

Public Abstract

First Name:Haunani

Middle Name:Marie

Last Name:Thomas

Adviser's First Name:Carol

Adviser's Last Name:Deakyne

Co-Adviser's First Name:

Co-Adviser's Last Name:

Graduation Term:FS 2011

Department:Chemistry

Degree:PhD

Title:Computational Studies of Three Chemical Systems

The subject of this dissertation is the use of electronic structure calculations to examine and supplement the experimental observations of three different chemical systems. The first topic is the study of pyrogallol[4]arene with R-groups R=H and R=phenyl. This macrocycle self-assembles into dimeric and hexameric nanocapsules. The purpose of this study is to use DFT methods to gain knowledge of this process. The relative energies of different structures and their solvent interactions are examined to better understand how self-assembly of the nanocapsule occurs. In the second study, electrospray ionization mass spectrometry, DFT and conventional ab initio calculations are used to study the addition and ligand-exchange reactions of vanadium oxide cations. Specifically investigated is the addition of H₂O and O₂ to vanadyl complexes of the form [VOX(NCCH₃)]⁺ where X = F⁻, Cl⁻, Br⁻, I⁻, and OH⁻. Changing the identity of X allows the observation of how the electron density on the metal center influences the addition of H₂O or O₂. The final chapters discuss the high-level quantum chemical calculations performed to study the structure and energetics of isomers of CH₂BF on both the singlet and triplet PES. MP2 optimizations were used to identify minima and transition states. A series of CCSD(T) single-point calculations were used to extrapolate to the complete basis set limit. A wide variety of structures with a large range of energies were found. All of these species are compared as well as the transition states that connect the most stable isomers.