

Massively-parallel intracavity trace molecular detection in the mid-infrared using broadband frequency combs

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ABSTRACT

Ultrasensitive detection of methane, isotopic carbon dioxide, carbon monoxide, formaldehyde, acetylene and ethylene is performed in the spectral range 2.5 – 5 μm using intracavity spectroscopy inside a broadband optical parametric oscillator (OPO). The two separate OPOs were operated near degeneracy and were synchronously pumped either by a mode-locked erbium (1560 nm) or thulium (2050 nm) fiber laser. A large instantaneous bandwidth of up to 800 cm^{-1} allowed for simultaneous detection of several gases. We observed an effective path length enhancement due to coherent interaction inside the OPO cavity and achieve part-per-billion sensitivity levels.

Keywords: molecular spectroscopy, middle infrared, optical parametric oscillator, frequency combs, intracavity spectroscopy, trace molecular detection.

1. INTRODUCTION

Optical spectroscopy in the mid-IR - the region of fundamental rotational-vibrational transitions - has potential for such applications as trace gas detection [1], remote chemical sensing [2], and human breath analysis [3–5]. For example, human breath is known to contain more than 500 different 'biomarker' volatile organic compounds and quantification of these gases may have clinical applications. Simultaneous detection of several gases requires a suitable broadband or a widely tunable CW source. A broadband source coupled with Fourier transform methods provides massive parallelism of data collection and elimination of the need for wavelength tuning. Optical frequency combs are particularly attractive broadband sources for spectroscopy [6], owing to their extraordinary coherence over broad bandwidth. This property has led to applications including trace gas detection, molecular fingerprinting and dual comb spectroscopy [7–10].

Synchronously pumped (sync-pumped) optical parametric oscillators represent an attractive way of generating mid-IR frequency combs suitable for molecular spectroscopy [14–17]. Recently a new method was implemented for generating broadband mid-IR combs, based on a doubly resonant, degenerate sync-pumped OPO, which rigorously downconverts and augments the spectrum of its pump frequency comb [18,19]. Exceptionally large parametric gain bandwidth at degeneracy combined with extensive cross mixing of comb components, resulted in extremely broad (> one-octave-wide) instantaneous mid-IR bandwidth extending the wavelength range beyond 6 μm [19]. Here we show that such a broadband source, combined with intracavity spectroscopy, becomes a useful tool for trace molecular detection.

We perform molecular spectroscopy using two such sources. One source is a periodically poled lithium niobate (PPLN) based OPO, pumped at 1560 nm by a femtosecond Er-doped fiber laser [18], and the other source is an orientation-patterned GaAs based OPO, pumped at 2050 nm by a Tm-doped fiber laser [19]. Both OPOs operate near degeneracy – to obtain broad instantaneous bandwidth. In this work the OPO cavity itself is used as an enhancement cavity to increase the effective path length [20–22]. Intracavity spectroscopy of methane, carbon monoxide, formaldehyde and several other gases is performed by injecting gas directly into the OPO enclosure, or by using an intracavity gas cell with Brewster windows. We observe significant effective path length enhancement due to the intracavity action. In addition, we find that the measured spectral line shapes may have dispersive features. Such features have previously been observed with cavity-enhanced frequency comb spectroscopy [14, 23], and in intracavity spectroscopy with sync-pumped OPOs and mode-locked lasers [19,24,25]. The measured spectra are compared to a simple model, based on the intracavity passive loss and round-trip dispersion, and excellent agreement between theory and measurements is found.

2. EXPERIMENTAL SETUP

The first OPO in our experiment was based on a PPLN crystal and was pumped by an Er: fiber laser (Toptica, 350 mW average power, 1.56 μm wavelength, 80 MHz repetition rate, 85 fs pulse duration), producing an output centered at $\sim 3.1 \mu\text{m}$. The length of the PPLN crystal was 0.5 mm or 0.8 mm and a ZnSe 1-degree wedge pair was used for dispersion compensation and for out-coupling, as shown in Fig. 1. The second OPO was based on a 0.5-mm-long orientation-patterned GaAs (OP-GaAs) crystal, and was pumped by a Tm: fiber laser (IMRA, 600 mW average power, 2.05 μm wavelength, 75 MHz rep. rate, 93 fs pulse duration), producing an output centered at 4.1 μm . The OPOs and their coherence properties are described in detail in Refs. [18, 19, 26]. Both OPOs were placed in Plexiglas enclosures and the pump lasers were free running. The output power of the OPOs was some tens of mW.

Oscillation occurs at a discrete set of cavity lengths, separated (in effective roundtrip cavity length) by approximately one pump wavelength, due to the doubly resonant operation [26]. Figure 2 shows measured output power of the Er: fiber pumped OPO, with 0.8 mm PPLN, as a function of cavity length detuning. The cavity length was locked to one of these oscillation peaks using a feedback loop including a piezo stage attached to one of the cavity mirrors.

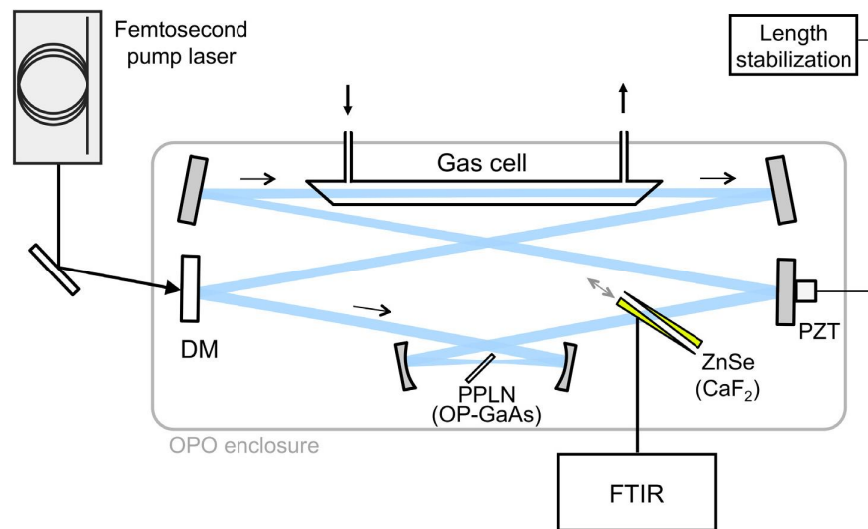


Figure 1. Schematic of the degenerate broadband OPO. The pump beam was introduced through the in-coupling dielectric mirror DM. The other five mirrors are gold coated. A pair of wedges made of ZnSe (Er: fiber-pumped system) or CaF₂ (Tm: fiber-pumped system) was used for (i) dispersion compensation and (ii) beam out-coupling. The nonlinear crystal was AR-coated (PPLN) or placed at Brewster's angle (OP-GaAs).

3. SPECTRAL MEASUREMENTS

We have performed spectroscopic measurements of six different molecules. Measurements of methane, formaldehyde, ethylene and acetylene were performed using the Er: fiber pumped OPO, while the absorption spectra of carbon monoxide and isotopic carbon dioxide (¹³CO₂) were measured with the Tm: fiber pumped OPO. Measurements of the absorption spectra were carried out by injecting a controlled amount of gas directly into the N₂-purged Plexiglas enclosure, or by using an intra-cavity gas cell with length 48 cm and a volume of $\sim 30 \text{ cm}^3$ (used for formaldehyde and carbon monoxide). The Brewster windows in the gas cell were made of 1-mm-thick ZnS that was chosen because of its comparatively low dispersion in the 2–5 μm range (with zero-dispersion at 3.7 μm).

The main advantages with injecting gas directly into the OPO enclosure were simplicity and the ability to exploit the entire cavity round-trip length as a physical path length through the gas. The disadvantages with this approach were the large volume of the Plexiglas enclosure (estimated to be 103 liter) and possible contamination of the optical surfaces of the OPO components. The advantages using the gas cell were the small volume of the cell, and the ability to easily control the flow rate and the pressure of the gas. The main disadvantage with the gas cell was the short cell length

compared to the cavity round-trip distance (~ 0.5 m vs. ~ 4 m), but this could in principle be improved by using a different resonator geometry allowing longer intracavity gas cells. All spectra were measured at 1 atm. pressure and a temperature of 21.5 °C. The flow rate of gas through the intra-cavity cell was 0.2 l/min. for formaldehyde, and a steady state gas concentration was reached after ~ 5 min. of flowing. No flowing was used for carbon monoxide. Unless otherwise noted, the OPO output spectra were measured with a commercial (Nicolet 6700) FTIR spectrometer with a liquid N₂-cooled HgCdTe detector. We used the maximum available resolution of 0.125 cm⁻¹ of the FTIR instrument for most of the measurements. The total measurement time was in the range of 30 seconds up to 4 minutes, which includes averaging over 8 to 32 scans. Reference spectra were obtained by filling the OPO enclosure and gas cell, respectively, with N₂ only. The free-running pump lasers resulted in drifts of the OPO spectra on a time scale of the order of minutes, affecting the baseline in the relative OPO spectra. We therefore apply a baseline correction (determined by parts of the spectra between the absorption lines) of up to a few percent of the measured spectral intensity.

4. RESULTS

Fig. 2 shows the spectrum of methane, obtained when a controlled amount of this gas was injected into the N₂-flushed OPO enclosure. Based on the volume of the enclosure, the concentration of methane in the OPO cavity was estimated to be 8.5 ppm. 'Dispersive' features seen in the spectrum result from the coherent interaction of intracavity light with the molecules. Due to small group dispersion of the OPO cavity, which results in the occurrence of an extra phase shift $\Delta\phi$, the cavity transmission coefficient becomes complex. Molecular dispersion imposes an additional phase shift near absorption resonances (antisymmetric with respect to the line center). This causes a distortion of the spectral line shapes depending on the mismatch. Our simple theory for intracavity spectroscopy with femtosecond OPOs [27] predicts dispersive features in the absorption spectrum, similar to those observed with frequency comb spectroscopy enhanced with an external cavity [23]. The calculated absorption of methane, also shown in Fig. 2, was based on the known line intensities and line widths from the HITRAN database. We also used the known dispersion of the OPO cavity elements and observe that the simulated spectrum reproduces the measured spectrum pretty well.

The results for spectral measurements of formaldehyde, acetylene+methane mixture, ethylene, carbon monoxide, and isotopic carbon dioxide are shown in Figures 3-7.

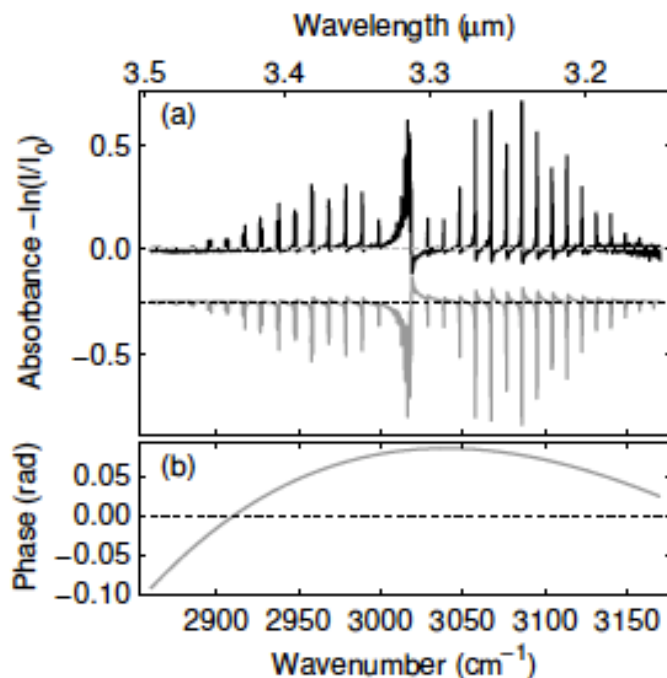


Figure 2. Measured (black) and calculated (gray) absorption spectra for 8.5 ppm methane in nitrogen at 1 atm. Pressure. The calculated spectrum is inverted and offset for clarity. (b) Phase shift $\Delta\phi$, which was used for the calculation in (a).

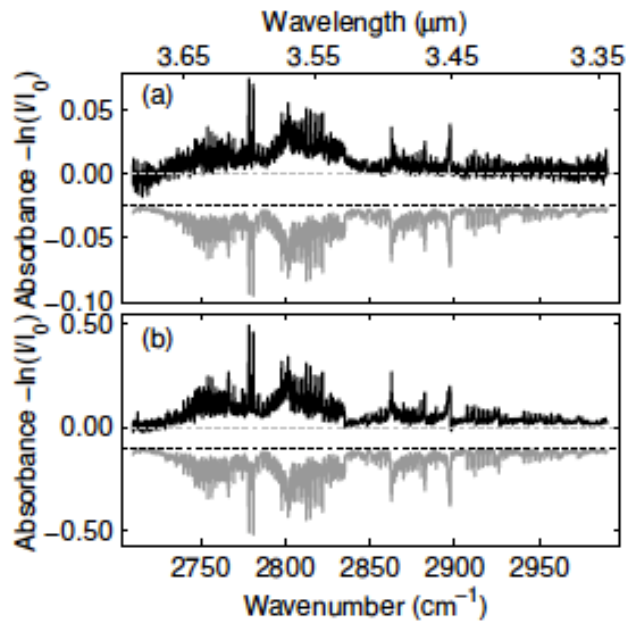


Figure 3. Measured (black) and calculated absorption spectra (gray) for 100 ppm formaldehyde in nitrogen at 1 atm. pressure. The calculated spectra are offset and shown on an inverted scale for clarity. (a) Extracavity spectra, (b) intracavity spectra. The effective path length is taken to be 6 times the length of the gas cell for the calculated spectrum in (b).

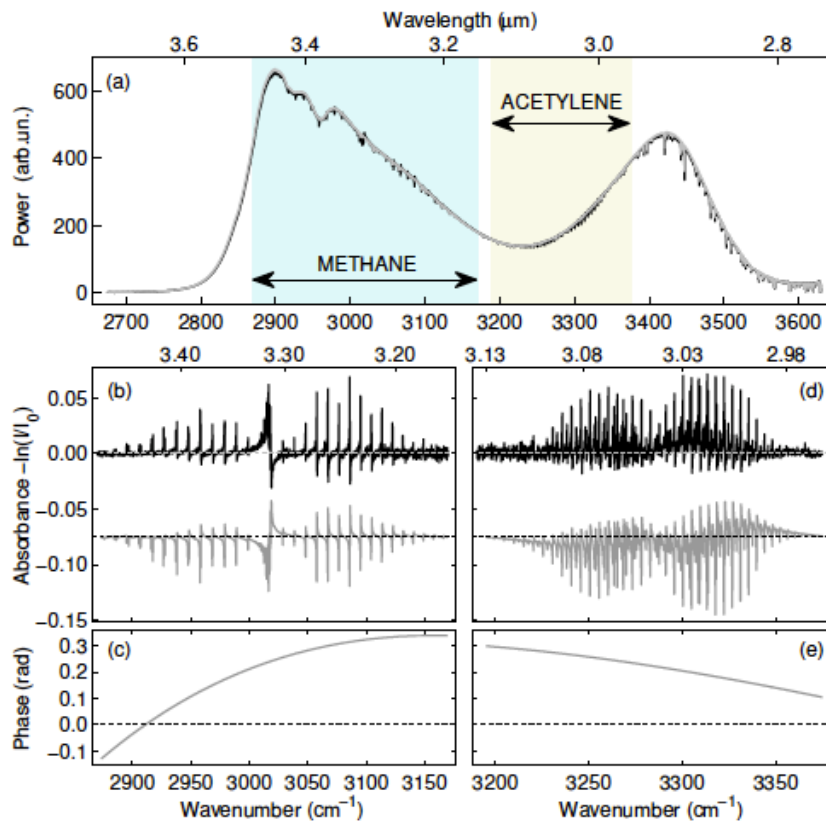


Figure 4. (a) Showing reference intracavity spectrum (gray) and, underneath, the intracavity spectrum (black) with the absorption features present, while detecting methane and acetylene simultaneously inside the OPO. (b) Experimentally measured methane spectrum (black) at a concentration of 1.4 ppm and the corresponding calculated spectrum (gray). (c) Round-trip phase shift for the calculated methane spectrum. (d) Experimentally measured acetylene spectrum (black) at a concentration of 3.8 ppm and the corresponding calculated spectrum (gray). (e) Round-trip phase shift for the calculated acetylene spectrum. The calculated spectra in (b) and (d) are offset and shown on an inverted scale for clarity.

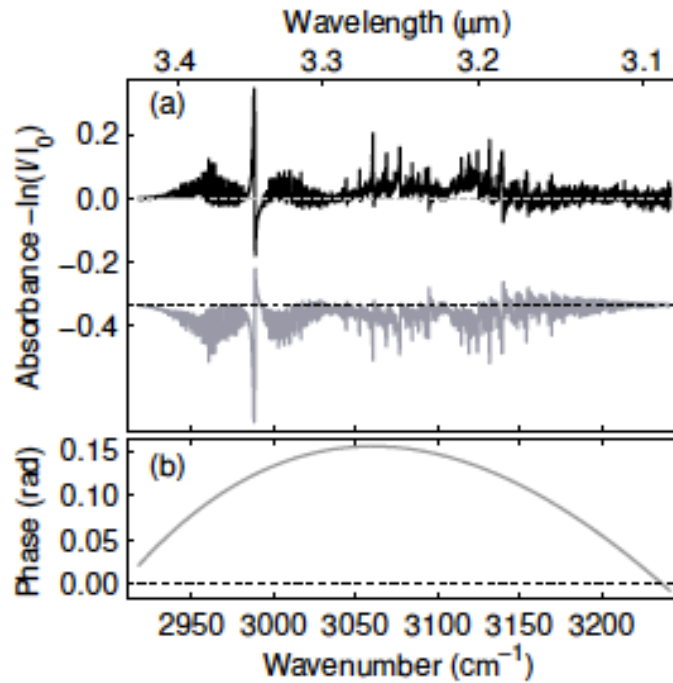


Figure 5. (a) Experimentally measured ethylene spectrum (black) at a concentration of 48 ppm and the corresponding calculated spectrum (gray). The calculated spectrum is inverted and offset for clarity. (b) Phase shift $\Delta\phi(\nu)$, which was used for the calculation in (a).

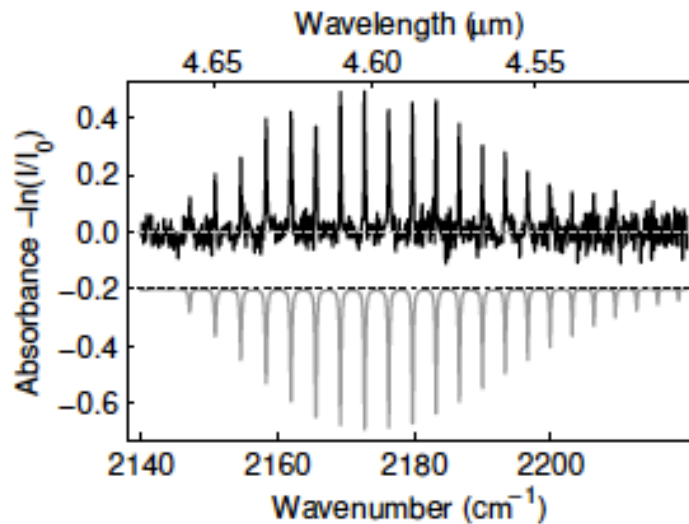


Figure 6. Measured (black) and calculated (gray) absorption spectra for 50 ppm carbon monoxide in helium at 1 atm. pressure. The calculated spectrum is offset and shown on an inverted scale for clarity. The effective path length is taken to be 7 times the length of the gas cell for the calculated spectrum

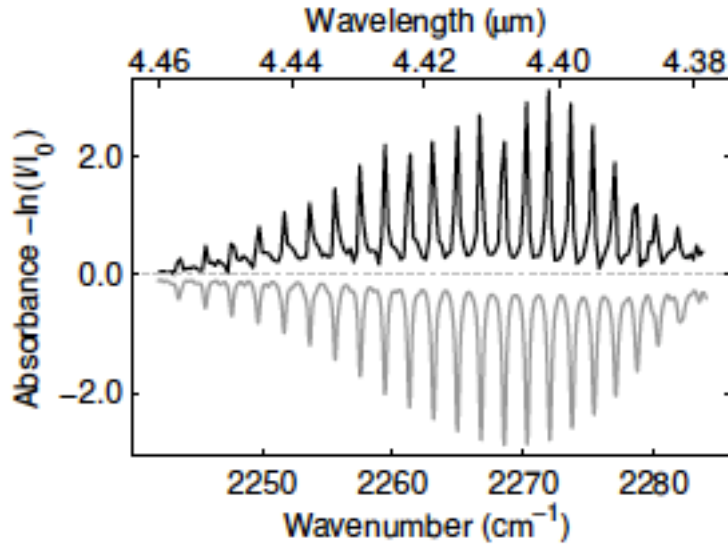


Figure 7. Measured (black) and calculated (gray) molecular spectra of isotopic ($^{13}\text{CO}_2$) carbon dioxide. The simulation is based on the HITRAN database and is inverted for clarity

Finally, Table 1 represents estimated detection limits for each of the six molecules investigated.

Table 1. Estimated detection limits.

Gas name	Det. Limit [ppb]	Meas. Time [s]	Phys. path length [m]	System
Methane (CH_4)	1.7	57	3.75	Er
Formaldehyde (CH_2O)	310	30	0.48	Er
Acetylene (C_2H_2)	110	60	3.75	Er
Ethylene (C_2H_4)	320	60	3.75	Er
Carbon monoxide (CO)	270	120	0.48	Tm
Isotopic carbon dioxide ($^{13}\text{CO}_2$)	2.4	90	4	Tm

5. CONCLUSION

By using synchronously pumped OPOs operating around degeneracy, we obtain ultrabroadband mid-IR radiation suitable for coherent spectroscopy in the Fourier domain. A large instantaneous bandwidth of up to 800 cm^{-1} allows detecting several trace gases simultaneously. Spectroscopic detection of six molecules in trace amounts has been performed in the wavelength range of $2.5 - 5\ \mu\text{m}$. By injecting the gases inside the OPO cavities we obtained substantial

enhancement of the effective path length and achieved detection limits down to part-per-billion level in volume. Our intracavity sensing approach offers great simplicity and compactness, which might be a great asset for future applications. The dispersive spectral features that we observe at some circumstances are well reproduced using a simple model for propagation in a dispersive Fabry-Perot cavity. These features can be predicted a priori from the knowledge of group dispersion of the intracavity elements. By decreasing the OPO loss and increasing the finesse of the OPO cavity we expect an improvement of detection limits, down to sub-ppb levels. This will also require better dispersion compensation, e.g. using chirped dielectric mirrors. Utilizing intracavity cells with low (~ 0.1 atm.) gas pressure will allow better specificity of molecular recognition because of sharper spectral features. With further development, this system may find important applications in trace gas detection and real time human breath analysis – with further enhancement possible through the use of dual-comb multi-heterodyne methods.

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