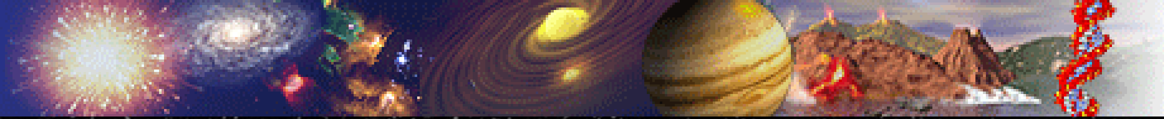
Chemistry of hydride-containing ices:

UV photoprocessing of a $H_2O:CH_4$ ice analog

R. Martín-Doménech[1] (rmartin@cab.inta-csic.es), G. M. Muñoz Caro[1], G. A. Cruz-Díaz[2], E. Moreno-Atahonero[1]

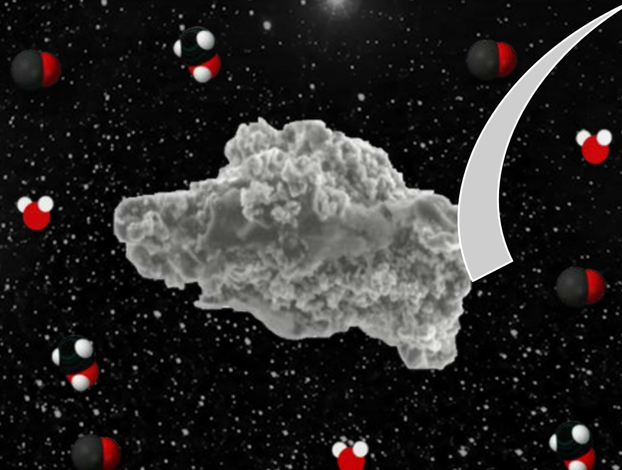
[1]Centro de Astrobiología (INTA-CSIC), Madrid, Spain
[2]NASA Ames Research Center, Mountain View, CA, USA



Astrophysical ice mantles composition

Low dust temperature

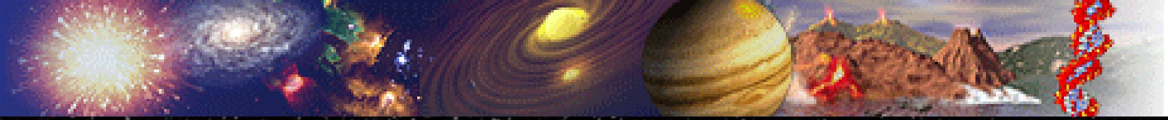
Molecules accrete
on top of dust grains
↓
ice mantles



Species	X_{H_2O} [%] MYSOs	LYSOs	BG Stars	Comets
Securely identified species :				
H_2O	100	100	100	100
CO	7^{15}_{4} (7)	21^{35}_{12} (18)	25^{43}_{20}	
	3-26	(<3)-85	9-67	0.4-30
CO_2	19^{25}_{12}	28^{37}_{23}	26^{39}_{18}	15^{24}_{10}
	11-27	12-50	14-43	4-30
CH_3OH	9^{23}_{5} (5)	6^{12}_{5} (5)	8^{10}_{6} (6)	
	(< 3)-31	(< 1)-25	(<1)-12	0.2-7
NH_3		6^{8}_{4} (4)		
	~7[f]	3-10	< 7	0.2-1.4
$\boxed{CH_4}$		4.5^{6}_{3} (3)		
	1-3	1-11	< 3	0.4-1.6
Likely identified species :				
H_2CO	~2-7	~6		0.11-1.0
OCN^-	$0.6^{0.7}_{0.3}$	$0.6^{0.8}_{0.4}$ (0.4)		
	0.1-1.9	(< 0.1)-1.1	<0.5	
OCS	0.03-0.16	≤1.6	<0.22	0.1-0.4

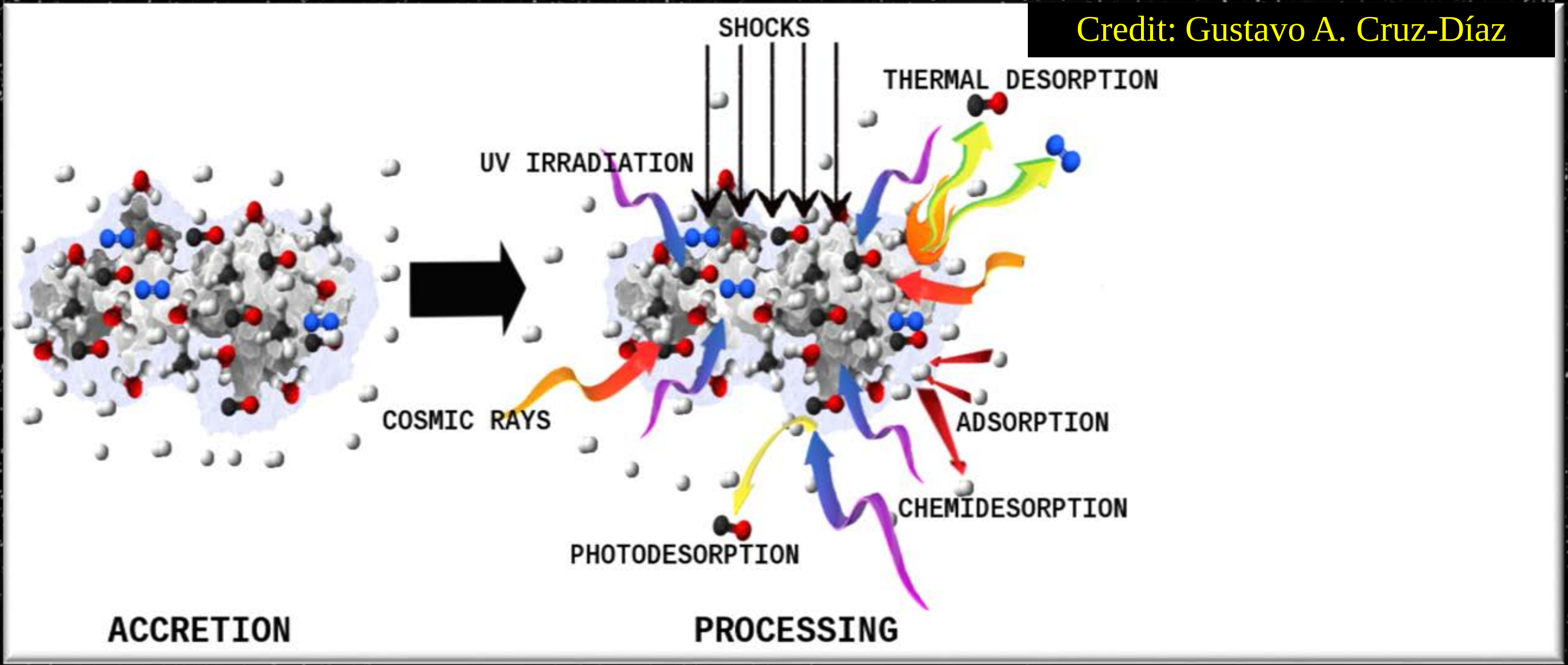
More species possibly present (e.g., N_2, O_2)

Boogert et al. 2015



1. Introduction

Energetic processing of ice mantles



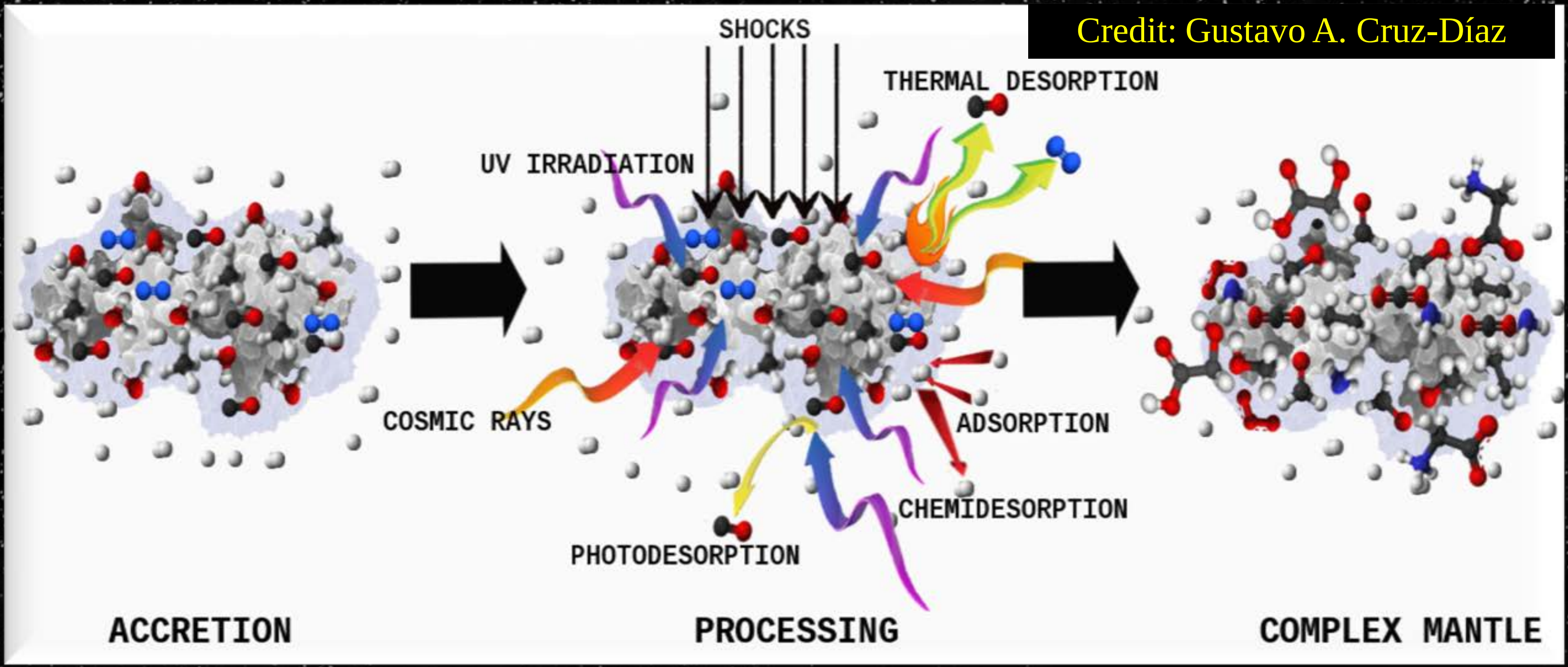
Ice mantles are energetically processed in dense cloud interiors

- Shocks
- Cosmic rays
- UV photons and X-rays

in circumstellar environmets

- Thermal processing

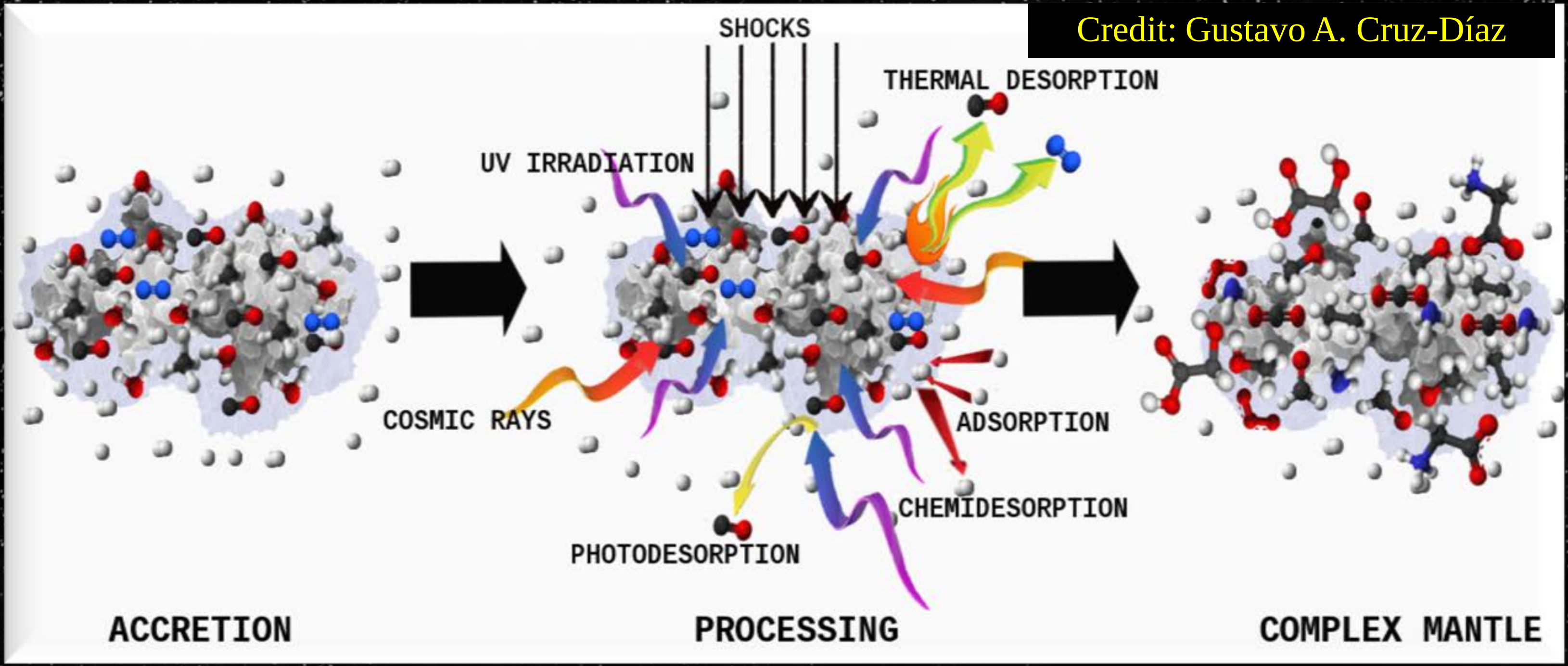
Energetic processing of ice mantles



Ice mantles are energetically processed in dense cloud interiors

- Shocks → Sputtering
- Cosmic rays → Non-thermal desorption / ice chemistry
- UV photons and X-rays → Non-thermal desorption / ice chemistry in circumstellar environments
- Thermal processing → Thermal desorption /ice chemistry

Energetic processing of ice mantles



Ice mantles are energetically processed in dense cloud interiors

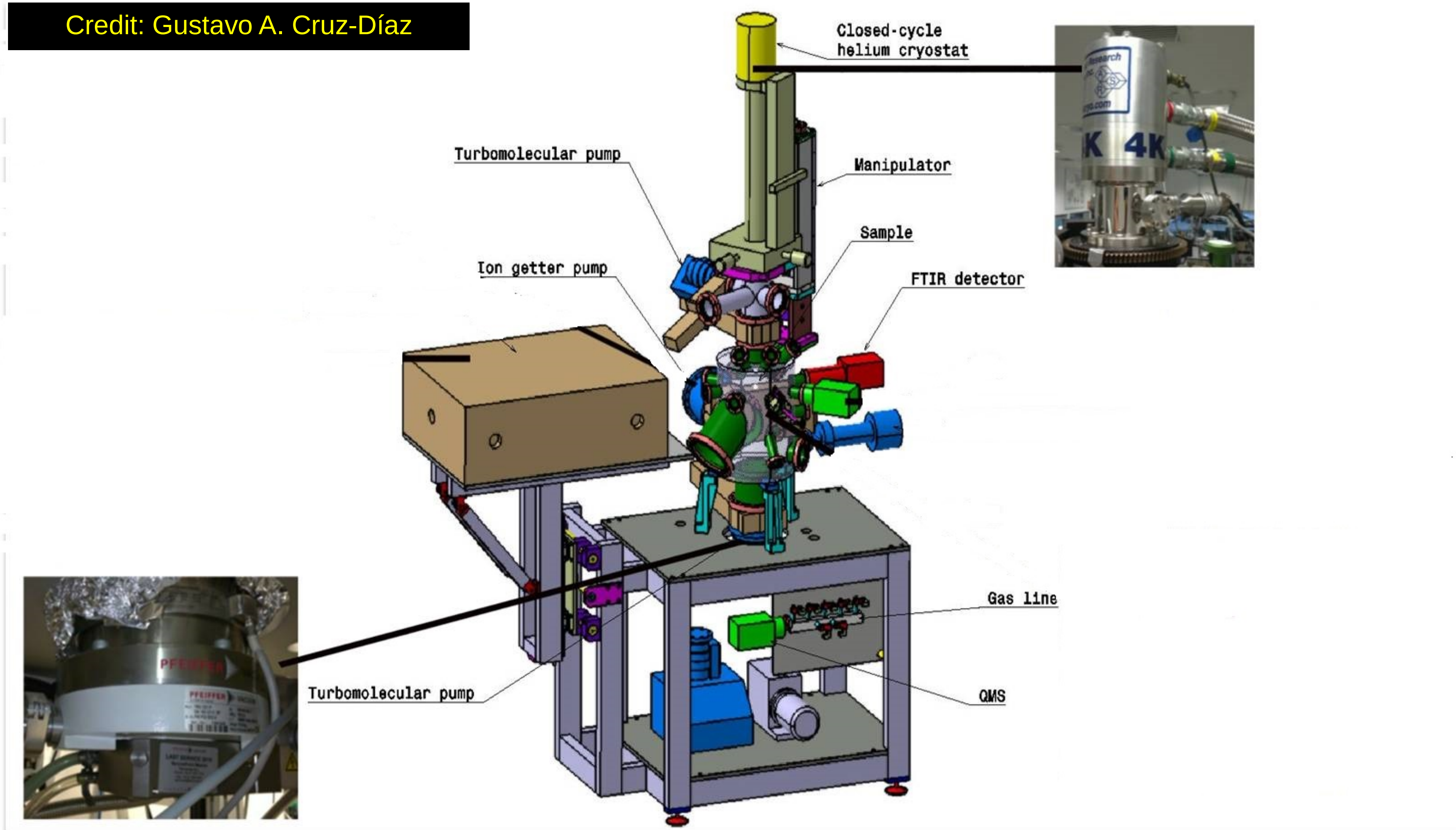
- Shocks → Sputtering
- Cosmic rays → Non-thermal desorption / ice chemistry
- UV photons and X-rays → Non-thermal desorption / ice chemistry in circumstellar environments
- Thermal processing → Thermal desorption /ice chemistry

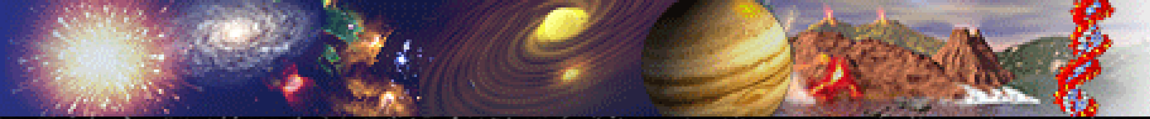
InterStellar Astrochemistry Chamber (ISAC)

ISAC is an UHV chamber with P~4 10^{-11} mbar (dense clouds interiors)

InterStellar Astrochemistry Chamber (ISAC)

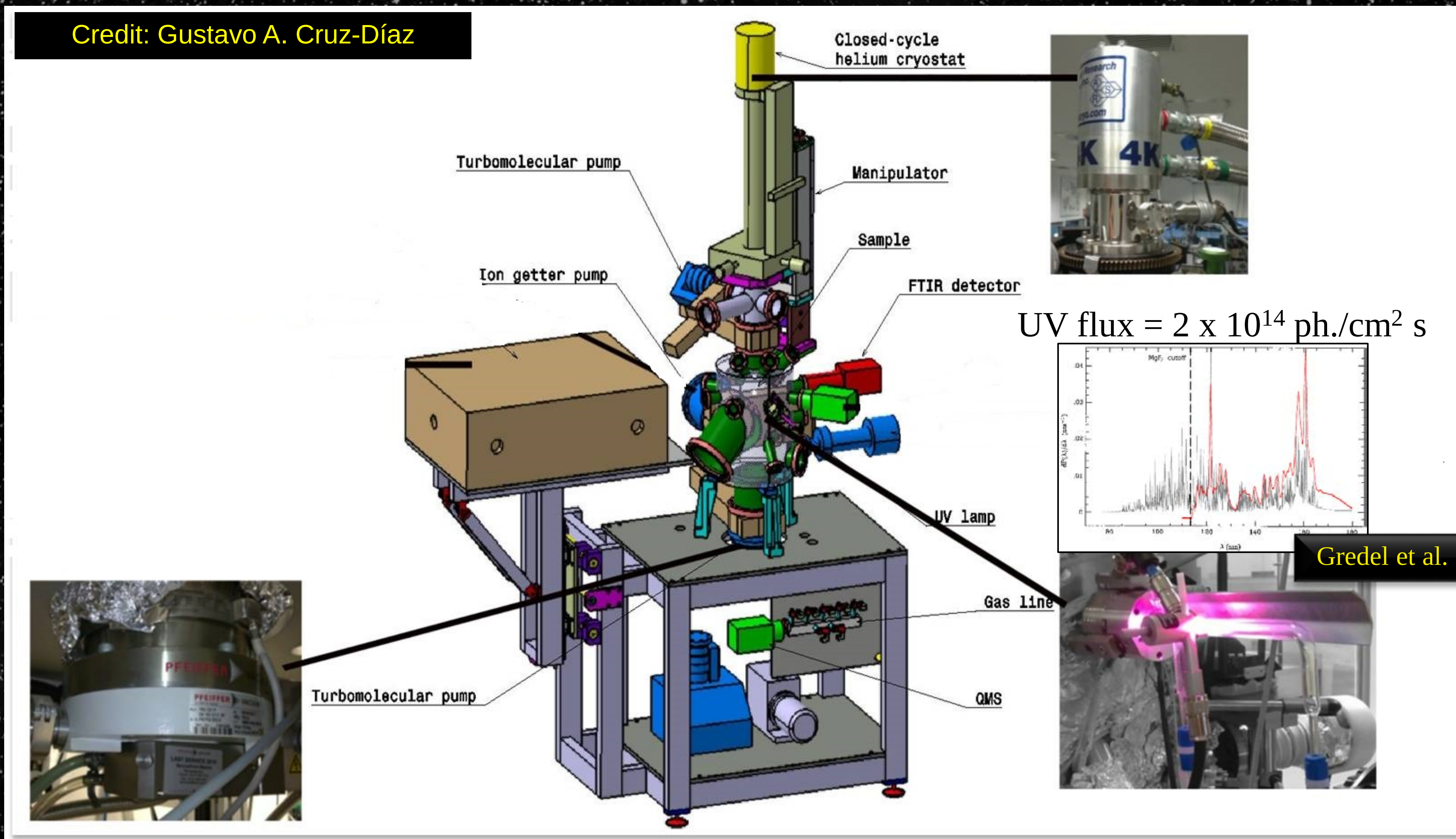
Credit: Gustavo A. Cruz-Díaz



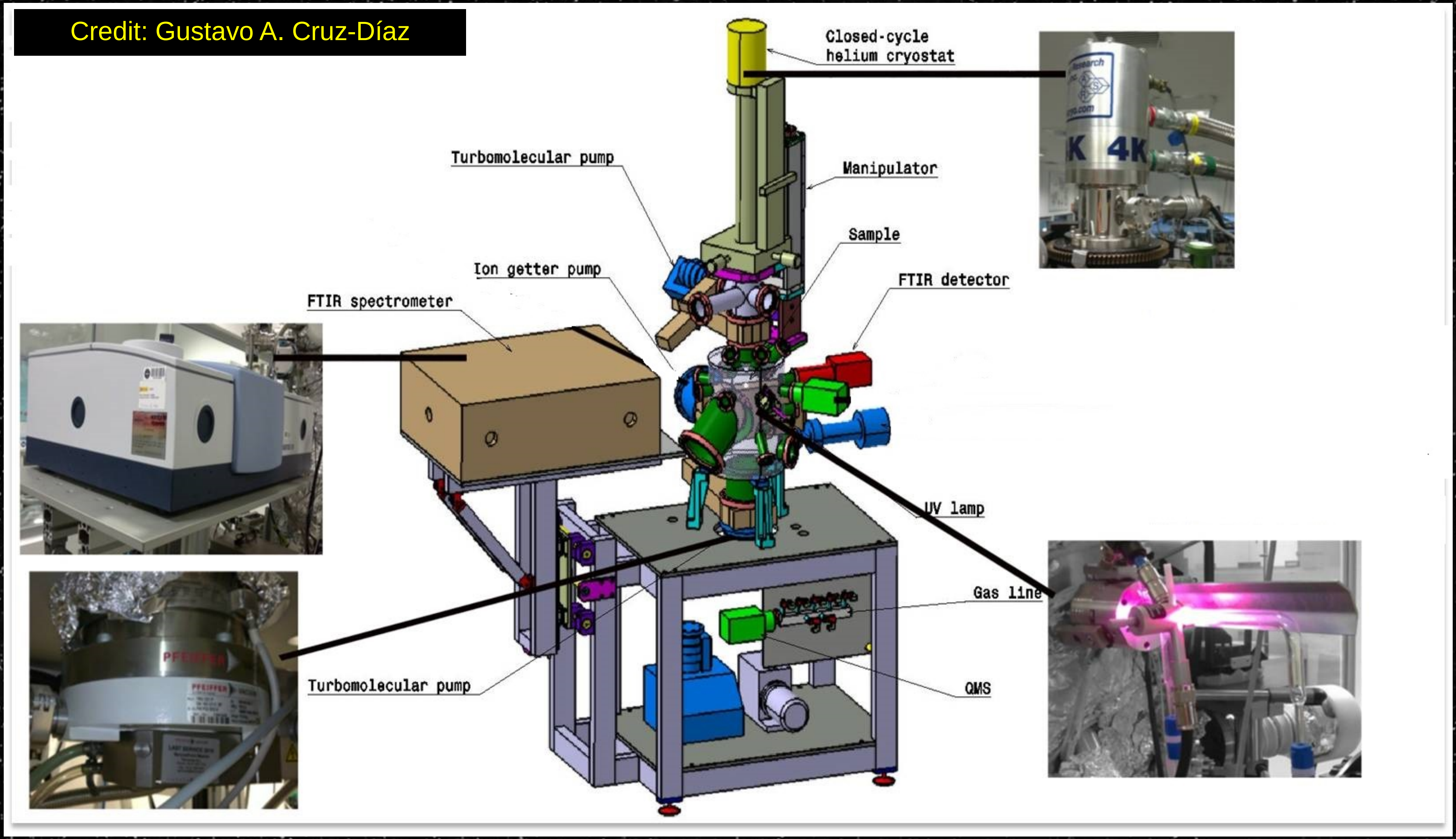


2. Experimental set-up

InterStellar Astrochemistry Chamber (ISAC)

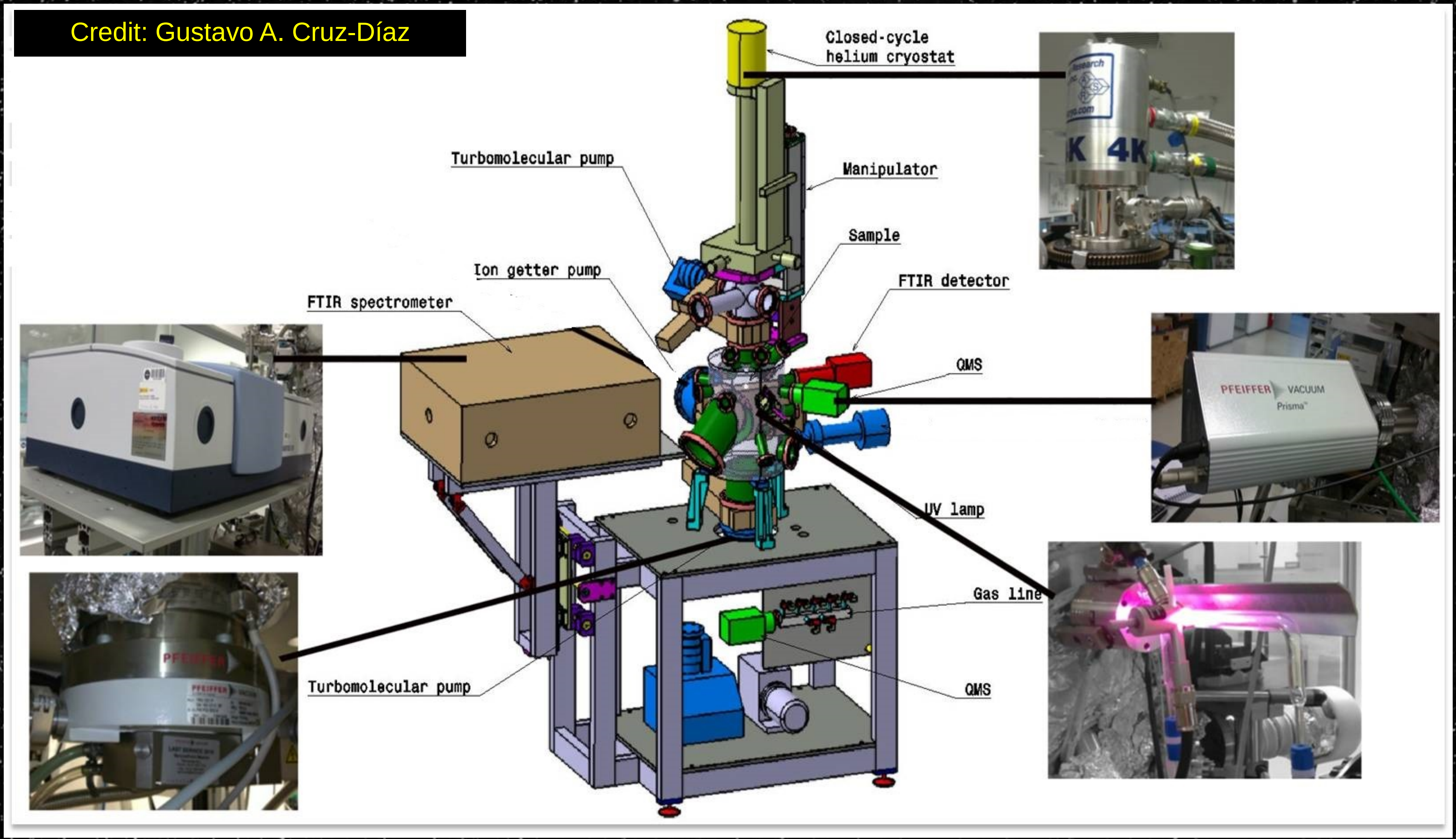


InterStellar Astrochemistry Chamber (ISAC)



InterStellar Astrochemistry Chamber (ISAC)

Credit: Gustavo A. Cruz-Díaz



Ice molecules divided in 2 groups depending on $E_d \leftrightarrow E_{h\nu}$

Different mechanisms?

Ice molecules divided in 2 groups depending on $E_d \leftrightarrow E_{h\nu}$

GROUP 1

ices with (*almost*) NO photodissociation ($E_{h\nu} < E_d$)

Example: CO[1] ice, N_2 ice

[1]No direct photodissociation, only occurs via

$$CO + h\nu \longrightarrow CO^*$$

$$CO^* + CO \longrightarrow CO_2 + C$$

Ice molecules divided in 2 groups depending on $E_d \leftrightarrow E_{h\nu}$

GROUP 1

ices with (*almost*) NO photodissociation ($E_{h\nu} < E_d$)

Example: CO[1] ice, N_2 ice

- Photodesorption of original ice components
- ~~Photodesorption of photoproducts~~ (no ph-chemistry)

[1] No direct photodissociation, only occurs via

$$CO + h\nu \longrightarrow CO^*$$

$$CO^* + CO \longrightarrow CO_2 + C$$

Ice molecules divided in 2 groups depending on $E_d \leftrightarrow E_{h\nu}$

GROUP 1

Photodesorption of original ice components via:

- ~~Direct photodesorption~~ (see, e.g., Bertin et al. 2012)
- Indirect photodesorption (DIET)

(Muñoz Caro et al. 2010, Fayolle et al. 2011, 2013, Bertin et al. 2012, 2014, Chen et al. 2014)

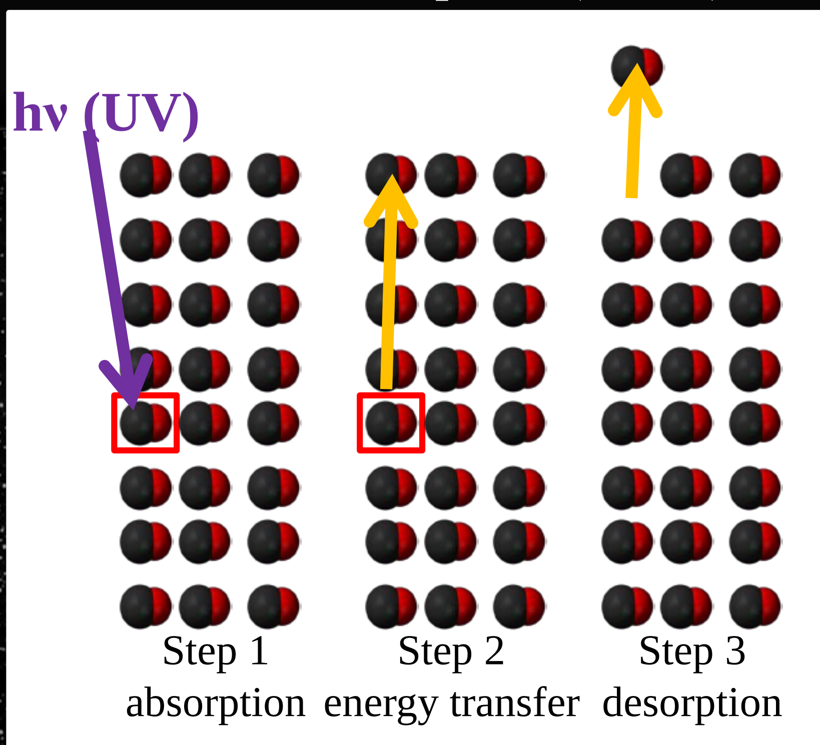
Ice molecules divided in 2 groups depending on $E_d \leftrightarrow E_{h\nu}$

GROUP 1

Photodesorption of original ice components via:

- ~~Direct desorption~~ (see, e.g., Bertin et al. 2012)
- Indirect desorption (DIET)

al. 2011, 2013, Bertin et al. 2012, 2014,



Indirect desorption induced by electronic transitions (**DIET**): Electronic excitation energy is transfered to neighbors and provides energy to surface molecules breaking intermolecular bonds.

Ice molecules divided in 2 groups depending on $E_d \leftrightarrow E_{h\nu}$

GROUP 2

ices with photodissociation ($E_{h\nu} < E_d$)

Example: CO_2 ice, CH_3OH ice, CH_4 ice, etc. (most molecules)

Ice molecules divided in 2 groups depending on $E_d \leftrightarrow E_{h\nu}$

GROUP 2

ices with photodissociation ($E_{h\nu} < E_d$)

Example: CO_2 ice, CH_3OH ice, CH_4 ice, etc. (most molecules)

- Photodesorption of original ice components
- Photodesorption of photoproducts (photochemistry)

Ice molecules divided in 2 groups depending on $E_d \leftrightarrow E_{h\nu}$

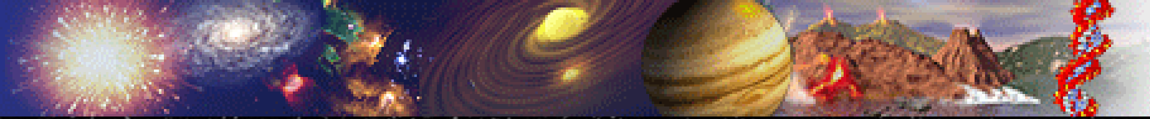
GROUP 2

ices with photodissociation ($E_{h\nu} < E_d$)

Example: CO_2 ice, CH_3OH ice, CH_4 ice, etc. (most molecules)

- Photodesorption of original ice components
- Photodesorption of photoproducts (photochemistry)

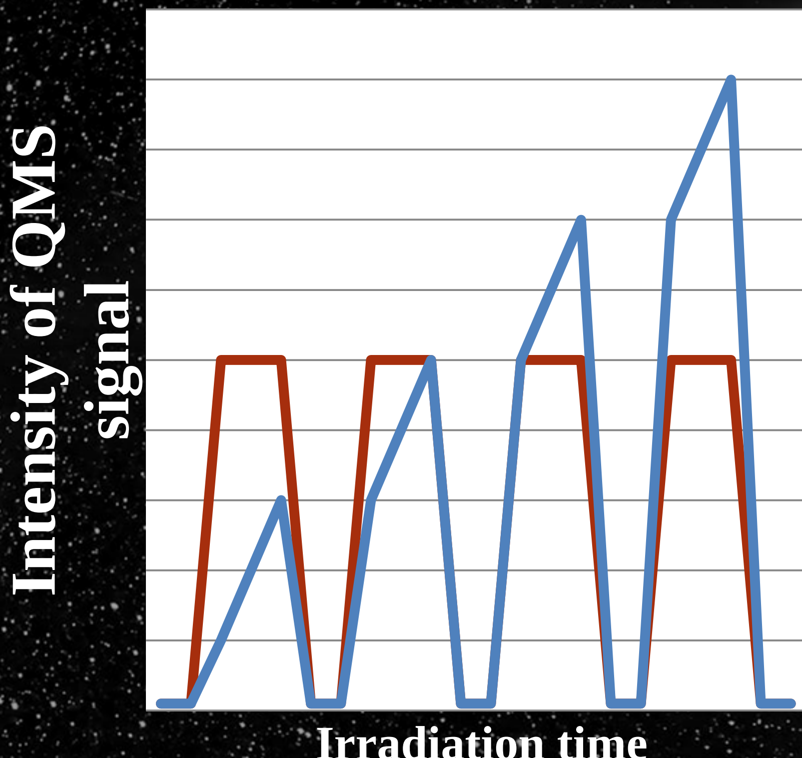
Additional photodesorption mechanisms!!



Additional desorption mechanisms upon photodissociation

GROUP 2

Photoproducts desorb with two yield vs fluence patterns



Two different photodesorption patterns

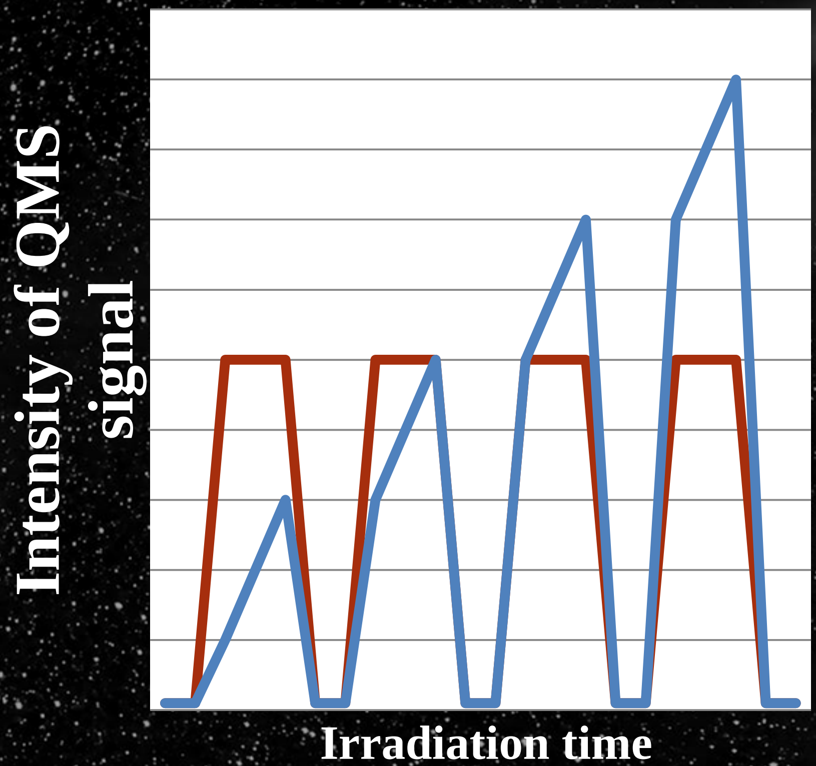
↕

Two different photodesorption mechanisms

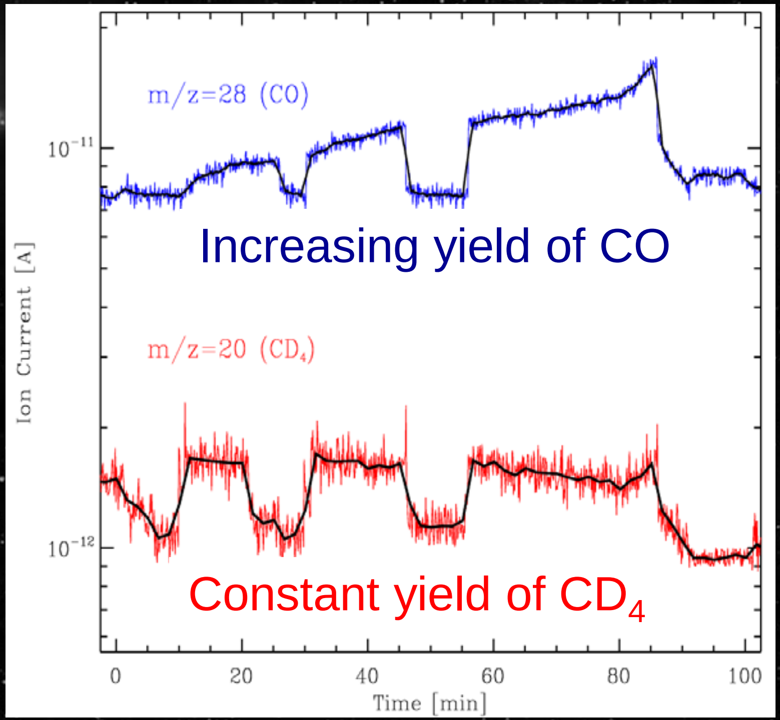
Additional desorption mechanisms upon photodissociation

GROUP 2

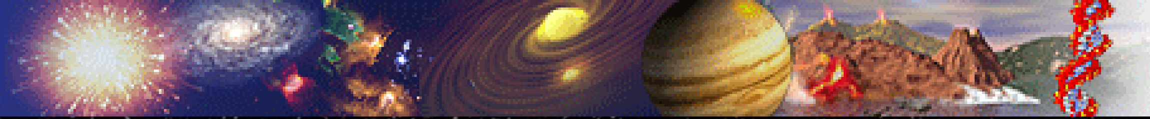
Photoproducts desorb with two yield vs fluence patterns



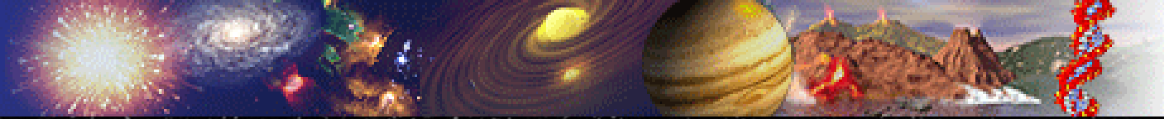
CD_3OD ice irradiation



Cruz-Díaz et al. 2016, A&A 592, A68

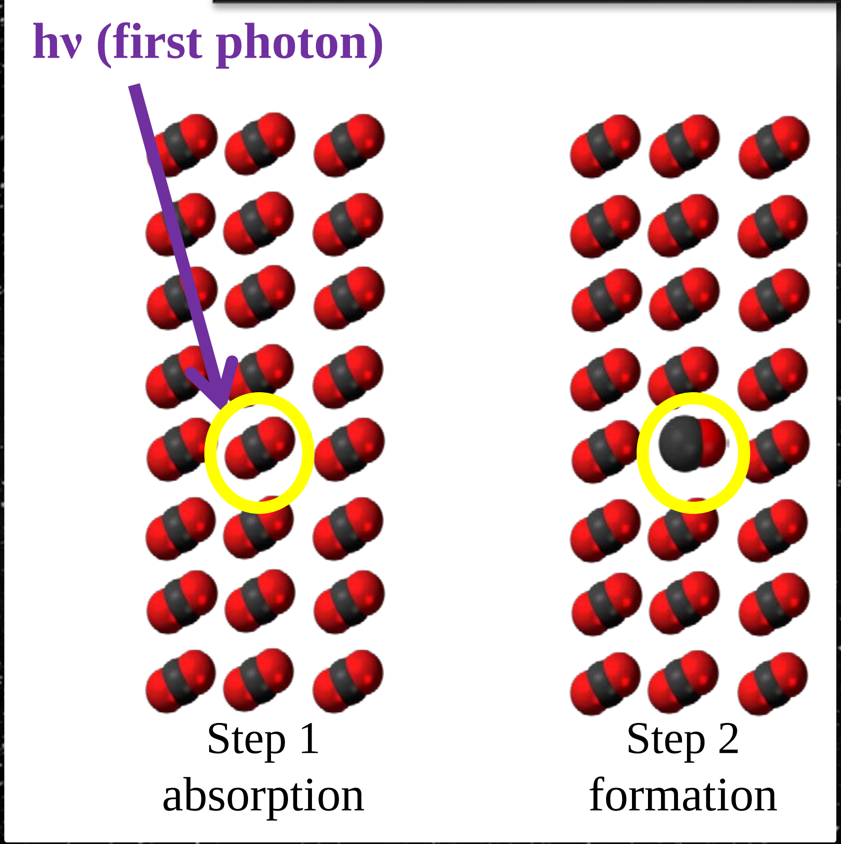


Increasing yield $\leftrightarrow$ indirect desorption of photoproducts (DIET)



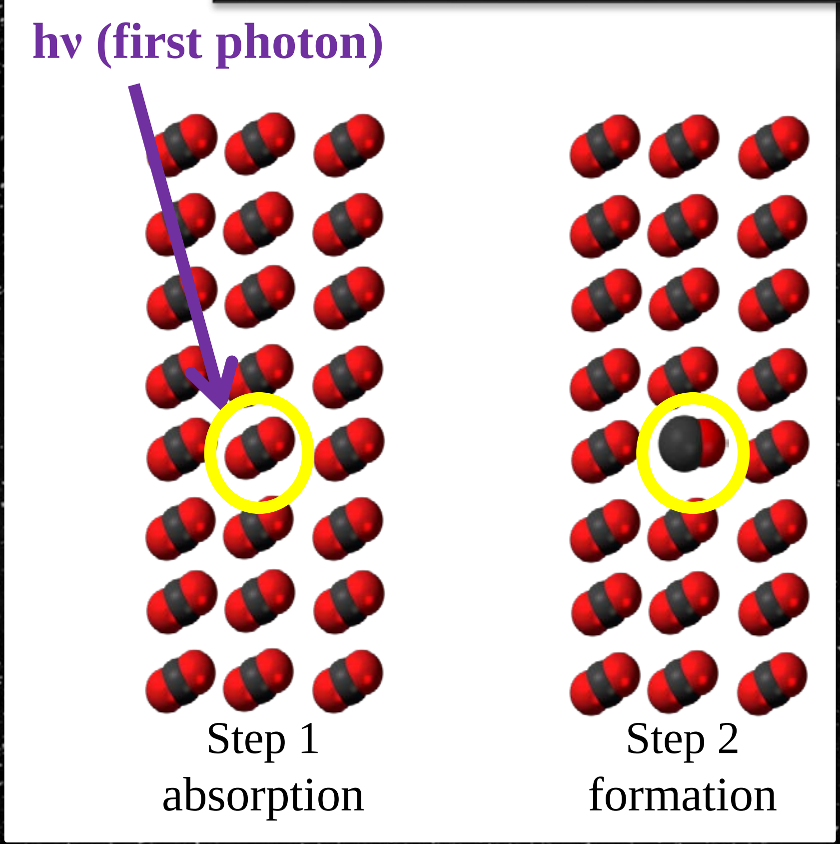
Increasing yield ↔ indirect desorption of photoproducts (DIET)

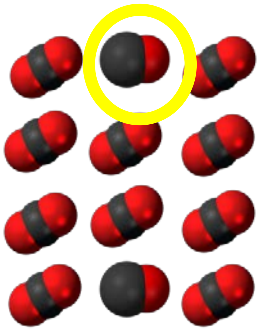
Photoproducts formed in the ice bulk (first photon)



Increasing yield ↔ indirect desorption of photoproducts (DIET)

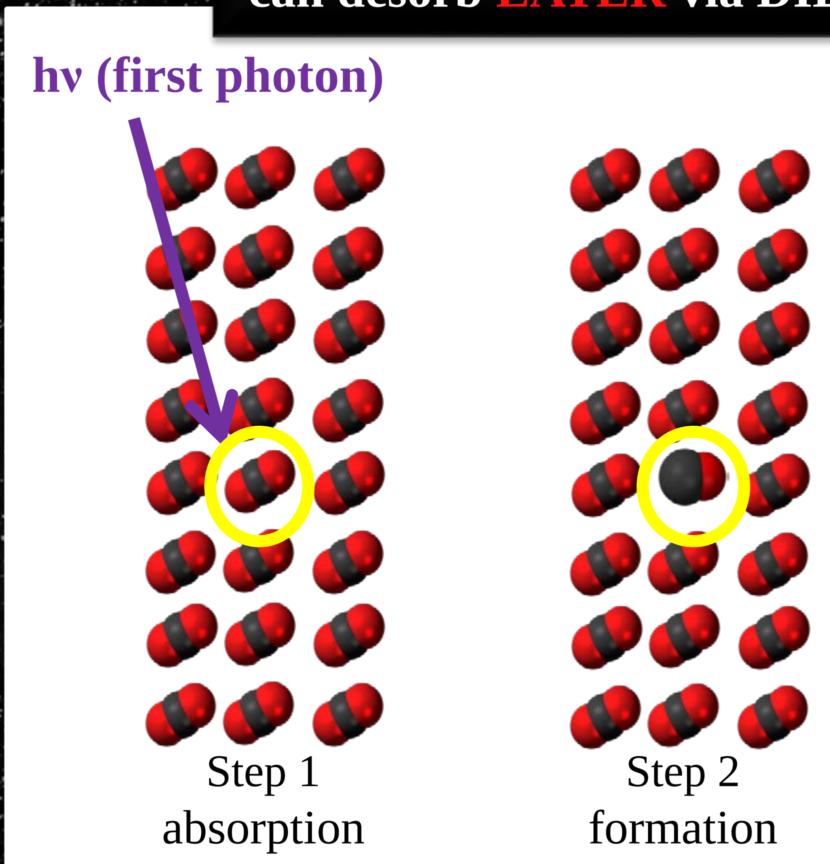
Photoproducts formed in the ice bulk (first photon)

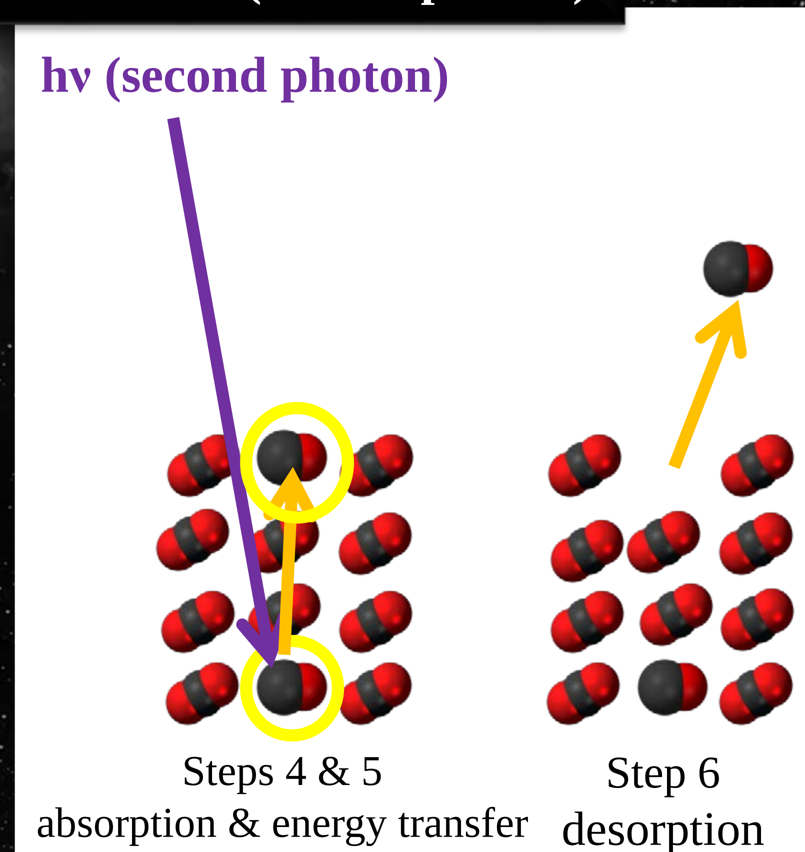


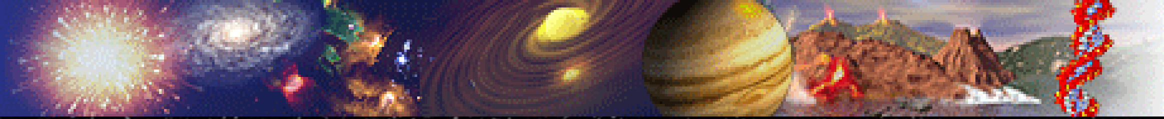


Increasing yield ↔ indirect desorption of photoproducts (DIET)

Photoproducts formed in the ice bulk (first photon) can desorb LATER via DIET mechanism (second photon)



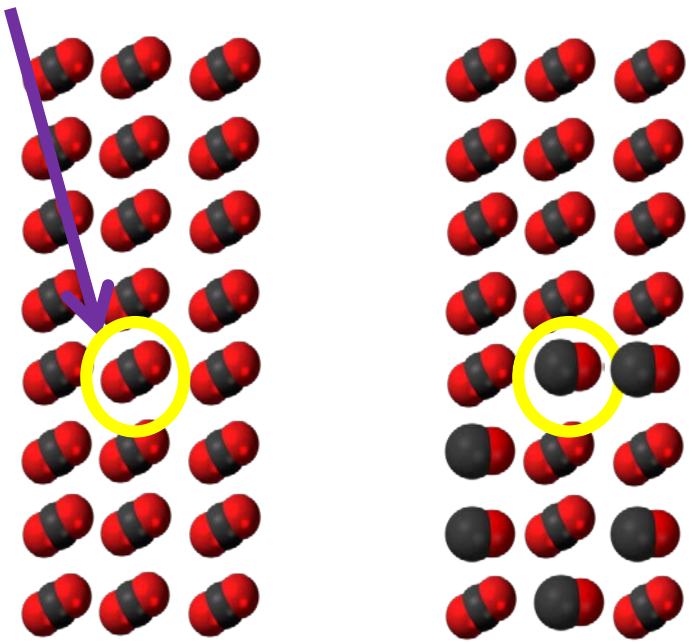




Increasing yield ↔ indirect desorption of photoproducts (DIET)

Photoproduct ACCUMULATES in the ice during irradiation
➔ photodesorption yield INCREASES with fluence

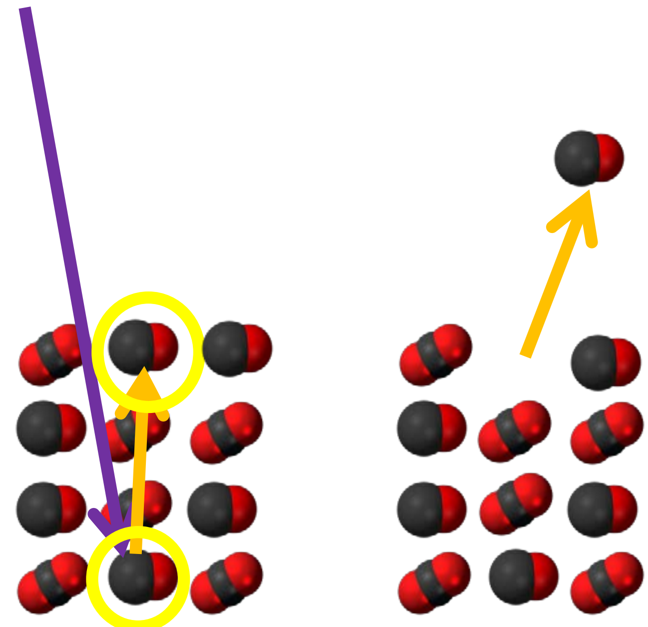
hν (first photon)



Step 1
absorption

Step 2
formation

hν (second photon)

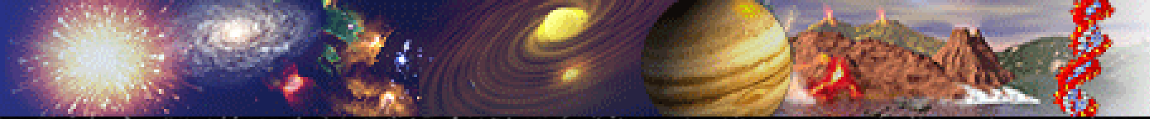


Steps 4 & 5
absorption & energy transfer

Step 6
desorption

Additional desorption mechanism upon photodissociation

Constant yield ↔ inmediate desorption of photoproducts



Additional desorption mechanism upon photodissociation

Constant yield ↔ inmediate desorption of photoproducts

Photoproducts formed on the ice surface (first photon)

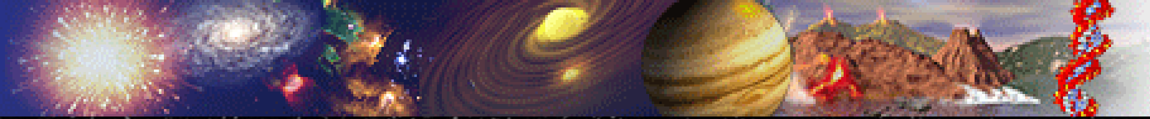
- **by photofragmentation**
- **by recombination of radicals**

$$CH_3OH + h\nu \rightarrow \left\{ \begin{array}{l} CH_3 + OH \\ CH_2OH + H \end{array} \right\} \rightarrow CH_3 + H \rightarrow CH_4$$

(first photon)

CH_3OH ice surface

Cruz-Díaz et al. 2016, A&A 592, A68



Additional desorption mechanism upon photodissociation

Constant yield ↔ inmediate desorption of photoproducts

Photoproducts formed on the ice surface (first photon)

- **by photofragmentation**
- **by recombination of radicals**

can desorb INMEDIATELY because of the excess energy (no more photons needed)

Fayolle et al. 2013, Fillion et al. 2014

$$CH_3OH + h\nu \rightarrow \left\{ \begin{array}{c} CH_3 + OH \\ CH_2OH + H \end{array} \right\} \rightarrow CH_3 + H \rightarrow CH_4$$

(first photon)

CH_3OH ice surface

Cruz-Díaz et al. 2016, A&A 592, A68

Additional desorption mechanism upon photodissociation

Constant yield ↔ inmediate desorption of photoproducts

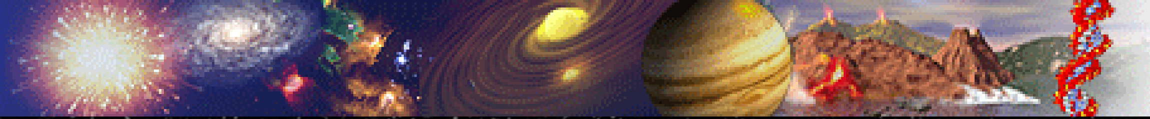
Photoproducts DO NOT ACCUMULATE on the ice surface during irradiation
→ photodesorption yield is CONSTANT with fluence

$$CH_3OH + h\nu \rightarrow \left\{ \begin{array}{l} CH_3 + OH \\ CH_2OH + H \end{array} \right\} \rightarrow CH_3 + H \rightarrow CH_4 \uparrow$$

(first photon)

CH_3OH ice surface

Cruz-Díaz et al. 2016, A&A 592, A68



Additional desorption mechanism upon photodissociation

Constant yield ↔ inmediate desorption of photoproducts

Photoproducts DO NOT ACCUMULATE on the ice surface during irradiation
→ photodesorption yield is CONSTANT with fluence

PHOTOCHEMIDESORPTION

Martín-Doménech et al. 2016, A&A 589, A107
Cruz Díaz et al. 2016, A&A 592, A68

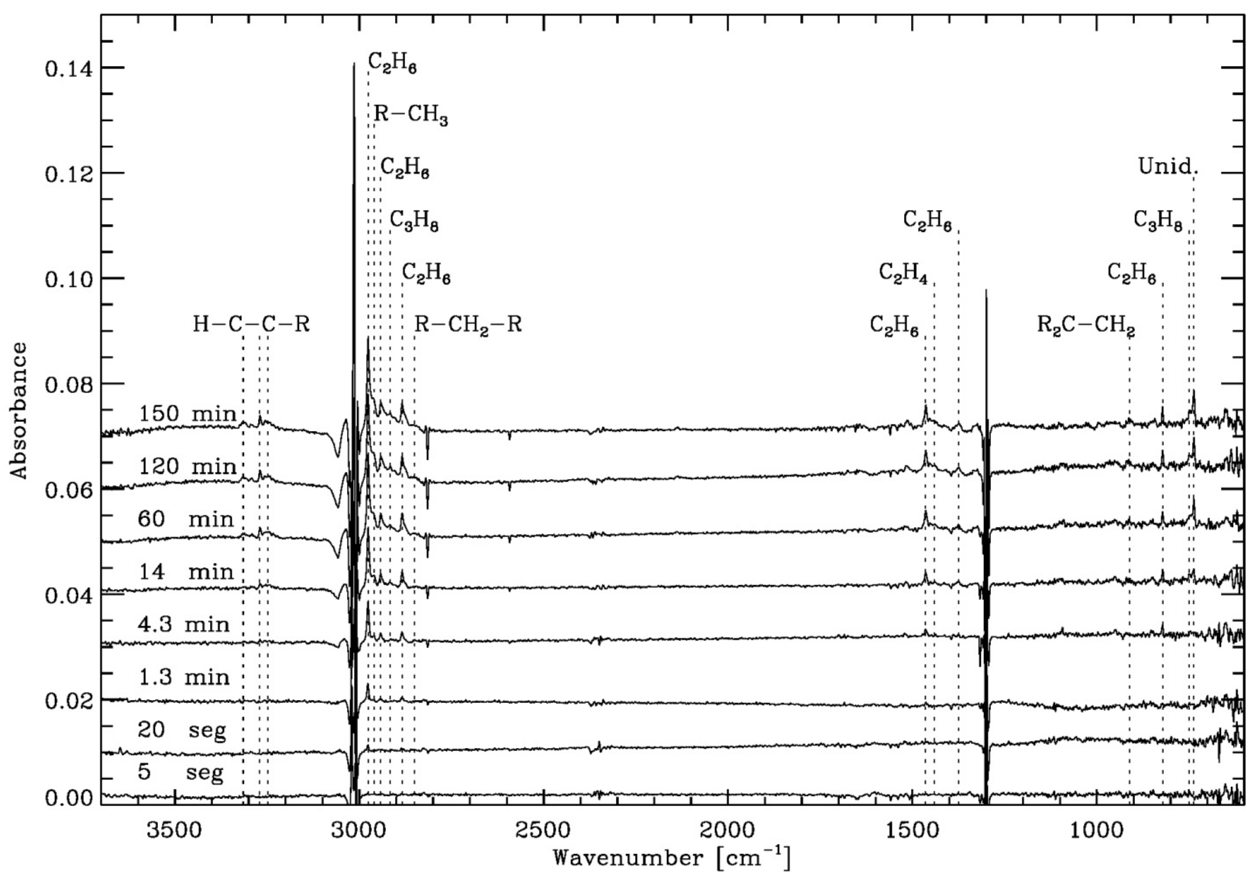
$$CH_3OH + h\nu \rightarrow \left\{ \begin{array}{c} CH_3 + OH \\ CH_2OH + H \end{array} \right\} \rightarrow CH_3 + H \rightarrow CH_4 \uparrow$$

(first photon)

CH_3OH ice surface

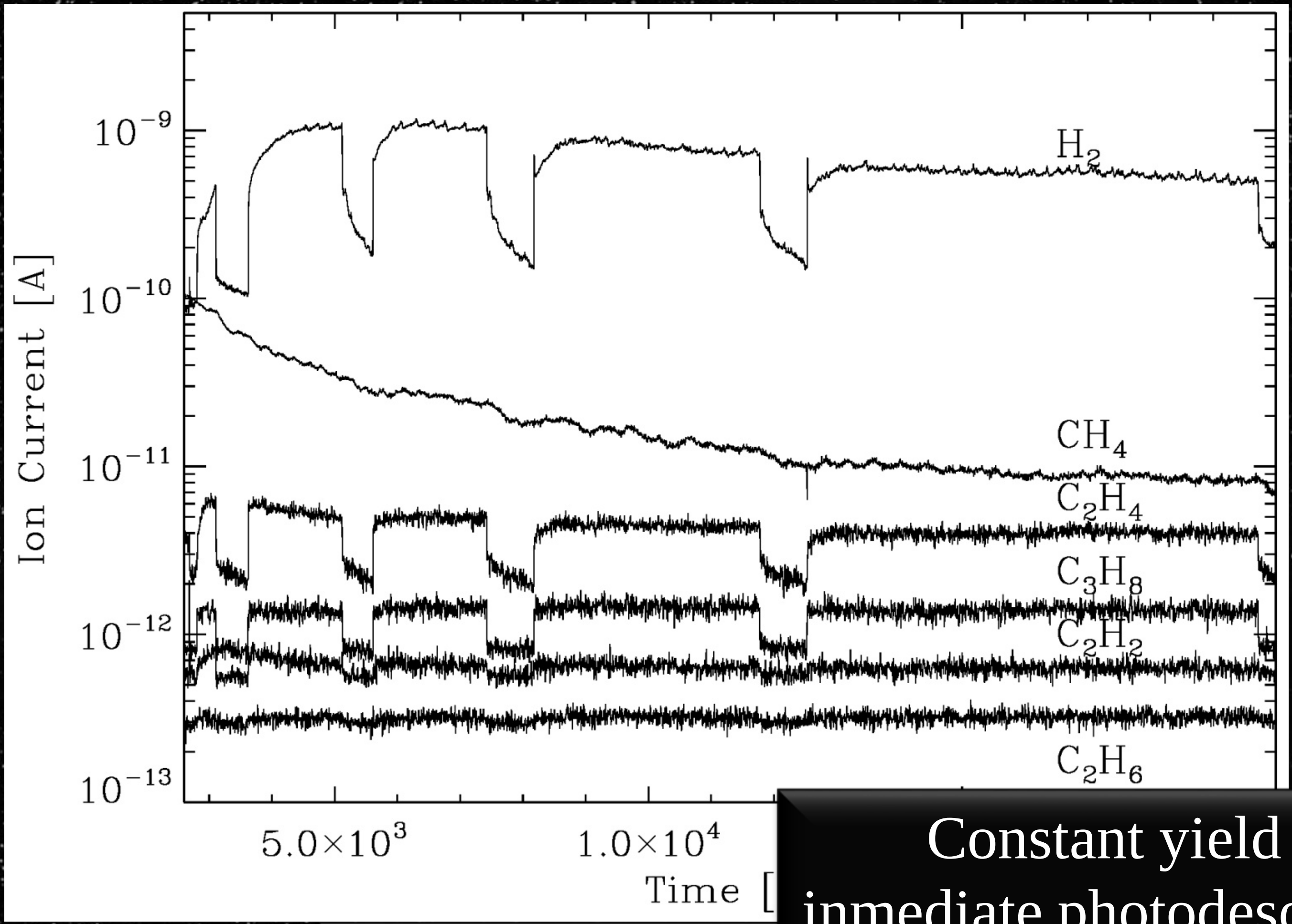
Cruz-Díaz et al. 2016, A&A 592, A68

Photodissociation of CH_4 → Formation of photoproducts



Cruz-Díaz et al., *in prep.*

Photodesorption of photoproducts observed by QMS

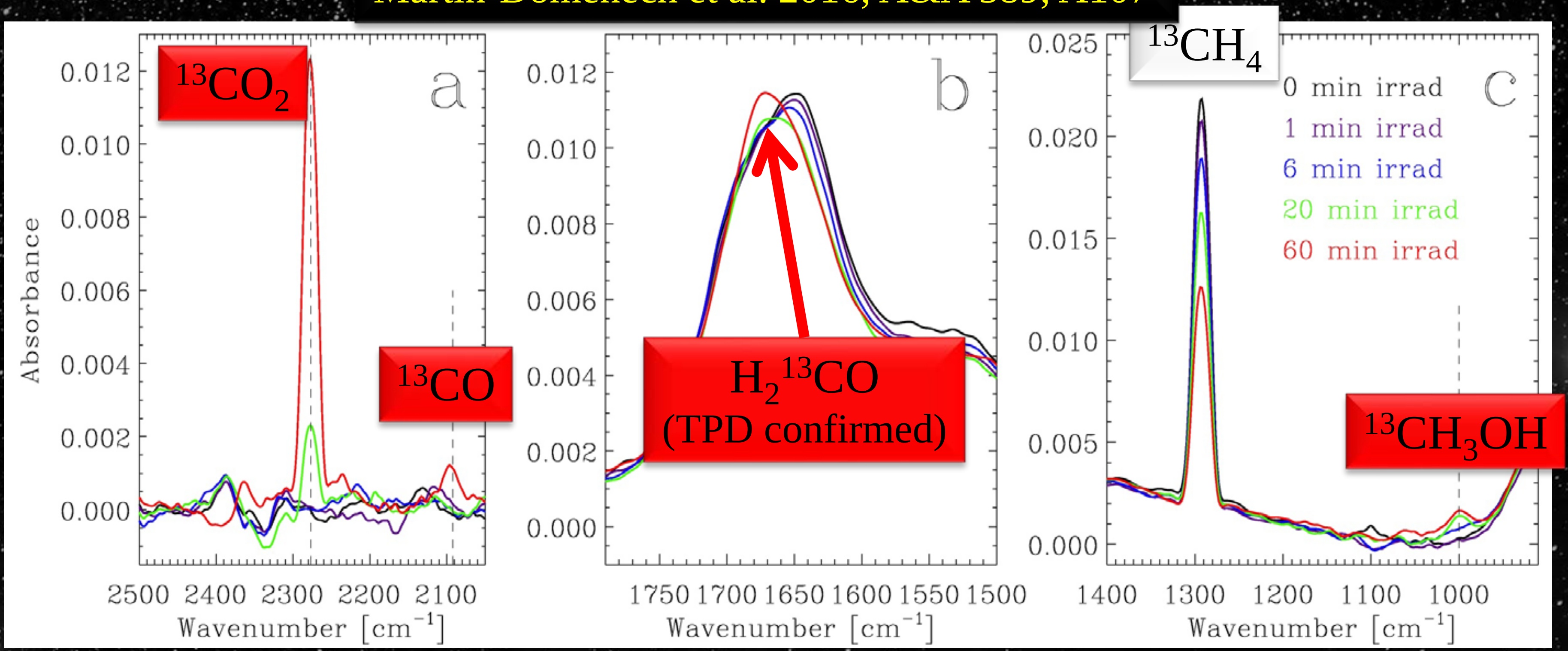


Cruz-Díaz et al., *in p*

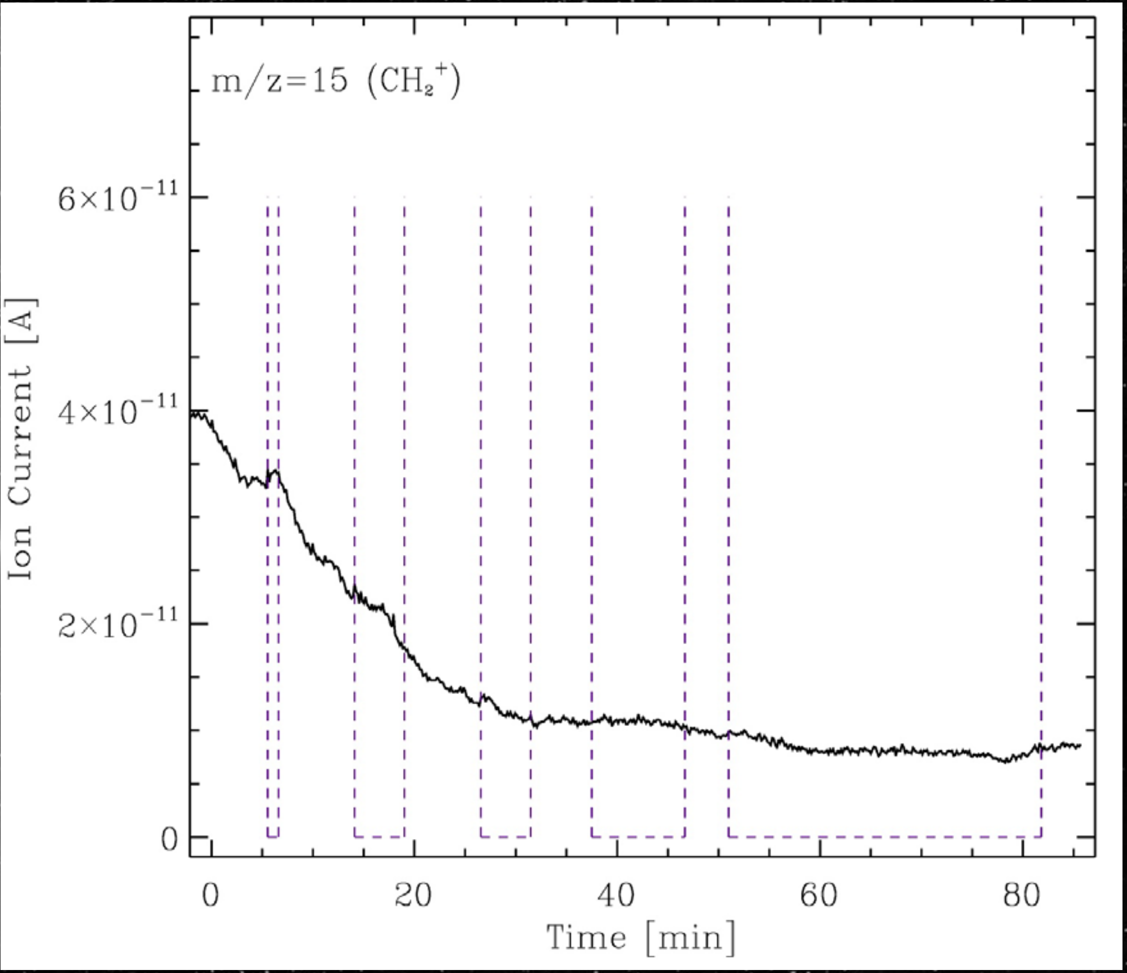
Constant yield = inmediate photodesorption (photochemidesorption)

Formation of photoproducts → new IR bands during irradiation

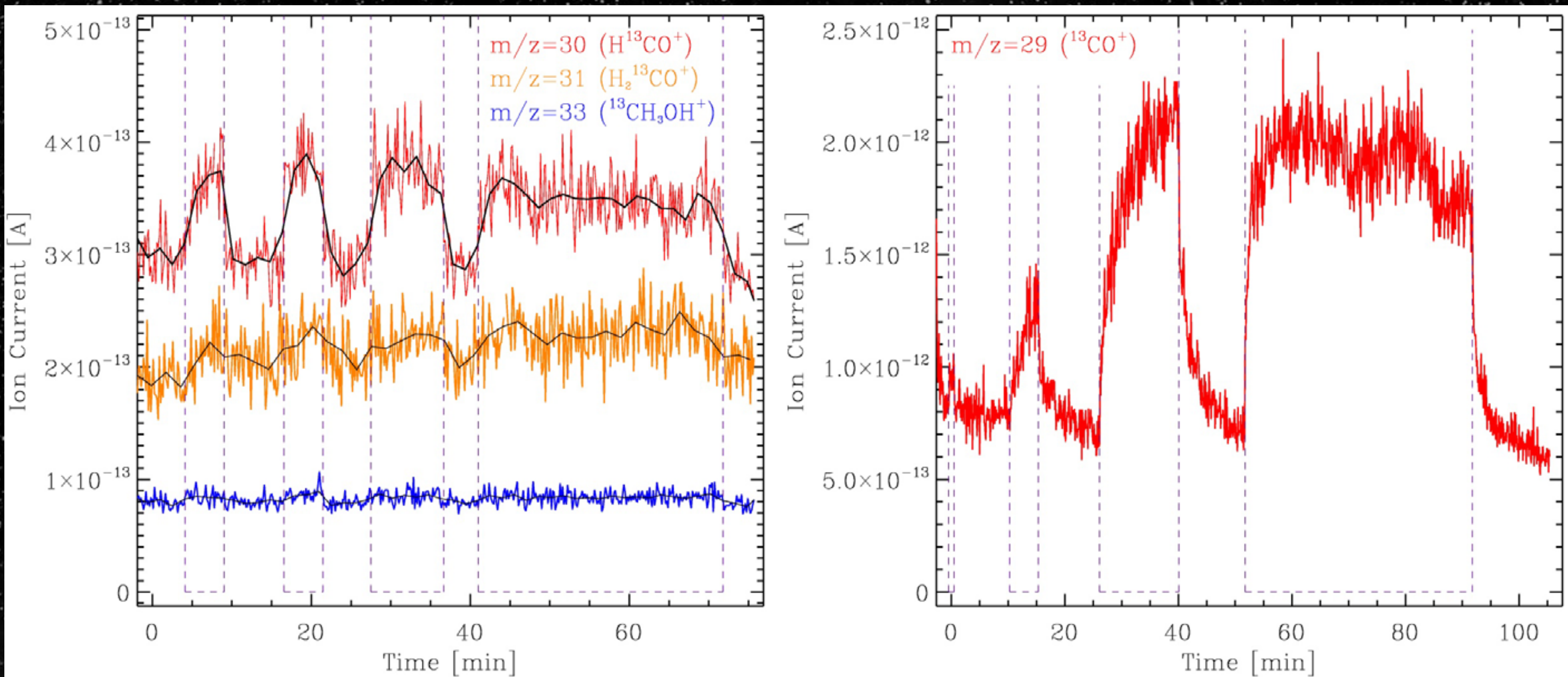
Martín-Doménech et al. 2016, A&A 589, A107



Photodesorption of CH_4 not observed by QMS



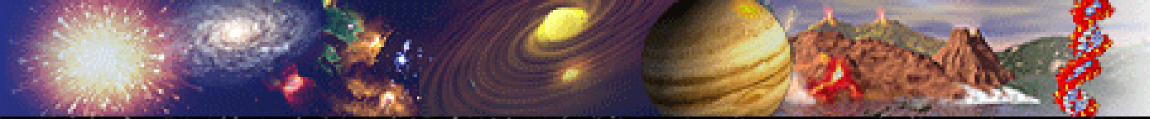
Photodesorption of H_2CO and CO observed by QMS



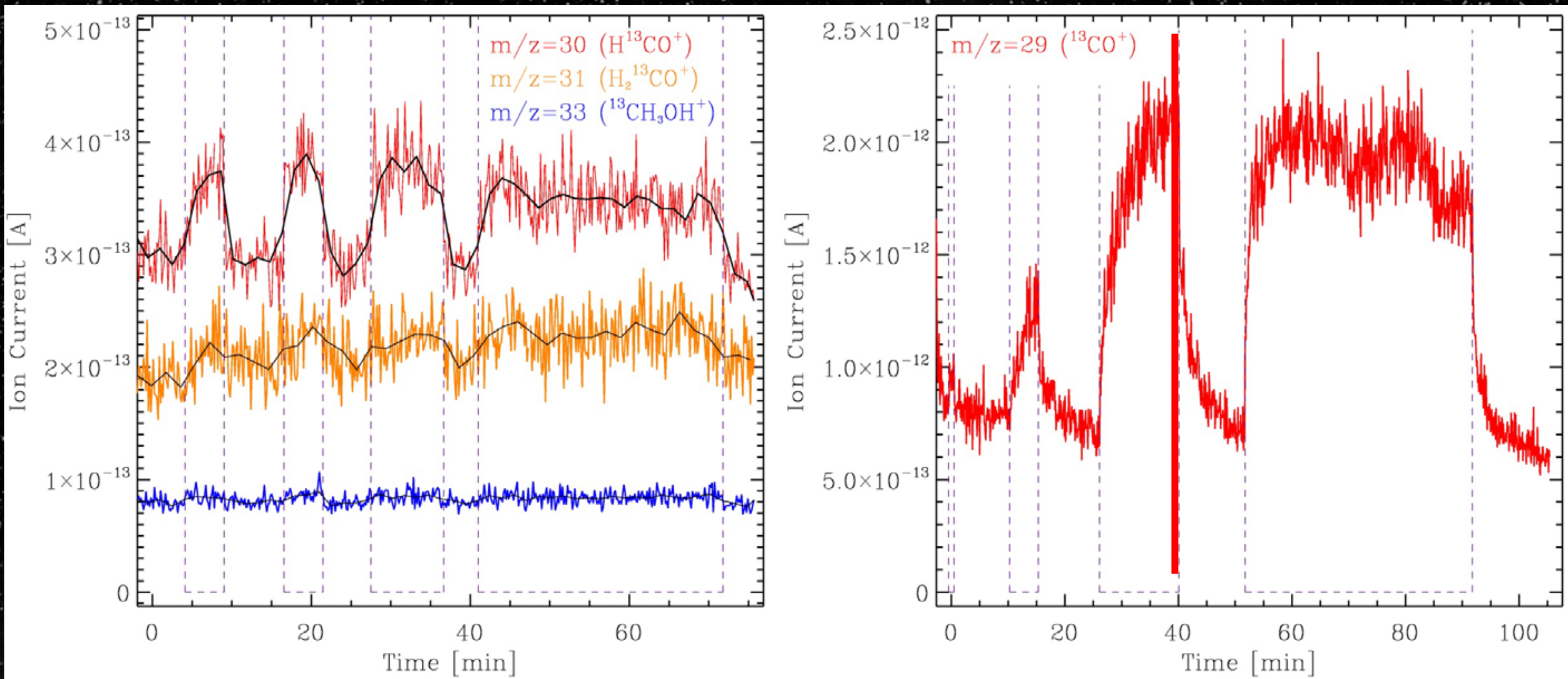
Martín-Doménech et al. 2016, A&A 589, A107

Constant yield = inmediate photodesorption (photochemidesorption)

Increasing yield = indirect photodesorption (DIET)



Photodesorption of H_2CO and CO quantified by QMS



Martín-Doménech et al. 2016, A&A 589, A107

Y_{pd} (H_2CO)= 4.4 x 10^{-5} mol. / inc. ph.

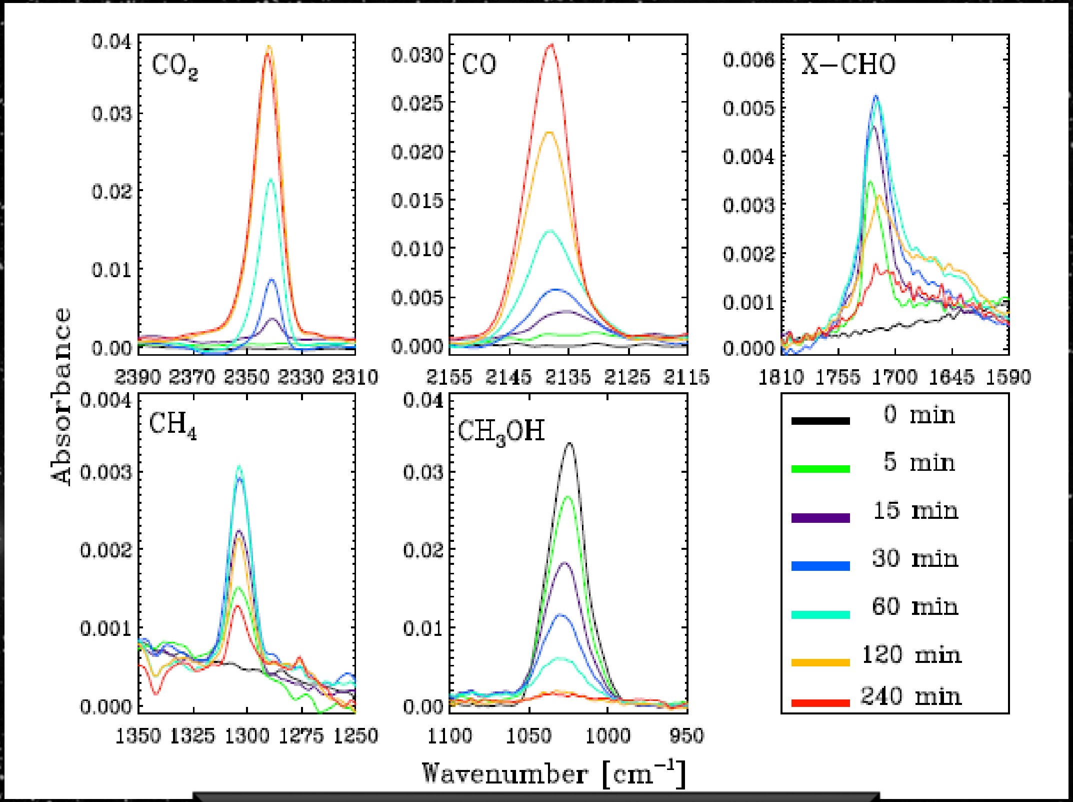
Y_{pd} (CO)= 1.5 x 10^{-4} mol. / inc. ph.

	Photodesorption of CH_4
CH_4 ice	⃠
H_2O:CH_4 ice	⃠
CH_3OH ice	O

↓

Additional desorption mechanism for photoproducts

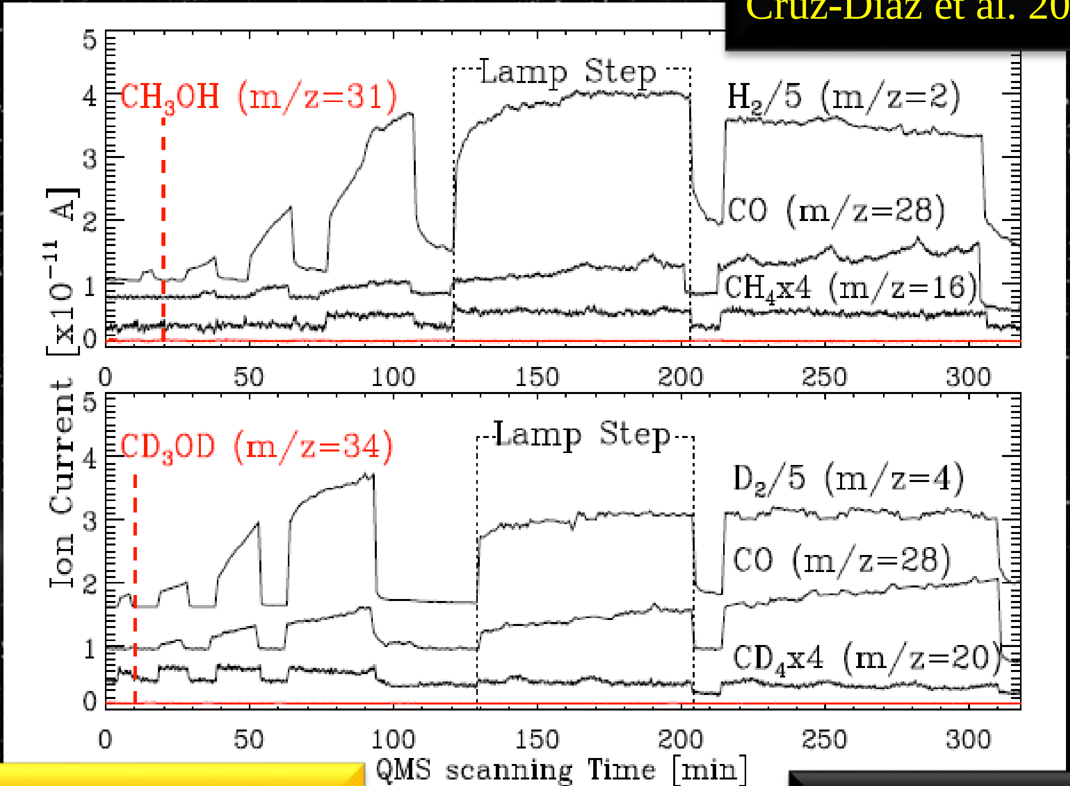
Formation of photoproducts → new IR bands during irradiation



Cruz-Díaz et al. 2016, A&A 592, A68

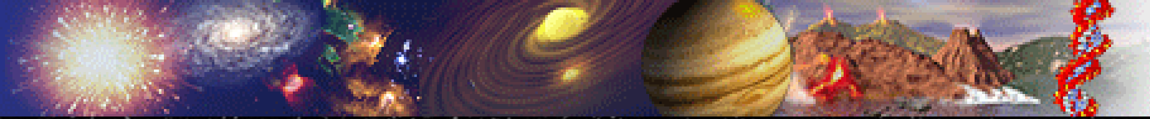
Photodesorption of H_2CO and CO observed by QMS

Cruz-Díaz et al. 2016, A&A 592, A68



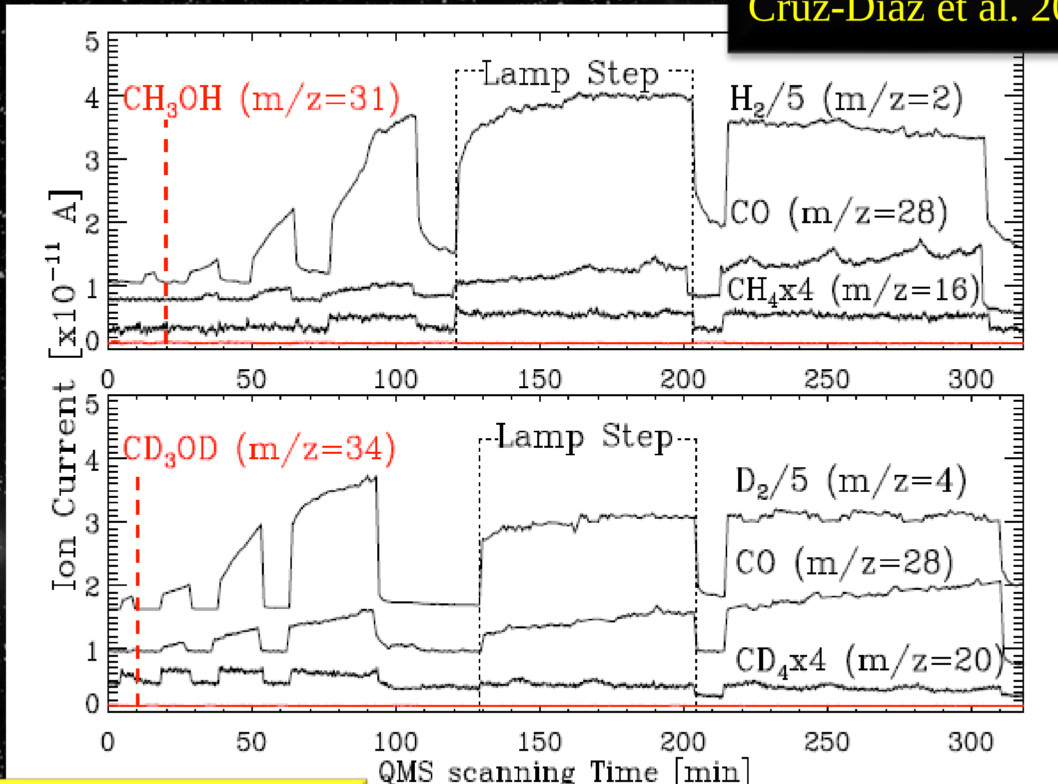
$CH_4 \rightarrow$ Constant yield = inmediate photodesorption (photochemidesorption)

CO $\rightarrow$Increasing yield = indirect photodesorption (DIET)



Photodesorption of H_2CO and CO observed by QMS

Cruz-Díaz et al. 2016, A&A 592, A68

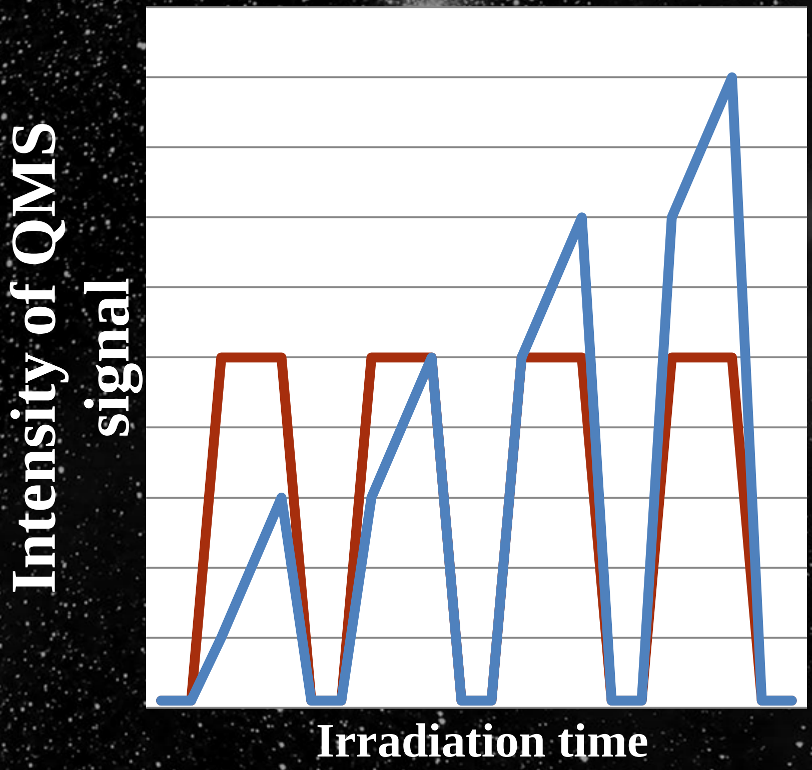


$CH_4 \rightarrow Y_{pd} =$
2.0×10^{-3} mol. / inc. ph.

$CO \rightarrow Y_{pd\ max} =$
9.0×10^{-3} mol. / inc. ph.

7. Conclussions

Photoproducts desorb with two yield vs fluence patterns



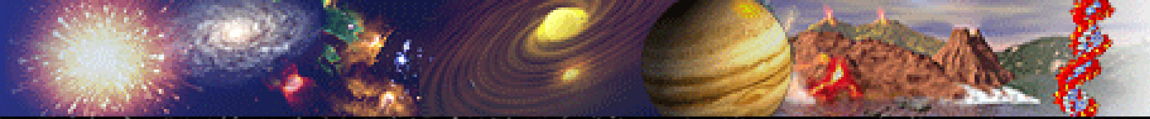
Increasing yield = INDIRECT desorption of accumulated photoproducts via ENERGY TRANSFER

Constant yield = INMEDIATE desorption of formed photoproducts due to EXCESS ENERGY

7. Conclussions

	Photodesorption of CH_4
CH_4 ice	
$H_2O:CH_4$ ice	
CH_3OH ice	

Additional desorption mechanism for photoproducts



Acknowledgments

Colaborators:

E. Dartois (IAS), Y. J. Chen (Taiwan), A. Ciaravella & C. Cecchi-Pestellini (O. Palermo), R. Escribano and B. Maté (IEM), W.-F. Thi (Grenoble), S. Cazaux (Groningen), I. Jiménez-Serra (London), COSAC-Rosetta team, etc.

Merci !