EXTENDING THE ABSOLUTE PROTON AFFINITY SCALE

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Accurate proton affinities (PAs) are important for the understanding of many chemical reactions. The extensive compilation of Hunter and Lias [1], which forms the basis of the NIST PA data base [2], lists values that range from 200 kJ/mol to well in excess of 1000 kJ/mol. The majority of these have been derived from relative gas-phase basicity measurements using equilibrium and bracketing techniques. Unfortunately the number of absolute reference PAs that have been obtained by experiment is minimal, spanning the relatively small range of 540 – 825 kJ/mol [1]. The Hunter and Lias evaluation lists just 21 species with a PA less than 540 kJ/mol, but approximately 1200 having a PA greater than 825 kJ/mol. Clearly it would be of great value to be able to extend this upper reference limit to minimize the unavoidable accumulation of systematic errors over such a large range. To this end we have used dissociative photoionization mass spectrometry to measure absolute PAs for several bases that increases the above high limit to more than 950 kJ/mol [3-5]. Apart from adding to the number of available anchor points, this expansion has reduced by 75% the number of compounds with tabulated PAs lying outside the range of absolute reference measurements. It also provides a set of experimental data to help evaluate the reliability of corresponding high-level *ab initio* molecular orbital calculations.

References

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