FARADAY ROTATION SPECTROSCOPY OF HO_2 FROM AN ATMOSPHERIC FLOW REACTOR

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The hydroperoxyl radical (HO_2) is a key reactive intermediate in the low-temperature ($<$1000 K) and high pressure ($\geq$1 atm) oxidation chemistry of hydrocarbons and oxygenated fuels. Chemical kinetic models have been developed for a number of fuels in the low-temperature and high-pressure regime, but validation of these models relies on quantitative measurements of radical intermediates such as HO_2. In situ optical measurements of HO_2 at high-pressure ($\geq$1 atm) by absorption spectroscopy are complicated by spectral overlap from non-radical species. Faraday rotation spectroscopy (FRS) is a sensitive magneto-optical dispersion-based technique that can be used to selectively observe signals from radicals while strongly suppressing signals from non-radicals,[a] effectively eliminating the problem of spectral overlap at high-pressures.

Recently FRS has been used in the first direct measurements of HO_2 at the exit of an atmospheric flow reactor during the oxidation of dimethyl ether (DME). An external-cavity quantum cascade laser was used to record FRS spectra of Q-branch transitions in the ν_2 vibrational band at 7.14 μm. To describe the experimental signals a numerical spectral model was developed using line positions and intensities provided by the HITRAN 2008 spectral database. HO_2 concentrations were determined through non-linear fitting of the spectral model to the experimental spectra. In this talk the non-linear fitting of the FRS spectra to the numerical model will be presented, and the measured temperature dependence on the concentration will be compared to results from chemical kinetic modeling of DME oxidation.

[a] Litfin et al., *J. Chem. Phys.* **72**, 6602 (1980).