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Water formation through O_2 + D pathway on cold silicate and amorphous water ice surfaces of interstellar interest

H. Chaabouni,[1,a)] M. Minissale,[1] G. Manicò,[2] E. Congiu,[1] J. A. Noble,[3] S. Baouche,[1] M. Accolla,[4] J. L. Lemaire,[1] V. Pirronello,[5] and F. Dulieu[1]
[1]*LERMA, UMR 8112 du CNRS, de l'Observatoire de Paris et de l'Université de Cergy Pontoise, 5 mail Gay Lussac, 95000 Cergy Pontoise Cedex, France*
[2]*Dipartimento di Fisica ed Astronomia Università degli Studi di Catania Via Santa Sofia, 64 95123 Catania, Italy*
[3]*Aix-Marseille Universit´e, PIIM UMR 7345, 13397 Marseille, France*
[4]*Dipartimento di Scienze Applicate - Università Parthenope di Napoli Centro Direzionale, Isola C4, 80143 Napoli, Italy*
[5]*Dipartimento di Metodologie Fisiche e Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Sicily, Italy*

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The formation of the first monolayer of water molecules on bare dust grains is of primary importance to understand the growth of the icy mantles that cover dust in the interstellar medium. In this work, we explore experimentally the formation of water molecules from O_2 + D reaction on bare silicate surfaces that simulates the grains present in the diffuse interstellar clouds at visual extinctions ($A_V < 3$ mag). For comparison, we also study the formation of water molecules on surfaces covered with amorphous water ice representing the dense clouds ($A_V \geq 3$ mag). Our studies focus on the formation of water molecules in the sub-monolayer and monolayer regimes using reflection absorption infrared spectroscopy and temperature-programmed desorption techniques. We provide the fractions of the products, such as D_2O and D_2O_2 molecules formed on three astrophysically relevant surfaces held at 10 K (amorphous olivine-type silicate, porous amorphous water ice, and nonporous amorphous water ice). Our results showed that the formation of D_2O molecules occurs with an efficiency of about 55%–60% on nonporous amorphous water ice and about 18% on bare silicate grains surfaces. We explain the low efficiency of D_2O water formation on the silicate surfaces by the desorption upon formation of certain products once the reaction occurs between O_2 and D atoms on the surface. A kinetic model taking into account the chemical desorption of newly formed water supports our conclusions. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4771663]

I. INTRODUCTION

Solid water ice is the most abundant condensed component in the cosmos and particularly on the icy mantle of dust grains in dense molecular clouds. It is also the most abundant species in the icy mantles covering dust grains[1] in the interstellar medium (ISM). The accretion of water from the gas phase cannot explain the observed abundances of solid water in dark molecular clouds.[2] It was suggested in the past that water ice is formed through surface reactions where dust grains play a role of catalyst.[3] Three different hydrogenation routes for water formation on the surface of dust grains have been proposed by Tielens and Hagen:[3] O + H, O_2 + H, and O_3 + H.

In dense molecular clouds, dust grains are covered with icy mantles which play the role of catalyst, and hydrogen is mainly in its molecular form. Hydrogen atoms are produced by cosmic rays with an abundance of (10^{-3} H_2).[4] O_3 and O_2 molecules have not so far been detected in interstellar ices on dust grains,[5] while the abundance of O atoms in these environments, is predicted by astrochemical models to be (O/H = 10^{-4}).[6]

The O_3 + H channel is demonstrated theoretically[7] and experimentally[5,8] to be the most effective route for water formation in dense clouds.

According to Cuppen and Herbst,[7] the O_2 + H channel is also responsible for water formation on cold dense clouds. Several laboratory studies demonstrated the high efficiency (∼50%) of water ice formation through O_2 and D atoms in the multilayer regime of oxygen ice at 10 K using reflection absorption infrared spectroscopy and temperature-programmed desorption (RAIRS)[9–14] and temperature-programmed desorption (TPD)[11] techniques.

The hydrogenation of molecular oxygen O_2 results in the formation of water through the following exothermic reactions:

$$H + O_2 \rightarrow HO_2, \quad (1)$$

$$H + HO_2 \rightarrow H_2O_2, \quad (2)$$

$$H + H_2O_2 \rightarrow H_2O + OH, \quad (3)$$

and

$$H + OH \rightarrow H_2O. \quad (4)$$

a)Electronic mail: henda.chaabouni@obspm.fr.

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Reaction (1) has a very low activation barrier of about 52 K in the gas phase,[9] while reaction (2) has no activation barrier.[7,15] However, despite the large activation barrier of the reaction (3) in the gas phase (∼1800 K),[14] the experimental studies of Miyauchi *et al.*[9] at surface temperature of 10 K and Ioppolo *et al.*[10,14] at 12–28 K have confirmed the high efficiency of water formation trough the O_2 + H/D pathway in the multilayer regime of O_2 ice. Both H_2O_2 (D_2O_2) and H_2O (D_2O) species were observed by RAIRS. Miyauchi *et al.*[9] and Oba *et al.*[12] have suggested a tunneling process for the reaction (3) because of the isotopic effect between H + H_2O_2 and D + D_2O_2 reaction rates. Recent experimental results of Cuppen *et al.*[13] showed that H_2O is not predominantly formed through the hydrogenation of H_2O_2 but also through the reaction (4) between H atoms and OH radicals.

In dense clouds in which typical temperatures are about 10 K, the UV flux is very low, and H_2 molecules the dominant H-bearing species.[3,7,14] Consequently, the reaction H_2 + OH (5) is often thought to be the most common route for the formation of H_2O on grain surfaces covered with water ices

$$H_2 + OH \rightarrow H_2O + H. \quad (5)$$

Despite the high activation barrier of this reaction in the gas phase (2100 K),[16] Oba *et al.*[17] have demonstrated experimentally the formation of water ice at low surface temperature 10 K.

The formation of water by successive hydrogenation of atomic oxygen proceeds through the barrierless radical-radical reactions

$$H + O \rightarrow OH, \quad (6)$$

$$H + OH \rightarrow H_2O. \quad (7)$$

Dulieu *et al.*[18] have demonstrated the high efficiency (50%) of water formation from O and D atoms on compact water ices substrates at 10 K using TPD experiments. Recently, Jing *et al.*[19] have studied experimentally the first stages of water formation through O + D reaction on the surface of an amorphous film of silicates at 15 K and 25 K using RAIRS and TPD techniques. They observed the formation of D_2O_2, D_2O, and O_3, and suggested that the formation of D_2O_2 molecules proceeds through OD + OD → D_2O_2 reaction because of the presence of the strong infrared absorption peak at 2300 cm^{-1} of OD radicals on the surface.

Theoretical simulations (Cuppen and Herbst[7]) suggest that the O + H reaction pathway is the most dominant process for water formation in diffuse clouds in the ISM where bare dust grains are mostly composed of silicates and/or carbonaceous materials.[20] In such places gas phase composition is mostly atomic because of the high UV radiation fields. In these gas environments, where the visual extinctions (A_V <1 mag), the densities of hydrogen and oxygen atoms are expected to be high (n_H = 100 atoms cm^{-3}) and (n_O = 0.03 atoms cm^{-3}), with an atomic abundance of O/H = 10^{-4} (see Ref. 6).

Silicates are among the most commonly found dust species in the (ISM) of galaxies. They are often assumed to be metallic and dielectric materials.[21] Their presence is established through the detection of the mid-infrared resonances due to the SiO stretching and the OSiO bending mode at 9.7 and 18 μm, respectively.[22]

Recent gas-surface chemical models of Goumans *et al.*[23] showed that the formation of H_2O water ice on cold silicate surface such as forsterite can occur via species (O and H) strongly bound to the surface that can dissipate efficiently their excess energy to the surface via phonons. However, the exothermicity of the H + OH → H_2O reaction could provide sufficient surplus energy to desorb H_2O water molecules into the gas phase from bare silicate surfaces. Certainly, the evaporation of water molecules at low surface temperatures (10 K) is inefficient, but their desorption into the gas phase upon formation on cold dust grains analogs, can be induced by the heat of formation released from the exothermic surface reaction H + OH. This desorption process of newly formed water species is called the chemical desorption,[24] it is also refereed as non-thermal desorption as opposed to TPD thermal desorption.[25] This process has a great impact on the chemical composition of interstellar gas.

Recently, Cazaux *et al.*[26] studied water formation on dust grains using Monte Carlo simulations and provided the fractions of physisorbed molecules (OH, HO_2, H_2O_2, H_2O, OD, DO_2, D_2O_2, D_2O) released into the gas phase upon formation in different astrophysical environments. These authors suggested that a significant part of the species are desorbed upon formation from bare surfaces because of the exothermicity of certain reactions on the surface. Then in diffuse clouds, 35% of OH desorbed upon formation from O + H reaction and 15% of H_2O is ejected in the gas phase from OH + H reaction H + OH.

In order to understand the growth of water ice mantle that covers the dust grains in dense molecular clouds, it is primordial to understand the process and the mechanism of water formation on the surface of bare dust grains composed either of silicates or carbonaceous materials. As previously mentioned, the formation of H_2O water ice in dense clouds is likely to occur from the hydrogenation of O_3, O_2, and O atoms. However, the reactivity of oxygen atoms on the surface may form again oxygen and ozone molecules, respectively, from O+O and O+O_2 reactions.[19,27] In this work, we investigate experimentally the formation of the first monolayer of D_2O water ice through O_2 and D atoms on amorphous silicate surface held at 10 K. In order to study the effect of the substrate on the efficiency of water formation in the submonolayer and monolayer regimes, the experiments were also investigated both on porous and nonporous amorphous solid water ices.

The plan of this paper is the following: In Sec. II, we describe the experimental setup and we explain the experimental procedures. In Sec. III, we present the experimental results for the synthesis of water ice through O_2 + D channel on silicate and amorphous water ices substrates at 10 K. We used D atoms instead of H atoms to increase the signal to noise ratio in spectrometric measurements. Surface reactions are analyzed both with RAIRS and TPD spectroscopy. In Sec. IV, we discuss the results and we propose a reaction route for water formation, and a chemical model to support our conclusions.

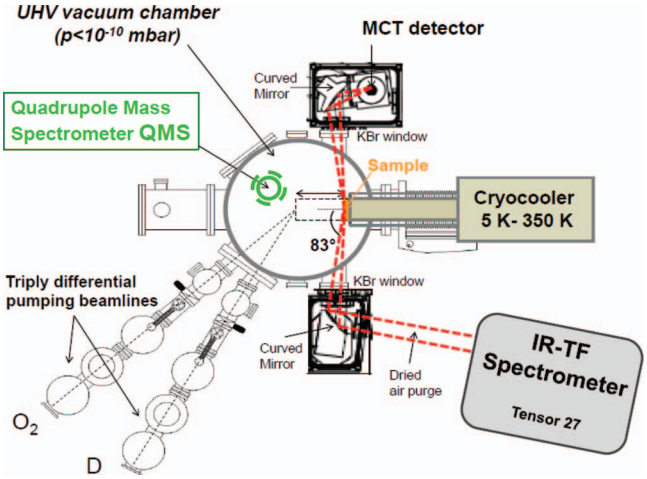


FIG. 1. Schematic of the experimental setup showing the UHV chamber, the atomic/molecular beam lines, the QMS, and the FTIR diagnostics.

II. EXPERIMENTS

The experiments were performed using the formation of molecules in the ISM setup. It is briefly described here and more details are given in Refs. 28–31. The apparatus displayed in Figure 1 consists of an ultra-high vacuum (UHV) stainless steel chamber with a base pressure lower than 1×10^{-10} mbar. In its center, we find the sample holder, which is thermally connected to a cold finger of a closed-cycle He cryostat ARS cryogenics 210SD. The temperature of the sample is measured in the range of 5.5–350 K with a calibrated silicon diode clamped to the sample and connected to a Lakeshore 336 controller. The temperature is controlled within ± 0.2 K precision and ± 1 K of absolute accuracy depending on how tight is the silicon diode clamped to the surface.

The sample holder is made of a 1 cm diameter copper block. Its optically polished and gold-coated surface is covered with an amorphous olivine type silicate film $[(Mg_xFe_{1-x})_2SiO_4]$ where $0 < x < 1$. Its exact chemical composition is unknown, but its amorphous propriety is evidenced by infrared spectroscopic studies,[32] and its nonporous surface structure is estimated from TPD experiments.

An analytical quadrupole mass spectrometer (QMS Hiden 3F) is used to quantify the reactants entering the chamber and the products desorbing from the sample surface. We used two triply differentially pumped beam-lines aimed at the sample to introduce the reactants (O_2, D) onto the surface of the sample holder. The two beam lines are equipped with micro-wave dissociation sources (a Surfatron cavity delivering 300 W at 2.45 GHz) that can generate deuterium atoms from their parent molecules. When the microwave sources are turned on, the dissociated efficiency of D_2 beam is $\tau = 65\%-70\%$. The flux of D atoms hitting the surface is defined as $\Phi_D = 2 \times \tau \times \Phi_{D2}$ where $\Phi_{D2} = (2.2 \pm 0.4) \times 10^{12}$ molecules $cm^{-2}\,s^{-1}$ is the flux of D_2 molecules. The flux of D atoms is estimated to be $(3.0 \pm 0.5) \times 10^{12}$ particles $cm^{-2}\,s^{-1}$, whereas the flux of O_2 molecules at the surface is evaluated to $(2.8 \pm 0.4) \times 10^{12}$ molecules $cm^{-2}\,s^{-1}$.

Since water molecules are polar and IR active, water ices are monitored *in situ* by means of RAIRS. RAIRS is a powerful surface infrared technique used to study the vibrational spectrum of very thin adsorbate on a surface.[33]

We used a Fourier transform infrared spectrometer (FTIR), Bruker Tensor 27 with a mid-IR source (Globar) emitting light between 2.5 μm and 25 μm. As shown in Figure 1, the spectrometer is coupled to the main UHV chamber through two differentially pumped potassium bromide (KBr) windows for the IR incident and reflected light. The spectrometer is used in external mode and the IR beam exiting it through a KBr window. Spectra are recorded in the 4000–400 cm^{-1} spectral region which includes absorption by several molecules detected in the ISM. As shown in Figure 1, the incoming IR beam is bent at 90° by a parabolic mirror with a focal distance f = 25 cm before entering in the main chamber. This mirror focuses the IR beam on the sample at an incidence angle of ~83° corresponding to a grazing angle of ~7°. The beam reflected from the highly reflective surface is then focused at 90° by an ellipsoidal mirror (f = 25 cm) onto a mercury-cadmium-telluride (model D316/6) detector cooled with liquid nitrogen N_2 (77 K). This detector is characterized by its fast response time and its high sensitivity. A spectral resolution of 4 cm^{-1} is used and 500 scans (about 400 s acquisition time) are co-added for one averaged spectrum in order to reduce the signal to noise ratio.

Our RAIRS experiments required two positions for the sample holder. During the exposure phase, the sample is placed in the center of the vacuum chamber where O_2 and D beams are aimed at the surface. Then, the sample is moved back ~9 cm from the exposure position for infrared measurements. Initially a spectrum of the clean surface at 10 K has been recorded before dosing which is called reference spectrum S_R. Then a sample spectrum S_S is acquired after exposure to O_2 and D-atoms. The RAIR spectrum of the sample compound (resulting from the difference between S_S and S_R) is plotted in absorbance (AB) mode for quantitative analysis.

Since the diatomic homonuclear molecule O_2 is infrared inactive, gas phase O_2 is monitored during the desorption by the QMS using TPD spectroscopy. It consists to heat the sample with a linear rate of heating $dT/dt = 0.04$ K s^{-1} until the sublimation of water species.

The experiments of water formation from O_2 and D-atoms has been performed at 10 K on different surface samples: (i) silicate (as described above), (ii) nonporous amorphous solid water (np-ASW) ice, and (iii) porous amorphous solid water (p-ASW) ice. The np-ASW ice film with a thickness of about 50 layers (1 ML = 10^{15} molecules $cm^{-2}\,s^{-1}$) is grown by spraying water vapor from a microchannel array doser located 2 cm in front of the surface held at 110 K. The np-water film (called also compact water ice) is then cooled down to 10 K for the exposure of O_2 molecules and D atoms. Otherwise the p-ASW ice film with 10 layers of thickness is introduced by background vapor deposition on the compact water ice substrate kept at 10 K using the same microchannel array doser placed in the remote position.

The D, O_2, and D_2O beams have been calibrated to estimate the exposure time required for each gas to form the first monolayer coverage of the species on the surface of the

silicate at 10 K. The O_2 beam calibration consists of depositing different amounts of oxygen molecules on the surface and monitoring their thermal desorption by the QMS. The calibration of D-atoms beam was estimated from King and Wells[34] type experiments for the sticking coefficient of particle incident on the surface using mass spectrometry (see Ref. 29 for details about this measurement). In our experimental conditions, the 1 ML of D-atoms is evaluated to 7 min of D deposition time, the 1 ML of O_2 ice was obtained after 6 min of O_2 exposure time.

For all the experiments, the coverages (in ML) of the nascent O_2 and D species are estimated from the ratio between the exposure time of gas phase and exposure time required to form 1 ML coverage. For D_2O and D_2O_2 species, the coverages (in ML) are obtained from the comparison of RAIRS integrated areas of the observed peaks and the integrated area corresponding to one monolayer coverage of D_2O molecules. Because the coverages of D_2O and D_2O_2 were not possible by TPD, we have used the yield calculation. The yields (in %) of species (O_2, D_2O...) in solid phase are obtained by dividing the (RAIRS or TPD) integrated area of the corresponding peak, by the expected integrated area when O_2 is fully consumed by D atoms following the reaction $O_2 + 4D \rightarrow 2D_2O$.

III. RESULTS

A. Formation of water on amorphous silicates

1. RAIRS results

In these experiments, we exposed the surface of the silicate held at 10 K to many cycles of 1 min of O_2 + 4 min of D (i.e., 0.18 ML of O_2 + 0.58 ML of D), by increasing progressively the deposition times of O_2 and D atoms under the condition $[D]/[O_2] \simeq 4$; it corresponds to the stoichiometric proportions of the reaction $O_2 + 4D \rightarrow 2D_2O$. This co-deposition method of O_2 and D atoms ensures that the reaction between O_2 and D atoms occurs in low-coverage regime until all O_2 molecules consumed by D atoms are transformed into D_2O molecules. We used this method of deposition to be able to observe the infrared signature of D_2O water ice formed on the silicate surface at 10 K in the sub-monolayer coverages.

Despite the low sticking coefficient of D atoms (~20%) on grain surfaces at 10 K,[35] the low fraction of the impinging D atoms that stuck on the surface react first with O_2 molecules and form DO_2 which can be deuterated into OD and D_2O_2 species. The final products of the deuteration are D_2O water molecules. The impinging D atoms can also react with another D atom on the surface and form D_2 molecules. The formation of hydrogen molecules occurs either via Eley-Rideal (E-R) mechanism between an adsorbed D atom and another one coming from the gas phase, or by Langmuir Hinshelwood mechanism which is enhanced by the diffusion of two adsorbed D atoms on the surface.[7]

In Figure 2 left panel, the RAIR spectra from (a) to (g) show the growth of the infrared absorption peaks of D_2O and D_2O_2 ices in the spectral region [3000 cm^{-1} − 1900 cm^{-1}] of the OD-stretching vibration bonds and in the spectral region [1300 cm^{-1} − 1000 cm^{-1}] of the OD-bending modes of D_2O and D_2O_2.

Because of the low sensitivity of our RAIRS diagnostic for low coverages, it was not obvious to observe clearly the IR absorption peaks of D_2O and D_2O_2 in the sub-monolayer regime (see spectra (a)–(c)). However, by increasing the exposure doses of O_2 and D atoms (1.1 ML O_2 + 4.2 ML D) to observe the monolayer regime (see spectrum (d)), we start observing a broad absorption peak at around 2404 cm^{-1} corresponding to the overlapping of D_2O and D_2O_2 –OD stretching vibrations. The small peak at around 2107 cm^{-1} is attributed to the $2\nu_6$ vibration mode of D_2O_2.[13,19] In addition, a small peak at around 1215 cm^{-1} is attributed to OD-bending mode of D_2O and a second small peak at around 1050 cm^{-1} is attributed to the OD-bending of D_2O_2.[9,19] RAIR spectra (e)–(g) in Figure 2 left panel show the growth of D_2O and D_2O_2

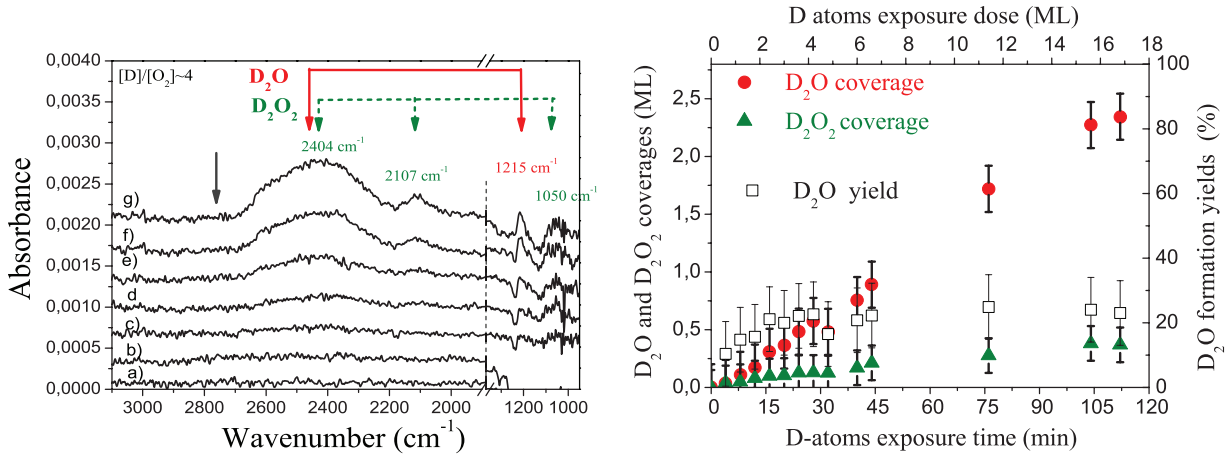


FIG. 2. (Left panel) RAIRS spectra (from (a) to (g)) of D_2O and D_2O_2 molecules formed on the silicate substrate held at 10 K by co-deposition of O_2 molecules and D atoms for several exposure times under the condition of $O_2/D = 4$. (a) 0.2 ML(O_2) + 0.6 ML(D), (b) 0.6ML(O_2) + 1.8 ML(D), (c) 0.7 ML(O_2) + 2.4 ML(D), (d) 1.1 ML(O_2) + 4.2 ML(D), (e) 2.0 ML(O_2) + 6.6 ML(D), (f) 3.5 ML(O_2) + 11 ML(D), and (g) 5.1 ML(O_2) + 17 ML(D). (Right panel) Full circles and triangles, the estimated coverages in (ML) of D_2O and D_2O_2 on the silicate surface, respectively, as a function of D exposure doses and times. Empty blue squares, the yield of D_2O molecules formed on the silicate surface, obtained from the formulae: $f_{D_2O} = \frac{D_2O\text{coverage}}{2\times O_2\text{coverage}}$. The uncertainties are given by the errors bars.

peaks in the multilayer regime. We note that neither OD radicals having an absorption peak at about 2300 cm^{-1} in solid phase,[19] nor DO_2 radicals peaking at around (2549 cm^{-1})[36] were observed in our spectra during the co-deposition phase of O_2 and D atoms on the silicate surface.

Figure 2 right panel shows the increase in the coverages (in ML) of D_2O and D_2O_2 species on the silicate surface held at 10 K as a function of D-atoms exposure times and doses. In this experiment, the coverages are estimated from the infrared integrated areas of the small D_2O_2 band ($2\nu_6$) at 2107 cm^{-1}, while the coverages of D_2O are estimated from the integrated areas of the wide band around 2404 cm^{-1} of D_2O molecules overlapping D_2O_2 species in the (ν –OD) stretching mode. The combination of D_2O and D_2O_2 modes in this spectral region leads to an over-estimation for D_2O formation. The ratio of the integrated areas for D_2O and D_2O_2 peaks is found to be $D_2O/D_2O_2 = \sim 4.0$ for very low surface coverages ($O_2 \leq 1$ ML) and $D_2O/D_2O_2 = \sim 6.5$ for ($O_2 > 1$ ML).

The Figure 2 right panel shows that the amount of D_2O molecules is always higher than D_2O_2 as the time of D atoms exposure increases. This is because in this co-deposition experiment, the monolayer fraction of O_2 molecules deposited on the surface reacts each time with D atoms and forms mostly D_2O species. In the case of the sub-monolayer regime, the high abundance of D_2O on the surface in comparison to D_2O_2 results from the diffusion of a sufficient number of D atoms on the surface of the silicate, favoring thus the conversion of most of OD and D_2O_2 surface products into D_2O molecules. These results are different from those of Miyauchi *et al.*[9] and Ioppolo *et al.*[10] who observed much more D_2O_2 than D_2O because of the diffusion of D(H) atoms in the multilayers of O_2 ice. The H_2O (D_2O) products formed on the top of hydrogen peroxide layers desorb into the gas phase by the heat released from the reactions.

The surface structure of the thin D_2O water ice formed on the silicate surface at 10 K from 5 ML of O_2 and 17 ML of D atoms (RAIR spectrum (g), Figure 2 left panel) is not well identified. The absence of a small dangling (–OD) absorption feature around (2730 cm^{-1})[37] (see the arrow in the spectrum (g)) may be due to the high signal to noise ratio. However, the compact (not micro-porous) structure of the newly formed water ices from O_2 + D reaction has been largely studied and confirmed experimentally.[12,38,39]

Knowing the initial coverage of O_2 molecules on the surface and that of D_2O molecules formed from D atoms and O_2 molecules, we have estimated the yields of D_2O molecules formed on the surface as a function of D-atoms exposure times (see Figure 2 right panel). The yield of D_2O defined as the ratio between the amount of D_2O molecules formed on the surface and the amount of D_2O molecules expected to be formed from one molecule of O_2 and four D atoms is given by the following formulae $f_{D_2O} = \frac{D_2O\text{coverage}}{2\times O_2\text{coverage}}$. As shown in this figure, for the very low coverages of O_2 and D atoms, the yield of D_2O is found to be lower than 15% probably because of the uncertainties of the infrared measurements. As soon as the coverage of water ice is about 0.5 ML, the formation yield of D_2O molecules stabilizes at about 20% and stagnates at this value for more than one monolayer coverage of D_2O ice.

It is possible that water molecules in the first monolayer do not cover uniformly the surface of the silicate because of the chemical desorption of the newly formed water molecules, which is enhanced by the metallic substrate. That is why the formation yield of water ice is low (20%). However, the deficiency of D_2O water molecules in some sites on the surface, may create small clustering water molecules[26] that may reduce the formation yield of water in the second and the subsequent layers.

2. TPD results

In these experiments, the surface of the silicate is uniformly covered with one monolayer coverage of solid O_2 at 10 K to eliminate the effect the substrate, and then irradiated with D atoms for several exposure doses (0, 0.9 ML, 1.8 ML, 3.3 ML, and 5.5 ML). In these conditions, D atoms are likely to meet with an O_2 molecule already adsorbed on the surface, react and form O_2D, D_2O_2, OD, and D_2O species via Eley-Rideal mechanism. The competitive $D + D \rightarrow D_2$ reaction with no activation barrier is always possible at low surface temperature,[11] but it is less probable at least as long as oxygen reactive species (O_2, DO_2 D_2O_2, and OD) are present on the surface. These oxygen populations consume D atoms via surface reactions with low energy barriers, reducing therefore the residence time of D atoms on the surface, and their density available for D_2 formation.[9–11,19]

In our experiments, after each D-atoms exposure dose on 1 ML coverage of O_2 ice film, the sample is then heated from 10 K to 220 K. Figures 3(a) and 3(b) left panel show the TPD curves of O_2 between 10 K and 60 K, D_2O between 120 K and 180 K, and D_2O_2 between 140 K and 220 K for different exposure doses of D atoms. By increasing the amount of D-atoms we see clearly the gradual destruction of O_2 molecules adsorbed on the surface, and the growth of D_2O and D_2O_2 ices. We point out that no intermediate species such as O_2D and OD radicals are detected by the QMS while heating the sample.

Figure 3 right panel shows the evolution of the yields (in %) of O_2, D_2O, and D_2O_2 species present on the surface as a function of D-atoms exposure doses on 1 ML coverage of O_2 ice. These yields are estimated from the TPD integrated areas "a" of O_2, D_2O, and D_2O_2 peaks using the following formulaes: $f_{O_2} = 100 \times (aO_2/aO_2$ consumed by D), $f_{D_2O_2} = 100 \times (aD_2O_2/aO_2$ consumed by D), and $f_{D_2O} = 100 \times (aD_2O/2\times aO_2$ consumed by D). As shown in the Figure 3 right panel, after the exposure of ~1.5 ML of D atoms, about 85% of O_2 molecules consumed by D atoms lead to the formation of ~19% of D_2O_2 and ~6% of D_2O on the surface. As four D atoms are required in order to form two molecules of D_2O, a dose four times higher than 1.5 ML of D atoms (i.e., $\sim 4 \times 1.5$ ML = 6 ML) destroys all the O_2 molecules present on the surface and forms only pure D_2O water ice with high efficiency (100%). However, our results show that by increasing the exposure of D atoms until 5.5 ML, the total amount of O_2 molecules destroyed by D atoms reaches 98%, while the yield of D_2O molecules formed on the surface increases up to ~18%.

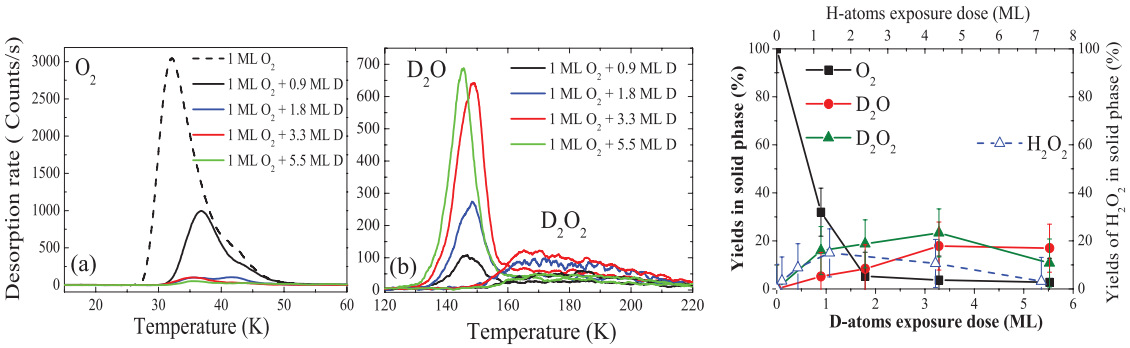


FIG. 3. (Left panel) (a) and (b) the desorption rates of O_2, D_2O, and D_2O_2 species as a function of D-atom exposure doses (0, 0.9 ML, 1.8 ML, 3.3 ML, and 5.5 ML) on 1 ML coverage of O_2 ice film deposited on the silicate surface held at 10 K. (Right panel) The evolution of the yields (in %) of O_2, D_2O, and D_2O_2 species present on the surface of the silicate as a function of D-atom exposure doses. The blue dashed line is the yields (in %) of H_2O_2 molecules present on the surface of the silicate as a function of H-atom exposure doses. The uncertainties of the measurements are marked by the errors bars.

For comparison, Figure 3 right panel displays the yields of H_2O_2 obtained from O_2 + H reaction on the silicate surface held at 10 K for the same experimental conditions. The TPD data are plotted in dashed lines for clarity. We note that H_2O_2 and D_2O_2 have the same behavior for the low coverages of H(D) atoms on the surface ($\leq$1.5 ML). Then by increasing H(D)-atoms exposure doses, the H_2O_2 + H reaction seems to be faster than the D_2O_2 + D one thus suggesting a tunneling process for the reaction (3) on the silicate substrate as previously suggested by Miyauchi *et al.*[9] and Oba *et al.*[12]

Following these results, we suggest that the low amount ($\sim$18%) of D_2O molecules formed on the surface of the silicate cannot be explained only by the tunneling process between D and D_2O_2 species. We should take into account the possible desorption of certain products of the reaction such as DO_2, D_2O_2, OD, and D_2O once the reactions with D atoms occur on the surface. The results of Secs. III A 1 and III A 2 are summarized in Table I for the silicate.

TABLE I. Yields in (%) obtained from TPD and RAIRS experiments of O_2 molecules consumed by D atoms, D_2O, and D_2O_2 molecules formed from the O_2 + D reaction on different substrates held at 10 K: silicate SiOx, np-ASW ice, and p-ASW ice.

	TPD			RAIRS
	$T_{surface} \in [10-220\,K]$			$T_{surface} = 10\,K$
Experiments	O_2,	D_2O_2,	D_2O,	D_2O
Silicate				
1 ML O_2	0	0	0	...
1 ML O_2 + 2.0 ML D	85	5	13	19
1 ML O_2 + 3.3 ML D	96	24	18	...
1 ML O_2 + 5.5 ML D	98	11	17	...
np-ASW ice				
1ML O_2 + 2.0 ML D	79	1	32	63
1ML O_2 + 3.3 ML D	85	5	55	...
p-ASW ice				
1 ML O_2 + 2.0 ML D	60	0.1	28	45

B. Effect of the substrate on the efficiency of the O_2 + D reaction

In Sec. VI, RAIRS results showed that the yield of D_2O water molecules formed from O_2 and D atoms on the silicate substrate held at 10 K reaches a steady state of $\sim$20% regime once the D_2O water ice coverage grows up to $\sim$0.5 ML. Such a result is supported by TPD experiments and stresses the ability of the silicate surfaces to desorb newly formed water species into the gas phase even for low surface coverages. In order to confirm these observations related to bare silicate grains, we have investigated the formation of the first D_2O water molecules from 1 ML coverage of O_2 and 2 ML of D atoms on two substrates with different compositions (bare silicate and water ices). In dark interstellar clouds, dust grains are covered with icy mantles mainly composed of amorphous water ice whose morphology still remains poorly known. So we have also studied the formation of D_2O water molecules on two types of amorphous water ices surfaces (porous amorphous water ice with a large effective surface area available for the adsorption and the nonporous (or compact) amorphous water ice). Thanks to the mobility of D atoms on the surface at 10 K, the formation of D_2O water ice via O_2 + D reaction has been already observed experimentally in the submonolayer regime on porous water ice surfaces by Matar *et al.*[11]

1. *RAIRS results*

Figure 4 displays the RAIR spectra recorded in the –OD stretching region after the exposure of 2.0 ML of D atoms on 1 ML coverage of O_2 ice film adsorbed on three substrates held at 10 K: amorphous silicate (spectrum (a)), p-ASW ice film with 10 ML of thickness (spectrum (b)), and np-ASW ice film with 50 ML of thickness (spectrum (c)). Here, the ratio D/O_2 between the deposition of D atoms and O_2 molecules is taken to be 2 and the flux of D atoms is 3.0×10^{12} atoms cm^{-2} s^{-1}.

As shown in Figure 4, the three spectra show a broad absorption band at around 2400 cm^{-1} attributed to D_2O water ice overlapping D_2O_2 molecules. The strong absorption bands observed in spectra (b) and (c) are an indication that

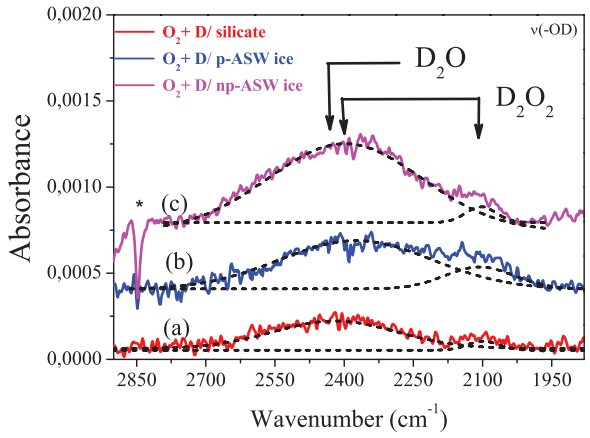


FIG. 4. RAIRS spectra of D_2O and D_2O_2 ices formed after the exposure of 1 ML of solid O_2 and 2.0 ML of D atoms on different substrates held at 10 K: (a) amorphous silicate, (b) p-ASW ice, and (c) np-ASW ice. The dashed curves are the Gaussian fits. (The star at 2850 cm^{-1} is an impurity.)

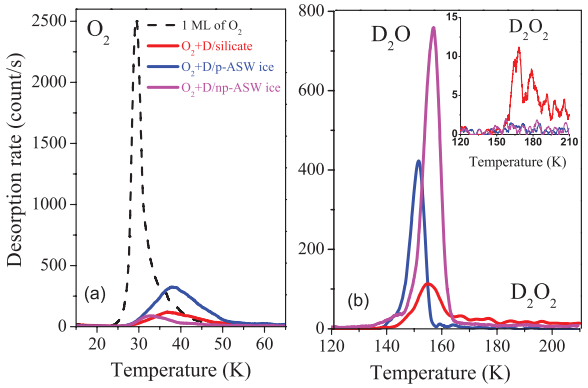


FIG. 5. Desorption peaks of D_2O, D_2O_2, and O_2 obtained after the exposure of 1 ML of O_2 and 2.0 ML of D atoms coverages on different substrates held at 10 K: red color (silicate), blue color (p-ASW ice), and magenta (np-ASW ice). The inset shows the TPD curves of D_2O_2 formed on three substrates.

the amounts of D_2O molecules formed both on p-ASW and np-ASW ices are higher than that formed on bare silicate substrate. The shoulder at 2105 cm^{-1} is clear evidence for D_2O_2 molecules formed from the $O_2 + D$ reaction.

Since D_2O band overlaps with D_2O_2, a multi-Gaussian fit is used to separate the contributions of D_2O at 2400 cm^{-1} and D_2O_2 at 2105 cm^{-1}, and to determine the area of the individual bands. The proportions between the different integrated area of D_2O bands are found to be 3.5/2.3/1, for np-ASW, p-ASW, and silicate, respectively. By dividing the area of the broad absorption bands at 2400 cm^{-1} by the integrated area of D_2O water peak corresponding to 1 ML coverage (not shown in Figure 4), we estimated the amount of D_2O water molecules formed on each substrate held at 10 K to be ~0.37 ML on the silicate surface, ~0.89 ML on the p-ASW ice, and ~1.25 ML on np-ASW ice surfaces. These results give preliminary estimations for the yields of the species formed on the surface. It appears that ~19% of the newly formed D_2O molecules remain on the silicate surface, while ~45% of D_2O molecules reside on the p-ASW ice, and ~63% on the np-ASW ice surfaces (see Table I).

2. TPD results

After the exposure of 2.0 ML of D atoms at 10 K on one monolayer coverage of O_2 ice film, the sample is then heated from 10 K to 220 K until the complete desorption of the species implicated in the $O_2 + D$ reaction. Figures 5(a) and 5(b) display for three substrates (silicate, p-ASW ice, and np-ASW ice films) the TPD curves of O_2, D_2O, and D_2O_2 molecules.

By comparing TPD curves of solid O_2 before and after D atoms irradiation for different substrates, we can assume from Figure 5(a) that ~85% of O_2 molecules adsorbed both on silicate and np-ASW ice film are consumed by D atoms, while ~60% of O_2 molecules present on the p-ASW ice are destroyed after the exposure of 2.0 ML of D atoms. The high amount (~40%) of O_2 molecules not struck by D atoms on the porous water ice can be explained by the lack of some D atoms on the surface because of their diffusion at 10 K in the micro-pores structures of the water ice film.[11]

In addition, Figure 5(b) displays the desorption peaks of D_2O molecules formed on three substrates. The blue and the magenta peaks of D_2O molecules are corrected from the contribution of HDO molecules (not shown in the figure), produced by isotopic exchange during heating sample between the newly formed D_2O molecules and the H_2O molecules of water substrates.[18] The inset in Figure 5(b) shows a small desorption peak of D_2O_2 molecules between 160 K and 210 K mainly for the silicate substrate. While the RAIR spectra in Figure 4 revealed the presence of D_2O_2 peak at 2107 cm^{-1} for the three substrates at 10 K (spectra (a)–(c)), the D_2O_2 products formed on each substrate are not converted to D_2O water ice either by lack of D atoms, or by the presence of a high activation barrier for the $D_2O_2 + D$ reaction. However, the quasi absence of D_2O_2 desorption peaks both for p-ASW and np-ASW ices (see Figure 5(b)) can be explained by the possible isotopic exchange between the newly formed hydrogen peroxide D_2O_2 and the H_2O molecules of water substrates during the heating phase of the sample. In fact, some other isotopic species than HDO (m/z = 19) have been observed as traces in our TPD experiments mainly with the porous and the nonporous water ices substrates, such as HDO_2 (m/z = 35) and H_2O_2 (m/z = 34), but their desorption peaks are not shown in Figure 5(b).

Knowing the TPD integrated area of the newly formed D_2O molecules and that of O_2 molecules consumed by D atoms, we have estimated the yields of D_2O molecules formed on each substrate to be 32% on np-ASW ice, 28% on p-ASW ice, and only 13% on the silicate substrate. These estimations are slightly lower than those previously obtained by RAIRS measurements.

Further TPD experiments were performed on the silicate and np-ASW ice substrates held at 10 K by lowering the flux of D-atoms to 2.5×10^{12} molecules cm^{-2} s^{-1} and increasing the D-atoms exposure doses up to 3.3 ML on one monolayer coverage of O_2. In this case, we observe much more D_2O_2 not converted into water ice on silicate substrate compared to the previous experiments performed with higher D-atom flux.

The TPD results showed the formation of 18% of D_2O and 24% of D_2O_2 on the silicate substrate at 10 K when most of O_2 molecules (96%) are consumed by D-atoms. While in the case of the np-ASW ice substrate, the yield of D_2O molecules reaches its maximum of about 55% and that of D_2O_2 5% when 85% of O_2 molecules are destroyed by D-atoms. Table I summarizes for the different substrates (silicate, np-ASW ice, and p-ASW ice) held at 10 K the yields of D_2O, D_2O_2, and O_2 species present on the surface after D-atoms exposure on 1 ML coverage of O_2 ice film. Table I shows that the TPD yields for D_2O water formation for the same experiments are always lower than the RAIRS ones because of the upper limits of water formation abundances by RAIRS measurements as previously mentioned in Sec. III A 1.

As previously stated, the combination of D_2O and D_2O_2 absorption modes in the –OD stretching region leads to an over-estimation of the RAIR water formation yields. Table I also shows that for the same TPD experiments, the very low yields of D_2O_2 for p- and np-ASW ices compared to silicate substrate, may result from an isotopic exchange between D_2O_2 and H_2O molecules of water ices substrates.

In addition, the low formation yields of D_2O by TPD experiments in comparison to the yields measured by RAIRS (see Table I), may be explained by the isotopic exchange between D_2O and H_2O water molecules of porous and non-porous ices between (140 and 160 K), leading to the formation of HDO species ($D_2O + H_2O \rightarrow 2HDO$).

C. The chemical desorption process of water

We have experimentally observed the desorption upon formation of D_2O molecules from the silicate substrate held at 10 K once the reaction occurs between O_2 and D atoms. Figure 6 shows the signal of D_2O (m/z = 20) as well as the signals of OD (m/z = 18) and D_2 (m/z = 4) species monitored in the gas phase with the QMS (placed very close to the sample) during 37 min (2220 s) of D-atoms on 1 ML of O_2 ice.

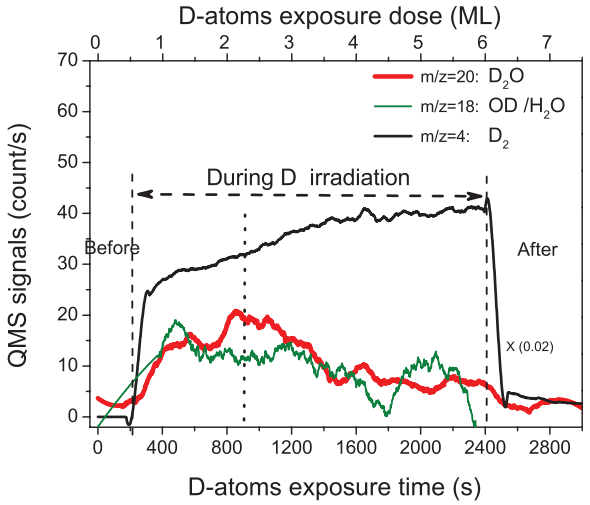


FIG. 6. The signals of D_2O, OD, and D_2 species monitored by the QMS in the gas phase during 37 min of D-atoms exposure on 1 ML coverage of O_2 ice deposited on the silicate surface held at 10 K.

The signal of mass (m/z = 18) is noisy and can be attributed either to OD products released into the gas phase and/or H_2O molecules present as an impurity in the vacuum chamber. Figure 6 also shows that during the first 1000 s of D-atoms exposure, the amount of the newly formed D_2O molecules which are released from the surface into the gas phase increases and reaches a maximum of desorption, meaning that the formation of D_2O water molecules occurs efficiently on the surface of the silicate in the beginning of the D irradiation phase, and probably through the barrierless $D + OD \rightarrow D_2O$ reaction. Afterwards, by increasing the D-atoms irradiation time until 2200 s, the signal of the newly formed D_2O molecules desorbing into the gas phase decreases gradually as the surface is depleted in O_2 molecules. We note that no desorption into the gas phase of DO_2 and D_2O_2 species was observed in this experiment during all the D-atoms exposure phase.

In parallel, Figure 6 also shows the increase in the signal of D_2 species during the exposure phase of D atoms, which corresponds to the desorption into the gas phase of D_2 molecules. The linear increase of D_2 molecules in the gas phase is enhanced by the increase of the coverage of D atoms and D_2 molecules coming either from the fraction (30%) of the non-dissociated deuterium molecules from the D atomic beam, or from the fraction of D atoms that recombine with other D atoms on the surface of the silicates and form D_2 by the exothermic D + D reaction. It is difficult to estimate the contribution of D_2 molecules due exclusively to D + D reaction taking place on the sample, since D atoms are also consumed by the oxygen species (O_2, DO_2, OD, D_2O_2) present on the surface forming thus D_2O ice which is released from the surface by chemical desorption. Even if D_2 are formed on the surface at 10 K, the local energy released from the D + D reaction does not affect the desorption of the newly formed D_2O and the other products.

The D_2 species that are stuck on the surface at 10 K do not react with O_2 molecules already adsorbed on the surface because of the very high activation barrier of the reaction.[26] The absence of any product when D_2 beam is exposed to O_2 ice has been already confirmed experimentally by Miyauchi *et al.*[9] and Cuppen *et al.*[13]

Moreover, Cuppen *et al.*[13] have suggested in their discussions using hydrogen instead of deuterium that some H_2 molecules present on the surface may react with reactive species not desorbed into the gas phase such as HO_2 and OH radicals and form H_2O_2 and H_2O, respectively, through the following reactions $H_2 + HO_2 \rightarrow H_2O_2 + H$ and $H_2 + OH \rightarrow H_2O + H$. But the efficiency of these reactions were below the detection limit.

IV. ANALYSIS AND DISCUSSIONS

RAIRS and TPD results show that the formation of water molecules on cold surfaces through O_2 + D pathway is efficient in the sub-monolayer and monolayer regimes, but the fraction of the newly formed D_2O molecules which remains in the solid phase on the surface depends significantly on the substrate (see Table I).

In the case of the silicate substrate, the fraction of D_2O water molecules that stays on the surface at 10 K upon formation through O_2 + D reaction is about 17% of the total amount of D_2O molecules expected to be formed on the surface from 1 ML of O_2 and 5.5 ML of D-atoms (see Table I). As previously mentioned in Sec. III C, the lack of D_2O molecules (∼83%) on the surface of the silicate results from the desorption into the gas phase of newly formed D_2O molecules.

Many factors enhance the desorption of species from a substrate: the surface roughness, the binding energies of the final products in the physisorbed sites of the surface, and mainly the energy of formation released from the exothermic reactions.

We have estimated the binding energies of D_2O and D_2O_2 molecules from our TPD experiments using the Polanyi-Wigner equation[40]

$$-\frac{dN}{dt} = r = AN^n exp(-E_d/k_BT), \tag{8}$$

where r is the rate of desorption, N is the number of molecules adsorbed, n is the order of reaction, E_d is the desorption energy, k_B is the Boltzmann constant, and T is the absolute temperature of the surface. Assuming $n = 0$ for water desorption in the sub-monolayer regime, the pre-exponential factor A is taken to be 10^{13} s^{-1}. The binding energies of species adsorbed on the silicate surface are estimated to be (465 ± 10) meV for D_2O and (525 ± 20) meV for D_2O_2 molecules and they are in agreement with the estimations of Jing *et al.*[19] on amorphous silicates held at 15 K. These values are also very close to the binding energies obtained from our estimations on nonporous amorphous water ice substrate for D_2O (480 ± 10) meV and D_2O_2 (520 ± 40) meV confirming thus the compact structure of our silicate surface.

In the case of the amorphous water ice substrates, the process of desorption upon formation is less significant than previously mentioned on bare grain silicates. It is possible that the catalytic effect of the water ice substrate enhances the reaction rates between D and O_2 by increasing the binding energies and reducing the exothermicity of the reactions. Such a catalytic effect of amorphous water ice has been demonstrated experimentally and theoretically by Hidaka, Kouchi, and Watanabe[41] for the successive H + CObrk reactions. As a result of this effect, the newly formed species (O_2D, OD, D_2O_2, and D_2O) are likely to remain trapped on the surface sites of the amorphous water ice and dissipate their excess energy of formation on the surface until the thermalization.[26] These assumptions are in agreement with Jones and Williams[42] who suggested that the product of the reactions $O + H \rightarrow OH$ and $OH + H \rightarrow H_2O$ should be retained on the grains with a probability of 70% and 100% for grain-mantle formation in dense clouds.

A. Possible reactions routes for water formation

We demonstrated experimentally that the efficiency of water formation through O_2 + D pathway depends significantly on the substrate (silicates or amorphous water ice) held at 10 K. Figure 7 illustrates the possible reaction routes for the formation of solid D_2O water ice on the silicate substrate involving O_2 and D atoms. As shown in Figure 7, the impinging D atoms are likely to react via Eley-Rideal mechanism with oxygen O_2 molecules adsorbed on the surface or with the newly formed species DO_2, D_2O_2, and OD. All these reactions are in competition with the $D + D \rightarrow D_2$ reaction leading to the formation of D_2 molecules either via E-R mechanism between a D atom already adsorbed on the surface and an impinging D atom coming from the gas, or Langmuir-Hinshelwood mechanism between two adsorbed D-atoms on the surface. D atoms start to react with O_2 molecules with one monolayer coverage and form DO_2 products. The reaction involving DO_2 and D atoms may proceed through two alternative pathways. The first pathway $D + DO_2 \rightarrow 2OD$ (9) leading to 2OD intermediates has been recently highlighted by Cuppen *et al.*[13] for the hydrogen species

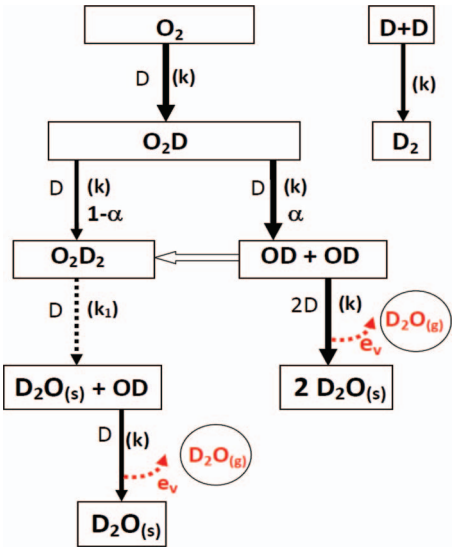


FIG. 7. Schematic illustration showing the possible reaction routes for the formation of solid D_2O involving O_2 and D atoms. The solid and the broken black arrows indicate the reactions without and with activation barriers, respectively. Thick arrows denote reactions investigated in the present study. White arrow indicates the reaction which is less probable on bare silicate substrate than on amorphous water ice. D_2O molecules desorbed in the gas phase upon formation are enclosed in circles. k is the rate constants of all the reactions without activation barrier and k_1 the rate constant of the reaction with barrier. α is the branching ratio of the reaction $D + DO_2$, and e_v denotes the evaporation of D_2O into the gas phase upon formation.

$$D + DO_2 \rightarrow OD + OD. \tag{9}$$

This exothermic reaction with an enthalpy $\Delta H = \sim -1500$ meV seems to be predominant over the second classical pathway $D + DO_2 \rightarrow D_2O_2$ with higher activation barrier ($\Delta H = -3540$ meV), because it favors both the formation of water ice through OD + D and its chemical desorption into the gas phase. If the two OD radicals are formed in pairs in the same reaction,[13] they can react together because they are very close to each other, and form D_2O_2 molecules on the surface following this reaction $OD + OD \rightarrow D_2O_2$ which has been recently evidenced by Cuppen *et al.*[13] and Jing *et al.*[19] Otherwise, the two OD intermediates react with D atoms and form D_2O water molecules through the $D + OD \rightarrow D_2O$ reaction without activation

barrier. We note that in the case of the silicate substrate, the two OD radicals are likely to be formed separately, and their association via Langmuir-Hinshelwood mechanism is difficult because of their low mobility at 10 K. This situation is different on amorphous water ice substrate, where the diffusion of the OD intermediates at low surface temperature can be enhanced by the hydrogen bonds of the nearest water molecules composing the substrate.

So most of D_2O molecules formed on the silicate surface from the barrierless D + OD reaction are likely to desorb into the gas phase upon formation because of the sufficient heat released from the exothermic reaction ($\Delta H = -4290$ meV). The formation of D_2O water molecules through $D + D_2O_2 \rightarrow D_2O + OD$ reaction is also possible but less probable because of the high activation barrier (~2000 K)[17] of the reaction. However, the amount of D_2O molecules formed slowly by quantum tunneling process during the D atoms irradiation is likely to remain on the surface, while some of OD radicals may react with D atoms coming from the gas phase or already adsorbed on the surface and form D_2O molecules without barrier. This scenario is in agreement with our previous TPD results concerning the slow evolution of D_2O_2 and D_2O species on the surface with the increase of D atoms exposure on 1 ML of O_2 ice (see Sec. III A 2, Figure 3 right panel).

In the case of the amorphous water ice substrates held at 10 K (porous and nonporous water ices), additional reaction routes can be suggested in order to explain the high percentages (42%–60%) of D_2O water formation on these surfaces through O_2 + D channel. In particular, the subsequent reaction $OD + OD \rightarrow D_2O_2$ seems to be non-negligible on the amorphous water ice, and can contribute efficiently to the formation of D_2O water molecules on the surface through the following deuteration reactions:

$$O_2 \xrightarrow{D} O_2D \xrightarrow{D} OD + OD \xrightarrow{D} D_2O_2 \xrightarrow{D} D_2O + OD. \quad (10)$$

Some OD radicals either react with D atoms to form D_2O molecules through the barrierless OD + D reaction (see Figure 7), or with some D_2 molecules present on the surface and form new D_2O molecules via reaction (11) with high activation barrier of ~2100 K[16,17]

$$D_2 + OD \rightarrow D_2O + D. \quad (11)$$

B. Modeling the O_2 + D reaction on the silicates

In order to confirm our previous suggestions concerning the effect of the desorption of the newly formed oxygen species on the efficiency of water formation through O_2 + D pathway, a simple kinetic chemical model was developed to reproduce our TPD experimental results for the reaction of O_2 with D on the silicate substrate held at 10 K. The model is made to fit the amounts $[O_2]$, $[D_2O_2]$, and $[D_2O]$ (in ML) of O_2, D_2O_2, and D_2O species present on the surface of the silicate sample as a function of D-atoms exposure doses (0, 0.9 ML, 1.8 ML, 3.3 ML, and 5.5 ML) on 1 ML coverage of O_2 ice film (see Sec. III A 2 and Figure 3 left panel).

Contrary to O_2 and D_2O species, we were not able to measure by TPD experiments the coverage in (ML) of D_2O_2 ice on the surface, the calibration of D_2O_2 beam was not possible. We then estimated the fractions in monolayer of the species present on the surface by normalization to the amount of O_2 in 1 ML exposure coverage, see the following formulae: $[O_2]$ = area O_2/(area of 1 ML O_2), $[D_2O_2]$ = area D_2O_2/(area of 1 ML O_2), and $[D_2O]$ = area D_2O/(area of 1 ML O_2). The experimental data are plotted in Figure 8.

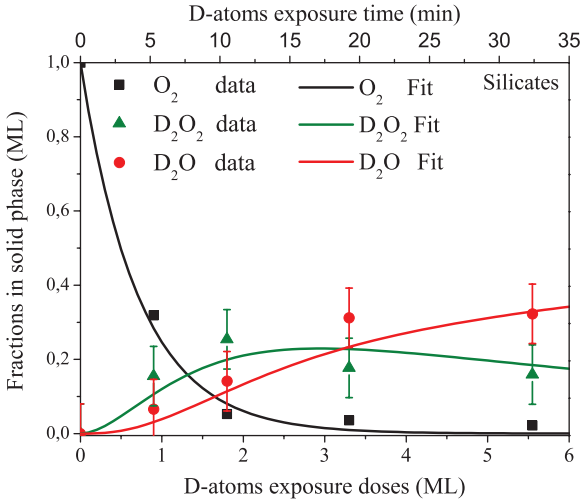


FIG. 8. (Full triangles, circles, and squares) The amount (in ML) of O_2, D_2O, and D_2O_2 species present on the surface as a function of D-atoms exposure doses on 1 ML coverage of O_2 ice deposited on the silicate sample at 10 K. (Solid lines) The fits of O_2, D_2O, and D_2O_2 obtained from the model with $\alpha = 0.69$, $k = 1$, $k_1 = 0.09$, $\mu = 1$, $\mu_1 = 0.14$, and the fraction of D_2O desorbed from upon formation by the exothermic OD + D reaction is $e_v = 86\%$. The uncertainties are given by the errors bars which are equal to 0.08 for D_2O and 0.1 for D_2O_2.

The model is described by the following reaction routes which are illustrated in Figure 7 of Sec. IV A

$$D + O_2 \xrightarrow{k} DO_2, \quad (12)$$

$$D + DO_2 \xrightarrow{k,(\alpha)} OD + OD, \quad (13)$$

$$D + DO_2 \xrightarrow{k,(1-\alpha)} D_2O_2, \quad (14)$$

$$D + D_2O_2 \xrightarrow{k_1} D_2O + OD, \quad (15)$$

$$D + OD \xrightarrow{k} D_2O. \quad (16)$$

The rate equations for the amount of O_2, O_2D, D_2O_2, OD, and D_2O species present on the surface are given by

$$\frac{d[O_2]}{dt} = -n_D k[O_2], \quad (17)$$

$$\frac{d[O_2D]}{dt} = n_D(\mu k[O_2] - k[O_2D]), \quad (18)$$

$$\frac{d[O_2D_2]}{dt} = n_D\left[(1-\alpha)\mu k[O_2D] - k_1[O_2D_2])\right], \quad (19)$$

$$\frac{d[D_2O]}{dt} = n_D(\mu k_1[D_2O_2] + \mu_1 k[OD]), \quad (20)$$

$$\frac{d[OD]}{dt} = n_D(2\alpha\mu k[O_2D] + \mu k_1[O_2D_2] - k[OD]). \quad (21)$$

We assume that D atoms coming from the gas phase react via Eley-Rideal mechanism with oxygen molecules covering the sample or with molecules previously formed. Where $n_D = 2\tau\phi = 3.4 \times 10^{12}$ molecules cm^{-2} s^{-1} is the number of D-atoms per second coming from the gas phase and hitting the surface (ϕ is the flux of deuterium molecules and $\tau = 70\%$ is the dissociation rate of the D_2 beam). k is the rate constant of the reactions (12)–(14) and (16), which are supposed to take place without a barrier. k_1 is the rate constant of Eq. (15) with activation barrier. The μ and μ_1 coefficients are the fractions of just formed species, for each reaction, which stay adsorbed on the sample. μ corresponds to the fraction of the newly formed species through the reactions (12), (13), and (15), and μ_1 that of D_2O formed through the reaction (16). In order to keep the model as simple as possible we assumed $\mu = 1$ and $\mu_1 = 0.14$ from the experiments, so 86% of D_2O molecules desorbs into the gas phase upon formation. The idea was that the main contribution to the desorption is due to D_2O formed through reaction OD + D (16). Reaction (13) may proceed through two alternative pathways, and α is the branching ratio (see Figure 7).

In our model, we assumed $k = 1$ and fitted our data using α and k_1 as free parameters. Figure 8 shows the kinetic curves obtained from the model (plotted in solid lines) for O_2, D_2O_2, and D_2O. The best fit is obtained with $\alpha = 0.69$ and $k_1 = 0.09$, and it is always better for D_2O than D_2O_2 because of the high uncertainty in the TPD measurements of hydrogen peroxide peak. The ratio of the reaction rate constants $k_1/k = 0.09$ for $D + O_2$ and $D + D_2O_2$ reactions is found to have the same order of magnitude as that obtained (0.04) by the gas-surface model of Miyauchi *et al.*[9]

The model shows that the evolution of O_2 molecules on the surface follows an exponential decay, and that ∼95% of O_2 molecules destroyed by ∼1.8 ML of D-atoms produce about 0.1 ML of D_2O ice and 0.2 ML of D_2O_2. The presence of D_2O_2 species on the surface even after a high exposure dose (5.5 ML) of D-atoms is an indication that the conversion of D_2O_2 into D_2O molecules occurs slowly through reaction (15) which proceeds through tunneling process. Although the reaction $D + OD \rightarrow D_2O$ is very efficient on cold silicate surface, Figure 8 shows the presence of only ∼0.30 ML of solid D_2O after the destruction of the oxygen ice by D atoms. This observation is well explained by the high desorption rate (88%) of water species. The most efficient pathway for water formation on the silicate substrate is through the formation of two OD radicals from Eq. (13) and the subsequent reaction (16) between OD and D atoms.

The reaction $D + OD \rightarrow D_2O$ is highly exothermic and is then enable to release into the gas most (∼90%) of D_2O molecules upon its formation on the surface. The formation of D_2O water ice from D + OD reaction and through 2OD as intermediates can explain our previous experimental results concerning the desorption of a large amount of D_2O molecules into the gas phase, mainly at the beginning (∼1000 s) of the D atoms-irradiation phase of O_2 ice film (1 ML) (see Figure 6).

As D atoms react with oxygen molecules without an activation barrier and in the experiments on a silicate substrate, we have initially one monolayer of O_2 on the sample, the formation of D_2 is highly improbable. So, even if included in our reaction scheme (see Figure 7), D + D reaction does not affect the fits of O_2, D_2O_2, and D_2O in Figure 8.

V. ASTROPHYSICAL IMPLICATIONS

Our results have a great relevance in astrochemistry. We demonstrated for the first time from the experiments that water formation in the sub-monolayer and monolayer regimes can occur on bare amorphous silicates grains under interstellar conditions through surface reactions between atomic hydrogen and molecular oxygen. However, the desorption of species upon formation induced by the heat released from the exothermic reactions affects the efficiency of water formation on bare silicate grains at 10 K. Such a process revealed in this work is considered as the first evidence for the chemical desorption of water molecules in astrophysical environments where dust grains are composed of silicates. The result of our work shows that bare silicate surfaces have a large propensity to release species into the gas phase upon formation. In the ISM, the desorption of water molecules upon formation on dust grains is enhanced by the strong UV radiations field which dissociate the remaining molecules into radicals such as OH, O, and H. These newly intermediate species produce again water ices that desorb into the gas phase by the exothermic surface reactions. Following this desorption process of water, the formation of the first monolayer of water ice on bare grain surfaces such as amorphous silicates requires very long timescales to be grown. The time required to form the first layer of water ice in diffuse clouds is estimated to vary between (∼10^4 years)[26] and (∼10^6 years)[7] according to Monte Carlo simulations.

VI. CONCLUSIONS

We have studied experimentally the initial stages of water formation through O_2 + D reaction on amorphous silicate surfaces analogous to bare dust grains in diffuse clouds. Co-deposition experiments of O_2 and D atoms on the silicate substrate held at 10 K, in the condition $[D]/[O_2] \sim 4$ have showed an effective formation of D_2O_2 and D_2O molecules in the sub-monolayer and monolayer regimes. RAIRS results showed that the yield of D_2O water ice formed on the surface reaches ∼20%.

The kinetic studies performed by TPD experiments for the deuteration of one monolayer of O_2 film, have revealed a H(D) isotopic effect for the formation of water through reaction (3) with activation barrier. The $D + D_2O_2$ reaction occurring with tunneling process is much slower than $H + H_2O_2$ reaction.

RAIRS and TPD experiments also showed that the efficiency of D_2O water formation via Eley-Rideal mechanism between O_2 molecules adsorbed on the surface and D atom coming from the gas, depends strongly on the substrate whether it is composed of silicate or amorphous (H_2O) water ice film analogous to dense molecular clouds. The fraction of D_2O water ice formed on the surface of the silicate at 10 K was found to be ∼20%, two and three times lower than the fractions of D_2O water molecules formed on the porous amorphous water ice (∼45%) and the nonporous amorphous water ice (∼55%–60%) surfaces, respectively. It is possible that the catalytic effect of the water ice substrate enhances the reaction rates between D and O_2 by reducing the activation barriers and the exothermicity of the reactions.

A schematic reactions routes for water formation through $O_2 + D$ pathway is proposed. It privileges the formation of two OD intermediates. Water ice is mainly formed on the silicate surface at 10 K through the barrierless and the exothermic $D + OD \rightarrow D_2O$ reaction. Experiments have evidenced the desorption into the gas phase of more than (∼85%) of D_2O water molecules upon formation on the surface through the $OD + D$ reaction. The high desorption rate of water molecules results from the excess energy released from the exothermic $OD + D$ reaction. Such a chemical desorption of water ice from the silicates was supported by a kinetic model.

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[1]E. L. Gibb, D. C. B. Whittet, A. C. A. Boogert, and A. G. G. M. Tielens, Astrophys. J. Soc. **151**, 35 (2004).
[2]T. I. Hasegawa, E. Herbst, and C. M. Leung, Astrophys. J. Soc. **82**, 167 (1992).
[3]A. G. G. M. Tielens and W. Hagen, Astron. Astrophys. **114**, 245 (1982).
[4]D. Li, P. F. Goldsmith, and K. Menten, Astrophys. J. **587**, 262 (2003).
[5]H. Mokrane, H. Chaabouni, M. Accolla, E. Congiu, F. Dulieu, M. Chehrouri, and J. L. Lemaire, Astrophys. J. Lett. **705**, L195 (2009).
[6]D. Hollenbach, M. J. Kaufman, E. A. Bergin, and G. J. Melnick, Astrophys. J. **690**, 1497 (2009).
[7]H. M. Cuppen and E. Herbst, Astrophys. J. Lett. **668**, 294 (2007).
[8]C. Romanzin, S. Ioppolo, H. M. Cuppen, E. F. van Dishoeck, and H. Linnartz, J. Chem. Phys. **134**, 084504 (2011).
[9]N. Miyauchi, H. Hidaka, T. Chigai, A. Nagaoka, N. Watanabe, and A. Kouchi, Chem. Phys. Lett. **456**, 27 (2008).
[10]S. Ioppolo, H. M. Cuppen, C. Romanzin, E. F. van Dishoeck, and H. Linnartz, Astrophys. J. **686**, 1474 (2008).
[11]E. Matar, E. Congiu, F. Dulieu, A. Momeni, and J. L. Lemaire, Astron. Astrophys. **492**, L17 (2008).
[12]Y. Oba, N. Miyauchi, H. Hidaka, T. Chigai, N. Watanabe, and A. Kouchi, Astrophys. J. **701**, 464 (2009).
[13]H. M. Cuppen, S. Ioppolo, C. Romanzin, and H. Linnartz, Phys. Chem. Chem. Phys. **12**, 12077 (2010).
[14]S. Ioppolo, H. M. Cuppen, C. Romanzin, E. F. van Dishoeck, and H. Linnartz, Phys. Chem. Chem. Phys. **12**, 12065 (2010).
[15]J. Troe and V. G. Ushakov, J. Chem. Phys. **128**, 204307 (2008).
[16]R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe, Atmos. Chem. Phys. **4**, 1461 (2004).
[17]Y. Oba, N. Watanabe, T. Hama, K. Kuwahata, H. Hidaka, and A. Kouchi, Astrophys. J. **749**, 67 (2012).
[18]F. Dulieu, L. Amiaud, E. Congiu, J.-H. Fillion, E. Matar, A. Momeni, V. Pirronello, and J. L. Lemaire, Astron. Astrophys. **512**, A30 (2010).
[19]D. Jing, J. He, J. Brucato, A. De Sio, L. Tozzetti, and G. Vidali, Astrophys. J. Lett. **741**, L9 (2011).
[20]B. T. Draine, Annu. Rev. Astron. Astrophys. **41**, 241 (2003).
[21]D. Williams and E. Herbst, Surf. Sci. **500**, 823 (2002).
[22]F. Kemper, A. J. Markwick, and P. M. Woods, Mon. Not. R. Astron. Soc. **413**, 1192 (2011).
[23]T. P. M. Goumans, C. R. A. Catlow, W. A. Brown, J. Kästner, and P. Sherwood, Phys. Chem. Chem. Phys. **11**, 5431 (2009).
[24]F. Dulieu, E. Congiu, J. Noble, S. Baouche, H. Chaabouni, A. Moudens, M. Minissale, and S. Cazaux, "How micron-sized dust particles determine the chemistry of our Universe," Sci. Rep. (unpublished).
[25]R. T. Garrod, V. Wakelam, and E. Herbst, Astron. Astrophys. **467**, 1103 (2007).
[26]S. Cazaux, V. Cobut, M. Marseille, M. Spaans, and P. Caselli, Astron. Astrophys. **522**, A74 (2010).
[27]E. A. Bergin, G. J. Melnick, J. R. Stauffer, M. L. N. Ashby, G. Chin, N. R. Erickson, P. F. Goldsmith, M. Harwit, J. E. Howe, S. C. Kleiner, D. G. Koch, D. A. Neufeld, B. M. Patten, R. Plume, R. Schieder, R. L. Snell, V. Tolls, Z. Wang, G. Winnewisser, and Y. F. Zhang, Astrophys. J. Lett. **539**, L129 (2000).
[28]S. Baouche, Ph.D. dissertation, University of Cergy, 2004, see http://www3.u-cergy.fr/LERMA-LAMAP/theses/Saoud_BAOUCHE_2004.pdf.
[29]L. Amiaud, F. Dulieu, J.-H. Fillion, A. Momeni, and J. L. Lemaire, J. Chem. Phys. **127**, 144709 (2007).
[30]J. L. Lemaire, G. Vidali, S. Baouche, M. Chehrouri, H. Chaabouni, and H. Mokrane, Astrophys. J. Lett. **725**, L156 (2010).
[31]E. Congiu, H. Chaabouni, C. Laffon, P. Parent, S. Baouche, and F. Dulieu, J. Chem. Phys. **137**, 054713 (2012).
[32]Z. Djouadi, L. D'Hendecourt, H. Leroux, A. P. Jones, J. Borg, D. Deboffle, and N. Chauvin, Astron. Astrophys. **440**, 179 (2005).
[33]F. M. Hoffman, "Infrared reflection-absorption spectroscopy of adsorbed molecules," Surf. Sci. Rep. **3**, 107 (1983).
[34]D. King and M. G. Wells, Surf. Sci. **29**, 454 (1972).
[35]H. Chaabouni, H. Bergeron, S. Baouche, F. Dulieu, E. Matar, E. Congiu, L. Gavilan, and J. L. Lemaire, Astron. Astrophys. **538**, A128 (2012).
[36]H. Uehara, K. Kawaguchi, and E. Hirota, J. Chem. Phys. **83**, 5479 (1985).
[37]S. Hawkins, G. Kumi, S. Malyk, H. Reisler, and C. Wittig, Chem. Phys. Lett. **404**, 19 (2005).
[38]M. Accolla, E. Congiu, F. Dulieu, G. Manicò, H. Chaabouni, E. Matar, H. Mokrane, J. L. Lemaire, and V. Pirronello, Phys. Chem. Chem. Phys. **13**, 8037 (2011).
[39]M. Accolla, H. Chaabouni, E. Congiu, F. Dulieu, J. L. Lemaire, G. Manicò, and V. Pirronello, "Morphology of the solid water synthesized through the pathway $D + O_2$ studied by the sensitive TPD technique," Mon. Not. R. Astron. Soc. (submitted).
[40]T. Zubkov, R. S. Smith, T. R. Engstrom, and B. D. Kay, J. Chem. Phys. **127**, 184707 (2007).
[41]H. Hidaka, A. Kouchi, and N. Watanabe, J. Chem. Phys. **126**, 204707 (2007).
[42]A. P. Jones and D. A. Williams, Mon. Not. R. Astron. Soc. **209**, 955 (1984).