Binding Enthalpies for Alkali Cation−Benzene Complexes Revisited

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The geometries and binding enthalpies of M^+(benzene) complexes (M = Li, Na, K, Rb, and Cs) were obtained from large basis set second-order perturbation theory and coupled cluster theory calculations. The best ΔH_{298} estimates (in kcal/mol) are Li^+(benzene) = −36.8 ± 0.2 (theory) vs −37.9 and −39.3 ± 3.2 (expt), Na^+(benzene) = −24.7 ± 0.3 (theory) vs −28.0 ± 1.5 and −22.5 ± 1.5 (expt), K^+(benzene) = −20.1 ± 0.4 (theory) vs −19.2 and −17.1 ± 0.9 (expt), Rb^+(benzene) = −16.4 ± 0.2 (theory) vs −16.4 ± 0.9 (expt), and Cs^+(benzene) = −12.5 ± 0.2 (theory) vs −15.1 ± 1.1 (expt). The present findings include small corrections for core/valence correlation effects and lead to binding enthalpies uniformly larger than those of previous theoretical studies.

1. Introduction

The binding enthalpies of M^+(benzene) complexes, where M is one of the alkali cations (Li, Na, K, Rb, and Cs), have recently been the subject of several gas-phase experimental and theoretical studies. These studies were motivated by the importance of alkali cation−ligand interactions in chemically related systems important to biological or chemical separations. In the case of Na^+(benzene), which is the most extensively studied of the complexes, the strength of the interaction exceeds that of the corresponding interaction in $Na^+(H_2O)$, despite the presence of a substantial dipole moment in water and the lack of a permanent dipole in benzene. The two available experimental measurements of the Na^+(benzene) binding enthalpy (ΔH) vary by more than 6 kcal/mol. Very recent collision-induced dissociation experiments by Armentrout and Rodgers[1] using guided ion beam mass spectrometry (CID-GIBMS) techniques were interpreted as indicating a value of ΔH_{298} = −21.5 ± 1.0 kcal/mol. Earlier equilibrium high-pressure mass spectrometry (HPMS) studies by Castleman and co-workers[2−4] found a value of ΔH_{610} = −28.0 ± 1.5 kcal/mol. Clearly, the two values lie well outside their respective error bars. Besides sodium, experimental data are also available for the Li^+(benzene)[5,6] and K^+(benzene)[7] complexes.

After this work was complete, we learned of new experimental and theoretical work on the M^+(benzene) and M^+(benzene)$_2$ complexes (M = alkali metals Li to Cs) by Amicangelo and Armentrout.[8] The experimental work was based on the same GIBMS-CID techniques as that in the earlier work of Armentrout and Rodgers. The theoretical work used second-order Møller−Plesset perturbation theory (MP2), combined with the 6-311+G(2d,2p) basis set on H, Li, C, O, and Na and effective core potentials (ECPs) for K, Rb, and Cs.

The majority of recent theoretical calculations are in good agreement with the smaller of the two ΔH experimental values for Na^+(benzene). An MP2 calculation with the 6-311+G(2d,2p) basis set by Hoyau et al.[9] yielded ΔH_0 = −21.4 kcal/mol after correcting for the undesirable effects of basis set superposition error (BSSE). Nicholas et al.[10] applied a combination of MP2 and density functional theory (DFT) to determine the binding enthalpies of all five complexes, Li^+(benzene) through Cs^+(benzene). The nonlocal DFT calculations included Becke exchange[11,12] and Perdew correlation[13] (BP86/DFT). The calculated Na^+(benzene) binding enthalpy was found to be −21.0 kcal/mol with both MP2 and BP86/DFT. Armentrout and Rodgers[1] reported similar findings from MP2, DFT, and composite electronic structure methods, such as Gaussian-2[14] and CBS-Q.[15] Their ΔH values ranged from approximately −21 to −23 kcal/mol, with the larger values coming from the composite methods. Recent literature values of the M^+(benzene) binding enthalpies are summarized in Table 1.

A somewhat different conclusion regarding the magnitude of ΔH was reached in a newly published study that attempted to minimize the uncertainty associated with the use of finite one-particle basis set expansions by estimating the MP2 complete basis set (CBS) limit. This limit can be approximated by carrying out a sequence of (typically 2−3) calculations with a well-defined collection of basis sets that is known to approach the CBS limit and then applying one or more extrapolation formulas to estimate the limit. In practice, this usually means performing calculations with basis sets of at least quadruple-ζ quality. The result of the CBS study was a ΔH_{298} value of −24.7 ± 0.3 kcal/mol, 3−4 kcal/mol larger than the comparable MP2 values in the literature that had been adjusted for BSSE.[16] The −24.7 kcal/mol value included minor corrections for core/valence and higher-order correlation effects. In light of the importance of this class of interactions and the attention they have received, in the present work, we extend the CBS approach to the other alkali metal complexes up through Cs^+.

2. Methods

As in the previous work, the present calculations were performed with three members of the diffuse function augmented correlation-consistent family of basis sets (i.e., aug-cc-pVxZ, x = D, T, and Q)[17−19] for carbon and hydrogen. For the sake of brevity, the collection of basis sets involving the aug-cc-pVDZ carbon and hydrogen basis sets on benzene and a comparable basis set on the metal cation will be referred to simply as "aVDZ", even though for K, Rb, and Cs their basis

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TABLE 1: Experimental and Theoretical M^+(Benzene) Binding Energies and Enthalpies[a]

M	method	basis	ΔE_e	ΔH_0	ΔH_{298}	ref
Li	MP2	6-31G*	−43.8			Caldwell and Kollman[b]
	MP2	6-311+G*	−36.0[c]		−35.0[c]	Nicholas et al.[d]
	BP86(DFT)	TZ94p	−34.5		−33.6	
	CCSD(T)	est. CBS	−38.0	−36.1 ± 0.2	−36.8 ± 0.2	present work
	MP2(full)	6-311+G(2d,2p)		−34.2[c]		Amicangelo and Armentrout[e]
	CID(expt)			−38.5 ± 3.2	−39.3 ± 3.2	
	ICR(expt)				−37.9	Woodin and Beauchamp[f]
Na	MP2	6-31G*	−29.4			Caldwell and Kollman[b]
	MP2	6-311+G*	−21.9[c]		−21.0[c]	Nicholas et al.[d]
	BP86(DFT)	TZ94p	−21.6		−21.0[g]	
	CCSD(T)	est. CBS	−25.4	−24.2 ± 0.3	−24.7 ± 0.3	present work
	MP2	6-311+G(2d,2p)	−22.7[c]		−21.8	Hoyau et al.[h]
	HPMS(expt)				−28.0 ± 1.5[i]	Guo et al.[j]
	MP2(full)	6-311+G(2d,2p)		−21.4[c]		Amicangelo and Armentrout[e]
	CID(expt)			−21.2 ± 1.1	−22.5 ± 1.5	
	CID(expt)				−21.5	Armentrout and Rodgers[k]
K	MP2	6-31G*	−15.0			Caldwell and Kollman[b]
	MP2	6-311+G*	−16.7[c]		−16.0[c]	Nicholas et al.[d]
	BP86(DFT)	TZ94p	−13.5		−13.0[l]	
	CCSD(T)	est. CBS	−20.6	−20.0 ± 0.4	−20.1 ± 0.4	present work
	MP2(full)	6-311+G(2d,2p)		−16.1		Amicangelo and Armentrout[e]
	CID(expt)			−17.5 ± 0.9	−17.1 ± 0.9	
	(expt)				−19.2 (−18.3)[m]	Sunner et al.[n]
Rb	MP2	6-311+G*	−13.9[c]		−13.3[c]	Nicholas et al.[d]
	BP86(DFT)	TZ94p	−11.5		−11.0	
	CCSD(T)	est. CBS	−17.1	−16.3 ± 0.2	−16.4 ± 0.2	present work
	MP2(full)	6-311+G(2d,2p)		−12.7		Amicangelo and Armentrout[e]
	CID(expt)			−16.4 ± 0.9	−16.4 ± 0.9	
Cs	MP2	6-311+G*	−12.1[c]		−11.6[c]	Nicholas et al.[d]
	BP86(DFT)	TZ94p	−9.5		−9.0	
	CCSD(T)	est. CBS	−13.1	−12.4 ± 0.2	−12.5 ± 0.2	present work
	MP2(full)	6-311+G(2d,2p)		−11.4		Amicangelo and Armentrout[e]
	CID(expt)			−15.4 ± 1.1	−15.5 ± 1.1	

[a] Theoretical values in kcal/mol. [b] Ref 35. [c] Corrected for BSSE. [d] Ref 10. [e] Ref 8. [f] Ref 5. [g] $T = 610$ K. [h] Ref 9. [i] Measured at $T = 610$ K. At 0 K, the estimated value is −27.6 kcal/mol. [j] Ref 4. [k] Ref 1. [l] $T = 500$ K. [m] Value corrected for assumed unimolecular decomposition in the vacuum of the mass analyzer. [n] Ref 7.

TABLE 2: Metal Cation Basis Sets and M^+ Energies (E_h)

M	name	composition	MP2 energy
Li	aVDZ	[4s,3p,2d]	−7.23612
	aVTZ	[5s,4p,3d,2f]	−7.23638
	aVQZ	[6s,5p,4d,3f,2g]	−7.23638
Na	CVDZ	[5s,4p,2d]	−161.85517
	CVTZ	[7s,6p,4d,2f]	−161.93701
	CVQZ	[9s,8p,6d,4f,2g]	−161.96805
K	CVDZ	[6s,5p,2d]	−599.16999
	CVTZ	[8s,7p,4d,2f]	−599.23072
	CVQZ	[10s,9p,6d,4f,2g]	−599.25987
Rb	CVDZ/ECP	[4s,4p,2d]	−23.51657
	CVTZ/ECP	[5s,5p,4d,2f]	−23.55593
	CVQZ/ECP	[9s,9p,6d,4f,2g]	−23.60604
Cs	CVDZ/ECP	[4s,4p,2d]	−19.53872
	CVTZ/ECP	[5s,5p,4d,2f]	−19.57749
	CVQZ/ECP	[9s,9p,6d,4f,2g]	−19.60378

sets will not be taken from the correlation-consistent family of basis sets. At present, no correlation-consistent basis sets have been published for these elements. The naming convention for the larger triple and quadruple-ζ basis sets follow in a similar fashion.

The metal cation basis sets were obtained from a variety of sources. For lithium, we used the augmented correlation-consistent sets. Since correlation-consistent basis sets were not available for potassium, we used a series of potassium basis sets developed for use on $K^+(H_2O)_n$ complexes.[20,21] Because of the importance of correlating the (2s,2p) shell of electrons on sodium, the potassium basis sets were developed for use in calculations in which the K (3s,3p) electrons would be included in the correlation treatment. Double- and triple-ζ quality Rb and Cs basis sets were taken from the literature,[20] and new quadruple-ζ sets for these elements were developed as part of the present study. The Rb and Cs inner shell electrons were replaced with the relativistic effective core potentials (RECP) of Hay and Wadt,[22] which excluded the (n-1) shell of metal electrons from the core. The metal cation basis sets and the corresponding total atomic energies are summarized in Table 2.

The lithium and potassium basis sets can be obtained from URL www.emsl.pnl.gov:2080/forms/basisform.html. The sodium basis sets were prerelease versions from Woon and Dunning.[23] The rubidium and cesium basis sets are available from the authors upon request. Only the spherical components of the Cartesian (d, f, and g) polarization functions were used.

Binding enthalpies were computed with respect to MP2-optimized structures obtained with each of the three levels of basis sets. That is, the binding enthalpies for the aVDZ were obtained as the difference in energy between MP2/aVDZ geometries, and the binding enthalpies for the aVTZ and aVQZ basis sets were obtained similarly. These optimizations and the complete basis set electronic binding energies to be discussed used the following frozen core definitions: Li, C, and Na (1s: 2e$^-$), K (1s,2s,2p:10e$^-$), Rb (1s,2s,2p,3s,3p,3d: 28e$^-$), and Cs (1s,2s,2p,3s,3p,3d, 4s,4p,4d:48e$^-$). Thus, the calculations involving Na, K, Rb, and CS included the (n-1) s and p alkali cation electrons in the correlation treatment. MP2 geometry optimizations employed a convergence criterion which corresponds to a maximum gradient component of approximately 1.5×10^{-5} E_h/bohr. Benzene geometries for the isolated molecule were taken from previous work on the H_2O-benzene complex.[24] The vibrational frequencies needed for zero-point and finite-temperature corrections were obtained from MP2/aVDZ calculations.

MP2 calculations were performed with a combination of the Gaussian-98[25] program on SGI Origin 2000 machines and the NWChem[26] program on an IBM SP computer. Higher-level, coupled cluster calculations, including single, double, and perturbative triple excitations (CCSD(T)) and the aVTZ basis set were performed with the MOLPRO-2000[27] and NWChem programs.

NWChem and Gaussian-98 attempt to minimize problems associated with linear dependency by transforming out the linearly dependent eigenvectors of the overlap matrix. NWChem uses a default threshold of $\tau_{\text{delete}} = 10^{-5}$, whereas Gaussian's threshold is 1 order of magnitude larger. A threshold of 10^{-5} results in ~25 vectors being eliminated for calculations performed with the large aVQZ basis set, whereas setting $\tau_{\text{delete}} = 10^{-6}$ reduces this number by a factor of 5, but increases the risk that the calculation will fail due to convergence problems associated with the near-linear dependence.

Energy differences were computed with consistent thresholds ($\tau_{\text{delete}} = 10^{-5}$) for all complexes and their fragments. Tests calculations were performed on the Na^+(benzene) complex, with a tighter threshold (10^{-6}) in order to determine its affect on the binding energy. While use of the tighter threshold did result in a lowering of the total energy of the complex and isolated benzene by ~0.0003 E_h, the binding energy changes by 3.0×10^{-5} E_h (0.02 kcal/mol).

The effect of including the inner shell carbon and lithium electrons in the correlation treatment was investigated in a series of calculations with the triple-ζ core/valence correlation-consistent basis sets, cc-pCVTZ. The MP2/aVTZ geometries were adopted for this purpose.

It is frequently possible to improve upon the raw aVxZ binding energies by performing an extrapolation to the CBS limit. Extrapolations are normally done by extrapolating the individual energies of the two fragments and then taking the difference of the extrapolated energies. However, in many cases the binding energy can also be extrapolated directly. Differences between these two approaches are typically small. A surprisingly large number of formulas have been proposed, but we find that while the total energy is somewhat sensitive to the choice of the formula, the energy differences are not. A mixed exponential/Gaussian function of the form[28]

$$E(\mathrm{x}) = E_{\mathrm{CBS}} + B\exp[-(x-1)] + C\exp[-(x-1)^2] \quad (1)$$

where $x = 2$(aVDZ), 3(aVTZ), or 4(aVQZ), has been found to be effective. Another expression consists of a simple exponential function of the form[29-31]

$$E(\mathrm{x}) = E_{\mathrm{CBS}} + b\exp(-cx) \quad (2)$$

Yet another involves the reciprocal of $l_{\max}$, the highest angular momentum in the basis set[32]

$$E(\mathrm{x}) = E_{\mathrm{CBS}} + B/(l_{\max} + 1)^4 \quad (3)$$

Whenever possible in the present work, we have chosen to report the CBS values obtained with the mixed exponential/Gaussian formula as our best estimates because of its statistically better performance on a large number of binding energies. The spread in estimated CBS binding energies among the various extrapolation methods will serve as a crude estimate of the uncertainty in extrapolating the MP2 frozen core limit. As will be seen, for the five complexes investigated in this work, no single approach to estimating the CBS limit was found to be universally effective. We believe that this stems in part from the lack of very high-quality correlation-consistent cation basis sets for the heavier elements.

Other potential sources of error, such as the need to resort to relativistic effective core potentials for Rb and Cs or the effect of correlation recovery beyond what was explicitly considered in our CCSD(T)/aVTZ calculations, were not estimated. In the former case, the only way of testing the reliability of the RECPs is to perform fully relativistic four-component calculations with large basis sets and high levels of correlation recovery. Software and hardware limitations made such calculations impractical.

The most widely used a posteriori correction for BSSE is the counterpoise (CP) method of Boys and Bernardi.[33] In this work, we used the relaxed geometries of the benzene fragments taken from the M^+(benzene) complexes when computing the CP correction.

3. Results and Discussion

The total energies at the optimized MP2 geometries and the distances between the metal ion and the center of the C_6 carbon ring, r_{MX}, are shown in Table 3 for each of the five complexes. Monotonic convergence in r_{MX} is observed for Li, Na, and K, with the aVQZ basis set results being essentially identical to the CBS limit. Although CBS values of r_{MX} could not be obtained for the Rb^+(benzene) and Cs^+(benzene) complexes due to the lack of monotonic convergence, we believe that the aVQZ values should similarly be very close to the limit. The reason for the somewhat irregular convergence in r_{MX} for the heavier cations is presumed to be caused by the manner in which the metal basis sets approach the CBS limit. The present values of r_{MX} are considerably shorter than previous MP2 results in the literature. For example, the MP2/aVQZ values of r_{MX} in K^+(benzene) and Cs^+(benzene) are ~0.10 Å shorter than the corresponding values reported by Nicholas et al.,[10] with the present results more closely matching the local DFT distances reported by those authors. A complete set of Cartesian coordinates is available from the present authors upon request.

MP2 electronic binding enthalpies, ΔE_{el}, and the corresponding CBS estimates are listed in Table 3 and depicted graphically in Figure 1, where a variety of convergence patterns are evident. The CP-corrected binding energies are observed to universally converge to the CBS limit in a monotonic fashion, but in most instances, the difference between the CP-corrected values of ΔE_{el} and the CBS limit are larger than the raw values. The poorer agreement between CP-corrected results and the CBS limit has been observed for other chemical systems[34] and is thought to be due to the fortuitous cancellation of BSSE and basis set incompleteness errors for the aVxZ basis sets.

The raw ΔE_{el} values for Li^+(benzene) show very little change as a function of basis set size, as was the case for Na^+(benzene). An extrapolation of the total energies yields an estimated CBS value of $\Delta E_{\mathrm{el}} = -36.6 \pm 0.2$ kcal/mol, essentially the same CBS limit obtained from extrapolating the CP-corrected binding energies. Our best estimate of ΔH_{298}, including the core/valence and CCSD(T) corrections, is -36.8 ± 0.2 kcal/mol. It is only slightly smaller than the ion cyclotron resonance (ICR) experimental value of Woodin and Beauchamp at −37.9 kcal/mol.[5] The later experimental value due to Taft et al.[6] is essentially identical to that of Woodin and Beauchamp. The present theoretical value also falls within the error bars of the very recent -39.3 ± 3.2 kcal/mol value, based on the CID measurements of Amicangelo and Armentrout.[8]

The core/valence effects on the binding energies, beyond what have already been considered by including the (n-1) shell of

TABLE 3: M$^+$(Benzene) Total Energies, Electronic Binding Energies, Zero-Point Energies, and Enthaplies[a]

M	basis	method	E	r_{MX}	ΔE_e	ΔE(CP)	E^b_{ZPT}	ΔH_0	ΔH_{298}	ref
Li	aVDZ	MP2	−238.83465	1.936	−36.6	−34.8	64.26			this work
	aVTZ	MP2	−239.04017	1.887	−37.1	−36.3				
	aVQZ	MP2	−239.10469	1.880	−36.8	−36.5				
	CBS	MP2	−239.1412[c]	1.879[d]	−36.6 ± 0.2					
	CBS	CCSD(T)+CV[e]			−38.0 ± 0.2			−36.1	−36.8 ± 0.2	
Na	aVDZ	MP2	−393.43570	2.420	−25.3	−22.8	63.35			Feller[f]
	aVTZ	MP2	−393.72109	2.393	−24.7	−23.8				
	aVQZ	MP2	−393.81749	2.390	−25.0	−24.6				
	CBS	MP2	−393.8728[c]	2.390[d]	−25.1 ± 0.3					
	CBS	CCSD(T)+CV[e]			−25.4 ± 0.3			−24.4	−24.7 ± 0.3	
K	aVDZ	MP2	−830.73979	2.848	−18.6	−17.1	62.97			this work
	aVTZ	MP2	−831.00684	2.789	−19.7	−18.6				
	aVQZ	MP2	−831.10203	2.786	−20.4	−19.9				
	CBS	MP2	−831.1571[c]	2.786[d]	−20.8 ± 0.4					
	CBS	CCSD(T)+CV[e]			−20.6 ± 0.4			−20.0	−20.1 ± 0.4	
Rb	aVDZ	MP2	−255.08118	3.148	−15.3	−13.7	63.15			this work
	aVTZ	MP2	−255.32703	3.089	−16.6	−14.9				
	aVQZ	MP2	−255.44095	3.100	−15.9	−15.6				
	CBS	MP2	−255.5095[c]		−15.8 ± 0.2					
	CBS	CCSD(T)+CV[e]			−17.1 ± 0.2			−16.3	−16.4 ± 0.2	
Cs	aVDZ	MP2	−251.09971	3.406	−13.0	−11.8	63.08			this work
	aVTZ	MP2	−251.34650	3.309	−15.3	−13.5				
	aVQZ	MP2	−251.46303	3.313	−14.2	−14.0				
	CBS	MP2	−251.5333[c]		−14.1 ± 0.2					
	CBS	CCSD(T)+CV[e]			−13.1 ± 0.2			−12.4	−12.5 ± 0.2	

[a] Total energies are given in hartrees. The distance from the metal to the center of the carbon ring (r_{MX}) is given in Å. Binding energies are in kcal/mol. The core/valence correction, ΔE_{CV}, was obtained from MP2/cc-pCVTZ calculations. [b] Zero-point energies for the M$^+$(benzene) complexes were obtained from MP2/aVDZ calculations. The zero-point energy of benzene at this level of theory is 62.35 kcal/mol. [c] Estimated complete basis set energies are based on the mixed Gaussian/exponential formula. [d] Estimated complete basis set distance based on the exponential formula. [e] Includes a correction to the complete basis set MP2 results for higher-order correlation via CCSD(T) and additional core/valence correlation, including the carbon 1s orbitals. [f] Ref.

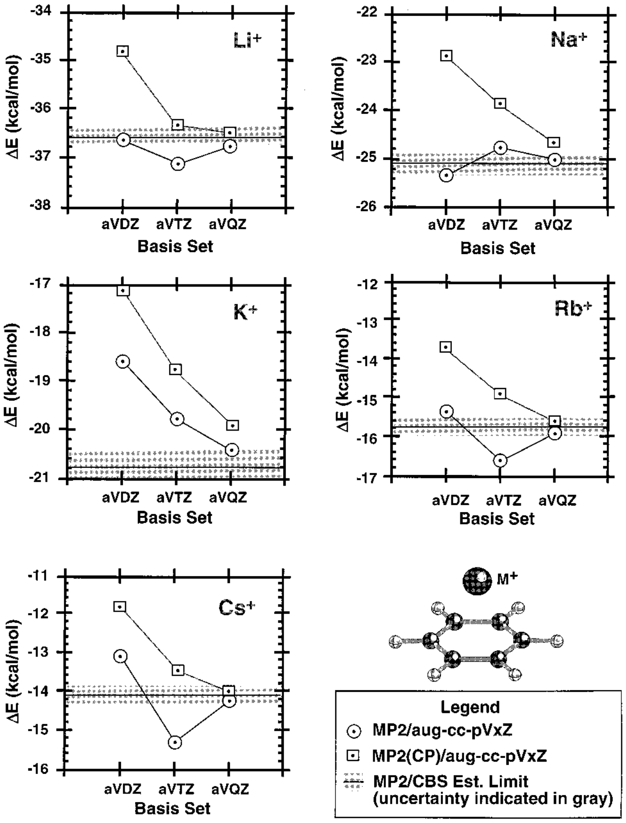

Figure 1. MP2 electronic binding energies for the M$^+$(benzene) complexes as a function of the basis set size.

metal atom electrons in our correlation treatment, were generally less than 1 kcal/mol. The only exception was Li$^+$(benzene), where the correction strengthened the binding energy by 1.3 kcal/mol. When all electrons are correlated in K$^+$(benzene), the binding energy increased by 0.50 kcal/mol. No change was found for Rb$^+$(benzene), and a 0.32 kcal/mol decrease in binding energy occurred in Cs$^+$(benzene). The correction for higher-order correlation effects, as estimated from CCSD(T) calculations, ranged from a minimum of −0.05 kcal/mol for Li$^+$(benzene) to a maximum of 1.29 kcal/mol for Rb$^+$(benzene).

With the exception of the small basis set results of Caldwell and Kollman,[35] the present approach leads to significantly stronger electronic binding energies than have previously been reported. This difference ranges from as little as 1.1 kcal/mol for Li$^+$(benzene) to as much as 3.9 kcal/mol for K$^+$(benzene). The MP2/6-31G* values of Caldwell and Kollman are clearly too large compared to both the higher-level ab initio results and the values from the experiment.

Although Woodin and Beauchamp[5] report no experimental uncertainty in ΔH, the corresponding ΔG value was assigned error bars of ±2 kcal/mol. We note that essentially the same theoretical approach gives a binding enthalpy of −34.2 kcal/mol for Li$^+$(H$_2$O), in almost exact agreement with the −34.0 kcal/mol reported by Woodin and Beauchamp. Part of the discrepancy between theory and experiment for ΔH_{298} is attributable to the value of TΔS used by Woodin and Beauchamp when computing ΔH from the observed free energy of binding, ΔG_{298}. The approximations which were adopted yielded a value of $T\Delta S = -8.2$ versus the −7.5 kcal/mol obtained from the MP2/aVDZ level of theory. Similar approximations were not required for Li$^+$(H$_2$O), and the corresponding TΔS value reported by Woodin and Beauchamp (−6.7 kcal/mol) is in exact agreement with the MP2/aVDZ value.

Some of the experimental uncertainty arises from uncertainty about the temperature and potentially nonequilibrium nature of the sample in the ICR technique, as discussed by Peurrung et al.[36] Presumably, there is also a cumulative uncertainty associated not just with the ΔG_{298} value for Li$^+$(benzene) but also

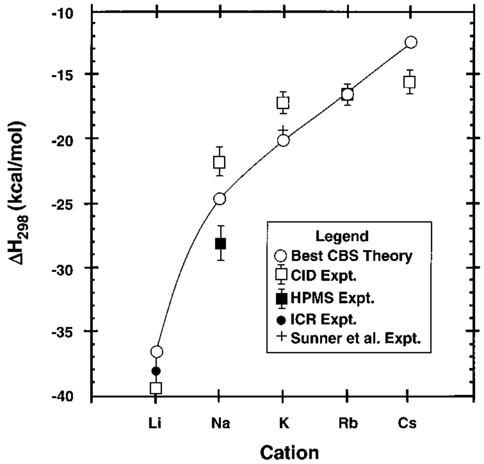

Figure 2. Comparison of the experimental and theoretical complete basis set binding enthalpies.

with the three complexes appearing below it on the ladder of experimental free energies.

As previously discussed,[16] the best theoretical binding enthalpy at 298 K for Na^+(benzene) sits approximately midway between the CID experimental value of Armentrout and Rodgers[1] and the HPMS value of Castleman and co-workers.[2-4] For K^+(benzene), the present $\Delta H_{298} = -20.1 \pm 0.4$ kcal/mol value is in good accord with the -19.2 kcal/mol experimental value of Sunner et al.[7] Adjusting the experimental value for the assumed effect of unimolecular decomposition slightly worsens the level of agreement.

In Figure 2, the best theoretical estimates of ΔH_{298} for all five complexes are compared to the recent CID results of Amicangelo and Armentrout.[8] The level of agreement is generally good, but Figure 2 shows considerable variation from system to system. As already mentioned, the theoretical value falls just inside the experimental error bars for Li. While theory underestimates the binding enthalpy in Li^+(benzene), for Na^+(benzene), and K^+(benzene), the theoretical values are both well outside the experimental error bars and too large. For Rb, there is fortuitously exact agreement, and for Cs, the theoretical value is again smaller than that of the experiment. The reason for these discrepancies is unclear.

In addition to the magnitude of the M^+(benzene) binding energies, it is of interest to compare the present results with the comparable MP2 binding energies where water has replaced benzene as the ligand. The relative strengths of these two interactions is important for molecular dynamics studies involving benzene, water, and the alkali cations.[37,38] MP2/CBS binding energies for $M^+(H_2O)$ have been reported by Feller et al.[20] For the complexes from Li through Rb, we find the M^+ binding enthalpies to benzene to be 1−3 kcal/mol stronger than that to to water. For Cs it is ~1 kcal/mol weaker. Although the individual benzene−potassium interaction is slightly stronger than the water−potassium interaction, the overall binding enthalpy to the first solvation shell is larger for water because approximately 6−8 waters, compared to at most four benzenes, comprise the first solvation shell around K^+.[38]

4. Conclusions

Large basis set ab initio calculations were performed on M^+(benzene) complexes (M = Li, Na, K, Rb, and Cs) to obtain optimized geometries and to estimate binding enthalpies in the complete basis set limit. Compared to previous theoretical predictions of ΔH_{298}, the present values are uniformly larger because the CBS limit was found to lie closer to the raw binding energies than to values corrected for BSSE. BSSE corrections always reduce the binding energy. Core/valence and higher-order correlation effects, estimated via CCSD(T) calculations, were found to contribute small amounts to ΔH. The present theoretical binding enthalpies are in relatively good agreement with the available experimental data. The origin of the often erratic differences between theory and CID experimental results is unclear.

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References and Notes

(1) Armentrout, P. B.; Rodgers, M. T. *J. Phys. Chem. A* **2000**, *104*, 2238.

(2) Castleman, A. W., Jr.; Peterson, K. I.; Upschulte, B. L.; Schelling, F. J. *Int. J. Mass Spectrom. Ion Processes* **1983**, *47*, 203.

(3) Guo, B. C.; Conklin, B. J.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6506.

(4) Guo, B. C.; Purnell, J. W.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1990**, *168*, 155.

(5) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.

(6) Taft, R. W.; Anvia, F.; Gal, J.-F.; Walsh, S.; Capon, M.; Holmes, M. C.; Hosn, K.; Oloumia, G.; Vasanwala, R.; Yazdani, S. *Pure Appl. Chem.* **1990**, *62*, 17.

(7) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem.* **1981**, *85*, 1814.

(8) Amicangelo, J. C.; Armentrout, P. B. Submitted for publication.

(9) Hoyau, S.; Norrman, K.; McMahon, T. B.; Ohanessian, G. *J. Am. Chem. Soc.* **1999**, *121*, 8864.

(10) Nicholas, J. B.; Hay, B. P.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 1394.

(11) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(12) Becke, A. D. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 599.

(13) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(14) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(15) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

(16) Feller, D. *Chem. Phys. Lett.* **2000**, *322*, 543.

(17) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(18) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(19) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(20) Feller, D.; Glendening, E. D.; Woon, D. E.; Feyereisen, M. W. *J. Chem. Phys.* **1995**, *103*, 3526.

(21) Partridge, H. *J. Chem. Phys.* **1989**, *90*, 1043.

(22) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(23) Woon, D. E.; Dunning, T. H., Jr. Submitted for publication.

(24) Feller, D. *J. Phys. Chem. A* **1999**, *103*, 7558.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Petersson, G. A.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaroni, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.;

Andreas, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, version A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(26) Anchell, J.; Apra, E.; Bernholdt, D.; Borowski, P.; Bylaska, E.; Clark, T.; Clerc, D.; Dachsel, H.; de Jong, B.; Deegan, M.; Dupuis, M.; Dyall, K.; Elwood, D.; Fann, G.; Fruchtl, H.; Glendening, E. D.; Gutowski, M.; Harrison, R.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kendall, R.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nichols, J.; Nieplocha, J.; Rendall, A.; Rosing, M.; Sandrone, G.; Stave, M.; Straatsma, T.; Taylor, H.; Thomas, G.; van Lenthe, J.; Windus, T.; Wolinski, K.; Wong, A.; Zhang, Z. *NWChem*, version 3.3; Pacific Northwest National Laboratory: Richland, WA, 1999.

(27) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R. M.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO-2000*; Universität Stüttgart: Stüttgart, Germany, 2000.

(28) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.

(29) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

(30) Xantheas, S. S.; Dunning, T. H., Jr. *J. Phys. Chem.* **1993**, *97*, 18.

(31) Feller, D. *J. Chem. Phys.* **1993**, *98*, 7059.

(32) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669.

(33) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(34) Feller, D.; Aprà, E.; Nichols, J. A.; Bernholdt, D. E. *J. Chem. Phys.* **1996**, *105*, 1940.

(35) Caldwell, J. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 4177.

(36) Peurrung, A. J.; Kouzes, R. T.; Barlow, S. E. *Int. J. Mass. Spectrom. and Ion Processes* **1996**, *157*, 39.

(37) Dang, L. X.; Feller, D. *J. Phys. Chem. B* **2000**, *104*, 4403.

(38) Dang, L. X. *J. Chem. Phys.* **2000**, *113*.