Hydration of NH_4F

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Abstract: Ab initio molecular orbital calculations have been carried out on hydrates of NH_4F. We have employed one- and two-body energies in a similar way to that used in our study of Li^+ hydration and predict that ion pair structures are favored when three or four waters per NH_4F are added. Solvent separated ion pairs become competitive with the contact ion pairs as more waters are added to the system.

The techniques of electronic structure theory have advanced to the point where intermolecular interactions of small molecules in the gas phase can be treated quite accurately.[2] However, it is a continuing challenge to apply these techniques to problems in condensed phases. There have been, in recent years, a number of approaches to examining intermolecular interactions in solids and liquids. Almlöf,[3] Santry,[4] and Tomasi[5] have shown that one can treat crystal environment effects quite well. Studies on the structure of water and ionic solutions by Clementi and co-workers,[6] the "super-molecule approach", to study the effect of H_2O on the conformations of biological molecules extensively employed by Pullman;[7] continuum model approaches to solvation by Beveridge,[8] Hylton et al.,[9] and Newton;[10] and the electrostatic partial charge representation of solvent by Morokuma and Noell[11] are all examples of interesting approaches to look at the effect of solvent on molecular properties and intermolecular interactions in liquids. It should be pointed out that the "supermolecule" and continuum approaches can be combined.[10]

In our previous work in this area we have studied the hydration of cations, examining the energy and structure of hydrates of Li^+, Be^{2+}, Na^+, Mg^{2+}, Al^{3+}, K^+, and Ca^{2+}.[12] We have used cation $\cdot 2H_2O$ surfaces to represent larger clusters of cation—water structures and have found that two- and three-body energies appear to suffice to build up qualitatively reasonable structures for Li^+ and Na^+ complexes. For more highly charged ions[13,14] the inclusion of at least cation—three water energies may be needed for semiquantitative accuracy.

Here we apply this many-body approach to the hydration of NH_4F. This complex is of great interest to us because we have calculated that $H_3N\cdots H{-}F$ has very little structural reorganization of the monomers, despite its very high binding energy.[15] The $H_2O\cdots H{-}Cl$ dimer is also calculated to be a complex of nearly unperturbed monomers.[15] This is in contrast to $H_3N\cdots HCl$, where the calculated equilibrium structure[16] has the proton half-transferred from the Cl to the N. We have confidence in the correctness of our predicted structure of $H_3N\cdots HF$[15,18] in view of the matrix isolation ir spectroscopic studies of $NH_3\cdots HCl$ and $H_2O\cdots HCl$[17] that support the theoretical calculations. However, one expects that ammonium fluoride will be an ionic salt in aqueous solutions, so it is of interest to study the perturbation of the properties of H_3NHF as one gradually "adds" water to the molecule. In our study of NH_4F we focus on two specific questions: First, how does the proton potential function in NH_3HF change as water is added? Second, what are the relative stabilities of different ion-pair structures as water is added? In addition to these specific questions, we also discuss the general properties of ion-water interactions.

Methods

We have employed the program GAUSSIAN 70 (QCPE No. 236) in these calculations using a basis set of "double ζ" quality (431-G).[19] This is the same basis set employed in our systematic study of H-bonded complexes. We have used the CDC 7600 version of this program which has the capability of treating molecules with up to 110 atomic orbitals.[20]

Results and Discussion

A. Hydration of Li^+, NH_4^+, Cl^-, and F^-. In order to assess the strengths and weaknesses of this 431-G basis set for studying ion hydration we have carried out an examination of the interaction of a single water with Li^+, NH_4^+, F^-, and Cl^-. More accurate calculations[21] and experiments[22] exist for these ion-water interactions; Table I contains the results of the various studies. As one can see, this basis set is capable of relatively good structural prediction but exaggerates the hydration energy. This error appears larger for anions than cations, but it is encouraging that the ratio of the ΔE's found in these calculations to the corresponding ΔE's found in accurate calculations is very similar for both anions ($F^-\cdots H_2O$, ratio = 1.707; $Cl^-\cdots H_2O$, ratio = 1.681). We are currently testing the generality of this scale factor of ~1.7 on other anions. The correction factor appears to be significantly smaller for cations than anions (for $Li^+\cdots H_2O$ it is 1.35).

The main reasons for the exaggerated interaction energy with the 431-G basis set are probably: (1) This basis set predicts a much larger dipole moment for H_2O (2.6 D vs. ~2.0 D) than the best basis set,[21] the latter being in much better agreement with experiment (1.85 D). (2) In limited basis set calculations of intermolecular interactions, the crude representation of the monomer wave functions causes them to be artificially stabilized in the presence of neighboring atoms. Using the counterpoise method to correct for basis set deficiencies[28] we find that $\Delta E(F^-\cdots H_2O) = -28.92$ kcal/mol and $\Delta E(Cl^-\cdots H_2O) = -15.74$ kcal/mol. Further scaling by the ratio of experimental and calculated H_2O dipole moments (1.85/2.60), one finds a $-\Delta E$ for fluoride-water of 20.58 kcal/mol and for chloride-H_2O of 11.20 kcal/mol. Both of these values are in respectable agreement with experiment. The agreement would be even better if we had scaled by the ratio of the Hartree-Fock limit dipole moment (ref 21 must be close to this) to our calculated moment (2.00/2.60); the hydration energies are then -22.08 and -12.11 kcal/mol.

Applying the same approach to $Li^+\cdots OH_2$ and $NH_4^+\cdots OH_2$, we find the counterpoise corrections to be 2.56 and 0.77 kcal/mol, respectively. Further scaling the interactions by 2.0/2.6 leads to $-\Delta E$'s of 34.9 ($Li^+\cdots OH_2$) and 20.4 ($NH_4^+\cdots OH_2$) kcal/mol. The former is in good agreement with the best calculation and experiment; the latter is somewhat too high, probably because this basis set also exaggerates the $N^+{-}H$ bond moment. If we assume that the bond moment is too high by the same factor as the water dipole, we calculate a $-\Delta E(NH_4^+\cdots OH_2)$ of 15.7 kcal/mol.

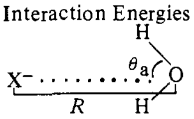
One can ask the question: what is the nature of these ion-water interactions? Both $Li^+{-}H_2O$ and $NH_4^+{-}H_2O$ surfaces show the minima expected from a consideration of simple

Table I. Comparison of Ion–Water Surfaces

Complex	E_T (ion),[a] au	ΔE(calcd), kcal/mol	ΔH(exptl), kcal/mol	R(calcd), Å	θ(calcd), deg
$Li^{+}\cdots OH_2$	−7.233 20[b]	47.90[b]	34.0[f]	1.80[b]	0[b]
	−7.236 3[c]	35.17[c]		1.84[c]	0[c]
				1.85[i]	
$NH_4^{+}\cdots OH_2$	−56.458 70[b]	27.34[b]	17.3[g]	2.64[b]	0[b]
	−56.534 8[d]	23.3[d]		2.71[d]	
$F^{-}\cdots H-O$	−99.247 82[b]	40.18[b]	23.3[h]	2.48[b]	7[b]
$\backslash H$	−99.456 82[e]	23.54[e]		2.51[d]	4.5[e]
$Cl^{-}\cdots H-O$	−459.026 41[b]	19.94[b]	13.1[h]	3.15	26[b]
$\backslash H$	−459.571 55[e]	11.86[e]		3.31[e]	14.6[e]

[a] The monomer energy of H_2O with this basis set is −75.907 39 au. In these studies, the monomers were fixed at the experimental geometry. (For NH_4^+, we employed the SCF optimized geometry found using Dunning's "double ζ basis set"[23] (r(N–H) = 1.02 Å). [b] This work. [c] Reference 24. [d] Reference 25. [e] Reference 21. [f] Reference 22. [g] Reference 26. [h] Reference 27. [i] Reference 1.

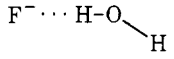
Table II. Point Charge Interaction Energies for Model



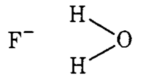
R, Å	Optimum θ_a, deg	Optimum $-\Delta E$, kcal/mol[a]
2.0	4	54.5
2.5	11	29.7
3.0	17	19.1
3.5	32	13.8
4.0	47	10.5
4.5	49	8.4
5.0	51	6.8

[a] These are the point charge energies. No repulsive terms are included.

electrostatics, that is, structures with $\theta_c = 0°$ that minimize the ion–dipole energy. (θ_c is the angle between the dipole of water and the O···Li^+ vector.) However, as pointed out by Popkie et al.,[21] there are two limiting structures to consider for anion–water interactions: $\theta_a = 0°$, a hydrogen-bonded structure



and $\theta_a = 52.25°$, C_{2v} dipolar



(see Table II for definition of θ_a). A simple ion point dipole model favors the $\theta = 52.25°$ structure. A more sophisticated model, in which the water is represented by a *finite* dipole, with partial charges on hydrogen and oxygen ($q_H = 0.465$ and $q_O = -0.93$) that reproduce the 431-G calculated dipole moment of 2.6 D, indicates that the minimum energy is a sensitive function of R, the distance between the ion and the water oxygen. These finite dipole calculations show that the interaction energies are sensitive to q_O ($q_H = -\frac{1}{2}q_O$), but the optimum θ_a is not; the θ_a values in Table II are constant (to ±2°) for $q_O = -0.5$ to -1.1. A value of q_O of −0.65 reproduces the experimental dipole moment (1.85 D) for H_2O. These results are quite intriguing in that they qualitatively reproduce the θ_a dependence for the ab initio calculated surfaces and reinforce one's view that much of the nature of these interactions can be understood from classical electrostatics.

The better basis set calculations for F^-···HOH and Cl^-···HOH predict smaller θ's than does the electrostatic model or the 431-G basis set; this is consistent with one's expectation that the extended basis set better represents charge redistribution effects, which would favor $\theta = 0$ for both complexes. If these finite dipole calculations apply to other anions they provide a nice model to predict the θ for structures of anion–solvent complexes whose approximate minimum energy separation is known. More specifically, one might expect interesting qualitative changes in the H_2O stretching modes (from uncoupled to "C_{2v}" like) as the size of the anion is increased.

B. Multiple Hydration of NH_4^+, F^-, and Li^+. Before we consider the hydration of the NH_4F complex, we need to examine the hydration of NH_4^+ and F^- separately and compare these with previous studies of $Li^+\cdots OH_2$ surfaces. For NH_4^+, we have done a very limited examination of $NH_4^+\cdots(OH_2)_2$ and $NH_4^+\cdots(OH_2)_3$ surfaces. For $NH_4^+\cdots(OH_2)_n$, we kept the water(s) at the optimized N···O distance (2.68 Å) and examined the one-, two-, and three-body energies for waters in the first coordination sphere of the ammonium ion. For the $NH_4^+\cdots 2H_2O$, the external hydrogens were oriented as in the $Li^+\cdots$water surfaces[1] and we only considered waters approaching directly along an N–H axis (maximum tetrahedral first coordination sphere). We also examined the interaction energy for $NH_4^+\cdots OH_2\cdots OH_2$. From these studies, we conclude: (1) three-body ($NH^+\cdots(H_2O)_2$) energies are important, as we earlier found for Li^+ hydrates; (2) the binding energy of $NH_4^+\cdots(H_2O)_4$ including two- and three-body energies, with the waters tetrahedrally disposed, is −83 kcal/mol; (3) the energy gain for a second coordination sphere water to act as a proton acceptor to a water in the first coordination sphere is −16 kcal/mol.

For $F^-\cdots(H_2O)_n$ (n = 1, 2, 3) we oriented the waters with the O–H bond pointing at the F^- and varied both $R(F^-\cdots O)$ and θ (the angle approach of different water molecules), considering octahedral and tetrahedral coordination. We also did a limited search varying the orientation of the external hydrogen on the water and found that those orientations that have "partial" H bonding between the waters are more stable. Having found the minimum energy R for tetrahedral and octahedral coordination by evaluating $F^-\cdots(HOH)_n$ surfaces with n = *1 to 3*, we calculated the energy of $F^-\cdots(H_2O)_4$ tetrahedral, $F^-\cdots(H_2O)_4(H_2O)_2$ with the two second coordination spheres acting as proton donors to two of the inner waters using water dimer optimum geometry,[14] and $F^-\cdots(H_2O)_6$ octahedral. The $F^-\cdots 6H_2O$ calculations include 87 atomic orbitals and take 7 min on the CDC 7600. From these studies we conclude that (1) octahedral coordination appears slightly favored

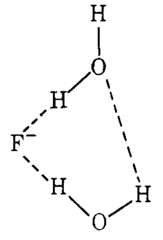


Table III. Energies of Hydration of $Li^+(H_2O)_6$ $-\Delta E = E_T$(complex) $- E_T$ (isolated species)

Complex[a]	Using two- and three-body energies: This study	Using two- and three-body energies: Ref 1	Complete calcn, this study
$Li^+\cdot(H_2O)_4\cdot(H_2O)_2$	168.2	132	171.4
$Li^+(H_2O)_5\cdot H_2O$		125	162.1
$Li^+(H_2O)_6$	146.7	119	157.4

[a] Reference 22 found $\Delta H(Li^+ + 6H_2O \rightarrow Li^+(H_2O)_6) = -123$ kcal/mol.

Table IV. Total Energies of Neutral ($NH_3\cdot HF$) and Ionic (NH_4F) Structures

Molecule	Structure	E_T, au
NH_3HF	H-bonded $R = 2.65$	−156.016 72
$NH_4^+F^-$	Ionic $R = 2.65$	−155.952 65
$NH_3HF\cdot H_2O$	H_2O on N	−231.934 70
$NH_3HF\cdot H_2O$	H_2O on F	−231.938 48
$NH_4^+F^-\cdot H_2O$	H_2O on N	−231.880 78
$NH_4^+F^-\cdot H_2O$	H_2O on F	−231.898 51
$NH_3HF\cdot 2H_2O$	Both H_2O on N	−307.849 86
$NH_4^+F^-\cdot 2H_2O$	Both H_2O on N	−307.802 14
$NH_3HF\cdot 2H_2O$	Both H_2O on F	−307.855 19
$NH_4^+F^-\cdot 2H_2O$	Both H_2O on F	−307.834 45
$NH_3HF\cdot 2H_2O$	One H_2O on N, one on F	−307.858 83
$NH_4^+F^-\cdot 2H_2O$	One H_2O on N, one on F	−307.829 36

Table V. Relative Energies of Hydrated NH_3HF (Neutral) and $NH_4^+F^-$ (Ionic), $\Delta E = E_{ionic} - E_{neutral}$

Hydration No.: H_2O on N	Hydration No.: H_2O on F	ΔE = relative stability of ionic structure, kcal/mol: Including nonadditivity[a]	ΔE = relative stability of ionic structure, kcal/mol: Excluding nonadditivity[a]
0	0	40.17	40.17
1	0	33.81	33.81
0	1	25.06	25.06
2	0	29.92	27.45
0	2	13.00	9.95
1	1	18.48	18.70
3	0	28.50	21.09
2	1	14.37	12.34
1	2	6.20	3.59
0	3	3.99	−5.16
3	1	12.73	5.98
2	2	1.87	−2.77
1	3	−3.03	−11.52
3	2	0.01	−9.13
2	3	−7.58	−17.88
3	3	−9.66	−24.24

[a] Nonadditivity means inclusion of three-body ($NH_4F\cdot 2H_2O$) energies in determining the relative energy.

over tetrahedral +2 waters in the second coordination sphere, but the difference is too small to be definitive (~4 kcal/mol); (2) the calculated binding energy for F^- with four waters tetrahedral is −115 kcal/mol, compared to −106 kcal/mol calculated by including only $F^-\cdots H_2O$ and $F^-\cdots 2\ H_2O$ surfaces, and (3) water in the second coodination sphere acting as a proton donor to water in the first coordination is bound to the complex by −14 kcal/mol.

In order to assess the reliability of our ion-many water surfaces and the correctness of our inclusion of only two- and three-body energies we carried out an extensive study of Li^+ hydration with the 431-G basis set. For Li^+, we have carried out examinations of the potential surfaces for $n = 1 \rightarrow 6$ H_2O's surrounding the ion. Using $Li^+(H_2O)$ and $Li^+(H_2O)_2$ surfaces, we have found that the basis set employed here predicts, as our earlier study with a more extended basis,[1] a preferred first coordination number of 4 for Li^+. We carried out these studies as in ref 1, except in this calculation we included $Li^+(H_2O)_3$ surfaces in estimating the minimum energy R for tetrahedral and octahedral coordination. We then calculated the energy for $Li^+(H_2O)_4$, $Li^+(H_2O)_5$, and $Li^+(H_2O)_6$. The $Li^+\cdots 6H_2O$ calculations include 87 atomic orbitals and take 7 min on the CDC 7600. With this 431-G basis set, we were also able to actually calculate the energy for $Li^+(H_2O)_6$ with four, five, and six waters molecules in first coordination sphere, and we found that the structure with a first coordination sphere of four waters (two water molecules in the second coordination sphere) was lower in energy than the structure with a first coordination sphere of five waters by 8.7 kcal/mol and lower than the octahedrally hydrated Li^+ by 14.0 kcal/mol (Table III).

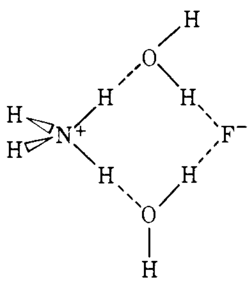
C. **Hydration of H-Bonded $H_3N\cdots H\text{-}F$.** We have previously examined the structure of this complex and have found, with rigid monomer geometries, that the minimum energy occurs for R(N–F) = 2.65 Å.[15] We fixed the position of all the atoms in this minimum energy geometry except the H-bonded proton and examined the energy as the H-bonded proton was transferred to the nitrogen. We also determined the energy for proton transfer with one and two water molecules hydrogen bonded to either the F lone pairs or the ammonia N–H's. To place waters on NH_3 and HF, we used the minimum energy geometries found for the $H\text{-}F\cdots HOH$ and $H_2O\cdots HNH_2$ complexes,[15] reoptimizing only R(F–O) and R(O–N). For the hydrated ionic structures ($NH_4^+\cdots F$) we used the best available $NH_4^+\cdots OH_2$ geometry (R(N–O) = 2.68 Å)[27] where the H-bonded proton is at an N–H distance of 1.02 Å and the best available $F^-\cdots HOH$ geometry (R(F–O) = 2.51 Å).[19] For the intermediate positions of proton transfer, we placed the water at linearly interpolated positions. For the $NH_4^+\cdots 2H_2O$ surfaces, we carried out similar calculations, considering the possibility of two waters on F^- or on NH_4^+ or one water on each. Then we calculated the energy for $NH_4F\cdot(H_2O)_n$ structures as a function of proton position for each structure both considering the nonadditivity terms (three-body energies) explicitly and leaving them out. In Tables IV and V we report the relative energies of neutral and ionic forms as a function of hydration. In Figure 1 we show the proton potential as a function of hydration; we plot only the energy of the most stable conformation for a given number of H_2O molecules. These results demonstrate the dramatic effect of solvation on the proton potential curve; in the absence of solvent, the neutral form is clearly much more stable; when one has four or more H_2O molecules, the ionic form is more stable. Noell and Morokuma[11] have carried out similar calculations on the solvent effect on the $H_3N\cdots HF$ potential, using partial charges (scaled to reproduce the ab initio calculated two-body energies) surrounding $H_3N\cdots HF$. The partial charges of three "waters" on NH_3 and three on HF do have a dramatic effect on $H_3N\cdots HF$ proton potential but they still find the neutral form to be more stable than the ionic.[11] In our calculations, at some intermediate hydration points there appears to be a "double well" potential. These calculations suggest interesting experiments using matrix isolation ir techniques. If NH_3 and HF are deposited in a matrix to which water (H_2O or D_2O) is slowly added one could detect the predicted neutral → ionic conversion by monitoring the loss of the H–F or the appearance of NH_4^+ vibration frequencies. The congruence between the structure derived from matrix isolation experiments[17a] and gas phase calculations for $NH_3\cdots HCl$[16] supports the "inertness" of the matrix itself in terms of influencing proton transfer. One also could examine the solvation of $NH_3\cdots HCl$. These are likely candidates to show dramatic changes in proton potential as a function of added H_2O. Mixed liquid solvent systems also offer an interesting area for studies of this sort; for example, what are the relative efficacies of protic and nonprotic solvents in enabling proton transfer. One complex of particular interest to us is $H_3N\cdots HCOOH$, since a study of its solvation may enable us to estimate the energetic cost of "burying" charges in nonaqueous environments such as occur in the interior of proteins. Such a calculation would reveal the energy penalty, if any, for internal ion pairs ("salt bridges").

There are a number of points to stress about the accuracy of these calculations. The hydration energies are clearly too great with this basis set and thus, with a better calculation, the number of water molecules required to make the ionic structures favored over the neutral may increase. However, more accurate SCF calculations such as those of Popkie et al.[21] are technically feasible for $NH_4F{\cdot}H_2O$ and $NH_4F{\cdot}2H_2O$. Correlation corrections (going beyond the Hartree-Fock approximation) are likely to decrease the difference between isolated $H_3N\cdots HF$ and $H_3NH^+F^-$ (since the reaction neutral → ionic involves bond breaking) and thus give an error of the opposite sign (but probably of much smaller magnitude) to the basis set error.

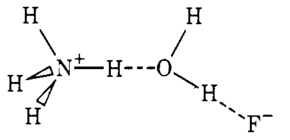
Our approximation of using at most surfaces containing only two water molecules also will cause us to underestimate the hydration energy since we have shown for $Be^{2+}(H_2O)_3$,[1] $Li^+(H_2O)_{3-6}$, and $F^-(H_2O)_{3-6}$ that the sign of the terms alternates (for a given type of coordination) (see also ref 14). For example, considering first coordination water molecules, the two-body Li^+-water energy is −40 kcal/mol, the three-body $Li^+\cdots 2H_2O$ term is +6 kcal/mol and the four-body $Li^+\cdots 3H_2O$ term is −1 kcal/mol. By neglecting higher nH_2O surfaces, we are underestimating the actual 431-G hydration energies. For example, $-\Delta E$ for $Li^+(H_2O)_6$ octahedral coordination is predicted to be 147 kcal/mol including only $Li^+(H_2O)$ and $Li^+(H_2O)_2$ surfaces but is 157 kcal/mol for the actual $Li^+(H_2O)_6$ calculations.

D. Other Structures of NH_4F Hydrates. What minimum energy structure (or structures) might be available to NH_4F in aqueous solution? To make an attempt to answer this question, we have examined "solvent separated" ion pair structures as well as the neutral and ionic H-bonded structures discussed previously. We have considered a "bridged" structure, a single water solvent separated structure, and a two water solvent separated structure.

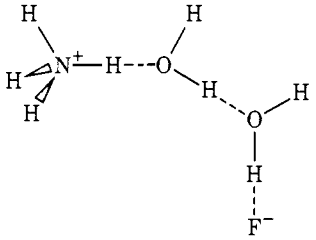
bridge



1 water separated structure



2 water separated structure



In the bridged structure, we used both R(N-O) and R(F-O) = 2.60 Å to make the central NOFO linkage a parallelogram; in other structures R(N-O) = 2.68 Å and R(F-O) = 2.51 Å. The calculated minimum energy structure for water dimer was used for O···O linkages. We then computed all one and two H_2O structures and compared the energies of these structures for $NH_4F(H_2O)_n$ using all $NH_4F{\cdot}H_2O$ and $NH_4F{\cdot}2H_2O$ interactions, with those discussed previously. We considered n = 1 to 8 because it requires at least eight waters to saturate the first coordination sphere of some of the structures.

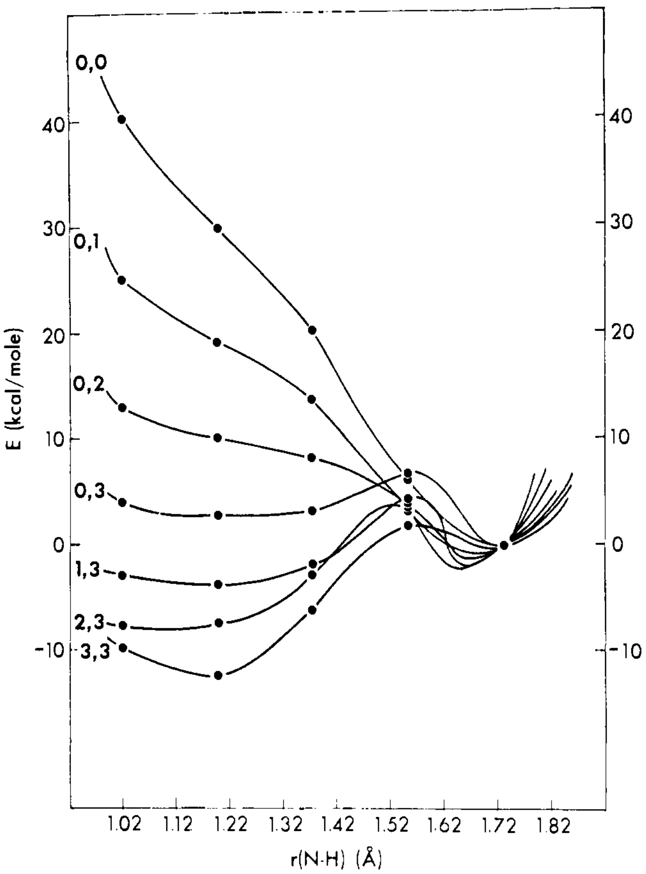


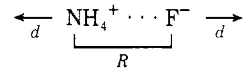
Figure 1. NH_4F proton potential as a function of added waters. X,Y refer to the number of waters H bonding to N and F, respectively. The N-F distance is 2.65 Å and the remaining protons on N are held fixed as the N···H···F bridge proton is moved.

Tables VI and VII contain the results (using the optimal coordination at each level of hydration). As one can see, the optimum hydration energy (Table VI) occurs for the two water solvent separation structure, although this is less stable (Table VII) than the ion pair model due to less $NH_4^+F^-$ attraction (the ions are further apart). Following a suggestion of a referee, we have made a crude estimate, based on Onsager's dipolar reaction field eq 1, of the interaction of the NH_4^+F structures with bulk solvent.[28]

$$-\Delta E = \frac{\epsilon - 1}{2\epsilon + 1}\frac{\mu^2}{a^3} \tag{1}$$

ΔE is the reaction field energy, ϵ is the dielectric constant (80 for H_2O), μ is the dipole moment of solute, and a is the cavity radius.

As the radius of our cavity, we used ½ the N···F distance ($R/2$) plus the distance (d) to the second coordination sphere



water, since we have included the first coordination sphere waters explicitly in our quantum mechanical surfaces. Table VIII contains the results of calculations on the reaction field stabilization of the various structures. For infinitely separated $NH_4^+\cdots F^-$ in water, we use an analogous reaction field stabilization[29]

$$-\Delta E = \frac{\epsilon - 1}{2\epsilon + 1}\frac{q^2}{a^2} \tag{2}$$

Table VI. Hydration Energy of Different Structures (kcal/mol)[a]

No. of water molecules	Neutral H bond	Ionic H bond	Bridge	Single	Double	∞ sep
1	−9.01	−24.12	−41.65	−73.09	−45.78	−39.22
2	−17.14	−44.31	−73.60	−96.05	−93.62	−69.94
3	−24.39	−60.57	−92.54	−113.20	−119.39	−97.03
4	−35.50	−78.70	−106.24	−130.19	−139.61	−119.91
5	−43.11	−90.86	−115.14	−143.75	−159.33	−142.13
6	−52.47	−102.30	−126.15	−154.77	−175.58	−160.80
7	−61.40	−112.57	−138.42	−164.74	−188.65	−175.26
8	−70.04	−122.55	−150.40	−174.78	−200.63	−188.98

[a] Lowest energy for a given number of water molecules is used. These hydration energies were determined using all two- and three-body terms.

Table VII. Relative Energy of Hydrated Structures (kcal/mol)[a]

No. of water molecules	Neutral H bond	Ionic H bond	Bridge	Single	Double	∞ sep
0	0.00	40.17	74.00	114.25	135.25	194.49
1	0.00	25.06	41.36	50.17	98.48	164.28
2	0.00	13.00	17.54	34.34	58.77	141.69
3	0.00	3.99	5.85	25.44	40.25	121.85
4	0.00	−3.03	3.26	19.56	31.14	110.08
5	0.00	−7.58	1.97	13.61	19.03	95.47
6	0.00	−9.66	0.32	11.95	12.14	86.16
7	0.00	−11.00	−3.02	10.91	8.00	80.63
8	0.00	−12.34	−6.36	9.51	4.66	75.55

[a] This table is determined by referencing the entries in Table VI to the hydration for the neutral H-bonded structure. Note that the various "solvent separated" ion pairs start out (with No. of water molecules = 0) at a very high energy because it costs a large amount of energy to dissociate $NH_4^+F^-$ in the absence of solvent.

Table VIII. Reaction Field Energies and Net Stabilization of Hydrated HN_4F Structures

Structure	R(N−F), Å	μ, D[a]	μ, D (point charge)[b]	−ΔE(reaction field),[c] kcal/mol	ΔE(rel energy),[d] kcal/mol
$NH_3\cdots HF$ neutral	2.65	5.30		3.2	0
$NH_4^+F^-$ ion pair	2.65	10.49	12.72	12.4	−21.5
$NH_4^+F^-$ bridge	3.00	13.08	14.40	17.0	−20.2
$NH_44^+F^-\cdot H_2O$ sep	4.24	19.90	20.35	25.8	−13.1
$NH_4^+F^-\cdot 2H_2O$ sep	5.57	26.62	26.75	31.2	−23.3
$NH_4^+\cdots F^-$ (sep)	∞	∞	∞	24.6	+54.2

[a] 431-G calculated dipole moment for $NH_4^+F^-$ structure. [b] Dipole moment calculated using point charge approximation. [c] Reaction field energy using eq 1 (eq 2 for last entry) using 431-G calculated dipole moment. [d] Relative energy after adding to the last row in Table VII, ΔE(reaction field).

where q is the charge of the solute (1 au) and the cavity radius is taken as 2.6 Å (the average distance to the edge of the first coordination sphere of NH_4^+ and F^-).

As one can see, all the ionic structures (with the exception of the ∞ separation) now become more stable than the neutral structure. Solvent separated structures (rows 2–4) are now competitive in energy with the H-bonded ion pair. The fact that the two water separated structure appears most stable is not of any great significance because of the many approximations involved in these calculations (both the ab initio and reaction field). However, the dramatic influence of solvent on the NH_4F structure is demonstrated. Using the $\Delta H_f°$ of NH_3 (aq), HF (aq), NH_4^+ (aq), and F^-, one finds that the ΔH for the reaction $NH_3\ (aq) + HF\ (aq) \rightarrow NH_4^+\ (aq) + F^-\ (aq)$ is −18.6 kcal/mol,[29] similar to our results for the energy difference between the ionic and neutral $NH_3\cdots HF$ structures (Table VIII). Even though the neutral $NH_3\cdots HF$ hydrate is not the same as the NH_3 (hydrate) + HF (hydrate), one expects comparable H-bond energies[30] and thus it is encouraging that our calculated ΔH's appear consistent with experimental solution reaction enthalpies.

Conclusion

We have examined the hydration of NH_4F using one and two water interaction energies. The results show the important role of water in stabilizing ionic structures, both of a "contact" ion pair and solvent separated variety. We would also like to put these studies in perspective in view of interesting related work by Newton and Ehrenson[32] on $H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$, Delpuech et al.[25] on $NH_4^+(H_2O)_n(NH_3)_m$ where $n = 2, m = 0$ or $n = 1, m = 1$, and Demoulin and Allen[33] on imidazole $H^+(H_2O)_n$. These authors all found that proton *transfer* would occur more easily in H-bonded species $A\text{-}H^+\cdots B\cdots C$ than corresponding $A\text{-}H^+\cdots B$ species, mainly because the positive charge can be stabilized by multiple H bonds when it resides on an interior molecule in an H-bonded chain. In this paper, we are looking at the role of solvent in *creating* an ion pair structure where there was none previously, which should be energetically less favorable to begin with than proton motion in a species whose charge remains +1 or −1 throughout. Thus, one needs more molecules of H_2O to allow proton transfer in our system than in those mentioned above.[34]

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(31) For example, using our previously calculated H-bond energies for NH_3 and HF with each other and with water, we estimate the energy for the reaction $H_3N\cdots HF$ (neutral, aq) $\rightarrow$ NH_3 (aq) + HF (aq) to be -6.0 kcal/mol. This leads one to expect a calculated difference between neutral and ionic ($NH_3\cdots HF$) of -24.6 kcal/mol, if it is to be quantitatively consistent with the experimental enthalpies. Our best "extrapolated" value as the number of H_2O approaches ∞ is -15 to -20 kcal/mol.
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Solvated Electron Reaction Rates in Alcohols and Water. Solvent Effect[1]

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Abstract: In alcohols electron capture by sulfur hexafluoride is less efficient than that by oxygen. This is the reverse of the relative efficiencies in the gas phase. Solvation affects the electron attachment efficiency by altering the energetics of the reaction. The ratio of electron capture rate constants for a given solute in methanol and ethanol, $k_{4,M}/k_{4,E}$, decreases with decreasing reactivity of the solute. The ratio varies from a maximum ≥ 2.0 for diffusion controlled reactions, with $k_{4,M} \geq 6 \times 10^{10}$ M^{-1} s^{-1}, to a minimum of 0.18 for $k_{4,M} \leq 10^7$ M^{-1} s^{-1}. The upper limit of the ratio is due to the higher diffusion coefficients in methanol. The decrease is due to the greater solvation energy of electrons in methanol, which makes electron transfer from the solvent trap to the less efficient solutes more endoergic in methanol than in ethanol. At 296 K the ratio of rate constants for neutral scavengers in the two alcohols is given by $(k_{4,M}/k_{4,E}) = \exp([1.6 - 0.38\Delta G^{\ddagger}{}_{4,M}]/0.59)$ when $\Delta G^{\ddagger}{}_{4,M} < 6.8$ kcal mol^{-1}, and by $(k_{4,M}/k_{4,E}) = 0.18$ when $\Delta G^{\ddagger}{}_{4,M} > 6.8$ kcal mol^{-1}, where $\Delta G^{\ddagger}{}_{4,M}$ is the free energy of activation of reaction of a given solute with solvated electrons in methanol. The free energies of activation in methanol and ethanol are related by the equations: $\Delta G^{\ddagger}{}_{4,E} = (0.62\Delta G^{\ddagger}{}_{4,M} + 1.6)$ when $\Delta G^{\ddagger}{}_{4,M} < 6.8$ kcal/mol^{-1}, and $\Delta G^{\ddagger}{}_{4,E} = (\Delta G^{\ddagger}{}_{4,M} - 1.0)$ when $\Delta G^{\ddagger}{}_{4,M} >$ 6.8 kcal/mol^{-1}.

Introduction

This article has two purposes, (a) to report values of rate constants for reactions of solvated electrons with dissolved gases, including common impurities and popular additives, and (b) to describe a solvent effect on electron reaction rates.

Nitrous oxide and sulfur hexafluoride are the most commonly used electron scavengers in alcohol radiolysis, yet the rate constants of their reaction with solvated electrons have not been measured.[2,3] Carbon dioxide is difficult to remove completely from liquids and is an efficient electron scavenger in water[4] and hydrocarbons,[5] but its rate constant has not been measured in alcohols. Oxygen is a common impurity whose rate constant for reaction with solvated electrons has been measured in water[4] and alcohols;[6] the rate constants have been remeasured for comparison. Acetylenes and conjugated olefins react with sodium-potassium alloy; electrons from the alloy react with acidic protons on acetylenes[7] to form hydrogen and a salt, while electrons simply add to conjugated olefins (hydrogen is not evolved). It was therefore interesting to measure and compare the rate constants of solvated electron reactions with these two types of compound.