# Diffusion-limited Reactivity in water ice

GHESQUIERE Pierre

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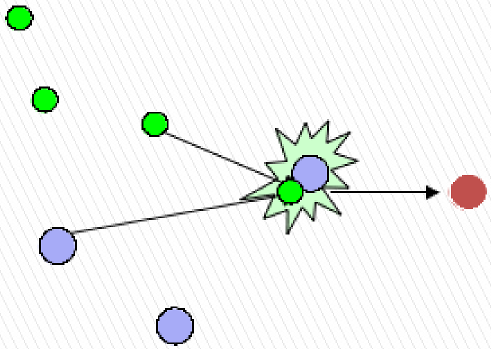
# INTRODUCTION

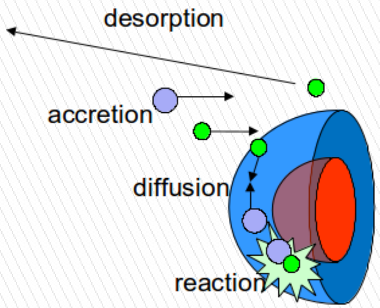
- Interstellar clouds

Star-forming regions T~100K

- Gas-phase reactions



- Interstellar ices
  - Solid-state reactions




- Chemistry induced by :
  - Thermal effects
  - Irradiation
  - Electrons…

Not sufficient

Good scenario for complex chemistry

# INTRODUCTION

Solide state chemistry :

- Reactivity

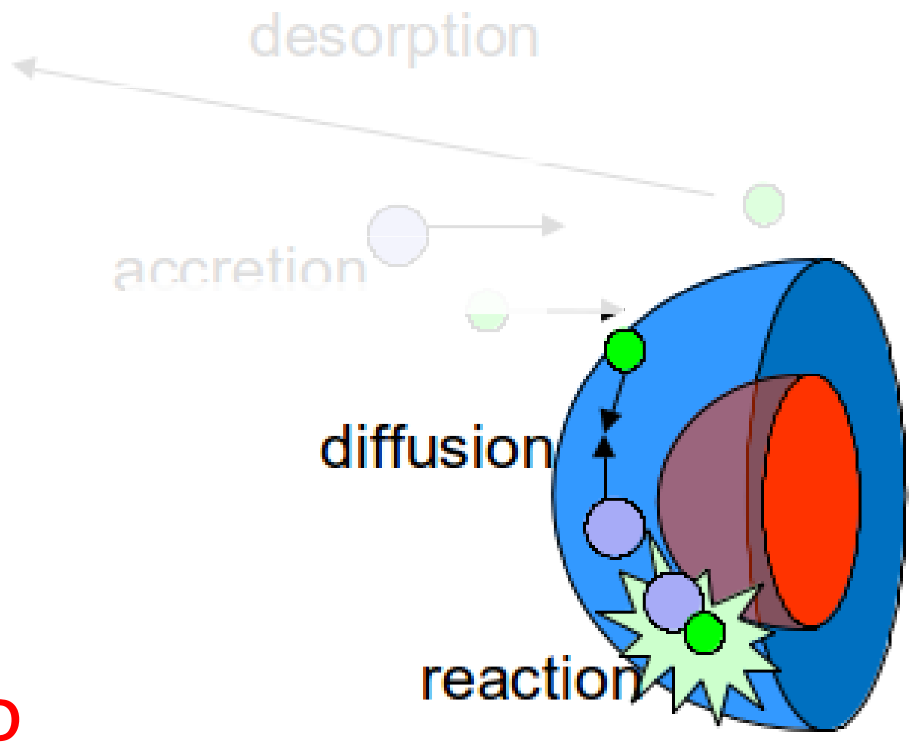
$$\frac{d[X]}{dt} = -k[X][Y]$$

  - **Rate constant k**

- Diffusion

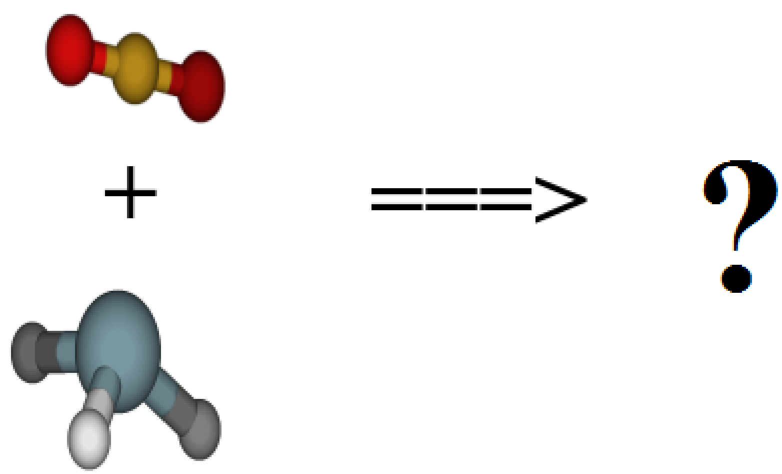
$$\frac{d[X]}{dt} = D\frac{d^2[X]}{dx^2}$$

  - **Diffusion Coefficient D**



# INTRODUCTION

- Coupled Theoretical and Experimental study :
  Reaction between $CO_2$ and $NH_3$ in the bulk of a low density amorphous (LDA) ice for T in [90–150K]



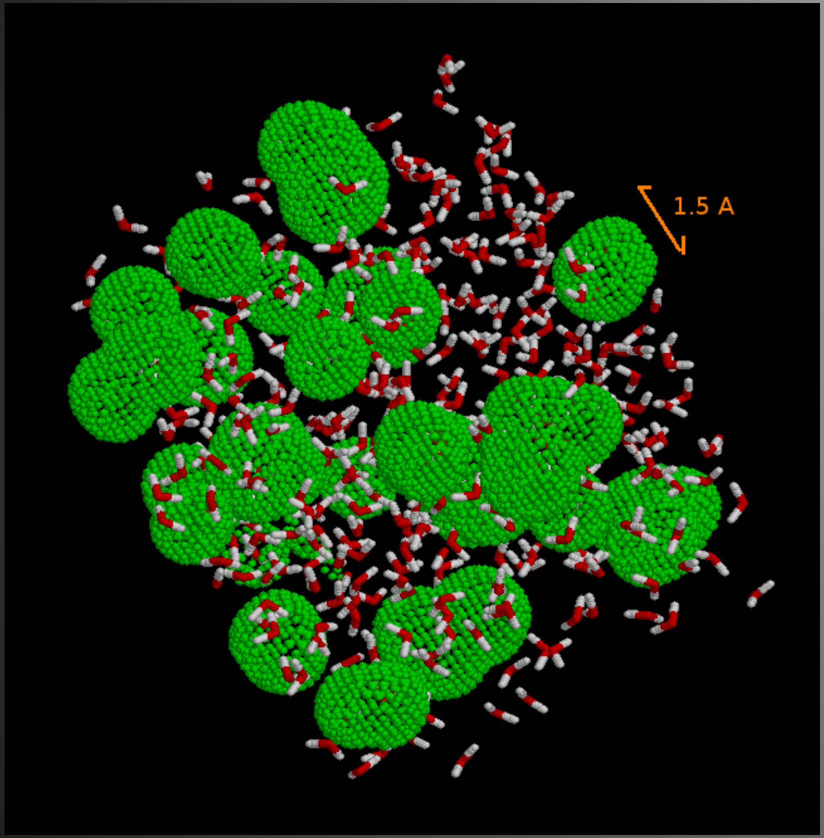
# DIFFUSION IN A LOW DENSITY AMORPHOUS ICES

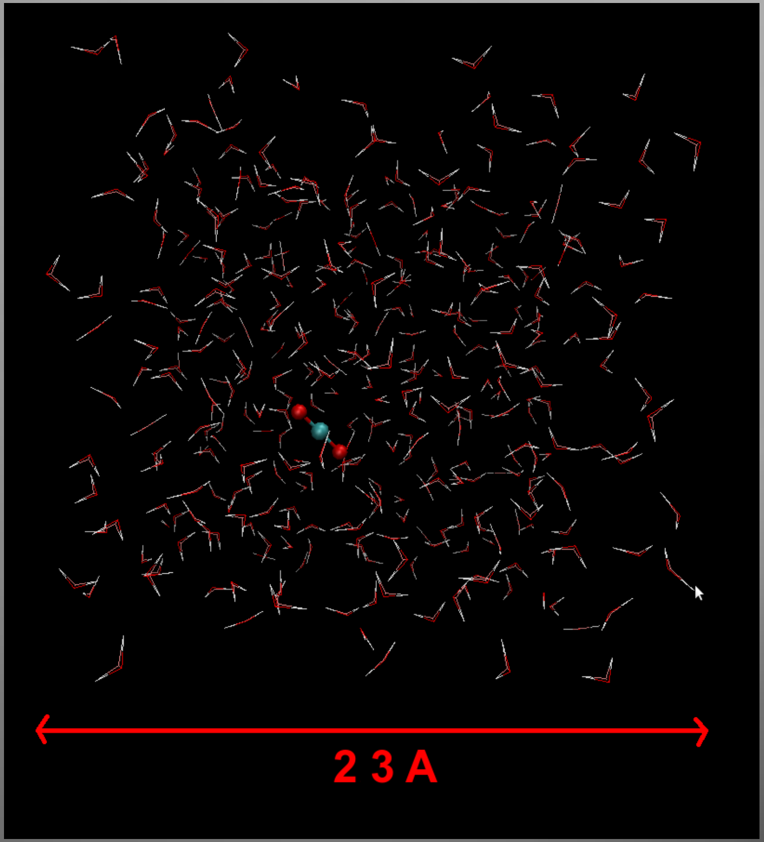
- A theoretical and experimental study

$$\frac{d[X]}{dt} = D\frac{d^2[X]}{dx^2}$$

# DIFFUSION IN AMORPHOUS ICES

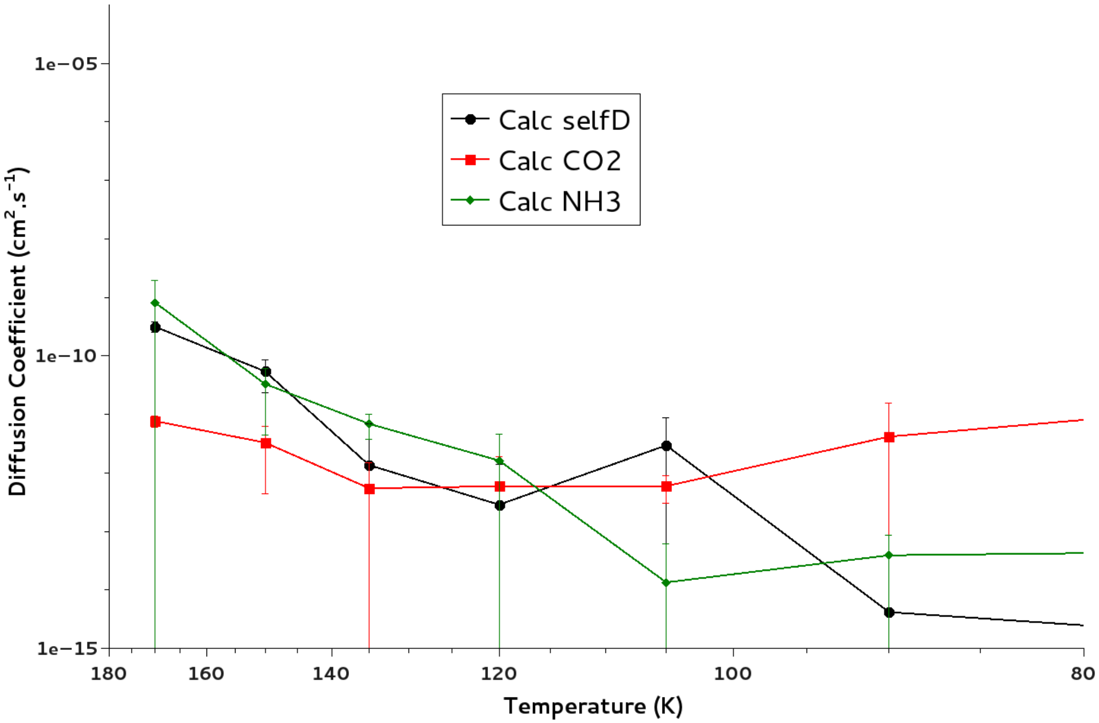
## Theoretical Approach




Modelisation of compact low-density amorphous (LDA) ice :
<u>no pores</u> and no phase transition 90K-170K

# DIFFUSION IN AMORPHOUS ICES
## Theoretical results




- Classical molecular dynamics trajectories of 5 µs [90K;170K]

$$\lim_{t \to \infty} \left\| r(t) - r(0) \right\|^2 = 6Dt$$

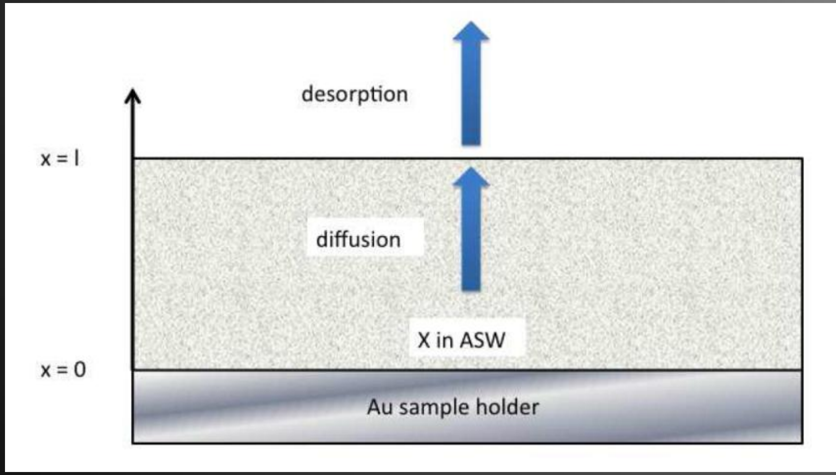
- Arrhenius fit

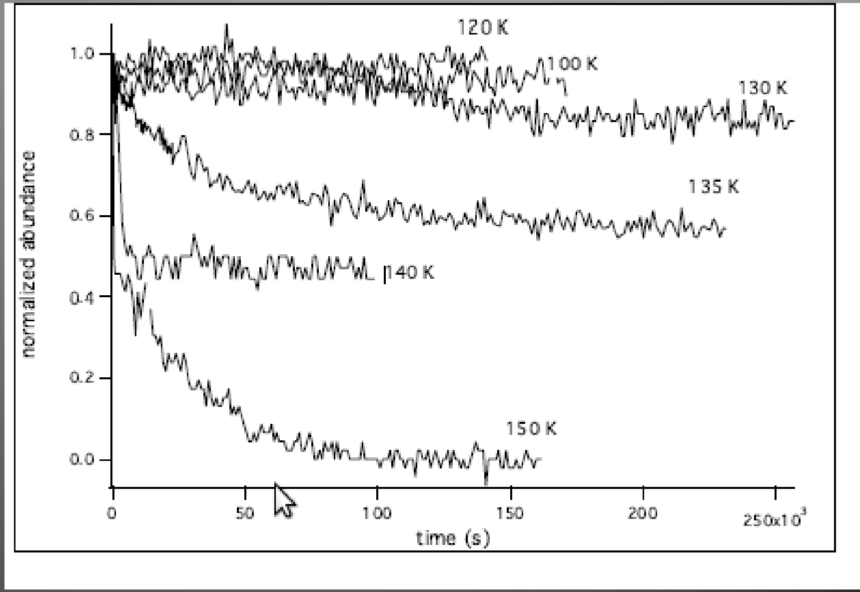
$$D = D_0 * \exp^{-\frac{E_a}{RT}}$$

- Diffusion following water self-diffusion
- Diffusion barrier of **10 – 20 kJ/mol** for $H_2O$, $CO_2$ and $NH_3$
- D for $H_2O$, $CO_2$ and $NH_3$ at 120K of the order of **$10^{-12}$ $cm^2s^{-1}$**
- Suggestion for **interstitial mechanism**

# DIFFUSION IN AMORPHOUS ICES
## Experimental approach

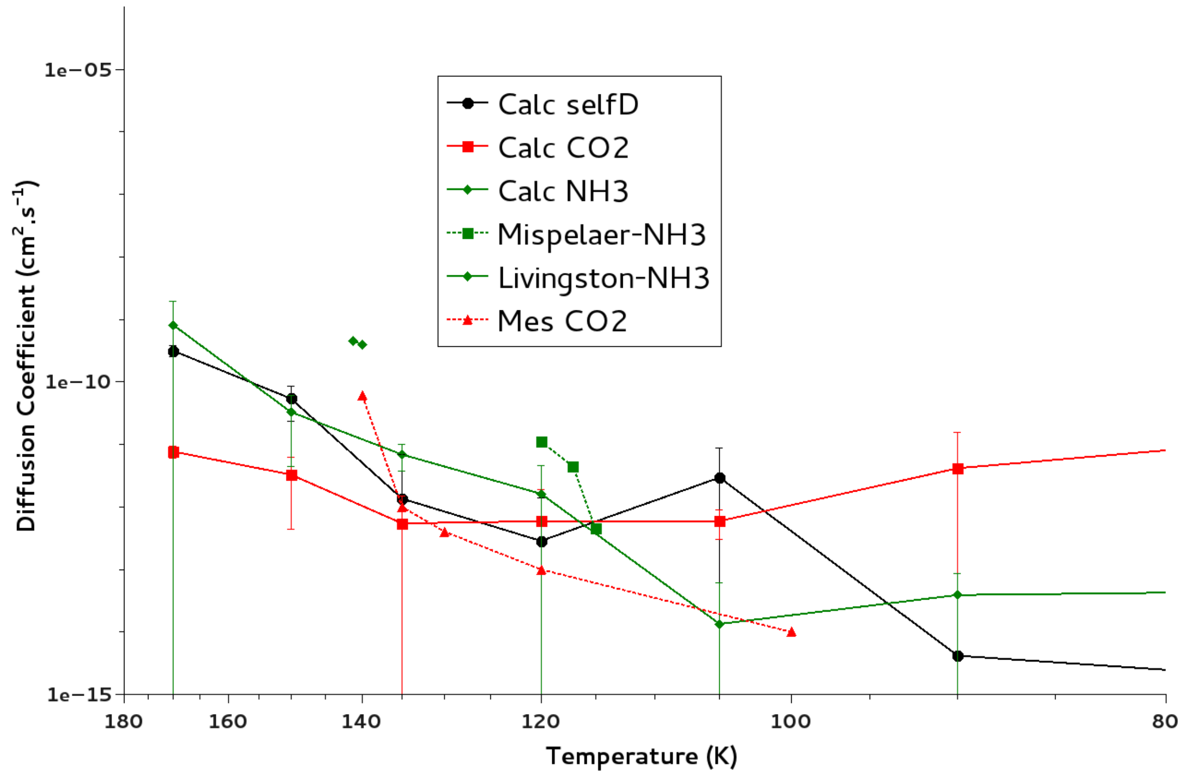
- Vapor Deposition of compact ices mixtures
- Isothermal Experiments at $T > T_{S\ desorption}$
- Analysis by IR spectroscopy
- Decay curve ajusted with Fick's law



# DIFFUSION IN AMORPHOUS ICES

## Theoretical and experimental results




- Good agreement between experiments and theory
- Measured diffusion barrier of **22 kJ/mol** for $CO_2$ **66 kJ/mol** for $NH_3$
- D $CO_2$ , $NH_3$ at 120K of the order of **$10^{-13}$ cm$^2$s$^{-1}$**

**Validates the use of MD simulations to compute diffusion coefficient at T 90K-170K**

# REACTIVITY IN AMORPHOUS ICES

- A theoretical and experimental approach

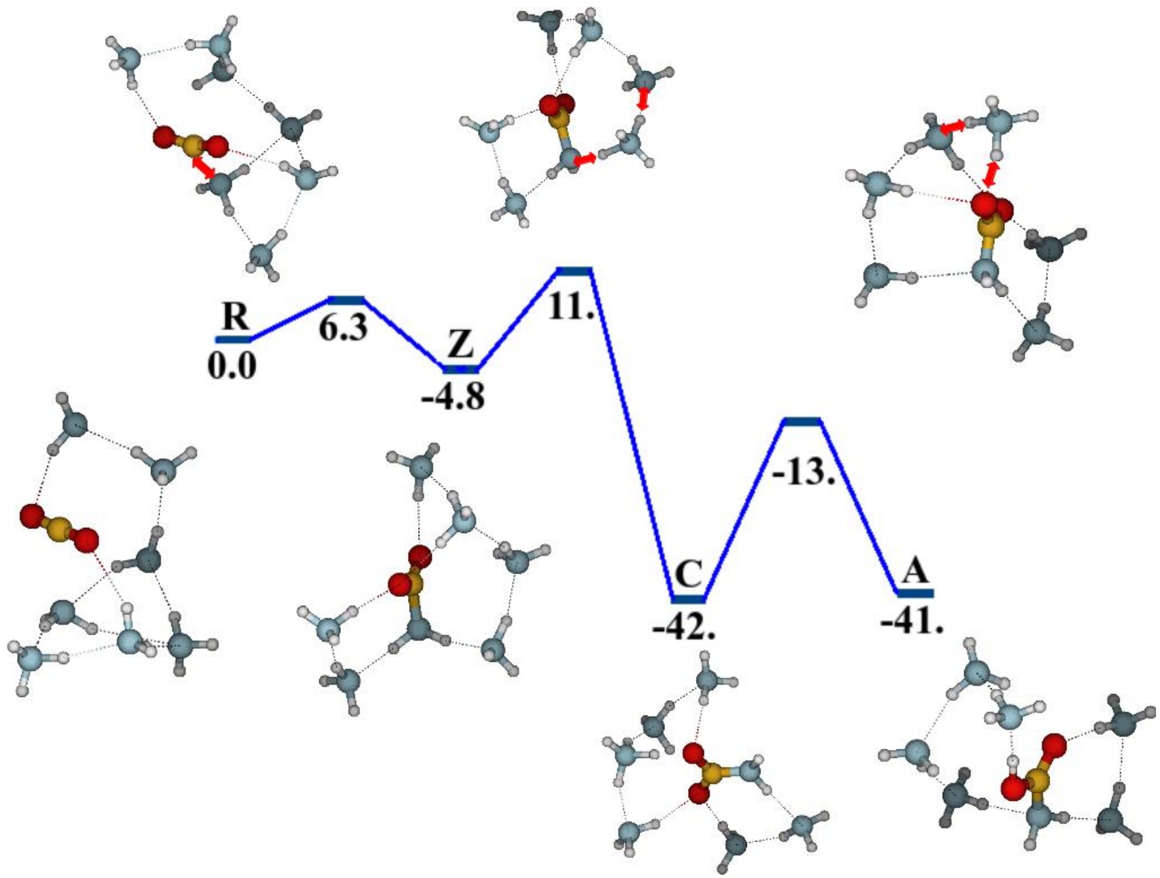
$$\frac{d[X]}{dt} = -k[X][Y]$$

# REACTIVITY IN AMMONIA ICES

## Theoretical and Experimental approaches

- OBJECTIVES
  - Study the reactivity without any solvation artifacts like diffusion
    - Reaction in ammonia ice
- EXPERIMENTAL METHOD
  - Isothermal experiments on $CO_2:NH_3$ 1:10 ices
- THEORETICAL METHOD
  - Calculation within a cluster approach of the reaction path using DFT (B3LYP/6-311G(d,p)

# REACTIVITY IN AMMONIA ICE

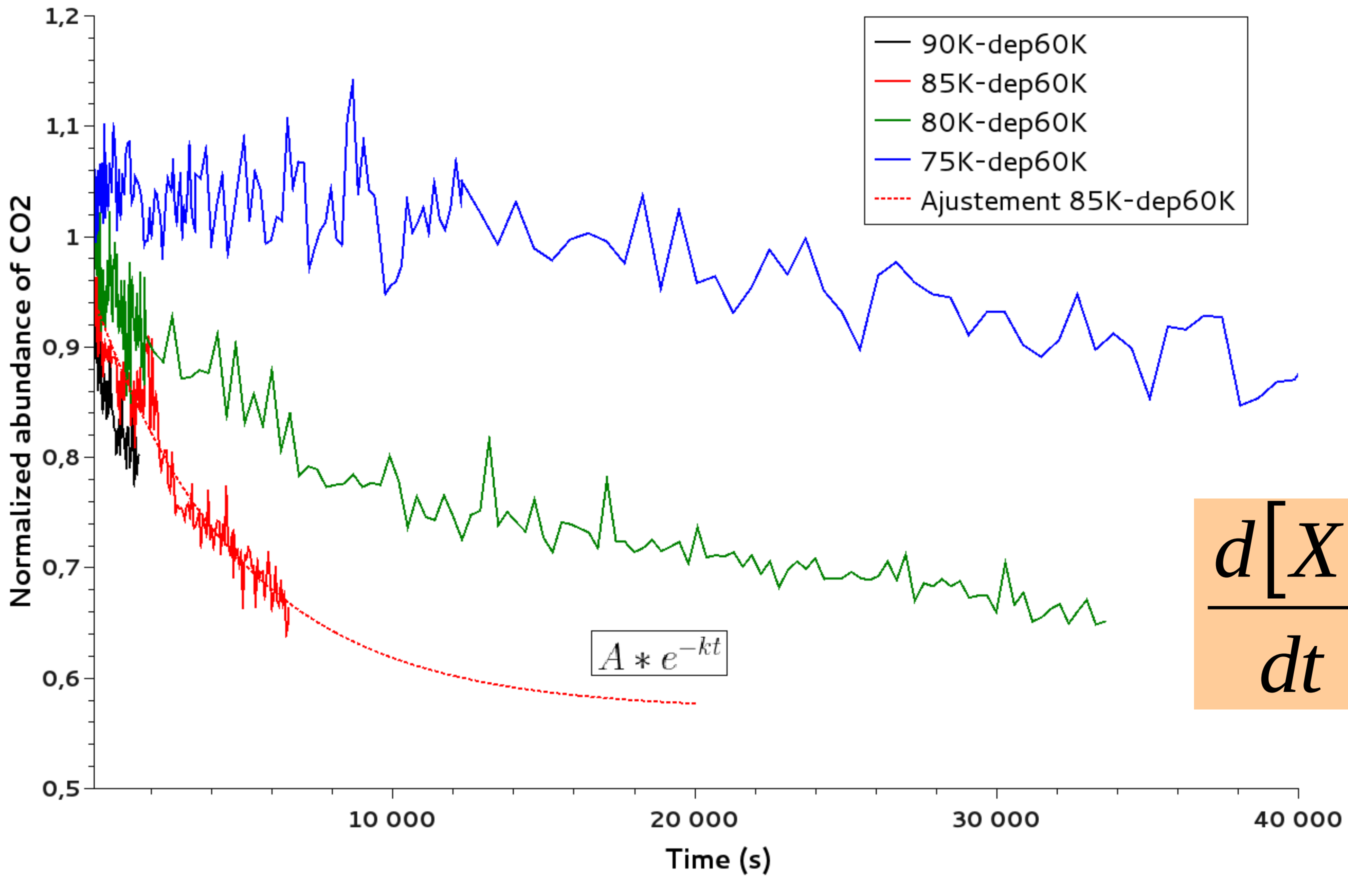



Cluster of $NH_3$:$CO_2$ 7:1

$NH_3 + CO_2$ -> $[H_2NCOO^-][NH_4^+]$ -> $H_2NCOOH$

Total energy barrier of 11 kJ/mol : **reaction possible**

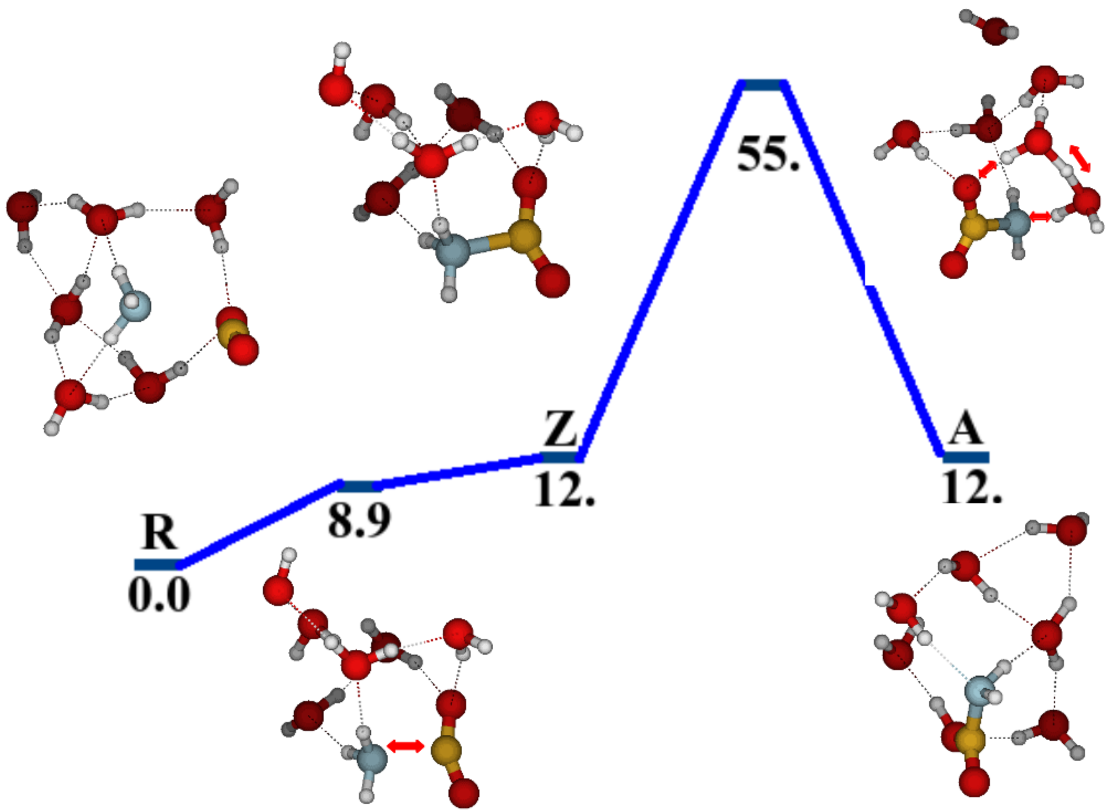
# REACTIVITY IN AMMONIA ICE




$$\frac{d[X]}{dt} = -k[X][Y]$$

- Formation of ammonium carbamate $[H_2NCOO^-][NH_4^+]$
- Fit of reaction constant with Arrhenius law :
  - Measured reaction barrier of **5kJ/mol / 11kJ/mol** from calculations

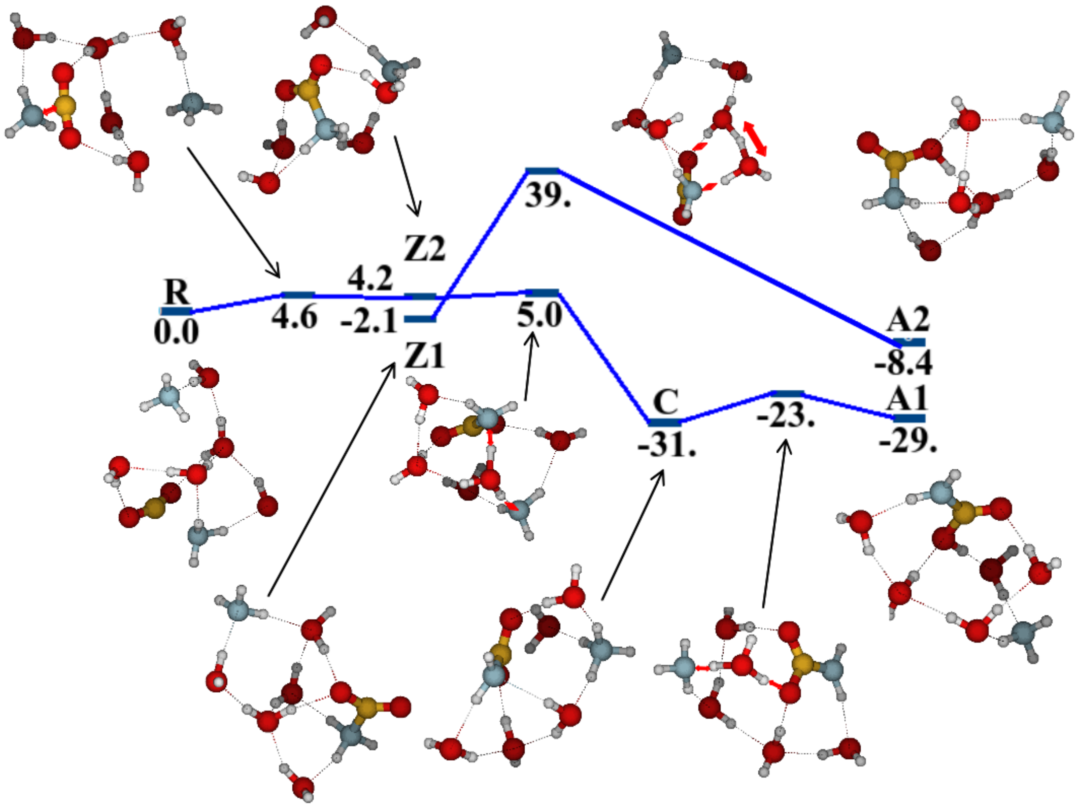
# REACTIVITY IN WATER ICE



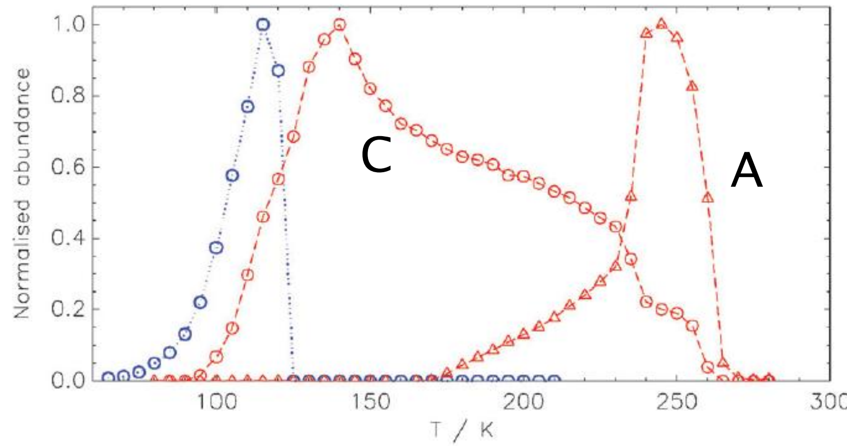

Cluster of $NH_3$:$CO_2$:$H_2O$
1:1:6

$NH_3 + CO_2$ -> $NH_2CO_2H$ : high barrier of 55kJ/mol
=> reaction difficult

# REACTIVITY IN WATER ICE




Cluster of
$NH_3$:$CO_2$:$H_2O$
2:1:5




2 $NH_3$ + $CO_2$ -> [$H_2NCOO^-$][$NH_4^+$] -> $NH_2CO_2H$ + $NH_3$

low barrier of 5kJ/mol : **reaction possible**

2 $NH_3$ +$CO_2$ -x> $NH_2CO_2H$ + $NH_3$

high barrier of 39 kJ/mol : reaction difficult

# SOLID-STATE REACTIVITY

- Experimentally : in ammonia ice
  - $2NH_3 + CO_2 \rightarrow [H_2NCOO^-][NH_4^+]$ : **5kJ/mol**

- Theoretically : in clusters
  - <u>In ammonia cluster :</u>

    $2NH_3 + CO_2 \rightarrow [H_2NCOO^-][NH_4^+]$ : **11kJ/mol**

  - <u>In water cluster :</u>

    $2NH_3 + CO_2 \rightarrow [H_2NCOO^-][NH_4^+]$ : **5kJ/mol**
    - Catalytic role of water

    $NH_3 + CO_2 \rightarrow NH_2CO_2H$ : **55kJ/mol : difficult**
    - Experimental detection of $NH_2CO_2H$ at higher temperature

# CONCLUSIONS AND PERSPECITVES

- A Diffusion-Reactivity Study

$$\frac{d[X]}{dt} = -k[X][Y] + D\frac{d^2[X]}{dx^2}$$

# CONCLUSIONS

- Diffusion :
  - **First calculation of D** for $CO_2$ and $NH_3$ for 90-170K in the bulk LDA ices
  - Likely **interstitial mechanism**
  - **High diffusivity** of $CO_2$ and $NH_3$ above 100K
- Reactivity
  - Thermal $2NH_3 + CO_2 \rightarrow [H_2NCOO^-][NH_4^+]$ reaction **possible in ISM**
  - **Proton transfer favored by $H_2O$** lowering the barrier
  - Indication of **concentration-dependent mechanism**

**Argue for combined experimental and theoretical studies for studying solide state chemistry**

# PERSPECTIVES

- **Theory : ab initio Molecular Dynamics**
  - Reaction in a periodic LDA ice at different temperatures
  - Comparison with cluster approach
  - Rate constants calculations

- **Experiments**
  - Dependency with concentration
  - Activation energy in water

**Towards the construction of a formalism for diffusion-limited reactivity …**

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