

## PHOTOIONIZATION MASS SPECTROMETRIC MEASUREMENTS OF COMBUSTION-RELATED TRANSIENT AND METASTABLE SPECIES

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Photoionization mass spectrometry is a versatile tool providing a wealth of spectroscopic, structural and dynamical details as well as information needed to successfully detect and monitor various species in real-life processes. It can also provide, through the use of the positive ion cycle, reliable and accurate thermochemical quantities, such as bond dissociation energies and enthalpies of formation. In the simplest variant, thermochemistry can be deduced from two correlated studies: the first aims to determine the ionization potential of a transient species and the second measures a related fragment appearance potential from a stable parent molecule. While the former involves challenges entailed in measuring ephemeral species, the latter involves the understanding of the shape of the fragmentation threshold resulting from the underlying unimolecular decomposition process. The fitting procedures developed to aid the extraction of thermodynamically significant values for fragmentation thresholds will be exemplified using several recent determinations of combustion-related bond dissociation energies. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. W-31-109-ENG-38.