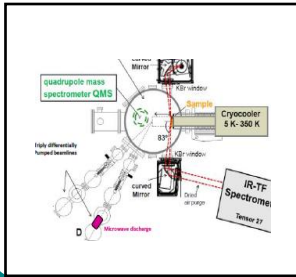


## Introduction

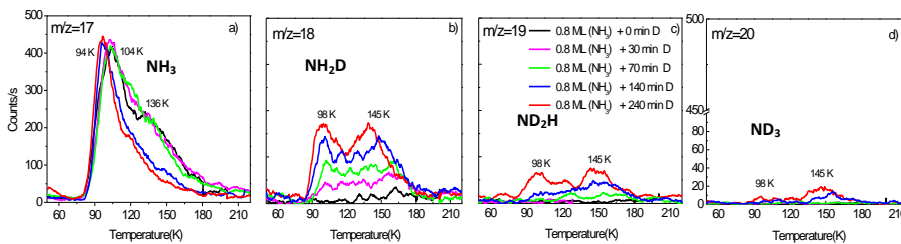
Singly and multiply deuterated ammonia species NH<sub>2</sub>D, NHD<sub>2</sub>, and ND<sub>3</sub> have been observed in many astrophysical sources, such as cold dense cores (10–20 K, 10<sup>6</sup> cm<sup>-3</sup>) and cold dense interstellar clouds (10 K, 10<sup>4</sup> cm<sup>-3</sup>) [1]. The abundances of these species in gas phase were found to be higher than the cosmic elemental D/H ratio (~ 2 · 10<sup>-5</sup>) [2]. In order to know if surface chemistry may contribute as well as gas phase chemistry for the deuteration of ammonia molecules, we have investigated laboratory experiments for the reaction between solid NH<sub>3</sub> and D atoms on cold surfaces of dust grains analogs. The experiments were performed in the sub-monolayer regime of solid ammonia [3]. For comparison, identical control experiments were performed with CH<sub>3</sub>OH + D.

## Experiment-FORMOLISM



- Experiments:** - The experiments were performed with the **FORMOLISM** (FORmation of MOlecules in the ISM) set-up located in Cergy Pontoise. It is composed of an ultra high vacuum chamber (<10<sup>-10</sup> mbar), two atomic and molecular differentially pumped beam-lines, a quadrupole masse spectrometer (QMS) and a Fourier Transform Infrared Spectrometer (IR-TF).
- Sample holder:** - The sample is made with an oxidized graphite slab of Highly Ordered Pyrolytic Graphite (HOPG).
- Exposure:**
  - About 0.8 ML of solid ammonia was pre-deposited on the oxidized graphite surface held at 10 K. The film is then exposed to D atoms for different deposition times.
  - NH<sub>3</sub> and D species were deposited successively by using the same beam line aimed at the surface.
  - D atoms are produced by microwave dissociation of D<sub>2</sub> molecules with an efficiency of 85 %. The same exposure experiments were realized with CH<sub>3</sub>OH and D atoms.
- TPD:** - After the deposition phase, we apply the Temperature Programmed Desorption (TPD) Technique, which consists to heat the films of NH<sub>3</sub>+D or (CH<sub>3</sub>OH +D) from 10 K to 210 K using a linear heating rate of 10 K/min. The desorbed species into the gas phase are detected with the QMS.

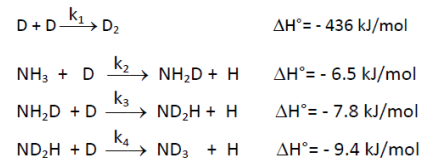
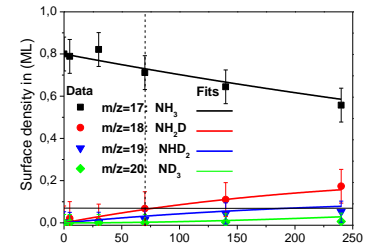
## Results : NH<sub>3</sub> + D



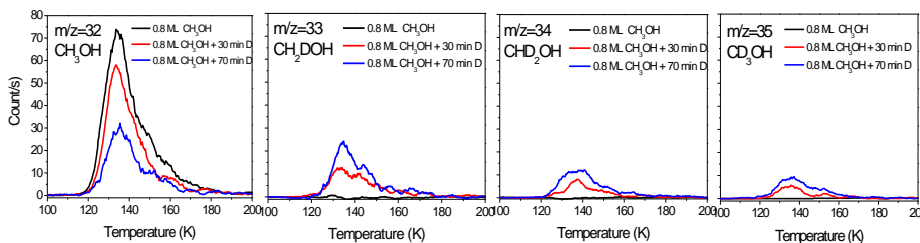
TPD experimental results showed a decrease in the desorption peak of NH<sub>3</sub> (m/z=17) at ~ 94 K, and an increase in the desorption peaks at ~ 98 K, attributed to ammonia isotopologue species: NH<sub>2</sub>D (m/z=18), NHD<sub>2</sub> (m/z=19), and ND<sub>3</sub> (m/z=20).

These species are formed by direct H-D substitution exothermic surface reactions between adsorbed ammonia species and D atoms.

Kinetic evolutions of NH<sub>3</sub>, NH<sub>2</sub>D, NHD<sub>2</sub>, ND<sub>3</sub> species as a function of D atoms exposure doses.



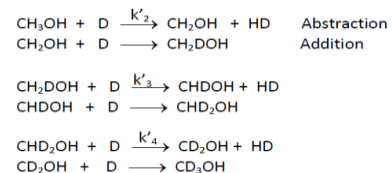
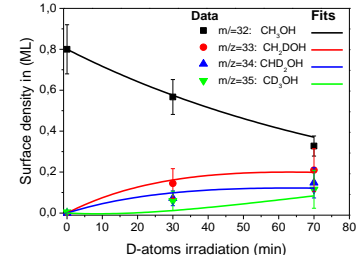
## Results : CH<sub>3</sub>OH + D



The TPD experimental results showed a rapid decrease in the desorption peak of CH<sub>3</sub>OH (m/z=32) at ~ 140 K, and the increase of three desorption peaks at ~ 140 K, attributed to methanol isotopologue species: CH<sub>2</sub>DOH (m/z=33), CHD<sub>2</sub>OH (m/z=34), and CD<sub>3</sub>OH (m/z=35).

These deuteration species are formed by surface process, which is ruled by quantum tunneling H abstraction and D addition exothermic surface reactions [4].

Kinetic evolutions of CH<sub>3</sub>OH, CH<sub>2</sub>DOH, CHD<sub>2</sub>OH and CD<sub>3</sub>OH<sub>3</sub> as a function of D atoms exposure doses.



## Activation barriers for reaction

Table 2: The width Z<sub>x</sub> and the height of the energy barriers E<sub>a</sub>, expressed in (Å) and in kelvin (K), respectively, of the successive H-D substitution reactions of NH<sub>3</sub> molecules by D atoms on the oxidized, partly ASW covered graphite surface at 10 K, for a fixed value of D-atom diffusion energy E<sub>diff</sub>. The minimum χ<sup>2</sup> value of the fits is found to vary between 0.3 and 0.1.

Reactions units	E <sub>diff</sub>	Z <sub>x</sub>	E <sub>a</sub>
	K	Å	K
NH <sub>3</sub> +D $\xrightarrow{\beta_1}$ NH <sub>2</sub> D+H	150	0.86	1950 ± 250
	250	0.83	1840 ± 270
	350	0.81	1750 ± 320
NH <sub>2</sub> D+D $\xrightarrow{\beta_2}$ NHD <sub>2</sub> +H	150	0.86	1820 ± 220
	250	0.83	1690 ± 245
	350	0.81	1610 ± 290
NHD <sub>2</sub> +D $\xrightarrow{\beta_3}$ ND <sub>3</sub> +H	150	0.86	1800 ± 210
	250	0.83	1670 ± 230
	350	0.81	1600 ± 250

Table 3: The width Z<sub>x</sub> and the height of the energy barriers E<sub>a</sub>, expressed in (Å) and in kelvin (K), respectively, of the successive H-D substitution reactions of CH<sub>3</sub>OH molecules by D atoms on the oxidized, partly ASW covered graphite surface at 10 K, for a fixed value of D-atom diffusion energy E<sub>diff</sub>. The χ<sup>2</sup> value of the fit vary between 0.3 and 0.1.

Reactions units	E <sub>diff</sub>	Z <sub>x</sub>	E <sub>a</sub>
	K	Å	K
CH <sub>3</sub> OH+D $\xrightarrow{\beta'_1}$ CH <sub>2</sub> DOH+H	150	0.86	1450 ± 210
	250	0.85	1080 ± 180
	350	0.84	860 ± 120
CH <sub>2</sub> DOH+D $\xrightarrow{\beta'_2}$ CHD <sub>2</sub> OH+H	150	0.86	1330 ± 200
	250	0.85	990 ± 180
	350	0.84	770 ± 145
CHD <sub>2</sub> OH+D $\xrightarrow{\beta'_3}$ CD <sub>3</sub> OH+H	150	0.86	1300 ± 205
	250	0.85	980 ± 170
	350	0.84	780 ± 150

## Conclusions

- Contribution of grain surface chemistry in the deuterium enrichment of NH<sub>3</sub> molecules.
- The deuteration process of ammonia by D atoms addition on cold grain surfaces is slower than that of methanol species, and occurs with higher activation energy barriers.

## References

- [1] Roueff, E., Tine, S., Coudert, L.H., et al. *Astronomy & Astrophysics*, 388, L53 (2002).
- [2] J. L. Linsky, *Space Sci. Rev.* **106**, 49 (2003).
- [4] Nagaoka, A., Watanabe, N., and Kouchi, A. *Journal of Physical Chemistry A*, 111, 3016 (2007)