Astron. Astrophys. 344, 681–686 (1999)

ASTRONOMY
AND
ASTROPHYSICS

Measurements of molecular hydrogen formation on carbonaceous grains*

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Received 9 October 1998 / Accepted 8 January 1999

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 (∼200 K) hydrogen-isotope beams, sample temperature between 5 K and 20 K. 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.

Key words: ISM: clouds – ISM: abundances – ISM: atoms – molecular processes – atomic processes – methods: laboratory

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 astrochemistry 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 et al. 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 $R_{\mathrm{H}_2}(cm^{-3}sec^{-1})$ 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:

$$R_{\mathrm{H}_2} = \frac{1}{2}(n_{\mathrm{H}} v_{\mathrm{H}} \sigma \xi t_{\mathrm{H}})^2 n_{\mathrm{g}} \alpha \gamma\prime, \quad (1)$$

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. $\gamma\prime$ takes into account the possibility that there is an activation energy for recombination. Notice that the quantity that is squared, i.e., $(n_{\mathrm{H}} v_{\mathrm{H}} \sigma \xi t_{\mathrm{H}})$, 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

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* Research supported in part by NASA under grants no. NAG5-4998 and NAG5-6822.

** *Present address:* American International Groups, NYC 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 $\gamma\prime$. $n_{\rm g}$ 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

$$R_{\rm H_2} = \frac{1}{2} n_{\rm H} v_{\rm H} \sigma \xi \eta n_{\rm g}, \qquad (2)$$

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 are always 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 Sect. 4, we present our experimental results, while a discussion of these results and implications to astrophysics is given in Sect. 5.

2. Carbon grains

Several forms of carbon exist in nature and several carbonaceous models of cosmic dust have been proposed (for an extensive review, see 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 causes 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

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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.

below 40 K, 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 ($\sim$ 0.6 K s^{-1}) 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):

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

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.

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 Fig. 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} (~ 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

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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 5 $\%$ instead of 50 $\%$. For example, as the number of atoms reaching the sample is concerned, an exposure of 4 minutes with a 5 $\%$ chopper, the configuration here employed, corresponds to an equivalent irradiation time of 24 sec. with a 50 $\%$ chopper used in Pirronello et al. (1997a).

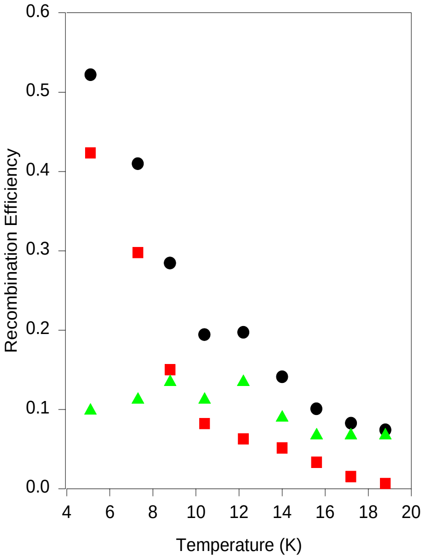

Fig. 1. Hydrogen recombination efficiency as a function of temperature on a surface of amorphous carbon. Circles: total recombination efficiency; triangles: contribution during irradiation; squares: contribution due to TPD runs. Equivalent irradiation time: 48 sec.

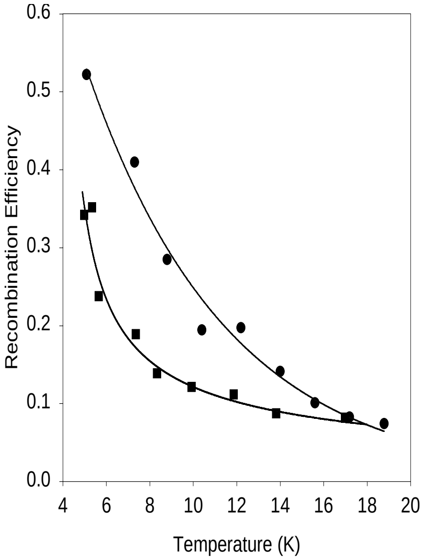

Fig. 2. *Hydrogen* recombination efficiency as a function of temperature on a surface of amorphous carbon (*top*) and olivine (*bottom*). Lines are guides to the eye.

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

As Fig. 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.

The recombination efficiency vs. exposure is presented in Fig. 3. Irradiation with H and D beams was carried out with the surface at ~ 7 K. Data in Fig. 3 are obtained from the thermal desorption contribution only; at this temperature the irradiation contribution is small, see Fig. 1.

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. Fig. 4 shows the kinetics of desorption of molecular hydrogen as a function of atomic hydrogen exposure (i.e, irradiation time at constant flux).

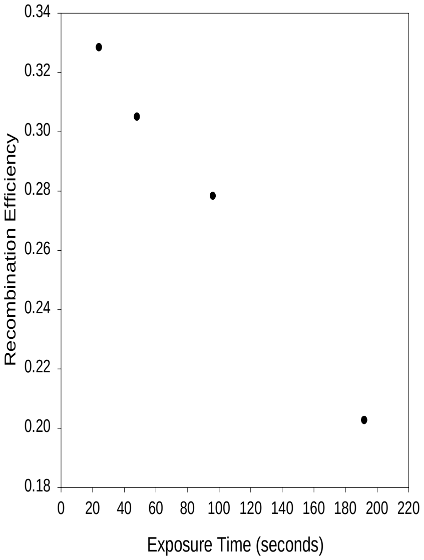

Fig. 3. Molecular hydrogen recombination efficiency vs. exposure time. Sample temperature $\sim 7 K$. The recombination efficiency is calculated using only the thermal desorption contribution.

An analysis of desorption runs (see also previous section) shows that the desorption kinetics is marginally of the second order, especially for the curve obtained at the highest exposure. Exposure times considered in these experiments are not quite short enough to see a dramatic shift of peaks towards lower temperatures as the exposure is increased, which is one of the hallmarks of second order kinetics, and as it was clearly seen

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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.

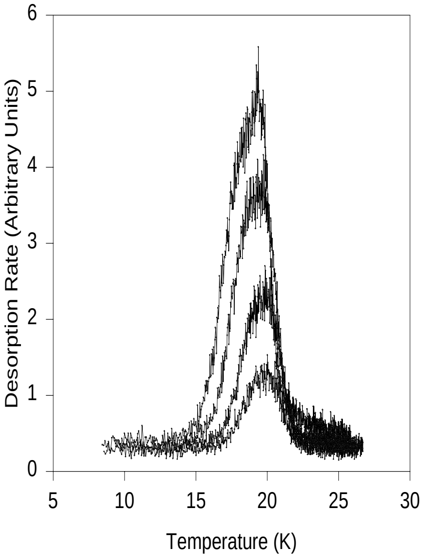

Fig. 4. HD desorption rate vs. surface temperature of an amorphous carbon sample during TPD runs following adsorption of H and D on amorphous carbon at ∼ 7 K for (*bottom* to *top*): 24, 48, 96, and 192 sec.

in the experiments on olivine (Pirronello et al. 1997b). Thus, Fig. 4 shows, in the case of amorphous carbon (and as already discussed in the olivine paper), that at higher coverage (but still much less than a layer) we are close to a transition from a second order to an "apparent" first order kinetics. Here the term "apparent" refers to the fact that the kinetics is still of the second order because atoms are still separated from each other but now so close that they need to migrate for a short distance to form a molecule. In such a case it is hard to see, from an experimental point of view, a clear shift of peaks.

Second order kinetics should conceivably hold 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 the experiment does not give the values of the energy barriers that enter in α and $\gamma\prime$ of Eq. (1) separately. However, we can get that the overall activation energy for formation of HD on amorphous carbon: $\sim$ 45 meV, while it is $\sim$ 26 meV for olivine. 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 can be seen from Fig. 4, the temperature for the beginning of significant HD production, and hence for mobility of adsorbed hydrogen atoms, occurs at a higher value 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.

This observation might lead one 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

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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.

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 into 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.

Acknowledgements. We thank Profs. Armando Blanco and Sergio Fonti of University of Lecce for carefully preparing and donating the amorphous carbon samples we used in this set of measurements and for helpful discussions. We thank Prof. Ofer Biham of the Hebrew University in Jerusalem for helpful discussions. V.P. acknowledges support from the Italian National Research Council (CNR) through grant CN96.00307.02.

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