Natcha Injan 2010: Computational and Theoretical Studies of Ionic Systems: From Gas Phase via Solutions to Heterogeneous Catalysis. Doctor of Philosophy (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisors: Professor Jumras Limtrakul, Ph.D. 143 pages.

Ionic systems covering from the gas phase via solutions to heterogeneous catalysis have been investigated using electronic structure theory and molecular dynamics studies.

Dissociative electron attachment (DEA) on the gas phase purine (Pu) and its derivatives (adenine (Ad) and 6-fluoropurine (6-fPu)) was studied by means of quantum chemical calculations. The resulting DEA products are dehydrogenated anions and hydrogen. The energies required for removing one hydrogen atom from the purine ring were calculated with the G2MP2 method. It was found that the hydrogen atom at the N9 site needs the least energy for dissociation (0.54 eV (6-fPu), 0.72 eV (Pu) and 0.94 eV (Ad)), which are in good agreement with experimental values. Adiabatic neutral and anionic potential energy surfaces were calculated at the UB3LYP/cc-pVTZ level of theory. From these the vibrational energy levels of the stretching vibrations were calculated in order to obtain the energy levels for the DEA reaction.

Potential energy functions for the interaction between Au^+ cation and dicyanoaurate (I) anion ($Au(CN)_2^-$) and nitromethane (NM) were constructed and then used in molecular dynamics simulations of $Au^+/Au(CN)_2^-$ ion in liquid NM. It was found that the first solvation shell around the ion contains 9-10 and 15-16 NM molecules, respectively for the Au^+ and $Au(CN)_2^-$ cases. An X-ray diffraction measurement on a diluted solution of $KAu(CN)_2$ in NM was in good agreement with the simulated one. Complementary, extensive quantum chemical calculations on Au^+-NM_n and $Au(CN)_2^-$-NM_n clusters were performed as well. They show the especially strong binding between Au and NM in $AuNM_2^+$. For higher values of n, the resulting geometries reflect the fact that the NM-NM interaction dominates over Au^+-NM and $Au(CN)_2^-$-NM interactions.

The direct benzene-to-phenol conversion on Fe-ZSM-5 was elucidated via density functional theory at M06/6-31G (d,p) level of theory. From the results, benzene is favorably activated by α-oxygen of the active dioxo-Fe center via electrophilic substitution to form the σ-adduct. This adduct can further transform into the very stable hydroxo-phenoxo intermediate by either via the proton shuttle of the σ-adduct or via the 1,5-H shift of 2,4-cyclohexadienone which is produced from 1,2-H shift of the σ-adduct. Finally, the hydroxo hydrogen shifts to the phenoxo oxygen to form phenol which is proposed to be a rate-determining step with the activation energy of 45.7 kcal/mol.

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