

Photoelectron Photoion Coincidence Spectroscopy for High-Accuracy Thermochemistry (···and More!)

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Photoelectron photoion coincidence (PEPICO) spectroscopy is a marriage of photoelectron spectroscopy and mass spectrometry. Electron / ion pairs are created by single photon ionization and the two charged species are measured in delayed coincidence with each other. Ions are selected in narrow range of internal energy by collecting only ions created in delayed coincidence with the photoelectrons. The use of the PEPICO technique is demonstrated on two systems. A) Methanol isotopologues were measured using iPEPICO and, from the four independent appearance energies from the isotopologue ions, very accurate heat of formation was determined for CH₂OH⁺. This value then yields the heat of formation of an important species in combustion processes, the CH₂OH radical. B) Protonation is arguably the most important basic chemical process and the proton affinity (PA) of water is a fundamental quantity in many areas. Yet, it is notoriously difficult to determine this number accurately. Using only very accurate literature spectroscopic data and two iPEPICO measurements, one on water and one on the water dimer leads directly to PA(H₂O) with an accuracy that is an order of magnitude better than the current literature value.

Photoionization mass spectrometry is a powerful detection method in gas-phase chemical kinetics. Tunable synchrotron light enables isomer separation based on unique photoionization (PI) spectra; however, mixtures of three or more isomers can be difficult to resolve by this method. By measuring the photoelectron spectrum corresponding to each cation m/z ratio, PEPICO spectroscopy provides a more detailed spectral fingerprint and higher isomer selectivity than PI spectra. Compared to PI spectra, the higher information content of mass-selected TPES spectra has been demonstrated for static mixtures and reacting systems and we believe this advance will be critical in achieving the next generation of highly multiplexed, isomer-resolved methods for time- or space-resolved chemical analysis.

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