Investigations of molecular properties by means of computational chemistry

Report for the Short Term Scientific Mission to Uppsala University
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The aim of this STSM at the University of Uppsala was to investigate molecular properties such as electron affinity, proton affinity etc. subject to different levels of theory (comparison between wavefunction based calculations and density functional theory) and the size of basis sets.

As first step different methods and different basis sets were used to find the best method comparing accuracy to computational costs. Hartree-Fock wavefunctions, post Hartree-Fock methods (MP2, CCSD), density functional theory (B3LYP) and the new G4(MP2)-method were used for the small systems like water and acetic acid. Compared to available experimental results it was found that B3LYP/6-311+G(2d,2p) gives slightly better values than G4(MP2), but computational costs are much higher with G4(MP2). Therefore B3LYP/6-311+G(2d,2p) was chosen for the further investigations of larger systems.
Electron affinity, proton affinity, dipole moment and polarizability were then calculated using density functional theory B3LYP/6-311+G(2d,2p) for Alphapinene, Betapinene, Levoglucosan, 1,2,4-Trichlorobenzene and 2-methyl-3-butene-2-ol.
To calculate the proton affinity the attachment of a proton the molecule on different sites was studied. This is shown for acetic acid in figure 1. If the molecule is dissociating the PA calculation fails. Else G4(MP2) shows slightly better results than B3LYP/6-311+G(2d,2c) but not sufficient to justify the higher computational costs. Further analysis of the obtained data is in progress.

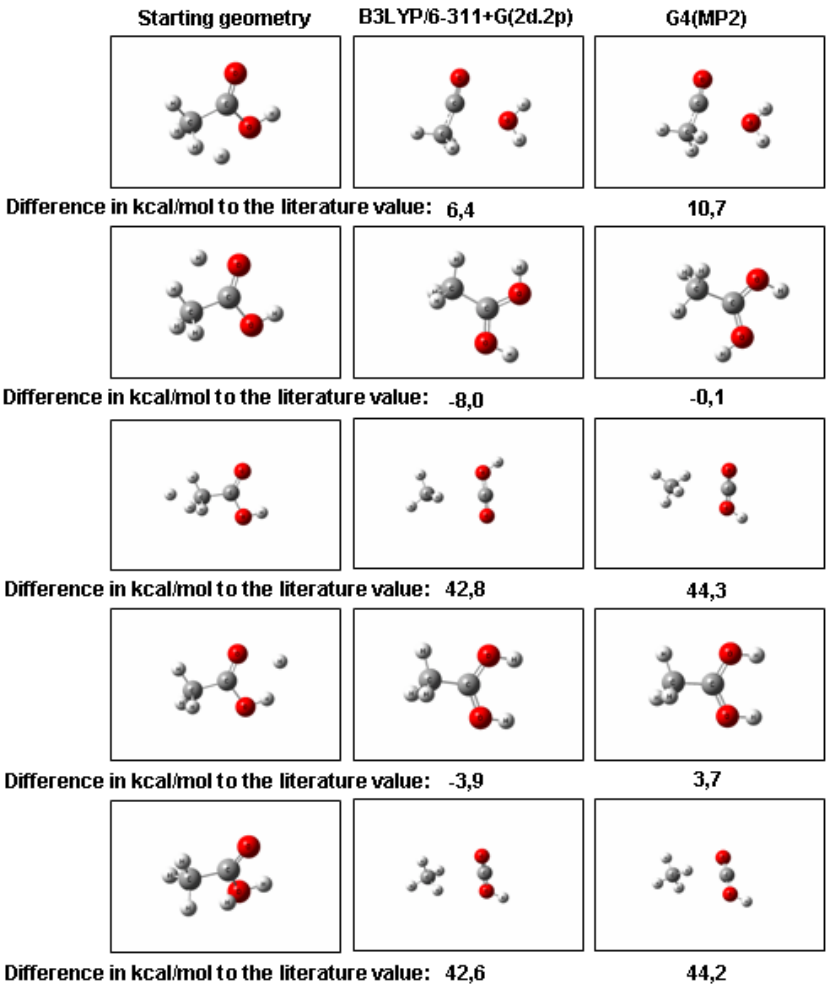

Figure 1

This STSM was a great opportunity to gain detailed understanding in the calculation process of molecular properties and will serve as a starting point for further collaboration between the Institute of Ion Physics and Applied Physics in Innsbruck and the Department of Materials Chemistry in Uppsala.