

NASA LAW, February 14-16, 2006, UNLV, Las Vegas

## Use of Laboratory Data to Model Interstellar Chemistry

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### ABSTRACT

Our laboratory research program is about the formation of molecules on dust grains analogues in conditions mimicking interstellar medium environments. Using surface science techniques, in the last ten years we have investigated the formation of molecular hydrogen and other molecules on different types of dust grain analogues. We analyzed the results to extract quantitative information on the processes of molecule formation on and ejection from dust grain analogues. The usefulness of these data lies in the fact that these results have been employed by theoreticians in models of the chemical evolution of ISM environments.

### 1. Introduction

It is well known that gas-phase formation of H<sub>2</sub> doesn't occur with the rate necessary to explain its abundance in the ISM. More than thirty years ago Hollenbach and Salpeter (1971) proposed that H<sub>2</sub> formation occurs on the surfaces of dust grains. They calculated that the migration of H atoms on the grain via tunneling was so fast that, if two atoms happened to be on a grain at a given time, they would encounter and bond before leaving the grain. For

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this rate of formation to match the observed destruction rate in diffuse clouds, thus achieving steady-state conditions, the sticking probability of H on a grain has to be about 0.3, a number close to what they obtained in semiclassical calculations of sticking of H atoms on model surfaces. Smoluchowski (1981) reasoned that, if interstellar ice is amorphous, the diffusion by tunneling would be greatly limited; in his calculation he obtained a recombination rate much smaller than the one necessary to explain observations.

In the late 90's we initiated a program to measure in the laboratory the formation on surfaces of H<sub>2</sub> and other key molecules in conditions as close to actual interstellar environments as technically feasible. The first measurement of H<sub>2</sub> formation on a surface at low temperature was performed by our group using a telluric polycrystalline sample of olivine as a proxy of a dust grain (Pirronello et al. 1997a). Since then we extended our measurements to samples of amorphous carbon and amorphous water ice (Vidali et al. 2006a). Besides the formation efficiency, to be defined below, we characterized the kinetics of the reaction in order to learn about the mechanisms of H<sub>2</sub> formation. In this presentation, we summarize our latest results of the determination of the mechanisms of H<sub>2</sub> formation on amorphous water ice.

## 2. Experimental Methods

The apparatus consists of two triply differentially pumped atomic beam lines, a sample chamber, and a time-of-flight section (Vidali et al. 2006a). The experiment is done in two stages. In the first, or irradiation stage, we send *low flux* beams of H and D atoms onto the surface of a dust grain analogue held at 5 to 30 K. The HD yield that comes off the sample during irradiation with H and D atoms is collected by a quadrupole mass spectrometer. In the second stage, or TPD - Thermal Programmed Desorption, in order to set H and D atoms in motion so they can react, or to remove HD molecules that formed on the surface during irradiation, the temperature of the surface is rapidly raised and the HD molecules coming off the surface are detected. The sum of the yields collected during the irradiation and the thermal desorption experiment is then divided by half of the number of atoms that are detected striking the surface during the irradiation phase. Corrections are applied for the detection geometry and sensitivity, and for the different reaction paths. The number obtained (between 0 and 1) is the recombination efficiency. From an analysis of the shape of the TPD traces information on the kinetics of the reaction and on the mechanisms of reaction can be obtained (Vidali et al. 2006b).

## 3. Results

In Fig. 1 we show the recombination efficiency of H<sub>2</sub> obtained on surfaces of polycrystalline olivine, amorphous carbon, and amorphous water ice (Vidali et al. 2006a).

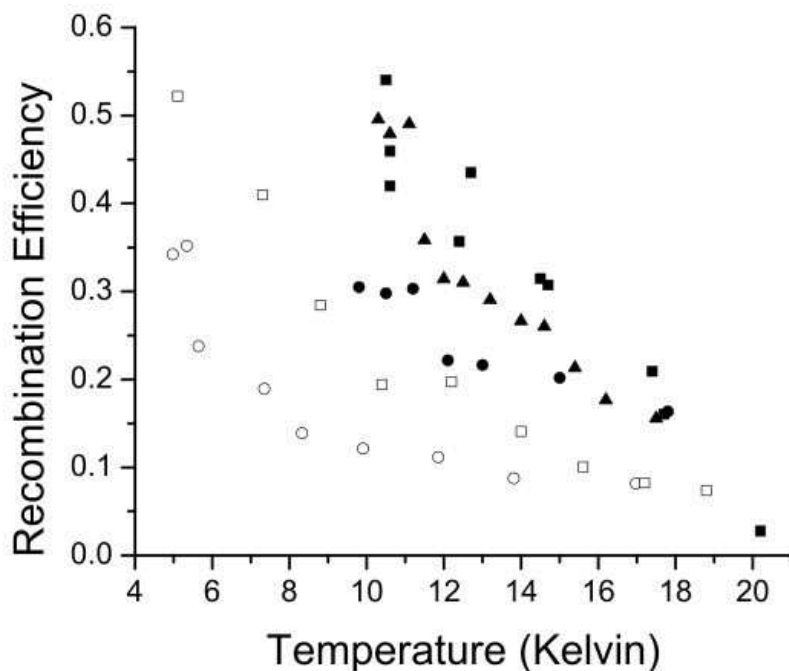


Fig. 1.— Recombination efficiency of molecular hydrogen vs. temperature of the sample at irradiation. High-density amorphous water ice: filled circles; low-density amorphous water: filled square; water vapor-deposited low-density amorphous ice: filled triangles; polycrystalline olivine: empty circles; amorphous carbon: empty squares. From Vidali et al. (2006a).

In Fig. 2 we plot the results of experiments designed to probe the mechanisms of reaction. We prepared an amorphous water ice sample (see Roser et al. (2003) for details) and deposited molecular HD at 10 K followed by a TPD (see trace with  $\circ$ ). After cleaning the surface, we sent H and D atoms and then we did a TPD that produced HD molecules. If HD molecules formed rapidly during the irradiation phase and stayed on the surface, then the TPD trace should have the same shape as the one in the experiment in which molecular HD was deposited and then made to leave the surface via a TPD. Clearly the two traces are different. Specifically, the figure shows that a good fraction of HD in the experiment of molecular deposition comes off at a lower temperature than in the experiment of deposition of H and D atoms. We conclude, as we did about the experiments of HD formation on polycrystalline olivine *at low irradiation doses* (Pirronello et al. 1997a), that H and D atoms remain on the surface as atoms until a thermal pulse is given. Thus, the formation of molecular hydrogen *is primarily initiated by thermal energy*.

In another experiment, see (Roser et al. 2003), we measured the time-of-flight of HD

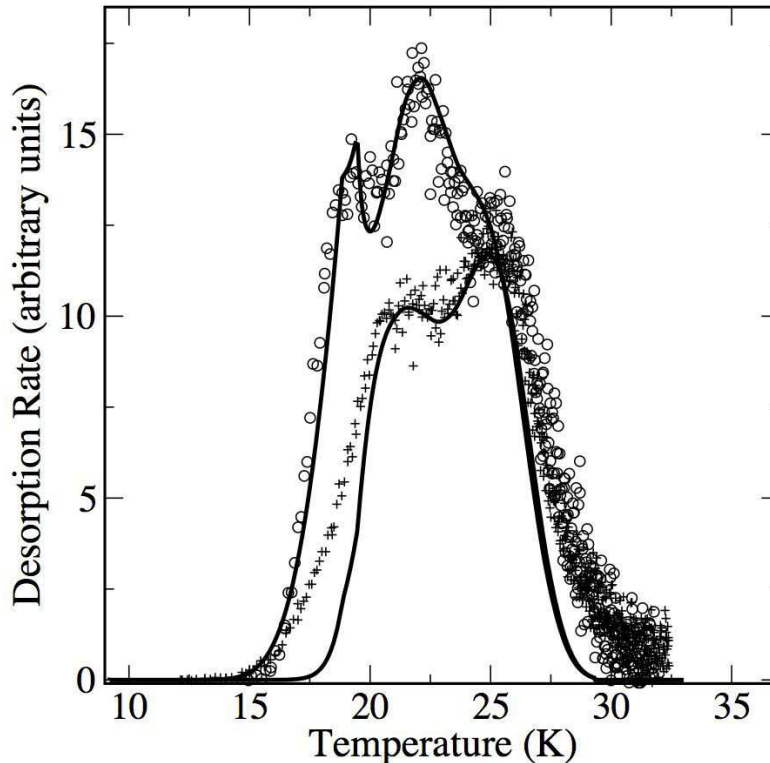


Fig. 2.— TPD traces of HD desorption after irradiation with HD molecules ( $\circ$ ) and H+D atoms ( $+$ ) on amorphous low density water ice. The solid lines are fits obtained by a rate equations model. (Perets et al. (2005)).

molecules flying off the surface after the formation process. The velocity distribution of the molecules was fit with a Maxwell-Boltzmann distribution with a translational speed around 20 K, depending on the conditions of the experiment. A similar result was obtained independently by Hornekaer et al. (2003). Recently, the ro-vibrational excitation of HD leaving a graphitic surface was measured (Creighan et al. 2006) giving a rotational energy of about 250 to 280 K.

#### 4. Discussion

Our experiments are designed to measure the formation efficiency and mechanisms of reactions in conditions as close as possible to ISM conditions. In order to use our results in models of the chemistry of ISM environments, theorists (Katz et al. 1999; Cazaux and Tielens 2004; Perets et al. 2005; Cuppen and Herbst 2005) have used models with rate or stochastic equations to fit our data and then to predict the formation of molecular hydrogen in ISM conditions and on grains with a distribution of sizes. From the analysis

of experimental data and the results of the models, one gets the following picture. The recombination efficiency is higher on amorphous surfaces, indicating that morphology plays a role. The efficiency is high in a narrow temperature range on polycrystalline olivine, but this range is wider on amorphous analogues. H atoms experience weak physisorption forces and thermal activation is needed to promote diffusion. The reaction proceeds either by the Langmuir-Hinshelwood or the hot atom mechanism, depending on the conditions (see Vidali et. al. 2006a,b for details).

## 5. Conclusion

Our work shows that through laboratory research and in close collaboration with theoreticians and modelers precious information can be obtained on the catalytic activity of surfaces, on the mechanisms of reaction and on the energy released in the reaction. This knowledge is useful for understanding the formation of hydrogen in the ISM and the role that dust grains play in the formation of molecules. Experiments on H<sub>2</sub> formation on other analogues (such as silicates) are in progress.

This work was supported in part by NASA through grants NAG5-9093 and NAG5-11438 (G.V) and by the Italian Ministry for University and Scientific Research through grant 21043088 (V.P).

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