



Atomistic and infrared study of CO-water amorphous ice onto olivine dust grain



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ABSTRACT

This work is a study of CO and H₂O molecules as adsorbates that interact on the surface of olivine dust grains. Olivine (forsterite) is present on the Earth, planetary dust, in the interstellar medium (ISM) and in particular in comets. The composition of amorphous ice is very important for the interpretation of processes that occur in the solar system and the ISM. Dust particles in ISM are composed of a heterogeneous mixture of amorphous or crystalline silicates (*e.g.* olivine) organic material, carbon, and other minor constituents. These dust grains are embedded in a matrix of ices, such as H₂O, CO, CO₂, NH₃, and CH₄. We consider that any amorphous ice will interact and grow faster on dust grain surfaces. In this work we explore the adsorption of CO-H₂O amorphous ice onto several (100) forsterite surfaces (dipolar and non-dipolar), by using first principle calculations based on density functional theory (DFT). These models are applied to two possible situations: *i*) adsorption of CO molecules mixed into an amorphous ice matrix (gas mixture) and adsorbed directly onto the forsterite surface. This interaction has lower adsorption energy than polar molecules (H₂O and NH₃) adsorbed on this surface; *ii*) adsorption of CO when the surface has previously been covered by amorphous water ice (onion model). In this case the calculations show that adsorption energy is low, indicating that this interaction is weak and therefore the CO can be desorbed with a small increase of temperature. Vibration spectroscopy for the most stable complex was also studied and the frequencies were in good agreement with experimental frequency values.

1. Introduction

The processes that occur on solid surfaces have great importance in materials science. In Astrophysics and Cosmochemistry, a mineral surface can be considered as a substrate on which several molecules in the vapour phase can be deposited. The mineral surface can then catalyse several reactions in the solid-gas interphase, where many interstellar molecules, such as NH₃, CH₄, can be produced (Ehrenfreund and Charnley, 2000). The mineral surface has an important role for understanding chemical reactions that occur with the interstellar dust. In the interstellar medium it is believed that H₂O ice is mainly component on amorphous phase (Al-Halabi et al., 2004), the amorphous ice can grow by vapour deposition onto the silicate grain (olivine), the most important component is the water and other volatile elements in low proportion such as: CO, CO₂, NH₃ and CH₄ (Ehrenfreund and Charnley, 2000), this ice is formed at a very low temperature (3–90 K). Water ice creates an amorphous network, the physical properties of this ice (density; conductivity, vapour pressure, and sublimation) depend of crystalline structure. The mixed of amorphous water ice with other components enhanced their interac-

tion with dust and organic molecules (Cartwright et al., 2008).

Carbon monoxide (CO) is an abundant molecule in the ISM and an important component of interstellar ice (Allamandola et al., 1999). This molecule has a small dipole moment and its affinity for water is poor. CO has been observed in planetary atmospheres, photosphere of the sun (Cooper and Kirby, 1987) and external galaxies (Scott et al., 2013). In the nucleus of comets, CO and CO₂ are the major constituent (Bockelee-Morvan et al., 2004). Observations of comet Hale-Bopp show that at large heliocentric distances, CO ice is the constituent of the cometary sublimation (Bockelee-Morvan et al., 2004; Hanner and Bradley, 2003) and this is the case in other comets such as 29 P/Schwassmann-Wachmann (Kossacki and Szutowicz, 2013). In comets, the origin of CO is unknown, for example there are several theories: *i*) CO molecule can be sublimated directly from the nucleus, *ii*) released from amorphous water ice, *iii*) sublimating from grains in the inner coma (Capria et al., 2000; Gunnarsson, 2003). Therefore we can study the several possibilities of interaction of CO molecule with mineral surface; one of them can be the interactions within the ice matrix or in a layering growth.

Water ice is the main component of comets and has the capacity to

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trap volatile molecules (Bockelee-Morvan et al., 2004). Several studies show that in comets CO molecule abundances can be between 2 and 30 per cent relative to water (Capria et al., 2000). In tele-spectroscopic studies, the stretching mode of CO has been observed in the ISM, with two absorption bands centred at 2136 cm^{-1} and 2152 cm^{-1} . These observations have been interpreted as the result of CO interactions with the ice surface (Manca et al., 2001), (Cuppen et al., 2011; Whittet et al., 1989). This vibration mode is sensitive to different environments. Frozen CO can be incorporated within H_2O -rich matrices called as polar ice matrices or in non-polar ice matrices formed by CO, CO_2 , N_2 , O_2 and CH_4 molecules (Allamandola et al., 1999). Previous astronomical observations attributed the stretching frequencies ($\nu(\text{CO})$) at 2136 cm^{-1} to non-polar environments (Cuppen et al., 2011). There are several experimental studies on the deposition of CO onto ice analogues models which reproduce these frequencies (Burke and Brown, 2010; Collings et al., 2003; Cuppen et al., 2011; Hibbitts and Szanyi, 2007). However, there are many discussions regarding to this $\nu(\text{CO})$.

This is a study, from an astrochemical point of view, of the phenomena that occur on the surface of dust grains (forsterite as a model of olivine) during the interactions in the gas-solid interphase, of carbon monoxide and water molecules as well as the growth of amorphous ice. According to astrophysical observations, we should consider two possible scenarios: *i*) a mixture of amorphous H_2O -CO ice that interacts at the same time with grain surface; *ii*) layer stacking, in which the interaction of CO occurs within a thin layer of amorphous water ice that previously grew on grain surface.

2. Methodology

Several theoretical models were explored in order to understand the stability of the CO and water molecules deposited onto surfaces grain. The spectroscopic property of the most stable structure was studied and compare with experimental results to validate our theoretical model. First principles calculations were used to optimize and describe the geometries and energies of the bulk and surfaces of forsterite and complexes adsorbed on the surfaces. This methodology has been previously used to describe the adsorption process successfully (Escamilla-Roa and Moreno, 2012, 2013). To obtain the energetic stability of the structures, the program of calculation has several electronic parameters such as: functional, pseudopotential, basis set, convergence gradient etc, these parameters will be describe in the next part.

All calculations were performed with the Dmol3 program (Accelrys, 2009), which applies Density Functional Theory (DFT) methods with the Generalized Gradient Approximation (GGA) and the PBE (Perdew Burke and Ernzerhof) (Perdew et al., 1996) exchange correlation functional with a double zeta basis set augmented with polarization function. DFT Semi-core Pseudopotentials (DSPP) was used to describe the core atoms. The convergence gradient for the self-consistent field for energy calculations was 1×10^{-6} eV. The vibration frequencies were calculated based on a harmonic approximation and were obtained by means of finite atomic displacements and forces by diagonalizing the mass-weighted second-derivative Hessian matrix. In order to estimate the contribution of the weak van der Waals interactions in the adsorption complexes, the correction with the semiempirical formalism of Grimme (Grimme, 2006) for the weak dispersion forces was included in some optimizations. The boxes of amorphous mixtures of carbon monoxide and water ices were generated using the amorphous cell builder modulus based on Monte Carlo simulations at 298 K and a density of 1 g/cm^3 with geometry optimization for refinement, using the Compass Force Field implemented in the Materials Studio (Accelrys, 2009).

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

$$E_{x\text{surf}}^{\text{ads}} = -(E^{x\text{surf}} - E^{\text{surf}} - nE^{\text{adsorbate}})$$

where $E^{x\text{surf}}$, E^{surf} , and $nE^{\text{adsorbate}}$ are the energies of the mineral surface with the X-chemical species (complex adsorbed) on the surface, the pristine surface, and the total electronic energies of the n chemical species involved, respectively.

In the adsorption processes, the geometry of all adsorbed molecules (carbon monoxide and water molecules) was optimized isolated within a periodical box of the same size as the adsorption complex periodic system at constant volume.

In the Monte Carlo (MC) simulated annealing of the adsorption of CO, periodical boundary conditions were applied and the energy calculations were based on empirical interatomic potentials using the Universal Force Field (Rappe and Goddard, 1991). The van der Waals interactions were calculated by an atom based direct method with a cut-off of 12.5 \AA and the coulombic electrostatic interactions were calculated by the Ewald method. The geometry of the configuration that was obtained after each simulation was fully optimized. Low energy adsorption sites were searched within the configurational space of the substrate-adsorbate complex for each value of a fictitious temperature. The MC simulated annealing method has been used satisfactorily in several works on silicates (Sainz-Díaz et al., 2003).

3. Models of the interphase surface amorphous ice

All chemical species were adsorbed on a $1 \times 2 \times 1$ supercell of the clean forsterite (100) surface as a model for an astrophysical dust mineral. In our previous works we observed that polar molecules (water, ammonia, glycine molecules) have interesting interactions with the (100) surface of forsterite (Escamilla-Roa and Moreno, 2012, 2013; Escamilla-Roa and Sainz-Díaz, 2014b). After the cleavage of the bulk forsterite crystal, we consider two possible and different (100) surfaces: a dipolar and a non-dipolar. We use these surfaces to simulate the solid-gas interface reactions. Besides, in the ISM the dust grains can suffer impacts which generate fractal particles with irregular surfaces and produce sites with low coordination Mg atoms associated with high reactivity (King et al., 2010). Furthermore, there is experimental and theoretical evidence which shows the (100) surface is reactive to water adsorption (Muralidharan et al., 2008; Stimpfl et al., 2006). In our previous works we showed the main geometric features of the pristine mineral surface, such as, Mg-O and Si-O bonds (Escamilla-Roa and Moreno, 2012). For both surfaces, the geometric parameters of Mg-O and Si-O distances are in good agreement with previous results (de Leeuw et al., 2000; Watson et al., 1997), when the (100) surface is created, several Mg atoms are under-coordinated in the exposed surface. In the dipolar surface (Fig. 1a) the under-coordinated Mg atoms can be: 4-fold (4f), 3-fold (3f) and 2-fold (2f) coordinated. In the non-dipolar surface (Fig. 2a), the Mg atoms can have the following coordination: 4-fold (4f and 4f*) (4f* indicates Mg atom in a top side on surface) and 3-fold (3f). It has been demonstrated that the low-coordination atoms, on exposed surface have a strong relation to the reactivity on mineral surface (Escamilla-Roa and Moreno, 2012, 2013; Escamilla-Roa et al., 2013, 2012).

To continue the study of the adsorption process on the surface of dust grains, we consider carbon monoxide which is a component of cometary ice. We start this study by analyzing the chemical interaction between surface grains and one CO molecule to determine the main reactive sites on the (100) surface where the Mg atoms show affinity to CO molecule. This affinity is measured through the adsorption energy. In the next step, we increased the concentration of CO and calculated the adsorption energy from one to three CO molecules to explore the chemical interaction of CO with the mineral surface. This model explores the intermolecular interactions between adsorbates and the adsorbent (surface). However, it does not pretend to reproduce a complete coverage of mineral surface because other molecules may also be presents. We considered a model which includes water molecules as the main component of amorphous ice and co-adsorbate with CO, in this model a mixture of amorphous water-carbon monoxide ice

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