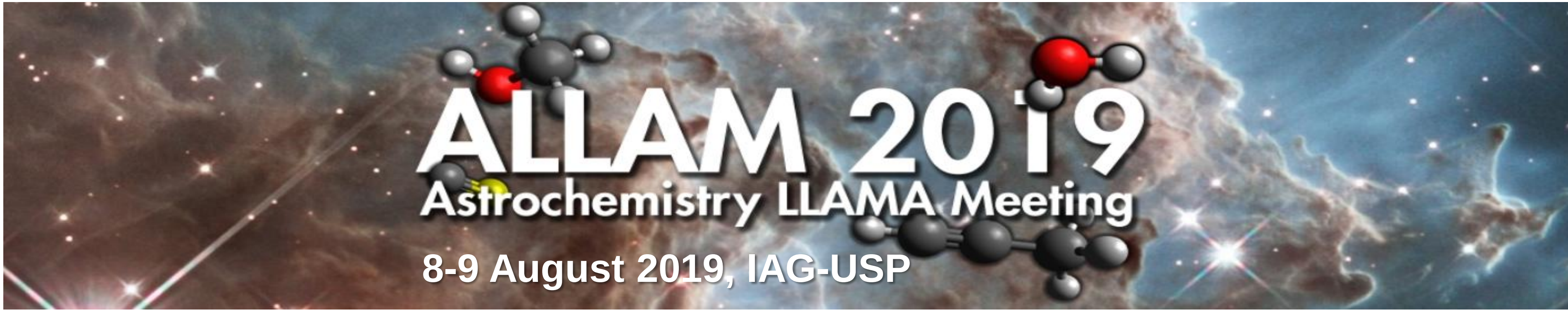


Liquid Astrophysical Ice:
A new state of matter?

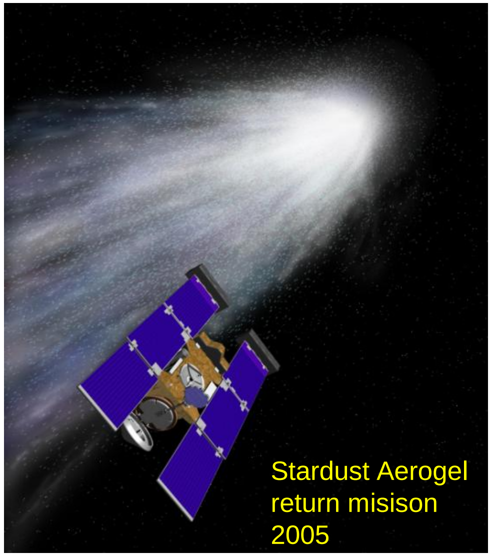
Prof. Dr. Sergio Pilling (UNIVAP)

UNIVERSIDADE DO VALE DO PARAIBA
São José dos Campos - SP

LASA
Laboratório de Astroquímica e Astrobiologia
da Universidade do Vale do Paraíba

P&D

Overview

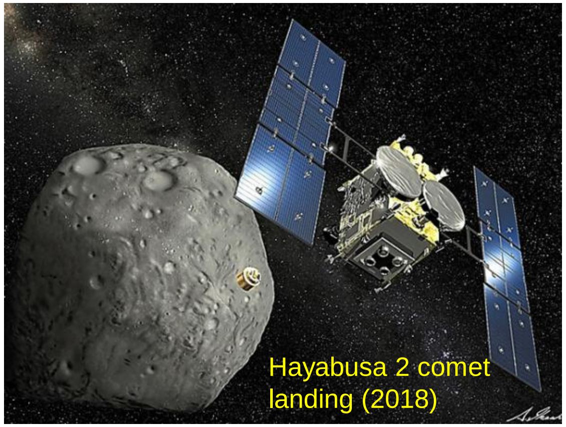


States of matter;

Astrophysical ices;

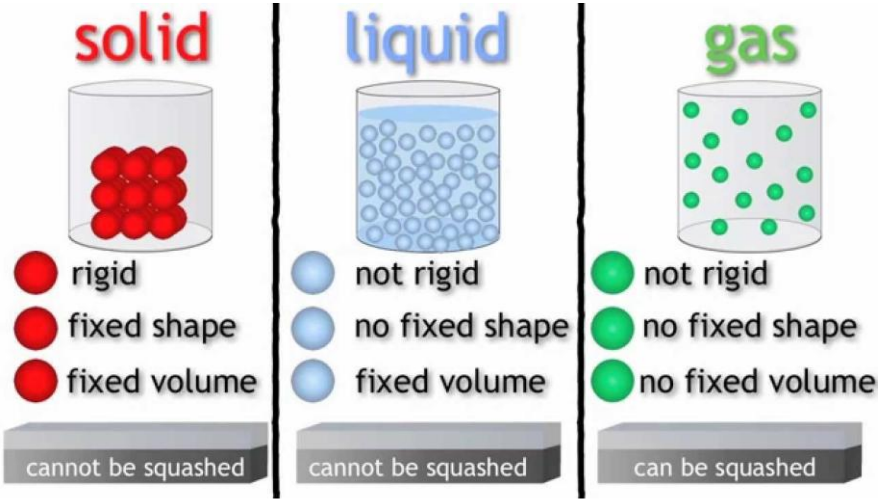
- What? Where? Detection? Formation?
- Simulations and experiments;
- Physicochemcial properties;
- Chemical processing;
- Chemical equilibrium at large fluences;

Liquid Astrophysical Ice!



States of Matter

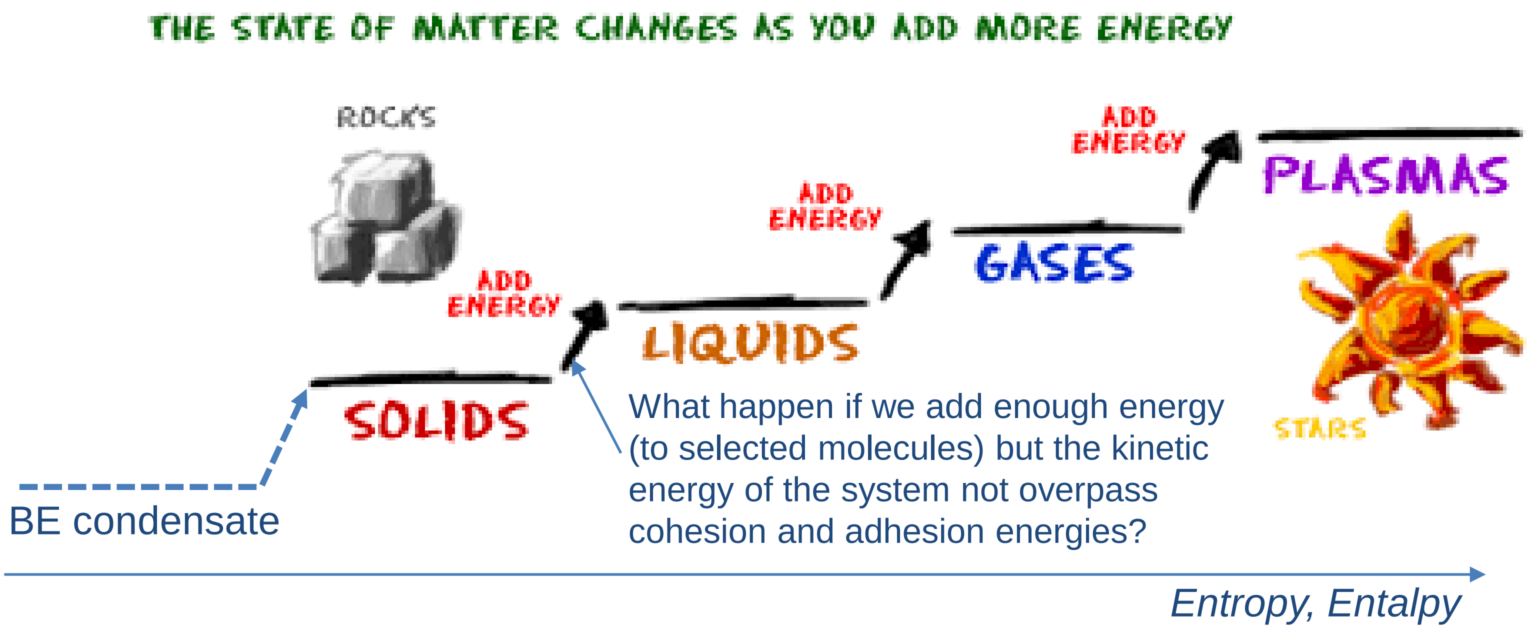
The different states are characterized by different physical and physicochemical properties such as cohesion, adhesion, evaporation, volatility, diffusion, viscosity, degree of ionization, degree of compaction ....



+ Plasma and Bose-Einstein condensate

Cohesion: The tendency of particles to attract their peers (affinity with their peers). Adhesion: Particle tendency to attract different particles (empathy with differences). Evaporation: When the kinetic energy of particles is greater than the energy that holds them together by cohesion and adhesion forces. More energetic particles evaporate first leaving the slower behind (emancipation). Diffusion: Movement of particles in the medium due to internal or external forces.

Energy → Changes in state of matter



More about solids.

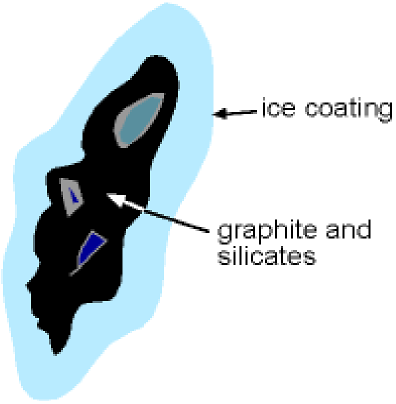
Two main categories: **crystalline** and **amorphous**. Crystalline solids are well ordered at the atomic level, and amorphous solids are disordered. There are **four different types** of crystalline solids: molecular solids, network solids, ionic solids, and metallic solids.

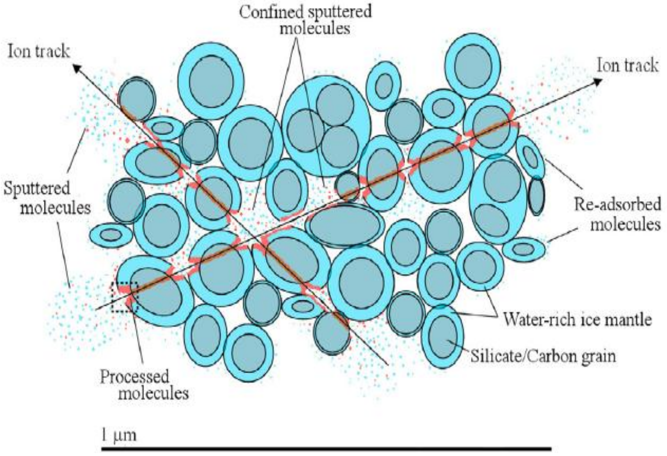
More about mixed states.

Gel (liquid dispersed in a solid; gelatin); **Sol** (Solid dispersed in a liquid; Ink), **Liquid foam (**gas dispersed in a liquid, soap foam, Chantilly); **Solid foam** (gas dispersed in a solid; sponge rock), **Liquid aerosol** (liquid dispersed in a gas; fog, clouds), **Solid aerosol** (solid dispersed in a gas, smoke). **Glass** (Amorphous solid or super cooled liquid with “high viscosity”), …….

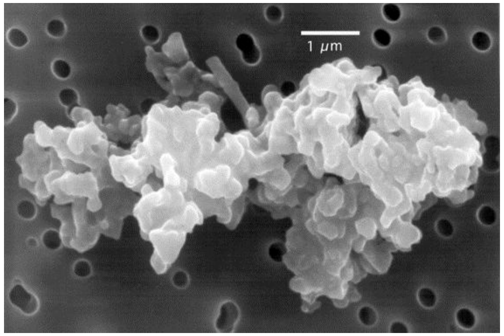
Astrophysical ices (What? Where?)

Amorphous solids (compact or not) with low temperatures <180 K
Present in space (or very low pressure environments – labs).
Sometimes they may be found in crystalline phase (due to annealing processes). Usually is a water-rich ice.





IMPORTANT: Not to be confused with astrophysical dust grain: tiny solids (sub microm and centim) rich in oxides, silicates, carbonaceous species such as amorphous carbon, graphite which may have temperatures from 3K to 5000K.
In many situations astrophysical grains are covered with ice (especially water) when temperature allows volatile molecules to condense on them.



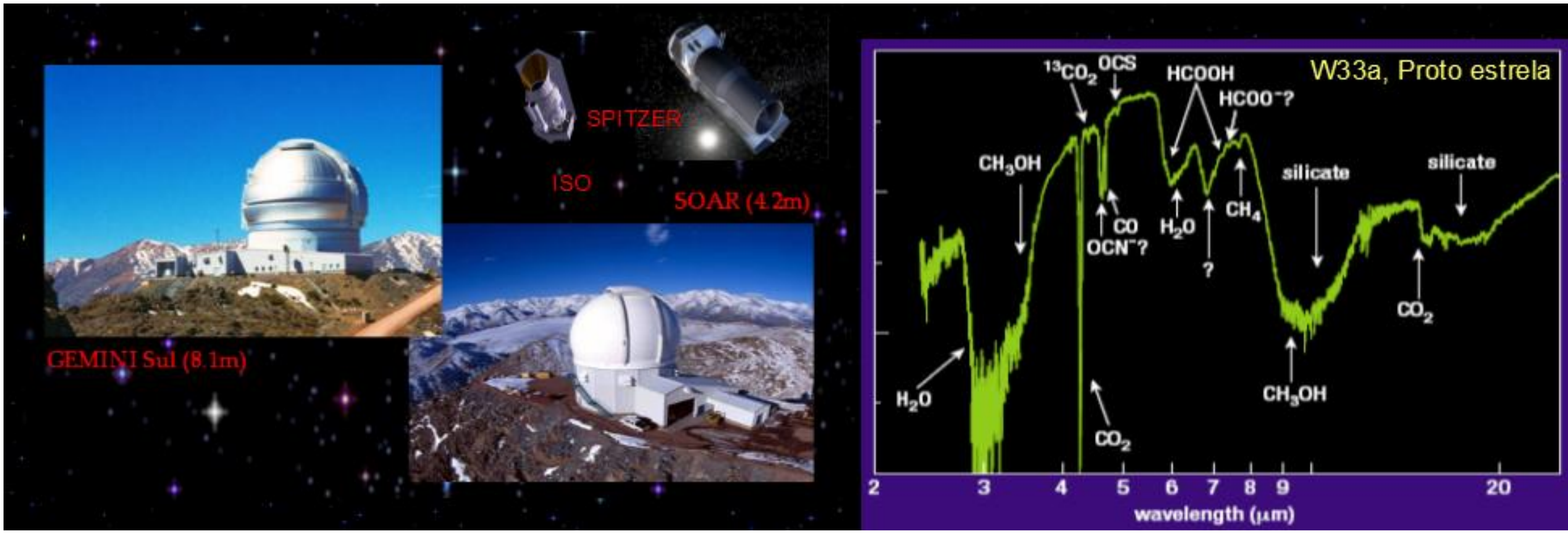
Astrophysical ices (What? Where?)

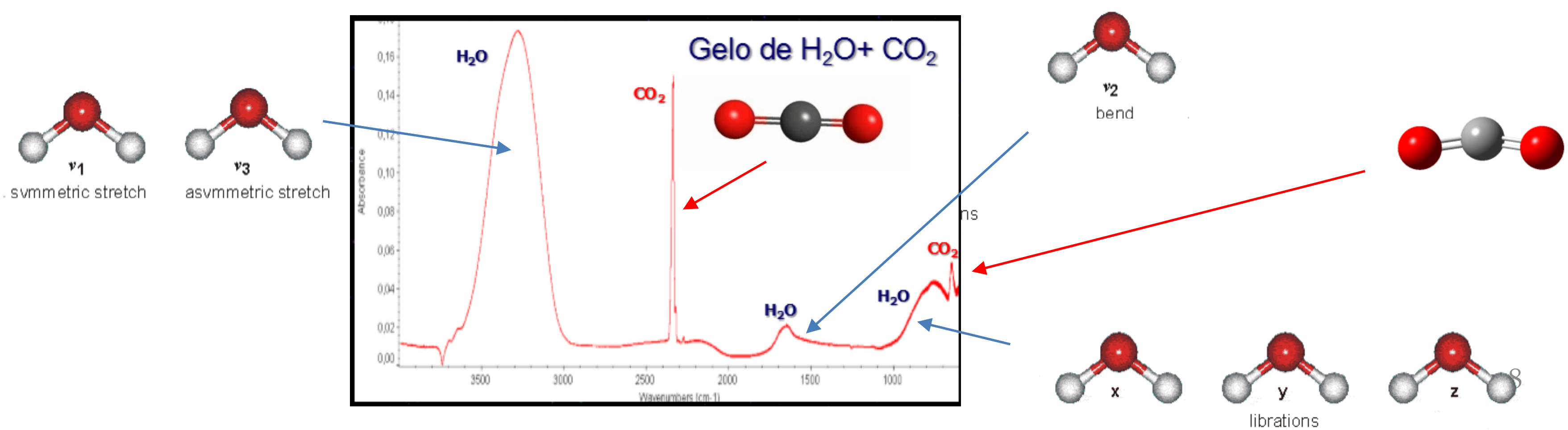
Cold (<180K) and dense regions (>1E4 cm-3) of ISM, Star forming regions, YSO, Protostellar disks, Dense Clouds.

Planetary nebulae, molecular clouds, cold regions in planetary systems (e.g. Comets, rings, moons, asteroids)

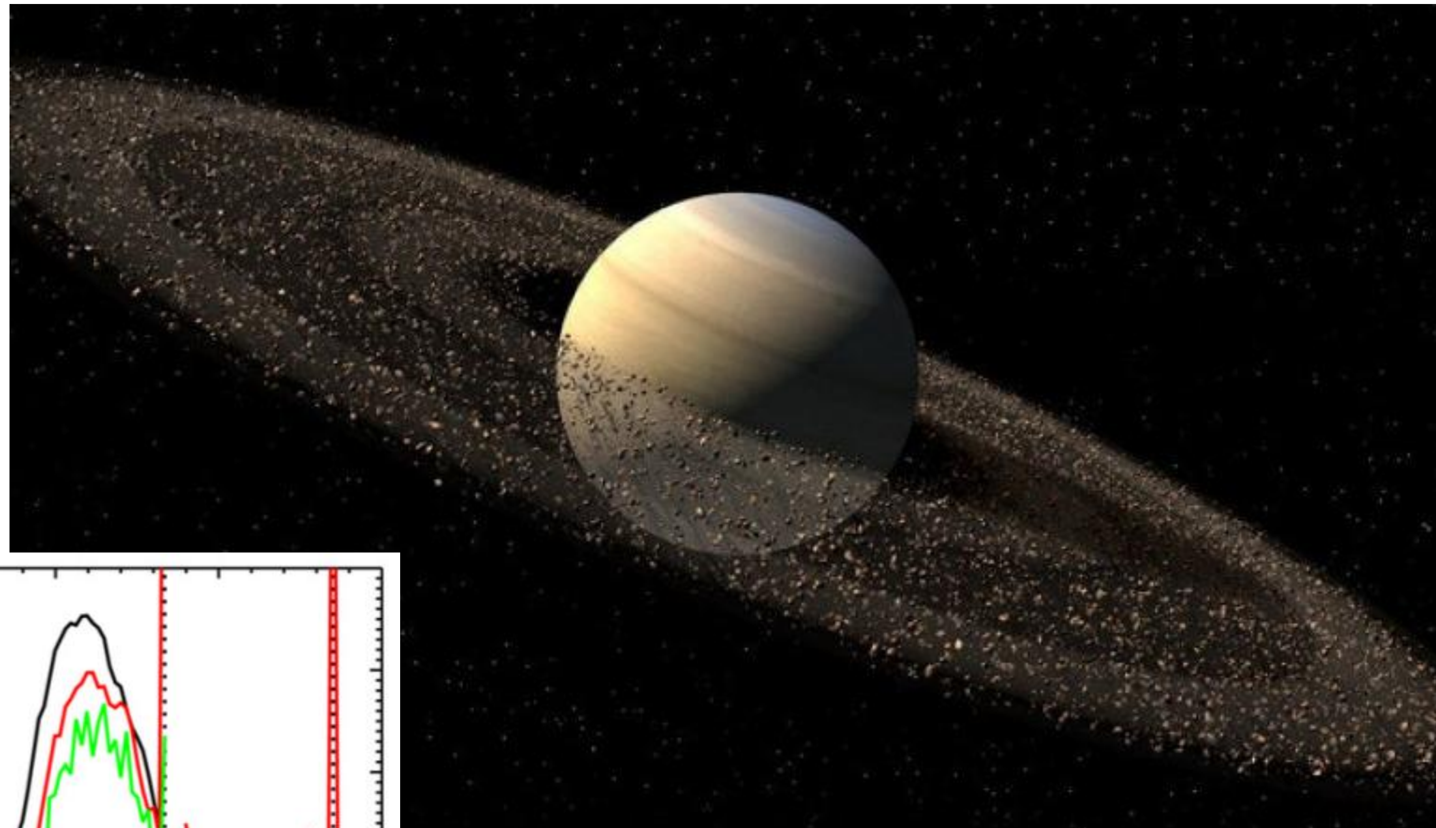
Astrophysical ices (Detection?)

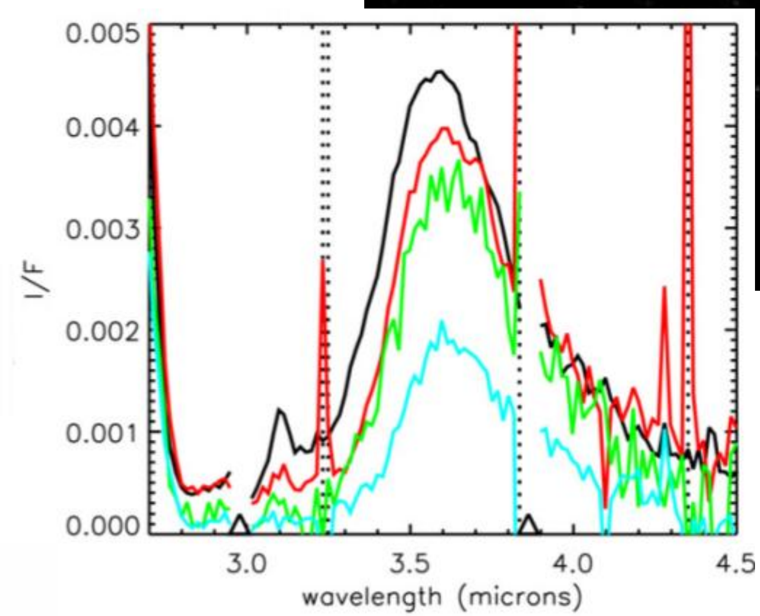
IR spectroscopy (molecular vibration modes)

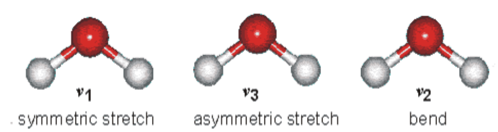




Astrophysical ices (Detection?)



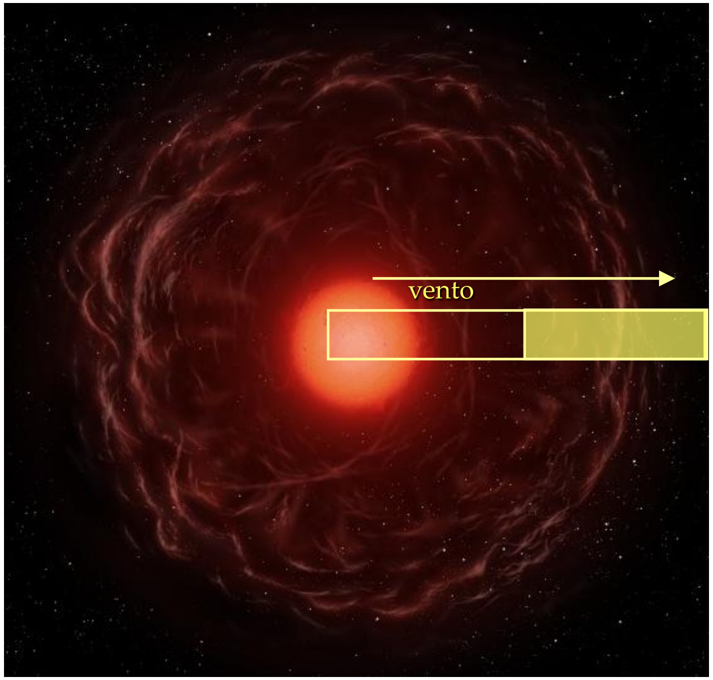


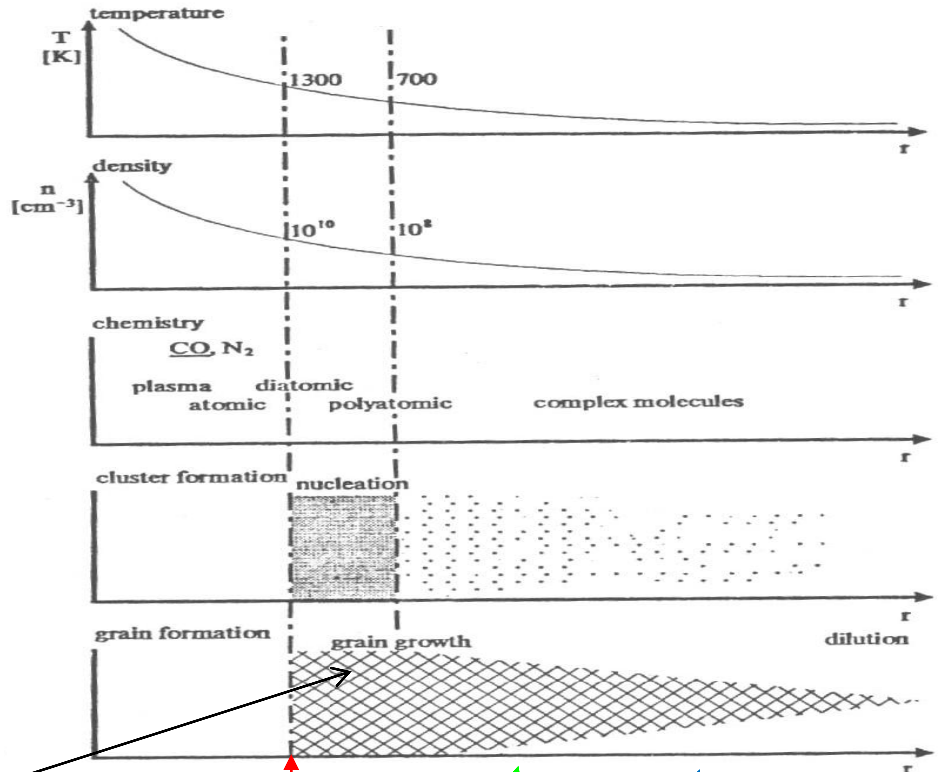


Nicholson et al. 2008, Icarus, 193, 182 (CASSINI VIMS)

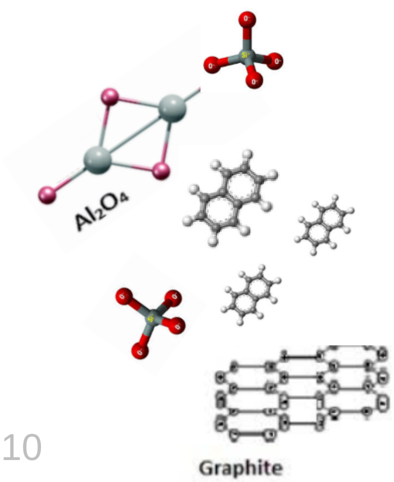
Astrophysical ices (Formation?)

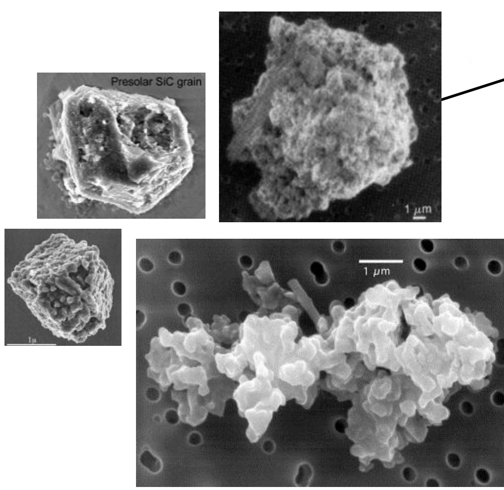
Grain seeds in stellar winds (RGB and SNe) + grain growth (mantles in cold ISM)





Sedlmayr 1994

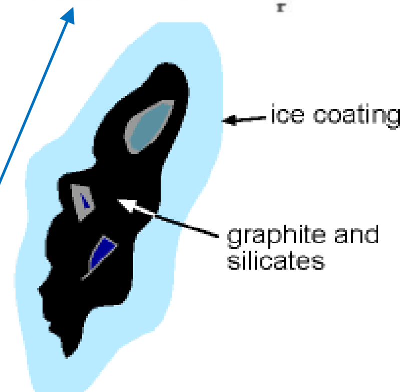




Al_2O_4 (temp ~ 1700K);
silicatos (temp ~ 1400K)

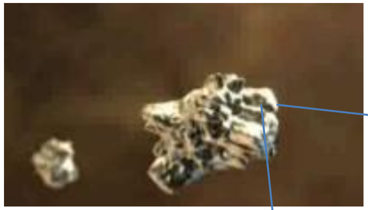
Moléculas carbonáceas
(C, PAHs, SiC)

Moléculas voláteis – mantos
de gelo (H_2O, CO, CH_4…)



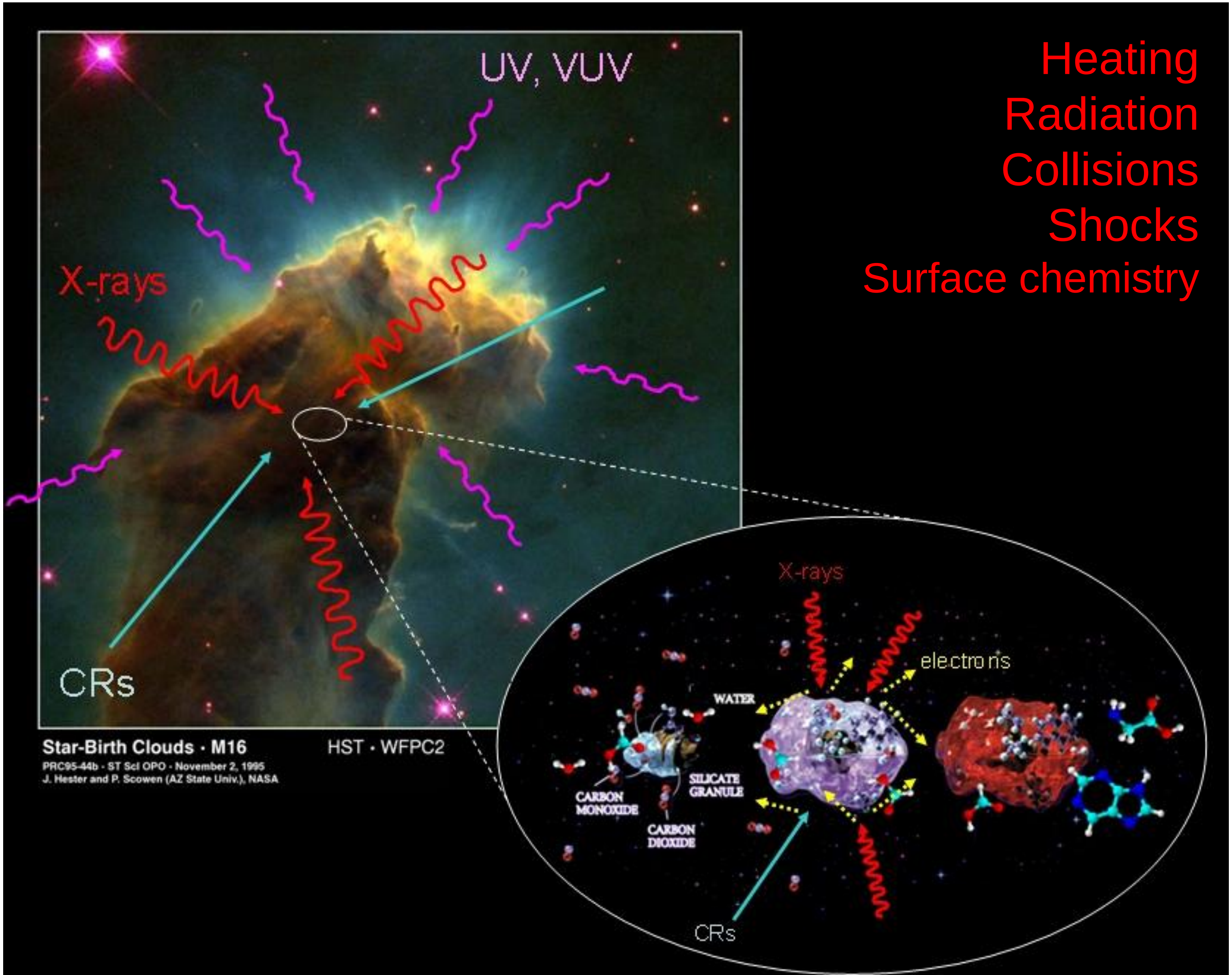
Astrophysical ices (Formation?)

Atom addition, molecular
adsorption, surface reactions



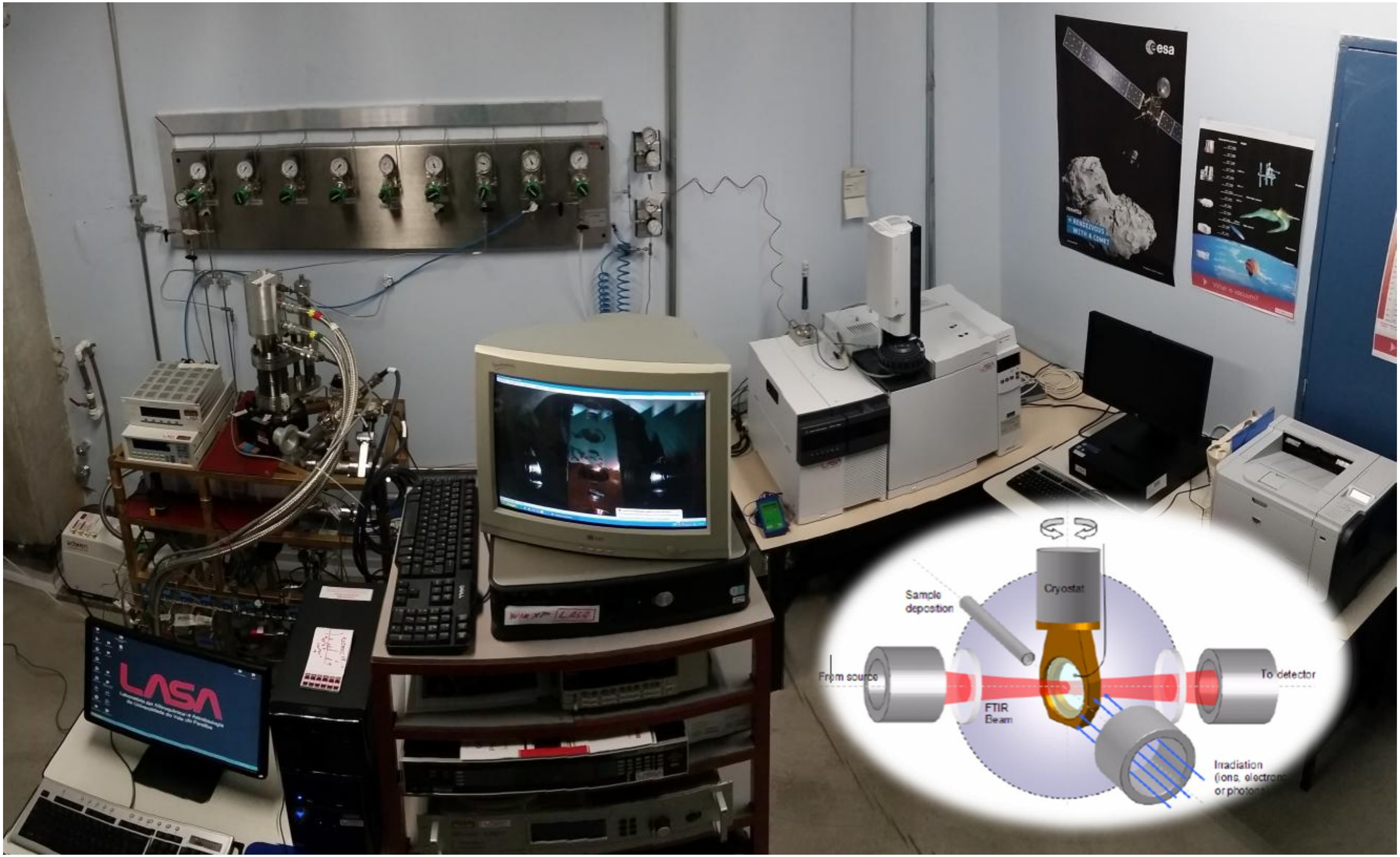
https://www.youtube.com/watch?v=X_jSenHTqFw (Leiden Univ.)

Astrophysical ices (Chemical processing)



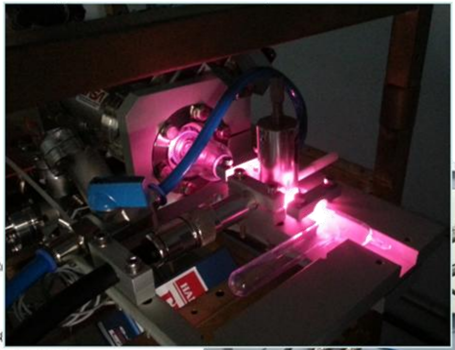
Astrophysical ices (Simulation: some laboratory setups)

UV and electrons at LASA (UNIVAP/Brazil)

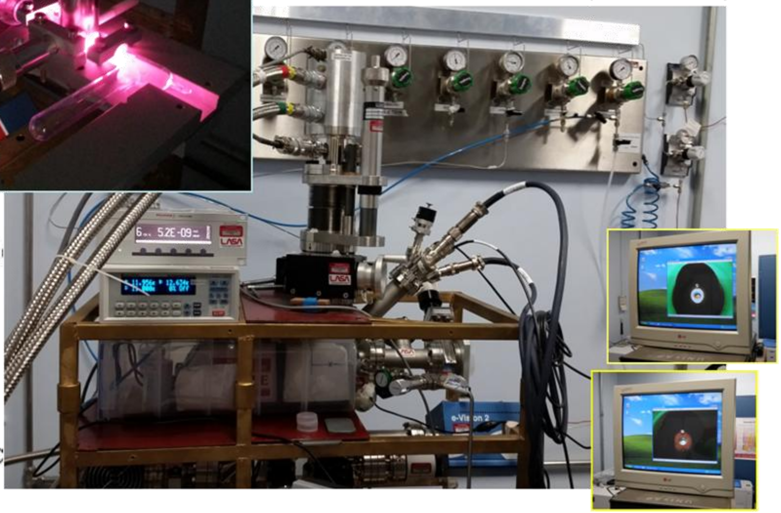


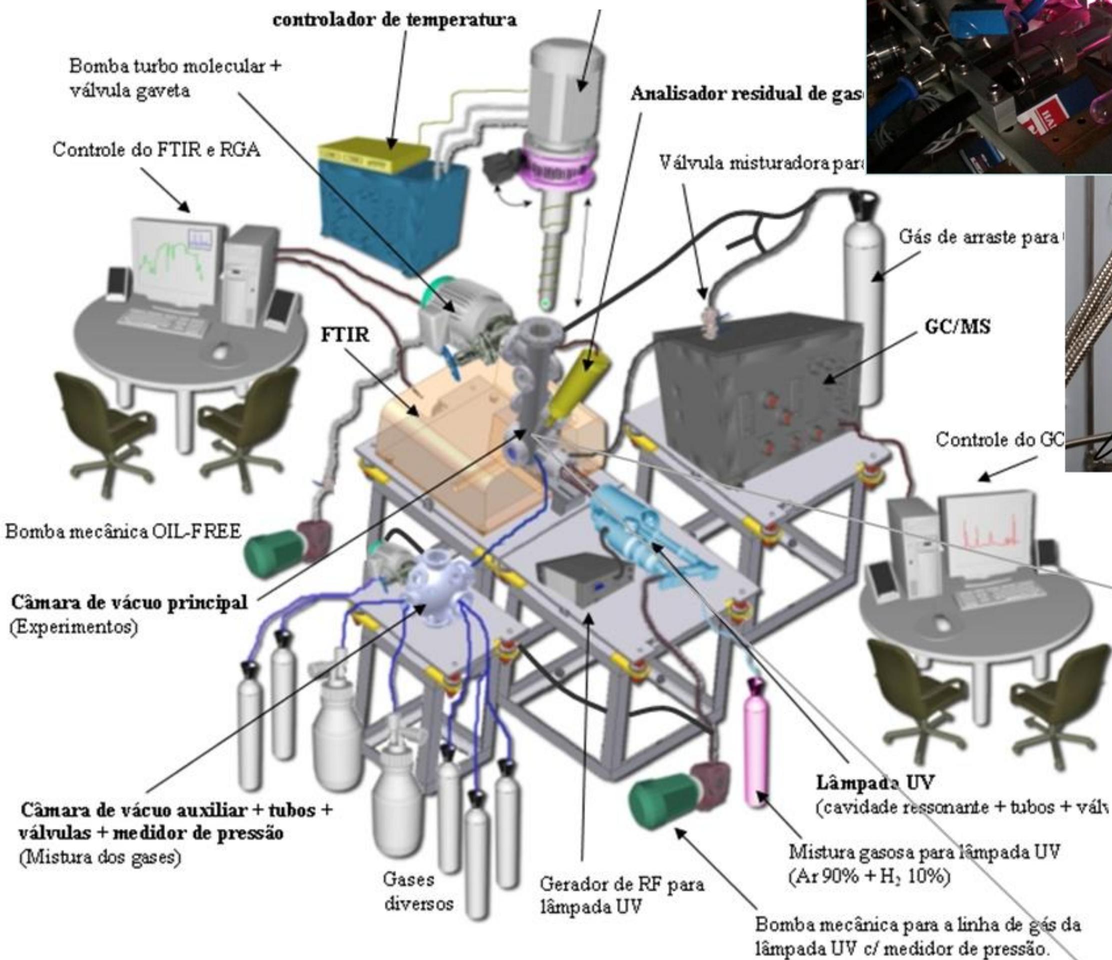
LASA (UNIVAP/Brazil)

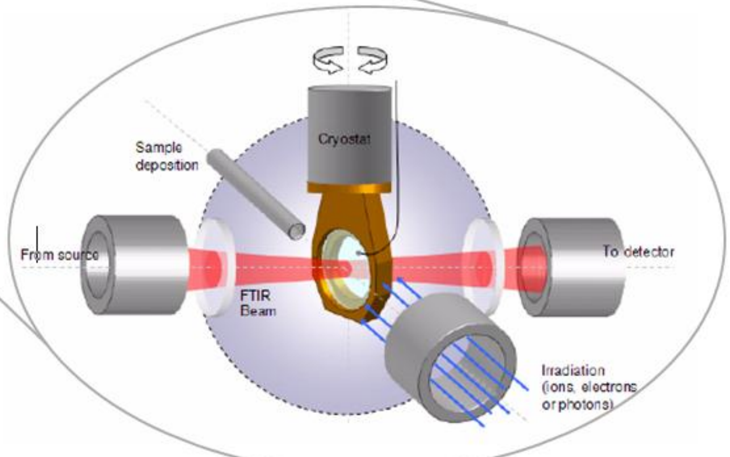
Lâmpada de UV 10.2 eV (Lyman alfa)



Canhão de Elétrons (100eV-5000eV)



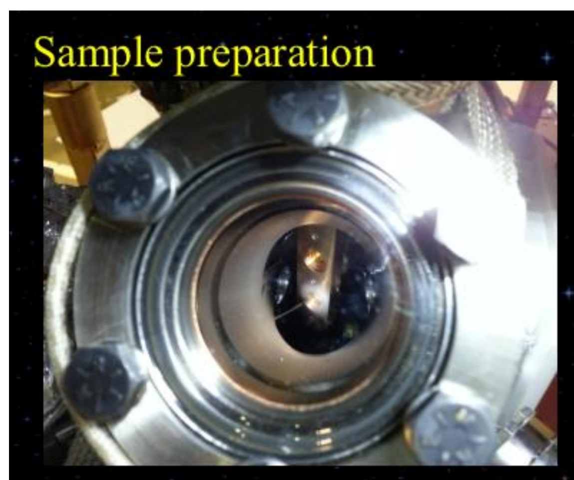




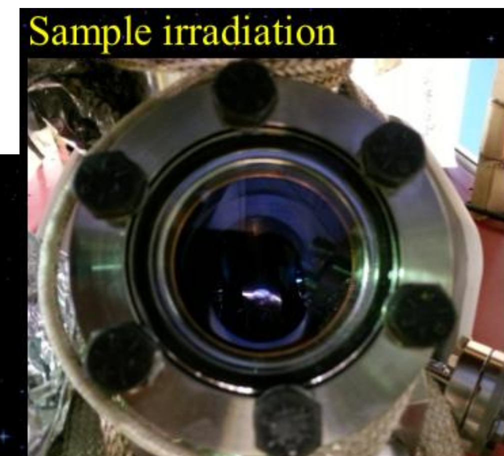
Laboratório de Astroquímica e Astrobiologia

UNIVERSIDADE DO VALE DO PARAÍBA
São José dos Campos - SP

X-rays at (LNLS/CNPEM/Brazil)



Sample preparation



Sample irradiation

The gas samples were deposited onto a ZnSe substrate at 13 K and then heated (when was the case) to specific temperatures to be irradiated. *In-situ* analysis were performed by a Fourier transform infrared (FTIR) spectrometer at different photon fluences. Cross section, photolysis yield and half-lives of the produced species were quantified.

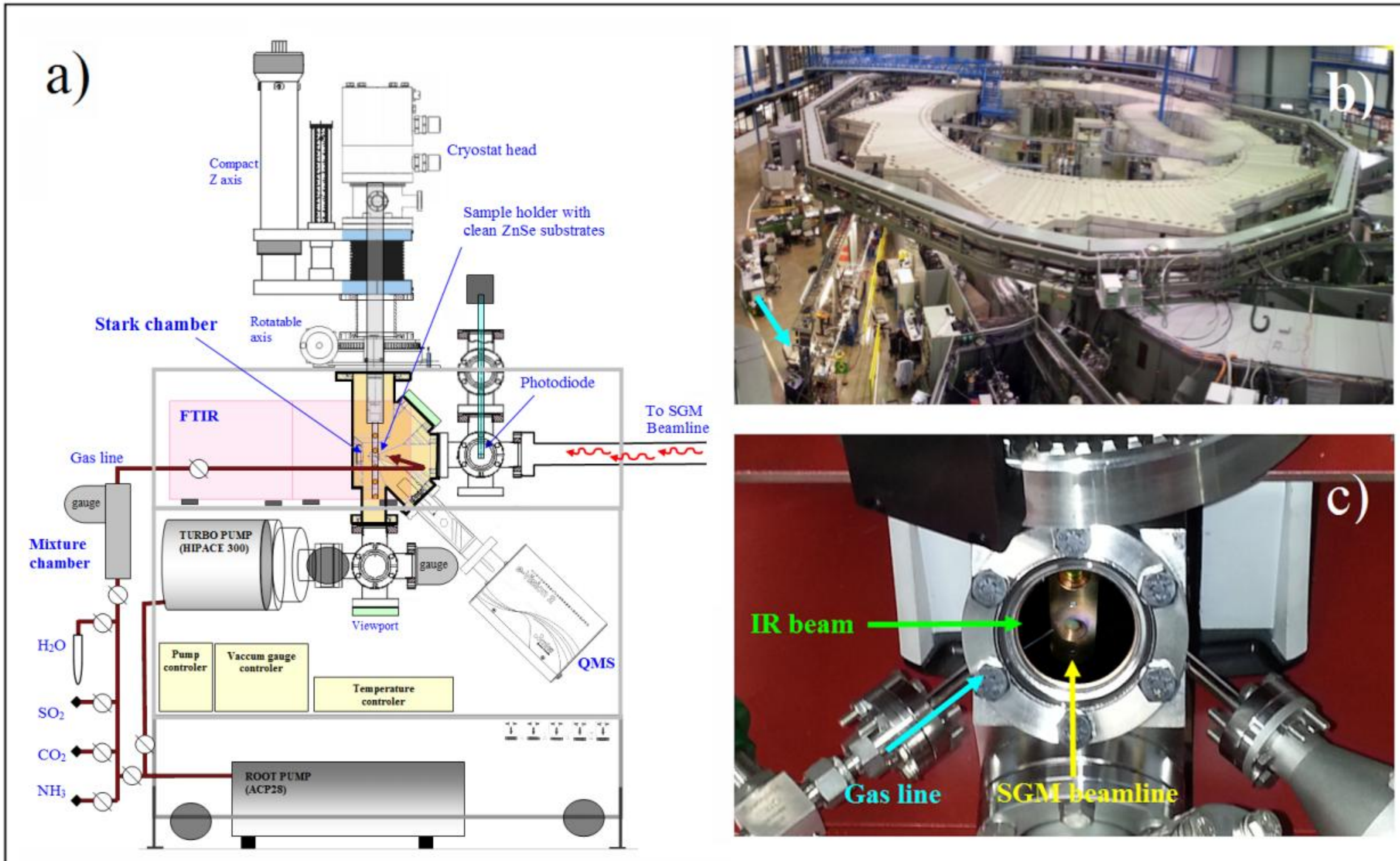


Figure 1. a) Diagram of the experimental setup (Stark chamber). b) Picture of the experimental hall of the Brazilian synchrotron source (LNLS) with the experimental chamber coupled at the SGM beam line (arrow). c) Picture showing the Europa surface analog inside the chamber ready to be irradiated by synchrotron light.

Pilling and Bergantini, MNRAS, 2015, APJ.

Swift ions GANIL/FR

ARIBE/GANIL → Solar wind (low energy ions, implantation)
E ~ 10 keV/u

Astrophysical ices (Physicochemical comparison)

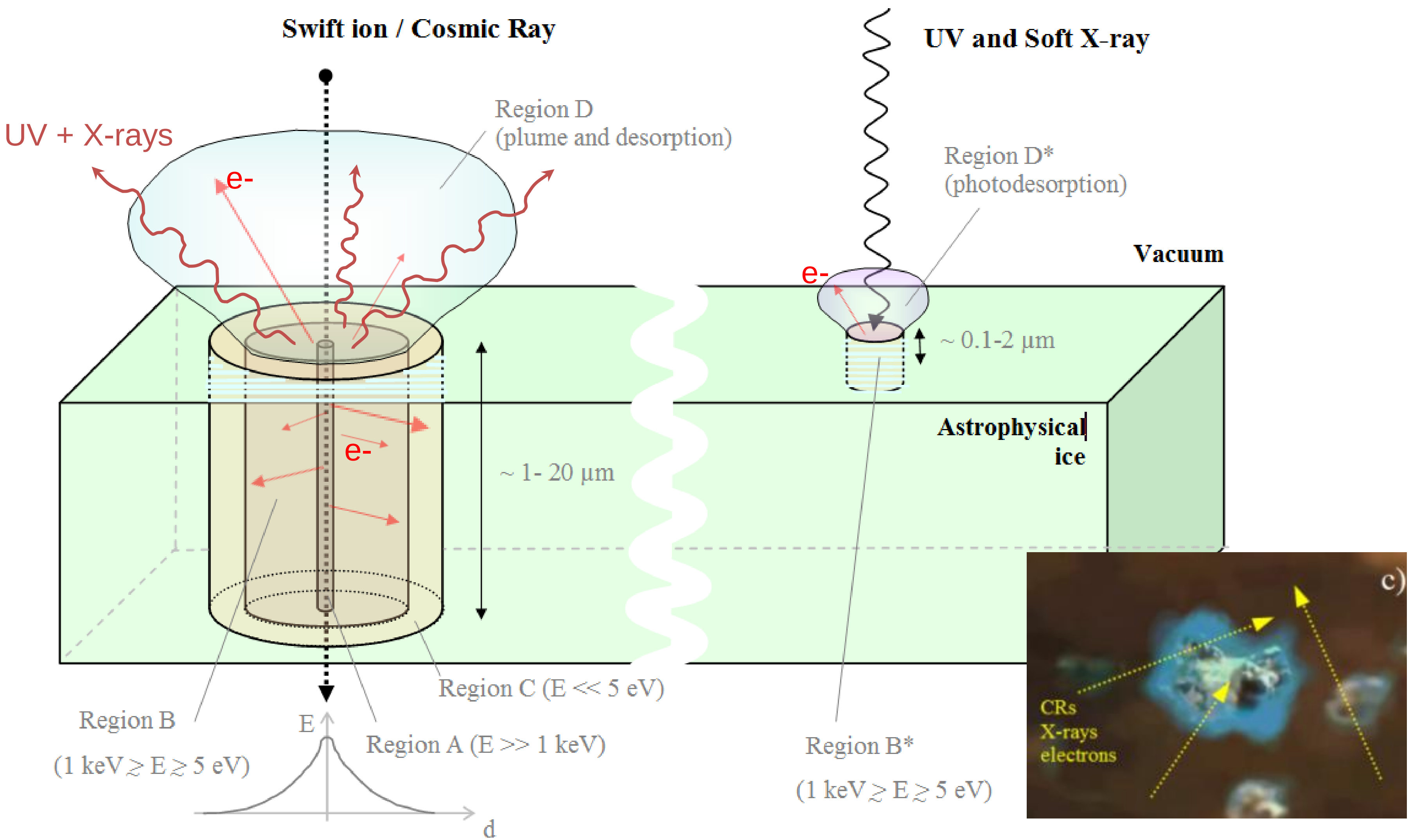


Figure 4: Schematic diagram of the different physicochemical regions surrounding the ion and photons track during the processing of the N_2:CH_4 (19:1) ice by ions (15.7 MeV $^{16}O^{5+}$) and soft X-ray photons. (Adapted from Vasconcelos et al. ApJ 2017)

Pilling et al 2018, IAUS

Astrophysical ices (heating or radiation processing)

1) Destruction of parent species and formation of new species in the ices during processing (lab experiments +IR spectroscopy)

Metanol ice at 12K
Unirradiated

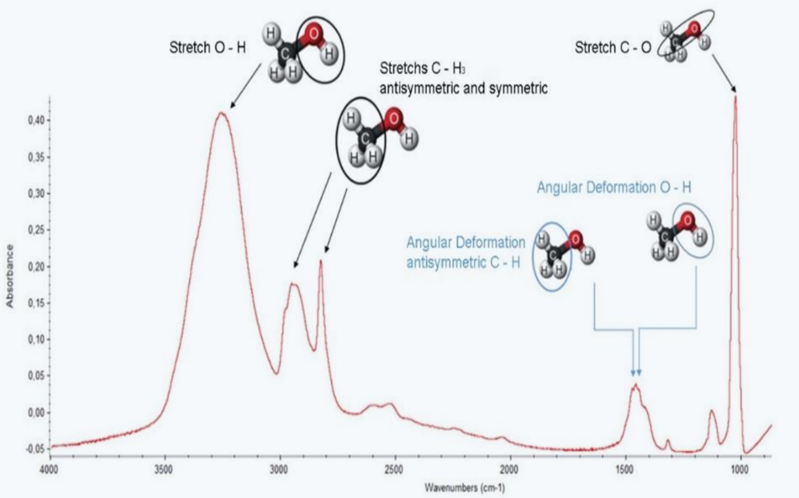


Figure 4. *Infrared spectrum of amorphous methanol ice at 12K indicating the main vibrational modes.*

Freitas and Pilling 2019, Quimica nova, Subm.

After irradiation with X-rays (6-2000 eV)

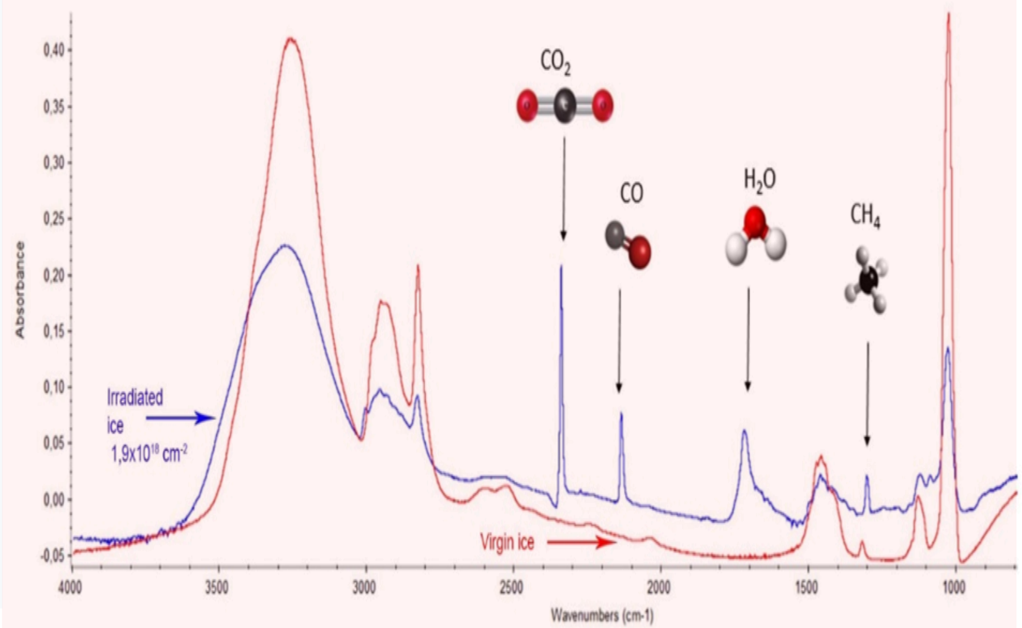
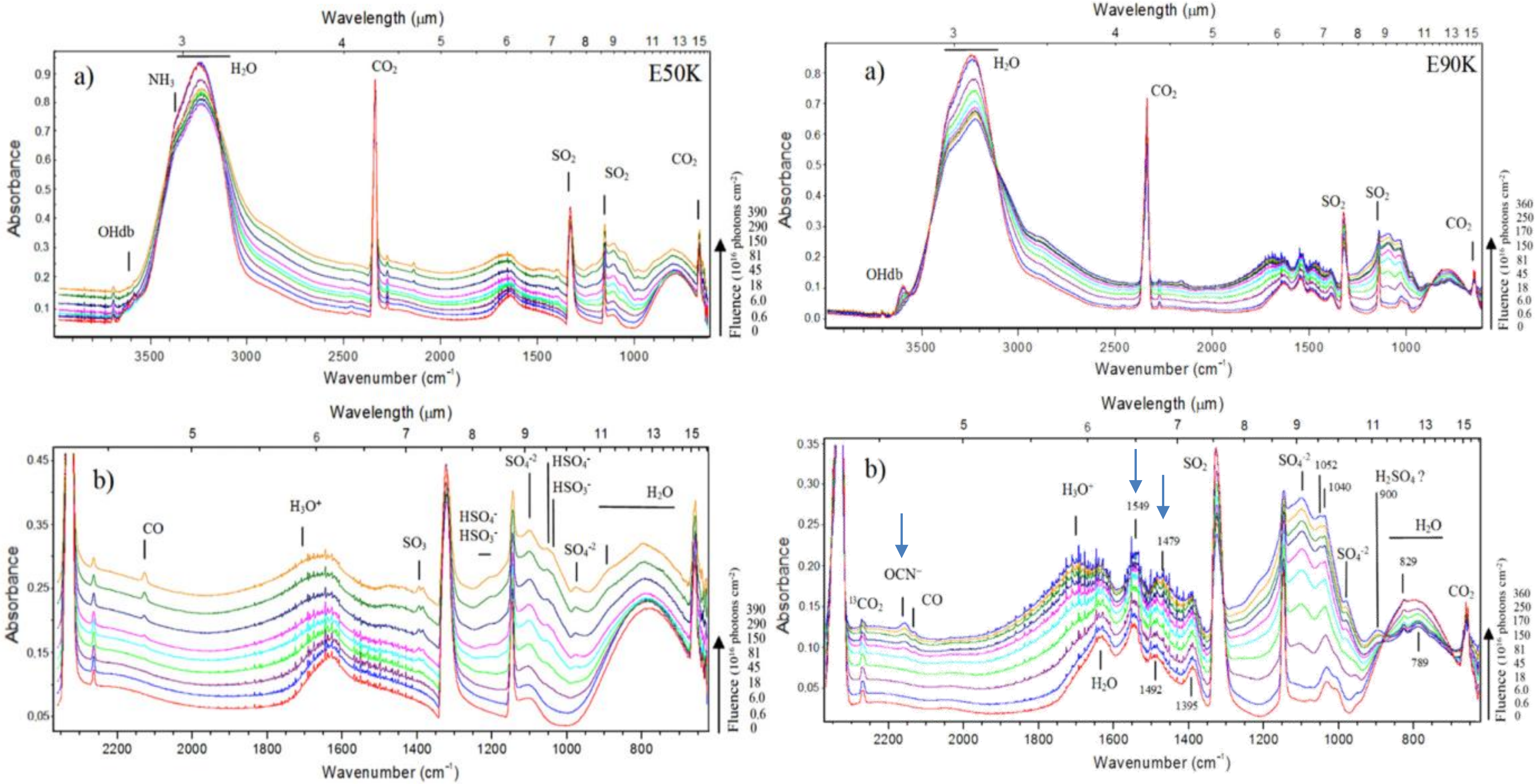


Figure 5. *Overlap of the virgin methanol ice (red line) and irradiated ice spectra after 250 minutes of exposure to photons in the soft X-ray range (6 to 2000 eV).*

Astrophysical ices (heating or radiation processing)

1) Destruction of parent species and formation of new species in the ices during processing (lab experiments +IR spectroscopy)

H_2O:CO_2: NH_3:SO_2 ices (50 and 90 K) irradiated by X-rays → Temp. also influences the chemical processing



Pilling and Bergantini, 2015, ApJ.

Astrophysical ices (heating or radiation processing)

2) Molecular segregation (diffusion and viscosity)

During ice heating the energy deposited allows molecular diffusion inside ice bulk which may also result in molecular segregation (diffusion processes) → Changes in chemical environment induce changes also in band position, shape and band intensity

(H_2O+CO_2 model)

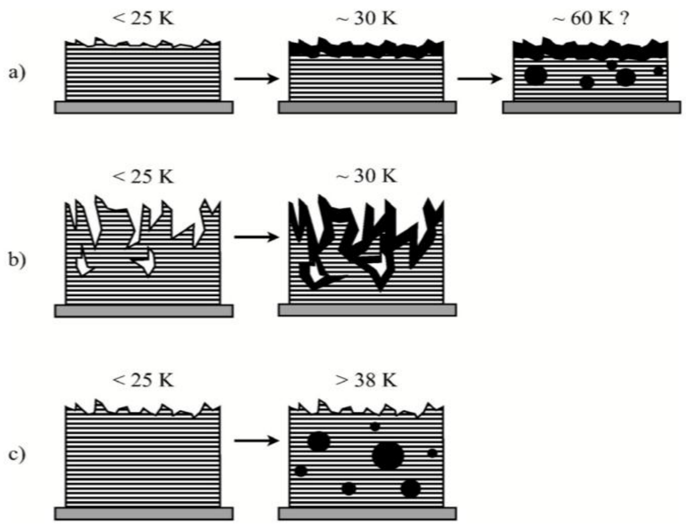
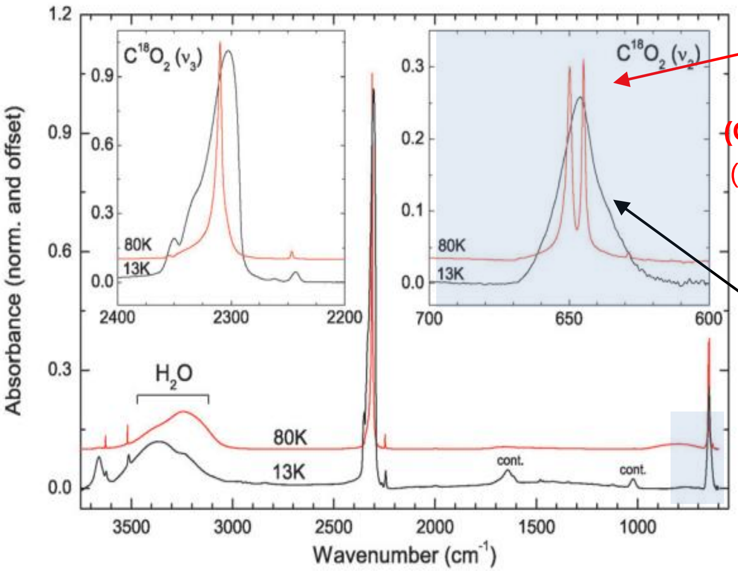


Fig. 13. The segregation mechanism in **a)** ices below 40 ML together with the two proposed segregation mechanisms for thick ices (>100 ML), through **b)** internal surface segregation and **c)** phase transitions. Black indicates segregated CO_2 ice and stripes the H_2O:CO_2 ice mixture. Each step is marked with the approximate temperature at which the mechanism becomes important at the time-scales of low-mass star formation, as discussed in Sect. 5.3.

Oberg et al. 2009, A&A, 505, 183

(H_2O+CO_2 IR spectroscopy)



Hot ice
(CO_2 segregated)
(CO_2 surround. by CO_2)
(heterogeneous sample)

Cold ice
(CO_2 mixed)
(homogeneous sample)

ig. 7 Infrared spectra of the mixed $H_2O:C^{18}O_2$ ices at 13 K and 0 K. Figure inset shows the IR profile of $C^{18}O_2$ ν_3 (left) and ν_2 (right) ibration modes.

Pilling et al. 2010, A&A, 523, A77

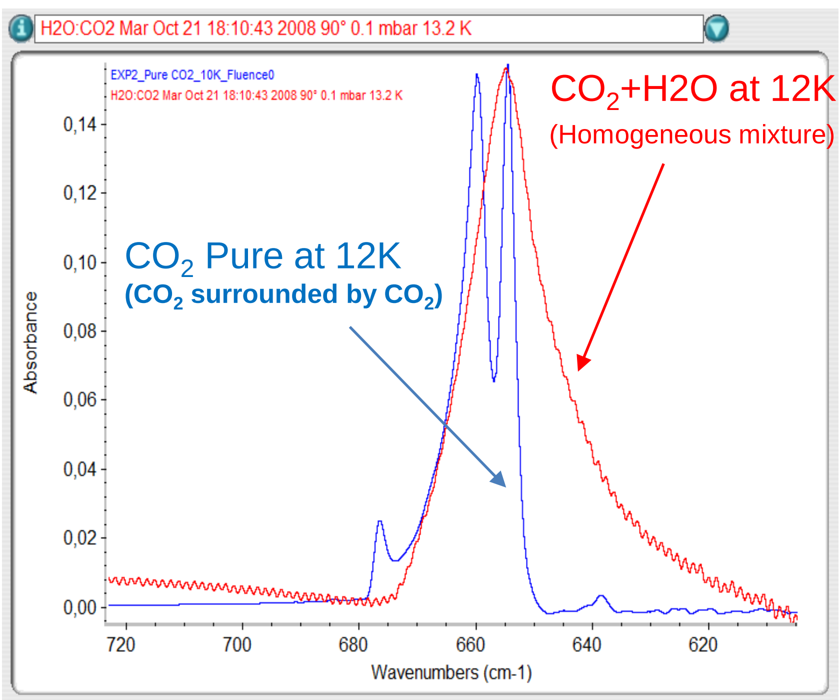
Astrophysical ices (radiation processing)

2) Molecular segregation

Changes in chemical environment induce changes also IR spectra. Effects also observed during irradiation of ices by

NON-IRRADIATED

(IR spectra of two CO_2 containing ices at 12K)
Pure CO_2 and $H2O+CO_2$(1:1)

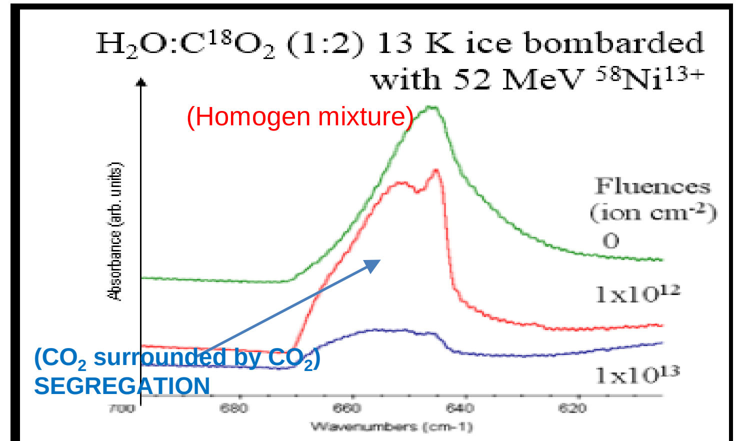


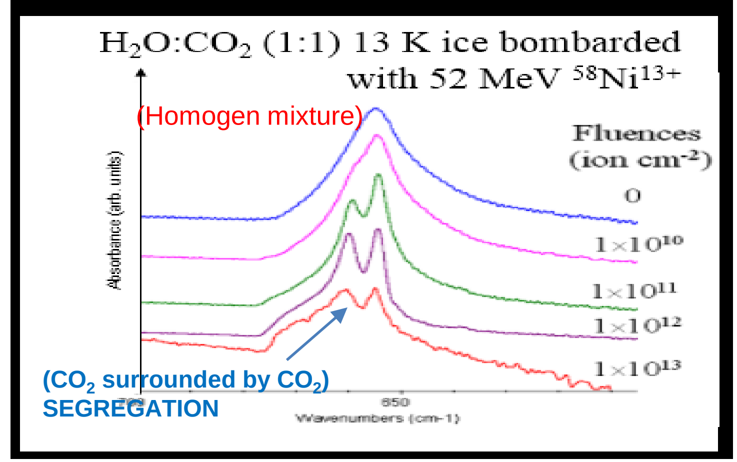
Pilling et al. 2010, A&A, 523, A77 Pilling et al. 2019, in prep.

IRRADIATED

(IR changes during ion bombardment)

$H2O+CO_2$ ices at 13K





Unpublish data + Pilling 2010 AeA 523, A77 e Pilling et al. 2011, PCCP, 13, 15755, Proc IAUS 2012 Toledo.

Astrophysical ices (radiation processing)

3) Compaction ("diffusion in large scale")

CR induced compaction

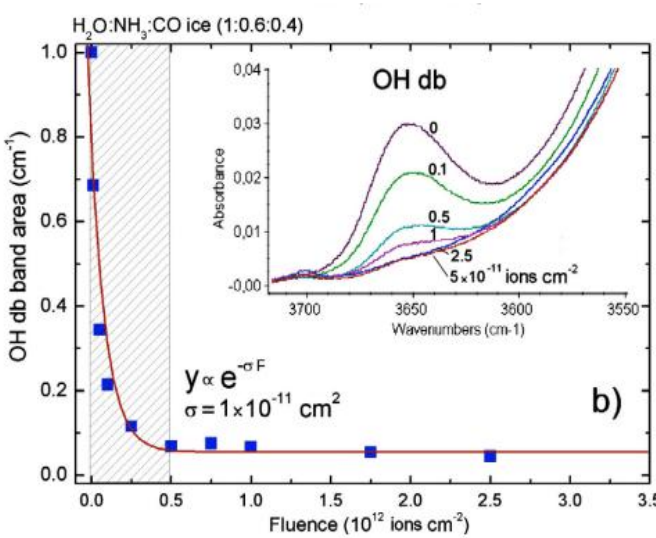
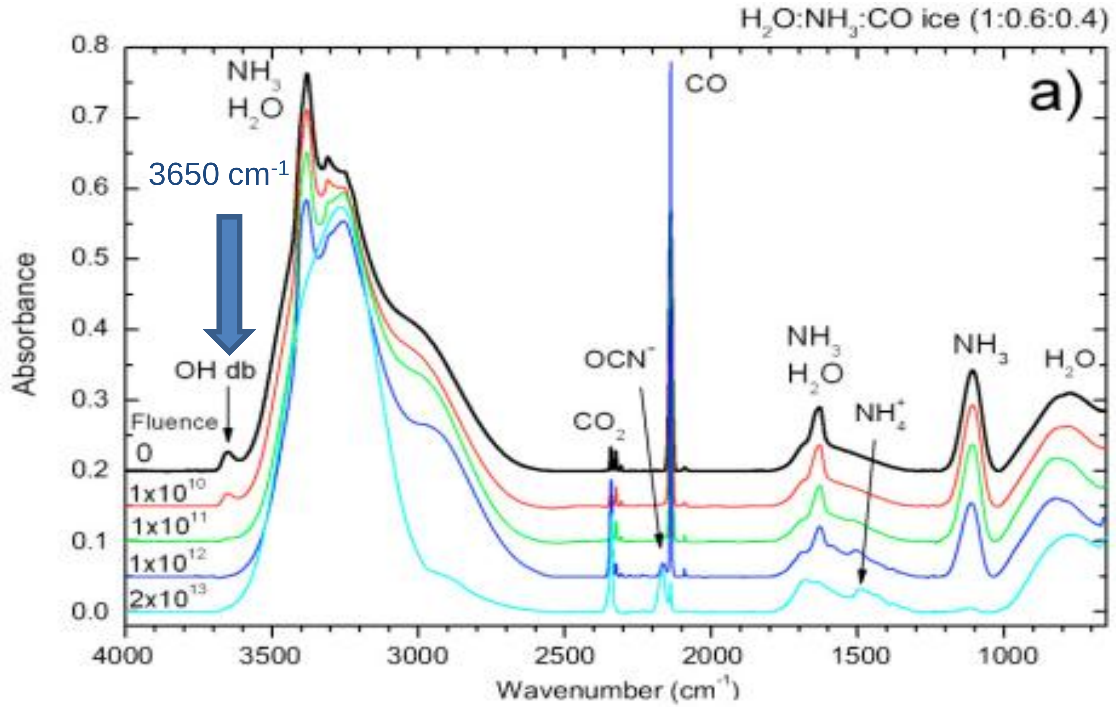
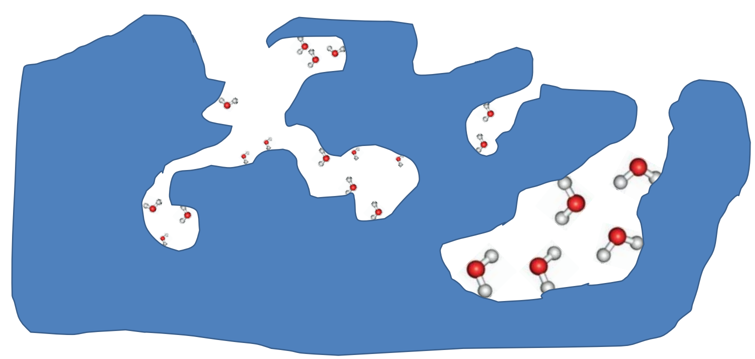


Fig. 4. a) Expanded view of Fig. 3 at the beginning of irradiation. Note the drastic changes in column density of water and ammonia up to fluence of 5×10^{11} ions cm^{-2}. The hashed area indicates the regions where compaction is occurring. **b)** OH dangling bond feature area (cm^{-1}) in the $H_2O:NH_3:CO$ ice (1:0.6:0.4) as a function of fluence. Figure inset is the OH db feature from non irradiated ice and at fluences 0.1, 0.5, 1, 2.5 and 5×10^{11} ions cm^{-2}.

Pilling et al. 2010, A&A, 509, A87





Astrophysical ices (radiation processing)

3) Compaction ("diffusion in large scale")

X-ray induced compaction

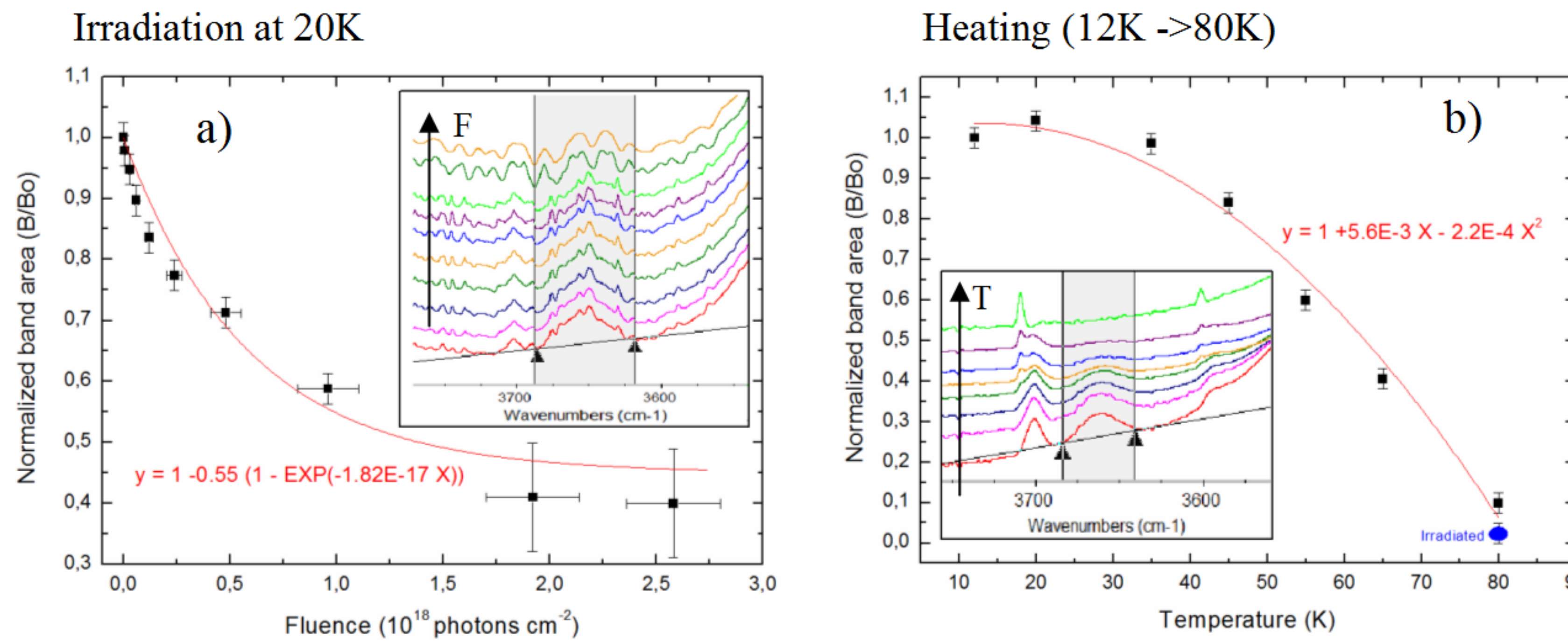
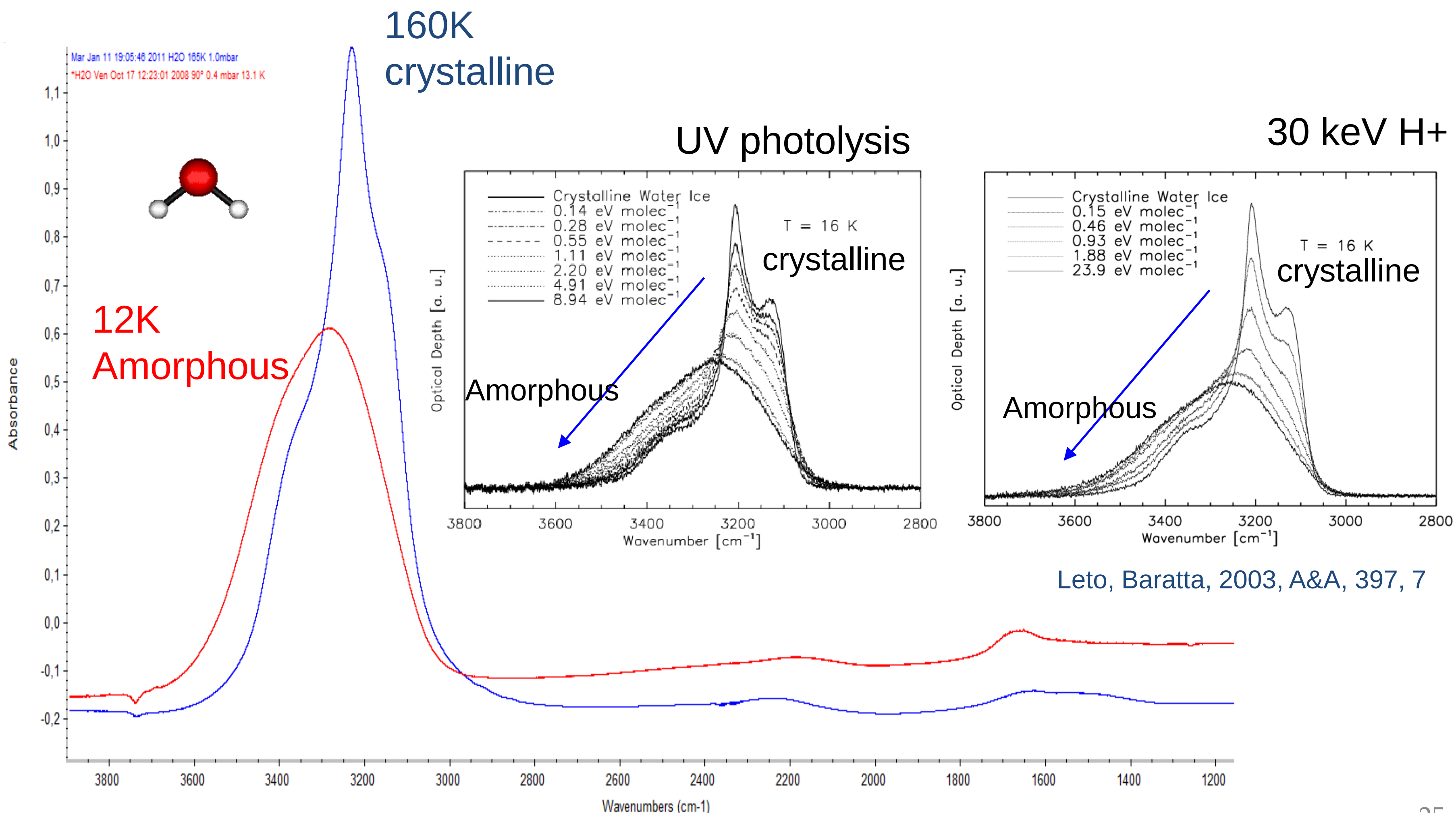


Fig. 7 - a) Compaction effect due to X-rays: Evolution of OHdb feature of sample at 20 K (experiment E20K) as a function of photon fluence; b) Pore collapse due to ice heating and diffusion of CH_4 and CO_2: Evolution of OHdb feature of un-irradiated sample as a function of temperature during heating phase from 12 K(sample deposition) to 80 K (experiment E80K). For comparison purpose, blue dot indicates the value for the irradiated sample (at the final fluence of 3.1E18 photons cm^{-2}). Both inset panels illustrate the part of IR spectra showing the evolution of OHdb feature.

Pilling et al. 2019, RSC advanced, Submitted

Astrophysical ices (radiation processing)

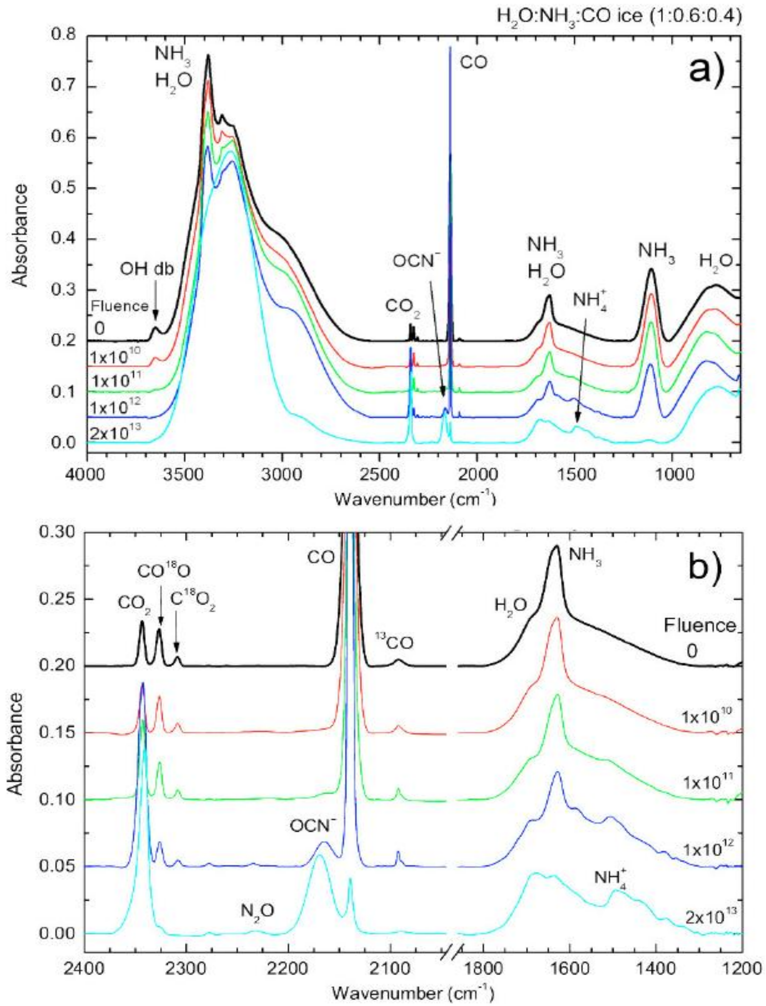
4) Amorphization (crystalline → amorphous)
 Destruction or rearranging of intermolecular bonds in the presence of extra energy.



Leto, Baratta, 2003, A&A, 397, 7

Astrophysical ices (radiation and chemical equilibrium)

5) At larger Fluences (ions or X-rays) with T=cte e P=cte → **Chemical Equilibrium** is reached (const. chemical composition not affected by further irradiation)



$H_2O:NH_3:CO$ ice (12K)
irradiated with 46 MeV Ni^{13+}

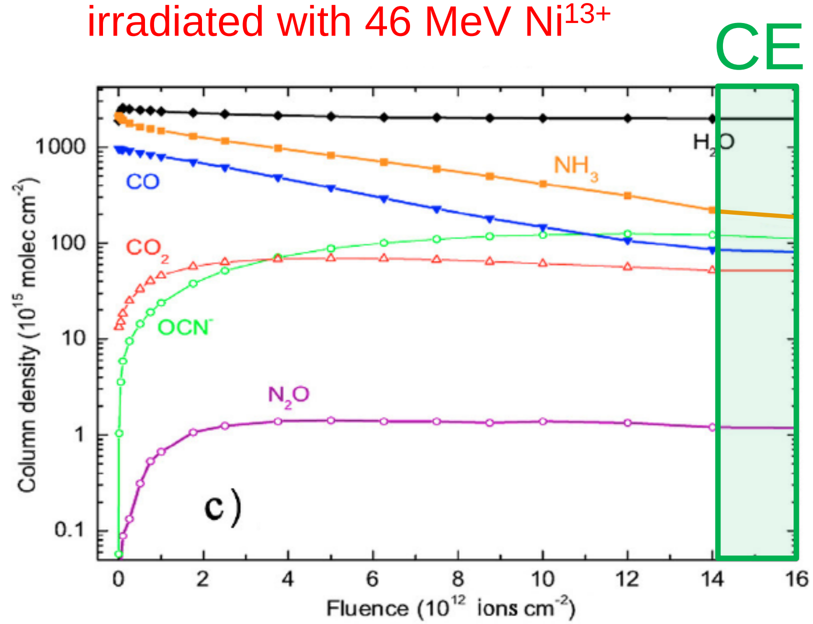


Fig. 2. **a)** Infrared spectra of $H_2O:NH_3:CO$ ice (1:0.6:0.4) before (top dark line) and after different irradiation fluences. **b)** Expanded view from 2400 to 1200 cm^{-1}. Each spectrum has an offset of 0.05 for better visualization. **c)** Molecular column density derived from the infrared spectra during the experiment.

Pilling et al. 2010, A&A, 509, A87

Astrophysical ices (radiation and chemical equilibrium)

5) At larger Fluences (ions or X-rays) with T=cte e P=cte → **Chemical Equilibrium** is reached (const. chemical composition not affected by further irradiation)

N_2:CH_4 (19:1) a 12K irradiated with X-rays (6 a 2000 eV)

N_2:CH_4 (19:1) a 19K irradiated with 15.7 MeV O^{5+}

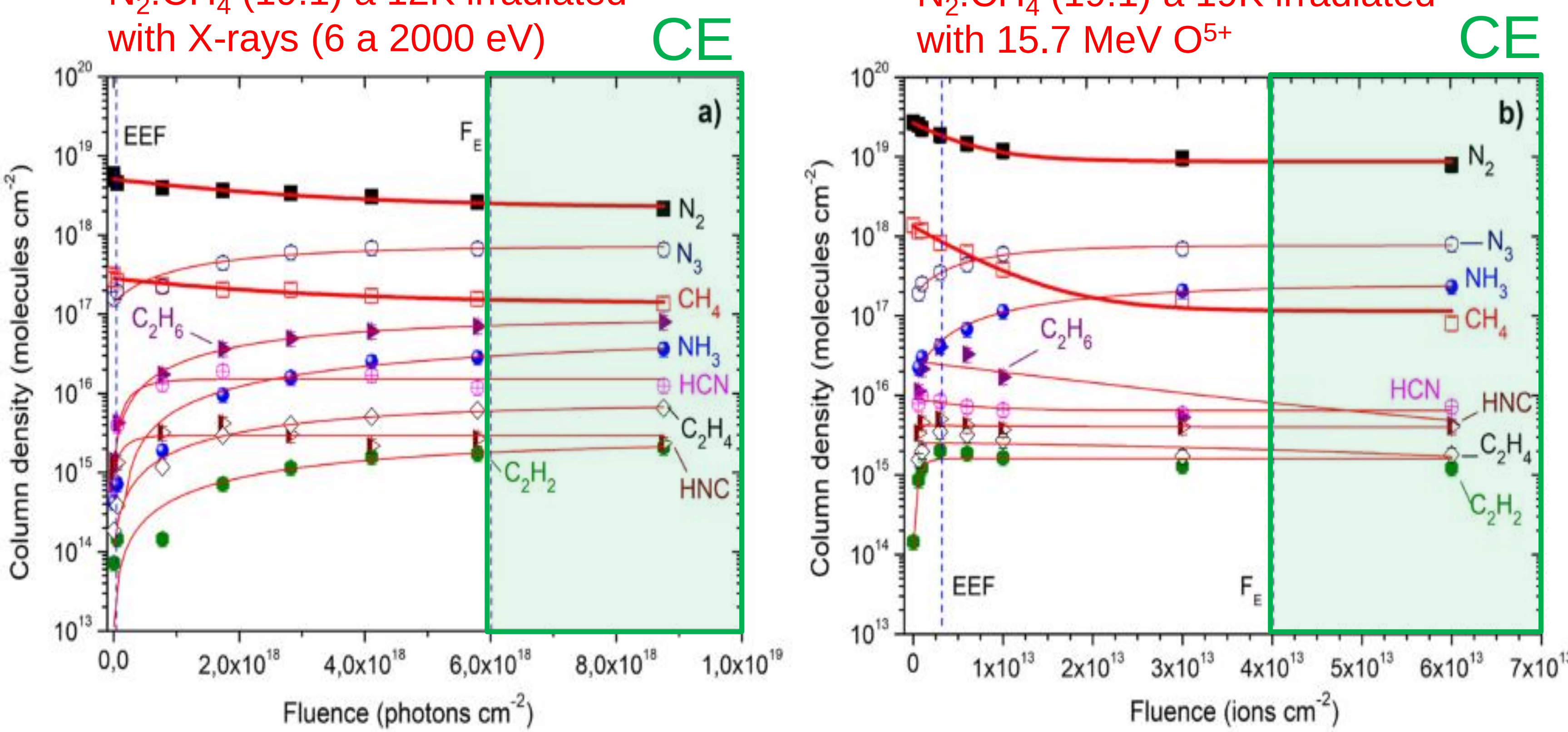


Figure 4. Column density evolution as a function of the fluence of (a) ionizing photons and (b) energetic ions. The lines indicate the best fit using Equation (2) (thick lines for parent species) and Equation (3) (thinner lines for daughter species). Uncertainties are about 20% (see details in the text). EEF represents the Equivalent Energy Fluence (eV cm^{-2}) and F_E is the Chemical Equilibrium Fluence (see discussion in Sections 4.2 and 4.3).

Vasconcelos et al. 2017, ApJ, 850, 174

Astrophysical ices (radiation and chemical equilibrium)

5) At larger Fluences (ions or X-rays) with T=cte e P=cte → **Chemical Equilibrium** is reached (const. chemical composition not affected by further irradiation)

H_2O:CO_2:CH_4:NH_3 at 20K and 80 K irradiated broadband X-rays

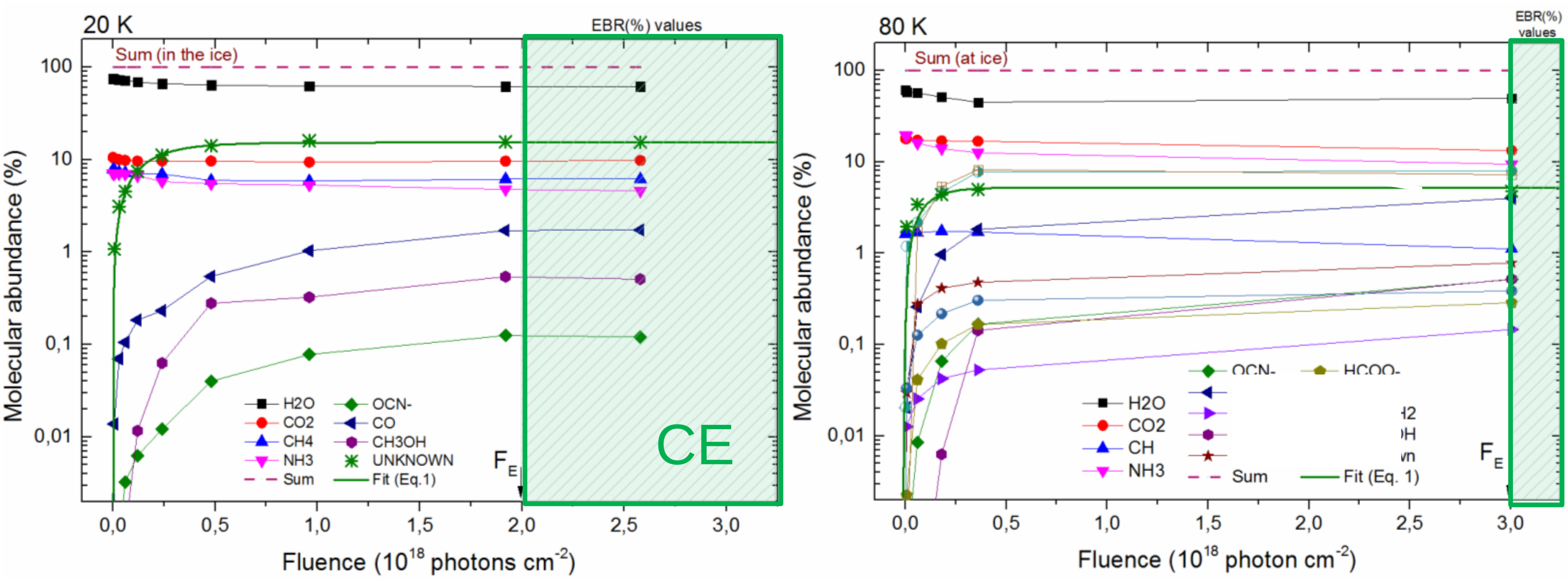


Fig. 5 - Molecular abundance in percentage as a function of fluence for the studied sample. Panel a and b present the calculated quantities for the experiment at 20 K and at 80 K, respectively. The estimated value for unknown species are also displayed. Hatched region indicates chemical equilibrium region. Solid green line is the best fit employing and adapted version of Eq 1. Other lines are employed here only to guide the eyes.

Pilling et al. 2019, PCCP, Submitted (see also also Pilling Bergantini, 2015)

Astrophysical ices (radiation and chemical equilibrium)

6) Homogenous dessorption during irradiation (after chemical equilibrium) ~ "vapor pressure?"

Dessorption yield induced by 6-2000 eV X-rays ~0.2 molecules /photon
Dessorption yield induced by 16 MeV O^{+5} ~ 1000 molecules /ion

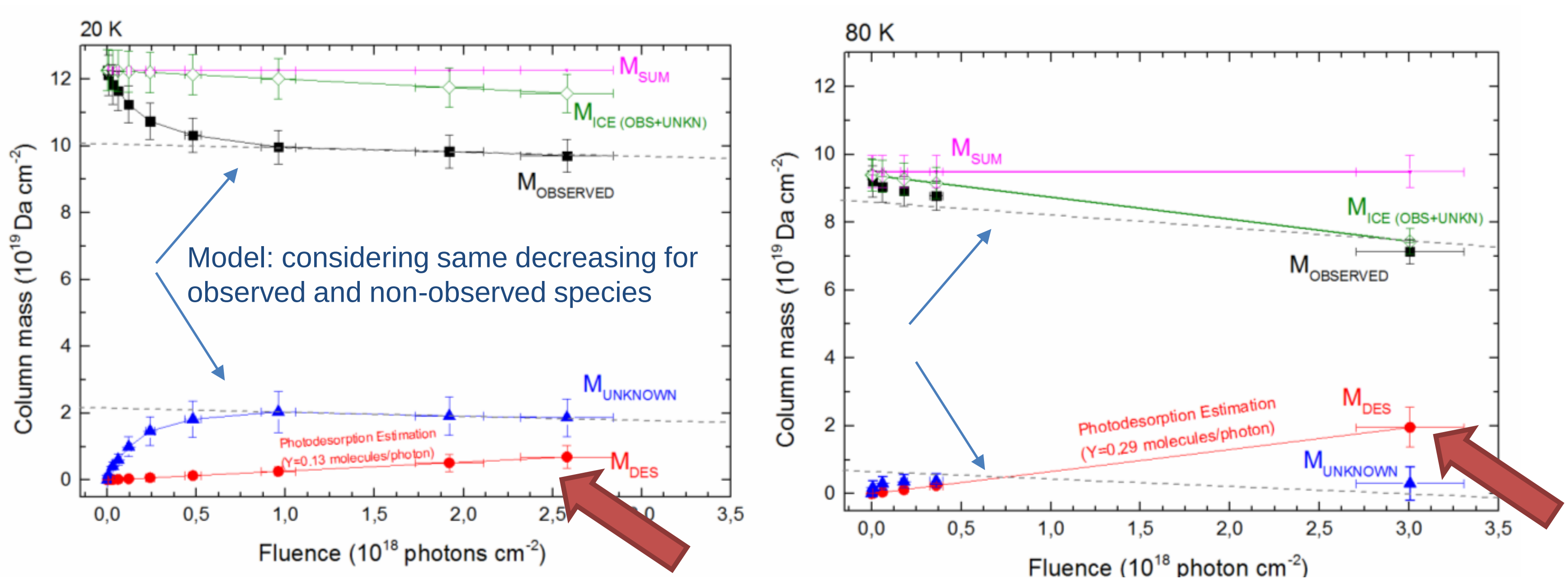


Fig 4 - The calculated column mass of molecular species in the ices using infrared spectroscopy as a function of fluence. Panel a and b show the data from the experiment at 20 K and 80 K, respectively. The chemical equilibrium is reached when $M_{observed}$ and $M_{unknown}$ reach linear decrease at large fluences (chemical equilibrium region). The total column mass (M_{sum}) is given in pink color (representing a constant value). The column mass of desorption species is a linear function with the fluence as indicated by Eq. 6. The sputtering yield modeled in both experiment are also indicated.

Pilling et al. 2019, RSC advances, Submitted

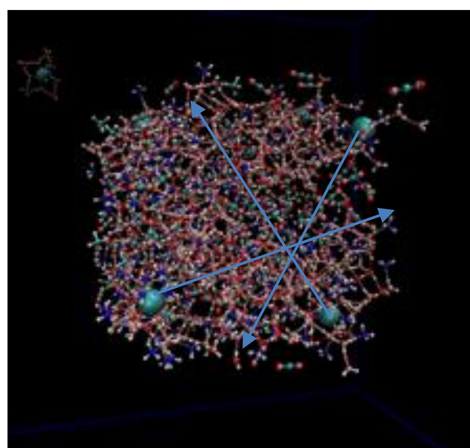
(See also Vasconcelos et al. 2017, ApJ and Rachid et al. 2019, MNRAS, Submited)

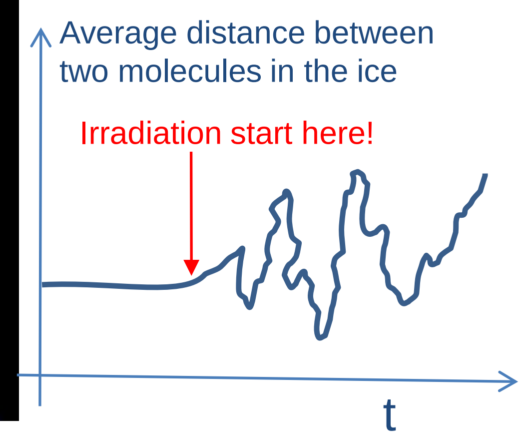
Astrophysical ices (chemical equilibrium properties)

- Thin ices irradiated at large fluence by X-ray (~2E18 photons cm-2) or ions (e.g. ~1E13 ions cm-2) with T=cte and P=cte.
- Chemical composition constant (even during further irradiation); parent species $\leftrightarrow$ daughter species
- Ephemeral Intermolecular bonds due to the continuous energy deposition by incoming radiation $\rightarrow$ molecular diffusion, segregation, amorphization, viscosity, const. dessorption (yield and chemistry) (~ " vapor pressure?")

Properties of liquids!??!

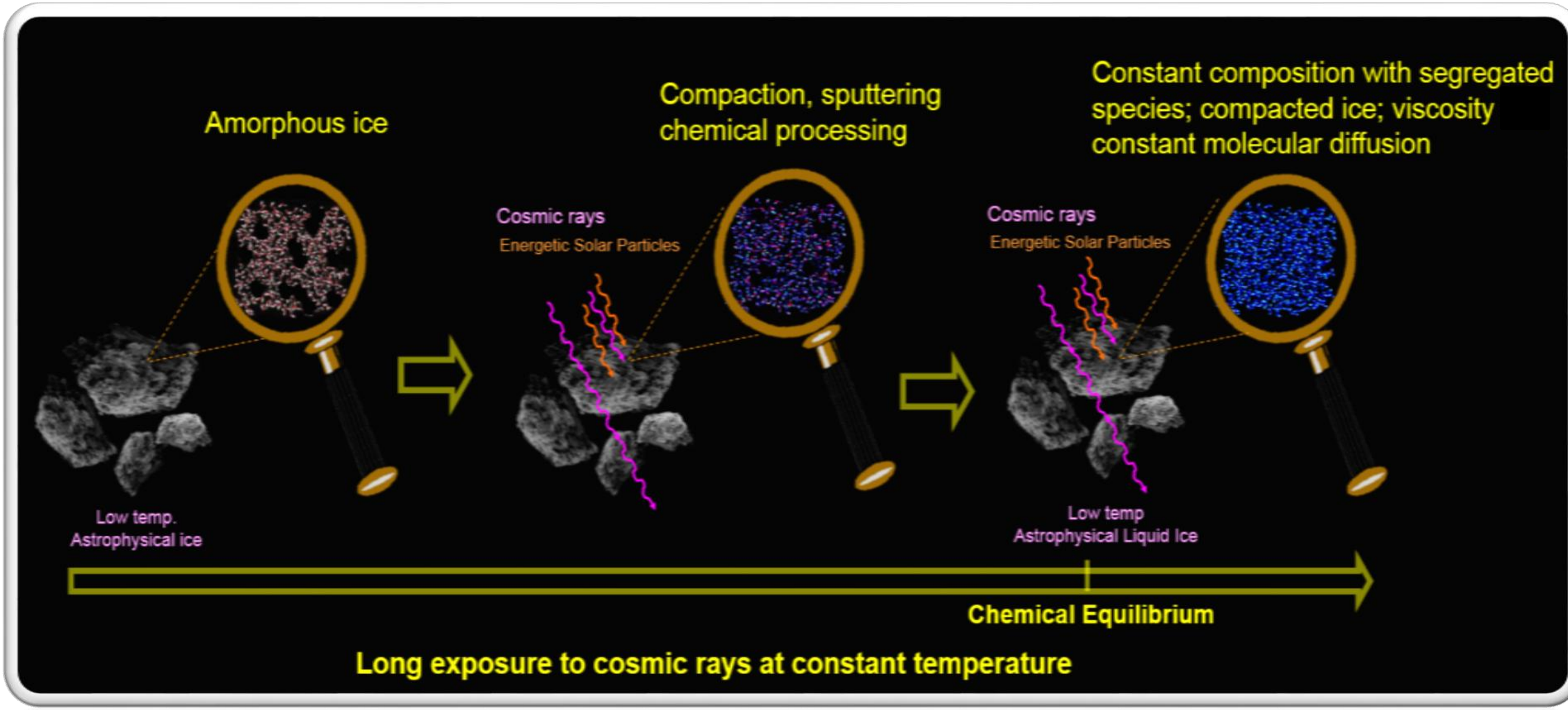
Properties also observed by molecular dynamics calculation (Alves da Silva, PhD thesis.in progress)





Liquid Astrophysical Ice

(Astrophysical ice after chemical equilibrium being reached (long exposure to ionizing radiation and kept at constant T and P)



Thank you for your attention!

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