

High-resolution spectroscopy with quantum cascade laser frequency combs

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ABSTRACT

Optical frequency comb spectroscopy has proven an indispensable tool for high-resolution spectroscopy. QCL frequency combs offer the possibility to explore the mid-infrared spectral range. However, they suffer from large repetition frequencies which make them seemingly unsuitable for high resolution spectroscopy. We present three measurement modes overcoming this limitation. The rapid-sweep technique allows to retrieve the full high-resolution spectrum in 6ms, the step-sweep technique allows for high-resolution spectroscopy with spectral resolution $<5 \times 10^{-4} \text{ cm}^{-1}$. As a last technique we present the time-resolved step-sweep approach enabling high-resolution spectra of sub-millisecond-lived samples. It was assessed in a study of cold gases in supersonic beams.

Keywords: Spectroscopy, high-resolution, QCL, dual-frequency comb

1. INTRODUCTION

Frequency combs spectroscopy based on QCLs [1], [2] offer the possibility to easily explore the mid-infrared spectral range (4-12 μm) and allow for microsecond time resolution. However, they suffer from large repetition frequencies.

Several techniques to overcome this limitation have been developed. In the rapid-sweep technique, the two frequency combs are simultaneously modulated to cover the gap between adjacent comb modes [3]. The simultaneous modulation and the inherently high time-resolution of QCL dual-comb spectroscopy makes it possible to retrieve the full high-resolution spectrum in only $\sim 6 \text{ ms}$.

In the step-sweep mode, the lasers are each individually modulated in small steps. This method guarantees an accurate knowledge of the frequency axis by directly measuring the optical step size from the heterodyne beat signal. The step-sweep technique is best adapted to studies of molecular line parameters such as line strength, line position and line broadening.

Recently, the high time resolution of QCL dual-comb spectroscopy has been used in combination with the step-sweep technique. This has allowed to measure broadband high-resolution spectra of sub-millisecond-lived samples. The resolution accuracy obtained using this technique have been assessed in a study of cold gases in supersonic beams.

2. DUAL-COMB SPECTROMETER

Precise sensing of molecules is critical for numerous markets in environmental, medical, industrial, and security applications. The dual-comb technique is disruptive [4], [5] for spectroscopy, as it combines high speed detection with outstanding sensitivity. It uses two optical frequency combs with a slightly different mode spacing to enable broadband spectroscopy with high resolution in a single shot. IRsweep is in a worldwide leading position in dual-comb systems operating in the mid-infrared (MIR), where nearly all biologically and technically relevant molecules have strong ro-vibrational absorptions. The QCL dual-comb [1], [2] technology gives the IRis-F1 spectrometer strong advantages compared to the currently dominant systems using Fourier Transform Interferometer (FTIRs) or external cavity QCL (EC-QCLs).



Figure 1 Tabletop IRis-F1 dual-comb QCL spectrometer. It consists of the optical unit and a computer to control the system. In the rack on the right side from top to bottom: control unit, acquisition unit and chiller unit.

IRsweep is the worldwide leader on the market of dual-comb infrared spectrometers. Figure 1 shows the IRis-F1, the tabletop dual-comb instrument. The optics unit is inspired by FTIR benchtop instruments and allows to easily couple common accessories developed for FTIRs. The control unit houses the drive electronics for the optic unit. The acquisition unit is responsible for the digital to analog conversion and subsequent signal processing of the dual comb signal. This instrument is intended for research laboratories and R&D departments of industries.

3. POINT SPACING VS. RESOLUTION

The terms spectral resolution and spectral point spacing may sometimes lead to confusion. Especially when talking about FTIR spectrometers, these two parameters are commonly used interchangeably. And such use is misleading. It is however important to understand this difference to fully grasp the potential of dual-comb spectroscopy.

3.1 Spectral resolution

Spectral resolution is the wavenumber, wavelength or frequency difference of two still distinguishable lines in a spectrum (after IUPAC, Green Book, 2nd ed., p. 31). Spectral resolution defines what would be the narrowest spectral feature that can be resolved, or the necessary spacing between two features that enables to distinguish them. On the other hand, the observed/registered signal is a convolution of spectral resolution of the spectrometer and the linewidth of the signal. If the spectral feature is substantially wider than the spectral resolution, the effect of the resolution is negligible.

FTIR spectrometers are equipped with broadband light sources (e.g. glowbars), and their spectral resolution is defined by the optical path difference in the interferometer. In the IRis-F1, the source is

a QCL frequency comb. When talking about laser sources, we attribute the resolution to the laser linewidth (or, more precisely to the full width at half maximum). In the IRis-F1, there is a laser source, but instead of one line, there are several – and the linewidth of each line, i.e. the spectral resolution, is $<3 \times 10^{-4} \text{ cm}^{-1}$.

3.2 Spectral point spacing

Point spacing– separation between two adjacent data points in the spectrum. It corresponds to points that can be probed. Commonly, spectral point spacing is smaller than spectral resolution. However, for the IRis-F1, the situation is reverse: the spectral resolution is $<3 \times 10^{-4} \text{ cm}^{-1}$, while the point spacing is $\sim 0.3 \text{ cm}^{-1}$.

A high-resolution spectrum ($<3 \times 10^{-4} \text{ cm}^{-1}$), yet under sampled spectrum due to the high-spectral point spacing of 3 cm^{-1} of a light molecule such as Methane, might look like pure noise. But good modeling and algorithms can retrieve spectroscopically relevant data. This is exactly why it is possible to retrieve high-temperature conditions as well as the mole fraction by measuring the absorbance of Methane using a high-temperature shock-tube [6]. None of the presented tuning techniques here were used to achieve this result.

Regardless, improving the point spacing and avoid an under sampled spectra is desirable for many applications. It makes modeling and identification of species easier, and it is of indispensable for research such as line-shape measurements.

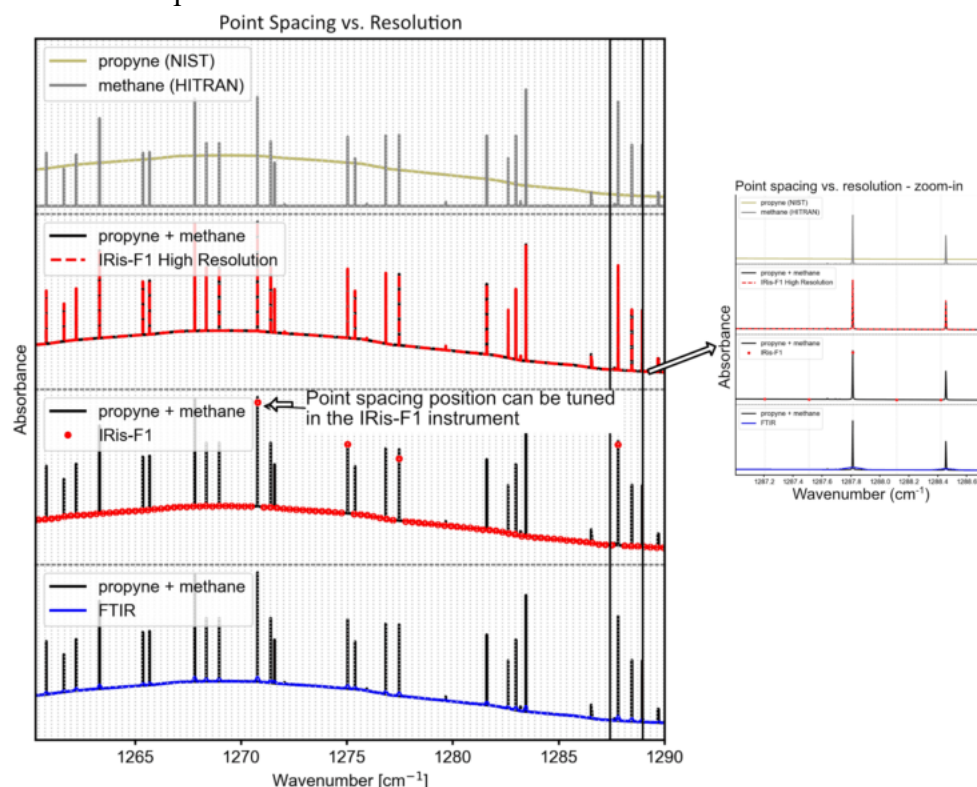


Figure 2 Khaki: experimental spectrum of propyne from NIST database as a model broadband absorber ($p = 67 \text{ matm}$ backfilled with N_2 to 800 matm , path length: 0.05 m). Gray: methane spectrum (HITRAN, $p = 0.01 \text{ atm}$, $T = 296 \text{ K}$, pathlength: 0.01 m) as a model narrow band absorber. Black: A sum of propyne and methane spectra from the top panel – a model mixture spectrum. Dashed red: the mixture spectrum as measured with the use of IRis-F1 in the high resolution option (point spacing $<0.001 \text{ cm}^{-1}$). Red points: the mixture spectrum as measured with the use of IRis-F1 (0.3 cm^{-1} point spacing). Blue: the mixture spectrum as measure with the use of FTIR (with 0.3 cm^{-1} resolution).

4. HIGH-RESOLUTION, HIGH-POINT SPACING SPECTROSCOPY WITH QCL FREQUENCY COMBS

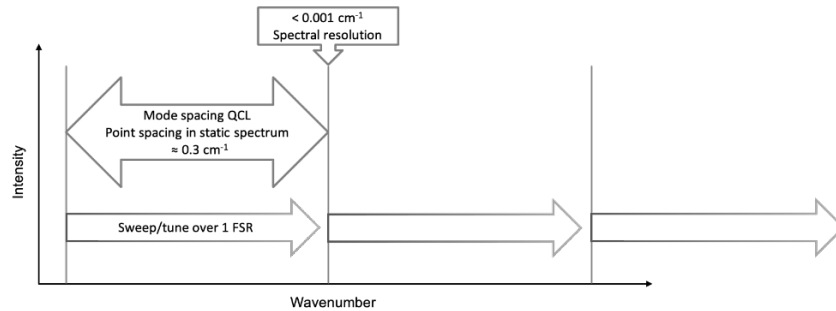
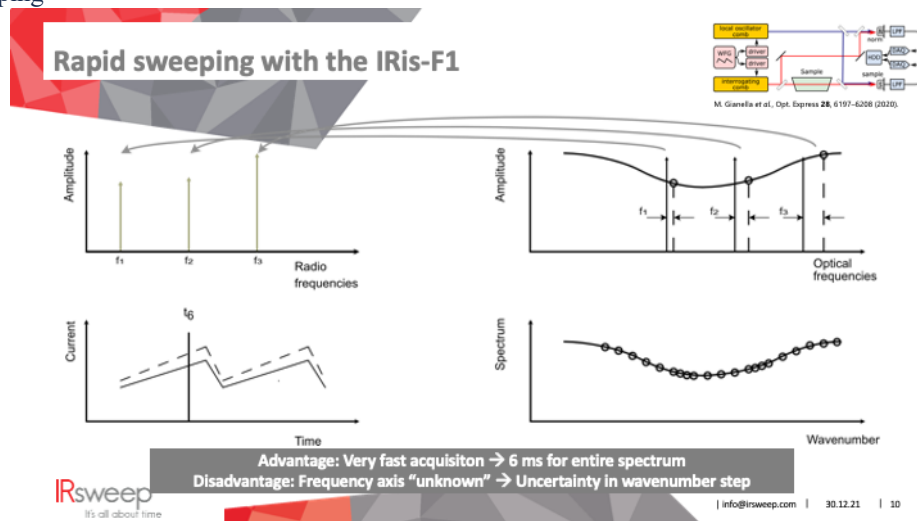


Figure 2 Description of sweeping in QCL dual-comb spectrometer to enable high-resolution spectroscopy.

To enable high-resolution spectroscopy featuring a high-point spacing to overcome the limitations illustrated in the above section, the QCL frequency comb can be tuned over 1 free-spectral range (FSR) by changing either the current or the temperature of the laser. This effectively changes the optical path length inside the laser cavity, leading to a sweeping of the optical frequencies, and thus enabling high-resolution spectroscopy. Indeed, this idea was pioneered very early on in early dual-comb spectroscopy measurements with QCL frequency combs [2], [7]. The tuning was however done manually, resulting in very long experimental times as well as limited SNR or the tuning was not carried out over the entire FSR of the laser.

5. HIGH-RESOLUTION SPECTROSCOPY DUAL-COMB METHODS

5.1 Rapid Sweeping

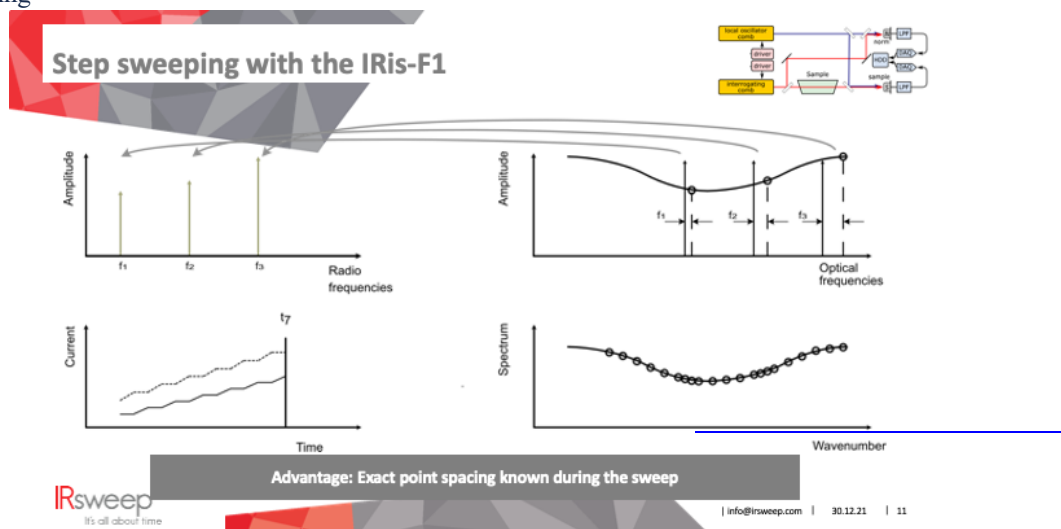


Video 1 “RapidSweep”. The video illustrates how rapid sweeping in the IRis-F1 works [8]. <http://dx.doi.org/10.1117/12.2609711.1>

Tuning both QCL combs at the same time allows for a very rapid acquisition of the entire dual-comb spectral bandwidth of 60cm^{-1} without any gaps, allowing fully resolved real-time spectra at acquisition speeds of $\sim 6\text{ms}$ [3], [9].

Video 1 illustrates how the rapid sweep technique works. The two lasers are tuned at the same time (bottom left). This leads to a simultaneous tuning of the optical frequencies (top right). This in turn results in a quasi-stationary multi-heterodyne signal (top left), allowing to fully recover the absorption spectrum (bottom right) after a full FSR of tuning. The rapid sweep video is also available for download [8].

5.2 Step Sweeping



Video 2 “StepSweep”. The video illustrates how step sweeping in the IRis-F1 works [10]. <http://dx.doi.org/10.1117/12.2609711.2>

Tuning each QCL comb sequentially on the other hand allows to measure the exact point spacing during a step sweep reaching an accuracy of $<1\text{e-}3\text{ cm}^{-1}$ [11]. Video 2 illustrates how the step sweep technique works. Each laser is tuned sequentially after one another (bottom left). This leads to a sequential tuning of the optical frequencies (top right). This in turn results in a tuning of the multi-heterodyne signal (top left). The exact tuning of the optical frequency can then be extracted from the multi-heterodyne signal (top left), allowing to fully recover the absorption spectrum including an exact point spacing (bottom right). The illustration of the step sweep video is also available for download [10].

5.3 Time-resolved step sweeping

The previously mentioned method of step sweeping can also be combined with the time-resolved mode of the IRis-F1. The dual-comb approach of the IRis-F1 gives the IRis-F1 a time-resolution of $\sim 1\mu\text{s}$. This allows for broadband and fast process monitoring as necessary in bio-applications [12] or combustion experiments [6]. In the time-resolved step-sweeping method, a time-resolved spectrum is acquired at each step. This allows for example the study of cold gases in supersonic beams. A study in collaboration with the Molecular Physics and Spectroscopy group of Prof. Frédéric Merkt at ETH Zürich revealed a $<0.0005\text{cm}^{-1}$ (15 MHz) linewidth, still limited by the Doppler linewidth of the cold gas.

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