

## Heats of formation and ionization energies of $\text{NH}_x$ , $x=0-3$

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The heats of formation of  $\text{NH}_3$ ,  $\text{NH}_2$ ,  $\text{NH}$  and the ionization energies of  $\text{NH}_3$ ,  $\text{NH}_2$ ,  $\text{NH}$ , and  $\text{N}$  have been calculated at high levels of *ab initio* molecular orbital theory at 0 K. Geometries and frequencies were calculated with coupled cluster theory, including a perturbative treatment of the connected triple excitations and with correlation consistent basis sets up through augmented sextuple zeta in quality. Subsequent extrapolation of the total energies to the complete one-particle basis set limit was performed to further reduce the basis set truncation error. Additional improvements in the atomization energy were achieved by applying corrections for core/valence correlation, scalar relativistic, spin-orbit, and higher order correlation effects. Zero point energies were taken from anharmonic force fields where available or are based on appropriately scaled values. Using the R/UCCSD(T) method, we find the following heats of formation (kcal/mol) at 0 K:  $\Delta H_f(\text{NH}_3) = -9.10 \pm 0.17$  (calc.) versus  $-9.30 \pm 0.10$  (expt.);  $\Delta H_f(\text{NH}_2) = 45.27 \pm 0.12$  (calc.) versus  $45.17 \pm 0.09$  (expt.);  $\Delta H_f(\text{NH}) = 85.92 \pm 0.08$  (calc.) versus  $90.0 \pm 4$  (expt.);  $\Delta H_f(\text{NH}_3^+) = 225.44 \pm 0.23$  (calc.) versus  $225.59 \pm 0.08$  (expt.);  $\Delta H_f(\text{NH}_2^+) = 303.00 \pm 0.20$  (calc.) versus  $302.60 \pm 0.08$  (expt.); and  $\Delta H_f(\text{NH}^+) = 396.56 \pm 0.12$  (calc.). © 2001 American Institute of Physics. [DOI: 10.1063/1.1367283]

### INTRODUCTION

There is significant interest in re-evaluating the heats of formation and bond energies of many small molecules, especially radicals, by using new experimental and computational methods that can significantly reduce the errors in these properties. The close interplay of theory and experiment allows us to evaluate both the experimental and computational methods and the inherent accuracies of each. We have recently shown that such a combination leads to a new heat of formation for the OH radical differing by 0.5 kcal/mol at 0 K from the accepted values adopted by most tabulations.<sup>1</sup> In collaboration with experimental groups at Iowa State University/Ames Laboratory and Lawrence Berkeley National Laboratory,<sup>2</sup> we have re-evaluated the heats of formation of the radicals due to loss of hydrogens from the simplest amine,  $\text{NH}_3$ , as well as ionization of  $\text{NH}_x$ ,  $x=0-3$ . The experimental work is published as a companion paper.

In an effort to predict uniformly accurate thermochemical properties across a range of small-to-intermediate size chemical systems, we have developed a composite theoretical approach that does not include empirically adjusted parameters.<sup>3</sup> This approach starts with existing, reliable thermodynamic values obtained from either experiment or theory. Normally we adopt experimental atomic heats of formation, which are difficult to obtain theoretically. We also make use of experimental molecular and atomic spin-orbit splittings (if available). As discussed below, in cases where high quality, anharmonic zero point energies are not avail-

able, we combine fundamental frequencies obtained from experiment with theoretical harmonic frequencies to calculate zero point vibrational energies. Aside from these areas, our approach relies on high-level *ab initio* electronic structure calculations in order to compute molecular atomization energies.

### COMPUTATIONAL APPROACH

Coupled cluster theory, including single, double and connected triple excitations (CCSD(T)), with the latter being handled perturbatively, is the method of choice for incorporating a large fraction of the valence correlation energy.<sup>4</sup> The CCSD(T) energies are extrapolated to the complete basis set (CBS) limit, a step facilitated by the uniform convergence properties of the correlation consistent basis sets (cc-pVXZ) from Dunning and co-workers.<sup>5</sup> For this study, we used the diffuse function augmented (aug-cc-pVXZ) basis sets for  $X=T, Q, 5$ , and 6. For the sake of brevity, the basis set names will be shortened to a VxZ throughout this text. Only the spherical components (5-d, 7-f, 9-g, 11-h and 13-i) of the Cartesian basis functions were used. All of the current work was performed with MOLPRO 2000.<sup>6</sup>

Three coupled cluster methods have been proposed for treating open shell systems. The first is a completely unrestricted method, built atop unrestricted Hartree-Fock (UHF) orbitals and designated UCCSD(T). The other two methods start with restricted open shell Hartree-Fock (ROHF) orbitals. One is a completely restricted method, which we label as

RCCSD(T).<sup>7</sup> The other relaxes the spin constraint in the coupled cluster calculation and is designated R/UCCSD(T).<sup>8</sup> At present, little is known about which open shell coupled cluster method produces the best agreement with the exact full configuration interaction (FCI) results. We have used the R/UCCSD(T) method in this study.

Three different formulas were used to extrapolate to the frozen core (FC) CBS limit. The first is a three-parameter, mixed exponential/Gaussian function of the form:

$$E(x) = A_{\text{CBS}} + B \exp[-(x-1)] + C \exp[-(x-1)^2] \quad (1)$$

where  $x=2$  (DZ), 3(TZ), etc.<sup>9</sup> In addition, we used two two-parameter formulas<sup>10,11</sup> that involve expansions in  $1/\ell_{\text{max}}$ , where  $\ell_{\text{max}}$  is the highest angular momentum in the basis set

$$E(x) = E_{\text{CBS}} + B/(\ell_{\text{max}} + 1)^4 \quad (2)$$

and

$$E(x) = E_{\text{CBS}} + B/(\ell_{\text{max}})^3. \quad (3)$$

On average, the mixed formula has been found to produce slightly better agreement with experiment when results from basis sets through quadruple zeta were used. However, the  $1/\ell_{\text{max}}$  formulas, which are based on the asymptotic  $1/Z$  perturbation theory convergence properties of two-electron systems,<sup>11</sup> may perform better for even larger basis sets which more closely match the conditions of saturated  $\ell$  spaces used in the perturbation theory analysis. As there is no compelling formal reason to choose one of the CBS extrapolation formulas over the others, we will adopt the average of

TABLE I. Frozen core electronic energies and estimated complete basis set frozen core energies.<sup>a</sup>

Calculation Basis	N( <sup>4</sup> S) $E_{\text{R/UCCSD(T)}}$	N <sup>+</sup> ( <sup>3</sup> P) $E_{\text{R/UCCSD(T)}}$	IE <sup>b</sup>			
aVQZ	-54.525 300	-53.992 467	334.35			
aV5Z	-54.528 001	-53.994 756	334.61			
aV6Z	-54.528 853	-53.995 444	334.71			
CBS(mix)/aVQ56 <sup>c</sup>	-54.529 349	-53.995 845	334.77			
CBS( $\ell_{\text{max}}^4$ )/aV56 <sup>d</sup>	-54.529 749	-53.996 168	334.82			
CBS( $\ell_{\text{max}}^3$ )/aV56 <sup>e</sup>	-54.530 023	-53.996 389	334.86			
Basis	NH( $X^3\Sigma^-$ ) $E_{\text{R/UCCSD(T)}}$	$D_e^f$	NH <sup>+</sup> ( $X^2\Pi$ ) $E_{\text{R/UCCSD(T)}}$	IE <sup>b</sup>		
aVQZ	-55.156 036	82.07	-54.661 603	310.26		
aV5Z	-55.159 323	82.41	-54.664 656	310.40		
aV6Z	-55.160 547	82.64	-54.665 633	310.56		
CBS(mix)/aVQ56 <sup>c</sup>	-55.161 238	82.76	-54.666 201	310.64		
CBS( $\ell_{\text{max}}^4$ )/aV56 <sup>d</sup>	-55.161 775	82.85	-54.666 660	310.68		
CBS( $\ell_{\text{max}}^3$ )/aV56 <sup>e</sup>	-55.162 143	82.91	-54.666 974	310.72		
Basis	NH <sub>2</sub> ( $X^2B_1$ ) $E_{\text{R/UCCSD(T)}}$	$\Sigma D_e^g$	NH <sub>2</sub> <sup>+</sup> ( $X^3B_1$ ) $E_{\text{R/UCCSD(T)}}$	IE <sup>b</sup>	NH <sub>2</sub> <sup>+</sup> ( $X^1A_1$ ) $E_{\text{R/UCCSD(T)}}$	IE <sup>b</sup>
aVQZ	-55.813 057	180.63	-55.401 739	258.10	-55.355 502	287.12
aV5Z	-55.817 084	181.41	-55.405 056	258.55	-55.359 179	287.34
aV6Z	-55.818 427	181.71	-55.406 120	258.72	-55.360 389	287.42
CBS(mix)/aVQ56 <sup>c</sup>	-55.819 209	181.89	-55.406 739	258.82	-55.361 086	287.47
CBS( $\ell_{\text{max}}^4$ )/aV56 <sup>d</sup>	-55.819 841	182.03	-55.407 239	258.91	-55.361 661	287.51
CBS( $\ell_{\text{max}}^3$ )/aV56 <sup>e</sup>	-55.820 273	182.13	-55.407 582	258.96	-55.362 050	287.53
Basis	NH <sub>3</sub> ( $X^1A_1$ ) $E_{\text{R/UCCSD(T)}}$	$\Sigma D_e^h$	NH <sub>3</sub> <sup>+</sup> ( $X^2A_2$ ) $E_{\text{R/UCCSD(T)}}$	IE	NH <sub>4</sub> <sup>+</sup> ( $X^1A_1$ ) $E_{\text{R/UCCSD(T)}}$	PA <sup>b</sup>
aVQZ	-56.495 732	295.29	-56.121 126	235.07	-56.833 285	211.81
AV5Z	-56.500 282	296.37	-56.125 153	235.39	-56.837 821	211.81
AV6Z	-56.501 812	296.78	-56.126 465	235.53	-56.839 322	211.79
CBS(mix)/aVQ56 <sup>c</sup>	-56.502 703	297.03	-56.127 228	235.61	-56.840 195	211.78
CBS( $\ell_{\text{max}}^4$ )/aV56 <sup>d</sup>	-56.503 422	297.23	-56.127 845	235.67	-56.840 900	211.77
CBS( $\ell_{\text{max}}^3$ )/aV56 <sup>e</sup>	-56.503 914	297.37	-56.128 267	235.72	-56.841 384	211.76

<sup>a</sup>Total energies are given in hartrees ( $E_h$ ). Calculations were performed at the optimal CCSD(T)/aug-cc-pVQZ geometries given by  $r_{\text{NH}}=1.0377$  Å (NH),  $r_{\text{NH}}=1.0696$  Å (NH<sup>+</sup>),  $r_{\text{NH}}=1.0255$  Å,  $\angle\text{HNH}=102.99^\circ$  (H<sub>2</sub>N, <sup>2</sup>B<sub>1</sub>),  $r_{\text{NH}}=1.0313$  Å,  $\angle\text{HNH}=152.20^\circ$  (H<sub>2</sub>N<sup>+</sup>, <sup>3</sup>B<sub>1</sub>),  $r_{\text{NH}}=1.0487$  Å,  $\angle\text{HNH}=107.76^\circ$  (H<sub>2</sub>N<sup>+</sup>, <sup>1</sup>A<sub>1</sub>),  $r_{\text{NH}}=1.0215$  Å (H<sub>3</sub>N<sup>+</sup>, <sup>2</sup>A<sub>2</sub>),  $r_{\text{NH}}=1.0216$  Å,  $\angle\text{HNH}=106.6^\circ$  (H<sub>3</sub>N, <sup>1</sup>A<sub>1</sub>), and  $r_{\text{NH}}=1.0217$  Å (NH<sub>4</sub><sup>+</sup>). Symmetry equivalencing of the NH( $\pi_x, \pi_y$ ) and N<sup>+</sup>( $p_x, p_y, p_z$ ) atomic orbitals was not imposed.

<sup>b</sup>Ionization energy (kcal/mol).

<sup>c</sup>Complete basis set extrapolation based on the mixed Gaussian/exponential formula.

<sup>d</sup>Complete basis set extrapolation based on the  $1/(\ell_{\text{max}}+1)^4$  formula.

<sup>e</sup>Complete basis set extrapolation based on the  $1/(\ell_{\text{max}})^3$  formula.

<sup>f</sup>Dissociation energy (kcal/mol).

<sup>g</sup>Atomization energy (kcal/mol).

<sup>h</sup>Electronic component of the molecular proton affinity.

TABLE II. Atomization energy, ionization energy, and proton affinity for NH<sub>3</sub>.

Component	$\Sigma D_0$ (kcal/mol)	IE (kcal/mol)	PA (kcal/mol)
R/UCCSD(T)(FC) <sup>a</sup>	297.21 ± 0.17	235.67 ± 0.06	211.77 ± 0.01
$\Delta E_{ZPE}$ <sup>b</sup>	-21.33	-1.09	-9.24
$\Delta E_{CV}$ R/UCCSD(T)/cc-pCVQZ	0.60	0.08	-0.13
$\Delta E_{SR}$ CISD/cc-pVQZ	-0.24	-0.02	0.03
$\Delta E_{FCI}$ FCI/cc-pVTZ <sup>c</sup>	0.28	-0.10	
Total	276.52 ± 0.17 <sup>d</sup>	234.54 ± 0.06 (10.171 eV)	202.43
Expt. <sup>e</sup>	276.72 ± 0.10	10.1862 eV	

<sup>a</sup>Based on the average of the aVQ56 mixed and two  $\ell_{\max}$  extrapolations. The uncertainty is taken from the spread in the extrapolations.

<sup>b</sup>The zero point vibrational energy of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> are taken from the empirically corrected potentials of Martin *et al.*, Ref. 14. For NH<sub>3</sub><sup>+</sup>, see the text.

<sup>c</sup>FCI correction obtained with a mixed cc-pVTZ(N)/cc-pVDZ(s)(H) basis set.

<sup>d</sup>The calculated  $\Delta H_f(0 \text{ K}, \text{NH}_3)$  is -9.10 kcal/mol and the experimental value  $\Delta H_f(0 \text{ K}, \text{NH}_3)$  is -9.30 ± 0.10 kcal/mol. See footnote e.

<sup>e</sup>NIST-JANAF, Ref. 24.

the three extrapolations as our best estimate. The spread among the values will serve as a measure of the uncertainty in the extrapolation.

Geometries were optimized at the CCSD(T)(FC) level of theory up through aug-cc-pVQZ. The CCSD(T)(FC)/aug-cc-pVQZ geometries (see footnote in Table I) were used for the larger basis set calculations. Table I shows the convergence behavior of the frozen core energies for N/N<sup>+</sup>, NH/NH<sup>+</sup>, NH<sub>2</sub>/NH<sub>2</sub><sup>+</sup>, NH<sub>3</sub>/NH<sub>3</sub><sup>+</sup>, and NH<sub>4</sub><sup>+</sup> as well as the convergence of the valence shell component of the corresponding ionization energies and dissociation energies.

The molecular zero point energies were taken from anharmonic corrected values where available and from combined experimental and calculated values and include anharmonic corrections where possible.<sup>12,13</sup> The zero point vibrational energies of NH and NH<sup>+</sup> were based on  $0.5\omega_e - 0.25\omega_e x_e$ , where  $\omega_e$  and  $\omega_e x_e$  values were taken from Huber and Herzberg<sup>12</sup> for NH and calculated at the CCSD(T)/aug-cc-pVQZ level for NH<sup>+</sup>. The latter values are  $\omega_e = 3047.1 \text{ cm}^{-1}$  and  $\omega_e x_e = 70.75 \text{ cm}^{-1}$ . For NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> the zero point energies were taken from the anharmonic force fields of Martin and co-workers.<sup>14</sup> For NH<sub>2</sub> the zero point energy was taken from the force field of Gabriel *et al.*<sup>15</sup> This value is within 0.02 kcal/mol of the value given by Martin and co-workers.<sup>16</sup> For triplet NH<sub>2</sub><sup>+</sup>, only the  $b_2$  (asymmetric) stretch is known reliably from experiment.<sup>13,17</sup> We have previously shown that averaging the calculated harmonic values at the CCSD(T) level with the experimental anharmonic values provides a good estimate of the zero point energy. If we do this for the one known mode of NH<sub>2</sub><sup>+</sup>, we obtain a scale factor of 0.979 at the CCSD(T)/aug-cc-pVTZ level which we apply to the  $a_1$  stretch. For the bend, we calculated a value of  $746.0 \text{ cm}^{-1}$  as compared to the uncertain experimental value of  $840 \pm 50 \text{ cm}^{-1}$ .<sup>13,18</sup> For NH<sub>3</sub><sup>+</sup>, we average the CCSD(T)/aug-cc-pVTZ frequencies for the  $a_2''$  bend, and the  $e'$  stretches and bends with the experimental values.<sup>13,17,19</sup> This yields a scale factor of 0.978 which we apply to the calculated  $a'$  stretch of  $3364.8 \text{ cm}^{-1}$ , as the experimental value<sup>19(a)</sup> of  $2740 \text{ cm}^{-1}$  for this stretch is clearly in error.

Additional corrections to the CCSD(T)(FC) atomization energies are needed when trying to achieve accuracies on the order of a few tenths of a kcal/mol. Core/valence corrections ( $\Delta E_{CV}$ ) to the dissociation energy were obtained from fully correlated (and valence only) CCSD(T) calculations with the cc-pCVQZ basis set<sup>20</sup> at the CCSD(T)/aug-cc-pVQZ geometries.

The effects of relativity must also be considered. 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. For N(<sup>4</sup>S), no such correction is needed, but a correction is needed for the <sup>3</sup>P state of N<sup>+</sup>, as well as the doublet ground state of NH<sup>+</sup>. In order to correct for this effect in N<sup>+</sup> and in the diatomic NH<sup>+</sup>, we calculated the spin-orbit matrix elements<sup>21</sup> at the CISD (configuration interaction with singles and double excitations) level using an uncontracted cc-pV5Z basis set. Due in part to program limitations, the  $g$  and  $h$  functions on N and the  $f$  and  $g$  functions on H were removed. Molecular scalar relativistic corrections ( $\Delta E_{SR}$ ) which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms were included at the CISD level of theory using the cc-pVQZ basis set in the frozen core approximation.  $\Delta E_{SR}$  is

TABLE III. Ionization energy for the nitrogen atom.

Component	IE (kcal/mol)
R/UCCSD(T)(FC) <sup>a</sup>	334.82 ± 0.05
$\Delta E_{CV}$ R/UCCSD(T)/cc-pCV5Z	0.65
$\Delta E_{SR}$ R/UCCSD(T)/unc-cc-pVQZ	-0.15
$\Delta E_{SO}$	-0.23
$\Delta E_{FCI}$	0.01
Total	335.10 ± 0.05 (14.532 eV)
Expt. <sup>b</sup>	335.15 (14.534 eV)

<sup>a</sup>Based on the average of the aVQ56 mixed and two  $\ell_{\max}$  extrapolations. The uncertainty is taken from the spread in the extrapolations.

<sup>b</sup>Reference 24.

TABLE IV. Atomization energy and ionization energy for  $\text{NH}_2$ .

Component	$\Sigma D_0$ (kcal/mol)	IE (kcal/mol) $^3B_1$	IE (kcal/mol) $^1A_1$
R/UCCSD(T)(FC) <sup>a</sup>	182.02±0.12	258.90±0.08	287.50±0.03
$\Delta E_{\text{ZPE}}^b$	-11.78	-1.27	-0.77
$\Delta E_{\text{CV}}$ R/UCCSD(T)/cc-pCVQZ	0.30	0.00	0.44
$\Delta E_{\text{SR}}$ CISD/cc-pVQZ	-0.14	0.01	-0.09
$\Delta E_{\text{FCI}}$ FCI/cc-pVTZ <sup>c</sup>	0.12	0.07	
Total	170.52±0.12 <sup>d</sup>	257.71±0.08 (11.176 eV)	287.08±0.03 (12.449 eV)
Expt. <sup>e</sup>	170.62±0.09	11.163 eV	

<sup>a</sup>Based on the average of the aVQ56 mixed and two  $\ell_{\text{max}}$  extrapolations. The uncertainty is taken from the spread in the extrapolations.

<sup>b</sup>The zero point vibrational energy of  $\text{NH}_2$  was taken from the empirically corrected potential of Gabriel *et al.*, Ref. 15. For the zero point energy of  $\text{NH}_2^+$ , see the text.

<sup>c</sup>Obtained with a mixed cc-pVTZ(N)/cc-pVDZ(H) basis set.

<sup>d</sup>The calculated  $\Delta H_f(0 \text{ K}, \text{NH}_2)$  is 45.29 kcal/mol and the experimental value  $\Delta H_f(0 \text{ K}, \text{NH}_2)=45.17 \pm 0.09$  kcal/mol. See footnote e.

<sup>e</sup>Reference 2.

taken as the sum of the mass-velocity and one-electron Darwin (MVD) terms in the Breit–Pauli Hamiltonian.<sup>22</sup>

We were able to estimate the effects of higher order correlation at the full configuration (FCI) level with the cc-pVTZ basis set for N,  $\text{N}^+$ , NH,  $\text{NH}^+$ , and with a mixed cc-pVTZ(N)/cc-pVDZ(H) basis set for  $\text{NH}_2$ ,  $\text{NH}_2^+$ ,  $\text{NH}_3$ , and  $\text{NH}_3^+$ . The FCI calculations were performed with the Knowles sparsity-driven, determinant-based FCI program.<sup>23</sup> Program thresholds were chosen to insure accuracy in the total energy to at least  $10^{-5}E_h$ .

By combining our computed  $\Sigma D_0$  values with the known<sup>24</sup> heats of formation at 0 K for the elements [ $\Delta H_f^0(\text{N})=112.53$  kcal/mol,  $\Delta H_f^0(\text{H})=51.63$  kcal/mol, and  $\Delta H_f^0(\text{H}^+)=365.22$  kcal/mol], we can derive  $\Delta H_f^0$  values for the molecules under study.

## RESULTS

The total electronic energies and the extrapolated results together with various electronic components to  $D_e$ ,  $\Sigma D_e$ , ionization energies (IE), and the proton affinity of  $\text{NH}_3$  (PA) are given in Table I. Details of the other terms for  $\text{NH}_3$  through N are given in Tables II–V.

The calculated result for  $\Delta H_f^0(\text{NH}_3)$  serves as a benchmark for our theoretical approach. We note that the theoretical  $\Sigma D_e$  value is 0.2 kcal/mol smaller than the experimental value (see Table II), which has an error bar of 0.10 kcal/mol.<sup>24</sup> This result is similar to what we found for  $\Delta H_f^0(\text{H}_2\text{O})$ .<sup>1</sup> The core-valence and full CI corrections increase  $\Sigma D_e$  by 0.60 and 0.28 kcal/mol, respectively, whereas the scalar relativistic term decreases  $\Sigma D_e$  by 0.24 kcal/mol. The ionization energy for  $\text{NH}_3$  differs from the latest experimental value<sup>2</sup> by 0.015 eV or 0.35 kcal/mol and the ionization energy is predicted to be too low. This gives  $\Delta H_f^0(\text{NH}_3^+)=225.44$  kcal/mol, 0.15 kcal/mol below the latest experimental value.<sup>2</sup> The proton affinity is predicted to be 202.43 kcal/mol at 0 K (203.91 kcal/mol at 298 K) in good agreement with previous high level calculated values.<sup>25</sup>

Another test of our methods is the calculation of the ionization energy of N. In this case the calculated IP is too low by 0.002 eV (0.05 kcal/mol) as compared to experiment

as shown in Table III. Together with the calculated value for the heat of formation of  $\text{NH}_3$ , this demonstrates that we can reliably calculate the properties that we are interested in within a few tenths of a kcal/mol.

The atomization energy and ionization energy of  $\text{NH}_2$  ( $X^2B_1$ ) are listed in Table IV. The calculated  $\Delta H_f(0 \text{ K}, \text{NH}_2)=45.27$  kcal/mol can be compared to the new experimental value<sup>2</sup> of  $\Delta H_f(0 \text{ K}, \text{NH}_2)=45.17$  kcal/mol, both of which are lower than the previously accepted value<sup>24</sup> of  $46.19 \pm 1.50$  kcal/mol. The calculated ionization energy of  $\text{NH}_2$  to form triplet  $\text{NH}_2^+$  is calculated to be too high by 0.013 eV (0.30 kcal/mol) as compared to the latest experimental results.<sup>2</sup> This gives  $\Delta H_f(0 \text{ K}, \text{NH}_2^+)=303.00$  kcal/mol, 0.40 kcal/mol above the experimental value.<sup>2</sup> We note that the ground state triplet has a very large bond angle of  $152.2^\circ$  as compared to the much smaller bond angle of  $103.0^\circ$  in  $\text{NH}_2$ . The singlet–triplet splitting for  $\text{NH}_2^+$  is predicted to be 29.37 kcal/mol at 0 K.

Table V contains the results for NH ( $X^3\Sigma^-$ ). The cal-

TABLE V. Dissociation energy and ionization energy for NH.

Component	$D_0$ (kcal/mol)	IE <sub>0</sub> (kcal/mol)
R/UCCSD(T)(FC) <sup>a</sup>	82.84±0.08	310.68±0.04
$\Delta E_{\text{ZPE}}^b$	-4.64	-0.33
$\Delta E_{\text{CV}}$ R/UCCSD(T)/cc-pCVQZ	0.10	0.53
$\Delta E_{\text{SR}}$ CISD/cc-pVQZ	-0.06	-0.11
$\Delta E_{\text{SO}}$		-0.07
$\Delta E_{\text{FCI}}$ FCI/cc-pVTZ	0.12	-0.06
Total	78.36±0.08 <sup>c</sup>	310.64±0.04 (13.471 eV)
Expt. <sup>d</sup>	74.2±4	(13.49±0.01 eV)

<sup>a</sup>Based on the average of the aVQ56 mixed and two  $\ell_{\text{max}}$  extrapolations. The uncertainty is taken from the spread in the extrapolations.

<sup>b</sup>The zero point vibrational energies of NH and  $\text{NH}^+$  were based on  $0.5\omega_e - 0.25\omega_e x_e$ , where  $\omega_e$  and  $\omega_e x_e$  values were taken from Huber and Herzberg, Ref. 11 for NH and calculated at the CCSD(T)/aug-cc-pVQZ level for  $\text{NH}^+$ . The latter values are  $\omega_e=3047.1 \text{ cm}^{-1}$  and  $\omega_e x_e=70.75 \text{ cm}^{-1}$ .

<sup>c</sup>The calculated  $\Delta H_f(0 \text{ K}, \text{NH})=85.92 \pm 0.08$  kcal/mol vs an experimental value of  $90.0 \pm 4$  kcal/mol. See footnote d.

<sup>d</sup>Reference 24.

TABLE VI. Calculated and experimental heats of formation at 0 K ( $\Delta H_f^0$ ) in kcal/mol.

Molecule	Calc.	Expt.
NH	85.92±0.08	90.0±4 <sup>a</sup>
NH <sub>2</sub>	45.27±0.12	45.17±0.09 <sup>b</sup>
NH <sub>3</sub>	-9.10±0.17	-9.30±0.10 <sup>a</sup>
NH <sup>+</sup>	396.56±0.12	
NH <sub>2</sub> <sup>+</sup>	303.00±0.20	302.60±0.08 <sup>b</sup>
NH <sub>3</sub> <sup>+</sup>	225.44±0.23	225.59±0.08 <sup>b</sup>

<sup>a</sup>Reference 24.<sup>b</sup>Reference 2.

culated value for  $\Delta H_f(0\text{ K, NH}) = 85.92 \pm 0.08$  kcal/mol. This can be compared to an experimental value<sup>24</sup> of  $90.0 \pm 4$  kcal/mol and the calculated value is just outside the large experimental error limits. The calculated value should be far more reliable than the experimental one. The ionization energy for NH is not as well established experimentally as that for NH<sub>3</sub> and NH<sub>2</sub>. Comparing the various ionization energies with experiment, we find that we are within less than 0.02 eV of the experimental value for NH by Dyke and co-workers,<sup>18</sup> confirming their value within 0.02 eV. The calculated heat of formation of NH<sup>+</sup> at 0 K is 389.00 kcal/mol.

Martin<sup>26</sup> has used a similar approach based on using CCSD(T) with somewhat smaller basis sets based on the cc-pVXZ and aug-cc-pVXZ basis sets to calculate the atomization energies. They account for zero point energies as well as spin-orbit and core correlation corrections and extrapolate to the complete basis set limit. For NH<sub>x</sub> species, they apply an empirical correction of 0.126 kcal/mol per N-H bond. For NH, they find  $D_0 = 78.37$  kcal/mol as compared to our value of  $78.36 \pm 0.08$  kcal/mol; for NH<sub>2</sub>, they find  $\Sigma D_0 = 170.73$  kcal/mol as compared to our value of  $170.52 \pm 0.12$  kcal/mol; and for NH<sub>3</sub>, they find  $\Sigma D_0 = 276.82$  kcal/mol as compared to our value of  $276.52 \pm 0.17$  kcal/mol. Our values are in excellent overall agreement within tenths of a kcal/mol. The exact, small differences between our values and the Martin values for NH<sub>2</sub> and NH<sub>3</sub> seem to be essentially due to their empirical corrections (0.25 kcal correction for NH<sub>2</sub> and 0.38 kcal/mol for NH<sub>3</sub>).<sup>26</sup>

The calculated heats of formation at 0 K are shown in Table VI where they are compared with the best available experimental results. The calculated heats of formation are all within 0.4 kcal/mol of the accurately determined experimental values which have small error bars. The largest difference is 0.4 kcal/mol for  $\Delta H_f^0(\text{NH}_2^+)$ . Table VI shows that we can reliably calculate the heats of formation of these types of species within a few tenths of a kcal/mol at the *ab initio* electronic structure theory level. It is likely that some of the error is due to our treatment of the zero point energies for these species which have A-H bonds with significant anharmonic corrections (e.g., an error of  $35\text{ cm}^{-1}$  is 0.1 kcal/mol).

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