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Nanosecond Mid-Infrared Detection for Pulse Radiolysis

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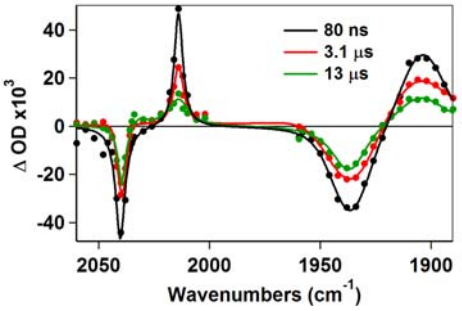
Pulse radiolysis, utilizing electron pulses from accelerators, is the definitive method for adding single positive or negative charges to molecules. It is also among the most effective means for creating free radicals. Such species are particularly important in applications such as redox catalysis relevant to solar energy conversion and advanced nuclear energy systems. Coupled with fast UV-visible detection, pulse radiolysis has become an extremely powerful method for monitoring the kinetics of the subsequent reactions of these species on timescales ranging from picoseconds to seconds. However, in many important contexts the radicals formed are difficult to identify due to their broad and featureless UV-visible absorption spectra. Time-resolved infrared (TRIR) absorption spectroscopy is a powerful structural probe of short-lived intermediates, which allows multiple transient species to be clearly identified and simultaneously monitored in a single process. Unfortunately, due to technical challenges the coupling of fast (sub-millisecond) TRIR with pulse radiolysis has received little attention, being confined to gas-phase studies.[1,2] Taking advantage of recent developments in mid-IR laser technology, we have recently begun developing nanosecond TRIR detection methodologies for *condensed-phase* samples at our Laser Electron Accelerator Facility (LEAF). The results of preliminary pulse radiolysis-TRIR investigations on the formation of the one-electron reduced forms of CO_2 reduction catalysts (*e.g.* see above) and their interactions with CO_2 will be presented.



TRIR spectra recorded after pulse radiolysis of $[Re(bpy)(CO)_3(CH_3CN)]^+$ in acetonitrile under argon.

References:

1. H. A. Schwarz, *J. Chem. Phys.* **1977**, *67*, 5525-5534; *J. Chem. Phys.* **1980**, *72*, 284-287.
2. P. Pagsberg, J. T. Jodkowski, E. Ratajczak, A. Sillesen, *Chem. Phys. Lett.* **1998**, *286*, 138-144, and refs. therein.