

## References and Notes

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### A Novel Class of Molecular Complexes: Li-NH<sub>3</sub>, Li-H<sub>2</sub>O, Li-HF, Li-H<sub>2</sub>S, Na-H<sub>2</sub>O, and Na-HF

Sir:

In recent years theoretical chemists have made considerable progress in understanding the gas phase hydration<sup>1-4</sup> of simple cations and anions. For example, theory and experiment agree that Li<sup>+</sup> and F<sup>-</sup> bind a single water molecule by 35 and 24 kcal/mol, respectively. In addition, ab initio calculations have been reported for systems as large as Li(H<sub>2</sub>O)<sub>6</sub><sup>+</sup>, leading to the conclusion<sup>4</sup> that Li<sup>+</sup> prefers a tetrahedral (rather than octahedral) coordination. There seems to be agreement<sup>4</sup> that much of the strength and directionality of these interactions can be qualitatively understood in terms of classical electrostatics.<sup>5</sup>

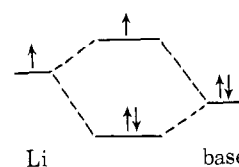
However, the analogous neutral systems (e.g., Li-H<sub>2</sub>O and F-H<sub>2</sub>O) have, for the most part, remained unexplored. This is in part due to the lack of charge, suggesting that such systems might not be significantly bound. In addition the unpaired electron makes standard closed-shell self-consistent-field theory<sup>6</sup> inapplicable. Nevertheless, there is at least one indication in the literature that such molecular complexes may be strongly bound. This is the work on Li-NH<sub>3</sub> by Nicely and

Dye,<sup>7</sup> who used SCF theory to predict a binding energy of ~20 kcal/mol. In the present communication we report SCF studies on a family of molecular complexes involving neutral alkali and halogen atoms and dipolar molecules. In particular, we have studied interactions between Li, Na, and F atoms and the dipolar molecules NH<sub>3</sub>, H<sub>2</sub>O, HF, PH<sub>3</sub>, H<sub>2</sub>S, and HCl.<sup>8</sup> The results of these calculations are summarized in Table I.

The minimum energy structure for alkali atom (M)-hydride (BH<sub>n</sub>) interactions is M...BH<sub>n</sub>, where the negatively charged end of the hydride approaches the neutral atom. There is charge transfer from the hydride to the metal and this leads to a rather substantial dipole moment for the complex. Comparing the Li atom interaction energies with different hydrides, we see that they qualitatively follow the order expected on the basis of the electrostatic potential model we developed<sup>9</sup> (NH<sub>3</sub> > H<sub>2</sub>O > HF > PH<sub>3</sub> > H<sub>2</sub>S > HCl), with the exception that H<sub>2</sub>S is more strongly bound than PH<sub>3</sub>. The reason for this discrepancy is not completely clear at this point. Another interesting feature of the calculations, which could have been predicted on the basis of the electrostatic potential of the hydrides,<sup>9</sup> is that the minimum energy  $\theta$ , the angle between the Li...B vector and the dipole vector of the base is ~0 for H<sub>2</sub>O and ~70-80° for H<sub>2</sub>S and HCl. This is another demonstration that there is much greater "lone pair directionality" in the hydrides of the second row than in the hydrides of the first row (H<sub>2</sub>O, HF).<sup>10</sup>

The Na...hydride interactions appear to have the same relative strength as the Li...hydride for NH<sub>3</sub>, H<sub>2</sub>O, and HF, although the interaction energies are smaller. Na is at least as polarizable as Li,<sup>11</sup> but the greater Na...hydride distances would be expected to decrease the interaction energies compared to those found for Li...hydride. If the Li...base interactions are analogous to Li<sub>2</sub>...base interactions,<sup>12</sup> we expect electrostatic and polarization energies (especially the latter) to dominate these alkali metal-hydride interaction potentials.

A simple orbital picture which describes these interactions and is consistent with the Mulliken populations changes<sup>13</sup> showing base → atom charge transfer is shown below. This



type of an orbital interaction would be net stabilizing. The less tightly bound the orbital of the base, the more strongly it would interact with that of Li, and this is consistent with the strength

Table I. Interaction Energies Geometries and Charge Redistribution in Complexes Studied

Complex	$-\Delta E$ (kcal/mol)	$R$ (Å) <sup>a</sup>	$\theta$ (deg) <sup>b</sup>	Charge transfer <sup>c</sup>	Dipole moment enhancement <sup>d</sup>
Li...NH <sub>3</sub>	14.5	2.07	(0)	0.059	4.05
Li...OH <sub>2</sub>	12.8	1.93	0	0.046	3.69
Li...FH	4.2	1.94	(0)	0.036	3.61
Li...PH <sub>3</sub>	0.5	3.03	(0)	0.054	3.51
Li...SH <sub>2</sub>	1.8	2.78	78°	0.081	3.32
Li...ClH	<0.1	(3.18)	71°	0.035	1.58
Na...NH <sub>3</sub>	6.0	2.75	(0)	0.030	3.33
Na...OH <sub>2</sub>	5.2	2.38	(0)	0.024	3.28
Na...FH	1.2	2.46	(0)	0.019	2.93
F...NH <sub>3</sub> ( <sup>2</sup> E)	-3.0	(2.80)	(0)	-0.002	0.37
F...NH <sub>3</sub> ( <sup>2</sup> A)	1.8	2.80	(0)	0.006	0.53

<sup>a</sup> Distance between atom and electronegative atom on the polar molecule; values in parentheses are nonoptimized values. <sup>b</sup> Angle between the  $R$  vector and the dipolar axis of the neutral molecule; values in parentheses are nonoptimized values. <sup>c</sup> Net Mulliken charge transfer from molecule to atom. <sup>d</sup> Dipole moment of complex minus dipole moment of isolated molecules (in Debyes).

of Li interaction energies in the first row of the periodic table ( $\text{NH}_3 > \text{H}_2\text{O} > \text{HF}$ ). However, this picture leads one to expect strong  $\text{H}\cdots\text{NH}_3$ ,  $\text{H}\cdots\text{OH}_2$ , and  $\text{H}\cdots\text{FH}$  interactions as well, and Lathan et al.<sup>14</sup> found that these interactions did not lead to bound species (at the SCF level). The  $\text{H}\cdots\text{NH}_3$  is isoelectronic with the  $\text{Li}\cdots\text{NH}_3$  so one must surmise that the key difference is the much greater polarizability of Li. The electrostatic potential at 2 Å from the atom is significantly more positive for Li than H, so electrostatic effects may play an important role as well.<sup>15</sup>

If charge transfer were of dominant importance in stabilizing these complexes, one might expect the F atom, which has a greater electron affinity than the alkali metals, to have a larger interaction energy with  $\text{NH}_3$  than does Li. As shown in Table I, the  $\text{F}\cdots\text{NH}_3$  complex ( ${}^2\text{A}$ ) is weakly bound and the  ${}^2\text{E}$  complex not bound at all. This is consistent with the directionality of the electrostatic potential in  ${}^2\Sigma$  and  ${}^2\Pi\text{F}$  atom, with a single electron in either the  $p_z$  ( $\sigma$ ) or  $p_{x,y}$  ( $\pi$ ) orbitals. An interaction of the type  $\text{H}_3\text{N}:\ddot{\text{F}}:$  ( ${}^2\text{A}$ ) is favorable, because the nitrogen is approaching an "electropositive side" of the fluorine. The interaction  $\text{H}_3\text{N}:\ddot{\text{F}}:$  ( ${}^2\text{E}$ ) is repulsive because the "negative end" of  $\text{NH}_3$  is approaching the "negative side" of F.<sup>16</sup>

Further studies are in progress on these complexes, specifically Morokuma component analysis<sup>17</sup> and configuration interaction calculations. The latter are of considerable interest, since the dispersion energy, which depends on the polarizabilities of the atom and hydride, is likely to be much larger in this case than that for  $(\text{H}_2\text{O})_2$  (1 kcal/mol).<sup>18</sup>

We thus expect that our SCF calculated interaction energies may be somewhat less than the actual  $\Delta E$ 's of complex formation. On the basis of the calculated dipole moments and interaction energies in Table I, molecular beam studies of a radical atom-dipolar molecule interactions would be of considerable interest.

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- The results are consistent with the potential surfaces reported by Noble and Kortzeborn for F atom interacting with HF. The  ${}^2\Pi$  state of  $\text{F}\cdots\text{H}-\text{F}$  was bound by  $\sim 2$  kcal/mol; the  ${}^2\Sigma$  state of  $\text{F}\cdots\text{H}-\text{F}$  was repulsive. This is consistent with the fact that in this case F is acting as the electron donor and can do so effectively only if its "negative side" points toward the HF molecule.
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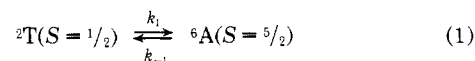
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## A Direct Measurement of Dynamic Spin-Interconversion Rates in the Spin-Equilibrium Protein Ferric Myoglobin Hydroxide

Sir:

Various heme proteins including cytochrome P-450,<sup>1-8</sup> catalase,<sup>9</sup> myoglobin, and hemoglobin,<sup>10,11</sup> have been reported to possess an electronic structure for Fe(III) in which two electronic states of differing spin multiplicity are in thermal equilibrium (a spin-equilibrium)<sup>12</sup> with one another. The question arises as to the existence and role of this unusual electronic structure for in vivo biological functions of these proteins and especially as to the nature of this involvement in electron transfer/storage activity. For an idealized Fe(III) heme center of  $O_h$  symmetry, the spin-equilibrium is between a low-spin  ${}^2\text{T}(S = 1/2)$  state and a high-spin  ${}^6\text{A}(S = 5/2)$  state,



In this work we wish to report on the dynamics of this spin-equilibrium process in which the spin-interconversion rates,  $k_1$  and  $k_{-1}$ , have been directly measured in solution for horse ferric myoglobin hydroxide using laser stimulated Raman temperature-jump kinetics.<sup>13</sup> The interpretation of the anomalous magnetic properties of ferric myoglobin hydroxide as arising from a thermal equilibrium between an  $S = 1/2$  low-spin and  $S = 5/2$  high-spin electronic state has been extensively documented in solution by the reversible temperature dependence of its electronic spectrum,<sup>10,14</sup> variable-temperature magnetic susceptibility data<sup>11</sup> (reproduced satisfactorily in our laboratory) and by its EPR spectrum<sup>15</sup> (see also ref 25). Beattie and West, using conventional capacitive discharge T-jump,<sup>14</sup> have previously established a lower limit of  $2 \times 10^5 \text{ s}^{-1}$  for the sum of the forward ( $k_1$ ) and reverse ( $k_{-1}$ ) rate constants for the spin change of the protein, while EPR studies have been used to estimate an upper limit for  $k$  of  $10^{10} \text{ s}^{-1}$ .<sup>15</sup> Furthermore, Beattie and West's correlation of the visible