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Cation−π Interactions: A Theoretical Investigation of the Interaction of Metallic and Organic Cations with Alkenes, Arenes, and Heteroarenes

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The nature of the cation−π interaction has been examined by carrying out high level ab initio calculations of both metallic (Li^+,Na^+,K^+, and Ag^+) and organic (NH_4^+, $C(NH_2)_3^+$, and $N(CH_3)_4^+$) cations with different classes of π systems, viz. alkenes (ethene), arenes (benzene), and heteroarenes (pyrrole). The calculations, which include a rigorous decomposition of the interaction energies, indicate that the interaction of these π systems with the metal cations is characterized by contributions from both electrostatic and induction energies, with the contribution of the latter being dominant. Though the contributions of dispersion energies are negligible in the cation−π complexes involving Li^+ and Na^+, they assume significant proportions in the complexes involving K^+ and Ag^+. In the π complexes of the organic cations, the repulsive exchange contributions are much larger than the attractive electrostatic contributions in the π complexes of organic cations, and thus, the contributions of both induction and dispersion energies are important. While inclusion of electron correlation is essential in obtaining accurate estimates of the dispersion energy, it also magnifies the contribution of the induction energies in the π complexes of the organic cations. This results in significant consequences in the evaluation of geometries and energies of these cation−π complexes. The major difference between the cation−π and cation−H_2O complexes stems from the differences in the relative contributions of electrostatic and induction energies, a foreknowledge of which is vital in the design of ion-selective ionophores and receptors. The blue shift in the highly IR active out-of-plane CH bending mode of the π systems in these complexes is representative of the strength of the cation−π interaction.

1. Introduction

Much interest has been generated during the recent past in the molecular level design of functional materials[1−6] because of the intense demand for precise functional devices of nanoscale or sub-nanoscale dimensions.[2,7−10] Noncovalent intermolecular interactions play an important role in this context, because they are responsible for the structures and properties exhibited by these functional materials. Much of the successes in the recent design of interesting molecules and energetically favorable functional materials have indeed benefited from a detailed understanding of the fundamental aspects of the underlying noncovalent intermolecular interactions.[11−16]

Among the plethora of noncovalent intermolecular interactions, the cation−π interactions have been at the forefront of a number of experimental and theoretical investigations,[17−20] owing to their importance in diverse fields of chemistry and biology.[21−59] While the strength of the cation−π interaction is generally greater than that of other interactions involving π systems (π−π, π−hydrogen bond),[17,18] its magnitude is extremely dependent on the nature of π system and cation involved in the interaction, as has been noted in several recent investigations.[60−67] In this context, a number of calculations have been carried out on several cation−π complexes.[60−79] However, the focus of most of these investigations has been the evaluation of optimal geometries or interaction energies of these complexes. While attempts have been made in some of these investigations to rationalize the large variation in the strength of these interactions,[60,64,67,76−78] little effort has been expended in understanding the origin of these interaction energies using rigorous quantum chemical methodologies. Furthermore, not much is known on how the origin of these interactions compare to the more well-understood hydrogen-bonding and ionic interactions.[18] We believe such a study would help obtain a detailed understanding of the interplay of competing noncovalent interactions and many-body effects prevailing in chemical and biological processes.[20,26,31,33,35,36,79] Since water is intimately associated with virtually all biochemical process, the interplay between cation−water, cation−π, and water−π interactions underscores the importance of understanding each constituent interaction.[20] It would also aid the design of ionophores, receptors, and novel functional materials, such as metallic nanostructures.[11−16]

Early studies of the interaction of alkali-metal cations with benzene indicate that purely electrostatic considerations can explain the observed trends of the interaction energies.[17,23,60] However, the problem associated with this approach is particularly accentuated, when one compares the binding of these cations to different π systems (olefinic, aromatic, and heteroaro-

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matic). Thus the most recent experimental estimates of the enthalpies of binding (ΔH_0) of Na^+ to ethene and benzene are -10.7 ± 1.0 and -21.5 ± 1.0 kcal/mol, respectively.[52] One might have the expectation that the enthalpy of binding of Na^+ to benzene to be three times than that to ethene since benzene has three times the number of π electrons although geometrical considerations make this quantitative relationship suspect. However, the general trend of increased binding is present. A more interesting problem arises when one compares the interaction energy of the benzene−Na^+ and the pyrrole−Na^+ complexes. Though both of them have equal number of π electrons, the cation−π interaction in the latter is stronger than in the former.

Even when comparisons are made across the interaction of different cations with a single π system, it is still difficult to come up with an a priori estimate of the interaction energy. This is because the magnitude of individual forces responsible for the interaction of these cations with different π systems is very much dependent on the nature of the cation and the π system. Thus, for example, the calculated interaction energies indicate that the binding of NH_4^+ to these π systems is much stronger than that of K^+.[13,61,64] This is very interesting because both K^+ and NH_4^+ have nearly the same ionic radii and have a single positive charge. Thus, the magnitude of the dispersion energies seems to play an important role in distinguishing between these two types of interaction, as reflected by the polarizability of the two ions: $K^+ = 5.52$,[80] while $NH_4^+ = 8.83$[81] (in au). It would therefore be useful to obtain a quantitative estimate of the dispersion energies. The importance of such an exercise has been highlighted in a recent experimental report.[82] Furthermore, it would also aid dispel some of the misconceptions regarding the cation−π interactions involving organic cations, with some recent reports attributing to emerge from a combination of cation−π and dispersion energies.[77]

As was mentioned earlier, several attempts have been made in the past to obtain the magnitudes of some of these individual energy components.[64,67,71,76−78] However, to the best of our knowledge, no attempt has been made in any of these studies to carry out comparisons across the interaction of different π systems with both metallic and organic cations.[18] In a number of studies carried out in our group in the recent past on different π-system-containing complexes,[83−86] we had shown the utility of using the symmetry adapted perturbation theory (SAPT) methodology[87−89] in obtaining a detailed picture of the various forces responsible for the interaction. A compelling justification for the use of SAPT is that electron correlation is explicitly taken into account. Consequently, reliable estimates of the dispersion and repulsive energies can be obtained.[87−89]

In view of our continuing interest in interactions involving π systems,[12,83−86,90−94] the present study presents a detailed investigation of the cation−π interaction. In addition to investigating the interaction of three different classes of π systems (olefinic, aromatic, and heteroaromatic), represented by ethene (Et), benzene (Bz), and pyrrole (Py), with several alkali-metal cations (Li^+, Na^+, and K^+), we have also investigated their interaction with the organic (NH_4^+,$C(NH_2)_3^+$, and $N(CH_3)_4^+$) cations. Since recent studies in our group as well as several recent reports have highlighted the importance of cation−π interactions involving Ag^+ cations,[11,95−100] we thought it would be useful to include the interaction of Ag^+ with the aforementioned π systems. Apart from evaluating the equilibrium geometries, interaction energies, and vibrational frequencies, the major focus of the present work is on the evaluation of the magnitude of the individual energy components. Furthermore, we also discuss the implications of these results in understanding the phenomena of molecular recognition, material design, and development of new force fields. Toward this end, we have compared the interaction energy components of these cation−π complexes with the more widely investigated cation−H_2O complexes.

2. Methods

All the calculations reported in this study were carried out using the supermolecular (SM) variational and perturbational (SAPT) methods.[87−89,101] Even though the SM method is conceptually and computationally simple, it does not provide a clear picture of the interaction forces responsible for the interaction. On the other hand, SAPT enables one to obtain a physical picture of the interactions prevailing between the various complex monomers. This is because of the fact that, in the SM method, the interaction energy is evaluated as the difference of the energy of the complex and the energy of the isolated monomers. However, in the SAPT method, the interaction energy is obtained as a sum of the individual *electrostatic, exchange, dispersion, and induction* energies. We briefly describe some of the details of the calculations to aid the discussion of the results.

2.1. Supermolecular Calculations. All the SM calculations, which included geometry optimizations and evaluation of the vibrational frequencies, were carried out at the second-order Møller−Plesset (MP2) level of theory using the 6-31+G* and aug-cc-pVDZ basis sets. On the suggestions of one of the referees, we have also evaluated the interaction energies of some of the smallest complexes using the much larger aug-cc-pVTZ basis set. To examine the effects of the inclusion of higher levels of correlation, we have also carried out 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. Even though comparable basis sets were used for the metal cations, for the sake of brevity, calculations are distinguished by the kind of basis set used to represent C, N, and H.

Except for Ag^+, the 6-31+G* basis set was used for all the other metal cations investigated in this study. In calculations of the π−K^+ complexes carried out using the aug-cc-pVDZ basis set, we used the Feller miscellaneous CVDZ basis set to represent the K^+ cation. In this basis set, the (s,p) exponents of K^+ are obtained from Schafer et al.,[102] and the core/valence exponents are obtained from Feller et al.[103] Given the importance of the inclusion of relativistic effects on inner shells in calculations involving Ag^+, we have used the small-core energy-consistent relativistic pseudopotentials developed by Andrae et al.,[104] plus an f function ($\zeta_f = 1.7$). In this basis set, the 28 core electrons ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$) are replaced by effective core potentials (ECPs) and the 18 remaining electrons ($4s^2 4p^6 4d^{10}$) are considered to be valence electrons. While the use of all-electron basis sets would have avoided the approximations inherent in effective core potentials, the substantial relativistic corrections in silver preclude their use. An alternative approach of using Dirac−Fock relativistic calculations is computationally too expensive for these large systems. It has been shown in earlier calculations on small Ag clusters and the interaction of Ag^+ with water and dimethyl ether that the above basis set yields the excitation and interaction energies that are close to those obtained experimentally.[105,106]

Basis set superposition error (BSSE) corrections for all these complexes were carried out using the counterpoise (CP) method of Boys and Bernardi.[107] Compared to other complexes involv-

TABLE 1: Total Binding Energies and Selected Geometries Obtained at the MP2 Level Using the 6-31+G* and aug-cc-pVDZ Basis Sets for Various Monocation−π Complexes[a]

	6-31+G*							aug-cc-pVDZ				
	Li^+	Na^+	K^+	NH_4^+	$C(NH_2)_3^+$	$N(CH_3)_4^+$	$Ag^{+\,b}$	K^+	NH_4^+	$C(NH_2)_3^+$	$N(CH_3)_4^+$	$Ag^{+\,b}$
						π = Ethene						
$R_\perp$	2.30	2.67	3.20	3.24	3.99	4.25	2.28	3.14	3.16	3.96	4.12	2.18
$-\Delta E_e^N$	21.63	14.53	8.37	10.99	7.85	5.12	35.24	9.25	12.74	9.80	6.92	46.99
$-\Delta E_e^B$	19.62	12.84	7.49	9.61	5.97	3.64	31.09	8.41	11.02	7.60	4.65	40.29
$-\Delta E_0$	18.46	12.04	6.84	8.33	5.33	2.93	29.58	7.82	9.86	6.81	3.96	38.86
$-H_{298}$	18.99	12.36	7.05	8.41	4.73	2.30	30.31	8.02	10.00	6.35	3.43	39.66
$-\Delta E_{corr}$	1.03	1.07	1.09	2.46	3.07	3.31	16.22	1.43	4.07	5.21	5.58	30.13
						π = Benzene						
$R_\perp$	1.91	2.40	2.90	2.99	3.98	4.25	2.21	2.83	2.88	3.88	4.12	2.06
$-\Delta E_e^N$	39.53	26.78	17.83	18.66	15.53	11.40	41.86	19.21	22.45	19.40	15.11	58.16
$-\Delta E_e^B$	34.60	22.14	15.47	15.74	11.71	7.99	32.01	17.01	18.60	14.21	9.48	42.38
$-\Delta E_0$	31.95	20.23	14.59	14.17	10.81	6.90	30.65	16.55	17.39	13.31[c]	8.39[c]	41.68
$-\Delta H_{298}$	32.91	20.79	14.79	14.12	10.22	6.34	30.90	16.67	18.75	12.72[c]	7.83[c]	41.91
$-\Delta E_{corr}$	3.02	3.53	3.27	4.98	7.33	7.58	22.72	3.55	8.21	11.50	12.03	42.63
						π = Pyrrole						
$R_\perp$	1.95	2.46	2.88	3.00	3.96	4.19	2.26	2.82	2.91	3.88	4.09	2.18
$-\Delta E_e^N$	42.34	28.85	20.75	21.95	18.84	13.17	48.40	21.28	24.88	21.96	16.53	61.47
$-\Delta E_e^B$	38.35	25.23	18.23	19.35	15.27	9.87	42.10	18.91	21.52	17.45	11.47	51.32
$-\Delta E_0$	36.30	23.87	17.36	17.96	14.38	8.75	40.75	18.16	20.39	16.56[c]	10.35[c]	50.38
$-\Delta H_{298}$	37.16	24.33	17.66	18.04	13.91	8.29	41.16	18.44	20.52	16.09[c]	9.89[c]	50.74
$-\Delta E_{corr}$	2.57	2.84	3.63	5.07	7.22	7.48	20.20	4.31	8.20	11.33	11.77	35.20

[a] All energies are in kcal/mol and distances are in angstroms. $R_\perp$ represents the perpendicular distance from the center-of-mass of the π system to the cation (the cation position in the organic cations corresponds to the central nitrogen or carbon atom). "$-\Delta E_e^N$" and "$-\Delta E_e^B$" represent the binding energies without and with BSSE correction, respectively. ΔE_0 is the ZPVE-corrected ΔE_e^B. The frequencies for ZPVE correction were evaluated at both the MP2/6-31+G* and MP2/aug-cc-pVDZ levels. ΔH_{298} is the enthalpy at 298.15 K and 1.0 atm. The electron correlation energy ΔE_{corr} is the value of the $E_e^{(MP2)}$ subtracted by $E_e^{(HF)}$ at the MP2 optimized geometry. [b] For Ag, we used a Stuttgart RECP potential augmented with a single set of f-type polarization function ($\zeta_f = 1.7$) (ref 104). [c] These values have been obtained using the ZPVE and thermal corrections evaluated at the MP2/6-31+G* level.

ing π systems, the BSSE corrections in these systems are small.[18] The zero point vibrational energy (ZPVE) corrections were computed from the frequencies evaluated at the MP2/6-31+G* and MP2/aug-cc-pVDZ levels of theory.

The natural bond orbital (NBO) analysis method has been employed to evaluate the atomic charges in all the complexes,[108] because unlike most other charge partitioning schemes, it is unaffected by the presence of diffuse functions in the basis set. The NBO charges reported in this study have been calculated using the densities obtained at the MP2 level. Since recent reports seem to indicate that the charges evaluated using the atomic polar tensors (APT) are more representative of the electron density distributions,[109,110] we have calculated the APT charges from the calculated wave functions of the optimized geometries of these complexes. As in case of the NBO evaluated charges, the APT evaluated charges are much less sensitive to basis set variations.[110]

The SM calculations were carried out using the GAUSSIAN suite of programs.[111]

2.2. Symmetry Adapted Perturbation Theory Calculations. In this study, the SAPT calculations were carried out using the optimized geometries (obtained from SM calculations) of all the complexes. The SAPT interaction energy accurate to third order $E_{int}^{(SAPT)}$ is given by eq 1

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

where $E_{elst}^{(1)}$ is the electrostatic energy of the monomers with the unperturbed electron distribution, $E_{exch}^{(1)}$ is their first-order valence repulsion energy due to the Pauli exclusion principle, $E_{ind}^{(2)}$ stands for the second-order energy gain resulting 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 δ_{int}^{HF} includes the higher order induction and exchange corrections. Since BSSE effects are explicitly included when evaluating the SAPT interaction energies, a comparison of the BSSE corrected supermolecular interaction energy ΔE_e^B and the SAPT interaction energy $E_{int}^{(SAPT)}$ is appropriate.

The SAPT interaction energy can also be represented 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 (HF) level and $E_{int}^{(corr)}$ is the sum of all the energy components evaluated at the correlated level. Given the size of the systems investigated and the level of theory employed in this study to evaluate the various energy components, it was not feasible to evaluate the computationally demanding higher order components ($n \leq 3$). Hence, one should expect a slight deviation of the total interaction energies evaluated using SAPT and SM calculations. This, however, does not affect our conclusions based on the magnitude of the individual interaction energy components, as was shown in recent papers.[83−86] A detailed description of SAPT and some of its applications can be found in some recent references.[87−89,112−114]

3. Results and Discussion

The values of the interaction energy (ΔE_e^N, ΔE_e^B, and ΔE_o), interaction enthalpy (ΔH_{298}), and intermolecular separation ($R_\perp$) obtained at various levels of theory for the optimized geometries of all the π−cation complexes considered in this study are listed in Table 1. The vibrational frequencies, which were calculated

TABLE 2: Total Binding Energies Evaluated at the MP2/aug-cc-pVTZ and CCSD(T)/Aug-cc-pVDZ//MP2/aug-cc-PVDZ Levels of Theory for the Ethene Complexes of the Organic Cations[a]

	MP2/aug-cc-pVTZ			CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ		
	Eth−NH_4^+	Eth−$C(NH_2)_3^+$	Eth−$N(CH_3)_4^+$	Eth−NH_4^+	Eth−$C(NH_2)_3^+$	Eth−$N(CH_3)_4^+$
$-\Delta E_e^N$	12.92	10.67	6.97	12.21	9.37	6.57
$-\Delta E_e^B$	11.51	8.06	4.92	10.42	7.09	4.27
$-\Delta E_0$	10.36	7.27	4.22	9.27	6.31	3.58
$-\Delta H_{298}$	10.49	6.81	3.69	9.40	5.85	3.04
$-\Delta E_{corr}$	4.82	6.99	6.71	3.53	4.77	5.23

[a] All energies are in kcal/mol. See Figure 1 for description of the various complex forms. See footnote of Table 1 for description of various terms. The ZPVE corrections have been evaluated using the frequencies obtained at the MP2/aug-cc-pVDZ level of theory.

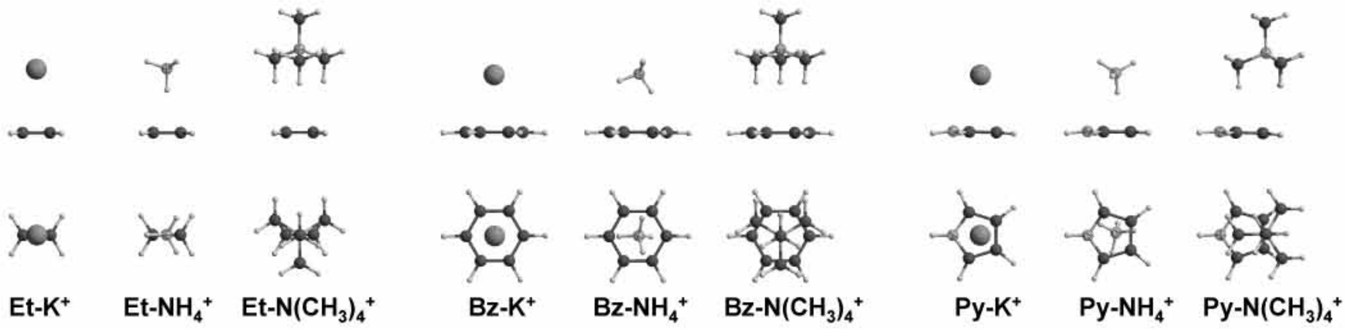

Figure 1. MP2/aug-cc-pVDZ optimized structures of the K^+, NH_4^+, and $N(CH_3)_4^+$ complexes of all the π systems (ethene, Et; benzene, Bz; and pyrrole, Py) investigated in this study. The top layer depicts the side view, and the bottom layer, the top view of the complexes.

for all the optimized structures, indicated that these structures were genuine minima. The data given in Table 1 indicate that the interaction energies of these cationic complexes increase with a decrease in the ionic radii for similarly charged cations. The interactions involving Ag^+ are, however, exceptions to these trends. For the smaller metal cations, the calculated enthalpies ΔH_{298} are in good agreement with the available experimental values. Thus, for instance, the calculated enthalpies ΔH_{298} of Et−Na^+ and Bz−Na^+ are −12.36 and −20.79 kcal/mol, respectively. The corresponding experimental enthalpies are −10.7 ± 1.0 and −21.5 ± 1.0 kcal/mol.[46−52] Similar observations were made in earlier studies by Feller et al.[63] The results obtained at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ levels of theory for the ethene complexes of the organic cations (Table 2) indicate a small increase in the interaction energies with the use of the much larger aug-cc-pVTZ basis set or the inclusion of higher correlation effects. However, this increase is more pronounced with the use of the larger basis set. While we elaborate on the origin of this increase in our subsequent discussion, it is interesting to note that the trends in the magnitudes of the interaction energies evaluated using different basis sets are consistent with the contributions of the dispersion energies. This is important in the context of the present study because the emphasis is more on the relative differences of the various interaction energy terms than on the absolute numbers. Furthermore, it can also be noted that the BSSE and ZPVE corrected interaction energies ΔE_o evaluated at the CCSD(T)/aug-cc-pVDZ level are close to the values obtained at the MP2/6-31+G* level.

The MP2/aug-cc-pVDZ optimized geometries of the π−K^+, π−NH_4^+, and π−$N(CH_3)_4^+$complexes (Figure 1) indicate that the metal cation or the positive charge bearing atom of the organic cation lies on top of the double bond in the ethene complexes and on the center of the aromatic ring in the benzene complexes. However, the pyrrole complexes are very distinct from both the ethene and the benzene complexes with both the metal cation and the organic cation being displaced away from the center. Thus, in the Py−$N(CH_3)_4^+$ complex, the organic cation lies on top of the C−C bond opposite to the nitrogen. This is despite the fact that one would expect the cation to be more localized over the more negative nitrogen atom of pyrrole because of its greater electronegativity.[116] Despite this geometrical anomaly, it is of interest to note that the pyrrole complexes exhibit the largest interaction energies for all classes of cations (Table 1).[23] This is illustrated in more detail in Figure 2 wherein we have plotted the BSSE and ZPVE corrected interaction energies (ΔE_o) of all the systems. The numbers obtained for the corresponding dications of the alkali earth metals have also been plotted to provide an interesting comparison. Expectedly, their interactions with these π systems are much stronger than that of monocations of alkali metals. In Figure 2, one also notes that both the Bz−K^+ and Bz−NH_4^+ complexes possess nearly similar interaction energies,[13,117] but we subsequently show that the origin of this similarity is very different.

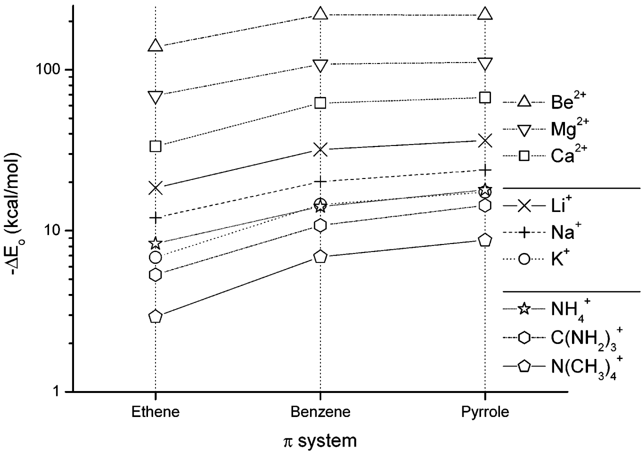

Figure 2. A logarithmic plot of the BSSE and ZPVE corrected interaction energies (ΔE_o) of the complexes evaluated at the MP2/6-31+G* level.

There are small changes in the geometries of the monomers upon complexation, and these changes are independent of the

TABLE 3: MP2 Equivalent Interaction Energy Components of All the Monocation−π Complexes Obtained Using the 6-31+G* Basis Set[a]

	Li^+	Na^+	K^+	NH_4^+	$C(NH_2)_3^+$	$N(CH_3)_4^+$	Ag^+
π = Ethene							
E_{int}[b]	−20.49	−13.50	−7.91	−10.15	−6.40	−3.83	−28.23
E_{corr}[c]	0.77	0.54	−0.21	−1.09	−1.69	−1.89	−7.30
E_{es}	−15.52	−12.79	−8.51	−10.16	−7.35	−4.29	−44.87
E_{exch}	15.30	19.45	14.61	13.80	10.55	5.95	139.17
E_{ind}	−20.11	−19.92	−13.15	−11.69	−6.99	−3.06	−110.44
E_{disp}	−0.16	−0.24	−0.85	−2.09	−2.61	−2.44	−12.10
π = Benzene							
E_{int}[b]	−35.80	−23.00	−16.19	−16.34	−11.77	−8.26	−29.93
E_{corr}[c]	1.23	0.76	−1.07	−2.57	−4.26	−4.45	−10.52
E_{es}	−17.59	−16.55	−13.53	−13.27	−10.98	−7.95	−40.88
E_{exch}	14.67	18.61	15.87	14.27	14.97	10.28	96.74
E_{ind}	−32.42	−24.47	−16.09	−13.20	−10.06	−5.11	−70.62
E_{disp}	−0.47	−0.59	−2.44	−4.13	−5.71	−5.48	−15.17
π = Pyrrole							
E_{int}[b]	−39.28	−26.14	−19.25	−20.41	−15.93	−10.50	−40.30
E_{corr}[c]	1.36	0.67	−1.21	−2.79	−4.16	−4.52	−9.66
E_{es}	−23.21	−21.71	−18.39	−18.69	−17.38	−10.96	−52.54
E_{exch}	16.28	20.80	20.23	18.18	21.10	12.05	124.20
E_{ind}	−31.86	−24.69	−18.58	−15.54	−13.77	−5.85	−98.60
E_{disp}	−0.49	−0.54	−2.51	−4.36	−5.88	−5.74	−13.37

[a] All energies are in kcal/mol. [b] $E_{\mathrm{int}} = E_{\mathrm{es}} + E_{\mathrm{exch}} + E_{\mathrm{ind}} + E_{\mathrm{disp}}$. [c] E_{corr} is the sum of all the energy components evaluated at the correlated level.

nature of the cation binding to the π system. Thus in the case of the benzene complexes, the elongation of the C−C bond length is maximal (0.012 Å) in the Ag^+ complex and minimal in its complex with $N(CH_3)_4^+$(0.002 Å). However, no discernible changes can be observed in the C−H bond lengths.

There is a broad consensus among the numerous studies, which have examined the interaction of these cations with these π systems that electrostatic and induction energies dominate the interaction energies.[17,67,71,74] However, little is known about the contribution of dispersion energies because of the difficulties in evaluating their magnitudes. Previously, a number of groups have tried to obtain a rough estimate of the magnitudes of the dispersion energy from the electron correlation energy ΔE_{corr} given in Table 1.[18,84,89] While such an approach is the only recourse in cases where the dispersion energy cannot be calculated, the problem in using the values of ΔE_{corr} is that the electron correlation energy contains contributions from numerous other terms, which are either attractive or repulsive.

Against this background, it is instructive to examine the trends exhibited by the various interaction energy components evaluated for these complexes. The interaction energy components obtained on the MP2/6-31+G* optimized geometries of the complexes using the 6-31+G* basis set are listed in Table 3. The correlation contribution $E_{\mathrm{int}}^{(\mathrm{corr})}$ to the total interaction energy, which is small (∼5%) for the alkali-metal cation−π complexes,[115] increases to as much as 50% for the π−$N(CH_3)_4^+$ complexes. Interestingly, the correlation contribution to the interaction energy of the Ag^+ complexes is quite substantial (∼30%). Apart from highlighting the importance of the inclusion of electron correlation in obtaining reliable interaction energies of the π complexes of the organic cations and Ag^+, the magnitude of the correlation contribution also gives an inkling of the role of electron correlation in influencing their equilibrium geometries.

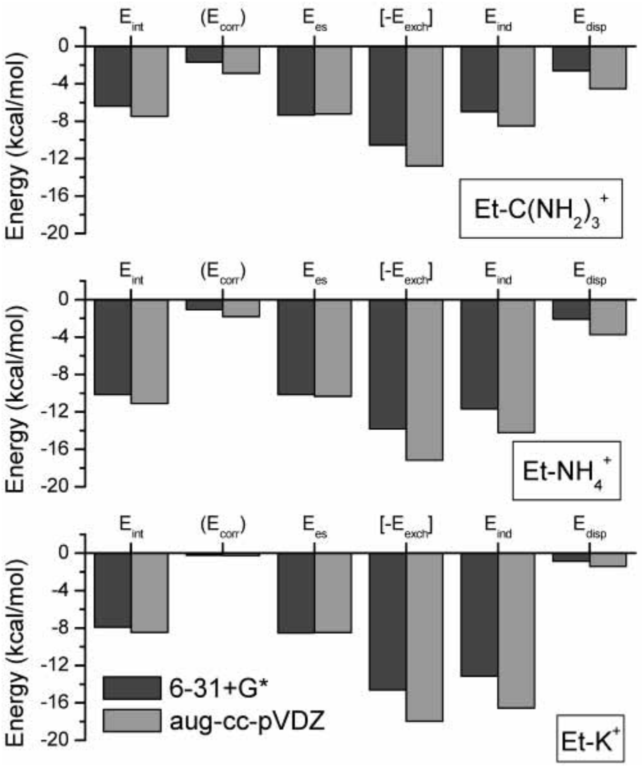

Figure 3. Comparison of the magnitude of the interaction energy components evaluated using the 6-31+G* and aug-cc-pVDZ basis sets, for the Et−K^+, Et−$N(CH_3)_4^+$, and Et−$C(NH_2)_3^+$ complexes. In the plot, E_{int} is the total interaction energy $E_{\mathrm{int}}^{(\mathrm{SAPT})}$, E_{corr} is the sum of all the interaction energy components evaluated at the correlated level $E_{\mathrm{int}}^{(\mathrm{corr})}$, E_{es} is the electrostatic energy E_{elst}, E_{ind} is the induction energy E_{ind}, E_{disp} is the dispersion energy (E_{disp}), and E_{exch} is the sum of the all the exchange components ($E_{\mathrm{exch}}^{(1)}$, $E_{\mathrm{exch-ind}}^{(2)}$, $E_{\mathrm{exch-disp}}^{(2)}$, and $\delta_{\mathrm{int}}^{(\mathrm{HF})}$).

Since we had stated earlier that the difference in interaction energies obtained using different basis sets is quite substantial, it is instructive to examine the magnitudes of the interaction energy components obtained using the 6-31+G* and aug-cc-pVDZ basis sets. Since it is practically impossible to carry out the energy decomposition using the larger basis set for all the complexes investigated in this study, we compare the results obtained for some of the ethene complexes in Figure 3. It can be seen that the increase in the total interaction energy $E_{\mathrm{int}}^{(\mathrm{SAPT})}$, which results from the use of the larger basis set, predominantly emerges from the increase in the correlation contribution $E_{\mathrm{int}}^{(\mathrm{corr})}$. In turn, the enhanced correlation contribution is due to

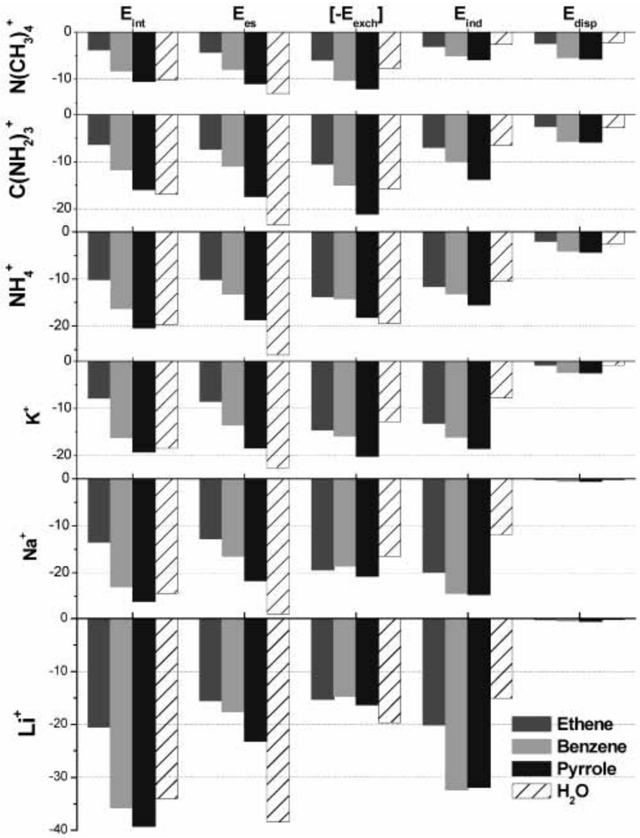

Figure 4. Comparison of the interaction energy components evaluated using the 6-31+G* basis set for both the alkali-metal cation and organic-cation complexes of these π systems. See caption of Figure 3 and the text for description of various interaction energy terms.

the increase in the dispersion energy E_{disp}. The use of the larger basis set also leads to an increase in the induction E_{ind} and exchange E_{exch} energies, which indicate that the induction and dispersion energy increases offset the increase in the exchange energy. Similar conclusions can be drawn on the relative contributions of various interaction energy components in the benzene and pyrrole complexes. With this information on the effect of basis sets, it is useful to examine in detail the magnitudes of the interaction energies listed in Table 3 and plotted in Figure 4. In Figure 4, the interaction energy components of the corresponding water complexes have also been plotted to highlight the similarities/differences in the binding of these cations to water and π systems.

The major attractive contributions to the total interaction energy in case of the alkali-metal complexes emerge from electrostatic E_{elst} and induction E_{ind} energies. In particular, the magnitude of the induction energies is nearly double that of the electrostatic energies. This predominance of the induction energies can be attributed to the interaction between the highest occupied molecular orbital (HOMO) of the π system and the empty *s* orbital of the metal cation. This MO interaction is in turn governed by the orbitals involved and the size of the cation, because a smaller sized cation can have a closer approach to π system due to a decrease of exchange repulsion at a given separation. Smaller intermolecular separation $R_{\perp}$ leads to a larger electrostatic stabilization and also facilitate an enhanced overlap of the constituting MO's and hence leads to larger induction energies. Though numerous authors have attributed this kind of MO interaction to be of the charge-transfer type, we feel that this interaction is more of the inductive type. One of the reasons for doing so is the fact that charge-transfer interactions cannot be distinguished from BSSE effects. It has been pointed out by Stone that when the charge-transfer energies are calculated rigorously, their magnitudes are very small and in some cases negligible.[118,119] Nevertheless in the course of our discussion on the charges, we show that the magnitude of the induction energies can be correlated to the charge transferred from the π system to the metal cation. Earlier attempts by Cubero et al. and Tsuzuki et al. to obtain empirical estimates of these induction energies have yielded numbers which are either much smaller than the electrostatic energies or much larger than both the electrostatic and total interaction energies.[67,71] The contribution of the dispersion energies, though negligible for both the Na^+ and Li^+ complexes, are substantial for the K^+ complexes.

The influence of the π system on the cation−π interaction, can be noted from the fact that the pyrrole complexes exhibit the largest electrostatic energies. The π electron density of pyrrole is much higher than that of either benzene or ethene because the nitrogen lone pair is a part of the delocalized π system of pyrrole.[116] The presence of the nitrogen atom in pyrrole, however, influences both the equilibrium geometries and the interaction energies exhibited by these pyrrole complexes. It can be seen that the magnitude of the induction energies in both the Li^+ and Na^+ complexes of pyrrole is nearly the same as that observed in the corresponding complexes of benzene. However, the induction energy increase in K^+ complex of pyrrole is nearly 16% higher than in the K^+ complex of benzene. The innate tendency of both the small-sized Li^+ and Na^+ cations is to maximize the electrostatic stabilization by a closer approach to the π system. However, the presence of the electronegative nitrogen atom prevents a closer approach of the cation to the π system, as can be noted by the magnitude of the exchange energies E_{exch} and the intermolecular separation $R_{\perp}$. The pyrrole complexes exhibit larger exchange energies and larger intermolecular separations as compared to the corresponding benzene complexes. This limits the extent of orbital overlap and consequently the magnitude of the induction energies are nearly similar in the Li^+ and Na^+ complexes of benzene and pyrrole. On the other hand, the larger size of the K^+ and NH_4^+ cations would prevent their closer approach to either benzene or pyrrole because of increased exchange−repulsion. As a result, both the benzene and pyrrole complexes exhibit nearly similar intermolecular separations indicating that the presence of the nitrogen atom has little effect. However, the enhanced π electron density of pyrrole results in increases in the magnitudes of both the induction and electrostatic energies.

The magnitudes of the electrostatic and induction energies in case of the organic-cation complexes of these π systems are much smaller than those observed in case of the π−alkali-metal cation complexes. While the repulsive exchange energies are relatively smaller, the dispersion energies exhibit large increases. Thus, a comparison of the pyrrole complexes of Li^+ and $N(CH_3)_4^+$ reveals that the dispersion energies of the latter are nearly 12 times larger than that of the former. However, the total interaction energy of the Py−Li^+ complex is only 4 times larger than the Py−$N(CH_3)_4^+$ complex. The relative magnitudes of the dispersion and induction energies in the organic-cation complexes raise the important issue of the role of electron correlation. It can be noted that in all the organic-cation complexes, the magnitude of the induction energies is much larger than that of the dispersion energies. Since by definition, induction energies are entirely obtained in calculations carried out at the HF level, it would be expected that HF calculations would yield accurate geometries and reliable interaction energies of these organic-cation complexes. However, it has been shown in studies in the past that HF calculations fail to yield both reliable geometries and interaction energies.[64−66] We therefore feel that in the presence of electron correlation, the $\pi-\sigma^*$ interaction (where π is the HOMO of the π system and σ^* is the LUMO of the organic cation), which is of the inductive type, is magnified.[64] Similar observations were made in our earlier studies on the interaction of the first-row hydrides with both ethene and benzene.[84] One of the reasons for the magnification of this induction energies upon inclusion of electron correlation is the fact that there is a depletion of electron density from the centers of the bonds and a concurrent increase in the shells around the atomic nuclei.[120] As a result, a much closer approach of the cation to the π system is facilitated. This results in an increased MO interaction and hence the larger induction energy. The increase in the electron density around the shells of the atomic nuclei and the closer approach of the cation to the π system results in the increased dispersion energy. More details on the role of the shifts in electron density on the magnitudes of the various interaction energy components can be found in our earlier work detailing the interaction of argon with various fluorine-substituted benzenes.[86] As in case of the interaction of these π systems with the alkali-metal cations, the electrostatic energies are largest in the case of the pyrrole containing complexes. However, unlike what is observed in the case of the alkali-metal cations, the induction energies are much larger in the case of the pyrrole containing complexes. Given the nearly similar intermolecular separations and the equal number of delocalized π electrons in both benzene and pyrrole, the dispersion energies are nearly similar in their organic-cation complexes.

A comparison of the cation−π and cation−water interactions in Figure 4, indicates that the total interaction energies $E_{\mathrm{int}}^{(\mathrm{SAPT})}$ of the water complexes of the various cations are comparable in magnitude to those exhibited by the corresponding pyrrole complexes. What distinguishes the interactions of these cations with the π systems and water is the magnitude of the electrostatic energies, with them being dominant contributors to the total interaction energy in case of the latter. Thus, in the case of the Li^+ complex of water, the electrostatic contribution to the total interaction energy of the water complexes (113%) is much larger than the induction (44%), dispersion (1%), and exchange (58%) contributions. In contrast, the induction contribution of the Li^+ complex of pyrrole (81%) is larger than the electrostatic (59%), dispersion (1%), and exchange (41%) contributions. It is pertinent to note here that the exchange contributions are repulsive and hence destabilizing. On the other hand, in the $N(CH_3)_4^+$ complexes of both water and pyrrole, the electrostatic contribution (H_2O, 128%; Py, 104%) is much larger than both the induction (H_2O, 26%; Py, 56%) and dispersion contributions (H_2O, 22%; Py, 55%). However, the exchange contribution to the total interaction energy of the water complex (76%) is much smaller than what is observed in the pyrrole complex (115%). More importantly, the magnitude of this repulsive contribution in the Py−$N(CH_3)_4^+$ complex is much larger than the attractive electrostatic contribution. Hence the contribution of the induction and dispersion energies is far more important in stabilizing the Py−$N(CH_3)_4^+$ complex than the H_2O−$N(CH_3)_4^+$ complex. The marked difference between the water and π complexes of these cations can be attributed to the nature of the donor. In water, the donor lone pair of the oxygen atom is more localized than the diffuse π cloud of the π system. As a result the polarizability of the former is much smaller than the latter. Consequently the electrostatic contributions are larger and the induction energy contributions are smaller in case of the water complexes. The repulsive energies are higher in case of the water complexes because the cation encounters another atom in contrast to a bond in ethene or the center of the aromatic ring (no atoms or bonds). As opposed to the electron-rich aromatic systems interacting with cations, one can speculate about similar types of complexes between electron-deficient systems such as boranes interacting with anions. In this case, the anion would be expected to interact with the molecule at the bond position instead of an atomic site.

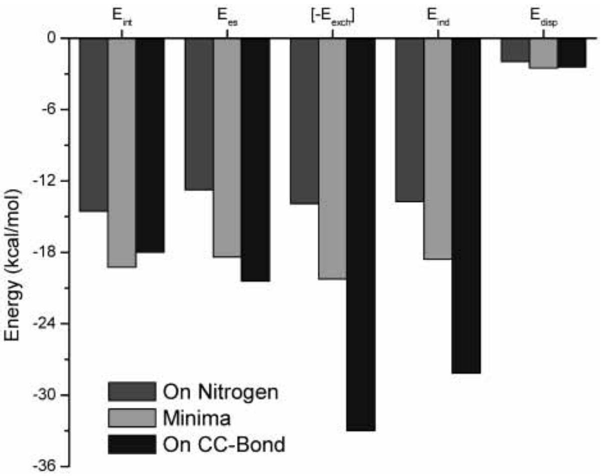

Figure 5. Comparison of the interaction energy components evaluated using the 6-31+G* basis set for three different orientations of the Py−K^+ complex. See caption of Figure 3 for description of various interaction energy terms.

An oft-encountered predicament in the context of the geometries and energies is the role of the magnitude of the various interaction energy components in governing the equilibrium geometry of the complex. We illustrate this by considering the example of the K^+ complex of pyrrole. We have evaluated the interaction energy components for three different orientations of the K^+ cation on pyrrole (i) above the nitrogen atom, (ii) above the CC bond opposite to the nitrogen atom, and (iii) the minimal energy conformation. To make an effective comparison, the intermolecular separation observed in the case of the minimal energy conformation was used for all the three conformations. The results shown in Figure 5 highlight some interesting details. As can be seen, the interaction energies are smallest for the conformation in which the K^+ cation is located over the nitrogen atom. The lower interaction energy results from smaller contributions of both the electrostatic and induction energies. The magnitude of the dispersion energy, though substantial, is nearly similar for all the three conformations. Interesting, however, is the case of the CC−bond conformation. Both the electrostatic and induction energies are much larger than that observed in the case of the minimal energy conformation. However, the repulsive exchange energies are much larger than that observed in case of the minimal energy conformation. While it is instructive to attribute this observation to the shape exhibited by the π electron density, i.e., the cations bind closer to the point where there is maximum charge density but not too close to result in a large exchange energy, it is pertinent to note that similar observations were made by us in previous studies of the fluorine-substituted benzene−argon complexes,[86] and the benzene−water-dimer complex.[83] We believe that this observation on the role of exchange energies in governing the equilibrium geometries has profound implications in explaining the structural manifestations of various intermolecular and host−guest complexes.

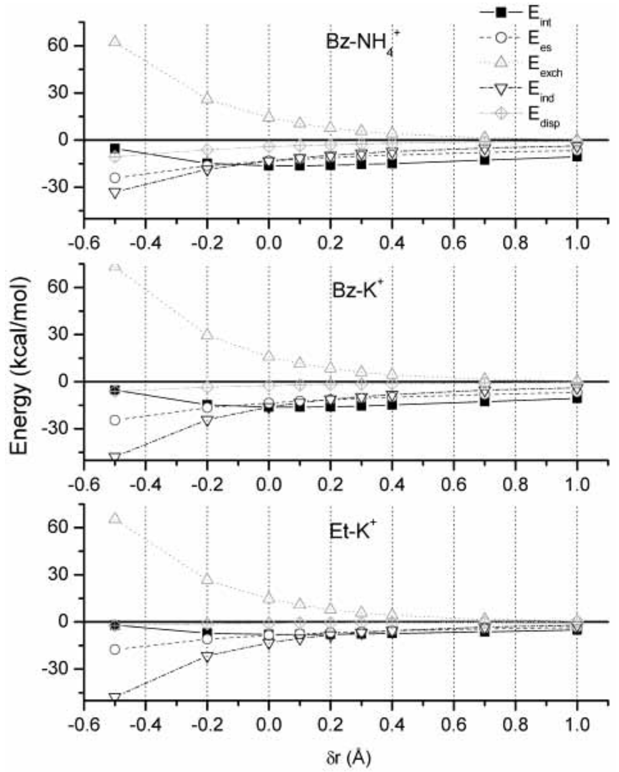

Figure 6. Comparison of the calculated SAPT interaction energy components of the Bz−NH$_4^+$, Bz−K$^+$, and Et−K$^+$ complexes at the 6-31+G* level. See caption of Figure 3 for description of various interaction energy terms. δr is the increment in the intermolecular separation, where $\delta r = 0.0$ corresponds to that in the equilibrium geometry.

The Ag$^+$ complexes of these π systems merit special attention owing to the large interaction energies and the presence of d electrons. As can be noted from Table 3, induction energies are dominant contributors to the interaction energy. The small size of the Ag$^+$ ion (1.26 Å) implies that the Ag$^+$ cation can approach much closer to the π system. However, the larger nuclear charge of the Ag leads to a much larger repulsive energy. The higher dispersion energy result both from a smaller intermolecular separation and the participation of the d electrons in the binding. The higher interaction energies also imply that the role of the π system in the binding is minimal. However, the equilibrium geometries can be expected to vary owing to the widely differing magnitudes of the various interaction energy components.

Since most instances of cation−π interactions in chemical and biological systems exhibit significant deviations from the kind of idealized behavior discussed in this study, it is, however, of interest to examine how the magnitude of the various interaction energy components are modulated when the cation is brought closer to the π system from larger distances. To do so, we have compared the interaction energy components of the Bz−NH$_4^+$, Bz−K$^+$, and Et−K$^+$ complexes for various intermolecular separations in Figure 6. While the former two complexes were chosen because of our interest in delineating the origins of their nearly similar binding energies, the latter was chosen because it allows us to examine the role of the π system. At large intermolecular separations, electrostatic energies dominate the interaction energies of these complexes. Consequently the interaction energies for the Bz−K$^+$ complex are much larger than those observed in the Et−K$^+$ complex but similar to those observed in the Bz−NH$_4^+$ complex. At shorter intermolecular separations, induction energies become dominant in the metal cation complexes with both the Et−K$^+$ and Bz−K$^+$ complexes exhibiting nearly similar induction energies. The predominance of the induction energies over that of the electrostatic energies can be observed much before the onset of the equilibrium geometry in the metal cation complexes. Unlike what is observed in the metal cation complexes, much larger increases in the dispersion energies are observed in the Bz−NH$_4^+$ complex when the intermolecular separation is decreased. The repulsive exchange energies are much smaller in the Bz−NH$_4^+$ complex than in the corresponding Bz−K$^+$ complex, and interestingly are similar in magnitude to those observed in the Et−K$^+$ complex. Thus, the nearly similar interaction energies of the Bz−NH$_4^+$ and Bz−K$^+$ complexes result from a balance of dispersion and induction energies because the electrostatic and exchange energies are nearly similar and hence cancel out. While the predominance of the dispersion energies in case of Bz−NH$_4^+$ complex explains the higher interaction energy obtained at the MP2/aug-cc-pVDZ level, it also implies that suitable receptors specific for the NH$_4^+$ cation could be designed by maximizing the dispersion energies.[13,117] Talking of the design of receptors, it is useful to examine the implications of the present study in understanding chemical and biological processes. By definition, a greater electrostatic contribution to the interaction energy of the complex implies that the magnitudes of the interaction energies are susceptible to the dielectric of the solvent. The fact that the electrostatic contributions are much lower in case of the cation−π complexes than in the corresponding cation−H$_2$O complexes might explain the wide prevalence of the former.

TABLE 4: Charge Transfer (ΔQ, in au) from the π Systems to the Cation Evaluated at the MP2/6-31+G* and MP2/aug-cc-pVDZ Levels[a]

	NBO[b]			APT[c]		
	Et	Bz	Py	Et	Bz	Py
Li$^+$	0.03	0.04	0.04	0.16	0.36	0.30
Na$^+$	0.02	0.02	0.02	0.10	0.22	0.18
K$^+$	0.01	0.01	0.01	0.06	0.14	0.11
NH$_4^+$	0.06	0.04	0.06	0.05	0.12	0.10
	(0.06)	(0.05)	(0.07)	(0.06)	(0.14)	(0.12)
C(NH$_2$)$_3^+$	0.03	0.04	0.06	0.04	0.07	0.07
	(0.03)	(0.05)	(0.07)	(0.04)		
N(CH$_3$)$_4^+$	0.01	0.02	0.03	0.01	0.03	0.03
	(0.02)	(0.04)	(0.04)	(0.02)		
Ag$^+$	0.08	0.04	0.09	0.27	0.26	0.27
	(0.09)	(0.02)	(0.09)	(0.35)	(0.35)	(0.34)

[a] The charges in the parantheses have been evaluated at the MP2/aug-cc-pVDZ level. [b] Natural population analysis of the MP2 electron density. [c] Atomic polar tensor charges evaluated from the mean dipole moment derivatives.

One of the prevailing notions is that the binding of these cations to various π systems can be explained by charge transfer.[71,76,77] It is therefore interesting to examine the charge transfer Δq evaluated using both the NBO and APT methods (Table 4). However, one can see that irrespective of the method employed to evaluate the charges, few correlations can be made between the charge transfer and the total interaction energy. In particular, neither the interaction energies nor the interaction energy components of the π complexes of the organic cations exhibit any correlation with the charge transferred. However, in the case of the alkali-metal−cation complexes, one can obtain a correlation of the charge transferred to the induction energies (Figure 7).

It would be useful to examine if the binding of the cation to the π system exhibits some characteristic spectral signatures. Indeed, as can be noted from Table 5, the highly IR active out-

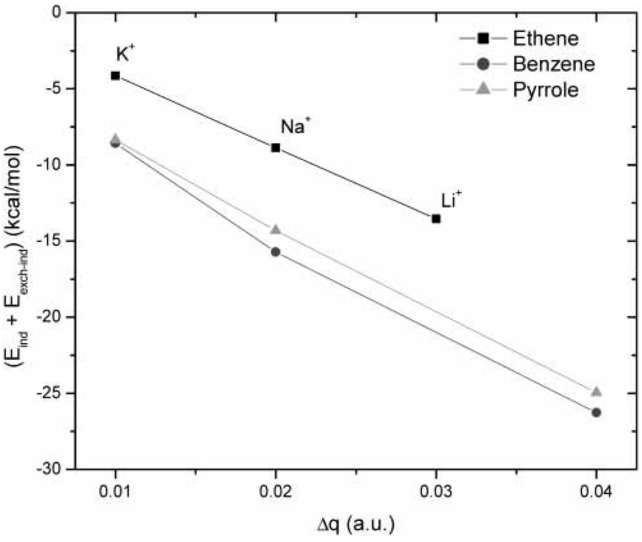

Figure 7. Correlation of the electronic charge transferred from the π system to the metal cation with the total induction energies in the π−alkali-metal cation complexes.

TABLE 5: Calculated (MP2/6-31+G*) Vibrational Frequency Shifts of the Symmetric Out-of-Plane CH Bend ($\nu^{H\perp}$) of the π System and the Frequencies of the Intermolecular Stretching (S_z) Mode in All the Cation−π Complexes[a]

	ethene		benzene		pyrrole	
	$\nu_7^{H\perp\ b}$	S_z	$\nu_4^{H\perp\ b}$	S_z	$\nu_{22}^{H\perp\ b}$	S_z
Li^+	83(141)	350(94)	77(181)	382(105)	106(240)	420(92)
Na^+	63(144)	193(23)	61(161)	205(34)	86(217)	228(32)
K^+	47(149)	117(12)	35(158)	133(20)	53(211)	161(19)
NH_4^+	56(166)	185(53)	41(154)	213(24)	280(176)	709(10)
$C(NH_2)_3^+$	40(160)	114(9)	33(175)	120(16)	179(188)	412(58)
$N(CH_3)_4^+$	23(169)	79(6)	24(173)	91(12)	139(227)	279(49)
Ag^+	101(90)	256(0)	60(149)	171(7)	152(93)	358(18)

[a] All frequencies and frequency shifts are in units of cm^{-1}. The calculated intensities (km/mol) are enclosed in parentheses beside them. [b] The modes are numbered according to Herzberg (ref 122). The calculated shifts are with respect to the corresponding frequency observed in the uncomplexed monomer {ethene = 983(133), benzene = 674(150), and pyrrole = 693(199)}.

of-plane CH bend of these π systems exhibits a characteristic blue shift. This blue shift, specific for each π system, gives an inkling of the strength of the cation−π interaction. It is of interest to note that the enthalpies of binding of the ethene−H_2O complex were also evaluated from the experimentally observed blue shifts of the out-of-plane CH bending modes of ethene.[121] On a similar note, the intermolecular stretching frequency S_z also yields similar information on the strength of the cation−π interaction. It would therefore be interesting to experimentally examine the relationships between these spectral features and the interaction energies.

4. Conclusions

Several issues have been highlighted in the present theoretical study, which details the interaction of various cations with different π systems. These include, (i) the most consistent, and rigorous theoretical comparison of the cation−π interaction involving various kinds of systems, (ii) a detailed and sophisticated energy decomposition of the cation−π interactions, and (iii) the comparison of the magnitudes of the interaction energy components of the cation−π and cation−water interactions. Such a consistent comparison for diverse systems, which include the interactions between various cations (alkali-metal, noble-metal, and organic) and different π systems (ethene, benzene, and pyrrole)/water, is very much essential in obtaining a thorough understanding of ion-specific recognition and would be useful in designing novel molecular systems and functional materials. In the absence of any report on the evaluation of the magnitude of repulsive energies and their role in governing the geometries of these cation−π complexes, the present study would aid understand the structural manifestations of various intermolecular and host−guest complexes. Given the wide prevalence of cation−π interactions in biological and chemical systems, the present study would help obtain a better perspective of noncovalent intermolecular interactions.

The interaction of π systems with metal cations is distinct from their interaction with organic cations, with electrostatic energies playing a far smaller role in the attractive stabilization of the latter. Consequently, the contribution of induction and dispersion energies becomes important in the binding of organic cations to various classes of π systems. The inclusion of electron correlation, apart from yielding accurate dispersion energies, also magnifies the contribution of the induction energies.

The presence of heteroatoms in the π system has important consequences both on the geometries and the interaction energies exhibited by these systems. In particular, the presence of an electronegative atom in a π system need not necessarily be the site of cation binding because the magnitude of repulsive energies dictates the geometry of the equilibrium structure.

Though both cation−π and cation−water interactions exhibit nearly similar interaction energies, the predominance of electrostatic energies in the interactions of the latter implies that the nature of the solvent would have a more pronounced effect in case of the latter.

The magnitude of charge transfer has little correlation with the total interaction energies exhibited by these cation−π complexes. However, in case of the metal cation complexes, the charge transfer can be correlated to the induction energies.

We believe that the results presented in this study could be employed to intelligently design and generate crafted molecular systems for size- and molecule-selective processes.

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Supporting Information Available: Table S1 containing the magnitudes of the individual interaction energy components of all the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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