Adsorption of Atoms on a Crystalline Ice Surface Model: Results from Periodic *ab Initio* Simulations

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Abstract. In cold and dense regions of the interstellar medium, such as molecular clouds, more than 200 gas-phase molecular species have been observed by means of infra-red and rotational spectroscopy techniques alongside solid sub-micrometer sized particles called dust grains. These grains are of uttermost importance because their surfaces serve as meeting points for chemical species that adsorb from the gas phase, diffuse and possibly react to form more complex molecules. These grains consist of a silicate or carbonaceous cores covered in layers of water dominated ices that contain other small volatile molecules such as CO, CO_2, NH_3, CH_3OH. Most of the ice components originate from the adsorption and reaction of bare atoms, e.g., H, C, N and O, on the grain surfaces. An important challenge in Astrochemistry is to characterize the thermodynamics and kinetics of the main reaction steps of the bare atoms forming the ice components on the grain surfaces. As a first step previous to the reaction of these atomic species, in this paper we present results based on quantum chemistry methods on the adsorption of atomic carbon, nitrogen and oxygen on a crystalline water ice surface model mimicking the icy grain surfaces.

1 Introduction

Surface chemistry plays a central role in Astrochemistry. Grain surface processes such as adsorption, diffusion and reactions are currently topics of great interest both for experimentalists and theoreticians of the field. Quantitative information such as binding energies (BE), diffusion energies and reaction rate constants are used as input data in astrochemical models that aim to reproduce the evolution of the chemical composition of the interstellar medium (ISM) [2]. However, the values implemented in these models are often roughly approximated, leading to

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incorrect predictions of the interstellar chemical evolution. Following the work of Shimonishi et al. [9] in which the adsorption of atomic C, N, O on different annealed 20-water molecule clusters was deeply investigated, here we explore the same adsorption processes on a periodic crystalline model for water ice. Our results are compared with those of Simonishi et al. as well as those from Wakelam et al. [13] in which BEs were calculated for a vast number of species (also for C, N and O) with a single water molecule. The aim of the work is to investigate the effect of the structural models used as water ice surfaces, including the size of the models, the structural state and the inclusion or not of periodicity, on the adsorption properties.

2 Computational Details

All the simulations were performed adopting the DFT formalism, using the CP2K software package [6]. Electronic structure calculations were carried out using the QUICKSTEP module, which employs the hybrid Gaussian and plane waves (GPW) approach (i.e., an hybrid scheme of Gaussian functions and plane waves as basis set) for the calculation of energies and forces [7,12]. In our DFT simulations we applied the norm-conserving GTH (Goedecker-Teter-Hutter) pseudopotentials, [3] replacing the core electrons and a triple-zeta valence basis set added with a single set of polarization Gaussian functions (TZVP) for valence electrons. The PBE DFT exchange-correlation functional in combination with the D3(BJ) Grimme's correction to account for dispersive forces (not taken into account in the pure PBE functional) was used [4,5,8].

Binding energies for the atomic species considered were calculated as:

$$-BE = \Delta E_{\text{int}} = E(SM) - E(S) - E(M) \tag{1}$$

in which the binding energy (BE) is the interaction energy (ΔE_{int}), with opposite sign, between the atom and the surface, $E(SM)$ is the energy of the optimized atom/slab adduct, $E(S)$ is the total energy of the optimized slab and $E(M)$ is the total energy of the atomic species. The BE values are not corrected for the basis set superposition error (BSSE).

3 Ice Surface Model

As a first step to simulate the atom adsorption processes on interstellar ice water, we adopted as ice model the P-ice system, a crystalline proton ordered water ice phase [1]. From its bulk structure, we cut a surface along the (010) plane. This surfaces slab model does not possess a net dipole moment along the z-axis, which ensures a electronic structure stability by increasing its thickness [11]. The PBE-D3(BJ)-optimized structure of the P-ice (101) surfaces (see Fig. 1) presents two main adsorption sites identified as dH (dangling hydrogen) and dO (dangling oxygen). We adopted a supercell model with unit cell parameters of $|\mathbf{a}| = 13.156\,\text{Å}$ and $|\mathbf{b}| = 14.162\,\text{Å}$ with the aim to simulate the adsorption of

fully isolated atoms, i.e., without contributions from lateral interactions between replica images, this way mimicking the actual low gas densities of the ISM. The thickness of the slab model is 11 Å (corresponding to 3 water layers). To avoid fictitious interactions between slab replicas, the c parameter (represented by the non-periodic z direction) was set to 30.156 Å. During the optimizations, the cell parameters remained fixed. Integrals were evaluated only at the Γ point, namely, point $k = 0$ in the first Brillouin zone (so-called the central zone).

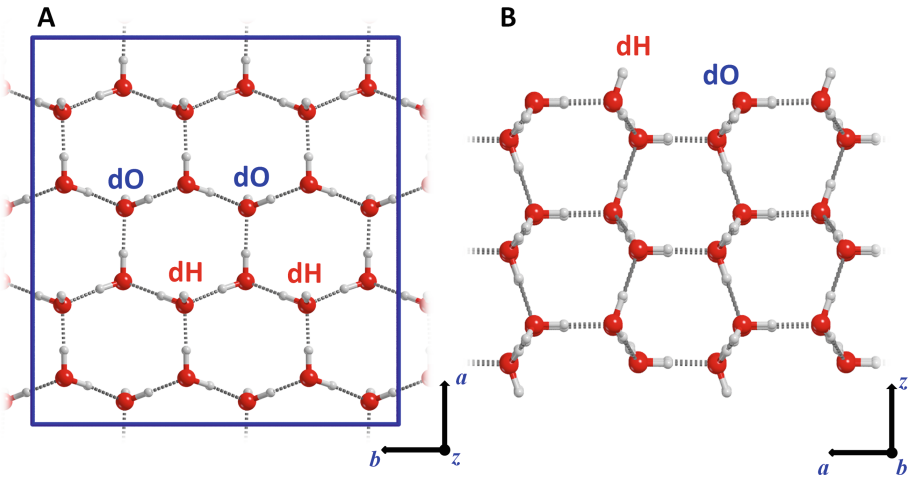

Fig. 1. Top view (A) of the first layer and side view (B) of the crystalline surface model, with dangling hydrogen (dH) and dangling oxygen (dO) sites highlighted in red and blue, respectively.

4 Adsorption of C, N and O

Several geometry optimizations were performed to simulate the atomic adsorptions on the crystalline water ice surface. For all cases, the initial guess structures consisted of the atoms placed over the centroid of the hexagon of the outermost water layer, rendering adsorption states either close to the dH or the dO sites. The adsorption of the atoms were simulated according to their electronic ground states, i.e., C(^3P), O(^3P) and N(^4S). In any case, adsorption does not lead to changes in the electronic states, that is, the first excited electronic states of the bare atoms (namely, singlet for C and O, and doublet for N) remain more unstable upon adsorption. These atoms do not possess any charge and electric dipole moment but can exhibit an electric quadrupole moment or higher moments since their electron density is not spherically symmetric around the nucleus. In our cases, C and O do possess a non-zero electric quadrupole moment whereas N has a null quadrupole moment but a non-zero octupole moment. Accordingly,

the interactions between these atoms and the surface are expected to be weak through a physisorption mechanism. Figure 2, Fig. 3 and Fig. 4 show the PBE-D3(BJ)-optimized structures of the computed complexes for every atom on both dH and dO sites. Table 1 reports the calculated BE values for these atoms, the comparison of which with those of Simonishi et al. and Wakelam et al. is also reported.

Table 1. Calculated BE values, given in Kelvin and in kJ mol^{-1} (in square brackets) of N, O and C on the dH and dO sites of the (101) P-ice surface model. The values by Shimonishi et al. [9] Wakelam et al. [13] are also reported for the sake of comparison.

	BE dH site PBE-D3	BE dO site PBE-D3	⟨BE⟩ Shimonishi ω-B97XD	BE Wakelam M06-2X
N	977[8.2]	937[7.8]	400[3.3]	1200[10.0]
O	4673[38.8]	3177[20.2]	1440[12.0]	1700–2200[14.1–18.3]
C	18449[153.2]	14605[127.3]	14100[116.4]	10000[83.1]

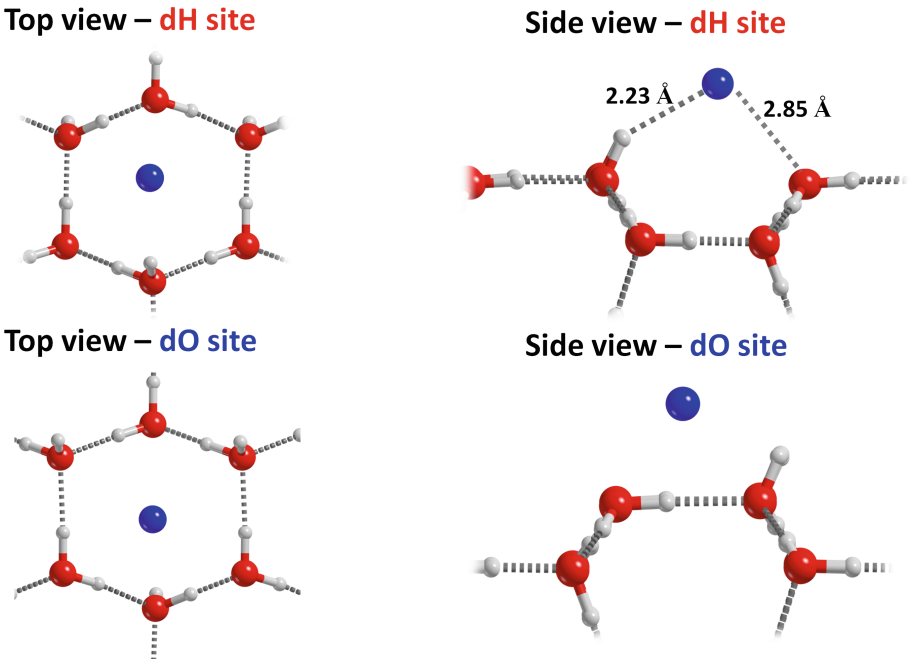

Fig. 2. Top and side views of the PBE-D3(BJ)-optimized geometries for the adsorption of N on the dH and dO sites. Bond distances are in Å

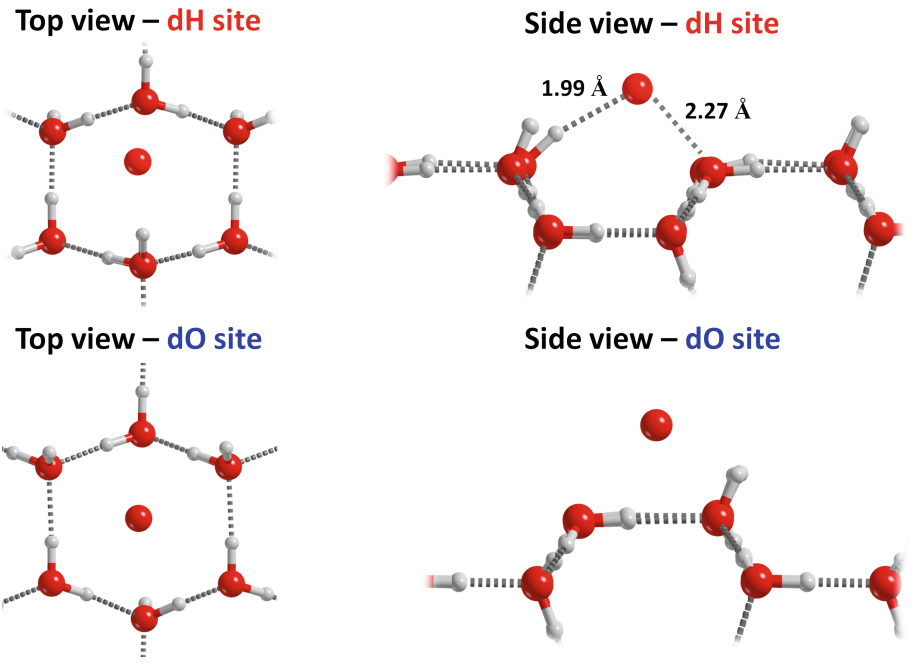

Fig. 3. Top and side views of the PBE-D3(BJ)-optimized geometries for the adsorption of O on the dH and dO sites. Bond distances are in Å

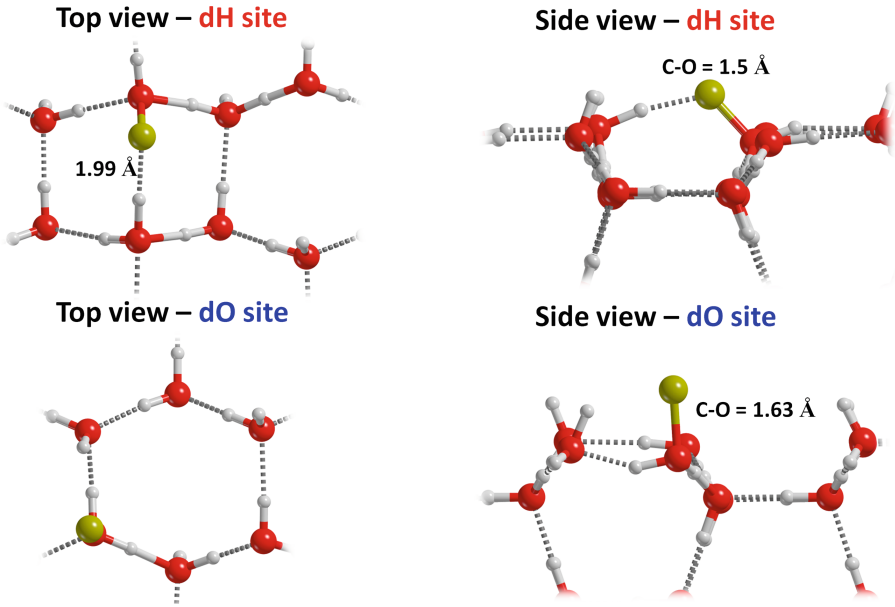

Fig. 4. Top and side views of the PBE-D3(BJ)-optimized geometries for the adsorption of C on the dH and dO sites. Bond distances are in Å

As one can seen in Fig. 2, for N adsorption, the atom remains over the water hexagon of the outermost ice layer and does not perturb the structure of the crystalline ice surface. Calculated BEs are small, dH being a more favourable adsorption site (977 K) than dO (937 K). In both complexes, the adsorption is dominated by dispersive forces. The computed values are in reasonable agreement with those reported in the other two computational works.

For O adsorption, the interaction with the surface is stronger than for the N case on both adsorption sites. Interestingly, adsorption on dH site (BE = 4673 K) is significantly more stable than the dO site (BE = 3177 K). As one can see in Fig. 3, on the dH site, the adsorbate O atom stays closer to the surface in comparison with the N case, as reflected by the O–O_{surf} and N–O_{surf} distances (2.27 and 2.85 Å, respectively). Due to that, the surface dangling H atom bents towards the O atom, thus presenting some distortion with respect to the pristine crystalline surface. Comparison of atomic O BEs on water, our values are clearly overestimated with respect to the values of the other works (see Table 1). This can be due to GGA nature of the PBE functional, which tends to overestimate electron delocalization situations [10]. This could indeed be our case since the O atom is an open-shell system with two unpaired electrons. Accordingly, more investigation as far as the quantum chemistry method is concerned on this system is required.

Adsorption of atomic C on our crystalline water ice surface model is the most peculiar case because it reacts spontaneously with an oxygen atom of the surface forming a •COH radical (see Fig. 4). This event triggers a chain displacement of a hydrogen atom to a nearby water molecule. The C-O distance (about 1.5 Å in the dH site) is similar to that of a single bond between these two atoms. From the Mulliken charges of the Carbon atom (−0.27 a.u.) and of the attached Oxygen atom (−0.41 a.u.), a charge transfer towards the carbon atom can be seen. Because of this spontaneous chemisorption process, the calculated BE is large, especially on the dH site (18449 K) an additional interaction between the C atom and the dangling hydrogen of the water matrix is estbalished. On the dO site, calculated BE is lower (14605 K) because (i) the C-O distance is longer (1.63 Å) and (ii) there are no additional interactions with the surface. In the work of Simonishi et al. [9] the same spontaneous chemisorption was also observed for the vast majority of the simulations carried out on the cluster models using ω-B97XD as DFT method, which is a range separated functional that can treat long range interactions better than PBE-D3 and therefore, probably more accurate. This could be indicative that the formation of the chemical bond between C and O is not an artifact of the PBE method. Our calculated BE value, moreover, is in good agreement with that reported by Simonishi et al. (14100 K) [9]. In Wakalem et al. [13] the interaction of C with one water molecule does not lead to a full formation of a C-O bond, but some interaction seems to be formed between these two atoms. The reason why they do not observe the chemical changes occurring in our system is probably due to the use of just one single water molecule. As mentioned above, the chemisorption brings associated with a H transfer from the reacting water to a nearby water molecule, which favors the formation of the

C-O chemical bond. This H transfer is not possible in the Wakelam's model and accordingly, the system does not evolve to fully form •COH. Because of that, the Wakelam's BE value is lower (10000 K) than the computed by us and by Shimonishi et al.

5 Conclusions and Perspective

The adsorption of atomic C(^3P), N(^4S) and O(^3P) on a crystalline water ice surface model based on the P-ice system has been investigated by means of DFT PBE-D3(BJ). Our results are in general in good agreement with those reported in the literature using smaller, non periodic water ice models and different DFT methods, although some differences have been detected. The physisorption of N and O and the chemisorption of C are qualitatively similar. Calculated BE values for N are in good agreement with the other computational data. For C adsorption, in which spontaneous formation of •COH takes place, results indicate the importance of using relatively large water ice surfaces, otherwise the chemisorption is not properly described (i.e., full formation of •COH does not occur). The major drawback of the present work is the overestimated BE value for atomic O, which is over stabilized with respect to the reported values, probably due to the GGA nature of the PBE functional. Further investigations in that aspect (e.g., to refinement of the BE values using highly accurate quantum chemical methods) are mandatory. As a perspective, the next step will be to simulate the same adsorption processes on an amorphous ice surface, which will resemble more closely astrochemical ices, to assess the changes that a disordered surface can bring to the BE values of these atomic species.

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