

Revisiting the Acid–Base Equilibrium in Aqueous Solutions of Hydrogen Halides: Study by the *ab Initio* Electronic Structure Theory Combined with the Statistical Mechanics of Molecular Liquids

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Abstract: The classical problem of acid strength of the hydrogen halides in aqueous solution is revisited by means of the RISM-SCF/MCSCF theory, an *ab initio* electronic structure theory combined with the statistical mechanics of molecular liquids. Free energy changes associated with the chemical equilibrium $\text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{X}^- + \text{H}_3\text{O}^+$ are studied for a series of hydrogen halides (X: F, Cl, Br, I). The free energy differences between hydrogen halides and the dissociated anions are mainly governed by the subtle balance of the two energetic components—formation energies of hydrogen halides and solvation energies of the anions. It is shown that hydration structure around hydrogen fluoride is qualitatively different from the other three hydrogen halides. The well-known specificity of the hydrogen fluoride with respect to the acidity in aqueous solution is explained in terms of the characteristic hydration structure. Molecular geometries and electronic structures of the solute molecule as well as the solvation structure and free energy components are also discussed in detail. The old concept of electronegativity proposed by Pauling is reexamined on the basis of the modern theoretical approach.

1. Introduction

The acidity of hydrogen halides (HX, where X = F, Cl, Br, I) is one of those phenomena which have been most intensively studied by means of the quantum chemistry in its earlier history. The quantum chemistry could have successfully predicted the order of acidity in the gas phase, namely, $\text{F} < \text{Cl} < \text{Br} < \text{I}$, from the bond energy or the formation energy of HX. However, there were several interesting questions in these phenomena, that could not have been solved just by the quantum chemistry. First, the formation energies are largely negative in all of the hydrogen halides and they cannot dissociate in the gas phase under normal conditions, which of course is not the case in aqueous solutions. Second, while hydrogen chloride, bromide, and iodide completely dissociate in aqueous solutions, hydrogen fluoride shows a small dissociation constant. Using the experimental data for the solvation free energies of the solutes in aqueous solution, Linus Pauling gave a heuristic explanation of the phenomena in terms of the electronegativity. According to the explanation by McCoubrey¹ and Pauling,² the dissociation constants are determined not only by the formation energy but also by the solvation free energy. Moreover, the dissociation constant of the hydrogen halide is determined by a different dependency of the two energetic components on the electronegativity x of the halogens, the formation energy that depends quadratically on x and the solvation free energy that depends linearly on x .² The explanation, however, is phenomenological, and many questions concerning the microscopic process remain to be resolved. Does the classical concept proposed by Pauling, “electronegativity”, still make sense after all the theoretical developments in quantum chemistry? If it does, how is the

concept interpreted in terms of the *ab initio* electronic structure theory? Are those dependencies of the formation energy and the solvation free energy on the electronegativity correct? If they are, what is the microscopic process to produce such dependencies? Answering such questions based on modern theoretical methods is of fundamental importance in general chemistry, because the classical concepts are still used in a broad field of chemistry, and have been taught in high-school text books as a pedagogical tool for explaining quantum processes in a molecule.

The phenomenon described above is a typical process in which the electronic structure of molecules and solvation processes is closely coupled. A theoretical treatment of such processes inevitably requires a method that is able to describe the electronic structure of molecules in question and statistical solvent effects on the electronic structure. This is a nontrivial theoretical problem by any standard, and that may be the reason the problems have not been challenged for a long time by modern quantum chemistry despite their importance in chemistry.³

Recently, we have developed a powerful method to treat the electronic structure of a molecule in solution based on the *ab initio* molecular orbital theory and the statistical mechanics of molecular liquids.^{4–7} The method referred to as RISM-SCF/MCSCF determines electronic structure (MO; molecular orbital) as well as the geometry of a solute molecule and the statistical solvent distribution around the solute in a consistent manner.

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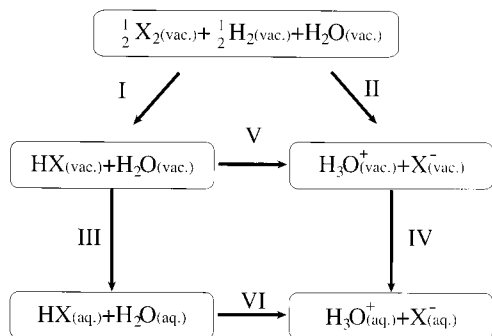
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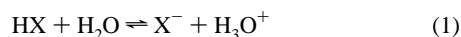
Scheme 1. Thermodynamic Cycle for Chemical Processes of Hydrogen Halides

All other physicochemical properties such as the solvation free energy are readily derived from the primary quantities. The theory has been successful in exploring a variety of physicochemical processes in solution.^{8–10}

In the present study, we revisit the classical problem of the acidity of a series of hydrogen halides in aqueous solutions using the new theoretical approach. In the following section, we describe briefly the model and methodologies employed in the study. Section 3 is devoted to the detailed analysis of the free energy change associated with the dissociation reaction as well as the solvation structure of the relevant species in the solutions. Pauling's electronegativity concept and his analysis regarding the acidity of hydrogen halides is examined in light of the new theoretical results.

2. Methods

2.1. Computational Procedure. In the present study, we assume the following dissociation process for hydrogen halides in water,



To facilitate the calculation of the free energy change associated with the reaction of eq 1 in aqueous solution, a thermodynamic cycle is employed which is shown in Scheme 1. Both “aq.” and “vac.” are used to distinguish aqueous and vacuum environments. A system containing homonuclear halide and hydrogen dimers was chosen as the standard state. In the study of aqueous solutions, we regard the species concerning the reaction, HX, X[−], H₂O, H₃O⁺, as “solutes” in the infinitely dilute solution. Then the free energy difference in aqueous solution, Δ*G*(VI), can be written in terms of the energy differences associated with the reaction in vacuo (Δ*G*(I), Δ*G*(II)) and the free energy change due to the solvation as

$$\Delta G(\text{VI}) = \{\Delta G(\text{II}) + \Delta G(\text{IV})\} - \{\Delta G(\text{I}) + \Delta G(\text{III})\} \quad (2)$$

where all free energy differences corresponding to the reaction process are shown in the scheme. The free energy differences, Δ*G*(I), Δ*G*(II), and Δ*G*(V), are concerned with the reaction in vacuo, and can be decomposed into electronic energy change, Δ*E*_{elec}, and kinetic (translational, rotational and vibrational) contributions, Δ*G*_{kin}. These components can be readily calculated from the elementary statistical mechanics for ideal gas.

There is a controversy concerning which state of an excess proton in liquid water is most stable, H₃O⁺, H₅O₂⁺, or others.¹¹ However, since our present interests are mainly in relative acidity of a series of hydrogen halides in water, in light of the thermodynamic cycle (Scheme 1), our

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main conclusion does not depend on the assumption regarding the state of an excess proton.

Δ*G*(III) and Δ*G*(IV) concern the solvation process and can be decoupled into two contributions as

$$\Delta G = \Delta\mu_{\text{HNC}} + \Delta E_{\text{reorg}} \quad (3)$$

where Δ*μ*_{HNC} is the excess chemical potential or the solvation free energy and Δ*E*_{reorg} is the electronic reorganization energy. It is assumed that the kinetic contributions do not change upon transferring solute from in vacuo to aqueous solution.

Δ*μ*_{HNC} can be computed from the Singer–Chandler equation¹² expressed in the total and direct site–site correlation functions in molecular liquid theory,

$$\Delta\mu_{\text{HNC}} = \frac{\rho}{\beta} \sum_{\alpha} \sum_{s} \int \text{d}\mathbf{r} \left[\frac{1}{2} h_{\alpha,s}^2(r) - c_{\alpha,s}(r) - \frac{1}{2} h_{\alpha,s}(r) c_{\alpha,s}(r) \right] \quad (4)$$

It is noted that these correlation functions are obtained by solving the RISM-SCF/MCSCF equation, which optimizes both the solute electronic structure and the solvation structure simultaneously.

Δ*E*_{reorg} is defined as the difference of the electronic energies in aqueous solution, *E*_{elec}^{aq}, and in vacuo, *E*_{elec}^{vac}.

$$\Delta E_{\text{reorg}} = E_{\text{elec}}^{\text{aq}} - E_{\text{elec}}^{\text{vac}} \quad (5)$$

This energy includes not only contributions from the distortion of electronic structure but also those due to the relaxation of molecular geometry upon transferring solute from the gas phase to the aqueous solutions.

2.2. Polarization Energy. Solving the RISM–SCF equations can determine the solute wave function in solution as well as the microscopic solvent distribution around the solute molecule described in terms of a set of total correlation functions. The polarization (or distortion) effects on the solute electronic structure are automatically treated in a framework of the mean field approximation. However, in the present study, polarization of atomic anions (X[−]) cannot be taken into account because of the spherical symmetry of the field around the anions. In this section, we discuss a procedure to estimate the contribution of electronic polarization of the halide anions to the solvation free energies.

Consider the components of the average electric field exerted on an anion in one direction along the each axis ⟨*F*_{*x*}⟩, ⟨*F*_{*y*}⟩, and ⟨*F*_{*z*}⟩. Due to the symmetry of the field around the anions, all the contributions from such induced polarization effects are exactly canceled,

$$\langle F_i \rangle = \langle \vec{F}_i \rangle + \langle \vec{F}_i \rangle = 0 \quad (6)$$

where *i* stands for *x*, *y*, or *z*. We approximate the stabilization energy Δ*E*_{stab} by an interaction between simple induced dipole moments and the electric fields as

$$\begin{aligned} \Delta E_{\text{stab}} &\approx -\frac{1}{2} \langle \mu_{\text{ind}} \rangle \cdot \langle \vec{F} \rangle \\ &= -\frac{1}{2} (\langle \mu_x \rangle \langle \vec{F}_x \rangle + \langle \mu_y \rangle \langle \vec{F}_y \rangle + \langle \mu_z \rangle \langle \vec{F}_z \rangle) \\ &= -\frac{\alpha}{2} (\langle \vec{F}_x \rangle^2 + \langle \vec{F}_y \rangle^2 + \langle \vec{F}_z \rangle^2) \end{aligned} \quad (7)$$

where α, μ_{ind} are the polarizability and the induced electronic dipole moment of an anion, respectively. The component of the electric field in each direction can be calculated by the following equation;

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$$\begin{aligned} \langle \vec{F}_i \rangle &= \int_{\text{one direction}} d\mathbf{r} \left(-\frac{\partial}{\partial i} \sum_s \frac{q_s}{|\mathbf{r}|} \right) g_s(\mathbf{r}) \\ &= \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \int_0^\infty dr \sum_s \frac{q_s}{r^3} g_s(r) r \cos \theta r^2 \sin \theta \end{aligned} \quad (8)$$

In the present method, the whole solvation energy, $\Delta E_{\text{solvation}}$, of the system is described as follows.

$$\begin{aligned} \Delta E_{\text{solvation}} &= (E_{\text{elec}}^{\text{aq}} + \Delta\mu_{\text{HNC}}) - E_{\text{elec}}^{\text{vac}} \\ &= \Delta\mu_{\text{HNC}} + \Delta E_{\text{reorg}} \end{aligned} \quad (9)$$

The latter $\Delta\mu$ can be further decomposed into two components: the first-order interaction $\Delta\mu_0$, representing the interaction energy of unpolarized solute with solvent molecules, and a solute–solvent stabilization energy arising from the polarization of solute electronic structure ($\Delta E_{\text{stab}} = \Delta\mu_{\text{HNC}} - \Delta\mu_0$). As discussed by Gao, a simple relationship,

$$\Delta E_{\text{stab}} = -2\Delta E_{\text{reorg}} \quad (10)$$

is obtained from a classical linear response theory.¹³ Thus it is possible to evaluate $\Delta E_{\text{solvation}}$ of an anion by the following equation.

$$\begin{aligned} \Delta E_{\text{solvation}} &= \Delta\mu_0 + \Delta E_{\text{stab}} + \Delta E_{\text{reorg}} \\ &\approx \Delta\mu_0 + \frac{1}{2}\Delta E_{\text{stab}} \end{aligned} \quad (11)$$

Note $\Delta\mu_0$ in the above equation is equivalent to the $\Delta\mu_{\text{HNC}}$ only in the case of an atomic anion since the RISM-SCF procedure does not affect the electronic structure in an atomic solute molecule. ΔE_{stab} can be computed from eqs 7 and 8 by using the pair correlation function around the anions.

2.3. Computational Detail. Since details of the RISM–SCF/MCSCF procedure have been reported previously,^{5–10} we shall make brief comments concerning the approximation and models used in the present study. The standard triple- ζ plus polarization basis sets with diffuse functions ($\alpha_{\text{p}}(\text{F}) = 0.0740$, $\alpha_{\text{p}}(\text{Cl}) = 0.0490$, $\alpha_{\text{p}}(\text{Br}) = 0.0376$, and $\alpha_{\text{p}}(\text{I}) = 0.0368$ ¹⁴) were employed in the Hartree–Fock (RHF) method and second-order Møller–Plesset (MP2) method. Note that second-order correlation energy is different from the usual one in the gas phase since the orbital energy is defined from the solvation Fock operator.¹⁰ It is well-known that the relativistic effects become serious problems in the MO calculation for heavy elements with many electrons. To take account of such effects, we have used the effective core potential (ECP) parameters suggested by Stevens et al.¹⁵ for bromine and iodine atoms.

The RISM equations are solved by using the hypernetted chain (HNC) approximation. The solvent water model used in the present study is the SPC-like¹⁶ model,⁸ which has been successful in liquid-phase calculations. A set of Lennard-Jones potential parameters for halide anions proposed by Kinoshita et al. was employed.¹⁷ Unfortunately, the parameters for hydrogen halides were not available in the literature, we therefore determined these parameters in the following manner. The same σ values as for halide ions are used for halogen atoms in hydrogen halides. The ϵ values are then calculated from those σ values, experimental values of polarizability,^{17,18} and total number

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Table 1. Lennard-Jones Potential Parameters for Solute–Water Interaction

	HX		X [−]	
	σ (Å)	ϵ (kcal/mol)	σ (Å)	ϵ (kcal/mol)
F	2.72	1.364	2.72	0.348
Cl	3.62	0.364	3.62	0.448
Br	3.90	0.529	3.90	0.658
I	4.32	0.633	4.32	0.806

Table 2. Optimized Geometry of the Homonuclear Halogen Dimers and Hydrogen Halides

	in vacuo			aq solution	
	RHF	MP2	exp ^a	RHF	MP2
	bond length (in Å)				
F ₂	1.336	1.419	1.435		
Cl ₂	2.005	2.027	1.988		
Br ₂	2.294	2.322	2.284		
I ₂	2.675	2.700	2.667		
HF	0.898	0.918	0.917	0.920	0.941
HCl	1.272	1.276	1.274	1.280	1.284
HBr	1.406	1.413	1.415	1.411	1.418
HI	1.594	1.597	1.609	1.595	1.599
H ₂ O	0.941	0.958	0.957	0.965	0.982
H ₃ O ⁺	0.960	0.976		0.982	1.000
	bond angle (in deg)				
H ₂ O	107.1	105.1	104.5	105.5	103.8
H ₃ O ⁺	115.5	113.4		108.7	106.7

^a Experimental value taken from ref 20.

of electrons by using the Mavroyannis–Stephen theory.¹⁹ The resultant parameters for halide atoms are summarized in Table 1. All the interactions between the atoms in solute and solvent molecules are determined by means of the standard combination rule.⁸ All the calculations were performed at 298.15 K and a density of 1.0 g/cm³.

3. Results and Discussion

3.1. Molecular Structure and Electronic Properties. In Table 2, the optimized geometry both in vacuo and in aqueous solution is reported. It is worth noting that the geometries determined by RHF and MP2 in vacuo are in good agreement with the experimental results²⁰ and with the previous theoretical estimates by ab initio MO calculations,^{21–23} except for the bond length of F₂, the present RHF reproduced the experimental data for HX and X₂ within 2% of accuracy. Inclusion of the electron correlation effect in the MP2 level makes the description of F–F and H–X bond lengths better, while it worsens the results for the other X–X bond lengths.

Solvent effects due to surrounding water molecules slightly increase the bond lengths. The most significant change was found in the HF molecule (+0.02 Å), and it becomes smaller going from HCl (+0.008 Å) to HI (+0.002 Å). Chipot et al. reported the optimized geometries for HF and HCl in aqueous solution, which were obtained by using the dielectric continuum model for solvent.²⁴ The trend of increasing bond lengths is very similar to our results, but the solvent effect found in their calculations is rather small (0.005 Å for HF and 0.003–0.004 Å for HCl) compared to ours. The difference between their calculations and ours lies in the treatment of solvent effect and

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Table 3. Dipole Moment and Effective Charge on Heavy Atoms^a

	dipole moment/D			Mulliken charge		ESP charge	
	gas	exp	aq	gas	aq	gas	aq
HF	2.08	1.82	2.51	-0.376	-0.460	-0.484	-0.569
HCl	1.47	1.11	2.10	-0.211	-0.293	-0.246	-0.345
HBr	1.03	0.83	1.66	-0.181	-0.249	-0.158	-0.248
HI	0.66	0.45	1.18	-0.078	-0.128	-0.089	-0.156
H ₂ O	2.27		2.99	-0.616	-0.788	-0.850	-1.067
H ₃ O ⁺	1.39		2.54	-0.406	-0.470	-0.607	-0.725

^a Calculated by the RHF method at each optimized geometry.

the basis set employed for the MO calculation. As we discuss later, we found very strong hydrogen bonding between the HX and surrounding water molecules in the present system, which has significant effects on the bond length of HX. It is very likely that the results by Chipot et al. might have underestimated the change of bond lengths, because the continuum model cannot take account of the hydrogen bond.

The results for dipole moments and effective charges both in vacuo and in aqueous solution are listed in Table 3. It is

known that the agreement of dipole moments calculated by the RHF method with experimental values is not generally good, but the method reproduces the qualitative trend of dipole moments in the series of hydrogen halides. HF has the largest dipole moment in both the gas and aqueous phases, suggesting that it has the most conspicuous ionic character in the electronic structure among the hydrogen halides. Dipole moments decrease in going from light to heavy halogen atoms. The enhancement of dipole moments on transferring from the gas phase to aqueous solution becomes greater as the ion size increases. The dipole moment of HF increases by 21% upon the transfer, while that of HI increases by 79%. This can be explained in terms of polarizability of the molecules: the polarizabilities increase in going from HF to HI. Chipot et al. reported that the enhancement of the dipole moment on transferring is about 10% in HF and 20% in HCl in the dielectric continuum approximation, showing qualitative agreement with our present calculations.

3.2. Solvation Structure. In Figure 1, we show the pair correlation functions (PCF) for all the combinations of atom pairs between solute and solvent: (a) halogen and solvent

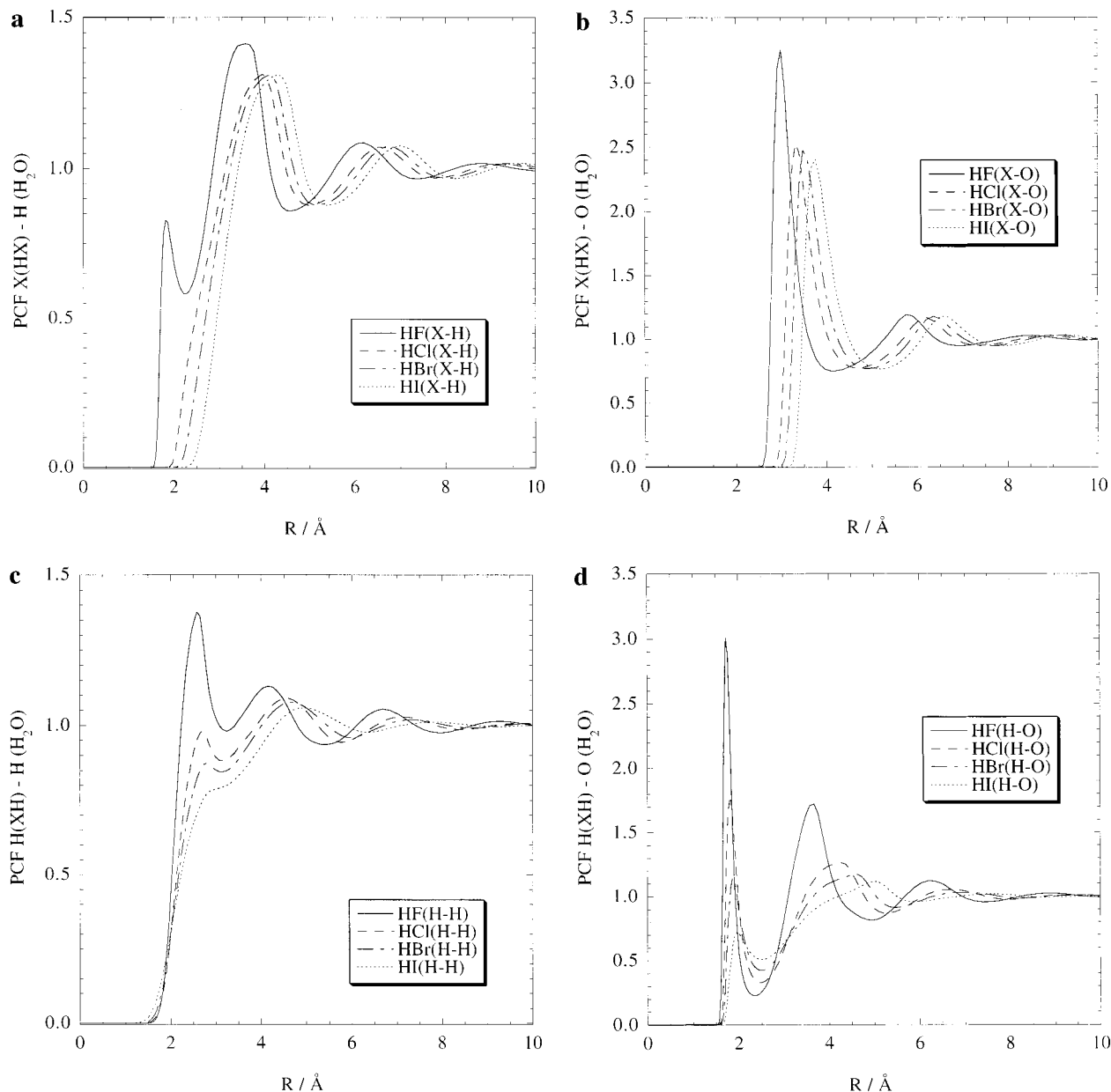


Figure 1. Pair correlation functions of hydrogen halides: (a) X-water[H], (b) X-water[O], (c) H-water[H] and (d) H-water[O].

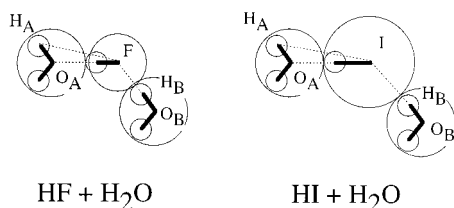


Figure 2. Illustrations of hydration structure of HF and HI. Note that the structure corresponding to the second water (B) does not appear in the calculated PCF of HI.

hydrogen (X–water[H]), (b) halogen and solvent oxygen (X–water[O]), (c) solute hydrogen and solvent hydrogen (H–water[H]), and (d) solute hydrogen and solvent oxygen (H–water[O]). One can find the sharp peaks in PCF between all the hydrogen halides and solvent water, of which height becomes lower on going from the fluoride to the iodide. These peaks can be assigned to the hydrogen bond between solute and solvent molecules by simple geometrical considerations. In these hydrogen halides, two types of hydrogen bonding can be considered: one is between the halogen atom and the solvent hydrogen, the other is between the solute hydrogen and solvent oxygen. Some of the plausible configurations for HF and HI are shown in Figure 2. (Here we assume that all the atoms in the molecules are in the same plane, and the interatomic distances are estimated from the Lennard-Jones σ given in Table 1.) Since the absolute values of effective charges in solute hydrogen are greater than those in the halogen atoms, it is expected that the hydrogen bond between solute hydrogen and solvent oxygen is stronger than that between halogen atom and solvent hydrogen.

The calculated distances of F–water[O] and I–water[O] in Figure 2 are 3.00 and 3.68 Å, respectively. These values are very close to the first peaks of F–water[O] in PCF (3.04 Å) and of I–O (3.76 Å). Consistent results can be obtained from the second peak position of F–water[H] PCF (3.58 Å) and the first peak position of I–water[H] (4.26 Å); these are close to the estimated values in the Figure 2 (3.70 Å for F–H_A and 4.36 Å for I–H_A, respectively).

The fluoride shows a distinct peak at 1.82 Å in the X–H correlation functions in Figure 1a. There is no corresponding peak in the other X–H correlation functions. From the geo-

metrical consideration, a “direct” hydrogen bond is expected to form around $r = 1.86$ Å. Undoubtedly, the distinct peak is assigned to this hydrogen bonding. Thus, we can conclude that hydrogen bonds between the solute hydrogen and the solvent oxygen are strong and found in all hydrogen halides, and only hydrogen fluoride forms a distinct F–water[H] hydrogen bonding. The hydrogen bond will cause the large change in the geometry of hydrogen fluoride, which is much greater compared to that of the other hydrogen halides. It is also expected that the liquid structure around HF is markedly different from those around the other hydrogen halides.

In Figure 3, PCFs between the halide anions and solvent hydrogen (a) as well as those between the halide anions and solvent oxygen (b) are shown. Hydrogen sites of solvent water are acutely attracted due to the negative charge on the anion, giving rise to much sharper and higher peaks than those in the series of hydrogen halides. Among the four anions, the first peak of the fluoride ion is more than three times higher than the others. Positions of the first peaks in (a) indicate that all the halide anions form hydrogen bonds, which is in striking contrast to the case of hydrogen halides.

3.3. Polarization Energy. Before proceeding to the discussion of the whole solvation free energy, we make a brief comment on the accuracy of relation 10 for the energies due to electronic polarization, ΔE_{stab} and ΔE_{reorg} . The accuracy of the relation is checked within the framework of the RISM-SCF/MCSCF procedure for the molecular solutes in the present study, for which direct calculations of ΔE_{reorg} are possible. The zeroth order interaction, $\Delta\mu_0$, can be evaluated by solving the RISM equation with fixed solute charges which are determined from the gas-phase electronic structure. By definition, the difference between $\Delta\mu_{\text{HNC}}$ and $\Delta\mu_0$ gives the solute–solvent stabilization energy, ΔE_{stab} , due to the solute polarization. According to Gao, the relation $\Delta E_{\text{stab}} = -2\Delta E_{\text{reorg}}$ should hold within the linear response theory. The estimated values for $-\Delta E_{\text{stab}}/2$ and ΔE_{reorg} are compared in Table 4. The results clearly demonstrate the reliability of relation 10 to estimate the polarization energies. It should be noted that values given in Table 4 were computed at optimized geometry in the gas phase. The values of μ_{HNC} calculated at optimized geometry in aqueous solution are larger negatives. Therefore, the descriptions based on the linear response theory are expected to become worse. However, in

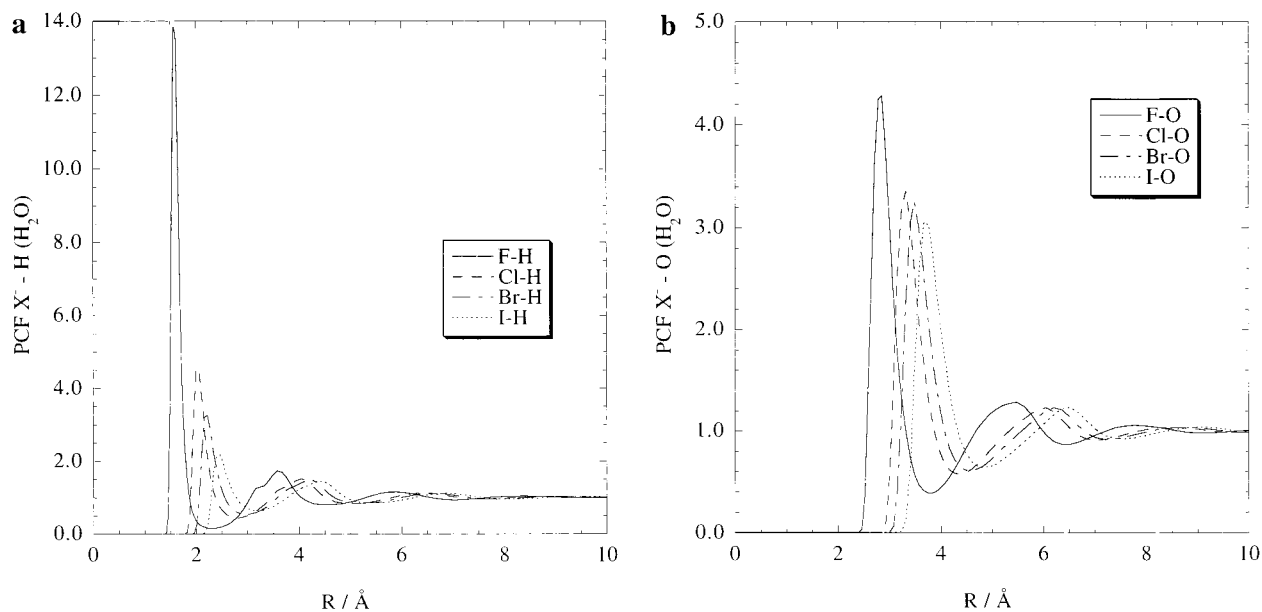


Figure 3. Pair correlation functions of halide anions: (a) X[−] – H and (b) X[−] – O.

Table 4. Computed Polarization Energies and Components^a

	$\Delta\mu_{\text{HNC}}$	$\Delta\mu_0$	$-(\Delta\mu_{\text{HNC}} - \Delta\mu_0)/2$	ΔE_{reorg}
HF	-8.6	-5.8	1.4	1.5
HCl	1.9	4.2	1.2	1.4
HBr	4.3	5.8	0.8	1.0
HI	6.9	7.6	0.4	0.5
H ₂ O	-9.4	-2.6	3.0	3.5
H ₃ O ⁺	-70.1	-67.8	1.2	0.9

^a All the values were computed at the optimized geometry in the gas phase by the RHF method and are given in kcal/mol.

Table 5. Calculated Energy Components (I)–Gas Phase^a

	process I	process II	process V	process V'
		ΔE_{elec}		
F	-70.3 (-72.3)	130.8 (132.6)	201.1 (204.9)	375.5 (381.6)
Cl	-24.1 (-26.1)	138.6 (129.6)	162.7 (155.7)	337.0 (332.3)
Br	-12.3 (-14.6)	136.9 (129.7)	149.2 (144.3)	323.6 (320.9)
I	-2.2 (-4.3)	138.3 (129.8)	140.5 (134.1)	314.9 (310.8)
		$\Delta G = \Delta E_{\text{elec}} + \Delta G_{\text{kin}}$		
F	-68.7 (-70.7)	136.0 (137.8)	204.7 (208.5)	364.2 (370.3)
Cl	-24.2 (-26.2)	144.4 (135.4)	168.6 (161.6)	328.1 (323.4)
Br	-12.8 (-15.1)	143.0 (135.8)	155.8 (150.9)	315.3 (312.7)
I	-3.2 (-5.3)	144.5 (136.0)	147.6 (141.3)	307.2 (303.0)

^a All the energies were computed by the MP2 method and are given in kcal/mol. Values in parentheses are by the RHF method.

the present case, such consideration for the internal degrees of freedom is not necessary, because we are concerned with the polarization energies for atomic anions.

3.4. Free Energies. In this section, we discuss the calculated free energy changes and their components corresponding to each chemical process in Scheme 1.

Reaction energies in the gas phase are collected in Table 5. To check the accuracy of the electronic structure description, we computed the following reaction (Process V') with the same level of calculations;



The experimental values of free energy change associated with this reaction are 365.6 (HF), 328.1 (HCl), and 318.5 (HBr) kcal/mol,²⁵ respectively. Our present results ($\Delta G = \Delta E_{\text{elec}} + \Delta G_{\text{kin}}$) are in excellent agreement with these experiments.

In Table 6, the energies related to the solvation process are listed. As is expected, the solvation energies of the ions (Process IV) are much greater than those of hydrogen halides (Process II). The solvation energy of hydrogen fluoride is more than three times larger than that of the other three hydrogen halides, being consistent with the solvation structure analysis based on the PCF in the previous section.

The free energy changes associated with the chemical processes in the Scheme 1 are plotted against the series of halogen atoms in Figure 4. One can see that contributions from $\Delta G(\text{II})$ (the energy associated with chemical reaction II) and $\Delta G(\text{IV})$ (solvation free energy of halogen anion and hydronium cation) are very large compared to those from the other two processes. It is also seen that $\Delta G(\text{I})$ and $\Delta G(\text{IV})$ show significant dependence on the halide atoms, while $\Delta G(\text{II})$ and $\Delta G(\text{III})$ are nearly constant. The dependence of $\Delta G(\text{I})$ can be explained in terms of the electronic character of bonding between hydrogen and halogen atoms. It is known that the bonding of hydrogen fluoride contains much more ionic character than that of the other hydrogen halides.²⁶ On the other hand, $\Delta G(\text{II})$ does not

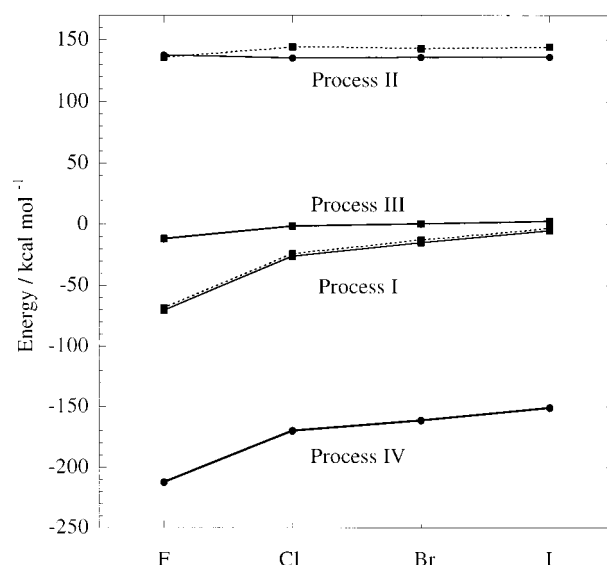


Figure 4. Free energy components of chemical processes in the thermodynamic cycle represented in Scheme 1: (I) Formation of HX, (II) formation of X⁻, (III) solvation of HX, and (IV) solvation of X⁻. Solid lines are computed by the RHF and dashed lines by the MP2 methods.

show such dependence on the halogen atoms. Thus the variation in $\Delta G(\text{V})$ associated with reaction V is mainly attributed to that in $\Delta G(\text{I})$, the energy associated with reaction I.

The dependence of $\Delta G(\text{IV})$ concerns the characteristics of the halide ions, especially the size of the anions. According to our previous calculation based on the RISM equation, the solvation free energy for anions is roughly proportional to the inverse of the ionic radius, which is qualitatively consistent with the behavior of the Born energy for ion hydration.²⁷ The hydration free energy of the fluoride ion deviates slightly in the negative direction from the regular behavior due to the extra hydrogen bond that was described in the previous section. Contributions from the polarization effects (ΔE_{stab}) on atomic anions were rather small and similar in all halide ions. But, taking account of this correction seems to be important to describe the difference in the solvation free energy between the dissociated and nondissociated hydrogen halides.

Very large contributions, from $\Delta G(\text{I})$, $\Delta G(\text{II})$, $\Delta G(\text{III})$, and $\Delta G(\text{IV})$, compensate each other, giving rise to $\Delta G(\text{VI})$ on the basis of the thermodynamic cycle (Scheme 1). The results are shown in Figure 5 with the earlier results by McCoubrey and Pauling. In the case of chloride, bromide, and iodide, the dissociated forms are more stable than the nondissociated forms, while fluoride is more stable in the nondissociated form of hydrogen halide. It should be noted that the behavior is primarily determined by the subtle balance of the two contributions, $G(\text{I})$ and $G(\text{IV})$, indicating the importance of an accurate description for both the electronic structure in a chemical reaction ($G(\text{I})$) and the solvation process ($G(\text{IV})$). It is also important to note that the enhanced stability of the nondissociated form in hydrogen fluoride due to the hydrogen bond between the fluorine atom and water oxygen makes the substance a weak acid.

The behavior is essentially the same with the earlier results reported by McCoubrey and Pauling. However, we must emphasize that the earlier results were those estimated, based on the various ad hoc assumptions, from the experimental data for the free energy changes associated with the chemical

(25) *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2.

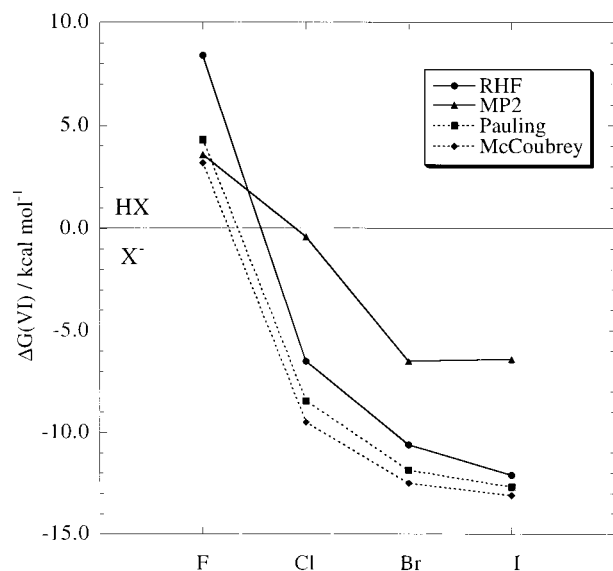
(26) Sato, H.; Nakano, H. In preparation.

(27) Hirata, F.; Redfern, P.; Levy, R. M. *Int. J. Quantum Chem., Quantum Biol. Symp.* **1988**, *15*, 179.

Table 6. Calculated Energy Components (2)—Solvation^a

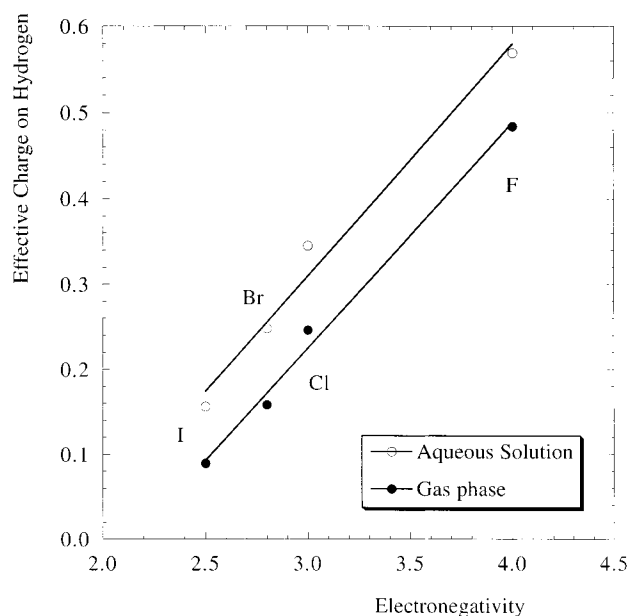
	process III	process IV	G(I)+G(III)	G(II)+G(IV)	process VI
			$\Delta\mu_{\text{HNC}^a}$		
F	-19.6 (-18.5)	-210.1 (-208.7)			
Cl	-8.2 (-7.6)	-169.2 (-167.9)			
Br	-5.8 (-5.2)	-160.6 (-159.2)			
I	-3.1 (-2.5)	-150.6 (-149.2)			
			$\Delta E_{\text{reorg}}^b$		
F	8.0 (6.6)	4.4 (3.6)			
Cl	6.9 (6.0)	4.4 (3.6)			
Br	6.3 (5.6)	4.4 (3.6)			
I	5.7 (5.1)	4.4 (3.6)			
			$1/2\Delta E_{\text{stab}}$		
F		-7.0 (-7.0)			
Cl		-5.5 (-5.5)			
Br		-5.5 (-5.5)			
I		-5.2 (-5.2)			
			$\Delta G = \Delta\mu_{\text{HNC}} + \Delta E_{\text{reorg}} (+1/2\Delta E_{\text{stab}})$		
F	-11.6 (-12.0)	-212.7 (-212.0)	-80.2 (-82.7)	-76.7 (-74.2)	3.6 (8.44)
Cl	-1.4 (-1.6)	-170.4 (-169.7)	-25.6 (-27.8)	-25.9 (-34.3)	-0.4 (-6.5)
Br	0.5 (0.4)	-161.7 (-161.1)	-12.3 (-14.7)	-18.8 (-25.3)	-6.5 (-10.6)
I	2.6 (2.5)	-151.5 (-150.8)	-0.6 (-2.7)	-7.0 (-14.8)	-6.4 (-12.1)

^a All the values are in kcal/mol. ^a $\Delta\mu_{\text{HNC}}(\text{H}_2\text{O}) = -10.0$ kcal/mol (MP2), -9.4 kcal/mol (RHF) and $\Delta\mu_{\text{HNC}}(\text{H}_3\text{O}^+) = -74.9$ kcal/mol (MP2), -73.5 kcal/mol (RHF). ^b $\Delta E_{\text{reorg}}(\text{H}_2\text{O}) = 5.2$ kcal/mol (MP2), 4.6 kcal/mol (RHF) and $\Delta E_{\text{reorg}}(\text{H}_3\text{O}^+) = 4.4$ kcal/mol (MP2), 3.6 kcal/mol (RHF).

**Figure 5.** Free energy differences between hydrogen halide (HX) and its dissociated anion (X^-).

processes illustrated in Scheme 1. Therefore the quantitative comparison between the present theoretical results and the earlier results does not make much sense. What is important is that both RHF and MP2 results show a qualitative agreement in the energetics with the earlier results. All the results unambiguously show the specific character of hydrogen fluoride in the electronic structure of the hydrogen halide and in the solvation free energy.

3.5. On Pauling's Electronegativity. It will be instructive to bring the present results into closer contact with Pauling's earlier prediction. As is well regarded, Pauling proposed the "electronegativity" to explain the character of a chemical bond, and used the concept to describe the acid strength of hydrogen halide in aqueous solutions.² Since the "electronegativity" is a measure of distortion in a chemical bond, it is expected that the electronegativity can be related to the partial charge on the atoms (hydrogen or halogen) in the present diatomic system. The partial charges of hydrogen halides in the gas phase and aqueous solutions are plotted against Pauling's electronegativity in Figure 6. As can be readily seen, these two quantities in fact

**Figure 6.** Computed effective charges against Pauling's electronegativity.

have a good correlation, indicating that the concept has some theoretical basis as an intuitive measure of the electronic distortion in a molecule at least for such simple systems. Then, the other important question is if the simple relations proposed by Pauling between the electronegativity and the free energy changes associated with the chemical processes are correct or not. Pauling has assumed that the solvation free energy depends linearly on the electronegativity, while the bond energy is a quadratic function of the parameter. The total free energy change obtained by the RISM-SCF/MCSCF calculation is plotted in Figure 7 against Pauling's electronegativity. Depicted in the same figure by the solid lines are Pauling's prediction based on the intuitive relations for the solvation free energies and the bond energies. The figure indicates that Pauling's heuristic relation between the electronegativity and the free energy changes associated with the chemical reactions, as well as the solvation processes, does have some theoretical foundation at least in the qualitative sense. However, the plot of the bond

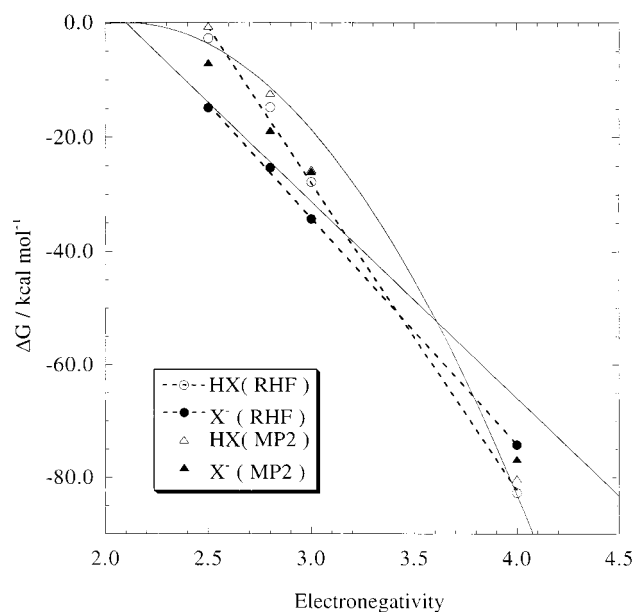


Figure 7. Computed formation energies of hydrogen halides and solvation free energies of halide anions plotted against Pauling's electronegativity. Solid lines are Pauling's predictions and dashed lines are best fit by linear functions.

energy against electronegativity also can be well fit by a straight line. So, the peculiar behavior of hydrogen fluoride can be explained as well in terms of crossing of the two free energy components, both of which depend linearly on the electronegativity.

4. Conclusion

We have revisited the acidity of a series of hydrogen halides in aqueous solution, one of the oldest problems in physical

chemistry, with a modern theoretical approach combining the *ab initio* MO theory and statistical mechanics of molecular liquids.

The well-known order of the acid strength for a series of hydrogen halides is reproduced by the theory as an interplay between the two free energy components: the formation energy or bond energy of hydrogen halides and the solvation free energy. The characteristic behavior of hydrogen fluoride as a weak acid was explained in terms of the enhanced stability of the nondissociated form of the molecule in aqueous solution due to hydrogen bonding. Hydrogen fluoride shows a distinct peak characteristic of a hydrogen bond in the pair correlation function between the fluorine atom and water oxygen, while the other hydrogen halides do not show such a peak.

The old concept of electronegativity proposed by Pauling was reexamined by the modern approach. It is found that there is a good correlation between the electronegativity of halogen atoms and effective charges on hydrogen in hydrogen halides. Regarding the functional dependency of the free energy components on the electronegativity, Pauling's heuristic argument seems to be correct in a qualitative sense. However, there remains some ambiguity, because the plot of the formation energy against the electronegativity can be well fit by a straight line as opposed to Pauling, who predicted the quadratic dependency. It is of great interest for a theoretical study to find detailed functional dependency of the bond energy upon the electronegativity.

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