

1 VALIDATION OF OPEN-PATH DUAL-COMB SPECTROSCOPY AGAINST AN O₂ 2 BACKGROUND

3 NATHAN A. MALARICH,^{1,3} BRIAN R. WASHBURN,¹ KEVIN C. COSSEL,¹
4 GRIFFIN J. MEAD,¹ FABRIZIO R. GIORGETTA,^{1,2} DANIEL I. HERMAN,^{1,2}
5 NATHAN R. NEWBURY,¹ AND IAN CODDINGTON^{1,4}

6 ¹NIST Spectrum Technology and Research Division, Boulder, CO 80305, USA

7 ²Department of Physics, University of Colorado Boulder, Boulder, CO 80309, USA

8 ³nathan.malarich@nist.gov

9 ⁴ian.coddington@nist.gov

10 **Abstract:** Dual-comb spectroscopy measures greenhouse gas concentrations over kilometers
11 of open air with high precision. However, the accuracy of these outdoor spectra is challenging
12 to disentangle from the absorption model and the fluctuating, heterogenous concentrations over
13 these paths. Relative to greenhouse gases, O₂ concentrations are well-known and evenly mixed
14 throughout the atmosphere. Assuming a constant O₂ background, we can use O₂ concentration
15 measurements to evaluate the consistency of open-path dual-comb spectroscopy with
16 laboratory-derived absorption models. To this end, we construct a dual-comb spectrometer
17 spanning 1240 nm to 1700 nm, which measures O₂ absorption features in addition to CO₂ and
18 CH₄. O₂ concentration measurements across a 560 m round-trip outdoor path reach 0.1%
19 precision in 10 minutes. Over seven days of shifting meteorology and spectrometer conditions,
20 the measured O₂ has -0.07% mean bias, and 90% of the measurements are within 0.4% of the
21 expected hemisphere-average concentration. The excursions of up to 0.4% seem to track
22 outdoor temperature and humidity, suggesting that accuracy may be limited by the O₂
23 absorption model or by water interference. This simultaneous O₂, CO₂, and CH₄ spectrometer
24 will be useful for measuring accurate CO₂ mole fractions over vertical or many-kilometer open-
25 air paths, where the air density varies.

26 Work of the U.S. government and not subject to copyright.

27 1. Introduction

28 Dual-comb spectroscopy (DCS) is an emerging technique for open-path greenhouse-gas
29 monitoring. These instruments can be operated with a negligible instrument line shape, broad
30 spectral bandwidth, high spectral resolution and near perfect frequency axis, enabling high-
31 precision measurements of path concentrations. Open-path DCS has shown CO₂ precisions
32 better than 0.2% over 2 km in 30 seconds [1], making DCS well-matched to the challenging
33 requirements of greenhouse gas measurements [2]. In principle, open-path DCS should be
34 capable of not just precision but also retrieving expected concentrations, which would allow
35 measurements taken across the world and over successive years to be readily intercompared.
36 Additionally, an accurate DCS could be used to calibrate other open path instruments or even
37 satellite measurements in a manner similar to the Total Carbon Column Observing Network
38 (TCCON) [3].

39 In earlier work, outdoor DCS concentration measurements have agreed to 0.3% between
40 adjacent systems, but have deviated ~1% from nearby laboratory calibrated point
41 measurements [1]. There are three possible causes for this deviation. First, the DCS instrument
42 might produce some unidentified, systematic bias in its recorded spectrum. Even if the DCS
43 spectrum is not distorted, the molecular absorption model (e.g. HITRAN [4]) used to fit
44 concentration from the DCS spectrum can have its own error. Lastly, there is a great deal of
45 atmospheric variability in greenhouse gas concentrations, so an open-path sensor measuring a
46 kilometer path may not see the same path-averaged concentration as a nearby point sensor. This

atmospheric variability in CH₄ and CO₂ enables instruments to detect emissions [5,6], but makes instrument biases challenging to diagnose.

It is possible to evaluate the accuracy of a DCS system using cell measurements, however this also has some drawbacks. The maximum pathlength possible in a cell is short compared to open paths and often forces one to work at mole fractions that are highly inconsistent with the outdoor environment. Additionally, it is difficult to mimic the rapidly varying return power seen on an open path (a possible driver of detection non-linearity and distortion) or the fluctuations of water and other interfering species. Lastly, a multi-pass cell will likely experience a different etalon realization than an open-path measurement. While cell based validation offers its own benefits in terms of being able to control gas parameters, we want to test these potential pitfalls unique to outdoor DCS measurements in the native measurement environment as well.

Fortunately, there is an ideal molecule to use to validate open-path DCS measurements: O₂. Unlike other greenhouse gases, O₂ concentrations are consistent to 0.005% throughout the hemisphere, and have remained constant to 0.06% over the past 30 years [7,8]. While local combustion and biosphere processes will exchange O₂ molecules for CO₂ (or vice versa), the fractional change in O₂ will be much smaller than to CO₂ due to a 500x higher background concentration. Additionally, considerable effort has been put into developing high-resolution O₂ absorption models to support satellite remote sensing, and the latest line parameters are believed to be accurate to within 0.2% [9]. Here, we leverage these advantages of O₂ to validate open-path DCS concentration retrievals in a cross-platform comparison against a laboratory-derived absorption model, using the O₂ band at 1270 nm.

In addition to DCS verification, O₂ measurements can improve open-path concentration accuracies for other greenhouse gases including CO₂. Extracting CO₂ concentration (in $\mu\text{mol CO}_2 / \text{mol dry air}$) from open-path spectroscopy requires knowledge of the air density throughout the path. Traditional open-path DCS determines air mass, or path-integrated air density, from the ideal gas law and a weather station [1]. An alternative is to simultaneously measure path-integrated O₂ absorption and calibrate the air-mass to the known O₂ concentration, as is often done in both satellite [10–14] and solar-based ground measurements [3,15]. Because O₂ concentrations are known and well-mixed in the atmosphere, the ratio of O₂ to CO₂ or CH₄ can be used to remove errors associated with imperfect air mass knowledge, provided the O₂ measurement is unbiased.

2. DCS system setup

2.1 Producing dual-comb spectra in the 1270 nm O₂ band

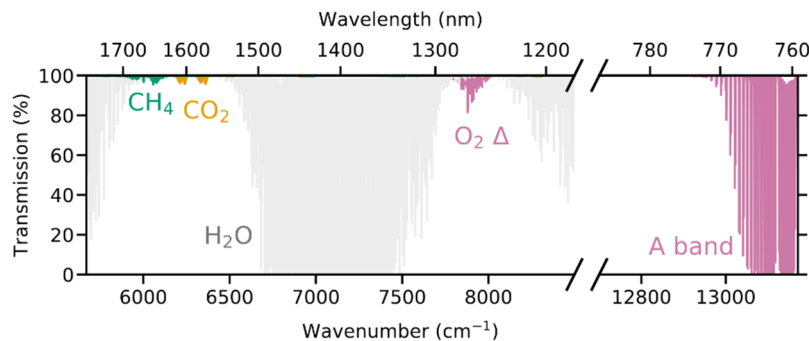


Fig 1. Simulation of transmission spectrum over 560 m (round-trip) outdoor path assuming 420 $\mu\text{mol/mol}$ CO₂ (orange), 2 $\mu\text{mol/mol}$ CH₄ (green), 209.5 mmol/mol O₂ (purple), and 5 mmol/mol H₂O (grey). O₂ a¹ Δ_g absorption at 1270 nm is more comparable to greenhouse gas bands at 1600 nm than the O₂ A-band at 760 nm.

O₂ absorbs near-infrared light in two wavelength regions commonly used for remote sensing, which are both shown in Fig. 1. Most satellite spectrometers use the A-band near 760 nm for

air-mass correction [10–13]. A second band, the $a^1\Delta_g$ band near 1270 nm, is more commonly used for ground-based Fourier Transform Spectrometers [3,15] as well as upcoming satellite missions [16,17].

This 1270 nm absorption band has several advantages over the 760 nm band for dual-comb ground-based measurements and CO₂/CH₄ air mass corrections. First, the 1270 nm band is only ~3x stronger than the 1600 nm CO₂/CH₄ band, whereas most of the 760 nm absorption features would fully attenuate dual-comb light over outdoor pathlengths as short as 500 m (Fig. 1). Second, the 1270 nm wavelengths are eye-safe at higher intensities than 760 nm, allowing more laser power and thus higher measurement precision. Finally, the same InGaAs photodetector can record the 1270 nm band in addition to the 1600 nm CO₂/CH₄ band, whereas the 760 nm band would require an additional silicon photodetector.

To generate phase-locked comb light in the 1270 nm O₂ band, we use an all-fiber setup shown in Fig. 2(a). Erbium-doped fiber oscillators operating at a 200 MHz pulse-repetition frequency (Fig. 2) provide a narrowband 1565 nm spectrum which is then split into two branches. The first branch performs the two phase locks [18] which provide the coherence across the spectrum which is required for accurate spectroscopy.

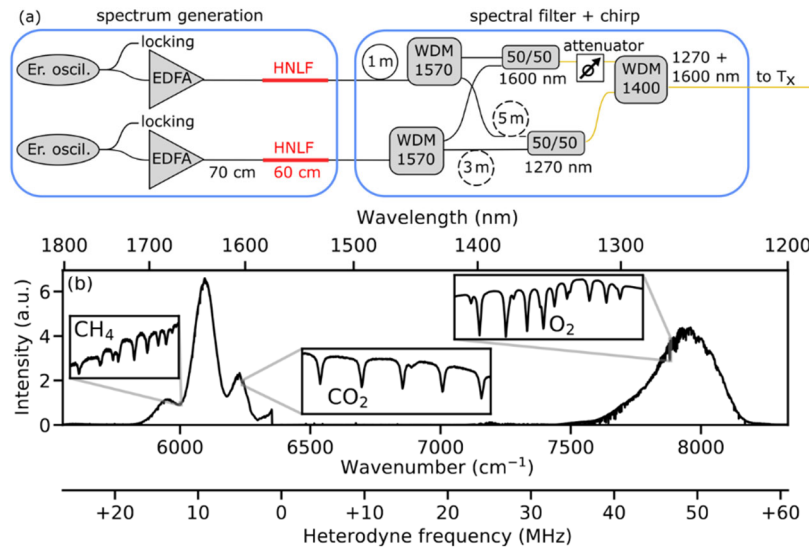


Fig 2. (a) All-fiber optical setup for producing spectrum in (b) for measurement of O₂, CO₂, and CH₄ features. EDFA: erbium-doped fiber amplifier, HNLF: highly nonlinear fiber, WDM: Wavelength Division Multiplexers, black lines: PM 1550 fiber, dashed black lines: PM980 fiber; yellow lines: SM1550 fiber. (b) DCS spectrum from outdoor measurement (160-minute average). The bottommost x-axis indicates the radio frequencies in the DCS heterodyne signal for the corresponding optical frequencies and wavelengths shown in the upper axes. Heterodyne frequencies exist at multiple wavenumbers due to the ambiguity in folding to one Nyquist window. Dither and DC signal below 1 MHz removed for clarity.

The second branch generates the light for spectroscopy using highly nonlinear fiber (HNLF). Unfortunately, many HNLF spectral broadening approaches produce negligible light in the 1270 nm O₂ band. Our approach to generating milliwatt powers at 1270 nm was to seed a long section of HNLF with a ~0.5 nJ pulse. To obtain this seed, we amplify the mode-locked erbium oscillator pulse in an erbium-doped fiber amplifier (EDFA), compress it to ~100 fs in ~70 cm of PM1550 fiber, and inject it into a 60 cm length of low anomalous group velocity dispersion (GVD) HNLF ($D = +2.2$ ps/nm/km). This approach requires lower amplification—the EDFA uses only 1 pump diode—as the dispersive wave blue-shifts below 1270 nm at higher pulse powers due to intra-pulse Raman scattering [19]. Each HNLF module produces 3 mW of comb light at 1270 nm and 5 mW at 1600 nm, which is less than the ~10 mW launch powers for typical open-path DCS instruments but adequate for outdoor spectroscopy.

After the HNLF, additional fiber components (Fig. 2(a), right) filter the spectroscopy light around the 1270 nm and 1600 nm bands and differentially chirp the combs before combining. The differential chirp effectively spreads out the interferogram power in time, allowing the receiver to maintain linear operation over a wider range of optical powers and thus avoid spectrum inaccuracies [20]. To filter and chirp the supercontinuum, first a 1570 nm fiber WDM separates the 1600 nm and 1270 nm light for each comb. The 1600 nm light from each comb is then chirped in PM1550 fiber, but the 1270 nm is inconveniently close to the zero-dispersion point of PM1550 fiber and requires a different approach. To apply the differential chirp at 1270 nm, we rely on the waveguide dispersion of PM980 fiber, which has an overall GVD magnitude of $\beta_2 \sim 15 \text{ ps}^2/\text{km}$ at 1270 nm. A 2 m section of differential PANDA PM980 fiber [43] thus reduces the height of the 1270 nm interferogram by a factor of four. To avoid cross-phase modulation [21] after the combs are combined, we further add a common 3 m of PM980 chirp fiber to the path of each comb. After the chirp fibers, an attenuator in the higher-power 1600 nm fiber branch balances the power in the two spectral bands before we recombine the bands on the 1400 nm WDM. The final filtered spectrum out of this Fig. 2(a) subsystem has no unwanted comb light between 1400 nm and 1570 nm, and 3 mW each in the 1270 nm and 1600 nm spectral regions.

We must phase lock the combs at a condition where all of the optical frequencies correspond to a unique RF heterodyne frequency, so that the 1270 nm and 1600 nm absorption bands can be recorded on a common detector. For phase locking, we lock a tooth of each frequency comb with the same +27 MHz offset to a RIO Orion 1560 nm reference laser [43], and set the repetition rates of the two combs at an offset of 208.8 Hz. This locking scheme maps the reference laser to 0 Hz and results in different radio frequencies for the 1270 nm and 1600 nm bands (as shown in Fig. 2(b), MHz axis).

The time base for the frequency combs was provided by a commercial oven-controlled quartz oscillator, which was low drift but had a $\sim 3 \times 10^{-7}$ bias. The frequency offset caused by this bias was determined by fitting one spectrum to known molecular features and then applying this shift to subsequent data.

2.2 Outdoor measurement of O_2

We launch the combined and filtered combs on a horizontal, two-way outdoor path between a 10-cm aperture transmit/receive telescope (T_x/R_x) and 12.5-cm diameter hollow corner-cube retroreflector (Fig. 3). A gimbal controls the telescope pointing to the retro. A single photodetector collects the 1270 nm and 1600 nm return light and sends the heterodyne signal to a data acquisition (DAQ) device.

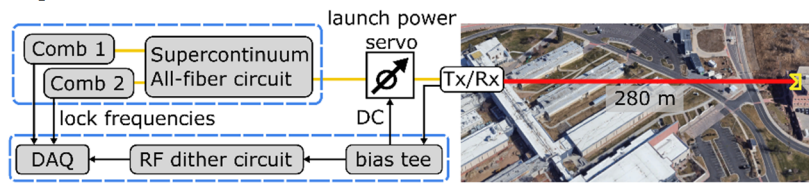


Fig 3. Outdoor measurement setup for simultaneous O_2 , CO_2 , CH_4 and H_2O concentrations. Measurement over horizontal 560 m round-trip path between balconies on NIST Boulder campus (image credit: Google Earth). Yellow lines indicate optical fiber, thick red line indicates free-space laser, and black arrows indicate radio-frequency (RF) cables. Larger dashed boxes surround subsystems further detailed in Figs. 2,4. DAQ: data acquisition system.

Fig. 3 includes three subsystems to ensure the 1270 nm spectrum is free of instrument distortions. The launch power servo between the fiber circuit and telescope avoids photodetector saturation. The DAQ with real-time phase-correction compensates for frequency-comb phase noise. The RF dither circuit surpasses digitization error on the DAQ. Next, we describe each of these subsystems in detail.

2.2.1 Power servo

Atmospheric turbulence moves and distorts the free-space laser beam, causing fluctuations in the optical power received on the photodetector [22]. These fluctuations can be particularly severe under sunny or windy turbulent conditions, and the brief bursts of maximum received power can exceed the requirements for linear photodetector operation [23]. To reduce these fluctuations in received power, a servo adjusts the launch power.

This power-servo consists of a closed-loop microcontroller and a variable optical attenuator that effectively clamps the maximum power on the detector. The fluctuations in transmitted power imprint on the DC photodetector voltage, read by the microcontroller. The microcontroller operates a fixed-gain feedback loop, adjusting the attenuation voltage of the variable fiber optical attenuator to stabilize this DC photodetector voltage at the prescribed setpoint. The 1 kHz bandwidth of the feedback loop is comparable or faster than the turbulence induced power variations observed over this path.

This power-servo acts equally on both the 1270 nm and 1600 nm spectral bands. The other manually operated attenuator in Fig. 2(a) controls the power in the 1600 nm band without any feedback. In Section 3.4 we change settings for each attenuator to test dependence of the concentration retrievals on optical power.

2.2.2 DAQ with real-time phase correction

In addition to moderate optical powers, accurate spectroscopy requires interferogram phase noise well below 1 radian [24]. The timing jitter of our oscillators causes the comb tooth phase noise to increase linearly with frequency offset from the carrier [25]. Since the CO₂/CH₄ absorption bands lie closer to the 1560 nm carrier, the phase-noise criterion is easier to meet for CO₂/CH₄ spectroscopy than for O₂ spectroscopy. In these combs, the residual phase noise on the self-referenced lock of carrier-envelope offset frequency is 4.5 radians (integrated from 1 Hz to 5 MHz), and the residual phase noise in the lock to the cw-laser at 1560 nm is ~0.2 rad, suggesting that the phase noise in the O₂ band should be ~1.8 radians. To remove this residual carrier-envelope offset phase noise from the recorded spectra, the FPGA-based DAQ records the residual phase noise from each comb phase lock and applies a point-by-point digital phase-correction described in [26], which is an adaptation of the work in [20,27] for our present comb-locking scheme. As is typically done, we also apply an interferogram-to-interferogram phase correction to remove slow, out-of-loop drifts. We average interferograms for 96 seconds before writing to disk. For the phase correction, we split the two spectral bands onto different DAQ channels (Fig. 4) allowing us to apply separate phase corrections to compensate for the independent fiber paths in each branch for the two spectral bands.

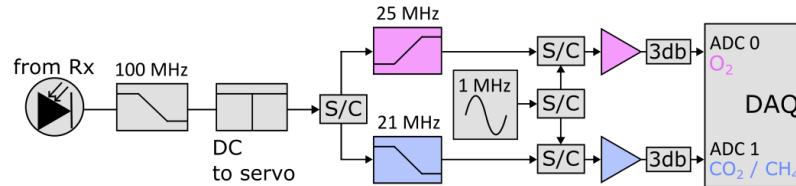


Fig 4. RF circuit between photodetector and DAQ allows power measurement and undistorted signal digitization. The circuit splits the heterodyne signal into O₂ and CO₂/CH₄ components. We dither both bands with a 1 MHz sinewave before recording on separate analog-to-digital converters (ADC). S/C is 50/50 splitter, which operates either as splitter or coupler.

2.2.3 Dither circuit

Interferograms are recorded on a 14 bit, 200 MS/s analog-to-digital converter (ADC). While such ADCs can be quite linear over their full voltage range, transitions between different subsections of the ADC circuit can lead to nonlinear behavior at the least-significant-bit (LSB) range. As the free induction decay portion of an interferogram typically spans only a couple

LSBs, this nonlinear behavior can lead to a bias in concentration [28]. We mitigate this ADC impact by adding a 1 MHz sinewave dither to the interferogram prior to digitizing (shown in Fig. 4) [29]. This dither amplitude spans 2000 LSBs, ensuring that the ADC samples the free induction decay over a large bit range. The dither frequency is asynchronous with the interferogram frame rate, allowing it to be suppressed during averaging of successive interferograms.

3. O₂ concentration retrievals

To test this O₂/CO₂/CH₄ spectrometer, we measure a short (560 m round-trip) horizontal path (Fig. 3) where a weather station positioned 10 m above the telescope records the air density. We first characterize the dry O₂ fit of a characteristic dataset. Then in Section 3.5 we evaluate the consistency of this O₂ concentration retrieval under a variety of laser and weather conditions. This work emphasizes O₂ rather than the CO₂ and CH₄ fits, because O₂ has the most stable concentrations. However, to apply the O₂ measurement for an air-mass correction, we must recover expected O₂ concentrations in this setup which simultaneously measures these other species.

3.1 Expected O₂ concentration

Inherent in this work is the assumption that our local dry O₂ mole fractions match the global mean to better than the precision of our measurement. This assumption is validated by the Scripps network which has observed global O₂ levels for decades. During our May 2022 measurements, Scripps had six active flask locations throughout the northern hemisphere; across this urban and rural spanning network the total spread in monthly dry O₂ mole fractions from all sites ranged from 0.20933-0.20934, a 0.005% variation [8].

An additional driver of O₂ uncertainty at our location is temporal fluctuations due to local sources and sinks from combustion and biogenic exchange. These fluctuations are difficult to measure directly, but their magnitude can be estimated from local CO₂ measurements and a theoretical O₂/CO₂ exchange ratio [30]. Previous, 5 minute resolution, paramagnetic measurements at the La Jolla site have shown O₂ concentrations are strongly anticorrelated with local CO₂ concentrations. For combustion the expected O₂: CO₂ exchange ratio is -1.4 O₂ : 1 CO₂ [31]. The La Jolla site actually sees a slightly lower ratio, indicating that 1.4:1 is a conservative estimate of O₂ variability. At our site, a collocated cavity ring-down spectrometer (CRDS) instrument measured a maximum CO₂ variation of 50 μmol/mol during our measurement periods, corresponding to a $50\text{e-}6 \cdot 1.4 / 0.20934 \cdot 100\% = 0.033\%$ uncertainty in O₂ concentration. Taking this temporal variation together with the global variation, we assume an uncertainty of 0.035% on the assumed dry O₂ mole fraction throughout the month of DCS measurements. This variation is comfortably below our 0.1% instrument precision.

3.2 Spectral fitting

The DCS spectrum at 1270 nm (Fig. 2(b)) contains many O₂ absorption features, but also water vapor features and structure from the initial laser intensity spectrum. To extract accurate O₂ concentrations from this spectrum, we fit with a time-domain technique which separates the absorption signature from the spectral fluctuations in laser background intensity [32]. This technique fits the modified free induction decay (mFID) signal in Fig. 5(a), which is the inverse-Fourier transform of the logarithm of the O₂ and H₂O portion of the intensity spectrum (7790 cm⁻¹-7960 cm⁻¹). The laser intensity background and etalons occupy only a few points of this mFID signal, so the least-squares algorithm applies zero weights to those high-residual regions (Fig. 5(a) shaded regions) and instead fits concentration over the majority of the mFID signal where there is negligible laser-intensity structure. This approach is essentially a spectral fit with a high-pass filter to ignore slowly-varying structure on the comb spectrum.

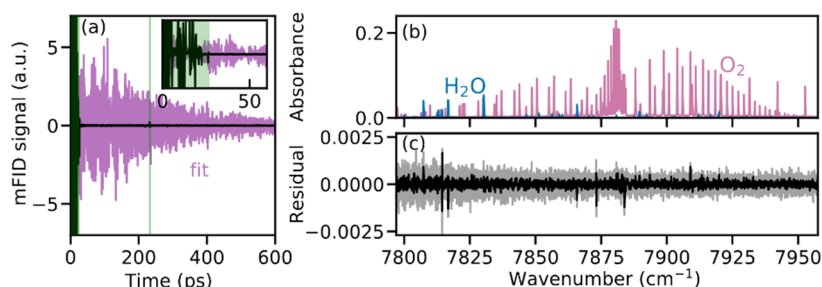


Fig 5. Fitting the 1270 nm O₂ band of a 160 minute time-averaged spectrum. (a) Time-domain fit result using mFID technique. Purple: best-fit model from O₂ + H₂O. Black: fit residual. Inset shows high-amplitude residual at early times due to laser intensity background. High-pass fit weighting function is zero in green-shaded regions. (b) Frequency-domain visualization of time-domain fit using β -qSDNGP+LM O₂ absorption model [9], and (c) Grey: high-pass weighted absorbance residual. Black: same residual apodized from 200 MHz to 1.6 GHz resolution.

The fits naturally return a path integrated number density (molecules/cm²) for each observed species of molecule, as well as a path averaged temperature and pressure. However, a dry air mole fraction (mol O₂/mol air) is the quantity of interest for atmospheric measurements and, equally importantly, O₂ dry air mole fraction is the atmospherically stable quantity that we hope to evaluate in this work. Conversion to mole fraction is straightforward through the ideal gas law, but requires additional knowledge of path length (measured to 0.05% precision with a laser ranger) to convert to path-averaged number density (molecules/cm³), as well as the path averaged temperature and pressure to determine the air number density. It is a strength of this approach that, between the resolution and bandwidth of the DCS and the quality of the O₂ absorption model, we can directly recover high quality temperature and pressure from the spectral fits, allowing us to retrieve a mole fraction almost entirely from a single self-consistent DCS measurement.

Our path-average fitting approach does assume constant pressure and temperature across the laser path. Partly this is justified by the fact that we avoid localized heating by having all but a few meters of the path be at least 5 m above any surface, but there could be inhomogeneity. The impact of an inhomogeneous path can be modeled and is small. Cross-comparison of weather stations within 1 km of the site shows that local temperatures may vary by up to 4 K. Local pressures are predictably more uniform, varying by up to 0.6 hPa. To quantify the effect of inhomogeneity we simulate a continuous 8 K gradient path and fit to a constant temperature. The model gives a 0.01% error in fit concentration and <0.01% error in the retrieved mean temperature. Similar analysis shows a negligible effect for a 0.6 hPa pressure gradient.

Finally, we use the retrieved O₂ and H₂O mole fractions ($\chi_{O_2,fit}$, $\chi_{H_2O,fit}$) to obtain the dry O₂ mole fraction according to Eq. 1:

$$\chi_{O_2,dry} = \frac{\chi_{O_2,fit}}{1 - \chi_{H_2O,fit}} \quad 1$$

Several observations suggest high fit quality. First, the frequency-domain spectrum (Fig. 5(b)) shows many high-SNR H₂O and O₂ features. Also, the frequency-domain residual of Fig. 5(c) (defined as Fourier transform of the product of the time-domain fit residual and weight function) shows that 95 out of the 99 O₂ modeled absorption features have a residual below 0.0005 absorbance. Finally, the mFID fit is only weakly sensitive to the size of the zero-weight region, and doubling this region (from 27 ps to 60 ps) changes the O₂ concentration by a factor of just 1.0005.

The residuals are more likely to be from H₂O and O₂ absorption model error than any other species. HDO is the only secondary isotopologue HITRAN predicts to produce absorption near our noise floor in this spectral region, and we include it in the fit, constraining its mole fraction to be equal to H₂O. CO₂ and CH₄ have a maximum 1e-5 absorbance in this region, far below

the noise floor and omitted from this spectral model. Aerosol effects on our short path are both weak and impart a smoothly-varying structure on the spectrum, which would be removed by the high-pass weighting filter.

3.3 O₂ absorption model

The DCS concentration measurement depends directly upon the molecular absorption model used to fit the spectrum. Absorption models include both an intensity and several lineshape parameters for each absorption feature. A model with incorrect lineshape parameters will extract incorrect areas and produce fit residual structure, while a model with an incorrect band strength will produce a constant concentration offset. We used the empirical O₂ line-by-line absorption model from [9] based on room-temperature, zero-humidity cavity ring-down measurements at a range of pressures with a stated uncertainty of 0.16%. This model includes several non-Voigt lineshape parameters to improve the pressure-dependence accuracy of the absorption model. Specifically, it is a beta quadratic speed-dependent Nelkin-Ghatak profile with line-mixing (β -qSDNGP+LM), which includes two line-narrowing parameters and an asymmetry parameter. To this room-temperature model, we add the linewidth temperature-exponents from HITRAN2020 [4], which were derived from atmospheric-column FTIR data [33].

We input this line-by-line model into the HITRAN Application Programming Interface [34] to calculate a lookup table of absorption spectra at 40 hPa pressure, 10 K temperature, and 0.04 O₂ mole fraction resolution. Then the fit uses rectangular interpolation to fit the measured spectrum with this pre-computed grid. This lookup table method reduces the time to fit each spectrum to under 1 second, rather than recalculating the non-Voigt absorption model each iteration of a slower nonlinear minimization routine. The tradeoff for this speed a maximum interpolation error (calculated at midpoint of grid) of 0.045% imposed on the retrieved mole fraction at this gridding resolution.

Using this β -qSDNGP+LM absorption model, the fit of the 160-minute data set matches the expected mole fraction to the stated 0.16% uncertainty in line intensity (Table 1). Furthermore, whereas previous open-path DCS studies have fixed pressure to a barometer measurement [1], we fit a pressure from the spectral linewidths that matches the barometer within the estimated 0.05% uncertainty in line broadening parameters [9]. Uncertainties of 0.8 K and 0.1 hPa in the expected path-average conditions are maximum discrepancies between two weather stations 1 km apart throughout the time period.

Table 1. Fit results to Fig. 2(b) spectrum using different absorption models. Expected T and P data comes from weather station and expected χ_{O_2} from Scripps O₂ program [8].

	Expected	HITRAN2020 Voigt [4]	% diff	β -qSDNGP+LM [9]	% diff
Dry χ_{O_2}	0.20934(7)	0.20682	-1.20	0.20967	0.16
T (K)	287.7(8)	284.0	1.27	287.6	0.02
P (hPa)	826.3(1)	819.7	-0.80	826.1	-0.04

For comparison, we also fit this spectrum with the HITRAN2020 Voigt model, which is a combination of the Voigt lineshapes from NIST Gaithersburg [9] and Universite Grenoble Alpes [35,36]. The resulting fit, shown in Table 1, changes the O₂ mole fraction by 1.2% relative to the β -qSDNGP+LM model and gives a worse estimate of all three parameters. A study of many absorption line models with TCCON data also found that the β -qSDNGP+LM model from [9] gave the lowest-residual spectral fits [37].

3.4 Precision of O₂ measurement

The fitted O₂ mole fractions over a 2.5-hour acquisition period are shown in Fig. 6(a). The corresponding Allan deviation (Fig. 6(b)) shows that O₂ achieves a 0.1% relative precision in 10 minutes. Concentration precision is proportional to pathlength [38], so extending the pathlength should reduce the Allan deviation provided that the received optical power is the

348 same, and the pathlength is not so long that the absorption features saturate. CO₂ and CH₄ had
 349 lower relative precisions, due to the weaker absorption signature of these molecules. However,
 350 the pathlength-normalized CH₄ precision of 3 $\mu\text{mol/mol}\cdot\text{m}$ at 900 s is comparable to previous
 351 open-path fiber-comb results [1,39].

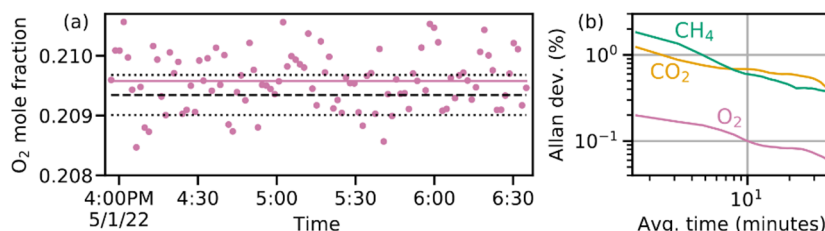


Fig 6. (a) O₂ fit time-series with 96-second averaging. Solid trace is mean of the fitted mole fractions, dashed line is expected mole fraction from [8] with dotted lines at $\pm 0.16\%$ uncertainty. (b) Corresponding Allan deviation of fitted dry mole fractions for each species, expressed in relative percent. CO₂ and CH₄ fits are from simultaneous 1600 nm measurement. O₂ achieves 0.1% precision in 10 minutes.

358 The dry O₂ mole fraction is constant with time, and the known value is shown as a dashed
 359 line in Fig. 6(a). The dotted horizontal lines in Fig. 6(a) indicate a relative concentration
 360 uncertainty of 0.16% from the absorption model [9]. Half of the individual, 96-second O₂
 361 measurements lie within this bound, as does the time-average of all 100 measurements (solid
 362 line). Average CO₂ and CH₄ concentrations matched the WMO-referenced point sensor to
 363 better than 0.5%, which is comparable to previous work [1], though spatial variability of these
 364 gases makes it difficult to compare too directly.

365 3.5. Consistency of O₂ measurement

366 To test whether this O₂ measurement remains stable over shifting conditions, we collected 13
 367 hours of data spread throughout one month, changing both meteorological conditions and DCS
 368 instrument parameters. We consider 10-minute time-averages of these datasets to distinguish
 369 potential measurement bias from low measurement precision (as the Fig. 6(b) Allan deviation
 370 shows 0.1% precision at 10 minutes).

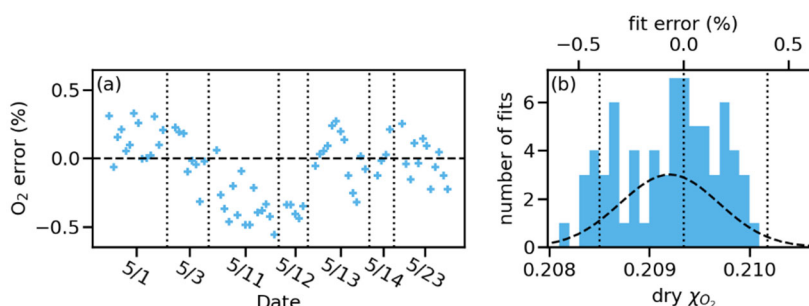


Fig 7. (a) Dry-O₂ fit errors for 10-minute-averaged spectra (markers). Dotted lines separate each day of measurement. (b) Histogram of same O₂ fits. The data have a mean $\chi_{O_2} = 0.20913$ (-0.07%), and 90% of fits are within 0.4% of O₂ background (dashed line). Dashed-line is Gaussian distribution with same mean and variance as histogram.

377
378

Table 2. Range of measurement conditions in Fig. 7 histogram. Top category is meteorology; bottom category is instrument parameters.

Parameter	Min	Max
T (K)	278	302
P (hPa)	824	833
H ₂ O (mmol/mol)	2	14
Dither amplitude on ADC (LSBs)	2600	5200
Power in O ₂ band (μW)	27	100
Total power in O ₂ + CO ₂ bands (μW)	30	160

379

380 The histogram of all the 10-minute-averaged data (Fig. 7(b)) has an average mole fraction
381 bias of -0.07%, within the 0.16% uncertainty due to the absorption model line intensities.
382 However, the O₂ error does not look like Gaussian noise, as the O₂ fit concentration drops by
383 ~0.4% on 5/11 and returns to typical values on 5/13. Even with this time-varying behavior,
384 90% of the fits are within 0.4% of expected concentration. This level of agreement between the
385 DCS, absorption model, and O₂ background is comparable to the agreement between the
386 TCCON and OCO-2 network, which has a mean 0.1% offset and RMS 0.4% offset [40].

387

Table 3. Summary of dry-O₂ error budget, expressed as percent uncertainties in dry O₂.

Source	% UC	Determination
O ₂ spatiotemporal variability	0.035	From global network [8] and local CO ₂ CRDS
Pathlength	0.05	Laser ranger precision
Path nonuniformity	0.01	Simulate 8 K, 0.6 hPa variation across laser path
Laser baseline masking	0.05	Change weight function gate time in fit [32]
Lookup table discretization	0.045	Interpolation from P, T, χ_{O_2} grid of simulated spectra
Absorption model intensities	0.16	From [9]
Quadrature sum	0.18	

388 This 0.4% variation exceeds the aggregate uncertainty from the sources we have already
389 discussed throughout Section 3, summarized in Table 3. It is an order of magnitude larger than
390 the atmospheric variability in O₂ concentration, larger than the uncertainties in the fitting
391 approach and the uncertainty in the room-temperature absorption model.

392 3.6. Possible explanations for the residual error and future directions

393 To diagnose the possible causes of this 0.4% deviation in the O₂ data, we consider the
394 conditions that vary across the measurement (Table 2). The meteorology conditions (Table 2,
395 top) alter the number density of O₂ measured by the DCS spectrum. As the fit relies on the
396 quality of the absorption model to disentangle dry O₂ mole fraction from these other variations
397 in O₂ number density, the meteorological variation might interact with absorption model error
398 to produce error in the O₂ fits. The second category of independent variables are instrument
399 variables (Table 2, bottom), which may act through instrument nonlinearities to distort the DCS
400 spectrum. While this time-varying bias could be an undiagnosed sporadic instrument issue, a
401 multi-variate analysis of O₂ error with respect to all the parameters in Table 2 point to a possible
402 absorption model error.

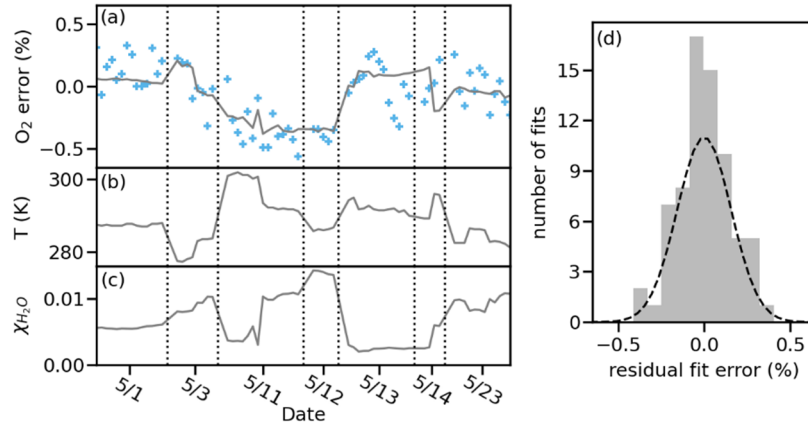


Fig 8. Time-varying O₂ fit error (from Fig 7) correlates with meteorology, possibly indicating error in the absorption model. (a) O₂ fits (markers) colored by day of measurement. Grey trace: regression ($R^2 = 0.55$) with respect to measured temperature (b) and H₂O mole fraction (c). (d) Histogram of residual O₂ fits after subtracting correlation line in (a) has deviation 0.16%.

Of these independent variables in Table 2, temperature and H₂O mole fraction variations track this time-varying O₂ error (Fig. 8). The low-biased O₂ data corresponds to a period of high temperature, followed by a period of high H₂O mole fraction across the laser path. The two-parameter regression reduces the standard deviation of the residual fit error to 0.16%, giving a more Gaussian histogram (Fig. 8(d)) with close to the expected 0.1% deviation from absorbance noise. This temperature and H₂O correlation was much stronger than error correlations with pressure, photodetector power, or dither amplitude across the dataset. As the dual-comb instrument was indoors, we would not expect any temperature-dependent instrument effects to correlate with the outdoor temperature shown here. However, absorption model error might be causing this correlation—while the empirical model was based on several pressures, there are no laboratory measurements at different temperatures or at significant humidity [9].

Eq. 2 describes the empirical regression trace in Fig. 8(a), expressed in terms of deviation from the laboratory temperature and H₂O conditions in [9]:

$$O_2 \text{ error (\%)} = 0.13 - 7.8 \frac{T - 296}{296} - 55 \chi_{H_2O} \quad 2$$

To investigate a theoretical basis of this empirically-derived equation, we simulate spectra with uncertainties in several absorption model parameters. The absorption model line intensities have a 0.16% uncertainty, producing an O₂ error of up to 0.16% at dry, 296 K conditions. This is larger than the 0.13% error in the empirical Eq. 2, so this first coefficient has a plausible magnitude. Temperature-dependence of the O₂ error may stem from uncertainty in the linewidth temperature-exponents, which are currently estimated from TCCON atmospheric data as no temperature-varying laboratory data is available. A sensitivity study of O₂ fit error due to a 7% bias in these temperature exponents (the change from HITRAN2016 to HITRAN2020) predicted a coefficient of 5.3, close to the observed 7.8 in Eq. 2. Finally, H₂O-dependence of O₂ error may stem from H₂O-broadening of the O₂ features. No H₂O-broadening laboratory data exists in this band, although a simulation using the best estimates of H₂O-broadening [41] suggests this coefficient could be 10, less than the observed 55. Of the three regression coefficients in Eq. 2, only H₂O-dependence substantially exceeds the expected sensitivity to uncertainty ranges in O₂ absorption model parameters. However, this remaining H₂O-dependence could possibly stem from overlapping absorption between O₂ features and a less-accurate model of H₂O features.

There is also the possibility that the 0.4% O₂ variations are coming from a different variable that isn't recorded in Table 2. However, our investigations suggest that the T and H₂O

dependence is plausible, and that improved absorption models can reduce the bias of future measurements. Additional data taken during periods of high meteorological variability could confirm this trend and allow construction of a calibrated absorption model. We hope to address this with future measurement efforts.

4. Summary

Here we constructed a dual-comb spectrometer capable of simultaneously measuring O₂ concentrations, water vapor concentrations, atmospheric temperature and pressure based on spectroscopy around 1270 nm. Measurements on a horizontal outdoor path achieved 0.1% precision in 10 minutes, and 90% of these time-averaged measurements agree with the expected dry-O₂ mole fraction to within 0.4% without bias correction. While different open-path dual-comb spectrometers have shown relative agreement over a range of concentrations and multiple molecules, this is the first validation of concentration retrievals with bias below 0.5%. The quality of the O₂ absorption model enabled this degree of agreement without using a weather station to provide temperature and pressure. Concentration retrievals with 0.4% accuracy are comparable to state-of-the-art for open-path instruments. Furthermore, as the 0.4% deviations from the expected background correlated with weather changes across the laser path, improvements in absorption models at the range of weather conditions has the potential to improve this agreement.

In addition to measuring O₂, the spectrometer simultaneously measured CO₂ and CH₄ at 1600 nm. Thus, this O₂ measurement eventually can correct the path-integrated air density of CO₂ and CH₄ measurements. Correcting for air mass by calculating CO₂/O₂ or CH₄/O₂ ratios will introduce a 0.4% uncertainty as demonstrated here. This air density correction could be advantageous for longer outdoor measurements where a single weather station cannot reliably provide the path-integrated air density.

Funding. NASA Earth Science Technology Office's Instrument Incubation Program. N.M. acknowledges support from the NIST NRC fellowship program. The equipment used in this study was partially funded by the NSF Division of Biological Infrastructure Award #1726304.

Acknowledgments. The authors thank Erin Adkins for assistance in implementing the β -qSDNGP O₂ absorption model, David Plusquellic and Jasper Stroud for weather station data, and Alexander Lind, David Long and Joe Hodges for instructive comments.

Disclosures. The authors declare no conflicts of interest. Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.

Data availability. Data underlying the results presented in this paper are available in [Dataset 1](#), Ref. [42].

References

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. A. Crotwell, M. Steinbacher, and World Meteorological Organization, *19th WMO/LAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques* (2018), p. 2.
3. 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. Math. Phys. Eng. Sci.* **369**, 2087–2112 (2011).
4. I. E. Gordon, L. S. Rothman, R. J. Hargreaves, R. Hashemi, E. V. Karlovets, F. M. Skinner, E. K. Conway, C. Hill, R. V. Kochanov, Y. Tan, P. Wcislo, A. A. Finenko, K. Nelson, P. F. Bernath, M. Birk, V. Boudon, A. Campargue, K. V. Chance, A. Coustenis, B. J. Drouin, J. -M. Flaud, R. R. Gamache, J. T. Hodges, D. Jacquemart, E. J. Mlawer, A. V. Nikitin, V. I. Perevalov, M. Rotger, J. Tennyson, G. C. Toon, H. Tran, V. G. Tyuterev, E. M. Adkins, A. Baker, A. Barbe, E. Canè, A. G. Császár, A. Dudaryonok, O. Egorov, A. J. Fleisher, H. Fleurbaey, A. Foltynowicz, T. Furtenbacher, J. J. Harrison, J. -M. Hartmann, V. -M. Horneman, X. Huang, T. Karman, J. Karns, S. Kass, I. Kleiner, V. Kofman, F. Kwabia-Tchana, N. N. Lavrentieva, T. J. Lee, D. A. Long, A. A. Lukashetskaya, O. M. Lyulin, V. Yu. Makhnev, W. Matt, S. T. Massie, M. Melosso, S. N. Mikhailenko, D. Mondelain, H. S. P. Müller, O. V. Naumenko, A. Perrin, O. L. Polyansky, E. Raddaoui, P. L. Raston, Z. D. Reed, M. Rey, C. Richard, R. Tóbiás, I. Sadiek, D. W. Schwenke, E. Starikova,

493 K. Sung, F. Tamassia, S. A. Tashkun, J. V. Auwera, I. A. Vasilenko, A. A. Vigasin, G. L. Villanueva, B.
494 Vispoel, G. Wagner, A. Yachmenev, and S. N. Yurchenko, "The HITRAN2020 molecular spectroscopic
495 database," *J. Quant. Spectrosc. Radiat. Transf.* **107**949 (2021).

496 5. Y. Chen, M. Soskind, J. McSpirt, J. Liu, R. Wang, N. Li, X. Guo, M. A. Zondlo, and G. Wysocki,
497 "Fugitive methane detection using open-path stand-off chirped laser dispersion spectroscopy," *Opt. Lett.* **46**,
498 3005–3008 (2021).

499 6. L. Balet, S. Chin, T. Herr, F. Lütolf, P. Renevey, J. van Zaen, S. Dasen, S. Droz, V. Schaffter, J. Gouman, G.
500 Buchs, F. J. M. Harren, A. Khodabakhsh, G. Vergara, J. Wigg, H. Martin, L. Huot, P. M. Moselund, C.
501 Hüglin, P. Arsenovic, L. Emmenegger, and S. Lecomte, "Airborne campaign results of a compact 2-4 μ m
502 broadband supercontinuum-based spectrometer system for multi-species atmospheric gas analysis at ppm
503 level," in *Photonic Instrumentation Engineering VIII* (SPIE, 2021), Vol. 11693, pp. 138–153.

504 7. R. F. Keeling and S. R. Shertz, "Seasonal and interannual variations in atmospheric oxygen and implications
505 for the global carbon cycle," *Nature* **358**, 723–727 (1992).

506 8. R. Keeling and S. Walker, "Scripps O₂ program," (n.d.).

507 9. H. Fleurbaey, Z. D. Reed, E. M. Adkins, D. A. Long, and J. T. Hodges, "High accuracy spectroscopic
508 parameters of the 1.27 μ m band of O₂ measured with comb-referenced, cavity ring-down spectroscopy," *J.*
509 *Quant. Spectrosc. Radiat. Transf.* **270**, 107684 (2021).

510 10. E. J. Llewellyn, N. D. Lloyd, D. A. Degenstein, R. L. Gattinger, S. V. Petelina, A. E. Bourassa, J. T. Wiensz,
511 E. V. Ivanov, I. C. McDade, B. H. Solheim, J. C. McConnell, C. S. Haley, C. von Savigny, C. E. Sioris, C. A.
512 McLinden, E. Griffioen, J. Kaminski, W. F. Evans, E. Puckrin, K. Strong, V. Wehrle, R. H. Hum, D. J.
513 Kendall, J. Matsushita, D. P. Murtagh, S. Brohede, J. Stegman, G. Witt, G. Barnes, W. F. Payne, L. Piché, K.
514 Smith, G. Warshaw, D.-L. Deslauniers, P. Marchand, E. H. Richardson, R. A. King, I. Wevers, W. McCreath,
515 E. Kyrölä, L. Oikarinen, G. W. Leppelmeier, H. Auvinen, G. Mégie, A. Hauchecorne, F. Lefèvre, J. de La
516 Nöe, P. Ricaud, U. Frisk, F. Sjöberg, F. von Schéele, and L. Nordh, "The OSIRIS instrument on the Odin
517 spacecraft," *Can. J. Phys.* **82**, 411–422 (2004).

518 11. M. Reuter, M. Buchwitz, O. Schneising, J. Heymann, H. Bovensmann, and J. P. Burrows, "A method for
519 improved SCIAMACHY CO₂ retrieval in the presence of optically thin clouds," *Atmos Meas Tech* **3**, 209–
520 232 (2010).

521 12. A. Butz, S. Guerlet, O. Hasekamp, D. Schepers, A. Galli, I. Aben, C. Frankenberg, J.-M. Hartmann, H. Tran,
522 A. Kuze, G. Keppel-Aleks, G. Toon, D. Wunch, P. Wennberg, N. Deutscher, D. Griffith, R. Macatangay, J.
523 Messerschmidt, J. Notholt, and T. Warneke, "Toward accurate CO₂ and CH₄ observations from GOSAT,"
524 *Geophys. Res. Lett.* **38**, (2011).

525 13. D. Crisp, "Measuring atmospheric carbon dioxide from space with the Orbiting Carbon Observatory-2
526 (OCO-2)," in (2015), Vol. 9607, p. 960702.

527 14. D. Crisp, B. M. Fisher, C. O'Dell, C. Frankenberg, R. Basilio, H. Bösch, L. R. Brown, R. Castano, B.
528 Connor, N. M. Deutscher, A. Eldering, D. Griffith, M. Gunson, A. Kuze, L. Mandrake, J. McDuffie, J.
529 Messerschmidt, C. E. Miller, I. Morino, V. Natraj, J. Notholt, D. M. O'Brien, F. Oyafuso, I. Polonsky, J.
530 Robinson, R. Salawitch, V. Sherlock, M. Smyth, H. Suto, T. E. Taylor, D. R. Thompson, P. O. Wennberg, D.
531 Wunch, and Y. L. Yung, "The ACOS CO₂ retrieval algorithm – Part II: Global XCO₂ data characterization,"
532 *Atmos Meas Tech* **5**, 687–707 (2012).

533 15. D. Fu, T. J. Pongetti, J.-F. L. Blavier, T. J. Crawford, K. S. Manatt, G. C. Toon, K. W. Wong, and S. P.
534 Sander, "Near-infrared remote sensing of Los Angeles trace gas distributions from a mountaintop site,"
535 *Atmospheric Meas. Tech.* **7**, 713–729 (2014).

536 16. F. Pasternak, P. Bernard, L. Georges, and V. Pascal, "The microcarb instrument," in *International*
537 *Conference on Space Optics — ICSSO 2016* (SPIE, 2017), Vol. 10562, pp. 485–497.

538 17. C. Staebell, K. Sun, J. Samra, J. Franklin, C. Chan Miller, X. Liu, E. Conway, K. Chance, S. Milligan, and S.
539 Wofsy, "Spectral calibration of the MethaneAIR instrument," *Atmospheric Meas. Tech.* **14**, 3737–3753
540 (2021).

541 18. L. C. Sinclair, J.-D. Deschênes, L. Sonderhouse, W. C. Swann, I. H. Khader, E. Baumann, N. R. Newbury,
542 and I. Coddington, "Invited Article: A compact optically coherent fiber frequency comb," *Rev. Sci. Instrum.*
543 **86**, 081301 (2015).

544 19. G. P. Agrawal, "Soliton fission and dispersive waves," in *Nonlinear Fiber Optics*, 5th ed. (Elsevier, 2013),
545 pp. 501–521.

546 20. J. Roy, J.-D. Deschênes, S. Potvin, and J. Genest, "Continuous real-time correction and averaging for
547 frequency comb interferometry," *Opt. Express* **20**, 21932–21939 (2012).

548 21. S. Singh and N. Singh, "Nonlinear effects in optical fibers: origin, management, and applications," *Prog.*
549 *Electromagn. Res.* **73**, 249–275 (2007).

550 22. M. A. Khalighi and M. Uysal, "Survey on Free Space Optical Communication: A Communication Theory
551 Perspective," *IEEE Commun. Surv. Tutor.* **16**, 2231–2258 (2014).

552 23. P. Guay, A. Tourigny-Plante, V. Michaud-Belleau, N. B. Hébert, A. Gouin, and J. Genest, "Understanding
553 photodetection nonlinearity in dual-comb interferometry," *OSA Contin.* **4**, 2460–2467 (2021).

554 24. G.-W. Truong, K. C. Cossel, E. Waxman, F. R. Giorgetta, I. Coddington, and N. R. Newbury, "Phase Noise-
555 Induced Biases in Coherent Dual-Comb Spectroscopy," in *CLEO* (OSA, 2016).

556 25. N. R. Newbury and W. C. Swann, "Low-noise fiber-laser frequency combs (Invited)," *J Opt Soc Am B* **24**,
557 1756–1770 (2007).

558 26. G. Ycas, F. R. Giorgetta, E. Baumann, I. Coddington, D. Herman, S. A. Diddams, and N. R. Newbury,
559 "High-coherence mid-infrared dual-comb spectroscopy spanning 2.6 to 5.2 μm ," *Nat. Photonics* **12**, 202–208
560 (2018).

561 27. J.-D. Deschênes, P. Giaccari, and J. Genest, "Optical referencing technique with CW lasers as intermediate
562 oscillators for continuous full delay range frequency comb interferometry," *Opt. Express* **18**, 23358–23370
563 (2010).

564 28. N. Malarich, K. Cossel, F. Giorgetta, E. Baumann, G. Mead, D. Herman, B. Washburn, N. Newbury, and I.
565 Coddington, "Countering nonlinearity in digitization for precise dual-frequency comb spectroscopy," in
566 (*Optica*, 2022).

567 29. R. Wannamaker, "The theory of dithered quantization," Waterloo (1997).

568 30. R. F. Keeling, S. C. Piper, and M. Heimann, "Global and hemispheric CO₂ sinks deduced from changes in
569 atmospheric O₂ concentration," *Nature* **381**, 218–221 (1996).

570 31. A. C. Manning, R. F. Keeling, and J. P. Severinghaus, "Precise atmospheric oxygen measurements with a
571 paramagnetic oxygen analyzer," *Glob. Biogeochem. Cycles* **13**, 1107–1115 (1999).

572 32. R. K. Cole, A. S. Makowiecki, N. Hoghooghi, and G. B. Rieker, "Baseline-free quantitative absorption
573 spectroscopy based on cepstral analysis," *Opt. Express* **27**, 37920–37939 (2019).

574 33. R. A. Washenfelder, G. C. Toon, J.-F. Blavier, Z. Yang, N. T. Allen, P. O. Wennberg, S. A. Vay, D. M.
575 Matross, and B. C. Daube, "Carbon dioxide column abundances at the Wisconsin Tall Tower site," *J.*
576 *Geophys. Res. Atmospheres* **111**, D22305 (2006).

577 34. R. V. Kochanov, I. E. Gordon, L. S. Rothman, P. Wcisło, C. Hill, and J. S. Wilzewski, "HITRAN
578 Application Programming Interface (HAPI): A comprehensive approach to working with spectroscopic data,"
579 *J. Quant. Spectrosc. Radiat. Transf.* **177**, 15–30 (2016).

580 35. M. Konefal, S. Kassi, D. Mondelain, and A. Campargue, "High sensitivity spectroscopy of the O₂ band at
581 1.27 μm : (I) pure O₂ line parameters above 7920 cm^{-1} ," *J. Quant. Spectrosc. Radiat. Transf.* **241**, 106653
582 (2020).

583 36. D. D. Tran, H. Tran, S. Vasilchenko, S. Kassi, A. Campargue, and D. Mondelain, "High sensitivity
584 spectroscopy of the O₂ band at 1.27 μm : (II) air-broadened line profile parameters," *J. Quant. Spectrosc.*
585 *Radiat. Transf.* **240**, 106673 (2020).

586 37. D. D. Tran, T. Delahaye, R. Armante, J.-M. Hartmann, D. Mondelain, A. Campargue, H. Fleurbaey, J. T.
587 Hodges, and H. Tran, "Validation of spectroscopic data in the 1.27 μm spectral region by comparisons with
588 ground-based atmospheric measurements," *J. Quant. Spectrosc. Radiat. Transf.* **261**, 107495 (2021).

589 38. N. R. Newbury, I. Coddington, and W. C. Swann, "Sensitivity of coherent dual-comb spectroscopy," *Opt.*
590 *Express* **18**, 7929–7945 (2010).

591 39. D. I. Herman, C. Weerasekara, L. C. Hutcherson, F. R. Giorgetta, K. C. Cossel, E. M. Waxman, G. M.
592 Colacion, N. R. Newbury, S. M. Welch, B. D. DePaola, I. Coddington, E. A. Santos, and B. R. Washburn,
593 "Precise multispecies agricultural gas flux determined using broadband open-path dual-comb spectroscopy,"
594 *Sci. Adv.* **7**, eabe9765 (2021).

595 40. D. Wunch, P. O. Wennberg, G. Osterman, B. Fisher, B. Naylor, C. M. Roehl, C. O'Dell, L. Mandrake, C.
596 Viatte, M. Kiel, D. W. T. Griffith, N. M. Deutscher, V. A. Velazco, J. Notholt, T. Warneke, C. Petri, M. De
597 Maziere, M. K. Sha, R. Sussmann, M. Rettinger, D. Pollard, J. Robinson, I. Morino, O. Uchino, F. Hase, T.
598 Blumenstock, D. G. Feist, S. G. Arnold, K. Strong, J. Mendonca, R. Kivi, P. Heikkinen, L. Iraci, J. Podolske,
599 P. W. Hillyard, S. Kawakami, M. K. Dubey, H. A. Parker, E. Sepulveda, O. E. García, Y. Te, P. Jeseck, M.
600 R. Gunson, D. Crisp, and A. Eldering, "Comparisons of the Orbiting Carbon Observatory-2 (OCO-2) XCO₂
601 measurements with TCCON," *Atmos Meas Tech* **10**, 2209–2238 (2017).

602 41. Y. Tan, R. V. Kochanov, L. S. Rothman, and I. E. Gordon, "Introduction of Water-Vapor Broadening
603 Parameters and Their Temperature-Dependent Exponents Into the HITRAN Database: Part I—CO₂, N₂O,
604 CO, CH₄, O₂, NH₃, and H₂S," *J. Geophys. Res. Atmospheres* **124**, 11580–11594 (2019).

605 42. N. Malarich, "Dataset 1" figshare (2022) doi.org/10.6084/m9.figshare.21506976

606 43. The use of tradenames in this manuscript is necessary to specify experimental results and does not imply
607 endorsement by the National Institute of Standards and Technology