



Adsorption of methane and CO₂ onto olivine surfaces in Martian dust conditions



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ABSTRACT

Methane has been detected on all planets of our Solar System, and most of the larger moons, as well as in dwarf-planets like Pluto and Eric. The presence of this molecule in rocky planets is very interesting because its presence in the Earth's atmosphere is mainly related to biotic processes. Space instrumentation in orbiters around Mars has detected olivine on the Martian soil and dust. On the other hand the measurements of methane from the Curiosity rover report detection of background levels of atmospheric methane with abundance that is lower than model estimates of ultraviolet degradation of accreted interplanetary dust particles or carbonaceous chondrite material. Additionally, elevated levels of methane about this background have been observed implying that Mars is episodically producing methane from an additional unknown source, making the reasons of these temporal fluctuations of methane a hot topic in planetary research. The goal of this study is to investigate at atomic level the interactions during the adsorption processes of methane and other Mars atmospheric species (CO₂, H₂O) on forsterite surfaces, through electronic structure calculations based on the Density Functional Theory (DFT). We propose two models to simulate the interaction of adsorbates with the surface of dust mineral, such as binary mixtures (5CH₄+5H₂O/5CH₄+5CO₂) and as a semi-clathrate adsorption. We have obtained interesting results of the adsorption process in the mixture 5CH₄+5CO₂. Associative and dissociative adsorptions were observed for water and CO₂ molecules. The methane molecules were only trapped and held by water or CO₂ molecules. In the dipolar surface, the adsorption of CO₂ molecules produced new species: one CO from a CO₂ dissociation, and, two CO₂ molecules chemisorbed to mineral surface forming in one case a carbonate group. Our results suggest that CO₂ has a strong interaction with the mineral surface when methane is present. These results could be confirmed after the analysis of the data from the upcoming remote and in-situ observations on Mars, as those to be performed by instruments on the ESA's ExoMars Trace Gas Orbiter and ExoMars rover.

1. Introduction

Methane is a molecule relatively abundant within the objects of our Solar System. It can be found on Earth, the Giant Planets (Jupiter, Saturn, Uranus, Neptune), in Saturn's planet-size moon Titan, and, very recently has been reported the indubitable detection of methane on Mars (Webster et al., 2015). The presence of this molecule in rocky planets is very interesting because its presence in our atmosphere is mainly related to biological production. For that reason some works speculate that microorganisms could produce methane in Mars (Hu et al., 2016). However, methane can be abiotically produced also. For example, minerals surfaces, such as olivine, can catalyze the formation of CH₄ at low temperatures (Neubeck et al., 2011). This process is known as serpentinization

of ultramafic rocks (Kelley et al., 2001; Russell, 2007), where some chemical reactions can produce H₂ and CH₄ in the mineral surface with the presence of iron ferrous (McCollom and Bach, 2009) Olivine is an ultramafic rock, and it is a major component in the lithosphere of Earth and other planets as Mars (Ody et al., 2013). It consists of magnesium, iron and silicates that form a complete solid solution between two end-members: forsterite (Mg-rich olivine) and fayalite (Fe-rich olivine). In space, forsterite has been found in meteorites and in the cometary dust of samples in the Stardust Mission (Lauretta et al., 2005). On Mars, olivine has been detected using remote sensing and in-situ observations (Blake et al., 2013), and the NASA's Curiosity rover of the Mars Science Laboratory mission, currently exploring the Gale crater on Mars, has detected methane by using the onboard Tunable Laser Spectrometer of

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the SAM (Sample Analysis at Mars). The results show fluctuations of 0.69 ppbv–7.2 ppbv during a short time (20-month) (Webster et al., 2015). The reasons of this increment of CH₄ are unknown.

There are several experimental and theoretical studies about the hydration process and stability of different surface faces of olivine (Asaduzzaman et al., 2013; de Leeuw et al., 2000; Price et al., 1987; Stimpfl et al., 2006). On the other hand, the interactions of surface of forsterite (Mg-rich olivine) with several molecules, such as, water, glycine, ammonia, CO, CO₂, CH₄ etc., have been studied using several methodologies (Asaduzzaman et al., 2014; Escamilla-Roa and Moreno, 2012, 2013; Escamilla-Roa et al., 2017). Chemisorption processes were reported in the interphase solid-gas of grain dust. The formation of methane and serpentinization process has been investigated from both experimental and theoretical points of view (Martos-Villa et al., 2013; McCollom and Bach, 2009; Neubeck et al., 2011).

The goal of this work is to investigate in depth the microscopic interactions of forsterite surfaces with different species with and without presence of water molecules, in order to understand the stability of methane inside surface (clathrate model) or onto dust particle (aerosol model). This could provide a light on the recent observations of methane on Mars. Interaction processes of methane and Mars atmospheric species (CO₂, H₂O) with two forsterite (100) surfaces were investigated at atomic level by through quantum mechanical calculations of electronic structure based on the Density Functional Theory (DFT). Dissociations of water and CO₂ along with the formation of carbonates were observed on these surfaces.

2. Methodology

In order to understand the adsorption energy of several molecules (CH₄, CO₂, H₂O) onto mineral surfaces and main geometrical parameters of adsorption complexes (bond distances, bond angles) onto the forsterite (100) surfaces (dipolar and non-dipolar), calculations based on the Density Functional Theory were performed by using the Dmol3 code.

To reproduce the amorphous mixture of ice components of CH₄ and H₂O, an Amorphous Cell Builder code based on Monte Carlo simulations (Accelrys, 2009) was used with geometry optimization for refinement of amorphous ice periodical boxes, using the Compass Force Field at 298 K and a density of 1 g/cm³. This density provides an enough coverage on the surface for the molecules-mineral surface interactions. The density value of 1 g/cm³ is found in this kind of ices at 50 K and this density can be considered an intermediate value between the so-called low-density amorphous water ice (0.95 g/cm³) and the higher density form (1.17 g/cm³) (Gómez and Escribano, 2017). On the other hand, the Adsorption Locator code (Accelrys, 2009) was used for exploration of the possible adsorption sites of adsorbate on the mineral surface. This exploration is based on Monte Carlo and simulated annealing method where the energy of the system is calculated with empirical interatomic potentials based on the Universal forcefield (Rappe and Goddard, 1991).

The quantum-mechanical calculations were performed by means of the Dmol3 code within the Materials Studio package (Accelrys, 2009). The optimization of these models was at DFT level including periodical boundary conditions. The Generalized Gradient Approximation (GGA) with the PBE exchange correlation functional was used (Perdew et al., 1996). The electronic calculations were made with a DNP basis set (double-zeta basis set augmented with polarization functions). The orbital cut-off quality was determined with a 0.1 eV atom⁻¹ of energy accuracy threshold. We used semi-core Pseudopotentials (DSPP). The convergence criterion for the self-consistent field was 1×10^{-6} . The optimization of geometries has been performed at 0 K. The harmonic vibrational frequencies were calculated diagonalizing the mass-weighted second-derivative Hessian matrix generated by finite atomic displacements.

In the adsorption processes, the geometry of the adsorbate (H₂O, CH₄ and CO₂ molecules) was optimized alone at constant volume within a large periodical box with the same size of the adsorption complex. This

adsorbate was also optimized with the periodical surface of mineral at constant volume with the same crystal cell parameters. This methodology has been previously used successfully to describe similar adsorption processes (Escamilla-Roa and Moreno, 2012, 2013). The geometry parameters and energies of the bulk and clean surfaces of forsterite and adsorption complexes were calculated. The structure of methane hydrate was taken from previous calculations on methane clathrate (Martos-Villa et al., 2013).

To determine the adsorption energy, we use the following equation:

$$E_{X/\text{forst}}^{\text{ads}} = -(E^{X/\text{forst-surf}} - E^{\text{forst-surf}} - nE^{\text{adsorbate}}) \quad (1)$$

where $E^{X/\text{forst-surf}}$, $E^{\text{forst-surf}}$, and E^X are the energies of the forsterite surface with the X-chemical species (adsorption complex) on the surface, the pristine forsterite surface, and the adsorbates involved, respectively.

As a model of olivine mineral, all chemical species were adsorbed on a $1 \times 2 \times 1$ unit cell of (100) surfaces of forsterite, component of dust grains. The optimization of these complexes was similar to that of the clean forsterite surface; in the slab, three upper SiO₄ planes were optimized and the rest of planes remained fixed. On the other hand, for the weak interactions we applied the semiempirical Grimme dispersion correction (Grimme, 2006) by fully optimizing adsorption complex and reactant with GGA/PBE/G06 method (McNellis et al., 2009). This correction was applied only in all the most stable complexes.

3. Models

3.1. Models of the surface

Two models of olivine were used. These models are based on optimized crystal structure of forsterite, which consists of independent SiO₄ tetrahedra linked by divalent Mg cations with octahedral coordination. There is evidence that the (100) and (010) surfaces are the most reactive and most stable surfaces for water adsorption, respectively (Muralidharan et al., 2008; Stimpfl et al., 2006). The forsterite (100) surfaces are built up with periodical boundary conditions by cleaving the bulk structure of forsterite optimized from the experimental bulk structure. This cleavage produced two kinds of (100) surfaces, dipolar and non-dipolar, whose difference is in the stacking sequence and in the surface atomic termination with different Mg atom coordination. The relaxed slab of the dipolar surface has several undercoordinated Mg atoms in the exposed surface: 4-fold (4f), 3-fold (3f) and 2-fold (2f). This surface contains steps and grooves, and it is more irregular than the non-dipolar one. Hence this undercoordination on the Mg exposed atoms is more remarkable than in the non-dipolar surface (Fig. 1). In the non-dipolar surface, the Mg atoms have different coordinations: 4-fold (4f) and 3-fold (3f) (Fig. 1). In our previous work we reported the geometrical parameters for the surface stacking sequences, these surfaces are in a good agreement with previous studies (de Leeuw et al., 2000; Escamilla-Roa and Moreno, 2012).

After this cleavage, supercells were generated and the vacuum volume was enlarged with respect to *c* axis until achieving a constant surface energy as a function of the vacuum distance. Previously we optimized the bulk and crystal surface. The geometrical parameters, such as Mg-O and Si-O distances are in good agreement with previous results (de Leeuw et al., 2000; Watson et al., 1997). The building and optimization conditions of these structures were detailed in previous works (Escamilla-Roa and Moreno, 2012, 2013). In both surfaces the slab generated contains five SiO₄ horizontal planes with alternate Mg atoms.

The high reactivity for adsorption process in the surface has a strong relationship with the steps, terrace, and corners that are generated from the Mg atoms with low coordination in surfaces (Escamilla-Roa and Sainz-Díaz, 2014a; King et al., 2010). The exploration of different terminations of the surface is important to determine the reactivity between adsorbent and adsorbates. The surface of Mars can support strong and intense solar radiation, cosmic particle impacts, and interstellar winds

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