Final Report on NASA Grant NAG5-4998: Experimental Studies of Hydrogenation and Other Reactions on Surfaces Under Astrophysically Relevant Conditions

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1   Summary

The goal of our project is to study hydrogen recombination reactions on solid surfaces under conditions that are relevant in astrophysics. Laboratory experiments were conducted using low-flux, cold atomic H and D beams impinging on a sample kept under ultra high vacuum conditions. Realistic analogues of interstellar dust grains were used. Our results show that current models for hydrogen recombination reactions have to be modified to take into account the role of activated diffusion of H on surfaces even at low temperature.

2   Introduction

The formation of molecular hydrogen is a very important process in astrochemistry, since H_2 is the most abundant molecule in space. Molecular hydrogen intervenes in many chemical reactions and provides an efficient mechanism for cooling clouds during a gravitational collapse. Once they are collisionally excited, H−2 and other molecules de-excite through roto-vibrational transitions, emitting photons to which the cloud itself is transparent. This cooling mechanism increases the formation rate of stars and has great impact in the structure and evolution of galaxies.

It has been known for some time that reaction schemes to form H_2 in the gas phase and in conditions present in interstellar clouds cannot explain the abundance of H_2. Several years ago Hollenbach and Salpeter proposed that molecular hydrogen could form on the surface of interstellar grains.

The main processes occurring in the formation of H_2 on interstellar dust grains proceeds are: collision and sticking of H atoms with a grain of interstellar dust, diffusion of atoms on the surface of the grain and formation of H_2 upon collision of two hydrogen atoms. The energy that is gained in the formation of the H_2 bond is likely shared between the molecule

leaving the surface and the solid. It is speculated that the molecule leaves the surface in a roto-vibrational excited state.

We know much less about processes occurring on surfaces than processes taking place in the gas-phase. Surface processes, as they occur in astrophysically relevant conditions, have not been studied thoroughly either experimentally or theoretically because of technical difficulties both in reproducing astrophysically relevant environmental conditions (low fluxes of H atoms, low kinetic energy in the atom-grain collision, and low grain temperature) and in carrying out calculations for processes dominated by quantum effects.

The experiments were conducted using an atomic beam scattering apparatus (see Fig.1) consisting of two atomic beam lines (one for H and the other for D), each triple differentially pumped and equipped with radio-frequency sources to dissociate the parent molecular species. Measured dissociation rates were in the $\sim$ 75-85 % range. Before entering the first vacuum chamber, the atoms in the beams are cooled to $\sim$ 150-200 K by passing through short aluminum channels connected via a copper braid to a liquid nitrogen reservoirs. The beams are aimed at the center of a sample located in an ultra-high vacuum chamber (p $\sim$ 10^{-10} torr). The reaction products ejected from the surface are detected by a quadrupole mass spectrometer. Two beam lines with isotopically labeled hydrogen have been used to avoid background counts due to the residual molecular hydrogen present in the chamber or to the undissociated hydrogen in the beam. The mass spectrometer is then tuned to mass 3 in order to detect HD. The possibility of using a second beam line is undoubtedly one of the most important features of our apparatus.

To investigate hydrogen recombination reactions, we conducted our experiments in two phases. In the first, the H and D beams are sent onto the surface for a given amount of time (exposure). During this phase of irradiation, the amount of HD produced right away is measured. One would expect HD to be produced promptly either because of a Eley-Rideal reaction (where a D atom from the gas phase reacts with an H atom at the surface to produce HD), or because H and D atoms move so fast on the surface that they recombine during the time of irradiation (from tens of seconds to tens of minutes). In the second phase, called TPD or thermal programmed desorption, a heat pulse is applied to the surface, raising its temperature to $\sim$ 30 K. Adsorbed atomic species that haven't yet recombined are set in motion. As H and D meet and form HD, the HD molecule is released in the gas phase and is detected by the mass spectrometer. The purpose of this second experiment is to measure the amount of recombination that would have occurred if enough time elapsed.

The efficiency of the process r, defined as the ratio of the HD signal I_{irr} (detected after placing the mass spectrometer in front of the surface) to the signal of the incoming beam I_{in} (previously measured placing the quadrupole in front of H and D lines), has been measured as a function of the surface temperature during irradiation (r is then corrected for instrumental effects and branching ratios for the A+B $\rightarrow$ AB reaction, where A,B is either H or D). Such an efficiency r has been measured for each run both during irradiation of the surface with H and D atoms: $r_{irr} = I_{irr} = I_{in}$ and after a TPD run: $r_{TPD} = I_{TPD} = I_{in}$. The total efficiency at each irradiation temperature is then given by: $r_{tot} = r_{irr} + r_{TPD}$.

Measurements were carried out of the sticking coefficient of H and D on various surfaces. The method used is the one of King and Wells, whereby the change in pressure in the

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scattering chamber is related to the degree of sticking of particles on the surface of the sample. If most atoms stick, the sample will collect most of the H beam, and the pressure will rise little. On the contrary, if there is little or no sticking, the atoms of the H and D beams will bounce off the surface and contribute to an increase of the chamber pressure.

3 Results

In Figure 2 the efficiency of molecular hydrogen recombination on a silicate (olivine) and amorphous carbon is shown as a function of the irradiation temperature, in the temperature range of interest in interstellar clouds.

Our sample of olivine is a natural polycrystalline stone that was polished until shiny. The amorphous carbon sample was prepared by Prof. Blanco of the the University of Lecce in a pure Ar atmosphere. Both samples should be considered realistic analogues of interstellar dust grain material. Additionally, we studied H sticking and recombination reactions on a sample of coronene (a polycyclic aromatic hydrocarbon) and a residue of a UV processed ice mantle. The latter two samples were given to us by Dr.Allamandola's group.

Besides these quantitative results that can be straightforwardly applied to interstellar cloud chemical models, experimental evidence was obtained on the type of processes that take place on the sample during irradiation with atomic hydrogen. This evidence comes from several TPD runs performed after irradiation with H and D atoms with the surface at the lowest temperature (5K-6K). TPD runs, where the surface temperature is raised quickly ($\sim$ 0.6 K/sec), were done after exposure of the sample to increasingly large amounts of H and D.

In a typical TPD run, we started from a temperature of 5-6K; no signal was detected until the olivine sample reached a temperature between 9 and 10K. Furthermore, going from the lowest to higher coverage, the position of the HD peak collected during TPD was seen to shift from higher to lower temperature. This is characteristic of second order desorption, where the desorption rate is proportional to the square of the concentration of the reactants. The physical picture that emerges is then one where atomic species are adsorbed on the surface and become mobile only when heat is provided (thermally activated diffusion). Once two H atoms meet, they form a molecule that then leaves the surface. Although tunneling of H atoms is expected to be present, this apparently is not the dominant mechanism, since thermal activation is required.

In a second order desorption, the desorption yield is proportional to the square of the coverage, hence at least in the low coverage regime (the important one in interstellar environments) the famous expression of Hollenbach, Werner and Salpeter for the production rate of molecular hydrogen should be substituted by an expression that was derived by us based on phenomenological grounds (Pirronello et al., 1997 - ApJ 483, L131):

$$R(cm^{-3}s^{-1}) = \frac{1}{2}(n_H v_H S_H \sigma t_H)^2 n_g \alpha \tag{1}$$

where
  n_H is the number density of atomic H in the gas phase
  v_H is the average speed of H atoms in the gas phase
  S_H is the sticking coefficient of H atoms on grains
  σ is the cross-sectional area of the grain
  t_H is the residence time of H adatoms on the grain
  n_g is the number density of grains in clouds
  α is mobility of H on the grain surface multiplied by the recombination probability.

In collaboration with the group of Prof. Ofer Biham, we worked on the theory of hydrogen recombination. We solved rate equations for the formation of molecular hydrogen on surfaces. Two physically distinct limits were obtained. In one, corresponding to a slow diffusion time compared to the residence time of H on the surface, an expression for the recombination rate was obtained that was quadratic in the concentration of H on the surface, as the expression obtained above from phenomenological considerations.

In the limit of a fast diffusion time compared to the residence time, an expression linear in the adsorption rate of H on the surface was derived from our analysis of the soluton of the rate equations: $R = \frac{1}{2} n_H v_H S \sigma n_g$. This expression is essentially the one proposed by Hollenbach and Salpeter.

Experiments of H recombination on surfaces of realistic dust grain analogues and theoretical work using rate equations have shown that H recombination, in the conditions appropriate to the diffuse interstellar medium, is initiated by thermally activated processes and that the recombination rate is lower for olivine than for amorphous carbon.

Thanks to NASA support through this grant, we were able to continue the investigations of hydrogen recombination reactions that were initiated in our laboratory, also through NASA support, a few years back. Our work has given us new insight on this important reaction. To our knowledge, these are the first experiments on measuring the efficiency of hydrogen recombination reactions using realistic analogues of dust grains and in conditions of astrophysical relevance. Experiments now continue under NASA sponsorship through a grant from the Ultraviolet, Visible & — Gravitational Astrophysics program.

4   Collaborators and Graduate Students

Prof. Valerio Pirronello (University of Catania, Sicily)was a visitor to our laboratory for one month in Winter 1998. He has been a longtime collaborator on this and other projects.

Prof. Ofer Biham (The Hebrew University, Jerusalem, Israel) and his group worked with us on setting up and solving rate equations for the recombination reactions of H on surfaces.

Three graduate students, one undergraduate student and a high school student were involved in this project.

Dr. Liyong Shen (now at the University of Alabama at Huntsville) worked on the initial stage of data collection using the amorphous carbon and coronene samples. Earlier on he worked on the setting up of the apparatus and in the collection and interpretation of data from olivine.

Dr. Chi Liu (now at the American Enterprise Group Co.) worked on the data collection and interpretation on the samples of amorphous carbon, coronene, and UV processed ice mantles.

Joe Roser has worked on the measurements of sticking and recombination of H and D on amorphous carbon, coronene, and UV processed residues of ice mantles.

The undergraduate student, Rob Conde, has worked on the data acquisition system, while the high school student has helped in data collection.

5   Presentations

-NASA Laboratory Space Science Workshop (April 1-3, 1998, Cambridge)
-Faraday Discussion No 109, University of Nottingham (April 1998)
-Invited talks at the University of Genoa and the University of Torino (Italy), University of Rochester

-Invited talks at the 23rd European Geophysical Assembly, Nice (France), April 1998 (Talk given by Prof. Pirronello)
-Invited talk at: Symposium on Atom Beam Scattering from Surfaces (Clemson University, S.C.) February 1998.
-191th Meeting of the American Astronomical Society (January 1998, Washington, D.C.)
-190th Meeting of the American Astronomical Society (June 1997, Winston-Salem, N.C.)
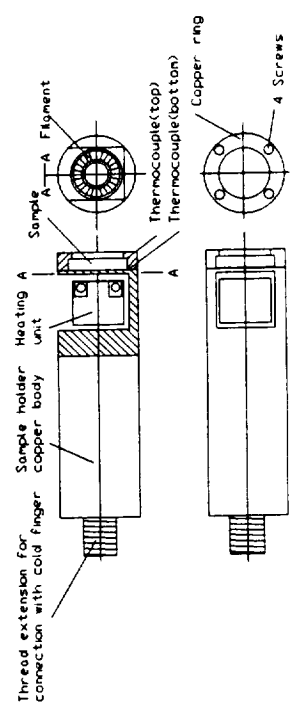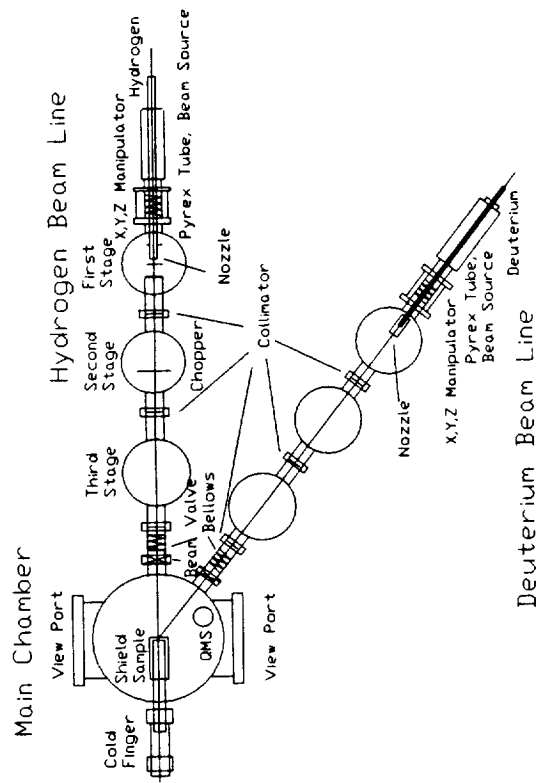
6 Published Works

-"H_2 Formation on Interstellar Grains in Different Physical Regimes", MNRAS 296, 869 (1998)
-"Experimental Studies of Chemical Reactions on Surfaces of Astrophysical Interest", Astro.Lett. and Communications 35, 423 (1998).
-"Laboratory Investigations of Molecular Hydrogen Formation on Dust Grain Analogues", Proceedings of NASA Laboratory Space Science Workshop, Cambridge April 1998 (in press).
-"Measurement of Molecular Hydrogen Formation on Carbonaceous Grains", submitted for publication to Astronomy and Astrophysics, Oct. 1998

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Main Chamber

Hydrogen Beam Line
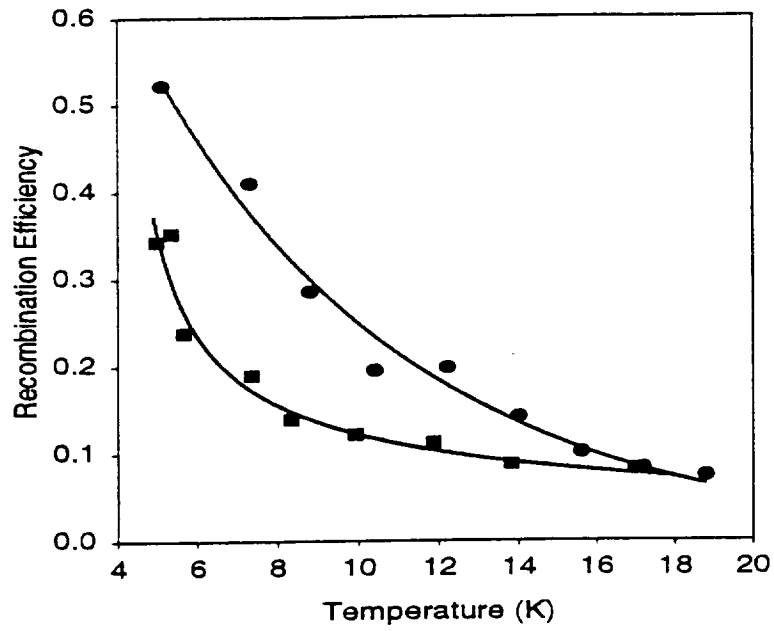
View Port

X,Y,Z Manipulator

Hydrogen

First
Stage

Pyrex Tube, Beam Source

Second
Stage

Nozzle

Cold
Finger

Third
Stage

Chopper

Collimator

Shield

Beam Valve

Sample

Bellows

Nozzle

QMS

X,Y,Z Manipulator
Pyrex Tube,
Beam Source

View Port

Deuterium

Deuterium Beam Line

Thread extension for
connection with cold finger

Sample holder
copper body

Heating
unit

Sample

A

A   Filament

Thermocouple(top)
Thermocouple(bottom)

Copper ring

A

A

4 Screws

Sample Holder Unit

fig 1

Fig 2. *Hydrogen* recombination efficiency as a function of temperature on a surface of amorphous carbon (top) and olivine (bottom). Lines are guides to the eye. (From Pirronello et al., submitted to Astronomy & Astrophysics, Oct. 1998).

H₂ formation on interstellar grains in different physical regimes

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ABSTRACT
An analysis of the kinetics of H₂ formation on interstellar dust grains is presented using rate equations. It is shown that semi-empirical expressions that have appeared in the literature represent two different physical regimes. In particular, it is shown that the expression given by Hollenbach, Werner & Salpeter applies when high flux, or high mobility, of H atoms on the surface of a grain makes it very unlikely that H atoms evaporate before they meet each other and recombine. The expression of Pirronello et al. – deduced on the basis of accurate measurements of a realistic dust analogue – applies to the opposite regime (low coverage and low mobility). The implications of this analysis for the understanding of the processes dominating in the interstellar medium are discussed.

Key words: atomic processes – molecular processes – ISM: abundances – ISM: atoms – ISM: molecules.

1 INTRODUCTION

The problem of the formation of molecular hydrogen, the most important species in the universe, is a fundamental open question in astrophysics (Duley & Williams 1984). It was recognised long ago (Gould & Salpeter 1963) that H₂ cannot form in the gas phase in the interstellar medium (ISM) efficiently enough to account for its abundance. It was proposed that dust grains act as catalysts, allowing a protomolecule to release quickly 4.5 eV of excess energy (in a time comparable to the vibration period of the highly vibrationally excited state in which it is formed). Briefly stated, the problem is as follows. An H atom approaching the surface of a grain has a probability ξ (sticking coefficient) of becoming trapped. The adsorbed H atom (adatom) will spend an average time t_H (residence time) before leaving the surface. If, during the residence time, the H adatom encounters another H adatom (which has just landed on the surface or was already trapped in a deeper adsorption site), an H₂ molecule will form with a certain probability. Given the fact that, until recently, there were no experiments performed in conditions relevant to the ISM, and also that little is known of the chemical composition and morphology of dust grains, it is not surprising that quite different models coexisted. This is an area, like many others in astrophysics and astrochemistry, in which, by far, more theoretical papers have been written (Gould & Salpeter

1963; Williams 1968; Hollenbach & Salpeter 1970, 1971; Hollenbach, Werner & Salpeter 1971; Smoluchowski 1981, 1983; Aronowitz & Chang 1985; Duley & Williams 1986; Buch & Zhang 1991; Sandford & Allamandola 1993) than experiments performed.

A milestone has been certainly set by Hollenbach & Salpeter (1970, 1971), who treated sticking and accommodation of H atoms in a semiclassical way, while the mobility was treated quantum mechanically. They concluded that tunnelling between adsorption sites, even at 10 K, would have assured the required mobility. Hollenbach et al. (1971) obtained for the steady-state production rate of molecular hydrogen per unit volume the simple expression

$$R_{H_2} = \tfrac{1}{2} n_H v_H \sigma \xi \eta n_g, \tag{1}$$

where n_H and v_H are the number density and speed of H atoms in the gas phase respectively, σ is the average cross-sectional area of a grain, n_g is the number density of dust grains and η is the probability that two H adatoms on the surface meet and recombine to form H₂. Note that in the original formulation by Hollenbach et al. (1971) $R_{H_2} = (1/2) n_H v_H \sigma \gamma n_g$, where γ is the fraction of H atoms striking the grain that eventually form a molecule, namely $\gamma = \xi \eta$. Equation (1) states, that for $\eta = 1$, whenever two H atoms are adsorbed on a grain, a H₂ molecule is formed.

From the experimental point of view, besides some pioneering work in the early 1960s (King & Wise 1963) and

1970s (Schutte et al. 1976), only recently has the problem been investigated again (Pirronello et al. 1997a,b). Pirronello et al. performed their measurements in an ultrahigh vacuum (UHV) chamber (typical experimental pressures were in the region of 10^{-10} torr), irradiating the sample, maintained at temperatures between 5 and 15 K, with H and D atoms from two different triple differentially pumped lines (D atoms were used to obtain a better signal-to-noise ratio). For the very first time they used as a substrate a natural 'olivine' (a Mg, Fe silicate) slab (mechanically polished until shiny), which has to be considered, for good reasons, a better analogue of interstellar dust than any model surface. A quadrupole mass spectrometer detected the amount of HD formed on the cold substrate. Measurements were performed both during and after irradiation with H and D atoms. In the latter case, a temperature programmed desorption (TPD) experiment was carried out in which the temperature of the sample was quickly ramped to over 30 K to desorb all weakly adsorbed species.

The main results obtained by Pirronello et al. (1997a,b) are as follows.

(i) In the temperature range of interest for interstellar applications (between 10 and 15 K), the formation rates deduced from their experimental data are up to one order of magnitude lower than those calculated by Hollenbach & Salpeter (1970,1971) and Hollenbach et al. (1971).

(ii) According to their desorption spectra, hydrogen, which is adsorbed as atomic, becomes mobile only around 10 K, even at the high coverage regime (see fig. 2 in Pirronello et al. 1997b). Thus, at the lowest temperatures (less than about 10 K) tunnelling alone does not provide enough mobility to H adatoms. Instead, they find that thermal activation is required. A possible scenario is that thermal energy is necessary to raise H adatoms inside the adsorption well to an energy level from which tunnelling can become effective.

(iii) According to a careful analysis of the kinetics of HD desorption spectra during TPDs, different regimes can be recognised during H_2 formation, depending on the values of certain parameters discussed below. This analysis has led to the proposal of the following expression for the steady state formation rate of H_2:

$$R_{H_2} = \tfrac{1}{2}(n_H v_H \sigma \xi t_H)^2 n_g \bar{N}^{-2} v f(T, a, \delta E) \gamma',$$ (2)

where $\bar{N}^2$ is the average number of hops an adatom needs to make to encounter another adatom while performing a random walk, and $vf(T, a, \delta e)$ describes the hopping rate of adatoms resulting from both thermal activation and tunnelling. Here, v is a characteristic attemp rate, T is the grain temperature, while a and δE are width and height of the energy barrier, respectively. γ' is the probability that two H adatoms recombine after encountering. In this expression the rate of H_2 formation is proportional to the square of the effective incoming H flux ($n_H v_H \sigma \xi$) on the grain surface, and is built on a purely phenomenological basis to interpret the experimental data on desorption kinetics.

In equation (1), which has been used by Hollenbach et al. (1971) and others in their chemical models, the recombination rate is linearly proportional to the effective incoming H flux. In this note it is shown that rate equations yield equa-

tions (1) and (2) as two distinct limiting cases of the H recombination rate.

2 THE CALCULATIONS

For simplicity we will consider the H_2 production rate on a single grain; the total production rate per unit volume can be obtained by multiplying it by n_g, the number density of dust grains. The number of H adatoms on the surface, N_1, and that of H_2 molecules, N_2, as a function of time are given by the rate equations

$$\dot{N}_1 = F - p_1 N_1 - 2\alpha N_1^2,$$ (3a)

$$\dot{N}_2 = \alpha N_1^2 - p_2 N_2,$$ (3b)

where F is the rate of adsorption of H atoms on the grain, α is the rate of H_2 recombination (given by the product of the diffusion coefficient and the recombination probability) and p_1 and p_2 are the desorption rates for H and H_2, respectively. The first term in equation (3a) represents the growth of the H population as a result of the incoming flux, the second term is the decrease in the H population resulting from the desorption of H adatoms and the third term represents the rate at which H adatoms are lost as a result of the recombination process. In equation (3b) the first term represents the rate of creation of H_2 molecules. It is related to the last term in equation (3a) through a factor $1/2$ because two H adatoms are needed to form one H_2 molecule. The second term in equation (3b) is the desorption rate of H_2 molecules and is equal to the desired production rate, $R_{H_2} = p_2 N_2$, of H_2 molecules released to the gas phase. Note that according to this formulation $F = n_H v_H \sigma \xi$, $p_1 = 1/t_H$ and $\alpha = \bar{N}^{-2} v f(T, a, \delta E) \gamma'$.

We will now consider the steady-state conditions, where $\dot{N}_1 = \dot{N}_2 \equiv 0$. In this case N_1 can be extracted from equation (3a), giving rise to $N_1 = [-p_1 + (p_1^2 + 8\alpha F)^{1/2}]/(4\alpha)$, where the unphysical negative solution is discarded. The steady-state condition and equation (3b) imply $R_{H_2} = p_2 N_2 = \alpha N_1^2$. By substituting the expression for N_1 into this equality we find an exact formula for the H_2 production rate of a single grain:

$$R_{H_2} = \frac{p_1^2 - p_1(p_1^2 + 8\alpha F)^{1/2} + 4\alpha F}{8\alpha}.$$ (4)

Note that the H_2 desorption rate p_2 does not affect the steady-state production rate R_{H_2}. However, it will affect the number of H_2 molecules on the grain N_2 in the steady state. We now evaluate expression (4) in two limiting cases. The first case is when the adatom desorption rate is negligible compared with the recombination rate on the surface. This is the limit of $p_1^2 \ll \alpha F$. We can neglect the first two terms in the numerator on the right-hand side of equation (4), finding

$$R_{H_2} = \tfrac{1}{2}F, \qquad p_1^2 \ll \alpha F,$$ (5)

namely all H atoms that attach to the surface recombine and desorb as H_2 molecules. In the other limit, $p_1^2 \gg \alpha F$, adatom desorption is important and we expect the production rate R_{H_2} to be dependent on p_1. Indeed, expanding the square

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root in equation (4) according to $(1 + x)^{1/2} \simeq 1 + x/2 - x^2/8$ with $x = (8\alpha F)/p_1^2$, we obtain

$$R_{H_2} = \frac{\alpha}{p_1^2} F^2, \qquad p_1^2 \gg \alpha F. \tag{6}$$

The important result of equations (5) and (6), which is the focus of this note, is that the production rate R_{H_2} can be *either linear or quadratic* in the adsorption rate F of H atoms, depending on the conditions stated above. Equation (6) also predicts the dependence of R_{H_2} on the recombination rate α and the adatom desorption rate p_1 when the latter is significant.

To make contact with equations (1) and (2) we substitute $F = n_H v_H \sigma \xi$, $p_1 = 1/t_H$ and $\alpha = \bar{N}^{-2}vf(T, a, \delta E)\gamma'$, and multiply the result by n_g, the grain density. Thus, equation (5) is transformed into equation (1) apart from a factor η, which is in fact equal to unity at the conditions studied by Hollenbach et al. (1971). Similarly, equation (6) is identical to equation (2), apart from a factor of $1/2$ that arises because of a different definition of α.

3 DISCUSSION

It has been shown analytically that the expressions to calculate the H$_2$ formation rate given in equations (1) and (2) are correct in two different regimes. Equation (1), introduced by Hollenbach et al. (1971) almost thirty years ago, holds when high flux, or high mobility of H adatoms, makes it very unlikely that H adatoms evaporate before they recombine. Specifically, it is the appropriate expression to use when $\alpha F \gg p_1^2$. The assumption of a high mobility has been experimentally proven (Pirronello et al. 1997a,b) to be inappropriate for the case in which a more realistic grain analogue surface is used rather than a monocrystalline one. Experimental data suggest that H adatoms have limited mobility and, in the low coverage regime, H$_2$ is not readily formed at the lowest temperature. Such a result had been already obtained theoretically by Smoluchowski (1981). In his calculations of H$_2$ formation on amorphous water, he obtained the result that the onset temperature for mobility and recombination was about 18 K, a value significantly higher than the 10 K measured by Pirronello et al. for olivine. In dense, cold clouds, Smoluchowski's value would be too high and would make H recombination too infrequent. The expression given in equation (2), introduced by Pirronello et al. (1997b), can be applied in the opposite limit or whenever the physical conditions maintain a low flux or low mobility of H adatoms, with respect to their desorption rate.

4 IMPLICATIONS FOR THE INTERSTELLAR MEDIUM

The results on the rate of formation of molecular hydrogen obtained experimentally (Pirronello et al. 1997a,b), and also shown to hold on theoretical grounds in this communication, can be used to speculate on how this fundamental process might proceed during the dynamical evolution of an interstellar cloud.

As is well known a typical interstellar cloud crosses diffuse and dense stages according to its energy balance with the surroundings. When a cloud loses more energy than it gains from the environment, it contracts; in the opposite limit, it expands. In the evaluation of the rate of formation of molecular hydrogen, the criteria of applicability of equations (1) and (2) will then depend on the particular stage the interstellar cloud is going through. In diffuse clouds, conditions favour equation (2). This is because of the low flux of H atoms (caused by the low gas phase density) and the relatively high grain temperature (hence low H residence time on the grain surface). If such a diffuse cloud evolves towards a denser stage, the conditions will probably tend to favour equqation (1) because of the increase of the gas phase density and the decrease of the grain temperature. In passing, we note that one must be aware that the processes described above of H$_2$ formation on bare refractory grains are influenced by at least two other processes, i.e. the decrease of H atom density in the gas phase (caused by the ongoing conversion into H$_2$) and the accretion of an icy mantle. In the latter case, the formation rate of H$_2$ might be quite different from that on a sparsely covered silicate surface because of the different depth distributions of adsorption sites and hence the different values of sticking and mobility of H adatoms. It would be very useful to have laboratory measurements of H$_2$ formation under these conditions.

Finally, when a full dense cloud environment is developed, equation (2) should apply again, because of the low density of H in the gas phase and because of the competition between H$_2$ and H adatoms in occupying available adsorption sites. Moreover, under these conditions, the grain surface may be covered by ice where binding energies for H$_2$ are slightly larger than for H. In this case, H adatoms will likely be far apart from each other and will have to undergo a long migration before encountering each other, which in turn favours equation (2). If we consider evolution from a dense toward a diffuse stage, the applicability of equations (1) and (2) will of course take place in the reverse order. Quantitative studies of time-dependent chemical models of interstellar clouds have been carried out under both static (d'Hendecourt, Allamandola & Greenberg 1985; Hasegawa & Herbst 1993; Bergin, Langer & Goldsmith 1995) and dynamically evolving conditions (Charnley et al. 1998a,b; Nejad, Williams & Charnley 1990; Prasad, Heere & Tarafdar 1991; Rawlings et al. 1992; Shalabiea & Greenberg 1995). The qualitative framework that we have just given has to be confirmed by quantitatively incorporating it into calculations describing the evolution of an interstellar cloud.

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Experimental Studies of Chemical Reactions on Surfaces of Astrophysical Interest

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Catalytic reactions involving hydrogen and heavier species take place on surfaces of dust particles in the extreme conditions of several astrophysical environments. Up to now, most investigations of surface catalysis have been carried out only on materials and in temperature ranges that are not of great relevance to space applications. In this review, we describe how surface science tools can be employed to study physical/chemical processes leading to formation of molecules at surfaces under astrophysically relevant conditions. An apparatus to study key reactions on low temperature surfaces is described in detail, as well as measurement procedures and selected results of astrophysical relevance.

KEYWORDS: Dust – ISM   abundances – ISM   molecules – molecular processes
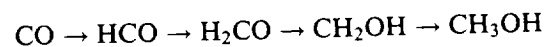
1. INTRODUCTION

Surfaces of solids in interstellar space are important mediators in many physical and chemical processes leading to the creation/modification/destruction of molecules in space.

In this review, we look at the use of surface science techniques to study physical and chemical processes under conditions of astrophysical interest. Although the discussion is particularized to reactions in interstellar cloud environments, our presentation is mostly about experimental methods which can be applied to the study of surface processes in several other environments, such as the interplanetary medium, aerosols in atmospheres and cometary ices (Singh, 1992).

Of particular importance are reactions involving hydrogen, since H and H_2 are the most abundant atom and molecule in space, respectively. H_2, once ionized either by UV photons in diffuse clouds or by cosmic rays in dense ones, enters and triggers the beginning of all reaction schemes that in the gas phase are able to synthesize other molecular species (Watson, 1976). Furthermore H_2, and molecules produced through its involvement, provide an efficient cooling mechanism of interstellar clouds that tends to reduce the time scale for their collapse, an hence for the formation of stars and star clusters, a fact that in turns has important implications for the structure, dynamics and evolution of galaxies.

The radiative association of two hydrogen atoms in the gas phase is a process too rare to be efficient, since it involves forbidden roto-vibrational transitions, and gas-

phase three-body reactions don't occur frequently enough in the diffuse interstellar medium (ISM) to explain H_2 abundance. Other reaction schemes, involving either positive or negative atomic or molecular ions, have also been shown to be ineffective in the ISM (Duley and Williams, 1984). It has long been recognized that hydrogen recombination occurs mostly on surfaces of dust, where grains act as the third body in the H + H reaction (Gould and Salpeter, 1963). In general, surface reactions compete with gas-phase reactions (especially neutral-ion reactions, which are usually very efficient since there is virtually no activation energy). However, in recent years, an increasing number of studies have shown that hydrogenation reactions on surfaces might be significant or even dominant in certain astronomical environments. For instance, observations of the Kleimann-Low nebula (KL) show a cluster of luminous infrared sources immersed in a molecular cloud. The presence of small hot clumps in star forming regions (where there is an overabundance of saturated nitrogen containing species – such as in the Orion Hot Core) is evident. NH_3, HCN, CH_3CN, C_2H_5CN and H_2S have an enhanced abundance in these regions which is not compatible with gas-phase chemistry (Irvine *et al.*, 1987). In hot molecular cores, $T > 100$ K, heavy atoms are believed to diffuse thermally to neighboring sites in 10^{-2} sec (Tielens and Allamandola, 1987). However, H atoms can tunnel in much shorter time-scales, so heavy species can still be considered almost immobile as long as H atoms fractional abundance is higher than 10^{-3}. They hydrogenate other species almost instantaneously via chain reactions of the type:

$$N \rightarrow NH \rightarrow NH_3$$

$$O \rightarrow OH \rightarrow H_2O$$

$$S \rightarrow SH \rightarrow H_2S$$

$$CO \rightarrow HCO \rightarrow H_2CO \rightarrow CH_2OH \rightarrow CH_3OH$$

Furthermore, Brown (Brown, 1990) suggested that radicals formed on grain surfaces could have large mobility if part of their heat of formation is retained as translational energy. Reactions of the type:

$$C + H \rightarrow CH$$

$$NH + H \rightarrow NH_2$$
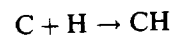
are exothermic by 3 to 4 eV. If this hypothesis is correct (and it would be interesting to check) surface chemistry would be open to a wide variety of possibilities.

In low mass stars forming regions ($T > 30$ K), NH_3, which typically has abundance in excess of 10^{-7} (relative to H_2), is overabundant with respect to standard gas phase chemistry. Gas phase chemistry is not able to sustain NH_3 fractional abundance greater than $2 \cdot 10^{-8}$ for the physical and chemical conditions of collapsing stars (Rawlings *et al.*, 1992). NH_3 could be formed on grains by hydrogenation reactions and remain frozen since there isn't an efficient desorption mechanisms in the dark cores where infall is high, as it is observationally suggested by the absence of wings in NH_3 lines.

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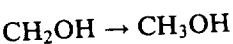
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There are other potentially important reactions at surfaces for which little is known from an astrophysical standpoint. For example, the oxidation reaction of CO into CO_2 might be important since CO is the second most abundant molecule in the ISM, and CO_2 has been detected in several objects in space (d'Hendecourt and deMuizon, 1989, de Graauw *et al.*, 1996). It is known that CO_2 can be synthesized in ice mixtures of water and CO or water and methane by UV (Grimm and d'Hendecourt, 1986) or particle irradiation (Pirronello *et al.*, 1982; Pirronello, 1993). Detection of CO_2 by the infrared satellite ISO in shielded regions (clouds where no UV can penetrate) might signify that serious consideration should be given to reactions on grains that could yield CO_2.

The formation of molecules on surfaces is an intensively studied problem in surface science. There are several ways in which reactions can occur. At one extreme, a molecule from the gas phase reacts directly with a species already on the surface (Eley-Rideal mechanism). In reality this mechanism has been positively identified, at the microscopic scale, only in a small number of systems, such as in the case of hydrogen and chlorine adsorption on low index single crystal copper surfaces (Rettner *et al.*, 1995; Rettner, 1994, Jackson *et al.*, 1994). On the other extreme, the reaction takes place between two atoms/molecules that are already adsorbed as one diffuses towards the other (Langmuir-Hinshelwood reaction). This is believed to be the mechanism by which most surface reactions occur. Reactions can give very different yields depending on the characteristics of surfaces, and the products of the reaction might be ejected into the gas phase in rotationally and vibrationally excited states. These reactions have been extensively studied at a microscopic level (see, for example: Zangwill, 1984) in conditions (well characterized single crystal metal surfaces at a room temperature or above) which are quite different from the ones prevailing in the ISM (where there are no active metal surfaces and other materials – such as oxides – might be passivated by H/OH groups).

A typical interstellar grain constitutes an important third body where reactions involving gas phase atoms/molecules can take place. Reactions leading to the productions of organic compounds in ISM and cometary ice analogs triggered by particle bombardment or UV radiation fall outside the scope of this review, since they involve physical/chemical processes occurring not necessarily on the surface, but in the bulk (For recent reviews of experimental work, see: Schmitt, 1994, Greenberg, 1996, Bernstein *et al.*, 1995; experimental procedures can be found in Allamadola *et al.*, 1988, Greenberg and Mendoza-Gomez, 1993). Several recent publications have been devoted to the study of interstellar dust matter (Whittet, 1992, Mathis, 1993, Bussoletti and Colangeli, 1990), and, thus, there is no need to summarize them here. On the other hand, hydrogen recombination reactions and hydrogenation reactions on ISM dust particles are typical surface phenomena for which little has been written about.

In the following section, we examine first the theoretical understanding of processes leading to recombination of hydrogen on grains (such as sticking and diffusion). Our discussion is focused primarily on hydrogen recombination, but extensions to other reactions, such as the hydrogenation reactions mentioned above, can be made. (Allamadola *et al.*, 1988, Greenberg and Li, 1996). In Section 3, a review of surface science techniques suitable for studies of gas-surface physical/

chemical processes is given. This is followed in Section 4 by a detailed presentation of the use of atomic beam techniques to study the recombination of H on surfaces of astrophysical interest.

2. CURRENT VIEW ON H_2 FORMATION IN THE ISM

The problem of H_2 formation on grains in interstellar conditions has been extensively studied, from a theoretical point of view, by, among others, Gould and Salpeter, 1963, Hollenbach and Salpeter, 1970; 1971, Leitch-Devlin and Williams, 1984, Duley and Williams, 1984, Buch and Zhang, 1991, Smoluchowski, 1979; 1983, and Aronowitz and Chang, 1985.

The critical physical steps of processes in which interstellar grains act as catalysts are: sticking and accomodation of gas phase atoms on grain surfaces; mobility of adatoms to encounter each other within their residence time on the cold grain; and, possibly, restoration of the reaction product into the gas phase. Depending on the nature of the interaction with the surface, adsorbed species might have significant mobilities to diffuse and react with radicals, or might become localized in physisorption or chemisorption sites. (Vidali *et al.*, 1991). The physical adsorption energy (up to $\sim$ a few hundred meV) originates from induced dipole – induced dipole van der Waals interactions (Bruch *et al.*, 1997); because of the relatively small activation energy for hopping, an atom/molecule might have considerable mobility while it is in physisorption wells (the activation energy barrier for diffusion is typically 1/4 of the adsorption potential well), except at very low temperature.

Hollenbach and Salpeter (Hollenbach and Salpeter, 1970; 1971) proposed a model for the recombination of H on ice deposited on interstellar grains. They recognize that surfaces of actual grains are likely to be rough and heterogeneous; consequently, they make the reasonable assumption that H or H_2 have a range of adsorption sites with a range of binding energies. They argue that if H atoms had only weak adsorption sites, H atoms wouldn't have enough time on the surface to find other H atoms to recombine with because they would evaporate at typical grain temperatures. Much stronger adsorption sites would lead to either a layer of H_2 or to immobile H atoms, depending on the role of diffusion. However, if the adsorption sites display a range of binding energies, with H more strongly bound than H_2 by 50 K or more, then reasonable recombination rates are obtained. Specifically, HS show that there is a high mobility, via a tunneling mechanism, of H atoms on the surface of the grain. This high mobility guarantees a very fast sampling of all possible adsorption sites on a grain surface in a fraction of the residence time; such high mobility is likely due to the fact that HS considered in their model a single crystal in which H moves in a periodic potential.

The production rate R_{H_2} ($cm^{-3}sec^{-1}$) or molecular hydrogen in this model is given by:

$$R_{H_2} = \frac{1}{2} S_H \, n_H \, v_H A \gamma n_g \qquad (1)$$

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where S_H is the sticking coefficient, n_H the number density of H atoms in the gas phase, v_H the speed of the H atom in the gas phase, A the cross-sectional area of the grain, and n_g the number density of dust grains. γ represents the probability that two hydrogen atoms on the surface recombine to form molecular hydrogen when they meet; such a probability is usually to be understood to be equal or colse to one.

Let us examine how Eq. (1) can be used to evaluate the production rate of H$_2$ in a typical diffuse/dense cloud and the implications of the assumptions used in the above models.

In the ISM, dust grain temperatures range from 10 to 70 K and hydrogen densities from 10^4 to 10 atoms/cm^3, for dense and diffuse clouds, respectively. If we take a typical diffuse cloud environment, $n_H \sim 10$ cm^{-3}, $v_H \sim 2 \cdot 10^5$ cm/sec, $A = \pi a^2 \sim 0.7 \cdot 10^{-9}$ cm^2 (where $a \sim 1.5 \cdot 10^{-5}$ cm is the radius of an average dust grain), $\gamma \sim 1$, and $n_g \sim 10^{-11}$ cm^{-3}, we get $R = S_H 7 \cdot 10^{-15}$ cm^{-3}/sec. From observations (Jura 1975) one obtains that the H$_2$ production rate is: $1 - 3 \cdot 10^{-17}$ n_H n(cm^{-3}/sec); here $n = n_H + 2n_{H_2} \sim n_H$. Thus, with $n_h = 10$ cm^{-3}, the sticking coefficient should be ~ 0.3 to reconcile the value of R obtained from Eq. (1) with the one from observation.

Let us now consider the process of H diffusion on a dust grain surface. In the ISM, collisions of H atoms with grains are not frequent. The collision rate is: $n_H \pi a^2 v_H$, or the average time between collisions is $10^4/n_H$ sec, thus of the order of tens to hundreds of seconds in typical diffuse clouds. The residence time of an atom on a surface at temperature T is $t = v^{-1} \exp(E_A/k_B T)$, where v is the typical vibrational frequency of H in the adsorption potential well, $\sim 10^{12}$ Hz; taking for the adsorption energy for H on graphite $E_A = 32$ me V (370 K) (Mattera et al., 1980) and $T = 10$ K, we get $t \sim 10^4$ sec, while for $T = 15$ K $t \sim 5 \cdot 10^{-2}$ sec. Thus, Eq. (1) would predict that R would be extraordinarily sensitive to grain temperature unless diffusion can occur in very short times and there are some binding sites with deeper wells, as both the HS and Smoluchowski models postulate.

The ratio of the activation energy for diffusion E_{diff} to the adsorption energy is of the order of 5% E_A for H chemisorbed (strongly bonded) on transition metal surfaces, but relatively larger, (15–20%) E_A, for physisorbed (Van der Waals bonded) atomic/molecular hydrogen on inert surfaces. At low temperature, where thermal diffusion becomes very slow, diffusion by tunneling – which is temperature independent – should dominate. If we consider a weakly adsorbed species, i.e. $E \sim 30$ meV, an E_{diff} could be ~ 6 meV; the hopping rate is then $h = v\exp(-E_{diff}/k_B T)$ or 10^{10} Hz at 15 K, 10^9 Hz at 10 K, and 10^6 Hz at 5 K. The diffusion coefficient for single thermally activated hopping events is $D = 1/4l^2 h$, l being the nearest neighbor distance ~ 2Å; thus, $D = 10^{-7}$ cm^2/sec (at 10 K), and the distance traveled in 10 seconds is $\sim \sqrt{(4Dt)}$ or $2 \cdot 10^{-3}$ cm, so once on the surface of a grain H atoms could find each other out quickly. Tunneling times are temperature independent and can be evaluated by using a simple one-dimensional model of a barrier of height V_0 and width s. For a particle of mass m and energy E, the transition probability is (Schiff, 1949): $\rho = (1 + V_0^2 \sin h^2(\beta s)/E(V_0 - E))^{-1}$. Taking $E \sim 2$ meV, $V_0 \sim 4$ meV, $s \sim 2$ Å, $\rho \sim 2 \cdot 10^{-2}$, and the tunneling time is $\sim (\rho v)^{-1} \sim 0.1$ nsec. (Duley and Williams, 1984). For random hopping at 10 K, the time to thermally hop onto the next site is, from the calculation above, of the order 10^{-9} sec.

Amorphous ice surfaces have been considered by Smoluchowski, 1979; 1983 and Buch and Zhang, 1991 who reached conclusions quite different from HS. Smoluchowski in particular used a quantum mechanical approach to study the mobility of H atoms. He found that the mobility of H adatoms is reduced to very low values due to the localization of H atoms in the deepest adsorption sites. Since he considered an amorphous surface, H diffusion is greatly reduced with respect to HS's. However, scuh point of view hasn't been followed by the astrophysical community because observational constraints (Jura 1975) require that the H_2 formation rate in clouds has to be a few orders of magnitude higher than the model of Smoluchowski.

HS and Smoluchowski's models differ, among other things, in how the diffusion is calculated; in HS diffusion is by tunneling and, for a single crystal, it is very fast. In Smoluchowski model, the macroscopic diffusion becomes slower because an atom has to travel in a random walk; thus, the distance traveled goes like $\sqrt{(t)}$ (t = time) rather than t as in tunneling in a perfect crystal.

The rates of key adsorption/diffusion/desorption processes depend on the stricking coeffcient and the composition and structure of the grain surface. In the HS model, S_H was calculated by treating the interaction between the adatom and the solid surface in a simple semiclassical way, i.e. as a harmonic oscillator. It was found that S_H should be between 10^{-1} and 1 for most species.

Other authors calculated specific processes that intervene in the H recombination reactions in the ISM. A quantum approach been used by Leitch-Devlin and Williams (Leitch-Devlin and Williams, 1984) in the calculation of the sticking coefficient. They considered a perfect crystal and assumed single phonon excitation as the energy loss mechanism. They found that S reaches a maximum at $k_B T$ (T = gas temperature) comparable with phonon energies and then decreases again. At low gas temperature it is not easy for the colliding atom to excite a phonon and at high $k_B T$ not enough energy is carried away by single phonons to produce a non-negligible energy loss of the incoming particle. Buch and Zhang (Buch and Zhang, 1991) numerically evaluated the sticking of hydrogen atoms on a cluster (amorphous in structure) of about one hundred water molecules, finding that S decreases monotonically with gas temperature, where $S = (k_B T/E_0 + 1)^{-2}$ and E_0 is a parameter. Buch (Buch, 1987) proposed a mechanism of H_2 formation on carbon grains where an adsorbed hydrogen atom tunnels through an activation energy barrier for abstraction of another H chemically bound to a carbon atom (CH bond). Recombination probability of order unity is obtained for low grain temperatures.

Astrophysically relevant surfaces include silicon-bearing (silicates can be not very stable in UV radiation fields, see, for example, Hong and Greenberg, 1984) and carbonaceous ones (carbon can possibly be distributed on silicon-bearing grains surfaces) or icy (Mathis, 1993). In the case of more chemically active surfaces, like carbonaceous ones, the possible presence of unsaturated bonds will increase the percentage of chemisorption events over the physisorption ones with relevant consequences on the quantitative effectiveness of the catalytic role of such grains. Furthermore, although most models and experimental studies consider or use crystalline surfaces, the most probable structure for grains in space is amorphous (Leger *et al.*, 1979). The chemical or morphological condition of the surface of grains

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should have an influence on rates of certain physical/chemical processes occurring on them. For example, rougher surfaces should yield a higher sticking coefficient, because atoms make multiple hits with the surface, and slower tunneling times.

3. EXPERIMENTAL TECHNIQUES

There are far fewer experimental studies of reactions occurring on surfaces in conditions of astrophysical relevance than there are theoretical studies. Below, we argue that surface science techniques can be used to elucidate some of the puzzles that have emerged in the study of the formation of H and other molecules in the ISM.

The employment of such techniques has been very successful in reaching an understanding, often in great detail, of a large number of physical and chemical processes at surfaces. (Zangwill, 1984) Unfortunately, the typical system studied using surface science probes is quite different from what is encountered in the ISM. Here we briefly describe techniques that have been or could be applied to the study of catalytic processes of surfaces in astrophysically interesting conditions. This is followed by a review of experimental results pertinent to the hydrogen recombination problem on ISM grain analogues.

3.1. Atomic/Molecular Beam Methods

In these experiments, atomic or molecular beams are produced by the expansion of a high pressure gas into vacuum. Beams of neutral atoms/molecules are sent into a scattering chamber where they interact with the surface of a sample. Scattered products are then detected either by a quadrupole mass spectrometer, which can give information about the composition of reactants, or by bolometer, a microcalorimeter that is particularly sensitive to energy releasing processes occurring on its surface. For a typical atomic/molecular beam apparatus, see the description in Section 4 and Figure 1. For more details on the use of reactive molecular beams, see Zangwill, 1984 and D'Evelyn and Madix, 1984.

3.1.1. Surface characterization

A chemically inert He beam at thermal energy is used to probe the surface condition, its dynamics or the structure and dynamics of atoms and molecules residing on top of the substrate (adsorbates) (Hulpke 1992). Modern He beams are supersonic, meaning that the flow velocity is much greater than the local sound velocity. Mach numbers of 80 and above are routinely achieved. Supersonic He beams are characterized by high forward intensity and narrow ($\delta v/v \sim 2\%$) velocity distributions; they are used to characterize the morphology, atomic structure and dynamics of the topmost layer of a solid surface. In a study of H and H_2 adsorption on a single graphite surface, Lin and Vidali, 1996 used a supersonic He beam to characterize the surface (A description of an atomic/molecular beam apparatus is given in the next
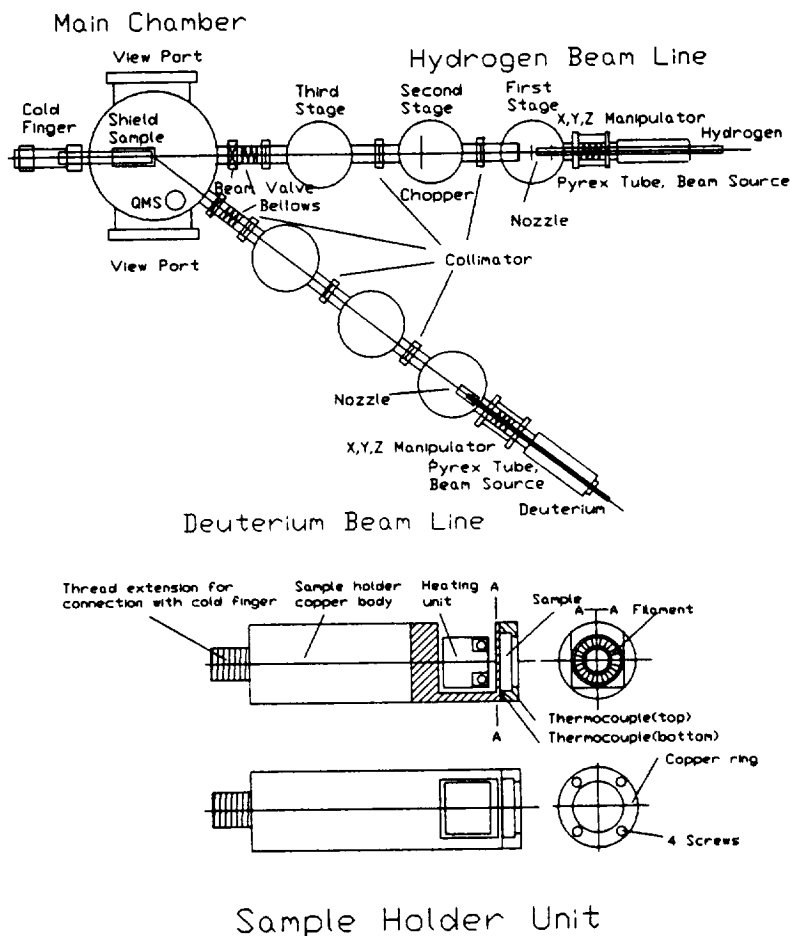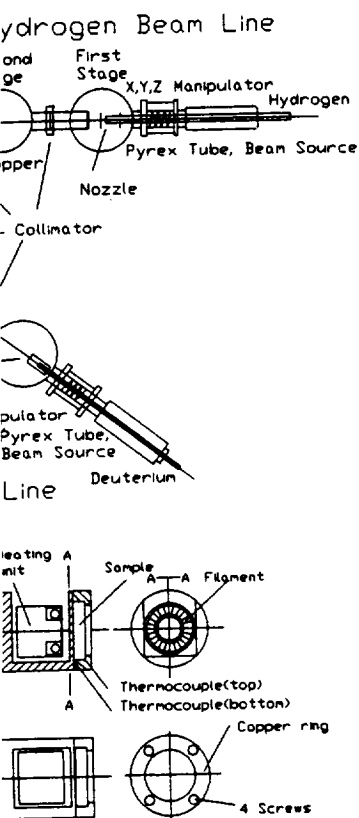
Main Chamber

FIGURE 1 Schematic of an atomic/molecular beam apparatus (a), and of a low temperature sample holder (b).

section). A supersonic He beam is sent onto the graphite crystal and the specularly reflected beam is monitored under various conditions. From the shape of the specular reflection, see Figure 2, one can deduce the average size of the crystalline platelets and their relative orientation. Lin and Vidali sent a H beam on the graphite surface while they monitored the reflection of a He beam with a quadrupole mass spectrometer. The attenuation in the reflection of the He beam due to the presence of the H beam, see Figure 3, is proportional to the fraction of H covering the surface: $I(t)/I(t_0) = (1 - \Sigma Jt\ S)$ (Poelsema and Comsa, 1989), where J is the flux, t the time, S the sticking coefficient, Σ the He-adsorbate scattering cross-section, and I_0 is the H reflected intensity before adsorption. From an estimate of the flux and of the He – adsorbed H scattering cross-section, the sticking coefficient of H on graphite at $\sim$ 16 K was estimated to be between 0.06 and 0.1. The method is sensitive down to parts of 1% of one layer in coverage, chiefly because of the large He-adatom

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Detector angle

FIGURE 2 He specularly reflected peak from a natural graphite crystal (Lin and Vidali, 1996) (He intensity *vs.* angular position of detector). Arrows indicate specular peaks from other facets, as deduced from deconvolution (for details, see: Lin and Vidali, 1996). In the inset: angular scan from another graphite sample.

scattering cross section Σ. Unfortunately, cross-sections of He scattering from adsorbates are not generally known, and they have to be measured to obtain absolute calibrations. Furthermore, this method can be applied when the sample surface is ordered enough on a $10-100$ Å scale, so that there is a measurable amount of specular He beam reflection.

3.1.2. Sticking

A beam of atoms or molecules is sent onto a surface. The pressure in the scattering chamber is measured with the beam on and with/without the sample in the beam path. A drop of the pressure when the sample is in the beam path is attributed to the sticking of atoms/molecules of the beam on the surface of the sample; in other words,
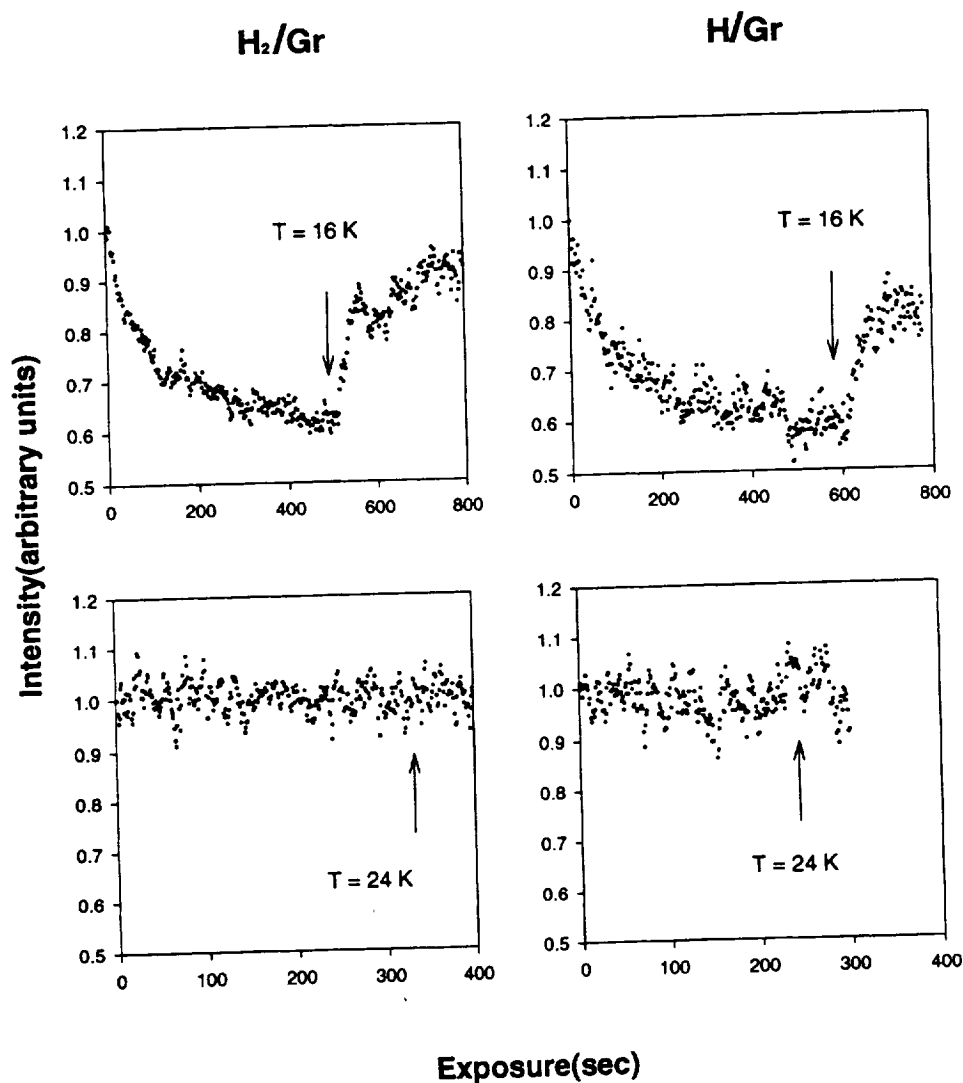
H₂/Gr

H/Gr

T = 16 K

T = 16 K

T = 24 K

T = 24 K

Intensity(arbitrary units)

Exposure(sec)

FIGURE 3   Helium specularly reflected peak from graphite as a function of adsorption time to H_2 (left) and H(right) fluxes (Lin and Vidali, 1996). The arrows indicate when the H, H_2 beam valve was closed.

the atoms/molecules in the beam stick onto the surface and don't contribute to the pressure in the scattering chamber. Figure 4 shows the increase of the partial pressure of D_2 in the presence of a "hot" and "cold" surface. In this specific case, almost no D_2 molecules stick at 70 K, but sticking is almost 1 (100 %) at 6 K. (For another example, see Figure 7 in Lin and Vidali, 1996 for sticking of hydrogen on graphite; for other cases, see Rettner et al., 1995; Rettner, 1994). Measurements can be difficult to make in cases in which the background pressure of the gas to be studied is already high, or when the gas reacts with the walls of the chamber. One

H/Gr

T = 16 K

T = 24 K
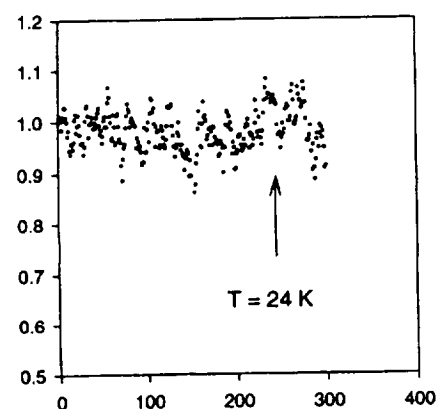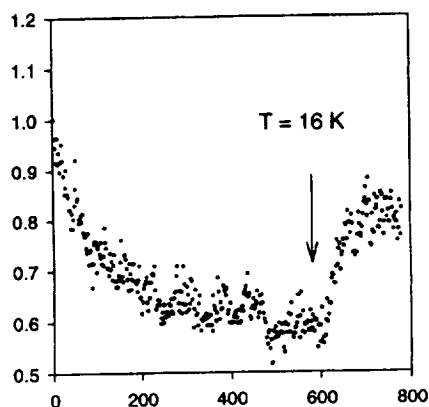
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phite as a function of adsorption time to H_2 (left)
ndicate when the H, H_2 beam valve was closed.

the surface and don't contribute to the
: 4 shows the increase of the partial
nd "cold" surface. In this specific case,
:icking is almost 1 (100 %) at 6 K. (For
'idali, 1996 for sticking of hydrogen on
1995; Rettner, 1994). Measurements can
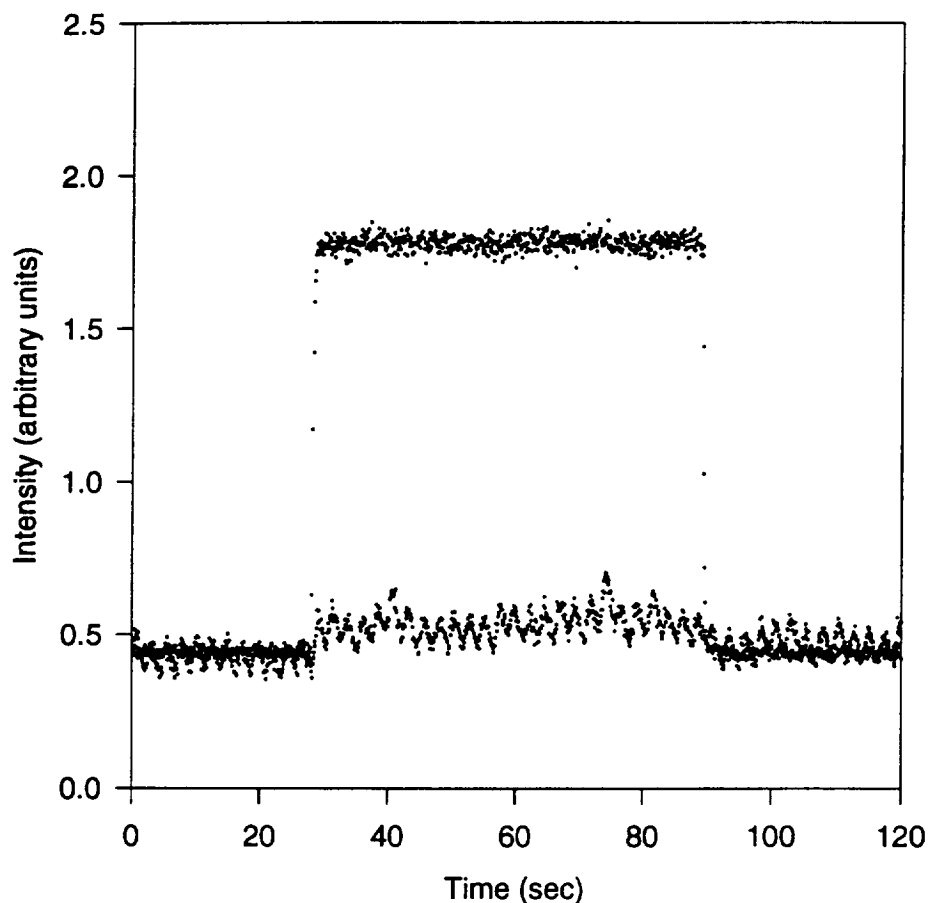background pressure of the gas to be
icts with the walls of the chamber. One

FIGURE 4 D_2 partial pressure *vs.* time. At 30 sec. a D_2 beam is sent on a copper disc coated with coronene; the beam is shut off at 90 sec. The detector is behind the sample. Upper trace for sample at 70 K, lower trace for sample at 6.1 K.

should also be aware that, in general, the sticking coefficient is coverage dependent (especially below one layer coverage). Thus, measurements of sticking probability should be taken at different coverages (Rettner *et al.*, 1986).

3.1.3. Residence time

If the beam is chopped by a mechanical selector, one can measure the scattered signal as a function of time. A time delay or change of shape of the scattered beam pulse yields information on residence times of atoms/molecules on the surface. Typical chopping frequencies go from a few Hertz to hundreds of Hertz (Comsa and David, 1985), depending on the typical times of adsorption/reaction/desorption. As for the characterization of the surface discussed above, this method relies on the detection of

a large enough signal scattered back into the gas phase. In practice, this method has been applied mostly to well-ordered surfaces.

A slightly different method is used to probe the residence time of atom/molecules when this time is expected to be much longer than a few seconds. In this method, the surface is exposed to a certain flux of atoms/molecules for a given amount of time. Then, the amount that stick is meaured with progressively large delay times between the end of the adsorption and the beginning of the desorption. The longer the delay time, the smaller the amount found on the surface, since some of the atoms and molecules will evaporate from the surface during the interval between the end of the adsorption and the beginning of the desorption. A result of an experiment of HD desorption on olivine is given in Figure 5 (see below for more details). In this case, the amount of HD desorbed is plotted as a function of delay time. The slope gives the residence time τ, in this case $\tau \sim 120$ mins.
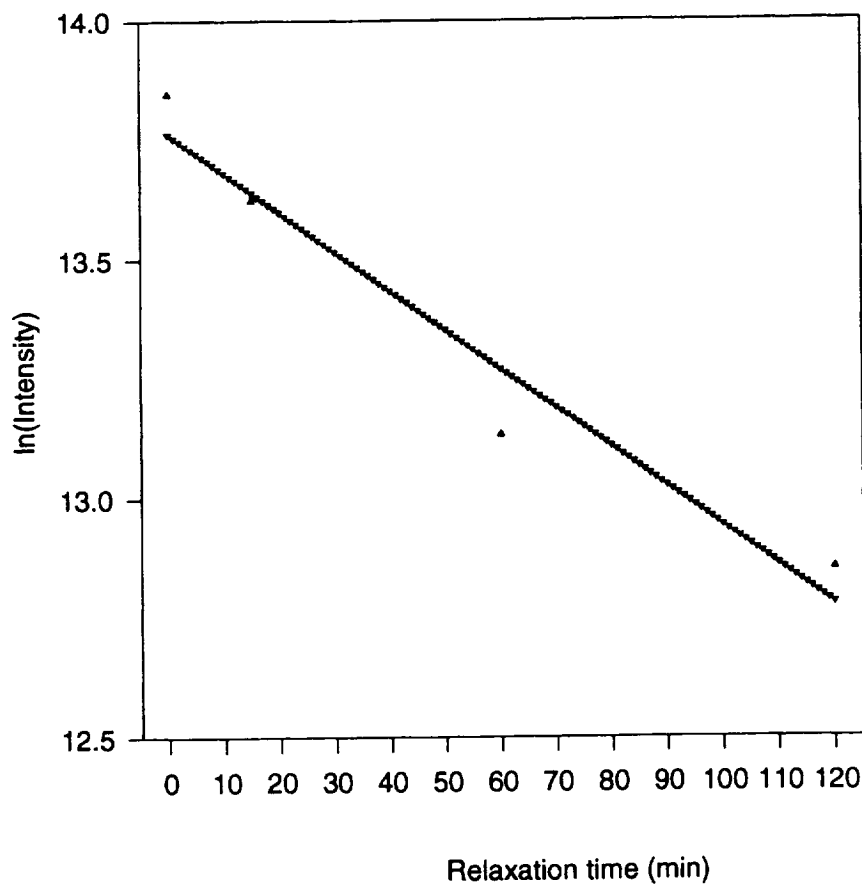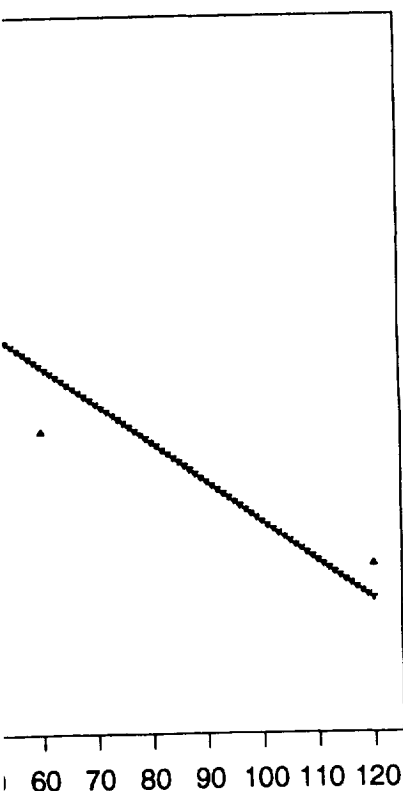

Relaxation time (min)

FIGURE 5   Amount of HD desorbed as a function of delay time between end of adsorption and beginning of desorption. The adsorption time is the same for all runs. The surface of olivine is at ~ 6 K.

gas phase. In practice, this method has

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e below for more details). In this case,
function of delay time. The slope gives
ns.

60 70 80 90 100 110 120

Relaxation time (min)

on of delay time between end of adsorption and
me for all runs. The surface of olivine is at ~ 6 K.

3.2. Thermal Programmed and Flash Desorption

In the technique of thermal programmed desorption (and/or flash desorption), the
sample temperature is ramped quickly (and usually, but not necessarily, linearly)
in order to desorb adatoms and molecules from a surface. A quadrupole mass
spectrometer placed in front of the sample is used to measure, as a function of time,
the reaction products desorbed form the surface, see Figure 6. From the maximum of
the desorption rate peaks, information about the energy of desorption can be
obtained, while its area is proportional to coverage (see Section 4 for more details).
Notice that there can be more than one desorption peak, since there can be multiple
adsorption sites. The kinetics of desorption can be studied by analyzing the shape of
the desorption peak (Menzel, 1975, Yates, 1985).

For example, let us assume that the temperature is ramped linearly. Fast
temperature ramps are needed to obtain a picture of the state of the adsorbate at the
time of desorption; otherwise, the adsorbate layer might go through changes, such as
phase transitions or quasi-isothermal desorption. Taking $T = T_0 + \beta t$, where T_0 is the
initial temperature, t is the time and β is the heating rate, we have:

$$-dN(t)/dt = k_m N(t)^m, \tag{2}$$

where $N(t)$ is the number of atoms on the surface at time t, $k_m = k^{(m)}\exp(-E_d/k_B T)$,
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
multilayer desorption, 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 fuction of coverage. Schematically these processes are
represented in Figure 6. Data of H desorption from a silicate are presented in Section
4. Other examples of actual desorption spectra displaying different desorption
orders, but not for astrophysically relevant substrates, can be found in Kay et al.,
1989.

The position of the maximum in $N(t)$ gives the desorption energy, if $k^{(m)}$ is known.
Setting $d^2N(t)/dt^2 = 0$, and for linear temperature ramp, we have: $E_d/k_B T_{max}^2 = k^{(m)}/\beta \exp(-E_d/k_B T_{max})$. In the $m = 2$ case, $k^{(2)}$ is proportional to the coverage; in
this case, the peak position (i.e., the max) shifts continuously to lower temperature as
a function of coverage, but the value of the desorption energy doesn't change.

3.3. Diffusion

Only in very few cases diffusion of adatoms on surfaces can be directly probed, for
example by using the technique of Field Ionization Microscopy (FIM) or Scanning
Tunneling Microscopy (Zangwill, 1984). In the first case, a sharp metal tip is placed
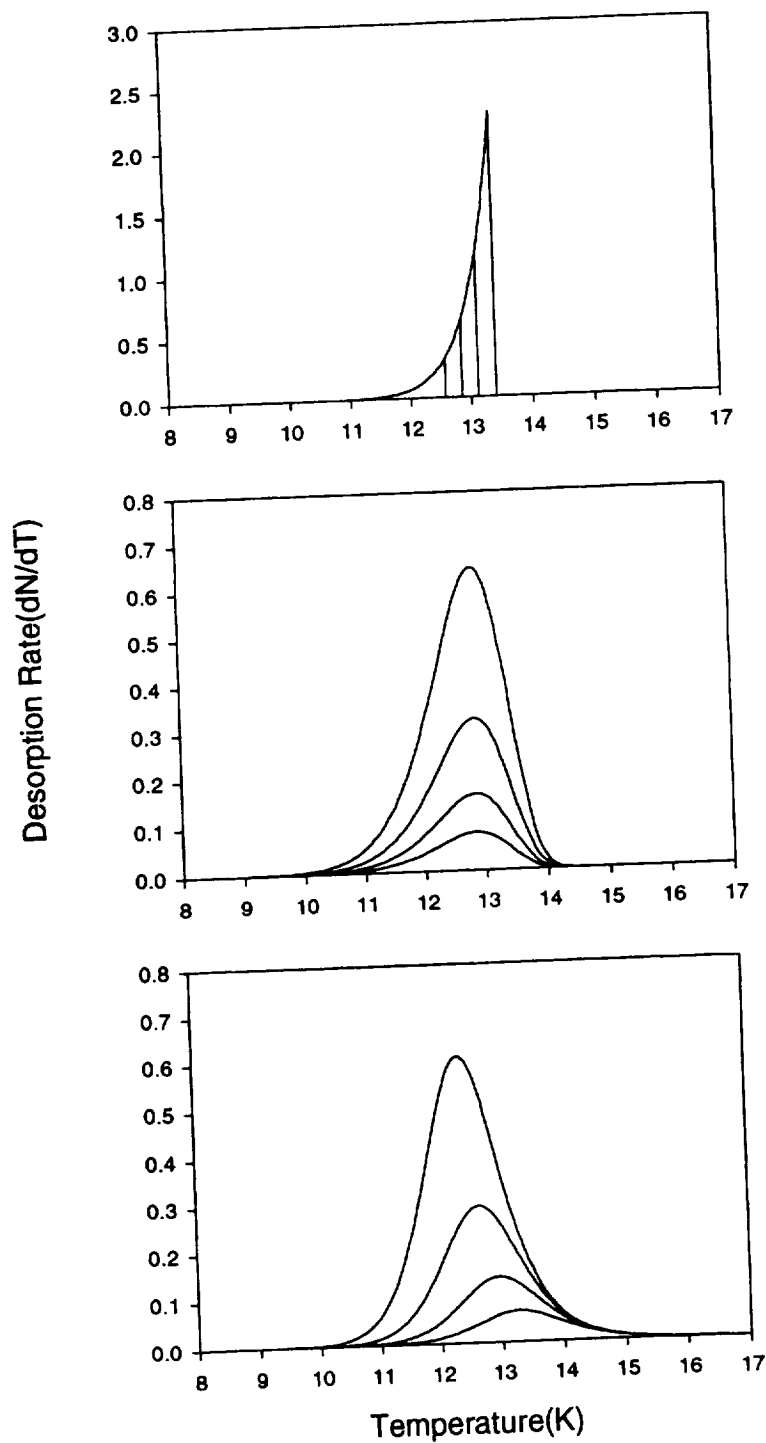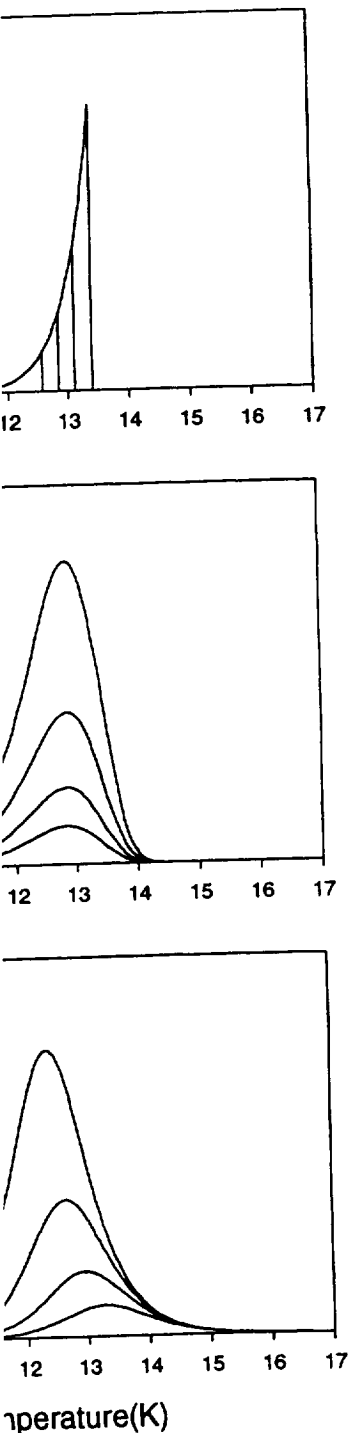
FIGURE 6 Schematic desorption curves for (top to bottom) zeroth, first, and second order desorption at different coverages generated with formulas given in the text. Coverage doubles from line to line.

at a high potential, so electric fields of the order of 10^9 volt/cm are reached at the tip. When a rare gas is admitted, it becomes ionized at the tip and the ions drift toward an imaging plate providing an image of the tip on the atomic scale. In the second case (STM) a sharp tip is placed near an electrically conductive sample and the tunneling current between tip and sample is used to regulate the distance of the tip from the sample. In both cases, by measuring the fluctuation of the electric current due to atoms adsorbed on the tip (in the FIM case) or on the sample just under the STM tip, the autocorrelation of the tip current can be evaluated. From it, one obtains the autocorrelation function of the atom's velocity and, thus, its mobility. To our knowledge, no experimental studies of diffusion on astrophysically relevant systems have been done, since FIM studies are confined to tips of refractory metals which can withstand the high electric fields without being stripped of their tip atoms. STM studies require a conductive sample; in principle, they could be applied to a variety of materials, but this technique for measuring atom mobility is still in its infancy.

3.4. Chemical Characterization

To find out what elements are present on the surface, Auger electron spectroscopy is often used. A 1.5– 3 KeV electron beam impinges on the surface and the emitted Auger electrons are detected. Unfortunately this technique cannot be used with hydrogen and insulating materials, and it is in general not very sensitive to elements with low electron number (Zangwill, 1984). Other methods to study the chemical composition of a surface include flash desorption, as discussed above, and SIMS, Static Secondary Ion Mass Spectrometry. In the latter case, an ion beam sputters a small portion of the surface, and the desorbing ions are studied with a quadrupole mass spectrometer and energy analyzer. Quantitative interpretation of the data is not always easy because certain materials are more easily sputtered than others.

4. STUDIES OF HYDROGEN RECOMBINATION REACTIONS UNDER ASTROPHYSICALLY RELEVANT CONDITIONS

In this section, we first review experiments conducted in the 1970s and aimed at studying specific processes of hydrogen interaction with surfaces at low temperature. We then describe recent experiments of hydrogen recombination reaction on surfaces of materials of interest to astrophysics.

4.1. Earlier Work

Although some of these studies were done on materials of no interest to astrophysics or with kinetic energies of hydrogen atoms considerably higher than found in diffuse clouds, we review those aspects of these studies which might be useful for an understanding of hydrogen physics/chemistry on dust grains.

The sticking of hydrogen has been extensively studied experimentally (Rendulic, 1992), but in conditions and on surfaces of little interest for any astrophysical

12   13   14   15   16   17

12   13   14   15   16   17

12   13   14   15   16   17

nperature(K)

bottom) zeroth, first, and second order desorption at
he text. Coverage doubles from line to line.

application. In a series of experiments, Scoles and his group measured the sticking of H and H_2, and the recombination of H on an otherwise uncharacterized surface of a silicon bolometer at low temperature (3 – 4 K) (Schutte *et al.*, 1976). Detection was achieved using two bolometers, which are essentially microcalorimeters. One of the bolometers acts also as the target surface, while the other detects the particles that have bounced off the first one. They found that the sticking coefficient of H_2 increases rapidly as coverage is increased; after the first layer, the sticking coefficient remains constant (about 1) as layer after layer of H_2 are formed. Adsorption energies of H and H_2 decrease with increasing coverage in the sub-monolayer regime; for H_2 it goes from 30 meV on a "clean" surface (as deduced from residence time measurements) to 10 meV (taken from the known adsorption energy of H_2 on H_2 solid). From their data they deduce that the recombinating fraction of H already present on a H_2-free surface is high (0.25) while on a H_2 covered surface is low (0.05 to 0.1). The advantage of their method is the use of very sensitive calorimeters; on the other hand, no particle discrimination was obtained, and characterization or processing of surfaces couldn't be done in that type of set-up.

In a subsequent experiment (Grovers *et al.*, 1980) the second bolometer was replaced by a rotatable quadrupole spectrometer. The authors concluded that sharp variations of the sticking coefficient and binding energy occur at submonolayer coverage. It was also found that the impingement of a H beam causes H_2 molecules to desorb from the target surface.

Commenting on the relevance of their results for astrophysical situations, they concluded that for grain temperatures of the order of 10 K, the sticking coefficient will be low; as H_2 starts to slowly accumulate, the binding energy will decrease leading to a balance of adsorption and desorption.

There have been a few experiments on H interaction with carbonaceous/graphitic surfaces at low temperature. However, the method by which H atoms were generated casts a few doubts about the validity of these experiments to describe recombination reactions in diffuse interstellar clouds.

Typical methods of generating H atoms include passing an effusive beam of H_2 through a hot filament, or dissociating H_2 in a hot oven. In both cases, H atoms with kinetic energies of 1,000 K and more are generated. In a surface science study, it was shown that these atoms can interact with carbon atoms of graphite (probably a defect sites) and formation of hydrocarbons were detected following the dosing of graphite with hydrogen (Kurpick *et al.*, 1992). Using a thermal energy H beam from a microwave dissociation source, the bound state energies of a H atom on a graphite surface were determined experimentally by H beam scattering from a single crystal graphite surface (Mattera *et al.*, 1980). The ground state energy (that is, the adsorption energy) is 32 meV while for H_2 scattering from graphite, the ground state energy is 42 meV. This indicates that the crystalline parts of graphite are inert as far interaction is concerned, that is, no chemical bond is formed. It is reasonable to suppose that the difference in hydrogen interaction with graphite is due to the different kinetic energies of H atoms. An experiment reported below on H adsorption on graphite at low temperature using a thermal energy H beam (Li and Vidali, 1996) lends support to the thermal energy H scattering result of Mattera *et al.*, 1980. Thus, we will not review here other experiments (King and Wise, 196

et al.

and his group measured the sticking of
otherwise uncharacterized surface of a
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known adsorption energy of H_2 on H_2
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was obtained, and characterization or
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al., 1980) the second bolometer was
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include passing an effusive beam of H_2
a hot oven. In both cases, H atoms with
nerated. In a surface science study, it was
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state energies of a H atom on a graphite
H beam scattering from a single crystal
The ground state energy (that is, the
scattering from graphite, the ground state
rystalline parts of graphite are inert as H
ical bond is formed. It is reasonable to
interaction with graphite is due to the
An experiment reported below on H
re using a thermal energy H beam (Lin
mal energy H scattering result of Mattera
other experiments (King and Wise, 1963,

Schermann *et al.*, 1994) where the kinetic energy of the H atoms is substantially higher than the one in the diffuse/dense interstellar clouds.

4.2. Current Work

In this section, we present in detail experimental methods to measure hydrogen recombination reactions using atomic beam methods in astrophycially relevant conditions. A description of the apparatus is followed by a presentation of measuring methods and selected results.

4.2.1. Experimental techniques and measuring methods

The apparatus used in the studies described below is a modified version of a helium beam scattering apparatus which has been used for the study of the growth of ultra-thin films in ultra-high vacuum (UHV) (Vidali and Zeng, 1996). Currently, our apparatus consists of two beam lines and a UHV scattering chamber, see Figure 1. One line is used to produce a supersonic, thermal energy, neutral He beam for structural and morphological characterization of surfaces. The beam line can be modified to carry a beam of hydrogen atoms. The other line, which is structurally very similar to the first one, is used to produce a beam of deuterium atoms. The two lines converge on a target in a ultra-high vacuum chamber and are 38° apart. Both lines are triple differentially pumped; with the beams on, the pressure in the third stages, just before the UHV chamber, is in the low 10^{-8} torr to mid 10^{-9} torr range. There is a mechanical chopper in each line for in-phase detection. When the He beam is not used for characterizing the sample, both lines are fitted with hydrogen/deuterium dissociation sources (Lin and Vidali, 1996). The atomic sources consist of water cooled Pyrex tubes surrounded by an inductor in a radiofrequency (RF) cavity. The sources are mounted on stainless steel bellows and x-y micrometer positioning stages. RF power from a 300 watt 13.6 MHz power supply is fed to the RF cavities via a power splitter and impedance matching networks. Typically 100 watts are fed into the sources with less than 5 watts of reflected power. Ultra-high pure molecular hydrogen or deuterium are inserted into the sources at pressure of 0.1–0.2 torr measured before dissociation. After dissociation, H or D pass through a short aluminum channel with a 1 mm diameter exit hole. The beams can be cooled to about ~150 K using copper braids connecting the aluminum block to liquid nitrogen reservoirs. Most of the data reported here, however, refer to room temperature operation. Peak dissociation rates over 90% have been measured downstream with the quadrupole mass spectrometer (see Fig. 7). Typically, the dissociation rate is betwen 70 and 85% and is stable during runs.

The beams enter a UHV scattering chamber with operating pressure in the high 10^{-10} torr range. The sample is attached to a OFHC (oxygen free high conductivity) copper block; it can be heated to over 200°C by a tungsten filament placed in the back of the sample (see bottom part of Fig. 1). There are two calibrated iron-gold/chromel thermocouples, one between the bottom of the sample and the top of the sample holder, and another between the top of the sample and a copper clamping ring. The OFHC Cu block, which is attached to a HeliTrans continuous flow
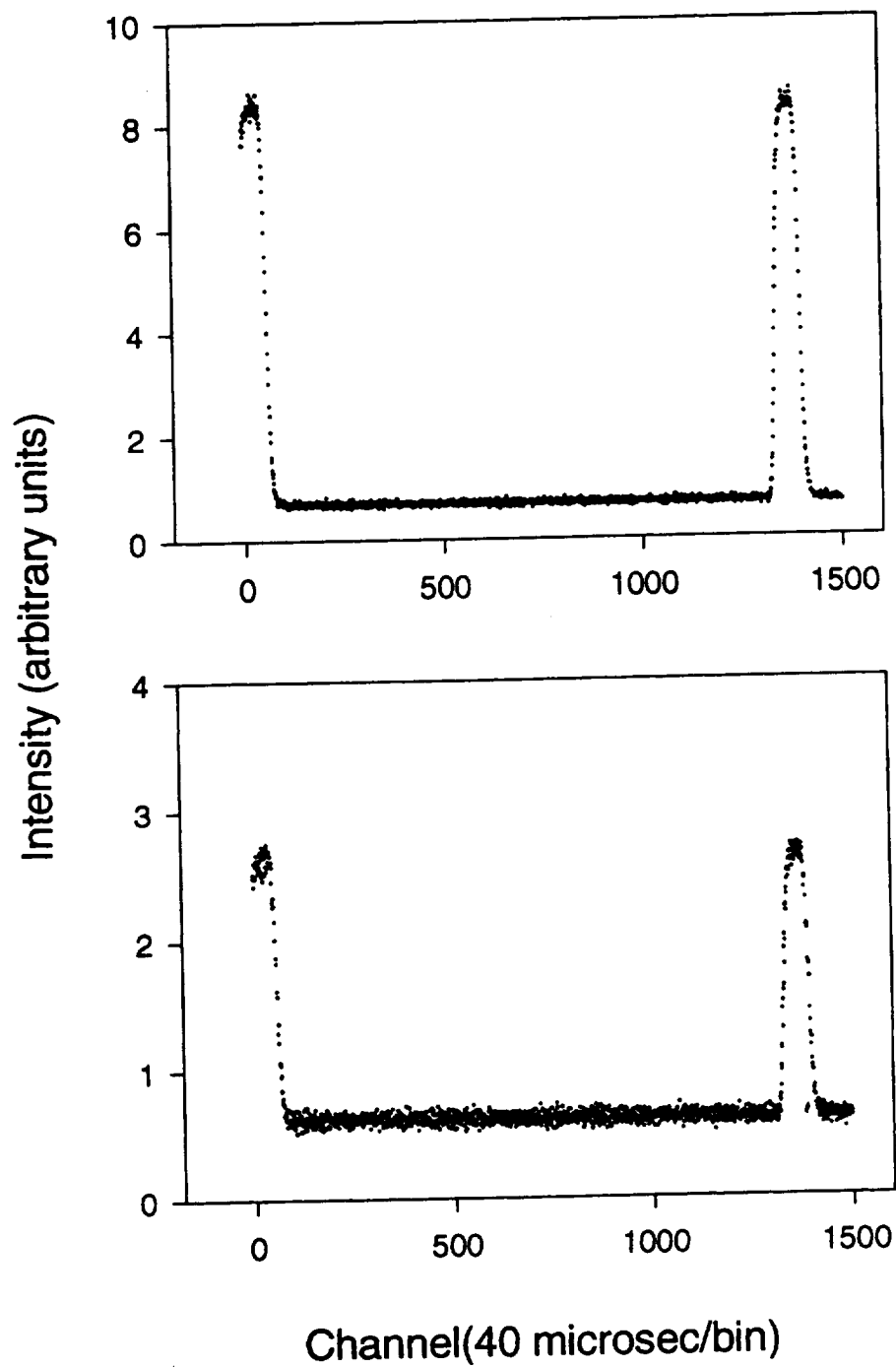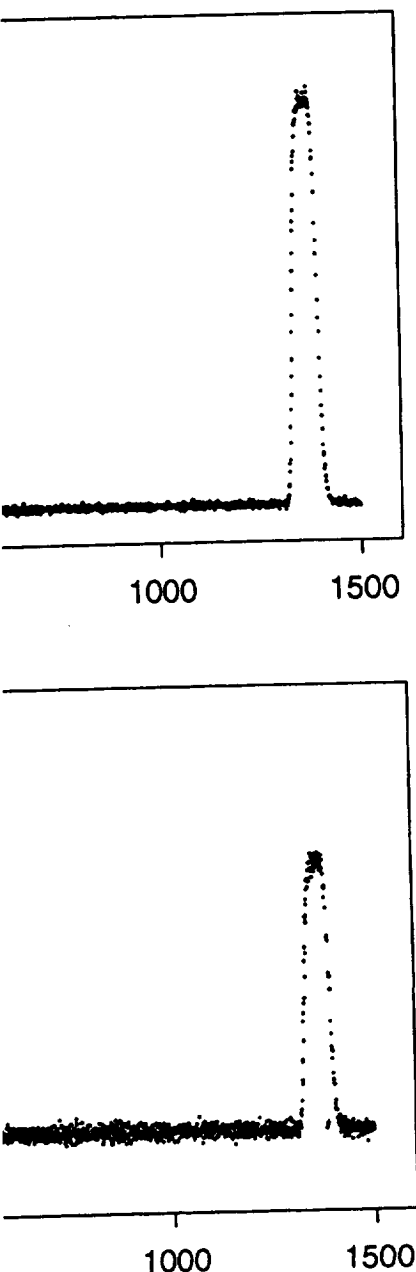
FIGURE 7 Direct D_2 beam pulses with RF off (top) and on (bottom). The dissociation rate can be obtained by comparing the two signals.

cryostat, is shrouded by a Cu shield. The shield is designed with a small aperture in front so deposition of H and D occurs only on the sample, since the shield is at too high a temperature for sticking to occur on it. The other parts of the cold finger are at much higher temperatures (≥ 160 K). A capillary stainless steel tubing can be positioned in front of the sample for depositing condensables. The system is pumped by a 400 l/s turbomolecular pump and a 10" He closed-cycle cryopump. At a pressure of $5 \cdot 10^{-10}$ torr, it would take 40 minutes to build up a layer of background gas if the sticking coefficient is 1.

The solid angles subtended by the sources to the entrance collimators to the UHV scattering chamber are about $6 \cdot 10^{-6}$ sr. Assuming a center-line intensity of 10^{17} atoms/sec/sr. (Scoles, 1988), and a 50 % duty cycle of the choppers, the beam at the sample is about $\sim 10^{12}$ atoms/sec with a ~ 3 mm diameter. The sample is typically $\sim$ 9 mm in diameter. The beams are adjusted to hit the same spot on the sample by using three laser beams, two mounted where the beam sources are, and the third at 90° from one of the beams. Lower fluxes have been obtained by using chopper wheels with a 5% duty cycle (see Fig. 7). In this condition of low beam flux, leakage of background hydrogen or deuterium from the third stage is small compared to the fluxes of the beams.

The beams are detected by a rotatable, differentially pumped quadrupole mass spectrometer. The signal is sent to either a lock-in amplifier or a multichannel scaler. Thermal desorption measurements, described below, are carried out with the detector in front of the sample and between the two beams (entrance hole of detector: 6.3 mm at 6.2 cm from sample; the center of the detector is at 8.25 cm from the sample). Our apparatus is equipped with other surface science probes, such as a LEED (Low Energy Electron Diffraction)/Auger electron spectroscopy set-up to determine the structure and chemical compositions of surfaces, an Ar-ion gun for sample cleaning, a two-rotation axes, (XYZ) sample manipulator with temperature range from 140 K to 1200 K.

Sample treatment varies according to the type of material and manipulator used. Graphite is peeled just prior insertion into the apparatus and then it is annealed at $\sim$ 200°C for several hours. Silicates are cleaned with solvents in ultrasonic baths (acetone, methanol, alcohol) and then placed in the UHV chamber. After UHV conditions are reached, the sample is flashed to $\sim 200°$C. The main background gas in a well baked UHV chamber is hydrogen. Once cooled to a few K, samples can be cleaned of physically adsorbed hydrogen by flashing them to 30 K.

4.2.2. Results of H recombination reaction studies

In a recent study we measured the recombination efficiency of hydrogen on HOPG (Highly Oriented Pyrolitic Graphite) and on an olivine (a silicate) sample (Pirronello *et al.*, 1997a, Pirronello *et al.*, 1997b) using two beams, one of H and the other of D. In this case the recombination product, HD, can form only on the sample surface, excluding any contribution of background gas (mostly H and H_2). Furthermore, since we use a quadrupole mass spectrometer, it is particularly convenient to work with HD (mass 3), since there is little background signal at that mass. On the contrary, detection of H, H_2, or D signals is more problematic, due to the presence of

1000   1500

1000   1500

10 microsec/bin)

p) and on (bottom). The dissociation rate can be

background gas (H and H_2 with mass 1 and 2, respectively). The signal from the quadrupole mass spectrometer is fed into a multichannel scaler which accumulates the counts in time bins. Due to the uncertainties in ionization probability and transmission efficiency down the filter, only relative measurements are meaningful.

In our studies of H recombination, we make the following measurements; we determine: a) the amount of H and D which is sent on the surface, I_H, b) the amount of HD which desorbs during exposure of the sample to H and D fluxes (irradiation), I_{irr}, and c) the amount of HD which sticks and remains on the surface, I_{des}.

The amount of HD that remains stuck on the surface is measured in a thermal desorption experiment, where the surface temperature is ramped quickly (~ 1 K/sec), from the temperature at which irradiation occurred to over 30 K. Figure 8 shows a cartoon of the adsorption and desorption process. In Figure 9, a typical trace of a thermal programmed desorption is shown. Most of HD comes out in a single peak and, from the temperature at which it comes off, one can deduce the desorption energy and the order of desorption kinetics. This type of study can be done at different coverages, from sub-monolayer to multilayer, to see the effect of particle-particle interaction on the desorption kinetics and ultimately on the recombination rates (Vidali et al., 1997).

This signal I_{des} is corrected for the acceptance angle of the detector, $\Omega = 4 \cdot 10^{-3}$, and the lower velocity of the particles coming from the surface (A quadrupole mass spectrometer gives a signal proportional to the gas density). Except at high temperatures, i.e., $T \sim 12-15$ K, I_{irr} is much smaller than I_{des}. I_{irr} is really an overestimate, since it accounts also for HD that could have formed on the chamber walls following scattering of H and D from the sample. Note that at low temperature, most of the HD that is formed remains on the surface; only a small part leaves the surface before the desorption run. Typically, it takes 45 sec from the end of the adsorption to the beginning of the temperature ramp. A plot of the area under the desorption peak vs. temperature or coverage gives the trend of how efficient the production of HD is. To obtain the recombination efficiency r, which is a pure number, the raw signals have to be analyzed as follows. r is given by: $f(I_{irr} + I_{des})/I_H$. I_H is the signal due to incoming hydrogen, f is a multiplicative factor that takes into account the fact that, besides HD, also H_2 and D_2 are formed, and that the incoming beams of H and D might have different intensities. Note that because of this correction factor, r is the recombination efficiency of H_2, and not of HD. r vs. T is plotted in Figure 10 for a sample of olivine. Furthermore, the gas let in the chamber by the sample in the thermal desorption run is not pumped out immediately; thus the background pressure rises a bit during the desorption. This background signal, measured with the detector behind the sample, needs to be subtracted from I_{des}. After each desorption run the sample is held at "high" (greater than 30 K) temperature to avoid recondensation of HD or H_2 on the surface. Test desorption runs were carried out with no prior adsorption of H and D. The desorption yield of HD was within the background level, indicating that HD doesn't form on the chamber walls in any significant way. Adsorption of H_2, a background gas in any UHV chamber, is negligible for the typical running times of experiments.

The recombination efficiency r is related to R_{H_2} (the recombination or production rate) by: $r = 2R_{H_2}/(n_H v_H A n_g)$. We find that at typical grain temperatures (10–15 K),

l 2, respectively). The signal from the
multichannel scaler which accumulates
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perature is ramped quickly ($\sim$ 1 K/sec),
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dicating that HD doesn't form on the
orption of H_2, a background gas in any
running times of experiments.
to R_{H_2} (the recombination or production
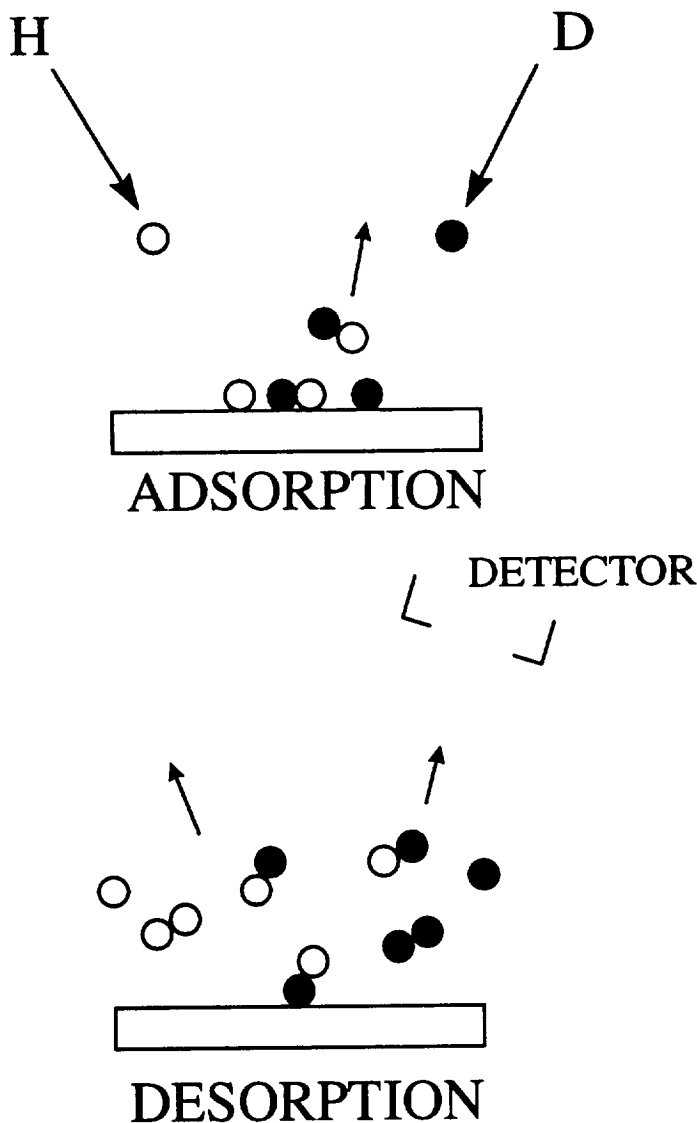at typical grain temperatures (10 – 15 K),

FIGURE 8   Cartoon of processes of H and D adsorption and HD desorption.

the recombination efficiency is of the order of $\sim 0.03 - 0.05$ (Pirronello *et al.*, 1997, Pirronello *et al.*, 1997b); if we take the model of HS, the recombination efficiency is 0.3, which is equal to the sticking coefficient, since in their model, all the H atoms landing on the grain recombine. This discrepancy could be due to several factors including:

a) the diffusion rate on actual grains is much less than the one calculated in HS due to the fact that actual surfaces are rather rough and chemically heterogeneous;
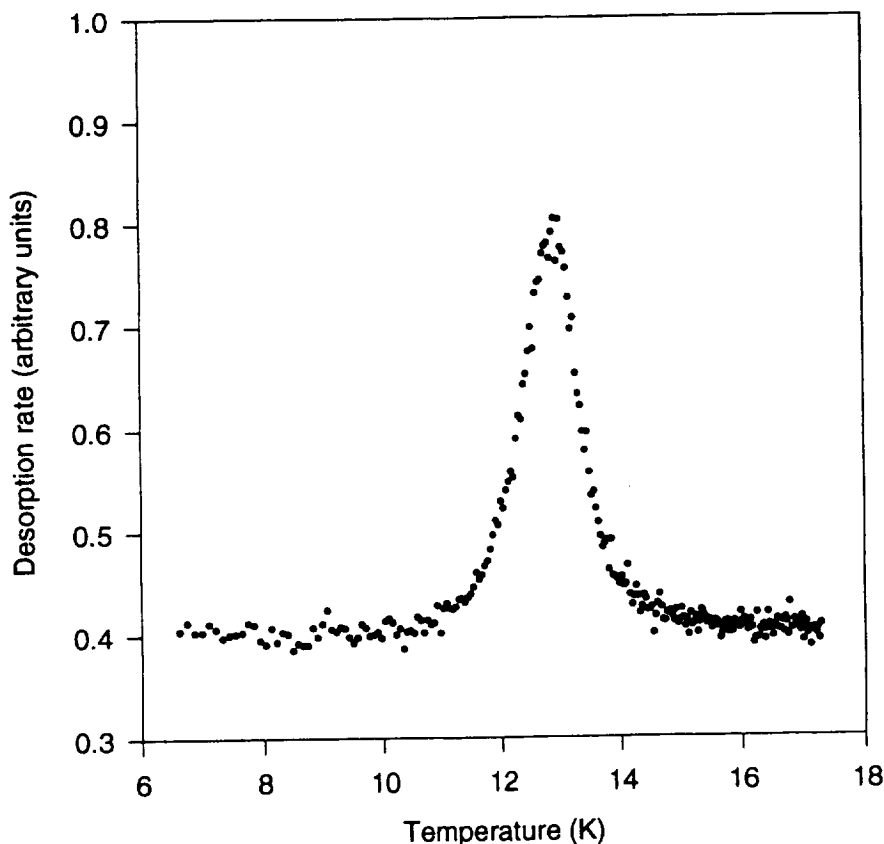
FIGURE 9   Desorption rate *vs.* temperature of HD from an olivine sample.

b) the expression for R in HS doesn't capture all the physical/chemical processes actually responsible for the recombination;

c) the probability that two atoms recombine when they meet (γ) is significantly less than one;

d) the olivine sample is not a good approximation of actual silicates in space.

In a recent paper Pirronello *et al.*, 1997b, suggested, based on the interpretation of desorption kinetics data, that H atoms form HD after diffusing on the olivine surface only when the surface temperature is sufficiently high. The evidence is given by thermal desorption experiments that show that the desorption rate is proportional to the square of the reactant concentration (this would correspond to the case of $m = 2$ in Eq. (2)). Furthermore, r is found to be temperature dependent. Thus, tunneling alone cannot explain the results reported in Figure 10. Based on these observations, Pirronello *et al.*, 1997b proposed a new expression for $R_{H_2}(cm^{-3}sec^{-1})$ of molecular hydrogen:

$$R_{H_2} = \frac{1}{2}(S_H n_H v_H A t_H)^2 n_g \tilde{N}^{-2} \nu f(T, a, \delta E) \gamma', \tag{3}$$
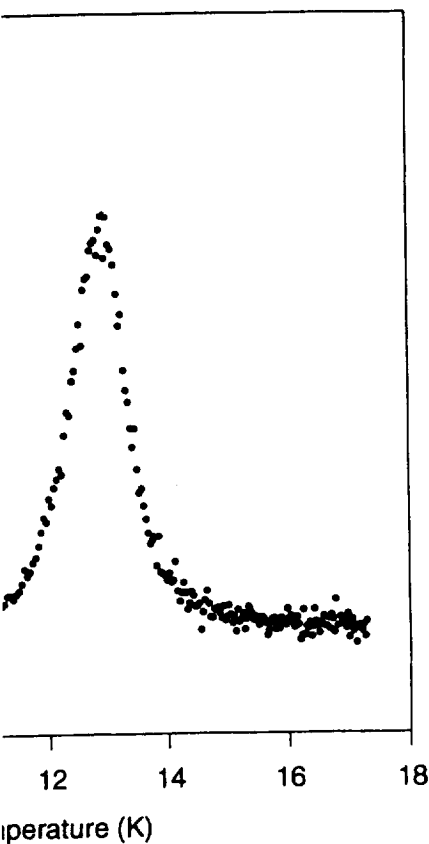
rature of HD from an olivine sample.

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cm^{-3}sec^{-1}) of molecular hydrogen:

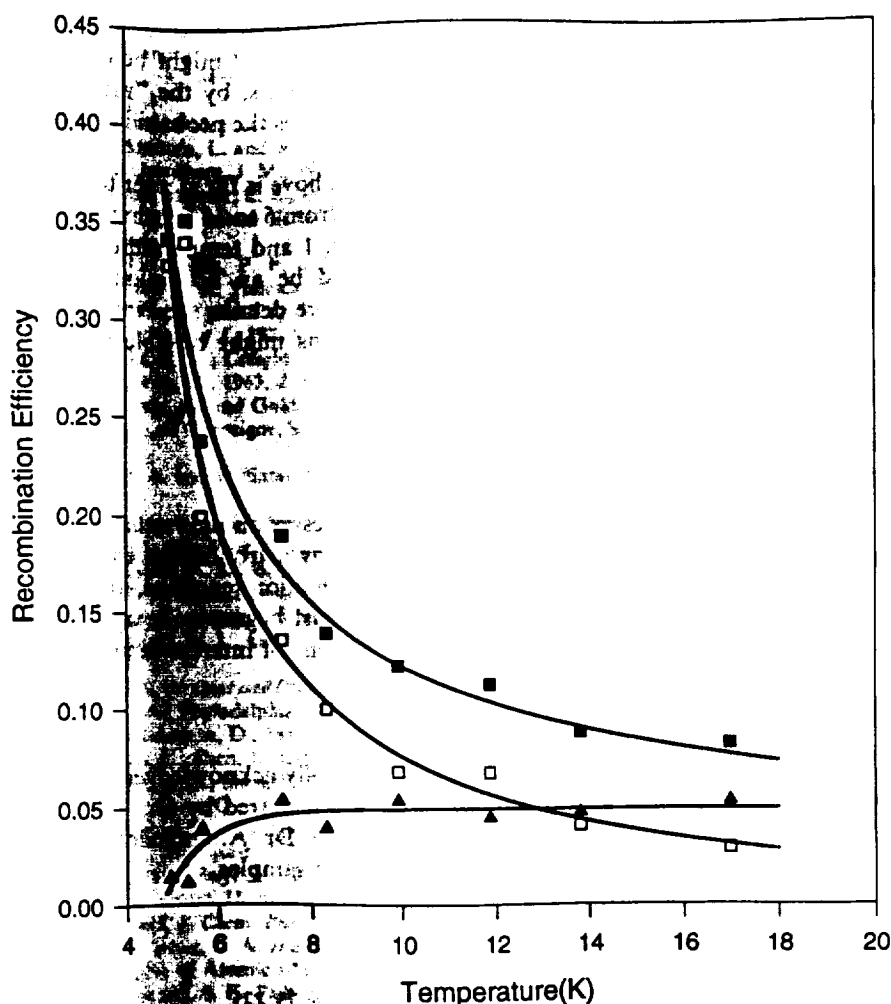$$)^2 n_g \tilde{N}^{-2} \nu f(T, a, \delta E) \gamma', \qquad (3)$$

FIGURE 10 Hydrogen recombination efficiency from an olivine sample (from Pirronello et al., 1997b). Lines are guides to the eye. Empty squares: r using the desorption yield only; triangles: contribution to r from the irradiation term (see text); filled squares: r with desorption yield and irradiation contributions.

The term squared in Eq. (3) represents the total number of H atoms on the grain surface and the $\tilde{N} \mu f(T, a, \delta, E)$ describes the mobility of adatoms due both to thermal activation and tunneling, two processes that can be in competition with or help each other. The cross-sectional area A is given as $N^{2/D} \sigma$, where N is the number of sites, σ the area of each adsorption site, and D is the fractal dimension (likely to be from 2 to ~ 2.6 for many non-porous carbon and silicon-bearing solids; see, Avnir et al., 1984); $t_H = t_o \exp(D_H/k_B T)$ is the residence time of H atoms (ν_H is characteristic frequency of an H atom in the energy level D_H inside the adsorption potential well), $\tilde{N}$ is the average number of sites between two adsorbed H atoms ($\tilde{N}$ is squared to take into account that adatoms perform random walks), ν an inverse

characteristic time related to atom diffusion, T is the temperature, δE and a are energy and width parameters for tunneling. The function f might be obtained, in analogy to electric conduction in non-cyrstalline materials, by the "variable range hopping" theory: $f = f_0 \exp(-B / k_B T^{1/3})$ (Mott 1987). γ' is the probability that two H adatoms recombine upon encountering.

However, the temperature dependence of Eq. (3) above is far steeper than the one observed (the latter one being about a factor 10 in r from 5 to 15 K); thus, it has been suggested that γ' (Eqs. (3)) might be different from 1 and temperature dependent. γ could be temperature dependent if there would be an activation energy for recombination of the order of $\sim 5 - 20$ meV. (For more details, see Pirronello et al., 1997b). More experiments and computer simulations might be able to prove or disprove this conjecture.

5. CONCLUSION

It is now recognized that physical and chemical processes on interstellar dust grains are important in the generation of molecules in many astronomical environments. Key processes in the ISM, such as hydrogen recombination reactions, are eminently surface processes. Surface science techniques have just begun to be applied to the study of fundamental reactions occurring in conditions of interest to astrophysics.

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Laboratory investigations of molecular hydrogen formation on dust grain analogues

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We report results on molecular hydrogen formation on surfaces of realistic analogues of dust grains under astrophysically relevant conditions. Experiments were conducted using two low energy hydrogen and deuterium beams impinging on samples kept at 6 to 20 K in an ultra-high vacuum chamber. Most of the results reported here are for molecular hydrogen formation on olivine (a silicate).

Our main results are:

a) diffusion of atomic hydrogen at the lowest temperature is slow;

b) recombination efficiency depends strongly on surface temperature in the 6-15 K range;

c) Recombination is thermally activated.

Based on these results, we propose a model consisting of a set of rate equations for the recombination of molecular hydrogen in different astrophysical environments.

Introduction

The formation of molecular hydrogen is certainly one of the most important processes occurring in astrophysical environments because H_2 is the most abundant molecule in space and, as such, is the most frequent collisional partner of all other particles in the gas phase.

Furthermore, molecular hydrogen, together with other species, provides an efficient mechanism for cooling clouds during a gravitational collapse. Once they are collisionally excited, molecules deexcite through roto-vibrational transitions, emitting photons to which the cloud itself is transparent. This cooling mechanism increases the formation rate of stars and has great impact in the structure and evolution of galaxies.

In this note we report on measurements of formation of molecular hydrogen that were performed, for the first time, in conditions and on materials that are relevant to environments in the diffuse interstellar medium (Pirronello et al., 1997a,b).

Molecular hydrogen is not efficiently formed in the reactions that are so efficient in producing other interstellar molecules. In a collision of two hydrogen atoms in the gas phase the proto-molecule forms in a high vibrational level. In order to become stable, the molecule has to shed a large fraction of the condensation energy (4.5 eV); radiative processes are very slow because they involve forbidden roto-vibrational transitions and the just formed molecule falls apart before it has the time to radiate the excess energy. Other ion-neutral collision schemes, as discussed in

detail by Duley and Williams (1984), don't work either since they are limited by the abundance of intermediate charged species.

It was proposed several years ago (Gould and Salpeter, 1963; Hollenbach and Salpeter, 1970; Hollenbach, Werner and Salpeter, 1971; Williams, 1968) that molecular hydrogen could form in three-body reactions where the third body is an interstellar grain that can take the excess energy. (In the diffuse interstellar medium, the density is so low - $n_H \sim 10 - 10^2$ cm^{-3} - that three-body reactions in the gas phase are very unlikely).

To form H_2 on interstellar dust grains, the following processes have to occur: collision and sticking of H atoms with a grain of interstellar dust, diffusion of hydrogen atoms on the surface of the grain and formation of H_2 upon collision of two hydrogen atoms. Part of the energy gained in the formation of the molecule is retained by the surface, while the other fraction might go into translational and internal energies of the molecule leaving the surface. Some of these processes have not been studied thoroughly either experimentally or theoretically on account of technical difficulties in reproducing astrophysically relevant environmental conditions and in carrying out calculations for processes dominated by quantum effects.

Experiment

A detailed description of the experimental set-up and measurement procedures is given in Vidali et al.(1998), while a presentation of results of hydrogen recombination reactions is given in Pirronello et al. (1997a, 1997b).

The experiments were conducted using a scattering beam apparatus consisting of two atomic beam lines (one for H and the other for D), each triple differentially pumped and equipped with radio-frequency sources to dissociate H_2 and D_2. The dissociation rate was measured to be $\sim$ 75-85 %. Before entering the first vacuum chamber, the atoms in the beams are cooled to $\sim$ 150-200 K by passing through a short aluminum channel connected via a copper braid to a liquid nitrogen reservoir. The beams are aimed at the center of a sample located in an ultra-high vacuum chamber (p $\sim 10^{-10}$ torr). The reaction products ejected from the surface are detected by a quadrupole mass spectrometer. Two beam lines with isotopically labeled hydrogen have been used to avoid background counts due to the residual molecular hydrogen present in the chamber or to the undissociated hydrogen in the beam. The mass spectrometer is then tuned to mass 3 in order to detect HD.

A typical experimental run is carried out in two stages. In the first, the H and D beams are sent onto the surface for a given amount of time (exposure). During this phase of irradiation, the amount of HD produced right away is measured. One would expect HD to be produced promptly either because of a Eley-Rideal reaction (where a D atom from the gas phase reacts with an H atom at the surface to produce HD), or because H and D atoms move so fast on the surface that they recombine during the time of irradiation (from tens of seconds to tens of minutes). In the second stage, a heat pulse is applied to the surface, raising its temperature to $\sim$ 30 K.. Adsorbed atomic species that haven't yet recombined are set in motion. As H and D meet and form HD, the HD molecule is released in the gas phase and is detected by the mass spectrometer. This second experiment is called Thermal Programmed Desorption, or TPD.

The efficiency of the process r, defined as the ratio of the HD signal I_{irr} (detected after placing the mass spectrometer in front of the surface and in between the two lines) to the signal of the incoming beam I_{in} (previously measured placing the quadrupole in front of H and D lines), has been measured as a function of the surface temperature during irradiation (r is then corrected

for instrumental effects and branching ratios for the A+B → AB reaction, where A,B is either H or D). Such an efficiency r has been measured for each run both during irradiation of the surface with H and D atoms: $r_{irr} = I_{irr}/I_{in}$ and after a TPD run: $r_{TPD} = I_{TPD}/I_{in}$. The total efficiency at each irradiation temperature is then given by: $r_{tot} = r_{irr} + r_{TPD}$.

Results and Discussion

In Table 1 the efficiency of molecular hydrogen recombination is shown as a function of the irradiation temperature, in the temperature range of interest in interstellar clouds.

TABLE 1. Efficiency of Molecular Hydrogen Recombination on Polycrystalline Olivine

T(K)	r_{irr}	r_{TPD}
10	.04	.08
12	.05	.06
14	.06	.05
16	.06	.04
18	.07	.03

These values are up to one order of magnitude lower than those estimated by Hollenbach and Salpeter (1971) for a monocrystalline water-ice surface under some simplifying assumptions.

Besides these quantitative results that can be straightforwardly applied to interstellar cloud chemical models, experimental evidence was obtained on the type of processes that take place on the sample during irradiation with atomic hydrogen. This evidence comes from several TPD runs performed after irradiation with H and D atoms with the surface at the lowest temperature (5K-6K). TPD runs, where the surface temperature is raised quickly (~ 0.6 K/sec), were done after exposure of the sample to increasingly large amounts of H and D. Absolute calibration of the amount of HD present is very difficult to obtain. An estimate can be made as follows. From a fit of the recombination efficiency vs. exposure (Fig.5 of Pirronello et al.1997a) with $r = r_0(1 + cr_0t)$, we get $c \sim 0.1$ layer/min. If we assume that r vs exposure depends on the change of sticking with coverage (a feature of Langmuir adsorption kinetics - see Fig. 3 in Pirronello et al. 1997a), then $S = S_0(1 - \Theta)$, where S_0 is the sticking probability at zero coverage. Since $\Theta = FSt$, where F is the flux, then $S = S_0(1 - FS_0t)$, which has the same functional dependence on time as r vs. exposure. Identifying c with F, we get that the flux is ~0.1 layer/min, and the smallest exposure (0.07 min in Fig.2 of Pirronello et al 1997b) corresponds to ~0.5 % of a layer, if $S \sim 0.6$ at 5-6 K, a reasonable assumption. During TPD, the mass spectrometer was tuned on mass 3 and the outcome of each of these runs was a peak of HD release versus temperature. Note that the amount of HD detected during irradiation at the lowest irradiation temperatures was always very small.

During TPD, starting from 5-6K, no signal was detected until the olivine sample reached a temperature between 9 and 10K. Furthermore, going from the lowest to higher coverage, the HD peak collected during TPD showed a peculiar behavior: the position of its maximum migrated from higher to lower temperatures. This is characteristic of second order desorption, where the desorption rate is proportional to the square of the concentration of the reactants. The physical picture that emerges is then one where atomic species are adsorbed on the surface and become mobile only when heat is provided (thermally activated diffusion). Once two H atoms meet, they form a molecule that then leaves the surface. Although tunneling of H atoms is expected to be

present, this apparently is not the dominant mechanism, since thermal activation is required.

In a second order desorption, the desorption yield is proportional to the square of the coverage, hence at least in the low coverage regime (the important one in interstellar environments) the famous expression of Hollenbach, Werner and Salpeter (1971) for the production rate of molecular hydrogen should be substituted by (Pirronello et al., 1997b):

$$R(cm^{-3}s^{-1}) = \frac{1}{2}(n_H v_H S_H \sigma t_H)^2 n_g \alpha \qquad (1)$$

where

n_H is the number density of atomic H in the gas phase

v_H is the average speed of H atoms in the gas phase

S_H is the sticking coefficient of H atoms on grains

σ is the cross-sectional area of the grain

t_H is the residence time of H adatoms on the grain

n_g is the number density of grains in clouds

α is mobility of H on the grain surface multiplied by the recombination probability.

Recently, Biham et al. (1998), solved rate equations for the formation of molecular hydrogen on surfaces. Two physically distinct limits were obtained. In one, corresponding to a slow diffusion time compared to the residence time of H on the surface, an expression for the recombination rate was obtained that was quadratic in the concentration of H on the surface, as the expression obtained above from phenomenological considerations.

In the limit of a fast diffusion time compared to the residence time, an expression linear in the adsorption rate of H on the surface was derived: $R = \frac{1}{2} n_H v_H S \sigma n_g$. This expression is essentially the one proposed by Hollenbach and Salpeter.

Experiments of H recombination on surfaces of realistic dust grain analogues and theoretical work using rate equations have shown that H recombination, in the conditions appropriate to the diffuse interstellar medium, is initiated by thermally activated processes and that the recombination rate is lower than predicted by Hollenbach and Salpeter. In order to reconcile our recombination values with observations (Jura 1975), it is speculated that grains in space have fluffy surfaces, where the sticking coefficient is much higher than considered by current models, and/or that there is a larger number of very small grains than previously estimated.

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Measurements of Molecular Hydrogen Formation on Carbonaceous Grains *,

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Abstract. Measurements of molecular hydrogen formation on an amorphous carbon sample have been carried out under astrophysically relevant conditions, i.e., using low fluxes of cold ($\sim$200 K) hydrogen-isotope beams, sample temperature between 5K and 20K. The experiments were conducted using the same methods as the ones employed for similar measurements on an olivine sample; therefore, results from the two experiments can be compared to each other. As in the case for the study of hydrogen recombination on a silicate surface, we find that mobility of hydrogen is thermally activated. However, differently from the olivine case, the activation energy for the overall process of diffusion and desorption is significantly higher, and the recombination efficiency, at similar total fluence of impinging atoms and sample temperature during irradiation, is also higher. Implications of these measurements for astrophysical environments are discussed.

1. Introduction

The relevance of dust grains in interstellar chemistry is now well recognized (see e.g. Rawlings et al. 1992, Hasegawa & Herbst 1993, Shalabiea & Greenberg 1995). The proper quantitative incorporation of their role in theoretical models needs experimental studies to provide the rate constants of chemical processes that take place on grains. Until a few years ago, laboratory investigations were principally aimed at the study of the chemistry

occurring in icy mantles irradiated either by UV photons (see e.g. Schutte 1996 and Bernstein et al. 1995) or by cosmic rays (see e.g. Pirronello 1996). On the other hand, due to intrinsic experimental difficulties, the experimental study of chemical reactions occurring on surfaces of grains, whose critical role in astrochemsitry has been discussed many times before, has been neglected.

In recent laboratory experiments, Pirronello et al. (1997a, 1997b) investigated the formation of molecular hydrogen on a natural iron-magnesium silicate, an olivine sample mechanically polished until shiny. This heterogeneous surface is polycrystalline and not amorphous as it has been deduced to be in interstellar space (Willner 1982), based on the measured high width of the 10 and 18 μm band (Day 1979, 1981; Stephens& Russel 1979; Dorschner et al. 1995). Nonetheless, it represents a better analogue than any model surface that has been proposed so far to estimate the production of molecular hydrogen in the interstellar medium. Quantitative values of the efficiency of the process of recombination (defined as the ratio between the number of molecules formed and one half of the number of hydrogen atoms sent onto the surface) were obtained in the temperature range between $5 \sim 6$ K and 18 K. The main results were: a) at the lowest temperatures, hydrogen atoms that stick and accommodate on the surface do not recombine, but rather they remain adsorbed as atoms; b) there is clear evidence in desorption kinetics studies that mobility of hydrogen adatoms requires thermal activation, therefore it does not proceed by tunneling alone, as commonly believed.

Our group used the results of a careful analysis of the desorption kinetics experiments to propose a new expression for the rate $R_{H_2}(cm^{-3}sec^{-1})$ of H_2 recombination in *astrophysical environments* (Pirronello et al. 1997b). This expression is valid in the regime of low coverage (defined as the percentage of surface sites occupied by hydrogen atoms), a regime that is the most important one in both diffuse and dense interstellar clouds:

$$R_{H_2} = \frac{1}{2}(n_H v_H \sigma \xi t_H)^2 n_g \alpha \gamma', \tag{1}$$

where n_H and v_H are the number density and the speed of H atoms in the gas phase respectively, σ the average cross-sectional area of a grain, t_H is the residence time of adsorbed H atoms on the surface, ξ is the sticking coefficient, n_g is the number density of dust grains, α is the hopping rate of a single H adatom . γ' takes into account the possibility that there is an activation energy for recombination. Notice that the quantity that is squared, i.e., $(n_H v_H \sigma \xi t_H)$, is the average number N of H atoms adsorbed on the surface at a given time.

The physical rationale behind this expression is the following. For an adatom that is localized on an adsorption site on the grain surface, α represents the number of hops it makes in the unit of time from one site to another and hence the number of sites it explores by a random walk in the unit of time; the probability for such an adatom to

encounter another H adatom is, of course, proportional to the number of other H adatoms that are on the grain surface (i.e., to the total number N of H adatoms on the surface minus one, that is neglected in Eq.1 and is important only when very few H atoms are adsorbed). This probability is then $(N - 1)\alpha$ for each single H adatom; the total rate of encounter between H adatoms on the surface is then $N(N - 1)/2\alpha$ because there are N adatoms on the surface. The factor 1/2 arises to avoid counting the number of encounters twice. The fraction that recombines is given by $\gamma\prime$. n_g gives the rate of H_2 recombination per unit volume in a cloud.

Subsequently Biham et al. (1998)[1] showed analytically, by means of a rate equations approach, that expression (1) for the formation rate of molecular hydrogen in interstellar clouds proposed by Pirronello et al. (1997b) and the well-known expression

$$R_{H_2} = \frac{1}{2} n_H v_H \sigma \xi \eta n_g, \tag{2}$$

given by Hollenbach at al. (1971) are just two extreme cases of the same general analytical solution to the steady state problem. Here η is the probability that two H adatoms on the surface meet and recombine to form H_2. Expression (1), that is quadratic in the total number N of H adatoms, holds when the coverage is low. Expression (2) is independent of coverage and really states that any two H atoms that stick on the grain always are released as molecular hydrogen. Expression (2) holds either when mobility is extremely high (as is the case if tunneling is effective) or when coverage is very high (in this case there is no need of high mobility because adatoms are so close to each other that they immediately react when they become mobile).

The measurements on the formation of molecular hydrogen on silicate surfaces need to be extended to other surfaces of materials likely to be part of interstellar grains (carbonaceous, other types of silicates, and icy and dirty ice UV irradiated residues) in order to obtain quantitatively the efficiency of heterogeneous catalysis for astrochemical applications. Furthermore, it needs to be checked whether the same kinetics observed for hydrogen recombination on olivine holds also in the case of these other substrates.

In this paper, we address some of these needs by presenting experimental results on the formation of molecular hydrogen on carbonaceous surfaces. The plan of the paper is as follows: in the next Section we describe the carbonaceous surfaces we have used in our experiments and their relationship with interstellar grains; this is followed by a brief review of the experimental apparatus and methods; in Section 4, we present our experimental results, while a discussion of these results and implications to astrophysics is given in Section 5.

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[1] In Biham et al.'s paper, a slightly different definition of α was used. In that paper the hopping rate was 2 α.

2. Carbon grains

Several forms of carbon exist in nature and several carbonaceous models of cosmic dust have been proposed (see for an extensive review Papoular et al. 1996). In particular small carbonaceous particles have been invoked (see e.g. Mathis et al. 1977; Hong & Greenberg 1980; Draine & Lee 1984; Sorrell 1990; Papoular at al. 1993; Blanco et al. 1996a; Li & Greenberg 1997) to explain the existence, position and width of the ubiquitous 2175 Å extinction hump, discovered in 1965 by Stecher & Donn (1965). Graphite grains, whose bulk optical properties were measured about thirty years ago (Taft & Phillip 1965; Tosatti & Bassani 1970), fit the average extinction curve, but are not able to reproduce the band width (Draine & Malhotra 1993). Furthermore, amorphous carbon seems more easily formed in astrophysical conditions than graphite (Donn et al. 1981; Duley & Najdowsky 1983). The role of hydrogenation of carbon amorphous grains in the physics of the interstellar medium and the evolution of grains due to UV and cosmic ray irradiation from the circumstellar to the interstellar medium have been considered by Sorrell (1990).

We used carbon samples prepared by A. Blanco and S. Fonti (University of Lecce) using an arc-discharge between two amorphous carbon rods in a 10 mbar Argon atmosphere. Carbon vapors are quenched collisionally by the background gas and condense into grains that are then collected on a copper substrate. The optical properties of these types of grains have been extensively studied in the laboratory (Blanco et al. 1991, 1993; Colangeli et al. 1993; Mennella et al. 1995) and it has been found that the extinction spectra of carbon grains condensed in a pure H_2 atmosphere show a continuous decrease with wavelength in the absorbance (there is no 2175 Å hump in this case). However, carbon grains condensed in a pure Ar atmosphere do show the interstellar bump, but around 2400 Å.

Recent results of Blanco et al. (1996b), relative to the formation of amorphous carbon grains in mixed atmospheres of Ar and H_2, show that an amount of 2 % or higher of hydrogen content in the quenching atmosphere already produces the disappearance of the hump, probably due to the fact that p electrons responsible for the UV absorption become localized, according to Fink et al. (1984), while with a lower percentage of H_2 the position of the hump is reproduced. Transmission electron microscopy performed on these samples have shown that, as in the case of carbon grains produced in either Ar or H_2 pure atmospheres, the samples consist of "clustered spheroidal amorphous carbon grains having an average diameter of about 10 nm" (Blanco et al. 1996b) and clustering of grains has been shown to have great relevance on their optical properties (Schnaiter et al. 1998).

For our experiments on the formation of molecular hydrogen on carbonaceous surfaces we chose to use samples of amorphous carbon condensed in a pure Argon atmosphere. The reason for such a choice is related to the evidence that even a small amount of hydrogenation sweeps out the presence of the hump, certainly the most relevant observable feature of the presence of carbonaceous grains in the interstellar medium.

We postpone to a future investigation the task to check the interesting prompt reaction model proposed by Duley (1996). He suggested that impinging H atoms from the gas phase could react (without being adsorbed and thermally accommodated on the surface) with "interstitial" H atoms at grain temperatures below 40K and with $-CH_3$, $-CH_2$ and $-CH$ groups in warm dust to form, by H abstraction, H_2. The probability of such a process should be proportional to the surface hydrogen concentration and should become particularly efficient in the case of a high hydrogen content in the grains.

In future experiments we will measure the formation efficiency of molecular hydrogen on organic residues of photolyzed ice mixtures. According to Greenberg's model of interstellar grains, such residues contain most of the carbon in solid form (Li & Greenberg 1997).

3. Experimental

The experimental apparatus and measurement methods have been described previously by Pirronello et al. (1997a, 1997b) and in greater details in the review paper by Vidali et al. (1998a); here we give a brief outline. The apparatus consists of a Ultra-High Vacuum (UHV) chamber pumped by a cryopump and a turbomolecular pump (operating pressure in the low 10^{-10} torr range). The sample is placed in the center of the UHV chamber and is mounted on a liquid helium continuous flow cryostat. By varying the flow of liquid helium and with the use of a heater located behind the sample, temperatures can be maintained in the range of 5-30 K. For cleaning purposes, the temperature of the sample can be raised to about 200 ° C (without liquid helium in the cryostat). The temperature is measured by a iron-gold/chromel thermocouple and a calibrated silicon diode placed in contact with the sample. Two triple differentially pumped atomic beam lines are aimed at the surface of the sample. Each has a radiofrequency cavity in which the molecular species is dissociated, cooled to $\sim$ 200 K by passing the atoms through a cooled Al channel, and then injected into the line. Dissociation rates are typically in the 75 to 90 % range, and are constant throughout a run. Estimated fluxes are as low as 10^{12} atoms $cm^{-2}s^{-1}$ (Vidali et al. 1998b).

The reason for using two different lines and two isotopes (one line for H and the other for D) is dictated by the fact that, in preliminary runs using only one line, it became evident that the signal of H_2 formation was hidden in the background given

by the undissociated fraction of molecules coming directly from the beam source. The possibility of using a second line is undoubtedly one of the most important features of this equipment.

By using H atoms in one line and D atoms in the other, we can look at the formation of HD on the surface, knowing that there are no other spurious sources of HD. The signal of HD is collected by a quadrupole mass spectrometer mounted on a rotatable flange. The experiment is done in two phases. First, H and D are sent onto the surface for a given period of time (from tens of seconds to tens of minutes) [2] At this time any HD formed and released is detected. In the second phase, the sample temperature is quickly (~ 0.6 K/sec) ramped and the HD signal is measured. This latter experiment is called Temperature Programmed Desorption (TPD).

By measuring the amount $\mathcal{N}(t)$ of HD that comes off the surface as a function of time, as well as the temperature of the surface as a function of time, information on the kinetics of desorption can be obtained. The desorption rate is given by (Vidali et al. 1998a):

$$d\mathcal{N}(t)/dt = -\mathcal{N}(t)'^m k^{(m)} exp(-E_d/k_B T), \qquad (3)$$

where $\mathcal{N}'$ on the right-hand side is the number density of reactants on the surface, m is the order of desorption, E_d is the activation energy for desorption and $T = T(t)$ is the temperature of the sample. For m=1, $k^{(1)}$ is associated, in the simplest model, with the frequency of vibration of the particle in the adsorption well. For m=2, $k^{(2)} \sim d(\pi k_B T/M)^{1/2}$, where d is the cross-section diameter and M is the mass of the adatom. Notice that $k^{(2)}$ has the dimension of $cm^2 \ sec^{-1}$., i.e. the dimension of a diffusion constant.

Second order desorption curves are characterized by a shift of the desorption peak to *lower temperatures* and a common high temperature tail as the coverage is increased; the peak shapes are symmetric, while first order ones have a sharp drop-off after the maximum (see Fig. 6 in Vidali et al. 1998a).

The so-called efficiency of the process, which is proportional to the ratio of the HD yield and the number of H and D atoms sent on the target, is computed by taking into account the fact that H and D yield also H_2 and D_2; in the figures below, the results are given for the total number of *hydrogen* molecules produced.

This efficiency depends, in general, on the total fluence of H and D atoms.

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[2] Note: the irradiation times given in the figure and elsewhere in this report are *equivalent irradiation times*. With respect to the data presented in Pirronello et al. (1997a), the amount of gas admitted was slowed down by using mechanical choppers with duty cycle of 1:20 instead of 1:2. For example, as the number of atoms reaching the sample is concerned, an exposure of 4 minutes with a 1:20 chopper, the configuration here employed, corresponds to an equivalent irradiation time of 24 sec. with a 1:2 chopper used in Pirronello et al. (1997a).

As in the case for olivine, and at the lowest sample temperatures, most of HD detected is formed because of thermal activation during the heat pulse. Only a small fraction of HD is formed during the irradiation process, showing that, at least under our experimental conditions, prompt-reaction mechanisms (Duley 1996) or fast tunneling (Hollenbach et al. 1971) are not that important.

4. Results

In Figure 1, the efficiency of formation of molecular hydrogen as a function of temperature is shown for a sample of amorphous carbon. The sample was irradiated with an estimated flux of H and D atoms of 10^{12} atoms $cm^{-2}s^{-1}$ ($\sim$ 0.1 layer/min) for 48 seconds of equivalent irradiation time (see also footnote 2). The total recombination efficiency is the sum of the contribution measured during H and D irradiation and after a TPD run. In the former case we measure HD production due to fast processes, such as the fast migration of H and D atoms across the surface or the direct reaction of an H atom from the gas phase with a D atom at the surface. In the latter case, we set H and D atoms in motion with a heat pulse, so as to probe the amount of H and D that would have formed by H and D migration if we had waited an amount of time that is technically impossible to reproduce in the laboratory.

As discussed in Pirronello et al. (1997b), the irradiation contribution is obtained by computing the difference of the HD background signal before and during irradiation. Thus, such difference represents an upper limit to the amount of HD formed promptly on the surface of the sample vs. other contributions due, for example, to recombination on the walls of the chamber.

In Figure 2, the total recombination efficiency of *molecular hydrogen* on olivine (Pirronello et al. 1997a) and on an amorphous carbon sample is compared.

As Figure 2 clearly shows, at equal substrate temperatures, the efficiency of molecular hydrogen formation on the amorphous surface is higher than that measured on olivine, especially at the lowest sample temperatures[3]. This may be due to the following factors: the intrinsic difference in the depth and surface distribution of adsorption sites; the probable increase in sticking and decrease in mobility of H atoms on the amorphous carbon surface with respect to the olivine polycrystalline surface; and the difference between the total area of the two exposed surfaces.

In order to better understand in detail the processes involved in the formation of molecular hydrogen, we studied the kinetics of HD desorption for several irradiation time intervals, corresponding to several values of H and D coverages. Figure 3 shows the

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[3] This is also true, particularly for temperatures below 10 K, if we assume that the recombination efficiency is given only by the TPD contribution.
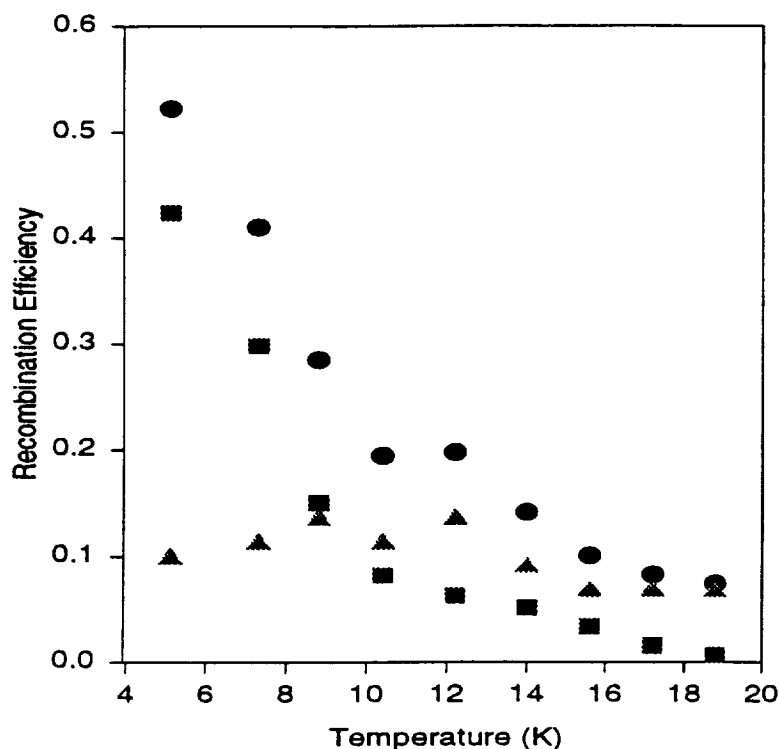
Fig. 1. Hydrogen recombination efficiency as a function of temperature on a surface of amorphous carbon. Circles: total recombination efficiency; triangles: contribution during irradiation; squares: contribution due to TPD runs. Equivalent irradiation time: 48 sec.

kinetics of desorption of molecular hydrogen as a function of atomic hydrogen exposure (i.e, irradiation time at constant flux).

An analysis of desorption runs (see also previous Section) shows that the desorption kinetics is of the second order from the lowest coverage used in the experiment. Hence, it should conceivably be so for even lower coverages that are encountered in dense and diffuse interstellar clouds because at higher exposure the kinetics becomes of the first order. Qualitatively, this means that desorption of the molecular species occurs after atoms are set in motion and recombine; in the first order desorption, the desorbing molecule was already present on the surface in that form.

From a quantitative point of view we get that the overall activation energy for desorption of HD from amorphous carbon is $\sim$ 45 meV, while it is $\sim$ 26 meV from olivine.
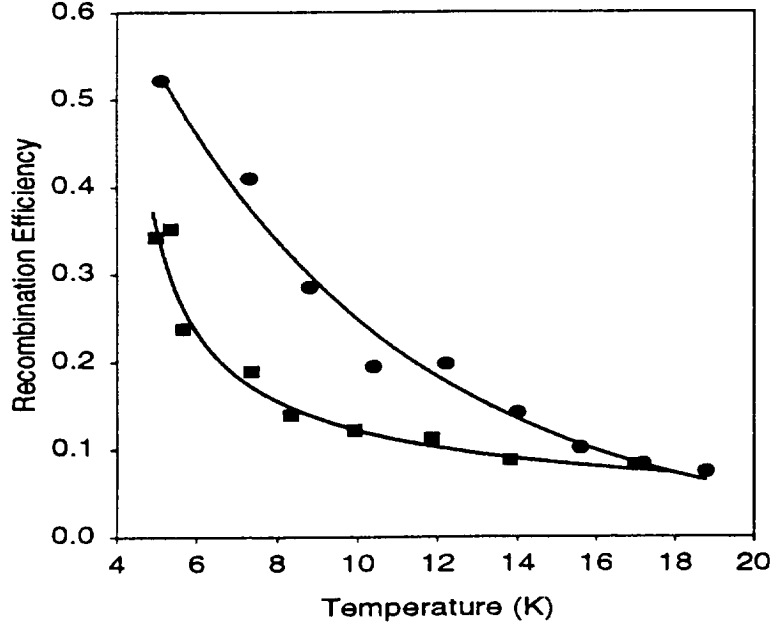
Fig. 2. *Hydrogen* recombination efficiency as a function of temperature on a surface of amorphous carbon (top) and olivine (bottom). Lines are guides to the eye.

We also get: $k^{(2)} \sim 10^{-3} cm^2 sec^{-1}$ (see Vidali et al. (1998a) for details), which is in the range of values for hydrogen desorption from most surfaces.

5. Discussion

The fact that the desorption kinetics is of the second order in the low coverage regime of H adatoms gives additional support to the expression (1) to evaluate the rate of H_2 formation in interstellar conditions. Such analysis is not valid only for olivine but also for amorphous carbon grains. Thus, recombination on amorphous carbon confirms the trend seen on olivine, although there are some differences, as explained below.

As it can be seen from Figure 3, the temperature for the beginning of significant HD production, and hence for mobility of adsorbed hydrogen atoms, occurs at a higher value
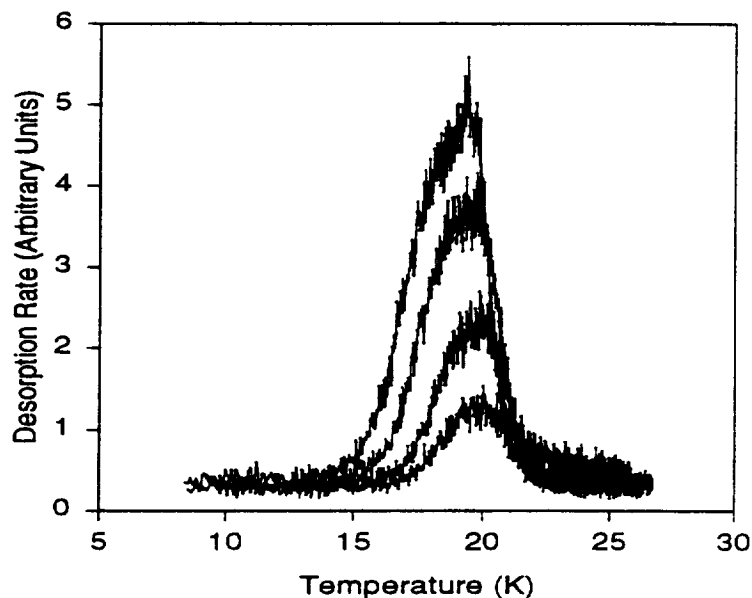
Fig. 3. HD desorption rate vs. surface temperature of an amorphous carbon sample during TPD runs following adsorption of H and D on amorphous carbon at $\sim$ 7 K for (bottom to top): 24, 48, 96, and 192 sec.

than the one observed for olivine (about 14 K instead of 9 K).[4] This is an important piece of evidence of the fact that the technique we are using is sensitive to surface peculiarities; it shows that even if the regime of adsorption is dominated by long-range physical adsorption forces, ("physisorption", see Vidali et al. 1991), there are important differences between olivine and amorphous carbon. The most relevant is that on carbon grains desorption of HD occurs at higher temperatures than on olivine, or, equivalently, that the activation energy for the overall combined process of diffusion, recombination and desorption is higher.

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[4] These values depend in general on the coverage and the heating rate (Vidali et al. 1998a); however, they can be compared in this case since both the coverage and the heating rate were the same.

This observation might lead to think that, at least in some environments, it is more difficult to form molecular hydrogen on carbon surfaces than on silicate ones. In our opinion this is not necessarily the case. Although the effective energy barrier for HD formation and desorption (as obtained from TPD runs) is higher on amorphous carbon than on olivine, one has to consider that, if we look at *experimental* work on single-crystal surfaces, H is more strongly held on a carbon surface than on the one of an insulator (Vidali et al. 1991). Thus, the residence time of H atoms on amorphous carbon is longer and this might allow them more time to overcome the higher energy barrier for recombination/desorption. Fig 2 shows that this should be the case.

Depending on the physical conditions of the region in which grains are immersed, their "steady-state" temperature T_g (obtained by the balance between the energy they absorb from the radiation field and the one they re-emit in the infrared) dictate how efficiently recombination takes place, given the size and chemical composition of the grain.

It is possible to envisage two main scenarios for the formation of molecular hydrogen on grains, depending on the mobility of H adatoms on the grain surface and hence on the value of $k_B T_g$ with respect to the energy barrier for their diffusion.

If $k_B T_g$ is such that diffusion of H adatoms on the grain surface occurs efficiently, H_2 synthesis may proceed without problems following the Langmuir-Hinshelwood mechanism in which adatoms migrate, meet and then recombine (see for details Vidali et al. 1998a). If, on the contrary, $k_B T_g$ is much lower than the barrier for diffusion, atomic hydrogen impinging from the gas phase on the grain surface will remain substantially immobile. H atoms will then accumulate on the surface and tend to saturate available adsorption sites. Progressively another mechanism, the so-called Eley-Rideal mechanism (in which atoms impinging from the gas phase react directly with adsorbed ones), will become more important, because its efficiency is proportional to adatom coverage. This latter mechanism (which resembles the prompt reaction model proposed by Duley (1996) and was also discussed by Guillois et al. (1998) in connection with the possible presence on grains of H atoms that have stronger and more localized bonds with surface atoms than in the physisorption case) will assure, after an initial delay, a more or less steady production of molecular hydrogen at a rate limited by the gas-phase H flux of H atoms.

The fact that two different mechanisms of H_2 formation might be operational, depending on grain temperature T_g, has interesting consequences in the case of very small grains (for instance of the size required to explain the Cirrus cloud infrared emission). It is interesting to analyze what would be the effect on H_2 formation of the absorption of UV photons by such small grains if they are at temperatures in which H adatom mobility is extremely low or almost absent and only the E-R mechanism might allow some synthesis of molecular hydrogen. For these small grains the recombination processes outlined

above can be totally perturbed by temperature spikes induced by the absorption of single energetic UV photons. Such spikes can increase the temperature of grains to several tens or hundreds K in times of the order of 10^{-10} seconds. The effect of such a sharp rise is to desorb H adatoms directly to the gas phase without allowing them to recombine. The spikes will reset the population of adsorbed hydrogen atoms on the surface of small grains to zero, leaving to the numerically smaller population of larger grains the duty of forming molecular hydrogen. The involvement of small grains in the production of H_2 is then dictated by the competition of two processes: a) collision and adsorption of H atoms; b) absorption of energetic UV photons. Only when the timescale for adsorption

$$t_{ad} = (n_H v_H \sigma \xi)^{-1} \tag{4}$$

is much shorter than the time for the absorption of a single UV photon (assuming that the grain behaves like a black body at UV wavelengths)

$$t_{UV} = (\sigma \Phi_{UV})^{-1} \tag{5}$$

where Φ_{UV} is the UV flux, then small grains will be able to participate to the production of molecular hydrogen.

In diffuse clouds that are permeated by almost unscreened UV radiation field, formation of H_2 on small grains can be almost certainly ruled out if their equilibrium temperature is below that for efficient mobility of H adatoms on their surface. In dense clouds UV photons do not penetrate, but grain cores are covered by a dirty ice mantle, hence it is important to delay such discussion when measurements of molecular hydrogen recombination will be performed on water ice (one of the aims of our future work). In clouds of intermediate density, between diffuse and dense ones, there may be room for H_2 synthesis even on small grains.

6. Acknowledgments

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