

JET COOLED LASER SPECTROSCOPY OF HYDROCARBON RADICALS AND MOLECULAR IONS IN SLIT SUPERSONIC EXPANSIONS

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The novel combination of pulsed slit supersonic expansions and pulsed electrical discharges results in a remarkably intense source of jet cooled chemical reactive species in a long path length geometry ideal for near shot noise limited direct absorption spectroscopy with high resolution tunable lasers. This proves particularly powerful in the near infrared, where the reduced Doppler linewidths in the slit jet permits rovibrational, open shell fine structure and sometimes even hyperfine structure to be resolved. Most importantly, this method provides access to spectra of transient species at very low temperatures (10K), which greatly simplifies the resulting spectroscopic assignment and analysis.

This talk will develop the background methodology of these slit discharge methods, and then discuss three sample hydrocarbon radical systems studied: from 1) the relatively simple methyl (CH_3) radical, which by virtue of sub-Doppler linewidths permits both Fermi contact information on gas phase spin densities to be extracted for the first time and elucidates the effects of spin polarization through CH molecular bonds, 2) the more complicated ethyl (CH_3CH_2) radical, which exhibits strongly coupled large amplitude motion between wagging of the CH_2 radical center and internal rotation around the C-C bond, to 3) the allyl (CH_2CHCH_2) radical, which represents the fundamental paradigm for electron delocalization in a π system. Time permitting, recent extensions to high frequency discharge modulation techniques and applications to jet cooled molecular ion spectroscopy will also be discussed.