

Probing Combustion Chemistry with molecular beams and synchrotron radiation

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Single photon ionization with vacuum ultraviolet (VUV) photons is an efficient (and “soft”) method of ionizing fragile molecules, whereby the tunable radiation provides precise threshold ionization imparting little excess internal energy into the molecular ion.¹ Furthermore, tunable VUV ionization has been shown to be a selective, yet universal technique in elucidating molecule-specific information since it can resolve isomers via ionization energy (IE), absorption cross-sections follow rules which are quantifiable, and all molecules will ionize beyond its IE and hence can be detected in a mass spectrometer. In this talk I will describe two recent results showcasing how tunable synchrotron radiation allows for an understanding of molecular growth processes relevant to combustion.

We in collaboration with Ralf Kaiser (University of Hawaii, Manoa), and Alex Mebel (Florida International University) have performed systematic and extensive studies of two- and three-membered ring polycyclic aromatic hydrocarbons (PAHs)² utilizing a high temperature chemical reactor coupled to synchrotron based VUV photoionization mass spectrometry. Moving beyond these studies, the critical step in the understanding of the mass-growth processes from simple PAHs to soot particles is to unravel the synthesis of key building blocks as present in two- and three-dimensional precursors to soot: coronene and corannulene. In this talk I will describe our recent results on the formation of larger compounds (four ringed pyrene) generated from the reaction of the anthracenyl radical with acetylene.³

Working with Martin Head-Gordon (UC Berkeley, LBNL), we have formulated an understanding as to how non covalent interactions can drive chemical reactivity in small acetylene clusters upon photoionization. A dramatic dependence of product distribution on the ionization conditions is demonstrated experimentally and understood from simulations. The products change from reactive fragmentation products in a higher temperature, higher density gas regime towards a very cold collision-free cluster regime that is dominated by products whose empirical formula is $(C_2H_2)_n^+$, just like ionized acetylene clusters. Formation of the benzene cation is demonstrated in Ab-Initio Molecular Dynamics simulations of clusters of acetylene clusters with $n > 3$, as well as other metastable $C_6H_6^+$ isomers.⁴

I will conclude by discussing how water affects the photoionization properties of PAH's and how these studies could shed light on processes relevant to energy science and astrochemistry.

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