

## THE NATURE OF THE BONDING OF $\text{Li}^+$ TO $\text{H}_2\text{O}$ AND $\text{NH}_3$ ; AB INITIO STUDIES

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Ab initio wavefunctions have been calculated for the complex of  $\text{Li}^+$  with  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in order to better characterize the nature of the bonding. Hartree–Fock and generalized valence bond calculations were performed using a double zeta basis plus polarization functions. The binding energies obtained at the GVB level are  $D_e(\text{Li}^+ - \text{NH}_3) = 40.4$  kcal/mol and  $D_e(\text{Li}^+ - \text{H}_2\text{O}) = 37.6$  kcal/mol, in reasonable agreement with experimental values. Model calculations indicate that the  $\text{Li}^+$ –base bond is basically electrostatic. Small basis sets were found to lead to  $D_e$  as large as 75 kcal/mol for  $\text{Li}^+ - \text{NH}_3$ , a significant overestimation. Repulsions due to the  $\text{Li}^+$  core are responsible for keeping the  $\text{Li}^+$  too far away for significant relaxation effects.

### 1. Introduction

A measure and characterization of the intrinsic Lewis basicity of a molecule is the strength of its interaction with various reference acids in the gas phase. The affinity of a particular base for an acid is strongly dependent upon the acid; thus

$$D_0(\text{H}^+ - \text{NH}_3) = 202.3 \pm 2 \text{ kcal/mol [1]}, \quad (1)$$

while

$$D_0(\text{Li}^+ - \text{NH}_3) = 38.8 \pm 2 \text{ kcal/mol [2]}.$$

For cases in which the base has a nonbonding lone pair of electrons to donate and the acid has an empty orbital to accept transfer of electrons from the base, one might expect the relative affinities of several bases to be independent of the reference acid. This is not the case; for example:

$$D_0(\text{H}^+ - \text{NH}_3) - D_0(\text{H}^+ - \text{H}_2\text{O}) = 38.3 \pm 2 \text{ kcal/mol [3]},$$

while

$$D_0(\text{Li}^+ - \text{NH}_3) - D_0(\text{Li}^+ - \text{H}_2\text{O}) = 4.8 \pm 2 \text{ kcal/mol [2]}.$$

Given that the strength of different bases such as  $\text{H}_2\text{O}$

and  $\text{NH}_3$  is acid dependent, we might still expect that the differential effect of substitutions (e.g.,  $\text{CH}_3$  for  $\text{H}$ ) on a particular base would be independent of the reference acid. This is also not the case since

$$\begin{aligned} D_0(\text{H}^+ - \text{N}(\text{CH}_3)_3) - D_0(\text{H}^+ - \text{NH}_3) \\ = 19.2 \pm 2 \text{ kcal/mol [1]}, \\ D_0(\text{Li}^+ - \text{N}(\text{CH}_3)_3) - D_0(\text{Li}^+ - \text{NH}_3) \\ = 2.9 \pm 2 \text{ kcal/mol [2]}. \end{aligned} \quad (3)$$

In this paper we will address ourselves to the nature of the  $\text{Li}^+ - \text{NH}_3$  bond and the  $\text{Li}^+ - \text{H}_2\text{O}$  bond, and how the bond to  $\text{Li}^+$  differs from the bond to  $\text{H}^+$ . The results are consistent with the data in both (2) and (3).

A second consideration in carrying out this work concerns discrepancies between calculations and experiments reported in the literature. The use of ion cyclotron resonance techniques has established relative  $\text{Li}^+$  affinities of a number of  $\pi$ - and  $n$ -donor bases [2]. These techniques are capable of providing these affinities to  $\pm 0.2$  kcal/mol. However, the *absolute* affinities are much more difficult to obtain and the current scale of absolute  $\text{Li}^+$  affinities is based on the estimate

$$D_0(\text{Li}^+ - \text{H}_2\text{O}) = 34.0 \text{ kcal/mol} \quad (4)$$

by Džidić and Kebarle [4], the result of extrapolation

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to  $n = 1$  of measurements of  $D_0(\text{Li}^+(\text{H}_2\text{O})_n)$  for  $\text{Li}^+-\text{H}_2\text{O}$  clusters. Previous ab initio calculations on  $\text{Li}^+-\text{H}_2\text{O}$  lead to  $D_0(\text{Li}^+-\text{H}_2\text{O}) = 34.13$  [5], 34.03 [6] and 32.87 [6], all consistent with (4). However previous calculations on  $D_e(\text{Li}^+-\text{NH}_3)$  report values of 50 [7] and 54.7 [8], quite inconsistent with the result of combining experimental results (4) with (2)

$$D_0(\text{Li}^+-\text{NH}_3) = 38.8 \pm 2.0 \text{ [9]}. \quad (5)$$

Our calculations are in agreement with both (4) and (5), confirming the experimental results. After completion of our work a paper appeared [10] reporting  $D_e(\text{Li}^+-\text{NH}_3) = 40.2$ , in reasonable agreement with our results and with experiment.

First we will outline the details of the theoretical calculations, and then present the results obtained. We will discuss these results in terms of simple model calculations.

## 2. Computational details

### 2.1. Wavefunctions

We carried out both Hartree–Fock (HF) and generalized valence bond (GVB) calculations on  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{Li}^+$ ,  $\text{Li}^+-\text{H}_2\text{O}$  and  $\text{Li}^+-\text{NH}_3$ . The HF wavefunction has the form

$$\mathcal{A}(\phi_1\phi_1\alpha\beta\phi_2\phi_2\alpha\beta\dots), \quad (6)$$

with all orbitals doubly-occupied ( $\mathcal{A}$  is the antisymmetrizer or determinant operator). In the GVB wavefunction we replace one or more of the HF pairs with correlated or valence bond pairs,

$$\phi_i(1)\phi_i(2) \rightarrow [\phi_{ia}(1)\phi_{ib}(2) + \phi_{ib}(1)\phi_{ia}(2)], \quad (7)$$

and then solve for all orbitals self-consistently [11].

For all of these molecules we carried out GVB (1) calculations, meaning that we included only one valence bond pair [eq. (7)] in each – the  $\text{Li}^+-\text{O}$  or  $\text{Li}^+-\text{N}$  bond and the corresponding lone pair in the free base. In addition we correlated all four bonding orbitals of  $\text{Li}^+\text{NH}_3$ , requiring each orbital to be orthogonal to all the other electron pairs, and requiring each electron pair to be singlet coupled. This is called perfect pairing and we denote this calculation as GVB (4/PP).

The orbital pairs from the GVB(4/PP) wavefunctions were then transformed to an equivalent natural orbital

representation

$$(\phi_a\phi_b + \phi_b\phi_a) \rightarrow C_1\phi_1^2 - C_2\phi_2^2,$$

where  $\phi_1$  and  $\phi_2$  are orthogonal. We then carried out a configuration interaction [12] calculation allowing all single excitations from the dominant configuration plus all double excitations within each pair. The calculations involve 255 determinants, relax the perfect pairing restriction and allow for inter-pair correlation effects.

### 2.2. Basis sets

In order to obtain such wavefunctions, each orbital is expanded in terms of a set of basis functions  $\{\chi_\mu\}$ .

$$\phi_i = \sum_{\mu} \chi_{\mu} C_{\mu i}$$

and the expansion coefficients solved for. The basis set used for O, N, and H was the double zeta (DZ) contracted gaussian type orbital basis of Dunning and Huzinaga [13], supplemented with a set of d polarization functions on each N and O; the basis used for  $\text{Li}^+$  was that of Kahn et al. [14]. This set of basis functions, denoted DZd, is expected to be sufficient for obtaining  $\text{Li}^+$  affinities to  $\sim 1$  kcal/mol. We repeated several of our calculations with the DZ basis alone, omitting the polarization functions, and found that the calculated bond energy increased by  $\sim 5$  kcal/mol. A third set of calculations at the minimal basis set (MBS) level (i.e., five basis functions per N, O and  $\text{Li}^+$  and one basis function per H) was carried out using both the STO-3G and STO-4G bases [15]. The MBS lead to very large positive errors ( $\sim 40$  kcal/mol) in the  $\text{Li}^+$  affinities.

### 2.3. Geometries

All geometries are indicated in table 1. For  $\text{H}_2\text{O}$  and  $\text{NH}_3$  we used the experimental geometries. Clementi and Popkie [18] carried out an extensive potential surface scan for  $\text{Li}^+\text{H}_2\text{O}$ , and we used their optimum geometry. We solved for the optimum geometry of the  $\text{Li}^+\text{NH}_3$  molecule using a minimal basis set (STO-4G) and the GAUS70 program [19]. In  $\text{Li}^+\text{H}_2\text{O}$ , the  $\text{Li}^+$  was found to lie on the axis of highest symmetry [18] and we retained this configuration for  $\text{NH}_3$ , arriving at  $r_{\text{Li}-\text{N}} = 1.899$  Å. The other coordinates were similar to those of free  $\text{NH}_3$ , as shown in table 1. It is expected

Table 1

Geometry parameters: bond lengths are in Å, bond angles are in degrees. X indicates O or N. The  $\text{Li}^+$  is along the symmetry axis of the molecule

	$r(\text{Li}^+-\text{X})$	$r(\text{X}-\text{H})$	$\angle(\text{Li}^+-\text{X}-\text{H})$	$\angle(\text{H}-\text{X}-\text{H})$
$\text{NH}_3$ <sup>a)</sup>	–	1.012	–	106.7
$\text{Li}^+\text{NH}_3$ <sup>b)</sup>	1.90	1.027	113.8	104.6
$\text{H}_2\text{O}$ <sup>c)</sup>	–	0.96	–	104.5
$\text{Li}^+\text{H}_2\text{O}$ <sup>d)</sup>	1.84	0.96	127.0	106.1

<sup>a)</sup> ref. [16]. <sup>b)</sup> This geometry calculated using the Hartree–Fock wavefunction with an STO-4G basis. <sup>c)</sup> Ref. [17].

<sup>d)</sup> Ref. [18].

that the use of MBS and HF will lead to a  $\text{Li}^+-\text{N}$  bond length somewhat too short.

### 3. Results

The energies are reported in table 2 and the calculated  $\text{Li}^+$  affinities appear in table 3. In order to compare our results with experiments we have to include zero-point energy corrections. Diercksen et al. [6], in their  $\text{Li}^+\text{H}_2\text{O}$  calculation, obtained force constants for the complex from a partial potential surface calculation, and estimated the zero point energy correction to be 2.0 kcal/mol. Because of the similarity in bond length and bond strength of  $\text{Li}^+-\text{N}$  and  $\text{Li}^+-\text{O}$ , we assumed the region of the  $\text{Li}^+-\text{N}$  coordinate on the  $\text{Li}^+\text{NH}_3$  hypersurface to have approximately the same shape as the corresponding region on the  $\text{Li}^+\text{H}_2\text{O}$  surface. We therefore have added 2.0 kcal/mol to the experimental

$D_0$  to give  $D_e(\text{Li}^+-\text{NH}_3) = 40.8$  and  $D_e(\text{Li}^+-\text{H}_2\text{O}) = 36.0$ .

Our calculated  $\text{Li}^+$  affinity for  $\text{Li}^+\text{NH}_3$  is within 1 kcal/mol of the experimental value while the number for  $\text{Li}^+\text{H}_2\text{O}$  is within 2 kcal/mol. For the former system, our HF result compares very well with the value reported by Hinchliffe and Dobson [10]. This is to be expected since they used a geometry and basis set similar to ours. Several other calculations on the latter system have been reported, leading to Hartree–Fock  $\text{Li}^+$  affinities ( $D_e$ ) of 34.9 [5], 35.2 [5] and 36.0 [6] kcal/mol. The 35.2 kcal/mol and 36.0 kcal/mol values are closer to experiment than ours, perhaps reflecting the larger basis sets used in those calculations [20]. Of interest here is the value of 34.4 kcal/mol obtained by Clementi with a slightly *smaller* basis. Primarily, this basis is not completely adequate for the  $\text{Li}^+$ . The effect of this is to lower the  $\text{Li}^+-\text{O}$  bond strength; this is the opposite of the effect of a deficient basis on the base, as will be discussed below. A second point to note is the effect of adding further polarization functions to the basis. Clementi's numbers indicate an energy lowering of approximately 1 kcal/mol with the addition of extra polarization functions. Thus we expect one set of polarization functions to be adequate.

The lone pair bonding orbitals of  $\text{Li}^+\text{H}_2\text{O}$  and  $\text{Li}^+\text{NH}_3$  are shown in fig. 1, where we see that they are little changed from their form in the free base. This result concurs with the Mulliken populations which indicate a movement of only about 0.06 to 0.09 electrons onto the  $\text{Li}^+$ . Furthermore, the population analysis shows that the polarization of the  $\text{X}-\text{H}$  bonds is *larger* than the delocalization of the bonding lone pair onto

Table 2

Total energies (in hartree<sup>a)</sup>). The geometries are given in table 1

	Basis set					
	MBS(STO-4G)	DZ	DZd	GVB(1) <sup>b)</sup>	GVB(4/PP) <sup>b)</sup>	GVB-CI <sup>b)</sup>
	HF	HF	HF			
$\text{Li}^+$	– 7.197837	– 7.236211	– 7.236211			
$\text{H}_2\text{O}$			–76.034483	–76.055221		
$\text{Li}^+\text{H}_2\text{O}$			–83.330154	–83.351393		
$\text{NH}_3$	–55.849245	–56.175987	–56.198279	–56.210039	–56.263088	–56.292999
$\text{Li}^+\text{NH}_3$	–63.167383	–63.484111	–63.498580	–63.510701	–63.563674	–63.594263

<sup>a)</sup> 1 hartree = 27.2117 eV = 627.507 kcal/mol = 2625.49 kJ/mol.

<sup>b)</sup> The GVB terminology is discussed in the text.

Table 3

Calculated  $\text{Li}^+$  affinities in kcal/mol. A zero point correction of 2 kcal/mol has been added to the experimental  $D_0$  values to obtain  $D_e$

	MBS	DZ a)	DZd a)	correlated	experimental
	HF	HF	HF		
$\text{Li}^+\text{NH}_3$	75.5 b)	45.1 b)	40.2 b)	40.4 b) GVB(1)	$40.8 \pm 2$ c)
	50.0 d)		40.3 e)	40.4 b) GVB(4/PP)	
	54.7 f)	45.2 f)		40.8 b) GVB-CI	
$\text{Li}^+\text{H}_2\text{O}$			37.3 b)	37.6 b) GVB(1)	$36.0 \pm 3$ g)
			35.3 h)		
			34.4 i)		
			35.2 j)		
			36.0 j)		

a) We include under DZ more extended bases. b) Present work. c) Ref. [2]. 2 kcal/mol was added to the experimental value to obtain  $D_e$ . d) Ref. [7]. e) Ref. [10]. f) Ref. [8]. g) Ref. [4]. Error estimated from data presented in ref. [4]. h) Ref. [18]. i) Ref. [5]. The 34.4 kcal/mol value is with a smaller basis and the 35.2 kcal/mol value is for a larger basis. j) Ref. [6].

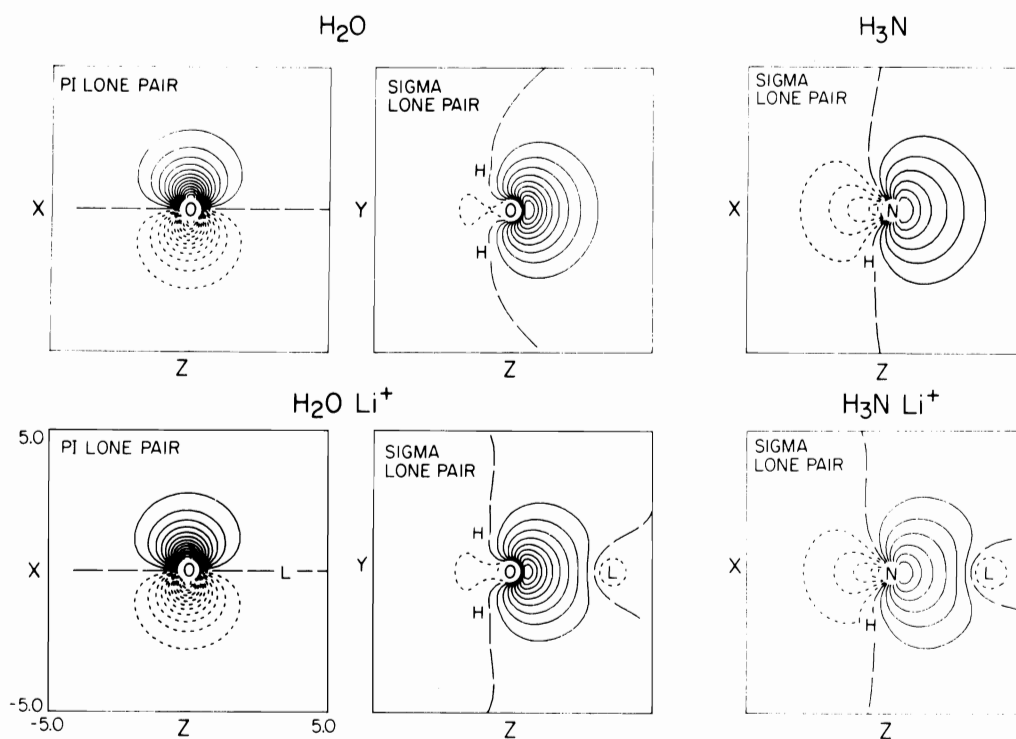


Fig. 1. The GVB(1) lone pair orbitals of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{Li}^+\text{H}_2\text{O}$  and  $\text{Li}^+\text{NH}_3$ . Dashed lines indicate negative amplitudes, and long dashes indicate zero amplitude. The contour interval is 0.05 au. H locates hydrogen, N locates nitrogen, O locates oxygen and L locates  $\text{Li}^+$ .

Table 4  
Population analyses differences. The numbers quoted are the changes in the Mulliken population analysis upon bringing the Li<sup>+</sup> up to the molecule

	MBS(STO-4G) HF	DZ HF	DZd HF	GVB
Li <sup>+</sup> H <sub>2</sub> O:	Li	-	0.058	0.064
	O	-	0.144	0.135
	H	-	-0.100	-0.100
Li <sup>+</sup> NH <sub>3</sub> :	Li	0.272	0.075	0.096
	N	-0.009	0.270	0.235
	H	-0.087	-0.115	-0.105

the Li<sup>+</sup>. One might expect that the second lone pair orbital ( $\pi$ ) on the oxygen would delocalize into a  $\pi$  orbital on the Li<sup>+</sup> to form a  $\pi$ -bond. In fact, as can be seen in fig. 1, no such delocalization occurs. We can conclude that both Li<sup>+</sup>-N and Li<sup>+</sup>-O are purely *sigma* bonds and therefore can be compared quite closely.

From table 3 it can be seen that the smaller basis sets lead to larger Li<sup>+</sup> affinities, with errors of 20–35 kcal/mol for the MBS. These effects can be understood as follows. The lone pair orbitals of n-donor bases are quite tight but are poorly described with a MBS; even with a DZ basis d polarization functions are required. On forming a bond with Li<sup>+</sup>, these orbitals tend to remain localized on the base, and hence do not make much use of the Li<sup>+</sup> basis functions. However, if the atomic orbital basis of the base is too small, the lone pair orbitals delocalize onto the Li<sup>+</sup> in order to compensate for the inadequate basis: the result is too large a Li<sup>+</sup> affinity. In other words, a deficient basis set raises the energy of the free base more than the Li<sup>+</sup>-base complex since in the latter case additional basis functions are available. For a MBS this effect is extreme, leading to affinity increases of up to 35 kcal/mol. Indeed, from table 4 we see that the MBS leads to a transfer of 0.27 electrons onto the Li<sup>+</sup> in Li<sup>+</sup>NH<sub>3</sub>, whereas with the DZd basis only 0.096 electrons are transferred onto the Li<sup>+</sup>. Such effects are not noticed for more typical bonding situations involving neutral molecules as it is usually the case that the orbitals on each center are already occupied.

As indicated in table 3, the calculated Li<sup>+</sup> affinity of NH<sub>3</sub> using the DZ basis is 5 kcal/mol *greater* than that obtained with the DZd basis. Usually, a DZ basis leads to a weaker bond energy rather than a stronger

one. Again, the problem is that the Li<sup>+</sup> basis functions can be used to compensate for the deficiency of the basis (i.e., the lack of d functions on the N), leading to a Li<sup>+</sup> affinity that is too large.

The Li<sup>+</sup>NH<sub>3</sub> results for the GVB(4/PP) and GVB-CI calculations shown in table 3 indicate that correlation effects play little role in the bonding. As can be seen in the total energies (table 2) or the energy lowerings (table 5), there are significant energy changes due to the additional correlations. However very nearly the same changes occur in Li<sup>+</sup>NH<sub>3</sub> as in NH<sub>3</sub>. This small differential effect indicates that the presence of the Li<sup>+</sup> constitutes only a small perturbation on the NH<sub>3</sub> electronic structure, and hence any extra correlation energy in Li<sup>+</sup>NH<sub>3</sub> due to the Li<sup>+</sup> is negligible. This is consistent with the very small degree of the delocalization of electrons on to the Li<sup>+</sup>.

#### 4. Discussion

As mentioned in the introduction: (1) the H<sup>+</sup> affinities of H<sub>2</sub>O and NH<sub>3</sub> differ by 38.3 kcal/mol whereas their Li<sup>+</sup> affinities differ by only 4.8 kcal/mol; (2) the H<sup>+</sup> affinities of NH<sub>3</sub> and N(CH<sub>3</sub>)<sub>3</sub> differ by 19.2 kcal/mol whereas their Li<sup>+</sup> affinities only differ by approximately 3 kcal/mol; (3) the H<sup>+</sup> affinities of the bases considered are several times larger than their Li<sup>+</sup> affinities.

In order to shed some light on these differences we carried out several model calculations. First, in order to determine the purely electrostatic contribution to the bond, we took the Hartree-Fock wavefunction for the free base and placed a proton at the optimum position for a Li<sup>+</sup>, but without relaxing the base orbitals (a *frozen orbital* calculation). The results are shown in fig. 2 and table 4. The value (52.8 kcal/mol) for NH<sub>3</sub> is about one-third larger than the value for H<sub>2</sub>O (39.9 kcal/mol). This difference is expected since the N lone pair orbitals are more extended and therefore have higher amplitude closer to the proton.

A common approximation used to estimate electrostatic bond energies is the replacement of the base by a point-dipole and the ion by a point charge. Using this approach for Li<sup>+</sup>NH<sub>3</sub> and Li<sup>+</sup>H<sub>2</sub>O (with the dipole centered at the N and O and the Li<sup>+</sup> positioned at the proper distance) leads to Li<sup>+</sup> bonding energies of 28.22 kcal/mol for NH<sub>3</sub> and 37.58 kcal/mol for H<sub>2</sub>O.

Table 5  
Summary of important contributions<sup>a)</sup> to the GVB-CI wavefunctions

	N1s	Configuration			Lone pair	Character	Equivalent configurations	Energy contributions <sup>b)</sup> (mh)					
		NH(1)	NH(2)	NH(3)									
$\text{NH}_3$	2	2	1	2	0	2	0	2	0	GVB	1	–	
	2	0	2	2	0	2	0	2	0	GVB	3	47.1	
	2	2	0	2	0	2	0	0	2	GVB	1	9.1	
	2	2	0	2	0	1	1	1	1	$\sigma\sigma^*$ , $nn^*$	3	15.1	
	2	1	1	1	1	2	0	2	0	$\sigma\sigma^*$ , $\sigma\sigma^*$	3	10.7	
	N1s	Li1s	Configuration			Lone pair	Character	Equivalent configurations	Energy contributions <sup>b)</sup> (mh)				
			NH(1)	NH(2)	NH(3)								
$\text{Li}^+\text{NH}_3$	2	2	2	0	2	0	2	0	2	0	GVB	1	–
	2	2	0	2	2	0	2	0	2	0	GVB	3	47.0
	2	2	2	0	2	0	2	0	0	2	GVB	1	9.3
	2	2	2	0	2	0	1	1	1	1	$\sigma\sigma^*$ , $nn^*$	3	15.5
	2	2	1	1	1	1	2	0	2	0	$\sigma\sigma^*$ , $\sigma\sigma^*$	3	10.9

a) All spatial configurations leading to an energy contribution larger than 1 mh are listed.

b) The energy contribution listed here is the increase in the energy that would result from deleting this configuration but without modifying the other CI coefficients.

These numbers are smaller than those obtained in the frozen orbital calculation (which is equivalent to using all moments of the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  rather than just the dipole term), and the ordering of their magnitudes has reversed. We can conclude that the truncation of the multipole series in calculating the electrostatic energies offers a poor description of the interaction. Therefore, we recommend using a direct frozen orbital calculation to determine the magnitude of the electrostatic contri-

bution to cation affinities.

Secondly, we replaced the  $\text{H}^+$  with a  $\text{Li}^+$  and repeated the calculations, again without allowing the orbitals to readjust. This leads to only minor changes in the electrostatic attractions – both ionic centers having a single positive charge – but has a large effect on the  $\text{Li}^+$  affinity. The value for  $\text{Li}^+\text{H}_2\text{O}$  is found to decrease by 11.3 kcal/mol, and that for  $\text{Li}^+\text{NH}_3$  to decrease by 20.8 kcal/mol. This effect is a result of the requirement of the Pauli principle that the  $\text{Li}^+$  core orbitals and the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  orbitals be orthogonal. The decrease for  $\text{NH}_3$  is much larger because this effect is directly related to the degree of overlap of the base and  $\text{Li}^+$  orbitals, which is higher in the  $\text{Li}^+-\text{NH}_3$  complex. Combining the electrostatic and Pauli principle effects gives a  $\text{Li}^+$  affinity of 28.6 kcal/mol for  $\text{H}_2\text{O}$  and 32.0 kcal/mol for  $\text{NH}_3$ . The difference of 3.4 kcal/mol between the two values is consistent with the difference between the results of the full calculations, but each is only about 80% of the actual values.

The remaining 20% can be broken down into two contributions. One is from the polarization of the base orbitals by the  $\text{Li}^+$  potential and the second is from the actual delocalization of the lone pair onto the  $\text{Li}^+$

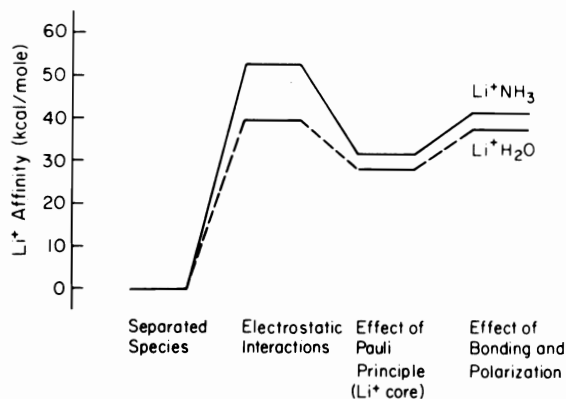


Fig. 2. Components of the  $\text{Li}^+$  binding energies.

to form the bond. These effects can be separated, but we did not do so. The net result of both terms is about the same for both systems: 8.7 kcal/mol for  $\text{H}_2\text{O}$  and 8.2 kcal/mol for  $\text{NH}_3$ .

Our conclusion is that (with a good basis set) 80% of the  $\text{Li}^+$  bond energy is accounted for without any readjustment of the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  orbitals. This suggests that initial molecular geometry searches for such systems be carried out with frozen orbital wavefunctions (no self-consistent calculations). Using effective potentials [21] for the core of the  $\text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$  would make the calculations particularly inexpensive.

As we have seen, the electrostatic interaction of a proton with  $\text{NH}_3$  is significantly larger than with  $\text{H}_2\text{O}$ . Since there are no Pauli principle effects, we can expect that polarization of the bonds in the base will be large and that the proton will be able to move much closer to the base. This causes the proton affinities of the bases to be far higher than their respective  $\text{Li}^+$  affinities. Furthermore, the variation in proton affinities with the base is more pronounced, since now the physical properties of the base (e.g., polarizability, dimensions of the orbitals) play a much greater role in determining the strength of the acid–base bond.

These considerations allow a qualitative picture of the effects of substituents on the base. In the case of  $\text{Li}^+$ , the lone pair orbital involved in the bond tends to remain localized on the base, so that the replacement of one or more hydrogens with some other functional group would not be expected to affect the affinity significantly. This is supported by current experimental results [2], indicating changes in  $D_0(\text{Li}^+-\text{N})$  of only 2 kcal upon  $\text{CH}_3$  substitution. However, the importance of polarizability contributions to the proton affinity suggests that the dependence of this affinity on the nature of the substituent will be large.

## 5. Summary

Three main conclusions can be drawn from this work. First, a good basis set with polarization functions is essential for these systems. However the inclusion of correlation effects is not critical, leading to corrections of about 1 kcal/mol to the binding energy. Secondly, the  $\text{Li}^+$  affinity is due primarily to an attractive electrostatic potential and a repulsive interaction resulting from the Pauli principle. Finally,

Table 6  
Components of the  $\text{Li}^+$  affinities of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . All quantities in kcal/mol

	Base	
	$\text{H}_2\text{O}$	$\text{NH}_3$
electrostatic interactions <sup>a)</sup>	39.91	52.83
Pauli principle effect <sup>b)</sup>	-11.30	-20.78
bonding and polarization effects	8.70	8.17
total	37.31	40.22

<sup>a)</sup> Obtained by placing a point positive charge at the position of the  $\text{Li}^+$  and re-evaluating the energy of the base.

<sup>b)</sup> The energy of the complex is evaluated using the orthogonalized free ion and free base orbitals, allowing for no readjustment of the orbitals.

simple models using charge–dipole and charge–polarizability interactions are not adequate.

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