Ab Initio Prediction of the Gas- and Solution-Phase Acidities of Strong Brønsted Acids: The Calculation of pK_a Values Less Than −10

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The intrinsic gas-phase acidities of a series of 21 Brønsted acids have been predicted with G3(MP2) theory. The G3(MP2) results agree with high level CCSD(T)/CBS acidities for H_2SO_4, FSO_3H, CH_3SO_3H, and CF_3SO_3H to within 1 kcal/mol. The G3(MP2) results are in excellent agreement with experimental gas-phase acidities in the range 342−302 kcal/mol to within <1 kcal/mol for 14 out of 15 acids. Five of the six acids in the range of 302−289 kcal/mol had an average deviation of 5.5 kcal/mol and the strongest acid, $(CF_3SO_2)_3CH$, deviated by 15.0 kcal/mol. These high-level calculations strongly suggest that the experimental acidities in this very acidic part of the scale need to be remeasured. The CCSD(T)/CBS (mixed exponential Gaussian) additive approach for CH_3CO_2H, HNO_3, H_2SO_4, CH_3SO_3H, FSO_3H, and CF_3SO_3H gives excellent agreement (±1 kcal/mol) with experiment for the ΔH_f^0's of non-sulfur containing species, and supports the low end of the experimental values for H_2SO_4 and FSO_3H. Use of a larger basis set (aug-cc-pV5Z) in the CBS extrapolation improves the agreement with experiment for both H_2SO_4 and FSO_3H. The G3(MP2) heats of formation for RSO_3H molecules tend to be underestimated as compared to the CCSD(T)/CBS approach by 2.5−7.0 kcal/mol. COSMO solvation calculations were used to predict solution free energies and pK_a values with pK_a's up to −17.4. Including the solvation of the proton gives good agreement with experimental pK_a values in the very acidic regime, whereas it is less reliable for weaker acids. The use of CH_3CO_2H and HNO_3 as reference acids in the less acidic and more acidic regions of the scale, respectively, provided improved results to within ±2 pK_a units in nearly all cases (±3 kcal/mol accuracy).

Introduction

The concept of Brønsted acids and bases was first introduced in 1923 to describe species that can donate or accept a proton in chemical reactions (generally referred to as the Brønsted−Lowry concept).[1] In 1927, Conant extended the concept by coining the term superacids, or acid systems that are more acidic than conventional mineral Brønsted acids.[2] In the 1960s, Olah advanced the use of superacids in studies of stable carbocations in highly acidic media.[3] Gillespie, in 1972, explicitly defined superacids as acid systems that are stronger than 100% sulfuric acid, or systems with a Hammett acidity function (H_0) < −12.[4] Brønsted acids that exceed this requirement include fluorosulfuric acid and trifluoromethanesulfonic acid, with H_0 values of −15.1 and −14.1, respectively, as well as carborane acids.[5] The modern study of superacids has significant importance in a variety of fields of research, including organic synthesis,[6] and electrochemical technologies including fuels cell[7] and batteries.[8] In addition, within the field of ionic liquids, studies involving strong acids have led to useful insights into speciation and acidity in these nonconventional media as well as their potential for synthesizing new ionic liquids.[9−12] Proton-transfer reactions form the foundation for research aimed at developing alternative methods for energy production.[13] Proton exchange membranes (PEMs) are critical parts of fuel cells, in which oxygen and hydrogen combine to form water, driven by the diffusion of H^+ ions across the membrane. Current research thrusts are focused on developing advanced PEM materials, which are typically composed of perfluorinated polymers.[14] The fluorinated polymers which comprise these membranes characteristically contain very strong acid sites, mainly sulfonic acids, which are responsible for the proton transfer needed for the fuel cells to function.

Developing the new materials needed to form the next generation of PEMs requires not only more durable, active, and temperature resistant materials, but also a more fundamental understanding of the chemistry involved in the proton-transfer process.[15] Measurement of the dissociation constant of very strong molecular acids which form the basis for PEM acid sites in a solvent environment, particularly water, is difficult for several reasons. First, the high dielectric constant of water and its ability to hydrogen bond leads to very strong solvation of the ionic components, thus interfering with the measurement of fundamental properties. Second, the solubility of fluorinated or organic materials in water is somewhat limited. Third, the autoprotolysis constant of water, although small, is not nearly small enough to allow for the measurement of very strong acid strengths such as those of sulfonic acids.[16] As a result, dissociation constants of very strong or very weak acids have been measured in alternative solvents of low dielectric constant which are not plagued by the difficulties of water as a solvent to develop relative acidity scales. However, simple extrapolation to predict acidities in different solvents is not possible, thus resulting in no simple way to develop a single acidity scale on which to gauge the properties of all acids. As a result, different acidity orders exist for families of acids in different media (and sometimes in the same medium), making comparisons difficult in the condensed phase.[17]

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The gas-phase acidity (ΔG) of a neutral acid, HA, defined as in eq 1

$$HA \leftrightarrow H^+ + A^- \quad (1)$$

provides valuable information about the intrinsic, solvent-independent properties of the acid. The gas-phase acidity of a neutral acid HA is equivalent to the gas-phase basicity of the conjugate base, A^-. The solvent-independent nature of the gas-phase acidity measurement allows for the development of an acidity scale that can range over orders of magnitude in acidity strength and can provide details regarding fundamental reactivity.[18] Experimental gas-phase acidities are usually measured by using mass spectrometric approaches, for example Fourier transform ion cyclotron resonance (FT-ICR) spectroscopy.[19] General principles have also been proposed for designing neutral superstrong Brønsted acids based on functional group additivities.[20] The measurement of equilibrium constants from proton-transfer reactions (eq 2)

$$AH + B^- \leftrightarrow BH + A^- \quad (2)$$

allows for a direct determination of relative $\delta\Delta G$. Absolute ΔG values are then obtained from several measurements of overlapping independent paths connecting a range of different acids which are then related to an absolute value. Absolute values can be obtained from other thermochemical properties. For the acidity scale, the acidities of HX (X is a halogen) are well established using the heats of formation of H^+, X^- from electron affinities determined by photoelectron spectroscopy, and HX and the X_2 bond energy. Reliable experimental measurement of gas-phase acidity, particularly with very strong Brønsted acids, can be complicated by a variety of factors, including volatile decomposition products, competing proton-transfer reactions, difficulties in measuring pressures, and too few independent path measurements.[21]

Viggiano et al. have measured the intrinsic superacidities of several strong sulfonic acids using the ion flow tube method.[22] Koppel et al.[17] measured equilibrium constants in an FT-ICR spectrometer to obtain the intrinsic gas-phase acidities of over 90 Brønsted acids. Several of the ΔG values measured by Koppel et al. are <300 kcal/mol, making them very strong acids in the gas-phase. They reported a ΔG value of 299.5 kcal/mol for trifluoromethanesulfonic acid or triflic acid, CF_3SO_3H. On the basis of MP2/aug-cc-pVnZ (n = D, T, Q) calculations extrapolated to the complete basis set (CBS) limit for CF_3SO_3H, we predicted a value which differed from the measured value by about 9 kcal/mol.[23] We can predict the acidity of triflic acid to be 290.2 kcal/mol on the basis of our previous calculated value of 297.3 kcal/mol for ΔH_{298} at this level.

A large discrepancy was also calculated by Koppel et al. (6.3 kcal/mol) at the G2(MP2) level,[24] who applied a scaling factor to this and other results to achieve agreement with their measured values.[25] Burk et al. performed semiempirical PM3 calculations and obtained similar results.[26] Dixon and co-workers used a composite approach at the CCSD(T) level with values extrapolated to the complete basis set limit to predict the acidity of the strong acids H_2SO_4, H_3PO_4, and HNO_3.[27,28] They found good agreement with the ion flow tube values[22] and lowered the error bars for these gas-phase quantities. In addition, they used a self-consistent field reaction field model[29] to include the effects of solvent and predicted the pK_a of H_2SO_4 in aqueous solution to be very negative, finding a value of −3.4 as compared to experimental values of −3.0[30] and −10.[31] On the basis of comparing other calculated acidities of strong acids with known values, they scaled the size of the cavity for the anion and estimated that the pK_a of H_2SO_4 is likely to be in the range of −6 to −8.

We have performed gas-phase electronic structure calculations at the B3LYP/DZVP2, MP2/CBS, CCSD(T)/CBS (for four compounds), and G3(MP2) levels on 18 of the Brønsted acids reported by Koppel et al.,[17] as well as H_2SO_4, HNO_3, and CH_3CO_2H to understand the origin of the discrepancy discovered in our ionic liquid study[23] and to evaluate the reported acidity scale at several points over the entire range of acidities. Based on the results for CF_3SO_3H, the potential exists for other discrepancies, particularly at the low end (most acidic) of the scale where the measurements are most difficult. We report the gas-phase acidities of CF_3COCH_3, $(CN)_2CH_2$, $(CF_3)_3COH$, $(CF_3)_2NH$, $(CH_3CO)_3CH$, $CF_3SO_2NH_2$, CF_3CO_2H, $(CF_3CO)_2CH_2$, CH_3SO_3H, CF_3COSH, $(FSO_2)_2CH_2$, $(CF_3CO)_2NH$, $(CF_3SO_2)_2CH_2$, FSO_3H, CF_3SO_3H, $(CF_3CO)_3CH$, $(CF_3SO_2)_2NH$, and $(CF_3SO_2)_3CH$. G3(MP2) heats of formation are reported for the gas-phase acids (HA) and their conjugate bases (A^-) and compared to experiment where available. In addition, for a number of HA and A^-, heats of formation were calculated at the CCSD(T)/CBS with additive corrections level. A self-consistent reaction field approach based on the COSMO (conductor-like screening model) model[32] has been used to model the aqueous solvation acidities so that we can predict the aqueous pK_a values and compare them to the available experimental (estimated) pK_a values.

Computational Details

The structures of the acids (HA) and conjugate bases (A^-) were optimized at the density functional theory (DFT) level with the B3LYP exchange correlation functional[33] and the DZVP2 DFT-optimized basis sets.[34] Vibrational frequencies were also calculated at this level to ensure that the structures corresponded to local minima on the potential energy surfaces and for thermochemical corrections. We broadly searched conformer space for all of the acids and anions to obtain the lowest energy structures. The coordinates from the B3LYP/DZVP2 optimized geometries were used for single point MP2 calculations[35] with aug-cc-pVnZ (n = D, T, Z) basis sets,[36] and the MP2 energies were extrapolated to the complete basis set (CBS) limit with a mixed Gaussian/exponential of the form in eq 3

$$E(n) = E_{CBS} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \quad (3)$$

with n = 2 (DZ), 3 (TZ), and 4 (QZ), as first proposed by Peterson et al.[37] The 1s core orbitals for the first row atoms and the 1s, 2s, and 2p core orbitals on sulfur were frozen in the MP2 calculations. The acids H_2SO_4, FSO_3H, CH_3SO_3H, and CF_3SO_3H and their conjugate bases were also optimized and frequencies calculated at the MP2/aug-cc-pVnZ (n = D, T) level including tight d functions on sulfur.[38] For these acids, single point calculations were done at the MP2/aug-cc-pVQZ level with tight d functions on sulfur using the MP2/aug-cc-pVTZ optimized geometry, and the energies were extrapolated to the CBS limit (labeled MP2/CBS(+d)). This was done to observe the effect of tight d functions on sulfur on the calculated acidities, as well as geometry effects. The former effect was observed to be negligible, so tight d functions were not included on sulfur for the remaining compounds.

We have been involved in developing an approach to the prediction of thermodynamic properties to chemical accuracy based on CCSD(T) valence electron calculations[39] extrapolated to the CBS limit with additional corrections.[40] Single-point frozen-core CCSD(T) calculations using the MP2/aug-cc-pVTZ optimized geometries were also performed on CH_3CO_2H, H_2SO_4, FSO_3H, CH_3SO_3H, and CF_3SO_3H and their conjugate bases using the aug-cc-pV*n*Z (n = D, T, Q) basis sets with tight d functions on sulfur, and the energies were extrapolated to the CBS limit (labeled CCSD(T)/CBS(+d)). Single point CCSD(T) calculations using aug-cc-pV(5+d)Z basis sets were run for H_2SO_4, HSO_4^-, FSO_5H and FSO_3^- and the energies (n = Q, 5) were extrapolated to the CBS limit using an expression (eq 4) suggested by Helgaker and co-workers;[41]

$$E(n) = E_{\mathrm{CBS}} + B/(l_{\mathrm{max}})^3 \tag{4}$$

eq 4 works well if at least results with the aug-cc-pV5Z basis set are available. Although eq 4 was originally proposed for describing only the correlation component of the energy, we have used it to fit the total CCSD(T) energy because the Hartree–Fock component of the CCSD(T) energy was found to be converged for such large basis sets. CCSD(T) calculations on CF_3SO_3H without tight d functions on sulfur were also done, and the effects of including tight d functions were once again observed to be negligible for the acidities. For the heats of formation of CH_3CO_2H, H_2SO_4, FSO_3H, CH_3SO_3H, and CF_3SO_3H and their conjugate bases at the CCSD(T)/CBS(+d) level, core-valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[36,42] Scalar relativistic corrections, ΔE_{SR}, which account for the changes in the relativistic contributions to the total energies of the molecule and constituent atoms, were included at the MP2 level with the cc-pVTZ DK basis set and the spin-free, one-electron Douglas–Kroll–Hess (DKH) Hamiltonian.[43,44,45] Relativistic corrections were also obtained at the CI–SD (configuration interaction singles and doubles) level of theory using the aug-cc-pVTZ basis sets for comparison. This relativistic correction is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit–Pauli Hamiltonian.[46] Most electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state. Instead, the energy is a weighted average of the available multiplets. Corrections are needed for C (0.08 kcal/mol), O (0.22 kcal/mol), F (0.38 kcal/mol), and S (0.56 kcal/mol) and were taken from the excitation energies of Moore.[47]

The calculated MP2/aug-cc-pVTZ vibrational frequencies of FSO_3H, CH_3SO_3H, and CF_3SO_3H (and conjugate bases) were scaled to the experimental frequencies of FSO_3H obtained from IR measurements.[48,49] The OH stretching frequency was scaled to the average of the experimental and calculated frequencies for FSO_3H, resulting in a scale factor of 0.979 following the recommendations of Grev et al.[50] A scale factor for the remaining frequencies was obtained from an average of the experimental and calculated frequencies, resulting in a value of 0.995. The calculated MP2/aug-cc-pVTZ vibrational frequencies of CH_3CO_2H and $CH_3CO_2^-$ were scaled to the experimental frequencies of CH_3CO_2H obtained from IR measurements.[51] The CH and OH stretching and bending vibrational modes were scaled to the average of experimental and calculated frequencies for CH_3CO_2H, resulting in a scale factor of 0.978. The C=O stretch scale factor of 0.994 was also derived using the same approach. Vibrational frequencies below 1100 cm^{-1} were unscaled for both species based on the comparison of the experimental and calculated values. The calculated MP2/aug-cc-pVTZ O–H stretch vibrational frequencies of H_2SO_4 and HSO_4^- were scaled to the average of the experimental[52] and calculated values. The remaining frequencies were in good agreement with experiment and were unscaled.

TABLE 1: G3(MP2) Reaction Enthalpies (ΔH_{298}, kcal/mol) and Reaction Free Energies (ΔG_{298}, kcal/mol) for Proton Loss of Brønsted Acids with Comparison to Experimental Reaction Free Energies

molecule	ΔE_{298}	ΔH_{298}	ΔG_{298}	$\Delta G_{298}(\mathrm{exp})^a$	$\delta\Delta G_{\mathrm{exp-theory}}$
CF_3COCH_3	349.0	349.6	343.3	342.1	−1.2
CH_3CO_2H	347.8	348.4	340.3	341.1	0.8
$(CN)_2CH_2$	334.9	335.5	327.9	328.3	0.4
$(CF_3)_3COH$	330.9	331.5	324.0	324.0	0.0
$(CF_3)_2NH$	329.8	330.4	323.2	324.3	1.1
$(CH_3CO)_3CH$	327.4	328.0	322.9	328.9	6.0
$CF_3SO_2NH_2$	327.3	327.9	320.8	321.3	0.5
HNO_3	324.3	324.9	317.5	317.8	0.3
CF_3CO_2H	324.2	324.8	316.9	316.3	−0.6
CF_3COSH	319.2	319.7	312.7	312.5	-0.2
CH_3SO_3H	317.7	318.3	312.2	315.0	2.8
$(CF_3CO)_2CH_2$	315.4	316.0	309.8	310.3	0.5
$(CF_3CO)_2NH$	315.5	316.1	308.5	307.5	−1.0
$(FSO_2)_2CH_2$	313.6	314.2	306.0	307.3	1.3
H_2SO_4	311.4	312.0	303.8	302.3	−1.5
$(CF_3SO_2)_2CH_2$	304.1	304.7	297.4	301.5	4.1
$(CF_3CO)_3CH$	299.7	300.3	295.1	300.6	5.5
FSO_3H	301.2	301.8	294.7	299.8	5.1
CF_3SO_3H	298.8	299.4	292.4	299.5	7.1
$(CF_3SO_2)_2NH$	292.6	293.2	286.0	291.8	5.8
$(CF_3SO_2)_3CH$	280.2	280.7	274.0	289.0	15.0

[a] Reference 17.

By combining our computed ΣD_0 values with the known heats of formation at 0 K for the elements ($\Delta H_f^0(\mathrm{H})$ = 51.63 ± 0.001 kcal/mol, $\Delta H_f^0(\mathrm{C})$ = 169.98 ± 0.1 kcal/mol, $\Delta H_f^0(\mathrm{O})$ = 58.99 ± 0.02 kcal/mol, $\Delta H_f^0(\mathrm{F})$ = 18.47 ± 0.07 kcal/mol, $\Delta H_f^0(\mathrm{S})$ = 65.66 ± 0.06 kcal/mol),[53] we can derive the ΔH_f^0 values at 0 K in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[54]

G3(MP2) calculations[55] were also performed on the entire set of acids and conjugate bases to obtain the heats of formation of the acids and conjugate bases and the acidities. Except for $(CF_3SO_2)_3CH$ and $(CF_3CO)_3CH$ and their conjugate bases, the G3(MP2) calculations were performed using the automated G3(MP2) protocol in Gaussian03. Due to hardware limitations, the G3(MP2) calculations on $(CF_3SO_2)_3CH$ and $(CF_3CO)_3CH$ and their conjugate bases had to be performed stepwise, with appropriate corrections applied based on the G3(MP2) procedure.

Solvation effects were included at the SCRF level through the use of the COSMO[32] model as implemented in Gaussian03. A dielectric constant of 78.39 corresponding to that of bulk water was applied to the gas-phase reaction energies to obtain solution energetics. The B3LYP/DZVP2 optimized geometries were used for the single point B3LYP/DZVP2 COSMO calculations.

All calculations were performed with the Gaussian03[56] suite of programs on the SGI Altix 350 and Cray XD1 at the Alabama Supercomputer Center and the MOLPRO suite of programs[57] and NWChem suite of programs[58] on the massively parallel 1980 processor HP Linux cluster in the Molecular Science Computing Facility in the William R. Wiley Environmental Molecular Sciences laboratory at the Pacific Northwest National Laboratory.

Results and Discussion

Gas-Phase Acidities. The gas-phase acidities of the 18 neutral Brønsted acids calculated at the G3(MP2) level are listed in Table 1, including the reference acids CH_3CO_2H, HNO_3, and H_2SO_4. Table 2 has heats of formation of CH_3CO_2H, H_2SO_4, HNO_3, FSO_3H, CH_3SO_3H, and CF_3SO_3H (and conjugate bases) at the composite CCSD(T)/CBS(+d) level as well as at the G3-

TABLE 2: Heats of Formation of CH_3CO_2H, HNO_3, H_2SO_4, CH_3SO_3H, FSO_3H, and CF_3SO_3H (and Conjugate Bases) at CCSD(T)/CBS(+d)[a] and G3(MP2) Levels

	CCSD(T)/CBS(+d)		G3(MP2)		experiment	
acid/conjugate base	ΔH_f (0 K)	ΔH_f^0 (298 K)	ΔH_f (0 K)	ΔH_f^0 (298 K)	ΔH_f (0 K)	ΔH_f^0 (298 K)
HA						
CH_3CO_2H	−99.3	−102.5	−99.3	−102.4	−99.9 ± 0.6[d,e]	−103.4 ± 0.6[d,e]
HNO_3[b]	−29.9	−32.2	−27.4	−29.8	−29.8 ± 0.1[f]	−32.1 ± 0.1[f]
H_2SO_4	−169.0 (−170.9)[c]	−172.5 (−174.3)[c]	−162.4	−165.8	−172.4 ± 2.0[f]	−175.7 ± 2.0[f]
CH_3SO_3H	−127.5	−131.9	−123.1	−127.3	−	−
FSO_3H	−175.0 (−176.8)[c]	−177.7 (−179.5)[c]	−168.0	−170.7	−	−180 ± 2.0[f]
CF_3SO_3H	−265.7	−268.9	−262.1	−265.3	−	−
A^-						
$CH_3CO_2^-$	−117.7	−119.9	−118.8	−121.0	−	−121.0 ± 2.8[g]
NO_3^-[b]	−70.8	−72.4	−70.3	−71.9	−71.7 ± 0.3[h]	−73.3 ± 0.3[i]
HSO_4^-	−223.4 (−225.4)[c]	−225.9 (−227.9)[c]	−218.2	−220.8	−	−231.8 ± 4.6[j]
CH_3SO_3-	−175.2	−179.0	−172.3	−176.0	−	−
FSO_3-	−239.2 (−241.1)[c]	−241.2 (−243.1)[c]	−233.9	−235.9	−	−
CF_3SO_3-	−332.7	−335.2	−330.4	−332.9	−	−

[a] (+d) means tight d functions were used on the S basis set. [b] Reference 28. [c] Values in parentheses correspond to heats of formation obtained from the l_{max} extrapolation (eq 4) of CCSD(T)/aug-cc-pV(Q,5)Z total energies for molecules and atoms. [d] Reference 59. [e] Reference 60. [f] Reference 53. [g] Reference 61. [h] Reference 62. [i] Reference 63. [j] Heat of formation at 298 K derived from the deprotonation reaction enthalpy (ref 22), experimental heat of formation of H^+ (ref 53), and experimental H_2SO_4 heat of formation (ref 53).

TABLE 3: Components for CCSD(T) Atomization Energies

acid/conjugate base	CBS	ΔE_{ZPE}	ΔE_{CV}	ΔE_{SR} (CI-SD)	ΔE_{SR} (DKH)	ΔE_{SO}	ΣD_0 (0 K)[a]
HA							
CH_3CO_2H	801.17	−38.31	2.66	−0.93	−1.14	−0.60	763.78
H_2SO_4	601.75 (603.59)[b]	−24.46	1.53	−2.99	−3.49	−1.44	573.89 (575.74)[b]
CH_3SO_3H	787.98	−39.25	2.41	−2.66	−3.19	−1.30	746.65
FSO_3H	508.62 (510.41)[b]	−17.17	1.26	−2.92	−3.38	−1.60	487.73 (489.52)
CF_3SO_3H	814.28	−24.70	2.32	−3.59	−4.15	−2.44	785.31
A^-							
$CH_3CO_2^-$	759.65	−29.92	2.49	−0.95	−1.12	−0.60	730.49
HSO_4^-	596.94 (598.94)[b]	−16.85	1.44	−3.02	−3.47	−1.44	576.63 (578.62)[b]
$CH_3SO_3^-$	776.89	−31.88	2.31	−2.79	−3.30	−1.30	742.73
FSO_3^-	513.75 (515.70)[b]	−9.76	1.22	−2.94	−3.36	−1.60	500.25 (502.20)
$CF_3SO_3^-$	822.57	−17.40	2.26	−3.73	−4.29	−2.44	800.69

[a] Contains ΔE_{SR} (DKH) correction. [b] Values in parentheses correspond to quantities derived from the l_{max} extrapolation (eq 4) of CCSD(T)/aug-cc-pV(Q,5)Z total energies for molecules and atoms.

(MP2) level for comparison. Details of the atomization energy calculations are given as in Table 3. Table 4 contains the heats of formation for the remaining acids and conjugate bases calculated at the G3(MP2) level.[55] Previously, G2 and G2(MP2) calculations were performed by Koppel et al.[25] on several strong Brønsted acids, including FSO_3H and CF_3SO_3H, and these are included in our set of acids. At the G2(MP2) level, the acidities for these two compounds were 295.4 and 293.3 kcal/mol, respectively. These two results differ from the experimentally determined values by 4.4 and 6.2 kcal/mol, respectively. Koppel et al. found a nearly linear scaling equation between their G2(MP2) results and their experimental results over a wide range of different Brønsted acids with close to unity slope and practically zero intercept. Thus, scaling the results for FSO_3H and CF_3SO_3H lowered the G2(MP2) results by only ∼0.4 kcal/mol and, in fact, led to worse agreement with experiment. However, they found excellent agreement with experiment for the predicted G2(MP2) acidities of H_2SO_4, HNO_3, and HPO_3, although we note that the experimental values have large error bars. The G2(MP2) results for H_2SO_4 and HNO_3 also agree with the higher level values at the corrected CCSD(T)/CBS level by Dixon and co-workers[27,28] to 0.7 and 0.9 kcal/mol, respectively. The deviations observed for FSO_3H and CF_3SO_3H at the G2(MP2) level fall well outside the ∼2 kcal/mol accuracy which is reported for G2(MP2) proton affinities.[24,54]

We used G3(MP2) theory to calculate the gas-phase acidities of the Brønsted acids originally reported by Koppel et al.,[17] as well as those reported by others using alternative methods.[22] As shown in Table 1, the acidities for FSO_3H and CF_3SO_3H previously calculated at the G2(MP2) level are in agreement with those obtained at the G3(MP2) level and both are much lower than the experimental values. We find differences from the reported experimental values of 5.1 and 7.1 kcal/mol, respectively, slightly larger than the differences reported by Koppel et al.[25] Experimentally, FSO_3H and CF_3SO_3H are equally strong acids in the gas phase, as indicated by both FT-ICR and ion flow tube measurements.[17,22] However, at the G3(MP2) level, CF_3SO_3H is 2.3 kcal/mol more acidic than FSO_3H

To benchmark the G3(MP2) method, higher-level CCSD(T)/CBS(+d) (derived from the full atomization approach) calculations were also performed for the gas-phase acidities of H_2SO_4, CH_3SO_3H, FSO_3H, and CF_3SO_3H and are the same to within 1 kcal/mol in all cases, as shown in Table 6. The excellent agreement between the G3(MP2) and CCSD(T) results strongly suggests that the G3(MP2) method is providing an accurate estimate of the gas-phase acidities. The calculated results at the G3(MP2) and CCSD(T)/CBS(+d) levels for methylsulfonic acid, CH_3SO_3H, are in good agreement with the lower end of the experimental range of 315.0 ± 2.0 kcal/mol. The calculated results at the G3(MP2) and CCSD(T)/CBS(+d) levels for H_2SO_4 are in good agreement with the upper range of the experimentally reported value of 302.3 ± 2.6 kcal/mol. In fact, all of the calculated results essentially fall within the error bars for the acidity of H_2SO_4. This suggests that the 5.1 and 7.1 kcal/mol differences predicted for FSO_3H and CF_3SO_3H are real and originate from the difficulties in the experimental measure-

TABLE 4: Heats of Formation of HA Acids and A^- Conjugate Bases at G3(MP2) Level (kcal/mol)

acid/conjugate base	ΔH_f (0 K)	ΔH_f^0 (298 K)
HA		
CF_3COCH_3	−196.7	−199.6
$(CN)_2CH_2$	62.6	61.5[a]
$(CF_3)_3COH$	−520.6	−524.5
$(CF_3)_2NH$	−322.3	−325.6
$(CH_3CO)_3CH$	−115.5	−122.2
$CF_3SO_2NH_2$	−216.7	−220.7
CF_3CO_2H	−243.2	−245.4[b]
CF_3COSH	−185.8	−187.6
$(CF_3CO)_2CH_2$	−375.1	−378.4
$(CF_3CO)_2NH$	−379.2	−382.6
$(FSO_2)_2CH_2$	−235.8	−240.3
$(CF_3SO_2)_2CH_2$	−416.4	−421.8
$(CF_3CO)_3CH$	−553.4	−556.8
$(CF_3SO_2)_2NH$	−415.0	−420.3
$(CF_3SO_2)_3CH$	−607.4	−614.1
A^-		
$CF_3COCH_2^-$	−214.6	−217.0
$(CN)_2CH^-$	30.2	30.0
$(CF_3)_3CO^-$	−556.9	−560.0
$(CF_3)_2N^-$	−359.8	−362.3
$(CH_3CO)_3C^-$	−154.8	−161.2
$CF_3SO_2NH^-$	−256.5	−259.8
$CF_3CO_2^-$	−286.4	−287.7
CF_3COS^-	−233.7	−234.9
$(CF_3CO)_2CH^-$	−426.8	−429.4
$(CF_3CO)_2N^-$	−431.0	−433.5
$(FSO_2)_2CH^-$	−289.6	−293.1
$(CF_3SO_2)_2CH^-$	−479.6	−484.2
$(CF_3CO)_3C^-$	−620.6	−623.6
$(CF_3SO_2)_2N^-$	−489.5	−494.1
$(CF_3SO_2)_3C^-$	−694.5	−700.4

[a] The experimental ΔH_f^0 at 298 K is 63.64 ± 0.24 kcal/mol (ref 65). [b] Two reported experimental ΔH_f^0's at 298 K are −243.2 ± 1.1 kcal/mol (ref 66a) and −246.52 ± 0.41 kcal/mol (ref 66b).

TABLE 5: MP2/CBS Reaction Enthalpies (ΔH_{298}, kcal/mol) and Reaction Free Energies (ΔG_{298}, kcal/mol) for Proton Loss of Brønsted Acids with Comparison to Experimental Reaction Free Energies

molecule	ΔE_{298}[a]	ΔH_{298}	ΔG_{298}	$\delta\Delta G_{\text{exp}-\text{theory}}$	$\delta\Delta G_{\text{G3(MP2)}-\text{MP2/CBS}}$[b]
CF_3COCH_3	345.5	346.1	339.4	2.7	3.9
CH_3CO_2H	344.7	345.3	337.2	3.9	3.1
$(CN)_2CH_2$	331.9	332.5	325.0	3.3	2.9
$(CF_3)_3COH$	328.3	328.9	321.2	2.8	2.8
$(CF_3)_2NH$	326.0	326.6	318.8	5.5	4.4
$CF_3SO_2NH_2$	325.1	325.7	318.4	2.9	2.4
$(CH_3CO)_3CH$	322.9	323.5	317.5	11.4	5.4
HNO_3	322.2	322.8	316.5	1.3	1.0
CF_3CO_2H	321.0	321.6	313.6	2.7	3.3
CH_3SO_3H	315.6	316.2	309.6	5.4	2.6
CF_3COSH	316.0	316.6	309.5	3.0	3.2
$(CF_3CO)_2NH$	312.7	313.3	305.4	2.1	3.1
$(FSO_2)_2CH_2$	311.5	312.1	304.0	3.3	2.0
$(CF_3CO)_2CH_2$	309.2	309.8	303.6	6.7	6.2
H_2SO_4	312.9	313.5	301.6	0.7	2.2
$(CF_3SO_2)_2CH_2$	300.8	301.4	293.8	7.7	3.6
FSO_3H	299.4	300.0	292.8	7.0	1.9
CF_3SO_3H	296.7	297.3	290.2	9.3	2.2
$(CF_3CO)_3CH$	294.5	295.1	290.1	10.5	5.0
$(CF_3SO_2)_2NH$	291.0	291.6	284.7	7.1	1.3
$(CF_3SO_2)_3CH$	277.1	277.7	270.1	18.9	3.9

[a] aug-cc-pV*n*Z (n = D, T, Q) contributions and zero-point energy differences provided in Supporting Information Table SM2. [b] Average ±standard deviation from average is 3.2 ± 1.3 kcal/mol.

ments of gas-phase acidities of very strong acids. Koppel et al.[17] noted that the experimental value for FSO_3H "may be significantly in error because the experimentally measured gross partial pressure for fluorosulfonic acid probably includes some unknown contributions from its highly volatile decomposition products, HF and SO_3." The discrepancy for CF_3SO_3H may in fact be due to the use of only a single equilibrium measurement for its determination, with a $-\delta\Delta G$ value of 2.0 kcal/mol.[17]

The MP2/CBS(+d) results for the four acids in Table 6 with geometries obtained at the MP2 level with the aug-cc-pV(D+d)Z and aug-cc-pV(T+d)Z basis sets are consistently lower than the G3(MP2) and CCSD(T)/CBS(+d) results by 2 to 3 kcal/ mol. The MP2/CBS calculations with the B3LYP/DZVP2 geometries resulted in differences of only 0.0−0.5 kcal/mol for H_2SO_4, FSO_3H, CF_3SO_3H, and CH_3SO_3H. We also reoptimized the geometries at the aug-cc-pVDZ and aug-cc-pVTZ levels and with these geometries, the MP2/CBS and MP2/CBS(+d) acidities are the same to within 0.2 kcal/mol.

The MP2/CBS results (Table 5) over all of the acids studied are consistently lower than the G3(MP2) results in all cases. Tight d functions in the basis set were not used for the sulfur-containing compounds in Table 5. The $\delta\Delta G$(G3(MP2)-MP2/CBS) differences fall in the range of +1.3 to +6.2 kcal/mol, with an average and standard deviation of 3.2 ± 1.3 kcal/mol. The MP2/CBS results were therefore not used to analyze the experimental gas-phase acidity results due to this systematic deviation or for predicting solution equilibria. The B3LYP/DZVP2 results for H_2SO_4, FSO_3H, CF_3SO_3H, and CH_3SO_3H are also shown in Table 6. The B3LYP results for CF_3SO_3H and CH_3SO_3H are consistent with the G3(MP2) results, but the B3LYP results for H_2SO_4 and FSO_3H are far too low relative to the G3(MP2) result. The B3LYP/DZVP2 results for the remaining acids are included in the Supporting Information. The B3LYP/DZVP2 calculations were simply used to optimize the structures and obtain thermochemical corrections for the MP2/CBS approach. The resulting acidities are not expected to be highly reliable as diffuse functions are not included in the basis sets but such functions will have little impact on the geometries or frequencies. Previous studies by Koppel et al.[25] using DFT for acidity calculations found that scaling equations were needed in order to obtain agreement with the available experimental results. However, as shown by our work, there may be significant errors in the experimental values which makes this scaling approach less reliable.

The G3(MP2) acidities for the remaining acids are listed in Table 1 (based on increasing gas-phase acidity which corresponds to decreasing ΔG_{298} values) and are compared with the experimentally determined values. The experimental values have error bars estimated to be ±2 kcal/mol.[17] The experimental acidity range of the acids under study is $289.0 \leq \Delta G_{298} \leq 342.1$ kcal/mol. The majority of the acids chosen were taken from the set measured by Koppel et al.,[17] excluding CF_3COCH_3, $(CN)_2CH_2$, and FSO_3H, which were provided by Koppel et al. for comparison, yet determined by other workers.[18,22] Based on the analysis of the CCSD(T)/CBS(+d) values for the acidities of H_2SO_4, FSO_3H, CH_3SO_3H, andCF_3SO_3H, the acidities listed in Table 1 show a distinct trend. Over the range of 302.3 to 342.1 kcal/mol, the calculated acidities are in excellent agreement with experiment, except for $(CH_3CO)_3CH$. Deviations from experiment in this acidity range are between −1.0 and 2.8 kcal/mol, within the error bars of the experiment as well as the accuracy of the G3(MP2) method. The 6.0 kcal/mol $\delta\Delta G$(exp-theory) observed for $(CH_3CO)_3CH$ is indicative of an obvious outlier. Interestingly, the acidity of 328.9 kcal/mol reported by Koppel et al.[17] was not included in the original set of 90 acids, but was included as an additional new ΔG_{acid} value obtained for comparison purposes from $\delta\Delta G$ values for proton-transfer equilibria between $(CN)_2CH_2$ and CF_3SH, two acids which were not included in the original study. As a result, the origin of this

TABLE 6: Reaction Enthalpies and Free Energies for Proton Loss of H_2SO_4, FSO_3H, CF_3SO_3H, and CH_3SO_3H at Various Levels of Theory (kcal/mol) Compared to Experimental Values ($\Delta\Delta G$)[a]

	H_2SO_4			FSO_3H			CF_3SO_3H			CH_3SO_3H		
method	ΔH_{298}	ΔG_{298}	$\delta\Delta G_{exp-theory}$	ΔH_{298}	ΔG_{298}	$\delta\Delta G_{exp-theory}$	ΔH_{298}	ΔG_{298}	$\delta\Delta G_{exp-theory}$	ΔH_{298}	ΔG_{298}	$\delta\Delta G_{exp-theory}$
B3LYP/DZVP2	309.2	300.9	1.4	297.5	290.3	9.5	299.1	292.0	7.5	319.8	313.2	1.8
MP2/CBS[b]	309.9	301.6	0.7	300.0	292.8	7.0	297.3	290.2	9.3	316.2	309.6	5.4
MP2/CBS(+d)[c]	309.9	301.6[d]	0.7	300.0	292.8	7.0	297.1	290.0	9.5	316.3	309.7	5.3
CCSD(T)/CBS(+d)[e]	312.3	304.0	−1.7	302.4	295.6	4.2	299.5	293.0[f]	6.5	318.8	312.4	2.6
G3(MP2)	312.0	303.8	−1.5	301.8	294.7	5.1	299.4	292.4	7.1	318.3	312.2	2.8

[a] H_2SO_4: $\Delta G_{exp} = 302.3 \pm 2.6$ (ref 53); FSO_3H: $\Delta G_{exp} = 299.8 \pm 2.0$ (ref 17); CF_3SO_3H: $\Delta G_{exp} = 299.5 \pm 2.0$ (ref 17); CH_3SO_3H: $\Delta G_{exp} = 315.0 \pm 2.0$ (ref 17). [b] Single points at B3LYP/DZVP2 opt geom (no tight d functions on S). [c] Optimized at MP2/aD+d and MP2/aT+d. Single point at MP2/aQ+d (with MP2/aT+d opt geom.) + d means additional tight d function on S. [d] Omission of tight d functions from S basis set results in negligible acidity difference (−0.1 kcal/mol). [e] Derived from dissociation energies ($\sum D_0$) in Table 3 at 0 K and MP2/aug-cc-pVTZ thermochemistry. [f] With no tight d functions on S: $\Delta G = 292.9$ kcal/mol.

6.0 kcal error difference is likely due to issues with different experimental scales. The G3(MP2) acidities for the remaining 14 acids in this range strongly support the experimental acidities and provide an excellent benchmark of the computational method, with an average deviation of 0.9 kcal/mol from experiments.

Over the experimental range of 289.0 to 301.5 kcal/mol (Table 1) the calculated acidities exhibit a distinctly opposing trend in $\delta\Delta G$(exp-theory) compared to acidities >302 kcal/mol. In this lower range of the acidity scale, the calculated acidities differ from experiment by 4.1, 5.5, 5.1, 7.1, and 5.8 kcal/mol for $(CF_3SO_2)_2CH_2$, $(CF_3CO)_3CH$, FSO_3H, CF_3SO_3H, and $(CF_3SO_2)_2NH$, respectively, and a much larger difference of 15.0 kcal/mol for $(CF_3SO_2)_3CH$. The acidity of the latter molecule is predicted to be substantially greater than that for the most acidic gas-phase molecule measured by 10.1 kcal/mol. Based on the excellent agreement of the G3(MP2) acidities with experiment for weaker acids and with the even more accurate CCSD(T)/CBS(+d) values, these differences in the very acidic part of the scale suggest that there are significant issues with the experimental values. We note that the measured $\delta\Delta G$ values below 301.5 kcal/mol are almost all tied to proton-transfer equilibria involving $(CF_3SO_2)_2CH_2$. Based on our calculated values, the measured acidity of $(CF_3SO_2)_2CH_2$ (301.5 ± 2.0) is too high by 4.1 kcal/mol. The issues with the experimental measurements for FSO_3H and CF_3SO_3H were discussed above. The experimental $\delta\Delta G$ values used for the assignment of the acidities for $(CF_3CO)_3CH$, $(CF_3SO_2)_2NH$, and $(CF_3SO_2)_3CH$ and other acids in the this range are, on average, larger in magnitude than those outside this range (large K values which are harder to measure), and the number of independent equilibria measurement paths is fewer. Thus, it is likely that the inherent experimental errors are large in this region of the acidity scale. In addition, the “superacidic” characteristics of these molecules make the acidity determination intrinsically difficult, due to multiple and competing equilibria and difficulties in making absolute pressure measurements. The G3(MP2) results show that the measured acidities for these very strong Brønsted acids need to be remeasured. On the basis of our values, we suggest that the CCSD(T)/CBS(+d) values are the best available values. Where the CCSD(T)/CBS(+d) values are not available, we recommend using the G3(MP2) values for the acidities of these strong acids.

The trends observed in Table 1 for the G3(MP2) calculations are consistent with the MP2/CBS results listed in Table 5. Although the MP2/CBS acidities are consistently lower, a break in the acidity scale in terms of the agreement with experiment occurs at the same point observed in the G3(MP2) acidities at $(CF_3SO_2)_2CH_2$, and an anomaly is still apparent for $(CH_3CO)_3CH$ in the less acidic region where the ΔG(exp-theory) values are generally much smaller. These results provide further support for the G3(MP2) results in the very acidic regime of the acidity scale. The B3LYP/DZVP2 acidities also indicate a break in the agreement with experiment in the acidities at around 310 kcal/mol, although the trend is less defined and less conclusive due to limitations in the basis set.

Gas-Phase Heats of Formation. The gas-phase heats of formation of the Brønsted acids (HA) and their conjugate bases (A^-) at 0 K (ΔH_f) and 298 K (ΔH_f^0) have been calculated at the G3(MP2) level (and CCSD(T)/CBS(d+) for several) and are listed in Tables 2 and 4. Components for the CCSD(T) atomization energies are listed in Table 3. Table 2 contains a comparison between the CCSD(T)/CBS(+d) and G3(MP2) heats of formation for CH_3CO_2H, HNO_3, H_2SO_4, CH_3SO_3H, FSO_3H, and CF_3SO_3H and their conjugate bases. The experimental heats of formation at 0 and 298 K for CH_3CO_2H,[59,60] $CH_3CO_2^-$,[61] HNO_3,[53] and NO_3^-[62,63] differ from CCSD(T)/CBS(+d) values by only 0.1 to 1.1 kcal/mol. CCSD(T)/CBS(+d) values at 298 K for H_2SO_4[53] and FSO_3H[53] are both less negative than experiment by 3.3 and 2.3 kcal/mol, respectively. The respective experimental error bars are given as ±2 kcal/mol but could be larger.

Previously, Alexeev et al.[27] reported the CCSD(T) heats of formation for H_2SO_4 of −171.3 kcal/mol at 298 K which is 1.1 kcal/mol higher than our current value obtained using eq 3 for the extrapolation. The difference between the two values is due to using different geometries and treatments of the scalar relativistic effect. The values in ref 27 were obtained using MP2/aug-cc-pVTZ optimized geometries, without tight d functions, and Douglas−Kroll−Hess (DKH) relativistic calculations were done with the aug-cc-pVTZ basis sets. These calculations do not change the acidity result but do impact the heat of formation. On the basis of comparing the valence electronic energy component at the CBS levels, we note a strong geometry dependence with an increase in the currently calculated component of 3.1 kcal/mol simply by inclusion of tight d functions in the MP2 geometry optimization. The use of the aug-cc-pVTZ basis set for the DKH calculation results in too small a correction as compared to use of cc-pVTZ DK basis sets. The lower DKH result in ref 27 almost cancels the effect of using the smaller valence electronic energy component at the CBS level so that these small errors approximately cancel as compared to the more rigorous calculations in the current work.

Single-point CCSD(T)/aug-cc-pV(5+d)Z calculations using the MP2/aug-cc-pV(T+d)Z geometries were performed for H_2SO_4, HSO_4^-, FSO_3H, and FSO_3^-. The CCSD(T)/CBS total energy was obtained using the l_{max} extrapolation of eq 4. The results of the extrapolation are shown in parentheses in Tables 2 and 3. The l_{max} extrapolation increases the CCSD(T)/CBS total energies by ∼1.8 to 2 kcal/ mol, resulting in predicted heats of formation that are more negative by the same amount. For both H_2SO_4 and FSO_3H, this has the effect of greatly improving the agreement with the experimental heat of formation, resulting in a differences of only 1.4 and 0.5 kcal/mol, respectively, well within 2 kcal/mol error bar of the experimental value.[53] For these compounds, the second row sulfur atom is in a high oxidation state of +6. In terms of the atomization energy, the S atom is in oxidation state 0 and the difference between the two oxidation states apparently requires going to a very large basis set to recover the valence correlation energy for the total dissociation energy. These results suggest that a correction of 1.8 to 2.0 kcal/mol making the heat of formation more negative should be applied to CF_3SO_3H and CH_3SO_3H, as the sulfur is in a similar oxidation state.

The relativistic corrections for the RSO_3H acids are high in comparison to those of many other compounds including other small molecules containing sulfur.[40i] Table 3 also contains a comparison of the DKH and CI−SD MVD scalar relativistic corrections. The DKH relativistic corrections are comparable to those obtained at the CI−SD MVD level and they are larger than what is often observed. The large values for ΔE_{SR} are consistent with the large change in the character of the sulfur atom going from the free atom to the nominal +6 charge on that atom in RSO_3H. The DKH corrections are in general 0.4 to 0.6 kcal/mol more negative than the CI−SD MVD corrections for the RSO_3H acids and anions, and ~0.2 kcal/mol more negative for acetic acid, consistent with previously observed differences.[64]

The G3(MP2) results at 0 and 298 K agree with the CCSD(T)/CBS results for CH_3CO_2H, $CH_3CO_2^-$, and NO_3^- and differ from experiment by 0.6 to 1.4 kcal/ mol. The G3(MP2) values for $\Delta H_f(HNO_3)$ at 0 and 298 K differ by 2.4 and 2.3 kcal/ mol, respectively. In addition, the G3(MP2) value for $\Delta H_f(FSO_3H)$ at 298 K is too low by 9.3 kcal/mol. This is consistent with the CCSD(T)/CBS(+d) and G3(MP2) differences for the other sulfur-containing species in Table 2. The G3(MP2) method consistently underestimates these heats of formation by 2.3 to 7.0 kcal/mol as compared to CCSD(T)/CBS(+d), suggesting that the G3(MP2) treatment of molecules containing second row elements needs to be improved. This is further supported by results in Table 4, particularly for $(CN)_2CH_2$[65] and CF_3CO_2H.[66] The G3(MP2) method predicts the heats of formation of these two acids to within 2.1 and 1.1 kcal/ mol, respectively, as compared to experiment. This is consistent with the G3(MP2) results from Table 2 for non-sulfur-containing species where G3(MP2) is consistent with experiment to within 0.6 to 2.4 kcal/ mol. Thus, the results in Table 4 for $CF_3SO_2NH_2$, CF_3SO_3H, $(FSO_2)_2CH_2$, $(CF_3SO_2)_2CH_2$, $(CF_3SO_2)_2NH$, $(CF_3SO_2)_3CH$, and their conjugate bases are likely to be underestimated, and a 3 to 7 kcal/mol correction factor probably needs to be applied. However, the heats of formation of the remaining acids and conjugate bases are predicted to be accurate to within 1 to 3 kcal/mol, consistent with benchmarks of the G3(MP2) method.[55] It is apparent from the above discussion that although the heats of formation of the acids are in error, most of this error cancels when predicting the acidity due to the similarity in the structures of the neutral and the anion.

TABLE 7: G3(MP2) Gas-Phase Reaction Energetics, COSMO Electostatic Solvation Contributions, and Solution (Water) Energetics (Including pK_a Values) for the Acidity Reaction HA → A^- + H^+

HA	ΔG_{298}	ΔG_{solv}	$\Delta G_{solution}$	pK_a	pK_a (exp)
CF_3COCH_3	343.3	−319.7	23.6	17.3	–
$(CN)_2CH_2$	327.9	−307.8	20.1	14.7	11.2[a]
$(CH_3CO)_3CH$	322.9	−307.7	15.2	11.2	5.9[a]
$(CF_3)_2NH$	323.2	−310.7	12.5	9.2	–
$(CF_3)_3COH$	324.0	−313.3	10.7	7.8	5.1[b]
CH_3CO_2H	340.3	−329.9	10.4	7.6	4.76[c]
$CF_3SO_2NH_2$	320.8	−311.6	9.2	6.8	6.3[d]
$(FSO_2)_2CH_2$	306.0	−299.3	6.7	4.9	–
$(CF_3CO)_2NH$	308.5	−303.4	5.1	3.8	–
$(CF_3CO)_2CH_2$	309.8	−305.1	4.7	3.4	–
CF_3CO_2H	316.9	−316.9	0.0	0.0	−0.6,[e] 0.3,[f] 0.5[g]
$(CF_3SO_2)_2CH_2$	297.4	−299.2	−1.8	−1.3	–
CF_3COSH	312.7	−313.8	−1.1	−0.8	–
HNO_3	317.5	−321.8	−4.3	−3.2	−1.4[h]
$(CF_3CO)_3CH$	295.1	−301.1	−6.0	−4.4	–
CH_3SO_3H	312.2	−320.7	−8.5	−6.2	−2.6,[I] −1.9[j]
H_2SO_4	303.8	−315.8	−12.0	−8.8	−3,[k] −10[h]
$(CF_3SO_2)_2NH$	286.0	−302.6	−16.6	−12.2	–
FSO_3H	294.7	−312.5	−17.8	−13.0	−6.4,[c] ≤−12[h]
CF_3SO_3H	292.4	−311.7	−19.3	−14.2	−5.9,[c] −14[i]
$(CF_3SO_2)_3CH$	274.0	−299.6	−25.6	−18.8	–

[a] Reference 74. [b] Reference 75. [c] Reference 71. [d] Reference 69. [e] Reference 70a. [f] Reference 70b. [g] Reference 70c. [h] Reference 31. [i] Reference 72. [j] Reference 76. [k] Reference 30.

Solution pK_a Values. Experimental measurements of pK_a values of very strong acids are difficult or impossible to make in aqueous solution. Acids with pK_a values less than that of the hydronium ion (H_3O^+), with pK_a = −1.74,[67] cannot be measured in aqueous solvent and require alternative methods for their estimation. Such methods typically involve some type of extrapolation from experimental data or solvent discrimination based on measurements in solvents with much lower autoprotolysis constants. Consequently, pK_a values for very strong acids are typically not well established and estimates can vary over many pK_a units for the same acid. To estimate the effects of solvation, we have calculated the free energies of solvation using the COSMO approach. Table 7 contains electrostatic solvation energy contributions to the solution free energy calculated using the COSMO solvation model for reaction 1 in solution incorporating the value for the free energy of solvation of the proton at 298 K of −264.3 kcal/mol (corrected for the proper standard state).[68] Individual neutral and anion electrostatic and nonelectrostatic solvation energies are included in Supporting Information. Combined with the G3(MP2) gas-phase reaction free energies, the solution free energies for reaction 1 were obtained for each acid in aqueous solution. The corresponding pK_a values were calculated using eq 5

$$pK_a(\mathrm{HA}) = \frac{\Delta G_{\mathrm{solution}}}{2.303RT} \qquad (5)$$

As shown in Table 7, the solvation free energy contributions (ΔG_{solv}) are all substantially negative quantities, due in large part to the very negative free energy of solvation of the proton. The solution free energies for eq 5 are divided into two distinct regions in Table 7. The first region, including CF_3COCH_3 through CF_3CO_2H, contains positive $\Delta G_{solution}$ values with pK_a > 0. Here, the gas-phase reaction free energy dominates the solvation free energy. The second region, including $(CF_3SO_2)_2CH_2$ through $(CF_3SO_2)_3CH$, contains negative $\Delta G_{solution}$ values with pK_a < 0. Here, the solvation free energy dominates the gas-phase free energy. The prediction of pK_a values using this approach works well for $CF_3SO_2NH_2$,[69] CF_3CO_2H,[70] FSO_3H,[31,71] and CF_3SO_3H,[71,72] with deviations of 0.5, 0.5, ~1.0, and ~0.2 pK_a units, respectively, from the experimental values. For the very strong acids FSO_3H and CF_3SO_3H, we prefer the experimental pK_a values of ≤−12[31] and −14,[72] respectively, and not the more positive values of Guthrie.[71] Although FSO_3H is known to hydrolyze to HF and H_2SO_4,[73] we have included the results

TABLE 8: Selected G3(MP2) Gas-phase Reaction Energetics, COSMO Solvation Contributions, and Solution (Water) Energetics (Including pK_a Values) for the Proton Exchange Reaction HA + $CH_3CO_2^-$ → A^- + CH_3CO_2H[a]

HA	ΔG_{298}	ΔG_{solv}[b]	$\Delta G_{solution}$	pK_a[c]	pK_a (exp)[d]
CF_3COCH_3	3.0	10.1	13.1	14.4	−
$(CN)_2CH_2$	−12.3	22.0	9.7	11.8	11.2
$(CH_3CO)_3CH$	−17.4	21.0	3.6	7.4	5.9
$(CF_3)_2NH$	−17.1	19.4	2.3	6.4	−
$(CF_3)_3COH$	−16.3	16.9	0.6	5.2	5.1
$CF_3SO_2NH_2$	−19.5	18.4	−1.1	4.0	6.3
$(FSO_2)_2CH_2$	−34.2	30.9	−3.3	2.3	−
$(CF_3CO)_2NH$	−31.7	27.1	−4.6	1.4	−
$(CF_3CO)_2CH_2$	−30.5	24.0	−6.5	0.0	−
CF_3CO_2H	−23.3	13.0	−10.3	−2.8	−0.6, 0.3, 0.5

[a] An all-inclusive list of solution energies is included in Supporting Information Tables SM4 and SM5. [b] Includes electrostatic and non-electrostatic contributions. [c] pK_a(HA) = pK_a(CH_3CO_2H) + ΔG_{soln}/(2.303RT); pK_a (CH_3CO_2H) = 4.76. [d] See Table 7 for references.

TABLE 9: Selected G3(MP2) Gas-Phase Reaction Energetics, COSMO Solvation Contributions,[a] and Solution (water) Energetics (including pK_a Values) for the Proton exchange reaction HA + NO_3^- → A^- + HNO_3[a]

HA	ΔG_{298}	ΔG_{solv}[b]	$\Delta G_{solution}$	pK_a[c]	pK_a (exp)[d]
CF_3CO_2H	−0.6	4.9	4.3	1.8	−0.6, 0.3, 0.5
$(CF_3SO_2)_2CH_2$	−20.1	23.6	3.5	1.2	−
CF_3COSH	−4.8	8.0	3.2	1.0	−
$(CF_3CO)_3CH$	−22.4	19.1	−3.3	−3.8	−
CH_3SO_3H	−5.3	1.0	−4.3	−4.6	−2.6, −1.9
H_2SO_4	−13.6	6.0	−7.6	−7.0	−3, −10
$(CF_3SO_2)_2NH$	−31.5	19.0	−12.5	−10.6	−
FSO_3H	−22.9	9.2	−13.7	−11.4	−6.4, ≤−12
CF_3SO_3H	−25.1	10.0	−15.1	−12.5	−5.9, −14
$(CF_3SO_2)_3CH$	−43.5	21.6	−21.9	−17.4	−

[a] An all-inclusive list of solution energies is included in Supporting Information Tables SM4 and SM5. [b] Includes electrostatic and non-electrostatic contributions. [c] pK_a(HA) = pK_a(HNO_3) + ΔG_{soln} /(2.303RT); pK_a (HNO_3) = −1.4. [d] See Table 7 for references.

to provide insight into the initial solution acidity due to FSO_3H. However, for the acids $(CN)_2CH_2$,[74] $(CH_3CO)_3CH$,[74] $(CF_3)_3COH$,[75] and CH_3SO_3H,[72,76] this approach generates differences with experiment of 3.5, 5.3, 2.7, and 4.3 pK_a units, respectively.

Because the consistency obtained with the simple approach just described varies considerably over the entire acid range, we prefer to use an approach which predicts the pK_a values relative to known standards in order to provide a better estimate. Reaction 1 involves the formation of charged species starting from neutral molecules and can pose a challenge for solvation models, especially as we are not including any waters of solvation about the anion. For example, it has been shown that such an approach can be used to calculate the solvation free energy of F^-, and hence its acidity, but that a large number of water molecules (12 to 16) are needed for convergence of the free energy of solvation.[77] HF is a relatively weak acid in the gas phase ($\Delta G_{298} = 365.50 \pm 0.20$ kcal/mol)[78] and is a modest acid in aqueous solution (pK_a = 3.2).[31] Reactions that conserve the number of charged species as reactants and products may be more suitable for accurate calculations of changes in solvation free energies as differences will tend to cancel. Following the work of Pliego and Riveros[79] and Houk[80] as well as our own work on H_xNO,[81] we reference our solution phase values to a molecule with a well-established pK_a using reaction 2. The reference acid was chosen such that the pK_a was comparable to the expected pK_a of the Brønsted acids determined in Table 7. Thus, for strong acids, with pK_a values near or less than zero, we chose the strong acid HNO_3 as the reference (pK_a = −1.4).[31] For the acids with positive pK_a values, we chose CH_3CO_2H as the reference (pK_a = 4.76).[71] Values for the acid standards CH_3CO_2H and HNO_3 using the simple approach given above show pK_a errors of 2.8 and 1.8, pK_a units, respectively. Table 8 contains differential solvation energy contributions to the solution free energy calculated using the COSMO solvation model for the reference reaction 6

$$\mathrm{HA} + \mathrm{CH_3CO_2}^- \leftrightarrow \mathrm{A}^- + \mathrm{CH_3CO_2H} \tag{6}$$

based on the proton-transfer equilibrium with acetic acid for 10 of the acids. The pK_a values in aqueous solution were calculated using the following relationship

$$\mathrm{p}K_\mathrm{a}(\mathrm{HA}) = \mathrm{p}K_\mathrm{a}(\mathrm{ref}) + \frac{\Delta G_{\mathrm{solution}}}{2.303RT} \tag{7}$$

where the $\Delta G_{solution}$ is taken from Table 8 and ref is CH_3CO_2H. The solvation contributions to the solution free energy for reaction 6 for the HA acids are all positive values and range in magnitude from 10.1 kcal/mol to 30.9 kcal/mol. These positive free energies indicate that the solution contribution to the reaction free energy is unfavorable, primarily due to better differential solvation of the small $CH_3CO_2^-$ anion. This is particularly evident in reactions with large bulky anions which have greater charge delocalization and larger volumes consistent with larger positive electrostatic contributions to the solution free energy. The nonelectrostatic solvation contributions to the solution free energy for reaction 6 for different HA acids are all very small and close to zero and may be neglected without affecting the results in a significant way (see Supporting Information). The improvement in the pK_a values using acetic acid as a reference is significant in the less acidic part of the scale as compared to the directly calculated values reported in Table 7. With this reference, small differences in pK_a are obtained for $(CN)_2CH_2$, $(CH_3CO)_3CH$, $(CF_3)_2COH$, of 0.6, 1.5, and 0.1, respectively. For $CF_3SO_2NH_2$ and CF_3CO_2H the differences from experiment are now larger at 2.3, and 2.2 pK_a units, respectively, but the approach of using a reference acid results in an overall improvement. This suggests that the solvation energy differences for these acids involving heterolytic cleavage of CH, NH, and OH bonds, and their conjugate bases are similar to those between CH_3CO_2H and $CH_3CO_2^-$.

Table 9 contains differential solvation energy contributions to the solution free energy calculated using the COSMO solvation model for the reference reaction

$$\mathrm{HA} + \mathrm{NO_3}^- \leftrightarrow \mathrm{A}^- + \mathrm{HNO_3} \tag{8}$$

on the basis of the proton-transfer equilibrium with nitric acid for 10 of the acids. The resultant solution free energies were obtained using the approach used for reaction 6. The pK_a values in aqueous solution were calculated using the eq 7 with ref = HNO_3 and $\Delta G_{solution}$ is taken from Table 9. Just as found with acetic acid as the standard, the solvation contributions to the solution free energy for reaction 8 for the HA acids are all positive values and range in magnitude from 1.0 kcal/mol to 23.6 kcal/mol. Again, use of a reference (HNO_3) results in pK_a values that are in agreement with the available experimental values to within 2 pK_a units in all cases. In particular, the predicted value for the pK_a of CH_3SO_3H is improved by nearly 2 pK_a units, whereas the results for the remaining acids for which experimental data is available are comparable to those obtained with reaction 1. Previously, Alexeev et al.[27] calculated the pK_a using the fully polarizable continuum model[82] and varied the isodensity contour. With an isodensity contour of 0.001 au for the neutral and anion, they found a pK_a of −3.4 for H_2SO_4. By comparing the calculated pK_a values with experiment for H_3PO_4, HNO_3, and H_2CO_3, they found that the calculated pK_a values were in agreement with experiment when a contour value of 0.0022 au was used for the anion and the value of 0.001 au for the neutral. This gave a value of −8.5 for pK_a(H_2SO_4), and they estimated that the actual pK_a value would fall in the range of −6 to −8. Our COSMO value for the pK_a(H_2SO_4) is −8.7 using eq 1. Using eq 2 with the HNO_3 reference gives pK_a(H_2SO_4) = −7.0, in the middle of the previously predicted range and essentially in the middle of the estimated experimental values of −3[30] and −10.[31] The HNO_3 reference works well for these OH acids, again suggesting that HA/A^- and HNO_3/NO_3^- solvation energy differences are comparable. The experimental pK_a values for $CF_3SO_2NH_2$ (see Supporting Information) and CF_3CO_2H are bracketed by the calculated values obtained from both CH_3CO_2H and HNO_3 as references. These two acids fall in the middle of the acidity range shown in Table 1, suggesting that either reference is suitable for this portion of the scale.

The strongest acids, those with negative solution free energy changes, are predicted (using HNO_3 as the reference) to have the following pK_a ordering in solution: $(CF_3SO_2)_3CH < CF_3SO_3H < FSO_3H < (CF_3SO_2)_2NH \ll CH_3SO_3H < (CF_3CO)_3CH$. Due to the simple model we are using for the solvation of anions without the inclusion of solvating water molecules,[77,83] our calculated free energies when calculated relative to a standard are good to ±3 kcal/mol which corresponds to ±2 pK_a units at 298 K. Overall, the predicted pK_a values are in relatively good agreement with experiment, even with the very acidic compounds for which only pK_a estimates are available, and all of the signs are predicted to be in the right direction.

A number of other methods have been used to predict pK_a's. For example, the COSMO−RS approach which includes additional empirical terms,[84] has been applied to a set of 64 acids, mostly with pK_a > 2 and a good correlation is found between the calculated and experimental values. On the basis of their results, Klamt et al.[84] concluded that the pK_a scale has a different dependence on the free energy of dissociation than is usually assumed, stating that eq 5 should be modified by including a constant times the right-hand side term which is less than one and with an additional constant representing the intercept. Whether this is the reason or that additional energy terms are needed for dealing with short-range interactions such as hydrogen bonding has not been established.[85]

Conclusions

A computational approach based on G3(MP2) theory was used to predict the gas-phase acidities of CF_3COCH_3, $(CN)_2CH_2$, $(CF_3)_3COH$, $(CF_3)_2NH$, $(CH_3CO)_3CH$, $CF_3SO_2NH_2$, CF_3CO_2H, $(CF_3CO)_2CH_2$, CH_3SO_3H, CF_3COSH, $(FSO_2)_2CH_2$, $(CF_3CO)_2NH$, $(CF_3SO_2)_2CH_2$, $(CF_3CO)_3CH$, FSO_3H, CF_3SO_3H, $(CF_3SO_2)_2NH$, $(CF_3SO_2)_3CH$, H_2SO_4, HNO_3, and CH_3CO_2H. High-level calculations at the CCSD(T) level using aug-cc-pVnZ (n = D, T, Q) basis sets including tight d functions extrapolated to the complete basis set limit for H_2SO_4, FSO_3H, CH_3SO_3H, and CF_3SO_3H were used to confirm the accuracy and reliability of the G3(MP2) method for the acidity of these strong acids. On the basis of comparisons to experimentally determined acidities, excellent agreement was found for acids with calculated gas-phase acidities ≥304 kcal/mol. However, acids with experimental acidities ≤302 kcal/mol were found to have large differences compared to the G3(MP2) results of between +4 to +15 kcal/mol, in particular for $(CF_3SO_2)_2CH_2$, $(CF_3CO)_3CH$, FSO_3H, CF_3SO_3H, $(CF_3SO_2)_2NH$, and $(CF_3SO_2)_3CH$. This trend is supported by MP2/CBS results, which exhibit an analogous break in the acidity scale in terms of the agreement with the experimental values. Our computational results suggest that the experimental values for the gas phase acidities of the strong acids are substantially in error and need to be remeasured.

The heats of formation of these acids have also been calculated using the G3(MP2) approach, as well as with the more accurate CCSD(T) additive approach for CH_3CO_2H, HNO_3, H_2SO_4, CH_3SO_3H, FSO_3H, and CF_3SO_3H. The CCSD(T) additive method gives excellent agreement (±1 kcal/mol) with experiment for the non-sulfur-containing species. This method predicts heats of formation in agreement with the low end of the experimental values for H_2SO_4 and FSO_3H. Use of a larger basis set (aug-cc-pV(5+d)Z) in the CBS extrapolation improves the agreement with experiment for both H_2SO_4 and FSO_3H. Compounds with a second row atom where there is a large change in oxidation state from the atom in the molecules to the bare atom may require use of very large basis sets to recover the valence correlation energy for the total dissociation energy. The G3(MP2) heats of formation for RSO_3H molecules (and anions) tend to be underestimated as compared to the CCSD(T) additive approach by 2.3 to 7.0 kcal/mol. The G3(MP2) heats of formation are within the error bars of the method for the remaining types of species. This suggests that additional corrections for RSO_3H type molecules may be needed at the G3(MP2) level.

Solution acidities and pK_a values were computed by using the COSMO approach either directly using a previously calculated value for the free energy of solvation of the proton or with respect to a reference acid. The direct approach successfully predicted pK_a values to within a few pK_a units, particularly in the very acidic region of the scale. However, in the less acidic region, the approach was not as reliable. The use of CH_3CO_2H and HNO_3 as reference acids in the less acidic and more acidic regions of the scale, respectively, provided more consistent results, typically to within ±2 pK_a units in nearly all cases, suggestive of better than 3 kcal/mol accuracy in the solution acidity prediction. Our results are consistent with the literature pK_a values of ≤−12 for FSO_3H and CF_3SO_3H, which are notoriously difficult to measure. These results suggest that high-level calculations of gas-phase acidities in conjunction with continuum solvation models can be used to predict the pK_a values of very strong acids in aqueous solution. The pK_a scale outlined above provides for the first time a reliable estimate of pK_a values of very strong acids for which very little experimental data exists. These results will aid in the unification of the acidity scale in aqueous solution for both strong and weak acids, thus minimizing the reliance on extrapolation methods based on solvent differentiation and related techniques.

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Supporting Information Available: Cartesian coordinates, additional solvation results, and energies at the different levels of theory described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Brønsted, J. N. *Recl. Trav. Chim. Pays-Bas* **1923**, *42*, 718−728.

(2) Hall, N. F.; Conant, J. B. *J. Am. Chem. Soc.* **1927**, *49*, 3047−3061.

(3) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985.

(4) (a) Gillespie, R. J.; Peel, T. E. *Adv. Phys. Org. Chem.* **1972**, *9*, 1−24. (b) Gillespie, R. J.; Peel, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 5173−5178.

(5) Juhasz, M.; Hoffmann, S.; Evgenii, S.; Kim, K.-C.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5352−5355.

(6) (a) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: Chichester, 1995; pp 5143−5146. (b) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69−92.

(7) (a) Heitner-Wirguin, C. *J. Membr. Sci.* **1996**, *120*, 1−33. (b) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535−4585.

(8) Xu, K. *Chem. Rev.* **2004**, *104*, 4303−4417.

(9) Yoshizawa, M.; Xu, W.; Angell, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 15411−15419.

(10) Thomazeau, C.; Olivier-Bourbigou, H.; Magna, L.; Luts, S.; Gilbert, B. *J. Am. Chem. Soc.* **2003**, *125*, 5264−5265.

(11) Noda, A.; Susan, M. A. B. H.; Kudo, K.; Mitsushima, S.; Hayamizu, K.; Wantanabe, M. *J. Phys. Chem. B* **2003**, *107*, 4024−4033.

(12) Xue, H.; Verma, R.; Shreeve, J. M. *J. Fluorine Chem.* **2006**, *127*, 159−176.

(13) Kerres, J. A. *J. Membr. Sci.* **2001**, *185*, 3−27.

(14) Smitha, B.; Sridhar, S.; Khan, A. A. *J. Membr. Sci.* **2005**, *259*, 10−26.

(15) Prater, K. B. *J. Power Sources* **1994**, *51*, 129−144.

(16) Stewart, R. *The Proton: Applications to Organic Chemistry*; Organic Chemistry, A Series of Monographs; Academic Press: Orlando, FL, 1985; Vol. 46, pp 1−8.

(17) Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignat'ev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047−3057.

(18) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. W. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(19) Ervin, K. M. *Chem. Rev.* **2001**, *101*, 391−444.

(20) Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I. *J. Am. Chem. Soc.* **2002**, *124*, 5594−5600.

(21) Gal, J.-F.; Maria, P.-C.; Raczyñska, E. D. *J. Mass Spectrosc.* **2001**, *36*, 699−716.

(22) Viggiano, A. A.; Henchman, M. J.; Dale, F.; Deakyne, C. A.; Paulson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 4299−4306.

(23) Gutowski, K. E.; Holbrey, J. D.; Rogers, R. D.; Dixon, D. A. *J. Phys. Chem. B* **2005**, *109*, 23196−23208.

(24) Curtiss, L. A.; Raghavachari, K.; Pople. J. A. *J. Chem. Phys.* **1993**, *98*, 1293−1298.

(25) Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I.; Sonoda, T.; Mishima, M. *J. Am. Chem. Soc.* **2000**, *122*, 5114−5124.

(26) Burk, P.; Koppel, I. A.; Koppel, I.; Yagupolskii, L. M.; Taft, R. W. *J. Comput. Chem.* **1996**, *17*, 30−41.

(27) (a) Alexeev, Y.; Windus, T. L.; Zhan, C.-G.; Dixon, D. A. *Int. J. Quantum Chem.* **2005**, *102*, 775−784. (b) *Int. J. Quantum Chem.* **2005** *104*, 379−380, erratum.

(28) Dixon, D. A.; Feller, D.; Zhan, C.-G.; Francisco, J. S. *Int. J. Mass Spectrosc.* **2003**, *227*, 421−438

(29) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999−3094.

(30) (a) Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry,* 3rd ed.; John Wiley & Sons: New York, 1994. (b) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; W. H. Freeman: New York, 1994. (c) Kolthoff, I. *Treatise on Analytical Chemistry*; Interscience Encyclopedia: New York, 1959.

(31) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; 5th ed.; John Wiley & Sons: New York, 2001.

(32) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799−805.

(33) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(34) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560−571.

(35) (a) Møller C.; Plesset M. S. *Phys. Rev.* **1934**, *46*, 618−622. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1−19.

(36) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(37) Peterson, K. A.; Woon, D. E.; Dunning, T. E., Jr. *J. Chem. Phys.* **1994**, *100*, 7410−7415.

(38) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244−9253.

(39) (a) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479−483. (c) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718−8733.

(40) (a) Peterson, K. A.; Xantheas, S. S.; Dixon, D. A.; Dunning, T. H., Jr. *J. Phys. Chem. A* **1998**, *102*, 2449−2454. (b) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154−176. (c) Dixon, D. A.; Feller, D. *J. Phys. Chem. A* **1998**, *102*, 8209−8216. (d) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1999**, *110*, 8384−8396. (e) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 6413−6419. (f) Feller, D. *J. Chem. Phys.* **1999**, *111*, 4373−4382. (g) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2000**, *104*, 3048−3056. (h) Feller, D.; Sordo, J. A. *J. Chem. Phys.* **2000**, *113*, 485−493. (i) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484−3496. (j) Dixon, D. A.; Feller, D.; Sandrone, G. *J. Phys. Chem. A* **1999**, *103*, 4744−4751. (k) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727−2747. (l) Feller, D.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem. A* **1998**, *102*, 7053−7059. (m) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Chem. Phys.* **2001**, *115*, 2576−2581. (n) Pollack, L.; Windus, T. L.; de Jong, W. A.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 6934−6938. (o) Dixon, D. A.; Gutowski, M. *J. Phys. Chem. A* **2005**, *109*, 5129−5135. (p) Dixon, D. A.; Arduengo, A. J., Jr. *J. Phys. Chem. A* **2006**, *110*, 1968−1974. (q) Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 10138−10147.

(41) (a) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669−678. (b) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639−9646. (c) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. L. *Chem. Phys. Lett.* **1998**, *286*, 243−252. (d) Klopper, W.; Bak, K. L.; Jørgensen, P.; Olsen, J.; Helgaker, T. *J. Phys. B* **1999**, *32*, R103−R130.

(42) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548−10560.

(43) (a) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89−155. (b) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756−763. (c) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742−3748.

(44) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48−53.

(45) EMSL basis set library. http://www.emsl.pnl.gov/forms/basisform.html.

(46) Davidson, E. R.; Ishikawa, Y.; Malli, G. L. *Chem. Phys. Lett.* **1981**, *84*, 226−227.

(47) Moore, C. E. Atomic energy levels as derived from the analysis of optical spectra, Volume 1, H to V; U.S. National Bureau of Standards Circular 467; U. S. Department of Commerce, National Technical Information Service, COM-72−50282; U.S. GPO: Washington, DC, 1949.

(48) Varetti, E. L. *J. Mol. Struct. (THEOCHEM)* **1998**, *429*, 121−130.

(49) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1979.

(50) Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128−5132.

(51) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidated Volume 1*; National Bureau of Standards (U.S.): Washington, DC, 1972.

(52) Chackalackal, M.; Stafford, F. E. *J. Am. Chem. Soc.* **1966**, *88*, 723−728.

(53) Chase, M. W., Jr. NIST-JANAF Tables (4th ed.) *J. Phys. Chem. Ref. Data, Monograph 9* **1998**, pp 1−1963.

(54) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063−1079.

(55) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703−4709.

(56) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J.

V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004..

(57) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R. M.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. MOLPRO-2002, a package of initio programs, Universität Stüttgart, Stüttgart, Germany, and University of Birmingham, Birmingham, United Kingdom, 2002.

(58) (a) Aprà, E.; Bylaska, E. J.; Jong, W. d.; Hackler, M. T.; Hirata, S.; Pollack, L.; Smith, D.; Straatsma, T. P.; Windus, T. L.; Harrison, R. J.; Nieplocha, J.; Tipparaju, V.; Kumar, M.; Brown, E.; Cisneros, G.; Dupuis, M.; Fann, G. I.; Fruchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J. A.; K. Tsemekhman; Valiev, M.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; D. Elwood; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; R. Kobayashi; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; T. Nakajima; Niu, S.; Rosing, M.; Sandrone, G.; Stave, M.; H. Taylor; G. Thomas; Lenthe, J. v.; Wong, A.; Zhang, Z. NWChem. PNNL, **2003**; (b) Kendall, R. A.; Aprà, E.; Bernholdt, D. E.; Bylaska, E. J.; Dupuis, M.; Fann, G. I.; Harrison, R. J.; Ju, J.; Nichols, J. A.; Nieplocha, J.; Straatsma, T. P.; Windus, T. L.; Wong, A. T. *Comput. Phys. Commun.* **2000**, *128*, 260−283.

(59) Frenkel, M.; Kabo, G. J.; Marsh, K. N.; Roganov, G. N.; Wilhoit, R. C. *Thermodynamics of Organic Compounds in the Gas State, Vol. 1*; Thermodynamics Research Center: College Station, TX, 1994.

(60) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds, Vol. 1.*; Thermodynamics Research Center: College Station, TX, 1994.

(61) Heat of formation derived from deprotonation reaction enthalpy (Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1−83), experimental heat of formation of H^+ (ref 53), and experimental CH_3CO_2H heat of formation.

(62) Davidson, J. A.; Fehsenfeld, F. C.; Howard, C. J. *Int. J. Chem. Kinet.* **1977**, *9*, 17−29.

(63) Heat of formation at 298 K derived from deprotonation reaction enthalpy (Davidson, J. A.; Fehsenfeld, F. C.; Howard, C. J. *Int. J. Chem. Kinet.* **1977**, *9*, 17−29), experimental heat of formation of H^+ (ref 53), and experimental HNO_3 heat of formation.

(64) Bauschlicher, C. W., Jr. *J. Phys. Chem. A* **2000**, *104*, 2281−2283.

(65) Beckhaus, H. D.; Dogan. B.; Pakusch, J.; Verevkin, S.; Ruechardt, C. *Chem. Ber.*. **1990**, *123*, 2153-2159.

(66) (a) Guthrie, J. P. *Can. J. Chem.* **1976**, *54*, 202−209. (b) Kolesov, V. P.; Slavutskaya, G. M.; Papina, T. S. *Russ. J. Phys. Chem. (Engl. Transl.)* **1972**, *46*, 474.

(67) Waser, J.; Trueblood, K. N.; Knobler, C. M. *Chem One*; McGraw-Hill: New York **1976**; pp 372 and 783.

(68) Zhan, C.-G.; Dixon, D. A. *J. Phys. Chem. A* **2001**, *105*, 11534−11540.

(69) Trepka, R. D.; Harrington, J. K.; Belisle, J. W. *J. Org. Chem.* **1974**, *39*, 1094−1098.

(70) (a) Bonner, O. D.; Prichard, P. R. *J. Solution Chem.* **1979**, *8*, 113−124. (b) Henne, A. L.; Fox, C. J. *J. Am. Chem. Soc.* **1951**, *73*, 2323−2325. (c) Kurz, J. L.; Farrar, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 6057−6062.

(71) Guthrie, J. P. *Can. J. Chem.* **1978**, *56*, 2342−2354.

(72) W. P. Jencks. http://daecr1.harvard.edu/pdf/evans_pK_a_table.pdf

(73) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202−209.

(74) Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439−2443.

(75) Jencks, W. P.; Brant, S. R.; Gandler, J. R.; Fendrich, G.; Nakamura, C. *J. Am. Chem. Soc.* **1982**, *104*, 7045−7051.

(76) Covington, A. K.; Thompson, R. *J. Solution Chem.* **1974**, *3*, 603−617.

(77) Zhan, C.-G.; Dixon, D. A. *J. Phys. Chem. A* **2004**, *108*, 2020−2029.

(78) Blondel, C.; Delsart, C.; Goldfarb, F. *J. Phys. B. − At. Mol. Opt. Phys.* **2001**, *34*, L281−L288.

(79) Pliego, J. R., Jr.; Riveros, J. M. *J. Phys. Chem. A* **2002**, *106*, 7434−7439.

(80) Takano, Y.; Houk, K. N. *J. Chem. Theory Comput.* **2005**, *1*, 70−77.

(81) Dixon, D. A.; Francisco, J. S.; Alexeev, Y. *J. Phys. Chem. A.* **2006**, *110*, 185−191.

(82) (a) Zhan, C.-G.; Bentley, J.; Chipman, D. M. *J. Chem. Phys.* **1998**, *108*, 177−192. (b) Zhan, C.-G.; Chipman, D. M. *J. Chem. Phys.* **1998**, *109*, 10543−10558. (c) Zhan, C.-G.; Chipman, D. M. *J. Chem. Phys.* **1999**, *110*, 1611−1622. (d) Zhan, C.-G.; Zheng, F. *J. Am. Chem. Soc.* **2001**, *123*, 2835−2838.

(83) Zhan, C.-G.; Dixon, D. A. *J. Phys. Chem. A* **2002**, *106*, 9737−9744.

(84) Klamt, A.; Eckert, F.; Diedenhofen, M.; Beck, M. E. *J. Phys. Chem. A* **2003**, *10*, 9380−9386.

(85) Chipman, D. M. *J. Phys. Chem. A* **2002**, *106*, 7413−7422.