

Near-Infrared Cavity Ringdown Spectroscopy of Intermediates in Complex Chemical Reactions

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A difficult challenge for any spectroscopic technique is the observation, characterization, and quantification of weakly absorbing molecular species in complex chemical mixtures. The species of interest may be weakly absorbing due to either low concentration or low oscillator strength, or a combination of both. Complex chemical mixtures have the additional difficulty of interference from typically stronger absorptions from other molecules. Near-infrared cavity ringdown spectroscopy (NIR-CRDS) offers a powerful tool to address these challenges. The NIR is a convenient spectral window, lower in frequency than the electronic transitions of most non-reactive molecules and containing only weak combination and overtone vibrational bands. However electronic transitions of many reactive chemical species fall into the NIR due to their open-shell electronic nature. The lowest singlet-triplet transitions of molecules are often in this region, e.g. the singlet-triplet transition of O₂ which is important in fields as far separated as atmospheric chemistry and photochromatic cancer therapy. Key oxidation intermediates in combustion often have low-lying electronic transitions, e.g. the peroxy radicals, RO₂, where R is any hydrocarbon functional group, like methyl, ethyl, etc. Atmospheric pollutants, like NO₃, likewise have a NIR electronic transition. This talk will discuss NIR-CRDS of both room temperature and jet-cooled reactive chemical intermediates. It will show the nature of the spectra at both temperatures. It will further discuss the analyses of the spectra and the information resulting therefrom as well as its significance for several areas, including chemical diagnostics and the benchmarking of electronic structure calculations.