

## Experimental studies on the behavior of hydrogen on bare grain surfaces and within icy grains

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In contrast to numerous experimental and theoretical investigations on the physicochemical processes involving hydrogen atoms and/or molecules on cosmic ice dust surfaces (especially on amorphous solid water, ASW), experimental studies on bare grain surfaces (i.e., silicate or carbonaceous materials) have been scarcely performed partly because it is difficult to prepare model surfaces. In our group, a laser ablation system was developed for in situ preparation of silicate and carbon films. Using an amorphous diamond-like carbon (DLC) film, we investigated the diffusion of physisorbed H atoms ( $H_2$  formation) and desorption energetics of  $H_2$ .<sup>1</sup> We found that  $H_2$  recombination reaction on a DLC surface efficiently occurs even at 20 K. Another important hydrogen process occurring on grain surfaces is ortho-to-para nuclear spin conversion (NSC) of  $H_2$ , since the ortho-to-para ratio not only affect chemical evolution but also affect the gas dynamics of core formation in star-forming regions. We determined, for the first time, the NSC-rates on an amorphous silicate ( $Mg_2SiO_4$ ), DLC, and graphite surfaces in a temperature range 10–18 K.<sup>2,3</sup> The NSC process on the silicate surface is very rapid; e.g., 980 s at 10 K and 260 s at 18 K. Numerical simulations indicated that ortho-to-para ratio of  $H_2$  in molecular clouds changes even on a bare silicate surface within an astronomically meaningful timescale. On the other hand, the NSC process on DLC and graphite surfaces are found to be several times slower than that on amorphous silicate surface.

$H_2O$ ,  $HCHO$ , and  $CH_3OH$  molecules have been found abundantly as solids in ice mantles that cover the cosmic dust. It has been demonstrated that the formation of these molecules involves the surface reaction of H atoms, which are accreted from the gas phase. For example,  $CH_3OH$  molecule is efficiently produced on ASW surface via a successive hydrogenation of carbon monoxide:  $CO \xrightarrow{H} HCO \xrightarrow{H} HCHO \xrightarrow{H} H_3CO/H_2COH \xrightarrow{H} CH_3OH$ . Such hydrogen reactions are thought to be active only at temperatures below  $\sim 20$  K because the sticking probability of H atoms and their residence time on the dust surface are significantly reduced at elevated temperatures. However, we found that reaction of non-energetic hydrogen atoms with CO molecule can occur even in ice mantles and at temperatures as high as 70 K: the diffusive hydrogenation process.<sup>4</sup> In this process, hydrogen atom colliding ASW surface penetrates into ice and diffuse within the ice to induce hydrogenation reactions. Recently, we investigated the diffusive hydrogenation processes of aromatic species (benzene and naphthalene) embedded in ASW and found that a part of molecules (up to 30%) can be fully hydrogenated by an H-atom fluence relevant to molecular cloud conditions.<sup>5</sup>

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<sup>1</sup> Tsuge, M.; Hama, T.; Kimura, Y.; Kouchi, A.; Watanabe, N. Interactions of Atomic and Molecular Hydrogen with a Diamond-like Carbon Surface:  $H_2$  Formation and Desorption. *Astrophys. J.* **2019**, *878*, 23.

<sup>2</sup> Tsuge, M.; Namiyoshi, T.; Furuya, K.; Yamazaki, T.; Kouchi, A.; Watanabe, N. Rapid Ortho-to-para Nuclear Spin Conversion of  $H_2$  on a Silicate Dust Surface. *Astrophys. J.* **2021**, *908*, 234.

<sup>3</sup> Tsuge, M.; Kouchi, A.; Watanabe, N. Measurements of Ortho-to-para Nuclear Spin Conversion of  $H_2$  on Low-temperature Carbonaceous Grain Analogs: Diamond-like Carbon and Graphite. *Astrophys. J.* **2021**, *923*, 71.

<sup>4</sup> Tsuge, M.; Hidaka, H.; Kouchi, A.; Watanabe, N. Diffusive Hydrogenation Reactions of CO Embedded in Amorphous Solid Water at Elevated Temperatures  $\sim 70$  K. *Astrophys. J.* **2020**, *900*, 187.

<sup>5</sup> Tsuge, M.; Kouchi, A.; Watanabe, N. Penetration of Non-energetic Hydrogen Atom into Amorphous Solid Water and its Reaction with Embedded Benzene and Naphthalene. *in preparation*.