J. Phys. Chem. A **1998,** *102,* 2449−2454

Predicting the Proton Affinities of H_2O and NH_3

Kirk A. Peterson

Department of Chemistry, Washington State University, and the Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352

Sotiris S. Xantheas, David A. Dixon,* and Thom H. Dunning, Jr.

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352

Received: May 5, 1997; In Final Form: November 12, 1997

High-level ab initio molecular orbital theory has been used to predict the proton affinities of H_2O and NH_3 at the CCSD(T) level with correlation-consistent basis sets through augmented quintuple-ζ for the former and augmented quadruple-ζ for the latter. Diffuse functions have been shown to yield faster convergence to the complete basis set limit for the prediction of highly accurate proton affinities. For these two systems, core−valence correlation effects are small, 0.13 kcal/mol, and were obtained from calculations with core−valence, correlation-consistent basis sets. The electronic component of the proton affinities are 171.56 kcal/mol for H_2O and 211.97 kcal/mol for NH_3. The zero-point vibrational corrections were taken from experimental values where available and from scaled theoretical values otherwise. The final proton affinity (PA) values at 298 K are $\mathrm{PA}(H_2O) = 165.1 \pm 0.3$ kcal/mol and $\mathrm{PA}(NH_3) = 204.1 \pm 0.3$ kcal/mol as compared to experimental values of $\mathrm{PA}(H_2O) = 166.5 \pm 1$ kcal/mol and $\mathrm{PA}(NH_3) = 204 \pm 1$ kcal/mol. The calculated values together with our estimated error limits suggest that the experimental value for H_2O is too high by 1.5 kcal/mol.

Introduction

Computational molecular science has made enormous strides over the past 2 decades due to advances in hardware, software, algorithms, and new theoretical methods so that it is now a full partner with experimental methods. An area in which computational chemistry is playing an ever increasing role is the one of thermodynamics, especially thermochemistry. As thermodynamic measurements become more difficult to make (e.g., due to the size of the molecules and/or to the accuracies demanded by needs such as chemical process models), computational methods will become more and more important in predicting thermodynamics properties.

Computational methods are now being used to define and confirm accurate points on various thermodynamic scales. One of the most important scales is the gas-phase proton affinity scale which is now 30 years old.[1,2] The proton affinity of A (PA(A)) is defined as the negative of ΔH for the following reaction (usually at 298K)

$$A + H^+ \rightarrow AH^+ \qquad (1)$$

The significance of this scale is due to the importance of acid−base chemistry, with proton-transfer reactions often being the most important processes. There is still significant interest in knowing the intrinsic molecular basicity of a molecule in order to understand how the surrounding molecular environment can affect the ability of a molecular species to transfer or accept a proton. This becomes very important when dealing with complex processes, such as those at mineral/aqueous or organic liquid/aqueous interfaces or in acid/base catalysts such as zeolites.

An inherent problem with the proton affinity scale is how to anchor it. Although a large number of equilibrium measurements of gas phase proton transfer processes have been made quite reliably, it is difficult to obtain absolute values with low absolute error bars because one is dealing with molecular ions. Furthermore, each equilibrium measurement has errors associated with it and these can propagate along the scale. Absolute values with high accuracy can be established from theoretical methods, especially for small systems.[3] For example, the lowest known proton affinity of a neutral system, that of He, can be calculated very accurately since it is a two electron system; the proton affinity of H_2 can be calculated very accurately for similar reasons. With normal molecular orbital methods, the only issues for calculations on the He/HeH$^+$ or H_2/H_3^+ systems are the adequacy of the basis set, since a full configuration interaction (FCI) calculation is possible. However, the proton affinities of the two electron systems are so low that they are of importance mostly to the astrophysics community. The more interesting region of the proton affinity scale for many compounds corresponds to values of PA > 150 kcal/mol.

The typical anchor for the high proton affinity region has been NH_3 from various equilibrium measurements, many of which are based on the heat of formation of the *tert*-butyl cation ($C(CH_3)_3^+$) and on photoionization measurements.[4,5] The proton affinity of NH_3 at 298 K is now given as 204 ± 1 kcal/mol. At the lower end of this region is $\mathrm{PA}(H_2O) = 166.5 \pm 1$ kcal/mol at 298K, which has been well-studied, but the experimental measurements are quite difficult due to problems in obtaining accurate pressure measurements of H_2O.

There have been many calculations of the proton affinity of H_2O and NH_3, and the most accurate through 1986 have been summarized and discussed.[3] At that time, the most accurate

S1089-5639(97)01510-7 CCC: $15.00

TABLE 1: Calculated Equilibrium Geometries and Energies for H_2O and H_3O^+

		H_2O			H_3O^+		
method	basis set	E_e (h)	r_e(OH) (Å)	θ_e(HOH) (deg)	E_e (h)	r_e(OH)	θ_e(HOH) (deg)
exptl[a]			0.9572	104.52		0.9758	111.84
HF	aug-cc-pVDZ	−76.041 844	0.9436	105.93	−76.318 580	0.9622	113.27
	aug-cc-pVTZ	−76.061 203	0.9411	106.32	−76.340 777	0.9602	113.77
	aug-cc-pVQZ	−76.066 676	0.9402	106.32	−76.346 600	0.9590	113.85
	aug-cc-pV5Z	−76.068 009	0.9400	106.34	−76.348 010	0.9588	113.88
MP2	aug-cc-pVDZ	−76.260 910	0.9659	103.87	−76.530 062	0.9831	111.03
	aug-cc-pVTZ	−76.328 992	0.9614	104.11	−76.600 209	0.9795	111.49
	aug-cc-pVQZ	−76.351 919	0.9590	104.28	−76.623 204	0.9770	111.74
	aug-cc-pV5Z	−76.360 228	0.9584	104.33	−76.631 388	0.9764	111.88
CCSD	aug-cc-pVDZ	−76.268 633	0.9648	104.17	−76.540 846	0.9815	111.16
	aug-cc-pVTZ	−76.333 670	0.9587	104.43	−76.608 323	0.9769	111.66
	aug-cc-pVQZ	−76.354 216	0.9556	104.62	−76.629 051	0.9742	111.97
MP4	aug-cc-pVDZ	−76.274 512	0.9670	103.88	−76.545 032	0.9832	110.97
	aug-cc-pVTZ	−76.343 678	0.9627	104.06	−76.616 107	0.9798	111.36
	aug-cc-pVQZ	−76.365 084	0.9605	104.23	−76.637 613	0.9771	111.65
	aug-cc-pV5Z	−76.371 847	0.9597	104.30	−76.644 304	0.9766	111.79
CCSD(T)	aug-cc-pVDZ	−76.273 903	0.9666	103.99	−76.545 198	0.9832	110.96
	aug-cc-pVTZ	−76.342 325	0.9616	104.04	−76.615 655	0.9792	111.41
	aug-cc-pVQZ	−76.363 587	0.9594	104.35	−76.637 019	0.9766	111.71
	aug-cc-pV5Z	−76.370 298	0.9584	104.43	−76.643 659	0.9761	111.84

[a] References 13 and 14.

calculated values for H_2O were in the range of 168−169 kcal/mol and that for NH_3 was 205.6 kcal/mol, both of which were higher than the experimental values of 166.5 and 204.0 kcal/mol. Since 1986, there have been significant advances in the general availability of high-quality correlation methods[6] such as coupled-cluster single and double excitations with perturbative treatment of triple excitations [CCSD(T)] for treating the *n*-particle space and important advances in the quality of atomic basis sets for treating the 1-particle space.[7] Furthermore, there have been significant advances in measuring the vibrational spectra of ions so that one can calculate reliable zero-point differences.[8] In a report published after our work was completed, Martin and Lee[9] have reported a high-level calculation of PA(NH_3) at the CCSD(T)/aug′-cc-pV5Z level where the accent mark (′) indicates that the diffuse functions on H have been omitted. They also teated the vibrational modes from CCSD(T) quartic force fields including the effects of anharmonicity through second-order perturbation theory.

Methods

Calculations were performed with the Gaussian-94[10] and MOLPRO-96[11] programs on SGI Power Challenge compute servers and on the Cray C90 at NERSC (National Energy Research Scientific Computing Center). The coupled cluster calculations included single and double excitations with a noniterative correction for triples [CCSD(T)].[6] The one-particle basis sets were taken from the correlation-consistent basis set family.[7] Unless otherwise noted, the nitrogen and oxygen (1s) electrons were not correlated. Only the spherical components of the d, f, and g functions were used. The geometries were optimized at a variety of computational levels including MP2, MP4, CCSD, and CCSD(T) with the correlation-consistent sets through aug-cc-pV5Z unless noted below. The frequencies for H_2O and H_3O^+ were calculated at the MP2/aug-cc-pVTZ level. To estimate values at the complete basis set (CBS) limit, we used a 3-parameter exponential fitting function[12] of the form:

$$F(n) = F_{\mathrm{CBS}} + B\exp(-Cn) \tag{2}$$

with $n = 2$, 3, 4, and 5 for DZ, TZ, QZ, and 5Z sets.

Results

The total energies and geometry parameters for H_2O and H_3O^+ are given in Table 1. For NH_3 and NH_4^+, the corresponding values are given in Table 2. The electronic proton affinities are given in Table 3.

The geometrical parameters for H_2O at the CCSD(T)/aug-cc-pV5Z level, 0.9584 Å for the bond distance and 104.43° for the bond angle, are in excellent agreement with the experimental values of 0.9572 Å and 104.52°.[13] The geometry shows a steady improvement toward the experimental values with increasing basis set at the CCSD(T) level. The geometries obtained with lower levels of correlation show similar values and trends to the CCSD(T) results. The geometry for H_3O^+ is nonplanar with experimental values of 0.9758 Å for the bond distance and 111.3° for the bond angle.[14] The calculated values at the CCSD(T)/aug-cc-pV5Z level are 0.9761 Å and 111.84°. As for H_2O, the bond distance is in excellent agreement with the experimental value but the bond angle shows a somewhat larger deviation.

For NH_3 the calculations were performed up to the CCSD(T)/aug-cc-pVQZ and CCSD(T)/cc-pV5Z levels. The bond distance and bond angle at the CCSD(T)/aug-cc-pVQZ level, 1.0126 Å and 106.61°, are in excellent agreement with the experimental values of 1.0116 Å and 106.7°.[15] The CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ results are essentially identical to those obtained previously by Martin, Lee, and Taylor.[16] It is interesting to note that the error of more than 0.5° in the bond angle with the cc-pVQZ basis set is due to the omission of diffuse functions. For NH_4^+ (T_d), the best calculated value for the bond distance, 1.0217 Å, is longer than the value in NH_3 by about 0.01 Å. Our results compare well with those of Martin and Lee[9] who obtained values at the CCSD(T) level of 1.0316 Å (cc-pVDZ), 1.0226 Å (cc-pVTZ), and 1.0214 Å (cc-pVQZ). The calculated value also is in good agreement with the experimental value of 1.0208 ± 0.0020 Å.[17]

The value of ΔE_{elec} for eq 1 for A = H_2O and NH_3 are given in Table 3. Plots of the CCSD(T) values of ΔE_{elec} for NH_3 in Figure 1 show the different convergence behavior for the augmented and unaugmented basis sets. For the aug-cc-pV*n*Z basis sets, the effect of different correlation treatments [MP*n*, CCSD, and CCSD(T)] for NH_3 and H_2O is shown in Figure 2.

TABLE 2: Calculated Equilibrium Geometries and Energies for NH_3 and NH_4^+

method	basis set	NH_3			NH_4^+	
		E_e (h)	r_e(NH) (Å)	θ_e(HNH) (deg)	E_e (h)	r_e(NH) (Å)
exptl[a]			1.0116	106.7		1.0210 ± 0.0020
MP2	cc-pVDZ	−56.382 497	1.0234	103.89	−56.730 684	1.0297
	cc-pVTZ	−56.452 986	1.0113	105.95	−56.793 495	1.0211
	cc-pVQZ	−56.474 652	1.0096	106.49	−56.812 248	1.0199
	cc-pV5Z/QZ[b]	−56.480 687	1.0098	106.89	−56.816 732	1.0202
	aug-cc-pVDZ	−56.404 884	1.0201	106.32	−56.739 780	1.0274
	aug-cc-pVTZ	−56.460 531	1.0120	106.77	−56.796 151	1.0220
	aug-cc-pVQZ	−56.477 774	1.0100	106.96	−56.813 372	1.0203
MP3	cc-pVDZ	−56.396 156	1.0231	103.95	−56.746 115	1.0290
	cc-pVTZ	−56.464 293	1.0098	106.08	−56.807 205	1.0197
	cc-pVQZ	−56.483 509	1.0080	106.61	−56.823 897	1.0185
	cc-pV5Z/QZ[b]	−56.488 214	1.0080	106.95	−56.827 387	1.0186
	aug-cc-pVDZ	−56.417 489	1.0193	106.33	−56.755 217	1.0268
	aug-cc-pVTZ	−56.470 999	1.0103	106.80	−56.809 749	1.0205
	aug-cc-pVQZ	−56.485 926	1.0082	107.01	−56.824 765	1.0188
MP4	cc-pVDZ	−56.402 103	1.0267	103.53	−56.751 798	1.0311
	cc-pVTZ	−56.473 429	1.0142	105.60	−56.815 170	1.0226
	cc-pVQZ	−56.493 532	1.0127	106.14	−56.832 375	1.0215
	cc-pV5Z/QZ[b]	−56.498 591	1.0128	106.49	−56.836 072	1.0218
	aug-cc-pVDZ	−56.425 165	1.0233	105.94	−56.761 337	1.0291
	aug-cc-pVTZ	−56.480 945	1.0151	106.36	−56.817 871	1.0235
	aug-cc-pVQZ	−56.496 277	1.0131	106.56	−56.833 291	1.0218
CCSD	cc-pVDZ	−56.398 832	1.0254	103.85	−56.748 953	1.0306
	cc-pVTZ	−56.465 530	1.0117	105.96	−56.808 705	1.0211
	cc-pVQZ	−56.484 354	1.0099	106.48	−56.825 061	1.0197
	cc-pV5Z/QZ[b]	−56.489 017	1.0099	106.81	−56.828 514	1.0199
	aug-cc-pVDZ	−56.419 957	1.0214	106.19	−56.757 699	1.0282
	aug-cc-pVTZ	−56.472 201	1.0123	106.66	−56.811 166	1.0218
	aug-cc-pVQZ	−56.486 781	1.0101	106.87	−56.825 901	1.0200
CCSD(T)	cc-pVDZ	−56.402 794	1.0272	103.51	−56.752 667	1.0316
	cc-pVTZ	−56.473 189	1.0140	105.64	−56.815 326	1.0226
	cc-pVQZ	−56.493 048	1.0123	106.19	−56.832 373	1.0214
	cc-pV5Z/QZ[b]	−56.498 000	1.0123	106.55	−56.836 000	1.0216
	cc-pV5Z	−56.499 451	1.0121	106.53	−56.837 410	1.0211
	aug-cc-pVDZ	−56.425 511	1.0236	105.94	−56.762 101	1.0295
	aug-cc-pVTZ	−56.480 552	1.0148	106.40	−56.818 016	1.0235
	aug-cc-pVQZ	−56.495 728	1.0126	106.61	−56.833 285	1.0217

[a] References 15 and 17. [b] The cc-pV5Z set was used on the nitrogen atom and the cc-pVQZ set was used on the hydrogen atoms.

Extrapolations of the total energies with subsequent subtraction to obtain ΔE or extrapolations of the ΔEs themselves as a function of the basis set by using eq 2 give essentially the same result (± 0.25 kcal/mol in the worst case).

The ΔE_{elec} values in Table 3 show some interesting trends. For example, the proton affinity is converged to ~0.1 kcal/mol of the complete basis set (CBS) limit for a given correlation treatment at the aug-cc-pVTZ level. The unaugmented basis sets (cc-pV*n*Z) do not converge as rapidly and even the cc-pV5Z result for NH_3 is not as converged to the CBS limit as the aug-cc-pVTZ value. Thus, as noted by others,[9,18] diffuse functions are important for predicting the last 1 to 2 kcal/mol for proton affinities. The diffuse functions decrease the proton affinity by stabilizing the neutral molecule relative to the cation.

The different correlation treatments give proton affinities within 1.5 kcal/mol of the CCSD(T) result. For NH_3, the MP2 level underestimates the value of ΔE_{elec} by 1.2 kcal/mol, while the MP4(SDTQ) result is within 0.3 kcal/mol of the CCSD(T) result. The MP3 and CCSD results overestimate the value of ΔE_{elec} by 0.8 and 1.0 kcal/mol, respectively. For H_2O, similar results are found. The MP2 result underestimates the value of ΔE_{elec} by 1.4 kcal/mol, and the MP4(SDTQ) result is 0.5 kcal/mol too low, compared to the CCSD(T) result. The CCSD result is, again, 1 kcal/mol too high.

The most accurate results are expected to be those from the CCSD(T) calculations. For H_2O at the CCSD(T) level, extrapolation to the CBS limit based on the total energies gives 171.43 kcal/mol for ΔE_{elec}. For NH_3, the extrapolated value is 211.84 kcal/mol in excellent agreement with the extrapolated values of 211.78−211.89 kcal/mol of Martin and Lee.[9] We note here that we used an exponential extrapolation as compared to Martin and Lee who also used the exponential extrapolation as well as an empirically scheme based on the types of bond pairs and the $1/l_{max}$ asymptotic limit three term expansion for the two-electron cusp.

To account for core-valence correlation effects, we carried out calculations at the CCSD(T)/aug-cc-pwCVTZ level[19] using the CCSD(T)/aug-cc-pVTZ optimized geometries. With only the valence electrons correlated, we obtain 211.67 kcal/mol for PA(NH_3), close to the value of 211.76 kcal/mol calculated without the core correlation functions, and 211.80 kcal/mol if all electrons are correlated. Thus, the difference of 0.13 kcal/mol can be added to our best extrapolated value to give $PA_{elec}(NH_3) = 211.97$ kcal/mol in agreement with the range of 211.91−212.02 kcal/mol given by Martin and Lee[9] who used a different basis set to treat core correlation corrections. For H_2O, the electronic proton affinity at the CCSD(T)/aug-cc-pwVTZ level with the valence electrons correlated is 171.34 kcal/mol as compared to a value of 171.47 kcal/mol if all electrons are correlated. The difference, 0.13 kcal/mol, is the same as for $PA_{elec}(NH_3)$, and we can add this value to the 171.43 kcal/mol given above to obtain PA_{elec} (H_2O) = 171.56 kcal/mol.

To calculate the proton affinity at 298 K, we need to calculate both the zero point energy and the thermal correction from *T*

TABLE 3: Calculated Values of ΔE_{Elec} for Predicting the Proton Affinities for H_2O and NH_3

method	basis set	ΔE_{elec} (H_2O) (kcal/mol)	ΔE_{elec} (NH_3) (kcal/mol)
MP2	cc-pVDZ		218.49
	cc-pVTZ		213.67
	cc-pVQZ		211.84
	cc-pV5Z/QZ[a]		210.87
	aug-cc-pVDZ	168.99	210.15
	aug-cc-pVTZ	170.19	210.60
	aug-cc-pVQZ	170.23	210.59
	aug-cc-pV5Z	170.15	
MP3	cc-pVDZ		219.60
	cc-pVTZ		215.18
	cc-pVQZ		213.60
	cc-pV5Z/QZ[a]		212.83
	aug-cc-pVDZ	171.21[b]	211.93
	aug-cc-pVTZ	172.69[b]	212.57
	aug-cc-pVQZ	172.74[b]	212.62
MP4	cc-pVDZ		219.44
	cc-pVTZ		214.45
	cc-pVQZ		212.63
	cc-pV5Z/QZ[a]		211.77
	aug-cc-pVDZ	169.75	210.95
	aug-cc-pVTZ	170.95	211.42
	aug-cc-pVQZ	171.01	211.48
	aug-cc-pV5Z	170.97	
CCSD	cc-pVDZ		219.70
	cc-pVTZ		215.35
	cc-pVQZ		213.80
	cc-pV5Z/QZ[a]		213.04
	aug-cc-pVDZ	170.81	211.94
	aug-cc-pVTZ	172.34	212.70
	aug-cc-pVQZ	172.46	212.80
CCSD(T)	cc-pVDZ		219.55
	cc-pVTZ		214.69
	cc-pVQZ		212.93
	cc-pV5Z/QZ[a]		212.10
	cc-pV5Z		212.07
	aug-cc-pVDZ	170.24	211.21
	aug-cc-pVTZ	171.51	211.76
	aug-cc-pVQZ	171.58	211.82
	aug-cc-pV5Z	171.53	

[a] The cc-pV5Z set was used on the nitrogen atom and the cc-pVQZ set was used on the hydrogen atoms. [b] The MP3 results for H_2O were obtained at the optimized MP4 geometry and are given for completeness.

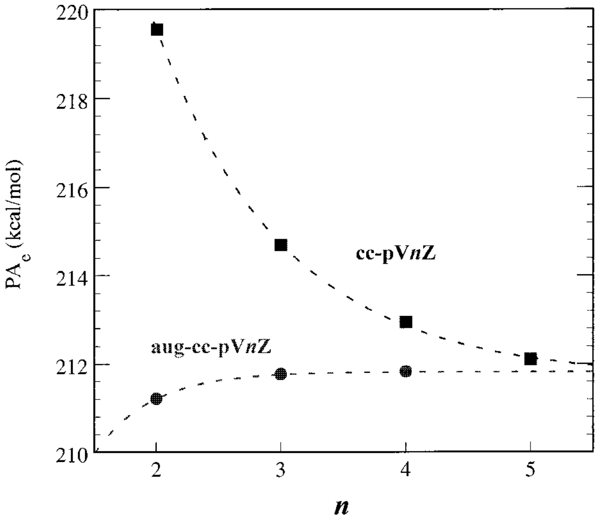

Figure 1. CCSD(T) values of ΔE_{elec} for the proton affinity of NH_3 calculated with the cc-pV*n*Z and aug-cc-pV*n*Z basis sets.

$= 0$ K to $T = 298$ K. The zero-point energy for H_2O can be taken from the known experimental frequencies.[20] For H_3O^+ all of the vibrational modes except for the (a_1) stretch have been measured.[8,14,21] We use the zero-point energy for the (a_2') inversion mode of 376.3 cm^{-1} reported by Oka and coworkers.[14] For the (e) degenerate stretches and bends, we use $0.5\nu_{0+\rightarrow 1+}$ giving a contribution of 1768 cm^{-1} for the stretch and 813 cm^{-1} for the bend. To obtain an estimate for the symmetric stretch, we calculated the harmonic frequencies at the MP2/aug-cc-pVTZ level for H_2O and H_3O^+. The values are given in Table 4. The scale factors for the (a_1) mode in H_2O is 0.955 and the scale factor for the (e) mode in H_3O^+ is 0.957, so we averaged the two to obtain a scale factor for the (a_1) stretch in H_3O^+. This gives a value of 3443 cm^{-1} and a

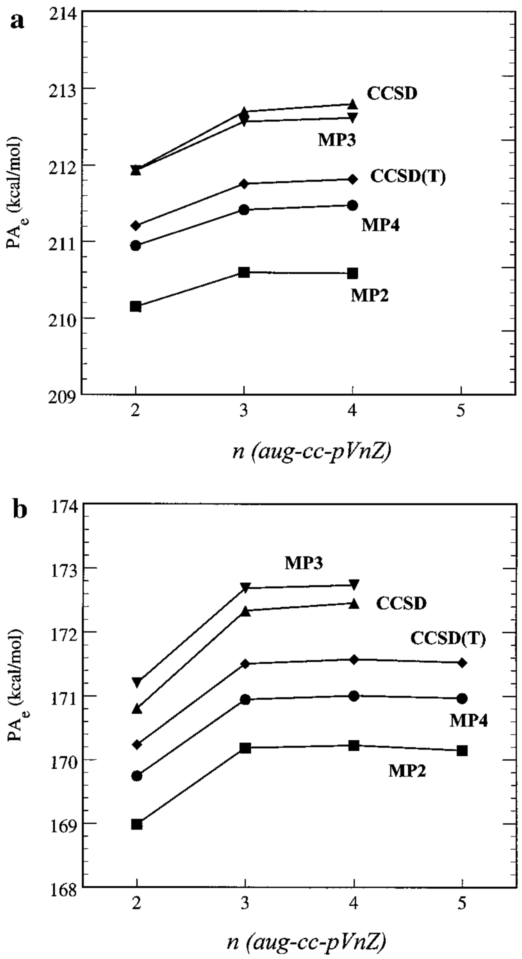

Figure 2. Comparison of ΔE_{elec} for the proton affinity of (a) NH_3 and (b) H_2O calculated using the aug-cc-pV*n*Z basis sets and MP2, MP3, MP4, CCSD, and CCSD(T).

TABLE 4: Calculated Vibrational Frequencies (cm^{-1}) for H_2O and H_3O^+ at the MP2/aug-cc-pVTZ Level

symmetry	ω_e(calc)[d]	ν(exptl)[a,b]
	H_2O	
a_1	3821.5	3656.6
	1628.4	1594.6
b_1	3947.3	3755.8
	H_3O^+	
a_1	3601.7	
	884.8	954.4 (525.8)
e	3704.4	3536.0 (3519.4)
	1692.2	1638.5 (1626.0)

[a] Reference 19 for H_2O frequencies. [b] Reference 14 for H_3O^+ frequencies. The values in parentheses are given because of the splitting of the frequencies in H_3O^+ due to the low energy barrier to inversion.

zero point energy of 1721.6 cm^{-1}. The $H_2O-H_3O^+$ zero-point energy difference is 7.87 kcal/mol, which can be compared to the value of 8.13 kcal/mol given by Botschwina.[22] Use of our ΔE_{ZPE} value gives a predicted PA(H_2O) = 163.7 kcal/mol at 0 K. Botschwina has previously reported a value of 164.2 kcal/mol in good agreement with our value.

Conversion of the energy to an enthalpy at 298 K involves adding the translational, rotational, and vibrational temperature-dependent energy terms as well as the $P\Delta V$ term, which is $-RT$ assuming ideal gas behavior, to the above value of PA(H_2O). To an excellent approximation, we can take the translational and rotational energy terms to have their classical values. Excluding the temperature dependence of the vibrations, we obtain PA(H_2O) = 165.2 kcal/mol. However, it is not possible to ignore the vibrational temperature dependence because of the low inversion energy of H_3O^+. Direct summation of the inversion frequency gives a correction of 0.13 kcal/mol, lowering the proton affinity to 165.1 kcal/mol at 298 K. We estimate that the error in the zero-point correction is less than 0.3 kcal/mol, giving a final value of PA(H_2O) = 165.1 ± 0.3 kcal/mol. We note here that the treatment of the zero-point energy difference is the largest source in the calculation of PA(H_2O). This can be compared to the experimental value of 166.5 kcal/mol which has error limits of at least 1 kcal/mol. We would thus favor a lower value for PA(H_2O), closer to 165 kcal/mol. Our value is in better agreement with the photoionization work of Ng et al.[4] who report 165.8 ± 1.8 kcal/mol.

Other theoretical results for PA(H_2O) are similar to ours. Del Bene[18] has reported an MP4 value of 163.8 kcal/mol and a CCSD(T) value of 164.2 kcal/mol, both of which are low by about 1 kcal/mol compared to our value. DeFrees and McLean[23] reported a value of 165.1 kcal/mol, essentially identical to our value. The G1 value[24] for PA(H_2O) is 164.8 kcal/mol and the G2 value[25] is 164.6 kcal/mol, both of which are in good agreement with our value. For proton affinities, we note that there are no empirical correction factors for these methods. The other calculated proton affinities have been based on geometries calculated at a variety of levels and zero-point energy differences calculated at different levels. The differences in the calculated values for PA(H_2O) could be due to the differences in geometry or in zero-point energy treatment.

For PA(NH_3), the zero-point energy for NH_3 is well-established but only the values of the (t_2) bend and stretch frequencies are known experimentally for NH_4^+.[26] The zero-point energy for NH_3 was taken as one-half the observed frequencies,[20] which yields 20.61 kcal/mol. For NH_4^+, the zero-point energies for the (t_2) modes are taken as $0.5\nu_{0\rightarrow 1}$ and are 1672 cm^{-1} for the stretch and 724 cm^{-1} for the bend. We can obtain the missing frequencies for NH_4^+ from the CCSD(T)/TZ(2df,2pd) calculations of Schaefer and co-workers[27] on the vibrational spectra of NH_3 and NH_4^+ and use the same type of scaling model as used above for H_3O^+. For NH_3, we obtain a scale factor of 0.97 for the (e) bend and the same scale factor for the (t_2) bend in NH_4^+. We can thus use this scale factor for the (e) bend in NH_4^+, giving a frequency of 1689 cm^{-1}. The scale factor for the (t_2) stretch in NH_4^+ is 0.956 and the scale factors for the (a_1) stretch in NH_3 is 0.961 and for the (e) stretch is 0.957. Averaging these values gives a scale factor of 0.958 for the (a_1) stretch in NH_4^+ giving a value of 3235 cm^{-1}. This results in a zero-point energy for NH_4^+ of 29.98 kcal/mol and a zero-point energy difference for the proton affinity calculation of 9.37 kcal/mol. This can be compared to the ΔE_{ZPE} value of 9.50 kcal/mol obtained by Martin and Lee,[9] based on CCSD(T) calculations of the quartic force field for NH_3 and NH_4^+. The elegant approach of Martin and Lee yields a more accurate representation of the zero-point energy difference but cannot be applied in general to larger, asymmetric molecules due to its computational expense. Our approach of using experimental frequencies or scaled theoretical frequencies can be applied more broadly and, as demonstrated here, yields results within 0.15 kcal/mol if those of Martin and Lee. Because of the modest barrier height for NH_3 inversion, the thermal vibrational energy correction is essentially zero. Thus, PA(NH_3) = 204.1 ± 0.3 kcal/mol where the error limits come from our zero-point energy estimates. Again, it is likely that the largest source of error in the calculation of PA(NH_3) is associated with the zero-point energy difference. This value is in excellent agreement with the experimental values of 204 ± 1[1,2] and 203.6 ± 1.3 kcal/mol,[5] as well as with the value of 203.9 ± 0.3 kcal/mol calculated by Martin and Lee.[9] Other calculated values include the value of 204.0 kcal/mol obtained by DeFrees and McLean[23] and the values of 203.2 and 203.7 kcal/mol obtained by Del Bene.[18] The G1 value for PA(NH_3) is 204.2 kcal/mol[24] and the G2 value is 204.0 kcal/mol,[25] both in good agreement with our values. All of the work points to a reliable value of 204 ± 0.5 kcal/mol for PA(NH_3). The slight variations among the theoretical values could be due to differences in geometries and treatment of zero-point effects as well as differences in the treatment of the electronic energy differences.

On the basis of our calculated PAs, the energy difference PA(NH_3) − PA(H_2O) = 39 ± 0.6 kcal/mol as compared to the experimental value of 37.5 kcal/mol. The experimental difference, as we noted above, is probably too small because of the error in PA(H_2O).

Acknowledgment. This research was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830 (Division of Chemical Sciences, Office of Basic Energy Sciences and the Environmental Technology Partnerships Program). The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute. We also thank the Mathematics, Informatics and Computer Science Division, Office of Energy Research, U.S. Department of Energy, for a grant of computer time at the National Energy Research Scientific Computing Center (Berkeley, CA). Helpful discussions with Dr. Greg Schenter of EMSL/PNNL are gratefully acknowledged.

References and Notes

(1) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

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

(3) Dixon, D. A.; Lias, S. G. In *Molecular Structure and Energetics*; Greenberg, A., Liebman, J. F., Eds.; VCH: Deerfield Beach, FL, **1987**; Vol. 2, Chapter 7, p 269.

(4) Ng, C. Y.; Trevor, D. J.; Tiedemann, P. W.; Ceyer, S. T.; Kronebusch, P. L.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys*. **1977**, *67*, 4235.

(5) Ceyer, S. T.; Tiedemann, P. W.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys*. **1979**, *70*, 14.

(6) Bartlett, R. J. *J. Phys. Chem*. **1989**, *93*, 1697. (b) Kucharski, S. A.; Bartlett, R. J. *Adv. Quantum Chem*. **1986**, *18*, 281. (c) Bartlett, R. J.; Stanton, J. F. In *Reviews of Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers: New York, 1995; Vol. V, Chapter 2, p 65.

(7) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989,** *90*, 1007. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796. (c) Woon, D. E.; Dunning T. H. Jr. *J. Chem. Phys.* **1993**, *99*, 1914. (d) Peterson, K. A.; Kendall, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, 99, 1930. (e) Peterson, K. A.; Kendall, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, 99, 9790.

(8) Jacox, M. E. *J. Phys. Chem. Ref. Data, Monogr.* **1994**, *3*.

(9) (a) Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1996**, *258*, 129. (b) Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1996**, *258*, 136.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; 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. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(11) MOLPRO is a package of ab initio molecular orbital theory programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlof, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, A. J. Stone, P. R. Taylor, and R. Lindh.

(12) (a) Xantheas, S. S.; Dunning, T. H., Jr., *J. Phys. Chem.* **1993**, *97*, 18. (b) Feller, D. J. *Chem. Phys.* **1992**, *96*, 6104.

(13) Benedick, W. S.; Jailar, N.; Plyler, E. K. *J. Chem. Phys*. **1956**, *24*, 1139.

(14) Liu, D.-J.; Oka, T.; Sears, T. J. *J. Chem. Phys*. **1986**, *84*, 1312.

(15) Duncan, J. L.; Mills, I. M. *Spectrochim. Acta* **1964**, *20*, 523.

(16) Martin, J. M. L.; Lee, T. J.; Taylor, P. R. *J. Chem. Phys.* **1992**, *97*, 8361.

(17) Crofton, M. W.; Oka, T. *J. Chem. Phys.* **1987**, 86, 5983.

(18) Del Bene, J. *J. Phys. Chem*. **1993**, *97*, 107.

(19) (a) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572. (b) Peterson, K. A.; Dunning, T. H., Jr. to be published.

(20) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated Volume 1*; NSRDS−NBS 39, Department of Commerce: Washington, DC, 1972.

(21) H_3O^+ (e) stretch: Begemann, M. H.; Gudeman, C. S.; Pfaff, J.; Saykally, R. J. *Phys. Rev. Lett*. **1983**, *51*, 554. Begemann, M. H.; Saykally, R. J. *J. Chem. Phys.* **1985**, *82*, 3570. Keim, E. R.; Polak, M. L.; Owrutsky, J. C.; Coe, J. V.; Saykally, R. J. *J. Chem. Phys.* **1990**, *92*, 3257. Ho, W. C.; Pursell, C. J.; Oka, T. *J. Mol. Spectrosc*. **1991**, *149*, 530. (e) bend: Grubele, M.; Polak, M.; Saykally, R. J. *J. Chem. Phys.* **1987**, *87*, 3347.

(22) Botschwina, P. *J. Chem. Phys.* **1986**, *84*, 6523.

(23) DeFrees, D. J.; McLean, A. D. *J. Comput. Chem*. **1986**, *7*, 321.

(24) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys*. **1989**, *90*, 5622.

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

(26) NH_4^+ (t_2) stretch: Crofton, M.; Oka, T. *Chem. Phys.* **1983**, *79*, 3187. Schaeffer, E.; Begemann, M. H.; Gudeman, C. S.; Saykally, R. J. *J. Chem. Phys.* **1983**, *79*, 3159. Schafer, E.; Saykally, R. J.; Robiette, A. G. *J. Chem. Phys.* **1984**, *80*, 3969. Keim, E. R.; Polak, M. L.; Owrutsky, J. C.; Coe, J. V.; Saykally, R. J. *J. Chem. Phys.* **1991**, *93*, 3111. (t_2) bend: Polak, M.; Gruebele, M.; DeKock, B. W.; Saykally, R. J. *Mol. Phys*. **1989**, *66*, 1193.

(27) Schaefer, H. F., III, Thomas, J. R.; Yamaguchi, Y.; DeLeeuw, B. J.; Vacek, G. In *Modern Electronic Structure Theory, Part 1*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1996, 3.