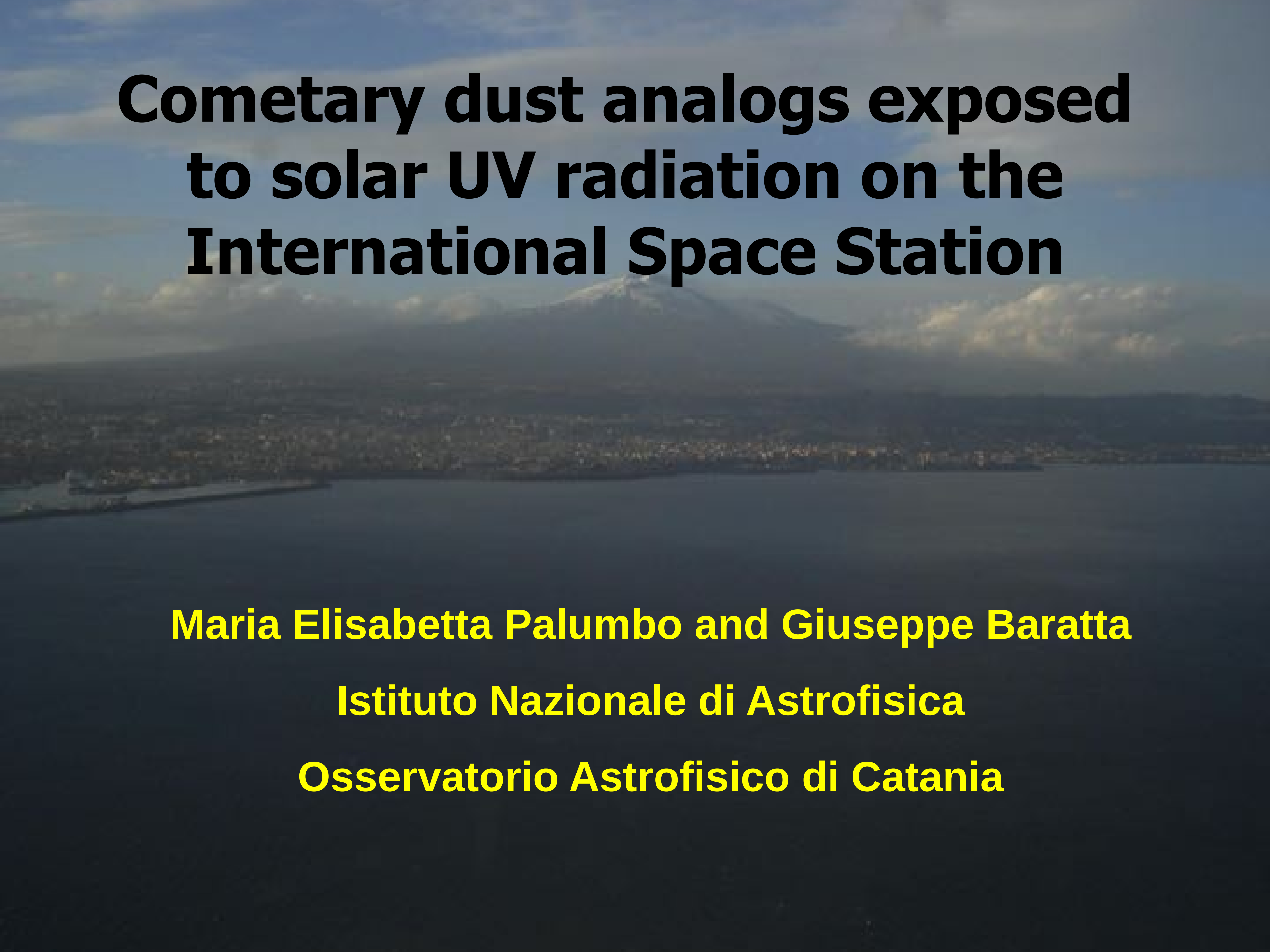


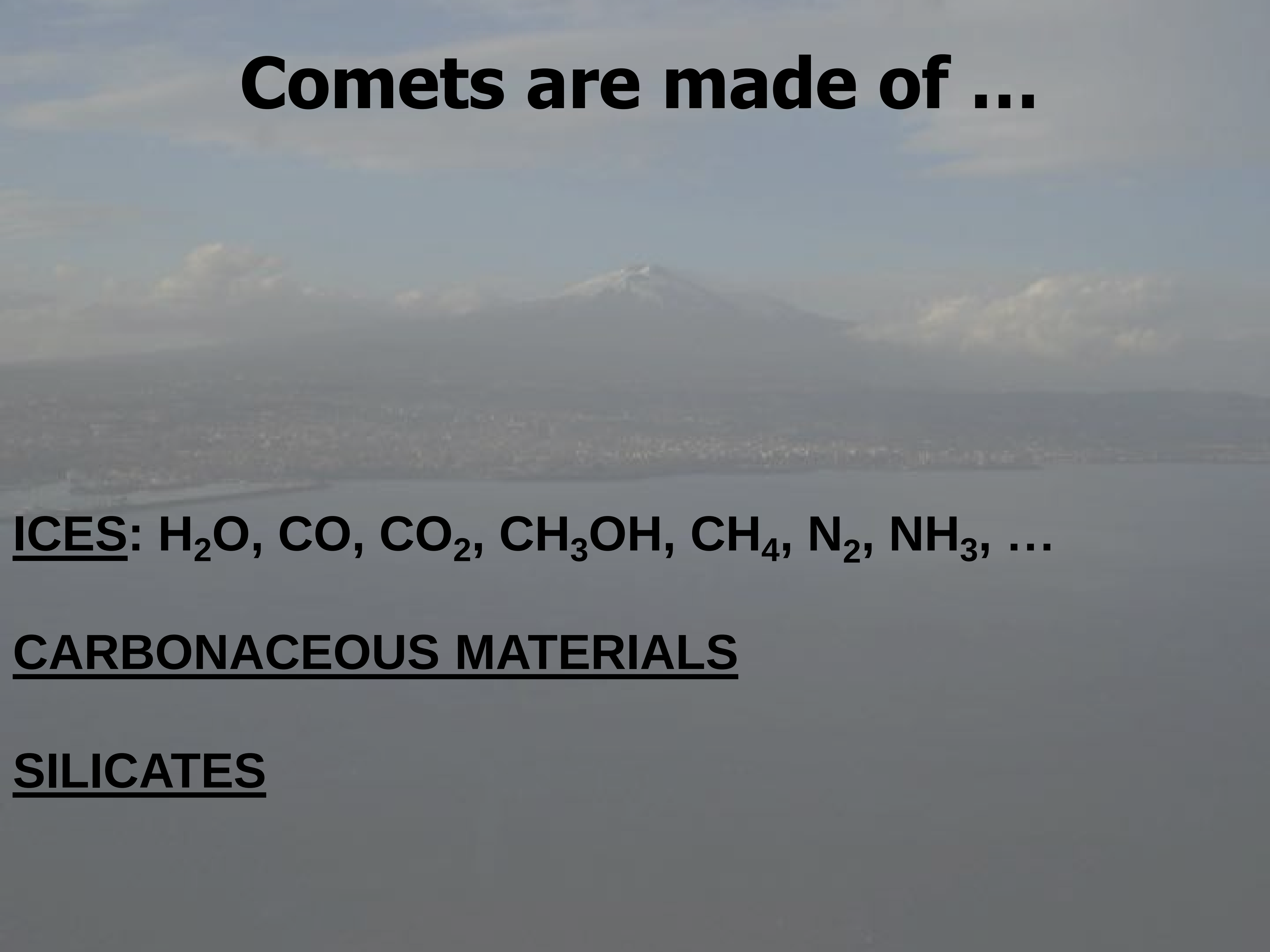
Cometary dust analogs exposed to solar UV radiation on the International Space Station

Maria Elisabetta Palumbo and Giuseppe Baratta

Istituto Nazionale di Astrofisica

Osservatorio Astrofisico di Catania

Comets are made of …



<u>ICES</u>: H_2O, CO, CO_2, CH_3OH, CH_4, N_2, NH_3, …

<u>CARBONACEOUS MATERIALS</u>

<u>SILICATES</u>

Laboratory investigation aims to study the processes which drive the evolution of cometary materials

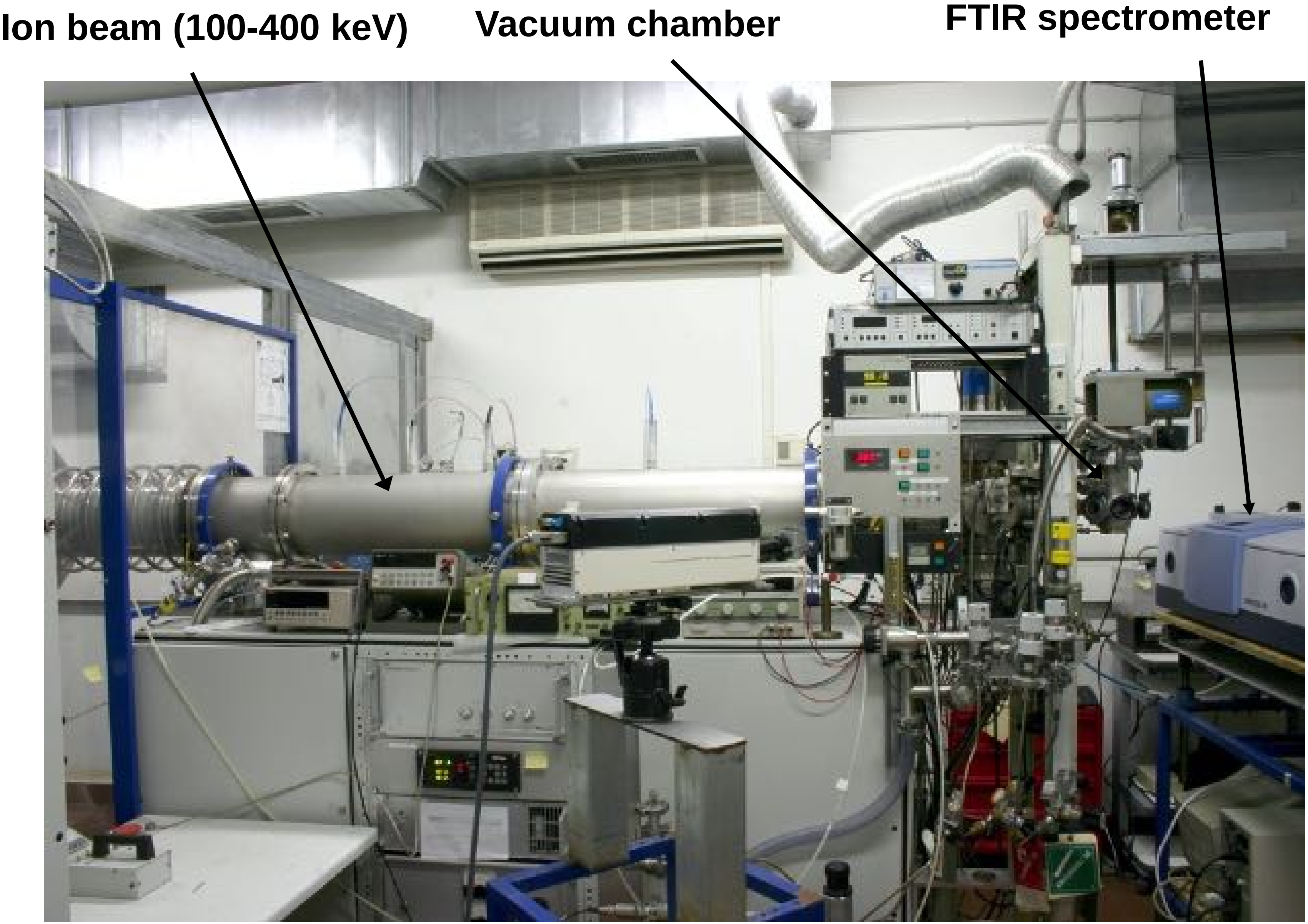
Energetic processing

✓*Galactic cosmic rays*
✓*UV photons*
✓*Solar wind*
✓*Solar energetic particles*

Thermal processing

✓*Warm-up phase during star formation*
✓*Variation of distance from the Sun*

Laboratory for Experimental Astrophysics INAF - Catania

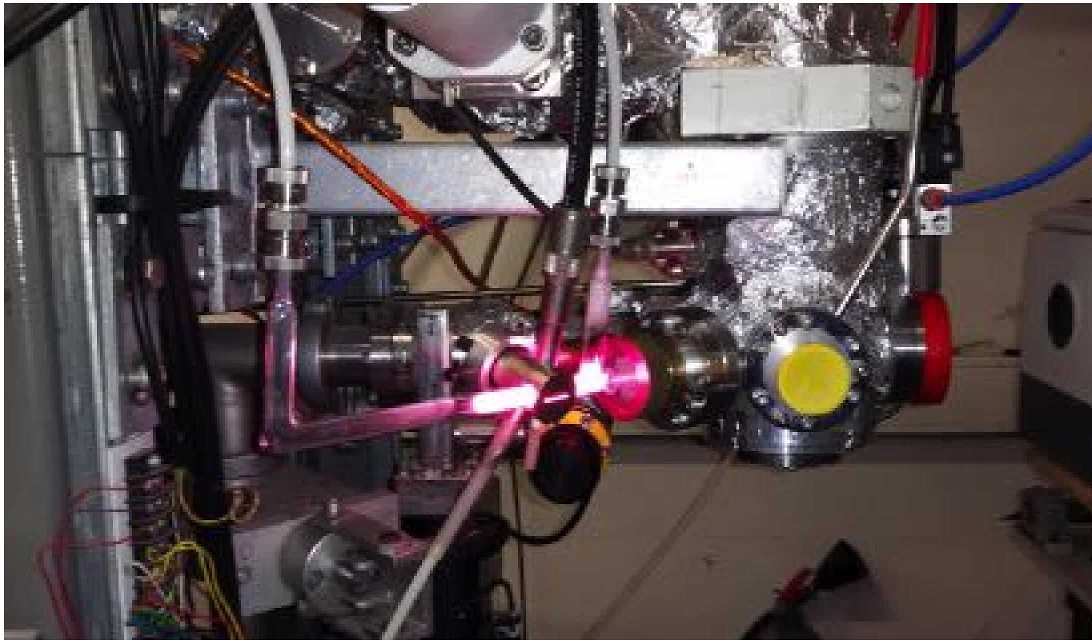


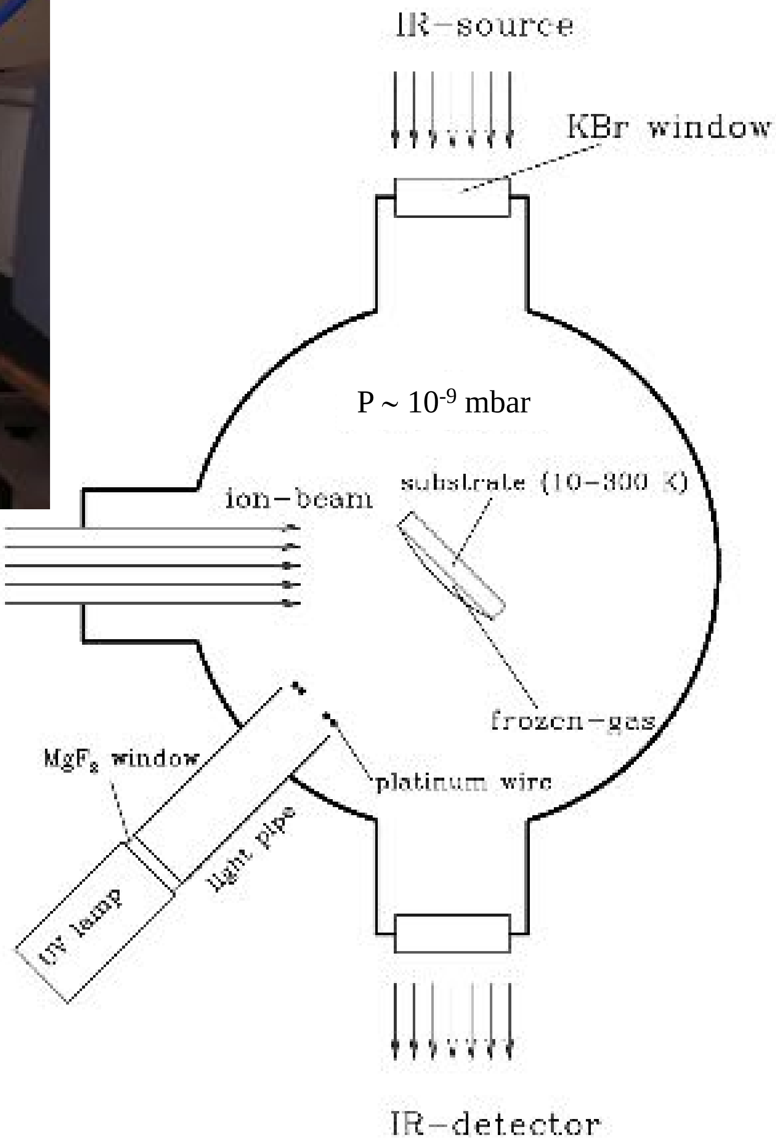
Ion beam (100-400 keV)

Vacuum chamber

FTIR spectrometer

Vacuum chamber



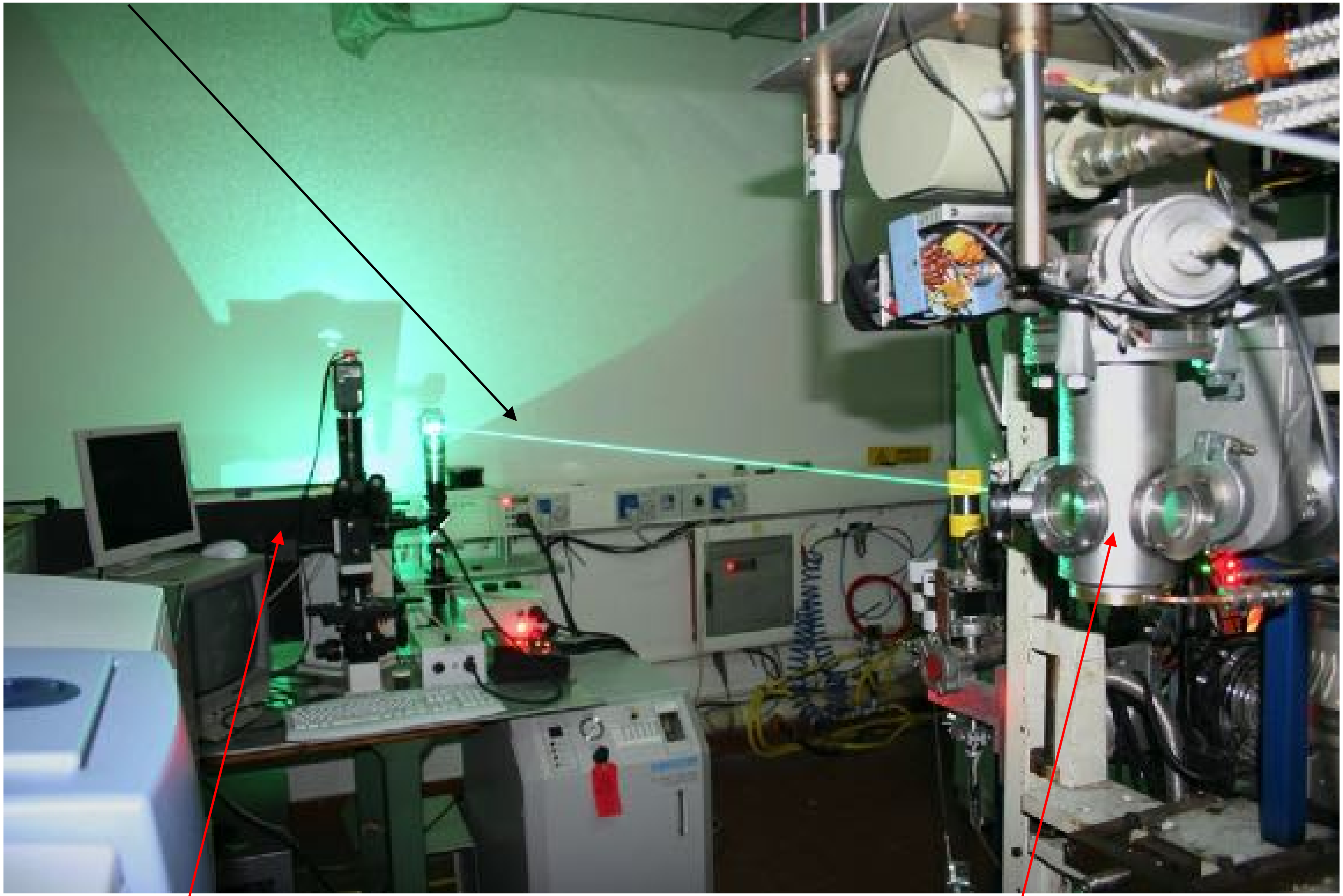


Analysis:

- **IR spectroscopy**
- **Raman spectroscopy**

In situ Raman spectroscopy

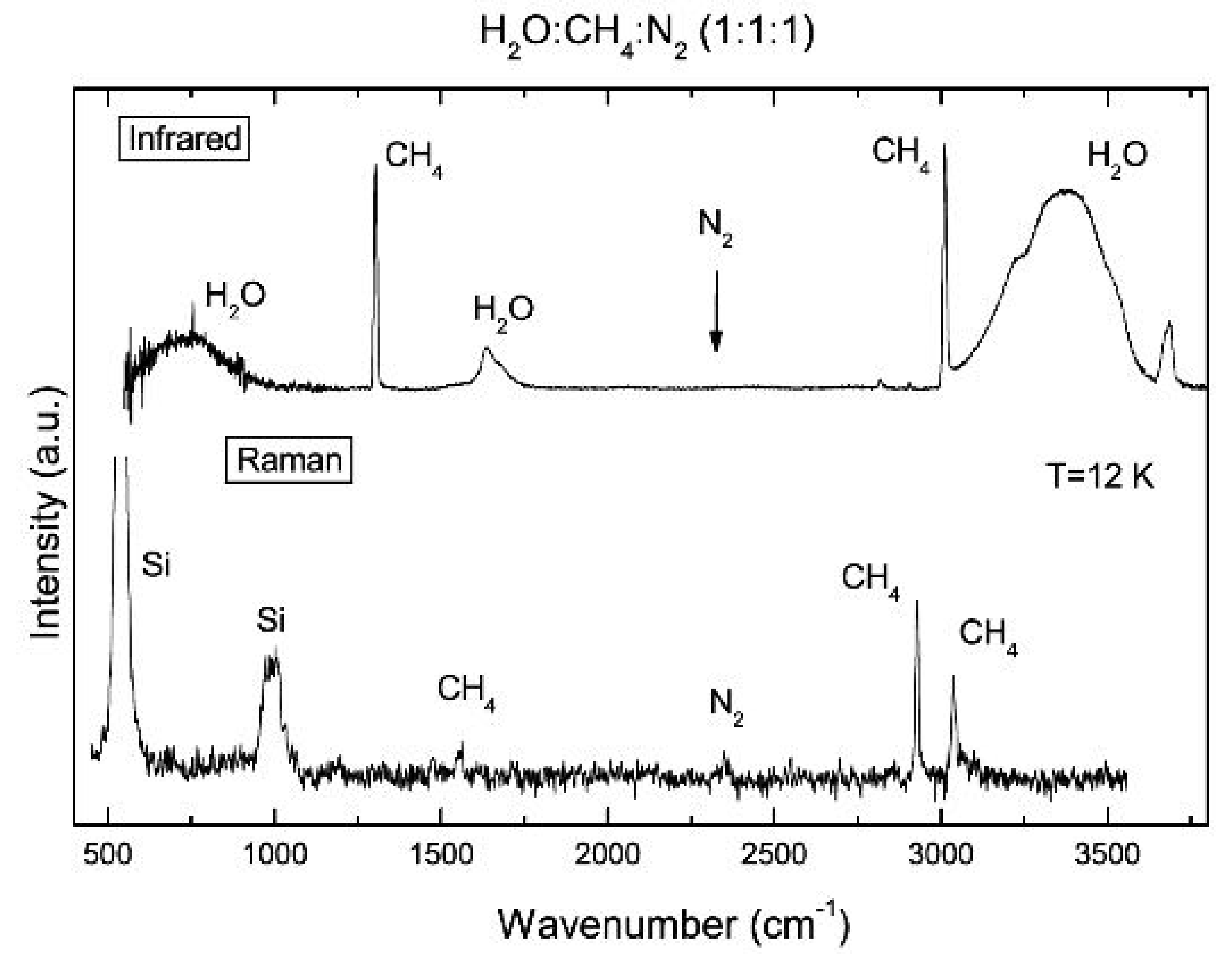
Laser Ar^+ (514.5 nm)



Raman spectrometer

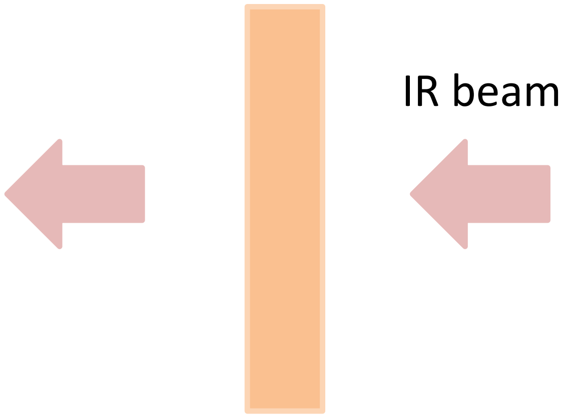
Vacuum chamber

IR and Raman spectroscopy



Palumbo M.E., Ferini G., Baratta G.A., 2004, Adv. Sp. Res. 33, 49

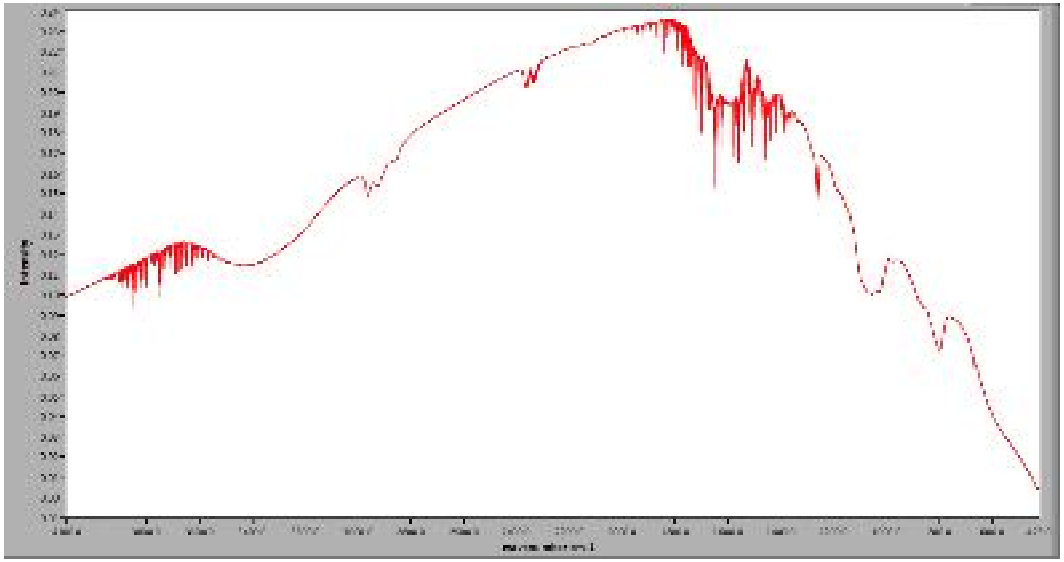
Experimental procedure



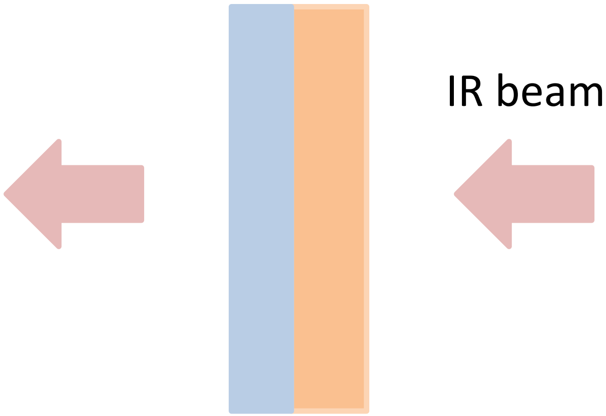
Substrate (Si, KBr, CsI)
T=10-300 K

IR beam

Background (mid-infrared) at 16 K
(KBr substrate)



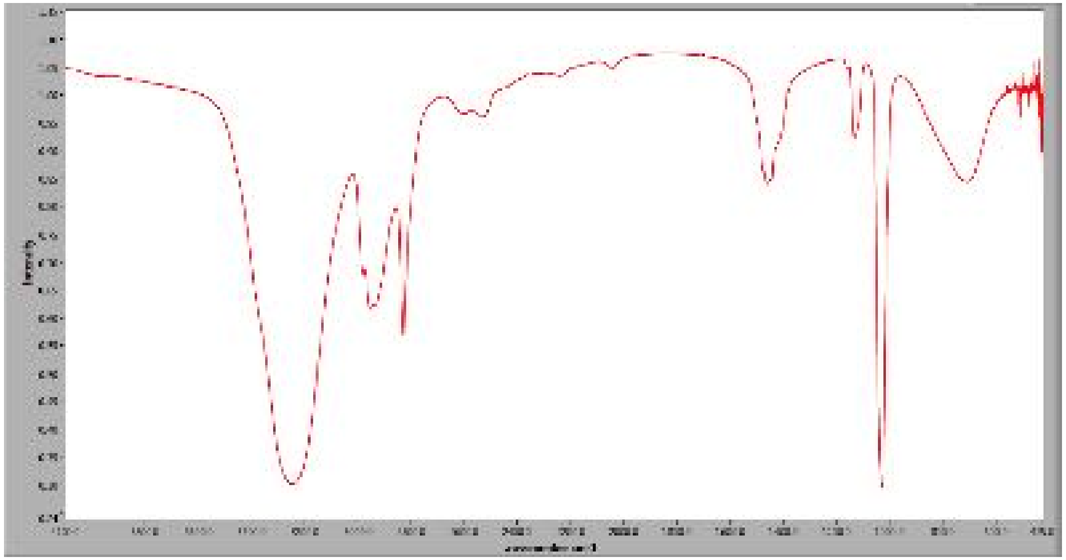
Experimental procedure



Sample
T=10-150 K

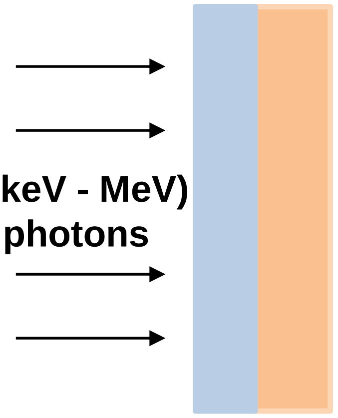
IR beam

Mid-IR spectrum of the sample as deposited
(CH_3OH at 16 K)



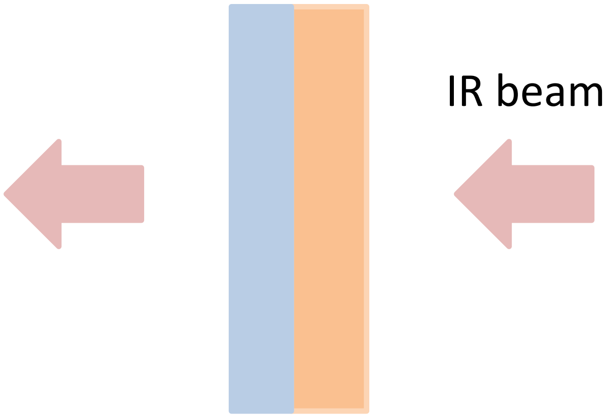
Experimental procedure

Bombardment or irradiation of the sample
T=10-150 K



Ions (keV - MeV)
UV photons

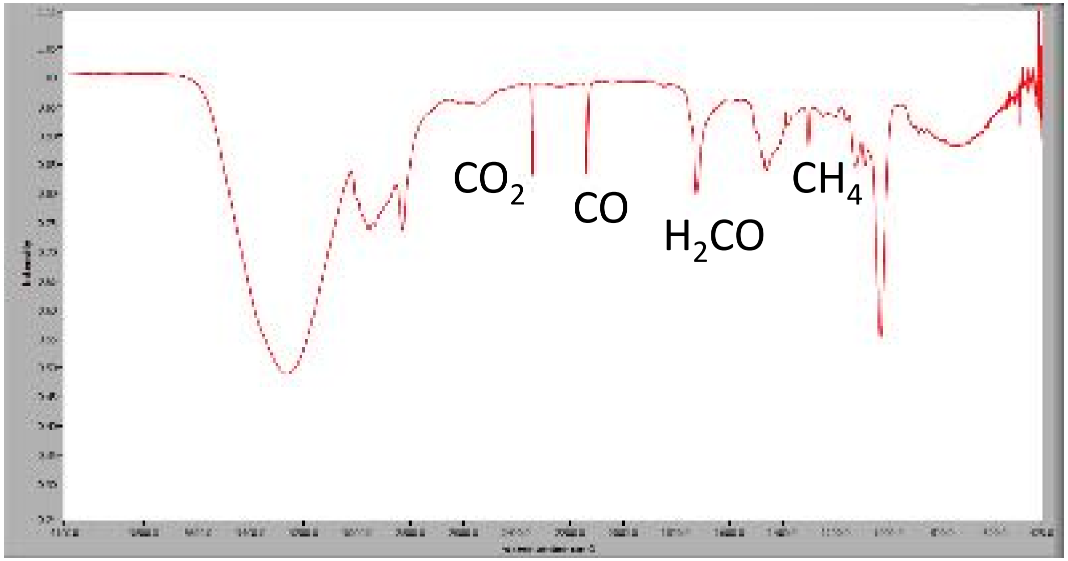
Experimental procedure



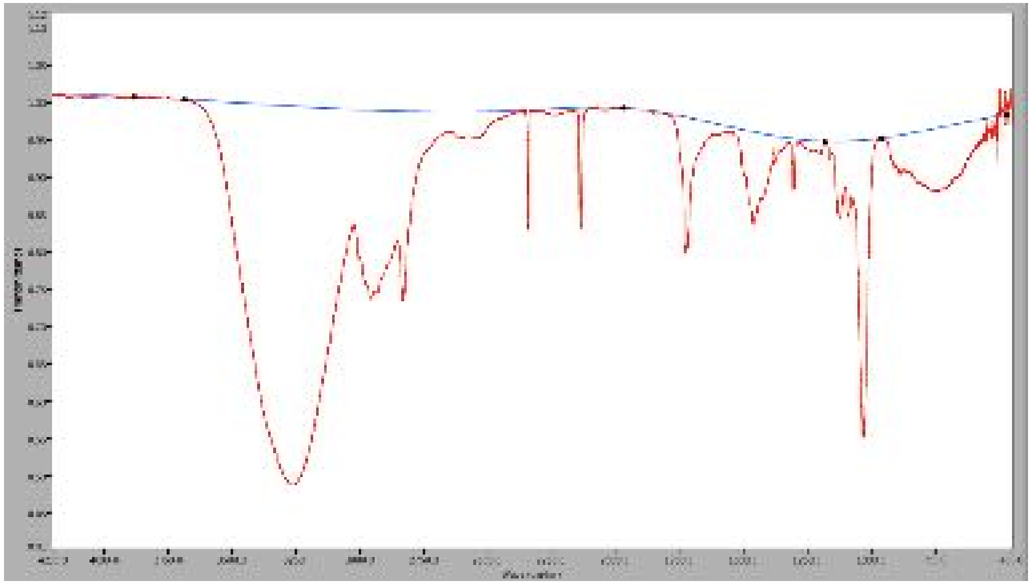
Processed sample
T=10-150 K

IR beam

Mid-IR spectrum of the sample after irradiation
(CH_3OH + 200 keV H^+ at 16 K)

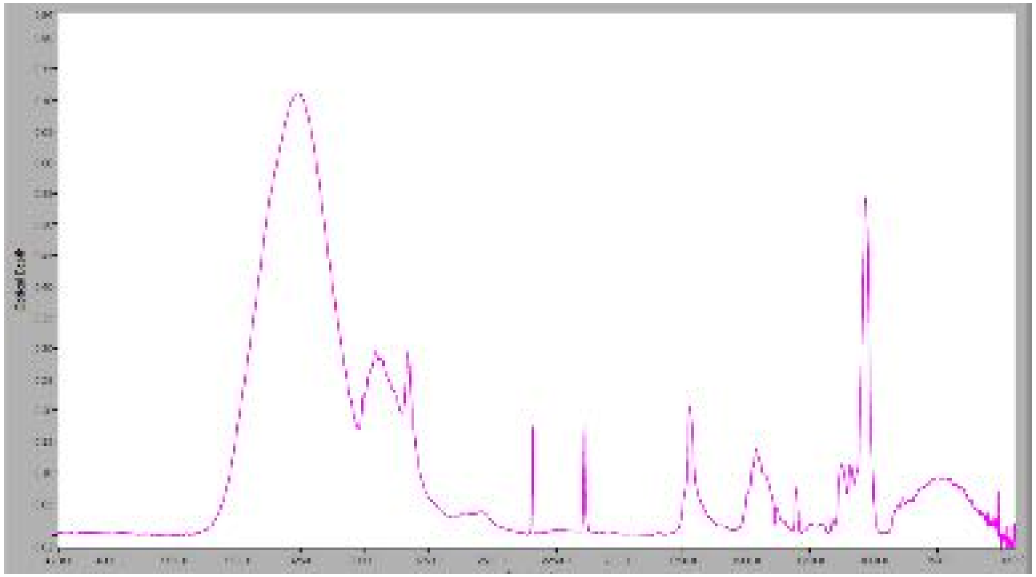


Experimental procedure

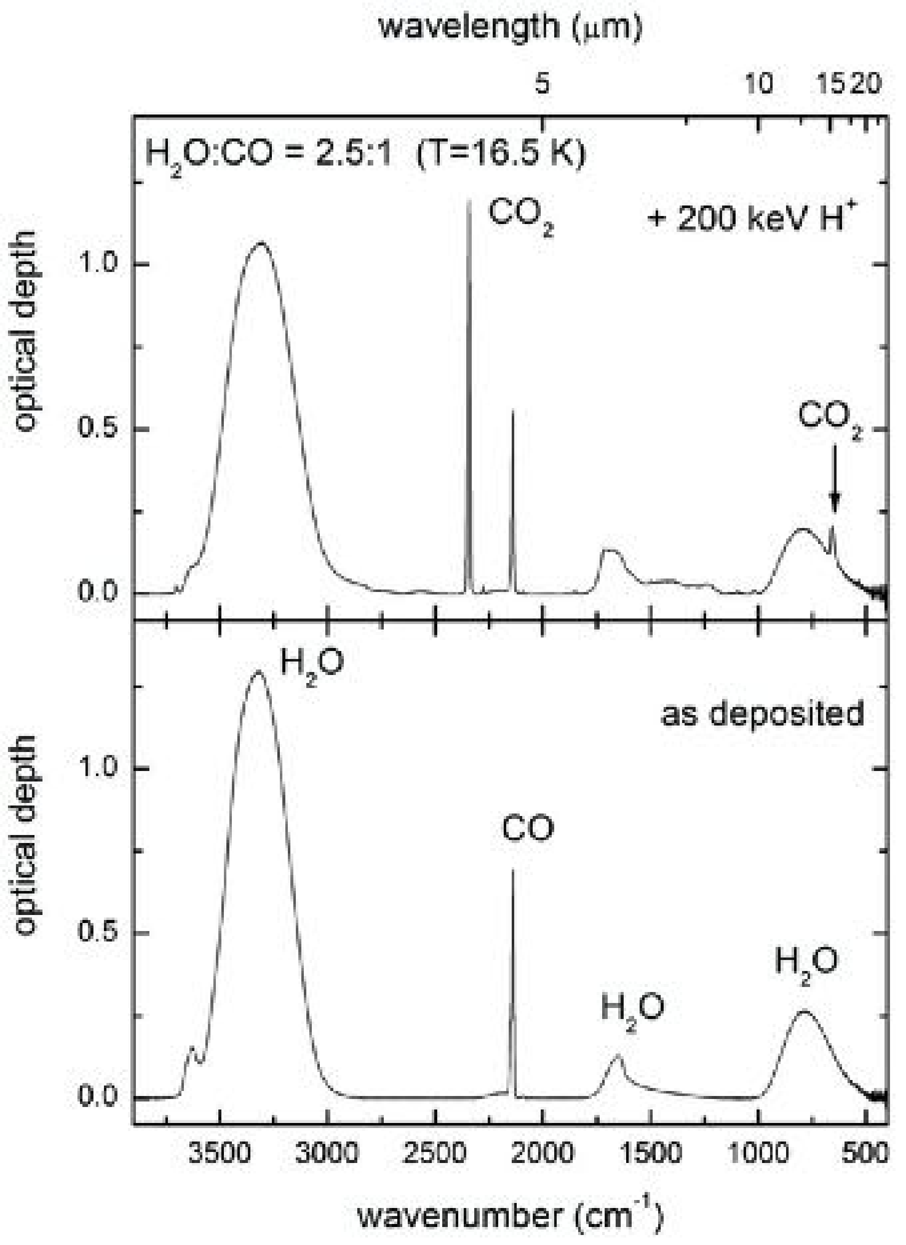


Continuum normalization

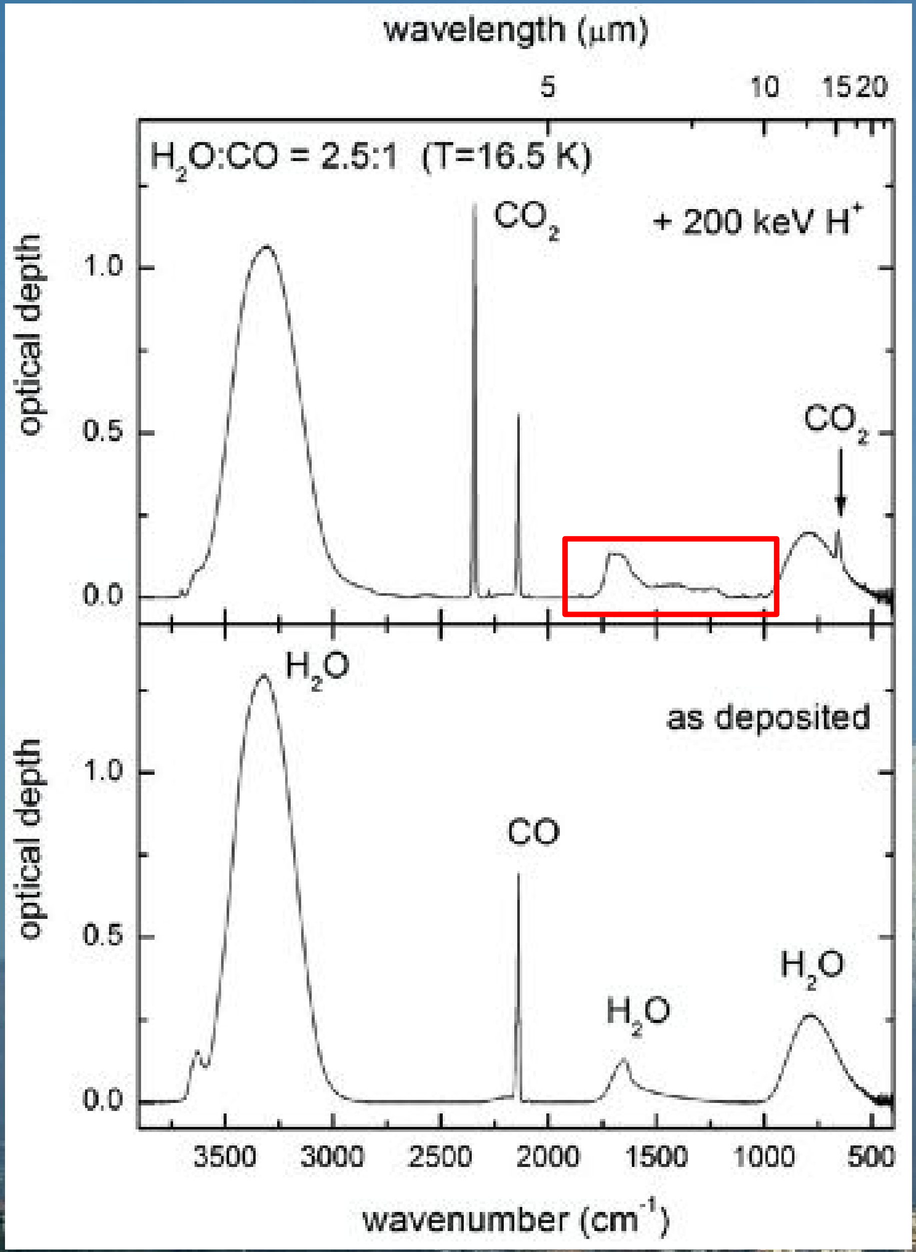
$$\tau = -\ln(I/I_0)$$



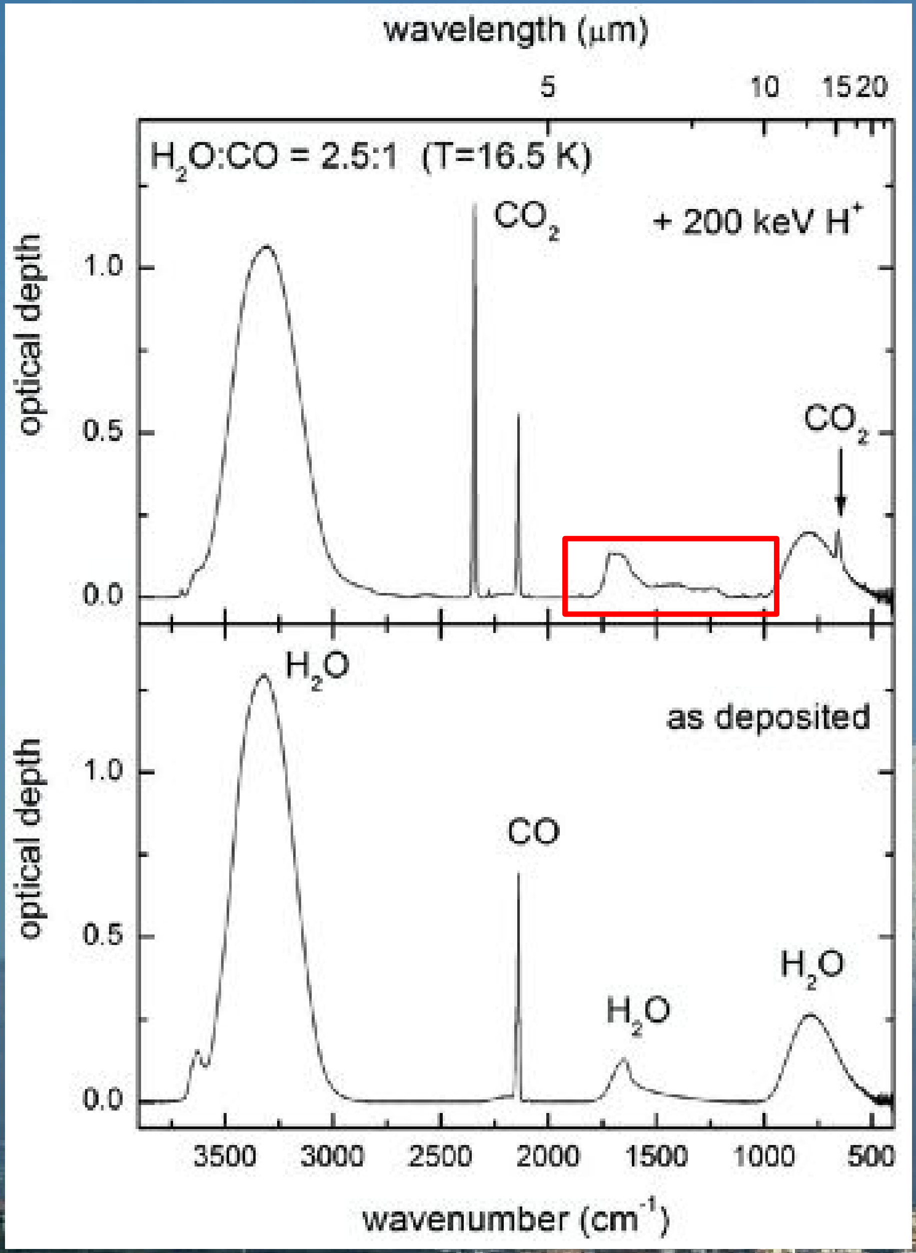
H_2O:CO

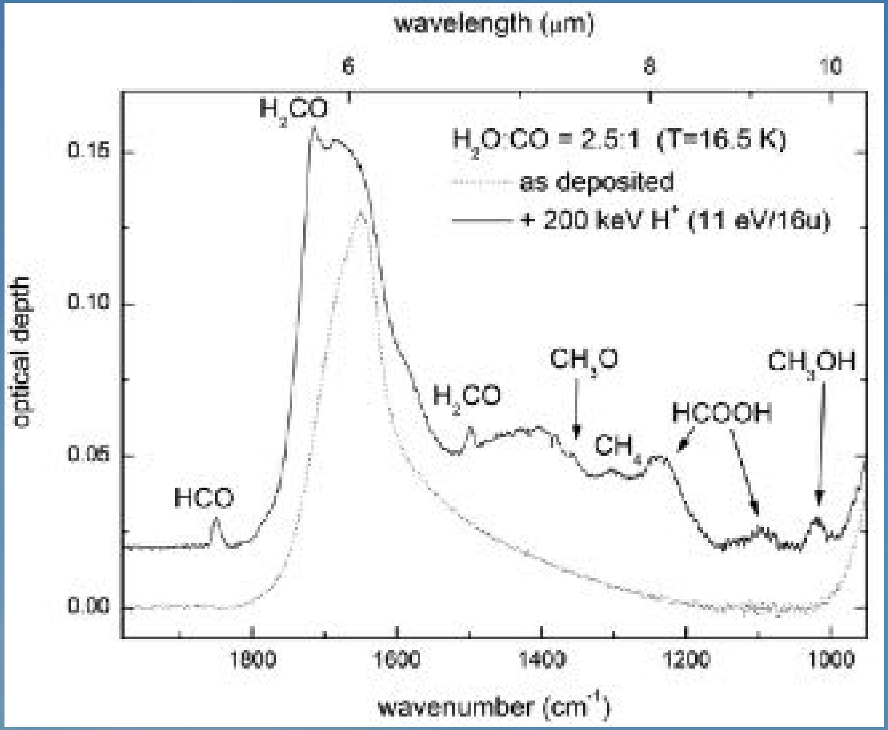

wavelength (μm)
5
10
15
20
H_2O:CO = 2.5:1 (T=16.5 K)
CO_2
+ 200 keV H^+
CO_2
optical depth
1.0
0.5
0.0
H_2O
as deposited
CO
H_2O
H_2O
optical depth
1.0
0.5
0.0
3500
3000
2500
2000
1500
1000
500
wavenumber (cm^{-1})

H_2O:CO

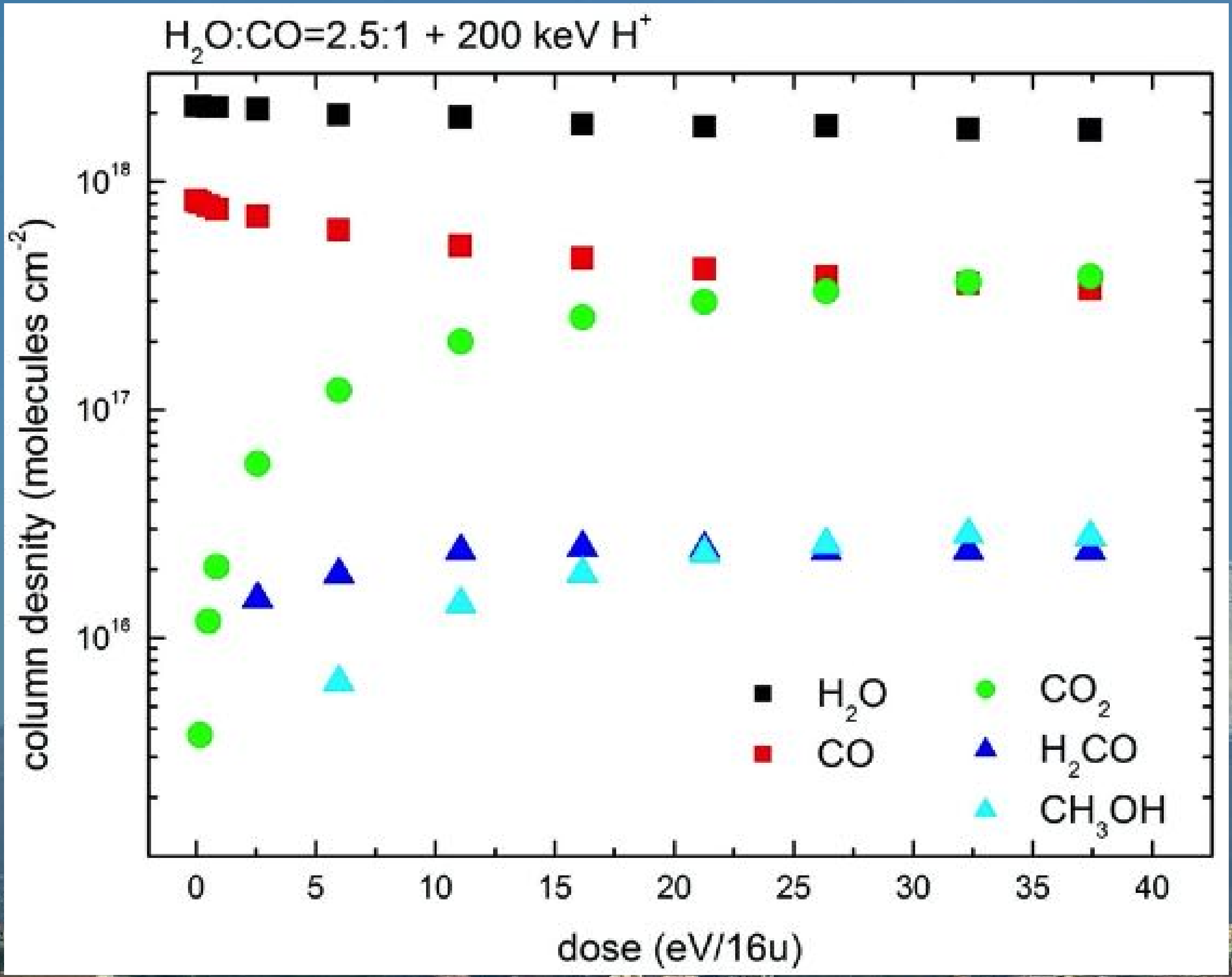

wavelength (μm)
5
10
15
20
H_2O:CO = 2.5:1 (T=16.5 K)
CO_2
+ 200 keV H^+
CO_2
optical depth
1.0
0.5
0.0
H_2O
as deposited
CO
H_2O
H_2O
optical depth
1.0
0.5
0.0
3500
3000
2500
2000
1500
1000
500
wavenumber (cm^{-1})

H_2O:CO

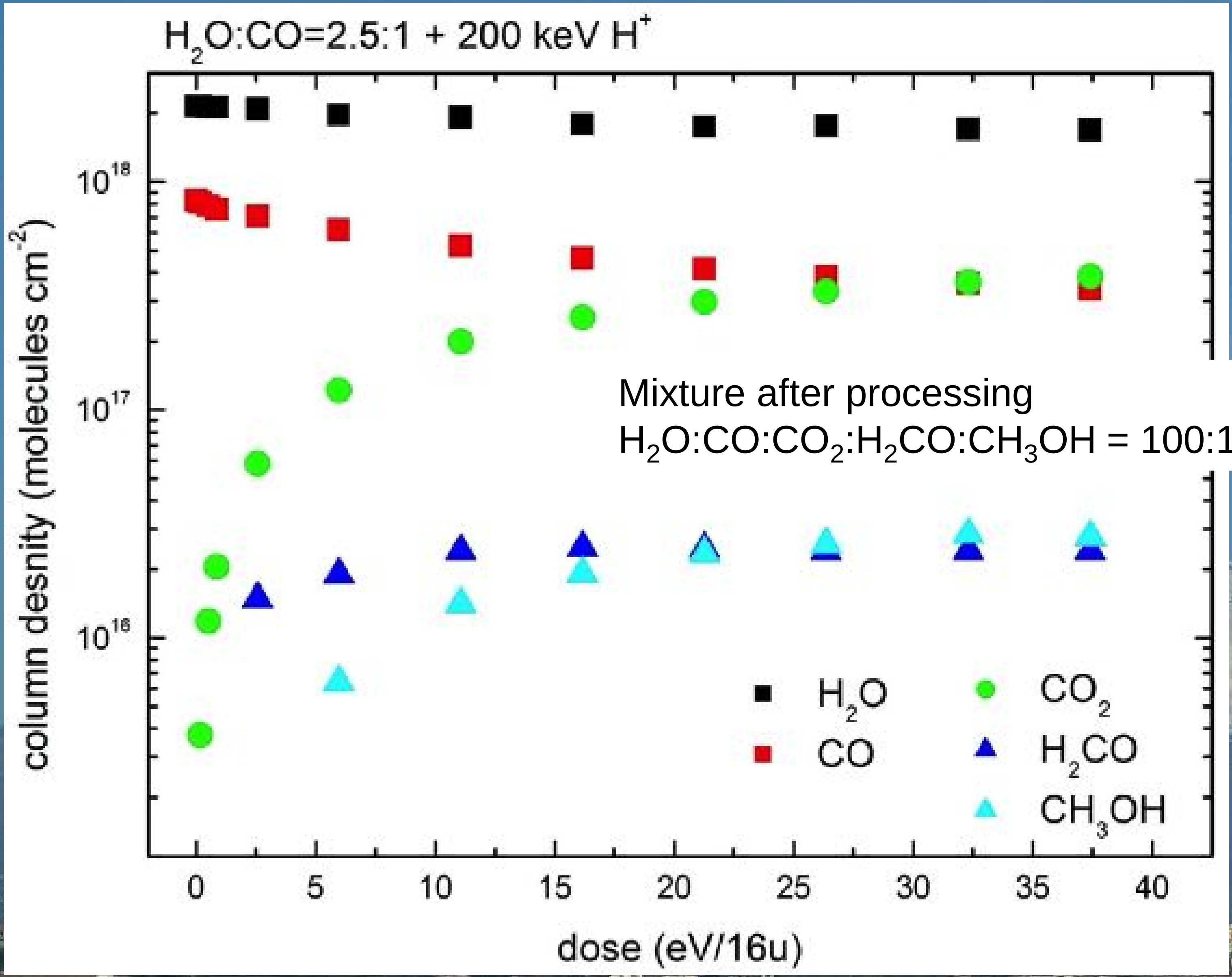

wavelength (μm)
5
10
15
20
H_2O:CO = 2.5:1 (T=16.5 K)
CO_2
+ 200 keV H^+
CO_2
optical depth
1.0
0.5
0.0
H_2O
as deposited
CO
H_2O
H_2O
optical depth
1.0
0.5
0.0
3500
3000
2500
2000
1500
1000
500
wavenumber (cm^{-1})


wavelength (μm)
6
8
10
H_2CO
H_2O:CO = 2.5:1 (T=16.5 K)
as deposited
+ 200 keV H^+ (11 eV/16u)
optical depth
0.15
0.10
0.05
0.00
H_2CO
CH_3O
CH_3OH
HCOOH
CH_4
HCO
1800
1600
1400
1200
1000
wavenumber (cm^{-1})

H_2O:CO

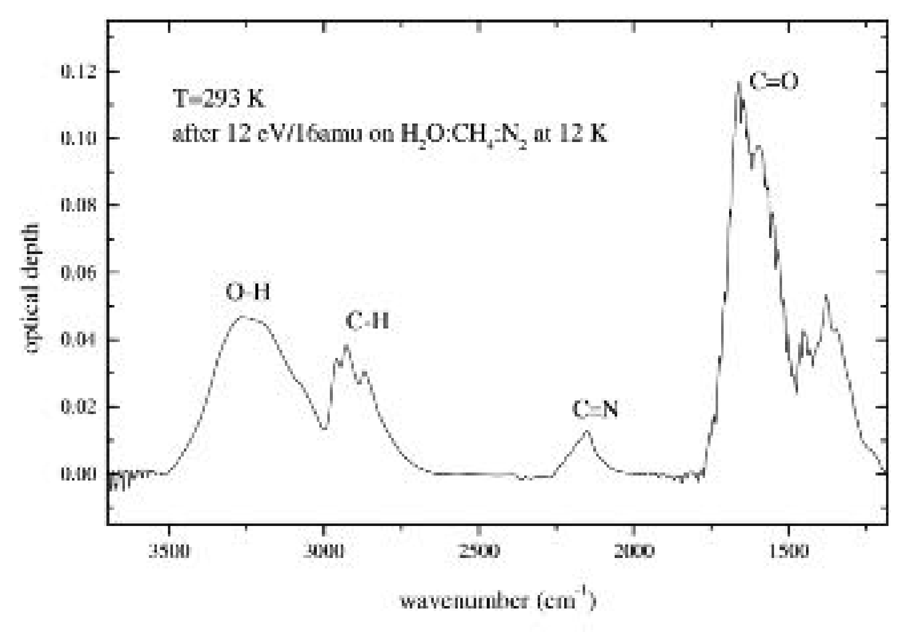

H_2O:CO=2.5:1 + 200 keV H^+
column desnity (molecules cm^{-2})
10^{18}
10^{17}
10^{16}
0
5
10
15
20
25
30
35
40
dose (eV/16u)
H_2O
CO
CO_2
H_2CO
CH_3OH

$H_2O:CO$



Mixture after processing
$H_2O:CO:CO_2:H_2CO:CH_3OH = 100:15:15:1.5:1.5$

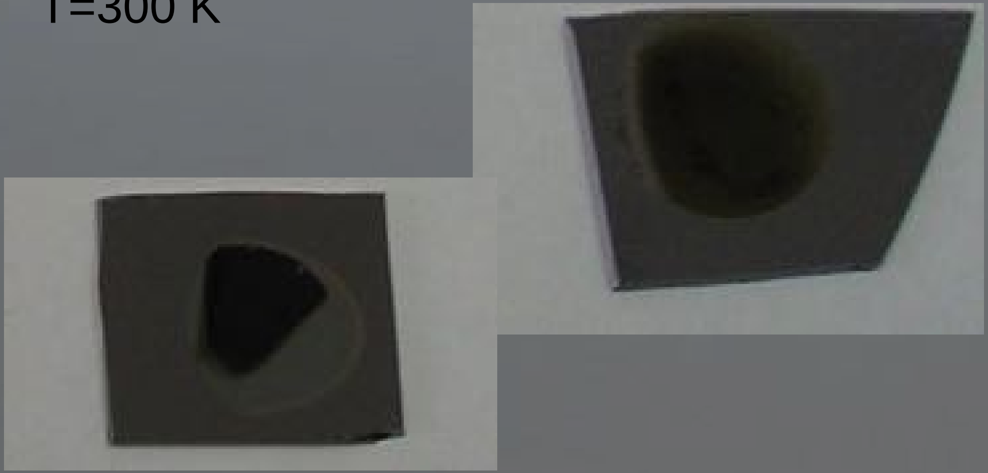
Organic refractory residue



Energetic processing modifies the chemical composition of the sample forming volatile species and a refractory residue

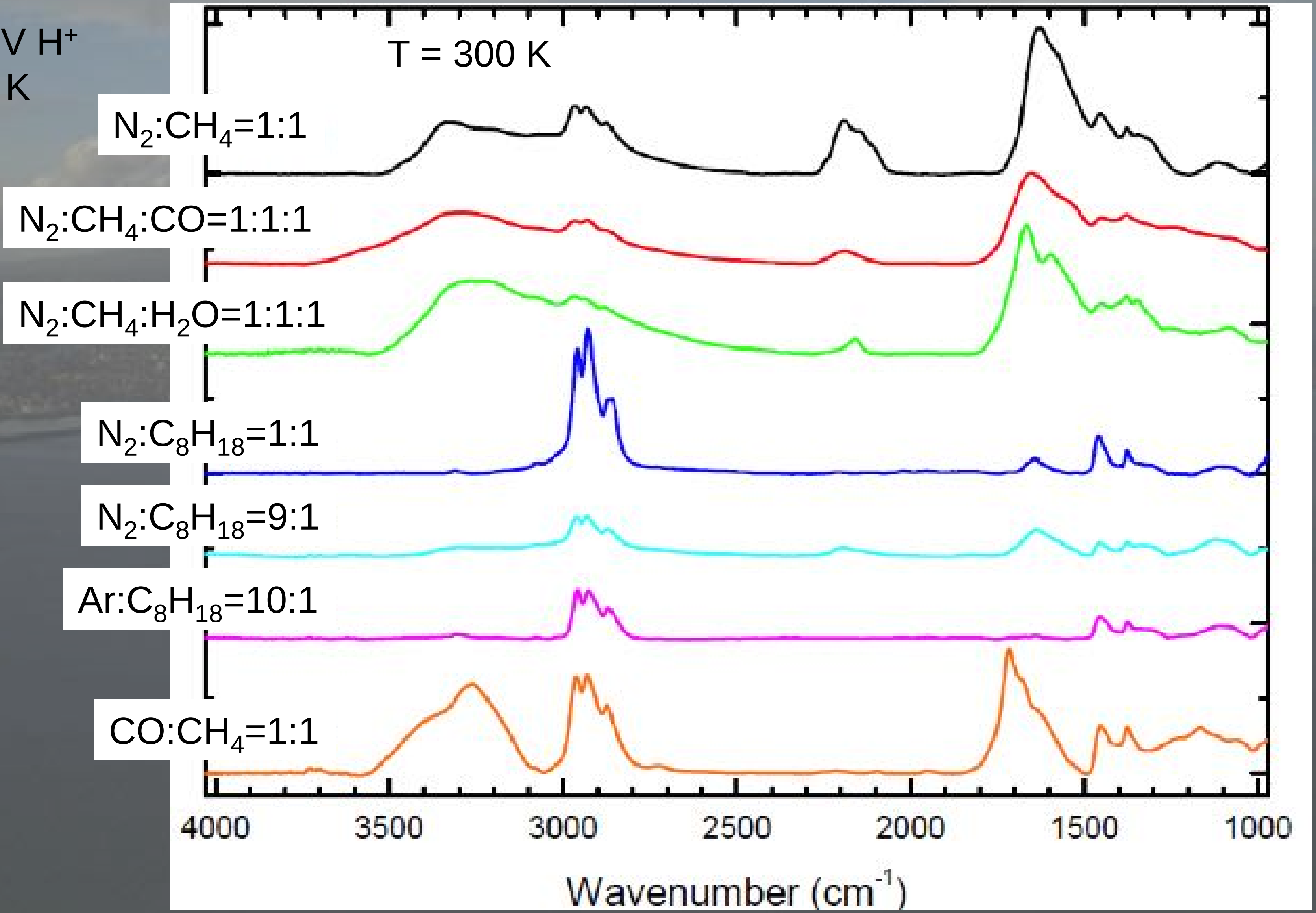
Strazzulla, Baratta, Palumbo 2001, Spectrochim. Acta A 57, 825
Palumbo, Ferini, Baratta, 2004, Ad Sp Res 33, 49
Baratta et al. 2015, Pl Sp Science 118, 211

T=300 K



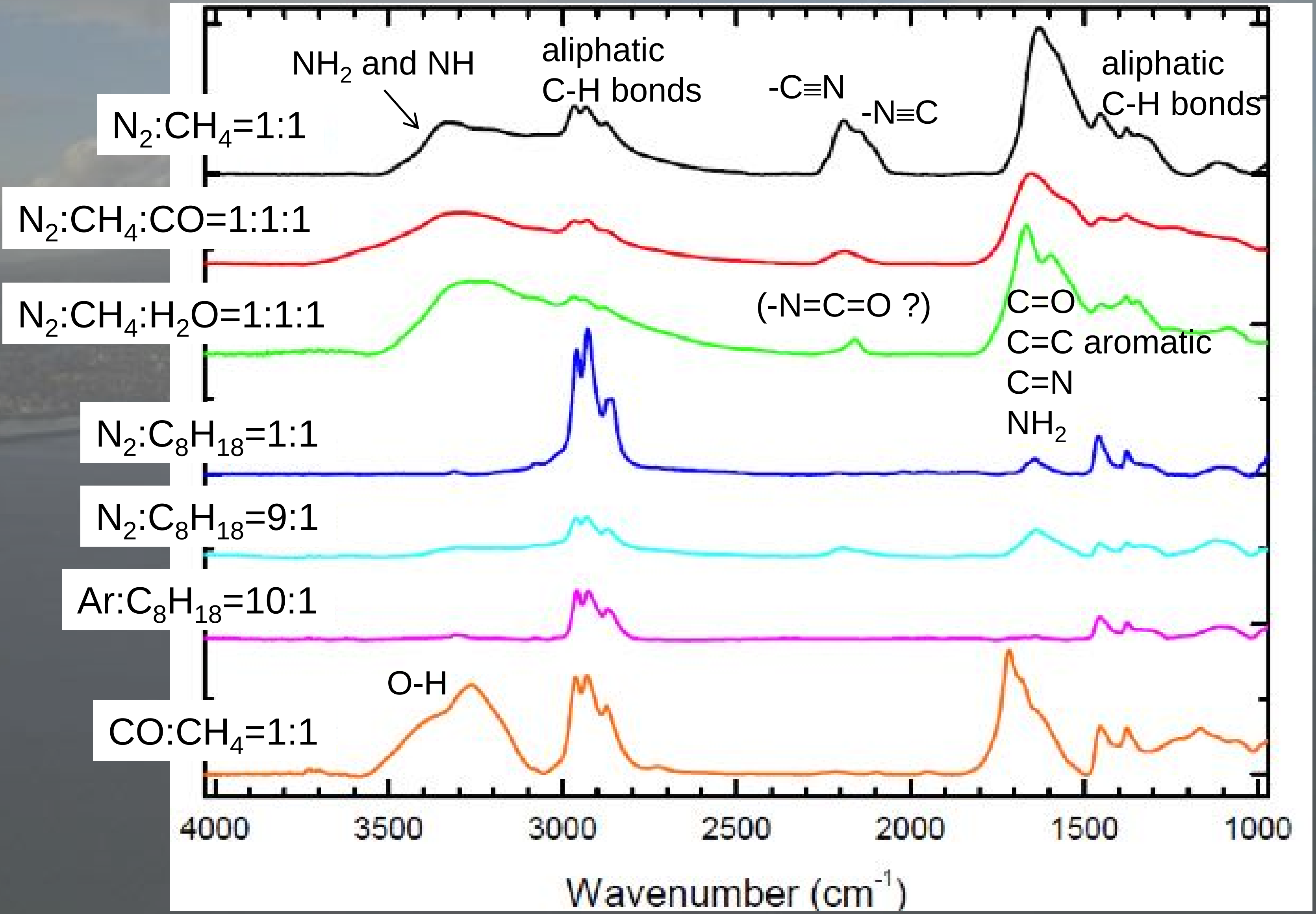
Complex molecules trapped in the residue

200 keV H^+
T = 17 K



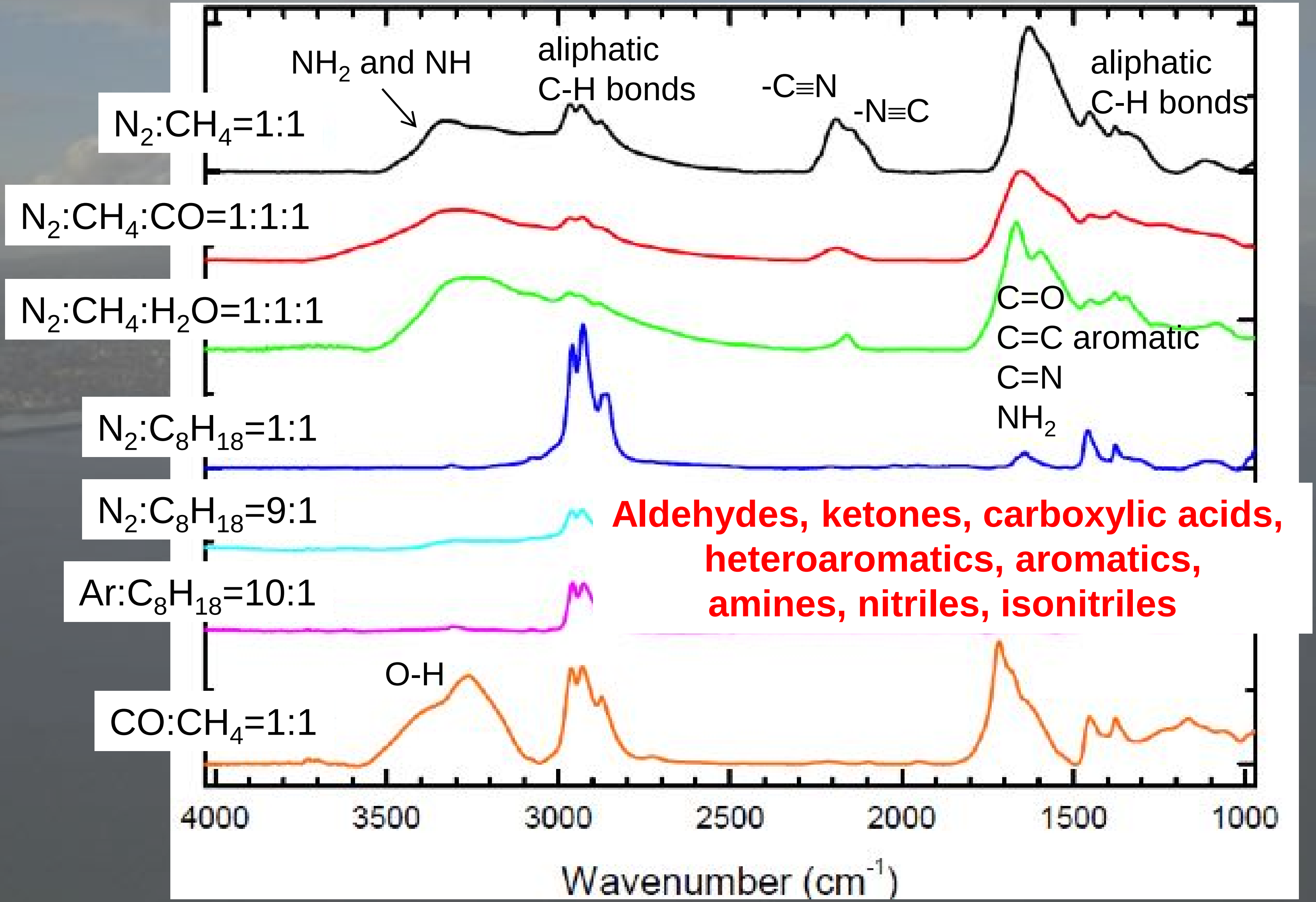
Accolla et al., 2018, A&A 620, A123

Complex molecules trapped in the residue



Accolla et al., 2018, A&A 620, A123

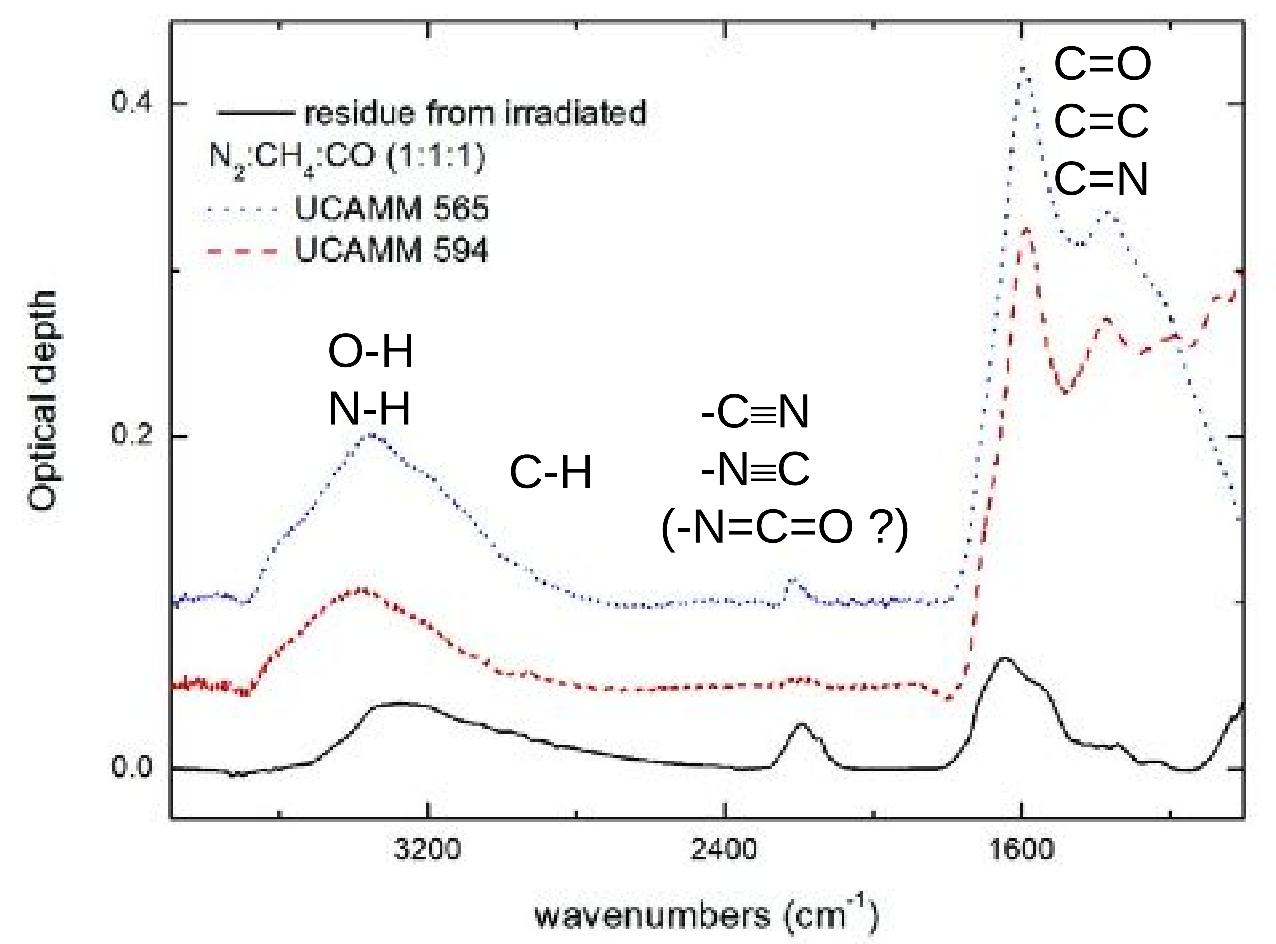
Complex molecules trapped in the residue



Aldehydes, ketones, carboxylic acids, heteroaromatics, aromatics, amines, nitriles, isonitriles

Accolla et al., 2018, A&A 620, A123

Ultra Carbonaceous Antarctic micrometeorites probing the Solar System beyond the nitrogen snow-line



Dartois et al. 2013, Icarus 224, 243; Baratta et al. 2015, Pl. Sp. Sci., 118, 211
Augé et al. 2016, A&A 592, A99; Dartois et al. 2018, A&A 609, A65

Do complex molecules survive in the interplanetary medium?

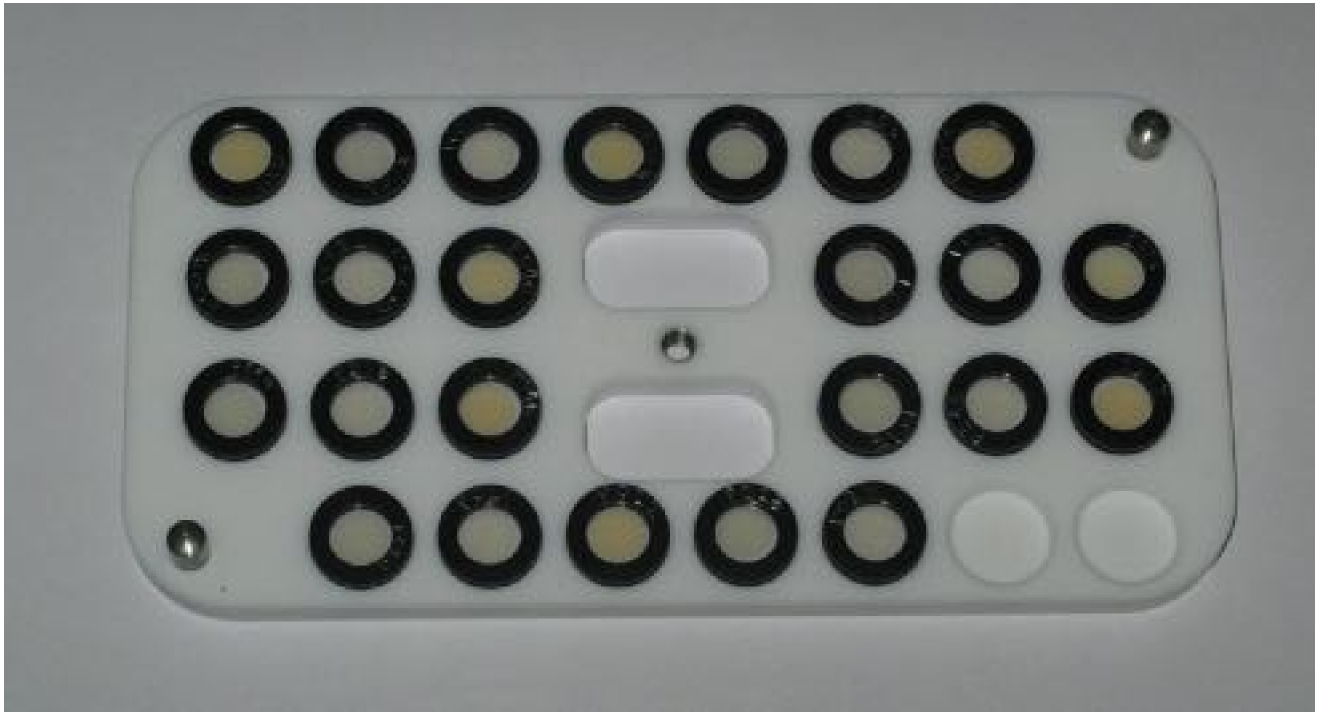
- ✓**Complex molecules formed after cosmic-ray bombardment of simple ices remain trapped in the refractory residue;**
- ✓**Nitriles are thought to be key intermediates to form amino acids providing one of the basic ingredients for life;**
- ✓**Infrared spectra of micrometeorites show the presence of astrobiologically relevant chemical bonds;**
- ✓**Formation of organic refractory material could have occurred in comets and TNOs and/or during the protostellar phase;**
- ✓**It has been suggested that comets, asteroids, and micrometeorites could have delivered organic material on the early Earth;**

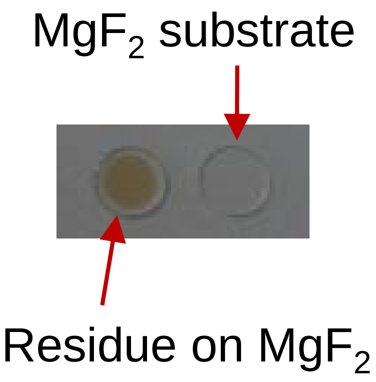
How long complex molecules trapped in the residue survive in the interplanetary medium exposed to UV solar photons?

Photochemistry on the Space Station

This is an international project related to ASTROBIOLOGY
This project is approved by ESA (European Space Agency)
The Italian participation is funded by ASI (Agenzia Spaziale Italiana)
The aim is to study the survival of organic material exposed to solar UV radiation
We prepared organic refractory residues that remained exposed for about 16 months

Photochemistry on the Space Station





MgF_2 transparent
110 nm < λ < 10 μm

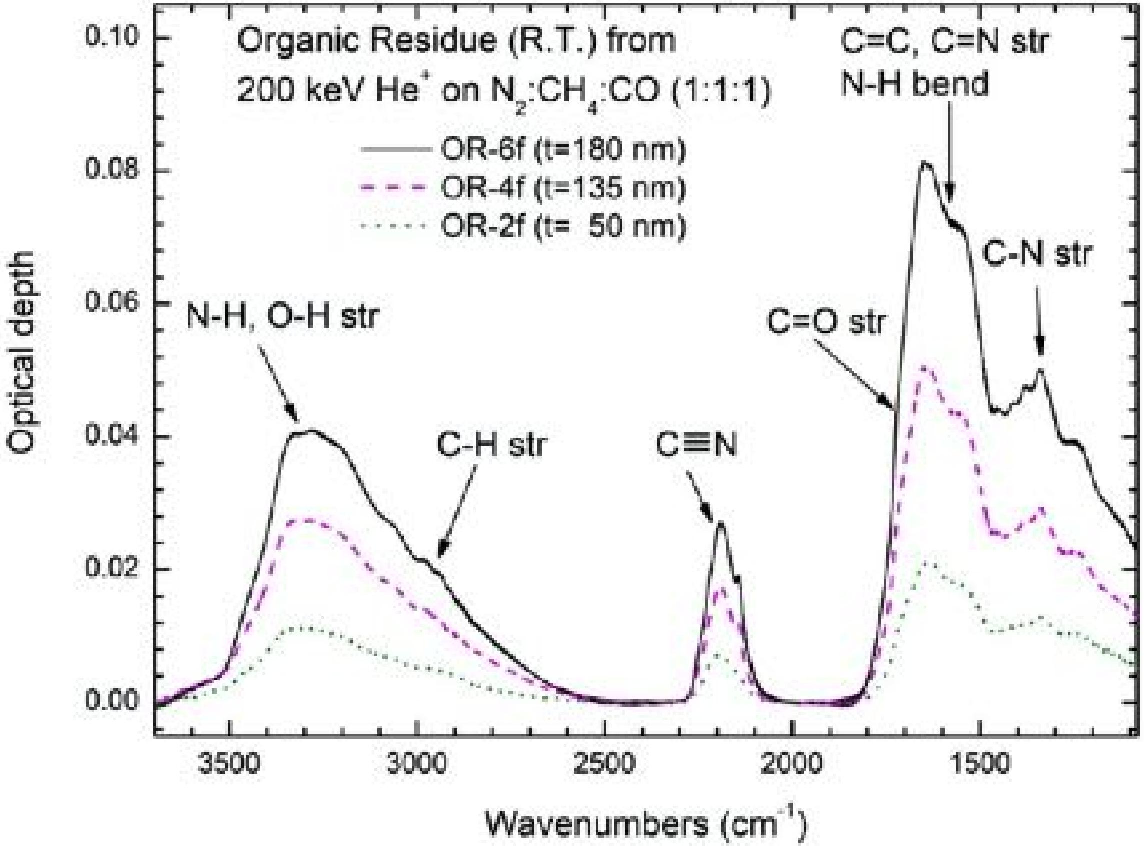
Residues after 200 keV He^+ on N_2:CH_4:CO at 16 K

3 different thicknesses of the residue
(180 nm; 135 nm; 50 nm)

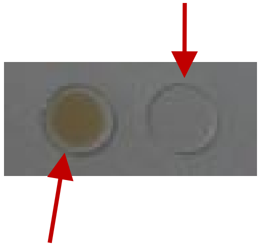
10 samples for each thickness

Baratta et al. 2015, Planet. Space Science 118, 211
Baratta et al. 2019, Astrobiology 19, 1018

Photochemistry on the Space Station



MgF$_2$ substrate



Residue on MgF$_2$

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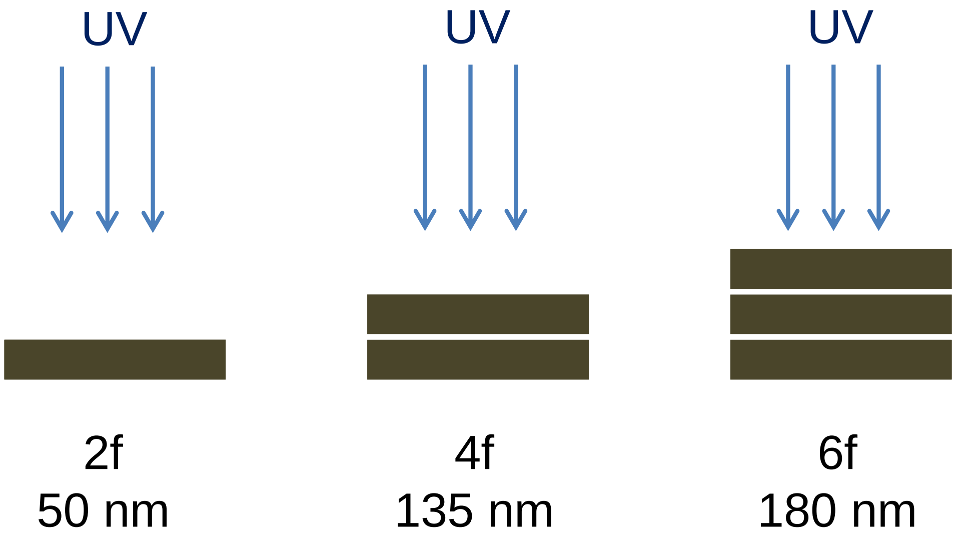
Photochemistry on the Space Station



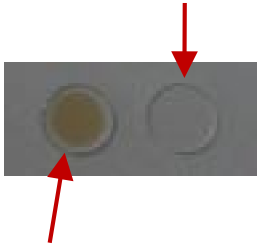
UV UV UV

2f
50 nm

4f
135 nm

6f
180 nm

MgF$_2$ substrate



Residue on MgF$_2$

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3 different thicknesses of the residue
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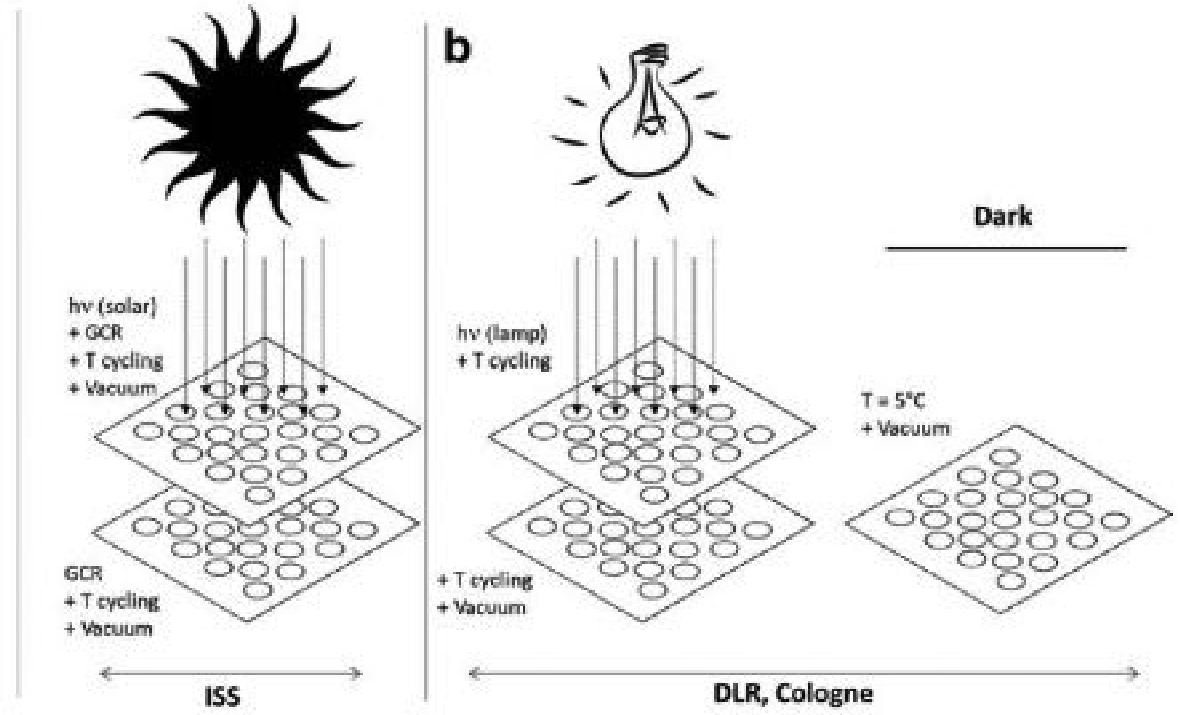
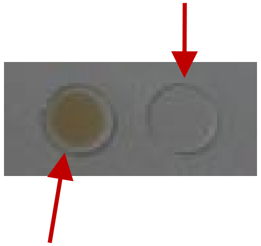
Baratta et al. 2015, Planet. Space Science, 118, 211
Baratta et al. 2019, Astrobiology 19, 1018

Photochemistry on the Space Station



MgF$_2$ substrate



Residue on MgF$_2$

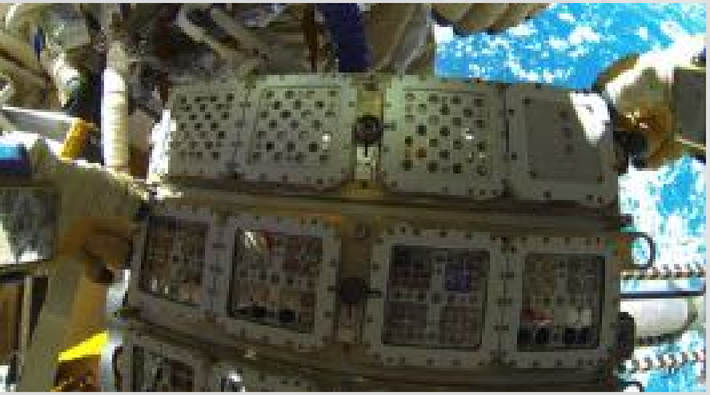
2 samples “exposed” on the ISS
2 samples “not exposed” on the ISS
2 samples exposed to UV lamp and temperature cycles (-20-60 ^{o}C) at DLR
2 samples suffered the same temperature cycles as those on ISS
2 samples stored at DLR at constant temperature (5 ^{o}C) under vacuum

Baratta et al. 2015, Planet. Space Science, 118, 211
Baratta et al. 2019, Astrobiology 19, 1018

Photochemistry on the Space Station

24 July 2014 launch of rocket "Soyuz-U" to transport cargo ship "Progress M-24M“ from Baikonur (Kazakhstan)

18 August 2014
Expose-R facility placed outside the ISS on the Universal Platform D of the Russian module Zvezda



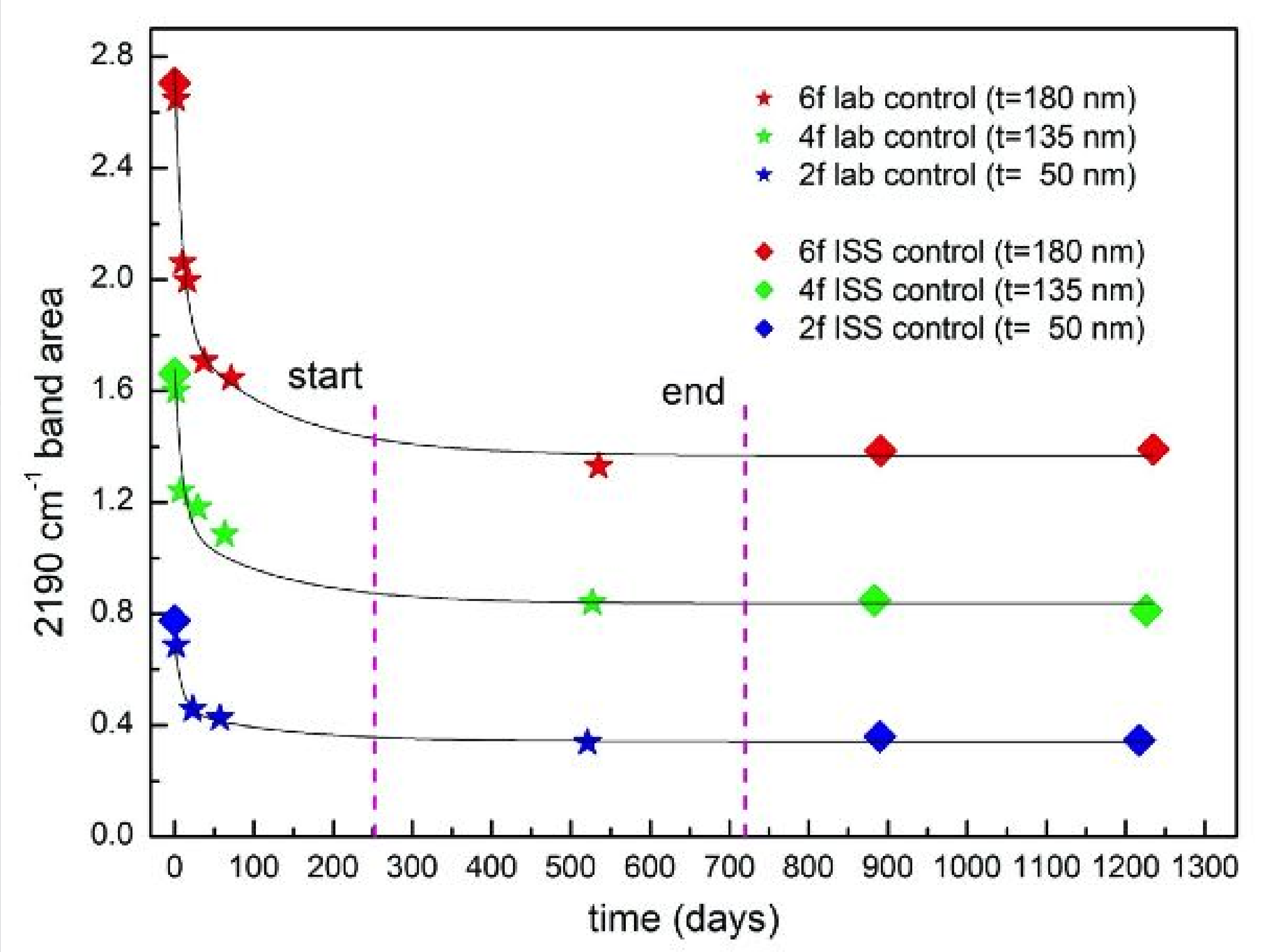
22 October 2014
Removal of protective cover

3 February 2016
Expose-R facility returned inside the ISS

2 March 2016 samples landed at Karaganda (Kazakhstan), on-board the Soyuz 44S return capsule

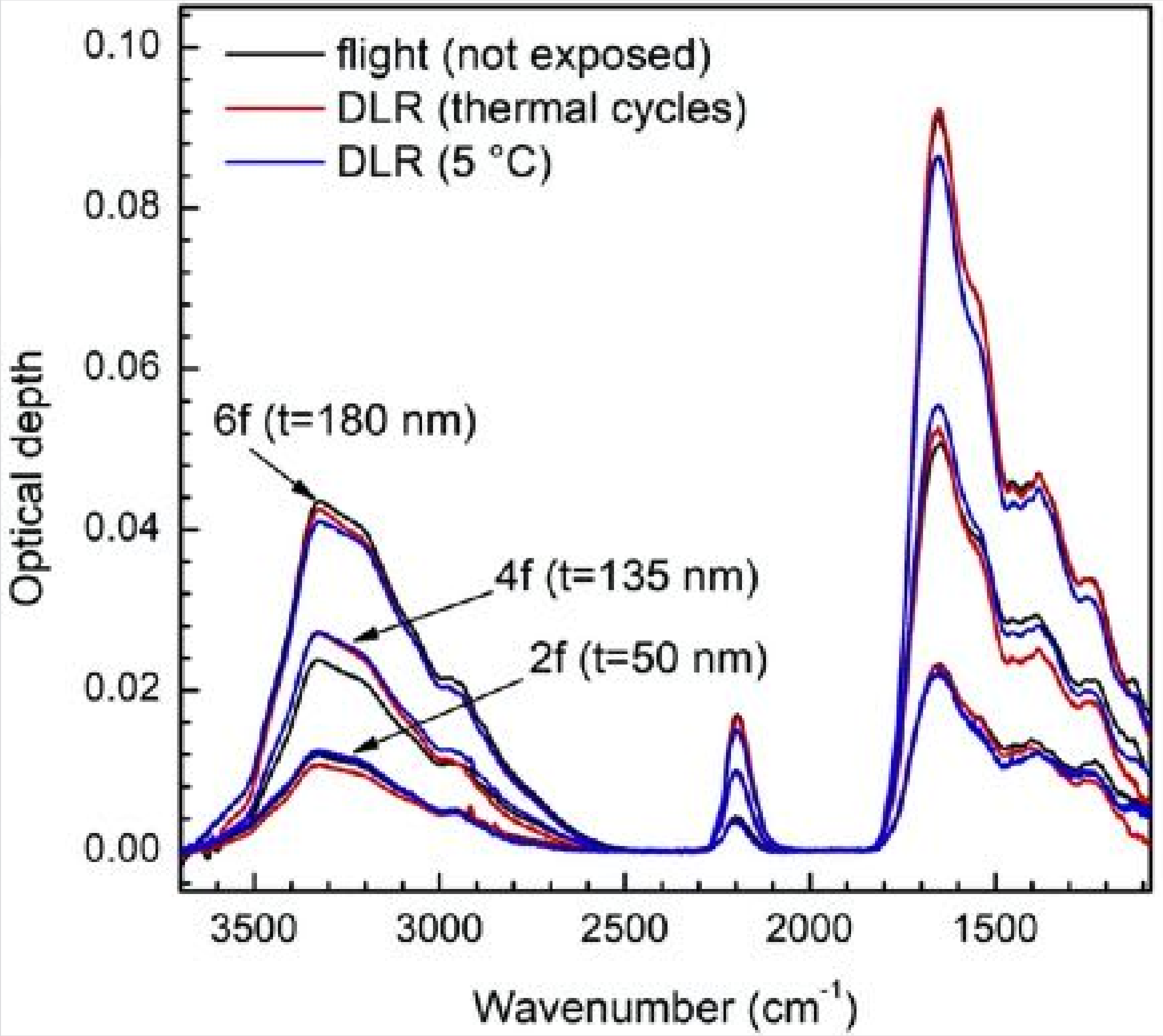
Exposure to space vacuum lasted **531 days**
Exposure to solar UV photons lasted **469 days**

Samples stability



Photochemistry on the Space Station

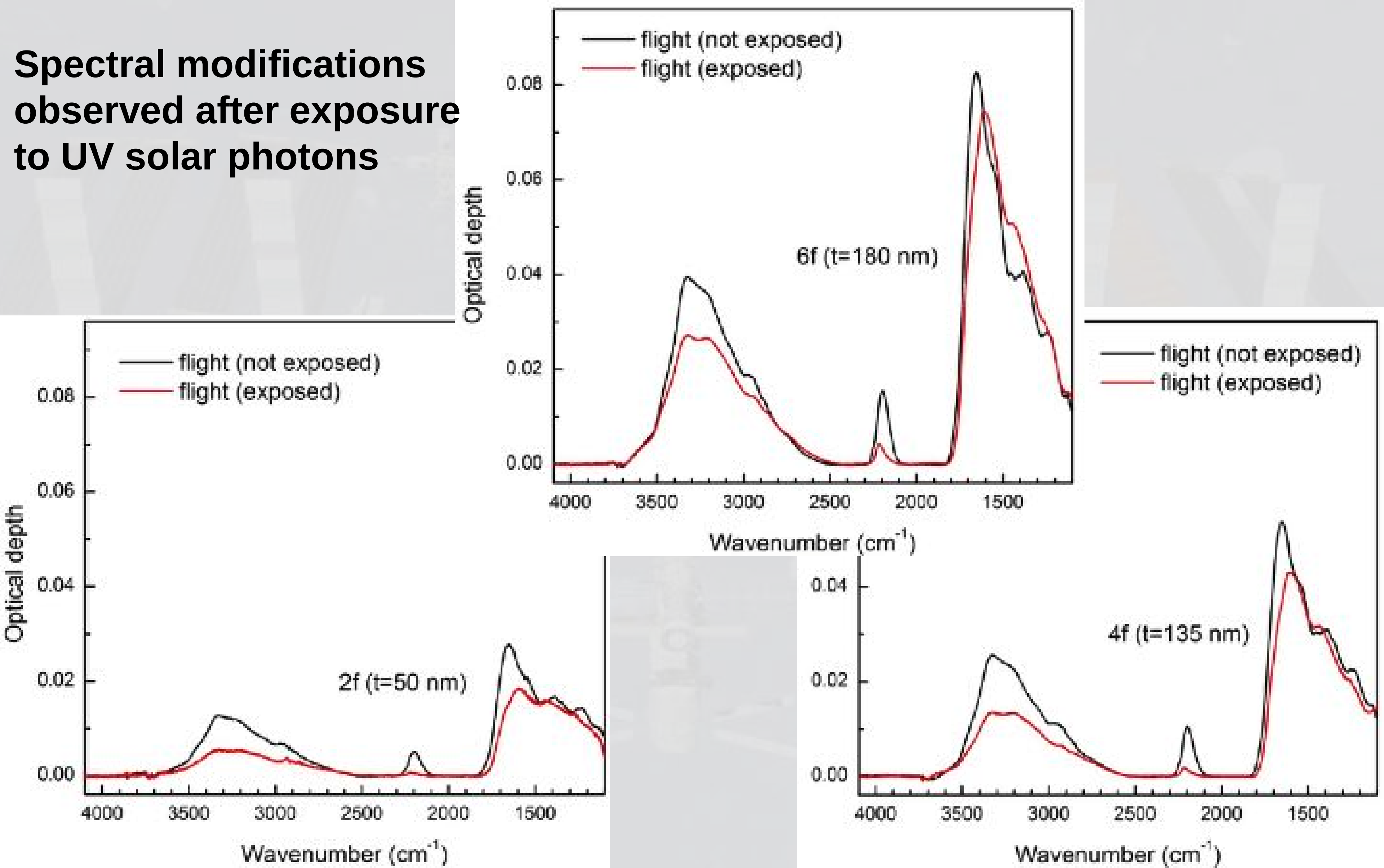
All control samples do not show any significant spectral modification



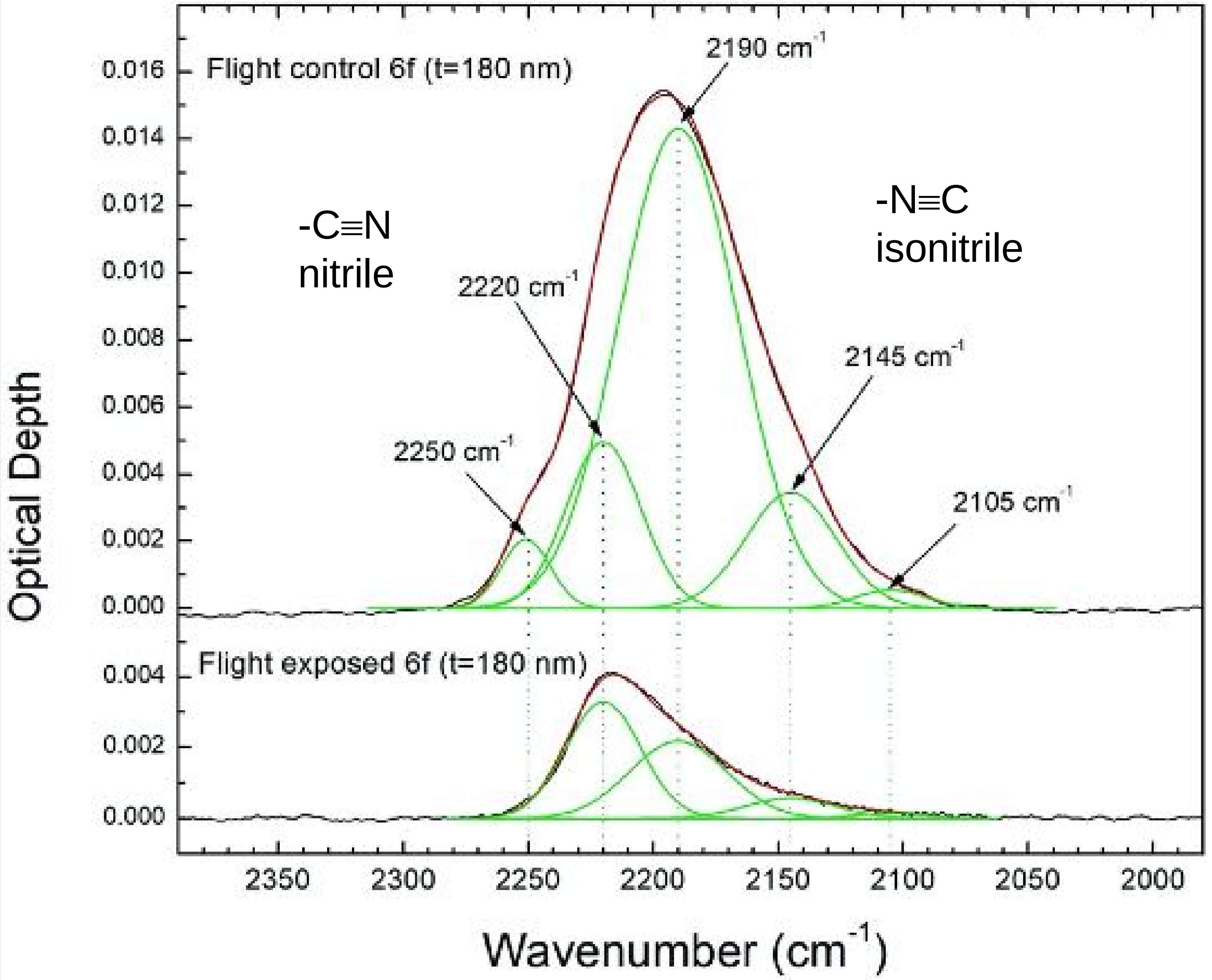
Baratta G., Accolla M., Chaput D., Cottin H., Palumbo, M.E., Strazzulla G. 2019, Astrobiology 19

Photochemistry on the Space Station

Spectral modifications observed after exposure to UV solar photons



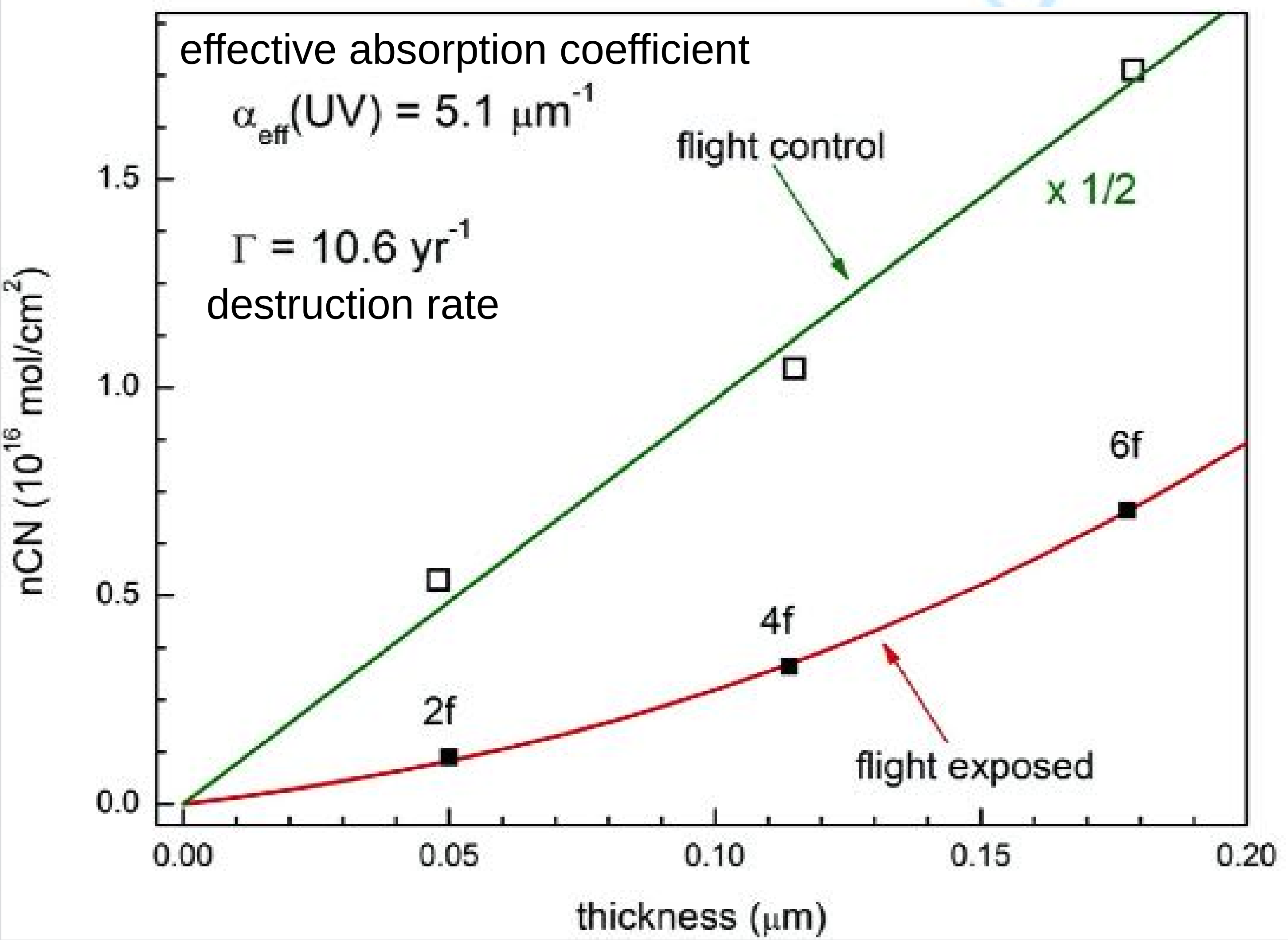
Photochemistry on the Space Station

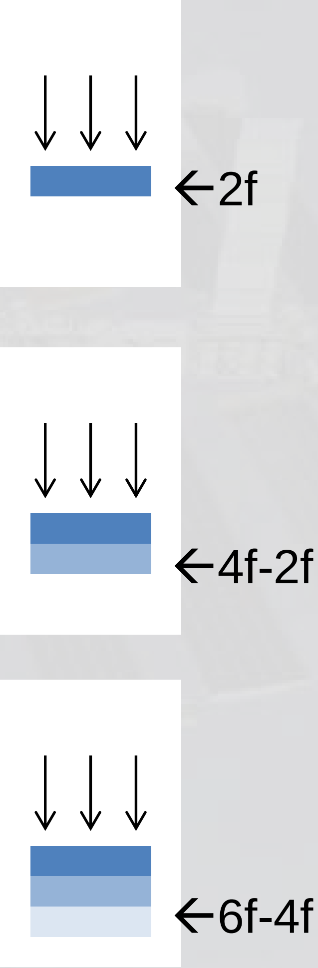


Baratta G., Accolla M., Chaput D., Cottin H., Palumbo, M.E., Strazzulla G. 2019, Astrobiology 19

Photochemistry on the Space Station

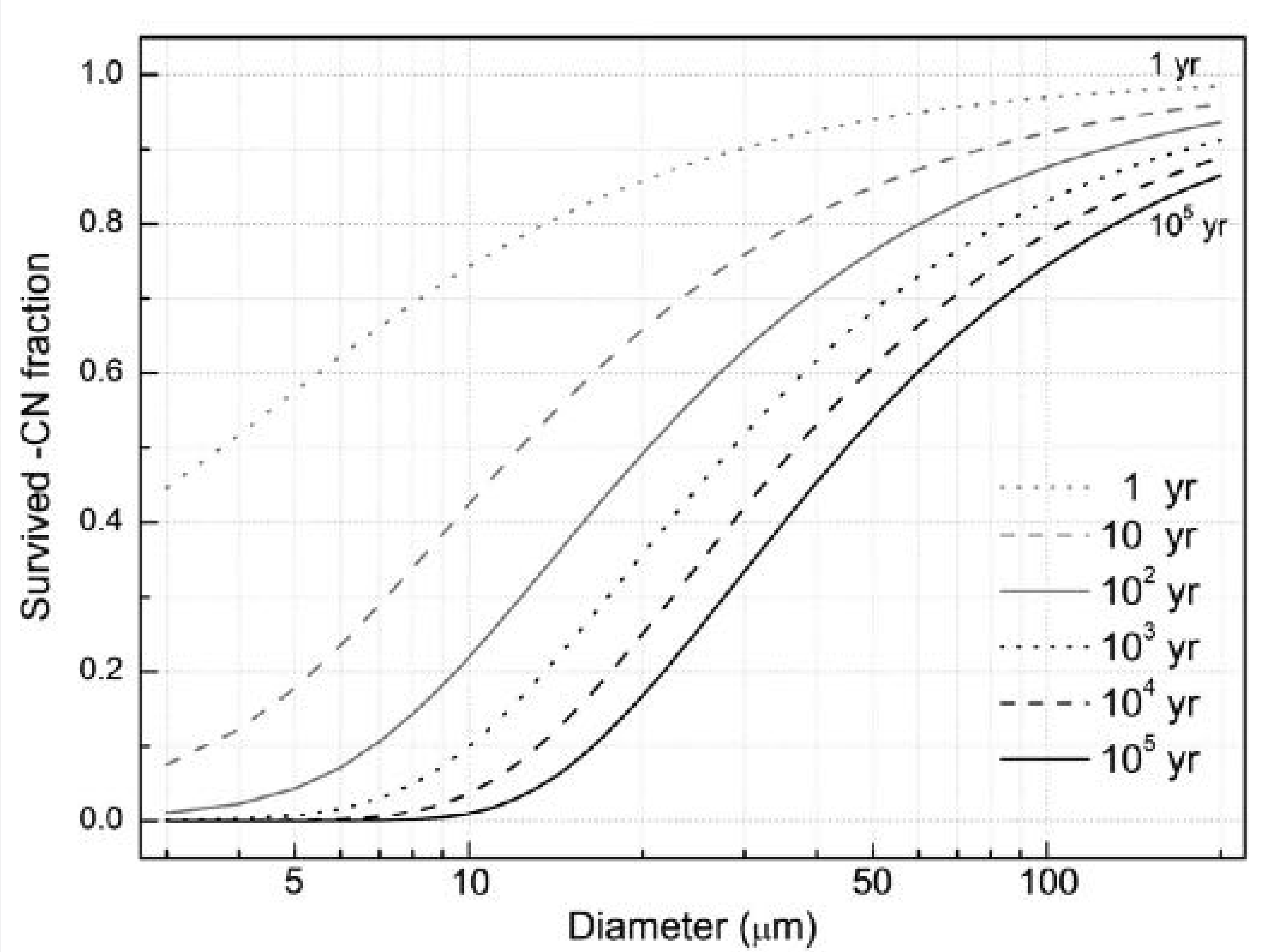
$$n_{CN} = \int_{x1}^{x2} dN_{CN} = N_{CN}^{0} \int_{x1}^{x2} e^{-\Gamma \cdot t \cdot e^{-\alpha(UV)_{eff} \cdot x}}\, dx$$





Baratta et al. 2019

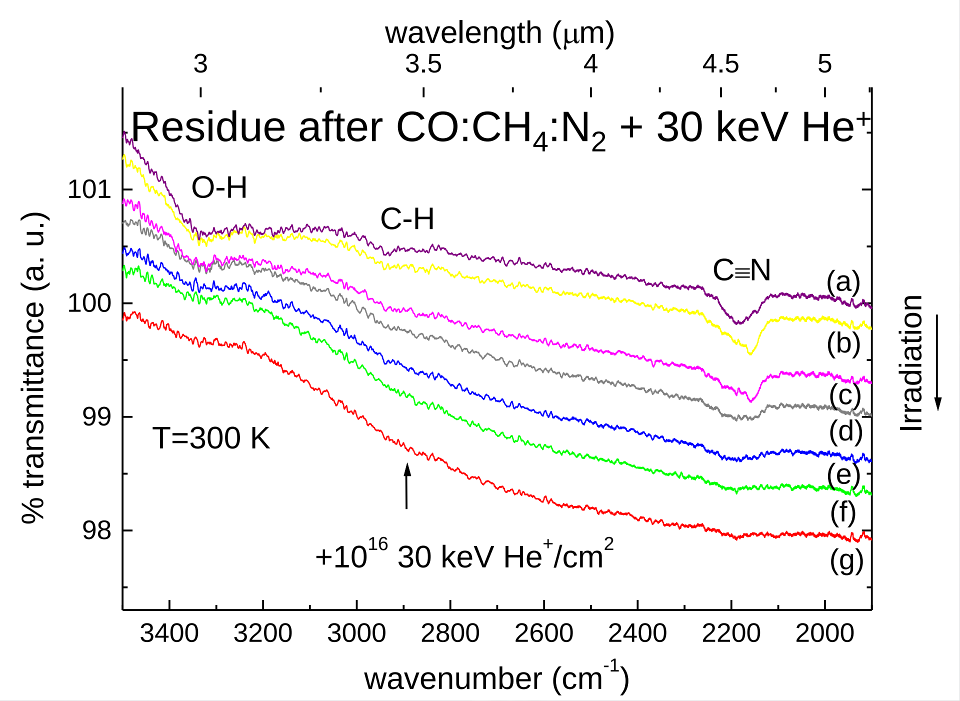
Photochemistry on the Space Station



Survival time of CN bonds in a particle made of 50% silicates and 50% organic matter placed at 1 au (Baratta et al. 2019)

Work in progress

Investigate the effects of solar wind ions and solar energetic particles (SEP)



Palumbo M.E., Ferini G., Baratta G.A., 2004, Adv. Space Res. 33, 49

Ferini G., Baratta G.A., Palumbo M.E., 2004, A&A 414, 757

Summary

Nitriles contained in Interplanetary Dust Particles as large as 20-30 µm can survive their journey in the interplanetary medium;

Nitriles contained in Interplanetary Dust Particles could have reached the prebiotic Earth providing one of the basic ingredient for life.

Acknowledgments

iALMA

REGIONE SICILIA

esa

cost
EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

MIUR PRIN

VAMDC
Virtual Atomic and Molecular Data Centre

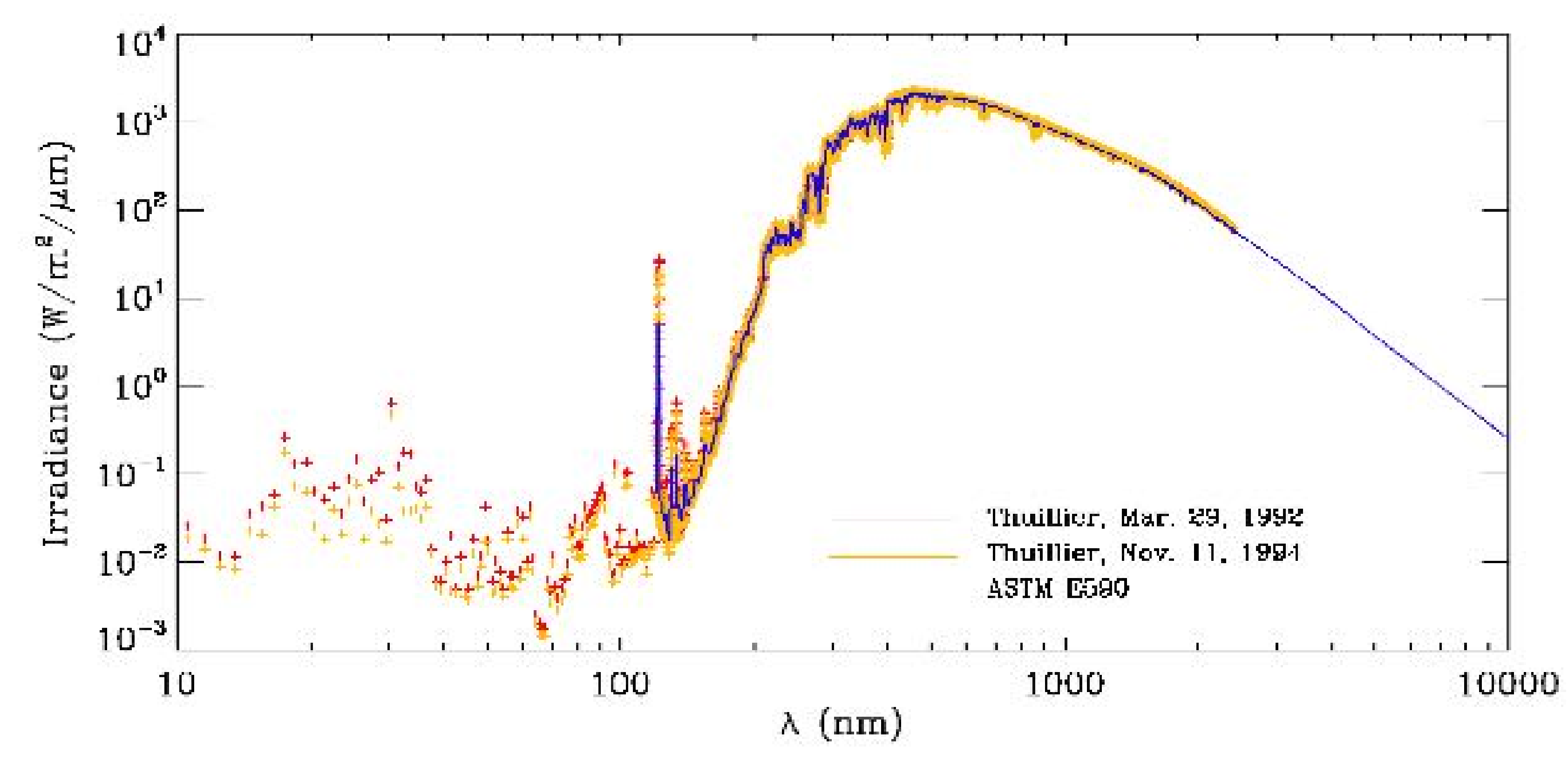
asi

LASSIE

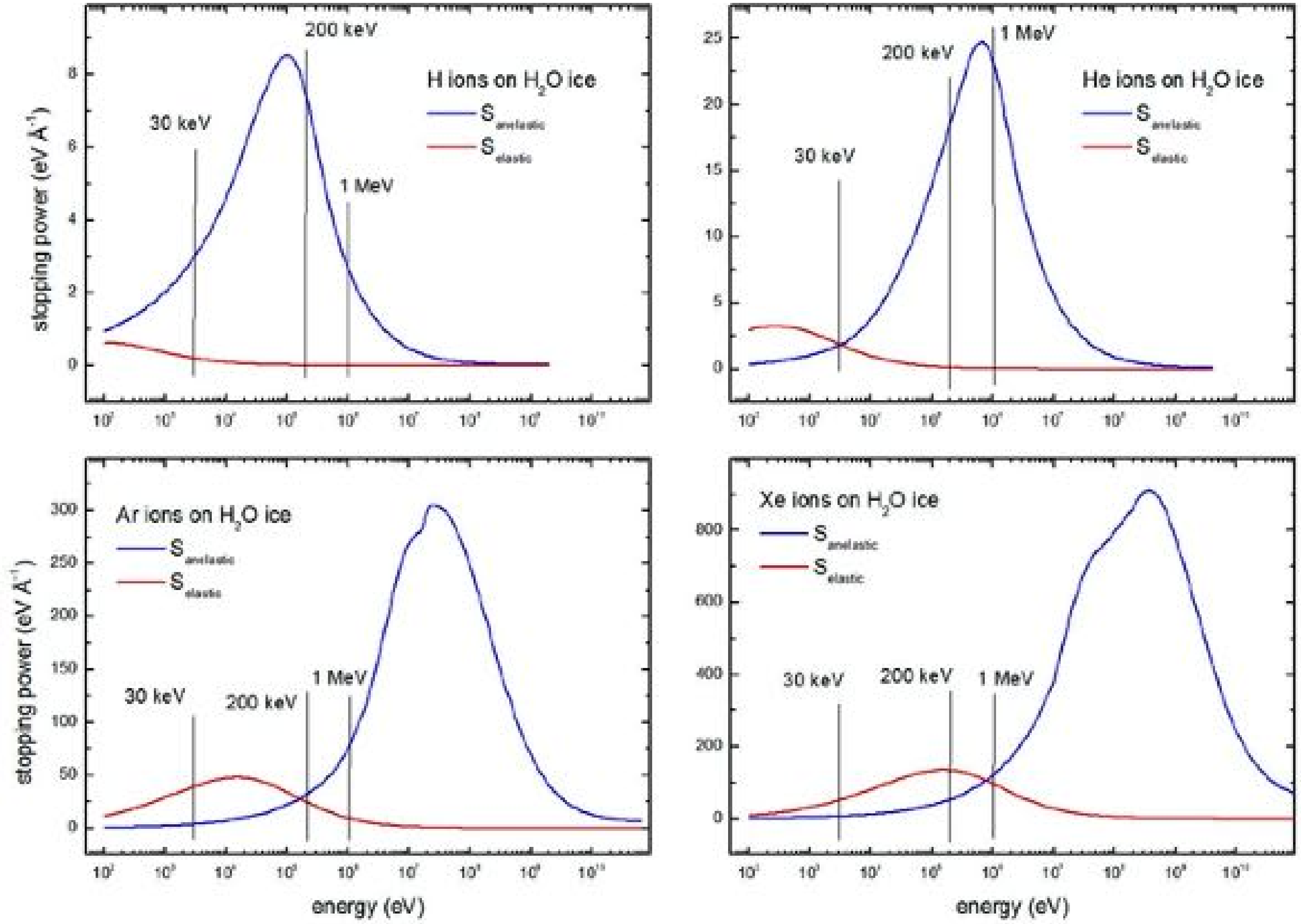
Vamos Seguro

INAF

Solar Irradiance



Interaction of ions with matter



J.F. Ziegler: SRIM (Stopping and Range of Ions in Matter); TRIM (TRansport of Ions in Matter)

Energetic processing in the Solar System

	Energy		Fluxes ($cm^{-2}\ s^{-1}$)
Solar Photons	2 eV	Visible	$2.0 \cdot 10^{17}$
	4 eV	NUV	$1.5 \cdot 10^{16}$
	6 eV	FUV	$3.0 \cdot 10^{13}$
Solar Wind (1 AU)			
	1keV	H^+	$3.0 \cdot 10^{8}$
	4keV	He^{2+}	
Solar Flares (1 AU)			
	>1 MeV	H^+	10^{10} ($cm^{-2}\ yr^{-1}$)
	>1 MeV	He^{2+}	
Galactic cosmic rays			
	>1 MeV	H^+	1-10
	>1 MeV	He^{2+}	

$$dN_{\mathrm{CN}} = N_{\mathrm{CN}}^{0} e^{-\phi_{\mathrm{UV}}^{\mathrm{eff}}(x) t \sigma(\mathrm{CN})} dx$$

$$\phi_{\mathrm{UV}}^{\mathrm{eff}}(x) = \phi_{\mathrm{UV}}^{\mathrm{eff}}(0) e^{-\alpha(\mathrm{UV})_{\mathrm{eff}} \cdot x}$$

$$n_{\mathrm{CN}} = \int_{x1}^{x2} dN_{\mathrm{CN}} = N_{\mathrm{CN}}^{0} \int_{x1}^{x2} e^{-\Gamma \cdot t \cdot e^{-\alpha(\mathrm{UV})_{eff} \cdot x}} dx$$

constant of the composite medium $\varepsilon_{\mathrm{av}} = \tilde{N}_{\mathrm{av}}^2$ (where $\tilde{N}$ is the complex index of refraction) is given by the relation

$$\varepsilon_{\mathrm{av}} = \varepsilon_{\mathrm{m}} \left[1 + \frac{3F_{\mathrm{v}} \dfrac{\epsilon - \epsilon_{\mathrm{m}}}{\epsilon + 2\epsilon_{\mathrm{m}}}}{1 - F_{\mathrm{v}} \dfrac{\epsilon - \epsilon_{\mathrm{m}}}{\varepsilon + 2\epsilon_{\mathrm{m}}}} \right] \tag{5}$$

where ε_{m} is the dielectric constant of the matrix, ϵ and F_{v} are the dielectric constant and the volume fraction of the inclusions, respectively. We assume that the organic material is the matrix and the inclusions are made of crystalline forsterite in Eq. 5. By

with $F\left(R_{\mathrm{sph}}, \tilde{N}_{\mathrm{av}}, r\right)$ the fraction of the incident radiation field transmitted within a sphere of radius R_{sph} down to a distance r from the center. For a sphere Eq. 4 can be modified in:

$$n_{\mathrm{CN}} = \int_0^{R_{\mathrm{sph}}} dN_{\mathrm{CN}} = V_{\mathrm{or}} N_{\mathrm{CN}}^0 4\pi \int_0^{R_{\mathrm{sph}}} e^{-\frac{1}{4}\Gamma \cdot t \cdot F\left(R_{\mathrm{sph}}, \tilde{N}_{\mathrm{av}}, r\right)}\, r^2 dr \tag{6}$$

fraction F_{CN} of survived $-\mathrm{C{\equiv}N}$ units, within a sphere of radius R_{sph} at 1 AU after a time t, is given by

$$F_{\mathrm{CN}} = \frac{n_{\mathrm{CN}}}{V_{\mathrm{or}} N^0_{\mathrm{CN}} \frac{4}{3}\pi R^3_{\mathrm{sph}}} = \frac{3}{R^3_{\mathrm{sph}}} \int_0^{R_{\mathrm{sph}}} e^{-\frac{1}{4}\Gamma \cdot t \cdot F\left(R_{\mathrm{sph}}, \tilde{N}_{\mathrm{av}}, r\right)}\, r^2 dr \tag{7}$$

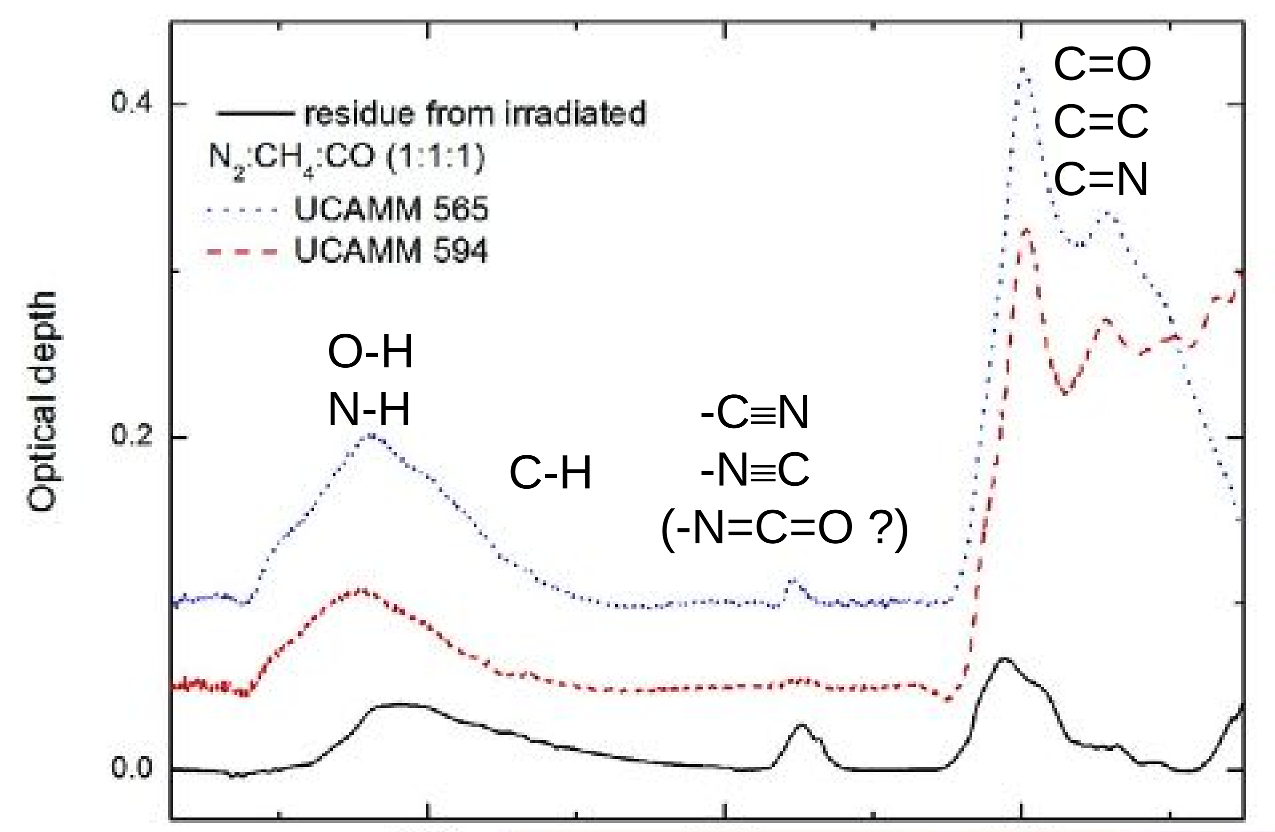
The time of flight of an IDP evolving inward (spiraling) under Poynting-Robertson (P-R) drag force from a heliocentric distance R down to 1 AU is given in the work of Pepin *et al.* (2000):

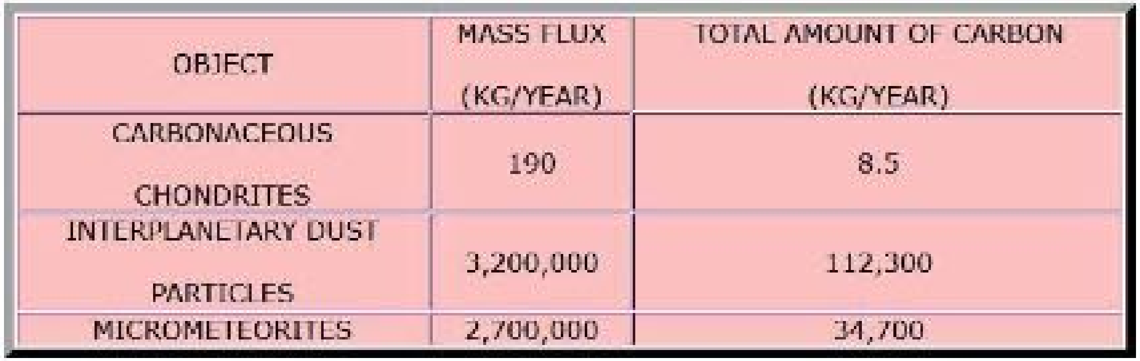
$$\tau = 1.1 \cdot 10^{14} \delta\rho (R/R_0)^2 \text{ (seconds)} \tag{8}$$

where δ and ρ are the diameter and the density of the particle in c.g.s units, respectively, R is the starting heliocentric distance, and R_0 is the distance that corresponds to 1 AU.

found that the fluence suffered by an IDP during its P-R drag from a heliocentric distance R down to 1 AU is the same as that the IDP would suffer at 1 AU in a χ times shorter period, where $\chi = 2 \cdot \ln(R/R_0) \cdot (R/R_0)^{-2}$. This relation can

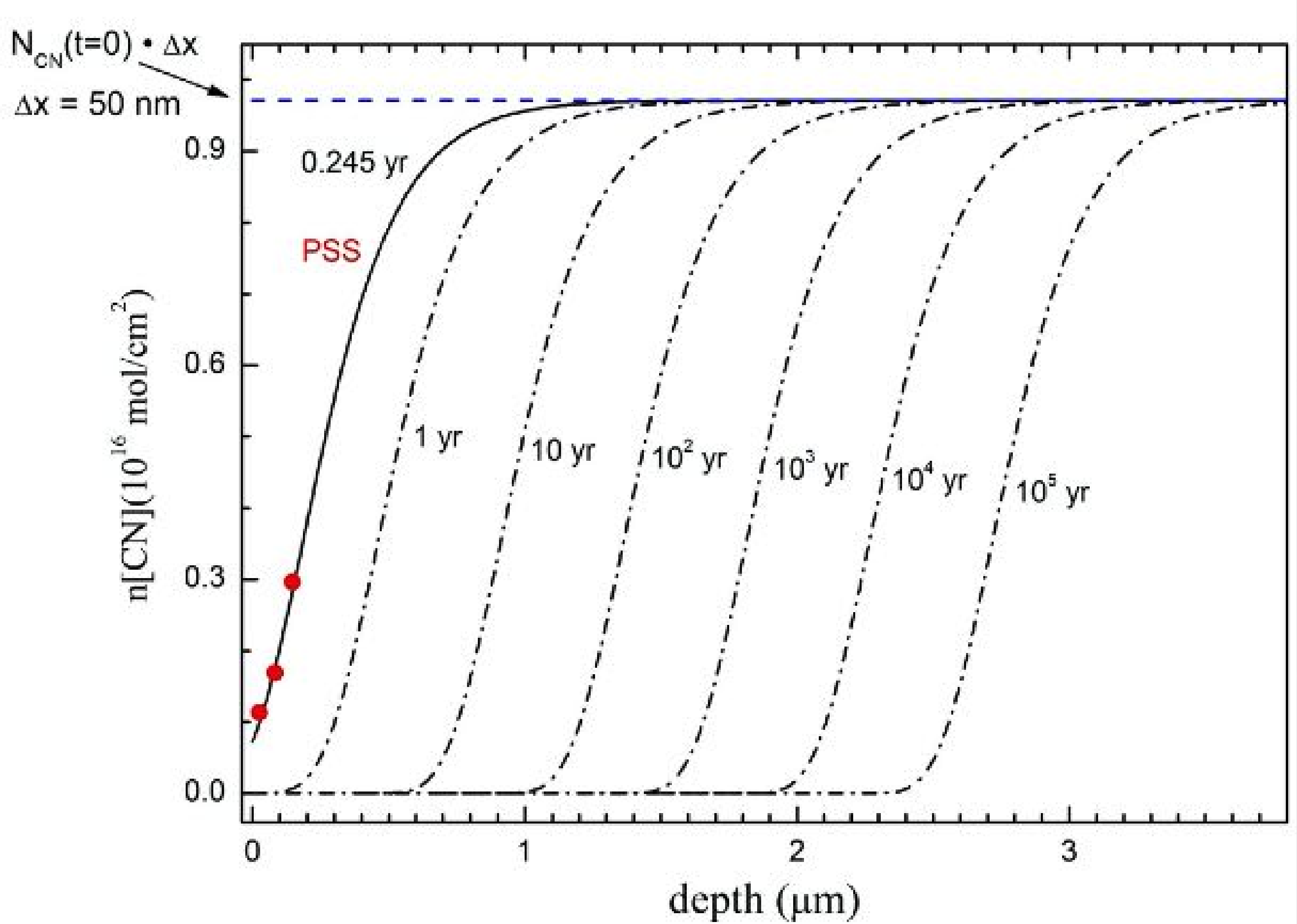
Ultra Carbonaceous Antarctic micrometeorites probing the Solar System beyond the nitrogen snow-line





OBJECT	MASS FLUX (KG/YEAR)	TOTAL AMOUNT OF CARBON (KG/YEAR)
CARBONACEOUS CHONDRITES	190	8.5
INTERPLANETARY DUST PARTICLES	3,200,000	112,300
MICROMETEORITES	2,700,000	34,700

Photochemistry on the Space Station



Baratta G., Accolla M., Chaput D., Cottin H., Palumbo, M.E., Strazzulla G. 2019, Astrobiology 19