Investigations of the Formation of Molecular Hydrogen on Dust Grain Analogues
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Abstract
In the last four years we have been working to investigate the formation of molecular hydrogen on surfaces of materials of astrophysical interest, such as silicates, carbonaceous particles and ices, and in conditions approximating the ones present in a variety of astrophysical environments. Our experimental studies - the first of their kind and complemented with computer simulations and theoretical analyses - have given not only hydrogen recombination rates under different ISM conditions, but they have also offered new insights into this fundamental astrophysical problem. Here we summarize our experimental methods and most significant results.

1. Introduction
Molecular hydrogen, the lightest and most abundant molecule in the Universe, plays several crucial roles, from aiding the formation of stars to being an active participant, in its neutral or charged state, to most of the reactions occurring in the interstellar medium.

It has long been realized that molecular hydrogen cannot form efficiently in the gas phase, because the release of the energy excess upon formation via radiative decay is not allowed by selection rules, while its formation via the reaction $H + H^- \rightarrow H_2 + e^-$ is not sufficient to explain its abundance except in very specific environments. It has been pointed out that dust grains can act as catalysts in the formation of molecular hydrogen, and simple models (Hollenbach & Salpeter 1971; Hollenbach et al. 1971) showed that, although dust grains are outnumbered by gas atoms $10^{12}$ to 1, under reasonable hypotheses and values of key parameters, molecular hydrogen can form on grains in numbers to match the observed abundance. However, the dynamics and the rate of formation of $H_2$ molecules on surfaces of grains have not been clarified yet (for a recent review, see: Pirronello et al. 2000 and references therein).

Smoluchowski (1979, 1981, 1983), in his theoretical work questioned the choice of a crystalline structure for the grain in earlier calculations (Hollenbach & Salpeter 1971; Hollenbach et al. 1971) and considered the formation of $H_2$ on amorphous surfaces, obtaining a formation efficiency much less than the one required by observations. This stimulated some authors to propose alternative mechanisms of formation of $H_2$ (Pirronello & Averna 1988; Averna & Pirronello 1991; Watanabe et al. 2000). A few years ago, our group at Syracuse University embarked in a program to conduct carefully designed experiments to study the formation of molecular hydrogen on surfaces in conditions as close to key ISM environments as technically feasible. The work concentrated on measuring the recombination efficiency on different candidates of actual dust grain surfaces and on elucidating the mechanism of $H_2$ formation (Pirronello et al. 1997a,b; Vidali et al. 1998; Pirronello et al. 1999). Other groups are now taking up the challenge of studying other important aspects of this problem.
2. Experimental

The apparatus used in these investigations was originally designed to study processes occurring on well-characterized surfaces. In state-of-the-art surface science work, probes are used to obtain knowledge of physical and chemical processes at the atomic level. The apparatus, see Fig. 1, was modified to address the study of the formation of molecules catalyzed on surfaces of materials of relevance to astrochemistry. It has been described several times in easily accessible publications (Vidali et al. 1998; Pirronello et al. 2000; Manicò et al. 2001). Because of space constraints, here we rather give some overall design considerations that we followed in order to carry out the measurements under conditions as closely as possible to the ones present in key astrophysical environments. First, the apparatus uses ultra-high vacuum (UHV) techniques to keep the background pressure, mostly made up of H₂, in the 10⁻¹⁰ torr range (or 10⁶ particles/cm³) to avoid the contamination of the sample. Second, there is the capability of keeping the temperature of the sample in the range of astrophysical interest (10 to 30 K) as well as higher (for cleaning purposes) and lower (for studying processes that, if conducted at higher temperature, would take place too rapidly on the laboratory time scale to be measured). Great care has been given to the design of the sample holder, so the sample is adequately thermally shielded and its temperature is measured reliably (using a calibrated silicon diode in good thermal contact with the sample). Third, the exposure of gases to the sample is obtained using atomic beams. The use of beams allows to control the size of the beam (so it strikes the sample and no other part of the apparatus), its temperature and density. For this application, the use of low energy and low flux beams is essential. Also essential in the study of H₂ formation is the use of beams of two isotopes, H and D, so that the formation of HD can be unequivocally traced to processes on the sample. Therefore, the presence of background H₂ gas or imperfect hydrogen dissociation in the beam source do not influence our measurements. Thus, the innovative aspect of this apparatus is the ability to study astrophysically relevant physical and chemical processes that occur at the surface of grains, whereby in the past lab studies have been carried out to study reactions in the bulk of dust grain analogues.

Fig. 1.— Schematic view of the apparatus at Syracuse University used to study physical and chemical processes on dust grain analogues in astrophysically relevant conditions. QMS is the quadrupole mass spectrometer; CH1, CH2 and CH3 are mechanical choppers (beam modulators); VP is the viewport to introduce the laser beam into the UHV chamber for the (2+1) REMPI investigation.
3. Review of Results

In Fig. 2 the recombination efficiency on different analogues of dust grain surfaces is plotted as a function of sample temperature. Here the recombination efficiency is obtained by taking the amount of HD collected in the reaction and dividing it by the measured amount of H and D sent onto the sample. This number is then corrected for the instrumental response and for the probability of forming HD versus H₂ or D₂. The amount of HD collected comes from two sources. The first is the HD that is formed during the time H and D atoms are sent to the surface. This contribution, which physically corresponds to a fast migration of H and D on the surface, is usually small at the lowest temperature. As mentioned elsewhere, the amount reported as the “fast reaction” contribution is typically an overestimate of the true HD formed under these conditions, since there are instrumental effects affecting the measurement that cannot be easily separated from the true contribution. The second source of the collected HD is the one formed during the thermal desorption, when the surface temperature is rapidly ramped providing mobility to atoms. Thus, the thermal desorption experiments can be thought as providing a means to accelerate processes that on grains in actual astrophysical environments would take much longer. Finally, it is worth reminding that in the experiments that we have done so far, the exposure of the surface to H and D was such that the sample is covered with much less than one layer of H or D. Thus, the contribution to HD formation from events in which H hits a D atom (or vice-versa) and forms HD without prior thermalization with the surface (the Eley-Rideal reaction) is expected to be small. The results presented in Fig. 2 were obtained on the following samples: a natural sample of polycrystalline olivine (Pirronello et al. 1997a,b), amorphous carbon samples (Pirronello et al. 1999), and amorphous water ice (Manicò et al. 2001). The size of the symbols gives a measure of the statistical errors, while the scatter of the points for each type of material gives an indication of reproducibility due to preparation methods and instrumental effects.

![Figure 2: Recombination efficiency of molecular hydrogen versus temperature on polycrystalline olivine (circles), amorphous carbon (squares), and high density amorphous ice (triangles). Only the contribution from the thermal desorption experiment is shown, see text. The samples were exposed to roughly comparable amounts of H and D. Data are from Pirronello et al. (1997a); Katz et al. (1999); Manicò et al. (2001).](image-url)
4. Discussion

It would be desirable to conduct a systematic study of which processes or characteristics of the surface are responsible for a given trend in the recombination efficiency. Given the challenges of conducting these types of experiments, it will take time to amass this needed detailed information. As a first step, we recently began a systematic study of the effect on molecular hydrogen formation of the morphology of different types of amorphous ice and of treatment with UV radiation (Roser et al. 2002). Experiments to provide more specific answers on other aspects influencing the recombination efficiency are currently being designed. In the meantime, one can look at the information provided in Fig. 2. It seems to indicate that surfaces that are more disordered, such as amorphous carbon or amorphous water ice, provide a more favorable locus for the formation of molecular hydrogen than polycrystalline olivine. Additional information on the formation of molecular hydrogen on surfaces comes from the study of the kinetics. First, as shown in Pirronello et al. (1997b), there is good experimental evidence that the kinetics of formation of molecular hydrogen on polycrystalline olivine at low temperature and at very low coverage of H is of the second order, signifying that the formation rate depends on the square of the concentration of the reactants. It is customary to obtain an insight into the desorption process by using the following approximation to relate the rate of desorption of particles \( \frac{dN(t)}{dt} \) to parameters related to surface processes:

\[ -\frac{dN(t)}{dt} = k_m N(t)^m, \]

where \( N(t) \) is the number of particles desorbing at time \( t \), \( N(T) \) is the number of atoms or molecules on the surface at time \( t \) (these particles could be of a different species than the ones desorbing), \( k_m = k^m \exp(-E_d/k_BT) \), \( E_d \) is the desorption energy, \( k^m \) is a constant, and \( m \) is the order of the desorption. For \( m = 0 \), desorption is independent of coverage, which is the case appropriate for desorption from several layers, since the desorption yield doesn't, in first approximation, depend on the coverage. A typical signature is the presence of a common leading edge for different coverages. \( m = 1 \) corresponds to first order desorption, and the molecules already formed on the surface leave during the desorption independently from each other; a distinguishing trait is the common trailing edge and the same peak position as a function of coverage. \( m = 2 \) corresponds to second order desorption, that is the reaction rate depends upon the products of the adatoms' concentrations; in this case, the peak shifts as a function of coverage. The observation that data can be fitted with an \( m = 2 \) kinetics indicates that the mechanism of formation involves the diffusion of the reactants, thus contradicting the long held assumption that molecular hydrogen would form quickly due to tunneling. Rather, it seems that H (and D) atoms are stuck in deeper wells and can move if given a thermal boost. This led Pirronello et al. (1977b) to propose an expression for the recombination rate that is quadratic in the density of H in ISM clouds:

\[ R_{H_2} = \frac{1}{2}(n_H v_H A S t_H)^2 n_g \alpha \gamma \gamma, \]

where \( n_H \) and \( v_H \) are the number density and the speed of H atoms in the gas phase, respectively; \( A \) is the average cross-sectional area of a grain; \( t_H \) is the residence time of adsorbed H atoms on the surface, \( S \) is the sticking coefficient, \( n_g \) is the number density of dust grains, and \( \alpha \) is the hopping rate of a single H adatom. \( \gamma \) takes into account the possibility that there is an activation energy for recombination. Notice that the quantity that is squared, i.e., \( (n_H v_H A S t_H) \), is the average number \( N \) of H atoms adsorbed on the surface at a given time. Biham et al. (1998) found from an analysis of the rate equations that this is the correct expression of the steady state solution in the case of slow diffusion of reactants on dust grains, while the Hollenbach et al.'s expression, which is linear in the concentration of H in the ISM, holds in the regime of very fast tunneling or large coverage of H on
the grain. The second type of information that can be extracted from the data is about the activation energy of the reaction. Using rate equations, Katz et al. (1999) fitted thermal desorption data of H and D on olivine and amorphous carbon to obtain activation energy barriers. No prior assumption on the order of the desorption was made. The results of this theoretical analysis confirmed the picture given above obtained with the use of Eq.(1), and gave a tool to extrapolate the experimental results to conditions in the ISM. The molecular hydrogen formation efficiency on amorphous carbon and water ice (Katz et al. 1999; Manicò et al. 2001) can explain the abundance of H₂ in diffuse and quiescent dense clouds. An analysis of the formation of HD on different types of amorphous water ice (Roser et al. 2002) gives information on the energetic of the reaction H_surface + D_surface → HD_desorbing as a function of different ice morphology.

5. Future Investigations

Thirty years ago, when the first model of the formation of molecular hydrogen on dust grains came out, there was no experimental evidence to verify its predictions or to point the way for further refinements. Now there are experimental data on recombination efficiencies and kinetics of recombination which have shed light on this fundamental process. As more experiments are being carried out at Syracuse University and soon elsewhere, detailed information on the influence of the morphology and chemical make-up of surfaces of dust grain analogues will soon be available. Furthermore, at Syracuse University we have set-up a measurement system to determine the kinetic energy of the departing molecules by using time-of-flight mass spectrometry (see Fig.1) as well as their roto-vibrational status - for detecting the internal quantum state of hydrogen molecules we use a (2+1) REMPI (Resonance Enhanced MultiPhoton Ionization) scheme. We are also planning to build an instrument to measure the energy released into the solid by the reaction of molecular hydrogen formation. From the theoretical standpoint, the sophistication of the calculations will have to match that of the experiments; the formation of molecular hydrogen will have to be studied on realistic, disordered surfaces.

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