Syracuse University
SUrface

Physics | College of Arts and Sciences

11-7-1996

Laboratory Synthesis of Molecular Hydrogen on Surfaces of Astrophysical Interest

Gianfranco Vidali
Syracuse University

V Pirronello
Universita di Catania

Chi Liu
Syracuse University

Liyong Shen
Syracuse University

Follow this and additional works at: http://surface.syr.edu/phy

Part of the Physics Commons

Repository Citation
Vidali, Gianfranco; Pirronello, V; Liu, Chi; and Shen, Liyong, "Laboratory Synthesis of Molecular Hydrogen on Surfaces of Astrophysical Interest" (1996). *Physics*. Paper 513.
http://surface.syr.edu/phy/513

This Article is brought to you for free and open access by the College of Arts and Sciences at SUrface. It has been accepted for inclusion in Physics by an authorized administrator of SUrface. For more information, please contact surface@syr.edu.

arXiv:astro-ph/9611022v2 7 Nov 1996

LABORATORY SYNTHESIS OF MOLECULAR HYDROGEN ON SURFACES OF ASTROPHYSICAL INTEREST

V.Pirronello

Istituto di Fisica, Universita' di Catania, Catania, Sicily, Italy and the Department of Physics, Syracuse University Syracuse, NY 13244-1130

Chi Liu, Liyong Shen, and Gianfranco Vidali *

The Solid State Science and Technology Program and the Department of Physics, Syracuse University, Syracuse, NY 13244-1130

Received _____; accepted _____

ABSTRACT

We report on the first results of experiments to measure the recombination rate of hydrogen on surfaces of astrophysical interest. Our measurements give lower values for the recombination efficiency (sticking probability S x probability of recombination upon H-H encounter γ) than model-based estimates. We propose that our results can be reconciled with *average* estimates of the recombination rate ($1/2 n_H n_g v_H A S \gamma$) from astronomical observations, if the actual surface of an average grain is rougher, and its area bigger, than the one considered in models.

Subject headings: dust— ISM; abundances — ISM; molecules — molecular processes

1. Introduction

H_2 formation in the ISM (interstellar medium) is a fundamental process in astrophysics. The radiative association of two hydrogen atoms is a process too rare to be efficient because it involves forbidden roto-vibrational transitions, and gas-phase three-body reactions are rare in the diffuse ISM to explain H_2 abundance. It has long been recognized that hydrogen recombination occurs on surfaces of dust grains, where the grains act as the third body in the $H + H$ reaction. (Duley and Williams 1984).

The critical physical steps in which interstellar grains act as catalysts for the H_2 synthesis are: sticking and accommodation of gas-phase atoms on the grain surface; mobility of H adatoms to meet each other within their residence time on the cold grain; and ejection of the newly formed molecule into the gas phase.

The efficiency of these processes depends on the structure and the chemical activity of the grain surface, whether it is silicon-bearing (silicates can be not very stable in UV radiation fields) Hong and Greenberg, 1980, Greenberg and Li, carbonaceous (carbon can possibly be distributed on silicon-bearing grain 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. The morphology of the surface should influence the sticking and tunneling processes; it is reasonable to assume that sticking will be higher and diffusion length lower on amorphous than on crystalline surfaces. Amorphous is the most probable structure for grains in space, as shown by observations (Leger et al. 1979).

Observed H_2 abundance in diffuse clouds can be explained if the formation rate R on grains balances its destruction rate; the canonical value of R is $\sim 3x10^{-17} cm^3 sec^{-1}$ (Jura 1975); on grain surfaces, the recombination rate can be described as $\sim 1/2 n_H n_g v_H A S \gamma$ where, n_H and n_g are the number densities of hydrogen atoms and dust grains, respectively,

and v_H is their relative velocity. S (sticking coefficient) is the probability that an atom hitting a dust grain remains on the surface, and γ is the probability that an atom, once on the surface, makes an encounter with another H atom and recombines with it. For a typical diffuse cloud environment, (Jura 1975) it is assumed that, on average, $S\gamma \sim 0.3$.

From a theoretical standpoint, the complexity of the problem lies in the fact that, due to the quantum nature of the H atom, a quantum mechanical calculation has to be done on a realistic, heterogeneous surface resembling dust grains in ISM. Hollenbach and Salpeter (HS) (Hollenbach and Salpeter 1970 and 1971) calculated S using simple semiclassical method for the atom-surface interaction, and found S to be between 10^{-1} and 1 in most cases. Leitch-Devlin and Williams (Leitch-Devlin and Williams 1984 and 1985) used a quantum mechanical approach and assumed a perfect single crystal with energy loss due to single phonon excitations. Their sticking coefficient increases with gas temperature, reaches a maximum at k_BT comparable with phonon energies and then decreases again. Buch and Zhang (Buch and Zhang 1991) numerically evaluated the sticking of hydrogen atoms on a cluster (amorphous in structure) of water molecules. They obtained $S = (k_BT/E_0 + 1)^{-2}$, where E_0 is a parameter($\sim 100k_BT$ for H and $\sim 200k_BT$ for D)

In HS's calculation (Hollenbach and Salpeter 1970 and 1971), the tunneling efficiency of adsorbed hydrogen was high enough to ensure a very fast scanning of virtually all possible adsorption sites on a grain surface in a fraction of the residence time of the adsorbed species. In their model, the grain surface has two adsorption sites for H, one weak ($\sim 400K$) and the other strong ($\sim 20,000K$). If only one weak adsorption site is present, H atoms wouldn't spend enough time on the surface to meet other H atoms and they would evaporate in a time $\tau \sim \tau_0 exp(E/k_BT)$, where τ_0 is a typical time of a vibration of a H atom in an adsorption site.

Smoluchowski (Smoluchowski 1981) did a quantum mechanical calculation and found

that H would get trapped in the deepest sites of an amorphous surface after a few hops. His efficiency of H_2 production is several orders of magnitude smaller than HS's. Pirronello and Averna (Pirronello and Averna 1988 and 1991) investigated the possibility that H_2 could be produced in dense clouds by cosmic rays bombardment of grain mantles. Within the Smoluchowsky's model, they found that the cosmic rays mechanism would be dominant over H_2 recombination on grains at 10 K.

Although sticking has been extensively studied experimentally (Rendulic 1992), it has been done in conditions and on surfaces of almost no astrophysical interest, except for the following studies. Brackmann and Fite (Brackmann and Fite 1961) measured a sticking probability of 0.2 on a H_2-free surface and 0.5 on top of a H_2 layer in the temperature range of 2.5 to 8 K. Due to poor vacuum conditions of their apparatus, it is assumed that their surfaces were covered with thick cryodeposits of background gas. There have been even fewer determinations in the laboratory of the hydrogen recombination coefficient on surfaces and up to now in conditions of no astrophysical relevancy. Schutte et al. (Schutte et al. 1976) measured the H recombination on a surface of a bolometer at 3 K, a temperature significantly smaller than the one of interstellar grains (10-15 K). They found $S\gamma \sim 0.05 - 0.1$ on a hypothetically H_2-free surface. Other experiments (Schermann et al. 1993, King and Wise 1963) measured recombination rates in situations where either the surface temperature or the kinetic energy of the H atoms were high. On the other hand, H beam scattering experiments have shown that the interaction of *low energy* H beams with single crystal graphite surfaces is rather weak; the ground state is ~ 32 meV deep. (Ghio et al. 1980) Experiments of scattering of H from graphite single crystals above ~ 16 K gave a sticking coefficient of less than 0.1 and negligibly small above 21 K. (Lin and Vidali 1996)

The experimental studies mentioned above, although gave interesting information about physical/chemical process at surfaces, didn't really address the question of measuring

the hydrogen recombination rate on surfaces in situations which could be related to astronomical observations. Our study attempts to address this need.

In this report, we present the results of a set of experiments to measure the recombination coefficient on the surface of an olivine slab (a silicate rich in Fe, Mg, Si and oxygen), an astrophysically relevant material, even if polycrystalline, as natural stones on Earth are, and not amorphous, as required by observations (Draine and Lee 1984). Low kinetic energy of H beams, low fluxes, and low surface temperature have been used.

2. Experimental Set-Up

The experiments were performed in an ultra-high vacuum apparatus consisting of a scattering chamber and of two triply differentially pumped beam lines (See Fig. 1). Each atomic beam is produced by RF dissociation of molecular hydrogen (or deuterium) in a water-cooled Pyrex tube placed in a RF cavity. An ENI power supply provides 100-150 watt of power to the cavities via a power splitter and impedance matching networks. By using H and D beams, the recombination product (HD) can be formed only on the surface, and not in the beam source due to imperfect dissociation, as in the case when using only one beam. The dissociation rate is measured by the quadrupole mass spectrometer in the main chamber. The maximum dissociation rate is over 90 %, but in most cases was lower, around 70-85 %, and it remained constant during experimental runs. Each beam is made by the expansion of a low pressure gas (0.1-0.2 torr) into vacuum through a short aluminum capillary of 1mm in diameter connected to a LN_2 reservoir. The beams enter the scattering chamber through 3 mm collimators. The estimated solid angle is $6x10^{-6}sr$ and the flux for H is $\sim 10^{12}$ atoms/cm^2/sec. To obtain a lower flux, a mechanical chopper with a duty cycle of $1:20$ was used. The H beam hits the surface of the sample perpendicularly, while the D beam hits it at 38 deg. from the normal. The sample is mounted on a copper sample

holder that is in good thermal contact with a HeliTrans cold finger and its temperature is measured via two calibrated chromel/iron-gold thermocouples pressed against the top and bottom surfaces of the sample. The lowest temperature reached with the cold finger is $\sim 5-6K$ (top thermocouple). The sample can be heated by radiation and electron-beam bombardment with a heater placed in a small cavity of the sample holder just behind the sample. The incoming and reflected beams are detected by a differentially-pumped quadrupole mass spectrometer.

3. Measuring Procedures and Results

Most of the results reported here are for a sample of olivine donated by Dr. P. Plescia of the CNR Institute for the Treatments of Minerals (Rome). It consists of a mixture of Fe_2SiO_4 and Mg_2SiO_4. Prior insertion into the apparatus, the sample was cleaned with mild solvents (acetone, methanol, freon) in an ultrasonic bath. The sample was then placed on the sample holder in the UHV chamber and the apparatus was baked to 150 °C for a couple of days. The base pressure was in the mid 10^{-10} torr range. In a typical experiment, the sample is first heated to 200 °C for cleaning. After cooling, it is exposed for a given amount of time to the H and D beams. During the adsorption time, the detector is placed in front of the sample and the mass is tuned to 3 (i.e., mass of HD. There is no other background gas contributing to the spectrometer signal at mass "3"). At the end of the exposure time, the sample temperature is quickly ($\sim$ 1 K/sec) raised to over 30 K by shutting the He flow to the tip of the cryostat; the amount of HD desorbed as a function of time is recorded into a multichannel scaler. A set of representative traces is shown in Fig. 2. An analysis of desorption kinetics is given elsewhere. (Liu et al. 1996)

The background pressure of HD due to finite pumping capacity and/or recombination of H and D on the walls of the chamber is measured prior to and after each

adsorption/desorption experiment, in front and back of the sample, and is subtracted from the recorded signal. We checked that after the blow-off of the HD layer there is no re-adsorption of HD from the gas phase. The sample holder is hugged by a copper radiation shield; no adsorption/desorption of HD has been detected on/from the shield whose temperature is considerably higher than the sample. Exposure times have been changed over several decades, see Fig. 3, where the desorption yield (which is the integral of curve in Fig.2) is plotted vs. exposure to H and D. The data are fitted well by a Langmuir adsorption kinetics. The saturation of the signal is interpreted as due to the completion of the first layer. The time it takes to form a HD layer is consistent with the calculated flux and a low (~ 0.1) sticking coefficient (Brackmann and Fite 1961, Schutte et al. 1976).

Fig. 4 shows the amount of HD desorbed following adsorption of H and D at various sample temperatures. The amount of HD produced and released *during* the adsorption process (as measured by the mass spectrometer) is typically much smaller than the amount released in the thermal desorption run. This means that at low sample temperatures (5-7 K), H sticks (although with a sticking probability well below 1) and readily recombines; because of the low temperature, just HD that has just formed remains on the surface. At higher sample temperatures (10-15 K), H doesn't stay on the surface long enough to recombine, and the HD yield is much smaller. Likely, only those H atoms which became trapped in strong binding sites are retained at these temperatures; HD is then produced at reduced rates because of slow diffusion of H atoms out of these deeper energy sites. We couldn't measure the H signal during adsorption/desorption in a quantitative way because of the presence of background of H in a stainless steel system (even at 5 10^{-10} torr total base pressure). An analysis of desorption kinetics after adsorption of H at high sample temperature could yield some valuable clues; at present, however, the desorption signals are too low for a meaningful quantitative analysis.

4. Discussion

The recombination efficiency of HD, here defined as the fraction of H atoms which stick and recombine to from HD - or $r \sim S\gamma$, is calculated as follows (Note that this is different from the recombination rate R defined earlier): $r = (I_a + I_d)/I_{in}$, where I_a is the HD signal during adsorption, I_d is the total amount of HD desorbed after the adsorption process, and I_{in} the the amount of H sent into the chamber. The signals are corrected for velocity-dependent detection efficiency and for the measured solid angle of the detector.r is also corrected for the probability of forming HD into other reaction channels, and for the different measured intensities of the H and D beams. As mentioned before, only a small fraction of the amount of HD which desorbs in the thermal programmed desorption leaves the sample during the *adsorption process*. Consequently, the recombination efficiency drops with increasing surface temperature similarly to the fall off of the desorption yield as a function of temperature, see Fig. 4. The recombination efficiency was measured for different exposures to H and D, as seen in Fig. 5.

Other candidate materials for grains in the ISM are: carbonaceous solids, both amorphous and crystalline, and icy mantles (Mathis 1993). We plan to investigate the formation of molecular hydrogen also on these other materials and we have already obtained some preliminar results (to be published elsewhere) for D_2 recombination on HOPG (Highly Oriented Pyrolitic Graphite).

Our estimate of r at 5 - 6 K is not far from Schutte et al.' s value obtained on a uncharacterized surface of a semiconductor bolometer but at considerably lower temperature (3K). At the astrophysically relevant grain temperature range of 10-15 K, our result, $r \sim 0.03 - 0.05$ is noticeably lower than the value of HS's model (Hollenbach and Salpeter 1970 and 1971), ~ 0.3 at 10-15 K.

We might try to speculate on the reason of this difference. Calculations are for very

idealized surfaces. There are a few assumptions that can influence the outcome of the calculation, such as the semiclassical description, the energetics of the binding sites, and the tunneling time between sites. The sample used by us presents a far more heterogeneous environment, both energetically and morphologically, than it has been considered in theoretical models. In a real surface, tunneling might proceed much more slowly, and the sticking coefficient for H on surfaces of olivine and graphite might be much different than previously calculated on model surfaces. Considering that many models (Duley and Williams 1984) assume $S \sim 0.3$, and that a determination of S for H on graphite at $\sim 16K$ gives $S \sim 0.06 - 0.1$ (Lin and Vidali 1996) , it is conceivable that S is only partially responsible for the fact that our $r = S\gamma$ is a factor 10 lower than Hollenbach's, and that γ might be appreciably less than 1, contrary to what is most often assumed in models.

What are the consequences of this determination of $S\gamma$ on the recombination rate R giving the constraints posed by astronomical observations? In order to reconcile our value for $r = S\gamma \sim 0.03 - 0.05$ with the accepted value (Jura 1975) for R ($\sim$ 1 to $3x10^{-17} cm^3 sec^{-1}$), we propose that the surface area of grains (which, in a simple model, enters the expression for $R \sim 1/2 n_H n_g v_H A S\gamma$ as a multiplicative factor) might be larger (by a factor 5 to 10 or even more for amorphous surfaces). This could be indeed the case if grains have a larger surface area (i.e, they are "fluffier') (Mathis and Whiffen 1989), than previously considered. This is not an unlikely scenario, considering the type of processing that grains are subjected to in the ISM, and more theoretical and experimental effort should be devoted to verify it.

REFERENCES

Duley,W.W. and Williams, D.A., "Interstellar Chemistry" (1984)

Hong, S.S. and Greenberg, J.M. 1980, Astron.Astrophys. 88, 194.

Greenberg, J.M. and Li, A. 1996, Astron.Astrophys. 309, 258, and references cited therein.

Mathis, J.M. 1993, Rep.Prog.Phys.56, 605.

Leger, A., Klein, J., de Cheveigne, S., Guinet, C., Defourneau, D., Belin, M., Astron. Astrophys. 1979, 79, 256.

Jura, M., Astrophys.J. 1975, 197, 575.

Hollenbach, D. and Salpeter, E.E., 1970, J. Chem Phys. 53, 79; 1971, Astrophys. J. 163, 155.

Leitch-Devlin, M.A. and Williams, D.A. 1984, M.N.R.A.S. 210, 577; 1985, ibidem 213, 295.

Buch, V. and Zhang, Q. 1991, Astrophys. J. 379, 647.

Smoluchowski, R. 1981, Astrophys. Space Sci. 75, 353; 1983, J. Phys. Chem. 87, 4229.

Pirronello, V., and Averna, D. 1988, Astron. Astrophys. 196, 201; Averna, D. and Pirronello, V. 1991, Astron. Astrophys. 245, 239.

Rendulic, K.D. 1992, Surf. Science 272, 34.

Brackmann, R.T., and Fite, W.L. 1961, J.Chem.Phys. 34, 1572.

Schutte, A., Bassi, D., Tommasini, F., Turelli, F., Scoles, G., Herman, L.J.F. 1976, J.Chem.Phys. 64, 4135.

Schermann, C., Gough, S.F., Pichou, F., Landau, M., Hall, R.I., Curie, M. 1993, in "Molecules and Grains in Space", Ed. by I.Nenner, (AIP Confer.Proc. 312), p.801

King, A.B., and Wise, H. 1963, J.Phys.Chem. 67, 1163.

Ghio, E., Mattera, L., Salvo, C., Tommasini, F., and Valbusa, U. 1980, J.Chem.Phys. 73, 556.

Lin, J., and G.Vidali, G. 1996, in "The Cosmic Dust Connection", Ed. by M.Greenberg and V.Pirronello (Kluwer, Dodrect) in press.

Draine, B.T., and Lee, H.M. 1984, Astophys. J. 285, 89.

Vidali, G., Liu, C., and Shen, L. 1996, to be submitted.

Mathis, J.S., and Whiffen, G. 1989, Astrophys.J. 341, 808.

Acknowledgments

Support from NASA-Astrophysics Division is gratefully acknowledged. We thank Dr. PLescia of the CNR - Rome for providing the olivine sample and ENI of Rochester, N.Y. for donating the RF splitter.

* To whom correspondence should be addressed; e-mail: gvidali@syr.edu

---

This manuscript was prepared with the AAS LaTeX macros v4.0.

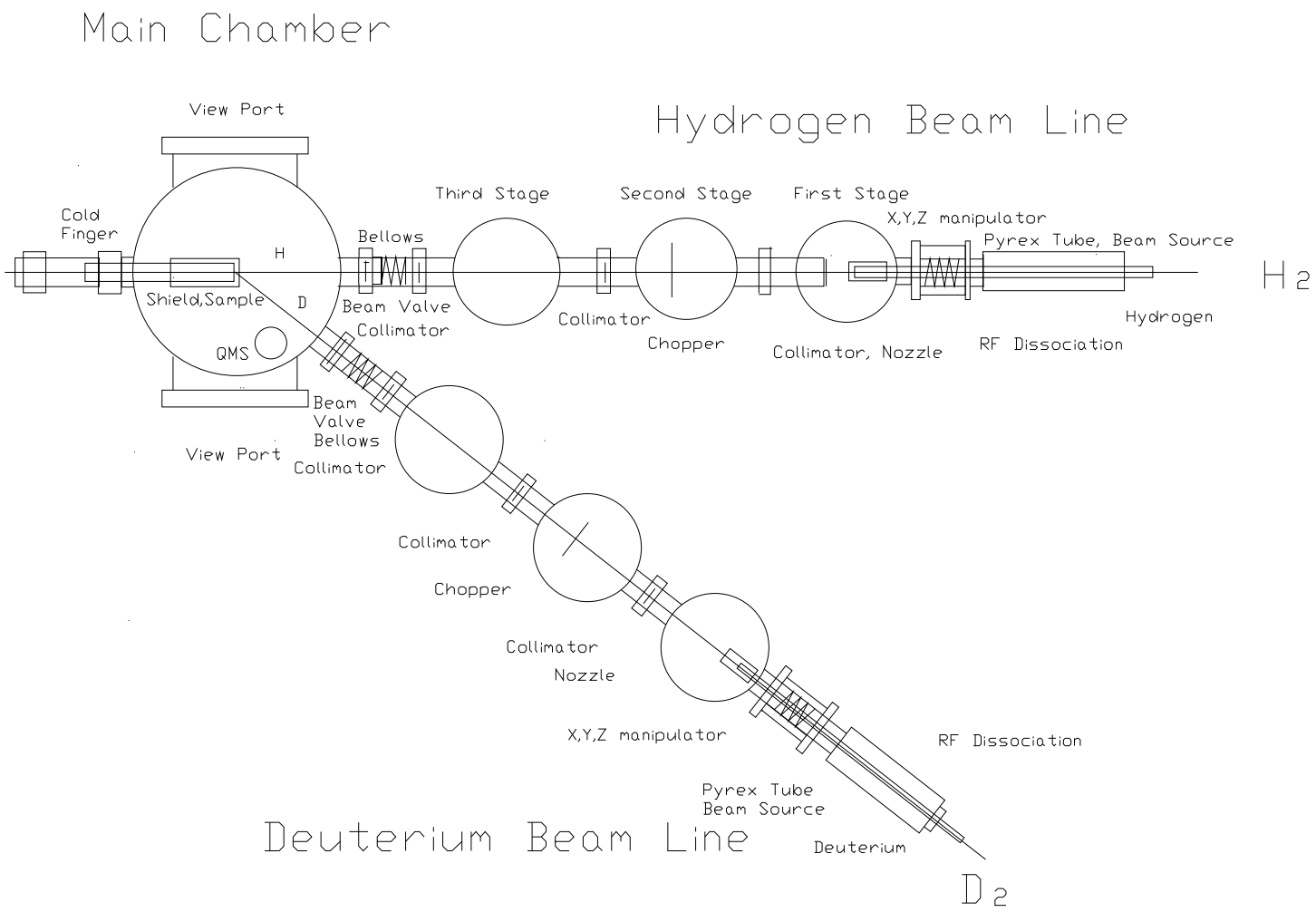
Fig. 1.— Schematic top-view of the apparatus

Fig. 2.— Representative thermal desorptpwd ion curves of HD from olivine; exposure to H and D for 1, 1.5, and 2 minutes (top to bottom) at 5 K; heating rate: $\sim 1K/sec$.

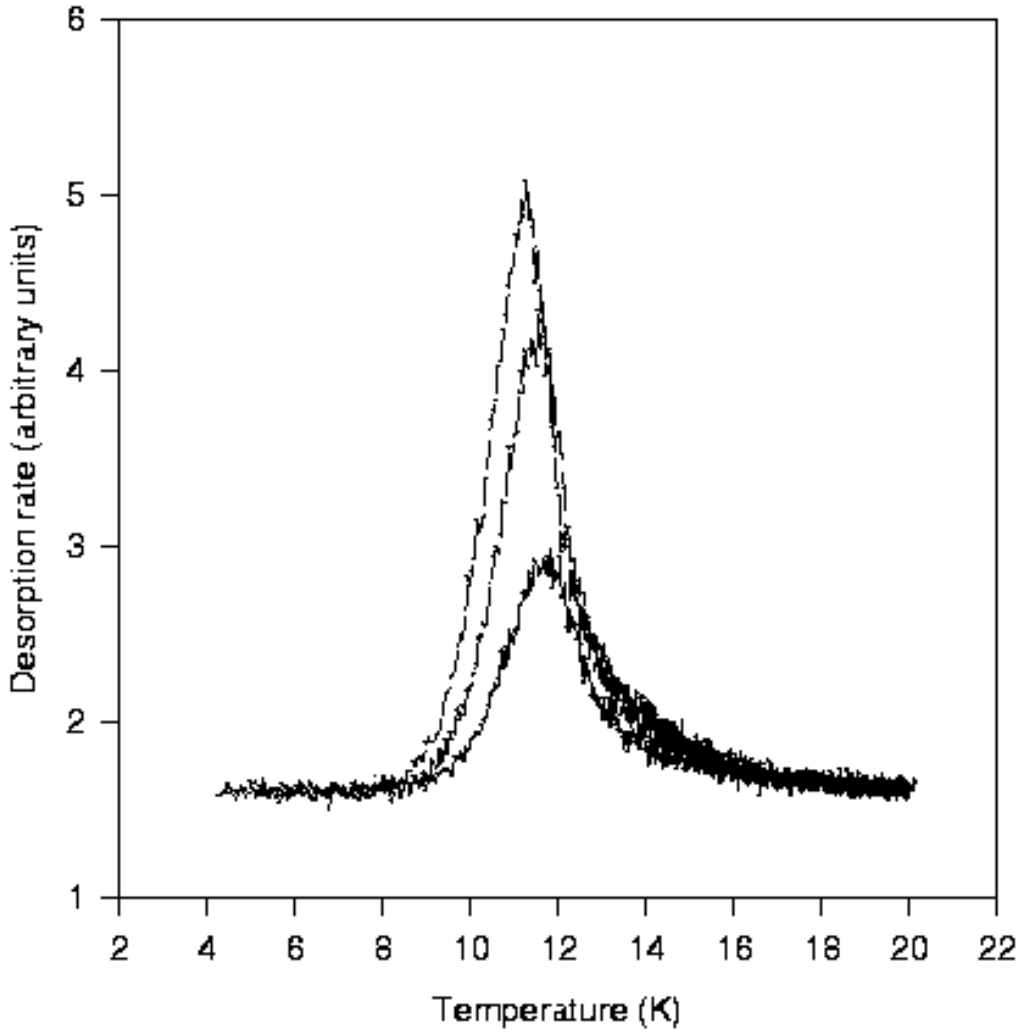
Fig. 3.— HD desorption rate from olivine vs. exposure. Notice the different units in the abscissa in the two panels. (Line: fit - see text)

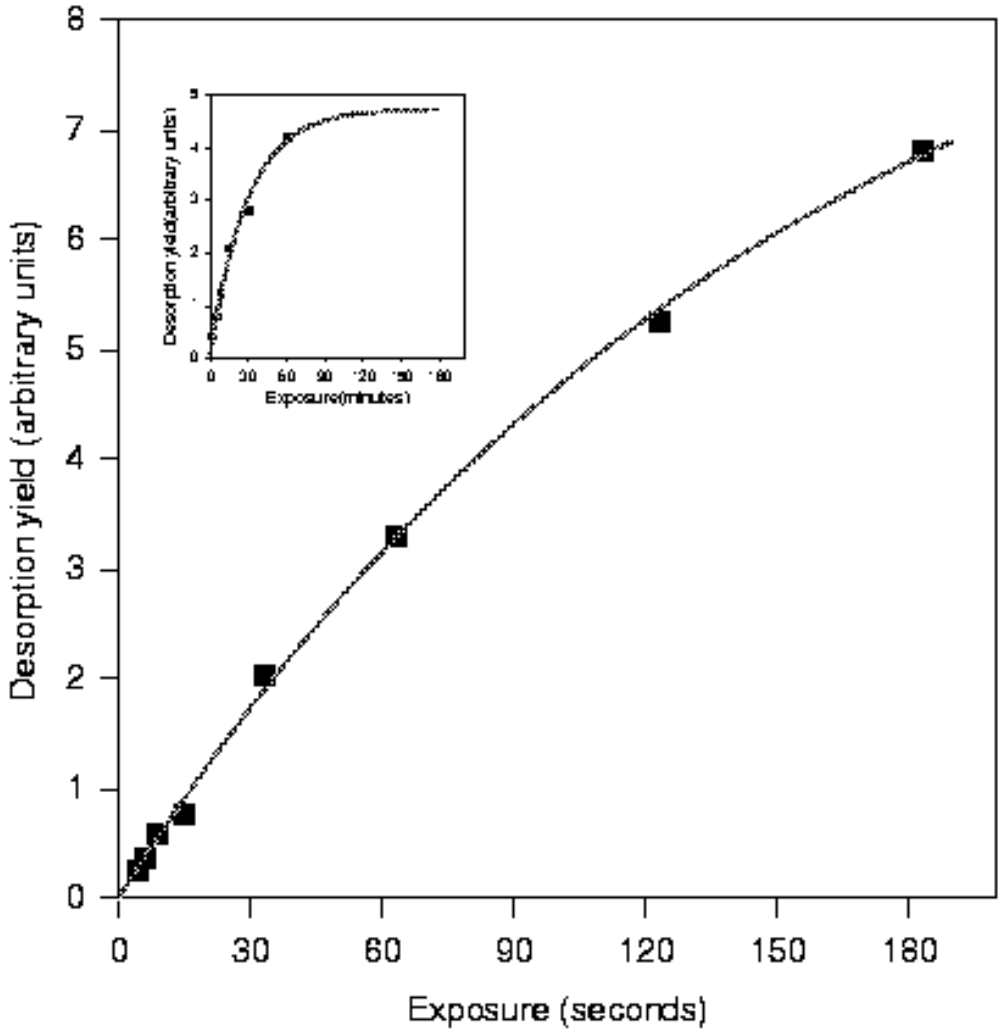
Fig. 4.— Desorption yield of HD from olivine after adsorption of H and D at the indicated temperatures. Exposure: 1 minute (Line: guide to the eye).

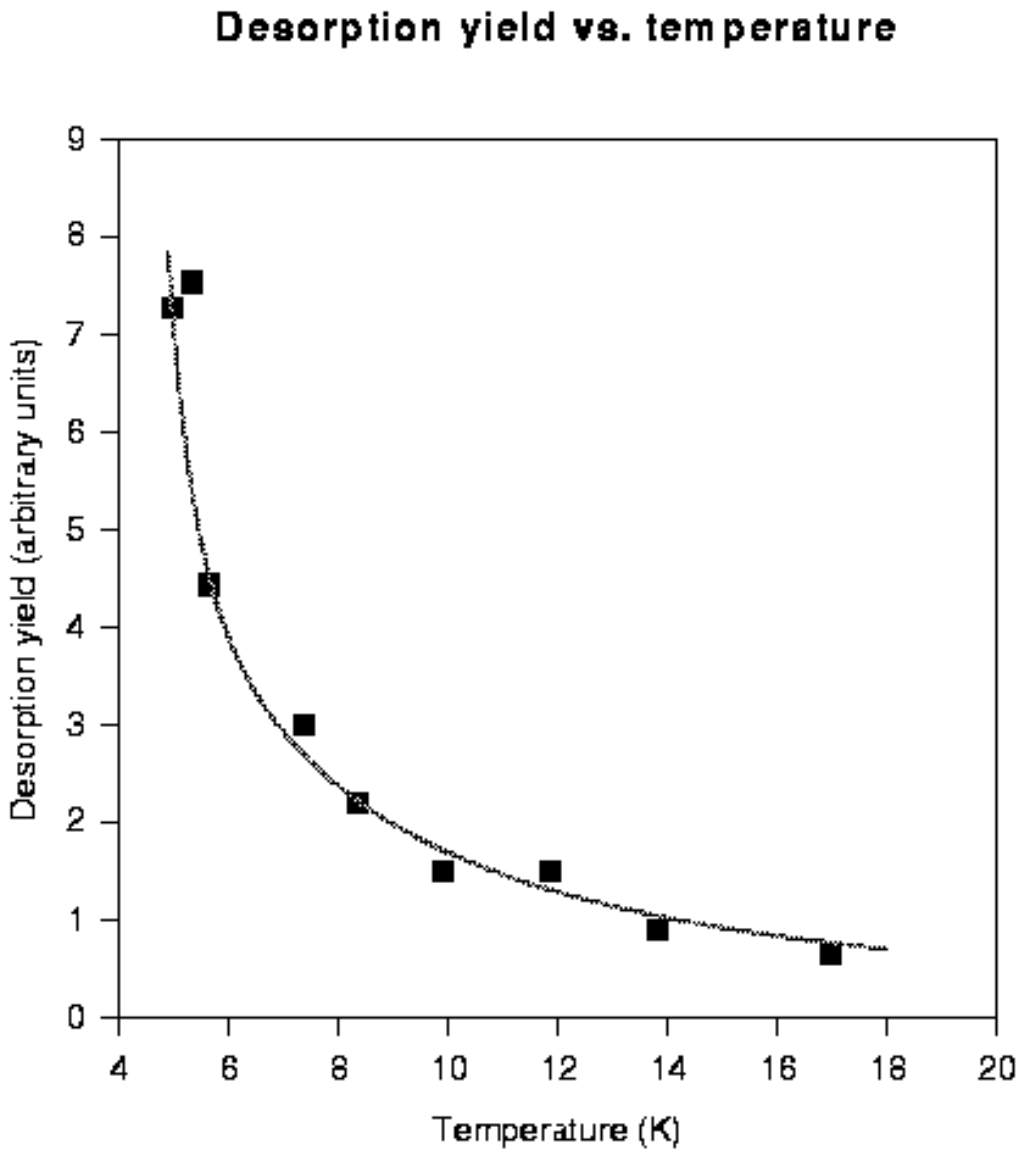
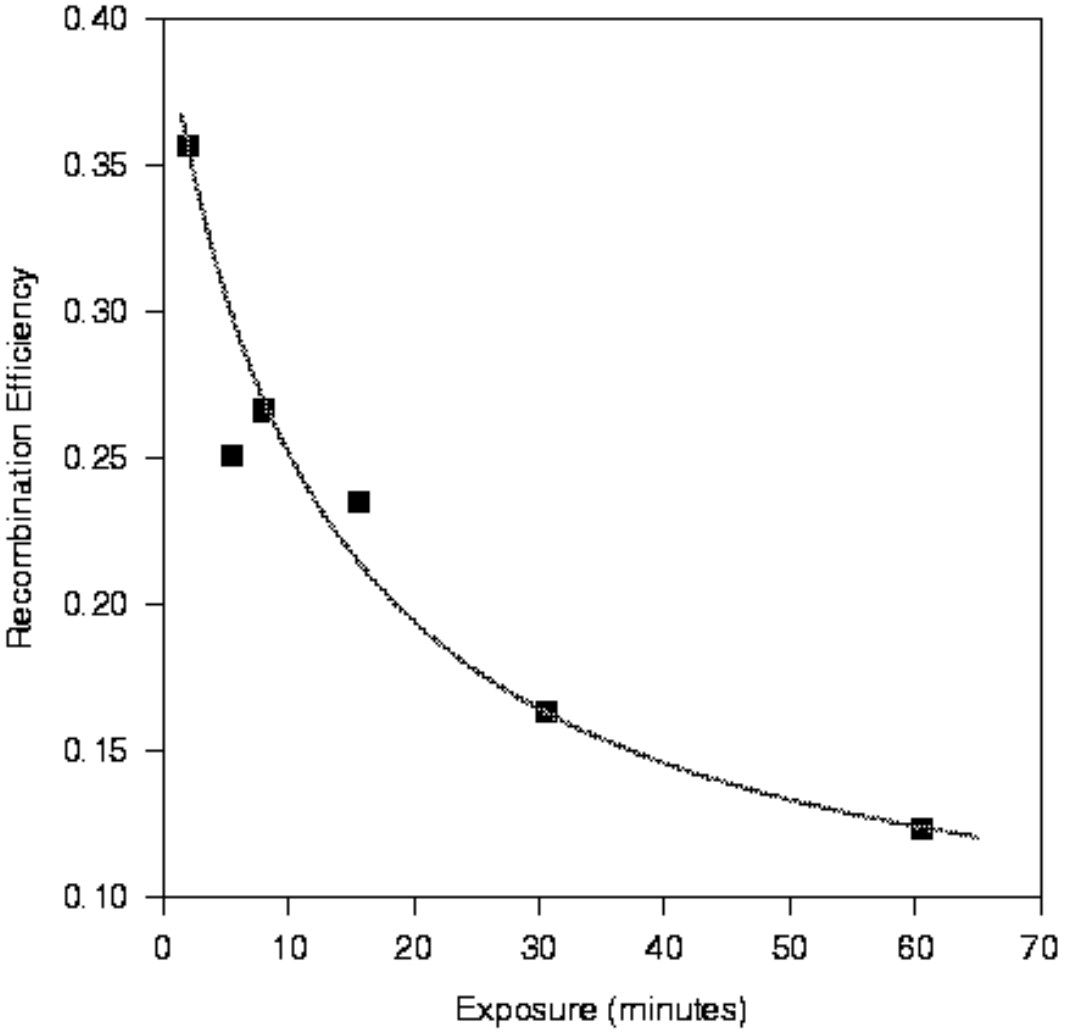
Fig. 5.— HD recombination efficiency r vs. exposure time at $\sim 6K$. (Line: guide to the eye).



Experimental Set-up


6
5
4
3
2
1
Desorption rate (arbitrary units)
2
4
6
8
10
12
14
16
18
20
22
Temperature (K)


Desorption yield (arbitrary units)
Exposure (seconds)
0
1
2
3
4
5
6
7
8
0
30
60
90
120
150
180
Desorption yield(arbitrary units)
Exposure(minutes)


Desorption yield vs. temperature
Desorption yield (arbitrary units)
Temperature (K)
0
1
2
3
4
5
6
7
8
9
4
6
8
10
12
14
16
18
20

Recombination efficiency vs. exposure