Photoionization mass spectrometric study of N_2H_2 and N_2H_3: N–H, N=N bond energies and proton affinity of N_2

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The photoion yield curves of $N_2H_2^+$, N_2H^+, and H_2^+ from N_2H_2 have been studied by photoionization mass spectrometry. The adiabatic ionization potential of N_2H_2 determined $(9.589 \pm 0.007$ eV) is in excellent agreement with that obtained by photoelectron spectroscopy (PES). The appearance potential of N_2H^+ $(10.954 \pm 0.019$ eV at 0 K) is in good agreement with earlier electron impact measurements. The appearance potential of H_2^+ $(<13.52_6 \pm 0.03$; probably $\leqslant 13.403 \pm 0.036$ eV, at 0 K) leads to $\Delta H^0_{f_0}$ (N_2H_2) $> 43.8 \pm 0.7$; probably $\geqslant 46.6 \pm 0.8$ kcal/mol. Consequently, proton affinity (PA) (N_2) $< 121.8 \pm 0.8$; probably $\leqslant 119.0 \pm 0.9$ kcal/mol, which is in good agreement with results from proton transfer experiments and with most *ab initio* calculations. The N=N "double bond" energy determined from $N_2H_2 \rightarrow 2NH$ is $< 126.6 \pm 1.0$; probably $\leqslant 123.8 \pm 1.1$ kcal/mol. The adiabatic ionization potential of N_2H_3 is found to be 7.61 ± 0.01 eV. This observation leads to D_0 $(H_2NNH–H) = 80.8 \pm 0.3$ kcal/mol, and $D_0(HNNH–H) \cong 43.8 \pm 1.1$ kcal/mol.

I. INTRODUCTION

The N_2H^+ species is a known constituent of interstellar clouds.[1] One of the most important reactions postulated[2] to occur in this medium is

$$H_3^+ + N_2 \rightarrow N_2H^+ + H_2.$$
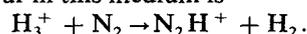
Although the molecular structure[3] and the three normal mode frequencies[4–6] are now known experimentally to high accuracy, the value of the proton affinity of N_2 [(PA) (N_2)], or alternatively ΔH^0_f (N_2H^+), is still a matter of some controversy. Two types of experiments have been applied to deducing this quantity.

(i) Determining the appearance potential (AP) of N_2H^+ from N_2H_2, after having established ΔH^0_f (N_2H_2).

(ii) Determining the difference in proton affinity between N_2 and some secondary standards from the kinetics of proton transfer reactions.

Unfortunately, the results from these experiments differ. In an experiment of type (ii), Bohme *et al.*[7] have determined the difference in proton affinity (ΔPA) between N_2 and O to be 1.3 ± 0.5 kcal/mol. Using as reference value PA $(O) = 116.1 \pm 0.2$ kcal/mol, they deduce PA $(N_2) = 117.4 \pm 0.7$ kcal/mol. A more circuitous route involves ΔPA $(CO_2–Xe) = 10.6 \pm 1.2$ kcal/mol and ΔPA $(Xe–N_2) = 0.63 \pm 0.19$ kcal/mol from Bohme *et al.*[7] together with our[8] recent value for PA $(CO_2) = 129.2 \pm 0.5$ kcal/mol to arrive at PA $(N_2) = 118.0 \pm 1.3$ kcal/mol. Lias *et al.*[9,10] give PA $(N_2) = 118.2$ kcal/mol in their compilations.

The type (i) experiment has been performed by Willis *et al.*[11] and by Foner and Hudson,[12,13] both using electron impact methods. They differ only slightly in their determinations of AP N_2H^+ (N_2H_2). Willis *et al.* obtain 10.98 ± 0.05 eV, while Foner and Hudson report 10.89 ± 0.08 eV. However, there is a major difference in their determinations of ΔH^0_f (N_2H_2). Willis *et al.* chose to measure AP N_2^+ (N_2H_2); they obtained 14.00 ± 0.05 eV for this quantity. Subtracting this value from the well-known ionization potential (IP) $(N_2) = 15.5808$ eV,[10] one obtains ΔH^0_f (N_2H_2) $= 1.58$ eV$\equiv 36$ kcal/mol. Their estimated error is ± 2 kcal/mol; no attempt is made to distinguish between $\Delta H^0_{f_0}$ and $\Delta H^0_{f_{298}}$. Combining their ΔH^0_f (N_2H_2) with their AP (N_2), they obtain ΔH^0_f $(N_2H^+) = 237$ kcal/mol, and PA $(N_2) = 128.7$ kcal/mol$\equiv 5.6$ eV.

Foner and Hudson[12] were unable to duplicate the measured AP N_2^+ (N_2H_2) reported by Willis *et al.* and questioned their result. Instead, they chose to measure AP $N_2H_2^+$ (N_2H_4). Their ion yield curve amounted to 2.5×10^6 counts/sec at 50 eV electron energy, 10^4 counts/sec at 15 eV, but in the critical onset region it was "a few counts/sec". In other words, there was significant curvature. "This unusually large diminution of intensity in going from high energy to the threshold region contributes substantially to the difficulty in measurement of AP $(N_2H_2^+)$."[12] They inferred 10.75 eV for this threshold. Utilizing a photoelectron spectroscopic value for IP (N_2H_2) of 9.59 eV and $\Delta H^0_{f_0}$ (N_2H_4) $= 26.155$ kcal/mol (Lias *et al.*[10] give 26.1 ± 0.2 kcal/mol), they extracted $\Delta H^0_{f_0}$ $(N_2H_2) = 52.4 \pm 2$ kcal/mol, and $\Delta H^0_{f_{298}}$ $(N_2H_2) = 50.7 \pm 2$ kcal/mol, about 15–17 kcal/mol higher than the result of Willis *et al.*[11] Upon introducing their value[13] for AP N_2H^+ (N_2H_2), they obtained PA $(N_2) = 4.93 \pm 0.11$ eV$\equiv 113.7 \pm 2.5$ kcal/mol.

In summary, experiments of type (ii) are consistent with PA $(N_2) = 118.2 \pm 1$ kcal/mol, whereas experiments of type (i) deviate significantly from this quantity, and in opposite directions. The critical factor in the type (i) experiments is the determination of ΔH^0_f (N_2H_2).

The elusive ΔH^0_f (N_2H_2) can also be related, through ΔH^0_f (NH), to a measure of the N=N double bond energy. Pauling[15] has used bond additivity arguments to arrive at single and double bond energies, which he then compares to the N≡N triple bond energy. Thus, an average N–H bond energy is deduced from ΔH^0_f (NH_3). This is then assumed to represent the N–H bond energies in (for example) N_2H_4. By subtracting four N–H bond energies from the heat of atom-

ization of N$_2$H$_4$, he arrives at 38.4 kcal/mol for the N–N single bond energy. An alternative approach, based on the reaction

$$N_2H_4 \rightarrow 2NH_2,$$
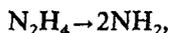
yields a very different value, 65.5 $\pm$ 0.4 kcal/mol [using $\Delta H^0_{f_0}$ (NH$_2$) = 45.8 $\pm$ 0.3 kcal/mol[16]].

From the heat of formation of azoisopropane and auxiliary average bond energies, Pauling obtains 100 kcal/mol for the N=N double bond energy. Since the triple N≡N bond energy is known[17] to be 225.0$_6$ kcal/mol, Pauling concludes "that there is an abnormality in the structure of the nitrogen molecule such as to increase the N≡N bond energy from 147 (*his inferred value*) to 226 (currently 225.06) kcal/mol. This abnormality is not shown by the N=N and N–N bonds. Its nature is not known."[15]

Our alternative approach to the single N–N bond energy gives a much higher value than Pauling's. It is interesting to inquire about an alternative to Pauling's approach to the N=N double bond energy.

The heat of formation of N$_2$H$_3$ is poorly known, at best. Our goal here was to obtain an accurate adiabatic ionization potential for this free radical[18] which, when combined with the appearance potential of N$_2$H$_3^+$ (N$_2$H$_4$), would provide us with ΔH^0_f (N$_2$H$_3$) and D_0 (H$_2$NNH–H). The latter could then be compared with Pauling's average N–H bond energy obtained from NH$_3$ to test the transferability hypothesis.

II. EXPERIMENTAL ARRANGEMENT

The basic approach was to use photoionization mass spectrometry, with an apparatus that has been described previously.[19] N$_2$H$_2$ was produced by the two methods described by Frost *et al.*[14]—a very weak microwave discharge

through N$_2$H$_4$, and pyrolysis of sodium tosylhydrazide.[20] Both methods produced N$_2$H$_2$ for study, but the pyrolysis method was more advantageous for examining weak fragments, since extraneous sources of these fragments were less likely. A more conventional experiment was also performed, searching for the N$_2$H$_2^+$ fragment from hydrazine. N$_2$H$_3$ was prepared *in situ* by the reaction of hydrogen atoms with hydrazine.[16]

III. EXPERIMENTAL RESULTS
A. N$_2$H$_2^+$ (N$_2$H$_4$)

This process was examined in earlier work from this laboratory.[16] We have repeated this experiment because of its potential value in establishing ΔH^0_f (N$_2$H$_2$), but our results were the same. The parent ion, N$_2$H$_4^+$, is four orders of magnitude larger than the background level of M30 in the relevant wavelength region ($\lambda > 1140$ Å). In fact, the wing of the M32 peak probably accounts for this background. As shown in Fig. 3 of Ref. 16, M30 does not display a significant signal above this background below ~ 15.2 eV (817 Å), which is approximately the energy for dissociative ionization into N$_2$H$_2^+$ + 2H, about 4.5 eV above N$_2$H$_2^+$ + H$_2$.

B. N$_2$H$_2^+$ (N$_2$H$_2$)

Parent diimine ion was observable from both the weak microwave discharge through hydrazine and from pyrolysis of sodium tosylhyrazide, but the latter proved to be a cleaner source. The photoion yield of the parent ion is shown in Fig. 1. Step structure is observed from threshold to ~ 10.35 eV (~ 1200 Å). This is roughly the energy region in which vibrational fine structure is seen in the He I photoelectron spectrum.[14] The midrise of the first observable step occurs at 1293 $\pm$ 1 Å $\equiv$ 9.589 $\pm$ 0.007 eV, in excellent agreement with
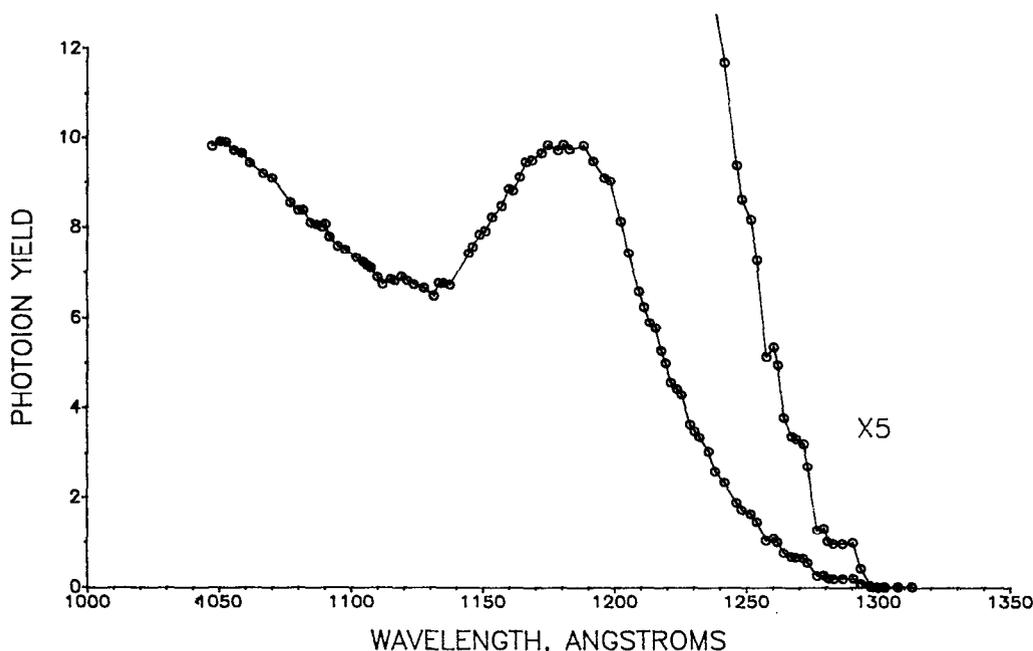

FIG. 1. The photoion yield curve of N$_2$H$_2^+$ (N$_2$H$_2$).

the adiabatic ionization potential obtained by PES $(9.59 \pm 0.01$ eV$)$.

C. N_2H^+ (N_2H_2)

Under the same conditions as III B (above), the M29 position was scanned. The threshold region for N_2H^+ (N_2H_2) is displayed in Fig. 2. The approach to threshold is linear, the onset occurring at 1137 ± 2 Å $\equiv 10.905 \pm 0.019$ eV. The sample was pyrolyzed at 70 °C, which was taken to be the temperature of the vapor. Hence, applying a correction for the internal thermal energy of N_2H_2, the 0 K threshold becomes 10.954 ± 0.019 eV. This value is consistent with the two electron impact thresholds (10.98 ± 0.05 eV[11] and 10.89 ± 0.08 eV[13]), but more precise and well defined with respect to temperature.

At 1047 Å $\equiv 11.84$ eV, the $N_2H^+/N_2H_2^+$ intensity ratio was 1/18.5.

D. N_2^+ and H_2^+ from N_2H_2

Even with the cleaner pyrolysis source, there was a persistent weak signal at M28 (attributed to an impurity) which masked the wavelength region of interest. Hence, we were unable to test the assertion of Willis et al.[11] that a threshold for N_2^+ could be observed, nor its negation by Foner and Hudson.[12] However, the M2 position did not suffer from this background. Furthermore, since IP (H_2) is 15.4259 eV,[10] and IP (N_2) is 15.5808 eV,[10] the H_2^+ (N_2H_2) threshold should be lower than N_2^+ (N_2H_2), in the absence of possible dynamic factors. It should be noted that both appearance potentials are expected to occur below their respective ionization potentials.

A weak H_2^+ signal was observed. At 810 Å $\equiv 15.31$ eV, the $H_2^+/N_2H_2^+$ intensity ratio was $\sim 1/200$–300. The photoion yield curve for H_2^+ (N_2H_2) is shown in Fig. 3. The approach to threshold is more gradual than that of N_2H^+ (N_2H_2) shown in Fig. 2. This is often the case for a higher energy process, and/or one which involves a tight complex. A smooth curve drawn through the last four points distinctly above the background level intersects the base line
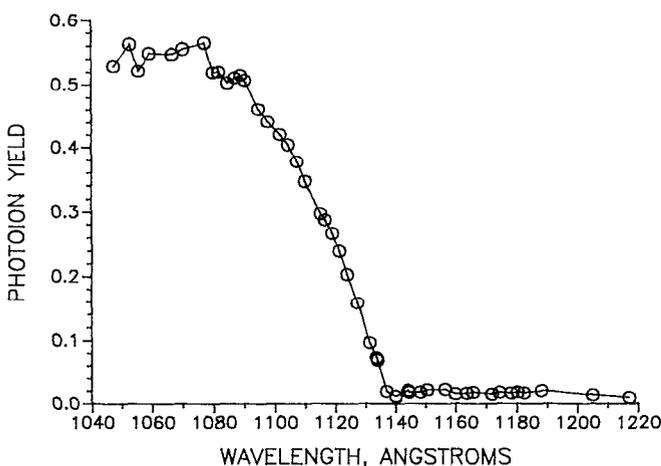
at 920 ± 2 Å $\equiv 13.47_7 \pm 0.03$ eV, or $13.52_6 \pm 0.03$ eV at 0 K. This is a clear upper limit for AP H_2^+ (N_2H_2). A more careful examination of the threshold reveals one additional lower energy point, still distinctly above background, but displaced from the smooth curve drawn through the four higher energy points. We choose as a less rigorous upper limit, but a probable value, the midpoint between the last significant point above background and the following point, i.e., 928.5 ± 2.5 Å $\equiv 13.353 \pm 0.036$ eV, or 13.403 ± 0.036 eV at 0 K.

E. $N_2H_3^+$ (N_2H_3)

The photoion yield curve of $N_2H_3^+$ (N_2H_3) is displayed in Fig. 4. The smooth curve is a spline function fitted to the experimental points. Steplike structure can be seen. The ion yield has not yet reached the background level at the longest wavelength (1620 Å) for which data points exist. Therefore, the adiabatic IP is < 7.65 eV. (With the grating used in these experiments, the light at longer wavelengths was extremely weak.)

Figure 5 is the energy derivative of the smooth curve, which should simulate a photoelectron spectrum if direct photoionization is the dominant mechanism. This derivative curve has peaks (in eV) at 7.81, 7.99, and 8.20 eV (± 0.01). The average spacing is 0.19_5 eV $\cong 1570 \pm 80$ cm^{-1}. If we take this spacing to be the dominant vibrational progression, then (since the photoion yield curve in Fig. 4 has not yet reached the background level) at least one more peak in this progression should exist, and consequently IP (N_2H_3) $\leqslant 7.61 \pm 0.01$ eV.

The integrals over peak intensities (or the step heights in Fig. 4), which we have assumed to be a Franck–Condon distribution of some vibrational progression, can be approximated by a Poisson distribution $(a^n/n!)e^{-a}$. The measured step heights form the proportion $0.38 : 0.95 : 1.00 : 0.67$, where 0.38 represents the sum of all possible step heights above ~ 1610 Å (below ~ 7.70 eV). We can calculate the expected relative intensities in a Poisson distribution corresponding to 1, 2, or 3 missing vibrational intensities at lower photon energy, and hence to adiabatic ionization potentials of $\sim 7.61 \pm 0.01$, $\sim 7.42 \pm 0.02$, or $\sim 7.22 \pm 0.03$ eV. From the ratio of step heights at 7.81 and 7.99 eV, a value for the parameter $a = 2.10$, 3.15, and 4.20, respectively, can be inferred. The resulting intensity patterns over the complete distribution can now be derived,

(1) $0.45 : 0.95 : 1.00 : 0.69$.
(2) 0.80 ($\equiv 0.20 + 0.60$) $: 0.95 : 1.00 : 0.79$.
(3) 1.08 ($\equiv 0.08 + 0.32 + 0.68$) $: 0.95 : 1.00 : 0.84$.

Pattern (3) can be ruled out, since this pattern deviates too strongly from their experimental one. Pattern (1) fits very well, pattern (2) less well. Hence, on the basis of the simple Poisson distribution, we select 7.61 ± 0.01 eV as the adiabatic ionization potential of N_2H_3. Pople and Curtiss[21] have calculated the structures of N_2H_3 and $N_2H_3^+$ in their ground states. They find that the N–N distance diminishes upon ionization by 0.112 Å, and hence one might expect the presumed vibrational progression in the experimental spectrum to be characteristic of an N–N stretching frequency.
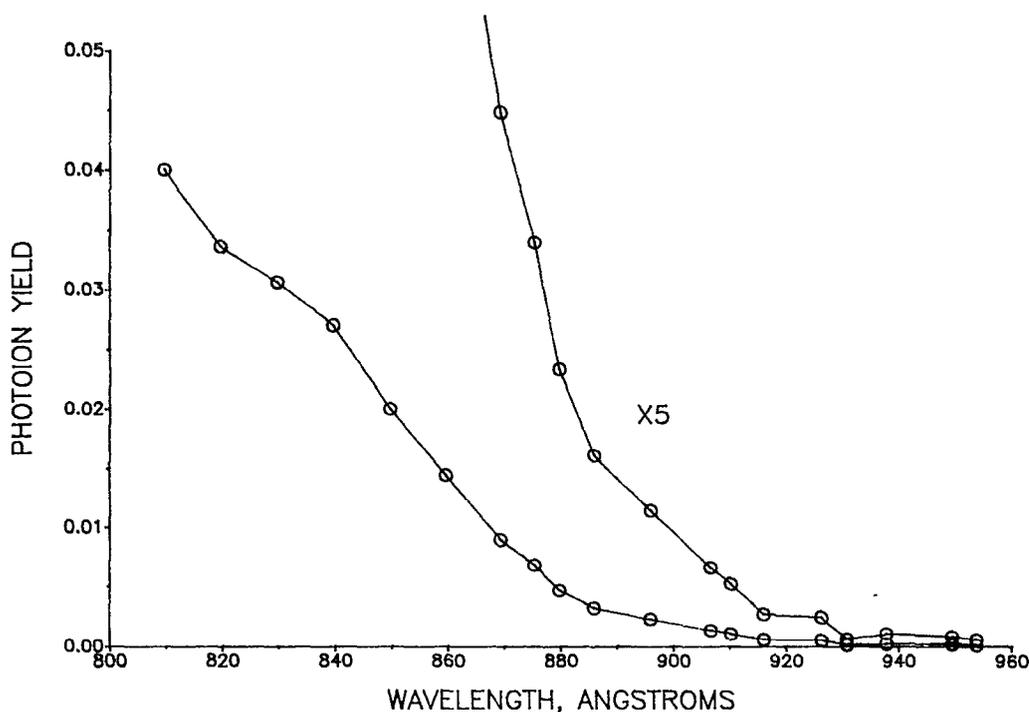

FIG. 2. The photoion yield curve of N_2H^+ (N_2H_2).

FIG. 3. The photoion yield curve of H_2^+ (N_2H_2).

The N–N stretching frequency in H_2N–NH_2 is only about 1100 cm^{-1},[22] considerably smaller than the observed spacing of 1570 $\pm$ 80 cm^{-1}. However, the N–N stretching frequency in HNNH is about 1530 cm^{-1} (Ref. 23), and that in trans H_3CN–NCH_3 is 1574 cm^{-1}. These latter molecules can be expected to exhibit N = N double bond characteristics, and hence have larger stretching frequencies. Perhaps surprisingly, the N–N distance in $N_2H_3^+$ calculated by Pople and Curtiss is 1.240 Å, whereas the N–N distance in trans-HNNH is found to be 1.252 $\pm$ 0.002 Å.[24] Hence, the observed frequency and the calculated N–N distance in $N_2H_3^+$ are characteristic of an N–N bond which is essentially a double bond.

IV. INTERPRETATION OF RESULTS
A. $\Delta H_f^0(N_2H_2)$

Of the various experiments attempted, the only one producing a significant result concerning ΔH_f^0 (N_2H_2) was AP H_2^+ (N_2H_2). The relevant energy relationship is

$$\Delta H_{f_0}^0(N_2H_2) = \Delta H_{f_0}^0(H_2^+) - \text{AP } H_2^+(N_2H_2),$$

where $\Delta H_{f_0}^0(H_2^+)$ is IP (H_2). Utilizing the two alternative values for AP H_2^+ (N_2H_2), we obtain

$$\Delta H_{f_0}^0(N_2H_2) \begin{matrix} > 43.8 \pm 0.7 \\ \geqslant 46.6 \pm 0.8 \end{matrix} \text{ kcal/mol,}$$
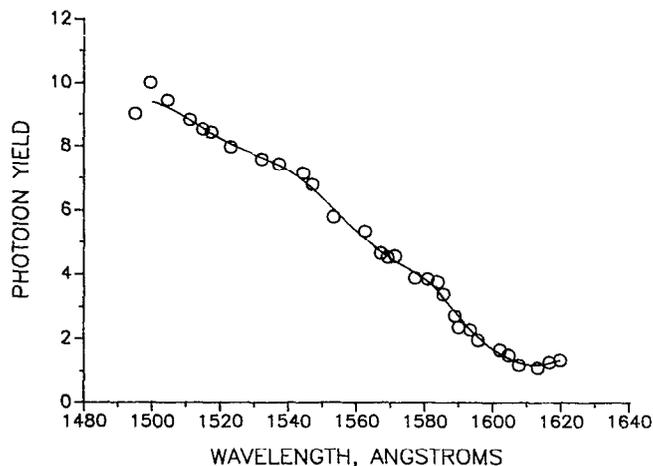
FIG. 4. The photoion yield curve of $N_2H_3^+$ (N_2H_3). The smooth curve is a spline function fitted to the data points.
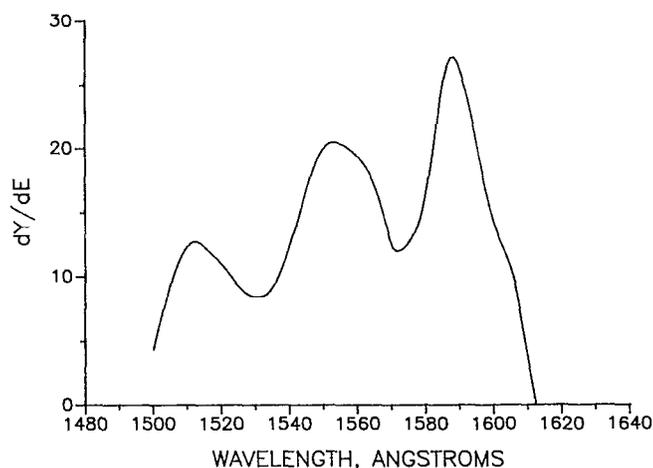
FIG. 5. The energy derivative of the smooth curve of Fig. 4, simulating a photoelectron spectrum of N_2H_3.

and (using the conversion from $\Delta H^0_{f_0}$ to $\Delta H^0_{f_{298}}$ given in Ref. 25),

$$\Delta H^0_{f_{298}}(N_2H_2) {> 42.1 \pm 0.7 \atop \geqslant 45.0 \pm 0.8} \quad \text{kcal/mol.}$$

B. $\Delta H^0_f(N_2H^+)$ and PA (N_2)

For $\Delta H^0_f(N_2H^+)$, the relevant energy relationship is

$$\Delta H^0_{f_0}(N_2H^+) = AP \ N_2H^+ (N_2H_2)$$
$$- \Delta H^0_{f_0}(H) + \Delta H^0_{f_0}(N_2H_2).$$

Utilizing our value for AP N_2H^+ (N_2H_2) = 10.954 $\pm$ 0.019 eV, the well-established[10] $\Delta H^0_{f_0}$ (H) and our derived limits for $\Delta H^0_{f_0}$ (N_2H_2), we obtain

$$\Delta H^0_{f_0}(N_2H^+) {> 244.8 \pm 0.8 \atop \geqslant 247.6 \pm 0.9} \quad \text{kcal/mol, or (Ref. 26),}$$

$$\Delta H^0_{f_{298}}(N_2H^+) {> 243.9 \atop \geqslant 246.7} \quad \text{kcal/mol.}$$

The proton affinity is conventionally compiled at 298 K. From $\Delta H^0_{f_{298}}$ (N_2H^+) and $\Delta H^0_{f_{298}}$ (H^+) = 365.7 kcal/mol, we obtain

$$PA \ (N_2) {< 121.8 \pm 0.8 \atop \leqslant 119.0 \pm 0.9} \quad \text{kcal/mol.}$$

These values, together with the results obtained by other methods directed at PA (N_2) are summarized in Table I.

TABLE I. Proton affinities of N_2 obtained from experiment and theory (kcal/mol).

	PA, 0 K	PA, 298 K
Type (i) experiment		
Willis, et al.[a]	(128.₇)[a]	(128.₇)
Foner and Hudson[b]		113.7 ± 2.5
Present results	< 120.4 ± 0.8	< 121.8 ± 0.8
	≤117.6 ± 0.9	≤119.0 ± 0.9
Type (ii) experiment		
Bohme et al.[c]		117.4 ± 0.7
Other combination[d]		118.0 ± 1.3
Lias et al.[e]		118.2
Ab initio calculation		
Forsen and Roos[f]	116.6	118.0
Vasudevan et al.[g]	119.6	121.0
DeFrees and McLean[h]	117.0	118.4
Kraemer et al.[i]	118.4	119.8
Pople and Curtiss[j]	116.8	118.2
Botschwina[k]	116.6	118.3
Ikuta[l]	118.7	120.1

[a] Reference 11. There is no distinction made here between PA (0 K) and PA (298 K).
[b] Reference 13.
[c] Reference 7.
[d] Δ PA (CO_2–N_2) from Ref. 7; PA (CO_2) from Ref. 8.
[e] Reference 9.
[f] Reference 29.
[g] Reference 30.
[h] Reference 32.
[i] Reference 33.
[j] Reference 21.
[k] Reference 31.
[l] Reference 34.

C. The N=N double bond energy

We assume that the energy relationship

$$N_2H_2 \rightarrow 2NH \qquad (1)$$

is representative of the N=N double bond energy. From a previous study,[16] $\Delta H^0_{f_0}$ (NH) = 85.2 $\pm$ 0.4 kcal/mol. Hence, the derived enthalpy for reaction (1) at 0 K is

$${< 126.6 \pm 1.0 \atop \leqslant 123.8 \pm 1.1} \quad \text{kcal/mol.}$$

D. $\Delta H^0_{f_0}(N_2H_3)$ and $D_0(H_2NNH–H)$

Earlier,[16] we had studied the reaction

$$N_2H_4 + h\nu \rightarrow N_2H_3^+ + H + e$$

in this laboratory, and obtained a threshold of 1121.2 ($\pm$ 1) $\mathring{A} \equiv 11.058 \pm 0.010$ eV. With an internal thermal energy correction of 0.054 eV this threshold becomes 11.112 $\pm$ 0.01 eV at 0 K. Upon subtracting from this quantity our selected adiabatic ionization potential of N_2H_3, 7.61 $\pm$ 0.01 eV, we obtain 3.50₂ $\pm$ 0.01₄ eV $\equiv$ 80.8 $\pm$ 0.3 kcal/mol for the dissociative reaction

$$N_2H_4 \rightarrow N_2H_3 + H.$$

Now taking $\Delta H^0_{f_0}$ (N_2H_4) = 26.13 $\pm$ 0.12 kcal/mol[27] and $\Delta H^0_{f_0}$ (H) = 51.634 kcal/mol, we obtain 55.3 $\pm$ 0.3 kcal/mol for $\Delta H^0_{f_0}$ (N_2H_3).

In Sec. IV A, we deduced $\Delta H^0_{f_0}$ (N_2H_2) $\geqslant$46.6 $\pm$ 0.8 kcal/mol. The preferred value for PA (N_2)₂₉₈ is 118.2 $\pm$ 1 kcal/mol (see Table I, vide infra), which can readily be related to $\Delta H^0_{f_0}$ (N_2H_2) = 47.4 $\pm$ 1.1 kcal/mol. From the latter value, and the aforementioned $\Delta H^0_{f_0}$ (N_2H_3) = 55.3 $\pm$ 0.3 kcal/mol, we infer D_0 (HNNH–H) = 43.8 $\pm$ 1.1 kcal/mol. The various ionization and appearance potentials, heats of formation, and bond energies discussed in this paper are summarized in Table II.

V. DISCUSSION AND CONCLUSIONS

The present results for PA (N_2), i.e., < 121.8 $\pm$ 0.8 and probably ≤119.0 $\pm$ 0.9 kcal/mol, based on a type (i) experiment, are now closer to the type (ii) value (118.2 $\pm$ 1 kcal/mol) than either of the two previous type (i) experiments cited. In their compilation, Lias et al.[9,10] have tried to recalculate PA (N_2) from the AP N_2H^+ (N_2H_2) given by Willis et al. and by Foner and Hudson, using a value for ΔH^0_f (N_2H_2) ostensibly obtained by an independent calculation (the reference is to Casewit and Goddard[28]). However, the value for ΔH^0_f (N_2H_2) used by Casewit and Goddard in their paper (see their Table IV) comes from Foner and Hudson.[12] A truly independent ab initio calculation has been performed by Pople and Curtiss,[21] who obtained $\Delta H^0_{f_0}$ (N_2H_2) = 49.6 kcal/mol, closer to our lower limit, $\geqslant$46.6 $\pm$ 0.8 kcal/mol.

Several ab initio calculations[21,29–34] have been directed at the determination of PA (N_2). These are summarized in Table I, together with the experimental results previously discussed. The calculated values usually refer to the minima of the respective potential wells, which we shall call PA

TABLE II. Ionization and appearance potentials, heats of formation, and bond energies for N_2H_n systems.

(A) Ionization and appearance potentials (eV) at 0 K	
$N_2H_4 \rightarrow N_2H_4^+ + e$	8.36 ± 0.03[a]
$N_2H_4 \rightarrow N_2H_3^+ + H + e$	11.112 ± 0.010[b]
$N_2H_3 \rightarrow N_2H_3^+ + e$	7.61 ± 0.01[c]
$N_2H_2 \rightarrow N_2H_2^+ + e$	9.589 ± 0.007[c]
	9.59 ± 0.01[d]
$N_2H_2 \rightarrow N_2H^+ + H + e$	10.954 ± 0.019[c]
	10.98 ± 0.05[e]
	10.89 ± 0.08[f]
$N_2H_2 \rightarrow H_2^+ + N_2 + e$	$\leqslant 13.403 \pm 0.036$[c]

(B) Heats of formation (kcal/mol at 0 K)	
N_2H_4	26.13 ± 0.12[g]
N_2H_3	55.3 ± 0.3[c]
N_2H_2	$> 46.6 \pm 0.8$[c]
	47.4 ± 1.1[h]

(C) Bond energies (kcal/mol at 0 K)	
$D_0(H_2NNH-H)$	80.8 ± 0.3[c]
$D_0(HNNH-H)$	43.8 ± 1.1[c]
$D_0(H_2N-NH_2)$	65.5 ± 0.4[b]
$D_0(HN-NH)$	$\leqslant 123.8 \pm 1.1$[c]

[a] M. E Akopyan, F. I. Vilesov, and A. N. Terenin, Izvest. Akad. Nauk USSR **27**, 1083 (1963).
[b] From Ref. 16, with internal energy correction.
[c] Present results.
[d] Reference 14.
[e] Reference 11.
[f] Reference 13.
[g] Reference 27.
[h] Based on PA $(N_2)_0 = 116.8$ kcal/mol (see Table I and text).

$(N_2)_e$. When zero point energies are included, the result becomes PA (N_2) 0 K. The zero point energy difference, when computed from the experimental frequencies of N_2H^+ [4–6] and N_2,[17] amounts to 6.45 kcal/mol. For consistency, we have used this quantity to correct each of the *ab initio* values of PA $(N_2)_e$ to PA (N_2) 0 K. Addition of 1.4 kcal/mol then gives PA $(N_2)_{298 K}$. The calculations of De-Frees and McLean, Pople and Curtiss, and Ikuta use a similar method, but Ikuta's calculation is at the MP3 level of perturbation theory, whereas the others are at a higher level. Hence, we assume that an extension of Ikuta's calculation would yield essentially the same value as the others using this method. With this proviso, five calculations result in PA $(N_2)_{298 K}$ between 118.0–118.4 kcal/mol. This range is in excellent agreement with PA $(N_2)_{298 K} = 118.2 \pm 1$ kcal/mol obtained from the type (ii) experiments, and also with the current type (i) experiment. The calculated values of Vasudevan *et al.* and (to a lesser extent) Kraemer *et al.* seem a bit high.

The N$=$N double bond energy obtained in this work

$$\left(\begin{array}{c} < 126.6 \pm 1.0 \\ \leqslant 123.8 \pm 1.1 \end{array} \text{kcal/mol} \right)$$

is more than Pauling's value[15] (100 kcal/mol), but still substantially smaller than the N$\equiv$N triple bond energy. The incremental increase between single and double bond now becomes

$$< 61.1 \atop \leqslant 58.3 \text{ kcal/mol,}$$

while that between triple and double bond is

$$> 98.5 \atop \geqslant 101.3 \text{ kcal/mol.}$$

Hence, the first and second bonds are more nearly equal, but the third bond is about 40 kcal/mol larger. Rather than concluding that the strength of the third bond is an indication of an abnormality in the structure of the nitrogen molecule, we prefer to view the discrepancy as a measure of the weakness of the first and second bonds, influenced as they are by the presence of N–H bonds.

We have found that D_0 (H$_2$NNH–H) $= 80.8 \pm 0.3$ kcal/mol. This is the closest we can come to "an N–H bond energy in N_2H_4". Previously,[16] we had found D_0 (N–H) $= 79.0 \pm 0.4$ kcal/mol, D_0(HN–H) $= 91.0 \pm 0.5$ kcal/mol, and D_0 (H$_2$N–H) $= 106.7 \pm 0.3$ kcal/mol. Hence, the N–H bond energy in N_2H_4 comes closest to the first H atom addition to nitrogen, and is quite far from the average bond energy in NH$_3$, 92.3 kcal/mol, which Pauling transferred to the hydrazine molecule in estimating the strength of the N–N single bond.

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