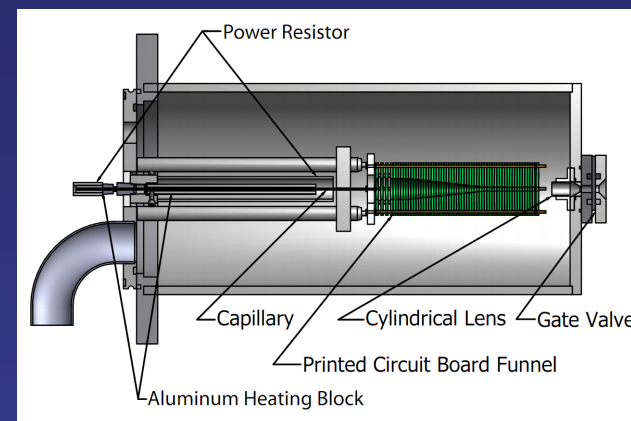


# Energetics and dynamics of biofuel reactive intermediates

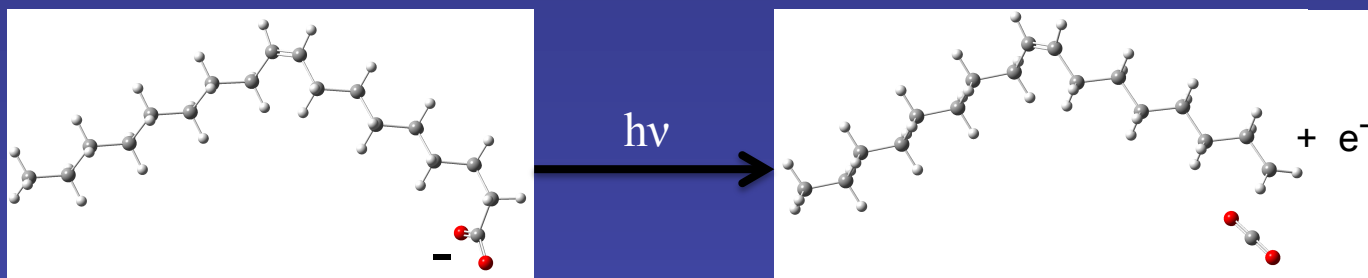
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This New Directions grant supports the investigation of the energetics and dynamics of reactive intermediates formed from long-chain esters and fatty acids prevalent in many biofuels. Relatively large oxygenated organic molecules such as the ester methyl linoleate ( $C_{19}H_{32}O_2$ ) typically form major fractions of biodiesel fuels. Fundamental experimental data on these species and reactive radicals derived from them is sparse. The goal of this project is to provide fundamental information including the heats of formation, electron affinities, and dissociation dynamics of the reactive radicals produced by hydrogen abstraction from a range of biofuel component molecules. This involves the use of negative ion photoelectron spectroscopy and photoelectron-photofragment coincidence (PPC) spectroscopy. The experimental efforts have focused on the incorporation of an electrospray ionization (ESI) ion source and an ion funnel onto an existing PPC spectrometer, and are nearly complete. The experimental efforts are being guided by DFT calculations (B3LYP/6311+G(d,p)) on the structure and energetics of these species. Interestingly, we found that even for molecules of this size the carboxylate radicals are often predicted to eliminate carbon dioxide when produced by photodetachment as shown in the figure below. The PPC experiment will allow us to experimentally probe such processes.



Electrospray Ionization Source and Ion Funnel for coupling to Photoelectron-Photofragment Coincidence Spectrometer



Dissociative photodetachment of the 18,1 Oleate Anion: Predicted elimination of  $CO_2$  from the neutral carboxyl radical