Cosmic Ray Chemistry 2

Cosmic Ray Irradiation of Ices

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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
3. Prepare targets for collisions – gas phase 'easy'
   - condensed/ice phase harder

     Temperature

     Morphology

     Compound mixture of ices

All needs to be prepared in ultra high vacuum to mimic space

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

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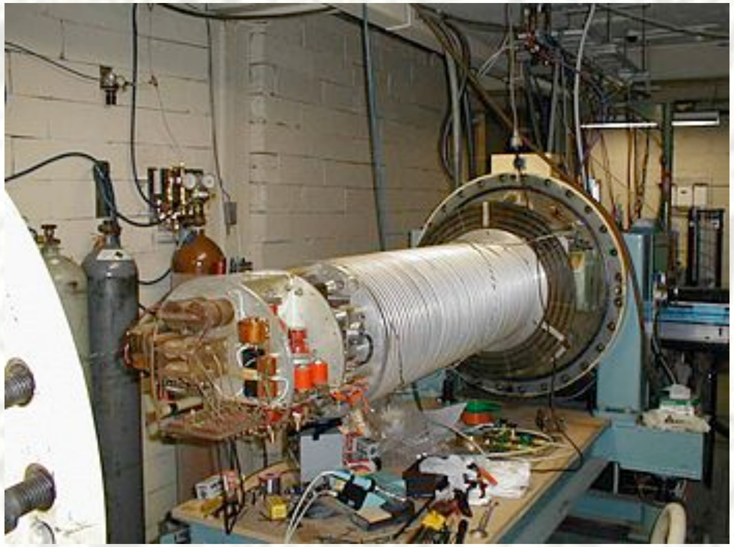
Use particle accelerators - Van der Graf Accelerators



Modern version ECRIS Ion source

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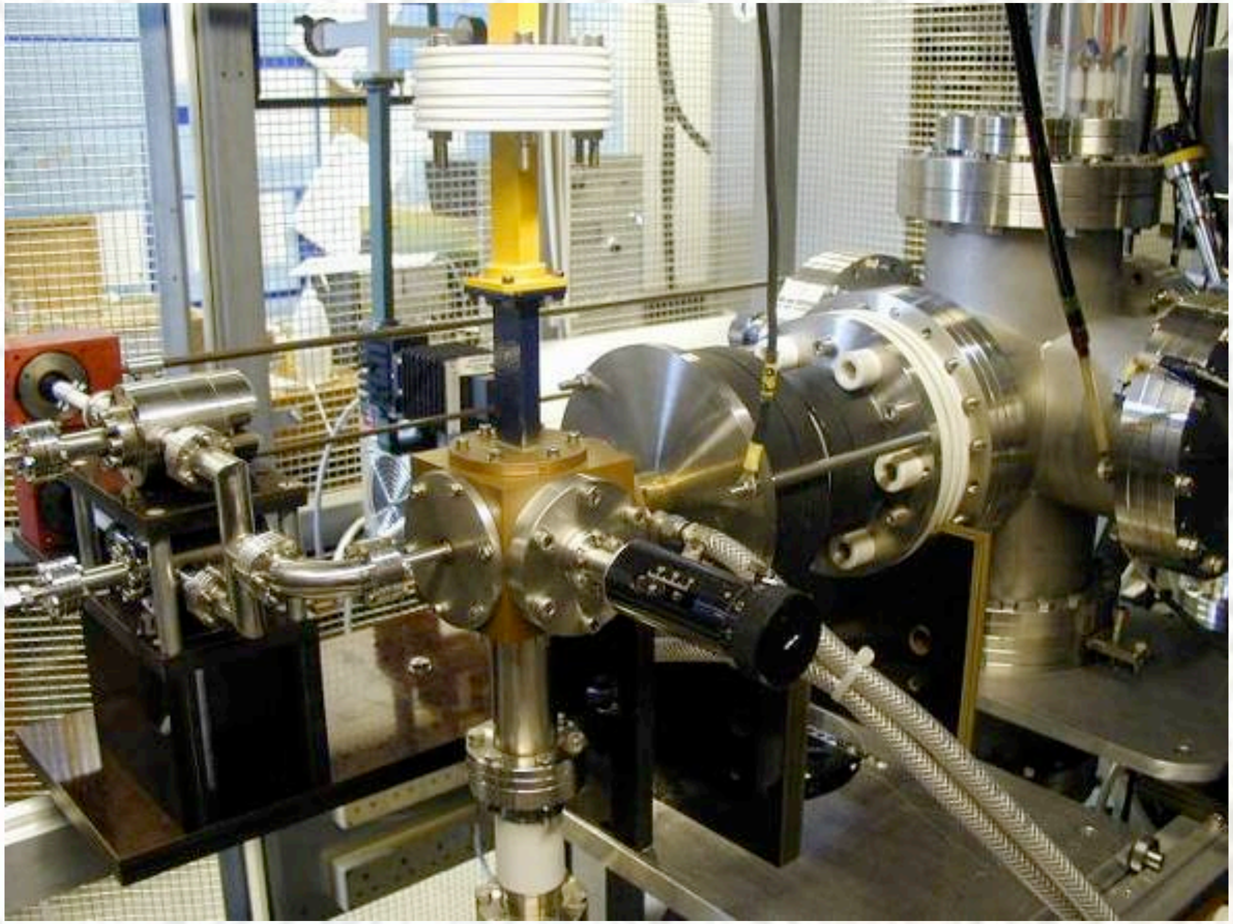
9.0 – 10.5 GHz Electron Cyclotron Resonance Ion Source at Belfast



- Produce beams of heavy ions in multiply charged state e.g. C^{+} to C^{4+} *(note beam may not all be in ground state)*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A Team
in ACTION

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

1. Prepare targets for collisions – gas phase 'easy'
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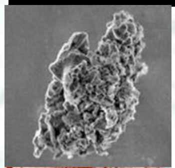
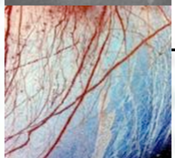
Nature of Astrochemical Ices and their Environments

- **Ices may be broadly characterised in terms of**
  - ice thickness, temperature and composition → **ice morphology**
  - energy, flux and type of processing radiation → **ice processing**

	Ice environment	Thickness	Temperature	Processing Radiation
	**ISM grain mantle**	1nm - 1μm	10 – 100 K	Stellar UV; Lyman-α photons (H_2 luminescence); Cosmic rays
	**Surfaces of planetary bodies in the outer solar system**	1μm – several km	30 – 150 K	Magnetospheric ions, Solar UV, solar wind, cosmic rays
	**Comets (in the Oort cloud)**	1m – several km	10 K	Cosmic rays

Experimental Set-up

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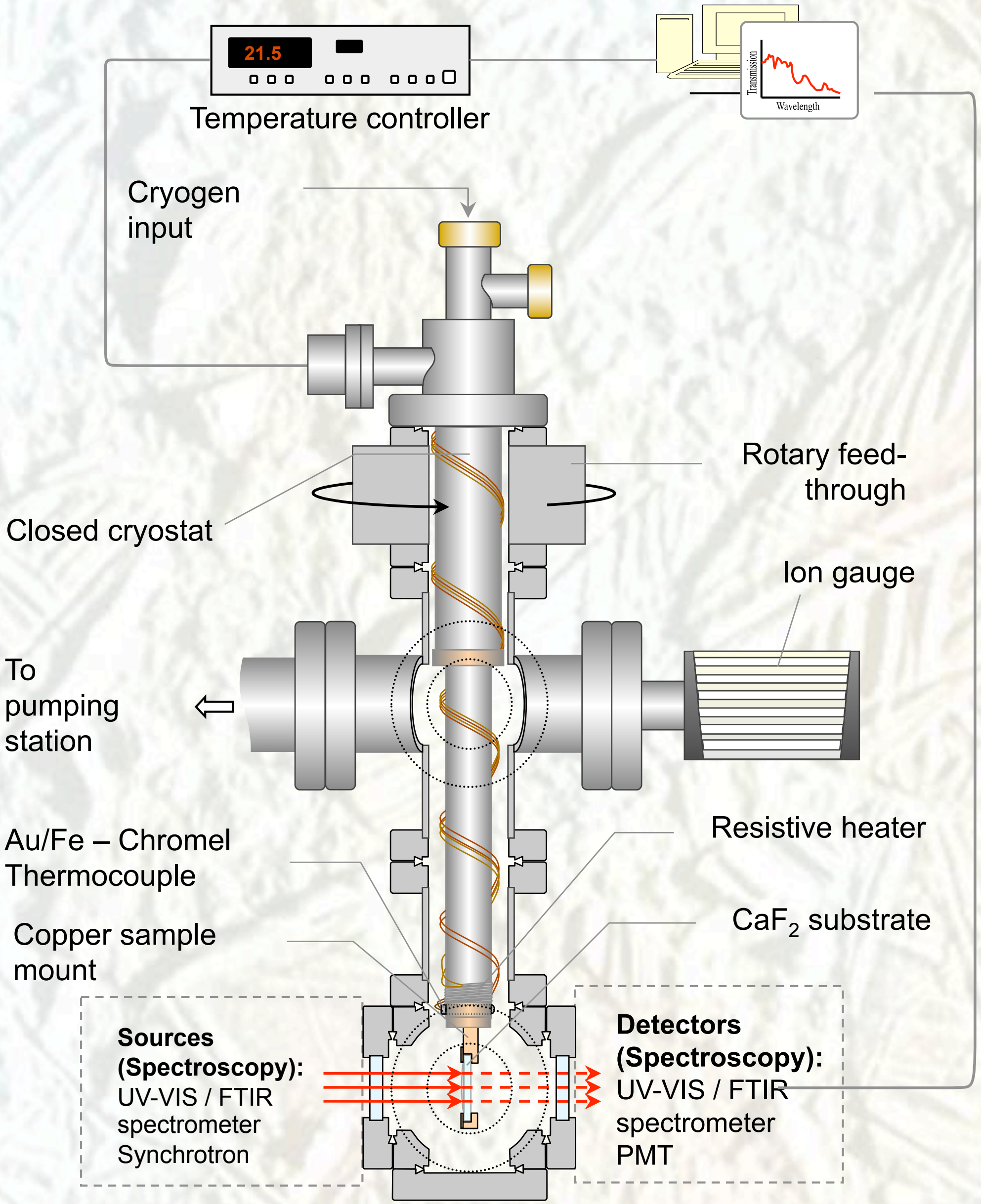
- HV (UHV) chamber :
  - P~10^{-8} - 10^{-10} mbar
  - Still 1000 higher than dense ISM !
- Temperature
  - Continuous flow or LHe/LN2 cryostat
    - 10K < T < 450 K
    - Mimics ISM and star forming regions
- Samples onto a substrate
  - deposited *in situ* by vapour deposition

What substrate ?



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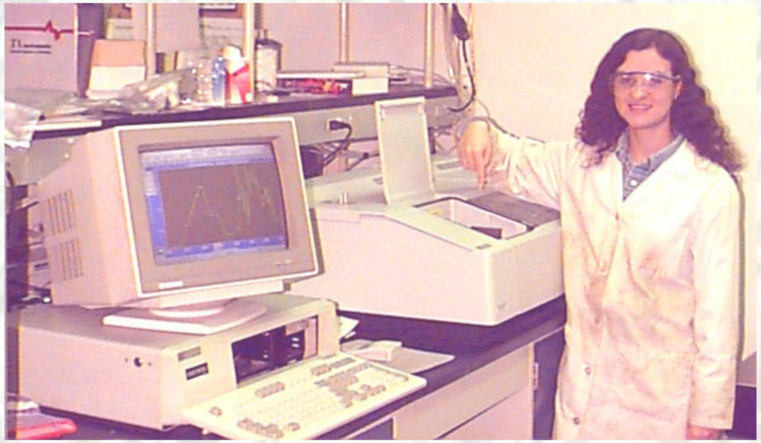
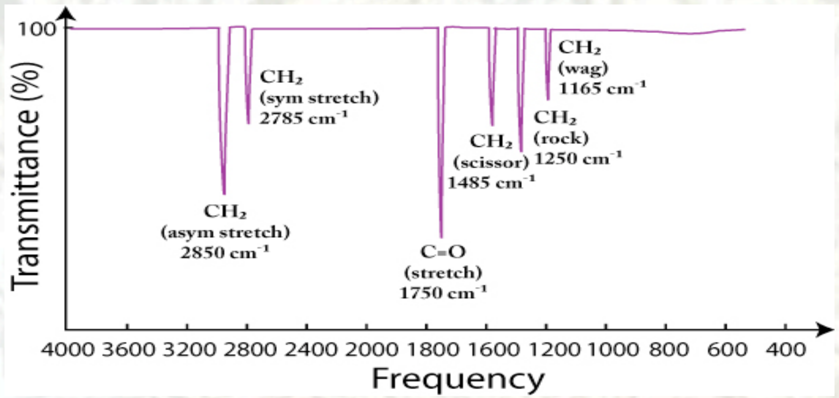
How do we study Cosmic Ray (CR) induced chemistry ?



How do we monitor chemical change ?

Use spectroscopy - molecules have *spectral fingerprint*

FTIR (Infrared spectroscopy)



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

How do we monitor chemical change?

Heat to desorb from surface

Temperature Programme Desorption (TPD)

Use mass spectroscopy to detect products

What ISM condition cant we reproduce in the lab ?

What ISM condition cant we reproduce in the lab ?

TIME !!

- Processes take places over 10s 100s or 1000s of year
- Flux is very low

- Low dose, long exposure time

What ISM condition cant we reproduce in the lab ?

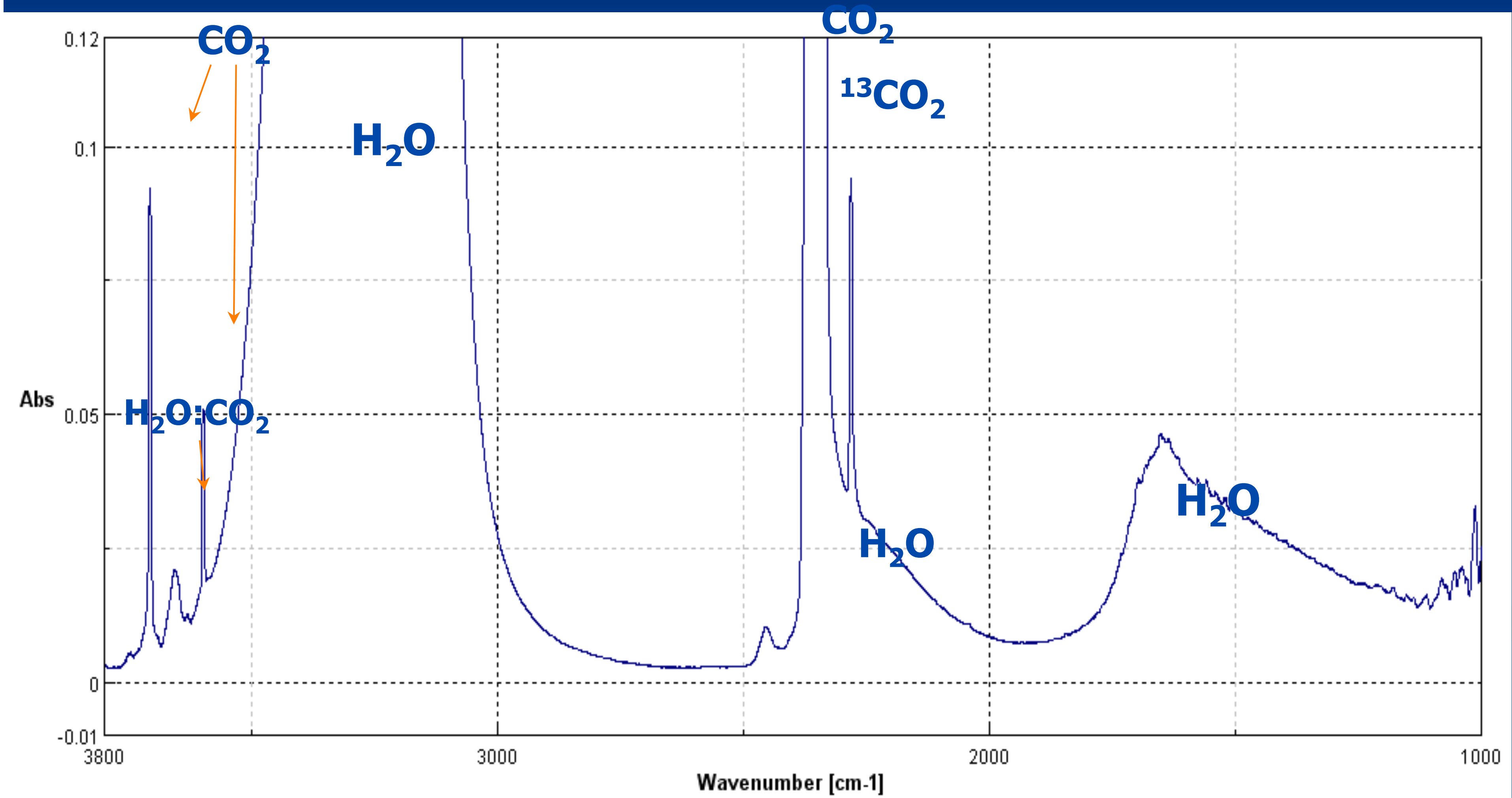
- Question

Is flux A for irradiation time Y same as flux B for time Z?

So lets do some chemistry !

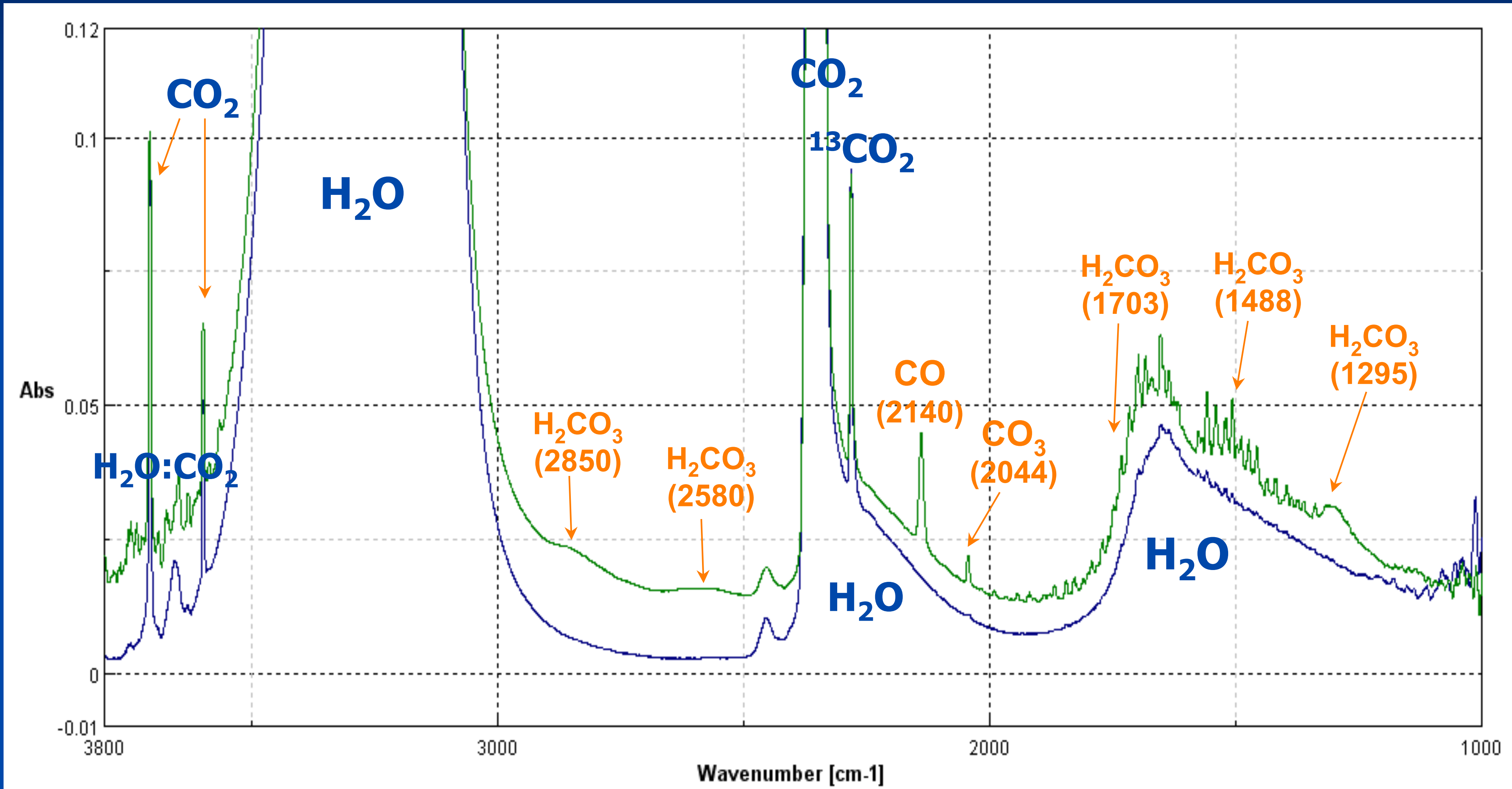
Irradiation of $H_2O:CO_2$ ice by protons

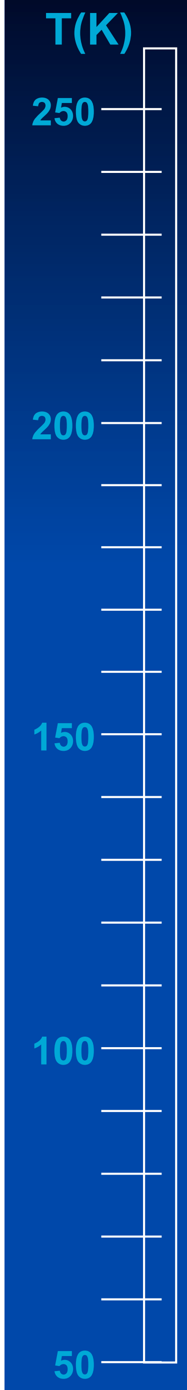
Before irradiation



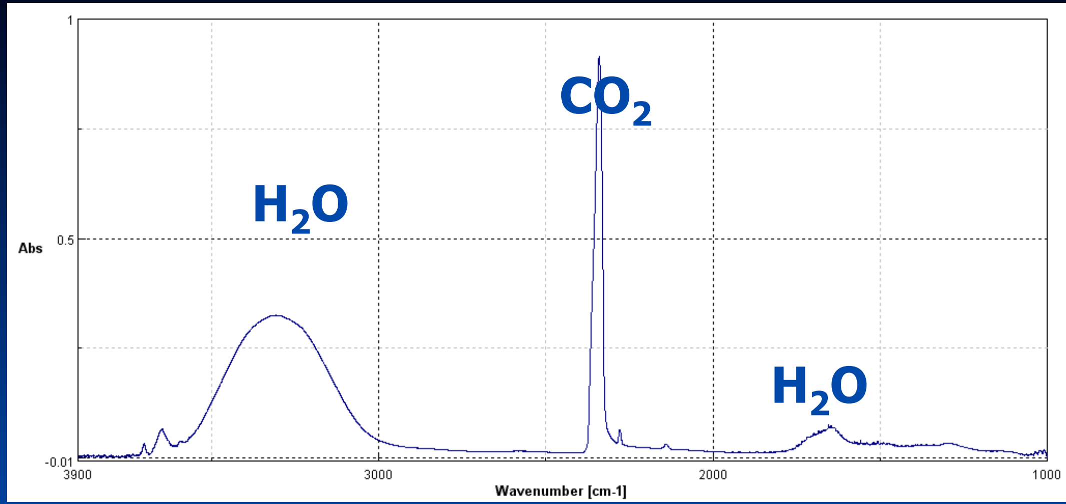
Irradiation of $H_2O:CO_2$ ice

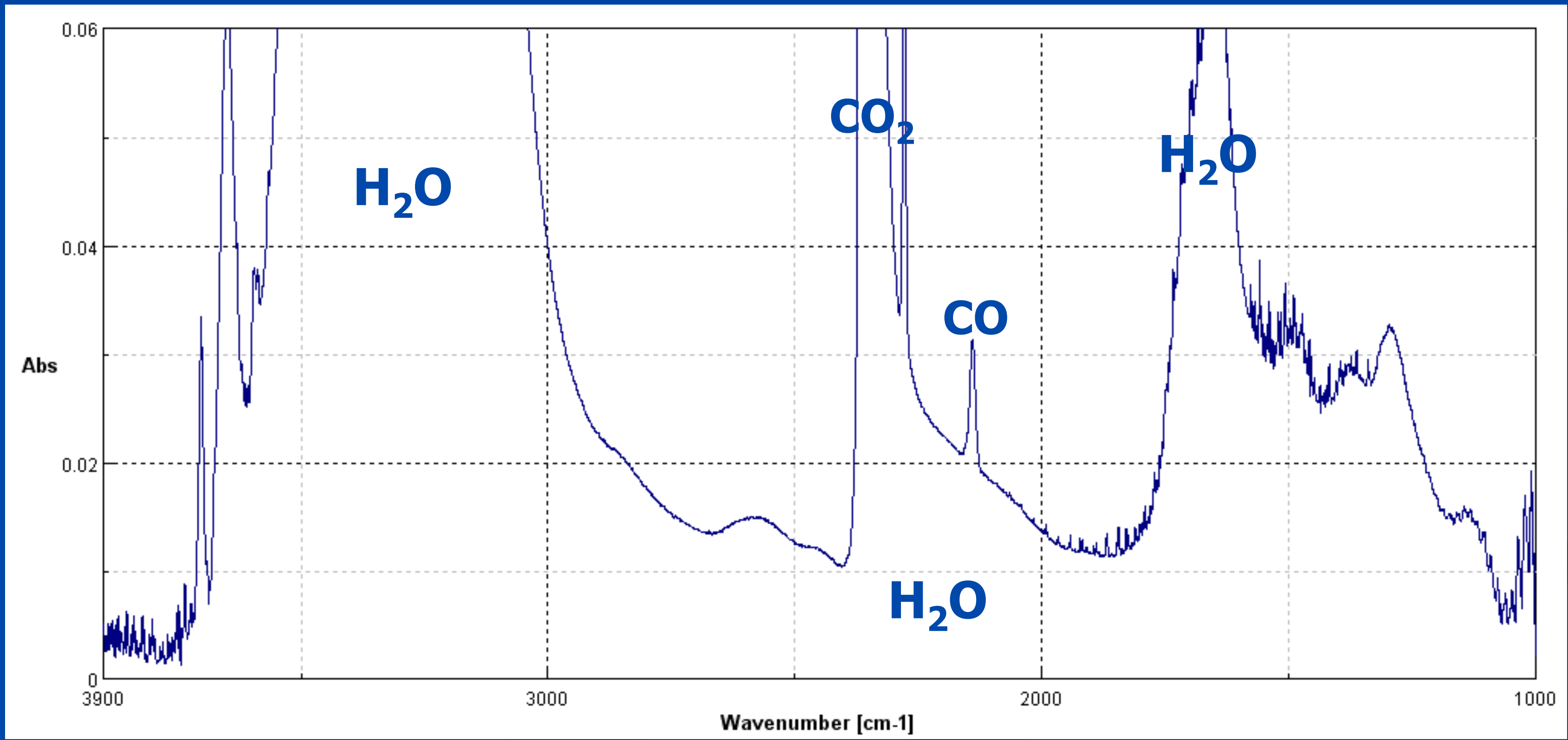
After irradiation for 1 hour



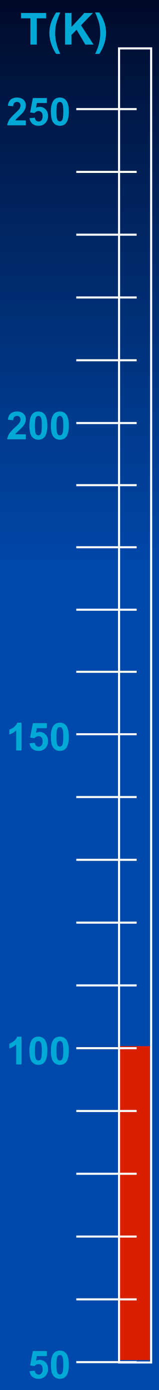


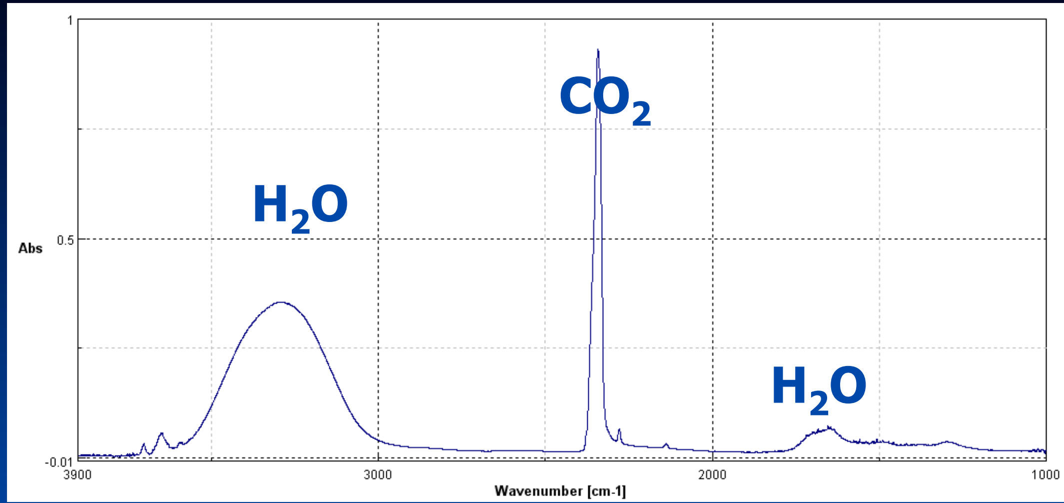
Warm-up
+Irradiation of H_2O:CO_2 ice

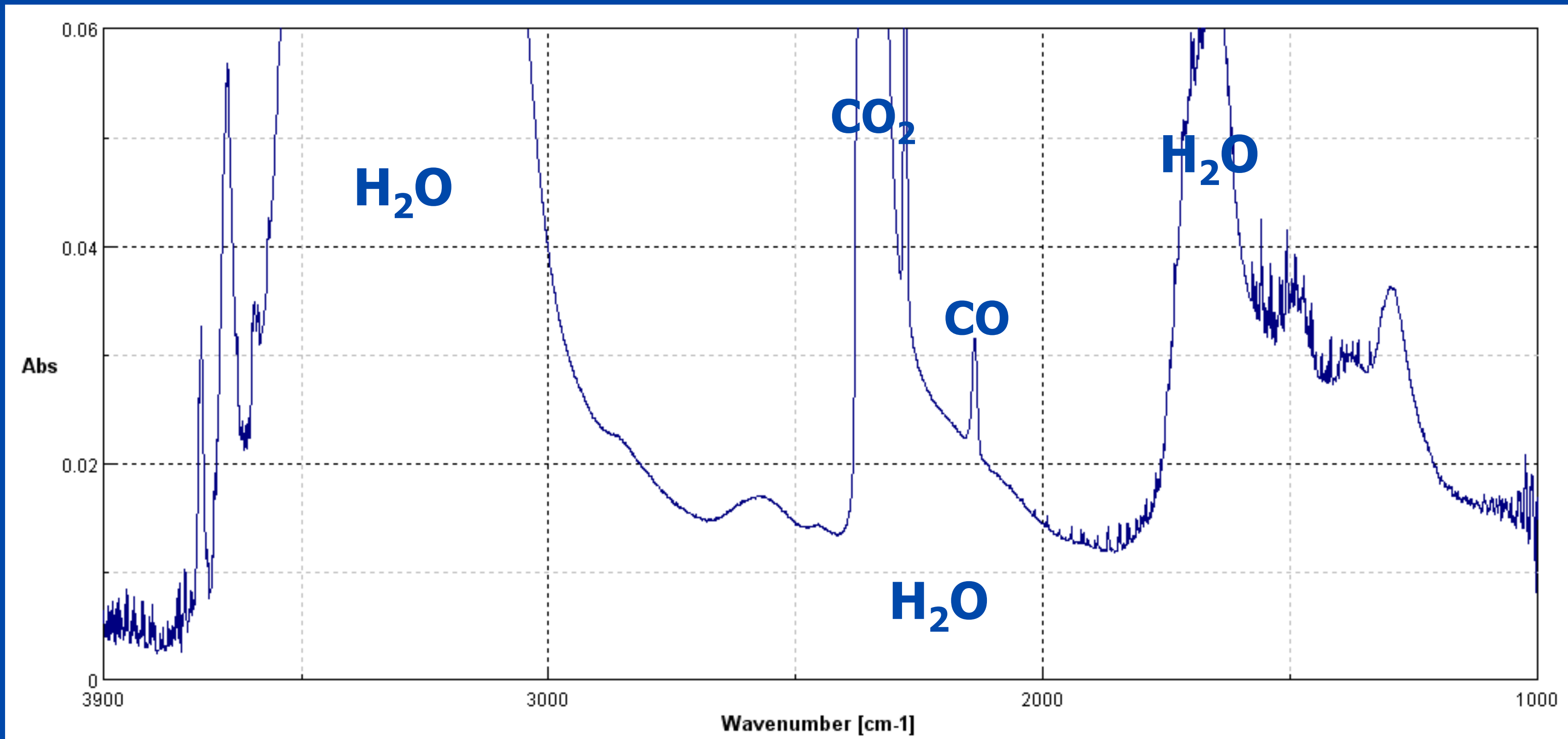


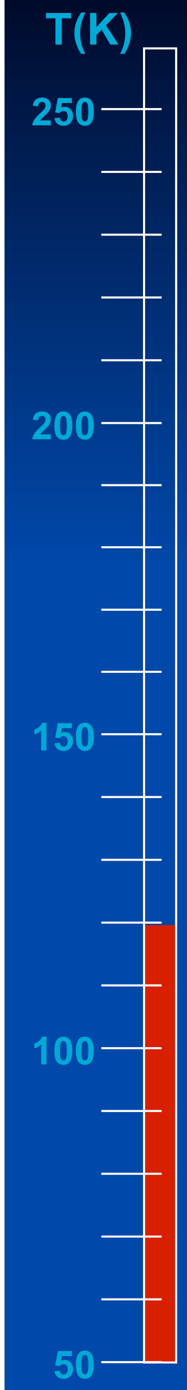


Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice

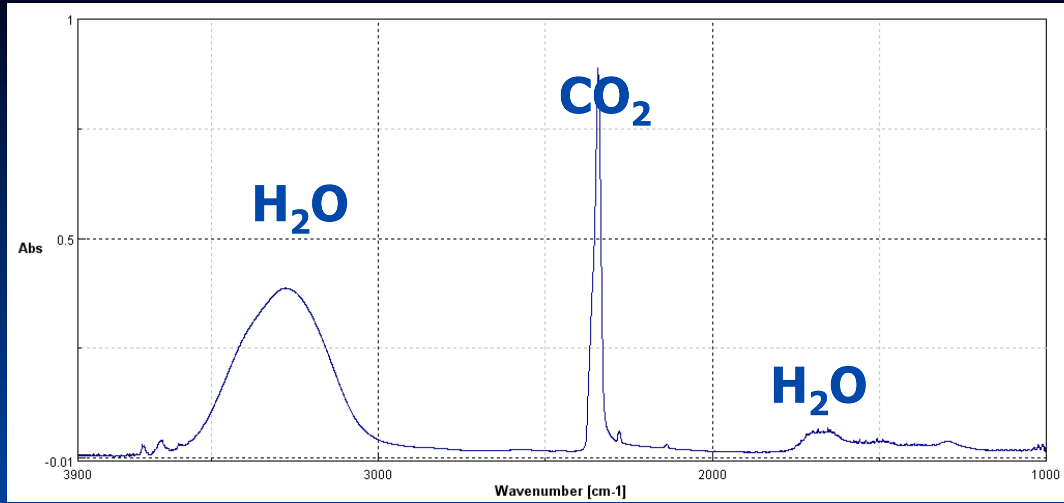


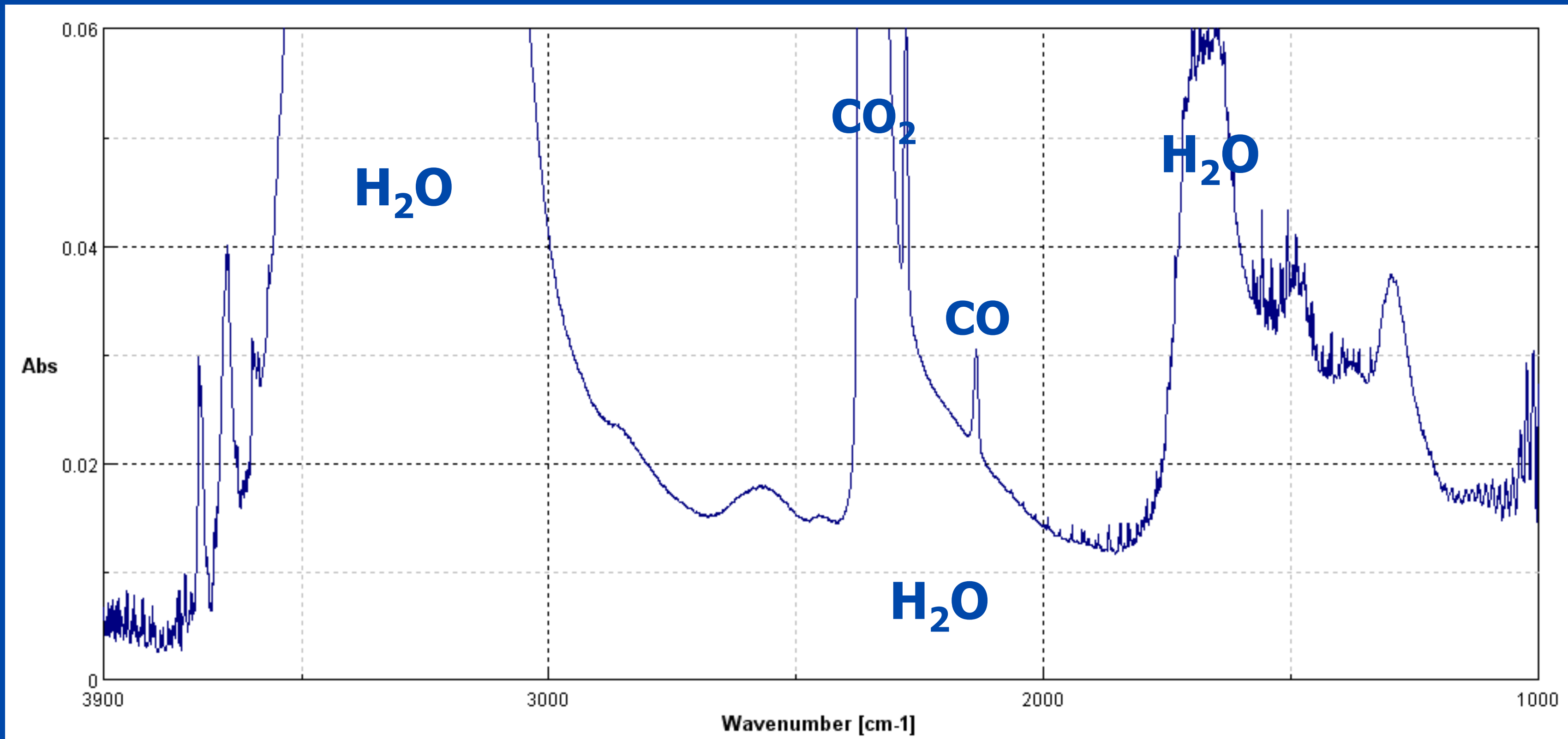


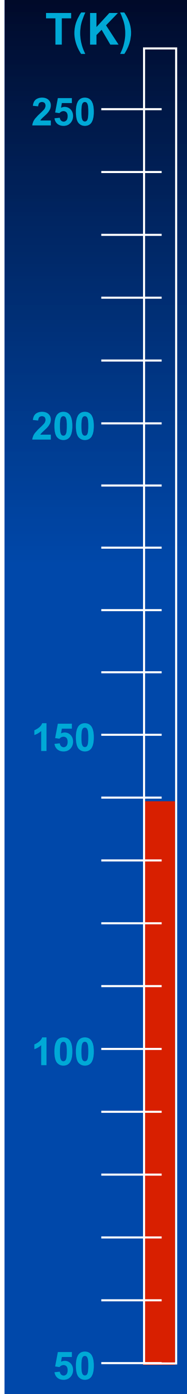




Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice







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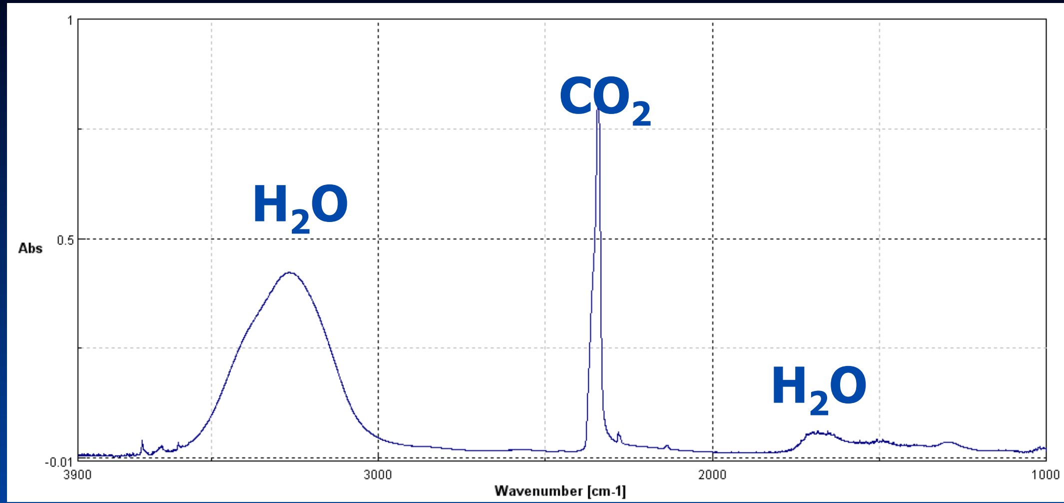

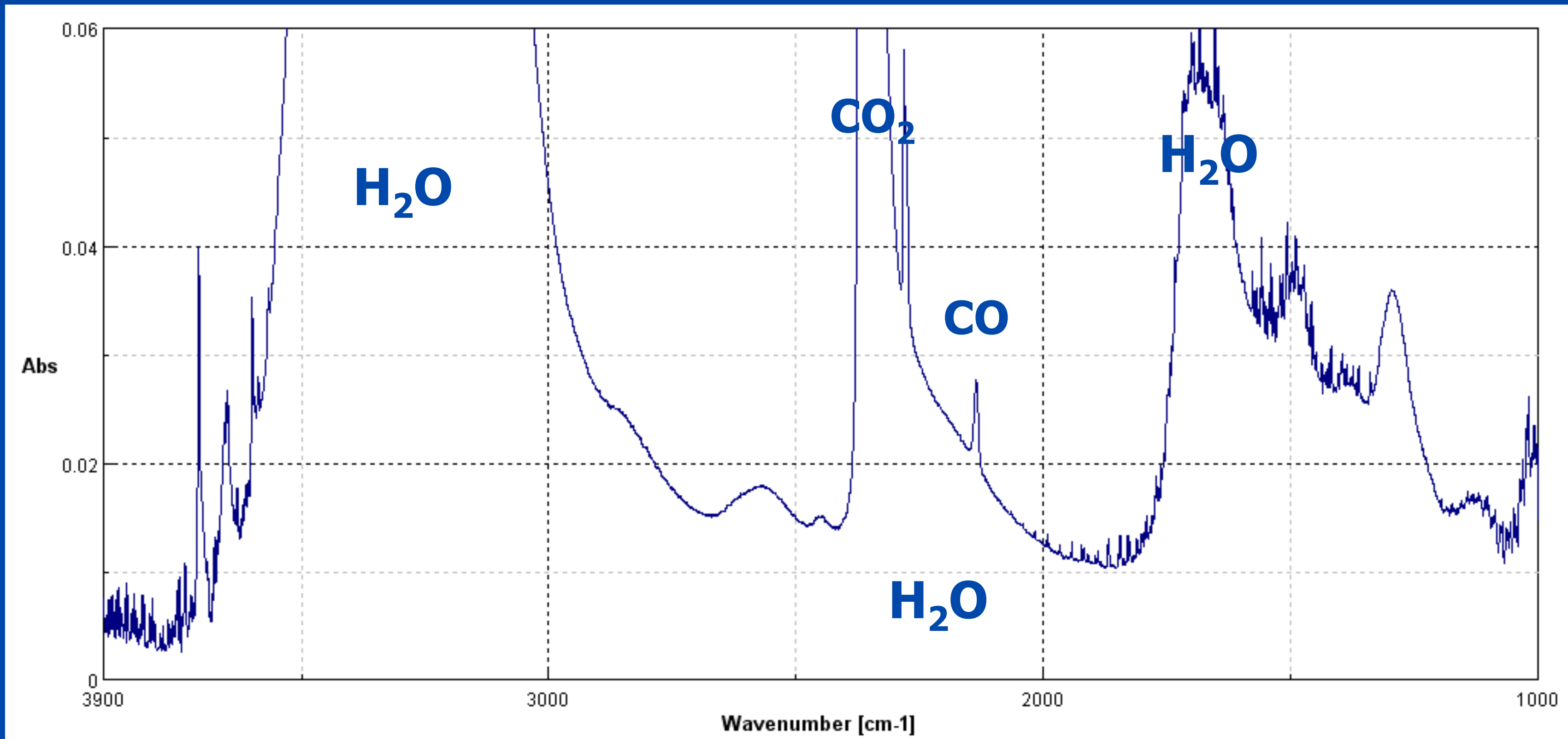

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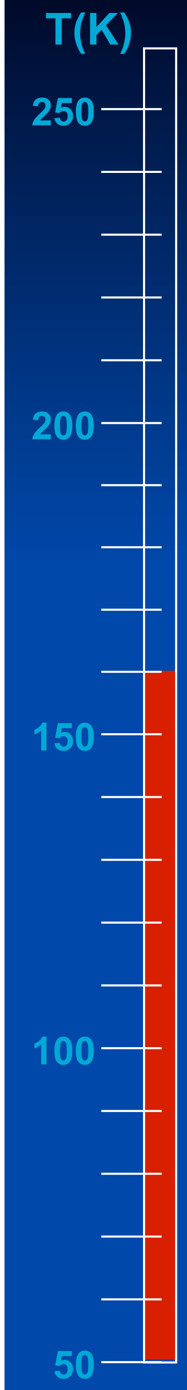
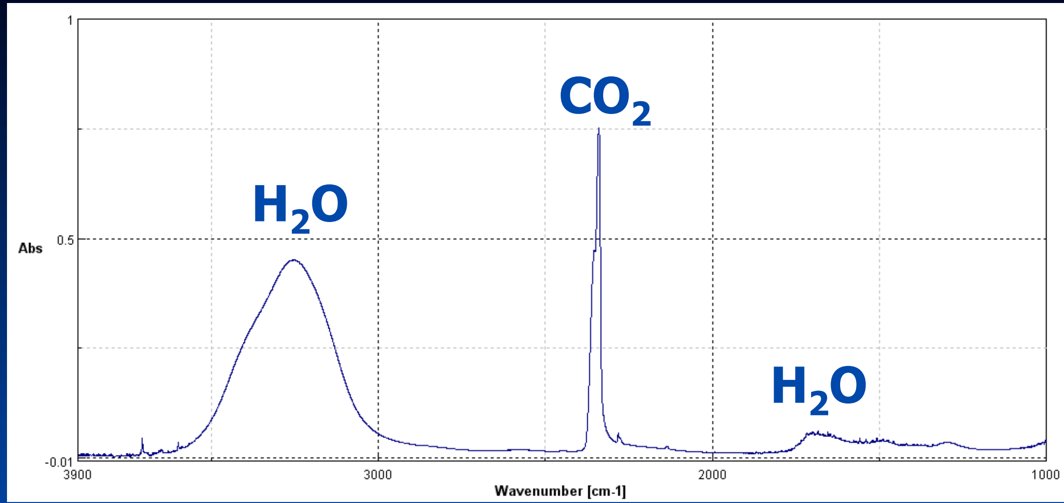
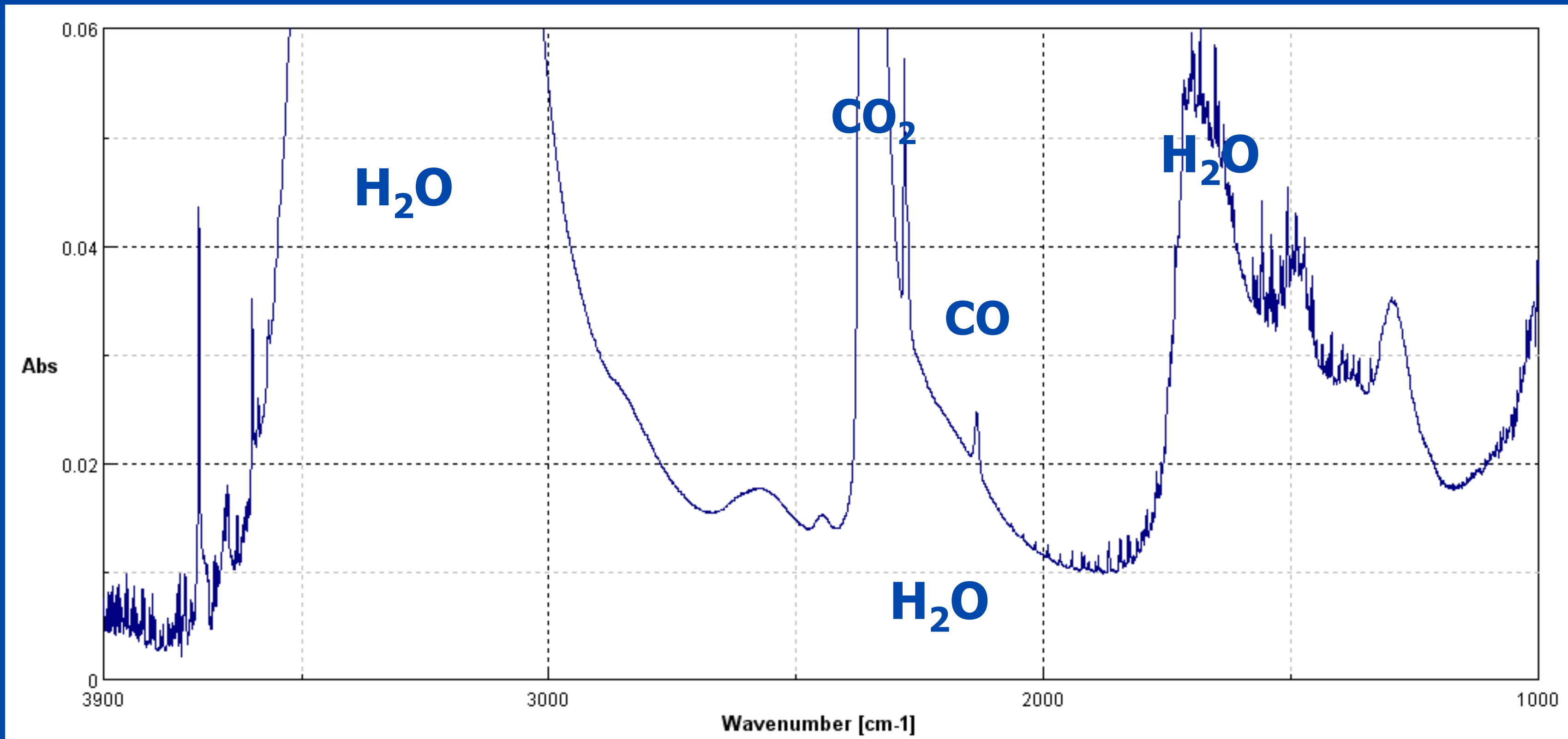
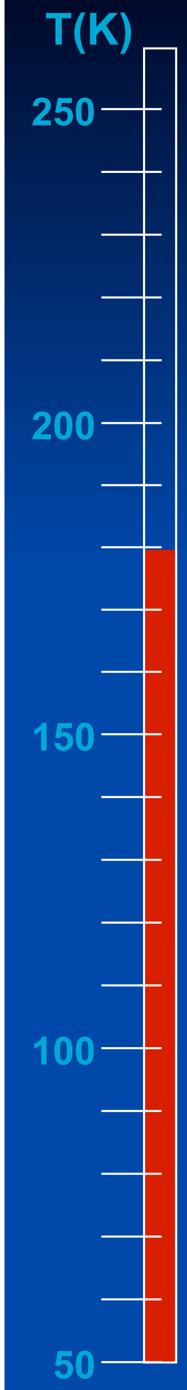
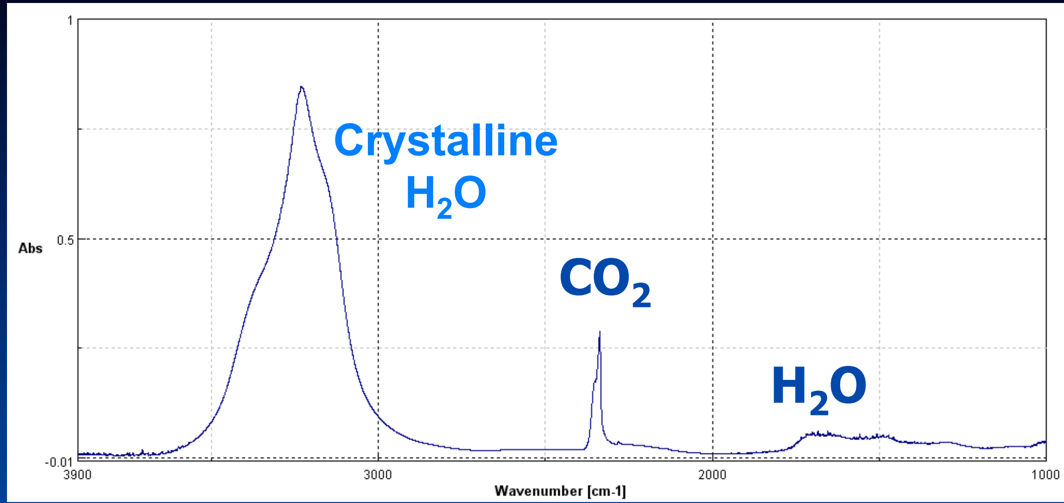


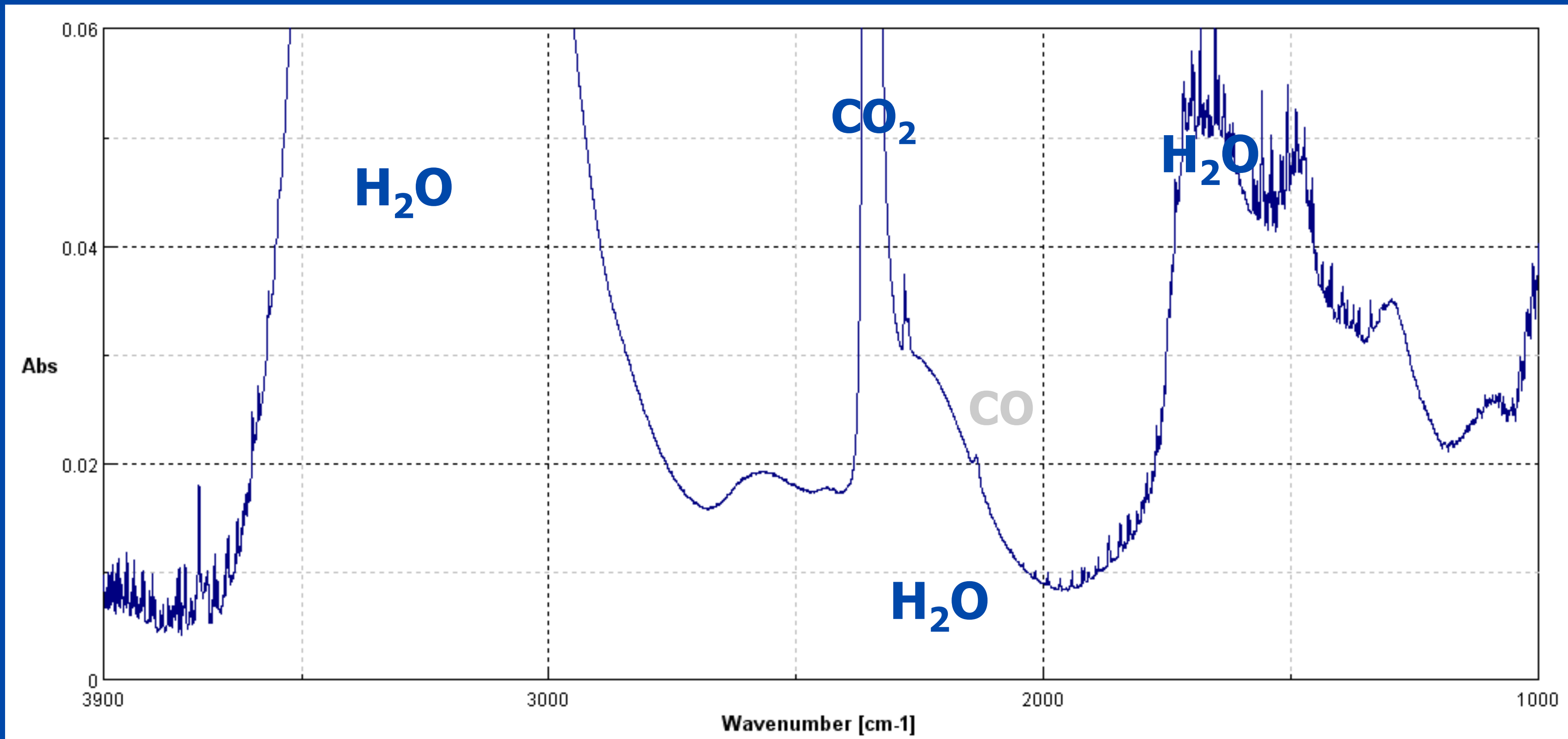


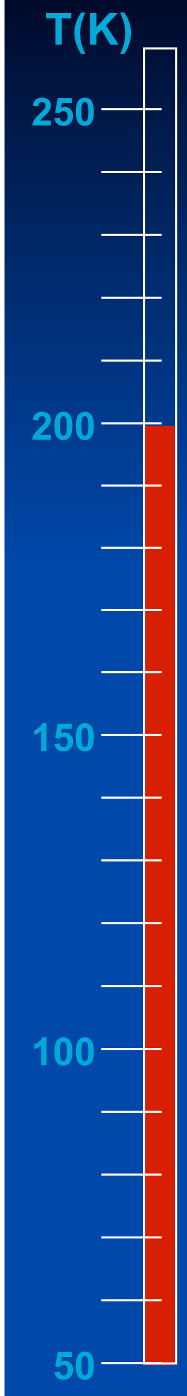




Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice







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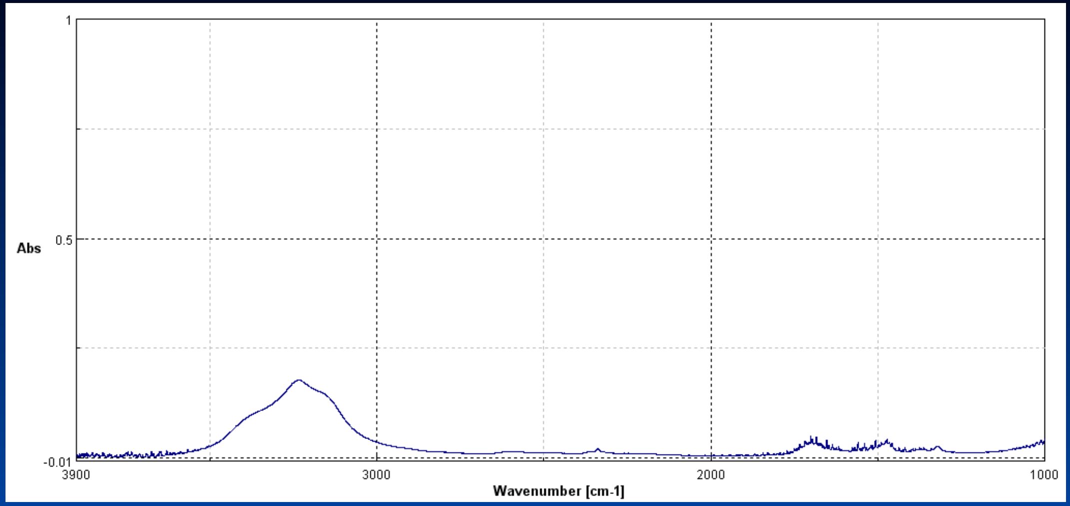
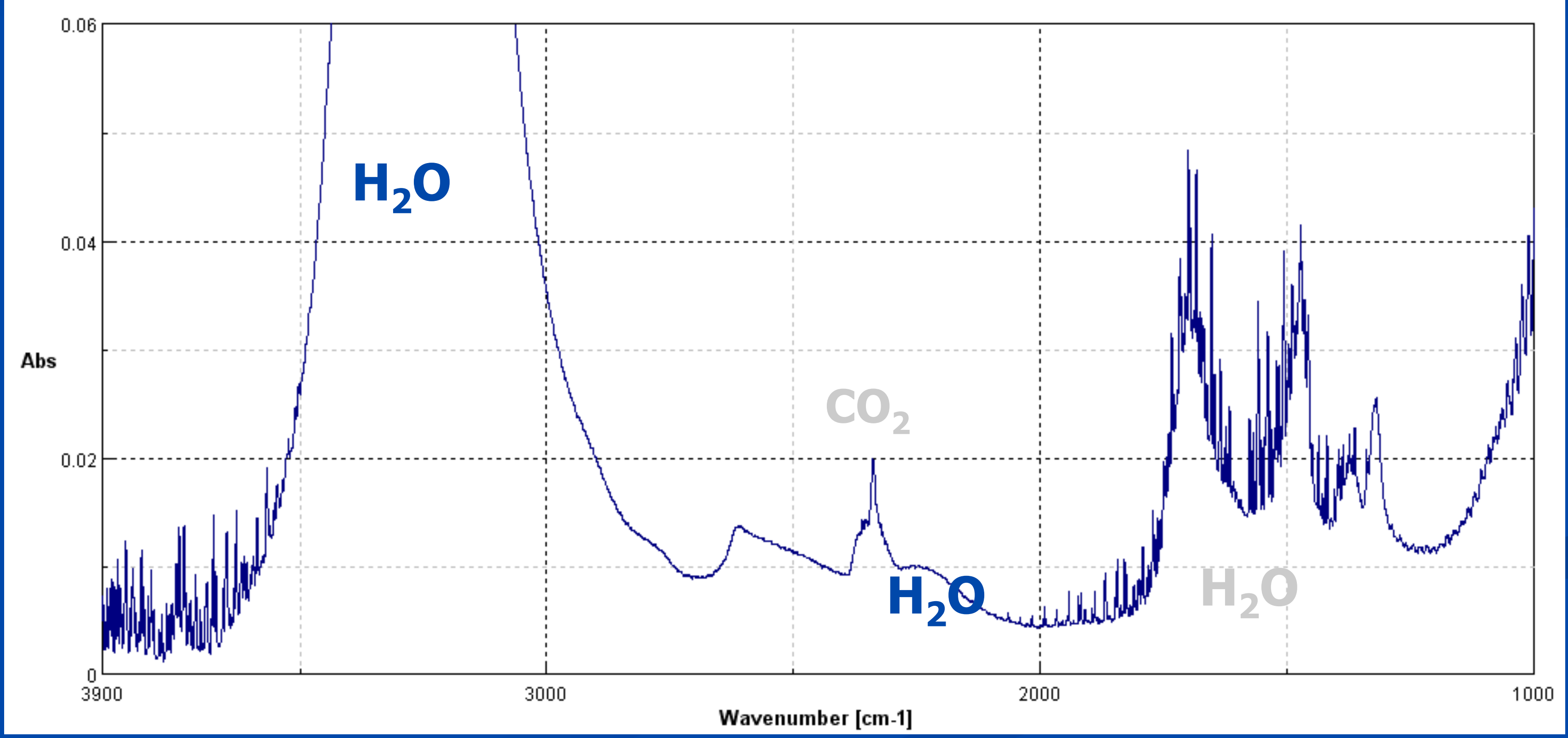
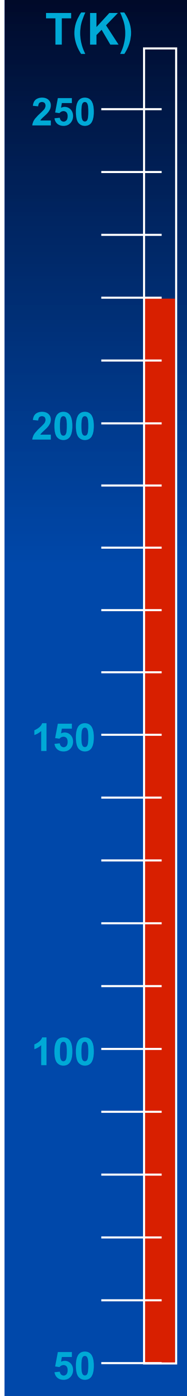
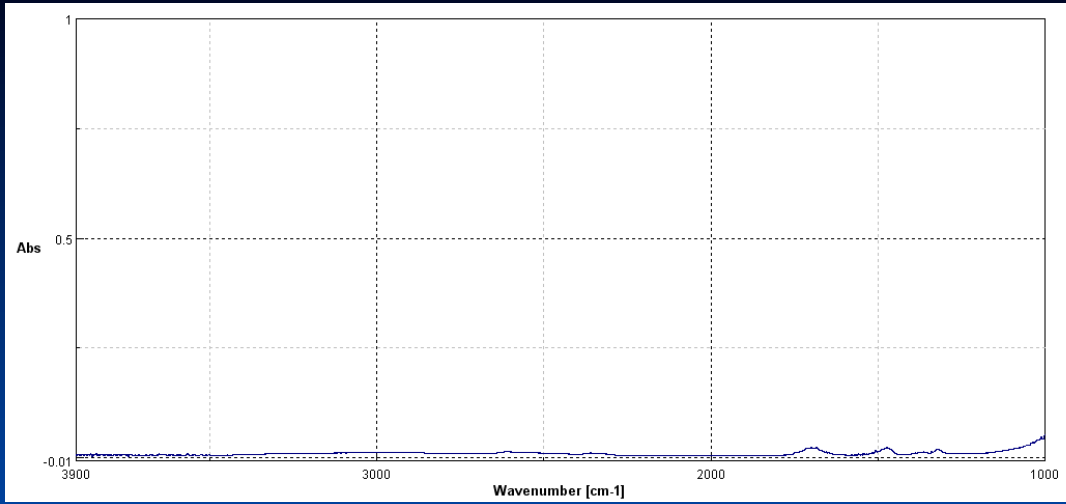
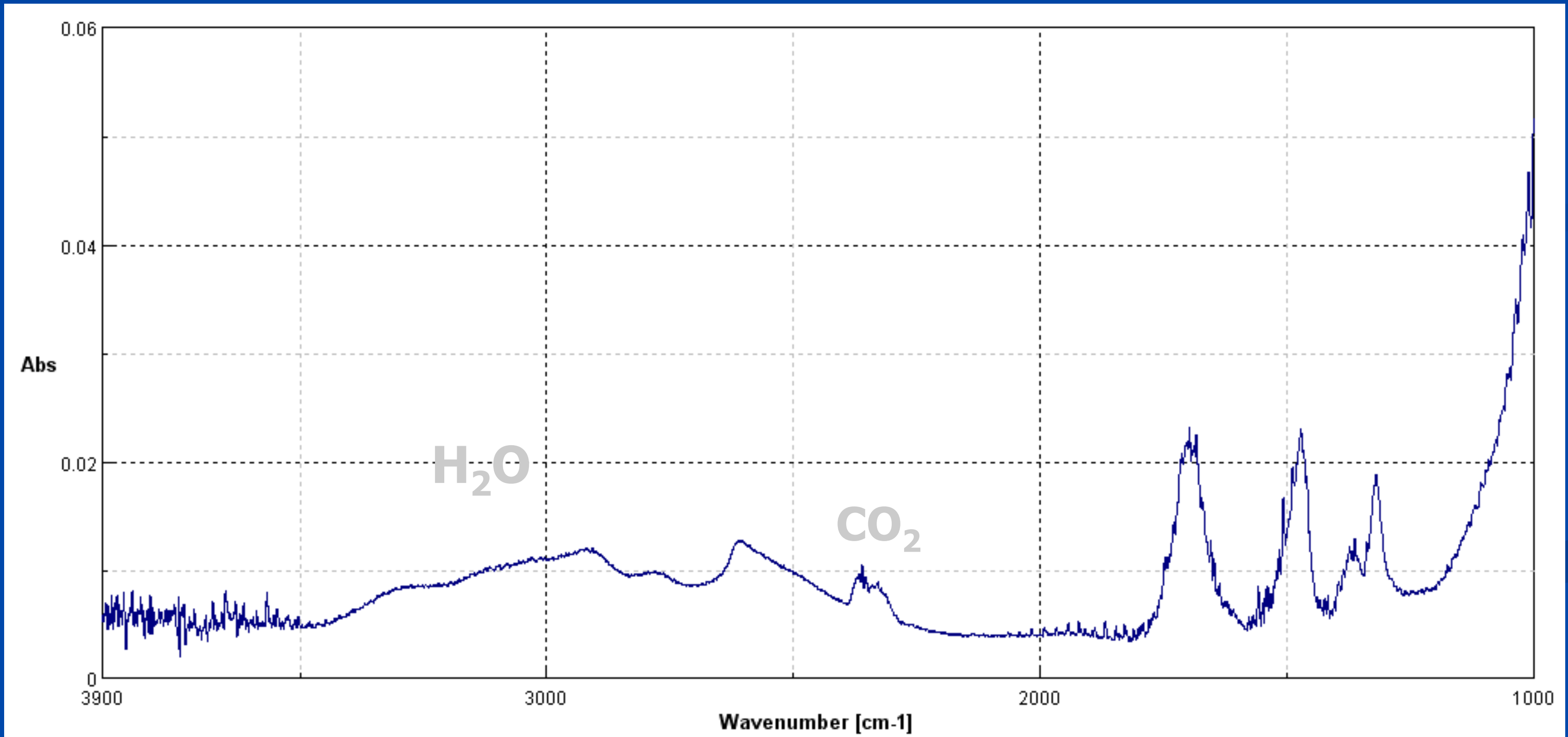


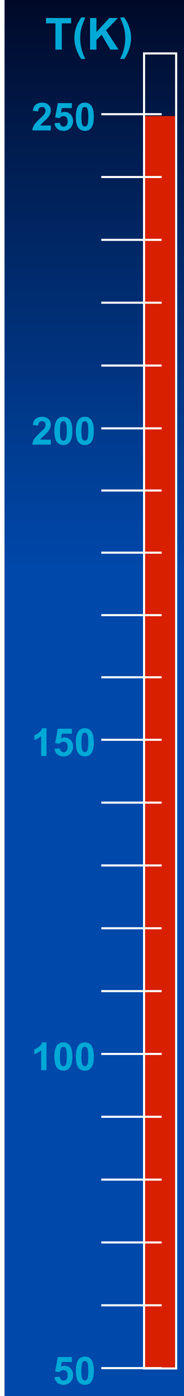




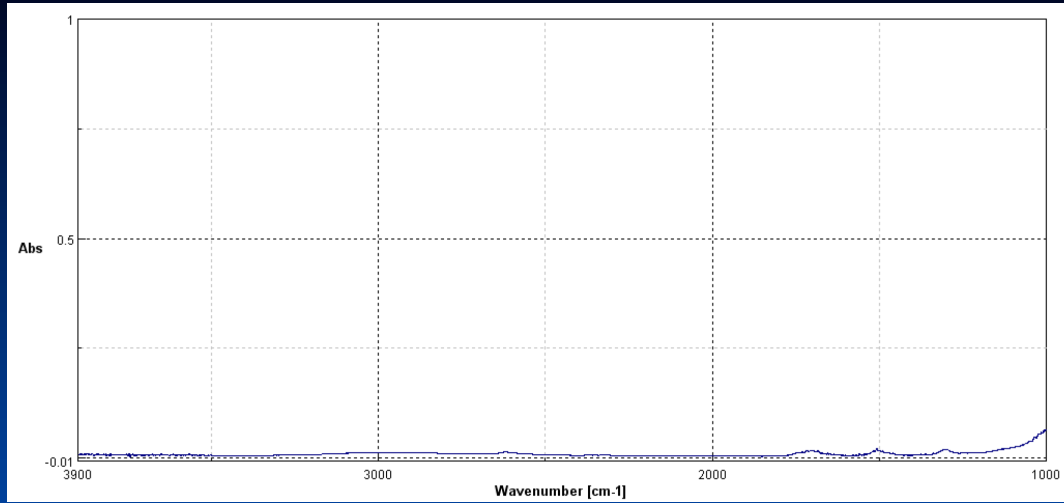
Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice

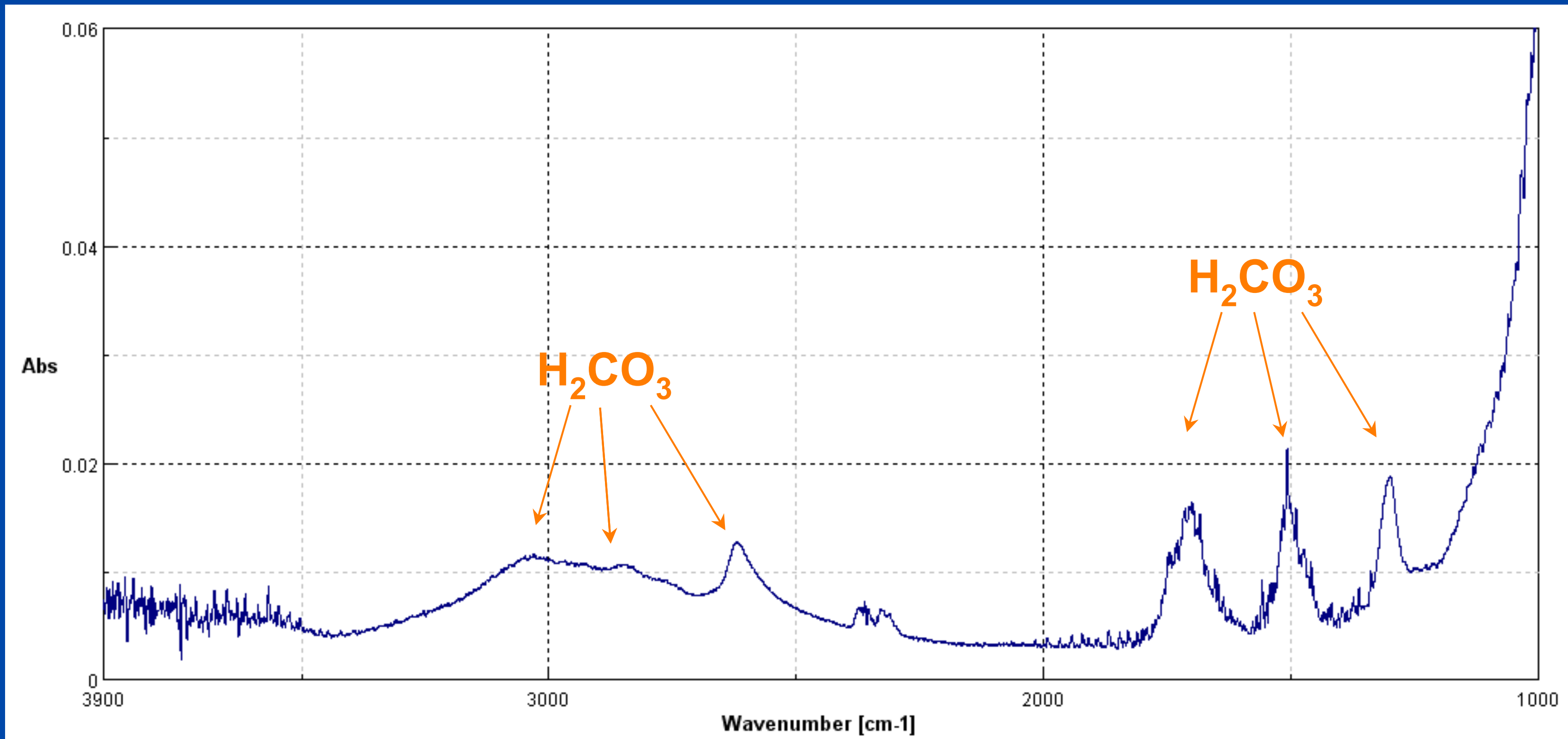






Warm-up after H^+ Irradiation of $H_2O:CO_2$ ice



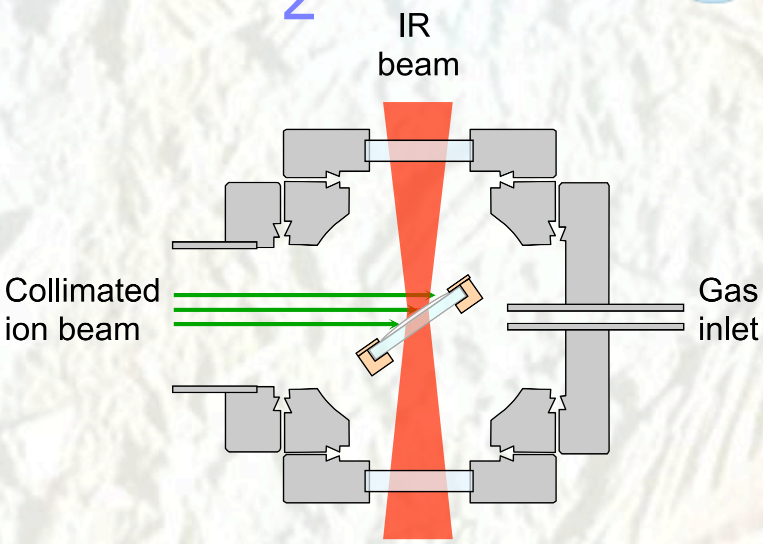


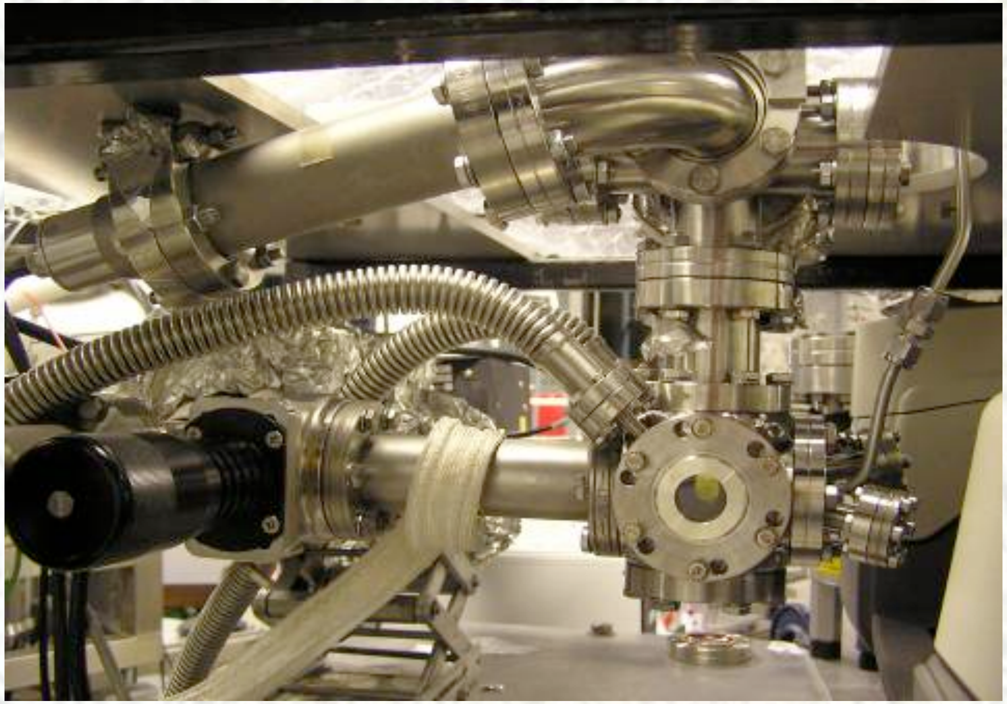
Example C^{n+} Irradiation of H_2O ice

- Ions: $^{13}C^{+}$ and $^{13}C^{2+}$ (45°)
- Energies: 2 and 4 keV
- Sample Temperature: 30 and 90 K
- Sample thickness: ~ 300 nm
- Analysis: FTIR transmission (45°)

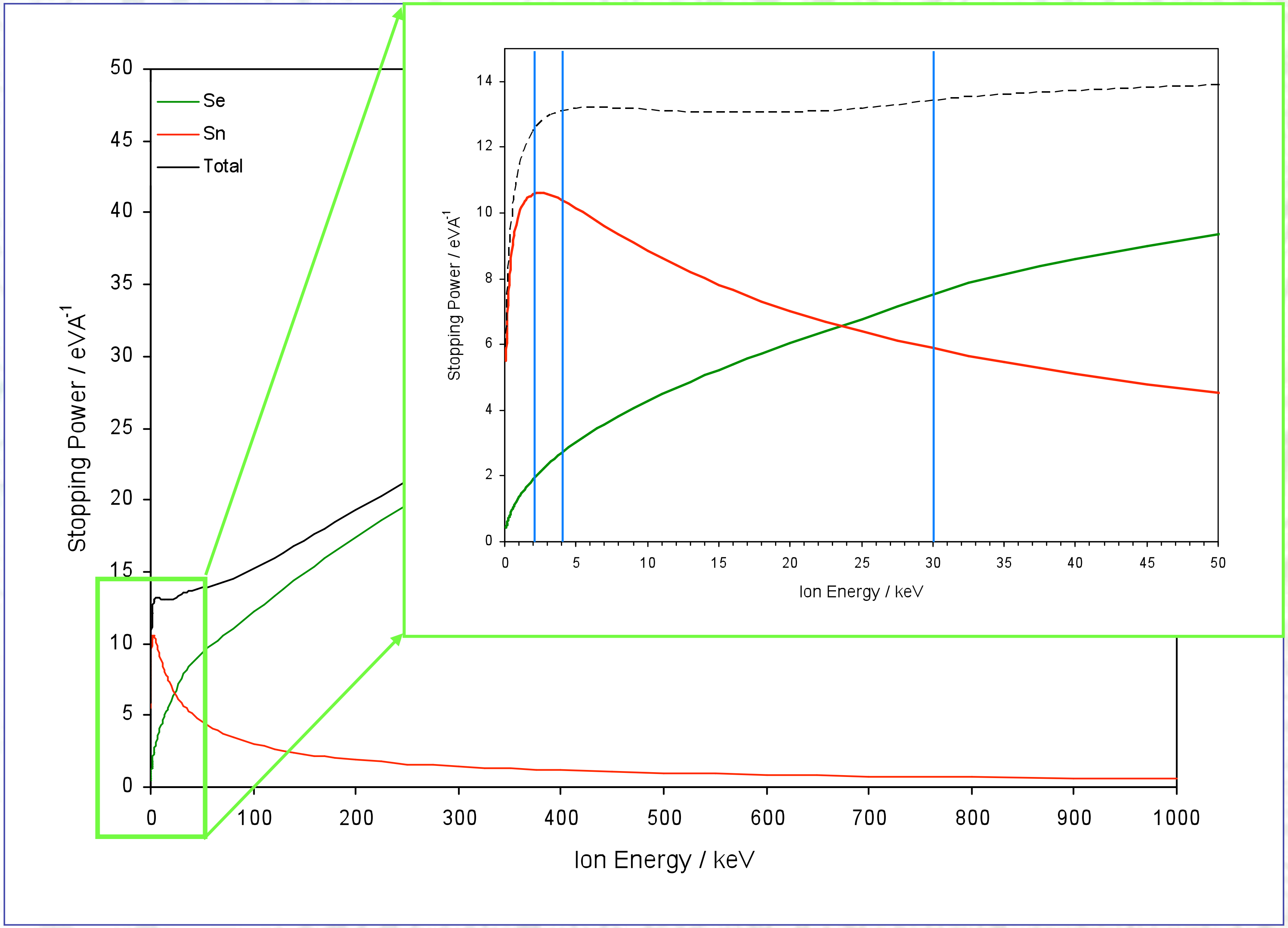
$$Fluence = \frac{It}{eqA}$$ *(ions cm^{-2})*

- Ion beam size measured for each ion type
- Faraday cup calibrated to determine ion current at the sample for each ion type
- Beam currents < 200 – 600 nA
- Preliminary Tests:
  - No ion intensity effects

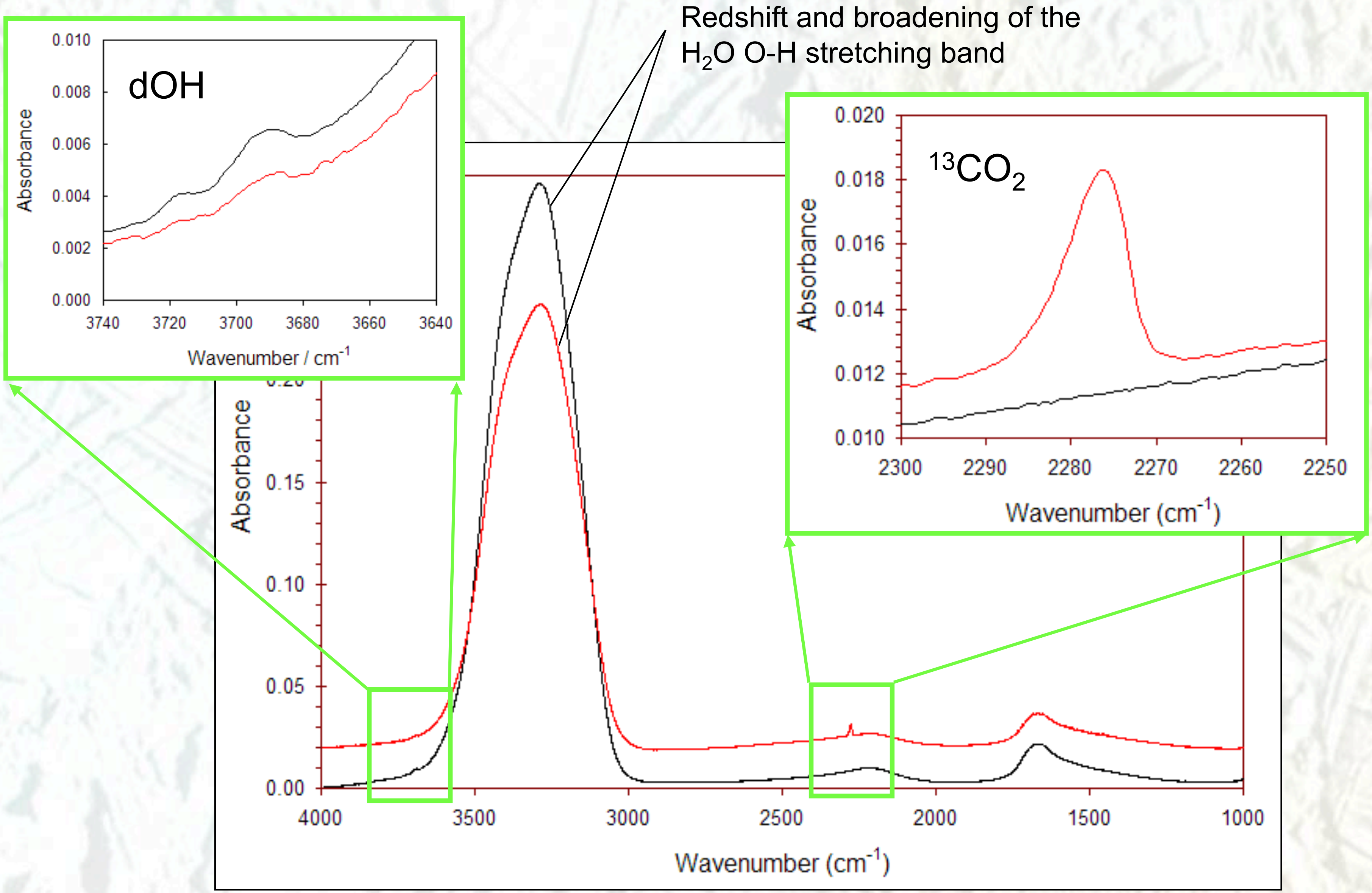




Stopping Power – C^+ in H_2O

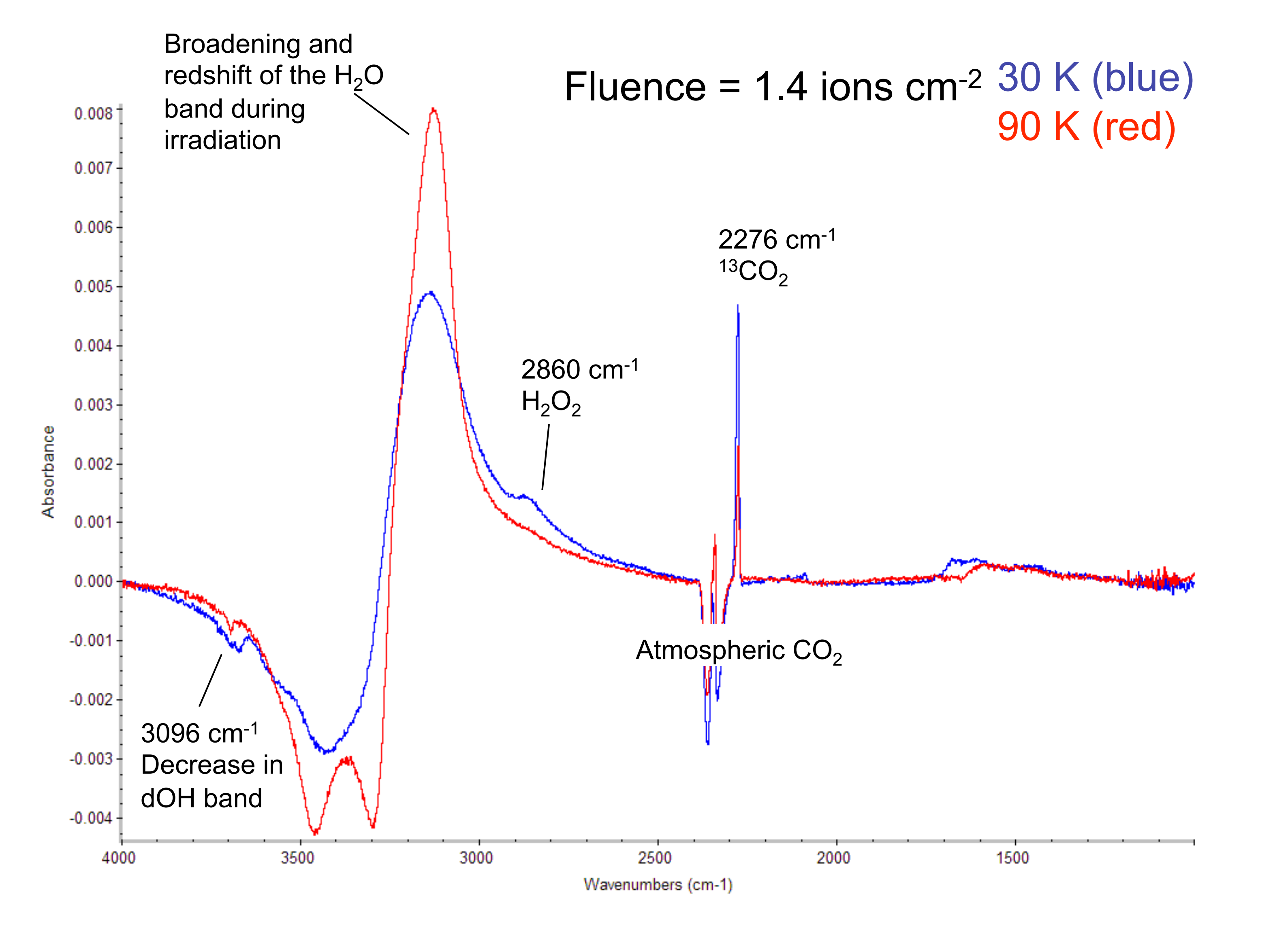


Results: FTIR Spectroscopy



Results: FTIR Spectroscopy

Subtraction before and after irradiation with 2 keV C^+



Temperature Dependence

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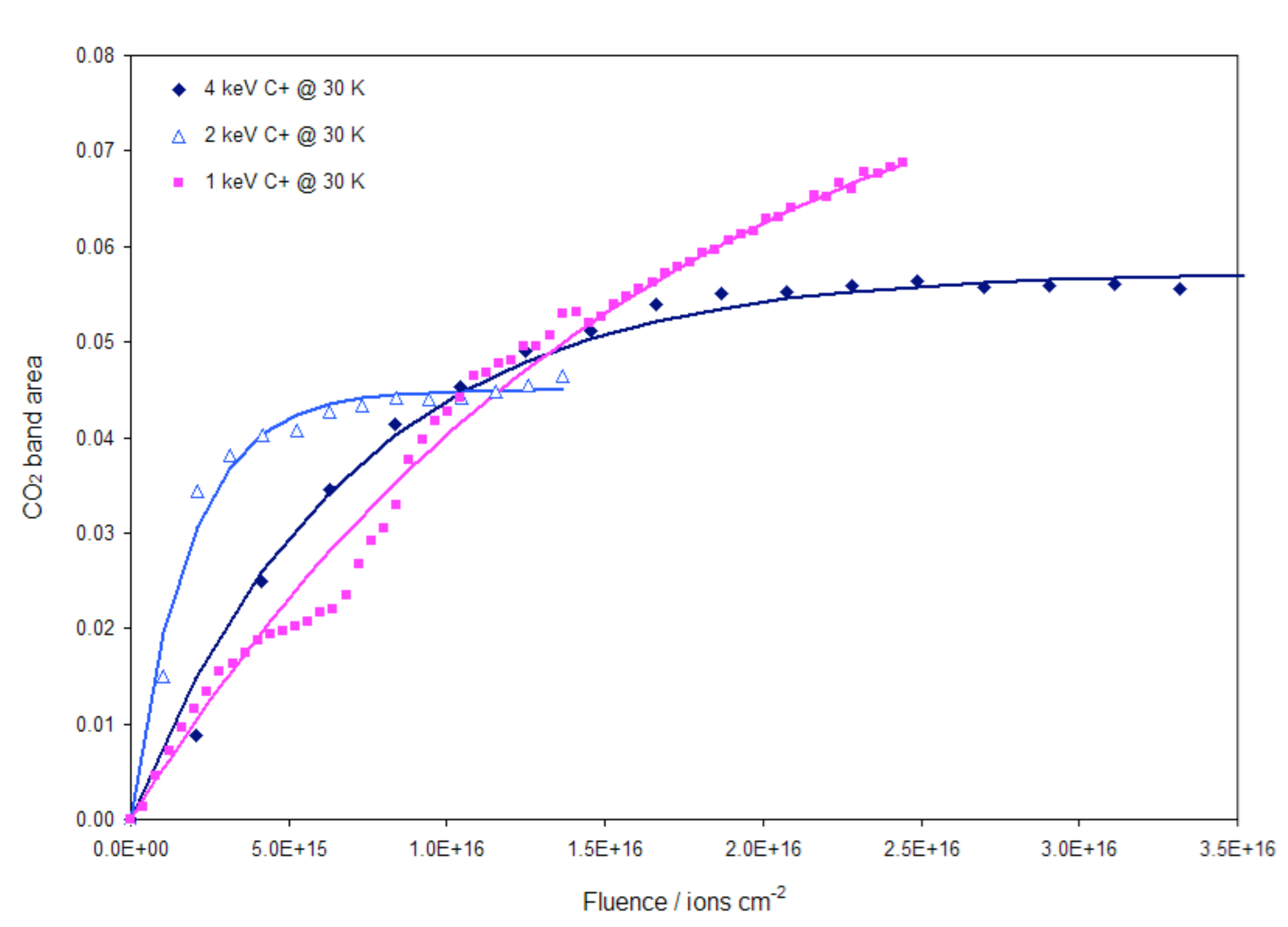
In all experiments a higher yield of CO_2 (and H_2O_2 – qualitatively) is observed at lower temperature! **This is general trend in many experiments**

Ice morphology

- Plays an important role in surface chemistry (surface area, pores…)
- Density/porosity → affect stopping power and range
- Formation of dimers ??

Preliminary → 1 keV C^+



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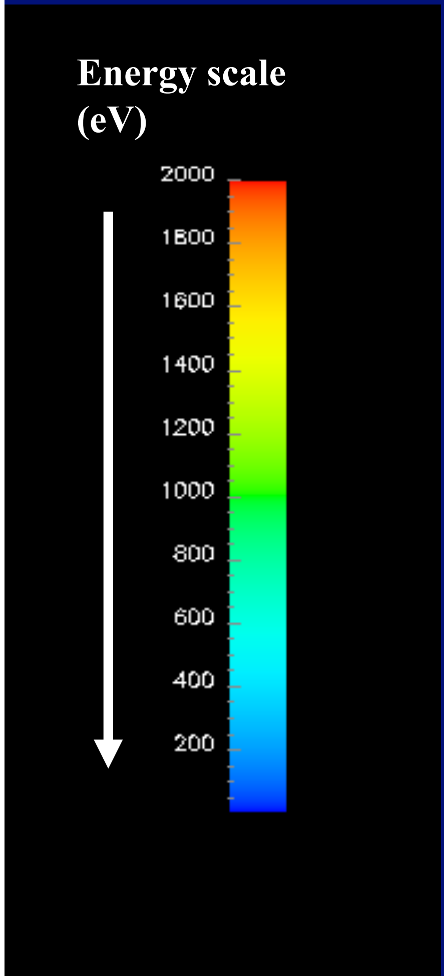
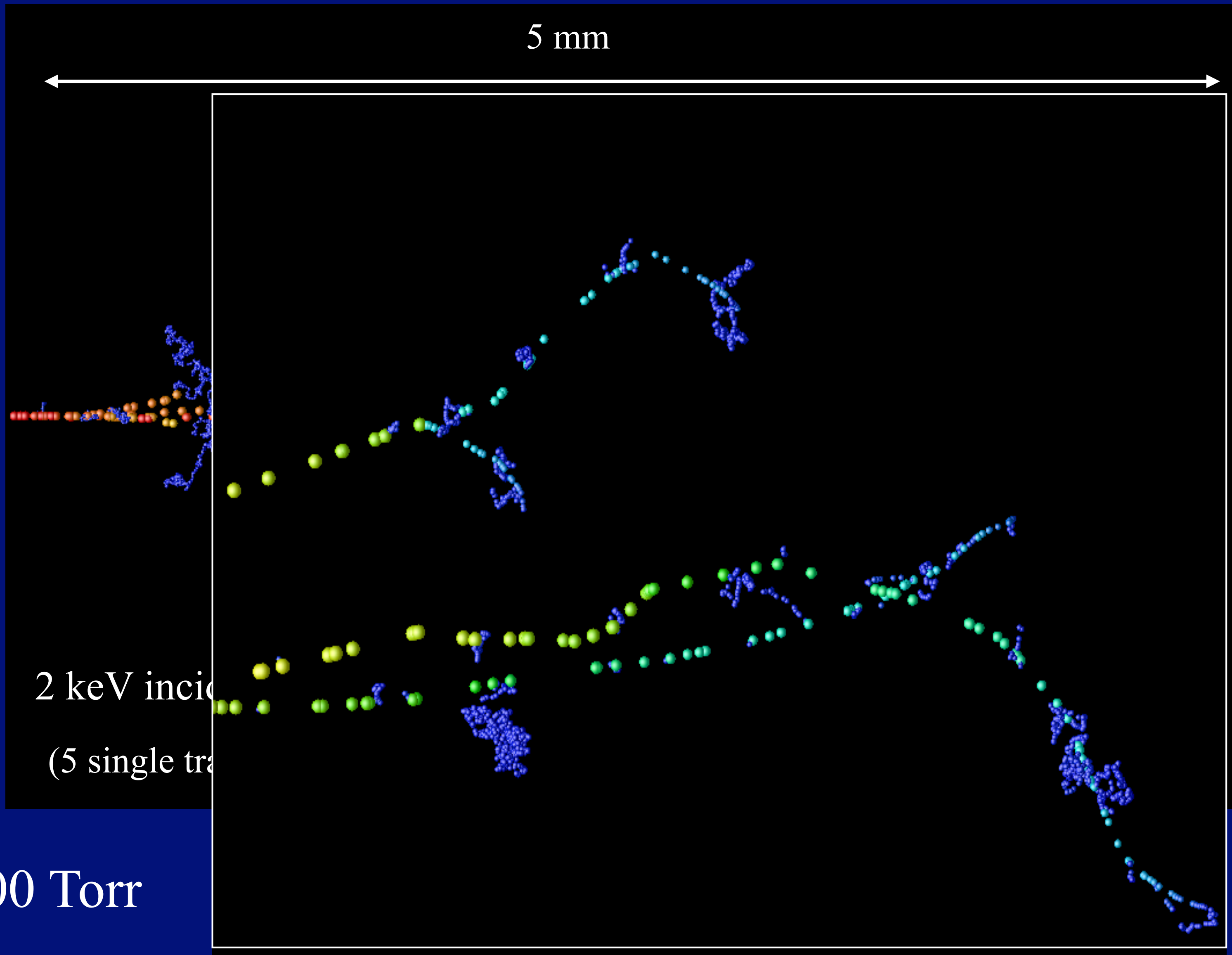
Role of Secondaries

- Major product of cosmic rays are more particles !
- Track modelling can explore this

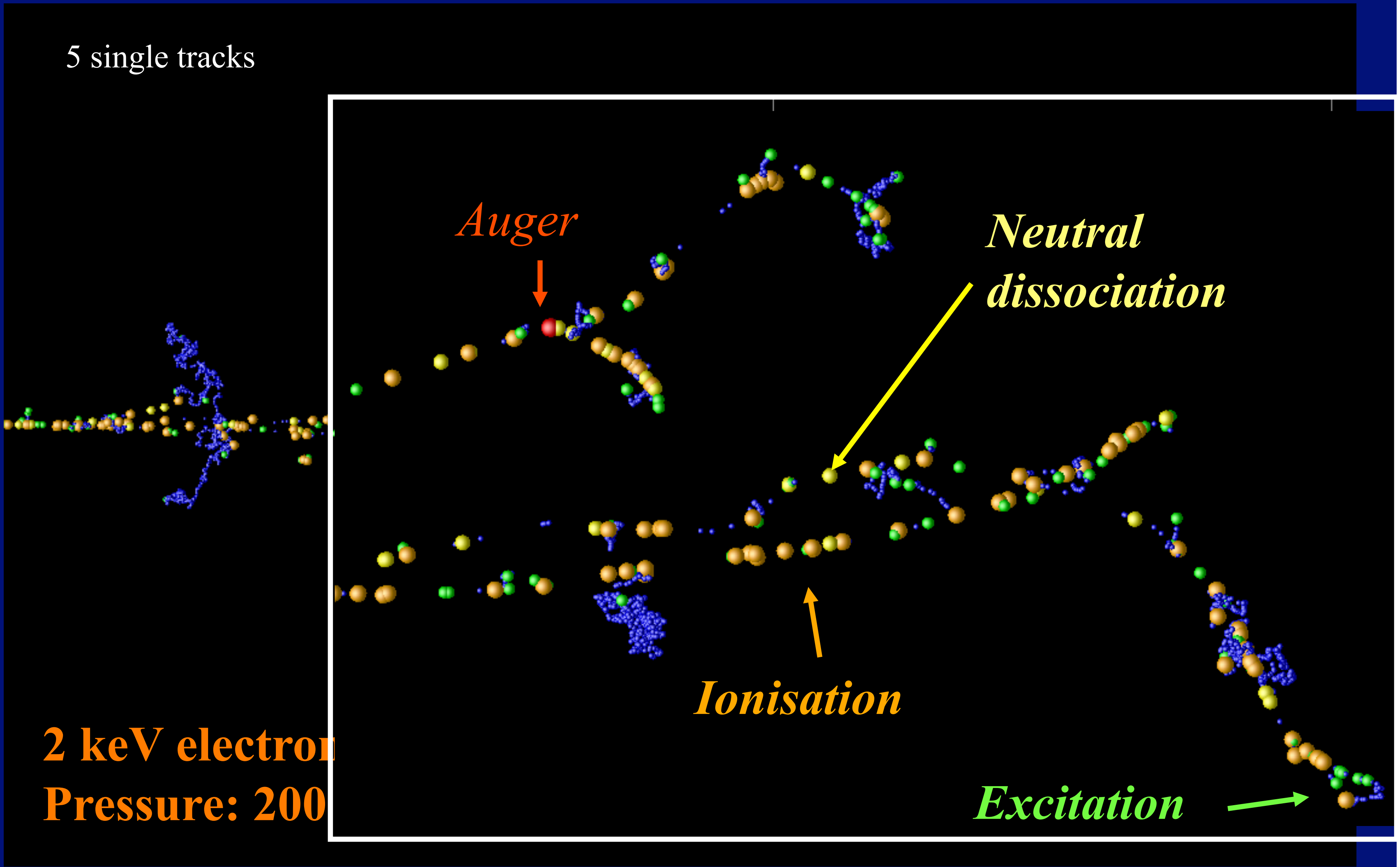
Energy degradation of electrons in H_2O





H_2O , 200 Torr

Different types of interactions



Role of Secondaries

- Major product of cosmic rays are more particles !
- Secondary electrons are the major species

  and they can induce chemistry as well as ions (but are not themselves reactive)

indeed one CR may produce an avalanche of 10^4 electrons whose energy vary from close to CR energy to thermal energy.

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5 keV Electron irradiation of methylammine and carbon dioxide ice makes glycine simple amino acid

Effects of Irradiation

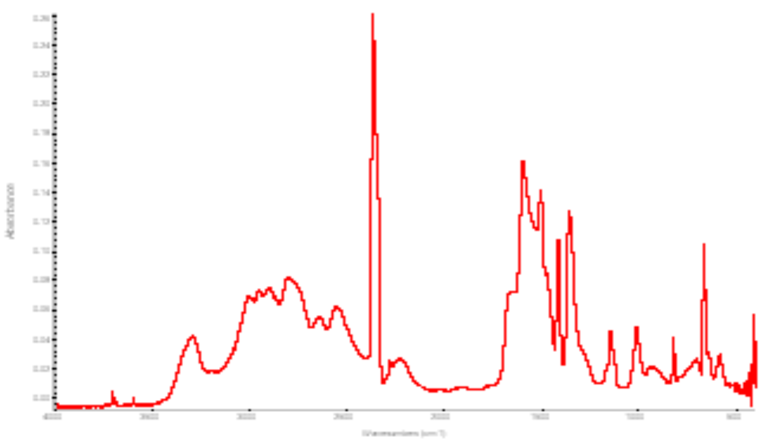


Figure 3 – Pristine CH_3NH_2 & CO_2 mixture

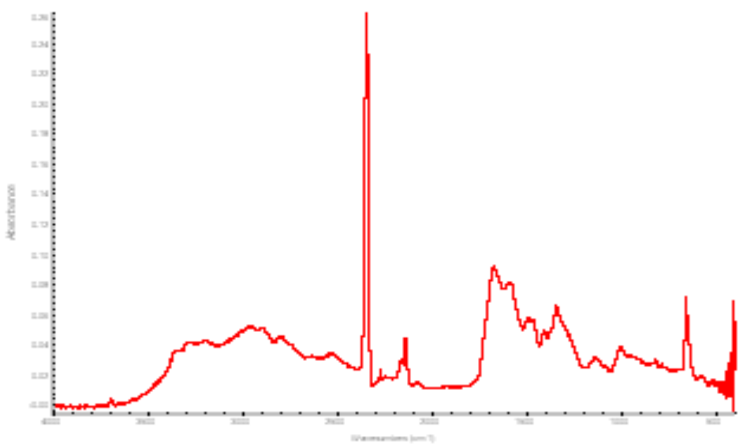


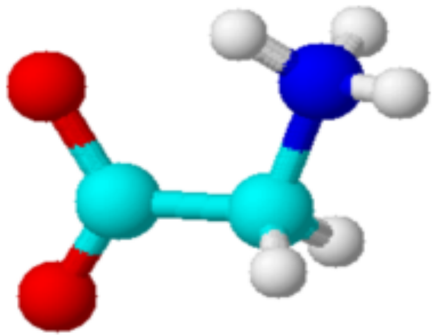
Figure 4 – 100 minute after irradiation of the mixture

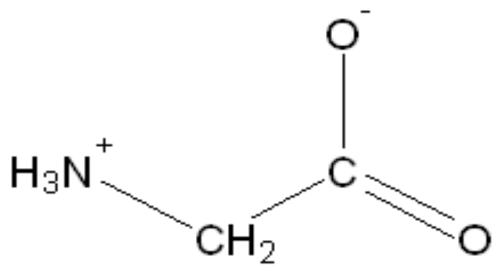
Forms of Glycine

- Zwittionic glycine

"A zwitterion is a dipolar ion that is capable of carrying both a positive and negative charge simultaneously"

E.G. $NH_3^+CH_2COO^-$

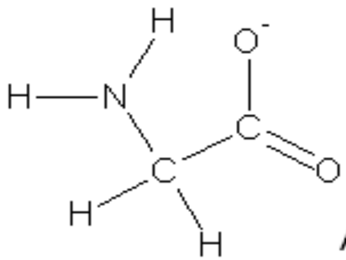




Zwittionic Glycine

- Anionic

Negatively charged, e.g. $NH_2CH_3COO^-$



Anionic Glycine

Electron Induced Chemistry

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- Some examples of laboratory study of electron induced synthesis of molecules under astrochemical conditions.

- Chemical synthesis in **1:1 Mixture of NH_3:CO_2 Ice with 1 keV electrons at 30 K**

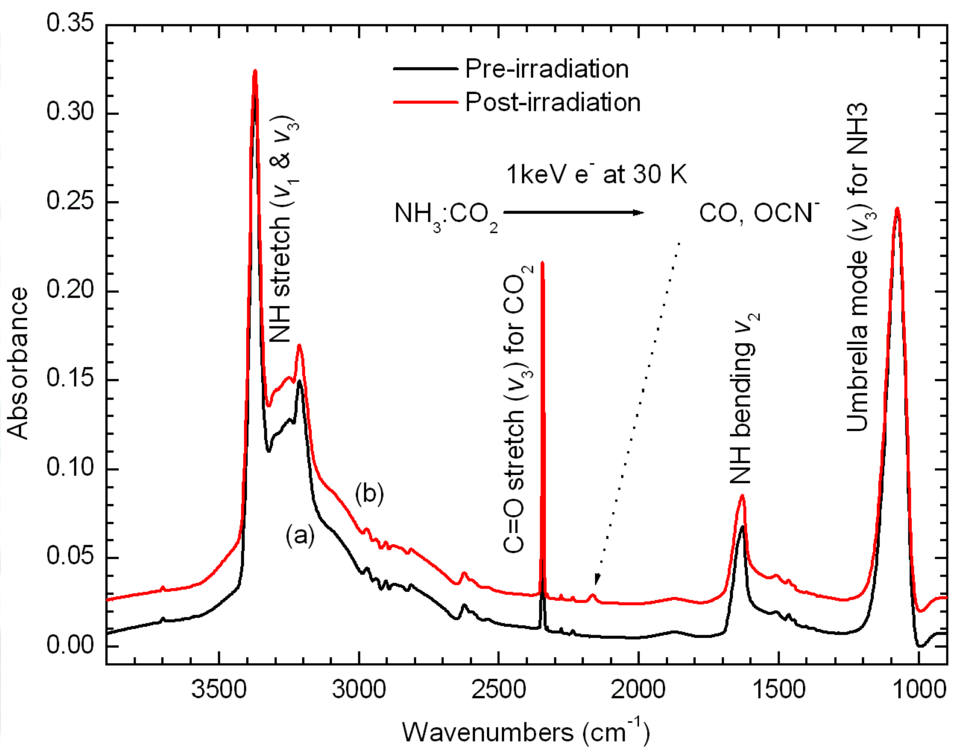

Fig 5-1: IR spectra of NH_3:CO_2 (1:1), (a) pre-irradiation (b) post irradiation (58 min). Both spectra at 30 K

Formation of ammonium carbamate

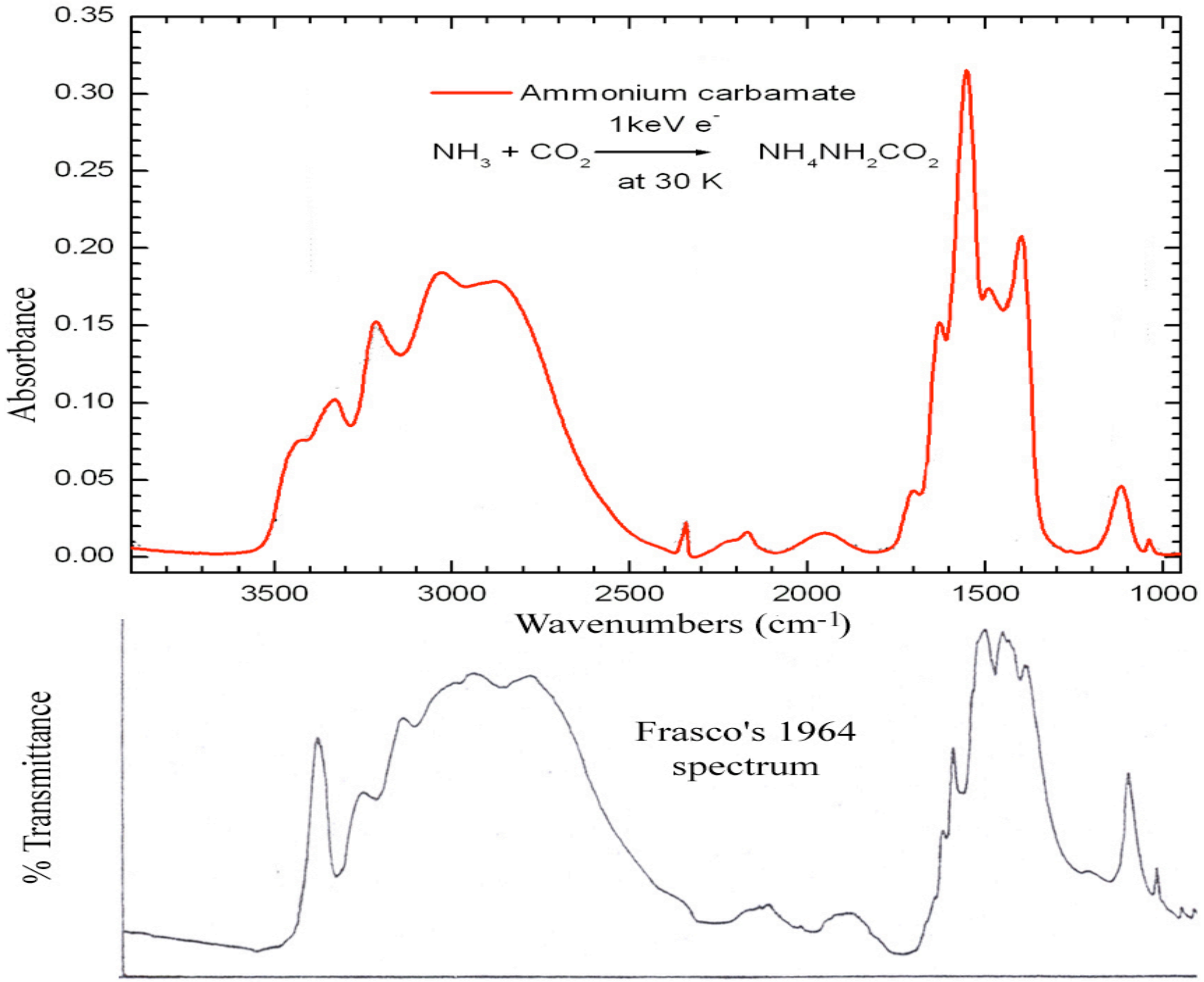

Fig. 5-5: IR spectra of NH_3 :CO_2 (1:1), (a) post-irradiation (58 min) and after warm-up (220 - 270 K); and (b) comparing Frasco's actual 1964 experimental spectrum at 248 K

Formation of ethylene glycol in pure methanol ice

$HOH_2C\text{-}CH_2OH$

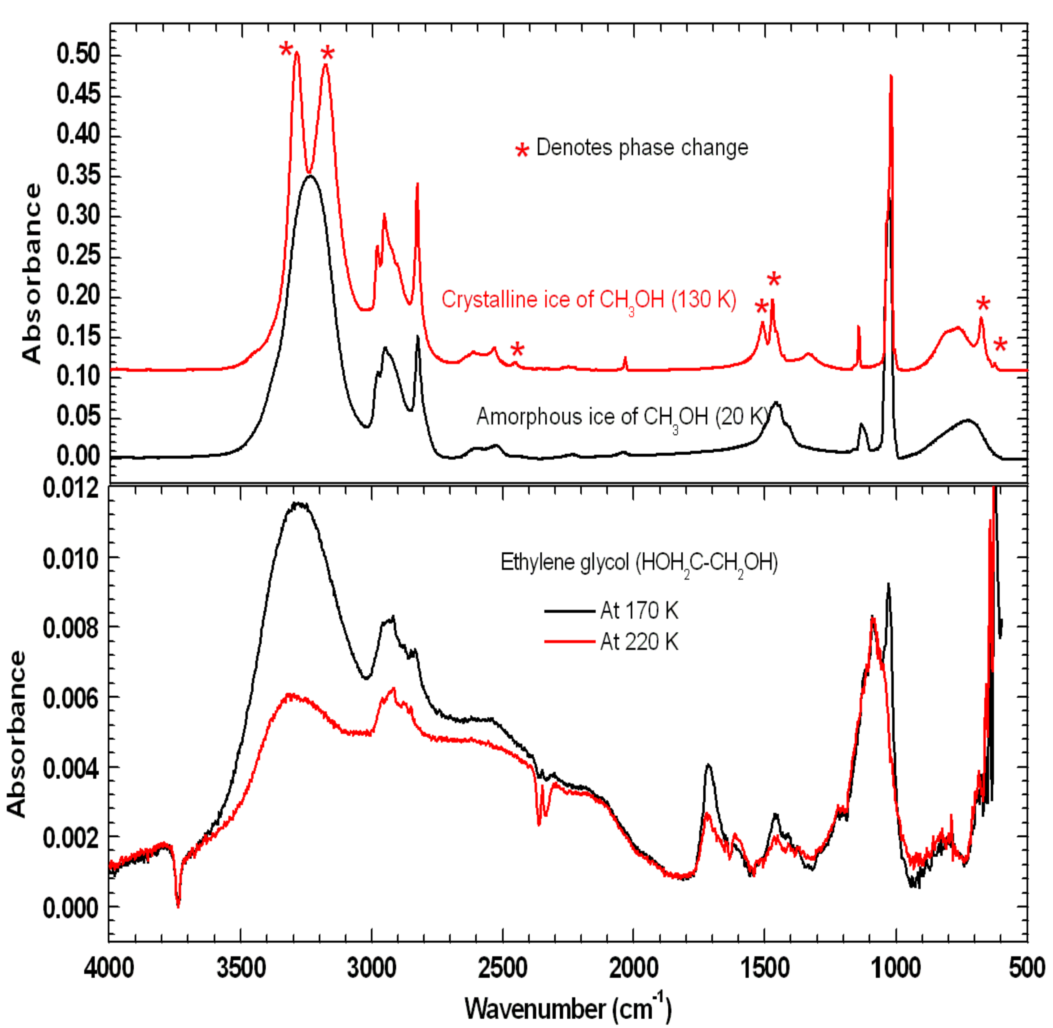

Fig. 6-3: Ethylene glycol was observed after irradiation of pure CH_3OH with 1 keV e^- at 30 K and then annealing process

Formation of methyl formate CH_3OHCO

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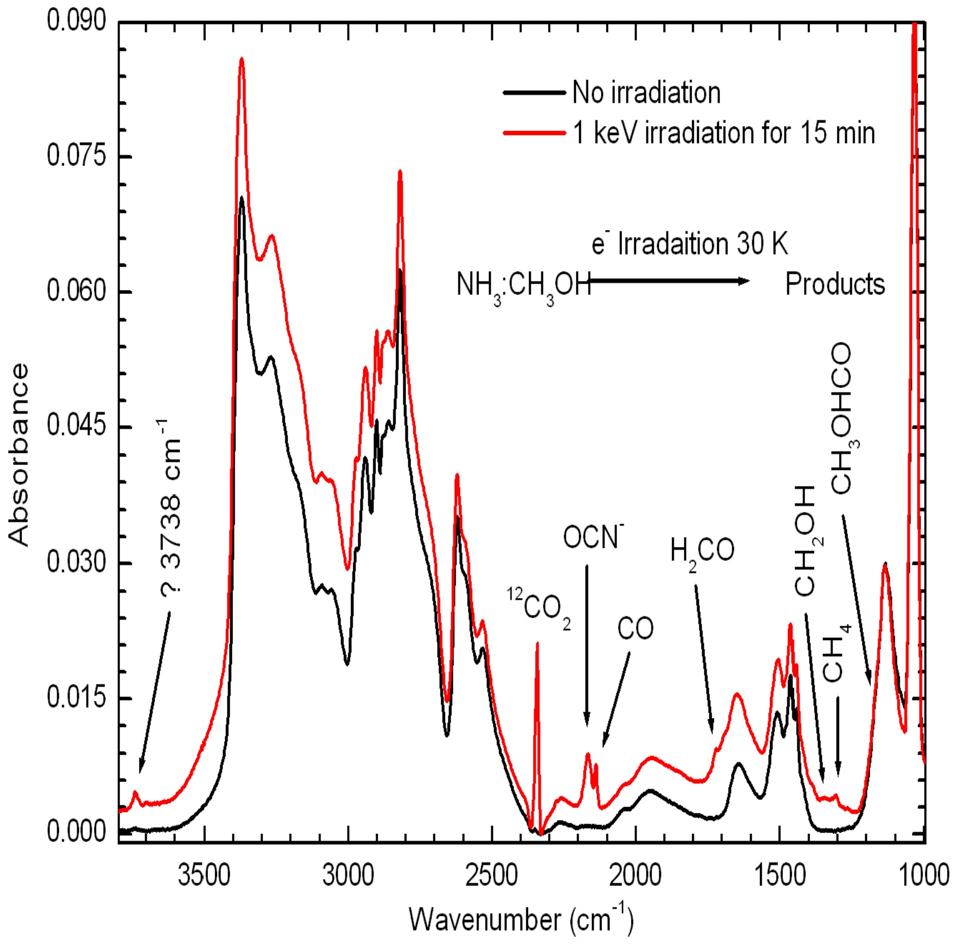

Fig. 6-9: Irradiation of 1:1 binary mixture of NH_3:CH_3OH with 1 keV e^- at 30 K

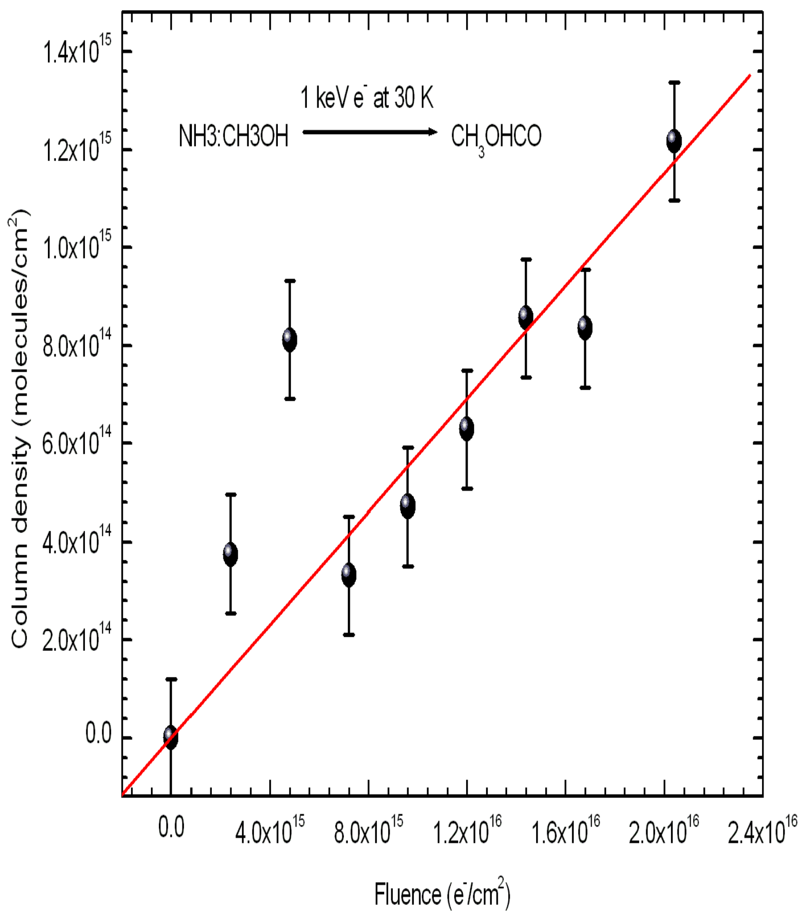

Fig 6-14: Formation of CH_3OHCO during the irradiation of binary mixture NH_3:CH_3OH with 1 keV e^- at 30 K

Formation of formamide $HCONH_2$

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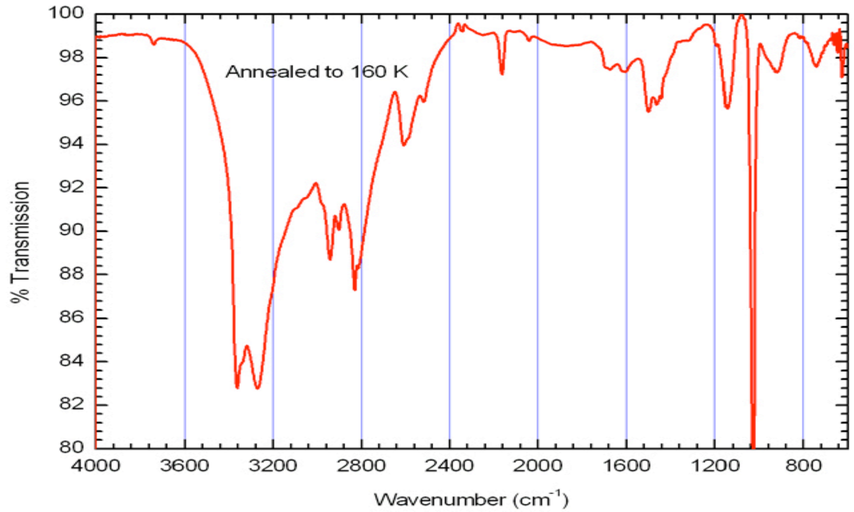


Fig. F6-16a: Spectrum of formamide formed during annealing to 160 K of irradiated ice of 1:1 binary mixture of NH_3:CH_3OH with 1 keV e^- at 30 K

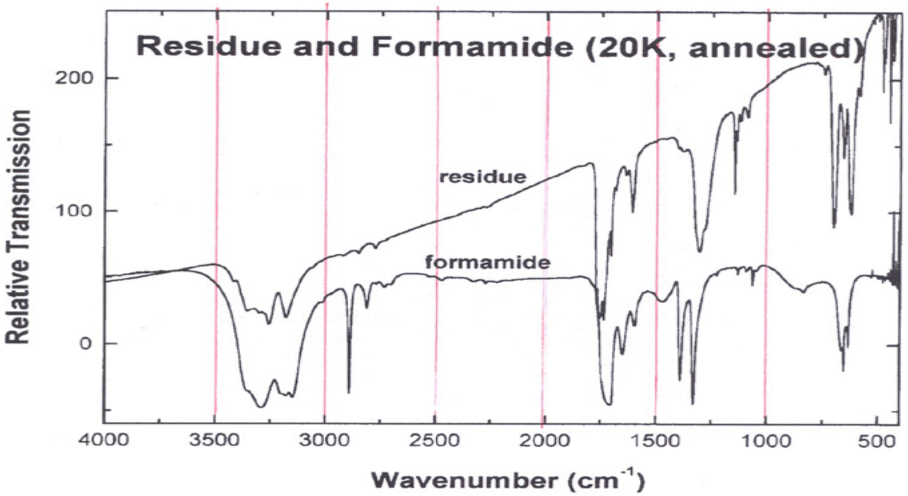


Fig. 6-16b: Comparison of infrared spectra of residue with formamide. Both deposits have been anealed (to 165 K) and recooled to 20 K to produce crystaline structure

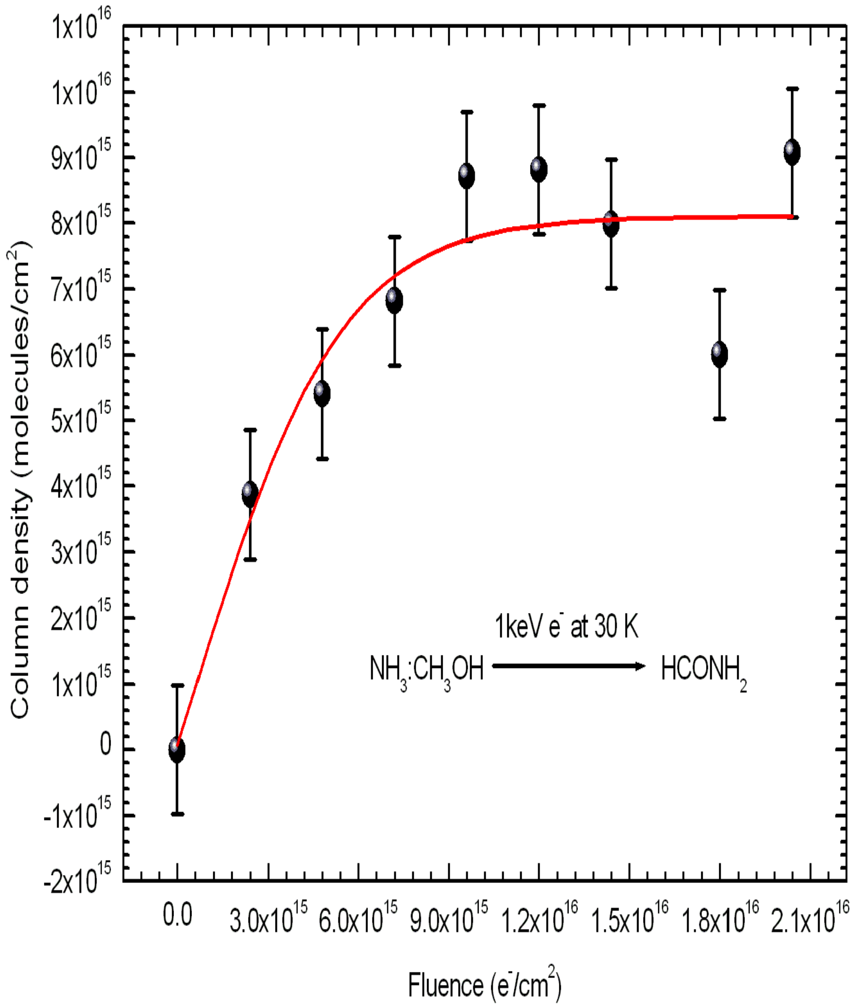


Fig. 6-15: Formation of $HCONH_2$ during the irradiation of 1:1 bianry mixture of NH_3:CH_3OH with 1 keV at 30 K

(Khanna, Lowenthal et al. 2002)

Electron Induced Chemistry

These are examples of high energy electrons 'Blasting' molecules apart or release of secondary electrons !!

But at low energies electrons can do surprising things !

Electron Induced Chemistry

The Open University

At low energies electrons can do surprising things !

- They can 'stick' to the molecule
- To form a **negative ion** or 'resonance'
- But only for a very short period of time (10^{-14} s)

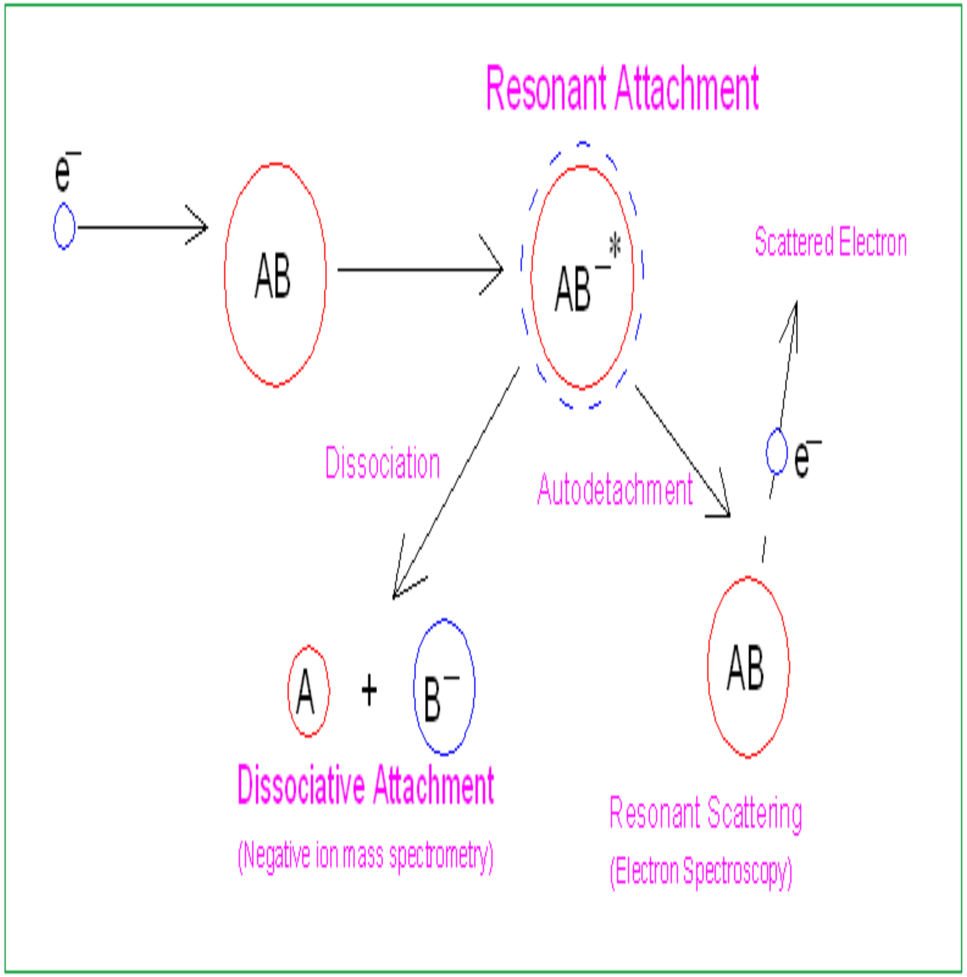
- Then the electron detaches
- Leaving molecule excited or not (elastic scattering)
- But this process can also lead to the dissociation of the molecule

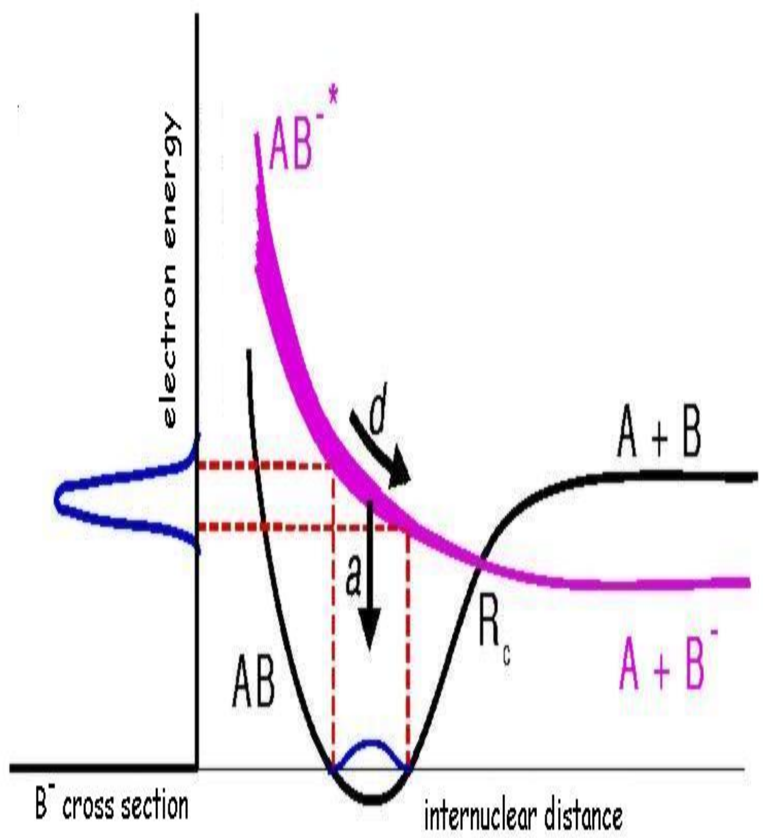
This is the process of **Dissociative Electron Attachment** (DEA)

Bond Selectivity using Electrons

Process of Dissociative Electron Attachment

Product is anion and neutral(s)





Electron Induced Chemistry; Chemical Control at the Molecular Level

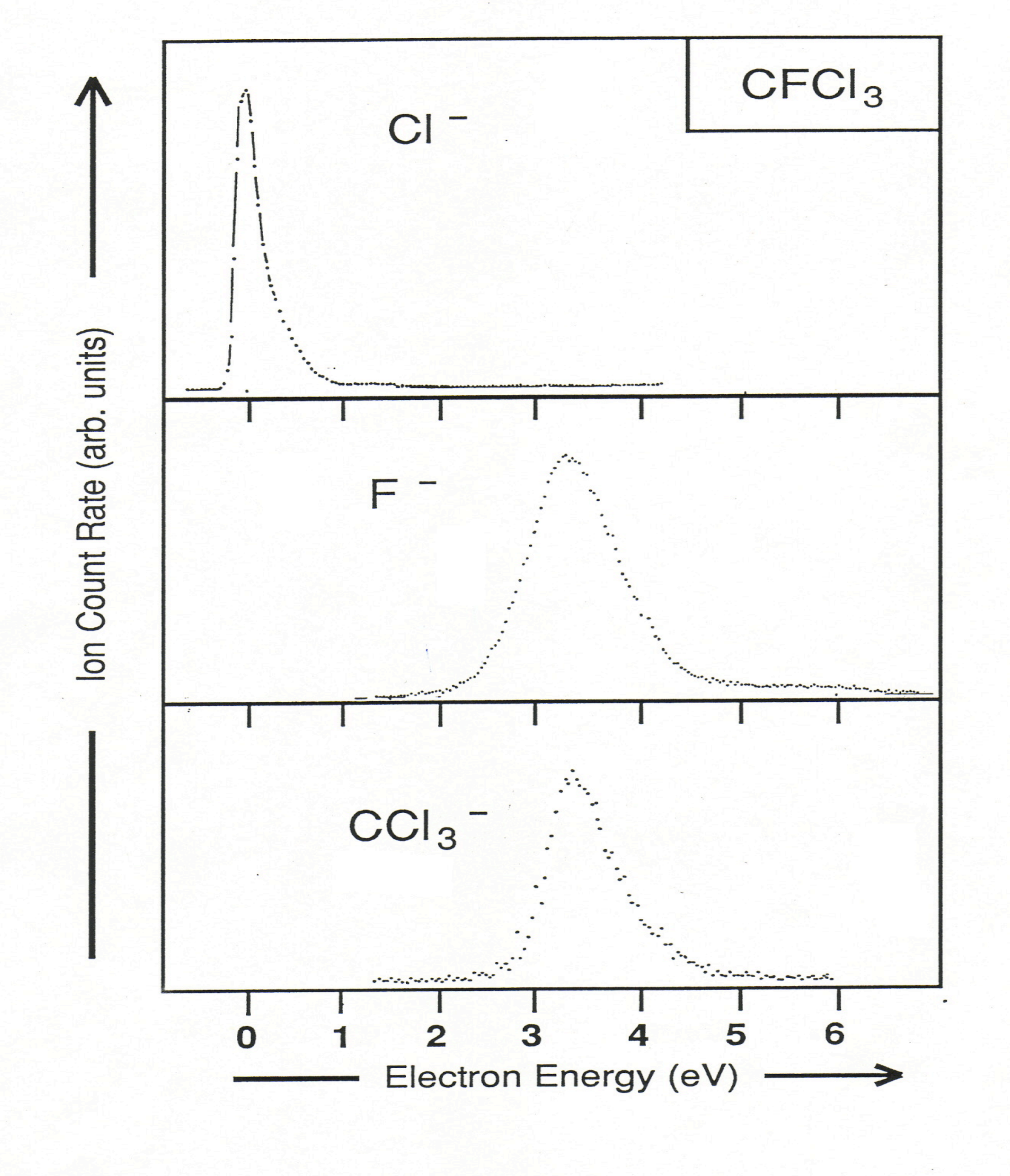
The Open University

Dissociative electron attachment therefore provides a method for breaking up molecules at low energies

Energies lower than the chemical bond energy !!!

Hence electrons can initiate chemistry

Electron Induced Chemistry; Chemical Control at the Molecular Level



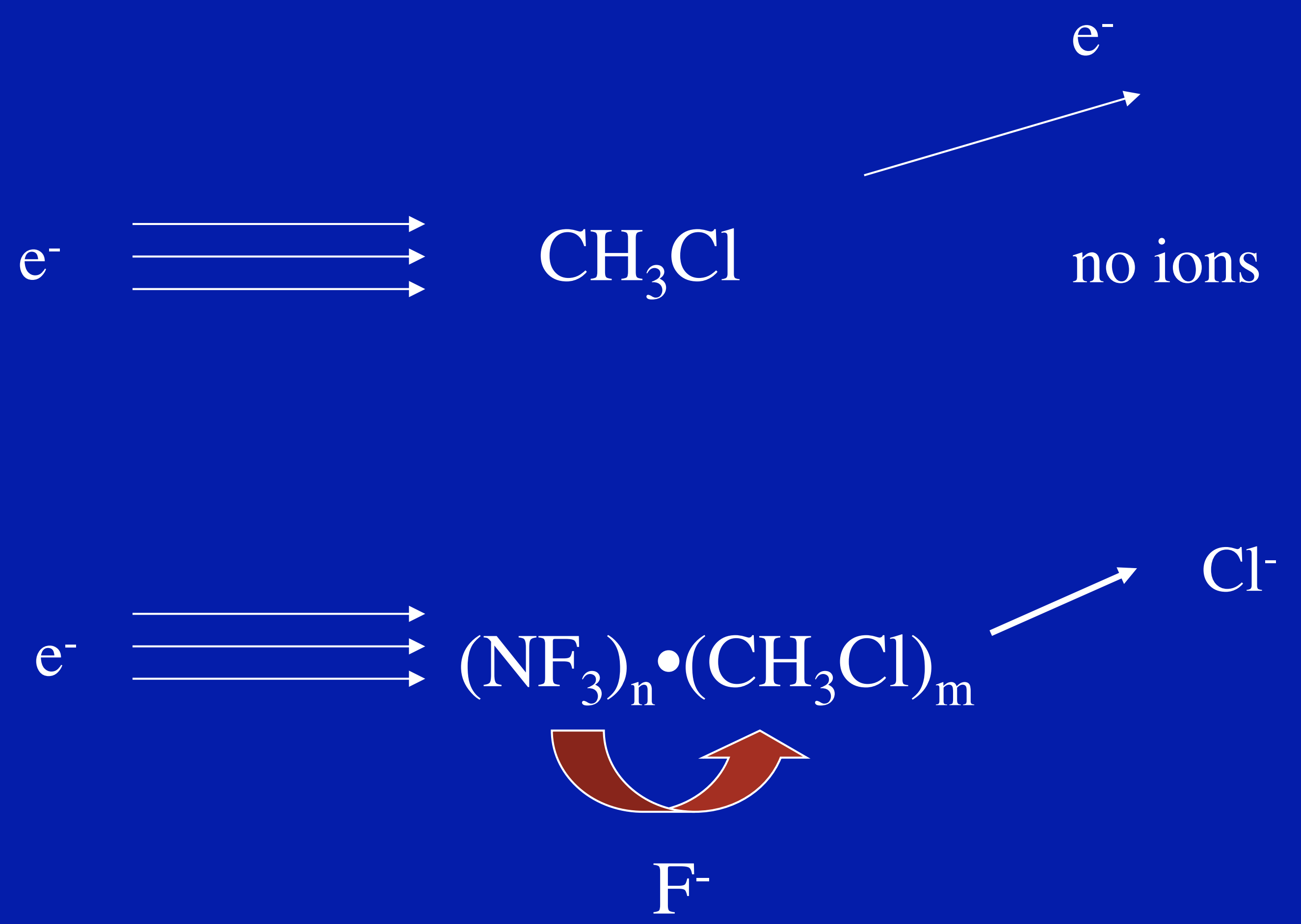
Selective C-Cl bond cleavage at 0 eV

Selective C-F bond cleavage at 3.2 eV

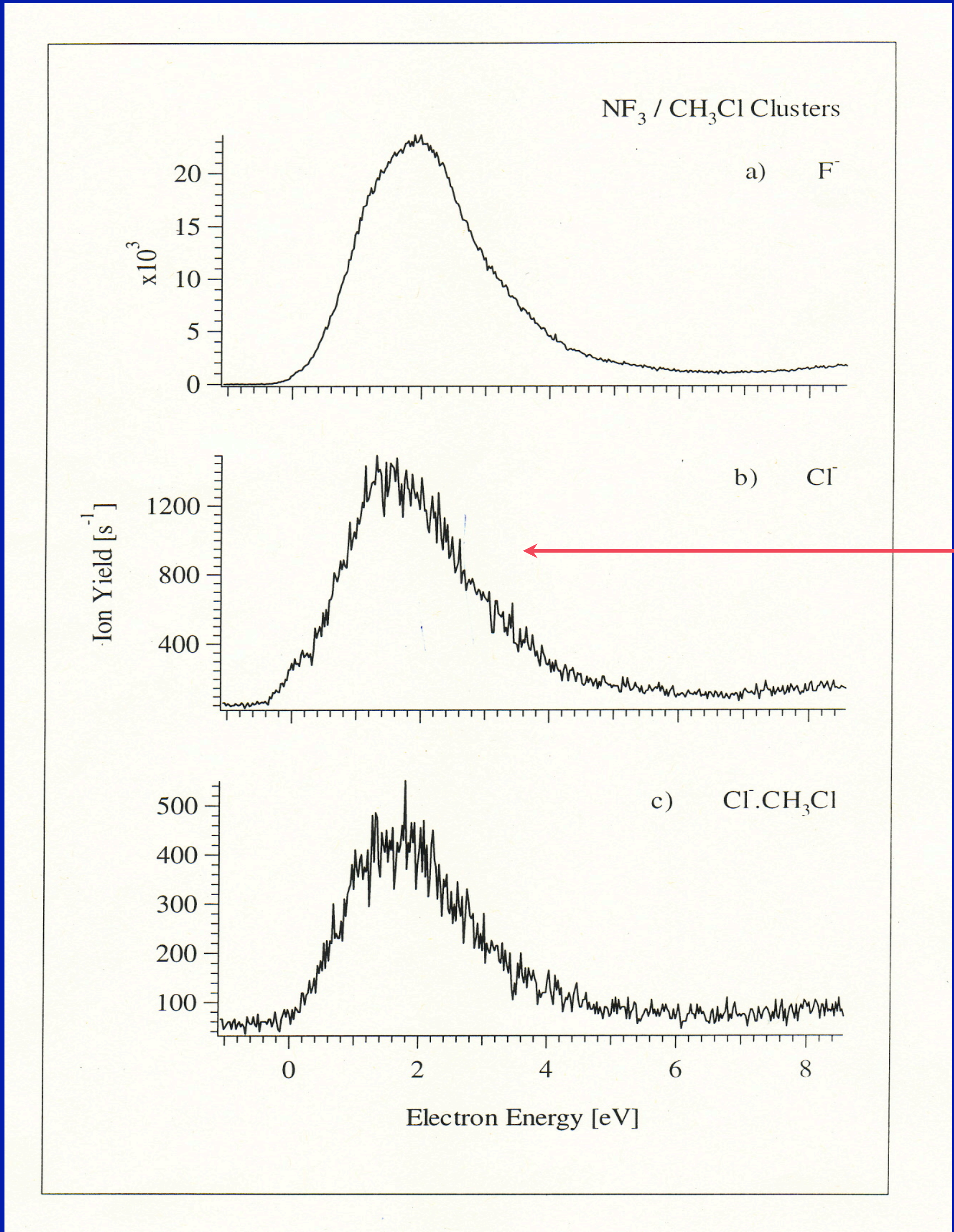
Illenberger et al Berlin

Nucleophilic Displacement (S_N2) Reaction

e.g. : $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$



e-
e-
CH3Cl
no ions
Cl-
e-
(NF3)n•(CH3Cl)m
F-



S_N2 Reaction

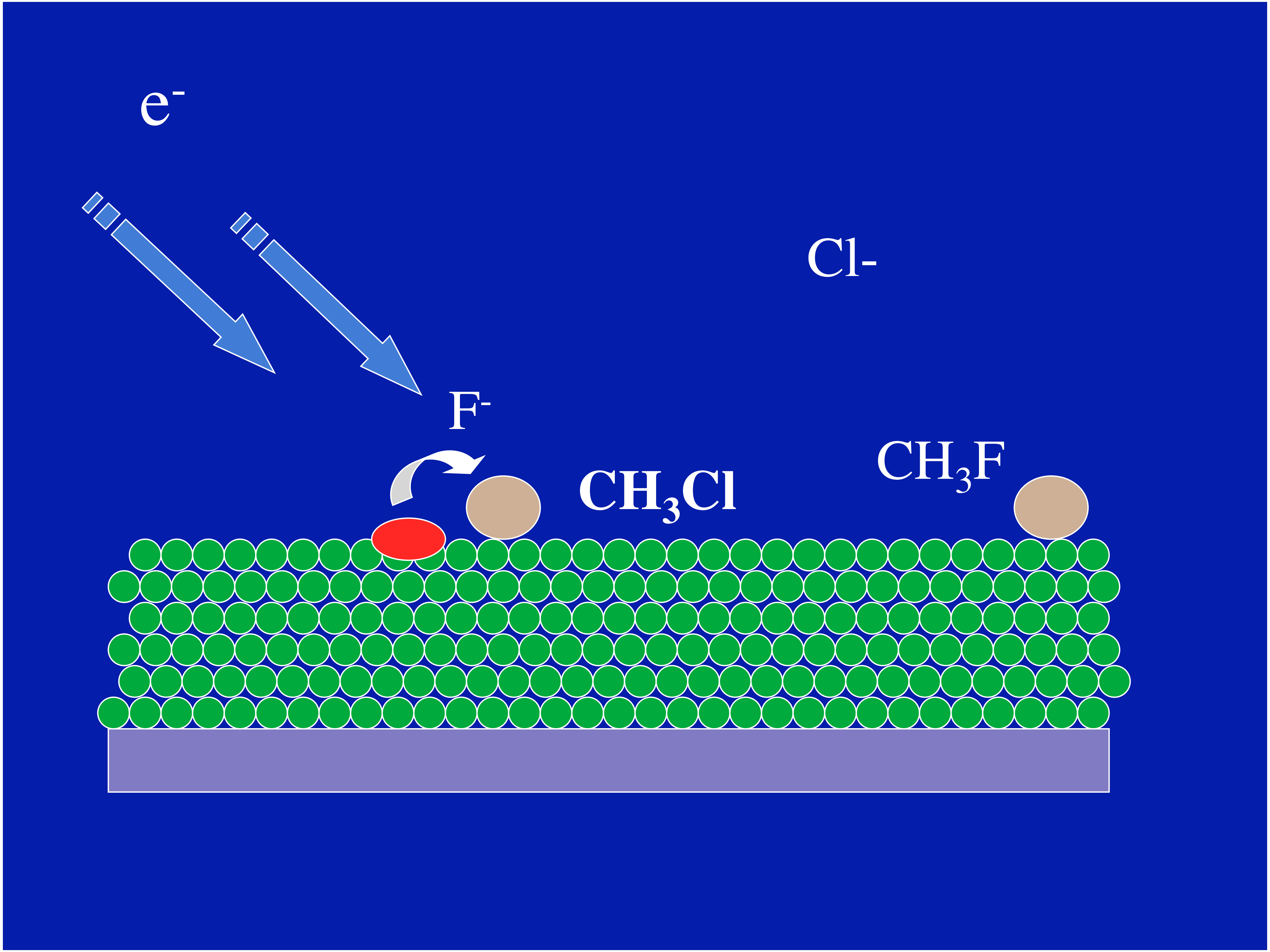
Illenberger et al Berlin

EIPAM

- Chemical surface transformations using electron induced reactions/

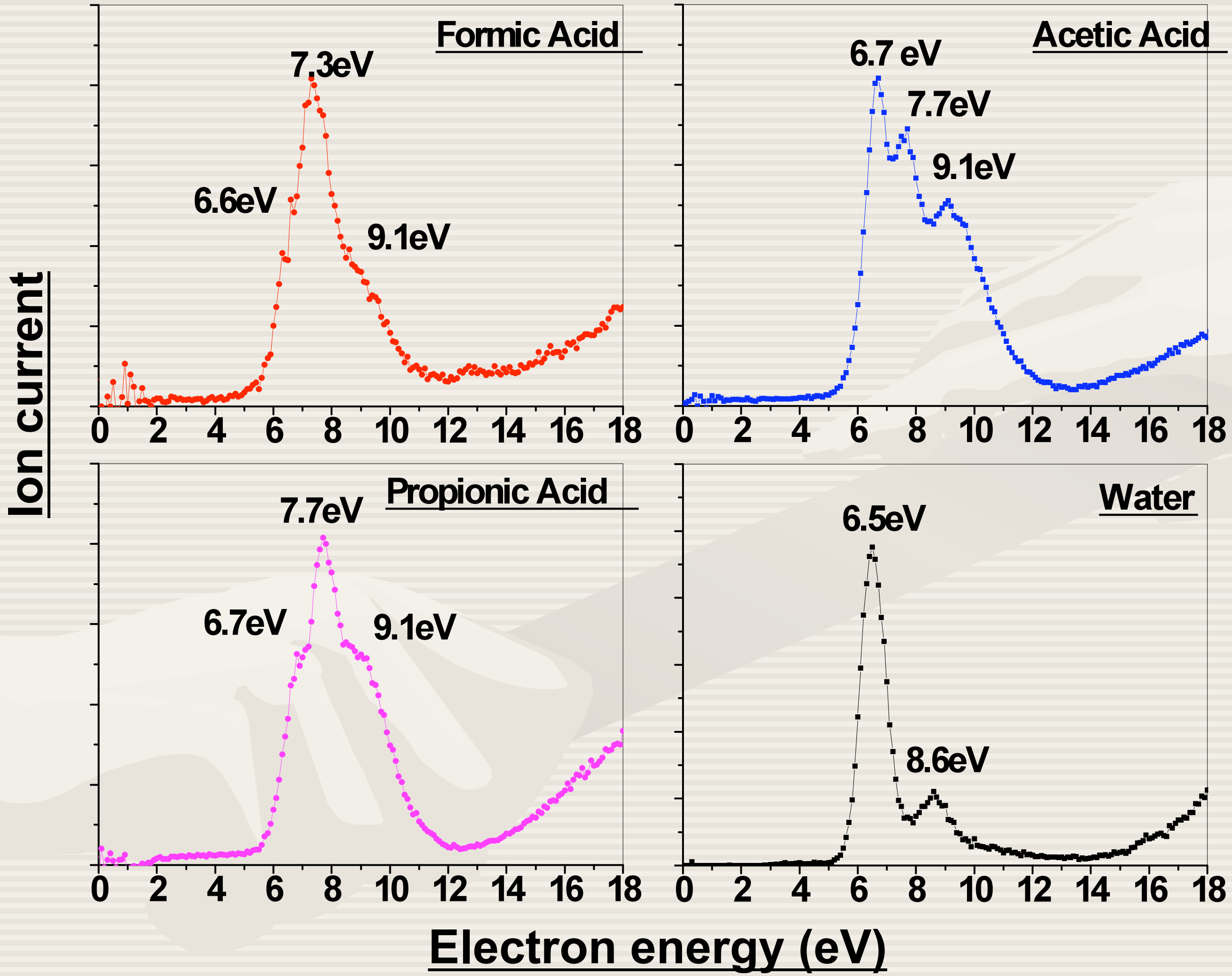
- DEA produces products that subsequently react on the surface

- E.g. Irradiate film of NF_3 and CH_3Cl
- Form CH_3F

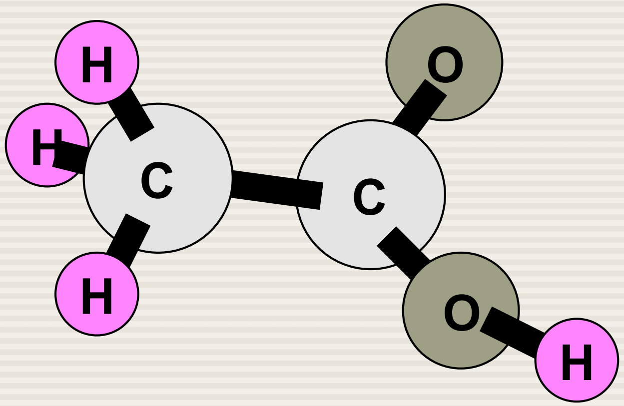

e^-
Cl-
F^-
CH_3Cl
CH_3F

DEA is universal

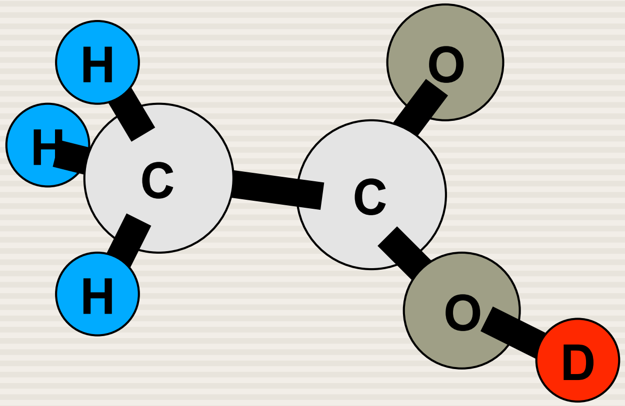
Relevant to most molecules in the ISM

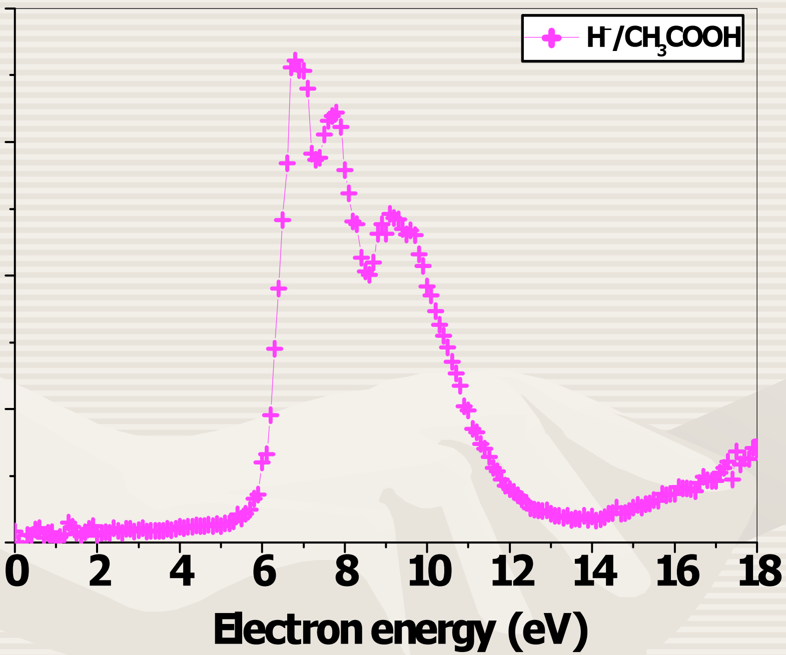


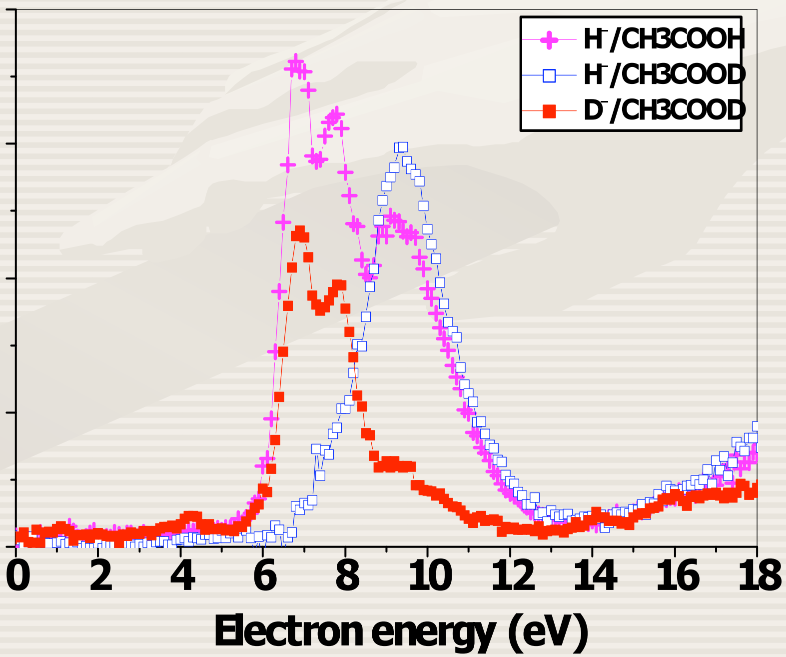
CH_3COOH



CH_3COOD

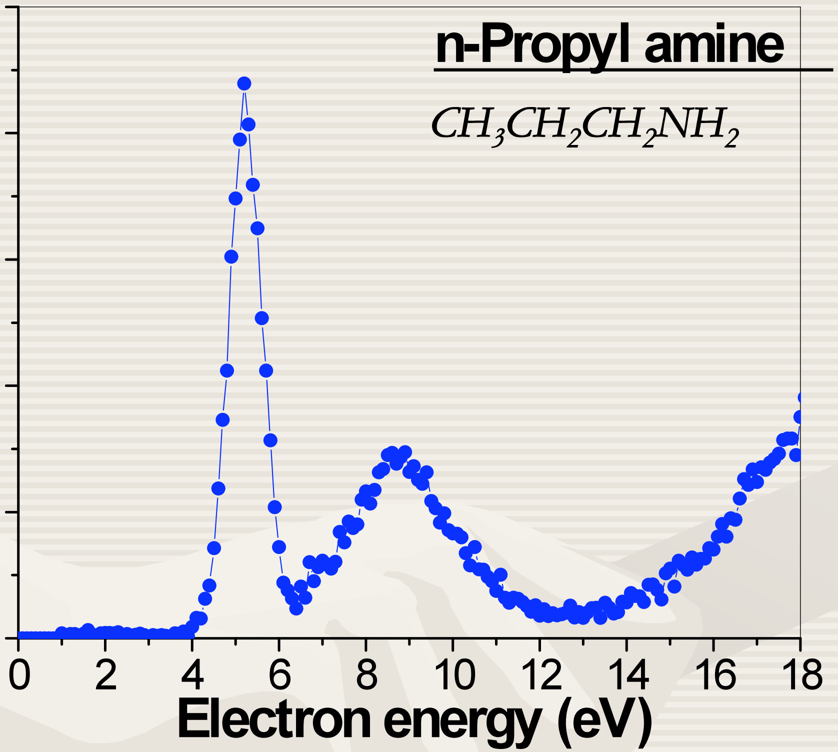




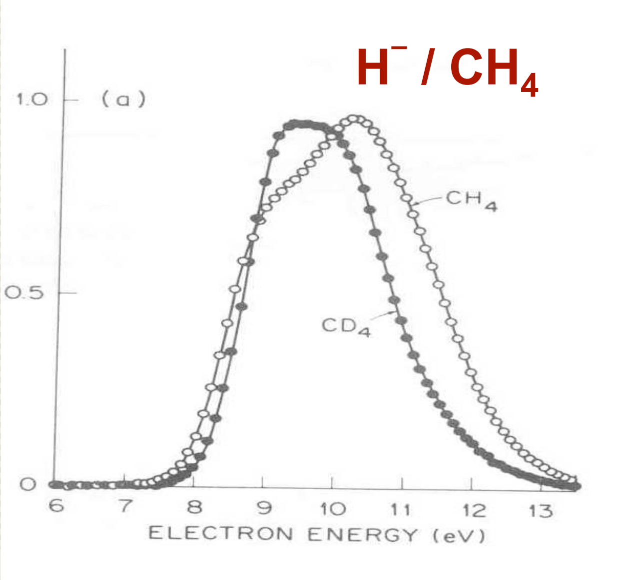


Prabhudesai et al. PRL (2005)

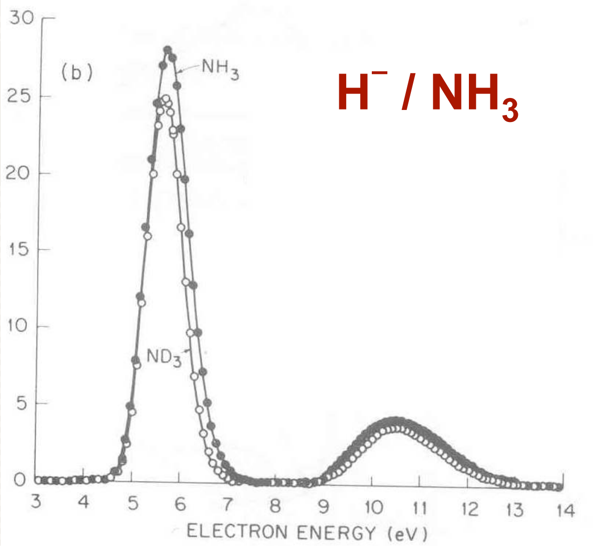
H^- from Amine



n-Propyl amine
$CH_3CH_2CH_2NH_2$
0
2
4
6
8
10
12
14
16
18
Electron energy (eV)



H^- / CH_4
1.0
(a)
0.5
0
CH4
CD4
6
7
8
9
10
11
12
13
ELECTRON ENERGY (eV)

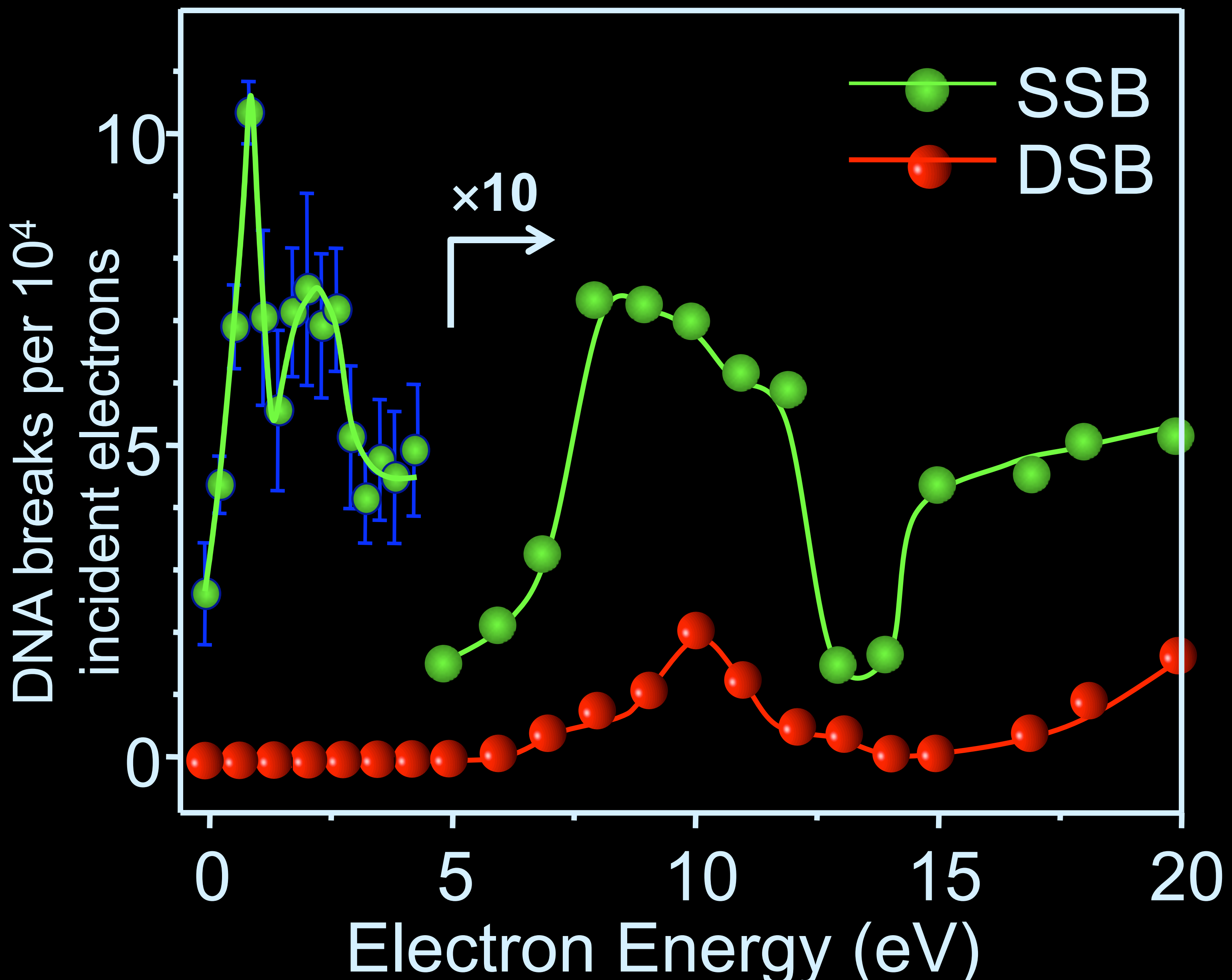


H^- / NH_3
30
25
20
15
10
5
0
(b)
NH3
ND3
3
4
5
6
7
8
9
10
11
12
13
14
ELECTRON ENERGY (eV)

DEA is universal

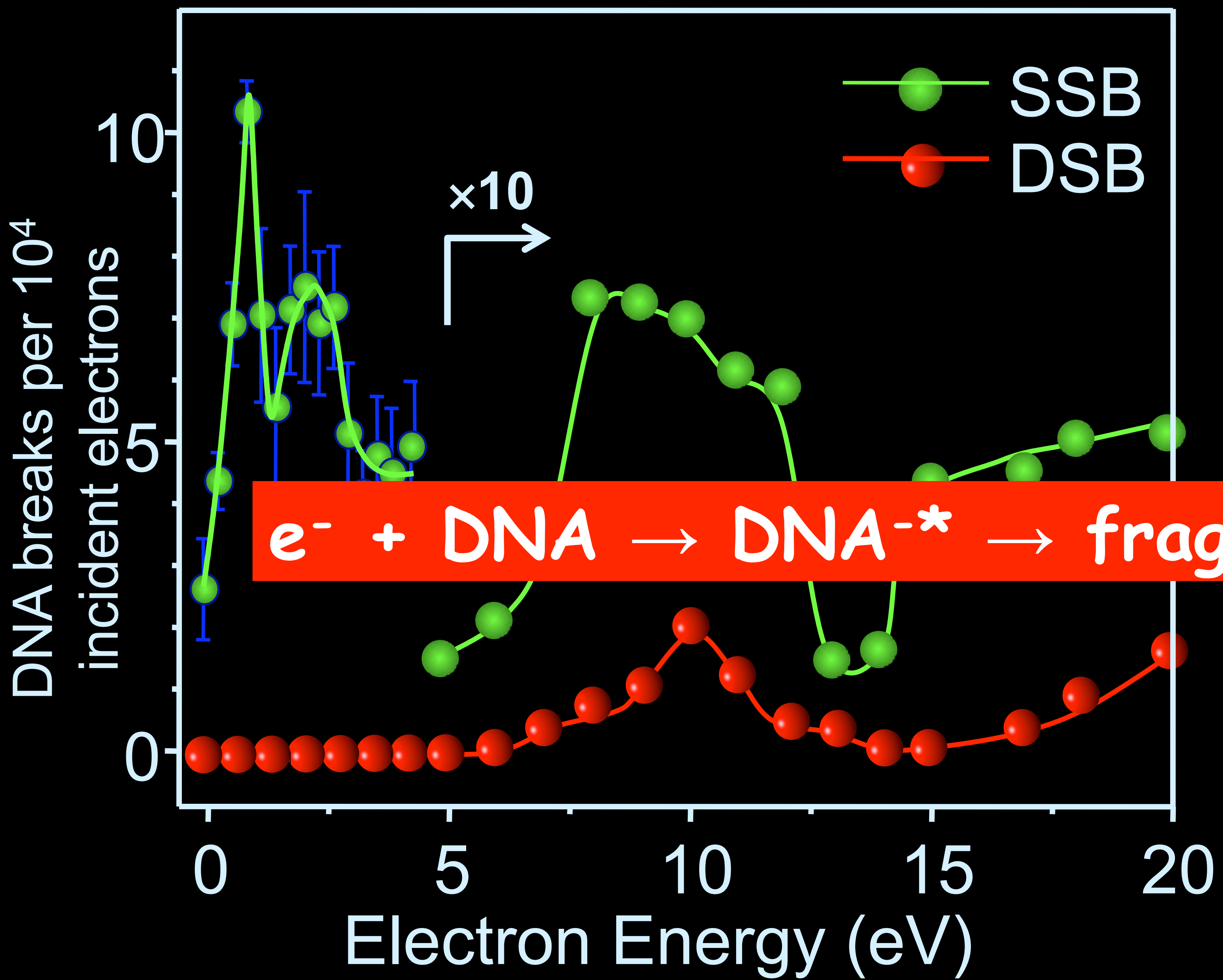
Even occurs in larger biomolecules such as DNA

Strand breaks of DNA



L. Sanche et al. Science, 287 (2000) 1659 and PRL (2004)

Strand breaks of DNA



$e^- + DNA \rightarrow DNA^{-*} \rightarrow$ fragments

L. Sanche et al. Science, 287 (2000) 1659 and PRL (2004)

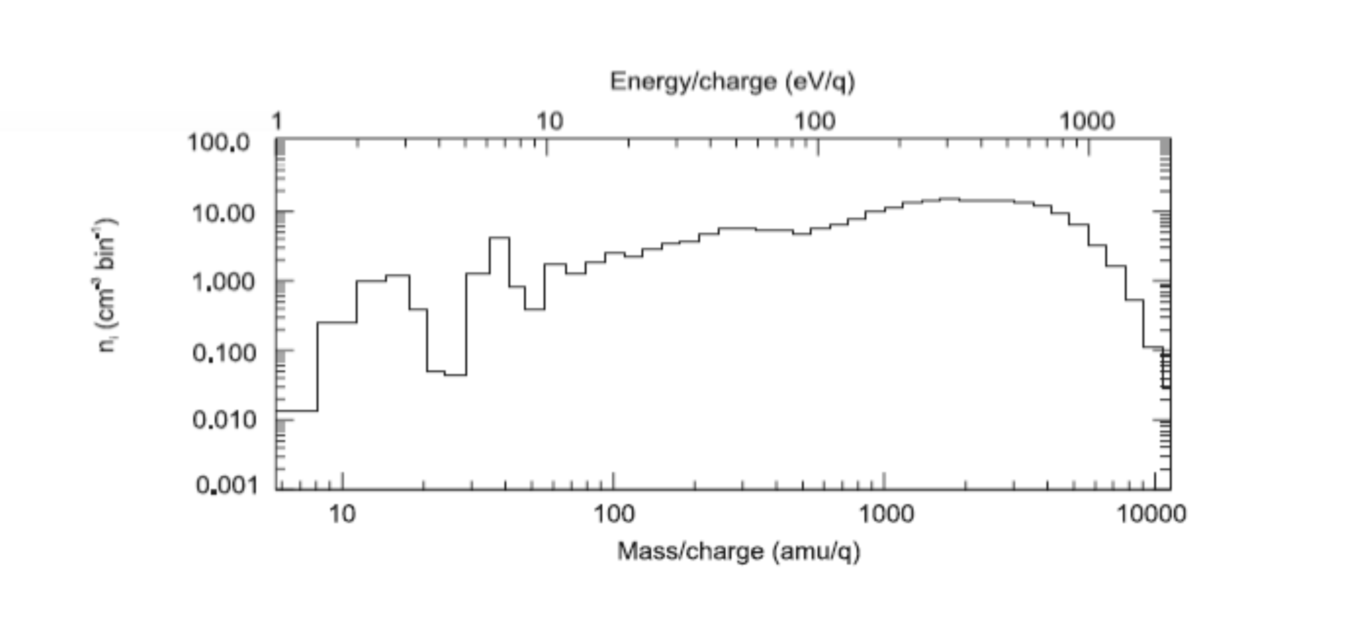
Presence of anions in space

The number of molecular anions detected in space is growing with the detection of;

C_4H^-, C_6H^-, C_8H^- and more recently the first nitriles **CN^- C_3N^- and C_5N^-**

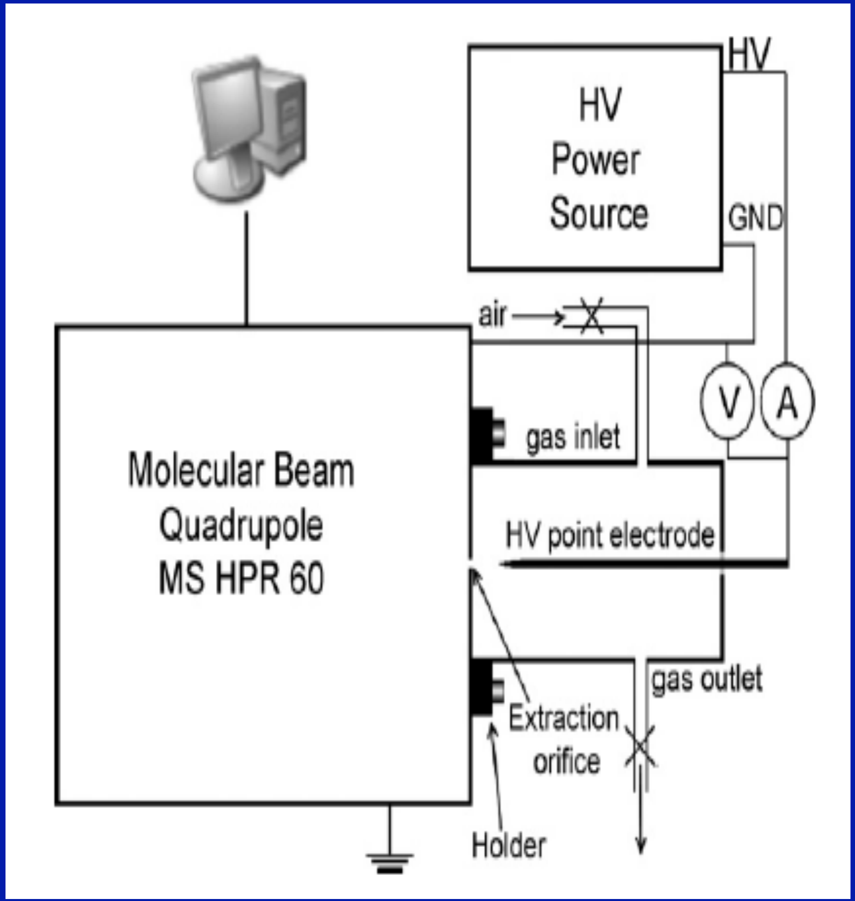
Anions on Titan

Negative ion density measured by ELS at an altitude of 953 km during the Titan (from Coates *et al. (2007))*.



Laboratory mimics of Titan's atmosphere

Use discharges to mimic the chemistry and physical conditions in Titan's atmosphere (5-10% CH_4 and 95-90% N_2)



Corona discharge

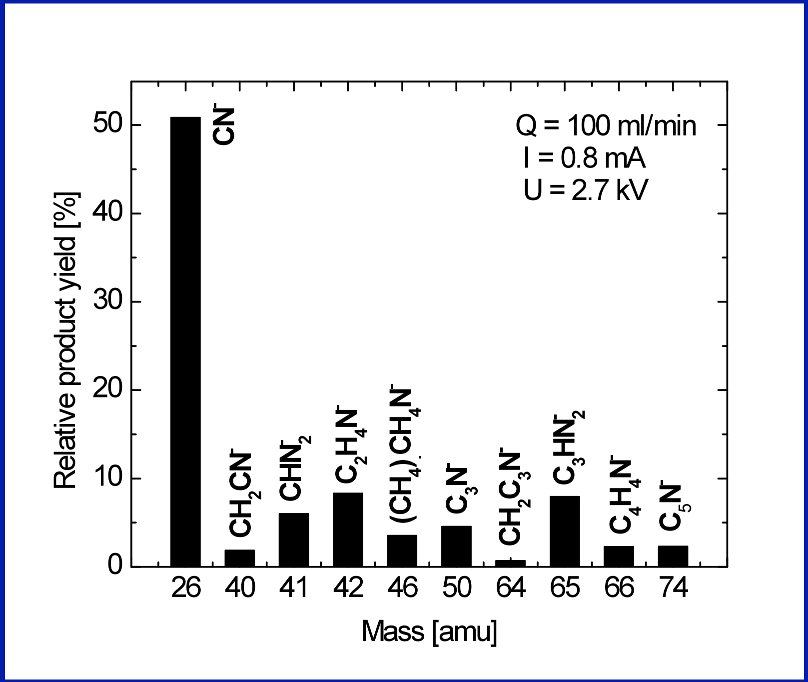
Dielectric Barrier Discharge

Laboratory mimics of Titan's atmosphere

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

provides good evidence of the presence of

HCN, CH_3CN,HC_3N and HC_5N neutrals



Learning Outcomes Lecture 2

- Cosmic rays induce chemistry in astrochemical/planetary ices
- Laboratory experiments can replicate these conditions
- CRs produce secondary species (electrons) which may in fact drive most of the chemistry.
- ALMA will provide fascinating new maps of molecular species that will allow the routes of synthesis to be explored – Surface and CR/ Electron chemistry may be highlighted