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Theoretical Study of Alkali Cation−Benzene Complexes: Potential Energy Surfaces and Binding Energies with Improved Results for Rubidium and Cesium

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High level ab initio quantum chemical calculations have been carried out on the binding of alkali metal to benzene with special attention to heavier metals for which the agreement between the most recent theoretical investigations and the experimental bond dissociation energies (BDEs) is not very good. We performed BSSE-corrected geometry optimizations employing the MP2 level of theory with large basis sets and a modified Stuttgart RSC 1997 basis set for rubidium and cesium and carried out single point energy calculations at the MP4 level, obtaining, also for the latter metals, BDE values in good agreement with the experimental results. Furthermore, in view of the development of empirical correction terms to force fields to describe cation−π interactions, we evaluated the potential energy surface along the benzene symmetry axis and discussed the role of the BSSE correction on the accuracy of our results.

Introduction

The interactions between cations and aromatic rings, generally referred to as cation−π interactions, have been the focus of many investigations in the past decade due to their importance in complex biological systems.[1−14] Such cation−π interactions are believed to play a key role in protein structural organization,[3−10] in the functioning of ionic channels in membranes,[11,12] and in molecular recognition processes.[15,16] Indeed, the three-dimensional structures of biological macromolecules are determined by a delicate balance of weak noncovalent interactions, such as hydrogen bonds, salt bridges, hydrophobic interactions, cation−π interactions,[3,15] charge-dipole interactions,[17,18] and π−π stacking[19,20] interactions. In particular, due to the full positive charge on the cation, the strength of cation−π interactions is much greater than other noncovalent interactions and they are now believed to be crucial determinants in protein structural organization.[3,5−10]

Moreover, the binding of alkali metal cations, and in particular Na^+ and K^+, to the exposed faces of aromatic amino acids such as phenylalanine, tyrosine, and tryptophan lying along the inner surfaces of ionic channels is thought to play a key role in the selective transport of these metal cations through the ion channel.[21,22] Sodium and potassium alkali metal ions are among the most abundant and important metals in biological systems,[23,24] and their interactions with π-systems are also important in several biological recognition processes such as the binding of acetylcholine to the active site of the enzyme acetylcholine esterase[5] and the stereoselective cyclization of squalene epoxide in the enzymatically catalyzed process of steroid biosynthesis.[5]

Cation−π interactions between a positively charged metal cation and an aromatic ligand with a delocalized π-electron cloud were first recognized and studied in the gas phase.[25−29] Extensive experimental and theoretical investigations have been subsequently performed with the objective of characterizing these interactions.[3,5] Several earlier gas-phase experimental studies have shown that the binding of lithium,[30,31,33] sodium,[28,32−34] potassium,[25,33] rubidium,[33] and cesium[33] ions with benzene is indeed strong and allowed to determine the corresponding bond dissociation energies (BDEs). Prior theoretical studies of alkali metal ion interactions with benzene were performed at the RHF and MP2 levels using basis sets of double-ζ quality and faced several difficulties to reproduce accurately the experimental BDEs.[35−37] Recent ab initio calculations have shown that good agreement with the available experimental data for lithium, sodium, and potassium is achieved only if the level of theory is extensive enough to include adequately correlated methods, MP2 or higher, large basis sets up to the complete basis set (CBS) limit, and the basis set superposition error (BSSE).[38−40] However, the agreement between the theoretical and experimental BDEs is not as good as that for rubidium and cesium.[33] For rubidium, an accurate BDE could be recently calculated but only through lengthy calculations employing the complete basis set limit and a highly correlated CCSD(T) method,[40] while this computationally expensive approach still led to a 20% error on the BDE of cesium.[40]

Computationally expensive ab initio quantum mechanical calculations are limited to small molecules (up to a few hundred atoms, depending on the available computer resources), and the theoretical investigation of large biological systems, such as proteins or enzymes, can only be performed with a molecular mechanics based approach. Since current force fields fail to account adequately for cation−π interactions when modeling the geometry of proteins or enzymes and the binding of ligands to their biological target, several approaches have been recently developed to modify these force fields by including empirical correction terms to describe cation−π interactions, that are determined by a multiple linear regression analysis fit to experimental data or ab initio calculations.[12,37,41]

Unfortunately, the experimental information is limited to BDEs and all of the high level theoretical calculations up to date are restricted to the most stable geometries and the corresponding binding energies, while the development of a corrected force field would greatly gain from the availability

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of large sections of the potential energy surface. For these reasons, we undertook a theoretical investigation to characterize more quantitatively the binding of alkali metal to benzene with special attention to the heavier metals and to evaluate the potential energy surface along the benzene symmetry axis. Rather than investigate the CBS limit, we aimed at analyzing the performance of increasingly larger basis sets and higher order correlation treatment to determine the optimal ones in terms of accuracy and computational load in view of their use in the calculation of potential energy surfaces.

Computational Details

All of the calculations were performed using Gaussian 03 [42] to obtain geometrical structures, vibrational frequencies, binding energies and enthalpies, and potential energy scans for the alkali−benzene complexes, using different levels of theory and a collection of basis sets. In each case, the basis set superposition error was evaluated following the Boys−Bernardi counterpoise (CP) correction method[43] and BSSE-corrected geometry optimizations were carried out employing the CP-corrected potential energy surface (PES) approach[44] implemented in Gaussian 03.

For M^+−benzene, where M = Li, Na, or K, the 6-311+G* basis set was first employed. Since there has been some debate[38,40] over the importance of the inclusion of the $(n-1)$ core electrons in energy calculations for alkali metal cation complexes, we have performed both frozen core (FC) (excluding C and Li 1s and Na 1s, 2s, and 2p electrons, as the standard in Gaussian 03) and full MP2 calculations (including all of the above listed core electrons) for both Li^+ and Na^+ complexes. To elucidate more in detail how neglect of the metal core electrons affects the energetics of the complexes, a calculation on Li^+−benzene was also performed with the inclusion of the 1s electrons of Li^+ only (i.e., excluding C 1s electrons). $(n-1)$ electrons are automatically considered in Gaussian 03 for potassium.

The effects arising from the increase of either the electron correlation treatment or the basis set size were investigated through two distinct sets of calculations. Since a previous work[38] has indicated that MP4 and CCSD(T) calculations on Li^+−benzene with medium to large basis sets give the same BDE, within 0.1 kcal/mol, a more extensive treatment of electron correlation was taken into account by carrying out single point energy calculations at the MP4 level. We therefore performed MP4/6-311+G* calculations for Li^+, Na^+, and K^+ (including core electrons for lithium and sodium) on the geometry optimized at the corresponding MP2 level. Larger basis sets were considered at the MP2 level (again employing a full treatment for Li^+ and Na^+). We have gradually increased the number of polarization functions by using the 6-311+G(2d,2p) and 6-311+G(3df,2p) sets. As the quality and number of functions used to describe the heavy atoms, and the metal in particular, seems to be an important requirement for the accurate determination of binding energies,[39,40] for lithium and sodium, we have further increased the description of the metal and of the carbon atom using the augmented correlation-consistent triple-ζ basis set (aug-cc-pVTZ), while employing a 6-311+G* basis set for the hydrogen atom, whose description is less important. To support the use of the smaller basis set for hydrogen, we have compared a few BDEs calculated using this basis set to those where hydrogens were also described by the aug-cc-pVTZ basis, finding an agreement within 0.1 kcal/mol. The mixed basis set will be hereafter globally indicated as aug-cc-pVTZ. MP4 single point energy calculations were also performed on the MP2-optimized geometry with the latter basis set for the Li^+ and Na^+ systems and with the 6-311+G(3df,2p) basis set for K^+−benzene.

Concerning the heavier metal cation (Rb^+ and Cs^+) complexes, the same type of computations was performed: MP2 and MP4 with a smaller and a larger basis set. In this case, effective core potentials (ECPs) and valence basis sets were employed for the description of the metal. In conjunction with the 6-311+G* set for the description of C and H atoms, we have used the Hay−Wadt[45] ECPs and valence basis sets, consisting of a (5s5p)/[3s2p] contraction, with the addition, as suggested by Glendening et al.,[46] of a single polarization d function with exponents of 0.64 and 0.19 for Rb and Cs, respectively. Geometry optimizations at the MP2 level and single point energy calculations at the MP4 level were both performed using this basis set, which, for the sake of simplicity, will be denoted as 6-311+G*.

The investigation of the performance of more complete basis sets was carried out by means of the Stuttgart relativistic small core (RSC) 1997 ECP basis set[47] in order to have sets comparable to those employed for the MP2/6-311+G(3df,2p) and MP2/aug-cc-pVTZ types of calculations for the lighter cations. Indeed, for rubidium and cesium, the Stuttagart RSC 1997 basis set consists of a (7s6p)/[5s4p] contraction. To this set, two polarization functions, d and f, were added, with exponents of 0.39 and 0.55, respectively, for Rb and 0.29 and 0.44 for Cs. These values were obtained by energy optimizing metal cation−water complexes at the RHF level using the 6-311+G* basis set for the description of water and the Stuttgart RSC 1997 ECP for the metal and adding the two polarization functions in subsequent steps. This set was used in combination with either the 6-311+G(3df,2p) set or the above-described aug-cc-pVTZ set for carbon and hydrogen. Furthermore, to investigate the effect of increasing the basis set on the sole metal, we used this modified Stuttgart ECP basis set on the metal together with a smaller 6-311+G* set on the benzene atoms. These basis sets will be hereafter called, respectively, 6-311+G(3df,2p), aug-cc-pVTZ, and mixed. MP4 single point energies were also obtained on the corresponding MP2-optimized geometries.

The determination of zero point energies (ZPEs) and thermal corrections was performed through frequency calculations at the MP2/6-31G* level for the whole metal series (including core electrons for Li and Na) using a scale factor of 0.9646.[49]

In addition to the structure and energetics of the optimized complexes, we also analyzed the performance of the same variety of methods and sets (including BSSE corrections) to investigate potential energy curves for the whole series. The results reported here were obtained by scanning the potential energy surface, placing the metal along the benzene D_{6h} symmetry axis at a variable distance, R, from the ring center.

Results and Discussion

Table 1 reports binding energies and enthalpies, together with the metal−benzene ring centroid distance, R_{M^+-bz}, and basis set superposition error, calculated at the employed levels of theory for the optimized M^+−benzene complexes, with M = Li, Na, and K, while Figures 1, 2, and 3, respectively, represent the corresponding potential energy scans. Analogously, Table 2 and Figures 4 and 5 illustrate the same data for rubidium and cesium complexes.

Optimized Complexes. As already noted in many preceding works,[33,38,40] all of the employed levels of theory show a correct qualitative trend both for the R_{M^+-bz} distance value, which

TABLE 1: Binding Energies and Enthalpies for M^+−Benzene Complexes (M = Li, Na, K)[a]

M	method	basis	R_{M^+-bz}	BSSE	$\Delta E^{CP\ b}$	ΔH_0	ΔH_{298}	ref
Li	MP2(FC)	6-311+G*	1.90	4.06	−36.0	−34.0		this work
	MP2(Window)	6-311+G*	1.88	4.34	−36.7	−34.7		this work
	MP2(Full)	6-311+G*	1.88	4.53	−36.7	−34.7	−35.5	this work
	MP4(Full)//MP2(Full)	6-311+G*	1.88	4.51	−36.7	−34.6	−35.4	this work
	MP2(Full)	6-311+G(2d,2p)	1.88	2.28	−36.4	−34.4	−35.2	this work
	MP2(Full)	6-311+G(3df,2p)	1.88	3.14	−36.8	−34.8	−35.6	this work
	MP2(Full)	aug-cc-pVTZ	1.87	4.46	−37.5	−35.5	−36.3	this work
	MP4(Full)//MP2(Full)	aug-cc-pVTZ	1.87	4.70	−37.6	−35.6	−36.4	this work
	MP2(FC)	CBS	1.88		−36.6 ± 0.2	−34.7		Feller et al.[40]
	CCSD(T)+CV	CBS			−38.0 ± 0.2	−36.1	−36.8	Feller et al.[40]
	CID(Expt.)					−38.5 ± 3.2	−39.3	Amicangelo et al.[33]
	ICR(Expt.)					−36.39	−37.9	Woodin et al.[30]
Na	MP2(FC)	6-311+G*	2.49	2.80	−22.0	−20.7		this work
	MP2(Full)	6-311+G*	2.47	3.42	−22.6	−21.3	−21.7	this work
	MP4(Full)//MP2(Full)	6-311+G*	2.47	3.43	−22.6	−21.3	−21.7	this work
	MP2(Full)	6-311+G(2d,2p)	2.44	2.15	−22.8	−21.6	−22.0	this work
	MP2(Full)	6-311+G(3df,2p)	2.41	3.55	−23.8	−22.5	−22.9	this work
	MP2(Full)	aug-cc-pVTZ	2.45	6.30	−22.8	−21.6	−22.0	this work
	MP4(Full)//MP2(Full)	aug-cc-pVTZ	2.45	6.70	−22.9	−21.7	−22.1	this work
	MP2	CBS	2.39		−25.1 ± 0.3	−24.1		Feller[39]
	CCSD(T)+CV	CBS			−25.4 ± 0.3	−24.4	−24.7	Feller[39]
	CID(Expt.)					−22.8 ± 1.4	−23.2	Amicangelo et al.[34]
	CID(Expt.)					−22.2 ± 1.4	−22.6	Amicangelo et al.[33]
	CID(Expt.)					−21.1 ± 1.0		Armentrout et al.[32]
	HPMS(Expt.)						−28.0 ± 1.5	Guo et al.[28]
K	MP2	6-311+G*	2.89	2.22	−17.8	−17.1	−17.3	this work
	MP4//MP2	6-311+G*	2.89	2.24	−17.2	−16.4	−16.6	this work
	MP2	6-311+G(2d,2p)	2.86	0.83	−17.9	−17.1	−17.3	this work
	MP2	6-311+G(3df,2p)	2.83	1.11	−18.9	−18.1	−18.3	this work
	MP4//MP2	6-311+G(3df,2p)	2.83	1.15	−18.1	−17.4	−17.6	this work
	MP2	CBS	2.79		−20.8 ± 0.4	−20.2		Feller et al.[40]
	CCSD(T)+CV	CBS			−20.6 ± 0.4	−20.0	−20.1	Feller et al.[40]
	CID(Expt.)					−17.5 ± 0.9	−17.6	Amicangelo et al.[33]
	Expt.					−18.2 ± 1.4		Sunner et al.[25]

[a] Energy and enthalpy values are in kilocalories per mole, and distances are in angstroms. [b] Counterpoise-corrected bond dissociation energy.

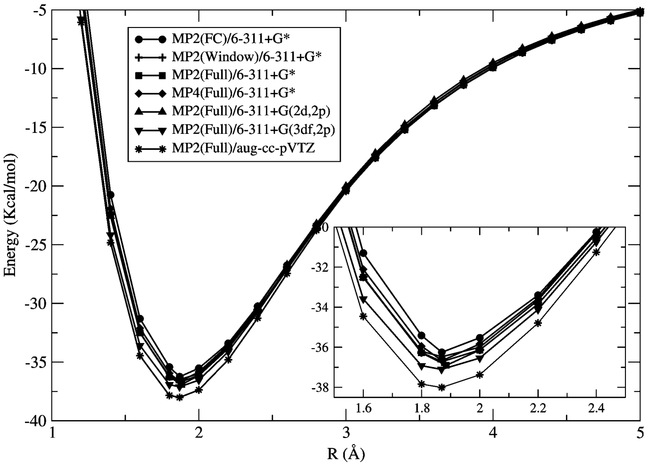

Figure 1. BSSE-corrected potential energy curves for Li^+−benzene, calculated at different levels of theory. The Li^+−benzene interaction energy is reported as a function of R, the distance between the metal ion and the ring center along the D_{6h} symmetry axis.

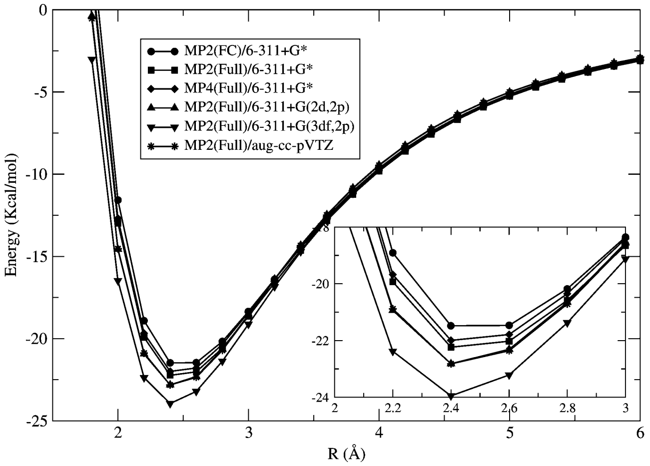

Figure 2. BSSE-corrected potential energy curves for Na^+−benzene, calculated at different levels of theory. The Na^+−benzene interaction energy is reported as a function of R, the distance between the metal ion and the ring center along the D_{6h} symmetry axis.

increases as the metal atomic mass increases, and for the binding energies and enthalpies, which decrease. However, from a quantitative point of view, there are large differences depending on the level of theory.

In the case of Li^+ and Na^+ complexes, it can be noted that the inclusion of the heavy atom core electrons strengthens the binding energies of about 0.6−0.7 kcal/mol. We have analyzed more in detail the origin of this effect in Li^+−benzene, by calculating at the same level of theory the binding energy with the inclusion of 1s core electrons just for Li^+ (MP2(Window)/6-311+G*). The values of binding energies obtained in this way are practically indistinguishable from those obtained when all core electrons are included, thus showing that the largest part of this effect derives from the explicit treatment of the metal core electrons.

The effect of an increase of the electron correlation treatment with the application of the MP4 method in the calculation of the binding energy is extremely small for both Li^+− and Na^+−benzene. On the other hand, an increase of the basis set size and quality strengthens the binding energy, especially when basis sets privileging the description of heavy atoms (MP2/6-311+G(3df,2p) and MP2/aug-cc-pVTZ) are employed.

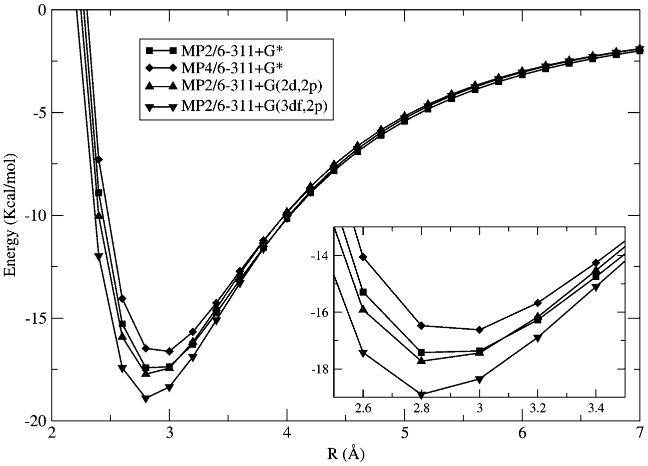

Figure 3. BSSE-corrected potential energy curves for K$^+$−benzene, calculated at different levels of theory. The K$^+$−benzene interaction energy is reported as a function of *R*, the distance between the metal ion and the ring center along the D_{6h} symmetry axis.

Table 1 also reports a comparison with recent experimental data and high level ab initio studies. As far as the Li$^+$−benzene complex is concerned, there is an improvement of the agreement with the experimental results with the quality of the basis set. In particular, the use of a correlation-consistent basis set (aug-cc-pVTZ) leads to the best performance. The value obtained with this basis set, $\Delta H_0 = -35.3$ kcal/mol, as a matter of fact, is quite close to the ion cyclotron resonance (ICR) experimental result of Woodin et al.[30] (−36.3 kcal/mol), differing more from the collision induced dissociation (CID) of Amicangelo and Armentrout[33] (−38.5 ± 3.2 kcal/mol), although still within the experimental uncertainty. The comparison with the ab initio values obtained by Feller et al.,[40] who have estimated the MP2 and CCSD(T) complete basis set limit, is particularly interesting. In the case of Li$^+$−benzene, the MP2 CBS value was obtained using a frozen core approach, and probably also for this reason, their calculated ΔH_0 value, although free of the well-known BSSE overcorrection problem (see below), is about 1 kcal/mol smaller than our MP2(Full)/aug-cc-pVTZ value. The latter value is close to the CCSD(T) CBS limit result (within 0.5 kcal/mol), where core-valence corrections were also included in the calculation. As for the 6-311+G* basis set, the MP4(Full)/aug-cc-pVTZ enthalpy value is very close to the corresponding MP2-(Full) one, providing only a small increase (∼0.1 kcal/mol) in the BDE value, thus confirming the reduced effect of an increase of the correlation treatment for the lighter Li$^+$ and Na$^+$ ions.

The Na$^+$−benzene results are very similar to those obtained for Li$^+$. There is a significant improvement in the binding energy when core electrons are explicitly considered and a gradual strengthening as the basis set size increases. However, in this case, the value obtained with the 6-311+G(3df,2p) basis set is about 1 kcal/mol larger than that obtained with the aug-cc-pVTZ basis set, contrary to what was found for Li$^+$. Particularly striking is the value of the BSSE correction for MP2(Full)/aug-cc-pVTZ, amounting to 6.10 kcal/mol, ∼2.5 kcal/mol larger than that for MP2(Full)/6-311+G(3df,2p), which could partly account for the discrepancy between the two values. The ΔH_0 values calculated with these two basis sets are both quite close to the CID experimental data of Amicangelo et al.[33,34] The 6-311+G-(3df,2p) and aug-cc-pVTZ results approach more closely, respectively, the CID experimental value of ref 34 and those of refs 32 and 33 within 0.5 kcal/mol. Both MP2 and CSSD(T) CBS limits[40] lead to much larger BDE values close to previous high pressure mass spectrometry (HPMS) experimental data,[28] which have been, however, recently recognized to be overestimated.[33] Once again, the MP4(Full)/aug-cc-pVTZ enthalpy value does not differ significantly from the corresponding MP2-(Full) one.

In the case of K$^+$−benzene, $n = 3$ core electrons were automatically included in the MP2 computations. Again, the effect of increasing the basis set size leads to more strongly bound complexes; however, in contrast with the Li$^+$− and Na$^+$−benzene systems, here the use of a higher correlation method (MP4 instead of MP2) gives significant differences: 0.6 kcal/mol when the 6-311+G* basis set is employed and 0.8 kcal/mol with 6-311+G(3df,2p). This correction for the latter set leads to a ΔH_0 value in better agreement with the experimental one.[33] As in Na$^+$−benzene, the MP2 and CCSD(T) CBS data of Feller et al.,[40] which were obtained by an ad hoc constructed aug-cc-pVTZ basis set, give BDE values about 2 kcal/mol larger.

Complexes involving heavy metal cations (Rb and Cs) need a special discussion. Indeed, the majority of theoretical studies on these systems[33,38] largely underestimate binding energies, with the exception of ref 40 for Rb$^+$−benzene, where the CCSD(T) CBS limit was obtained using double- and triple-ζ basis sets taken from the literature and an ad hoc developed quadruple-ζ basis set in conjunction with the Hay−Wadt relativistic effective core potential. The same scheme, however, gave for Cs$^+$−benzene a value for the binding enthalpy 3 kcal/mol smaller than the experimental one (Table 2).

As described in the preceding section, we first employed Hay−Wadt ECPs and valence basis sets for the metal, obtaining the same kind of poor performance of the available ab initio studies. Because of the emerging importance of an accurate description of these metal ions, we have then made use of the small core RSC Stuttgart 97 ECPs and basis sets. Such basis sets are able to describe core-valence correlation effects of M$^+$ and were found[48] to give good results in the description of both bond lengths and binding energies when heavy metal cations are involved. Binding enthalpies obtained with this basis set enriched with d and f polarization functions (Table 2) show an increase of 3−4 kcal/mol, leading to an agreement with the experimental value of about 0.2−0.3 kcal/mol when used in conjunction with either 6-311+G(3df,2p) and aug-cc-pVTZ basis sets for the description of the benzene atoms. Test calculations with the same RSC Stuttgart 97 ECP basis set used in conjunction with the smaller 6-311+G* basis set on the benzene atoms (indicated as mixed in Table 2) lead to an increase of the BDE by about 2−3 kcal/mol, thus showing the higher importance of the accurate description of the metal atom. Energies calculated at the MP4/aug-cc-pVTZ level are smaller than the corresponding MP2 ones, by 0.3 kcal/mol for Rb$^+$−benzene and by 0.7 kcal/mol for Cs$^+$−benzene. The difference between the MP4 values and the experimental ones is, in any case, within 0.5 kcal/mol.

Potential Energy Curves. The examination of the potential energy curves, Figures 1−5, can shed some more light on the analysis of bonding in these systems and on the performance of different levels of theory, besides confirming some of the features that already emerged when investigating optimized complexes.

As expected from the electrostatic nature of the interaction between a metal cation with the benzene π-electrons, the long range attraction contribution is quite large, leading, for example, to an interaction energy of at least 5 kcal/mol at a metal cation−benzene distance of about 5 Å. The depth and extent of the potential energy well obviously depend on the atomic mass of

TABLE 2: Binding Energies and Enthalpies for M^+−Benzene Complexes (M = Rb, Cs)[a]

M	method	basis	R_{M^+-bz}	BSSE	$\Delta E^{CP\ b}$	ΔH_0	ΔH_{298}	ref
Rb	MP2	6-311+G*	3.21	1.69	−13.9	−13.3	−13.4	this work
	MP4//MP2	6-311+G*	3.21	1.71	−13.4	−12.8	−12.9	this work
	MP2	mixed	3.09	1.24	−15.9	−15.3	−15.4	this work
	MP2	6-311+G(3df,2p)	3.02	1.01	−16.7	−16.1	−16.2	this work
	MP2	aug-cc-pVTZ	3.03	1.36	−16.8	−16.2	−16.3	this work
	MP4//MP2	aug-cc-pVTZ	3.03	1.46	−16.5	−15.9	−16.0	this work
	MP2	CBS			−15.8 ± 0.2	−15.0		Feller et al.[40]
	CCSD(T)+CV	CBS			−17.1 ± 0.2	−16.3	−16.4	Feller et al.[40]
	CID(Expt.)					−16.4 ± 0.9	−16.5	Amicangelo et al.[33]
Cs	MP2	6-311+G*	3.51	1.67	−12.1	−11.6	−11.6	this work
	MP4//MP2	6-311+G*	3.51	1.69	−11.6	−11.1	−11.2	this work
	MP2	mixed	3.25	1.50	−15.3	−14.8	−14.9	this work
	MP2	6-311+G(3df,2p)	3.19	1.53	−16.2	−15.7	−15.8	this work
	MP2	aug-cc-pVTZ	3.18	2.08	−16.3	−15.8	−15.9	this work
	MP4//MP2	aug-cc-pVTZ	3.18	2.24	−15.6	−15.1	−15.2	this work
	MP2	CBS			−14.1 ± 0.2	−13.4		Feller et al.[40]
	CCSD(T)+CV	CBS			−13.1 ± 0.2	−12.4	−12.5	Feller et al.[40]
	CID(Expt.)					−15.5 ± 1.1	−15.5	Amicangelo et al.[33]

[a] Energy and enthalpy values are in kilocalories per mole, and distances are in angstroms. [b] Counterpoise-corrected bond dissociation energy.

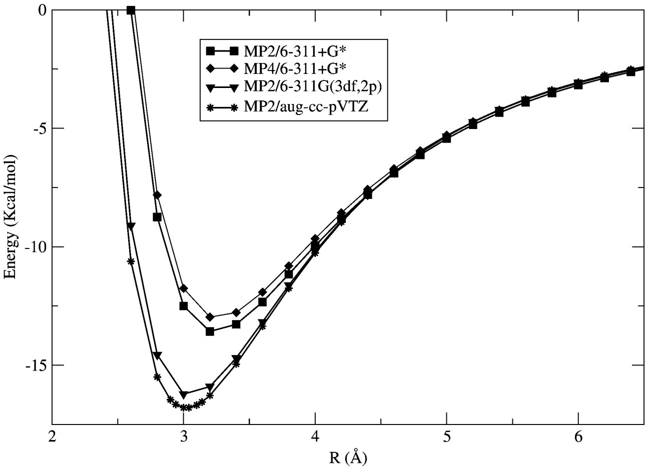

Figure 4. BSSE-corrected potential energy curves for Rb^+−benzene, calculated at different levels of theory. The Rb^+−benzene interaction energy is reported as a function of *R*, the distance between the metal ion and the ring center along the D_{6h} symmetry axis.

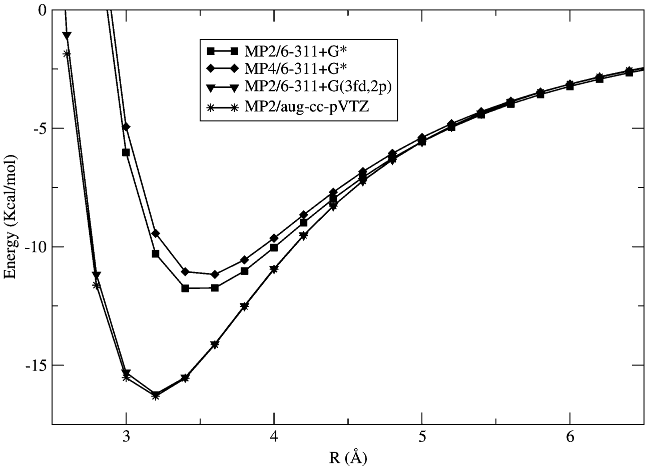

Figure 5. BSSE-corrected potential energy curves for Cs^+−benzene, calculated at different levels of theory. The Cs^+−benzene interaction energy is reported as a function of *R*, the distance between the metal ion and the ring center along the D_{6h} symmetry axis.

the cation and on its ability to penetrate the electron cloud of benzene, being thus deeper and wider for smaller cations.

About the performance of the basis sets and methods, for all of the investigated cases, the differences are quite small at long range and increase as the *R* distance decreases, suggesting that the long range attractive component of the interaction energy is well described at all levels of theory. On the other hand, large differences arise at small values of *R*, that is, in the description of the repulsive component of the interaction, leading to rather relevant discrepancies in the calculated minimum positions, in the well size, as well as in the overall shape of the curve. In the case of K^+−benzene, for instance, while the difference between the MP2/6-311+G* and MP2/6-311+G(3df,2p) values amounts to less than 0.2 kcal/mol at $R = 4$ Å, it becomes about 2 kcal/mol at $R = 3$ Å, rising up to nearly 5 kcal/mol at $R = 2.4$ Å.

In Figures 1−3, for Li^+, Na^+, and K^+ complexes, as noted for the corresponding optimized systems, there is a gradual lowering of the potential energy curves, together with a widening of the well, as the size of the basis set increases, in particular when considering sets belonging to the same family. However, as already mentioned, the behavior of the larger basis sets, 6-311+G(3df,2p) and aug-cc-pVTZ, which have nearly a comparable size, for Li^+−benzene and Na^+−benzene is quite different. In the first case, the largest lowering is found when using the aug-cc-pVTZ set, while for Na^+−benzene the latter set gives results which are very similar to 6-311+G(2d,2p), that is, higher in energy with respect to the 6-311+G(3df,2p) basis set.

As in the optimized complexes, the potential energy curve at the MP4(Full)/6-311+G* level of theory is extremely close to the corresponding MP2(Full) one for both Li^+ and Na^+. This is not the case for K^+−benzene where the MP4 curve is sensibly higher at short range and slightly lower at long range than the corresponding MP2 one.

Once again, results change more drastically for heavy metal cations described by core potentials as for Rb^+ and Cs^+ (Figures 4 and 5). Here, the choice of the basis set has a strong impact on the whole shape of the potential energy well: the use of the modified Stuttgart RSC 1997 ECPs basis set, instead of the Hay−Wadt basis set, in conjunction with a small 6-311+G*, larger 6-311+G(3df,2p), or aug-cc-pVTZ basis set for the description of the benzene atoms, leads to much more strongly bound systems (larger BDEs and smaller R_{M^+-bz}) for both Rb^+ and Cs^+. Indeed, as shown in Table 2, BDEs are increased by 2−3 or 3−4 kcal/mol, respectively, for the smaller and larger benzene basis sets, while equilibrium ion−benzene distances are reduced by about 0.2−0.3 Å. More in detail, the repulsive part of the potential obtained with the Stuttgart RSC 1997

TABLE 3: Effects of the Use of BSSE-Uncorrected and -Corrected PES on the Geometry and Bond Dissociation Energies of M$^+$−Benzene Complexes[a]

		BSSE-uncorrected PES			BSSE-corrected PES		
M	method	$R_{\mathrm{M^+-bz}}$	ΔE	ΔE^{CP}	$R_{\mathrm{M^+-bz}}$	ΔE	ΔE^{CP}
Li	MP2/6-311+G*	1.84	−41.3	−36.6	1.88	−41.2	−36.7
	MP2/aug-cc-pVTZ	1.81	−42.1	−37.4	1.87	−42.0	−37.5
Na	MP2/6-311+G*	2.46	−26.2	−22.4	2.47	−26.0	−22.6
	MP2/aug-cc-pVTZ	2.34	−29.5	−22.5	2.45	−29.1	−22.8
K	MP2/6-311+G*	2.82	−20.1	−17.7	2.89	−20.0	−17.8
	MP2/6-311+G(3df,2p)	2.80	−20.0	−18.9	2.83	−20.0	−18.9
Rb	MP2/6-311+G*	3.16	−15.6	−13.8	3.21	−15.6	−13.9
	MP2/aug-cc-pVTZ	2.89	−18.2	−16.1	3.03	−18.2	−16.8
Cs	MP2/6-311+G*	3.41	−13.9	−12.0	3.51	−13.8	−12.1
	MP2/aug-cc-pVTZ	3.11	−18.5	−16.2	3.18	−18.4	−16.3

[a] Energy values are in kilocalories per mole, and distances are in angstroms.

basis set is correspondingly larger than that obtained when using the Hay−Wadt one, leading to much wider and deeper wells.

Again, it can be noted that employing 6-311+G(3df,2p) or aug-cc-pVTZ basis sets for benzene gives very similar energy values along the whole curve and not only for the optimized systems.

BSSE Corrections. The question of BSSE corrections has been affecting the determination of geometries and binding energies for weakly bonded systems for a long time. Because the description of the atoms of one fragment in the complex is improved by the basis functions of the other one with respect to the isolated monomers, uncorrected approaches lead to an overestimate of the interaction energies and to too close interaction distances. Corrections to this error are generally evaluated by the counterpoise technique proposed by Boys and Bernardi;[43] however, this approach was sometimes reported to lead to overcorrected values of energy,[50] to the extent that in some cases uncorrected results seemed to be preferable. Recent studies[51−53] have pointed out that this apparent better performance is actually often due to a fortuitous cancellation of error between BSSE and basis set incompleteness error. Furthermore, since BSSE corrections to the whole potential energy surface have important consequences on the minima position and on its topology,[54] BSSE corrections calculated on the uncorrected potential energy surface minima should be avoided: they are in fact too large and lead to too weak interaction energies. Such effects are displayed in Table 3, where we reported metal−benzene distances, CP-corrected and -uncorrected bond dissociation energies obtained by performing geometry optimization on both BSSE-corrected and -uncorrected potential energy surfaces. This comparison has been carried out at the MP2 level of theory with both the smallest and the largest basis sets for all the alkali metal ion−benzene series. M$^+$−benzene equilibrium distances are systematically larger on the BSSE-corrected surface, even if the extent of the lengthening does not follow a regular pattern, being linked to both the strength of the interaction and the value of the BSSE corrections which are strongly dependent on the specific basis set (see below). The lengthening of the metal−benzene distance ranges from 0.01 to 0.11 Å, thus potentially affecting the determination of properties connected to the minimum geometry. The effect on bond dissociation energies is, in general, less marked (about 0.1−0.2 kcal/mol), although, in some cases (e.g., Rb$^+$−benzene), it leads to a discrepancy (0.7 kcal/mol) larger than the accuracy of the method.

Nonetheless, the strong dependence of the BSSE corrections on the theoretical model and on the basis set type and their slow convergence with the basis set size require a certain care when considering CP-corrected energy values. In this context, an analysis on the CP correction behavior along the potential energy curves for the various basis sets could be of interest.

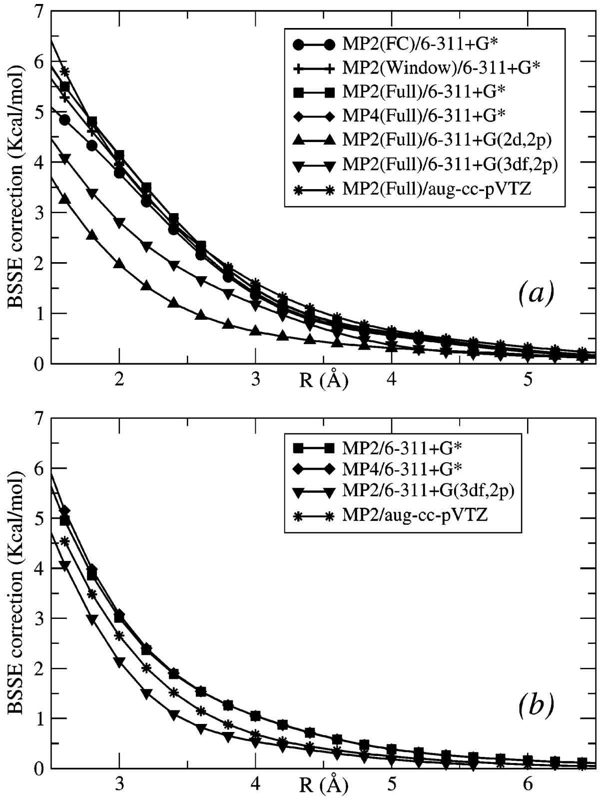

Figure 6. BSSE corrections, calculated at different levels of theory, as a function of the distance, *R*, for Li$^+$−benzene (panel a) and Cs$^+$−benzene (panel b).

In Figure 6, we have reported counterpoise BSSE corrections to the potential energy curves for Li$^+$−benzene and Cs$^+$−benzene. As expected, the BSSE decreases as the metal cation−benzene distance increases: At long range (R > 4 Å), the correction amounts to 1 kcal/mol at most. At short range, there is a sharp enhancement of the BSSE, which, at comparable distances, is larger for Cs$^+$ than for Li$^+$, due to the higher *n* basis functions employed for Cs. However, for values of *R* corresponding to the complex equilibrium distance, BSSE corrections are smaller for Cs$^+$−benzene than for Li$^+$−benzene. There is in fact a gradual lowering of the BSSE correction of the optimized complexes going from lighter to heavier metals (see Tables 1 and 2), mostly due to the increase in the equilibrium distance. ΔH values for Rb$^+$ and Cs$^+$ complexes will thus be less affected by possible overcorrection problems connected to the CP approach, while values for Li$^+$ and Na$^+$ complexes should be taken more carefully. In this sense, the larger discrepancies between the calculated values and the experimental ones for the latter systems could be partly explained by the correspondingly large, and probably overestimated, BSSE values (∼4−5 kcal/mol).

As far as the correlation level of the employed method is concerned (MP2 or MP4), no significant variation can be noted for the BSSE corrections along the whole potential energy curve. The extent of the correction is on the other hand linked to the different basis sets. For the 6-311G family, as already noted,[56] although the general trend is a reduction of the BSSE corrections as the number of basis functions increases, an irregular behavior is shown, with minimum values reached when the 6-311+G-(2d,2p) set is used. In particular, the addition of diffuse functions (such as d functions), leading to a better description of both the isolated fragment and the whole complex, does result in an improvement of the binding energy but also results in a larger BSSE.[57] MP2/aug-cc-pVTZ bond dissociation energies show higher BSSEs when compared with those obtained with 6-311+G(3df,2p) of similar size.

Conclusions

In this work, we carried out high level ab initio quantum chemical calculations on the binding of alkali metal (M = Li, Na, K, Rb, Cs) to benzene. Special attention was devoted to the heavier metals, rubidium and cesium, for which the agreement between the most recent theoretical investigations and the experimental BDEs is not very good. Rather than investigate the CBS limit, we analyzed the performance of increasingly larger basis sets and higher order correlation treatments to determine the optimal ones in terms of accuracy and computational load in view of their use in the calculation of potential energy surfaces for these systems. We performed BSSE-corrected geometry optimizations employing MP2 and MP4 levels of theory with several large basis sets to estimate equilibrium geometries and binding energies. The effects arising from the increase of either electron correlation treatment and of the basis set size were investigated and showed that the basis set increase, especially that of the metal atom, is much more important for the accuracy of the results. Binding energies calculated at the MP2 level with large basis sets of at least triple-ζ quality and including d and possibly f polarization functions, such as 6-311+G(3df,2p) or aug-cc-pVTZ, are in good agreement with the experimental results. In particular, the use of an energy-optimized modification of the Stuttgart RSC 1997 ECP basis set including d and f polarization functions allowed us to obtain also for rubidium and cesium accurate bonding energies. Furthermore, in view of the development of empirical correction terms to force fields to describe cation−π interactions, we evaluated the potential energy surface along the benzene symmetry axis and discussed the role of the BSSE correction on the accuracy of our results.

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