Ion Dissociation of Hydrazoic Acid Investigated by Synchrotron-radiation-based Photoionization Mass Spectrometry

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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 appearance energies observed here are all lower than the previously reported ones obtained with electron impact ionization,[1] which were the only ones available in the literature prior to this work. Our results can be compared to predicted dissociative ionization energies using literature values of neutral bond dissociation energies and fragment ionization energies and are generally found to be in good agreement with the results of such an analysis. We observe the appearance energy of the parent ion (HN_3^+) to be 10.56 ± 0.015 eV, substantially 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.

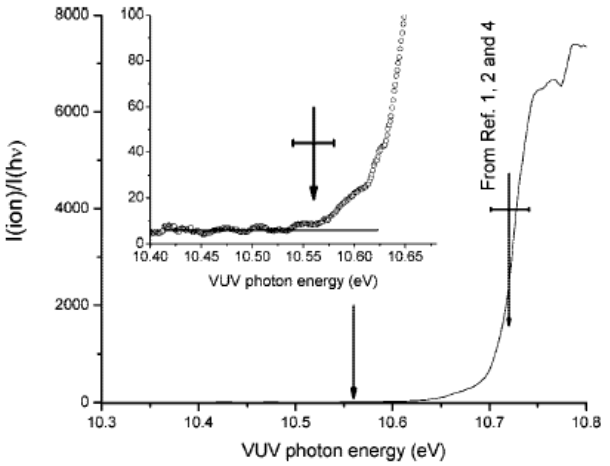

Fig. 1: Photoionization yield spectra for *m/z*) 43 ($HN3^+$), threshold region of reaction $HN_3 + h\nu \rightarrow HN_3^+ + e^-$, seeding ratio of 2% in He, using a pulsed valve.

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 kcal/mol ≤ PA(N_2) ≤ 121.4 kcal/mol. We also derive an upper limit to the ionization energy of N_2H (IE(N_2H) ≤ 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 $\Delta fH°0$ (HN3), nearly 5 kcal/mol larger than prior evaluations

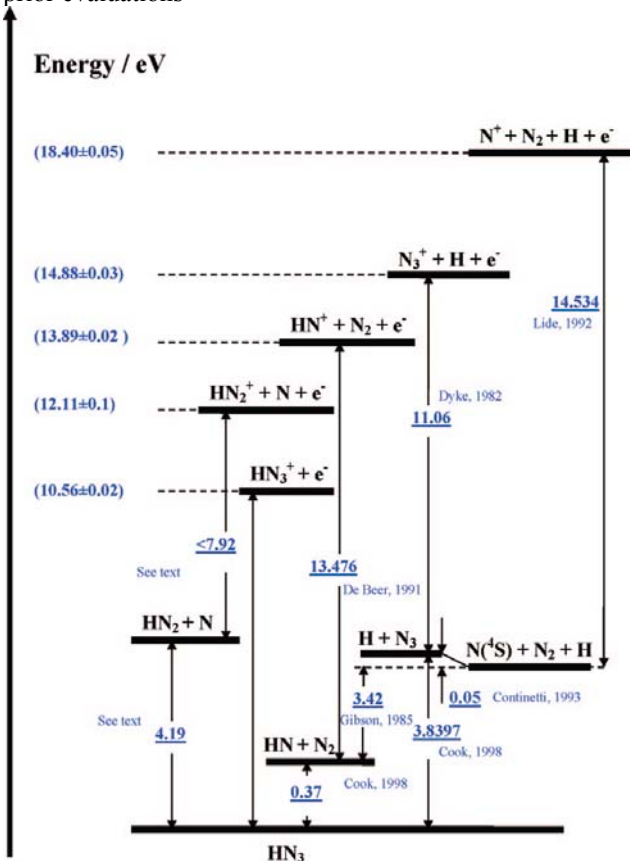

Fig. 2: Energy diagram for the hydrazoic acid dissociation study and summary of the results of this work and the literature review. The results derived from this work are shown in parentheses, while the literature values are underlined. See the text for further details.

Reference

[1] A. Q.-Hernandez, A. M. Wodtke,Y.-Y. Lee, T.-P. Huang, W.-C. Pan, and J. J. Lin, J. Phys. Chem. A **113**, 3822 (2009).