

Formation du glycéraldéhyde par des processus radicalaires dans des analogues de glaces: approche mécanistique

Yohann Layssac, Fabrice Duvernay, Albert Rimola, Alejandro Gutiérrez Quintanilla, Thierry Chiavassa

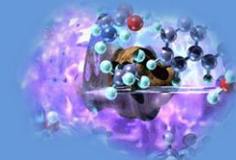
Laboratoire de Physique des Interactions Ioniques et Moléculaires (PIIM)

Aix Marseille Université (AMU), Centre de St Jérôme, Marseille

Les glaces interstellaires

Deux phases distinctes : gazeuse (99% en masse) et solide (1% en masse)

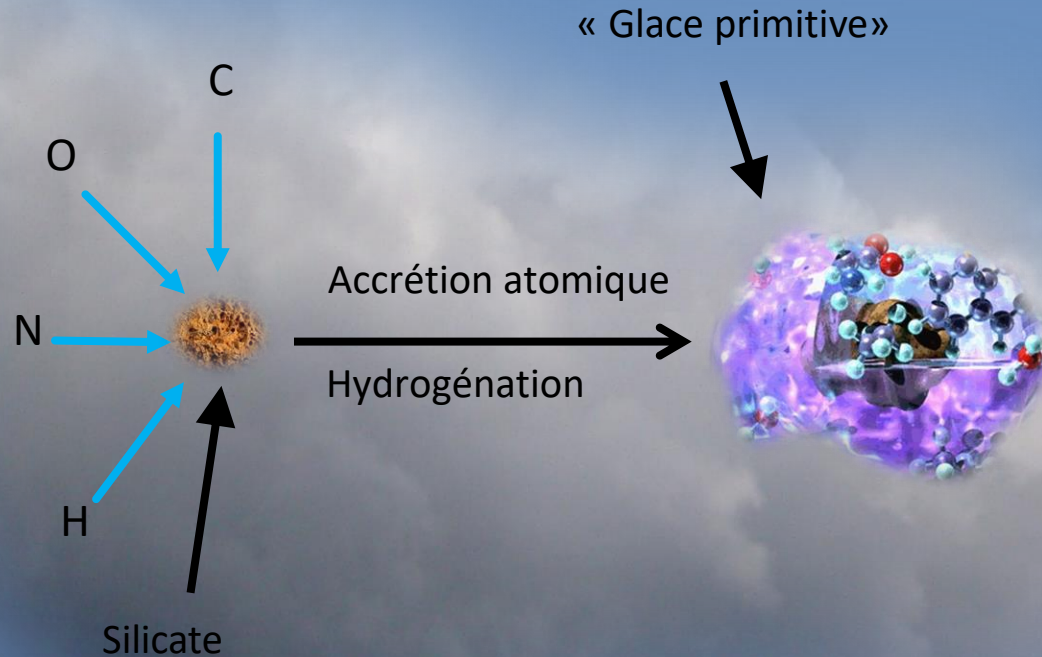
Environnements denses, froids
($T < 20$ K)



« glaces »
(H_2O , CO , CO_2 ,
 NH_3 , MeOH ...)

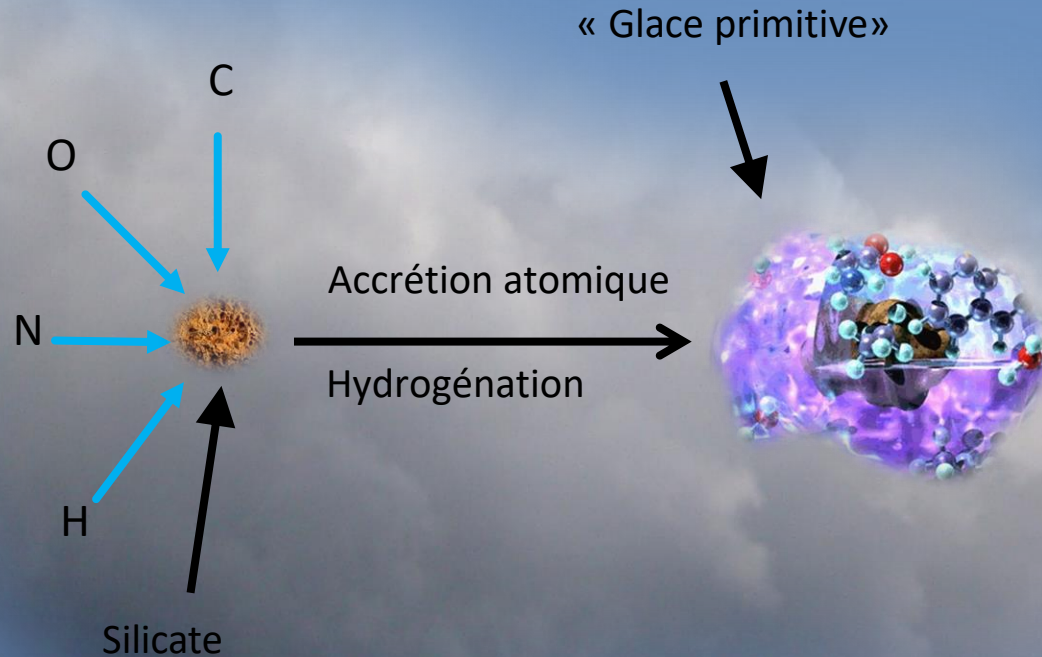
Chimie de surface sur les grains interstellaires

Nuage moléculaire dense : 10 K , 10^4 10^6 part cm^{-3}



Chimie de surface sur les grains interstellaires

Nuage moléculaire dense : 10 K , 10^4 - 10^6 part cm^{-3}



Réactions de surface



S. Nourry, L. Krim MNRAS 2015



T. Hama, N. Watanabe. Chem. Rev., 2013, 113, 8783

Chimie sur les grains interstellaires

« Glaces primitives »

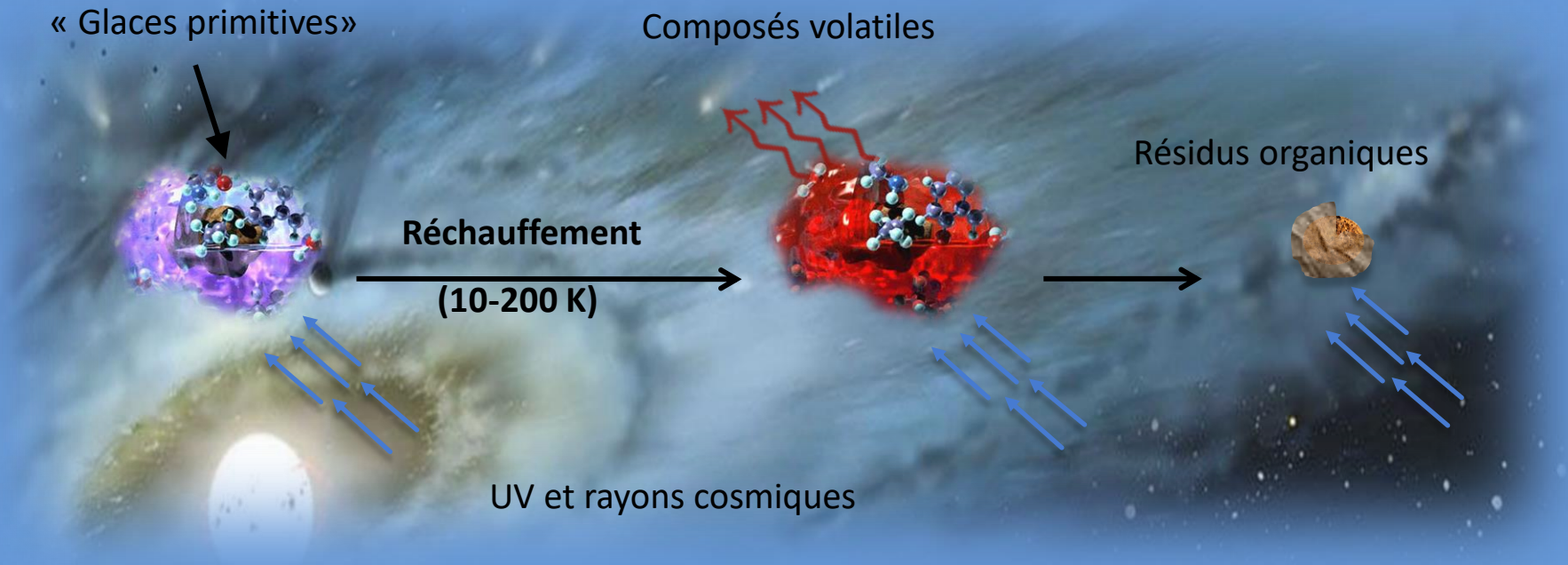
Composés volatiles

Résidus organiques

Réchauffement

(10-200 K)

UV et rayons cosmiques



Chimie sur les grains interstellaires

« Glaces primitives »

Composés volatiles

Résidus organiques

Réchauffement

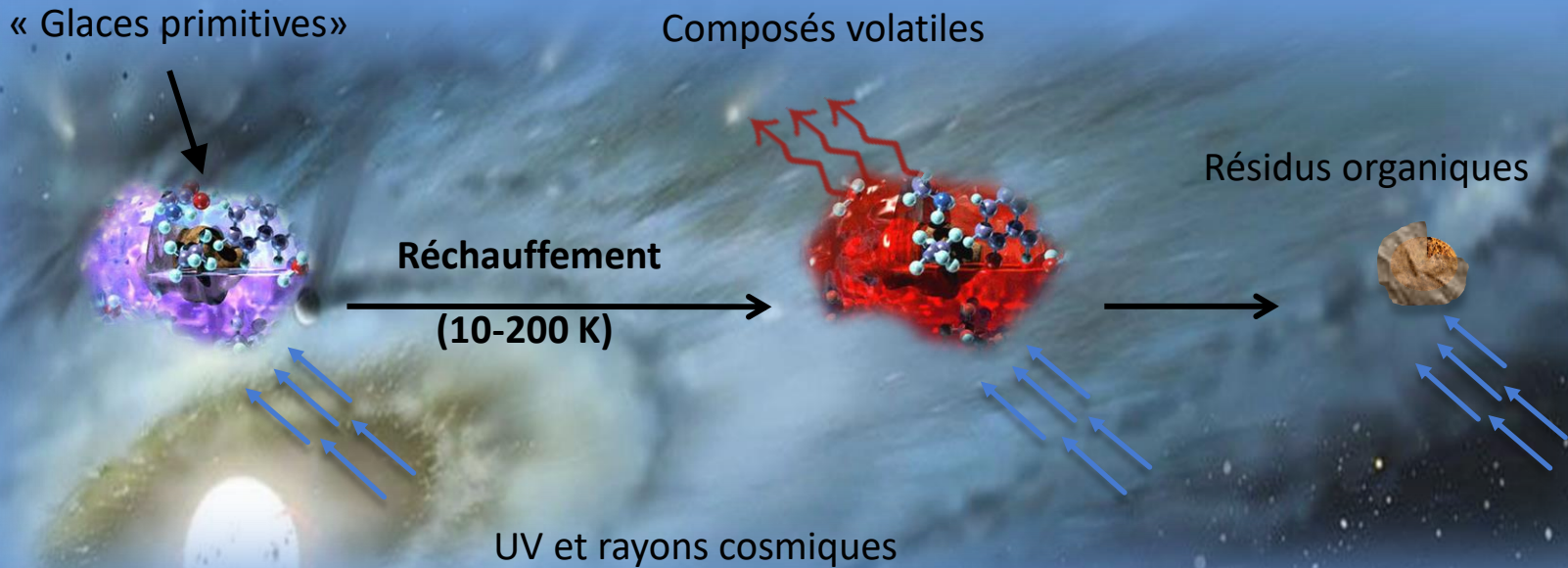
(10-200 K)

UV et rayons cosmiques

Réactions de surface et de volume

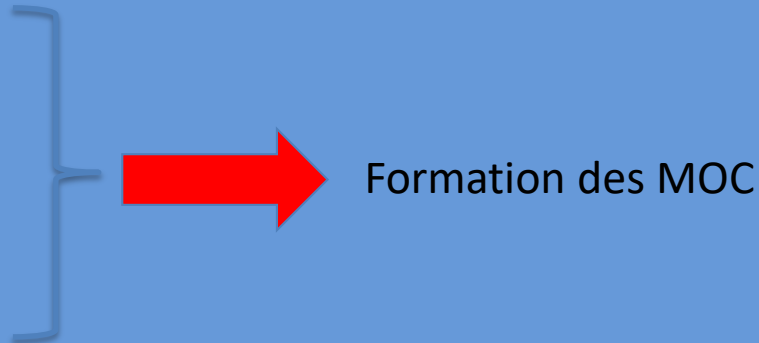
- Réactions neutre-neutre
- Réactions radical-radical
- Réactions radical-neutre

Chimie sur les grains interstellaires

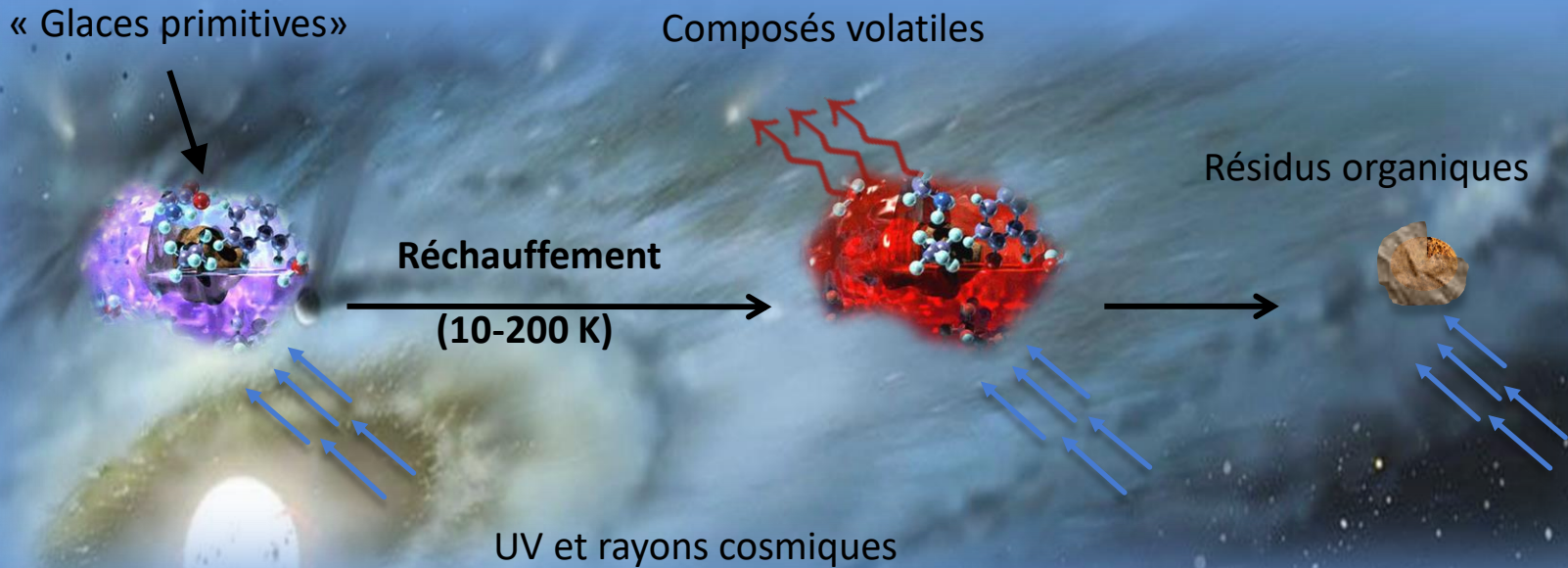


Réactions de surface et de volume

- Réactions neutre-neutre
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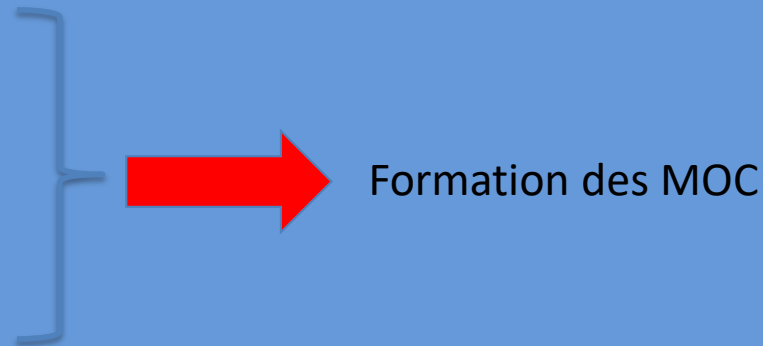


Chimie sur les grains interstellaires



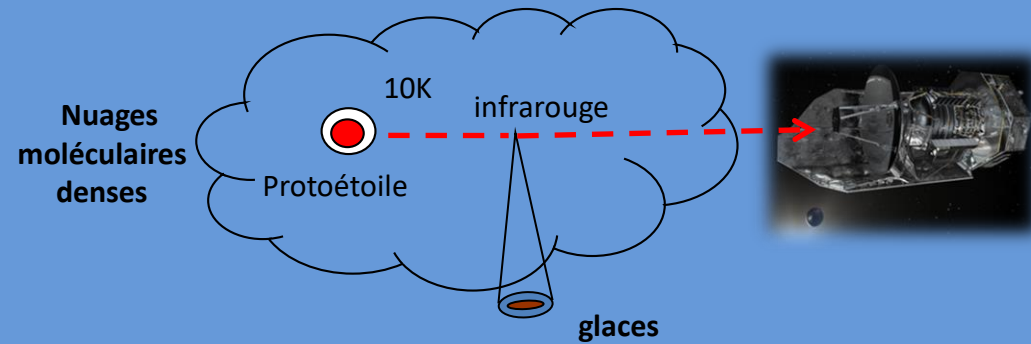
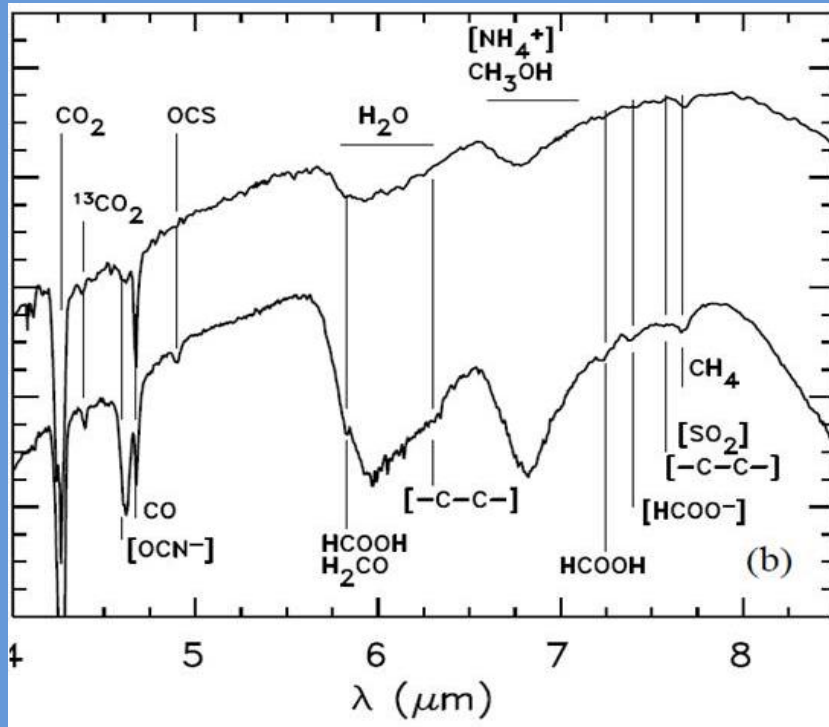
Réactions de surface et de volume

- Réactions neutre-neutre
- Réactions radical-radical
- Réactions radical-neutre



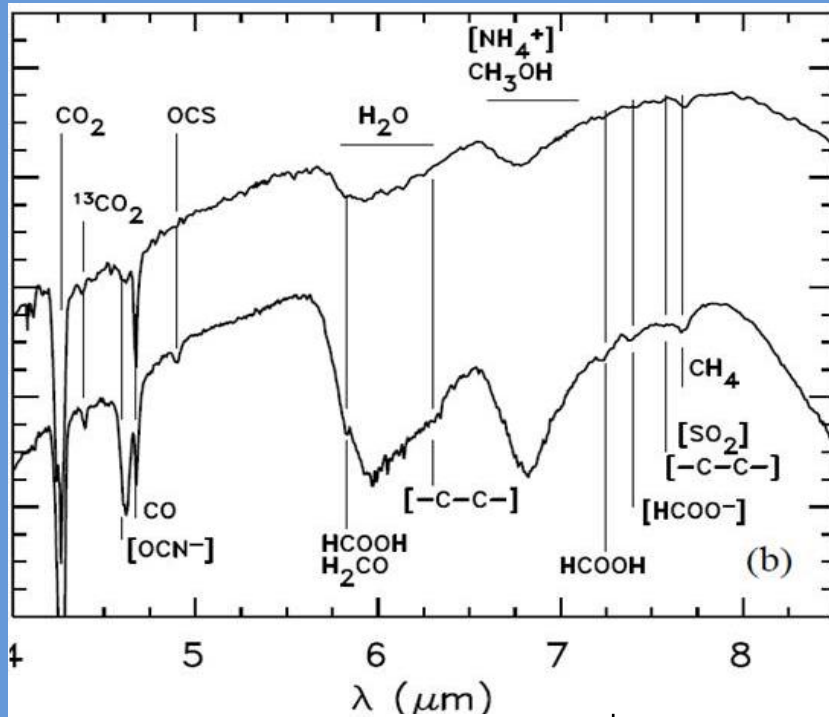
Composition du MIS

Phase solide



Composition du MIS

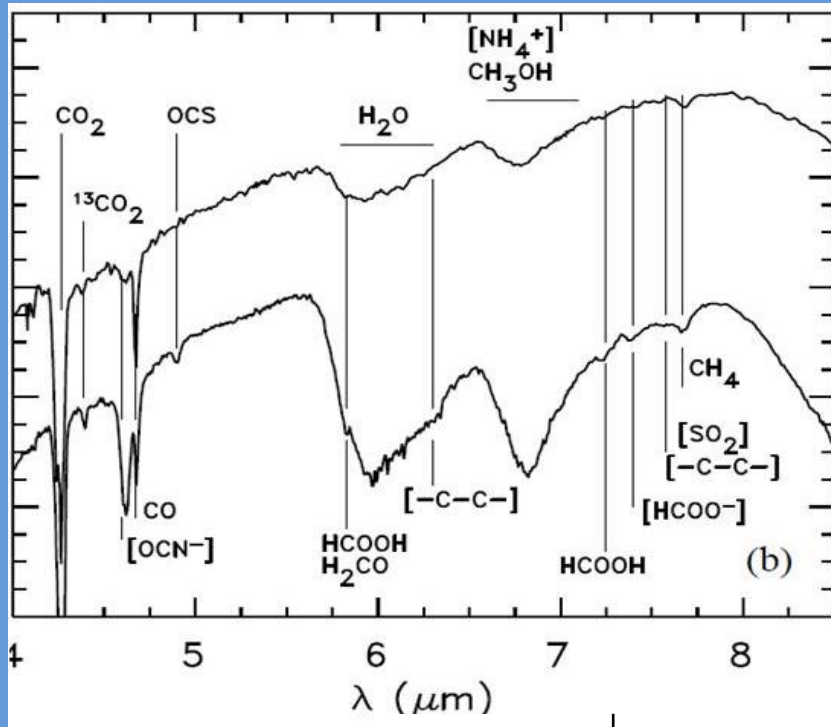
Phase solide



Molécules	Abondance en % / H_2O
H_2O	100
CO	3-35
CO_2	7-25
CH_3OH	2-25
NH_3	10-20
H_2CO	2-10
CH_4	1-8
HCOOH	1-5

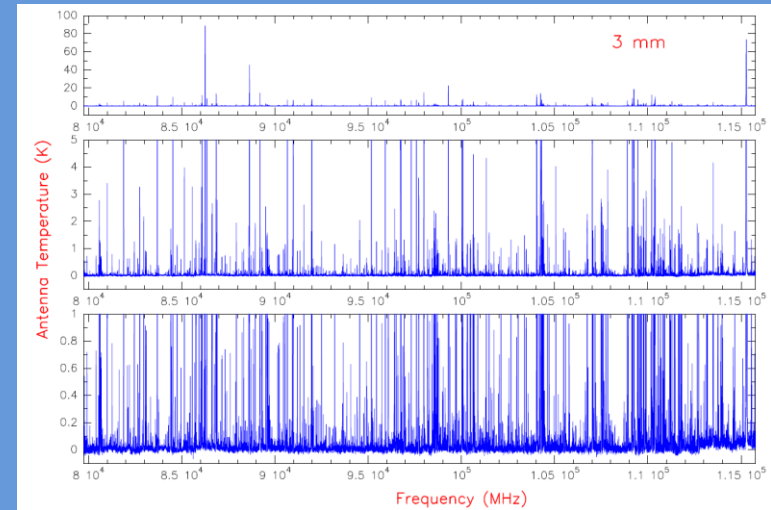
Composition du MIS

Phase solide



Molécules	Abondance en % / H ₂ O
H ₂ O	100
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CH ₃ OH	2-25
NH ₃	10-20
H ₂ CO	2-10
CH ₄	1-8
HCOOH	1-5

Phase gazeuse

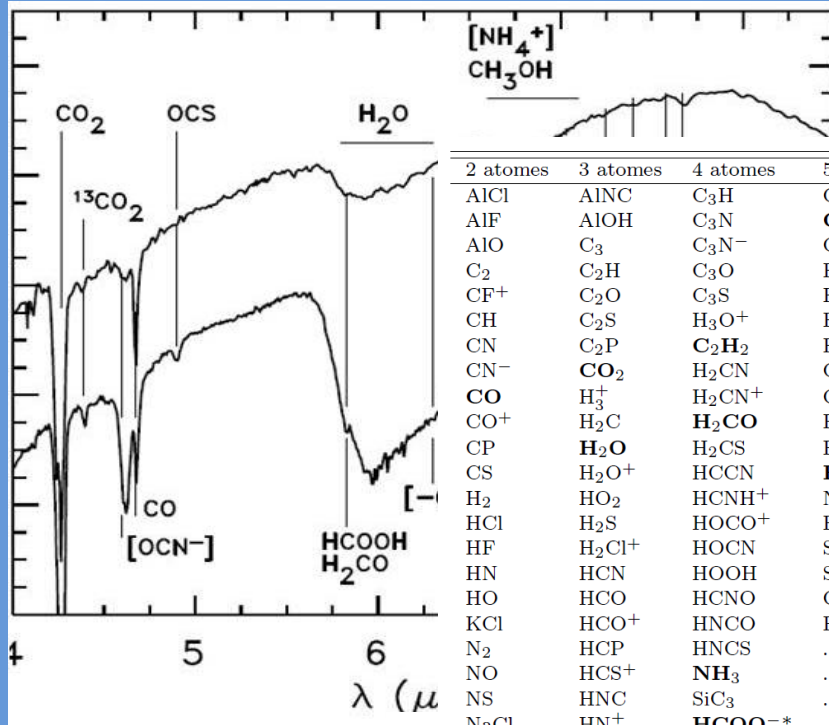


Tercero et al, A&A, A96, 2010.

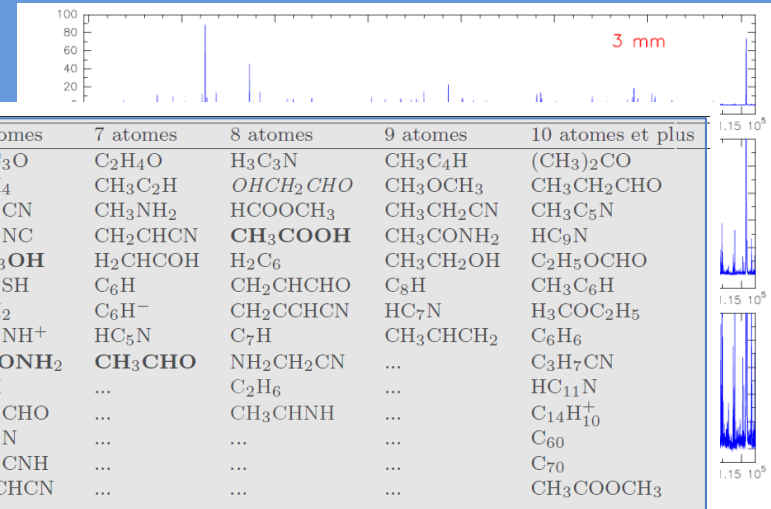


Composition du MIS

Phase solide



Phase gazeuse



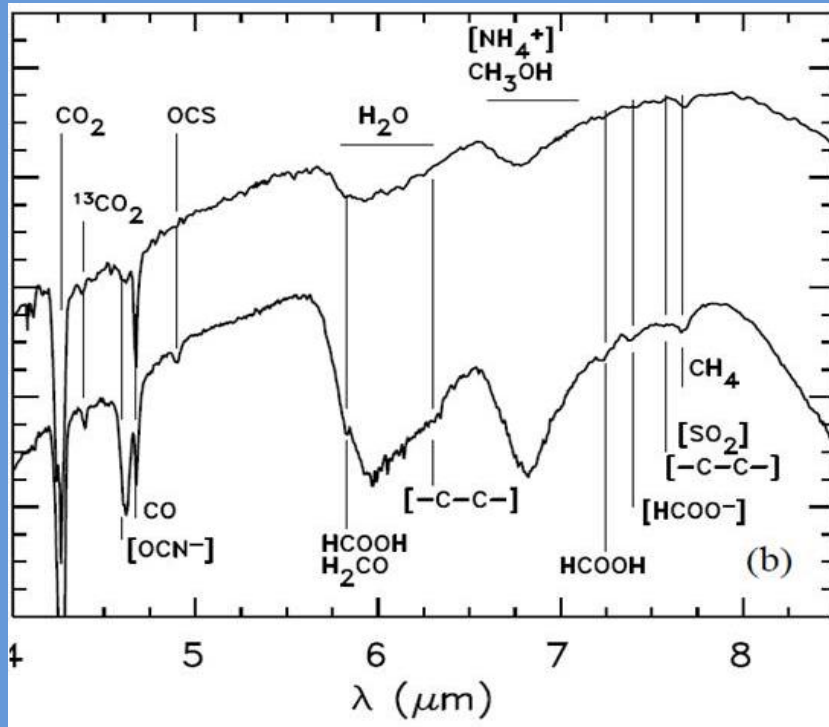
2 atomes	3 atomes	4 atomes	5 atomes	6 atomes	7 atomes	8 atomes	9 atomes	10 atomes et plus
AlCl	AlNC	C ₃ H	C ₅	H ₂ C ₃ O	C ₂ H ₄ O	H ₃ C ₃ N	CH ₃ C ₄ H	(CH ₃) ₂ CO
AlF	AlOH	C ₃ N	CH₄	C ₂ H ₄	CH ₃ C ₂ H	<i>OHCH₂CHO</i>	CH ₃ OCH ₃	CH ₃ CH ₂ CHO
AlO	C ₃	C ₃ N ⁻	C ₃ H ₂	CH ₃ CN	CH ₃ NH ₂	HCOOCH ₃	CH ₃ CH ₂ CN	CH ₃ C ₅ N
C ₂	C ₂ H	C ₃ O	H ₂ CCN	CH ₃ NC	CH ₂ CHCN	CH₃COOH	CH ₃ CONH ₂	HC ₉ N
CF ⁺	C ₂ O	C ₃ S	H ₂ C ₂ O	CH₃OH	H ₂ CHCOH	H ₂ C ₆	CH ₃ CH ₂ OH	C ₂ H ₅ OCHO
CH	C ₂ S	H ₃ O ⁺	H ₂ CNH	CH ₃ SH	C ₆ H	CH ₂ CHCHO	C ₈ H	CH ₃ C ₆ H
CN	C ₂ P	C₂H₂	H ₂ COH ⁺	C ₄ H ₂	C ₆ H ⁻	CH ₂ CCHCN	HC ₇ N	H ₃ COC ₂ H ₅
CN ⁻	CO₂	H ₂ CN	C ₄ H	HC ₃ NH ⁺	HC ₅ N	C ₇ H	CH ₃ CHCH ₂	C ₆ H ₆
CO	H ₃ ⁺	H ₂ CN ⁺	C ₄ H ⁻	HCONH₂	CH₃CHO	NH ₂ CH ₂ CN	...	C ₃ H ₇ CN
CO ⁺	H ₂ C	H₂CO	HC ₃ N	C ₅ H	...	C ₂ H ₆	...	HC ₁₁ N
CP	H₂O	H ₂ CS	HC ₂ NC	HC ₂ CHO	...	CH ₃ CHNH	...	C ₁₄ H ₁₀ ⁺
CS	H ₂ O ⁺	HCCN	HCOOH	HC ₄ N	C ₆₀
H ₂	HO ₂	HCNH ⁺	NH ₂ CN	CH ₂ CNH	C ₇₀
HCl	H ₂ S	HOCO ⁺	HC(O)CN	HNCHCN	CH ₃ COOCH ₃
HF	H ₂ Cl ⁺	HOCN	SiC ₄
HN	HCN	HOOH	SiH ₄
HO	HCO	HCNO	CH ₃ O
KCl	HCO ⁺	HNCO	HNCNH
N ₂	HCP	HNCS
NO	HCS ⁺	NH₃
NS	HNC	SiC ₃
NaCl	HN ₂ ⁺	HCOO^{-*}
O ₂	HNO
PN	HOC ⁺
PO	FeCN
SH	KCN
SH ⁺	MgCN
SO	MgNC
SO ⁺	NH ₂
SiC	NH ₂ ⁺
SiN	N ₂ O
SiO	NaCN
SiS	OCS
OH ⁺	SO ₂
FeO	SiC ₂
HCl ⁺	SiCN
TiO	SiNC
...	OCN⁻
...	TiO ₂

Molécules organiques complexes
MOC (COMs): 62 molécules

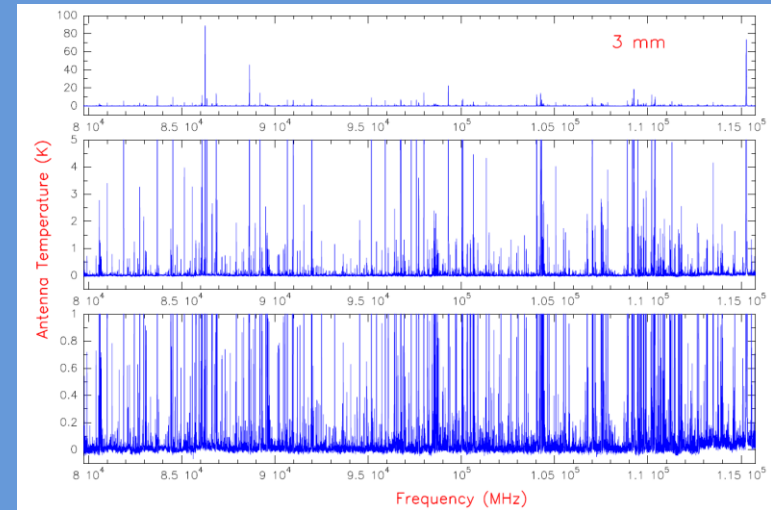
Environ 200 molécules !

Composition du MIS

Phase solide



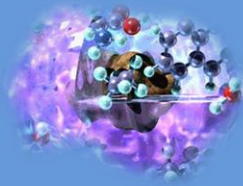
Phase gazeuse



Tercero et al, A&A, A96, 2010.

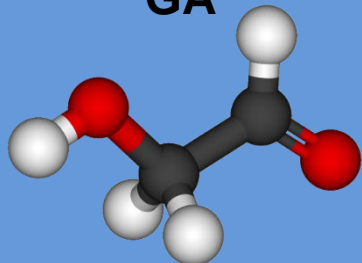


Mécanismes de formation des MOC



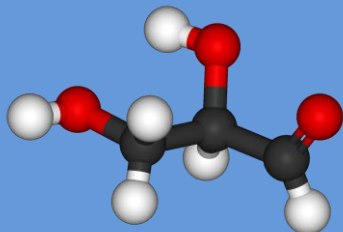
Sucres et leurs dérivés

GA



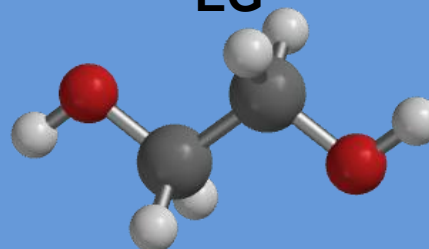
Glycolaldéhyde

GCA



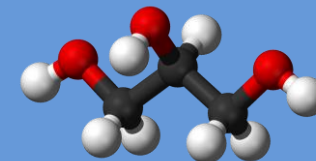
Glycéraldéhyde

EG



Ethylène glycol

GCO

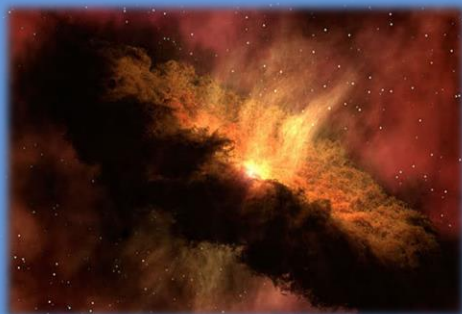


glycérol

Sucre (aldose, $C_nH_{2n}O_n$)

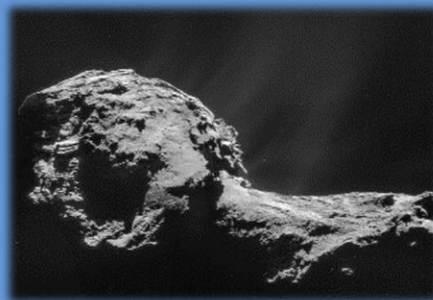
Polyol (glycol) $C_nH_{2n+2}O_n$

Objets protostellaires



Jorgensen et al. 2016; Coutens et al. 2015

Comètes



Crovisier et al. 2004 ; Goesmann et al. 2015
Altwegg et al. 2017

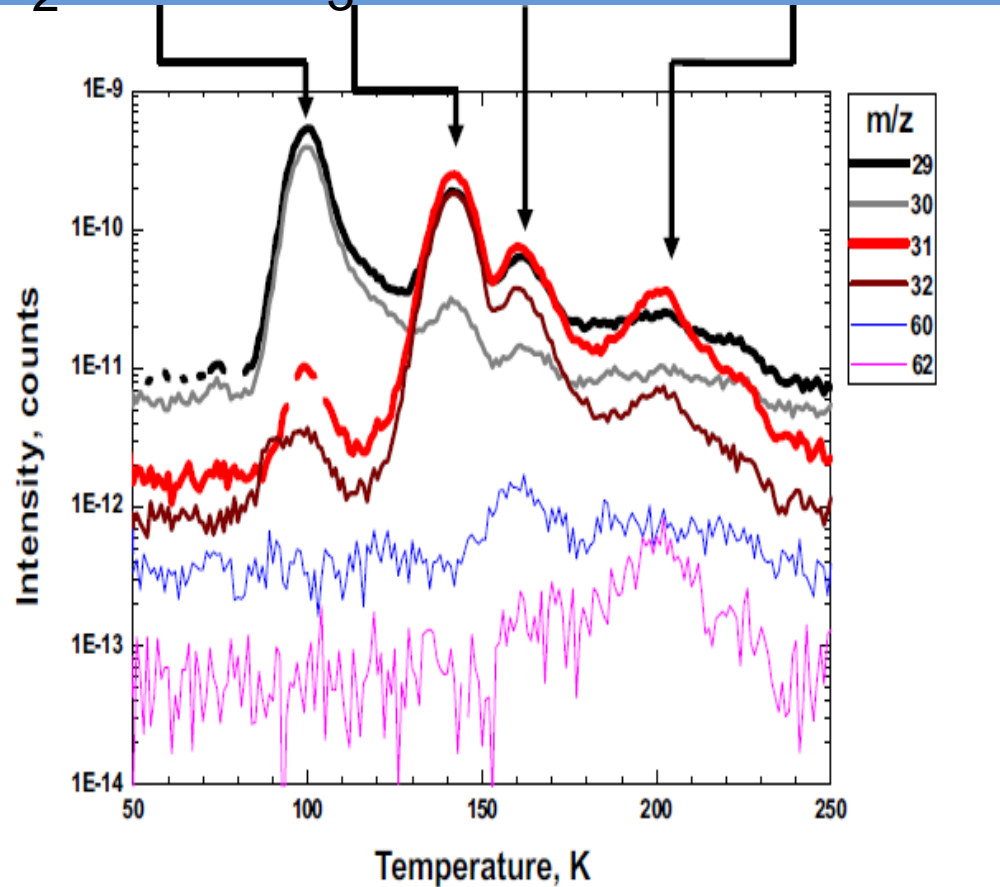
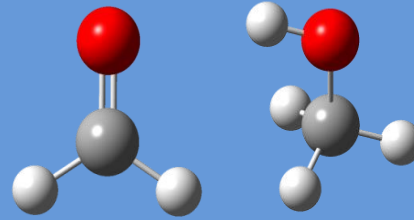
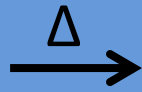
Météorites



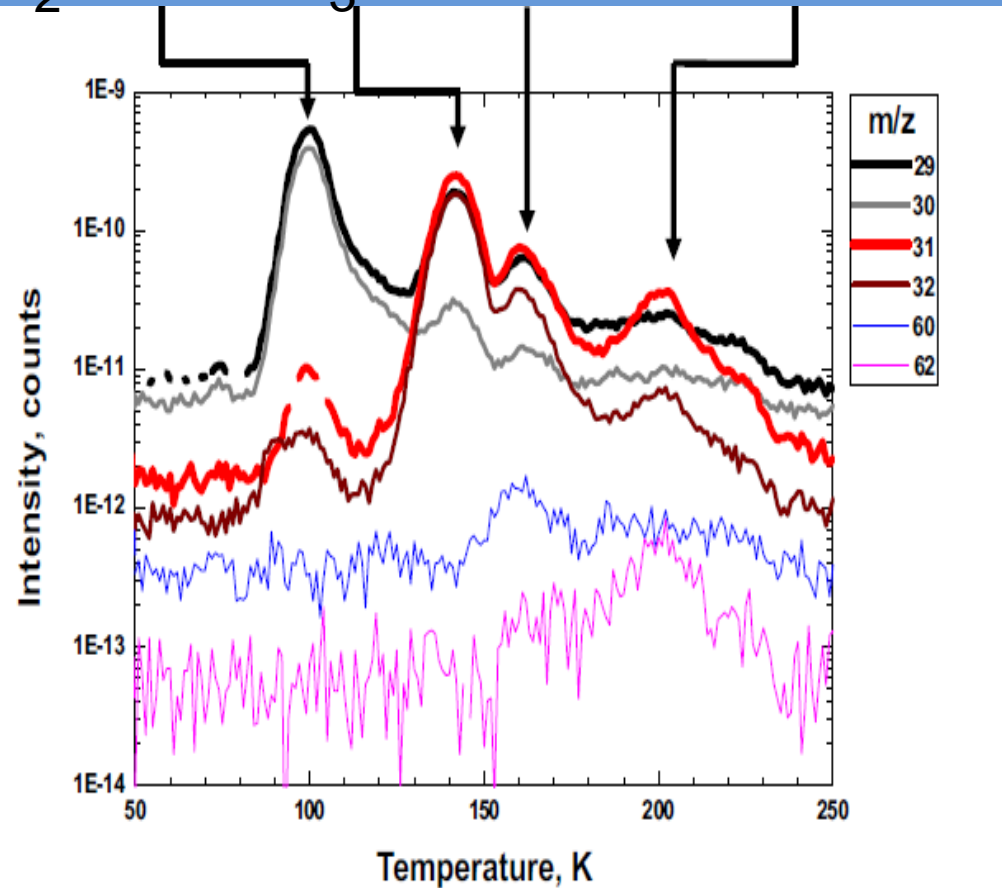
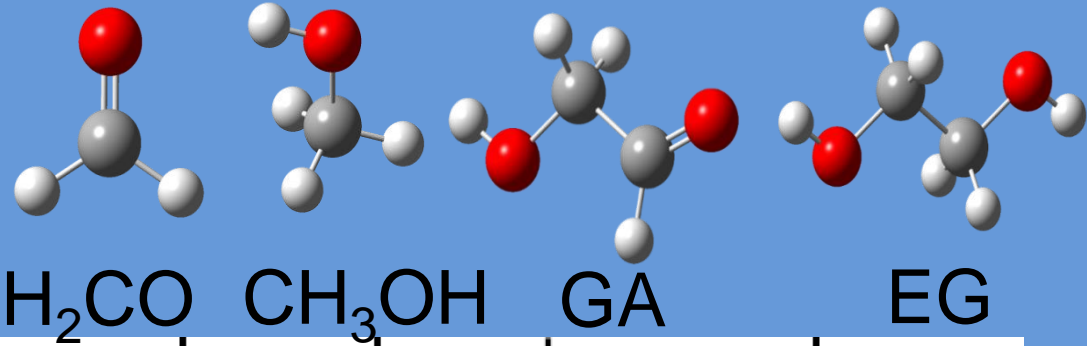
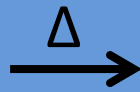
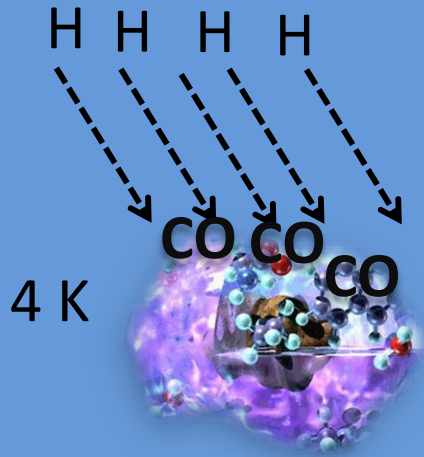
Cooper et al. Nature 2001

Formation possible dans les glaces interstellaires?
Mécanisme de formation?

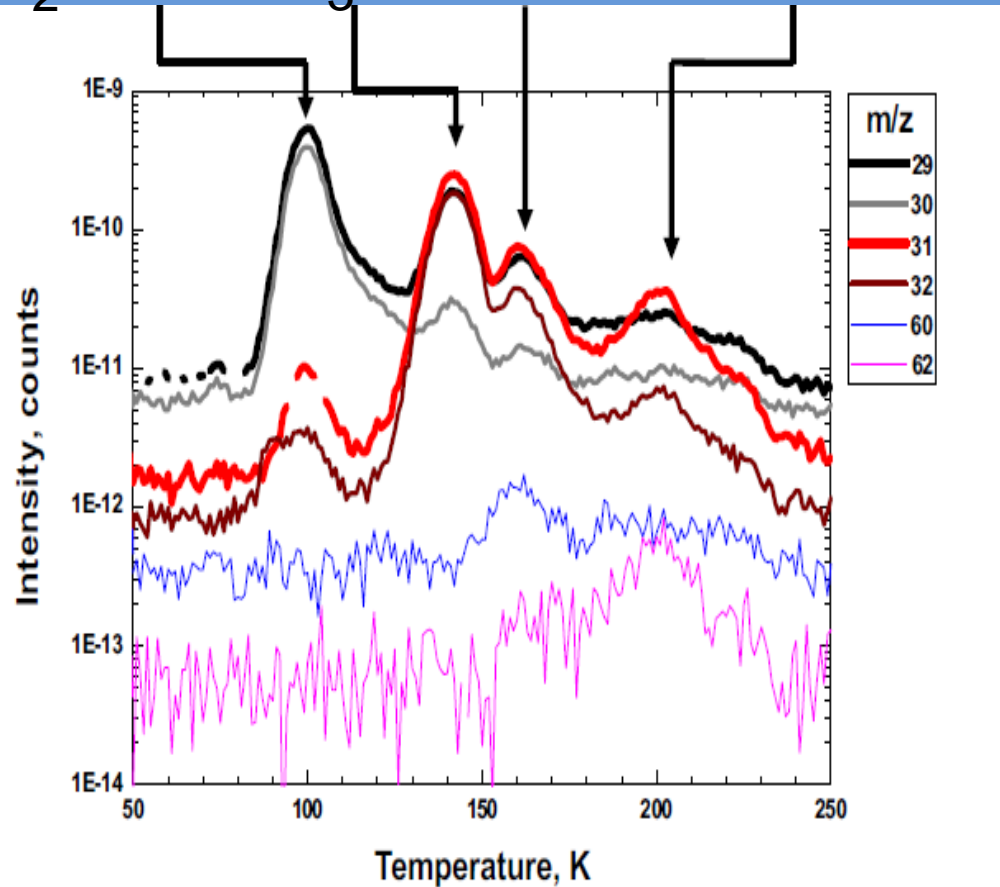
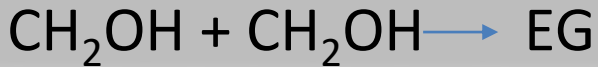
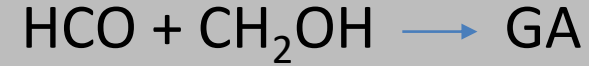
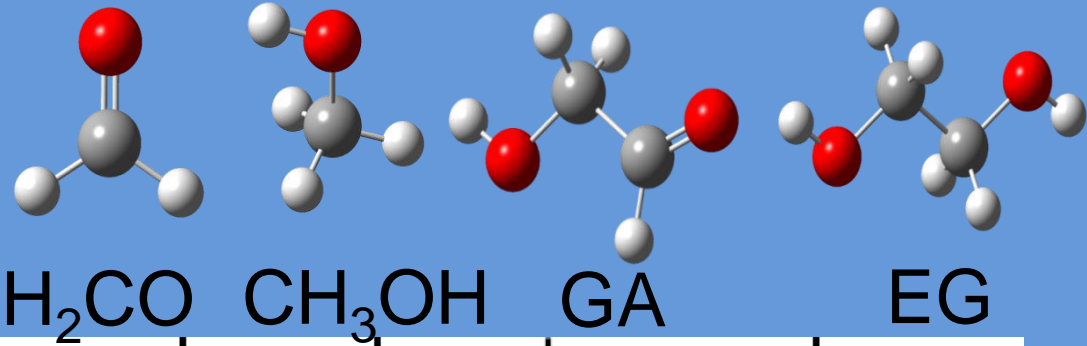
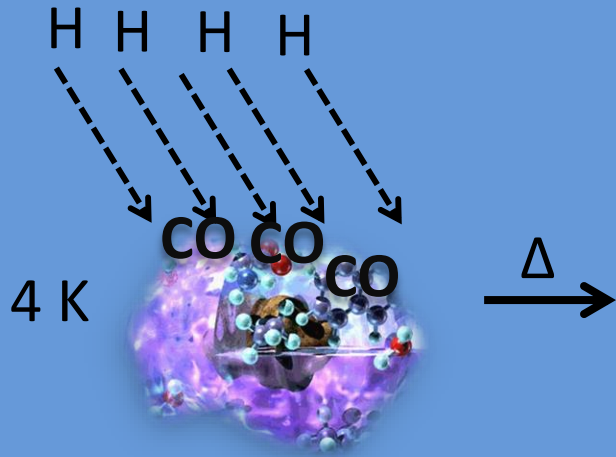
Hydrogénation du CO



Hydrogénation du CO



Hydrogénation du CO

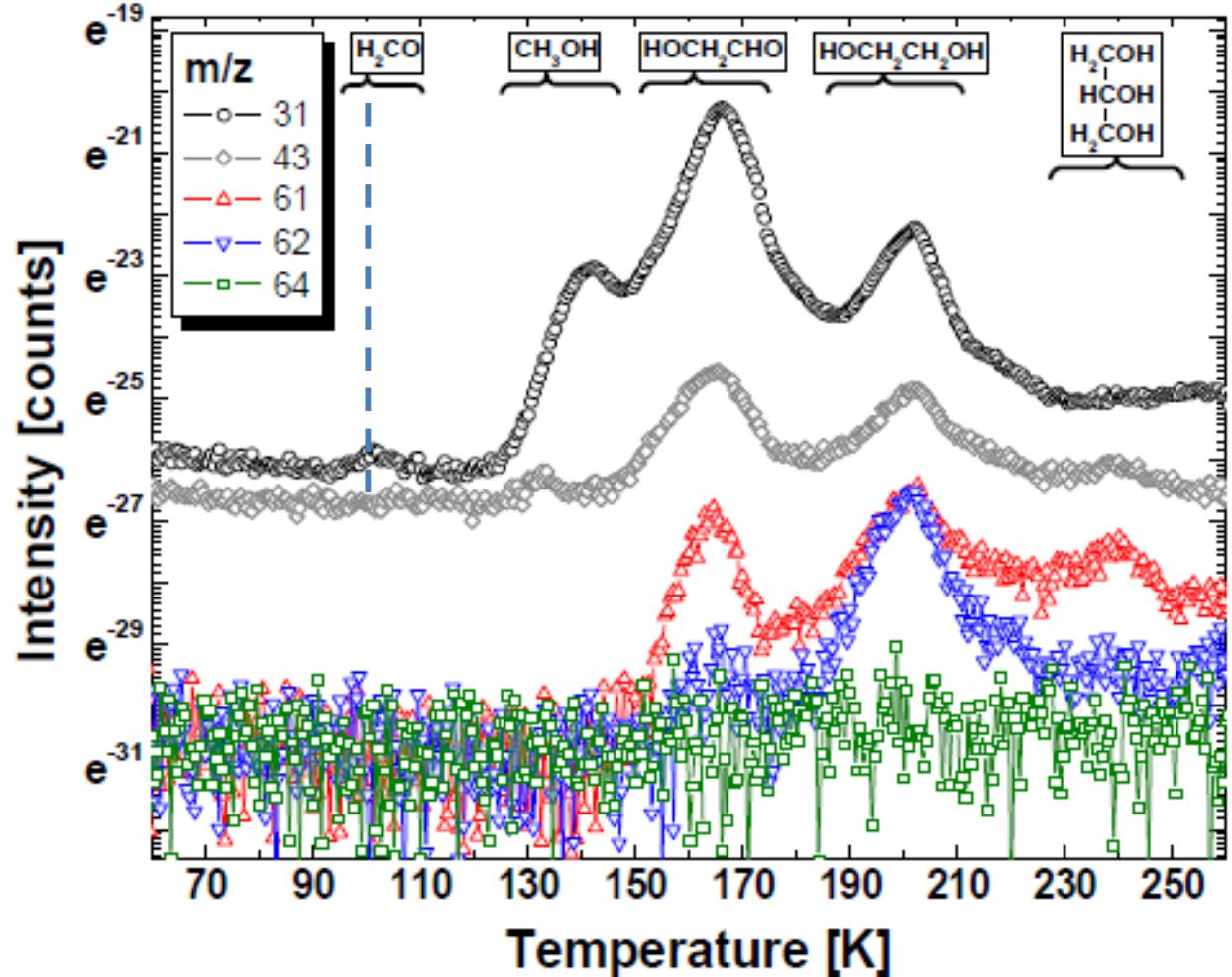
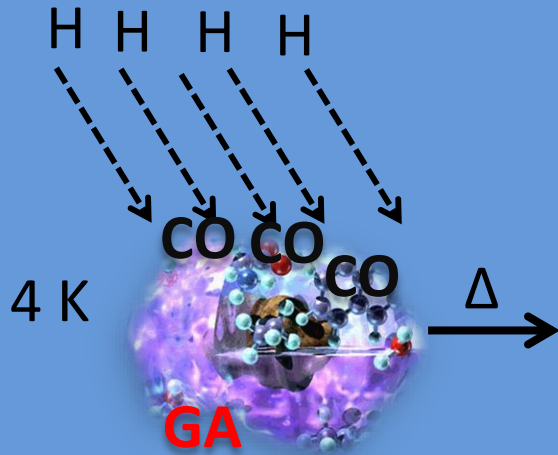


Bennet and Kaiser ApJ 2007

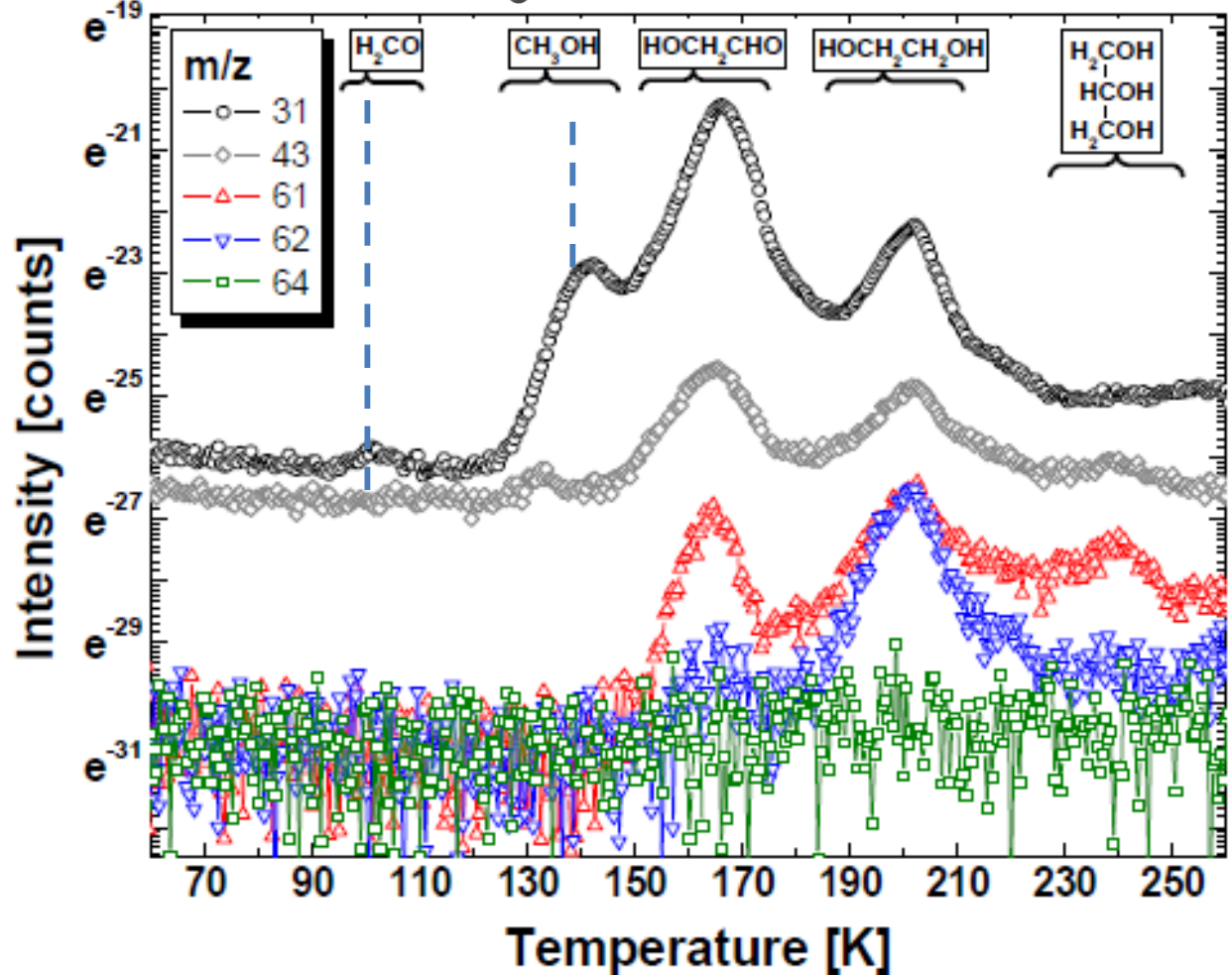
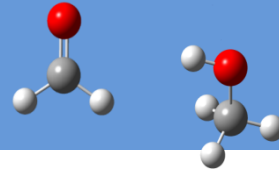
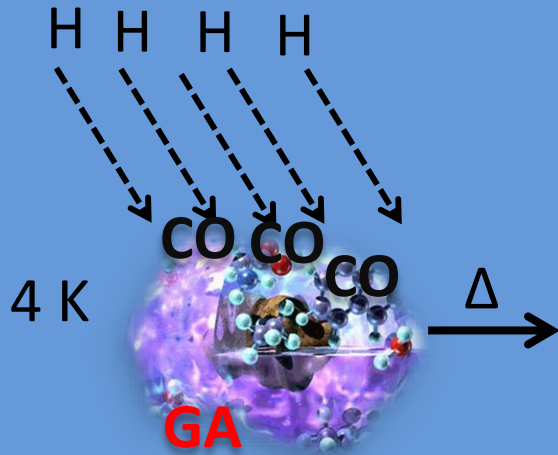
Butscher et al. MNRAS 2015

Fedoseev et al. MNRAS 2015

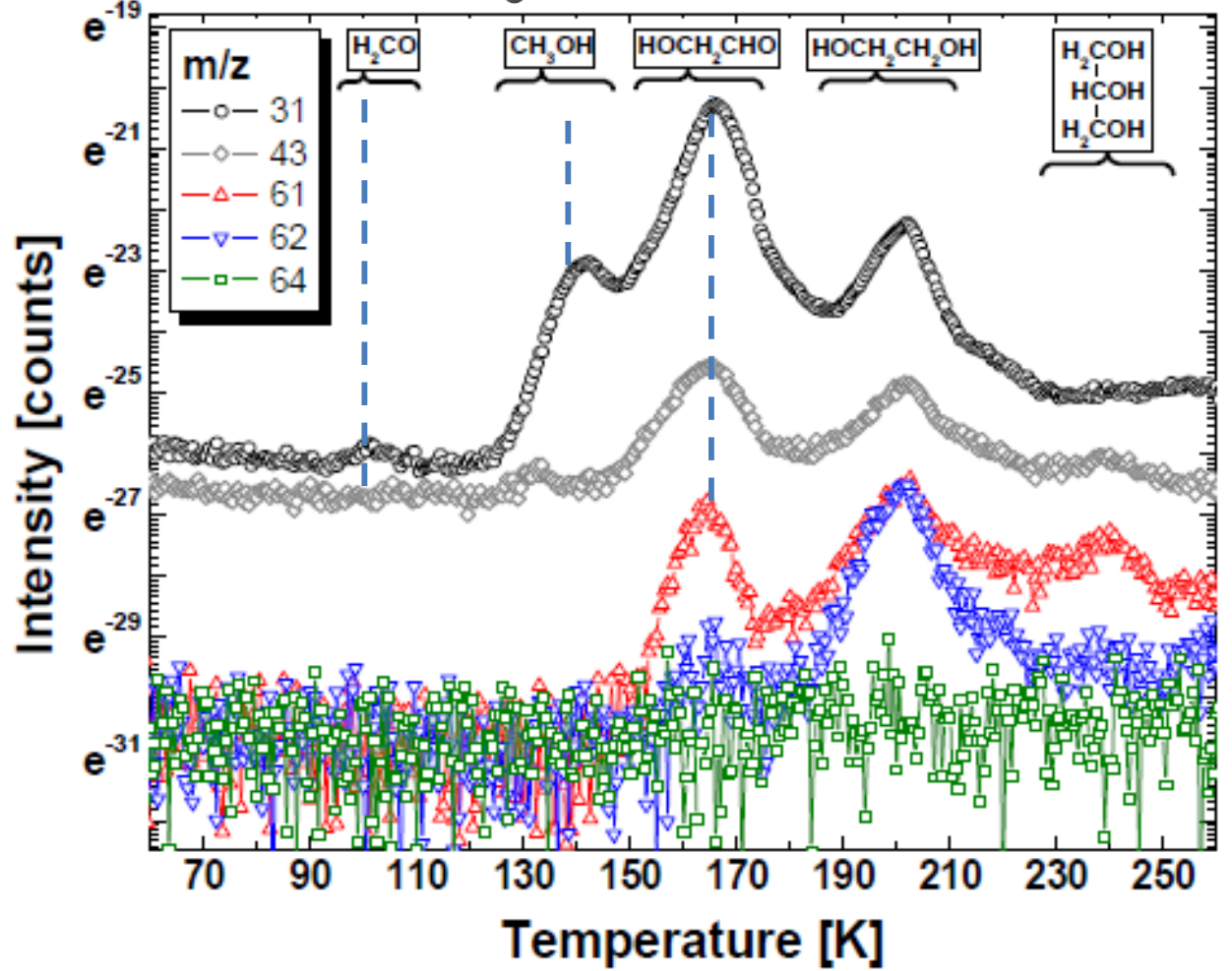
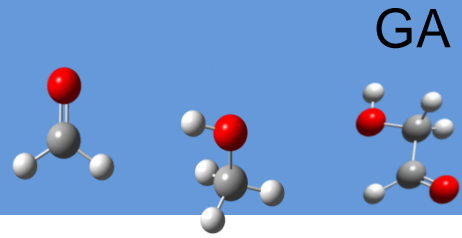
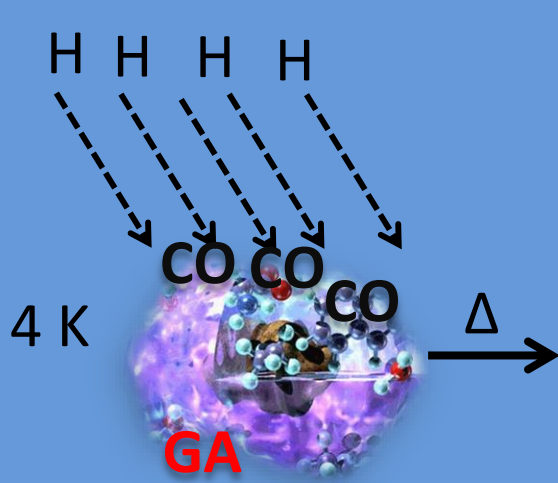
Hydrogénation du CO/GA



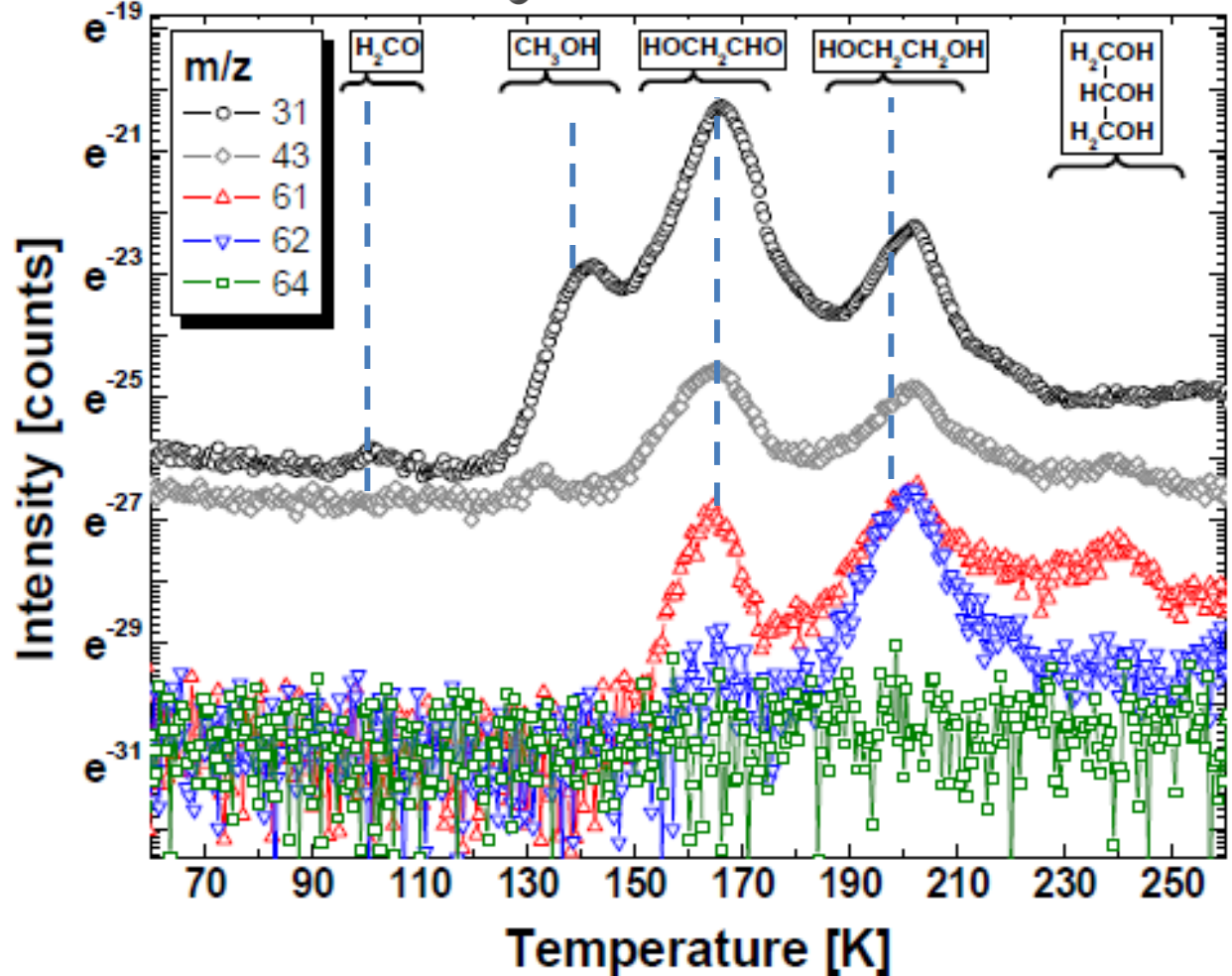
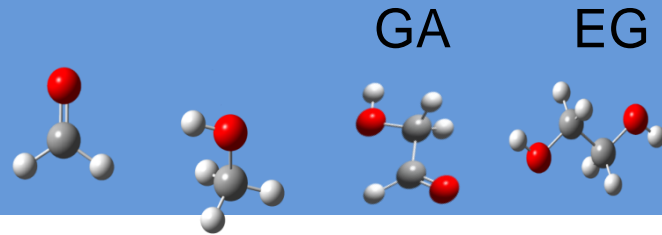
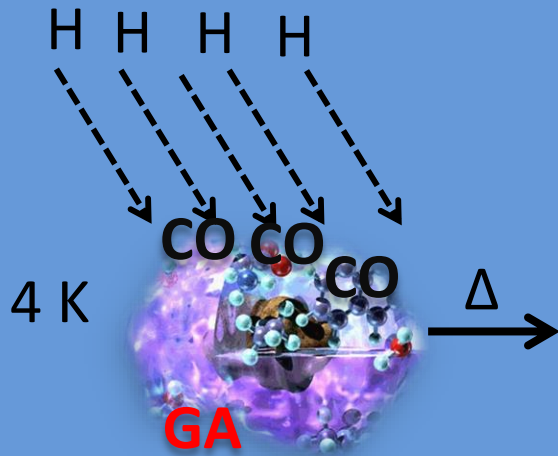
Hydrogénation du CO/GA



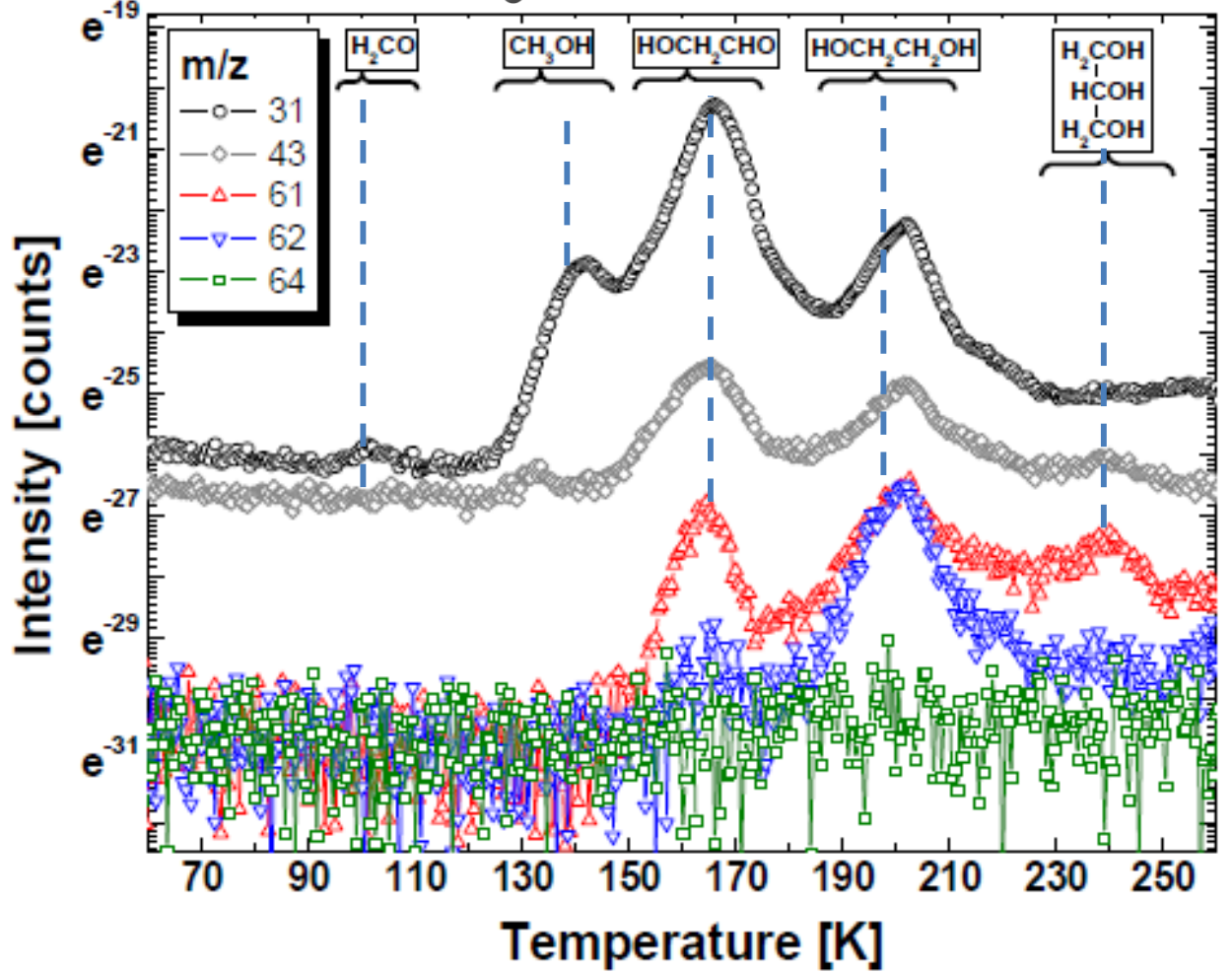
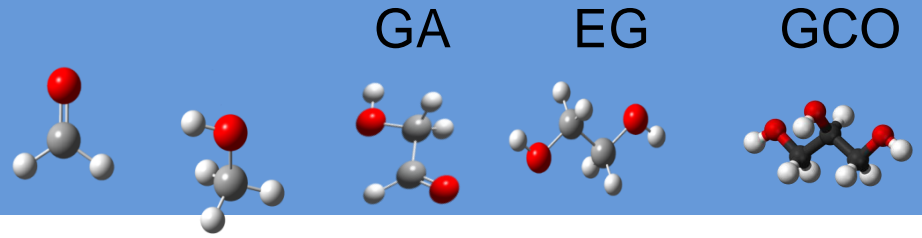
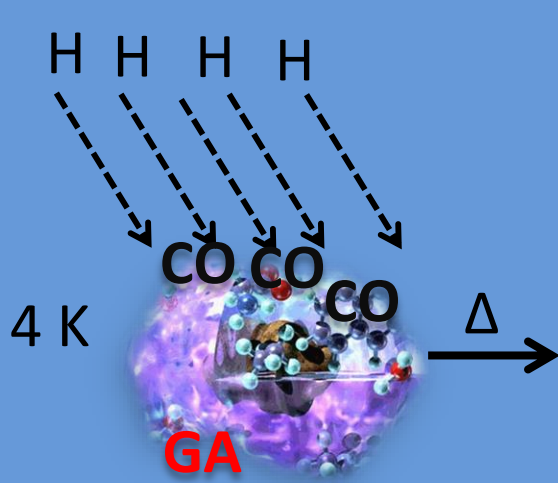
Hydrogénation du CO/GA



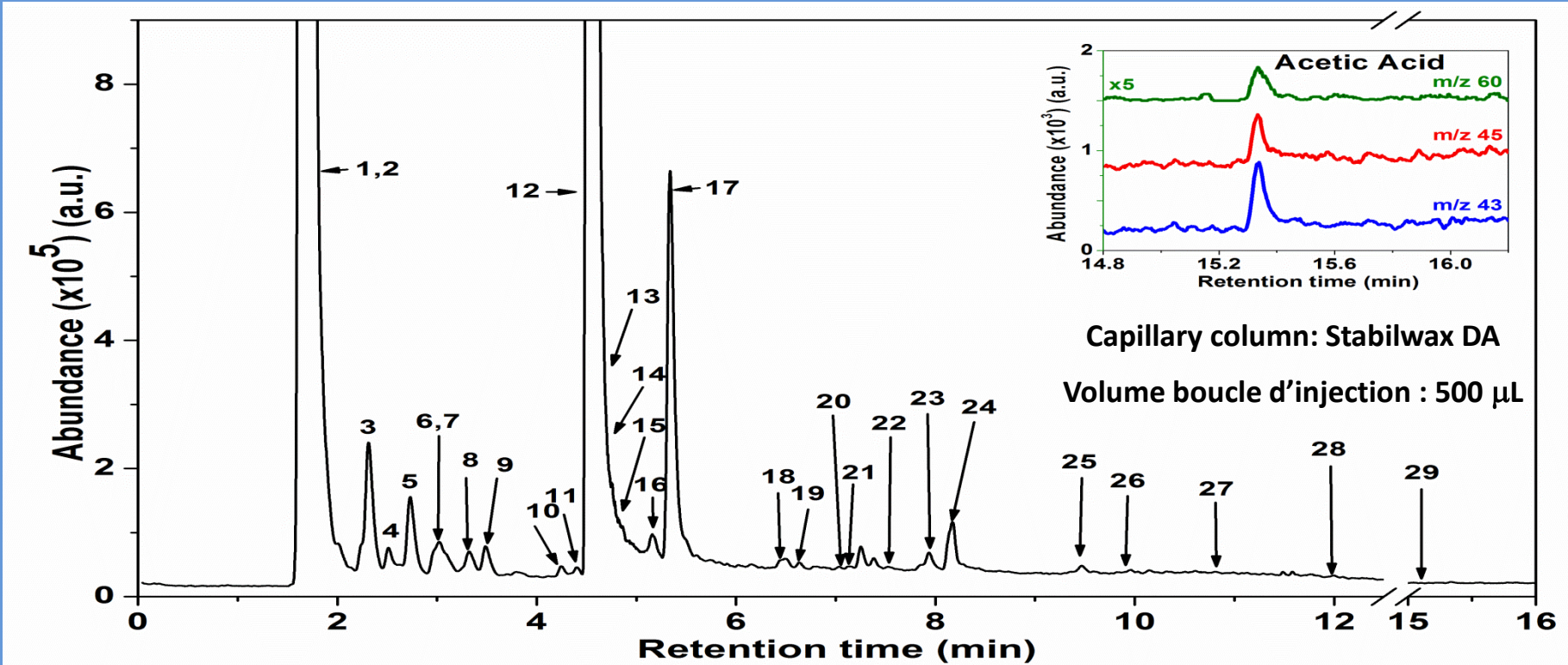
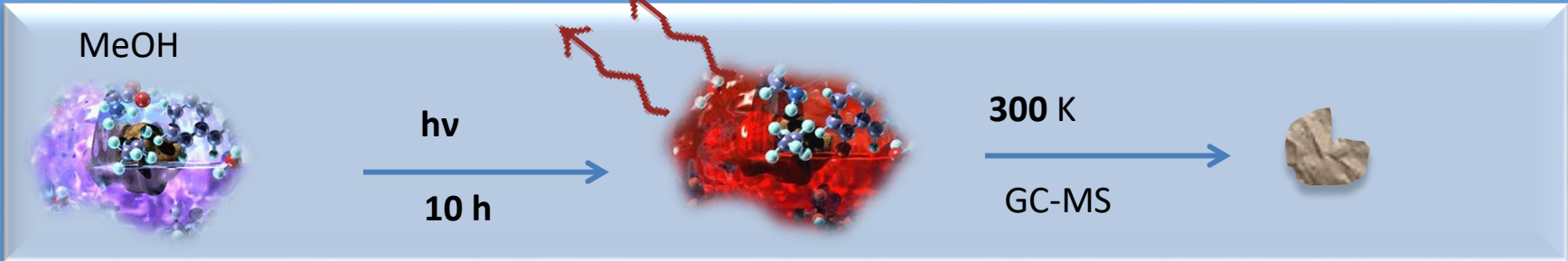
Hydrogénation du CO/GA



Hydrogénation du CO/GA

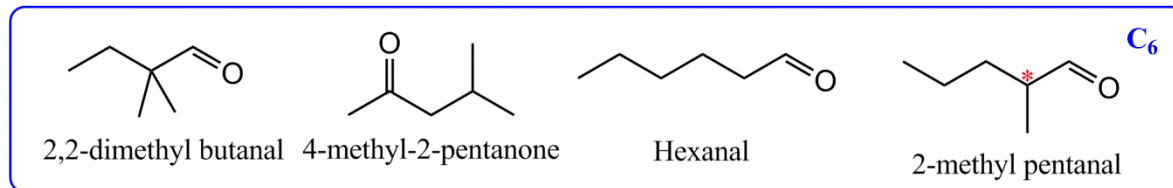
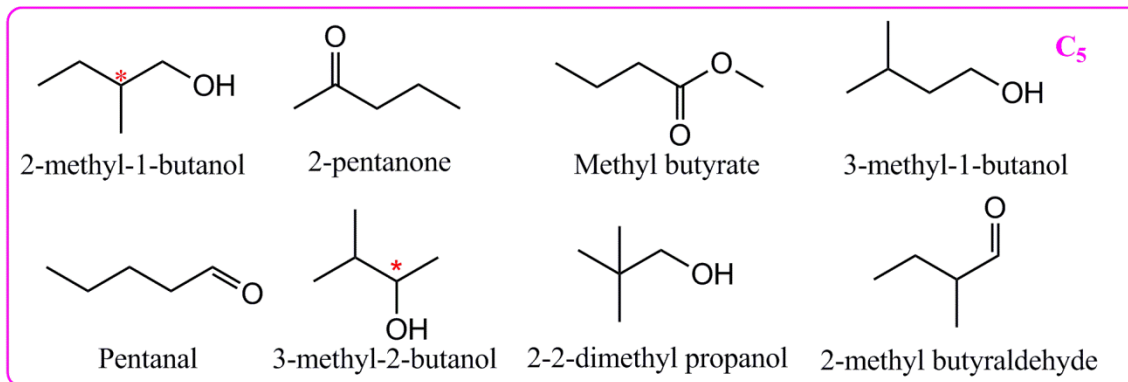
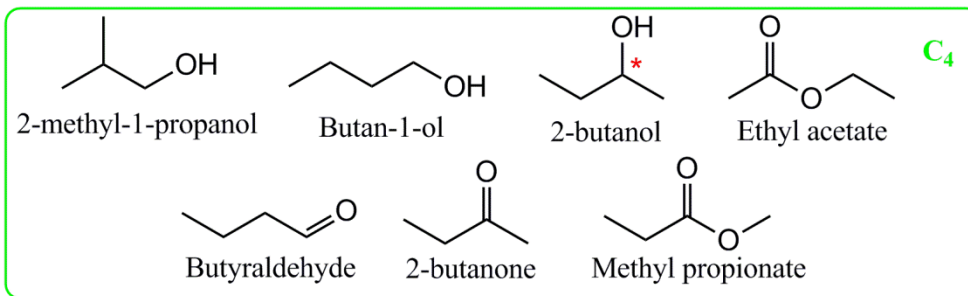
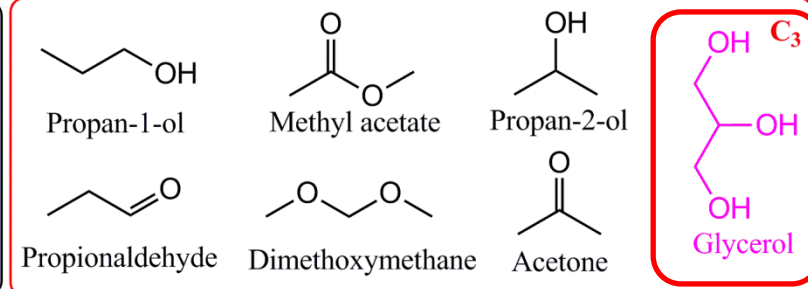
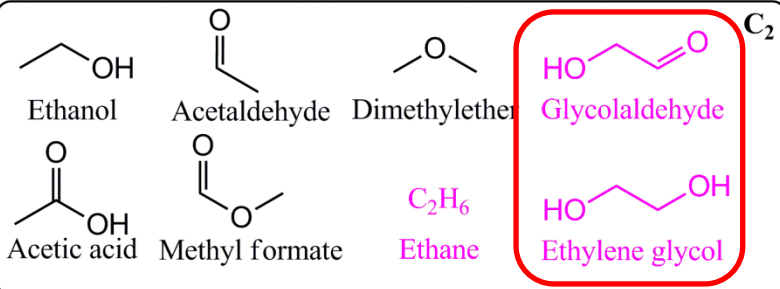


Irradiation du Methanol CH₃OH



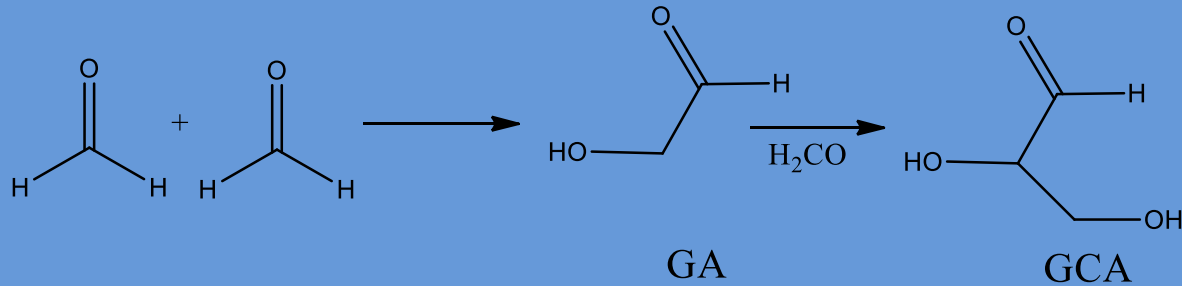
Irradiation du Methanol CH₃OH

CO C₁
Carbon monoxide
CO₂
Carbon dioxide
CH₂O
Formaldehyde
HCOOH
Formic acid
CH₄
Carbon monoxide

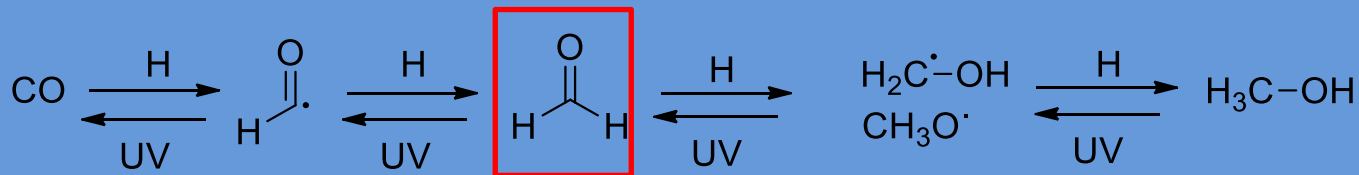


Formation des sucres en chimie organique

Réaction de Formose:



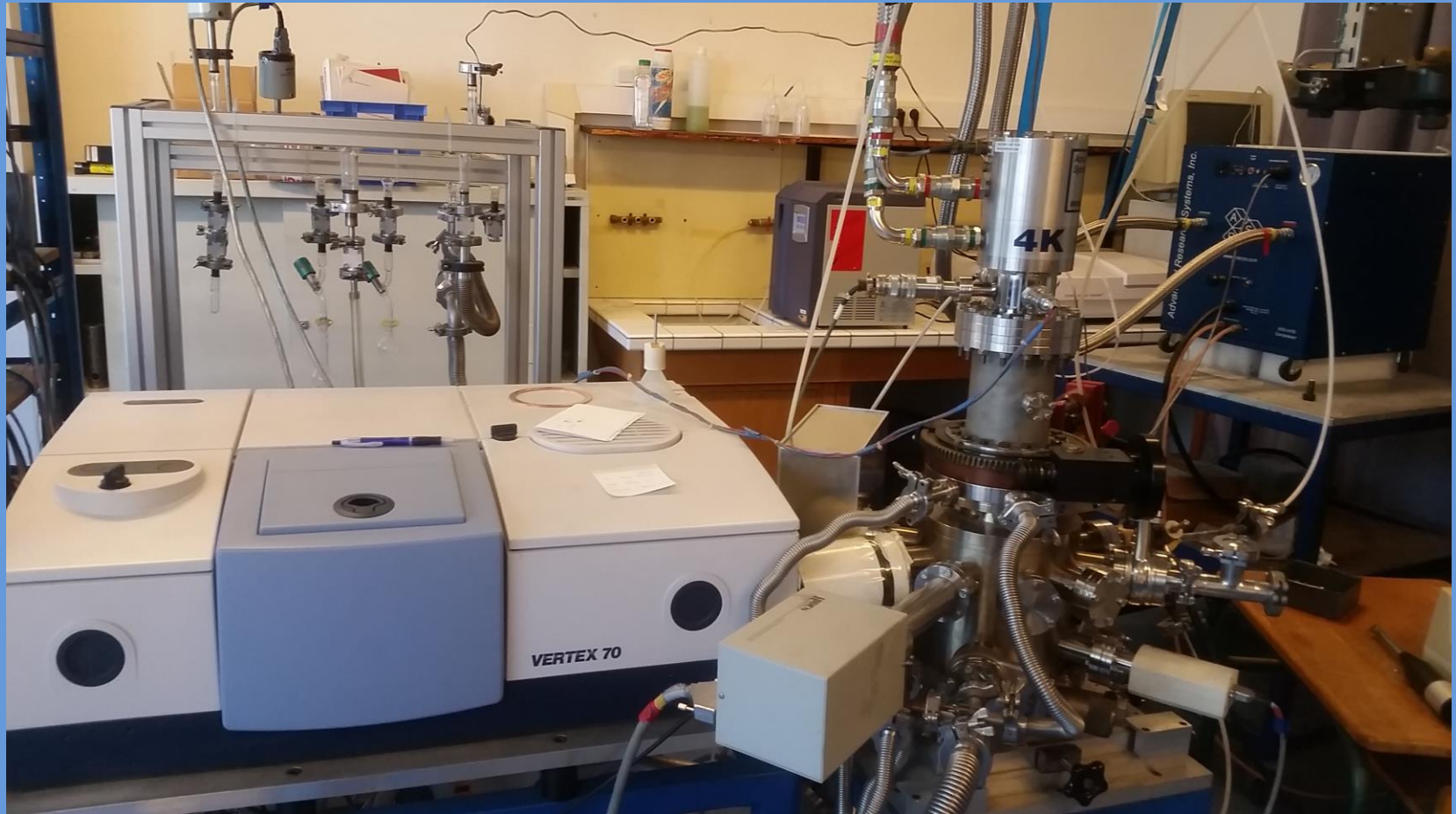
- Formaldéhyde est le précurseur clé dans le formation des sucres
- Formation par hydrogénation du CO ou la photolyse du méthanol



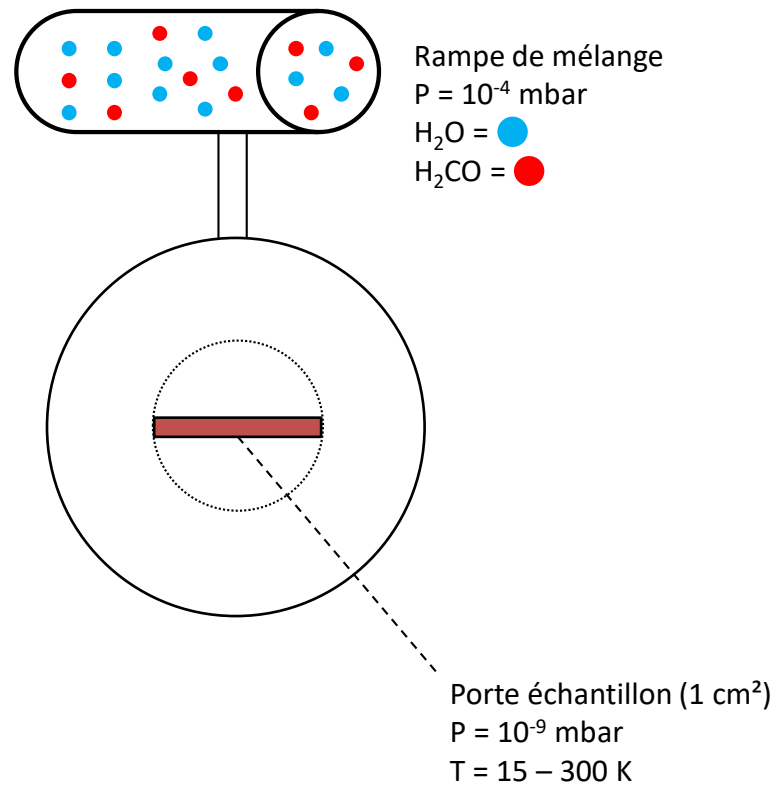
**Irradiation d'analogues de glace contenant du formaldéhyde:
Formation des sucres et polyols**



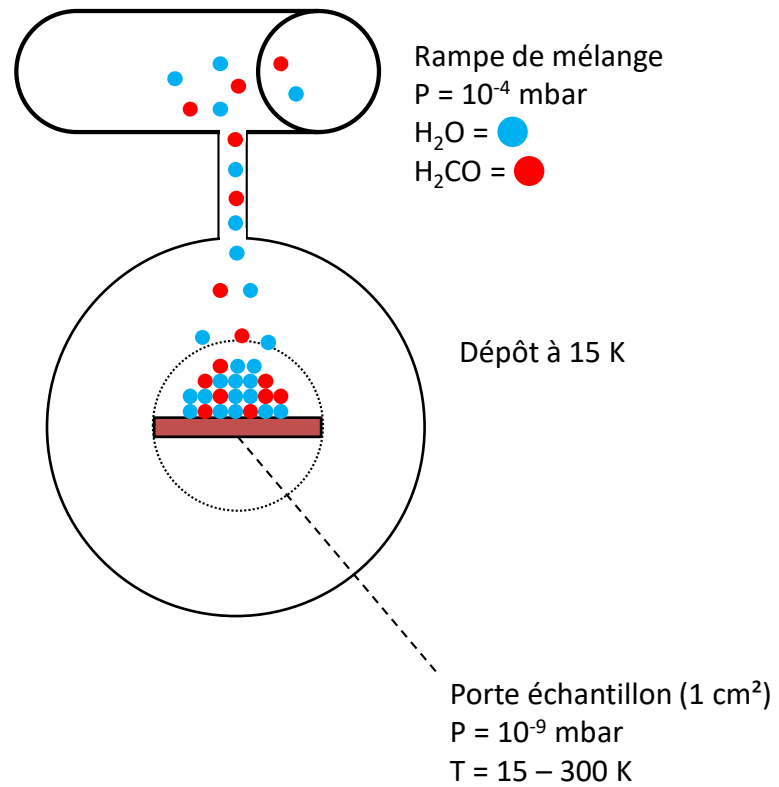
L'expérience RING



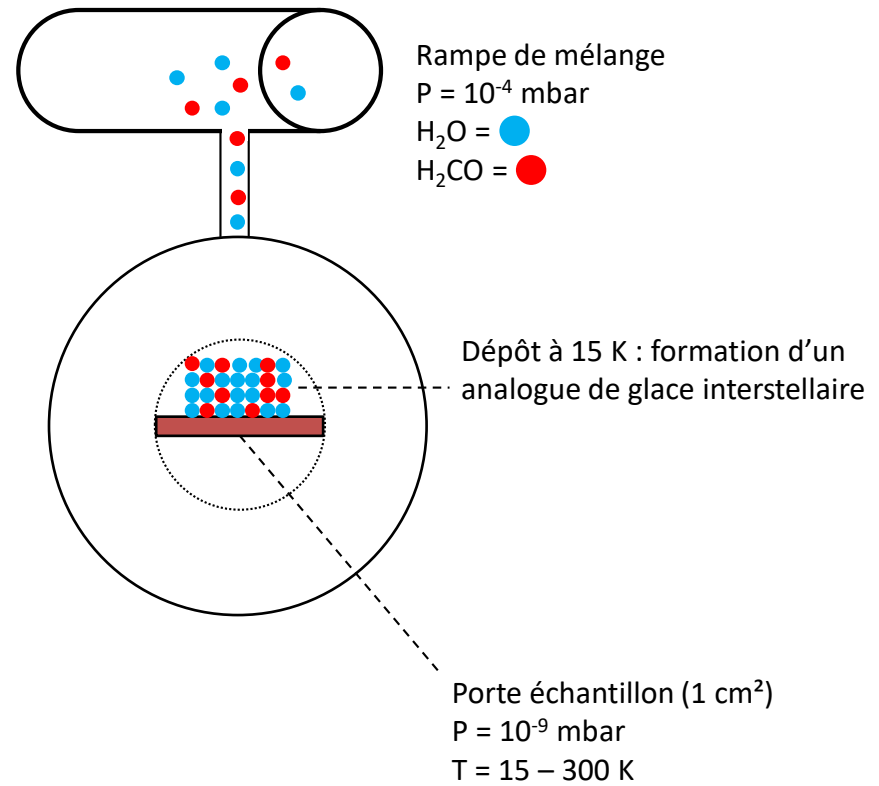
L'expérience RING



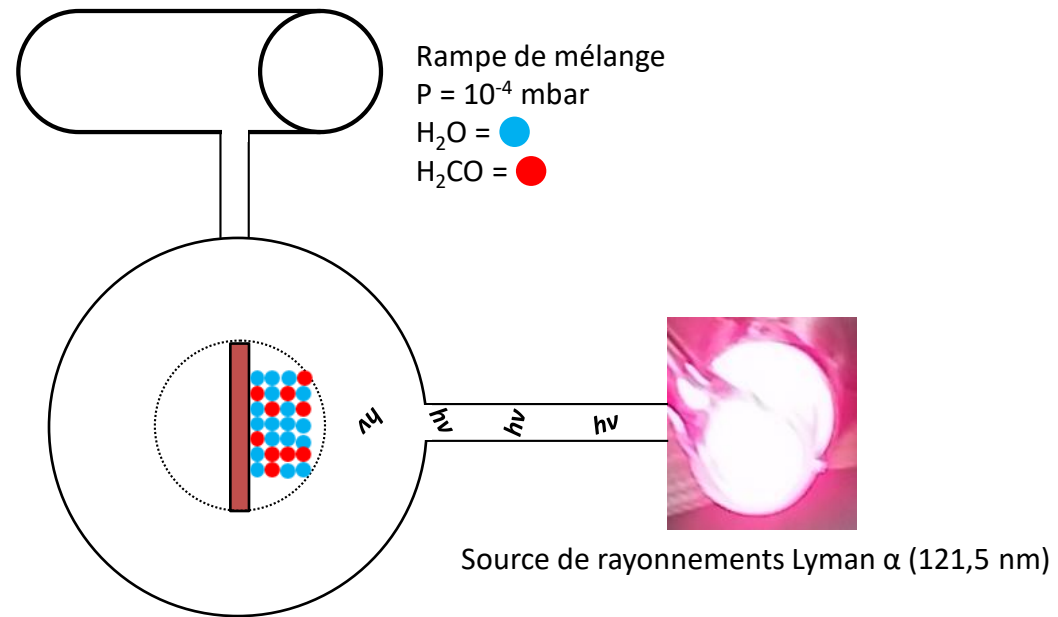
L'expérience RING



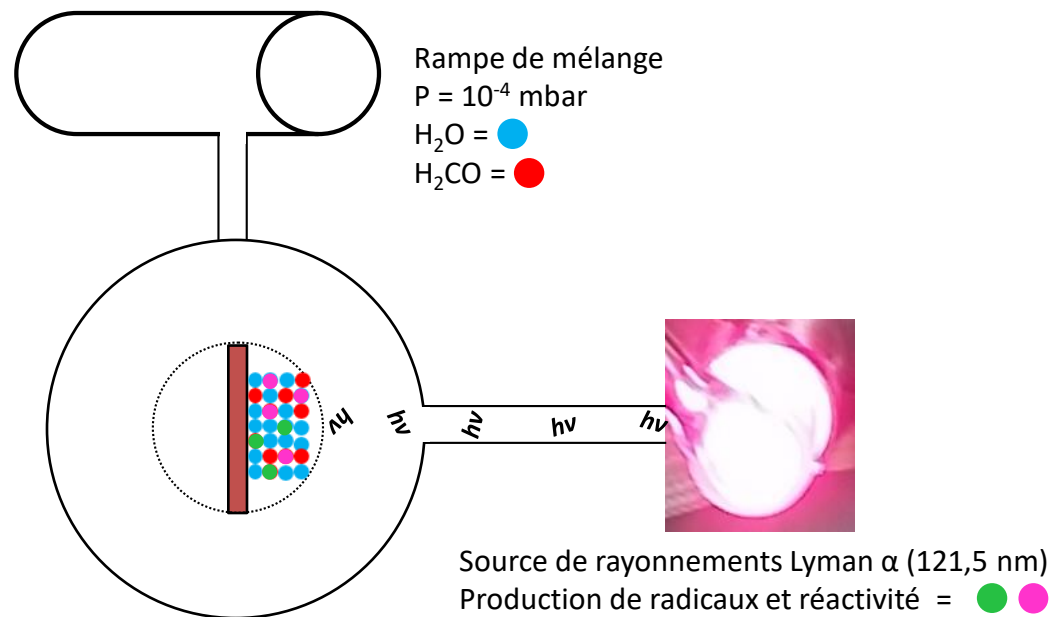
L'expérience RING



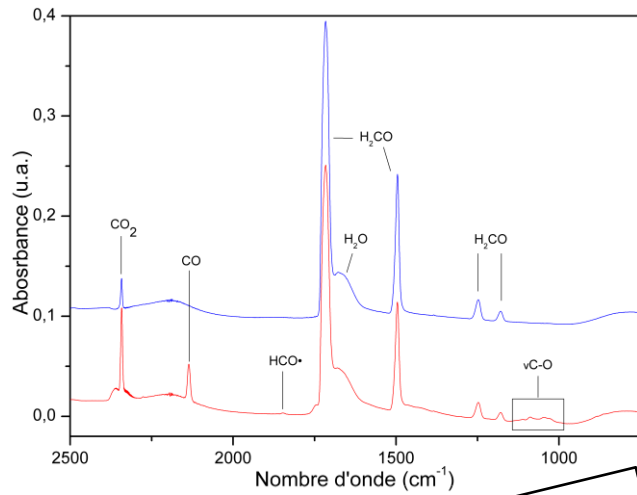
L'expérience RING



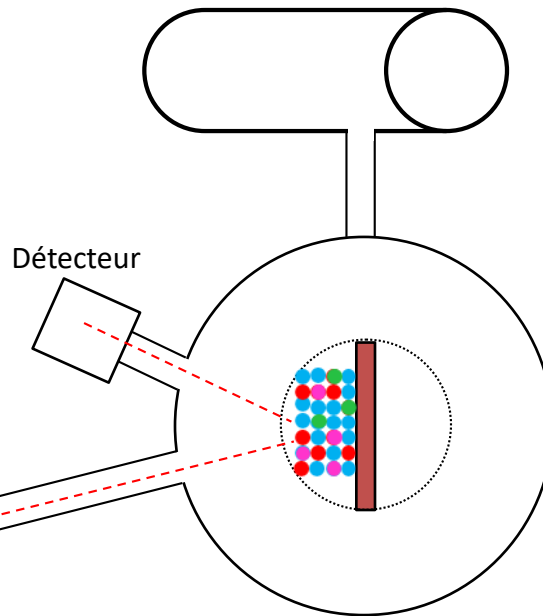
L'expérience RING



L'expérience RING



Spectromètre
infrarouge



Rampe de mélange

$P = 10^{-4}$ mbar

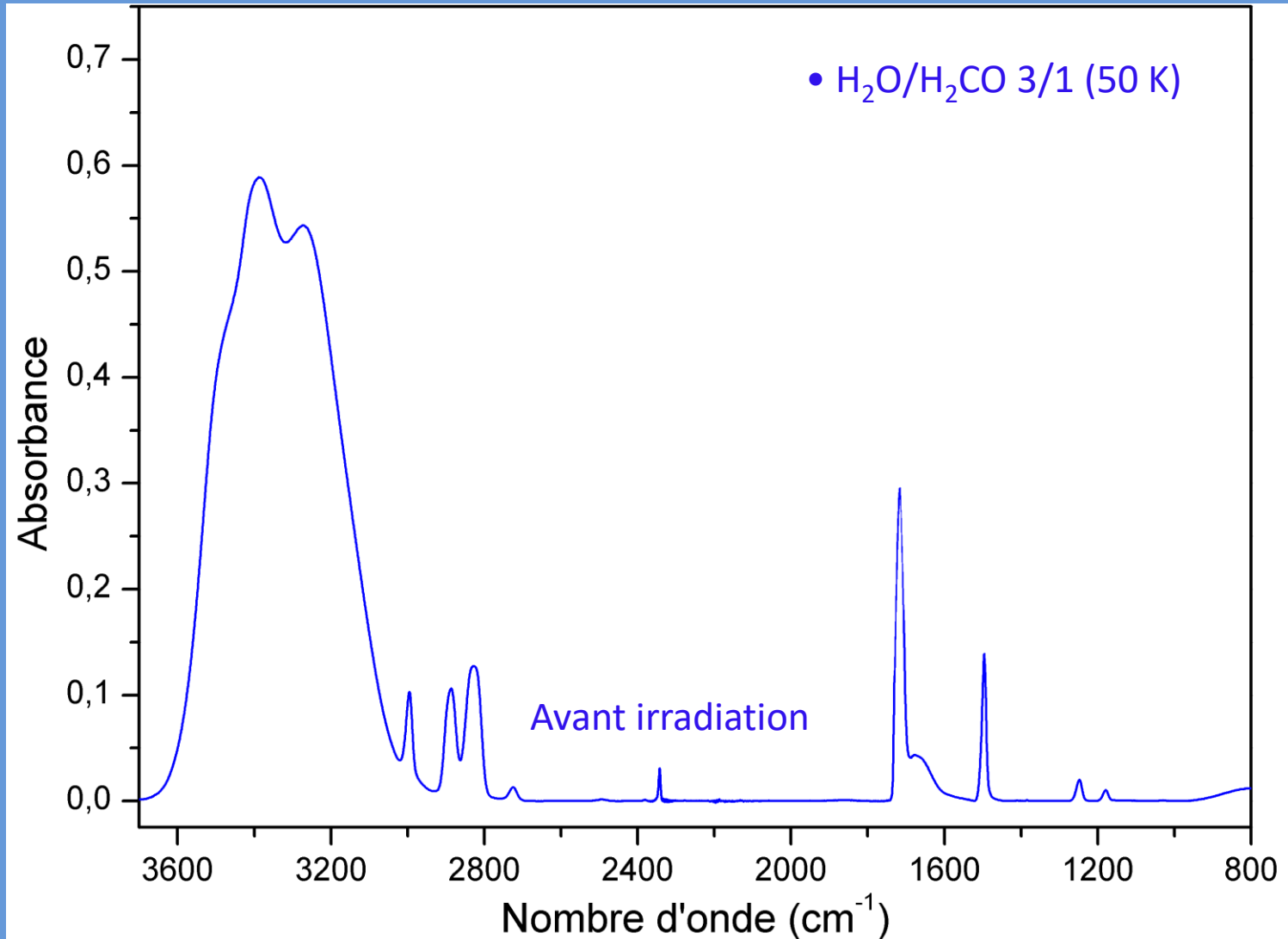
H₂O = ●

H₂CO = ●

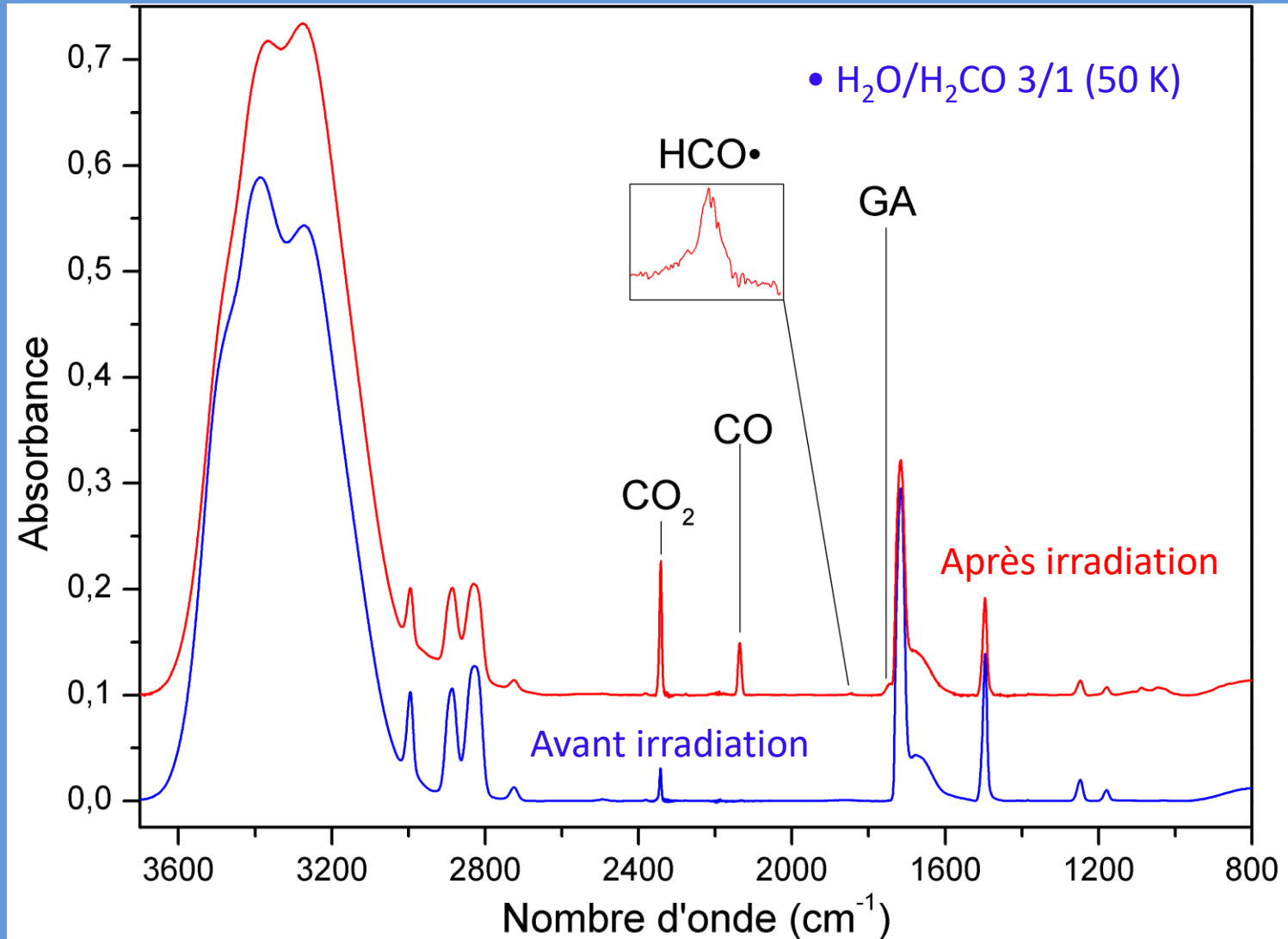
Source de rayonnements Lyman α (121,5 nm)

Production de radicaux et réactivité = ● ●

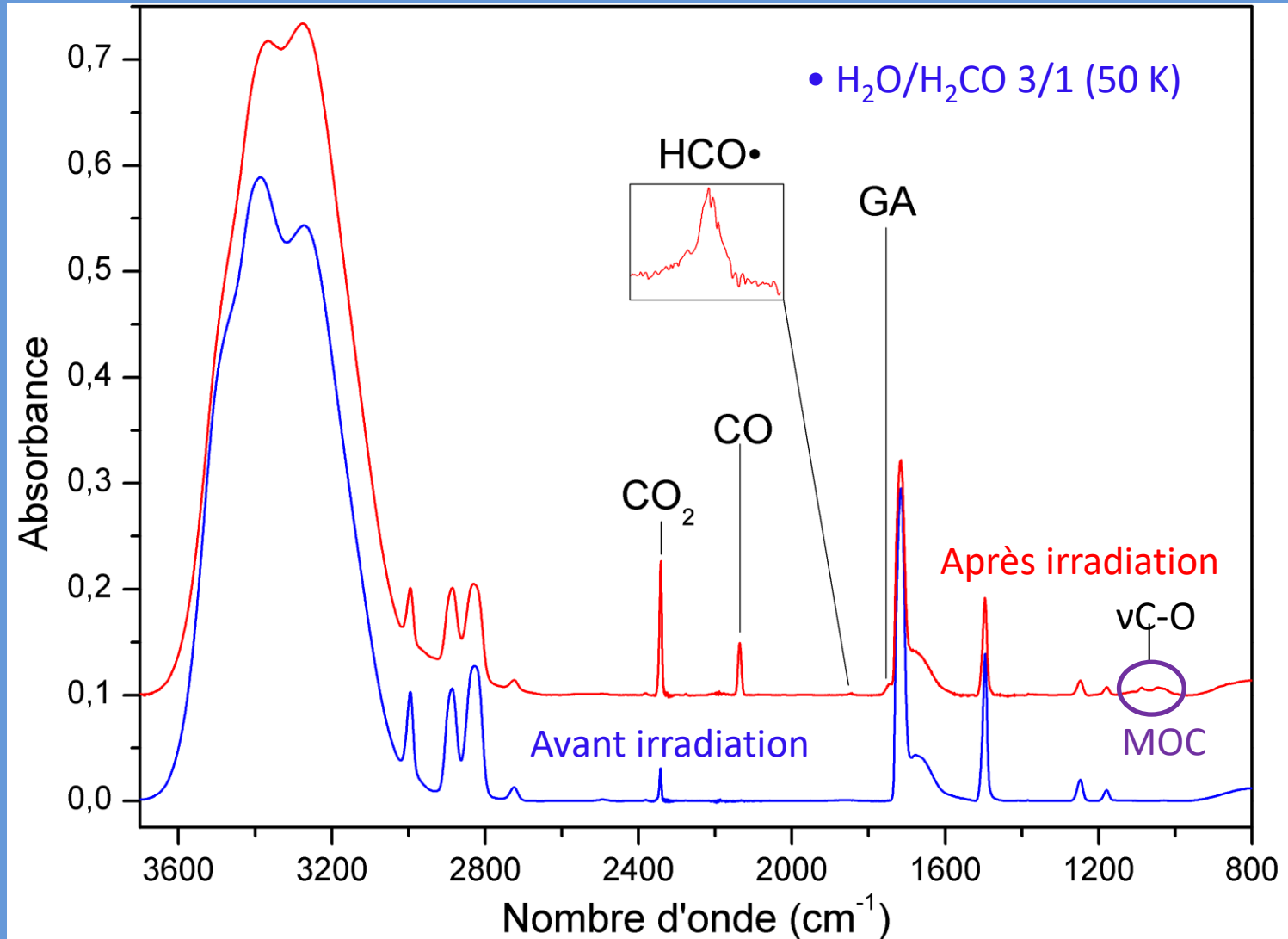
Irradiation UV H₂O/H₂CO 3/1 (50K)



Irradiation UV H₂O/H₂CO 3/1 (50K)

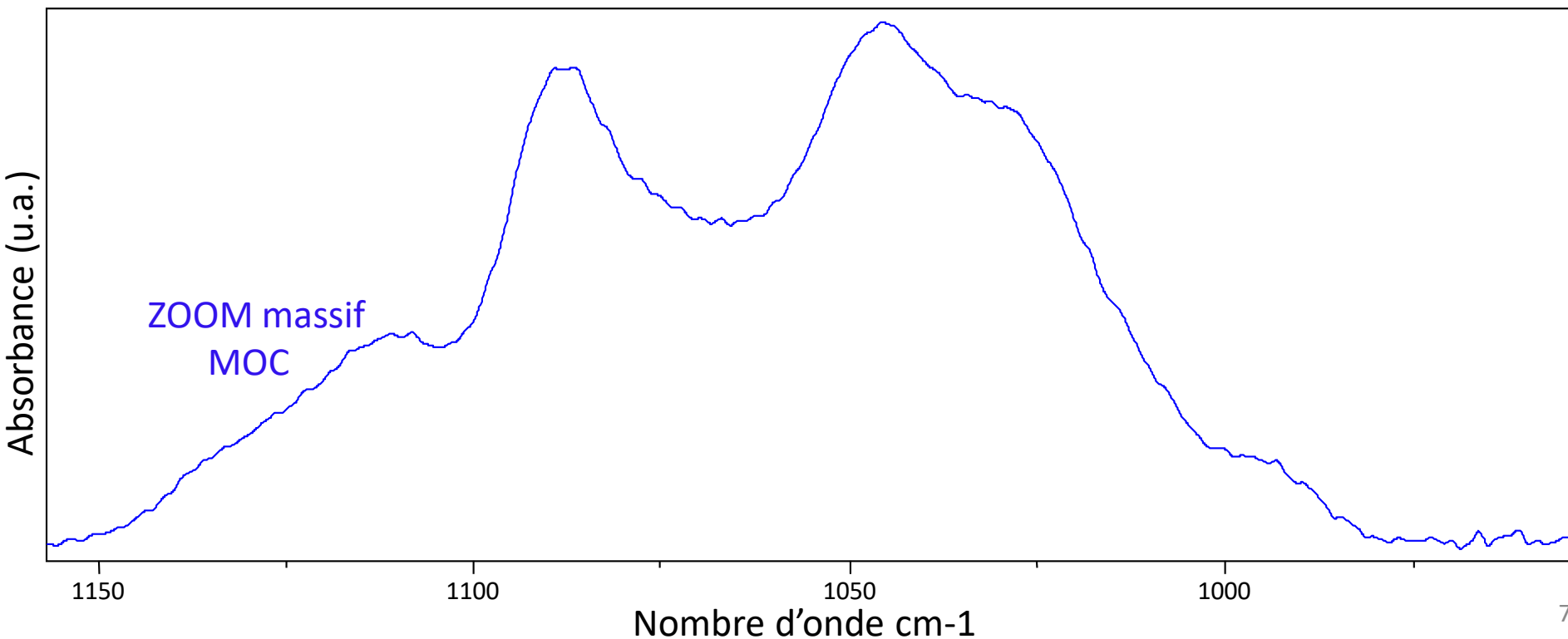


Irradiation UV H₂O/H₂CO 3/1 (50K)



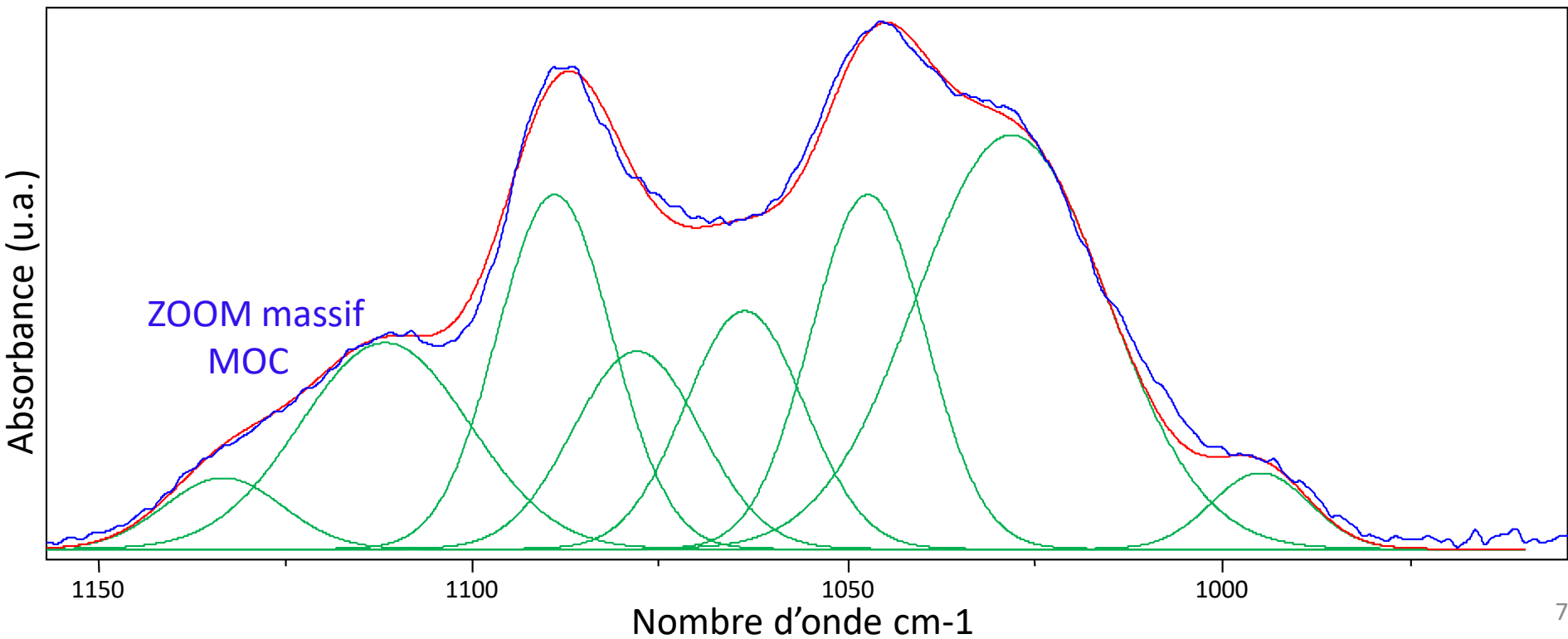
Irradiation UV H₂O/H₂CO 3/1 (50K)

Spectroscopie IRTF



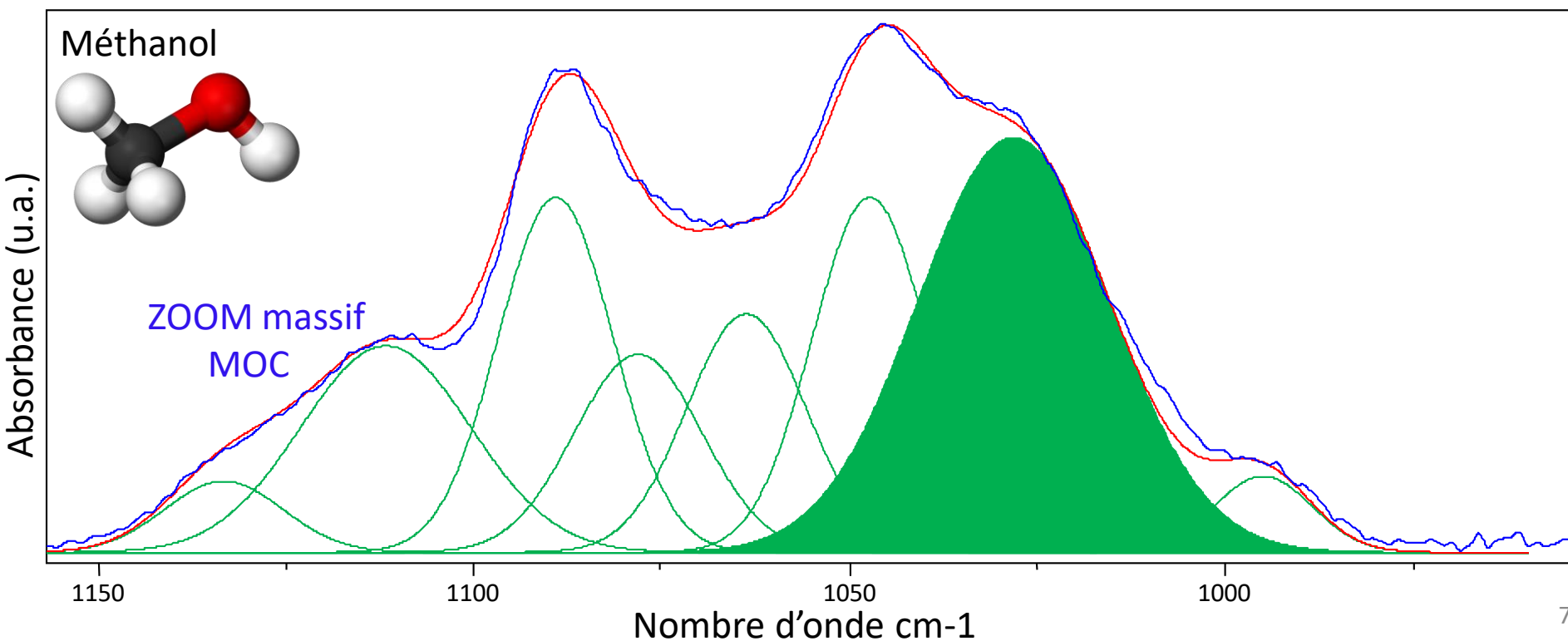
Irradiation UV H₂O/H₂CO 3/1 (50K)

Spectroscopie IRTF



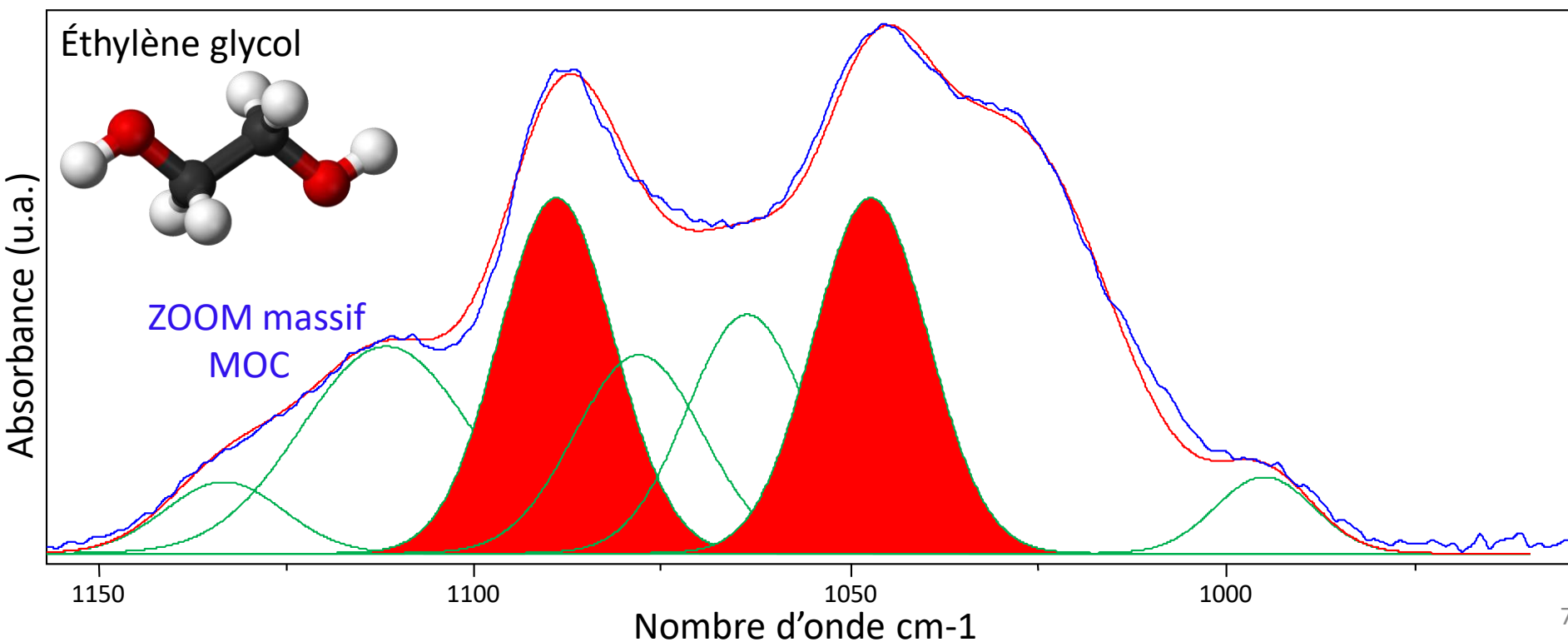
Irradiation UV H₂O/H₂CO 3/1 (50K)

Spectroscopie IRTF



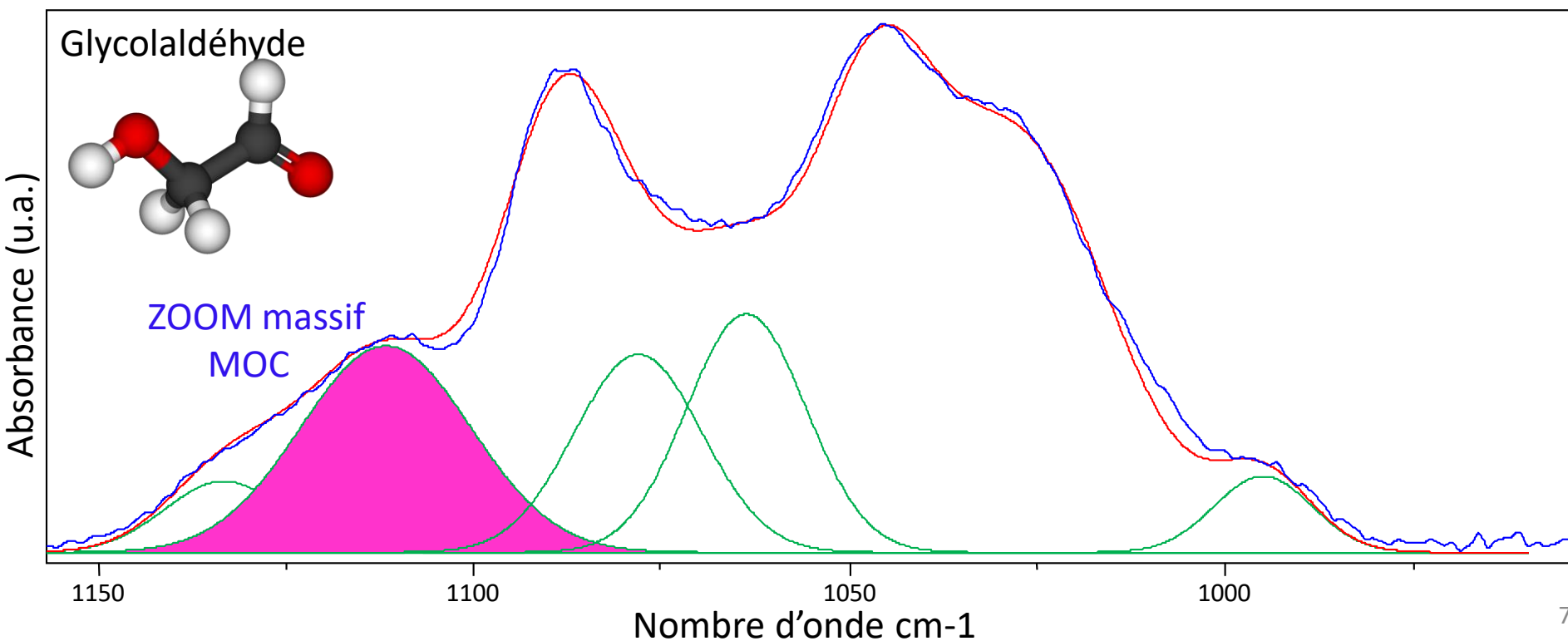
Irradiation UV H₂O/H₂CO 3/1 (50K)

Spectroscopie IRTF

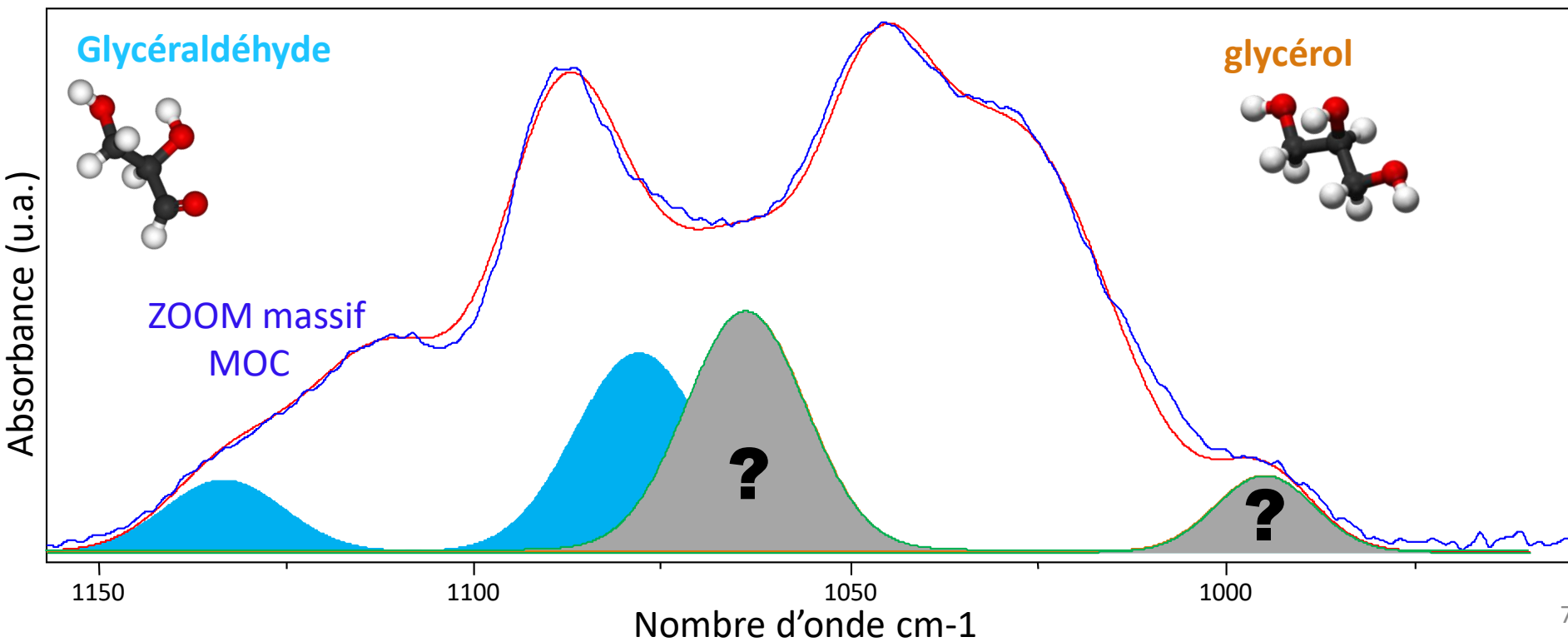


Irradiation UV H₂O/H₂CO 3/1 (50K)

Spectroscopie IRTF

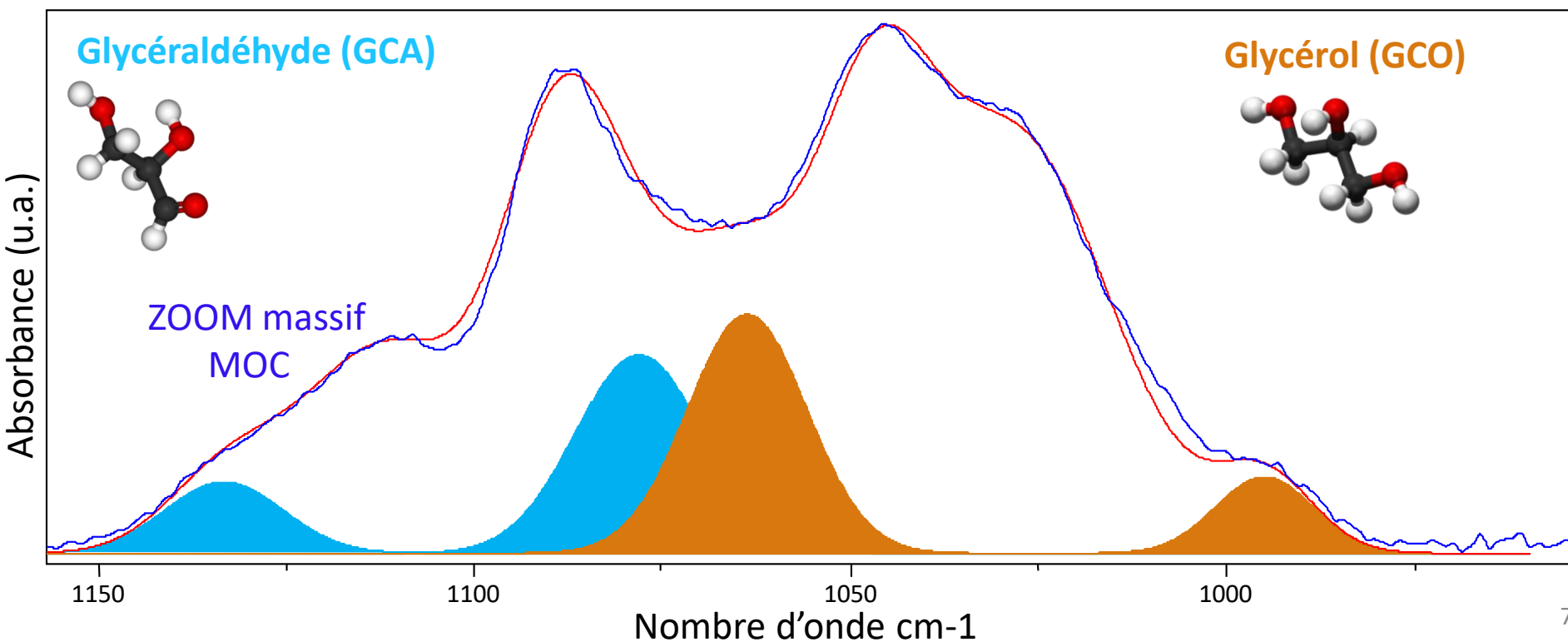


Irradiation UV H₂O/H₂CO 3/1 (50K)

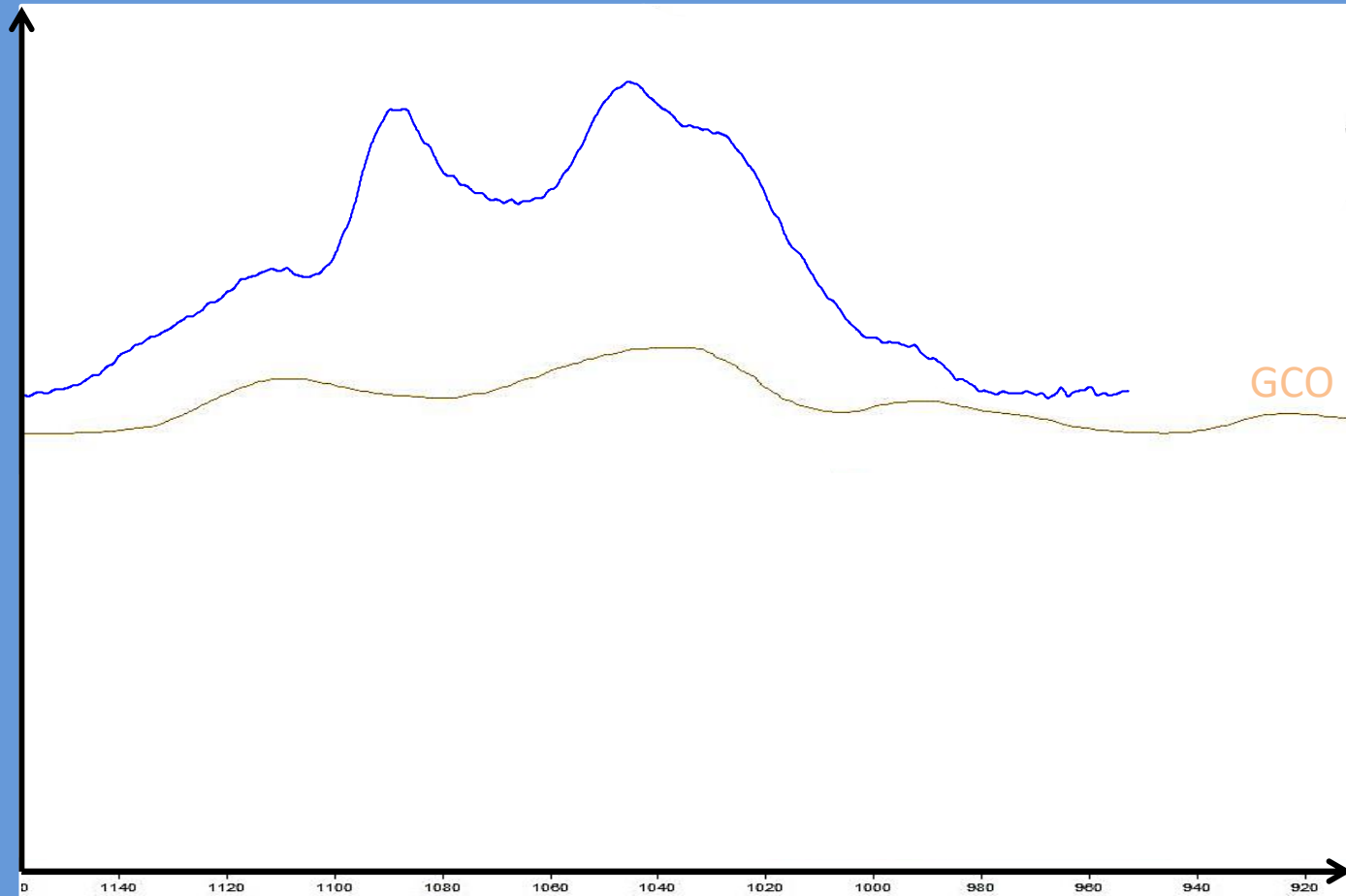


Irradiation UV H₂O/H₂CO 3/1 (50K)

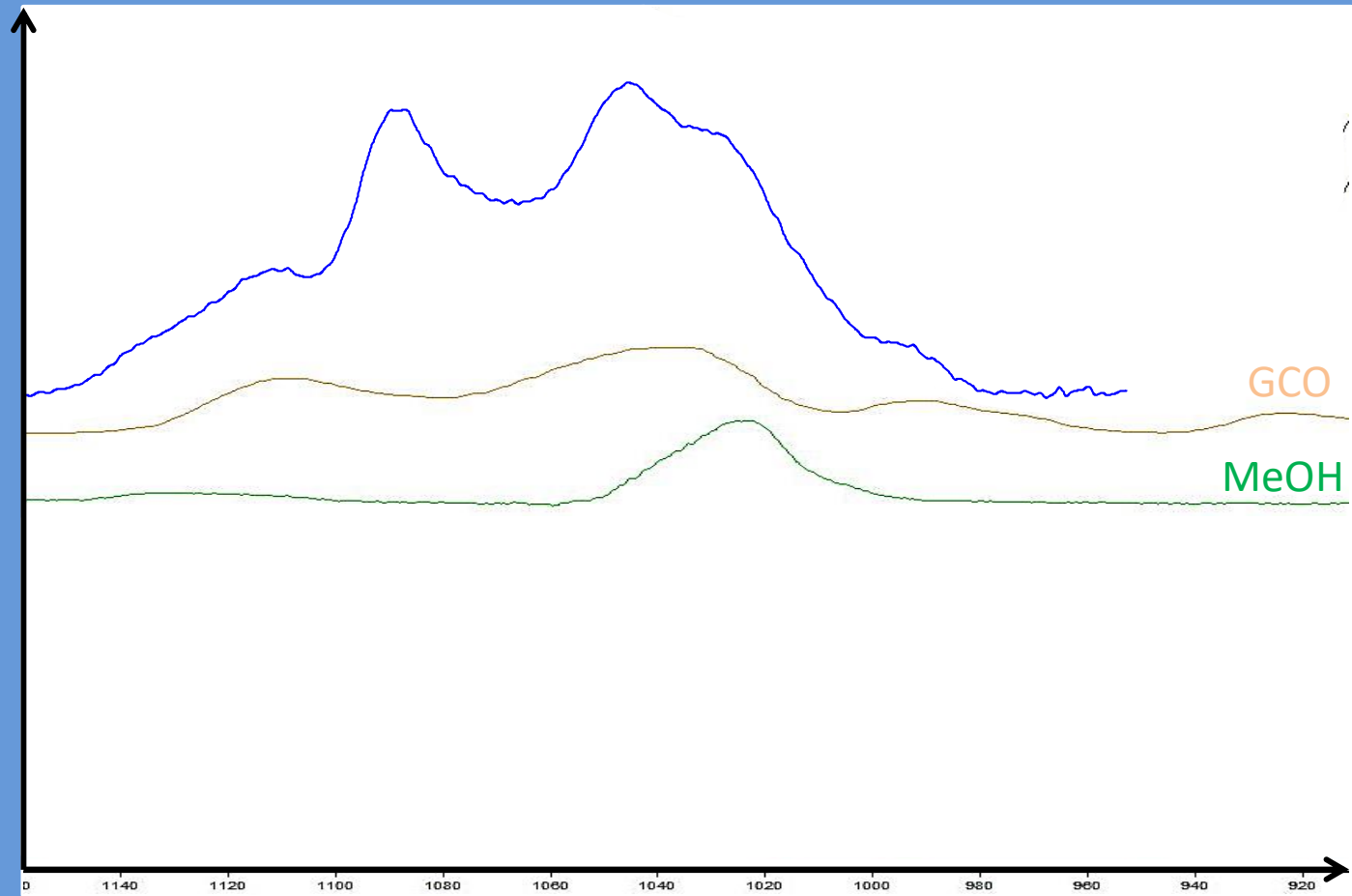
Spectroscopie IRTF



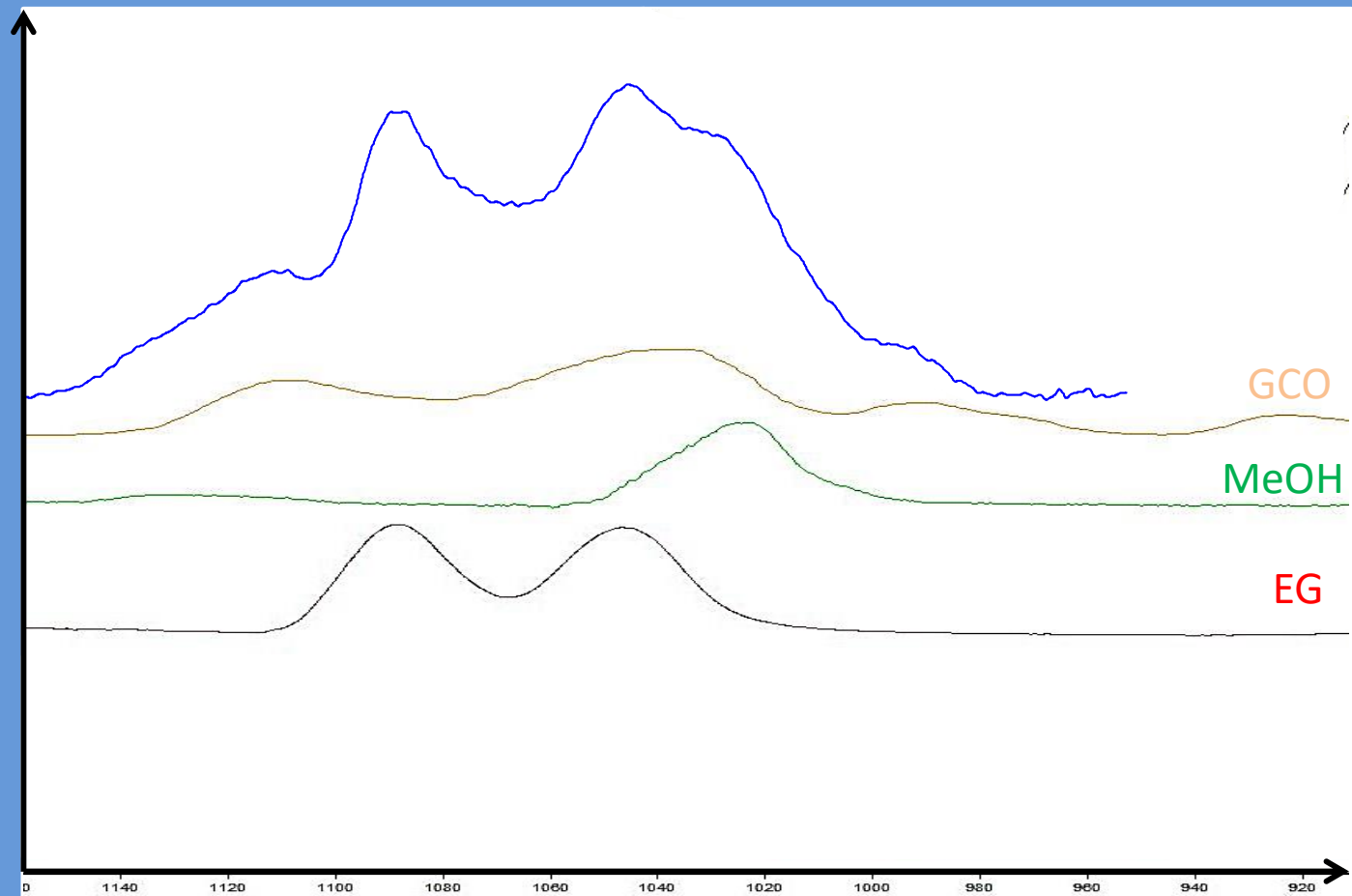
Irradiation UV H₂O/H₂CO 3/1 (50K)



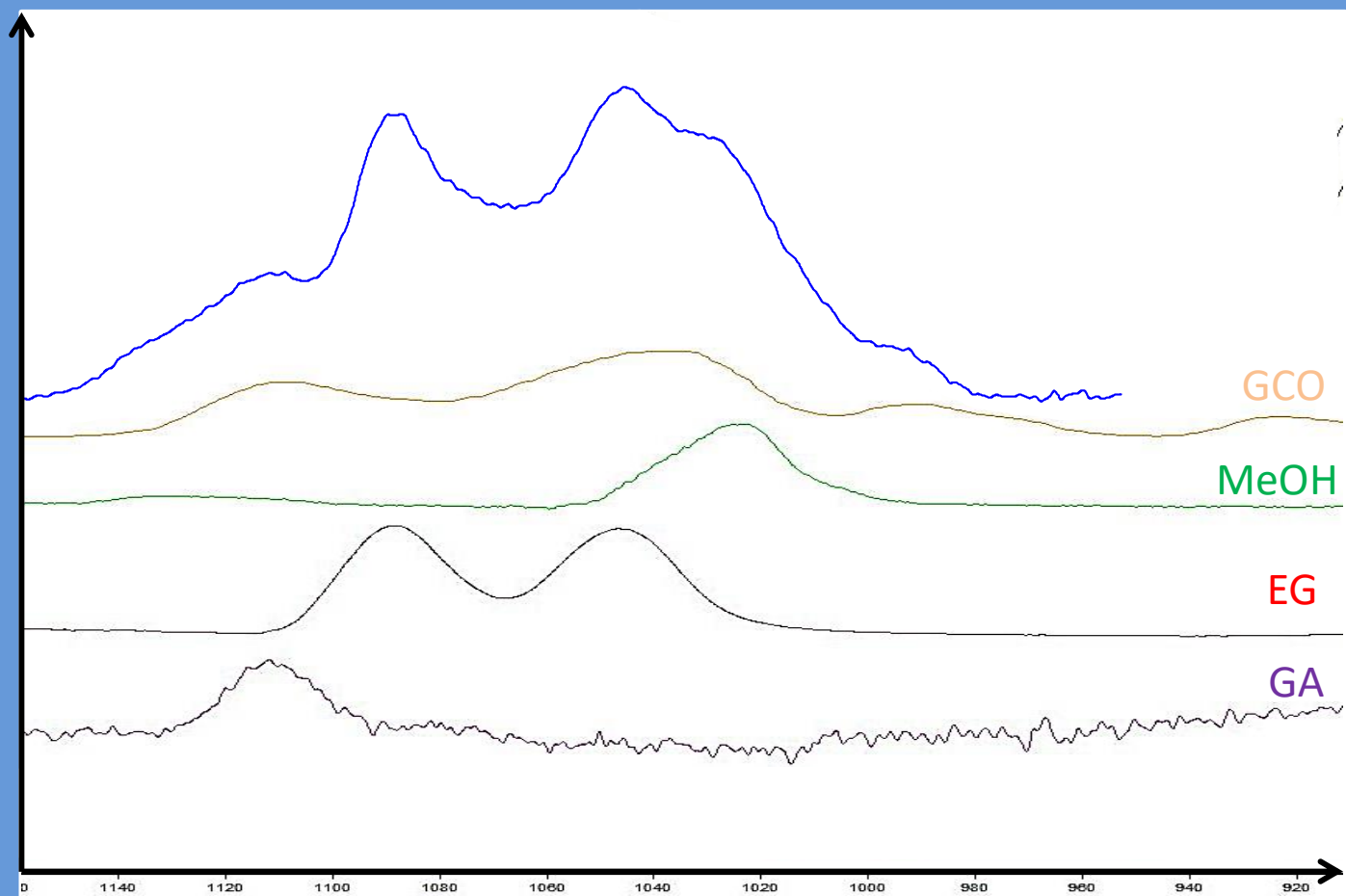
Irradiation UV H₂O/H₂CO 3/1 (50K)



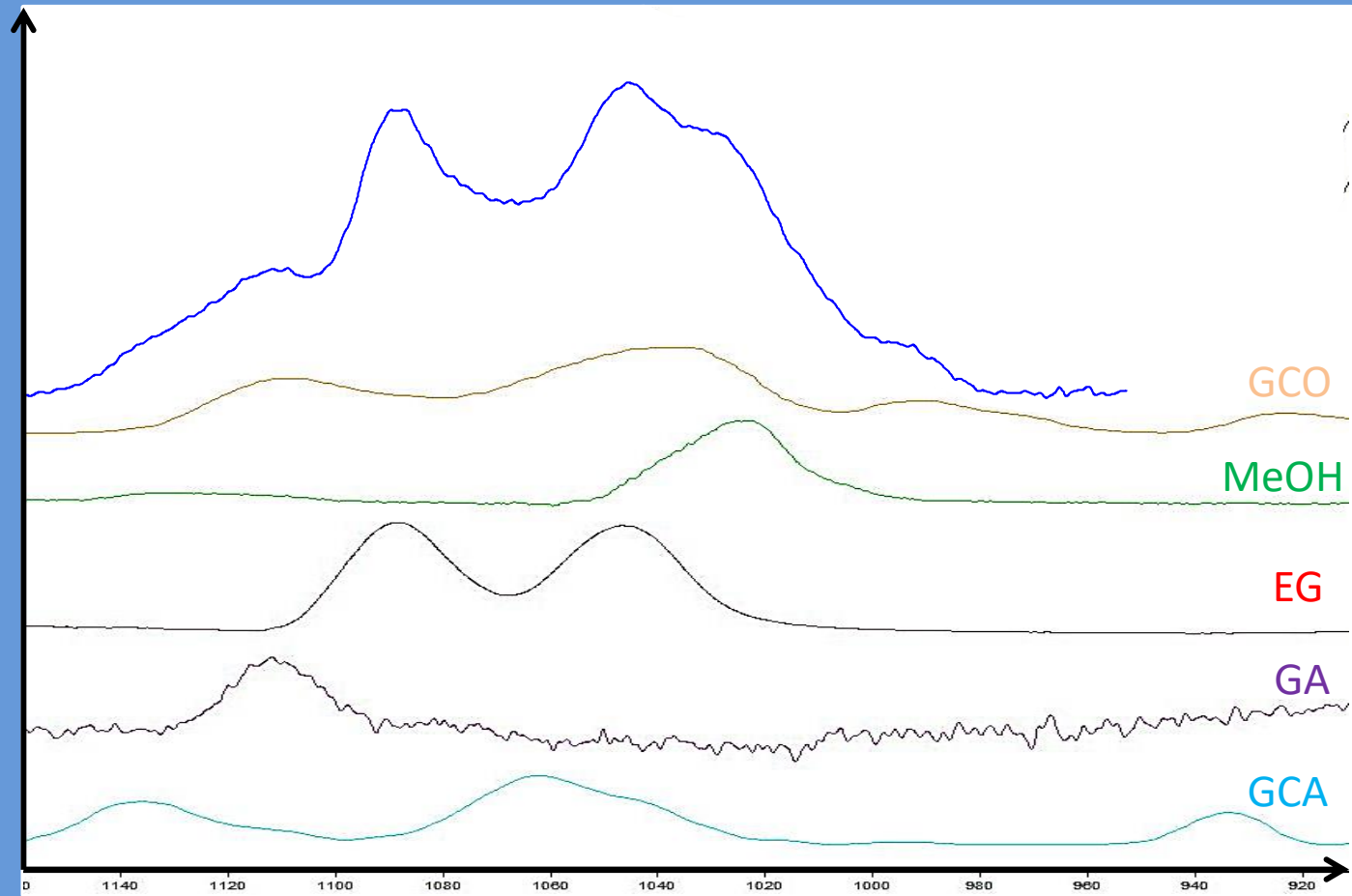
Irradiation UV H₂O/H₂CO 3/1 (50K)



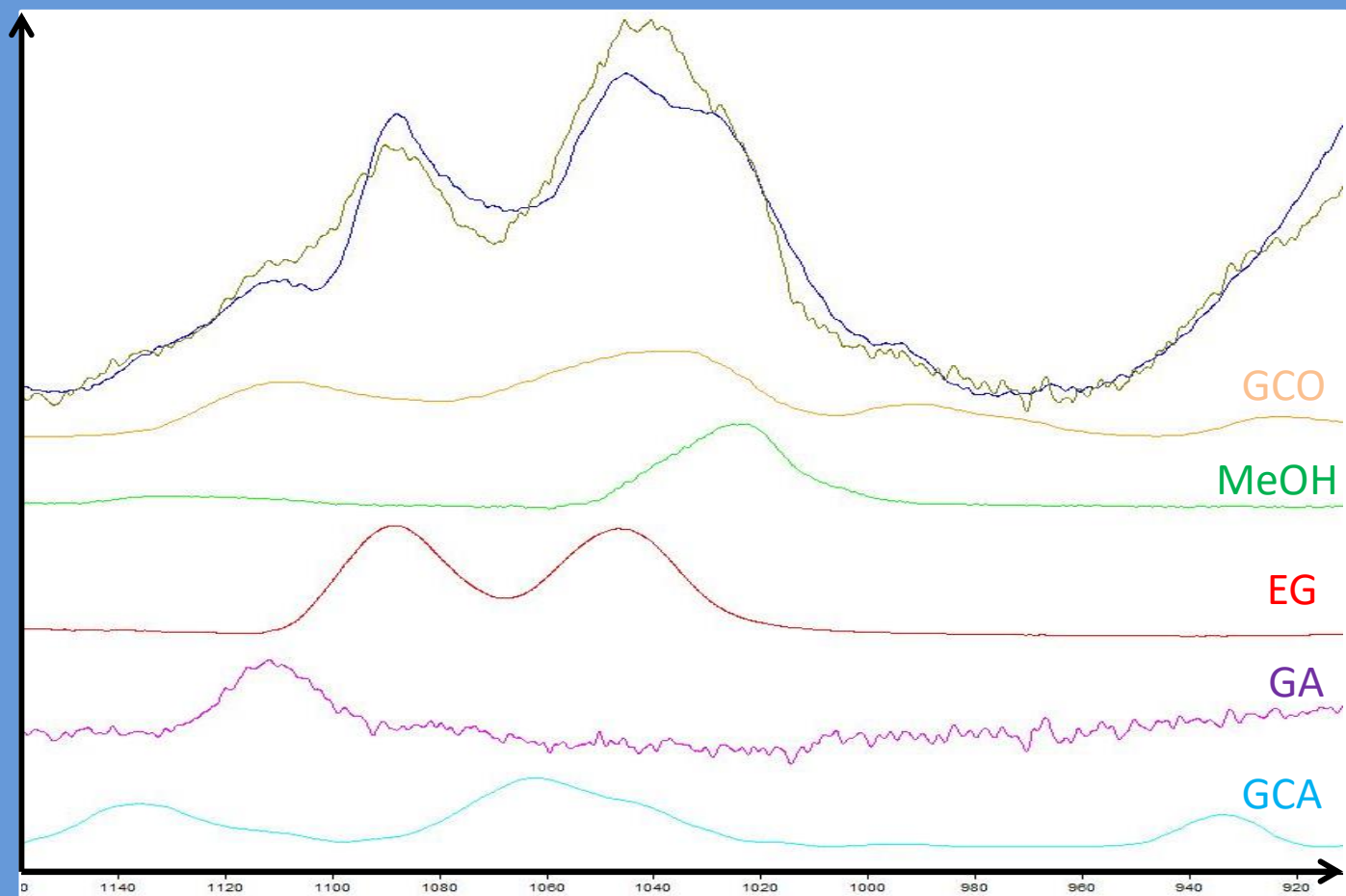
Irradiation UV H₂O/H₂CO 3/1 (50K)



Irradiation UV H₂O/H₂CO 3/1 (50K)

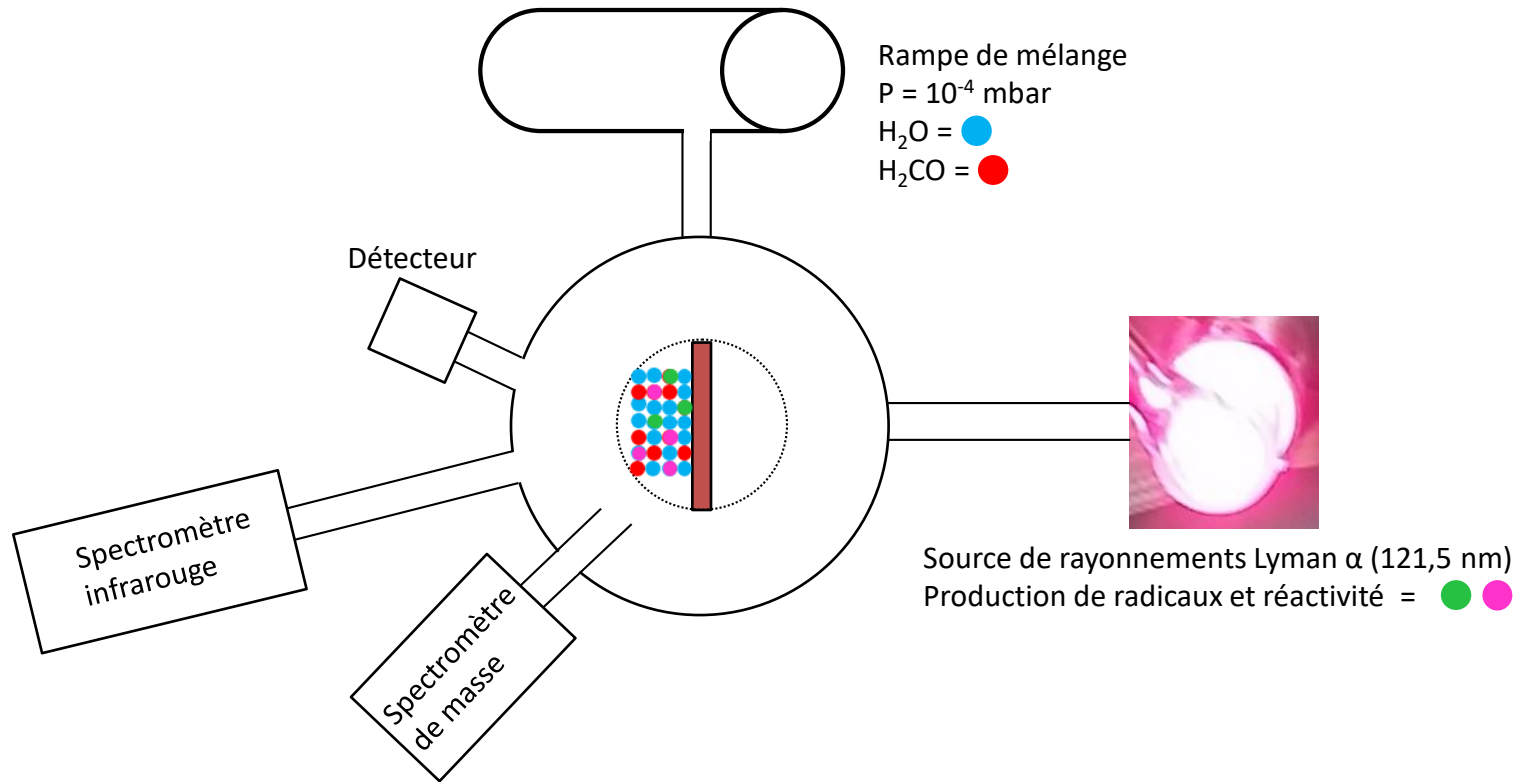


Irradiation UV H₂O/H₂CO 3/1 (50K)

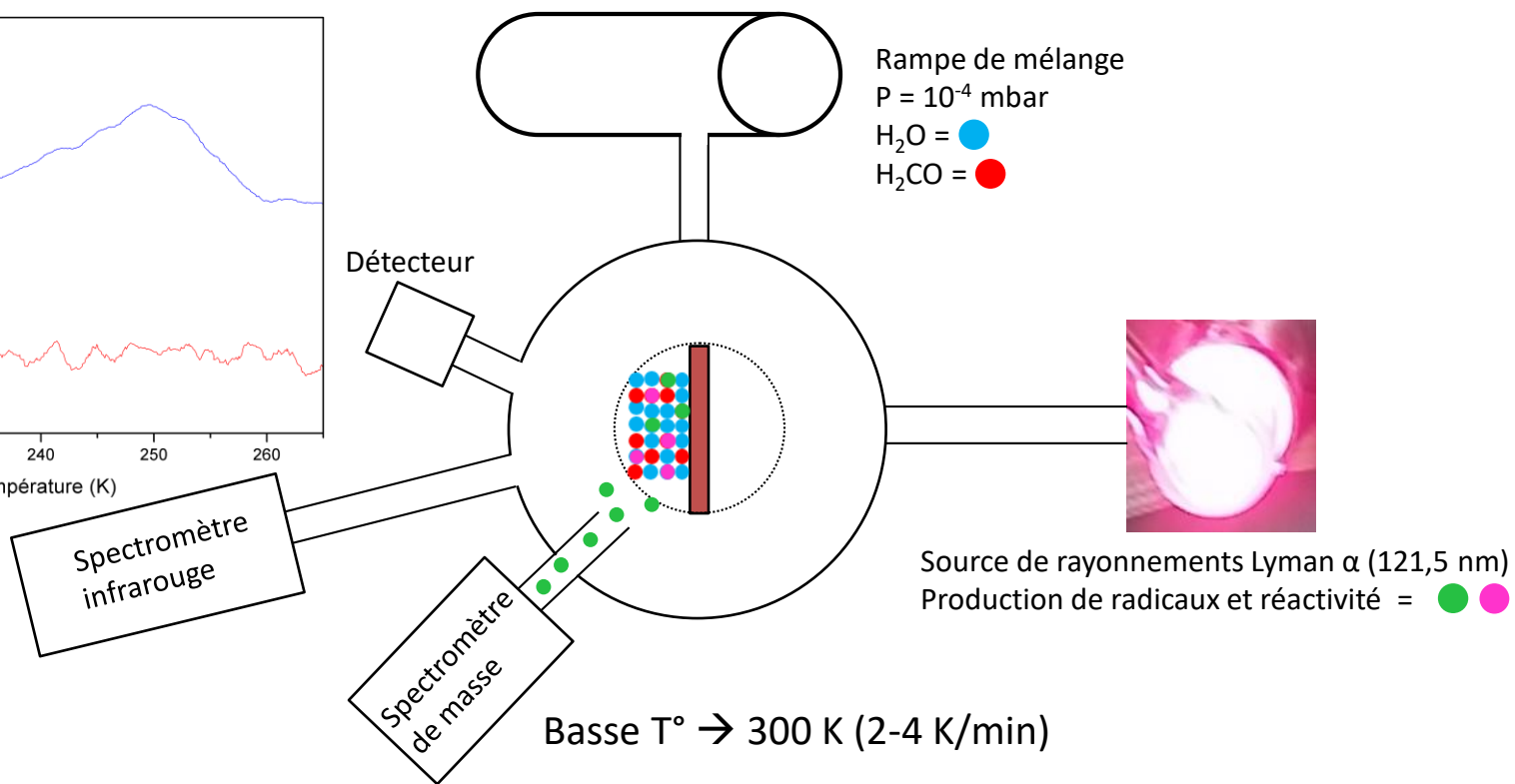
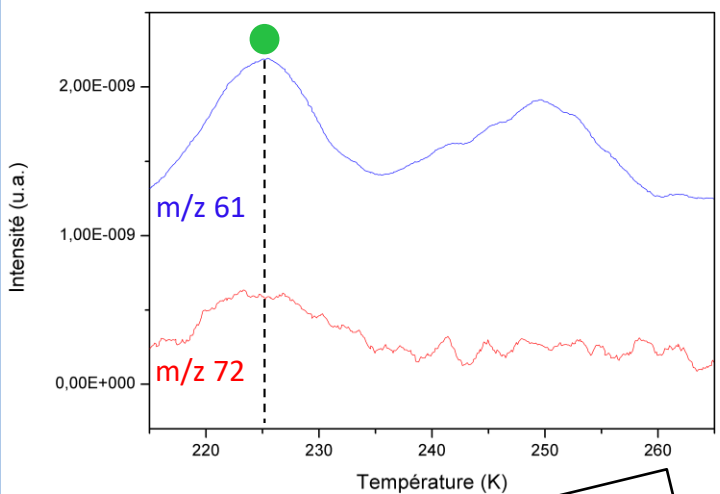


Identification par spectroscopie IR: MeOH, GA, GCA, EG, GCO

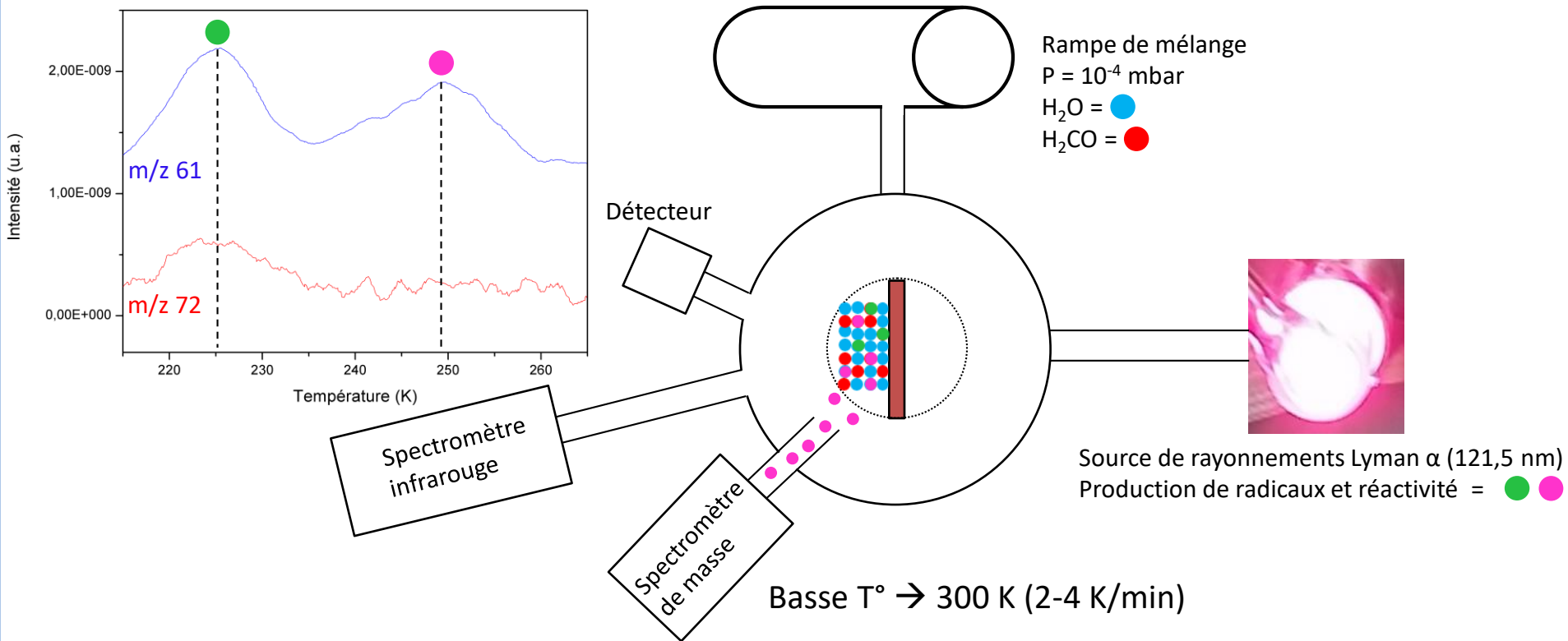
L'expérience RING



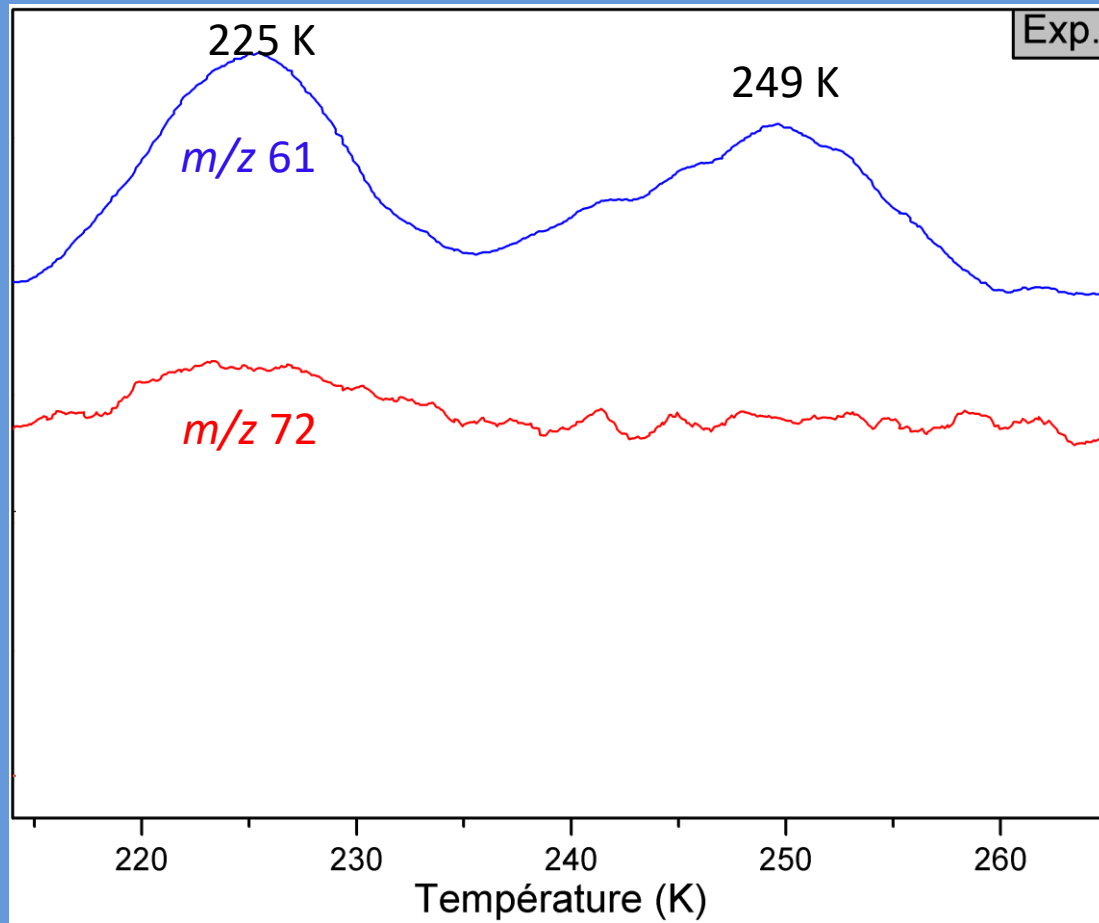
L'expérience RING



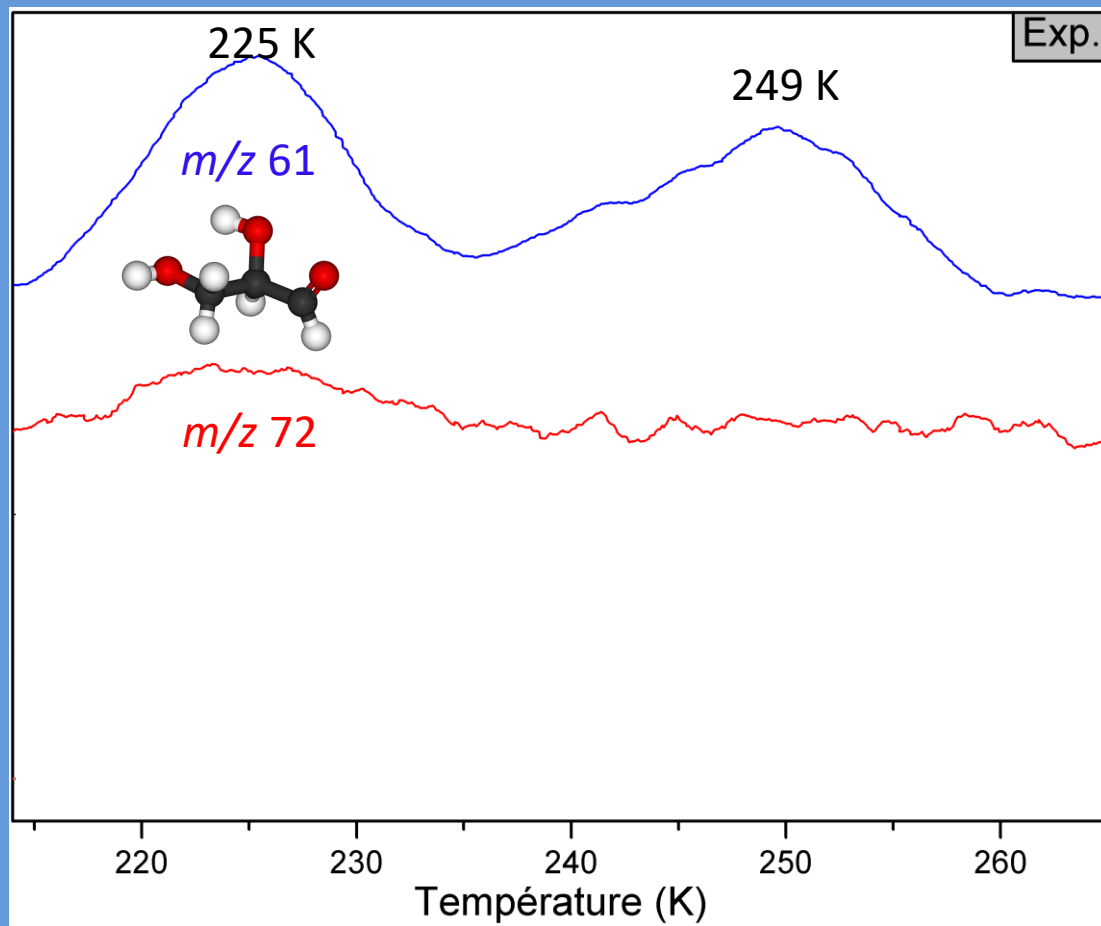
L'expérience RING



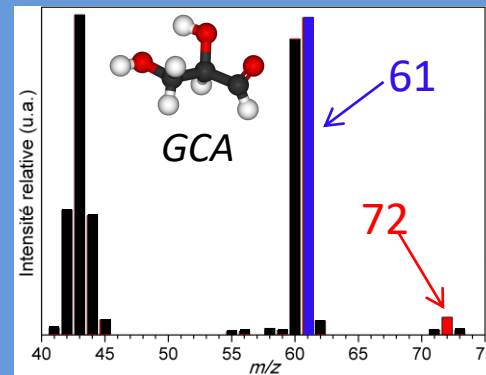
Irradiation UV H₂O/H₂CO 3/1 (50K)



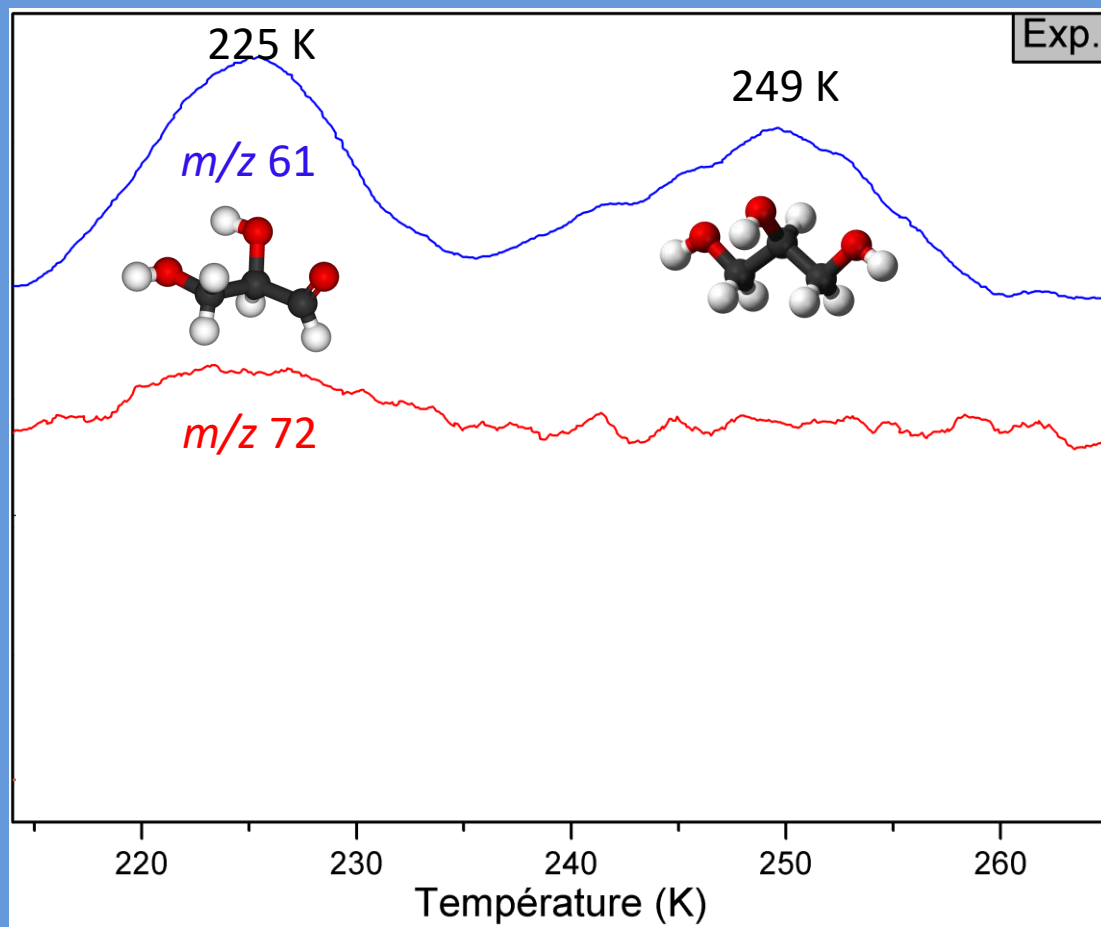
Irradiation UV H₂O/H₂CO 3/1 (50K)



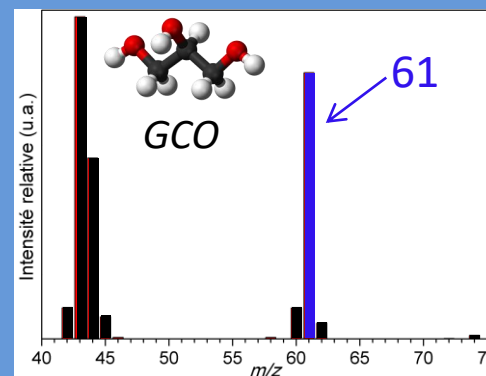
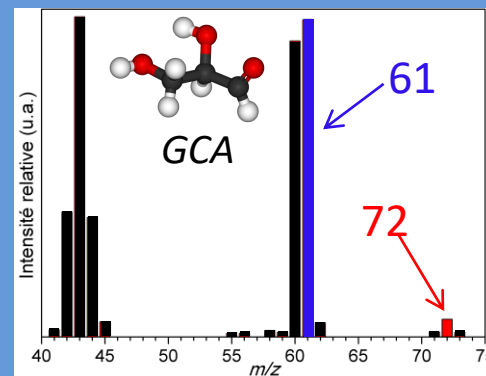
Références 70 eV

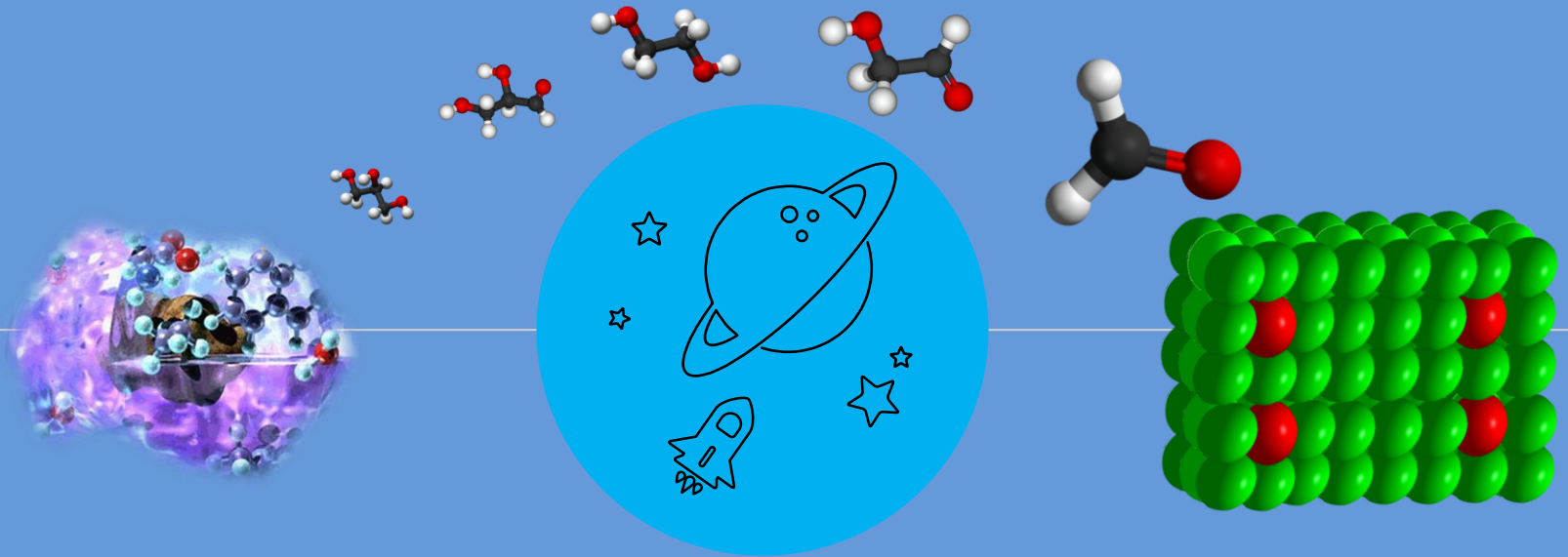


Irradiation UV H₂O/H₂CO 3/1 (50K)



Références 70 eV

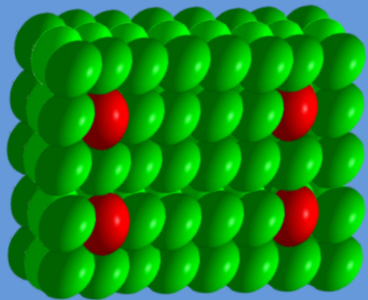
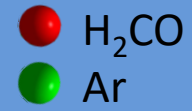




Mécanisme de formation?

- Etudes en matrices cryogéniques
- Calculs théoriques

Irradiation H₂CO en matrice d'argon (15 K)

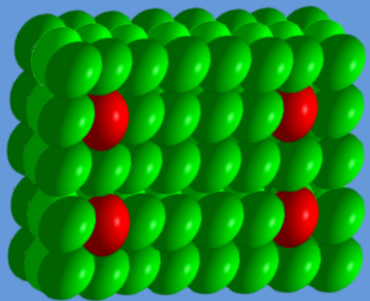


H₂CO / Ar=2/1000

Irradiation H₂CO en matrice d'argon (15 K)

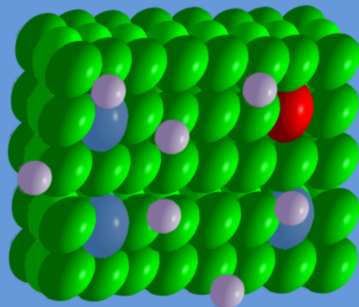
- H₂CO
- Ar
- HCO•
- H•

Irradiation (15 K)



H₂CO / Ar=2/1000

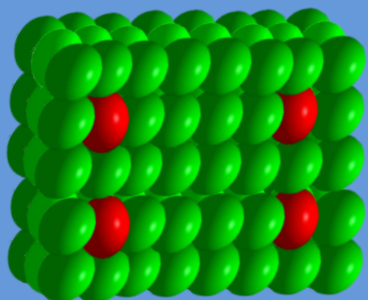
85 %



Irradiation H₂CO en matrice d'argon (15 K)

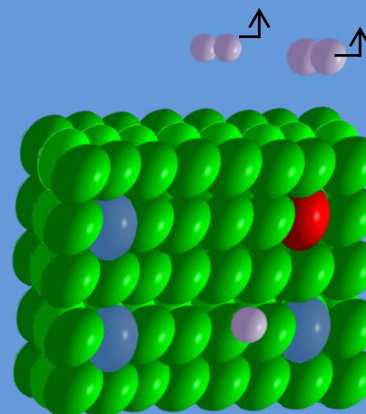
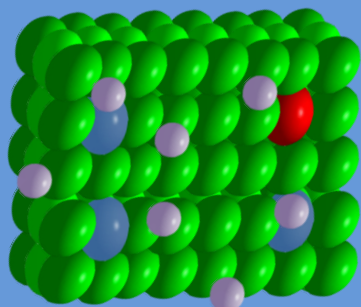
- H₂CO
- Ar
- HCO•
- H•

Irradiation (15 K)



Recuit :
15 K → 30 K → 15 K

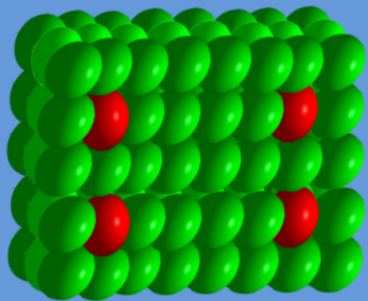
85 %



Irradiation H₂CO en matrice d'argon (15 K)

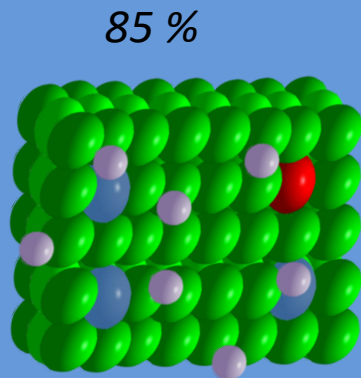
- H₂CO
- Ar
- HCO●
- H●

Irradiation (15 K)

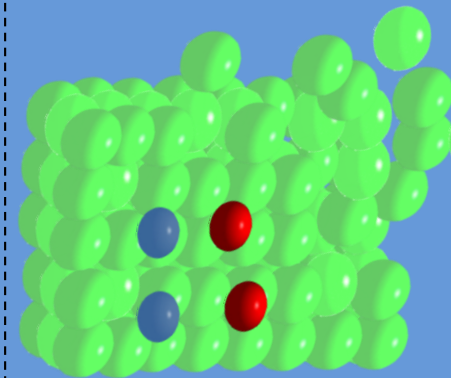
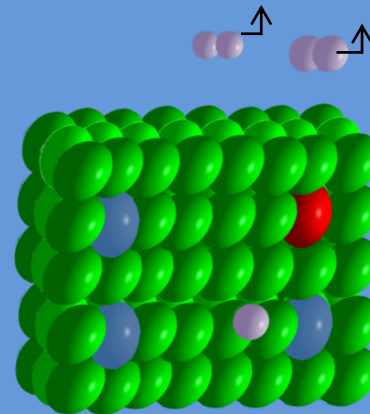


H₂CO / Ar=2/1000

Recuit :
15 K → 30 K → 15 K



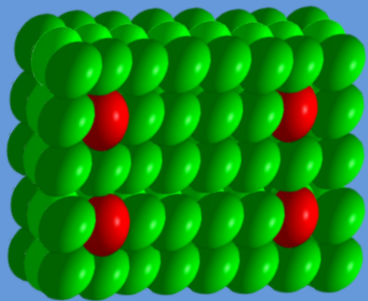
Sublimation matrice :
15 K → 35 K



Irradiation H₂CO en matrice d'argon (15 K)

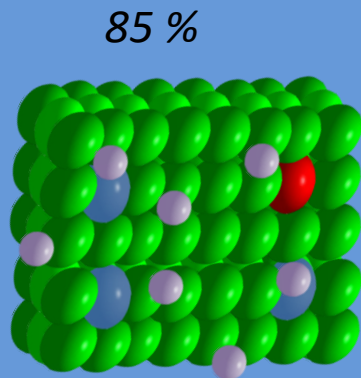
- H₂CO
- Ar
- HCO•
- H•

Irradiation (15 K)

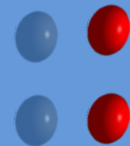
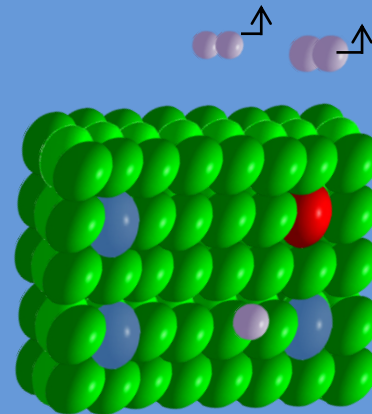


H₂CO / Ar=2/1000

Recuit :
15 K → 30 K → 15 K



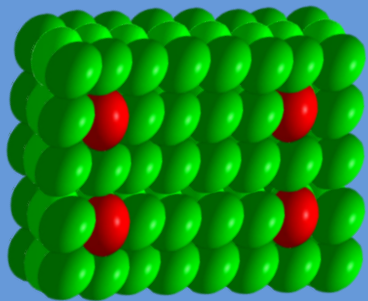
Sublimation matrice :
15 K → 35 K



Irradiation H₂CO en matrice d'argon (15 K)

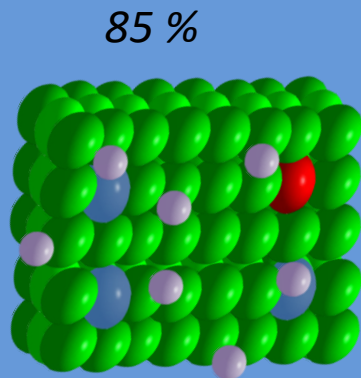
- H₂CO
- Ar
- HCO•
- H•

Irradiation (15 K)

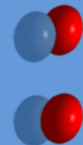
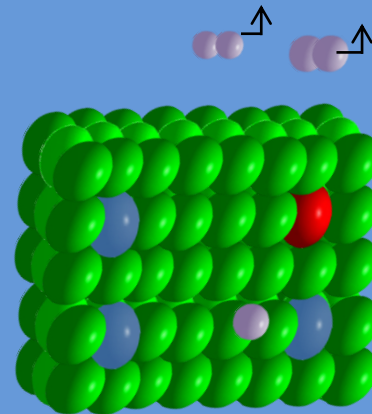


H₂CO / Ar=2/1000

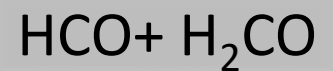
Recuit :
15 K → 30 K → 15 K



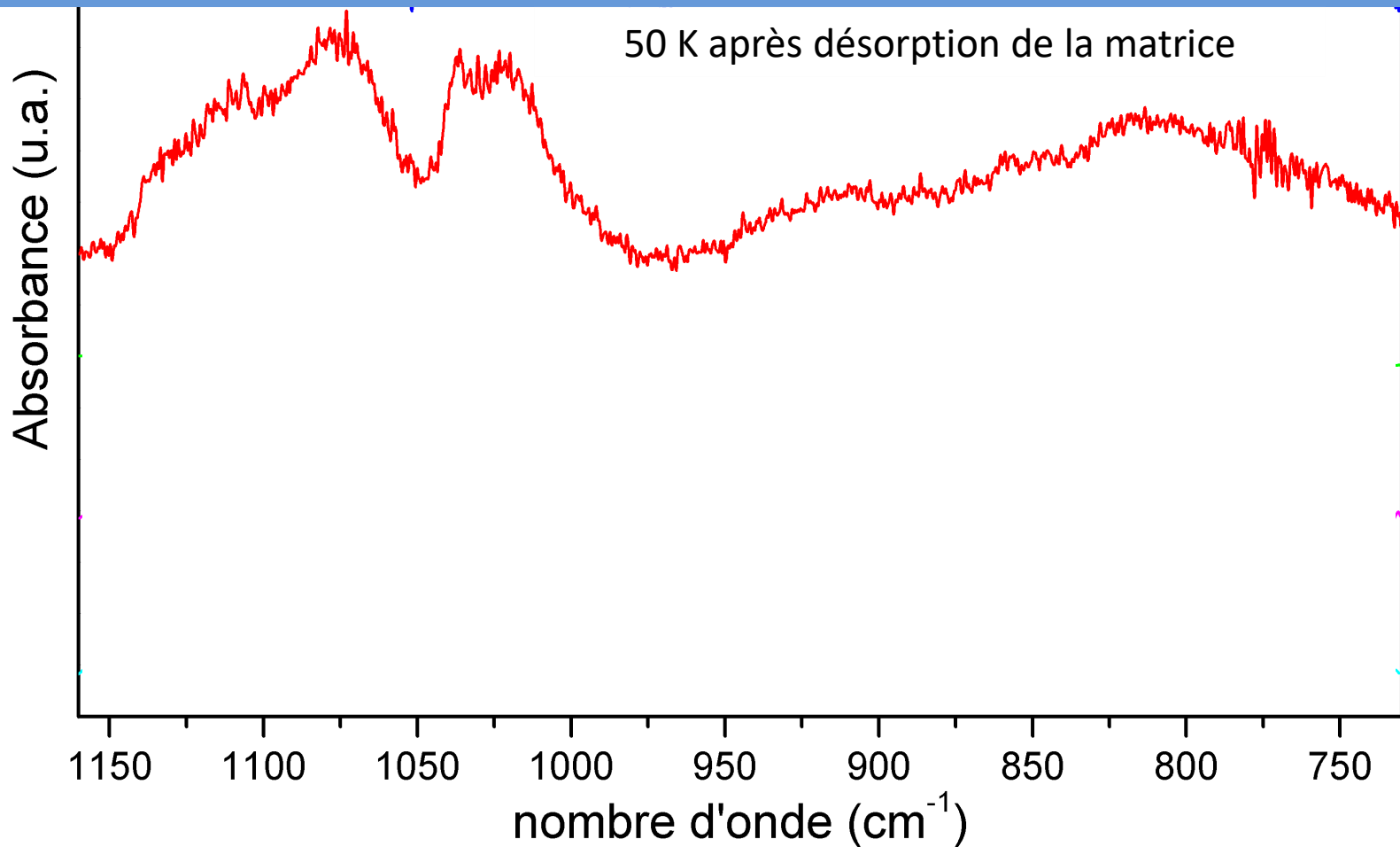
Sublimation matrice :
15 K → 35 K



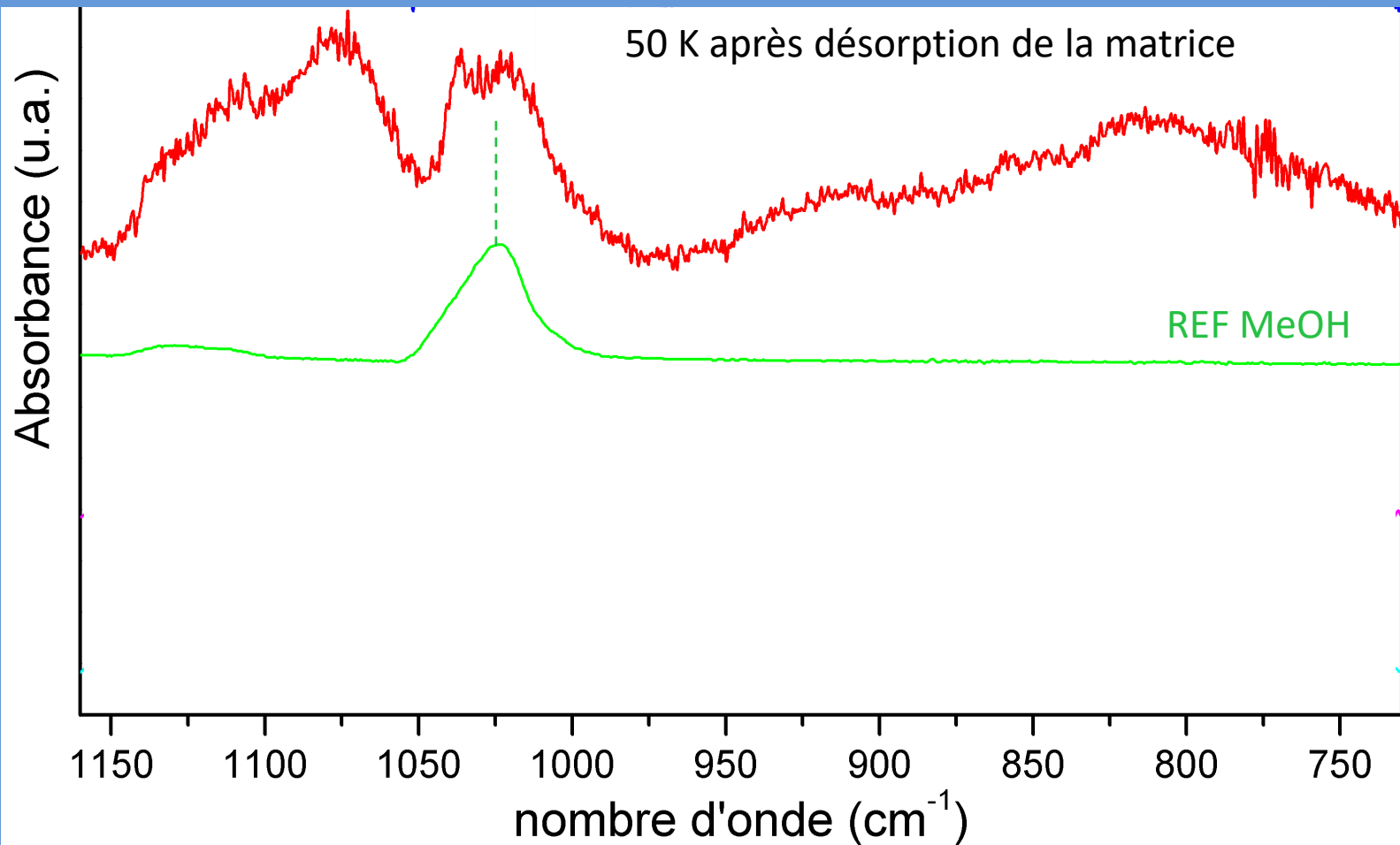
recombinaison⁹



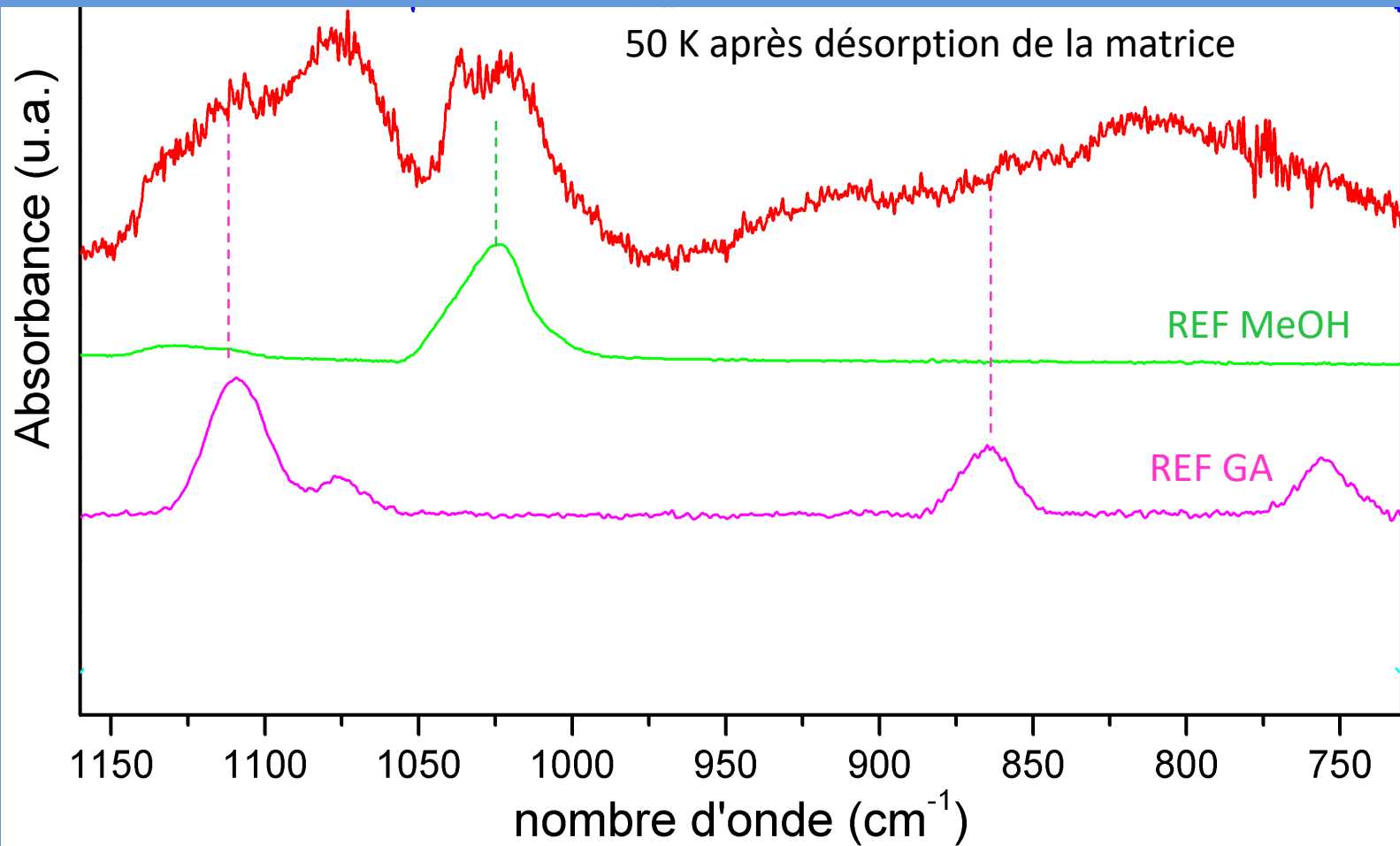
Irradiation H₂CO en matrice d'argon (15 K)



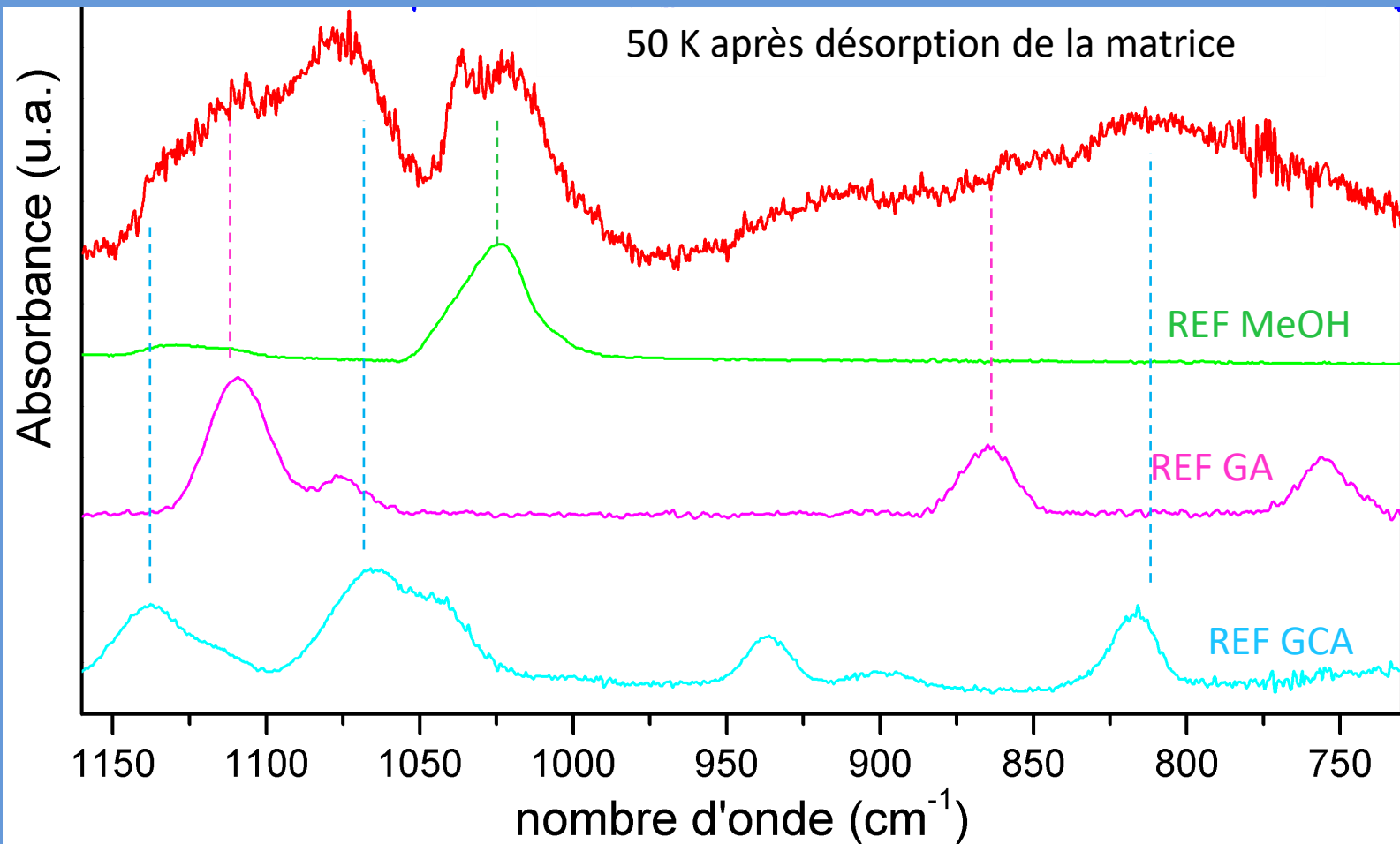
Irradiation H₂CO en matrice d'argon (15 K)



Irradiation H₂CO en matrice d'argon (15 K)



Irradiation H₂CO en matrice d'argon (15 K)

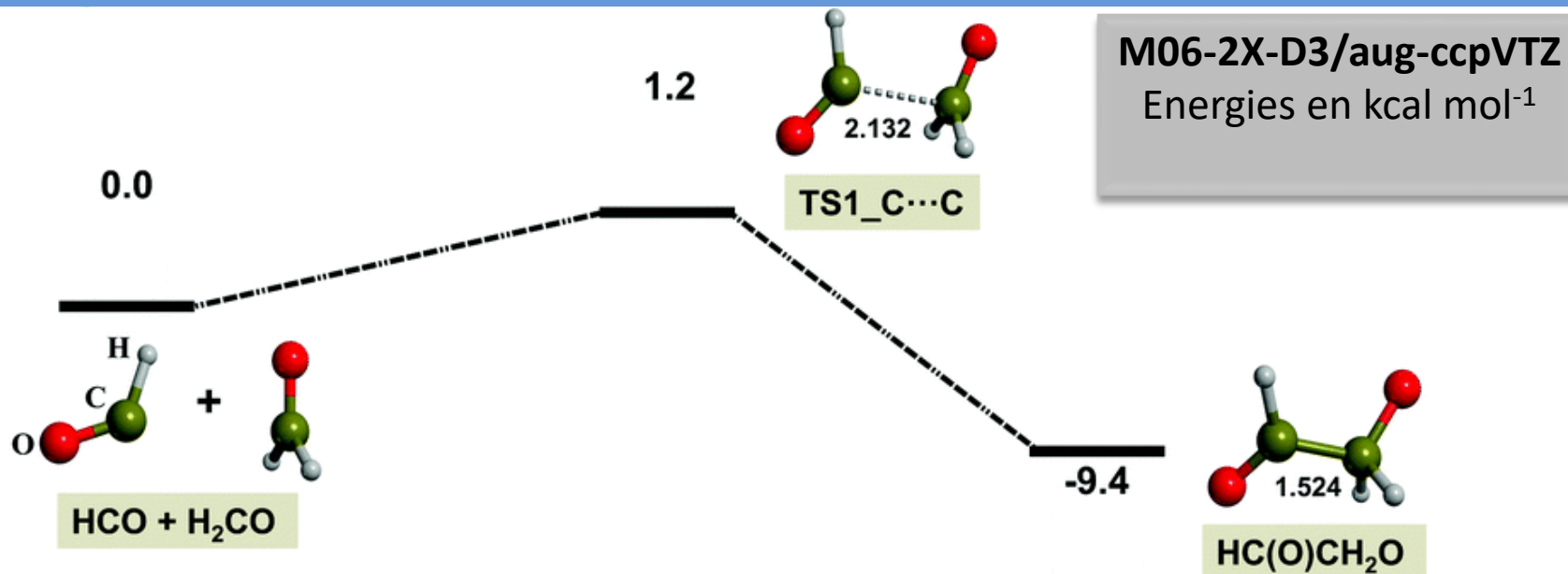


→ Principalement MeOH, GA et GCA

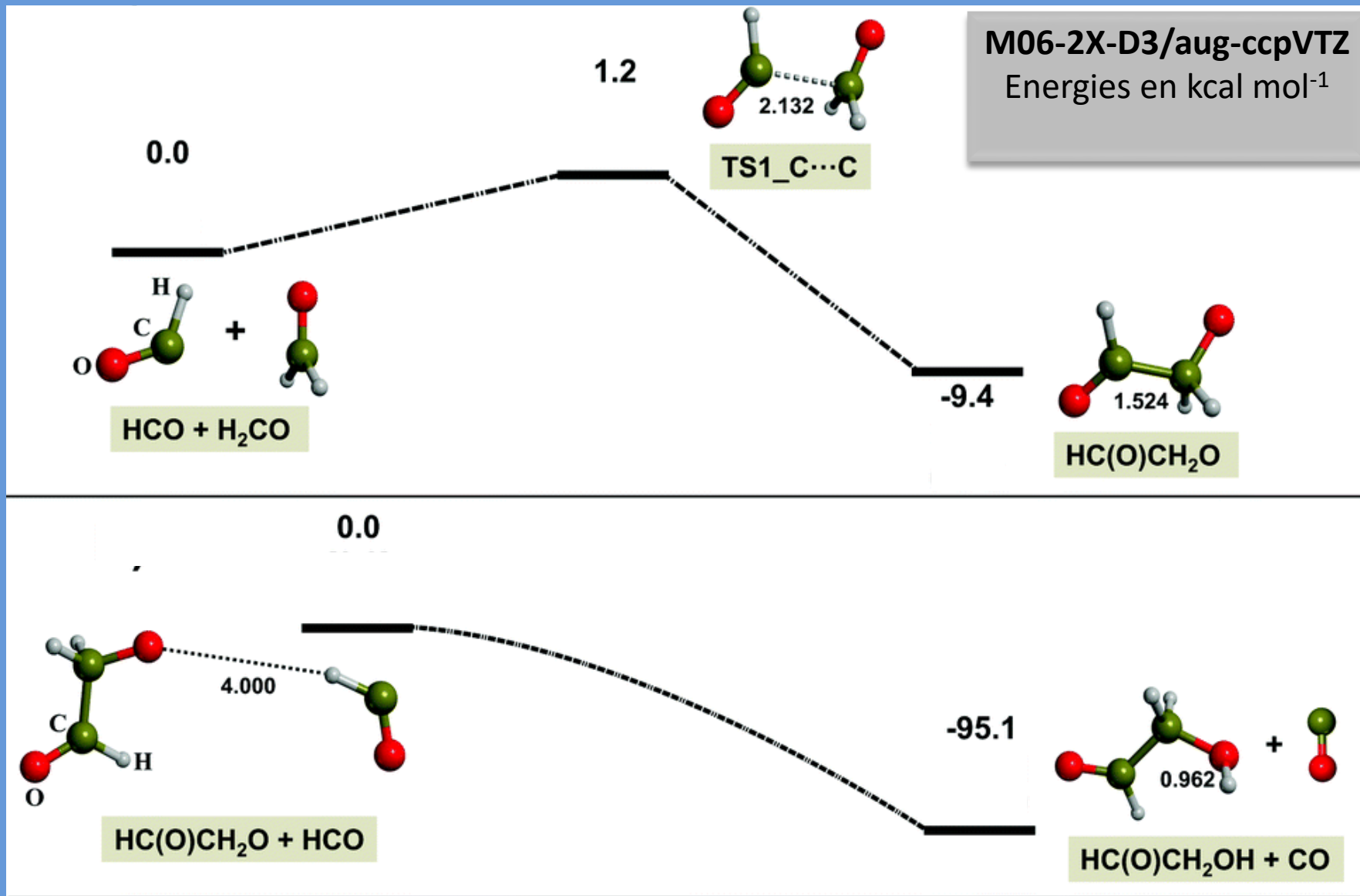
→ La réaction HCO + H₂CO conduit aux aldoses (GA et GCA)

→ Pas d'EG ni de GCO (•CH₂OH probablement nécessaire)

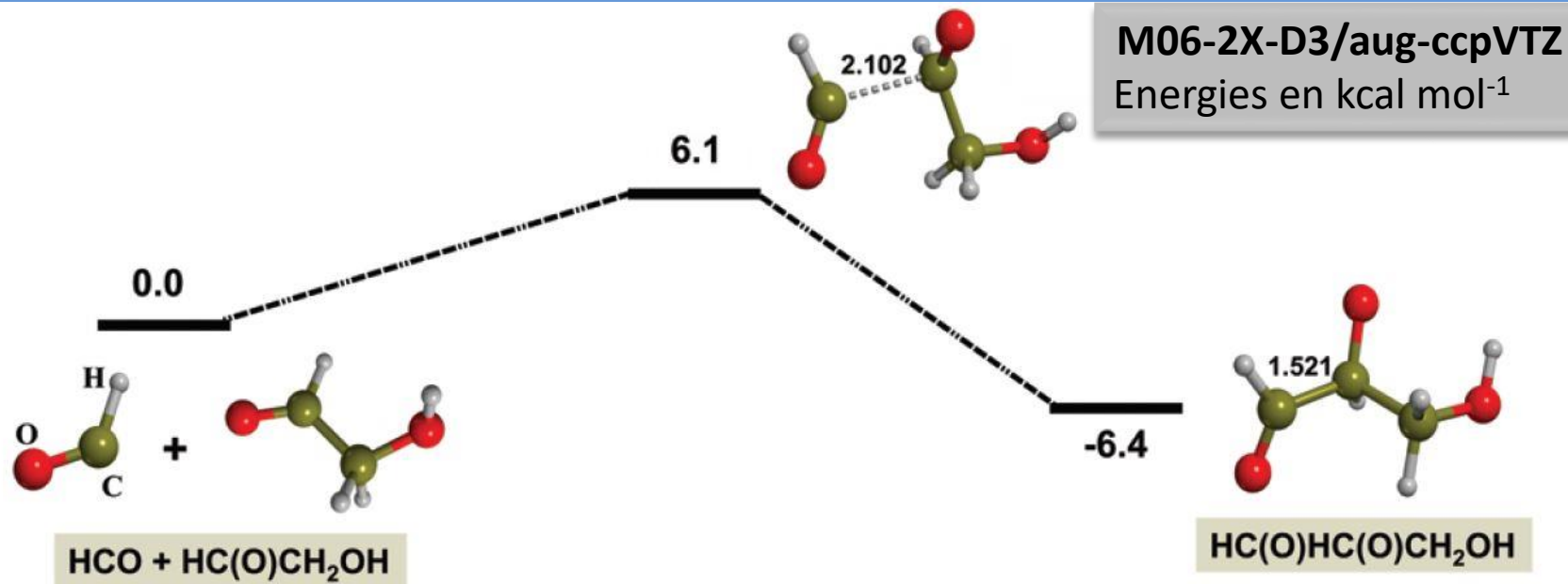
Mécanisme de formation du GA: HCO + H₂CO



Mécanisme de formation du GA: HCO + H₂CO

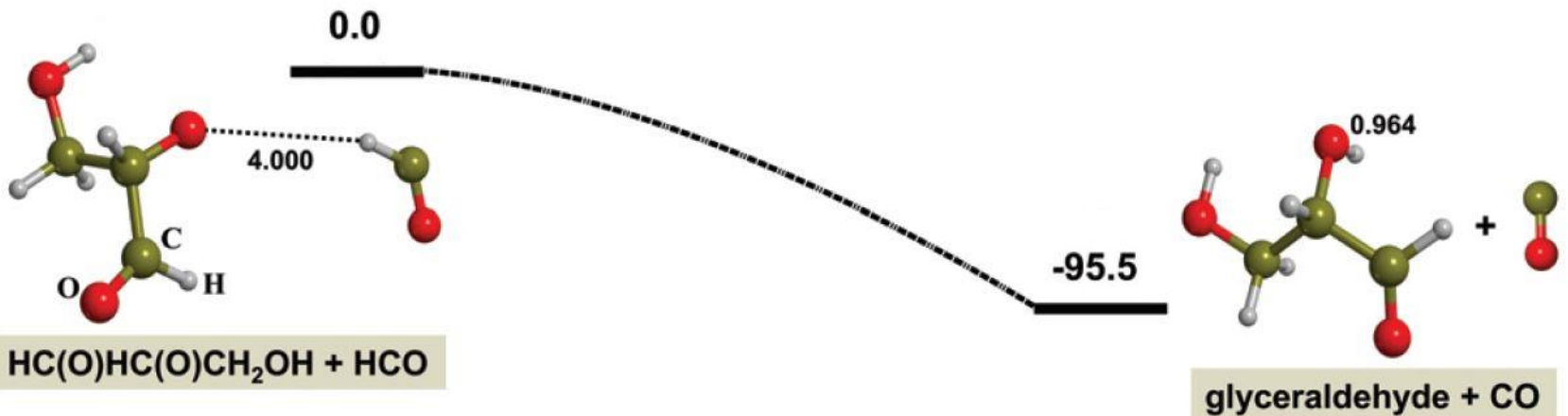
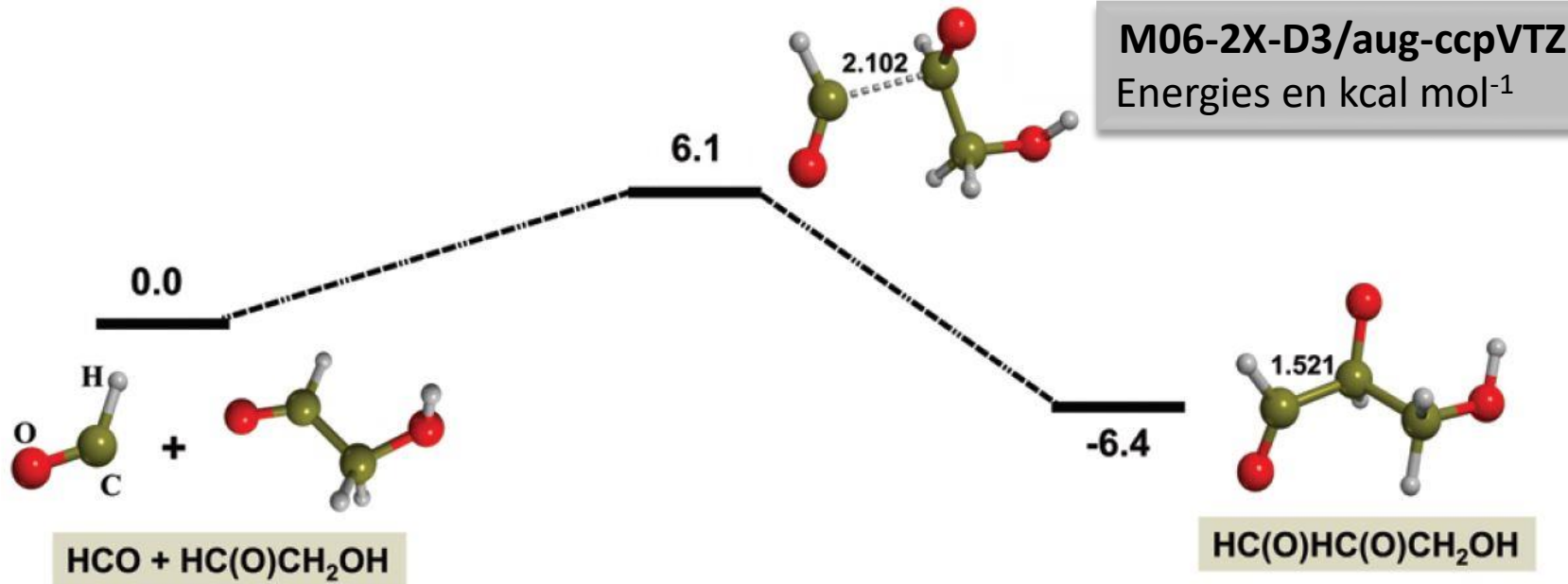


Formation du GCA : HCO+ GA



Formation du GCA : HCO+ GA

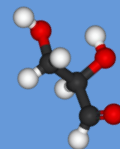
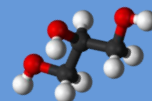
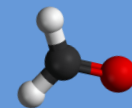
M06-2X-D3/aug-ccpVTZ
Energies en kcal mol⁻¹





Take-Home messages

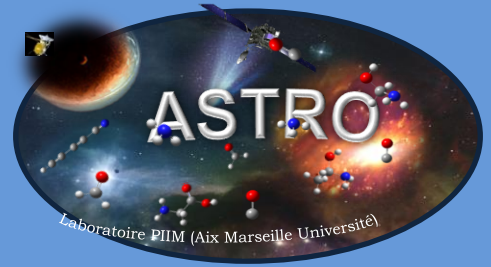
- GA, GCA et EG, GCO formées en analogues de glaces interstellaires contenant du formaldéhyde
- Contraintes apportées concernant l'étude des mécanismes:
 - Mécanisme radicalaire du type radical- H_2CO
 - La formation des aldoses (sucres) est initiée par le radical HCO
 - La formation des polyols est probablement initiée par le radical CH_2OH (expériences/calculs complémentaires nécessaires)



MERCI 😊



Equipe ASTRO



Pr. Thierry Chiavassa



Fabien Borget



Isabelle Couturier



Grégoire Danger



Nathalie Pietri



Fabrice Duvernay



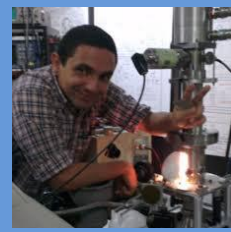
V. Vinogradoff



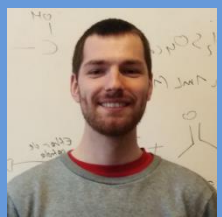
Louis D'hendecourt



Alexander Ruf



Alejandro Gutierrez Quintanilla



Yohann Layssac



Adeline Garcia



Julie Mouzay



Thomas Javelle

