Available online at
www.ijacskros.com

Ground State Sodium Cation Affinities 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 Solvent Phase

Biswarup Mandal[1], Bhudeb Ranjan De[2], Umasankar Senapati[3]*

[1]*Department of Chemistry, Sitananda College, Nandigram, Purbo Medinipur, West Bengal, India,* [2]*Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapur, West Bengal, India,* [3]*Department of Chemistry, Belda College, Belda, Paschim Medinipur, West Bengal, India*

ABSTRACT

A detailed quantum mechanical study of ground state sodium cation (Na^+) affinities (SCA) and some associated parameters of 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]) has been computed in gas phase and in different solvents (water, dimethyl sulfoxide, CCl_4) phase using DFT [B3LYP] method employing 6-311G (d,p) basis set. Sodium complexes are stabilized by solvation in all cases. ACR exhibits the highest SCA in all medium. In gas phase, computed Na^+ affinity of the compounds are in following order ACR > MA > HNE > MVK ≥ EMA > ACL whereas upon solvation it shows different trend, follow ACR ≥ MA > EMA ≥ MVK> ACL ≥ HNE order. Sodium cation basicity (SCB) has been calculated from Gibbs free energies obtained in frequency calculation at the same level of theory. Calculated SCA and SCB values in gas phase are higher in comparison to the solvent phases. Entropy of the complex formation reactions has been estimated. Atomic charges of the complexes have been calculated in two schemes Mulliken population analysis and natural population analysis. The interactions sodium cation (Na^+) with ligand is electrostatic ion-dipole interaction in all case. The local stereochemical disposition of the Na^+ is found to be almost same in each case.

Key words: *Unsaturated, Sodium cation affinities, Sodium cation basicity, Aqueous, B3LYP, DFT.*

1. INTRODUCTION

This work is part of a continuing effort from our laboratory to provide additional information in ion-molecular interaction in gas phase as well as in different solvent phases using sodium cation affinities (SCA), ligand-cation bond distance and charge on different atom including metal cation with other quantum mechanical parameters. The interaction of alkali metal cation (Lewis acid) with carbonyl compounds (Lewis base) extended the area of theoretical and computational research. It is known that a Lewis acid is an electron pair acceptor because of having one or more empty orbitals which make easier to complex formation by coordinating ligands. The reactivity of alkali metal cations toward ligand is quite simple compared to transition metal ion and it can form clusters or adducts which are ions "solvated" by one or several ligands [1]. Due to easy production under vacuum, alkali metal ions

became the first metal cations studied in the gas phase. The bioinorganic chemistry of the alkali metal ions has been extensively reviewed [2]. Solid state crystal structures have been determined for many complexes of alkali metal ions in small peptides, nucleic acid constituents, carbohydrates, and ionophore complexes [3]. Sodium occurs in all known biological systems, generally functioning as electrolytes inside and outside cells [4]. Sodium is an essential nutrient that regulates blood volume, blood pressure, osmotic equilibrium, and pH. The minimum physiological requirement for sodium is 500 mg per day [5]. Ion-molecule complexes help to remove metal cation from contaminated area with their active involvement in molecular recognition processes [6]. Carbonyl compounds taken in this theoretical study are known as environmental pollutants and dietary contaminants. Exposure to these type-2 alkenes produces major toxicity in organ systems and to probable carcinogenicity in humans and laboratory

*Corresponding Author:
E-mail: biswarupmandal75@gmail.com*

animals [7-12]. Some experimental procedure such as high pressure mass spectrometry high pressure mass spectrometry [13-16], ion cyclotron resonance [17-21], or unimolecular dissociation–Cooke's kinetic method [22,23] has been employed for measuring most accurate alkali metal cation affinities. The ground state SCA of a series of substituted acetophenones was reported earlier [24]. The Na^+ ion affinity of asparagine, glutamine, histidine, and arginine were also studied theoretically [25]. Metal ion affinities and geometrical features of formohydroxamic acids derivatives have been investigated theoretically in gas and water phase [26]. On the basis of some previously evaluated [27,28] sodium ion affinities, it may be assessed that sodium will bind most preferentially with the acid function. Although several important functional groups have been studied, coverage might be not exhaustive and some key groups would be of considerable interest. To the best of our knowledge, no such computational studies were performed systematically for six selected carbonyl compounds to investigate comparative SCA values in different phases. In this chapter, we have systematically analyzed the structures, ground state SCA, basicities, and some other computed parameters of α,β-unsaturated carbonyl derivatives RC(H) = C(A) – C(= O)B [A= –H, –CH$_3$, B = –H, –NH$_2$, –CH$_3$, –OCH$_3$, –OC$_2$H$_5$] both before and after complex formation in gas phase and in different solvents of low, medium and high dielectric constant (ε). The calculations have been carried out with the help of most reliable B3LYP [DFT] method using most accurate atom centered split valence with polarization function 6-311(d,p) basis set [29,30]. The compounds (Figure 1) undertaken in this study are acrolein (ACL), 4-hydroxy-2-nonenal (HNE), methyl vinyl ketone (MVK), acrylamide (ACR), methyl acrylate (MA), and ethyl methacrylate (EMA). The gas phase SCA values are evaluated considering reaction between free base (B$_1$) and metal cation (M^{n+}) that is,

$$B_1 + M^{n+} \leftrightarrow [B_1 - M^{n+}] \qquad (1)$$
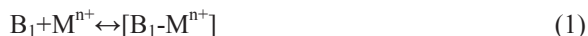
It was seen that sodium cation (Na^+) interacted with carbonyl oxygen ligand of the unsaturated carbonyl compounds and formed metal complexes in each case (Figure 2). Compounds have more than one donor atom (N and O in acrylamide) were optimized with free Na^+ (not directly bonded with carbonyl oxygen). We observed that Na^+ cation prefers to bind with carbonyl oxygen (C=O) to form stable complexes. Before attempting the ion-molecular optimization in solvent phase, a detail idea of gas phase ion-molecular interaction energies, geometrical features are required [31]. We have observed the solvents effect on equilibrium geometry and atomic charge distribution of the complexes, because inclusion of solvents may change the geometrical and electronic parameters. The goal of our present study to supply a bunch of reliable

quantum mechanical parameters including SCA in gas phase and in three different solvents water (ε=78.39), dimethyl sulfoxide (ε=46.7) and CCl$_4$ (ε=2.228). The data obtained from this theoretical analysis has been discussed comprehensively. It is expected that the model system chosen above will provide some initial insight into the binding of a univalent cation, i.e. ,Na^+ to carbonyl oxygen of unsaturated compounds. Compounds studied in this theoretical calculation are listed bellow with their name and proper abbreviation.

2. COMPUTATIONAL DETAILS

The geometry of the six α,β-unsaturated carbonyl compounds and their metal ion complexes in gas phase and different solvent phases has been completely optimized with hybrid B3LYP/DFT method using most accurate 6-311G(d,p) basis set of Gaussian "9" program package [32]. To optimize these systems in solvents, we used polarization continuum model (PCM) [33] and water, dimethyl sulfoxide (DMSO) and CCl$_4$ have been selected from given solvents list in the programme. Specifically three dielectric constants were utilized to create the solvents environment. Thermodynamics data of ion-molecule complexes (cation-Lewis base) obtained from B3LYP/DFT calculations at 6-311G(d,p) basis set level are very close to accuracy [34] and differed only by 10 kj/mol therefore DFT method can be used as an appropriate alternative to conventional *ab initio* methods for investigating larger ion-molecular interactions. Mulliken population analysis (MPA) [35] and NBO analysis (natural population analysis [NPA] only) are used to determine equivalent charges on all atoms of the free bases and their O–Na^+ complexes. Basis set superposition error (BSSE) was not made in this calculations. The magnitude of BSSE was evaluated at the B3LYP/6-311G (d,p) level for a small test set of molecules using counterpoise correction [36] and found to be small (0.5 kcal/mol or less). Gibbs free energies (G) and enthalpies (H) were evaluated using un-scaled frequencies calculation at the same level of basis set.

3. RESULTS AND DISCUSSION

A general geometrical structure of the studied α,β-unsaturated carbonyl compounds and their O-Na^+ complexes are given bellow.

The gas phase SCA of the selected unsaturated carbonyl compounds has been evaluated as negative value of the enthalpy change ($\Delta H^{298.15K}$) of the reaction.

$$B_1 + Na^+ \leftrightarrow B_1 Na^+ \qquad (2)$$

Where SCA is defined as $-\Delta H_{Na+}$. In the similar way, sodium cation basicity (SCB) is defined as negative of the Gibbs free energy change associated with the above thermodynamic equation, where SCB = $-\Delta G_{Na+}$. We also report the entropies ($\Delta S^{298.15K}$) of the same reaction. The interaction enthalpy ($\Delta H^{298.15K}$) for the
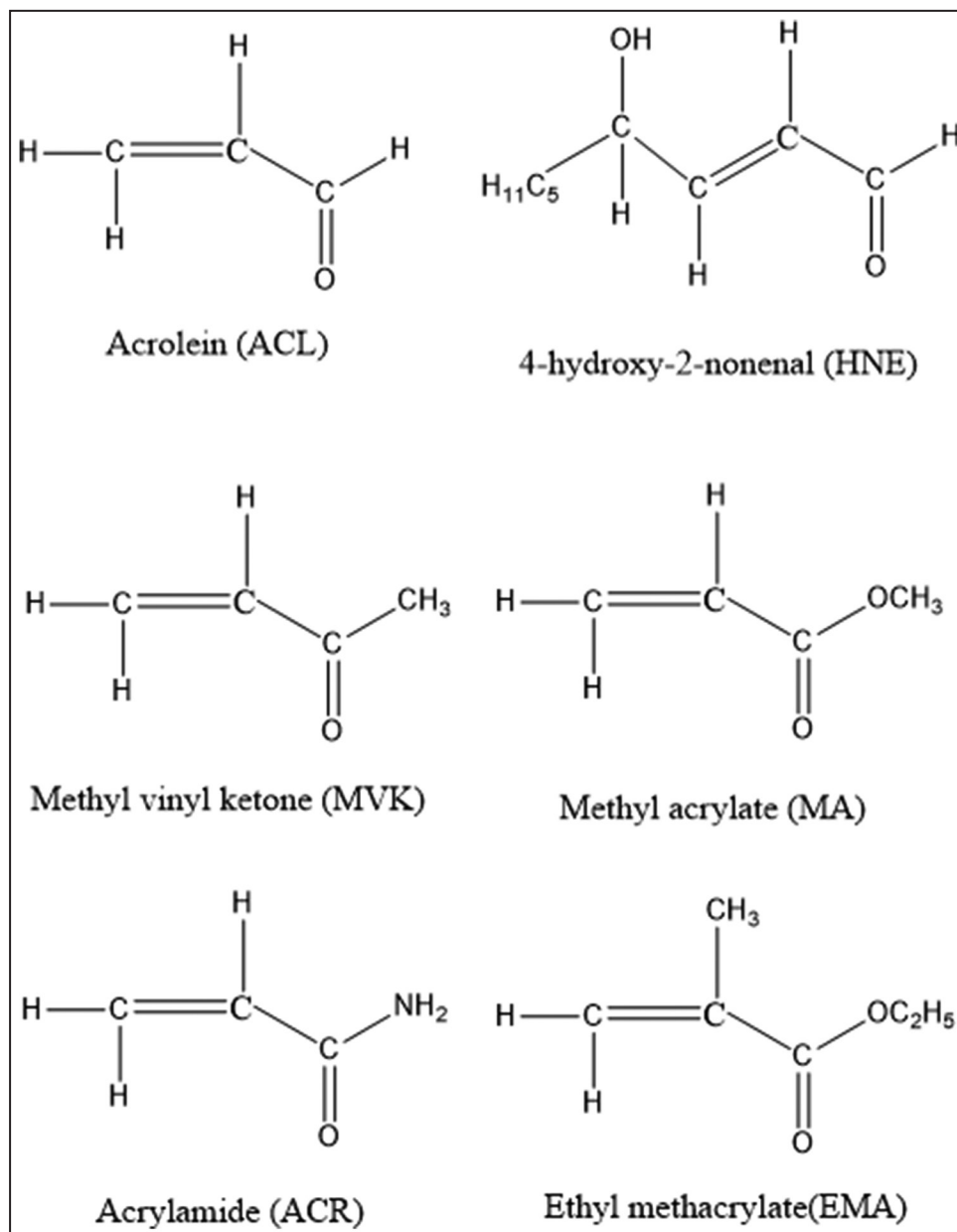
Figure 1: Structure of several α,β-unsaturated carbonyl compounds.

metal ion–Lewis base complexes can also be obtained by following equation:

$$\Delta H^{298.15K} = \{E^{298.15}(B_1M) - [E^{298.15}(B_1) + E^{298.15}(M)]\} + \Delta(pV) \tag{3}$$

The compounds studied are listed in Table 1 along with their respective abbreviated names and total energies of the free bases (B_1) and their sodium complexes (B_1Na^+) in gas phase and in different solvents. Table 2 reports the calculated SCA of the carbonyl compounds using equation 3. Where ΔE_g are the gas phase SCA values and $\Delta E_{(sol)}$ are the SCA in solvent phases. Table 3 summarized the total enthalpies (H), Gibbs free energies (G), SCA, and SCB results of
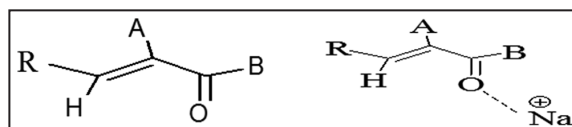
Figure 2: General structures for conjugated α,β-unsaturated carbonyl compounds of type-2-alkene chemical class. (R = –H or alkyl group, A = –H or –CH$_3$ and B = –H, –CH$_3$, –OCH$_3$, –NH$_2$, –OC$_2$H$_5$).

the compounds. We observed that SCA values of the compounds obtained in two different calculations do not differ significantly. It is very much expected for a thermodynamic equilibrium reaction. Difference of SCA values evaluated in two methods of calculation

Table 1: Computed total energies (hartree) of the carbonyl derivatives and their sodium complexes (B_1Na^+) for both gas phase and in different solvent phase at the equilibrium geometry of the ground state.

Carbonyl compounds	Total energy (hartree)							
	Gas phase		Aqueous phase		DMSO		CCl$_4$	
	B_1	B_1Na^+	B_1	B_1Na^+	B_1	B_1Na^+	B_1	B_1Na^+
ACL	−191.96	−354.11	−191.97	−354.23	−191.94	−354.22	−191.97	−354.17
HNE	−503.15	−665.30	−503.16	−665.42	−503.16	−665.41	−503.15	−665.36
MVK	−231.30	−393.44	−231.30	−393.56	−231.30	−393.56	−231.30	−393.51
ACR	−247.36	−409.52	−247.37	−409.63	−247.37	−409.63	−247.37	−409.58
MA	−306.54	−468.69	−306.55	−468.80	−306.55	−468.80	−306.54	−468.75
EMA	−385.21	−547.35	−385.21	−547.47	−385.21	−547.47	−385.20	−547.41

DMSO: Dimethyl sulfoxide

Table 2: Calculated Sodium cation affinities (SCA) of six conjugated α,β-unsaturated carbonyl derivatives in equilibrium ground state both in gas phase and solvents.

Compounds	Gas phase [ΔEg], kcal/mol	Solvent phase [ΔEsol], kcal/mol		
		Water	DMSO	CCl$_4$
ACL	−34.67	−5.367	−5.55	−17.15
HNE	−37.62	−5.18	−5.43	−17.91
MVK	−35.61	−5.43	−5.682	−17.60
ACR	−42.265	−7.43	−7.68	−22.24
MA	−41.70	−6.43	−6.74	−21.18
EMA	−35.42	−5.55	−5.80	−21.05

DMSO: Dimethyl sulfoxide. SCA calculated as $\Delta H^{298.15K} = \{E^{298.15}(B_1M) - [E^{298.15}(B_1) + E^{298.15}(M)]\} + \Delta(pV)$. Here SCA values are expressed in term of $[\Delta E_g]$ for gas phase and $[\Delta E_{sol}]$ for solvents.

[E_{Na+} (Gas) = −162.0874 hartree, E_{Na+} (aqueous) = −162.2468 hartree. E_{Na+} (DMSO) = −162.2454 hartree, E_{Na+} (CCl$_4$) = − 162.1764 hartree]

can be neglected considering minor computational errors. The calculated ΔE_g values have a variation in the range of −34.67 to −42.265 kcal/mol in gas phase. In solvents, $\Delta E_{1(sol)}$ varying in the range of −5.18 to −7.43 kcal/mol, −5.43 to −7.68 kcal/mol and −17.15 to −22.24 kcal/mol in water, DMSO and CCl$_4$, respectively. Acrylamide (ACR) exhibits the highest affinity for sodium cation in both gas and in all solvent phases in comparison to other compounds in the series. Differences of SCA values of selected unsaturated carbonyl derivatives obtained due to the non-unique effect of conjugated double bond on binding oxygen. SCA values are also influenced by different substituent attached to carbonyl carbon and by the substituent at α-carbon of the alkyl chain of the compound.

In Acrylamide, −NH$_2$ group is present at carbonyl carbon. Lone pair electron of amide nitrogen helps

to increase electron density on binding oxygen which enhances the ligand–cation interaction. Magnitudes of SCA's for all six compounds are found to be smaller in all solvents relative to the gas phase. Based on the ΔE_{sol} values, SCA's are found to follow the order as ACR ≥ MA > EMA ≥ MVK > ACL ≥ HNE in all solvents.

SCA of the compounds in solvent phase are in the order Water ≤ DMSO < CCl$_4$. $\Delta E_{1(sol)}$ values in DMSO observed little bit more (0.183-0.31 kcal/mol) compared to water, while in carbon tetra chloride, it increased markedly. This trend indicates that solvent polarity has marked influence on SCA values. In Table 3, total enthalpies (H), Gibbs free energies (G) of the free bases and their O–Na$^+$ complexes and SCA as −ΔH_{Na}^+ and SCB as −ΔG_{Na}^+ are tabulated (−ΔH_{Na}^+ has been calculated as difference between enthalpies of the product and reactants [SCA = $H_{Na+} + H_{free base} - H_{complex}$] and −$\Delta G_{Na}^+$ has been calculated as difference between free energies of the product and reactants [SCA = $G_{Na+} + G_{free base} - G_{complex}$]).

The SCA values reported in Tables 2 and 3 are differ only by 0.03-2.35 kcal/mol in gas phase, while in solvents, this difference become distinctly less. The calculated SCA values of all unsaturated derivatives reported in Tables 2 and 3 maintain same trend in both gas and different solvent phases. The computed Gibbs free energies (ΔG_{Na}^+) are negative and have a large energy difference from −27.79 kcal/mol to −34.32 kcal/mol in gas phase. On solvation (water, DMSO), interaction Gibbs energies difference reduced a lot [(0.9412 to −0.3765 kcal/mol in water and 0.5647 to −0.502 kcal/mol in DMSO)] and positive value also obtain in some cases. In non-polar CCl$_4$ solvent, ΔG_{Na}^+ values has a variation in the range −9.78 to −14.11 kcal/mol clears the fact that SCB values are somehow influenced by solvent polarity.

We know, for molecular complexes, the associating tendency is described by Gibbs free energies. Hence,

Table 3: Obtained enthalpy, free energy of six α,β-unsaturated carbonyl derivatives and sodium cation affinities (SCA, in kcal/mol), sodium cation basicities (SCB, in kcal/mol) and entropies (ΔS) in cal/mol by B3LYP/DFT method at 6-311G (d, p) level in gas and different solvents. SCA calculated as: $H_{Na+} + H_{free\ base} - H_{Complex}$.

At 298.15° K	H	G	SCA (ΔH_{Na}^+)	SCB (ΔG_{Na}^+)	ΔS
Gas phase					
Na+	−162.0851	−162.1018	−33.88	−27.79	−20.42
ACL	−191.9027	−191.9334			
ACL-Na$^+$	−354.0418	−354.0795			
Aqueous phase					
Na+	−162.2445	−162.2613	−5.39	1.25	−22.27
ACL	−191.9077	−191.9393			
ACL-Na$^+$	−354.1608	−354.1986			
In DMSO					
Na+	−162.2431	−162.2599	−5.58	1.00	−22.08
ACL	−191.9076	−191.9392			
ACL-Na$^+$	−354.1596	−354.1975			
In CCl$_4$					
Na+	−162.1741	−162.1908	−17.005	−9.78	−24.24
ACL	−191.9044	−191.9359			
ACL –Na$^+$	−354.1056	−354.1423			
Gas phase					
HNE	−502.9046	502.9601	−37.65	−31.31	−21.26
HNE-Na$^+$	−665.0497	−665.1118			
In aqueous phase					
HNE	−502.9142	−502.9699	−5.33	0.941	−21.033
HNE-Na$^+$	−665.1672	−665.2297			
In DMSO					
HNE	−502.9140	−502.9697	−5.64	0.7531	−21.44
HNE-Na$^+$	−665.1661	−665.2284			
In CCl$_4$					
HNE	−502.9086	−502.9641	−18.07	−11.10	−23.37
HNE-Na$^+$	−665.1115	−665.1726			
Gas phase					
MVK	−231.2063	−231.2420	−35.51	− 29.053	−21.65
MVK-Na$^+$	−393.3480	−393.3901			
In aqueous phase					
MVK	−231.2123	−231.2481	−5.584	1.06	−22.28
MVK-Na$^+$	393.4657	−393.5077			
In DMSO					
MVK	−231.2122	−231.2480	−5.773	0.815	−22.09
MVK-Na$^+$	−393.4645	−393.5066			
In CCl$_4$					
MVK	−231.2089	−231.2446	−17.63	−11.546	−20.40
MVK-Na$^+$	−393.4111	−393.4538			

(*Contd...***)**

Table 3: (*Continued*)

At 298.15° K	H	G	SCA (ΔH_{Na}^+)	SCB (ΔG_{Na}^+)	ΔS
Gas phase					
ACR	−247.2839	−247.3195	−40.72	−33.25	−25.05
ACR-Na$^+$	−409.4339	−409.4743			
In aqueous phase					
ACR	−247.2946	−247.3295	−6.96	−0.125	−22.92
ACR-Na$^+$	−409.5502	−409.5910			
In DMSO					
ACR	−247.2945	−247.3294	−7.21	−0.313	−23.13
ACR-Na$^+$	−409.5491	−409.5898			
In CCl$_4$					
ACR	−247.2885	−247.3238	−21.14	−14.11	−23.57
ACR-Na$^+$	−409.4963	−409.5371			
Gas phase					
MA	−306.4391	−306.4775	−41.603	−34.324	−24.41
MA-Na$^+$	−468.5905	−468.6340			
In aqueous phase					
MA	−306.4492	−306.4878	−6.463	−0.3765	−20.41
MA-Na$^+$	−468.7040	−468.7497			
In DMSO					
MA	−306.4490	−306.4876	−6.777	−0.502	−21.04
MA-Na$^+$	−468.7029	−468.7483			
In CCl$_4$					
MA	−306.4434	−306.4819	−21.021	−14.056	−23.36
MA-Na$^+$	−468.6510	−468.6951			
Gas phase					
EMA	−385.0356	−385.0812	−37.776	−30.81	−23.36
EMA-Na$^+$	−547.1809	−547.2321			
In aqueous phase					
EMA	−385.0448	−385.0903	−5.647	0.753	−21.46
EMA-Na$^+$	−547.2983	−547.3504			
In DMSO					
EMA	−385.0447	−385.0902	−5.898	0.5647	−21.67
EMA-Na$^+$	−547.2972	−547.3492			
In CCl$_4$					
EMA	−385.0394	−385.0849	−20.833	−12.612	−27.57
EMA-Na$^+$	−547.2467	−547.2958			

SCB calculated as: $G_{Na+} + G_{Free\ base} - G_{Complex}$

it is important to know the significance of entropy in the process studied. Since a single cationic metal-ligand complex is formed from a couple of reactant, loss of entropy should be involved in the process which exactly happened in our study. From Table 3 we observed that entropy change due to complex formation of the studied carbonyl derivatives vary in the range of −20.42 to −25.05 cal/mol in gas phase, it is −20.41 to −22.92 cal/mol, −21.04 to −23.13 cal/mol and −20.40 to −27.57 cal/mol in aqueous, DMSO and CCl$_4$, respectively. Loss of entropy in the gas phase for six α,β-unsaturated carbonyl complexes is differ by −4.63 cal/mol only. This difference is reduced to −2.51 cal/mol in water, −2.09 cal/mol in DMSO and −7.17 cal/mol in CCl$_4$.

We are unable to compare the energetic values obtained in this theoretical analysis due to the unavailability of

exact experimental data of this class of compounds. However, metal cation affinity, basicity values obtained from B3LYP level of theory provide good accuracy in comparison to experimental results [37,38].

Atomic charge on the atoms are non-unique, depend on the basis set used in the theoretical calculation [39] but till it used in theoretical calculations. Table 4 reported the computed Mulliken net charge on the carbonyl oxygen atom of the free bases and the Na^+ complexes both in their equilibrium ground state in gas phase and in solvents. Mulliken net charge carried out by Na^+ cation of the metal complexes in different phases at the equilibrium ground state are tabulated in Table 5. Charge on oxygen atom of the free bases and of their metal complexes and charge on Na^+ cation in complexes are also evaluated by means of NPA. The calculated NPA results are listed in Table 6. The atomic charges obtained in MPA by dividing orbital overlap equally by two shared atoms.

It is observed from Tables 4 and 5, the charge density on oxygen is higher in solvents relative to gas phase. Charge on Na^+ cation in sodium complexes vary in

the range of 0.7544-0.7925 in gas phase, 0.8479-0.877 in water, 0.89-0.911 in DMSO and 0.8756-0.8933 in CCl_4. The relative magnitudes of the charges on Na^+ cation indicate that, the bond formed by the sodium cation is largely ionic. Therefore, the interactions between Na^+ cation and carbonyl oxygen of the Lewis base is predominantly an ion-dipole attraction and ion induced dipole interaction as well rather than a covalent interactions. Increases of dipole moment (μ in Debye) in all solvents (Table 6a) clearly indicate the higher charge separation in solution phase (as it is expected for polar molecules). The magnitudes of the charges also indicate that both pre- and post-complex correlations with local charge densities of the adjoining locality of the carbonyl oxygen sites are not strong. Hence, SCA of the corresponding unsaturated carbonyl compounds (Lewis bases) cannot be explained properly considering the binding site properties only.

A significant ligand to metal charge transfer values (Δq_{CT}) calculated from NPA in both gas and different solvent phase are summarized in Table 7. The extent of charge transfer (Δq_{CT}) might have expected

Table 4: Calculated Mulliken net charges on oxygen atom (q_O-) in unit "e" in free bases and in sodium complexes in equilibrium ground state both in gas phase and in different solvent phases.

Compounds	(q_O-) Gas phase		(q_O-) Solvent phase					
	Free base	Sodium complex	Water		DMSO		CCl_4	
			Free base	Sodium complex	Free base	Sodium complex	Free base	Sodium complex
ACL	−0.2864	−0.4283	−0.4675	−0.3728	−0.4668	−0.3732	−0.4352	−0.3972
HNE	−0.2944	−0.4514	−0.3520	−0.3796	−0.3483	−0.3804	−0.3185	−0.4148
MVK	−0.3022	−0.4608	−0.3574	−0.3935	−0.3567	−0.3944	−0.3260	−0.4277
ACR	−0.3594	−0.5181	−0.4316	−0.4607	−0.4307	−0.4612	−0.3904	−0.4903
MA	−0.3525	−0.4173	−0.3778	−0.4249	−0.3770	−0.4253	−0.3424	−0.4503
EMA	−0.3071	−0.5099	−0.3701	−0.3974	−0.3691	−0.3981	−0.3339	−0.4373

DMSO: Dimethyl sulfoxide

Table 5: Mulliken net charges (unit "e") on sodium ion (q_{Na+}) in sodium complexes (B_1Na^+) and ligand to metal charge transfer (Q_{CT}) in the complexes in equilibrium ground state in both gas phase and in different solvent phase.

Compound	(q_O-) Gas phase		(q_O-) Solvent phase					
			Water		DMSO		Water	
	B_1Na^+	Q_{CT}	B_1Na^+	Q_{CT}	B_1Na^+	Q_{CT}	B_1Na^+	Q_{CT}
ACL	0.7925	0.2075	0.8742	0.1258	0.9110	0.089	0.8933	0.1067
HNE	0.7724	0.2286	0.877	0.123	0.9116	0.088	0.8883	0.1117
MVK	0.7765	0.2235	0.8746	0.1246	0.909	0.091	0.8901	0.1099
ACR	0.7544	0.2456	0.8479	0.1521	0.896	0.104	0.8769	0.1231
MA	0.7643	0.2357	0.8545	0.1455	0.890	0.11	0.8764	0.1236
EMA	0.7666	0.2334	0.8561	0.1439	0.903	0.097	0.8756	0.1244

DMSO: Dimethyl sulfoxide

Table 6: Computed partial atomic charges (units 'e') on the carbonyl oxygen (q_O^-) of the free bases (B_1) and charge on alkali metal ion (q_{Na}^+) and on carbonyl oxygen (q_O^-) of the O-Na$^+$ complexes (B_1Na^+) obtained from NPA analysis in both gaseous and different solvents.

Compound	(q_O^-) Gas phase		q_{Na}^+	(q_O^-) Water		q_{Na}^+	(q_O^-) DMSO		q_{Na}^+	(q_O^-) CCl$_4$		q_{Na}^+
	B_1	B_1Na^+	B_1Na^+	B_1	B_1Na^+	B_1Na^+	B_1	B_1Na^+	B_1Na^+	B_1	B_1Na^+	B_1Na^+
ACL	−0.505	−0.716	0.977	−0.567	−0.624	0.983	−0.566	−0.625	0.982	−0.538	−0.669	0.980
HNE	−0.521	−0.723	0.975	−0.553	−0.650	0.984	−0.554	−0.651	0.983	−0.535	−0.698	0.979
MVK	−0.549	−0.751	0.970	−0.597	−0.660	0.978	−0.597	−0.661	0.978	−0.570	−0.710	0.974
ACR	−0.604	−0.812	0.954	−0.671	−0.744	0.979	−0.683	−0.745	0.977	−0.649	−0.780	0.975
MA	−0.567	−0.679	0.953	−0.626	−0.686	0.974	−0.625	−0.687	0.974	−0.592	−0.729	0.973
EMA	−0.558	−0.759	0.964	−0.618	−0.689	0.979	−0.617	−0.690	0.979	−0.583	−0.727	0.973

DMSO: Dimethyl sulfoxide

Table 6a: Selected computed parameters of six conjugated α,β-unsaturated carbonyl derivatives in gas phase as well as in various solvent phase.

Carbonyl compound	Hardness ($\eta=[(\in_{LUMO}-\in_{HOMO})/2]$ hartree				Dipole moment (Debye)			
	Gas phase	Solvent phase			Gas phase	Solvent phase		
		Water	DMSO	CCl$_4$		Water	DMSO	CCl$_4$
ACL	0.0957	0.0982	0.0981	0.0968	3.15	4.04	4.032	3.54
HNE	0.0943	0.0964	0.0963	0.0952	2.12	2.83	2.82	2.40
MVK	0.0963	0.0983	0.0983	0.0971	2.70	3.51	3.49	3.03
ACR	0.1058	0.1099	0.1098	0.1076	3.88	5.14	5.12	4.40
MA	0.1083	0.1127	0.1127	0.1102	4.32	5.56	5.54	4.84
EMA	0.1137	0.1172	0.1172	0.1167	1.78	5.51	5.48	4.64

DMSO: Dimethyl sulfoxide

parallel to the alkali metal binding affinities of the compounds, but this is not occurred. The NPA results gave uncooperatively MA ≥ ACR > EMA > MVK > HNE > ACL in gas, MA > MVK > ACR = EMA > ACL > HNE in water, MA > ACR > MVK > EMA > HNE ≥ ACL in DMSO and MA = EMA ≥ MVK ≥ ACR> HNE > ACL in CCl$_4$. No direct correlation between SCA and Δq_{CT} has been observed. It was seen from a previous study of dichalcogen-bridged complexes with divalent metal cation (Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}) by Jeanvoine and Spezia [40] using B3LYP and MP2 method that there was also no direct good correlation between (Δq_{CT}) and binding affinities.

We observed the calculated NPA atomic charge on carbonyl oxygen and sodium cation in complexes is higher compared to MPA charges. Magnitudes of Δq_{CT} are smaller than Q_{CT} (Tables 5 and 7). Although the relative order of charge transfer in MPA and NPA follows a parallel trend. Both Δq_{CT} and Q_{CT} values have been predicted to be highest in ACR in gas phase and it is found minimum for ACL which satisfy their obtained SCA results.

Optimized geometry of free base and complexes are shown in Figure 3. Important geometrical parameters

Table 7: Charge transfer (Δq_{CT}) (unit e) in different phase. Calculated from the data of (q_{Na}^+) listed in Table 7 [the ligand to metal charge transfer (Δq_{CT})] = [(Formal + 1 charge on the metal ion) – (charge on the metal in the complex)] obtained in NPA.

Carbonyl compounds	Gas Δq_{CT}	Water Δq_{CT}	DMSO Δq_{CT}	CCl4 Δq_{CT}
ACL	0.023	0.017	0.018	0.020
HNE	0.025	0.016	0.017	0.021
MVK	0.030	0.022	0.022	0.026
ACR	0.046	0.021	0.023	0.025
MA	0.047	0.026	0.026	0.027
EMA	0.036	0.021	0.021	0.027

DMSO: Dimethyl sulfoxide

such as bond angle (in degree), bond distance (Å), and dihedral or torsion angle (in degree) of the optimized structures are summarized systematically in Table 8. The local streochemical properties around the carbonyl moiety are found to be almost identical in each compound. The C = O bond length of the free bases elongated by 0.023Å-0.029Å in complexes in the gas phase, whereas in solvents atmosphere, it is remain almost same (increased slightly by 0.001-0.015Å).
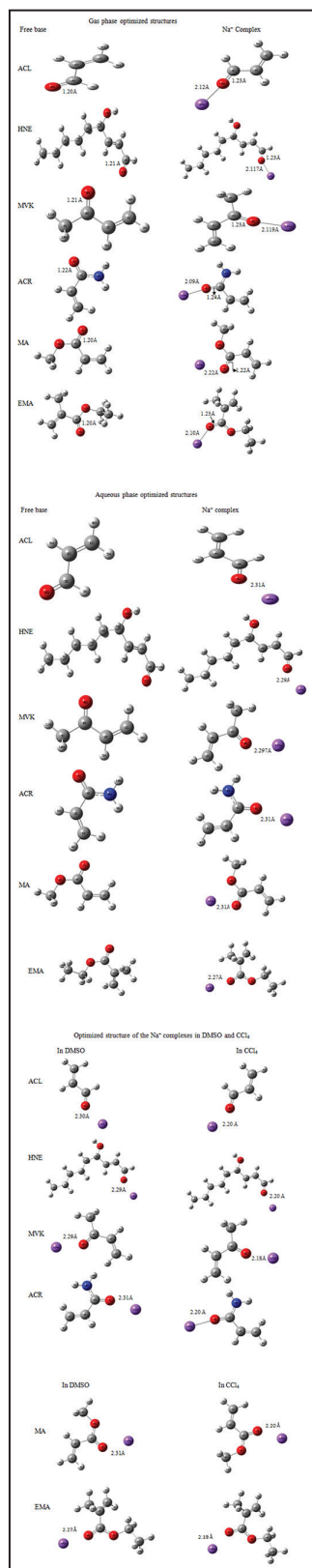
Figure 3: Optimized structure of the studied α,β-unsaturated carbonyl compounds and their O-Na⁺ complexes in gas phase and in different solvents [optimized structures of the free bases in dimethyl sulfoxide and CCl₄ are almost similar as they obtained in aqueous phase thus not given].

In solvents, distance between carbonyl carbon and donor oxygen of the free bases and their Na⁺ complexes has a variation in the range 1.20-1.23Å and 1.22-1.24Å, respectively. Analysis of the C = O bond length in each compounds are tend to suggest that substituent's effect on bond length is marginal. Since the sodium-ligand interaction is electrostatic, the bond length between ligand and cation should be a supporting parameter to realize the strength of interaction. From Table 8, it is seen that O-Na⁺ distance remains within the range from 2.092 to 2.22Å in the gas phase. The O-Na⁺ bond length is found to be shortest in ACR in gas phase as well as in all solvents. Thus, it can be predicted partially that ligand-cation interaction is stronger in ACR compared to other compounds.

Employing PCM type solvents model leads to increase of O–Na⁺ bond distance of the given class of compounds. Ligand-cation bond lengths are elongated by 0.09-0.189Å, 0.09-0.176Å, and 0.058 to 0.083Å in aqueous, DMSO and CCl₄ with an exception of MA complex in carbon tetra chloride where it is reduced by 0.02Å. We also observed that O-Na⁺ bond distances are reduced by 0.08-0.11Å in CCl₄ compared to other two solvents. This may be occurred in non-polar solvent where solvent particles compress the electron density between the nuclei of two bonding atom responsible for decreased bond length. The equilibrium geometrical optimized structures of the unsaturated carbonyl compounds obtained with DFT/B3LYP/6-311G (d,p) calculation in gas phase and in different solvents do not changed significantly. Concerning torsion angles [τ (adjacent to carbonyl C–carbonyl C–carbonyl O – Na⁺ cation)] for all metal complexes, it should be noticed that except the sodium complex of ACR and EMA, all complexes have planar structure in all gas and solvent phases. ACR has non-planar structure in all medium (dihedral angles are 13.5°, −4.18°, −5.82° and 3.24°). EMA has planar geometry in CCl₄ (τ=−178.86°) but in gas, water and DMSO, non planar structures have been obtained.

In ACL torsion angle (τ) is 180° in all medium, in HNE it is −175-172°, in MVK, τ=179-180° and which estimated −179° in MA. The almost invariant stereochemistry around the complex formation site of bases forced to suggest that the entire contribution from different substituent effects to SCA cannot be described comprehensively without considering the contribution from far away centers.

We have analyzed hardness (η) as a single global parameter for all compounds in the equilibrium ground state in gas phase as well as in solvents. Hardness (η) = [Î$_{LUMO}$-Î$_{HOMO}$]/2 parameters are listed in Table 6a.

Calculated η values clearly reflects that, EMA is more hard (η=0.1137-0.1172 hartree) in all medium while HNE exhibit lowest η values (0.0943-0.0964 hartree)

211

Table 8: Some selected geometrical features of six α,β-unsaturated carbonyl derivatives and their sodium complexes at ground state equilibrium geometry [bond distance (carbonyl carbon-binding oxygen [r (C-O) and binding oxygen sodium cation $r(O-Na^+)$ in Å, <carbonyl carbon-carbonyl oxygen-sodium ion ($<C-O-Na^+$) and $\tau(C-C-O-Na^+)$ angles in].

Carbonyl compound	Gas phase		Water		DMSO		CCl4	
	r(C-O)		r(C-O)		r(C-O)		r(C-O)	
	B_1	B_1Na^+	B_1	B_1Na^+	B_1	B_1Na^+	B_1	B_1Na^+
ACL	1.208	1.231	1.221	1.222	1.221	1.227	1.218	1.226
HNE	1.212	1.239	1.21	1.225	1.217	1.225	1.214	1.232
MVK	1.213	1.238	1.219	1.226	1.219	1.226	1.215	1.231
ACR	1.22	1.248	1.230	1.237	1.23	1.23	1.224	1.242
MA	1.203	1.229	1.212	1.22	1.212	1.221	1.206	1.226
EMA	1.208	1.237	1.212	1.22	1.211	1.22	1.20	1.227
		$r(O-Na^+)$		$r(O-Na^+)$		$r(O-Na^+)$		$r(O-Na^+)$
ACL	-	2.124	-	2.313	-	2.30		2.20
HNE	-	2.117	-	2.29	-	2.29		2.20
MVK	-	2.119	-	2.297	-	2.293		2.18
ACR	-	2.092	-	2.238	-	2.23		2.15
MA	-	2.22	-	2.31	-	2.31		2.20
EMA	-	2.107	-	2.27	-	2.27		2.19

Carbonyl compound	Gas phase		Water		DMSO		CCl4	
	$<C-O-Na^+$	$\tau(C-C-O-Na^+)$	$<C-O-Na^+$	$\tau(C-C-O-Na^+)$	$<C-O-Na^+$	$\tau(C-C-O-Na^+)$	$<C-O-Na^+$	$\tau(C-C-O-Na^+)$
ACL	174.228	180.00	134.082	180.00	134.946	180.00	151.525	180.00
HNE	159.216	−175.537	143.12	−175.537	143.146	−175.51	147.534	172.547
MVK	167.869	180.034	141.356	179.934	141.697	−179.96	162.248	179.939
ACR	170.425	13.5137	162.338	−4.189	163.175	−5.823	171.834	3.248
MA	103.925	−179.966	126.752	−179.995	126.639	−179.986	145.398	−179.966
EMA	164.829	13.001	164.829	13.0016	165.544	−13.235	149.544	−178.869

**<C-O-Na+: 3C-8O-9Na+ (ACL), 20C-21O-28Na+ (HNE), 5C-8O-12Na+ (HNE), 5C-7O-11Na+ (MVK), 3C-7O-11Na+ (ACR), 5C-7O-13Na+ (MA), 5C-6O-19Na+ (EMA). *τ(C-C-O-Na+): 2C-3C-8O-9Na+ (ACL), 19C-20C-21O-28Na+ (HNE), 2C-5C-8O-12Na+ (HNE), 2C-3C-7O-11Na+ (ACR), 2C-5C-7O-13Na+ (MA), 2C-5C-6O-19Na+ (EMA), DMSO: Dimethyl sulfoxide

Table 9: Calculated salvation energies (hartree) of the six α,β-unsaturated carbonyl compounds by DFT/B3LYP method at 6-311 G(d, p) basis set level. Solvation energy (ΔE_s) = [(total energy in solvent phase) - (total energy in gas phase)].

Carbonyl compound	Solvation energy (ΔE_s) (hartree)		
	Water	**DMSO**	**CCl$_4$**
ACL	−0.0059	−0.0058	−0.0025
HNE	−0.0093	−0.0091	−0.0040
MVK	−0.0060	−0.0059	−0.0026
ACR	−0.0108	−0.0107	−0.0047
MA	−0.0101	−0.0099	−0.0043
EMA	−0.0059	−0.0093	−0.0038

DMSO: Dimethyl sulfoxide

in gas and also in solvents. Compounds are stabilized in all solvents. The solvation energy (ΔE_s) of all studied α,β-unsaturated compounds listed in Table 9. Solvation energy of the compounds follows the order water > DMSO> CCl$_4$ which fulfil the chemical expectation raised from the dielectric constant of the solvents.

CONCLUSION

The theoretical calculation of six α,β-unsaturated carbonyl compounds using DFT [B3LYP] method at hybrid triple zeta 6-311G (d,p) basis set level provides a set of important data like SCA, SCB, entropy of the reactions process in gas phase as well as in different solvents. The applications of PCM-SCRF model in the study not influence markedly on geometrical structures of the compounds but it change a lot of chemical properties. The calculations indicate that Na^+ cation prefer to bind with carbonyl oxygen of the studied bases. SCA is predicted to be highest in ACR in all medium of reactions. The interaction enthalpies, Gibbs free energies of the complexation reactions reduced in solvents in each case.

The SCA of the unsaturated compounds 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. Finally, from the different electronic properties of the complexes, we can conclude that the interactions are predominantly an ion-dipole attraction and ion-induced dipole interaction as well rather than covalent interaction.

REFERENCES

1. P. Burk, M. L. Sults, T. T. Jaana, (2007) Comparative calculations of alkali metal cation basicities of some Lewis bases, *Proceedings of the Estonian Academy of Sciences Chemistry,* **56(3):** 107.

2. K. Aoki, K. Murayama, H. Ning-Hai, (2016) *Solid State Structures of Alkali Metal Ion Complexes Formed by Low-Molecular-Weight Ligands of Biological Relevance,* Ch. 3. US: Springer. p27-101.

3. A. Sigel, H. Sigel, R. K. O. Sigel, (2016) The alkali metal ions: Their role for life, *Metal Ions in Life Sciences, (Springer),* **16:** 27-101.

4. W. Mark, (2012) WebElements Periodic Table of the Elements|Sodium|Biological Information. WebElements. Available from: https://en.wikipedia.org/wiki/alkali_metal#cite_note-webelements-sodium-230. [Last retrieved on 2015 Jan 13].

5. North-western University. Archived from the Original (PDF). Available from: https://en.wikipedia.org/wiki/alkali-metal#cite_note-r31-231. [Last accessed on 2011 Aug 23; Last retrieved on 2011 Nov 21].

6. J. C. Ma, D. A. Dongherty, (1997) The cation-π interaction, *Chemical Review,* **97:** 1303-1324.

7. R. M. LoPachin, D. S. Barber, T. Gavin, (2008) Molecular mechanisms of the conjugated α,β-unsaturated carbonyl derivatives: Relevance to neurotoxicity and neurodegenerative diseases, *Toxicological Sciences*, **104:** 235-249.

8. M. Friedman, (2003) Chemistry, biochemistry and safety of acrylamide. A review, *Journal of Agricultural and Food Chemistry*, **51:** 4504-4526.

9. R. M. LoPachin, T. Gavin, (2008) Acrylamide-induced nerve terminal damage: Relevance to neurotoxic and neurodegenerative mechanisms, *Journal of Agricultural and Food Chemistry*, **56:** 5994-6003.

10. R. L. Stedman, (1968) The chemical composition of tobacco and tobacco smoke, *Chemical Review,* **68:** 153-207.

11. W. Parzefall, (2008) Minireview on the toxicity of dietary acrylamide, *Food and Chemical Toxicology,* **46:** 1360-1364.

12. J. F. Stevens, C. S. Maier, (2008) Acrolein: Sources, metabolism and biomolecular interactions relevant to human health and disease, *Molecular Nutrition and Food Research*, **52:** 7-25.

13. I. Dzidic, P. Kebarle, (1970) Hydration of the alkali ions in the gas phase. Enthalpies and entropies of reactions M+(H_2O)n–1 + H_2O = M+(H_2O)n, *Journal of Physical Chemistry,* **74:** 1466-1474.

14. J. Sunner, P. Kebarle, (1984) Ion-solvent molecule interactions in the gas phase. The potassium ion and Me2SO, DMA, DMF and Me2O, *Journal of the American Chemical Society*, **106:** 6135-6139.

15. M. D. Tissandier, K. A. Cowen, W. Y. Feng, E. Gundlach, M. H. Cohen, A. D. Earhart, J. V. Coe, T. R. Jr. Tuttle, (1998) The proton's absolute aqueous enthalpy and Gibbs free

energy of solvation from cluster-ion solvation data, *Journal of Physical Chemistry A*, **102:** 7787-7794.

16. A. W. Castleman, R. G. Keesee, (1986) Ionic clusters, *Chemical Review*, **86:** 589-618.

17. R. D. Wieting, R. H. Staley, J. L. Beauchamp, (1975) Reactions of alkali ions with organic molecules in the gas phase. Low energy pathways for carbonium ion formation and novel methods for generating alkali ion complexes with .pi.- and n-donor bases, *Journal of the American Chemical Society*, **97:** 924-926.

18. R. H. Staley, J. L. Beauchamp, (1975) Intrinsic acid-base properties of molecules. Binding energies of lithium(1+) ion to .pi.- and n-donor bases, *Journal of the American Chemical Society*, **97:** 5920-5921.

19. R. L. Woodin, J. L. Beauchamp, (1978) Binding of lithium(1+) ion to Lewis bases in the gas phase. Reversals in methyl substituent effects for different reference acids, *Journal of the American Chemical Society*, **100:** 501-508.

20. R. L. Woodin, J. L. Beauchamp, (1979) Bimolecular infrared radiative association reactions. Attachment of Li+ to carbonyl compounds in the gas phase, *Chemical Physics*, **41:** 1-9.

21. R. W. Taft, F. Anvia, J. F. Gal, S. Walsh, M. Capon, M. C. Holmes, K. Hosn, G. Oloumi, R. Vasanwala, S. Yazdani, (1990) Free-energies of cation molecule complex-formation and of cation solvent transfers, *Pure and Applied Chemistry*, **62:** 17-23.

22. S. A. McLuckey, D. Cameron, R. G. Cook, (1981) Proton affinities from dissociations of proton bound dimmers, *Journal of the American Chemical Society*, **103:** 1313-1317.

23. R. G. Cook, J. S. Patrick, T. Kotiaho, S. A. McLuckey, (1994) Thermochemical determinations by the kinetic method, *Mass Spectrometry Reviews*, **13:** 287-339.

24. U. Senapati, D. De, B. R. De, (2010) The ground-state Na$^+$ affinities of a series of substituted acetophenones: A DFT study, *Molecular Simulation*, **36(6):** 448-453.

25. W. Ping, O. Gilles, W. Chrys, (2008) The sodium ion affinities of asparagine, glutamine, histidine and arginine, *International Journal of Mass Spectrometry*, **269:** 34-45.

26. J. Sille, V. Garaj, P. Jezko, M. Remco, (2010) AED Gas phase and solution state stability of complexes LM, where M = Li+, Na+, K+, Mg2+, or Ca2+ and L = R−C(=O)NHOH (R = H, NH2, CH3, CF3, or Phenyl)/J. Šille, *Acta Facultatis Pharmaceuticae Universitatis Comenianae*, **17:** 96-113.

27. S. Hoyau, K. Norman, T. B. Mcmohon, G. Ohanessian, (1990) A quantitative basis for a scale of Na+ affinities of organic and small biological molecules in the gas phase, *Journal of the American Chemical Society*, **121:** 8864.

28. P. B. Armentrout, M. T. Rodgers, (2000) An absolute sodium cation affinity scale: Threshold collision-induced dissociation experiments and ab initio theory, *Journal of Physical Chemistry A*, **104:** 2238.

29. C. Lee, W. Yang, R. G. Parr, (1988) Development of the colle-salvetti correlation-energy formula into a functional of the electron density, *Physical Review*, **B37:** 785-789.

30. W. J. Hehre, (1969) Self-consistent molecular-orbital methods. I. Use of gaussian expansions of slater-type atomic orbitals, *Journal of Chemical Physics*, **51(6):** 2657-2664.

31. F. Jensen, (1992) Structure and stability of complexes of glycine and glycine methyl analogs with H$^+$, Li$^+$ and Na$^+$, *Journal of the American Chemical Society*, **114:** 9533-9537.

32. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, (2009) *Gaussian 09, Revision A.02,* Wallingford, CT: Gaussian Inc.

33. J. Tomasi, B. Mennucci, E. Cancès, (1999) The IEF version of the PCM solvation method: An overview of a new method addressed to study molecular solutes at the QM ab initio level, *Journal of Molecular Structure (Theochem)*, **464(1-3):** 211-226.

34. M. Remko, B. M. Rode, (2000) Thermodynamics of binding of Li+, Na+, Mg+2, Zn+2 to Lewis base in gas phase, *Journal of Molecular Structure (Theochem)*, **505:** 269-281.

35. R. S. Mulliken, (1955) Electronic population analysis on LCAO-MO molecular wave functions, *Journal of Chemical Physics*, **23(10):** 1833-1840.

36. S. F. Boys, F. Bernardi, (1970) The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors, *Molecular*

Physics, **19:** 553-566.

37. H. Nagase, J. F. Jr. Woessner, (1999) Matrix metalloproteinases, *Journal of Biological Chemistry*, **274:** 21491-21494.

38. L. R. Scolnick, A. M. Clements, J. Liao, L. Crenshaw, M. Heliberg, J. May, T. R. Dean, D. W. Christianson, (1997) Novel binding mode of hydroxamate inhibators to human carbonic anhydrase II, *Journal of the American Chemical Society*, **119:** 850-851.

39. D. De, S. Dalai, B. R. De, (2010) The ground state structure and properties of erythritol in gas phase and in different solvents: A DFT/SC-IPCM approach, *African Journal of Pure and Applied Chemistry*, **4(9):** 177-182.

40. Y. Jeanvoine, R. Spezia, (2009) Mn2+-, Fe2+-, Co2+-, Ni2+-, Cu2+-, and Zn2+-binding chalcogen-chalcogen bridges: A Compared MP2 and B3LYP Study, *Journal of Physical Chemistry A*, **113:** 7878-7887.

*Bibliographical Sketch

Dr. Umasankar Senapati presently working as Assistant Professor of Chemistry in Belda college (Govt. aided College), Belda-721424, Paschim Medinipur, West Bengal, India. He did his B.Sc. in Chemistry from Midnapore College in the year 2000 and obtained his M.Sc. degree (with Physical Chemistry special) from Vidyasagar University, Midnapore in 2002. He qualified CSIR-UGC (JRF)-NET in December-2002. He also qualified in GATE-2002 with 96.13 Percentile Score. He also did his Ph.D. under the faculty of Science from Vidyasagar University in 2010. Dr. Senapati published 15 papers in national and international journals and he also actively engaged himself in research in the field of Computational Chemistry.