

Interaction of chlorinated species with soot surfaces and influence on water adsorption. A theoretical study.

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Theoretical studies devoted to the characterization of the interaction between halogenated species and large carbonaceous surfaces as present in soot are very scarce and recent. This is quite surprising because the interaction of chlorinated species with soot is an old question related to the transport of irritant gases into the lungs during/after combustion of polyvinyl chloride in domestic or industrial fires.[Stone,1973] Indeed, it has been long inferred that smoke aerosols including soot could be particularly effective in transporting hydrogen chloride behind the respiratory defences. [Ramskill,1967] More recently, experimental measurements have actually shown that small chlorinated species can be efficiently trapped at the surface of soot and that they can even modify the hydrophilicity of soot.[Ouf,2016]

In this work, we have thus performed DFT calculations to characterize the adsorption of chlorine species (Cl, HCl) on small C_nH_m carbonaceous clusters modelling the surface of soot. Both perfect and defective surfaces have been considered, by removing one H atom at the edge or one C atom on the face of the carbonaceous surfaces. Whereas a physisorption process corresponding to weak adsorption energy has been obtained on a perfect carbonaceous cluster, larger interaction energies have been calculated on defective clusters, characterizing chemisorption of the chlorinated species on the carbonaceous surface.

Then, the first steps of water adsorption on the corresponding chlorinated clusters have been characterized, by adding up to 6 water molecules in the DFT calculations. The results shown that the presence of chlorine atoms on the carbonaceous surfaces favoured water adsorption when compared to pure carbon surfaces. Comparison with previous works shown that chlorinated carbonaceous surfaces can in fact attract water at least as much as oxidized carbonaceous surfaces can do.

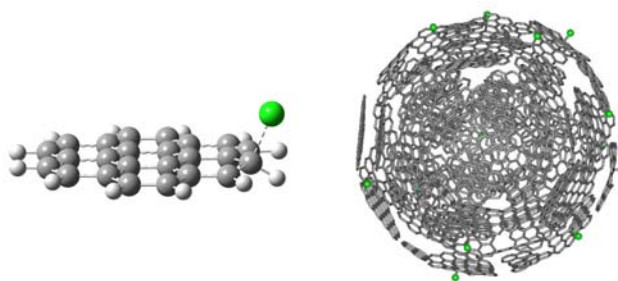


Figure 1. (left) Equilibrium structure of Cl adsorbed on a small carbonaceous cluster $C_{24}H_{12}$ as obtained from DFT calculations (BH&HLYP / 6-31G++(d,p) level of theory). (right) Model of soot nanoparticle containing a few % of Cl atom adsorbed at its surface, as used in the GCMC calculations of water adsorption.

Finally, optimized carbonaceous clusters (made of carbon or containing also chlorine atoms) have been randomly scattered on concentric layers to model the experimentally evidenced onion-like structure of soot nanoparticles.[Parent,2016] The chlorinated carbonaceous clusters have been randomly distributed either at the surface, only, or also in the bulk of the nanoparticle to model soot resulting from domestic or industrial fires.

Then, adsorption isotherms of water on these soot nanoparticles have been simulated by using the Grand Canonical Monte Carlo (GCMC) approach and the results have been compared to the isotherms obtained in similar conditions on soot nanoparticles made of carbon atoms only, or containing a few % of oxygen atoms.

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