

Quantum mechanical investigation on the formation of silicate building blocks on interstellar ice mantles

A. Gelli,^{1,2} J. Perrero,^{1,2,3} S. Ferrero,⁴ J. Enrique-Romero,⁵ C. Ceccarelli^{1,6}, P. Ugliengo^{1,2},
N. Balucani^{1,3★} and A. Rimola^{1,7★}

¹Department de Química, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Catalonia, Spain

²Department of Chemistry, Interdepartmental Centre NIS, University of Torino, via P. Giuria 7, I-10125 Torino, Italy

³Dipartimento di Chimica, Università degli Studi di Perugia, via dell' Elce di Sotto 8, I-06123 Perugia, Italy

⁴Muséum National d'Histoire Naturelle, Institut de Recherche pour le Développement, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Université, UMR CNRS 7590, F-75252 Paris, France

⁵Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, NL-2300 RA Leiden, the Netherlands

⁶Université Grenoble Alpes, CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), F-38000 Grenoble, France

⁷Accademia delle Scienze di Torino, Via Maria Vittoria, 3, I-10123 Torino, Italy

Accepted 2025 July 17. Received 2025 July 16; in original form 2025 June 3

ABSTRACT

Silicon monoxide (SiO), a diatomic molecule present in the interstellar medium, probably contributes to the formation of silicate dust grains since orthosilicic acid (Si(OH)₄), a SiO derivative, is a precursor of silica and silicates. The formation of Si(OH)₄ is investigated here by means of quantum chemical computations, characterizing the interaction and reactivity of SiO with water ice mantles (modelled through different cluster systems) that coat interstellar dust grains in dense clouds. Several reaction pathways involving SiO and H₂O were simulated with the aim of forming Si(OH)₂ and subsequently Si(OH)₄. Results highlight that the ice mantle not only supplies a reactant, H₂O, but also acts as a chemical catalyst, reducing the energy barrier of the process. The formation of the Si(OH)₂ precursor is a crucial step, occurring easily by reaction of SiO with H₂O. Subsequently, both the Si(OH)₂ $\xrightarrow{+O}$ OSi(OH)₂ $\xrightarrow{+H_2O}$ Si(OH)₄ and Si(OH)₂ $\xrightarrow{+2O}$ O₂Si(OH)₂ $\xrightarrow{+2H}$ Si(OH)₄ paths have been found to be energetically favourable towards Si(OH)₄ formation due to being barrierless, although formation of H₂Si(OH)₂ by H addition to Si(OH)₂ is a potential competitive channel. This study provides evidence that orthosilicic acid can form due to the addition of H₂O, O, and H to SiO on water ice mantles, indicating that silicate grains can potentially form and grow in cold interstellar regions, in addition to originating from material ejected by asymptotic giant branch stars and supernovae remnants. Our results show that grain surface reactions in dense clouds are important not only in the synthesis of volatile molecular species but also in the formation of silicate refractory material precursors.

Key words: astrochemistry – molecular processes – solid state: refractory – methods: numerical – ISM: clouds – ISM: molecules.

1 INTRODUCTION

The interstellar medium (ISM) consists primarily of gas-phase species and solid-state dust grains. Although the gaseous phase accounts for 99 per cent of the mass of the ISM, dust grains play a crucial role in its chemical composition, despite their smaller mass fraction (e.g. Tielens 2005). These interstellar dust grains, averaging about 0.2 μm in diameter, are mainly composed of silicates and carbonaceous materials (Draine 2003; Henning 2010; Potapov & McCoustra 2021). Their origins remain debated, but prevailing theories suggest that they form within the outflows of dying stars through condensation reactions at high temperatures (Zhukovska & Henning 2014). Specifically, silicate dust grains are believed to nucleate from gas-phase seeds (e.g. SiO, Mg, H₂, and H₂O: Goumans & Bromley 2012) under high-temperature conditions

(1000–1200 K) and pressures between 0.1 and 0.001 Pa (Jeong et al. 2003), primarily in environments associated with dying stars such as asymptotic giant branch (AGB) stars. While studies on silicate grain formation in AGB star outflows have provided valuable insights (Andersson 2023; Andersson, Gobrecht & Valero 2023), definitive conclusions are still lacking. Further potential sources of stardust are Type Ia supernovae (SNe) and, at lesser extent, red supergiants, Wolf–Rayet stars, Classical Novae, where similar high-temperature, high-pressure conditions are possible, although no definitive evidence for their specific contribution exists yet (e.g. Galliano, Galametz & Jones 2018; Schneider & Maiolino 2024).

In the Milky Way and nearby galaxies, dust grains produced by stellar sources undergo significant reprocessing once injected into the ISM, such as destruction by interstellar shock waves from SNe explosions (Jones, Tielens & Hollenbach 1996) or sputtering by thermal collisions (Tielens et al. 1994). As a result, it has been estimated that just a few per cent of the Milky Way dust is pristine stardust, while the vast majority is reprocessed (by shattering, sputtering,

* E-mail: albert.rimola@uab.cat (AR), nadia.balucani@unipg.it (NB)

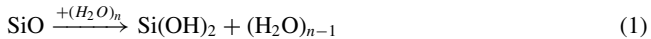
fragmentation, and coagulation) (e.g. Tielens 2005; Galliano et al. 2018).

The discovery of significant dust amounts in galaxies up to redshifts $z \simeq 8$, where low-mass stars have not had time to evolve into AGBs, has opened new avenues for investigating dust origins (e.g. Schneider & Maiolino 2024). Some studies suggest that silicate formation could also occur within cold dense molecular clouds through the freeze-out of Si atoms or SiO molecules on to the icy mantles that envelop the grain refractory cores (Krasnokutski et al. 2014; Ferrara, Viti & Ceccarelli 2016; Ginolfi et al. 2017). However, because of the relatively low abundance of Si and SiO with respect to the iced water molecules, only a small fraction of these frozen Si and SiO would be next to each other, reducing the potential contribute to silicate growth (Ceccarelli et al. 2018). That said, another major uncertainty is the fate of frozen Si and SiO.

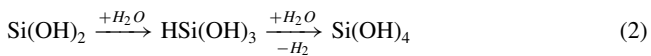
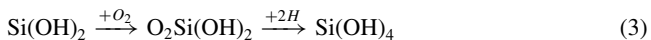
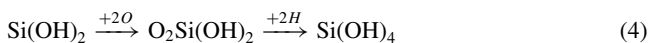
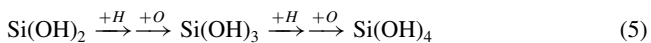
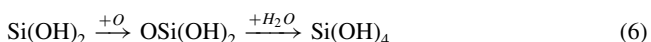
In general, interstellar grains have different roles in the chemistry of molecular clouds (Boogert, Gerakines & Whittet 2015; Ceccarelli et al. 2022): (i) they act as chemical catalysts, reducing energy barriers and accelerating reactions (e.g. Potapov & McCoustra 2021; Pareras et al. 2023, 2024; Perrero & Rimola 2024), (ii) they serve as reactant concentrators and suppliers (e.g. Molpeceres et al. 2021; Ferrero et al. 2023b, 2024; Bariosco et al. 2024), and (iii) they act as third bodies, dissipating the energy released by exothermic reactions taking place on their surfaces (e.g. Pantaleone et al. 2020, 2021; Molpeceres et al. 2023; Ferrero et al. 2023a). However, while the presence of interstellar dust grains is not argued, it is still not totally clear their initial formation process and whether Si-bearing species have a role in facilitating it. In particular, SiO is observed in star-forming regions where shocks of various nature liberate some silicon trapped in the dust grains (e.g. Wilson et al. 1971; Bouvier et al. 2025; Codella et al. 2025; Molinari et al. 2025): once in the gas-phase it is oxidized into SiO (e.g. Caselli, Hartquist & Havnes 1997; Schilke et al. 1997; Gusdorf et al. 2008; Jiménez-Serra et al. 2008). With time, the gaseous SiO freeze-out on to the icy dust grains in the cold/cooled regions (e.g. De Simone et al. 2022), where its fate is so far unknown.

In this study, we investigate the interaction and reactivity of SiO with the water molecules of the icy mantles coating interstellar grains, which can lead to form orthosilicic acid ($\text{Si}(\text{OH})_4$, the main precursor of silica and silicates), by means of quantum chemical computations. The icy mantle has been mimicked by means of different atomistic structural models of pure water ice, namely, clusters reproduced by the $(\text{H}_2\text{O})_n$ ($n = 1, 2, 18$, and 33) systems.

The very first step investigated is the reaction of SiO with an H_2O molecule from the ice mantle to form dihydroxysilicon ($\text{Si}(\text{OH})_2$) as the primary intermediate:



Subsequently, several reactions between the newly formed $\text{Si}(\text{OH})_2$ species and highly abundant species (i.e. H, O, O_2 , and H_2O) were investigated to finally obtain $\text{Si}(\text{OH})_4$:



Additionally, due to the high atomic H abundance in these environments, the following competitive reaction involving $\text{Si}(\text{OH})_2$ and H was also examined:



The binding energies (BEs) of the species adsorbed on the ice surfaces, selecting only the reaction products that originate from barrierless or very low energy barrier reactions, have also been computed. The BEs describe the strength of the interaction between the species and the ice surfaces, which is crucial for the chemical composition of the gas and dust phases. Not in vain, BEs are fundamental parameters in astrochemical models aiming to reproduce the occurring chemistry in interstellar environments (Minissale et al. 2022), and hence the relevance to calculate them.

The paper is organized as follows: in Section 2, the methodology employed in this work is presented; in Section 3, the results obtained in the gas phase (i.e. considering only one and two water molecules in the reaction scenario, Section 3.1) and on two different water clusters, $(\text{H}_2\text{O})_{18}$ and $(\text{H}_2\text{O})_{33}$, are presented, focusing on the formation of $\text{Si}(\text{OH})_2$ (Section 3.2) and its reactivity towards forming $\text{Si}(\text{OH})_4$ (Section 3.3). Finally, a discussion of the results, including the astrophysical implications, is outlined in Section 4, ending with the conclusions (Section 5) that summarize the most important issues of the work.

2 METHODS

All calculations were conducted using the ORCA 5.0.3 and ORCA 6.0.0 software packages (Neese et al. 2020; Neese 2022). The quantum mechanical methods were grounded on the density functional theory (DFT).

An initial benchmarking study was performed to identify the DFT method that is most suitable to describe the electronic structure of the systems and the processes investigated. This was done considering the $\text{SiO} + \text{H}_2\text{O}$ reaction, which was computed in the absence of the water ice clusters and using six different DFT functionals: the hybrid generalized gradient approximation (GGA) B3LYP-D3(BJ) (Lee, Yang & Parr 1988; Becke 1993) and PW6B95-D3(BJ) (Zhao & Truhlar 2005) functionals, the hybrid meta-GGA M062X-D3 and M06 functionals (Zhao & Truhlar 2008a, b) [this latter due to have been shown to be accurate enough in similar systems (Andersson 2023)], and the range-separated hybrid $\omega\text{B97X-D3}$ (Chai & Head-Gordon 2008) and $\omega\text{B97M-V}$ (Mardirossian & Head-Gordon 2016) functionals. As it can be noted, to account for dispersion interactions, the B3LYP and PW6B95 functionals were used in combination with Grimme's D3(BJ) dispersion correction. For the M06-2X functional, the zero-damping variant of the D3 correction (D3ZERO) was applied, as recommended for Minnesota functionals. The range-separated hybrid functionals, $\omega\text{B97X-D3}$ and $\omega\text{B97M-V}$, employed their respective built-in dispersion treatments: $\omega\text{B97X-D3}$ incorporates the D3ZERO correction by design, whereas $\omega\text{B97M-V}$ includes a non-local VV10 dispersion term, making additional corrections unnecessary (Grimme 2006; Grimme et al. 2010; Grimme, Ehrlich & Goerigk 2011).

As basis set, the def2-TVZP was used (Weigend & Ahlrichs 2005). This preliminary benchmarking was based on comparing the interaction energies of SiO with H_2O calculated at the different DFT levels and through single point (SP) energy calculations at coupled cluster single-double and perturbative triple, CCSD(T), theory level using the Dunning correlation consistent aug-cc-pVTZ basis set (Kendall, Dunning & Harrison 1992; Woon & Dunning 1993) on the DFT-optimized structures. The comparison was based on the error

percentage of the interaction energies between SiO and H₂O species, in which ω B97X-D3 emerged as the most suitable DFT method. To further increase the accuracy of the reference methodology, additional CCSD(T) single-point calculations were performed using the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets, and extrapolated to the complete basis set (CBS) limit. The results (see Table A2 in the Appendix A) confirm that, although the errors on the interaction energies are slightly overestimated when only relying on the aug-cc-pVTZ basis set, ω B97X-D3 remains the most accurate method throughout. For further confirmation, we also performed a benchmark on the energy barriers and reaction energies of the $\text{SiO} \xrightarrow{+\text{H}_2\text{O}} \text{Si(OH)}_2$ and $\text{SiO} \xrightarrow{+2\text{H}_2\text{O}} \text{Si(OH)}_2 + \text{H}_2\text{O}$ reactions, comparing ω B97X-D3 results with those obtained at CCSD(T) level SP calculations. For these reactions, ω B97X-D3 was also shown to be still an accurate method, in agreement with previous studies of similar reactions such as CCH with H₂O (Perrero et al. 2022).

Based on the benchmarking results, in the presence of the water ice clusters, geometry optimizations and frequency calculations were performed using the standard convergence criteria at the ω B97X-D3/def2-TZVP level of theory. Additionally, the energies of these systems were refined with SP calculations at CCSD(T), within the Domain-Based Local Pair Natural Orbital (DLPNO) approach (Riplinger & Neese 2013) (DLPNO-CCSD(T)) and utilizing the aug-cc-pVTZ basis set with an auxiliary aug-cc-pVQZ/C basis set (Dunning, Peterson & Wilson 2001).

Transition state (TS) structures were found using the climbing image nudged elastic band (CI-NEB) technique (Åsgerisson et al. 2021), which can characterize reaction pathways by gradually adjusting a series of images along the reaction coordinate, facilitating the identification of the minimum energy path at the same level of theory as for geometry optimization.

To determine the nature of stationary points on the potential energy surface (PES), harmonic frequencies were analytically calculated, characterizing them as minima (reactants and products) and saddle points (transition states). Thermochemical corrections were added to the potential energy values using a standard protocol with rigid rotor/harmonic oscillator to calculate zero-point energy (ZPE) corrections.

The cases involving open-shell species were treated within the unrestricted formalism. Furthermore, the broken symmetry approach was employed specifically when dealing with biradical systems (Neese, Wennmohs & Hansen 2009).

The cluster modelling approach was adopted to mimic the ice mantles covering interstellar grains. Considering that interstellar ices are predominantly composed of amorphous solid water (ASW; Watanabe & Kouchi 2008), two clusters comprised of 18 and 33 water molecules, respectively (referred to as W18 and W33 and shown in Fig. 1), were utilized, after being successfully adopted in past simulations. The former model features a flat surface, while the latter one is characterized by the presence of a cavity that better represents the surface defects of an amorphous ice (Rimola et al. 2014). These medium-sized cluster models allowed us to describe the investigated reactions at a high level of theory such as the DLPNO-CCSD(T) one.

The BEs of SiO, Si(OH)₂, H₂Si(OH)₂, and Si(OH)₄ were obtained as follows. First, the interaction energy of the species with the water ice surfaces (ΔE_{int}) was computed as

$$\Delta E_{\text{int}} = E_{\text{complex}} - (E_{\text{surface}} + E_{\text{molecule}}), \quad (8)$$

where E_{complex} , E_{surface} , and E_{molecule} are the absolute potential energies of the species adsorbed on the ice models, of the isolated ice models, and of the isolated reactive species, respectively.

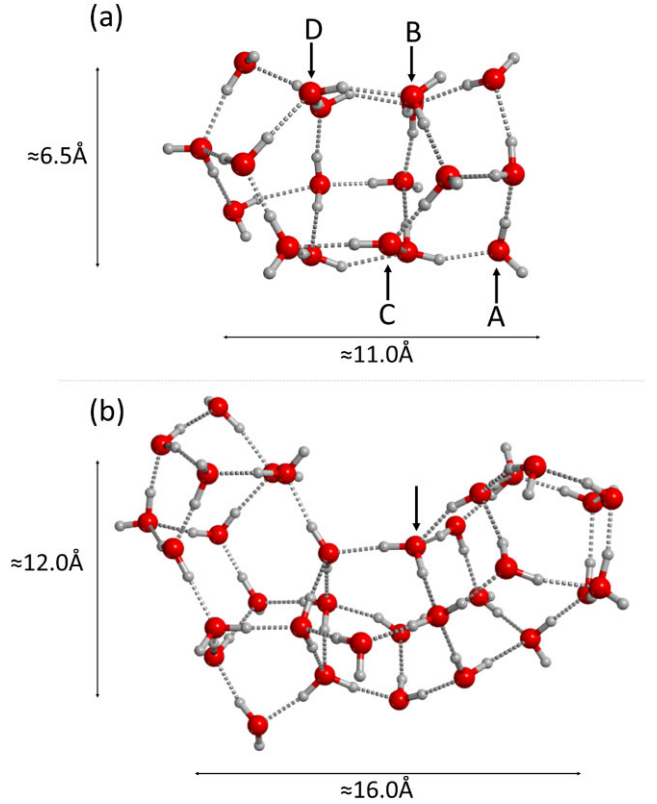


Figure 1. Structures of the 18 (a) and 33 (b) water molecule clusters, optimized at the ω B97X-D3/def2-TZVP. Model (b) was optimized with constraints in that the dangling oxygen atoms of the central cavity were fixed to prevent the collapse of the structure. The arrows indicate the investigated adsorption sites.

Then, the ZPE corrections were introduced into ΔE_{int} to obtain the ZPE-corrected interaction energies (ΔU_{int}):

$$\Delta U_{\text{int}} = \Delta E_{\text{int}} + \Delta \text{ZPE}, \quad (9)$$

where ΔZPE is the difference in ZPE between the complex and the individual components.

The final BE is defined as the opposite of ΔU_{int} .

$$\text{BE} = -\Delta U_{\text{int}}, \quad (10)$$

which is a positive quantity in case of a favourable interaction.

In principle, E_{surface} represents the energy of the bare water cluster previous to the adsorption of the species of interest (e.g. Ferrero et al. 2020). However, the formation of Si(OH)₂, H₂Si(OH)₂, and Si(OH)₄ involves the reaction with water molecules belonging to the cluster. Therefore, the BE of SiO was calculated on the W18 clusters, while for the rest, the BEs were determined using the cluster obtained after the formation of Si(OH)₂, which consists of 17 water molecules, and the one composed of 16 water molecules after the formation of Si(OH)₄, since the remaining water molecules became part of the products, respectively.

3 RESULTS

3.1 Benchmarking study

As mentioned above, we first carried out a preliminary benchmarking analysis focusing on two specific aspects: (i) the interaction between SiO and H₂O, and (ii) the PES associated with the reaction between

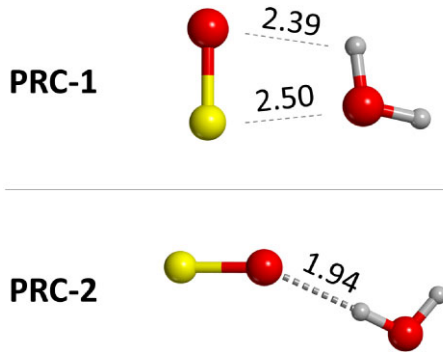


Figure 2. The two pre-reactant structures resulting from the interaction of SiO with H₂O, calculated at the ω B97X-D3 theory level. Distances are in Å.

SiO and H₂O in strict gas-phase conditions (i.e. $\text{SiO} \xrightarrow{+\text{H}_2\text{O}} \text{Si}(\text{OH})_2$) and in presence of an additional H₂O molecule (i.e. $\text{SiO} \xrightarrow{+2\text{H}_2\text{O}} \text{Si}(\text{OH})_2 + \text{H}_2\text{O}$).

We first compared the interaction energies between SiO and H₂O. Four initial guess structures consisting of the SiO molecule and a H₂O molecule placed in different initial orientations were fully optimized using the different DFT methods. After the geometry optimization, two distinct pre-reactant complexes were finally identified (PRC-1 and PRC-2 in Fig. 2), characterized by different geometrical features. PRC-1 is dominated by dispersive interactions, while PRC-2 by a hydrogen bond (H-bond) between the O atom of SiO and a H atom of H₂O.

The comparison of the interaction energies of the several DFT functionals against the CCSD(T)/aug-cc-pVTZ energies (reported in the table of Appendix A1) shows that ω B97X-D3 yields the smallest percentage error in the interaction energy. PRC-1 is the most stable structure despite the absence of a conventional H-bond, as there is interaction between the O atom of SiO and a H atom of H₂O, as well as between the Si atom of SiO and the O atom of H₂O. PRC-2 is stabilized by the presence of a well-defined H-bond. Thus, the stability trend is: PRC-1 > PRC-2.

To gain a comprehensive understanding of the reaction energetics, we characterized the PES of the gas-phase $\text{SiO} \xrightarrow{+\text{H}_2\text{O}} \text{Si}(\text{OH})_2$ reaction (using PRC-1 as the reactive structure), calculated with the ω B97X-D3 functional. Results are reported in Fig. 3(a) and extended in Table A3. At CCSD(T), although the reaction energy is large and negative, the energy barrier is relatively high, 39.7 kJ mol⁻¹, due to the formation of a geometrically strained (i.e. a 4-membered ring) TS structure. The error over the energy barrier reaches 15 per cent when compared to CCSD(T). This serves as a further confirmation that ω B97X-D3/def2-TZVP is the most suitable method for the description of our chemical process. Table A3 also includes results for the reaction incorporating results at DLPNO-CCSD(T) to assess its performance for the forthcoming reactions on the W18 cluster. From the outcomes, it is evident that the mean error (on the energy barrier and reaction energy) of DLPNO-CCSD(T) results with respect to the full CCSD(T) ones amounts to a mere 0.7 per cent, making it suitable for subsequent calculations.

With the aim of characterizing the role of water ice in the reaction mechanism and energetics, we studied the same process by adding an extra water molecule, therefore modelling the $\text{SiO} \xrightarrow{+2\text{H}_2\text{O}} \text{Si}(\text{OH})_2 + \text{H}_2\text{O}$ reaction. This is an intermediate situation, serving as a link between the absence and presence of icy water molecules. Results are shown in Fig. 3(b).

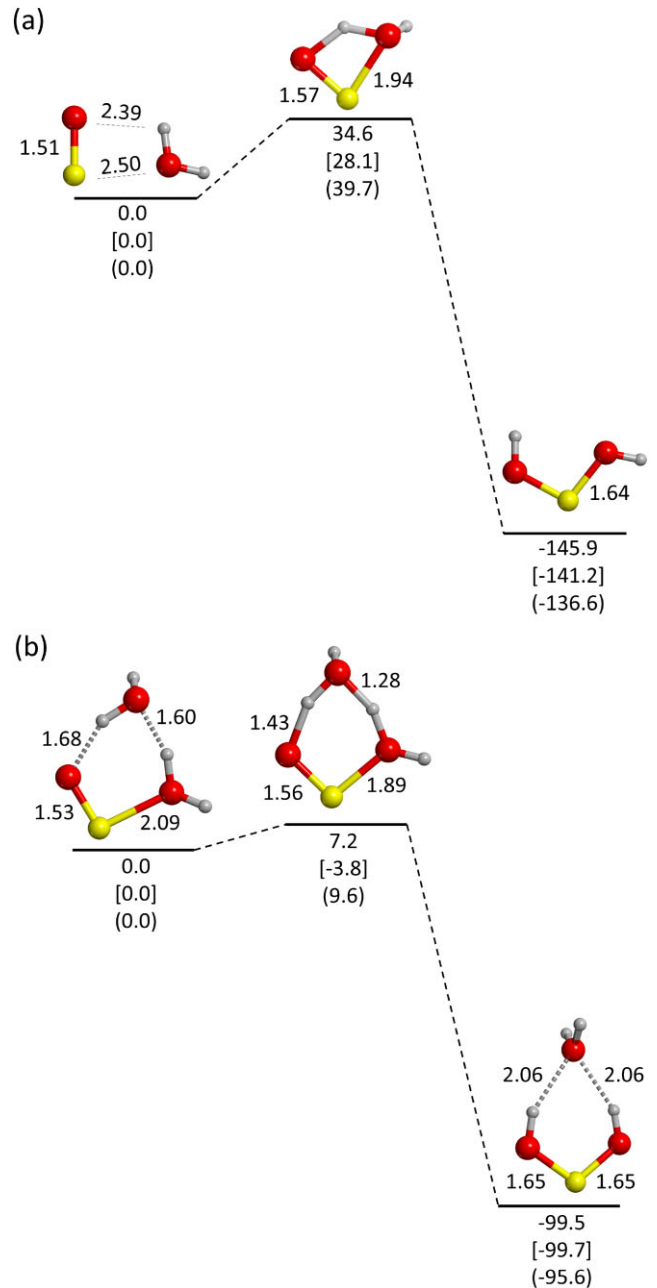


Figure 3. Relative energy profiles (in kJ mol⁻¹) of (a) $\text{SiO} \xrightarrow{+\text{H}_2\text{O}} \text{Si}(\text{OH})_2$ reaction and (b) $\text{SiO} \xrightarrow{+2\text{H}_2\text{O}} \text{Si}(\text{OH})_2 + \text{H}_2\text{O}$ reactions. The geometries of the stationary points are optimized at the DFT ω B97X-D3/def2-TZVP theory level. The bare values refer to DFT electronic energies, the values in square brackets include ZPE corrections applied to the DFT energies, and the values in parentheses correspond to DLPNO-CCSD(T)//DFT energies without ZPE corrections. Distances are in Å.

In this scenario, we see in the reactants that the Si–O chemical bond is almost formed (2.09 Å), which does not happen when only one water molecule is used. This is due to polarizing effects exerted by the additional H₂O molecule, at forming H-bonds with both the SiO and the reactive H₂O. Indeed, the H-bond with SiO (this species acting as acceptor) induces a polarization of the SiO species, which decreases the electron density on the Si atom and hence increases its Lewis acid character. In contrast, the H-bond with the reactive water (this species acting as a donor) also polarizes the H–O bond, but

in this case it increments the electron density on the O atom, hence increasing its Lewis base character. Due to these complementary electronic effects, the new Si–O chemical bond between SiO and the reactive H₂O is almost barrierless. Moreover, the second H₂O molecule behaves as a proton transfer assistant, facilitating the conversion of the reactants into the products, and hence reducing the structural strain of the TS compared to the gas-phase reaction (6-membered ring versus 4-membered ring, respectively; see TS structures of Fig. 3). Accordingly, the addition of just one water molecule significantly reduces the energy barrier, dropping from 39.7 to 9.6 kJ mol^{−1} (at CCSD(T)//DFT theory level, see Fig. 3). Finally, in the SiO + 2H₂O reaction, ZPE corrections not only significantly reduce the energy barrier but also lower the TS energy below that of the reactant, effectively resulting in a barrierless reaction.

3.2 Si(OH)₂ formation on water ice mantles

3.2.1 On W18 ASW ice cluster model

The W18 cluster shows different dangling hydrogen (dH) and oxygen (dO) atoms, which represent potential binding sites for SiO and, therefore, potential reactive sites. To investigate the impact of the local ice structure on the reaction, we selected four representative adsorption sites (A, B, C, and D, highlighted in Fig. 1). These sites were chosen based on their different characteristics: site A is located on the outer edge of the cluster, characterized by an outward-facing dH, easily accessible for adsorption; site B is positioned on a flatter region, where a dH and a dO are close together, and the SiO can form interactions with both of them; site C is closer to the interior of the cluster and has a neighbourhood that can allow different orientations of the adsorbed molecule; and site D is located in a corner of the cluster, where dO is the primary interaction point, in contrast to the dH-dominated sites.

Irrespective of the binding site, and similarly to the SiO + 2H₂O → Si(OH)₂ + H₂O reaction, the adsorption of SiO on to the W18 cluster results in the almost formation of the chemical bond between Si and an O atom of an ice water molecule (with a bond length within the range of 1.86 and 2.09 Å), facilitated by H-bond cooperativity within the W18 cluster.

The initial position of the reactants significantly affects the TS geometries, as well as that of the Si(OH)₂ products formed (see the different outcomes in Fig. 4), because the proton transfer can be assisted by a different number of water molecules (forming different *n*-membered rings). Thus, the energy barriers can vary, leading to a more or less favoured reaction path. The energy barriers relative to the SiO + H₂O reaction simulated at binding sites A, B, C, and D, and involving a different number of water molecules in the TS structures, are provided in Table 1. Please note that the notation (*x* + *y*) stands for *x* being the number of reacting H₂O molecules (in our reaction *x* = 1 in all the cases) and *y* being the number of H₂O molecules assisting the proton transfer. Table 1 also shows the calculated reaction energies, which indicates a thermodynamically favoured process in all the cases.

Starting from the binding site A (resulting in product A of Fig. 4), the reaction is fully barrierless, that is, once the Si–O bond is formed, the proton transfer occurs spontaneously during the optimization process. On site C, two possible reactions can take place (with 1 or 2 water molecules assisting the proton transfer, ending with products C₁ and C₂ of Fig. 4, respectively). Both pathways are characterized by a potential energy barrier, which after consideration of the ZPE corrections becomes submerged with respect to the initial state. In both A and C binding sites, SiO interacts with the

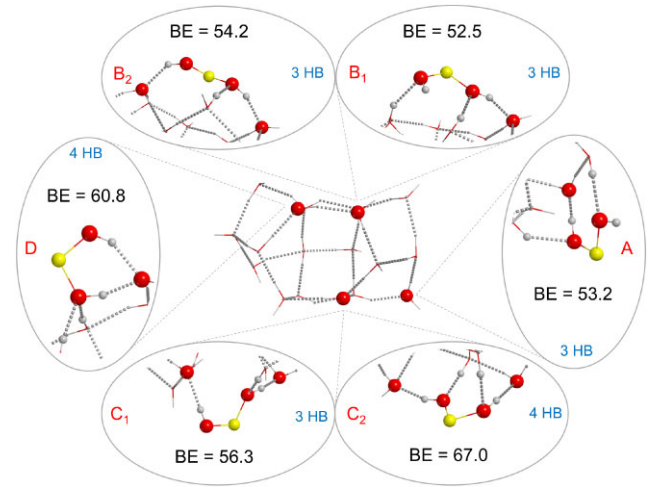


Figure 4. Adsorption complexes and their BE for the interaction of Si(OH)₂ considering different binding sites. BE values are in kJ mol^{−1}. HB stands for the number of H-bonds.

Table 1. Energetics involved in the reaction pathways for the SiO + W18 reaction to form Si(OH)₂. The initial binding site of SiO and the final product (shown in Fig. 4) are also included. The notation (*x* + *y*) indicates the reacting molecules (*x*) and the assisting molecules (*y*). The columns relative to energy barriers and reaction energies report potential energy values calculated at DFT = ωB97X-D3 as bare values, while values in square brackets include ZPE corrections. Energy units are in kJ mol^{−1}.

SiO + 18H ₂ O → Si(OH) ₂ + 17H ₂ O				
Binding site	Final product (Fig. 4)	Water-assisted scheme	Energy barrier	Reaction energy
A	A	(1 + 1)	barrierless	−176.8 [−170.5]
C	C ₁	(1 + 1)	16.3 [−0.4]	−172.8 [−169.4]
B	B ₁	(1 + 1)	12.6 [1.4]	−195.8 [−187.8]
C	C ₂	(1 + 2)	7.5 [−1.9]	−180.9 [−172.9]
D	D	(1 + 3)	33.6 [20.9]	−188.2 [−183.5]
B	B ₂	(1 + 5)	66.7 [43.0]	−192.0 [−186.1]

water molecules placed at the edges of the cluster, which exposes dH sites. In the other cases (sites B and D), the potential energy barriers are considerably higher, reaching the maximum value of 66.7 kJ mol^{−1} (for the reaction starting from the binding site B and resulting in structure B₂ of Fig. 4). This variation is attributed to the efficiency of the proton transfer assistant role of the water molecules comprising the ice matrix (see below). Like in the reaction with two water molecules, for the water-assisted proton transfer mechanism, the inclusion of ZPE corrections yields a significant energy barrier reduction. This trend can be rationalized through the consideration of an imaginary transition mode that also includes collective high-frequency stretching modes of water molecules, which is not so relevant in reactants and products.

To assess the efficiency of the water ice as a proton transfer assistant in the reaction, we compare the data obtained for the binding site B (see Fig. 1), in which a different number of water molecules is involved in the proton transfer. The well-oriented H-bond network within the cluster facilitates multiple paths from this site, allowing the water-assisted mechanism to operate in two limiting cases: through the assistance of either one or five water molecules, i.e. (1+1) and (1 + 5) mechanisms, which result in the formation of products B₁

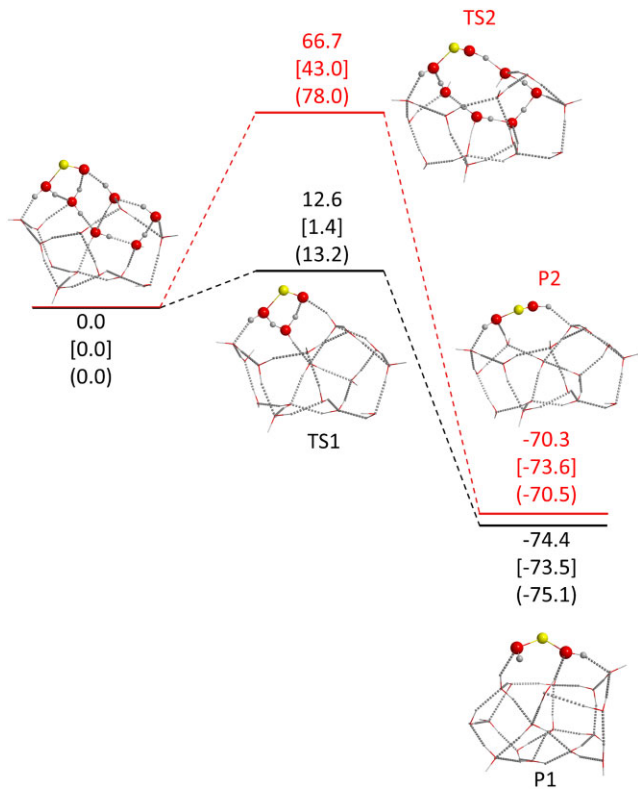


Figure 5. Relative energy profile (in kJ mol^{-1}) of the reaction of an adsorbed SiO with H_2O on the W18 cluster model (site B), the geometries of the stationary points being optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The bare values refer to DFT potential energies, the values in square brackets include the ZPE corrections and the values in parentheses correspond to DLPNO-CCSD(T)//DFT energies without ZPE corrections. The black pathway (involving the TS1 and P1 structures) corresponds to a (1+1) mechanism; the red pathway (involving the TS2 and P2 structures) corresponds to a (1 + 5) mechanism.

and B_2 , respectively (see Fig. 5). The results clearly indicate that the (1+1) mechanism presents a lower energy barrier than the (1+5) one. This is because in the (1+5) mechanism more chemical bonds must be broken/formed to transfer the proton, increasing the cost of the path. Thus, the effectiveness of a water-catalysed proton transfer process is determined by the number of water molecules involved. Indeed, it consists of a delicate trade-off between the geometry relaxation induced by the water assistant molecules and the number of chemical bonds broken/formed during the proton transfer. In our case, if we exclude the spontaneous path, the balance reaches its optimum situation in the (1 + 2) mechanism.

3.2.2 W33 ASW ice cluster model

The W33 cluster model features a structure resembling a cavity; therefore, we explored whether a different ice morphology can influence the outcome of the reaction. We ruled out simulating the reaction on the flat portion of the W33 cluster assuming similar results to those obtained for the W18 cluster. The reaction pathway involving a (1 + 2) water-assisted proton transfer mechanism mirrors the most favourable situation observed on W18. The energy profile and the structures of the stationary points are reported in Fig. 6. For proton transfer, the energy barrier calculated at $\omega\text{B97X-D3}$ is 13.8 kJ mol^{-1} , which upon inclusion of ZPE decreases to 2.8 kJ mol^{-1} .

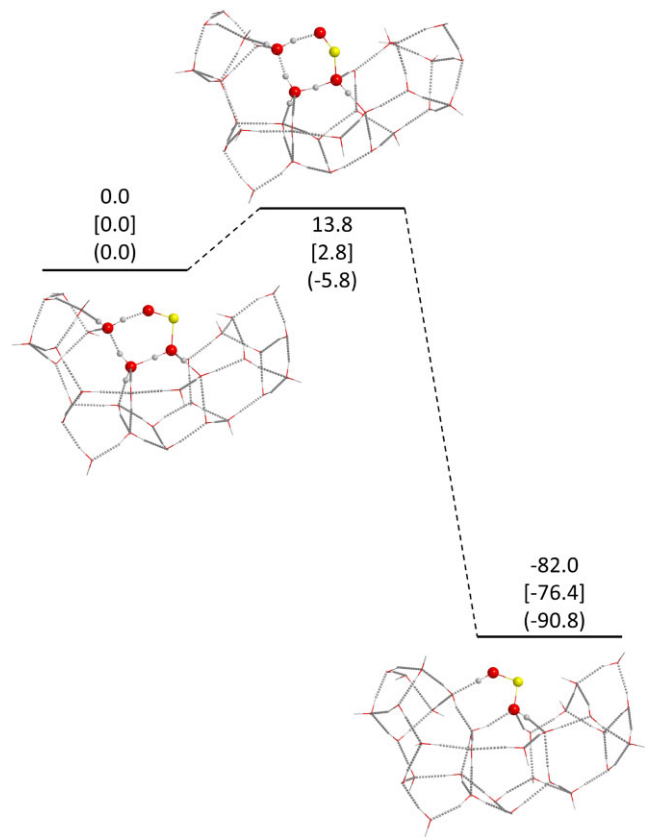
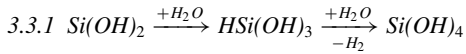


Figure 6. Relative energy profile (in kJ mol^{-1}) of the reaction of an adsorbed SiO with H_2O on the W33 cluster model, the geometries of the stationary points being optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The bare values refer to DFT electronic energies, the values in square brackets include ZPE corrections applied to the DFT energies, and the values in parentheses correspond to DLPNO-CCSD(T)//DFT energies without ZPE corrections.

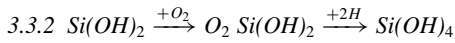
These are similar values to those obtained on the W18 cluster model (potential energy barrier of 12.6 kJ mol^{-1} , reduced to 1.4 kJ mol^{-1} with ZPE corrections). According to this reactive scheme, since there is no evidence that the ice cavity promotes or hampers the reaction, subsequent simulations concerning the evolution of the newly formed $\text{Si}(\text{OH})_2$ species towards orthosilicic acid ($\text{Si}(\text{OH})_4$) were performed on the W18 ice model.

3.3 Towards orthosilicic acid formation

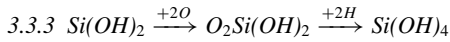
Most of the following reactions (reactions 2–6 leading to the formation of $\text{Si}(\text{OH})_4$, and reaction 7 leading to the formation of $\text{H}_2\text{Si}(\text{OH})_2$, see above) were simulated starting from more than one configuration of $\text{Si}(\text{OH})_2$ adsorbed on the cluster. The values reported here refer to the reactions having the C_2 structure as reactant (Fig. 4), i.e. starting from the $\text{Si}(\text{OH})_2$ structure that is formed through the most energetically favourable path (considering both the energy barrier and the reaction energy, see Table 1). Unless stated otherwise in the text, the energy barrier values obtained from the other $\text{Si}(\text{OH})_2$ sites were found to be very similar.



As a first step, we examined the possibility that Si(OH)_2 undergoes a new reaction with another water ice molecule (the first elementary step of reaction 2), as an intermediate process towards forming Si(OH)_4 . From our results (see Fig. B1 in the appendix), the energy barrier for this new water addition is very high, $139.3 \text{ kJ mol}^{-1}$ ($123.3 \text{ kJ mol}^{-1}$ after accounting ZPE corrections), and stems from both the requirement to break water O–H bonds and the unfavourable orientation of the two reactants. Being this process impeded by this high energy barrier, the subsequent elementary step along this reaction to form Si(OH)_4 was not investigated.



Another possible pathway for the formation of Si(OH)_4 involves the formation of $\text{O}_2\text{Si(OH)}_2$ by the reaction of Si(OH)_2 with molecular oxygen (electronic ground state $^3\Sigma_g^-$), followed by the addition of two H atoms (reaction 3). However, the addition of O_2 is characterized by a very high energy barrier (88.0 kJ mol^{-1} , 82.6 kJ mol^{-1} including ZPE, see Appendix Fig. B2) due to the need to break the double bond of the O_2 molecule. Consequently, this process is not expected to significantly contribute and we did not examine the subsequent H additions.



For this process, we initially investigated the addition of one oxygen atom, in its ^3P electronic ground state, to Si(OH)_2 in the gas phase to assess its intrinsic nature. Results indicate that the reaction is barrierless, forming OSi(OH)_2 spontaneously.

On the W18 cluster model, the $\text{O}(^3\text{P})$ atom can form a H-bond with a water molecule close to Si(OH)_2 . From our calculations, we noticed that, depending on the initial SiO binding, this interaction may or may not induce a diffusion energy barrier. Specifically, when O does not react directly with Si(OH)_2 (starting from the B_1 structure), it is because one hydrogen atom of the newly formed Si(OH)_2 remains unbound, and O forms a H-bond with this H atom. In this scenario, the calculated diffusion energy barrier is 20.8 kJ mol^{-1} (18.2 kJ mol^{-1} with ZPE corrections). The reaction pathway for this case is detailed in the Appendix, Fig. B3. In contrast, starting from the C_2 structure, no barrier is observed (see Fig. 7a). In other words, the barrierless nature of the reaction is determined by the presence or absence of an oxygen diffusion barrier, which arises from the formation or not of an H-bond with Si(OH)_2 . Regardless of the pathway, the reaction yields OSi(OH)_2 in a triplet state due to the spin conservation rule. However, it can be assumed that the excited state will relax to the ground singlet state via physical quenching and release the excess energy to the lattice. Also, given the presence of silicon and the expected strong spin–orbit coupling, intersystem crossing (ISC) from the triplet to the singlet is possible, which is energetically largely favourable (Fig. 7b).

We characterized the subsequent addition of a second $\text{O}(^3\text{P})$ atom to form $\text{O}_2\text{Si(OH)}_2$ along an adiabatic triplet PES. Our optimization shows that the addition is barrierless, with Si forming five chemical bonds: two with the two original OH groups, two with the two added O atoms (1.78 and $1.63 \text{ \AA}$, respectively) and an additional one with a surrounding water molecule ($1.90 \text{ \AA}$), see Fig. 8a. The reaction energy associated with the addition of this second O atom is $-307.6 \text{ kJ mol}^{-1}$ (including ZPE corrections).

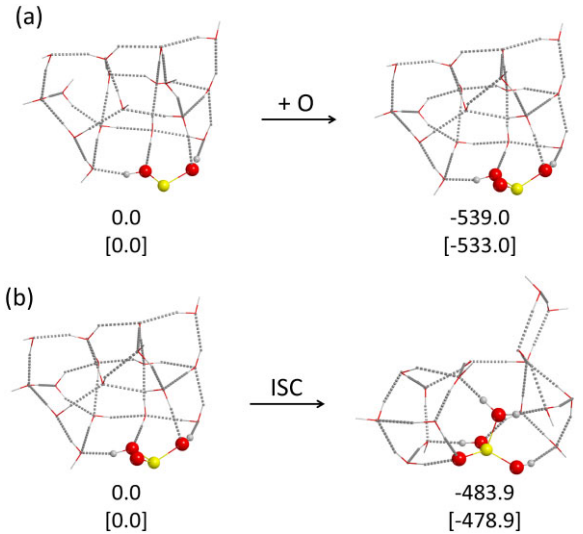
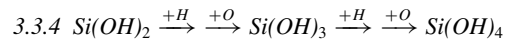


Figure 7. Relative energies (in kJ mol^{-1}) of stationary points of the reaction $\text{Si(OH)}_2 \xrightarrow{+\text{O}(^3\text{P})} {}^3\text{OSi(OH)}_2 \rightarrow {}^1\text{OSi(OH)}_2$, the geometries being optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The first step is represented in (a), while the second step (consisting of an intersystem crossing, ISC) in (b). The bare values refer to DFT potential energies, and the values in square brackets include the ZPE corrections.

The first H addition to the newly formed triplet $\text{O}_2\text{Si(OH)}_2$ species (shown in Fig. 8b) is also barrierless and leads to a product (in a doublet electronic state) in which Si retains the five bonds, of which three are now with OH groups, one with the O atom ($1.71 \text{ \AA}$) and one with a water molecule of the cluster ($2.03 \text{ \AA}$). The reaction energy (including ZPE corrections) was calculated to be $-449.5 \text{ kJ mol}^{-1}$. Finally, the second H addition also occurs without an energy barrier (see Fig. 8c) and leads to the formation of Si(OH)_4 . For this step, we employed a broken-symmetry approach due to the bi-radical nature of the system. Our results indicate that the product collapses on to the closed-shell singlet ground state, with a calculated reaction energy of $-524.8 \text{ kJ mol}^{-1}$ (including ZPE corrections).



Results shown above, in the Section 3.3.3, indicate that both atomic oxygen and atomic hydrogen additions on Si(OH)_2 (reaction 4) occur without barriers. However, the global mechanism resulting from the combined addition of O and H depends on the addition sequence. If the O addition takes place first followed by the H addition, Si(OH)_3 and then Si(OH)_4 (by repeating the same sequence) are formed and the global process can be assumed to occur in a barrierless way. However, considering the larger abundance of H atoms, this scenario is not realistic. Thus, we explored the formation of Si(OH)_3 , assuming that the addition of a H atom occurs first, followed by the O addition. Both additions are barrierless, but the final product is $(\text{O})(\text{H})\text{Si(OH)}_2$ since both H and O establish a chemical bond with the Si atom rather than forming the OH groups. Thus, to form Si(OH)_3 a migration of the H atom on to the O atom to form a hydroxyl group is necessary, but a barrier of 60.2 kJ mol^{-1} (considering ZPE corrections) is associated with this step (see Fig. B4). Although tunneling effects may improve the feasibility of these reactions, they seem less likely to form Si(OH)_4 compared to reaction (4).

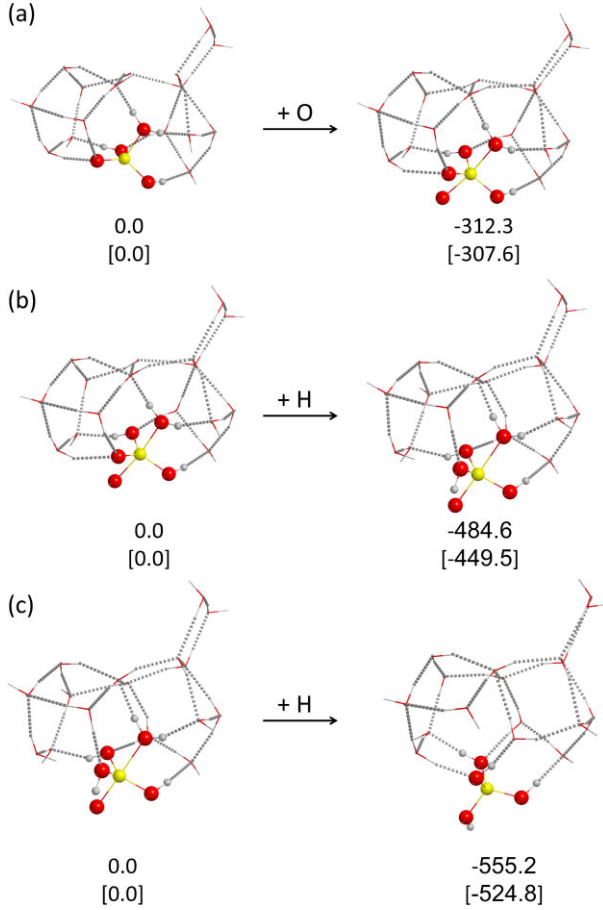


Figure 8. Relative energies (in kJ mol⁻¹) of stationary points of the reaction $\text{Si(OH)}_2 \xrightarrow{+\text{O}} \text{OSi(OH)}_2 \xrightarrow{+\text{H}_2\text{O}} \text{Si(OH)}_4$, the geometries being optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The bare values refer to DFT potential energies, and the values in square brackets include the ZPE corrections.

3.3.5 $\text{Si(OH)}_2 \xrightarrow{+\text{O}} \text{OSi(OH)}_2 \xrightarrow{+\text{H}_2\text{O}} \text{Si(OH)}_4$

The absence of an energy barrier in the addition of atomic oxygen to Si(OH)_2 with the formation of OSi(OH)_2 (the first step of reaction (4), shown in the Section 3.3.3) leads us to consider a subsequent water addition. As described above, the optimization of the geometry of the OSi(OH)_2 molecule was performed both in the triplet and singlet electronic states because of the possible ISC occurrence. While the structure of the triplet state is such that the Si atom is far from other water molecules, the optimization of the singlet state structure leads to the formation of a Si–O bond with a contiguous water molecule of the cluster (see Fig. 7b).

Following the ISC, the system constituted by OSi(OH)_2 and the W18 becomes more stable (with a $\Delta E_{\text{singlet-triplet}} = -478.9$ kJ mol⁻¹ including ZPE corrections). However, it is worth pointing out that ISC significantly deforms the cluster geometry. That is, in the singlet state structure, a water molecule of the cluster spontaneously couples with the Si atom. For this reason, we investigated the H atom transfer from the added water molecule to the previously incorporated O atom and verify that Si(OH)_4 can be formed (see Fig. 9). The hydrogen atom transfer can occur through a proton relay mechanism assisted by two water molecules and, therefore, the potential energy barrier is relatively low (8.8 kJ mol⁻¹), submerged below the energy of the reactants when ZPE corrections are included

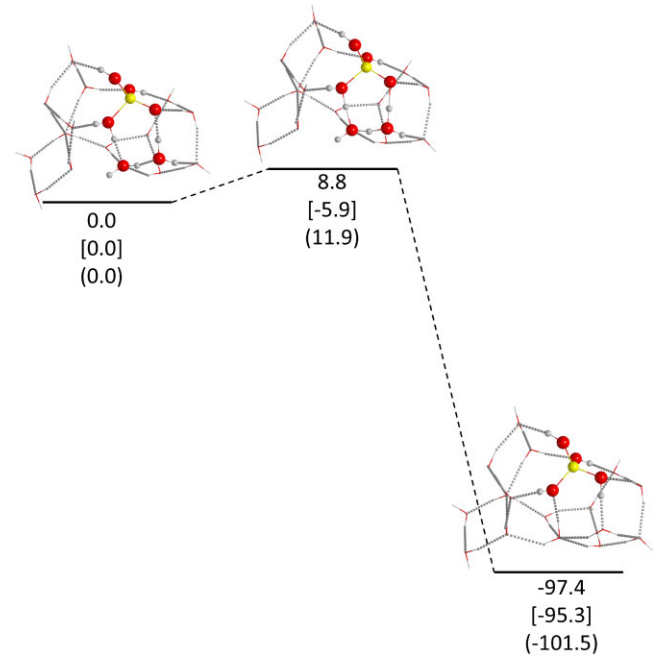


Figure 9. Relative energy profile (in kJ mol⁻¹) of the reaction $\text{OSi(OH)}_2 \xrightarrow{+\text{H}_2\text{O}} \text{Si(OH)}_4$ on the W18 cluster model, after following steps (a) and (b) of Fig. 7. The geometries of the stationary points are optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The bare values refer to DFT electronic energies, the values in square brackets include ZPE corrections applied to the DFT energies, and the values in parentheses correspond to DLPNO-CCSD(T)/DFT energies without ZPE corrections.

(-5.9 kJ mol⁻¹). Therefore, this mechanism can indeed occur without a barrier, leading to the formation of Si(OH)_4 in fewer steps compared to reaction (4).

3.4 Formation of other products: the $\text{Si(OH)}_2 \xrightarrow{+\text{H}} \text{H}_2\text{Si(OH)}_2$ reaction

Since, even at a temperature as low as 10 K, the H atoms on ice can diffuse and encounter adsorbed reactive species, it is important to consider H addition to Si(OH)_2 . Therefore, we have considered the successive addition of two H atoms leading to the formation of silanediol ($\text{H}_2\text{Si(OH)}_2$, reaction 7), which, being a closed-shell molecule, can be considered an end-product in competition with Si(OH)_4 .

The first hydrogenation ($\text{Si(OH)}_2 \xrightarrow{+\text{H}} \text{HSi(OH)}_2$) has already been described above as a barrierless process, presenting a highly favourable reaction energy (-199.4 kJ mol⁻¹). A systematic scan of the Si–H bond distance confirmed the absence of any discernible barrier and indicates that the bond formation is largely favourable at the Si–H equilibrium bond length (1.49 Å). The same results are found for different initial positions of the H atom, indicating that the position of the H atom on the ice surface does not affect its interaction with Si(OH)_2 , due to the negligible diffusion barrier of atomic H on the water ice surface. Results of the second hydrogenation also indicate a barrierless H addition, with a reaction energy of -416.7 kJ mol⁻¹ for the formation of $\text{H}_2\text{Si(OH)}_2$. Therefore, the formation of $\text{H}_2\text{Si(OH)}_2$ by two successive H additions to Si(OH)_2 competes with the formation of Si(OH)_4 .

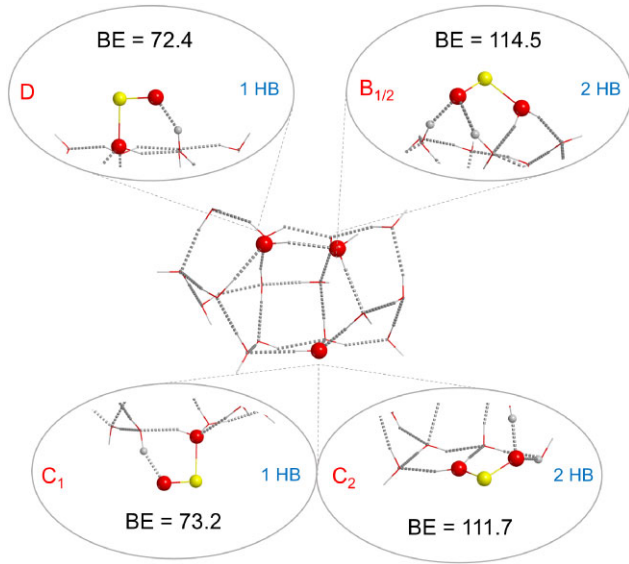


Figure 10. Adsorption complexes and their BE for the interaction of SiO on the different binding sites considered in the W18 cluster model (see Fig. 1). BE values are in kJ mol^{-1} . HB stands for the number of H-bonds.

3.5 Binding energies

3.5.1 SiO

As represented in Fig. 1, SiO was adsorbed on several sites of the W18 cluster model, the resulting different complexes shown in Fig. 10. It is worth reminding that on site A, the BE of SiO can not be directly calculated because SiO reacts spontaneously upon adsorption forming Si(OH)_2 , such that SiO already undergoes a chemical transformation. The calculated BEs are significantly high (spanning the 72.4–114.5 kJ mol^{-1} range), because (as mentioned earlier) in all the cases a Si–O chemical bond forms, i.e. chemisorption occurs. In the most stable binding sites, the O atom of SiO forms two H-bonds with the cluster model. This occurs on site B (the most favourable one, with $\text{BE} = 114.5 \text{ kJ mol}^{-1}$, indicated as $\text{B}_{1/2}$ in Fig. 10) and on site C (the second most favourable one, $\text{BE} = 111.7 \text{ kJ mol}^{-1}$, labelled as C_2 in Fig. 10). Interestingly, on site C, even though SiO adsorbs on the same O atoms of the water cluster, two different adsorption complexes can be formed, depending on the orientation of the adsorbate. One is the above-mentioned C_2 structure, and the other is the C_1 structure, in which only one H-bond is formed, resulting in a lower BE (73.2 kJ mol^{-1}). Finally, on site D, the SiO also forms a single H-bond, resulting in a BE of 72.4 kJ mol^{-1} .

3.5.2 Si(OH)_2 , $\text{H}_2\text{Si(OH)}_2$ and Si(OH)_4

For Si(OH)_2 and $\text{H}_2\text{Si(OH)}_2$, which are products of key processes involved in the reactions described above, a direct calculation of the BE with W18 is not possible. This is because a water molecule from the ice reacts during the formation of Si(OH)_2 , thus leaving an interaction of the species with a ‘reacted’ cluster of 17 water molecules. Therefore, we calculated the BEs of these species as the extraction energy of the molecules (as the opposite of the interaction energy) on the re-optimized cluster of 17 water molecules after the species removal.

The BE of Si(OH)_2 and $\text{H}_2\text{Si(OH)}_2$ is a function of the number of established H-bonds, as summarized in Fig. 4. For the adsorption of Si(OH)_2 , we performed the calculations using the products obtained

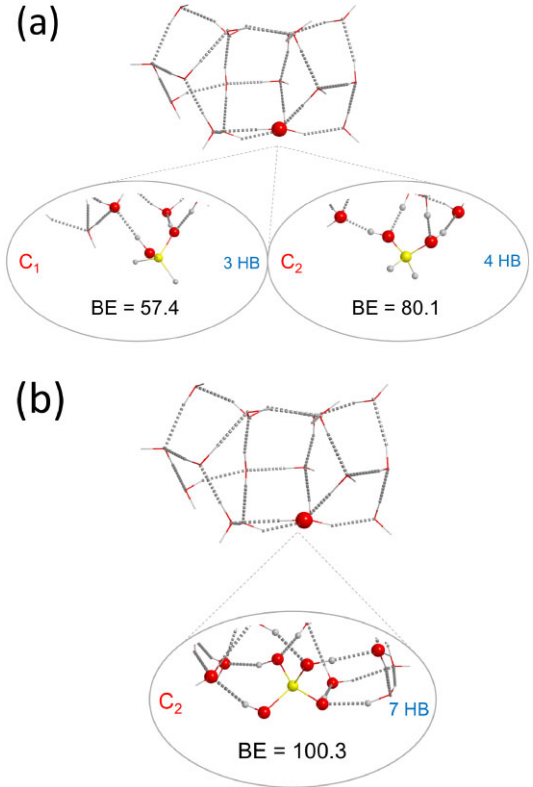


Figure 11. Adsorption complexes and their BE for the interaction of $\text{H}_2\text{Si(OH)}_2$ (a) and Si(OH)_4 (b), considering different binding sites. BE values are in kJ mol^{-1} . HB stands for the number of H-bonds.

at the different sites where SiO was previously adsorbed. Depending on the outcome, Si(OH)_2 establishes three or four H-bonds with the water ice cluster, leading to BEs in the range of 52–57 kJ mol^{-1} in the first case and 60–67 kJ mol^{-1} in the second. The formation of $\text{H}_2\text{Si(OH)}_2$ requires the addition of two hydrogen atoms to Si(OH)_2 . Thus, to calculate its BE, and considering the influence of the H-bonds in their values, two cases (shown in Fig. 11a) have been adopted, which correspond to the C_1 and C_2 positions of Si(OH)_2 and that are the most stable complexes presenting three and four H-bonds, respectively. Consistently, the number of H-bonds plays a predominant role in the BEs between $\text{H}_2\text{Si(OH)}_2$ and the water cluster model, for which we obtained BE in the range 57.4–80.1 kJ mol^{-1} , depending on the structure.

For Si(OH)_4 , as its formation requires two water ice molecules, the reference pristine ice cluster contains 16 water molecules. Our product presents seven H-bonds (see Fig. 11b), which causes the molecule to be more ‘embedded’ within the system. As a result, a BE of 100.3 kJ mol^{-1} was obtained.

These calculations provide insights into how the products of the investigated reactions interact with the ice surface. However, it is important to notice that investigating the BEs across multiple adsorption sites is compulsory to have a meaningful representation of the BE distribution that accounts for the various possible adsorption sites, as it has been done for other species in more dedicated studies on this topic (e.g. Duflet, Toubin & Monnerville 2021; Bovolenta et al. 2022; Tinacci et al. 2022; Bariosco et al. 2024). Moreover, since a detailed study of the BEs is not the primary goal of this work, the results were calculated not taking into account the BSSE correction.

4 DISCUSSION

In this study, the reactivity of SiO on the icy mantles covering interstellar dust grains has been explored, with the aim to elucidate the formation pathways of Si(OH)_2 , Si(OH)_4 , and $\text{H}_2\text{Si(OH)}_2$ in molecular clouds. We verified that the reaction between SiO and a H_2O molecule belonging to the ice efficiently leads to Si(OH)_2 following the ‘molecule + ice’ scheme proposed by some of us (Rimola et al. 2018; Perrero et al. 2022) and going beyond the more commonly studied radical–radical coupling mechanisms (Garrod & Herbst 2006; Garrod, Weaver & Herbst 2008; Enrique-Romero et al. 2022). This is a somewhat unexpected result since, differently from previous cases, the gas–grain reaction involving closed-shell species, like SiO and H_2O , are expected to be forbidden in ISM due to high kinetic barriers. To the best of our knowledge, this is the first documented case ever in which closed shell molecules are so reactive. In astrochemical models, these processes are usually overlooked because they are expected to present high energy barriers (Woon & Herbst 2009). However, for atoms beyond the second-period elements, the presence of d empty atomic orbitals can significantly change the chemistry (see, for instance, Goettl et al. 2024). This is the case of SiO in which, besides the high polarity of the bond, the frontier molecular orbitals are arranged such that there is a relatively low-lying empty orbital on the silicon. This orbital can readily accept electron density from H_2O , further promoting chemical reactions.

Our findings highlight the significant role of ice mantles, not only as reactant suppliers and reactant concentrators but also as chemical catalysts, particularly as proton transfer assistants, here facilitating the formation of Si(OH)_2 and Si(OH)_4 . The mechanism, supported by bridging water molecules, effectively links proton transfer processes [a phenomenon known as proton-transport catalysis (Chalk & Radom 1997)] and alleviates the geometrical strains of the TS structures. These proton relay mechanisms have been proven to substantially diminish energy barriers when contrasted with their non-water-assisted counterparts. In this study, we identified several pathways on the W18 cluster that enable proton-transfer catalysis, among which a different number of water molecules are involved. We found that the cavity shape (and, by extension, the morphology of the grain) does not significantly affect the energetics of the processes. While we did not explicitly analyse all these pathways on the W33 cluster, it is clear that other paths involving varying numbers of water molecules are certainly possible.

The significance of such catalytic effects extends to processes of interstellar interest occurring on icy surfaces, as already demonstrated by other previous studies (e.g. Rimola, Sodupe & Ugliengo 2010; Rimola et al. 2018; Molpeceres et al. 2021). However, the effectiveness of these transfers is closely related to the H-bond network connecting water molecules along the proton transfer pathway, as any disruption in this connectivity arising from impurities can reduce the catalytic efficiency. Indeed, given the compositional complexity of interstellar ices, the presence of minor volatile species can potentially inhibit (particularly the non-protic ones like CO and CO_2) the contiguous proton relays essential for these catalytic transfers.

The prompt SiO reaction with the ice water molecules, even in the extreme conditions of cold and dense regions (where the grains adopt this core/mantle structure), is quite relevant because in those conditions Si(OH)_2 will be easily converted into $\text{H}_2\text{Si(OH)}_2$ via a barrierless process. Therefore, $\text{H}_2\text{Si(OH)}_2$ (silanediol) is expected to be the predominant silicon species in those environments.

Furthermore, Si(OH)_2 can be converted via a series of steps to Si(OH)_4 (orthosilicic acid), the precursor of silica and silicates with the fundamental $[\text{SiO}_4]^{4-}$ unit. By testing different reaction sequences, we found cases with exceedingly high reaction barriers (3.3.1 and 3.3.2) and others involving only barrierless steps (3.3.3 and 3.3.5). These two last ones are, thus, viable routes, but since the pathway described in 3.3.5 only requires two steps (one of which involving a contiguous water molecule), according to the present investigation this is the most favourable one. It is worth remembering that Si(OH)_4 is very reactive towards its polymerization products, like silica and silicates. Moreover, our result is in line with previous findings in the gas phase: Plane et al. (2016) reported that the formation of Si(OH)_4 from OSi(OH)_2 and H_2O also proceeds via a very low energy barrier in the gas phase, following the formation of a molecular complex. Our results confirm that, on ice surfaces, this process remains barrierless and even benefits from catalytic assistance by the ice, supporting the efficiency of this transformation under both interstellar and atmospheric conditions.

In protoplanetary discs, species snow lines mark the regions where gaseous species condense on to dust grains (e.g. Hartmann et al. 2017; Öberg & Bergin 2021). The position of these snow lines is influenced by the dust temperature and the BE of the species. Generally, as you move farther from the centre of the disc, the dust temperature drops, causing species with lower BEs to stay gaseous at greater distances, while those with higher BEs condense closer to the centre. Consequently, snow lines (and thus BEs) significantly impact the balance between gaseous and solid chemical compositions in protoplanetary discs, playing a vital role in the formation of rocky and gaseous bodies in these regions (e.g. Öberg, Murray-Clay & Bergin 2011; Öberg & Wordsworth 2019; Mollière et al. 2022). The high BE of SiO, which is due to chemisorption, combined with the fact that its reaction with water is barrierless, suggests that SiO does not desorb but it is likely to stick on the ice mantle and eventually participate in chemical reactions. Likewise, the BEs obtained for Si(OH)_2 , $\text{H}_2\text{Si(OH)}_2$, and Si(OH)_4 suggest that these molecules strongly interact with the ice surface (due to the formation of multiple H-bonds) and are unlikely to desorb once they are formed. Within this context, it is interesting to compare the BEs of these species with those of water. The water BE distribution computed in Tinacci et al. (2023) peaks at 35.4 kJ mol^{-1} and extends over the range between 14.2 kJ mol^{-1} and 61.6 kJ mol^{-1} , while the BEs of the Si-bearing species considered here span the $52.5\text{--}100.3 \text{ kJ mol}^{-1}$ range. Thus, these species will very likely be retained by water-rich grains, forming part of their refractory component, which eventually aggregate forming first pebbles and subsequently planetesimals, contributing to the formation of rocky planets and other asteroidal bodies through their polymerization.

We recognize potential avenues for further research to enhance our understanding of interstellar chemistry. Future investigations could explore kinetic aspects, consider quantum effects such as tunneling, and better evaluate adsorption and desorption processes. In any case, even if this study cannot solve the problem related to the origin of silicate grains, it must be said that these results must be coupled with other considerations (Ceccarelli et al. 2018; Andersson et al. 2023). Indeed, because of the current difficulties in explaining grain growth, it has even been suggested that reconsidering some of the underlying arguments (mainly based on the comparison of dust production rates from various sources such as planetary nebulae, evolved stars, and SNe and destruction rates in SN shocks) might provide a workable solution (e.g. Ferrara et al. 2016; Schneider & Maiolino 2024). While uncertainties persist regarding the formation of dust grains

in molecular clouds, especially silicates, our study sheds light on the behaviour of silicon-bearing species.

5 CONCLUSIONS

In this study, we conducted a thorough quantum chemical investigation into the reactivity of the closed shell silicon monoxide (SiO) with water molecules of the ice mantles covering interstellar dust grains. The $\text{SiO} \xrightarrow{+\text{H}_2\text{O}} \text{Si(OH)}_2$ reaction was simulated by adopting atomistic cluster models representing interstellar water ices with the W18 and W33 systems. We found that some pathways are spontaneous or nearly barrierless, due to the significant role of icy water molecules as chemical catalysts, which help the proton transfer processes, a somehow surprising results due to the closed shell nature of the involved species. Furthermore, we observed that the size of the water cluster does not affect the reaction, but the number of water molecules involved in the TS does. After the formation of Si(OH)_2 , subsequent pathways were simulated, aiming to obtain Si(OH)_4 as the final product. Among the pathways, we considered the addition of relatively abundant species such as H, O, O_2 , and H_2O , finding cases where the product formation occurs in a barrierless manner. Additionally, the BEs of the investigated species suggest that once formed, these molecules remain strongly bound to the ice surfaces, making desorption unlikely and supporting the idea that they remain as part of the ice to participate in further chemical processes. The high BEs also indicate that the Si-bearing species can be incorporated in water-rich pebbles and planetesimals as part of the refractory materials, eventually constituting rocky planets and asteroids through their polymerization. This study thus provides valuable insights into the puzzling origin of dust grains in molecular clouds.

ACKNOWLEDGEMENTS

This project has received funding within the European Union's Horizon 2020 research and innovation programme from the European Research Council (ERC) for the projects 'Quantum Chemistry on Interstellar Grains' (QUANTUMGRAIN), grant agreement No. 865657. JER acknowledges the funding from the Horizon Europe Framework Programme (HORIZON) under the Marie Skłodowska-Curie grant agreement No. 101149067, 'ICE-CN'. Authors JP and PU acknowledge support from the Project CH4.0 under the MUR program 'Dipartimenti di Eccellenza 2023–2027' (CUP: D13C22003520001). PU and NB acknowledge support from Italian MUR via the project PRIN2020 2020AFB3FX- 'Astrochemistry beyond the second period elements'. Support from the Italian Space Agency (Bando ASI Prot. n. DC-DSR-UVS-2022-231, Grant no. 2023-10-U.0 MIGLIORA) is also acknowledged (JP, PU, and NB). The Spanish MICINN is also acknowledged for funding the projects PID2021-126427NB-I00 (AR) and CNS2023-144902 (AR). The authors thankfully acknowledge the supercomputational facilities provided by CSUC. AR acknowledges Accademia delle Scienze di Torino for supporting the project 'In silico interstellar grain-surface chemistry'. AR gratefully acknowledges support through 2023 ICREA Award.

DATA AVAILABILITY

The data underlying this article are freely available in Zenodo at <https://doi.org/10.5281/zenodo.14893264>.

REFERENCES

- Andersson S., 2023, *J. Phys. Chem. A*, 127, 4015
 Andersson S., Gobrecht D., Valero R., 2023, *Front. Astron. Space Sci.*, 10, 1135156
 Ásgeirsson V., Birgisson B. O., Björnsson R., Becker U., Neese F., Riplinger C., Jónsson H., 2021, *J. Chem. Theory Comput.*, 17, 4929
 Barriosco V., Pantaleone S., Ceccarelli C., Rimola A., Balucani N., Corno M., Ugliengo P., 2024, *MNRAS*, 531, 1371
 Becke A. D., 1993, *J. Chem. Phys.*, 98, 1372
 Boogert A. A., Gerakines P. A., Whittet D. C., 2015, *ARA&A*, 53, 541
 Bouvier M., Giani L., Chahine L., López-Sepulcre A., Ceccarelli C., Podio L., 2025, *MNRAS*, 539, 2380
 Bovolenta G. M., Vogt-Geisse S., Bovino S., Grassi T., 2022, *ApJS*, 262, 17
 Caselli P., Hartquist T. W., Havnes O., 1997, *A&A*, 322, 296
 Ceccarelli C., Viti S., Balucani N., Taquet V., 2018, *MNRAS*, 476, 1371
 Ceccarelli C. et al., 2022, Organic Chemistry in the First Phases of Solar-Type Protostars, 379, Protostars and Planets VII
 Chai J.-D., Head-Gordon M., 2008, *J. Chem. Phys.*, 128, 084106
 Chalk A. J., Radom L., 1997, *J. Am. Chem. Soc.*, 119, 7573
 Codella C., Bianchi E., Podio L., De Simone M., López-Sepulcre A., Ceccarelli C., Caselli P., 2025, *A&A*, 696, A219
 De Simone M. et al., 2022, *MNRAS*, 512, 5214
 Draine B., 2003, *ARA&A*, 41, 241
 Duflot D., Toubin C., Monnerville M., 2021, *Front. Astron. Space Sci.*, 8, 645243
 Dunning Thom H. J., Peterson K. A., Wilson A. K., 2001, *J. Chem. Phys.*, 114, 9244
 Enrique-Romero J., Rimola A., Ceccarelli C., Ugliengo P., Balucani N., Skouteris D., 2022, *ApJS*, 259, 39
 Ferrara A., Viti S., Ceccarelli C., 2016, *MNRAS*, 463, L112
 Ferrero S., Zamirri L., Ceccarelli C., Witzel A., Rimola A., Ugliengo P., 2020, *ApJ*, 904, 11
 Ferrero S., Pantaleone S., Ceccarelli C., Ugliengo P., Sodupe M., Rimola A., 2023a, *ApJ*, 944, 142
 Ferrero S., Ceccarelli C., Ugliengo P., Sodupe M., Rimola A., 2023b, *ApJ*, 951, 150
 Ferrero S., Ceccarelli C., Ugliengo P., Sodupe M., Rimola A., 2024, *ApJ*, 960, 22
 Galliano F., Galametz M., Jones A. P., 2018, *ARA&A*, 56, 673
 Garrod R. T., Herbst E., 2006, *A&A*, 457, 927
 Garrod R. T., Weaver S. L. W., Herbst E., 2008, *ApJ*, 682, 283
 Ginolfi M., Graziani L., Schneider R., Marassi S., Valiante R., Dell'Agli F., Ventura P., Hunt L. K., 2017, *MNRAS*, 473, 4538
 Goettl S. J., Vincent A., Silva M. X., Yang Z., ao B. R. L. G., Sun R., Kaiser R. I., 2024, *Sci. Adv.*, 10, eadq5018
 Goumans T. P. M., Bromley S. T., 2012, *MNRAS*, 420, 3344
 Grimme S., 2006, *J. Comput. Chem.*, 27, 1787
 Grimme S., Antony J., Ehrlich S., Krieg H., 2010, *J. Chem. Phys.*, 132, 154104
 Grimme S., Ehrlich S., Goerigk L., 2011, *J. Comp. Chem.*, 32, 1456
 Gusdorf A., Pineau Des Forêts G., Cabrit S., Flower D. R., 2008, *A&A*, 490, 695
 Hartmann L., Ciesla F., Gressel O., Alexander R., 2017, *Space Sci. Rev.*, 212, 813
 Henning T., 2010, *ARA&A*, 48, 21
 Jeong K. S., Winters J. M., Le Bertre T., Sedlmayr E., 2003, *A&A*, 407, 191
 Jiménez-Serra I., Caselli P., Martín-Pintado J., Hartquist T. W., 2008, *A&A*, 482, 549
 Jones A. P., Tielens A. G. G. M., Hollenbach D. J., 1996, *ApJ*, 469, 740
 Kendall R. A., Dunning Thom H. J., Harrison R. J., 1992, *J. Chem. Phys.*, 96, 6796
 Krasnokutski S. A., Rouillé G., Jäger C., Huysen F., Zhukovska S., Henning T., 2014, *ApJ*, 782, 15

Lee C., Yang W., Parr R., 1988, *Phys. Rev. B Condens. Matter*, 37, 785

Mardirossian N., Head-Gordon M., 2016, *J. Chem. Phys.*, 144, 214110

Minissale M. et al., 2022, *ACS Earth Space Chem.*, 6, 597

Molinari S. et al., 2025, *A&A*, 696, A149

Mollière P. et al., 2022, *ApJ*, 934, 74

Molpeceres G., Kästner J., Fedoseev G., Qasim D., Schömig R., Linnartz H., Lamberts T., 2021, *J. Phys. Chem. Lett.*, 12, 10854

Molpeceres G., Zaverkin V., Furuya K., Aikawa Y., Kästner J., 2023, *A&A*, 673, A51

Neese F., 2022, *WIREs Comput. Mol. Sci.*, 12, e1606

Neese F., Wennmohs F., Hansen A., 2009, *J. Chem. Phys.*, 130, 114108

Neese F., Wennmohs F., Becker U., Riplinger C., 2020, *J. Chem. Phys.*, 152, 224108

Öberg K. I., Bergin E. A., 2021, *Phys. Rep.*, 893, 1

Öberg K. I., Wordsworth R., 2019, *AJ*, 158, 194

Öberg K. I., Murray-Clay R., Bergin E. A., 2011, *ApJ*, 743, L16

Pantaleone S., Enrique-Romero J., Ceccarelli C., Ugliengo P., Balucani N., Rimola A., 2020, *ApJ*, 897, 56

Pantaleone S., Enrique-Romero J., Ceccarelli C., Ferrero S., Balucani N., Rimola A., Ugliengo P., 2021, *ApJ*, 917, 49

Pareras G., Cabedo V., McCoustra M., Rimola A., 2023, *A&A*, 680, A57

Pareras G., Cabedo V., McCoustra M., Rimola A., 2024, *A&A*, 687, A230

Perrero J., Rimola A., 2024, *Icarus*, 410, 115848

Perrero J., Enrique-Romero J., Martínez-Bachs B., Ceccarelli C., Balucani N., Ugliengo P., Rimola A., 2022, *ACS Earth Space Chem.*, 6, 496

Plane J. M. C., Gómez-Martín J. C., Feng W., Janches D., 2016, *J. Geophys. Res.: Atmos.*, 121, 3718 <https://doi.org/10.1002/2015JD024691>

Potapov A., McCoustra M., 2021, *Int. Rev. Phys. Chem.*, 40, 299

Rimola A., Sodupe M., Ugliengo P., 2010, *Phys. Chem. Chem. Phys.*, 12, 5285

Rimola A., Taquet V., Ugliengo P., Balucani N., Ceccarelli C., 2014, *A&A*, 572, A70

Rimola A., Skouteris D., Balucani N., Ceccarelli C., Enrique-Romero J., Taquet V., Ugliengo P., 2018, *ACS Earth Space Chem.*, 2, 720

Riplinger C., Neese F., 2013, *J. Chem. Phys.*, 138, 034106

Schilke P., Walmsley C. M., Pineau des Forets G., Flower D. R., 1997, *A&A*, 321, 293

Schneider R., Maiolino R., 2024, *A&AR*, 32, 2

Tielens A. G. G. M., 2005, *The Physics and Chemistry of the Interstellar Medium*, Cambridge University Press, UK

Tielens A. G. G. M., McKee C. F., Seab C. G., Hollenbach D. J., 1994, *ApJ*, 431, 321

Tinacci L., Germain A., Pantaleone S., Ferrero S., Ceccarelli C., Ugliengo P., 2022, *ACS Earth Space Chem.*, 6, 1514

Tinacci L., Germain A., Pantaleone S., Ceccarelli C., Balucani N., Ugliengo P., 2023, *ApJ*, 951, 32

Watanabe N., Kouchi A., 2008, *Prog. Surf. Sci.*, 83, 439

Weigend F., Ahlrichs R., 2005, *Phys. Chem. Chem. Phys.*, 7, 3297

Wilson R. W., Penzias A. A., Jefferts K. B., Kutner M., Thaddeus P., 1971, *ApJ*, 167, L97

Woon D. E., Dunning Thom H. J., 1993, *J. Chem. Phys.*, 98, 1358

Woon D. E., Herbst E., 2009, *ApJS*, 185, 273

Zhao Y., Truhlar D. G., 2005, *J. Phys. Chem.*, 109, 5656

Zhao Y., Truhlar D. G., 2008a, *Acc. Chem. Res.*, 41, 157

Zhao Y., Truhlar D. G., 2008b, *Theor. Chem. Acc.*, 120, 215

Zhukovska S., Henning T., 2014, *Proc. Sci., Life Cycle of Dust in the Magellanic Clouds and the Milky Way*. SISSA, Trieste, PoS#016

APPENDIX A: BENCHMARK

Table A1. Interaction energies (DE) between the SiO molecule and a water molecule for PRC-1 and PRC-2, calculated using six different DFT functionals: BHLYP-D3(BJ), PW6B95-D3(BJ), M062X-D3, ω B97X-D3, ω B97M-V, and M06. Corresponding interaction energies are calculated at the single point CCSD(T) level on each DFT-optimized structure. The table includes the relative percentage errors of each functional for each structure. Units are in kJ mol^{-1} .

struct	PRC-1		PRC-2	
	DE	err%	DE	err%
ω B97X-D3	−30.9	28.9	−25.1	1.0
CCSD(T)//DFT	−24.0		−25.3	
BHLYP-D3(BJ)	−33.8	34.9	−28.2	13.6
CCSD(T)//DFT	−25.0		−24.8	
PW6B95-D3(BJ)	−32.8	38.5	−25.2	0.2
CCSD(T)//DFT	−23.7		−25.3	
M062X-D3	−36.0	38.4	−26.0	2.9
CCSD(T)//DFT	−24.6		−25.2	
ω B97M-V	−34.0	41.9	−26.0	2.7
CCSD(T)//DFT	−23.9		−25.3	
M06	−34.5	40.9	−24.6	2.7
CCSD(T)//DFT	−24.5		−25.3	

Table A2. Interaction energies (DE) between the SiO molecule and a water molecule for PRC-1, calculated using ω B97X-D3. DE values are calculated at the single point CCSD(T) level on the ω B97X-D3-optimized structure with different basis set and through the complete basis set limit. The table includes the relative percentage errors of each functional for each structure. Energies are in kJ mol^{-1} .

struct	PRC-1	
	DE	err%
ω B97X-D3	−30.9	
CCSD(T)/aug-cc-pVTZ	−24.0	28.9
CCSD(T)/aug-cc-pVQZ	−24.6	25.4
CBS	−25.2	22.7

Table A3. Relative energies of the stationary points involved in the gas-phase reaction pathway of $\text{SiO} + \text{H}_2\text{O}$. DFT = electronic energy, ZPE DFT = electronic energy + zero-point energy corrections, CCSD(T) = CCSD(T)/aug-cc-pVTZ, and DLPNO = DLPNO-CCSD(T)/aug-cc-pVTZ/aug-cc-pVTZ-C. Values are in kJ mol^{-1} .

	$\text{SiO} + \text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_2$		DFT = ω B97X-D3/def2-TZVP	
	DFT	ZPE DFT	CCSD(T)//DFT	DLPNO//DFT
Reactants	0	0	0	0
TS	34.6	28.1	39.7	39.8
Products	−145.9	−141.2	−136.6	−137.8
	$\text{SiO} + \text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_2$		DFT = M062X-D3/def2-TZVP	
	DFT	ZPE DFT	CCSD(T)//DFT	DLPNO//DFT
Reactants	0	0	0	0
TS	27.8	22.8	39.8	39.8
Products	−152.4	−147.2	−136.1	−137.8

APPENDIX B: DISCARDED PATHS

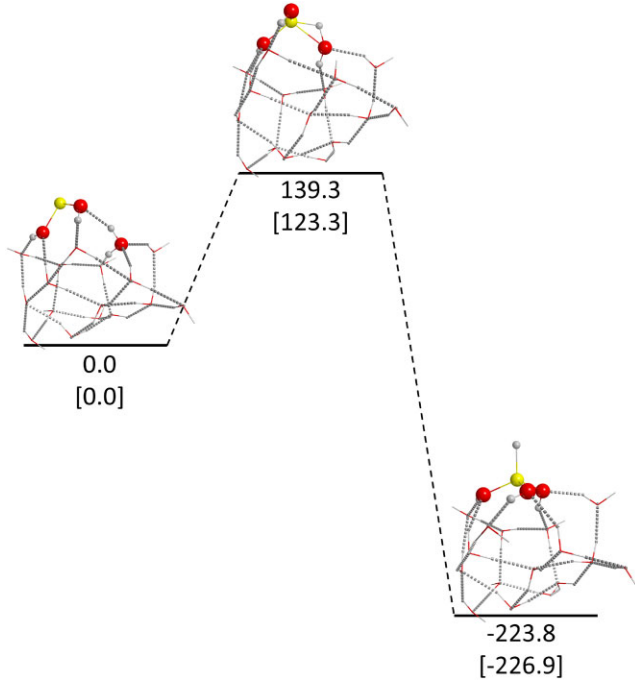


Figure B1. Relative energy profile (in kJ mol^{-1}) of the reaction of Si(OH)_2 with H_2O , the geometries of the stationary points being optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The bare values refer to DFT potential energies, and the values in square brackets include the ZPE corrections. All values are given in kJ mol^{-1} .

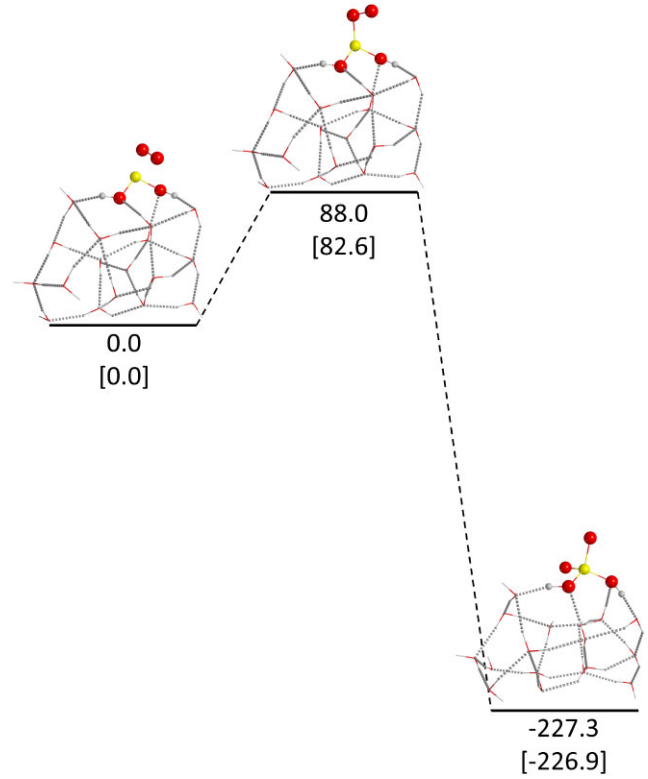


Figure B2. Relative energy profile (in kJ mol^{-1}) of the reaction between Si(OH)_2 and O_2 , the geometries of the stationary points being optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The bare values refer to DFT potential energies, and the values in square brackets include the ZPE corrections. All values are given in kJ mol^{-1} .

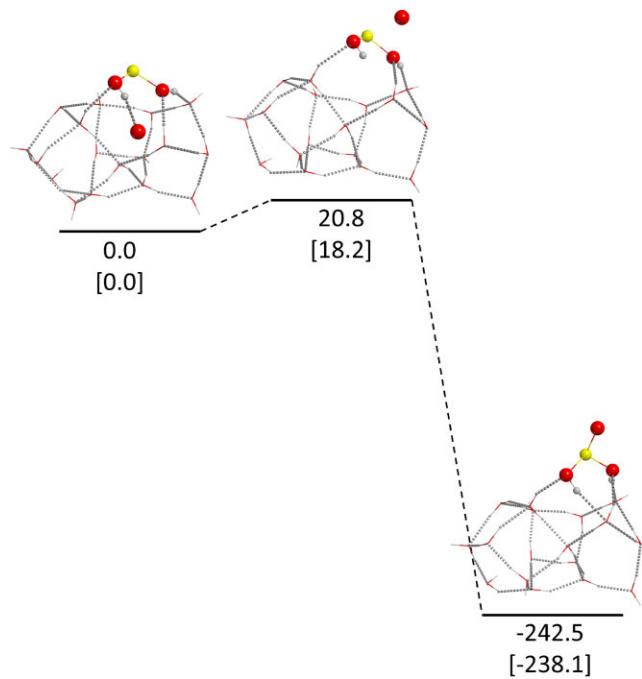


Figure B3. Relative energy profile (in kJ mol⁻¹) of the reaction between Si(OH)_2 and O starting from adsorption site B2, the geometries of the stationary points being optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The bare values refer to DFT potential energies, and the values in square brackets include the ZPE corrections. All values are given in kJ mol⁻¹.

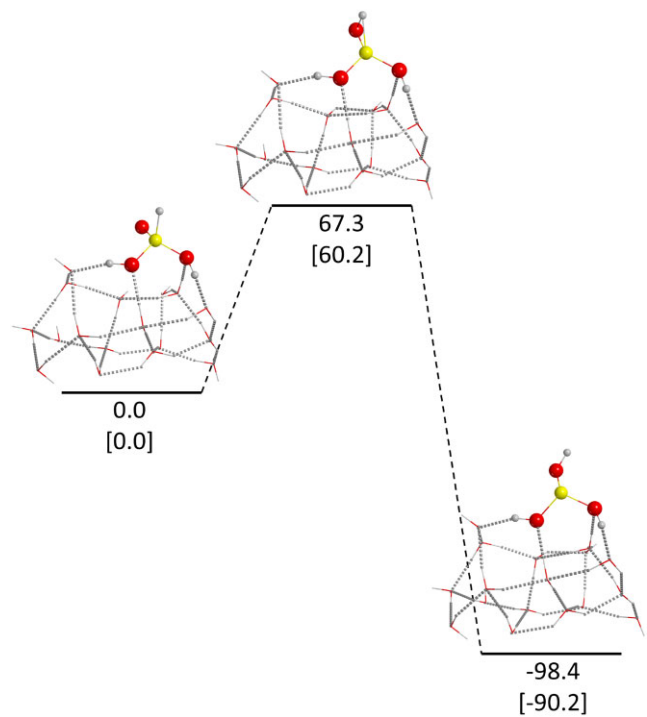


Figure B4. Relative energy profile (in kJ mol⁻¹) of the reaction $(\text{O})(\text{H})\text{Si(OH)}_2 \rightarrow \text{Si(OH)}_3$. The geometries of the stationary points being optimized at the DFT $\omega\text{B97X-D3/def2-TZVP}$ theory level. The bare values refer to DFT potential energies, and the values in square brackets include the ZPE corrections. All values are given in kJ mol⁻¹.

This paper has been typeset from a $\text{\LaTeX}$ file prepared by the author.