

## Anchoring the Absolute Proton Affinity Scale

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**Abstract:** Converged first-principles proton affinities (PA) of ammonia and carbon monoxide have been determined by the focal-point analysis (FPA) approach, thus fixing the high and low ends of the molecular proton affinity scale. The electronic structure computations employed the all-electron (AE) coupled-cluster (CC) method up to single, double, triple, quadruple, and pentuple excitations. Aug-cc-pCVXZ [ $X = 2(\text{D}), 3(\text{T}), 4(\text{Q}), 5$ , and  $6$ ] correlation-consistent (cc) Gaussian basis sets for C, N, and O were used in conjunction with the corresponding aug-cc-pVXZ ( $X = 2–6$ ) sets for H. Our FPA study supersedes previous computational work by accounting for (a) electron correlation beyond the “gold standard” CCSD(T) level; (b) the nonadditivity of core electron correlation effects; (c) scalar relativity; (d) diagonal Born–Oppenheimer corrections (DBOC); (e) anharmonicity of zero-point vibrational energies, based on accurate AE-CCSD(T)/cc-pCVQZ internal coordinate quartic force fields and fully variational vibrational computations; and (f) thermal corrections to enthalpies by direct summation over rovibrational energy levels. Our final proton affinities at 298.15(0.0) K are  $\Delta_{\text{pa}}H^\circ(\text{NH}_3) = 852.6(846.4) \pm 0.3 \text{ kJ mol}^{-1}$  and  $\Delta_{\text{pa}}H^\circ(\text{CO}) = 592.4(586.5) \pm 0.2 \text{ kJ mol}^{-1}$ . These values have better accuracy and considerably lower uncertainty than the best previous recommendations and thus anchor the proton affinity scale of molecules for future use.

### I. Introduction

Modern mass spectrometry (MS) is an advanced and highly versatile experimental technique that allows studies of fundamental energetic quantities in the gas phase, including proton affinities (PA) and the related gas-phase basicities (GB). PAs and GBs have special relevance for MS fragmentation processes in tandem mass spectrometry (MS/MS) experiments. MS/MS fragments yield not only essential structural data for a wide variety of compounds but also information about dissociation processes. Among these fragmentation processes, those of protonated peptides and proteins are of particular importance because they provide the basis of protein identification by mass spectrometry in proteomics studies.

The “mobile proton model” has been developed for understanding peptide fragmentation in MS experiments.<sup>1–10</sup> In essence, this relatively simple but now widely accepted model states that upon ion activation the proton(s) added to a peptide will migrate to various sites prior to fragmentation and will thereby trigger charge-directed cleavages. Proton migration is crucial in inducing fragmentation and, as indicated by simple quantum chemical computations, the thermodynamically most stable protonated forms are not the preferred fragmenting structures.<sup>11–13</sup> The ease or difficulty of proton migration depends on the PA (or GB) values of the protonation sites; for example, peptides containing the most basic amino acids, such as arginine (R) or lysine (K), require higher internal energy (more efficient ion activation) to fragment. Statistical evaluations of the MS/MS data of a large number of protonated peptides clearly show that the extent of fragmentation for particular amide bonds can be related to the PAs of the amino acids.<sup>14–16</sup>

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As eloquently pointed out by Paizs and Suhai in their recent review<sup>17</sup> on peptide fragmentation, a significant simplification embodied in the mobile proton model is that it focuses mostly on the step(s) prior to dissociation. To overcome this limitation, they proposed the “pathways in competition” (PIC) description involving a detailed energetic and kinetic characterization of the major fragmentation pathways, requiring the computation of parts of the potential energy surfaces (PES). While electronic structure computations of ever increasing accuracy have started to appear for amino acids, peptide models, and small peptides,<sup>18–24</sup> for oligopeptides of practical interest computations at higher levels of electronic structure theory are still not routine, and a full, reliable mapping of the PES is time-consuming even for relatively small dipeptides. For example, several fragmentation pathways for the loss of ammonia have been found for a small protonated dipeptide.<sup>25</sup> The complexity of fragmentation pathways and the practical limitations of rigorous theoretical computations justify the use of experimental MS/MS data and their relatively simple interpretation based on relative proton affinities of possible protonation sites. Therefore, anchoring the PA scale is not only of theoretical but also of practical importance.

Several studies,<sup>26–33</sup> including elaborate reviews and critical compilations, have been published that attempted to fix the absolute proton affinity scale of organic compounds. To accomplish this goal, the PAs of molecules at both the high and low end of the scale must be pinpointed. The purpose of the present study is to determine benchmark first-principles PAs of ammonia (NH<sub>3</sub>) and carbon monoxide (CO). These molecules have been chosen because they are small species amenable to highly sophisticated methods of electronic structure and nuclear motion theory, and they have extremely different proton affinities at the low (CO) and the high (NH<sub>3</sub>) ends of the absolute PA scale. Among other things, very precise proton affinities of NH<sub>3</sub> and CO will facilitate the determination of ion energetics from measurements of equilibrium constants for reversible proton-transfer reactions



The proton affinities at 298.15(0.00) K,  $\Delta_{\text{pa}}H_{298}^0$  ( $\Delta_{\text{pa}}H_0^0$ ), of NH<sub>3</sub> and CO have been studied frequently, and numerous data with varying uncertainties are available for both species. Tables 1 and 2 and their footnotes contain a compilation and assessment of literature data for the PAs of NH<sub>3</sub> and CO, respectively.

In 1984, a  $\Delta_{\text{pa}}H_{298}^0$ (NH<sub>3</sub>) value of 853.5 kJ mol<sup>-1</sup> was recommended by Lias and co-workers<sup>32</sup> based on critical evaluation of different measurements. In the 1990s, the best ab initio computations gave the 298.15 K PA of ammonia as 853.6 kJ mol<sup>-1</sup> (ref 34, with no uncertainty reported), 853.1 ± 1.3 kJ mol<sup>-1</sup> (ref 35), and 854.0 ± 1.3 kJ mol<sup>-1</sup> (ref 36). In 1998, in the most recent compilation of PAs, Hunter and Lias<sup>31</sup> selected the proton affinity of NH<sub>3</sub> computed by Smith and Radom,<sup>34</sup> considering its close match with experimental measurements and the earlier recommendation.<sup>32</sup> At the beginning of this decade, more sophisticated ab initio results were computed for PA(NH<sub>3</sub>), which

translate to 853.2 kJ mol<sup>-1</sup> (ref 37) and 853.1 (ref 38) at 298.15 K. The best experimental  $\Delta_{\text{pa}}H_{298}^0$ (CO) was obtained by Traeger<sup>39</sup> in 1985 as 594 ± 3 kJ mol<sup>-1</sup> by means of dissociative photoionization of formic acid. This value was recommended by Hunter and Lias in their 1998 critical evaluation of literature data.<sup>31</sup> The best previously computed values of  $\Delta_{\text{pa}}H_{298}^0$ (CO) are 593.3 ± 2.1 kJ mol<sup>-1</sup> published by Komornicki and Dixon<sup>40</sup> and 593.0 kJ mol<sup>-1</sup> reported by Smith and Radom.<sup>34</sup>

Despite the large amount of information for the PAs of these two molecules, the attendant uncertainties are still considerably larger than what can be achieved from state-of-the-art computations on molecules of this size.<sup>41–55</sup> For small molecules and radicals (at present up to 5–6 “heavy” atoms), first-principles computations of thermochemical quantities are often more accurate than experimental measurements; frequently, the uncertainties of the best computed values can only be surpassed by comprehensively incorporating both empirical and theoretical data in schemes such as the Active Thermochemical Tables (ATcT).<sup>56</sup> Previous computations of energetic quantities other than PAs,<sup>41–55</sup> employing variants of the focal-point analysis (FPA) approach,<sup>57,58</sup> clearly prove the effectiveness of the sophisticated first-principles methods employed in this study.

The present FPA study pushes the ab initio treatment of PAs to new heights by means of the following advances: (a) electron correlation beyond the “gold standard” CCSD(T) level is taken into account by performing coupled cluster computations complete through quadruple excitations and, for NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, even considering the effect of connected pentuples; (b) FPA limits are determined with all electrons correlated (AE), avoiding any additivity assumptions regarding valence and core correlation; (c) relativistic shifts are evaluated by first-order perturbation theory applied to the mass-velocity and one-electron Darwin terms (MVD1);<sup>59,60</sup> (d) the electronic structure computations go beyond the clamped nucleus assumption by appending diagonal Born–Oppenheimer corrections (DBOC);<sup>61–64</sup> (e) anharmonic zero-point vibrational energies (ZPVEs) have been determined by computing new AE-CCSD(T)/cc-pCVQZ internal coordinate quartic force field representations of the ground-state potential energy surfaces and executing variational vibrational motion computations using exact kinetic energy operators; and (f) the enthalpy increments needed to convert the 0 K computational results to finite temperatures, in the present case 298.15 K, have been obtained by explicitly summing over (ro)vibrational energy levels, obtained mostly through our variational vibrational motion computations, within standard statistical mechanical expressions.

## II. Computational Methods

The (aug)-cc-p(C)VXZ [X = 2(D), 3(T), 4(Q), 5, and 6] families of correlation-consistent, atom-centered Gaussian basis sets<sup>65–68</sup> were employed in this study. The orbital contraction schemes of these basis sets range from [11s6p2d] → [5s4p2d] to [22s16p10d8f6g4h2i] → [13s12p10d8f6g4h2i] for N, C, O, and from [5s2p] → [3s2p] to [11s6p5d4f3g2h] → [7s6p5d4f3g2h] for H. These atomic-orbital basis sets give superior performance in approaching the complete basis set

**Table 1.** Literature Data for the Proton Affinity of NH<sub>3</sub> (in kJ mol<sup>-1</sup>)

| $\Delta_{\text{pa}}H_{298}^{\circ}$ ( $\Delta_{\text{pa}}H^{\circ}$ ) | authors and references                     | comments | $\Delta_{\text{pa}}H_{298}^{\circ}$ ( $\Delta_{\text{pa}}H^{\circ}$ ) | authors and references                    | comments |
|---|--|----------|---|---|----------|
| Measurements  |  |          |   |   |          |
| 851.9 ± 5.4   | Ceyer et al. (1979) <sup>110</sup>         | <i>a</i> | 851.4 ± 3.3   | Szulejko and McMahon (1993) <sup>27</sup> | <i>c</i> |
| 867.8 ± 6.7   | Meot-Ner and Sieck (1991) <sup>111</sup>   | <i>b</i> |   |   |          |
| Ab Initio Computations  |  |          |   |   |          |
| 860.2 ± 4.2   | Eades et al. (1980) <sup>112</sup>         | <i>d</i> | 852.8   | Smith and Radom (1995) <sup>118</sup>     | <i>k</i> |
| 853.5   | DeFrees and McLean (1986) <sup>113</sup>   | <i>e</i> | 853.1 ± 1.3 (846.8)   | Martin and Lee (1996) <sup>35</sup>       | <i>l</i> |
| 853.5 (847.3)   | Pople and Curtiss (1987) <sup>114</sup>    | <i>f</i> | 854.0 ± 1.3   | Peterson et al. (1998) <sup>36</sup>      | <i>m</i> |
| 858.6   | Del Bene and Shavitt (1990) <sup>115</sup> | <i>g</i> | 849.3   | Seo et al. (2001) <sup>119</sup>          | <i>n</i> |
| 853.5 (847.3)   | Curtiss et al. (1991) <sup>116</sup>       | <i>h</i> | 853.2 (847.0)   | Dixon et al. (2001) <sup>37</sup>         | <i>o</i> |
| 852.3   | Del Bene (1993) <sup>117</sup>             | <i>i</i> | 853.1   | Parthiban and Martin (2001) <sup>38</sup> | <i>p</i> |
| 853.6 (847.4)   | Smith and Radom (1993) <sup>34</sup>       | <i>j</i> |   |   |          |
| Reviews and Evaluations   |  |          |   |   |          |
| 853.5 ± 8   | Lias et al. (1984) <sup>32</sup>           | <i>q</i> | 853.6   | Hunter and Lias (1998) <sup>31</sup>      | <i>r</i> |

<sup>a</sup> Examination of the photoionization threshold for the appearance of the ammonium ion generated from the ammonia van der Waals dimer gave  $\text{PA}(\text{NH}_3) = 203.6 \pm 1.3 \text{ kcal mol}^{-1}$ . <sup>b</sup> Originally reported as  $208.3 \text{ kcal mol}^{-1}$  at 600 K, or  $\text{PA}(\text{NH}_3) = 207.4 \pm 1.6 \text{ kcal mol}^{-1}$  at 300 K. This value was soon challenged in ref 27. <sup>c</sup> From temperature-dependent proton transfer equilibrium experiments, originally reported as  $\text{PA}(\text{NH}_3) = 203.5 \pm 0.8 \text{ kcal mol}^{-1}$ . <sup>d</sup> Originally reported as  $205.6 \pm 1 \text{ kcal mol}^{-1}$ . The proton affinity of ammonia was computed at different levels of theory. The SCF calculations were performed using both Gaussian-type orbitals (GTO) and Slater-type orbitals (STO). The STO basis was used in CI calculations with all single and double excitations excluding the top virtual orbital ( $\epsilon > 10 E_h$ ); correction was made for quadruple excitations. The ZPVE contribution was obtained from SCF harmonic frequencies computed with the GTO basis and scaled to experiment. <sup>e</sup> Computed at the MP4/6-311++G(3df,3pd) level; originally reported as  $204.0 \text{ kcal mol}^{-1}$ . <sup>f</sup> Obtained from MP perturbation theory through fourth order with a combination of isogyric reactions and basis set additivity approximations; originally reported as  $204.0(202.5) \text{ kcal mol}^{-1}$ . <sup>g</sup> Computed at the CISD+Q/6-31+G(2d,2p) level; originally reported as  $213.2 \text{ kcal mol}^{-1}$ , at 0 K and without a ZPVE correction. With a MP2/6-31+G(d,p) harmonic ZPVE correction, the PA estimate becomes  $205.2 \text{ kcal mol}^{-1}$ . <sup>h</sup> From G2 computations; originally reported as  $204.0(202.5) \text{ kcal mol}^{-1}$ . <sup>i</sup> Computed at the CCSD + T(CCSD)/aug-cc-pVTZ level; originally reported as  $203.7 \text{ kcal mol}^{-1}$ . <sup>j</sup> Proton affinities of 31 molecules (including NH<sub>3</sub> and CO) were computed at the G2 level of theory. G2 corresponds to QCISD(T)/6-311+G(3df,2p)/MP2/6-31G(d) computations with zero-point vibrational and empirical "higher-level" corrections. In this case, the higher-level corrections cancel, and thus the G2 proton affinities are purely ab initio. <sup>k</sup> The proton affinities of several molecules, including NH<sub>3</sub> and CO, were computed using the G2(MP2,SVP) procedure, which is similar to G2(MP2) but uses the split-valence plus polarization (SVP) 6-31G(d) basis set for the QCISD(T) computations. ZPVE and enthalpy corrections were obtained from scaled HF/6-31G(d) vibrational frequencies. <sup>l</sup> Based on CCSD(T)/(aug)-cc-pVXZ (X = 2-5) computations. The largest basis set employed was aug'-cc-pV5Z, where the diffuse functions on hydrogen were removed. Frozen-core CCSD(T) energies were extrapolated to the CBS limit; core correlation and ZPVE corrections were appended. Anharmonic ZPVEs were obtained from a CCSD(T)/cc-pVTZ quartic force field by means of VPT2 with the  $G_0$  term included. Not considered were the following: (a) electron correlation beyond the CCSD(T) level, (b) relativistic shifts, (c) DBOC terms, and (d) nonadditivity of the core correlation effect. With a thermal contribution of  $1.50 \text{ kcal mol}^{-1}$ , a final result of  $\Delta_{\text{pa}}H_{298}^{\circ}(\text{NH}_3) = 203.9 \pm 0.3 \text{ kcal mol}^{-1}$  was originally reported. We have subtracted off the thermal correction to obtain the 0 K proton affinity listed in the table. <sup>m</sup> Based on computations up to the frozen-core CCSD(T)/aug-cc-pVQZ and CCSD(T)/cc-pV5Z levels; originally reported as  $204.1 \pm 0.3 \text{ kcal mol}^{-1}$ . CCSD(T)/aug-cc-pwCVTZ//CCSD(T)/aug-cc-pVTZ core-valence correlation effects were included. ZPVE contributions were taken from experiment and from scaled theoretical results. <sup>n</sup> Proton affinities of several molecules, including NH<sub>3</sub> and CO, were obtained at the multicoefficient QCISD (MC-QCISD) level of theory. For  $\Delta_{\text{pa}}H_{298}^{\circ}(\text{NH}_3)$ , both MP2/6-31G(d,p) and full multilevel (ML) optimum geometries gave the same results. Zero-point and thermal energies were obtained from MP2/6-31G(d,p) frequencies scaled by 0.9676. <sup>o</sup> Originally reported as  $202.43 \text{ kcal mol}^{-1}$  at 0 K; our thermal correction has been used to obtain the corresponding  $298.15 \text{ K}$  value. A vibrationless proton affinity of  $886.05 \pm 0.04 \text{ kJ mol}^{-1}$  was inferred as the CBS limit of frozen-core CCSD(T). A core correlation correction of  $-0.54 \text{ kJ mol}^{-1}$  was then appended, which may have a sign error considering that our CBS AE-CCSD(T) vibrationless proton affinity is  $886.61 \text{ kJ mol}^{-1}$ . The approximate ZPVE correction of Dixon et al. deviates from the more accurate result of this study by  $1 \text{ kJ mol}^{-1}$ . <sup>p</sup> From W2 theory, originally reported as  $203.9 \text{ kcal mol}^{-1}$ . The corresponding W1 values are  $853.9(847.6) \text{ kJ mol}^{-1}$  at  $298.15(0.0) \text{ K}$ . This paper also gives a  $298.15 \text{ K}$  value of  $849.8 \text{ kJ mol}^{-1}$  from the G3 method. <sup>q</sup> Recommendation based on a critical evaluation of different measurements. The uncertainty is a general value stated in the Introduction. <sup>r</sup> The recommended proton affinity was based on a close match between the computed value of Smith and Radom<sup>34</sup> and the previously recommended<sup>32</sup> value.

(CBS) limit in a systematic fashion during traditional electronic structure computations. When (aug)-cc-pCVXZ sets were used to effectuate the correlation of core electrons for C, N, and O, the corresponding (aug)-cc-pVXZ functions were utilized for H.

Reference electronic wave functions were determined by the single-configuration restricted Hartree-Fock (RHF) method.<sup>69</sup> Electron correlation was accounted for by the coupled-cluster (CC) method<sup>70,71</sup> including all single and double (CCSD), triple (CCSDT), and quadruple (CCSDTQ) excitations.<sup>72</sup> The CCSD(T)<sup>73</sup> and CCSDT(Q)<sup>74,75</sup> methods, which include perturbative (T) and (Q) terms for connected triple and quadruple excitations, respectively, were also used extensively. For NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, the CCSDTQ(P) method<sup>74</sup> was also employed with the aug-cc-pCVDZ basis set. All electrons were included, unless otherwise noted, in the active space for the correlation energy computations.

In the spirit of the FPA approach,<sup>52-55,57,58</sup> the aug-cc-pCVXZ sequences of electronic energies were extrapolated to determine CBS limits. For extrapolation of the Hartree-Fock energies, two-<sup>76,77</sup> and three-parameter<sup>78</sup> exponential functions of the cardinal number  $X$  were used

$$E_X^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + a(X+1)e^{-9\sqrt{X}} \quad (2)$$

and

$$E_X^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + ae^{-bX} \quad (3)$$

For the molecules considered here, the two extrapolation formulas, when applied with the largest possible  $X$  values, gave RHF energies and PAs in agreement to better than 0.04 and 0.001 kJ mol<sup>-1</sup>, respectively. The perhaps slightly more accurate<sup>76,79</sup> two-parameter results are reported in Tables 3 and 4 as the CBS RHF proton affinities for NH<sub>3</sub> and CO,

**Table 2.** Literature Data for the Proton Affinity of CO (in kJ mol<sup>-1</sup>)

| $\Delta_{\text{pa}}H_{298}^{\circ}$ ( $\Delta_{\text{pa}}H^{\circ}$ ) | authors and references                    | comments | $\Delta_{\text{pa}}H_{298}^{\circ}$ ( $\Delta_{\text{pa}}H^{\circ}$ ) | authors and references                      | comments |
|---|---|----------|---|---|----------|
| Measurements  |   |          |   |   |          |
| 594 ± 3   | Traeger (1985) <sup>39</sup>              | <i>a</i> | 591.6 ± 4.2   | Adams et al. (1989) <sup>28</sup>           | <i>b</i> |
| Ab Initio Computations  |   |          |   |   |          |
| (597.5)   | Del Bene et al. (1982) <sup>120</sup>     | <i>c</i> | 592.4(586.5) ± 2.1  | Martin et al. (1993) <sup>104</sup>         | <i>j</i> |
| 599.6   | Ikuta (1984) <sup>121</sup>               | <i>d</i> | 594.1   | Botschwina et al. (1993) <sup>124</sup>     | <i>k</i> |
| 591.6   | Dixon et al. (1984) <sup>122</sup>        | <i>e</i> | 597.1   | Smith and Radom (1995) <sup>118</sup>       | <i>l</i> |
| 599.1   | DeFrees and McLean (1986) <sup>113</sup>  | <i>f</i> | 594.1   | Mladenović and Schmatz (1998) <sup>98</sup> | <i>m</i> |
| 593.3 ± 2.1   | Komornicki and Dixon (1992) <sup>40</sup> | <i>g</i> | (587.8) ± 2.1   | van Mourik et al. (2000) <sup>125</sup>     | <i>n</i> |
| (589.3)   | Ma et al. (1992) <sup>123</sup>           | <i>h</i> | 599.9   | Seo et al. (2001) <sup>119</sup>            | <i>o</i> |
| 593.0 (587.1)   | Smith and Radom (1993) <sup>34</sup>      | <i>i</i> |   |   |          |
| Reviews and Evaluations   |   |          |   |   |          |
| 594 ± 6   | Lias et al. (1984) <sup>32</sup>          | <i>p</i> | 594 ± 3   | Hunter and Lias (1998) <sup>31</sup>        | <i>r</i> |
| 593.7   | Szulejko and McMahon (1993) <sup>27</sup> | <i>q</i> |   |   |          |

<sup>a</sup> From examination of the dissociative photoionization of a number of formyl compounds (in this case HCOOH) to yield the formyl cation HCO<sup>+</sup>. <sup>b</sup> The enthalpy of the reaction HN<sub>2</sub>O<sup>+</sup> + CO → HCO<sup>+</sup> + N<sub>2</sub>O was obtained from a van't Hoff plot of the measured equilibrium constant at different temperatures, yielding PA(CO) = 141.4 ± 1 kcal mol<sup>-1</sup> at 300 K. <sup>c</sup> PA at 0 K is 142.8 kcal mol<sup>-1</sup> as originally reported. SCF geometries and frequencies were used along with partial fourth-order perturbation theory and the 6-31G\*\* basis. <sup>d</sup> The PA value at 0 K computed at the MP3/6-31G\*\* level is originally reported as 149.7 kcal mol<sup>-1</sup>. This value does not contain the ZPVE correction. In this table a value of 143.3 kcal mol<sup>-1</sup> is given as originally cited by Komornicki and Dixon.<sup>40</sup> <sup>e</sup> Originally reported as 141.4 kcal mol<sup>-1</sup>. Geometries and frequencies were determined at the CI(SD) level using a TZP basis set. <sup>f</sup> PA(CO) = 143.2 kcal mol<sup>-1</sup> was computed using MP4-SDTQ fourth-order perturbation theory with an extensive one-particle basis including *f* and *d* double polarization functions on the heavy atoms and hydrogen, respectively. CI(D)/6-31G(*d*) optimum geometries and scaled SCF frequencies were used. <sup>g</sup> PA(CO) was computed at the SCF, MP2, CCSD, and CCSD(T) levels of theory using three different basis sets, with account of BSSE. Empirical geometrical parameters and vibrational frequencies were used. A final value of 141.8 ± 0.5 kcal mol<sup>-1</sup> was originally reported. <sup>h</sup> Based on QCISD(T)/6-311+G(3df,2p) energies and scaled MP2/6-31G(*d*) harmonic ZPVE estimates. <sup>i</sup> See comment *j* of Table 1. <sup>j</sup> Reported as 141.59(140.17) kcal mol<sup>-1</sup>, based on frozen-core CCSD(T)/cc-pVQZ computations. <sup>k</sup> Originally reported as 142.0 kcal mol<sup>-1</sup>. This value was based on an equilibrium CBS CCSD(T) proton affinity of 147.6 kcal mol<sup>-1</sup>, a ZPVE contribution of -7.0 kcal mol<sup>-1</sup>, a difference in the mean vibrational energies between HCO<sup>+</sup> and CO of -0.1 kcal mol<sup>-1</sup>, a difference in the translational energies of 0.9 kcal mol<sup>-1</sup>, and a  $\Delta(PV)$  term of 0.6 kcal mol<sup>-1</sup>. <sup>l</sup> See comment *k* of Table 1. <sup>m</sup> Originally reported as 142.0 kcal mol<sup>-1</sup>, based on frozen-core CCSD(T)/cc-pVQZ (no *f* functions on hydrogens) energies and variational ZPVE estimates. <sup>n</sup> The 0 K value, 140.49 kcal mol<sup>-1</sup> with an uncertainty estimate of ±0.5 kcal mol<sup>-1</sup>, was reported in Table 6 as  $D_0(\text{HCO}^+)$ . <sup>o</sup> See comment *n* of Table 1. The MC-QCISD/ML value is listed in the table; at the MC-QCISD//MP2/6-31G(*d,p*) level, the PA is 598.7 kJ mol<sup>-1</sup>. <sup>p</sup> Selected value from experimental measurements, taken from Table 2 of the compilation. The uncertainty is a general value stated in the Introduction. <sup>q</sup> PA(CO) = 141.9 kcal mol<sup>-1</sup> was chosen because it was midway between the Traeger<sup>39</sup> experimental value and the ab initio calculation of Komornicki and Dixon<sup>40</sup> and because it agreed with the previous assessment from the NIST proton affinity tables. <sup>r</sup> Recommended value is the proton affinity originally measured by Traeger.<sup>39</sup>

**Table 3.** Focal-Point Analysis of the All-Electron Nonrelativistic Born–Oppenheimer Proton Affinity ( $\Delta E_e$ , kJ mol<sup>-1</sup>) of NH<sub>3</sub> at 0 K<sup>a,b</sup>

|                    | $\Delta E_e(\text{RHF})$ | $\delta[\text{CCSD}]$ | $\delta[\text{CCSD(T)}]$ | $\delta[\text{CCSDT}]$ | $\delta[\text{CCSDT(Q)}]$ | $\delta[\text{CCSDTQ}]$ | $\delta[\text{CCSDTQ(P)}]$ | $\Delta E_e[\text{CCSDTQ(P)}]$ |
|--------------------|--------------------------|-----------------------|--------------------------|------------------------|---------------------------|-------------------------|----------------------------|--------------------------------|
| aug-cc-pCVDZ       | 898.68                   | -11.59                | -2.95                    | -0.08                  | -0.30                     | +0.04                   | -0.005                     | 883.80                         |
| aug-cc-pCVTZ       | 903.28                   | -13.04                | -4.00                    | +0.04                  | -0.33                     | [+0.04]                 | [-0.005]                   | [885.98]                       |
| aug-cc-pCVQZ       | 903.87                   | -13.08                | -4.18                    | +0.08                  | [-0.33]                   | [+0.04]                 | [-0.005]                   | [886.39]                       |
| aug-cc-pCV5Z       | 904.03                   | -13.06                | -4.24                    | [+0.09]                | [-0.33]                   | [+0.04]                 | [-0.005]                   | [886.52]                       |
| aug-cc-pCV6Z       | 904.06                   | -13.10                | -4.26                    | [+0.10]                | [-0.33]                   | [+0.04]                 | [-0.005]                   | [886.48]                       |
| CBS <sup>c,d</sup> | [904.06]                 | [-13.15]              | [-4.30]                  | [+0.11]                | [-0.33]                   | [+0.04]                 | [-0.005]                   | [886.43]                       |

<sup>a</sup> Based on AE-CCSD(T)/aug-cc-pCVQZ reference structures. <sup>b</sup> For the all-electron coupled cluster computations, the symbol  $\delta$  denotes the increments in the proton affinity,  $\Delta E_e$ , with respect to the preceding level of theory. Brackets signify increments obtained from basis set extrapolations or additivity approximations. <sup>c</sup> The complete basis set RHF, CCSD, and CCSD(T) entries were obtained from aug-cc-pCV(5,6)Z energies using the two-parameter extrapolation formulas given in eqs 2 and 4. The bracketed CCSDT entries result from direct extrapolation of aug-cc-pCV(T,Q)Z increments (rather than individual energies). <sup>d</sup> Application of the three-parameter formula (eq 3) with aug-cc-pCV(Q,5,6)Z energies for the extrapolation to the RHF CBS limit also results in 904.06 kJ mol<sup>-1</sup>.

respectively. The CCSD and CCSD(T) electron correlation energies ( $\varepsilon_X \equiv E_X^{\text{CC}} - E_X^{\text{HF}}$ ) were extrapolated using a two-parameter polynomial formula<sup>80</sup>

$$\varepsilon_X = \varepsilon_{\text{CBS}} + bX^{-3} \quad (4)$$

The  $\delta[\text{CCSDT}]$  correlation increments in the focal-point analyses were extrapolated likewise.

The program packages ACESII,<sup>81,82</sup> MRCC (interfaced to ACESII),<sup>83,84</sup> and MOLPRO<sup>85,86</sup> were used for the electronic structure computations. Analytic gradient techniques<sup>87–89</sup> were utilized to obtain optimum geometric structures at the all-electron CCSD(T) level with the cc-pVQZ, cc-pCVQZ, and aug-cc-pCVQZ basis sets. The

AE-CCSD(T)/aug-cc-pCVQZ structures were adopted for all electronic structure computations involved in the FPA analyses. The DBOC corrections were computed at the frozen-core CCSD/aug-cc-pVDZ level within the formalism of ref 62 utilizing a private version of the conjoined ACESII and MRCC program packages. Relativistic effects were evaluated by first-order perturbation theory applied to the mass-velocity and one-electron Darwin terms (MVD1),<sup>59</sup> as implemented in ACESII. For this purpose, AE-CCSD(T)/aug-cc-pCVTZ wave functions were employed.

The full quartic force fields of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> were determined in internal coordinates at the AE-CCSD(T)/cc-

**Table 4.** Focal-Point Analysis of the All-Electron Nonrelativistic Born-Oppenheimer Proton Affinity ( $\Delta E_e$ , kJ mol<sup>-1</sup>) of CO at 0 K<sup>a</sup>

|                  | $\Delta E_e(\text{RHF})$ | $\delta[\text{CCSD}]$ | $\delta[\text{CCSD(T)}]$ | $\delta[\text{CCSDT}]$ | $\delta[\text{CCSDT(Q)}]$ | $\delta[\text{CCSDTQ}]$ | $\Delta E_e(\text{CCSDTQ})$ |
|------------------|--------------------------|-----------------------|--------------------------|------------------------|---------------------------|-------------------------|-----------------------------|
| aug-cc-pCVDZ     | 597.14                   | +17.12                | +0.04                    | -0.03                  | +0.29                     | -0.23                   | 614.34                      |
| aug-cc-pCVTZ     | 603.37                   | +14.28                | -0.17                    | -0.19                  | +0.28                     | [-0.23]                 | [617.33]                    |
| aug-cc-pCVQZ     | 604.07                   | +13.50                | -0.23                    | -0.17                  | [+0.28]                   | [-0.23]                 | [617.22]                    |
| aug-cc-pCV5Z     | 604.14                   | +13.06                | -0.27                    | [-0.17]                | [+0.28]                   | [-0.23]                 | [616.81]                    |
| aug-cc-pCV6Z     | 604.16                   | +12.83                | -0.29                    | [-0.17]                | [+0.28]                   | [-0.23]                 | [616.58]                    |
| CBS <sup>b</sup> | [604.16]                 | [+12.52]              | [-0.32]                  | [-0.17]                | [+0.28]                   | [-0.23]                 | [616.25]                    |

<sup>a</sup> See footnotes a, b, and c of Table 3. <sup>b</sup> Application of the three-parameter formula (eq 3) with aug-cc-pCV(Q,5,6)Z energies for the extrapolation to the RHF CBS limit yields the same value as given in the table.

**Table 5.** Auxiliary Corrections (DBOC, MVD1, and ZPVE) and Final Proton Affinities, All in kJ mol<sup>-1</sup>, for the NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> and CO/HCO<sup>+</sup> Systems

|                              | DBOC <sup>a</sup> | relativistic MVD1 <sup>b</sup> | ZPVE <sup>c</sup> | final $\Delta_{\text{pa}}H_0^{\text{f}}$ |
|------------------------------|-------------------|--------------------------------|-------------------|--|
| NH <sub>3</sub>              | 7.038             | -76.251                        | 89.17             | 846.40                                   |
| NH <sub>4</sub> <sup>+</sup> | 7.225             | -76.112                        | 128.87            |  |
| CO                           | 10.637            | -176.656                       | 12.94             | 586.51                                   |
| HCO <sup>+</sup>             | 11.052            | -176.533                       | 42.14             |  |

<sup>a</sup> Frozen-core CCSD/aug-cc-pVDZ//AE-CCSD(T)/aug-cc-pCVQZ level. <sup>b</sup> AE-CCSD(T)/aug-cc-pCVTZ//CCSD(T)/aug-cc-pCVQZ level. <sup>c</sup> For NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> accurate anharmonic ZPVEs were computed in this study by variational vibrational methods, as described in the text. The ZPVEs for CO and HCO<sup>+</sup> were taken from refs 97 and 98, respectively.

pCVQZ level of theory, using high-precision energy points from the MOLPRO package and carefully validated higher-order finite-difference procedures built into the code INTDIF2005.<sup>90,91</sup> The force fields were transformed by INTDER2005<sup>92-94</sup> into a representation with Simons–Parr–Finlan (SPF)<sup>95</sup> bond-stretching coordinates for use in the variational vibrational procedures.

The variational vibrational computations were performed with a recently developed program called DEWE,<sup>96</sup> which employs a discrete variable representation (DVR) of the Eckart–Watson (EW) Hamiltonian and involves an exact transformation from normal to internal coordinates, thus allowing the exact inclusion of an arbitrary potential. For NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, the AE-CCSD(T)/cc-pCVQZ quartic force fields in SPF coordinates were used to obtain accurate zero-point vibrational energies (ZPVEs), as well as low-lying vibrational band origins (VBOs) used for evaluating thermal enthalpy increments via direct summation. Variational ZPVEs were taken from the literature for carbon monoxide<sup>97</sup> and the HCO<sup>+</sup> cation.<sup>98</sup>

### III. Results and Discussion

The primary focal-point analyses of the proton affinities of NH<sub>3</sub> and CO are presented in Tables 3 and 4, respectively. The auxiliary data for the DBOC, relativistic, and ZPVE corrections are given in Table 5. The absolute total energies of the NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, CO, and HCO<sup>+</sup> species, from which the relative energies are derived, are tabulated in Supporting Information (Tables S1–S4) for this paper. The less stable HOC<sup>+</sup> isomer, with a relative energy and isomerization barrier of 166 and 321 kJ mol<sup>-1</sup> above HCO<sup>+</sup>, respectively,<sup>98</sup> was not considered in this study.

**III.1. Reference Structures.** For all species, AE-CCSD(T)/aug-cc-pCVQZ equilibrium structures were used as reference

geometries in our final FPA computations. Accordingly, for NH<sub>3</sub> we employed  $[r_e(\text{N-H}), \theta_e(\text{H-N-H})] = (1.0115 \text{ \AA}, 106.71^\circ)$ , which are in almost perfect agreement with both a longstanding empirical structure<sup>99</sup> (1.0116 Å, 106.7°), and the optimum parameters (1.0109 Å, 106.81°) given by the highest current levels of ab initio theory.<sup>100</sup> Our AE-CCSD(T)/aug-cc-pCVQZ bond distance in NH<sub>4</sub><sup>+</sup> (*T<sub>d</sub>* point-group symmetry) is 1.0208 Å. The corresponding bond length in CO is 1.1293 Å, while for the linear HCO<sup>+</sup> cation,  $r_e(\text{C-H}) = 1.0925 \text{ \AA}$  and  $r_e(\text{C-O}) = 1.1066 \text{ \AA}$ . These AE-CCSD(T)/aug-cc-pCVQZ equilibrium distances are also in excellent agreement with the best experimental bond lengths, namely,  $r_e(\text{C-O}) = 1.1283 \text{ \AA}$  for carbon monoxide<sup>101</sup> and  $[r_e(\text{C-H}), r_e(\text{C-O})] = (1.0916, 1.1056) \text{ \AA}$  for HCO<sup>+</sup>.<sup>102</sup> As expected,<sup>103</sup> the close matching of experimental and computed structures requires the correlation of all electrons, as demonstrated also by previously reported<sup>104</sup> frozen-core CCSD(T)/cc-pVQZ results:  $r_e(\text{C-O}) = 1.1314 \text{ \AA}$  for CO and  $[r_e(\text{C-H}), r_e(\text{C-O})] = (1.0935, 1.1086) \text{ \AA}$  for HCO<sup>+</sup>.

FPA energies and corresponding proton affinities were also determined at our AE-CCSD(T)/cc-pVQZ equilibrium structures, as reported in the Supporting Information (Tables S5–S10). These alternative results show that when the reference structures have an accuracy better than about 0.001 Å and 0.5°, the precise choice has a rather small influence, less than 0.15 kJ mol<sup>-1</sup>, on the computed PA values. Nevertheless, unlike most previous studies, the level of precision sought here requires the choice of the reference structures to be taken into account in computing proton affinities and ascribing uncertainties to them.

**III.2. Nonrelativistic Born–Oppenheimer Proton Affinities of NH<sub>3</sub> and CO.** The present FPA analysis starts at the RHF/aug-cc-pCVDZ level, which yields 898.68 and 597.14 kJ mol<sup>-1</sup> for the vibrationless proton affinities of NH<sub>3</sub> and CO, respectively. Enlarging the basis set to aug-cc-pCV6Z increases the Hartree–Fock PAs of NH<sub>3</sub> and CO by 5.38 and 7.02 kJ mol<sup>-1</sup>, respectively. The differences between the aug-cc-pCV6Z and CBS Hartree–Fock proton affinities are minuscule, less than 0.005 kJ mol<sup>-1</sup> for both molecules.

As expected, the electron correlation energies and the lowest-order FPA increments exhibit considerably slower basis set convergence. The aug-cc-pCV6Z and extrapolated (CBS)  $\delta[\text{CCSD}]$  increments deviate by 0.05 and 0.31 kJ mol<sup>-1</sup> for the proton affinities of NH<sub>3</sub> and CO, respectively. The level of convergence of the CCSD increment in the CO case largely determines the eventual uncertainty in the FPA value of  $\Delta_{\text{pa}}H_0^{\text{f}}(\text{CO})$ . Consistent with the foundations of the

FPA approach, all of the higher-order correlation increments converge rapidly to their respective CBS limits; for example, the changes in the  $\delta[\text{CCSD(T)}]$  increments beyond aug-cc-pCV6Z are only about  $0.03 \text{ kJ mol}^{-1}$ .

The final CBS estimates of the coupled-cluster correlation energy increments for  $\Delta_{\text{pa}}H_0^0(\text{NH}_3)$  are  $-13.15$ ,  $-4.19$ , and  $-0.28 \text{ kJ mol}^{-1}$  for the full treatments of single and double (SD), triple (T), and quadruple (Q) excitations, in order. The same increments for  $\Delta_{\text{pa}}H_0^0(\text{CO})$  are  $+12.52$ ,  $-0.48$ , and  $+0.05 \text{ kJ mol}^{-1}$ , in order. For both  $\text{NH}_3$  and  $\text{CO}$ , the total correlation contribution to the proton affinity is about 2.0%. Interestingly, the effect of higher-order electron correlation past CCSD on the proton affinity of carbon monoxide is 1 order of magnitude smaller than in the  $\text{NH}_3$  case, contrary to general expectations for an electron-dense, multiply bonded system such as  $\text{CO/HCO}^+$ . From the sequences of CCSD, CCSDT, and CCSDTQ values, it appears that full inclusion of pentuple excitations would decrease both  $\Delta_{\text{pa}}H_0^0(\text{NH}_3)$  and  $\Delta_{\text{pa}}H_0^0(\text{CO})$  on the order of  $0.01 \text{ kJ mol}^{-1}$ . The actual CCSDTQ(P)/aug-cc-pCVDZ increment of  $-0.005 \text{ kJ mol}^{-1}$  computed for the proton affinity of  $\text{NH}_3$  supports this expectation.

Our final values from Tables 3 and 4, with conservative uncertainty estimates, for the all-electron nonrelativistic proton affinities (without ZPVE) at 0 K are  $886.43 \pm 0.10$  and  $616.25 \pm 0.20 \text{ kJ mol}^{-1}$  for  $\text{NH}_3$  and  $\text{CO}$ , respectively.

**III.3. Relativistic Effects.** Relativistic effects on the proton affinities were computed by applying first-order perturbation theory to the mass-velocity and one-electron Darwin terms (MVD1).<sup>59,60</sup> Detailed previous studies, *e.g.*, refs 60 and 105, suggest that for systems such as those investigated here, the accuracy of MVD1 relative energy corrections is excellent, as compared to those from more complicated multicomponent methods. Employing the AE-CCSD(T)/aug-cc-pCVTZ level of theory, the relativistic energy shifts for the PAs of  $\text{NH}_3$  and  $\text{CO}$  are  $-0.14$  and  $-0.12 \text{ kJ mol}^{-1}$ , respectively. Similar results,  $-0.15$  and  $-0.11 \text{ kJ mol}^{-1}$ , are obtained from the lower-level CCSD/aug-cc-pCVDZ method, suggesting that these quantities do not contribute any significant amount to the uncertainties of our final PAs.

**III.4. DBOC Contributions.** The effects of computing electronic wave functions beyond the clamped nucleus formalism can be estimated from diagonal Born–Oppenheimer corrections (DBOCs).<sup>106</sup> The DBOC contributions to the proton affinities at the frozen-core CCSD/aug-cc-pVDZ level of theory are  $-0.19 \text{ kJ mol}^{-1}$  ( $\text{NH}_3$ ) and  $-0.42 \text{ kJ mol}^{-1}$  ( $\text{CO}$ ). For comparison, the corresponding HF/aug-cc-pVDZ numbers are  $-0.14 \text{ kJ mol}^{-1}$  ( $\text{NH}_3$ ) and  $-0.36 \text{ kJ mol}^{-1}$  ( $\text{CO}$ ). Although the DBOCs for the total energies of the individual species are 1 order of magnitude smaller than their relativistic counterparts (Table 5), the DBOC shifts in the proton affinities are sizable, especially for carbon monoxide. To achieve the level of accuracy sought in this study for proton affinities, the standard Born–Oppenheimer approximation is clearly not sufficient.

**III.5. Zero-Point Vibrational Energies.** The ZPVEs of all four species were obtained from variational nuclear motion computations. The PESs of  $\text{NH}_3$  and  $\text{NH}_4^+$  were represented by newly determined quartic internal coordinate

force fields obtained at the AE-CCSD(T)/cc-pCVQZ level of theory. The force constants are tabulated in the Supporting Information (Tables S11 and S12), in terms of SPF coordinates for the bond stretches with reference distances corresponding to the optimized equilibrium ones.

The converged variational, anharmonic ZPVEs of  $\text{NH}_3$  and  $\text{NH}_4^+$  are  $89.17$  and  $128.87 \text{ kJ mol}^{-1}$ , respectively. For comparison, the harmonic ZPVEs are  $90.69 \text{ kJ mol}^{-1}$  ( $\text{NH}_3$ ) and  $131.02 \text{ kJ mol}^{-1}$  ( $\text{NH}_4^+$ ). Our anharmonic ZPVE for ammonia is consistent with earlier variational ZPVEs of  $88.87 \text{ kJ mol}^{-1}$ ,<sup>107</sup>  $89.08 \text{ kJ mol}^{-1}$ ,<sup>108</sup> and  $89.25 \text{ kJ mol}^{-1}$ .<sup>109</sup> It is likely that our computation on the 5-atomic  $\text{NH}_4^+$  molecular ion is the first variational determination of the low-lying vibrational levels of this cation. Therefore, the ZPVEs and the first several vibrational band origins (VBOs) are reported for  $\text{NH}_3$  and  $\text{NH}_4^+$  in the Supporting Information (Table S13). Our computed anharmonic (harmonic) ZPVE contribution to the PA of ammonia is  $-39.70$  ( $-40.33$ )  $\text{kJ mol}^{-1}$ .

Because our vibrational computations employed a uniform, converged variational method and potentials from the same level of electronic structure theory, the uncertainty in our ZPVE contribution to the proton affinity should be considerably smaller than the uncertainties in the individual ZPVEs. In support of this contention, the AE-CCSD(T)/cc-pCVQZ harmonic ZPVEs for  $\text{NH}_3$  and  $\text{NH}_4^+$  are  $1.52$  and  $2.15 \text{ kJ mol}^{-1}$  too large, respectively, compared to the corresponding variational anharmonic values, but the harmonic  $\text{NH}_3 - \text{NH}_4^+$  ZPVE difference is in error by only  $-0.63 \text{ kJ mol}^{-1}$ . In comparison to previous ZPVE contributions ( $\Delta_{\text{ZPVE}}$ ) computed for  $\text{PA}(\text{NH}_3)$ ,<sup>35–38</sup> our value is within  $0.05 \text{ kJ mol}^{-1}$  of the second-order vibrational perturbation theory (VPT2) result of Martin and Lee,<sup>35</sup> who included the leading  $G_0$  term in their analysis and employed slightly less accurate quartic force fields from the frozen-core CCSD(T)/cc-pVTZ level of theory; however, previous  $\Delta_{\text{ZPVE}}$  estimates of  $-38.66 \text{ kJ mol}^{-1}$  (ref 37) and  $-39.25 \text{ kJ mol}^{-1}$  (determined by the standard W1 protocol from scaled B3LYP harmonic frequencies)<sup>38</sup> are significantly different. Overall, we are confident that the uncertainty in our ZPVE term for  $\text{PA}(\text{NH}_3)$  is no larger than  $0.15 \text{ kJ mol}^{-1}$ .

The variationally computed ZPVE values for  $\text{CO}$  and  $\text{HCO}^+$  were taken from the literature. We chose  $\text{ZPVE}(\text{CO}) = 12.94 \text{ kJ mol}^{-1}$  from an experimentally derived RKR potential,<sup>97</sup> which is confirmed by the  $12.96 \text{ kJ mol}^{-1}$  value we obtained variationally from the SPF quartic force field given by AE-CCSD(T)/cc-pCVQZ theory. In 1998, Mladenović and Schmatz<sup>98</sup> performed variational rovibrational computations using a new analytic global PES of  $\text{HCO}^+/\text{HOC}^+$  determined at the frozen-core CCSD(T)/cc-pVQZ level of theory; this work yielded  $\text{ZPVE}(\text{HCO}^+) = 42.14 \text{ kJ mol}^{-1}$ . Thus, the ZPVE contribution to the proton affinity of  $\text{CO}$  is  $-29.20 \text{ kJ mol}^{-1}$ , with an uncertainty not larger than  $0.05 \text{ kJ mol}^{-1}$ . This value is considerably different from that used by Komornicki and Dixon,<sup>40</sup>  $-28.5 \text{ kJ mol}^{-1}$ , based on experimental fundamental frequencies.

**III.6. Final Proton Affinities at 0 K.** The final proton affinities of ( $\text{NH}_3$ ,  $\text{CO}$ ) at 0 K are obtained by summing the vibrationless all-electron nonrelativistic proton affinities

(886.43, 616.25) kJ mol<sup>-1</sup>, the relativistic energy shifts (-0.14, -0.12 kJ mol<sup>-1</sup>), the DBOC corrections (-0.19, -0.42 kJ mol<sup>-1</sup>), and the ZPVE contributions (-39.70, -29.20 kJ mol<sup>-1</sup>). Accordingly, we determine  $\Delta_{\text{pa}}H_0^0(\text{NH}_3) = 846.4 \pm 0.3$  and  $\Delta_{\text{pa}}H_0^0(\text{CO}) = 586.5 \pm 0.2$  kJ mol<sup>-1</sup>. The uncertainties ascribed to these values correspond to  $2\sigma$  and arise mostly from the reference geometry and ZPVE effects for NH<sub>3</sub> and the CBS extrapolation of the  $\delta[\text{CCSD}]$  correlation increment for CO. We estimate that all other sources of error collectively contribute no more than 0.1 kJ mol<sup>-1</sup> to the uncertainties of our proton affinities. The best previous theoretical  $\Delta_{\text{pa}}H_0^0(\text{NH}_3)$  value (846.8 kJ mol<sup>-1</sup>), computed by Martin and Lee,<sup>35</sup> agrees well with our improved result. For  $\Delta_{\text{pa}}H_0^0(\text{CO})$ , the G2 computation (587.1 kJ mol<sup>-1</sup>) of Smith and Radom<sup>34</sup> is within 0.6 kJ mol<sup>-1</sup> of our converged ab initio result.

**III.7. Final Proton Affinities at 298.15 K.** Proton affinities, as universally employed, are quantities defined at a finite temperature, usually 298.15 K. Therefore, the ab initio PA values determined in the previous subsection, referring to 0 K, need to be converted to 298.15 K.

The proton affinity of a neutral molecule A is defined as the enthalpy change for the isogyric reaction  $\text{AH}^+ \rightarrow \text{A} + \text{H}^+$ . The proton affinity at 0 K can be obtained by performing quantum chemical computations for the electronic energies and zero-point vibrational energies of the A and  $\text{AH}^+$  species. To compute PAs at a nonzero temperature ( $\Delta_{\text{pa}}H_T^0$ ), the heat capacities of the species have to be taken into account as

$$\Delta_{\text{pa}}H_T^0 = \Delta_{\text{pa}}H_0^0 + \int_0^T C_p(\text{A})dT - \int_0^T C_p(\text{AH}^+)dT + \frac{5}{2}RT \quad (5)$$

The most important term in eq 5 is the last one, which is the translational enthalpy of H<sup>+</sup>. The two integrals in eq 5 cancel if one assumes that A and  $\text{AH}^+$  are classical rigid rotors of the same type (linear or nonlinear). Therefore, some studies have considered only the  $5/2RT$  term (6.20 kJ mol<sup>-1</sup> at 298.15 K) as the thermal contribution to PAs.

Vibrational enthalpy effects can be treated by evaluating partition functions via direct summation of variationally computed vibrational energy levels (Table S13). In this way, we obtained vibrational enthalpy contributions of +0.06 and -0.35 kJ mol<sup>-1</sup> to the 298.15 K proton affinities of NH<sub>3</sub> and CO, respectively. These corrections are certainly not negligible for our target accuracy, especially in the carbon monoxide case. The large effect on PA(CO) is due to the disparity between the relatively low bending frequency (830.7 cm<sup>-1</sup>) of HCO<sup>+</sup> and the stretching fundamental of CO (2143.3 cm<sup>-1</sup>).

To evaluate rotational enthalpy contributions, we employed the usual rigid-rotor analytic formulas for rotational energy levels of linear molecules and symmetric and spherical tops in terms of equilibrium rotational constants. The rigid-rotor rotational energies were appended to our variationally computed vibrational levels in the direct summations for the rotational-vibrational partition functions. We found that the rotational contribution to the 298.15 K proton affinity of NH<sub>3</sub> is -0.02 kJ mol<sup>-1</sup>, whereas the corresponding rotational effect for CO is negligible (<10<sup>-3</sup> kJ mol<sup>-1</sup>).

Adding the translational enthalpy of H<sup>+</sup> (6.20 kJ mol<sup>-1</sup>) to our vibrational and rotational corrections yields total thermal contributions of +6.24 and +5.85 kJ mol<sup>-1</sup> for the 298.15 K proton affinities of NH<sub>3</sub> and CO, respectively. Therefore, we arrive at the final values  $\Delta_{\text{pa}}H_{298}^0(\text{NH}_3) = 852.6 \pm 0.3$  kJ mol<sup>-1</sup> and  $\Delta_{\text{pa}}H_{298}^0(\text{CO}) = 592.4 \pm 0.2$  kJ mol<sup>-1</sup>.

## IV. Conclusions

The highest levels of electronic structure theory currently feasible have been employed in focal-point analyses to systematically converge on the 0 K proton affinities of NH<sub>3</sub> and CO, two molecules fixing the high and low ends of the absolute PA scale. Moreover, thermal contributions to these proton affinities have been evaluated by direct summation of partition functions over computed (ro)vibrational energy levels. The current study is another methodological milestone for ab initio quantum chemistry because we pinpoint proton affinities to 0.2–0.3 kJ mol<sup>-1</sup>, roughly an order of magnitude more precise than previous PA measurements and critical evaluations. In the process, a number of valuable observations are made regarding the performance of state-of-the-art theoretical methods: (1) each step in the coupled cluster series  $\text{CCSD} \rightarrow \text{CCSDT} \rightarrow \text{CCSDTQ} \rightarrow \text{CCSDTQ(P)}$  reduces the electron correlation error in the PAs by at least 90%, and CCSDTQ appears sufficient to converge within 0.01 kJ mol<sup>-1</sup> of the full configuration interaction (FCI) limit; (2) somewhat surprisingly, the coupled cluster convergence to the FCI proton affinity is slower for NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> than for the electron-dense, multiply bonded CO/HCO<sup>+</sup> system; (3) the perturbative CCSDT(Q) method reproduces the full CCSDTQ effect quite well for PA(NH<sub>3</sub>) but not for PA(CO); (4) conventional CCSD(T) computations with the aug-cc-pCV6Z basis appear to be within 0.05 kJ mol<sup>-1</sup> of the corresponding CBS limit for PA(NH<sub>3</sub>), but the aug-cc-pCV6Z incompleteness error is still 0.3 kJ mol<sup>-1</sup> for PA(CO); (5) one of the largest sources of uncertainty in the first-principles determination of highly accurate PAs of polyatomic molecules is clearly the ZPVE correction; for example, use of the harmonic approximation in evaluating the effect of ZPVE on PA(NH<sub>3</sub>) engenders a 0.63 kJ mol<sup>-1</sup> error; (6) the Born–Oppenheimer approximation is not satisfactory in predicting PA(CO) to our target accuracy, as DBOCs shift this quantity by 0.42 kJ mol<sup>-1</sup>; (7) neglecting terms other than the translation enthalpy of H<sup>+</sup> in determining the 298.15 K proton affinity of CO causes a 0.35 kJ mol<sup>-1</sup> error; and (8) MVD1 relativistic effects shift both PA(NH<sub>3</sub>) and PA(CO) downward by just over 0.1 kJ mol<sup>-1</sup> and are the smallest auxiliary corrections considered here.

The final 298.15 K results determined in this study are  $\Delta_{\text{pa}}H_{298}^0(\text{NH}_3) = 852.6 \pm 0.3$  kJ mol<sup>-1</sup> and  $\Delta_{\text{pa}}H_{298}^0(\text{CO}) = 592.4 \pm 0.2$  kJ mol<sup>-1</sup>. These values supersede all previous determinations due to the rigor and precision with which they have been pinpointed. In particular, our proton affinities improve on the values recommended in the 1998 critical evaluation of Hunter and Lias:<sup>31</sup> 853.6 kJ mol<sup>-1</sup> for NH<sub>3</sub> based on the computations of Smith and Radom,<sup>34</sup> and 594 ± 3 kJ mol<sup>-1</sup> for CO given by the experiments of Traeger.<sup>39</sup> It is not likely that the uncertainties in our proton affinities

can be significantly lowered anytime soon, and thus these PAs should anchor the proton affinity scale for the foreseeable future.

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**Supporting Information Available:** Compilation of all total energies utilized in the focal point analyses of the proton affinities and tabulation of the quartic force fields and lowest-lying variational vibrational levels of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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