Intracavity molecular spectroscopy in the mid-IR using ultra-broadband optical parametric oscillator

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ABSTRACT

We have performed intracavity molecular spectroscopy of water vapor, isotopic carbon dioxide, methane, acetylene, carbon monoxide, formaldehyde and other gases using broadband mid-IR sync-pumped OPO sources (PPLN-based OPO pumped by a femtosecond Er-fiber laser, or OP-GaAs-based OPO pumped by a femtosecond Tm-fiber laser) operating near degeneracy, with up to 2.5–6.1 μm instantaneous bandwidth. We found that the measured spectral line shapes may show dispersive features. The measured spectra were compared to a simple model, based on the intracavity round-trip dispersion, and excellent agreement between theory and measurements was found. Detection limits in the ppb-range were demonstrated.

Keywords: Infrared spectroscopy, frequency combs, optical parametric oscillator

1. INTRODUCTION

Optical spectroscopy in the mid-IR region has potential for several applications including trace gas detection,[1] remote chemical sensing,[2] and human breath analysis.[3–5] For simultaneous detection of several gasses a broadband source or a widely tunable CW source is required. Optical frequency combs are especially attractive broadband sources for spectroscopy,[6] due to their extraordinary coherence over broad bandwidth and good beam quality.

Recently, our group implemented a new method suitable for generating broadband mid-IR combs, based on a doubly resonant, degenerate sync-pumped OPO.[7,8] Exceptionally large parametric gain bandwidth at degeneracy combined with extensive cross mixing of comb components, resulted in extremely broad (> one octave) instantaneous mid-IR bandwidth extending the wavelength range beyond 6 μm.[8] Here we show that such a broadband source becomes a powerful tool for trace molecular detection. The OPO cavity itself is used as an enhancement cavity to increase the effective path length. We observe one order of magnitude enhancement of the absorption features. 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,[9,10] and in intracavity spectroscopy with sync-pumped OPOs and mode-locked lasers.[8,11,12] A simple model is developed to model such dispersive features in sync-pumped OPOs, and we compare the model to the experimental results.

2. EXPERIMENTAL SETUP

We perform broadband molecular spectroscopy using two degenerate, doubly resonant OPO sources. The doubly resonant operation makes oscillation occur at a discrete set of cavity lengths, separated (in effective round-trip cavity length) by approximately one pump wavelength.[13] One source is a periodically-poled lithium niobate (PPLN) based OPO, pumped at 1.56 μm by a femtosecond Er-doped fiber laser (Toptica, 350 mW average power, 1.56 μm wavelength, 80 MHz repetition rate, 85 fs pulse duration), producing an output centered at

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~ 3.1 μm.[7] 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 other source is based on a 0.5-mm long orientation-patterned GaAs crystal, which is pumped at 2.05 μm by a Tm-doped 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.[8] The OPOs and their properties are described in detail in Refs.[7,8,13] 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.

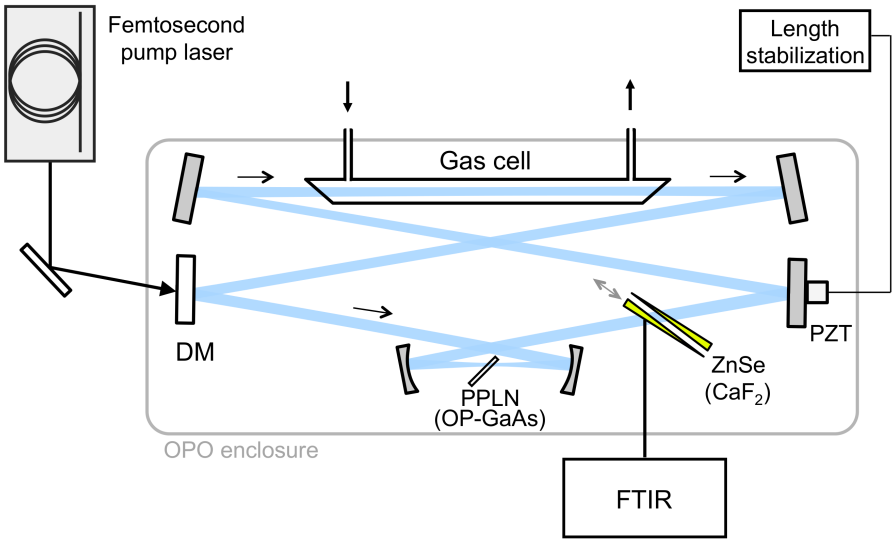

Figure 1. The degenerate broadband OPO. The pump beam was introduced through the in-coupling dielectric mirror DM. The other five mirrors are gold coated. A pair of wedges made of ZnSe (Er:fiber-pumped system) or CaF_2 (Tm:fiber-pumped system) was used for (i) dispersion compensation and (ii) beam out-coupling. The nonlinear crystal was AR-coated (PPLN) or placed at Brewster's angle (OP-GaAs).

Measurements of methane, formaldehyde, ethylene and acetylene were performed using the Er:fiber pumped OPO, while absorption spectra of carbon monoxide and isotopic carbon dioxide ($^{13}CO_2$) 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 N_2-purged Plexiglas enclosure, or by using an intra-cavity gas cell with length 48 cm and a volume of ~ 30 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).

All spectra were measured at 1 atm. pressure and a temperature of 21.5 °C. The OPO output spectra were measured with a commercial (Nicolet 6700) FTIR spectrometer with a liquid N_2-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. First, the OPO was locked to an appropriate oscillation peak during measurements using the dither-and-lock technique. Then reference spectra were obtained by filling the OPO enclosure and gas cell, respectively, with N_2 only. Finally, the trace gases were injected and the absorption spectra were determined from the ratio between these two measurements. 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. In addition, an offset in wavenumber of up to ~ 1 cm^{-1} was applied to the measured data, to compensate FTIR instrument errors and to match the positions of the measured absorption peaks to the HITRAN data.

3. MODEL FOR INTRACAVITY MOLECULAR SPECTROSCOPY

We here present a simple model for intracavity gas spectroscopy with femtosecond OPOs. Consider a synchronously pumped femtosecond OPO where we assume steady-state conditions. The round-trip evolution of the resonating pulse (signal) is given by

$$A(\omega_n) = t(\omega_n)A(\omega_n) + \Delta A(\omega_n). \tag{1}$$

Here $A(\omega_n)$ is the spectral amplitude of comb tooth No. n of the signal, $t = |t| \exp(-i\Delta\phi)$ is the round-trip amplitude transmission coefficient of the OPO-cavity, ΔA is the gain due to the nonlinear crystal, and $\Delta\phi$ is the linear round-trip phase shift. ΔA can in principle be found using the coupled-wave equations, but we here make the approximation that ΔA is not significantly affected by weak, narrow molecular absorption features. One can argue for this both in the time domain and in the frequency domain. In the frequency domain, the nonlinear interaction results in a cross-coupling between large manifolds of pump and OPO comb lines. Given the extremely broad spectra for both the pump and the OPO, the presence of narrow molecular absorption features in the spectra will be averaged out in in the coupled-wave equations describing the evolution of the signal in the nonlinear crystal. Consequently, ΔA is unaffected by narrow molecular absorption lines. In the time domain the effect of a narrow absorption feature is to add a tail to the initial pulse, with a time-constant determined by the absorption line width. If the absorption line width is much smaller than the bandwidth of the main pulse, there will be negligible temporal overlap between the main pulse and its tail, and the non-linearity will only affect the initial pulse. The approximation of a constant ΔA makes Eq. (1) similar to transmission through a dispersive Fabry-Perot cavity. Accordingly, our simple theory for intracavity spectroscopy with femtosecond OPOs predicts dispersive features in the absorption spectrum, similar to those observed with frequency comb spectroscopy enhanced with an external cavity.[9,17] Physically, dispersion in the OPO cavity introduces a mismatch $\Delta\phi(\nu)$ between the OPO frequency comb and the cavity resonances. Molecular dispersion imposes an additional phase shift near absorption resonances. This causes a change of the spectral line shapes depending on the mismatch.

4. RESULTS

We here present the results from a selection of the measurements on the gasses.

4.1 Simultaneous measurement of acetylene and methane with the PPLN OPO

This experiment was performed to measure acetylene on one hand but also to show the capabilities of the intracavity OPO spectroscopy to detect more than one trace gas at once with reasonable high resolution. The use of a syringe allowed a precisely controlled injection of 400 ml of 1000 ppm acetylene in N_2, followed by 15.0 ml of 1% methane in N_2, into the N_2-flushed OPO enclosure, resulting in an estimated 3.78 ppm acetylene concentration and 1.40 ppm methane concentration, respectively. Figure 2(a) shows the measured reference spectrum (gray) and, underneath, the absorption intracavity spectrum (black), covering the absorption region of methane and acetylene, with the OPO operated with 0.8 mm of PPLN crystal length. Figure 2(b) indicates the measured dispersive absorption spectrum of methane and the corresponding calculated spectrum. Figure 2(d) contains the detected absorption spectrum for acetylene, which shows a similar amount of dispersion. Setting the FTIR to 17 scans per trace with a resolution of 0.125 cm^{-1} resulted in an acquisition time of 60 s for the reference as well as the absorption measurements. The simulated spectra were obtained using the fitted linear round-trip phase shifts in Fig. 2(c) and (e) for methane and acetylene, respectively, while assuming a cavity round-trip loss of 25%. We estimate a detection limit of 105 ppb for acetylene and 1.7 ppb for methane using a matched-filter approach.

4.2 Measurement of carbon monoxide with the Tm-pumped OPO

The Tm-system represents an attractive system because of its wide bandwidth from 2.6–6.1 μm at the -30 dB level. Initial measurements of intracavity spectra of water vapor and isotopic CO_2 in standard air have previously been presented in Refs.[8,18] for this system.

Carbon monoxide absorbs around 4.7 μm, and the Tm-system was tuned to this wavelength region by selecting an appropriate oscillation peak. The gas cell was filled with 50 ppm CO in He and placed inside the OPO cavity.

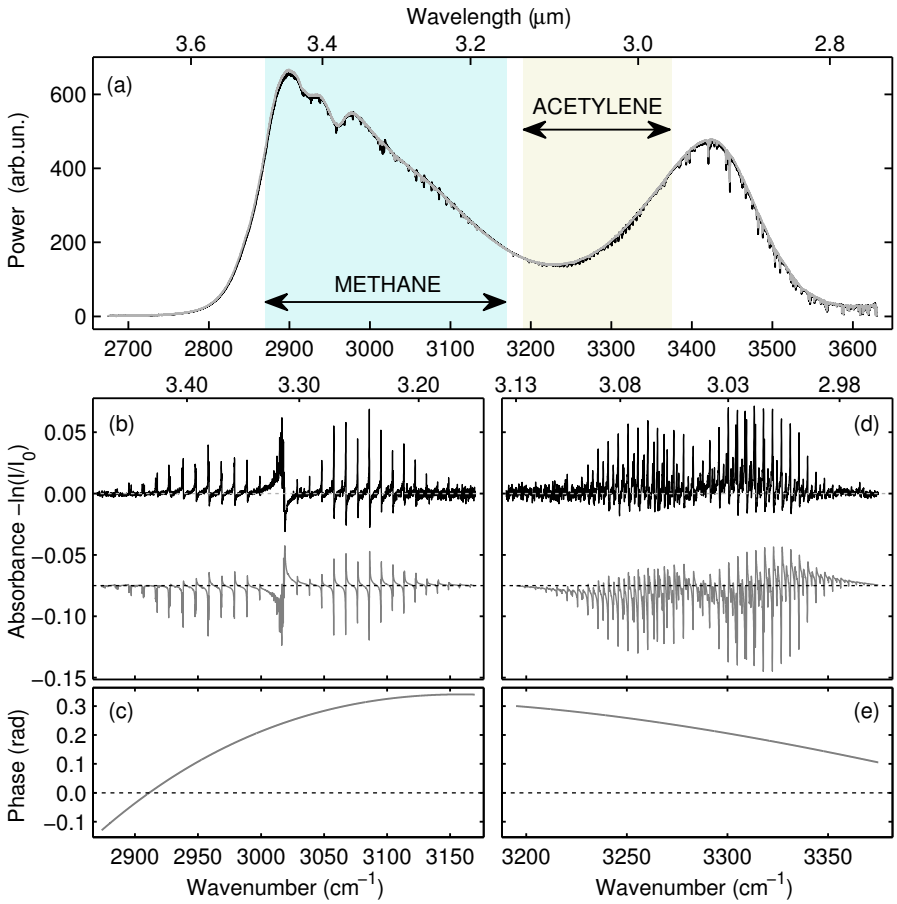

Figure 2. (a) Showing reference intracavity spectrum (gray) and, underneath, the intracavity spectrum (black) with the absorption features present, while detecting methane and acetylene simultaneously inside the OPO. (b) Experimentally measured methane spectrum (black) at a concentration of 1.40 ppm and the corresponding calculated spectrum (gray). (d) Experimentally measured acetylene spectrum (black) at a concentration of 3.78 ppm and the corresponding calculated spectrum (gray). The calculated spectra are offset and shown on an inverted scale for clarity.

Figure 3 shows the measured and calculated absorption spectrum of CO, with a measurement time of 2 min. In the calculations we assume a round-trip phase shift of $\Delta\phi = 0$, which provided a reasonable fit to the measured data. The detection limit for CO is estimated to be 270 ppb. The increased noise properties of the Tm-system, compared to the Er-system, are attributed to instabilities (mode hopping) in the 790-nm laser diodes used for pumping the Tm:fiber amplifier. We observe that the intracavity absorption is enhanced by a factor of ~ 7, corresponding to a round-trip loss of approximately 30%. However, this is higher than the expected round-trip loss of approximately 20%, estimated in a previous publication of the Tm-system,[8] and might be due to clipping of the signal beam introduced by the intracavity gas cell. For a perfectly aligned gas cell, the clipping is estimated to be a few percent.

5. CONCLUSIONS

By using synchronously pumped OPOs operating around degeneracy, we obtain ultra-broadband mid-IR radiation suitable for coherent spectroscopy in the Fourier domain. A large instantaneous bandwidth of up to 800 cm^{-1} allows detection of several trace gases simultaneously. 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. 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 pre-

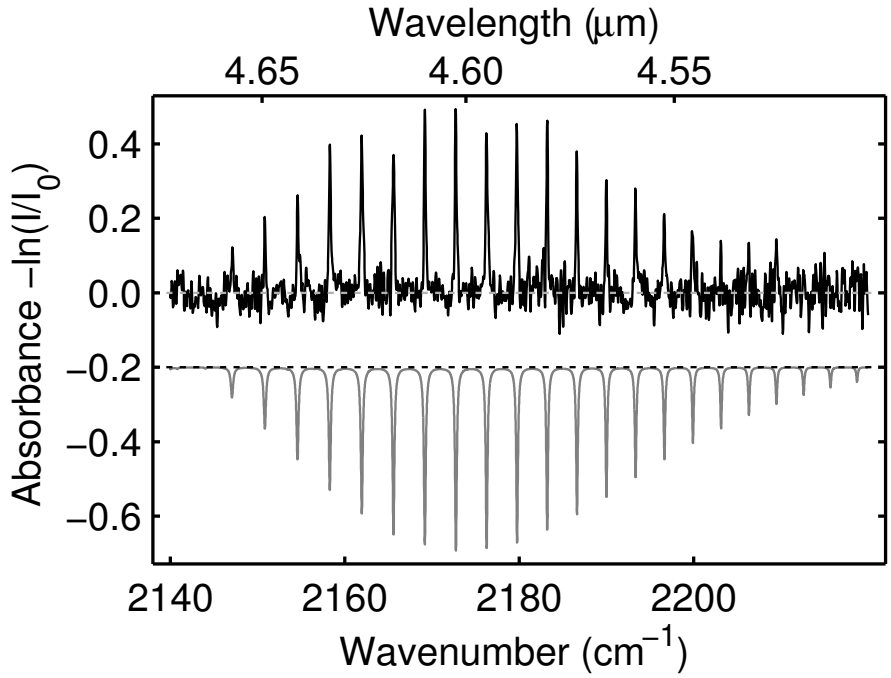

Figure 3. Measured and calculated absorption spectra for 50 ppm carbon monoxide in helium at 1 atm. pressure. The calculated spectrum is offset and shown on an inverted scale for clarity. The effective path length is taken to be 7 times the length of the gas cell for the calculated spectrum.

dicted a priori from knowledge of dispersion of the intracavity elements; on the other hand, if the dispersion of the individual components is not known, the overall dispersion can be precisely mapped by injecting trace amounts of known molecules and analyzing the shapes of spectral peaks. 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. With further development, this system may find important applications in trace gas detection and real time human breath analysis – with even further enhancement possible through the use of dual-comb multi-heterodyne methods

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