

Adsorption of Organic Molecules on Calcite Surfaces

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Abstract:

Calcium carbonate is a common mineral in nature. It is the main constituent of geological formations where significant quantities of oil and drinking water reserves are found, it plays an essential role for some marine organisms and it is widely encountered in everyday life. Calcite is the most stable polymorph of calcium carbonate and there is a vast literature concerning the interactions of various organic molecules with surfaces of calcite. However, each study focuses on adsorption of only a few molecules and therefore reaches conclusions of limited general applicability. In this talk I will try to show the big picture concerning the organic molecule calcite interface and answer two fundamental questions: (i) how do the common functional groups of organic molecules interact with calcite? And (ii) what is the effect of side groups on adsorption?

For this purpose, adsorption energies and geometries for 36 oxygen, nitrogen and sulfur containing molecules were calculated on calcite {10.4} surface, using density functional theory with semiempirical dispersion corrections (DFT-D2). From the adsorption energies, within the transition state theory approximation, desorption temperatures for all molecules were determined and results were compared with 8 measurements from temperature programmed X-ray photoelectron spectroscopy (XPS). The results show that carboxylic acids (R-COOH) have the strongest interactions with the surface, followed by primary amines (R-NH₂) and alcohols (R-OH). Thiols (R-SH), nitriles (R-CN) and aldehydes (R-CHO) have the weakest interactions. Attachment of a H atom or methyl (-CH₃), ethyl (-C₂H₅) and phenyl (-C₆H₅) side groups changes the strength of the surface–molecule interactions and significantly affects the adsorption behavior.