

# Cation- $\pi$ Interactions in 1:1 Systems

Dr. Sharon Achamma Abraham

Department of Chemistry  
Mar Thoma College Tiruvalla, Kerala, India

**Abstract:** Noncovalent interactions play an important role in many areas of Chemistry. Compared to the more conventional interactions such as Ionic interactions, Vander Waal's interactions, Hydrogen bonds, Hydrophobic Interactions, cation  $\pi$  interactions has been emerging as a useful tool in Supramolecular complexes and protein ligand systems. The present study will give a detailed understanding of cation –  $\pi$  interactions in 1:1 systems. In this paper, various metallic cations like  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ag}^+$  and organic cations like  $\text{NH}_4^+$ ,  $\text{C}(\text{NH}_2)_3^+$ ,  $\text{N}(\text{CH}_3)_4^+$  bind with different  $\pi$  systems like ethene, benzene, pyrrole. Interaction energies are calculated using MP2 level 6-31+G(d,p) and aug-cc-pVDZ basis sets. Interaction energy components of all 1:1 systems are discussed. Among the energies, the total energy  $E_{int}$  mainly comes from electrostatic energy component and is higher for Pyrrole.. $\text{Li}^+$  complexes. The interaction of organic cations contributes a little to the complexes. But the contribution of induction and dispersion energies becomes important in the binding of organic cations to  $\pi$  systems. When  $\pi$  system is plotted against interaction energies, curved lines are obtained. Similarly interaction energy components are plotted against  $\pi$  system column graphs are formed.

**Keywords:** Interaction Energy; Mollé-Plesset level; Induction energy; Perturbation theory; Natural Bond Orbital Analysis

## I. INTRODUCTION

Non-covalent Interactions play an important role in Supramolecular chemistry, Crown ethers to calixarenes, Modification and assembly of DNA as well as inorganic based systems, receptor-ligand, antigen-antibody, DNA-protein, RNA-ribosome, molecular recognition and in biological systems. These non-covalent interactions are host-guest interactions in biological systems. It refers to the specific interaction between two or more molecules through non-covalent bonding such as hydrogen bonding, metal co-ordination, hydrophobic forces, Vanderwaals forces,  $\pi$ - $\pi$  interactions, Electrostatic or Electromagnetic effects [1,2]. Among the non-covalent interactions, Cation  $\pi$  interactions is the most important and has many applications in drug delivery, supramolecular complexes and in molecular recognition. These interactions are used to design molecular materials, protein-ligand structures and as one-dimensional materials [3,4].

## Methods

All the calculations were performed using the supermolecular (SM) variational and perturbational (SAPT) methods. Even though the SM method is conceptually and computationally simple, it does not give any information of the interaction forces responsible for the interaction. SAPT method helps one to obtain the different interactions existing between the various complex monomers. In SM method, the interaction energy is calculated as the difference of the energy of the complex and the energy of the isolated monomers. In the SAPT method, the interaction energy is given as a sum of the individual electrostatic, exchange, dispersion and induction energies. Here, some calculations are discussed which helps in the results [5,6,7].

## Supermolecular Calculations

All the SM calculations, which included geometry optimizations and vibrational frequencies were done at the second-order Moller-Plesset (MP2) level of theory using the 6-31+G(d,p) and aug-cc-pVDZ basis sets. Interaction energies of



the complexes were also calculated using the much larger aug-cc-pVDZ basis set. For higher levels of correlation, single point calculations at the coupled-cluster with single, double, and perturbative triple substitutions [CCSD(T)] levels of theory. All the electrons were explicitly correlated in the MP2 and CCSD(T) calculations.

Except for  $\text{Ag}^+$ , the 6-31+G(d,p) basis set was used for all other metal cations investigated in this study. In calculations of  $\pi\text{-K}^+$  carried out using aug-cc-pVDZ basis set, we used the Feller miscellaneous CVDZ basis set to represent the  $\text{K}^+$  cation. In this basis set, the (s,p) exponents of  $\text{K}^+$  are obtained from Schafer et al [8] and the core/valence exponents are obtained from Feller et al. Basis set superposition error (BSSE) for all these complexes were obtained using the counterpoise (CP) method of Boys and Bernardi. Compared to other complexes involving  $\pi$  systems, the BSSE corrections in these systems are small. The zero point vibrational energy (ZPVE) corrections were computed from the frequencies evaluated at the MP2/6-31+G(d,p) and MP2/aug-cc-pVDZ levels of theory. For  $\text{Ag}^+$ , small-core energy-consistent relativistic pseudopotentials developed by Andrae et al [9] plus an f function ( $\zeta_f=1.7$ ). In this basis set, the 28 core electrons are replaced by effective core potentials and 18 remaining electrons are considered to be valence electrons.

The natural bond orbital (NBO) analysis method has been used to calculate the atomic charges in all the complexes, because unlike most other charge partitioning schemes, it is not affected by the presence of diffuse functions in the basis set. The NBO charges got in this study have been calculated using the densities at the MP2 functional. Since the charges evaluated using the atomic polar tensors (APT) are similar to electron density distributions, calculated the APT charges from the calculated wave functions of the optimized geometries of these complexes. NBO charges and the APT charges are calculated for all the complexes. As in the case of NBO calculated charges, the APT calculated charges are much less sensitive to basis set variations. NBO and APT charges are calculated for  $\pi$  systems Ethene, benzene, pyrrole with cation like  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{C}(\text{NH}_2)_3^+$ ,  $\text{N}(\text{CH}_3)_4^+$  and  $\text{Ag}^+$ .

**Table 1: Total Binding Energies obtained at the MP2 level using 6-31+G(d,p) and aug-cc-pVDZ Basis Sets for Various Monocation- $\pi$  Complexes**

	6-31+G(d,p)						aug-cc-pVDZ					
	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{NH}_4^+$	$\text{C}(\text{NH}_2)_3^+$	$\text{N}(\text{CH}_3)_4^+$	$\text{Ag}^+$	$\text{K}^+$	$\text{NH}_4^+$	$\text{C}(\text{NH}_2)_3^+$	$\text{N}(\text{CH}_3)_4^+$	$\text{Ag}^+$
$\pi$ =Ethene												
R	2.4	2.7	3.3	3.4	4.0	5	3.4	4.5	4.6	4.96	5.1	3.3
$\Delta E_e^N$	-22.5	-16.5	-9.2	-12.3	-8.5	-6.2	-36.2	-10.5	-13.7	-10.9	-7.9	-47.8
$\Delta E_e^B$	-20	-14.5	-9.7	-11.3	-6.7	-4.7	-30.2	-9.5	-12.8	-8.6	-5.7	-41.4
$\Delta E_0$	-19.2	-13.6	-7.5	-	-7.2	-	-	-8.8	-10.8	-7.7	-4.5	-39.6
				10.3		3.5	30.8					
$\Delta H_{298}$	-20	-13.4	-8.7	-9.5	-5.8	-	-	-9.02	-11	-7.8	-4.8	-40.8
						3.7	32.4					
$\Delta E_{cor}$	-2.3	-2.7	-2.8	-3.5	-4.2	-	-	-2.7	-5.08	-6.2	-6.5	-31.6
						4.8	17.6					
$\pi$ =Benzene												
R	2.8	3.5	3.9	3.7	4.98	5.85	3.21	3.83	3.88	4.57	5.12	3.06
$\Delta E_e^N$	-40.53	-36.78	-	-	-	-	-	-	-	-	-16.11	-
			18.76	19.66	16.80	12.40	51.86	20.98	23.45	20.40		59.14
$\Delta E_e^B$	-35.7	-23.98	-	-	-	-8.99	-	-	-	-	-10.48	-
			16.48	16.74	12.71		33.01	18.21	19.60	15.21		43.38
$\Delta E_0$	-32.95	-21.23	-	-	-	-7.90	-	-	-	-	-9.39	-
			15.89	15.87	11.81		31.65	17.95	18.39	14.31		42.68



$\Delta H_{298}$	-33.91	-21.9	-15.6	-15.5	-	-7.98	-31.9	-	-	-	-8.83	-
					11.97			17.87	19.85	13.85		42.97
$\Delta E_{corr}$	-4.02	-4.56	-4.27	-5.97	-8.33	-8.56	-23.7	-4.99	-9.21	-	-13.65	-
										12.42		43.43
$\pi$ -Pyrrole												
R	2	3.5	3.4	4	4	5.6	3.26	3.82	3.91	4.88	5.09	3.18
$\Delta E_e^N$	-43.5	-29.2	-	-22.5	-19.6	-	-49.5	-	-25.6	-22.7	-17.53	-
			21.76			14.45		22.24				62.78
$\Delta E_e^B$	-39.5	-26.5	-	-20.5	-16.3	-10.6	-	-19.9	-	-	-12.67	-
			19.54				43.32		22.52	18.45		61.67
$\Delta E_0$	-37.2	-24.9	-	-	-	-9.75	-	-	-21.4	-	-11.45	-
			18.36	18.97	15.46		41.75	19.16		17.56		51.82
$\Delta H_{298}$	-38.5	-25.6	-18.5	-	-	-9.87	-	-	-	-	-10.89	-
				19.04	14.91		42.12	19.44	21.65	17.23		51.81
$\Delta E_{corr}$	-3.6	-3.7	-4.3	-6.8	-8.2	-8.4	-21.0	-5.6	-9.20	-	-12.78	-
										12.45		36.43

All energies are in kcal/mol and distances are in Angstroms. R represents the perpendicular distance from the center-of-mass of the  $\pi$  system to the cation.  $\Delta E_e^N$  and  $\Delta E_e^B$  represent the binding energies without and with BSSE correcton.  $\Delta E_0$  is the ZPVE-corrected  $\Delta E_e^B$ .  $\Delta H_{298}$  is the enthalpy at 298.15K and 1atm. The electron correlation energy  $\Delta E_{corr}$  is the value of the  $E_e^{MP2}$  subtracted by  $E_e^{HF}$  at the MP2 optimized geometry.

#### Symmetry Adapted Perturbation Theory Calculations.

In this study, the SAPT calculations were carried out using the optimized geometries of all the complexes. The SAPT interaction energy accurate to third order  $E_{int}^{SAPT}$  is given by

$$E_{int}^{SAPT} = E_{elst}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{exch-ind}^{(2)} + E_{disp}^{(2)} + E_{exch-disp}^{(2)} + \delta_{int}^{HF}$$

where  $E_{elst}^{(1)}$  is the electrostatic energy of the reactants with unperturbed electron distribution,  $E_{exch}^{(1)}$  is their first-order valence repulsion energy because of the Pauli exclusion principle,  $E_{ind}^{(2)}$  indicates the second-order energy gain from the induction interaction,  $E_{exch-ind}^{(2)}$  represents the repulsion change due to the electronic cloud deformation,  $E_{disp}^{(2)}$  is the second-order dispersion energy,  $E_{exch-disp}^{(2)}$  denotes the second-order correction for a coupling between the exchange repulsion and the dispersion interaction and  $\delta_{int}^{HF}$  includes the higher order induction and exchange corrections[10].

The SAPT interaction energy can also be calculated as the sum of

$E_{int}^{HF}$  and  $E_{int}^{corr}$ , where  $E_{int}^{HF}$  is the sum of all the energy components evaluated at the Hartree Fock level and  $E_{int}^{corr}$  is the sum of all the energy components evaluated at the correlated level. Various energy components are included in the SAPT calculations. SAPT energy is the sum of all energy component ie, electrostatic, exchange, induction, exchange induction, dispersion, exchange dispersion components, higher order exchange and induction corrections etc.



**Table 2:MP2 Equivalent Interaction Energy Components of all the Monocation- $\pi$ complexes using the 6-31+G(d,p) Basis set**

	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	C(NH <sub>2</sub> ) <sub>3</sub> <sup>+</sup>	N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	Ag <sup>+</sup>
$\pi$ =Ethene							
E <sub>int</sub>	-21.09	-13.97	-9.66	-11.65	-10	-8.38	-37.71
E <sub>corr</sub>	0.67	0.64	-0.32	-2.95	-1.68	-2.89	-8.30
E <sub>es</sub>	-16.78	-13.79	-9.75	-11.26	-8.35	-4.76	-45.2
E <sub>exch</sub>	16.5	20.45	15.78	14.89	11.55	5.98	140.21
E <sub>ind</sub>	-21.3	-20.93	-14.42	-12.56	-7.87	-4.06	-111.32
E <sub>disp</sub>	-0.18	-0.34	-0.95	-3.08	-3.65	-2.65	-13.10
$\pi$ =benzene							
E <sub>int</sub>	-34.13	-23.62	-20.04	-20.55	-18	-13.45	-42.6
E <sub>corr</sub>	2.23	0.87	-2.0	-2.8	-4.7	-4.8	-11
E <sub>es</sub>	-17.78	-17.5	-14.54	-14.23	-11.1	-8.0	-41.2
E <sub>exch</sub>	15.32	19.3	16.22	15.1	15.0	11.0	97.2
E <sub>ind</sub>	-33.4	-25.67	-17.2	-14.12	-11.3	-6.0	-71.4
E <sub>disp</sub>	-0.5	-0.62	-2.52	-4.5	-5.9	-5.65	-16.2
$\pi$ =Pyrrole							
E <sub>int</sub>	-38.06	-26.2	-21	-23.29	-20.56	-14.98	-50.85
E <sub>corr</sub>	1.43	0.7	-1.5	-3.0	-4.86	-4.78	-10.0
E <sub>es</sub>	-24.0	-22.0	-19.0	-19.0	-18.0	-11.0	-53.0
E <sub>exch</sub>	17.31	21.4	21.3	19.21	22.3	12.9	125.25
E <sub>ind</sub>	-32.3	-25.7	-19.0	-16.0	-14.0	-6.0	-99.2
E <sub>disp</sub>	-0.5	-0.6	-2.8	-4.5	-6.0	-6.1	-13.9

## II. RESULTS AND DISCUSSION

Here various cations with the  $\pi$  system such as Li<sup>+</sup>,Na<sup>+</sup>,K<sup>+</sup>,NH<sub>4</sub><sup>+</sup>,C(NH<sub>2</sub>)<sub>3</sub><sup>+</sup>,N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup>,Ag<sup>+</sup> with the  $\pi$  system such as Ethene,benzene and Pyrrole are discussed[11].The values of the interaction energy,interaction enthalpy and intermolecular separation obtained at MP2 level of theory using 6-31+G(d,p) and aug-cc-p VDZ basis sets are listed in the Table 1. Local minimum structures are obtained for all the complexes.  $\Delta E_e^N$  and  $\Delta E_e^B$  are the binding energies without and with BSSE correction.

$\Delta E_0$  is the ZPVE-corrected  $\Delta E_e^B$ .  $\Delta H_{298}$  is the enthalpy at 298.15K.The electron correlation energy  $\Delta E_{corr}$  is the value of the  $E_e^{MP2}$  subtracted by  $E_e^{HF}$  at the MP2 optimized geometry.As the size of the cation increases, the distance R between the  $\pi$  system and the cation increases[12,13].So Lithium cation binds more than NH<sub>4</sub><sup>+</sup>, C(NH<sub>2</sub>)<sub>3</sub><sup>+</sup>,N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> cations.It is observed that Binding energy decreases as the size of the cation increases.The binding energy with bsse correction is more than the binding energy without bsse correction.When the binding energies  $-\Delta E$  of the cations are plotted against the  $\pi$  system using 6-31+G(d,p), it is observed that curved lines are obtained.It is noticed that Pyrrole complexes have highest binding energies for all cations.The interaction energies decreases as the size of the cation increases.Binding energy curve for K<sup>+</sup> passes along with NH<sub>4</sub><sup>+</sup>, BenzeneK<sup>+</sup> and BenzeneNH<sub>4</sub><sup>+</sup> have similar interaction energies. Ethene cations have lowest binding energies, it binds weakly with the cations.Pyrrole cation complexes binds strongly as shown in the curve.Interaction energies are also calculated using aug-cc-pVDZ basis set, where the binding energies as the size of the cation increases.  $\Delta E_0$  is also decreasing as the size of cation increasing. Similar plots are obtained when  $\Delta E_0$  is plotted against the  $\pi$  system.  $\Delta H_{298}$  is decreasing as the size of the cations increases.  $\Delta E_{corr}$  is the electron correlation energy is calculated in the table. Among the different metallic and organic cations,Lithium



cation shows the highest binding and enthalpy value, which binds more strongly. For the smaller metallic cations, the calculated enthalpies  $\Delta H_{298}$  are in good agreement with the experimental values. The calculated enthalpies  $\Delta H_{298}$  of Ethene..Na + and BenzeneNa + are  $-13.4$  and  $-21.9$  kcal/mol respectively. The corresponding experimental enthalpies are  $-10.7 \pm 1.0$  and  $-21.5 \pm 1.0$  kcal/mol [14,15].

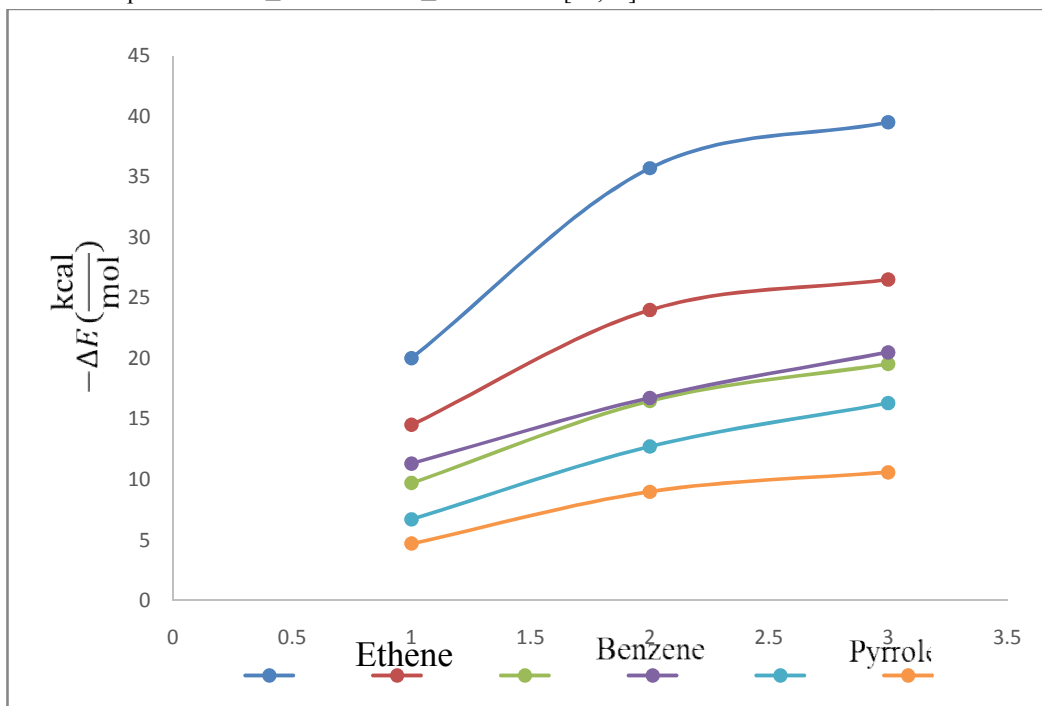


Figure 1 . A plot of Binding energies against  $\pi$  system evaluated at the MP2/6-31+G(d,p) level



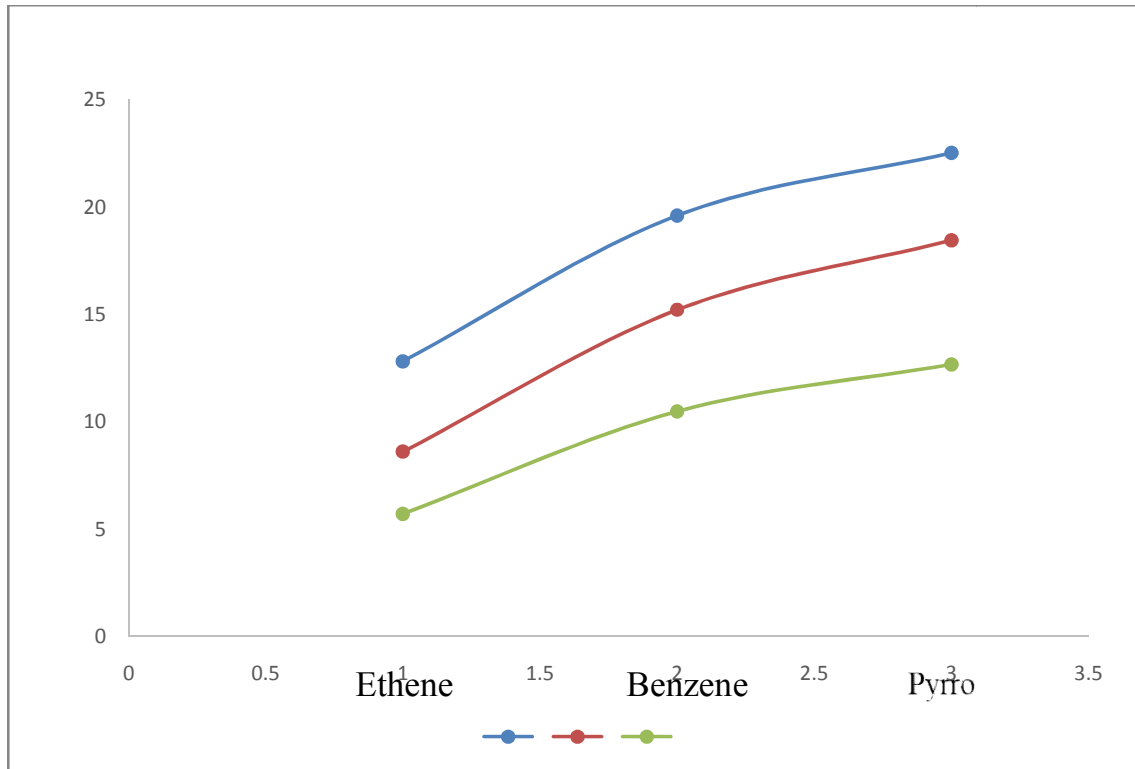
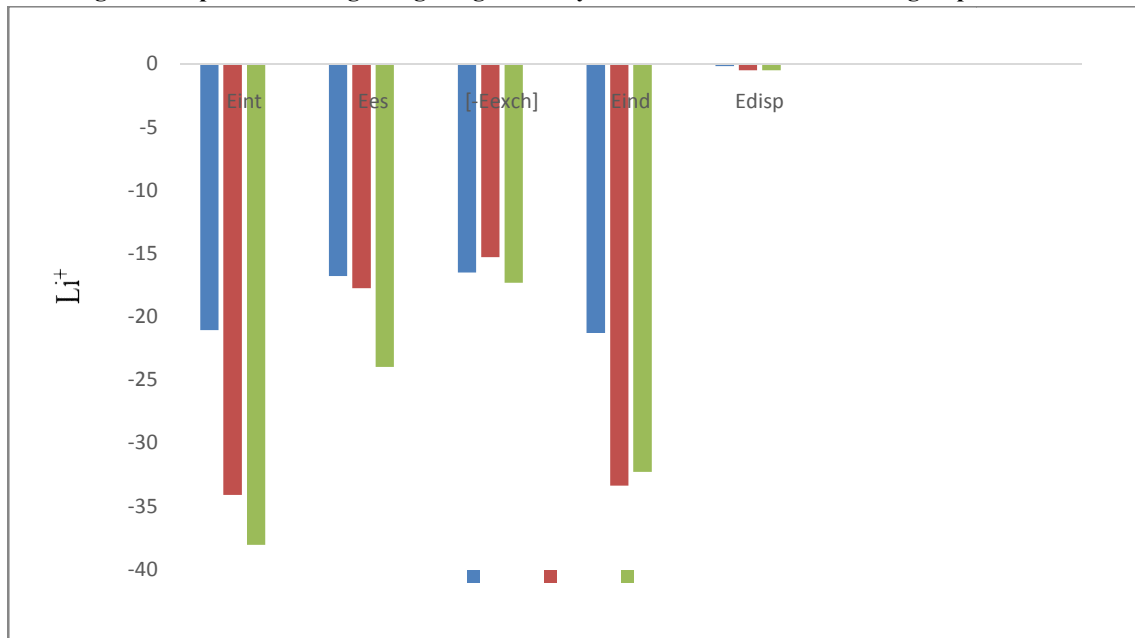
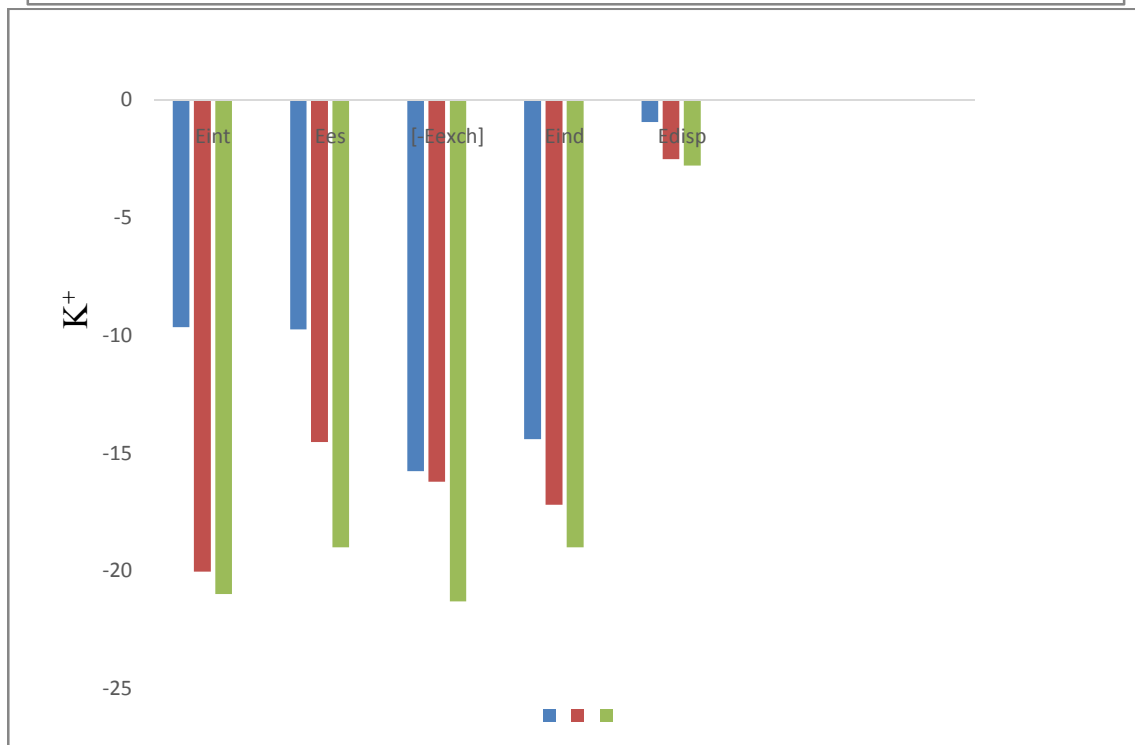
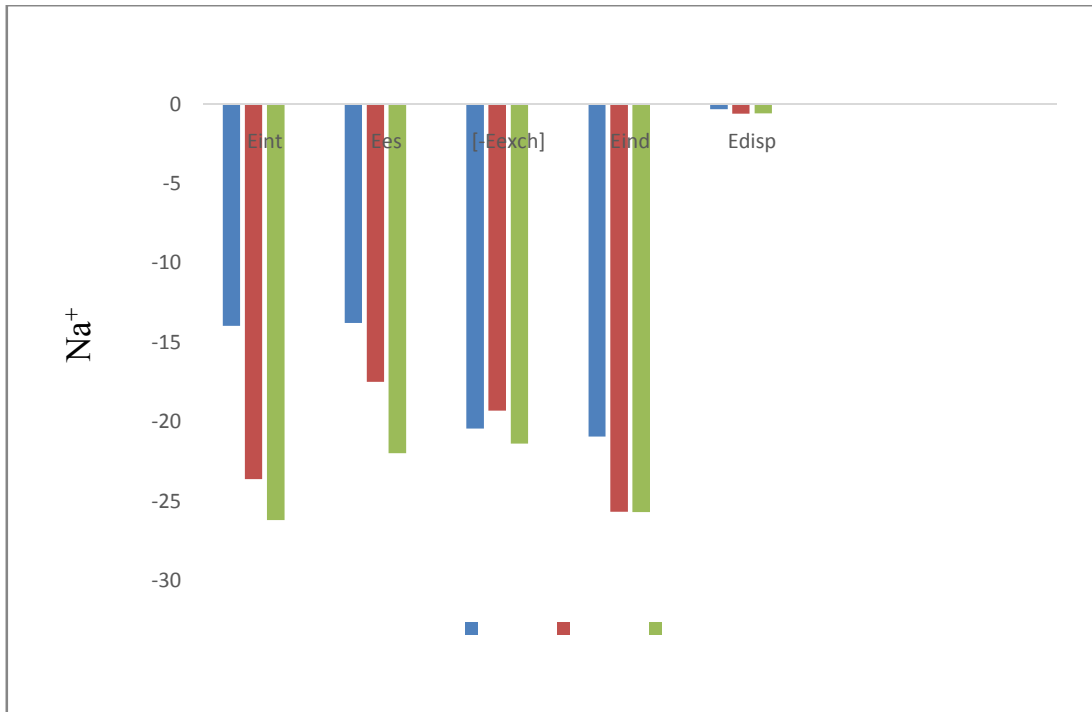
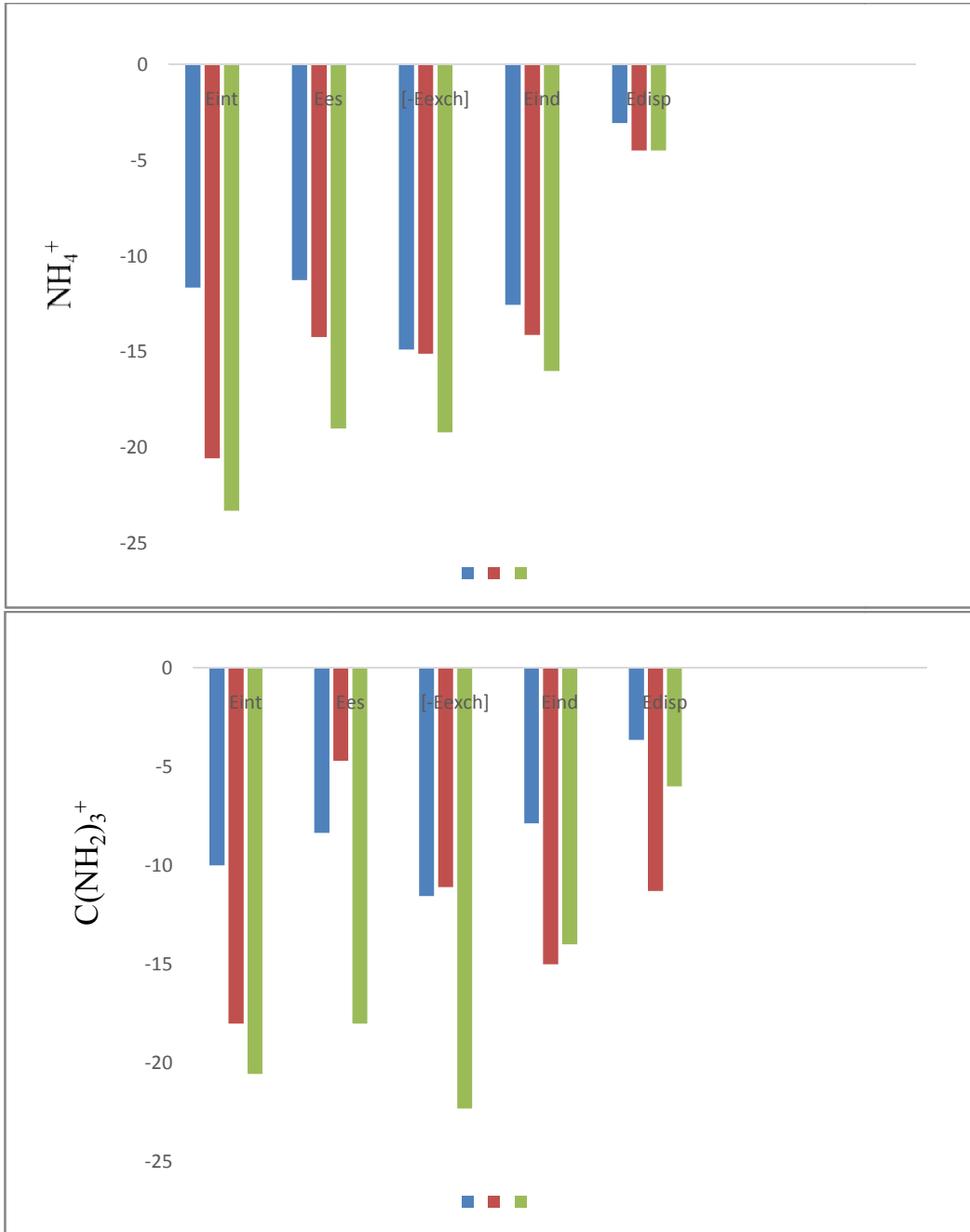
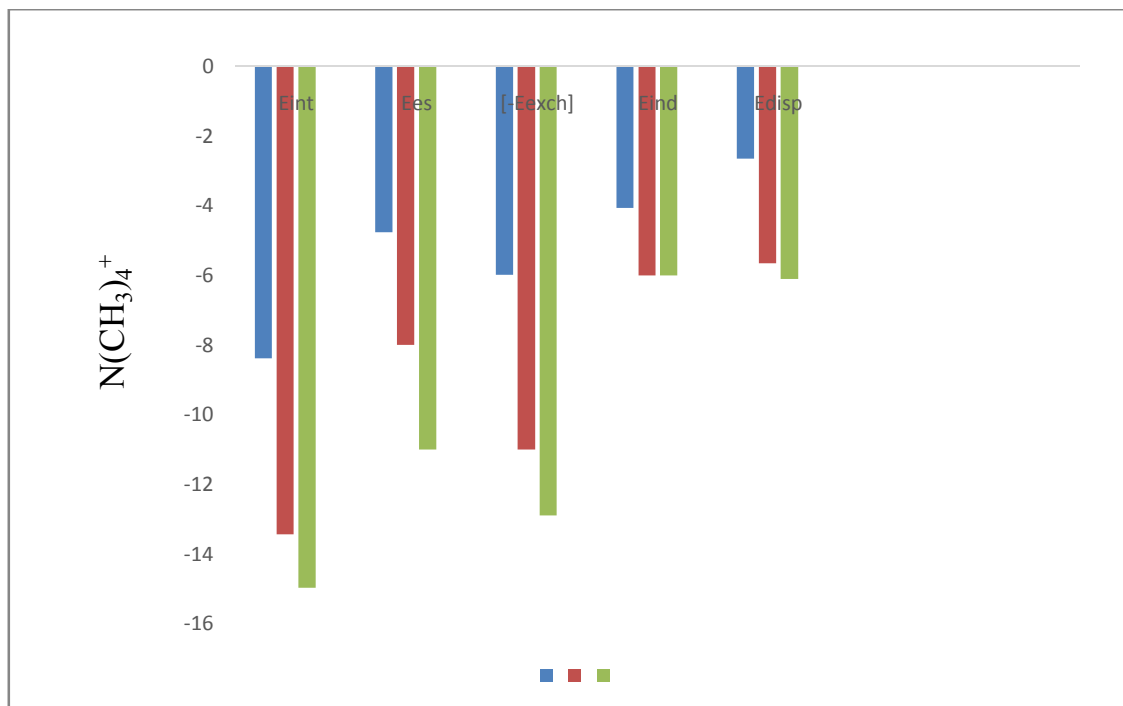


Figure 2. A plot of Binding energies against  $\pi$  system evaluated at the MP2/aug-cc pVDZ level









**Figure 3. Comparison of the interaction energy components evaluated using the 6-31+G(d,p) basis set for both the alkali -metal cation and organic-cation complexes of these  $\pi$  systems**

When the interaction energy components are plotted against different energy values, column graph is obtained.  $E_{int}$  is the total energy and is defined as the sum of  $E_{es} + E_{exch} + E_{ind} + E_{disp}$  where  $e_s$  is the electrostatic energy,  $exch$  is the exchange energy,  $ind$  is the induction energy and  $disp$  is the dispersion energy. From the column graphs obtained,  $E_{int}$  is higher for the  $\pi$  system Pyrrole and it is inferred that Lithium cation is more stable. PyrroleLithium cation complex is more stable because the binding energy value is highly negative.  $E_{corr}$  is the sum of all energy components evaluated at the correlated level. The electrostatic energy component  $E_{es}$  is more for Pyrrole and the metallic cation Lithium is more stable.  $E_{es}$  is less for  $N(CH_3)_4^+$  cation and least binding for Ethene $N(CH_3)_4^+$  complex. The total energy is also less for  $N(CH_3)_4^+$  Ethene complex. The exchange energy component  $E_{exch}$  taken as  $[-E_{exch}]$  is more for PyrroleLithium complex due to the lone pair of electrons on

Nitrogen[16]. The total Interaction energy  $E_{int}$  is due to larger basis set and correlation contribution  $E_{corr}$ . Another reason for increased correlation contribution is due to increase in dispersion energy  $E_{disp}$ . The use of larger basis set also results in an increase in induction  $E_{ind}$  and exchange  $E_{exch}$  energies. The major attractive contribution to total interaction energy in alkali-metal complexes results from electrostatic  $E_{els}$  and induction  $E_{ind}$  energies. The magnitude of induction energy is nearly double that of electrostatic energies. This induction energy is due to interaction between highest occupied molecular orbital of  $\pi$  system and empty s orbital of metal cation. The pyrrole complexes exhibit larger exchange energies and larger induction energy. The induction energy component also decreases as the size of the cation increases. The induction energy increase in  $K^+$  complex of pyrrole is nearly 16% higher than that of  $K^+$  complex of benzene. While the repulsive exchange energies are relatively smaller, the dispersion show large increases. When we compare the pyrrole complexes of  $Li^+$  and  $N(CH_3)_4^+$  shows that the dispersion energies of the latter are nearly 12 times larger than that of the former. In organic cation complexes, the magnitude of induction energies is more than that of dispersion energies[17,18]. The reason where the magnification of induction energies upon inclusion of electron correlation is that there is depletion of electron density from the centers of the bonds and a concurrent increase in the shells around the atomic nuclei. As a result, closer approach of cation to the  $\pi$  system is formed. This results in an



increased MO interaction and the induction energy increases. Dispersion energy increases as the size of cation increases. Organic cation  $N(CH_3)_4^+$  has the highest dispersion energy among these complexes. Pyrrole  $N(CH_3)_4^+$  Complex has the highest dispersion energy-5.74kcal/mol where as the lowest dispersion energy-0.16kcal/mol is for Ethene  $Li^+$  complex. Dispersion component adds little energy to the cation  $\pi$  interaction about 2-3kcal/mol. Among the different energy components, dispersion component has the least energy values and is negative.

**Table 3. Charge Transfer from the  $\pi$  systems to the cation Evaluated at the MP2/6-31+G(d,p) level**

	NBO			APT		
	Et	Bz	Py	Et	Bz	Py
$Li^+$	0.04	0.05	0.05	0.18	0.46	0.4
$Na^+$	0.03	0.03	0.03	0.2	0.4	0.19
$K^+$	0.02	0.02	0.02	0.07	0.15	0.3
$NH_4^+$	0.07	0.05	0.07	0.06	0.14	0.2
$C(NH_2)_3^+$	0.04	0.05	0.07	0.05	0.08	0.08
$N(CH_3)_4^+$	0.02	0.03	0.04	0.02	0.04	0.04
$Ag^+$	0.09	0.05	0.1	0.37	0.36	0.29

NBO and APT charges are calculated. The different  $\pi$  systems are Ethene, benzene and Pyrrole. Natural Bond Orbital Analysis and Atomic Polar Tensor are used to calculate the different charge from  $\pi$  system to metallic and organic cations.

#### Summary

Total Binding energies are calculated for various cations with different  $\pi$  systems. Interaction energies with and without BSSE correction,  $-\Delta E_0$ ,  $\Delta H_{298}$ ,  $\Delta E_{corr}$  are discussed. Of these negative value energies, Lithium cation complexes with Pyrrole are most stable and high binding energies, where as Ethene complexes are least stable. Ethene  $N(CH_3)_4^+$  is least stable. Pyrrole Lithium cation binds strongly. Among the different cations Lithium cation is most suitable for binding. Curved lines are obtained on plotting  $\pi$  system against Binding energies. Column graphs are obtained on plotting energy components against energies. Interaction energy components of all the monocation  $\pi$  complexes are found out. Total interaction energy is higher for Lithium complexes. This study has many applications in molecular structures,

solid-state Graphene battery, and in organic synthesis etc.

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