

**SURFACE CHEMICAL REACTIONS TO THE FORMATION OF SOLID H<sub>2</sub>O AND ITS ISOTOPOLOGUES ON INTERSTELLAR GRAINS AT 10 K.** Y. Oba<sup>1</sup>, N. Watanabe<sup>1</sup>, H. Hama<sup>1</sup>, K. Kuwahata<sup>1</sup>, H. Hidaka<sup>1</sup> and A. Kouchi<sup>1</sup>, <sup>1</sup>Institute of Low Temperature Science, Hokkaido University, N19W8, Kita-ku, Sapporo, Hokkaido 060-0189 JAPAN, oba@lowtem.hokudai.ac.jp

**Introduction:** It is well known that solid H<sub>2</sub>O is the most abundant component not only in cometary nuclei but also in icy grain mantles in molecular clouds (MCs). Because the observed abundance of solid H<sub>2</sub>O in MCs cannot be explained only by synthesis in the gas phase, it has been considered that solid H<sub>2</sub>O is formed on grain surfaces in MCs. Tielens and Hagen [1] proposed possible pathways to form solid H<sub>2</sub>O in those environments. In their model, H<sub>2</sub>O formation initiates by hydrogenation of O, O<sub>2</sub>, or O<sub>3</sub>. Previous experimental studies reported that solid H<sub>2</sub>O is produced in each hydrogenation at low temperatures [2-4]. For example, Miyauchi et al. [2] found that H<sub>2</sub>O is formed by hydrogenation of O<sub>2</sub> via the formation of H<sub>2</sub>O<sub>2</sub> as an intermediate at 10 K. Moreover, a significant isotope effect was observed on the reaction of H<sub>2</sub>O<sub>2</sub> with H, indicating that this reaction proceeds via quantum tunneling [2].

In addition to these hydrogenation processes, reactions of hydroxyl radicals (OH) with H<sub>2</sub> (E<sub>a</sub>~2000 K) have been regarded as an important route to the formation of H<sub>2</sub>O especially in dense MCs [5], where the UV flux is very low. Since UV-induced energetic reactions are not expected to occur under those conditions, the reaction OH + H<sub>2</sub> may proceed only through quantum tunneling on grains at ~10 K. However, it remains unclear whether the tunneling reaction occurs, unless the experiment using “cold” (i.e. non-energetic) OH is performed.

We have recently succeeded in utilizing cold OH as a reactant for surface reactions at very low temperatures [e.g. 6,7]. In the present study, we will show experimental results on the formation of H<sub>2</sub>O and its isotopologues (HDO and D<sub>2</sub>O) through the reaction of OH/OD with H<sub>2</sub>/HD/D<sub>2</sub> at 10 K, and discuss its astrophysical implications.

**Experimental Details:** Experiments were performed in the apparatus named ASURA. The ASURA consists of a main chamber and radical source. An aluminum substrate was mounted at the center of the main chamber. OH was produced in a microwave-induced H<sub>2</sub>O plasma and cooled by many collisions with the inner wall of a cold Al pipe (100 K) at the outlet of the source. We verified that the OH radical impinging on the surface was electronically and vibrationally in the ground states [7]. H<sub>2</sub> was induced from a separate gas line through a capillary plate. OH (OD) and H<sub>2</sub> (HD or D<sub>2</sub>) were continuously codeposited on

the substrate at 10 K and the reaction products were monitored in-situ by FTIR.

**Results:** We found that solid H<sub>2</sub>O is produced by the surface reaction of cold OH with H<sub>2</sub> at 10 K despite its significant barrier of about 2000 K. This is the first experimental result to show that solid H<sub>2</sub>O is produced from reaction with molecular hydrogen via non-energetic processes. In addition, when cold OH was codeposited with D<sub>2</sub>, solid HDO was formed but its abundance was about one order of magnitude lower than that of H<sub>2</sub>O by the reaction OH + H<sub>2</sub> under the same experimental conditions (e.g. H<sub>2</sub> and D<sub>2</sub> fluence, OH fluence, and substrate temperature).

**Relative reaction efficiency.** In all experiments performed, H<sub>2</sub>O or its isotopologues (HDO and D<sub>2</sub>O) was produced through surface reactions of cold OH or OD with H<sub>2</sub>, HD, or D<sub>2</sub> at 10 K. These reactions are categorized into two groups depending on whether the reaction involves H- or D-atom abstraction, where H-atom abstraction reactions are about 10 times more effective than D-atom abstraction ones. This is attributable to the difference in the effective masses between 0.47 and 0.90 for H-atom and D-atom abstraction reactions, respectively. This effective-mass dependence on tunneling reactions were also reported in the different reaction systems [8].

**Astrophysical Implications:** The present results show that H-atom abstraction is much preferable to D-atom abstraction. It is therefore reasonable to consider that H<sub>2</sub>O is produced from OH (OH + H<sub>2</sub> or OH + HD), HDO is from OD (OD + H<sub>2</sub> or OD + HD), and D<sub>2</sub>O production is not favored in this reaction system. That is, the crucial factor to determine the D/H ratio of water (= HDO/H<sub>2</sub>O) formed by these reactions is not the D/H of molecular hydrogen (i.e. HD or D<sub>2</sub>/H<sub>2</sub>) but that of atomic D/H if OH and OD is mainly produced on grain surfaces through the reaction O + H (D).

**References:** [1] Tielens A. G. G. M. and Hagen W. (1982) *A&A*, 114, 245–260. [2] Miyauchi N. et al. (2008) *Chem. Phys. Lett.*, 456, 27–30. [3] Mokurane H. et al. (2009) *ApJ*, 705, L195–L198. [4] Dulieu F. et al. (2010) *A&A*, 512, A30. [5] Cuppen H. M. and Herbst E. (2007) *ApJ*, 668, 294–309. [6] Oba Y. et al. (2010) *ApJ*, 712, L174–L178. [7] Oba et al. (2012) to appear in *ApJ*. [8] Hidaka et al. (2009) *ApJ*, 702, 291–300.