Abstract

The objective of this investigation is to further develop the Cavity Enhanced Magneto-Optic Rotation (CEMOR) laser spectroscopy technique for measuring the small peroxy radicals in combustion systems. CEMOR combines the sensitivity of Cavity Ringdown Spectroscopy (CRDS) with the selectivity of Magneto-Optic Rotation (MOR) to allow sensitive and selective measurements of paramagnetic species (e.g., OH and HO₂) in spectral regions with interferences from stable diamagnetic species (e.g., CO and CO₂). Previous work in our laboratory utilized CEMOR for selective detection of OH in the A²Σ⁺-X²Σ⁻(0,0) vibronic band near 308 nm, demonstrating an improvement in sensitivity of the MOR technique to detect weakly absorbing paramagnetic molecules in a region congested by diamagnetic molecules. In our flash photolysis cell facility, we have also generated and measured HO₂ using a pulsed Nd:YAG/OPO laser. The present work represents the next step in development of the CEMOR diagnostic. Specifically, this experimental study explores the increase in resolution by application of a narrow bandwidth DFB telecom laser near 1430 nm to measurement of HO₂ in our flash photolysis facility using continuous wave CRDS and continuous wave CEMOR. Following this effort, the photolysis cell will be used to provide HO₂ and RO₂ calibration of the diagnostics including high resolution spectroscopy for these species and then application of CEMOR to quantification of OH, HO₂, and RO₂ in combustion systems.

Motivation

Combustion is the main energy utilization method: 80 quadrillion BTU in 2014, 81% of U.S. energy consumed comes from fossil fuels. In order to minimize the environmental impact from combustion, efficiency gains and emissions reduction methods need to be implemented. New engine designs which are more efficient and produce fewer emissions depend on control through reaction chemistry. The reaction chemistry in premixed and cool flame conditions is controlled by radicals OH, HO₂, and RO₂. The HO₂ and RO₂ radicals are difficult to measure due to their small absorption cross section and interference from stable species, specifically H₂O and CO₂.

Fortunately, these radicals (HO₂ and RO₂) interact with a magnetic field (they are paramagnetic) while the stable species (H₂O and CO₂) do not. CEMOR spectroscopy can sensitively and selectively measure combustion radicals by combining Magneto-Optic Rotation and CRDS.

Oxidation Process

A. Low temperature regime – Chemical synthesis that produces oxygen-containing organic molecules
   - Oxidation can only occur through the agency of initiators or catalysts, otherwise reaction rates are negligibly slow
   - RO₂ controls oxidation process

B. Intermediate temperature regime – Pale blue emissions characteristic of peroxides and formaldehyde
   - Reaction rates are much slower than high temperatures
   - HO₂ and OH controls oxidation process

C. Intermediate temperature regime – Negative temperature coefficient (NTC) for the reaction rate
   - Reaction rates slow down until a complete stop

D. High temperature regime – Explosion
   - OH, O, and H controls oxidation process

Conclusion

CEMOR has demonstrated sensitivity and selectivity in measurement of OH in a slot burner flame. HO₂ can be generated and measured in the Flash Photolysis Cell using CRDS. Pulsed Nd:YAG laser bandwidth is too broad to measure vibronic spectral features of HO₂.

Continuous wave DFB lasers offer promising solutions to resolve vibronic spectra.

Future Work

Apply cw-CRS and cw-CEMOR to Flash Photolysis Cell to measure [HO₂] and create calibration data. Use calibration data to make [HO₂] measurements using cw-CEMOR.

Seed controlled amounts of H₂O vapor in with HO₂ and demonstrate selectivity of cw-CEMOR.