# ROTATIONAL SPECTROSCOPY OF ORGANIC RADICALS AND CARBENES RELEVANT TO COMBUSTION

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Spectroscopy at centimeter and millimeter wavelengths provides unambiguous identification and accurate structures of complex radicals and carbenes that form when stable hydrocarbons disintegrate in the hostile environment of combustion systems. Kineticists modeling combustion systems often rely on quantum theoretical calculations to obtain estimates of the thermochemical properties of radical species, however our work shows that the theoretical structures of open-shell molecules are uncertain when there is a low-lying excited electronic state. Forty-six new reactive organic molecules, including 13 metastable isomers, have been detected in supersonic molecular beams with a sensitive Fourier transform microwave (FTM) spectrometer and the densities of the reactive species have been determined fairly precisely. We think that most of the precursors to the PAHs and other carbon clusters observed in flames with up to about $10 - 15$ carbon atoms can probably be detected by the present technique or refinements thereof. The FTM studies lay the ground work for the development of laser diagnostic probes of flames, because they establish a means for producing reactive molecules in supersonic molecular beams at densities that are high by the standards of modern laser spectroscopy. Finally, we will discuss the feasibility of using millimeter-wave spectroscopy to probe the same collisionless supersonic molecular beam of stable molecules and free radicals formed from "standard" flames characterized by mass spectrometry.