Kinetics of hydrogen/deuterium exchanges in cometary ices

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A B S T R A C T

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 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 H2O:CD3OD, H2O:CD3ND2 and D2O:HCN. Our results show that fast exchanges occur on the –OH and –NH2 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 H2O:CD3OD and H2O:CD3ND2 ice mixtures, respectively. The corresponding pre-exponential factors ln(A(s−1)) are 25 ± 7 and 20 ± 1, respectively. No exchange was observed in the case of HCN trapped in D2O ice. These results strongly suggest that upon thermal heating (1) –OH and –NH2 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 (H2O) along with CO and CO2, and to a lesser extent of CH3OH, H2CO, HCN, CH4, C2H2, C2H6, NH3 and H2S. 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 CH3, NH3, HCCOH, HNCO and NH2CHO 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 CH4, 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; Cleaves 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/H2O was found to lie above the Standard Mean Ocean Water (SMOW) in the range 2.75 × 10−4–3.25 × 10−4 (765–1086‰), and with a larger value of 5.3 × 10−4 ± 0.7 (1968–2871‰) for the Comet 67P/Churyumov–Gerasimenko (Altwegg et al., 2015), the primordial solar nebula nD/nH value being 2 × 10−5. For one Comet (Hartley 2), the isotopic ratio HDO/H2O 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...
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 [HDO]/[H2O] 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 H2O 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 H2O and CH3OH 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 –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 (CH3OH), methylamine (CH3NH2) 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 CH3OH 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 CH3OH and CH3NH2 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](https://example.com/table1.png)

**Table 1**

The observed vibrational frequencies (cm⁻¹) of H2O, HOD, CD3OD and CD3ND2 in the condensed H2O:CD3OD and H2O:CD3ND2 thin films.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Band position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>ν1 &amp; ν3, ν2 + ν1</td>
</tr>
<tr>
<td>HOD</td>
<td>νOD, amorphous</td>
</tr>
<tr>
<td></td>
<td>νOD, crystallized</td>
</tr>
<tr>
<td>D2O</td>
<td>ν1 &amp; ν3</td>
</tr>
<tr>
<td>CD3OD</td>
<td>νOD (OD)</td>
</tr>
<tr>
<td></td>
<td>ν11, ν2, ν3 (CD3)</td>
</tr>
<tr>
<td>CD3ND2</td>
<td>ν11, ν2, ν3 (ND2)</td>
</tr>
<tr>
<td></td>
<td>ν1s, ν1 (CD3)</td>
</tr>
<tr>
<td>HCN</td>
<td>ν1 (CN) in water</td>
</tr>
<tr>
<td></td>
<td>ν1 (CN) cluster</td>
</tr>
<tr>
<td>DCN</td>
<td>ν1 (CN) in water</td>
</tr>
<tr>
<td></td>
<td>ν1 (CN) cluster</td>
</tr>
</tbody>
</table>
Laboratoire de Physique des Interactions Ioniques et Moléculaires de Marseille (PIIM, Marseille – France). At IPAG, films (~1 μm) of amorphous solid water (ASW) containing ~2% of deuterated methanol (CD3OD – 99.8%) or methylamine (CD3ND2 – 98%) were produced in a vacuum chamber at ~10⁻⁸ mbar. A co-injection system allowed to co-condense both gases on a KBr window held at 20 K with a SHI CH-202B-HC-4E two-stage He closed cycle refrigerator APD. No isotopic exchanges occurred in the gas phase prior condensation. The deposition rate of each compound (H₂O, CD3OD and CD3ND2) was calibrated with a He–Ne interferometric system and adjusted with a microvalve. It is around 5.5 monolayers s⁻¹ (ML s⁻¹) for H₂O and 0.1 ML s⁻¹ for organic compounds. Typical concentration of CD3OD or CD3ND2 was around 2% (molecular ratio). Films were warmed up with a resistor and a PID controller (Lake Shore 331). In a first step, the sample was heated up to 100 K through a 1 K min⁻¹ ramp. Then, it was heated up to a temperature between 110 and 150 K (temperature ramp 5 K min⁻¹). As the sample reach this temperature, it was monitored with infrared spectroscopy, with time intervals ranging from minute to hours. Mid-infrared spectra (4000–400 cm⁻¹) with 1 cm⁻¹ spectral resolution were collected with a Vertex 70v FTIR spectrometer equipped with a GLOBAR source and a DTGS detector.

At PIIM, thin films of deuterated amorphous solid water (D-ASW) containing hydrogen cyanide (HCN) were condensed onto a gold plated copper surface held at 50 K in the reflection–absorption mode. As above, the films were formed in a vacuum chamber by a co-injection system. The gas-phase HCN monomer was synthesized via the thermal reaction of potassium cyanide, KCN, with an excess of stearic acid, CH₃(CH₂)₁₆COOH, in a primary pumped vacuum line. HDO was also present in the D-ASW sample as a contamination, with an abundance as high as 15%. The HCN percentage in the ice sample was estimated using the integrated absorbance of the ν₃ stretching mode of HCN at 35 K (A = 2.3 × 10⁵ cm⁻²; Dello Russo and Khanna (1996)), of the blended ν₁ and ν₂ stretching modes of D₂O (A = 72.6 × 10³ cm mmol⁻¹) and the ν₃OH and ν₃OD stretching modes of HDO (A = 80.9 × 10³ cm mmol⁻¹ and A = 30.3 × 10³ cm mmol⁻¹, respectively; Ikawa and Maeda (1968)). The deposition rate was >15 ML s⁻¹ for D₂O and the HCN concentration was estimated to be ~25%. The sample was warmed at 2 K min⁻¹ from 50 K to

Fig. 2. Temperature and time evolution of the FTIR absorption spectra for a mixture of D₂O:HCN. The plots show the three frequency ranges corresponding to (a) HCN, (b) DCN and (c) D₂O. While heating to 150 K, HCN (resp. DCN) molecules segregate to form clusters. At 150 K, the sample crystallizes (as observed on the spectra centered on D₂O vibrational modes) while HCN (resp. DCN) molecules desorb. Spectra are vertically offset to ensure clarity of the figure.

Fig. 3. The sum of the integrated absorbance of the CN bands of HCN at 2091 cm⁻¹ and 2100 cm⁻¹ (Fig. 2a) versus the sum of the integrated absorbance of the CN bands of DCN at 1856 cm⁻¹ and 1890 cm⁻¹ (Fig. 2b). Both remain linearly correlated as suggested by the linear fit (dash line).
150 K and hold at this temperature a few hours while H/D exchanges were examined. During the experiment, mid-infrared spectra (4000–650 cm$^{-1}$) with a 1 cm$^{-1}$ spectral resolution were collected with a Bruker Vertex 70 FTIR spectrometer, equipped with a GLOBAR source and a MCT detector.

3. Results

3.1. Infrared spectra of ice mixtures

3.1.1. H$_2$O:CD$_3$OD and H$_2$O:CD$_3$ND$_2$ ice mixtures

Isothermal experiments were conducted at different temperatures (110 K, 115 K, 120 K, 125 K, 130 K and 135 K). Fig. 1 shows the spectral evolution of infrared spectra collected at 130 K over time for the H$_2$O:CD$_3$OD (Fig. 1a) and H$_2$O:CD$_3$ND$_2$ ice (Fig. 1b) mixtures (1:50 ratio). At $t=0$ h, the broad vibrational mode at ~2250 cm$^{-1}$ ($v_3+v_1$) of water ice, $v_1$ being the libration mode, dominates the infrared spectrum. Weaker and narrower vibrational modes of the CD$_3$ or ND$_2$ functional groups of CD$_3$OD or CD$_3$ND$_2$ are superimposed on this broad water band (see also Table 1). The CD$_3$ symmetric stretching mode peaks at ~2080 cm$^{-1}$, two CD$_3$ antisymmetric stretching modes peak in the range 2210–2250 cm$^{-1}$. In addition, the OD stretching mode of CD$_3$OD peaks at 2450 cm$^{-1}$, the ND$_2$ symmetric stretching mode at ~2380 cm$^{-1}$ and the ND$_2$ antisymmetric stretching mode at ~2526 cm$^{-1}$. Within a few hours, the $v_{OD}$ stretching band of HOD appears at 2425 cm$^{-1}$ and continuously increases upon time. This evidences that H/D exchanges occurred between water and the deuterated organic molecules. These exchanges are observed at the laboratory time scale above 120 K for the CD$_3$OD:H$_2$O mixture, in agreement with the measurements of Ratajczak et al. (2009).

They are slightly faster for the H$_2$O:CD$_3$ND$_2$ ice mixture and were observed above 110 K. We note that the integrated absorbance of the CD$_3$ symmetric stretching mode at ~2080 cm$^{-1}$ decreases by ~20%. This decrease is larger in the case of H$_2$O:CD$_3$OD than in
the case of H$_2$O:CD$_3$ND$_2$. Several effects may explain this result, such as environmental modifications (crystallization modifies the shape of the band) and sublimation of the organic molecule. A slight decrease is also observed on other organic chemical groups of the same molecule, such as the CO stretching mode of CD$_3$OD. This supports the idea that H/D exchanges on the methyl group are not of concern here, accordingly to the fact that such exchanges are negligible in liquid water at room temperature (England and Kallenbach, 1983). By contrast, the ND$_2$ antisymmetric stretching mode of CD$_3$ND$_2$ at $\sim$2526 cm$^{-1}$ seems to disappear entirely. Therefore, thermally-activated H/D exchanges seem to proceed on the amine and hydroxyl functional groups of CD$_3$ND$_2$ and CD$_3$OD respectively, but not on the methyl functional group. Interestingly, the V$_{OD}$ stretching band of HOD gets thinner and shifts toward smaller wavenumbers during the process. This spectral change is controlled by the crystallization of water ice (Hage et al., 1994) and suggests a close link between the H/D exchange and the morphological changes (see below).

3.1.2. D$_2$O:HCN ice mixture

In this experiment performed at PIIM, the sample was studied at 150 K. This temperature is a compromise in order to optimize exchange conditions, but it is low enough to avoid sublimation. After formation at 50 K, the sample was heated up to 150 K (2 K min$^{-1}$ temperature ramp) and held a few hours at this temperature. Fig. 2a–c shows the temperature and time evolution of the infrared spectra of D$_2$O:HCN ice mixture. At 100 K, the CN stretching mode $v_1$ of HCN appears at $\sim$2091 cm$^{-1}$. This band is interpreted as small clusters ($n \geq 2$) of HCN, as observed in Pacansky (1977). The shoulder observed at 2101 cm$^{-1}$ is assigned to HCN large aggregates as this band peaks at the same position as pure HCN (Moore et al., 2010). The weak bands that peak between 1830 cm$^{-1}$ and 1900 cm$^{-1}$ are presumably due to a DCN contamination (<1%). DCN may indeed have been formed from H/D exchanges at 300 K in the primary pumped vacuum line with residual adsorbed D$_2$O from previous experiments.

![Fig. 6. Reduced-time plots for the crystallization of (a) a mixture of H$_2$O:CD$_3$OD, (b) a mixture of H$_2$O:CD$_3$ND$_2$, and (c) pure H$_2$O at different temperatures. The fits (dotted lines) are plotted for a second order kinetic model at 125 K (a), an Avrami ($n=2$) kinetic model at 125 K (b) and an Avrami ($n=2$) kinetic model at 130 K (c). The very first data points, related to the induction period, are not considered in the Avrami fits.](image)

![Fig. 7. Arrhenius plots for the crystallization process for (c) pure ASW ice and mixtures of (a) H$_2$O:CD$_3$OD and (b) H$_2$O:CD$_3$ND$_2$.](image)
Interestingly, the behavior of the DCN bands in the 1830–1900 cm\(^{-1}\) range mimics that of the HCN bands. Upon heating the intensity of the 1891 cm\(^{-1}\) band correlates with that at 2101 cm\(^{-1}\) (HCN aggregates), while that of the 1856 cm\(^{-1}\) correlates with the (small clusters) HCN band at 2091 cm\(^{-1}\). We therefore assign the 1856 and 1891 cm\(^{-1}\) bands to “small cluster” and “aggregate” DCN, respectively. Intensity variations of those features suggest that aggregation occurs at temperatures as low as 120 K. At 150 K, the shift toward low wavenumbers of the aggregated molecule bands may be triggered by the crystallization of deuterated ASW. The relative abundances of HCN and DCN were determined through their CN integrated band absorbances in the 2070–2110 and 1830–1900 cm\(^{-1}\) ranges. The C–H and C–D bands could not be used, because the C–D band at ~2500 cm\(^{-1}\) is merged within the broad \(v_1\) and \(v_3\) bands of D\(_2\)O ice in the 2250–2550 cm\(^{-1}\) ranges (Fig. 2c). The integrated absorbance of the CN bands of HCN and DCN were found to decrease and to remain linearly correlated (Fig. 3). We conclude that no exchange occurred and that the decrease of the intensity of the CN bands of HCN and DCN was fully controlled by sublimation. The high concentration of HCN in our sample (~25%) may partly explain this observation, as aggregation prevents close interactions with D\(_2\)O. However, at 150 K (\(t \approx 0\)), the fraction of HCN molecules neighbored by D\(_2\)O molecules should be large as ~20% of HCN is still in the form of small clusters (see Fig. 2a). Still, at 150 K these HCN molecules did not exchange, whereas at this temperature the exchange should be completed within a few minutes for –OH or –NH\(_2\) chemical groups. These results suggest that the kinetics of exchange with HCN is definitely much slower than that of –OH and –NH\(_2\) chemical groups, and is also much slower than ASW crystallization in our experimental conditions.

### 3.2. Kinetic approach

The rate of a solid-state chemical reaction \(dx/dt\) is generally described by a single step kinetic equation:

\[
\frac{dx}{dt} = k_i(T) f_i(x)
\]

where \(x\) is the time, \(k_i\) is the rate constant, \(T\) is the temperature, \(f_i\) is the kinetic model and \(x\) is the degree of conversion (e.g. \(x \in [0,1]\)) that represents the progression of the studied physical process. The integrated form of the kinetic equation for isothermal conditions is then given by:

\[
g_i(x) = k_i(T) t
\]

where \(g_i(x)\) is the integrated kinetic model, defined by \(g_i(x) = \int_0^x \frac{dx}{f_i(x)}\).

For thermally induced processes, the temperature dependence of the rate constant can be described in general by an Arrhenius type equation:

\[
k_i(T) = A_i \exp \left( \frac{-E_i}{T} \right)
\]

**Fig. 8.** Schematic representation of H/D exchanges mechanism which is the conversion of CH\(_3\)OD to isolated CH\(_3\)OH via proton hopping and propagation of orientational defects (adapted from Fisher and Devlin, 1995).
where $A_i$ is the pre-exponential factor (in s$^{-1}$), $E_{A_i}$ is the activation energy (in K).

Kinetic models are theoretical and empirical mathematical descriptions of experimental processes. Some of the kinetic models used in the literature are presented in Table 2 and theoretical developments can be found in the review by Khawam and Flanagan (2006). In contrast to gas phase kinetics, it is difficult to retrieve information about individual reaction steps in condensed phase (liquid or solid phases) and a single kinetic model is used to represent the entire process. As the kinetic equation describes the overall process, it is hazardous to draw conclusion on the reaction mechanism from the kinetic model.

A chemical process is kinetically described by the kinetic triplet, which consists of the kinetic model $f_i(x)$ and the two Arrhenius parameters ($E_{A_i}$ and $A_i$). Our strategy was to use a model-fitting method in order to determine the best adapted kinetic model. This model must be identical for different isothermal experiments, which means for different temperatures. The reduced time variable

![Fig. 9. Half-life of H/D exchange, crystallization and desorption processes as function of temperature. Values for H/D exchange and crystallization are derived from this work: a second-order kinetic model is used to determine the half-life of H/D exchanges and crystallization of the H$_2$O:CD$_3$OD ice mixture. For the crystallization of pure H$_2$O and H$_2$O:CD$_3$ND$_2$ ice mixture, the half-life includes both the induction and Avrami periods. The half-life for desorption is derived from the work of Brown and Bolina (2007), see their Eq. (4), with a sample thickness $h_0$ of 0.9 $\mu$m.](image)

![Fig. 10. Physical differentiation of the comet as a function of the distance to the Sun, during one revolution. Calculations have been performed at latitude $\theta = 10^\circ$ with the same initial parameters as in Marboeuf and Schmitt (2014). Thermal inertia is $=40$ W m$^{-2}$ K$^{-1}$ s$^{1/2}$.](image)
other band contributions to the integrated absorbance of the OD stretching band. Indeed, the OD stretching band at the end of the experiment, when the integrated absorbance no longer increases. The superposition of the plots $\alpha$ versus $t/t_\alpha$ at different temperatures is shown in Fig. 4. The displayed error bars correspond mainly to the correction for overlap within error bars, therefore indicating that a unique kinetic model can then be evaluated by performing a linear fit of the plots $g_i(\alpha)$ versus $t/t_\alpha$. A standard $\chi^2$-test on these linear fits is used to select the best model. The reduced $\chi^2$ associated with the kinetic model $i$ ($\overline{\chi^2}_i$) is the average of the reduced $\chi^2$ obtained for this model at different temperatures ($\chi^2_i(T)$). The lowest $\overline{\chi^2}_i$ gives our best model. The rate constant $k_i(T)$ at each temperature is simply evaluated as the slope of the plot $g_i(\alpha)$ versus $t/t_\alpha$. Finally, the Arrhenius parameters ($E_a$ and $A_i$) are deduced from an Arrhenius diagram, $\ln(k(T))$ versus $1/T$.

3.3. Kinetics of H/D exchange

The formation of HOD molecules in the sample results from the process of H/D exchange between the deuterated organic molecule ($R\rightarrow D$) and water ($H_2O$) in large excess.

$$R\rightarrow D + H_2O \rightarrow R-H + HOD$$

(4)

The integrated absorbance of the $\nu_{OD}$ stretching band of HOD is proportional to the fraction of HOD molecules (the $\nu_{OD}$ stretching band is unsaturated as the maximal absorbance for this band is under 0.2). Thus, this band was employed as a tracer of H/D exchanges. The degree of conversion for H/D exchanges can be described by:

$$\alpha = \frac{I_{\nu_{OD}}(t)}{I_{\nu_{OD}}(t_\alpha)}$$

(5)

where $I_{\nu_{OD}}(t)$ is the integrated absorbance of the $\nu_{OD}$ stretching band at a time $t$ and $I_{\nu_{OD}}(t_\alpha)$ is the integrated absorbance of the $\nu_{OD}$ stretching band at the end of the experiment, when the integrated absorbance no longer increases. The superposition of the plots $\alpha$ versus $t/t_\alpha$ at different temperatures is shown in Fig. 4. The data overlap within error bars, therefore indicating that a unique kinetic model can be employed for temperatures between 110 K and 135 K. The displayed error bars correspond mainly to the correction for other band contributions to the integrated absorbance of the $\nu_{OD}$ stretching band. Indeed, the $\nu_{OD}$ stretching band is mixed with other vibrational bands in the spectra, mainly the combination mode $\nu_3 + \nu_1$ of water (see Fig. 1). The plots of $g_i(\alpha)$ versus time for different kinetic models were linearly fitted, as plotted in Figs. A1 and A2. The corresponding $\overline{\chi^2}_i$ are shown in Fig. A3. It is clear that pseudo second and third order (O2 and O3) kinetic models, with $\overline{\chi^2}_i \sim 1$, are the most accurate to describe the H/D exchanges in both mixtures ($H_2O:CD_3ND_2$ and $H_2O:CD_3OD$). Kinetic constants were derived from the simplest O2 kinetic model to draw the Arrhenius diagrams shown in Fig. 5. The obtained activation energy $E_a$ and frequency factor $A$ values are listed in Table 3. Activation energies are $4300 \pm 900$ K and $3300 \pm 100$ K for $H_2O:CD_3OD$ and $H_2O:CD_3ND_2$ ice mixtures, respectively. The larger error bars for the $H_2O:CD_3OD$ ice mixture are due to the higher spectral congestion (extracting the $\nu_{OD}$ stretching band of HOD was trickier than in the case of methylamine) and sublimation effects. These activation energies are similar to those derived for the $H_2O:D_2O$ mixture, which range between $3000$ K and $5000$ K (Collier et al., 1984; Fisher and Devlin, 1995; Lamberts et al., 2015).

Although the best models for the two H/D exchange reactions are O2 and O3, it should be noted that astrochemical models generally adopt a pseudo first-order (O1) formulation for bimolecular reactive processes (a total second-order with partial first-order for each molecule) (e.g., Hasegawa et al., 1992). Kinetic parameters deduced from pseudo second-order models are obviously not applicable in such models. To circumvent this problem we provide Arrhenius parameters assuming a pseudo first-order kinetic model (Table 3) for the organic molecule. The activation energies are $4100 \pm 900$ K and $3350 \pm 100$ K for $H_2O:CD_3OD$ and $H_2O:CD_3ND_2$ ice mixtures, respectively. These values are thus very similar to those obtained using the pseudo second-order model. In particular, the difference in the activation energies between the two ice mixtures remains significant. We note, however, that in the case of methanol the pre-exponential factor is larger by a factor of $\sim 7$ in the O2 model with respect to the O1 model.

3.4. Kinetics of crystallization

In the range of temperature where H/D exchanges occur (110–150 K), crystallization of the sample is observed. This well studied process consists in the physical transformation of a metastable phase of water ice, the amorphous solid water (ASW), to the stable cubic crystalline form (Ic). This molecular reorganization may be intimately related to the feasibility of isotopic exchange in amorphous solid water, as discussed by Devlin (2001). Here, the kinetics of crystallization of the $H_2O:CD_3OD$ and $H_2O:CD_3ND_2$ ice mixtures is described using the formalism employed above for H/D exchanges. The rate of crystallization of pure ASW has been investigated in many previous studies (Schmitt et al., 1989; Dohnálek et al., 1999, 2000; Hage et al., 1994, 1995; Jenniskens and Blake, 1996; Maté et al., 2012; Safari et al., 2003; Safari and Mullins, 2004; Smith et al., 2011). The kinetics has been shown to follow nucleation models but a large variation in the Avrami exponents and in the activation energies (from $\sim 5000$ K to $10,000$ K) was observed. Thus, in order to compare the two ice mixtures crystallization with pure ASW ice crystallization under the same experimental conditions, isothermal experiments on pure ASW were performed in the same temperature range.

Our approach to measure the crystallization kinetics consists of assuming that the blended water stretching band ($\nu_1$ and $\nu_3$) at $\sim 3250$ cm$^{-1}$ is a linear combination of an amorphous spectrum and a crystallized spectrum, as shown in Fig. A4. The degree of conversion $\alpha$ for the crystallization is then simply described by the linear combination coefficient. The superposition of the plots $\alpha$ versus $t/t_\alpha$ for different temperatures is shown in Fig. 6. The displayed error...
bars result from the linear decomposition method. For pure ASW ice and H$_2$O:CD$_3$ND$_2$ ice mixtures, it is observed that the degree of conversion is close to zero for a significant period of time, which decreases when increasing temperature. Hage et al. (1995) observed the same phenomenon in a deuterated ASW film. This is not specific to water crystallization as it appears frequently in phase change kinetic. It is called an induction period and is interpreted as the time for nucleus of new solid phase to form and grow to detectable size (Brown et al., 1980; Söhnel and Mullin, 1988). In the present work, modifications of the IR bands are too faint to be detectable during this induction period even if structural rearrangement processes are already taking place. As kinetic models do not account for such an induction period, the corresponding data points were excluded and they are not reported in Figs. A5–A7 where $g_i (\alpha)$ is plotted as function of $t/t_i$ for different kinetic models.

The $\chi^2$ associated to the kinetic models are shown in Fig. A8. It is interesting to note that the best model to describe the crystalization kinetics is not unique. Thus, for the H$_2$O:CD$_3$OD ice mixture, the best models are O2 and O3, while for pure ASW ice and H$_2$O:CD$_3$ND$_2$ mixture the best model is an Avrami model (A2). The fits at 125 K (or 130 K) can be found in Fig. 6. Arrhenius diagrams are shown in Fig. 7 and the calculated Arrhenius parameters are given in Table 3. In the case of the H$_2$O:CD$_3$OD mixture, the activation energy associated to the crystallization process is found to be 4550 ± 150 K. As mentioned above, in the case of pure ASW ice and H$_2$O:CD$_3$ND$_2$ mixture, an induction period precedes the Avrami period. The temperature dependence of this induction period is well described by an Arrhenius type equation:

$$k_{\text{ind}} = \frac{1}{t_{\text{ind}}} = A_{\text{ind}} \exp \left( - \frac{E_{\text{ind}}}{T} \right)$$  

(6)

where $t_{\text{ind}}$ is the total duration of the induction period and $A_{\text{ind}}$ and $E_{\text{ind}}$ are the Arrhenius parameters. The corresponding Arrhenius diagrams are also shown in Fig. 7 and the Arrhenius parameters for the induction period are listed in Table 3. It should be noted that both the Avrami and induction periods must be considered when estimating the characteristic time for crystallization at a given temperature (see Section 4).

Table 3 shows that for our 1 $\mu$m ($\approx$3000 ML) ASW film, pure or enriched with 2% organic molecules (CD$_2$ND$_2$ and CD$_3$OD), the activation energies lie in the range 4500–7000 K, consistent with literature values (see above). It should be noted, however, that the organic molecules modify both the rate of ice crystallization (higher for CD$_3$OD than CD$_3$ND$_2$) and the kinetic law.

Finally, we note that the crystallization kinetics of deuterated water is slightly different from that of hydrogenated water. Hage et al. (1995) and Smith et al. (2011) have thus measured the Arrhenius parameters ($A$: $E_a$) for the crystallization of H$_2$O and D$_2$O and they found that the onset temperature and the time needed for complete crystallization is higher in the case of deuterated ASW. For instance, at 140 K, 5 h are needed for D$_2$O crystallization against half an hour for H$_2$O. D$_2$O is therefore less mobile than H$_2$O but, on the other hand, more time is given to defect activity before the completion of crystallization. The kinetics of H/D exchange is therefore expected to be similar in H$_2$O:DCN and D$_2$O:HCN mixtures.

4. Discussion

4.1. Exchange mechanisms

We have shown that H/D exchanges occur quickly between water and both hydroxyl (–OD) and amine (–ND$_2$) functional groups above 110 K, with activation energies in the range 3000–5000 K. In contrast, no exchange is observed with CH$_3$ alkyl groups or with HCN. Many studies on H/D exchanges between H$_2$O and D$_2$O in solid state suggest the strong implication of the hydrogen bond, although controversy exists in the detailed mechanism (Collier et al., 1984; Devlin, 2001; Fisher and Devlin, 1995; Gálvez et al., 2011; Lee et al., 2007; Lamberts et al., 2015; Pat-El et al., 2009). Two successive steps are generally invoked within the so-called “hop-and-turn” process (Eq. (6)): (1) a mechanism of proton hopping via hydrogen bond from D$_2$O to H$_2$O to form two coupled HOD molecules; (2) the propagation of orientational defects to form two isolated HOD molecules.

$$D_2O + H_2O \rightarrow 2(HOD)_{sp} \rightarrow 2(HOD)_{is}$$  

(7)

The two steps have been investigated by Collier et al. (1984). A schematic representation of the “hop-and-turn” process in H$_2$O:CD$_3$OD is shown in Fig. 8.

Our experiments have shown that H/D exchanges proceed through molecular groups able to form strong hydrogen bonds with water. Indeed, the proton affinities of CH$_3$NH$_2$ and CH$_3$OH are 107.7 $\times 10^3$ K and 91.5 $\times 10^3$ K, respectively, while it is only ~86.2 $\times 10^3$ K for HCN (e.g. Rablen et al., 1998). Proton affinity is a measure of the gas-phase basicity and it is correlated with the hydrogen bond strength (Rablen et al., 1998) or the polarizability of the atoms. It may thus give an estimate of the binding energy in solution or in ice. In this respect, the relative values for the proton affinity of CH$_3$NH$_2$, CH$_3$OH and HCN are consistent with our observations, supporting the interpretation that H/D exchanges are promoted in species with functional groups capable of strong hydrogen bonds with water. We also note that since the activation energies for H/D exchanges and crystallization are close, small differences in hydrogen bonding energy can simply make H/D exchanges too slow with respect to the water reorganization, as suggested by our D$_2$O:HCN experiment.

Although the detailed mechanism for propagation of charge and orientational defects in ice is still debated (see Gálvez et al. (2011) and references therein), it appears that thermally activated H/D exchanges and crystallization are intimately related phenomena. As mentioned above, ASW crystallization has been widely studied but large variations in the kinetics parameters are reported in literature. These variations are primarily due to different experimental conditions. The crystallization process is indeed sensitive to many factors including the underlying substrate, film deposition temperature (Dohnálek et al., 2000; Maté et al., 2012), film thickness and density and, most importantly, deposition and heating rates. The induced variations are rather complex. Dohnálek et al. (2000) and Löfgren et al. (1996) have thus shown that the Avrami exponent increases (the slope of the sigmoid is steeper) and that the crystallization process is faster when decreasing thickness to 10–110 monolayers (ML) films. On the contrary, Safarik et al. (2003) observed crystallization acceleration with increasing thickness for films thicker than 55 nm (177 ML). The dependence of ASW crystallization with dopant was studied by Souda (2007). It was found that the incorporation of methanol molecules in the bulk of ASW ice lowers the crystallization temperature, which is in agreement with our observations (the lowest activation energy is for CD$_3$OD, see Table 3). In addition, our results show that crystallization follows a second order kinetics, in contrast to pure ASW and H$_2$O:CD$_3$ND$_2$ ice mixture for which the best model is A2. In Avrami kinetics, a first period with a slow rate, which corresponds to the nucleation of a significant number of new phase nuclei, is followed by a rapid transformation as nuclei grow. The transformation then slows down until completion. The first stage is drastically reduced in the case of H$_2$O:CD$_3$OD ice.
mixture as if the nucleation process was instantaneous. The apparent O2 kinetics may thus simply reflect a truncated Avrami law.

4.2. D/H composition of cometary ices

4.2.1. Isotopic evolution of OH and NH2 bearing molecules

In comets, water ice is the main compound in which other molecular species are probably diluted. Except CO and CO2, most molecular species are neighbored with water molecules. Ice sublimation is processed through a succession of physical processes involving energy and mass exchanges and transports within the porous cometary nucleus (Marboeuf et al., 2012). As a consequence of the control of the surface energy balance by solar illumination, a stratified medium takes place whose upper icy layer is composed of crystalline water ice and possibly clathrates. The more volatile species (e.g. CO, CH4) are partly released by ASW ice at low temperature and propagates from some depth through the porous medium by diffusion and successive adsorption and desorption on the walls of open pores, while others are mostly released at shallower depths during water ice crystallization or during decomposition of clathrates earlier formed during crystallization or by gas–ice reaction (Marboeuf et al., 2010). In this regard, all molecules expelled from the nucleus have strongly interacted with water molecules in the solid state.

Our experiments show that exchanges triggered by ASW crystallization occur over couples of minutes or hours on –OH and –NH2 chemical groups at temperature above 110 K. Fig. 9 shows the half-time of three main thermal processes in ASW, i.e. H/D exchange, crystallization and H2O desorption, as function of the ice temperature. It is observed that H/D exchanges on –OH functional groups and ASW crystallization occur within similar timescales. In contrast, in the case of –NH2 groups, H/D exchanges proceed at a significantly larger rate (smaller half-life) than crystallization, as expected from the activation energies listed in Table 3. Since in both cases H/D exchanges are faster than crystallization and desorption above 100 K, the fractionation of the –OH and –NH2 groups should change upon thermal heating. The heating timescales are however different in the laboratory and in a comet. In particular, the temperature profile within a nucleus subsurface evolves slowly over months when a comet approaches the Sun.

A model of cometary nucleus evolution was applied to Comet 67P/Churyumov–Gerasimenko (67P/CG) in Marboeuf and Schmitt (2014). The crystallization timescale is reported in Fig. 10 where it is found to be about 40 days on a thickness of a few tens of centimeters. Further simulations performed for the present study reveals variation of this timescale, from 4 days to several months, by varying the thickness of the dust crust mantle at the surface of the comet, the thermal conductivity of the porous medium and the CO/CO2/H2O composition. As a result, cometary ASW crystallizes on timescales which are rather similar to those of our laboratory experiments.

We note that the formation of clathrates instead of pure crystalline water ice is an alternative process, which in the case of coexistence with proton acceptor guest species also favors water orientational mobility and hydrogen bonding (Devlin, 2001; Richardson et al., 1985). In addition, CH3OH is able to form weak hydrogen bond with the oxygen of the water molecules of the cages and seems to promote the formation of clathrates of other gases in specific conditions during the crystallization of amorphous ice mixtures (Williams and Devlin, 1997; Notesco and Bar-Nun, 2000). In summary, the D/H composition of all molecular species that contain –OH or –NH2 functional groups will evolve during nucleus activity. In addition, water molecules should exchange with themselves, and will tend to homogenize their composition if the primitive ice is isotopically heterogeneous.

Now, the final composition of the chemical groups on these molecular species depends on whether thermodynamic equilibrium is attained. In fact, we can reasonably assume that this equilibrium is reached considering the faster H/D exchange kinetics with respect to the crystallization kinetics: Fig. 11 shows, on the same graph, the degree of conversion for both processes versus time at 125 K in the case of methyleneamine. It is clear that an H/D exchange equilibrium is attained around 10 - 103 s, before the crystallization process runaway at 25 - 103 s. H/D exchanges thus proceed during the very initial phase of the crystallization process. Smith and Kay (1999) have provided evidences that ice melts into a deeply metastable extension of normal liquid water during this phase (also called the glass transition). This liquid-like behavior naturally favors H/D exchange equilibrium. In this regard, the D/H ratio of the organic species may be related to the thermodynamic constant K(T) of Eq. (4) via the equilibrium equation:

\[ K(T) = \frac{[R-H][HOD]}{[R-D][H_2O]} \]

The K(T) constant depends at first order on the nature of the molecular species (number of atoms, molecular structure) and at second-order on the nature and energetics of the chemical group (–OH versus –NH2). Hence, these parameters controls mobility and reorganization, and finally the ability to establish hydrogen bonds during ice crystallization. Unfortunately, we lack thermodynamic constant values for reactions between water and many of the molecules detected so far in comets, and experimental studies appear here necessary. An alternative strategy is however possible in the case of Comet 67P/CG, if D/H ratios can be obtained for a broad set of molecules.

4.2.2. The HCN molecule

Our experiments show that H/D exchanges operate through hydrogen bonds. Strictly speaking, hydrogen bond requires a proton bound to an electronegative atom as N or O. But for the HCN molecule, H is bound to a carbon atom. Nevertheless, HCN is known as a very weak organic acid, and therefore weakly releases protons in liquid water. A strong hydrogen bond is reported in HCN dimers and HCN molecular crystal, involving H and N atoms from adjacent molecules (Müller et al., 1993; Panczyk, 1977). Studies also report that a hydrogen bond is present in H2O and HCN dimers (Bernstein et al., 1997). Therefore, a similar mechanism as that proposed for –OH and –NH2 functional groups cannot be excluded. Our experiments do not support H/D exchanges between HCN and deuterated ASW. As reported above, this result is consistent with the proton affinity, but it does not rule out the possibility of exchanges in different conditions.

5. Conclusions

The main conclusions are the following:

1. D/H exchanges between –OH and –NH2/NH functional groups of organic molecules and amorphous water ice are controlled by proton exchange through hydrogen bonds. The process requires molecular motion and is strongly catalyzed by water ice crystallization.

2. The kinetics of the H/D exchanges have been determined experimentally. H/D exchange kinetics is best described by a pseudo second-order kinetic law with activation energies of 4300 ± 900 K (36 ± 7 K mol⁻¹) and 3300 ± 100 K (27.5 ± 0.8 K mol⁻¹) for H2O:CD3OD and H2O:CD3ND2 ice mixtures, respectively. The corresponding pre-exponential factors ln(A(s⁻¹)) are 25 ± 7 and 20 ± 1, respectively. Physical conditions within
cometary nucleus when a comet approaches the Sun make it plausible that –OH and –NH functional groups of organic molecules equilibrate with water ice. The D/H composition of X–OH and X–NH species may therefore not be representative of their initial composition prior to sublimation.

3. In contrast, the H/D exchange between –CH bond and water ice is not of concern on the timescale of cometary subsurface evolution.

4. H/D exchanges between HCN and amorphous solid water are probably inhibited by the low kinetics of proton exchanges (through the water–HCN hydrogen bond) with respect to ASW crystallization.

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Appendix A

Fig. A1. H/D exchange function g, for a mixture of H2O:CD3OD at different temperatures for various kinetic models i listed in Table 2. The linear fit for the isothermal experiment at 125 K is shown for each model (dotted line).
Fig. A2. H/D exchange function $g_i$ for a mixture of $\text{H}_2\text{O}:\text{CD}_3\text{ND}_2$ at different temperatures for various kinetic models $i$ listed in Table 2. The linear fit for the isothermal experiment at 125 K is shown for each model (dotted line).
Fig. A3. Average reduced $\chi^2$ for various kinetic models fitting the time dependence of integrated kinetic model $g_i$ (Figs. A1 and A2). The average is done over 5 isothermal experiments ($T = 110$ K, 115 K, 120 K, 125 K and 130 K) in the case of methylamine and 4 experiments ($T = 120$ K, 125 K, 130 K and 135 K) in the case of methanol.

Fig. A4. Fourier transform infrared absorption spectra of the water stretching band $v_1$ & $v_2$ at $\sim 3250$ cm$^{-1}$ obtained during an isothermal experiment (in gray). The dotted line corresponds to the theoretical spectrum ($St$). It is the linear combination of an amorphous spectrum ($\times (1 - \alpha) \times Sa$) (in red) and a crystallized spectrum ($\times \alpha \times Sc$) (in green), the combination coefficient being the degree of conversion $\alpha$ (i.e. $St = (1 - \alpha) \times Sa + \alpha \times Sc$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Fig. A5. Crystallization function $g_i$ for a mixture of H$_2$O:CD$_3$OD at different temperatures for the various kinetic models listed in Table 2. Linear fits for the isothermal experiment at 125 K are shown (dotted line).
Fig. A6. Crystallization function $g_i$ for a mixture of H$_2$O:CD$_3$ND$_2$ at different temperatures for the various kinetic models listed in Table 2. Linear fits for the isothermal experiment at 125 K are shown (dotted line).
Fig. A7. Crystallization function $g_i$ for H$_2$O pure at different temperatures for the various kinetic models listed in Table 2. Linear fits for the isothermal experiment at 125 K are shown (dotted line).

Fig. A8. Average reduced $\chi^2$ for various integrated kinetic models $g_i$ fitting the crystallization versus time showed in Figs. A5–A7. The average is done over 3 experiments ($T = 120$ K, $T = 125$ K and $T = 130$ K) in the case of methyamine, 4 experiments ($T = 120$ K, $T = 125$ K, $T = 130$ K, $T = 135$ K) in the case of methanol and 5 experiments ($T = 125$ K, $T = 130$ K, $T = 135$ K, $T = 140$ K, $T = 143$ K) in the case of pure H$_2$O.