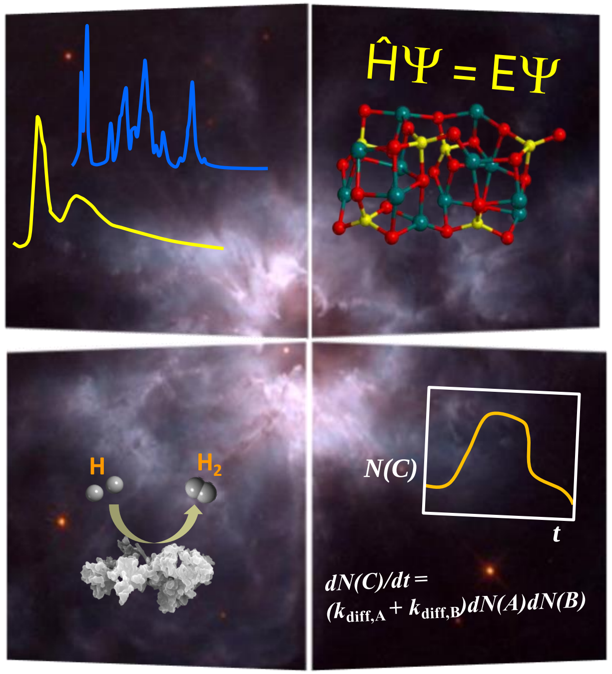
Chemistry on Dust Surfaces



Albert RIMOLA
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QUANTUMGRAIN
Quantum Chemistry on Interstellar Grains

Department of Chemistry

UAB
Universitat Autònoma de Barcelona

6th Institute of Space Sciences Summer School: Life Cycle of Dust

3-13 July 2023
Institute of Space Sciences
Europe/Madrid timezone

European Research Council
Established by the European Commission

MARIE CURIE ACTIONS

Who am I?

- **Chemist** (Degree of Chemistry, 2002 UAB)
- **Computational chemist** (PhD in Theoretical and Computational Chemistry, 2007 UAB)
- Postdoc in Univ. Turin (2007-2009)
- Postdoc + tenure track researcher (2010 – 2022)
- **Professor Dept. Chemistry** UAB (Physical Chemistry, Quantum chemistry & spectroscopy)

- **Use of computational chemistry to solve chemical problems**

Surface phenomena of interstellar grains

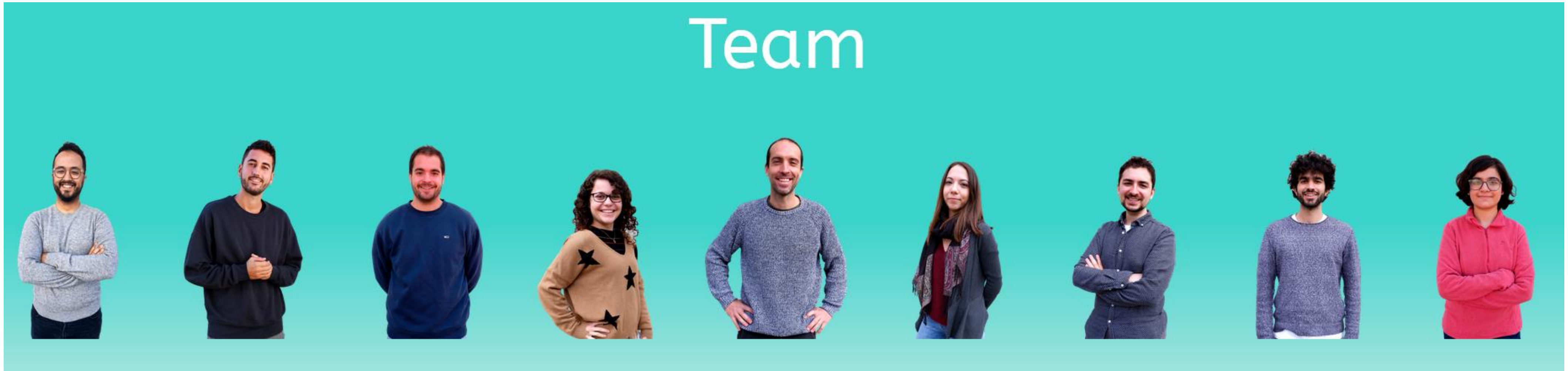
Who am I?

PI of Quantum Chemistry on Interstellar Grains (QUANTUMGRAIN)

ERC Consolidator Grant

https://www.quantumgrain.eu

@QuantumGrain

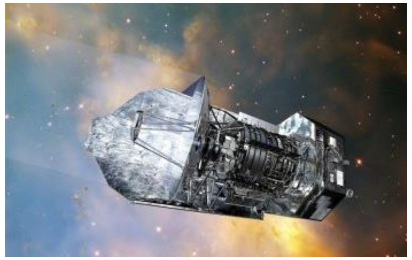


Astrochemistry: Definition

- The **Chemistry** of the **Universe**.
- Area of the Astronomy dedicated to **study the chemical species** (atoms, molecules and ions) occurring in celestial bodies (e.g., stars), interstellar space and other **astrophysical environments**.
- Astrochemistry is the study of the composition and reactions of atoms, molecules and ions in space. The topic includes the gathering of spectroscopic information from ground-, air- and space-based **observatories, lab-based studies** that replicate the harsh environments of space and **modelling**.

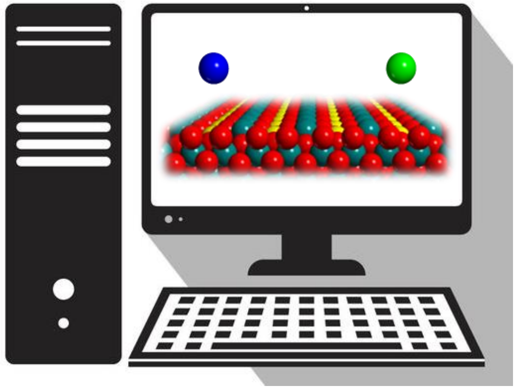
natureresearch

INTERDISCIPLINARITY



Astronomical Observations

Laboratory Experiments



Modeling

INTERSTELLAR CLOUDS OF GAS AND SOLID GRAINS

99% of the interstellar matter

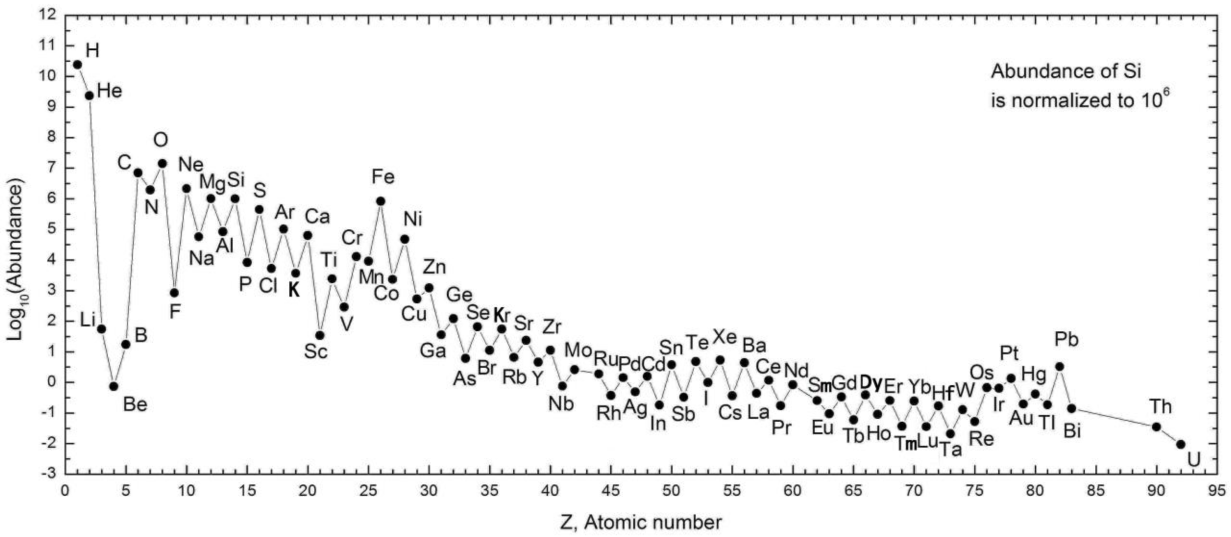
1% of the interstellar matter

Pilars of Creation

Horsehead Nebula

Solar elemental abundances

Element	Abundance	Element	Abundance
H	1.00	Mg	4.0×10^{-5}
He	0.085	Al	2.8×10^{-6}
C	2.7×10^{-4}	Si	3.2×10^{-5}
N	6.8×10^{-5}	S	1.3×10^{-5}
O	4.9×10^{-4}	P	2.6×10^{-7}
Na	1.7×10^{-6}	Fe	3.2×10^{-5}



Gas-phase molecules

2 àtoms	3 àtoms	4 àtoms	5 àtoms	6 àtoms	7 àtoms	8 àtoms	9 àtoms	10 àtoms	11 àtoms	12 àtoms	> 12 àtoms
H_2	AlNC	c-C_3H	C_5	C_5H	C_6H	C_7H	C_8H	$(CH_3)_2CO$	C_2H_5OCHO	$C_6H_6^+$	$HC_{11}N$
AlF	AlOH	i-C_3H	C_4H	C_5N	C_6H^-	CH_3C_3N	C_8H^-	$(CH_2OH)_2$	CH_3C_6H	*n*-C_3H_7CN	$HC_{10}CN$
AlCl	C_3	C_3N	C_4H^-	C_5N-	CH_3C_2H	CH_3CH_3	C_3H_6	CH_3C_5N	HC_9N	$C_2H_5OCH_3$	$C_{14}H_{10}$
AlO	C_2H	C_3N^-	C_4Si	C_2H_4	CH_3NH_2	$HC(O)OCH_3$	$(CH_3)_2O$	CH_3CH_2CHO			C_{60}
C_2	C_2O	C_3O	i-C_3H_2	CH_3CN	CH_2CHCN	CH_3COOH	CH_3C_4H				C_{70}
CH	C_2P	C_3S	c-C_3H_2	CH_3NC	c-C_2H_4O	CH_2CCHCN	CH_3CH_2CN				
CH^+	C_2S	C_2H_2	CH_4	CH_3OH	H_2CCHOH	CH_2CHCHO	CH_3CH_2OH				
CF^+	CH_2	CH_3	H_2C_2N	CH_3SH	HC_5N	CH_2OHCHO	$CH_3C(O)NH_2$				
CN	CN_2	HCCN	H_2C_2O	i-H_2C_4	CH_3CHO	H_2C_6	HC_7N				
CN^+	CO_2	$HCNH^+$	H_2CNH	c-H_2C_3O		i-HC_6H					
CN^-	CO_2^+	HCNO	H_2COH^+	i-HC_4H		NH_2CH_2CN					
CO	CS_2	HNCO	H_2NCN	i-HC_4N							
CO^+	FeCN	HNCS	HCCCN	HC_3NH^+							
CP	H_3^+	HOCN	HCCNC	HC_2CHO							
CS	H_2D^+	$HOCO^+$	HCOOH	H_2CCNH							
CSi	HD_2^+	HSCN	HC(O)CN	NH_2CHO							
FeO	H_2Cl^+	H_2CO	HNC_3								
HD	H_2O	H_2CN	SiH_4								
HCl	H_2O^+	H_2CS									
HF	HDO	H_2O_2									
KCl	H_2S	H_3O^+									
NH	H_2S^+	NH_3									
N_2^+	HCN	PH_3									
NO	HCO	c-SiC_3									
NS	HCO^+										
NaCl	HCP										
O_2	HCS^+										
OH	HOC^+										
OH^+	HNC										
PN	HNO										
PO	KCN										
S_2	MgCN										
SH	MgNC										
SH^+	N_2H^+										
SO	N_2O										
SO^+	NH_2										
SiH	NaCN										
SiN	OCN^-										
SiO	OCS										
SiS	SO_2										
	c-SiC_2										
	SiCN										
	SiNC										

- **More tan 250 GAS-PHASE molecular species detected**
- **Of interstellar, circumstellar and cometary origin**
- **Based on emission from rotational transitions (radio/microwave region of the EM spectrum)**

ALMA

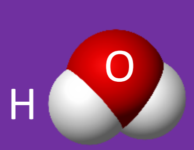
NOEMA

Brett A. McGuire 2022 *ApJS* **259** 30

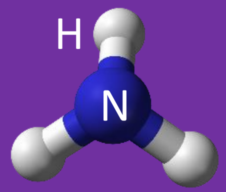
Gas-phase molecules: simple molecules

2 atoms	3 atoms	4 atoms	5 atoms
H_2	AlNC	$c\text{-}C_3H$	C_5
AlF	AlOH	$i\text{-}C_3H$	C_4H
AlCl	C_3	C_3N	C_4H^-
AlO	C_2H	C_3N^-	C_4Si
C_2	C_2O	C_3O	$i\text{-}C_3H_2$
CH	C_2P	C_3S	$c\text{-}C_3H_2$
CH^+	C_2S	**CH_3**	CH_4
CF^+	CH_2	$HCNH^+$	H_2C_2N
CN	CN_2	HCNO	H_2C_2O
CN^+	CO_2	HNCO	H_2CNH
CN^-	CO_2^+	HNCS	H_2COH^+
CO	**FeCN**	HOCN	H_2NCN
CO^+	H_2D^+	$HOCO^+$	HCCCN
CP	HD_2^+	HSCN	HCCNC
CS	**H_2O**	H_2CO	HCOOH
CSi	HDO	H_2CN	HC(O)CN
FeO	H_2S	H_2CS	HNC_3
HD	H_2S^+	H_2O_2	SiH_4
HCl	HCN	**NH_3**	
HF	**HCO^+**	$c\text{-}SiC_3$	
KCl	HCS^+		
NH	HOC^+		
N_2^+	HNC		
NO	HNO		
NS	**MgCN**		
NaCl	N_2H^+		
OH	N_2O		
PN	**OCN^-**		
PO	SO_2		
S_2	$c\text{-}SiC_2$		
SH	SiCN		
SH^+	SiNC		
SO			
SO^+			
SiH			
SiN			
SiO			
SiS			

- neutral (closed-shell) molecules

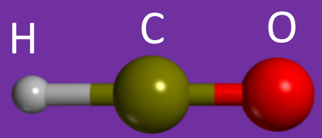


H_2O
(water)

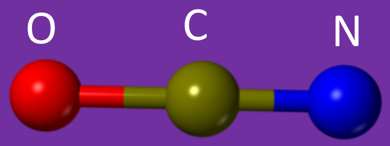


NH_3
(ammonia)

- Ions (charged species)

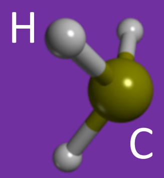


HCO^+
(formyl cation)

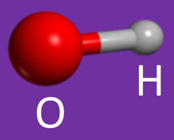


OCN^-
(cyanate anion)

- Radicals (neutral open-shell species)

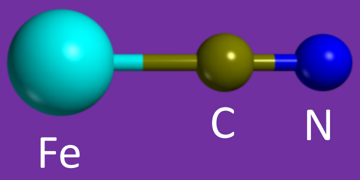


CH_3
(methyl rad.)

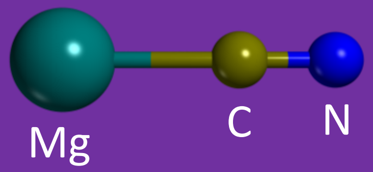


OH
(hydroxyl rad.)

- Organometallic components (Metal-C bonds)



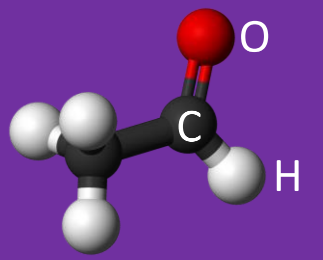
FeCN
(ferrocyanide)



MgCN
(magnesium
cyanide)

Gas-phase molecules: interstellar complex organic molecules (iCOMs)

- **iCOMs**: Molecules between 6-12 atoms in which at least one is C

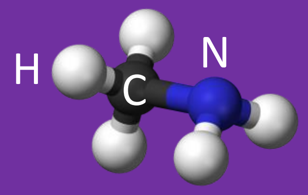


CH_3CHO (acetaldehyde)

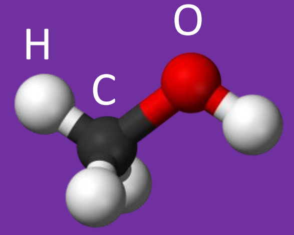
6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms
C_5H	C_6H	C_7H	C_8H	$(CH_3)_2CO$	C_2H_5OCHO	$C_6H_6^+$
C_5N	C_6H^-	CH_3C_3N	C_8H^-	$(CH_2OH)_2$	CH_3C_6H	n-C_3H_7CN
C_5N-	c-C_2H_4O	CH_3CH_3	C_3H_6	CH_3C_5N	HC_9N	$C_2H_5OCH_3$
i-HC_4H	H_2CCHOH	NH_2CH_2CN	$(CH_3)_2O$	CH_3CH_2CHO		
i-HC_4N			CH_3CH_2OH			
HC_3NH^+						
HC_2CHO						
H_2CCNH						

CH_3OH **CH_3SH** **NH_2CHO** **CH_3NH_2** **CH_3CHO** **CH_3COOH** **$HOCH_2CHO$**

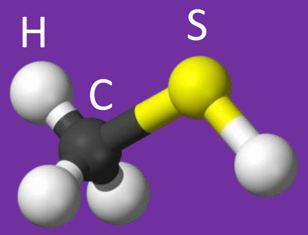
- Most of them contain heteroatoms (N, O, S)



CH_3NH_2 (methylamine)

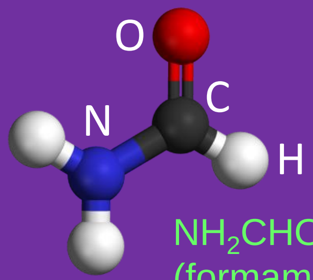


CH_3OH (methanol)

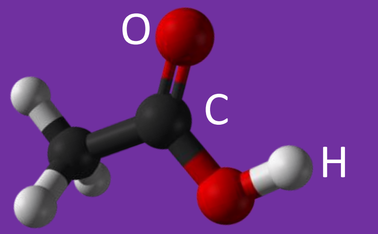


CH_3SH (methanethiol)

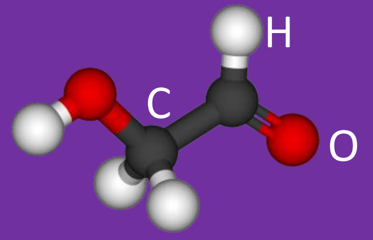
- Some of them are of biological potential (prebiotic relevance)



NH_2CHO (formamide)



CH_3COOH (acetic acid)



$HOCH_2CHO$ (glycolaldehyde)

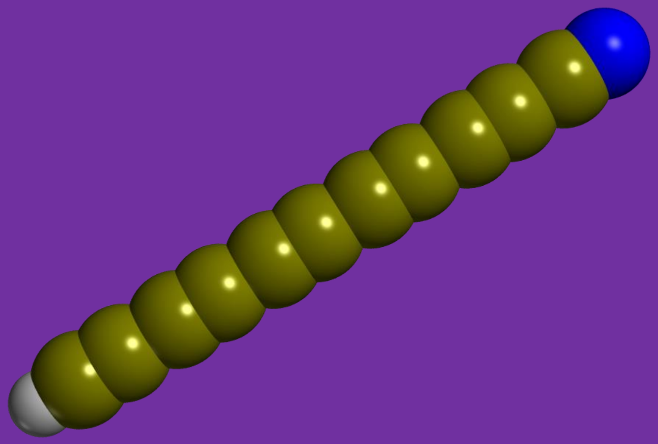
Gas-phase molecules: molecules of enhanced complexity

> 12 atoms

$HC_{11}N$

$C_{14}H_{10}$

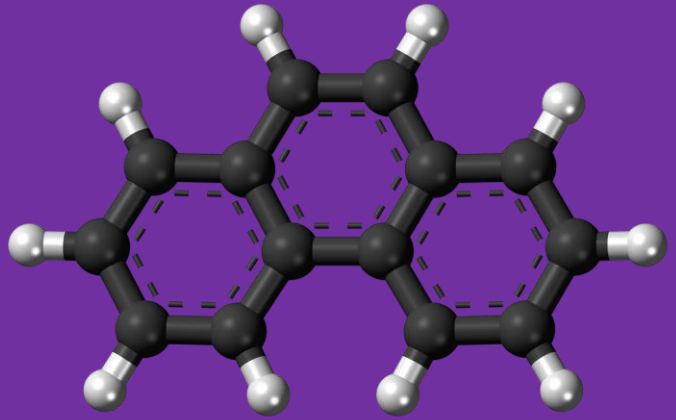
C_{60}



$HC_{11}N$ (cyanodecapentayne)

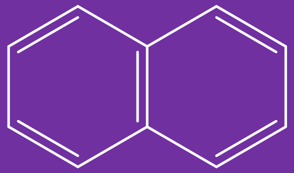
Cyanopolyynes

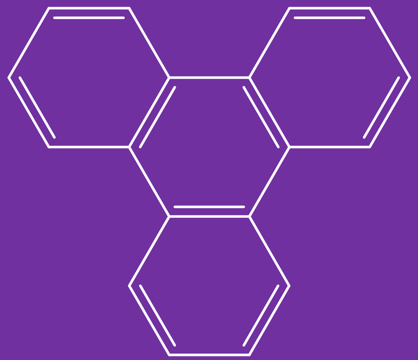
(HC_nN, n: 1, 3, 5 ...)

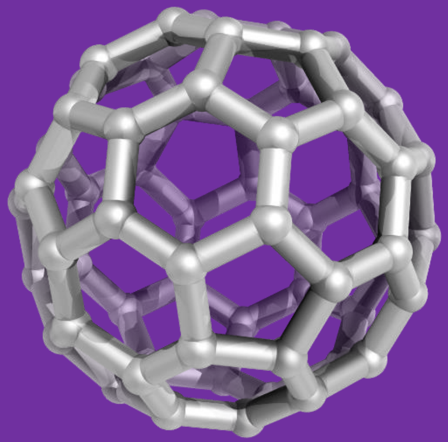


$C_{14}H_{10}$ (phenanthrene)

PAHs







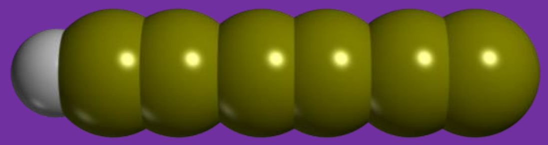
C_{60} (fullerene)

Buckyballs

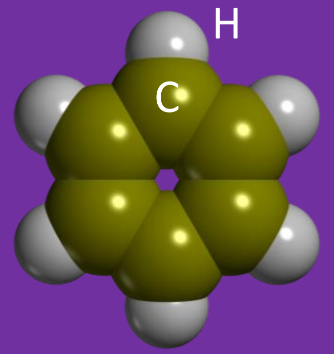
(C_{60}^+, C_{70})

Gas-phase molecules: “exotic” molecules

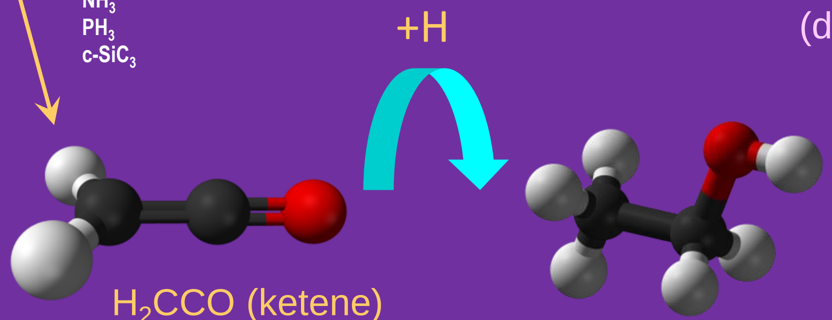
2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	> 12 atoms
H_2	AlNC	c-C_3H	C_5	C_5H	C_6H^-	C_7H	C_8H	$(CH_3)_2CO$	C_2H_5OCHO	$C_6H_6^+$	$HC_{11}N$
AlF	CCH	i-C_3H	C_4H	C_5N	CH_3NH_2	CH_3C_3N	C_8H^-	$(CH_2OH)_2$	CH_3C_6H	$C_2H_5OCH_3$	$HC_{10}CN$
AlCl	CCO	C_3N	C_4H^-	C_5N-	CH_2CHCN	CH_3CH_3	C_3H_6	CH_3C_5N	HC_9N		$C_{14}H_{10}$
AlO	CN_2	C_3N^-	C_4Si	C_2H_4	c-C_2H_4O	$HC(O)OCH_3$	$(CH_3)_2O$	CH_3CH_2CHO			C_{60}
C_2	CO_2	C_3O	i-C_3H_2	CH_3CN	H_2CCHOH	CH_3COOH	CH_3C_4H				C_{70}
CH	CO_2^+	C_3S	c-C_3H_2	CH_3NC	HC_5N	CH_2CCHCN	CH_3CH_2CN				
CH^+	CS_2	C_2H_2	CH_4	CH_3OH	CH_3CHO	CH_2CHCHO	CH_3CH_2OH				
CF^+	FeCN	CH_3	H_2C_2N	CH_3SH		CH_2OHCHO	$CH_3C(O)NH_2$				
CN	H_3^+	HCCN	H_2C_2O	i-H_2C_4		H_2C_6	HC_7N				
CN^+	H_2D^+	$HCNH^+$	H_2CNH	c-H_2C_3O		i-HC_6H					
CN^-	HD_2^+	HCNO	H_2COH^+	i-HC_4H		NH_2CH_2CN					
CO	H_2Cl^+	HNCO	H_2NCN	i-HC_4N							
CO^+	H_2O	HNCS	HCCCN	HC_3NH^+							
CP	H_2O^+	HOCN	HCCNC	HC_2CHO							
CS	HDO	$HOCO^+$	HCOOH	H_2CCNH							
CSi	H_2S	HSCN	HC(O)CN	NH_2CHO							
FeO	HCN	H_2CO	HNC_3								
HD	HCO^+	H_2CN	SiH_4								
HCl	HCP	H_2CS									
HF	HCS^+	H_2O_2									
KCl	HNC	H_3O^+									
NH	KCN	NH_3									
N_2^+	MgCN	PH_3									
NO	MgNC	c-SiC_3									
NS	N_2H^+										
NaCl	N_2O										
O_2	NH_2										
OH	NaCN										
OH^+	OCN^-										
PN	OCS										
PO	SO_2										
S_2	c-SiC_2										
SH	SiCN										
SH^+	SiNC										
SO											
SO^+											
SiH											
SiN											
SiO											
SiS											



C_6H^- (deprotonated polyyne)

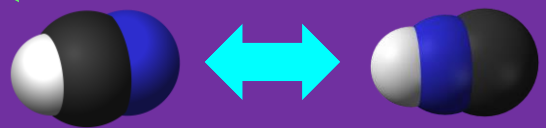


$C_6H_6^+$ (Ionized benzene)



H_2CCO (ketene)

CH_3CH_2OH (ethanol)

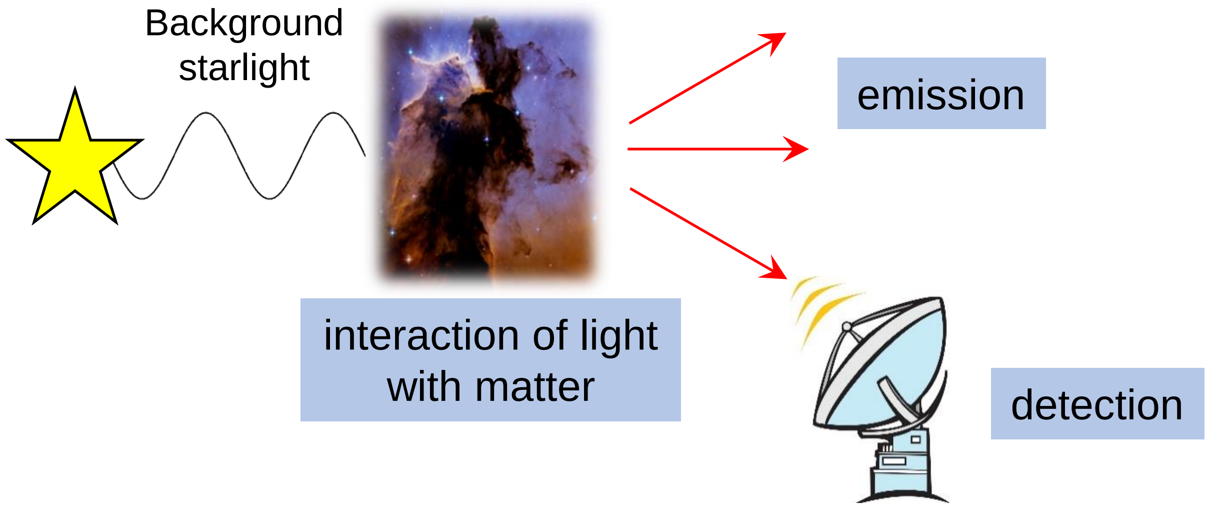


HCN

HNC (unstable isomer)

- molecules that are unstable in the terrestrial environment and yet observed in space
- **free radicals, ions & metastable isomers**

Observational Measurements of the Gas-Phase Components



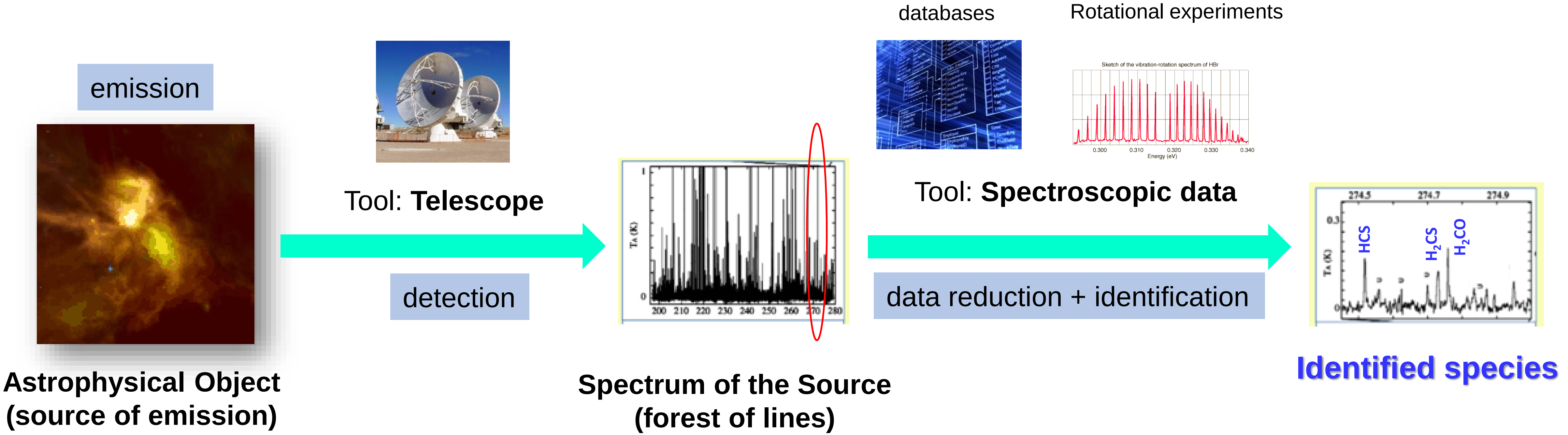
- **Radiofrequency range**

  e.g., SKA radiotelescope: λ = 6 m – 1.5 cm

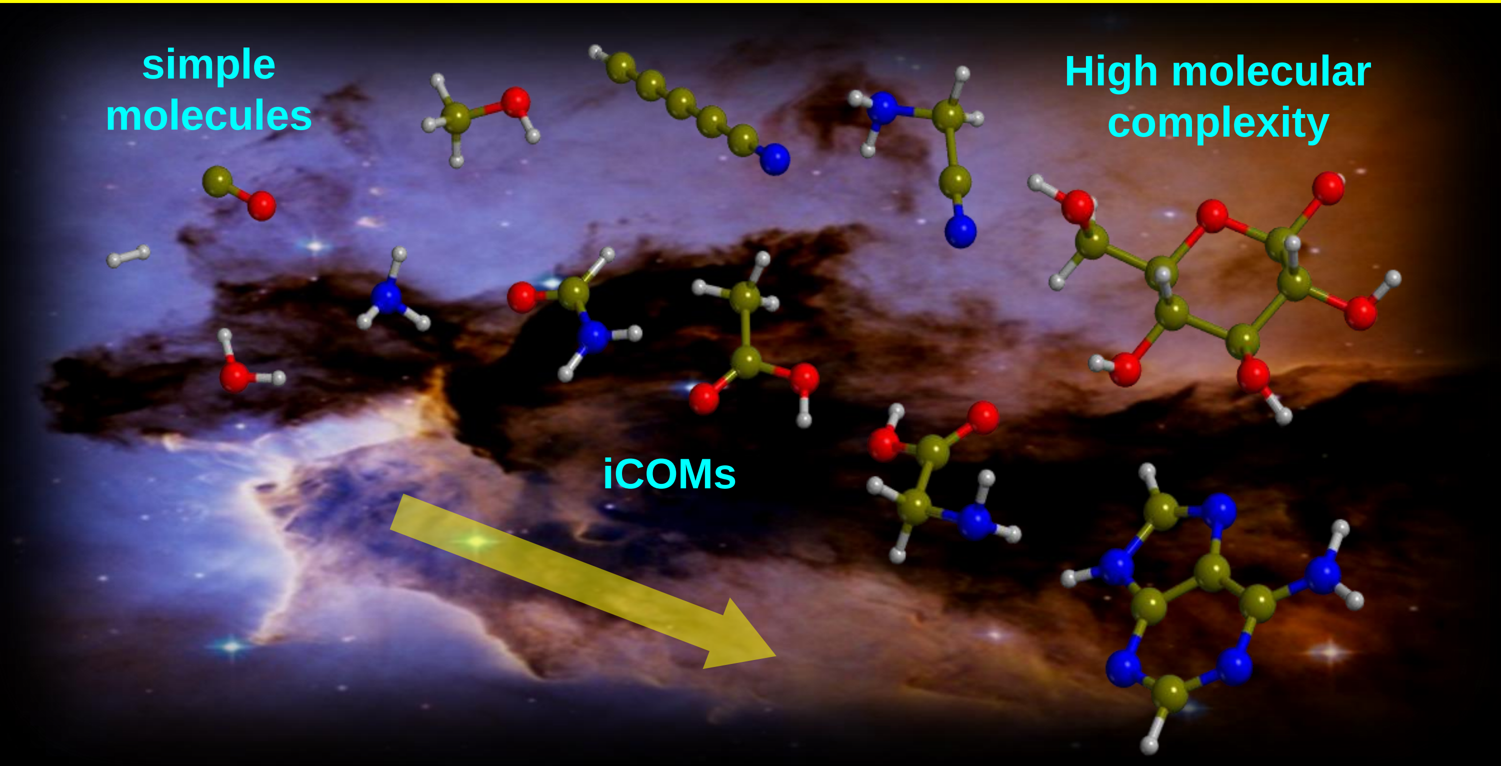
- **Microwave (mm/submm) range**

  e.g., ALMA: λ = 3.6 mm – 0.3 mm

  e.g., NOEMA: λ = 3 mm – 0.8 mm



Chemical evolution in Solar-type planetary formation



Evolution of the molecular complexity goes hand-in-hand with the physical phases involved in the formation of Solar-type planetary systems

Caselli & Ceccarelli, Astron. Astrophys. Rev., 2012, 20, 1

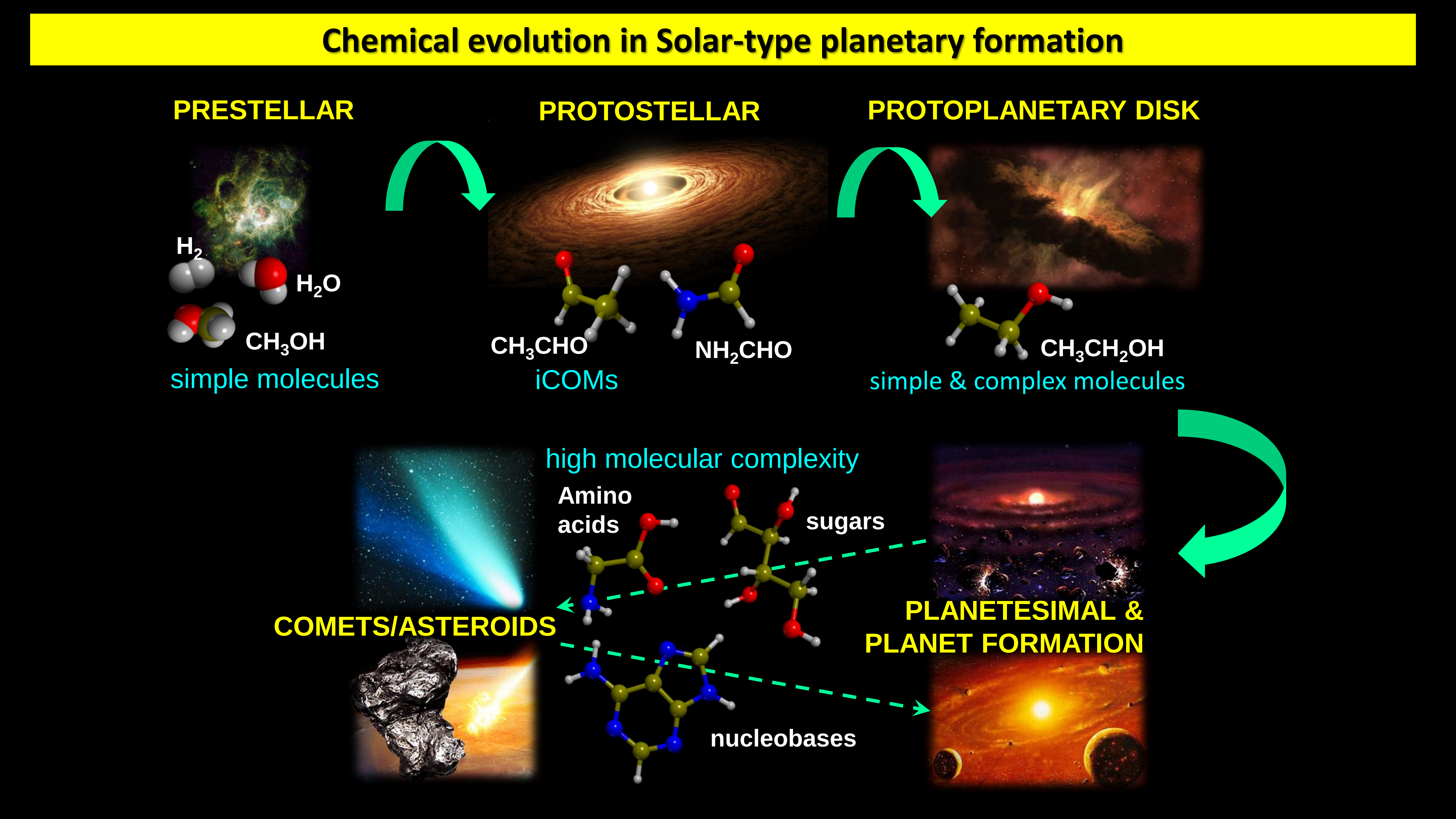
prestellar

protostellar

Protoplanetary disk

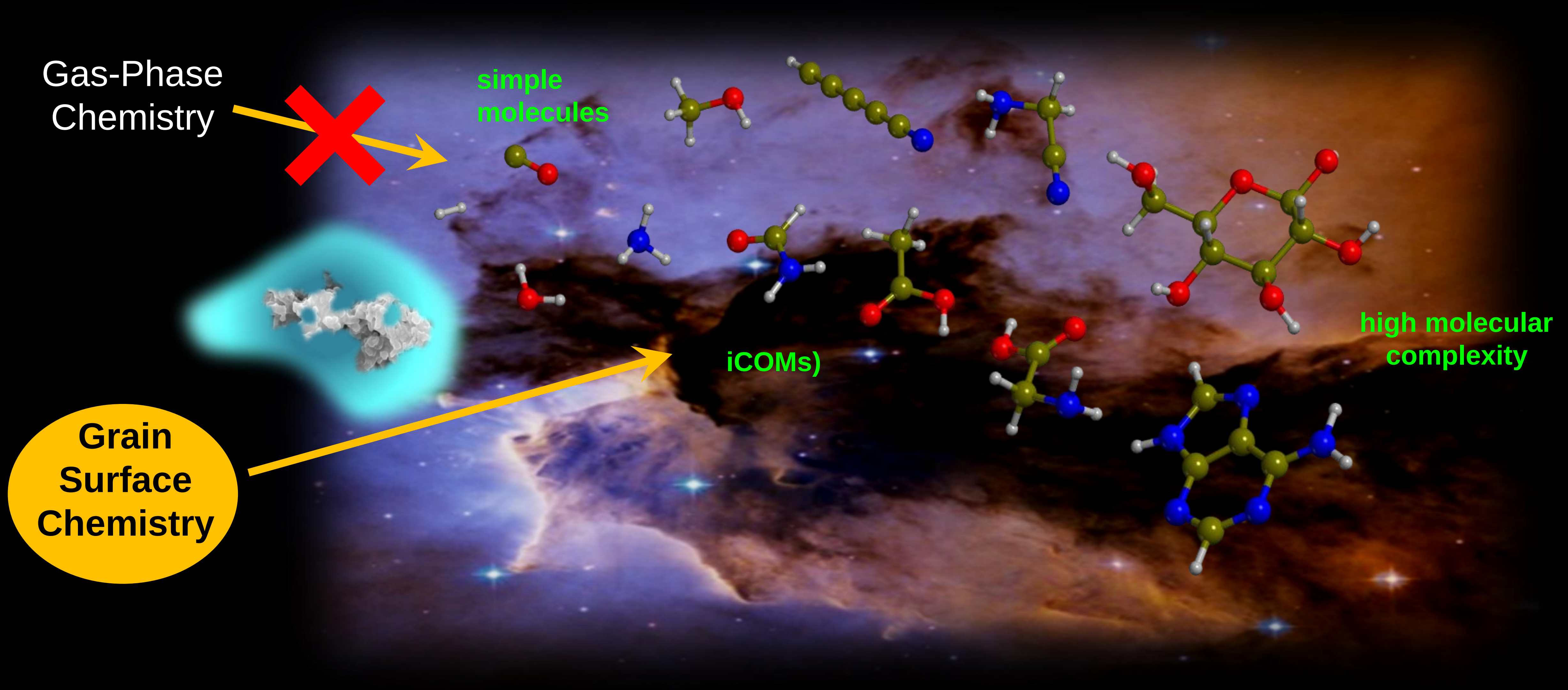
Planetesimal formation

Planet formation



Chemical evolution in Solar-type planetary formation
PRESTELLAR
PROTOSTELLAR
PROTOPLANETARY DISK
H_2
H_2O
CH_3OH
simple molecules
CH_3CHO
NH_2CHO
iCOMs
CH_3CH_2OH
simple & complex molecules
high molecular complexity
Amino acids
sugars
nucleobases
COMETS/ASTEROIDS
PLANETESIMAL & PLANET FORMATION

Chemical Evolution & Grains



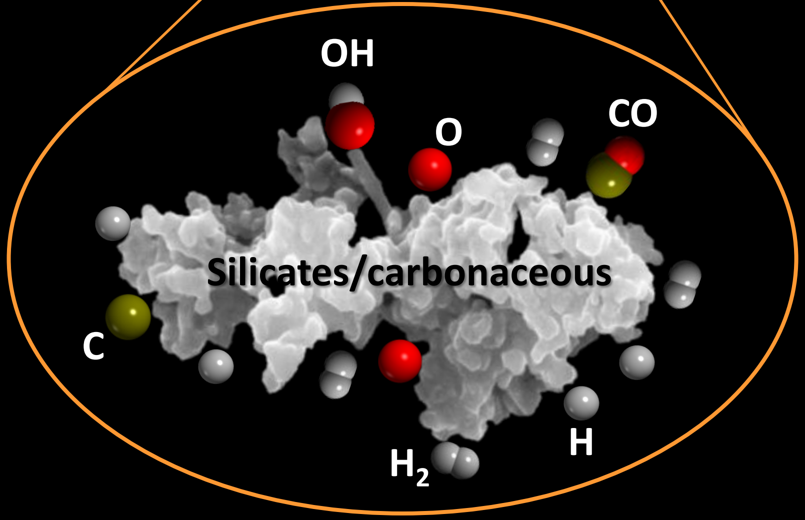
Interstellar Grains

Interstellar matter
99% gas
1% solid

Celestial Valentine
W5 star-forming region
Protrait from NASA's Spitzer Space Telescope

Diffuse Clouds

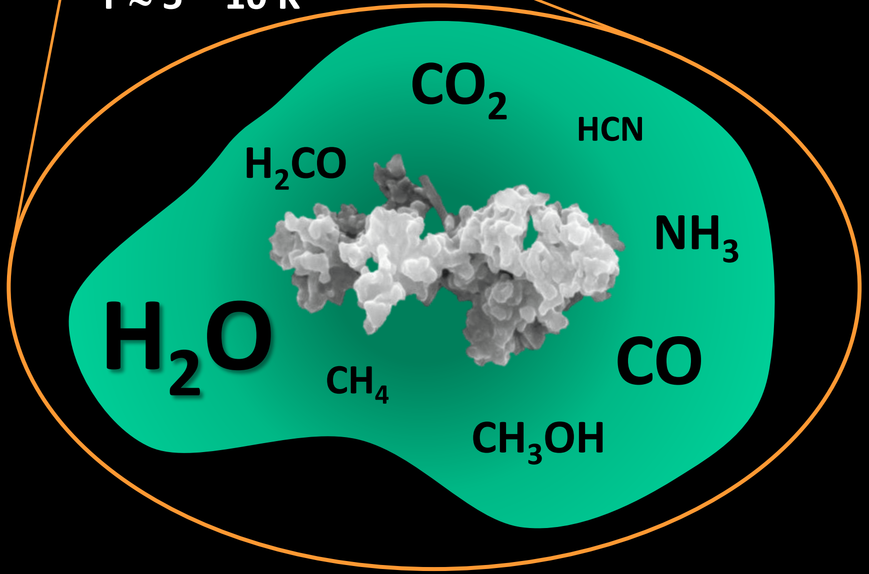
$n \approx 10 - 10^2$ cm^{-3}
T ≈ 50 – 100 K



Bare DUST grains

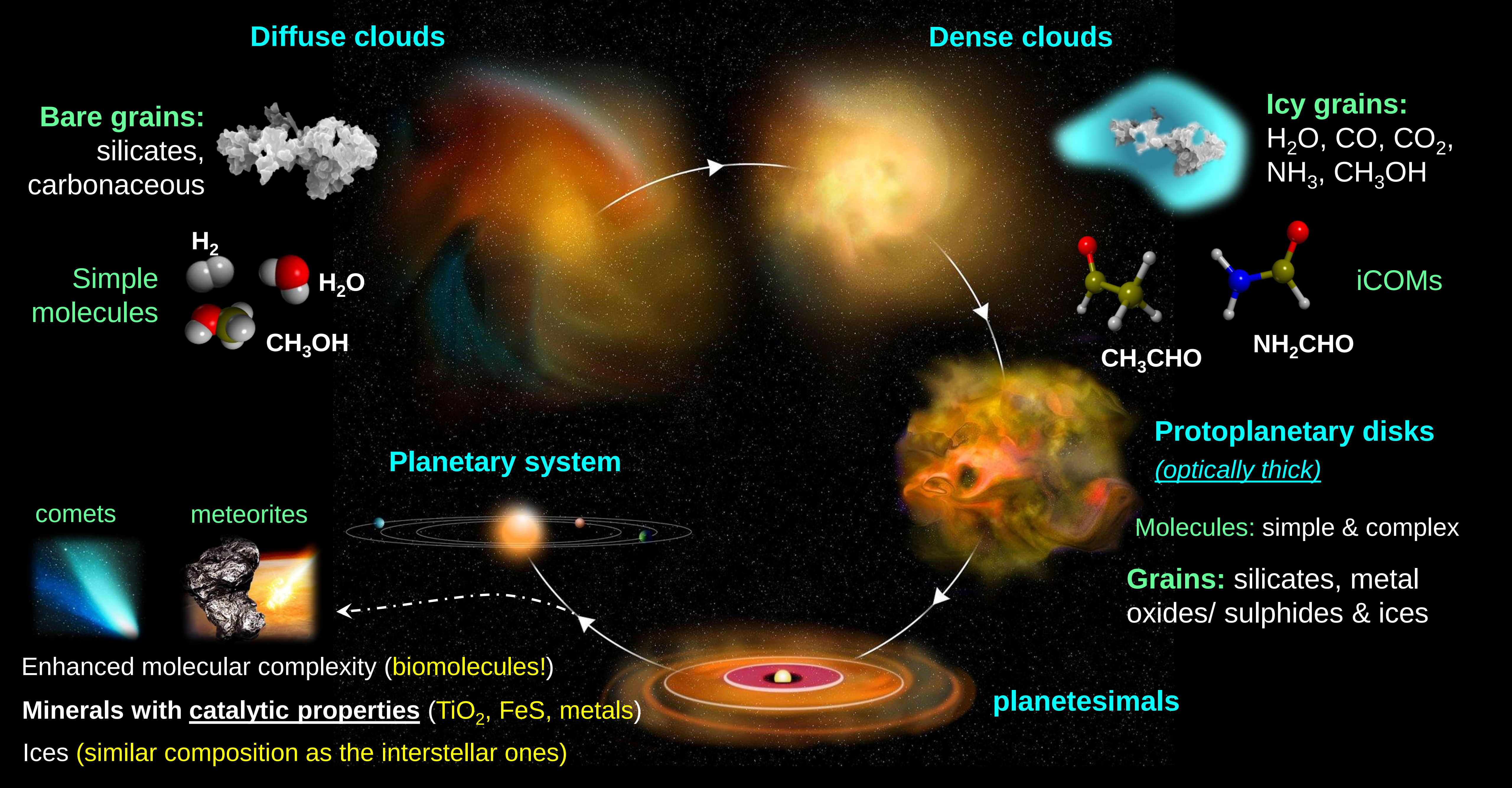
Dense Clouds

$n \approx 10^4$ cm^{-3}
T ≈ 5 – 10 K



Dust grains covered in ICE mantles

Formation of a Solar-type planetary system & Mineralogical Evolution

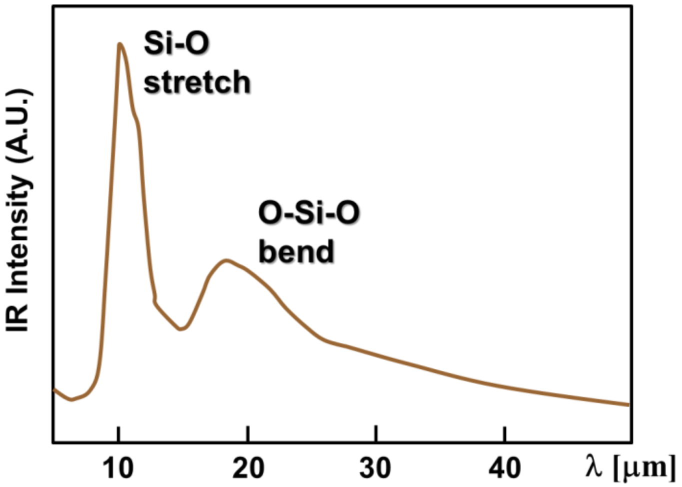


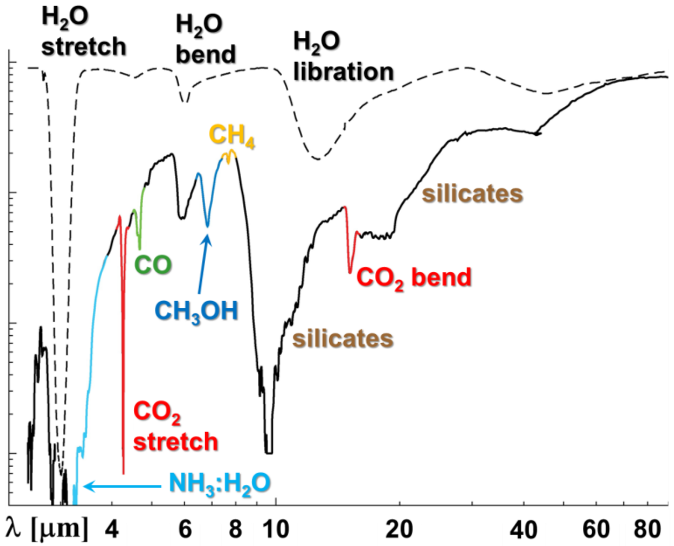
Observational Measurements of the Solid-Phase Component

- Range of the mid-Infrared (IR) region: 4000 – 200 cm^{-1} (2 – 40 μm)

➢ **Obs. IR for silicate dust grains**

Henning, ARA&A 2010, 48, 21

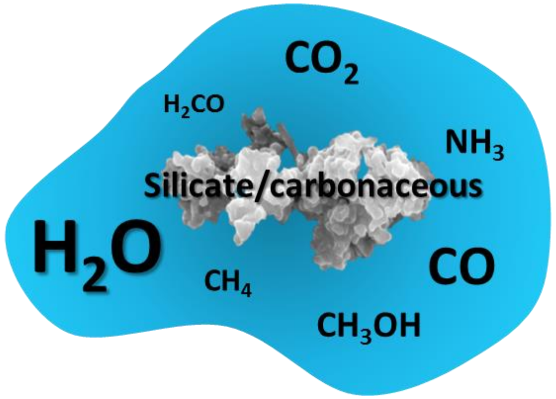




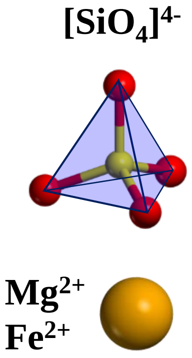
➢ **Obs. IR for ice mantles**

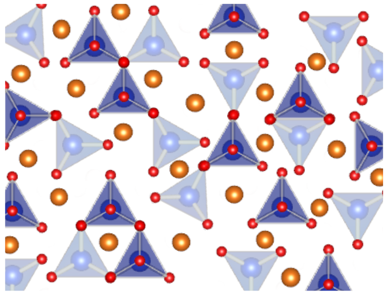
Boogert, ARA&A 2015, 53, 541

CHEMICAL COMPOSITION

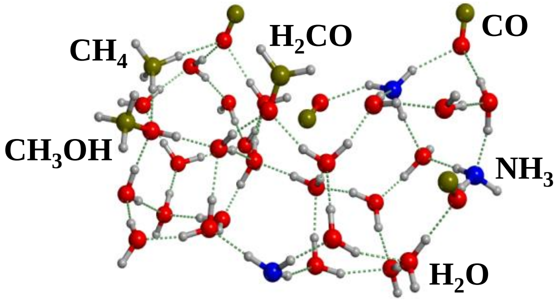


STRUCTURAL STATE: AMORPHOUS





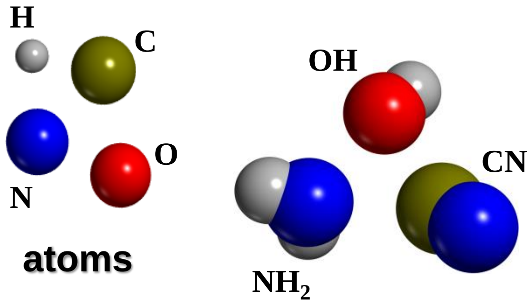
silicates



dirty ices

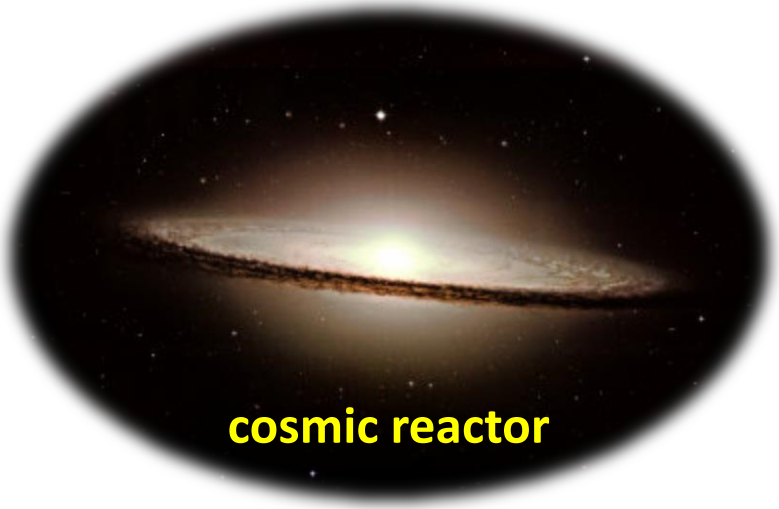
Need for grains: Key ingredient for Cosmic Reactions

REACTANTS

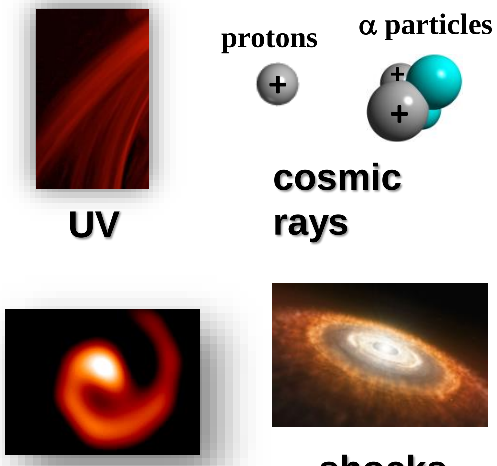


atoms

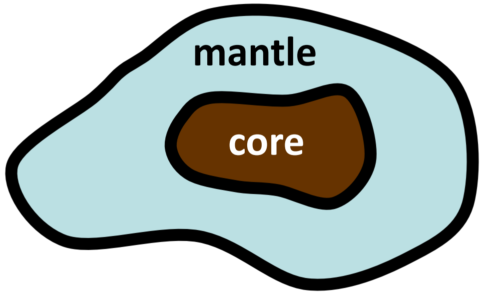
simple molecules



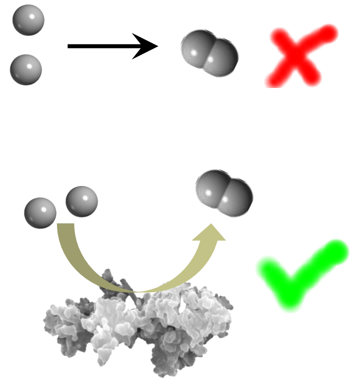
ENERGY SOURCES



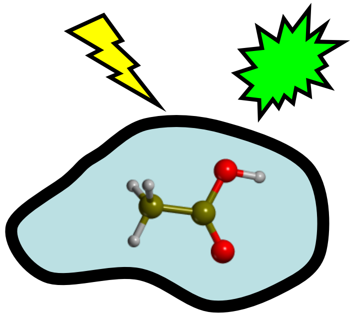
GRAIN PARTICLES



Reaction helper



Product Protector



Grains in Chemical Evolution

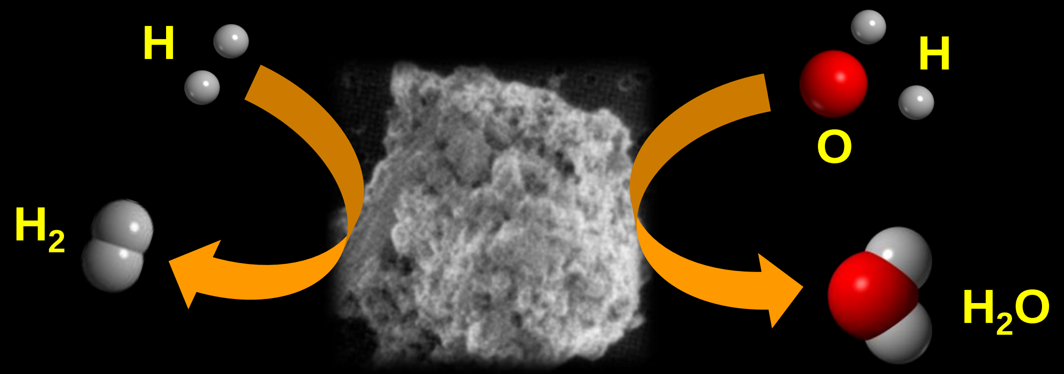
Most of the interstellar molecules form through a series of gas-phase reactions. However, in some cases, we need the presence of grains.

- Question: **When do we need grains?**

- Answer: When gas-phase reactions cannot justify the large abundances detected by astronomical observations.

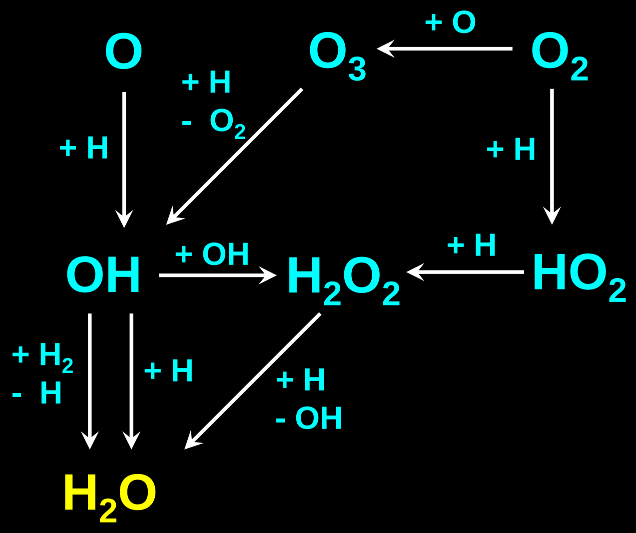
In dust we trust!

- **Grain-dricen reactions In Diffuse Clouds**



Reactions occurring on the surfaces of bare dust grains

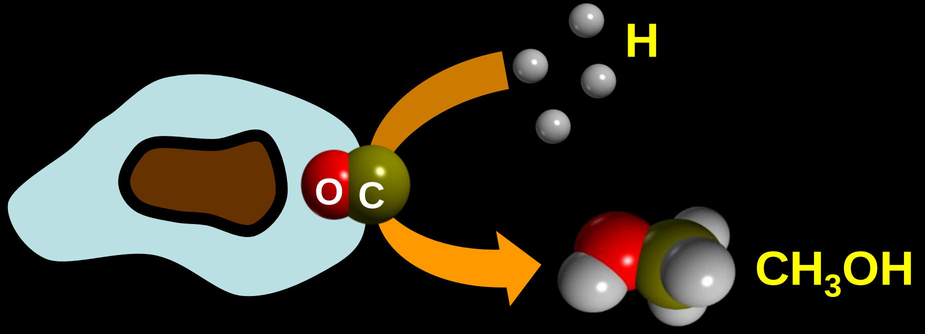
H_2, H_2O, NH_3, N_xO_y, ...



Grains in Chemical Evolution

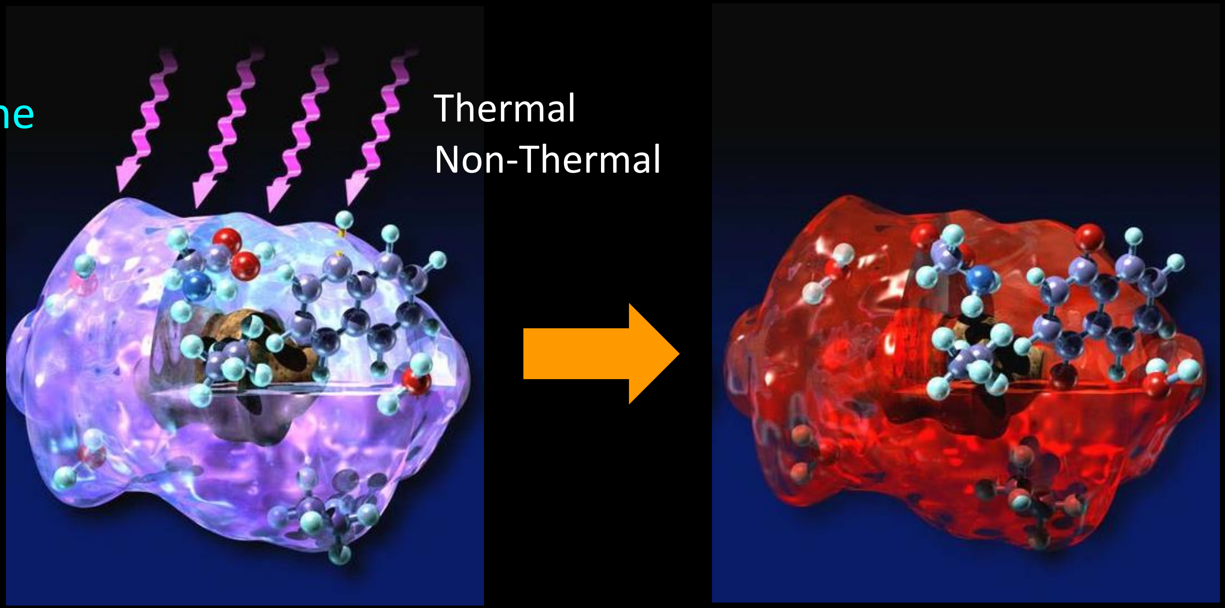
- Grain-driven reactions in Dense Clouds

Reactions occurring on the **SURFACE** of the ice mantles



H_2, H_2O, H_2CO, CH_3OH, CH_3NH_2, ...

Reactions occurring inside the **BULK** of the ice mantles

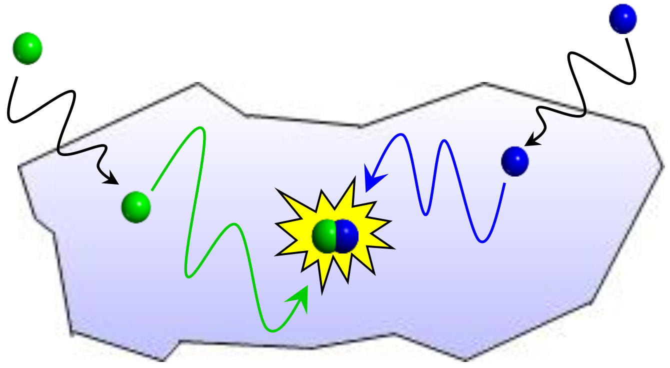


COMs

...

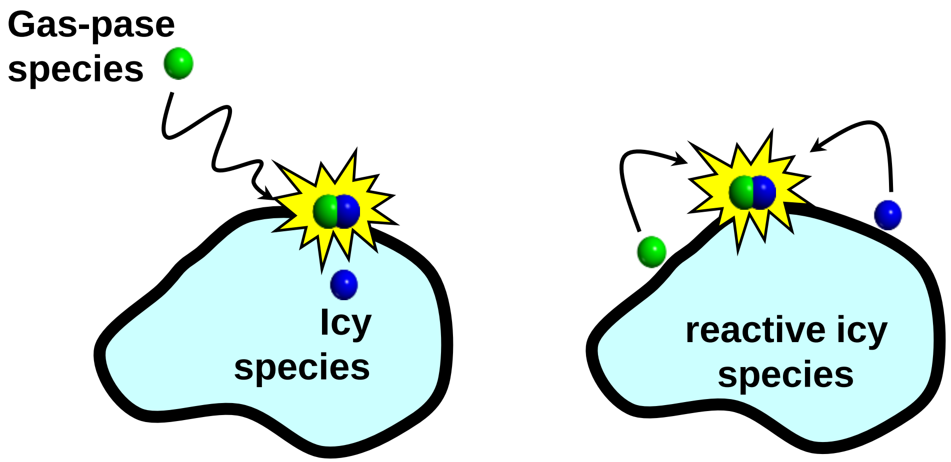
Role of Grains in Chemical Reactions

➢ Reactant concentrator



adsorption + diffusion

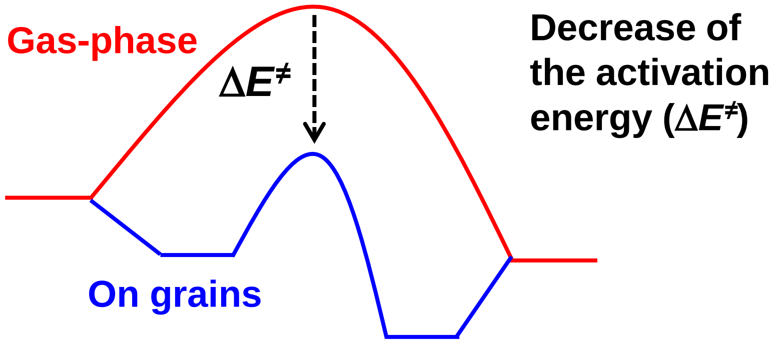
➢ Reactant supplier



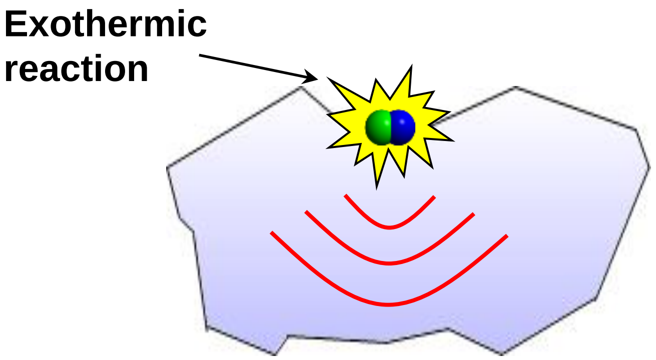
adsorption + reaction

diffusion + reaction

➢ Chemical catalyst



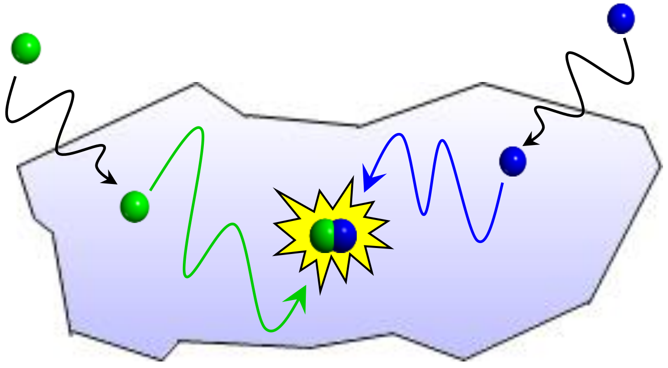
➢ Third body



Energy dissipation

Role of Grains in Chemical Reactions

➢ Reactant concentrator



adsorption + diffusion

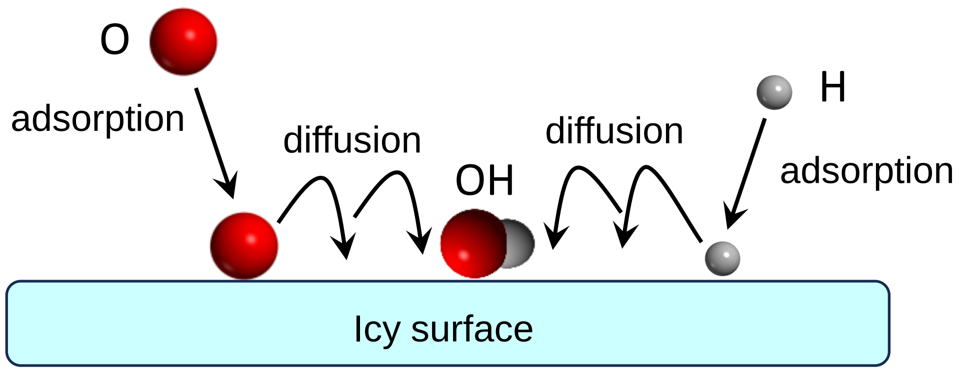
- Important due to the **low densities** of the ISM

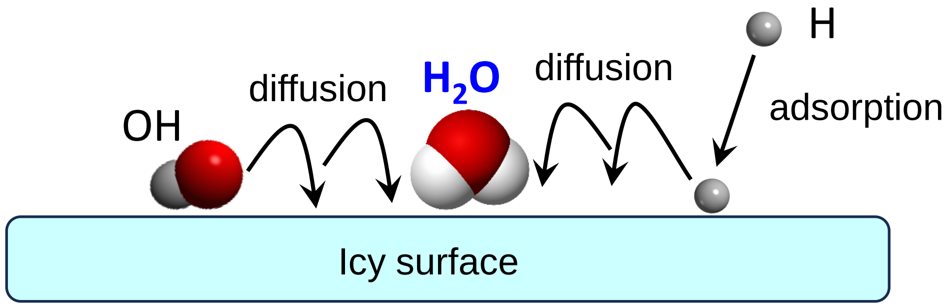
- Key parameter: **Binding Energy** (**BE**)

  - Adsorption rate constant: $k_{ads} \propto exp\left(\frac{BE}{k_B T}\right)$

  - Diffusion rate constant: $k_{diff} \propto exp\left(\frac{-f \cdot BE}{k_B T}\right)$ $\quad f \cong 0.3 - 0.6$

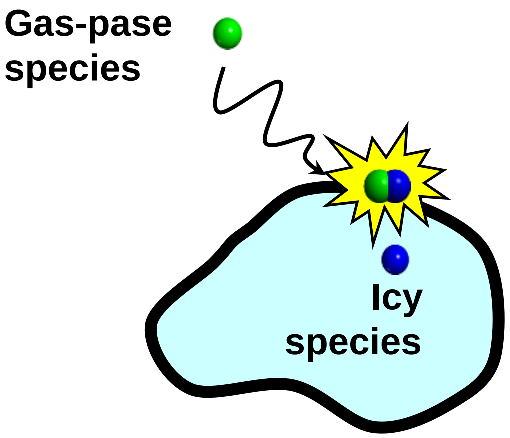
E.g., H_2O formation on ices





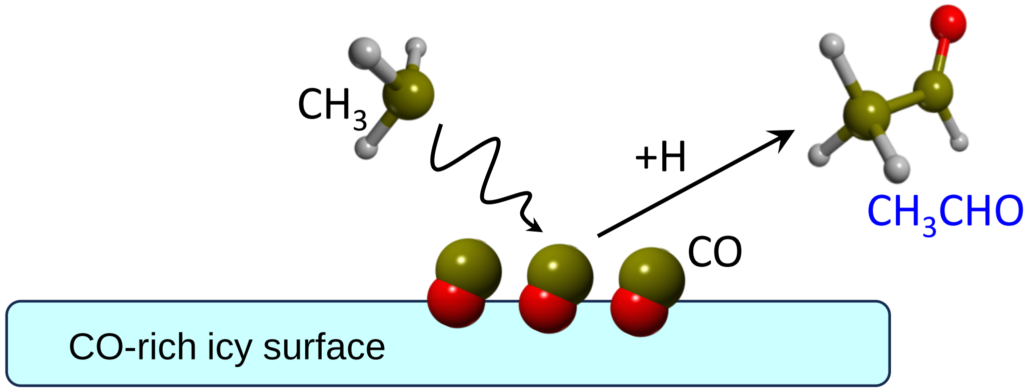
Role of Grains in Chemical Reactions

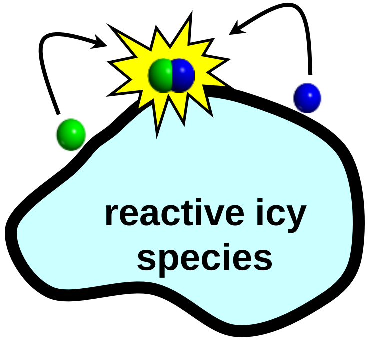
➢ Reactant supplier



Essentially on icy mantles (i.e., with H_2O, CO, CO_2, NH_3, CH_3OH, CH_4...)

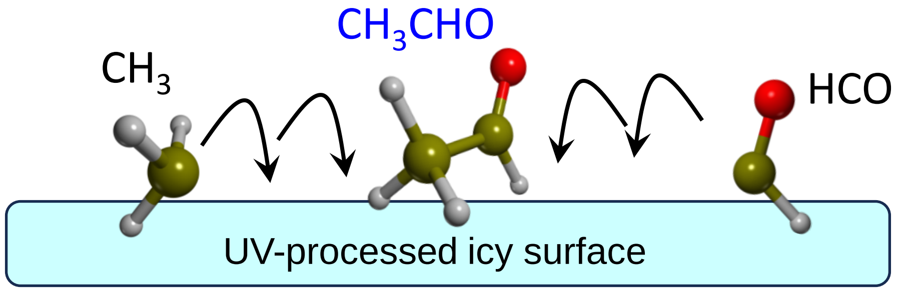
E.g., CH_3CHO formation on CO-rich ices





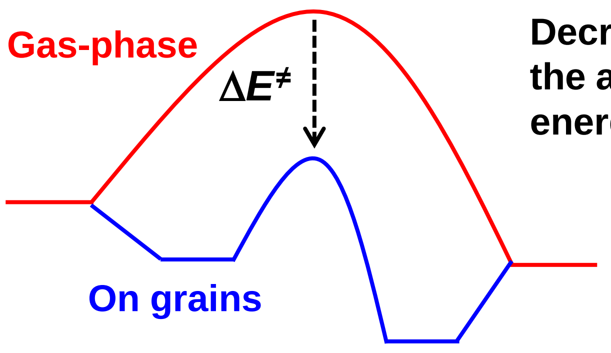
UV incidence on the ice mantles gives rise radicals (CH_3, NH_2, HCO, CH_3O,...)

E.g., CH_3CHO formation via radical coupling



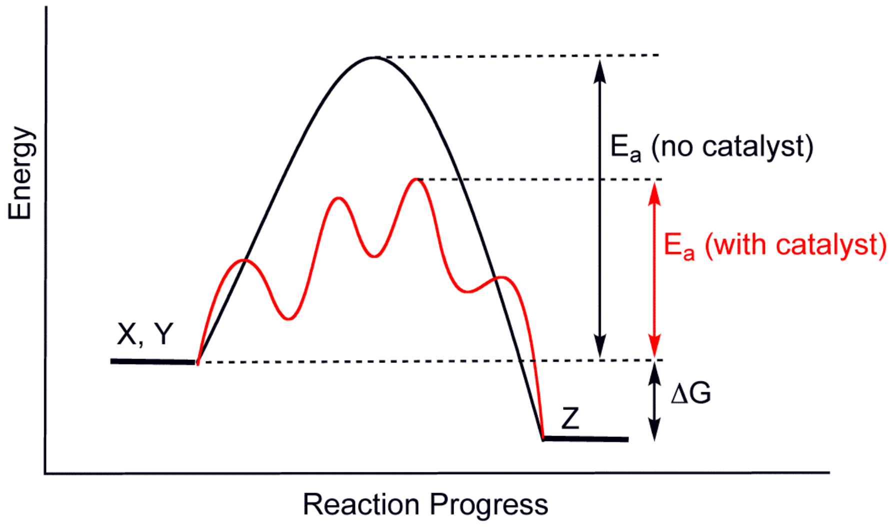
Role of Grains in Chemical Reactions

➢ Chemical catalyst



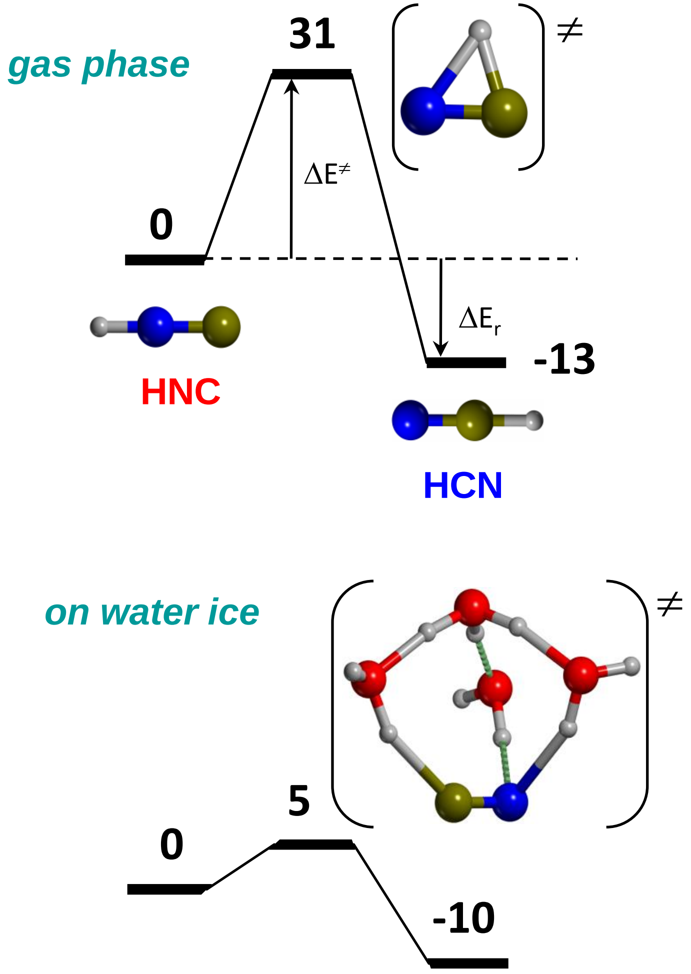
Decrease of the activation energy (ΔE≠)

A **chemical catalyst** is a substance that provides an **alternative, less energetic pathway** increasing the chemical reaction's speed, but is not included in its end-products



E.g., HNC → HCN isomerization on water ices

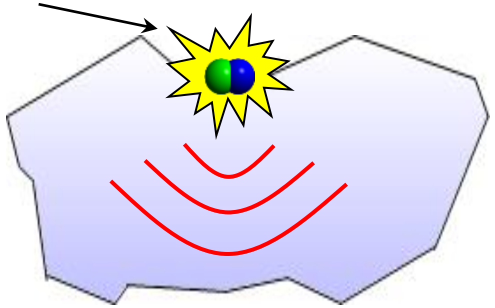
Energy units in kcal/mol



Role of Grains in Chemical Reactions

➢ Third body

Exothermic reaction

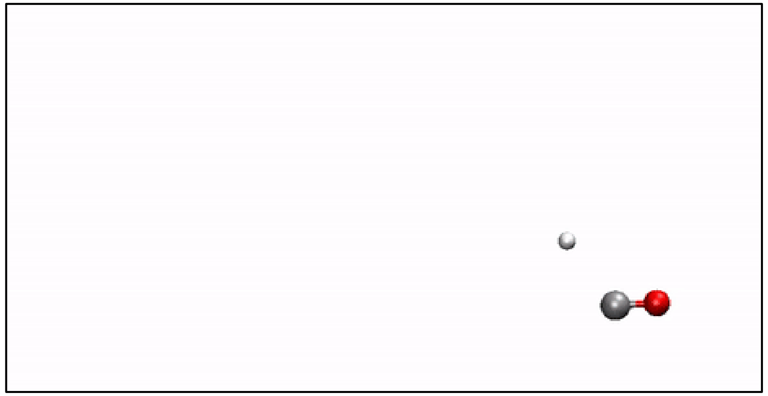


Energy dissipation

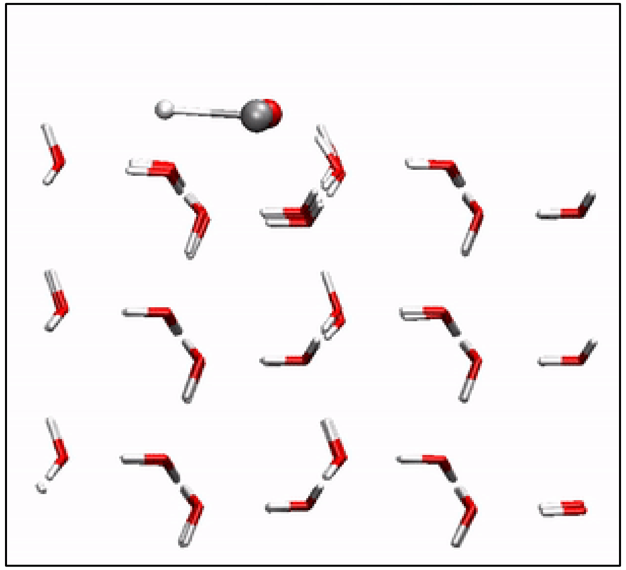
- Water ices have been demonstrated to be effective third bodies
- The third body effect in refractory materials is commonly advocated but it has never been unambiguosly determined

E.g., H + CO → HCO on water ices

➢ In absence of grains (gas phase)



➢ In the presence of grains (grain surface)



Types of Molecular Processes

Bond formation processes	
Radiative association	$X + Y \rightarrow XY + h\nu$
Associative detachment	$X^{-} + Y \rightarrow XY + e$
Grain Surface formation	$[X + Y]:g \rightarrow [XY]:g$

Grain Surface reactions

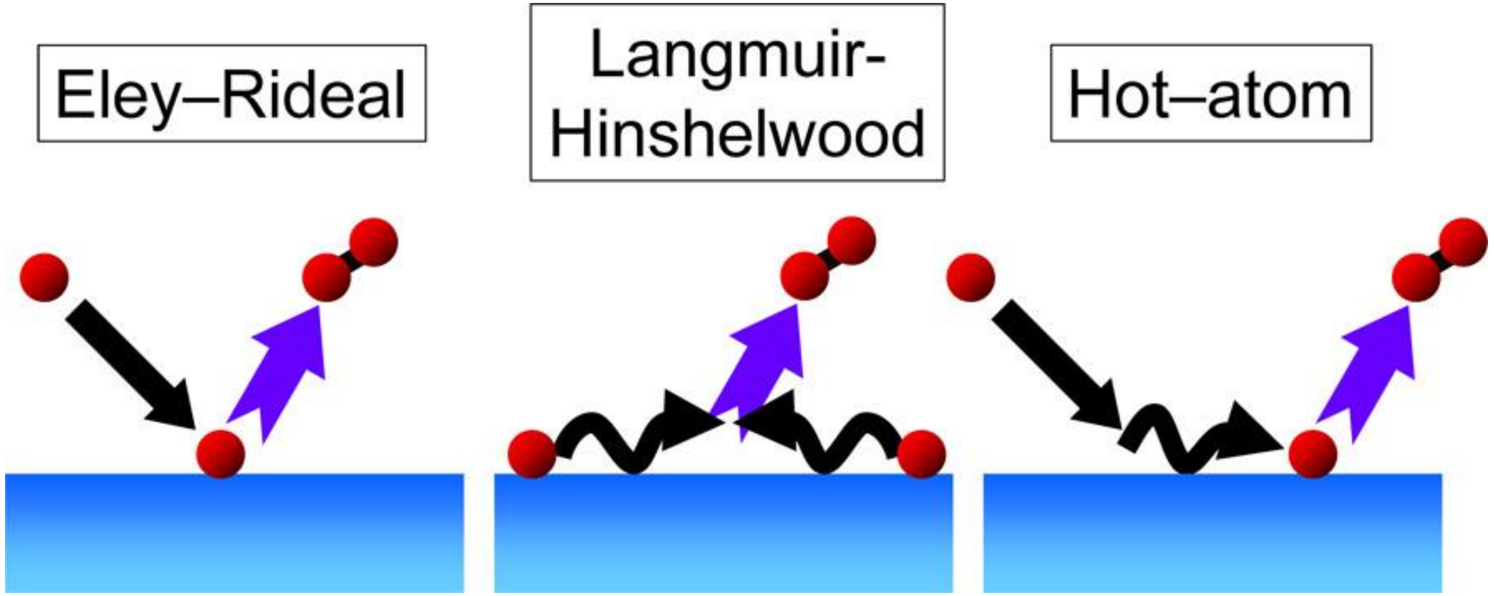
Coupling reactions
(2 → 1)

Bond destruction processes	
Photodissociation	$XY + h\nu \rightarrow X + Y$
Dissociative recombination	$XY^{+} + e \rightarrow X + Y$
Collisional dissociation	$XY + M \rightarrow X + Y + M$

Bond rearrangement processes	
Ion-molecule Exchange	$X^{+} + YZ \rightarrow XY^{+} + Z$
Charge-transfer	$X^{+} + YZ \rightarrow X + YZ^{+}$
Neutral-neutral	$X + YZ \rightarrow XY + Z$
	$X + [YZ]:g \rightarrow XY + [Z]:g$

Exchange reaction on a surface
($\Delta E >> 0$)

Chemical Mechanisms on Grains



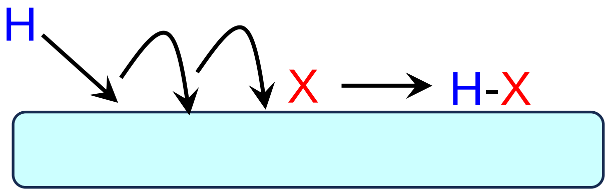
an adsorbed species on the surface is directly hit by another coming from the gas phase, thereby leading to the reaction

Two adsorbed species diffuse and encounter to react on the surface

A species from the gas phase reacts with and adsorbed one during its transient diffusion before being fully thermalized on the surface.

Chemical Reactions on Grains

- **H additions** (i.e., hydrogenations)



$H + H \rightarrow H_2$

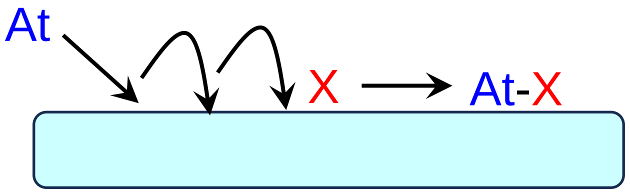
$O + H \rightarrow OH + H \rightarrow H_2O$

$N + H \rightarrow NH + H \rightarrow NH_2 + H \rightarrow NH_3$

$CO + H \rightarrow HCO + H \rightarrow H_2CO + H \rightarrow CH_3O + H \rightarrow CH_3OH$

mobile + open-shell species

- **Other atom additions** (i.e., O > C > N)



$CO + O \rightarrow CO_2$

$NH_3 + O \rightarrow NH_2OH$

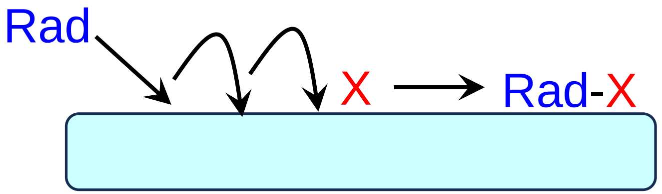
$CO + C \rightarrow CCO$

$OH + N \rightarrow HNO$

open-shell character of the atoms

$O(^3P)$, $C(^3P)$, $N(^4S)$

- **Radical additions**



$CN + H_2O_{(ice)} \rightarrow NH_2CO + H \rightarrow NH_2CHO$

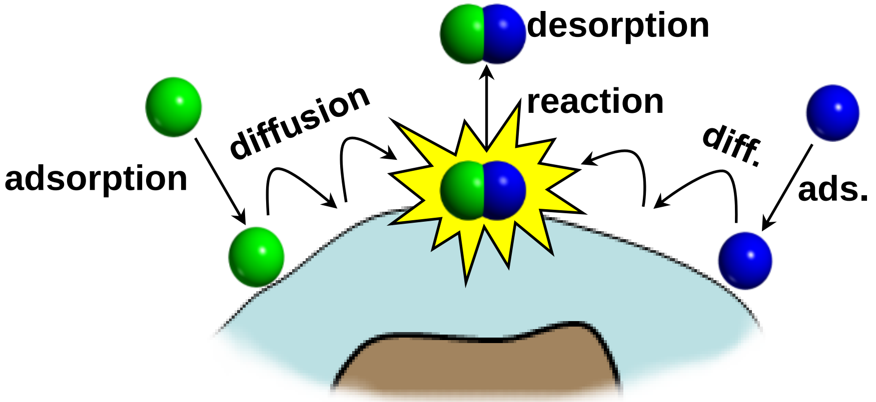
$CCH + H_2O \rightarrow CO_2 + H \rightarrow CH_2{=}CHOH$

$CH_3 + HCO \rightarrow CH_3CHO$

(and many other radical-radical couplings)

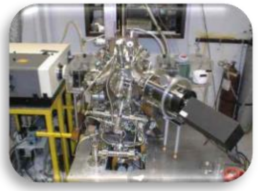
open-shell species
(one unpaired electron)

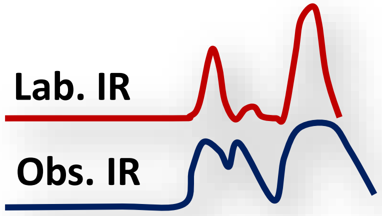
Investigations on Grain Surface Chemistry



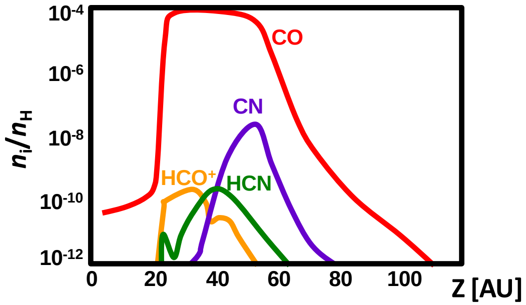
(traditional interdisciplinar approach)

Astron. Observations

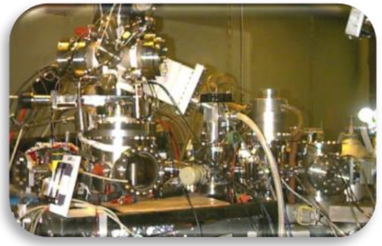


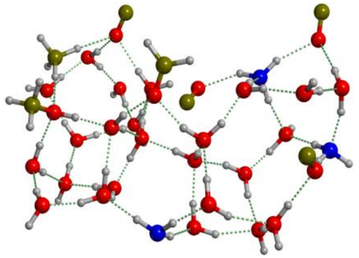


Astrochemical Modeling



Laboratory Experiments



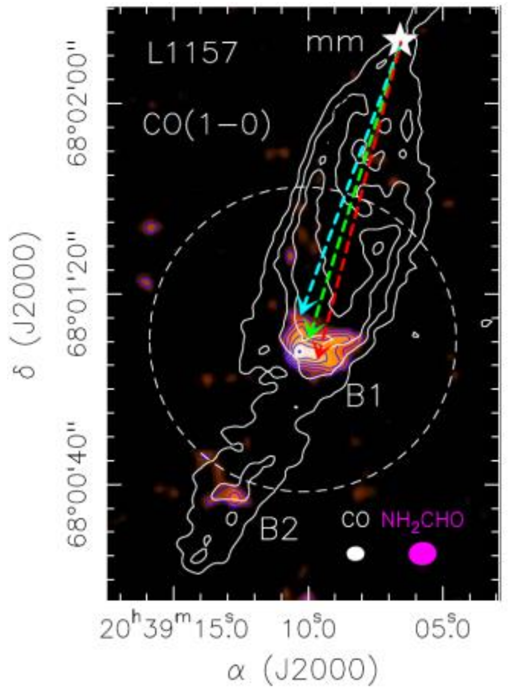


Astronomical Observations

- **Aim:** to **identify molecular species** that have been synthesised in different astrophysical environments

E.g.: Formamide (NH_2CHO) detection

Codella et al. A&A, 2017



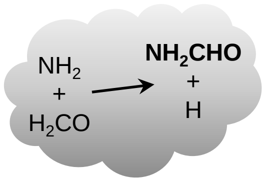
Detection & Identification

Abundances & quantities

Limitations

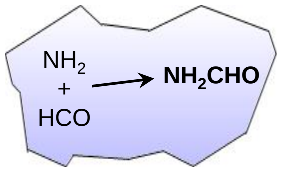
- **No information on the synthetic routes**
  - **- Reactants**
  - **- Mechanisms**
  - **- Gas phase *vs* on grain**

gas phase



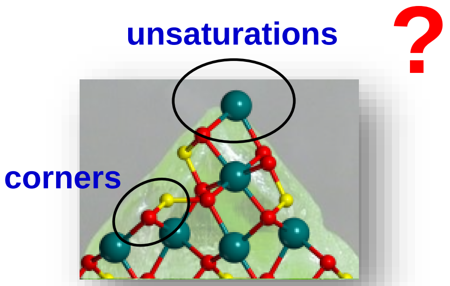
Barone et al., MNRAS, 2015

on grains

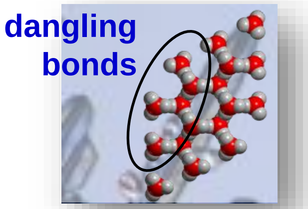


Rimola et al., ACS Earth Space Chem., 2018

- **No information on specific grain structural details (e.g., presence and nature of surface defects)**



SILICATE DUST



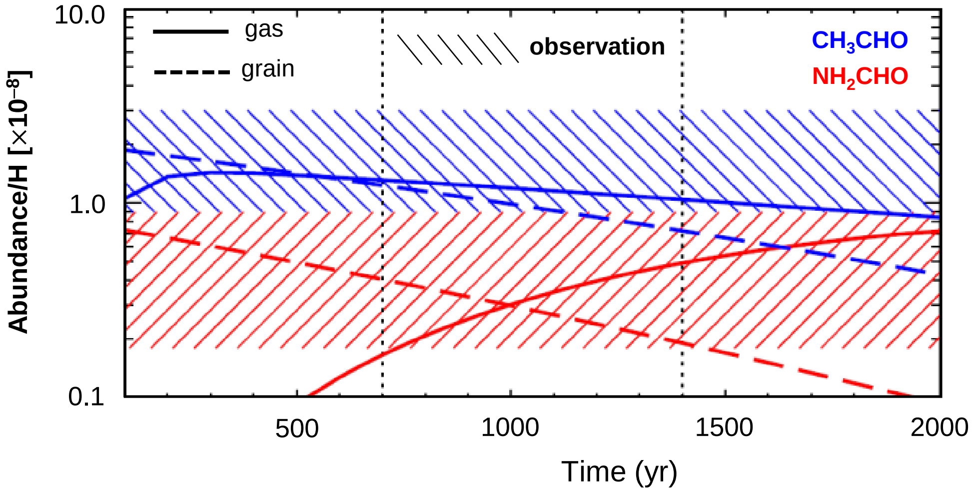
WATER ICE

Astrochemical Models

- **Numerical (e.g., kinetic) equations** that allow us to predict the **overall behaviour of the species** involved in a given **interstellar chemical process**

***E.g.*: NH_2CHO and CH_3CHO abundance predictions**

Codella,…,Rimola... A&A, 2017



Need of Input Data

- **Physical Parameters:** initial abundances, size of the grains, ...
- **Energetic Parameters:** activation energies, binding/desorption energies, ...

⬆ **Rationalization of the observations**

⬇ **Limitation**

- **Energetic input data** often based on **empirical estimates**, **gas-phase values** or even **guess values.**

Uncertainties on the parameters ↷ **Uncertainties on the predictions**

- **Effect of the uncertainties**

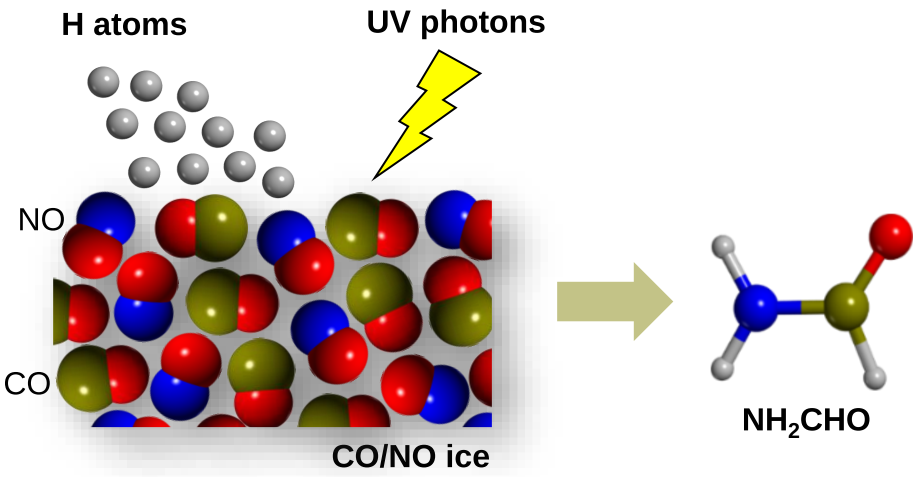
Source	CH_3NH_2/NH_2CHO
IRAS 16293–2422B (Obs.)	**≤ 0.053**
Gas-grain Model	**0.2 – 2.3**

Ligterink et al., A&A, 2018, 619, A28

Laboratory Experiments

- **Aim:** to **reproduce reactions of astrochemical interest** by simulating astrophysical regimes (low T and UHV) under well controlled conditions (i.e., lab instrumentation).

***E.g.*: Formamide (NH_2CHO) synthesis**



Fedoseev et al., MNRAS, 2016

Experimental conditions

NO:CO = 1:12

T_{ice} = 13 K

$p_{chamber} \approx 10^{-10}$ mbar

H-atom flux = 1.2×10^{13} cm^{-2} s^{-1}

UV-photon flux = 1.3×10^{13} cm^{-2} s^{-1}

↑ **Determination of the newly formed products**

↑ **Macroscopic thermodynamic and kinetic data: BEs, Ea**

(by empirical fiting)

↓ **Limitations**

- **Unable to reproduce truly occurring reactions**
  - Grain compositions
  - Individual processes
  - Fluxes
- **No information on the reaction mechanisms**
  (unless intermediates are identified)

Current Limitation

Limitations

- **Observations**: no information on the synthetic routes
- **Astrochemical models**: uncertainties
- **Experiments**: ISM conditions + mechanisms

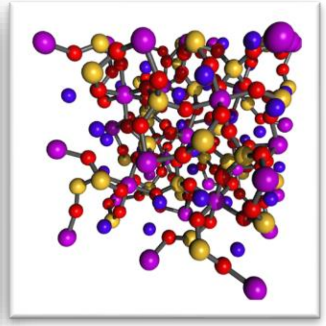
LACK OF ATOMIC-SCALE INFORMATION

The chemist paradox

we only have AVERAGE/MACROSCOPIC data

Chemists deal with molecules: synthesize them, determine their properties, make them to react,… but **we have limitations to obtain**

ATOMIC-SCALE INFORMATION



How to obtain information at the atomistic level?

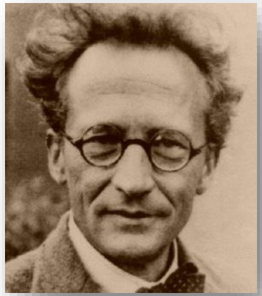
- ❑ Spectroscopy

  (IR, NMR, UV-Vis, EPR, X-ray…. but not atomic resolution)

- ❑ **Computational Modeling and Simulation**

Obtaining Atomic-Scale Information

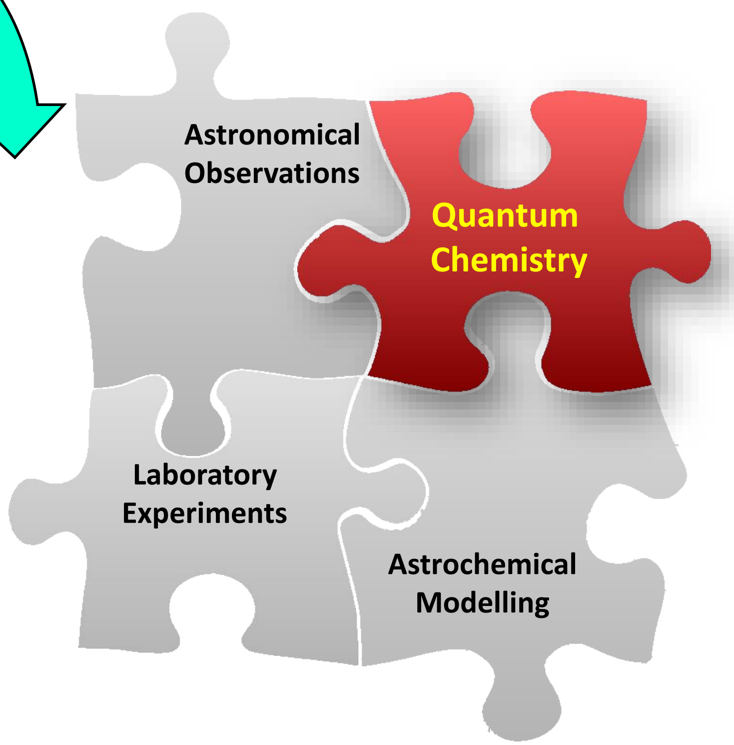
Molecular Simulations Based on QUANTUM MECHANICAL METHODS



The Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

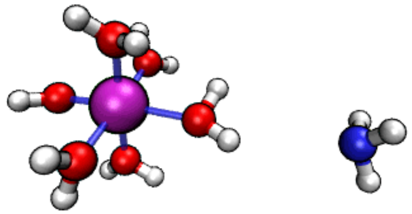
"If we can solve this equation we know everything about the systems"



Complementary tool to investigate grain surface chemical phenomena

Information from Computational Simulations

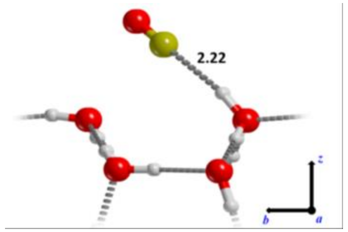
- **Computational Chemistry:** Area of the Chemistry that uses **molecular simulations** to solve **chemical problems**.

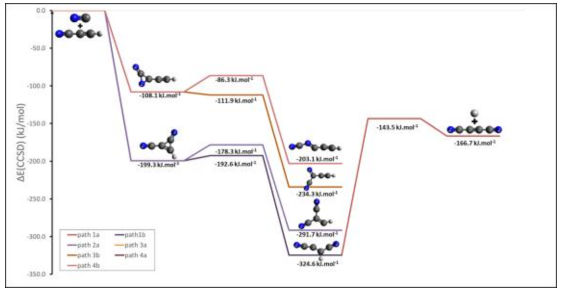


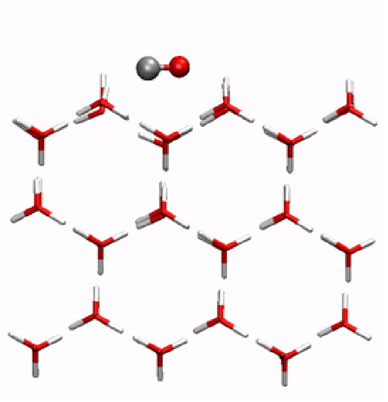
It covers the use of **theoretical chemistry** methods and **molecular modeling** techniques to calculate the **structure and properties** of chemical systems (molecular, biological, materials) with the goal to obtain unique **atomic scale information**

- **Atomic Scale Information:**

  - **Structure & related properties**
  - **Energetics & kinetics**
  - **Dynamics**





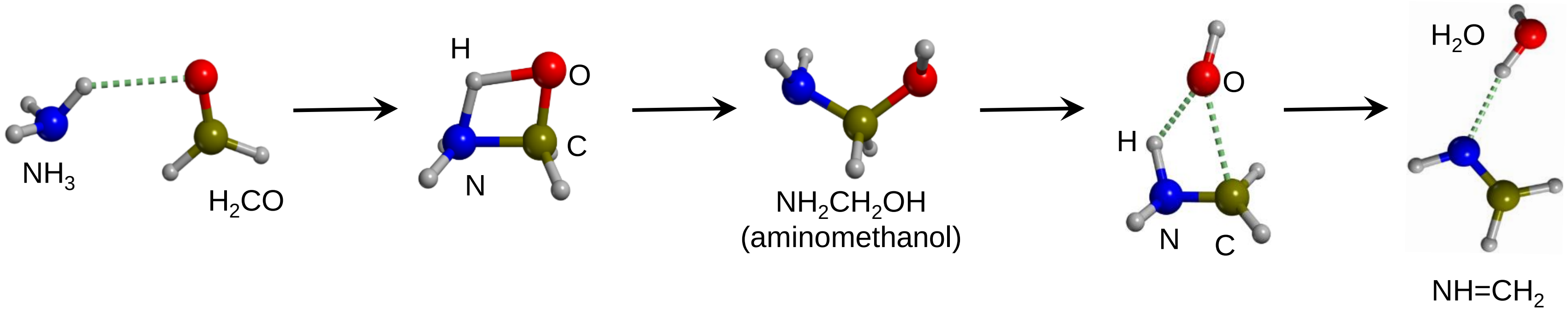


Information from Computational Simulations

❑ Structure and Related properties

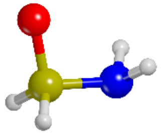
- **Reaction mechanisms: reactants, products, intermediates & transition states**

E.g.: $NH_3 + H_2CO \rightarrow NH{=}CH_2 + H_2O$

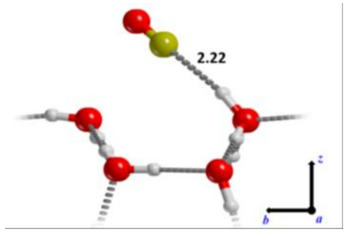


- **Van der Waal complexes, surface complexes**

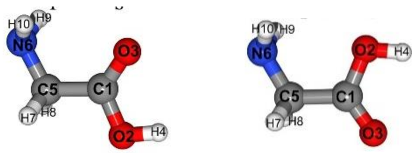
$H_2CO\cdots NH_2$



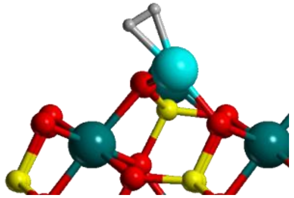
CO/H_2O(ice)



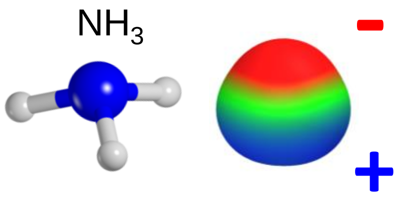
- **Related properties**



Rotational parameters

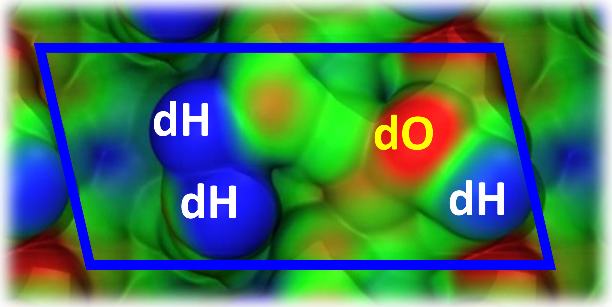


Frequencies & IR



Elecrostatic potential maps

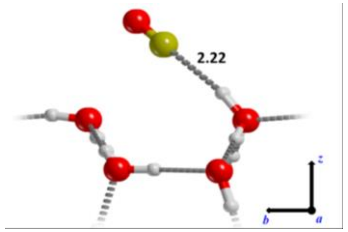
H_2O ice



Information from Computational Simulations

❑ Energetics & kinetics

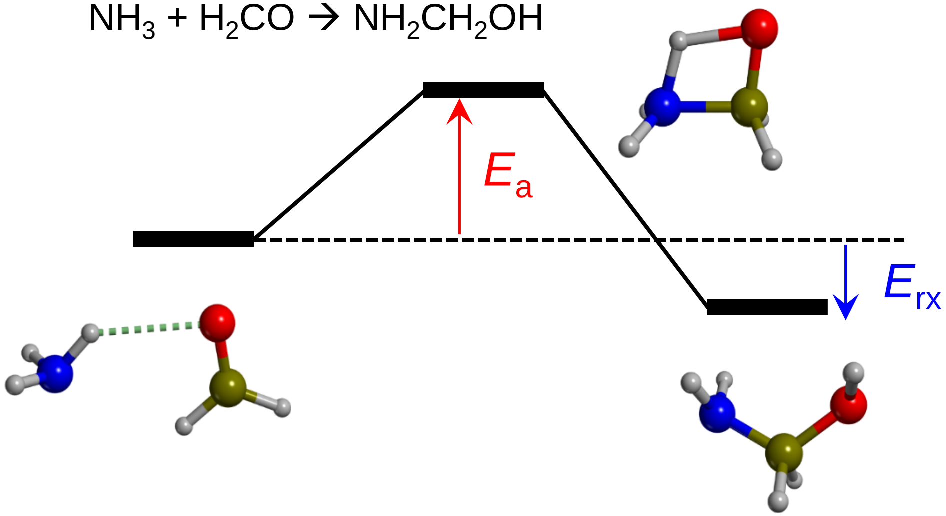
- **Binding energies**



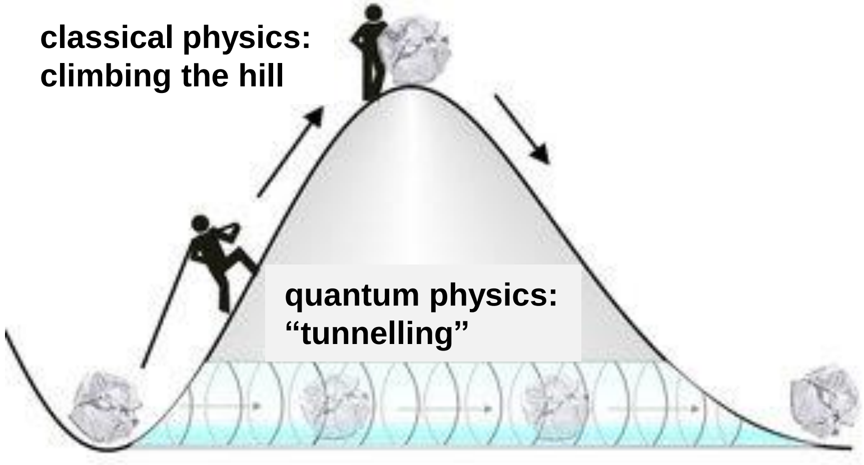
BE = 18.4 kJ/mol

- **Potential energy surfaces**

$NH_3 + H_2CO \rightarrow NH_2CH_2OH$



- **Kinetics**

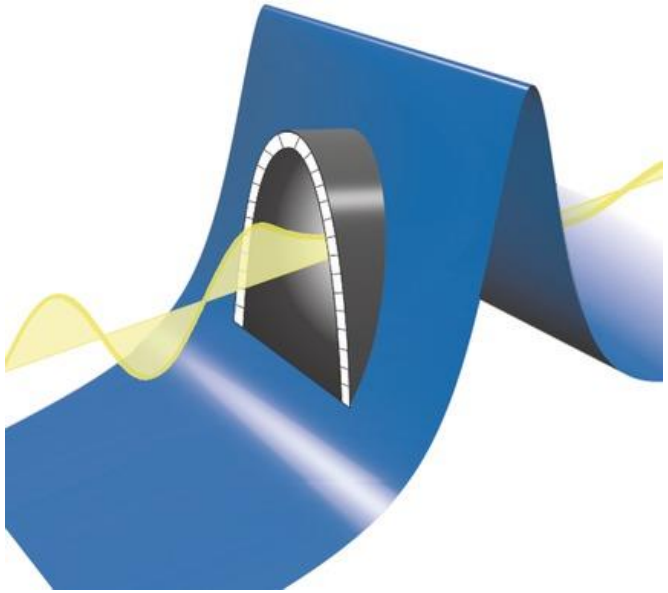


Calculation of Rate Constants:

- **Classical Transition State Theory (TST)**
- **Tunneling via:**
  - **Semi-classical approach**
  - **Quiantum approach**

Information from Computational Simulations

- **Relevance of Tunneling in Astrochemistry**

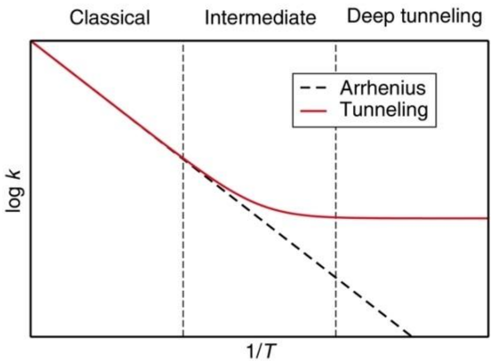


- **Tunnelling** is the **quantum phenomenon** where a chemical process occurs by **passing through** a potential barrier.

- Play an **important role** in many chemical transformations:
  - It enables astrochemical reactions that would be **impossible** by thermal transition.
  - It **changes** reaction paths and branching ratios
  - It **influences** biochemical processes

- Experimentally, it can be indirectly detected by:

temperature independent rate constants at low temperature



The influence of tunneling on the reaction rates can be monitored directly through computational investigations

Information from Computational Simulations

❑ Relevance of Tunneling in Astrochemistry

- **General conditions**
  - Low temperatures
  - Light species (i.e., particle+wave behaviour), e.g., **H atoms**
  - High potential barriers
  - Narrow potential barriers (particle wave wider than the barrier width)

- **Crossover Temperature (T_X)**

Temperature below which tunneling becomes dominant and above which becomes negligible.

$$T_X = \frac{\hbar\nu^{\neq}}{2\pi k_B}$$

$$T_X = \frac{h\nu^{\neq}\Delta U_0^{\neq}/k_B}{2\pi\Delta U_0^{\neq} - h\nu^{\neq} ln2}$$

(derived from different tunneling formalisms)

- **Rate constant via semi-classical approach**

$$k^{SC-TST} = \Gamma^{tun} \times k^{TST}$$

$$k^{TST} = \frac{q^{\neq}}{q^R}\frac{k_B T}{h} e^{\left(-\frac{\Delta E^{\neq}}{k_B T}\right)}$$

Γ^{tun}: tunneling **transmission coefficient**

values of **≥ 1**

depends on the **transmission probability P(E)**

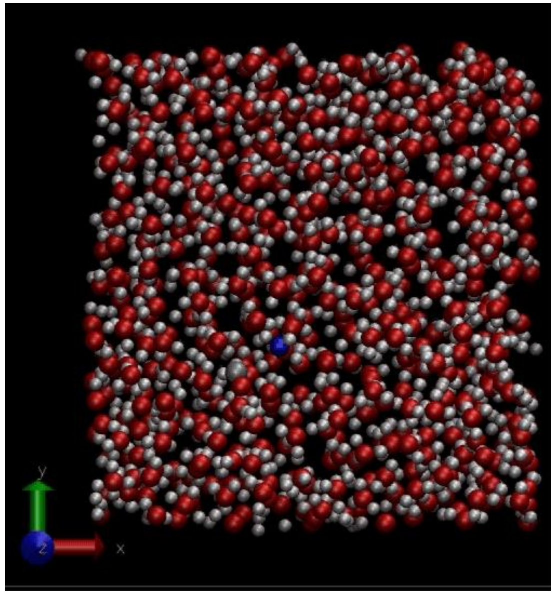
Information from Computational Simulations

- **Dynamics**

Useful to study non-equilibrium systems: diffusion, reactions, energy dissipation

- **Molecular Dynamics Simulations**

  Evolution of the system with time by introducing energy (e.g., T, collisions).

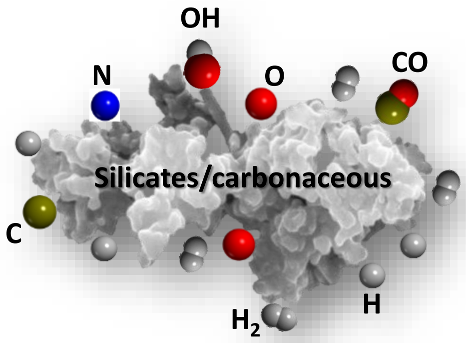


MD evolution for the $HCO + NH_2 \rightarrow NH_2CHO$ reaction at 10 K

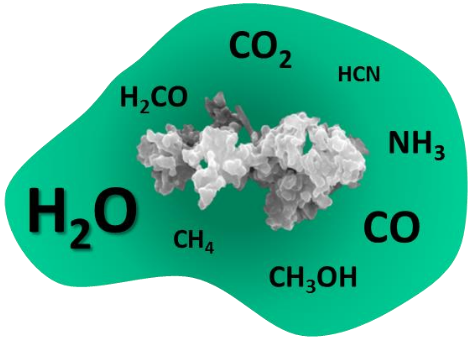
Surface modeling of interstellar grains

REAL SYSTEM

dust grains



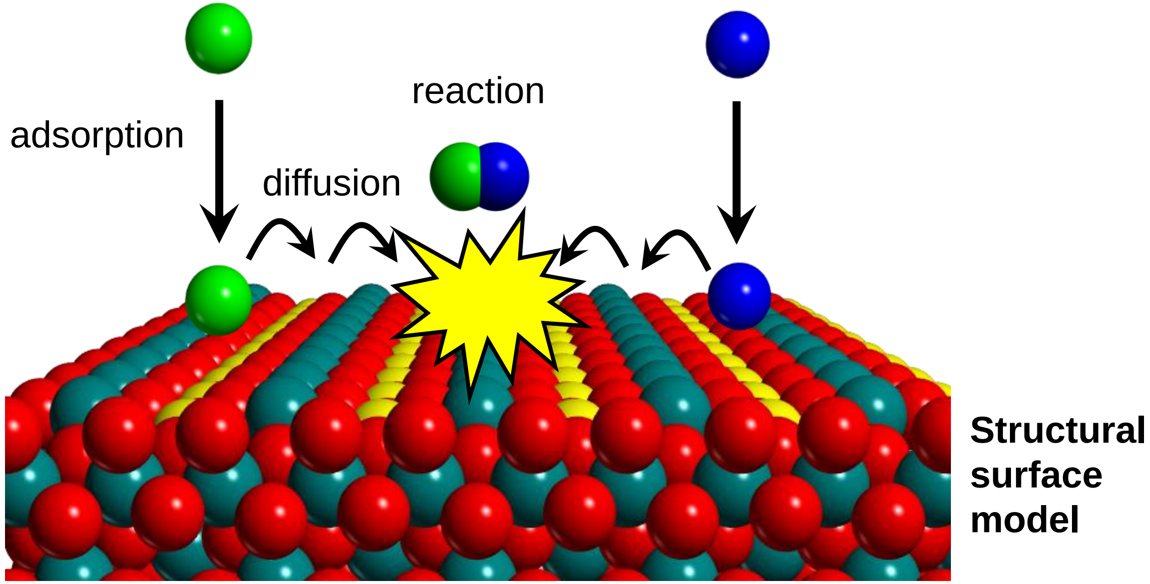
icy grains



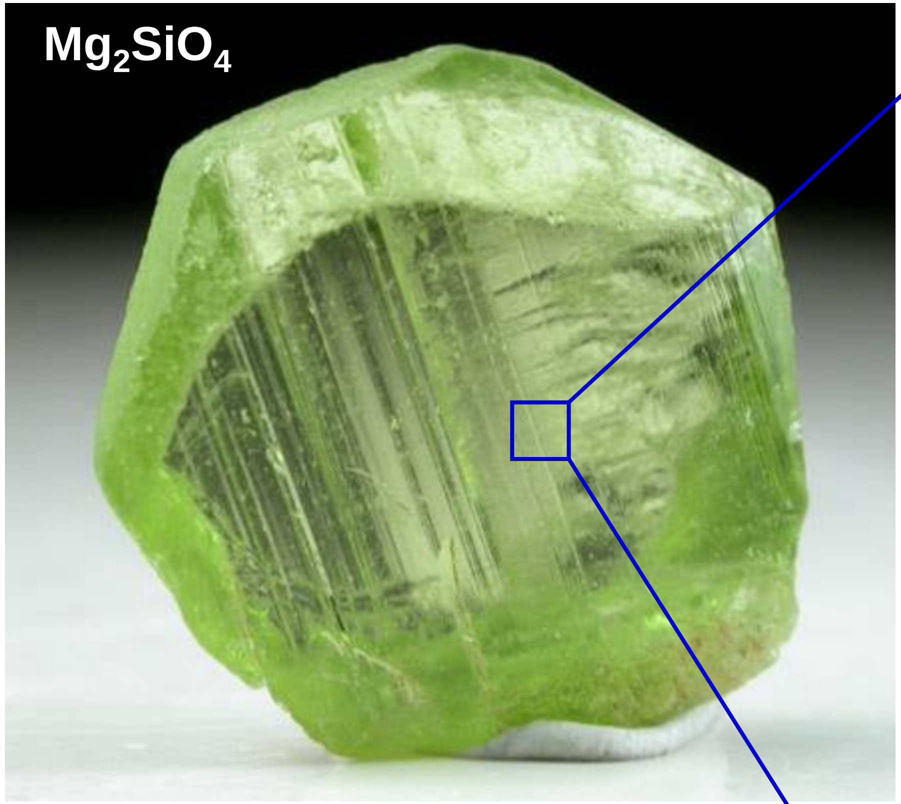
MODEL SYSTEM

1. **Modeling a suitable structure for the surface**

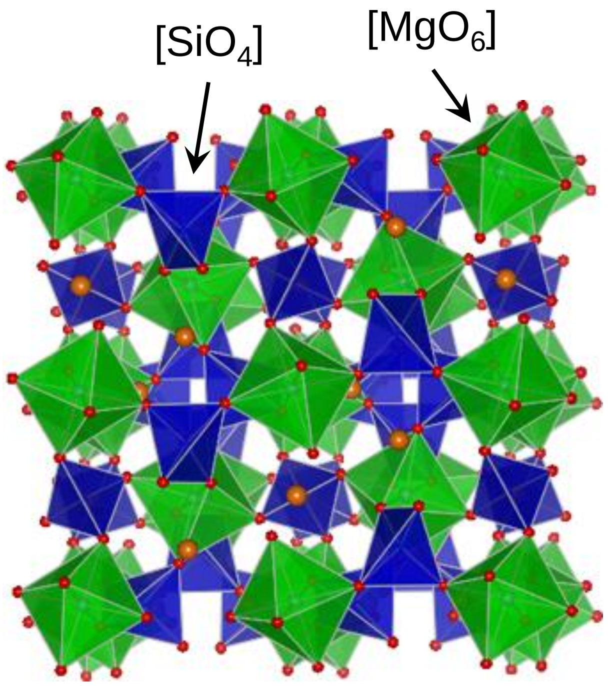
2. **Simulation of the surface phenomena on the model**



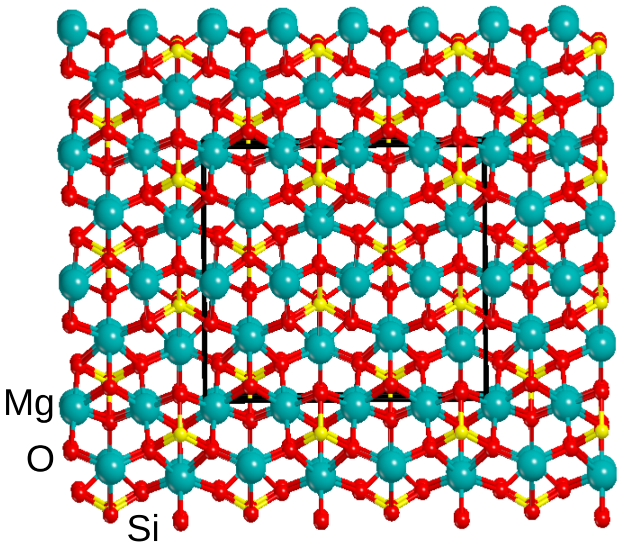
Surface modeling of interstellar grains. Top-down approach



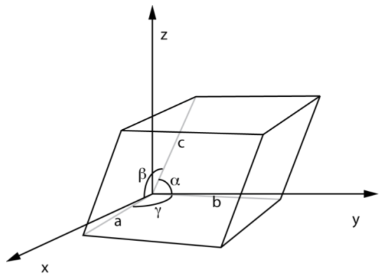
crystalline bulk structures obtained from X-Ray Diffraction



Polyhedric view

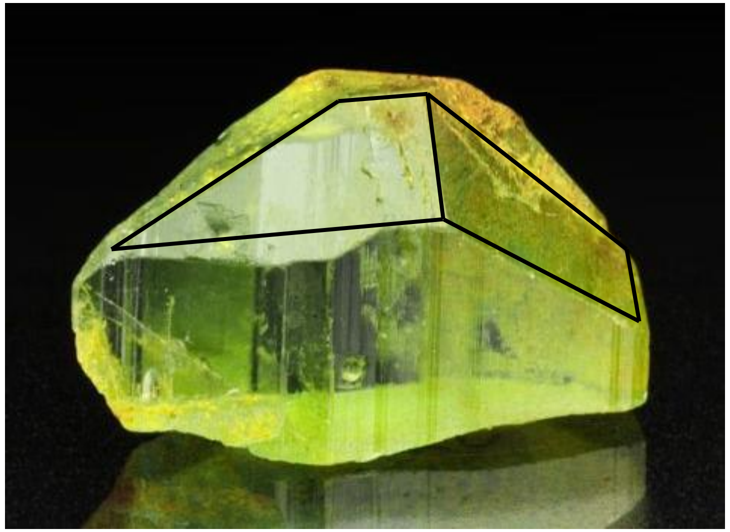


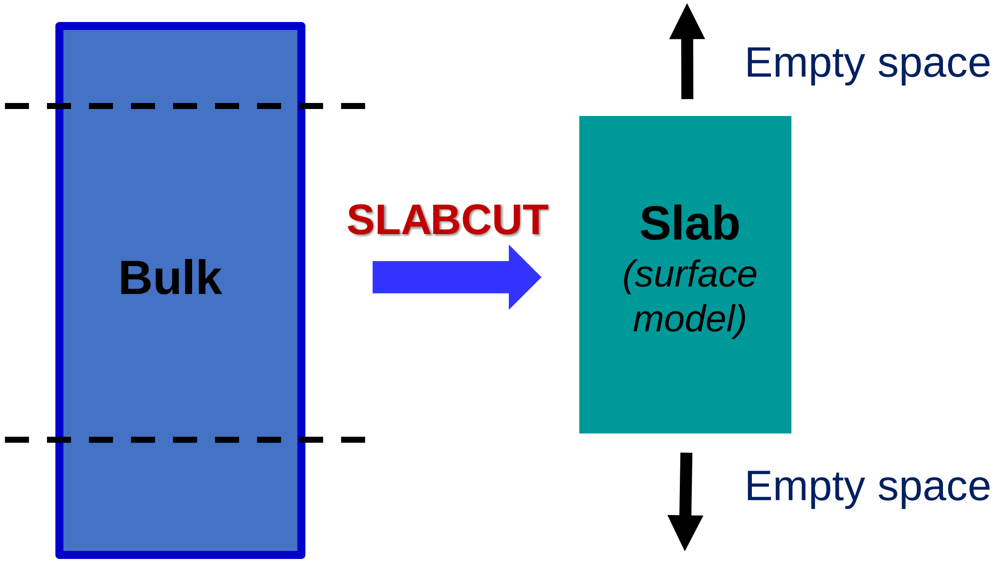
Atomistic view

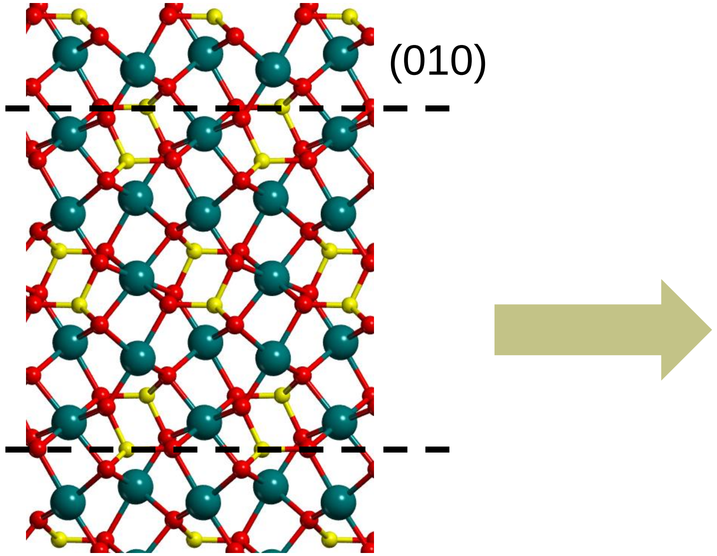


3D periodicity

Surface modeling of interstellar grains. Top-down approach

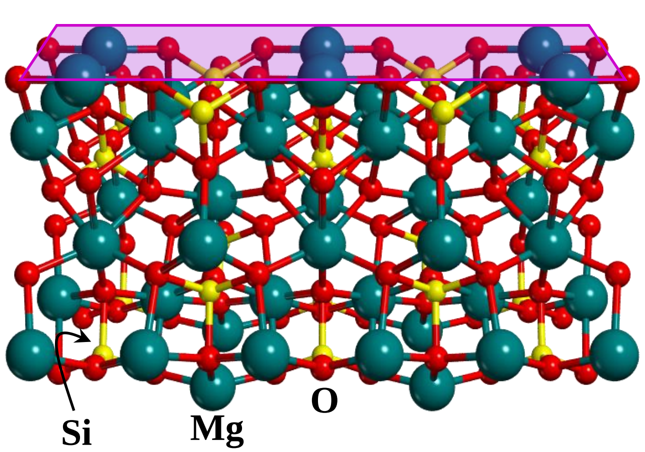




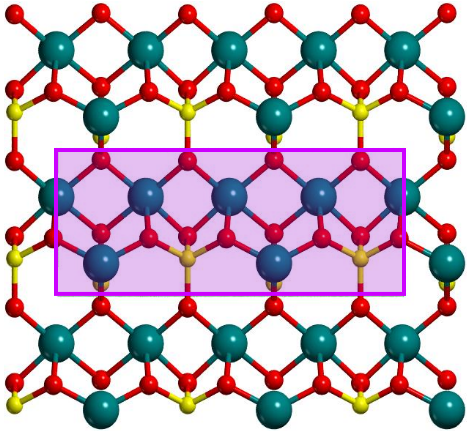


Mg_2SiO_4 bulk crystal

Mg_2SiO_4 (010) surface



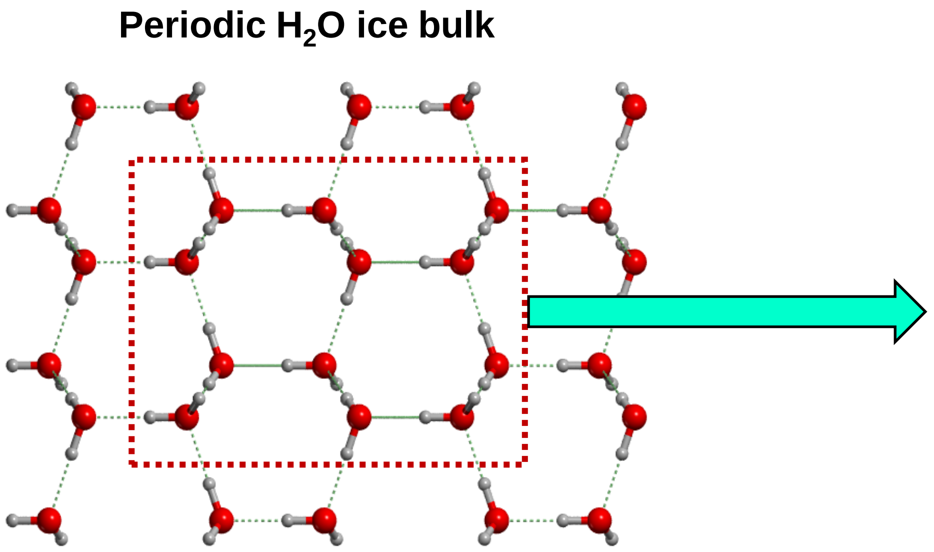
(lateral view)

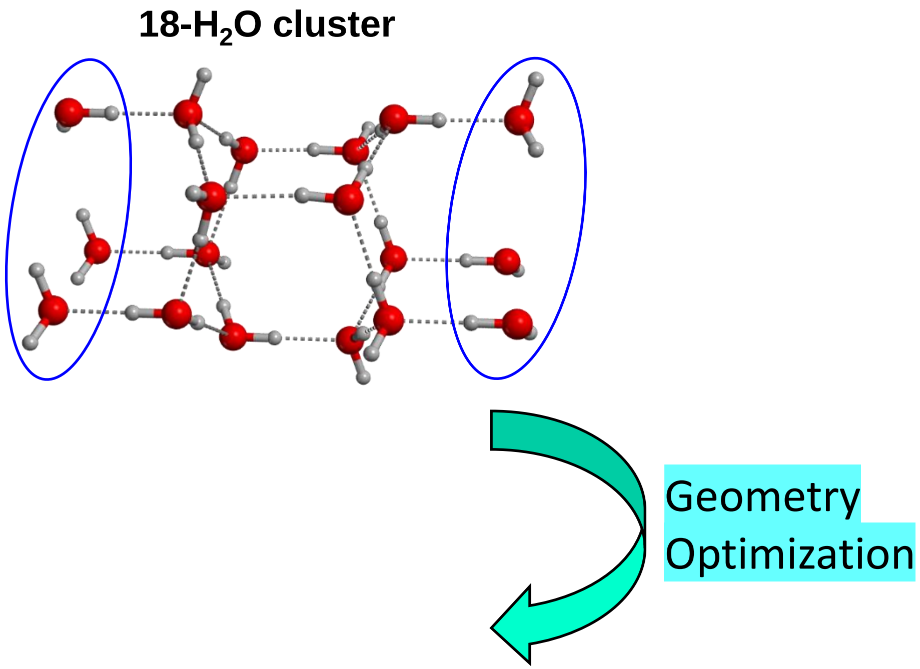


(top view)

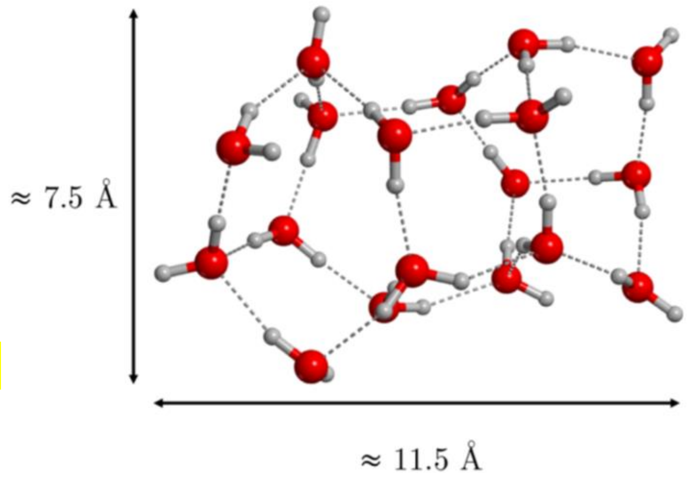
- 2D periodicity
- Finite thickness

Surface modeling of interstellar grains. Top-down approach





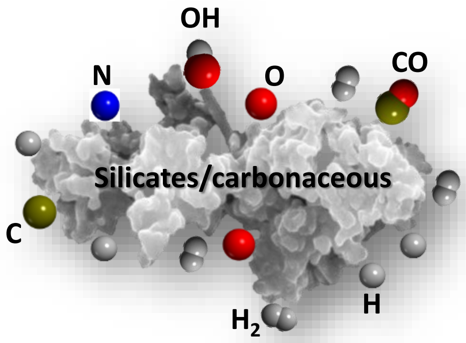
- Geometry resulting from the cut will change dramatically upon relaxation
- Molecules at the **border** will move to maximize the intermolecular interactions (H-bond)
- Optimized structures are no longer representative of the crystal to which they initially belong (inherent amorphisation!)



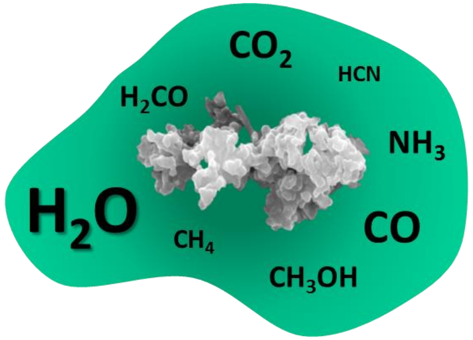
Surface modeling of interstellar grains

REAL SYSTEM

dust grains



icy grains



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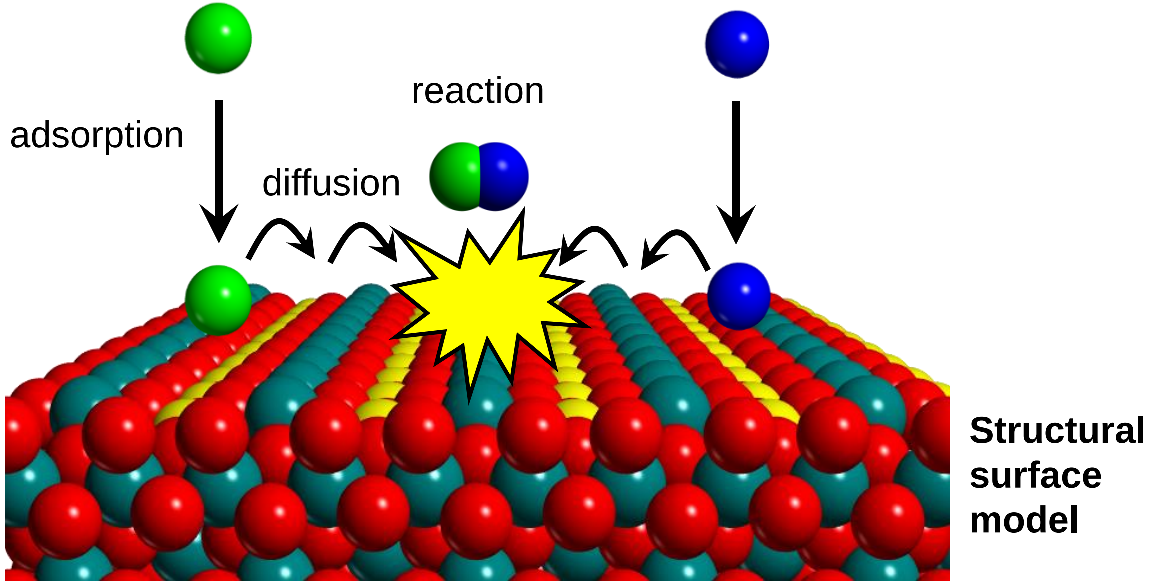
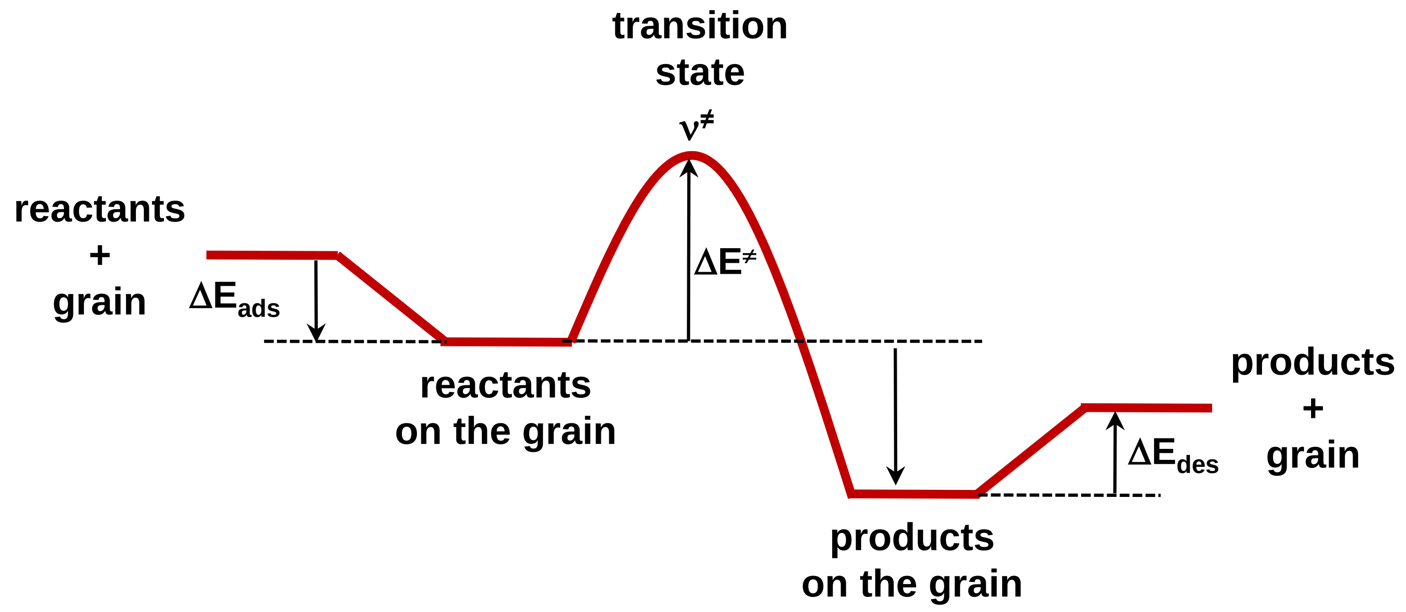
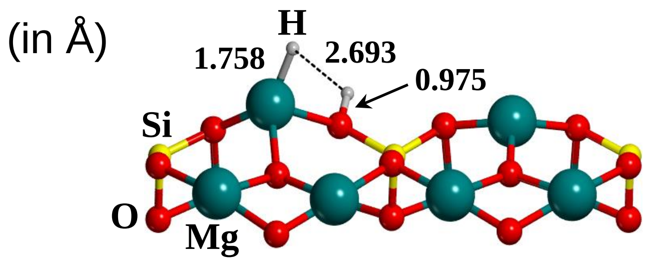


Potential Energy Surface of a grain surface reaction



Structural Information



Energetic Information

- Adsorption energies (ΔE_{ads} = -BE)
- Energy Barriers ($\Delta E^{\neq}$)
- Reaction Energies (ΔE_{r})
- Desorption energies (ΔE_{des})
- Transition Frequency ($\nu^{\neq}$)

Useful in astrochemical modeling studies

Kinetics & Tunneling

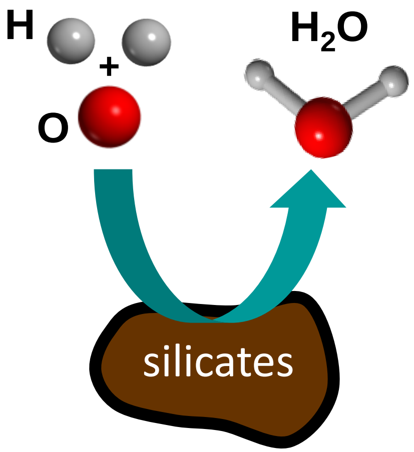
- Classical rate constant

$$k^{TST} = \frac{q^{\neq}}{q^{R}}\frac{k_B T}{h} e^{\left(-\frac{\Delta E^{\neq}}{k_B T}\right)}$$

- Tunneling through semi-classical approach

$$k^{SC-TST} = \Gamma^{tun} \times k^{TST}$$

H_2O formation on silicates



Molpeceres et al., MNRAS, 2019, 482, 5389

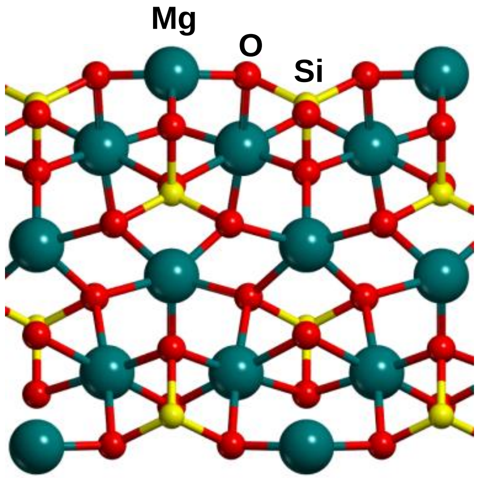
i) $O_{(g)} \rightarrow O_{(surf)}$ (O adsorption)

ii) $H_{(surf)} + O_{(surf)} \rightarrow OH_{(surf)}$ (1st H additon)

iii) $H_{(surf)} + OH_{(surf)} \rightarrow H_2O_{(surf)}$ (2nd H additon)

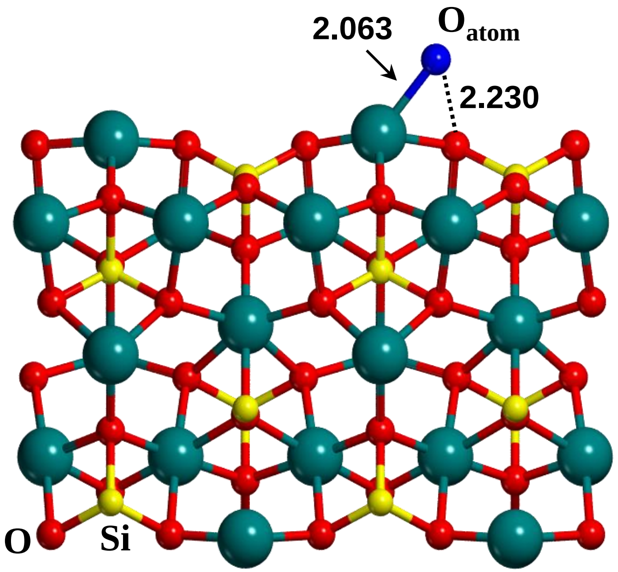
H_2O formation on silicates. O adsorption

Step 1: adsorption of atomic $O(^3P)$ on the silicate surface



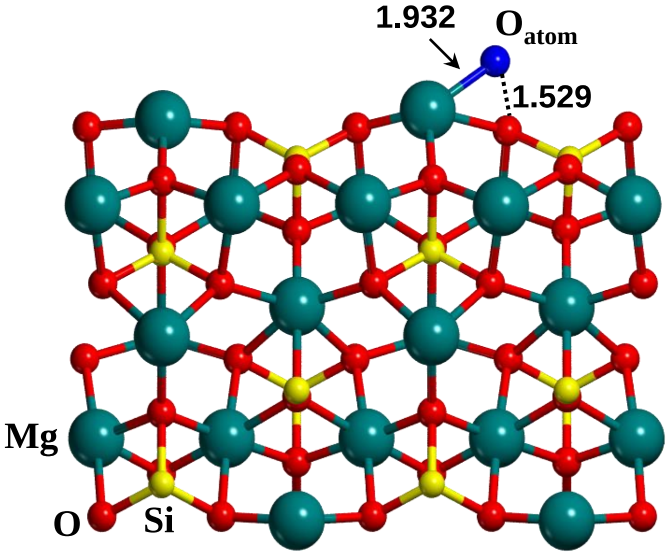
Mg_2SiO_4 (010) surface

$O\ (^3P)$



$\Delta_{ads}U_0$ = -3.2 kcal mol^{-1}

TRIPLET STATE



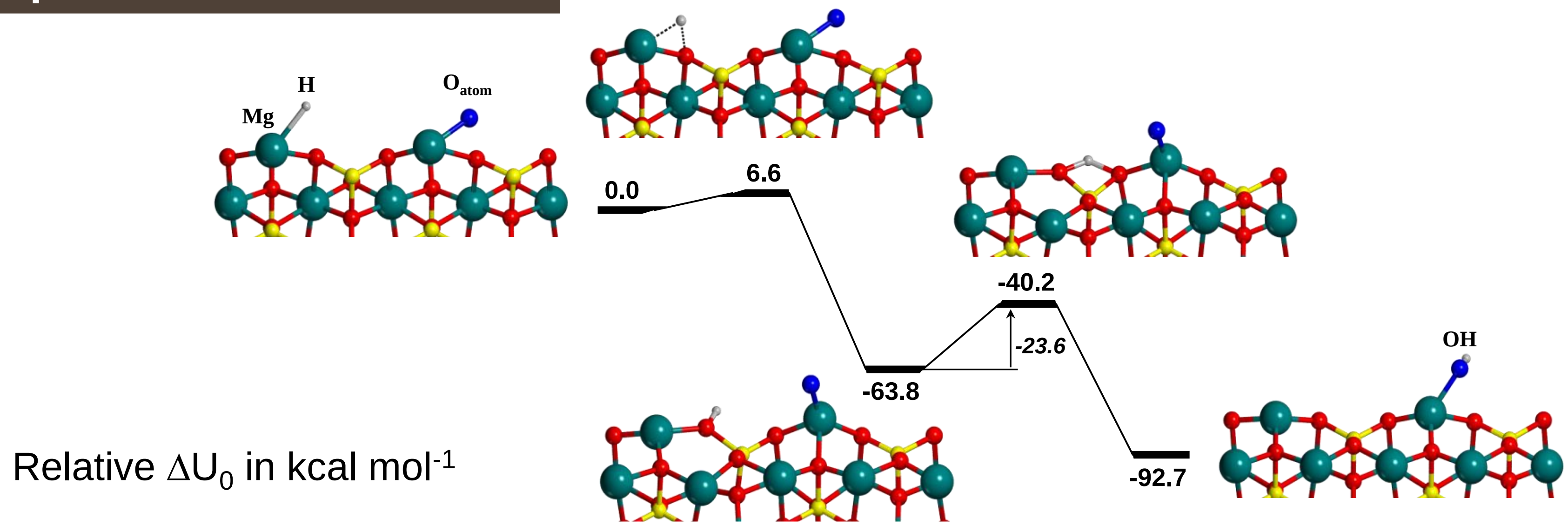
$\Delta_{ads}U_0$ = -33.6 kcal mol^{-1}

SINGLET STATE

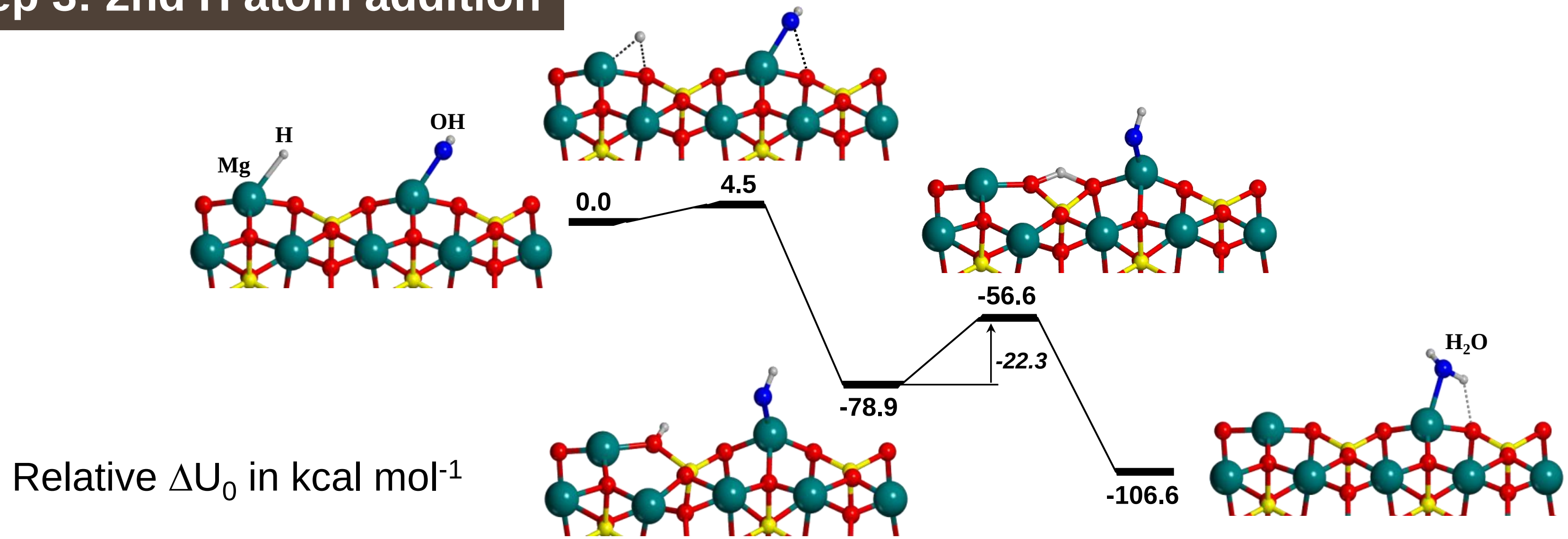
Electronic Spin Inter-System Crossing

H_2O formation on silicates. H additions to O

Step 2: 1st H atom additon



Step 3: 2nd H atom addition



H_2O formation on silicates. Tunneling effects

Final semi-classical rate constant

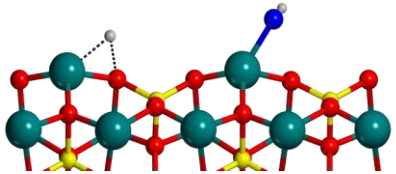
$$k^{SC-TST} = \Gamma(T) \times k^{TST}$$

Fermann & Auerbach (FA) Correction

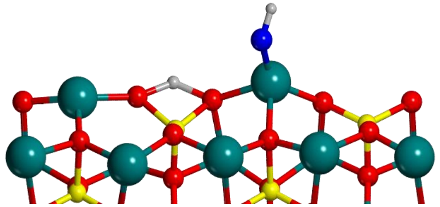
$$\Gamma^{FA}(T) = \exp\left(\frac{\Delta U_0^{\neq}}{k_B T}\right) \exp\left(\frac{2\pi \Delta U_0^{\neq}}{h\nu^{\neq}}\right)\left(1 + \frac{2\pi k_B T}{h\nu^{\neq}}\right)$$

Eckart Correction

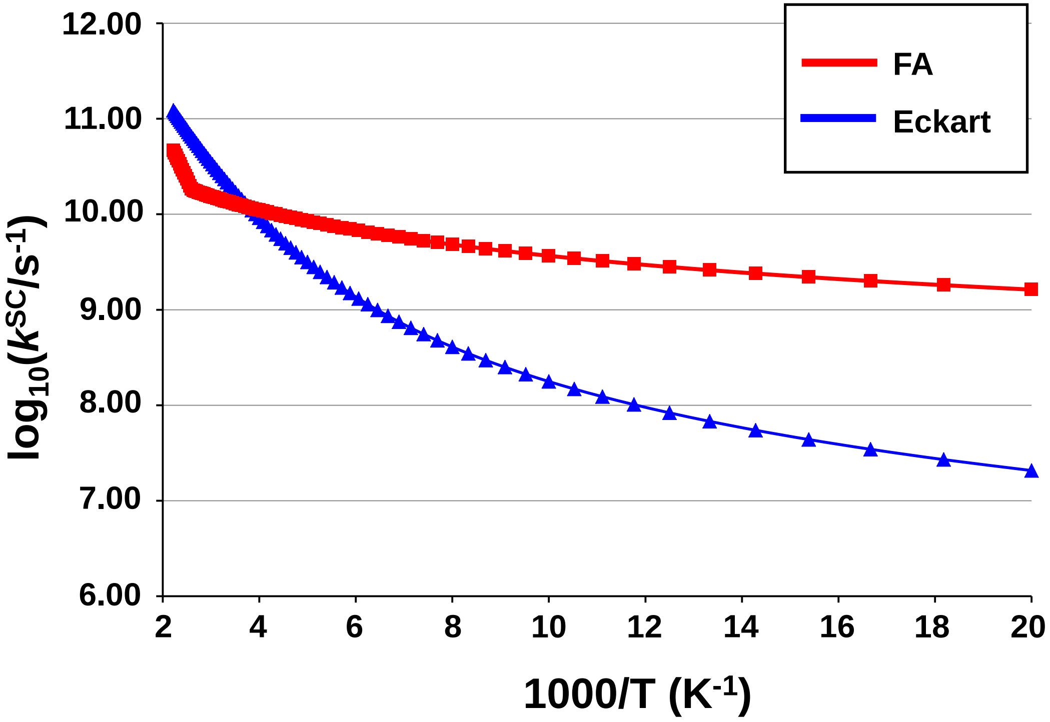
$$\Gamma^{Eckart}(T) = \exp\left(-\frac{\Delta U_0^{\neq}}{RT}\right) \int_0^{\infty} P(E) \exp\left(-\frac{E}{RT}\right) dE$$

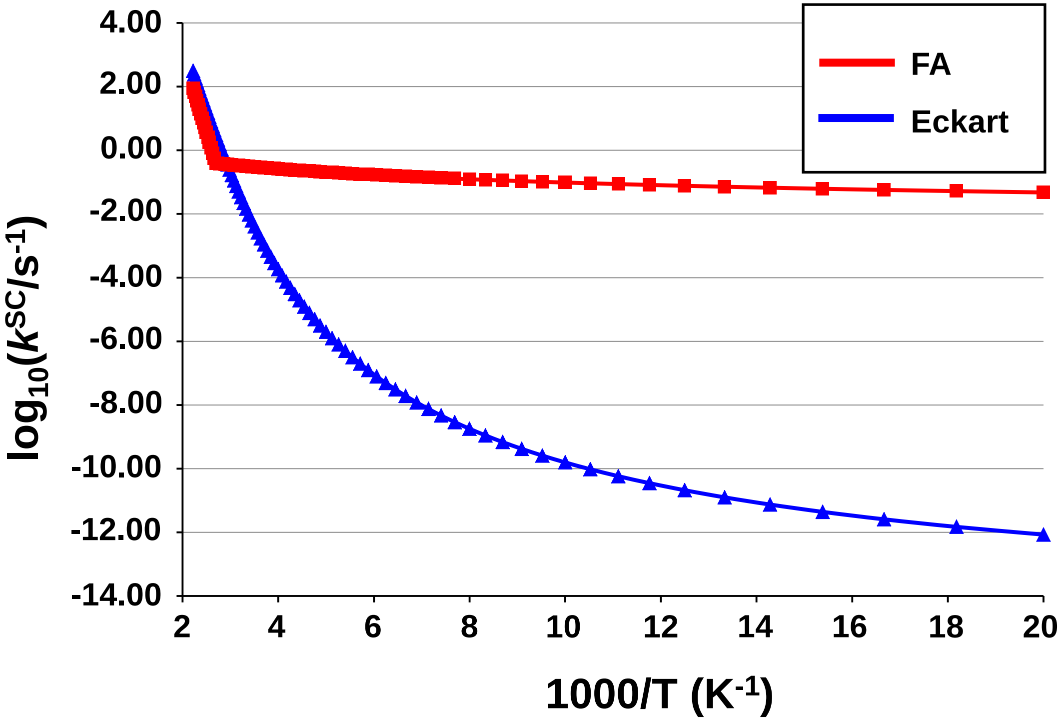


$\Delta U^{\neq}_0$ = 4.2 kcal mol^{-1}

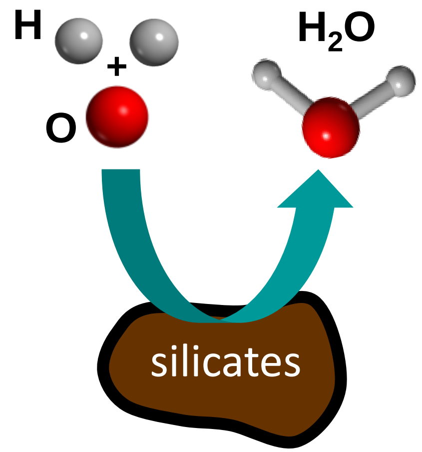


$\Delta U^{\neq}_0$ = 22.3 kcal mol^{-1}





H_2O formation on silicates



Molpeceres et al.,
MNRAS, 2019, 482, 5389

i) $O_{(g)} \rightarrow O_{(surf)}$ (O adsorption)

ii) $H_{(surf)} + O_{(surf)} \rightarrow OH_{(surf)}$ (1st H additon)

iii) $H_{(surf)} + OH_{(surf)} \rightarrow H_2O_{(surf)}$ (2nd H additon)

No catalytic effects

ii) $H_{(g)} + O_{(g)} \rightarrow OH_{(g)}$

iii) $H_{(g)} + OH_{(g)} \rightarrow H_2O_{(g)}$

barrierless processes

Silicate grains as reactant concentrators
+
(probably) third bodies

iCOMs formation on Ices

- **iCOMs**: Interstellar Complex Organic Molecules

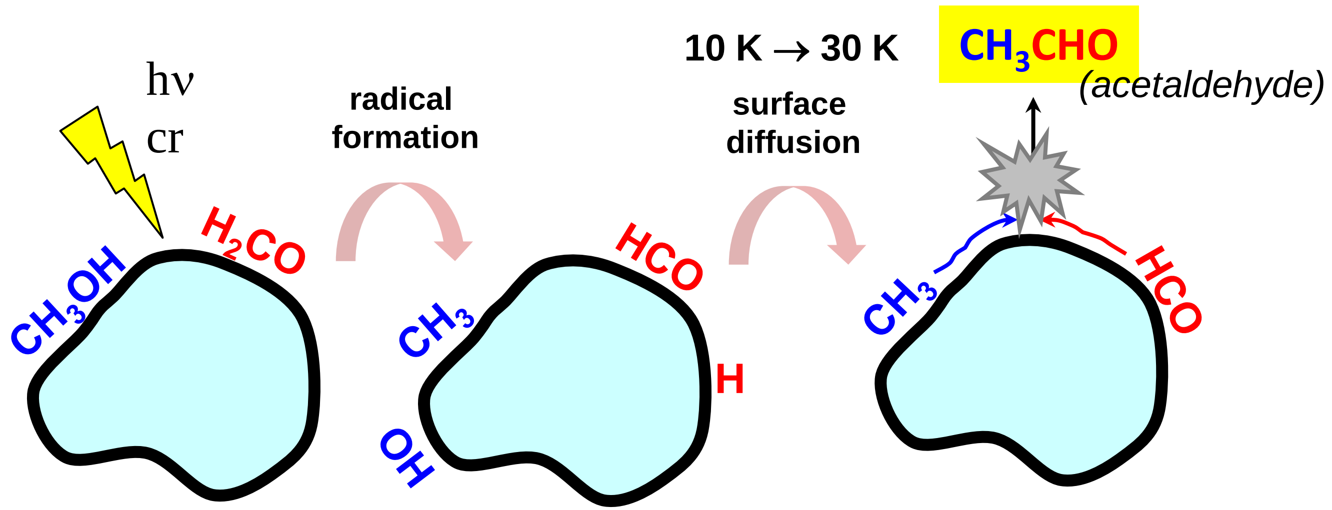
  Molecules with 6 – 12 atoms in which at least one is C

- Prevailing **mechanism** on the **icy grain surfaces:**

  Radical-radical coupling

  (Garrod & Herbst, 2006, A&A, 457, 927)

E.g., **CH_3CHO formation**



Ice grains as reactant suppliers

Considered to be **barrierles** (like in the gas pase). **BUT** on water ice they **exhibit energy barriers**

(it goes against the role of chemical catalyst!)

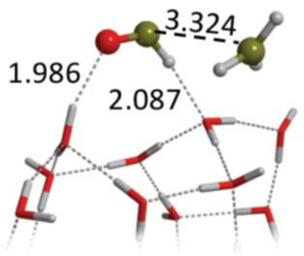
Radical pairs	iCOM formation	ΔE≠ (kJ/mol)
CH_3 + HCO	CH_3CHO	**2–6**
CH_3 + CH_3	CH_3CH_3	**5**
CH_3 + NH_2	CH_3NH_2	**1–2**
CH_3 + CH_3O	CH_3OCH_3	**1–3**
CH_3 + CH_2OH	CH_3CH_2OH	**2–3**
HCO + NH_2	NH_2CHO	**2–4**
HCO + HCO	HCOHCO	**4**
HCO + CH_3O	HC(=O)CH_2OH	**4–5**
HCO + CH_2OH	HC(=O)CH_2OH	**2**
CH_3O + CH_3O	CH_3OOCH_3	**10–20**
CH_2OH + CH_2OH	$CH_2(OH)CH_2OH$	**3–5**

Enrique-Romero et al., Astrophys. J., Suppl. Ser., 259:39 (2022)

CH_3 + HCO

↓

CH_3CHO



Radical/Surface interactions

iCOMs formation on Ices

➢ Limitations of the radical-radical couplings:

- They exhibit **energy barriers**
- Present **competitive reactions**: H-abstractions
  e.g., $CH_3 + HCO \rightarrow CH_4 + CO$
- Delicate **trade-off** between the diffusion and desorption of the radicals (**T window**).

Example: formation of CH_3CH_2OH via **"$\cdot CCH + H_2O_{(ice)}$"**

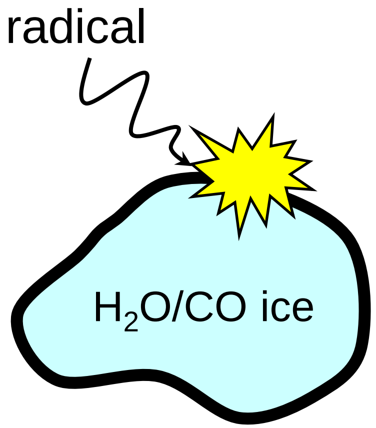
step i): $\cdot CCH + H_2O \rightarrow \cdot CHCHOH$ **(with barrier)**

step ii): $\cdot CHCHOH + \cdot H \rightarrow CH_2CHOH$ **(barrierles)**

step iii): $CH_2CHOH + \cdot H \rightarrow CH_3CHOH$ **(with barrier)**

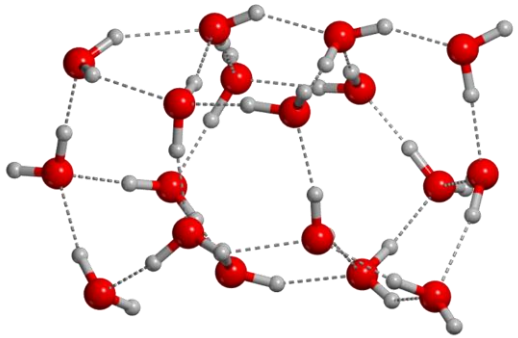
step iv): $\cdot CH_3CHOH + \cdot H \rightarrow CH_3CH_2OH$ **(barrierles)**

➢ Alternative pathway: "radical + ice" reactions



- It **avoids** direct **competitive reactions**
- It **avoids** the **T window**
- It **DOES NOT avoid** the presence of **energy barriers**

Rimola et al., ACS Earth Space Chem., 2, 720 (2018)



- ✓ Cluster model of 18 H_2O (also tested for 33 H_2O)
- ✓ DFT vs CCSD(T) benchmarking study

Perrero et al., ACS Earth Space Chem., 6, 496 (2022)

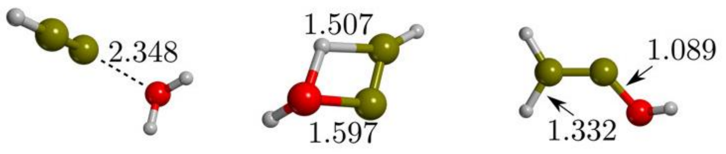
Ices as catalysts? (III). Formation of COMs via "radical + ice" reactions

Example: formation of CH_3CH_2OH via **"·CCH + $H_2O_{(ice)}$"**

ωB97x-D3/6-311++G(d,p)
ZPE-corrected energies (potential energies)
In kJ/mol

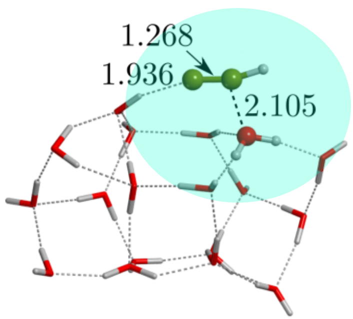
step i): ·CCH + $H_2O \rightarrow$ ·CHCHOH

In the gas phase:

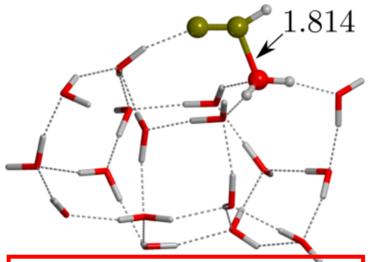


$\Delta E^{\neq}$= 113 kJ/mol
(without ZPE)

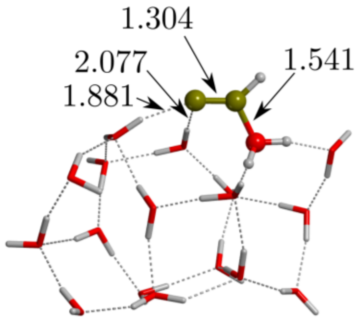
Formation of a hemi-bonded complex



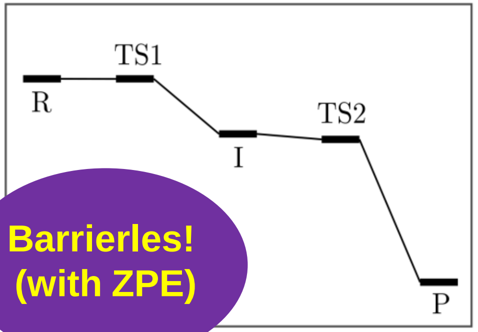
R: 0.0



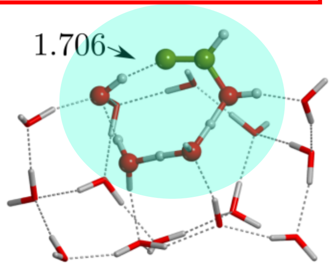
TS1: 0.0 (0.7)



I: -10.5 (-12.5)

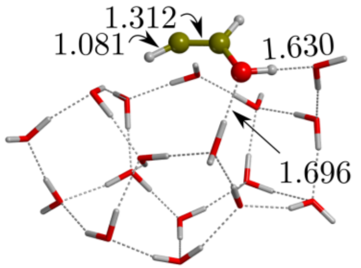


Barrierles!
(with ZPE)



TS2: -10.6 (5.1)

Water-assisted proton transfer

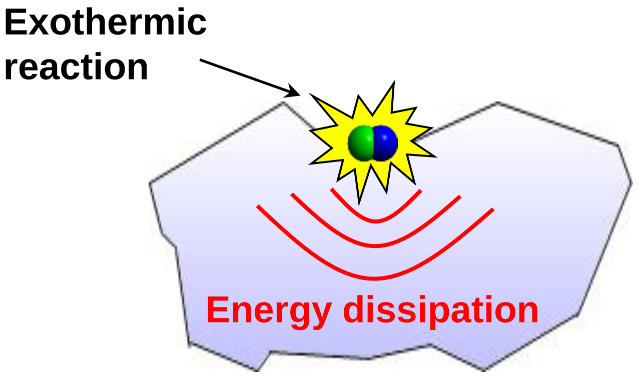


P: -185.5 (-192.3)

Ice grains as:
reactant suppliers
+
chemical catalyts

Perrero et al., ACS Earth Space Chem., 6, 496 (2022)

The third body effect



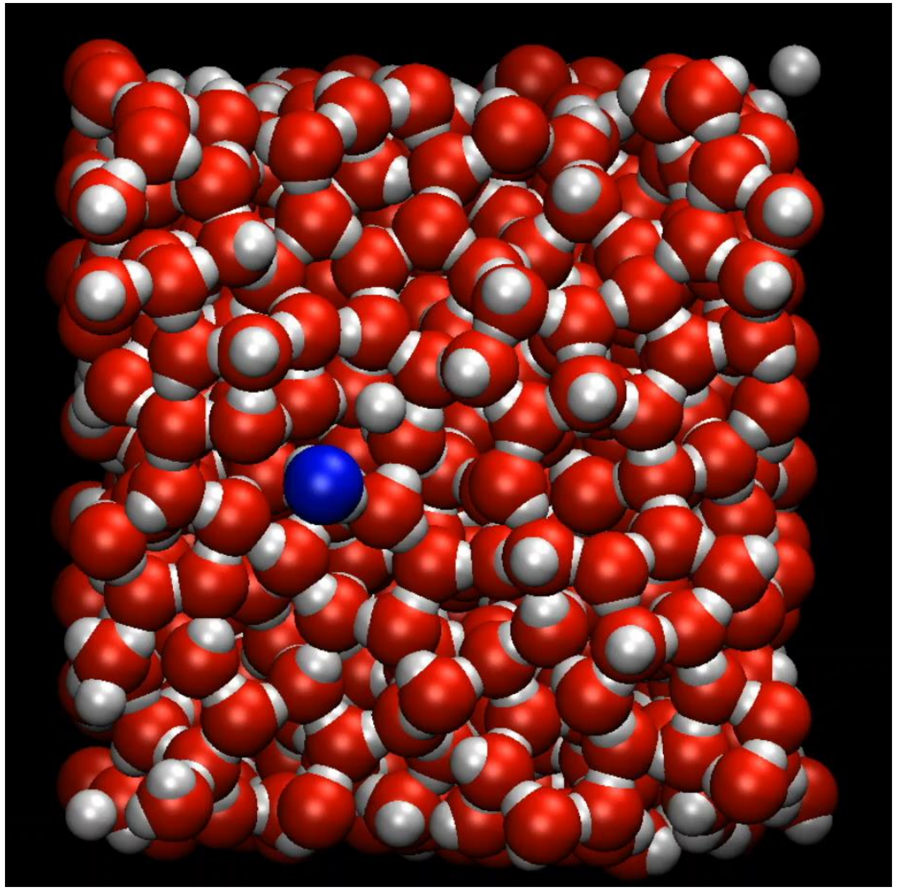
- What is the **fate** of the **nascent reaction energy**?
  - Amount of energy excess **transferred to the grain** (energy dissipation)?
  - Amount of energy excess into **kinetic energy** of the newly formed product?

Ferrero et al., ApJ, 944, 142 (2023)

- Ab Initio Molecular Dynamics (**AIMD**) simulations
- (NVE), microcanonicle ensemble

  The total Energy is conserved

- Case of study: **H + NH_2 → NH_3** on water ice
  - Barrierless reaction & reaction energy ≈-440 kJ/mol
  - Amorphous periodi water ice: 1728 atoms (576)
  - Initial T=10K, time-scale=1ps, time-step=0.2fs
  - DFT PBE-D3/TZVP (CP2K code)

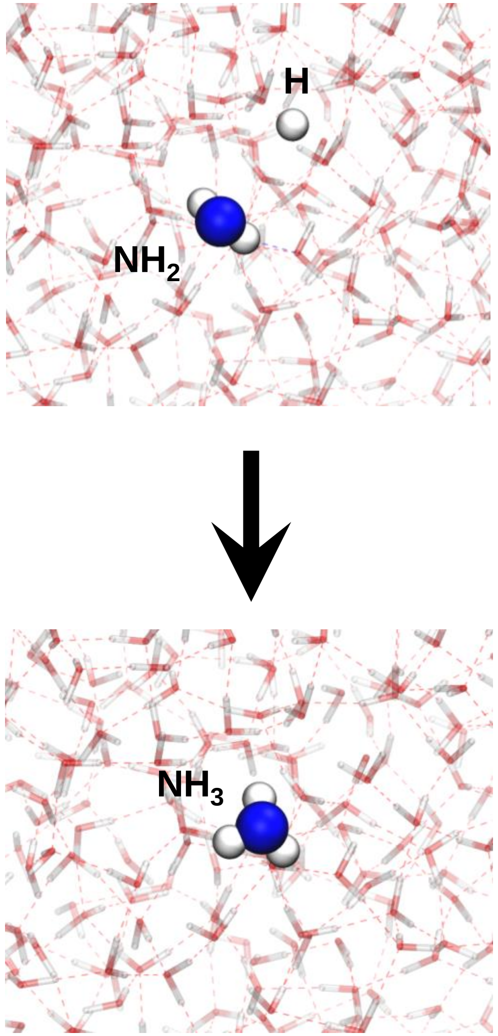


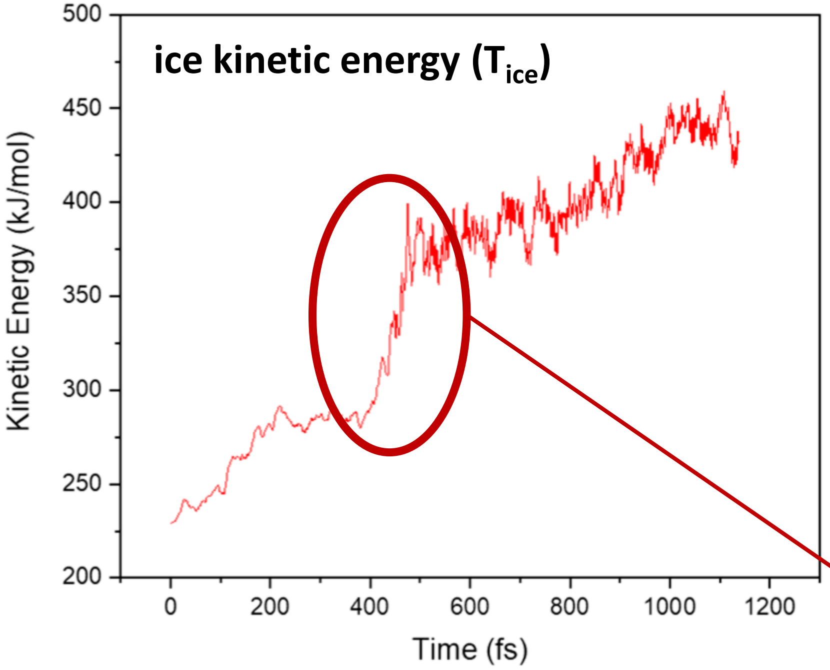
The third body effect

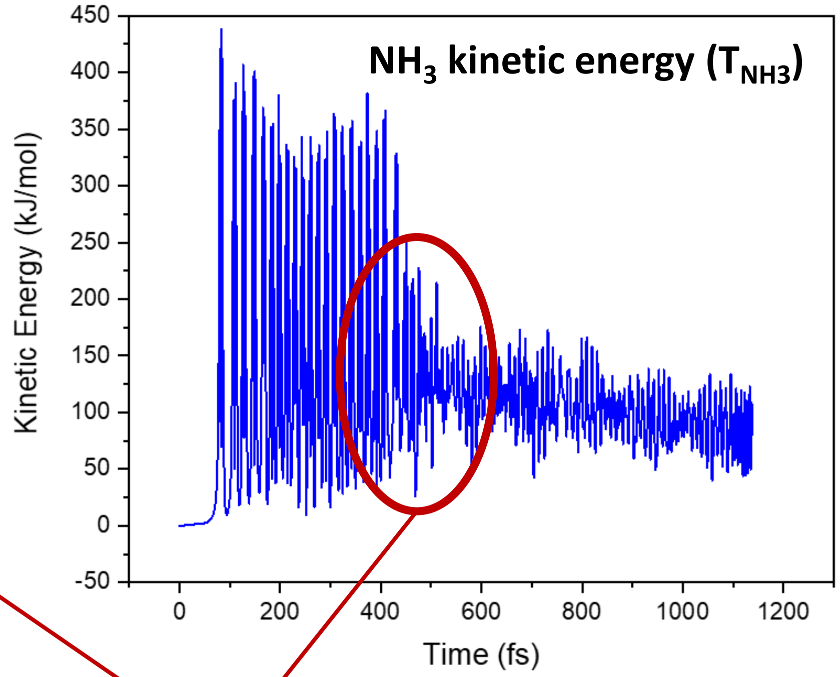
- Analysis of the data: energy **partitioning** and **monitoring**

Ferrero et al., ApJ, 944, 142 (2023)

NH_3 formation on amorphous water ice surface:



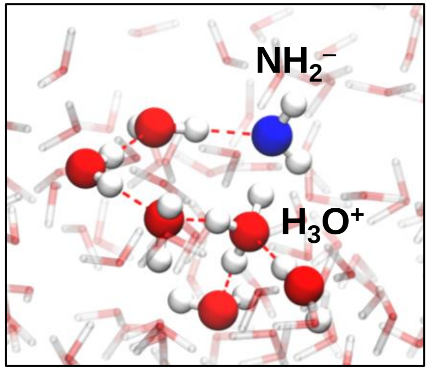




	T_{ice}/T_{TOT}	T_{NH3}/T_{TOT}
H + NH_2	0.73	0.27

- **energy transfer of ≈210 kJ/mol** to the surface
- BE_{NH3} (22.4) << T_{NH3} (5.2)

NH_3 do not leave the surface



Formation of a transient **NH_2^-/H_3O^+** ion pair

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