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High-Resolution Energy-Selected Study of the Reaction $NH_3^+ \rightarrow NH_2^+ + H$: Accurate Thermochemistry for the NH_2/NH_2^+ and NH_3/NH_3^+ Systems

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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 ($D_0=4.6017\pm0.0025$ eV) for NH_3, allows the determination of the $D_0(NH_2^+\text{-}H)$ 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 (ΔH°_{f0}) for NH_3 and H and the $AE(NH_2^+)$, we obtain the $\Delta H^\circ_{f0}(NH_2^+) = 302.60\pm0.08$ 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 $\leq10^{-7}$ 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_2/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).[1]

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

$$D_0(NH_2\text{-H}) = AE(NH_2^+) - IE(NH_2) \qquad\qquad (2)$$

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.[2,3] 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,[2] 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,[4,5] 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.[4,5] 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.[5] 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.[2,3] 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.[6-8] 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 NH_3, the rotationally resolved PFI-PE spectrum has been measured using the non-resonant two-photon (N2P) PFI-PE scheme.[9] This measurement, together with the rotational-resolved infrared study of NH_3^+,[10] provides an IE(NH_3) value of 10.1864±0.0001 eV.[9]

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.[1,11,12] 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.[13] 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 CH_3^+ from CH_4 and C_2H^+ from C_2H_2 can be determined unambiguously with unprecedented precision using this PFI-PEPICO scheme.[14,15] Furthermore, step-like features in the PFI-PE spectrum for CH_4 and C_2H_2 were observed,[16] 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 (3).

$$NH_3 + h\nu \rightarrow NH_2^+ + H + e^- \tag{3}$$

On the basis of the AE(NH$_2^+$) 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$_2^+$ [ΔH_{f0}^0(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 (hν) 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 hν calibration was achieved using the Ne$^+$(^{2}P$_{3/2}$), Ar$^+$(^{2}P$_{3/2}$), and Xe$^+$(^{2}P$_{3/2}$) 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.[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.[13] The average accumulation time for a PFI-PEPICO TOF spectrum is ≈20 min. The PFI-PEPICO resolution achieved is ≈1.0 meV (FWHM).[13-15]

The NH_3 sample (obtained from Aldrich, purity = 99.99%) is introduced into the PI/PEX region as a skimmed neat NH_3 supersonic beam (stagnation pressure = 600 Torr and stagnation temperature = 298 K). We estimate that NH_3 at the PI/PEX region consists of ≈85% cold beam sample and ≈15% thermal background in the photoionization chamber.[13-15]

III.   Results and discussion

A.   PFI-PEPICO TOF spectra for NH_2^+ and NH_3^+

We have obtained PFI-PEPICO TOF spectra for NH_2^+ and NH_3^+ in the hν region of 15.65-15.85 eV, which is near the NH_3^+ dissociation threshold. Selected PFI-PEPICO TOF spectra measured at hν=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.[13-15] At hν=15.7129 eV, which is below the AE(NH_2^+), only the parent ion TOF peak at 20.34 μs was observed. As the hν is increased, the relative abundance for the daughter ion at 19.78 μs increases correspondingly. The spectra shown at hν=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_3^+ was found to remain essentially constant at 0.10 at hν values above the AE(NH_2^+). The residual coincidence intensity for the parent NH_3^+ ion peak observed at hν=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_2^+ and NH_3^+

Similar to previous PFI-PEPICO studies,[13-15] the TOF peak shapes for the parent NH_3^+ and daughter NH_2^+ ions are analyzed to consist of the contribution of a narrow component due to the cold NH_3 beam sample and a broad component arising from the thermal NH_3 background. As shown in Fig. 1, the daughter ion TOF peak is broad at hν=15.7513 eV, indicating that daughter ions are mostly formed at this

energy by photoionization of thermal (298 K) background NH_3. The daughter peak at $h\nu$=15.7561 eV clearly exhibits a narrow cold component and a broad thermal component. The broad shape of the TOF peak for NH_2^+ observed at $h\nu$=15.8279 eV can be attributed to the finite kinetic energy release of process (3). We note that the NH_3^+ PFI-PEPICO peaks at $h\nu$=15.7561, 15.7513, and 15.7129 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 NH_3^+ and daughter NH_2^+ ions, we first obtained the relative intensities for NH_3^+ and NH_2^+ ions based on their respective TOF peak areas observed in the PFI-PEPICO TOF spectra. The fractional abundance for NH_3^+ (NH_2^+) at a given $h\nu$ was obtained by dividing the NH_3^+ (NH_2^+) ion intensity by the sum of the NH_3^+ and NH_2^+ ion intensities. These breakdown curves for NH_3^+ (open circles) and NH_2^+ (open squares) representing the plots of the fractional abundances for NH_3^+ and NH_2^+ as a function of $h\nu$ are shown in Fig. 2(a). These breakdown curves include both the cold and thermal ion signals for NH_2^+ and NH_3^+. In order to derive the relative abundances for NH_3^+ and NH_2^+ due to the cold beam NH_3 sample, we have simulated the NH_2^+ and NH_3^+ ion peaks resolved in PFI-PEPICO TOF spectra obtained in the $h\nu$ range of $h\nu$=15.65-15.85 eV using two Gaussian functions with widths of $\approx$100 ns and $\approx$300 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 NH_3^+ (solid circles) and NH_2^+ (solid squares) taking into account only the cold NH_2^+ and NH_3^+ ion signals. As expected, due to the rotational cooling of NH_3 achieved by the supersonic expansion, the cold breakdown curves shown in Fig. 2(b) are sharper, showing that the dissociation of NH_3^+ to NH_2^+ + H is complete in an energy interval of $\approx$15 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 NH_3. The thermal energy distribution in NH_3 was determined by calculating the density of rovibrational states using the Beyer-Swinehart direct count algorithm[28] based on the known vibrational frequencies and rotational constants for NH_3. Due to the relatively high vibration frequencies for NH_3, 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.

$$(NH_3)_2 + h\nu \rightarrow NH_3^+ + NH_3 + e^- \tag{4}$$

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 CH_4 (C_2H_2), the 0 K AE(CH_3^+) [AE(C_2H^+)] is found to be marked by the disappearance energy for the parent CH_4^+ ($C_2H_2^+$), i.e., the energy at which the fractional abundance for the parent CH_4^+ ($C_2H_2^+$) equal to *zero*.[14,15] Although the fractional abundance for the parent NH_3^+ ion does not go to zero at the AE in this case, the 0 K AE(NH_2^+) 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 NH_3^+ 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(NH_2^+) 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(NH_2^+) 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 NH_3^+ in the hν range of 15.755-15.830 eV. Here, the breakdown data for NH_3^+ obtained using the entire (thermal and cold) NH_3^+ and NH_2^+ ion signals are shown as open squares and those using only the cold NH_3^+ and NH_2^+ 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(NH_2^+).

C.   PFI-PE spectrum for NH_3

Figure 2(c) depicts the PFI-PE spectrum for NH_3 in the energy range of 15.68-15.84 eV. In addition to some sharp spectral features (notably at hν = 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(NH_2^+) 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.[16] This step, which marks the 0 K AE in the PFI-PE spectrum, is attributed to the lifetime switching effect[16] at the AE, where NH_3^* species with shorter lifetimes are converted into NH_2^* fragments with longer lifetimes. Here, NH_3^* and NH_2^* represent excited NH_3 and NH_2, respectively, in long-lived high-n (n≥100) Rydberg states. The longer lifetime for NH_2^* results from the fact that NH_2^* formed at the AE has an energy below the IE(CD_3) and thus cannot decay via autoionization. The observation of the sharp step in the PFI-PE spectrum indicates[16] that the conversion from NH_3^* to NH_2^* 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±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±0.001 eV for the AE(NH_2^+) determined here is consistent with the PIE value (15.768±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±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 10.1864±0.0001 eV derived from these experiments should be the most reliable. This value, together with the AE(NH_2^+) = 15.765±0.001 eV determined here, gives the D_0(H-NH_2^+) = 5.579±0.001 eV.

The adiabatic IE(NH_2) has been measured to be 11.14±0.01 eV (see Table I) in a PIE study of NH_2 formed in the reaction of N_2H_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±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±0.0025 eV for IE(NH_2). The latter value is higher than the PIE value by ≈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.[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.[39] Taking into account the experimental error limits, the latter value would have agreed with the IE(NH_2) of 11.1633±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.[40]

The ΔH°_{f0}(NH_3) value is well known. A 1977 *JANAF* revision[41] recommends -9.30±0.1 kcal/mol, which is in excellent accord with the -9.31±0.08 kcal/mol[42] given by the compilation of Glushko *et al*. Using the latter value, IE(NH_3)=234.9034±0.0023 kcal/mol (10.1864±0.0001 eV), ΔH°_{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 ΔH°_{f0}(NH_3^+) = 225.59±0.08 kcal/mol, ΔH°_{f0}(NH_2)= 45.17±0.09 kcal/mol, and ΔH°_{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 ΔH°_{f0}(NH_2) and ΔH°_{f0}(NH_2^+) values are now predominantly limited by the uncertainty of ΔH°_{f0}(NH_3).[41,42]

These highly precise energetic data (values in bold fonts in Table I) would provide a challenge for state-of-the-art *ab initio* computational quantum theories. Currently, the Gaussian-2/Gaussian-3 (G2/G3) procedures are among the most popular quantum chemical computation schemes.[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,[43] whereas that for the G3 theory[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[37] and other[2,3] compilations.

We have compiled the AE(NH_2^+), IE(NH_3), IE(NH_2), and $\Delta H°_{f0}/\Delta H°_{f298}$ values for NH_2, NH_2^+, NH_3, and NH_3^+ at the G2/G3 levels of theory for comparison with experimental values in Table I.[42,43] The theoretical G2 and G3 values for $D_0(H-NH_2)$ [$D_0(H-NH_2^+)$] are 4.62 eV [5.60 eV] and 4.57 eV [5.54 eV], respectively. These latter values are found to deviate by ≈0.02-0.03 eV from the best experimental $D_0(H-NH_2)$ [$D_0(H-NH_2^+)$] value of 4.6017±0.0025 eV (5.5786 ±0.0010 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_3) and G3 IE(NH_2) are ≈40 meV lower than the corresponding best experimental values. While the G3 $\Delta H°_{f0}(NH_2)$ is in excellent agreement with the most precise experimental value, the G3 $\Delta H°_{f0}(NH_3)$ 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 $\Delta H°_{f0}(NH_3^+)$ and G3 value for $\Delta H°_{f0}(NH_3^+)$ [obtained by summing up G3 IE(NH_3) and G3 $\Delta H°_{f0}(NH_3^+)$ values] is fortuitous and is due mostly to the cancellation of errors. The maximum deviation of ≈0.09 eV (2 kcal/mol) is observed between the best experimental value and G3 prediction for AE(NH_2^+). The range of errors (≤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_2/NH_2^+ and NH_3/NH_3^+ 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 Gaussion type theories would require a better set of experimental energetic data with smaller error limits. Without doubt, accurate AE, IE, and $\Delta H°_{f0}$ 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 *ab initio* quantum computational procedures.[43,44]

Highly precise energetic data obtained in the present and previous[9,17] PFI-PE studies have stimulated a state-of-the-art *ab initio* quantum chemical calculation by Dixon *et al.*,[45] that is published as an accompanying theoretical article in this journal issue.   The computational scheme used is purely *ab*

initio except for the use of experimental $\Delta H°_{f0}$'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 $IE(NH_3) = 10.171$ eV and $IE(NH_2) = 11.176$ 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 ≤ 0.4 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 $AE(NH_2^+)$ thus measured has made possible the determination of highly accurate values for $D_0(H-NH_2^+)$, $IE(NH_2)$, and $\Delta H°_{f0}(NH_2^+)$ 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 $AE(NH_2^+)$ determined based on the PFI-PEPICO data. Thus, the observation can be taken as a confirmation for the 0 K $AE(NH_2^+)$ 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 $\leq 10^{-7}$ s. We believe that accurate thermochemical data with well-founded error limits obtained in the present and similar experiments[13-15] using the PFI-PFIPECO technique would play an essential role for development of the next generation of *ab initio* quantum chemical calculation schemes.

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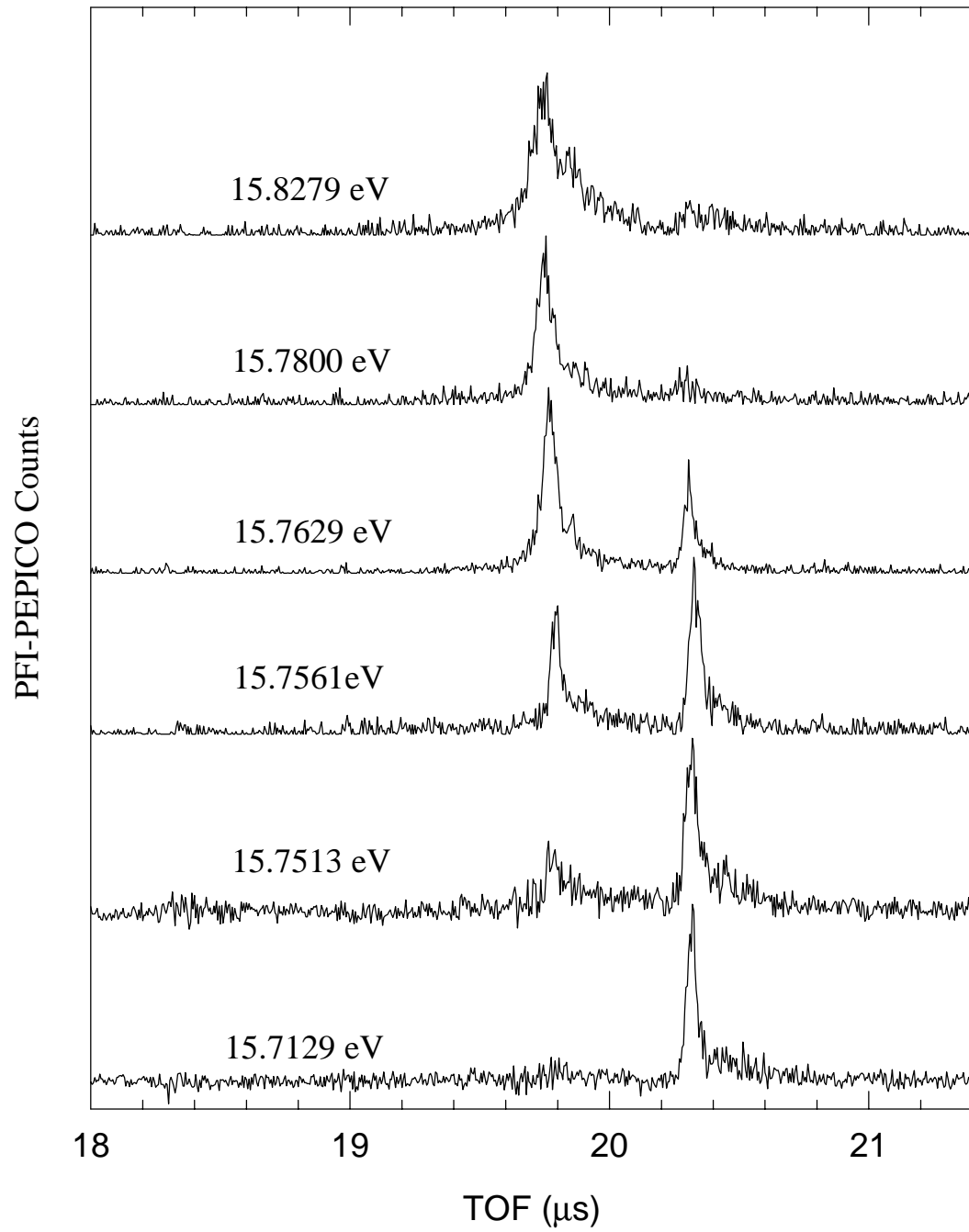
Table I. Comparison of values for 0 K heats of formation ($\Delta H°_{f0}$) for NH_2, NH_2^+, NH_3, and NH_3^+ and 0 K AE for NH_2^+ [$AE(NH_2^+)$] from NH_3.[a]

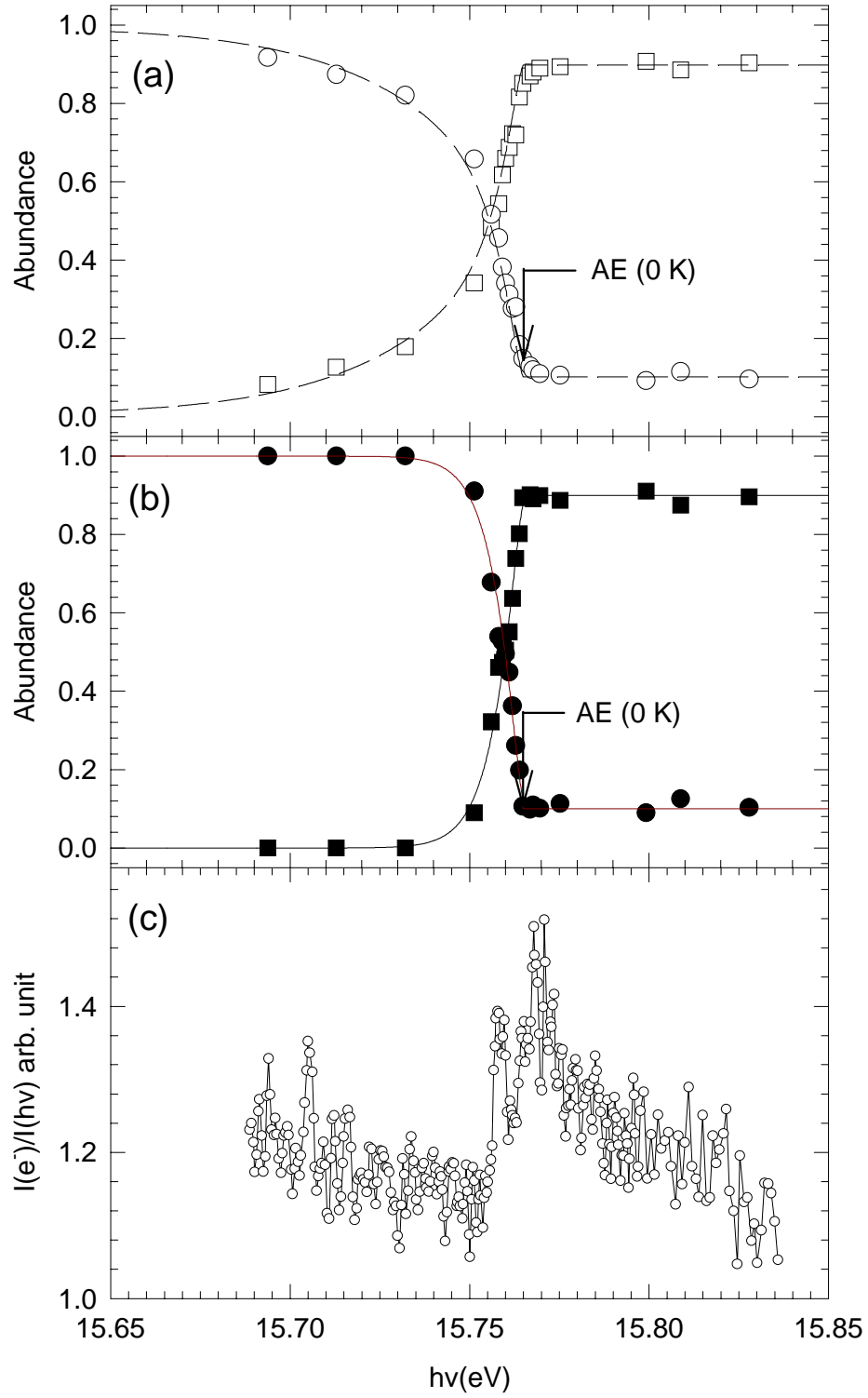| AE(NH$_2^+$) (eV)	IE (eV)		ΔH°$_{f0}$ (kcal/mol)			
	NH$_3$	NH$_2$	NH$_3$	NH$_3^+$	NH$_2$	NH$_2^+$
15.765±0.001[b]	**10.1864±0.0001[c]**	**11.1633±0.0025[b]**	**-9.31±0.08[d]** **(-10.98±0.08)**	**225.59±0.08[e]** **(223.92±0.08)**	**45.17±0.09[f]** **(44.50±0.09)**	**302.60±0.08[b]** **(301.93±0.08)**
15.768±0.004[g]	10.069±0.02[h]	11.14±0.01[g]	-9.30±0.10[i]	222.9±0.09[j]	45.8±0.2[k]	302.7±0.3[k]
15.60±0.02[l]	10.07±0.01[l,m]	11.46±0.01[n]				
15.76±0.05[o]	10.17[p]					
15.50[q]	10.160 ±0.008[r]					
15.75[s]	10.154 ±0.010[t]					
15.73±0.02[r]	10.02 ±0.02[u]					
Semi-empirical G3/G2 values[v]						
15.68/15.79	10.14/10.19	11.12/11.18	-8.5/-9.1 (-10.2/-10.8)	225.4/225.9 (223.6/224.3)	45.2/45.7 (44.5/45.0)	301.6/303.4 (300.9/302.8)
Ab initio predictions[w]						
15.77	10.171	11.176	-9.1 (-10.8)	225.4 (223.7)	45.3 (44.6)	303.0 (302.3)

a. The values in bold are recommended values. The values in parentheses are ΔH°_{f298} values. The thermal corrections from ΔH°_{f0}'s to ΔH°_{f298}'s are computed at the MP2 level of theory.
b. This work.
c. Reference 9.
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 IE(NH$_3$)=10.07±0.02 eV as recommended by Ref. 37 and ΔH°_{f0}(NH$_3$) = -9.31±0.08 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 hν=15.7129, 15.7513, 15.7561, 15,7629, 15.7800, and 15.8279 eV. The TOF peaks centered at 19.78 and 20.34 μs are due to NH_2^+ and NH_3^+, respectively.

Figure 2   (a) Breakdown curves for NH_3^+ (O) and NH_2^+ (□) in the hν 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 hν 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 hν range of 15.69-15.83 eV.

Figure 3   A magnified view of the breakdown curves for NH_3^+ in the hν 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
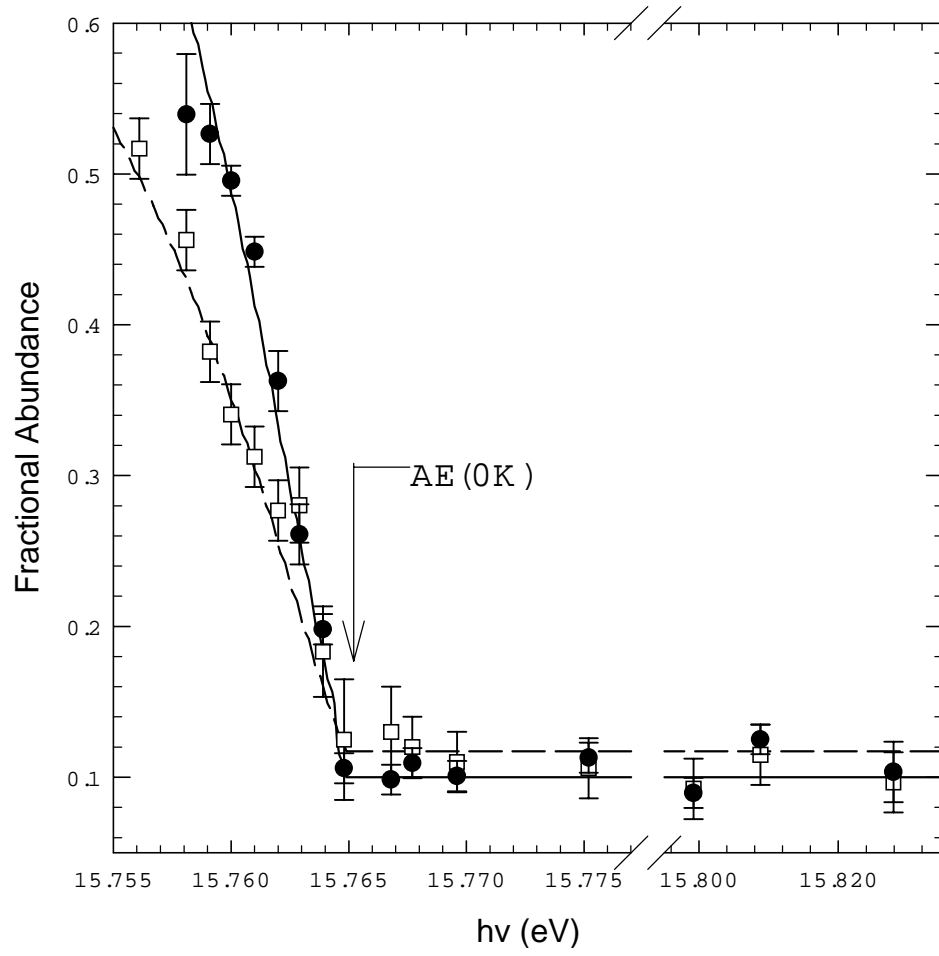
Figs. 2(a), 2(b), and 2(c)

Fig. 3