

# Proton Solvation in Nonaqueous HF as a Main Factor That Determines Its Superacidic Properties

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**Abstract**—The Hartree–Fock method and electron correlation at the MP2 level in the 6-31++G\*\* basis set is used together with the combined method for taking into account solvation (the discrete model of microsolvation and the polarizable continuum model (PCM)) to study the following molecular systems in the medium of liquid HF:  $[\text{HFH}]^+$ ,  $[\text{HFHFH}]^+$ ,  $[\text{HF} \dots \text{HF} \dots \text{FH}]^+$ ,  $[\text{HF} \dots \text{HFHFH} \dots \text{FH}]^+$ , and  $[\text{HF} \dots \text{HF} \dots \text{HFH} \dots \text{FH}]^+$ . The results of calculation make it possible to explain the anomalously high activity of protons in nonaqueous HF by a lower solvation energy of protons in liquid HF (by 48 kcal/mol) than in water. A conclusion is drawn that the combined method used in this work (the discrete model of microsolvation and PCM) is an efficient tool in estimating the contribution from the solvation to the thermodynamic parameters of the reaction in liquid HF.

## INTRODUCTION

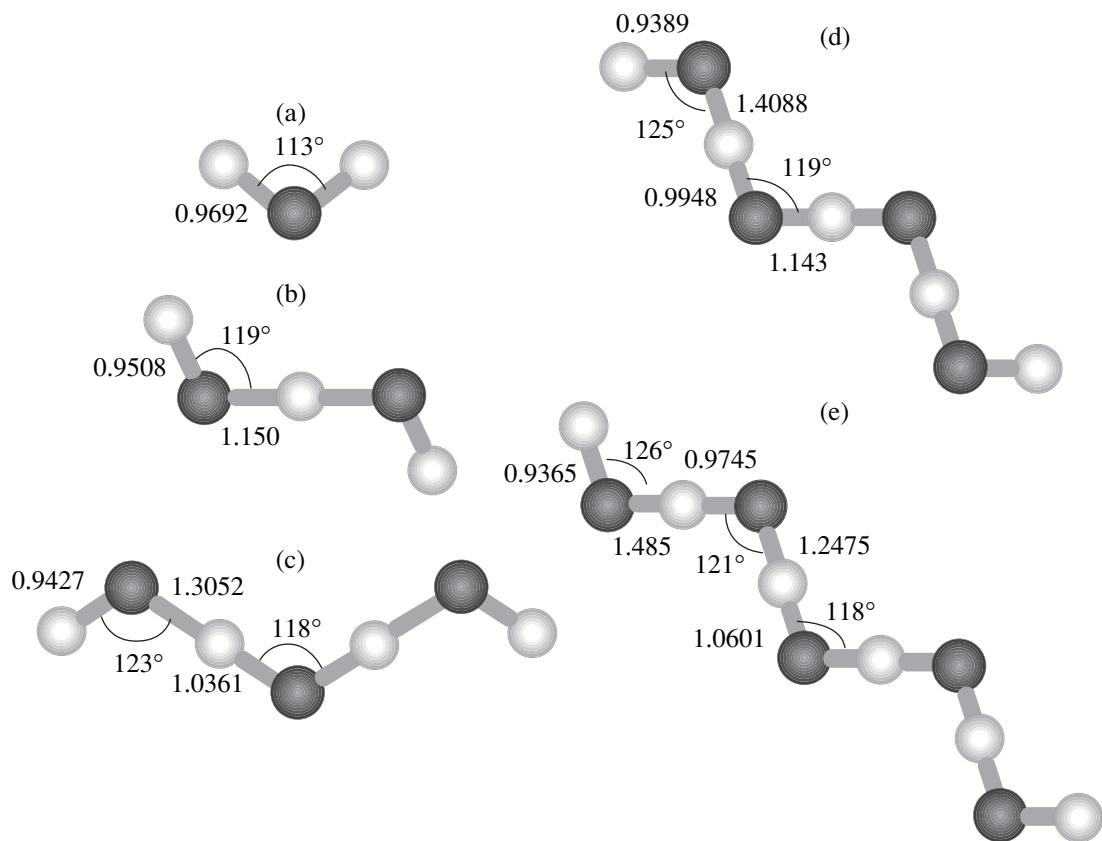
Superacids are acids capable of protonating even very weak bases. Their strength is usually measured in terms of the Hammett acidity function  $H_0$ . The use of dissociation constants  $K_0$  or  $pK_a$  for this purpose does not make sense because the extent of dissociation of superacids is very low. For instance, the dissociation constant of 100% sulfuric acid is as low as  $10^{-4}$  [1], and that of liquefied HF is  $10^{-10}$  [2]. The dilution of acids with water leads to an increase in the extent of their dissociation and to a decrease in their strength. In our opinion, the cited features of superacids are due to the fact that the main factor that determines the unusual properties of superacids is the low energy of proton solvation by superacid molecules. Since the 1940s, liquefied HF has been widely used as a catalyst for isoparaffin alkylation by olefins in industrial practice [3]. Therefore, energetics data on the dissociation of nonaqueous hydrogen fluoride and the solvation of protons formed in this process are of interest for understanding the mechanism of formation and the nature of HF-solvated alkylcarbenium ions, which are active intermediates in HF-catalyzed hydrocarbon conversions.

The goal of this work is to estimate the energy of proton solvation in 100% hydrofluoric acid and to analyze the energy balance of HF self-dissociation taking into account solvation effects using *ab initio* quantum-chemical calculations taking into account electron correlation according to the perturbation theory MP2 and modern models of solvation.

## QUANTUM-CHEMICAL CALCULATION

When calculating the proton solvation energy in liquefied HF, we used the experimental value of the proton affinity of an HF molecule in the gas phase

(112 kcal/mol [4]) and the solvation energy of  $[\text{HFH}]^+$  in liquefied HF calculated using a quantum-chemical method. The solvation energy calculation was carried out in two stages. First, the cluster approximation was used together with the Hartree–Fock method in the 6-31++G\*\* basis set and electron correlation at the MP2 perturbation theory level, and the structures and the energies of formation of the  $[(\text{HFH})^+ \cdot (\text{HF})_n]$  clusters ( $n = 1–4$ ) in the gas phase were calculated with full geometry optimization. We also calculated the force-constant matrices and analyzed normal vibrations of stationary points on the potential energy surface. Vibration frequencies thus calculated were used without correcting multipliers in estimating the zero-point energies (ZPE). Then, in the framework of the continuum model of solvation using the polarizable continuum model (PCM) [5], we estimated the additional contribution from the electrostatic interactions of these clusters with surrounding molecules of liquid HF to the solvation energy. Liquid HF was modeled by the continual medium with a dielectric constant  $\epsilon$  of 84. The electrostatic component of the free energy of solvation  $\Delta G_{\text{el}}$  was calculated in the framework of the PCM model at the MP2 level. To analyze the electron structure, we used effective Mulliken charges obtained by the Hartree–Fock method. When calculating the reaction enthalpies of cluster formation, we used full energies calculated at the MP2 level in the 6-31++G\*\* basis set. This makes it possible to reduce the error that appears due to basis incompleteness. The calculated full energies, zero-point energies, and the  $\Delta G_{\text{el}}$  components of the solvation energies for the clusters are presented in the table. The structures of clusters are shown in the figure with calculated distances between the HF molecules and between a proton and neighboring HF molecules. Based on these data, we calculated the enthalpies



Structures of clusters (a)  $[\text{HFH}]^+$ , (b)  $[\text{H}(\text{FH})_2]^+$ , (c)  $[\text{H}(\text{FH})_3]^+$ , (d)  $[\text{H}(\text{FH})_4]^+$ , and (e)  $[\text{H}(\text{FH})_5]^+$ . Distances are given in angstroms.

of cluster formation, which are also presented in the table. Quantum-chemical calculations were carried out using the program packages GAMESS [6] and GAUSSIAN 98 [7] and SGI Power Challenge (Zelinskii Institute of Organic Chemistry, Moscow) and Pentium II (300 MHz) computers.

## RESULTS AND DISCUSSION

The results of our calculations showed that the interaction of the  $[\text{HFH}]^+$  ions with one HF molecule results in the formation of a symmetric cation with two equivalent very short hydrogen bonds of 1.151 Å (see figure). To be more exact, we deal with the  $[\text{HFHFH}]^+$  cat-

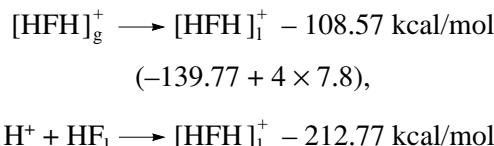
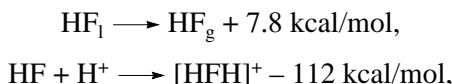
Full energies ( $E$ ), energies of interaction in the gas phase ( $\Delta E$ ), zero-point energies ( $ZPE$ ), and the electrostatic contribution to the free energy of solvation ( $\Delta G_{\text{el}}$ ) of the most stable complexes according to MP2/6-31++G\*\* calculations

Molecule or complex	$E$ , a.u.	$ZPE$ , kcal/mol	$\Delta E$ , kcal/mol	$\Delta H^0 = \Delta E + ZPE$ , kcal/mol	$\Delta G_{\text{el}}$ , kcal/mol	$\Delta H^0 + \Delta G_{\text{el}}$ , kcal/mol	$\Delta H^0 + \Delta G_{\text{el}} - n\Delta E_{\text{HB}} (\text{FH})^*$ , kcal/mol
FH	-100.2159192	5.89	—	—	—	—	—
$[\text{HFH}]^+$	-100.406401	12.05	119.53	113.37	94.96	208.33	200.53
$[\text{H}(\text{FH})_2]^+$	-200.6753069	19.48	152.78	145.08	79.26	224.34	208.74
$[\text{H}(\text{FH})_3]^+$	-300.9270679	27.32	175.27	165.61	69.42	235.24	211.84
$[\text{H}(\text{FH})_4]^+$	-401.1705967	34.69	192.59	181.46	63.19	244.65	213.45
$[\text{H}(\text{FH})_5]^+$	-501.4098333	42.25	207.23	194.42	58.72	253.12	214.12

\*  $E_{\text{HB}}(\text{FH}) = 7.8$  kcal/mol [8] (HB is for hydrogen bond).

ion in this case. The energy of its formation in the gas phase corrected for the zero-point energy is 31.71 kcal/mol. The estimated contribution of the additional electrostatic interaction with the surrounding molecules of liquid HF is 79.26 kcal/mol in the framework of the continuum model. As can be seen from the figure, the interaction of the  $[\text{HFH}]^+$  ion with two HF molecules occurs with the formation of a trimer with two equivalent short hydrogen bonds between the  $[\text{HFH}]^+$  cation and two HF molecules, which have symmetric positions. The lengths of these bonds are 1.305 Å. The energy of trimer formation in the gas phase with the correction for the zero-point energy is 52.24 kcal/mol. The estimated contribution of the additional electrostatic interaction with the surrounding molecules of liquid HF further increases the solvation energy by 69.42 kcal/mol in the framework of the continuum model. When the  $[\text{HFH}]^+$  ion interacts with three HF molecules, a local minimum appears on the potential energy surface. It corresponds to a tetramer with two very short hydrogen bonds (1.1436 Å) and two hydrogen bonds with a medium length 1.409 Å (see the figure). In this case, it is more exact to speak about the  $[\text{HFHFH}]^+$  cation, which was solvated by HF molecules. The energy of tetramer formation in the gas phase with the correction for the zero-point energy is 68.09 kcal/mol. The estimated contribution to the solvation energy of liquid HF is 63.19 kcal/mol in the framework of the continuum model. When the  $[\text{HFH}]^+$  ion interacts with four HF molecules, a local minimum appears on the potential energy surface. It corresponds to a pentamer in which the  $[\text{HFH}]^+$  cation is bound to two HF molecules in the first solvate shell via very short hydrogen bonds (1.247 Å). Two HF molecules enter the second solvate shell of the  $[\text{HFH}]^+$  cation. They are bound to the HF molecules of the first solvate shell via two medium-length hydrogen bonds (1.485 Å, see the figure). The energy of pentamer formation in the gas phase corrected for the zero-point energy is 81.05 kcal/mol, and this value additionally increases by 58.72 kcal/mol due to the effect of liquid HF according to the estimates of the solvation energy in the framework of the continuum model. As can be seen from these data, the overall value of the solvation energy (microsolvation plus the contribution from the continuum electrostatic model) of the  $[\text{HFH}]^+$  ion is close to 253 kcal/mol.

To find the full energy of  $[\text{HFH}]^+$  cation solvation by liquid HF, we subtracted the correction for the transfer of four HF molecules ( $n = 4$ ) from liquefied HF to the gas phase from the calculated solvation energy. It can be taken as equal to the experimental value of hydrogen bond energy in liquefied HF (7.8 kcal/mol [8]). Thus, the full energy of  $[\text{HFH}]^+$  ion solvation by liquid HF can be determined from the following thermodynamic cycle:



The resulting value is 48 kcal/mol lower than the heat of proton hydration in an aqueous solution, which is equal to 261 kcal/mol [9].

To check the accuracy of our quantum-chemical calculations, we also calculated the energy of self-dissociation of liquid hydrofluoric acid. This value can be compared with an experimental value of +14 kcal/mol [2]. The calculated value of the heat of solvation for the octahedral complex containing six HF molecules in the first coordination shell of the fluoride ion equal to ~145 kcal/mol [11] was used as an estimate of the energy of fluoride ion solvation by HF molecules in the liquefied acid. To estimate the self-dissociation energy of hydrofluoric acid, we used the experimental value of HF self-dissociation in the gas phase equal to 370 kcal/mol [9]. Then, taking into account the calculated energy of  $[\text{HFH}]^+$  cation solvation (213 kcal/mol) and  $\text{F}^-$  anion solvation (145 kcal/mol), the energy of self-dissociation of liquid hydrofluoric acid is 12 kcal/mol. The coincidence of the calculated and experimental values of the self-dissociation heat is almost quantitative in this case. This fact confirms that our calculations are accurate.

Earlier, the anomalously high activity of protons in liquefied HF was noted in [10]. It is well known that, due to the high strength of the H–F bond, the heterolytic dissociation of an HF molecule requires much more energy than the dissociation of other hydrogen halides. Indeed, the energies of heterolytic dissociation of HF, HCl, HBr, and HI molecules in the gas phase are 370, 333, 324, and 314 kcal/mol, respectively [9]. In an aqueous solution, these differences are much less pronounced because of hydration of protons and halide anions, and the energy of the heterolytic dissociation of HF is higher than the corresponding values for other hydrogen halide acids by only 11–12 kcal/mol. The reason for this phenomenon is the higher energy of fluorine ion hydration compared to  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  [9]. Nevertheless, despite this fact, the aqueous solutions of hydrofluoric acid belong to the medium-strength acids with an ionization constant as low as  $10^{-3}$  mol/l. On the other hand, although the dissociation constant of liquefied HF is still lower ( $10^{-10}$  mol/l), nonaqueous HF is a superacid because the corresponding value of the Hammett function is  $H_0 = -10$ , almost the same as for 100% sulfuric acid. This strong difference in the behavior of nonaqueous hydrofluoric acid from the behavior of its aqueous solutions is associated with the difference in the solvation energy of protons and fluorine ions by HF and water molecules. Indeed, according to our calculations, the energy of fluorine ion solvation in liquid HF is 145 kcal/mol [11], which is ~35 kcal/mol higher than the corresponding value for aqueous solutions. A sub-

stantial difference in proton solvation by HF and water molecules also follows from our results (213 and 261 kcal/mol, respectively). Thus, the superacidic properties of liquefied nonaqueous HF are not due to the high extent of its dissociation. Rather, they are due to the weaker solvation of protons compared to aqueous solutions. Therefore, protons have a higher chemical potential and anomalously high reactivity.

To conclude, we would like to note that the anomalously high activity of protons in liquid HF is general and is also relevant to other superacids as well. To be a superacid, the strong acid itself should play the role of a solvent and it should solvate anions formed by acid dissociation to a maximum degree and protons to a lesser degree. In agreement with this statement, all superacids known to date are nonaqueous solutions of strong acids or mixtures based on strong acids. Note that the accuracy of calculations based on the combined method of taking into account solvation permits us to anticipate its applicability to estimating the contributions of solvation to thermodynamic parameters of reactions in the medium of liquefied HF.

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#### REFERENCES

1. Nekrasov, B.V., *Osnovy obshchei khimii* (Foundations of General Chemistry), Moscow: Khimiya, 1969, vol. 1, p. 518.
2. Cotton, F. and Wilkinson, J., *Advanced Inorganic Chemistry: A Comprehensive Text*, New York: Wiley, 1965, part 2.
3. Corma, A. and Martinez, A., *Catal. Rev. – Sci. Eng.*, 1993, vol. 35, p. 483.
4. Foster, M.S. and Beauchamp, J.L., *Inorg. Chem.*, 1975, vol. 14, p. 1229.
5. Miertus, S., Scrocco, E., and Tomasi, J., *Chem. Phys.*, 1981, vol. 55, p. 117.
6. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S.J., Windus, T.L., Dupuis, M., and Montgomery, J.A., Jr., *J. Comput. Chem.*, 1993, vol. 14, no. 12, p. 1347.
7. *Gaussian 98, Revision A.7*, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.J., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, G.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A., Pittsburgh: Gaussian, 1998.
8. *Kratkaya khimicheskaya entsiklopediya* (Abridged Chemical Encyclopedia), Knunyants, I.L., Ed., Lenigrad: Sov. Entsiklopediya, 1961, vol. 1.
9. Bell, R.P., *The Proton in Chemistry*, London: Chapman and Hall, 1973.
10. Hammett, L.P., *Physical Organic Chemistry*, New York: McGraw Hill, 1970.
11. Kazansky, V.B., *Top. Catal.*, 2000, no. 11/12, p. 55.