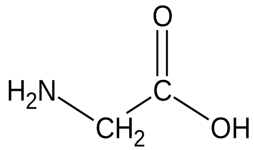
Amino acid

Urey Miller Results

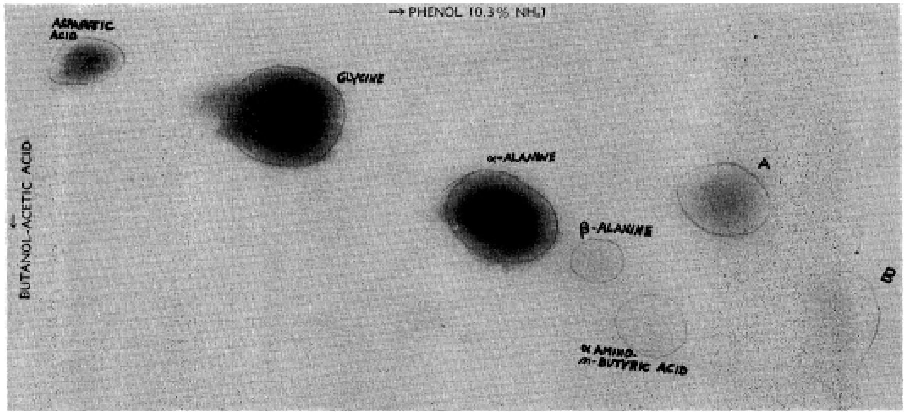
- Urey-Miller was run for a week, liquid was extracted from the flask
- Analysed with paper chromatogram
- 3 Amino acids identified, Glycine, α-alanine and β-alanine
- Hence it is possible to form prebiotic molecules from basic chemistry



Alanine **(Ala)**



Glycine **(Gly)**



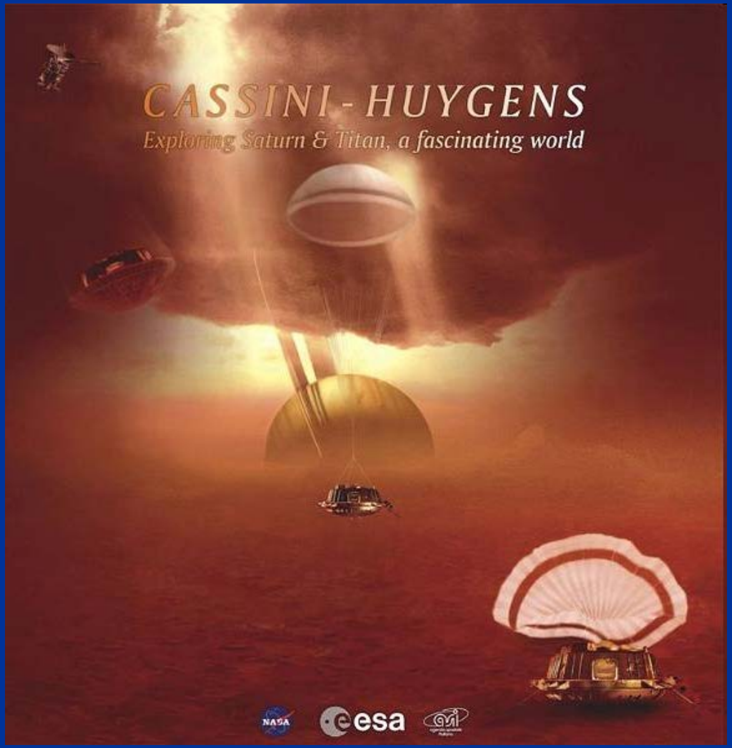
Planetary atmospheres

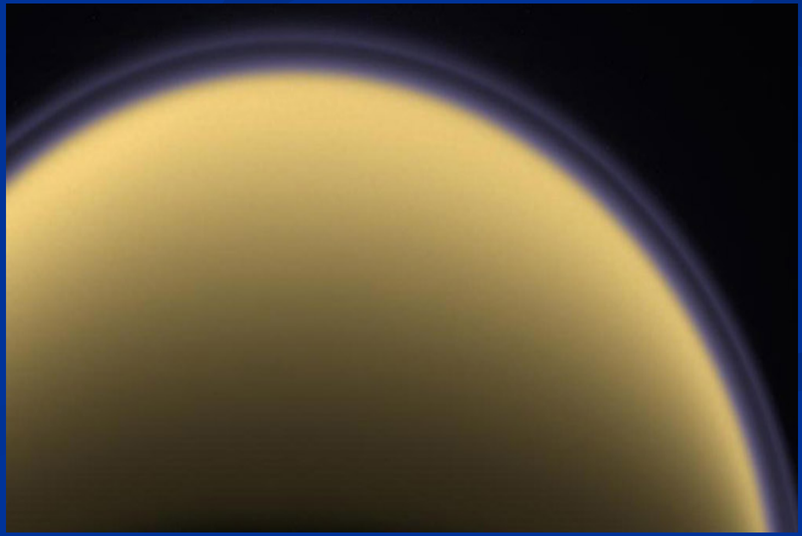
- One area of current and developing research is the study of planetary atmospheres
- Observational studies
- Models (e.g. climate models of Mars and Venus)

Exploring Titan's atmosphere
-- the early Earth ?

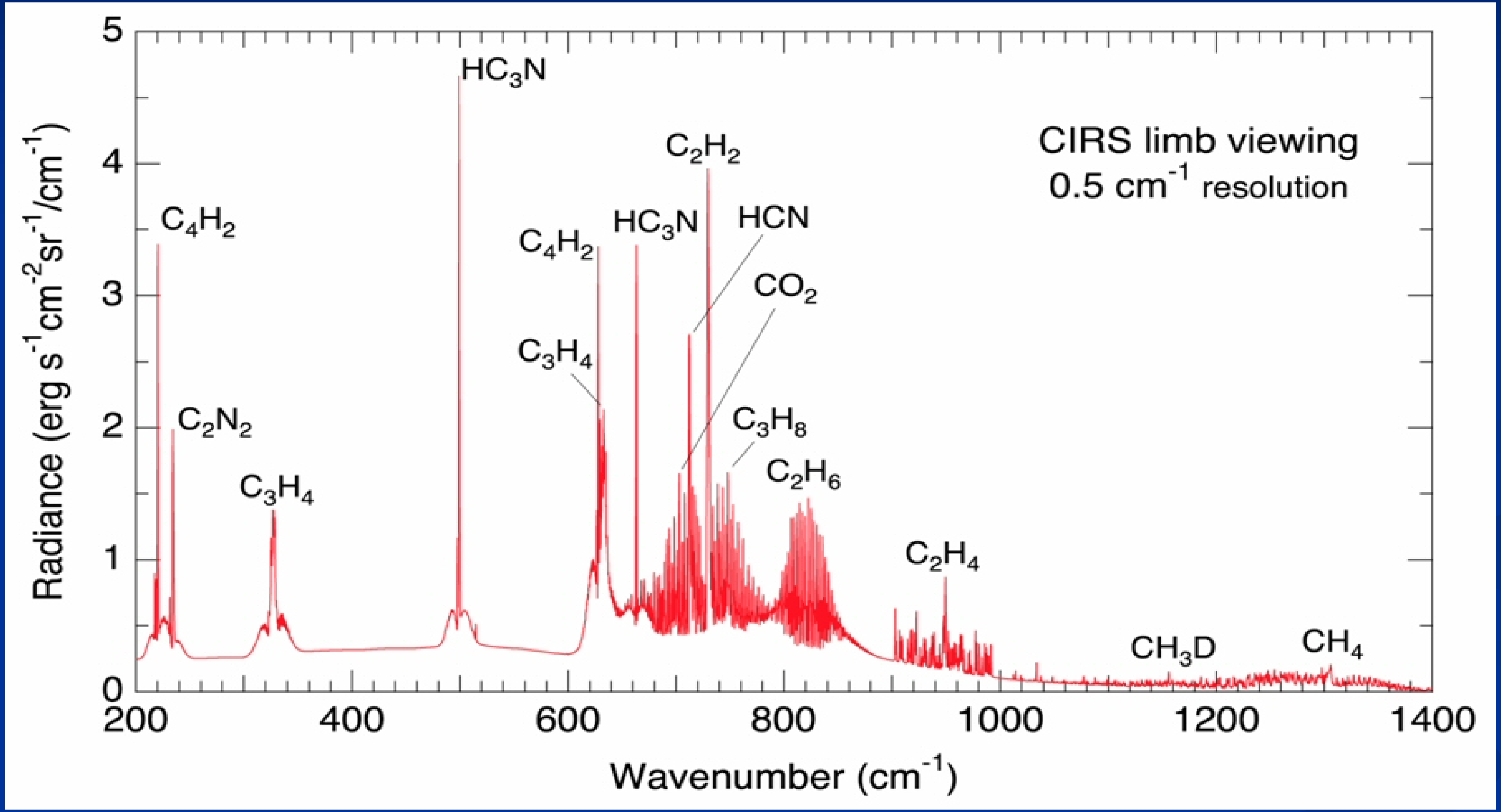
Cassini-Huygens

Mission to Titan



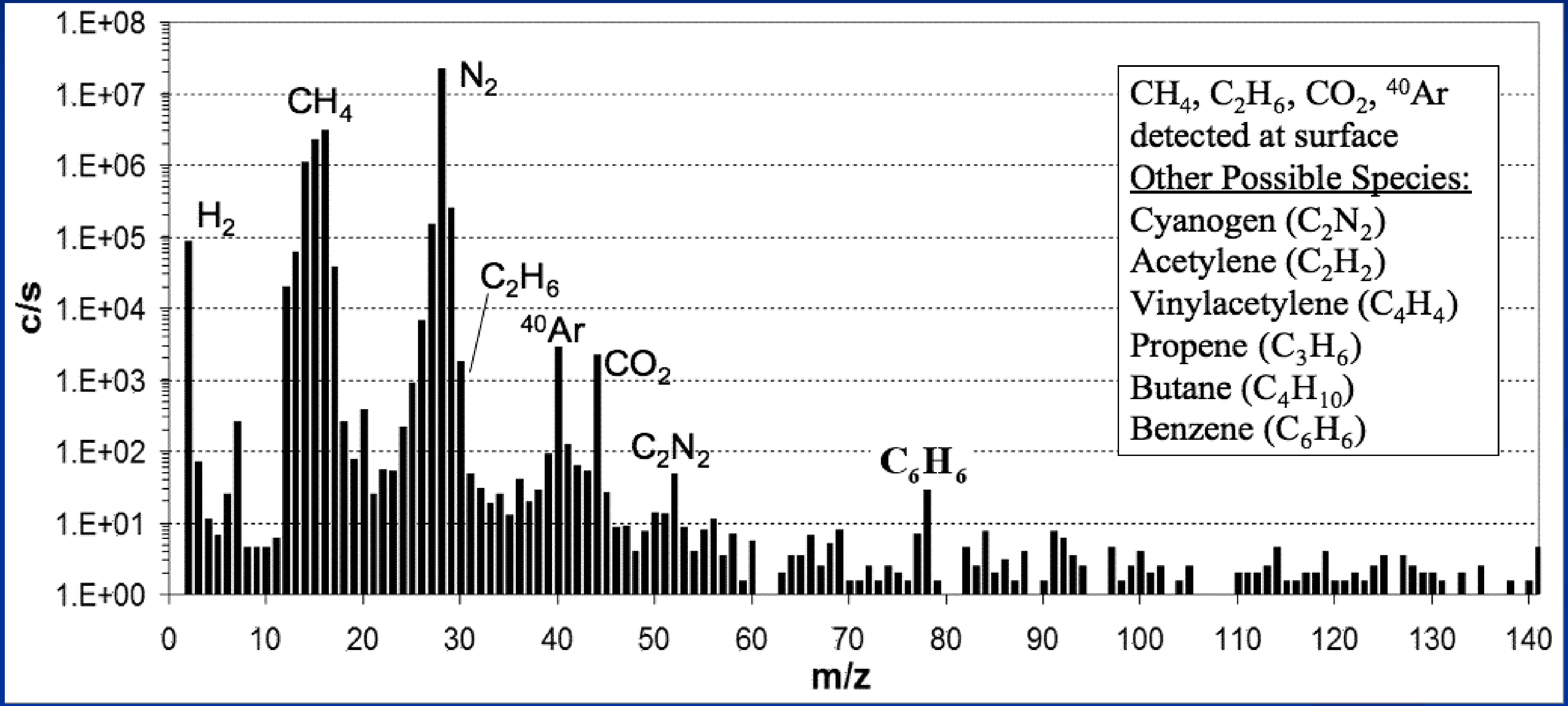


Titan's atmosphere – chemical composition



Hunter Waite et al **Science** 308 982 (2005)

Titan's atmosphere – chemical composition



Titan's surface

Hunter Waite et al **Science** 308 982 (2005)

Nitrogen	N_2	90–97%
Argon	Ar	0–6%
Methane	CH_4	2–5%
Hydrogen	H_2	0.2%
Ethane	C_2H_6	10 p.p.m.
Carbon monoxide	CO	~10 p.p.m.
Acetylene	C_2H_2	2 p.p.m.
Propane	C_3H_8	500 p.p.b.
Hydrogen cyanide	HCN	170 p.p.b.
Ethylene	C_2H_4	100 p.p.b.
Acetonitrile	CH_3CN	5 p.p.b.
Carbon dioxide	CO_2	10 p.p.b.
Cyanoacetylene	HC_3N	10 p.p.b.
Methylacetylene	CH_3C_2H	5 p.p.b.
Cyanogen	C_2N_2	5 p.p.b.
Water vapour	H_2O	8 p.p.b.
Diacetylene	C_4H_2	1 p.p.b.

Question

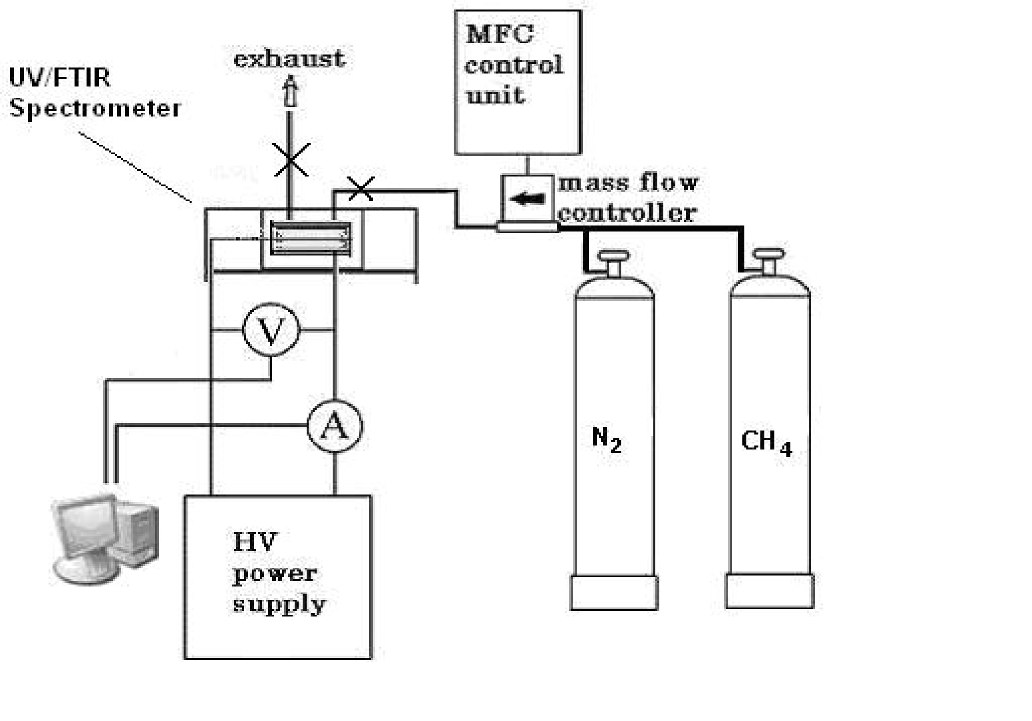
- What organic chemistry may be prevalent ?
- Can prebiotic molecules form in a Titan atmosphere ?

Use laboratory plasma/discharge as mimic of planetary atmosphere

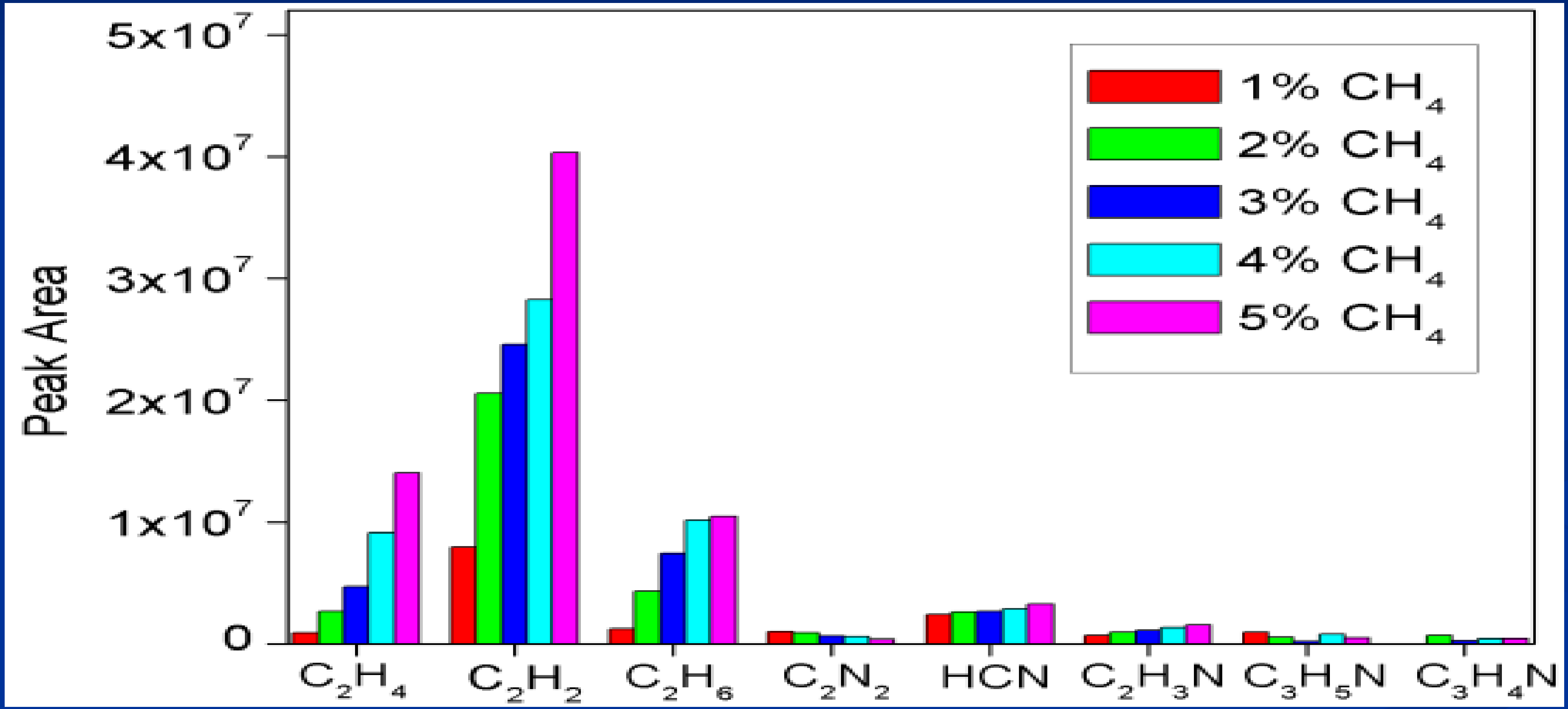
- Study discharge in N_2/CH_4

Make Titan dust analogues

Detect anions

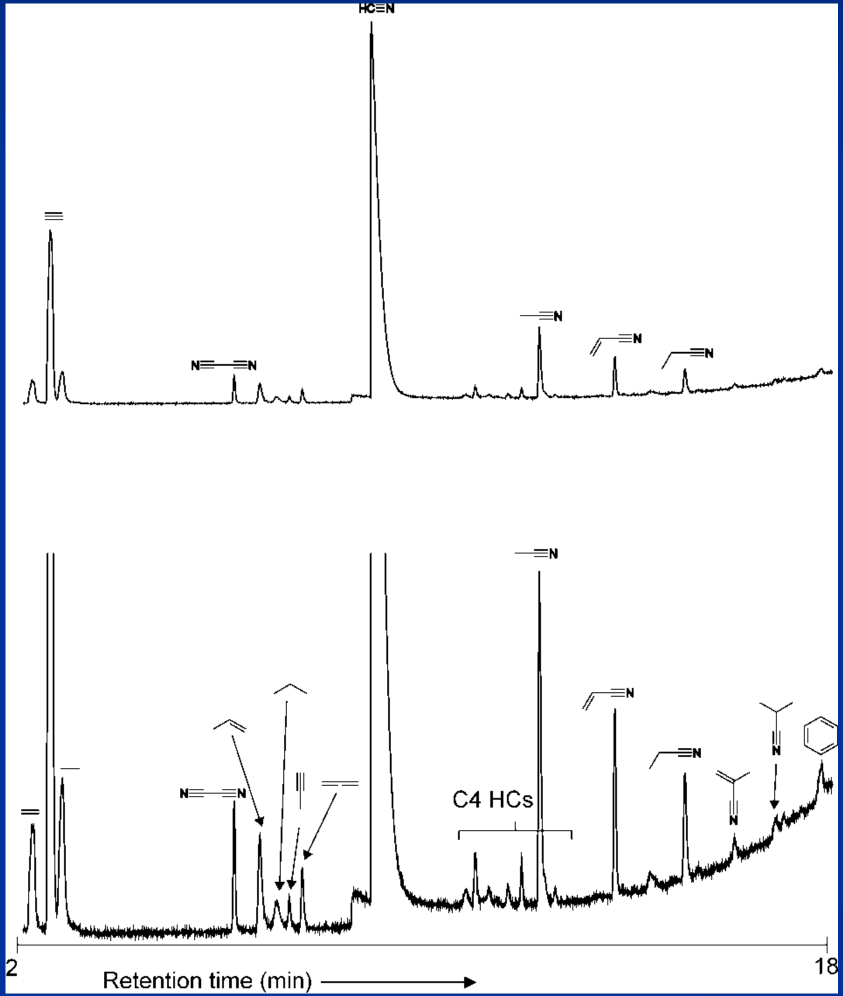


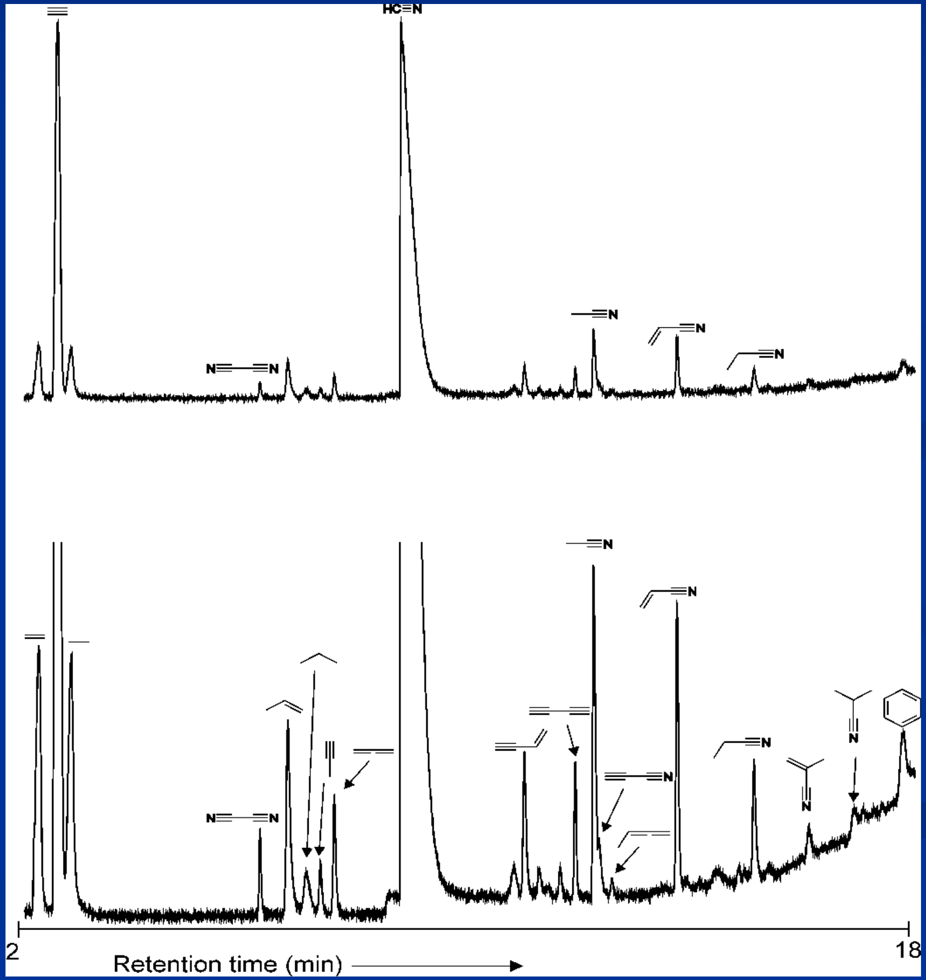
Molecular formation in glow discharge



Form main hydrocarbons and nitriles
seen in Titan atmosphere

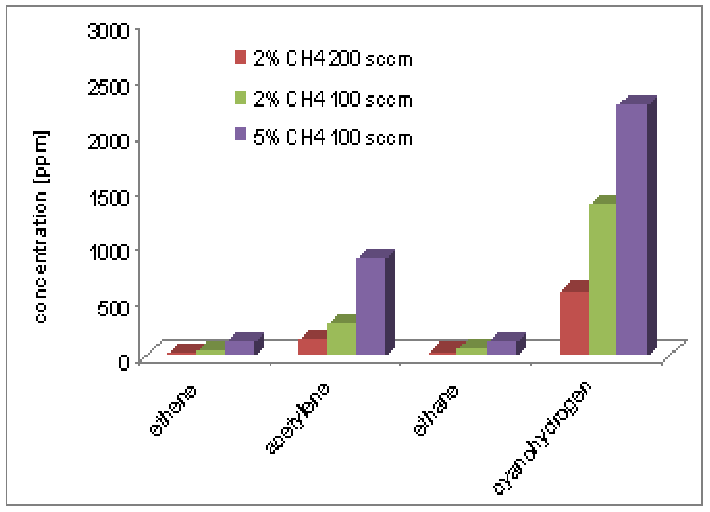
Neutral chemistry
Optical Emission --
FTIR –or GC-MS

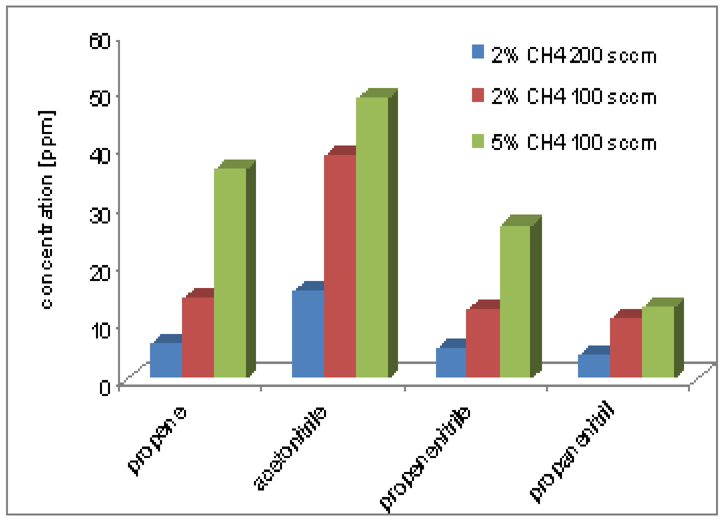




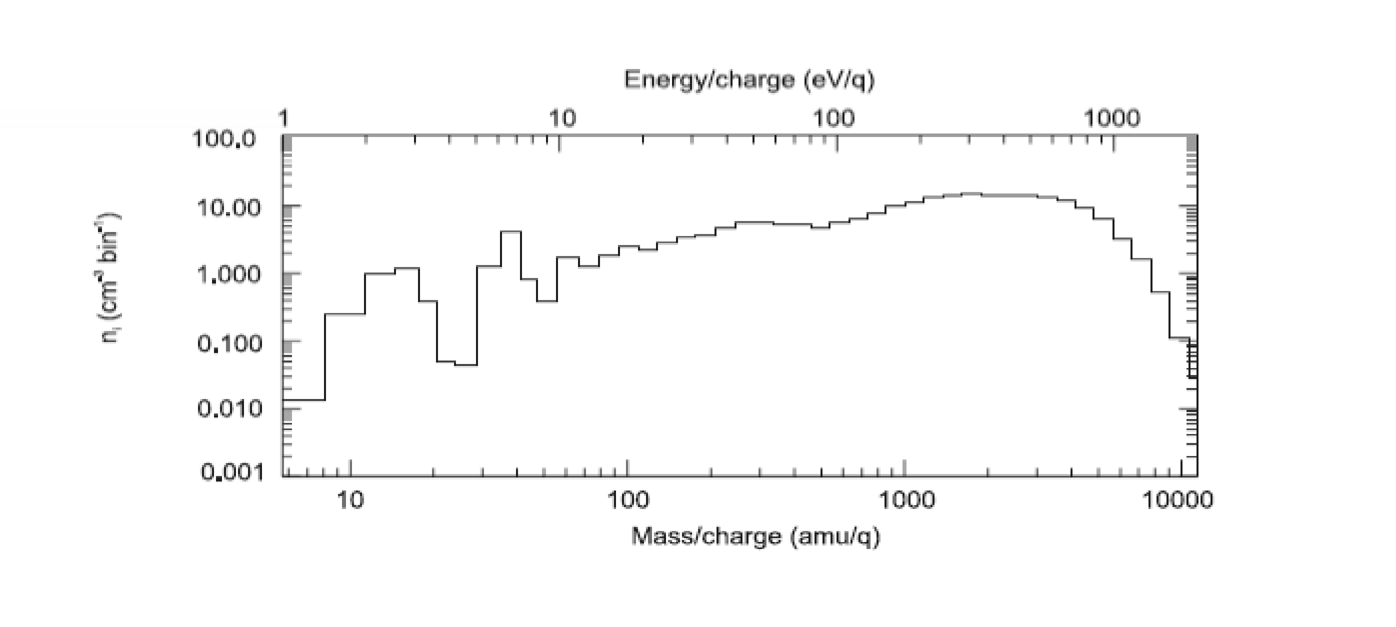
Neutral Chemistry – GC-MS

Ethane, ethene, cyanogens, propene, propane,propyne, propadiene, butenyene, butadiene, butadiyne, Acetonitrile,propenenitrile, benzene and toluene.



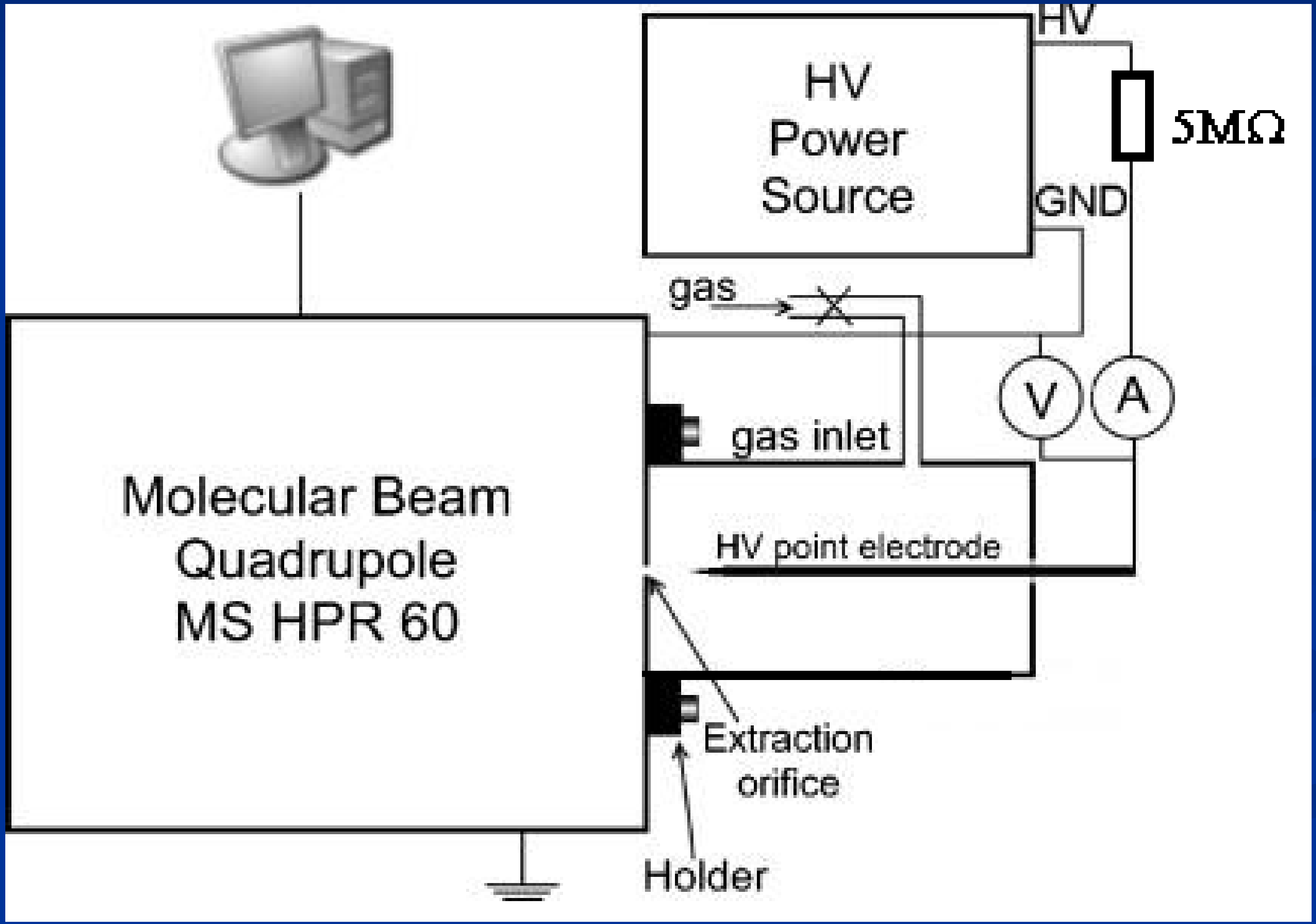


What about anions in Titan atmosphere ?

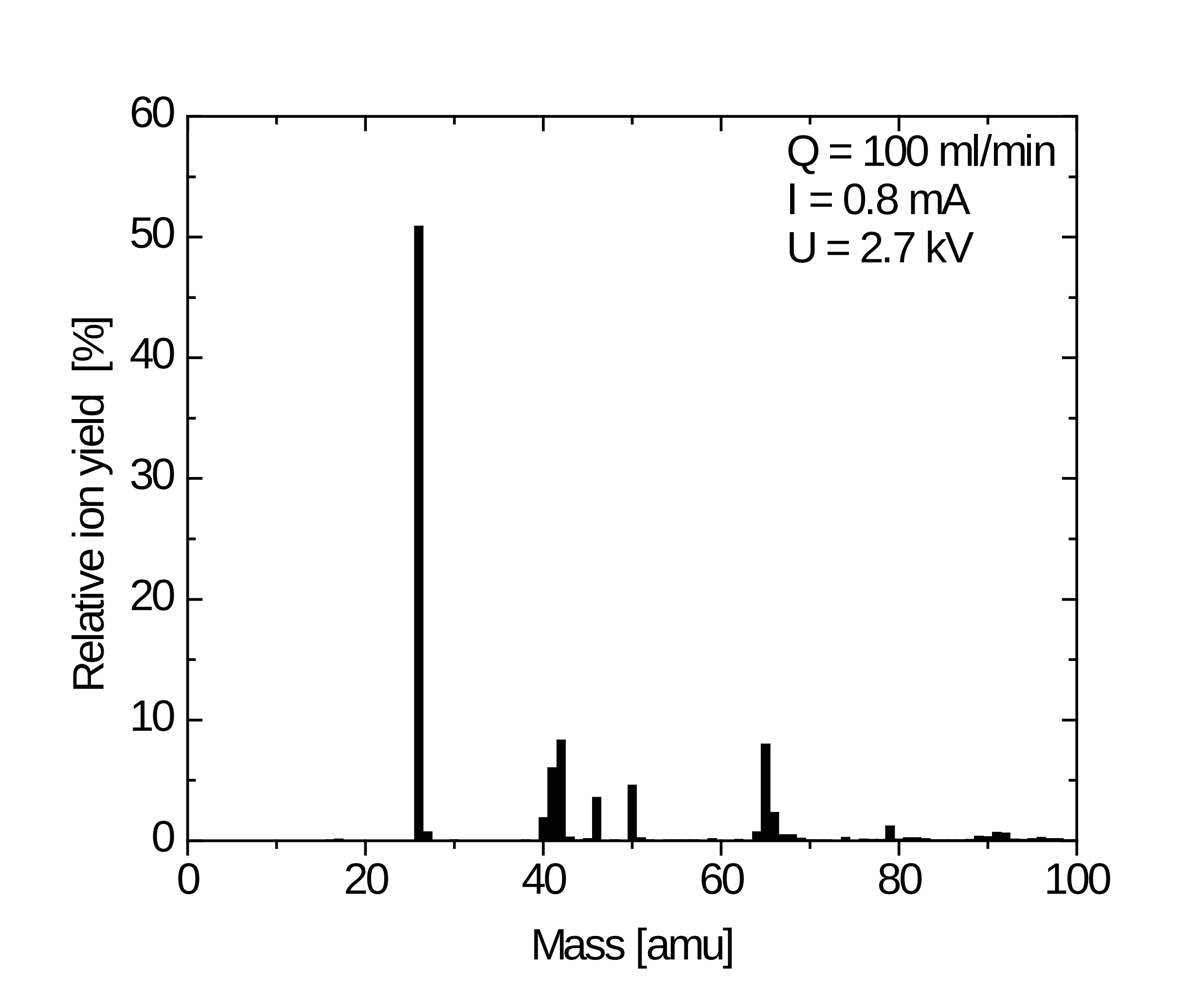


The anion spectrum recorded by the Cassini-Huygens mission at an altitude of 953 km (Coates et al (2007)).

Experimental set-up for exploring anion formation in point-to-plane corona discharge



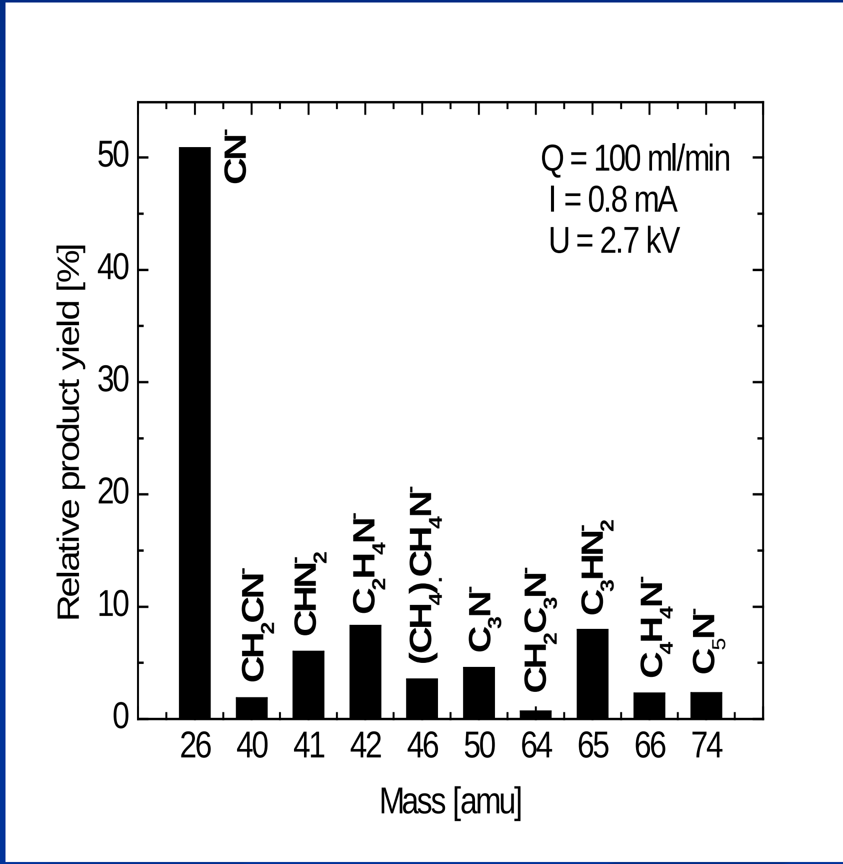
Mass spectra of negative ions extracted from point-to-plain corona discharges.



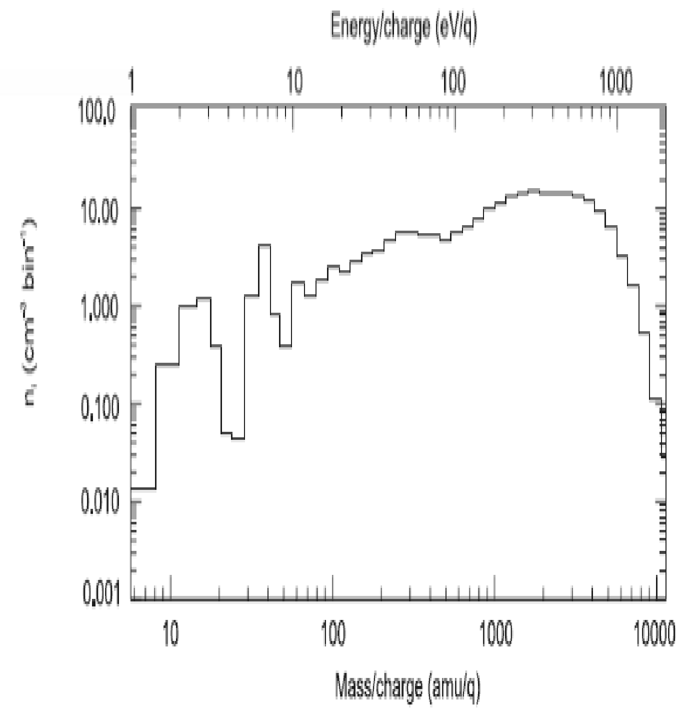
Anions in the discharge

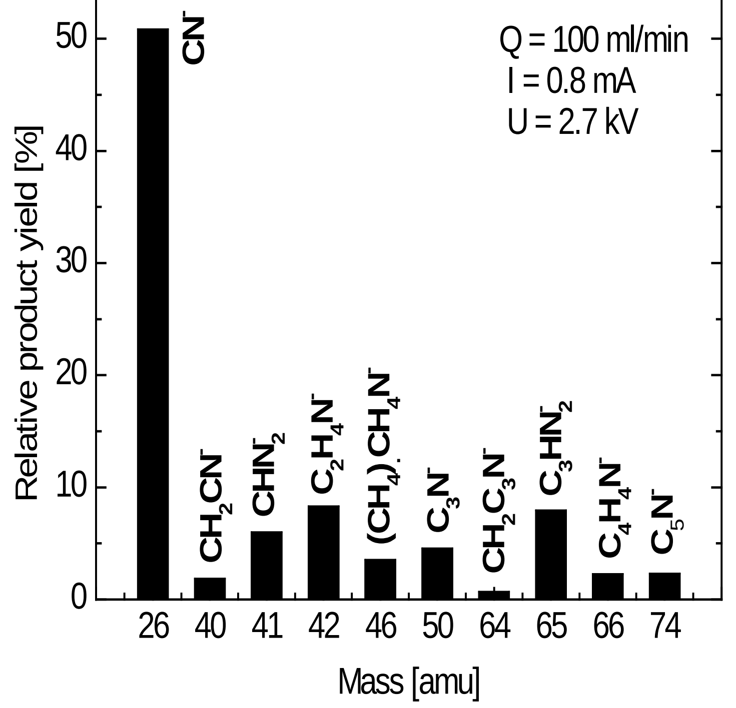
The detection of CN^-, CH_2CN^-, C_3N^-, CH_2CN^- and C_5N^- anions

provides good evidence of the presence of HCN, CH_3CN, HC_3N, and HC_5N neutrals



Anions in Titan's atmosphere





Future Research/Challenges in astrochemistry

- Reproduceability
- Different experiments do not agree on molecules synthesized and/or concentrations of species produced.

- Cross Sections/rate constants
- Ill defined and hence hard to produce data for models

- Same ingredients mixed and bake make different cakes

Future Research/Challenges in astrochemistry

- Do experiments mimic nature?
- ISM surface chemistry is on micron sized dust grains - is this replicated in bulk ice films?
- Time – do laboratory experiments replicate the slow, unimolecular events of space ?
- Planetary atmospheres – How to make a real mimic (no walls) Terrestrial atmospheric chambers

Future Research/Challenges in astrochemistry

- Understand the physics/chemistry
- Role of (secondary) electrons and electron induced mechanisms compared to direct ion bombardment and UV absorption
- Morphology – Surface cluster chemistry and three body reactions
- Synthesis when/where – Direct or through diffusion of radicals (In-situ spectroscopy vs TPD results)

Future Research/Challenges in astrochemistry

- How do we know we have 'got it right'

- Experiments tested against/predict observations
- ALMA spatial chemical maps.
-

Future Research/Challenges in astrochemistry

- Towards biology
- Energetic processing of prebiotic and biological molecules
- Look for routes of formation and stability

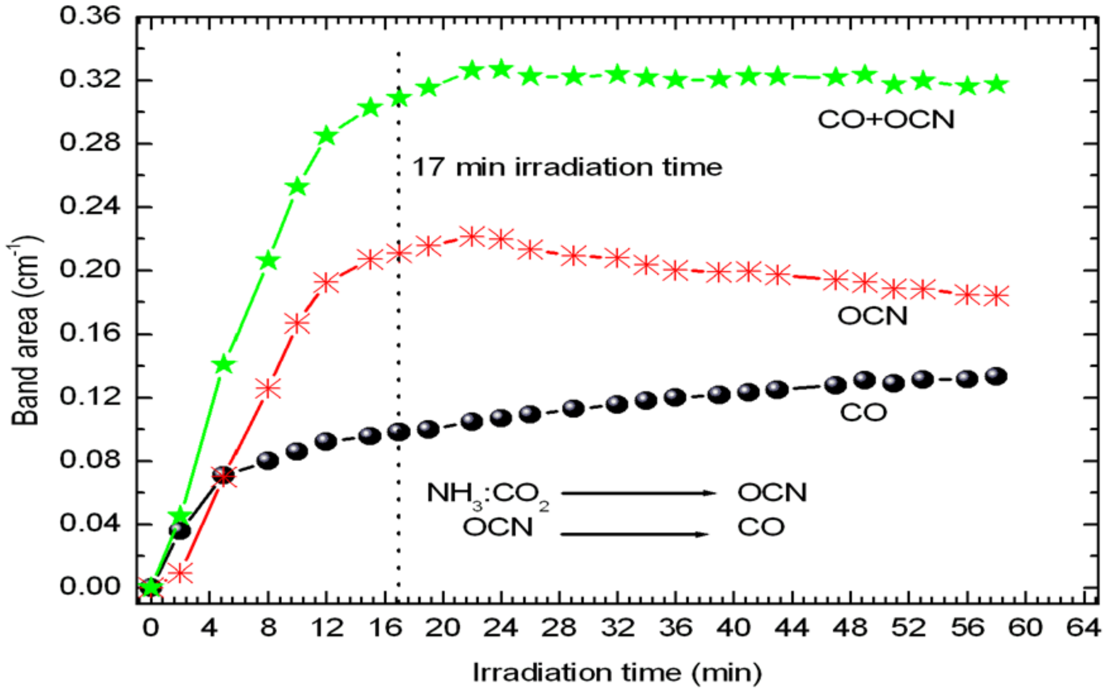


Fig. 5-9: Destruction of OCN during the irradiation of NH_3:CO_2 (1:1 ratio)

Future Research/Challenges in astrochemistry astrobiology

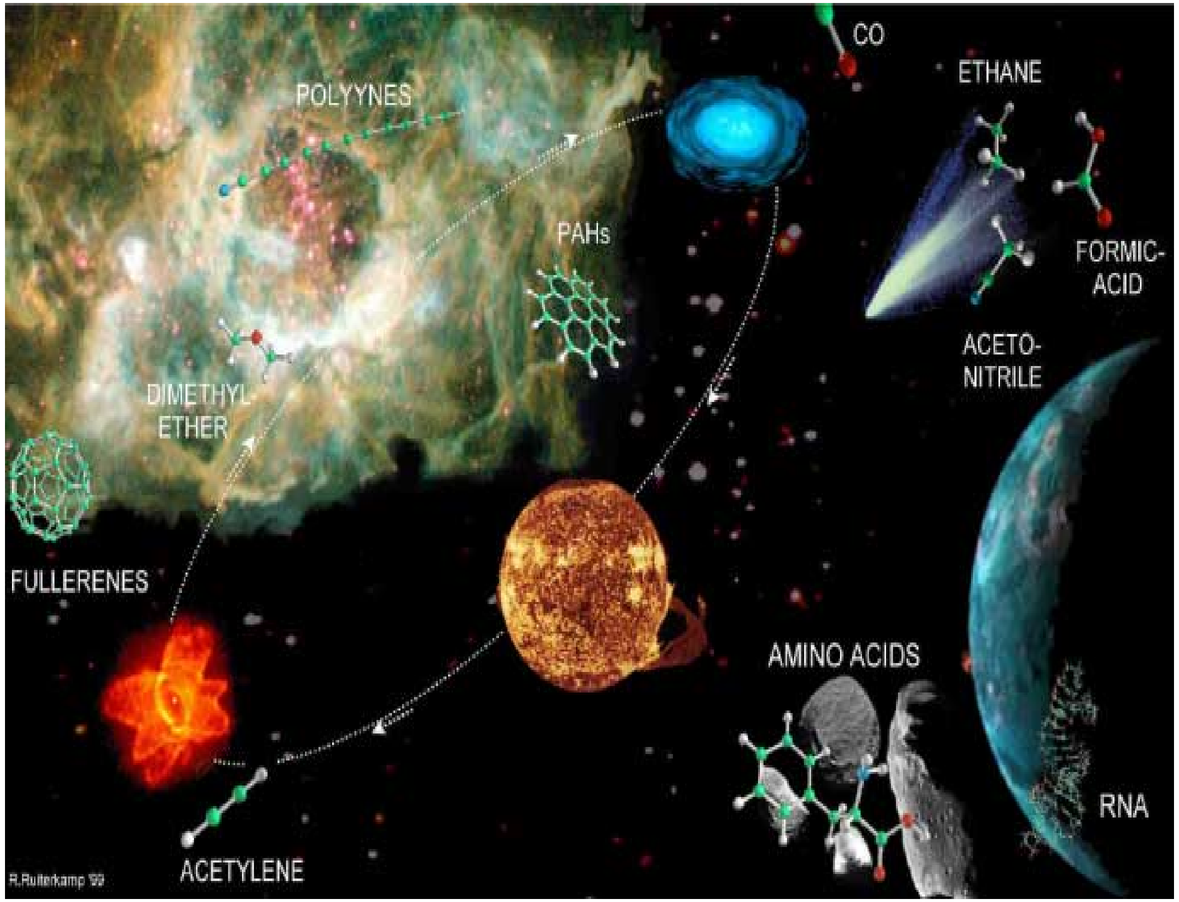
- How do prebiotic molecules assemble to form biomolecular systems e.g. DNA
- Role of the host planet ?
- Is life inevitable or rare ?

Core Questions for Astrochemistry & Astrobiology

- Where are the building blocks of life synthesised ? ISM or on planet?

- Are the conditions for such synthesis common/universal ?

- European Astrobiology Roadmap. Published 2016



and finally thanks to..

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