Decreasing uncertainties in photoionization mass spectrometry introduced by photoionization crosssections

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Photoionization-Molecular-Beam-Mass spectrometry has developed in the last ten years into a staple technic for the investigation of gas phase reactive systems including comprehensive Flame data, pyrolysis, micro reactors, crossbeam systems, photolysis reactors, jet stirred reactors and most recently a mini shock tube. The quantitative and already the qualitative results of all these experiments and many more rely heavily on the knowledge of ionizations properties of the investigated molecules (Thresholds, cross-sections, electronic structure of the ground and ion states, maybe even interaction between different components). The NIST Chemistry Webbook [1] only list ionization thresholds and fragment appearance energies stating all the measurements known to them and sometimes an evaluated value. Even this database is maintained only sporadically and already outdated to a large extend by measurements conducted by the above mentioned groups alone let alone other communities which also rely on such data and measure them as byproducts of their work. Most recently Fei Qi et al at NSRL made an attempt to gather all the published cross-sections in a database which the made available on the internet.[2] This list is by no means comprehensive as new cross-sections are generated every day and buried in files and databases which are used in specific collaborations and projects. Furthermore an evaluation if the cross-sections in respect to their accuracy and applicability to the different Experiments would be most useful. For instance it is known that the referencing is done differently by different groups, leading to different shape of a given photoionization efficiency curve measured on different machines although at the same beamline. Obtaining cross-sections by computational methods is a route employed recently. The calculations can yield cross-sections with reasonable trustworthiness. The problem is that this work either needs some serious time commitment by the scientist who needs the cross section or a computational chemist/physicist who normally does not have funding which this work can be performed on. This with the onset of usage of photoelectron photoion coincidence spectroscopy by the combustion community the need for reference data will increase even more. One possible route to establish, maintain and expand a crucial database of reference data like this is to share the load on many groups and via collaboration with the national metrology institutes whose core competence and scope are to establish traceability and reduction of uncertainties.

[1] http://webbook.nist.gov/chemistry/
[2] http://flame.nsrl.ustc.edu.cn/database/