

Theoretical Study of $\text{Fe}^-(\text{H}_2\text{O})_m$, $m \leq 4$ and $\text{Fe}_n-(\text{C}_6\text{H}_6)_m$, $n \leq 7$, $m \leq 4$

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ABSTRACT

The structural, electronic, energetic and vibrational properties of transition-metal-ligand clusters which are formed by magnetic iron clusters interacting with benzene and water moieties are studied by means of density functional theory, including dispersion corrections. The obtained results for $\text{Fe}^+(\text{H}_2\text{O})-\text{Ar}_2$ and $\text{Fe}^+(\text{H}_2\text{O})_2\text{Ar}$, jointly with the experimental IRPD (infrared photo-dissociation spectra), provides insight on the nascent hydration for $\text{Fe}^+(\text{H}_2\text{O})_m$ clusters in the gas phase. Solvation of one electron, localized on the iron atom, was addressed through the $\text{Fe}^-(\text{H}_2\text{O})_6$ ions. For these clusters the B3LYP method was used. Further, using the BPW91 functional and dispersion corrections as proposed by Grimme (DFT-D2), the $\text{Fe}^+(\text{C}_6\text{H}_6)_m$, $m \leq 4$, systems were studied. It was found that the tilted-T-shape structure, appearing as the ground state for the isolated benzene dimer, play an important role in the stabilization and growing of $\text{Fe}^+(\text{C}_6\text{H}_6)_m$. Solvent behavior for $m \geq 3$ was found. Bigger clusters were also addressed: $\text{Fe}_2-(\text{C}_6\text{H}_6)_m$, $\text{Fe}_4-(\text{C}_6\text{H}_6)_m$; $\text{Fe}_6(\text{C}_6\text{H}_6)_m$, and $\text{Fe}_7-\text{C}_6\text{H}_6$; on which all-electron calculations are done at the BPW91/6-311++G(2d,2p) level of theory. The obtained results allow to determinate the geometry of the ground state, GS, clusters. $\text{Fe}_6(\text{C}_6\text{H}_6)_m$ and $\text{Fe}_7(\text{C}_6\text{H}_6)$ present the so called “rice-ball” structures where the geometry of the bare cluster is preserved and the benzene molecules are bonded through 3d- π Fe—C bonding with hapticity equal to six, η^6 , and equilibrium bond lengths of 2.1 to 2.2 Å. The ionization energies of the formed complexes are smaller than those of the bare Fe_n clusters confirming the existence of 3d- π bond interactions. Also the electronic affinities are smaller. The magnetic moments of these complexes are quenched strongly with respect to those of the isolated Fe_n clusters, suggesting that the magnetization play an important role in the adsorption or bonding properties of these complexes. The IR spectra was also addressed showing IR resonances near to those of bare benzene with blue shifts for the CH bending out of the plane and red shifts for the in plane C-H bending and for the in plane carbon ring distortion, implying a weakening of the bonding in the carbon ring. In some cases, some IR forbidden vibrational bands of benzene becomes active in the $\text{Fe}_n-(\text{C}_6\text{H}_6)_m$ complexes and, conversely, some become deactivated.

References

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