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Experimental evidence for water formation on interstellar dust grains by hydrogen and oxygen atoms

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ABSTRACT

Context. The synthesis of water is one necessary step in the origin and development of life. It is believed that pristine water is formed and grows on the surface of icy dust grains in dark interstellar clouds. Until now, there has been no experimental evidence whether this scenario is feasible or not on an astrophysically relevant template and by hydrogen and oxygen atom reactions.
Aims. We present here the first experimental evidence of water synthesis by such a process on a realistic analogue of grain surface in dense clouds, i.e., amorphous water ice.
Methods. Atomic beams of oxygen and deuterium are aimed at a porous water ice substrate (H_2O) held at 10 K. Products are analyzed by the temperature-programmed desorption technique.
Results. We observe the production of HDO and D_2O, indicating that water is formed under conditions of the dense interstellar medium from hydrogen and oxygen atoms. This experiment opens up the field of a little explored complex chemistry that could occur on dust grains, which is believed to be the site where key processes lead to the molecular diversity and complexity observed in the Universe.

Key words. astrochemistry – ISM: molecules – dust, extinction – methods: laboratory – molecular processes

1. Introduction

Water, the spring of life (Brack 2002), is the most abundant molecule in biological systems, and it is almost certainly of extraterrestrial origin. Water has been detected in gaseous or solid form in numerous astrophysical environments such as planets, comets, interstellar clouds and star forming regions where strong maser emissions are observed (Ehrenfreund et al. 2003; Dartois 2005). Amorphous water ice was directly detected in dark interstellar clouds through infra-red absorption (Leger et al. 1979). During the formation of stars deep inside molecular clouds, gas and dust become part of the infalling material feeding the central object. Part of these gas and dust grains, covered with icy mantles (mainly composed of water), ends up in the rotating disks surrounding young stars and forms the basic material from which icy planetesimals and later planets are formed together with comets in the external regions (van Dishoeck 2004). While the means of delivery of water to Earth remain a subject of debate (Morbidelli et al. 2000), the synthesis of water in the Universe is a fundamental link in establishing our origins. Water molecule formation in the gas phase is not efficient enough to reproduce the observed abundances in dark clouds, especially in its solid form (Parise et al. 2005; Ceccarelli et al. 2007). Therefore water ice must form directly on the cold interstellar grains and not as a condensate after being formed in the gas phase. A complete review of the processes involved both in the gas and solid phase has been recently published (Tielens 2005).

It was suggested many years ago that interstellar dust grains act as catalysts (Oort & van de Hulst 1946; van de Hulst 1946). Starting from simple atoms or molecules such as H, O, C, N, CO, grains are believed to be chemical nanofactories on which more complex molecules are synthesized, leading eventually to prebiotic species produced concurrently by surface reactions and by UV photons and cosmic rays irradiation, as already shown long ago (Hagen et al. 1979; Pironello et al. 1982). The most volatile species may be released in the gas phase upon formation (Garrod et al. 2007), while the refractory ones remain on the grain surface, building up a so called "dirty icy mantle", and may at least partially be sputtered by the heavy component of cosmic rays (Johnson et al. 1991). Such mantles, which typically have a thickness of a hundred monolayers, are mainly composed of water, the most abundant solid phase species in the Universe. Under dark cloud conditions, the very first monolayer has to grow on bare silicate or carbonaceous grains (Papoular 2005). For most of the water molecules, they should be synthesized on a surface mainly composed of water. Studying the growth of water on water ice substrate is therefore of high relevance.

Chemical models that include water formation on grain surfaces were proposed years ago by Tielens & Hagen (1982). They suggested that H_2O formation would be initiated by H-atoms reacting with O, O_2 and O_3, although the O_3+H pathway was considered the most effective and O_2 would play a mere catalytic role. Recent Monte Carlo simulations (Cuppen & Herbst 2007) show that while the main route to water formation on cosmic dust grains in diffuse and translucent clouds is the reaction H + OH, in dense clouds the principal source of H_2O is the reaction between H_2 and OH. This study also emphasizes the

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non-negligible contribution from the H + H_2O_2 reaction (H_2O_2 being a product of the H + O_2 pathway) and the unusual high abundance of reactants such as OH and O_3. Interestingly, another code by Parise (2004) proposed a water formation scheme where O_3 molecules react with H- or D-atoms to form OH or OD, and subsequently the reaction H_2 + OH/OD leads to H_2O/HDO. It should be noted that this scheme was in part also constrained by the observed abundances of deuterated species.

In dense clouds, observations show that hydrogen in the gas phase is mainly in molecular form (H/H_2 $\sim$ 10^{-3}, Li & Goldsmith 2003) and astrochemical models assume that H-atoms are present on the surface of interstellar dust grains as the dominant reactive partner. A great many theoretical papers and subsequently several experiments have accordingly treated the H+H reaction and other hydrogenation reactions on the surface of ice mantles in molecular clouds (see, e.g., Watanabe & Kouchi 2008, for an exhaustive review). The number density of H-atoms is mostly ruled by the destruction of H_2 due to cosmic rays and, whatever the density of the cloud, is about 1 cm^{-3}. On the other hand, the O/H_2 ratio remains approximately constant (10^{-4}), thus the number of atomic O, unlike H, is proportional to the density of the cloud. Therefore, in a cloud with a density of 10^3 cm^{-3}, H/O is 10, but in a cloud with a density of 10^5 cm^{-3} the ratio H/O is around 1/10. See for example Caselli et al. (2002) where the H/O ratio is 1/7 for a cloud density of 10^5 cm^{-3}. O is consequently the most abundant species in atomic form for very dense clouds and it can accrete on grains and subsequently react with either H- or O-atoms.

In previous laboratory works, Hiraoka et al. (1998) succeeded in producing water molecules from the reaction of H- and O-atoms initially trapped in a N_2O matrix. In 2006, using the set-up FORMOLISM (see Sect. 2), we studied the formation of water molecules by exposing a water ice substrate to D- and O-atoms and O_2 molecules, and simulated thus water formation in dense interstellar clouds (Dulieu et al. 2007). Very recently Miyauchi et al. (2008) investigated the reaction between cold H-atoms and an O_2 ice at 10 K, demonstrated the production of H_2O_2 and H_2O molecules and estimated the efficiency of the reactions. Ioppolo et al. (2008) performed a similar experiment, but with varying O_2 substrate temperatures. They confirmed the production of H_2O_2 and H_2O, made an estimate of the reactions efficiency and also drew conclusions upon the temperature dependence of the amount of species produced. These two experiments dealt with the H_2O production pathway in which O_2 is the species consumed to produce water.

In this paper, we present for the first time a quantitative study of the formation of water molecules through hydrogen and oxygen atoms on the surface of an amorphous solid water (ASW) ice film held at 10 K, hence under conditions that are much more relevant to the interstellar medium. The experiments are complemented by a statistical model to qualitatively disentangle the final products from ambiguities in the mass spectra. The aim of this first attempt to synthesize water under conditions close to those encountered in dense clouds is to investigate how water formation continues on the icy surfaces of cosmic grains, and also to give an estimate of the efficiency of the chemical path(s) actually active.

2. Experimental procedures

Several experiments were performed with the FORMOLISM set-up (Amiaud et al. 2006). In brief, a copper sample surface whose temperature can be controlled in the 8–800 K range is maintained under ultra-high vacuum conditions; on

it an amorphous solid water ice substrate, on which water formation is studied, is prepared in two steps. First, a 100-layer film of non-porous ASW ice is deposited at 120 K (Kimmel et al. 2001), then an overlayer of 10 mono-layers (1 ML = 10^{15} molecules/cm^2) of porous ASW ice is grown at 10 K. The underlying non-porous water film isolates the ice layer from the copper substrate (Engquist et al. 1995). This double ASW ice film is annealed to 90 K prior to each experimental run to avoid any further collapse of the pores between 10 and 80 K in the subsequent temperature-programmed desorption (TPD) experiments (see below). In fact, the species D_2, O and O_2 used in this experiment will be thoroughly evaporated by 80 K and that is before any rearrangement in the porous structure of the ice template takes place.

The annealed water ice substrate is still porous (Kimmel et al. 2001) and mimics an amorphous ice processed by UV and cosmic rays (Palumbo 2006) that is thought to constitute the icy mantle of interstellar grains. By using an architecture with two separate channels (Pirronello et al. 1997), where each consists of a triply differentially pumped beam line, two atomic beams of O and D are aimed at the ASW ice substrate held at 10 K. Atoms are produced by dissociation of O_2 and D_2 in microwave discharges. The dissociation efficiency of the oxygen beam is typically 40%, meaning that for 100 O_2 molecules that initially feed the discharge, 60 O_2 molecules and 80 O-atoms will finally reach the cold target. Trace quantities of residual gases (i.e., CO, N_2, CO_2 and H_2O) were detected in the beam. Great experimental attention has been paid, however, to confirm that neither O_3 nor deuterated compounds were present in the O-atom beam. The D-atom beam has a 60% dissociation efficiency, and no UV photons from the D_2-discharge plasma can reach the water ice sample. The purity of the beams was checked with a rotatable quadrupole mass spectrometer (QMS) that intercepted the incoming beam. The O- and D-beams have a flux of 10^{12} atoms/cm^{2}s and 5×10^{12} atoms/cm^{2}s, respectively. After concurrent or sequential injection of the beams, a TPD is performed at a heating rate of 20 K/min from 10 K to 200 K, and the desorbing species are simultaneously monitored with the QMS. The signals of mass 19 (HDO) and mass 20 (D_2O) presented are corrected by subtracting the contribution of the H_2O water substrate, which naturally includes some isotopes.

3. Results and discussion

Several experiments have been performed. In the first one D-atoms were sent onto the water surface to confirm that hydrogen atoms do not react with water molecules in the substrate to produce deuterated water molecules (see the solid thick line in Fig. 1), as already mentioned by Nagaoka et al. (2005). In addition, we determined that D_2 molecules do not react with O-atoms or with O_2 molecules residing on the ASW ice surface. This is a decisive result in itself that proves that the water formation process requires hydrogen in atomic form.

Figure 1 shows the mass spectrum recorded during the TPD performed after the irradiation of the water substrate with D-atoms and ^{16}O-atoms (and $^{16}O_2$ molecules). Water formation clearly occurs, as is testified by the presence of D_2^{16}O and HD^{16}O peaks. These findings are not surprising, although one could expect that mainly D_2O should be formed, because D is used as precursor. But it is also known that during the heating an isotope exchange between water molecules will occur (Smith et al. 1997). For a very thin layer of deuterated water, a complete isotope exchange with the underlying H_2O substrate molecules is expected around 150 K. In such a context, even if D_2O is formed
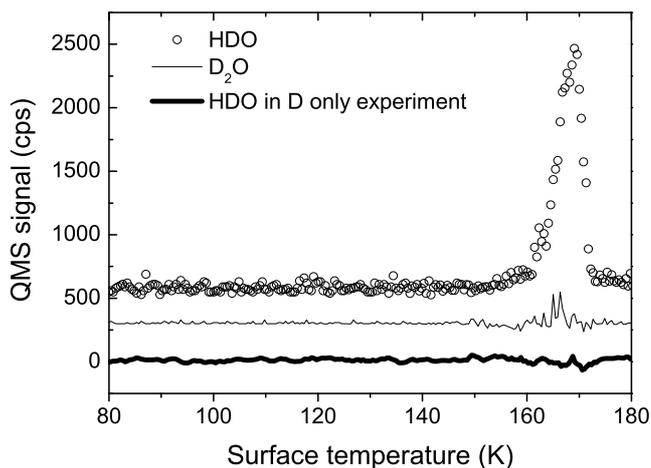
Fig. 1. TPD profiles of $D_2^{16}O$ (thin line) and $HD^{16}O$ (circles) after irradiation of the water substrate ($H_2^{16}O$) with D-atoms, ^{16}O-atoms and $^{16}O_2$ molecules. Thick line: TPD profile of $HD^{16}O$, after 30 min of D irradiation of the water ice substrate. The water ice substrate is held at 10 K during all exposures. Traces are vertically shifted for clarity.

at 10 K, most of the deuterated water will desorb as $HD^{16}O$, as is observed in our experiments.

Due to the mass spectrometric detection method of water molecules in the gas phase one could say that molecules synthesized by the reaction of D-atoms and O-atoms or O_2 were formed during the warm-up of the whole ice substrate, a fact that would render the result less relevant to interstellar space. But this is certainly not the case because reactions involving D-atoms must proceed at a temperature below 20 K. At temperatures higher than this the residence time of H-/D-atoms becomes exceedingly small for the reactions to occur.

To confirm unequivocally that water was formed starting from the reactants deposited from the gas phase and to provide quantitative results, we repeated the experiment presented above with the oxygen beam line fed with $^{18}O_2$ molecules. To ensure that the concentration of D-atoms on the surface was always much higher than that of O-atoms and O_2 molecules, we opened the oxygen beam by time-slices of 20 s every 2 min while the D-beam was constantly running and irradiated the target held at 10 K. Thus, the relative concentration on the surface consisted of $\gtrsim$10 D-atoms per O-nucleus (either in atoms or molecules). Matar et al. (2008) have shown that D reacts very efficiently with O_2, and that O_2 disappears from the surface in a ratio of one D for one O_2. In such a scenario it is reasonable to assume that O and O_2 surface concentration reflects the proportions in which they were produced in the beam due to the very low mobility of O-atoms (Tielens & Hagen 1982) and O_2 molecules at the irradiation temperature and in the temperature range in which H- and D-atoms remain adsorbed on the substrate. O-atoms have therefore a very low probability to form O_2 and to encounter O_2 molecules to form O_3, especially because they react with D with a higher probability. Under our experimental conditions we estimate that the surface concentration of O and O_2 never exceeds 1%. The mobility of D-atoms, however, is high enough to observe the formation of water molecules.

Figure 2 shows a TPD mass spectrum obtained after a 10-min dose of ^{18}O-atoms (30 time-windows of 20 s every 2 min, i.e., corresponding a total dose of ~0.6 ML) and simultaneous D-atom irradiation of the ASW ice substrate at 10 K. The two peaks at mass 21 and 22 can only be assigned to $HD^{18}O$
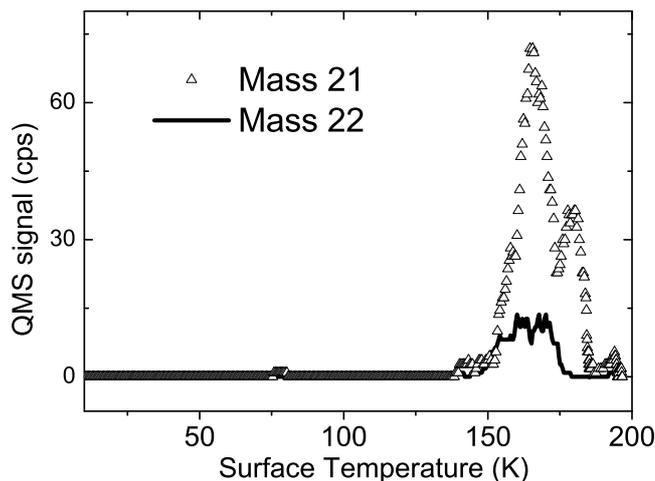

Fig. 2. $HD^{18}O$ (open triangles) and $D_2^{18}O$ (solid line) desorption profiles after ten minutes of simultaneous exposure of the amorphous H_2O ice substrate (held at 10 K) to ^{18}O- and D-atoms.

and $D_2^{18}O$, and this clearly shows again that formation of water molecules has occurred on the amorphous H_2O ice substrate, namely, a realistic analogue of cosmic dust surfaces in dense clouds.

In Table 1 the relative abundances (in terms of uncorrected ion counts) of the species detected during the TPD are shown, and in addition the total number of oxygen nuclei (^{18}O atoms and twice the number of $^{18}O_2$ molecules) that have been exposed to the substrate during the irradiation phase. We have not performed any corrections here (except the correction from the H_2O substrate).

As a preliminary remark, the signal at mass 23 is expected to be 0, and it serves as a good indicator of the level of noise. The number of $^{18}O_2$ molecules sent to the target was calculated by measuring the corresponding counts per second following the TPDs of a series of given $^{18}O_2$ exposures (with the microwave discharge OFF), and then calibrating the $^{18}O_2$-beam flux accordingly. The number of ^{18}O-atoms was calculated by scaling by the dissociation efficiency of O_2 (40%) with the discharge ON; namely, the number of ^{18}O-atoms = ($^{18}O_2$ counts × 0.40) × 2. To evaluate the conversion efficiency of O-atoms into water molecules in our experiment, we may evaluate the ratio α between the sum of mass 20 (^{18}OD and $H_2^{18}O$), mass 21 ($HD^{18}O$), mass 22 ($D_2^{18}O$) and the total amount of ^{18}O nuclei:

$$\alpha = \frac{M20 + M21 + M22}{total\ ^{18}O} = 0.76.$$

This ratio represents an upper limit of the formation of water molecules from ^{18}O, assuming that the contribution of $D_2^{16}O$ to the signal at mass 20 is negligible, as we have actually seen above (Fig. 1). α, however, is not 1. The missing ^{18}O nuclei are likely to have partially desorbed during the reaction or ended up in the form ^{18}OH radicals or even as $H_2^{18}O_2$ (and its deuterated isotopologues).

The formation of water molecules through the D + O_2 pathway has already been studied and confirmed experimentally by Miyauchi et al. (2008); Ioppolo et al. (2008); Matar et al. (2008). In the present experiment, we can deduce a lower limit for the formation efficiency for the D+O pathway. Actually, 60% of the available ^{18}O on the surface is contained in molecules. We can then see that, even if we assume that the molecular pathway has a 100% efficiency, it is less than α and that consequently

Table 1. Surface area under the TPD mass spectra of the species produced in the $^{18}O + D$ experiment. The results of a statistical model are given as a comparison (*see text*).

	Total ^{18}O	Mass 19	Mass 20	Mass 21	Mass 22	Mass 23
Area (cps)	$15\,000 \pm 1000$	$30\,000 \pm 2000$	$10\,000 \pm 500$	1250 ± 150	250 ± 70	20
Model	$15\,000$	31 802	8076	1434	188	0

a lower limit for water formation via the D + O pathway is about 0.16 (0.76–0.60). Therefore, if we define the formation efficiency via atoms as the ratio between the fraction of water molecules that certainly formed via the D + O route (0.16) and the fraction of O-atoms available (0.4), we obtain 0.4 as a lower limit for the formation efficiency. On the other hand we can also deduce an upper limit. If we assume that O and O_2 react with equal probability with D, we can estimate that 31% (0.76×0.4) of the water we have formed is the product of the D + O pathway and the efficiency of water formation via atoms is equal to α. Considering both boundary conditions, we conclude that a reasonable estimate for the efficiency of water formation via D- and O-atoms is about 0.5. An upper boundary value of the conversion efficiency of 76% – and not a closer value to 100% – may also be due to a non-perfect overlapping of the two beams (D and O) on the target sample. In fact, we found that not all O_2 molecules on the surface were consumed during the irradiation of D-atoms (cf. Matar et al. 2008). Moreover, it should be noted that our purpose was to provide a plausible value of the conversion efficiency from O-atom to water molecules. The value of α actually increases up to 0.88 if we take into account water fragments produced in the QMS ionizer, although this does not greatly affect the final estimate of the conversion efficiency of 0.5. Should the real value of α be comprised between 0.76 and 1, we point out that under our experimental conditions the value of 0.76 can still be considered a reasonable lower boundary value for the maximum conversion efficiency of O-atoms into D_2O.

We succeeded to build a very simple statistical model able to correctly reproduce the data (see Table 1). It allows us to discuss of the different pathways of water formation. The model considers only statistical equilibrium. For the sake of clarity we give here a simple example. Suppose there is an initial population of 90 H_2O and 10 OD, the final equilibrium obtained by randomly mixing the isotopes is OD = 0.5, OH = 9.5, H_2O = 81.225, HDO = 8.55, D_2O = 0.225. We also include oxygen scrambling and calculate the statistical weight of all the final species. Finally, we sum the final products by mass taking into account the QMS fractionation and are able to compare this with the experimental results. In Table 1, experimental yields are given as raw ion counts per second (cps); namely, without any correction due to the branching ratio of the cracking pattern of each species in the QMS. So in every one hundred $H_2^{18}O$ molecules about 87 are detected as mass 20 while the remaining 13 contribute to the counts at mass 19 ($H^{18}O$). ^{18}OD molecules also contribute to mass 20 although the cracking branching ratio is different. It is impossible to correct the data to express the initial parent molecules without making a choice on the relative concentrations on the surface. Therefore the experimental data are presented without correction. The model calculates final yields and only then, given the concentration of molecules on the surface before desorption, the contribution of each species can be distributed to the specific mass(es) (e.g., $H^{16}O$ contributes to mass 18, 17 and in minimal amount to mass 16).

In the light of the results we obtained, the obvious question is whether it is possible that the OH + H reaction has an activation barrier as sometimes previously suggested, and as occurs for

the gas phase? In this case, ^{18}OD could be mixed with H_2O at higher temperatures during the isotope exchange. We first assume that the OD + D reaction is actually negligible compared to the O_2 + D reaction, which leads to a formation of OD and D_2O in equal amounts. Therefore, at the end of the D irradiation the ratio $a = {}^{18}OD / D_2^{18}O$ is equal to $(40 + 30 = 70)/30$ because ^{18}O-atoms will form ^{18}OD and $^{18}O_2$ molecules will form an equal amount of ^{18}OD and $D_2^{18}O$ (via $D_2^{18}O_2$). The ratio $b = {}^{16}O/{}^{18}O$ is the only free parameter in the model and specifies the proportion of O-nuclei that will exchange during the TPD and statistically equilibrate their populations via isotope exchanges. The best fit of the data is found for a value of $b = 15$ (see model results in Table 1). This means that the overlayer of products (^{18}OD and $D_2^{18}O$) is mixed with 15 layers of the H_2O substrate which is reasonably consistent with previous results. Smith et al. (2000) found an efficient mixing of about 50 ML of both isotopes, although they used a lower heating ramp and a different amorphous ice. If one believes in our simple statistical model, it is also possible to explain our data starting with a high population of OD, and therefore with the assumption that an activation barrier for the OD + D reaction exists at 10 K. Indeed, the isotope exchange blurs the chemical pathways, and our data give not enough constraints to make a firm conclusion about which pathway is more efficient. None the less, on average we have estimated that water formation via the D + O pathway is highly efficient ($\sim$50%) and certainly is responsible for producing a significant fraction of water molecules. More laboratory investigations should be performed, and we actually plan to do that by combining TPD and infrared spectroscopy.

The relevance of our results to astrochemistry is clear and gives strong experimental support to simulations of the formation and time scale of growth of water ice mantles in dense clouds. For the first time it is demonstrated on experimental grounds that water molecules can form on an amorphous water ice substrate under interstellar conditions (i.e., through surface reactions between atomic hydrogen and atomic and molecular oxygen on ASW ice), allowing the growth of the icy mantles that are observed in dense clouds. Also, in our experiments as on interstellar grains, the formation of water ice via reactions between hydrogen and oxygen atoms suffers from the competition between the formation of H_2 and O_2, and this competition could probably reflect on the depth profile inside the ice layer and in the time evolution of the mantle itself.

Several issues still need to be investigated: the efficiency at various coverages and with an abundance ratio between hydrogen and oxygen atoms closer to the interstellar one; the interaction of the atoms that land from the gas phase and those belonging to the surface; other chemical pathways that contribute to the formation of water and so on. A key issue that provides an important observational counterpart and then has to be investigated also experimentally is the study of the effects of UV irradiation (photodesorption of radicals and molecules, photolysis) on the forming mantles that reflect the evidence of a threshold value (around $A_V = 3.2$) for the detection of thick icy mantles in dense clouds (Whittet et al. 2001). This issue has been already studied in a laboratory, but only considering photodesorption of

already formed water molecules (Westley et al. 1995). Besides all these investigations, of course, we have also to study how the first monolayer of water molecules may form efficiently on amorphous silicate and amorphous carbon. If it cannot form efficiently enough, it will be compulsory to accept that the very first monolayer has to be built by water molecules formed by gas-phase reactions and then accreted on the bare refractory grain surface; a fact of major interest inside dense clouds near the threshold of observability of icy mantles. These and other issues will be addressed in forthcoming papers.

4. Conclusions

We presented the first laboratory attempt to reproduce the formation of water molecules on a realistic analogue of grain surface in dense molecular clouds. By exposing O- and D-atoms to an amorphous water ice substrate held at 10 K, deuterated water molecules were formed with a high efficiency ($\sim$0.5). Our results imply that the O + H reaction pathway is an important route for water formation in interstellar environments with a number density greater than 10^4/cm^3. Furthermore, it is fair to believe that the same mechanism turns out to be the most efficient in diffuse clouds and (particularly) in the boundary layers of dense clouds where UV photons and atomic species dominate. Hence, for clouds where $A_V < 3$, the O + H route may be the only process for the efficient formation of the first monolayer of water ice on bare interstellar grains.

References

Amiaud, L., Fillion, J. H., Baouche, S., et al. 2006, J. Chem. Phys., 124, 094702
Borget, F., Chiavassa, T., Allouche, A., & Aycard, J. P. 2001, J. Phys. Chem. B, 105, 449
Brack, A. 2002, in Astrobiology: The quest for the conditions of life, ed. G. Horneck, & C. Baumstark-Khan (Berlin: Physics and astronomy online library, Springer), 79
Caselli, P., Stantcheva, T., Shalabiea, O. M., Shematovich, V. I., & Herbst, E. 2002, Planet. Space Sci., 50, 1257
Ceccarelli, C., Caselli, P., Herbst, E., Tielens, A. G. G. M., & Caux, E. 2007, in Protostars and Planets, ed. V. B. Reipurth, D. Jewitt, & K. Keil (U. Arizona Press) 47
Cuppen, H. M., & Herbst, E. 2007, ApJ, 668, 294
Dartois, E. 2005, Space Sci. Rev., 119, 293
Dulieu, F., Amiaud, L., Fillion, J.-H., et al. 2007, in Molecules in Space and Laboratory, Ed. J. L. Lemaire, F. Combes, 79
Ehrenfreund, P., Fraser, H. J., Blum, J., et al. 2003, Planet. Space Sci., 51, 473
Engquist, I., Lundström, I., & Lieberg, B. 1995, J. Phys. Chem., 99, 12257
Garrod, R. T., Wakelam, V., & Herbst, E. 2007, A&A, 467, 1103
Hagen, W., Allamandola, L. J., & Greenberg, J. M. 1979, Ap&SS, 65, 215
Hiraoka, K., Miyagoshi, T., Takayama, T., Yamamoto, K., & Kihara, Y. 1998, ApJ, 498, 710
Ioppolo, S., Cuppen, H. M., Romanzin, C., van Dishoeck, E. F., & Linnartz, H. 2008, ApJ, 686, 1474
Johnson, R. E., Pirronello, V., Donn, B., & Sundqvist, B. 1991, ApJ, 379, L75
Kimmel, G. A., Stevenson, K. P., Dohnalek, Z., Smith, R. S., & Kay, B. D. 2001, J. Chem. Phys., 114, 5284
Li, D., & Goldsmith, P. F. 2003, ApJ, 125, 1177
Leger, A., Klein, J., de Cheveigne, S., et al. 1979, A&A, 79, 256
Matar, E., Congiu, E., Dulieu, F., Momeni, A., & Lemaire, J. L. 2008, A&A, 492, L17-L20
Meyer, D. M., Jura, M., & Cardelli, J. A. 1998, ApJ, 493, 222
Miyauchi, N., Hidaka, H., Chigai, T., et al. 2008, Chem. Phys. Lett., 456, 27
Morbidelli, A., Chambers, J., Lunine, J. I., et al. 2000, Meteoritics & Planetary Science, 35, 1309
Nagaoka, A., Watanabe, N., & Kouchi, A. 2005, ApJ, 624, L29
Oort, J. H., & van de Hulst, H. C. 1946, Bull. Astron. Inst. The Netherlands, 10, 187
Palumbo, M. E. 2006, A&A, 453, 903
Papoular, R. 2005, Mon. Not. R. Astron. Soc., 362, 489
Parise, B. 2004, PhD Thesis, CESR (Toulouse, France)
Parise, B., Ceccarelli, C., & Maret, S. 2005, A&A, 441, 171
Pirronello, V., Brown, W. L., Lanzerotti, L. J., Marcantonio, K. J., & Simmons, E. H. 1982, ApJ, 262, 636
Pirronello, V., Liu, C., Shen, L., & Vidali, G. 1997, ApJ, 475, L69
Smith, S. R., Huang, C., & Kay , B. D. 1997, J. Phys. Chem. B, 101, 6123-6126
Smith, S. R., Dohalek, Z., Kimmel, G. A., & Kay, B. D. 2000, Chem. Phys., 258, 291
Tielens, A. G. G. M. 2005, The Physics and Chemistry of the Interstellar Medium (Cambridge University Press)
Tielens, A. G. G. M., & Hagen, W. 1982, A&A, 114, 245
van de Hulst, H. C. 1946, Recherches Astronomiques de l'Observatoire d'Utrecht, 11, 2
van Dishoeck, E. F. 2004, ARA&A, 42, 119
Watanabe, N., & Kouchi, A. 2008, PrSS., 83, 439
Westley, M. S., Baragiola, R. A., Johnson, R. E., & Baratta, G. A. 1995, Nature, 373, 405
Whittet, D. C. B., Gerakines, P. A., Hough, J. H., & Shenoy, S. S. 2001, ApJ, 547, 872