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Extending, and Repositioning, a Thermochemical Ladder: High-Level Quantum Chemical Calculations on the Sodium Cation Affinity Scale

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High-level ab initio quantum chemical calculations, at the CP-dG2thaw level of theory, are reported for coordination of Na^+ to a wide assortment of small organic and inorganic ligands. The ligands range in size from H to C_6H_6, and include 22 of the ligands for which precise relative sodium ion binding free energies have been determined by recent Fourier transform ion cyclotron resonance and guided ion beam studies. Agreement with the relative experimental values is excellent (± 1.1 kJ mol^{-1}), and agreement with the absolute scale (obtained when these relative values are pegged to the CH_3NH_2 "anchor" value measured in a high-pressure mass spectrometric study) is only marginally poorer, with CP-dG2thaw values exceeding the absolute experimental ΔG_{298} values by an average of 2.1 kJ mol^{-1}. The excellent agreement between experiment and the CP-dG2thaw technique also suggests that the additional 97 ligands surveyed here (which, in many cases, are not readily susceptible to laboratory investigation) can also be reliably fitted to the existing experimental scale. However, while CP-dG2thaw and the experimental ladder are in close accord, a small set of higher level ab initio calculations on sodium ion/ligand complexes (including several values obtained here using the W1 protocol) suggests that the CP-dG2thaw values are themselves too low by approximately 2.5 kJ mol^{-1}, thereby implying that the accepted laboratory values are typically 4.6 kJ mol^{-1} too low. The present work also highlights the importance of Na^+/ligand binding energy determinations (whether by experimental or theoretical approaches) on a case-by-case basis: trends in increasing binding energy along homologous series of compounds are not reliably predictable, nor are binding site preferences or chelating tendencies in polyfunctional compounds.

1. Introduction

The cation of sodium, the most abundant alkali metal, is ubiquitous in aqueous solution: Na^+ dominates the metal-ion contribution to the ionic strength of seawater and, in concert with K^+, is crucial to biochemical function. In the gas phase also, Na^+ displays a multifaceted chemistry, encompassing its involvement in sudden layer formation within Earth's upper atmosphere,[1−4] its application in the generation of ionized biomolecules under "soft" ionization techniques in mass spectrometers,[5,6] and its postulated participation in the formation of metal-containing molecules within various astrophysical environments.[7,8]

In addition to the role of Na^+ in the fields noted above, there are several motivating factors underscoring the many studies of gas-phase sodium ion ligation thermochemistry which have been undertaken to date.[1−3,6,7,9−28] The sodium ion formally lacks valence electrons and therefore forms ion/ligand complexes which are virtually purely electrostatic in character, providing an important avenue for the investigation of ionic bonding between charged and uncharged species. In the literature, sodium ion/ligand bond strengths are variously expressed as "sodium cation affinity" (SCA) or "bond dissociation enthalpy" (BDE) measurements, which for a given ligand X can be expressed as $SCA(X) = BDE(Na^+{-}X) = \Delta H^\circ_f(X) + \Delta H^\circ_f(Na^+) - \Delta H^\circ_f(NaX^+)$. Several studies have expressed the hope that, by establishing a scale of Na^+ binding energies to monofunctional organic molecules (e.g., to CH_3COOH and CH_3NH_2), the preferred binding site in polyfunctional molecules of biochemical interest (e.g., glycine, H_2NCH_2COOH)[11] can be satisfactorily identified. This is an important "blind spot" in the existing mass-spectrometric laboratory techniques which are often able to determine absolute or relative binding energies to admirably high precision but which are generally incapable of providing any accompanying structural information on the metal ion/ligand complexes under study. Some high-level theoretical studies (on ligand binding energies of Na^+ and other main-group metal ions) have in fact shown that the coordination to metal ions of ligands such as H_2NCN,[29] $HCONH_2$,[30] and C_6H_5OH[24] is often contrary to the expectations derived from binding energies of simpler compounds. For this reason, there remains a pressing need for an extensive data set of high-level, accurate theoretical BDE values for metal ion/ligand complexes involving both mono- and polyfunctional ligands. The present work is a continuation of efforts in this direction.

In an earlier study, CP-dG2thaw was employed to determine a sodium cation affinity scale comprising over 30 small (mostly organic) ligands.[22] The focus of the previous work was on assessing the theoretical values against the precise experimental measurements of McMahon, Ohanessian, and co-workers.[14,20] The agreement between experiment and theory was excellent, with the CP-dG2thaw values[22] lying uniformly 2.8 ± 1.3 kJ mol^{-1} higher than the corresponding experimental data.[20] In the present work, which extends the coverage of the CP-dG2thaw sodium cation affinity scale to 119 ligands (featuring, among them, approximately 140 Na^+ coordination sites), we have focused on species whose ligation to Na^+ may be considered

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prototypical, but which are less readily amenable to experimental study. We have also included many ligands which are bifunctional and for which competition between different coordination sites is evident. To further aid direct comparison with the McMahon/Ohanessian measurements, we have incorporated several of the larger ligands, including C_6H_6, for which precise laboratory data exist[20] but which were too large for CP-dG2thaw treatment at the time of our earlier computational study.[22] Finally, in an effort to "bridge the gap" between the few extant very-high-level calculations (on Na^+ coordination to small or highly symmetric ligands) and the precise laboratory measurements (on Na^+ coordination to often asymmetric, larger organic ligands), we have also performed calculations, using the W1 protocol of Martin and de Oliveira,[31] on over 20 of the complexes within our new CP-dG2thaw data set.

2. Theoretical Methods

Most of the calculations reported here were performed using the CP-dG2thaw quantum chemical methodology.[22] The CP-dG2thaw method is an offshoot of Gaussian-2 (G2) theory.[32] While G2 itself is a "generalist" method designed to yield highly accurate thermochemical values for small molecules comprised of first-, second-, and third-row main-group atoms,[32] CP-dG2thaw is a more specialized tool tailored for calculations on molecules and molecular ions featuring one or more metal atoms, since such species are often poorly treated by standard G2 theory. A detailed description of standard G2 theory,[32] and of the CP-dG2thaw method,[22] has been presented before and is consequently not explored here, but a summary of G2 itself, and an outline of the key differences between G2 and CP-dG2thaw, is relevant for the purposes of the current work. G2 theory[32] emulates[33] a calculation using the "quadratic configuration interaction with single, double, and perturbative triple excitations" (QCISD(T)) treatment of electron correlation and a triple-split-valence contracted Gaussian basis set with diffuse functions on non-hydrogenic atoms and multiple polarization functions (6-311+G(3df,2p)). This emulation is achieved by combination of a sequence of less computationally intensive calculations at lower levels of theory, with inclusion of zero point vibrational energy, and with treatment of higher order effects through an empirical correction factor.[32] G2 theory neglects correlation of the "inner-valence" electrons of first- and second-row metal atoms (e.g., the 2s and 2p orbitals of Na), omits any correction for basis set superposition error (BSSE), and uses a basis set for Na which is ill-designed for calculations on species featuring the sodium cation. The CP-dG2thaw technique redresses these shortcomings by incorporation of the inner-valence metal-based molecular orbitals among those correlated,[10,34,35] by inclusion[22,23] of a counterpoise correction[36] for BSSE, and by the use of a "partially decontracted" sodium basis set which offers a more flexible description of Na^+.[22] CP-dG2thaw also omits the empirical correction factor of the standard method[32] (which, in any event, has no impact on metal ion/ligand binding energy determinations). It is anticipated that CP-dG2thaw metal ion/ligand binding energies are accurate to well within the "standard G2" target of ±8 kJ mol^{-1}; comparison of the 10 Na^+/ligand binding energy values common to our previous CP-dG2thaw study[22] of sodium ion complexes and to the precise sodium cation affinity ladder of McMahon, Ohanessian, and co-workers[14,20] found a consistent agreement within 2.8 ± 1.3 kJ mol^{-1} in all cases.

Calculations were also performed, in some cases, using the W1 technique of Martin and de Oliveira.[31] This method uses the "coupled cluster with single and double excitations" (CCSD) and "CCSD with perturbative triple excitations" (CCSD(T)) treatments of electron correlation, with correlation-consistent basis sets of double-, triple-, and quadruple-ζ quality augmented with polarization and diffuse functions. Extrapolation of the total-energy trends from these calculations provides an estimate of the basis set limit, with treatment also given for core correlation, scalar relativistic correction, and spin–orbit coupling effects.

To assist in comparison with literature values, bond strengths calculated at both the CP-dG2thaw and W1 levels of theory are reported here both as 0 K bond dissociation enthalpies (BDEs) and as 298 K complexation free energies.

All calculations reported herein were obtained using the GAUSSIAN98[37] and GAUSSIAN03[38] program suites.

3. Results and Discussion

3.1. Assessment against Literature Values. The laboratory data on Na^+ complexation thermochemistry can usefully be subdivided into three categories. The first category, of complexation free energies at 298 K, includes the recent studies by McMahon, Ohanessian, and co-workers,[14,20] which have established a high-precision ladder encompassing approximately 40 ligands. This ladder is comprised mostly of relative free energies obtained through Fourier transform ion cyclotron resonance (FT-ICR) measurements,[20] but is anchored at four points to the absolute free energy values resulting from a high-pressure mass spectrometer (HPMS) study[14] of the $Na^+ + X \leftrightarrow NaX^+$ complexation equilibria for CH_3NH_2, NH_3, CH_3OH, and CH_3COCH_3. Category 1 also includes the recent guided ion beam (GIB) study of Amicangelo and Armentrout,[27] which has yielded relative free energies in very good agreement with the McMahon/Ohanessian scale. Uncertainties of less than ±2.6 kJ mol^{-1} are ascribed to the values on this ladder. The second category comprises recent guided ion beam (GIB) and triple quadrupole mass spectrometer measurements of 0 K absolute bond dissociation enthalpies, obtained through collision induced dissociation (CID) experiments by the groups of Armentrout[12,17] and Siu;[25,39] also in this category are competitive CID measurements of doubly ligated clusters,[21] yielding relative bond enthalpy values for several ligands. The uncertainties on these values are typically ~5–10 kJ mol^{-1}. The third category encompasses the extensive set of earlier measurements (i.e., before ca. 1995) on Na^+ complexes, using several different experimental techniques and performed by many different research groups, typically again with uncertainties of ~5–10 kJ mol^{-1}. The fourth category covers the numerous theoretical studies on sodium ion/ligand BDEs and related properties. It should be noted that agreement between measurements in categories 1 and 2 is generally good to excellent, while there are several instances of significant or severe discrepancy between category 3 values and those of categories 1 and 2.[17] Since the several (category 1 and 2) experimental studies to have appeared over the past six years have, almost without exception, highlighted discrepancies between the recent internally consistent measurements and those of certain earlier laboratory investigations, we have chosen in the present work to restrict our focus to a comparison of the new CP-dG2thaw sodium cation affinity scale (see Table 1) with the more recent (categories 1 and 2) laboratory studies, with the highest level theoretical data currently available from earlier quantum chemical investigations, and with the results of a limited set of calculations using the W1 computational protocol. This comparison is set out in the following four subsections.

3.1.1. Comparison with Laboratory Free Energy Meaurements at 298 K. The theoretical 298 K complexation free energy

TABLE 1: Sodium Cation Bond Dissociation Enthalpy (BDE) Values and Coordination Preferences for Many Ligands, Obtained at the CP-dG2thaw Level of Theory

	BDE(Na^+−ligand)[a]/kJ mol^{-1}					
	preferred site			other site(s)		
ligand	(B)[b]	(M)[c]	coord[d]	(B)[b]	coord[d]	$-\Delta G^\circ_{298}$ [e]/kJ mol^{-1}
He	2.2	2.7				−13.8
H	4.7	4.2[f]				−10.1
Ne	5.1[g]	4.2				−10.4
H_2	8.7	10.5	2 H			−7.2
Ar	13.5	13.9				−2.8
F_2	14.1					−2.2
CH_4	25.6	26.6				2.2
BH_3	28.4		2 H			7.6
N_2	28.9[h]	29.4	N			8.6
SiH_4	30.6					12.6
C_2H_6	33.0	32.3				5.2
Cl_2	34.2					13.8
CH_3	34.7	31.8[f]	C			12.4
$CH_3CH_2CH_3$	36.3					10.8
FCl	36.8		F			11.9
CO	37.9	38.2	C	27.0	O	13.7
HCl	38.1	38.2	Cl			19.3
HBr	39.7		Br			21.0
HCCF	40.7		π	27.5	F	20.2
SCS	42.4		S			24.2
HBeH	47.6		H			27.3
C_2H_5	47.9	46.5[f]	C			22.0
c-C_3H_4	49.2		π			24.7
HCCCl	49.8		π			29.1
CO_2	49.8	51.3	O			23.8
C_2H_3	53.0	52.0[f]	π			29.2
C_2H_2	53.7[g]	54.0	π			33.8
C_2H_4	53.7[g]	54.2	π			31.1
CH_2CCH_2	54.8		π			31.6
H_2S	56.9	56.7				34.9
H_2CCHCl	56.9		π			33.0
c-C_3H_6	58.4		(C_{2v})	24.2	(C_{3v})	34.6
H_2Se	58.6					36.5
CH_3Cl	60.7	60.6				40.6
HF	61.7[g]	62.1				40.1
PH_3	62.4	63.4				40.5
CH_3CHCH_2	62.6					36.8
OCS	62.8		O	28.7	S	36.3
H_2CCO	65.9		O	52.7	π (C=C)	41.3
CH_3CCH	68.0					47.0
NCCN	68.8[h]		N			44.2
H_2CCHF	69.0		F			43.7
C_2H	69.3	44.8[f]	π[i]			34.5
CH_3CH_2Cl	69.4	69.4				45.4
i-C_4H_8	69.8					45.3
H_2CS	71.5		S			48.5
C_4H_6 (butadiene)	72.8		(*trans*)			48.4
CH_2Cl_2	73.0		2 Cl			45.7
CH_2F_2	73.8		2 F			46.4
CH_3SH	74.8	74.1				49.2
C_4H_4O (furan)	76.8		π	73.3	σ (O)	51.1
CH_2FCl	75.6		F			48.0
t-C_4H_9Cl	77.7					58.4
AlCl	80.5					56.5
CH_3F	80.8	81.8				55.1
CH_3CH_2SH	81.7	80.1				55.6
CNCN	83.3		N (term.)	58.6	C (term.)	56.6
HNCO	83.6		O	63.2	N	56.5
$(CH_3)_2S$	87.0	86.9				60.3
H_2O	90.0[g]	90.8				66.3
H_2CCHOH	90.5		$\sigma + \pi$	86.8	O	64.8
CS	92.6		C			66.2
FCN	93.9		N	−12.1	F	67.1
C_6H_6	96.1					68.3
HCOCN	96.5		N	70.2	O	66.9
H_2CO	98.7	99.9	O			72.6
HCCNC	99.9		N*C*			72.4
CH_3OH	100.3	101.6				74.3
HNC	101.3		C			75.2
HCN	102.3[h]	103.2	N			76.8

TABLE 1 (Continued)

	BDE(Na^+−ligand)[a]/kJ mol^{-1}					
	preferred site			other site(s)		
ligand	(B)[b]	(M)[c]	coord[d]	(B)[b]	coord[d]	$-\Delta G°_{298}$ [e]/kJ mol^{-1}
$(CH_3)_2O$	102.4	102.5				76.0
HCOOH	102.9		C*O*	46.9	*O*H	76.4
AlF	103.1					76.2
NH_3	104.3[g]	104.7				79.5
HCNO	104.9		O			77.9
ClCN	106.6		N			79.5
c-C_2H_4O	107.2					82.8
H_2NOH	108.5		N, O	79.3	O	81.6
FCH_2CH_2F	108.8		2 F	62.7	F	78.4
CH_3CH_2OH	109.3	109.6				82.2
n-C_3H_7OH	109.8					83.4
$(CH_3)_3N$	109.9					81.5
CH_3NH_2	110.5	111.3				83.7
$(CH_3)_2NH$	111.4	111.4				83.7
HCCCN	112.3 [h]		N			85.8
H_2CNH	112.4		N			85.8
$HCOOCH_3$	114.3		C*O*	53.9	−O−	87.0
i-C_3H_7OH	114.6					87.3
CH_3CHO	115.9	116.0				88.9
$CH_3CH_2NH_2$	116.1	115.8				88.5
CH_3COOH	116.2		C*O*	57.8	*O*H	90.8
t-C_4H_9OH	118.3					90.4
$(C_2H_5)_2O$	118.4					90.5
H_2NNH_2	118.9		2 N			91.7
HOCN	121.6		C*N*	22.6	*O*H	94.5
CH_3NC	125.3		C			98.0
HOOH	126.6		2 O			100.4
CH_2CHCN	127.1		N			99.9
CH_3CN	128.7	128.5	N			101.5
CH_3COCH_3	128.9		O			101.1
FCH_2CH_2OH	131.8		F, O			101.2
CH_3CH_2CN	132.8		N			105.5
H_2NCN	138.9		C*N*			111.9
CH_2OHCHO	140.0		2 O	98.8 (96.6)	C*O* (−O−)	109.4
$HCONH_2$	144.6		O			116.6
c-C_3H_2	145.4		C:			118.7
CH_3SOCH_3	159.3		O			131.9
LiCl	160.0					135.5
$HOCH_2CH_2OH$	165.1		2 O	89.0	O	126.4
LiOH	178.2					155.6
$H_2NCH_2CH_2NH_2$	184.4		2 N	116.7	N	151.3
NaCl	192.7	194.5				165.4
LiNC	198.2					170.1
LiF	205.5					178.6
BeO	210.3					183.5
Na(CN)	214.0					182.5
MgO	218.1					191.2
NaOH	229.7					204.2
NaF	247.6					218.4

[a] Bond dissociation enthalpy at 0 K, calculated at the CP-dG2thaw level of theory. [b] Obtained in the present work (unless otherwise indicated), using optimized geometries and unscaled vibrational frequencies calculated at the B3-LYP/6-311+G** level of theory. [c] Previously reported in ref 22, unless otherwise indicated, using MP2(full)/6-31G* optimized geometries and scaled HF/6-31G* vibrational frequencies. [d] Identified donor atom(s) connected to, or mode of coordination to, Na^+ in instances where some ambiguity may exist. [e] Free energy of complexation, obtained in the present work. The values shown use optimized geometries, unscaled vibrational frequencies, and thermal corrections calculated at the B3-LYP/6-311+G** level of theory. [f] Previously reported in ref 26. [g] Previously reported in ref 9u. [h] Previously reported in ref 28. [i] See text for discussion.

values reported in Table 1 were obtained from the computed CP-dG2thaw ΔE_e values (at 0 K) by inclusion of the unscaled calculated 298 K free energy corrections for Na^+, ligand X, and complex NaX^+ yielded by B3-LYP/6-311+G** frequency calculations.

Figure 1 displays the level of agreement between our calculated 298 K free energy values and the experimental $\Delta G°_{298}$ ladder of McMahon and Ohanessian,[20] augmented by the recent laboratory values of Amicangelo and Armentrout. There are 22 ligands, ranging in size from H_2O to C_6H_6, which are common to the McMahon/Ohanessian ladder[20] and to the present work, with seven of these ligands featured also in the GIB study of Amicangelo and Armentrout.[27] As noted above, it should be reiterated that the experimental data points are almost exclusively *relative* values which are pegged to the absolute $\Delta G°_{298}$ value for the Na^+/CH_3NH_2 complex obtained in a HPMS study.[14]

Comparing first the relative values, the agreement between CP-dG2thaw and the FT-ICR free energies is very good indeed. Across a data set spanning approximately 90 kJ mol^{-1} (and centered on the pivotal CH_3NH_2 value), the best-fit line in Figure 1 deviates from a slope of unity by only ~0.6 kJ mol^{-1} at either

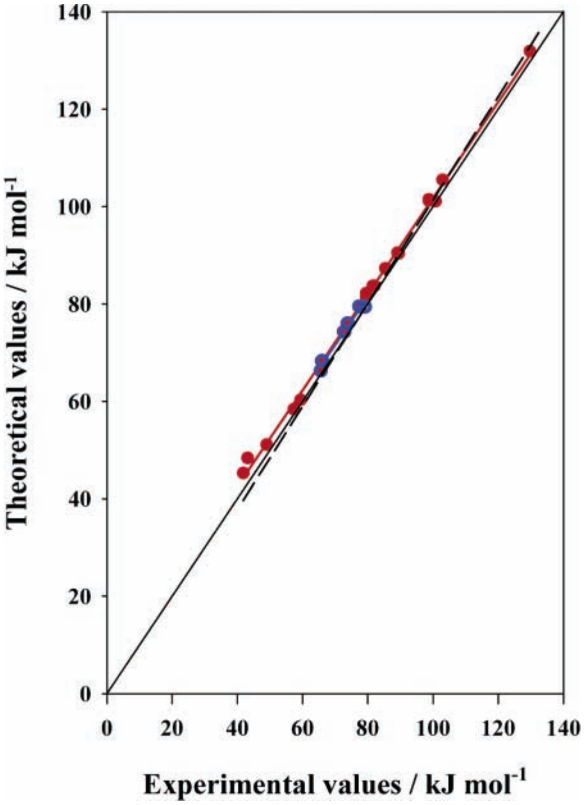

Figure 1. Comparison of CP-dG2thaw complexation free energies (at 298 K) with the corresponding experimental ladders of McMahon and Ohanessian (obtained from FT-ICR ligand exchange experiments,[20] shown in red) and Amicangelo and Armentrout (shown in blue; obtained via GIB studies[27] and normalized to the FT-ICR data[20]). The solid black line is the 1:1 line, provided as a visual aid, while the dashed line is the best fit to the MP2(full)/6-311+G(2d,2p) calculations reported by McMahon and Ohanessian,[20] plotted against their own experimental results.

end. Note that this deviation is well within the attributed cumulative uncertainty (of ∼ ±2.6 kJ mol^{-1}) for the top and bottom values of the experimental ladder. The scatter of individual data points from this best-fit line is also minimal, suggesting (a) that the experimental ladder is indeed reliably constructed and (b) that the CP-dG2thaw technique is well able to reproduce the spacings on the experimental ladder. Similarly good agreement is seen also with the more limited data set of Amicangelo and Armentrout.[27]

For the absolute free energies, the agreement between theory and experiment is less striking. Across the 22 ligands common to this study and the McMahon/Ohanessian ladder,[20] our calculated complexation free energies (expressed, following the convention of the experimental studies, as positive values) consistently exceed the laboratory values by an increment of 2.1 ± 1.1 kJ mol^{-1}, where the stated uncertainly is 1 standard deviation (SD). For comparison, the counterpoise-corrected MP2(full)/6-311+G(2d,2p) values used by McMahon and Ohanessian[20] as a theoretical reference set display a deviation from experiment of -0.1 ± 2.0 kJ mol^{-1}, again with 1 SD uncertainty. It is worth noting that the uncertainties quoted above describe the agreement between theory and the *relative* laboratory free energy values, while the discrepancies themselves denote agreement (or disagreement) with the *absolute* values. Thus, while the lower level of theory (MP2/6-311+G(2d,2p)) displays greater conformity to the absolute free energy ladder (anchored to the HPMS methylamine complexation value),[14] the higher level of theory (CP-dG2thaw) is clearly superior in its ability to reproduce the relative free energy values. This variation in performance, between relative and absolute values, raises the question of whether the HPMS methylamine value is, in fact, a sufficiently reliable reference point for the complete free energy ladder. Perhaps coincidentally, our CP-dG2thaw complexation free energy is 2.2 kJ mol^{-1} higher than the HPMS laboratory value,[14] i.e., displaying almost exactly the mean discrepancy of CP-dG2thaw with the entire ladder. This shows that an upward revision of the experimental scale, so as to remove the discrepancy with CP-dG2thaw *for this one ligand*, would result in near-perfect agreement between experiment and CP-dG2thaw theory (as represented by a mean deviation of -0.1 ± 1.1 kJ mol^{-1}). We will return to this point in subsequent sections.

3.1.2. Comparison with Laboratory Bond Dissociation Enthalpy (BDE) Meaurements at 0 K. As with the free energy values discussed above, we turn first to the *relative* bond dissociation enthalpies at 0 K. These values, with stated uncertainties of between 1.2 and 2.7 kJ mol^{-1}, were measured in the laboratory by competitive CID of doubly ligated sodium ions in a GIB apparatus.[21] Relative to ammonia, the laboratory values for ethanol, dimethyl ether, methanol, benzene, and water are 7.8 ± 1.2, -1.6 ± 1.0, -4.9 ± 1.0, -6.9 ± 2.0, and -14.4 ± 2.7 kJ mol^{-1}, with the corresponding CP-dG2thaw values of 5.0, −1.9, −4.0, −8.2, and −14.3 kJ mol^{-1}. Only for ethanol does the calculated CP-dG2thaw relative bond enthalpy lie outside the stated uncertainty. The laboratory values used in this comparison are those recommended in the competitive CID study,[21] which treat the internal rotors of the ethanol product as hindered rotors; if ethanol's internal rotors are instead treated as free vibrations, the discrepancy between theory and experiment for the ethanol relative bond enthalpy is reduced to 0.3 kJ mol^{-1}, while discrepancies for the other ligands are not greatly affected.

With regard to recent absolute values,[17,25,39] the performance of CP-dG2thaw is shown in Figure 2. Scatter is obviously larger than for the free energy values assessed in Figure 1, but this appears to be a function largely of the comparatively large error bars on the laboratory BDE values. The CP-dG2thaw values diverge from experiment by greater than the stated uncertainty only for the guided ion beam CID values for C_2H_4, C_6H_6, CH_3OH, CH_3OCH_3, and CH_3CH_2OH, and for the triple quadrupole value for H_2O. For all of these ligands except C_2H_4, the GIB competitive CID study of Amicangelo and Armentrout[21] provides an alternative and generally more internally consistent data set with which our CP-dG2thaw values are invariably in agreement.

3.1.3. Comparison with Existing High-Level Quantum Chemical Data. The Na^+ complexes of many of the ligands studied here have not been subjected to previous computational scrutiny. Of those which have been studied previously, the Na^+/H_2O complex has received particularly close attention. Our BDE value of 90.0 kJ mol^{-1} for this ligand is somewhat lower than the theoretical values of 90.8 kJ mol^{-1} (CP-dG2thaw//MP2(full)/6-31G*),[22] 91.2 kJ mol^{-1} (G3(GCP)),[23] 91.4 kJ mol^{-1} (c-SLW3),[22] 92.1 kJ mol^{-1} (CCSD(T)(CV)/aug-cc-pVTZ),[40] 94.3 kJ mol^{-1} (CCSD(T)/aug-cc-pV5Z),[16] 95.0 kJ mol^{-1} (CCSD(T)(fc)/6-311++G(2df,p)//B3-LYP/6-311++G**),[39] and 97.5 kJ mol^{-1} (estimated complete basis set (CBS) limit MP2(full) value).[40] For all but the CCSD(T)(fc)/6-311++G(2df,p) value, the computational method includes treatment of Na 2s and 2p orbital electron correlation, while only the extrapolated CBS value of Feller and co-workers[40] does not include a counterpoise correction for BSSE. While there is a significant scatter among these data points, the consistency with which they

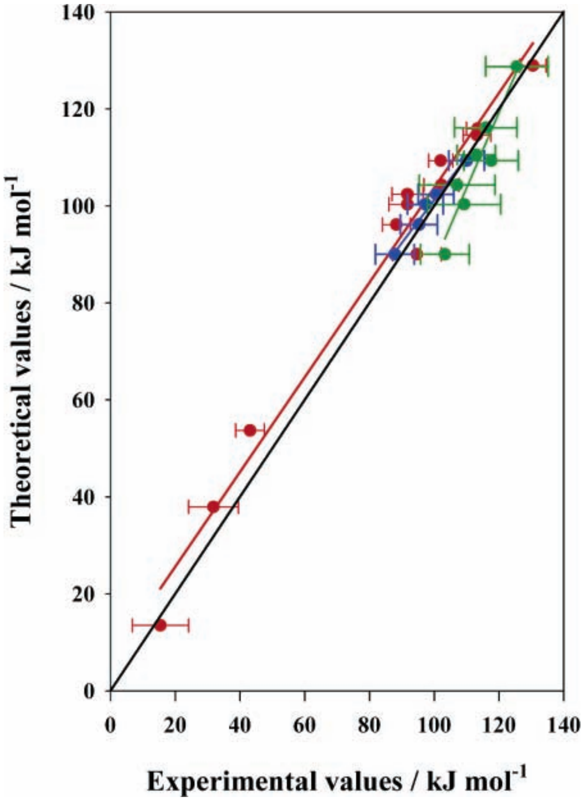

Figure 2. Comparison of CP-dG2thaw bond dissociation enthalpies (at 0 K) with recent experimental measurements. Data points shown (with associated experimental error bars) are, in blue, the competitive CID values of Amicangelo and Armentrout;[21] in red, the CID measurements of Armentrout and co-workers;[12,17] and, in green, the CID results of El Aribi et al.[25,39] The latter set of results were obtained using the HPMS technique, while the former two sets of experimental data were measured in a GIB apparatus. The black line is the 1:1 line, provided as a visual aid, while the colored lines are fits to the respective subsets of data. It is notable that the considerably wider scatter seen in this plot than that in Figure 1 appears entirely attributable to the substantially greater uncertainties in the experimental 0 K enthalpies than in the experimental 298 K free energies.

estimate BDE values which are significantly in excess of the experimental value of 89.1 ± 2.0 kJ mol^{-1}, obtained in the McMahon/Ohanessian FT-ICR study of sodium ion ligand transfer reactions,[20] is a cause for some concern.

It is worth focusing on the discrepancies between our present CP-dG2thaw results and those of Soldan, Lee, and Wright,[2−4,13,15,16] who in a series of studies have used coupled-cluster methods with very large correlation-consistent basis sets (which for the case of sodium have been specifically optimized to yield superior results for Na^+) in calculations including BSSE correction and correlation of all pertinent electrons. The "benchmark" BDE values obtained in this manner for Na^+ complexes of He, Ne, Ar, N_2, CO_2, and H_2O are consistently higher than the CP-dG2thaw values reported here, typically by ~1 kJ mol^{-1} for the nonpolar ligands (but by a markedly larger increment for H_2O, as noted above). The regularity of this discrepancy, coupled with the results of other studies which indicate that very large ligand basis sets are required to accurately encompass the ligand's electronic response to an adjacent cation, suggests that our tabulation of CP-dG2thaw bond dissociation enthalpies in Table 1 very likely consistently underestimates the true BDE values by perhaps up to 5%. Adding weight to this argument, the CBS extrapolations of Feller et al.[18,19,40] (also employing large correlation-consistent basis sets and, for the two π-complexes, using coupled-cluster theory) have yielded BDE values for the complexes of ethylene, H_2O, and benzene of respectively 56.9, 97.5, and 102.1 kJ mol^{-1}, consistently above our values of 53.7, 90.0, and 96.1 kJ mol^{-1} for these ligands. The few very high-level calculations on Na^+ complexes which have been reported by the groups of Wright[2−4,13,15,16] and Feller[18,19,40] are consistently a few kilojoules per mole higher than the corresponding CP-dG2thaw values, which in turn are typically around 2 kJ mol^{-1} higher than the BDE values obtained by conversion to 0 K enthalpy values of the complexation free energy ladder of McMahon and Ohanessian.[20] If it is assumed (as is generally the case) that the "benchmark" computational results obtained at a higher level of theory, or with larger basis sets, are more reliable than those which are less computationally intensive than these benchmarks, then it follows that the CP-dG2thaw ladder presented here tends to underestimate the true BDE values, implying also that the McMahon/Ohanessian[20] scale is apparently too low by several kilojoules per mole. This is clearly a contentious assertion but, given the usefulness of Na^+ complexation energies as a probe of ion/ligand electrostatic interactions, one which should be subjected to serious scrutiny, both through further very high-level calculations and through further laboratory studies targeting precise binding energies against which to assess the reliability of the Na^+/CH_3NH_2 "anchor" used in the McMahon/Ohanessian ladder.[20]

On some technical aspects of the present calculations, we note that even with the use of a sodium basis set (dB4G), which is designed to minimize basis set superposition error, the counterpoise (CP) corrections to BSSE are still of significant magnitude. For almost all complexes the "ligand" contribution to CP (i.e., involving ligand electron occupation of the metal atom's virtual orbitals) exceeds the "metal" contribution (involving Na^+ electron occupation of the ligand's virtual orbitals), with ligand contributions of between 60 and 90% in most cases. This is not true, however, for H_2, or for saturated hydrocarbons or hydrocarbon radicals, all of which bond rather weakly and which have approximately equal CP contributions from the ligand and metal terms. As absolute values, the largest counterpoise corrections are those for π-coordinating aromatics [$CP(Na^+/C_6H_6) = 9.3$ kJ mol^{-1}, $CP(Na^+/C_4H_4O) = 6.9$ kJ mol^{-1}], inorganic chlorides [$CP(Na^+/Cl_2) = 8.5$ kJ mol^{-1}, $CP(Na^+/ClNa) = 8.4$ kJ mol^{-1}, $CP(Na^+/ClLi) = 6.8$ kJ mol^{-1}], and chelating organic molecules [$CP(Na^+/CH_2Cl_2) = 8.0$ kJ mol^{-1}, $CP(Na^+/HOCH_2CH_2OH) = 6.4$ kJ mol^{-1}, $CP(Na^+/H_2NCH_2CH_2NH_2) = 6.3$ kJ mol^{-1}, $CP(Na^+/HOCH_2CHO) = 5.9$ kJ mol^{-1}]. In almost all other instances the CP correction is less than 5 kJ mol^{-1}. Proportionately, the CP correction has the greatest influence on weakly bound complexes, notably those of the rare gases [$CP(Na^+/He) = 28\%$ (of uncorrected BDE); $CP(Na^+/Ar) = 17\%$] and of chlorine [$CP(Cl_2) = 20\%$], while for the polar O- or N-containing organic molecules the CP correction seldom amounts to more than 4% of the BDE for the preferred complex geometry. Since the counterpoise correction is expected to overcompensate for the true basis set superposition error, these trends suggest that, over the BDE range of greatest interest to biochemical applications (i.e., BDE ~ 100 kJ mol^{-1} and greater), the calculated values are perhaps low by up to appromixately 4%. However, this consideration is based only on BSSE trends and does not treat the separate issue of basis set incompleteness (metal ion/ligand BDEs tend to increase with increasing basis set size, as do ligand contributions to the counterpoise correction). There are several aspects of the computational technique, such as basis set incompleteness and counterpoise correction overestimation of

BSSE, which engender systematic underestimation of the true metal ion/ligand BDE values, but few if any aspects which lead us to suspect that the CP-dG2thaw values might generally overestimate the true BDE.

Is it appropriate to include a counterpoise correction for BSSE, in calculation of sodium ion/ligand BDE values? This is a point of some division in the literature. The theoretical studies of Siu et al.[23] and Wright and coauthors,[3,13,16] employing respectively G2-based composite computational techniques and CCSD(T) calculations featuring large, correlation-consistent basis sets, have incorporated and recommended counterpoise correction in Na^+ binding energy calculations. This approach has also been followed in the theoretical results accompanying experimental measurements, in the studies of Armentrout and Rogers[17] and McMahon and Ohanessian.[20] However, Feller has urged caution: in calculations on the Na^+ complexes of ethylene and benzene,[19] performed using correlation-consistent basis sets and with extrapolation to the complete basis set (CBS) limit, he found that inclusion of a counterpoise correction led to an apparently systematic deterioration in the convergence of MP2 binding energy calculations to the CBS limit. In the present work we have attempted to address the question of counterpoise correction appropriateness through a statistical analysis, as follows. Twenty-two of the ligands surveyed in the present work are also featured in the McMahon/Ohanessian ladder of experimental complexation free energies.[20] When counterpoise corrections are included, our calculated 298 K free energy values are systematically higher than the McMahon/Ohanessian values by 2.0 ± 1.1 kJ mol^{-1}, where the stated uncertainty is 1 standard deviation. However, when counterpoise corrections are omitted from the free energy calculation sequence, our values exceed the McMahon/Ohanessian ladder values by 6.7 ± 2.0 kJ mol^{-1} (again with a 1 SD uncertainty). Thus our theoretical results show substantially better agreement with both the *absolute* and *relative* values on the experimental ladder when counterpoise corrections are included. One particularly striking illustration concerns water and benzene, for which previous high-level theoretical and experimental studies both find essentially equal Na^+ complexation free energies at 298 K.[17,20,27] At the CP-dG2thaw level of theory, these two ligands differ in $\Delta G°_{298}$ by 2.0 kJ mol^{-1}, but when counterpoise corrections are omitted (i.e., at the "dG2thaw" level of theory), the difference is 7.7 kJ mol^{-1}. The improved agreement between our calculated results and the relative values on the experimental ladder, resulting from inclusion of counterpoise corrections, is particularly compelling since the McMahon/Ohanessian ladder is primarily a sequence of relative values: our analysis shows quite clearly that the best agreement with these relative values is obtained when counterpoise corrections are included. (This is, however, a separate issue from the accuracy of the absolute experimental values, as discussed in some of the preceding paragraphs, and we contend that further study is required to better establish an absolute anchor for the existing experimental ladder.)

We should also note that our previous study of sodium ion complexes[22] used the CP-dG2thaw method in conjunction with MP2(full)/6-31G* optimized geometries and scaled HF/6-31G* zero point vibrational energies (ZPE). In the present work, we have used B3-LYP/6-311+G** optimized geometries and unscaled ZPE, and this difference in method results in different BDE values than those reported in the earlier work. For all closed-shell ligands, the calculated BDE has little dependence on the method used to obtain geometries and ZPE: in almost all instances, discrepancies are less than 1 kJ mol^{-1}. For the Na^+/C_2H BDE value, however, the choice of optimized geometry is significantly more important, as at MP2/6-31G* this complex is found to possess a π-complex global minimum whereas with B3-LYP/6-311+G** a linear σ-complex is obtained.[26] The B3-LYP optimized geometry yields a markedly stronger Na^+/ligand interaction as shown by the BDE values in Table 1, suggesting that in this instance at least the B3-LYP geometry is to be preferred.

3.1.4. Comparison with W1 Values of Sodium Cation BDEs for Small Ligands. As stated above, few previous studies have employed very high levels of theory to characterize binding energies of Na^+ to small ligands. This paucity of benchmarks is an impediment to our wish to provide, to the best extent possible, sound theoretical guidelines for evaluating the existing experimental scale. Consequently, we have performed a limited series of calculations using the W1 method of Martin and de Oliveira,[31] for Na^+ complexation by small ligands.

Comparison between CP-dG2thaw and W1 values for over 20 Na^+/ligand complexes is afforded by Table 2, which also specifies the McMahon/Ohanessian[20] scale ligands for which we have performed CP-dG2thaw calculations, as well as the small set of very high level ab initio results obtained by Soldan, Lee, and Wright.[3,13,16] Turning first to the trend evident between CP-dG2thaw and W1, there are two species which deliver anomalous results. The Na^+/Ne BDE and complexation free energy values obtained by W1 exceed their CP-dG2thaw counterparts by over 12 kJ mol^{-1}, while the Na^+/AlF values determined using W1 are lower than CP-dG2thaw by more than 5 kJ mol^{-1}. In all other cases the W1 values for "covalent" ligands are within a zone ranging from 1 kJ mol^{-1} below to 4 kJ mol^{-1} above the corresponding CP-dG2thaw value, while for the "ionic" ligands LiCl, NaCl, AlCl, and NaF the W1 values exceed CP-dG2thaw by a slightly larger margin. We believe that the CP-dG2thaw value for BDE($Na^+{-}Ne$) is, in this instance, the more reliable: the weakly bound $NaNe^+$ complex has been previously identified[22,34] as a species for which the standard method of "frozen-core" assignment is particularly problematic, since the (nominally "core") molecular orbitals derived from Na 2p lie higher in energy than the "valence" molecular orbitals derived from Ne 2s. Any method employing routine application of the frozen-core approximation in some component of its calculation is therefore subject to error on a species with interspersed "core" and "valence" orbitals, and W1 is such a method. The W1 value for $NaNe^+$ is high not just with respect to CP-dG2thaw, but also in comparison to the set of all-electron CCSD(T) calculations performed by Soldan, Lee, and Wright[13] using large correlation-consistent basis sets; further, the W1 calculation also gives a result out of step with the tendency, found in both our CP-dG2thaw calculations and the work of Soldan et al.,[13] for the BDE values of Na^+ complexes of the rare gases to increase in systematic fashion with increasing row number. For BDE($Na^+{-}FAl$) the resolution of the discrepancy between CP-dG2thaw and W1 is less clear-cut, although fluorides are known to share neon's propensity for inducing frozen-core mayhem in calculations featuring Na^+.[34]

It is useful also to compare the W1 values with the other Na^+-containing complexes studied by Soldan et al.[3,13,16] using the CCSD(T)/aV*X*Z method. Here the overlap encompasses only four ligands: Ar, N_2, CO_2 and H_2O. In all four instances, the agreement between W1 and CCSD(T)/aV*X*Z is excellent, with both methods showing substantially closer accord with each other than either does with CP-dG2thaw for these ligands.

What can we infer from a comparison of the W1 values and the McMahon/Ohanessian[20] experimental ladder? Direct com-

TABLE 2: Summary of Complexation Free Energy and/or BDE Trends between Four Data Sets: McMahon/Ohanessian Relative Scale Anchored to $\Delta G_{298}(CH_3NH_2)$ (Ref 20); CP-dG2thaw Values (This Work); W1 Values for Small Ligands (This Work); and CCSD(T)/aV*X*Z Values ($X = Q, 5$) of Soldan, Lee, and Wright (Refs 3, 13, and 16)

	ΔG_{298}/kJ mol^{-1}			BDE/kJ mol^{-1}		
ligand	MM/O[a]	CP-dG2thaw	W1	CP-dG2thaw	W1	SLW[b]
He		−13.8		2.2		2.8
Ne		−10.4	2.0	5.1	18.4	5.3
H_2		−7.2	−5.9	8.7	9.8	
Ar		−2.8	−1.1	13.5	15.2	15.1
CH_4		2.2	4.6	25.6	27.9	
N_2		6.6	7.8	28.9	30.3	30.1
CO		13.7	14.6	37.9	39.2	
HCl		19.3	22.4	38.1	41.1	
CO_2		23.8	27.6	49.8	51.1	50.8
C_2H_2		33.8	33.2	53.7	52.8	
C_2H_4		31.1	32.9	53.7	56.0	
HF		40.1	41.6	61.7	63.1	
i-C_4H_8	41.8	45.3		69.8		
$CH_2CHCHCH_2$	43.1	48.4		72.8		
c-C_4H_4O (furan)	49.0	51.1		76.8		
t-C_4H_9Cl	57.3	58.4		77.7		
AlCl		56.5	62.6	80.5	84.5	
$(CH_3)_2S$	59.4	60.3		87.0		
C_6H_6	65.7	68.3		96.1		
H_2O	65.7	66.3	69.8	90.0	93.4	94.3
H_2CO		72.6	75.5	98.7	101.2	
CH_3OH	72.4	74.3	77.5	100.3	103.2	
HCN		76.8	78.8	102.3	104.6	
$(CH_3)_2O$	73.6	76.0		102.4		
AlF		76.2	70.5	103.1	96.5	
NH_3	77.8	79.5	82.5	104.3	107.2	
$(CH_3)_3N$	79.5	81.5		109.9		
C_2H_5OH	79.5	82.4		109.3		
CH_3NH_2	81.5	83.7	86.3	110.5	112.9	
$(CH_3)_2NH$	82.0	83.7		111.4		
i-C_3H_7OH	85.4	87.3		114.6		
$(C_2H_5)_2O$	89.1	90.5		118.4		
t-C_4H_9OH	89.5	90.4		118.3		
CH_3CN	98.7	101.5		128.7		
CH_2FCH_2OH	98.7	101.2		131.8		
$(CH_3)_2CO$	100.8	101.1		128.9		
CH_3CH_2CN	102.9	105.5		132.8		
$(CH_3)_2SO$	129.7	131.9		159.3		
LiCl		135.5	140.5	160.0	163.3	
NaCl		165.4	172.4	192.7	198.2	
NaF		218.4	223.7	247.6	252.5	

[a] McMahon and Ohanessian.[20] [b] Soldan et al.[3,13,16]

parison is feasible only in four instances: the complexes of water, ammonia, methanol, and methylamine. In all four instances the W1 complexation free energy is at least 4 kJ mol^{-1} above the experimental value, a greater discrepancy than that seen between experiment and CP-dG2thaw. The result for CH_3NH_2 is of heightened importance given the pivotal role of this ligand as the "anchor point" of the experimental scale,[14,20] although NH_3 and CH_3OH are also species for which precise experimental ΔG_{298} values[14] of 79.9 ± 3 and 74.9 ± 3 kJ mol^{-1} have been reported by McMahon, Ohanessian, and co-workers. The absolute values for the latter two ligands are, like the relative values fixed to CH_3NH_2, consistently lower than W1 values.

In summary, the existing experimental ladder[14] lies systematically lower than that obtained theoretically using the CP-dG2thaw technique, while the CP-dG2thaw ladder is itself noticeably low according to W1. "Normalization" of the experimental ΔG_{298} scale[14] to the CP-dG2thaw values can be achieved by application of the formula $\Delta G_{298}(\text{adjusted}) = 0.986\Delta G_{298}(\text{exptl}) + 3.10$ kJ mol^{-1}, while resolution of the experimental scale with W1 requires $\Delta G_{298}(\text{adjusted}) = 1.013\Delta G_{298}(\text{exptl}) + 4.66$ kJ mol^{-1}. The first of these formulas results from a direct fitting of CP-dG2thaw to the experimental data, while the second formula relies also on the trend evident between CP-dG2thaw and W1 (discounting the fluorine-containing and neon complexes for which W1 may be less reliable for reasons of core/valence electronic ordering). By most criteria, the W1 protocol would be regarded as more rigorous than CP-dG2thaw, and therefore by implication more reliable, although the reliance of W1 on the frozen-core approximation in some components of its calculation is somewhat problematic. It would be an audacious theoretician who claimed that, in this instance, the W1 values for sodium ion complexes called for a substantial correction to the experimental ladder, but the W1 calculations which we have performed here do certainly substantiate the inference, drawn from CP-dG2thaw as well as the work of Soldan et al.[3,13,16] and the calculations of Feller and co-workers,[18,19,40] that the experimental ladder appears low by comparison with high-level theoretical values.

3.2. BDE Trends Apparent in the CP-dG2thaw Data Set. The bonding character in Na^+/ligand complexes has been shown to be almost purely electrostatic, and dominated by ion/dipole and ion/induced dipole attractive terms which are offset, to a fair approximation, by hard-sphere repulsive terms as the interaction distance diminishes. We would therefore expect that among the Table 1 values, for monofunctional ligands at least, a dependence of BDE on ligand polarity should be evident. This is, to a reasonable degree, borne out in the calculated results. The BDE values of nonpolar inorganic ligands (rare gases, homonuclear diatomics, etc.) and saturated hydrocarbons are uniformly lower than those of polar O- and N-containing organic molecules, while the 10 highest BDE values for monofunctional ligands are for highly polar halides, cyanides, and oxides of the main-group metals. The halides of aluminum are seen to have much lower BDEs than those of lithium and sodium, in keeping also with dipole moment trends (μ_D(LiCl) = 7.3 D, μ_D(NaCl) = 9.3 D, μ_D(AlCl) = 1.8 D according to calculations at the MP2/dB4G level of theory). For ligands lacking a significant permanent dipole moment, the polarizability of the ligand becomes significant, accounting for BDE trends such as Ar > Ne > He, $C_3H_8 > C_2H_6 > CH_4 > H_2$, and NCCN > $CO_2 > N_2$. However, issues such as donor atom effective radius can sometimes override trends in polarizability even for nonpolar ligands. For example, the BDE for CO_2 exceeds that for CS_2 by 7 kJ mol^{-1}, despite the latter ligand having a much larger polarizability: the respective Na$^+$/donor atom separations for these complexes are 2.25 and 2.79 Å, accounting for the comparatively "efficient" bond to CO_2.

Is it possible, using only the relative Na$^+$/ligand bond strengths of prototypical monofunctional ligands, to reliably predict or assign the mode of Na$^+$ coordination to a di- or polyfunctional ligand? In keeping with previous theoretical studies,[24,29,30] the Table 1 data strongly suggest that it is not. For example, the bond dissociation enthalpy of the σ-complex Na$^+$−FH exceeds BDE(Na$^+$−C_2H_2) by 8 kJ mol^{-1}, yet π-coordination of Na$^+$ to HCCF wins out over σ-coordination to its F atom by 13 kJ mol^{-1}. The trend is reversed for H_2CCHF, which exclusively forms an F-coordinated σ-complex, yet the BDE values for the C_2H_2 and C_2H_4 complexes are almost identical. The stability only of an O-coordinated $HCONH_2$ complex, with no N-coordinated minimum, is also contrary to the greater BDE of the NH_3 complex than of H_2CO.

There also do not appear to be consistent trends across homologous series. For example, the bond dissociation enthalpy of the NH_3 complex exceeds that for H_2CO as well as those of HCN, HNC, and HCOOH, but this trend is reversed on methylation: the BDEs of the CH_3CHO, CH_3COCH_3, CH_3CN, CH_3NC, $HCOOCH_3$, and CH_3COOH complexes all exceed the values for mono-, di-, and trimethylamine. Within these complexes, the rise in nitrile BDE on methylation is particularly steep: BDE(Na$^+$−$NCCH_3$) exceeds the corresponding CH_3COOH value by 12.5 kJ mol^{-1}, although the value for HCOOH is marginally greater than that for HCN. The F-coordinated σ-complex of HCCF is less strongly bound than the π-complexes of HCCF and HCCCl, yet H_2CCHF (which forms a σ-complex) coordinates much more strongly to Na$^+$ than does H_2CCHCl, which yields a π-complex. For CH_3Cl, substituting H by either F or Cl (to produce CH_2ClF or CH_2Cl_2) results in a BDE increase, but for CH_3F the same substitutions *decrease* the BDE. The complex of the smallest thioether, $(CH_3)_2S$, has a BDE 5 kJ mol^{-1} greater than that of its isomer CH_3CH_2SH, in contrast to the larger BDE (by a margin of 7 kJ mol^{-1}) for CH_3CH_2OH than for $(CH_3)_2O$. Hydrogen peroxide, HOOH, has a BDE which is 8 kJ mol^{-1} greater than that of hydrazine, H_2NNH_2, counter to the trend between H_2O and NH_3 BDE values. Finally, dehydrogenation of CH_3CH_2CN to CH_2CHCN reduces the complexation BDE by only 6 kJ mol^{-1}, while dehydrogenation of CH_3CH_2OH to CH_2CHOH engenders a reduction by 19 kJ mol^{-1}, *despite* the additional stabilization imbued on the Na$^+$/CH_2CHOH complex by a weak π-coordination which augments the σ-coordination to the hydroxyl group, a chelation pathway which is not geometrically attainable for the CH_2CHCN complex.

On this note, what governs chelation (or its absence) in the complexation of bifunctional ligands? Coordination is strictly to one donor atom (nitrile N or carbonyl O) in the cases of H_2NCN and HCOCN, an occurrence which can be rationalized on geometric grounds: the ligand is simply not sufficiently flexible to permit the distortion required for simultaneous σ-complexation at both donor atoms. Nor does chelation feature in the Na$^+$ complexes of $HCONH_2$ or of any ligand bearing a carboxyl group, although geometric constraints do not appear so problematic for these ligands. Chelation of a sort is encountered for CH_2CHOH (as noted above) and for CH_2F_2 and CH_2Cl_2, although the contribution from the second donor site in each instance is rather slight: the additional π-coordination in CH_2CHOH only stabilizes the complex by 4 kJ mol^{-1} relative to the value found for coordination to the OH group alone, while the CH_2Cl_2 and CH_2F_2 values are respectively slightly higher and lower than those of CH_3Cl and CH_3F. The 1,2-disubstituted ethanes provide the "best" examples of chelation among the present data set: FCH_2CH_2F, $HOCH_2CH_2OH$, and $H_2NCH_2CH_2NH_2$ all form complexes in which the second Na$^+$/donor atom interaction contributes, respectively, an additional 58−86% of the BDE calculated for the singly coordinated complex, while the FCH_2CH_2OH complex is also very significantly stabilized by chelation.

In previous CP-dG2thaw studies on magnesium ion complexes,[29,41] we have contrasted the trends evident in Na$^+$/ligand bond dissociation enthalpies to those of Mg$^+$ and Mg^{2+}. While the present study offers many more points of comparison, it does not materially alter the conclusions of these earlier studies:[29,41] the lone valence electron of Mg$^+$ hinders the formation of purely electrostatic complexes to small nonpolar ligands such as H_2 and N_2, but assists in strengthening the bond between Mg$^+$ and polar organic ligands due to covalency effects, while dicationic Mg^{2+} forms much stronger complexes than either Na$^+$ or Mg$^+$ due especially to the greatly enhanced ion−induced dipole interaction.

Finally, are there useful trends which can be identified, for example in the dependence of metal ion/ligand bond strength on the distance separating Na$^+$ from the ligand's donor atom(s), which might be sufficiently general to permit prediction of BDE values from a knowledge of the complex ion's geometry? In an attempt to address this question, we have further explored some concepts (originally described by Dunbar)[42] which were assessed in our previous work on metal ion complexes of linear NC-terminated molecules.[28] In the earlier work,[28] metal ion/ligand binding energies were compared to the ionic stabilization energies ΔE_{ionic} obtained by replacing the metal ion with a unit point charge:

$$\mathrm{BDE(Na^+{-}X)} = -(\Delta E_{\text{ionic}} + \Delta E_{\text{orbital}} + \Delta E_{\text{repuls}})$$

where the other terms concern the (attractive, nominally covalent) electronic orbital interactions associated with complexation and the short-range repulsion energy arising from the metal ion's finite size. The CP-dG2thaw calculations return BDE values, while calculations on ligand complexation to a point charge (at the same level of theory) yield the corresponding ΔE_{ionic} terms, allowing determination of the "difference energy" ($\Delta E_{\text{orbital}} + \Delta E_{\text{repuls}}$). When calculations of this type were undertaken on linear NC-containing molecules,[28] we found that the alkali metal ion complexes invariably were well fitted by a dependence of the difference energy on $r^{-12\pm1.2}$ (where r is the M$^+$−N interatomic distance) while complexes of Mg$^+$, Al$^+$,

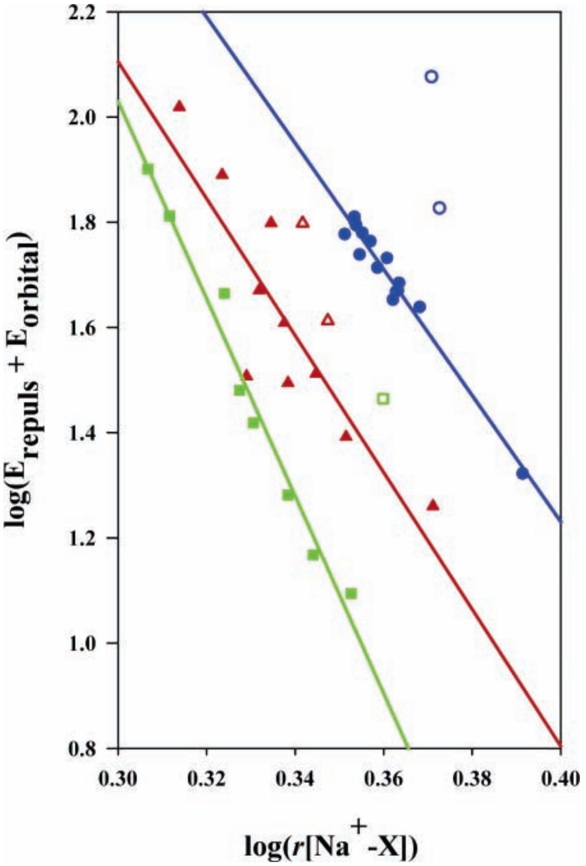

Figure 3. Log−log graph of "difference energy" versus sodium/donor atom internuclear separation for complexes of various N-, O-, and F-containing ligands. Line fits and solid symbols are displayed for nitriles (blue), sp^2-hybridized O donors (red), and monocoordinated fluorides (green), while the open symbols represent other donor types for each coordinating atom: the sp^3-hybridized N donors ammonia and trimethylamine, sp^3-hybridized O donors water and dimethyl ether, and F donor chlorofluoromethane, which is weakly chelating.

and Ca$^+$ with the same ligands obeyed much less steep power laws. The conformity of the Na$^+$ data to the r^{-12} dependence of the standard Lennard-Jones potential was held to be fortuitous, but nonetheless indicative of a metal ion/ligand interaction in which covalent effects were essentially negligible.[28] When the analysis is extended to include all of the NC-terminated ligands in Table 1, we find that the conclusions of our earlier study[28] (originally applied to the rather restrictive set of linear nitriles) hold up remarkably well also for planar and nonplanar nitriles (see Figure 3). The log/log graph of difference energy versus Na$^+$−N distance obeys a dependence on $r^{-12.3}$, minimally changed from the result of $r^{-12.8}$ obtained in our earlier work.[28] This leads us to conclude that the Na$^+$/ligand repulsive interaction preventing further compression of these complexes is dominated by repulsion between Na$^+$ and sp-hybridized N, with negligible involvement from the ligand's more remote atoms. In contrast, the two data points (shown as open circles in Figure 3) for sp^3-hybridized N-coordinated complexes, namely those of ammonia and trimethylamine, categorically do not adhere to the r^{-12} dependence followed by the NC-containing compounds, instead displaying an apparent "excess" of the difference energy. This result suggests that the repulsion between Na$^+$ and sp^3-hybridized N is intrinsically stronger, at any separation, than the corresponding repulsive interaction between Na$^+$ and sp-hybridized N, consistent with the more extended radial size generally attributed to orbitals with a higher admixture of p character. It is also likely that the bulky methyl groups on trimethylamine are sufficiently close to Na$^+$ to further augment the ion/ligand repulsion through a simple steric effect.

Figure 3 also depicts analogous data for the Na$^+$ complexes of sp^2-hybridized O-coordinating compounds and of F-coordinating ligands. To a first approximation, results from these compounds are broadly consistent with the nitrile data, when allowance is made for the progressively smaller atomic radii of O and of F. However, while the fluorinated ligand results show a reasonably convincing straight-line fit to the data (excluding the outlying point for H_2CClF, which forms a sodium ion complex featuring a weak Cl/Na$^+$ interaction at an interatomic distance of $r(\text{Na}-\text{Cl}) = 2.884$ Å in conjunction with $r(\text{Na}-\text{F}) = 2.290$ Å and which can therefore be expected to possess a significant repulsive term from the sodium/chlorine interaction as well as that attributable to fluorine), the fitted dependence of difference energy on $r^{-18.7}$ is considerably at variance from the nitrile results. The oxygen-containing complexes are better matched to the nitrile data, with a dependence on $r^{-13.0}$ (once the points for sp^3-hybridized H_2O and $(CH_3)_2O$, shown as open triangles, are excluded) but exhibit a much wider scatter from the best-fit line. It appears that the results for Na$^+$ coordination to nitriles are anomalous in the sense that the difference in energy—between a "point-charge" complexed ligand and the true sodium ion complex—is a particularly straightforward function of the Na−N interatomic distance. The inability to reliably generalize from this class of complexes to other classes (in Figure 3, doubly bonded O-containing ligands, or fluorinated ligands) suggests that few, if any, "shortcuts" exist for the determination of sodium ion/ligand BDE values for larger ligands.

4. Conclusions

The remarkable consistency between CP-dG2thaw sodium ion/ligand bond strengths, and the recently constructed ladder of experimental complexation free energy values, is gratifying but does not ultimately provide a reconciliation between theory and experiment. While agreement between experimental and theoretical *relative* complexation free energies is extremely close, the reliability of the *absolute* experimental ladder is still open to question: our CP-dG2thaw values are clustered 2.1 ± 1.1 kJ mol^{-1} higher than the experimental values (fixed according to the Na$^+$/CH_3NH_2 binding energy), while a small set of higher level calculations on Na$^+$-containing complexes (including W1 calculations performed in this work) has delivered complexation free energies which are generally higher than the experimental ladder values by ~5 kJ mol^{-1}. This modest disagreement between experiment and theory is not likely to be satisfactorily resolved without additional high-level theoretical investigations as well as further high-precision laboratory study of absolute sodium ion binding energies.

The breadth of ligands considered in the present work, in tandem with the regularity with which CP-dG2thaw delivers relative complexation free energies in accordance with experimental values, has allowed us to uncover several inconsistencies in bond strengths for different classes of compounds. For example, ammonia has a larger BDE to Na$^+$ than does H_2CO, HCN, HNC, or HCOOH, but the monomethylated analogues of the latter compounds all have larger BDEs (in some instances, by a considerable margin) than does CH_3NH_2. As another example, ethanol binds more strongly to Na$^+$ than does CH_3OCH_3, but for the analogous sulfur-containing ligands CH_3CH_2SH and CH_3SCH_3 the trend is reversed. It is also difficult to predict when chelation is preferred as a mode of coordination: a weak chelation effect is seen with CH_2CHOH and with H_2CF_2; CH_3COOH and $HCOOCH_3$ prefer coordination geometries with Na^+ in which chelation is not feasible, while their isomer $HCOCH_2OH$ shows a very definite tendency for simultaneous coordination at both O atoms. In the face of these variations in ligand behavior, it seems that the binding site preferences and energetics of larger Na^+/ligand complexes (particularly those featuring polyfunctional ligands) are not susceptible to determination by simple extrapolation of results for smaller ligands, but must be obtained by reliable experimental or theoretical measurements (or both).

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