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, dualcomb 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, ¹ and optically pumped gas-phase molecular lasers, ² 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.^{3,4} 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 package⁵ makes them particularly intriguing for in-situ applications in industry and consumer products.

The recent demonstrations of THz frequency combs^{6,7} and proof-of-concept spectroscopy results obtained with a GaAs etalon,^{8,9} as well as solids¹⁰ 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.^{8,10} 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 $\sim 10 \mu$ W. 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



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 $\Delta f_{\rm rep}=39$ 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 ~1 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} $(i, j \in \{1..., 11\}$ 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 $\Delta f_{\rm rep}=39$ MHz with approximately 500 MHz of electrical bandwidth, which corresponds to ~180 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,⁸ 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.

hardware phase-locked loops¹¹ for rf frequency stabilization or digital post-correction algorithms for recovering the comb nature of the dual-comb signals.^{12,13} The short-term coherence between the sources was sufficient to permit power spectrum averaging of the data within a 1.2 MHz resolution bandwidth, which additionally reduced the amount of stored data for prolonged (dozen of seconds) acquisitions. Fig. 2a plots the persistence spectrum of a thousand 1 millisecond free-running spectra. Upon close examination, mechanical vibrations are not completely suppressed despite elaborate dampening mechanisms in the cryostat design. A zoom of the strongest beat note shown in Fig. 2b reveals maximum fluctuations in frequency of approximately 3 MHz (3 dB linewidth) over 1 second, while the standard deviation of the peak amplitude is 1.2 dB. This value is surprisingly high for the relatively long 1 ms acquisition time of each spectral frame in the MH spectrum, yet can be attributed to vibration noise affecting the combs. The (vibration) frequency spectrum of the quasi-instantaneous amplitude of the beat note is shown in Fig. 2c. In addition to the fundamental cryostat pump frequency of ~ 1 Hz, we observe a dominant contribution of even harmonics of 60 Hz known to appear in resonant mechanical systems. Also the appearance of broader resonant features close to typical eigenfrequencies of the inner shield and the vacuum chamber of the cryostat (i.e. 50 Hz) suggest a mechanical origin.^{14–16}

An analysis of all the beat note amplitudes in the system, retrieved using a quadratic peak interpolation algorithm,¹⁸ shows highly correlated fluctuations. The transient dips in amplitude shown in Fig. 2d clearly show that the cryostat pump-related slowly-varying components appear at the same instances of time for all beat notes. The pair-wise correlation coefficient map computed from the amplitude data set



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 open 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 HITRAN¹⁷ 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. 2e has 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_2O_4) , was added to the gas mixture. At lower temperatures, the formation of (N_2O_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_2O_4) . The latter has shown to exhibit intensive absorption peaks around 113 cm^{-1} (3.39 THz)¹⁹ with an unchanged molecular structure in the liquid, gaseous and solid state.²⁰ 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_2O_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. 10



Figure 5: Fitted absorbance spectrum of 99% anhydrous NH₃ 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.³ Fig. 4a 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%-90% 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 $t_{\min} = 1/\Delta f_{rep}$, 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 HITRAN¹⁷ database. The minimum detection limit (MDL, 1σ) reaches sub-ppm·m after two periods of cryostat vibrations (1.8 s), while at 1 ms it reaches 12 ppm \cdot 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 NH₃ 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.⁸) should help mitigate these issues in the future. After the nonlinearity correction, good agreement between the spectroscopic data and the fitted model has been obtained as shown in Fig. 5.

In conclusion, we have demonstrated rapid-response QCLbased dual-comb THz measurements of gas mixtures around 3.4 THz. We probe an equilibrium reaction of NO_2/N_2O_4 as well as fast changes in concentrations of NH_3 and H_2O 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 nonlinearities. 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 schemes⁶ and future broadband QCL gain designs.⁷ To unlock the full potential of multi-species sensing, a multi-wavelength framework²¹ for estimating the pressure and concentration of individual components can be implemented.

Notes

The authors declare no conflicts of interest.

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References

- Berry, C. W.; Wang, N.; Hashemi, M. R.; Unlu, M.; Jarrahi, M. Significant performance enhancement in photoconductive terahertz optoelectronics by incorporating plasmonic contact electrodes. *Nature communications* 2013, 4, 1622.
- (2) Chevalier, P.; Armizhan, A.; Wang, F.; Piccardo, M.; Johnson, S. G.; Capasso, F.; Everitt, H. O. Widely tunable compact terahertz gas lasers. *Science* 2019, *366*, 856–860.
- (3) Klocke, J. L.; Mangold, M.; Allmendinger, P.; Hugi, A.; Geiser, M.; Jouy, P.; Faist, J.; Kottke, T. Single-shot sub-microsecond mid-infrared spectroscopy on protein reactions with quantum cascade laser frequency combs. *Analytical chemistry* **2018**, *90*, 10494–10500.
- (4) Pinkowski, N. H.; Ding, Y.; Strand, C. L.; Hanson, R. K.; Horvath, R.; Geiser, M. Dual-comb spectroscopy for high-temperature reaction kinetics. arXiv preprint arXiv:1903.07578 2019,
- (5) Villares, G.; Wolf, J.; Kazakov, D.; Süess, M. J.; Hugi, A.; Beck, M.; Faist, J. On-chip dual-comb based on quantum cascade laser frequency combs. *Applied Physics Letters* **2015**, *107*, 251104.

- (6) Burghoff, D.; Kao, T.-Y.; Han, N.; Chan, C. W. I.; Cai, X.; Yang, Y.; Hayton, D. J.; Gao, J.-R.; Reno, J. L.; Hu, Q. Terahertz Laser Frequency Combs. *Nature Photonics* **2014**, *8*, 462–467.
- (7) Rösch, M.; Scalari, G.; Beck, M.; Faist, J. Octavespanning semiconductor laser. *Nature Photonics* 2014, 9, 42.
- (8) Yang, Y.; Burghoff, D.; Hayton, D. J.; Gao, J.-R.; Reno, J. L.; Hu, Q. Terahertz Multiheterodyne Spectroscopy Using Laser Frequency Combs. *Optica* 2016, *3*, 499.
- (9) Li, H.; Li, Z.; Wan, W.; Zhou, K.; Liao, X.; Yang, S.; Wang, C.; Cao, J. C.; Zeng, H. Compact and realtime terahertz dual-comb spectroscopy using a selfdetection scheme. arXiv preprint arXiv:1904.03330 2019,
- (10) Sterczewski, L. A.; Westberg, J.; Yang, Y.; Burghoff, D.; Reno, J.; Hu, Q.; Wysocki, G. Terahertz hyperspectral imaging with dual chip-scale combs. *Optica* **2019**, *6*, 766–771.
- (11) Westberg, J.; Sterczewski, L.; Wysocki, G. Midinfrared multiheterodyne spectroscopy with phaselocked quantum cascade lasers. *Applied Physics Letters* 2017, 110, 141108.
- (12) Burghoff, D.; Yang, Y.; Hu, Q. Computational Multiheterodyne Spectroscopy. *Science Advances* 2016, 2.
- (13) Sterczewski, L. A.; Westberg, J.; Wysocki, G. Computational coherent averaging for free-running dual-comb spectroscopy. *Optics express* **2019**, *27*, 23875–23893.
- (14) Massot, M.; Oleaga, A.; Salazar, A. Photopyroelectric Calorimetry down to 10 K. *Measurement Science and Technology* **2006**, *17*, 3245–3249.
- (15) Caparrelli, S.; Majorana, E.; Moscatelli, V.; Pascucci, E.; Perciballi, M.; Puppo, P.; Rapagnani, P.; Ricci, F. Vibration-Free Cryostat for Low-Noise Applications of a Pulse Tube Cryocooler. *Review of Scientific Instruments* **2006**, 77, 095102.
- (16) Brandl, M. F.; van Mourik, M. W.; Postler, L.; Nolf, A.; Lakhmanskiy, K.; Paiva, R. R.; Möller, S., et al. Cryogenic Setup for Trapped Ion Quantum Computing. *Review of Scientific Instruments* **2016**, *87*, 113103.
- (17) Rothman, L. S.; Gordon, I. E.; Babikov, Y.; Barbe, A.; Benner, D. C.; Bernath, P. F.; Birk, M.; Bizzocchi, L.; Boudon, V.; Brown, L. R., et al. The HITRAN2012 molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer* **2013**, 130, 4–50.
- (18) Smith III, J. O. Spectral audio signal processing; W3K publishing, 2011.
- (19) Givan, A.; Loewenschuss, A. Fourier transform infrared spectrum of well ordered solid dinitrogen tetroxide. *The Journal of Chemical Physics* **1990**, *93*, 866– 867.

- (20) Snyder, R. G.; Hisatsune, I. Infrared spectrum of dinitrogen tetroxide. *Journal of Molecular Spectroscopy* **1957**, *1*, 139–150.
- (21) Pinkowski, N. H.; Ding, Y.; Johnson, S. E.; Wang, Y.; Parise, T. C.; Davidson, D. F.; Hanson, R. K. A multiwavelength speciation framework for high-temperature hydrocarbon pyrolysis. *Journal of Quantitative Spectroscopy and Radiative Transfer* **2019**, *225*, 180–205.