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Ab initio studies of methane and carbon dioxide affinity to carbon compounds and minerals

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Understanding of physico-chemistry of capture and storage of carbon dioxide and methane might be crucial for development of the novel technologies meant: (i) to deal with the global warming process through the reduction of the CO_2 atmospheric concentration by sequestration, and (ii) to enhance oil recovery, on the other hand. The accurate description of CO_2 and CH4 adsorption to minerals and carbonaceous systems (which constitute the main component of sedimentary rocks) is essential to reach this goal. We have employed the ab initio molecular dynamics AIMD) based on the density functional theory (DFT) to study the affinity of CO_2 and CH4 from gaseous phase, also at elevated temperatures and hydrostatic pressure, to pristine and defected graphene, spiral carbon nanoparticles (spiroids), calcite rocks (represented by the most stable (10-14) surface of $CaCoO_3$), CaO, MgO, illite, and kaolonite. In the case of kaolonite that exhibits layered crystallographic structure, we have also studied the intercalation of CO_2.
These studies provide valuable quantitative predictions and shed light on physical mechanisms governing the processes of chemisorption and physisorption of the CO_2 and CH4 molecules, revealing also the essential role of Van der Waals interaction.
In particular, we find out that CO_2 molecules in supercritical gaseous phase (i.e. at temperature of order 60oC and moderate hydrostatic pressure of 20-30 MPa) change their shape from linear one to the water like bended V-shape with angle between C-O chemical bonds smaller than 180 degrees. This shape change of CO_2 molecules facilitates the CO_2 adsorption. Therefore, in the temperature-pressure conditions of shale deposits, the adsorption probability of CO_2 can be enhanced in comparison to the ambient conditions.
It turns out that the carbon atoms in the surrounding of characteristic Stone-Wales (or 5-7) defects in graphene are more reactive towards adsorption of CO_2 and CH4 molecules.
In the case of CO_2 adsorption to the most stable (10-14) surface of $CaCO_3$, the AIMD studies demonstrate that the carbon atom of CO_2 is attracted to calcium atoms at the (10-14) calcite surface. The performed studies also show that CH4 molecule can be accumulated at the calcite surface in parallel to CO_3 groups at low temperatures, and even it can induce reconfiguration of the surface by dehydrogenation process with the increase of temperature.