

## Kinetics of hydrogen/deuterium exchanges in cometary ices



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### ABSTRACT

The D/H composition of volatile molecules composing cometary ices brings key constraints on the origin of comets, on the extent of their presolar heritage, as well as on the origin of atmospheres and hydro-spheres of terrestrial planets. Nevertheless, the D/H composition may have been modified to various extents in the nucleus when a comet approaches the Sun and experiences deep physical and chemical modifications in its subsurface. We question here the evolution of the D/H ratio of organic species by proton exchanges with water ice. We experimentally studied the kinetics of D/H exchanges on the ice mixtures H<sub>2</sub>O:CD<sub>3</sub>OD, H<sub>2</sub>O:CD<sub>3</sub>ND<sub>2</sub> and D<sub>2</sub>O:HCN. Our results show that fast exchanges occur on the –OH and –NH<sub>2</sub> chemical groups, which are processed through hydrogen bonds exchanges with water and by the molecular mobility triggered by structural changes, such as glass transition or crystallization. D/H exchanges kinetic is best described by a second-order kinetic law with activation energies of 4300 ± 900 K and 3300 ± 100 K for H<sub>2</sub>O:CD<sub>3</sub>OD and H<sub>2</sub>O:CD<sub>3</sub>ND<sub>2</sub> ice mixtures, respectively. The corresponding pre-exponential factors ln(A(s<sup>-1</sup>)) are 25 ± 7 and 20 ± 1, respectively. No exchange was observed in the case of HCN trapped in D<sub>2</sub>O ice. These results strongly suggest that upon thermal heating (1) –OH and –NH<sub>2</sub> chemical groups of any organic molecules loose their primordial D/H composition and equilibrate with water ice, (2) HCN does not experience proton transfer and keeps a primordial D/H composition and (3) C–H chemical groups are not isotopically modified.

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## 1. Introduction

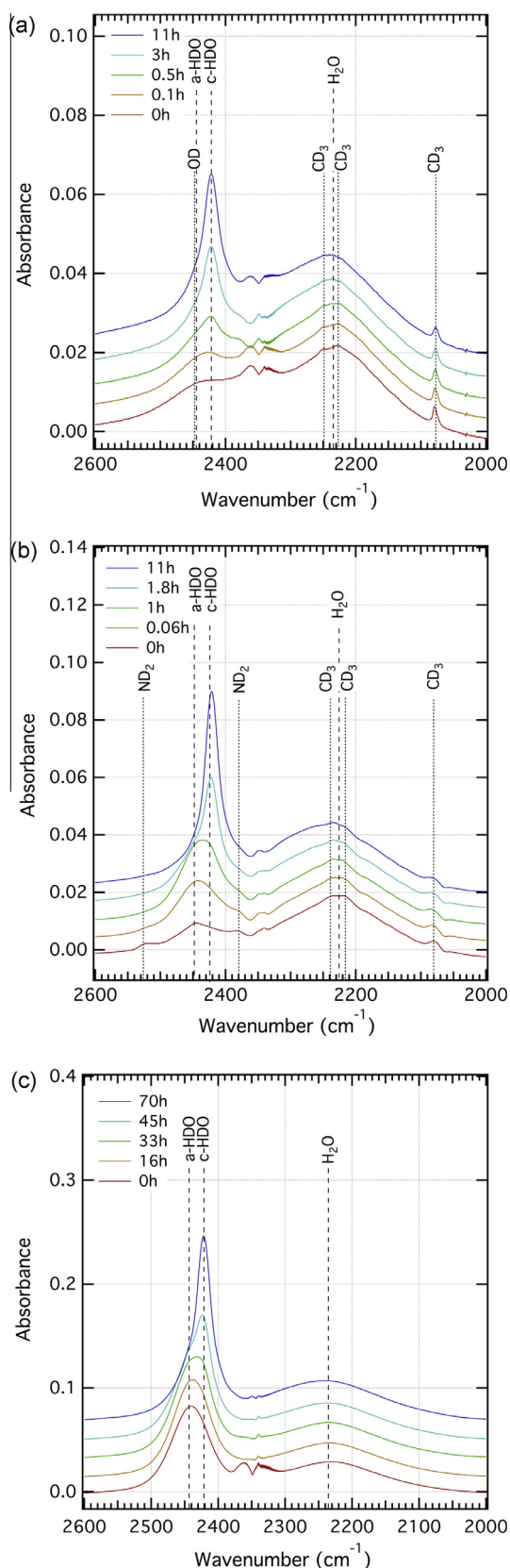
Cometary ices are composed primarily of water (H<sub>2</sub>O) along with CO and CO<sub>2</sub>, and to a lesser extent of CH<sub>3</sub>OH, H<sub>2</sub>CO, HCN, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub> and H<sub>2</sub>S. The abundance of these species varies from a comet to another, and some comets display a larger array of molecular species. This is the case of Comet Hale–Bopp for instance, for which CH<sub>4</sub>, NH<sub>3</sub>, HCCOH, HNCO and NH<sub>2</sub>CHO have been identified with abundances at the ~0.1–1.5% level (Bockelée-Morvan et al., 2004; Crovisier et al., 2004; Mumma and Charnley, 2011). Cometary ices resemble interstellar ices in the sense that all cometary molecules, except C<sub>2</sub>H<sub>6</sub>, have been detected in molecular clouds or in protostar environments with rather similar relative abundances (Bockelée-Morvan et al., 2000; Mumma and Charnley, 2011). Before the late 1990s, it was generally believed that they were inherited from the local interstellar medium 4.55 Gyr ago (Greenberg, 1982; Encrenaz et al., 1991). However, ISO observations of Comet Hale–Bopp, and the analysis of grains from Comet Wild 2 brought back by to Earth by the Stardust

mission have shown that comets accreted crystalline minerals formed in the hot region of the protosolar disk (Crovisier et al., 1999; Brownlee et al., 2006). The simple paradigm that had prevailed for long was thus seriously challenged, and a key issue emerged as whether cometary ices were partly or fully formed within the proto-solar disk (Blake et al., 1999; Cleeves et al., 2014).

One way to investigate the source of cometary materials is to use the deuterium fractionation as a tracer of the chemical and physical processes that led to their formation (Robert et al., 1979; Ceccarelli et al., 2014). Two deuterated molecules, HDO and DCN, have been so far detected in a limited number of comets. The isotopic ratio HDO/H<sub>2</sub>O was found to lie above the Standard Mean Ocean Water (SMOW) in the range 2.75 × 10<sup>-4</sup>–3.25 × 10<sup>-4</sup> (765–1086‰), and with a larger value of 5.3 × 10<sup>-4</sup> ± 0.7 (1968–2871‰) for the Comet 67P/Churyumov–Gerasimenko (Altwegg et al., 2015), the primordial solar nebula n<sub>D</sub>/n<sub>H</sub> value being 2 × 10<sup>-5</sup>. For one Comet (Hartley 2), the isotopic ratio HDO/H<sub>2</sub>O was around the SMOW value (Hartogh et al., 2011). The DCN/HCN ratio was measured in Comet Hale–Bopp and found to be ~0.002 (11,900‰) (Meier et al., 1998). Using high-resolution observations, Blake et al. (1999) derived higher values in the icy jets of this comet, up to 0.025 (~160,000‰). In cold molecular

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**Fig. 1.** Time evolution of the FTIR absorption spectra at 130 K for (a) a mixture of  $\text{H}_2\text{O}:\text{CD}_3\text{OD}$  and (b) a mixture of  $\text{H}_2\text{O}:\text{CD}_3\text{ND}_2$  and (c) time evolution of the FTIR absorption spectra at 125 K for a mixture of  $\text{H}_2\text{O}$  with 2% of  $\text{D}_2\text{O}$ . The isotopic H/D exchange between  $\text{H}_2\text{O}$  and the deuterated organic molecule is traced by the amorphous HDO (a-HDO) and the crystallized HDO (c-HDO)  $\nu_{\text{OD}}$  bands, respectively at  $2445\text{ cm}^{-1}$  and  $2425\text{ cm}^{-1}$ . Spectra are vertically offset to ensure clarity of the figure.

clouds, dense cores and star forming regions, the D/H fractionation results from zero-point energy effects and it probes chemistry at very low temperature. Extreme fractionations are observed in environments where CO is depleted from the gas phase by condensation onto the grains (Linsky, 2007; Parise et al., 2006). Regarding water deuteration, large variations have been reported among different low-mass protostars, with  $[\text{HDO}]/[\text{H}_2\text{O}]$  ranging from typically 0.1% to 2% (Parise et al., 2005; Coutens et al., 2012, 2013; Persson et al., 2014). Comparing comets with interstellar medium (ISM) and star forming regions is thus not straightforward and requires a systematic characterization of deuteration at the different stages of the protostellar and cometary evolutions (Caselli and Ceccarelli, 2012).

The interferometric data on Hale-Bopp obtained by Blake et al. (1999) suggested a higher deuteration of  $\text{H}_2\text{O}$  and HCN in icy jets with respect to the whole coma, interpreted by hydrogen/deuterium (H/D) exchanges. This process was also proposed to account for the selective deuteration of methanol observed in hot corinos where icy grain mantles have evaporated (Ratajczak et al., 2009). In this study, we question further the evolution of the D/H ratio of organic molecules through H/D exchanges between water and organic molecules in the solid state. Ratajczak et al. (2009) experimentally demonstrated that thermally-activated exchanges occur between solid  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  at temperatures as low as 120 K, that they are controlled by ice crystallization, and that they take place on the hydroxyl functional group of methanol. We report here an experimental study that aims at (i) extending earlier studies to  $-\text{NH}$  bearing species, as well as to the HCN molecule, and (ii) deriving kinetic order and rate constants for both the H/D exchange and the crystallization processes. We show how these new data will help constrain different issues regarding the D/H composition of ices in comets, and how they could be used to feed evolution models of volatiles in cometary nuclei (e.g. Lasue et al., 2008; Marboeuf and Schmitt, 2014). The organic molecules employed in our study are methanol ( $\text{CH}_3\text{OH}$ ), methylamine ( $\text{CH}_3\text{NH}_2$ ) and hydrogen cyanide (HCN). All three species have been observed in interstellar clouds (Ball et al., 1970; Ziurys and Turner, 1986) and cometary atmospheres (Bockelee-Morvan et al., 1991; Despois et al., 1986; Glavin et al., 2008). The deuterated isotopologues of  $\text{CH}_3\text{OH}$  and HCN have also been detected in the ISM (Jefferts et al., 1973; Mauersberger et al., 1988; Parise et al., 2004) while only DCN has been observed in comets (Meier et al., 1998). Upper limits on the abundance of the deuterated isotopologues of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{NH}_2$  have been estimated by Crovisier et al. (2004).

## 2. Experiments and method

Experiments were performed at Institut de Planétologie et d'Astrophysique de Grenoble (IPAG, Grenoble – France) and at

**Table 1**

The observed vibrational frequencies ( $\text{cm}^{-1}$ ) of  $\text{H}_2\text{O}$ , HOD,  $\text{CD}_3\text{OD}$  and  $\text{CD}_3\text{ND}_2$  in the condensed  $\text{H}_2\text{O}:\text{CD}_3\text{OD}$  and  $\text{H}_2\text{O}:\text{CD}_3\text{ND}_2$  thin films.

	Vibrational mode	Band position ( $\text{cm}^{-1}$ )
$\text{H}_2\text{O}$	$\nu_1$ & $\nu_3$ , $\nu_2 + \nu_L$	$\sim 3300$ , 2230
HOD	$\nu_{\text{OD}}$ amorphous	2425
	$\nu_{\text{OD}}$ crystallized	2450
$\text{D}_2\text{O}$	$\nu_1$ & $\nu_3$	$\sim 2400$
	$\nu_{\text{OD}}$ (OD)	2450
$\text{CD}_3\text{OD}$	$\nu_{11}$ , $\nu_2$ , $\nu_3$ ( $\text{CD}_3$ )	2250, 2220, 2080
	$\nu_{10}$ , $\nu_1$ ( $\text{ND}_2$ )	2526, 2380
	$\nu_{11}$ , $\nu_2$ , $\nu_3$ ( $\text{CD}_3$ )	2238, 2215, 2080
HCN	$\nu_1$ (CN) in water	2091
	$\nu_1$ (CN) cluster	2100–2103
DCN	$\nu_1$ (CN) in water	1856
	$\nu_1$ (CN) cluster	1894–1890

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