

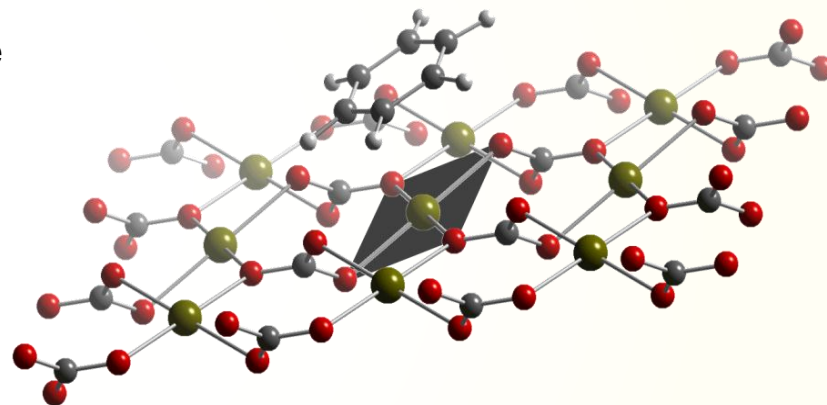


# Nanostructures Formation by Aromatic Hydrocarbons on Calcite

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We attempted to better understand the nature of the cation- $\pi$  interaction between benzene ( $C_6H_6$ ) molecule and the calcite ( $CaCO_3$ ) surface using quantum chemical calculations. The calculations were performed for the benzene-calcite interaction at the density functional theory (DFT) level using the program package Gaussian.

A benzene molecule was placed on top of the cleavage surface of a calcite slab consisting of 18  $CaCO_3$  units. The position and structure of the benzene molecule were optimized with the M06 functional and a 6-31G\* basis set. During optimization, the calcite surface was structurally constrained. The result of the optimization was the structure of the calcite-BTE complex associated with the global minimal total energy.



After optimization the benzene molecule was arranged by the cation- $\pi$  interaction with its aromatic ring facing the exposed surface calcium ions. The aromatic ring of the benzene molecule was oriented most perpendicular to the surface so that the  $\pi$  electrons can enter the empty orbital of the surface calcium atom. The aromatic ring was not centered over the calcium atoms but rather shifted toward the recessed surface oxygen atom bonded to the calcium atom. The energy of the cation- $\pi$  interaction was estimated to be  $58.4 \text{ kJ mol}^{-1}$ , of which 31% from the charge-quadrupole interaction and 69% from the hydrogen bonding between the aryl hydrogen atoms and the calcite oxygen atoms.

