High-Resolution Photoionization and Photoelectron Studies: Determination of Accurate Energetic Database for Combustion, Atmospheric, and Interstellar Chemistry

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We have developed a unique high-resolution vacuum ultraviolet (VUV) photoion-photoelectron facility at the Chemical Dynamics Beamline of the Advanced Light Source (ALS).[1] Using this facility, we have introduced novel synchrotron- based pulsed field (PFI) ionization-photoelectron (PFI-PE) schemes, attaining resolutions of 1-5 cm^{-1} (FWHM).[2] We have also established a generally applicable synchrotron-based PFI-PE-photoion coincidence (PFI-PEPICO) method for unimolecular dissociation studies of ions with internal energy resolutions only limited by the PFI-PE measurement.[3] Recent studies have shown that by combining PFI-PE and PFI-PEPICO measurements, highly reliable energetic data, such as ionization energies (IEs), 0 K AEs, 0 K bond dissociation energies (D_0's), and 0 K heats of formation (ΔH°_{f0}'s), for a range of small molecules and their ions can be obtained with unprecedented precision.[3-8] An improvement of this PFI-PEPICO scheme using the radio frequency octopole ion guide technique should made possible the application of the PFI-PEPICO scheme for accurate measurements of 0 K dissociative photoionization thresholds or appearance energies (AEs) for medium size molecules with dissociation lifetimes up to the millisecond ranges. In addition to our experimental effort at the ALS, we have also engaged in laboratory VUV laser ionization studies. A comprehensive VUV laser system [tunable range = 6-19 eV, optical bandwidth=0.12 cm^{-1} (FWHM)] based on four-wave sum- or difference-frequency mixing schemes, together with a reflectron time-of-flight mass spectrometer and a PFI-PE detector, has also been constructed and operational in our laboratory.[9] These developments have opened up a unique opportunity for initiating an experimental program for a systematic PFI-PE and PFI-PEPICO measurement of small and medium sizes molecules of relevance to combustion, plasma, atmospheric, and interstellar chemistry. The goal of this project is to obtain accurate IEs, 0 K AEs, D_0's, and ΔH°_{f0}'s, for selected polyatomic neutrals and their ions. These highly reliable energetic measurements would contribute to an indispensable database for the development of the next generation of *ab initio* quantum computational procedures.

References:

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