Title
High-resolution energy-selected study of the reaction NH3+ -> NH2 ++H: Accurate thermochemistry for the NH2/NH2+ and NH3/NH3 + systems

Permalink
https://escholarship.org/uc/item/126565v2

Journal
Journal of Chemical Physics, 115(6)

Authors
Song, Y.
Qian, X.M.
Lau, K.C.
et al.

Publication Date
2001-03-01
High-Resolution Energy-Selected Study of the Reaction $\text{NH}_3^+ \rightarrow \text{NH}_2^+ + \text{H}$: Accurate Thermochemistry for the NH$_2$/NH$_2^+$ and NH$_3$/NH$_3^+$ Systems

Y. Song, X.-M. Qian, K.-C. Lau, and C. Y. Ng*

Ames Laboratory,
U. S. Department of Energy,
and
Department of Chemistry,
Iowa State University,
Ames IA 50011, USA

Jianbo Liu and Wenwu Chen

Lawrence Berkeley National Laboratory,
Chemical Science Division,
Berkeley, CA 94720, USA

*Author to whom correspondence should be addressed. Email address: CYNG@AMESLAB.GOV
Abstract:

Employing the newly developed high-resolution pulsed field ionization-photoelectron (PFI-PE)-photoion coincidence (PFI-PEPICO) technique, we have examined the dissociation of energy-selected NH$_3^+$ to form NH$_2^+$ + H near its threshold. The breakdown curves for NH$_2^+$ and NH$_3^+$ thus obtained yield a value of 15.765±0.001 eV for the 0 K dissociation threshold or appearance energy (AE) for NH$_2^+$ from NH$_3$. This value, together with the known ionization energy (IE=10.1864±0.0001 eV) and 0 K bond dissociation energy (D$_0$=4.6017±0.0025 eV) for NH$_3$, allows the determination of the D$_0$(NH$_2^+$-H) and IE(NH$_2$), which are 5.5786±0.0010 and 11.1633±0.0025 eV, respectively. Using the known 0 K heats of formation ($\Delta H^\circ_{\text{f},0}$) for NH$_3$ and H and the AE(NH$_2^+$), we obtain the $\Delta H^\circ_{\text{f},0}$(NH$_2^+$) = 302.60±0.08 kcal/mol. The PFI-PE spectrum for NH$_3$ exhibits a step-like feature at the 0 K AE(NH$_2^+$), indicating that the dissociation of excited NH$_3$ in high-n (n≥100) Rydberg states at energies slightly above the dissociation threshold occurs on a time scale ≤10$^{-7}$ s. This step confirms the AE(NH$_2^+$) value derived from the PFI-PEPICO measurements. Highly accurate energetic data with well-founded error limits, such as those obtained in the present and other studies using the PFI techniques, are expected to play an important role for the development of the next generation of *ab initio* quantum computation procedures. This experiment has stimulated a state-of-the-art *ab initio* quantum chemical calculation (Dixon et al., J. Chem. Phys., accepted). The comparison between theoretical predictions and the best experimental results for the NH$_3$/NH$_2^+$ and NH$_3$/NH$_3^+$ systems indicates that the accuracy of the computational scheme used is ≤0.4 kcal/mol.
I. Introduction

As the simplest amine, ammonia (NH$_3$) is of fundamental interest to both chemistry and biology, especially considering its ability of forming hydrogen bond. For this reason, it is important to establish accurate energetic information for NH$_2$, NH$_3$, NH$_2^+$, and NH$_3^+$. Bond dissociation energies at 0 K (D$_0$) for NH$_2$-H [D$_0$(NH$_2$-H)] and NH$_2^+$-H [D$_0$(NH$_2^+$-H)] can be determined by measurements of the ionization energies (IEs) for NH$_2$ [IE(NH$_2$)] and NH$_3$ [IE(NH$_3$)] and the 0 K dissociation threshold or appearance energy (AE) for NH$_2^+$ [AE(NH$_2^+$)] from NH$_3$ according to Eqs. (1) and (2).

$$D_0(NH_2^+-H) = AE(NH_2^+) - IE(NH_3)$$  \hspace{1cm} (1)

$$D_0(NH_2-H) = AE(NH_2^+) - IE(NH_2)$$  \hspace{1cm} (2)

The uncertainties for $D_0$(NH$_2^+$-H) and $D_0$(NH$_2$-H) thus obtained depend on the error limits of IE(NH$_2$), IE(NH$_3$), and AE(NH$_2^+$).

In traditional photoionization and photoelectron studies using laboratory discharge lamps and second generation synchrotron radiation sources, the uncertainties for IE and AE values obtained for polyatomic molecules generally fall in the range of 5-100 meV. The AE values for most molecules have been determined by dissociative photoionization onsets of fragment ions obtained in photoionization efficiency (PIE) measurements. Although the PIE measurement is straightforward, the determination of the “true” ion dissociation threshold based on the PIE onset for a fragment ion can be ambiguous. Partly due to the hot band and kinetic shift effects and/or the lack of Franck-Condon factors for photoionization transitions, the PIE onset for a fragment ion formed in the dissociative photoionization of a polyatomic molecule can be very gradual, resulting in a large uncertainty.

A more reliable method for AE determinations is the conventional vacuum ultraviolet (VUV) threshold photoelectron (TPE)-photoion coincidence (TPEPICO) technique, which involves the detection of correlated TPE-photoion pairs. The TPEPICO scheme has been widely used for the study of state- or energy-selected ion dissociation dynamics. The analysis of the breakdown curves for parent and fragment ions based on TPEPICO time-of-flight (TOF) data is made to recover information concerning the AE for the fragment ion. The simulation of the breakdown curves applies statistical theories and takes into account the internal energy population of the parent ion. However, the precision of AE values derived from this method has been limited by the relatively low TPE resolution. In
TPEPICO measurements, a particular difficulty is that the intensity for the cold parent ion is always finite at energies above the 0 K AE because of the hot-electron tail associated with the TPE transmission function. Since the actual shape of the TPE transmission function can also be complicated by near resonance autoionization features, the detailed simulation of breakdown curves can be difficult. As a result of these difficulties, uncertainties for 0 K AE values derived in previous TPEPICO studies are often comparable to those obtained in PIE measurements. Since the actual contributions of these various experimental difficulties to the error limits are hard to account for, experimental uncertainties for IE and AE values obtained in many previous PIE and TPEPICO measurements, especially those for polyatomic molecules, are often assigned improperly. Thus, it is not surprising to find that most IE and AE values thus obtained and reported in the literature do not agree after taking into account their assigned experimental uncertainties.

The development of laser based pulsed field ionization (PFI) techniques has made possible the measurement of PFI-photoelectron (PFI-PE) spectra for diatomic molecules and simple triatomic and polyatomic hydrides to the rotational resolved level. The proper analyses of rotationally resolved PFI-PE spectra have provided definitive IE values for these molecules with uncertainties limited only by energy calibrations. In the case of NH3, the rotationally resolved PFI-PE spectrum has been measured using the non-resonant two-photon (N2P) PFI-PE scheme. This measurement, together with the rotational-resolved infrared study of NH3+, provides an IE(NH3) value of 10.1864±0.0001 eV.

The recent successful implementation of synchrotron-based high-resolution PFI techniques using the monochromatized VUV facility at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) has greatly enhanced the potential of the PFI-PE method for routine, accurate IE measurements of gaseous molecules. Most recently, we have developed a synchrotron based PFI-PE-photoion coincidence (PFI-PEPICO) scheme achieving resolutions for ion internal energy selections similar to that made in PFI-PE measurements. Since the transmission function for PFI-PEs is free from the hot-electron tail problem, we have demonstrated previously that highly reliable 0 K AEs for CH3+ from CH4 and C2H+ from C2H2 can be determined unambiguously with unprecedented precision using this PFI-PEPICO scheme. Furthermore, step-like features in the PFI-PE spectrum for CH4 and C2H2 were observed, which confirm the AE values. In this report, we present the results of a similar PFI-PE and PFI-PEPICO study of the dissociative photoionization process.
\[ \text{NH}_3 + h\nu \rightarrow \text{NH}_2^+ + \text{H} + e^- \]  \hspace{1cm} (3)

On the basis of the AE(NH2\(^{+}\)) value determined in the present study, together with the known IE(NH\(_3\))\(^{9,10}\) we have obtained an accurate value for the D\(_0\)(H\(_2\)N\(^{+}\)-H). By using the known D\(_0\)(H\(_2\)N-H)\(^{17}\) and appropriate thermochemical cycle, we have derived values for the IE(NH\(_2\)), and the 0 K heat of formation of NH\(_2^+\) [\(\Delta H^0_{f0}(\text{NH}_2^+)\)].

We note that in early PIE measurements, Dibeler et al.\(^{18}\) and McCulloh\(^{19}\) reported AE(NH\(_2^+\)) values of 15.73±0.02 and 15.768±0.004 eV, respectively. However, in later TPEPICO studies, significantly lower AE(NH\(_2^+\)) values of 15.60±0.02 and 15.50 eV were obtained by Ruede et al.\(^{20}\) and Powis,\(^{21}\) respectively. The 0 K AE(NH\(_2^+\)) value of 15.768±0.004 eV, which was deduced by McCulloh based on a simulation of PIE curves for NH\(_2^+\) from NH\(_3\) recorded at 160 K and 298 K, was likely the most reliable among previous measurements. Similar to the conclusion of previous PFI-PEPICO studies,\(^{14-16}\) the 0 K AE(NH\(_2^+\)) value determined in the present PFI-PEPICO study is marked unambiguously by the disappearance energy\(^{14,15}\) of the parent NH\(_3^+\) ion and the step-like feature resolved in the PFI-PE spectrum of NH\(_3\) and is thus not dependent on any simulation. This, together with a higher energy resolution used, has resulted in a smaller error limit for the 0 K AE(NH\(_2^+\)) obtained in the present experiment.

II. Experiment

The PFI-PE and PFI-PEPICO experiments were conducted using the high-resolution VUV photoelectron-photoion facility of the Chemical Dynamics Beamline at the ALS, which was operated in the multibunch mode (period=656 ns, dark gap=112 ns).\(^{1,10,12,22-25}\) In the present experiment, Ar was used in the gas filter to suppress higher undulator harmonics with photon energies (hv) greater than 15.76 eV. A 2400 lines/mm grating (dispersion = 0.64 Å/mm) was used to disperse the first order harmonic of the undulator VUV beam with entrance/exit slits set in the range of 30-100 µm. The resulting monochromatic VUV beam was then focused into the photoionization/photoexcitation (PI/PEX) center of the photoelectron-photoion apparatus. The hv calibration was achieved using the Ne\(^{+}(^2P_{3/2})\), Ar\(^{+}(^2P_{3/2})\), and Xe\(^{+}(^2P_{3/2})\) PFI-PE bands. On the basis of previous experiments, the accuracy of the energy calibration is believed to be within ±0.5 meV.\(^{1,11,26}\)
The PFI-PE and PFI-PEPCO measurements were achieved by employing the TOF scheme.\textsuperscript{13,24} The PFI pulse (height =7.3 V/cm, width=180 ns) was applied ≈10 ns after the start of the dark gap. The PFI pulse also served to extract PFI-photoions toward the ion detector.\textsuperscript{13} The average accumulation time for a PFI-PEPICO TOF spectrum is ≈20 min. The PFI-PEPICO resolution achieved is ≈1.0 meV (FWHM).\textsuperscript{13-15}

The NH\textsubscript{3} sample (obtained from Aldrich, purity = 99.99\%) is introduced into the PI/PEX region as a skimmed neat NH\textsubscript{3} supersonic beam (stagnation pressure = 600 Torr and stagnation temperature = 298 K). We estimate that NH\textsubscript{3} at the PI/PEX region consists of ≈85\% cold beam sample and ≈15\% thermal background in the photoionization chamber.\textsuperscript{13-15}

III. Results and discussion
A. PFI-PEPICO TOF spectra for NH\textsubscript{2}\textsuperscript{+} and NH\textsubscript{3}\textsuperscript{+}

We have obtained PFI-PEPICO TOF spectra for NH\textsubscript{2}\textsuperscript{+} and NH\textsubscript{3}\textsuperscript{+} in the hv region of 15.65-15.85 eV, which is near the NH\textsubscript{3}\textsuperscript{+} dissociation threshold. Selected PFI-PEPICO TOF spectra measured at hv=15.7129, 15.7513, 15.7561, 15.7629, 15.7800 and 15.8279 eV are depicted in Fig. 1. These spectra have been background corrected using procedures as described in previous studies.\textsuperscript{13-15} At hv=15.7129 eV, which is below the AE(NH\textsubscript{2}\textsuperscript{+}), only the parent ion TOF peak at 20.34 µs was observed. As the hv is increased, the relative abundance for the daughter ion at 19.78 µs increases correspondingly. The spectra shown at hv=15.7800 and 15.8279 eV are dominated by the TOF peak for the daughter ion with only a small residual parent ion peak. As shown in the analysis below, the relative abundance for the parent NH\textsubscript{3}\textsuperscript{+} was found to remain essentially constant at 0.10 at hv values above the AE(NH\textsubscript{2}\textsuperscript{+}). The residual coincidence intensity for the parent NH\textsubscript{3}\textsuperscript{+} ion peak observed at hv=15.7800 and 15.8279 eV can be attributed to background coincidences associated with hot electrons dispersed into the dark gap and the dissociative photoionization of ammonia dimers and clusters formed in the supersonic expansion.

B. Simulation of breakdown curves for NH\textsubscript{2}\textsuperscript{+} and NH\textsubscript{3}\textsuperscript{+}

Similar to previous PFI-PEPICO studies,\textsuperscript{13-15} the TOF peak shapes for the parent NH\textsubscript{3}\textsuperscript{+} and daughter NH\textsubscript{2}\textsuperscript{+} ions are analyzed to consist of the contribution of a narrow component due to the cold NH\textsubscript{3} beam sample and a broad component arising from the thermal NH\textsubscript{3} background. As shown in Fig. 1, the daughter ion TOF peak is broad at hv=15.7513 eV, indicating that daughter ions are mostly formed at this
energy by photoionization of thermal (298 K) background NH₃. The daughter peak at \( hν = 15.7561 \text{ eV} \) clearly exhibits a narrow cold component and a broad thermal component. The broad shape of the TOF peak for NH₂⁺ observed at \( hν = 15.8279 \text{ eV} \) can be attributed to the finite kinetic energy release of process (3). We note that the NH₅⁺ PFI-PEPICO peaks at \( hν = 15.7561, 15.7513, \) and \( 15.7129 \text{ eV} \) appear to be asymmetric. This is likely caused by a finite misalignment of the molecular beam and the VUV beam, such that the average flight times for ions formed by photoionization of the thermal and cold samples are slightly different. The previous studies indicated that the TOF peak could be distorted due to the pulsed extraction scheme used in the PFI-PEPICO measurements.¹³

In order to construct the breakdown curves for the parent NH₃⁺ and daughter NH₂⁺ ions, we first obtained the relative intensities for NH₃⁺ and NH₂⁺ ions based on their respective TOF peak areas observed in the PFI-PEPICO TOF spectra. The fractional abundance for NH₃⁺ (NH₂⁺) at a given \( hν \) was obtained by dividing the NH₃⁺ (NH₂⁺) ion intensity by the sum of the NH₃⁺ and NH₂⁺ ion intensities. These breakdown curves for NH₃⁺ (open circles) and NH₂⁺ (open squares) representing the plots of the fractional abundances for NH₃⁺ and NH₂⁺ as a function of \( hν \) are shown in Fig. 2(a). These breakdown curves include both the cold and thermal ion signals for NH₂⁺ and NH₃⁺. In order to derive the relative abundances for NH₃⁺ and NH₂⁺ due to the cold beam NH₃ sample, we have simulated the NH₂⁺ and NH₃⁺ ion peaks resolved in PFI-PEPICO TOF spectra obtained in the \( hν \) range of \( 15.65-15.85 \text{ eV} \) using two Gaussian functions with widths of \( \approx 100 \text{ ns} \) and \( \approx 300 \text{ ns} \) for the cold and thermal components, respectively, as described in the previous PFI-PEPICO studies.¹⁴,¹⁵ Figure 2(b) depicts the breakdown curves for NH₃⁺ (solid circles) and NH₂⁺ (solid squares) taking into account only the cold NH₂⁺ and NH₃⁺ ion signals. As expected, due to the rotational cooling of NH₃ achieved by the supersonic expansion, the cold breakdown curves shown in Fig. 2(b) are sharper, showing that the dissociation of NH₃⁺ to NH₂⁺ + H is complete in an energy interval of \( \approx 15 \text{ meV} \).

We have simulated the breakdown diagrams of Figs. 2(a) and 2(b) using procedure described previously.²⁷ The simulation assumes that the ion energy resolution is infinitely narrow and that the broadening of the breakdown diagram is due solely to the thermal excitation of parent NH₃. The thermal energy distribution in NH₃ was determined by calculating the density of rovibrational states using the Beyer-Swinehart direct count algorithm²⁸ based on the known vibrational frequencies and rotational constants for NH₃. Due to the relatively high vibration frequencies for NH₃, the thermal energy for this
system is mainly contributed by rotational excitations. By assuming a temperature of 60 K for NH$_3$ in the molecular beam, we have obtained an excellent fit (solid lines) of the cold breakdown curves shown in Fig. 2(b), yielding a value of 15.765±0.001 eV for the 0 K AE(NH$_2^+$) from NH$_3$. The dashed lines in Fig. 2(a) are calculated breakdown curves assuming the NH$_3$ sample to consist of ≈10 % thermal background and ≈90 % cold (60 K) beam sample. The simulation of the breakdown curves also assumes a constant false coincidence background of 10% at hν values above the AE, resulting in the fractional abundances for parent NH$_3^+$ and daughter NH$_2^+$ to attain constant values of 0.1 and 0.90, respectively, at the hν ≥ AE.

There are two types of coincidence background associated with the present PFI-PEPICO experiment. One does not correlate with PFI-PEs formed at the dark gap. In this experiment, the ALS gap (112 ns) is narrower than that (144 ns) used in the PFI-PEPICO studies.$^{13-15}$ Thus, the contamination due to a finite dispersion of hot electrons into the dark gap in the present study is higher than that in the latter studies. The hot electrons occur at the dark gap are probably responsible for the majority of background coincidences, manifesting as stable, cold parent ions in the PFI-PEPICO TOF spectra detected at hν≥AE(NH$_2^+$), e.g., at hν = 15.7800 and 15.8279 eV (see Fig. 1).

The other type of coincidence background arises from PFI-PEs produced by the electric field pulses applied during the dark gaps. Under the conditions for supersonic expansion of NH$_3$ in the present experiment, we expect the formation of NH$_3$ dimers [(NH$_3$)$_2$] and clusters in the beam sample.$^{29}$ At photon energies well above the IE(NH$_3$), the dissociative photoionization of (NH$_3$)$_2$ according to reaction (4) is expected to be the dominant channel.

\[(\text{NH}_3)_2 + h\nu \rightarrow \text{NH}_3^+ + \text{NH}_3 + e^- \quad (4)\]

In this reaction, NH$_3^+$ is stabilized by the ejection of NH$_3$. We believe that this type of background is also responsible for the observation of a finite intensity for the NH$_3^+$ TOF peak at photon energies above the AE for reaction (3). Since these photon energies involved here are well above the dissociative photoionization threshold for (NH$_3$)$_2$, the cross section of reaction (4) should be essentially independent of energy in the narrow energy range of concern in the present study. Thus, the constant, finite fractional abundance for NH$_3^+$ beyond the AE(NH$_2^+$) from NH$_3$ as observed in Figs. 2(a) and 2(b) may also be partly attributed to dissociative photoionization processes such as reaction (4).
In the previous experiment on CH₄ (C₂H₂), the 0 K AE(CH₃⁺) [AE(C₂H⁺)] is found to be marked by the disappearance energy for the parent CH₄⁺ (C₂H₂⁺), i.e., the energy at which the fractional abundance for the parent CH₄⁺ (C₂H₂⁺) equal to zero.⁴⁻⁵ Although the fractional abundance for the parent NH₃⁺ ion does not go to zero at the AE in this case, the 0 K AE(NH₂⁺) value is distinctly identified by the sharp break [marked as 0 K AE in Figs. 2(a) and 2(b)] of the breakdown curves, at which the fractional abundance for the parent NH₃⁺ reaches its lowest value. The use of the sharp breaks of the breakdown curves observed both in Figs. 2(a) and 2(b) for the 0 K AE determination is supported by the simulation. Nevertheless, we emphasize that the 0 K AE(NH₂⁺) value determined here by the sharp break is distinct and does not depend on a detailed simulation of the breakdown curves.

To illustrate the high precision of the 0 K AE(NH₂⁺) value determined in this study, we have shown in Fig. 3 a magnified view of the breakdown data, together with their error bars, for parent NH₃⁺ in the hv range of 15.755-15.830 eV. Here, the breakdown data for NH₃⁺ obtained using the entire (thermal and cold) NH₃⁺ and NH₂⁺ ion signals are shown as open squares and those using only the cold NH₃⁺ and NH₂⁺ ion signals are given as solid circles. The dashed and solid curves are simulation curves for the open squares and solid circles data, respectively. As clearly shown in Fig. 3, both breakdown curves resolved a sharp break at 15.765±0.001 eV, which is taken here as the 0 K AE(NH₂⁺).

C. PFI-PE spectrum for NH₃

Figure 2(c) depicts the PFI-PE spectrum for NH₃ in the energy range of 15.68-15.84 eV. In addition to some sharp spectral features (notably at hv = 15.705, 15.757, and 15.768 eV; not discussed here) an obvious step is observed in the region of 15.755-15.765 eV. The top of this step at 15.7652 eV coincides with the 0 K AE(NH₂⁺) identified in the breakdown diagrams of Figs. 2(a) and 2(b). A detailed discussion concerning the conditions for the observation of a step at the 0 K ion dissociation threshold has been given previously.⁶ This step, which marks the 0 K AE in the PFI-PE spectrum, is attributed to the lifetime switching effect⁶ at the AE, where NH₃⁺ species with shorter lifetimes are converted into NH₂⁺ fragments with longer lifetimes. Here, NH₃⁺ and NH₂⁺ represent excited NH₃ and NH₂, respectively, in long-lived high-n (n≥100) Rydberg states. The longer lifetime for NH₂⁺ results from the fact that NH₂⁺ formed at the AE has an energy below the IE(CD₃) and thus cannot decay via autoionization. The observation of the sharp step in the PFI-PE spectrum indicates⁶ that the conversion from NH₃⁺ to NH₂⁺ at energy above the AE of reaction (3) is complete prior to PFI and that process (3) has a dissociation rate...
constant $\geq 10^7$ s$^{-1}$. This step resolved in the PFI-PE spectrum for NH$_3$ can be taken as a confirmation for the 0 K AE(NH$_3^+$) = 15.765$\pm$0.001 eV determined in the PFI-PEPICO study.

The dissociation leading to the production of NH$_2^*$ from NH$_3^*$ formed by VUV excitation of thermally excited NH$_3$ molecules occurs below the 0 K AE. Considering the fact that the lifetimes for NH$_2^*$ are longer than those for NH$_3^*$, we expect that the PFI-PE signal from NH$_2^*$ produced by thermally excited NH$_3$ molecules at photon energies below the 0 K AE is also magnified. As a result of this magnification effect of PFI events for NH$_2^*$, the nominal temperature of 60 K estimated in the simulation for the breakdown curves of NH$_2^+$ and NH$_3^+$ is likely higher than the actual temperature for the cold NH$_3$ sample achieved in the supersonic expansion.

**D. Thermochemistry of the NH$_2$/NH$_2^+$ and NH$_3$/NH$_3^+$ systems**

Table I compares the AE(NH$_2^+$) value obtained in the present experiment with literature values determined by photoionization$^{18,19,30-33}$ and TPEPEPCO$^{20,21}$ studies. Taking into account the experimental uncertainties, the value of 15.765$\pm$0.001 eV for the AE(NH$_2^+$) determined here is consistent with the PIE value (15.768$\pm$0.004 eV) of McCulloh.$^{19}$

We have included in Table I IE values for NH$_3$ measured in previous PIE,$^{18,30,32-36}$ TPEPICO,$^{20}$ and N2P-PFI-PE$^{9,10}$ studies. These IE values fall in the range of 10.07-10.186 eV. The latest NIST compilation$^{37}$ recommended an IE(NH$_3$) value of 10.070$\pm$0.020 eV. However, since the recent N2P-PFI-PE measurement$^{9}$ and infrared study$^{10}$ of NH$_3^+$ are rotationally resolved studies, the IE(NH$_3$) value of 10.186$\pm$0.0001 eV derived from these experiments should be the most reliable. This value, together with the AE(NH$_3^+$) = 15.765$\pm$0.001 eV determined here, gives the $D_0$(H-NH$_3^+$) = 5.579$\pm$0.001 eV.

The adiabatic IE(NH$_2$) has been measured to be 11.14$\pm$0.01 eV (see Table I) in a PIE study of NH$_2$ formed in the reaction of N$_2$H$_4$ + H.$^{38}$ In a recent photodissociation study using the high-resolution TOF technique involving the PFI detection of H atoms formed in high-n Rydberg states, Mordaunt $et$ $al.$ obtained a value of 4.6017$\pm$0.0025 eV for $D_0$(H-NH$_2$).$^{17}$ Combining this $D_0$(H-NH$_2$) value and the AE(NH$_2^+$) value of the present study, we obtain a value of 11.1633$\pm$0.0025 eV for IE(NH$_2$). The latter value is higher than the PIE value by $\approx 23$ meV. The ionization of NH$_2$ involves the transition from the bent NH$_2$ radical (103°) to the less bent NH$_2^+$ (140°-150°). The unfavorable Franck-Condon factors for photoionization transitions, together with finite internal excitations of NH$_2$ acquired in the reaction, results in a very gradual PIE onset for NH$_2^+$. Although a substantial effort was made, calculating P, Q
and R branches, to fit the rotational tailing near the onset, the IE(NH$_2$) value thus determined is subject to a certain uncertainty of such a fitting scheme. Gibson et al.\textsuperscript{38} assigned the IE(NH$_2$) to be 1113±1 Å (11.14±0.01 eV). Referring to Fig. 5 of Ref. 38, the IE(NH$_2$) assignment may also be influenced by an autoionization feature at 1110 Å. Hence, a more conservative estimate for the IE(NH$_2$) would be 1112±2 Å = 11.15±0.02 eV.\textsuperscript{39} Taking into account the experimental error limits, the latter value would have agreed with the IE(NH$_2$) of 11.163±0.0025 eV derived using the AE(NH$_2^+$) value obtained here and the D$_0$(H-NH$_2$) value of Ref. 17. To confirm the consistency of these AE(NH$_2^+$) and D$_0$(H-NH$_2$) values, it is necessary to re-examine the IE(NH$_2$) value at a higher resolution using a cold NH$_2$ sample. We note that an IE(NH$_2$)=11.46±0.01 eV has also been reported by Dunlavey et al. in a photoelectron study.\textsuperscript{40}

The ∆H$_{f0}$(NH$_3$) value is well known. A 1977 JANAF revision\textsuperscript{41} recommends -9.30±0.1 kcal/mol, which is in excellent accord with the -9.31±0.08 kcal/mol\textsuperscript{42} given by the compilation of Glushko \textit{et al.} Using the latter value, IE(NH$_3$)=234.9034±0.0023 kcal/mol (10.1864±0.0001 eV), ∆H$_{f0}$(H)=51.643±0.001 kcal/mol, D$_0$(H-NH$_2$) = 106.118±0.046 kcal/mol (4.6017±0.0025 eV), and AE(NH$_2^+$) = 363.549±0.023 kcal/mol (15.765±0.001 eV), we have calculated the ∆H$_{f0}$(NH$_3^+$) = 225.59±0.08 kcal/mol, ∆H$_{f0}$(NH$_2$)= 45.17±0.09 kcal/mol, and ∆H$_{f0}$(NH$_2^+$)= 302.60±0.08 kcal/mol. The values in bold fonts given in Table I represent the most precise energetic data for the NH$_2$/NH$_2^+$ and NH$_3$/NH$_3^+$ systems. It is interesting to note that the error limits of the best ∆H$_{f0}$(NH$_2$) and ∆H$_{f0}$(NH$_2^+$) values are now predominantly limited by the uncertainty of ∆H$_{f0}$(NH$_3$).\textsuperscript{41,42}

These highly precise energetic data (values in bold fonts in Table I) would provide a challenge for state-of-the-art \textit{ab initio} computational quantum theories. Currently, the Gaussian-2/Gaussian-3 (G2/G3) procedures are among the most popular quantum chemical computation schemes.\textsuperscript{43,44} The G2/G3 theories are “slightly” semi-empirical in nature because they contain a high level correction (HLC) obtained empirically from a fit to a set of experimental energetic data, such as IEs, electron affinities, and heats of formation, by minimizing the deviations between corresponding experimental results and calculated values for atomic and molecular energies. The G2 theory has a more primitive HLC fitting scheme, which only involves a test set of 55 molecules,\textsuperscript{43} whereas that for the G3 theory\textsuperscript{44} is obtained by fitting a test set of 299 molecules. The reliability of such a fitting scheme demands a precise set of experimental energetic data. As shown Table I, even for a small molecule such as NH$_3$, the literature IE and AE values have maximum discrepancies of ≈0.17 and ≈0.27 eV, respectively. We note that the error limits assigned
for many of these previous experiments do not correspond, indicating that the error assignments for many
previous experiments are ill founded. This situation is general for most molecules listed in the NIST\textsuperscript{17}
and other\textsuperscript{2,3} compilations.

We have compiled the AE(NH\textsubscript{2}\textsuperscript{+}), IE(NH\textsubscript{3}), IE(NH\textsubscript{2}), and \(\Delta H^\circ_{\text{f0}}/\Delta H^\circ_{\text{f298}}\) values for NH\textsubscript{2}, NH\textsubscript{2}\textsuperscript{+},
NH\textsubscript{3}, and NH\textsubscript{3}\textsuperscript{+} at the G2/G3 levels of theory for comparison with experimental values in Table I.\textsuperscript{42,43} The
theoretical G2 and G3 values for D\textsubscript{0}(H-NH\textsubscript{2}) [D\textsubscript{0}(H-NH\textsubscript{2}\textsuperscript{+})] are 4.62 eV [5.60 eV] and 4.57 eV [5.54 eV],
respectively. These latter values are found to deviate by \(\approx\)0.02-0.03 eV from the best experimental D\textsubscript{0}(H-
NH\textsubscript{2}) [D\textsubscript{0}(H-NH\textsubscript{2}\textsuperscript{+})] value of 4.6017\pm0.0025 eV (5.5786 \pm0.0010 eV). It is interesting to note that the
comparisons show that the G2 predictions are in better agreement with the most precise experimental
results. The G3 IE(NH\textsubscript{3}) and G3 IE(NH\textsubscript{2}) are \(\approx\)40 meV lower than the corresponding best experimental
values. While the G3 \(\Delta H^\circ_{\text{f0}}(\text{NH}_2)\) is in excellent agreement with the most precise experimental value, the
G3 \(\Delta H^\circ_{\text{f0}}(\text{NH}_3)\) is higher than the most precise experimental value by 0.8 kcal/mol. This observation
indicates that the excellent agreement found between the most precise experimental \(\Delta H^\circ_{\text{f0}}(\text{NH}_3^+)\) and G3
value for \(\Delta H^\circ_{\text{f0}}(\text{NH}_3^+)\) [obtained by summing up G3 IE(NH\textsubscript{3}) and G3 \(\Delta H^\circ_{\text{f0}}(\text{NH}_3^+)\) values] is fortuitous
and is due mostly to the cancellation of errors. The maximum deviation of \(\approx\)0.09 eV (2 kcal/mol) is
observed between the best experimental value and G3 prediction for AE(NH\textsubscript{2}\textsuperscript{+}). The range of errors (\(\leq\)2
kcal/mol) observed here between the best experimental results and G2/G3 predictions is consistent with
the error limits targeted in the formulation of G2/G3 procedures.

The better theoretical predictions of G2 over G3 in comparison with the best experimental values
of Table I indicates that the HLC fitting scheme in G3 is not better than that in G2 for the NH\textsubscript{2}/NH\textsubscript{2}\textsuperscript{+}
and NH\textsubscript{3}/NH\textsubscript{3}\textsuperscript{+} systems. This is expected because the error limits for experimental data set used in the HLC
fitting for G3 theory is not improved compared to those for G2 theory. In order to yield more accurate
theoretical predictions, the HLC fitting for Gaussian type theories would require a better set of
experimental energetic data with smaller error limits. Without doubt, accurate AE, IE, and \(\Delta H^\circ_{\text{f0}}\) values,
such as those presented here with well-founded error limits in the meV range, would serve as an impetus
for the development of the next generation of \textit{ab initio} quantum computational procedures.\textsuperscript{43,44}

Highly precise energetic data obtained in the present and previous\textsuperscript{9,17} PFI-PE studies have
stimulated a state-of-the-art \textit{ab initio} quantum chemical calculation by Dixon \textit{et al.},\textsuperscript{45} that is published as
an accompanying theoretical article in this journal issue. The computational scheme used is purely \textit{ab
initio except for the use of experimental $\Delta H^\circ_{f0}$'s for the atoms and available experimental vibrational frequencies for the molecular species. The ab initio predictions of Dixon et al. are listed in the last row of Table I. The $\text{IE}(\text{NH}_3) = 10.171 \text{ eV}$ and $\text{IE}(\text{NH}_2) = 11.176 \text{ eV}$ predictions obtained in this calculation are in better agreement with the best experimental values than are the G2/G3 results. The comparison between theoretical results and the best experimental energetic data listed in Table I for the NH$_2$/NH$_2^+$ and NH$_3$/NH$_3^+$ systems shows that the accuracy of the ab initio theory of Dixon et al is $\leq 0.4 \text{ kcal/mol}$.

III. Conclusions

We have examined the unimolecular dissociation of energy-selected NH$_3^+$ near its threshold for the formation of NH$_2^+$ + H using a high-resolution PFI-PEPICO technique. The 0 K $\text{AE}(\text{NH}_2^+)$ thus measured has made possible the determination of highly accurate values for $D_0(\text{H-NH}_2^+)$, $\text{IE}(\text{NH}_2)$, and $\Delta H^\circ_{f0}(\text{NH}_2^+)$ through appropriate thermochemical cycles. Similar to previous studies, a sharp step-like feature is observed in the PFI-PE spectrum of NH$_3$. The position of this step is in excellent agreement with the 0 K $\text{AE}(\text{NH}_2^+)$ determined based on the PFI-PEPICO data. Thus, the observation can be taken as a confirmation for the 0 K $\text{AE}(\text{NH}_2^+)$ determined in the PFI-PEPICO measurement. Furthermore, the observation of the step, together with the breakdown curves for NH$_3^+$ and NH$_2^+$, shows that the production of NH$_2^*$ + H (NH$_2^+$ + H) from excited NH$_3^*$ (NH$_3^*$+) at the dissociation threshold is prompt, occurring in a time scale $\leq 10^{-7} \text{ s}$. We believe that accurate thermochemical data with well-founded error limits obtained in the present and similar experiments using the PFI-PFIPECO technique would play an essential role for development of the next generation of ab initio quantum chemical calculation schemes.

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under Contract No. W-7405-Eng-82 for the Ames Laboratory and Contract No. DE-AC03-76SF00098 for the Lawrence Berkeley National Laboratory. Y.S. is the recipient of the 2000 Henry Gilman Fellowship at Iowa State University. C.Y.N. is grateful for discussions with Prof. T. Baer, Dr. J. Berkowitz, Dr. D. A. Dixon, and Prof. K. M. Ervin.
References


<table>
<thead>
<tr>
<th>AE(NH$_2^+$) (eV)</th>
<th>Ie (eV)</th>
<th>ΔH° (kcal/mol)</th>
<th>NH$_3$</th>
<th>NH$_2$</th>
<th>NH$_3$</th>
<th>NH$_2^+$</th>
<th>NH$_3$</th>
<th>NH$_2$</th>
<th>NH$_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.765±0.001</td>
<td>10.186±0.0001</td>
<td>11.163±0.0025</td>
<td>-9.31±0.08</td>
<td>225.59±0.08</td>
<td>45.17±0.09</td>
<td>302.60±0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.768±0.004</td>
<td>10.069±0.02</td>
<td>11.14±0.01</td>
<td>-9.30±0.10</td>
<td>222.9±0.09</td>
<td>45.8±0.2</td>
<td>302.7±0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.60±0.02</td>
<td>10.07±0.01</td>
<td>11.46±0.01</td>
<td>222.9±0.09</td>
<td>45.8±0.2</td>
<td>302.7±0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.76±0.05</td>
<td>10.17</td>
<td></td>
<td>222.9±0.09</td>
<td>45.8±0.2</td>
<td>302.7±0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.50</td>
<td>10.160±0.008</td>
<td></td>
<td>222.9±0.09</td>
<td>45.8±0.2</td>
<td>302.7±0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.75</td>
<td>10.154±0.010</td>
<td></td>
<td>222.9±0.09</td>
<td>45.8±0.2</td>
<td>302.7±0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.73±0.02</td>
<td>10.02±0.02</td>
<td></td>
<td>222.9±0.09</td>
<td>45.8±0.2</td>
<td>302.7±0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Semi-empirical G3/G2 values

| 15.68/15.79 | 10.14/10.19 | 11.12/11.18 | -8.5/-9.1 | 225.4/225.9 | 45.2/45.7 | 301.6/303.4 |

Ab initio predictions

| 15.77 | 10.171 | 11.176 | -9.1 | 225.4 | 45.3 | 303.0 |

\(^a\) Values from NH$_3$.
a. The values in bold are recommended values. The values in parentheses are \( \Delta H^\circ_{298} \) values. The thermal corrections from \( \Delta H^\circ \)'s to \( \Delta H^\circ_{298} \)'s are computed at the MP2 level of theory.
b. This work.
d. Reference 42.
e. References 9 and 42.
f. References 17 and 42.
g. Reference 19.
h. Reference 32.
i. Reference 41.
j. Calculated using \( \text{IE}(\text{NH}_3)=10.07\pm0.02 \text{ eV as recommended by Ref. 37 and } \Delta H^\circ_{\text{f0}}(\text{NH}_3) = -9.31\pm0.08 \text{ kcal/mol of Ref. 42.} 
$k. References 19 and 38.
$l. Reference 20.
m. Reference 33.
n. Reference 40.
o. Reference 31.
p. Reference 35.
$q. Reference 21.
r. Reference 18.
s. References 30 and 32.
t. Reference 36.
u. Reference 30.
v. References 43 and 44.
w. Reference 45.
Figure Captions

Figure 1  Selected PFI-PEPICO TOF spectra for NH$_2^+$ and NH$_3^+$ at photon energies $h\nu=15.7129$, 15.7513, 15.7561, 15.7629, 15.7800, and 15.8279 eV. The TOF peaks centered at 19.78 and 20.34 $\mu$s are due to NH$_2^+$ and NH$_3^+$, respectively.

Figure 2  (a) Breakdown curves for NH$_3^+$ (○) and NH$_2^+$ (□) in the $h\nu$ range of 15.69-15.83 eV obtained using the entire (thermal and cold) NH$_3^+$ and NH$_2^+$ ion signals. The dashed (−−) curves are simulation calculated assuming 10% thermal (298 K) and 90% cold (60 K) NH$_3$ sample. (b) Breakdown curves for NH$_3^+$ (●) and NH$_2^+$ (■) in the $h\nu$ range of 15.69-15.83 eV obtained using only the cold NH$_2^+$ and NH$_3^+$ ion signals. The solid lines (−−) are simulated curves obtained assuming a cold NH$_3$ sample at 60 K. See the text. (c) The PFI-PE spectrum of NH$_3$ in the $h\nu$ range of 15.69-15.83 eV.

Figure 3  A magnified view of the breakdown curves for NH$_3^+$ in the $h\nu$ range of 15.755-15.830 eV. The breakdown data for NH$_3^+$ obtained using the entire NH$_3^+$ and NH$_2^+$ ion signals are shown as open squares (□) and those obtained using only the cold ion signals are shown as solid circles (●). The dashed (−−) and solid (−−) curves are simulated curves for the open squares and solid circles breakdown data, respectively.
Fig. 1
Figs. 2(a), 2(b), and 2(c)
Fig. 3