

# EXPERIMENTAL EVIDENCE FOR WATER FORMATION VIA OZONE HYDROGENATION ON DUST GRAINS AT 10 K

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## ABSTRACT

The formation of water molecules from the reaction between ozone (O<sub>3</sub>) and D-atoms is studied experimentally for the first time. Ozone is deposited on non-porous amorphous solid water ice (H<sub>2</sub>O), and D-atoms are then sent onto the sample held at 10 K. HDO molecules are detected during the desorption of the whole substrate where isotope mixing takes place, indicating that water synthesis has occurred. The efficiency of water formation via hydrogenation of ozone is of the same order of magnitude as that found for reactions involving O-atoms or O<sub>2</sub> molecules and exhibits no apparent activation barrier. These experiments validate the assumption made by models using ozone as one of the precursors of water formation via solid-state chemistry on interstellar dust grains.

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

## 1. INTRODUCTION

Solid water is a very abundant material. Indeed, it is believed to be the most abundant condensed material in the universe, thanks to its propensity for remaining as a deposit on interstellar dust particles in dense clouds. Amorphous solid water ice, together with a wealth of other condensed species, is widely observed spectroscopically via infrared absorption lines present in the spectrum of a field star or of the embedded object in star-forming regions (Gibb et al. 2000; Boogert et al. 2004). Icy mantles covering dust grains are reputed to form after direct freezeout of gas phase species and after surface reactions of atoms and radicals.

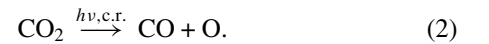
Although water ice is by far the most abundant species in icy mantles, the chemical origin of water molecules in interstellar icy mantles is still uncertain. Water molecule formation in the gas phase is not efficient enough to reproduce the observed abundances in dark clouds, especially in its solid form (Parise et al. 2005; Ceccarelli et al. 2007). Therefore, water ice is likely to form directly on the cold interstellar grains and not as a condensate after formation in the gas phase.

A reaction scheme including water formation on grain surfaces was proposed some years ago by Tielens & Hagen (1982). They suggested that H<sub>2</sub>O formation would be initiated by H-atoms reacting with O, O<sub>2</sub>, and O<sub>3</sub>, although the O<sub>3</sub> + H pathway was considered to be the most effective and O<sub>2</sub> would merely play a catalytic role.

Nonetheless, O<sub>2</sub> and O<sub>3</sub> molecules have not so far been detected in interstellar ices on dust grains, although their presence is presumed. Ozone non-detection may be partly explained because its strongest ν<sub>3</sub> (O–O) vibrational transition band at 1040 cm<sup>−1</sup> (9.6 μm) is swamped by the strong infrared absorption band of silicates at 10 μm, which has been observed by the *Infrared Space Observatory (ISO)* in the 2.4–25 μm region (e.g., spectrum toward the protostar W33A, resolution ~ 500–1000; Gibb et al. 2000).

Astrochemical models of dark clouds predict that condensed oxygen is likely to be a major component of apolar dust grains within interstellar clouds at 10 K. Recently, the O + H pathway (Dulieu et al. 2009) and the O<sub>2</sub> + H pathway (Miyachi et al. 2008; Ioppolo et al. 2008; Matar et al. 2008)

have been explored experimentally. All these experiments show that these reactions lead to water formation, even though the efficiencies of intermediate reactions are still under debate. Besides O and O<sub>2</sub>, ozone, too, can be present in icy mantles chemically processed by irradiation from Galactic cosmic-ray particles and internal secondary UV field (Tielens & Hagen 1982; Mathis et al. 1983; Greenberg 1984; Strazzulla & Johnson 1991). Several laboratory works confirm the efficient production of O<sub>3</sub> following energetic electron irradiation of pure oxygen ices (Bennett & Kaiser 2005; Sivaraman et al. 2007), and UV, proton and ion irradiation of ice mixtures simulating realistic analogs of interstellar ices (Ehrenfreund et al. 1992; Strazzulla et al. 1997; Cooper et al. 2008). In solid phase, O<sub>2</sub> and CO<sub>2</sub> are easily dissociated by UV radiations (λ < 240 nm) and cosmic rays (c.r.), producing atomic O in the electronic ground state (<sup>3</sup>P) and in the first electronically excited (<sup>1</sup>D) state (Sivaraman et al. 2007):

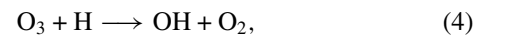


In the interstellar grain mantles, the O(<sup>3</sup>P) atoms in the ground state, which are in thermal equilibrium with the ice surface, react with O<sub>2</sub> molecules to form O<sub>3</sub> via the following reaction pathway:



The formation of ozone via Equation (3) is exothermic (Δ<sub>f</sub> H° = −1.48 eV).

The main ozone destruction reactions are



In addition, in dark clouds, hydrogen is mainly in its molecular form, so H-atoms are a rather rare reactant with H/H<sub>2</sub> ~ 10<sup>−3</sup> (Li & Goldsmith 2003). The number density of H-atoms is mostly governed by the destruction of H<sub>2</sub> due to cosmic rays. This value, whatever the density of the cloud, is about 1 cm<sup>−3</sup>. The O/H<sub>2</sub> ratio remains approximately constant (10<sup>−4</sup>), thus

the number of atomic O, unlike H, is proportional to the density of the cloud. See, for example, Table 1 of Caselli et al. (2002). For a cloud density of  $10^4 \text{ cm}^{-3}$ , the H/O ratio is  $\sim 1/0.75$ , while for a denser cloud with a density of  $10^5 \text{ cm}^{-3}$ , the H/O ratio is  $\sim 1/7$ . Therefore, for very dense clouds, O is the most abundant species in atomic form, and it can accrete on grains and subsequently form  $\text{O}_2$  and  $\text{O}_3$ .

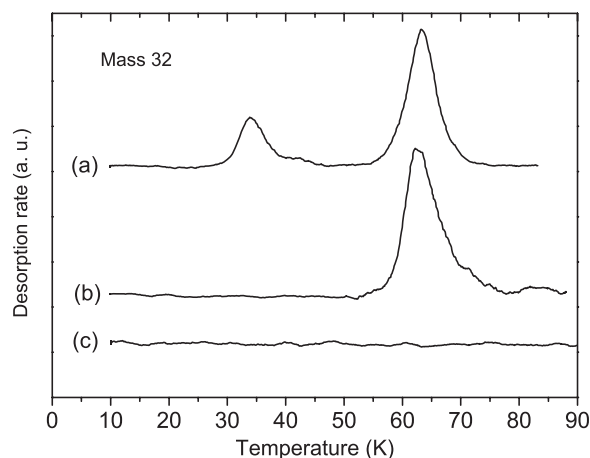
In their model, using a Monte Carlo approach, Cuppen & Herbst (2007) showed that under dense cloud conditions the  $(\text{O}_3 + \text{H})$  pathway is the most efficient route leading to the formation of  $\text{H}_2\text{O}$ . Finally, it should be noted that in the diverse models, some barriers can be raised in order to increase one of the competitive reactions (Lee et al. 1978; Caselli et al. 2002; Parise 2004). Yet, such barriers can only be experimentally probed, because extrapolations from the gaseous data are quite uncertain.

This Letter is the first report of water formation via ozone hydrogenation in the series of recent experiments that aim to investigate water synthesis in the interstellar medium. We present the evidence for the formation of water molecules from the reaction of  $\text{O}_3$  with D-atoms on non-porous amorphous solid water ice under conditions relevant to the dense interstellar clouds.

## 2. EXPERIMENTAL PROCEDURES

Our experiments were performed using the FORMOLISM setup developed to study the reaction and the interaction of atoms and molecules on surfaces simulating dust grains under interstellar conditions. The apparatus is composed of an ultrahigh-vacuum chamber with a base operating pressure of around  $10^{-10}$  mbar. The sample holder, a copper cylinder block, is attached to the cold finger of a closed-cycle He cryostat. It can be cooled to 8 K. The temperature of the sample is measured using a calibrated silicon diode and a thermocouple (Cromel-AuFe) clamped on the back of the sample holder. The copper surface is covered with 100 layers of non-porous amorphous solid water (np-ASW) by condensation of water vapor on the cold sample maintained at 120 K. Water is sprayed through a microchannel array doser located 2 cm in front of the surface. This ice is amorphous but non-porous (Kimmel et al. 2001). The water ice substrate is then cooled to 10 K. More details can be obtained in Amiaud et al. (2006).

Ozone can be synthesized by two methods. One is an ex situ method:  $\text{O}_3$  is prepared from gaseous  $\text{O}_2$  introduced in a glass bottle at a pressure of about 30 mbar. The  $\text{O}_2$  gas is then excited by a radio-frequency electric discharge ( $\sim 2$  MHz) through a copper coil placed around the  $\text{O}_2$  container. The blue ozone gas produced by the recombination of  $\text{O}_2$  and O-atoms during the discharge is condensed on the bottom wall plunged in liquid nitrogen (77 K). Residual  $\text{O}_2$  is then removed by primary pumping. The glass bottle is then mounted onto the main setup. Ozone is introduced into the vacuum chamber via a triply differentially pumped beam line aimed at the cold surface covered with  $\text{H}_2\text{O}$  ice. Due to the metallic parts of the inlet system on which  $\text{O}_3$  in part dissociates, the beam is composed of 70% ozone and 30%  $\text{O}_2$ . However,  $\text{O}_2$  is easily removed from the surface when the sample is held at 50 K. By varying the exposure time of the ozone beam, it is possible to vary the initial coverage of the surface. The  $\text{O}_3$  flux was previously calibrated using temperature-programmed desorption (TPD) by determining the exposure time of a pure  $\text{O}_2$  beam required to saturate the  $\text{O}_2$  monolayer (1 monolayer =  $10^{15}$  molecules  $\text{cm}^{-2}$ ) on np-ASW ice. In the experiments described below, we have deposited a maximum of half a monolayer of ozone under the same beam



**Figure 1.** TPD spectra of mass 32 obtained after depositing  $\sim 5 \times 10^{14}$  molecules  $\text{cm}^{-2}$  of  $\text{O}_3$  on np-ASW: (a)  $\text{O}_3$  deposited at 10 K, (b)  $\text{O}_3$  deposited at 50 K and cooled to 10 K, and (c)  $\text{O}_3$  deposited at 50 K, cooled to 10 K and irradiated with  $5 \times 10^{15}$   $\text{cm}^{-2}$  of D-atoms.

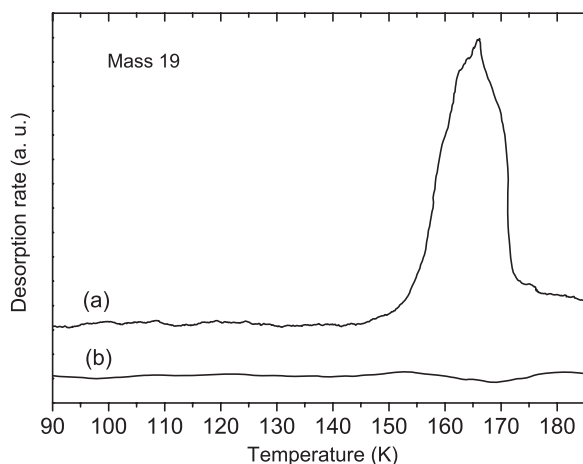
conditions used for calibrating the  $\text{O}_2$  flux. Owing to the non-pure  $\text{O}_3$  beam, however, ozone exposures had a relative accuracy of  $\sim 20\%$  and an absolute accuracy of  $\sim 30\%$ . Nevertheless, we did not see any significant effect due to the initial coverage (between 0.1 and 0.5 monolayers  $\pm 30\%$ ).

An alternative technique of ozone production was also used, namely, by depositing an atomic O on top of an  $\text{O}_2$  layer preadsorbed on the surface and then producing ozone in situ. The disadvantage of this technique is that the control of the initial amount of ozone has to be checked after each exposure. Whichever technique was used to deposit ozone onto the surface, we obtained the same final results.

After depositing ozone, an atomic D-beam aimed at the surface of the sample irradiates the  $\text{O}_3$ - $\text{H}_2\text{O}$  film maintained at 10 K. The D-atoms are produced by the dissociation of  $\text{D}_2$  molecules in a quartz tube using a Surfatron microwave discharge at 2.45 GHz. The rate of dissociation is  $\sim 60\%$ . After the irradiation of  $\sim 5 \times 10^{15}$  D-atoms  $\text{cm}^{-2}$ , a TPD is performed up to 180 K so that all the water ice desorbs. The TPD heating rate is  $10 \text{ K min}^{-1}$  from 10 to 180 K. The desorbed species are detected using a quadrupole mass spectrometer (QMS).

## 3. RESULTS AND DISCUSSION

The spectrum (a) in Figure 1 shows the TPD curve of mass 32 obtained after the exposure of half a layer of  $\text{O}_3$  on a np-ASW substrate held at 10 K (ex situ synthesis). We observe two peaks: the desorption peak at low temperature ( $\sim 30$  K) represents the desorption of  $\text{O}_2$  molecules. These molecules have been deposited by the  $\text{O}_2$  fraction in the  $\text{O}_3$  beam, probably due to ozone destruction on the metallic walls of the gas inlet system. The high-temperature peak at  $\sim 60$  K is the desorption of ozone. Mass 48 of  $\text{O}_3$  is also simultaneously detected in smaller amount and is always proportional to the signal at mass 32. In fact, for the most part  $\text{O}_2^+$  fragments are detected, as a result of the  $\text{O}_3$  cracking in the head of the QMS. Also, the desorption of ozone from ASW surfaces is known to occur at around 60 K (Chaabouni et al. 2000; Borget et al. 2001). Although this may be seen as an indirect measure, mass 32 gives information about  $\text{O}_2$  (below 50 K) and  $\text{O}_3$  (above 50 K) desorption. As shown in the spectrum (a) of Figure 1,  $\text{O}_3$  desorption is about three times larger than that of  $\text{O}_2$ . This indicates that the ozone fraction deposited with the ex situ method is  $\sim 70\%$ , the rest



**Figure 2.** TPD spectra of mass 19 (HDO) obtained after: (a) deposition of  $5 \times 10^{15} \text{ cm}^{-2}$  D-atoms on the np-ASW substrate at 10 K previously exposed to  $5 \times 10^{14} \text{ molecules cm}^{-2}$  of  $\text{O}_3$  and (b) deposition of  $2 \times 10^{16} \text{ cm}^{-2}$  D-atoms on the ozone-free water ice surface at 10 K.

being  $\text{O}_2$  molecules. In order to deposit only ozone molecules on the cold surface, we performed the exposure step with the water ice substrate held at 50 K. Thus,  $\text{O}_2$  molecules desorbing at 30 K were eliminated. Then, we cooled the sample to 10 K before proceeding with the TPD. As shown in the spectrum (b) of Figure 1, the TPD peak observed comes from  $\text{O}_3$  desorbing at 60 K. By using these procedures, we are sure that at 10 K only reactions involving ozone and D-atoms will occur.

For this work, we performed a set of experiments with various D-atom exposures. In the first one, D-atoms were sent onto the ozone-free water ice surface to check that no reaction occurred between D and the  $\text{H}_2\text{O}$  substrate to produce deuterated water molecules. This result is displayed in the mass 19 spectrum (b) of Figure 2. There is neither HDO nor  $\text{D}_2\text{O}$  desorption peak when D-atoms alone are deposited on the ASW ice substrate at 10 K as was previously noticed by Nagaoka et al. (2005) and Dulieu et al. (2009).

In a second experiment, we exposed the np-ASW sample held at 10 K to D-atoms before ozone deposition. In this experiment, ozone desorbs as if no atoms had been sent to the surface. This is because D-atoms form promptly  $\text{D}_2$  on non-porous water ice (e.g., Congiu et al. 2009) and apparently because ozone does not react with  $\text{D}_2$  (see below). This proves that hydrogenation reactions take place at around 10 K and not at higher temperatures since D-atoms react promptly at 10 K and furthermore they will have completely desorbed above 13 K (Amiaud et al. 2007).

In another experiment, D-atoms were sent onto the np-ASW surface previously exposed to 0.5 monolayers of  $\text{O}_3$ . In the spectrum (c) of Figure 1, we first observe the disappearance of the  $\text{O}_3$  peak. This suggests that all the ozone molecules have reacted. We also note that the reaction  $\text{D} + \text{O}_3$  is very efficient, because the number of D-atoms sent to the surface is only 10 times the number of  $\text{O}_3$  on the surface. Consequently, we can conclude that the  $\text{D} + \text{O}_3$  reaction—which is in competition with the  $\text{D} + \text{D}$  reaction in our experiment—proceeds on the ice surface with a small energy barrier. An estimation of the reaction rate can be made, for example, with the formula used by Cuppen & Herbst (2007) to simulate the surface reactions in their model:

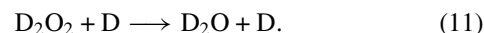
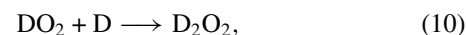
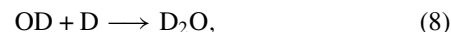
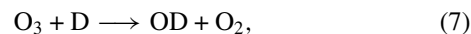
$$R_{\text{react}} = \nu_r \exp\left(-\frac{2a}{h}\sqrt{2E_a\mu}\right), \quad (6)$$

where  $\nu_r$  is the attempt frequency for reaction,  $a$  is the width of the barrier,  $\mu$  is the reduced mass, and  $E_a$  is the activation barrier. By taking  $E_a/k_B = 450 \text{ K}$  for the  $\text{D} + \text{O}_3$  reaction (Lee et al. 1978; Cuppen & Herbst 2007), we found that this reaction is very rapid ( $\sim 1 \text{ ps}$ ) if compared with the diffusion time of D-atoms on an amorphous water ice ( $\tau_{\text{diff}} = \sim 10 \text{ ms}$  on porous ASW ice; Matar et al. 2008).

In passing, we would like to point out that, over the last years, we have performed experiments on water formation in space starting from O,  $\text{O}_2$ , and now  $\text{O}_3$ . Even though we cannot infer absolute reaction rates which are very hard to estimate we can attempt to make relative comparisons. It should be noted that the destruction rate of ozone following D exposures is as important as the one for  $\text{O} + \text{D}$  and  $\text{D} + \text{O}_3$  reactions within the error bar of our experimental data. Hence, we conclude that the  $\text{D} + \text{O}_3$  reaction proceeds without a measurable activation barrier in the solid phase.

Obtained subsequently to the  $\text{D} + \text{O}_3$  experiment, the spectrum (a) of Figure 2 shows a desorption peak of mass 19 at 160 K attributed to the singly deuterated water (HDO). This clearly indicates that the reaction of D-atoms with  $\text{O}_3$  molecules on the ice surface is efficient and produces deuterated water molecules detected upon desorption of the whole ice film. We also notice that nearly no desorption peak of  $\text{D}_2\text{O}$  (mass 20) is detected. This is due to thermally activated H/D exchanges during the phase transition of the water ice (Smith et al. 1997). Therefore, even if  $\text{D}_2\text{O}$  is actually formed on the surface, mostly water molecules in the form of HDO are likely to desorb and be detected.

The formation of deuterated water molecules at  $T_s = 10 \text{ K}$  from D-atoms and  $\text{O}_3$  molecules may then follow the successive reaction pathways:



Whereas at  $T_s$  greater than 130 K, as mentioned above, the following isotope exchange reaction is active:



Of course, the reversal of reaction (12) is also possible, but in our case it is statistically negligible.

As for what concerns the intermediate products of the reaction scheme, we performed again the  $\text{D} + \text{O}_3$  experiment but with a low exposure of D-atoms (0.01 monolayers) on 0.15 monolayers of  $\text{O}_3$ , thus with a dose of D insufficient to go on with the hydrogenation reactions leading to water molecules. This experiment shows that  $\text{O}_3$  molecules are not thoroughly consumed and also that  $\text{O}_2$  molecules appear on the surface indicating that reaction (7) proceeds at 10 K and that the formation of  $\text{D}_2\text{O}$  can proceed as well from the intermediate reaction (9).

The studied mechanism for water formation from the hydrogenation of ozone might be an explanation for the non-detection of  $\text{O}_3$  in the interstellar ices. In fact, ozone reacts rapidly with hydrogen atoms to form water molecules on a water ice surface

at 10 K and under conditions similar to those found in dense interstellar clouds. Likewise, the lack of a clear detection of O<sub>2</sub> in interstellar ices may be explained by the high reactivity between O<sub>2</sub> and H-atoms reported in Miyauchi et al. (2008), Ioppolo et al. (2008), and Matar et al. (2008).

In addition, the OH + H<sub>2</sub> reaction could also be a key surface reaction in dark clouds, because H<sub>2</sub> (and D<sub>2</sub>) is present on the surface of the grains in large amounts (Kristensen et al. 2009). In our experiments too, there is a large amount of molecular deuterium because of the incomplete dissociation of D<sub>2</sub> in the D-beam. At the moment, it is not possible to us to probe explicitly the OH + H<sub>2</sub> reaction, but we can investigate the role of D<sub>2</sub>, by testing the O<sub>3</sub> + D<sub>2</sub> reaction. In order to do that, we have deposited a very large amount of D<sub>2</sub> ( $\sim 10^{17}$  cm<sup>-2</sup>) on np-ASW ice held at 10 K and previously dosed with O<sub>3</sub>. In this experiment, we did not detect any HDO, even when the surface was held at 50 K during D<sub>2</sub> deposition in order to overcome a possible activation barrier. Therefore, we can fairly conclude that the D<sub>2</sub> + O<sub>3</sub> reaction does not proceed under our experimental conditions.

Unlike the O<sub>3</sub> + D<sub>2</sub> reaction, O<sub>3</sub> + D shows no barrier under our experimental conditions and this result shows clearly that ozone is a likely precursor to water formation on a water ice layer at 10 K as proposed by Cuppen & Herbst (2007). This pathway is to be preferred in environments where the number of O-atoms exceeds the number of H-atoms, which is supposed to be the case in dark clouds with a density higher than 10<sup>4</sup> cm<sup>-3</sup> (Caselli et al. 2002). Unfortunately, our present data do not allow us to disentangle the different intermediate reactions that lead to the formation of water. In order to investigate in more detail the kinetics of water formation at 10 K via ozone, we are developing an additional IR diagnostic on FORMOLISM. This will allow us to see the appearance of some of the intermediate reactants and to provide accurate quantitative results.

#### 4. CONCLUSIONS

In this Letter, we have shown that it is possible to form efficiently water molecules from the reaction of O<sub>3</sub> with hydrogen atoms on non-porous water ice. This reaction exhibits no activation barrier at 10 K, and is about as efficient as the pathways having O or O<sub>2</sub> as precursors. This experimental result corroborates theoretical studies that consider ozone as one of the major actors of water formation in dark clouds.

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