

Carboxyl groups on hydrated calcite from first principles

Mario Canu, Danilo Addari, and Alessandra Satta

CNR-IOM UOS Cagliari

c/o Dipartimento di Fisica, Università degli studi di Cagliari, Italy

Understanding the mechanisms that rule the interaction between minerals and the biosphere is crucial for predicting both the stability and the reactivity of minerals. In particular, calcium carbonate (CaCO_3) is here considered in the form of calcite, as calcium-bearing minerals are the most abundant among all biominerals, with applications in geosciences, material science, bioengineering, and medical sciences. In order to understand and control the chemical processes occurring during biomineralization, functionalized headgroups on self-assembled monolayers are widely used as growth templates. More specifically, some experiments [1] show that $-\text{COOH}$ moieties used to induce a controlled crystallization enabled the growth of several nucleating planes of calcite with the exclusion of the $\{10.4\}$. A detailed knowledge of the reactivity of the calcite surface and the exact mechanism of how COOH -terminated molecules interact with calcite surface stands for a real need of investigation. In this work the inhibiting effects of protonated $-\text{COOH}$ and deprotonated $-\text{COO}^-$ headgroups on top of the $\{10.4\}$ hydrated surface of calcium carbonate are investigated by means of ab initio DFT-GGA simulations. The interfacial properties and the trend of adsorption energies for different coverages are given in details and show that the adsorption is favored by the presence of water.

- [1] A.B. Han, T. Y.-J.; Aizenberg, J. *Chemistry of Materials*, **20** 1064 (2008).