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Astrochemical models of water

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Abstract. We will review the chemical reaction network models of water and its D/H ratio coupled with the dynamics of star formation. Infrared observations show that water ice is abundant even in molecular clouds with relatively low visual extinction (~ 3 mag), which indicates that water ice is formed in early stage of molecular clouds. We thus start from a possible formation site of molecular clouds, i.e. the converging flow of diffuse gas. Then we proceed to dense cloud cores and its gravitational collapse, during which a significant deuterium enrichment occurs. The gas and ice accrete onto the circumstellar disks, which evolve to protoplanetary disks in T Tauri phase. If the disks are turbulent, water could be photodissociated in the disk surface and re-formed in deeper layers. The cycle continues until the dust grains with ice mantle are decoupled from the turbulence and settle to the midplane. The water D/H ratio could thus vary within the disk.

Keywords. astrochemistry, star formation

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1. Introduction

The D/H ratios of molecules (DX/HX) in molecular clouds are much higher than the elemental D/H ratio (1.5×10^{-5}; Linsky 2003). The deuterium enrichment is basically caused by exothermic exchange reactions such as

$$H_3^+ + HD \rightarrow H_2D^+ + H_2. \tag{1.1}$$

At a typical temperature of molecular clouds, ~ 10 K, the backward reaction is inefficient. The high D/H ratios of H_3^+ and some other molecules which are subject to such direct exchange reactions propagate to other molecules via chemical reactions. Recombination of deuterated H_3^+ produces D atoms, which are adsorbed onto grain surfaces to form deuterated ice such as HDO via hydrogenation of atoms and molecules. If molecules are formed or re-formed at high temperatures, where the backward reactions of exchange (e.g. Eq. 1.1) are efficient, the molecular D/H ratios could be lowered. The D/H ratios are thus considered to be a probe to investigate where the molecules are formed and reprocessed.

In planetary science and astrobiology, water is a key molecule for habitability. In order to reveal the origin of water in the Solar system, especially on Earth, the HDO/H_2O ratio is intensively studied. HDO/H_2O ratio of Earth's ocean is 3×10^{-4} (Lécuyer *et al.* 1998), which corresponds to the D/H ratio of 1.5×10^{-5}, considering that H_2O has two hydrogens. The D/H ratio in comets varies among objects; the ratio in Oorto cloud comets is $\sim 3 \times 10^{-4}$ (Mumma & Charnley 2011). As for Jupitar family comets, D/H ratio of 103P/Hartley 2 is observed to be $(1.61 \pm 0.24) \times 10^{-4}$ (Hartogh *et al.* 2011), while Rosetta measured the D/H ratio of 67P/Churyumov-Gerasimenko to be $5.3 \pm 0.7 \times 10^{-3}$ (Altwegg *et al.* 2015). These values, all higher than the elemental D/H ratio, indicate the contribution of low-temperature chemistry to the solar system material, although the variation among comets indicates some reprocessing.

How do these HDO/H_2O ratios in the Solar system objects compare with the ratio in molecular clouds, which is presumably an initial value for planetary system formation? In molecular clouds, water is mostly contained in ice mantle of dust grains (e.g. Whittet 2010). While the absorption band of water at 3.05 μm is ubiquitously detected, HDO band (4.1 μm) has not been firmly detected (Dartois *et al.* 2003; Parise *et al.* 2003, Aikawa *et al.* 2012). The upper limit of HDO/H_2O in ice mantle is $2 \times 10^{-3} - 0.02$. Alternatively, the D/H ratio can be constrained by observing the protostellar core in which the water ice is sublimated. Recent observations succeeded in detection of HDO and H_2O lines towards several protostellar cores to derive the HDO/H_2O ratio of $3 \times 10^{-4} - 10^{-3}$ (Persson *et al.* 2014, see also Coutens *et al.* 2013 and refereces therein). While it is consistent with the upper limits from the ice observation, it is significantly lower than the D/H ratio of other molecules in protostellar cores (e.g. NH_2D/NH_3 is 0.28 and 0.04 towards NGC1333 and L1527, respectively)(Roueff *et al.* 2005; Sakai *et al.* 2009). The relatively low D/H ratio of water could be due to its formation in the early evolutionary stage of molecular clouds. The high abundance of water ice ($\sim 10^{-4}$ relative to hydrogen) in clouds with low visual extinction (~ 3 mag) supports this idea.

In the following, we will review theoretical models of water chemistry from the cloud formation to protoplanetary disks. Relevant observational studies are also discussed briefly. Section 2 describes the epoch of cloud formation. Prestellar and protostellar cores are discussed in section 3. Models of disk water are reviewed in section 4.

2. Molecular cloud formation

Molecular clouds are formed by multiple episodes of super-sonic compression of diffuse gas (Inutsuka *et al.* 2015). While the 3D simulations of cloud formation are performed with simple chemistry (e.g. Inoue & Inutsuka 2012), more detailed chemistry in the post-shock region is investigated by Bergin *et al.* (2004) and Hassel *et al.* (2010) using the 1D steady-state shock models. Recently, Furuya *et al.* (submitted to ApJ) updated the 1D model to include the deuterium chemistry and ortho-para ratio (OPR) of H_2, which is relevant for deuteration. Since the ground-state energy of ortho-H_2 is 170 K higher than that of para-H_2, the backward reaction of (1.1) is more efficient, if o-H_2 is abundant (Hugo *et al.* 2009). In molecular cloud models, molecular D/H ratios thus depend on the initial OPR of H_2, which has not been well constrained by observations. By starting from the converging flow of diffuse HI gas, Furuya *et al.* calculate the OPR of H_2 within the model. Their findings are summarized as follows

- In the H/H_2 transition region, the OPR of H_2 is already much less than the statistical value (o/p= 3), because the timescale of spin conversion through the reaction of o-H_2 with H^+ is shorter than the timescale of H_2 formation.
- Water ice is the major oxygen reservoir at $A_v \geqslant 1$ mag.
- The HDO/H_2O ratio in the bulk ice is as low as 10^{-4}, when the column density of post-shock gas reaches $A_v = 3$ mag. The key mechanism to set the water ice D/H ratio is the cycle of photodissociation and reformation of water ice on grain surfaces. The OPR of H_2 plays a minor role in water ice deuteration at the main formation stage of water ice.

3. Prestellar and protostellar cores

In the central region of dense cloud cores, CO is frozen onto grains (Ceccareli *et al.* 2007 and references therein). Since CO is the dominant reactant of deuterated isotopomers of H_3^+, deuterium fractionation is further enhanced via CO freeze-out. A fraction of CO

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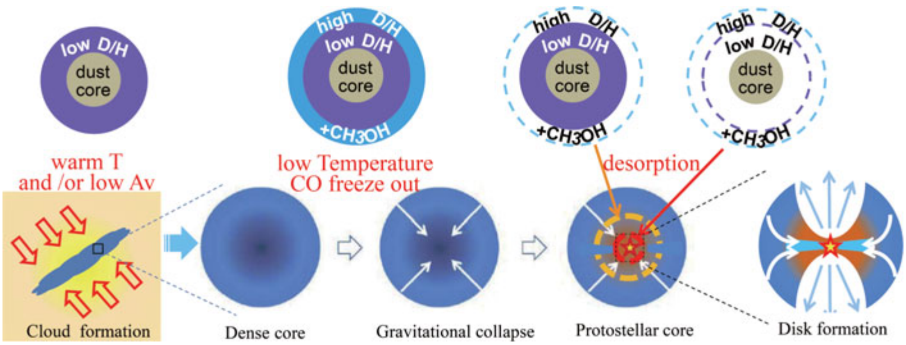

Figure 1. Schematic view of low-mass star formation and the evolution of water ice.

ice is hydrogenated to form H_2CO and CH_3OH, which are efficiently deuterated via the direct exchange, abstraction, and addition reactions (Hidaka *et al.* 2009 and references therein). When the compressional heating overwhelms the radiation cooling, a core starts to heat up, and eventually evolves to a protostar. When the infalling material reaches the warm central regions, ice mantle evaporates. Observations of the sublimated water have been a hot topic in recent years (§1). Interestingly, the initial observations with single dish telescopes derived relatively high D/H ratios ($1-10$ %), while lower D/H ratios of $\sim 0.1-1$ % are obtained by interferometric observations (Persson *et al.* 2014 and references therein). It suggests that the gaseous HDO/H_2O ratio decreases inwards in protostellar cores.

Several groups (Aikawa *et al.* 2012, Wakelam *et al.* 2014, Taquet *et al.* 2014) have investigated deuterium chemistry in collapsing star-forming cores, from a presetllar core to a protostellar core. Among them, Taquet *et al.* (2014) considered the layering of ice mantle, and showed that it could be a key to explain the radial gradient of HDO/H_2O observed in protostellar cores. The water ice in the deeper layers of ice mantle is formed in early phases before the significant freeze-out of CO, and thus has a relatively low D/H ratio, while water in the surface layer is formed in the CO freeze-out region to have a higher D/H ratio. When the grains fall towards the central warm regions, the highly-deuterated ice is desorbed first at larger radii, while the ice in the deeper ice-mantle layer sublimates only at smaller radii. Combining this model with §2, the evolution of water and its D/H ratio are schematically summarized in Figure 1. The models also suggest that the D/H ratios of various molecules decrease as the warm region extends and gas density decreases with evolution in protostellar cores (Aikawa *et al.* 2012), which could account for the observed variation among cores.

4. Protoplanetary Disks

A protoplanetray disk is ubiquitously formed by the collapse of a rotating core. Visser *et al.* (2011) investigated chemistry in disk formation using a semi-analytical model, while Furuya *et al.* (2012) and Hincelin *et al.* (2013) investigated chemistry as a post process in the 3D radiation hydrodynamics of the first-core formation. The models predict that the majority of water formed in cold cloud era will enter the disk intact, as their trajectories do not cross the hot regions, while a small fraction of water which passes through the vicinity of outflow cavity will be photodissociated and reformed (Visser *et al.* 2011).

In protoplanetary disks, ion-molecule reactions are triggered by X-rays from the central star and/or cosmic-rays. In the outer cold regions ($T \leqslant 20$ K), deuterium fractionation

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could proceed as in molecular clouds. Time-dependent chemistry models in protoplanetary disks show that the resultant HDO/H_2O ratio depends on the ionization rate (e.g. if the cosmic rays are hampered by stellar winds), initial HDO/H_2O ratio, and the initial abundance of oxygen which is not locked up in CO and H_2O (Aikawa & Herbst 1999; Wilacy 2007; Willacy & Woods 2009; Cleeves *et al.* 2014).

Furuya *et al.* (2013) considered the effect of vertical mixing on water chemistry in the disk. They showed that H_2O can be transported from the midplane to the disk surface, where H_2O is efficiently photodesorbed and photodissociated. The product, O atom is then transported to the midplane to reform water. Both the abundance and D/H ratio of water can thus be re-set depending on the temperature in the midplane. It should be noted that the efficiency of this process depends on the strength of the turbulence and (de-)couping of dust grains with turbulence, which are one of the hot topics in the current studies of disk physical structures.

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