

**QUANTUM CHEMISTRY OF ION-
MOLECULE INTERACTIONS IN GROUND
AND LOW-LYING EXCITED STATE**

**SYNOPSIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN SCIENCE (CHEMISTRY)
OF THE
VIDYASAGAR UNIVERSITY**

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February-2017

This thesis describes the “Quantum Chemistry of ion-molecule interaction in ground and low-lying excited state. This theoretical works have been using semiempirical AM1 and density functional theory (DFT)/B3LYP method at 6-311G(d,p) basis set level of Gaussian ‘09’ and ‘03’ program package. Ion-molecule interactions have been studied in gas phase and some of them in solvent phase. Molecules chosen for this theoretical works are (1) Series of a conjugated α,β -unsaturated carbonyl compounds [acrolein (ACL), 4-hydroxy-2-nonenal (HNE), methyl vinyl ketone (MVK), acrylamide (ACR), methyl acrylate (MA) and ethyl methacrylate (EMA)]. (2) Series of heterocyclic molecules [Pyrrole, furan, thiophene and pyridine]. (3) Three essential amino acids [Glycine, alanine and cysteine]. The thesis consists of twelve chapters.

Chapter 1: General introduction and objectives

This chapter deals with a brief introduction, literature survey (though not sufficiently exhaustive) and objectives of the present thesis.

The work will focus on the electronic and molecular structure of the above mentioned series of compounds in ground and some low-lying excited states.

Chapter 2:

This chapter deals briefly with the AM1 and DFT theories and their parameterization scheme. In order to understand the structural behavior and electronic properties in solvents, the work has been carried out using SCRF-PCM (Polarizable Continuum Model) optimization process at the same level of theory.

Chapter 3:

In Chapter 3, proton affinities of the carbonyl compounds have been predicted in both gas and aqueous phases. Proton affinities of the bases markedly changes due to solvation. Proton affinities are strongly affected by the different substituents attached to the carbonyl carbon.

Chapter 4:

In this chapter, lithium cation affinities and some associated quantum mechanical parameters of conjugated α,β -unsaturated carbonyl compounds have been calculated in gas phase as well as in aqueous phase.

Chapter 5:

The sodium cation affinities (SCA) and basicities of the unsaturated compounds have been calculated in gas and different solvent phases. SCA's are obtained from a delicate balance between inductive and resonance effect of different substituent or group present at the carbonyl carbon or any other position in the compound. The interaction enthalpies, Gibbs free energies of the complexation reactions reduced in solvents in each case.

Chapter 6:

In this chapter, ground state gas phase proton affinities (PA) of a series of β -substituted acrylamide and their O-protonated counterparts have been theoretically studied using B3LYP(DFT) method of Gaussian '03' program package. The presence of β -substituent is seen to cause change of the proton affinities relative to unsubstituted acrylamide.

Chapter 7:

Ground state gas phase proton affinities, alkali metal cation (Li^+ , Na^+) affinities and basicities of pyrrole, furan, thiophene and pyridine have been calculated. Different binding sites of pyrrole, furan and thiophene for protonation were observed. Results obtained in this calculation shows good agreement with experimental values.

Chapter 8:

A detail study of Cu^{2+} ion affinities of the amino acids namely Glycine, Alanine and Cysteine and their Cu^{2+} complexes have been investigated. The computed Cu^{2+} affinity for both O- Cu^{2+}

and N-Cu²⁺ interaction in gas phase is in this order $\Delta E_{\text{Cys}} > \Delta E_{\text{Ala}} > \Delta E_{\text{Gly}}$. In N-Cu²⁺ interaction Zwitterterionic complexes (Cu²⁺ bind with both nitrogen and carbonyl oxygen atom) have been formed.

Chapter 9:

Proton affinities (PA) and transition energies of carbonyl compounds have been calculated in gas phase as well as in aqueous phase at the relevant low-lying excited state. The proton affinity values are little higher in this particular electronic state relative to their ground state in both gas and aqueous phase.

Chapter 10:

Quantum mechanical properties of several conjugated α , β unsaturated carbonyl compounds and interactions with lithium cation were studied at the low-lying excited triplet state. Lithium cation affinities and basicities have been evaluated in gas phase as well as in aqueous phase.

Chapter 11:

Gas phase proton affinities (PAs), basicities (ΔG) and transition energies ($^1S_0 \rightarrow T_1$) of heterocyclic molecules have been investigated. Geometries and electronic properties of the protonated complexes have been searched extensively.

Chapter 12:

Comparative gas phase lithium cation affinities and basicities and transition energies of heterocyclic compounds have been calculated at low-lying excited triplet state. Cation affinity values are lower in all cases relative to their ground state with the exception of furan molecule.

LIST OF PUBLICATIONS

1. The Ground state Comparative Study of Proton affinities and Associated Parameters of Conjugated α,β -Unsaturated Carbonyl Compounds in Gas and Aqueous phases by Density functional Theory Method.
B. Mandal, U. Senapati, B. R. De. Indian Journal of Advances in Chemical Science. Vol. 4(4), (2016), 401-408.
2. Proton Affinities of a Series of α, β Unsaturated Carbonyl Compounds of Type-2-alkene (Acrolein, 4-hydroxy-2-nonenal, Methyl Vinyl Ketone, Acrylamide, Methyl Acrylate, and Ethylmethacrylate), in the Gas and Aqueous Phase in their Low-lying Excited Triplet State: A Density Functional Theory/Polarizable Continuum Model and Self-Consistent Reaction Field Approach
B. Mandal, U. Senapati, B. R. De. Indian Journal of Advances in Chemical Science. Vol. 5(1), (2017) 2017, 65-75.
3. The proton affinities of a series of β - substituted Acrylamide in the ground state: A DFT based computational study.
B. Mandal, U. Senapati, B. R. De. Discovery Chemistry, 2015, 1(3) 64-71.
4. The lithium affinities of a series of heterocyclic compounds pyrrole, furan, thiophene and pyridine in their low lying excited triplet state: A DFT based comparative study.
B. Mandal, U. Senapati, B. Panda, S. Sengupta. Indian Journal of Science, 2015, 15(44), 20-24.
5. The proton affinities of a series of heterocyclic compounds pyrrole, furan, thiophene and pyridine in their low lying excited triplet state: A DFT based comparative study.
B. Mandal, U. Senapati, B. Panda, S. Sengupta. Indian Journal of Science, 2014, 11(28), 49-53.
6. The Comparative study of basicities, Li^+ , Na^+ ion affinities of a series of heterocyclic molecules (pyrrole, furan, thiophene and pyridine) in the ground state, A DFT study.
B. Mandal*, B. Panda, S. Sengupta, Indian Journal of science, 2014, 8(19), 16-20.
7. Ground state lithium cation affinities (LCA) and associate parameter of a series of α,β -unsaturated carbonyl compounds of type-2-alkene chemical class (ACL, HNE, MVK, ACR, MA and EMA): A Comparative DFT based computational study in both gas and aqueous phase.
B. Mandal, U. Senapati, B. R. De. Communicated.