

INVITED LECTURES, C1

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Fourier-transform and cw-laser spectroscopies of matrix isolated  
radicals and ions

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Abstract not available.

LASER SPECTROSCOPY OF COLD, REACTIVE CHEMICAL  
INTERMEDIATES

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The spectroscopic detection and characterization of chemical intermediates, e.g., free radicals, is a basis for the fundamental understanding of their structure and reactivity as well as being a prerequisite for spectroscopic diagnostics of complex chemical reactions. The methoxy family,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3\text{S}$ ,  $\text{CF}_3\text{O}$ , and  $\text{CF}_3\text{S}$  is a most interesting set of chemical intermediates from a number of perspectives. We have prepared these radicals at very low temperatures in a supersonic free jet expansion and have used a variety of laser based spectroscopic techniques to probe the rovibronic structure of their ground  $\tilde{X}^2\text{E}$  and lowest excited  $\tilde{A}^2\text{A}_1$  states. Our results include geometric structures in both states based upon detailed rotational analyses. The vibrational structure of both electronic states has been characterized including the effects of Jahn-Teller interactions in the  $\tilde{X}$  state. Recent experiments have additionally characterized "dark" photochemically active levels in the  $\tilde{A}$  state. These results demonstrate the extreme mode and frequency selectivity of photofragmentation in these radicals.