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Mid-infrared dual-comb spectroscopy with absolute frequency calibration using a passive optical reference

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Abstract: We demonstrate an absolute-frequency-calibrated mid-infrared dual-comb spectrometer by using a reference absorption cell. The source is based on a singly-resonant OPO containing two MgO:PPLN crystals in a common ring cavity, synchronously pumped by two mode-locked Yb-fiber lasers. The repetition-rate of the two pumps are stabilized while their offset frequencies and the OPO cavity length are not actively controlled. The reference spectrum is used to correct the frequency fluctuations in the sample spectrum providing a high-quality averaged spectrum with spectral resolution of 6 GHz and calibration precision of 120 MHz, without adding any complexity to the experimental setup or signal processing.

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1. Introduction

Dual-comb spectroscopy (DCS) [1–3] is a powerful alternative for traditional or comb-based Fourier-transform spectroscopy (FTS) using a mechanical moving mirror [4,5]. DCS provides a broad spectral coverage with a high spectral resolution in a very short acquisition time. For majority of the spectroscopic applications, the mid-infrared (mid-IR) spectral region beyond 2.5 µm is of particular interest, as most of the molecules have their strongest rotational-vibrational transitions in this wavelength region. The optical frequency comb (OFC) sources suitable for spectroscopy are usually generated from mode-locked femtosecond lasers. However, mode-locked lasers are mostly limited to the visible and near-infrared (near-IR) wavelength ranges and robust mid-IR mode-lock lasers are still under development [6]. Therefore, the main approach to generate mid-IR combs for spectroscopy is nonlinear conversion from near-IR combs by optical parametric oscillation (OPO) or difference frequency generation (DFG) [7]. Compared to femtosecond DFG-based sources, femtosecond OPOs [8,9] usually offer higher conversion efficiency and as a result have higher output power. The higher output power yields a dual-comb spectrum with higher signal-to-noise ratio (SNR) and, hence, a better detection sensitivity. On the other hand, femtosecond DFG-based sources [10,11] do not need a resonance cavity and can generate carrier-envelope-offset-free frequency combs, which simplifies the experimental setup and/or signal processing of dual-comb spectrometers [12]. Recent developments on dual-comb spectrometers based on both OPO [13] and DFG [14,15] enhance the available spectral bandwidth, spectral resolution, spectral precision and detection sensitivity of these systems. However, these improvements are achieved at the cost of more bulky and complicated experimental setups including f-2f interferometry, several stabilization loops and/or extensive signal processing.

Using OPOs for mid-infrared dual-comb spectroscopy, while keeping the experimental setup simple, remains a challenge since the optical cavity of the OPO introduces instability into the generated signal and idler combs, both in amplitude and frequency. Two independent, fully stabilized, degenerate doubly-resonant OPOs (DROPOs) have demonstrated the best amplitude and frequency stability, as well as spectral precision in a DCS setup [13]. This is
especially due to the fact that the carrier-envelope offset frequencies (f_{ceo}) of the signal and idler combs from a DROPO do not change randomly, but linearly depend on the offset frequency of the pump [16]. Therefore, stabilizing the f_{ceo} of the pump laser is sufficient to have a stable f_{ceo} of the signal and idler. In addition, working in a degenerate regime (subharmonic OPO), yields a well-known f_{ceo} of the signal/idler, which is equal to half of the f_{ceo} of the pump laser (or the alias of this frequency with respect to f_{rep}). To implement a DCS system based on two well-stabilized degenerate DROPOS, the f_{ceo} value of each pump is first detected by f-2f interferometry and then independently stabilized to a radio frequency (RF) signal [17]. Since the repetition rates (f_{rep}) and the length of the DROPO cavities should be stabilized as well, the final system consists of two f-2f interferometry setups and at least six (medium to high bandwidth) stabilization loops [13].

One can also use two singly-resonance OPOs (SROPOs), which eliminates the need for active stabilization of the length of the OPO cavities. DCS is demonstrated by using two free-running mode-locked lasers pumping two singly-resonance OPOs [18,19]. In the first demonstration, the repetition rate difference (\Delta f_{rep}) as well as the f_{ceo} of the two pump lasers were recorded along with the time domain interferogram. The \Delta f_{rep} and f_{ceo} values were used to correct for distortions in the spectrum, due to their instantaneous fluctuations. The residual linear frequency mismatch between the individual spectra was revealed by a cross-correlation algorithm and compensated before averaging, yielding a spectral resolution of 0.5 cm\(^{-1}\) for the averaged spectra [18]. In the second demonstration the f_{ceo} of the pumps were not monitored, which simplified the setup due to elimination of two f-2f interferometers. Each single interferogram was recorded in a time much faster than the de-coherence time of the two idler combs (specially the fluctuations in f_{ceo} values of the two idler combs), thus the spectral information remains intact in each spectrum obtained after Fourier transform, and is only shifted to a different center frequency. The same cross-correlation algorithm is used to correct for the shifts, achieving a spectral resolution of \sim 0.3 cm\(^{-1}\) after averaging [19]. In both cases the averaged spectrum needs to be shifted manually (by comparison to the simulated spectrum) to achieve absolute frequency calibration. In addition, the efficiency of the cross-correlation algorithm in revealing the frequency mismatch values largely depends on the SNR of the spectrum retrieved from a single interferogram. Therefore, the usability of this method is mainly limited to highly absorbing samples.

The alternative approach to two independent SROPOs is to merge the two OPO cavities into one [8,9,20,21]. Despite the disadvantage that the \Delta f_{rep} between the two combs should be small to maintain synchronously pumping operation, this approach offers significant advantage in term of relative stability and coherence between the two idler combs. Our previous work yielded a rather fair spectral resolution (0.5 cm\(^{-1}\)) for a limited averaging time, without stabilization/correction of the f_{ceo} of the idler combs [9,21]. Here, we adopt a passive optical referencing method, similar to what is proposed in [10] and implemented in [22] for near-IR DCS. The general idea is to monitor an absorption line of a known gas sample, as well as the broadband spectrum of the sample under test. Similar to [19], as long as the measurement time for each individual interferogram is shorter than the de-coherence time of the two idler combs, we can assume that the f_{ceo} of the idler combs are constant for each individual measurement. Therefore, a simple frequency shift after Fourier transform would correct for the f_{ceo} changes in consecutive measurements. This allows for a DCS with longer averaging time, and potentially finer spectral resolution, as well as an absolute frequency calibration, thanks to the known frequency position of the monitored absorption line. Here, we also demonstrate the possibility of retrieving the concentration value of the sample species by fitting a theoretical model spectrum to the measurement.

2. Experimental setup

The experimental setup is demonstrated in Fig. 1. The OPO has already been explained in details in [9,21]. Briefly, two femtosecond Yb-fiber lasers (Menlo Systems, Germany) are
used as pump sources. They have cross polarized beams, emitting around 1040 nm and delivering 80 fs pulses at a repetition rate of ~90 MHz, with a maximum average power of 2.5 W. The OPO is based on a singly resonant ring cavity, in which the two cross-polarized pump beams counter propagate, and the cavity contains two 5 mm-long MgO:PPLN (Periodically Poled Lithium Niobate, Covesion Ltd., UK) crystals. The length of the cavity is designed to achieve synchronously pumped operation, i.e. ~3.3 m long. The OPO cavity consists of 4 curved dielectric mirrors with 100 mm radius of curvature (AR coated at 1064 & 3650-4850 nm and HR coated at 1350-1500 nm) and 6 flat, chirped, dielectric mirrors for group velocity dispersion compensation (HR coated at 1370-1750 nm, all from Layertec GmbH, Germany). The OPO cavity has two idler outputs, each delivering pulses with 200 mW of maximum average power, a spectral full width at half maximum (FWHM) bandwidth of up to 300 cm$^{-1}$ and tunable between 2380 cm$^{-1}$ and 3570 cm$^{-1}$ (2.8-4.2 µm), using different poling periods of the crystals. The $f_{\text{rep}}$ of each pump laser is controlled by a piezo-electric transducer (PZT) inside the corresponding oscillator cavity. We stabilize the $f_{\text{rep}}$ of each pump laser by locking their 10th harmonic at ~900 MHz to a separate RF signal generator (R&S, SMB100A, Germany) using a proportional-integral (PI) controller (Digilock 110, Toptica, Germany) with a closed-loop bandwidth of ~100 Hz. One signal generator acts as the master and provides the clock for the slave one. The two $f_{\text{rep}}$ values are slightly different to make the repetition rate difference of $\Delta f_{\text{rep}}=250$ Hz. The $f_{\text{rep}}$ of the two pumps are free running and not monitored. A PZT actuator is connected to one of the OPO cavity mirrors and used to manually tune the cavity length for synchronous pumping. The OPO keeps running for several hours without any need to correct or stabilize the cavity length.

![Fig. 1. The experimental setup. SG1,2: signal generator, DBM: double-balanced mixer, PI: proportional-integral controller, BPF: band-pass filter, PD1,2: near-IR photodetector (1 GHz), BS1-3: beam splitter, $\lambda/2$: half-waveplate, L1-4: lens, M1-6: curved dielectric mirror, CM1-6: flat chirped dielectric mirror, DM1,2: dichroic mirror, BD: beam dump, PD3,4: mid-IR photodetector (50 MHz), LPF: low-pass filter.](image)

For dual-comb spectroscopy, the polarization of one of the idler beams is rotated (the idler beams are cross-polarized in the OPO cavity following the polarization of their pumps), to align the polarizations of the two beams. Afterward, they are recombined on a pellicle
beamsplitter, producing two pair of beams on reflection and transmission. One pair of idler beams are used for the dual-comb spectroscopy of the sample and sent through a 50 cm single-pass absorption cell. A gas flow of 1-5 l/h can be maintained through the cell at a pressure of 20-1013 mbar. The transmission through the cell is detected by a thermoelectrically cooled photodetector (PVI-4TE, Vigo, Poland) with a bandwidth of 50 MHz. The detected signal, i.e. the interferogram, is low pass filtered (corner frequency at 50 MHz) and sampled at a rate of 125 Msample/s using a fast data acquisition card (NI-5762 coupled with a PXI FPGA Module, National Instruments, US). The second pair of idler beams is used to monitor a single absorption line of a reference gas. This allows absolute frequency calibration and effective averaging of the recorded sample spectra. For this, a single pass absorption cell of 20 cm is used, containing a pure reference gas at low pressure. The composition of the gas can vary depending on the wavelength of the idler beam. For measurements at the spectral window around 3.3 µm, methane (CH₄) is used at a pressure of ~100 mbar. A single absorption line (at ~3038.5 cm⁻¹) is isolated by the use of a diffraction grating and a mechanical slit forming an optical band-pass filter. The beam is finally focused by a cylindrical concave mirror on a thermoelectrically cooled photodetector (PVI-4TE, Vigo, Poland) with a bandwidth of 50 MHz. The output of the detector is sampled on the second channel of the same data acquisition card that samples the main interferogram. The clock of the data acquisition card is locked to the clock of the master signal generator by an internal phase-locked loop (PLL). The reference interferogram is also used as the trigger to start the data acquisition. The data acquisition card is set to save a pre-defined number of samples (30,000 samples, recorded in ~240 μs) equally before and after the trigger event. Therefore, a symmetrical interferogram is recorded around the central burst for the two channels. Both interferograms are saved on a regular PC for post-processing.

3. Spectral calibration

The recorded interferograms are post-processed in MATLAB. A Blackman apodization function [23] is applied to both sample and reference interferograms to minimize the ringing effect around the (narrow) absorption lines (especially in the reference spectrum). The ringing is due to the original box-car (uniform) apodization function that arose from abrupt cutting of the interferogram, which limits the precision of detecting the center of the reference absorption line. The Fourier transform of each individual interferogram of the reference and sample yield the Radio frequency (RF) down-converted image of the corresponding optical spectrum. The reference spectrum contains the spectral information of a single absorption line, with a spectral bandwidth of about 20 cm⁻¹ [see Fig. 2(a)]. The RF domain spectral grid for both of the spectra is converted to the optical frequency domain grid by the corresponding scaling factor (f_{rep}/Δf_{rep}). The known position of the absorption line in the optical frequency domain is used to calculate the frequency shift correction needed to bring each reference and sample spectrum to the absolutely-calibrated optical frequency scale. Figure 2 shows five single-shot reference spectra [absorption line at 3038.498 cm⁻¹ in Figs. 2(a) and 2(b)] and broadband spectra [a part of the spectra around the Q branch of CH₄ in Figs. 2(c) and 2(d)]; both are consecutively recorded on the same frequency scale. The reference absorption cell contains pure CH₄ at 100 mbar, while the 50-cm-long sample absorption cell contains 5% CH₄ in N₂ at 100 mbar. Figures 2(a) and 2(c) demonstrate the spectra in RF domain, where strong variations in the recorded spectra is clearly visible. Figures 2(b) and 2(d) depicts the same spectra, in absolutely-calibrated wavenumber domain, after frequency scaling and shift correction. The sample spectra are averaged after this frequency scaling and shift correction (not shown in the figure).
4. Results

4.1. Single species detection

Figure 3(a) shows the measured absorption spectrum of 250 ppm CH$_4$ diluted in N$_2$ at atmospheric pressure (in black) averaged for ~4 s (1000 averages). The spectrum is normalized to an averaged background spectrum, the latter is recorded when the sample absorption cell is filled with pure N$_2$ at atmospheric pressure. We compare this experimental absorption spectrum to the theoretical model (in blue) developed based on the corresponding parameters from the HITRAN database [24] using a Voigt profile, and convoluted with a Blackman instrument line-shape function corresponding to the applied apodization function. Note that the simulated spectrum is inverted and the two measured and simulated spectra are offset for clarity. We fit the developed model spectrum to the measured spectrum (with the CH$_4$ concentration as the fitting parameter), as well as a sum of a low order polynomial and few low frequency sinewave functions to correct for the remaining baseline and etalon fringes. The retrieved concentration is 249(3) ppm where the error is the standard deviation of 10 consecutive measurements. The residual of the fit is shown in Fig. 3(b) and indicate an excellent agreement between the measurement and the model. The spectral resolution of the retrieved spectra is ~6 GHz (~0.2 cm$^{-1}$). The precision of the frequency calibration is dictated by the precision of detecting the center of the reference absorption line, which is ~120 MHz (~0.004 cm$^{-1}$). To demonstrate the capability of the system for measuring low pressure gas absorption spectra, we measured 1% CH$_4$ diluted in N$_2$ at 100 mbar. The measured normalized absorption spectrum averaged for ~4 s (in black) is shown in Fig. 4(a) compared to the theoretical model (in blue) developed based on HITRAN database parameters, Voigt profile and Blackman instrument line-shape function, as described earlier. The retrieved concentration from the fit is 0.99(2)% where the error is the standard deviation of 10 consecutive measurements and the residual of the fit is shown in Fig. 4(b). The general agreement between the measurement and the fit is good; however, there are some features in the residual at the position of the absorption lines. This discrepancy is mainly due to the...
narrower absorption lines of the sample at lower pressures, where absorption linewidth would be comparable to the precision of the frequency shift correction and calibration. Therefore, the efficiency of the averaging degrades and the averaged measured spectrum deviates from the developed model.

Fig. 3. (a) Normalized transmission spectrum of 250 ppm CH$_4$ diluted in N$_2$ at atmospheric pressure (black, 1000 averages), along with a theoretical fit model (blue, inverted) developed based on the corresponding parameters from the HITRAN database, Voigt profile and Blackman instrument line-shape function. (b) Residual of the fit.

Fig. 4. (a) Normalized transmission spectrum of 1% CH$_4$ diluted in N$_2$ at 100 mbar (black, 1000 averages), along with a theoretical fit model (blue, inverted) developed based on the corresponding parameters from the HITRAN database, Voigt profile and Blackman instrument line-shape function. (b) Residual of the fit.

4.2. Multispecies detection of broadband absorbers

We measured broadband absorption spectrum of a mixture of acetone and ethyl acetate in a 6.5-cm long, windowless, absorption cell containing one liquid droplet of each species at atmospheric pressure. We normalize the measured spectrum to a background spectrum that is recorded after removing the absorption cell. We fit the model spectra of the two species calculated using PNNL database [25] (spectral resolution of 6 GHz) along with a sum of a low order polynomial and few low frequency sinewave functions (for removing any remaining baseline and etalon fringes) to the measured normalized transmission spectrum. Figure 5(a) shows the measured normalized transmission spectrum (in black) averaged for ~4 s, along with the fitted model spectra of acetone (in blue), ethyl acetate (in red), and the sum of the two fitted spectra (in green). The retrieved concentrations from the fit are 1.13% for
acetone and 1.21% for ethyl acetate. The residual of the fit is shown in Fig. 5(b). The featureless residual demonstrates the excellent agreement between measurements and PNNL database.

4.3. Absorption spectrum of the laboratory air over a free path

The DCS system is also capable of retrieving the concentration of a trace gas in the presence of an interfering species with much stronger absorption. To demonstrate this, we measured the absorption spectrum of the laboratory air without any sample cell. The interaction length between the idler beams and the laboratory air, i.e. the distance between the crystal(s) in the OPO cavity and the photodetector, is ~5.4 m. Figure 6 shows the measured transmission spectrum for different number of averages (with different offset for clarity). The H2O absorption lines due to the water vapor are hardly distinguishable from noise on a single-shot spectrum without averaging (blue curve in Fig. 6). However, after ~4 s averaging (1000 spectra), not only the H2O absorption lines are clear, we can also observe atmospheric CH4 absorption lines and retrieve both concentrations by multispecies fitting. We normalize the measured spectrum to its slow-varying envelope to obtain the normalized transmission. Figure 7(a) shows this normalized transmission in black, compare to the fitted simulated spectra of H2O and CH4 in red and blue, respectively (inverted and offset for clarity). The theoretical models are calculated from HITRAN database parameters for H2O and CH4, Voigt profiles, and Blackman line-shape function. The developed model spectra, as well as a sum of a low order polynomial and few low frequency sinewave functions (to correct for the remaining baseline and etalon fringes), are fitted to the measured spectrum with concentrations of H2O and CH4 as the fitting parameters. The residual of the fit is depicted in Fig. 7(b). The retrieved concentrations are 1.95(8) ppm for CH4 and 0.691(3)% for H2O, which match to the expected atmospheric concentrations. The two enlargements in Fig. 7(a), show two different spectral regions with stronger absorption features of CH4.
4.4. Long term stability and detection limit

To estimate the long term stability and minimum detection limit of the system, we measure the background spectra with the sample absorption cell filled with N₂, at atmospheric pressure for 80 s, and normalize each consecutively measured spectrum to the first spectrum. Afterwards we fit a sum of the model spectrum of CH₄ at atmospheric pressure (based on the corresponding parameters from the HITRAN database, Voigt profile and Blackman instrument line-shape function) and a slowly varying baseline, to these normalized spectra with CH₄ concentration (per interaction length) as the fitting parameter. The concentrations found from these fits are shown in Fig. 8(a). The Allan-Werle plot of the retrieved concentrations is shown in Fig. 8(b) in black (dots), as well as a $\tau^{-1/2}$ dependence characteristic line in red (dashed line) for the white-noise-dominated regime fitted to the corresponding measurement points. The Allan-Werle plot shows more than three decades of white-noise-dominated regime, with a minimum detectable concentration of ~100 ppb.m for CH₄ after ~10 s of integration.
Fig. 8. (a) CH4 concentrations found from fitting the theoretical model to the normalized background of atmospheric pressure N2. (b) Allan–Werle plot of the retrieved concentrations (black dots) along with the fitted $\tau^{-1/2}$ dependence characteristic line (red dashed line) for the white-noise-dominated regime.

5. Conclusions

We used a passive optical reference for absolute-calibration of a dual-comb spectrometer based on femtosecond OPOs, eliminating the need for the stabilization of the comb offset frequency and OPO cavity length. To achieve a distortion-free spectrum the measurement time should be shorter than the de-coherence time between the two idler combs. Since the spectral resolution is proportional to the acquired number of points around the central burst of the interferogram, the short measurement time limits the resolution of the spectrometer to a few GHz range. We used a Blackman apodization function to minimize the ringing effect around the (narrow) absorption lines and applied the corresponding Blackman instrument line-shape function to the simulated spectra. We demonstrated multispecies detection and concentration retrieval of different species using the developed model spectra for both small and large molecules. The measured spectra in atmospheric pressure demonstrate excellent agreement to the developed models based on existing molecular databases, while spectra measured at low pressure show slight discrepancy compared to the simulations. This discrepancy is mainly due to the narrower absorption lines at lower pressures, whose linewidth would be comparable to the precision of the frequency shift correction and calibration.

Compared to fully stabilized dual-comb spectrometers based on femtosecond OPOs [13], our developed system is less complicated and demanding; but it provides coarser spectral resolution and frequency precision. On the other hand, compared to similar OPO-based DCS systems using cross-correlation of the measured spectrum for offset correction [18,19], our method provides an absolute-frequency-calibrated spectrum, with a consistent and good frequency precision, long term stability and spectral resolution; fully independent from the SNR of the sample spectrum. Finally, compared to conventional Fourier transform spectrometers, our method provides similar spectral resolution and precision, but the measurement time is a few orders of magnitude shorter than a typical mechanical FTS. This feature makes our method suitable for applications that require a fast measurement, e.g., time-resolved spectroscopy.

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