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Alkali metal cation-ligand affinities: Basis set superposition correction for the Gaussian protocols

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The effect of basis set superposition error (BSSE) on Gaussian-2 and Gaussian-3 calculated alkali metal cation-ligand affinities has been studied. For these systems, we found that the standard Boys–Bernadi full counterpoise (CP) method often leads to correction terms that are physically incorrect. This problem may be rectified by using the geometry corrected counterpoise (GCP) method. The relationship between CP, GCP corrections, and deformation energy is discussed. In order to yield good agreement with existing experimental Li^+ and Na^+ ligand affinities, we recommend the adoption of either the G3 (with GCP correction) or the G2(MP2,SVP)-FC (without GCP correction) protocols. In the case of K^+, the GCP correction is of negligible magnitude, and hence GCP corrections may be omitted in the G2(MP2,SVP)-ASC affinity calculations for these complexes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1360196]

I. INTRODUCTION

The Gaussian protocols (Gaussian-1, Gaussian-2, and Gaussian-3)[1–3] and their variants have been very successful in reproducing thermochemistry data for a whole range of organic and inorganic species. As a result, these protocols have become indispensable tools for the estimation for heats of formation, ionization energies, and proton affinities. However, the question remains whether the Gaussian protocols are able to provide equally precise interaction energies for electrostatically bound alkali metal cation-ligand complexes. This is a valid question because in the set of 299 experimental data used in the development of the recent Gaussian-3 (G3) protocol, only 10 were associated with Li and Na. Moreover, it should be noted that the major source of these experimental values comes from precisely determined heats of formation, ionization energies, and electron affinities. As the reactants and products for the processes tested in Gaussian protocols are likely to have different number of alpha and beta electrons pairs (nonisogyric), the deficiencies in the Gaussian protocol might be corrected in the empirical ''higher level correction'' (HLC) terms. Since formation of the alkali metal cation-ligand complex is an isogyric process, calculations on such systems are, in fact, more stringent tests for the Gaussian protocols.

The calibration of the Gaussian protocols for alkali metal cation-ligand complexes has been hampered by the lack of accurate experimental data. However, with the improvement of experimental methodologies, accurate affinities are becoming available.[4–9] Accurate gas phase cation-ligand affinities not only are relevant to interpretations in metal cation-ization mass spectrometry, they also provide a basic framework for understanding the *in vivo* interaction of metal cations with biologically relevant ligands or functional groups.[10]

Our group has been interested in obtaining accurate cation affinities for biologically relevant ligands. Recently, we have investigated the core size effect on the theoretical alkali metal cation (Li^+, Na^+, and K^+) affinities for short chain alcohols, as well as the ionization energies of alkali atoms. We have shown that in order to achieve good agreement with experimental ionization energies for Li, Na, and K, the $1s^2$, $2s^2 2p^6$, and $3s^2 3p^6$ electrons of these atoms has to be included in the electron correlation treatment.[11] With such treatment, the core size would be smaller than the default core size in popular *ab initio* packages like GAUSSIAN94, and our findings are also supported by other studies.[12] Accordingly, we have modified the G2(MP2,SVP) protocol by adopting the aforementioned smaller core sizes, and denote it as G2(MP2,SVP)–MSC/ASC.[11] The affinities determined by this modified protocol are in very good agreement with experimentally determined Li^+–alcohol and K^+–H_2O/NH_3/amide (Refs. 9 and 26) affinities. However, at the same time, we found that the theoretical Na^+–alcohol affinities were, on average, higher than the experimental values reported by Rogers and Armentrout by 15 kJ mol^{-1},[13,14] which is larger than the expected accuracy of the theoretical procedure employed. The object of the present paper is to resolve this discrepancy.

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One possible source of theoretical discrepancy could arise from the basis set superposition error (BSSE). Consider the formation of a species M^+L from M^+ and L. Prior to the formation of M^+L, the two reactants M^+ and L can only make use of its own basis set. In the complexed form, not only can M^+ (and L) make use of its own basis set, it can also gain access to the basis set on L (and M^+). This unbalance in the theoretical treatment of the reactant and product leads to an unphysical lowering of the electronic energy of the complexes, hence artificially enhancing the theoretical affinity.

The most often used strategy for correcting BSSE is via the full counterpoise (CP) method.[15,16] The CP correction is typically performed with uncorrected free ligand geometries. In the context of the calculation of M^+L affinities, it means that the geometry of the free ligand is assumed to be identical to that of the ligand in the complexed state. More recently, the CP method has been modified to take into the account of the change of ligand geometry due to complexation.[17,18]

In this work, we studied the affinities between the three alkali metal cations (Li$^+$, Na$^+$, and K$^+$) and 16 ligands (water, ammonia, eight alcohols, and six amides). Detailed analysis is carried out to understand how the level of theory, core size, and geometry could affect the magnitude of BSSE. The calculated affinities are further compared with existing experimental values so that a suitable level of theory can be recommended for future studies.

II. THEORETICAL METHODS

The lithium, sodium, and potassium cation (M^+) binding affinities of ligand (L) are defined as the enthalpy (ΔH) change of reaction 1 and calculated by Eq. (2):

$$M^+L \rightarrow M^+ + L, \tag{1}$$

$$\Delta H = E(M^+) + E(L) - E(M^+L). \tag{2}$$

The electronic energies, $E(M^+)$, $E(L)$, and $E(M^+ - L)$ in Eq. (2) were calculated at four different levels: G2(MP2,SVP)-FU, G2(MP2,SVP)-MSC/ASC, G2(MP2,SVP)-FC or G3. All these protocols aimed at reproducing the QCISD(T) energy of a particular target basis set using successive additivity approximations and the major difference between the four protocols lies in the core size used in the correlation treatment for the alkali metal cation. Briefly, ''FU'' (fully electron correlated) indicates that all electrons in the alkali metal cations are included in the electron correlation treatment, while ''FC'' (frozen core) employs the default alkali metal cation core size of the GAUSS-IAN94 package. The ''MSC/ASC'' model releases some of the ''FC'' core electrons into the valence shell so that the $1s^2$, $2s^2 2p^6$, and $3s^2 3p^6$ electrons of Li, Na, and K, respectively, are now included in the electron correlation treatment. Further details of these protocols can be found in our previous work[11] and their original references.[3,19]

In this paper, the BSSE was estimated using both the full counterpoise method of Boys and Bernadi[15] and the geometry corrected counterpoise method of Daza et al.[18] Here, we present the derivation of the geometry corrected counterpoise

method with a slightly different point of view from that of Daza et al. We follow the notation of $E_{\text{geom}}^{\text{basis}}(\text{species})$[18] to indicate that the electronic energy of the species is calculated using a particular geometry (either the geometry of the free species or that in the complexed state) with a particular basis set (either the basis set of the free species or that of the complex). Using this notation, the familiar Eq. (2) can be rewritten as

$$\Delta H = E_{M^+}^{M^+}(M^+) + E_L^L(L) - E_{M^+L}^{M^+L}(M^+L), \tag{3}$$

where the energy of the cation, the ligand and the cation-ligand complex are evaluated using their own basis sets in their individually optimized geometries.

Here, we correct for BSSE using the full counterpoise (CP) method. In the CP method, the energies of the cation, ligand, and the complex, are uniformly calculated using the basis set of the complex. We denote the CP corrected affinity as $\Delta H(\text{CP})$:

$$\Delta H(\text{CP}) = E_{M^+L}^{M^+L}(M^+) + E_{M^+L}^{M^+L}(L) - E_{M^+L}^{M^+L}(M^+L). \tag{4}$$

$\Delta H(\text{CP})$ can be related to ΔH [Eq. (3)] via a correction term, $\delta(\text{CP})$:

$$\delta(\text{CP}) = \Delta H - \Delta H(\text{CP})$$
$$= E_{M^+}^{M^+}(M^+) - E_{M^+L}^{M^+L}(M^+) + E_L^L(L) - E_{M^+L}^{M^+L}(L). \tag{5}$$

We can rearrange Eq. (5) to

$$\delta(\text{CP}) = [E_{M^+}^{M^+}(M^+) - E_{M^+L}^{M^+L}(M^+) + E_{M^+L}^L(L) - E_{M^+L}^{M^+L}(L)]$$
$$- [E_{M^+L}^L(L) - E_L^L(L)] \tag{6}$$
$$= \delta(\text{GCP}) - E_{\text{def}}. \tag{7}$$

Equation (6) suggests that two effects contribute to $\delta(\text{CP})$. The sum of the first four terms in Eq. (6) arises purely from basis set effects. This correction is free from geometry effect, and we denote this as $\delta(\text{GCP})$ as shown in Eq. (7). When the $M^+(L)$ complex gains access to the $L(M^+)$ basis set, its electronic energy decreases. As a result, $\delta(\text{GCP})$ is always positive. On the other hand, the energy difference between the last two terms in Eq. (6) corresponds to the energy deficit of the ligand upon complexation with the cation, and we simply call it the ''deformation energy,'' E_{def}, in Eq. (7). As the deformed ligand in the complexed form is always less stable than the free ligand, E_{def} is always positive. Hence, the sign of $\delta(\text{CP})$ will depend on the relative magnitude of $\delta(\text{GCP})$ and E_{def}. We denote the affinity obtained by geometry effect corrected CP as ($\Delta H(\text{GCP})$):

$$\Delta H(\text{GCP}) = \Delta H - \delta(\text{GCP}). \tag{8}$$

In this study, four protocols had been used to calculate the ΔH: G2(MP2,SVP)–FC, G2(MP2,SVP)–MSC/ASC, G2(MP2,SVP)–FU, and G3. Then, the $\delta(\text{CP})$ and $\delta(\text{GCP})$ calculated with the corresponding basis set and core sizes were subtracted from ΔH to obtain the $\Delta H(\text{CP})$ [Eq. (5)] and $\Delta H(\text{GCP})$ [Eq. (8)] terms, respectively. In this paper, we are interested in elucidating the effect of core size (fully
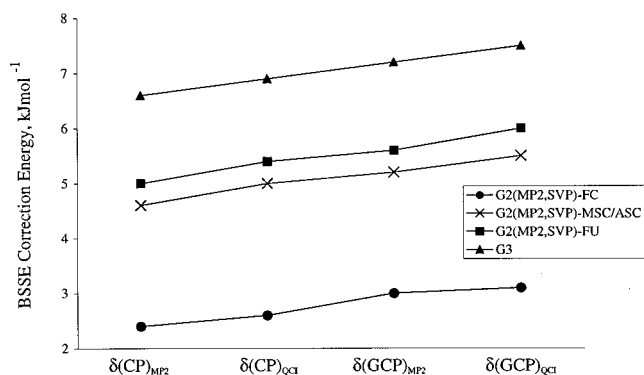
FIG. 1. Comparison of counterpoise correction [δ(CP)] and geometry corrected counterpoise correction [δ(GCP)], calculated at various levels of theories for Na^+-H_2O complex.

electron correlated, smaller and default core size), basis set [$6\text{-}311+G(3df,2p)$ and G3large]; and electron correlation method [MP2 and QCISD(T)] on δ(CP) and δ(GCP).

Standard *ab initio* molecular orbital calculations were carried out using the GAUSSIAN-94[20] and GAUSSIAN-98[21] package of programs on IBM RS6000, SGI Indigo 2, and Octane workstations. The potassium basis set developed by Blaudeau *et al.*[22] was used throughout this work.

III. RESULTS AND DISCUSSIONS

A. Counterpoise correction for Na^+-H_2O complex

In order to understand the underlying factors affecting BSSE, we considered the correction terms: δ(CP)$_{MP2}$, δ(CP)$_{QCI}$, δ(GCP)$_{MP2}$, and δ(GCP)$_{QCI}$, which correspond to the full counterpoise correction terms calculated with the MP2 and QCISD(T) Hamiltonian, and the geometry corrected counterpoise correction terms calculated with the MP2 and QCISD(T) Hamiltonian, respectively. At the same time, we varied the core size and basis set to match the corresponding target level of the Gaussian protocols of G2(MP2,SVP)–FC, G2(MP2,SVP)–MSC/ASC, G2(MP2,SVP)–FU, and G3. We have calculated these 16 correction terms for the alkali metal cation (Li^+, Na^+, and K^+) bound complexes with H_2O and NH_3 ligands. All the complexes were found to show very similar trends. As a representative example, the results for the Na^+-H_2O complex are illustrated in Fig. 1.

Given the same basis set and core size, we noted that δ(CP)$_{MP2}$ is within 1 kJ mol^{-1} of δ(CP)$_{QCI}$. Similar difference is found between δ(GCP)$_{MP2}$ and δ(GCP)$_{QCI}$. This suggests that, as far as the correction terms are concerned, even though the target level of the G2 and G3 protocols involve a QCISD(T) Hamiltonian, counterpoised correction at the MP2 level is already sufficient. Hence, for the rest of our discussions, we will only consider the correction at the MP2 level, and the subscripts in the δ(CP) and δ(GCP) notation will be omitted.

As expected, δ(GCP) is larger than δ(CP) (Fig. 1). In the case of Na^+-H_2O, this difference is quite small, around 1 kJ mol^{-1}. This is expected, as complexing an alkali metal cation to a small ligand like water is not likely to change the

geometry of the water molecule dramatically. However, we will show in the following discussion that geometry effect in counterpoise correction for even slightly larger systems are not negligible at all, and hence a geometry corrected counterpoise correction term is definitely needed in general.

It is commonly believed that smaller basis sets, due to their incompleteness, tend to yield larger BSSE than larger basis set. Comparing the four levels of calculation (Fig. 1), the magnitude for a given correction term follows the order

$$G2(MP2,SVP)-FC < G2(MP2,SVP)-ASC/MSC$$

$$\sim G2(MP2,SVP)-FU < G3.$$

The above trend may be viewed as counterintuitive as the basis set used in the G3 protocol is larger than that used in the G2-type protocol. However, it has already been pointed out that larger basis sets do not necessarily yield smaller counterpoise correction terms.[15] In the case of the alkali metal cation-ligand complexes, we observe a general positive correlation between the raw affinity, ΔH, with the magnitude of the counterpoise correction.

More importantly, it should be noted that δ(CP) and δ(GCP) are often not negligible in magnitude. While the calculated Na^+ affinity for water is approximately 95 kJ mol^{-1}, the largest correction term is 7 kJ mol^{-1} at the G3 level, which amounts to 7% of the calculated affinity. Moreover, as the target accuracy for G2 and G3 protocols is approximately 10 kJ mol^{-1}, a potentially significant correction term of this magnitude should not be overlooked.

B. Contribution to the counterpoise correction

We now wish to look into the details of what contribute to the counterpoise correction terms. We calculated the δ(CP) and δ(GCP) of alkali metal cations affinities for H_2O and NH_3, eight alcohols [methanol (MeOH), ethanol (EtOH), *n*-propanol (*n*-PrOH), *i*-propanol (*i*-PrOH), *n*-butanol (*n*-BuOH), *i*-butanol (*i*-BuOH), *s*-butanol (*s*-BuOH), and *t*-butanol (*t*-BuOH)], and six amides [formamide (F), *n*-methylformamide (MF), *n,n*-dimethylformamide (DMF), acetamide (A), *n*-methylacetamide (MA), and *n,n*-dimethylacetamide (DMA)]. We only tabulated the δ(CP) and δ(GCP) terms at the G2(MP2,SVP)–MSC/ASC level for these species in Table I and similar trends are observed in the other three levels of theory.

The results shown in Table I reveal the problem of using the Boys–Bernadi full counterpoise correction method.[15] For the 48 species tabulated in Table I, about one-third of them have a negative δ(CP). This means that, for these cases, applying the δ(CP) correction to ΔH will lead to an increase rather than the expected decrease of raw affinity. This is most significant and clearly demonstrated in the case of Li^+-n-BuOH, where the calculated δ(CP) value is -6.6 kJ mol^{-1}. While *n*-BuOH is an open chain in its free ligand state, the most stable Li^+-n-BuOH complex involves the alkyl chain of the ligand wrapping around the Li^+ so as to maximize binding due to ion-induced dipole interaction. This not only changes the dihedral angles, but some bond angles and bond lengths are also affected upon complexation (Fig. 2). These changes in geometry of *n*-BuOH between the free

TABLE I. Full counterpoise correction term $[\delta(CP)]$ and geometry corrected counterpoise correction term $[\delta(GCP)]$, and contribution of $\delta(GCP)$ from the metal cation $[\delta(GCP\_M)]$ and from the ligand $[\delta(GCP\_L)]$ at the G2(MP2,SVP)–MSC/ASC level of theory for various alkali metal cation-ligand complexes.

	G2(MP2,SVP)–MSC/ASC			
	$\delta(CP)$ (kJ mol^{-1})	$\delta(GCP)$ (kJ mol^{-1})	$\delta(GCP\_M)$ (kJ mol^{-1})	$\delta(GCP\_L)$ (kJ mol^{-1})
Li$^+$–H$_2$O	4.0	5.0	1.6	3.4
Li$^+$–NH$_3$	3.0	3.9	1.8	2.1
Li$^+$–MeOH	1.3	4.8	1.8	3.0
Li$^+$–EtOH	1.8	6.0	2.5	3.5
Li$^+$–n-PrOH	−5.5	7.4	3.4	4.0
Li$^+$–i-PrOH	1.2	6.3	2.8	3.5
Li$^+$–n-BuOH(cyclic)	−6.6	8.6	4.2	4.4
Li$^+$–n-BuOH(linear)	1.1	6.9	3.2	3.7
Li$^+$–i-BuOH	−5.2	7.6	3.7	3.9
Li$^+$–s-BuOH	1.2	6.4	2.9	3.5
Li$^+$–t-BuOH	0.8	6.6	3.1	3.5
Li$^+$–F	−2.0	5.1	2.1	3.0
Li$^+$–MF	−1.7	5.3	2.2	3.1
Li$^+$–DMF	−3.7	5.6	2.4	3.2
Li$^+$–A	−2.3	5.4	2.4	3.0
Li$^+$–MA	−1.8	5.5	2.5	3.0
Li$^+$–DMA	−5.0	5.8	2.6	3.2
Na$^+$–H$_2$O	4.6	5.1	2.4	2.7
Na$^+$–NH$_3$	4.2	4.9	2.9	2.0
Na$^+$–MeOH	3.5	5.5	3.2	2.3
Na$^+$–EtOH	5.0	7.5	4.8	2.7
Na$^+$–n-PrOH	2.5	6.3	3.9	2.4
Na$^+$–i-PrOH	4.9	7.8	5.2	2.6
Na$^+$–n-BuOH(cyclic)	−0.8	10.3	7.1	3.2
Na$^+$–n-BuOH(linear)	4.8	8.7	5.9	2.8
Na$^+$–i-BuOH	3.6	6.5	4.1	2.4
Na$^+$–s-BuOH	5.0	8.1	5.4	2.7
Na$^+$–t-BuOH	4.9	8.4	5.7	2.7
Na$^+$–F	1.5	6.1	3.8	2.3
Na$^+$–MF	2.2	6.4	4.1	2.3
Na$^+$–DMF	0.9	6.8	4.5	2.3
Na$^+$–A	2.1	6.6	4.4	2.2
Na$^+$–MA	3.0	6.9	4.7	2.2
Na$^+$–DMA	−0.2	7.2	4.9	2.3
K$^+$–H$_2$O	1.5	1.9	0.5	1.4
K$^+$–NH$_3$	0.5	1.6	0.6	1.0
K$^+$–MeOH	0.5	1.8	0.8	1.0
K$^+$–EtOH	0.5	2.2	1.0	1.2
K$^+$–n-PrOH	−1.0	2.3	1.1	1.2
K$^+$–i-PrOH	0.3	2.3	1.1	1.2
K$^+$–n-BuOH(cyclic)	−7.0	2.9	1.5	1.4
K$^+$–n-BuOH(linear)	−0.5	2.5	1.3	1.2
K$^+$–i-BuOH	0.1	2.4	1.2	1.2
K$^+$–s-BuOH	0.3	2.4	1.2	1.2
K$^+$–t-BuOH	0.1	2.5	1.3	1.2
K$^+$–F	−1.0	2.0	1.0	1.0
K$^+$–MF	−0.4	2.1	1.1	1.0
K$^+$–DMF	−1.6	2.2	1.2	1.0
K$^+$–A	−0.5	2.1	1.1	1.0
K$^+$–MA	0.2	2.2	1.2	1.0
K$^+$–DMA	−3.1	2.3	1.3	1.0

and the complexes lead to a qualitatively incorrect estimation of BSSE. For comparison, we also calculated the $\delta(CP)$ for a less stable Li$^+$–n-BuOH complex where the n-BuOH skeleton more or less retains its ''linear'' conformation in the free ligand. In this case, the full counterpoise correction term is comparable to other alcohols that do not cyclize after complexation (MeOH, EtOH, etc.).

Even when there is no obvious changes in the ligand geometry upon complexation, the $\delta(CP)$ term can still be negative as in the case of all the Li$^+$–amide complexes. The most notable example in the amide series is that of Li$^+$–DMA (-5.0 kJ mol^{-1}) (Fig. 2). We can understand this by inspecting Table I. Here we observe that the $\delta(GCP)$ for amides are smaller than that of alcohols in general. Hence, relatively small changes in geometry (i.e., E_{def}) can lead to negative $\delta(CP)$ values [Eq. (7)]. We noted that in the case of Li$^+$–(NH$_3$)$_n$ (where $n=1$ to 4) complexes, the MP2 deformation energies could be twice as large as the value obtained at the theoretically more sophisticated MP4 level.[23] However, our calculated E_{def} for Li$^+$–NH$_3$ at the MP2 and QCISD(T) levels using the 6-311+G(3df,2p) basis only differs by 0.3 kJ mol^{-1}. We also investigated a M^+–amide complex, Li$^+$–formaide (Li$^+$–F), which has a negative $\delta(CP)$ with no obvious geometrical change upon complexation. The E_{def} for Li$^+$–F calculated at MP2, MP4, and QCISD(T), with the same core size and basis sets, were 7.2, 8.1, and 7.7 kJ mol^{-1}, respectively. Because of these large E_{def}, it appears that $\delta(CP)$ will remain negative, regardless of the level of calculation. Given this, we concluded that BSSE correction at the MP2 level is indeed adequate for the Gaussian protocols.

It is pleasing to note that when geometry effect is considered, a much more reasonable correction term is obtained. The value of $\delta(GCP)$ ranges from 1.6 to 10.3 kJ mol^{-1} and is generally small for complexes of K$^+$ but large for Na$^+$ complexes. We have further broken the $\delta(GCP)$ term down into its two components: $\delta(GCP\_M)$ and $\delta(GCP\_L)$ accounting for the contribution from alkali metal cation and the ligand, respectively,

$$\delta(GCP) = [E_{M^+}^{M^+}(M^+) - E_{M^+L}^{M^+}(M^+)]$$
$$+ [E_{M^+L}^{L}(L) - E_{M^+-L}^{M^+-L}(L)]$$
$$= \delta(GCP\_M) + \delta(GCP\_L). \quad (9)$$

We observe two trends here. For a given complex, $\delta(GCP\_M)$ follows the order of Na$^+$>Li$^+$>K$^+$, while $\delta(GCP\_L)$ increases from Li$^+$>Na$^+$>K$^+$.

We suggest that two factors are at work here, namely, the number of basis functions and the distances between the metal cation and the binding sites. In terms of the number of basis functions, the number of basis for K$^+$ is largest amongst the three cations. Hence, incorporating the ligand basis set is likely to have the least effect on affinity. At the same time, as the distance between K$^+$ and the binding site is also the longest in the three cations considered, it is comparatively more difficult for the K$^+$ ion to utilize the ligand's basis set effectively. Both factors favor a small BSSE correction for K$^+$ complexes. Using the same argument, one expects the BSSE correction for Li$^+$ to be larger than that for Na$^+$, and this trend is observed in the $\delta(GCP\_L)$ term. However, either $\delta(GCP\_M)$ is too small for Li$^+$ or too large for Na$^+$, so that a reversal of order is observed here. The

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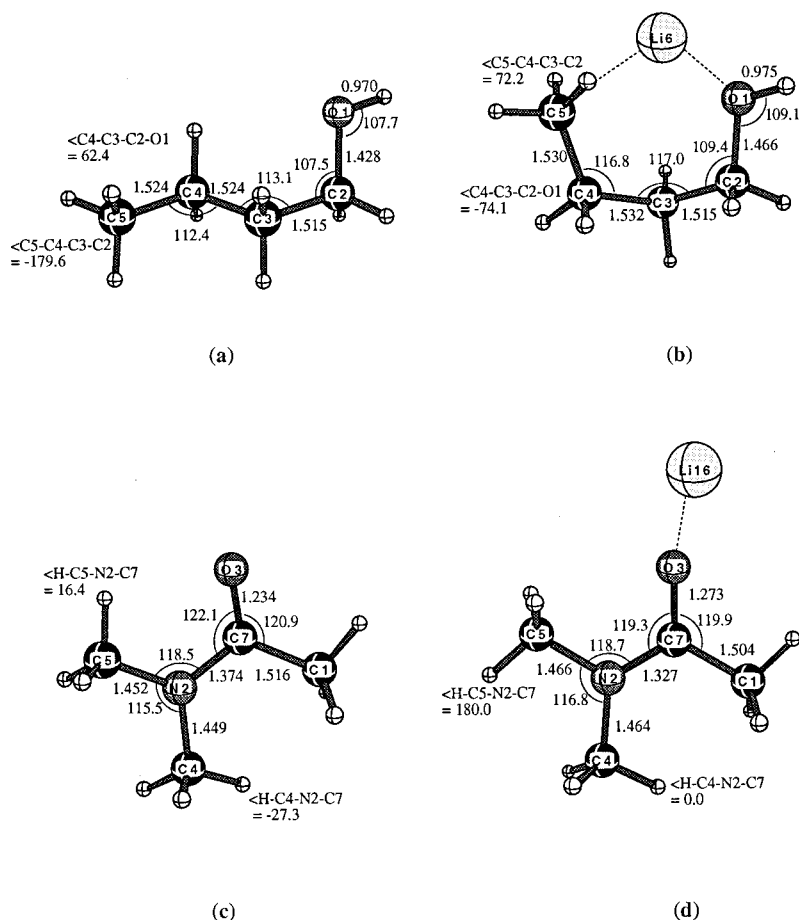
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FIG. 2. Geometry of (a) n-BuOH, (b) Li^+-n-BuOH, (c) DMA, and (d) Li^+-DMA. Bond lengths and angles are in units of Å and degrees (°), respectively.

same trend is observed at other levels of theory where the $\delta(GCP\_M)$ term for Na^+ is larger than that of Li^+, but the origin of this observation is not clear.

Finally, for a given series of ligands, we found very good linear correlation between $\delta(CP)$ and the deformation energy, E_{def}. For the amide series (Fig. 3), the R^2 for Li^+, Na^+, and K^+ are 0.99, 0.91, and 0.99, respectively. It suggests that the basis set effects on $\delta(CP)$, i.e., $\delta(GCP)$ for the

amides series are nearly constant [Eq. (7)]. This is apparently true for a series of structurally similar or related ligands.

C. Comparison with experimental affinity

In the discussions so far, we have shown that BSSE is not of negligible magnitude. We have also analyzed how various factors contribute to BSSE correction. The remaining question is: does one need to correct for BSSE to obtain good agreement with experimental values? In order to answer this question, we have summarized our best theoretical Li^+, Na^+, and K^+ affinities for 16 ligands in Table II. Experimental affinities are also tabulated if they are available.

The case for potassium complexes is the simplest. The $\delta(GCP)$ corrected G2(MP2,SVP)–ASC affinities are in excellent agreement with existing experimental values. However, as $\delta(GCP)$ is generally small (around 2 kJ mol^{-1}), and as long as the appropriate potassium cation core size of [Ne] is used, the BSSE correction appears to be not essential.

All six theoretical[27] estimates for Li^+-ligand complexes are in good agreement with experimental values. The best level of theory appears to be G3(GCP) and G2(MP2,SVP)– FC, with mean absolute deviation of 3.0 and 3.1 kJ mol^{-1}, respectively.

The situation is most complicated for Na^+ containing complexes. By comparing with the well-established ionization energy of sodium atom, we have shown previously that the appropriate core size for Na^+ should be the same as that
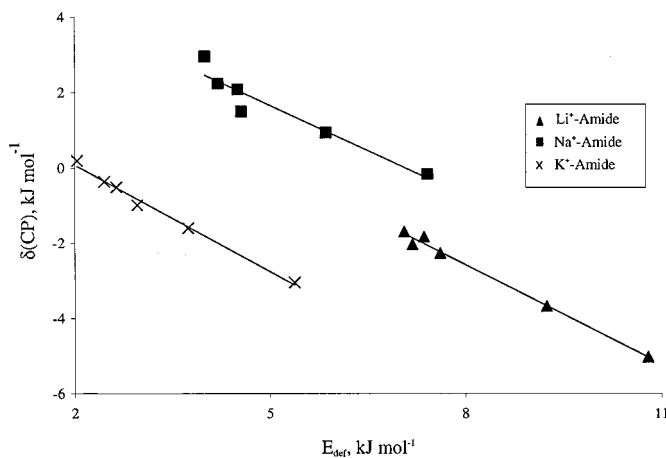

FIG. 3. The relation between counterpoise correction terms [$\delta(CP)$] and deformation energy (E_{def}) for Li^+-, Na^+-, and K^+-amide complexes.

TABLE II. Theoretical affinities[a] (ΔH, at 0 K) for the Li$^+$, Na$^+$, and K$^+$ containing complexes. Experimental affinities (ΔH_{expt}) are included if available.

	ΔH (kJ mol^{-1})	ΔH_{expt} (kJ mol^{-1})
Li$^+$–H$_2$O	131.3	138.1 (8)[b]
Li$^+$–NH$_3$	152.1	159.0 (8)[b]
Li$^+$–MeOH	147.2	155.0 (8.5)[c]
Li$^+$–EtOH	158.7	163.5 (6.5)[c]
Li$^+$–n-PrOH	167.4	170.3 (8.6)[c]
Li$^+$–i-Proh	166.1	172.8 (7.5)[c]
Li$^+$–n-Buoh (cyclic)	175.8	177.5 (8.0)[d]
Li$^+$–n-BuOH (linear)	166.8	
Li$^+$–i-Buoh	169.8	174.0 (8.0)[d]
Li$^+$–s-Buoh	169.7	174.3 (8.9)[c]
Li$^+$–t-Buoh	171.8	178.2 (10.2)[c]
Li$^+$–F	195.7	195.7[e]
Li$^+$–MF	209.2	209.2[e]
Li$^+$–DMF	220.0	220.0[e]
Li$^+$–A	211.7	209.7[e]
Li$^+$–MA	222.5	221.3[e]
Li$^+$–DMA	230.1	232.3[e]
Na$^+$–H$_2$O	91.2	95.0 (8)[f]
Na$^+$–NH$_3$	105.3	115.2[g]
Na$^+$–MeOH	101.3	91.7 (5.7)[d]
Na$^+$–EtOH	110.2	102.0 (3.7)[d]
Na$^+$–n-PrOH	109.7	108.0 (4.1)[d]
Na$^+$–i-Proh	115.4	113.2 (4.3)[d]
Na$^+$–n-Buoh (cyclic)	115.3	109.4 (4.7)[d]
Na$^+$–n-BuOH (linear)	116.2	
Na$^+$–i-Buoh	111.3	105.2 (5.7)[d]
Na$^+$–s-Buoh	118.2	117.2 (5.1)[d]
Na$^+$–t-Buoh	119.3	116.5 (4.1)[d]
Na$^+$–F	140.9	138.5[h]
Na$^+$–MF	150.9	148.5[h]
Na$^+$–DMF	158.7	156.3[h]
Na$^+$–A	152.7	148.6[h]
Na$^+$–MA	160.6	157.5[h]
Na$^+$–DMA	165.5	164.5[h]
K$^+$–H$_2$O	65.5	67.8[i]
K$^+$–NH$_3$	72.0	71.0[i]
K$^+$–MeOH	73.9	
K$^+$–EtOH	80.5	
K$^+$–n-PrOH	80.6	
K$^+$–i-Proh	84.6	
K$^+$–n-Buoh (cyclic)	80.0	
K$^+$–n-BuOH (linear)	85.3	
K$^+$–i-Buoh	83.2	
K$^+$–s-Buoh	86.9	
K$^+$–t-Buoh	88.2	
K$^+$–F	109.2	109.3[h]
K$^+$–MF	117.7	116.7[h]
K$^+$–DMF	123.9	123.6[h]
K$^+$–A	118.7	118.7[h]
K$^+$–MA	125.6	124.8[h]
K$^+$–DMA	129.2	129.1[h]

[a]Theoretical affinities obtained at the G3(GCP) level for complexes containing Li$^+$,Na$^+$; and at the G2(MP2,SVP)–ASC(GCP) levels for K$^+$ containing complexes. See Ref. 27.
[b]Reference 4.
[c]Reference 5.
[d]Reference 14.
[e]Reference 8.
[f]Reference 24.
[g]Reference 25.
[h]Reference 9.
[i]Reference 26.

of helium atom.[11] However, this core size leads to an increase in theoretical affinity so that both G2(MP2,SVP)–MSC and G3 values are systematically too high, with maximum error of 15.4 and 18.2 kJ mol^{-1}, respectively. Applying δ(GCP) corrections to these two levels decrease the raw affinities so that the maximum deviation is reduced to 9.0 and 9.6 kJ mol^{-1}, respectively. Interestingly, the increase of affinity due to core size effect is very similar in magnitude to the decrease of affinity due to the δ(GCP) corrections. As a result, the computationally least expensive G2(MP2,SVP)–FC without GCP correction[27] level also yields good agreement with existing experimental values, with mean absolute deviation of 3.0 kJ mol^{-1}.

IV. CONCLUSION AND RECOMMENDATION

In this paper, we have given a detailed analysis on how various factors affect the full counterpoise correction for basis set superposition error in the Gaussian-type protocols. We found that applying the standard full counterpoise correction often leads to misleading results. One can correct for this by taking the geometry effect into account.

As the δ(GCP) term for K$^+$ complexes are negligible, theoretical affinities calculated by G2(MP2,SVP)–ASC and G2(MP2,SVP)–ASC(GCP) protocols are both in good agreement with existing experimental K$^+$ affinities. For Li$^+$ and Na$^+$ complexes, δ(GCP) values are in general large, and of similar magnitude but opposite in sign to the core size effect. As a result, we found that both the G3(GCP) and G2(MP2,SVP)–FC protocols could yield Li$^+$ and Na$^+$ affinity values which are in good agreement with experimental data.

Finally, we would like to stress that while the conclusions drawn in this paper are based on Gaussian-type protocol calculations, the conceptual framework developed here is applicable to quantum chemical calculations in general.

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[27] See EPAPS Document No. E-JCPSA6-114-306117 for theoretical affinities obtained at G2(MP2,SVP) and G3 levels without the GCP correction. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.