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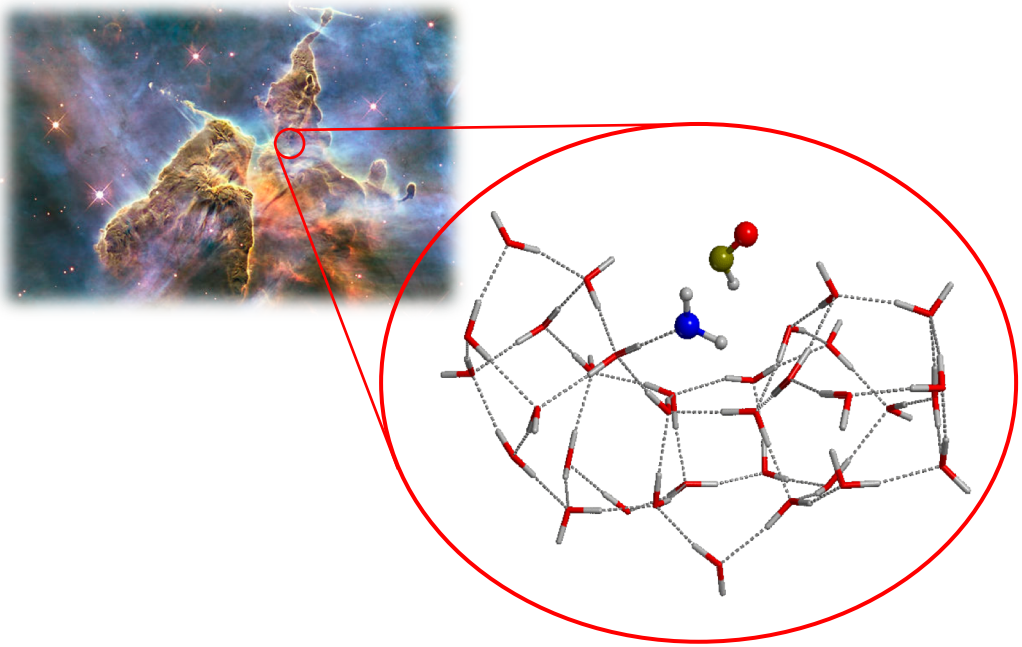

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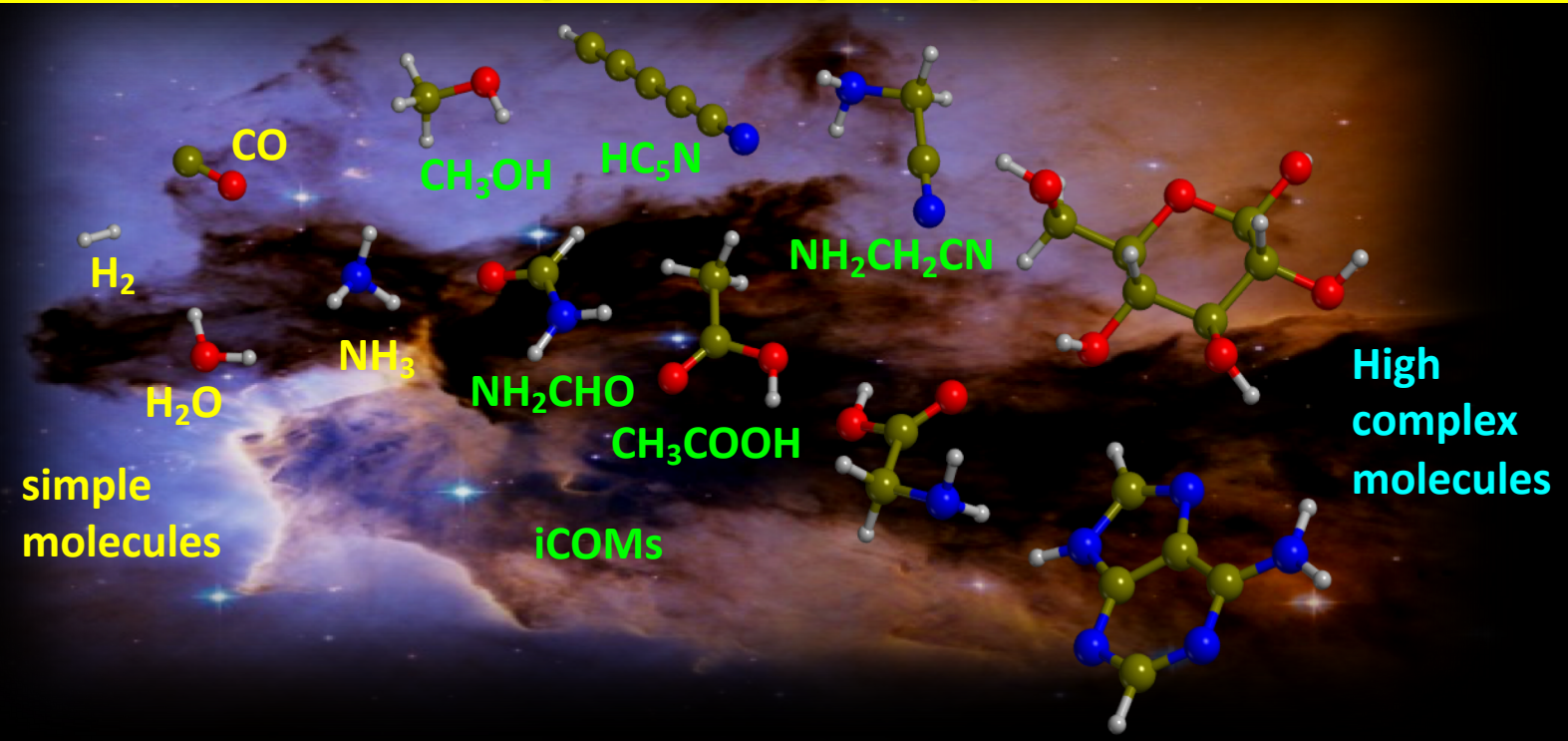
Celebrating the first 40 years of

Alexander Tielens' contribution to science:

The Physics and Chemistry of the Interstellar Medium

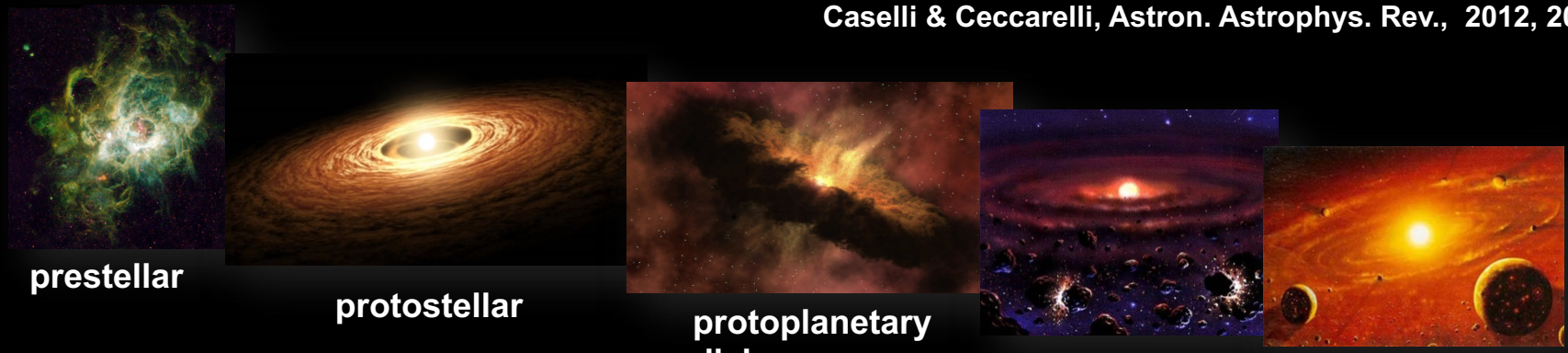
2 – 6 September 2019, Avignon

Molecular Diversity and Complexity in the Universe

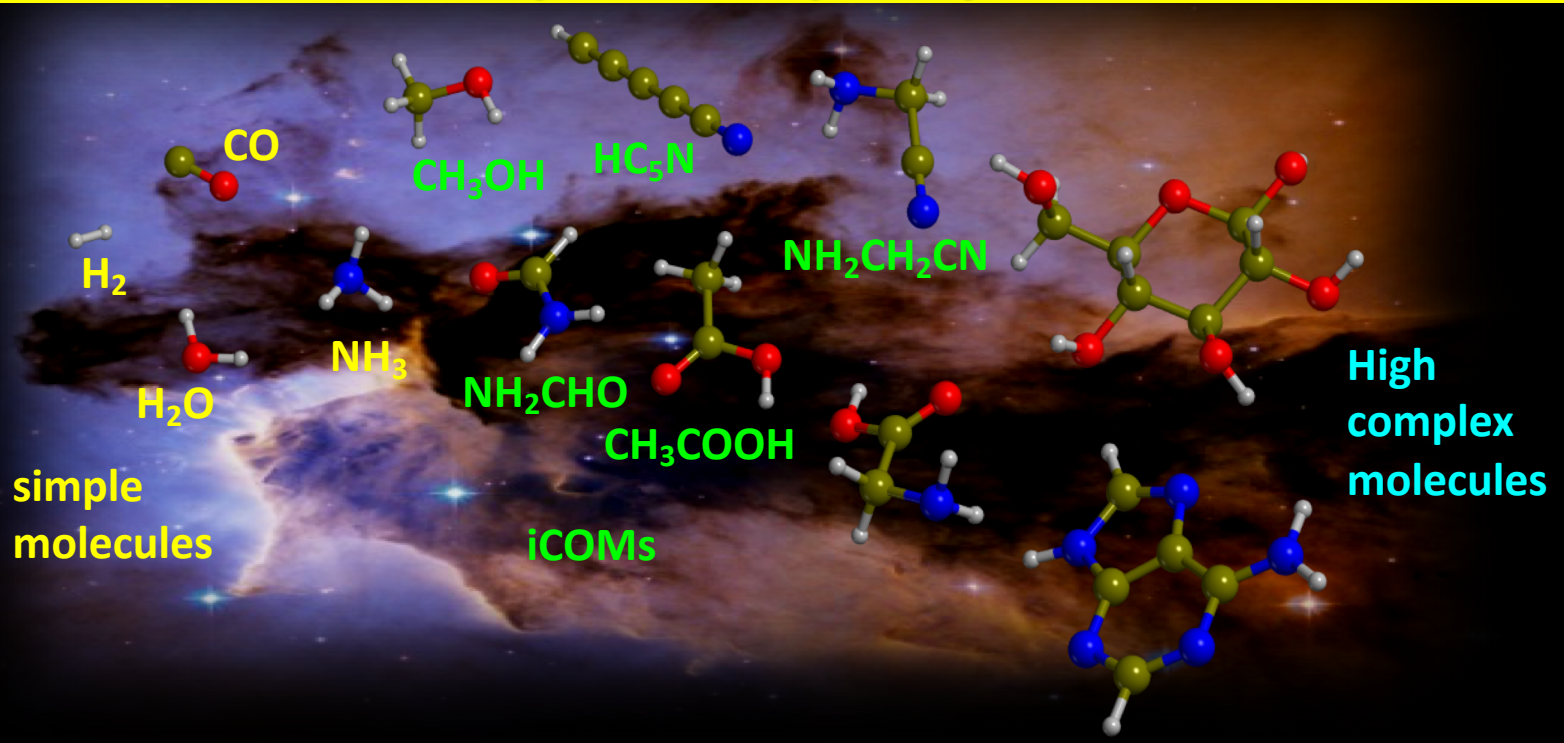


Evolution of the molecular complexity goes hand-in-hand with the physical phases involved in the formation of Solar-type planetary systems

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



Molecular Diversity and Complexity in the Universe



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

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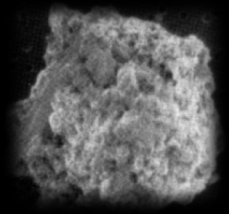
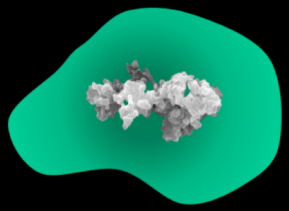
Need of GRAINS



dust particles



Ice mantles

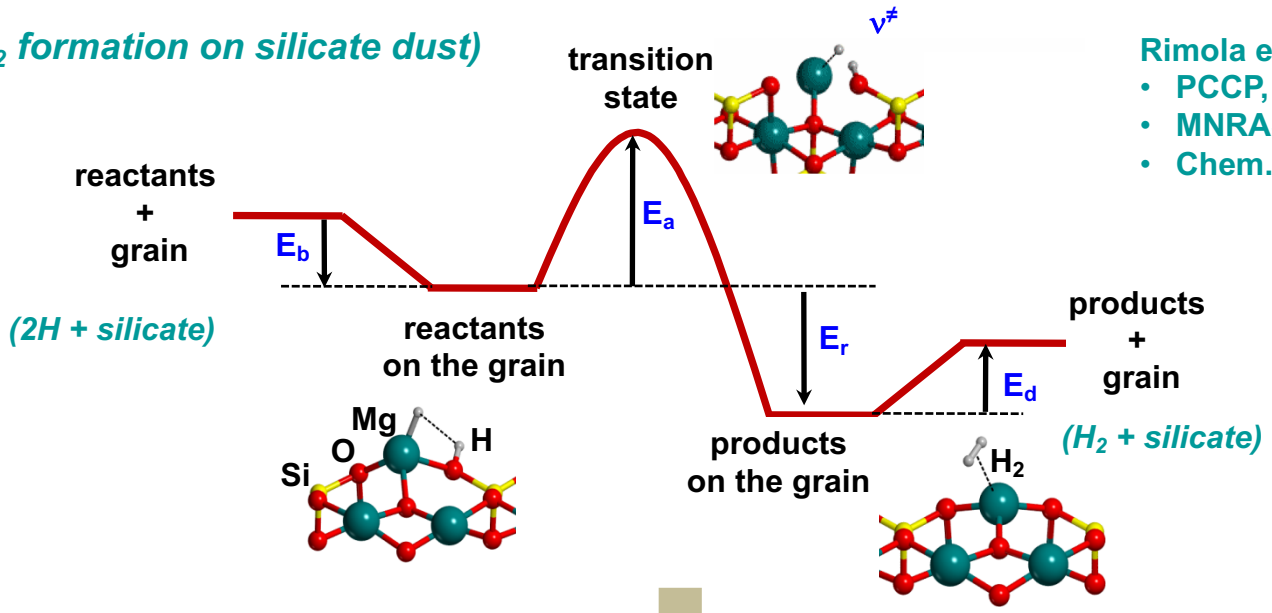
Synthetic reaction channels?

Role of grains?

Quantum Chemical Simulations

A Utility of Quantum Chemical Simulations: Characterization of Potential Energy Surfaces (PES)

(Ex: H_2 formation on silicate dust)



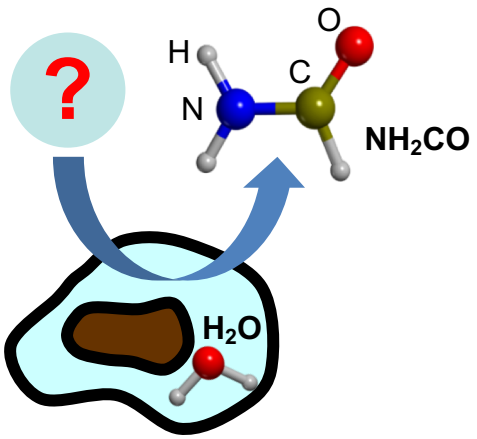
Rimola et al.
- PCCP, 2014, 16, 17447
- MNRAS, 2015, 453, 914
- Chem. Comm, 2016,52, 6873

Elucidation of Reaction Mechanisms

Quantum Chemical Simulations = Interpretation + Prediction

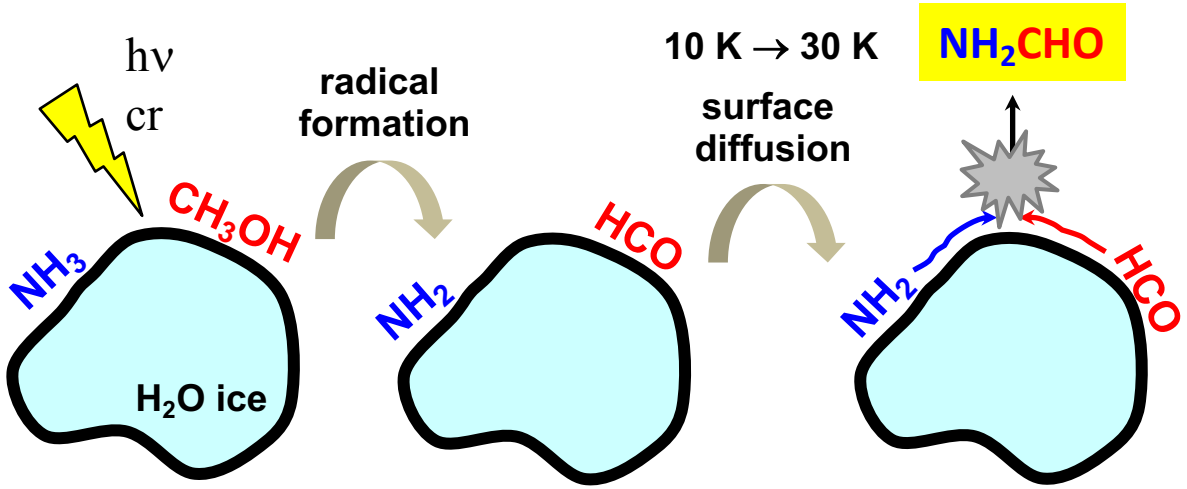
Quantum chemistry computations as an interpretative and predictive tool for grain-induced astrochemical processes. The formamide formation case.

NH_2CHO formation on **H_2O-dominated Ices**



Rimola et al.
ACS Earth and Space Chemistry, 2018, 2 (7), 720 – 734.

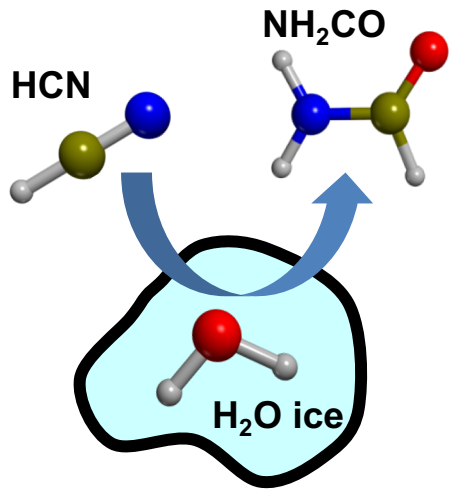
According to the iCOMs "on-surface" paradigm formation



- Garrod, et al., ApJ, 2008, 682, 283
- Öberg, Chem. Rev. 2016, 116, 9631-9663.

$NH_2 + HCO \rightarrow NH_2CHO$

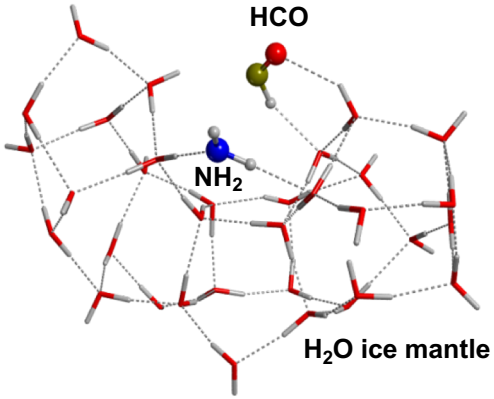
New syntehtic route



$HCN + H_2O \rightarrow NH_2CHO$

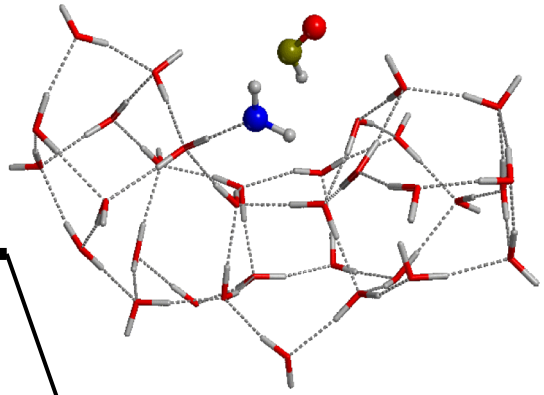
Formamide Formation: NH_2 + HCO reaction

BHLYP/6-311++G(d,p)
Potential Energy Surface (PES) including zero-point energy (ZPE) corrections
Energy units in kJ/mol (1 kJ/mol ≈ 120 K)

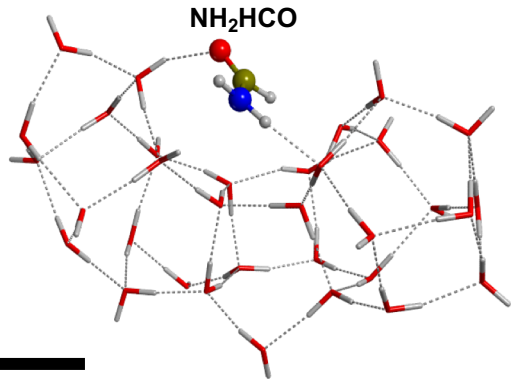


0.0

Transition State:
transition frequency in motion



2.6



-388.0

Product (formamide)

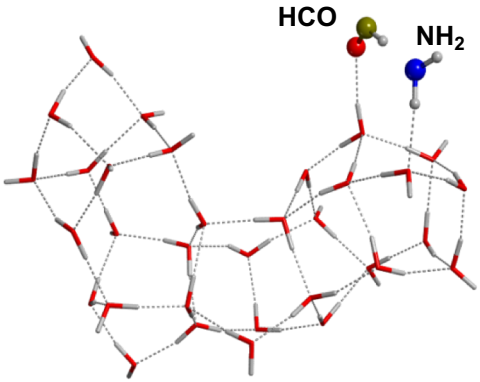
Reactant:
biradical system (singlet) is stable
- Spin on NH_2: +1/2
- Spin on HCO: -1/2

$$NH_{2(on\ ice)} + HCO_{(on\ ice)} \rightarrow NH_2CHO_{(on\ ice)}$$

Quantum Chemistry as an Interpretative tool

Formamide Formation: NH_2 + HCO reaction

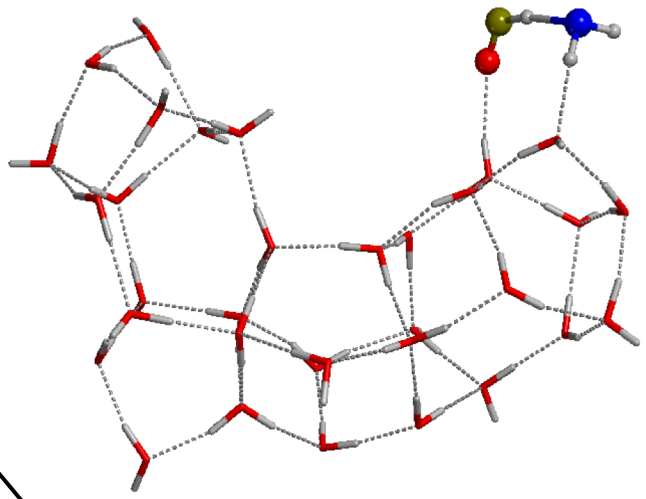
BHLYP/6-311++G(d,p)
Potential Energy Surface (PES) including zero-point energy (ZPE) corrections
Energy units in kJ/mol (1 kJ/mol ≈ 120 K)



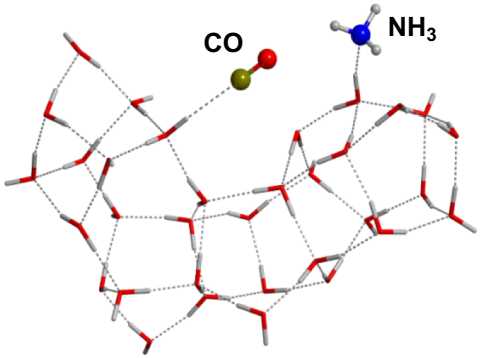
Reactant
Only the triplet state is stable
- **Spin on NH_2: +1/2**
- **Spin on HCO: +1/2**

0.0

Triplet → Singlet



-342.8



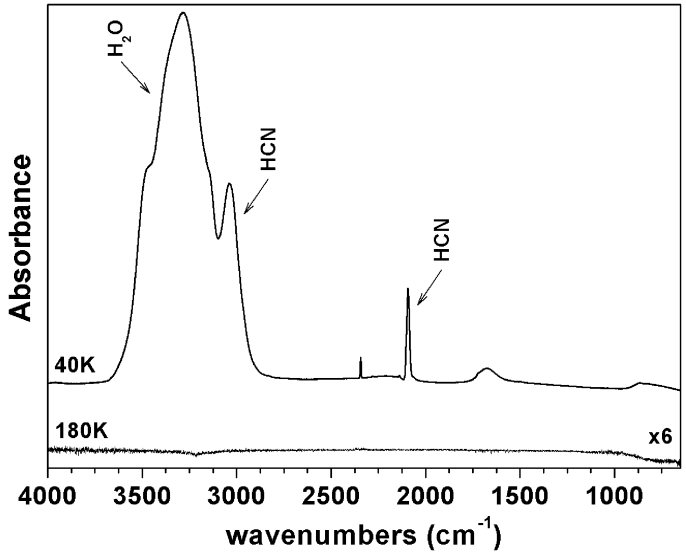
$NH_{2(on\ ice)} + HCO_{(on\ ice)}$

$NH_2CHO_{(on\ ice)}$

$NH_{3(on\ ice)} + CO_{(on\ ice)}$

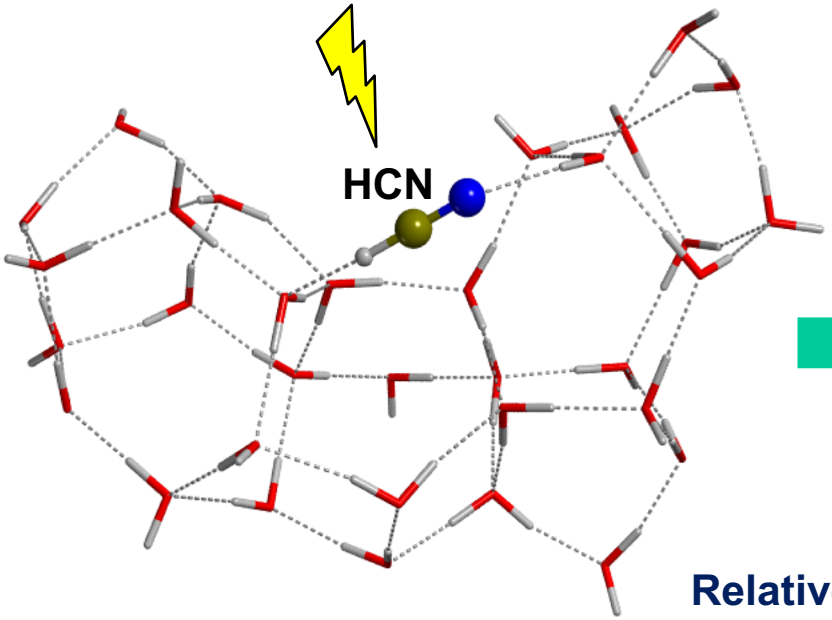
Quantum Chemistry as an Interpretative + Predictive tool

Formamide Formation. HCN + H_2O



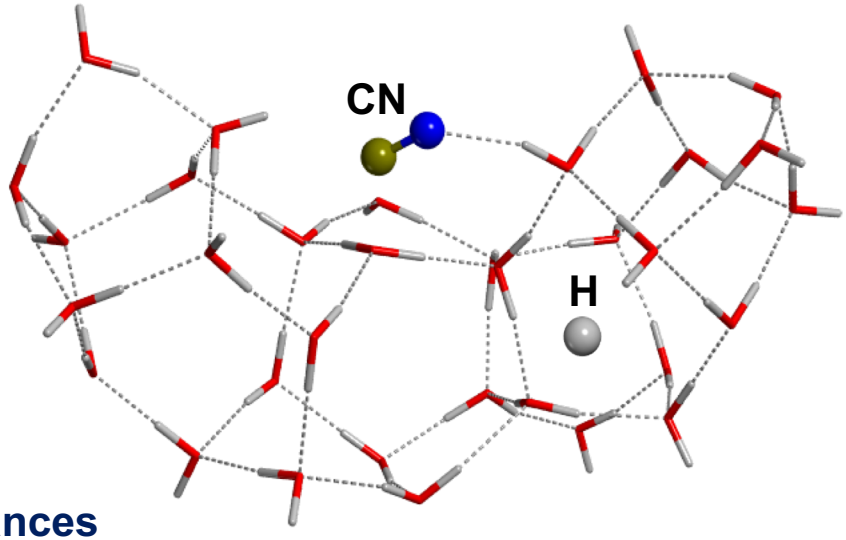
- **Ice mixture of H_2O:HCN**
- **Progressive warm: 40 K → 180 K**
- **No reaction between H_2O and HCN:** desorption of the ice components before reactivity

Danger et al., PCCP, 16, 3360 (2014)



$HCN/H_2 \approx 2\times10^{-8}$

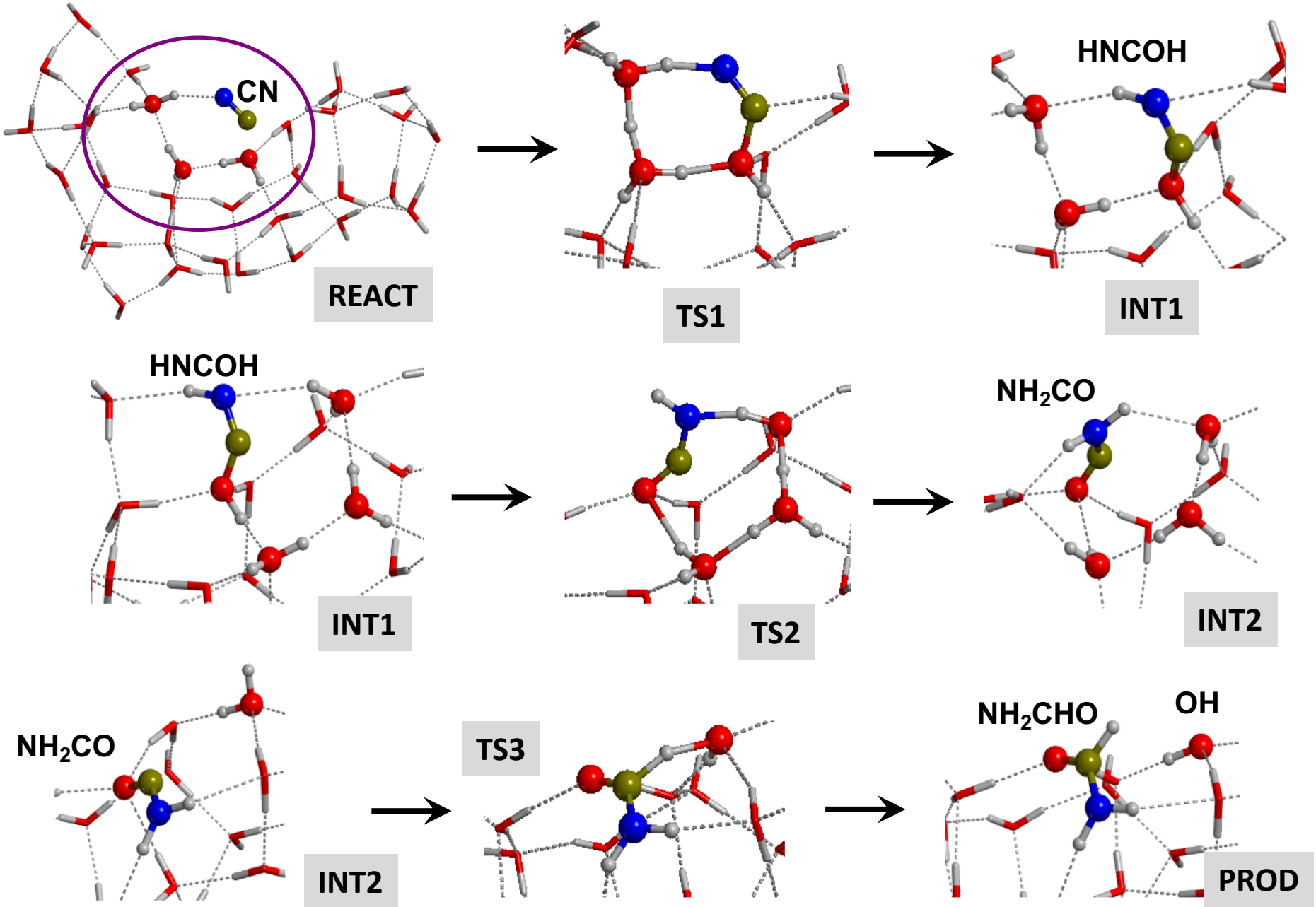
Relative abundances in molecular clouds



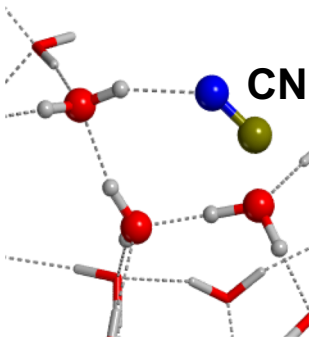
$CN/H_2 \approx 3\times10^{-10}$

(Tielens, Rev. Modern Phys., 2013, 85, 1021)

Formamide Formation. CN + H_2O . Mechanistic Proposal



Formamide Formation. CN + H_2O . Energy Profile



REACT

0.0

16.0

TS1

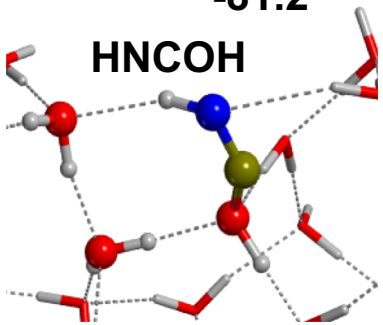
16.0

-81.2

TS2

-74.8

6.4



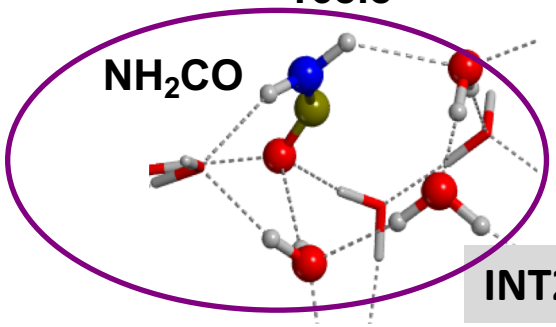
INT1

TS3

-57.2

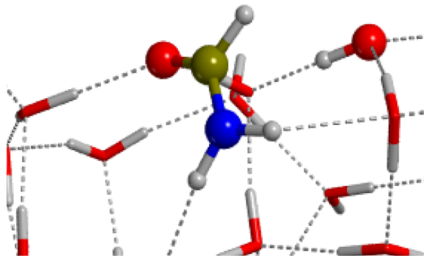
111.6

-168.8



INT2

-100.5

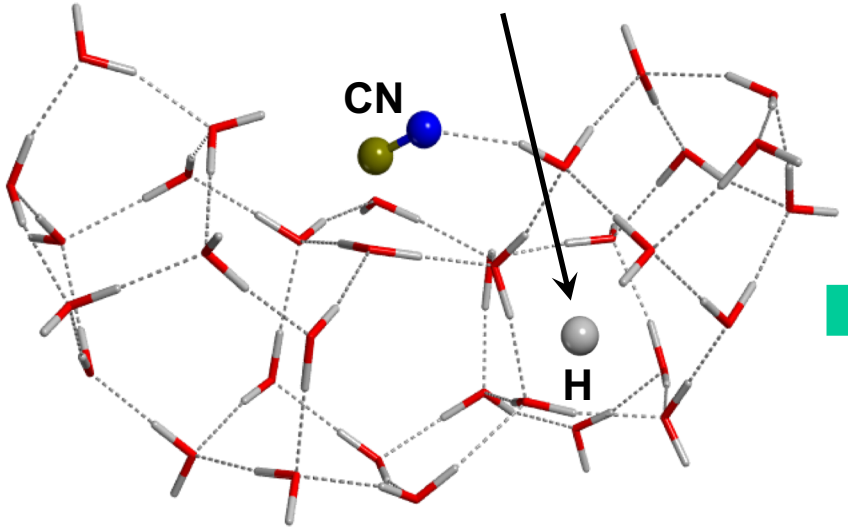


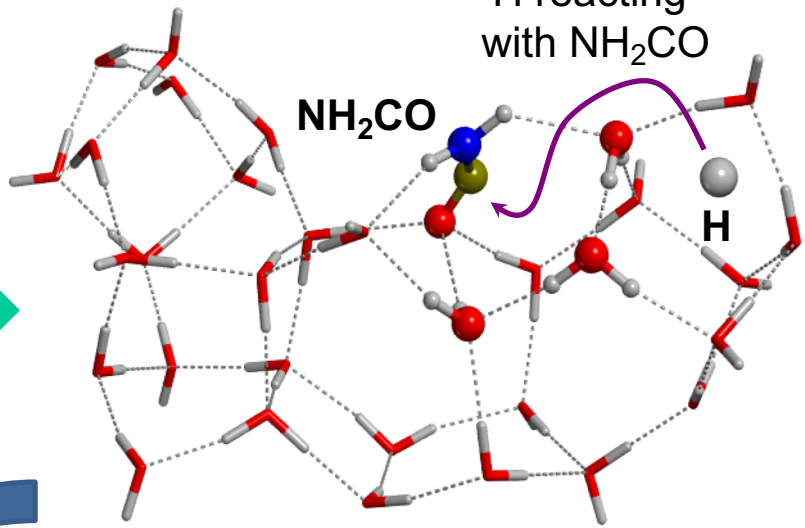
PROD

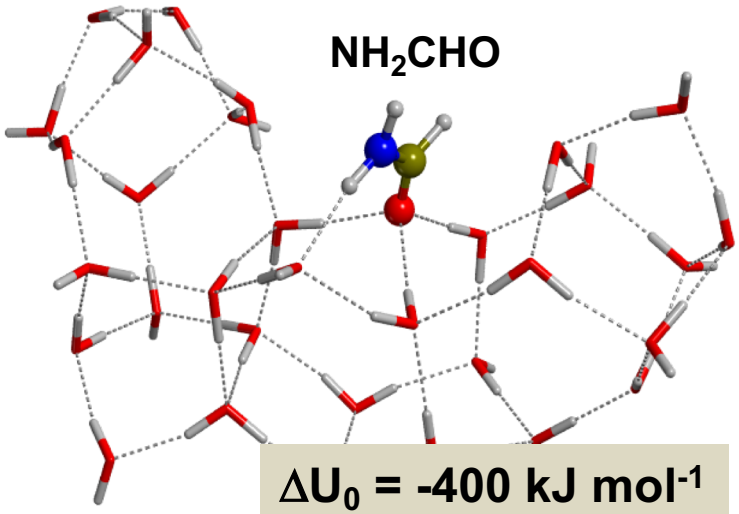
BHLYP/6-311++G(d,p)
PES including ZPE corrections
Energy units in kJ/mol
(1 kJ/mol ≈ 120 K)

Formamide Formation. CN + H_2O . Final Step

H diffuses and remains trapped in the ice







$HCN \rightarrow H + CN$

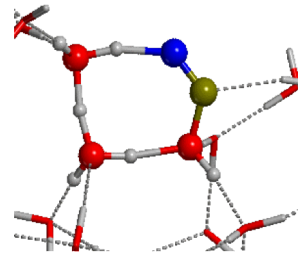
$CN_{(on\ ice)} + H_2O_{(of\ ice)} \rightarrow NH_2CO_{(on\ ice)}$

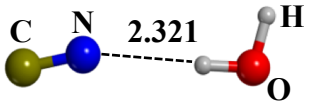
$NH_2CO_{(on\ ice)} + H \rightarrow NH_2CHO_{(on\ ice)}$

Quantum Chemistry as a Predictive tool

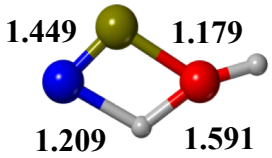
ΔU_0 = -400 kJ mol^{-1}

Formamide Formation. CN + H_2O . Water as Catalyst





PREREACT

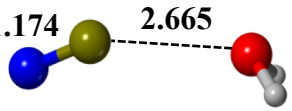


TS1

0.0

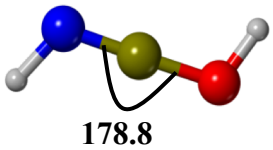
178.4

-3.6



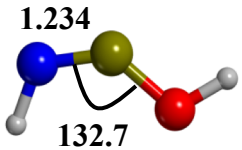
REACT

-107.4



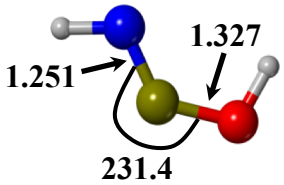
TS2

28.3



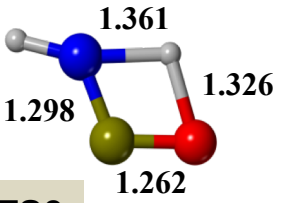
INT1

-130.3



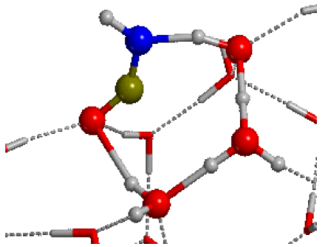
INT2

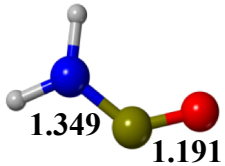
81.1



TS3

-213.7





PROD

BHLYP/6-311++G(d,p)
PES including ZPE corrections
Energy units in kJ/mol
(1 kJ/mol ≈ 120 K)

Conclusions

Take home message

- Quantum chemistry has great potentialities to be used as both an **interpretative** and a **predictive** tool in Astrochemistry

NH_2CHO Formation:

- NH_2 + HCO reaction on H_2O water ice mantles: NH_2CHO vs NH_3+CO. Importance of the relative orientation of the initial reactants.
- Dissociation of HCN and subsequent reaction of CN with H_2O ice can be a plausible grain surface reaction for NH_2CHO formation.
- Dual role of H_2O ice: **reactant** and **catalyst**

Acknowledgements

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Scuola Normale Superiore di Pisa

Catalan Supercomputer Center

Supercomputer time

2017SGR-1323
Catalan Government

Ramón y Cajal contract
CTQ2017-89132-P
Spanish Government

Funding organisms

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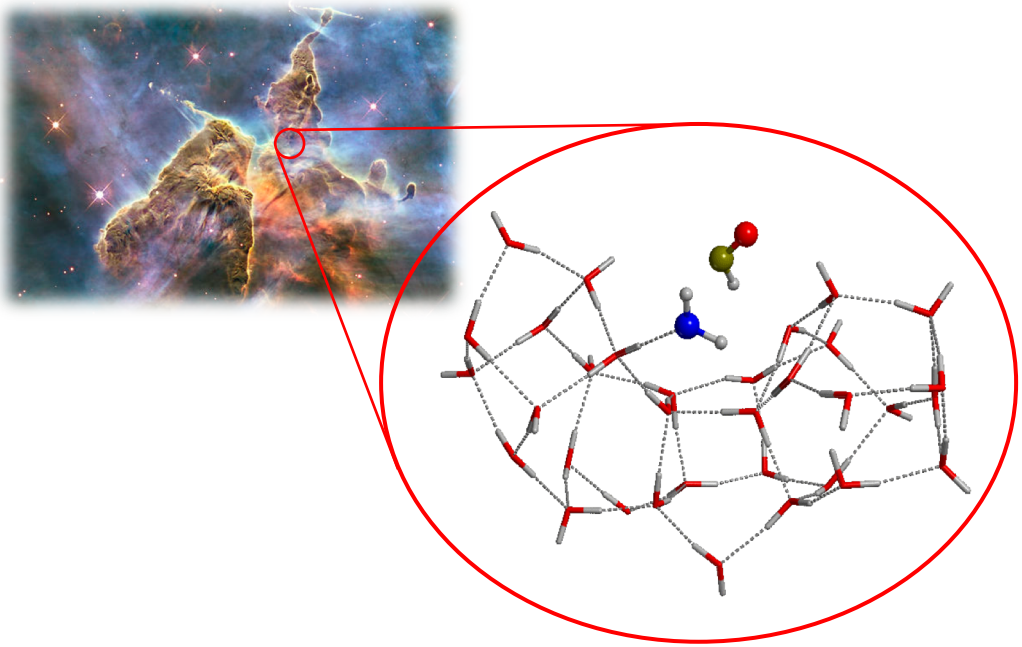

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2 – 6 September 2019, Avignon