

# Studies of *trans*-DOCO by Mid-IR Time-Resolved Frequency Comb Spectroscopy

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Spectral multiplexing techniques such as broad-band cavity enhanced absorption spectroscopy and step-scan FTIR are powerful tools in kinetics that allow one to observe the time-resolved spectra of reactants, intermediates and products over a wide spectral band. The recent development of optical frequency comb lasers take advantage of the phase coherence of stabilized ultra-fast lasers to provide enhanced sensitivity and spectral resolution for time-resolved spectroscopy of gas phase molecules. The Ye group at Boulder has developed a Mid-Infra-Red Time-Resolved Frequency Comb Laser Spectrometer (TRFCS) with applications in the study of the spectra and kinetics of free radicals. In this system, high-resolution frequency combs are generated as the coherent output of a stabilized mode-locked laser. Pulsed-laser-photolysis (PL) experiments are performed in a slow flow cell enclosed in a high-finesse cavity. The frequency comb output is matched to the modes of the external cavity for cavity-enhanced absorption detection of radical spectra with 25-50  $\mu$ s time resolution and 0.01  $\text{cm}^{-1}$  spectral resolution, with minimum detectable concentrations on the order of  $10^{11} \text{ cm}^{-3}$ .

The reaction of OH + CO plays a central role in the chemistry of the atmosphere as well as in combustion and has been studied extensively. This reaction possesses an anomalous temperature dependence, and is known to proceed through an energized HOCO intermediate; reaction can form either H + CO products or HOCO intermediates; it serves as a benchmark for examining fundamental kinetics on complex potential energy surfaces. Detailed master equation calculations rely on fitting the temperature and pressure dependences. In this work, we describe experiments which seek to exploit the sensitivity, temporal and spectral resolution, and broad-band coverage of TRFCS to detect directly the DOCO intermediate both in the photolysis of acrylic acid and in the reaction OD + CO.

## References

- (1) Fleisher, A.J.; Bjork, B.J.; Bui, T.Q.; Cossel, K.C.; Okumura, M.; and Ye, J. *J. Phys. Chem. Letters*, **2014**, 5, 2241-1146.