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‘L’eau peut aussi être bonne pour le coeur...’ is what the little prince said in the book written by Antoine de Saint-Exupéry. Indeed, water is at the very least important for the physical life on Earth. Contrary to what might be expected considering its importance, how and if water was delivered to our planet is still under debate. It has been postulated that Earth’s water reservoir has been formed already before the formation of the Sun. Moreover, water is abundantly observed throughout the interstellar medium. Not only in the cold quiescent birth places of new stars, but also in highly energetic flows of material surrounding a young star. Many of these astronomical observations have proven the existence of gas-phase water. It seems to be most likely though that these vapors originate from the sublimation of ices covering small dust grains. Oxygen and hydrogen atoms or molecules freeze out on the cold grain surface ($10^{-20} \text{ K}$) in regions of relatively high densities ($10^4 - 10^5 \text{ cm}^{-3}$). Given enough time, several hundred thousand years, thick layers of water-dominated ices are formed through consecutive reactions of the frozen-out material. Surface chemistry is thus crucial in understanding the abundances of water found in space. Next to the formation of regular water, the combination of oxygen, hydrogen, and deuterium atoms, results in heavy, or singly-deuterated water. As a result of the low temperatures involved, deuterium is preferentially incorporated into water molecules, enhancing the ratio of deuterated over regular water with respect to its elemental ratio. This ratio is therefore often used as a tracer in relating the water found in the interstellar medium to that of Earth’s oceans.

This thesis focuses on the surface formation of water at low temperatures, both experimentally and under interstellar conditions. It describes the use of a large reaction network as well as the studies of particular reaction routes of regular and deuterated water.
Low-mass star formation is relatively well-understood, and therefore this sequence of events is described below in conjunction with the water detections in the various stages of star and planet formation. A number of different regions corresponding to these stages with their representative density, temperature, and $A_V$ is summarized in Table 1.1.

![Table 1.1: Types of interstellar and circumstellar clouds and their physical characteristics, adapted from van Dishoeck et al. (2013).](image)

It is in the cold, dense regions of the interstellar medium (ISM) that star formation commences (Shu et al., 1987). The dense regions, or dark clouds, originate from more dilute, or diffuse, environments thanks to gravitational attraction or external shockwaves. In the diffuse regions, the interstellar radiation field (IRF) is the cause of efficient destruction of molecules and ices, whereas in dense regions $H_2$ is largely responsible for shielding from the IRF which keeps the temperature low in the center of the cloud ($\sim 10^{-20}$ K). Therefore, ices are abundantly present in the denser regions (e.g., Whitsett et al. (1988) and Chapter 5). The name ‘dark’ is given, because visible light at cannot penetrate through the clouds and reach a telescope. At this point, the cloud needs a cooling mechanism different from molecular radiation and it is the far-infrared light radiated by dust grains that mediates the further collapse. Since a cloud accumulates mass, the gravitational force increases and, eventually, the cloud collapses to form a prestellar core ($\sim 8 - 15$ K). The first water vapor detection towards a cloud on the verge of star formation, namely the prestellar core L1544, has been reported recently (Caselli et al., 2013). The high sensitivity of the Herschel Space Observatory (HSO) has made this detection possible. Further contraction of the cloud eventually raises the temperature of the inner region until the internal pressure can support the resulting protostar against a continuing collapse. The protostar is still surrounded by an envelope of atoms and molecules which continue to accrete onto the center. The outer envelope remains cold and ices can thus be present there as detected by the ISO and the SST, but the inner envelope is heated by the star and molecules evaporate. The rotating envelope eventually forms an accretion disk which dissipates its angular momentum via bipolar outflows. Water has been detected in the gas phase in a variety of regions around protostars thanks to the Water In Star forming regions with Herschel (WISH) program. It is seen in an infalling motion in the envelope, in shocked regions along the outflow cavity walls, and in the outflows themselves (Nisini et al., 2010; Kristensen et al., 2012).
The dust in the disks is known to grow up to cm-sized particles (Kessler-Silacci et al., 2006) and grain growth in general is thought to be the start of planet formation. The 13 orders of magnitude separating the sub-micron particles from terrestrial planets, however, are not easily connected (Williams & Cieza, 2011). Also in planet forming disks, water vapor has been detected by the Heterodyne Instrument for the Far-Infrared (HIFI) on the HSO. Cold water vapor around the young star TW Hydrae are observed and this likely originates from icy grains near the disk surface. The correlation between the observed gas to the water ice reservoir from which it originates hints at a reservoir equivalent to several thousand Earth oceans in mass (Hogerheijde et al., 2011). Not all material present in the disk ends up in planets and the remaining material can nowadays be found in comets and asteroids. Comets contain mainly ice, dust, rocky materials, and organic compounds, whereas asteroids are dry and consist of metals and rocky material. A comet can lose material upon approaching the Sun, as a part of the ice melts and evaporates, in the coma – consisting of sublimated cometary material – water has indeed been observed. For example as a part of the recent Rosetta mission towards the comet 67P/Churyumov-Gerasimenko both HDO and H₂O have been detected (see also Section 1.4) (Altwegg et al., 2015). Eventually a protostar will start to burn, or rather fuse, hydrogen and the star enters the main sequence phase in the Hertzsprung-Russell diagram (Rosenberg, 1910).

The star formation process of high-mass stars, those with masses exceeding that of 8 times the solar mass, is not well-understood. This is partially related to the shorter lifetime and the large distances associated with the molecular outflows. Therefore, the outflow of one star-forming core can influence that of the neighboring cores. Recently, however, within the WISH key programme, it was suggested from a study of 51 young stellar objects (YSOs) that physical processes in protostellar envelopes have similar characteristics in high- and low-mass stars (San José-García et al., 2013).

When the fuel, not only hydrogen, but also the heavier elements, has run out, the remnants of a star can take several forms depending on the mass during its lifetime: a white dwarf, neutron star, pulsar, or black hole. Most importantly for the present discussion is that during stellar death there are various ways for a star to inject mass into the ISM. This can be through winds, planetary nebulae, or supernovae. In this way, the cycle of matter is completed.

1.2 ICES IN THE INTERSTELLAR MEDIUM

The existence of water ice in the ISM had been postulated several decades prior to its detection: ‘In view of the high boiling-point of water (...) is it not likely that this would precipitate the most freely?’ (Eddington, 1937). After the realization that interstellar particles, i.e., grains, indeed are present, ‘It may now be asked of what kind of molecules they exist’ (van de Hulst, 1949). Water was already thought to be the main component of the ices, but it took until 1973 for solid water to be observed by Gillett & Forrest through its 3 µm feature.

The infrared absorption feature of the solid water OH stretch can be observed superimposed on the continuum spectrum of an embedded YSO or a background star. The Infrared Space Observatory (ISO), in the 1990’s, played a large role in the observations of interstellar ices in the spectral range of 2.5 – 30 µm. It observed 23 relatively bright sources in various regions of the ISM: embedded YSOs and field stars sampling quiescent dark clouds and the diffuse interstellar medium (Gibb et al., 2004). Furthermore, the cores-to-disks (ctd) program combined Spitzer Space Telescope (SST) observations in the spectral range of 3 – 38 µm of 41 low-luminosity YSOs with ground-based observations (Keck NIRSPEC or VLT ISAAC) (Boogert et al., 2008). It is thanks to these large-scale projects that the average composition of interstellar ice has been determined. Indeed the main component of interstellar ices is water, followed
by carbon monoxide (CO), carbon dioxide (CO₂), and minor contributions from methanol (CH₃OH), formic acid (HCOOH), formaldehyde (H₂CO), and methane (CH₄) (van Dishoeck, 2004). The name ‘ices’ in astrochemistry is actually not only reserved for water ice, but for all solids that consist of volatiles (molecules that are liquid or gaseous at room temperature).

1.3 SOLID STATE WATER FORMATION: SURFACE CHEMISTRY

Most of the ice species form on the surface of dust grains, even though the dust constitutes only 1% of the total mass in the ISM. Freeze-out of atoms and molecules takes place only when the temperature is low enough. In that case, there is a local high density of species present on the surface, allowing the formation of water from oxygen atoms and hydrogen atoms and molecules. Since frozen molecules are not isolated when they react with each other, gas-phase reaction dynamics cannot be directly extended to the solid phase; although the initially proposed surface reaction networks were largely constructed based on analogies with gas-phase data (Tielens & Hagen, 1982). The four main processes that occur on the surface – accretion, desorption, diffusion, and reaction – are always in competition with each other. For an accurate understanding of the microscopic interplay between them, both detailed experiments and models are needed.

**Accretion** is governed by the gas-phase abundance, \( n \), of a species. The rate of deposition, \( R_{\text{deposition}} \), also depends on the gas-phase mean velocity of the species, \( v \), and the surface site density, \( \rho \), scaled by a factor 4 taking to account for the fact that accretion takes place only from one direction:

\[
R_{\text{deposition}} = \frac{n v}{4 \rho}.
\]

**Desorption** depends on the binding energy of a particle to the grain surface or neighboring ice molecules. There are several ways to define the binding energy. One way is to derive an overall average value experimentally (see Chapter 2), but if a microscopic model is used, the interaction with a variety of adjacent sites can be taken into account explicitly.

**Diffusion** is also associated with the binding energy, albeit in a less stringent way. In this case it is not only the binding energy of a species in its initial state, but also the gain or loss in energy upon moving that determines its trajectory in astrochemical models. Both the desorption and diffusion rates are often assumed to be thermally activated and follow Arrhenius type expressions (see Chapter 3).

**Surface reactions** are generally devided into three types – schematically depicted in Figure 1.1: the Langmuir-Hinshelwood (LH) mechanism is a diffusive mechanism in which the species move over the surface and attempt to react upon meeting, the Eley-Rideal (ER) mechanism, where one (stationary) reactant is hit by another species from the gas phase, and the hot-atom (HA) mechanism, which is a combination of both mechanisms where non-thermalized species travel some distance over the surface finding reactants on their way. In all cases, the excess heat which becomes available through the reaction can be used for desorption of the products. Since in dense clouds the temperature of the gas phase is similar to the grain temperature, the hot-atom mechanism is generally not considered. It can be important in experimental conditions or, for instance, in shock regions where the gas phase is often much warmer than the grain. It is worth mentioning that the reaction rate is different for Eley-Rideal and Langmuir-Hinshelwood: for the former the two reactants have one attempt to cross the reaction barrier, whereas for the latter the two reactants will remain adsorbed in close vicinity until they react or one of them diffuses away or desorbs. Furthermore, energetic processing of an ice can result in the breaking of a bond, which is typically also considered to be a ‘reaction’ with a photon or an energetic particle (see Chapter 2).
1.4 ORIGIN OF WATER ON EARTH: HDO

Water is not only abundant in the ISM, in its liquid phase it also plays an ultimate role for the origin of life on Earth. The origin of the ocean’s water is nonetheless unclear, because Earth was formed within the so-called snow line. This is the line around a protostar that separates the inner area where bare grains exist from the outer area where grains are covered with ice. Planets formed within the snow line are therefore rather dry compared to those formed outside this line (Min et al., 2011).

Several hypotheses exist on how water arrived in the inner Solar System. One of these was put forward by Drake (2005) and Stimpfl et al. (2006) who showed that chemisorption sites exist on forsterite grains where water can absorb. Grains can retain a submonolayer of water well beyond the snow line in this way. Muralidharan et al. (2008) build on this work by applying a lattice-gas Kinetic Monte Carlo (KMC) simulation. Due to the many and conservative assumptions used in the model, the authors argue that the results only give a conservative lower limit to the amount of water that can be absorbed onto grains prior to accretion into planets. Their results show that this amount can indeed be substantial. Furthermore, the bombardment of carbonaceous asteroids or comets that originate from the ice-rich outer region of the early solar system is another plausible mechanism, accounting at least partially for water on Earth (Owen et al., 1992; Morbidelli et al., 2000; Cleeves et al., 2014). Such a scenario is supported by recent models where water delivery takes place during the formation phase of terrestrial planets (O’Brien et al., 2014). Finally, a large part of the carbonaceous chondrites contains hydrated silicates and hydrous carbon (Robert, 2003). Dynamic solar system models for planetary water delivery seem to indicate that carbonaceous chondritic planetesimals could have delivered water during primary accretion of Earth (Sarafian et al., 2014).

A common tracer in the origin of water on Earth is the HD$\text{O}/\text{H}_2\text{O}$ ratio, of which the Earth ocean value is found to be higher than the primordial ratio of $\sim 1.5 \times 10^{-5}$ (Piskunov et al., 1997; Oliveira et al., 2003). Linking the HD$\text{O}/\text{H}_2\text{O}$ ratio found in cometary, interstellar, and laboratory ices as well as those found through gas-phase observations to the ratio in our oceans is therefore one of the challenges currently faced by the community (Rodgers & Charnley, 2002; Hartogh et al., 2011). Figure 1.2 summarizes the HD$\text{O}/\text{H}_2\text{O}$ ratio in various astrochemically in-

![Figure 1.1: Schematic representation of the three mechanisms for surface reaction: the Langmuir-Hinshelwood mechanism, a diffusive mechanism in which the species move over the surface and try to react upon meeting, the Eley-Rideal mechanism where one (stationary) reactant is hit by another species from the gas phase, and the hot-atom mechanism which is a combination of both mechanisms where non-thermalized species travel some distance over the surface finding reactants on their way.](image-url)
Figure 1.2: D/H ratio for water in various regions in space. Retrieved from Persson (2015), references can be found in Persson et al. (2014), Albertsson et al. (2014), and Altwegg et al. (2015).

...regions and compares it to the primordial interstellar D/H ratio, the protosolar D/H ratio, the Standard Mean Ocean Water (SMOW) HDO/H\(_2\)O value, and a recently modeled HDO/H\(_2\)O value in the early solar nebula. From the figure it can be deduced that there is a considerable spread in the ratios found in both Jupiter Family Comets (JFC) and Oort Cloud Comets (OCC). The hypothesis that JFCs can be entirely responsible for the delivery of water to Earth therefore seems unlikely (Altwegg et al., 2015). It is very likely, though, that a considerable fraction of the solar system’s water originates from primitive sources (Cleeves et al., 2014; O’Brien et al., 2014).

The main causes of preferential incorporation of deuterium over hydrogen in molecules, or fractionation, find their origin in the lower zero-point energy of an X-D bond with respect to an X-H bond as a result of the larger mass of deuterium. Firstly, the molecule H\(_2\)D\(^+\) is more stable than the ubiquitous H\(_3^+\), and the reaction H\(_3^+\) + HD → H\(_2\)D\(^+\) + H\(_2\) enhances the H\(_2\)D\(^+\)/H\(_3^+\) ratio in the gas-phase. Following the freeze-out of the main destruction partners of H\(_2\)D\(^+\), namely CO and O, dissociative recombination with an electron takes place H\(_2\)D\(^+\) + e\(^-\) → D + H\(_2\) liberating D atoms. This process can increase the gas-phase D/H ratio to values larger than 0.1 (Roberts et al., 2003). The number of deuterium atoms landing on the grain surface is larger, thus increasing its probability to be incorporated into (water) molecules (Tielens, 1983; Caselli et al., 2012). Secondly, the binding energy of D atoms to a grain or water surface is larger, increasing the time that it spends on the surface, e.g., Lipshat et al. (2004). Finally, specific surface reaction rates are influenced by the enthalpy of the bonds that are destroyed and formed, which in itself is subject to zero-point energy. One 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 (Nagaoka et al., 2005).
1.5 THIS THESIS

This thesis is devoted to the study of regular and deuterated water in ices and on surfaces against an interstellar background. A large network for the formation of regular water has been studied with the use of a Kinetic Monte Carlo model. A specific reaction has been investigated as well: $\text{H}_2 + \text{O} \longrightarrow \text{OH} + \text{H}$. Furthermore, in the light of deuterium fractionation, a thermal study on deuteron scrambling in the ice has been performed: $\text{H}_2\text{O} + \text{D}_2\text{O} \longrightarrow 2\text{HDO}$. Finally, two low-temperature routes relevant to HDO formation have been investigated: $\text{H}_2\text{O} + \text{OD} \longrightarrow \text{OH} + \text{HDO}$ and $\text{D}_2\text{O} + \text{OH} \longrightarrow \text{OD} + \text{HDO}$.

First of all, Chapter 2 describes the use of an Ultra-High Vacuum (UHV) experimental setup equipped with a Reflection Absorption Infrared (RAIR) spectrometer and a Quadrupole Mass Spectrometer (QMS) in the context of various other possible techniques used in the field of astrochemistry. Furthermore, the specific experimental setup used in the Sakcler Laboratory for Astrophysics is introduced and its calibration is outlined.

In Chapter 3 the Continuous-Time Random-Walk (CTRW), or KMC, model is compared to other commonly used astrochemical models. The technical aspects, such as neccessary input parameters, are introduced along with the algorithm implemented in the code used for this thesis. Finally, a number of published astrochemical studies making use of KMC are summarized.

Chapters 4 and 5 build on the laboratory studies of molecular oxygen hydrogenation: $\text{O}_2 + \text{H}$. This route was chosen because it consists of reaction pathways that are relatively well-separated from the $\text{O} + \text{H}$ and $\text{O}_3 + \text{H}$ reaction routes: it starts out with two barrierless reactions $\text{H} + \text{O}_2 \longrightarrow \text{HO}_2$ and $\text{H} + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2$. The experiments have been performed and analyzed previously by Ioppolo et al. (2010) and Cuppen et al. (2010). Being able to use KMC simulations to reproduce the main experimental conclusions provides a benchmarked model that can then be used to run simulations under interstellar conditions. Four different experiments are chosen to be modeled to probe a large region of the parameter space spanned by the large number of reaction, diffusion and desorption rates. First, experiments in which a layer of pre-deposited $\text{O}_2$ was hydrogenated are modeled at 15 and 25 K. Then, again at both temperatures, so-called co-deposition experiments are used, in which hydrogen and oxygen were frozen out simultaneously. The full water surface formation chemical network is included in the model, but to understand the influence of separate parameters, a single process rate is varied at the time, either diffusion or reaction rates. Although initially a number of key reactions ($\text{H} + \text{O}_2$, $\text{H} + \text{HO}_2$, $\text{OH} + \text{OH}$, $\text{H} + \text{H}_2\text{O}_2$, $\text{H} + \text{OH}$) and the neccessity for including a high hydrogen diffusion rate was established, the diffusion of radicals other than $\text{H}$ turned out to play an important role. Therefore, a follow-up study focuses on the breakdown of the so-called Markov chain assumption for the formation of two OH radicals by the reaction $\text{H} + \text{HO}_2$. A combined effect of directionality of the OH radical movement together with energy dissipation can explain the experimental observation of OH radicals. This optimized model is then used to run simulations under diffuse, translucent, and dense cloud conditions. From these model runs information is obtained about the main reaction routes producing water in the different interstellar regions.

In astrochemical environments it is possible that one reaction within a network dominates water formation as a result of the relative abundances of the species involved. Such a behavior has been previously postulated for the role of the endothermic reaction $\text{H}_2 + \text{O} \longrightarrow \text{OH} + \text{H}$. 
in dark clouds. In **Chapter 6** precisely executed temperature-programmed desorption (TPD) experiments are described that determine an absolute conservative upper limit to the production of water on the surface after co-deposition of H\(_2\) and O. Furthermore, a set of KMC simulations – using the optimized parameters from Chapter 5 – is used to establish an upper limit to the reaction rate itself. Incorporating this rate into the same model, but run with astrochemically relevant parameters, allows to find the upper limit to the contribution of the reaction H\(_2\) + O for the formation of OH, and hence water formation. This value is 11% in dense interstellar clouds and therefore we conclude that the reaction H\(_2\) + O does not dominate water formation in these regions.

**Chapter 7** shifts focus towards the processes that influence the HDO/H\(_2\)O ratio in the ice. Here, the thermally induced proton/deuteron exchange in mixed amorphous H\(_2\)O:D\(_2\)O ices is monitored. The characteristic vibrational bending modes of the three isotopes involved – H\(_2\)O, HDO, and D\(_2\)O – are evaluated over time and as a function of temperature (90 – 140 K). The amorphous nature of the interstellar ice analogues investigated implies a high concentration of structural defects compared to crystalline samples. These deviations from perfect crystallinity aid the H and D atoms in exchanging from one oxygen centre to another. Therefore, the activation energy of the reaction H\(_2\)O + D\(_2\)O \(\rightarrow\) 2HDO obtained from an Arrhenius plot is lower than that of crystalline ices: 3840 versus 5000 K. The characteristic timescales that can be derived for the reaction (\(\tau\) < 10\(^4\) years at \(T > 70\) K) indicate that the process can be important in interstellar environments. Therefore, astronomical detections of D\(_2\)O remain challenging because of its potential to react with H\(_2\)O to form HDO. Furthermore, it has been demonstrated experimentally previously as well as in this chapter that proton/deuteron exchange also takes place in ice mixtures incorporating other hydrogen bonded molecules, i.e., those with OH and NH moieties. In general, H/D exchange should thus be included in models that are applied to protoplanetary disks or to simulate the warming up of cometary ices in their passage of the perihelion, to examine the extent of its influence on the final deuteron over hydrogen ratio.

Lastly, **Chapter 8** investigates two reactions that provide a cross link between the oxygen hydrogenation and deuteration networks. Hydrogen abstraction by hydroxyl radicals is reported to be important in the framework of complex hydrocarbon molecules. The OH radical is furthermore known to play a key role as intermediate species in the solid state formation of water on icy grains in space. Therefore, the reactions H\(_2\)O + OD \(\rightarrow\) OH + HDO and D\(_2\)O + OH \(\rightarrow\) OD + HDO are studied experimentally at 15 K. It is established that the reaction rate or efficiency of the second reaction is maximum 20% of that of the first. In other words, hydrogen transfer is more efficient than deuterium transfer, which is supported theoretically both by arguments of Gibbs free energy as well as through assuming tunneling plays a role. Including abstraction reactions in the H\(_2\)O, HDO, and D\(_2\)O surface formation reaction network can play an important role in the ISM. KMC simulations including all six possible abstraction reactions between water and hydroxyl radicals show that the HDO/H\(_2\)O ice ratio indeed changes with respect to simulations excluding these reactions. This conclusion holds provided that enough hydroxyl radicals are generated via photodissociation, i.e., in a translucent cloud.
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