Ab Initio Gas-Phase Acidities of NaH, MgH_2, and AlH_3

Robert J. Hinde*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Received: November 22, 1999; In Final Form: April 7, 2000

We present ab initio estimates of the gas-phase acidities ΔH_{acid} of the second-row metal hydrides NaH, MgH_2, and AlH_3. Our estimates are based on frozen-core CCSD(T) calculations using augmented triple- and quadruple-ζ correlation-consistent basis sets that include core polarization functions; these single-point calculations are extrapolated to the complete basis set limit and then adjusted to incorporate core−valence correlation effects, vibrational zero-point energy contributions, and thermal corrections. The final ΔH_{acid} values we obtain at $T = 298$ K are 345.26 kcal/mol for NaH, 363.83 kcal/mol for MgH_2, and 372.93 kcal/mol for AlH_3; the estimated uncertainty in these values is ±0.8 kcal/mol. Our results suggest that the current NIST−JANAF recommended bond dissociation energy for NaH is too high by roughly 2 kcal/mol.

Introduction

Considerable progress has recently been made in the treatment of electron correlation in molecules[1,2] and in the creation of systematic sequences of atomic basis sets[3−5] for highly correlated ab initio calculations. These advances, coupled with the development of extrapolation schemes[6−10] that provide estimates of the complete basis set limit of correlated ab initio calculations, have made it possible to compute, in a purely ab initio manner, highly accurate thermodynamic properties for small molecules composed of first- and second-row atoms. Computations of this type are important in a variety of applications. For example, we may want to estimate the thermodynamic properties of proposed energy-rich propellants or explosives before synthesizing them in the laboratory. Computational thermochemistry can also give us insight into the energetics of transition states and reactive intermediates that may be difficult to isolate experimentally.

In this work, we present ab initio estimates of the gas-phase acidities ΔH_{acid} of the second-row metal hydrides NaH, MgH_2, and AlH_3. The paper is organized as follows. In the Computational Methods section we describe our ab initio methods in detail and calibrate them against experimental results. The Results section summarizes our calculations and reports ab initio ΔH_{acid} values for NaH, MgH_2, and AlH_3. We then conclude in the Discussion section by comparing our results with those obtained by using computationally less-demanding methods and by discussing the current status of NaH thermochemistry.

Computational Methods

We begin by compiling a body of experimental data that we can use to test our ab initio protocol for computing gas-phase acidities. The energy change ΔE_{acid} at $T = 0$ K for the deprotonation reaction

$$\mathrm{XH}_n \rightarrow \mathrm{XH}_{n-1}^- + \mathrm{H}^+ \qquad (1)$$

is $\Delta E_{\mathrm{acid}} = \mathrm{BDE}(\mathrm{H{-}XH}_{n-1}) + \mathrm{IE(H)} - \mathrm{EA}(\mathrm{XH}_{n-1})$ where $\mathrm{BDE}(\mathrm{H{-}XH}_{n-1})$ is the $\mathrm{H{-}XH}_{n-1}$ bond dissociation energy at $T = 0$ K, IE(H) is the ionization energy of the hydrogen atom, and $\mathrm{EA}(\mathrm{XH}_{n-1})$ is the electron affinity of XH_{n-1}. Experimental values for the quantities $\mathrm{BDE}(\mathrm{H{-}XH}_{n-1})$ and $\mathrm{EA}(\mathrm{XH}_{n-1})$ are available for X = O, F, Na, S, and Cl (see Table 1); from these data we can define a set of "benchmark" first- and second-row ΔE_{acid} values against which our ab initio techniques can be calibrated.

However, ΔE_{acid} for reaction 1 at $T = 0$ K is not directly accessible from ab initio calculations; instead, these calculations give $\Delta E_{\mathrm{eq}} = E(\mathrm{XH}_{n-1}^-) - E(\mathrm{XH}_n)$, where E(M) is the total energy of species M at its equilibrium geometry. If we define Z(M) to be the vibrational zero-point energy of species M, then $\Delta E_{\mathrm{eq}} = \Delta E_{\mathrm{acid}} + Z(\mathrm{XH}_n) - Z(\mathrm{XH}_{n-1}^-)$. Accurate zero-point energies for the diatomic species HF, NaH, and HCl are available from spectroscopic measurements; these are listed in Table 2. We estimated the vibrational zero-point energies for H_2O, SH^-, and H_2S as the sum of the zero-point energies of the molecules' vibrational modes; these are in turn obtained from the experimental $v = 0 \rightarrow 1$ and $v = 0 \rightarrow 2$ transition energies under the assumption that each vibrational mode behaves like a Morse oscillator. The vibrational zero-point energy for OH^- was estimated in a similar fashion from the ω_e and $\omega_e x_e$ values given in ref 19.

Combining the experimental data in Table 1 with the zero-point energies listed in Table 2, we obtain the "experimental" $\Delta E_{\mathrm{eq,expt}}$ values listed in the first row of Table 3; these are the targets against which we calibrate our ab initio techniques. Because all of our ab initio calculations are performed within the Born−Oppenheimer approximation, we set IE(H) = 0.5 hartree to obtain the values listed in Table 3. (We use the energy conversion factors[24] 1 eV = 0.036749 hartree = 23.0495 kcal/mol = 8065.54 cm^{-1} throughout this paper.)

We begin our calibration with estimates of the total energies E of XH_n and XH_{n-1}^- for X = O, F, Na, S, and Cl, obtained by extrapolating a series of frozen-core ab initio energy calculations to the complete basis set (CBS) limit and then correcting for core−valence correlation effects. Specifically, we compute the electronic energy of XH_n and XH_{n-1}^- at their respective equilibrium geometries, correlating only valence electrons by using the coupled cluster singles-and-doubles method[1] with noniterative inclusion of connected triples,[2] or CCSD(T). We use the aug-cc-pVxZ (x = D, T, Q) series of basis sets for

---

* To whom correspondence should be addressed. E-mail: rhinde@utk.edu.

10.1021/jp994138j CCC: $19.00

TABLE 1: Experimental $H-XH_{n-1}$ Bond Dissociation Energies (in kcal/mol) and XH_{n-1} Electron Affinities (in eV)[a]

XH_n	BDE ($H-XH_{n-1}$)	ref	EA (XH_{n-1})	ref
H_2O	118.0	11	1.8277	14
HF	135.20	12	3.40119	15
NaH	43.8	13	0.54793	16
H_2S	89.0[b]	11	2.317	17
HCl	102.2	11	3.6136	18

[a] Unless otherwise indicated, estimated uncertainties are ±3 or smaller in the last significant figure. [b] Uncertainty is ±1.5 kcal/mol.

TABLE 2: Vibrational Zero-Point Energies Z(M) (in kcal/mol)

M	Z (M	ref
OH^-	5.28	19
H_2O	13.11	20
HF	5.86	12
NaH	1.66	13
SH^-	3.74	21
H_2S	9.30	22
HCl	4.24	23

hydrogen[3] and for first-row atoms[4] and the aug-cc-pVxZ+1 series of basis sets described below for second-row atoms.[5,25] We then extrapolate these energies to the frozen-core CCSD(T) CBS limit by fitting the triple- and quadruple-ζ CCSD(T) energies to the equation proposed by Martin:[8]

$$E(s) = E_{\mathrm{CBS}} - A(s + 1/2)^{-4} \tag{2}$$

where $s = 3$ for the aug-cc-pVTZ (or aug-cc-pVTZ+1) basis set and $s = 4$ for the aug-cc-pVQZ (or aug-cc-pVQZ+1) basis set. The energy E_{CBS} is our estimate of the complete basis set CCSD(T) energy when only valence electrons are correlated; the fitting parameter A indicates the speed with which the aug-cc-pVxZ energies converge to E_{CBS}. The results of these calculations are listed in Tables 3 and 4. All of the CCSD(T) calculations presented in this paper were performed by using ACES II.[27]

We then add to E_{CBS} the core−valence correlation energy for each molecule, defined as the difference between the CCSD(T)/aug-cc-pCVTZ energy obtained by correlating all electrons and the CCSD(T)/aug-cc-pCVTZ energy obtained by correlating only valence electrons. The aug-cc-pCVTZ basis sets we use are those derived from the aug-cc-pVTZ basis sets following the prescription of Martin and Taylor.[28] Tables 3 and 4 give the results of these core−valence calculations and our final estimates E (including core−valence correlation) of the total energy of each molecule at its equilibrium geometry. Table 3 also gives our ab initio estimates of ΔE_{eq} for reaction 1, obtained from the estimated total energies E of the species XH_n and XH_{n-1}^-.

The ab initio ΔE_{eq} values in Table 3 agree very well with the experimentally derived results, which indicates that our ab initio protocol is reliable. The largest deviation between our computed ΔE_{eq} and experiment is 0.95 kcal/mol for the deprotonation of H_2S; our ab initio ΔE_{eq} values for the other four molecules agree with experiment to better than 0.5 kcal/mol. The case of H_2S is somewhat anomalous because the H−SH BDE is uncertain by ±1.5 kcal/mol (see Table 1).

Martin and Uzan[29] showed that the properties of molecules with second-row atoms approach the CBS limit much faster if a tight d Gaussian function is added to the conventional aug-cc-pVxZ basis set. This tight d function accounts for the polarization of core orbitals in molecular environments; the basis set consisting of the original aug-cc-pVxZ basis set plus the additional d function is denoted aug-cc-pVxZ+1. The exponents of the tight d functions used in this work were obtained by minimizing the Hartree−Fock aug-cc-pVTZ+1 energies of NaH, H_2S, and HCl at their equilibrium geometries; the resulting exponents are $a = 0.81$ for Na, $\alpha = 3.53$ for S, and $\alpha = 4.51$ for Cl. (Note that we have used these tight d functions only in our frozen-core coupled cluster calculations.)

When this work was begun, no aug-cc-pVxZ basis sets had been developed for Na; we therefore constructed ad hoc aug-cc-pVxZ Na basis sets by adding to the cc-pVxZ basis sets one diffuse function of each symmetry, with an exponent $\alpha = \alpha_{\mathrm{min}}/3.5$ where α_{min} is the exponent of the most diffuse function of that symmetry in the original cc-pVxZ basis set.

Results

We now use the same ab initio protocol to calculate ΔE_{eq} for the deprotonation of MgH_2 and AlH_3. Experimental equilibrium geometries for these two molecules and their conjugate bases are not known; consequently, our ab initio calculations employ B3LYP/aug-cc-pVTZ equilibrium geometries, which are listed in Table 5. To assess the error introduced by using these approximate equilibrium geometries, we decided to calculate ΔE_{eq} for the other second-row hydrides by using B3LYP/aug-cc-pVTZ geometries, which are also listed in Table 5. The B3LYP[30,31] equilibrium geometries presented in this table were computed by using Gaussian 94.[32] [Note: A programming error in Gaussian 94, Revision C.2, forced us to delete the most diffuse primitive from the contracted Na 1s orbital in the aug-cc-pVTZ basis set when performing these calculations.]

Tables 6 and 7 summarize our CCSD(T) results. For these calculations, we used ad hoc augmented Mg basis sets analogous to those defined previously for Na. We also computed the exponents of the additional tight d functions used in the Mg and Al aug-cc-pVxZ+1 basis sets by minimizing the Hartree−Fock aug-cc-pVTZ+1 energy of MgH_2 and AlH_3 at their respective B3LYP/aug-cc-pVTZ geometries; these tight d exponents are $\alpha = 0.99$ for Mg and $\alpha = 1.34$ for Al.

Note that the ΔE_{eq} values listed in Table 6 for NaH, H_2S, and HCl are within 0.05 kcal/mol of the values given in Table 3. This indicates that the use of B3LYP/aug-cc-pVTZ geometries does not introduce significant error into our calculation of ΔE_{eq}.

The gas-phase acidity ΔH_{acid} of XH_n is defined as ΔH for reaction 1 at $T = 298$ K. To convert the ab initio ΔE_{eq} values listed in Table 6 to ab initio gas-phase acidities, we first account for the change in vibrational zero-point energy upon deprotonation, thereby converting ΔE_{eq} to ΔE_{acid} for reaction 1 at $T = 0$ K. We then evaluate the thermal contribution to ΔE_{acid} that arises from heating reactants and products to $T = 298$ K. Finally, we assume ideal gas behavior in reaction 1 and set $\Delta H_{\mathrm{acid}}(T) = \Delta E_{\mathrm{acid}}(T) + RT$.

To account for the change in zero-point energy in reaction 1 we assume that the vibrational zero-point energies Z of the species in Table 5 are given by 0.99 times the harmonic zero-point energies computed by using the B3LYP/aug-cc-pVTZ frequencies listed in that table. The factor of 0.99 was chosen to give the best agreement with the zero-point energies listed in Table 2 and accounts for the slight vibrational anharmonicity of the underlying potential surfaces. (The maximum deviation between our computed zero-point energies and those listed in Table 2 is 0.1 kcal/mol.) Pople et al.[34] recommended that accurate zero-point energies be obtained by scaling MP2/6-31G(d,p) harmonic zero-point energies by the factor 0.9646. Our scaling factor is slightly higher because we begin with B3LYP/aug-cc-pVTZ harmonic frequencies, and the agreement with

TABLE 3: "Experimental" $\Delta E_{eq,expt}$ Values, Equilibrium Geometries (with Literature References), Hartree−Fock Energies E_{HF}, Frozen-Core CCSD(T) Energies E_{CC}, Core−Valence Energies, Estimated CBS Energies E (Which Include Core−Valence Correlation), and Ab Initio ΔE_{eq} Values for H_2O, HF, NaH, H_2S, and HCl[a]

	H_2O	HF	NaH	H_2S	HCl
$\Delta E_{eq,expt}$	397.27	376.23	346.39	354.72	336.72
r_{eq} (Å)	0.9578	0.9170	1.8870	1.3366	1.2746
θ_{eq} (deg)	104.54			92.23	
ref	20	26	13	22	23
E_{HF}					
aug-cc-pVDZ	76.041395	100.033466	162.385736	398.701500	460.094267
aug-cc-pVTZ	76.060575	100.061069	162.391716	398.715957	460.108660
aug-cc-pVQZ	76.065960	100.068559	162.392888	398.719290	460.112011
E_{CC}					
aug-cc-pVDZ	76.273760	100.263586	162.420631	398.886064	460.277243
aug-cc-pVTZ	76.342298	100.349559	162.428947	398.943525	460.345632
aug-cc-pVQZ	76.363585	100.377384	162.430578	398.958828	460.365685
CBS limit	76.375871	100.393444	162.431519	398.967660	460.377259
CCSD(T)/aug-cc-pCVTZ energies					
frozen-core	76.351657	100.362945	162.429591	398.947901	460.350808
all-electron	76.410856	100.424863	162.747184	399.311923	460.700870
E	76.435070	100.455362	162.749112	399.331682	460.727321
ΔE_{eq}	397.42	376.65	346.08	355.66	336.56

[a] All total energies are given in hartrees with minus signs omitted; ΔE_{eq} and $\Delta E_{eq,expt}$ are given in kcal/mol. The E_{HF} and frozen-core E_{CC} calculations use aug-cc-pVxZ+1 basis sets for Na, S, and Cl atoms.

TABLE 4: Equilibrium Geometries, Hartree−Fock Energies E_{HF}, Frozen-Core CCSD(T) Energies E_{CC}, Core−Valence Energies, and Estimated CBS Energies E (Which Include Core−Valence Correlation) for OH^-, F^-, Na^-, SH^-, and Cl^-[a]

	OH^-	F^-	Na^-	SH^-	Cl^-
r_{eq} (Å)	0.9643[b]			1.3433[c]	
E_{HF}					
aug-cc-pVDZ	75.395879	99.428282	161.848874	398.135266	459.563645
aug-cc-pVTZ	75.412165	99.450807	161.853936	398.146256	459.573481
aug-cc-pVQZ	75.416949	99.457462	161.854882	398.149180	459.576353
E_{CC}					
aug-cc-pVDZ	75.643810	99.668634	161.872325	398.319670	459.741914
aug-cc-pVTZ	75.709414	99.749538	161.877972	398.375265	459.806513
aug-cc-pVQZ	75.730335	99.777073	161.878692	398.391454	459.828268
CBS limit	75.742410	99.792965	161.879108	398.400798	459.840824
CCSD(T)/aug-cc-pCVTZ energies					
frozen-core	75.718826	99.763310	161.878157	398.379300	459.811551
all-electron	75.777754	99.825104	162.196288	398.743052	460.161362
E	75.801338	99.854759	162.197239	398.764550	460.190635

[a] All energies are given in hartrees with minus signs omitted. The E_{HF} and frozen-core E_{CC} calculations use aug-cc-pVxZ+1 basis sets for Na, S, and Cl atoms. [b] Reference 19. [c] Reference 21.

TABLE 5: Equilibrium Geometries, Total Energies E (with Minus Signs Omitted), and Harmonic Vibrational Frequencies Calculated at the B3LYP/aug-cc-pVTZ Level for NaH, MgH_2, MgH^-, AlH_3, AlH_2^-, H_2S, SH^-, and HCl[a]

molecule	r_{eq} (Å)	θ_{eq} (deg)	E (hartrees)	vibrational frequencies (cm^{-1})
NaH	1.8833		162.871390	1180 (σ)
MgH_2	1.7012	180.0	201.269974	440 (π), 1611 (σ_g), 1636 (σ_u)
AlH_3	1.5815	120.0	244.233607	712 (a_2''), 788 (e'), 1927 (a_1'), 1936 (e')
H_2S	1.3446	92.57	399.432270	1209 (a_1), 2684 (a_1), 2697 (b_2)
HCl	1.2833		460.844267	2948 (σ)
MgH^-	1.8737		200.683919	1094 (σ)
AlH_2^-	1.6928	95.04	243.632224	799 (a_1), 1463 (a_1), 1464 (b_2)
SH^-	1.3494		398.867125	2626 (σ)

[a] Symmetries of vibrational modes are listed in parentheses.

experimental zero-point energies obtained here is substantially better than that obtained in ref 34.

To compute the thermal contribution to ΔE_{acid} at $T = 298$ K, we treat the rotational and translational degrees of freedom classically and assume that the vibrational modes are harmonic oscillators with the frequencies given in Table 5.

Our final ab initio gas-phase acidities ΔH_{acid} at $T = 298$ K are 345.26 kcal/mol for NaH, 363.83 kcal/mol for MgH_2, and 372.93 kcal/mol for AlH_3. The main sources of error in these estimates are (1) errors in our calculation of vibrational zero-point energies and (2) errors in our extrapolation to the CBS limit. We estimate the uncertainty in our zero-point energy differences to be ±0.3 kcal/mol or smaller on the basis of the results obtained for species whose zero-point energies are known experimentally. We estimate our extrapolation error to be ±0.5 kcal/mol or smaller on the basis of the very good agreement

TABLE 6: Hartree−Fock Energies E_{HF}, Frozen-Core CCSD(T) energies E_{CC}, Core−Valence Energies, Estimated CBS Energies E (Which Include Core−Valence Correlation), and ΔE_{eq} Values for NaH, MgH_2, AlH_3, H_2S, and HCl at the B3LYP Geometries Given in Table 5[a]

	NaH	MgH_2	AlH_3	H_2S	HCl
E_{HF}					
aug-cc-pVDZ	162.385715	200.730127	243.636558	398.701454	460.094208
aug-cc-pVTZ	162.391927	200.738617	243.646238	398.715768	460.108506
aug-cc-pVQZ	162.392867	200.740032	243.648902	398.719093	460.111852
E_{CC}					
aug-cc-pVDZ	162.420606	200.798735	243.743859	398.886235	460.277344
aug-cc-pVTZ	162.429154	200.813588	243.766816	398.943496	460.345605
aug-cc-pVQZ	162.430553	200.816362	243.772943	398.958792	460.365658
CBS limit	162.431360	200.817963	243.776749	398.967620	460.377232
CCSD(T)/aug-cc-pCVTZ energies					
frozen-core	162.429567	200.814249	243.768453	398.947845	460.350769
all-electron	162.747180	201.153346	244.104466	399.311836	460.700816
E	162.748973	201.157063	244.112492	399.331611	460.727279
ΔE_{eq}	346.06	366.97	377.74	355.68	336.59

[a] All total energies are given in hartrees with minus signs omitted; ΔE_{eq} is given in kcal/mol. The E_{HF} and frozen-core E_{CC} calculations use aug-cc-pVxZ+1 basis sets for all non-hydrogen atoms.

TABLE 7: Hartree−Fock Energies E_{HF}, Frozen-Core CCSD(T) Energies E_{CC}, Core−Valence Energies, and Estimated CBS Energies E (Which Include Core−Valence Correlation) for MgH^-, AlH_2^-, and SH^- at the B3LYP Geometries Given in Table 5[a]

	MgH^-	AlH_2^-	SH^-
E_{HF}			
aug-cc-pVDZ	200.148590	243.029624	398.135240
aug-cc-pVTZ	200.155554	243.037875	398.146179
aug-cc-pVQZ	200.156722	243.040032	398.149098
E_{CC}			
aug-cc-pVDZ	200.217984	243.144997	398.319745
aug-cc-pVTZ	200.229179	243.165696	398.375265
aug-cc-pVQZ	200.231227	243.170865	398.391450
CBS limit	200.232409	243.173848	398.400791
CCSD(T)/aug-cc-pCVTZ energies			
frozen-core	200.229612	243.166839	398.379290
all-electron	200.569103	243.503141	398.743030
E	200.571900	243.510150	398.764531

[a] All energies are given in hartrees with minus signs omitted. The E_{HF} and frozen-core E_{CC} calculations use aug-cc-pVxZ+1 basis sets for all non-hydrogen atoms.

between the ab initio and experimental values given in Table 3 (excluding the case of H_2S for the reason discussed earlier). A conservative estimate of the uncertainty in our ΔH_{acid} values is therefore ±0.8 kcal/mol.

Discussion

The estimated gas-phase acidities presented here are based on moderately demanding ab initio calculations, including CCSD(T)/aug-cc-pVQZ+1 single-point calculations. Although these calculations are feasible for the species studied here, which each have high point group symmetry and only one non-hydrogen atom, it is of interest to compare our results with those obtained by using less-expensive extrapolation schemes[10] based on double- and triple-ζ calculations or using less-expensive quantum chemstry methods such as density functional theory and Gaussian-2 (G2) theory.[33]

Alternative Extrapolation Schemes. Truhlar[10] has demonstrated that for H_2O, HF, and Ne, the CBS limit for a given level of electron correlation can be estimated inexpensively from cc-pVDZ and cc-pVTZ calculations by *separately* extrapolating the Hartree−Fock energy and the (frozen-core) correlation energy to their respective CBS limits by using the equation

$$E(s) = E_{CBS} - As^{-\beta} \qquad (3)$$

where $s = 2$ for the cc-pVDZ basis set and $s = 3$ for the cc-pVTZ basis set. Truhlar found that for a CCSD(T) treatment of electron correlation, the optimal extrapolation exponents β for these three first-row species were 3.4 for the Hartree−Fock energy and 2.4 for the correlation energy.

Table 8 lists the ΔE_{eq} values obtained by applying this extrapolation scheme to our frozen-core aug-cc-pVxZ+1 energies and compares them with the frozen-core CBS estimates obtained by using eq 2. The two sets of ΔE_{eq} values agree to within 0.6 kcal/mol, which indicates that Truhlar's extrapolation scheme may provide inexpensive but accurate estimates for heats of reaction for species involving both first- and second-row atoms.

Density Functional Theory and G2 Theory. From the B3LYP/aug-cc-pVTZ energies listed in Table 5, along with the B3LYP/aug-cc-pVTZ energy of Na^- ($E = -162.318369$ hartree) we obtain ΔE_{eq} values of 346.86 kcal/mol for NaH, 367.58 kcal/mol for MgH_2, and 377.20 kcal/mol for AlH_3. These values agree with our CBS estimates to within 0.8 kcal/mol, which suggests that B3LYP calculations may also provide reasonably accurate acidities at low computational cost.

In Table 8 we also compare our frozen-core CBS ΔE_{eq} values for NaH, MgH_2, and AlH_3 with those calculated by using several variants of G2 theory. (We performed all of our G2-style calculations by using Gaussian 94;[32] we removed the zero-point

TABLE 8: Estimated ΔE_{eq} Values from This Work (Omitting Core−Valence Correlation Effects) for NaH, MgH_2, and AlH_3 Compared with ΔE_{eq} Values Computed Using the Extrapolation Scheme of Eq 3 and Using Several Variants of Gaussian-2 Theory[a]

method	NaH	MgH_2	AlH_3
this work	346.38	367.28	377.98
eq 3	346.62	367.68	377.65
G2	344.59	366.08	377.53
QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d,p)	344.89	366.19	377.19
QCISD(T)/6-311(DD)G(3df,2p)//MP2(full)/6-31G(d,p)	344.90	366.14	377.04
QCISD(T)/6-311++G(3df,2p)//MP2(full)/6-31G(d,p)	344.90	366.09	377.12
QCISD(T)/6-311++G(3df,2p)//B3LYP/aug-cc-pVTZ	344.84	366.05	377.11

[a] All values are given in kcal/mol.

energy correction term to obtain ΔE_{eq} values.) Note that the ΔE_{eq} values obtained for NaH and MgH_2 by using the original G2 protocol[33] are somewhat below our estimated CBS limits. For MgH_2, the G2 ΔE_{eq} is 1.2 kcal/mol smaller than our CBS estimate; for NaH, the G2 value is 1.8 kcal/mol smaller than our CBS estimate. By comparison, the G2 and CBS values of ΔE_{eq} for AlH_3 agree to better than 0.5 kcal/mol. Our observation of a relatively large deviation between the G2 and CBS values for ΔE_{eq} for NaH and the systematic improvement in the G2 results on going from NaH to MgH_2 to AlH_3 prompted us to investigate the origin of this deviation.

G2 theory attempts to approximate QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d,p) energies by using a sequence of less-expensive ab initio calculations. Previous studies of G2 energies[35,36] have found that the additivity assumptions inherent in G2 theory can break down for small anions, thereby leading to inaccurate G2 predictions for deprotonation energies. To investigate this possibility, we calculated ΔE_{eq} for NaH, MgH_2, and AlH_3 at the QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31+G(d,p) level, avoiding any use of these additivity assumptions. The results, shown in Table 8, indicate that the additivity assumptions of G2 theory are justified for these molecules and are therefore not the source of the discrepancies observed here.

Other studies[37,38] have shown that the neglect of core−valence correlation effects in standard G2 theory can lead to inaccurate results for compounds including alkali metals and alkaline earths. However, the core−valence correlation contributions to ΔE_{eq} obtained in this work are quite small (0.35 kcal/mol or less), which suggests that the default G2 choice of core orbitals is adequate for the metal hydrides considered here.

Gronert[39] showed that adding a second set of diffuse functions to non-hydrogen atoms improved G2-style predictions for the acidities of first- and second-row nonmetal hydrides; additional diffuse functions are known[4] to be required for highly accurate ab initio calculations of anions. We therefore computed ΔE_{eq} for reaction 1 at the QCISD(T)/6-311(DD)G(3df,2p)//MP2(full)/6-31G(d,p) level, where (DD) indicates that non-hydrogen atoms carry a double set of diffuse s and p Gaussian functions. (The first set of diffuse functions was obtained from the 6-311+G(3df,2p) basis set; the second set of diffuse functions was assigned an exponent 1/3.5 times that of the first set.) These ΔE_{eq} values do not differ significantly from the values computed by using a single set of diffuse functions on non-hydrogen atoms.

Because Na and Mg are highly electropositive, we suspected that the discrepancy between our estimated CBS acidities and the G2 acidities might arise from the omission of diffuse orbitals on hydrogen atoms in the standard G2 basis sets. We therefore recalculated ΔE_{eq} at the QCISD(T)/6-311++G(3df,2p)//MP2(full)/6-31G(d,p) level; as Table 8 shows, inclusion of a diffuse s orbital on hydrogen changes ΔE_{eq} very little.

Finally, we investigated whether the discrepancy between our CBS estimates and G2 theory might arise from the use of MP2(full)/6-31G(d,p) equilibrium geometries in the G2-style calculations. We calculated QCISD(T)/6-311++G(3df,2p) values for ΔE_{eq} for NaH, MgH_2, and AlH_3 by using the B3LYP geometries listed in Table 5 instead of the MP2(full)/6-31G(d,p) geometries. As Table 8 shows, this also made very little difference in the computed ΔE_{eq} values.

It therefore seems that the discrepancies between our CBS and G2 NaH and MgH_2 ΔE_{eq} values originate in basis set deficiencies at the 6-311+G(3df,2p) level that cannot be remedied simply by the addition of further diffuse orbitals on either hydrogen or non-hydrogen atoms. We suspect that these deficiencies stem from an inadequate complement of high angular momentum functions on hydrogen, which is an electron-rich center in NaH and, to a lesser extent, in MgH_2. An accurate treatment of the *angular* correlation of the valence electrons in these molecules requires a reasonably large set of high angular momentum functions centered on hydrogen; these are provided in a systematic fashion by the aug-cc-pVxZ basis sets but are absent from the 6-311+G(3df,2p) basis set used in G2 theory.

An examination of the values obtained here for the fitting parameter A appearing in eq 2 provides support for this hypothesis. Recall that A measures the speed with which our calculated ab initio energies approach the CBS limit. A direct comparison of the A values obtained for different molecules is not very illuminating, primarily because the magnitudes of molecular energies vary strongly with the total number of electrons. We therefore compare the *ratios* of the A values obtained for XH_n and XH_{n-1}^-, defined $r(X) = A(XH_n)/A(XH_{n-1}^-)$. A large value for $r(X)$ indicates that the energy of XH_n is much more sensitive to basis set extension than is the energy of XH_{n-1}^-.

The r values we obtain are 1.18, 1.35, and 1.94 for Al, Mg, and Na, respectively. This indicates that the ab initio energy of NaH is especially sensitive to the quality of the underlying basis set. This sensitivity seems to arise from the considerable negative partial charge acquired by hydrogen in NaH because the r values for F and Cl are much smaller at 1.01 and 0.92, respectively.

NaH Thermochemistry. We conclude with a brief discussion of the current status of NaH thermochemistry. The experimental gas-phase acidity of NaH derived from data in the most recent NIST−JANAF compilation[11] is $\Delta H_{acid} = 348.13 \pm 4.63$ kcal/mol. The very large uncertainty in this value arises from a corresponding uncertainty in the $T = 0$ K BDE of NaH, which ref 11 cites as 2.05 ± 0.2 eV, or 47.25 ± 4.61 kcal/mol. This BDE value is a 1947 estimate[40] based on a modified Birge−Sponer[41] analysis of the $0 \leq v \leq 8$ vibrational levels of NaH. A more recent estimate[13] of the NaH BDE, based on the $0 \leq v \leq 11$ vibrational levels of NaH, is 45.43 ± 0.29 kcal/mol.

To obtain an ab initio estimate of the BDE of NaH, we extrapolated single-point CCSD(T) calculations for NaH, Na, and H to the CBS limit by using eq 2. These calculations were performed by using Martin−Taylor-style[28] aug-cc-pCVTZ and aug-cc-pCVQZ basis sets and correlating all electrons; NaH was held fixed at its equilibrium bond length given in Table 3. After subtracting the vibrational zero-point energy of NaH (Table 2) we obtain a CBS estimate of the $T = 0$ K NaH BDE of 45.16 kcal/mol, in good agreement with the more recent estimate. Hence it appears that the NIST−JANAF recommended BDE for NaH is too high by roughly 2 kcal/mol.

Acknowledgment. R.J.H. thanks Prof. J. E. Bartmess for posing a question that stimulated this work and for several helpful conversations. Some basis sets were obtained from version 1.0 of the Extensible Computational Chemistry Environment Basis Set Database, which was developed and distributed by the Molecular Science Computing Facility at Pacific Northwest National Laboratory's Environmental and Molecular Sciences Laboratory (http://www.emsl.pnl.gov/). We thank Dr. D. Feller and the authors of ref 25 for providing us with basis sets from this paper prior to publication.

References and Notes

(1) Purvis, G. D., III.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(2) Pople, J. A.; Head-Gordon, M.; Ragavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(3) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(4) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6769.

(5) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(6) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

(7) Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1996**, *248*, 336.

(8) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669.

(9) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olson, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(10) Truhlar, D. G. *Chem. Phys. Lett.* **1998**, *294*, 45.

(11) Chase, M. W., Jr. *NIST−JANAF Thermochemical Tables*, 4th ed. (Monograph 9 of *J. Phys. Chem. Ref. Data*); American Institute of Physics: Woodbury, NY, 1998.

(12) Zemke, W. T.; Stwalley, W. C.; Coxon, J. A.; Hajigeorgiou, P. G. *Chem. Phys. Lett.* **1991**, *177*, 412.

(13) Stwalley, W. C.; Zemke, W. T.; Yang, S. C. *J. Phys. Chem. Ref. Data* **1991**, *20*, 153.

(14) Schulz, P. A.; Mead, R. D.; Jones, P. L.; Lineberger, W. C. *J. Chem. Phys.* **1982**, *77*, 1153.

(15) Blondel, C.; Cacciani, P.; Delsart, C.; Trainham, R. *Phys. Rev. A: At., Mol., Opt. Phys.* **1989**, *40*, 3698.

(16) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 731.

(17) Breyer, F.; Frey, P.; Hotop, H. *Z. Phys. A: At. Nucl.* **1981**, *300*, 7.

(18) Berzinsh, U.; Gustafsson, M.; Hanstorp, D.; Klinkmuller, A.; Ljungblad, U.; Martenssonpendrill, A. M. *Phys. Rev. A: At., Mol., Opt. Phys.* **1995**, *51*, 231.

(19) Rosenbaum, N. H.; Owrutsky, J. C.; Tack, L. M.; Saykally, R. J. *J. Chem. Phys.* **1986**, *84*, 5308.

(20) Jensen, P.; Tashkun, S. A.; Tuyterev, V. G. *J. Mol. Spectrosc.* **1994**, *168*, 271.

(21) Gruebele, M.; Polak, M.; Saykally, R. J. *J. Chem. Phys.* **1987**, *86*, 1698.

(22) Kozin, I. N.; Jensen, P. *J. Mol. Spectrosc.* **1994**, *163*, 483.

(23) Coxon, J. A. *J. Mol. Spectrosc.* **1986**, *117*, 361.

(24) *Atomic, Molecular, and Optical Physics Handbook*; Drake, G. W. F., Ed.; American Institute of Physics: Woodbury, NY, 1996.

(25) The Na and Mg cc-pVxZ basis sets used in this work were obtained from Woon, D. E.; Dunning, T. H., Jr. Manuscript in preparation.

(26) Coxon, J. A.; Hajigeorgiou, P. G. *J. Mol. Spectrosc.* **1990**, *142*, 254.

(27) ACES II is an ab initio program system written by Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; and Bartlett, R. J. that incorporates the MOLECULE molecular integral program by Almlöf, J.; Taylor, P. R. and a modified version of the ABACUS integral derivative package by Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; and Taylor, P. R. See http://www.qtp.ufl.edu/ for more information.

(28) Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1994**, *225*, 473.

(29) Martin, J. M. L.; Uzan, O. *Chem. Phys. Lett.* **1998**, *282*, 16.

(30) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(31) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. P. *Gaussian 94 Revision C.2*; Gaussian, Inc.: Pittsburgh, 1995.

(33) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(34) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(35) Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K. *J. Chem. Phys.* **1992**, *96*, 9030.

(36) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258.

(37) Petrie, S. *J. Phys. Chem. A* **1998**, *102*, 6138.

(38) Schulz, A.; Smith, B. J.; Radom, L. *J. Phys. Chem. A* **1999**, *103*, 7522.

(39) Gronert, S. *Chem. Phys. Lett.* **1996**, *252*, 415.

(40) Gaydon, A. G. *Dissociation Energies and Spectra of Diatomic Molecules*; Wiley: New York, 1947.

(41) Birge, R. T.; Sponer, H. *Phys. Rev.* **1926**, *28*, 259.