Characterization of the adsorption of bio-organic molecules on metal, oxide and molecular surfaces, a molecular picture

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The adsorption of small molecules on inorganic surfaces is present in many (probably all) technological applications concerning interfaces. We study adsorption phenomena on three main families of surfaces : Metals, oxides and molecular solid surfaces.

On metal surfaces we present a typical example, which is the one of self-assembled monolayers (SAMs) consisting of a layer of functionalized long-chain molecules tethered to a solid substrate. SAMs have attracted significant interest of both the fundamental and applied scientific communities. Their presence as a "coating" on a surface is attractive in a number of applications due to the possibility to provide tuning of the surface properties by selectively modifying functional groups on the SAM.

Alkanethiols ($CH_3(CH_2)_nSH$) and alkylthiolate radicals ($CH_3(CH_2)_nS^{\bullet}$) adsorption on Au(111) surface is one of the most studied and best-known SAM systems, but also other bioorganic molecules such as amino acids organize at the surface. The nature of the corresponding structure at the surface has been controversial for a long time, as well as other aspects such as the adsorption site on which the thiol chain is anchored, and if the thiol adsorbs by S–H bond breaking process or not. In this context we will show here a series of results on the characterization of alkyl thiol SAMs and amino acids investigated in detail by means of periodic density functional calculations.[1-3]

In a second part we introduce recent results on the characterization of biomaterials. Solids like silica, might have been important in the origin of life on earth, but is also used as drug carrier; other solids of biological origin such as hydroxyapatite or calcium oxalates are directly involved in chemistry of "life": Hydroxyapatite as the main compound of human bones and calcium oxalate as main compound of kidney stones. In this broad study around chemistry of life, materials chemistry and computational chemistry we focus on three materials in particular: Silica, Calcium Oxalate and Hydroxyapatite.

We have performed DFT studies on different interfaces and investigated the interaction with a series of bio-organic molecules, such as glycine, benzoic acid, ibuprofen and Alendronate. Here we present the special case of the interaction of ibuprofen with a representative model of amorphous silica surface.[4,5]

From the bulk crystal structures of calcium oxalate polymorphs obtained through DFT methods[6] one can build for example the low index surfaces. Since the thermodynamic stability depends on the medium in which the surface is introduced, the calculation of the interaction of the calcium oxalate surface with water, urea, and other small molecules will give us the possibility to understand the change in crystal morphology of the final oxalate crystal in its natural medium. The final aim is the prediction of the shape of the kidney stone in its natural medium.

References

1. N.B. Luque, E. Santos, J. Andres, F. Tielens, *Langmuir*, **27**, 14514 (2011).

2. D. Costa, M. Smerieri, L. Savio, L. Vattuone, I. Tranca, F. Tielens, *J. Phys. Chem. C*, **118**, 29874 (2014)

3. V. Humblot, A. Naitabdi, A. Vallée, F. Tielens, C.-M. Pradier. *J. Am. Chem. Soc.* **134**, 6579 (2012).

4. F. Tielens, C. Gervais, J.-F. Lambert, F. Mauri, D. Costa, *Chem. Mater.* **20**, 3336 (2008).

5. N. Folliet, C. Gervais, D. Costa, G. Laurent, F. Babonneau, L. Stievano, J.-F. Lambert, F. Tielens, *J. Phys. Chem. C*, **117**, 4104, (2013).

6. H. Colas, L. Bonhomme-Coury, C. Coelho, F. Tielens, F. Babonneau, C. Gervais, D. Bazin, D. Laurencin,M.E. Smith, J.V. Hanna, M. Daudon, C. Bonhomme, *Cryst. Eng. Comm.* **15**, 8840 (2013).