

## A New Determination of the Fluoride Ion–Water Bond Energy

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The investigation of gas-phase ion–water clusters provides fundamental information about the forces involved in ionic solvation. Since understanding the properties of aqueous ionic clusters represents a key factor in elucidating the much more complex condensed phase environments, a large number of experimental and theoretical studies have discussed the properties of gas-phase clusters of water with single negative ions such as OH<sup>-</sup>,<sup>1–8</sup> or halide anions.<sup>9–23</sup>

Among the most important properties accessible both theoretically and experimentally are the incremental association energies of the clusters. These provide a measure of the combined strengths of the ion–water and water–water interactions in these clusters and serve as important benchmarks in the parametrization of interaction potentials used to model condensed phase processes. Ab initio calculations usually provide reliable estimates of the association energies in the absence of experimental data and can even assist in deciding between several sets of conflicting experimental data.<sup>1</sup> Quite surprisingly, in one of the most simple systems, namely the gas-phase “solvation” of fluoride by one water molecule, there exists a large discrepancy in the 0 K association enthalpy ( $\Delta H_0^\circ$ ) between the previous<sup>12</sup> experimental result of  $-23.3$  kcal/mol and values obtained from recent high-level (MP2, MP4) calculations, which range from  $-25$  to  $-28$  kcal/mol.<sup>9,10,24</sup> The effect of the strength of the fluoride–water interaction in determining structural trends in small ( $n < 8$ )

fluoride–water clusters as well as the F<sup>-</sup> ion’s enthalpy of solvation has been demonstrated previously.<sup>9</sup> An interaction potential parametrized with use of the previously available experimental value for the fluoride–water bond energy produced cluster geometries resembling “surface” states, i.e., configurations in which the ion resides on the surface of a water cluster. In contrast, when the stronger ion–water interaction obtained from the ab initio calculations was used to reparametrize the same potential, the resulting cluster geometries resembled “interior” states with the ion residing inside a water cluster. This discrepancy between theoretical and experimental estimates for the F<sup>-</sup>–H<sub>2</sub>O bond dissociation energy (BDE) is also disturbing since many other gas-phase ion/molecule equilibria are calibrated against this system. This communication presents new experimental and theoretical results to resolve this discrepancy.

In the present experiment<sup>25</sup> fluoride ions are produced by electron impact on gaseous difluoromethane. The ions are mass selected in a quadrupole mass spectrometer and injected into a high-pressure drift reaction cell filled with 1–5 Torr of water vapor at a temperature in the range between 400 and 800 K. The ions are guided through this bath gas with a small electric field (1–10 V/cm). The ions exiting the drift reactor are mass analyzed by a second quadrupole. The integrated F<sup>-</sup> and F<sup>-</sup>(H<sub>2</sub>O) intensities together with the water pressure and temperature in the reaction cell determine the association equilibrium constant and hence  $\Delta G_T^\circ$  as a function of temperature.

Over our experimental temperature range,  $\Delta G_T^\circ$  is a linear function of the temperature according to  $\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$  with the reaction enthalpy ( $\Delta H_T^\circ$ ) and entropy ( $\Delta S_T^\circ$ ) almost independent of temperature. The reaction enthalpy at the average experimental temperature  $T$  ( $\Delta H_T^\circ$ ) is then given by the 0 K intercept of the  $\Delta G_T^\circ$  vs  $T$  plot and the entropy ( $\Delta S_T^\circ$ ) by the slope. In reality, both  $\Delta H_T^\circ$  and  $\Delta S_T^\circ$  vary with temperature and the calculation of  $\Delta H_0^\circ$  ( $\equiv -D_0$ , the 0 K bond dissociation energy) is performed with a statistical mechanical fit to the data.<sup>25</sup> This requires knowledge of the rotational constants and the vibrational frequencies of the reactants and products which are obtained from theory.<sup>10,24</sup> Details of this calculation are given in the Supporting Information.

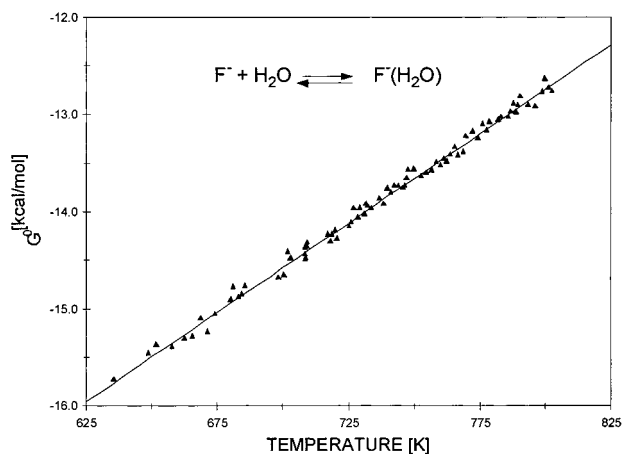
Equilibrium data for the fluoride–water cluster in the temperature range between 630 and 800 K are shown in Figure 1. Most data were taken at a bath gas (H<sub>2</sub>O) pressure of 2 Torr. Control experiments at lower and higher pressure (1–5 Torr) showed no significant pressure dependence. The  $\Delta G_T^\circ$  values were also independent of the drift time (i.e., the electric field across the reaction cell), indicating that the reaction was in equilibrium. Linear extrapolation of  $\Delta G_T^\circ$  to 0 K yields a reaction enthalpy  $\Delta H_T^\circ = -27.4 \pm 0.5$  kcal/mol, a value 4.1 kcal/mol larger than the  $\Delta H_T^\circ$  obtained previously by Kebarle and co-workers.<sup>12</sup> The statistical mechanical fit to the present yields a value of  $\Delta H_0^\circ = -26.2 \pm 0.8$  kcal/mol for the 0 K bond energy.

The objective of the ab initio calculations is to obtain a value for the electronic energy difference ( $D_e$ ) for the association of F<sup>-</sup> and H<sub>2</sub>O that is converged with respect to the size of the orbital basis set and the level of electron correlation. Previous studies<sup>11,24</sup> have suggested that the effect of the correlation on  $D_e$  is on the order of 4 kcal/mol. For example, the Hartree–Fock (HF)  $D_e$  value calculated with a triple- $\zeta$  basis set plus diffuse functions (TZ2P+diff) is<sup>11</sup>  $-23.2$  kcal/mol whereas the complete basis set limit (CBS) at the second-order Møller–Plesset perturbation (MP2) level of theory is reported<sup>24</sup> to be  $-27.1$  kcal/mol. In this study we examine the effects of higher electron correlation at the coupled cluster [CCSD(T)] level of theory (including single

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**Figure 1.** A plot of the experimentally determined free energy versus temperature for the  $F^- + H_2O \leftrightarrow F^-(H_2O)$  equilibrium.

**Table 1.** Calculated  $F^-(H_2O)$  Bond Dissociation Energies, in kcal/mol<sup>a</sup>

quantity	basis set	MP2 <sup>b</sup>	CCSD(T)
$D_e$	aug-cc-pVDZ	-26.82 (-25.30)	-27.07 (-25.38)
	aug-cc-pVTZ	-27.60 (-26.46)	-27.83 (-26.71)
	aug-cc-pVQZ	-27.48 (-26.72)	-27.64 (-27.02)
	aug-cc-pV5Z	-27.26 (-26.86)	
	CBS limit	-27.05 (-26.93)	-27.24 (-27.20)
$\Delta H_0^c$ (harmonic) <sup>c</sup>			-26.4
$\Delta H_0^c$ (anharmonic) <sup>d</sup>			-26.5
$\Delta H_0^c$ (exp - this study)			-26.2 ± 0.8

<sup>a</sup> Parentheses denote BSSE-corrected numbers. The  $\Delta H_0^c$  values are calculated with the CBS estimates for  $D_e$ . <sup>b</sup> Reference 24. <sup>c</sup> At the CCSD(T) or MP4 level with the aug-cc-pVTZ basis set. <sup>d</sup> Includes estimates for anharmonic corrections for  $F^-(H_2O)$  from ref 11 and the anharmonic frequencies for water.

and double excitations with perturbative estimation of the triple excitations). To investigate convergence with basis set size, we employed the family of augmented correlation consistent polarized valence sets of double through quadruple- $\zeta$  quality<sup>26</sup> and the usual exponential and  $(1 + \lambda)^{-n}$  extrapolation techniques<sup>24,27</sup> to obtain estimates for the CBS limit. Basis set superposition error (BSSE) corrections were taken into account by using the function counterpoise method.<sup>24,28</sup> Calculations were performed with the MOLPRO program suite.<sup>29</sup>

The calculated  $D_e$  values for  $F^-(H_2O)$  dissociation at the CCSD(T) level of theory with the aug-cc-pVxZ ( $x = D, T, Q$ ) sets are listed in Table 1. These are computed at the corresponding optimal cluster geometries. For comparison, the previously reported<sup>24</sup> MP2 results with basis sets up to quintuple- $\zeta$  are also included. The CCSD(T)/CBS limits are estimated<sup>27</sup> at -27.24 (uncorrected) and -27.20 (BSSE-corrected) kcal/mol. The CBS extrapolation scheme amounts to about 0.4 (uncorrected) and 0.2 (BSSE-corrected) kcal/mol when compared to the "best-computed" CCSD(T)/aug-cc-pVQZ values of -27.64 (uncorrected) and -27.02 (BSSE-corrected) kcal/mol. The CCSD(T)/CBS estimates are only 0.2 kcal/mol higher than those previously calculated at the MP2 level.<sup>24</sup> We therefore adopt a value of -27.2 kcal/mol as the best computed estimate for  $D_e$ . The harmonic zero-point energy (ZPE) correction amounts to +0.8 kcal/mol, yielding a

$D_0$  (harmonic) of -26.4 kcal/mol. The harmonic ZPE correction was found to be insensitive to both the level of electron correlation and the size of the basis set as evident from the small difference (<0.1 kcal/mol) between the MP2, MP4, and CCSD(T) harmonic corrections with the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ sets, respectively. To best compare the calculated and experimental bond dissociation energies ( $D_0 \equiv -\Delta H_0^c$ ), reliable estimates of the anharmonicities of the cluster frequencies must be made. The mode associated with the  $F^- \cdots H \cdots OH$  stretch exhibits<sup>11</sup> the largest anharmonicity. This is due to the existence of a "shoulder" on the potential energy surface corresponding to the unstable  $FH \cdots OH^-$  configuration. We compute an anharmonic correction for this mode equal to  $-539 \text{ cm}^{-1}$  at the MP2/aug-cc-pVTZ level by solving the 1-dimensional vibrational Schrödinger equation along this normal coordinate. The zero-point energy including anharmonic corrections is computed according to:<sup>30</sup>

$$G(0) = \frac{1}{2} \sum_r \omega_r + \frac{1}{4} \sum_{r \geq s} \chi_{rs} \quad (1)$$

where  $\omega_r$  are the harmonic frequencies and  $\chi_{rs}$  are the anharmonic constants. For water,  $G(0) = 13.25 \text{ kcal/mol}$ .<sup>30</sup> Combining the previously reported<sup>11</sup> anharmonic constants (computed at the HF/TZP+diff. level of theory with a complete quartic force field) with our best estimates for the harmonic frequencies at the CCSD(T)/aug-cc-pVTZ level of theory, we obtain  $G(0) = 13.98 \text{ kcal/mol}$  for the  $F^-(H_2O)$  zero-point energy (the corresponding value using the MP2/aug-cc-pVQZ  $\omega_r$  values is 13.90 kcal/mol). The difference between the reactant and product  $G(0)$  values therefore amounts to a correction of +0.73 kcal/mol (including anharmonic corrections) and our best theoretical estimate for  $\Delta H_0^c$  is -26.5 kcal/mol. Possible sources of error in the calculation include the extrapolation process used to obtain the CBS estimate for  $D_e$ , the estimate of harmonic frequencies and anharmonicities used to calculate the zero-point energies, and the intrinsic accuracy of the CCSD(T) method. Sources of uncertainty in the experimentally determined number include the usual errors in temperature and pressure measurement (negligible) together with the fitting process used to obtain  $\Delta H_0^c$  (see Appendix). Recent studies<sup>31,32</sup> have discussed corrections to  $\Delta H_T^c$  at finite temperatures for small  $Cl^-(H_2O)_n$  and  $I^-(H_2O)_n$  clusters using analytic interaction potentials. Despite these minor uncertainties, the above combined experimental and theoretical analysis strongly suggests that the new estimate for the bond dissociation energy of  $F^-(H_2O)$  is ~13% larger than that reported previously. Similar disagreements in bond energy also exist for the second and third water additions to  $F^-(H_2O)_n$  clusters and work is underway to resolve them.

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**Supporting Information Available:** Calculation of the experimental  $\Delta H_0^c$  for  $F^-(H_2O)$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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