Ion Dissociation of Hydrazoic Acid Investigated by Synchrotron-Radiation-Based Photoionization Mass Spectrometry[†]

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Received: October 29, 2008; Revised Manuscript Received: February 18, 2009

We report mass resolved photoionization yield spectra of a molecular-beam cooled sample of HN_3 using photoionization mass spectrometry based on high-resolution monochromatized synchrotron radiation. Spectra are reported at mass-to-charge ratios of 14(N^+), 15(NH^+), 29(N_2H^+), 42(N_3^+), and 43(HN_3^+) in the region of each ionization threshold. The thresholds observed here are all lower than the previously reported ones obtained with electron impact ionization, which were the only ones available in the literature prior to this work. The appearance energies can be used to evaluate four key thermochemical quantities of relevance to HN_3: $D_0(H-N_3)$, $D_0(N-N_2)$, $D_0(N-H)$, and IE(NH). We observe the appearance energy of the parent ion (HN_3^+) to be 10.56 ± 0.02 eV, somewhat below the reported ionization energies derived from photoelectron spectroscopy. Great care was taken to evaluate the importance of vibrational hot bands to the photoionization yield spectra. This experiment also provides a *lower* limit to the proton affinity of N_2 allowing us to bracket this quantity with improved certainty: $119.3\ \text{kcal/mol} \le PA(N_2) \le 121.4\ \text{kcal/mol}$. We also derive an upper limit to the ionization energy of N_2H ($IE(N_2H) \le 7.92$ eV), a molecule that has yet to be observed. We hope that knowledge of this ionization energy might help in future attempts to detect this interesting radical. We also take this opportunity to review the status of the thermodynamics of many molecules and ions containing N and H within the context of these new results and make new recommendations. In particular, we recommend a new value for $\Delta_f H^\circ_0(HN_3)$, nearly 5 kcal/mol larger than prior evaluations.

Introduction

Despite its simplicity and fundamental character, remarkably few photoionization studies have been performed on hydrazoic acid. Several studies of the photoelectron spectroscopy (PES) of HN_3 with fixed-frequency VUV sources have been applied to obtain information on the energetics of process 1[1−4]

$$HN_3 + h\nu \rightarrow HN_3^+ + e^- \qquad (1)$$

however, only a single 1957 study[5] using Electron Impact (EI) is presently available to characterize the energetics of reactions 2−5.

$$HN_3 \rightarrow HN_2^+ + N + e^- \qquad (2)$$

$$HN_3 \rightarrow HN^+ + N_2 + e^- \qquad (3)$$

$$HN_3 \rightarrow N_3^+ + H + e^- \qquad (4)$$

$$HN_3 \rightarrow N^+ + N_2 + H + e^- \qquad (5)$$

Although knowledge of ionization thresholds derived by EI methods can be quite helpful in the determination of thermodynamics quantities, this approach has become dramatically more successful with the advent of intense sources of tunable narrowband vacuum ultraviolet radiation, for example with synchrotron-based sources or various vacuum ultraviolet laser sources. The strategy behind such experiments is based on the idea that as the energy of the absorbed VUV photon is increased, one provides increasing amounts of energy to the molecule and by scanning over various ionization thresholds, adiabatic thermodynamics can be obtained. Such experiments assume that ionization via the channel of interest is indeed possible at the energetic threshold. This is, of course, not always the case. Thus, one must carefully evaluate the results of experiments like this

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[†] Part of the "George C. Schatz Festschrift".

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10.1021/jp809577t CCC: $40.75

within the context of other work and be aware of the possible pitfalls. These include the presence of exit barriers in the dissociation coordinate, and excitation to repulsive states, which can result in products with substantial excess energy—either internal or translational—that leads to ion formation only above the energetic threshold. When one detects ions of only one polarity, ion pair formation can lead to apparent thresholds below the energetic threshold. Finally, vibrational energy remaining in the molecular beam cooled sample (hot bands) can result in ion formation below the apparent threshold.

In this work we report appearance energies (AEs) for the various photoions resulting from HN_3, specifically, those associated with the thresholds of reactions 1−5 above. This is accomplished by scanning high-resolution VUV light in the 10−19 eV photon energy range and detecting ions formed from a molecular beam sample with an estimated effective internal temperature of 10 K. The threshold of reaction 1 leads to a new value for IE(HN_3) that is less than that predicted from PES. Thresholds associated with reactions 3 and 4 allows us to validate four key thermodynamic quantities from the literature: $D_0(H-N_3)$,[6] $D_0(N-N_2)$,[7,8] $D_0(N-H)$,[9−11] and IE(NH).[12,13] Within this context, we review many thermochemical quantities and make recommendations, the most fundamental of which is a new recommendation for $\Delta_f H°_0(HN_3)$.

Experimental Section

To safely prepare samples, HN_3 is synthesized with NaN_3 as the limiting reagent in a 1:20 molar ratio with stearic acid under vacuum conditions.[14] Once the two compounds are melted, they are maintained at 100−110 °C as the HN_3 vapor is collected into an already evacuated ($<1 \times 10^{-3}$ Torr) 50 L stainless steel container. To avoid contamination, no product was collected during the first 15 min after the reactants melted. To avoid the possibility of explosion the total pressure of HN_3 was maintained below 50 Torr.

Photoionization was performed on the 21B U9-CGM beamline of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The apparatus has been described in detail elsewhere[15,16] and only a brief description of the experiments is presented here. Mixtures of HN_3 in He (mixing ratios of 0.1%, 1% and 10% were employed) or Ne (with a mixing ratio of 5%) were prepared in a stainless steel container and expanded supersonically with a stagnation pressure of between 600 and 700 Torr through a pulsed valve (Even-Lavie valve) to generate a molecular beam. After being skimmed[17] and entering a differentially pumped chamber the beam was photoionized by high-resolution, tunable, VUV synchrotron radiation and the generated ions were mass-selected by a quadrupole mass filter. The ion signal at the output of the quadrupole was detected with a channeltron detector and normalized to the vacuum ultraviolet intensity. By tuning the synchrotron radiation wavelength by simultaneously scanning a monochromator and the gap of the undulator, we recorded photoionization efficiency spectra for m/z 43 (HN_3^+), 42 (N_3^+), 29 (HN_2^+), 15 (HN^+), and 14 (N^+), over a photon energy range of 10−19 eV. We did observe signal for m/z 28 (N_2^+) from HN_3 in the 14−16 eV range, but we discarded these spectra as they were dominated by signals produced by N_2 background.

VUV radiation was generated by passing the undulator output (bandwidth-FWHM ~3%) through a monochromator, resulting in tunable VUV radiation with a bandwidth of 1.5 meV FWHM. Higher undulator harmonics were suppressed by an inert gas (He or Ar) in a gas cell in a design similar to that described by Suits et al.[18] located after the monochromator. To determine the calibration of the monochromator, we recorded the strongest lines of the absorption spectra of Xe (8.42−11.7 eV), Ar (12.56−15.8 eV), and Ne (16.5−20.5 eV) and compared those with tabulated transition energies.[19] These measurements show that the deviation between actual and apparent photon energies, as displayed by the monochromator read-out, is less than 0.03 eV. Indeed, the performance of the monochromator is nearly sufficient to ignore a calibration procedure altogether. However, we proceeded to fit the measured deviation to a simple second order polynomial function, which was used to correct apparent wavelengths obtained from the monochromator.

To obtain an optimal signal-to-noise ratio and acceptable threshold determinations in these spectra, multiple scans were averaged together. The weight of each contributing data set to the average was obtained by observation of the ion intensity at a reference VUV wavelength. In this way variations in molecular beam and VUV intensity were automatically accounted for. During scans of the monochromator, ion signal was recorded every 0.001 or 0.0005 eV. Ten-point adjacent-point averaging was performed on these raw data, degrading the spectral resolution by about a factor of 10 (0.01−0.005 eV). As the error associated with identifying the ionization thresholds was never better than ±0.02 eV, this approach provided the advantage of optimizing S/N, without compromising experimental accuracy.

In the course of these studies, special attention was paid to vibrationally excited HN_3, populated in the molecular beam, and its possible contribution to observed ion signals, especially near the several thresholds we observed. To evaluate the role of these vibrational "hot-bands" several additional experiments were carried out with a continuous molecular beam with variable nozzle temperatures and three carrier gases—He, Ne, and Ar. For He carrier gas, mixing ratios of 2% and 4% were used at nozzle temperatures of $T_{NOZZLE} = 0$, 4, 25, 71, 97, and 100 °C. For Ar and Ne, mixing ratios of 0.1% and 5% were used at nozzle temperatures of $T_{NOZZLE} = -38$, −30, 0, 4, 25, 71, 97, and 100 °C.

Results and Discussion

Mass resolved photoionization yield spectra for m/z 42 (N_3^+), 15 (NH^+), 29 (N_2H^+), and 14 (N^+) are shown in Figure 1a−d. We identified the appearance energies for each ion by drawing a line through the background as shown and detecting where the ion signal begins to rise above the background. The derived threshold is indicated by arrows. This is equivalent (although perhaps not as mathematically rigorous) to finding the change in slope associated with the threshold. Using this approach, we determined four appearance energies and the ionization energy for of HN_3 (Table 1). We now discuss the implications of each of these threshold determinations.

The observed thresholds can be used to construct a variety of thermochemical cycles, from which the present results may be compared against previously reported thermochemical quantities and in some cases new thermochemistry can be derived. An overview of all of the possible thermochemical cycles is shown in Figure 2. Here appearance energies obtained in this work are shown in parentheses; values obtained from the literature are underlined with citations indicated.

We first discuss the appearance energies of NH^+ and N_3^+, which provide a means of validating the present approach to deriving thermochemical results. We then move to a discussion of HN_3^+, N^+, and HN_2^+.

The Appearance Energy for N_3^+ and NH^+. Consider the appearance energy for N_3^+ measured in this work: AE(N_3^+) = 14.88 ± 0.03 eV. Assuming that dissociative ionization is

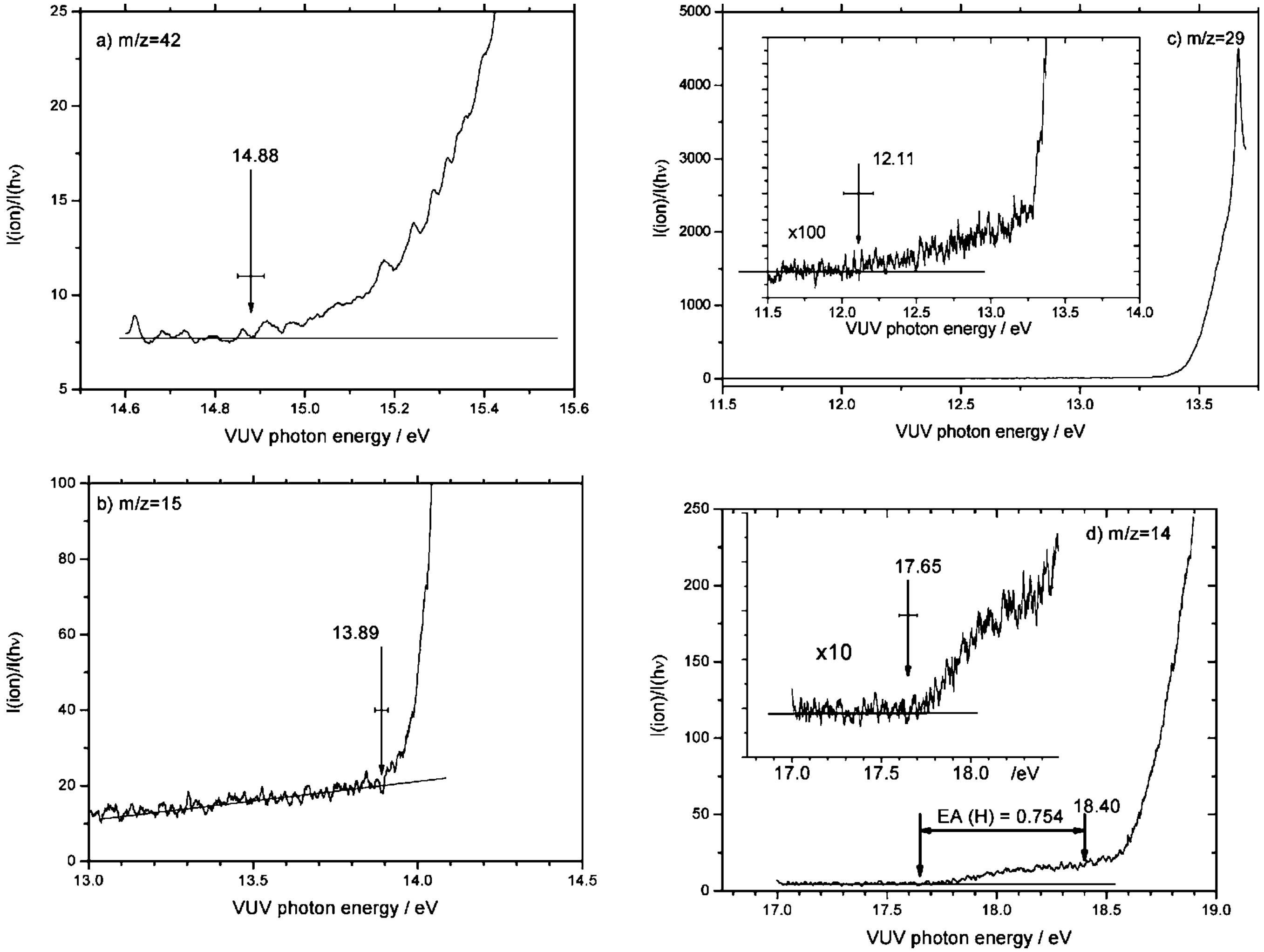

Figure 1. Photoionization yield spectra near threshold for (a) m/z = 42 (N_3^+), threshold region of reaction 4, seeding ratios of 0.1−10% in He (results averaged together, using a pulsed valve); (b) m/z = 15 (HN^+), threshold region of reaction 3, seeding ratio of 5% in Ne, using a pulsed valve; (c) m/z = 29 (HN_2^+) threshold region of reaction 2, seeding ratio of 5% in Ne, using a pulsed valve; and (d) m/z = 14 (N^+), threshold region of reaction 5, seeding ratio of 5% in Ne, using a pulsed valve. Also see Table 1. The solid lines indicate the subthreshold background level. The thresholds are identified by vertical down-pointing arrows. Horizontal error bars indicate the uncertainty associated with indentifying the threshold.

TABLE 1: Ionization Thresholds for HN_3 Dissociative Photoionization

reaction	threshold (eV)	EI results[5]
$HN_3(\tilde{X}^1A') + h\nu \rightarrow HN_3^+ + e^-$	10.56 ± 0.02	10.3 ± 0.2
$HN_3(\tilde{X}^1A') + h\nu \rightarrow HN_2^+ + N + e^-$	12.11 ± 0.1	13.8 ± 0.2
$HN_3(\tilde{X}^1A') + h\nu \rightarrow HN^+ + N_2 + e^-$	13.89 ± 0.02	14.4 ± 0.2
$HN_3(\tilde{X}^1A') + h\nu \rightarrow N_3^+ + H + e^-$	14.88 ± 0.03	16.0 ± 0.2
$HN_3(\tilde{X}^1A') + h\nu \rightarrow N^+ + N_2 + H + e^-$	18.40 ± 0.05	19.7 ± 0.3

possible at the energetic threshold, this appearance energy must be equal to the sum of the dissociation energy of HN_3 and the ionization energy of the azide radical, both of which are well determined from previous work

$$\mathrm{AE}(N_3^{\ +}) = D_0(\mathrm{H} - \mathrm{N}_3) + \mathrm{IE}(\mathrm{N}_3) \qquad (6)$$

Cook et al.[6] used H-atom Rydberg tagging to derive $D_0(\mathrm{H{-}N_3})$ = 3.8397 ± 0.006 eV. This value is extraordinarily precise and, in our view, the most accurate determination of this quantity available. Dyke et al.[20] obtained the $\mathrm{IE(N_3)}$ = 11.06 ± 0.01 eV from PES. Using these values with eq 6 we obtain $\mathrm{AE}(N_3^+)$ = 14.90 ± 0.01 eV. This is to be compared with our measured threshold of 14.88 ± 0.03 eV, shown in Table 1. The good agreement is strong evidence that, not only does reaction 4 occur at threshold, but additionally the above values of $D_0(\mathrm{H{-}N_3})$ and $\mathrm{IE(N_3)}$ are reliable.

In a similar fashion, we may calculate the HN^+ appearance energy from eq 7:

$$\mathrm{AE}(\mathrm{HN}^+) = D_0(\mathrm{HN} - \mathrm{N}_2) + \mathrm{IE}(\mathrm{HN}) \qquad (7)$$

Here, we turn to Cook et al.,[6] who showed how to derive the bond strength $D_0(\mathrm{HN{-}N_2}) = D_0(\mathrm{H{-}N_3})$[6] + $D_0(\mathrm{N{-}N_2})$[7,8] − $D_0(\mathrm{N{-}H})$[9−11] = 0.372 eV. Several determinations of IE(NH) have been reported including computational studies of Jursic and Dixon et al.,[12,21] which are expected to be quite accurate for such a small molecule as NH and experimental results using EI[22] as well as PES.[13,23] Indeed the high-level quantum chemical work of Dixon[12] (IE(NH) = 13.47 ± 0.01 eV) and the rotationally resolved REMPI photoelectron spectroscopy of de Beer[13] (IE(NH) = 13.476 ± 0.0002 eV) show the degree of accuracy that can be obtained. Combining the values from Cook et al.[6] and de Beer[13] in eq 7, we obtain $\mathrm{AE}(\mathrm{HN}^+)$ = 13.85 eV, which is also in good agreement with the threshold observed in this work, 13.89 eV (see Table 1). This level of agreement strongly supports the analysis of Cook et

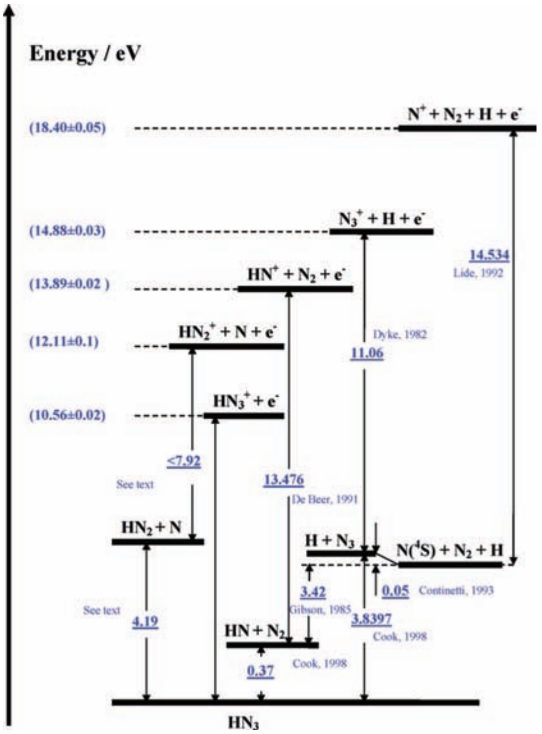

Figure 2. Energy diagram for the hydrazoic acid dissociation study and summary of the results of this work and the literature review. The results derived from this work are shown in parentheses, while the literature values are underlined. See the text for further details.

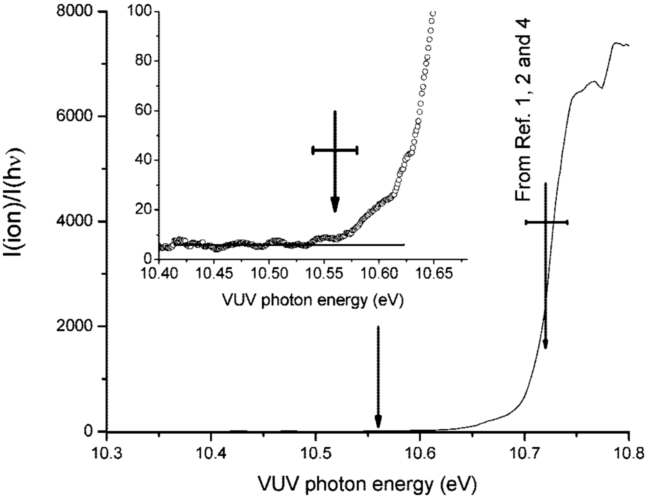

Figure 3. Photoionization yield spectra for $m/z = 43$ (HN_3^+), threshold region of reaction 1, seeding ratio of 2% in He, using a pulsed valve. The region below the observed threshold up to and surpassing the presently accepted ionization energy of HN_3 (IE(HN_3) = 10.72 eV) is shown here. The inset shows a magnified view of the threshold region. The thresholds are identified by vertical down-pointing arrows. Horizontal error bars indicate the uncertainty associated with indentifying the threshold.

al. concerning D_0(HN−N$_2$), from which we conclude that the values of de Beer and Continetti for IE(NH) and D_0(N−N$_2$) are highly reliable. In passing, we note that one could use the experimentally observed threshold AE(NH$^+$) to obtain D_0(N−N$_2$) = −0.01 eV. This may be somewhat more accurate than the nominal value reported in the literature.[7,8]

The agreement found in these two sets of analyses is better than 0.04 eV (1 kcal/mol). We take this level of agreement as validation of a number of assumptions made in this work. First, the use of photoionization appearance energies to derive thermodynamic quantities assumes that dissociative ionization can occur at the energetic threshold for dissociation. That is, dissociation products can be formed with little or no excess energy and a near zero energy photoelectron can be produced. This means that there must be (essentially) no barrier to dissociation and that dissociation does not occur on a repulsive potential energy surface. While this assumption may not hold in general, it does appear to be valid for reactions 3 and 4. Second, this level of agreement could not be obtained unless specific values of thermochemical quantities used from the literature were not highly accurate.

$$D_0(\mathrm{H-N_3}) = 3.8397 \pm 0.006\ \mathrm{eV}^{6} \qquad (8)$$

$$D_0(\mathrm{N-N_2}) = -0.05 \pm 0.1\ \mathrm{eV}^{7,8} \qquad (9)$$

$$D_0(\mathrm{N-H}) = 3.419 \pm 0.017\ \mathrm{eV}^{9-11} \qquad (10)$$

$$\mathrm{IE(NH)} = 13.476 \pm 0.0002\ \mathrm{eV}^{12,13} \qquad (11)$$

Hence, we rely on the values shown in eqs 8−11, which we consider validated by this work, in further analysis below. Note that the error bar reported in previous work for D_0(N−N$_2$) appears to be overly conservative if judged on the basis of the comparison with this work.

The Ionization Energy for HN$_3$. We now consider the nondissociative ionization energy for HN$_3$. Figure 3 shows the photoionization yield spectrum over the range including the values reported previously from PES, IE(HN$_3$) = (10.70−10.74) eV.[1,2,4] See the inset to Figure 3. The threshold observed in this work is somewhat lower, but agrees reasonably well with theoretical results in a range between 10.5 and 10.86 eV.[24−26]

$$\mathrm{IE(HN_3)} = 10.56 \pm 0.02\ \mathrm{eV} \qquad (12)$$

The discrepancy between this result and those from PES caused us to consider factors that could lead to errors in our experiment. Most importantly, we carried out extensive investigations using a wide variety of molecular beam conditions to evaluate the importance of hot-bands to the threshold determination. We also considered the possible influence of $(HN_3)_2$, which might also yield subthreshold HN_3^+. By using a continuous molecular beam expansion designed to suppress cluster formation, photoionization yield spectra were obtained at a variety of nozzle temperatures between −38 and 100 °C and with a variety of carrier gases and mixing ratios. None of the conditions explored in this work gave any evidence of hot-band or dimer contributions to the threshold region. Figure 4 shows some of these data, where the nozzle temperature has been varied. This range of temperature variation would be expected to dramatically change the hot-band and dimer population in the molecular beam. As can easily be seen from Figure 4, there is no evidence that the observed threshold depends on the nozzle temperature. Thus we conclude that the reported threshold is not significantly influenced by hot bands or HN$_3$ dimers.

One might be concerned that PES results appear to favor the origin band, whereas the photoionization mass spectrometry spectra ones of this work show a long tailing threshold. That is, the photoelectron spectra used to derive IE(HN$_3$) suggest that the structure of the ion is similar to that of the neutral. In

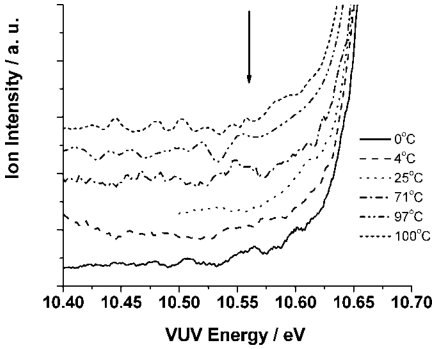

Fig. 4

Figure 4. The influence of nozzle temperature on the HN_3^+ threshold region. CW molecular beams were prepared at various nozzle temperatures and with a variety of carrier gases. See text for details. This figure shows a representative sample of data obtained in this work with a seeding ratio of 2% HN_3 in He at nozzle temperatures of $T_{\mathrm{NOZZLE}} =$ 0, 4, 25, 71, 97, and 100 °C. The results of the different experiments are vertically offset from one another and the thresholds are identified by vertical down-pointing arrows. No evidence of hot band contributions to ionization could be found.

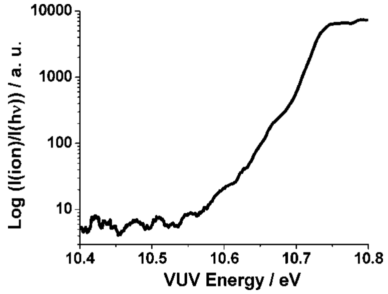

Figure 5. Photoionization yield spectrum for $m/z = 43$ (HN_3^+) shown in Figure 3 on a semilogarithmic scale. From ref 27 it has been shown that such a linear semilogarithmic threshold region is typical of ionization events that reflect significant structure change.

contrast, the near threshold photoionization mass spectrometry reported here exhibits a threshold region typical of ionization events that occur through a large geometry change.[27] This can be seen most clearly in Figure 5, where a long semilogarithmic linear region[27] is seen between 10.55 and 10.8 eV. We speculate that the near threshold ionization in HN_3 may result from excited electronic states, where the ionization continuum is quantum mechanically mixed with excited valence states whose structure is different than either the ground state or the ion.

The tailing threshold behavior seen between 10.5 and 10.7 eV in Figure 3 cannot be explained by the photon energy distribution of the synchrotron light. In measuring rare gas absorption features for calibration — see above — we found that the observed features were well fit by a Gaussian with a FWHM of 1.7 meV. Thus, when the VUV is turned to 10.72 eV — the nominal threshold from PES — the amount of VUV light at 10.55 eV is negligible. Indeed, the light intensity drops by a factor of one thousand just 30 meV from line center.

There are also potential problems with the PES experiments. Most importantly, none of that work employed a molecular beam cooled sample. In light of the fact that the reported error bars associated with IE(HN_3) derived from PES are much narrower than the actual line widths of the features in those spectra, if the broadening of the spectral features were not fully understood in that work, it is possible that the error bars may have been underestimated.

In conclusion, the origin of this relatively small disagreement with PES remains unclear. Nevertheless, our experiments cannot simply be dismissed as they exhibit high S/N and employ narrow bandwidth VUV light and molecular beam cooled HN_3 samples. There would appear to be no compelling reason not to revise the IE(HN_3) downward by about 0.16 eV to IE(HN_3) = 10.56 ± 0.02 eV.

The thermodynamic and energetic values recommended above can be used to obtain a number of new thermodynamic quantities.

We first consider $\Delta_f H°_0(HN_3)$. Gutowski has applied large basis set electronic structure calculations to obtain a first principles value of $\Delta_f H°_0(HN_3) = 72.6$ kcal/mol.[28] Reviewing work carried out with classical thermochemical methods[29] such as calorimetry[30] and vapor pressure measurements of HN_3 above water,[31] Gurvich recommends a value of $\Delta_f H°_{298}(HN_3) = 70.3$ kcal/mol,[32] from which we can derive a corresponding value of $\Delta_f H°_0(HN_3) = 71.9 \pm 1$ kcal/mol.[33] While these values appear to substantiate one another, we note that no heat of formation for HN_3 has been reported since the advent of mass spectrometric, laser, and molecular beam based methods have begun to be applied to thermochemistry. Thus, we have attempted to derive here what we believe to be the most accurate experimental value of $\Delta_f H°_0(HN_3)$ using eq 13.

$$\Delta_f H°_0(HN_3) = \Delta_f H°_0(H) + \Delta_f H°_0(N) - D_0(N_2-N) - D_0(H - N_3) \quad (13)$$

This approach to $\Delta_f H°_0(HN_3)$ has the advantage that it relies on validated thermochemical quantities that connect HN_3 to dissociated H + N + N_2, whose heats of formation are highly accurate. From diatomic dissociation energies, we may obtain the heats of formation of H[34] and N.[35]

$$\Delta_f H°_0(H) = 51.63 \text{ kcal/mol} \quad (14)$$

and

$$\Delta_f H°_0(N) = 112.469 \pm 0.012 \text{ kcal/mol} \quad (15)$$

Taking eqs 13−15 and the recommended values above, eqs 8 and 9, we may obtain

$$\Delta_f H°_0(HN_3) = 76.7 \pm 2.3 \text{ kcal/mol} \quad (16)$$

from which we may obtain

$$\Delta_f H°_{298}(HN_3) = 75.1 \pm 2.3 \text{ kcal/mol} \quad (17)$$

The greatest uncertainty in this analysis comes from the work of Continetti et al., who reported an error bar of ±2.3 kcal/mol in connection with $D_0(N_2-N)$.[7,8] However, as mentioned above this reported error bar appears to us to be conservative. Furthermore, the type of experiment performed in their work yields an upper limit to $D_0(N_2-N)$. Inspection of eq 13 shows us that, to the extent that the true value of $D_0(N_2-N)$ is lower than that assumed in this work, the value of $\Delta_f H°_0(HN_3)$ would be even higher than that shown in eq 16. Thus, the presently accepted value of $\Delta_f H°_0(HN_3) = 71.9 \pm 1$ kcal/mol appears untenable.

There is yet more evidence in favor of the newly recommended value of $\Delta_f H°_0(HN_3)$. Gibson et al. made careful measurements of the ionization thresholds of NH_2 produced by the reaction H + N_2H_4 → NH_3 + NH_2. From ionization thresholds forming NH_2^+ and NH^+, and the use of auxiliary thermochemical data, these authors arrived at $\Delta_f H°_0(NH^+) = 396.3 \pm 0.3$ kcal/mol. Using the threshold for reaction 3 obtained in this work, NH^+ formation from HN_3 (13.89 eV = 320.3 kcal/mol), we can quickly calculate $\Delta_f H°_0(HN_3) = 76.0$ kcal/mol, which agrees well with eq 16.

Next, we use the new value, $\Delta_f H°_0(HN_3) = 76.7 \pm 2.3$ kcal/mol, to derive a few other thermodynamic quantities. For example, using the IE for HN_3 derived in this work we may obtain the heat for formation of HN_3^+

$$\Delta_f H°_0(HN_3^+) = \Delta_f H°_0(HN_3) + IE(HN_3) = 320.2 \pm 2.3 \text{ kcal/mol} \quad (18)$$

We can also obtain the heat of formation for N_3.[7,8]

$$\Delta_f H°_0(N_3) = D_0(H - N_3) - \Delta_f H°_0(H) + \Delta_f H°_0(HN_3) = 113.6 \pm 2.3 \text{ kcal/mol} \quad (19)$$

This value is in excellent agreement with multireference configuration interaction (complete singles double and triples partial quadruples (MRCISDT(Q))-aug-cc-pVTZ) calculations of Morokuma et al.,[36] which show $\Delta_f H°_0(N_3)$ (=112.7 kcal/mol) to be 0.23 kcal/mol higher than that for N + N_2. Use of the Gurvich recommendation for $\Delta_f H°_0(HN_3)$ in this line of reasoning leads to $\Delta_f H°_0(N_3) = 108.8$ kcal/mol, which disagrees with the high level theory of Morokuma.

We may also use Continetti et al.'s value of the electron affinity of N_3 (2.68 ± 0.01 eV)[7] to obtain the heat of formation of N_3^-.

$$\Delta_f H°_0(N_3^-) = 51.8 \pm 2.3 \text{ kcal/mol} \quad (20)$$

Combining this result with $\Delta_f H°_0(HN_3)$ and $\Delta_f H°_0(H^+) = 365.213$ kcal/mol, we may obtain the proton affinity of N_3^-, $PA(N_3^-) = 340.2$ kcal/mol, which is in reasonable agreement with bracketing experiments of Pellerite et al., who reported $PA(N_3^-) = 344 \pm 2$ kcal/mol.[37] One should note that the bracketing result implies $D_0(H-N_3) = 92$ kcal/mol, inconsistent with the highly accurate determination (88.5 ± 0.1 kcal/mol) of Cook et al. (eq 8).

Finally, we may combine this information with the heat of formation of H^+, $\Delta_f H°_0(H^+)$, to obtain the proton affinity of the azide radical.

$$PA(N_3) = \Delta_f H°_0(HN_3^+) - \Delta_f H°_0(H^+) - \Delta_f H°_0(N_3) = 158.6 \pm 2.3 \text{ kcal/mol} \quad (21)$$

To our knowledge, this quantity has not been previously reported.

To summarize the sections above, we have used experimental values for the appearance energies of NH^+ and N_3^+ in dissociative ionization of HN_3 to at once validate our experimental approach and to use as a basis for validating specific thermochemical quantities, eqs 8−11. These have been used to derive a variety of other thermochemical quantities.

The Appearance Energy for HN_2^+. As described above, the use of appearance energies to derive thermochemical results assumes that ions may be created at threshold. For reaction 2 this may not be the case as HN_2^+ is isoelectronic with HCN and the electronic reorganization associated with formation of the N−N triple bond in this molecule may lead to an exit barrier. Even in the absence of a barrier, the large change in N−N bond length associated with the change in bond order could suppress ion production near threshold as the likelihood of forming HN_2^+ without vibrational excitation might be quite small. Indeed Figure 1c shows that HN_2^+ becomes most likely above about 13.3 eV; but there is a long tail extending out to 12.11 eV that can only be seen clearly when the data are magnified by a fact of 100. Assuming this is a rigorous upper limit to the adiabatic threshold ($AE(HN_2^+) \leq 12.11$ eV), our results may be used to derive the heat of formation of HN_2^+,

$$\Delta_f H°_0(HN_2^+) = AE(HN_2^+) + \Delta_f H°_0(HN_3) - \Delta_f H°_0(N) \leq 243.5 \pm 2.4 \text{ kcal/mol} \quad (22)$$

and from eq 22 we obtain the proton affinity of N_2.

$$PA(N_2) = \Delta_f H°_0(H^+) - \Delta_f H°_0(HN_2^+) \geq 121.7 \pm 2.4 \text{ kcal/mol} \quad (23)$$

As a consequence of the difficulties in finding the threshold of reaction 2 mentioned above, we denote the thermochemical quantities in eqs 22 and 23 as limiting values. Here a lower bound to $PA(N_2)$ is obtained.

A previous report of $PA(N_2)$ comes from Ruscic et al.[38] In that work the dissociative ionization threshold $N_2H_2 \rightarrow N_2H^+ + H + e^-$ was observed at 10.954 ± 0.019 eV, which was in good agreement with previous electron impact ionization threshold work.[39] Furthermore, the threshold for the reaction $N_2H_2 \rightarrow H_2^+ + N_2 + e^-$ could be observed, 13.52 ± 0.03 eV. This may be combined with the bond energy in H_2^+, $D_0(H-H^+) = 2.65078$ eV,[34] to obtain $PA(N_2) \leq 120.4 \pm 1$ kcal/mol. Again, we cannot ignore the possibility of energy release in the products of these two dissociative ionization reactions; hence these values are also presented as limits.

Conveniently, in contrast to the present work, Ruscic's analysis leads to an upper limit to the $PA(N_2)$. Hence, the two experiments bracket $PA(N_2)$ between 121.7 ± 2.4 kcal/mol on the lower energy side and 120.4 ± 1 kcal/mol on the high energy side. This can be equivalently expressed as $121.7 - 2.4 = 119.3$ kcal/mol $\leq PA(N_2) \leq 120.4 + 1 = 121.4$ kcal/mol by considering the error bars of the two experimental values. To our knowledge this is the first experimental route to a lower limit to the proton affinity of N_2. It is likely that improved experiments of the kind described here can improve the degree to which this important thermodynamic quantity may be bracketed.

We also note that had we attempted the analysis of the last paragraph using Gurvich's recommendation for $\Delta_f H°_0(HN_3)$, we would have arrived at a lower limit to $PA(N_2)$ of 126.5 kcal/mol, inconsistent with Ruscic's reported upper limit. This is further evidence supporting the new recommendation for $\Delta_f H°_0(HN_3)$.

In passing we note that we may impose additional constraints on the ionization energy of HN_2, $IE(HN_2)$, by suggesting an approach to the outer N−N bond dissociation energy in HN_3, $D_0(HN_2-N)$. To see this first consider eq 24

$$AE(HN_2^+) = D_0(HN_2-N) + IE(HN_2) \quad (24)$$

Note that $D_0(HN_2{-}N)$ can be quite accurately estimated by using eq 25

$$D_0(HN_2{-}N) = D_0(H - N_3) + D_0(N_2{-}N) - D_0(H - N_2) \tag{25}$$

For this, we may use the recommended values from eqs 8 and 9. The HN_2 molecule has never been observed. Here we must rely on theoretical calculations, which are expected to be accurate—that is, with associated error bars of ±2.5 kcal/mol or better. A variety of calculations have been performed.[40−44] Representative is that of Matus et al.,[40] who report $\Delta_f H°_0(HN_2) = 60.8$ kcal/mol, from which one may obtain $D_0(H{-}N_2) = -9.2$ kcal/mol (0.40 eV), using the heat of formation of H ($\Delta_f H°_0(H) = 51.6$ kcal/mol).[34] From eq 25, we obtain an accurate value of

$$D_0(HN_2 - N) = 96.6 \pm 2.3\ \text{kcal/mol} \tag{26}$$

Using this together with the measured appearance energy $AE(HN_2^+)$ we may obtain a bound on $IE(HN_2) < 7.92 \pm 0.1$ eV. As HN_2 is isoelectronic with NO, the low ionization energy should not come completely as a surprise. Matus' calculation on HN_2 shows that despite its low bond energy, the N−N bond length is extended to 1.18 Å,[40] which is to be compared to 1.097 Å for N_2 and 1.15 Å for NO. Clearly, H-atom attack on the N_2 molecule forming HN_2 dramatically reduces the N−N bond order and results in a covalent N−H bond.

We hope that this outcome may be helpful in designing new experiments to detect the HN_2 directly for the first time; for example, two-photon nonresonant ionization at wavelengths shorter than 313 nm would appear to be a reasonable approach to the detection of this molecule. Even one photon ionization with an F_2 laser ($h\nu = 7.897$ eV) would appear plausible.

The Appearance Energy for N$^+$. We expect the dissociation reaction 5 may occur through one or both of the following pathways.

$$HN_3 \rightarrow HN_3^+ + e^- \tag{27}$$

$$HN_3^+ \rightarrow N^+ + N_2H \tag{28}$$

$$N_2H \rightarrow H + N_2 \tag{29}$$

or

$$HN_3 \rightarrow HN_3^+ + e^- \tag{30}$$

$$HN_3^+ \rightarrow N_3^+ + H \tag{31}$$

$$N_3^+ \rightarrow N_2 + N^+ \tag{32}$$

Again, as for any of the work presented here, there is the possibility of encountering exit barriers and the possible role of repulsive electronic states that might prevent the products from being formed with no excess energy—that is, at the energetic threshold. Beyond this, we note that the electron affinity of H is quite large (EA(H) = 0.754 eV).[45] The fact that we have made no effort to detect negative ions in this work means that we cannot rule out the possible importance of reaction 33.

TABLE 2: Thermochemical Results of the Photoionization Mass Spectrometry Study of HN_3

Estimated Thermochemical Quantities in This Work (kcal/mol)	
(1) heats of formation	
$\Delta_f H°_0(HN_3)$	76.7 ± 2.3
$\Delta_f H°_{298}(HN_3)$	75.1 ± 2.3
$\Delta_f H°_0(HN_3^+)$	320.2 ± 2.3
$\Delta_f H°_0(N_3)$	113.6 ± 2.3
$\Delta_f H°_0(N_3^-)$	51.8 ± 2.3
$\Delta_f H°_0(HN_2^+)$	≤243.5 ± 2.4
(2) proton affinities	
$PA(N_3)$	158.6 ± 2.3
(3) bond dissociation energies	
$D_0(HN_2{-}N)$	96.6 ± 2.3
Validated Thermochemical Quantities from Previous Works	
(1) bond dissociation energies	
$D_0(H{-}N_3)$	3.8397 ± 0.006 eV[6]
$D_0(N{-}N_2)$	−0.05 ± 0.1 eV[7,8]
$D_0(N{-}H)$	3.419 ± 0.017 eV[9−11]
(2) ionization energies	
IE(NH)	13.476 ± 0.0002 eV[12,13]
$IE(N_3)$	11.06 ± 0.01 eV[20]

$$HN_3 \rightarrow N^+ + N_2 + H^- + e^- \tag{33}$$

On the basis of the thermochemistry validated above we may calculate the expected ionization threshold using eq 34 with the recommended values of eqs 8 and 9 as well as the ionization energy of the N-atom, IE(N)= 14.534 eV.[46]

$$AE(N^+) = D_0(H - N_3) + D_0(N - N_2) + IE(N) \tag{34}$$

This leads us to $AE(N^+) = 18.33 \pm 0.1$ eV. Should the ion pair channel be present, the threshold would be reduced to 17.6 ± 0.1 eV as the electron affinity of H is well-known. Inspection of Figure 1d shows a threshold at 17.65 ± 0.05 eV, which we assign to the onset of the ion pair channel.

Conclusions

We report photoionization mass spectrometry of HN_3 near the thresholds of several ionization reactions. The observed thresholds of reactions 3 and 4 allow us to validate several previously reported thermochemical quantities. We use this together with the observed threshold for nondissociative ionization to carry out a review of thermochemical quantities of relevance to HN_3 (see Table 2). We also find that the $IE(HN_3)$ is significantly less than that derived from PES. We are also able to bracket the proton affinity of N_2, $PA(N_2)$ (119.3 kcal/mol ≤ $PA(N_2)$ ≤ 121.4 kcal/mol), as well as obtain the ionization energy of HN_2 (7.92 ± 0.1 eV).

Acknowledgment. This work was in part supported by a grant from the Air Force Office of Scientific Research (Grant. No. FA9550-07-1-0206). A.Q.H. wishes to express his thanks to the National Council for Science and Technology (CONACYT-Mexico) and the University of California Institute for Mexico and the United States (UC-MEXUS) for his financial support during the development of these experiments. We thank the National Synchrotron Radiation Research Center personnel for their assistance during the present research and the Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan for support. We are grateful to Professor Yuan T. Lee, who took great effort to help us improve the original manuscript.

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JP809577T