Conclusion

From the data presented in this work we conclude that quasiergodicity is reached relatively quickly and that the used equilibration times are adequate. For bulk water and the solvated calcium ion, static properties seem to be plausibly represented by the present potential, as are also qualitatively dynamic properties. The failure to quantitatively reproduce dynamic, experimental data is mainly due to the absence of dynamic data in constructing the intermolecular potential. A water model that allows for intramolecular motion while correctly reproducing dynamic properties is desirable but lacking. Also for the larger EDTA molecule, structural properties are qualitatively reproduced but are more sensitive to the imperfections of the potential. The binding of the calcium ion to EDTA is adequately treated in most respects. The $CaEDTA^{2-}$ overall mobility is too large, but this may be corrected for by use of the known properties of the water model and experimental data. While shortcomings of the intramolecular EDTA potential render the simulation dynamics locally incorrect, the mechanism of this seems well understood and can be taken into account in the interpretation of simulations. We think the present simulations contribute substantially to the understanding of calcium binding, which; in view of its biological importance, certainly merits further investigation.

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Registry No. Ca, 7440-70-2; H_2O, 7732-18-5; EDTA, 60-00-4.

Calculated Structures and Fluoride Affinities for Fluorides

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Abstract: It is shown that SCF–MO calculations provide good estimates of the energies of the processes $MF_n \rightarrow M^{n+} + nF^-$ where M^{n+} is an ion of a first- or second-row element in a closed-shell or s^2 configuration. The fluoride ion affinities are then calculated for a number of molecules and ions. Where comparison with experiment is possible, the agreement is generally good when allowance is made for experimental uncertainties. In favorable cases, accurate heats of formation may be calculated from fluoride affinities.

Fluoride ion affinities of molecules and ions are of considerable theoretical and experimental interest. Experimental values come mainly from ion cyclotron resonance (ICR) experiments[1–3] or from Born–Haber (BH) thermodynamic cycles.[4,5] Most of the derived results are indirect, and it is often quite difficult to assess uncertainties reliably. It is important therefore to have an independent set of fluoride affinities to compare with experimental values and to provide estimates of values as yet not determined.

In this work it is shown that ab initio SCF–MO calculations can provide reliable fluoride affinities, at least in certain instances. The important point about such calculations is that they should be made only for processes in which there is no change in multiplicity and ideally for singlet state species.[6] Previous calculations of the fluoride affinity of HF[7,8] and of H_2O[9] have shown that in these cases at least the change of correlation energy is only a small fraction of the energy change and less than experimental error, which is typically >5 kJ mol^{-1}.

Methods

Equilibrium geometries and SCF energies have been calculated for a number of first- and second-row fluoride molecules and ions in singlet states. The 6-31G* basis set[10] was chosen as a reasonable compromise between the desire, on the one hand, to have a sufficiently flexible basis set to predict geometries reliably and to avoid basis set superposition errors and, on the other hand, to allow reasonably heavy molecules to be studied without untoward cost. It is well-known[11] that for negative ions (F^-, etc.) additional diffuse valence orbitals are necessary, so the F basis was supplemented

Table I. Energy (kJ mol^{-1}) for $MF_n \rightarrow M^{n+} + nF^-$

MF_n	expt[a]	theor	ratio[b]
HF	1573	1591	0.989
LiF	772	764	1.011
BeF_2	3285	3273	1.004
BF	1241	1196	1.038
BF_3	7859	7800	1.008
CF_2[c]	3848	3762	1.023
CF_4	14949	14775	1.012
NF_3	8700	8510	1.022
NaF	650	635	1.024
MgF_2	2564	2533	1.012
AlF	913	906	1.008
AlF_3	5931	5869	1.011
SiF_2	2943	2866	1.027
SiF_4	11036	10863	1.016
PF_3	6369	6191	1.029
PF_5	17789	17421	1.021
SF_4	11272	10917	1.033
SF_6	26701	26161	1.021

[a] Data from ref 13 except electron affinity of F from ref 14 and zero point energies estimated from frequencies given in ref 15. [b] Expt/theor. [c] Heat of formation from ref 15.

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Table II. Calculated Geometries and Energies[a]

species	symmetry	energy	dimensions	E_F
F^-	K_h	−99.4178		
HF	$C_{\infty v}$	−100.0237	0.902 (0.917)	177
HF_2^-	$D_{\infty h}$	−199.5098	1.125	
Li^+	K_h	−7.2355		774
LiF	$C_{\infty v}$	−106.9443	1.589 (1.564)	309
LiF_2^-	$D_{\infty h}$	−206.4786	1.695	
Be^{2+}	K_h	−13.6098		2009
BeF^+	$C_{\infty v}$	−113.7903	1.321	1276
BeF_2	$D_{\infty h}$	−213.6921	1.378	391
BeF_3^-	D_{3h}	−313.2586	1.474	−256
BeF_4^{2-}	T_d	−412.5785	1.597	
Be	K_h	−14.5669		276
BeF^-	$C_{\infty v}$	−114.0894	1.454	
B^{3+}	K_h	−21.9839		3930
BF^{2+}	$C_{\infty v}$	−122.8868	1.176	2671
BF_2^+	$D_{\infty h}$	−223.3138	1.218	1262
BF_3	D_{3h}	−323.2083	1.303 (1.313)	358
BF_4^-	T_d	−422.7612	1.397	
B^+	K_h	−24.2341		1241
BF	$C_{\infty v}$	−124.1074	1.266 (1.265)	187
BF_2^-	C_{2v}	−223.5936	1.422, 100.6	
C^{4+}	K_h	−32.3577		6913
CF^{3+}	$C_{\infty v}$	−134.3773	1.112	4559
CF_2^{2+}	$D_{\infty h}$	−235.5110	1.134	2344
CF_3^+	D_{3h}	−335.8109	1.218	1136
CF_4	T_d	−435.6565	1.304 (1.320)	
C^{2+}	K_h	−36.3992		2767
CF^+	$C_{\infty v}$	−136.8472	1.146	1081
CF_2	C_{2v}	−236.6677	1.288, 104.2 (1.300, 104.9)	169
CF_3^-	C_{3v}	−336.1484	1.420, 99.1	
N^{3+}	K_h	−51.0574		5247
NF^{2+}	$C_{\infty v}$	−152.4309	1.068	2367
NF_2^+	C_{2v}	−252.7310	1.212, 108.4	1082
NF_3	C_{3v}	−352.5523	1.330, 102.7 (1.365, 102.4)	
Na^+	K_h	−161.6595		650
NaF	$C_{\infty v}$	−261.3192	1.933 (1.926)	273
NaF_2^-	$D_{\infty h}$	−360.8393	2.036	
Mg^{2+}	K_h	−198.8119		1526
MgF^+	$C_{\infty v}$	−298.8041	1.693	1037
MgF_2	$D_{\infty h}$	−398.6124	1.742	404
MgF_3^-	D_{3h}	−498.1821	1.809	−128
MgF_4^{2-}	T_d	−597.5521	1.905	
Mg	K_h	−199.3243		956
MgF^-	$C_{\infty v}$	−299.1022	1.838	
Al^{3+}	K_h	−239.9789		2708
AlF^{2+}	$C_{\infty v}$	−340.4171	1.564	2029
AlF_2^+	$D_{\infty h}$	−440.5995	1.585	1196
AlF_3	D_{3h}	−540.4677	1.630 (1.63)	510
AlF_4^-	T_d	−640.0778	1.690	−243
AlF_5^{2-}	D_{3h}	−739.4043	1.814,[b] 1.768	−680
AlF_6^{3-}	O_h	−838.5658	1.883	
Al^+	K_h	−241.6528		913
AlF	$C_{\infty v}$	−341.4156	1.670	306
AlF_2^{2-}	C_{2v}	−440.9491	1.735, 99.3	
Si^{4+}	K_h	−285.1563		4302
SiF^{3+}	$C_{\infty v}$	−386.1869	1.524	3274
SiF_2^{2+}	$D_{\infty h}$	−486.8321	1.485	2167
SiF_3^+	D_{3h}	−587.0623	1.515	1294
SiF_4	T_d	−686.9652	1.561 (1.554)	323
SiF_5^-	D_{3h}	−786.5042	1.663,[b], 1.623	−187
SiF_6^{2-}	O_h	−885.8519	1.710 (1.708)	
Si^{2+}	K_h	−287.9704		1896
SiF^+	$C_{\infty v}$	−388.0914	1.539	1048
SiF_2	C_{2v}	−487.8976	1.604, 99.2 (1.590, 100.8)	366
SiF_3^-	C_{3v}	−587.4506	1.673, 96.1	
P^{5+}	K_h	−334.3411		
PF_2^{3+}	$D_{\infty h}$	−537.3863	1.437	3310
PF_3^{2+}	D_{3h}	−638.0389	1.443	2192
PF_4^+	T_d	−738.2785	1.480	1561
PF_5	D_{3h}	−838.0654	1.572,[b] 1.536 (1.577, 1.534)	406
PF_6^-	O_h	−937.6346	1.610	
P^{3+}	K_h	−338.5328		3220
PF^{2+}	$C_{\infty v}$	−439.1424	1.442	2022
PF_2^+	C_{2v}	−539.3086	1.504, 100.9	1129
PF_3	C_{3v}	−639.1442	1.570, 97.1 (1.570, 97.8)	189
PF_4^-	C_{2v}	−738.6321	1.751, 167.8 1.611, 99.8	
S^{6+}	K_h	−387.5316		
SF_3^{3+}	D_{3h}	−693.4955	1.415	3200
SF_4^{2+}	T_d	−794.1071	1.439	1590
SF_5^+	D_{3h}	−894.1179	1.524,[b] 1.492	1252
SF_6	O_h	−994.0028	1.557 (1.564)	
S^{4+}	K_h	−393.3312		
SF_3^+	C_{3v}	−695.4164	1.501, 99.0	885
SF_4	C_{2v}	−795.1603	1.643, 170.1 (1.646, 173.1) 1.544, 102.5 (1.545, 101.6)	211
SF_5^-	C_{4v}	−894.6560	1.588,[c] 84.4[d] 1.711, 89.5	

[a] Experimental values[e] in parentheses with distances in angstroms and angles between equivalent bonds in degrees and energies in hartrees for fluorides, and fluoride affinities, E_F (in kJ mol^{-1}). [b] Axial. [c] Apical. [d] Angle between apical and basal bonds. [e] References 15 and 17.

with an additional p gaussian orbital with exponent (0.090 au) optimized for F^-. A similarly augmented F basis was found to give a good account of the energetics of formation of oligomers of LiF and NaF.[12]

Thermochemical data were taken from the revision of NBS circular 500[13] except that I have taken the heat of formation of F^- to be $\Delta H^\circ = -251.1$ kJ mol^{-1} calculated from the revised electron affinity of fluorine (3.399 eV) reported by Milstein and Berry.[14] Zero point energies were calculated from the frequencies listed in the JANAF thermochemical tables.[15]

Results

The results are listed in Tables I and II. In Table I I compare the calculated energies for $MF_n \rightarrow M^{n+}$ with thermochemical data (corrected for zero point energy). The agreement can be seen to be very good, with the calculated values generally smaller by about 2% and no systematic variation across the periodic table. Indeed, for smaller values of *n* the absolute error is small, of the order often found for experimental uncertainties. As the heats of formation of *atomic* ions are very well-known, it can be seen that the data could be used to calculate heats of formation of molecules in much the same way as proposed by Hurley.[6]

The origin of the difference between the experimental and the calculated values is of interest. The difference per fluoride ion increases fairly systematically from left to right across the periodic table ruling out the possibility of there being a significant error in either the heat of formation of F^- or the theoretical modeling of F^-. In the case of $BF \rightarrow B^+ + F^-$, the calculation was repeated at the level of configuration interaction with all double substitutions. The energy difference changed by only 3 kJ mol^{-1}, suggesting that the neglect of correlation energy is not important. On the other hand, the fact that the sign of the discrepancy is such that the molecule is calculated to be less stable with respect to the ions than is observed suggests that a more flexible basis set might result in better results at the SCF level. One obvious approach would to be to use scale factors optimized for each molecule, but as the results are considered sufficiently good for the purpose of predicting fluoride affinities, it did not appear that

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the additional expense that this would entail was justified.

Table II lists the calculated geometries and energies of a number of species $X = MF^{p+}_{n-p}$; and in the last column, the fluoride affinity (E_F) of X, i.e., the energy change for the process $XF^- \rightarrow X + F^-$. In determining this quantity, the calculated energy difference has been multiplied by the ratio experimental:theoretical from Table I on the assumption that the errors in the calculated values for a given sequence are systematic. This correction is very small anyway for the fluoride affinities of most current interest (such as that of BF_3, for which it is only 3 kJ mol^{-1}).

The very good relative agreement between experimental and theoretical energies shown in Table I suggests that the calculated fluoride affinities should be sufficiently reliable to provide useful checks of reported values and reliable estimates of previously unknown ones.

Comparison with Experiment

A number of fluoride affinities have been estimated from experimental data. They are usually reported as ΔH for the process

$$XF^- \rightarrow X + F^-$$

(here X may be a neutral or a charged species). To compare these results with the E_F of Table II, there must be added to E_F (i) a correction for the change in zero point energy (typically ~9 kJ mol^{-1}) and (ii) a correction for heating from 0 K to the temperature at which ΔH is measured (usually ~298 K, but not always clear); this is $\sim -5RT/2 \sim -6$ kJ mol^{-1}. As the two corrections are in the opposite sense and their sum is less than typical uncertainties, in the following the calculated E_F is compared directly with reported values of $\Delta H°$. Sometimes it is not clear what value of the electron affinity of fluorine or other reference data are assumed; this introduces further difficulties into comparison of theory and experiment.

(**a**) **BF_3.** The fluoride affinity of BF_3 is important to the experimental evaluation of other affinities. Reported values range from 259 ± 40 kJ mol^{-1} (BH)[4] to 385 ± 25 kJ mol^{-1} (BH),[5] with 297 kJ mol^{-1} (ICR) also being quoted.[3] Mallouk et al.[5] make a strong case for the higher value being preferred. The value of E_F reported here (358 kJ mol^{-1}) supports that contention.

(**b**) **SF_4.** Murphy and Beauchamp[2] estimate for the fluoride affinity of SF_4 the value of 226 ± 50 kJ mol^{-1} (ICR) and Larson and McMahon[1a] give 183 kJ mol^{-1} (ICR). The higher value is in better agreement with $E_F = 211$ kJ mol^{-1} reported here.

(**c**) **PF_5.** Larson and McMahon[1] give for the fluoride ion affinity of PF_5 the value 356 ± 40 kJ mol^{-1} (ICR). Mallouk et al.,[5] on the other hand, prefer 423 ± 33 kJ mol^{-1} (BH). The latter value is closer to the calculated $E_F = 406$ kJ mol^{-1}.

(**d**) **SF_3^+.** Mallouk et al.[5] quote 883 ± 33 kJ mol^{-1} for the fluoride affinity of SF_3^+ (BH). This is very close to the calculated $E_F = 885$ kJ mol^{-1}.

(**e**) **PF_3.** Larsen and McMahon[1] give 168 kJ mol^{-1} (ICR) compared with a calculated $E_F = 189$ kJ mol^{-1} for PF_3.

(**f**) **SiF_4.** The same authors give 251 ± 20 kJ mol^{-1} (ICR) compared with a calculated $E_F = 323$ kJ mol^{-1} for SiF_4. On the other hand, Jenkins and Pratt[16] calculate (BH) for the double electron affinity of SiF_4 ($\rightarrow SiF_6^{2-}$) $\Delta E = 138$ kJ mol^{-1} in excellent agreement with the value (136 kJ mol^{-1}) calculated from Table II.

(**g**) **CF_3^+.** Data from ref 13 give for $\Delta H°_{298} = 1158$ kJ mol^{-1} (provenance unknown) for $CF_4 \rightarrow CF_3^+ + F^-$. The calculated value is $E_F = 1136$ kJ mol^{-1}.

(**h**) **BF_2^+.** Data from ref 15 (based on appearance potentials) yield $\Delta H°_{298} = 1227 \pm 12$ kJ mol^{-1} for $BF_3 \rightarrow BF_2^+ + F^-$. The calculated $E_F = 1262$ kJ mol^{-1}.

The comparison above shows generally good agreement between calculated values and experimental fluoride affinities determined by using a Born–Haber cycle (some of the residual differences may well be traced to the use of different reference data) providing a useful confirmation of the validity of that technique. The agreement reported in (g) and (h) above is also very satisfactory. On the other hand the fluoride affinities reported in the ICR[1-3] literature are generally lower than those calculated suggesting a possible systematic error due to an incorrect reference value.

Comparison of calculated and observed geometries show that for the neutral molecules distances are generally in agreement within ±0.02 Å and angles within ±1.0°, so that the data provided here should also provide useful estimates of the dimensions of species not as yet studied experimentally.

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Registry No. F^-, 16984-48-8; HF, 7664-39-3; HF_2^-, 18130-74-0; Li^+, 17341-24-1; LiF, 7789-24-4; LiF_2^-, 50561-24-5; Be^{2+}, 22537-20-8; BeF^+, 33808-13-8; BeF_2, 7787-49-7; BeF_3^-, 19181-26-1; BeF_4^{2-}, 18539-20-3; Be, 7440-41-7; BeF^-, 51233-20-6; B^{3+}, 22537-21-9; BF^{2+}, 86686-93-3; BF_2^+, 12355-90-7; BF_3, 7637-07-2; BF_4^-, 14874-70-5; B^+, 14594-80-0; BF, 13768-60-0; BF_2^-, 26202-31-3; C^{4+}, 16092-62-9; CF^{3+}, 102519-41-5; CF_2^{2+}, 97411-56-8; CF_3^+, 18851-76-8; CF_4, 75-73-0; C^{2+}, 16092-61-8; CF^+, 2154-59-8; CF_2, 2154-59-8; CF_3^-, 54128-17-5; N^{3+}, 18396-22-0; NF^{2+}, 102519-42-6; NF_2^+, 31685-31-1; NF_3, 7783-54-2; Na^+, 17341-25-2; NaF, 7681-49-4; NaF_2^-, 50417-28-2; Mg^{2+}, 22537-22-0; MgF^+, 21308-25-8; MgF_2, 7783-40-6; MgF_3^-, 55161-80-3; MgF_4^{2-}, 54097-16-4; Mg, 7439-95-4; MgF^-, 39343-43-6; Al^{3+}, 22537-23-1; AlF^{2+}, 21330-18-7; AlF_2^+, 21559-03-5; AlF_3, 7784-18-1; AlF_4^-, 21340-02-3; AlF_5^{2-}, 28747-75-3; AlF_6^{3-}, 21340-03-4; Al^+, 14903-36-7; AlF, 13595-82-9; AlF_2^-, 12758-11-1; Si^{4+}, 22537-24-2; SiF^{3+}, 102519-43-7; SiF_2^{2+}, 102519-44-8; SiF_3^+, 38192-99-3; SiF_4, 7783-61-1; SiF_5^-, 21476-45-9; SiF_6^{2-}, 17084-08-1; Si^{2+}, 14175-55-4; SiF^+, 12518-09-1; SiF_2, 13966-66-0; SiF_3^-, 54711-93-2; P^{5+}, 22537-25-3; PF_2^{3+}, 102519-45-9; PF_3^{2+}, 102519-46-0; PF_4^+, 29075-80-7; PF_5, 7647-19-0; PF_6^-, 16919-18-9; P^{3+}, 20337-88-6; PF^{2+}, 11080-57-2; PF_2^+, 37366-67-9; PF_3, 7783-55-3; PF_4^-, 25443-47-4; S^{6+}, 22537-26-4; SF_3^{3+}, 102519-47-1; SF_4^{2+}, 69754-88-7; SF_5^+, 19167-14-7; SF_6, 2551-62-4; S^{4+}, 20681-10-1; SF_3^+, 25431-36-1; SF_4, 7783-60-0; SF_5^-, 31140-82-6.

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