The XIII International Conference on the Physics of Non-Crystalline

Solids

Adherence of model molecules to silica surfaces: first principle calculations.

Matías Nuñez[a,b,c*], Miguel Oscar Prado[b,c,d]

[a]Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, 8400 Bariloche, Argentina.
[b]Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, 8400 Bariloche, Argentina.
[c]Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina.
[d]Instituto Balseiro, Universidad Nacional de Cuyo, Mendoza, Argentina.
Av. E. Bustillo Km.9.5, 8400 San Carlos de Bariloche, Río Negro, Argentina.

Abstract

The adherence of "model molecules" methylene blue and eosine Y (¨positive¨ and ¨negatively¨ charged respectively) to crystal SiO_2 surfaces is studied from first principle calculations at the DFT level. Adsorption energies are calculated which follow the experimental threads obtained elsewhere (Rivera et al.,2013). We study the quantum nature of the electronic charge transfer between the surface and the molecules, showing the localized and delocalized patterns associated to the repulsive and attractive case respectively.

Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

Understanding the nature of the interaction of molecules with glass surfaces represents not only a very interesting academic topic but also has important technological applications. In recent experiments (Rivera et al., 2013), model molecules with positive (Methylene Blue) and negative (Eosin Y) net charges have been used in order to characterize the adherence properties of a glass surface at a given pH value.

In order to understand in depth the physical and chemical processes involved at the interaction between the molecules and surface, we carried first principle calculations, in the framework of Density Functional theory (DFT) with the purpose of simulating the process and calculate the charge transfer that occurs at the local level as well as the adsorption energies.

The surface of an amorphous material still represents a challenge at the DFT theory level. A large unit cell must be used for the calculations in order to obtain a representative distribution of atom positions that reproduces the thermodynamic properties of an amorphous material. Currently there are limitations for these kind of calculations due to the large computational resources needed. Despite this drawback, something still can be learnt at the local spatial scale by analyzing the processes involved in the interaction between molecules and *crystal* silicon dioxide surfaces.

Fig. 1. (a) Electronic charge transfer between Eosine Y molecule and a hydroxylated SiO2 surface. Excess of electric density is shown in dark and its diminution in white (representative isosurfaces).

Among the different possible silica polymorphs, β-crystoballite is the most stable one at high temperatures up to its melting point. It also presents similar properties to those of amorphous silica (Arasa et al., 2005) (e.g. density, refractive index, etc.).

The surface chemistry of a silica surface in contact with an aqueous solution is determined to a large extent by the dissociation of the hydroxyl groups. The equilibria may be expressed as

$$Si\text{-}OH_2^+ \Leftrightarrow M\text{-}OH \Leftrightarrow Si\text{-}O^- + H^+$$

$$\xleftarrow{\hspace{1.5cm}} \quad \xrightarrow{\hspace{1.5cm}}$$
$$pH$$

Which indicates that by an appropriate adjustment of the pH the surface may carry either a positive or negative charge. At an intermediate pH value the hydroxyl groups are undissociated, and the surface has zero charge. This "point of zero charge" (PZC) defines the situation of a fully hydroxylated surface and corresponds to a pH value of 1-2 for a silica surface (Parfitt et al.).

The adsorption energy (see Eq. 1) represents the work that has to be done in order to take the molecule from it original position close to the surface to an infinite distance. We can define an upper and lower bound

for its value for negative and positive molecules respectively by calculating the adsorption energies for the fully hydroxylated silica surfaces.

If we take as reference the adsorption energy of a molecule interacting with a surface immersed in a media with a pH that corresponds to the PZC, then for higher pH values we would expect lower absorption energies if the lone molecule presents a negative net charge and higher adsorption energies if it presents a positive net charge.

The chosen model molecules that were simulated, were used as probes for surface adherence experiments (Rivera et al., 2013). Methylene Blue (MB) is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18} N_3SCl$. When dissociated in a solution it looses its Cl-, becoming $C_{16}H_{18} N_3S$ and positively charged while yields a blue color for the solution.

Eosin Y is also usually found as a salt and carries two extra negative charges when dissociated in a solution. It molecular formula is $C_{20}H_6 Br_4O_5$ in its deprotonated form (see Fig. 3) and yields a yellow color in the solution. By monitoring the color change in the solution one could estimate the quantity of molecules that adhere to the given surface and infer its characteristics.

In the next section we will give details about the methods used, then we will show and discuss the results and finally give the conclusion.

2. Methods

The energetics of the different structures were investigated by electronic structure calculations within the framework of the Density Functional Theory (DFT) (Hohenberg et al.,1964). To do that we used mainly the Quantum ESPRESSO code (QE) (Giannozzi et al., 2009) that uses a plane wave basis to describe the electronic wave functions and ultrasoft pseudopotentials to represent the interaction between electrons and ions (Vanderbilt et al.,1995) . The exchange and correlation potential was considered at the level of the Generalized Gradient approximation (GGA) based on the Perdew-Burke-Ernzerhof (PBE) expression (Perdew et al.,1996 and Perdew et al.,1981). Results using the Local Density Approximation (LDA) (Ceperley et al.,1980) were conceptually similar showing only minor differences in the energetics.

Reciprocal space integrations were checked to converge using only Gamma k point for 4x4 supercells. Van der Walls interactions were taken into account in the formalism detailed in Refs. (Roman-Perez et al, 2009 and Dion et al., 2004) as implemented in QE. The usual dipole correction (Bengtsson et l.,1999) was applied in all calculations. Relaxation was carried on until forces on each atom were below 0.002 eV/Angstrom. Graphics were prepared using the VMD code (Humphrey et al., 1996).

2.1. Surface Model

Surface (001) slabs were built starting from an optimized bulk crystoballite crystal structure.

The lattice parameter obtained at the minimum total energy bulk structure was a=7.463 Å using GGA functional. The distance between Si atoms and the first neighbors O atoms was 1.616 Å while the angle formed between O-Si-O atoms was 109.47 degrees. These values obtained are similar to the ones obtained in previous works (ref 1).

We used a 4x4 supercell and slab composed by 6 layer of atoms for modeling the crystalline SiO_2 surface. The outermost layer was formed by Si atoms, each connected to an hydroxyl group, defining in this way a surface with zero net charge, or point of zero charge as we named it before. An additional hydrogen back layer was added to saturate the O or Si dangling bonds (Ma et al., 2000; Baraille et al., 2003; Akiyama et al., 2003). In this was, the supercell for the clean slab was composed by 88 atoms (see Fig. 2). The slabs were separated by 15-20 Å in such a way that the repeated images were far enough so they do not interact.

All atoms were fully relaxed except the ones belonging to the two deepest layers which were fixed at their bulk ionic positions. Geometries obtained for ions positions after relaxation for the clean slab were similar to previously reported results (Arasa et al., 2005).
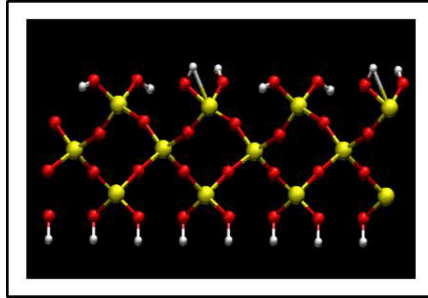

Fig. 2. (a) Fully relaxed slab. Hydroxilated (001) cristoballite. H is shown in white color, O in red, Si in yellow.

2.2. Model Molecules

Molecules were full relaxed before positioning them on top of the slab described in the previous section (see Fig.3). For the full system composed by the slab plus the model molecule, a 15-20 Å vacuum layer is used, which is found to be sufficient to ensure negligible coupling between periodic replicas of the slab.
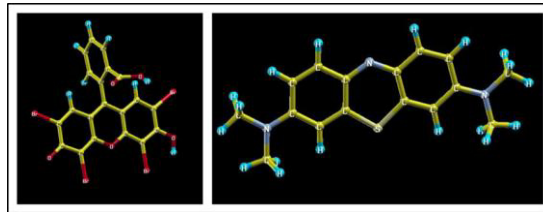
Fig. 3. (a) Left, Eosin Y molecule in it deprotonated form. (b) Right panel, Blue methyl molecule.

Absorption energies were calculated as follows

$$E_{Ads} = -\left(E_{Tot} - E_{Sur} - E_{Mol}\right) \, , \qquad\qquad (1)$$

where E_{Tot} is the total energy of the fully relaxed system, slab plus the molecule, E_{Sur} is the energy of the optimized clean hydroxylated surface system, E_{Mol} is the energy for an isolated molecule in gas phase at the global minimum. Defined in this way, a positive value for Eads would imply an adsorbed molecule while a repulsive interaction would be true for a negative value.

While the electronic density differences, that shows the electronic charge transfer due to the interaction, is calculated as

$$\Delta\rho = \rho_{Tot} - \rho_{Sur} - \rho_{Mol} \qquad\qquad (2),$$

where ρ_{Tot} is the electronic density of the relaxed total system, ρ_{Sur} is the electronic density of the hydroxylated surface using the same supercell and keeping the ionic coordinates frozen while ρ_{Mol} is the electronic density for an isolated molecule in gas phase at the global minimum.

3. Results and Discussion

Molecules were positioned above the surface at different starting positions and orientations before relaxation with the aim of sampling the configuration space. We found the global minimum configurations shown in Fig. 4. The corresponding adsorption energies E_{Ads}, calculated using Eq. (1), were -2,7 eV for the case of Eosine Y and and 4 eV for the case of MB. Similar threads are found for the nearby local minima structures indicating the repulsive nature of the interaction for Eosine Y and attractive for MB.

Results for the charge transfer, calculated with Eq. (2), are shown in Fig. 4 where we can see surfaces for representative isovalues, positive and negative, indicating where electronic charge has migrated to and from respectively. We can see that Eosin Y interacts with the surface mainly thru the C-O-O group and with some of the close by silanols thru H bridges. A weak dipole dipole interaction is formed through a depletion of electronic charge.

For MB we can see an asymmetric charge transfer pattern. A complex bonding pattern is developed, indicating a delocalized electronic migration that reaches deep into the surface. Hydrogen bridges are formed, and charge flows between methyl groups and silanol groups due to dipole dipole interactions.
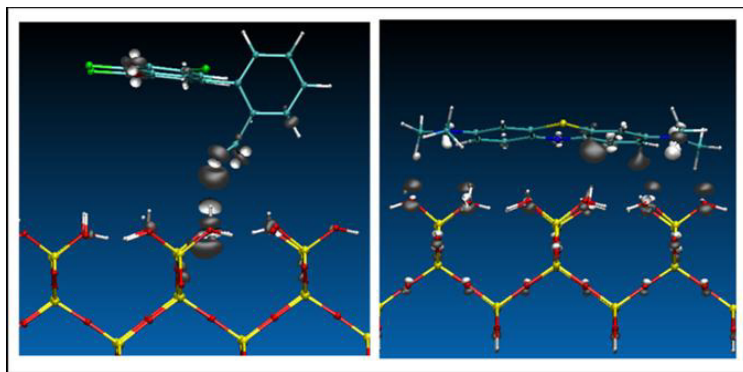

Fig. 4. Electronic charge transfer between molecule and surface for Eosine Y (a) Left panel, and (b) Right panel, Blue Methyl. The localized nature of the electronic redistribution is shown on the Eosine Y case while it is fully delocalized in the case of the Blue Methyl.

4. Conclusions

We have peformed calculations at the DFT level of theory, in order to simulate the interaction between model molecules (Eosine Y and MB) and a crystoballite SiO_2 surface. Adsorption energies were calculated and the values are consistent with experimental results published elsewhere (Rivera et al.) predicting an attractive interaction between the surface and the MB molecules while a repulsive interaction for the Eosine Y case. The adsorption energies calculated, simulating the case of a fully hydroxylated surface, represent a

lower bound for Eosine Y and a higher bound for BM. The calculated electronic charge transfer shows a spatially localized nature for the repulsive case and a complex delocalized nature for the attractive case.

Acknowledgements

References

Rivera, E., Prado, M.O., Nuñez M., to be published in Physics Procedia, 2013.

Arasa, C., Gamallo, P., Sayós, R., 2005. Adsorption of Atomic Oxygen and Nitrogen at β-Cristobalite (100): A Density Functional Theory Study. The Journal of Physical Chemistry B 109, p. 14954.

Parfitt, G., D., 1976. Pure & App. Chem., Vol. 48, pp. 415—418. Pergamon Press.

P. Hohenberg, and W. Kohn, Phys. Rev. 136, B864 (1964).

P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, Journal of Physics: Condensed Matter 39 395502 (2009).

D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).

J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

J. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

D. Ceperley and B. Alder, Phys. Rev. Lett. 45, 566 (1980).

G. Roman-Perez and J. M. Soler, PRL 103, 096102 (2009); M. Dion, H. Rydberg, E. Schroeder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 92, 246401 (2004).

L. Bengtsson, PRB 59, 12301 (1999).

Humphrey, W., Dalke, A. and Schulten, K., ``VMD - Visual Molecular Dynamics'' J. Molec. Graphics 1996, 14.1, 33-38

Ma, Q.; Klier, K.; Cheng, H.; Mitchell, J. W.; Hayes, K. S. J. Phys.Chem. B 2000, 104, 10618.

Baraille, I.; Loudet, M.; Lacombe, S.; Cardy, H.; Pisani, C. J. Mol. Struct. (THEOCHEM) 2003, 620, 291.

Akiyama, T.; Kageshima, H. Appl. Surf. Sci. 2003, 216, 270.