An Experimental and Ab Initio Study of the Nature of the Binding in Gas-Phase Complexes of Sodium Ions

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Abstract: Fourier transform ion cyclotron resonance (FT-ICR) ligand exchange equilibrium experiments have been used to establish a relative scale of sodium binding free energies of about fifty organic molecules. Ab initio calculations yield accurate enthalpies and entropies of complexation for a new set of 30 molecules. These calculations establish an absolute basis for the relative experimental free energy scale. In addition, they provide structural information for the complexes which permits considerable insight into the nature of sodium ion binding. We found that when the binding site is a first row atom, the sodium ion aligns with the molecular dipole axis in order to maximize charge–dipole electrostatic interactions. Strong deviations from this behavior occur when the ion is attached to a heavier atom such as sulfur, chlorine or bromine. For flexible molecules such as the isomers of butyl chloride, there are several isomers of low energy, and differences exist between the enthalpy and free energy orders of stability. Finally, sodium ion affinities have been obtained for several aromatic molecules which lend support to the importance of charge–quadrupole interactions in such cation–π complexes.

Keywords: ab initio calculations · enthalpies · gas-phase complexes · sodium

Introduction

Due to the importance of sodium compounds in organic chemistry and biochemistry, and to the use of sodium complexes in mass spectrometric studies, there has been a heightened recent interest in the study of the energetics of binding of sodium ions to organic and biological molecules in the gas phase. A compilation of experimental and computational data up to 1998 has recently been published.[1] Two studies have also succeeded in establishing both relative and absolute scales of sodium binding energies to organic molecules in the gas phase.[1, 2] The knowledge of accurate binding interactions to many small molecules is required to predict where, in a polyfunctional molecule, sodium cationization might occur. For example, in *para*-amino benzoic acid there are three possible sites for sodium complexation: on the amine nitrogen, on the carboxyl oxygens, or on the aromatic ring. On the basis of the sodium ion affinities recently determined,[1, 2] it might be predicted that sodium will associate most favorably with the acid function in the molecular plane with a favorable alignment with the molecular dipole moment. While several key functional groups have been studied, the coverage has by no means been exhaustive and several important groups would be of considerable interest. In addition, relatively little discussion has been directed toward a more detailed view of the nature of the bond formed to Na^+. We have therefore undertaken the current study to extend the range of types of molecules as well as to provide quantitative insight into the factors affecting structure and binding energetics in sodium ion complexes in general. Fourier transform ion cyclotron resonance (FT-ICR) ligand exchange equilibrium experiments have been used to establish a relative scale of sodium binding free energies of about fifty molecules. In addition, ab initio calculations have been carried out for a new set of 30 molecules to yield accurate enthalpies and entropies of complexation. This then establishes an absolute basis for the relative experimental free energy scale. In addition, such calculations provide structural information for the complexes which permits considerable insight into the nature of sodium ion binding.

Experimental and Theoretical Section

Experimental details: FT-ICR experiments were carried out on a Bruker-spectrospin CMS-47X spectrometer. Instrumentation and techniques of FT-ICR experiments have been described in detail previously.[3, 4]

Metallic sodium was placed in the sample holder of a direct insertion probe and heated to ≈400 °C. Ionization by 14 eV electrons in the external ion

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source resulted in the exclusive production of Na^+. The sodium ion thus generated was transferred to the FT-ICR cell where it was trapped and allowed to react with *tert*-butyl chloride via elimination of HCl, yielding the sodium ion adduct of isobutene, see Equation (1). This reaction has been previously shown by Allison and Ridge[5] to be an effective means of generating sodium adducts of small molecules. The $Na^+(i\text{-}C_4H_8)$ adduct thus formed subsequently reacts:

$$Na^+ + t\text{-}C_4H_9Cl \rightarrow Na^+(i\text{-}C_4H_8) + HCl \tag{1}$$

$$Na^+(i\text{-}C_4H_8) + t\text{-}C_4H_9Cl \rightarrow Na^+(t\text{-}C_4H_9Cl) + i\text{-}C_4H_8 \tag{2}$$

$$Na^+(t\text{-}C_4H_9Cl) + H_2O \rightarrow Na^+(H_2O) + t\text{-}C_4H_9Cl \tag{3}$$

with the parent neutral to generate the sodium ion adduct of *tert*-butyl chloride, Equation (2). Both reactions occur at the collision rate. Typical variation of ion intensities with trapping time is shown in Figure 1. The appearance of the sodium ion adduct with H_2O is due to the sodium ion transfer to water, Equation (3), introduced in the FT-ICR cell as an impurity in CH_4 which was used as a thermalization reagent. The background pressure of water in the ICR cell is on the order 2×10^{-9} mbar, however, this displacement reaction also occurs at the collision rate; this leads $Na^+(H_2O)$ to become the dominant ion after 10 s. However, when a species such as CH_3CN is also added to the FT-ICR cell in considerable excess the temporal behavior shown in Figure 2 results. Since the CH_3CN is in considerable excess and has a sodium ion affinity greater than that of water, the $Na^+(i\text{-}C_4H_8)$ reacts more rapidly than it is formed, leading to the efficient appearance of the $Na^+(CH_3CN)$ complex. Significantly, no appreciable amount of $Na^+(t\text{-}C_4H_9Cl)$ nor $Na^+(H_2O)$ is observed at any reaction time. If two species such as CH_3CN and $(CH_3)_2CO$, with comparable sodium ion affinities are added to the cell, a sodium ion transfer equilibrium, Equation (4), can be established such as that shown in Figure 3. If the ratio of pressures of CH_3CN and $(CH_3)_2CO$ is known, these, together with the equilibrium abundances of the two complexes, can be used to calculate the equilibrium constant, K_{eq}, for the sodium transfer, Equation (5). Pressures of each of the neutrals were determined using ionization gauge readings corrected for the polarizability of the molecule involved. Previous experiments in this laboratory have shown that this leads to very accurate pressure determinations.[6] From this equilibrium constant, the free energy change can then be calculated, Equation (6). In this way a number of sodium ion transfer equilibrium measurements could be carried out to permit the construction of a scale of relative sodium ion binding free energies.

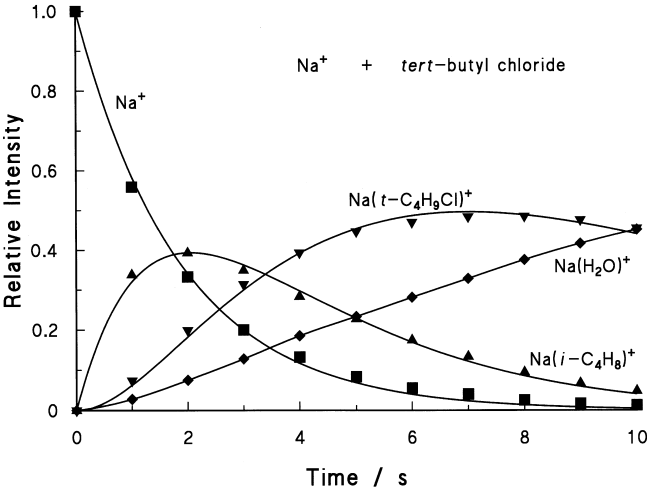

Figure 1. Variation of relative ionic abundances with reaction time for the sequence of reactions used to generate Na^+ complexes. The pressure of *tert*-butyl chloride is 1.3×10^{-8} mbar and that of CH_4, present as a thermalizing agent, is 5.8×10^{-7} mbar. The pressure of water, introduced as an impurity in the CH_4 is 1.7×10^{-9} mbar.

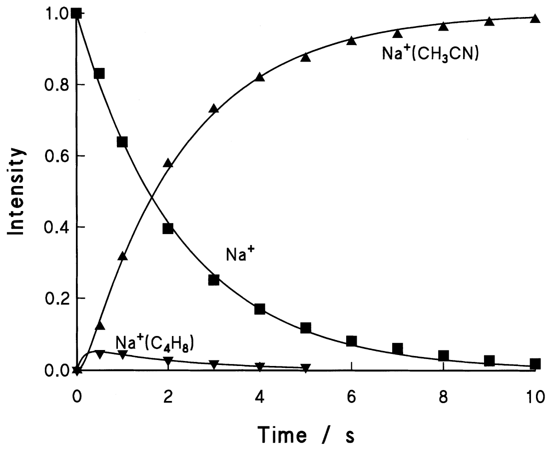

Figure 2. Variation of relative ionic abundances with reaction time for the sequence of reactions used to generate $Na^+(CH_3CN)$ adducts. The pressure of *tert*-butyl chloride is 1.2×10^{-8} mbar and 1.5×10^{-7} mbar for CH_3CN.

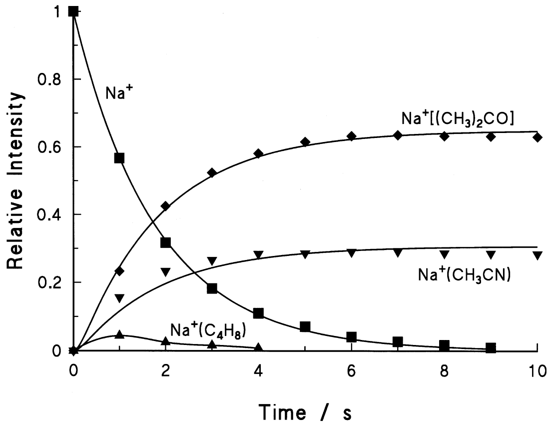

Figure 3. Variation of relative ionic abundances with reaction time leading to Na^+ exchange equilibrium between acetone and acetonitrile. The pressure of *tert*-butyl chloride is 1.2×10^{-8} mbar, 1.0×10^{-7} mbar for CH_3CN and 7.4×10^{-8} mbar for acetone.

$$Na^+(CH_3CN) + (CH_3)_2CO \rightarrow Na^+[(CH_3)_2CO] + CH_3CN \tag{4}$$

$$K_{eq} = \frac{I_{Na^+[(CH_3)_2CO]}}{_{Na^+(CH_3CN)}} \cdot \frac{P_{Na^+(CH_3CN)}}{P_{Na^+[(CH_3)_2CO]}} \tag{5}$$

$$\Delta G = -RT\ln(K_{eq}) \tag{6}$$

Experiments were also carried out in which, after equilibrium had been established, one of the equilibrium ionic partners was isolated using rf ejection techniques and allowed to react until equilibrium was re-established. Following this, the other equilibrium partner was isolated and allowed to react in the same fashion. Kinetic analysis of the resulting curves permitted the forward and reverse rate constants to be determined. In this way, the equilibrium constant could also be determined as the ratio of forward and reverse rate constants. In all cases where this was carried out, equilibrium constants in excellent agreement with those obtained from steady state intensities were obtained. For example, the data shown in Figure 4 for the equilibrium between the sodium complexes of benzene and methanol were obtained.

All experiments were performed at ambient temperature which varied from 23–25 °C depending upon the day. This small variation in temperature does not lead to any appreciable difference in the ΔG values cited.

Computational details: Sodium affinities were determined with a procedure already detailed in previous papers.[7, 8] Geometries of neutral and sodium-bound molecules were first optimized at the MP2(full)/6-31G* level. Vibrational frequencies were also obtained at this level. Test calculations on formamide and dimethyl ether at the MP2/6-31+G* level

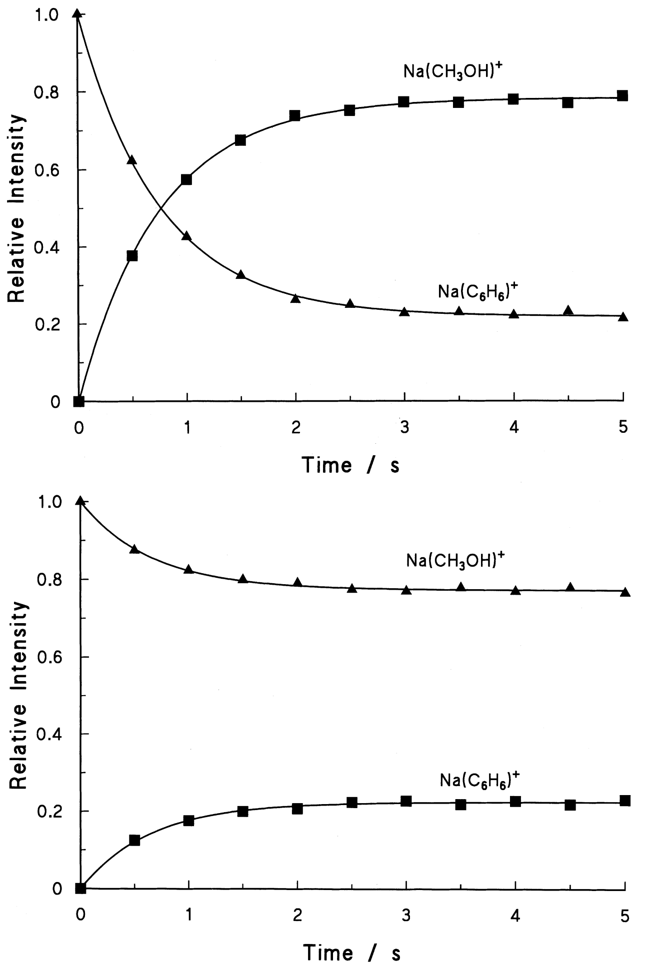

Figure 4. Variation of relative ionic abundances as a function of reaction time after isolation of each of the equilibrium partners in the Na^+ exchange equilibrium between C_6H_6 and CH_3OH. The pressure of *tert*-butyl chloride is 1.5×10^{-8} mbar, 1.9×10^{-7} mbar for C_6H_6 and 3.8×10^{-8} mbar for CH_3OH. Top: initial selection of $Na^+(C_6H_6)$; bottom: initial selection of $Na^+(CH_3OH)$.

showed negligible structural differences. Final energetics were obtained at the MP2(full)/6-311 + G(2d,2p)//MP2/6-31G* level in order to minimize basis set superposition errors (BSSE). Even so, BSSE remains non negligible and was subtracted from the computed interaction energies in the full counterpoise approximation. This is known to lead to slightly overestimated BSSE corrections, but the use of the 6-311 + G(2d,2p) basis set ensures that the magnitude of this overestimation will be small since the computed total BSSE is small (less than 2 kcal mol^{-1} in most cases). The largest BSSE values (between 2.0 and 2.5 kcal mol^{-1}) occurred for complexes of aromatic molecules. The influence of excluding the 1s shell of all non-hydrogen atoms in the MP2 calculation was assessed in the case of the $Na^+(C_6H_6)$ complex. It was found that both the raw D_e value and the BSSE correction were slightly diminished, such that the change to the corrected D_e value was negligible. Zero point vibrational energies and thermal corrections at 298 K were obtained from the unscaled MP2/6-31G* vibrational frequencies. Finally, these complexation energies were converted to enthalpies by the addition of a factor of RT (0.6 kcal mol^{-1} at 298 K). Calibration calculations at the CCSD(T) level for small sodium complexes have shown that this procedure based on MP2 wavefunctions leads to well converged energetics.[9, 23] This method also has the advantage of remaining tractable for molecules with up to $\approx$10 non hydrogen atoms. The excellent agreement found between experimental and calculated complexation enthalpies indicates that for molecules of reasonable size, calculated enthalpies should be accurate to within ± 2 kcal mol^{-1}. Recent computational studies by Feller et al.[23] indicate that binding energies converge very slowly when the basis set is systematically enlarged, and that applying the BSSE correction might actually degrade accuracy. Our own calculations indicate that the reason for this behavior is that the sodium basis brings a significant improvement in the description of the electrical properties of the complexed molecule, which require very large basis sets for high accuracy. If BSSE corrections are not applied, binding enthalpies are generally 1.0–1.5 kcal mol^{-1} larger than those reported in Table 1, and 2.0–2.5 kcal mol^{-1} larger for π complexes of aromatic compounds. Given the very good agreement of these values with experimental results (HPMS, FT-ICR and GIB) we have nevertheless chosen to give BSSE-corrected values.

Table 1. Ab initio calculated enthalpies, entropies, and free energies of complexation to the sodium cation. All values are in kcal mol^{-1} except for ΔS in cal mol^{-1} K^{-1}.

Molecule	ΔH_{298}	ΔS	ΔG_{298}
C_3H_6	14.6	21.4	8.2
i-C_4H_8	16.3	21.3	10.0
C_4H_6	16.9	23.1	10.0
CH_3SCH_3	20.2	20.6	14.1
HBr	9.4	17.0	4.3
CH_3Br	13.9	16.7	8.9
t-C_4H_9Br	18.1	13.8	14.0
HCl	8.9	17.2	3.8
CH_3Cl	13.7	16.9	8.7
C_2H_5Cl	15.9	18.8	10.3
n-C_3H_7Cl	16.4	18.2	11.0
i-C_3H_7Cl	17.5	17.0	12.4
n-C_4H_9Cl	17.0	18.6	11.5
s-C_4H_9Cl	17.6	17.6	12.4
i-C_4H_9Cl	16.8	19.3	11.0
t-C_4H_9Cl	18.3	17.2	13.2
Cl_2	7.3	17.5	2.1
C_6H_5Cl	18.2	24.0	11.0
furan	17.8	22.8	11.0
$(CH_3)_2CCHCHO$	33.3	21.6	26.9
cyclopentenone	33.5	22.4	26.8
$CH_3CO_2COCH_3$	39.9	25.9	32.2
$(CH_3)_3P$	25.2	23.3	18.3
DMSO	38.7	22.1	32.1
$HO(CH_2)_2OH$	37.5	27.2	29.4
$HO(CH_2)_3OH$	39.0	27.1	30.9
$NH(CH_3)_2$	26.6	23.5	19.6
$N(CH_3)_3$	26.2	23.6	19.2
$C_2H_5NH_2$	27.7	23.4	20.7
C_2H_5CN	31.2	22.3	24.6

Complexation entropies were also computed from the MP2/6-31G* frequencies and geometries. Comparisons with known entropies of stable neutral molecules show that this level of theory accurately reproduces absolute entropies. It must be noted that in the sodium adducts the three new vibrational modes will sometimes have very low frequencies which make significant contributions to the entropy. Inspection of the individual contributions of such modes suggests that typical accuracies for the complexation entropies should be ± 2 cal mol^{-1} K^{-1}.

All calculations were run using the Gaussian94 package.[10]

Results

The values of complexation enthalpy, entropy and free energy at 298 K obtained from the ab initio calculations are given in Table 1. Similar data for a number of other compounds used to establish an absolute sodium ion affinity scale have also been published by us recently elsewhere.[1]

The individual ΔG^0_{298} values for the majority of the sodium exchange equilibria studied are summarized in Table 2. Also

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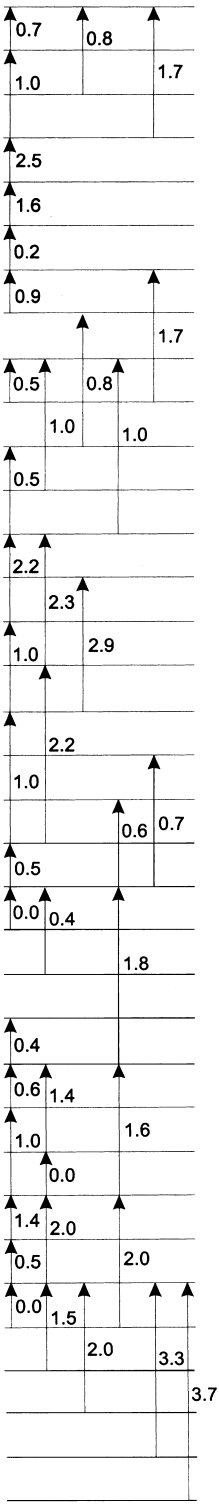
Table 2. Ladder of free energies of complexation of molecules to the sodium cation from FT-ICR ligand exchange equilibria, anchored at the HPMS and ab initio value for methylamine. Uncertainties in FT-ICR values increase with increasing number of steps away from the reference compound (CH_3NH_2) to a maximum of 0.6 kcal mol^{-1} at the top of the ladder. Ab initio values are from the present work or from ref. [1], while other values are from ref. [2].

Compounds	Energy difference	ΔG^0_{298} (FT-ICR)	ΔG^0_{298} (ab initio)	ΔG^0_{298} (other)
$CH_3OCH_2CH_2OCH_3$		31.8	32.9	30.7
$CH_3CO_2COCH_3$		31.1	32.2	
$(CH_3)_2SO$		31.0	32.1	
$HCON(CH_3)_2$		30.1	30.3	31.2
$CH_2(OC_2H_5)_2$		27.6		
$HCOCHC(CH_3)_2$		26.0	26.9	
$c\text{-}C_5H_6O$		25.8	26.8	
$CH_3COCH_2CH_2CH_3$		24.9		
CH_3CH_2CN		24.6	24.6	
$c\text{-}C_4H_6O_2$		24.1		
$(CH_3)_2CO$		24.1	23.7	25.3
CH_2FCH_2OH		23.6		
CH_3CN		23.6	23.6	
$CH_3CO_2CH_3$		23.3	22.6	
$t\text{-}C_4H_9OH$		21.4	21.4	21.3
$(C_2H_5)_2O$		21.3	21.3	
$i\text{-}C_3H_7OH$		20.4	20.4	20.4
$n\text{-}C_4H_9OH$		19.7	20.9	19.6
$(CH_3)_2NH$		19.6	19.6	
CH_3NH_2		19.5	19.5	20.1
C_2H_5OH		19.0	19.6	18.0
$(CH_3)_3N$		19.0	19.2	
NH_3		18.6	18.5	19.5
$(CH_3)_2O$		17.6	18.0	15.9
CH_3OH		17.3	17.7	15.7
C_6H_5OH		16.7	15.4	15.4
H_2O		15.7	15.6	17.8
C_6H_6		15.7	14.5	14.2
$(CH_3)_2S$		14.2	14.1	
$t\text{-}C_4H_9Cl$		13.7	13.2	
$t\text{-}C_4H_9Br$		13.7	14.0	
$n\text{-}C_4H_9Br$		12.2		
$c\text{-}C_4H_4O$		11.7	11.0	
C_4H_6		10.3	10.0	
$i\text{-}C_4H_8$		10.0	10.0	

given are absolute values of ΔG^0_{298} for the complexation of sodium to the neutral molecules. In order to assign these values, it was necessary to choose one compounds of known sodium ion binding free energy. High pressure mass spectrometric (HPMS) experiments give accurate ΔH^0_{298}, ΔS^0, and ΔG^0_{298} values for sodium ion binding and our previously published work[1] has shown that excellent agreement is obtained with ab initio calculations carried out at the level used in the current study. Methylamine has been chosen as the anchor point for the present sodium ion binding free energy scale since virtually exact agreement was obtained between ab initio calculations and experiment in this case. Choice of either of the other three compounds in the previous study would result in very minor changes in this scale. The uncertainty assigned to the HPMS ΔG^0_{298} value for methylamine is 0.2 kcal mol^{-1}. The uncertainty on the difference in ΔG^0_{298} for two molecules, obtained from an equilibrium in the FT-ICR conditions described above, may be estimated to be 0.1 kcal mol^{-1}. Propagating such uncertainties along the affinity scale leads to slowly increasing uncertainties on each absolute value, up to a maximum of 0.6 kcal mol^{-1} at the top of the ladder.

Since it was necessary to use *tert*-butyl chloride as the reagent to generate sodium ion complexes, it was not possible to examine equilibria involving compounds with sodium ion binding energies significantly less than that of *tert*-butyl chloride. Correspondingly, isobutene which binds sodium 3.7 kcal mol^{-1} more weakly than $t\text{-}C_4H_9Cl$ represents the lower limit of the present scale. All species whose sodium ion binding affinities are less than that of *tert*-butyl chloride have been examined relative to this compound. As a result, in order to maintain clarity in Table 2, not all equilibria examined in this region have been included. All of the energetics obtained are given in Table 3 (alkyl chlorides), Table 5 (alcohols), Table 6 (amines), Table 7 (aromatics) and Table 8 (carbonyl compounds) together with ab initio and literature results where available.

Also included in Table 2 are the ΔG^0_{298} values obtained from ab initio calculations from this or previous work as well as those obtained by HPMS or guided ion beam experiments.[2, 11]

Discussion

It is of interest to examine the thermochemistry of the reaction used in the current experiments to generate sodium ion adducts as in Equation (1). Available thermochemical data[12] reveal that the decomposition of *tert*-butyl chloride into isobutene and hydrogen chloride is endothermic by 16.6 kcal mol^{-1}. The reaction of Na^+ with $t\text{-}C_4H_9Cl$ is observed to proceed essentially at the collision rate, which would imply that it is thermoneutral or exothermic, with no barrier in excess of the energy of reactants. The calculated value of the complexation energy of Na^+ with isobutene of 16.3 kcal mol^{-1} thus shows that the reaction is thermoneutral. Ab initio calculations of the ΔH^0_{298} for this reaction yield a value of 2.5 kcal mol^{-1}, in qualitative support of this conclusion. Similarly, the analogous reaction of $t\text{-}C_4H_9Br$ (2.3 kcal mol^{-1}

endothermic) is found to proceed rapidly while, consistent with the calculated thermochemistry, no reaction with isopropyl halides is observed (3.4 kcal mol^{-1} endothermic for i-C_3H_7Cl). In the case of *tert*-butyl halides, each of the reactions involves a negative free energy change.

Larrivee and Allison[13] have proposed a mechanism for the analogous reaction of Li^+ with haloalkanes RX. The process begins by abstraction of a halide ion X^- followed by transfer of a proton from the resulting carbocation to LiX. Rotation of the $LiXH^+$ results in a lithium bound dimer of HX and an olefin, which dissociates either to $Li^+(HX)$ or Li^+(olefin), depending on the relative binding energies. Calculations of sodium binding energetics indicate that the proton transfer from t-$C_4H_9^+$ to NaCl is 17 kcal mol^{-1} exothermic and the transfer of Na^+ from HCl to i-C_4H_8 is 7.4 kcal mol^{-1} exothermic. The fact that the reaction is so efficient would indicate that the intermediate barriers on the potential energy surface (PES) lie significantly below reactants. In contrast, the analogous reaction of Na^+ with t-C_4H_9OH is not observed, even though production of $Na^+(i\text{-}C_4H_8)$ or $Na^+(H_2O)$ is predicted to be exothermic by 3.7 and 9.5 kcal mol^{-1}, respectively. Thus, in this case there must be an intermediate barrier which impedes the reaction. It is possible that the abstraction of OH^- is the limiting step of the mechanism.

In order to understand better the factors influencing sodium ion binding to molecules, various functional groups are discussed separately below.

Alkenes: Previous work[1] has shown that the sodium complexation to ethylene results in a symmetric π-bonded structure, in which the C=C bond length is essentially unchanged relative to that in isolated ethylene, with a Na–C distance of 2.74 Å, and a bond enthalpy at 298 K of 12.7 kcal mol^{-1}. As shown in Figure 5, for the sodium complex of propene, Na^+ is displaced towards the unsubstituted carbon atom with a Na–C distance of 2.641 Å and an increased bond enthalpy of 14.6 kcal mol^{-1}. These trends continue for isobutene where the shortest Na–C distance becomes 2.582 Å and the bond enthalpy 16.3 kcal mol^{-1}. This can perhaps be best understood from natural net charges on the sp^2 carbons, computed at the MP2 level. In propene the unsubstituted carbon bears a charge of -0.535, while the other has a significantly smaller charge of -0.221, due to the methyl group. In isobutene the two methyls lead to an increased polarization of the C=C bond, with net charges of -0.570 and $+0.001$ on the unsubstituted and substituted carbon, respectively. Thus simple electrostatics dominate the trend in shaping such cation–π complexes.

The situation for butadiene is somewhat more complicated because of the existence of two conformations of low energy for the neutral molecule. The *trans* form is more stable than the *gauche* form by approximately 3 kcal mol^{-1}. For the Na^+ complexes of butadiene, no minimum could be found in which a sodium was associated with one of the double bonds. Rather, the lowest energy structure **1** (see Figure 5) was found to be one in which the sodium lies above the central C–C bond of *trans*-butadiene. The Na–C distance of 2.64 Å and bond enthalpy of 16.9 kcal mol^{-1} closely resemble those in isobutene. A second minimum **2** was found to lie 2.3 kcal mol^{-1} higher in energy, in which Na^+ interacts with a *gauche* butadiene. In this case there is considerable interaction between sodium and each of the carbon atoms. It is evident that as the size of the alkene increases, so too does the enthalpy of interaction, a consequence of the increased polarization interaction.

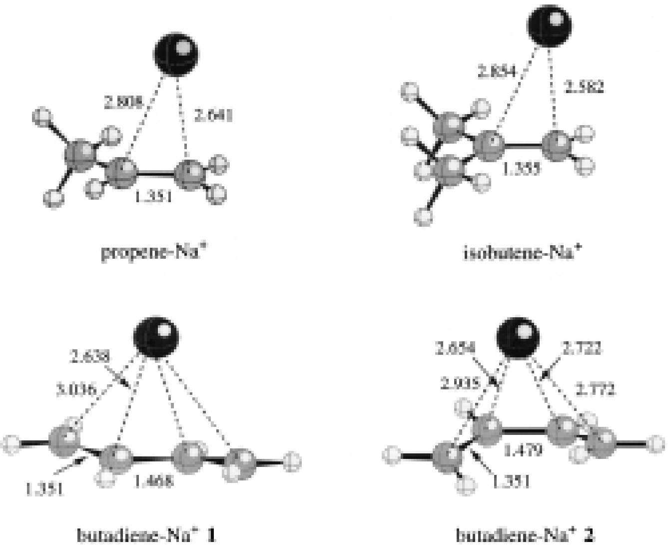


Figure 5. Optimized structures for the sodium complexes of propene, isobutene, and butadiene at the MP2/6-31G* level.

Alkyl halides: Ab initio and experimental sodium binding free energies for the series of alkyl halides investigated are summarized in Table 3. It can be seen that there is generally excellent agreement between both sets of data. In general, as the alkyl group increases in size, so does the energy of interaction with sodium. However, there are interesting differences observed for the various propyl and butyl isomers. In order to understand these differences, it is useful to examine the details of the structures of both the neutral alkyl halides and their sodium complexes. The pertinent details for the most favorable (see below) structures of the sodium complexes of the alkyl halides are summarized in Table 4. As a general feature, it should be noted that alignment of the sodium to the neutral molecule does not coincide with the molecular dipole moment as with several other types of compounds.[1] For example, even with HCl, where the ΔH_{298} of binding is only 8.9 kcal mol^{-1}, the Na-Cl-H bond angle is found to be 114° and in $HBrNa^+$ where the bond energy is slightly greater (9.4 kcal mol^{-1}) the angle is even smaller (103°).[14] One possible interpretation is that these species begin to more closely resemble protonated NaCl and NaBr than sodium complexes of HCl and HBr and, since the interaction between the proton and halogen will have substantial covalent character this “complex” readily adopts a bent configuration characteristic of species such as CH_3ClH^+ and CH_3BrH^+ for example.[15] This appears to be a general feature for species involving second-row atoms since sodium complexes of H_2S, CH_3SH, and $(CH_3)_2S$ are also observed to be non planar and therefore the Na^+ is not aligned with the molecular dipole.

Table 3. Free energies of complexation of alkyl chlorides to the sodium cation in kcal mol^{-1}.

Molecule	FT-ICR[a]	MP2[b]
CH_3Cl	–	8.7
C_2H_5Cl	10.8	10.3
n-C_3H_7Cl	11.6	11.0
i-C_3H_7Cl	12.3	12.4
n-C_4H_9Cl	12.1	11.5
i-C_4H_9Cl	12.3	11.0
s-C_4H_9Cl	13.0	12.4
t-C_4H_9Cl	13.7	13.2
CH_3Br	–	8.9
n-C_4H_9Br	12.2	–
t-C_4H_9Br	13.7	14.0

[a]FT-ICR values from the present work. [b] Computed values from the present work.

Table 4. Selected structural parameters for the complexes of alkyl halides to the sodium cation (distances in Å, angles in degrees).

Molecule	C-X[a]	X-Na[a]	CXNa[a]
CH_3Cl	1.804	2.690	120.7
C_2H_5Cl	1.828	2.672	120.9
n-C_3H_7Cl	1.829	2.667	120.3
n-C_4H_9Cl	1.831	2.664	120.2
i-C_4H_9Cl	1.84	2.66	119.5
i-C_3H_7Cl	1.841	2.654	111.4
s-C_4H_9Cl	1.840	2.649	106.5
t-C_4H_9Cl	1.861	2.640	106.7
CH_3Br	1.973	2.834	113.6
t-C_4H_9Br	2.060	2.778	117.6

[a] X = Cl or Br.

From the data in Table 4, it can be seen that the complexes of alkyl halides form two groups, depending upon whether the alkyl halide is primary or not. For example, the primary chlorides have NaClC bond angles of 120 ± 1° and the structures involve a staggered conformation about the C–Cl bond, with the next carbon (H in CH_3Cl) *anti* to Na. For the secondary and tertiary alkyl chlorides, the Na-Cl-C bond angle is noticeably smaller and the structure adopts a conformation about the C–Cl bond in which an alkyl group eclipses the Na–Cl bond. The secondary propyl and tertiary butyl chlorides have noticeably stronger bond energies than their primary counterparts which likely arises from the favorable polarization interaction with the methyl group which the Na–Cl bond eclipses. This also likely leads to the contraction of the Na-Cl-C bond angles to 109 ± 2°.

The calculated values of ΔH^0_{298} for binding Na^+ are 13.7 and 15.4 kcal mol^{-1} for CH_3Cl and C_2H_5Cl, respectively, and once again these species might be regarded as having the character of methylated and ethylated NaCl as evidenced by the Na-Cl-C bond angles. For C_2H_5Cl, FT-ICR experiments have also established a ΔG^0_{298} for binding Na^+ of 10.8 kcal mol^{-1} in good agreement with the calculated value of 10.3 kcal mol^{-1}.

The ab initio calculations actually reveal that there are at least two forms of n-propyl chloride and four forms of the sodium complexes of n-propyl chloride, as shown in Figure 6. The two conformers of the isolated molecule are extremely close in both enthalpy and free energy, with **2** marginally more favorable (0.1 kcal mol^{-1}).

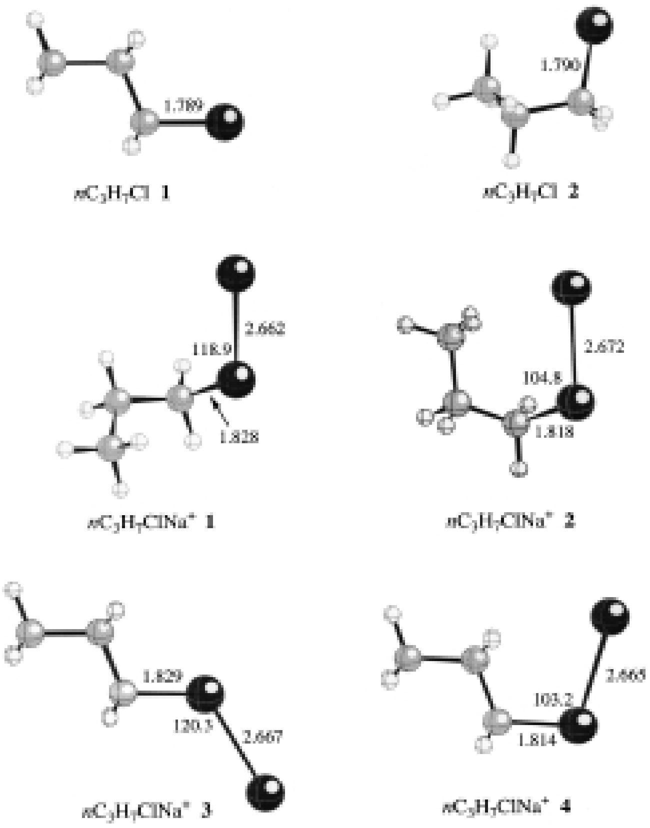


Figure 6. Optimized structures for the conformers of n-propyl chloride and its sodium complex at the MP2/6-31G* level.

The lowest energy structure of the sodiated complex, **2**, has a *gauche* conformation about the C–Cl and the adjacent C–C bond, giving the closest possible approach of the sodium to the terminal methyl group. This thus maximizes the polarization interaction between the positive charge and the alkyl chain. This *gauche* form has the most favorable enthalpy of binding (16.7 kcal mol^{-1}) but the loss of internal rotations makes it considerably entropically less favorable (ΔS^0 = 23.4 cal mol^{-1}K^{-1}) than the other three possible forms with the result that it has the least favorable free energy of binding (9.7 kcal mol^{-1}). Structure **1** for the ion derives from structure **2** by a 120° rotation about the internal C–C bond. The diminished polarization interaction lowers the enthalpy of binding to 15.9 kcal mol^{-1} while the increased flexibility in the alkyl chain results in a more favorable entropy of complexation (17.8 cal mol^{-1}K^{-1}) with the end result that the free energy of binding is more favorable than that in **2** (10.6 kcal mol^{-1}). Binding of Na^+ to the all *trans* conformation of n-C_3H_7Cl resulted in structures **3** and **4**. Both enthalpies of binding are very similar (16.4 and 16.3 kcal mol^{-1} for **3** and **4**, respectively); however, in **3** the sodium is farther away from the alkyl chain, leading to slightly less inhibition of internal rotation. The resulting entropy changes of 18.2 and 19.4 cal mol^{-1}K^{-1} for **3** and **4**, respectively, give rise to corresponding free energy changes of 11.0 and 10.5 kcal mol^{-1}. The computed ΔG^0_{298} of 11.0 kcal mol^{-1} for structure **3** is in good agreement with the experimental value of 11.6 kcal mol^{-1}. This is a particularly illustrative case for the need not only to explore the potential energy surface somewhat extensively for such flexible molecules, but also to investigate the subtle differences between the free energy and enthalpy surfaces. In cases such as that described above where several structures of comparable free energy exist with no significant barriers between them, a statistical mixture of these structures will be present under the experimental conditions employed here. As such, the sodium binding free energies obtained will reflect an average value for the structures of the neutral and the complex involved. In contrast, the calculations report free energy differences between the most favorable structures of the ion and neutral. In such cases therefore the experiments and the calculations do not give exactly the same quantity, but quantitatively the differences will always be minor.

In the case of isopropyl chloride, only one stable minimum was found. As described above, the sodium is oriented in such a way that there is a favorable polarization interaction with one methyl group. For the neutral the only possible structures are conformers due to rotation of the methyl groups and these differ very marginally in energy. The computed ΔG^0_{298} of 12.4 kcal mol^{-1} is in nearly exact agreement with the experimental value of 12.3 kcal mol^{-1}.

Similar considerations apply in the possible conformers of the butyl chlorides and their sodium complexes. Based on the intuition gained from the investigation of the smaller alkyl systems, the several most probable minima were explored. The very good agreement between the calculated and experimental values would indicate that this intuition was probably valid. However, since the experimental values are usually slightly larger than those calculated, the existence of still more favorable conformers of these sodiated complexes cannot be excluded. As expected *n*-butyl chloride exhibits the lowest sodium binding ΔH^0_{298} value. This is followed by the other primary species, isobutyl chloride, then *sec*-butyl chloride and finally the most stable, *tert*-butyl chloride. The unusually low entropies of association found for the Na^+ complexes of the alkyl chlorides is the result of the very low frequency, large amplitude C-C-Cl-Na torsional mode. Again the non-linear nature of the bond is a result of the fact that these species might be regarded as alkylated NaCl complexes.

The more limited data for alkyl bromide complexes reveal that there is almost no difference in energetics between a given bromide and its analogous alkyl chloride. The dipole moments of each alkyl chloride/alkyl bromide pair are nearly identical and thus the greater polarizability of the bromide is compensated for by the fact that the Na^+ can approach more closely in the case of the alkyl chlorides. For the complexes of methyl and *tert*-butyl bromide, essentially identical types of structure were found as those of the analogous chlorides. The free energy of complexation calculated for *tert*-butyl bromide is probably somewhat overestimated due to an unusually favorable entropy of the complex arising from an extremely small frequency of 5 cm^{-1} for the C-C-Br-Na torsional mode. It is likely that the harmonic approximation is not valid for modes of this type, therefore there is a larger uncertainty on the calculation in this case.

Out of a simple curiosity, calculations were also carried out for the sodium complex of Cl_2. The equilibrium structure was found to be of C_{2v} symmetry with a sodium binding energy of 7.3 kcal mol^{-1}. A linear structure was also optimized and found to be only very weakly bound at the MP2/6-31G* level. Vibrational frequency calculations revealed that this structure is a second order transition state with two equal imaginary frequencies corresponding to the degenerate NaClCl bending modes.

Alcohols and ethers: Sodium transfer equilibrium measurements were carried out for H_2O and all possible C_1–C_4 aliphatic alcohols. The free energy changes obtained are summarized in Table 5. Previous HPMS measurements and ab initio calculations for methanol[1] (17.9 and 17.8 kcal mol^{-1}, respectively) are in good agreement with the FT-ICR data obtained in the current work. In addition, Rodgers and Armentrout[11] have carried out guided ion beam measurements and ab initio calculations for the same series of alcohols. Their data are also given in Table 5. As expected, the sodium binding free energies increase with increasing size within the homologous series of primary alcohols. Since the dipole moments of the eight alcohols studied are essentially identical, this increase is primarily attributable to the increasing polarizability.

Table 5. Free energies of complexation of aliphatic alcohols to the sodium cation in kcal mol^{-1}.

Molecule	FT-ICR[a]	GIB[b]	MP2[c]
CH_3OH	17.3	15.7	17.7
C_2H_5OH	19.0	18.0	19.6
n-C_3H_7OH	19.5	19.2	20.2
i-C_3H_7OH	20.4	20.4	20.4
n-C_4H_9OH	19.7	19.6	20.9
i-C_4H_9OH	19.7	18.4	20.1
s-C_4H_9OH	20.9	21.1	21.1
t-C_4H_9OH	21.4	21.3	21.4

[a] FT-ICR values from the present work. [b] Guided ion beam values from ref. [11]. [c] Computed values from ref. [11].

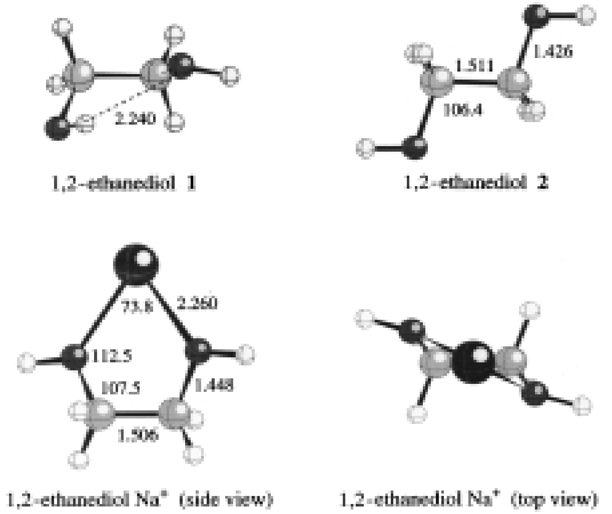
As observed for methanol, there is excellent agreement between the FT-ICR data and ab initio calculations for ethanol. However, for water, methanol and ethanol, the sodium binding free energies obtained from guided ion beam experiments are lower than FT-ICR and ab initio values. For the remaining alcohols with the exception of isobutanol, there is excellent agreement between FT-ICR and guided ion beam results.

It is interesting to compare the variation in binding energetics for the two series of isomeric alcohols. The experimental data find the ΔG^0_{298} for isopropanol to be $\approx$1 kcal mol^{-1} more favorable than that for *n*-propanol. However, the ab initio calculations reported by Rodgers and Armentrout[11] lead to an almost negligible difference (0.2 kcal mol^{-1}). By analogy to the ab initio results described above for the corresponding propyl chlorides, it is possible that the difference experimentally observed between these two alcohols also arises from both enthalpic and entropic factors. Given the small difference found by the calculations, it is therefore possible that the ab initio calculations for the complexed and uncomplexed alcohols did not explore the potential energy surface fully, taking both enthalpic and entropic factors into account.

The disagreement between calculated and experimental values is even more pronounced for *n*-butanol, while agreement is excellent with the FT-ICR values for the three other butanols. The apparent overestimation of the computed free energy of binding of Na^+ to *n*-butanol might be due to the use of an inappropriate conformation of the free molecule. These results thus suggest that due to the very subtle conformational differences possible in flexible alkyl chains, great care must be taken to find the structures with the most favorable free energies.

Experiments were also carried out for CH_2FCH_2OH as a model for simple bidentate binding. The free energy difference relative to ethanol of 4.6 kcal mol^{-1} reflects the increased enthalpy of binding due to the second site of attachment. It is known from microwave spectroscopy that the most stable conformation of CH_2FCH_2OH involves an intramolecular $F\cdots H{-}O$ hydrogen bond.[16] The bidentate complexation of sodium results in the breaking of this hydrogen bond. Since the CH_2FCH_2OH moiety is then in a different conformation, it is not possible to assess the effect of the increased dipole moment on the sodium binding free energy. The enthalpic and entropic effects of bidentate complexation are explored in more detail below for the analogous diol.

1,2-Ethanediol did not have sufficient vapor pressure to permit equilibrium experiments to be carried out. Optimized structures for 1,2-ethanediol (**1** and **2**) and the most stable of its possible sodium complexes are shown in Figure 7. As shown by Yeh and Su[17] other, less stable, monodentate structures are possible. Ab initio calculations reveal the complex interplay of enthalpic and entropic factors. The hydrogen-bonded conformer **1** is computed to be 2.3 kcal mol^{-1} more stable than the open conformer **2**; however, entropy favors the latter by 2 cal mol^{-1}K^{-1}. Thus, at 298 K, 95 % of molecules will exist in the hydrogen-bonded form. The enthalpy of binding of sodium of 37.4 kcal mol^{-1}, relative to **1**, is ≈ 11 kcal mol^{-1} greater than that for ethanol,[11] illustrating the increase of binding due to chelation. The entropy change found of 27.2 cal mol^{-1}K^{-1} is approximately 5 cal mol^{-1}K^{-1} less favorable than that found for ethanol;[11] this illustrates the greater restriction of internal degrees of freedom in the sodium chelated complex relative to the hydrogen bonded neutral form. If **2** is used as the reference conformer, an entropy change for complexation of 29.2 cal mol^{-1}K^{-1} is obtained, demonstrating the true loss of entropy in the sodium chelated diol. Ab initio calculations on 1,2-ethanediol and its sodium complex have recently been reported by Yeh and Su.[17] Using a comparable type of wavefunction, they obtained a D_0 value of 39.7 kcal mol^{-1}. This is slightly larger than the present value, probably because no BSSE correction was applied.



1,2-ethanediol 1 1,2-ethanediol 2

1,2-ethanediol Na$^+$ (side view) 1,2-ethanediol Na$^+$ (top view)

Figure 7. Optimized structures for the conformers of 1,2-ethanediol and its sodium complex at the MP2/6-31G* level.

Similarly, 1,3-propanediol exhibits an enhanced sodium ion binding relative to ethanol. Again the most stable conformer of the free molecule is that in which a hydrogen bond connects the two alcohol groups. In this case the sodium-binding enthalpy of 39.4 kcal mol^{-1} shows that the resulting six-membered ring conveys slightly stronger bonding than the corresponding five-membered ring in 1,2-ethanediol.

It was possible to carry out FT-ICR equilibrium experiments on 1,2-dimethoxyethane. The free energy of binding obtained of 31.8 kcal mol^{-1} also illustrates the substantially increased interaction due to chelation. The corresponding free energy values for dimethyl ether and diethyl ether of 17.6 and 21.3 kcal mol^{-1}, respectively, are in nearly exact agreement with ab initio values (18.0 and 21.3 kcal mol^{-1}) and are substantially smaller than that for dimethoxyethane. Considerations of relative data for 1-propanol and 1,2-ethanediol would lead to the conclusion that the additional $Na^+\cdots O$ interaction increases the enthalpy of binding by ≈ 11 kcal mol^{-1}, while leading to a more negative entropy change of ≈ 6 cal mol^{-1}K^{-1}. Based on this entropy estimate and the experimental free energy results above for dimethoxyethane, the enthalpy of binding of Na^+ to this diether can be predicted to be 40.6 kcal mol^{-1}, which is in excellent agreement with the MP2 value[2] of 40.4 kcal mol^{-1} but somewhat larger than the guided ion beam value[2] of 38.2 kcal mol^{-1}. Alternatively, these data could be used to predict a complexation enthalpy to methyl *n*-butyl ether of 29.6 kcal mol^{-1}, and a complexation entropy of 23 cal mol^{-1} K^{-1}. These values are each in excellent agreement with those which would be qualitatively predicted from the dimethyl- and diethyl ether data.

Experiments were also carried out for diethoxymethane. The sodium binding free energy obtained of 27.6 kcal mol^{-1} is more than 4 kcal mol^{-1} less than that found for dimethoxyethane, which demonstrates the poor chelation interaction resulting from a four-membered ring relative to the five-membered ring structure in the complex of dimethoxyethane.

Amines: Sodium transfer equilibrium measurements were carried out for NH_3, RNH_2, and R_2NH aliphatic amines with $R = CH_3$ or C_2H_5, and for $N(CH_3)_3$. The free energy changes obtained are summarized in Table 6. Previous HPMS measurements and ab initio calculations for ammonia[1] (19.1 and 18.5 kcal mol^{-1}, respectively) and methylamine (19.6 and 19.5 kcal mol^{-1}, respectively) are in good agreement with the FT-ICR data obtained in the current work of 18.6 kcal mol^{-1}

Table 6. Free energies of complexation of aliphatic amines to the sodium cation in kcal mol^{-1}.

Molecule	FT-ICR[a]	MP2[b]
NH_3	18.6	18.5
CH_3NH_2	19.5	19.5
$(CH_3)_2NH$	19.6	19.6
$(CH_3)_3N$	19.0	19.2
$C_2H_5NH_2$	20.8	20.7
$(C_2H_5)_2NH$	21.9	–

[a] FT-ICR values from the present work. [b] Computed values from the present work.

for NH_3 and 19.5 kcal mol^{-1} for CH_3NH_2. For $(CH_3)_3N$ and $C_2H_5NH_2$ excellent agreement is also obtained between the ICR and ab initio values. In addition calculations were carried out for trimethylphosphine, which is found to bind sodium by 25.2 kcal mol^{-1}. This value is 1 kcal mol^{-1} less than that for trimethylamine even though the dipole moment of $P(CH_3)_3$ is significantly larger (1.2 vs 0.6 D). This is a simple consequence of the Na–P distance being 0.46 Å longer than the Na–N distance. A similar trend applies to the comparison between oxygen and sulfur containing complexes.

Effect of methyl substitution: It is interesting to examine the relative trends observed for increasing methyl substitution at the basic center. In the case of increasing methyl substitution at oxygen, dimethyl ether was found to bind sodium only slightly more strongly than methanol which in turn has a sodium binding energy 2.2 kcal mol^{-1} greater than that of water. Similarly, while methylamine binds sodium 1 kcal mol^{-1} more strongly than ammonia, there is an almost negligible increase of 0.1 kcal mol^{-1} for dimethylamine. However, a slight decrease of 0.4 kcal mol^{-1} is found in proceeding to trimethylamine. This can be best understood from the variations in dipole moments and polarizabilities for these two series of compounds. Na^+ aligns with the direction of the dipole moment of the molecule as the charge–dipole interaction is the main component of binding of Na^+ to polar molecules. The decrease in dipole moment in proceeding from H_2O to CH_3OH to $(CH_3)_2O$ (1.85, 1.70 and 1.30 D, respectively) is small enough that it is compensated for by the regular increase in polarizability, leading to a plateau in sodium binding energies. However, the decrease in dipole moment observed for the series of amines (1.47, 1.31, 1.03, and 0.61 D for NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$) is much greater; this leads to first a plateau and then a decrease in sodium binding energies. An analogous trend is observed for the lithium and potassium free energies of binding of these amines.[18, 19] This is at variance with gas-phase basicities, which increase steadily with methyl substitution, reflecting the importance of formation of covalent bonds in the protonated amines. The observed order of alkali cation binding free energies demonstrates that the bonds formed in these adducts are primarily electrostatic and polarization in nature. A similar but slightly less pronounced effect is noticeable in the lithium complexes of H_2O, CH_3OH, and $(CH_3)_2O$ with binding free energies of 24.7, 28.5, and 29.5 kcal mol^{-1}, respectively.[18] Substitution of methyl by ethyl in amines, alcohols and chorides, leads to increases of 1–2 kcal mol^{-1} in ΔH^0_{298}. Dipole moment changes are less than 0.2 D in all cases of such substitution and thus the increases in binding free energies are largely due to increases in polarization interactions.

Results have previously been reported for the sodium affinities of H_2S and CH_3SH.[1] In the present work, both experiments and calculations were carried out for $(CH_3)_2S$, leading to free energies of interaction of 14.2 and 14.1 kcal mol^{-1}, respectively. The effect of methyl substitution is different for sulfur containing molecules since the sodium ion does not align with the molecular dipole. Increases of 3.7 and 2.7 kcal mol^{-1}, respectively, are observed for the first and second methyl substitutions on H_2S, even though the dipole moments of CH_3SH and $(CH_3)_2S$ are essentially identical. The increase is thus simply a reflection of the increase of the polarization interaction due to successive methyl substitution.

Aromatic compounds: FT-ICR and ab initio data obtained for benzene, chlorobenzene, bromobenzene, phenol, and furan are summarized in Table 7. In all cases the experimental and calculated values are in good agreement, although differences are slightly larger than for other classes of compounds, with the experimental value being greater in each case. The corresponding ab initio binding enthalpies (Table 1) are consistently smaller than those previously published by Dougherty et al.[20] because of the limited computational level used by the latter authors, as discussed previously.[1] However, the trends in binding energies are the same. Calculations at a comparable level by Nicholas et al.[21] give excellent agreement for the enthalpy of binding of sodium to benzene. Recent guided ion beam experiments by Armentrout and Rodgers[2] on sodium complexes of benzene and phenol yield binding enthalpies at 298 K of 21.5 and 24.0 kcal mol^{-1}, respectively. Using MP2 calculated thermal corrections and entropies, these translate to ΔG^0_{298} values of 14.2 and 16.7 kcal mol^{-1}. The former value is in agreement with the present calculations, while the latter agrees exactly with the present experiments. However, it should be noted that the structure which they calculated for sodium complexes of phenol is not the one with the lowest free energy at 298 K. We have shown previously[1] that there are in fact two stable minima for sodiated phenol, the more favorable of which involves a Na–O interaction rather than a pure cation–π interaction as observed in benzene.

The nature of intermolecular interaction involving aromatic systems has been discussed previously by several authors.[20, 22] In order to understand the bonding between sodium ion and aromatic systems, it is important to consider the various components of the interaction energy. Natural orbital population analysis shows that less than 0.03 electrons are transferred to the sodium in these complexes, thus, charge transfer can be neglected. The remaining forces arise from electrostatic and polarization interactions. Normally, a combination of charge–dipole and charge–induced dipole interactions have been considered to be sufficient. However, Dougherty et al. have pointed out the importance of charge–quadrupole interactions in determining structure of aromatic complexes of Na^+.[20] In the case of benzene, the π complex of C_{6v}

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symmetry can be readily understood qualitatively to be the most stable geometry as a result of the maximum combination of charge–quadrupole and charge–induced dipole forces. The quadrupole moment tensor has a large attractive component in the axial direction, while the in-plane components are smaller and repulsive toward a positive charge. The polarizability in the plane is significantly larger than the axial component, however, a sodium ion is able to approach the ring more closely in the axial direction. Therefore, the closer approach and favorable quadrupole interaction combine to make a π complex the most stable structure. However, for substituted benzenes such simple qualitative interpretations of structure are not immediately apparent. For example, for chlorobenzene it might be initially expected that a structure in which the sodium is aligned with the molecular dipole would be the most favorable. It might then be expected that a planar sodium complex of chlorobenzene might be formed in which favorable charge–dipole and charge–induced dipole forces dominate. As shown above, however, complexes between sodium and HCl and H_3CCl do not adopt a linear HClNa or CClNa arrangement but rather are bent. This weakens the charge–dipole significantly, which makes the maximization of the charge–quadrupole interaction the dominant effect. In fact, ab initio calculations show in this case that a cation–π complex in which the sodium is situated above the ring is the most stable if not the only form.

The free energies of binding to Na^+ in Table 7 fall in the range 11–17 kcal mol^{-1}. As a consequence, some predictions can be made on the most favorable site of attachment to other substituted aromatics. Since the binding interaction to halides is slightly smaller than that to benzene, it is likely that cation–π structures will be favored even for larger substituents. The binding of Na^+ to alcohols is stronger than that to halides, making both types of complexation, to the oxygen and to the aromatic ring, competitive. Indeed, two structures of very similar stabilities exist for phenol.[1] Since the binding of Na^+ to amines is even stronger than that to alcohols, the best attachment site in amino-substituted aromatics is likely to be the nitrogen. Imines are yet one step higher in the Na^+ binding scale as exemplified by formaldimine which has a ΔG^0_{298} of binding of 20.1 kcal mol^{-1}.[1] Consistently, the binding of Na^+ to imidazole occurs in plane on the imino nitrogen,[1, 20] and no stable minimum of the cation–π type exists.[20]

Table 7. Free energies of complexation of aromatic compounds to the sodium cation in kcal mol^{-1}.

Molecule	FT-ICR[a]	MP2[b]
furan	11.7	11.0
C_6H_5Cl	12.4	11.0
C_6H_5Br	12.8	–
C_6H_6	15.7	14.5
C_6H_5OH	16.7	15.4

[a] FT-ICR values from the present work. [b] Computed values from the present work.

Carbonyl compounds: In order to have a series of equilibrium measurements connecting all compounds of interest with a range of sodium ion affinities extending from the weakly binding compounds such as alkenes, to the much more strongly binding species such as dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and dimethoxyethane, experiments were carried out with a number of carbonyl compounds. In this way, a continuous scale of sodium ion binding free energies could be constructed. As noted previously,[1] carbonyl compounds exhibit sodium ion affinities which appear to increase roughly as the molecular dipole moment increases. Therefore carbonyl compounds were sought with regularly increasing dipole moments. The series of molecules used included methyl acetate, simple ketones (acetone and 2-pentanone), *β*-butyrolactone, cyclopenten-2-one, 3,3-dimethylacrolein, DMF, and acetic anhydride. Although the dipole moment of acetic anhydride is significantly smaller than that of other carbonyl compounds considered, its binding free energy is the largest because Na^+ is able to bind to both carbonyl oxygens in a symmetrical structure. As shown in Table 8, the agreement between experimental and calculated values is generally very good, except for the compounds with the higher sodium ion affinities for which a systematic difference of about one kcal mol^{-1} is obtained. The reason for this larger than normal difference is not clear.

Table 8. Free energies of complexation of carbonyl compounds to the sodium cation in kcal mol^{-1}.

Molecule	FT-ICR[a]	MP2
methyl acetate	23.3	22.6[b]
acetone	24.1	23.7[b]
pentan-2-one	24.9	–
β-butyrolactone	24.1	–
cyclopenten-2-one	25.8	26.8[c]
3,3-dimethylacrolein	26.0	26.9
N,N-dimethylformamide	30.1	30.3[b]
acetic anhydride	31.1	32.2[c]

[a] FT-ICR values from the present work. [b] Computed values from ref. [1]. [c] Computed values from the present work.

Miscellaneous: In addition to the compound classes described above, experiments and/or calculations were also carried out for CH_3CN, C_2H_5CN, and DMSO. Each of these molecules has a substantial dipole moment and, correspondingly, each binds sodium relatively strongly. The experimental and calculated free energies of binding for CH_3CN are in exact agreement, while those for DMSO are in good agreement, with a difference of 1.1 kcal mol^{-1} (see Table 2). Calculations show that in both cases the sodium ion aligns with the molecular dipole. It is interesting to note that CH_3CN, DMSO, and DMF are commonly used dipolar aprotic solvents in solution-phase organic chemistry. Given the strong binding that each of these species has towards the sodium ion (see Table 1), the reason for their use in ionic organic reactions is evident.

Conclusion

The results presented above provide a coherent view of the binding of sodium ion to a wide variety of molecules. Together with our previously published data,[1] this provides a scale of binding enthalpies of molecules ranging from 6 to 45 kcal mol^{-1}. The excellent agreement between experimental and calculated free energies lends confidence to the accuracy of the thermochemical data presented here. The structures obtained for the complexes reveal the importance of electrostatic and polarization interactions in determining the geometry of the adducts. Very little if any covalent character is associated with the newly formed bond(s). The interesting structures found for aromatic compounds as well as molecules containing second row atoms show that prediction of geometry of the sodium adducts is not necessarily straightforward. It is likely that the data presented herein will prove to be extremely useful in the estimation of both energetics and structure of sodium complexes of other molecules.

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