Microsolvation of Anions by Molecules Forming CH $\cdots$ X $^-$ Hydrogen Bonds

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Abstract

Various anions were surrounded by n molecules of CF₃H, which was used as a prototype CH donor solvent, and the structures and energies studied by M06-2X calculations with a 6-31+G** basis set. Anions considered included the halides F $^-$, Cl $^-$, Br $^-$ and I $^-$, as well as those with multiple proton acceptor sites: CN $^-$, NO₃ $^-$, HCOO $^-$, CH₃COO $^-$, HSO₄ $^-$, H₂PO₄ $^-$, and anions with higher charges SO₄²⁻, HPO₄²⁻ and PO₄³⁻. Well structured cages were formed and the average H-bond energy decreases steadily as the number of surrounding solvent molecules rises, even when n exceeds 6 and the CF₃H molecules begin to interact with one another rather than with the central anion. Total binding energies are very nearly proportional to the magnitude of the negative charge on the anion. The free energy of complexation becomes more negative for larger n initially, but then reaches a minimum and begins to rise for larger values of n .

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keywords: M06-2X; halides; free energy

INTRODUCTION

Solvation of ions in various media plays a crucial role in a large number of chemical, biochemical and environmental phenomena. The microsolvation of ionic species occurs not only in the liquid but also in the gas phase in the form of clusters. A number of studies [1-3] show that various types of ionic pollutants, both cationic and anionic, are present in the atmosphere in the form of aerosols causing atmospheric pollution. The study of microsolvation of ions provides an important tool for understanding their structure, energetics, spectroscopic properties, and reaction mechanisms and kinetics in the solution phase as well as in the gas phase. For example, in an ion pair S_N2 reaction between sodium p-nitrophenoxide and halomethanes in acetone [4], the rate of reaction is found to be drastically affected by the microsolvation of anions by acetone molecules. As another example, the α -effect in an S_N2 reaction has been found [5] to be strongly affected by the microsolvation of anions by solvent molecules. Additionally, the properties of isolated ions can be substantially different from their solvated cluster structure. For example, the isolated $(SO_4)^{2-}$ ion is unstable in the gas phase as a dianion due to its very high Coulombic repulsion; the same is true [6] for PO_4^{3-} . However, these same ions become stable when microsolvated by a cluster of solvent molecules, or in the solid state [7,8].

Since water is the most common and the most abundant solvent in nature, most studies of microsolvation of anions have been centered on aqueous systems. Water interacts with the ionic species via its strong H-bonding capacity as well as charge-dipole interactions. On the other hand, a great deal of recent work has shown that the CH group can serve as a potent proton donor in H-bonds (HBs) in parallel fashion to OH and NH donors [9-26]. $CH\cdots X$ HBs are quite prevalent in nature, in biological [27-35] as well as chemical [36-44] contexts. The ability of CH to act in this capacity is related first to the hybridization of the C atom, in the order $sp > sp^2 > sp^3$. The placement of electron-withdrawing substituents on the C atom, e.g. F or Cl, helps to polarize the CH bond, thereby strengthening the incipient HB. As with more conventional HBs, a cationic CH donor is particularly powerful [45-49], with related $CH^+\cdots X$ HBs surpassing some of the strongest conventional HBs. Likewise, one would expect that a $CH\cdots X^-$ HB with an anion ought to be quite strong as well, for which there is some evidence [50-55].

Hence, one would anticipate that a CH-donating solvent could serve in a microsolvating role, as do OH and NH donors. However, there has been very limited work to date dealing with clusters in which $CH\cdots O$ HBs play a dominant role. Indeed the first direct evidence of aromatic $CH\cdots O$ HBs in gas phase clusters did not arise until 2005 [56] wherein 1,2,4,5-tetrafluorobenzene served as proton donor to a variety of bases. In terms of calculations, most work has been limited to only small clusters [57-62]. For example, homo-oligomers of CH_3CN up to tetramer were examined [63] so as to measure the degree of cooperativity, as were clusters of H_2CO up to the pentamer level [64]. In a similar vein, aldehyde clusters up to the octamer [65] all contained $CH\cdots O$ HBs. H_2CO was inserted into cyclic clusters of HF and HOH [66] with a particular interest in the frequency shift of the CH bonds. But there is little that deals with larger clusters in which a central species is surrounded by a number of CH proton donors, as a simulation of the first steps of solvation. And data is even more limited when it comes to the microsolvation of anions by such donors.

This work is intended to answer a number of fundamental questions on this topic. As an overarching issue, how effective are CH donors in forming clusters around an anion? Do these molecules form well defined solvation shells around an anion? How does one anion differ from another in terms of the structure and energetics of these clusters? Do dianions and trianions behave qualitatively differently than do

monoanions? For those anions that have more than one proton-accepting atom, do they engage in bifurcated $\text{CH}\cdots\text{X}$ HBs or is there a preference for single, linear bonds?

Quantum chemical calculations have been recruited in an effort to answer these questions. Such calculations permit the study of a given number of surrounding solvent molecules without complications of smaller and larger clusters complicating the analysis. For any given cluster, all minima on the surface can be identified, and ordered with respect to energy. Analysis of each structure provides unambiguous information about the nature of the forces that hold it together, those between solvent molecules as well as ion-solvent. The comparison of data for different numbers of solvent molecules n reveals whether there is a smooth progression as n increases, or a break in character at some particular cluster size.

F_3CH was chosen as the CH proton donor for a number of reasons. The three strongly electron-withdrawing F atoms make the CH group particularly polar and a correspondingly good donor. Indeed, this molecule has been used in numerous studies [67-74] for just this reason. Secondly, the presence of only a single CH proton on the molecule simplifies the analysis, allowing a focus on a particular $\text{CH}\cdots\text{O}$ HB, as compared to larger molecules with numerous protons. A number of different anions were taken as proton acceptors, due in part to their ability to form strong HBs. Secondly, as anions, they would be unlikely to act as proton donors to the F atoms of F_3CH which would complicate the analysis. The first group of anions selected for study were the halides: F^- , Cl^- , Br^- and I^- . Their simplicity offers a first step, and their varying size provides a gradation of charge density. CN^- is an interesting anion as both atoms are potential proton acceptors, as is the π -system that connects them. There are several proton-accepting atoms present in the NO_3^- and HCOO^- anions; extension to CH_3COO^- permits an examination of the effect of an alkyl group. HSO_4^- and H_2PO_4^- each present four possible proton-accepting O atoms. It is then possible to study how increasing the charge on the anion affects the results by including SO_4^{2-} , HPO_4^{2-} , and the triply charged PO_4^{3-} .

COMPUTATIONAL DETAILS

Calculations were carried out with Gaussian-09 [75], applying the M06-2X [76] variant of density functional theory, in conjunction with the 6-31+G** basis set. The LAND2Z pseudopotential [77] from the EMSL basis set library [78] was used for I. Geometries were fully optimized and assured to be minima via vibrational calculations that found all positive frequencies. Binding energies were computed as the difference between the energy of the complex and the sum of the energies of fully optimized monomers. Each binding energy was corrected for basis set superposition error using the counterpoise method [79,80], [evaluating the superposition error between each pair of molecules within the cluster, both solute-solvent and solvent-solvent pairs.](#)

RESULTS AND DISCUSSION

Halide Ions

The optimized geometries of the fluoride anion complexes are presented in Fig 1, and those of the Cl^- , Br^- , and I^- anions in Figs S1-S3. In some cases, notably for $n=4$, there was a second minimum encountered, some not much higher in energy. The total numbers of minima are summarized in Table S1 of the SI, along with the spans of energy. The solvating CF_3H molecules generally adopt the classic arrangements around these halides, viz. those that might be predicted by VSEPR. But this is not always the case, and there are some other geometries that can be quite competitive in energy in some cases. More specifically, a

linear arrangement is preferred for $n=2$, but a bent structure occurs for Br^- and I^- , which is only slightly higher in energy. For $n=3$, the planar and trigonal pyramids are both minima for these same two anions, with I^- showing a slight preference for the latter. The tetrahedral and square planar geometries are both minima for all four halides, with the former slightly favored. A trigonal bipyramid represents the global minimum for $n=5$, and octahedral arrangement for $n=6$.

There are certain perturbations from the standard structures that are noted. Most notably, the $n=2$ geometries are not necessarily strictly linear, with $\text{H}\cdots\text{X}\cdots\text{H}$ angles varying between 163° for F^- , 114° for Cl^- . Two structures with very similar energies are observed for Br^- and I^- , one with a $\theta(\text{H}\cdots\text{I}\cdots\text{H})$ angle of $105-109^\circ$ and the other with 180° . It may be noted as well that for $n<6$, the CH groups point directly toward the central anion, with $\theta(\text{CH}\cdots\text{X})$ angles in the neighborhood of 180° . The exception to this rule is the hexacoordinated F^- , where the $\theta(\text{CH}\cdots\text{F})$ angles for $\text{F}^-(\text{CF}_3\text{H})_6$ are around $130-150^\circ$. This disruption of the linear HBs is likely due to the small size of the F^- anion, which would pull the various protons too close to one another without any such distortion.

When n grows larger than 6, the structures become less regular, less symmetric. The heptameric arrangement around F^- , for example, shows $\text{R}(\text{H}\cdots\text{F}^-)$ over a range covering 1.985 to 2.192 Å, and 1.997 - 2.221 Å for $n=8$. Also, the H-bonds grow less linear. Several of these HBs vary by as much as 70° from linearity for the octamer. In summary, since the central halide cannot fully accommodate more than 6 HBs, these solvating molecules turn so that they engage in HBs with their neighboring solvent molecules. The level of misalignment with the central halide varies from one molecule to the next: the $\theta(\text{CH}\cdots\text{F}^-)$ angle varies from 168° down to 111° . And indeed, this inter-solvent H-bonding is evident in the NBO analysis as well, which reveals charge transfers from the F lone pairs of one molecule to the $\sigma^*(\text{CH})$ antibonding orbitals of another. The same sort of pattern is evident in Figs S1-S3 which illustrate the geometries of the various clusters for the other halide anions.

As the number of solvent molecules rises, they become further separated from the halide anion, as may be seen by the average $\text{R}(\text{X}\cdots\text{H})$ distances displayed in Table 1. This increasing distance, shown pictorially in Fig 2, is very nearly linearly related to n , and is most sensitive to the growing solvation shell size for the smallest F^- anion, where each additional molecule elongates the HB distance by 0.10 Å. It is interesting to note that the linearity of each curve continues beyond $n=6$, even after some of the solvent molecules shift their HBs from the central halide to one another.

In concert with the progressively longer HBs, the average HB energy declines regularly with n . This quantity was computed as the total complexation energy (Table S2) divided by the number of solvent molecules n . As indicated in Table 2 and Fig 3, this mean HB energy decline is nearly proportional to n , with the exception of fluoride where a slight asymptotic behavior is apparent. The absence of any clear break around $n=6$ is consistent with Fig 2, and suggests that the complexation energy does not suffer when the solvent molecules begin to bind to one another.

A more complete treatment of the thermodynamics of binding of F_3CH to the halides is presented in Table 3. These quantities were evaluated at 298 K and 1 atm. The changes in entropy are negative, and progressively so with larger n , which is consistent with the process of binding multiple species into a single entity. The favorable enthalpy of binding is manifested by the progressively larger negative values of ΔH as n increases, consistent with the electronic energies in Table 2. Reflecting the smaller average binding energies as n increases (Table 2), ΔH behaves in an asymptotic manner. After accounting for the negative entropy change, ΔG is much less negative than ΔH , and even positive for some of the larger clusters. As

illustrated in Fig 4, ΔG first becomes more negative as n increases, reaches a minimum, and then begins to climb. This shape can be attributed to two factors. First, ΔH does not decrease linearly with n , but rather flattens out, due to the progressively smaller individual HB energy as illustrated in Fig 3. ΔS , on the other hand, does not flatten with increasing n ; in fact the $\Delta S/n$ ratio becomes larger as n increases. Thus ΔS becomes more prominent for larger n , while ΔH plays a diminishing role, accounting for the curvature of the ΔG curve. ΔG reaches a maximal negative value for small clusters; $n=4$ for F^- and Cl^- , 3 for Br^- , and 2 for I^- . And consistent with the energetic data, ΔG also obeys the trend that F^- forms the strongest bonds: $F^- < Cl^- < Br^- < I^-$.

CN⁻, NO₃⁻, HCOO⁻ and CH₃COO⁻

The optimized geometries of the CN⁻ complexes with increasing number of CF₃H molecules are presented in Fig 5. For a single solvent molecule, a proton can be donated to either atom of the CN⁻ anion, with near equal energy. When $n=2$, the two CF₃H molecules can either be located at the two ends of CN⁻, or both donating a proton to the N atom, again with little energetic difference between the two. All three solvent molecules can donate to N for $n=3$, or only two of them, with the third interacting with the C; the latter is favored by 1.5 kcal/mol. The pattern is repeated for larger values of n , wherein most of the CF₃H molecules interact with the N, leaving only a single molecule H-bonded to C. As displayed in Table S3, as n climbs above 3, the total number of minima increases as well. It is only for $n=7$ that a second solvent molecule interacts with C. It is for $n \geq 6$ that the geometries suggest appreciable intersolvent H-bonding, which is supported by NBO analysis. As in the cases of the halide anions, the average H-bond energy declines smoothly as n increases, with no sharp dropoff at any particular number of solvent molecules, as reported in Table S4.

The same pattern of approximately linear drop of average interaction energy is noted as well for the NO₃⁻, HCOO⁻ and CH₃COO⁻ anions as well, as illustrated in Fig 6 and displayed numerically in Table S4. In fact, the quantitative values indicate that there is little distinction between CN⁻ and NO₃⁻ anions with regard to binding energies. The same is true for formate and acetate, which form somewhat stronger bonds, than do CN⁻ and NO₃⁻. When the total binding energies are expanded to free energies (Table S5), one obtains the pattern exhibited in Fig 7. Whereas CN⁻ and NO₃⁻ have very similar binding energies to F₃CH, the former corresponds to a more negative ΔG than does the latter for any value of n ; again the HCOO⁻ and CH₃COO⁻ anions display a stronger interaction than do their smaller counterparts. ΔG is most negative for $n=3$, as was also the case for Br⁻.

The geometries of the complexes for NO₃⁻, HCOO⁻ and CH₃COO⁻ are displayed in Figs S4-S6, respectively. The presence of 2 or 3 O atoms on each anion creates a tendency for the F₃CH proton to engage in bifurcated HBs, although deviation from this pattern is not terribly costly energetically. As n increases it is no longer possible for all solvent molecules to engage in such bifurcated HBs, and single acceptor HBs become more prominent. For larger values of n , the plane of the anion becomes more crowded, and the solvent molecules consequently deviate further and further from that plane.

HSO₄⁻, SO₄²⁻, H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻

The presence of four O atoms on the sulfate and phosphate series presents certain interesting possibilities, as does the differing charge on each of these anions. In the first place, these anions present a

larger set of secondary minima, as reported in Table S6. The patterns of average HB energy of the global minima (Table S7) in Fig 8 reveal first of all that this quantity is highly dependent upon the total charge. In fact, for any given value of n , the average binding energy is roughly proportional to the charge on the anion. Taking $n=3$ as an example, the average binding energies for H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} , are respectively 13.6, 27.1, and 44.1 kcal/mol. It is also intriguing to note that the nature of the anion is largely irrelevant, in the sense that the SO_4^{2-} and HPO_4^{2-} dianions have nearly identical energies, as do the HSO_4^- and H_2PO_4^- monoanions, true for any given value of n . A third point worthy of note is related to the slopes of the curves. The average binding energies for the anions in Fig 8 decline more gradually with n than is the case for the halides in Fig 3, or the monoanions in Fig 6. For example, this quantity declines from 16.2 kcal/mol for CN^- when $n=1$ to 10.3 kcal/mol for $n=7$, a drop of 5.9 kcal/mol or 36%. The same quantities for the HSO_4^- anion drop from 13.9 to 10.0 kcal/mol, declining by only 4.0 kcal/mol which translates to 28%. While the dianions experience a larger absolute decrease (by 7.8 kcal/mol in the case of SO_4^{2-}) this change is proportionately the same, 27%.

The free energies of binding in Fig 9 (and Tables S8 and S9) also present certain comparisons with the smaller anions. Like the binding energies, ΔG is also very sensitive to the total charge. For the monoanions, ΔG can be as large as -11 kcal/mol, comparable to the smaller monoanions. But for higher charges, this quantity can be quite large, even in excess of -180 kcal/mol for PO_4^{3-} . It is also interesting to note that the value of n for which ΔG exhibits a minimum is closely related to the total charge. This minimum occurs for $n=3$ for the monoanions, rises to 6-7 for the dianions, and has not yet reached a minimum for the PO_4^{3-} trianion, even for n as large as 10.

The geometries of the various clusters including these anions are displayed in Figs S7-S11. The overall pattern for the HSO_4^- , SO_4^{2-} series is consistent with the earlier anions in that the proton of each CF_3H molecule prefers a position roughly midway between two O atoms, in bidentate $\text{CH}\cdots\text{O}$ HBs. This situation becomes less tenable for larger values of n , at which point non-bifurcated HBs begin to proliferate. In contrast, the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ series displays a propensity for single, linear $\text{CH}\cdots\text{O}$ HBs, even when this leaves the proton-accepting ability of O atoms unsatisfied. As a final point, it might be noted that the very high charge of PO_4^{3-} induced a spontaneous proton transfer from one of the CF_3H molecules, for $n=1-4$. In order to avoid this transfer, geometry optimizations were carried out by fixing all C-H bond lengths to 1.600. (The latter value was chosen based on the optimized CH bond lengths in the $\text{F}_3\text{CH}\cdots\text{H}_2\text{PO}_4^-$ and $\text{F}_3\text{CH}\cdots\text{HPO}_4^{2-}$ series of complexes.)

Perturbations in Monomers

The formation of a $\text{AH}\cdots\text{D}$ HB is well known to induce characteristic changes within the participating monomers. Perhaps most notable of these is the traditional elongation of the A-H covalent bond, accompanied by a red shift of its stretching frequency. However, in a number of cases which have become well known in recent years, these patterns can be reversed in the case of a CH proton donor [81]. The changes undergone in the CH bond length within CF_3H are reported in Tables 4 and 5 as the average of all the n molecules within a given cluster. In the majority of cases, this bond is stretched, most notably for the fluoride anion. Particularly large stretches are also observed for the multiply charged anions in Table 5, again reflecting the strength of the HBs. There is also a clear pattern that the amount of stretching diminishes as the number of solvent molecules enlarges. This pattern mirrors that of the average binding energy, although it is more dramatic. In fact, as n increases further, beyond a first solvation shell, $\Delta r(\text{CH})$

reverses sign in certain cases, reflecting a small contraction. The principal exception to these patterns is associated with the monoanion, where CH bond contractions occur for all size clusters. This reversal may be associated with the predilection for bifurcated HBs for this anion.

It is usually anticipated that the stretch of the CH bond ought to be associated with a red shift of its stretching frequency. This expectation is indeed realized in these clusters, as may be seen by comparison of Tables 4 and 5 with the frequency shifts in Tables S10 and S11. The largest red shift, amounting to 1099 cm^{-1} , occurs for $\text{F}_3\text{CH}\cdots\text{F}^-$, which matches the largest bond elongation of 84 mÅ . Progressive weakening of the average HB via larger numbers of solvent molecules is accompanied by reduced red shift. Those CH bonds which contracted as a result of complexation are also generally characterized by a blue shift of the stretching frequency.

CONCLUSIONS

Very much like the case of H-bonding solvent molecules such as water, CF_3H which engages in non-classical $\text{CH}\cdots\text{X}$ HBs, forms a well-structured solvation cage around anions of various types. Small numbers n of solvent molecules form highly structured geometries, with the $\text{CH}\cdots\text{X}$ bonding molecules disposed in well-defined positions. The most stable structures are very much akin to standard ideas of VSEPR theory for the simple halides. For larger anions with multiple H-bond acceptor atoms, the global minima favor simple HBs in many cases, but in others there is a tendency to form bifurcated HBs wherein the bridging proton lies roughly midway between two O atoms. Such bifurcated geometries switch to single proton-acceptor HBs as the number of solvent molecules grows. This pattern is different for the phosphate series however, where linear $\text{CH}\cdots\text{O}$ HBs are slightly favored, even when such a structure leaves the H-bonding capacity of some O atoms unsatisfied. As n increases beyond 6, steric crowding prevents all of the surrounding CF_3H molecules from forming a $\text{CH}\cdots\text{X}$ bond with the central anion. As a consequence, some of the solvent molecules reorient so as to engage in $\text{CH}\cdots\text{F}$ HBs with one another. This process is a gradual one in the sense that these solvent molecules tend to retain at least a marginal engagement with the central anion as well.

The binding energy per solvent molecule undergoes a steady decline as n increases, accompanied by a parallel elongation of the average distance between the central anion and the surrounding solvent molecules. There is no sharp change that occurs for $n\sim 6$, when solvent molecules disengage from the central anion and form $\text{CH}\cdots\text{F}$ HBs with one another. In contrast to the asymptotic decline of ΔE , the entropy loss of formation of the complex is nearly a linear function of n , even showing a slight uptick for larger complexes. As a result, the free energy of formation attains its most negative value for a small value of n (2-4) for monoanions, becoming less favorable for larger complexes. The binding energies are roughly proportional to the magnitude of the negative charge on the anion. The value of n for which ΔG is most negative is larger for di and trianions than for monoanions. It should finally be stressed that the results described above relate direct to clusters in the gas phase. Extrapolation to the liquid would involve a much larger number of surrounding solvent molecules, as well as dynamic treatment of molecular motions.

The results presented here were computed with the 6-31+G** basis set. One might wonder if a larger set would significantly alter the trends. In order to examine this possibility, additional calculations were carried out with the much larger and more flexible aug-cc-pVTZ set, within the context of the originally optimized geometries. As may be seen from examination of Table 6, such an expansion yielded only very small changes in the binding energies of either a monoanion (F^-) or a dianion (SO_4^{2-}) with any number of

F₃CH molecules. Use of the larger set reduced binding energies by only 1-3%. and had no effect on any of the trends. It may thus be concluded that the results presented above are quite insensitive to basis set expansion.

ACKNOWLEDGMENTS

Computer, storage and other resources from the Division of Research Computing in the Office of Research and Graduate Studies at Utah State University are gratefully acknowledged.

SUPPORTING INFORMATION

Total number of minima for each combination, binding energies, thermodynamic properties, and CH vibrational frequency shifts are reported in the tables of the Supplementary Information. Figures depict optimized geometries of those complexes not shown in the article.

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Table 1. Average H-bond lengths $R(H\cdots X)$ (Å) of the halide complexes with increasing number n of F_3CH molecules.

n	F^-	Cl^-	Br^-	I^-
1	1.420	2.276	2.440	2.712
2	1.614	2.315	2.492	2.743
3	1.720	2.350	2.500	2.794
4	1.800	2.390	2.531	2.830
5	1.867	2.437	2.550	2.873
6	1.984	2.474	2.569	2.890
7	2.063	2.543	2.676	2.966
8	2.146	2.586	2.723	2.988

Table 2. Average binding energies (kcal/mol) per F_3CH molecule of halide complexes

n	F^-	Cl^-	Br^-	I^-
1	29.31	16.08	14.01	11.69
2	25.05	14.98	13.10	10.33
3	22.08	14.06	12.36	9.31
4	19.66	12.89	11.50	8.47
5	17.50	11.84	10.65	7.76
6	15.93	10.97	9.88	7.15
7	14.60	10.65	9.29	7.12
8	13.57	10.51	9.15	6.80

Table 3. Thermodynamic parameters for binding of halide anions by n F_3CH molecules at 25 °C and 1 atm. ΔH and ΔG are in units of kcal/mol, and ΔS in cal mol⁻¹ K⁻¹.

	F^-			Cl^-			Br^-			I^-		
n	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG
1	-24.09	-30.71	-23.53	-20.63	-15.89	-9.74	-20.58	-13.89	-7.75	-20.51	-11.53	-5.41
2	-46.88	-50.26	-36.28	-48.35	-28.51	-14.09	-43.97	-25.01	-11.90	-44.40	-19.57	-6.33
3	-82.33	-64.75	-40.20	-75.54	-39.29	-16.77	-74.18	-34.73	-12.61	-70.11	-25.50	-4.60
4	-107.42	-75.50	-43.47	-98.75	-47.98	-18.54	-101.37	-42.33	-12.11	-97.31	-30.40	-1.39
5	-147.37	-82.78	-38.84	-130.07	-54.38	-15.60	-127.23	-48.71	-10.78	-118.54	-33.98	1.36
6	-172.51	-89.20	-37.77	-156.32	-59.72	-13.11	-159.01	-52.72	-5.31	-138.44	-36.84	4.44
7	-237.31	-94.34	-23.59	-212.16	-66.88	-3.62	-219.20	-57.19	8.16	-207.52	-42.29	19.58
8	-286.66	-99.12	-13.65	-270.93	-75.08	5.70	-279.63	-63.75	19.62	-250.42	-45.29	29.37

Table 4. Average CH bond length change (mÅ) within CF₃H upon complexation of monoanions with *n* CF₃H molecules (mÅ)

<i>n</i>	F ⁻	Cl ⁻	Br ⁻	I ⁻	CN ⁻	NO ₃ ⁻	HCOO ⁻	CH ₃ COO ⁻
1	83.94	9.67	7.05	5.16	10.70	1.22	3.56	4.08
2	29.62	6.52	5.03	3.57	8.96	0.04	5.85	6.66
3	15.98	4.41	3.28	2.73	4.88	-0.46	3.17	5.41
4	9.47	3.27	1.94	2.31	2.64	-0.46	3.46	2.88
5	6.07	2.04	1.28	1.42	0.02	-1.17	0.57	0.65
6	-2.83	1.35	0.48	1.46	-0.90	-2.69	-0.71	-0.89
7	0.19	-1.56	-2.71	-0.96	-2.32	-1.40	-0.83	-1.76
8	0.50	-2.58	-2.81	-1.45				

Table 5. Average CH bond length change (mÅ) within CF₃H upon complexation of mono-, di- and trianions with *n* CF₃H molecules (mÅ)

<i>n</i>	HSO ₄ ⁻	SO ₄ ²⁻	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	PO ₄ ³⁻
1	-3.48	11.84	4.14	41.15	-
2	-2.89	7.60	2.42	22.85	-
3	-2.80	4.36	2.16	10.94	-
4	-2.11	2.51	-0.18	12.16	-
5	-2.84	1.39	-0.67	6.21	62.67
6	-2.69	0.86	-1.82	5.03	31.12
7	-2.68	1.09	-3.11	4.96	24.56
8		0.71		2.82	16.83
9		0.02		3.29	13.79
10		0.44		2.80	9.97

Table 6. Binding energies (kcal/mol) of complexes of anions with *n* CF₃H molecules, calculated by M06-2X method with two different basis sets.

<i>n</i>	F ⁻		SO ₄ ²⁻	
	6-31+G**	aug-cc-pVTZ	6-31+G**	aug-cc-pVTZ
1	29.31	28.29	28.79	28.37
2	50.09	48.89	54.86	54.01
3	66.25	64.48	77.72	76.19
4	78.65	76.39	98.47	96.56
5	87.51	85.41	116.96	114.54

Fig 1. Optimized geometries of complexes with n molecules of CF_3H surrounding the F^- anion. Distance in Å, and binding energies in kcal/mol.

Fig. 2. Average H-bond length vs number n of surrounding F₃CH molecules for complexes with halide anions.

Fig. 3. Average H-bond energy vs number n of surrounding F₃CH molecules for complexes with halide anions.

Fig 4. Free energy of complexation for binding of halides as function of number of F_3CH molecules.

Fig 5. Optimized geometries of complexes with n molecules of CF_3H surrounding the CN^- anion. Distance in Å, angles in degs, and binding energies in kcal/mol.

Fig. 6. Average H-bond energy vs number n of surrounding F_3CH molecules for complexes with CN^- , NO_3^- , $HCOO^-$ and CH_3COO^- .

Fig 7. Free energy of complexation for binding of CN^- , NO_3^- , HCOO^- and CH_3COO^- with n molecules of F_3CH .

Fig. 8. Average H-bond energy vs number n of surrounding F_3CH molecules for complexes with HSO_4^- , SO_4^{2-} , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} .

Fig 9. Free energy of complexation for binding of HSO_4^- , SO_4^{2-} , $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} with n molecules of F_3CH .

SUPPLEMENTARY INFORMATION
 Microsolvation of Anions by Molecules Forming CH $\cdots$ X $^-$ Hydrogen Bonds
 Binod Nepal and Steve Scheiner

Table S1. Total number of minima identified for the complexes of anions with n F₃CH molecules. The number in parentheses indicates the energy difference between the global minimum and the least stable minimum in kcal/mol.

n	F $^-$	Cl $^-$	Br $^-$	I $^-$
1	1	1	1	1
2	1	1	2 (0.04)	2(0.36)
3	1	1	2(1.4)	2(0.24)
4	2 (1.5)	2 (0.8)	2(0.50)	2(0.33)
5	1	1	2(0.63)	1
6	1	1	1	1
7	1	1	1	1
8	1	1	1	1

Table S2. Counterpoise-corrected binding energies (kcal/mol) of halide complexes with n F₃CH molecules.

n	F $^-$	Cl $^-$	Br $^-$	I $^-$
1	29.31	16.08	14.01	11.69
2	50.09	29.96	26.20	20.65
3	66.25	42.19	37.07	27.93
4	78.65	51.54	45.99	33.89
5	87.51	59.18	53.27	38.78
6	95.55	65.82	59.26	42.92
7	102.23	74.56	65.01	49.84
8	108.59	84.11	73.16	54.38

Table S3. Total number of minima identified for the complexes of anions with n F₃CH molecules. The number in parentheses indicates the energy difference between the global minimum and the least stable minimum in kcal/mol.

n	CN $^-$	NO ₃ $^-$	HCOO $^-$	CH ₃ COO $^-$
1	2(0.77)	1	2(1.11)	2(1.40)
2	2(1.21)	1	3(1.54)	5(2.33)
3	2(1.50)	3(2.71)	3(1.87)	4(1.29)
4	3 (1.96)	4(2.09)	6(2.41)	11(1.04)
5	6(1.26)	9(1.27)	8(1.91)	7(1.73)
6	10(3.08)	10(1.74)	8(3.93)	5(2.64)
7	8(2.50)	4(1.29)	13(1.47)	2(1.07)

Table S4. Average binding energies (kcal/mol) per F_3CH molecule of CN^- , NO_3^- , $HCOO^-$ and CH_3COO^- complexes with n F_3CH molecules

n	CN^-	NO_3^-	$HCOO^-$	CH_3COO^-
1	16.17	15.46	17.99	18.43
2	14.88	14.47	16.06	16.49
3	13.53	13.53	14.85	15.25
4	12.43	12.30	13.79	14.07
5	11.49	11.30	12.80	13.14
6	10.94	10.58	11.99	12.24
7	10.32	10.05	11.30	11.69

Table S5. Thermodynamic parameters for binding of CN^- , NO_3^- , $HCOO^-$ and CH_3COO^- anions by n F_3CH molecules at 25 °C and 1 atm. ΔH and ΔG are in units of kcal/mol, and ΔS in cal mol⁻¹ K⁻¹.

	CN^-			NO_3^-			$HCOO^-$			CH_3COO^-		
n	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG
1	-24.79	-15.49	-8.10	-29.06	-14.27	-5.61	-25.23	-16.80	-9.28	-20.84	-16.59	-10.38
2	-53.14	-27.99	-12.15	-56.79	-26.58	-9.65	-55.37	-29.88	-13.37	-53.29	-30.10	-14.21
3	-81.06	-37.58	-13.41	-84.24	-36.97	-11.85	-89.12	-40.80	-14.23	-84.07	-41.52	-16.45
4	-110.87	-45.31	-12.25	-126.49	-44.16	-6.45	-124.05	-49.99	-13.00	-120.72	-50.62	-14.63
5	-152.30	-51.59	-6.18	-167.88	-50.14	-0.09	-164.13	-57.23	-8.29	-164.73	-58.55	-9.44
6	-198.43	-58.38	0.78	-199.08	-55.74	3.62	-196.07	-63.81	-5.35	-201.35	-64.82	-4.79
7	-230.29	-63.76	4.90	-241.96	-61.14	11.00	-232.86	-69.79	-0.36	-246.62	-71.78	1.75

Table S6. Total number of minima identified for the complexes of anions with n F_3CH molecules. The number in parentheses indicates the energy difference between the global minimum and the least stable minimum in kcal/mol.

n	HSO_4^-	SO_4^{2-}	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
1	3(0.60)	1	3(1.31)	4(0.32)	1
2	9(1.94)	2(0.42)	10(3.15)	8(1.23)	4(15.5)
3	8(2.90)	3(0.49)	11(3.26)	7(0.86)	3(12.95)
4	11(4.90)	4(4.49)	13(2.39)	9(1.00)	4(12.14)
5	8(1.83)	5(3.96)	15(5.45)	6(0.69)	1
6	8(2.49)	5(3.29)	18(2.52)	9(0.61)	7(5.74)
7	10(4.28)	5(2.97)	8(3.20)	8(1.69)	5(7.93)
8		8(1.90)		7(3.21)	8(2.67)
9		5(0.06)		7(1.63)	4(1.02)
10		5(2.19)		4(4.53)	3(3.47)

Table S7. Average binding energies (kcal/mol) of HSO_4^- , SO_4^{2-} , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} complexes with n F_3CH molecules.

n	HSO_4^-	SO_4^{2-}	H_2PO_4^-	HPO_4^{2-}	PO_4^{3-}
1	13.92	28.79	15.37	30.19	46.65
2	13.13	27.43	14.43	28.72	50.68
3	12.31	25.91	13.62	27.14	44.10
4	11.51	24.62	12.85	25.72	41.16
5	10.83	23.39	12.30	24.46	38.84
6	10.37	22.27	11.57	23.21	37.80
7	9.96	21.00	11.16	21.89	35.88
8		19.88		20.79	33.19
9		18.92		19.60	31.41
10		18.08		18.55	29.86

Table S8. Thermodynamic parameters for binding of HSO_4^- and SO_4^{2-} by n F_3CH molecules at 25 °C and 1 atm. ΔH and ΔG are in units of kcal/mol, and ΔS in $\text{cal mol}^{-1} \text{K}^{-1}$.

n	HSO_4^-			SO_4^{2-}		
	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG
1	-33.67	-13.14	-3.10	-30.14	-28.08	-19.09
2	-61.55	-23.68	-5.33	-61.53	-53.24	-34.89
3	-88.89	-33.05	-6.55	-94.20	-74.89	-46.80
4	-128.71	-40.82	-2.45	-125.03	-94.33	-57.05
5	-164.51	-47.76	1.29	-154.82	-111.47	-65.31
6	-204.05	-54.31	6.53	-189.94	-126.91	-70.28
7	-240.85	-60.47	11.34	-222.08	-139.23	-73.02
8				-275.78	-149.53	-67.31
9				-310.44	-158.83	-66.27
10				-356.91	-168.48	-62.07

Table S9. Thermodynamic parameters for binding of H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} by n F_3CH molecules at 25 °C and 1 atm. ΔH and ΔG are in units of kcal/mol, and ΔS in cal mol⁻¹ K⁻¹.

	H_2PO_4^-			HPO_4^{2-}			PO_4^{3-}		
n	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG
1	-30.11	-14.29	-5.31	-30.22	-30.10	-21.09	-41.62	-48.95	-36.54
2	-63.69	-26.46	-7.47	-63.01	-56.53	-37.74	-77.66	-107.38	-84.23
3	-88.55	-37.45	-11.05	-95.59	-79.07	-50.57	-107.11	-138.26	-106.33
4	-127.91	-46.61	-8.47	-124.52	-99.31	-62.18	-153.79	-169.01	-123.16
5	-162.85	-55.32	-6.77	-159.41	-117.38	-69.85	-162.16	-195.53	-147.18
6	-200.73	-61.97	-2.12	-185.02	-133.06	-77.90	-192.23	-224.98	-167.67
7	-251.97	-69.03	6.09	-232.66	-146.03	-76.66	-226.38	-247.83	-180.33
8				-271.46	-156.99	-76.05	-271.51	-259.10	-178.15
9				-311.71	-166.04	-73.10	-309.23	-275.67	-183.47
10				-340.10	-174.20	-72.80	-358.91	-290.11	-183.10

Table S10. Average CH bond stretching frequency change (cm^{-1}) within CF_3H upon complexation of monoanions with n CF_3H molecules

n	F^-	Cl^-	Br^-	I^-	CN^-	NO_3^-	HCOO^-	CH_3COO^-
1	-1099	-162	-94	-62	-192	26	-27	-35
2	-500	-138	-110	-32	-163	29	-122	-112
3	-259	-88	-53	-53	-92	38	-35	-84
4	-130	-43	-39	-49	-39	26	-37	-48
5	-69	-22	-17	-18	9	32	13	-2
6	57	-30	-4	-6	24	58	31	43
7	10	44	52	36	55	44	36	44
8	24	58	69	37				

Table S11. Average CH bond stretching frequency change (cm^{-1}) within CF_3H upon complexation of mono-, di- and trianions with n CF_3H molecules.

n	HSO_4^-	SO_4^{2-}	H_2PO_4^-	HPO_4^{2-}	PO_4^{3-}
1	107	-170	-42	-629	-
2	53	-121	2	-411	-
3	82	-49	-34	-192	-
4	58	-1	1	-220	-
5	64	12	32	-103	-860
6	62	4	46	-70	-500
7	68	-9	63	-82	-413
8		6		-27	-289
9		32		-34	-240
10		16		-22	-165

Fig S1. Optimized geometries of complexes with n molecules of CF_3H surrounding the Cl^- anion. Distance in Å, and binding energies in kcal/mol.

n=1 **14.01**

n=2 **26.24**

n=2 **26.20**

n=3 **37.07**

n=3 **36.46**

n=4 **45.99**

n=4 **45.49**

n=5 **53.27**

n=5 **52.64**

Fig S2. Optimized geometries of complexes with n molecules of CF_3H surrounding the Br^- anion. Distance in Å, and binding energies in kcal/mol.

Fig S3. Optimized geometries of complexes with n molecules of CF_3H surrounding the I^- anion. Distance in Å, and binding energies in kcal/mol.

n=1 **15.46**

n=2 **28.94**

n=3 **40.58**

n=3 **38.47**

n=3 **37.87**

n=4 **49.20**

n=4 **48.76**

n=4 **47.99**

Fig S4. Optimized geometries of complexes with n molecules of CF_3H surrounding the NO_3^- anion. Distance in Å, and binding energies in kcal/mol.

Fig S5. Optimized geometries of complexes with n molecules of CF_3H surrounding the HCOO^- anion. Distance in Å, and binding energies in kcal/mol.

Fig S6. Optimized geometries of complexes with n molecules of CF_3H surrounding the CH_3COO^- anion. Distance in Å, and binding energies in kcal/mol.

n=1 13.92

n=2 26.26

n=3 36.94

n=4 46.03

n=5 54.17

n=6 62.21

Fig S7. Optimized geometries of complexes with n molecules of CF_3H surrounding the HSO_4^- anion. Distance in Å, and binding energies in kcal/mol.

n=1 **28.79**

n=2 **54.86**

n=3 **77.72**

n=4 **98.47**

n=5 **116.96**

n=6 **133.61**

Fig S8. Optimized geometries of complexes with n molecules of CF_3H surrounding the SO_4^{2-} anion. Distance in Å, and binding energies in kcal/mol.

Fig S9. Optimized geometries of complexes with n molecules of CF_3H surrounding the H_2PO_4^- anion. Distance in Å, and binding energies in kcal/mol.

Fig S10. Optimized geometries of complexes with n molecules of CF_3H surrounding the HPO_4^{2-} anion. Distance in Å, and binding energies in kcal/mol.

n=1 **46.65**

n=2 **101.35**

n=3 **132.30**

n=4 **164.63**

n=5 **194.19**

n=6 **226.81**

Fig S11. Optimized geometries of complexes with n molecules of CF_3H surrounding the PO_4^{3-} anion. Distance in Å, and binding energies in kcal/mol.