Thermodynamic Calculations for Reactions Involving Hydrogen Halide Polymers, Ions, and Lewis Acid Adducts. 1. Polyfluorohydrogenate(1−) Anions ($H_nF_{n+1}^-$), Polyfluorohydrogen(I) Cations ($H_{n+1}F_n^+$), and Hydrogen Fluoride Polymers ($(HF)_n$)

W. David Chandler,* Keith E. Johnson, and John L. E. Campbell[†]

Department of Chemistry, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

Received January 12, 1995[®]

Semiempirical (MNDO, AM1 and PM3) and *ab initio* (HF/3-21+G(d,p), MP2/3-21+G(d,p), HF/6-311+G(d,p) and MP2/6-311+G(d,p)) energy minimization and frequency calculations have been carried out on five hydrogen fluoride polymers, $(HF)_n$, $n = 2, 3, 4, 5$, and 6; on four polyfluorohydrogenate(1−) anions, $H_nF_{n+1}^-$, $n = 1, 2, 3$, and 4; and on two polyfluorohydrogen(I) cations, $H_{n+1}F_n^+$ n = 1 and 2. From the results, ΔG°, ΔH°, and ΔS° values have been calculated for a number of reactions involving these species. The thermodynamic data are presented for 23 reactions using calculations at the MP2/6-311+G(d,p) level, along with a comparison of ΔG° values obtained from all seven molecular orbital methods.

Introduction

In previous work we have discussed solubility, ^1H NMR and IR spectroscopic, as well as electrochemical behavior of the HCl:AlCl$_3$:ImCl (Im ≡ 1-ethyl-3-methyl-1*H*-imidazolium) ambient temperature liquid systems.[1] Some of the anionic species present in melts containing an excess of chloride ion are governed by the equilibria

$$HCl + H_nCl_{n+1}^- \rightarrow H_{n+1}Cl_{n+2}^- \ (n = 0, 1, 2, ...) \qquad (1)$$

and possibly

$$Cl^- + H_nCl_n \rightarrow H_nCl_{n+1}^- \ (n = 1, 2, 3, ...) \qquad (2)$$

In particular, we have found evidence for the existence of the dichlorohydrogenate(1−) and trichlorodihydrogenate(1−) anions, HCl_2^- and $H_2Cl_3^-$ respectively. One might also expect that, in those media where an excess of protons occurs, cations could arise as the result of similar equilibria

$$HCl + H_{m+1}Cl_m^+ \rightarrow H_{m+2}Cl_{m+1} \ (m = 0, 1, 2, ...) \qquad (3)$$

$$H^+ + H_mCl_m \rightarrow H_{m+1}Cl_m^+ \ (m = 1, 2, 3, ...) \qquad (4)$$

These is a considerable body of literature dealing with the synthesis, properties and structures of some of these ions and their fluorine analogs: HCl_2^-,[2] HF_2^-,[2dhi,3] H_2Cl^+,[2dh,4] H_2F^+,[2dhi,3a,4a,5] larger anions (primarily fluorides) $H_nX_{n+1}^-$,[2f,3adf,6] larger cations $H_{n+1}F_n^+$,[3a,f,5b,c] and polymers H_nF_n or $(HF)_n$ particularly for $n = 2$ and 3.[2d,3ag,7,8a]

At the same time, there have been many theoretical treatments of structures and their energies, of complete energy surfaces, and of vibrational frequencies particularly of the fluorine species: HCl_2^-,[2b,8] HF_2^-,[3a,8a−c,9] H_2Cl^+,[8a,10] H_2F^+,[3a,5a,8a,10bc,11] larger anions $H_nF_{n+1}^-$,[3a,9a,d] larger cations $H_{n+1}F_n^+$,[9a,10c] $(HCl)_n$,[8a,12] and $(HF)_n$.[7b,8ad,12,13]

Our major interest, as an adjunct to studying melt compositions by various experimental techniques, is to use molecular orbital calculations in predicting which hydrogen chloride species would be expected to occur in the melts, and what their relative concentrations might be. Many people have examined some of the reactions we are interested in as well as those involving HF and fluoride ion, but, for the most part, little in the way of true thermodynamic data is available. Previous theoretical studies have tended to provide relative energies, often

---

* Author to whom correspondence should be addressed.

[†] Present address: Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.

[®] Abstract published in *Advance ACS Abstracts,* September 1, 1995.

(1) (a) Campbell, J. L. E.; Johnson, K. E. *Inorg. Chem.* **1993**, *32*, 3809. (b) Campbell, J. L.; Johnson, K. E. *J. Electrochem. Soc.* **1994**, *141*, L19. (c) Campbell, J. L. E.; Johnson, K. E.; Torkelson, J. R. *Inorg. Chem.* **1994**, *33*, 3340. (d) Campbell, J. L. E. Ph.D. Thesis, University of Regina, Regina, SK, 1994.

(2) (a) Atwood, J. L.; Bott, S. G.; Means, C. M.; Coleman, A. W.; Zhang, H.; May, M. T. *J. Am. Chem. Soc.* **1990**, *29*, 467. (b) Ikuta, S.; Saitoh, T.; Nomura, O. *J. Chem. Phys.* **1989**, *91*, 3539, and references cited therein. (c) Kawaguchi, K. *J. Chem. Phys.* **1988**, *88*, 4186. (d) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984; Chapter 17, and references cited therein. (e) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91, and references cited therein. (f) Shuppert, J. W.; Angell, C. A. *J. Chem. Phys.* **1977**, *67*, 3050. (g) Tuck, D. *Prog. Inorg. Chem.* **1968**, *9*, 161, and references cited therein. (h) Klanberg, F. In *The Chemistry of Non-Aqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1967; Volume II, Chapter 1. (i) Peach, P. E.; Waddington, T. C. In *Non-Aqueous Solvent Systems*; Waddington, T. C., Ed.; Academic Press: London, 1965; Chapter 3.

(3) (a) Hibbert, F.; Emsley. J. *Adv. Phys. Org. Chem.* **1990**, *26*, 255 and references cited therein. (b) Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1987**, *87*, 6838. (c) Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1986**, *84*, 2953. (d) Gennick, I; Harmon, K. M.; Potvin, M. M. *Inorg. Chem.* **1977**, *16*, 2033. (e) Pratt, J. C.; Smith, J. A. S. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 596. (f) Hyman, H. H.; Katz, J. J. In *Non-Aqueous Solvent Systems*; Waddington, T. C., Ed.; Academic Press: London, 1965; Chapter 2. (g) Kilpatrick, M.; Jones, J. G. In *The Chemistry of Non-Aqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1967; Volume II, Chapter 2.

(4) (a) Tedemann, P. W.; Anderson, S. L.; Ceyer, S. T.; Hirooka, T.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys.* **1979**, *71*, 605. (b) Polley, C. W.; Munson, B. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 49.

(5) (a) Petsalakis, I. D.; Theodorakopoulos, G.; Wright, J. S.; Hamilton, I. P. *J. Chem. Phys.* **1990**, *92*, 2440, and references cited therein. (b) Mootz, D.; Bartmann, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 291. (c) Bonnet, B.; Mascherpa, G. *Inorg. Chem.* **1980**, 19, 785. (d) Schafer, E.; Saykally, R. J. *J. Chem. Phys.* **1984**, *81*, 4189.

(6) (a) Coyle, B. A.; Schroeder, L. W.; Ibers, J. A. *J. Solid. State Chem.* **1970**, *1*, 386. (b) Forrester, J. D.; Senko, M. E.; Zalkin, A.; Templeton, D. H. *Acta. Crystallogr.* **1963**, *16*, 58. (c) Ibers, J. A. *J. Chem. Phys.* **1964**, *40*, 402.

corrected for zero-point energies, at 0 K (ΔU) for reactions such as 5,[2e,3a,8a−c,9d] 6,[2b,e,7d,8a−f] 7,[5a,8a,10b,c] 8,[8a,10b,c] 9,[8a,12b,13b,d,g−i] 10,[8a,12b] 11,[8a,7a,13b,g,h] 12,[8a] 13,[9d] 14,[3a,10c] 15,[9d] and 16.[9d] Ikuta, Saitoh, and Numura have converted their calculations for reaction 6 into standard free energy ($\Delta G° = -69.0$ kJ/mol), entropy ($\Delta S° = -98.3$ J/K/mol) and enthalpy ($\Delta H° = -98.3$ kJ/mol) changes at 298 K.[2b] Redington has calculated standard thermodynamic parameters such as $\Delta H°$ and equilibrium constants for the formation of clusters H_nF_n ($n = 2-6$) from HF (e.g. reactions 9 and 11) using experimental vapor density, heat capacity, IR data, excess entropy and excess enthalpy data in a nonideal vapor model.[7i,k] A more recent study has adopted a central force model to calculate $\Delta U°$, $\Delta S°$, and $\Delta G°$ at 273 K for the same HF cluster formation reactions.[13h]

$$F^- + HF \rightarrow HF_2^- \tag{5}$$

$$Cl^- + HCl \rightarrow HCl_2^- \tag{6}$$

$$H^+ + HF \rightarrow H_2F^+ \tag{7}$$

$$H^+ + HCl \rightarrow H_2Cl^+ \tag{8}$$

$$2HF \rightarrow H_2F_2 \tag{9}$$

$$2HCl \rightarrow H_2Cl_2 \tag{10}$$

$$3HF \rightarrow H_3F_3 \tag{11}$$

$$3HCl \rightarrow H_3Cl_3 \tag{12}$$

$$HF + HF_2^- \rightarrow H_2F_3^- \tag{13}$$

$$HF + H_2F^+ \rightarrow H_3F_2^+ \tag{14}$$

$$HF + H_2F_3^- \rightarrow H_3F_4^- \tag{15}$$

$$HF + H_3F_4^- \rightarrow H_4F_5^- \tag{16}$$

Comparable experimental values are not as readily available. Proton affinities for HF and HCl (reactions 7 and 8) are known,[4ab,14] as are the corresponding halide affinities (reactions 5 and 6).[2e,3a,15] Payzant and Cunningham determined ΔH for reaction 14,[16] and dissociation energies for the dimers (reactions 9 and 10) have been estimated.[7c,e] For reaction 6, the equilibrium constant has been reported to be 500 in nitrobenzene at 298 K ($\Delta G° = -15$ kJ/mol),[17] ≈600 at 304 K in *s*-tetrachloroethane ($\Delta G° = -16$ kJ/mol),[18] and 67 ± 18 in $AlCl_3$:ImCl at 363 K ($\Delta G° = -13$ kJ/mol).[19] In his review of dihalohydrogenate(1−) ions, Tuck quotes $\Delta G°$ values ranging from −4 to −18 kJ/mol for that same reaction, and $\Delta H = -160$ to -240 kJ/mol for reaction 5.[2f] Our own NMR and pressure-composition isotherm studies estimate K to be 715 ± 76 ($\Delta G° = -16.2$ kJ/mol), 3.28 ± 0.05 ($\Delta G° = -2.93$ kJ/mol), 0.72 ± 0.02 ($\Delta G° = +0.81$ kJ/mol), and 220 ± 20 ($\Delta G° = -13.3$ kJ/mol, $\Delta H° = -22.8$ kJ/mol and $\Delta S° = -31.8$ J/K/mol) for reactions 6, 17, 18, and 19 respectively in HCl:ImCl melts.[1d]

$$HCl + HCl_2^- \rightarrow H_2Cl_3^- \tag{17}$$

$$HCl + H_2Cl_3^- \rightarrow H_3Cl_4^- \tag{18}$$

$$Cl^- + H_2Cl_3^- \rightarrow 2HCl_2^- \tag{19}$$

If theoretical calculations are to be truly helpful in predicting the outcomes of reactions at equilibrium, they should provide $\Delta G°$, $\Delta H°$ and $\Delta S°$. The difference between ΔH at 298 K and ΔU at 0 K, even with zero point energy differences taken into account, involves thermal energy (usually small) as well as the term ΔnRT, where Δn is the change in the total number of moles of gas during the reaction. This PV work term can be as much as 12 kJ/mol in reactions we are interested in although it is more frequently 2.5 or 5.0 kJ/mol. At the same time, while $T\Delta S$ can be as large as 160 kJ/mol in cluster formations, it is usually found to be significantly smaller, of the order of 30 kJ/mol. Clearly the ΔE or ΔU values usually reported by theoreticians for reactions, while informative, simply do not

---

(7) (a) Quack, M.; Schmidt, V.; Suhm, M. *Chem. Phys. Lett.* **1993**, *208*, 446, and references cited therein. (b) Quack, M.; Stohner, J.; Suhm, M. *J. Mol. Struct.* **1993**, *294*, 33, and references cited therein. (c) Dayton, D. C.; Jucks, K. W.; Miller, R. E. *J. Chem. Phys.* **1989**, *90*, 2631. (d) Kofranek, M.; Lischka H.; Karpfen, A. *Chem Phys.* **1988**, *121*, 137, and references cited therein. (e) Pine, A. S.; Howard, B. J. *J. Chem. Phys.* **1986**, *84*, 590. (f) Pine, A. S.; Lafferty, W. J.; Howard, B. J. *J. Chem. Phys.* **1984**, *81*, 2939. (g) Howard, B. J.; Dyke, T. R.; Klemperer, W. *J. Chem. Phys.* **1984**, *81*, 5417. (h) Barton, A. E.; Howard, B. J. *Faraday Discuss. Chem. Soc.* **1982**, *73*, 45. (i) Redington, R. L. *J. Phys. Chem.* **1982**, *86*, 553. (j) Redington, R. L. *J. Phys. Chem.* **1982**, *86*, 561. (k) Redington, R. L. *J. Chem. Phys.* **1981**, *75*, 4417. (l) Janzen, J.; Bartell, L. *J. Chem. Phys.* **1969**, *50*, 3611. (m) Chase, M. W., Jr.; Davies C. A.; Downey, J. R. Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF* Thermochemical Tables, 3rd. ed. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

(8) (a) Heidrich, D.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R. *J. Comput. Chem.* **1993**, *14*, 1149, and references cited therein. (b) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258. (c) Sannigrahi, A. B.; Har, T.; Nandi, P. K. *Chem Phys. Lett.* **1992**, *198*, 67. (d) Botschwina, P.; Sebald, P.; Burmeister, R. *J. Chem. Phys.* **1988**, *88*, 5246. (e) Sannigrahi, A. B.; Peyerimhoff, S. D. *J. Mol. Struct.* **1985**, *122*, 127. (f) Saitoh, T.; Mori, K.; Sasagane, K.; Itoh, R. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2877. (g) Almlof, J. *J. Mol. Struct., THEOCHEM* **1981**, *79*, 179.

(9) (a) Karpfen, A.; Yanovitskii, O. *J. Mol. Struct., THEOCHEM* **1994**, *307*, 81. (b) Spirko, V.; Diercksen, G. H. F.; Sadlej, A.; Urban, M. *Chem. Phys. Lett.* **1989**, *161*, 519. (c) Jansen, C. L.; Allen, W. D.; Schaefer, H. F.; Bowman, J. M. *Chem. Phys. Lett.* **1986**, *131*, 352. (d) Clark, J. H.; Emsley, J.; Jones, D. J.; Overill, R. E. *J. Chem. Soc., Dalton Trans.* **1981**, *100*, 1219.

(10) (a) Kuntz, P. J.; Whitton, W. N. *J. Chem. Phys.* **1991**, *95*, 5149. (b) Del Bene, J. E.; Shavitt, I. *J. Phys. Chem.* **1990**, *94*, 5514. (c) Del Bene, J. E., Frisch, M. J.; Pople, J. A. *J. Phys. Chem.* **1985**, *89*, 3669.

(11) (a) Gianturco, F. A.; Buonomo, E.; Semprini, E.; Stefani, F.; Palma, A. *Int. J. Quantum Chem.* **1993**, *47*, 335. (b) Diercksen, G. H. F.; von Niessen, W.; Kraemer, W. P. *Theor. Chim. Acta.* **1973**, *31*, 205.

(12) (a) Szczesniak, M. M.; Chalasinski, J. *J. Mol. Struct., THEOCHEM* **1992**, *261*, 37. (b) Frisch, M. J.; Pople, J. A.; Del Bene, J. E. *J. Phys. Chem.* **1985**, *89*, 3664.

(13) (a) Quack, M.; Stohner, J.; Suhm, M. A. *Chem. Phys. Lett.* **1993**, *208*, 446. (b) Sun, H.; Watts, R. O.; Buck, U. *J. Chem. Phys.* **1992**, *96*, 1810. (c) Bonaccorsi, R.; Cammi, R.; Tomasi, J. *J. Comput. Chem.* **1991**, *12*, 301. (d) Smith, B. J.; Swanton, D. J.; Pople, J. A.; Schafer, H. F., III; Radom, L. *J. Chem. Phys.* **1990**, *92*, 1240. (e) Jensen, P.; Bunker, P. R.; Karpfen, A.; Kofranek, M.; Lischka, H. *J. Chem. Phys.* **1990**, *93*, 6266. (f) Bunker, P. R.; Jensen, P.; Karpfen, A.; Kofranek, M.; Lischka, H. *J. Chem. Phys.* **1990**, *92*, 7432. (g) Karpfen, A. *Int. J. Quantum Chem. Symp.* **1990**, *24*, 129. (h) Zhang, C.; Freeman, D. L.; Doll, J. D. *J. Chem. Phys.* **1989**, *91*, 2489. (i) Bunker, P. R.; Kofranek, M.; Lischka, H.; Karpfen, A. *J. Chem. Phys.* **1988**, *89*, 3002. (j) Jansen, R. W.; Bertoncini, R.; Pinnick, D. A.; Katz, A. I.; Hanson, R. C.; Sankey, O. F.; O'Keefe, M. *Phys. Rev.* **1987**, *B35*, 9830. (k) Del Bene, J. E.; Pople, J. A. *J. Chem. Phys.* **1971**, *55*, 2296.

(14) (a) Lias, S. G.; Bartmoss, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. (b) Foster, M. S.; Beauchamp, J. L. *Inorg. Chem.* **1975**, *14*, 1229.

(15) (a) Larson, J. W.; McMahon, T. B. *Inorg. Chem.* **1984**, *23*, 2029. (b) Yamdagni, R.; Kebarle, P. *Can. J. Chem.* **1974**, *52*, 2449.

(16) Payzant, J. D.; Cunningham, A. J. *Can. J. Chem.* **1973**, *51*, 3242.

(17) Herbrandson, H. F.; Dickerson, R. T., Jr.; Weinstein, J. *J. Am. Chem. Soc.* **1954**, *76*, 4046.

(18) Fujiwara, F. Y.; Martin, J. S. *J. Chem. Phys.* **1972**, *56*, 4091.

(19) Trulove, P. C.; Sukumaran, D. K.; Osteryoung, R. A. *Inorg. Chem.* **1993**, *32*, 4396.

provide the most reliable picture of what a chemical change will be like under equilibrium conditions.

Our purpose in this paper is to use thermodynamic data obtained from semiempirical and *ab initio* molecular orbital calculations to explore the feasibility of a number of reactions involving polyfluorohydrogenate(1−) anions, polyfluorohydrogen(I) cations, and hydrogen fluoride polymers. We chose the fluorides as a test of the calculational methods since they represent simpler cases for molecular orbital calculations and have been more extensively studied than their chlorine analogs. It is also important to see whether semiempirical calculations, which can be carried out in shorter time and with less computing resources, are able to provide results that are comparable with those obtained by *ab initio* methods. Since for some of the chlorine and aluminum systems we are interested in exploring experimentally *ab initio* calculations at the level of sophistication employed in this paper are less feasible, semiempirical methods must be relied upon to provide thermodynamic information. In a subsequent paper we will extend the analysis to many of the corresponding chloride species along with a variety of chloroaluminates expected in $HCl:AlCl_3:ImCl$ melts.[20]

Calculations

Ab initio and semiempirical calculations were performed using GAUSSIAN 92.[21] Geometries were optimized using MNDO, AM1, and PM3 semiempirical methods as well as with 3-21+G(d,p) and 6-311+G(d,p) basis sets taken from the GAUSSIAN 92 program at the Hartree−Fock and MP2 levels. Vibrational frequencies were also calculated using the same methods and basis sets. From these latter calculations, it was possible (a) to determine that a structure represented a true minimum and not a saddle point in the energy surface, (b) to obtain entropies ($S°$) at 298 K, and (c) to obtain zero-point energy corrections and thermal energies at 298 K and 1 atm pressure. All *ab initio* energies were corrected for thermal energies, including zero-point vibrations (Hartree−Fock zero point energy values were scaled by 0.90[22] and MP2 values by 0.95[8a]), to give U values at 298 K. The reaction internal energies ($\Delta U°$) were converted to reaction enthalpies ($\Delta H°$) with eq 20 which assumes ideal gas behavior for all species.[23] $\Delta S°$ values were obtained using $S°$'s taken from GAUSSIAN 92 frequency calculations for polyatomic ions and molecules, and employing the Sackur−Tetrode equation for monatomic ions.[23]

$$\Delta H° = \Delta U° + \Delta nRT \qquad (20)$$

Results

Figures 1 and 2 present structures of the species studied as determined by MP2/6-311+G(d,p) optimizations. Structures for all have been presented in the literature before in some form (*vide supra*), and our results are essentially the same as the most reliable of them. The agreement with experimental data, where available, is exceptionally good (Table 1). As n increases from 1 to 4 in the anionic series, $H_nX_{n+1}^-$, the shorter of the HF bond lengths decreases (1.138, 0.997, 0.967, and 0.950 Å respectively). There is a similar bond length decrease with the two cations studied, $H_{n+1}F_n^+$, (0.960 and 0.941 Å) indicating that, as ionic species become larger, HF molecules increasingly act in a solvating capacity around either a F^- or a H^+ ion, and less true covalent bonding occurs. While it is well-known that the cyclic H_2F_2, with C_{2h} symmetry, is a saddle point and not a minimum in the energy surface,[8a,9c,12b,13] the cyclic C_{nh} structures **are** minima for the other four hydrogen fluoride polymers.[7b,8a,9c,13g,j]

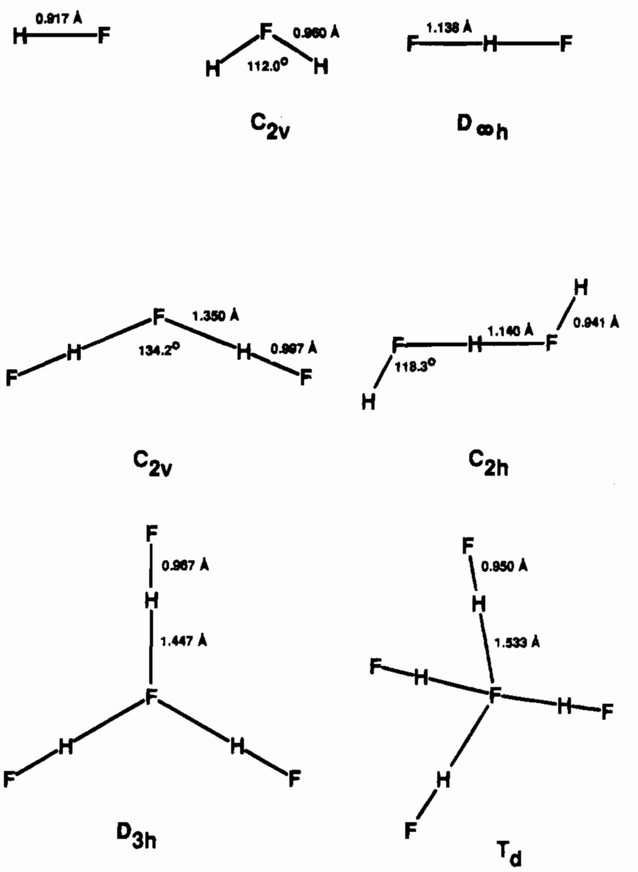

Figure 1. Structures of HF, some fluorohydrogenate(1−) anions and fluorohydrogen(I) cations as determined by MP2/6-311+G** *ab initio* methods. Bond lengths are in Å and angles in deg.

Structures obtained from the other methods (Hartree−Fock, MP2 and semiempirical) are qualitatively the same as those shown in Figures 1 and 2, with the following exceptions:

(i) AM1 optimization of HF_2^- finds a minimum structure with HF bonds of **different** length (0.884 and 1.608 A).

(ii) Structures obtained for H_2F^+ using semiempirical methods have a significantly larger HFH bond angle. In fact, the ion is predicted to be linear by both AM1 and PM3.

(iii) Optimizations using the 3-21+G(d,p) basis sets suggest that $H_2F_3^-$ should be linear. The HFH bond angle for the MNDO structure is also large but less than 180°.

(iv) For $H_3F_2^+$ the PM3 structure is linear and the MNDO structure has HFH angles of 152°. The AM1 structure is quite different; it has a C_{2v} "kite" shape, formed by the F of one HF being placed equidistant between the two H's at the ends of the inverted V of an H_2F^+ ion. In this case HF "solvates" H_2F^+ in a cyclic rather than linear form.

(v) MNDO optimization of $H_3F_4^-$ predicts a C_{2v} structure with the H of one HF molecule bonded to the central F of $H_2F_3^-$ but with a different bond length from the other two HF bonds (*i.e.* not quite D_{3h}). The same general observation occurs for the MNDO optimization of $H_3F_4^-$. Since one of the HF's is positioned differently relative to the central F, the symmetry is really C_{3v} rather than tetrahedral.

(vi) In contrast to **all** other methods, AM1 predicts that the global energy minimum occurs for the cyclic H_2F_2 of C_{2h} symmetry.

---

(20) Chandler, W. D.; Johnson, K. E.; Campbell, J. L. E. *Inorg. Chem.*, manuscript in preparation.

(21) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92, Revision A. Gaussian Inc., Pittsburgh, PA, 1992.

(22) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269.

(23) Atkins, P. W. *Physical Chemistry*, 5th ed.; Freeman: New York, 1994.

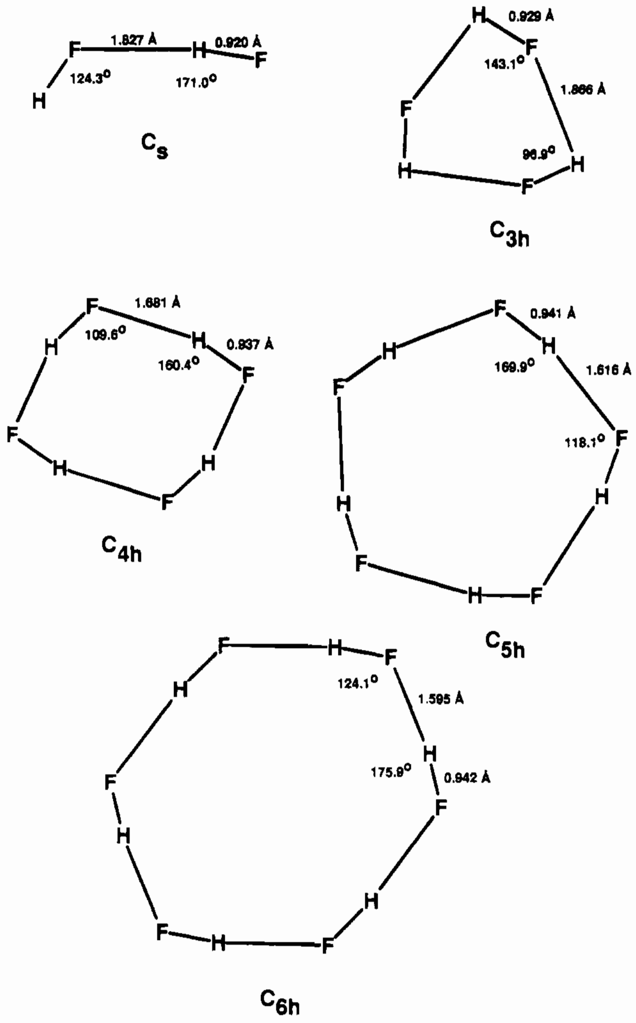

Figure 2. Structures of some hydrogen fluoride polymers as determined by MP2/6-311+G** *ab initio* methods. Bond lengths are in angstroms and angles in degrees.

Table 1. Comparison of Experimental and Calculated Structures

	structural params[a]			
species	param	exptl	ref	calcd[b]
HF	R_{HF}	0.9256	24	0.917
HF_2^-	R_{HF}	1.138	3e	1.138
	R_{FF}	2.278	3b	
H_2F^+	R_{HF}	0.9577	5d	0.960
	∠HFH	114.6	5d	112.0
$H_3F_2^+$	R_{FF}	2.30	5b	2.280
	∠HFH	115.2	5b	118.3
$H_3F_4^-$	R_{FF}	2.33−2.40	3a	2.414
	R_{HF}	0.70, 1.76	6c	0.967, 1.447
H_2F_2	*c*	2.72	7g	2.718
		67.5, 12	7h	57.8, 6.9
H_6F_6	R_{FF}	~2.55	71	2.537

[a] All lengths are in Å, and angles are in deg. [b] Calculated structures were obtained from MP2/6-311+G(d,p) optimizations. [c] Distance between centers of mass of two HF monomers and angles between line connecting the two centers of mass and the two short HF bonds.

(vii) In general, AM1 optimizations find that the shorter of the two HF bond lengths (the "HF molecules") in a structure is significantly smaller when compared with *ab initio* optimizations while the longer one is larger. MNDO and PM3 tend to give larger values for both bond lengths although differences are not as large in the AM1 cases.

Table 2 presents thermodynamic data, calculated at the MP2/6-311+G(d,p) for 23 reactions. Figures 3−8 are comparisons of the $\Delta G°$ values calculated for these reactions by the various *ab initio* and semiempirical molecular orbital methods. It is not surprising that any reaction that results either in neutral molecules forming ions or in an increase in the number of ions is highly endergonic in the gas phase (reactions 22, 23, and 25−29). It is also no surprise that reactions that turn smaller ions into larger ones are exergonic (reactions 5, 7, 13−16, and 32−35).

$$HF \rightarrow F^- + H^+ \tag{21}$$

$$3HF \rightarrow H_2F^+ + HF_2^- \tag{22}$$

$$2HF_2^- \rightarrow F^- + H_2F_3^- \tag{23}$$

$$HF_2^- \rightarrow H^+ + 2F^- \tag{24}$$

$$H_2F_2 \rightarrow F^- + H_2F^+ \tag{25}$$

$$H_2F_2 \rightarrow H^+ + HF_2^- \tag{26}$$

$$H_3F_3 \rightarrow F^- + H_3F_2^+ \tag{27}$$

$$H_3F_3 \rightarrow H^+ + H_2F_3^- \tag{28}$$

$$4HF \rightarrow H_4F_4 \tag{29}$$

$$5HF \rightarrow H_5F_5 \tag{30}$$

$$6HF \rightarrow H_6F_6 \tag{31}$$

$$H^+ + H_2F_2 \rightarrow H_3F_2^+ \tag{32}$$

$$F^- + H_2F_2 \rightarrow H_2F_3^- \tag{33}$$

$$F^- + H_3F_3 \rightarrow H_3F_4^- \tag{34}$$

$$F^- + H_4F_4 \rightarrow H_4F_5^- \tag{35}$$

For the gas phase formation of the polymers $(HF)_n$ (reactions 9, 11, and 29−31), $\Delta G°$ is a small positive number for all values of n at the MP2/6-311+G(d,p) level, reaching a maximum for $n = 3$ but decreasing through the remaining members of the series ($n = 4$, 5, and 6) in spite of the increasingly unfavorable entropy change that occurs in that direction. Since Hartree−Fock calculations, using the same basis set, predict that $\Delta G°$ keeps increasing as n does, electron correlation must be considered in these polymerization reactions for reliable results. Vapor pressure measurements, as well as a variety of spectral studies and model-fitting calculations, do support the existence of hydrogen fluoride polymers in liquid HF[2d,3g] and in other media.[3a,7,13h] Our calculated value of −16.0 kJ/mol for $\Delta H°$ (reaction 9) compares reasonably well with experimentally determined dissociation energies, of 12.41 and 12.73 kJ/mol for $(HF)_2$.[7c,e] The data in Table 2 predict that 13% of gaseous HF could exist in the various polymeric forms (7% hexamer, 3% pentamer, 1% tetramer and 2% dimer), qualitatively in agreement with the thermodynamic data quoted by Chase *et al.*[7m] for the polymers, and with the calculations of Redington which suggest that approximately 25% of gaseous HF is polymeric, primarily $(HF)_6$ at 299 K.[7i] The model used by Zhang *et al.* predicts even more polymer in the gaseous state.[13h] A comparison of our $\Delta G°$ values with the others mentioned above for these reactions is given in Table 3. The differences between the present work, the published thermodynamic data and the results of Redington are really quite small; predicted $\Delta H°$ values for the five clustering reactions are almost identical.

Table 2. Thermodynamic Data Calculated at 298 K for a Number of Reactions Involving H_nF_n, $H_nF_{n+1}^-$, and $H_{n+1}F_n^+$ Species[a]

	$\Delta H°$/ kJ mol^{-1}	$\Delta S°$/ J mol^{-1} K^{-1}	$\Delta G°$/ kJ mol^{-1}
$HF \rightarrow F^- + H^+$	1555.5	81.1	1531.3
$F^- + HF \rightarrow HF_2^-$	−189.1	−106.9	−157.3
$H^+ + HF \rightarrow H_2F^+$	−485.6	−92.1	−458.1
$3HF \rightarrow H_2F^+ + HF_2^-$	880.8	−117.9	915.9
$HF + HF_2^- \rightarrow H_2F_3^-$	−114.5	−101.6	−84.2
$2HF_2^- \rightarrow F^- + H_2F_3^-$	74.7	5.28	73.1
$HF + H_2F^+ \rightarrow H_3F_2^+$	−135.9	−112.8	−102.3
$HF + H_2F_3^- \rightarrow H_3F_4^-$	−88.6	−117.9	−53.5
$HF + H_3F_4^- \rightarrow H_4F_5^-$	−61.1	−113.3	−27.3
$H_2F_2 \rightarrow F^- + H_2F^+$	1085.9	72.5	1064.3
$H_2F_2 \rightarrow H^+ + HF_2^-$	1382.3	57.7	1365.1
$H_3F_3 \rightarrow F^- + H_3F_2^+$	982.9	97.7	953.7
$H_3F_3 \rightarrow H^+ + H_2F_3^-$	1300.8	94.2	1272.7
$HF_2^- \rightarrow H^+ + 2F^-$	1744.6	187.9	1688.5
$2HF \rightarrow H_2F_2$	−16.0	−83.6	8.9
$3HF \rightarrow H_3F_3$	−48.9	−221.6	17.2
$4HF \rightarrow H_4F_4$	−92.8	−348.9	11.2
$5HF \rightarrow H_5F_5$	−130.5	−460.9	6.9
$6HF \rightarrow H_6F_6$	−162.1	−559.2	4.7
$H^+ + H_2F_2 \rightarrow H_3F_2^+$	−605.5	−121.4	−569.3
$F^- + H_2F_2 \rightarrow H_2F_3^-$	−287.6	−124.9	−250.3
$F^- + H_3F_3 \rightarrow H_3F_4^-$	−343.3	−104.8	−312.1
$F^- + H_4F_4 \rightarrow H_4F_5^-$	−360.5	−90.7	−333.4

[a] All data were obtained using MP2/6-311+G(d,p) optimizations and frequency determinations.

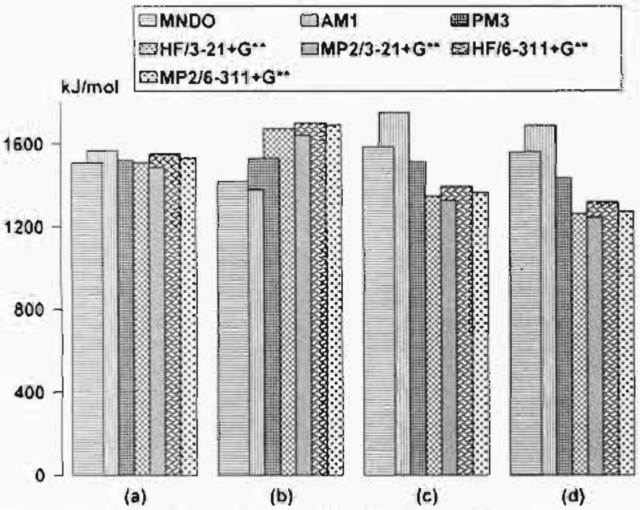

Figure 3. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods for: (a) $HF \rightarrow F^- + H^+$; (b) $HF_2^- \rightarrow H^+ + 2F^-$; (c) $H_2F_2 \rightarrow H^+ + HF_2^-$; (d) $H_3F_3 \rightarrow H^+ + H_2F_3^-$.

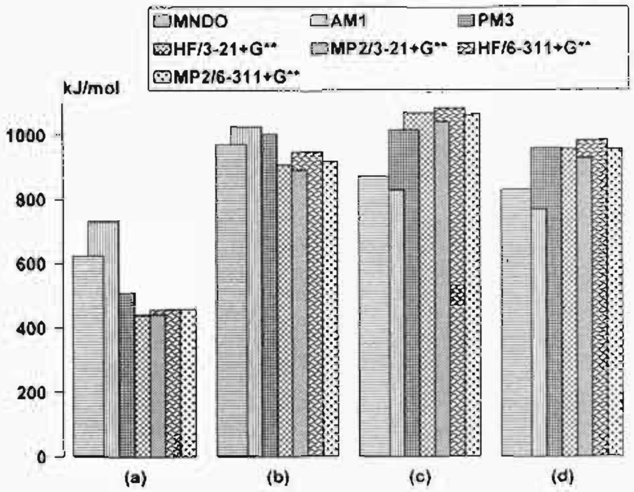

Figure 4. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods: (a) $H_2F^+ \rightarrow H^+ + HF$; (b) $3HF \rightarrow H_2F^+ + HF_2^-$; (c) $H_2F_2 \rightarrow F^- + H_2F^+$; (d) $H_3F_3 \rightarrow F^- + H_3F_2^+$.

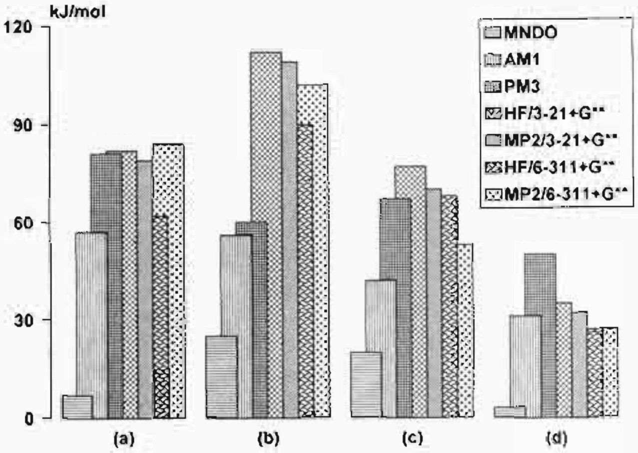

Figure 5. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods: (a) $H_2F_3^- \rightarrow HF + HF_2^-$; (b) $H_3F_2^+ \rightarrow HF + H_2F^+$; (c) $H_3F_4^- \rightarrow HF + H_2F_3^-$; (d) $H_4F_5^- \rightarrow HF + H_3F_4^-$.

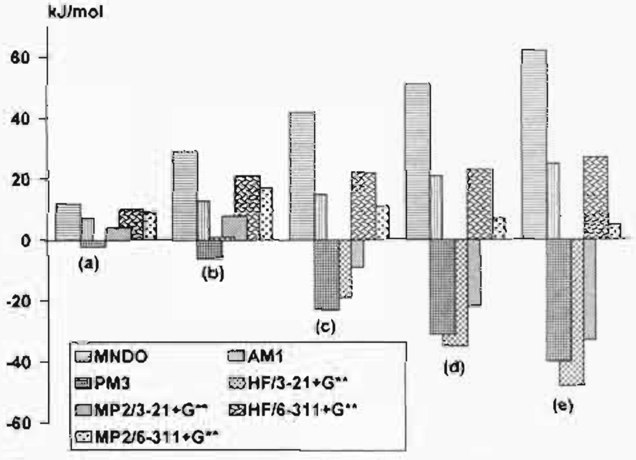

Figure 6. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods: (a) $2HF \rightarrow H_2F_2$; (b) $3HF \rightarrow H_3F_3$; (c) $4HF \rightarrow H_4F_4$; (d) $5HF \rightarrow H_5F_5$; (e) $6HF \rightarrow H_6F_6$.

Both MNDO and AM1 predict qualitatively the same result as the HF/6-311+G(d,p) calculation, whereas PM3, MP2/6-311+G(d,p), and *ab initio* methods using the 3-21+G(d,p) basis set suggest roughly the converse, namely that polymer formation becomes **more likely** as *n* increases from 3 to 6, qualitatively more in keeping with the calculations of Redington[7i] and of Zhang *et al.*[13h]

The formation of the two members of the cation series monofluorodihydrogen(I), H_2F^+, and difluorotrihydrogen(I), $H_3F_2^+$ (reactions 7 and 14) from H^+ and H_2F^+ respectively is spontaneous, a result qualitatively the same for all methods of calculation although the semiempirical methods seem to make H_2F^+ more stable *vis a vis* other species. Our $\Delta H°$ of −485.6 kJ/mol for reaction 7 at the MP2/6-311+G(d,p) level compares favorably with gas phase proton affinities of HF of −469 ± 8[14b] and −490 kJ/mol.[14a] Figure 9 illustrates what happens as H^+ is added to HF (at 1 atm) as determined by using equilibrium constants from MP2/6-311+G(d,p) calculations. For low initial pressures of H^+, $H_3F_2^+$ is the dominant cationic species. However, as the H^+ pressure increases $H_3F_2^+$ is formed in lesser amounts and the pressure of H_2F^+ increases to a maximum of 1 atm.

The four members of the polyfluorohydrogenate(1−) anion series, $H_nF_{n+1}^-$, are all favored with respect to the previous homologue or F^- (reactions 5, 13, 15, and 16), with the

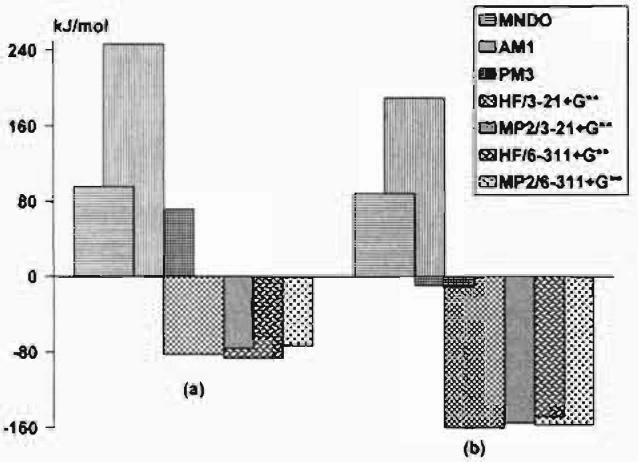

Figure 7. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods: (a) $F^- + H_2F_3^- \rightarrow 2HF_2^-$; (b) $F^- + HF \rightarrow HF_2^-$.

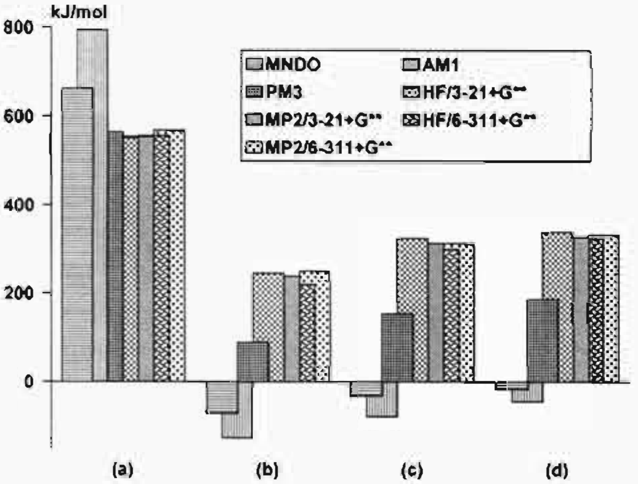

Figure 8. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods: (a) $H_3F_2^+ \rightarrow H^+ + H_2F_2$; (b) $H_2F_3^- \rightarrow F^- + H_2F_2$; (c) $H_3F_4^- \rightarrow F^- + H_3F_3$; (d) $H_4F_5^- \rightarrow F^- + H_4F_4$.

Table 3. $\Delta G°$ Values for the Reactions nHF → $(HF)_n$

n	$\Delta G°$/kJ mol^{-1}	ref
2	8.9	this work (298 K)
	10.3	7i (299 K)
	4.8	7m (298 K)
	4.1	13h (273 K)
3	17.2	this work (298 K)
	15.7	7i (299 K)
	8.0	7m (298 K)
	4.0	13h (273 K)
4	11.2	this work (298 K)
	9.0	7i (299 K)
	9.6	7m (298 K)
	−1.2	13h (273 K)
5	6.9	this work (298 K)
	2.7	7i (299 K)
	10.3	7m (298 K)
	−3.6	13h (273 K)
6	4.7	this work (298 K)
	−0.23	7i (299 K)
	−0.57	7m (298 K)
	−4.2	13h (273 K)

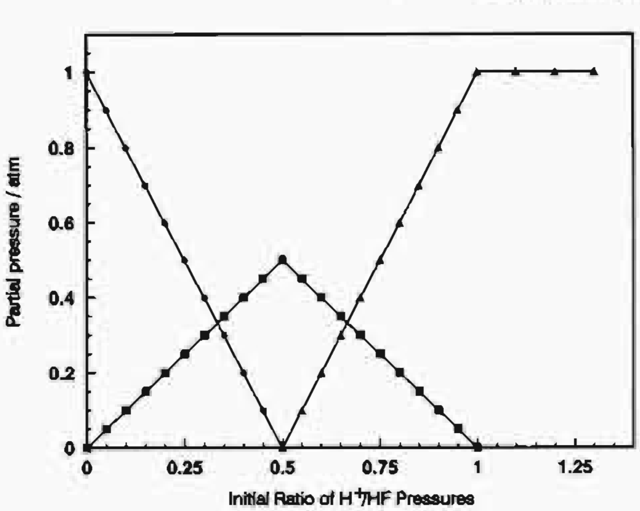

Figure 9. Partial pressures of various species as H^+ is added to HF (1 atm) using data from MP2/6-311+G** calculations: closed circles, HF; closed triangles, H_2F^+; closed squares, $H_3F_2^+$.

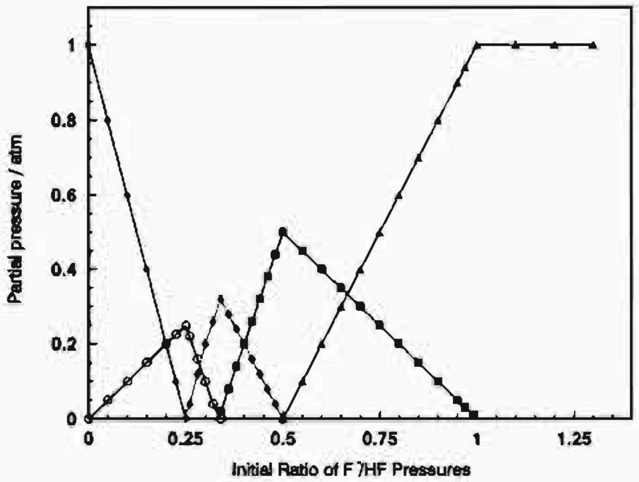

Figure 10. Partial pressures of various species as F^- is added to HF (1 atm) using data from MP2/6-311+G** calculations: closed circles, HF; closed triangles, HF_2^-; closed squares, $H_2F_3^-$; closed triangles, $H_3F_4^-$; open circles, $H_4F_5^-$.

equilibrium constant decreasing as n increases from 1 to 4. In the case of MNDO and AM1 calculations, however, the formation of HF_2^- is not predicted to be exergonic relative to HF and F^-. At the same time, MNDO and, to a lesser degree, AM1 underestimate the stability of members of the series relative to the preceding homologue. Our $\Delta H°$ of −189.1 kJ/mol for reaction 5 at the MP2/6-311+G(d,p) level compares favorably with the HF gas phase fluoride ion affinity of −162 kJ/mol.[15a] Figure 10 is an illustration of what MP2/6-311+G(d,p) calculations predict will happen to the anionic species as F^- is added to HF (1 atm). Initially, at low pressures of F^- relative to HF, $H_4F_5^-$ is the predominant anion. At higher F^- pressures $H_3F_4^-$ comes to dominate the mixture, followed in turn by $H_2F_3^-$ and HF_2^-, the latter reaching a constant pressure of 1 atm.

Because of the importance of the analogous reaction in the $HCl:AlCl_3$:ImCl melts, the disproportionation reaction (23) is particularly interesting. The gas phase value for K of 1.53×10^{-13} compares with 4.67×10^{-3} for the chlorine analogs in melts.[1d] In contrast to the four *ab initio* calculations, all three of the semiempirical methods suggest that K, for reaction 23, is much larger than 1.

A final word of caution is in order. Any thermodynamic calculation that contains a classic evaluation of $S°$ will underestimate the entropy for nonrigid molecules if conformations other than the lowest energy one are significantly populated. This entropy of mixing may mean that these molecules or ions are even **more favored** or **less disfavored**, by several kJ/mol, relative to their more rigid precursors than one would infer from our calculations.

Summary

While it is unwise to over interpret data arising from molecular orbital calculations it does seem that, based on the results of calculations at the MP2/6-311+G(d,p) level, the following conclusions may be drawn for reactions of HF, F^-, and H^+ occurring in the gas phase:

(i) At 298 K and 1 atm, 13% of HF will exist in a polymeric form, $(HF)_n$, the actual amount depending on the size of the polymer. Polymerization becomes more likely as n increases from 3 to 6. The amount of cluster formation is calculated to be only slightly less than that predicted in some earlier literature.

(ii) Reactions that form ions (reactions 5, 22, and 25–28) are extremely unlikely in the gas phase although one would expect solvation and other forces to increase the equilibrium constants substantially in condensed phases. For example, whereas $\Delta G°$ is over 1500 kJ/mol for the ionization of gaseous HF, it is 19.7 kJ/mol in aqueous solutions, meaning that a 1 M solution of HF produces 0.02 M H^+ and F^-.[23]

(iii) Once fluoride ion is available, the formation of the polyfluorohydrogenate(1−) anions, according to reaction 36, can proceed. Since $\Delta G°$ becomes less negative as n increases any one or several of the four anions could occur depending on the relative amounts of HF and F^-.

$$HF + H_nF_{n+1}^- \rightarrow H_{n+1}F_{n+2}^- \ (n = 0, 1, 2, \text{and } 3) \quad (36)$$

(iv) Once H^+ is available, the formation of the polyfluorohydrogen(I) cations according to reaction 37 can occur. $\Delta G°$ is less negative for $n = 0$ than $n = 1$ and either or both of the cations are possible depending on conditions.

$$HF + H_{n+1}F_n^+ \rightarrow H_{n+2}F_{n+1}^+ \ (n = 0 \text{ and } 1) \quad (37)$$

(v) The reactions of either H^+ or F^- with hydrogen fluoride polymers, to produce larger cations and anions (reactions 32–35), is highly improbable. Formation of these ions is more likely to occur by "solvation" of other ions by HF molecule(s).

In addition, the use of pure Hartree–Fock calculations or of the 3-21+G(d,p) basis set does not make a substantial difference in the thermodynamic results with the exception of those reactions in which the hydrogen fluoride polymers are formed. Generally speaking, of the semiempirical methods, PM3 gives results closest to those of *ab initio* methods although all methods give the same qualitative result when the absolute value of $\Delta G°$ is large. When $\Delta G°$ is small there may be a larger disagreement in percentage terms and even differences in sign. MNDO and, to a lesser degree, AM1 underestimate the stability of members of the anion series relative to the preceding homologue. In fact, both predict that HF_2^- would **not** be formed to any extent from F^- and HF contrary to all other methods. These two methods also overestimate the stability of H_2F^+ and, as a result, underestimate the stability of $H_3F_2^+$ from H_2F^+. For formation of HF polymers, MNDO, AM1 and HF/6-311+G(d,p) calculations do not agree with the known relative order of stability while PM3, MP2/6-311+G(D,p), and 3-21+G(d,p) results do.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada for support in the form of a scholarship to J.L.C.

IC950030G