Simultaneous measurement of outdoor O_2, CO_2, and CH_4 with a dual-comb spectrometer

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Abstract: We configure a fiber-laser based dual-comb spectrometer to measure the O_2 delta band (1260 nm) in addition to CO_2 and CH_4 absorption features (1600 nm). Work of the US Government and not subject to copyright.

Dual-comb absorption spectroscopy (DCS) is a proven method to monitor outdoor carbon dioxide and methane concentrations [1]. One remaining challenge limiting accuracy of optical outdoor measurements is determining the total air mass over a path that may have pressure variations. To date, high precision dual-comb measurements of greenhouse gases have relied on pressure measurements from a co-located pressure sensor for this critical input. However, as dual-comb is deployed over longer or vertical paths this pressure sensor approach may not be feasible as the assumption of a homogenous pressure across the path is almost certainly invalid. Fortunately, path averaged pressure can also be determined with high fidelity with a simultaneous O_2 measurement, an approach long used by solar-based spectrometers [2]. DCS light has been frequency-doubled to measure oxygen features at 770 nm [3]. We instead measure the O_2 delta ($a^1\Delta_g$-$X^3\Sigma^-_g$) band (1240-1290 nm, 7800-8000 cm^{-1} [4]). This band allows us to safely launch more free-space light, and to measure longer distances before the absorption features saturate.

To produce the supercontinuum light, we first temporally compress the amplified comb light in PM1550 fiber, then pass the light through 50cm of low-dispersion (+2.3 ps/nm/km) highly nonlinear fiber. Pulse power and chirp into the nonlinear fiber were designed to produce a dispersive wave at 1265 nm and self-phase-modulated light throughout 1400-1700 nm. The light is spectrally filtered using the setup in Fig. 1, in order to maximize the optical power in the O_2, CO_2, and CH_4 absorption bands while satisfying the free-space eye-safe limit. To maintain an all-fiber setup, a wavelength-division multiplexer (WDM) separates the CO_2/CH_4 light from the short-wavelength O_2 light, and a second WDM removes the light from 1400-1560 nm before a final WDM recombines the CO_2 and O_2 wavelengths. In this configuration, each comb produces 6.0 mW of filtered light, of which 20% is in the O_2 band (1240-1290 nm) and 30% is in the CH_4 band (1640-1690 nm).

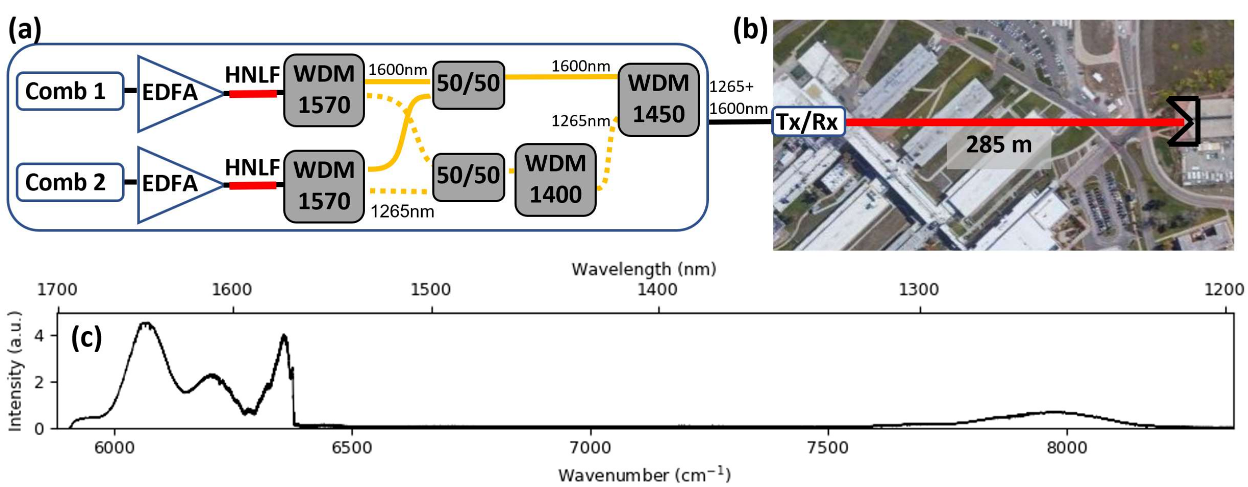

Figure 1: (a) All-fiber setup for comb generation, filtering, and combining. Highly nonlinear fiber (HNLF) produces supercontinuum light from 1200-1800 nm. Wavelength-division multiplexers (WDM) reflect light below the labelled transition wavelength (nm). (b) Transmit/receive (Tx/Rx) telescope launches light out window on round-trip path to retroreflector placed on building 285 m away, and focuses return light on InGaAs photodetector. Image: Google Earth (c) DCS intensity spectrum (linear y-axis scale) measured from outdoor path in (b).

An optical transceiver launches the DCS light between two buildings on the NIST campus, providing a round-trip optical path of 570 m. The heterodyne detection of the two combs produces an RF spectrum from 0-100MHz, which maps to optical wavelengths from 1100-1700 nm. The combs have a ~200 MHz repetition frequency (f_{rep}) and difference in repetition frequencies of 208 Hz.

The resulting spectrum is fit with the cepstral method [5] and the HITRAN2020 database [6]. Figure 2 shows the fit result for a spectrum with 96 seconds of averaging. The O_2 band is fit for temperature (286.8 K) and pressure (79.3 kPa), while the molefraction is fixed at 20.95% O_2. The features fit the data to within the 0.003 Gaussian absorbance noise. A nearby meteorology station measured 290. K and 82.2 kPa. The CH_4 and CO_2 bands (5940-6220 cm^{-1}) were fit separately, using the pressure determined from the O_2 band, giving 408 μmol/mol CO_2 and 1905 nmol/mol CH_4. We are exploring different fitting approaches and molecular absorption databases and we expect these to affect the concentration and pressure retrievals.

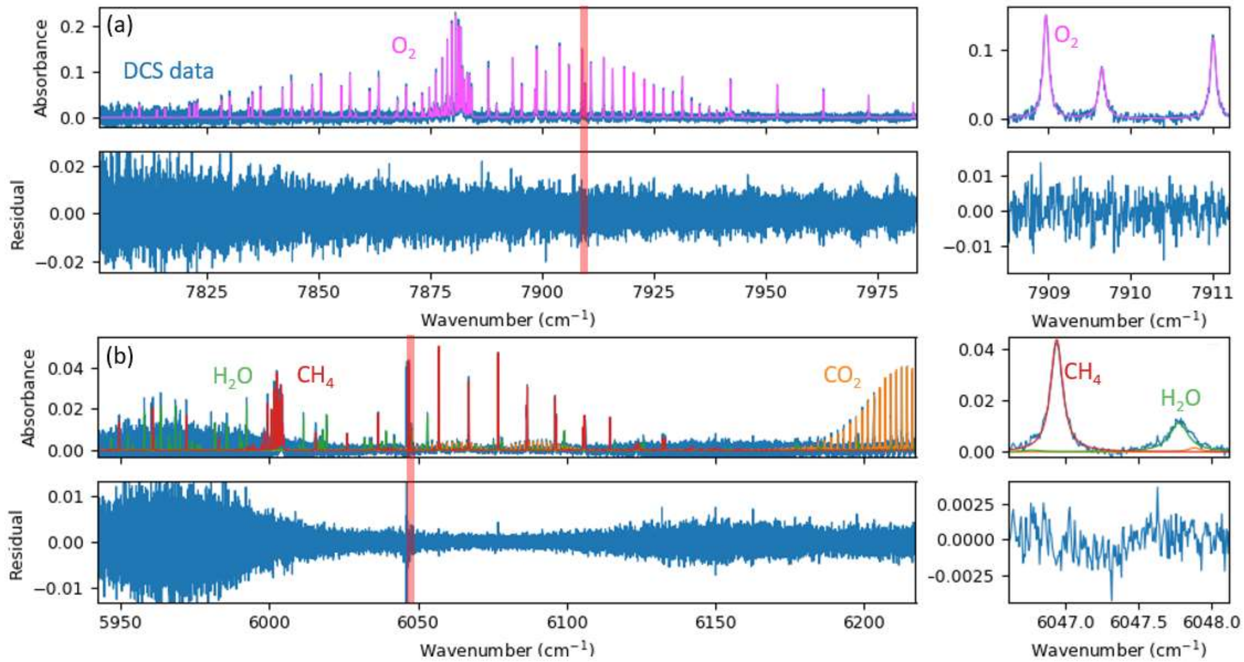

Figure 2: Fits to (top) O_2 and (bottom) CH_4/CO_2 absorption bands of outdoor DCS spectrum (the cepstra are transformed to magnitude spectra, in plotted units of the natural-logarithm of transmission). Blue trace is DCS measurement, other colors are fitted species spectral models. Residual is DCS data minus the sum of absorption models. (right) Zoomed-in portions of same fits.

This dual frequency comb spectrometer simultaneously measured absorption signatures of different molecules in spectral regions 2000 cm^{-1} apart from each other. Both spectral regions achieved sub-0.01 absorbance noise in under two minutes. This demonstration shows promise for using oxygen to determine the total number of molecules in an open-path laser greenhouse gas measurement when the average pressure, pathlength, and humidity is unknown. Additionally, future satellite missions plan to measure this O_2 band for air-mass correction [7], so DCS measurements could be useful for calibrating the oxygen absorption database.

[1] E. M. Waxman, K. C. Cossel, G.-W. Truong, F. R. Giorgetta, W. C. Swann, S. Coburn, R. J. Wright, G. B. Rieker, I. Coddington, and N. R. Newbury, "Intercomparison of Open-Path Trace Gas Measurements with Two Dual Frequency Comb Spectrometers," Atmospheric Meas. Tech. **10**, 3295–3311 (2017).

[2] D. Wunch, G. C. Toon, J.-F. L. Blavier, R. A. Washenfelder, J. Notholt, B. J. Connor, D. W. T. Griffith, V. Sherlock, and P. O. Wennberg, "The Total Carbon Column Observing Network," Philos. Trans. R. Soc. Lond. Math. Phys. Eng. Sci. **369**, 2087–2112 (2011).

[3] S. Potvin and J. Genest, "Dual-comb spectroscopy using frequency-doubled combs around 775 nm," Opt. Express **21**, 30707–30715 (2013).

[4] O. Leshchishina, S. Kassi, I. E. Gordon, L. S. Rothman, L. Wang, and A. Campargue, "High sensitivity CRDS of the a1Δg−X3Σg− band of oxygen near 1.27μm: Extended observations, quadrupole transitions, hot bands and minor isotopologues," J. Quant. Spectrosc. Radiat. Transf. **111**, 2236–2245 (2010).

[5] R. K. Cole, A. S. Makowiecki, N. Hoghooghi, and G. B. Rieker, "Baseline-free Quantitative Absorption Spectroscopy Based on Cepstral Analysis," Opt. Express **27**, (2019).

[6] I.E. Gordon et al. "The HITRAN2020 molecular spectroscopic database." J. Quant. Spectrosc. Radiat. Transf. **277,** 107949 (2022)

[7] J-L Bertaux et al. "The use of the 1.27μm O_2 absorption band for greenhouse gas monitoring from space and application to MicroCarb." Atmos. Meas. Tech. **13** 3329-3374 (2020)