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# $H_2$ formation on Mg-rich amorphous silicates

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**Abstract.** We present the results of an experimental study on the interaction of D atoms with Mg-rich amorphous silicates. The effects of D irradiation have been analyzed by infrared spectroscopy. The results indicate that HD forms by abstraction of hydrogen atoms chemisorbed in the hydroxyl groups of silicate grains. The formation process occurs for grain and atom temperatures relevant to photodissociation regions.

**Keywords.** Astrochemistry, molecular processes, methods: laboratory, techniques: spectroscopic

## 1. Introduction

It is generally accepted that $H_2$ molecules form at the surface of interstellar grains. The catalytic role of silicates, carbon grains and water ice has been demonstrated at low temperature through a series of experiments (e. g. Pirronello *et al.* 1997, Manicò *et al.* 2001, Hornekær *et al.* 2003). The recombination efficiency of H atoms is high only at low grain temperatures ($T_{grain} < 20$ K). Laboratory results fail to explain $H_2$ production at higher grain temperatures such as those expected in photodissociation regions (PDRs). At these temperatures, the residence time of H atoms in physisorption sites on the surface is too short for recombination to take place (Vidali *et al.* 2005). For an exhaustive review of observational, experimental and theoretical work on $H_2$ see Wakelam *et al.* (2017). To overcome this problem, H atom recombination with other H atoms on chemisorbed sites on aromatic structures such as graphite and coronene-like carbon clusters were proposed (Cazaux & Tielens 2004). Aliphatic C-H bonds were initially neglected for long since their binding energy was considered too high for those atoms to take part in $H_2$ formation. However, the catalytic formation of molecular hydrogen on the aliphatic C-H sites of hydrogenated carbon grains has successfully been demonstrated experimentally for grain and H atom temperatures relevant to ISM clouds and PDRs (Mennella 2008). $H_2$ formation was also observed in H atom irradiation experiments carried out on aromatic carbon materials such as coronene film and carbon soots with a marked aromatic character (Mennella *et al.* 2012, Thrower *et al.* 2012). On the basis of this experimental activity, one can conclude that carbon based structures varying from PAH molecules to complex disordered materials with mixed aromatic and aliphatic hydrogen bonding configurations act as catalysts for the molecular hydrogen formation.

Silicate grains are another basic and ubiquitous dust population in the ISM. Silicates have generally a Mg-rich composition and an amorphous structure: the crystalline fraction is less than 5% in the ISM and a bit higher (10%) around evolved stars with medium and high mass-loss rates (e.g. Molster *et al.* 2002, Kemper *et al.* 2004). Therefore, it is of primary interest to investigate their role in the formation of molecular hydrogen at high grain temperatures.

## 2. Experimental and Results

As analogues of interstellar silicates we have considered a Mg-rich amorphous silicates produced by laser ablation of an oxide mixture. We have used a Nd-YAG solid state pulsed laser

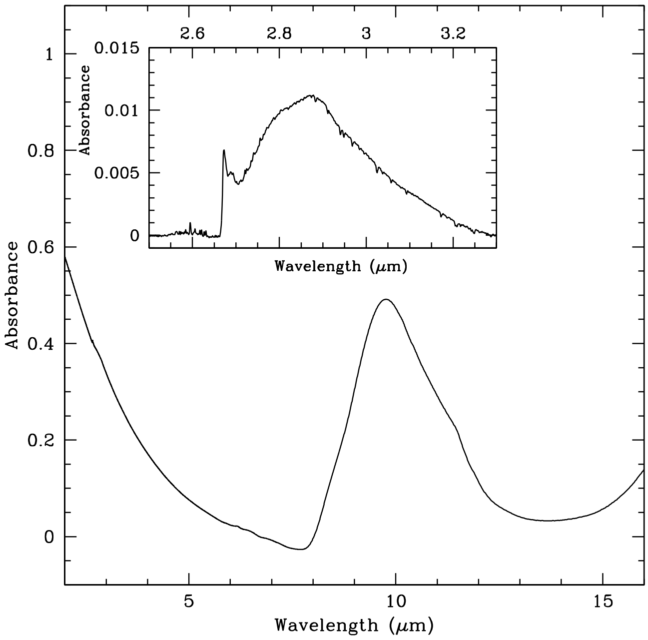

**Figure 1.** IR spectrum of Mg-rich silicate grains showing Si-O stretching at 9.8 μm. The inset shows O-H stretching around 3 μm after continuum removal.

at 1024 nm equipped with II and IV harmonics at 532 and 266 nm, respectively. By using a focusing lens, the power density on the target was $1\times10^8$ W cm$^{-2}$. The target to be ablated was mounted inside a chamber on a rotating sample holder placed in front of the laser beam. Silicate grains were collected at a distance of 5 cm from the target on ZnSe windows and carbon stubs, respectively, for infrared (IR) spectroscopy and scanning electron microscopy. We have used a Mg-rich oxide mixture [MgO:$SiO_2$ (1:1)] as target. The mixture was prepared by weighing the exact amount of MgO and $SiO_2$ in order to have the starting stoichiometric composition of enstatite ($MgSiO_3$) The mixture was produced in the form of a pellet (13 mm in diameter and a few millimeters in thickness) by pressing finely ground oxides at 10 tons. The chemical composition resulting from the process of vaporization and condensation was analyzed with an Electron Dispersive X-ray (EDX) system (Oxford Inca Energy 350) linked to a Field Emission Scanning Electron Microscope ZEISS SUPRA 25. The atomic ratio of the sample obtained by EDX was 1.1, in agreement with the corresponding value of the starting oxide mixture.

Figure 1 shows the infrared absorbance spectrum of the sample, in the range 2–16 μm, measured at a spectral resolution of 2 cm$^{-1}$. It is characterized by a strong Si-O stretching band at 9.8 μm, in agreement with the trend of the peak position as a function of the Mg/Si ratio reported by Jäger *et al.* (2003). The inset to Figure 1 shows the silicate absorbance in the O-H stretching spectral region after continuum removal. A broad band at 2.88 μm (3478 cm$^{-1}$), produced by adsorbed water and chemisorbed hydroxyl groups, characterizes this region. Two narrow bands at 2.67 μm (3741 cm$^{-1}$) and 2.69 μm (3716 cm$^{-1}$), are respectively, attributed to isolated Si-OH and Mg-OH groups (Iler 1979, Shinoda *et al.* 2002). Similar bands have been detected in silicates produced by sol-gel method, suggesting that laser ablation and sol-gel techniques provide materials with chemical properties expected for cosmic silicates. In fact, the formation of silicates with a small content of isolated Si-OH and Mg-OH bonds can be considered highly probable, since $H_2O$, the most abundant oxygen-bearing molecule, participates in the formation of olivine and pyroxene-type silicates (Gail & Sedlmayr 1998, Jäger *et al.* 2003).

To study the interaction of hydrogen with silicates, the samples were mounted in a vacuum

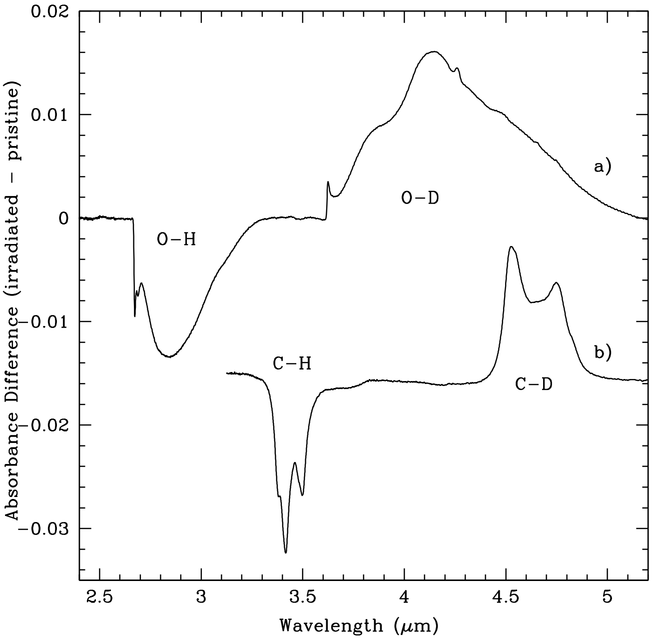

**Figure 2.** IR spectrum of silicate grains after irradiation (shown after subtraction of the initial spectrum) of $3.8\times10^{18}$ D atoms cm$^{-2}$ a). The evolution with D irradiation of hydrogenated carbon grains is also shown for comparison b). The spectra are shifted in ordinate for the sake of clarity.

chamber, with a base pressure of $2\times10^{-8}$ mbar, on a rotating sample holder at the right angle intersection between an atomic hydrogen beam and the IR beam of an FTIR spectrophotometer (Bruker model Vertex 80). We used D atoms to distinguish impinging atom from H atoms already present in hydroxyl groups of silicate grains. D atoms were produced by microwave dissociation of molecular deuterium; they have a Maxwellian distribution of the velocity at 300 K (Mennella 2006). After D atom exposure of silicate grains at room temperature and rotating the sample by 90° it was possible to measure the IR spectrum with a resolution of 2 cm$^{-1}$ in the range 2–5 $\mu$m (5000 – 2000 cm$^{-1}$).

Figure 2 shows the spectral changes induced by D atom irradiation in the considered amorphous silicate. The absorbance band centered at 2.84 $\mu$m due to O-H groups decreases, while the activation of a broad band centered at about 4.15 $\mu$m takes place. In addition, a sharp feature at 3.62 $\mu$m and a shoulder at 3.86 $\mu$m are also observed.

## 3. Discussion and Conclusions

The spectral variations induced in Mg-rich silicates by atomic deuterium are clear evidence for chemical reactions resulting in the formation of : 1) HD molecules via exchange reactions and 2) new OD bonds (hydroxylation) on silicate grains. The decrease in absorbance in Figure 2 indicates a reduction in the number of O-H stretching modes due to abstraction of already bonded H atoms in OH groups of silicates by the incoming D atom. Abstraction determines the formation of HD molecules in the gas phase. This reaction is the first step of a two-step exchange reaction, the second step being the addition of a second D atom to form again the OD group. The absorption of this groups is shifted at longer wavelengths due to isotopic substitution. The wavelength shift of a factor of 1.36 measured for the sharp Mg-OH feature is in good agreement with the expected value of 1.37 due to the variation in the reduced mass. There is a striking similarity between the present results and the evolution with D irradiation of the aliphatic C-H bonds in hydrogenated carbon grains (see Figure 2).

In addition to exchange reactions new O-D bonds are formed during irradiation. This is testified by the appearance of a band, activated by D atoms, wider then that present in the pristine silicates. This result is a consequence of multiple and independent overlapping absorptions of hydroxyl groups activated by hydrogen atom interaction in the defects on amorphous silicates, which determine a wider range of binding sites enhancing both physisorption and chemisorption of hydrogen (Dyar *et al.* 2010).

The formation of OH bonds has been reported after implantation of protons in silicates with different composition and structure (e.g. Schaible & Baragiola 2014). The substantial difference between the present work and previous implantation experiments concerns the interaction energy. Unlike proton implantation in silicates, where ions with an energy spanning from keV to MeV have been considered, the present experiment shows the possibility to hydroxylize amorphous silicates via reactions with thermal (a few tens of meV) hydrogen atoms. The results agree with density functional quantum mechanical calculations on the formation of OH groups in Mg–rich silicate nanoclusters by impinging H atoms that takes place without any significant energy barrier (Bromley 2019, private communication).

The preliminary results presented here clearly indicate that OH groups in Mg rich amorphous silicates act as catalysts for the molecular hydrogen formation. This result has a broader relevance in the context of $H_2$ formation in PDRs where grains resides at a higher temperature than interstellar clouds.

## 4. Ackowledgements

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