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**Author:** Lamberts, Agneta Luciana Matthanja (Thanja)

**Title:** Unraveling the surface formation of regular and deuterated water in space: a combined laboratory and computational study

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Sets of systematic laboratory experiments are presented - combining UHV cryogenic and plasma-line deposition techniques - that allow to compare H/D isotopic effects in the reaction of H$_2$O (D$_2$O) ice with the hydroxyl radical OD (OH). The latter is known to play a key role as intermediate species in the solid state formation of water on icy grains in space. The main finding of our work is that the reaction H$_2$O + OD $\rightarrow$ OH + HDO occurs and that this may affect the HDO/H$_2$O abundances in space. The opposite reaction D$_2$O + OH $\rightarrow$ OD + HDO is much less effective, and also given the lower D$_2$O abundances in space not expected to be of astronomical relevance. The experimental results are extended to the other four possible reactions between hydroxyl and water isotopes and are subsequently used as input for kinetic Monte Carlo simulations. This way we interpret our findings in an astronomical context, qualitatively testing the influence of the reaction rates, excess energy, and cloud extinction.

8.1 Introduction

Surface reactions on grains have been proposed as an effective way to form water at the low temperatures typical for the interstellar medium (van de Hulst, 1949; Tielens & Hagen, 1982). Over the last ten years many of the possible reactions have been tested in various laboratories and reaction routes, rates, and branching ratios have been determined (Hiraoka et al., 1998; Miyauchi et al., 2008; Ioppolo et al., 2008, 2010; Cuppen et al., 2010; Romanzin et al., 2011). The general conclusions obtained in these studies are in line with each other (Dulieu, 2011) and have been summarized by van Dishoeck et al. (2013).

A detailed characterization of the solid state formation of water also holds the potential to study deuteration effects. With the goal to understand how water was delivered to Earth, there has been much interest in linking the HDO/H$_2$O ratio in cometary, interstellar, and laboratory ices as well as astronomical (gas-phase) observations to ratios as found in our oceans (Rodgers & Charnley, 2002; Hartogh et al., 2011). Therefore, both the origin of the HDO/H$_2$O ratio in the ices and their subsequent chemical and thermal processing are currently widely studied (Caselli & Ceccarelli, 2012). It is in fact during the water formation on dust surfaces when the deuterium fractionation commences. This preferential incorporation of D over H in molecules can lead to D/H ratios in molecules that are much larger than the primordial ratio of $\sim 1.5 \times 10^{-5}$ (Piskunov et al., 1997; Oliveira et al., 2003). To understand the origin of this fractionation, it is neccessary to consider both the gas-phase and solid-state processes that are at play. The driving forces behind these processes are the lower zero-point energy of an X-D bond with respect to an X-H bond and the difference in tunneling behavior, both as a result of the larger mass of deuterium (Roberts et al., 2003; Tielens, 1983; Caselli & Ceccarelli, 2012; Lipshtat et al., 2004). One of the possible enhancement routes for hydrocarbon bonds is the simple replacement of a hydrogen by a deuterium via a deuteron mediated abstraction mechanism: $\text{CH + D} \rightarrow \text{C + HD}$ followed by $\text{C + D} \rightarrow \text{CD}$ (Nagaoka et al., 2005, 2007). An example is substitution of H for D in solid methanol, which has been found to be efficient, whereas the reverse reaction (substituting D for H) is not. Note that Nagaoka et al. (2005) have also attempted to substitute hydrogen in water by the same process, but did not find any deuteration upon D exposure. The non-occurence of reaction H$_2$O + D has been confirmed in our laboratory (unpublished data).

Another abstraction process, so far studied in less detail, involves OH and OD radicals. Hydroxyl radicals play an important role as reactive intermediates in water formation (see e.g. Cuppen et al., 2010; Chapter 5). Furthermore, recent microscopic models have shown that the radical concentration in the ice can be very high if photon penetration is included (Chang & Herbst, 2014). Garrod (2013) indicated the importance of abstraction reactions by the hydroxyl radical in the framework of complex hydrocarbon molecules. Such an OH induced abstraction mechanism is particularly important in water-rich ices, because both OH and OD radicals are produced on the surface by radical chemistry and by photodissociation of water isotopologues (Ioppolo et al., 2008; Andersson & van Dishoeck, 2008; Öberg et al., 2009).

Considering again the formation of HDO in the ice, the water surface reaction network needs to be duplicated, involving both reactions with hydrogen and deuterium. As a result of the large number of reactions that are in competition with each other and with diffusion, it is experimentally challenging to study hydrogenation and deuteration simultaneously. Therefore, in the past, either the deuteration pathways have been studied separately, e.g., O$_2$ + D (Chaabouni et al., 2012), or specific reaction routes are tackled theoretically and experimentally, e.g., OH (OD) + H$_2$ (HD or D$_2$) and H$_2$O$_2$ (D$_2$O$_2$) + H (D) (Kristensen et al., 2011; Oba et al., 2012, 2014). Here, we add to these studies and investigate the cross links between the
hydrogenation and deuteration networks by the following four hydrogen abstraction reaction via hydroxyl radicals:

\[
\begin{align*}
H_2O + OD & \xrightarrow{k_1} OH + HDO \\
HDO + OD & \xrightarrow{k_2} OH + D_2O \\
HDO + OH & \xrightarrow{k_3} OD + H_2O \\
D_2O + OD & \xrightarrow{k_4} OD + HDO .
\end{align*}
\]

Hydrogen abstraction of OH from H$_2$O (or the fully deuterated analog) can also take place

\[
\begin{align*}
H_2O + OH & \xrightarrow{k_5} OH + H_2O \\
D_2O + OD & \xrightarrow{k_6} OD + D_2O 
\end{align*}
\]

and although this does not have a net effect on the abundances in the ice, it can be seen as an analog of bulk diffusion, of which models indicate it is of great importance in ice chemistry (Vasyunin & Herbst, 2013; Chang & Herbst, 2014; Chapter 5).

Reactions R2 and R3 cannot be studied in the laboratory, because it is not feasible to deposit pure HDO. Room-temperature rapid proton transfer reactions scramble the protons and deuterons and yield a statistical $\sim 1:2:1$ mixture of H$_2$O:HDO:D$_2$O if one were to start from a pure HDO liquid. Such scrambling has been found to take place efficiently even in ices at temperatures far below room temperature (Chapter 7). Therefore, here, only reactions R1 and R4 are tested experimentally, at low temperature and using reflection absorption infrared (RAIR) spectroscopy as an in-situ diagnostic tool.

Note that from an astrochemical point-of-view, reactions R2, R4, and R6 are unlikely to be relevant as a result of the low concentrations of the reactants (D$_2$O and OD) present in the ice. Nevertheless, we put efforts in characterizing R4, as an understanding of the underlying mechanism helps in painting the full picture. Reactions R1 and R3, on the contrary, could occur in regions with a high photon flux as this causes water and isotopologues to dissociate, thus generating additional hydroxyl radicals.

In the following, we outline the experimental setup and sets of experiments performed (Section 8.2), the analysis of the resulting RAIR spectra (Section 8.3), the astrochemical implications by means of a kinetic Monte Carlo model (Section 8.4), and we conclude with summarizing remarks (Section 8.5).

### 8.2 Experimental Methods

Two sets of representative experiments and their corresponding control experiments are summarized in Table 8.1. All measurements are performed at a surface temperature of 15 K for a duration of 90 minutes. The two experiments that are used for this study are part of a larger set, varying mixing ratios and temperatures, and found to be optimum for the goals set in this work. The findings of the other experiments are largely in line with the ones discussed here, but do not add additional information.

Experiments are performed using the SURFRESIDE$^2$ setup, which was constructed to systematically investigate solid-state reactions leading to the formation of molecules of astrophysical interest at cryogenic temperatures. The setup has already been extensively described in Ioppolo et al. (2013) and therefore only a brief description of the procedure is given here.

SURFRESIDE$^2$ consists of three UHV chambers with a room-temperature base-pressure between $10^{-9} - 10^{-10}$ mbar. A rotatable gold-coated copper substrate in the center of the
main chamber is cooled to the desired temperature using a He closed-cycle cryostat with an absolute temperature accuracy of $\leq 2$ K.

Both reactions R1 and R4 require a water isotopologue to be co-deposited along with a hydroxyl isotopologue. The former are deposited through a metal deposition line under an angle of 90° and are prepared in a separate pre-pumped ($\leq 10^{-5}$ mbar) dosing line. After undergoing several freeze-pump-thaw cycles room-temperature vapor of H$_2$O or D$_2$O can partake in the co-deposition. Secondly, the hydroxyl radicals are generated in a Microwave Atom Source (MWAS, Oxford Scientific Ltd, Anton et al. (2000)) using a microwave discharge (300 W at 2.45 GHz) of pure water or heavy water. This discharge is located in a separate UHV beam line with an angle of 45° with respect to the surface. This beam line can be operated independently and is separated from the main chamber by a metal shutter. We cannot quantify the relative deposition rates of all fragments – O, O$_2$, H, H$_2$, OH, HO$_2$, and H$_2$O (or deuterated equivalents). However, an upper limit can be derived from the H$_2$O deposition rate when the microwave source is turned off: $\sim 10^{13}$ cm$^2$ s$^{-1}$. Many discharge products are thus deposited onto the surface, but only one reacts with D$_2$O (or H$_2$O). First, during the calibration stage of our setup the reaction O + H$_2$O is found not to take place, indicating that discharge fragments that reach the surface are no longer in an excited state (Ioppolo et al., 2013). Both H$_2$ and O$_2$ are inert to reactions with other non-radical species as confirmed previously (Ioppolo et al., 2010). The reaction of H with water isotopologues has been dicussed in the Introduction and does not take place in ices for which the water molecules are hydrogen bonded (Nagaoka et al., 2005). The reaction of HO$_2$ with water is endergonic and has been found to occur in the gas phase only with high barriers (several thousand Kelvin) (Lloyd, 1974). This leaves only the hydroxyl radical to react with a water isotopologue.

To confirm the presence of OH among the H$_2$O discharge products, we co-deposited H$_2$O discharge dissociation products with N$_2$ in a ~ 1:20 ratio during a separate experiment (not listed in Table 8.1). The presence of the OH radical is confirmed via its infrared absorption

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Table 8.1: Summary of the performed experiments with additional calibration and control experiments and corresponding parameters, $T_{\text{surf}} = 15$ K and $t_{\text{exp}} = 90$ min in all cases. The deposition rate of the species is denoted as $f_{\text{dep}}$ and the angle represents the angle of the deposition line with respect to the surface.

<table>
<thead>
<tr>
<th></th>
<th>$f_{\text{dep}}$ (cm$^2$ s$^{-1}$)</th>
<th>45° Discharge</th>
<th>$f_{\text{dep}}$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H$_2^{18}$O 4 × 10$^{12}$</td>
<td>D$_2$O</td>
<td>$\leq 1 \times 10^{13}$ a</td>
</tr>
<tr>
<td>1b</td>
<td>H$_2^{18}$O 4 × 10$^{12}$</td>
<td>D$_2$O</td>
<td>$\leq 1 \times 10^{13}$ a</td>
</tr>
<tr>
<td>1c</td>
<td>–</td>
<td>–</td>
<td>1 × 10$^{13}$</td>
</tr>
<tr>
<td>1d</td>
<td>H$_2^{18}$O 4 × 10$^{12}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2a</td>
<td>D$_2$O 4 × 10$^{12}$</td>
<td>H$_2^{18}$O</td>
<td>$\leq 1 \times 10^{13}$ a</td>
</tr>
<tr>
<td>2b</td>
<td>D$_2$O 4 × 10$^{12}$</td>
<td>H$_2^{18}$O</td>
<td>1 × 10$^{13}$</td>
</tr>
<tr>
<td>2c</td>
<td>–</td>
<td>–</td>
<td>$\leq 1 \times 10^{13}$ a</td>
</tr>
<tr>
<td>2d</td>
<td>D$_2$O 4 × 10$^{12}$</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

a The upper limit is derived from the D$_2$O and H$_2^{18}$O deposition rate when the microwave source is turned off.
at 3547 cm\(^{-1}\) (Cheng et al., 1988). Furthermore, both \(\text{O} + \text{H} \rightarrow \text{OH}\) and \(\text{O}_2 \rightarrow \text{HO}_2 \rightarrow \text{OH} + \text{OH}\) can lead to additional hydroxyl radicals on the surface, which we expect to thermalize quickly on a picosecond timescale (Arasa et al., 2013; Meyer & Reuter, 2014). Finally, the produced \(\text{H}_2\text{O}_2\) that forms upon OH recombination on the surface exhibits a comparable temperature dependent behavior to the \(\text{H}_2\text{O}_2\) features apparent after depositing \(\text{H}_2\text{O}\) dissociation fragments from a similar microwave-discharge plasma by Oba et al. (2011).

A RAIR difference spectrum with respect to the background is acquired every 5 minutes up to the final time of the experiment, 90 minutes. RAIR spectra comprise a spectral range between 4000 and 700 cm\(^{-1}\) with a spectral resolution of 1 cm\(^{-1}\) and are averaged over 512 scans. Our region of interest lies in the 2000-1000 cm\(^{-1}\) range, \(i.e.\), the bending modes of \(\text{H}_2\text{O}\), \(\text{HDO}\) and \(\text{D}_2\text{O}\): 1660, 1490, and 1250 cm\(^{-1}\), respectively. Although the bands are broad, the modes are relatively well separated and can be distinguished from each other, whereas that is not the case in the stretching regions. To further enhance the peak separation between the bands of different species we made use of \(\text{H}_2^{18}\text{O}\) instead of regular \(\text{H}_2^{16}\text{O}\). In the end the effect was limited as in matrix isolation experiments the bending mode of \(\text{H}_2^{18}\text{O}\) is redshifted instead of blueshifted with respect to that of \(\text{H}_2^{16}\text{O}\). In the following, we will refer to all species without mentioning explicitly the oxygen isotope at hand. Band strengths for the bending modes are typically ill-constrained and therefore we focus here on drawing qualitative conclusions.

The fluxes mentioned in Table 8.1 are calculated using the following relation

\[
f_{X,O} = \frac{c_{X,O} P_{X,O} \langle v \rangle}{4 k_B T}
\]

where \(P_{X,O}\) is the pressure, \(c_{X,O}\) is the calibration factor for the pressure gauge for the isotopologues of water, \(\langle v \rangle\) is the thermal velocity of the vapor molecules at 300 K, \(k_B\) is the Boltzmann constant, and \(T\) corresponds to the (room) temperature. The calibration factors for both water and heavy water are found to be equal (Straub et al., 1998; Itikawa & Mason, 2005) and we assume here that this also holds for \(\text{H}_2^{18}\text{O}\).

The separate experiments within a series, 1a – 1d and 2a – 2d (Table 8.1), are performed sequentially, \(i.e.\), on top of each other to make sure that the plasma conditions and deposition rates do not vary between experiments focusing on the abstraction process and the corresponding control experiments. The order in which the measurements are performed is (c)-(a)-(b)-(d). In this particular way first the plasma is able to stabilize before experiment (c) is started. During experiment (c) only the plasma products are deposited and spectra of the accumulated products are recorded. Subsequently the shutter of the plasma chamber is closed, while the plasma remains switched on and a new background spectrum is recorded. It is then possible to perform experiment (a), simply by opening the shutter of both the plasma chamber and the regular deposition line. At the end of this experiment, the discharge is switched off, the shutters of both beamlines are closed and another background spectrum is recorded. By opening the shutters, experiment (b) is performed, \(i.e.\) no plasma fragments are deposited, but rather the parent molecule itself. Finally, both shutters are closed and a background spectrum is recorded, followed by recording the deposition of non-dissociated species, experiment (d).

### 8.3 Results and Discussion

In Figures 8.1 and 8.2 the RAIR spectra recorded after 90 minutes of co-deposition are depicted for experiments 1a - 1c (to investigate reaction R1) and 2a - 2c (idem reaction R4) mentioned in Table 8.1. An overview of the products found in the various spectra and their respective origins is given in Table 8.2. A clear finding is that HDO is only seen in Figure 8.1 and not in Figure 8.2, indicative for different reaction efficiencies.
Figure 8.1: H$_2$O + OD. RAIR spectra acquired after 90 minutes of co-deposition for experiments (1a)-(1c), Table 8.1. Graphs are offset for reasons of clarity.

Figure 8.2: D$_2$O + OH. RAIR spectra acquired after 90 minutes of co-deposition for experiments (2a)-(2c), Table 8.1. Graphs are offset for reasons of clarity.
In Figure 8.1, five characteristic infrared features are visible, namely for H$_2$O, HDO, D$_2$O, D$_2$O$_2$, and $^{16}$O$_3$. The presence of these species can be explained either by deposition, by (re-)combination of discharge products, or through additional reactions. During experiment 1a (H$_2$O + OD), three molecules are formed in the course of the co-deposition: HDO, D$_2$O$_2$, and O$_3$. Both deuterated peroxide and ozone are also visible in experiment 1c when only dissociated D$_2$O is deposited on the surface. This indicates that reactions between discharge fragments are responsible for the production of these species. The formation of HDO is, however, observed as a result of reaction R1 which only takes place when the plasma is switched on. The small amount of HDO observed in control experiment 1b, is attributed to contamination in the D$_2$O sample and is clearly much weaker compared to the feature present in experiment 1a.

In Figure 8.2, four characteristic infrared features are observed, corresponding to H$_2$O, H$_2$O$_2$, D$_2$O, and $^{18}$O$_3$. Here, the ozone consists of $^{18}$O atoms, as a result of the H$_2$$^{18}$O plasma that produces both $^{18}$O$_2$ and $^{18}$O. Again, ozone and hydrogen peroxide are generated as a result of discharge fragment (re-)combinations. Throughout experiment 2a (D$_2$O + OH), these are the only two molecules that are formed while HDO production seems to be lacking. However, the peak positions of hydrogenperoxide and singly deuterated water in water-rich environments are very close to each other: ~1435 versus ~1475 cm$^{-1}$ (Devlin, 1990; Oba et al., 2014). Therefore special care is needed to conclude that HDO is not formed efficiently, as its absorption feature may be buried in the H$_2$O$_2$ signal. For a detectable level one expects to see a clear shift and a change in total integrated intensity of the peak. In Figure 8.3 a direct comparison between experiment 2a and control experiment 2c is shown. The right panel zooms in on the region of the OH bending mode of both HDO and H$_2$O$_2$ (discussed here), while the left panel zooms in on the $\nu_2 + \nu_6$ combination band of H$_2$O$_2$ at 2860 cm$^{-1}$. The latter is the only H$_2$O$_2$ band which does not overlap with other species (Lannon et al., 1971) and, as such, can be used as a reference point.

The figure shows that the spectra shift. The OH bending mode band shifts by about 20 cm$^{-1}$, halfway the peak positions of the H$_2$O$_2$ and HDO bands. This would be consistent with HDO formation, but a closer look learns that this shift is due to the changing matrix environment, i.e., the presence of D$_2$O in experiment 2a or lack thereof in experiment 2c, rather than a detectable amount of HDO formation. The first argument to support this is that also the combination band shifts, roughly 7 cm$^{-1}$, but in this case the band does not overlap with HDO and is therefore expected not to shift unless the matrix plays a role.

Second, to further study the influence of a mixed HDO and H$_2$O$_2$ ice on the bandwidth of the OH bending mode, we artificially added an HDO component to the H$_2$O$_2$ component of the H$_2$O plasma deposition. This is done by selecting specifically the HDO band in experiment 1a in Fig. 8.1, setting its baseline to zero around 1350 and 1530 cm$^{-1}$ and adding it to the same region of the spectrum obtained in experiment 2c. This shows that the final band should then exhibit a larger bandwidth. Clearly the observed band in Fig. 8.3 seems to have shifted rather than to have changed its profile because of merging features. This is only possible when the reaction D$_2$O + OH $\rightarrow$ OD + HDO is not efficient.

The third argument follows from a comparison of the integrated band areas (A) of the OH bending mode in experiments 1a, 2a and 2c. Since this involves the rather arbitrary choice of the range over which to integrate, the three experiments were all integrated over several ranges. The first point was chosen between 1340 and 1365 cm$^{-1}$ and the second point between 1520 and 1550 cm$^{-1}$. Subsequently, the ratio between (A$_{\text{exp.~2a}}$ − A$_{\text{exp.~2c}}$) and A$_{\text{exp.~1a}}$ is derived for all possible combinations of the two limits for the integration range. The maximum ratio poses a strict upper limit on the ratio $k_4/k_1 = 0.2$. We therefore conclude that the observed
Table 8.2: List of assigned species in the experiments and their respective origins.

<table>
<thead>
<tr>
<th>Products</th>
<th>Origin</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>Deposition</td>
<td></td>
</tr>
<tr>
<td>HDO</td>
<td>H₂O reacts with discharge fragments: H₂O + OD → OH + HDO OH + D → HDO</td>
<td></td>
</tr>
<tr>
<td>D₂O</td>
<td>Undissociated molecules in the discharge</td>
<td></td>
</tr>
<tr>
<td>D₂O₂</td>
<td>Reaction of discharge fragments: OD + OD → D₂O₂ O₂ + D + D → D₂O₂</td>
<td></td>
</tr>
<tr>
<td>O₃</td>
<td>Reaction of discharge fragments: O + O → O₂ O + O₂ → O₃</td>
<td></td>
</tr>
<tr>
<td>Experiment 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>Undissociated molecules in the discharge</td>
<td></td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Reaction of discharge fragments: OH + OH → H₂O₂ O₂ + H + H → H₂O₂</td>
<td></td>
</tr>
<tr>
<td>D₂O</td>
<td>Deposition</td>
<td></td>
</tr>
<tr>
<td>O₃</td>
<td>Reaction of discharge fragments: O + O → O₂ O + O₂ → O₃</td>
<td></td>
</tr>
</tbody>
</table>

Figure 8.3: Comparison of H₂O₂ RAIR spectra acquired after 90 minutes of co-deposition for experiments (2a) and (2c), Table 8.1. The right panel shows the wavelength domain studied here. The left panel is an additional spectrum in a combination band domain. Graphs are offset in such a way that the bands in both experiments overlap regardless of the baseline.
A final, independent argument comes from theory. From the experimental set presented here, we conclude that reaction R1 does, and reaction R4 does not efficiently take place at a detectable level for the specific conditions studied. To understand this difference and the overall likelihood of the reactions to take place at low temperatures, the gas-phase Gibbs free energies at 15 K are calculated using the enthalpies and entropies given by Chase (1998):

\[
\begin{align*}
R_1: & \quad -1.21 \text{ kJ mol}^{-1} = -145.66 \text{ K} \\
R_2: & \quad -1.32 \text{ kJ mol}^{-1} = -159.15 \text{ K} \\
R_3: & \quad 1.21 \text{ kJ mol}^{-1} = 145.66 \text{ K} \\
R_4: & \quad 1.32 \text{ kJ mol}^{-1} = 159.15 \text{ K}.
\end{align*}
\]

The experimentally found difference in reaction probability for reactions R1 and R4 is in line with the predictions from gas-phase Gibbs free energies. Extrapolating the experiments, a similar behavior for reactions R2 and R3 is expected.

Additionally, from a tunneling point-of-view, the first two reactions transfer a hydrogen atom, whereas the final two reactions transfer a deuteron. Calculating the effective mass, \( \mu \), for this system as outlined by Oba et al. (2012) to find the kinetic isotope effect involved, we find a \( \sim 25\% \) decrease in the reaction probabilities assuming that the tunneling rate is well-described by the Wentzel-Kramers-Brillouin or square-potential with width \( a \) and height \( E \) approximation:

\[
k_{\text{tunneling}} \propto \exp \left( -\frac{2a}{h} \sqrt{2\mu E} \right). \tag{56}
\]

This is in agreement with our experimental comparison between the first and the last reaction. Note, however, that the endergonicity still plays a role when tunneling is considered to further decrease the reaction probability (Chapter 6).

To summarize all experimental and theoretical findings and considerations, we expect the following relations to hold:

\[
\begin{align*}
k_4 & \ll k_1 \quad \text{(with an absolute upper limit } k_4 < 0.2 k_1) \\
k_1 & \approx k_2 \quad \text{(assuming thermal activation only)} \\
k_1 & > k_2 \quad \text{(assuming that tunneling plays a role)} \\
k_3 & \approx k_4.
\end{align*}
\]

We cannot draw any definitive conclusions concerning reactions R5 and R6, although it is important to note that the change in Gibbs free is zero on average and if tunneling is involved \( k_6 < k_5 \).

8.4 Astrochemical Implications

The key to the astrochemical relevance of the reactions studied here lies in the relative abundances of the water isotopes \( N(H_2O) > N(\text{HDO}) > N(D_2O) \) and the ice abundance of both hydroxyl radical isotopes, OH and OD. These species can be either formed on the interstellar dust surfaces via \( O + H \) and \( O + D \) reactions or via photodissociation of frozen \( H_2O, \text{HDO} \), or \( D_2O \). Therefore, especially in rather low-\( A_V \), and relatively high density regions such as translucent clouds the deuterium enrichment effect of the reactions studied here can be substantial. In these regions water is continuously formed and destroyed on the surface until a steady state is reached (Cuppen & Herbst (2007); Cazaux et al. (2010), Chapter 5). Each
time a formed HDO molecule is dissociated into OH + D or, more likely, OD + H (Koning et al., 2013), there is a chance that the hydroxyl radical evaporates. The OD evaporation is in competition with three solid-state reactions creating or recreating HDO:

\[
\begin{align*}
H + OD & \rightarrow HDO \quad (R7) \\
H_2 + OD & \rightarrow H + HDO \quad (R8) \\
H_2O + OD & \rightarrow OH + HDO \quad (R1)
\end{align*}
\]

To further characterize this, a previously-used continuous-time random-walk KMC model for water formation is adapted here (Chapters 4 and 5) with an extension of the chemical surface network including all deuteration reactions. All hydrogenation reactions are duplicated and replaced with deuterium analogue(s), initiated by surface reactions with HD or D. If tunneling is expected to be involved, the activation energies are altered accordingly (Oba et al., 2012, 2014). Furthermore, for reactions that can result in more than one product, the branching ratios between the product channels are distributed statistically. We realize that this model is a rather crude approximation, which is necessary, however, as a full model has to take into account too many aspects. It merely serves to test which parameters are crucial when including OH and OD abstraction reactions in the solid state water formation network.

The parameters of the ‘translucent cloud’ studied here are summarized below. They are chosen such to have a high enough photon flux to induce photodissociation of water, but simulatenously to allow for a minimal build-up of an icy layer. First, a low H_2 gas-phase abundance of 4 cm\(^{-3}\) is chosen to minimize the computational cost related to H_2 diffusion on the surface. The validity of this assumption has been tested by changing the H_2 abundance to 500 cm\(^{-3}\) and indeed we find no significant difference between the simulations. Second, a high D abundance (one or two orders of magnitude higher compared to Figure 4 in Le Petit et al. (2002) for a molecular fraction of \(\sim 0.9\)) is adapted to enhance the HDO abundance on the surface to reduce the total simulation time. The atomic hydrogen density is chosen to be 2 cm\(^{-3}\) (Goldsmith & Li, 2005). The remaining fractional densities of the species involved have been chosen typical for a cloud with \(n_H = 1000\) cm\(^{-3}\), i.e., \(n_{HD}/n_H = 8 \times 10^{-7}\) and \(n_{OHH}/n_H = 3 \times 10^{-4}\) (Le Petit et al., 2002; Nguyen et al., 2002). Several simulation runs have been performed three times, from which the uncertainty in the HDO/H_2O ratio is found to be \(\sim 10 - 30\%\) as a result of the low HDO abundances.

An intricate interplay is brought about between several of the simulation input parameters regarding their respective impact on the HDO/H_2O ice ratio, the evaporation of hydroxyl radicals, and the total ice thickness. This is discussed qualitatively below.

**Influence of including reactions R1-R6**

Reactions R1 and R3 become important after sufficient HDO has been produced on the surface, i.e., either at later stages in the simulation (\(> 5 \times 10^4\) years) or upon artificial increase of the D abundance. Indeed, reactions R2, R4 and R6 do not take place efficiently in the simulations, as a result of the low concentrations.

The relations for \(k_1 - k_4\) derived experimentally are implemented in the Monte Carlo routine in two ways. First, all reactions are incorporated with a non-zero rate, assuming a conservative upper limit corresponding with \((k_3, k_4) < 0.2 (k_1, k_2)\). Second, as experimentally no clear evidence of the occurence of reaction R4 is found, therefore both \(k_3\) and \(k_4\) are set to zero. These simulations are compared to runs where reactions R1-R6 are excluded from the network. We find that the HDO/H_2O ice ratio increases in both cases, since each time that an HDO molecule dissociates, the OD fragment can easily regenerate deuterated water. This is because the likelihood of an OD radical finding an H_2O neighbor is larger than that of finding an H atom. Furthermore, if several values of the ratio \((k_3, k_4)/(k_1, k_2)\) are tested, the
highest ratio results in the lowest amount of fractionation as a result of the allowed reverse reaction R3. Note that it is often implicitly assumed that the ratios in the ice and in the gas are coupled. This is, however, not always the case (Taquet et al., 2014; Furuya, 2015) and this should be kept in mind.

**Excess energy - heat of reaction**

All simulations include an excess heat given to each reaction product of a two-product atom addition or photodissociation reaction. For reactions R1 and R2 this value is set to 150 K, whereas reactions R3-R6 receive no excess energy as a result of their endergonicity or net zero Gibbs free energy (Chapter 5). For all other two-product reactions we chose two values, namely 150 and 700 K.

Firstly, a high excess energy allows for more desorption of photodisassociation products and therefore the ice thickness decreases by ~ 20%. Furthermore, since reaction R1 provides its products with excess energy this is another source of OH evaporation. Coutens et al. (2014) found a discrepancy between the modeled, predicted D\textsubscript{2}O/HDO and HDO/H\textsubscript{2}O ratios and the limited set found observationally. They indicated that a possible explanation may be following a higher gas-phase production of H\textsubscript{2}O starting from OH. Here, we find that the excess energy is an important parameter in leading to an enhancement of OH in the gas phase.

A lower excess energy keeps more products on the surface and therefore they recycle creating more HDO thus increasing the HDO/H\textsubscript{2}O ratio.

**Cloud extinction**

The cloud extinction also plays an important role in determining the HDO/H\textsubscript{2}O ratio, because a lower A\textsubscript{V} is associated with a higher degree of photodissociation and therefore more hydroxyl radicals are created. These species can evaporate depending on the excess energy they obtain. Therefore, a low extinction decreases the thickness of the ice, especially when combined with a high excess energy. As a consequence, the HDO/H\textsubscript{2}O ratio increases at low A\textsubscript{V} as a result of the recycling of OD radicals.

### 8.5 Conclusions

We demonstrated experimentally that the reaction between water and a deuterated hydroxyl radical produces singly deuterated water, but the deuterated analogue of this reaction does not proceed with the same efficiency:

\[
\begin{align*}
\text{H}_2\text{O} + \text{OD} & \xrightarrow{k_1} \text{OH} + \text{HDO} \\
\text{D}_2\text{O} + \text{OH} & \xrightarrow{k_4} \text{OD} + \text{HDO}
\end{align*}
\]

with \(k_4 < 0.2 \, k_1\)

This result is theoretically supported by the difference in gas-phase Gibbs free energy of the reactions which renders the reaction R1 exergonic, but the reaction R4 endergonic. If such a proton/deuteron transfer reaction was to occur (partially) via tunneling, the kinetic isotope effect also points towards a lower reaction rate for the deuteron transfer, \textit{i.e.}, \(k_4 < k_1\).

Furthermore, a deuterated-water-formation KMC model shows that including reactions between water and hydroxyl radical isotopes can change the ice ratio of HDO/H\textsubscript{2}O with respect to its surface formation. The extend of this change depends on the exact parameters included as well as on the astronomical conditions. More information on the exact role of crucial parameters, such as precise values for the reaction rates and the role of the excess heat upon reaction, in general, is needed before this model can be further extended.
Placing this in context with other studies, we want to stress that the previous experimental solid-state reactions involving different reaction efficiencies for different isotopologues all point towards the involvement of tunneling in overcoming the reaction activation barrier (Oba et al., 2012, 2014). This essentially results in H-enrichment of the ices since tunneling favors reactions with hydrogen over those with deuterium. The reactions discussed in the present work, however, could offer a pathway to D-enrichment. In the light of the recent investigations of the HDO/H₂O and D₂O/H₂O ratios it is thus pivotal to understand the isotopic effect of all single reactions included in the water formation network (van Dishoeck et al., 2013). The present study adds one specific reaction channel that is relevant within the large picture.

Finally, the importance of the abstraction reactions induced by the hydroxyl radical previously reported (Oba et al., 2012; Garrod, 2013) is reinforced by the present results especially since this radical plays an important role as reactive intermediate in water formation. Such reactions can strongly affect the local OH (and OD) abundance in interstellar ices, not only via abstraction reactions, but also influence, e.g., CO₂ formation, via the diffusion analog reaction R₅ (H₂O + OH → H₂O + OH), in the case that CO₂ forms through CO + OH recombination (Mennella et al., 2004). In this light, further efforts are needed to establish an accurate estimate of the comparison of the reaction rates of reactions R₅ to R₁.