TIME-RESOLVED FREQUENCY COMB SPECTROSCOPY OF TRANSIENT FREE RADICALS IN THE MID-INFRARED SPECTRAL REGION

BRYCE J BJORK, *Department of Physics, JILA - University of Colorado, Boulder, CO, USA*; ADAM J. FLEISHER, *Materials Measurement Laboratory - Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD, USA*; BRYAN CHANGALA, *Department of Physics, JILA - University of Colorado, Boulder, CO, USA*; THINH QUOC BUI, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; KEVIN COSSEL, *JILA, National Institute of Standards and Technology and Univ. of Colorado Department of Physics, University of Colorado, Boulder, CO, USA*; MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; JUN YE, *JILA, National Institute of Standards and Technology and Univ. of Colorado Department of Physics, University of Colorado, Boulder, CO, USA*.

The chemical kinetics of transient free radicals, such as HOCO and Criegee intermediates, play important roles in combustion and atmospheric processes. Establishing accurate kinetics models for these complex systems require knowledge of the reaction rates and lifetimes of all molecules along a particular reaction pathway. However, standard spectroscopic techniques lack a combination of sensitivity, frequency resolution, and adequate temporal resolution to survey these reactions on the μs timescale. To answer this challenge, we have developed time-resolved frequency comb spectroscopy (TRFCS). This novel technique allows for the detection of transient intermediates with high time-resolution and sensitivity while also permitting the direct determination of rotational state distributions of all relevant molecules. We demonstrate this technique in the mid-infrared spectral region, at 3.7 μm, by studying the photolysis of deuterated acrylic acid. We simultaneously observe the time-dependent concentrations of photoproducts trans-DOCO, HOD, and D_2O, identified through their unique rovibrational structure, with 5×10^{10} molecules cm^{-3} sensitivity, and with a time resolution of 25 μs. We aim to apply this technique to detect directly the formation of the DOCO intermediate in the OD + CO chemical reaction at atmospherically relevant pressures, in order to validate statistical rate models of this reaction.