Terahertz Spectroscopy of Gas Mixtures with Dual Quantum Cascade Laser Frequency Combs

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Abstract

Terahertz laser frequency combs based on quantum cascade lasers provide coherent, broadband, electrically pumped, THz radiation sources for use in future spectroscopic applications. Here, we explore the feasibility of such lasers in a dual-comb spectroscopy configuration for detection of multiple molecular samples in gas phase. The lasers span approximately 180 GHz of optical bandwidth, centered around 3.4 THz with sub-milliwatt total optical power. One of the main advantages of dual-comb spectroscopy is its high speed, which opens up the possibility for direct observations of chemical reaction dynamics in the terahertz spectral region. As a proof-of-concept, we recorded continuously evolving spectra from gas mixtures with 1 ms temporal resolution.

Keywords

Terahertz, quantum cascade laser, frequency comb, dual-comb spectroscopy, multi-species, real-time

For a long time, the terahertz part of the electromagnetic spectrum (0.1–20 THz) was experimentally inaccessible since it was too high in frequency for electronic circuitry and too low in frequency for coherent optical sources. However, recent advances in the generation of THz radiation, primarily provided by the developments of photoconductive antennas, and optically pumped gas-phase molecular lasers, have resulted in a massive increase of research activity in the field of THz spectroscopy over the last decennia. This field is predominantly occupied by THz time-domain spectroscopy (TDS) with commercially available turn-key systems that provide reliable spectral coverage over a few THz. However, just like THz spectrometers based on the Fourier transform spectroscopy technique, these instruments often require an optical delay line with mechanically moving parts, which make them inherently slow with spectral acquisition times in the order of seconds or longer.

Multiheterodyne spectroscopy or dual-comb spectroscopy (DCS) using quantum cascade lasers (QCLs) optical frequency combs (OFCs) is an interesting alternative that has proven to be viable in the mid-infrared spectral region, where broadband spectroscopy with high temporal resolution has been repeatedly demonstrated. These all-solid-state semiconductor-based spectrometers do not require moving parts and can record spectra spanning several hundreds of GHz in just a few microseconds. Furthermore, the possibility of complete integration into a small package makes them particularly intriguing for in-situ applications in industry and consumer products. The recent demonstrations of THz frequency combs and proof-of-concept spectroscopy results obtained with a GaAs etalon as well as solids indicate the potential of extending this technology to perform spectroscopy of gases in the THz region. This work aims to further establish the feasibility of high temporal resolution THz spectroscopy using QCL OFCs by presenting the first QCL-based THz-DCS measurements of gas phase molecular samples with millisecond time-resolution.

The experimental setup shown in Fig. 1a is similar to our earlier works. Two THz-QCL OFCs emitting light centered around 3.4 THz are housed in a pulsed tube cryostat with a cold finger temperature of 25 K. After collimation, the estimated optical power per tooth in each comb is ~10 µW. Only one of the combs, here labeled as signal (Sig.), interrogates the sample gas mixture, which is housed in a home-made 14-cm long stainless steel absorption cell with Polymethylpentene (TPX) windows. After propagating through the absorbing species, the signal comb is combined with the local oscillator comb (LO) on a silicon beam splitter, and guided to a superconducting NbN hot-electron bolometer (HEB) for multiheterodyne down-conversion of the THz spectrum to the radio-frequency (rf) domain. The entire system is enclosed in an acrylic chamber purged with dry gaseous nitrogen to suppress the absorption of atmospheric humidity on the THz spectrum. Due to a mismatch in the repetition rates of the combs (16.988 GHz and 17.027 GHz for the Sig. and LO comb, respectively), the

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Figure 1: (a) Dual-comb spectroscopic system. Two free-running THz-QCL OFCs mounted anti-parallel in a pulsed tube cryostat emit light centered around 3.4 THz collected using external off-axis parabolic mirrors. Only the signal (Sig) OFC interrogates the gas absorption cell. The transmitted light is combined with the local oscillator (LO) comb on a silicon beam splitter and next beaten on a GHz-bandwidth hot electron bolometer. A microwave spectrum analyzer records data in real time without the need for computational coherent averaging or active feedback loop stabilization; (b) 9 seconds of THz-DCS data recorded with the microwave spectrum analyzers with 1 millisecond temporal resolution (9000 spectra). Each 1 ms frame corresponds to 39000 quasi-coherently averaged interferograms with a fundamental refresh rate defined by the spacing of the radio-frequency comb equal to \( \Delta f_{\text{rep}} = 39 \text{ MHz} \).

Figure 2: (a) Stacked 1000 rf dual-comb spectra measured in 1 ms each with the spectrum analyzer under free-running operation of the system. Due to cryostat vibrations, the beat notes jitter in amplitude and frequency, albeit even over such extended time scales, they do not drift by more than a megahertz. 11 beat notes are used for spectroscopy marked with colored dots; (b) Zoom on the most intensive beat note. The 3 dB linewidth is lower than 3 MHz, while the peak amplitude fluctuates from shot to shot by 1.2 dB (standard deviation); (c) Fourier analysis of the most intensive peak amplitude showing the dominant oscillation frequency at 480 Hz, which is the 8th harmonic of the AC mains driving the cryostat motor. Additionally, strong resonances occur around 300 Hz, 120 Hz, and the fundamental operation frequency of the cryocooler of \( \sim 1 \text{ Hz} \); (d) Time series of all the 11 beat notes’ rf powers used for the reference measurement showing high visual similarity. The right panel zooms over 300 milliseconds illustrating the synchronicity of amplitude fluctuations; (e) Mutual correlation analysis of beat note amplitudes. The mean pairwise correlation coefficient \( r_{ij} \) (\( i, j \in \{1 \ldots 11\} \) and \( i \neq j \)) is 90.4\%, while the maximum is 98.7\%. Amplitude noise is highly correlated in our system.

down-converted comb in the rf has a frequency separation of \( \Delta f_{\text{rep}} = 39 \text{ MHz} \) with approximately 500 MHz of electrical bandwidth, which corresponds to \( \sim 180 \text{ GHz} \) of optical spectral coverage at 3.4 THz. The resulting microwave spectrum is recorded with a real-time spectrum analyzer (FSW-43, Rohde & Schwarz) with an acquisition time of 1 ms per spectra, as visualized in Fig. 1b using a waterfall representation of the recorded short-term amplitude spectrum (spectrogram). The down-converted THz spectrum shows characteristic beat note amplitude attenuations induced by wavelength-dependent changes in the transmission through the sample cell when different gas mixtures are introduced.

Compared to earlier preliminary dual-comb experiments using THz-QCL combs,

our system shows improved robustness against optical feedback and mechanical vibrations, which enables a completely free-running system without
Figure 3: Time-resolved decadic (base-10) absorbance retrieved from the dual-comb spectrogram at the four phases of the experiment. Bold lines are 10-point moving averages.

Figure 4: (a) Rapid response THz spectroscopy of water vapor. Three beat notes are strongly affected due to water vapor absorption as the measurement chamber is rapidly opened and hence exposed to atmospheric humidity. The 10%–90% rise time \( (t_r) \) on the beat note mapping 3.338 THz is 20 ms. Solid lines are 10-point moving averages of raw data sampled every 1 ms. (b) Allan deviation of path-integrated water vapor concentration based on a HITRAN database model. The curve shows a highly oscillatory shape with the global minimum at 1.8 s, corresponding to approximately two periods of cryostat vibrations. Inset shows the fitted concentrations.

In panel (d) plotted in Fig. 2, there is a mean value (excluding the diagonal) of 90.4% and a maximum of 98.7%, which indicates strong correlation. In principle, the fluctuations of individual modes could be suppressed by the use of a reference detector, and the high correlation between the beat notes could allow a simpler amplitude suppression scheme using a slow THz power detector rather than a costly HEB. However in this study, amplitude noise was suppressed through ordinary extended time-scale averaging.

Our proof-of-concept multi-species spectroscopic detection experiment was conducted in four phases, visualized by the background colors of the time-resolved dual-comb absorbance spectra in Fig. 3. In each phase, we measured the final cell pressure with a gauge to validate our spectroscopic model. In the first phase, the absorption cell was held under vacuum to obtain a zero-gas background spectrum used for calibration. Next, at time \( t=0 \) s, anhydrous ammonia (NH\(_3\)) was introduced to the cell up to a total pressure of 200 Torr, which is accompanied by a step in absorbance (phase 2). In phase 3, starting at \( t=1.6 \) s, nitrogen dioxide (NO\(_2\)), which exists in chemical equilibrium with dinitrogen tetroxide (N\(_2\)O\(_4\)), was added to the gas mixture. At lower temperatures, the formation of (N\(_2\)O\(_4\)) is a preferred process, whereas at higher temperatures formation of nitrogen dioxide predominates. A pressurized (NO\(_2\)) cylinder is used to deliver the gas to the system. When the gas expands into the measurement gas cell, it rapidly lowers its temperature, thus favoring the formation of solid and gaseous (N\(_2\)O\(_4\)). The latter has shown to exhibit intensive absorption peaks around 113 cm\(^{-1}\) (3.39 THz)\(^{12}\) with an unchanged molecular structure in the liquid, gaseous and solid state.\(^{18}\) Thus, the sudden increase of the absorption around 3.40 THz and its slow decay over several seconds is consistent with the formation of (N\(_2\)O\(_4\)) through dimerization followed by a slow transition to (NO\(_2\)) when the system again reaches thermal equilibrium. The last phase starting at \( t=4.4 \) s corresponds to a sudden opening of the purged measurement chamber, which allowed atmospheric air (10% relative humidity) to leak into the system and thus cause severe water absorption around 3.34 THz. The optical frequencies were retrieved from a multi-point spectroscopic fit to a separate water vapor measurement by using the measured comb repetition
rate, while leaving the center frequency as a free parameter like in Ref.\textsuperscript{29}

![Diagram showing absorbance vs wavenumber](image)

Figure 5: Fitted absorbance spectrum of 99% anhydrous NH\textsubscript{3} contaminated with residual amounts of water vapor measured from 0.5 s to 1.5 s in 100 ms intervals.

The fast rise time of the absorption (dotted frame in Fig. 3) demonstrates the rapid response time of the THz DCS spectrometer. This is one of the main advantages of the dual-comb technique that differentiates it from other broadband spectroscopic techniques and allows for the study of non-repeatable transient processes that occur on very fast time-scales.\textsuperscript{3} Fig. 4 plots the absorbance of beat notes that map three optical frequencies: 3.338 THz, 3.355 THz, and 3.321 THz, of which the strongest absorption occurs at 3.338 THz. The 10\textsuperscript{th}–90\textsuperscript{th} rise time (\(t_r\)) of the signal is 20 ms, which is not a fundamental limitation of our instrument but rather reflects the time it takes for water vapor to diffuse into the measurement chamber. The fundamental temporal resolution limit is given by the time between consecutive DCS interferograms and is related to the rf beat note frequency spacing through \(t_{\text{min}} = 1/\Delta f_{\text{rep}}\), which in our case is approximately 25 ns. However, this temporal resolution is accompanied by a significant reduction in signal-to-noise ratio due to random noise sources that cannot be effectively averaged. From an analogous measurement taken over 5 s, we generated an Allan deviation plot of the path-integrated water vapor concentration estimated using the HITRAN database. The minimum detection limit (MDL, \(\sigma\)) reaches sub-ppm-m after two periods of cryostat vibrations (1.8 s), while at 1 ms it reaches 12 ppm-m.

To demonstrate a spectral fitting capability, the DCS spectral data measured between 0.5–1.5 s in Fig. 3 have been fitted with a HITRAN simulated mixture model containing NH\textsubscript{3} and residual water vapor. It should be noted that the HEB shows quadratic response with respect to optical power that is dependent on the operating temperature of the bolometer, and if not properly corrected, this non-linearity could cause up to a factor of 2 overestimation in absorbance. Optical power management or use of Schottky mixers for dual-comb beating (Ref.\textsuperscript{29}) should help mitigate these issues in the future. After the non-linearity correction, good agreement between the spectroscopic data and the fitted model has been obtained as shown in Fig. 4.

In conclusion, we have demonstrated rapid-response QCL-based dual-comb THz measurements of gas mixtures around 3.4 THz. We probe an equilibrium reaction of NO\textsubscript{2}/N\textsubscript{2}O\textsubscript{4} as well as fast changes in concentrations of NH\textsubscript{3} and H\textsubscript{2}O with a temporal resolution of 1 ms. We identify the main current limitations of the system as related to a noisy cryostat environment and bolometer non-linearities. Another area of improvement is the spectral coverage (~180 GHz), which is constrained by the comb regime of the THz-QCL and can be addressed by dispersion compensation schemes\textsuperscript{3} and future broadband QCL gain designs.\textsuperscript{4} To unlock the full potential of multi-species sensing, a multi-wavelength framework\textsuperscript{21} for estimating the pressure and concentration of individual components can be implemented.

Notes

The authors declare no conflicts of interest.

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