Deconstructing Cation-pi Interactions: Understanding the Binding Energies in Metal Benzene Complexes

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The Effective Fragment Potential (EFP) method is a computationally efficient technique for describing non-covalent interactions, such as hydrogen bonding and van der Waals forces. Cation-pi interactions are a type of non-covalent interactions that are thought to be important in biological processes, such as permittivity of ion channels. The goal of this work is to establish that the EFP method reliably describes the strength, directionality, and composition of cation-pi interactions. Optimal geometries were found for several cations (K^+, Li^+, Na^+, Ca^{2+}, and Mg^{2+}) paired with the benzene molecule using the MP2 level of theory and cc-pVTZ basis set, aside from benzene and K^+ which used the 6-311G** basis set. Then the cation was displaced along a line normal to the face of the benzene ring between 1 and 7 Angstroms of separation. EFP and Symmetry-Adapted Pertubation Theory (SAPT) calculations were executed for each distance, and the binding energies and energy components from both methods were compared. Damping functions for electrostatic and polarization terms in EFP were carefully selected. It was found that the EFP method is able to accurately predict the binding energy of cation-pi interactions along the given trajectories. This implies that the EFP method has the potential to be expanded to cation-pi interactions in larger systems.