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Catalytic Role of Refractory Interstellar Grain Analogs on H₂ Formation

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Refractory dust grains have an important role to play in the chemistry of star and planet-forming regions. Their surfaces interact with interstellar gas and act as a catalyst for the formation of simple and complex molecules in space. Several mechanisms have been invoked to explain how molecular hydrogen is formed in reactions on dust grain surfaces in different regions of space. In this article, we give an overview of our understanding of the laboratory experiments, conducted over the last 20 years, that deal with H₂ formation on interstellar grain analogs in space simulated conditions.

Keywords: laboratory astrochemistry, dust analogs, molecular hydrogen, surface chemistry, interstellar medium

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1. INTRODUCTION

The interstellar medium (ISM) is the tenuous gas and dust that pervades space between the stars in a galaxy. Interstellar gas is the major component that accounts for 99% of the interstellar mass, of which 70% is hydrogen either in atomic or molecular form (Ferriere, 2001). Solid refractory dust, which is made up of either silicates or carbonaceous materials, forms the remaining 1% of the interstellar mass. Molecular hydrogen (H₂) is by far the most abundant molecule in the Universe and it plays a crucial role in star formation. It also directly or indirectly contributes to all the reactions involved in the formation of simple and complex molecules in the ISM.

Naturally, a lot of interest lies in the understanding of how H atoms convert to H₂ in different environments of space. In regions of low gas density and temperatures, H₂ cannot form efficiently in the gas phase by the association of two H atoms. Therefore, the need to explore an alternative route of molecule formation becomes crucial to explain the observed abundances. Van de Hulst (1948) was the first to propose a significant role of dust grains in molecule formation. Dust grain surfaces can impart catalytic effect by (i) acting as a site for atoms to rapidly diffuse and react; (ii) acting as the third body to dissipate the recombination energy; (iii) reducing the reaction activation barriers. Based on the rate constant calculations of formation and destruction processes of H₂ in interstellar space, it was suggested that recombination of H atoms on dust grain surface could proceed efficiently between 5 and 20 K (Gould and Salpeter, 1963). To explore the possibility of extending an efficient recombination of H atoms on the grain surface beyond 20 K, calculations were made with a more realistic model of interstellar grain having lattice defects or impurity sites rather than regular grain surface (Hollenbach and Salpeter, 1971). The H₂ formation rate, calculated for the dust grain catalyzed reaction, was found to be compatible with the observed H₂ abundances in diffuse ISM. A large number of experimental studies was also devoted to the understanding of H₂ formation. However, their relevance to astrophysical conditions is not easy to derive since these studies were not performed on realistic interstellar grain analog surfaces and conditions encountered in space. For an account of those studies, see Pirronello et al. (2000). It was only in the late 1990s that laboratory experiments were performed on well-characterized interstellar

grain analogs in simulated space conditions to examine the nuances of gas-grain chemistry relating to H₂ formation. For a systematic review on H₂ formation on interstellar dust grains, see Vidali (2013) and Wakelam et al. (2017). The aim of the present paper is to outline relevant laboratory experiments that discuss the catalytic role of the refractory dust grains in H₂ formation on different grain temperatures found in varied regions of space.

2. REFRACTORY INTERSTELLAR DUST GRAINS

Refractory dust grains are primarily formed in the circumstellar envelope of evolved stars during the asymptotic giant branch phase. The chemical composition of the dust is determined by the composition of the evolved stars producing it. There are two main classes of grains whose composition depends on the C/O abundance ratio in the stellar atmosphere. The carbon-rich outflows (C/O > 1) lead to the production of carbonaceous grains (e.g., amorphous carbon, silicon carbide, titanium carbide, etc.). In oxygen-rich envelopes (C/O < 1), silicates (olivine and pyroxene composition) and other metal oxides (e.g., MgO, FeO, Fe₃O₄, Al₂O₃) are formed. Other sources of refractory grains are the nova and supernova ejecta and R Coronae Borealis variable stars.

During the journey of dust grains through the ISM, they interact with cosmic rays, UV photons, atoms which induce many effects such as amorphization, sputtering, and implantation. As the dust traverses through dense and UV-shielded molecular clouds, various simple molecules (mainly H₂O) accrete on them forming icy mantles. Observational evidence suggest that silicates, carbonaceous grains and water ice mantles are predominantly amorphous in the ISM. According to interstellar dust models, silicate grains are mainly sub-micron in size, while carbon grains range in size from nano to sub-micron (Draine, 2003; Jones et al., 2013). Krugel (2007) and Draine (2010) study provide a detailed review of the structure and composition of dust.

3. PREPARATION OF LABORATORY DUST ANALOGS

Laboratory dust analogs are prepared with the aim to understand how dust grains are formed, destroyed and altered in different astrophysical environments, and how these processes affect their spectral properties. Realistic analogs, which simulate the chemical composition and properties of the cosmic dust, have also been considered to investigate the role of dust grain surfaces for molecule formation. Different methods, such as arc discharge, laser ablation, chemical vapor deposition, flame synthesis, ion sputtering, sol-gel, have been applied in the laboratory for the production of dust analogs. The prepared analogs are thoroughly characterized by different techniques among which wet chemical analysis, scanning electron microscope, energy dispersive x-ray and x-ray diffraction are commonly used. A detailed report on the preparation and characterization of silicate and carbonaceous

grain analogs can be found in Colangeli et al. (2003), Henning (2010), and Jäger et al. (2015).

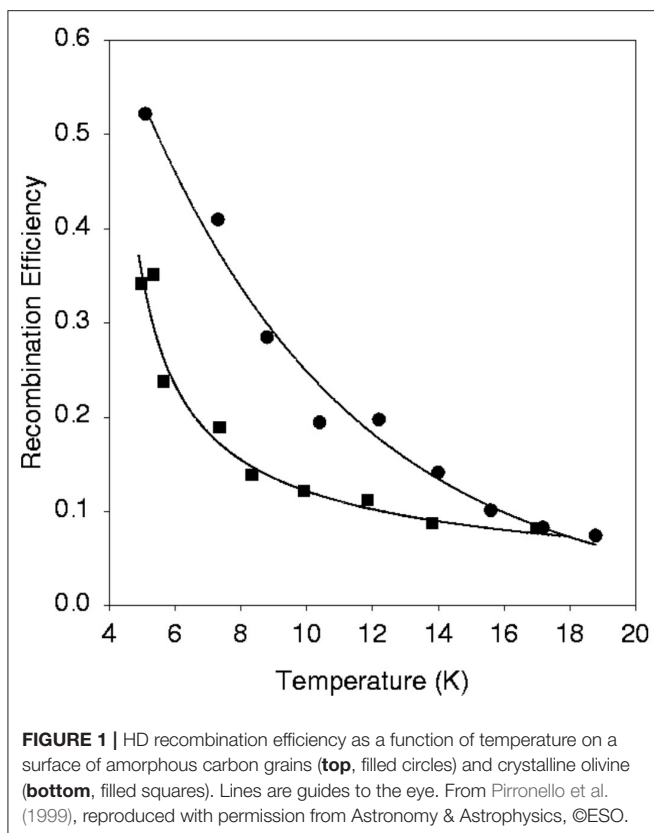
4. REACTION MECHANISMS BETWEEN ADSORBATE AND SURFACE

Physisorption and chemisorption are the two types of interactions that are important to consider between an atom and a surface. The former refers to weak and long range van der Waals forces that involve binding energy of the order of tens of meV. In the second case, there are strong and localized chemical bonds with a binding energy of the order of a few eV. Formation of H₂ on surfaces can occur through three main mechanisms namely Langmuir–Hinshelwood (LH), Eley–Rideal (ER), and Harris–Kasemo (HK, commonly known as hot atom). In LH mechanism, at first atoms are thermally accommodated on the surface, then they diffuse (via thermal hopping or quantum tunneling) and react to form molecules at the surface temperature. In the other two processes, atoms from the gas phase directly (for ER) or indirectly (for HK) hit other pre-adsorbed atoms on the surface. The HK is considered as an intermediate mechanism between LH and ER.

In the case of H₂ formation in space, H atoms can remain physisorbed on the grain surface until its temperature is low enough to prevent desorption. This happens in the cold interstellar clouds where grain temperatures are typically < 20 K. However, in these conditions H atoms are mobile enough to initiate reactions mainly through LH mechanism. Besides, in warmer environments such as photodissociation regions (PDRs), while physisorption fails to hold H atoms on the grain surface, chemisorbed H atoms that remain on the surface take part in formation reaction. In this regard, atoms are immobile and LH pathway can be fairly ruled out. Atoms from the gas phase with enough energy are needed to overcome the activation barrier to react on the surface, and molecule formation takes place via ER and HK mechanism. In the sub-sections that follow, we describe the H₂ formation in laboratory experiments performed at low and high grain surface temperatures.

4.1. H₂ Formation at Low Grain Surface Temperature

The first set of experiments to investigate H₂ formation on a dust grain analog was performed on a natural, polycrystalline olivine sample (Pirronello et al., 1997a,b). Together with the prompt formation of molecular hydrogen during irradiation of the surface by H atoms, the temperature programmed desorption (TPD) technique was applied to measure the recombination efficiency of H and D atoms (possessing low kinetic energies) that were still on the surface for a range of dust grain temperatures (< 20 K) encountered in the ISM (see **Figure 1**). The HD formation efficiency was found to be lower than the other theoretical model based estimates. The efficiency decreases with increasing sample temperature due to a short residence time of physisorbed H/D atoms at high temperatures. This aspect is also demonstrated by the trend with temperature of the sticking probability of H atoms on a dust analog surface (see **Figure 2**).



HD formation on olivine followed a second order kinetics at low coverages of H and D atoms. This means that atoms continued to remain localized on the surface without recombining till the surface temperature was raised. HD formation experiments were also carried out on amorphous carbon grains (prepared using the arc-discharge method) in the experimental conditions identical to the previous set (Pirronello et al., 1999). HD recombination efficiency was found to be higher in amorphous carbon grains than the silicates (Figure 1). The authors attributed this difference to the variation in surface morphology. A rate equation model, reproducing the above experimental data, confirmed that H_2 molecules can form efficiently only at low temperatures i.e., in the range 6–10 K for olivine and 10–20 K for amorphous carbon grains (Katz et al., 1999). Identical experiments of HD formation, as discussed above, were performed on amorphous olivine with different compositions prepared by laser ablation of mixed oxides used in varying proportions (Perets et al., 2007; Vidali et al., 2007, 2009). Amorphous silicate grains were found to be a more efficient catalyst for H_2 formation than polycrystalline olivine because H_2 formation efficiency is extended and shifted to higher grain temperature in the case of amorphous silicates. It was also suggested that H_2 molecules thermalize to the grain temperature before desorption. In another study, HD formation on single crystal olivine was found to be less effective than both amorphous and polycrystalline silicates (He et al., 2011). An interesting class of laboratory experiments that concerns H_2 formation at low dust grain temperature are reactions on amorphous water ice mantles

covering the refractory dust grains. It has been shown that such surfaces at 8 K possess shallow and deep adsorption sites that allows trapped H atoms to wait for the arrival of other H atoms from the gas phase in the low flux conditions of interstellar clouds and facilitate H_2 formation (Watanabe et al., 2010). Although H_2 formation on interstellar ices has been a topic of much interest, it is beyond the scope of the present article (see, for example, Watanabe and Kouchi (2008) and Hama and Watanabe (2013) for a review on this subject.

The process of H_2 formation raises an important concern about the fate of the 4.5 eV energy released during H atom recombination. In other words, we need to understand how this energy is distributed between a grain surface and the nascent molecule ejecting from the surface. TPD and resonance enhanced multiphoton ionization (REMPI) spectroscopy were simultaneously applied to study energy partitioning as a function of sample temperature during D_2 formation on amorphous silicate films (Lemaire et al., 2010). The films were prepared by electron beam evaporation of a San Carlos olivine on a gold coated substrate. The D_2 molecules, desorbed promptly just after formation, were detected in high excited states (vibrational level = 4, rotational level = 2). It was inferred that the morphology of the surface influences the internal energy of the formed molecules. In fact, D_2 molecules ejected from the crystalline sample were found to have a lower rotational energy distribution than those desorbed from amorphous samples of varying stoichiometry prepared by laser ablation technique (Gavilan et al., 2014). Similar sort of experiments were also performed on highly oriented pyrolytic graphite (HOPG), an idealized representation of an interstellar grain surface, between 15 and 50 K (Creighan et al., 2006; Islam et al., 2007; Latimer et al., 2008). In these experiments, HD molecules that were leaving the surface upon formation were detected in the vibrationally excited state up to the 7th level. Such investigations are important not only to look for observational signatures during H_2 formation in space, but also to develop accurate theoretical models.

4.2. H_2 Formation at High Grain Surface Temperature

For H_2 formation at high dust grain temperatures, reaction mechanisms that involve tightly bound chemisorbed H atoms on graphite and highly defected carbon/ silicate surface were theoretically proposed (Cazaux and Tielens, 2004; Cuppen and Herbst, 2005). Experimentally, adsorption behavior of H (D) atoms on HOPG was investigated and recombinative desorption of H_2 (D_2) showed a double peak in the TPD spectra (Zecho et al., 2002a). The desorption activation energy of H (D) on the surface was estimated to be ~ 0.6 (0.9) eV. Scanning tunneling microscopy (STM) images revealed that H_2 recombination is possible from two hydrogen dimer states on HOPG (Hornekær et al., 2006b). These dimer states were identified as the origin of the unusual double peak in TPD traces for hydrogen on graphite. Moreover, activation barriers of ~ 1.2 and ~ 1.6 eV were calculated for H_2 formation. STM images further revealed that H atoms have a preferential sticking on HOPG on those sites where an H atom is already pre-adsorbed, resulting in the formation of

large clusters that favor H₂ formation (Hornekær et al., 2006a). In another study, HD formation via ER or HK abstraction was investigated after exposure of H atoms with kinetic energies of 2,000 K on deuterated HOPG at 150 K (Zecho et al., 2002b). Depending on the coverage of the chemisorbed D atoms on the surface, the abstraction cross-section varied between 4 and 17 Å². Concerning the partitioning of 4.5 eV, the kinetic energy of H₂/D₂ molecules formed by laser assisted associative desorption of H/D atoms on HOPG at room temperature showed a broad distribution with a peak at ~ 1.3 eV (Baouche et al., 2006).

H₂ formation on amorphous carbonaceous surface with aliphatic C–H bonds was initially ignored since the binding energies of H atoms were considered very high (~ 4 eV). Mennella (2006) has experimentally estimated an activation barrier of 6 meV (70 K) for H atoms to form the aliphatic CH_{2,3} groups on hydrogen free nano-sized amorphous carbon grains. The barrier is much lower than the typical values of few tenths of an eV derived for H atoms on graphite (Hornekær et al., 2006b). On such hydrogenated amorphous carbon surface, HD formation has been observed for a range of surface temperatures 13–300 K, and for impinging D atoms between 80 and 300 K through ER mechanism (Mennella, 2008). At the aliphatic CH_{2,3} groups, H/D exchange occurs through a two-step reaction sequence: (1) dehydrogenation via H atom abstraction with the formation of an HD molecule and (2) deuteration with the addition of a D atom. **Figure 3** (red curve a) depicts the intensity decrease of the C–H stretching feature of aliphatic CH_{2,3} groups and the simultaneous increase of the corresponding aliphatic C–D bonds during the process. The net result of the exchange reaction sequence is formation of an HD molecule. This process was found to be barrierless at low surface temperatures, while an activation barrier of 130 K was found for surface above

100 K. An abstraction cross-section of 0.03 Å² was evaluated for H atoms (300 K) impinging on the analog sample at room temperature. Furthermore, the nascent HD molecules formed in the aliphatic sites should not be in a highly excited state as exoenergeticity of formation reaction is reduced by ~4 eV which is necessary to break the C–H bond. H₂ formation is not specific to H atom chemisorbed on aliphatic carbon sites. In fact, H₂ formation was observed in experiments carried out on hydrogenated aromatic carbon material with varying complexity starting from a simple polyaromatic hydrocarbon molecule (coronene film) (Mennella et al., 2012; Thrower et al., 2012) to complex carbon soots with a marked aromatic character (Mennella, 2011). In these cases, an initial carbon aromatic sp² to aliphatic sp³ rehybridization reaction was followed by the same exchange reactions as those observed in the aliphatic carbon sample. VUV photolysis of hydrogenated amorphous carbon was suggested to be a feasible route to H₂ formation (Alata et al., 2014). However, this mechanism alone can not explain the catalytic role of carbon grains and can only be a marginal source of H₂ in the absence of efficient H atom addition process.

H₂ formation involving chemisorbed H atoms has recently been investigated using Mg-rich hydroxylated amorphous silicates (Mennella and Suhasaria, 2019). The dust grain analogs prepared by laser ablation of an oxide mixture showed a broad infrared band resulting from chemisorbed hydroxyl groups. These hydroxylated silicate surfaces were exposed to D atoms with an energy of a few tens of meV. The catalytic H₂ formation

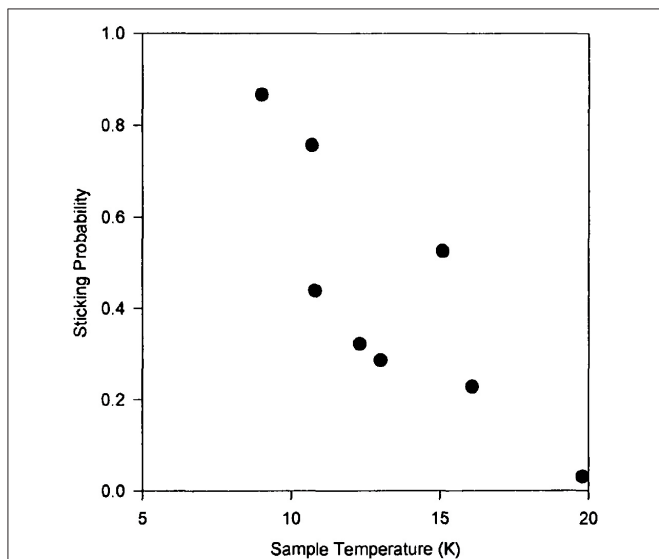


FIGURE 2 | Sticking probability of H atoms on amorphous carbon sample as a function of the sample temperature. From Pirronello et al. (2000), reproduced with permission of the Cambridge University Press through PLSclear.

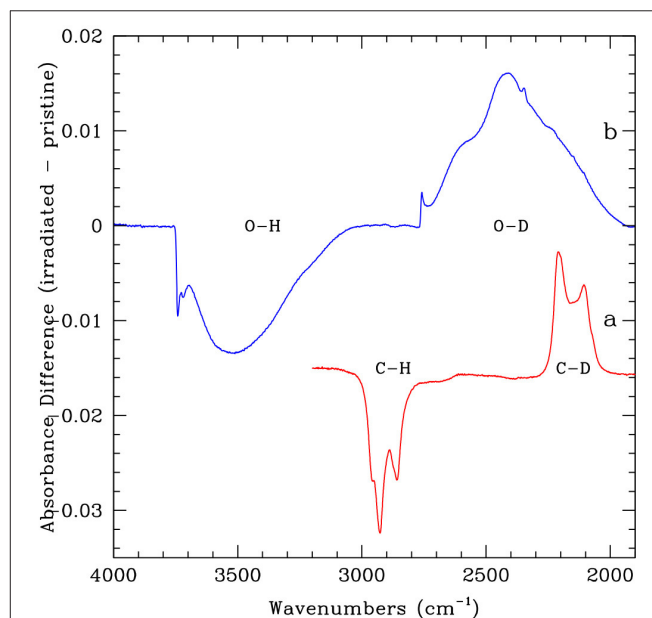


FIGURE 3 | The evolution of IR spectrum of hydrogenated nano sized carbon grains after irradiation of 1×10^{19} D atoms cm^{-2} (red curve a). The spectral evolution of Mg-rich hydroxylated amorphous silicate grains after irradiation of 3.8×10^{18} D atoms cm^{-2} is also reported (blue curve b). The spectra are shown after subtraction of the initial spectrum and are shifted in ordinate for the sake of clarity.

was a result of the exchange reaction similar to those on hydrogenated carbon surfaces. **Figure 3** (blue curve b) shows a reduction in the number of O–H stretching modes due to the abstraction of already bonded H atoms in O–H groups of silicates. At the same time, new O–D bonds are formed on silicate grains. In the process, HD molecules are formed via exchange reactions.

5. FINAL REMARKS

Laboratory investigations are crucial to the understanding of the physico-chemical processes involved in H₂ formation. They have demonstrated how weakly adsorbed H atoms on refractory grain analogs at temperatures <20 K migrate to another H atom and recombine to H₂ via Langmuir–Hinshelwood mechanism. It is also evident that the ejected H₂ molecules after formation on such grain analogs are likely to be vibrationally hot but rotationally cold. In the limited number of studies that concerns H₂ formation involving chemisorbed H atoms, LH mechanism was found to be inefficient at higher grain temperature and H₂ formation relies on ER/HK mechanism. Laboratory investigations have also indicated that varying carbon based structures altering from a simple aliphatic to an aromatic to a mixed aliphatic–aromatic system catalyze H₂ molecules.

This occurs through an exchange reaction when H atoms are already pre-adsorbed on them. The role of hydroxylated amorphous silicates as catalysts for H₂ formation has also been highlighted in a recent study. It is apparent that so far, most laboratory investigations have focused either on physisorption or chemisorption formation mechanism. However, the presence of H₂ in a wide variety of space environments hints to the fact that the two formation mechanism are not discrete but they should be operating at the same time. Thus, there is a need for a systematic approach that underlines the intertwining of the two formation mechanisms.

AUTHOR CONTRIBUTIONS

All authors contributed to the article and approved the submitted version.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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