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Letter to the Editor

Mobility of D atoms on porous amorphous water ice surfaces under interstellar conditions

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ABSTRACT

Aims. The mobility of H atoms on the surface of interstellar dust grains at low temperature is still a matter of debate. In dense clouds, the hydrogenation of adsorbed species (i.e., CO), as well as the subsequent deuteration of the accreted molecules depend on the mobility of H atoms on water ice. Astrochemical models widely assume that H atoms are mobile on the surface of dust grains even if controversy still exists. We present here direct experimental evidence of the mobility of H atoms on porous water ice surfaces at 10 K.
Methods. In a UHV chamber, O_2 is deposited on a porous amorphous water ice substrate. Then D atoms are deposited onto the surface held at 10 K. Temperature-Programmed Desorption (TPD) is used and desorptions of O_2 and D_2 are simultaneously monitored.
Results. We find that the amount of O_2 that desorbs during the TPD diminishes if we increase the deposition time of D atoms. O_2 is thus destroyed by D atoms even though these molecules have previously diffused inside the pores of thick water ice. Our results can be easily interpreted if D is mobile at 10 K on the water ice surface. A simple rate equation model fits our experimental data and best fit curves were obtained for a D atom diffusion barrier of 22 ± 2 meV. Therefore hydrogenation can take place efficiently on interstellar dust grains. These experimental results are consistent with most calculations and validate the hypothesis used in several models.

Key words. astrochemistry – ISM: atoms – dust, extinction – methods: laboratory

1. Introduction

Among the numerous molecules detected in different astrophysical environments, a large fraction is composed of hydrogenated species (Chang et al. 2007, and references therein). It has been established that dust grains play a major role in the hydrogenation of compounds (Herbst & Klemperer 1973; Smith et al. 2006). In the dense interstellar medium where most of the hydrogenated species have been detected (especially during the star formation stage, Tegmark et al. 1997; Cazaux & Tielens 2004; Cazaux & Spaans 2004), grains are covered in a molecular mantle mainly composed of water ice. In all the theoretical chemical models that describe the hydrogenation of compounds on grains (Tielens & Hagen 1982; Cuppen & Herbst 2007), mobility of hydrogen is hypothesised, though some calculations on amorphous water surfaces (Smoluchowski 1981) and modelling of experimental data (Perets et al. 2005) rule out such a mobility. On the other hand, other calculations (Buch & Zhang 1991; Masuda et al. 1998) and interpretations of experimental data (Hornekær et al. 2003) validate the hypothesis that H is mobile at 10 K, a temperature supposed to be close to that of dust grains in interstellar dense clouds where hydrogenation takes place. We have already demonstrated that D atoms are mobile at 10 K (in our experiment time scale) on non-porous amorphous solid water (np-ASW) ices (Amiaud et al. 2007), but the porosity and the roughness of the water ice films grown at low temperatures (10 K) may considerably lower the D atom mobility.

Yet the debate upon the mobility of hydrogen atoms is not closed, and much controversy exists regarding the interpretation of experiments (Vidali et al. 2006; Dulieu 2006). If one considers only the latest estimated value of 51 meV (Perets et al. 2005) for the diffusion energy barrier of H on porous amorphous solid water (p-ASW) ice, the hopping time between two adjacent adsorption sites is about 10 million years at 10 K. In such a context, no hydrogenation chemistry can occur on icy mantles of dust grains on a reasonable time scale. Hence, observational evidence of hydrogenated and deuterated species is a good argument for an experimental investigation of the mobility of H-atoms.

The aim of this paper is to provide new experimental evidence that directly addresses – without the prism of a sophisticated model – the question of hydrogen mobility on p-ASW ice at 10 K. By using O_2 as a tracer of D mobility we present a set of experiments that are straightforward to interpret if D is mobile on the surface of porous amorphous water ice, as is expected from almost all calculations and included in several astrochemical models. In Sect. 2 we briefly describe the experimental set-up and procedures. In Sect. 3 we present our experimental results and explain them assuming that D is mobile on p-ASW ice at 10 K. In Sect. 4, we describe a simple rate equation model that we used to fit our experimental results. In Sect. 5 we discuss other interpretations before concluding.

2. Experimental section

The FORmation of MOLecules in the InterStellar Medium (FORMOLISM) experimental set-up has been developed with the purpose of studying the reaction and interaction of atoms and molecules on surfaces simulating dust grains under interstellar conditions (the relevance of substrate, low density, and very low temperatures ∼10 K). FORMOLISM is composed of an ultra-high vacuum chamber with a base pressure of $\sim10^{-10}$ mbar, a

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rotatable quadrupole mass spectrometer (QMS) and an oxygen-free high-conductivity copper sample holder. The sample holder is attached to the cold finger of a closed-cycle He cryostat and can be cooled to 8 K. The temperature is measured with a calibrated silicon diode clamped on the sample holder and controlled by a Lakeshore 334 controller to ±0.2 K with an accuracy of ±1 K in the 8−400 K range. Reactants are introduced into the vacuum chamber via two separated triply differentially pumped beam lines aimed at the surface. The first one is used to deposit O_2 while the second beam line is used to introduce the D atoms. This second beam line, in its first stage, consists of an air-cooled quartz tube surrounded by a microwave cavity for dissociating D_2. To cool the D atoms exiting the dissociation region, the source is terminated with an aluminum nozzle connected to a closed cycle He cryostat that can be cooled to ∼25 K. For the experiments presented here the D beam has a temperature of 50 K and a flux of $\sim 1 \times 10^{13}$ cm^{-2}. The dissociation rate is constant at ∼50%.

For this work we grow composite ice films of p-ASW on np-ASW. The sub-layer of np-ASW has a thickness of ∼50 ML (1 ML = 10^{15} cm^{-2}) and is grown at 120 K with a micro-channel array doser. The only purpose of the compact ice sub-layer is to isolate the ensuing p-ASW films from the Cu surface (Engquist et al. 1995). The p-ASW films are grown at 10 K on top of the np-ASW substrate. In the present study we use two different thickness of p-ASW, namely 20 ML and 250 ML. The 20 ML p-ASW film is grown from a background flux formed by controlling the H_2O partial pressure in the vacuum chamber. Since ASW films deposited from ambient vapour take a long time to form and since a long time is needed to reach the base pressure again, the 250 ML p-ASW films are deposited with the micro-channel array doser. A previous calibration has shown that under these conditions we grow 0.33 ML of ASW per second. Although p-ASW films grown by this method exhibit a lower degree of porosity, the greater thickness ensures a more complex pore structure than that of thin p-ASW ices grown by background dosing. After the growth of the composite ice films, they are annealed to 70 K to avoid any subsequent morphological changes. Although the porous structure is not completely destroyed by the annealing process, this reduces irreversibly the porosity of the p-ASW films (Kimmel et al. 2001a,b). This is verified by looking at the shift in temperature of the D_2 desorption peak as described in Hornekær et al. (2005).

Our experimental procedures are the following:

- After the preparation of a stable and pure O_2 beam, the p-ASW surface held at 10 K (or 25 K in another set of experiments) is exposed to 0.5 ML of O_2 molecules. The flux was previously calibrated using TPD by determining the O_2 exposure time required to saturate the O_2 monolayer on np-ASW ice (Kimmel et al. 2001b).
- The p-ASW substrate kept at 10 K is then exposed to varying amounts of cold D atoms (50 K) ranging from 0 exposed monolayers (EML) to 2 EML. We use EML and not directly ML because in the case of light molecules the sticking coefficient is not necessarily unity. Thus fewer molecules than those actually impinging on the surface are adsorbed. Moreover, in the case of p-ASW ice more than 1 ML of D_2 can be adsorbed on the surface, and still the coverage can be low, since the effective surface area is very large due to the 3D conformation of the substrate (Amiaud et al. 2006).
- Finally, the QMS is placed in front of the surface and TPD mass spectra of D_2 and O_2 are recorded simultaneously. All TPDs are done with a linear heating rate of 10 K/min starting from 10 K up to a temperature above which the O_2 molecules have completely desorbed (∼65 K) (see Fig. 1).
- The same series of experiments are also done by depositing D and D_2 followed by O_2.

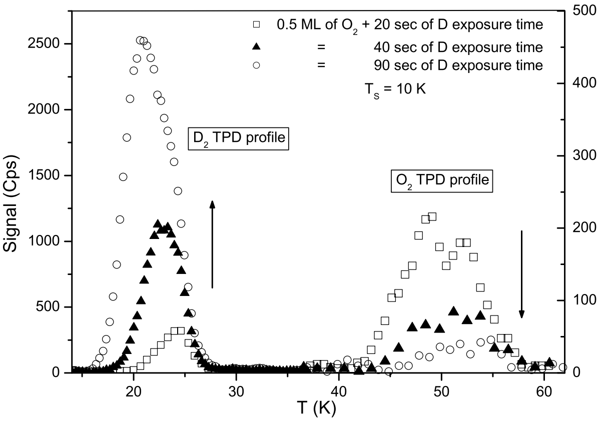

Fig. 1. TPD profiles of D_2 and O_2 after deposition of 0.5 ML of O_2 and followed by different deposition times of D at $T_S = 10$ K. The arrows emphasise that the quantity of desorbed O_2 decreases as the amount of exposed D grows.

3. Results

We find that O_2 is only sensitive to D and not to D_2. When D is deposited on the surface and then exposed to O_2, we find that the amount of desorbed O_2 is constant (within the experimental error bars (<10%)) irrespective of the D amounts. This series of experiments was done in order to rule out the possibility that D atoms were mobile only during the heating phase of the TPD. Indeed these results demonstrate that D atoms that adsorb on the ice surface diffuse immediately and either react with each other or desorb before O_2 is deposited. The amounts of desorbing O_2 are the same regardless of the amounts of D atoms deposited on the surface. Hence, in what follows, we restrict ourselves to experiments where O_2 is deposited first and then followed by various D exposure times.

Figure 1 shows the TPD profiles of O_2 and D_2 after the exposure of 0.5 ML of O_2 to 20, 40 and 90 s of D irradiation. The O_2 peak area decreases with the D deposition time and this proves that D atoms "consume" O_2 molecules adsorbed on the surface by reacting with them. Figure 2 displays the normalised TPD peak areas of O_2 and D_2, as a function of D exposure time (lower axis) or D EML (upper axis). Figures 1 and 2 show clearly that the quantity of desorbing O_2 decreases with the increase of the exposed dose of D. A sudden change in the slope of the monotonic decrease occurs after ∼0.5 EML of D exposure. At first, the drop of O_2 that desorbs from the surface occurs rapidly, then it becomes much slower. On the other hand, as expected, the amount of D_2 desorbing from the p-ASW surface increases with the exposure time of D (Fig. 2). Yet, in this case too, we observe that a change in the slope of the D_2 desorption raise takes place almost exactly after ∼0.5 EML of D exposure. Here the increase of D_2 TPD peak areas is slightly accelerated after the slope change.

These observations can be explained as follows: as D atoms are deposited onto the p-ASW sample, two competing mechanisms occur, namely O_2 destruction and D_2 formation. If D atoms are mobile, they are likely to encounter either another

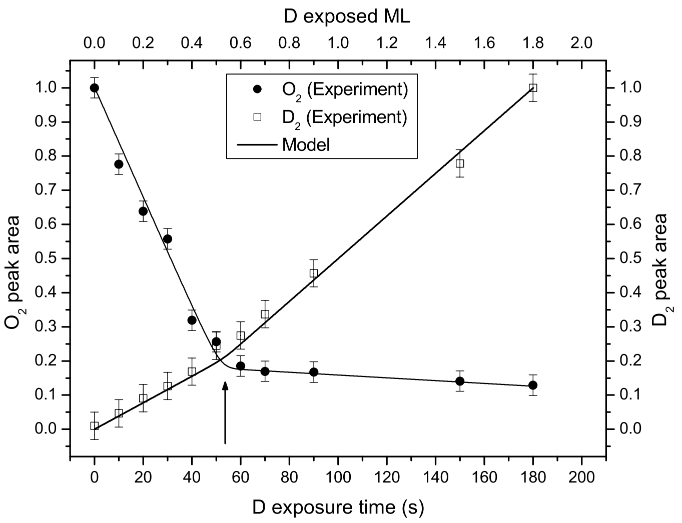

Fig. 2. Normalised O_2 (circles) and D_2 (squares) TPD peak areas following different D exposures on 20 ML of p-ASW ice. O_2 normalisation was performed with respect to the TPD peak area corresponding to 0.5 ML of O_2 alone and that of D_2 was made with respect to the TPD peak area corresponding to 1.8 EML of D. O_2 and D both deposited at a surface temperature of 10 K. The solid lines represent the model results (see text).

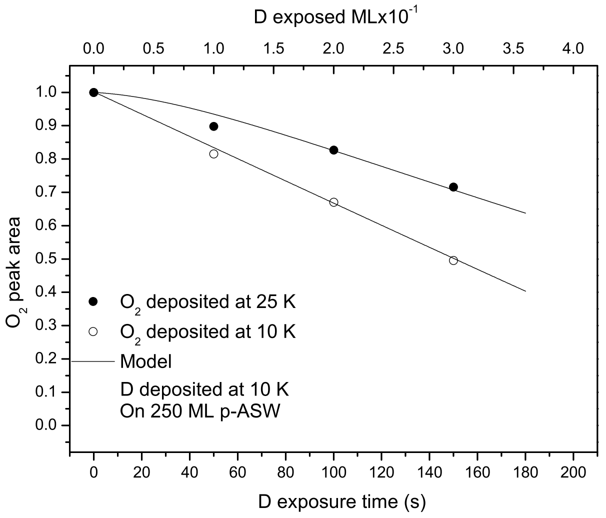

Fig. 3. Comparison between normalised TPD peak areas of 0.5 ML of O_2 deposited at 10 K (blank dots) and 25 K (black dots) and then irradiated with 0, 50, 100 and 150 s of D atoms on 250 ML of p-ASW ice. The solid line represents the model results (see text).

D atom to form D_2 (D+D formation) or an O_2 molecule and react with it (O_2 destruction). It is significant that in both cases of O_2 and D_2 desorptions, the change in slope occurs after the same amount of D exposure time (see arrow in Fig. 2). This suggests that after ~50 s (0.5 EML) of D irradiation, when most O_2 has been destroyed, a greater number of D atoms are available to form D_2. The presence of a rapid regime of O_2 destruction (80% of the initial dose destroyed by 0.5 EML of D) and of a slow regime (for the remaining 20% of the O_2 initial dose) can be ascribed to the non-perfect overlapping of the two beams. It has been checked that the two beams have in fact ~80% overlap on the surface.

We then performed the same experiment using a thicker p-ASW ice film in order to check whether the destruction of O_2 on a 20 ML p-ASW ice substrate is actually due to mobile D atoms being able to scan the porous surface. This time, on 250 ML p-ASW films, we deposited O_2 at a higher temperature (25 K), to favour O_2 mobility and to have O_2 not only adsorbed on the surface of the film but also deeper into the porous structure. The results are shown in Fig. 3. Plain circles represent the yield of desorbed O_2 after cooling the surface to 10 K and then irradiating with 0, 50, 100 and 150 s of D exposure at 10 K, while empty circles show the case of desorption of O_2 initially deposited at 10 K and then exposed to the same D exposure times. First, we notice in these experiments that the O_2 destruction rate is much slower than in the case of a 20 ML p-ASW substrate. We then only observe the first part of the curve in Fig. 2 at a slower rate. This can be due to the fact that the roughness is greater in the case of a 250 ML substrate. The structures (holes, pores, piles ...) are more pronounced. The total accessible surface is also higher and subsequently the average density of O_2 is reduced. In this case D_2 formation is more favoured. Secondly, we find that if O_2 is deposited at 25 K, the destruction rate is even lower. This can be due to the fact that at 25 K O_2 is more mobile on the surface of the ASW ice than at 10 K. Therefore O_2 molecules are spread over all the accessible porous surface. O_2 density is again lower and D_2 formation is favoured. We also notice the disappearance of the elbow that was present in Fig. 2 at 0.5 EML of D. It is due to the fact that we should have exposed the surface to longer times of D atoms in order to reach 80% destruction of the adsorbed O_2 to observe it. Finally we have checked that all the O_2 deposited at 25 K disappears, after very large exposure times (600 s), even on the 250 ML p-ASW film.

4. Model and data fit

A very simple model based upon the formalism of Katz et al. (1999) was used to fit the experimental results already obtained and shown in Fig. 2. If $F_{\rm tot}$ is the initial beam flux of D_2, after the dissociation $F_{\rm tot}$ is divided into a flux of D, $F_{\rm D}$, and a flux of D_2, $F_{\rm D2}$. Both fluences on the surface are determined knowing the sticking probabilities of D_2 and of D, $S_{\rm D2}$ and $S_{\rm D}$ respectively, and the dissociation rate τ at a beam temperature of 50 K. The fluxes are given by:

$$F_{\rm D} = 2\tau P_{\rm D} F_{\rm tot} \text{ and;} F_{\rm D_2} = (1-\tau) P_{\rm D_2} F_{\rm tot}.$$

Taking into account the porosity of the ice surface, the surface density of D, D_2 and O_2, and depending on the diffusion barrier $E_{\rm diff}$ of D atoms on the surface, this model simulates the number of D + D reactions as well as the number of D + O_2 reactions. As Figs. 2 and 3 clearly show, our simple model is able to reproduce the experimental results under the same conditions, namely, dissociation efficiency of the D_2 beam, sticking probabilities of D and D_2 (measured at a given beam temperature, Matar et al., *in preparation*), and porosity of the ice. A best fit of the experimental data has given a diffusion barrier of 22 ± 2 meV.

5. Discussion

In the previous section we proposed a direct interpretation of our experimental data assuming that D is mobile at 10 K. But other hypotheses also should be discussed in the light of these new experimental data, in particular the possible thermally induced mobility of the atoms. This process implies that atoms are not mobile at 10 K and that they require higher temperature to move and react. If atoms are not mobile at 10 K, they should stay in the vicinity of the external surface, especially under our experimental conditions where D atoms have a kinetic temperature of 50 K (in the beam) which considerably reduces the mobility of D atoms resulting from the hot atom (Harris-Kasemo) mechanism.

The total number of D atoms sent to the surface can be quite high (2×10^{15} cm^{-2}, i.e. 2 ML) which corresponds to a value of full coverage of the external surface. Consequently, if atoms are not mobile, the surface density becomes high, and two further mechanisms invoked in the literature should become non-negligible. One is the direct Eley-Ridel formation mechanism for D_2 (an adsorbed atom forms a molecule with an atom incoming from the gas phase, a fraction of the molecules formed is then directly released in the gas phase), the second is the rejection mechanism (Perets et al. 2005) (adsorbed atoms prohibit atoms from the gas phase sticking on the surface). In both cases a fraction of D or D_2 evaporates during the exposure and therefore does not desorb later during the heating ramp. If so, D_2 should not be proportional to the exposure, which is not the case in Fig. 2 where we observe proportionality. We can thus conclude that either the surface density does not increase to reach a value of the coverage close to unity or the two cited mechanisms (the Eley-Ridel and rejection mechanisms) are not efficient. However, it is unlikely that the E-R mechanism does not occur, therefore the coverage remaining low implies that D diffuses through the pores.

Calculations (Buch & Czerminski 1991) show that the adsorption energy of H on a water cluster and the height of the energy barrier between two adjacent sites are both described by large distributions, the latter being peaked in the 19.4–34.5 meV range. This means that the mobility is site dependent. Some deep adsorption sites can bind atoms more than others and release them less easily in the gas phase. Thus it is possible that a fraction of the atoms are not mobile at 10 K on the time scale of the experiment, and require thermal activation to react. Our experiments show that globally D atoms are able to penetrate the porous structure of the ice. In fact, we find a non-infinite D atom mobility ($E_{\rm diff} = 22 \pm 2$ meV, in agreement with calculations). This value is about half the one obtained by Perets et al. (2005). The discrepancy between the two results stems probably from different assumptions made on the surface coverage. Despite the fact that the atom fluence is about the same in both works (up to 2 ML of D), Perets et al. assume that their coverage is always less than 1%. Our results do not show if this mobility is dominated by thermal hopping or tunnelling. More experiments should be done at lower surface temperature (below 8 K) to fully understand how this mobility occurs. Another aspect of these experiments concerns the efficiency of the $O_2 + D$ reaction in comparison with the D + D reaction. We can see that $O_2 + D \rightarrow O_2D$ is a very efficient reaction (Miyauchi et al. 2008; Ioppolo et al. 2008), because the proportion of D required to destroy O_2 is close to 1, at the accuracy of our flux estimation (∼50%), because O_2+D is believed to have a low energy barrier (Walch et al. 1988). In our experiments the fact that the O_2+D reaction seems to be favoured in comparison with the D+D reaction when the exposition is low does not signify that the D+D reaction is less efficient because of an activation barrier. Indeed, our model assumes that both D+D and O_2+D reactions have 100% efficiency. Once again, if atoms are mobile, the density of D atoms stays low because they are consumed by the O_2 population. It is only when the density of D atoms is equal to that of O_2 atoms that the production of D_2 can be effective. This consideration allows us to conclude that at any moment in our experiment, the density of D atoms is low, initially because they are consumed by O_2 and subsequently because they form D_2.

At the end of the experiment, when the ice is sublimated we detect a high fraction of HDO and not D_2O owing to thermally activated H/D exchanges (Smith et al. 1997). Therefore O_2 is one of the possible precursors for water formation. Finally these experiments show that no O_2 should survive on grains in dark interstellar clouds. Apart from specific detection limitations, it can be a fundamental reason for the non detection of O_2 on icy grains in dark clouds.

6. Conclusions

We have reported the results of experiments on the mobility of deuterium at 10 K on porous ASW ice surfaces under interstellar conditions, using a temperature programmed desorption technique. Beams of O_2 and D were irradiated on the surface of an p-ASW ice film and the mobility of D atoms at 10 K was investigated via their property of reacting with the O_2 molecules. By using a simple rate equation model we found that the D atoms diffusion barrier at 10 K is 22 ± 2 meV. Our experimental results demonstrate that D atoms are mobile on ASW ice surfaces at 10 K, and validate the chemical models that hypothesized the mobility of H atoms at 10 K.

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