

TRACE MOLECULAR SENSOR BASED ON MID-INFRARED / THZ FREQUENCY COMBS.

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Introduction: In-situ detection of atmospheric gas-phase trace molecules and key isotopologues can reveal a wealth of information about a planet's physical, chemical, and geological history and help discover signatures of life that the planet may harbor. Laser-based spectroscopic methods are exceedingly advantageous for molecular sensing in terms of both high sensitivity and specificity in analyte identification. However, modern high spectral resolution laser spectrometers based on frequency-swept lasers are inherently limited in their tuning range so that simultaneous identification of multiple molecules and isotopologues by a single instrument is challenging.

We propose a radically new concept for *in-situ* precision trace gas measurements based on the latest revolutionary advances in *laser frequency combs* (Physics Nobel Prize 2005) and their applications in high-resolution spectroscopy. The proposed technique, **dual-comb spectroscopy (DCS)** – takes advantage of coherent properties of laser light – both in time and space. To achieve ultrasensitive and parallel detection of trace gases, we will target, **in one device**, ultra-broadband MIR (3–20 μm) and THz (1–5 THz) regions of the electromagnetic spectrum, where the strongest molecular signatures (ro-vibrational and rotational, correspondingly) are found. The DCS method does not only allow massively parallel identification of numerous molecules and key isotopologues with high detection sensitivity and specificity, but features near real-time detection capability and sub-Doppler spectral resolution

Optical frequency combs – manifolds of evenly spaced narrow spectral lines emitted by phase-stabilized femtosecond lasers – were introduced in the late 1990s and have revolutionized accurate measurements of frequency and time as well as high-resolution spectroscopic measurements [1,2]. Dual comb spectroscopy (DCS) is currently the most advanced spectroscopic technique in the MIR/THz range. The second frequency comb, with a small offset of the mode spacing (same as an offset of the comb pulse repetition rate) with respect to the first comb, effectively plays the role of the Doppler-shifted second arm in the Michelson interferometer. In the frequency domain, DCS can be thought of as multiheterodyne spectroscopy. The advent of frequency combs in the MIR 'signature' region considerably improved the sensitivity of molecular sensing, although the spectral coverage in these studies

was limited to a few 100 cm^{-1} . For the simultaneous detection of species with different functional groups, a wider frequency coverage is required, ideally exceeding 1000 cm^{-1} . In the last decade, our group pioneered a new method for producing ultra-broadband MIR frequency combs using a sync-pumped optical parametric oscillator (OPO) operating at degeneracy, also referred to as a subharmonic or frequency-divide-by-2 OPO. In such a device, the down converted output is inherently phase locked to the frequency comb of the pump laser while the spectral span is greatly augmented and can exceed an octave in the frequency span [3–5].

Based on this development, we implemented a DCS system using on a pair of subharmonic OPOs pumped by two phase-locked Tm-fiber combs that provided fast (up to 100 spectra per second), moving-parts-free, simultaneous acquisition of 350,000 spectral data points, spaced by a 115 MHz (comb-line spacing) over the whole wavelength range of 3.1–5.5 μm . Figs. 1–2 illustrate massively parallel trace molecular sensing in a mixture of ten gases (OCS, N_2O , NO, CO, CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , CO_2 , and H_2O) at ppm-level concentrations [6].

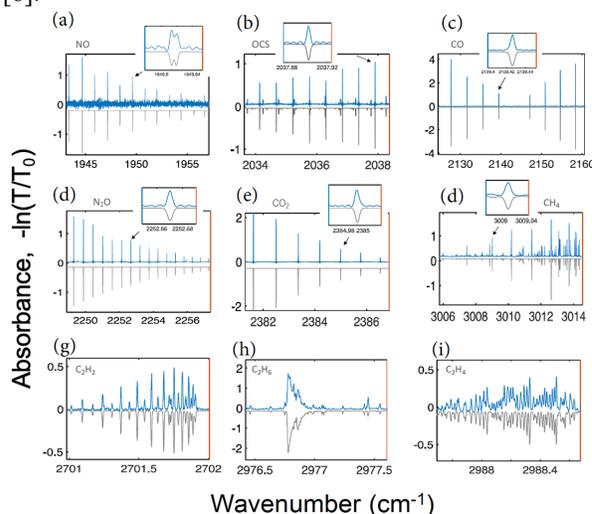


Fig. 1. Absorbance spectra of individual molecules obtained via DCS from a mixture of nine species (OCS, N_2O , NO, CO, CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , and CO_2) at ppm-level concentrations (buffer gas N_2 at 3-mbar total pressure). Simulated (HITRAN) absorption spectra are shown as inverted peaks [6].

Shown in Fig. 1 are spectra of molecules in the mixture along with simulated (HITRAN2016) absorption spectra, inverted for clarity.

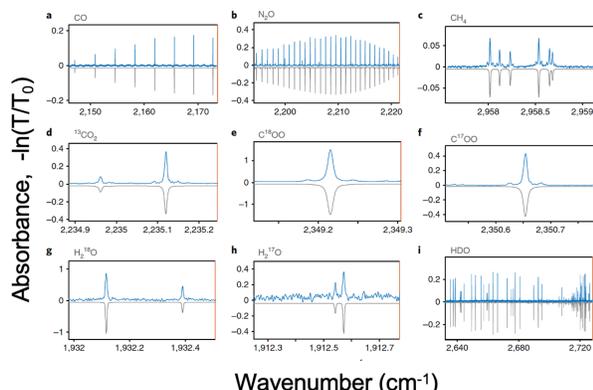


Fig. 2. Spectra of trace molecules present in ambient air ($p=10$ mbar). (a) CO, (b) N₂O, (c) CH₄, (d-f) three isotopologues of CO₂, (g-i) three isotopologues of H₂O. Simulated (HITRAN) absorption spectra are shown as inverted peaks [6].

Fig. 2 shows spectra of trace molecules measured just in ambient air. We detected CO, N₂O, CH₄, three isotopologues of CO₂, and three isotopologues of H₂O – with part-per-billion (ppb) sensitivity and sub-Doppler resolution. Due to the fact that the absolute frequency scale in our DCS setup was referenced to a Rb clock providing the absolute fractional accuracy of 10^{-10} , the acquired molecular spectra were in excellent agreement with the simulated ones. Overall, parallel detection of numerous trace species in a mixture, including isotopologues containing ¹³C, ¹⁸O, ¹⁷O, ¹⁵N, ³⁴S, ³³S and deuterium (D), with ppb sensitivity was demonstrated [6].

We also explore a new approach that will extend the DCS technique to the longwave IR and even THz range in a compact setup. The proposed sensing is based on **intra-pulse difference frequency generation (IDFG)**, also known as optical rectification, combined with electro-optic sampling (EOS) for detection.

IDFG takes advantage of the fact that near infrared ‘pump’ pulses consisting of only a few optical cycles have a very wide spectrum. Self-mixing of these spectral components in a nonlinear crystal produces a frequency down converted output that can range from 0.5 to 100 THz. The center frequency of the IDFG comb (either MIR or THz) is determined by the phase-matching condition and can be adjusted, for example, by angle tuning of a nonlinear crystal.

As a pump source, we will use a compact Kerr-lens mode-locked 2.35- μm Cr:ZnS laser producing pulses consisting of 2-3 optical cycles. Our preliminary results with these lasers show that we can generate super-wide IDFG outputs spanning more than two octaves in frequency with up to 10% conversion efficiency [7].

The key features of the proposed instrument are:

- Very broad spectral bandwidth for simultaneous detection of species in a significant portion of the MIR (3-20 μm) and terahertz (1-5 THz) ranges, while the device can easily switch between MIR and THz.
- Superior spectral resolution corresponding to the comb line spacing of 80 MHz ($2.7 \times 10^{-3} \text{ cm}^{-1}$) that can be reduced to 1 MHz ($3.3 \times 10^{-5} \text{ cm}^{-1}$) via sweeping the frequency comb lines.
- High speed of data acquisition - up to 100 spectra/sec combined with a massive amount of spectral information (up to 1M comb-line resolved data points).
- EOS based detection in the whole MIR/THz range allows avoiding cryogenically cooled detectors (especially bulky in the THz range).
- Outstanding dynamic range (150dB) provided by EOS since it senses MIR/THz field amplitude, not intensity.

Molecules that can be detected. The molecules that the instrument can detect include (but not limited to): CO₂ (carbon dioxide), CO (carbon monoxide), CH₄ (methane), C₂H₆ (ethane), CH₂O (formaldehyde), N₂O (nitrous oxide), OCS (carbonyl sulfide), H₂O (water vapor), NO (nitric oxide), C₂H₄ (ethylene), C₂H₂ (acetylene), CH₃OH (methanol), CS₂ (sulfur dioxide), PH₃ (phosphine), and their isotopologues containing isotopes: ¹³C, ¹⁸O, ¹⁷O, ¹⁵N, ³⁴S, ³³S and ²H (deuterium).

In summary, our instrument will advance the state of science across several major areas of planetary science and, in particular the investigation of Venus cloud region. It may help to:

- detect new atmospheric trace gases on Venus (and other planets).
- understand isotopic composition based on molecular spectra.
- determine the vertical and horizontal structure of the atmosphere and distribution of gases and study its daily or seasonal changes.
- investigate the correlation between the fluctuations of molecular abundances

References

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