Coordination Chemistry Reviews
197 (2000) 125–139

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Complexation of Li^+, Na^+, and K^+ by water and ammonia☆

Keith E. Laidig [a], Peter Speers [b], Andrew Streitwieser [c,]*

[a] *Department of Medicinal Chemistry, University of Washington, Seattle, WA 98195, USA*
[b] *Department of Pharmacy, University of Manchester, Oxford Road, Manchester M13 9P2, UK*
[c] *Department of Chemistry, University of California, Berkeley, CA 94720-1460, USA*

Received 29 January 1999; accepted 30 April 1999

Contents

Abstract

The energetics of complexation and the resulting polarization of solvent molecules were investigated for complexation of lithium, sodium, and potassium cations with water and with ammonia molecules. The mono-, di-, and tri-complexes were investigated using a double-zeta, polarized, diffuse, and balanced basis at both the molecular and atomic levels, using subsystem quantum mechanics. The stabilization at the molecular level during complexation results from large gains in the attractive energies overcoming the increases in repulsion. The cation–solvent interactions are closed-shell and involve only small transfers of electronic charge to the cations. On the atomic level, the cations are stabilized by inter-atom attraction, whereas the heavy atoms of the solvent molecules are destabilized by a small withdrawal of

---

☆ Dedicated to Professor R. Gillespie on the occasion of his 75th birthday.

* Corresponding author.

E-mail address: astreit@socrates.berkeley.edu (A. Streitwieser)

PII: S0010-8545(99)00152-6

charge to the cation. Additional solvation continues to stabilize the cations, but each additional solvent molecule is less stabilized because of competition among solvent molecules. The solvent molecules are dipole polarized by a transfer of electronic charge from the bonded hydrogen atoms towards the heavy atom, a polarization that decreases with each additional solvent molecule and with increasing cation size.

Keywords: Complexation; Solvation; Alkali cations; Atoms-in-molecule; Polarization

1. Introduction

Solvation is a crucial factor in the energetics and reaction pathways of a wide variety of systems. The field generated by the surrounding solvent perturbs the structures and energetics of reactions, in addition to the direct interaction of individual solvent molecules with the solute. The development of models that take into account the effect of solvation upon chemical processes for use in classical simulation requires a detailed understanding of the process of complexation of solvent with the different species in solution. There is also an interest in understanding the driving forces in the complexation of alkali cations by calixarenes, clathrates in order to design better and more selective material sensors and extractors.

Our purpose is to add to this understanding by performing detailed analyses of the direct interaction and the changes in atomic and molecular properties resulting from the complexation of solvent molecules (water and ammonia) with alkali cations typically found in solution (Li^+, Na^+, K^+). We plan to use this information as a guide for developing simple, accurate, and robust representations for use in large scale dynamic simulations which accurately model the effect of direct solvation.

Earlier work has focused upon the total energetics and structures of the alkali metal-solvent complexes, both from the theoretical [1–15] and experimental [16–21] points of view. An overlapping area of interest has been the understanding of and developing models for chelation of cations [22]. Energy decompositions within the Morokuma model [23] of many of these complexes have been done [5,24] and have shown that the energy of complexation is due principally to ion-dipole and polarization contributions and without significant charge transfer contributions.

This work is an extension of these previous investigations. We shall present a much more detailed energy picture of the consequences of solvation of cations using subsystem quantum mechanics, as developed within the theory of atoms-in-molecules [25]. This approach will uncover the driving forces at the atomic level by determining the consequences of complexation for each atom within the solvent molecules as well as the cation [26,27]. These studies also add a detailed description of the effects of complexation upon the multipole moments of the solvent molecules. The polarizations will be broken into the atomic contributions within each solvent molecule, to provide a detailed analysis of the perturbation resulting from complexation with alkali cations. Using subsystem quantum mechanics allows discussion of the changes, both in energies and moments, in terms of well-defined, physical observables, each of which is based upon the form of the electronic charge distributions of the system.

2. Methodology

We have considered mono-, di-, and tri-substituted alkai metal cations, Li^+, Na^+, and K^+, with water and ammonia as ligands, $M^+(X)_n$. All the atomic and molecular properties were determined from HF/6-31 + + G** wavefunctions calculated at conformations optimized using the same level of theory, excepting those complexes involving potassium [28–33]. For potassium, a Dunning–Hay double zeta basis with additional polarized and diffuse functions was adopted [34]. All stationary points were characterized via the determination of the analytical second derivatives, and all were found to be minima. The molecular calculations were performed using both Gaussian 92 [35] and GAMESS [36] and the properties of the charge distribution and the atomic properties were determined using the AIMPAC [37] suite of programs.

Our energy analysis, at both the atomic and molecular levels, is presented in terms of the terms of the usual fixed-nucleus Hamiltonian, i.e. the contributions to the potential energy of the system. This approach has been shown to provide a detailed analysis of energy changes and the corresponding changes in the electronic charge distributions [26,38]. The dipole moments of the solvent molecules within the complexes are determined from the appropriate summation of atomic contributions [27]. The geometry of the solvent molecules changes but little in complexation, and the center of mass of the solvent molecule correspondingly moves only slightly, making it ideal for direct comparisons between systems. We use the center of mass of the solvent molecule as the origin of our multipole moments because there is no unique origin for the dipole moment in charged species.

3. Results and discussion

The total and contributing energies of the adducts and the complexes are listed in Table 1. Our predicted relative complexation energies are in excellent agreement with those observed in the gas-phase, with the complexation energy ordered as $Li^+ > Na^+ > K^+$. The addition of the first solvent molecule is most favored, with each successive addition being somewhat less exothermic. The contributions to the total potential energy reveal the overall driving force for complexation; the interaction of a cation with a solvent molecule results in large gains in attractive energies for the complex. There are accompanying increases in repulsive energies between the nuclei and between the electronic distributions of the adducts, but these are overcome by the binding attraction of the nucleus of the cation with the charge distribution of the heavy atom of each solvent molecule.

Table 1
Molecular energetics of individual adducts and mono-, di-, and tri-solvated alkali cations[a]

	Li^+	Na^+	K^+	NH_3	H_2O
E	−7.2355	−161.6593	−598.9961	−56.2011	−76.0313
V_{NE}	−16.1233	−386.4419	−1418.6498	−156.0463	−199.2875
V_{EE}	1.6523	63.1234	220.6575	31.5400	37.8852
V_{NN}	0.0000	0.0000	0.0000	12.1040	9.3397
V	−14.4710	−323.3186	−1197.9922	−112.4023	−152.0626
ZPE				23.05	14.50
	$Li^+(NH_3)$	$Li^+(NH_3)_2$	$Li^+(NH_3)_3$		
ΔE	−0.0650	−0.0559	−0.0380		
ΔV_{NE}	−12.8329	−37.6216	−70.9743		
ΔV_{EE}	+5.3010	+17.9326	+34.8570		
ΔV_{NN}	+7.4020	+19.5773	+36.0415		
ΔV	−0.1300	−0.1118	−0.0757		
ΔZPE	+2.66	+2.53	+2.01		
ΔE_{comp}	−38.13	−32.55	−21.84		
	$Li^+(H_2O)$	$Li^+(H_2O)_2$	$Li^+(H_2O)_3$		
ΔE	−0.0578	−0.0509	−0.0372		
ΔV_{NE}	−13.9455	−40.6803	−77.4717		
ΔV_{EE}	+5.7580	+19.6361	+37.9994		
ΔV_{NN}	+8.0720	+21.2153	+39.3981		
ΔV	−0.1156	−0.1018	−0.0744		
ΔZPE	+2.12	+2.11	+1.69		
ΔE_{comp}	−34.15	−29.83	−21.65		
	$Na^+(NH_3)$	$Na^+(NH_3)_2$	$Na^+(NH_3)_3$		
ΔE	−0.0453	−0.0401	−0.0311		
ΔV_{NE}	−45.0463	−65.1878	−93.1873		
ΔV_{EE}	+21.8242	+32.0315	+46.1581		
ΔV_{NN}	+23.1314	+33.0764	+46.9743		
ΔV	−0.0906	−0.0799	−0.0623		
ΔZPE	+2.06	+1.95	+1.66		
ΔE_{comp}	−26.37	−23.21	−17.87		
	$Na^+(H_2O)$	$Na^+(H_2O)_2$	$Na^+(H_2O)_3$		
ΔE	−0.0409	−0.0370	−0.0302		
ΔV_{NE}	−48.2110	−69.9929	−100.5846		
ΔV_{EE}	+23.3015	+34.3296	+49.7635		
ΔV_{NN}	+24.8278	+35.5892	+50.7607		
ΔV	−0.0818	−0.0741	−0.0603		
ΔZPE	+1.66	+1.66	+1.37		
ΔE_{comp}	−25.01	−21.56	−17.58		
	$K^+(NH_3)$	$K^+(NH_3)_2$	$K^+(NH_3)_3$		
ΔE	−0.0301	−0.0269	−0.0230		
ΔV_{NE}	−66.0367	−82.1589	−106.3195		
ΔV_{EE}	+32.5270	+40.6909	+52.9050		
ΔV_{NN}	+33.4499	+41.4146	+53.3754		
ΔV	−0.0601	−0.0535	−0.0463		
ΔZPE	+1.66	+1.49			
ΔE_{comp}	−17.23	−15.39	−(14.43)		

Table 1 (*Continued*)

	Li^+	Na^+	K^+	NH_3	H_2O
	$K^+(H_2O)$	$K^+(H_2O)_2$	$K^+(H_2O)_3$		
ΔE	−0.0285	−0.0259	−0.0226		
ΔV_{NE}	−70.6293	−88.0088	−113.9255		
ΔV_{EE}	+34.7329	+43.5317	+56.5681		
ΔV_{NN}	+35.8394	+44.4255	+57.3121		
ΔV	−0.0571	−0.0516	−0.0453		
ΔZPE	+1.43		47.502		
ΔE_{comp}	−16.45	−(16.25)	−(14.18)		

[a] All values are in atomic units, determined from the HF/6-31++G** wavefunctions, excepting the zero-point energies (ZPE) and the total complexation energies, both of which are in kcal mol^{-1}. The energy differences are with respect to a complex with one less solvent molecule.

The geometry parameters of the isolated solvent molecules and those in complexes are given in Table 2. The interaction of the alkali cation with the solvent molecules produces a small X–H bond lengthening and a small H–X–H bond angle decrease, with the changes in NH_3 being greater than in H_2O. The effect is

Table 2
The geometry parameters within neutral and complexed ammonia and water[a]

	X–N	N–H	M–N–H	H–N–H	bpa[b]
NH_3		1.000		108.81	106.31
$Li^+(NH_3)$	1.987	1.007	113.11	105.61	103.69
$Li^+(NH_3)_2$	2.013	1.006	112.85	105.88	103.80
$Li^+(NH_3)_3$	2.073	1.005	112.42	106.09	103.82
$Na^+(NH_3)$	2.372	1.006	113.01	105.71	103.69
$Na^+(NH_3)_2$	2.401	1.005	112.84	105.90	103.79
$Na^+(NH_3)_3$	2.444	1.004	112.66	106.16	103.60
$K^+(NH_3)$	2.863	1.005	112.86	105.88	103.67
$K^+(NH_3)_2$	2.900	1.004	112.68	106.08	103.81
$K^+(NH_3)_3$	2.930	1.004	112.51	106.30	103.98
	X–O	O–H	M–O–H	H–O–H	bpa[b]
H_2O		0.943		107.09	102.16
$Li^+(H_2O)$	1.849	0.950	126.61	106.77	103.01
$Li^+(H_2O)_2$	1.875	0.949	126.55	106.91	102.93
$Li^+(H_2O)_3$	1.920	0.947	126.62	106.78	102.68
$Na^+(H_2O)$	2.234	0.948	126.97	106.06	102.28
$Na^+(H_2O)_2$	2.255	0.948	126.90	106.19	102.29
$Na^+(H_2O)_3$	2.287	0.947	126.89	106.20	102.19
$K^+(H_2O)$	2.692	0.947	127.10	105.81	101.77
$K^+(H_2O)_2$	2.722	0.947	127.07	105.86	101.77
$K^+(H_2O)_3$	2.747	0.946	127.00	105.99	101.80

[a] All bond lengths are given in angstroms and all bond angles in degrees.
[b] The bond path angle is the angle between the X–H bond paths.

largest for the Li^+ cation, which has the shortest M^+–X distance, and smallest for K^+, which has the largest corresponding distance. The effects decrease as each successive solvent molecule is added, shortening up the X–H distance and opening up the H–X–H angle.

Atomic interaction is quantitatively characterized using the properties of the charge density at bond critical points, and these values are listed in Table 3. The interaction between M^+ and the solvent molecule(s) is (are) closed-shell, or ionic, as shown by the small amount of electronic charge and the positive value of the Laplacian at the bond critical point(s). The bonded radii, the distance from that nucleus to the bond critical point, to the cation are about 75% that from the solvent's heavy atom, signalling a dominance of the heavy atom in the interaction. The X–H interactions within the solvent molecules change only a little upon complexation. There is a small decrease in the amount of charge at the bond critical points, the Laplacian changes by less than 5% (decreasing slightly in M^+–NH_3 and increasing slightly in M^+–H_2O), the bonded radius from the heavy atom increases and that from the hydrogen decreasing slightly. The change follows the same pattern as the overall geometry changes; namely, that the deviations are greatest for the Li^+ cation and decrease as the cation increases in size and/or the number of complexed solvent molecules increases.

The atomic populations and atomic contributions to the molecular energies are listed in Table 4. The charge transfer from the solvent molecules to the cation is small in all of the complexes and with each added solvent molecule, the cation gains a successively smaller amount of charge. The solvent's heavy atom gains much more charge in complexation than does the cation, with electronic charge being transferred from the bonded hydrogen atoms. This transfer of charge from H to X results from the proximity of the alkali cation, which polarizes the charge within the heavy atom towards the ion and away from the bonded hydrogens. This decreases the screening experienced by the hydrogen atoms from within the X–H bonding region and makes the X atom effectively more electronegative with respect to the bonded hydrogens. The cations produce the largest transfer of charge to the heavy atoms when they are mono-complexed and the cation is small; the largest transfer of charge to the N atom is in the ammonia clusters with Li^+. Adding additional solvent molecules or increasing the size of the cation decreases this polarization of the solvent heavy atom and thus decreases the transfer of charge to the heavy atom from the hydrogen atoms.

The atomic contributions to the molecular energetics shows which atoms are stabilized and which terms determine the total energy change within the complex. In all of the complexes the cation is stabilized by inter-atomic attraction with the solvent molecule. There is a small stabilization from the increased population (shown by the larger absolute value of $V_{NEO}(M^+)$, the intra-, or self-stabilization of the atom) and from an increase in the atomic repulsion energy, but it is the attraction between the electron density of the cations and the nuclei in the solvent molecule, $V_{NET}(M^+)$, that dominates. The hydrogen atoms of the solvent molecules are all destabilized by complexation because the withdrawal of charge to the heavy atom decreases the attractive energies available to each hydrogen atom.

Table 3
Properties at the bond critical point in the water and ammonia complexes[a]

	$\rho(r)$	$^2\rho(r)$	ε	r_a	r_b
NH_3					
N–H	0.358	–1.952	0.049	1.416	0.474
$Li^+(NH_3)$					
Li^+–N	0.033	0.214	0.000	1.357	2.396
N–H	0.351	−1.951	0.029	1.452	0.451
$Li^+(NH_3)_2$					
Li^+–N	0.031	0.191	0.000	1.381	2.423
N–H	0.352	−1.952	0.030	1.447	0.454
$Li^+(NH_3)_3$					
Li^+–N	0.026	0.161	0.007	1.417	2.501
N–H	0.354	−1.953	0.033	1.440	0.459
$Na^+(NH_3)$					
Na^+–N	0.024	0.135	0.000	1.941	2.541
N–H	0.353	−1.951	0.033	1.443	0.457
$Na^+(NH_3)_2$					
Na^+–N	0.022	0.124	0.000	1.963	2.574
N–H	0.354	−1.951	0.034	1.440	0.459
$Na^+(NH_3)_3$					
Na^+–N	0.020	0.109	0.002	1.994	2.625
N–H	0.354	−1.950	0.036	1.436	0.462
$K^+(NH_3)$					
K^+–N	0.016	0.067	0.000	2.640	2.771
N–H	0.354	−1.948	0.036	1.435	0.463
$K^+(NH_3)_2$					
K^+–N	0.015	0.061	0.000	2.671	2.808
N–H	0.355	−1.948	0.037	1.433	0.465
$K^+(NH_3)_3$					
K^+–N	0.014	0.057	0.003	2.695	2.842
N–H	0.355	−1.948	0.038	1.431	0.466
H_2O					
O–H	0.390	−2.479	0.027	1.443	0.340
$Li^+(H_2O)$					
Li^+–O	0.034	0.286	0.087	1.324	2.169
O–H	0.374	−2.590	0.023	1.474	0.320
$Li^+(H_2O)_2$					
Li^+–O	0.032	0.254	0.084	1.348	2.196
O–H	0.376	−2.582	0.024	1.470	0.322
$Li^+(H_2O)_3$					
Li^+–O	0.028	0.218	0.076	1.378	2.250
O–H	0.380	−2.567	0.025	1.464	0.325
$Na^+(H_2O)$					
Na^+–O	0.024	0.169	0.107	1.913	2.308

Table 3 (*Continued*)

	$\rho(r)$	$^2\rho(r)$	ε	r_a	r_b
O–H	0.378	−2.556	0.024	1.467	0.325
$Na^+(H_2O)_2$					
Na^+–O	0.023	0.157	0.107	1.930	2.331
O–H	0.379	−2.551	0.024	1.464	0.326
$Na^+(H_2O)_3$					
Na^+–O	0.021	0.141	0.102	1.955	2.367
O–H	0.381	−2.544	0.024	1.461	0.328
$K^+(H_2O)$					
K^+–O	0.017	0.085	0.121	2.593	2.495
O–H	0.381	−2.532	0.024	1.460	0.329
$K^+(H_2O)_2$					
K^+–O	0.016	0.079	0.121	2.622	2.523
O–H	0.382	−2.528	0.024	1.459	0.330
$K^+(H_2O)_3$					
K^+–O	0.015	0.074	0.118	2.643	2.549
O–H	0.383	−2.523	0.025	1.457	0.331

[a] All values are in atomic units. The properties are determined at the (3, −1) critical point between the atoms; $\rho(r)$, the total electronic charge density, $^2\rho(\mathrm{r})$, the Laplacian of the electronic charge density, ε, the ellipticity, r_a and r_b the bonded radii to atoms A and B.

The heavy atoms of the solvent have interesting changes in properties. The N atom is stabilized in the Li^+ and Na^+ complexes, but is destabilized in the K^+ complexes, whereas the O atom is only stabilized in the Li^+ complexes. The destabilizations occur despite the gain in population by all heavy atom in all of the complexes. With the lighter cations, the charge gained by the polarization of the heavy atoms (vide infra) stabilizes the X atom. But with the heavier cations, the repulsion (both electronic and nuclear) between the cation and the heavy atom becomes appreciable, overcoming any gained self-stabilization, and results in an overall atomic destabilization. This can be seen in the previously mentioned atomic energy pattern; the N of ammonia is stabilized by Li^+ and Na^+, whereas the O of water, having a larger nuclear charge and more electronic charge, is stabilized only by Li^+.

Complexation results in a change of the charge distribution within the solvent molecule. The transfer of charge from the heavy atom to the binding region between the cation and X atom polarizes the charge distribution within the solvent, changing its multipole moments. This can be addressed using the spatial partitioning implemented within AIM theory, which allows one to determine the dipole polarizations of the solvent molecules within the complexes; see Tables 5 and 6. The dipole polarization of the solvent molecules results primarily from the transfer of charge from hydrogen to the heavy atoms (vide infra) with smaller contributions from the polarization of the charge of the heavy atom. The total solvent dipole

Table 4
Atomic properties of the cations, solvent molecules, and complexes[a]

	Li^+	Na^+	K^+
N (Ω)	2.000	10.000	18.000
E (Ω)	−7.236	−161.659	−598.996
V_{NEO} (Ω)	−16.123	−386.442	−1418.650
V_{NET} (Ω)	−16.123	−386.442	−1418.650
V_{REP} (Ω)	1.652	63.123	220.657
NH_3	N	H	
N (Ω)	8.166	0.611	
E (Ω)	−54.807	−0.465	
V_{NEO} (Ω)	−134.041	−0.930	
V_{NET} (Ω)	−146.435	−3.204	
V_{REP} (Ω)	36.809	2.273	
Li^+–NH_3	Li	N	H
N (Ω)	2.039	8.340	0.540
E (Ω)	−7.315	−54.912	−0.425
V_{NEO} (Ω)	−16.272	−134.791	−0.850
V_{NET} (Ω)	−21.352	−154.114	−3.179
V_{REP} (Ω)	67.189	44.274	2.328
Li^+–$(NH_3)_2$	Li	N	H
N (Ω)	2.075	8.311	0.550
E (Ω)	−7.385	−54.895	−0.430
V_{NEO} (Ω)	−16.406	−134.682	−0.862
V_{NET} (Ω)	−26.605	−164.490	−3.848
V_{REP} (Ω)	11.830	54.679	2.985
Li^+–$(NH_3)_3$	Li	N	H
N (Ω)	2.089	8.274	0.565
E (Ω)	−7.405	−54.880	−0.439
V_{NEO} (Ω)	−16.453	−134.546	−0.879
V_{NET} (Ω)	−31.442	−177.204	−4.720
V_{REP} (Ω)	16.624	67.415	3.840
Na^+–NH_3	Na	N	H
N (Ω)	10.039	8.283	0.559
E (Ω)	−161.774	−54.826	−0.435
V_{NEO} (Ω)	−386.818	−134.490	−0.872
V_{NET} (Ω)	−407.983	−167.479	−4.025
V_{REP} (Ω)	84.428	57.813	3.153
Na^+–$(NH_3)_2$	Na	N	H
N (Ω)	10.070	8.269	0.565
E (Ω)	−161.860	−54.828	−0.439
V_{NEO} (Ω)	−387.115	−134.446	−0.879
V_{NET} (Ω)	−429.081	−176.036	−4.603
V_{REP} (Ω)	105.346	66.362	3.724
Na^+–$(NH_3)_3$	Na	N	H
N (Ω)	10.087	8.249	0.574
E (Ω)	−161.912	−54.825	−0.443
V_{NEO} (Ω)	−387.290	−134.378	−0.888
V_{NET} (Ω)	−449.318	−186.799	−5.354
V_{REP} (Ω)	125.468	77.124	4.466

Table 4 (*Continued*)

K^+–NH_3	K	N	H
N (Ω)	18.022	8.247	0.577
E (Ω)	–599.204	−54.731	−0.444
V_{NEO} (Ω)	−1419.041	−134.246	−0.890
V_{NET} (Ω)	−1450.804	−175.846	−4.695
V_{REP} (Ω)	252.394	66.383	3.806
K^+–$(NH_3)_2$	K	N	H
N (Ω)	18.039	8.238	0.581
E (Ω)	−599.333	−54.356	−0.447
V_{NEO} (Ω)	−1419.389	−134.219	−0.891
V_{NET} (Ω)	−1482.246	−182.789	−5.186
V_{REP} (Ω)	283.576	73.314	4.292
K^+–$(NH_3)_3$	K	N	H
N (Ω)	18.052	8.227	0.585
E (Ω)	−599.440	−54.739	−0.449
V_{NEO} (Ω)	−1419.642	−134.188	−0.900
V_{NET} (Ω)	−1513.085	−191.873	−5.824
V_{REP} (Ω)	314.194	82.388	4.926
H_2O	O	H	
N (Ω)	9.259	0.370	
E (Ω)	−75.356	−0.338	
V_{NEO} (Ω)	−184.910	−0.651	
V_{NET} (Ω)	−195.062	−2.113	
V_{REP} (Ω)	44.337	1.437	
Li^+–H_2O	Li	O	H
N (Ω)	2.028	9.364	0.305
E (Ω)	−7.303	−75.437	−0.292
V_{NEO} (Ω)	−16.243	−185.538	−0.564
V_{NET} (Ω)	−21.746	−203.726	−1.952
V_{REP} (Ω)	7.136	52.833	1.367
Li^+–$(H_2O)_2$	Li	O	H
N (Ω)	2.056	9.315	0.344
E (Ω)	−7.361	−75.428	−0.300
V_{NEO} (Ω)	−16.651	−185.474	−0.578
V_{NET} (Ω)	−27.346	−216.320	−2.593
V_{REP} (Ω)	12.616	65.435	1.991
Li^+–$(H_2O)_3$	Li	O	H
N (Ω)	2.068	9.336	0.321
E (Ω)	−7.384	−75.421	−0.305
V_{NEO} (Ω)	−16.398	−185.398	−0.587
V_{NET} (Ω)	−32.620	−232.074	−2.873
V_{REP} (Ω)	17.841	81.191	2.262
Na^+–H_2O	Na	O	H
N (Ω)	10.024	9.337	0.326
E (Ω)	−161.814	−75.312	−0.300
V_{NEO} (Ω)	−386.787	−185.244	−0.586
V_{NET} (Ω)	−409.459	−219.578	−2.511
V_{REP} (Ω)	85.822	68.936	1.910

Table 4 (*Continued*)

Na^+–$(H_2O)_2$	Na	O	H
N (Ω)	10.043	9.332	0.359
E (Ω)	−161.912	−75.332	−0.308
V_{NEO} (Ω)	−387.041	−185.243	−0.595
V_{NET} (Ω)	−432.061	−229.992	−3.143
V_{REP} (Ω)	108.214	79.301	2.526
Na^+–$(H_2O)_3$	Na	O	H
N (Ω)	10.056	9.322	0.330
E (Ω)	−161.973	−75.343	−0.310
V_{NEO} (Ω)	−387.206	−185.215	−0.598
V_{NET} (Ω)	−453.924	−243.211	−3.256
V_{REP} (Ω)	129.940	92.489	2.634
K^+–H_2O	K	O	H
N (Ω)	18.011	9.323	0.333
E (Ω)	−599.303	−75.185	−0.312
V_{NEO} (Ω)	−1419.071	−185.004	−0.602
V_{NET} (Ω)	−1453.067	−229.767	−2.867
V_{REP} (Ω)	254.458	79.392	2.243
K^+–$(H_2O)_2$	K	O	H
N (Ω)	18.020	9.318	0.336
E (Ω)	−599.498	−75.204	−0.314
V_{NEO} (Ω)	−1419.431	−185.005	−0.606
V_{NET} (Ω)	−1486.759	−238.222	−3.165
V_{REP} (Ω)	287.755	87.806	2.536
K^+–$(H_2O)_3$	K	O	H
N (Ω)	18.027	9.312	0.340
E (Ω)	−599.651	−75.219	−0.316
V_{NEO} (Ω)	−1419.697	−184.997	−0.611
V_{NET} (Ω)	−1519.863	−249.283	−3.561
V_{REP} (Ω)	320.542	98.830	2.928

[a] All atomic properties are in atomic units. N, is the population within the atomic basin; E, is the atomic energy; V_{NEO}, is the nuclear–electron attraction from charge within the atom's basin; V_{NET}, is the total nuclear–electron attraction between the atom's charge and all nuclei within the molecule; V_{REP}, is the atomic contribution to the total molecular repulsion energy. The energetics have been corrected for the virial defect.

enhancement, which always points towards the cation, falls off with each additional solvent molecule or with the larger cations, in parallel to the energetic changes. The contributions to the solvent molecule dipole moment also show the falloff with additional solvation or increased cation size. The contributions from transfer of electronic charge from the bonded hydrogens to the solvent heavy atom falls off slowly with further complexation for a given cation and decreases slowly as the size of the cation increases. The polarization of the heavy atom decreases more rapidly with additional solvent molecules and is larger for the smaller cations.

Table 5
Dipole moments of ammonia ligands within complexes[a]

	N	H	H	H	Sum
NH_3					
q (Ω)	−1.1663	0.3888	0.3888	0.3888	0.0001
M (Ω)	−0.1668	0.0770	0.0770	0.0770	
M^{W}	−0.3944	−0.0999	−0.1001	−0.1001	−0.6944
$Li^+(NH_3)_1$					
q (Ω)	−1.3401	0.4597	0.4597	0.4597	0.0390
M (Ω)	−0.2464	0.0678	0.0678	0.0678	
M^{W}	−0.5466	−0.1725	−0.1725	−0.1725	−1.0640
$Li^+(NH_3)_2$					
q (Ω)	−1.3114	0.4496	0.4496	0.4496	0.0374
M (Ω)	−0.2259	0.0691	0.0691	0.0691	
M^{W}	−0.5165	−0.1632	−0.1634	−0.1634	−1.0064
$Li^+(NH_3)_3$					
q (Ω)	−1.2740	0.4351	0.4342	0.4342	0.0295
M (Ω)	−0.1925	0.0705	0.0705	0.0705	
M^{W}	−0.4725	−0.1491	−0.1539	−0.1539	−0.9294
$Na^+(NH_3)_1$					
q (Ω)	−1.2834	0.4407	0.4407	0.4407	0.0387
M (Ω)	−0.1889	0.0715	0.0715	0.0715	
M^{W}	−0.4749	−0.1576	−0.1576	−0.1576	−0.9477
$Na^+(NH_3)_2$					
q (Ω)	−1.2690	0.4345	0.4345	0.4345	0.0345
M (Ω)	−0.1807	0.0723	0.0723	0.0723	
M^{W}	−0.4614	−0.1519	−0.1519	−0.1519	−0.9171
$Na^+(NH_3)_3$					
q (Ω)	−1.2487	0.4261	0.4287	0.4287	0.0348
M (Ω)	−0.1664	0.0727	0.0750	0.0750	
M^{W}	−0.4400	−0.1408	−0.1464	−0.1464	−0.8737
$K^+(NH_3)_1$					
q (Ω)	−1.2473	0.4230	0.4230	0.4230	0.0217
M (Ω)	−0.1810	0.0748	0.0748	0.0748	
M^{W}	−0.4569	−0.1435	−0.1435	−0.1435	−0.8874
$K^+(NH_3)_2$					
q (Ω)	−1.2380	0.4191	0.4191	0.4191	0.0193
M (Ω)	−0.1825	0.0751	0.0751	0.0751	
M^{W}	−0.4542	−0.1395	−0.1395	−0.1395	−0.8728
$K^+(NH_3)_3$					
q (Ω)	−1.2274	0.4149	0.4149	0.4149	0.0173
M (Ω)	−0.1757	0.0734	0.0769	0.1209	
M^{W}	−0.4427	−0.1272	−0.1387	−0.0947	−0.8033

[a] All values are listed in atomic units, are given with respect to the center of mass of the ammonia ligand, and have been transformed for direct comparison. The values are; q, the atomic charge; M, the atomic first moment, and the superscripted value, M^{W}, is the atomic contribution to the molecular dipole moments.

Table 6
Dipole moments of water ligands in complexes[a]

	O	H	H	Sum
H_2O				
q (Ω)	−1.2595	0.6297	0.6297	−0.0001
M (Ω)	0.2716	0.0931	0.0931	
M^W	0.0048	−0.4405	−0.4405	−0.8762
$Li^+(H_2O)_1$				
q (Ω)	−1.3644	0.6949	0.6949	0.0254
M (Ω)	0.2110	0.0676	0.0676	
M^W	−0.0810	−0.5273	−0.5273	−1.1357
$Li^+(H_2O)_2$				
q (Ω)	−1.3516	0.6897	0.6897	−0.0396
M (Ω)	0.2276	0.0737	0.0737	
M^W	−0.0609	−0.5152	−0.5152	−1.0913
$Li^+(H_2O)_3$				
q (Ω)	−1.3361	0.6795	0.6795	0.0229
M (Ω)	0.2526	0.0769	0.0769	
M^W	−0.0327	−0.5034	−0.5034	−1.0394
$Na^+(H_2O)_1$				
q (Ω)	−1.3374	0.6738	0.6738	0.0102
M (Ω)	0.2704	0.0459	0.0459	
M^W	−0.0178	−0.5349	−0.5349	−1.0876
$Na^+(H_2O)_2$				
q (Ω)	−1.3316	0.6765	0.6765	
M (Ω)	0.2771	0.0791	0.0791	
M^W	−0.0092	−0.5028	−0.5028	−1.0148
$Na^+(H_2O)_3$				
q (Ω)	−1.3224	0.6705	0.6705	0.0186
M (Ω)	0.2863	0.0811	0.0811	
M^W	−0.0022	−0.4950	−0.4950	−0.9877
$K^+(H_2O)_1$				
q (Ω)	−1.3228	0.6671	0.6671	0.0114
M (Ω)	0.2772	0.0823	0.0823	
M^W	−0.0083	−0.4937	−0.4937	−0.9957
$K^+(H_2O)_2$				
q (Ω)	−1.3183	0.6641	0.6641	0.0099
M (Ω)	0.2783	0.0833	0.0833	
M^W	−0.0060	−0.4895	−0.4895	−0.9850
$K^+(H_2O)_3$				
q (Ω)	−1.3121	0.6605	0.6605	0.0089
M (Ω)	0.2800	0.0843	0.0843	
M^W	−0.0024	−0.4843	−0.4843	−0.9709

[a] All values are listed in atomic units, are given with respect to the center of mass of the water ligand, and have been transformed for direct comparison. The values are; q, the atomic charge; M, the atomic first moment, and the superscripted value; M^W, is the atomic contribution to the molecular dipole moments.

4. Conclusions

The driving force for complexation is the stabilization of the alkali cations by increased nuclear–electron attraction between the heavy nucleus and the electron density on the solvent heavy atom, a density that is increased significantly on complexation as a result of the transfer of electronic charge from the hydrogen atoms. This stabilization is at the expense of increased repulsion between the charge distributions and nuclei within the adducts. This combination is to first order an ionic interaction between cation and the solvent dipole but polarization effects contribute significantly.. There is little charge transfer to the cation, but on the order of 0.1 e is transferred from the hydrogens to the X atoms of the solvent, in agreement with the results of Jorgenson et al. [5]; the role of hydrogens in stabilizing anions has been discussed previously by Wiberg et al. [39] Because of the transfer of electron density from H to X, $V_{\mathrm{NEO}}(\mathrm{H})$ increases in all cases and the hydrogens are destabilized in spite of a necessary increase in the magnitude of the interaction of their density with the nucleus of the cation, that is, an overall increase in $V_{\mathrm{NET}}(\mathrm{H})$.

The heavy atoms of the solvent have an increased effective electronegativity, pulling charge from its bonded neighbors, because of the decreased screening of the hydrogen atoms due to the polarization of the heavy atom. These effects are largest for the Li^+ complexes, decreasing as the cation gets larger due to increased repulsion. Similarly, the effects are largest for the $\mathrm{M}^+–(\mathrm{L})_n$, with $n = 1$, and decrease as the number of solvent molecules increase. The polarization of the solvent molecule is large for the smallest cation and for the first added solvent molecule. The polarization falls off with the increased size of the cations and more added solvent molecules.

Acknowledgements

We benefited from many insightful discussions with Dr J.A. Krom at UC-Berkeley. KEL thanks Professor V. Daggett for financial support at the University of Washington and PS would like to thank Professors M. Rowland and K.T. Douglas, and GlaxoWellcome UK for financial support at Manchester. This research was supported in part by grants from the National Science Foundation.

References

[1] C.W. Bauschlicher Jr., S.R. Langhoff, H. Partridge, J.E. Rice, A. Kormonicki, J. Chem. Phys. 95 (1991) 5142.
[2] T.C. Kuan, R.C. Jiang, T.M. Su, J. Chem. Phys. 92 (1990) 2553.
[3] L.A. Curtiss, E. Kraka, J. Guass, D. Cremer, J. Phys. Chem 91 (1987) 1080.
[4] P. Perez, W.K. Lee, E.W. Prohofsky, J. Chem. Phys 79 (1983) 388.
[5] S.F. Smith, J. Chandrasekhar, W.L. Jorgenson, J. Phys. Chem. 86 (1982) 3308.
[6] K.G. Spears, J. Phys. Chem. 81 (1977) 283.

[7] K.G. Spears, S.H. Kim, J. Phys. Chem. 80 (1976) 673.
[8] H. Kistenmacher, H. Popkie, E. Clementi, J. Chem. Phys. 6 (1974) 799.
[9] P.A. Kollman, I.D. Kuntz, J. Am. Chem. Soc. 96 (1974) 4766.
[10] P. Speers, K.E. Laidig, J. Chem. Soc. Perkin 2 (1994) 799.
[11] E. Kaufmann, B. Tidor, P.v.R. Schleyer, J. Comput. Chem. 7 (1986) 334.
[12] (a) D. Feller, E.D. Glendening, R.A. Kendall, K.A. Peterson, J. Chem. Phys. 100 (1994) 4981. (b) D. Feller, E.D. Glendening, D.E. Woon, M.W. Feyerisen, J. Chem. Phys. 103 (1995) 3526.
[13] E.D. Glendening, D. Feller, J. Chem. Phys. 103 (1995) 3060.
[14] S.H. Lee, J.C. Rasaiah, J. Chem. Phys. 101 (1994) 6964.
[15] J. Cioslowski, A. Nanayakkara, Int. J. Mod. Phys. B 6 (1992) 3687.
[16] A.W. Castleman Jr., P.M. Holland, D.M. Lindsay, K.I. Peterson, J. Am. Chem. Soc. 100 (1978) 6039.
[17] A.W. Castleman Jr., Chem. Phys. Lett. 53 (1978) 560.
[18] P. Kebarle, Annu. Rev. Phys. Chem. 28 (1977) 445.
[19] B.C. Guo, B.J. Conklin, A.W. Castleman Jr., J. Am. Chem. Soc. 111 (1989) 6506.
[20] L. Manceron, A. Loutellier, J.P. Perchard, Chem. Phys. 92 (1985) 75.
[21] E.A. Steel, K.M. Merz, A. Selinger, A.W. Castleman, J. Phys. Chem. 99 (1995) 7829.
[22] H. Bruning, D. Feil, J. Comput. Chem. 12 (1991) 1.
[23] K. Morokuma, K. Kituara, in: H.W. Ratajczak, J. Orville-Thomas (Eds.), Molecular Interactions, Wiley, New York, 1980.
[24] H.J. Hofmann, P. Hobza, R. Camini, J. Tomasi, R. Zahradnik, J. Mol. Struct. (THEOCHEM) 60 (1989) 339.
[25] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University, Oxford, 1990.
[26] R.F.W. Bader, J.R. Cheeseman, K.E. Laidig, K.B. Wiberg, C.M. Breneman, J. Am. Chem. Soc. 112 (1990) 6530.
[27] K.E. Laidig, J. Phys. Chem. 97 (1993) 12760.
[28] R. Ditchfield, W.J. Hehre, J.A. Pople, J. Chem. Phys. 54 (1971) 724.
[29] J.D. Dill, J.A. Pople, J. Chem. Phys. 62 (1975) 2921.
[30] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.
[31] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, J. Chem. Phys. 77 (1982) 3665.
[32] M.J. Frisch, J.A. Pople, J.S. Binkley, J. Chem. Phys 80 (1984) 3265.
[33] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
[34] B.C. Binning Jr., L.A. Curtiss, J. Comput. Chem. 11 (1990) 1206.
[35] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart, J.A. Pople, Gaussian 92, Revision E.2, Gaussian, Inc., Pittsburgh PA, 1992.
[36] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
[37] F.W. Biegler-König, R.F.W. Bader, T.H. Tang, J. Comput. Chem. 3 (1982) 317.
[38] K.E. Laidig, J. Mol. Struc. (THEOCHEM) 255 (1992) 93.
[39] K.B. Wiberg, P.v.R. Schleyer, A. Streitwieser, Can. J. Chem. 74 (1996) 892.