HO_2 Radical Measurements in a Photolysis Reactor using Line-Locked Faraday Rotation Spectroscopy

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Abstract: We report measurements of HO_2 radicals using wavelength modulated Faraday Rotation Spectroscopy in a multi-pass photolysis reactor. The current setup enables line-locked measurements to improve sensitivity and time resolution compared to the line-scanning system.
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1. Introduction

Tunable diode laser absorption spectroscopy (TDLAS) performed in the fingerprint spectral region (mid-infrared) has been widely employed in kinetic studies for *in-situ* gas concentration measurements. However, measuring active intermediate radicals such as HO_2 in a combustion setting is challenging due to spectral interference from water vapor and hydrocarbons. Therefore, Faraday rotation spectroscopy (FRS) is used to selectively detect paramagnetic molecules with strongly suppressed spectral interference from non-paramagnetic species [1,2]. In this work, we implement wavelength modulation on the experimental system reported in [3,4] to allow continuous line-locked measurements of HO_2 using FRS.

2. Photolysis system setup

Fig. 1 illustrates our setup. A UV photolysis laser (266 nm) is used to generates $O(^1D)$ atoms from O_3 and enables the formation of radicals (HO_2 and OH) by reacting with fuels. The photolysis reactor also serves as a Herriot multi-pass cell (MPC) with 21 passes for the quantum cascade laser (QCL) operating at 7.2 µm. A solenoid is placed around the photolysis reactor to generate an axial magnetic field (~300 G at the center of the reactor) that is utilized for FRS measurements. Accounting for 21 passes through the reactor and considering the overlap between the QCL and UV beam, the FRS signal is generated over an effective pathlength of ~6.3 m (limited by solenoid length of 30 cm) while the TDLAS signal is attributed to a pathlength of ~7.5 m.

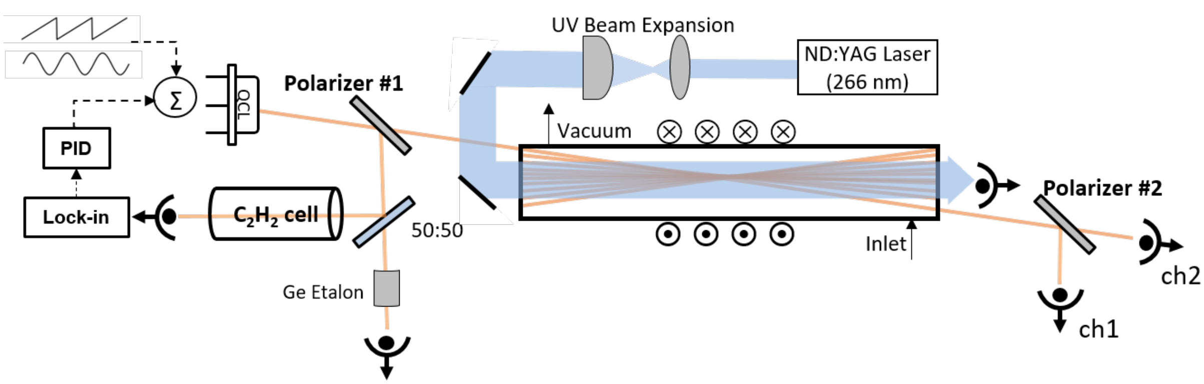

Fig. 1: System setup. The photolysis reactor is equipped with a 21-pass Herriot cell for the mid-IR probe beam while allowing the ultra-violet (UV) photolysis beam directly through the center of the cell. A solenoid around the center region of the cell generates an axial magnetic field for FRS. Polarizer #1 ensures linearly polarized light incident on the cell while Polarizer #2 is used to split the exiting beam into orthogonal polarizations, each of which is detected by a photodetector (PVI-4TE-8, VIGO). A reference cell filled with C_2H_2 is used for frequency reference through the 2nd harmonic signal from a lock-in amplifier (SR7280). A germanium etalon is also used for line-scanning measurements to correct for nonlinear laser frequency scanning.

2. Line-locked HO_2 detection

In FRS, the presence of paramagnetic species results in polarization rotation of the incident light. As Fig.1 shows, Polarizer #1 ensures linear polarization upon entering the MPC while Polarizer #2 is set to 45˚ with respect to the incident polarization angle, allowing roughly equal splitting of the *p* and *s* polarizations. In the wavelength modulated case, the digitized signals from the two detectors are individually demodulated in signal post-processing using

MATLAB, and the 2nd harmonic signals are digitally balanced to compensate for detector gain mismatch between the two detectors. Fig. 2a. shows the demodulated 2nd harmonic spectra corresponding to the *s* and *p* polarizations, where common-mode spectral interference from C_2H_2 within the photolysis cell is dominant. The FRS spectrum plotted in Fig. 2b is obtained from the differential signal between the *s* and *p* polarizations shown in Fig. 2a. Note that effective suppression of C_2H_2 interference is achieved in the demodulated FRS spectrum.

Although HO_2 is a highly reactive and unstable species, frequency reference can be obtained using a stable gas such as C_2H_2 (also used here as a fuel, which clearly has absorption features that closely coincide with HO_2 absorption lines). In this case, the 2nd harmonic signal of a nearby C_2H_2 transition conveniently provides a linear slope for laser frequency stabilization. The C_2H_2 is used in the reference cell at experimentally determined optimum pressure of 100 Torr to provide a suitable HO_2 line-locking location marked on the left wing of the 2nd harmonic wavelength modulation spectra shown in Fig. 2b.

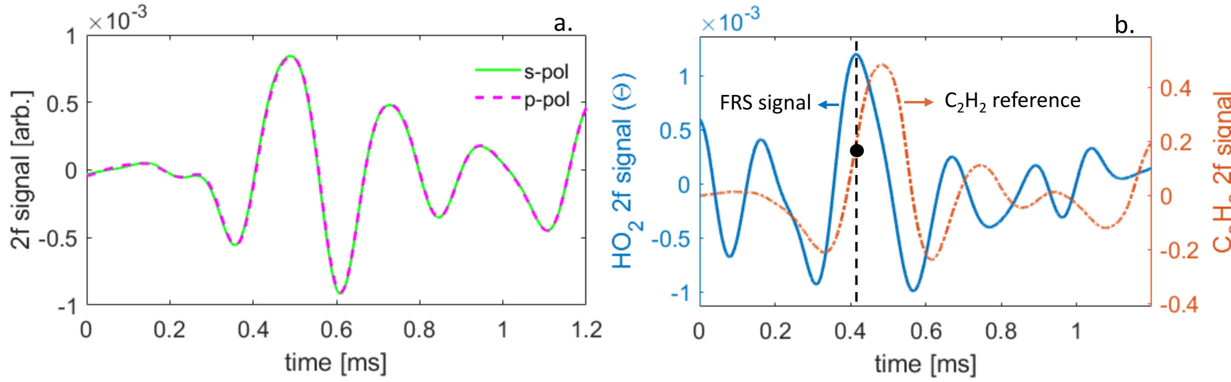

Fig. 2: a) Digitally balanced spectra corresponding to the *s* and *p* polarizations. b) The 2nd harmonic FRS signal of HO_2 acquired simultaneously with the C_2H_2 reference signal. The line-locking position is labeled in black.

3. Conclusion

With line-locked detection scheme, fast and convenient data analysis allows for instant concentration retrieval of HO_2 following each photolysis event. HO_2 detection sensitivity is enhanced from 1.9 ppmv for line-scanning mode to 1.2 ppmv for line-locked mode obtained with averaging of 100 photolysis events. In addition, time resolution within the single photolysis event is improved from 100 µs to 20 µs in a line-locked mode and can be further improved with faster laser modulation.

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4. References

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