DENSITY FUNCTIONAL THEORY CAPACITANCE MOLECULAR MECHANICS CALCULATIONS OF CORE-ELECTRON BINDING ENERGIES OF METHANOL AND METHYL NITRITE ON SILVER SURFACE

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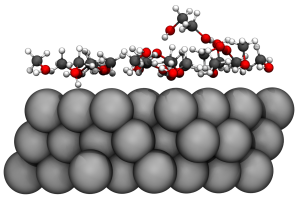
In this study we tested the capabilities of the density functional theory capacitance molecular mechanics (DFT/CMM) method [1] in core-electron binding energy (BE) calculations in systems with monolayer of methanol and methyl nitrite molecules physisorbed on silver surface. The method is able to model systems containing metallic parts by applying the capacitance-polarization model in DFT/MM framework.

We started our analysis by performing classical molecular dynamics simulations for the systems at 100 K temperature using the Gromacs program [2]. After equilibration, 100 structures were extracted from the simulations and the BEs were calculated by applying the Δ-DFT/CMM method using development version of the Dalton program [3]. In the calculations the DFT region included one of the molecules on top of the surface, while the rest of them were described by point charges, and the silver atoms were modelled by the capacitance-polarization model. The optimization of the core-hole orbitals was done with a stepwise process which prevented so called variational collapse. During the calculations it was noticed that the energies of the core-hole states converge slowly as a function of the size of the MM and CMM regions and thus fitting procedure was required.

In general, a good agreement was found between the calculated and the experimental BEs [4, 5]. However, in some structures the core-hole atoms were lying so close to the surface that the lack of charge transfer between the DFT and CMM regions caused problems, especially in case of oxygen atom of methanol. In addition we studied the charge distribution on the silver surface, where polarization effects from the MM molecules and especially from the core-hole DFT molecule were seen.



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