Time-Resolved Broadband Cavity-Enhanced Absorption Spectroscopy: a new tool for Chemical Kinetics

Leonid Sheps
Sandia National Lab, Livermore, CA

I will describe a new apparatus, constructed recently with the goal of developing novel probe methods for the study of short-lived radical intermediates in a wide range of gas-phase reactions. This approach brings a unique combination of capabilities to our experimental chemical kinetics toolkit: good time resolution, simultaneous detection of multiple species, sufficient sensitivity for dilute gas samples, and fast data acquisition. The apparatus is based on a moderate-finesse optical cavity that uses a continuous white-light probe radiation source (Xe arc lamp) and operates over broad wavelength ranges of 300 - 450 nm or 370 - 700 nm. The cavity is integrated into a flow chamber, where chemical reactions are initiated by laser photolysis. The cavity output is monitored by a CCD detector that records the time evolution over the entire spectral range for every photolysis laser shot. The spectra are averaged directly on the CCD chip, enabling the acquisition of transient absorption data with sub-nm spectral resolution and microsecond time resolution at high repetition rates in a simple, robust, and inexpensive experimental setup. I will also cover the application of this technique to our studies of Combustion and Atmospheric Chemistry. I will focus specifically on the spectroscopy and reactivity of Criegee intermediates - an elusive class of carbonyl oxides, formed in ozonolysis reactions of unsaturated hydrocarbons in the Earth's troposphere. These highly reactive transient species may influence the global budgets of VOCs, NO_x, SO_x, and OH, yet direct studies of their reactivity have only recently became feasible. Our work on the transient UV spectroscopy of two prototype Criegee intermediates, formaldehyde oxide (CH_2OO) and acetaldehyde oxide (CH_3CHOO), sheds light on their complex electronic structure and allows direct measurements of their reactions with SO_2, water, carboxylic acids, and other potentially important tropospheric compounds.