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An Improved Theoretical Sodium Cation Affinity Scale?

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We have used two novel “model chemistry” composite computational techniques, CPd-G2thaw and c-SLW3, to determine a sodium cation affinity (SCA) scale comprising 38 small ligands. The CPd-G2thaw and c-SLW3 methods have been developed to yield accurate thermochemical parameters for sodium-containing compounds by redressing shortcomings of existing computational techniques for such compounds. The SCA scale established here shows excellent internal consistency between CPd-G2thaw and c-SLW3 values. These theoretical SCA values are consistently higher (by an increment of 2.8 ± 1.3 kJ mol^{-1}) than the set of precise high-pressure mass spectrometry and Fourier transform ion cyclotron values recently reported and generally also exceed the recent threshold collision-induced dissociation values. Our values are typically 2 to 3 kJ mol^{-1} lower than those of a small set of previously reported theoretical “benchmark” values.

1. Introduction

Ligation of the gas-phase sodium ion[1] is important in contexts as diverse as the facile generation of ionized biomolecules in a variety of analytical techniques,[2−6] the persistence of “sporadic-E layer” effects within the Earth’s upper atmosphere,[7−9] the examination of solvent effects in metal-ion complexation,[10−12] and the possible formation of metal-containing molecules within extraterrestrial environments.[13−16] The thermochemistry of sodium ion association reactions is most conveniently expressed in terms of a given neutral’s sodium cation affinity (SCA), which, by analogy with the concept of proton affinity,[17,18] is defined as the enthalpy change associated with reaction 1:

$$\mathrm{NaX^+} \rightarrow \mathrm{Na^+} + \mathrm{X} \qquad (1)$$

Experimental measurement of SCA values has been ongoing for more than three decades,[19] involving a variety of methods including high-pressure mass spectrometric equilibrium studies,[19−25] temperature-dependent equilibrium measurements,[26] collision-induced dissociation,[27−31] Fourier transform ion cyclotron resonance measurements,[32] the kinetic method used by Cooks and co-workers,[33] and flame mass spectrometry.[34] Despite the comparatively large body of SCA measurements that now exists, a significant degree of uncertainty still exists regarding absolute SCA values, with several recent values obtained by the high-pressure mass spectrometry (HPMS),[25] Fourier transform ion cyclotron (FT-ICR),[32] and threshold collision-induced dissociation[31] techniques lying considerably below the recommended SCA values from earlier studies.[20−24]

Theoretical quantum chemical methods, which have proved valuable in resolving discrepancies between competing proton affinity measurements,[35−37] do not fare very well in the SCA arena; large differences are evident between the SCA values calculated by using generally reliable ab initio techniques. For example, the mean deviation between G3 and CBS-Q values for the SCAs of small molecules exceeds 10 kJ mol^{-1} [31]; G3 and CBS-Q are arguably the two most accurate, widely used “model chemistry” techniques for molecules and ions comprising first- and second-row atoms,[38,39] and the mean deviation between SCA values obtained by these two methods is much greater than that typically seen for their performance on other thermochemical parameters. The G3 SCA values show particularly poor performance against the latest experimental values[31]; Siu et al.[40] have recently argued that this is a consequence of the absence of any correction for basis-set superposition error (BSSE) in any model chemistry techniques, and have shown[40] that incorporation of such a correction in SCA calculations leads to dramatically improved performance for G3, but yielding poorer values in G2 and related methods. McMahon and Ohanessian[32] have also found that correction for BSSE is crucial in obtaining reliable calculated SCA values. Feller[41] has conversely concluded, from a complete-basis-set extrapolation of calculations performed by using large core/valence correlation-consistent basis sets, that inclusion of a BSSE correction has an adverse effect. Furthermore, despite a growing recognition[42−46] that “frozen-core” calculations on sodium-containing species can produce extremely large errors (because the “core” Na 2s and/or 2p orbitals may lie higher in energy than one or other “valence” orbital on a less electropositive atom), such frozen-core methods are still used routinely in SCA calculations, with the most recently recommended methods, G2(MP2, SVP) and G3(GCP), [40] both featuring frozen-core single-point calculations.

This study was motivated, in part, by the apparent failure of an earlier “improvement” to G2 theory, G2(thaw),[44,45] which sought to yield better thermochemical values for sodium-containing species by inclusion of a correlation space more appropriate than the standard “frozen core” featured in G2 itself. Although G2(thaw) undeniably performs better than G2 for calculating the SCA values of several fluorine-containing ligands,[44,45] it has also become apparent[47] that G2(thaw) otherwise offers poorer agreement with the most recent experimental values[25,31,32] than does the less rigorous standard G2 method.

2. Theoretical Methods

2.1. CPd-G2thaw. The CPd-G2thaw technique is a modification of standard G2 theory, and is most usefully defined with

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TABLE 1: Sodium Ion and Ligand Contributions (in kJ mol^{-1}) to the Counterpoise Corrections Obtained with Standard (B4G) and with Decontracted (d-B4G) Basis Sets, Applicable to BSSE-Corrected Calculations at the G2(thaw) and dG2thaw Levels of Theory

	Δ_{CP}(MP2/B4G)[a]		Δ_{CP}(MP2/d-B4G)[a]		Δ_{CP}(QCISD(T)/d-B4G)[a]	
ligand (X)	(Na^+)	(X)	(Na^+)	(X)	(Na^+)	(X)
H_2	−0.76	−0.29	−0.20	−0.31	−0.21	−0.28
He	−0.61	−0.53	−0.23	−0.54	−0.24	−0.58
CH_4	−3.35	−0.73	−1.04	−0.78	−1.08	−0.80
NH_3	−5.34	−2.00	−0.91	−2.11	−0.94	−2.23
H_2O	−4.85	−2.72	−0.83	−2.82	−0.86	−2.98
HF	−4.78	−2.45	−0.71	−2.48	−0.74	−2.67
Ne	−3.74	−2.98	−0.46	−3.10	−0.48	−3.21
PH_3	−4.42	−2.51	−0.71	−2.60	−0.73	−2.69
H_2S	−4.56	−3.23	−0.76	−3.36	−0.78	−3.59
HCl	−4.45	−3.75	−0.70	−3.93	−0.72	−4.22
Ar	−4.03	−2.10	−0.56	−2.22	−0.58	−2.42

[a] Counterpoise correction contribution at the indicated level of theory (in kJ mol^{-1}), with assignment of a "thawed" correlation space as detailed in the text.

reference to the structure of the G2 method itself. The G2 total energy can be expressed as

$$
\begin{aligned}
E_0(\mathrm{G2}) = {} & \mathrm{QCISD(T)/B1G} + \mathrm{MP2/B1G} - 2(\mathrm{MP4SDTQ/B1G}) \\
& + \mathrm{MP4SDTQ/B2G} - \mathrm{MP2/B2G} \\
& + \mathrm{MP4SDTQ/B3G} - \mathrm{MP2/B3G} \\
& + \mathrm{MP2/B4G} \\
& + E_{\mathrm{ZPE}} + \mathrm{HLC}, \qquad (2)
\end{aligned}
$$

where the basis sets B1G to B4G are, respectively, 6-311G**, 6-311+G**, 6-311G(2df,p), and 6-311+G(3df,2p), where all single-point calculations used in expression 2 are frozen-core values, in which only valence electrons are correlated, and where the zero-point vibrational energy (E_{ZPE}) and the higher-level correction (HLC) are as defined in the original reference.[48] The CPd-G2thaw method differs from G2 as follows.

1. All single-point calculations in CPd-G2thaw include the Na 2s and 2p orbitals within the correlation space, from which other "core" orbitals are excluded. This mode of correlation is subsequently identified as "thaw", to distinguish this method from the "frozen-core" or "full-correlation" approaches.

2. The largest basis set used is d-B4G instead of B4G, although these basis sets differ only for sodium; the standard G2 basis of 6-311+G(3df,2p) is retained for other atoms. The d-B4G basis for Na is modified from 6-311+G(3df); the second set of contracted s functions, and the second set of contracted p functions,[49] are decontracted, effecting a conversion from [631111+1/42111+1/111/1] to [61111111+1/411111+1/111/1]. This decontraction significantly improves the description of the sodium "inner-valence" 2s and 2p orbitals in calculations featuring electron correlation.

3. A geometry-corrected counterpoise correction, Δ_{CP}, is applied to the Na^+/ligand-binding energy obtained via expression 2. This correction

$$\Delta_{CP} = E_e(\underline{\mathbf{Na}}^+X) - E_e(\underline{\mathbf{Na}}^+) + E_e(\underline{\mathbf{X}}Na^+) - E_e(\underline{\mathbf{X}}) \qquad (3)$$

is obtained by calculations at the MP2(thaw)/d-B4G level of theory, where the various fragments Na^+ and X are composed of real (bold, underlined) or "ghost" (italic) atoms within the optimized NaX^+ molecular ion geometry. We have found that the MP2 level of theory yields correction factors very close to the CCSD(T) or QCISD(T) value with the same basis set. This result echoes the finding of Siu et al.[40] and justifies the use of a comparatively modest level of theory to correct for BSSE in a calculation designed to emulate the QCISD(T)/6-311+G(3df,2p) level overall.

Initial tests of the performance of this method have been very encouraging. The Na^+ component of the BSSE correction Δ_{CP}, in Na^+/ligand adduct ions (see Table 1), is uniformly much smaller in magnitude (by a factor of 2.5 to 7.5) than that obtained with the standard 6-311+G(3df) basis for sodium, indicating that the decontracted d-B4G basis for sodium gives a much better treatment of Na^+ than the standard basis. Modification of the sodium basis has little impact on the ligand component to the counterpoise correction (also shown in Table 1), with the result that the total absolute counterpoise correction for the d-B4G basis set is generally a factor of 2 (or more) below that for the standard B4G basis, for which the Na^+ term is the dominant component. The improvement in the sodium basis set is also reflected in calculations on the sodium ionization energy, for which CPd-G2thaw performs extremely well [IE(Na) = 5.103 eV, cf. the 5.139 eV literature value],[50] compared with the "standard" G2 value of 4.949 eV[48] and the G2(thaw) value of 5.066 eV.[45]

2.2. c-SLW3. The c-SLW3 method is defined by the formula

$$E_0(\text{c-SLW3}) = \mathrm{CCSD(T)/B1SLW} + \mathrm{MP2/B2SLW} - \mathrm{MP2/B1SLW} + E_{\mathrm{ZPE}}, \qquad (4)$$

where the constituent single-point CCSD(T) and MP2 calculations (all using a thawed correlation space as in CPd-G2thaw) are performed on species optimized at the B3-LYP/B1SLW level of theory; zero-point energy is also determined at B3-LYP/B1SLW, and is unscaled. The B2SLW basis set is aug-cc-PVTZ (except for sodium, for which the AVTZ basis of Soldán et al.[51] is used), whereas the B1SLW basis is cc-PVTZ (except for sodium, for which B1 equals AVTZ[51] with the outermost sp, d, and f functions removed). Counterpoise correction to the NaX^+ total energy is applied, in a manner entirely analogous to CPd-G2thaw, via MP2(thaw)/B2SLW calculations. The "additivity assumption" implicit in eq 4, that is, the method's ability to emulate a calculation at the CCSD(T)thaw/B2SLW level of theory, holds to within ±0.75 mHartrees (~2 kJ mol^{-1}) for single-point calculations on small ligands or Na-containing adduct ions, and to within ±1 kJ mol^{-1} in the resulting sodium cation affinities (see Table 2). Note that there is generally a significantly smaller error in additivity for the calculated SCA than for the ligand or adduct ion total energy because of cancellation of errors in the SCA determination.

TABLE 2: Deviations from Additivity of the c-SLW3 Method for Small Ligands and Adduct Ions

ligand (X)	$\Delta_{add}(X)^a$ (mHartrees)	$\Delta_{add}(NaX^+)^a$ (mHartrees)	$\Delta_{add}(SCA)^a$ (kJ mol^{-1})
H_2	−0.078	−0.039	−0.07
He	−0.148	−0.095	−0.11
CH_4	0.022	0.053	−0.05
NH_3	−0.177	0.083	−0.65
H_2O	−0.231	0.118	−0.88
HF	0.122	0.407	−0.72
Ne	0.587	0.704	−0.28
PH_3	0.104	0.139	−0.06
H_2S	0.249	0.332	−0.19
HCl	0.339	0.417	−0.17
Ar	0.451	0.492	−0.08
(Na^+)		0.012	

[a] Deviation from additivity, E_e(c-SLW3) − E_e(CCSD(T)/B2SLW), in the indicated units. The target B2SLW basis set is the AVTZ basis of Soldán et al.[51] for Na, and aug-cc-PVTZ for other atoms[68]; in all calculations, a "thawed" correlation space (i.e., Na 2s and 2p orbitals correlated, but other "core" orbitals frozen) was used.

TABLE 3: Comparison of "Model Chemistry" Results for the Sodium Cation Affinities of Water, Hydrogen Fluoride, and Neon

method^a	SCA^b H_2O	HF	Ne
MP2(full)/6-311+G(2d,2p)^c	89.4	61.7	2.3
G2(MP2,SVP)	88.7	−109.5	−153.5
G2(MP2)	94.2	−108.4	−152.1
G2	88.8	−119.0	−162.0
G2(GCP)	86.1	−121.5	−164.8
G2QCI	89.7	−117.3	−161.5
G2QCI(GCP)	86.8	−120.0	−164.4
G2(thaw)	98.3	69.2	11.0
G2(thaw)(GCP)	90.7	62.0	4.3
G2QCI(thaw)	99.0	70.0	9.0
G2QCI(thaw)(GCP)	91.4	62.7	2.4
CBS-Q	88.8	−126.8	−177.3
CBS-Q(G98)^d	88.7	−127.3	−177.8
G3(noFULL)	90.3	−96.0	−137.9
G3	98.4	56.0	1.0
G3(GCP)	91.2	48.0	−5.2
G3QCI^e	99.7	72.0	10.1
G3QCI(GCP)	92.2	63.6	3.5
G3(thaw)	98.7	71.2	11.0
G3(thaw)(GCP)	88.2	59.6	0.4
G3QCI(thaw)	99.1	71.4	9.7
G3QCI(thaw)(GCP)	88.7	59.9	−0.5
CPd-G2thaw	90.8	62.1	4.2
c-SLW3	91.4	63.1	4.6

[a] Standard model chemistry methods are as defined in the literature.[48,53,69−71] Nonstandard methods, identified by (thaw) and/or by (GCP), are modified from these methods by incorporation of a "thawed" correlation space and/or by implementation of a GCP as outlined in the text. [b] Sodium cation affinity in kilojoules per mole. [c] Incorporating a counterpoise correction for BSSE, as recommended by Hoyau et al.[25] [d] The Gaussian-98 implementation[52] of the CBS-Q method differs from the method as defined in ref 53. See text for discussion. [e] This method (abbreviated as G3QCI, by analogy with G2QCI)[70] is equivalent to calculation at the QCISD(T)(full)/G3Large[71] level of theory.

All calculations reported in this article were performed with the GAUSSIAN98 program suite.[52]

3. Results and Discussion

3.1. Critique/Appraisal of Existing Theoretical Methods. It is now reasonably well established[42−46] that inclusion of the sodium "inner-valence" orbitals (2s and 2p) within the correlation space is necessary, in particular, to obtain reliable results for species containing Na^+ and oxygen, fluorine, or neon; and yet several widely used quantum chemical methods [including some methods specifically recommended for SCA calculations, such as CBS-Q and G2(MP2,SVP)][31,40] are largely or wholly built around single-point post-Hartree−Fock "frozen-core" calculations in which these sodium "inner-valence" orbitals are not correlated. The hazards associated with use of the frozen-core approximation in SCA calculations are illustrated by the SCA values for H_2O, HF, and Ne as listed in Table 3, and as discussed below.

3.1.1. Model Chemistries. The three "standard" ab initio model chemistry methods, G2, CBS-Q, and G3, differ in their treatment of Na 2s and 2p electron correlation. Only G3 contains any single-point calculations [an MP2(full) calculation using the "G3Large" basis set] in which the Na 2s and 2p orbitals are included in the correlation space. An empirical factor in CBS-Q attempts to redress the lack of explicit sodium inner-valence correlation in the constituent single-point calculations: this correction factor, ΔE_{core}

$$\Delta E_{core}\ (\text{mHartrees}) = 3.92\ q_{Na} + 2.83\ {q_{Na}}^2, \qquad (5)$$

where q_{Na} is the Mulliken charge on Na obtained in the 6-31G† basis calculation, was obtained by fitting CBS2 values of IE(Na) and EA(Na) to experimental values.[53] Although inclusion of this correction factor ensures that CBS-Q[54] delivers a much better value (5.128 eV) than does G2 (4.949 eV) for the ionization energy of sodium (literature value = 5.139 eV),[50] it cannot compensate for the inappropriate assignment of valence orbitals in the CBS-Q frozen-core calculations. Consequently, CBS-Q delivers large *negative* values for the sodium cation affinities of HF and Ne (see Table 3), parameters that must (according to the fundamental principles of electrostatics) have *positive* values by virtue of the attractive ion/dipole and ion/induced dipole interactions. A similar failure of G2 for the SCAs of HF and Ne is evident, as reported previously.[45] The G3 method fares better on the SCAs of these problematic species (see Table 3), and on IE(Na) (5.114 eV), but otherwise yields SCA values that are systematically about 10−15 kJ mol^{-1} higher than the experimental values obtained by HPMS, FT-ICR, and guided ion beam (GIB) studies.[25,31,32]

Siu et al.[40] recently reported that the generally good performance of standard G2 for sodium cation affinities (when assessed against the most recent experimental results)[31] arises from a fortuitous cancellation of errors. The errors concerned are the neglect of BSSE [which causes an overestimation in SCA values by ∼5−10 kJ mol^{-1} in most cases, as diagnosed by geometry-corrected counterpoise correction (GCP) calculations] and neglect of sodium inner-valence correlation (which typically leads to SCA values ∼8 kJ mol^{-1} lower than those obtained when the Na 2s and 2p electrons are systematically included in the correlation space).[55] Sodium inner-valence correlation is generally better accommodated within G3, but neglect of BSSE in this method leads to overestimated SCA values. When a GCP correction for BSSE is included, G3 delivers SCA values closer to the recent experimental values in most cases,[40] but now yields a *negative* SCA(Ne) value (see Table 3) because of inappropriate core orbital assignment in its constituent frozen-core calculations.[56]

For a Na^+/ligand adduct NaX^+, there are two components of the BSSE, which we may denote $\delta(\underline{\mathbf{Na}}^+X)$ and $\delta(\underline{\mathbf{X}}Na)$. In GCP calculations,[40] these two components to the BSSE (which are of approximately equal value for SCA determinations, within the G3 protocol) represent the improved description of both the Na^+ and X constituent fragments within the adduct ion because of the accessibility to either fragment of basis functions on the neighboring fragment. The occurrence of a significant Na^+ component, $\delta(\underline{\mathbf{Na}}^+X)$ (which Siu et al.[40] note is systematically larger in magnitude than both the Li^+ and K^+ components in calculations on adduct ions containing these alkali metals), is troubling. This is a closed-shell metal ion that should make very little use of outer basis functions, and should already be well described by an atomic basis set such as 6-311+G(3df) (as in G2) or the more extensive G3Large basis, without requiring access to basis functions on neighboring atoms. In this respect, the comparatively large $\delta(\underline{\mathbf{Na}}^+X)$ term in SCA calculations (for the largest basis sets used, respectively, in G2, in CBS-Q, or in G3) suggests an underlying deficiency in the ability of these split-valence basis sets to describe Na^+ itself. The basis function contractions for the 6-31G* and 6-311G* Na basis sets (which, with various additional polarization and/or diffuse functions, are used throughout G2, CBS-Q, and G3) were originally optimized at the self-consistent-field (SCF) level in calculations on the sodium atom (for which the "valence" orbitals are 3s and 3p). Apparently, these contractions are inappropriate for post-SCF calculations on Na^+ (with 2s and 2p valence orbitals). Similar shortcomings in the applicability of "atom-optimized" contracted basis sets for alkali metal ions have been noted previously by Magnusson[57] for the 6-31G* Li basis set and by Soldán et al.[51] for the augmented correlation-consistent PVxZ Na basis sets. Magnusson has reported that partial decontraction of the 6-31G* Li basis offers substantially improved performance in calculations on Li-containing adduct ions, whereas Soldán et al.[51] have developed a set of ion-optimized Na^+ basis sets of comparable quality to aug-cc-PVxZ bases for other main-group atoms, again apparently offering improved reliability in adduct ion calculations. We have found that partial decontraction of the 6-311+G(3df) sodium basis, as in the d-B4G basis used herein, has two benefits: first, it yields a closer approximation [5.079 eV (MP2) vs 5.042 eV at MP2/6-311+G(3df), with Na 2s and 2p orbitals correlated in either case] to the literature value of IE(Na); second, it results in a much smaller $\delta(\underline{\mathbf{Na}}^+X)$ term (typically by an approximately 6-fold reduction) in electron-correlated SCA calculations.[58] Both of these observations demonstrate that this partially decontracted d-B4G basis is substantially more able to accurately describe the sodium ion, without recourse to basis functions on neighboring atoms, than is the standard 6-311+G(3df) basis set. This conclusion underpins our use of this decontracted basis set in the CPd-G2thaw method described in Section 2.1.[59]

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3.1.2. Other ab Initio Methods. The generally poor performance of "model chemistry" methods for SCA determination has resulted in a tendency for experimentalists to use cheaper methods, such as MP2/6-311+G(2d,2p), whereas theoreticians have opted to use expensive coupled-cluster methods, such as CCSD(T), with large correlation-consistent basis sets. In general, agreement between recent experimental results[25,31,32] and the economical MP2 calculations recommended by Ohanessian and co-workers[25,32,60] has been excellent, whereas the large-basis-set calculations performed on water, ethylene, benzene, and dimethyl ether[41,61−63] have predicted SCA values for these compounds that are between 2 and 5 kJ mol^{-1} higher than those observed experimentally.[31,32]

3.2. The CPd-G2thaw and c-SLW3 SCA Scales. Sodium cation affinity values were obtained for a series of 38 neutrals comprising up to 3 heavy atoms by the CPd-G2thaw method, and for a smaller series of neutrals (those containing 2 heavy atoms or less, and CO_2) by the more computationally expensive c-SLW3 method. These values, at 0 K, are detailed in Table 4.

One important test of these values is their internal consistency. On the basis of this criterion, the CPd-G2thaw and c-SLW3 methods perform extremely well. Of the 25 ligands for which SCA values have been determined by both methods, there is only one reversal in relative SCAs (between HF and PH_3), there is only one example (Ar) for which the two methods differ by as much as 1.5 kJ mol^{-1}, and the mean absolute discrepancy is less than 1 kJ mol^{-1}. This level of agreement (between two techniques for which the methods of geometry optimization, ZPE calculation, single-point total-energy calculation, and BSSE correction, are all distinctly different) is excellent, and contrasts sharply with the >10 kJ mol^{-1} discrepancy between SCA values calculated by using otherwise generally reliable methods such as, for example, CBS-Q and G3.[31] In this respect, the accord between CPd-G2thaw and c-SLW3 for SCA values for such a broad range of ligands (which seems to bode well for the reliability of both methods) is comparable with the excellent "internal consistency" of model chemistry methods such as G2, CBS-Q, and CBS-APNO when applied to proton affinity determinations, for which extremely good agreement with accepted experimental values is also seen.[35,36]

Various trends within the calculated SCA scale are apparent, and are generally consistent with previous observations. Molecules lacking lone pairs or double bonds (and for which neither σ- nor π-coordination is therefore possible) have the lowest SCA values, whereas polar organics display significantly larger SCAs than nonpolar species. The largest SCA found in the present study, by far, is for the sole ionic molecule, NaCl. For ligands having the formula RX (R = H, CH_3, C_2H_5; X = H, OH, NH_2, SH, Cl) the SCA increases systematically with increasing size of the alkyl group R, with the greatest impact of R size seen on the SCA values for the chlorides and sulfides (for which the ligand's polarizability seems to be much more significant than its dipole moment).[64] First-row heteroatoms promote stronger bonding to Na^+ than do second-row atoms.

3.3. Comparison with Previous Theoretical Results. Several previous theoretical studies have reported SCA values. To make the task of properly assessing the previous results more manageable, we limit our comparison here to those values obtained by either highly computationally intensive methods of presumed high accuracy, or by somewhat less expensive methods, which are nevertheless recommended elsewhere as being highly reliable for SCA determinations. In the first category (for which the values are also quoted, for comparison, in Table 4) belong the CCSD(T) calculations, which use large correlation-consistent basis sets, of the Wright[51,61,65,66] and Feller[41,62,63] groups and the EXGF/MP3-D model potential calculations of Ahmadi et al.[67] The second category includes the MP2(full)/6-311+G(2d,2p)//MP2(full)/6-31G* calculations of Hoyau et al.,[25] Armentrout and Rodgers,[31] and McMahon and Ohanessian[32] and the G3(GCP) calculations of Siu et al.[40]

Our calculated values are, in most instances, marginally lower than the SCA values obtained from the previously reported CCSD(T) calculations of the Wright[51,61,65,66] and Feller[41,62,63] groups (the sole exception is CO_2, for which our CPd-G2thaw value is 0.5 kJ mol^{-1} greater than the value in ref 61). The discrepancy of greatest concern is probably that for SCA(Ar), for which the c-SLW3 calculation is 2.7 kJ mol^{-1} (or 18%) lower than the CCSD(T)/aug-cc-PVQZ value of Soldán et al.,[51] which it might be expected to approximate more closely. Apparently [because the additivity assuption implicit in the c-SLW3 method holds well for SCA(Ar), as shown in Section

TABLE 4: SCA Values of Various Ligands

	SCA (kJ mol^{-1})			
species	CPd-G2thaw	c-SLW3	lit.[a]	technique
He	2.7	2.5	2.8	CCSD(T)/aug-cc-PV5Z[b,c]
			2.8	EXGF/MP3-D[d]
Ne	4.2	4.6	5.3	CCSD(T)/aug-cc-PVQZ[b,c]
			5.3	EXGF/MP3-D[d]
H_2	10.5	9.2	10.3 (0.8)	TDE[e]
Ar	13.9	12.4	15.1	CCSD(T)/aug-cc-PVQZ[b,c]
			14.8	EXGF/MP3-D[d]
			15.4 (8.7)	GIB[f]
CH_4	26.6	27.0		
N_2	29.4	29.1	30.1	CCSD(T)/aug-cc-PV5Z[c,g]
C_2H_6	32.3	33.5		
HCl	38.2	38.1		
CO	38.2	38.2	31.8 (7.7)	GIB[f]
CO_2	51.3	50.7	50.8	CCSD(T)/aug-cc-PV5Z[c,h]
C_2H_2	54.0	55.2		
C_2H_4	54.2	55.4	56.9	CCSD(T)(CV)/CBS[i]
			43.1 (4.4)	GIB[f]
H_2S	56.7	56.6		
CH_3Cl	60.6	61.1		
HF	62.1	63.1		
PH_3	63.4	62.4		
CH_3CH_2Cl	69.4			
CH_3SH	74.1	74.7		
CH_3CH_2SH	80.1			
CH_3F	81.8	82.8		
$(CH_3)_2S$	86.9		83.4 (2.0)	FT-ICR[j]
H_2O	90.8	91.4	94.3	CCSD(T)/aug-cc-PV5Z[c,h]
			92.1	CCSD(T)(CV)/aug-cc-PVTZ[c,k]
			89.1 (2.0)	FT-ICR[j]
			94.6 (7.5)	GIB[f]
H_2CO	99.9	100.6		
CH_3OH	101.6	102.3	97.8 (1.6)	FT-ICR[j]
			98.9 (0.8)	HPMS[l]
			91.7 (5.7)	GIB[f]
			109.8 (0.8)	HPMS[m]
$(CH_3)_2O$	102.5		99.7 (1.6)	FT-ICR[j]
			91.7 (4.8)	GIB[f]
HCN	103.2	103.7		
NH_3	104.7	105.6	102.4 (1.6)	FT-ICR[j]
			103.1 (0.8)	HPMS[l]
			102.2 (5.4)	GIB[f]
			117.8 (1.7)	HPMS[n]
CH_3CH_2OH	109.6		105.8 (1.2)	FT-ICR[j]
			102.0 (3.7)	GIB[f]
CH_3NH_2	111.3	112.1	108.1 (0.8)	FT-ICR[j]
			107.7 (0.8)	HPMS[l]
$(CH_3)_2NH$	111.4		109.4 (1.6)	FT-ICR[j]
$CH_3CH_2NH_2$	115.8		114.1 (1.6)	FT-ICR[j]
CH_3CHO	116.0		113.4 (3.4)	GIB[f]
CH_3CN	128.5		125.1 (1.6)	FT-ICR[j]
NaCl	194.5	193.9		

[a] With experimental error, where given, in parentheses. [b] Na basis = AVQZ or AV5Z.[51] [c] D_e value, adjusted by using ZPE values calculated at the B3LYP/B1SLW level of theory. [d] EXGF/MP3-D model potential calculation.[67] [e] Temperature-dependent equilibrium measurement.[26] [f] GIB measurement.[31] [g] Na basis = AV5Z.[66] [h] Na basis = AV5Z.[61] [i] Complete basis set extrapolation of aug-cc-PVxZ (x = T, Q, 5) results; not corrected for BSSE.[41] [j] FT- ICR $\Delta G°$ (298 K) measurement,[32] adjusted to 0 K SCA by using G2 thermal correction factors. [k] Calculated by using the cc-PCVTZ basis for Na and cc-PVTZ for other atoms.[62] [l] HPMS result,[25] adjusted to 0 K SCA by using thermal correction factors calculated in ref 31. [m] HPMS measurement,[20] adjusted to 0 K SCA by using thermal correction factors calculated in ref 31. [n] HPMS measurement,[23] adjusted to 0 K SCA by using thermal correction factors calculated in ref 31.

2.2], the largest basis set used in c-SLW3 is inadequate to obtain a well-converged binding energy for this species; Ahmadi et al. have noted that very large basis sets are required to properly characterize the Na^+/rare gas interaction.[67] Comparatively large discrepancies (2.7 kJ mol^{-1} and 3.5 kJ mol^{-1}) are also seen between CPd-G2thaw and the CCSD(T) calculations for C_2H_4[41] and for H_2O,[61] but these differences in calculated values are less troubling for two reasons: first, the CPd-G2thaw is quite different in its architecture than these CCSD(T)/correlation-consistent basis set methods, and so discrepancies to some degree are to be expected (whereas the c-SLW3 technique is patterned on the work of Soldán et al.[51]); second, the percentage discrepancy between the SCA values for C_2H_4 and for H_2O (always <5%) is much less than that seen for Ar.

Agreement with the G3(GCP) values of Siu et al.[40] for the four ligands common to this study and theirs (i.e., NH_3, H_2O, CH_3OH, and C_2H_5OH) is very good, with the largest discrepancy between CPd-G2thaw and G3(GCP) at 0.6 kJ mol^{-1} [and only slightly larger between c-SLW3 and G3(GCP)].

SCA values for many of the species in Table 4 have been obtained at the MP2(full)/6-311+G(2d,2p)//MP2(full)/6-31G* level (with BSSE correction), which Hoyau and Ohanessian[25,60] have recommended on the basis of the very good agreement seen with recent experimental values. We find that these MP2 values (most conveniently expressed as ΔH_0 values in the study of Armentrout and Rodgers[31]) are almost always lower than our CPd-G2thaw and c-SLW3 values, typically by between 1.5 and 4 kJ mol^{-1}. Of the 10 species in ref 31, which appear also in Table 4 (i.e., Ar, CO, C_2H_4, CH_3OH, CH_3OCH_3, H_2O, C_2H_5OH, NH_3, CH_3NH_2, and CH_3CHO), only CO has a calculated MP2 value (39.7 kJ mol^{-1}) that exceeds our CPd-G2thaw or c-SLW3 value. Armentrout and Rodgers have also reported B3-LYP calculations by using the same 6-311+G(2d,2p) basis[31]; the B3-LYP results always exceed our high-level SCA values, and generally by a greater margin than the disparity between our values and the corresponding MP2 results. On the basis of the results of test calculations using various basis sets, it would seem that the major factor contributing to the difference between the Hoyau/Ohanessian method[60] and our own calculations is basis-set size; addition of further polarization functions generally results in a higher SCA value, even after BSSE correction. This issue of basis-set size is relevant also in comparing our CPd-G2thaw or c-SLW3 values with those obtained with significantly larger basis sets. As noted above, our own values generally lie up to 3 kJ mol^{-1} below the large basis-set values obtained by Ahmadi et al.,[67] Soldán et al.,[51,61,65,66] and Feller and co-workers.[41,62,63]

Because there is a more-or-less consistent trend toward both larger SCA values (after BSSE correction) and smaller counterpoise correction terms with increasing basis-set size, and because it is anticipated that the counterpoise correction for BSSE is usually an overcorrection, we can infer that our calculated CPd-G2thaw and c-SLW3 SCA values are very probably too low. Other sources of inaccuracy in the present calculations (use of adduct ion geometries not corrected for BSSE, uncertainty in the calculated zero-point energy change upon adduct ion formation, and assumption of single-point total energy additivity in obtaining a composite total energy value) are unlikely to be of sufficient magnitude to overturn this conclusion.

3.4. Comparison with Existing Experimental Values. The most extensive series of precise SCA values for small organic molecules is that recently reported by McMahon and Ohanessian,[32] which is based on FT-ICR measurements of ligand-exchange equilibria. For the 10 species common to the FT-ICR study and the present work, we find a remarkable consistency; our CPd-G2thaw values are always between 1.5 and 4.0 kJ mol^{-1} higher than the 0 K SCAs obtained by correcting the 298 K $\Delta G°$ FT-ICR values. The FT-ICR SCA ladder is, however, largely based on *relative* SCA values (with which our calculated values show agreement within ±3 kJ mol^{-1}) and is anchored to one of only four *absolute* Na^+-binding energy measurements previously obtained by McMahon and co-workers by using the HPMS technique.[25] The discrepancy between our calculated values and the McMahon/Ohanessian ladder of experimental values[32] is, therefore, largely a matter of disagreement over the SCA of their chosen anchor, CH_3NH_2 (see Table 4). An adjustment to the experimental SCA value of methylamine[25] by +2.5 kJ mol^{-1}, with a concomitant shift in the Na^+-binding energy ladder, would essentially resolve all discrepancies with our calculated values. Comparison between our theoretical values and the larger basis-set results of the Wright[51,61,65,66] and Feller[41,62,63] groups also supports the notion of such a shift, although there are very few species that have been studied with such large basis sets and for which FT-ICR measurements have also been reported.[32]

We have already noted above the discrepancy between our calculated SCA values and the HPMS result[25] for methylamine. Two other species for which Hoyau et al.[25] also reported absolute Na^+-binding energies (viz., NH_3 and CH_3OH) are included in Table 4, and the HPMS values for these species are also between 1.5 and 4.0 kJ mol^{-1} below our CPd-G2thaw and c-SLW3 values. Although the absolute precision of our calculated values is difficult to assess, it is (as noted above) much more probable that the CPd-G2thaw and c-SLW3 methods provide underestimates, rather than overestimates, of the true values. We may observe, also, that previous reports by the Castleman group[20−24] of HPMS Na^+-binding energies, with a high quoted precision, are now generally discredited,[25,31,32] although the source of the apparent systematic error in the techniques of Castleman and co-workers remains unidentified. Interpretation of the McMahon/Ohanessian HPMS measurements[25] should therefore be tempered by the possibility that a small systematic error may also remain in these values.

The other recent set of SCA measurements is that of Armentrout and Rodgers,[31] who used the GIB technique to obtain thresholds to collision-induced dissociation of ligated Na^+ with xenon. The accepted experimental uncertainties of the GIB technique (∼4−8 kJ mol^{-1}) are considerably larger than those of HPMS, and this is reflected by the generally greater discrepancy of our calculated values with the GIB results than with the McMahon/Ohanessian HPMS results.[32] There are nine ligands in the present study for which GIB values have also been reported[31]; these are Ar, CO, C_2H_4, H_2O, CH_3OH, $(CH_3)_2O$, NH_3, C_2H_5OH, and CH_3CHO. In most instances, the GIB results are lower than our calculated values (most markedly for ethylene, methanol, and dimethyl ether, where the difference exceeds 10 kJ mol^{-1}, also outside the apparent combined uncertainties of the experimental and theoretical methods), with only the GIB values for Ar and H_2O lying above our results (and incidentally offering very good agreement, in these instances, with the large-basis-set CCSD(T) calculations of Soldán and co-workers[51,61]).

The other experimental determination of note is that of Bowers and co-workers,[26] who used a temperature-dependent equilibrium technique to determine $SCA(H_2) = 10.3 \pm 0.8$ kJ mol^{-1}. This value shows excellent agreement with CPd-G2thaw and an acceptable accord also with the c-SLW3 value. The measurement of $SCA(H_2)$[26] is particularly important because it is the sole precise low-end value for the SCA scale offering direct comparison with high-level ab initio techniques. The GIB technique[31] has been used to obtain SCA values for Ar, CO, and C_2H_4, but these have much greater experimental uncertainties (and, in C_2H_4, seem unreliable beyond these uncertainties). Thus, although there are now several precise experimental SCA values for more strongly binding ligands (the McMahon/Ohanessian ladder[32] starts at about 50 kJ mol^{-1}), the low end of the experimental SCA scale remains poorly defined. Further studies in this range would be particularly helpful.

4. Conclusions

Theoretical SCA values obtained for a set of 38 small ligands by using the newly developed CPd-G2thaw and c-SLW3 composite quantum chemical techniques show excellent internal consistency and generally offer very good agreement with the *relative* SCA values reported by the experimental research groups of McMahon, Ohanessian, and Armentrout during recent years. However, we note also that the SCA values delivered by CPd-G2thaw and c-SLW3 are almost uniformly higher than the *absolute* SCA values resulting from those experimental studies.

Furthermore, there is some evidence that the discrepancy between existing experimental and theoretical SCA values increases with increasing "level of theory" [as seen, for example, in the progression from MP2(full)/6-311+G(2d,2p) calculations, through CPd-G2thaw and c-SLW3, to the small number of CCSD(T) calculations using large aug-cc-PVQZ or aug-cc-PV5Z basis sets], perhaps indicating that the currently established experimental SCA scale is systematically too low, most likely by an increment of 3−5 kJ mol^{-1}. Further studies, both experimental and theoretical, thus seem necessary to resolve the continuing apparent discrepancy between the most precise extant laboratory and computational SCA values.

Evaluation of SCA results obtained by using a wide variety of quantum chemical techniques indicates three important principles for calculating sodium cation affinities. First, the basis set used must be sufficiently flexible to reliably characterize the sodium ion/ligand adduct NaX^+ and the separated species Na^+ and X; in practice, this requires the use of large basis sets to obtain convergence. Second, correction for BSSE is desirable, so as not to overestimate the SCA. Third, inclusion of the sodium 2s and 2p orbitals within the correlation space is essential in all single-point calculations. The inability of "standard" methods such as G2, CBS-Q, and G3, and of suggested "improved" methods such as G2(thaw) and G3(GCP), to consistently return accurate SCA values is invariably a result of the neglect of one or more of these principles, although in several instances these methods perform very well for SCA values for a limited range of ligands because of a fortuitous cancellation of errors.

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(55) Inclusion of sodium inner-valence correlation, but neglect of ion/ligand BSSE, in the original formulation of G2(thaw)[44,45] might therefore be expected to yield SCA values that are systematically too high, thus explaining the apparently poor performance of the more computationally expensive G2(thaw) method noted in the Introduction.

(56) This effect is also apparent in the evident failure of the additivity assumption for G3 with respect to the SCAs of HF and Ne, which are significantly lower than the corresponding G3(QCI) values that G3 seeks to emulate. Inclusion of a GCP correction for BSSE does nothing to rectify this discrepancy. These results suggest that the G3(GCP) method, recently

recommended for SCA calculations,[40] should not be used for this purpose without careful attention to core orbital assignment.

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(58) The $\delta(\underline{\mathbf{X}}\mathit{Na})$ term shows negligible dependence on Na basis set decontraction.

(59) Although decontraction of the G3Large and CBSB3 basis sets for sodium was also explored, these being the largest basis sets used, respectively, in the G3 and CBS-Q methods, we found that other features of these model chemistry methods, such as the combination of 6-31G- and 6-311G-style basis sets in each method, and difficulty in applying the complete-basis-set extrapolation in CBS-Q to a “thawed” correlation space, yielded a generally poorer ability of G3 and CBS-Q variants to emulate QCISD(T) or CCSD(T) calculations featuring large basis sets. In contrast, the additivity assumption [in this case, the ability to reproduce a QCISD-(T) calculation with the decontracted 6-311+G(3df) sodium basis set] held extremely well for the CPd-G2thaw method, with a deviation from additivity typically <0.5 kJ mol^{-1}.

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