

## MEASUREMENT OF THE KINETIC ENERGY OF HYDROGEN MOLECULES DESORBING FROM AMORPHOUS WATER ICE

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Received 2003 July 16; accepted 2003 August 15; published 2003 September 15

### ABSTRACT

A hydrogen molecule that is formed on an interstellar grain might retain some of the 4.48 eV of energy that is released in the recombination reaction of two hydrogen atoms. We set up an experiment to measure the translational (kinetic) energy of hydrogen molecules after they are formed on and are ejected from the surface of an interstellar dust grain analog. Here we report the first measurements of the kinetic energy of molecular deuterium as it leaves the surface of an amorphous water sample. The astrophysical implications of such measurements are discussed.

*Subject headings:* astrochemistry — dust, extinction — ISM: molecules — methods: laboratory — molecular processes

### 1. INTRODUCTION

H<sub>2</sub> formation is the most common and the most fundamental reaction taking place in the interstellar medium (ISM), since molecular hydrogen has an important role in the formation of protostars and, when ionized, intervenes in most of the important gas-phase chemical reactions occurring in interstellar clouds (Shull & Beckwith 1982). In a series of recent papers, we described the results and the analysis of the first laboratory investigations of the formation of molecular hydrogen on realistic analogs of interstellar grain surfaces. We measured the efficiency of the recombination on three main classes of surfaces: silicate and amorphous carbon analogs to simulate diffuse interstellar cloud grains (Pirronello et al. 1997a, 1997b, 1999), and amorphous water ices that are a component of ice mantles on dust grains in dense clouds (Manicò et al. 2001; Roser et al. 2002). From an astrophysical point of view, the most important surfaces are the exposed surfaces in diffuse clouds, where the high photodestruction rate due to the penetrating UV flux requires efficient production of H<sub>2</sub>. Amorphous water ices are also of interest because of the potentially high porosity of the ice layers and of the possibility that the ice layers may trap volatile atomic or molecular species within the ice matrix (Roser et al. 2001; Collings et al. 2003).

Of the 4.48 eV of energy that is released in the H<sub>2</sub> formation reaction, the fraction of this energy that is absorbed by the dust grain may cause at least a localized heating of the grain that may drive chemical reactions among adsorbed species on the grain surface. The released energy may also cause the desorption of the newly formed H<sub>2</sub> molecule, and it is of interest to know how this energy is partitioned in kinetic energy and in energy of the rovibrational excitations of the desorbing molecules (Duley & Williams 1993). There have been a few theoretical studies of the interaction of H with a surface under conditions that are of interest in astrophysics. Of the ones most relevant to the work presented here, we cite the molecular hydrogen formation on ice (Takahashi, Masuda, & Nagaoka 1999) and on a graphite surface (Parneix & Brechignac 1998; Farebrother et al. 2000). Since the early studies, swift progress has been made to obtain better potentials and more realistic geometries of scattering (Meijer,

Farebrother, & Clary 2002). Experiments at probing the rovibrational spectrum of the just-formed molecule are under way at the University College London (Perry et al. 2002) and in our own laboratory. Once a detailed knowledge of the rovibrational excitations is available, a constraint on the energy adsorbed by the surface can also be obtained.

The importance of a detailed knowledge of the energy distribution of the newly formed H<sub>2</sub> on the dust grains is due to the fact that it is closely related to the energy budget and hence to the dynamics of interstellar clouds. The fraction of energy released into the grain or taken by the molecule as kinetic energy is not subtracted from the energy budget of the cloud, but it will rather be collisionally redistributed to the other particles that are present in the cloud. The rovibrational energy of H<sub>2</sub> will be irradiated away in the infrared where the cloud is transparent. Thus, this energy loss together with the energy loss of other species such as CO help the cloud to contract.

The motivation for studying the formation of hydrogen on high-density amorphous water ice is that amorphous ice is the dominant water ice component of the icy mantles that form on interstellar grains in the dense ISM (Jenniskens et al. 1995). The icy mantles are in general mixtures of H<sub>2</sub>O, CO, CO<sub>2</sub>, and CH<sub>3</sub>OH ices that are chemically processed by the background cosmic-ray and photon fluxes. The more volatile of these components, such as CO, could be desorbed by the localized heating of the grain from the H<sub>2</sub> formation events on the surface, thus altering the gas-phase and solid-phase compositions of the dense interstellar clouds (Willacy, Williams, & Duley 1994). More detailed information on the energy of the H<sub>2</sub> formation available for surface heating should permit the refinement of this type of calculations.

### 2. EXPERIMENTAL

The apparatus consists of two atomic beam lines, an ultrahigh vacuum (UHV) chamber where the sample is kept, and a time-of-flight (TOF) section. The main apparatus has been described before (Roser et al. 2002; Biham, Pirronello, & Vidali 2003), and therefore only a summary of its salient characteristics will be given here. Briefly, the main apparatus consists of two triply

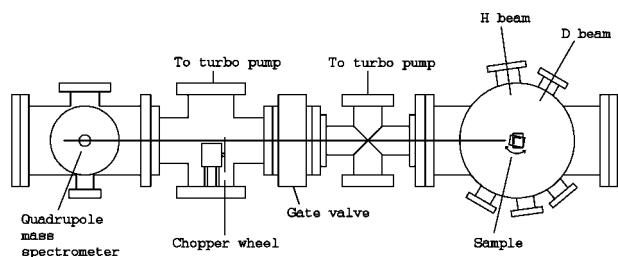


FIG. 1.—Schematic of the TOF section of the apparatus (*top view*)

differentially pumped beam lines aimed at the sample. Radio-frequency dissociation sources mounted on the beam lines produce hydrogen and deuterium atoms that are sent on to the target. The sample is attached to a copper holder in good thermal contact with a liquid-helium-cooled stage. A copper shield cooled by one of the stages of the refrigerator protects the sample from room-temperature radiation. The sample can be taken to a temperature of 4.5 K as measured by a calibrated silicon diode thermometer situated on the back of the sample; an indium foil between the sample and the diode improves the thermal contact.

The sample can be heated by a constantan filament housed in a Mycor (ceramic) box in the back of the sample. Thermal desorption experiments, in which the sample temperature is rapidly raised in order to increase thermal mobility of species on the surface and/or to desorb atoms and molecules, are typically done by cutting the flow of liquid helium to the sample holder, yielding a very reproducible and fast heating. A quadrupole mass spectrometer detects the products coming out of the surface.

The TOF section (see Fig. 1) consists of three chambers each pumped by a different turbopump and separated from the other chambers by 5 mm collimators. The turbopumps of the last two chambers are backed by another turbopump to reduce the amount of light-mass particles in the detection chamber. The TOF of molecules desorbing from the sample is measured by chopping the beam of desorbing particles defined by the collimators with a slotted wheel attached to an in vacuo AC motor located in the second stage of the TOF line. The pulse of molecules disperses in time as it travels toward the detector (33 cm from the chopper wheel). The signal from the quadrupole mass spectrometer in the final stage is recorded as a function of time in a multichannel scaler that is synchronized with the chopper rotation, thus yielding the time distribution of molecules arriving in each pulse.

In order to compute the average kinetic energy of the molecules reaching the detector, the TOF apparatus has to be calibrated. For this purpose, we directed the flow of either He or  $D_2$  into the TOF line from a room-temperature capillary temporarily mounted in the main UHV chamber. To obtain information on the velocity distribution of the desorbing molecules and their average translational energy from the recorded TOF signal, one has to take into account that the quadrupole mass spectrometer is a density and not a flux detector (since the detected flux should be multiplied by the probability of ionization and detection that is inversely proportional to the speed of the molecules) and that the measured TOF distribution has to be deconvolved for the finite time of the aperture of the slit of the chopper. Time lags in the instrumentation that could affect the measurement have also been investigated and assessed (Auerbach 1988).

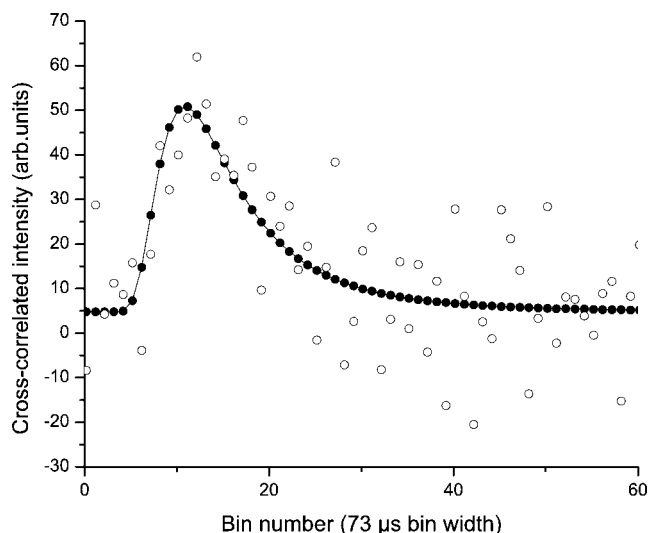


FIG. 2.—TOF trace of  $D_2$  desorbing from an amorphous ice surface (*open circles*) and fitted using a Maxwell-Boltzmann distribution (see text). The temperature at which D atoms were adsorbed on the ice was  $\sim 10$  K. Exposure time is 1 hr. The flux of D atoms is approximately half of the one typically used in previous investigations (Roser et al. 2002).

The experiment consists in dosing the surface with H and D atoms, or alternatively D atoms only, at the lowest sample temperature that we can reach in our apparatus (5–7 K depending on the particular run), then quickly raising the temperature with the sample rotated to face the TOF line for the TOF measurement. The temperature ramp applied to the sample accelerates the diffusion of H or D atoms on the ice surface, increasing the rates of  $D_2$ , HD, and  $H_2$  formation and desorption from the surface (Biham et al. 2003). The results reported here are of experiments conducted on the surface of high-density amorphous water ice. The preparation and characterization methods are the same as employed in a recent work by our group (Roser et al. 2002).

The differentially pumped stages of the TOF line provide a low background of light gases in the detection region. Furthermore, this arrangement guarantees that any thermalized gas load in the UHV chamber is only partially transmitted into the TOF section. It is important to make sure that the TOF signal is only of molecules leaving the surface with a direct flight path to the quadrupole mass spectrometer and not of molecules that have thermalized with the walls of the chambers before scattering into the final UHV chamber. We tested that this is so by directing the flux of  $D_2$  desorbing from water ice away from the TOF line, and we found that no TOF signal could be detected in this case.

Because the signal is expected to be very small, in some of the experiments we used a chopper wheel with a pseudorandom pattern of slots and bars that, per cycle, permits more of the beam through the wheel than a disk with equally spaced slots. A reasonably good signal-to-noise ratio could be attained using the pseudorandom method once the TOF pattern is recovered by cross-correlating the actual signal with the known pattern of the wheel (Comsa, David, & Schumacher 1981; Auerbach 1988).

### 3. RESULTS

Here we report the first TOF data for molecular deuterium formed from D exposure of amorphous ice during a thermal programmed desorption (TPD) experiment. Figure 2 shows the trace of a TOF distribution of  $D_2$  molecules departing from a

high-density amorphous water ice sample; the ice surface had been previously exposed to a beam of D atoms. Qualitatively similar results were obtained for the TOF of HD formed after dosing the surface with H and D atoms, except that in this case a lower duty cycle wheel with equally spaced slots was used, yielding a weaker signal. The peak of our TOF distribution can be identified with a parameter  $T_{\text{kin}}$ , the temperature of a Maxwell-Boltzmann distribution with a peak at the same flight time as in our data, while we denote the temperature at which the desorption rate is greatest by  $T_{\text{des}}$ .

For an effusive flow of distinguishable particles at thermal equilibrium, the number density of particles with a velocity between  $v$  and  $v + dv$  is proportional to a Maxwell-Boltzmann distribution:

$$f(v)dv \propto v^2 e^{-mv^2/2kT} dv.$$

To convert from a velocity distribution to a flight time distribution, we use  $v = L/t$  for the fixed chopper-to-detector distance  $L$ , and  $dv = (L/t^2) dt$ , so that

$$f(t)dt \propto \frac{1}{t^4} e^{-mL^2/2kTt^2} dt.$$

To obtain  $T_{\text{kin}}$ , we calculate the most probable TOF of molecules in the beam. For this purpose, we perform a least-squares fit of our data to  $f(t)$ . However, the maximum of this distribution  $t_{\text{peak}}$  is not the true most probable TOF. In fact, it includes temperature-independent offsets caused by the lag between triggering and measurement, deconvolution in the case of a pseudorandom chopper, and miscellaneous delays in electronics (Auerbach 1988). To compensate for these shifts, we calibrated our system by using an effusive flow of room-temperature D<sub>2</sub> from a capillary in the main UHV chamber as described in the previous section. By comparing this TOF distribution with the expected distribution for an effusive flow of gas, we were able to measure the total time shift  $t_{\text{shift}}$  necessary for agreement between the two. Knowing  $t_{\text{shift}}$ , we can calculate the most probable TOF,  $t_{\text{mp}} = t_{\text{peak}} - t_{\text{shift}}$ . By maximizing the previous expression for  $f(t)$ , we obtain

$$T_{\text{kin}} = \frac{mL^2}{4kt_{\text{mp}}^2}.$$

The effective kinetic temperature obtained from the fit to our TOF data is  $T \sim 16$  K. Since our typical time resolution was 73  $\mu\text{s}$ , an error of  $\pm 1$  channel gives a temperature error of  $\pm 2.6$  K. The maximum of the desorption rate occurs at a temperature comparable to the temperature range at which there is the maximum of the desorption rate.

We also conducted experiments in which molecular D<sub>2</sub> was adsorbed onto the ice surface. The TOF curve in such an experiment is virtually identical to the TOF curve of the product of the  $\text{D}_{\text{ads}} + \text{D}_{\text{ads}} \rightarrow \text{D}_2$  reaction. Thus, to be able to discriminate between these two models, it will be necessary to use shorter exposure times, better TOF resolution, and/or solids without the degree of high porosity of amorphous water ice. Such investigations are underway.

#### 4. DISCUSSION

To place our result in context, we briefly recall what is known about the distribution of the energy gained in a  $\text{H} + \text{H} \rightarrow \text{H}_2$  reaction on a solid surface. Most of the work has been done

on well-characterized, single-crystal metal surfaces (Bertino & Toennies 1999). In such cases, it is found that associative desorption of HD and D<sub>2</sub>, i.e., occurring via reactions of the type  $\text{A} + \text{B} \rightarrow \text{AB}$ , can proceed via either energy-activated or energy-nonactivated channels, depending on the specific surface and initial state of the particle (Allers et al. 1993). Molecules desorbing from metal surfaces via nonactivated channels (i.e., reaction paths along which the particles do not have to overcome an activation energy barrier) have a measured velocity distribution that is a Maxwell-Boltzmann distribution with a translational energy of  $2k_{\text{B}}T_{\text{surface}}$  and a  $\cos(\theta)$  angular distribution (where  $\theta$  is the angle with respect to the surface normal) as expected from detailed balance considerations (Brenig 1987). On the contrary, when reaction activation channels are involved, the molecule typically has a peaked angular distribution, such as  $\cos^n(\theta)$ , where  $n$  can be much greater than 1, and a hyperthermal translational energy,  $E_{\text{kin}} \gg 2k_{\text{B}}T$ . It has been found that the larger the number of defects that the surface has, the more the nonactivated channels should dominate the desorption process (Rendulic 1989). Activated and nonactivated energy channels can be simultaneously available to a reactant, as was shown, for example, in the dissociative adsorption and associative desorption of HD and D<sub>2</sub> from the (001) face of a nickel single crystal (Allers et al. 1993). Obviously, for as complex a surface as amorphous ice, such information at a microscopic level is not yet available, and we must wait for better characterization methods of the surface and a more sensitive detection of the reaction products.

From the analysis of our data in the previous section, we conclude that the D<sub>2</sub> molecules desorb from the ice surface as if they were thermally accommodated to it. In support of this analysis, a parameter  $\mu$ , such that  $(1 - \mu)$  is the probability of D<sub>2</sub> desorption immediately after recombination, had been incorporated into a rate equation model of our previously acquired thermal desorption data (Katz et al. 1999). A value of  $\mu = 0.33$  for olivine and  $\mu = 0.413$  for amorphous carbon was obtained by a fit of the model equations to the entire range of experimental TPD results. This indicates that a significant fraction of the newly formed hydrogen molecules may thermally accommodate to the sample. One possible mechanism for accommodation is that D<sub>2</sub> molecules newly formed on the ice layer suffer several hits with surface structures in escaping from the water ice film during the thermal desorption experiment, as amorphous ice is more porous than the samples of olivine and amorphous carbon used in our previous investigations.

Classical molecular dynamics simulations for H<sub>2</sub> formation on amorphous ice performed by Takahashi et al. (1999 and Takahashi & Uehara (2001) give a larger average kinetic energy ( $\sim 530$  meV) for the desorbing molecules than our experiments do ( $T_{\text{kin}} = 16$  K gives  $E_{\text{avg}} = 2k_{\text{B}}T_{\text{kin}} \sim 3$  meV). The disagreement is likely to come from the fact that they did not consider in their calculations the possibility of multiple collisions of the H<sub>2</sub> molecules with the ice surface as they find their way out of the pores.

In the calculation of the formation of H<sub>2</sub> and isotopes on the basal plane of graphite via the Eley-Rideal mechanism, i.e., via the direct reaction of an H atom from the gas phase with an H atom held on the surface, Meijer et al. (2002) found that H<sub>2</sub> is produced with a low vibrational quantum number and that a significant fraction, 40%–50%, of the available energy goes in translational motion.

We acknowledge financial support from NASA through

grants NAG5-6822 and NAG5-9093 to G. V. V. P. acknowledges support from the Italian Ministry for University and Scientific Research and from the Italian Space Agency. We

thank Robert D'Agostino, Chris Nagele, Scott Barbarow, Heather Gangemi, and Emily Watkins of Syracuse University for technical assistance in the laboratory.

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