High Precision Comb-Assisted Molecular Spectroscopy in the Mid-Infrared

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ABSTRACT

High precision comb-assisted molecular spectroscopy in mid-infrared

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In several fields, such as biology, chemistry, combustion and environmental science, laser absorption spectroscopy represents an invaluable tool for the detection and identification of a variety of molecular species in the gas phase. For this detection to be quantitative, it is of paramount importance to rely on accurate spectroscopic parameters for the involved absorption lines in terms of line strength, line center frequency, pressure broadening, and pressure shift coefficients. The mid-infrared region offers the most favorable conditions for sensitive and chemically selective detection. The sensitivity derives from the presence of intense fundamental ro-vibrational transitions of molecules, whereas chemical selectivity relates to the unique absorption spectrum that molecules possess in the mid-IR region, thereby known as the fingerprint region.

In this thesis, we combine the accelerating technology of optical frequency combs (OFC), which are powerful tools for accurate optical frequency measurements, with the wide tunability and single line emission in the mid-IR of extended cavity quantum cascade lasers (EC-QCL), to perform highly resolved, accurate and sensitive measurements in the fingerprint region, from 7.25 to 8 μm. Specifically, we have been able to lock for the first time the optical frequency of an EC-QCL to an OFC by utilizing nonlinear optics in the form of sum frequency generation (SFG) (Lamperti, AlSaif et al., 2018) and have exploited this comb-locked EC-QCL for an accurate survey of the entire
ν₁ ro-vibrational band of one of the most important greenhouse gases, nitrous oxide (N₂O). The developed spectrometer is able to operate over a wide region of ~ 100 cm⁻¹, in a fully automated fashion, while affording a 63 kHz uncertainty on the retrieved line center frequencies. The measurement allowed us to determine very accurately rotational constants of both ground and excited states of the ν₁ band of N₂O through the measurements of tens of lines of the P and R branches (AlSaif et al., JQSRT 2018). The spectrometer was then upgraded with a more recent and narrower linewidth EC-QCL to perform sub-Doppler saturated spectroscopy on the same N₂O sample at a spectral resolution below 1 MHz, the sharpest ever observed with this type of laser. Finally, we worked at adding high sensitivity to the apparatus by introducing the gas in a high-finesse passive resonator and by developing a system to measure the intra-cavity absorption with cavity ring-down spectroscopy (CRDS) together with comb calibration.
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The reward of this work is devoted to the spirit of my father Rasool Mohammed Al Saif, who passed away on Thursday 25/05/2017.

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AOFS: Acousto-optic frequency shifter.
AOM: Acousto-optic modulators.
CRDS: Cavity ringdown spectroscopy.
CTE: Coefficient of thermal expansion.
CW-CRDS: Continuous wave cavity ringdown spectroscopy.
DFG: Different frequency generation.
EC-QCL: Extended cavity quantum cascade lasers.
EM: Electromagnetic.
EOM: Electro optical modulator.
FC: Frequency comb.
FRS: Faraday rotational spectroscopy.
FS-CRDS: Fast swept cavity ringdown spectroscopy.
FSR: free spectral range.
FTS: Fourier transform spectroscopy.
GPS: Global positioning system.
GS: ground state.
HHG: High harmonic generation.
ICL: Interband cascade lasers.
IR: Infrared.
MCT: Mercury cadmium telluride.
MIR: Mid infrared.
NIR: Near infrared.
OFC: Optical frequency comb.

OPO: Optical parametric oscillator.

OP-GaP: Orientation-patterned gallium phosphide.

OR: Optical rectification.


PPLN: Periodically-poled lithium-niobate.

QCL: Quantum cascade laser.

RF: Radio frequency.

SC: Supper continuum.

SFG: sum frequency generation.

SSM: Single-sideband modulators.

Tm: Thulium.

UV: Ultraviolet.

VCO: Voltage controlled oscillator.

XUV: Extreme ultraviolet.

ZGP: Zing germanium phosphide.
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Chapter One: Introduction

The continuously growing development of semiconductor laser technology, providing access to a wider and wider spectral range along with single-mode operation and narrow-linewidth emission, makes such lasers highly favorable for optical spectroscopy. In the mid-infrared (MIR) region, in particular, where one can take advantage of the high absorption strength given by fundamental ro-vibrational transitions, the advent of quantum cascade lasers (QCL) and more recently of interband cascade lasers (ICLs) has opened up new avenues for the detection and identification of gases at trace levels, for applications to environmental monitoring, industrial process control and combustion science. Within the family of QCLs, extended-cavity QCLs (EC-QCLs) have generated considerable interest for multi-species gas detection due to their ability to cover several hundred wavenumbers in the MIR region.

Another area where QCLs and ICLs have been conquering more and more interest is precision optical spectroscopy, with experiments devoted to precise investigations of the absorption profiles and to accurate determinations of spectroscopic parameters such as line center frequency, Doppler width, pressure broadening and pressure shift coefficients through the fitting of the measured spectra. Ideally, these experiments require a narrow laser linewidth to measure the absorption profiles with negligible instrumental broadening, a linear frequency scan to avoid distortions of the profiles themselves and a repeatable frequency scale to average over many spectra and enhance the signal-to-noise ratio and the quality of spectroscopic determinations. Traditionally, these features have been achieved by stabilization techniques where the
frequency or even the optical phase of the laser field is actively locked to a stable passive optical cavity or to a molecular transition by feedback to the laser current or to a piezo-actuator in the laser cavity. The arsenal of tools for laser stabilization has been enriched at the end of the past millennium by the so-called optical frequency comb (OFC), a unique and unprecedented tool to calibrate optical frequencies in both the short and the long term, also against primary frequency references as given by Cesium fountain clocks. An OFC may provide an absolute frequency scale to any cw laser stabilized against it, with a fractional uncertainty that may go from $10^{-11}$ down to $10^{-16}$ at 1 s depending on how the comb itself is stabilized. For gas molecules at room temperature and in a collisional environment, where absorption lines are typically limited by a Doppler width at a level of a few hundreds megahertz, no sophisticated comb stabilization techniques are actually needed to squeeze the uncertainty on the line positions to the level of a few kHz [1–6], representing a gain by 3 to 4 orders of magnitude as compared to what offered so far by Fourier Transform Spectroscopy (FTS).

The stabilization of an EC-QCL to an OFC and its application to precision spectroscopy is the subject of this thesis. The motivation comes from the great potential that such a combination boasts to redefine spectroscopic databases such as HITRAN where their line parameters suffer from uncertainties at the 3–30 MHz level ($10^{-4} – 10^{-3}$ cm$^{-1}$) due to the limited accuracy given by the underlying spectroscopic data, mostly relying on FTS. The current accuracy limit is susceptible for being improved by decades as long as the frequency axis of a widely tunable laser such as an EC-QCL, which may cover hundreds of absorption lines from several bands and from
several molecules, is calibrated against the absolute frequency axis given by an OFC. Actually, this endeavor has been frustrated over the years by the difficulty to get an EC-QCLs locked to an OFC. Because of their particularly high amount of frequency noise, the only relevant result previously to this thesis was the real-time calibration of the frequency of a scanning EC-QCL against an OFC by acquiring and Fast-Fourier-Transform (FFT) processing of their beat-note [7].

In this thesis, we go one step further by demonstrating for the first time the frequency locking of a widely tunable commercial EC-QCL to a near-infrared (NIR) OFC. Despite the large linewidth of an early EC-QCL version, at a level of 21 MHz, we managed to measure line center frequencies with an accuracy up to 60 kHz. We applied this tool to the spectroscopic investigation of several lines of the P and R branches of the ν₁ band of N₂O around 7.8 μm, obtaining highly accurate values for the rotational constants of ground and excited state by a global fitting of the measured line centers. With a more recent EC-QCL version featuring a free-running linewidth of 1.7 MHz, we could obtain OFC locking and line narrowing down to 700 kHz, which was sufficient to observe for the first time with such a type of laser a sub-Doppler feature as narrow as 800 kHz. Finally, we have also worked at adding high detection sensitivity to the spectrometer through an approach of cavity-ring-down spectroscopy, where the gas sample is housed in a high-finesse passive optical resonator and the intra-cavity absorption is extracted from the measurement of the cavity photon lifetime. We arrived at a point of a preliminary validation of the apparatus that looks promising in view of obtaining absorption spectra with high-resolution over both the absorption and frequency scales.
The thesis is organized as follows. Chapter Two provides an introductory overview of the main concepts of optical spectroscopy exploited here and a description of the spectroscopy tools adopted here, namely OFCs and EC-QCLs.

Chapter Three discusses the proposed frequency locking schemes of a widely tunable MIR EC-QCL to a NIR-OFCC which was demonstrated in this work for the first time. The stabilized EC-QCL was applied for precision spectroscopy to measure the central frequency of R(18) line of the fundamental band, \( v_1 \), of N\(_2\)O gas at 1269 cm\(^{-1}\) with an uncertainty of 60 kHz.

Encouraged by the high accuracy achieved for a single N\(_2\)O transition, Chapter Four describes a line survey of the \( v_1 \) band of N\(_2\)O in the spectral range near 7.8 \( \mu \)m with our developed spectrometer to retrieve central frequencies and rotational constants. This work reports, for the first time, comb-assisted spectroscopy of 70 MIR transitions with uncertainty ranging from 10 to 170 kHz [8]. Furthermore, by a slight modification of the experimental setup and the adoption of a more recent and less noisy EC-QCL, sub-Doppler spectroscopy is also performed in the same absorption band.

In Chapter Five, moving from the high accuracy achieved on the x-axis (frequency), we demonstrate high sensitivity on the y-axis (absorption) by employing cavity ringdown spectroscopy (CRDS). For frequency referencing, we introduce an open loop control to trace the EC-QCL frequency against the frequency comb at extremely high acquisition rates.
Chapter Two: The Infrastructure of a Precise and Sensitive Mid-Infrared (MIR) Spectrometer
2.1 Introduction

Laser absorption spectroscopy provides a methodology for quantitative, rather than qualitative, analysis and monitoring of trace exhaust gases in industrial processes and atmospheric and environmental pollution. The possibility to identify and quantify several molecular species within a given gas volume relies on the fact that each molecules has a characteristic optical absorption. Thus, laser absorption techniques will enable a sensitive, a selective, a real-time gas monitoring, moreover in portable instruments.

The MIR spectral region provides very high absorption cross-sections compared to the NIR region, as illustrated in Figure 2.1(a) for a few relevant greenhouse gases in MIR. Larger cross-sections are highly favorable to increase the sensitivity of the absorption measurement.

Typically, NIR spectra are related to overtones transitions (see appendix A for more details) which make them significantly weaker than the fundamental ones that exist in the MIR. For instance, in the case of methane, NIR lines are 100 times weaker

![Figure 2.1: a) Line strength of several atmospheric gases. b) Absorption spectra of several gases in mid-infrared (MIR) (for pure gases at 296°C, 760Torr, and 1m, HITRAN 2008)](image-url)
than those in the MIR. Many molecules have their fundamental absorption bands in the MIR spectral region, which make it a target region for spectroscopists, particularly for gas tracing applications. Besides higher sensitivity, the MIR offers a better chemical selectivity because absorption lines are affected by a reduced Doppler broadening and because absorption bands of different species are more disentangled from each other: this is why the MIR is considered as a "fingerprint" region. This is demonstrated in Figure 2.1(b) which depicts large absorption cross-section and hence coefficient of various gases in the MIR region.

In this chapter, to be aligned with the framework of the thesis, the foundation of several techniques that have been used to develop our highly precise molecular spectrometer is discussed.

This chapter is organized as follows:

1. A description of the light interaction with molecules through the Beer-Lambert law, with focus on optical absorption, absorption line shape broadening mechanisms and Doppler-free absorption spectroscopy.

2. An introduction to optical frequency combs (OFCs) to discuss their basic principles, common synthesizers and applications. Since one of the fundamental methodologies in this work is comb assisted spectroscopy, this section concludes with a discussion on how this approach is implemented in the MIR.

3. An overview of one of the most unique MIR laser sources, namely extended-cavity quantum-cascade-lasers (EC-QCL), which has been adopted in this thesis as a probe laser source of molecular absorption.
4. A basic foundation of continuous-wave cavity ring-down spectroscopy (CW-CRDS).

2.2 Interaction of light with molecules

The energy associated with a photon (E) is related to the frequency of the associated electromagnetic radiation (ν) through the equation:

\[ E = hν = \frac{hc}{λ} = h\bar{ν} \]  \hspace{1cm} (2.1)

Where the parameters in (2.1) are:

- \( c \) is the speed of light in vacuum \( c = 2997925 \times 10^8 \text{ m/s} \).
- \( h \) is Planck’s constant: \( 6.62607004 \times 10^{-34} \text{ m}^2 \text{ kg/s} \).
- ν is the frequency in Hertz (Hz), \( \lambda \) is the wavelength in meter (m) and \( \bar{ν} \) is the wavenumber in (m\(^{-1}\)). From quantum mechanics, the absorbed or emitted energy of the radiation is equal to the energy gap between the involved quantized energy levels.

\[ ΔE = E_f - E_i = hν \]  \hspace{1cm} (2.2)

where \( E_f \) and \( E_i \) in (2.2) are the final and initial energy levels during the transition.

The transition from a lower energy level to a higher one is known as the absorption process. This is contrary to emission, either spontaneous or stimulated, where the

![Figure 2.2: Representation of the two types of transitions between energy levels by photon absorption or emission.](image-url)
occurring transition is from a higher to a lower energy level and, as a result, matter will emit radiation in an energy release process [Figure 2.2].

Optical absorption is one of the dominant processes that is used extensively in the spectroscopy field in different regimes to study matter structure or retrieve spectroscopic parameters experimentally. In the following section, we describe the Beer-Lambert law that rules out the phenomenon of absorption in a gas medium and that we have deeply used to fit the absorption spectra. We complement the discussion with an overview of the Doppler and collisional mechanisms that are mainly responsible for line broadening. We conclude the section with the saturation absorption regime, which allows to overcome the Doppler limit and considerably enhance the precision of line center determinations.

2.2.1 Beer-Lambert Law

When a monochromatic light (i.e. laser) passes through an absorber medium without affecting it chemically [Figure 2.3], its intensity is attenuated by an amount that depends on the light frequency. The Beer-Lambert rules out this phenomenon and shows that attenuation is exponentially decaying with the length of the medium:

\[ I(\nu) = I_0 e^{-\sigma(\nu)L} \]  \hspace{1cm} (2.3)

Figure 2.3: Simple schematic of Beer-Lambert absorption experimental setup.
where $I_0(\nu)$ and $I(\nu)$ are the light intensity before and after passing through the absorber medium in (W/m$^2$), respectively, $a(\nu)$ is the absorption coefficient (cm$^{-1}$), $L$ the depth of the absorption path (m), and $\nu$ is the light frequency (Hz).

Another way to express the Beer-Lambert law is through relative absorption, $A=\Delta I/I_0$, which is expressed as:

$$A(\nu) = \frac{\Delta I(\nu)}{I_0} = \frac{I_0 - I(\nu)}{I_0} = 1 - e^{-a(\nu)L}$$

(2.4)

where $\frac{I(\nu)}{I_0}$ is the optical transmission $T$. Experimentally, it is of major interest to get information from the gas sample such as mole faction, pressure, or temperature. These parameters may be directly retrieved from the absorbance quantity, which is a practical quantity for quantitative analysis defined as:

$$A = -\ln \left( \frac{I}{I_0} \right) = S\chi\phi(\nu)L$$

(2.5)

Equation (2.5) shows that the absorbance is related to the relative molecular concentration $\chi$, the total gas pressure $P$ (atm), and the strength of the molecular absorption line (or line strength) $S$ in (cm$^{-2}$atm$^{-1}$) and $\phi(\nu)$ is the normalized function of the spectral line shape function. Thus, absorption is a quantitative technique that is typically used for estimating species quantities in the medium, when the measurement is performed at known pressure for a given absorption length and at known temperature, the species mole fraction could be extracted by using the corresponding tabulated line strength from data base. Moreover, since the line strength depends on the medium temperature, the absorption measurement could be used as a
thermometric tool for temperature measurements as well as pressure evaluations. The line shape function describes the frequency dependence of the absorption coefficient. Comparing (2.3) and (2.5), the absorption coefficient can be indeed expressed as:

$$\alpha(\nu) = S \chi P \varphi(\nu)$$

(2.6)

The energy of the absorbed or emitted photon is equal to the difference between energy levels that correspond to that transitions. Line strength, line shape, and line position are typical target quantities in spectroscopy diagnostic applications. For instance, line shape is applicable to recognizing gas pressure, and Line strength for composition, or gas temperature identification. Whereas line positions and spacing information could be useful to identify molecular spectroscopic parameters including energy level structure of the molecule.

**2.2.2 Line shapes and broadening mechanisms**

The observed spectral lines exhibit a spectral distribution $I(\nu)$ around a central frequency $\nu_c$. For a two-level molecular system, with energy $E_i$ and $E_f$ being the initial and final levels, respectively, the central frequency of such a transition is related to the difference of the two energy levels by Eq. (2.2), namely: $\nu_c = (E_i - E_f)/\hbar$.

According to the Heisenberg’s uncertainty principle, , the energy of the photons involved in a given absorption process is not given by a delta-like function centered around the central frequency $\nu_c$, but by a distribution of width $\Delta E$ given by:

$$\Delta E \times \tau \geq \frac{\hbar}{2\pi}$$

(2.7)
where $\tau$ is the total lifetime of the involved levels. This translates into a distribution of frequencies that can be expressed as:

$$
\Delta \nu_N = \frac{1}{2\pi} \left( \frac{1}{\tau_i} + \frac{1}{\tau_f} \right) \quad (2.8)
$$

This distribution reflects a primary broadening mechanism of any absorption process that is typically referred to as natural line broadening. The resulting linewidth is known as natural width [Figure 2.4] and can be regarded as a sum of the Einstein coefficients $A$ for each level, if one considers that $A = 1/\tau$.

![Figure 2.4: Schematic diagram to illustrate the origin of natural broadening in the absorption line along with absorption line profile and its figure of merits: central frequency $\nu_c$ and linewidth: full width at half maximum (FWHM).](image)

Since all molecules of a given ensemble behave in the same manner relative to lifetime, natural broadening belongs to the so-called class of homogeneous broadening mechanisms, which are governed by the Lorentzian distribution around the central frequency of the transition [9,10]. Mathematically, the natural line profile or line shape, $\varphi(\nu)$ in (2.6), with its own natural linewidth $\Delta \nu_N$, is expressed as:

$$
\varphi_L(\nu) = \frac{1}{2\pi} \frac{\Delta \nu_N}{(\nu - \nu_c)^2 + \left( \frac{\Delta \nu_N}{2} \right)^2} \quad (2.9)
$$
For the ro-vibrational transitions involved in this thesis, natural broadening is at the Hertz level and thus negligible as compared to other broadening phenomena such as collisional (pressure) and Doppler (thermal) broadening. These two mechanisms are dominant in gas spectroscopy at environmental pressure and temperature.

Doppler broadening is an inhomogenous broadening mechanism as it originates from the different responses of the molecules to the probe light because of the different speeds of the molecules. Due to the Doppler effect, molecules traveling along the same direction of the probe light will undergo blue-shift of the expected frequency. On the other hand, the molecules that are moving towards the probe light will have red-shift. Because of the Maxwell’s distribution of molecular velocities in a gas medium, Doppler broadening results in a Gaussian profile with a characteristic full width at half maximum, FWHM, \( \Delta v_D \) of \([9]\)

\[
\Delta v_D = \frac{v_c}{c} \sqrt{\frac{2 \ln 2 k_B}{m}}
\]

(2.10)

where \( m \) is the molecular mass (kg), \( k_B \) is the Boltzmann constant: \( 1.380 \times 10^{-23} \) J/K and \( T \) is the temperature in Kelvins (K). The resulting absorption profile, as it is typical for inhomogeneous broadening, is described by a Gaussian profile:

\[
\phi_D (v) = \frac{2}{\Delta v_D} \sqrt{\frac{\ln 2}{\pi}} \cdot e^{-4 \ln^2 \left( \frac{v-v_c}{\Delta v_D} \right)}
\]

(2.11)

The collisions between atoms/molecules in a gas medium lead to an exchange of energy between the molecules that eventually reduces the effective transition lifetime and sets conditions for a homogenous broadening described by a Lorentzian distribution. It can be seen as a consequence of Eq. (2.8) due to the shorter effective
lifetime \( \tau \). Collisional broadening becomes more and more dominant at high pressures due to the increased collisional rate. The *Collisional width* \( \Delta v_c \) typically scales linearly with the gas pressure and can be calculated as the product of the total pressure of the sample gas system with their pressure broadening coefficients \( \gamma \) in \( \text{cm}^{-1}/\text{atm} \), which depends on the gas sample and on the specific absorption transition:

\[
\Delta v_c = 2P \sum_{i} \chi_i \gamma_i
\]  
(2.12)

The factor two in (2.12) is due to the fact that \( \Delta v_c \) in (2.12) is the FWHM, and \( \chi_i \) and \( \gamma_i \) are the mole fraction and pressure broadening coefficients for the present species, respectively, in the gas sample and \( P \) is the total pressure.

Practically, Doppler and pressure broadening always occur together and one has to take both effects into account through a proper line shape. This is the *Voigt profile* \( \varphi_v \), which arises from the convolution of the Lorentzian profile \( \varphi_c \) given by collision with the Gaussian profile \( \varphi_D \) given by the Doppler effect [11]:

\[
\varphi_v (\nu) = \int_{-\infty}^{+\infty} \varphi_c (u) \varphi_D (\nu - u) du
\]  
(2.13)

Using (2.9) and (2.11) in (2.13) one can obtain:

\[
\varphi_v (\nu) = \frac{2 \ln 2 \Delta v_c}{\pi^{3/2} \left( \Delta v_D \right)^2} \int_{-\infty}^{+\infty} e^{-y^2} dy
\]  
(2.14)

where \( y \) is the integration variable given by:

\[
y = 2\sqrt{\ln 2} \frac{u}{\Delta v_D}
\]  
(2.15)
The above formula holds in a linear interaction regime, where the absorption process occurs at a small rate that leaves the population of ground excited states unaltered. In contrast, when the rate is high and the phenomenon of absorption saturation occurs [10], further broadening of the profile can be observed, as well as the insurgence of extremely narrow Doppler-free spectral features called Lamb dips that can be highly favorable to precisely measure the transition line center. The saturation regime is described in the next section.

### 2.2.3 Doppler-free absorption spectroscopy

As discussed in the previous section, one of the dominant broadening mechanisms in gas spectroscopic measurement is Doppler broadening. Even at an ultra-low pressure where one can eliminate pressure broadening, the velocity distribution of the molecules will dominate the absorption linewidth along with natural width. With laser development, it has become possible to overcome this limitation by exploiting a saturation regime. The discovery of a “hole” in the Doppler broadened line corresponds to the “Lamb dip” phenomenon named after Lamb’s work [12] which inspired spectroscopists to create a novel experimental approach to extract natural linewidth. The first experimental Lamb dip was reported by two independent groups Szöke and Bennett [13,14]. They proposed to saturate the absorption line at a low
pressure in a maser cavity, which revealed a narrow dip at the center of the absorption line.

![Image](image.png)

*Figure 2.5: Experimental generic setup for Lamb-Dip spectroscopy with counter propagating laser beam, with the possible particle speed (υ), see the text for more detail. b) The expected direct transmission profile in single path. c) The expected transmission line profile from counter propagating beam setup observed at the detector (PD) after being reflected by the end mirror (M), with the emergence of a Lamb dip.*

Generally, the technique is based on using two counter-propagating beams from the same laser source [Figure 2.5], and hence the same frequency, that will travel twice in the gas medium but in opposite directions in a low pressure gas cell to minimize collisional broadening. However, a typical transition line profile at room temperature in gases will be strongly affected by Doppler broadening with Gaussian profile [Figure 2.5(b)]. In such cases, the absorption linewidth will exceed natural linewidth by several orders of magnitude. By introducing a “pump” beam which is counter propagating to the “probe” beam through the gas sample, a sharp peak will occur at the resonance frequency of that transition [Figure 2.5(c)]. Figure 2.5 illustrates an absorption experiment in which the laser source is reflected back through the cell, by a reflecting mirror M, to the detector. We assume that the laser emission linewidth is narrow compared with the absorption linewidth, a condition that may be satisfied
with, for example, the MIR sources. Molecules such as 1, 4 and 6 in Figure 2.5, which have a zero velocity axial component away from the source, behave uniquely in that they absorb radiation of the same frequency $\nu_c$ whether the radiation is travelling towards or away from the mirror M. If saturation occurs when the intensity of the pump beam is high enough to significantly deplete the ground state and reduce the absorbance of the probe beam, for those set of molecules (1, 4 and 6) while the radiation is travelling towards M, no further absorption takes place as it travels back from M. The result is that a dip in the absorbance curve is observed at $\nu_c$. This is known as a Lamb dip. It is worth mentioning that the lamb dip width can be as narrow as the natural linewidth if the probe laser beam linewidth is sufficiently narrow.

A parameter that is commonly used to quantify the phenomenon of saturation is the saturation intensity $I_{sat}$, whose expression for a two-level system can be shown equal to [15]:

$$
I_{sat} = \frac{3c\varepsilon_0h^2}{2\mu^2} \left( \Gamma_{tt} + \gamma_p P \right)^2
$$

(2.16)

where $P$ (Torr) is the gas pressure, $\mu$ (C.m) is the dipole moment of the transition, $\varepsilon_0$ is the electric permittivity of free space, $\gamma_p$ is the collisional half width and $\Gamma_{tt}$ is the half-width of a further broadening mechanism called transit-time broadening:

$$
\Gamma_{tt} = \frac{1}{8w} \sqrt{\frac{2k_BT}{m}}
$$

(2.17)

This broadening emerges due to the finite interaction time between the radiation and the molecules that cross a laser beam of radius $w$ with a mean velocity $(2k_BT/m)^{0.5}$ set by the Maxwell distribution. The contrast of the Lamb dip, defined as the
ratio between the depth of the dip and the amount of linear absorption at the line center, is a function of the saturation parameter $S$. The saturation parameter is defined as the ratio between the pump laser intensity and the saturation intensity, $S = I/I_{\text{sat}}$. Under low saturation, the contrast almost equals $S/2$, with the consequence that a smaller pressure and a larger beam, thus a lower $I_{\text{sat}}$, are favorable for the contrast. On the other hand, if the pressure is very low, the linear absorption vanishes, with the result that the Lamb dip may be obscured by technical noise even if the contrast is relatively high. In typical experimental conditions the Lamb dips are observed at a few Pascal with a contrast of a few %. The width of the dip, as it is limited by the transit time and by the collisional broadening, can easily attain the MHz level, thus orders of magnitude smaller than Doppler broadening. This explain the reason why saturation spectroscopy and the observation of Lamb dips through counter-propagating beams is a viable way for Doppler-free spectroscopy and for highly accurate determinations of the transition line centers. In the mid-infrared, thanks to the presence of the very intense fundamental ro-vibrational lines, the observation of Lamb dips is in general highly facilitated.
2.3 Optical frequency comb (OFC)

Traditionally, the OFC is generated by means of a “mode-locked” laser. For an understanding of the mode structure of a frequency comb, one could start by recalling the output coupled pulse from a laser resonator with carrier frequency $f_c$. Since the pulse is circulating in the laser cavity, the modulated amplitude of the carrier wave will be emitted from of the cavity every time the pulse completes one round trip in the resonator. Figure 2.6(a) is a representation of the oscillator electrical field in both time and frequency domains and will be explained below.

As a result of the pulse periodicity, the envelope function $A(t)$ is expressed as:

![Diagram of Optical Frequency Comb](image-url)

*Figure 2.6: An illustration of the discrete structure of the comb lines by representing time domain of frequency comb pulse train and b) is the corresponding frequency-domain.*
Accordingly, the electric field at the laser’s output is:

$$E(t) = A(t)e^{-i(2\pi f_{\text{rep}})t} + c.c. \quad (2.19)$$

where complex conjugation has been added to work on real quantities. From (2.18) and (2.19), the electric field becomes:

$$E(t) = \sum_{l=-\infty}^{\infty} A_n e^{-i\left(2\pi f_{\text{rep}} + i\frac{2\pi}{2L}\right)t} + c.c. \quad (2.20)$$

Accordingly, in a laser oscillator, a large number of pulses are oscillating simultaneously in the resonator maintaining a fixed phase relationship from pulse to pulse. The inverse of temporal pulse spacing gives the laser repetition rate $f_{\text{rep}}$ and the pulse width reflects the spectral tuning of the laser. In the frequency domain, the repetition rate frequency, $f_{\text{rep}}$, is related to the group velocity $v_g$ and resonator length $L$ by:

$$f_{\text{rep}} = \frac{v_g}{2L} \quad (2.21)$$

The temporal representation of the oscillated electric field is depicted in Figure 2.6(a), the electric field envelope is represented by the red line, while the oscillating field is represented by the blue line. Moreover, the phase variation from pulse to pulse will be affected by the resonator dispersion which will create a phase “slippage” in the electric field with respect to the pulse envelope represented in carrier envelope offset from pulse to pulse $\Delta\phi_{\text{CEO}}$. In the frequency domain [Figure 2.6(b)] this phase offset will produce a constant offset frequency, $f_{\text{CEO}}$, given by:
\[ f_{CEO} = \frac{\Delta \phi_{CEO}}{2\pi} f_{\text{rep}} \]  

(2.22)

Since the phase variation, is sensitive to any perturbation of the laser cavity, such as optical refractive index, nonlinear effects, or cavity length changes, active stabilization of the carrier frequency offset is essential to make the pulse train spectrum become a discrete set of evenly spaced frequency components \( \nu_n \). These frequency components are radially revived by both repetition rate frequency \( f_{\text{rep}} \) and carrier envelope offset frequency.

The carrier frequency \( f_c \) in (2.20) could be broken down to the offset frequency \( f_{CEO} \) and an integer multiple of repetition rate frequency \( mf_{\text{rep}} \). Therefore, we could rewrite (2.20) to represent the transmitted electric field of coherent pulse train

\[
E(t) = \sum_{n=-\infty}^{\infty} A_n e^{i\left(2\pi(f_{CEO} + nf_{\text{rep}})t\right)} + c.c. \tag{2.23}
\]

where \( n=m+l \).

In the frequency domain [Figure 2.6(b)], equation (2.23) will reveal a discrete set of narrow and equidistantly spaced frequency components, \( \nu_n \) which could be represented by:

\[
\nu_n = nf_{\text{rep}} + f_{CEO} \tag{2.24}
\]

With the previous straightforward formula, it becomes easier to link optical frequencies (\( \sim 10^{13} - 10^{16} \) THz) with radio frequencies (\( \leq 300 \)GHz) and consequently transfer the accuracy of radio frequency standards to the optical frequency in the wide electromagnetic spectrum. This regular pulse train of a mode-locked femtosecond laser will deliver a regular comb spectrum of millions of equidistant laser modes; this
spacing is equal to the pulse repetition rate frequency [16]. A primary technique to generate the light ruler in femtosecond mode-locked lasers is to stabilize the $f_{\text{rep}}$ as well as $f_{\text{CEO}}$ [17,18]. The absolute frequency measurements of those equidistant spectral lines can be measured with an accuracy ultimately limited by the primary atomic clock as $f_{\text{rep}}$ is locked to a highly stable frequency reference.

The realization of OFC synthesizers has become an extended field which covers a wide spectral range with different repetition rates. Figure 2.7 summarizes the most common way to generate OFC in the wide spectral regions with their unique characteristics of wavelength range, output power, and repetition rate. As the figure demonstrate, the most commercialized and well-established OFC synthesizers are IR mode-locked femtosecond lasers. However, reaching other spectral regions, such as ultraviolet (UV) and extreme UV (XUV), is feasible through frequency up-conversion of NIR combs, such as double frequency, quadruple frequency, sum harmonic generation (SHG) and high harmonic generation (HHG). For instance, the shortest
wavelength which has been achieved is 63nm at 0.7mW and repetition rate of 77MHz [19].

At the other end of the spectral region, i.e. deep MIR (5-20 μm), generally, combs are achieved through a down-conversion frequency process, namely different frequency generation (DFG), optical parametric oscillator (OPO), or even micro-resonators that mainly exploit third order nonlinear susceptibility $\chi^{(3)}$[16].

The most common of mode-locked femtosecond lasers, which are unique with their high stability and robust setup are fiber lasers, particularly doping fluoride glass fibers with Thulium (Tm), Holmium (Ho) and Erbium (Er) ions. For instance, Er$^{3+}$ doped fiber laser which deliver 200 fs pulses at 2.8 μm [20] or Thulium-doped fiber lasers with emission around 1.9 μm with a tunability over 190 cm$^{-1}$ [21], are examples of the promising fiber-based systems that could evolve into a free-alignment and turn-key system commercially available to laboratories.

Since the realization of OFCs, several avenues of research have expanded beyond their original purpose[18]. With the outstanding growth of OFC synthesizers which cover the wide spectral range of EM radiations from the sub-terahertz to the XUV regions, these applications have grown in parallel with OFC developments to cover a wide applications spectrum. These application include, but are not limited to, frequency and length metrology, fundamental science, precision spectroscopy, ultrafast phenomena, telecommunications, laser noise characterization and even long-term calibration in astronomical spectrographs.
2.3.1 Comb assisted spectroscopy

The precise regular frequency pattern of OFCs empowers precision spectroscopy of a frequency ruler for calibrating and referencing optical frequencies.

Comb-assisted spectroscopy is based on using a probe laser that interacts with an absorbing medium over a given distance and referring the frequency of the probe laser to one of the spectral components (comb tooth) of the frequency comb. Frequency referencing is performed by shining the comb and the cw laser on a detector and measuring or stabilizing a “beat-note” frequency between the two lasers, probe and reference: $f_{\text{beat}} = |\nu_n - \nu_{\text{probe}}|$.

$\nu_{\text{probe}} = n f_{\text{rep}} + f_{\text{CEO}} + f_{\text{beat}}$  \hspace{1cm} (2.25)
where $v_{probe}$ is the optical frequency of the probe laser and $f_{beat}$ is the frequency of the beat-note. As depicted in Figure 2.8, absolute frequency measurements could be accomplished by measuring all radiofrequencies involved in (2.25), namely $f_{beat}$, $f_{rep}$, and $f_{CEO}$, with respect to an atomic clock. This may be easily obtained in a laboratory by linking all frequencies to the time standard given by a GPS signal.

In comb-assisted spectroscopy, to improve the spectral resolution, the temporal coherence of the comb may be transferred to the probe laser via “phase-lock” of the probe laser to the nearest tooth of the comb. This scheme is accomplished through two phase-locking steps: firstly the comb needs to be phase locked to a low noise microwave or optical oscillator to enhance its temporal coherence and achieve narrower comb modes, secondly the probe laser needs to be phase locked to the comb. Both phase locking steps need a servo loop, in the first case acting on an intra-cavity electro-optic modulator and/or piezo transducer, in second case acting on the laser current and/or a piezo transducer that modifies the cavity length. [18].

Historically, Diddams et al. (2000) presented the first absolute frequency measurements of molecular iodine [18] where he used a combination of femtosecond Ti:sapphire comb, He-Ne laser, and a frequency doubled Nd:YAG laser to measure two lines of $^{127}$I$_2$. The same molecules were studied by Holzwarth et al. extensively [1] using a widely tunable Nd:YAG laser locked on several I$_2$ saturated absorption lines to reach a relative accuracy which is superior to $10^{-11}$. Another target molecule was acetylene (C$_2$H$_2$). In the NIR, the first absolute frequency of P(16) in the combination
band ($v_1+v_3$) of C$_2$H$_2$ lines with a retrieved central frequency uncertainty at $10^{-12}$ level was measured by Hong et al. (2003) [2].

Measurements of quite intense lines have been reported in the NIR for the $10^10$-00$^90$ band of ammonia [22], and 101-000 band of water [23]. While in the MIR a theoretical retrieval, as well as an experimental comb-reference for several bands of nitrous oxide, have been reported [24].

Combining the precision provided by OFCs with the MIR laser sources such as QCLs, one could perform precision spectroscopy in the MIR at high sensitivity. However, as most comb sources lie in the NIR, one has to resort to nonlinear optics to create a beat-note signal between a NIR comb and a MIR laser. There are two ways to do this, either by difference-frequency-generation or by sum-frequency generation [25].

![Figure 2.9: Different referencing approaches of a MIR laser, such as QCL, to a NIR comb: a) DFG generated by CW optical oscillators, b) Direct link to the comb by DFG, c) Direct link to the comb by SFG, and d) SFG generated by CW optical oscillators.](image-url)
As summarized in Figure 2.9, four possible schemes can be used where the second order nonlinear process is utilized. In the first two approaches, two extra NIR-CW laser sources are utilized along with MIR probe laser and OFC. The frequencies of the CW lasers, $\nu_1$ and $\nu_2$, are related to the MIR probe laser frequency by $\nu_{\text{probe}} = \nu_2 - \nu_1$. The two lasers are being locked to the OFC mode at two different order $n_1$ and $n_2$ with some offset, for simplicity let’s assume that they have the same offset $\Delta f$. And hence, the two laser frequencies $\nu_1$ and $\nu_2$ could be retrieved from OFC repetition rate ($f_{\text{rep}}$) and offset frequency ($f_{\text{CEO}}$) to be: $\nu_1 = n_1 f_{\text{rep}} + f_{\text{CEO}} + \Delta f$ and $\nu_2 = n_2 f_{\text{rep}} + f_{\text{CEO}} + \Delta f$, respectively. The beat-note could be readily detected either by mixing $\nu_{\text{probe}}$ with the DFG signal ($\nu_{\text{DFG}} = \nu_2 - \nu_1$) between the two lasers (Figure 2.9(a)), thus the beat-note frequency will be $f_{\text{beat}} = |\nu_{\text{probe}} - \nu_{\text{DFG}}| = |\nu_{\text{probe}} - \nu_2 + \nu_1|$. In the other way around, The SFG signal between the MIR probe laser and the $\nu_1$ (longest wavelength among the two CW lasers) could be also used for the beat-note detection, where $\nu_{\text{SFG}} = \nu_{\text{probe}} + \nu_1$ as illustrated in Figure 2.9(b).

Both schemes lead to the same beat-note frequency, $f_{\text{beat}} = |\nu_{\text{probe}} - (n_2 - n_1) f_{\text{rep}}|$, which allows calibrating the probe frequency against the comb repetition frequency and, in principle, against any primary RF reference through the simple $f_{\text{CEO}}$-free referencing formula:

$$\nu_{\text{probe}} = (n_2 - n_1) f_{\text{rep}} + f_{\text{beat}} \quad (2.26)$$

Another two simple approaches, either through SFG or DFG could be used without the use of extra lasers, simply by direct referencing of the probe laser to the comb [Figure 2.9 (c) and (d)]. In DFG case, a difference frequency between the broadband
comb spectral portions $v_2$ and $v_1$ is produced at an offset MIR-comb that will overlapped with the probe MIR laser. By measuring the beat-note between the probe laser and the nearest comb mode of the MIR generated difference frequency-comb (DF-comb), the frequency of the probe laser is calibrated by (2.26).

Alternatively, one could perform SFG between the NIR-comb and MIR-probe laser to produce sum frequency comb (SF-comb) that has the frequency components: $v_{SFG} = v_1 + v_{probe} = n_1 f_{rep} + f_{CEO} + v_{probe}$. The overlapping of the generated SF-comb with the high frequency ($v_2$) part of the comb will generates a beat-note of frequency $f_{beat} = |v_{SFG} - v_2|$. Thus, the MIR probe laser frequency could be retrieved by Eq. In the two aforementioned configurations (c and d in Figure 2.9), it is necessary to implement a delay line in the experimental setup that is not required in the cases (a) and (b).

While using intermediate CW-lasers in the approaches in (a) and (b) suffers from additional costs and complexity of the setup with the need to more servo loops, the SFG-approach in (d) has the advantage of simplicity and generating SF-comb in NIR region which will give an access to facilitate the experiment with optical fibers. Moreover, low-noise with high bandwidth and cost-effective detectors are available in NIR. For these attractive outcomes in that strategy, in this thesis, we are adopting the SFG approach with balanced detection scheme that will provide a 3-dB enhancement of SNR for our referencing experiments.
Following the SFG configuration mentioned in previous discussion to generate a beat-note for our referencing scheme, the first step will bring the two lasers (the probe in MIR and the comb in the NIR) to the same spectral region. Therefore, a sum frequency generation (SFG) between the probe and the reference laser is performed to up-convert the probe laser frequency. Thereafter, a spectrally broadened replica of the comb is generated in a highly nonlinear optical fiber through a supercontinuum (SC) process as illustrated in Figure 2.10 to beat with the previously generated SFG comb, and then to use the resultant beat-note in the locking servo loop.

\[ f_{\text{SFG}} = n f_{\text{rep}} + f_{\text{CEO}} + f_{\text{probe}} \]  

\[ f_{\text{SC}} = m f_{\text{rep}} + f_{\text{CEO}} \]  

Thus, the probe laser frequency is readily obtained by

\[ f_{\text{probe}} = (m-n) f_{\text{rep}} + f_{\text{beat}} \]
while $f_{CEO}$ is canceled out since both combs, SFG and SC, are generated from the same origin comb. The first measurement in comb-calibrated spectroscopy without the need to measure $f_{CEO}$ was in developed in 2005 [26], and as a result, sub-kilo hertz accuracy was demonstrated with this method.

Several approaches have been proposed so far in the framework of comb-assisted spectroscopy to tune the probe laser frequency over the target spectral range. For instance, one elegant approach is to take advantage of frequency actuators such as Single-Sideband Modulators (SSM) or Electro-Optic Modulators (EOM). In SSM, tunable sidebands of the probe laser are generated, but the carrier is kept fixed and maintains a tight phase lock to the comb [27,28]. The strength of the above-mentioned strategy lies in its functionality as a very fast and accurate approach.

Another strategy, which is not trivial, of probe laser scanning could be via changing the offset frequency of the phase-locking loops. A tradeoff in this technique is the aliasing effect when the beat-note between the probe laser and the nearest comb tooth overlaps with the beat note from the conjugated comb tooth. However, several proposed schemes to solve the ambiguity problem have been proposed. One particular solution was suggested by Benkler et al. [29], where they managed to remove this ambiguity in the “endless frequency shifting” approach by shifting the carrier frequency of the comb using an electro-optical crystal with a programmed phase evolution while keeping fixed the RF beat-note.

Another straightforward strategy to scan the locked probe laser over a specific bandwidth is via tuning of the repetition rate of the frequency comb through a piezo
transducer that changes the oscillator length. The limitations of this approach is the modest tuning speed due to the limited bandwidth given by the piezo.

In the framework of this thesis, we adopt the repetition rate scanning for tuning the probed laser over our target absorption lines. Yet, the limitation of this approach was not an obstacle for this work as another technique was implemented to cover wide tunable spectral span in MIR as will be discussed in Chapter Three.

Comb-assisted spectroscopy is a powerful tool to populate spectroscopic atomic/molecular databases of high quality data and to trigger a cooperation between theoretical and experimental spectroscopists for either comparison purposes with existing data or to verify theoretical models. Accuracies down to sub kHz levels at environmental conditions with compact and even portable spectroscopic tools have been realized thanks to OFCs, thus 3-to-4 orders of magnitude than the 1-10MHz accuracy limit of traditional Fourier Transform spectrometers. It is worth noting that the accuracy afforded by combs also relates to the repeatability of the frequency scale, which is highly favorable to acquire and average many spectra and thus improve their signal to noise ratio (SNR).

2.4 **Mid-infrared extended cavity quantum cascade lasers (EC-QCLs)**

The availability of QCLs has revolutionized MIR spectroscopy. The operation principle of QCLs, fundamentally, is different from the operation of conventional diode lasers. Reaching wavelengths of 3-12 μm or even those of the so-called THz range is made possible by controlling the quantum well thickness, and thereby the energy
levels of the confined electronic states that are involved in laser transition. The advancement in molecular beam epitaxy (MBE) along with the engineering of the band structure in QCLs opens up a promising development of laser sources in MIR.

In diode lasers that rely on the recombination of injected electrons and holes to emit photons, the radiative transitions take place between the conduction and valence bands where the emission wavelength is determined by the width of the bandgap, which is an intrinsic material property. Thus, in order to change the wavelength, a different material needs to be used. In III-V semiconductors such as gallium arsenide, indium phosphide, and gallium antimonide, typical bandgaps are in the range of 0.7-1.4 eV and reach up to 3.4 eV in gallium nitride. Photonic energies corresponding to these transitions lie in the range spanning from the near infrared to the ultraviolet and can be modified by mixing various percentages of different elements into the compounds, creating ternary or quaternary alloys.

Figure 2.11: a) Principle of intersubband transitions in the conduction band to form the cascade process of electron transition and a photon is being emitted between subbands in QCLs, b) Littrow-configuration that was proposed to extend the tunable range of QCLs through external cavity implementation to form EC-QCLs.

For the MIR emission in the 3-12 μm range the bandgap needs to be in the range of 0.1-0.4 eV. This is barely achievable in interband lasers with extreme mixing ratios
within the lead-salt family, e.g. Pb$_x$Sn$_{1-x}$Te, and certain quaternary alloys [30]. These lasers are known for their low power levels and usually require cryogenic temperatures for operation, not to mention their poor mechanical properties that severely limit their lifetime.

Unlike diode lasers, QCL emissions are based on intersubband transitions [Figure 2.11(a)] in the heterostructure where the emitted wavelength is determined by quantum confinement [31,32], where the electron transitions occur among potential staircases leading to photons emission at each step. Since a wide tuning laser is desired in many applications, wide tunable QCLs have been demonstrated with two main approaches. One approach to tune the laser emission over a few wavenumbers could be achieved through the integration of a Bragg grating into the laser waveguide, which will lead to a distributed feedback (DFB) laser that operates at cryogenic temperatures [33]. A second approach that offers tunability over multiple tens of wavenumbers exploits an external cavity configuration by adapting a grating to the laser setup by means of the external cavity (EC) [Figure 2.11(b)]. A tunable range up to 91 cm$^{-1}$ [34] was reached with this configuration. Further extension of the tunable range to reach up to 150 cm$^{-1}$ was also achieved [35]. One of the simplest and most dominant approaches [Figure 2.11(b)] to extend and improve QCLs spectral range is through Littrow configuration where the beam is coupled out of the external cavity facet. In this design, large output power is achieved and because of this configuration, the output beam direction is not shifted during the laser frequency tuning.

The first experimental report on an external cavity MIR QCL was given by Le et al. [36] in 1996 using a Littrow configuration, which was followed by an in-depth analysis
in 1997 [37]. The first single mode emission of EC-QCLs was introduced Totschnig, et al in 2002 by [38]. In 2005, the first mode-hop free EC-QCL was realized by Wysocki et al. [39] where they actively controlled the cavity length by mounting the grating on a piezo-controlled actuator. Later, this laser was applied to chemical sensing [40].

EC-QCLs became at some point commercially available from two main suppliers. One of them, Daylight Solution, was founded by Timothy Day in Poway CA, USA in 2005. Their core development is based on Littrow technology for EC-QCLs [41]. The other main supplier is Pranalytica Inc, founded by Kumar Patel, in Santa Monica, CA, USA. Their laser techniques are based on Littrow and Littman-Metcalf designs. Pranalytica has built a full EC-QCL based gas sensor for harsh environment [42] or security and defense applications. Both suppliers have developed their products extensively to build laser systems in compact housings using multiple QCLs to span a wide tuning range, for instance Daylight’s MIRcat (TM) and Pranalytica’s OmniLux (TM) product lines.

EC-QCL is a promising laser source with its relatively high output power and extended, wide tunable spectral coverage in the MIR. These lasers have proved their ability to delivered single mode emissions and frequency tunability in the MIR (from 4 to 12 μm) over ranges in excess of 100 cm⁻¹, with a 100 mW optical power [32]. With such strong outputs, these lasers provides strong motivation to utilized broadband spectroscopic applications in both sensing and metrology since they are able to be swept over a molecule’s entire ro-vibrational band.

The experimental work of this thesis employs a CW EC-QCL from Daylight Solution, which has a tunable range up to 100 cm⁻¹ around 7.8 μm, and another laser around 7.6
μm with output power that can reach up to 100 mW. These lasers are designed to have a wide tunability range with single-mode emissions around their central wavelength.

2.5 Cavity ringdown spectroscopy (CRDS)

In the following pages, a short theoretical summary is provided to cover the basics of optical cavities followed by a quick treatment of the ringdown approach in the cavities. The following treatment is based on several widely used textbooks that discuss optical resonators or cavities [43–46]. For more details on how the formulae are derived and background information on Gaussian beam propagation in optical cavities, readers are encouraged to explore the references which extensively discuss the foundation of optical resonators. It is worth noticing that the first treatment of the optical cavities starts with the Fabry-Pérot resonator of two flat mirrors. The literature usually refers to the cavities as resonators, as they will be named in the following text.

2.5.1 Optical resonator foundation

As introduced in the previous sections, the higher the interaction length, the higher the absorption of an electromagnetic field from a gas medium is. In a single-pass configurations, this length is necessarily limited by the geometrical length of the cell, which may be not sufficient to detect weak lines or highly diluted species. One of the most effective techniques for optical path length enhancement is the use of the optical cavity. For simplicity, the discussion below will be based on a simple linear cavity that contains two identical, parallel and highly-reflective mirrors with a radius of curvature $r$, separated by a distance $L_c$ to form a symmetric cavity [Figure 2.12]. A standing wave will result from the multiple reflections that the injecting undergoes along the
resonator axis if this is coupled perpendicularly to the entrance mirror of the cavity. Due to the generation of standing waves inside the cavity, only specific frequencies \( \nu_q \) may lead to an intra-cavity field build up, that satisfy the resonance condition:

\[
\nu_q = q \frac{c}{2nL_c}
\]  

where \( q \) is a positive integer, and \( n \) is the refractive index of the material inside the cavity. These frequencies are called "fundamental modes" of the cavity. The spacing between two consecutive fundamental modes is known as a free spectral range (FSR), which in the absence of dispersion is:

\[
FSR = \nu_q - \nu_{q-1} = \frac{c}{2nL_c}
\]  

Other entities of the cavity are the FWHM of cavity mode:

\[
\Gamma_c = \frac{FSR}{\pi} \frac{1-R}{\sqrt{R}}
\]  

where in (2.32) is the mirror reflectivity \( R \). The two mirrors are identical in the symmetric cavity and we defined \( R = \sqrt{R_1 R_2} \), where R1 and R2 are the input and rear
mirror's reflectivity respectively. The reflectivity $R$ is related to the mirror transmittance ($T$) and losses ($l$) by energy conservation, so that $R + T + l = 1$.

The ratio of the cavity FSR to the cavity mode width $\Gamma_c$ will give an important property of the cavity known as cavity *finesse* ($F$):

$$F = \frac{\text{FSR}}{\Gamma_c} = \frac{\pi \sqrt{R}}{1 - R}$$  \hspace{1cm} (2.33)

Essentially, the finesse defines the effective interaction length besides its impact on the cavity mode width. From (2.31) and (2.33), the higher the mirror reflectivity, the narrower the cavity modes, and hence, the larger the cavity Finesse and the larger the effective optical length $L_{\text{eff}}$ of the cavity:

$$L_{\text{eff}} = \beta \frac{F}{\pi} L_c$$  \hspace{1cm} (2.34)

where $\beta$ can be shown to be equal to 2 in the case of a steady coupling of the laser into the cavity and equal to 1 in the case of a transient coupling as it happens in CRDS. The typical reason for using an optical cavity is the enhanced interaction length given by (2.34). However, as an optical cavity also produces an enhancement of the field intensity because of constructive interface within the resonator, it may helpful to

---

Figure 2.12: Linear symmetric optical cavity, MMO is the spatial mode matching optic represent in the focusing lens. $w_0$ is the beam waist inside the cavity of length $L_c$. a). Illustration of Optical cavity fundamental modes with a description of cavity mode width and its FSR.
achieve saturation and thus sub-Doppler spectroscopy. The maximum build-up of power could be estimated from the cavity finesse $F$, if the initial power $P_{in}$ is known:

$$P_{cavity} = FP_{in}$$  \hspace{1cm} (2.35)

### 2.5.2 CW-Cavity ringdown spectroscopy (CW-CRDS)

In CRDS spectroscopy, the absorption coefficient is retrieved by measuring the temporal response of the transmitted beam. For more insight on the cavity temporal response to the incoming laser beam which is the core of the CRDS technique, and for simplicity treatment as well, let us assume a pulsed laser that is coupled to a linear symmetrical optical cavity with mirrors’ reflectivity represented by $R_1$ and $R_2$ and an absorbing medium between the two mirrors represented by absorption coefficient $\alpha(v)$. If the pulsed laser has an intensity $I_{in}$ and a pulse duration shorter than the round trip time ($\tau = 2L_c/c$) of the pulse in the cavity, and the mirrors have a transmittance factor of $T$, the monitor and transmitted intensity ($I_0$) after the first pass through the cavity, from Beer-Lambert’s law (2.3) will be:

$$I_0 = I_{in} T^2 e^{-\alpha(v)L_c}$$  \hspace{1cm} (2.36)

where $\alpha(v)$ is the frequency dependent absorption coefficient of the medium inside the cavity. The intensity after a complete round trip will be

$$I_1 = I_0 R^2 e^{-2\alpha(v)L_c}$$  \hspace{1cm} (2.37)

where the factor 2 represents a complete one round trip of the reflected pulse inside the cavity. Consequently, after $u$ complete rounds, the overall intensity $I_u$ will be:

$$I_u = R^{2u} e^{-2u\alpha(v)L_c}$$  \hspace{1cm} (2.38)
The overall cavity characteristic time will then be: \( t = \mu \times 2L_c/c \), and we rewrite the factor \( R^2u \) as: \( R^2u = e^{2u\ln R} \). Accordingly, (2.38) could be written as:

\[
I = I_0 e^{-\frac{c}{L_c} (1-R + \alpha(v)L_c) t}
\]

(2.39)

At this point, one can define ringdown time (\( \tau \)) as the time where the light intensity reduces to its \( 1/e \):

\[
\tau = \frac{L_c}{c(1-R + \alpha(v)L_c)}
\]

(2.40)

Rewriting (2.41) using (2.40):

\[
I = I_0 e^{-\frac{t}{\tau_0}}
\]

(2.41)

From Equation (2.41), the absorption coefficient of a medium that fills the cavity directly impacts on by the ringdown time of the cavity itself. In a more comprehensive way, and taking into account several species that could be within the cavity as well as frequency dependence of both mirror reflectivity and absorption coefficient, one could rewrite (2.40):

\[
\tau(v) = \frac{L_c}{c \left(1-R(v) + \sum_j \alpha_j(v) L_c \right)}
\]

(2.42)

By defining an empty cavity decay constant \( \tau_0 \) as:

\[
\tau_0 = \frac{L}{c(1-R)}
\]

(2.43)

The absorption coefficient may be directly expressed in terms of the cavity decays constants with \( \tau \) and without \( \tau_0 \) absorber as:
\[
\alpha(\nu) = \frac{1}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)
\]

(2.44)

The empty cavity decay constant \(\tau_0\), (2.43) is proportional to the mirror loss divided by the cavity length, which will imply that the higher reflectivity and the longer cavity length, the higher the sensitivity is (2.45). Nevertheless, higher reflectivity will also lead to less coupled light into the cavity.

![Schematic illustration of continuous-wave cavity ring-down spectroscopy (CW-CRDS). A CW laser is injected into a high-finesse cavity of mirror reflectivity \(R\) containing a gas sample. As soon as a certain cavity transmission threshold is reached, the injection is shut off by a fast optical switch, leading to exponential decay of the light transmitted intensity.](image)

The detection limit in CRDS depends on the ratio between the standard deviation of the acquired ringdown times, which mainly depends on the signal-to-noise ratio of the measured RD decay, and the empty cavity ting-down time \(\tau_0\). One could define the minimum detectable absorption in CRDS as:

\[
\alpha_{\text{min}} = \frac{1}{c\tau_0^2} \Delta\tau_{\text{min}} = \frac{1 - R}{L_c} \left( \frac{\Delta\tau}{\tau_0} \right)_{\text{min}}
\]

(2.45)
where $\Delta \tau_{\text{min}}$ is minimum detectable change in the decay time. The more are accurate the measurements of the ringdown time, the better is the detection limit of the absorption. Moreover, to some extent, the minimum measured absorption coefficient in CRD techniques is limited by mirror reflectivity and cavity length. Since the above-mentioned reflectivity $R$ is the effective reflectivity that includes all the losses inside the cavity, it could be less or equal to the reflectivity of the mirrors.

Another way to increase the detection limits of CRDS is to increase the accuracy of ringdown time determination by minimizing the quantity $\Delta \tau_{\min}/\tau_0$. Therefore, using a high resolution digitizer to record the ringdown time is essential, however, in reality, the fluctuation of ringdown event also limits the accuracy. The ratio $\Delta \tau_{\min}/\tau_0$ depends on several parameters, such as the mechanical and thermal stability of the cavity, the laser linewidth, the detector noise, and the circuitry or the number of bits in the digitalization. The thermal and mechanical fluctuations of the cavity cause long term drifts of the baseline noise, while the laser linewidth and detection noise are responsible for a low Signal-to-Noise Ratio (SNR) of the measured exponential decay.

In addition, the shot noise affects the signal on the detector since the detector signal will have a noise that proportional to the square root of the number of detected photons $\sqrt{N}$.

Therefore, the accuracy of measuring ringdown time will be affected, and hence the absorption coefficient. Moreover, CRDS at a higher pressure, such as atmospheric pressure, will increase the loss as well because of scattering.
A basic schematic diagram of the CW-CRDS is given in Figure 2.13 involving experimental setup in its most basic condition with a typical ringdown event that could be observed in CW-CRDS. In this form, the CW-CRDS setup as shown in Figure 2.13 consists of a tunable CW-laser followed by an acousto optical modulator AOM to switch the laser off/on, a high finesse optical cavity in placed after the AOM then fast photodetector to acquire the ringdown events.

A remarkable observation when using tunable CW semiconductor lasers (such as DFB, EC-TDL, QCL or EC-QCL) in CW-CRDS experiment, is their relatively large and noisy linewidth. If the laser linewidth is larger than the cavity mode, which is a typical case since cavity modes have a sub kHz level width while typical CW-lasers have a linewidth of MHz level(s), the intensity buildup will be noisy due to a laser jittering effect, as shown in Figure 2.13. Implementing a fast optical switch (AOM) that has a response time which is faster than the rise time of the ringdown event, based on its bandwidth, will help in cleaning up the noisy signal and results in clean events. Another advantage of the AOM is that it works as an optical isolator which prevents any perturbation into the laser coming from the feedback reflection from the high finesse cavity. In CW-CRDS setup, the first order diffracted beam is used to pump the high finesse cavity. A TTL signal is sent to the digital port of the RF driver of the AOM that will turn the first order diffracted beam on/off fast enough to pump and re-pump the optical cavity. Moreover, setting up a particular threshold of the cavity output signal to decide when to switch off the laser has the advantage to select the most intense and low order modes. In that step, other TEM modes which have a different diffraction loss are avoided, and hence, single exponential decay time is achieved.
In the acquiring procedure, usually measuring $\tau_0$ will be sufficient to estimate the scattering and transmission losses of the cavity mirrors. Also, one should pay attention to the detector bandwidth which is used in CRDS; a sufficiently fast detector is required to measure the ringdown events.

The CW laser linewidth, usually, is narrower than the optical cavity FSR and much larger than the cavity fundamental modes. To achieve the resonance, one can scan the cavity length, by implementing a piezoelectric transducer (PZT) attached to one of the cavity mirrors, usually the rear one. Applying periodic voltage to the PZT will allow us to periodically modulate the cavity length to cross the resonance several times. Another way to obtain resonance events is by scanning the laser frequency over the cavity modes in order to observe the resonance when the laser passes over the cavity mode.

The scanning rate of either the cavity length or laser frequency will affect the signal to noise ratio (SNR) of ringdown events. The relevant parameters that define the coupled power and thus the SNR are the ratio $\eta_L$ between the cavity-mode width and the laser linewidth, and the ratio $\eta_T$ between the time taken by the laser to cross a cavity resonance and the cavity response time, which may be assumed equal to the empty-cavity ting down time $\tau_0$. Under ideal conditions of lossless mirrors, equal reflectivity for the two mirrors, perfect spatial matching between the incoming radiation and field distribution of the coupled cavity mode of the cavity, a unitary coupling efficiency requires both ratios to be at least 1, which implies laser linewidth equal or lower than the cavity resonance, and crossing time equal or longer than $\tau_0$. If any of these ratios is lower than 1, the coupling efficiency will be correspondingly
decreased: as an example, in the case of a low scanning rate ($\eta = 1$) the fraction of laser power within the cavity mode width, fixes the overall coupling efficiency. Therefore, the drawback of a slow scanning rate is a noisy signal due to the laser linewidth effect. On the other hand, a fast scanning rate is desirable as it has the advantage of increasing the data collection rates.
Chapter Three: Absolute Spectroscopy with an Extended Cavity

Quantum Cascade Laser
For the first time, frequency locking of an EC-QCL to a near-infrared frequency comb has been demonstrated, enabling high-accuracy molecular spectroscopy measurements near 7.8 μm over an extremely wide spectral range of ~ 100 cm⁻¹. Line-center frequency measurements of P(40), P(18) and R(31) lines of N₂O fundamental ro-vibrational band show a combined uncertainty of ~ 63 kHz. This spectrometer has the potential to be extended to 12 μm, which is the current wavelength limit for commercial cw EC-QCLs.
3.1 Introduction: Highly precise MIR laser source

The precision that can be attained in optical metrology measurements is ultimately limited by the frequency noise of the probe lasers. Probing a spectroscopic feature at a sub-kHz or even sub-Hz level requires using a comparable laser linewidth. Since, the laser frequency noise, which drives from phase noise, causes linewidth broadening of the probe lasers, an active frequency stabilization of these lasers is a highly favorable implementation in metrology. Several techniques have been developed over the past few decades to achieve frequency stabilization of lasers. Since QCLs are the most widely used sources for MIR spectroscopy, several locking schemes were proposed to frequency stabilize these laser sources. The first implementation of an active stabilization of a distributed feedback-QCL (DFB-QCL) has been achieved in 1999 by Williams et al. [47]. In their experiment, DFB-QCL laser at 8.5 μm was locked against the edge of an N₂O molecular absorption and obtained linewidth narrowed to ~12 kHz. Another very well established, widely and frequently used approach to stabilize and also narrow a laser against the resonance of an optical cavity is the Pound-Drever-Hall (PDH). Nevertheless, these advantages come at the expense of system complexity. For instance, a lock of an 8.5 μm QCL to a passive optical cavity was reported by Taubmann, with linewidth shrank from 150 to 5.6 kHz [48]. Further linewidth reduction and coherence transfer to a 9.2 μm DFB-QCL laser has been developed by Bielsa, et al. [49] who phase locked the QCL to a single mode CO₂ laser and applied the locked laser to measure formic acid with sub-kHz resolution level.

The recent development of frequency combs, permits an additionally way for stabilizing QCLs. Absolute frequency measurements in the MIR became possible with
coherent transfer of OFCs to MIR semiconductor sources. Frequency or phase locking of QCLs has been successfully achieved against either visible Ti:Sapphire comb [50], NIR fiber combs [51], or IR thulium fiber combs [21]. With a frequency comb locking, an absolute frequency accuracy is achieved which provides a more accurate determination of transition line-center and absorption profile parameters.

In this chapter, the combined use of these two spectroscopic tools, namely EC-QCL and optical frequency comb, is shown to push the accuracy performance of the spectroscopic measurements to high level. We managed to do this over the entire tuning range of the EC-QCL. Moreover, the developed tool opens the possibility to massively average multiple spectra to improve the signal-to-noise-ratio and thus the precision of the spectroscopic measurements.
3.2 MIR Precise Spectrometer

3.2.1 MIR EC-QCL referencing to IR-OFC

The development of spectrometers that join an accurate frequency axis to a wide spectral coverage (> 100 cm⁻¹), which is the typical extension of absorption bands in the fundamental ro-vibrational band, is mandatory to fulfill the redefinition of spectroscopic databases such as HITRAN [52], which are still based on data prior to OFC invention. This has been realized in the near-infrared, thanks to the availability of commercial OFCs and of a variety of widely tunable diode-laser-based solutions [5,6,22,23,53–55].

In the mid-infrared region, the development of precise spectrometer is more challenging. A first requirement is the comb-referencing of the MIR probe laser to a NIR frequency comb which is not as straightforward as in the NIR because the emission ranges of the two sources do not superimpose. For that, an accomplishment of an efficient nonlinear frequency mixing scheme to relate the probe EC-QCL emitting in the MIR, to the OFC laser in the NIR is required. This has been obtained by a variety of approaches, such as down-conversion of the frequency comb to the mid-IR through difference frequency generation (DFG) [56,57] or optical parametric oscillation (OPO) [58], up-conversion of the probe laser to the near-IR through sum-frequency or second-harmonic generation (SFG/SHG) [59,60], as well as referencing schemes applied to DFG- and OPO- based cw sources [4,61].
A second requirement is a widely tunable laser source. Up to a wavelength of 4.5 μm, a viable solution is represented by cw sources based on DFG or OPO processes in periodically-poled lithium-niobate crystals (PPLN). These have been exploited for sub-Doppler surveys over more than 50 cm⁻¹ on CH₄ lines near 3 μm and N₂O lines near 4.5 μm [62]. DFB-QCLs are a valuable alternatively, but only over a narrower spectral range, as demonstrated by Galli et al. [63] on CO₂ lines near 4.3 μm. The widest spectral coverage achieved so far was obtained by a dual-comb approach [64] that affords multi-parallel detection and extremely fast acquisition time. However, this comes at the price of an accuracy limited to ~300 kHz.

In this chapter we are using a commercial EC-QCL from Daylight Solution with a tuning range of 1217-1328 cm⁻¹ and maximum output power of ~ 100 mW referenced to a Tm:fiber comb emitting around 5200 cm⁻¹ through SFG process. The referencing scheme is based on comb-assisted approach that is illustrated in Figure 3.1, where it is based on the frequency conversion of both MIR EC-QCL and IR Thulium (Tm) comb down to around 6500 cm⁻¹ (1.5 μm) in the NIR. As already demonstrated in Chapter Two, the beat-note is the core of such referencing scheme where it links the optical frequency of EC-QCL (ν_QCL) to the Tm-OFC repetition rate (f_{rep}) (2.25). Taking into

\[ f_{LO} \]

**Figure 3.1: Generic diagram for proposed frequency locking of EC-QCL to an OFC. f_{LO}: frequency local oscillator, f_{beat}: beat-note frequency, e(t) is the error signal.**
account the other frequency components in our locking chain, such as AOFS RF frequency $f_{AOFS}$, equation (2.25) could be rewritten to reference the EC-QCL optical frequency ($v_{QCL}$) as:

$$v_{QCL} = nf_{rep} + f_{AOFS} \pm f_{beat}$$

(3.1)

where the ± sign is referring to the sign of our locking servo loop. It is worth noticing that with our approach, both SFG and SC combs have the same contribution of $f_{CEO}$ which cancel out in the generated beat signal. That is an advantage to our approach as it saves the effort to stabilize the carrier envelope offset and remove the ambiguity of its determination.

### 3.2.2 Experimental setup

The layout of the experimental setup is illustrated in Figure 3.2. The near-IR frequency comb is based on an amplified Tm-fiber oscillator at 100 MHz delivering up

to 1.5 W at 1.9 µm [21], see the red trace Figure B.3(b) for Tm-FC spectral output. The EC-QCL (from Daylight Solutions, MHF series) operates at room temperature and provides single-mode emission in the range of 7.55-8.2 µm with output power up to 50 mW after optical isolation. The SF-comb is generated by collinearly combined [65] part of the Tm output (100 mW) and of the EC-QCL (16 mW) and focused by an off-axis parabolic mirror into an 8 mm long ZGP crystal. The new generated comb will be at ~ 1.54 µm. The frequency of the SF-comb is offset from the original comb by the EC-QCL frequency. By heterodyning the SF-comb against a spectrally broadened replica of the near-IR comb, whose spectrum is depicted in Figure B.3(b), a radio-frequency (RF) beat-note $f_{\text{beat}}$ is detected and then steadily locked to a local RF oscillator.

Two locking schemes have been implemented and tested for the 7.8 µm laser. A first scheme makes use of only one servo loop, providing feedback to the EC-QCL piezo modulation port. Due to a bandwidth limit of 100 Hz, it was not possible by this approach to go beyond frequency locking, essentially compensating for the laser frequency drift.

In a second scheme, to achieve a faster frequency correction and to explore the feasibility of phase locking, we added a second servo loop acting on an acousto-optic frequency shifter (AOFS). We recurred to external frequency actuation rather than to the laser current control because for our laser the current tuning was high-passed at 10 kHz by the manufacturer, thus inhibiting any laser frequency control in the 100 Hz-10 kHz range. As shown in Figure 3.2, the SFG branch of the setup is aligned to the beam diffracted by the AOFS. This was arranged in a double-pass configuration to
benefit from doubled frequency shifts while suppressing misalignments due to the changing diffraction angle.

### 3.2.3 Results and discussions

The obtained beat-note spectrum reflects the EC-QCL linewidth, and hence it could be radially estimated. In a free-running regime, the acquired beat-note with a sweep time of six ms at a 50 kHz resolution bandwidth of the EC-QCL is displayed in Figure 3.3(a). It can be noticed that the EC-QCL frequency experiences a jitter of about 20 MHz at the ms timescale which is comparable with the value reported by the Newbury group in the unique frequency characterization of an EC-QCL present in the literature [66]. The satisfactorily high signal-to-noise ratio (SNR) of more than 30 dB derives from an efficient nonlinear interaction in ZGP, which leads to an SF-comb power of $\sim 80$ nW, and from the use of balanced detection, which gives a reduced intensity noise floor and a 3 dB higher SNR as compared to direct detection. [Figure 3.3(b)] reports the averaged profiles of the beat-note under slow (blue) and fast (red) locking.

In the slow case, where the servo loop actively control the PZT driver of the EC-QCL, the lock compensates for the frequency drifts of the laser and maintains its average frequency at a predetermined offset from the comb mode pattern. On the other hand, it is not able to provide an appreciable line narrowing since the laser is affected by large frequency excursions beyond 100 Hz, thus beyond the available control bandwidth. This leads to an effective linewidth of about 21 MHz, slightly worse than the 15 MHz value observed in [66] for a 4.5 µm EC-QCL.

The addition of a second faster feedback loop, through an external actuator which is AOFS, a better compensates for the laser frequency jitter and narrows the emission
line down to 2.5 MHz [Figure 3.3(b)], which corresponds to an improvement by a factor of 8 in the available spectral resolution, once the laser is applied to spectroscopy.

The electrical spectra of the error signal reported in Figure 3.3(c) for the free-running and locking regimes show that the second loop provides an efficient noise suppression up to about 30 kHz. Extending further the control bandwidth resulted in an unstable behavior due to the rather high 1.6 \( \mu \text{s} \) delay introduced by the AOFS, which is responsible for the servo-bump at 100 kHz and for the excess noise beyond it. Over a measurement time of 100 ms, the counted beat-note suffers from an rms fluctuation of 100 kHz and 35 kHz for the slow and fast lock, respectively.
The higher frequency stability and spectral resolution afforded by the fast locking were found to be traded off by a severely degraded intensity noise. The oscilloscope traces reported in Figure 3.3(d) show that the intensity drops by more than 50%. These oscillations emerge because the frequency jitter of the laser forces the AOFS to work outside its modulation bandwidth, i.e., at frequencies where its diffraction efficiency is degraded. This is better quantified in Figure 3.3(b) by the comparison between the beat-note spectrum (blue curve) and the diffraction response of the AOFS (dashed grey curve), which have comparable widths. It is worth noting that the

Figure 3.3: Color code: green (free running), blue (slow locking), red (fast locking). (a) Beat note signal spectrum acquired with a sweep time of 6 ms at a 50 kHz resolution bandwidth, showing a nearly 20 MHz large laser jittering window at a ms time scale. (b) Averaged electrical spectrum of the beat note signal under slow and fast locking, as compared to the diffraction efficiency response of the AOFS (grey dashed dotted line). (c) Power spectral density of the error signal. (d) Scope traces of the laser intensity in locking condition.
intensity noise deriving from such an issue also impacts the quality of the feedback locking loop and could not be trivially solved by adoption of a faster AOFS.

3.3 Absolute frequency measurements of Nitrous oxide (N₂O) in MIR

3.1.1 Scanning strategies

To benefit from a constant power level, spectroscopy measurements were performed with the 7.8 μm EC-QCL locked to the comb using only the PZT as an actuator (Figure 3.3 (d) blue trace) in the slow locking condition. The acquisition has been performed using two different frequency scanning strategies. The first one exploits the application of a step-wise modulation to the EC-QCL piezo, forcing the laser frequency to jump from one comb mode to the next one, which implies unlocking and relocking at every spectral step. The procedure is robust due to the capture range of more than 20 MHz afforded by the large laser linewidth, which could easily accommodate piezo nonlinearities. The voltage/frequency steps result in an evenly spaced frequency axis with spectral points at every \( f_{\text{rep}} \) (100 MHz in our case). This approach can be applied for spectral scans up to 0.9 cm\(^{-1}\), which is the limit given by the piezo. However, this methodology can be easily extended to tens of wavenumbers with a remote control system that takes charge of driving both piezo and rotation stage of the grating in the extended cavity of the laser. To achieve a denser sampling of narrow spectral features, we tested both an interleaving of spectra acquired with
different comb repetition rates and, as a second frequency scanning strategy, the
tuning of the rep-rate while keeping a steady lock between the EC-QCL and the comb.

Figure 3.4: (a) Absorption spectrum at 298 K of an 85% air-diluted N₂O sample at a pressure of 0.25 mbar near 1269 cm⁻¹, with a comb-defined frequency axis. Inset: zoomed-in view of the P(25) doublet, with interleaved spectra for a denser spectral sampling. (b) Absorption spectrum of the P(18) line of N₂O with a 0.07% dilution at 131 mbar with a 100-MHz frequency grid (bottom panel) and residuals from a Voigt fitting (top panel). (c) Absorption spectrum of the same line in a pure sample at 0.013 mbar (bottom panel), and residuals from a Gaussian fitting (top panel). The spectrum is in this case acquired by a 4 Hz stepping of the comb repetition rate frequency (1.5 MHz spaced optical frequency grid). In the figure, χ is the diluted factor.

Figure 3.4(a) reports an example of absorption spectrum near 1269 cm⁻¹ of an 85%-air-diluted N₂O sample housed in a 66 cm long optical cell at a pressure of 0.25 mbar. The spectrum extends over 0.6 cm⁻¹ and presents 12.5 MHz-spaced points due to the interleaving of eight scans acquired at slightly detuned repetition frequencies (by ~30 Hz). The inset provides a zoomed-in view of the P(25) doublet and better highlights repeatability and absolute positioning of spectral points.
3.1.2 Results and Discussions

Quantitative analysis has been performed for the spectra reported in Figure 3.4(b) and Figure 3.4(c), both referring to the P(18) N₂O line of the 1000→000 band. The notation for the band transitions are $\nu_1\nu_2\nu_3$ where $\nu_i$ is the vibrational quantum number associated with the vibrational mode, and $l$ is the angular quantum number. The transition understudy is referred to the $\nu_1$ fundamental band. In the first case, thanks to a 0.07%-diluted sample at a relatively high pressure of 130 mbar, a 100-MHz sampling is sufficiently dense to reproduce the spectral shape and enable a reliable fitting with a Voigt profile. On a statistical ensemble of 100 acquisitions, the fitting provides an rms deviation of 500 kHz for the line-center frequency, which is equivalent to 7 parts over $10^4$ with respect to a 750 MHz linewidth. The uncertainty primarily reflects the SNR of the measurement, which amounts to ~1000 for the single spectrum. Apart from the interference of a weak neighboring line and from the presence of etalon effects at the $10^{-3}$ level, the residuals from the fitting do not show, at such a level of SNR, any appreciable departure from the Voigt profile. A more stringent test on precision [Figure 3.4(c)] was obtained on the same line at a pressure of 0.013 mbar, i.e. in conditions where the collisional broadening is negligible and the absorption linewidth is Doppler dominated to an estimated value of 70.5 MHz. A 1.5 MHz spectral sampling is ensured by a 4 Hz stepping of the comb rep-rate. This occurs at every 100 ms so that a 540 MHz large spectrum is acquired in 36 s.

The statistical uncertainty on the line-center frequency was inferred by repeating several times the measurement of the same absorption spectrum; the line-centers retrieved from the fitting of those spectra are described by a Gaussian distribution.
with a rms deviation of 47 kHz, which implies that when 10 spectra are averaged together (as it is shown in Figure 3.4(c), the resulting statistical uncertainty can be safely estimated at the 15 kHz level. Despite the relatively fast scanning speed of the rep-rate, no appreciable bias from the frequency comb rep-rate scanning direction was found. The averaged residuals of 10 consecutive spectra fitted with a Gaussian profile Figure 3.4(c) reveal an SNR of 900. Apart from small etalons whose contribution is below the $10^{-3}$ level, the residuals are almost flat within the SNR of the measurement. In terms of systematic uncertainty, several sources have been identified and quantified.

The stability of the Global-Positioning-System-based frequency standard (5 parts over $10^{12}$ at 36 s), which serves as a reference for the comb and the frequency offset between the comb and EC-QCL as well, translates into a frequency error of $\sim 0.5$ kHz. The uncertainty of the absolute pressure gauge used in the experiments (10% at the pressure of 0.013 mbar) provides a contribution of less than 0.5 kHz. The cell leakage, of the order of 0.0065 mbar/h, gives a sub-kHz impact over a typical measurement time of 6 minutes corresponding to an averaging of 10 spectra. The extrapolation of line-center frequencies to zero pressure through the air pressure shift coefficients instead of self-pressure shift coefficients [67] does not impact the accuracy by more than two kHz at the very low pressure adopted herein.

Baseline distortions occurring due to etalons and laser power drifts have been found to give a higher contribution, up to 10 kHz at the edges of the tuning range, but the major systematic limitation derives from an asymmetrical jittering of the laser around the local oscillator frequency, which leads to a beat-note barycentre slightly
detuned from the local oscillator, see Figure 3.4(b). Such detuning has been accounted for by registering the laser lineshape, as well as its absolute position from the nearest comb mode, through the electrical spectrum of the beat-note between the EC-QCL and the comb during the spectral scans, then deconvolving each absorption profile by the beat-note itself.

As the beat-note could be measured with a very high SNR (>10⁴) over the six minutes-long measurement time, the remaining uncertainty relates to the calibration of the frequency responses of the detector and of the RF filters and amplifiers used to detect the beat-note itself. This has been estimated at a level of 60 kHz by comparing the center of the same absorption line measured under different conditions, either reversing the sign of the lock or changing the local oscillator frequency. It is worth noting that the impact of an asymmetric jittering behavior is not appreciable from the residuals [Figure 3.4(c)].

The total systematic (Type B) uncertainty amounts to about 61 kHz and gives rise to an overall uncertainty of 63 kHz by quadrature addition with a statistical (Type A) contribution of 15 kHz (10 averaged spectra). The resulting line center-frequency of

![Graph](image_url)

*Figure 3.5: N₂O spectroscopy at 0.013 mbar over 65 cm⁻¹. Green line: P(40), 374.35005.26(10) MHz; blue line: P(18), 380.52238.584(63) MHz; red line: R(31), 392.68217.812(78) MHz.*
the \( P(18) \) line is 38052238584(63) kHz; the HITRAN value for the line-center frequency is only 2.7 MHz above our determination while the HITRAN value has a relatively large nominal uncertainty range of 3-30 MHz. The Doppler width retrieved from spectral fitting is equal to 73.9 MHz, thus 2.4 MHz higher than the expected value, but this precisely reflects the instrumental broadening (21 MHz) of our laser, once the typical quadrature addition law for Gaussian widths is applied.

The spectrometer is able to fully exploit the emission range of the EC-QCL, which extends over more than 100 cm\(^{-1}\). A demonstration of such large tunability is given in Figure 3.5, which reports spectroscopy of lines in the P and R branches of \( \text{N}_2\text{O} \), namely \( P(40) \) and \( R(31) \), lies 65 cm\(^{-1}\) far apart.

The lines have been measured by a remote control system that allows the uploading of the desired line list from HITRAN, the tuning of the EC-QCL to the target frequencies by an active loop fed by the reading of a wavemeter, the locking of the laser to the comb, the scanning of the comb rep-rate and the absorption line acquisition, finally the laser unlocking and the tuning to the next line frequency. More details on the fully automated system will be discussed in the next chapter, as well as application of this spectrometer in a widely tunable line survey of \( \text{N}_2\text{O} \).
Chapter Four: Highly accurate frequency measurements of N$_2$O laser transitions around 7.8 μm
The ν₁ fundamental band of nitrous oxide (N₂O) is addressed by a novel spectrometer that relies on the frequency locking of an extended-cavity quantum cascade laser around 7.8 μm to a near-infrared Tm:based frequency comb at 1.9 μm. Thanks to the large tunability of our probe laser, nearly 70 lines in the 1240-1310 cm⁻¹ range of the ν₁ band of N₂O, from P(40) to R(31), are measured with an absolute frequency calibration and an estimated systematic uncertainty of 60 kHz. Accurate values of the spectroscopic constants of the upper state are derived from a fit of the line centers (rms≈ 4.8×10⁻⁶ cm⁻¹ or 144 kHz). The ν₁ transitions presently measured in a Doppler regime validate high accuracy predictions based on sub-Doppler measurements of the ν₃ and (ν₃-ν₁) transitions.

Thanks to the availability, at a certain point of the thesis, an upgraded EC-QCL with a significant improved free running linewidth, from 21 to 1.7 MH, we managed to apply the spectrometer in sub-Doppler regime. We could resolve the Lamb dip associated to the R(16) line of N₂O and extracted the line center with higher accuracy without the need for deconvolving the measured absorption line with the laser line profile.
4.1 Introduction

OFCs have seldom been applied to a broad line survey to extract spectroscopic parameters of molecular absorption bands. In the near-infrared (NIR), extended measurements have been performed only on a few bands of acetylene (C$_2$H$_2$), ammonia (NH$_3$) and water (H$_2$O) in a sub-Doppler regime [5,6,22,23,53] and of carbon monoxide (CO), carbon dioxide (CO$_2$) and H$_2$O in a Doppler broadening regime [54,55,68–70], quite often in conjunction with optical cavities to extend the effective absorption path length (as well as to enhance the laser intensity in saturated surveys). In the mid-IR, surveys over more than 50 cm$^{-1}$ have been provided for the $\nu_3$ band of N$_2$O [24] and of CH$_4$ [64,71], as well as for CO$_2$ near 4.3 and 2.7 μm [72]. A technological hurdle here originating from the lack of commercial mid-IR comb synthesizers and hence from the need to resort to nonlinear optics to get referencing of a mid-IR probe laser to a NIR comb [26,56–61,73]. A second nontrivial requirement is a widely tunable single-mode laser, most of all beyond 5 μm, where cw sources based on difference-frequency-generation or optical parametric oscillation are not available. DFB-QCLs are an option only for rather narrow ranges of about 10 cm$^{-1}$ [63], whereas for ranges of ~100 cm$^{-1}$, which is typical range to cover an entire absorption band, the only solution available commercially is given by EC-QCLs. Their use in combination with frequency combs has been firstly demonstrated in an
unlocked regime, with an accuracy of 800 kHz [7], and only recently in a comb-locked regime with an accuracy of 60 kHz [74] as demonstrated in Chapter Three.

![Figure 4.1: Nitrous oxide (N₂O) bands and their corresponding transitions. In red, the target band in this work ν₁ fundamental band. “*” refer to the fundamental transitions.](image)

In this chapter we describe the spectroscopic measurements of 70 lines from ν₁ fundamental band of N₂O exploiting the spectrometer configuration reported in the previous chapter. N₂O is one of the most important greenhouse gases that is emitted during industrial processes, such as fuel combustion or solid waste, agriculture and even in wastewater treatments. With a lifetime of 110 year, N₂O impact is not only limited to the global warming, as it is occupied six percentage of the other greenhouse in the air, but also it is a main cause of Ozone depletion that decomposes to N₂. Which make a target for our case study to prove the concept of our highly precise developed spectrometer in MIR. N₂O shows quite strong line strength in the MIR as it can be appreciated from Figure 4.1 which shows that N₂O has three fundamental bands: 589, 1285, and at 2224 cm⁻¹. In particular the ν₁ fundamental band that related to the transition 00⁰0-10⁰0, lays in the 7.6 μm (1285 cm⁻¹) region matching the emission range of the EC-QCL with the line strength of the order of 10⁻²⁰. The possibility to improve the precision of the spectrometer are then investigated arranging the
experimental setup to perform spectroscopic measurement in sub-Doppler condition.

In the following sections, we are starting with the Doppler-limited experimental approach followed by the line position analysis for the measured lines in direct absorption spectroscopy (DAS). Moreover, Doppler-free saturation measurements of the R(16) line from the same band of N$_2$O are reviewed to show a potential improvement of widely tunable high precision spectrometer in the saturation regime.

**4.2 High accuracy line central frequency of N$_2$O**

The spectrometer proposed in Chapter Three, [74], is applied to the first experimental line center determination of the ν$_1$ fundamental band of $^{14}$N$_2^{16}$O in the 1240-1310 cm$^{-1}$ range. The measured positions are used to derive spectroscopic parameters of the upper state. Specifically, nearly 70 lines among the P and R branches have been measured with a systematic uncertainty of 60 kHz and a statistical uncertainty varying from 10 to 170 kHz depending on the line. It is worth noting that the impact of the statistical uncertainty on the spectroscopic parameters is strongly reduced by the averaging effect that takes place when all lines are considered in a global fitting procedure, this being one of the major strengths of the broadband comb-calibrated approach described herein.

**4.2.1. Experimental approach and results**

The spectrometer is described in detail in Chapter Three. The layout of the spectrometer is reported in Figure 4.2 Recalling the referencing schemes that was
used in previous chapter which relies on the generated beat-note ($f_{\text{beat}}$) between SF-comb and SC-comb which has the information of EC-QCL. The stabilization of $f_{\text{beat}}$ against an RF local oscillator ($f_{\text{LO}}$) is obtained by driving the EC-QCL piezo modulation port with a servo PID controller; resulting in $f_{\text{beat}} = f_{\text{LO}}$. The scanning procedure also was done through the OFC repetition rate while maintaining a steady frequency lock of the EC-QCL against the comb itself. By that one can finely tune the EC-QCL over ~600 MHz maximum without losing the locking to the comb. The absolute frequency calibration derives from the fact that all radio frequencies, namely $f_{\text{rep}}$ and $f_{\text{LO}}$, and hence all optical frequencies are referenced to a primary clock based on a GPS-disciplined Rb oscillator. As compared to the setup described in Chapter Three, stabilization of the laser intensity was added to compensate for the laser fluctuations during the spectral scans and thus to achieve a flatter baseline. This was obtained by
introducing an AOM in the beam path and by actively controlling its input RF power in such a way as to keep the diffracted field power stable around a 0.5 mW set-point. Adding the AOM will influence the calibration equation (2.29), where its RF frequency has to be taken into account in the calibration of optical frequency of EC-QCL by adding 50 MHz to the calibration equation. A photodetector placed upstream the optical cell serves as a monitor for the intensity stabilization feedback loop.

We fully exploit the wide tunability of the EC-QCL to cover 70 absorption lines of nitrous oxide spanning the 1240 – 1310 cm\(^{-1}\) range.

![Figure 4.3: Schematic diagram to illustrate the developed fully automated system for comb-assisted N\(_2\)O spectroscopy. The EC-QCL frequency is tuned by rotating its grating motor, on the basis of the list of N\(_2\)O center frequencies uploaded from HITRAN data base. The beat-note (BN) electrical spectrum is recorded during comb repetition rate (RR) scanning over absorption line, followed by barycenter (BC) calculation to evaluate BN frequency. The last step in the acquisition, is saving the required experimental data for post processing.](image)

The measurements are performed by a fully automated real-time acquisition system, see Figure 4.3. The acquisition program has several stages that occur in consecutive or parallel way as needed. It start with reading the EC-QCL frequency out of a wavemeter (WM) that has uncertainty of ~ 5MHz. Then a signal send from the
acquisition board (c-RIO from national instrument 24-bit with 50 kSample/sec) to EC-QCL controller to tune its frequency to the target absorption line. The list of the fundamental $\nu_1$ band of N$_2$O was uploaded and saved in the program from HITRAN database, for acquiring each line, the EC-QCL frequency was tuned to the target line through the grating motor of it. During the tuning of EC-QCL, the frequency locking switched off by a TTL signal that is sent to the PID of the frequency locking servo loop. Then re-lock the EC-QCL to the frequency comb, and steps the comb repetition rate by 4 Hz (1.5 MHz in the optical domain) to scan over and acquire the target absorption line, then switched off the lock, then again tunes the laser frequency to the next line from the preliminarily uploaded line list from HITRAN database. To maintain locking condition and avoid the jump of the locked laser between OFC frequency components, as well as maintaining the lock of OFC repetition rate, the scanning step was kept with the stability of the OFC rep rate stabilizing servo loops. Typically, a 540 MHz-wide spectrum consists of 360 evenly spaced points acquired with a dwell time of 100 ms. For x-axis calibration, the beat-note was averaged and recorded from electrical spectrum analyzer (ESA) during absorption line recording. Then it was processed to retrieve the barycenter and estimate its frequency. The last stage of the program was saving the acquired data, transmission spectrum and the corresponding beat-note for each line in a systematic and consecutive way for keeping track of the information of each line, then the post processing was perform offline.
An overview of the measurements of the $v_1$ band of N$_2$O is presented in Figure 4.4(a). The absorption spectra cover most parts of the $P$ and $R$ lines up to $J = 40$ and $J = 31$, respectively. Each line results from the average of 10 spectra and the total acquisition takes around six minutes. To maintain an almost uniform signal-to-noise ratio for lines with different strengths, the acquisition has been split into different separated runs at slightly different pressures, from 0.01 to 0.04 mbar (1 – 4 Pa). For representation purposes, the experimental absorbance values have been normalized in Figure 4.4 to the same pressure condition of 0.018 mbar.

![Absorption spectrum](image)

**Figure 4.4:** (a) Absorption spectrum of the $v_1$ band of N$_2$O at room temperature and at a 0.018 mbar pressure. (b) zoomed-in view of the $P(3)$ line together with residuals from a Gaussian fitting

In such a low-pressure regime absorption profiles are almost exclusively determined by Doppler broadening allowing us to fit the measured spectra with a simple Gaussian profile. As a representative case, Figure 4.4(b) reports a zoomed-in view of a 10-times averaged spectrum of the $P(3)$ line together with the residuals obtained from the fitting. The quality of the intensity stabilization is such that a linear contribution in the fit is enough to get rid of the most part of the baseline distortion as you can notice from Figure 4.4(c) where only very small residuals, at the level of
10^{-4}, due to some residual parasitic etalon are present. Thus the signal-to-noise ratio is considerably high reaching up to 890.

The overall uncertainty is estimated as follows: the statistical uncertainty (Type A error calculated as the standard deviation of the mean) of the line centers varies, depending on the line, from 10 kHz to 170 kHz. These numbers reflect the noise level on the vertical axis of the measurement, some nonlinearity of the spectral baseline and also the stability of the laser frequency.

The sources of systematic uncertainty (Type B error) are quantified and detailed in Table 4.1. Minor contributions come from the stability of the GPS frequency standard (~ 0.5 kHz over a 6 minute long measurement), from the uncertainty of the absolute pressure gauge used in the experiments (10 %) and from the cell leakage (0.0065 mbar/h); the latter two terms, as weighted by pressure shift coefficients of the order of -26 kHz/mbar, contribute to an uncertainty of about 1 kHz. Those coefficients have been taken from HITRAN [75], and refer to an air mixture instead of a pure sample, but as the pressure adopted herein is very low, this does not affect the accuracy budget by more than 2 kHz. The major systematic limitation is ascribed to an asymmetric shape of the laser emission, as described in Chapter Three, which we accounted for by recording, during each spectral scan, the electrical spectrum of the beat-note between the laser and comb, then by deconvolving every absorption profile by the laser emission line. In the error budget table Table 4.1, the 60 kHz uncertainty assigned to the laser line shape corresponds to the rms value of a distribution of line centers (of a single transition) acquired in different experimental locking conditions: either reversing the sign of the frequency lock or changing the local oscillator
frequency. The quadrature addition of Type A and Type B errors returns global uncertainty ranging from 62 to 180 kHz depending on the line. The ν1 line positions with their corresponding experimental errors are listed in Table 4.2 in the appendix.

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Type A (kHz)</th>
<th>Type B (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental reproducibility</td>
<td>10 – 170 kHz</td>
<td></td>
</tr>
<tr>
<td>Frequency scale uncertainty</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Pressure reading &amp; leakage</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Pressure shift calibration</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Laser lineshape asymmetry</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Total uncertainty</td>
<td>62 – 180 kHz</td>
<td></td>
</tr>
</tbody>
</table>

*Table 4.1: Uncertainty budget for the individual line center*

### 4.2.2. Line Position Analysis

#### I. Spectroscopic Parameters

The set of measured transition frequencies was used to derive the parameters of the 1000 upper vibrational state through the standard expression for ro-vibrational energy levels:

\[
F_v(J) = G_v + B_vJ(J+1) - D_v J^2 (J+1)^2 + H_v J^3 (J+1)^3 + L_v J^4 (J+1)^4
\]  

(4.1)

where \( G_v \) is the vibrational term value, \( B_v \) is the rotational constant, \( D_v, H_v \) and \( L_v \) are centrifugal distortion constants, and \( J \) is the angular momentum quantum number.

The ground state (GS) constants were constrained to the accurate values reported by Ting et al. [24]. These GS constants were obtained from a global fit involving different
sets of highly accurate measurements including fourteen line center values of GS rotational transitions with accuracy better than 1 kHz. Here, after excluding six weak $P(J)$ lines with $J$ values between 29 and 43 measured with lower accuracy, an $rms$ deviation of $4.8 \times 10^{-6}$ cm$^{-1}$ (144 kHz) is achieved for 66 line positions covering the $P(40) - R(31)$ range. This $rms$ value is consistent with the error budget described in Table 4.1. The obtained spectroscopic constants are listed in Table 4.3 together with the GS constants of [24] in the appendix.

Differences of measured and calculated line positions are displayed in Figure 4.5 and listed in Table 4.2 together with the corresponding calculated GS energy levels and $v_1$ line position values for all transitions up to $J_{up}=45$. 


II. Comparison to Literature

The HITRAN2016 database [75] reproduces the $v_1$ line positions calculated using the spectroscopic parameters (SP) given by Toth on his website [76] (see Table 4.3). By using long absorption path lengths (up to 70 m), Toth could detect high J rotational lines up to P(86) and R(89) which are listed in [76]. Toth’s line list, as reproduced in HITRAN, covers the P(87) – R(87) range of transitions. $H_v$ and $L_v$ distortion terms were needed to reproduce the measured dataset. In Ref. [76], Toth did not provide line position uncertainties or error bars on his band parameters. The deviations of HITRAN values to our fitted values are plotted in Figure 4.5 together with the deviations of Toth’s original measurements [76]. Compared to HITRAN, deviations up to $6 \times 10^{-5} \text{ cm}^{-1}$ (1.8 MHz) are observed in the range of our observations. These values

![Figure 4.5: Deviations from the fitted position values of the $v_1$ fundamental band of $^{14}$N$_2$:$^{16}$O of: the experimental values measured in this work (full blue circles; open circles correspond to transitions excluded from the fit), the HITRAN2016 values [1] (full black circles) and the original measurements by Toth [76] (grey squares).]
are fully consistent with the uniform HITRAN error bar (<10^{-3} \text{ cm}^{-1}) attached to the \nu_1 line positions.

An exhaustive literature review of the $^{14}\text{N}_2^{16}\text{O}$ line position measurements from 0 to 10000 cm$^{-1}$ can be found in [77], which includes estimated values for the precision of each experimental source. According to this review, a number of studies have reported positions of pure $R(J)$ rotational lines with an accuracy of ~ tens of kHz in both the ground [78–81] and $10^{00}$ excited states [78,79,82,83]. The $10^{00}$ upper state of the $\nu_1$ band is also involved in sub-Doppler frequency measurements of the ($\nu_3-\nu_1$) band near 9 µm performed by Tachikawa et al. [69] by using a heterodyne difference frequency technique with fluorescence-stabilized CO$_2$ lasers. The ($\nu_3-\nu_1$) transition frequencies of the $P(38)-R(18)$ lines were reported with an accuracy better than 5 kHz for most of the lines. The authors combined their results with literature measurements (including Toth's measurements) to derive effective spectroscopic parameters (SP) for the $10^{00}$, $00^{01}$, $02^{00}$ and $02^{20}$ states. The derived SPs of the $10^{00}$ state considered as an isolated state (as in our analysis) are included in Table 4.3. The most significant difference concerns the vibrational term which was reported with a 107 kHz and 750 kHz relative and absolute 1\sigma uncertainty, respectively [69]. Our vibrational term value obtained from the direct measurement of the $\nu_1$ band transitions is determined with a 36 kHz and 100 kHz relative and absolute uncertainty and differs by about 920 kHz compared to Ref. [69].

As mentioned above, the results recently reported by Ting et al. [24] in the sub-Doppler regime have supplanted most of the previous studies in terms of accuracy of rotational transitions in N$_2$O. By locking their synthesizer to a cesium clock, they
determined the frequency of 175 pure rotational transitions within five vibrational states (including the $10^00$ state). Overall, 33 values with sub-Doppler precision (0.5 – 3 kHz) and 142 with Doppler-limited precision were reported. In addition, using a difference frequency generation (DFG) source calibrated by an OFC, Ting et al. determined 44 saturated absorption line centers of the $v_3$ band near 2223 cm$^{-1}$, with an accuracy better than 10 kHz for most transitions [24]. Using their sets of microwave and infrared data with $J$ up to 100 and combined with literature precision measurements (in particular those by Tachikawa et al. [69]), Ting et al. developed an effective Hamiltonian (EH) model to reproduce the transition frequencies involving the $00^00$, $01^10$, $10^00$, $00^01$, $02^00$ and $02^{\pm20}$ interacting states. An overall ensemble of 860 selected transitions was used to fit the model parameters and predictions were obtained for the pure rotational band and for the fundamental bands, including the $v_1$ band of present interest. The combination of the $v_3$ measurements by Ting et al. with those of Tachikawa et al. for the ($v_3$-$v_1$) band, both with accuracy at the kHz level, allows for very accurate predictions of the frequency of the $v_1$ transitions. The resulting calculated line list was not provided in the supplemental material [24] but can be found in the JPL spectral line catalog [84]. In the range of our measurements, the $v_1$ band predicted frequencies are provided with a typical accuracy of 3 kHz. The average and $rms$ of the differences between the position values computed from our $v_1$ band spectroscopic parameters and those predicted in [24] are -72 and 54 kHz, respectively, then fully consistent with our claimed error bars [Table 4.1].
4.3 Sub-Doppler comb assisted molecular spectroscopy

We improve the precision characteristics of spectrometer used for the extensive line center determination of $v_1$ band of N$_2$O arranging it in order to perform Doppler-free saturation spectroscopy. The spectrometer performance is then evaluated measuring R16e line from the same band of N$_2$O. Repeated acquisition of the absorption line shows a statistical uncertainty on the single measurement below 5 kHz in the retrieval of the center frequency and an overall uncertainty at the 50 kHz level when compared with independent measurements at two different metrological institutes.

4.3.1. Experimental setup

The modified spectrometer configuration to perform sub-Doppler molecular spectroscopy is displayed in Figure 4.6. There are two main differences with respect to the Doppler configuration. The first one is related to the probe source, which is in

![Figure 4.6: Experimental Setup for Saturation spectroscopy.](image)
this experiment an improved generation of the EC-QCL from Daylight Solution used above. The probe laser tunability range covers 1250-1380 cm\(^{-1}\) with average power over tunability range of 120 mW. The improvements in-comparison with the previous EC-QCL is represented by a narrower free-running as demonstrated in the measurements described below. Moreover, an important improvement in this laser which gave as a continuum access to both PZT and current modulation controllers bandwidth. As the current controller is not high pass at 10 kHz like previous one. Where gap between the two controllers bandwidth that exist in previous used EC-QCL, prevented us from having full control on the laser jittering and drifting using current modulator. Differently, in the new laser we managed to shrink the laser linewidth for precision spectroscopy in a sub-Doppler regime.

The second difference is the position of the AOFS that is placed immediately after the OI. The zeroth order of diffraction is used for SFG generation and frequency locking in a similar way as in the previous section. The detected beat-note is then stabilized against a RF reference. Since the new generation of EC-QCL can rely on two actuators with complementary control bandwidth the first actuator was applied on the PZT driver of the EC-QCL laser limited to the PZT bandwidth of 100 Hz. The fast servo loop, in parallel with the slow one, was applied to the current controller within the current bandwidth of 20 kHz. The first order of diffraction is then collimated and sent to cross the same cell used in previous scheme in a double pass configuration. At the cell output, the beam is back-reflected along the same optical path to monitor out the saturation imprinted by the incoming pump beam. A lens with a long focal length (1 m) helps in compensating the natural divergence of the laser due to diffraction
while guaranteeing a good spatial overlap between the two beams. Then the spectroscopic signal is collected by a liquid nitrogen-cooled MCT detector.

The AOM serves two purposes. First, it reduces the laser instabilities that arise because of optical feedback from the counter-propagating geometry imposed by the saturated absorption measurements along with the optical isolator (OI) implemented before AOM. Second, in combination with an implemented servo loop, it is used to stabilize laser intensity fluctuation that might affect the absorption baseline. The intensity fluctuation was adjusted through the RF driver of the AOM. The intensity stabilization loop is performed with the assistance of a photodetector, which monitors a reflected power before the gas cell, and PID controller for intensity feedback stabilization loop To characterize the frequency noise of the EC-QCL we measured the electrical spectrum of the beat-note signal between the EC-QCL in free-running conditions and the comb with a measurement time of 1 ms, i.e. before the onset of evident laser drifts. As the comb modes are stable and narrow (below 100 kHz linewidth), this spectrum mimics the EC-QCL emission line. The beat-note shown in Figure 4.8(a) (blue line) exhibits a nearly Gaussian profile due to a prevailing $1/f$ noise contribution, with a full width at half maximum as narrow as 1.7 MHz. Using two servo loops, the first providing feedback to the EC-QCL piezo till tens of Hz, the second acting on the EC-QCL current above 100 Hz, we managed to lock the EC-QCL to the comb. The beat-note spectrum modifies according to the red line in Figure
4.8(a), with the appearance of a coherent peak. This is the signatures of a robust locking but not yet of a phase locking because of the small contrast of the peak.

To have a deeper insight into the laser noise under free-running and locked conditions, we exploited the edge of an intense N\textsubscript{2}O absorption line as a frequency discriminator to infer the frequency noise power spectral density of the laser. One of the techniques used to measure lasers frequency noise and convert the laser optical frequency fluctuations into intensity fluctuations is a frequency discriminator [85]. In the frequency discriminator, the transmission, or reflection) has frequency dependence such as molecular transition in gas absorption or a resonance of optical cavity. In our case we are using an absorption gas cell of N\textsubscript{2}O to measure the EC-QCL frequency noise. The laser frequency is tuned to the side of the transmission line to a linear region to linearly convert the frequency fluctuations to an amplitude fluctuation that is measured with a photodiode. A low pressure for such measurement is required to get very narrow linewidth and subsequently high conversion factor of frequency noise into intensity noise. This conversion factor, also known as discriminator slope, must be high for the reason that, the frequency contribution noise is overcome the laser intensity noise that in return impact the photo detector signal. Thereafter, the measured voltage fluctuation of the photodiode output signal
is measured by ESA which in return will give the frequency components of the measured signal by measuring its fast Fourier transform (FFT). Then the power spectral density (PSD) of the photodiode voltage signal is scaled by the square of the discriminator slope to convert it to the frequency noise PSD of the laser.

Figure 4.7 shows the measurement principle of the converting factor (D) from frequency modulation to amplitude modulation. The calibration of the frequency-to-amplitude conversion coefficient was readily obtained by a controlled scan of the comb repetition rate while keeping the EC-QCL locked to the comb. The measured frequency discriminator was 9.4 nV/Hz which was used to retrieved EC-QCL frequency noise PSD.

Figure 4.8(a) Electrical spectrum of the beat-note signal in free-running (inset) and locking condition. (b) Power spectral density of the laser frequency noise in the two conditions together with 1/f asymptote.

The resulting frequency noise spectrum is shown in Figure 4.8(b). In free-running conditions, the noise behavior is completely different from the one shown in Chapter Three. The old version of the used EC-QCL, as reported by [66], has frequency noise that falls off as 1/f at high frequencies and as 1/f² at low frequencies. While in the
used EC-QCL in this chapter, the noise does not show any $1/f^2$ dependence and of the $1/f$ contribution is reduced by nearly two orders of magnitude with respect to the characterization provided by Bartalini et al. [66], thus representing a significant advancement. The locking loop provides noise reduction until a frequency of 100 kHz but with a rather small depth, which explains why phase locking was not achieved. By integrating the frequency noise spectrum down to 100 Hz we infer an EC-QCL linewidth of 1.7 MHz and 690 kHz in free-running and locking conditions, respectively, thus in good agreement with the beat-note spectra measured at a 10 ms observation time. These values are almost one decade above the comb mode limit [65] and constitute the first demonstration of an EC-QCL suitable for measurements with sub-MHz spectral resolution.
4.3.2. Sub-Doppler spectroscopic results

We applied the comb-locked laser source to the sub-Doppler study of the R16 line in the ν₁ band of N₂O. Figure 4.9 shows the Doppler spectra acquired at different pressures by tuning the rep rate of the comb over 880 Hz with steps of one Hz, corresponding to spectral points separated by 380 kHz. The Lamb dips are clearly evident even with such coarse spacing, with a contrast that reaches 20 % compared with the linear absorption.

Further fine acquisitions were performed over the dip with smaller scanning step size and an average of four consecutive spectra over a measurement time of about one minute, at different pressures and at different power levels. An example of those dips, at a pressure of 10 mTorr (0.0133 mbar), is highlighted in Figure 4.9(b).

![Figure 4.9: (a) Measured spectra of the R(16) N₂O line at a wavelength of 7.70055 µm at different pressures (Inset) Zoomed in view of the Lamb dip. (b) Lamb dip measured with a denser spectral grid at a pressure of 10 mTorr and at a power of 1 mW. A fitting procedure with a Voigt profile at fixed Lorentzian collisional contribution returns a total linewidth that increases with the optical power as displayed in the inset. (c) Fit residuals reveal a distortion around 2 % and a signal-to-noise ratio in excess of 200.](image)
The solid line represents the fit with the Voigt profile with Lorentzian width fixed at 80 kHz on the basis of the expected pressure broadening [75].

The fitting returns a Gaussian width that varies from 850 to 1150 kHz depending on the optical power, as it is shown in the inset. Interestingly, the minimum width closely approaches the laser linewidth of 700 kHz previously measured. On the one hand, this is the signature of a relevant instrumental broadening given by the laser, on the other hand, this attests the feasibility, for the first time, of sub-MHz resolution with an EC-QCL.

The comparison between line centers obtained from repeated measurements of the same dip returns a statistical uncertainty of 4.5 kHz on the single measurement, is consistent with a signal to noise ratio of about 200 (for a measurement time of one minute). The retrieved line center frequency calculated as the weighted mean of the line center obtained at different power values is \( 38931326476.0(3.5) \) kHz. It is found to differ by 57 kHz from a recent measurement performed in a Doppler broadening regime with a declared uncertainty of 2.4 kHz [24]. This allows us to infer for our system accuracy of about 50 kHz.
### Table 4.2: Measured and calculated values of the line positions of the ν₁ band of 14N216O and corresponding deviations.

<table>
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<th>Calculated (cm⁻¹)</th>
<th>Meas.-Calc. (10⁻⁶cm⁻¹)</th>
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</tr>
<tr>
<td>R39</td>
<td>1315.5094670</td>
<td></td>
<td></td>
<td>653.2285561</td>
</tr>
<tr>
<td>R40</td>
<td>1316.2011033</td>
<td></td>
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<td>686.7043444</td>
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<td>R41</td>
<td>1316.8891399</td>
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<td>R42</td>
<td>1317.5735775</td>
<td></td>
<td></td>
<td>756.1594102</td>
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<tr>
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<td></td>
<td>792.1383367</td>
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<tr>
<td>R44</td>
<td>1318.9316588</td>
<td></td>
<td></td>
<td>828.9512843</td>
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</table>

*a Values with an asterisk (*) were excluded from the fit.

b The ground state energy levels given in the last column were calculated using the parameters values reported by Ting et al. [24].
The uncertainties (1σ) are given in parentheses in the unit of the last quoted digit.

The absolute (1σ) uncertainties are 100 kHz and 750 kHz (3.3×10⁻⁶ and 2.5×10⁻⁵ cm⁻¹) for this work and Ref. [69], respectively.

- **Table 4.3**: Spectroscopic parameters (in cm⁻¹) of the ground and (1000) upper vibrational states of 14N216O derived from the ν1 line positions measured between 1248 and 1310 cm⁻¹ using a comb-locked extended-cavity quantum-cascade laser together with a comparison.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>RMS</th>
<th>Δν1×10⁻⁶</th>
<th>H ν1×10⁻⁶</th>
<th>D ν1×10⁻⁶</th>
<th>B</th>
<th>V/AIE</th>
<th>G′</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tachikawa et al. [69]</td>
<td>(p(38)-γ(18))</td>
<td>0.1164(46)</td>
<td>0.172768(13)</td>
<td>0.172750738(14)</td>
<td>0.17275073(14)</td>
<td>1284.9033624(36)</td>
<td>1284.9033344(13)</td>
</tr>
<tr>
<td><em>This work</em></td>
<td>(p(43)-γ(31))</td>
<td>0.1307(86)</td>
<td>0.172597(18)</td>
<td>0.1725547(18)</td>
<td>0.1725547(18)</td>
<td>0.176106765(20)</td>
<td>0.17269780(20)</td>
</tr>
<tr>
<td>Ting et al. [74]</td>
<td>(p(57)-γ(87))</td>
<td>0.01666</td>
<td>0.14666</td>
<td>0.016529(2400)</td>
<td>0.015547</td>
<td>1.853</td>
<td>0.308</td>
</tr>
<tr>
<td>Tach. [86]</td>
<td>(p(38)-γ(27))</td>
<td>0.1307(86)</td>
<td>0.172597(18)</td>
<td>0.1725547(18)</td>
<td>0.1725547(18)</td>
<td>0.176106765(20)</td>
<td>0.17269780(20)</td>
</tr>
<tr>
<td>Tach. [76,86]</td>
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Chapter Five: Comb-Assisted Frequency Swept Cavity Ringdown Spectroscopy (FS-CRDS)
A cavity ring down spectrometer based on an EC-QCL probe laser has been implemented with comb referencing over an extremely broad spectral window. The frequency calibration has been realized without any lock of the EC-QCL to the comb. Acquiring the running beat-note and estimating its frequency value is performed through a fast FPGA-based board through FFT real-time algorithms. Ringdown (RD) events are acquired with the same board at 100 MS/s sampling rate. Preliminary tests show an encouraging SNR at a level of 300 per spectral point per second.
5.1 Introduction

Cavity rigdown spectroscopy (CRDS) is an ultrasensitive laser absorption technique that evolved from previous accurate techniques to measure the mirrors’ reflectivity down to 100 ppm [87]. The term cavity ringdown was first introduced by Crawford [88] to refer to the decay lifetime of the intracavity light intensity for reflectance measurements. In 1988, O’keefe et. al. [89] performed the first CRDS to measure atmospheric oxygen with pulsed laser. Thereafter in 1997, Romanini et al. introduced the CW-CRDS to measure \( \text{C}_2\text{H}_2 \) absorption lines at 570 nm with a sensitivity of \( \sim 10^{-9} \text{ cm}^{-1} \)[90].

CRDS approach has several advantages in the spectroscopic field. For instance, it exhibits high sensitivity due to the enhancement of the interaction length between probe laser and the gas that could reach up to ten kilometers. Since it based on the measurement of the decay time this technique is inherently immune to the frequency and amplitude laser noise. Moreover, it gives access to the absolute absorption coefficient without the need of any cavity-length calibration.

The CW-CRDS sensing applications has benefited from the advanced and very well demonstrated developments of the CW diode lasers. Those lasers has been developed for optical communication in the NIR region where they are reinforced by versatile range of optical fibers, operating at room temperature, and a single longitudinal mode; plus those lasers are inexpensive, low power and compact sources. Hence, the CW laser sources give a full access to explore overtone- and combination band of numerous species, such as \( \text{H}_2, \text{CO}_2, \text{CO}, \text{DHO}, \text{D}_2\text{O}, \text{H}_2\text{O}, \text{NH}_3, \text{CH}_4 \) and \( \text{C}_2\text{H}_2 \) in the NIR.
frequency region for gas sensing in the environment, the industry, and the medicine applications.

Tremendous efforts have been employed to improve the CW-CRDS sensitivity. The highest reported sensitivity was by Kassi et al. [91], when they reported a sensitivity of $5 \times 10^{-13}$ cm$^{-1}$ in the spectral region of 1450 nm using DFB laser.

The use of an optical frequency comb to calibrate the frequency of cavity ring down spectra allows to improve the accuracy and enabling massive averaging, due to the reproducibility of the frequency axis, increment the sensitivity of the system by SNR reduction. Because of very well established semiconductor communication lasers in near-IR, the state-of-art comb assisted CRDS is done in that region. For instance, Truong et al. (2013) managed to performed comb-linked frequency stabilized CRDS system that is consisted of an ECDL (at 1.57 μm) and a high finesse cavity of 20000 [92]. By acquiring the beat-note between the probe laser and the nearest comb tooth, an absolute frequency calibration was achieved for an isolated CO$_2$ line at SNR of $10^{4}$ and uncertainty of $\sim 9$ kHz. The same CO$_2$ line was tested with another unique approach in comb-assisted CRDS that was proposed by Gatti et al. (2015) [93]. Their system based on frequency lock of the extended cavity diode laser (ECDL) to the nearest optical frequency comb mode via feed-forward servo loop was characterized by an uncertainty of the central frequency of CO$_2$ line of 3 kHz.

In terms of wide tunable comb assisted CRDS, a system was developed by Mondelain et al. [54] where the probe laser was a wide tunable DFB laser in NIR to retrieve central frequency of CO with uncertainty of 500 kHz. Applying this approach
to measure buffer-gas-cooled molecular beam was performed to measure acetylene in 1.6 μm wavelength region by Santamaria et al. [94]. In comb-assisted CRDS scope, using CRDS as primary thermometry has been also demonstrated in comb assisted regime by Gotti et al. [27].

The development efforts is also extended to the MIR spectral region. Galli et al. measured ν3 fundamental band of CO2 in the range of 2190-2250 cm⁻¹[95]. An accuracy of 50 kHz in the range of 2.5-3.4 μm was achieved by Peltola et al. in measuring multiple species like water, carbon dioxide and nitrous oxide [97].

As discussed in Chapter Two, two strategies could be used to bring the incoming light into cavity resonance: either through scanning the cavity length or by scanning the laser frequency. Implemented a rapid scan of either laser frequency or cavity length in CW-CRDS is favorable to increase data collection rates, simplifying the CW-CRDS setup and avoiding the use of fast optical switch which could be very costy in the MIR spectral region. Rapidly swept-cavity is performed by using PZT to sweep the optical cavity length and hence the cavity FSR [98–100]. Another way around is laser frequency sweeping to permit spectroscopic surveys over wide tuning spectral range [101,102]. Moreover, demonstration of a high rate of the ringdown events acquisition with wide tunable range was reported by Truong et al. [103], in Frequency-agile Rapid-Scanning spectroscopy (FARS). Moreover, an off-axis CRDS, at 766 nm, has been reported by Courtois et al. [104] with detection limits of 3x10⁻⁶ cm⁻¹ to reach a normalized baseline spectral noise level of 1.6x10⁻⁸ cm⁻¹ Hz⁻¹/² at 50 kHz ringdown repetition rate.
5.2 Comb-assisted frequency swept cavity ringdown spectroscopy (FS-CRDS)

After the demonstration of high precision and high accuracy over the wide tunable range of mid-IR EC-QCL in the previous chapters, a new cavity-based configuration has been explored and demonstrated to increase the sensitivity of our mid-IR spectrometer. A comb-assisted cavity ringdown approach is implemented in our experimental setup measuring the free running beat-note between OFC and EC-QCL for referencing. In the following sections, we will discuss the proposed acquisition approach as well as the preliminary results obtained with our new system. The implementation of an algorithm which allows to reconstruct the calibrated absorption spectrum from both the acquisition of the ring-down and the beat-note signal is still under development.

5.2.1 Experimental setup

The optical setup depicted in Figure 5.1 is composed by two main parts: one aimed at beat-note generation for referencing purposes and a second one for the laser injection into a high-finesse cavity and the following detection of the ring-down events. As already demonstrated in previous chapters, an EC-QCL emitting at 7.6 μm is focused into an AOM: the zero-order diffracted beam was mixed up with the optical frequency comb in a high nonlinear crystal (ZGP) to generate a SF-comb in the NIR wavelength around 1540 nm. This SF-comb was then combined with the spectral broadened
replica of the original Tm:comb. The beat-note is detected and sent to the acquisition board after suitable filtering and amplification.

Conversely, the first order diffracted beam was injected into a high finesse cavity. The solution for cavity length stability and minimize the change in its length that occur as a results of thermal expansion, one could use in building the cavity an ultra-low expansion ceramic, that has very low coefficient of thermal expansion (CTE) $10^{-8}$ K$^{-1}$. For that the cavity was built with a 54 cm ZERODUR spacer and two high reflectivity zinc selenide (ZnSe) mirrors ($>99.985\%$) with a radius of curvature of 1 m. In this configuration the cavity is characterized by a finesse of 15700, an FSR of 285.5 MHz, and cavity modes linewidth of $\sim 18$ kHz. The expected empty cavity ring down time is around 14 $\mu$s. Two lenses of -75 mm and 200 mm were used to mode-matched the EC-QCL beam to the cavity spatial mode to maximize the injection efficiency and minimize the light coupled to the transverse modes. The transmitted light was focused to an MCT nitrogen-cooled photodetector with a bandwidth of 20 MHz and a gain of 10 V/μW to be sent to and acquired by the acquisition board.

5.2.2 Acquisition methodology

Due to the microsecond level of the ring-down and to the need of a real time monitoring of the beat-note to calibrate the frequency axis an FPGA based board with
high sampling rate is needed for acquisition. The scheme of our acquisition system is illustrated in Figure 5.2.

The acquisition system included an FPGA-based PXI board with 2 analog inputs (±1 V 100 MS/s 14 bit) and two additional digital inputs/outputs. The idea was to simultaneously and synchronously acquire the ringdown events from a photodetector and the varying beat-notes during laser frequency scanning via PZT or current driver modulation and then to postprocess the acquired data to retrieve the absorption from ring down time calibrating it with the acquired beat-note.

The data are streamed from the board to a PC with a maximum throughput of 250 MB/s. In principle, this is sufficient to stream both channels at 50 MS/s, but this limit is strongly influenced in real systems by the operating system (OS) that has priority over any other process. Therefore, lowering the throughput without affecting our sampling rate became a necessity in our data acquisition. For that, we processed the
beat-note (BN) signal directly in the FPGA implementing the Fast Fourier Transform algorithm (FFT), 256-samples, and the barycenter calculation to evaluate the instantaneous frequency of the beat-note. The instantaneous frequency reflects the frequency difference between the EC-QCL and the nearest comb tooth. In this way, we calculated a frequency value every 2.56 μs and the streaming of the barycenter was calculated to be at 390 kS/s. On the other hand, the photodetector (PD) channel was only decimated by a factor of 2 (50 MS/s), allowing us to sample the ringdown trace with a 20 ns resolution.

Every time the EC-QCL laser resonated with the cavity mode, the photodetector signal overcame a predetermined threshold and hence, a TTL signal provided by the digital port of the PXI board was used to switch off the acousto-optic modulator. The time needed to switch off the laser was based on the time response of the AOM driver and flight-time of the acoustic wave inside the AOM between the EC-QCL beam and the piezoelectric actuator. The flight-time is minimized by translating the laser beam as close as possible to the PZT without cutting the beam. After optimization, the overall delay time of the TTL signal was estimated to be 550 ns, which is sufficiently short in comparison with ringdown times at a few microsecond level. Every time the AOM was switched off, the acquisition system added a marker (a specific value at the end of the dynamic range of the board) to both the ring down channel and the beat note. This marker allows to correlate the ring down events with the corresponding beat-note frequency. Since the EC-QCL frequency is also scanned back and forth, a second digital port of the board was used to identify the scanning direction. This was used later on to unfold the sequence of back-and-forth beat-note spectra. Streaming of both the BN
barycenter and the PD signal was stored in a TDMS file format. This is the only binary type of file that supports the fast saving of huge amounts of data with the possibility of including additional experimental data (temperature, pressure, scan frequency, etc.) that might be needed for post-processing. In our experimental conditions, the typical file size is slightly more than 100 MB every second.

5.2.3 Beat-note acquisition and frequency unwrapping

As illustrated in Figure 5.3(a), beat-note frequency oscillates between 0 and \( f_{\text{rep}}/2 \) (50 MHz) and this is related to the periodic structure of the OFC. When the beat-note is close to 50 MHz, it cannot be measured correctly as the beat-note is low-pass filtered at 43 MHz by the antialiasing filter of the 100 MS/s board. To recognize this point in the frequency value of the beat-note is manually set to 50 MHz. While the laser is scanning, the BN barycenter Figure 5.3(b) moves up and down in a triangle-like behavior (a perfect triangle if the scanning speed is constant), with an oscillation between 0 and \( f_{\text{rep}}/2 = 50 \) MHz due to the beating between the EC-QCL changing frequency (red line in panel (c)) and the comb modes (blue lines in panel (c)).

![Figure 5.3: (a) Beat-note barycenter given by the BN channel. (b) A general schematic of the scanning laser across the manifold of comb modes.](image-url)

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**Figure 5.3:** (a) Beat-note barycenter given by the BN channel. (b) A general schematic of the scanning laser across the manifold of comb modes.
Three phases can be distinguished to understand the behavior of the swept beat-note:

1) At the beginning, the EC-QCL beats with the n-tooth of the comb. The beat-note with the n+1-tooth is greater than 50 MHz and is then filtered out (by the antialiasing filter) and the beat-note increases during the time from 0 to 50 MHz.

2) Once the EC-QCL frequency is at 50 MHz away from the n-tooth (dashed line in (c)), the beat-note acquired is no longer that with the n+1-tooth, but rather with the n-tooth, decreasing from 50 MHz to 0 as long as the EC-QCL approaches the n-1-tooth.

3) Once $\nu_{QCL}$ overcomes $\nu_{n+1}$ the beat-note increases again from 0 to 50 MHz and so on. One can notice that this description corresponds exactly to the measured barycenter behavior in the top panel Figure 5.3(a).

5.2.4 Sensitivity analysis of ringdown time

Figure 5.4 shows two ringdown events which start when the predetermined threshold value of 1 V is overcome. The acquisition system adds a marker (red line) to indicate the starting time of each ringdown decay. The additional peaks present in the figure are related to the EC-QCL light which is coupled to the transverse mode of the cavity. Being minimized they cannot reach the threshold.

For sensitivity analysis, a preliminary test to evaluate the performances of the CRDS spectrometer was performed with an empty cavity modulating the current port of the EC-QCL laser with 1 Vpp sinusoidal signal at 200 Hz. This corresponds to a 145 MHz scan depth (obtained using a previously calibrated $K= 145.4$ MHz/V tuning coefficient) which is less than one FSR of the cavity (FSR $\sim$280.7 MHz). Accordingly, only one resonance of the cavity was probed and if we neglect the slow drift of the
cavity modes due to vibration and temperature, we can assume that we always measured the ringdown at the same frequency.

The ringdown calculated from 10 s ring down trace is displayed in Figure 5.5 (a), corresponding to 17400 ringdown events at a sweeping speed of 131 GHz/s. The averaged value of the ringdown is $\tau_0=12.53$ μs, so very close to the theoretical value showing that the system is properly aligned, with a standard deviation of 0.02 μs which corresponds to a sensitivity of $\alpha_{\text{min}}=4 \cdot 10^{-9}$ cm$^{-1}$ (162 ppm) on the single ringdown measurement. In Figure 5.5(b) the Allan deviation of the same data is displayed. This value it is very helpful to characterize the drift of the system and consequently to estimate what is the best averaging time for sensitivity maximization. If the system is affected only by the white noise, the expected behavior would follow a $T^{-1/2}$ dependence on the averaging time $T$ (red trace in Figure 5.5(b)). In our case after 10-20 ms, the measured Allan curve departed from the theoretical one, showing that some drifts of the system affect the long-term reproducibility beyond 100 ms. This is not, however, a limitation in a spectrometer where each line can be measured in a time much shorter than 100 ms, thus before the onset of drifts.

![Figure 5.4: A sample of ringdown streaming that covers slightly more than one FSR. Red lines indicates the position of the markers indicating the start of RD events. The two small peaks between the highest ones represent the coupled transfer modes. A zoom-in inset shows the ringdown event.](image)
The choice of the specific line was strongly influenced by the EC-QCL behavior. To properly acquire an absorption line, a mode hop free scan of at least 0.4 cm\(^{-1}\) would have been required, but this was impossible due to the frequent mode hops. The laser frequency was found to jump in the entire tuning range of the laser for all possible combinations of grating position, temperature, current and voltage provided to the piezo.

**Figure 5.5:** a) An upper panel ringdown trace. b) Normalized Allan deviation trace over 10 s at 1273.36 cm\(^{-1}\) with 1 kHz current modulation over 1 FSR, speed of 131 GHz/s.
Chapter Six: Summary and Future Directions

In this work, two exceptional laser sources, namely a widely tunable extended-cavity quantum cascade laser (EC-QCL) and an optical frequency comb (OFC), were successfully combined and applied to precision spectroscopy.

This thesis shows how two extremely powerful laser tools, namely extended-cavity quantum-cascade-lasers (EC-QCLs) and optical frequency combs (OFCs), can be fruitfully combined for precision spectroscopy of molecular samples in the gas phase in a variety of approaches. The thesis demonstrated: i) linear spectroscopy over broad bands in the mid-infrared for the retrieval of high-quality spectroscopic parameters, ii) nonlinear spectroscopy for detection of sub-Doppler features and highly accurate determination of line center frequencies, and iii) cavity-enhanced spectroscopy to measure highly diluted samples and/or weak lines with very high detection sensitivity. For all such purposes, EC-QCLs represent a unique solution because of single mode operation joined with large optical power and tuning range. On the other hand, due to their large emission linewidth, the prior art in the field counted only two examples of comb calibration, in both cases without a steady locking regime. The thesis here promotes a leap forward under several aspects, with the first demonstration of frequency locking to an OFC, the first observation of a sub-Doppler feature at sub-MHz resolution, and the first demonstration of a broadband cavity-enhanced comb-calibrated spectrometer in the mid-IR.

We have reported for the first time frequency locking of an EC-QCL to a near-IR frequency comb, the former tuned from 7.6 to 8 μm, the latter at 1.9 μm from a
Tm:fiber oscillator. The locking was obtained by slow feedback to the EC-QCL piezo actuator port with a 100 Hz servo bandwidth, which resulted in a 100 kHz frequency stability over 100 ms. In these conditions, nitrous oxide absorption spectra were acquired and fitted with an overall uncertainty of about 63 kHz on the line center frequency. The addition of a fast feedback loop acting on an external acousto-optic frequency shifter was also discussed; this allows a narrowing of the laser emission line by a factor of eight but it introduced a severe laser intensity noise that made this choice counterproductive for the spectrometer performance.

In terms of applicability of the proposed scheme to other wavelengths, it is worth noting that the spectrometer range can be easily extended up to 12 µm simply by changing the laser head. It is even possible to replace the Tm:comb with a more common Er:comb. For the SFG process, either the long-wavelength part of its supercontinuum could be used or its main output at 1.55 µm. In the former case, the ZGP (or silver gallium selenide AgGaSe\textsubscript{2}) crystal could be used. In the latter case, either AgGaS\textsubscript{2} or orientation patterned GaP crystal could be used.

The developed spectrometer in this thesis lends itself to a broad line survey and to the redefinition of the HITRAN database in a region where previous experiments primarily relied on FTIR spectroscopy. The transition frequencies of 72 lines of the ν\textsubscript{1} fundamental band of $^{14}$N\textsubscript{2}$^{16}$O\textsubscript{2} have been directly measured, for the first time, with high accuracy. Line centers were obtained with uncertainty ranging between 62 and 180 kHz uncertainty. Surprisingly, the rather large jittering of the laser facilitated the relocking procedure in our acquisition system, allowing tens of lines to be repeatedly
and robustly acquired. For such a broad survey, statistical uncertainties have been averaged out consistently.

Using an isolated band model, line positions were reproduced with an $rms$ of 144 kHz allowing for an accurate determination of the spectroscopic parameters of the $^{10}_{00}$ level. Compared to the HITRAN line list of N$_2$O, based on FTS measurements by Toth [76,86], significant deviations are evidenced but their amplitude is largely below the HITRAN error bar ($<10^{-3}$ cm$^{-1}$). Those data, listed in Chapter Four, provide a validation of the predicted data by Ting et al. within 72 kHz, which is consistent with our $1\sigma$ uncertainty. This prompts the incorporation of Ting’s data into future versions of spectroscopic databases.

With the assistance of the OFC, the fully automated system helped to overcome the jittering and mode-hopping problems of the EC-QCL. This provided us with the opportunity to develop a spectrometer not limited to precision application only, but also could be applied for monitoring and sensing environmental applications. There are a large number of species, such as H$_2$O$_2$ and CH$_4$, which would be interesting to monitor and likely to be targeted to be studied in the currently used spectral region.

In a second part of the research activity, thanks to the availability of a more recent EC-QCL with narrower linewidth, we oriented the spectrometer development to the observation of sub-Doppler spectral features. Previously, only one demonstration was obtained using an EC-QCL with emission linewidth of 2.5 MHz as inferred from the instrumental broadening of the observed Lamb dips[105]. In our work, we showed saturated spectroscopy at variable pressures on the R(16) line in the $v_1$ band of N$_2$O. At about 1 mTorr, the FWHM of the dip is around 800 kHz without any deconvolution
with the laser line. To the best of our knowledge, this is the narrowest feature ever observed with an EC-QCL.

We demonstrated a narrow emission linewidth down to ~ 700 kHz observed over ten ms by frequency locking. This was, also confirmed by the instrumentally broadened observed Lamb dip profile. The reported sub-Doppler measurements delivered a potential application for using EC-QCLs in MIR comb-assisted saturation spectroscopy.

The proposed methodology could be further developed to target a coherent transfer from the OFC to the EC-QCL and thus further narrowing. Possible improvement and further work for stabilizing EC-QCLs could be accomplished by overcoming one of the technical limitations we faced in our experiment, such as the steep efficiency response curve of AOFS which gave rise to large intensity fluctuations in our first attempt of achieving phase locking via acousto-optic frequency modulation. Using an improved AOFS with nearly flat efficiency and a larger bandwidth, these problems are likely to be solved.

As a third step of my research activity, I took active part to the development of a comb-calibrated cavity-ringdown spectrometer. Cavity-ringdown spectroscopy in free running with the state-of-the-art high speed acquisition system aims for fast, precise, and sensitive system in MIR. Our developed spectrometer system has been upgraded to the CRDS domain to detect trace quantities of target species. It was tested with a high finesse empty cavity to estimate the sensitivity of $4 \times 10^{-9}$ cm$^{-1}$ at a speed of 131 GHz/s. The initial acquisition speed was 100 M sample/sec sampling rate to acquire
both decimated ringdown event and beat-note signal that undergoes FFT calculation for frequency referencing of the x-axis.

Potentially, with this system, it would be possible to measure several transitions of several molecules and specifically to survey the entire 10002-00001 transition of the $^{16}$O$^{13}$C$^{18}$O isotopologue of carbon dioxide in 7.6 μm. Moreover, targeting low concentration species is also feasible for sensing and monitoring environmental applications. One of the interesting species that could be used in our spectral region as a biomarker for diabetes is acetone. Acetone has a strong absorption coefficient around 7.6 μm, which could have a potential use in breath analyzing sensors and it is applicable with the fast swept CW-CRDS developed herein.

We believe that the research activities provided in this thesis suggest a promising route to exploit the widely tunable EC-QCLs for a coherent transfer from OFCs. Moreover, the versatility in the experimental and algorithmic approach makes our spectrometer applicable in different spectral regions that could be a promising tool for sensing and metrology applications.
APPENDICES
Appendix A: Infrared absorption: ro-vibrational bands

In the scope of molecular absorption, this appendix will focus on gas molecules and provides a brief background in IR molecular spectroscopy that is well explained in several textbooks [9,10,75,106–108] for reader’s interest.

Quantum mechanics explains optical absorption (excitations) or emission (relaxation) phenomena as a consequence of molecular energy transfer during interaction with electromagnetic radiation where the molecules or the atoms that exist in particular “quantum” states, will be associated with characteristic quantum “numbers”. Each quantum state has its own discrete energy and angular momentum leading to “quantization” of molecular energy. These energy levels are classified into three different transitions of the molecules: electronic, vibrational, and rotational transition because of the chemical bonds (in classical interpretation) between the atoms which form the molecules [Figure A.1].

As illustrated in Figure A.1 electronic transitions require more energy than vibrational and rotational transitions. Therefore, absorption or emission that involves such transitions will be located in high frequency regions visible or ultraviolet (UV).
Using the “Born-Oppenheimer” approximation to solve the Schrödinger wave equation that describes molecular motion, and because of the heavy mass of the nuclei, will results in considering the nuclei movements is being static in comparison to the movements of the electrons. Thus, the total energy of molecules could be expressed as a sum of several contributions from interactive parts, namely, nuclei and electrons.

\[
E_{\text{tot}} = E_{\text{elec}} + G(\nu) + F(J) \tag{A.1}
\]

where \(\nu\) and \(J\) are the vibrational and rotational quantum numbers, respectively. The approximation in (A.1) is valid because of the several orders of magnitude in the energy span in the different molecular transitions, where \(\Delta E_{\text{elec}} \gg \Delta G(\nu) \gg \Delta F(J)\).
In the following pages, we will introduce a general discussion about molecular ro-vibrational transitions, highlighting the quantum mechanics treatments for molecular structures, rotational and vibrational coupling, selective rules and spectral bands in MIR.

For a molecule to be IR active and exhibiting an infrared absorption, it has to possess electrical dipole moment ($\mu$) response to the oscillation of the light electrical field. During the change of the electrical dipole moment, molecular vibration appears as the contract or expand of molecular bonds in response to the change of energy levels. Since the change of dipole moments in homonuclear molecules is zero, those molecules are said to be IR-inactive.

In IR absorption, the absorbed energy is not sufficient for electronic transitions, thus, the molecule’s dipole will reorient itself as the electric field of the radiation oscillates. This reorientation occurs within discrete vibrational or rotational levels, and hence the IR inactive molecules have a zero, or unchanged, dipole moment. In the MIR region, particularly, the fundamental transitions will be excited by incident radiation. Both rotational and vibrational transitions will be involved. To drive both rotational and vibrational energy along with their selective rules that govern the transitions, we will follow the simple model that is used to drive each.

The approach used to drive rotational energy is a mix of classical and quantum treatments, namely “rigid rotator.” In this model, the atoms in molecules are treated as a point of mass with a constant, “rigid”, separation distance. The rotational energy for the rigid rotator will be governed by the rigid rotational constant $B$ and the
rotational quantum number $J$, that in return appears from quantum treatment to angular momentum for the rotator, so the rotational energy will be given by:

$$F(J) = BJ(J + 1)$$ (A.2)

where $J$ will take the values $J= 0, 1, 2, ...$

For an elastic rotator, centrifugal distortion effect is taken into account leading to the appearance of other terms in (A.2), to be rewritten as:

$$F(J) = BJ(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 - ...$$ (A.3)

where $D$ and $H$ are the centrifugal rotational constants.

For the rotational "selective rules" that will appear while solving the Schrödinger equation, the transitions allowed will be only when:

$$\Delta J = \pm 1$$ (A.4)

For the case of vibrational transition treatments, the molecular vibration will be treated as a simple harmonic oscillator. This model treats the chemical bonds that link the atoms as springs that oscillate around the equilibrium. The quantum mechanics treatment for this harmonic oscillator yields a vibrational energy $G(\nu)$:

$$G(\nu) = h\nu \left( \nu + \frac{1}{2} \right)$$ (A.5)

where $\nu$ is an integer of 0,1,2,...; and the governed selection rules for it is:

$$\Delta \nu = \pm 1, \pm 2, \pm 3,...$$ (A.6)

The difference between the transition levels of the quantum number in a harmonic oscillator will be strictly ±1. And this will give rise to fundamental transitions. In anharmonicity, another term would be added to (A.3) which will affect the selection
rules of vibrational transitions giving rise to overtone transitions [Figure A.3 (c)]. It is worth mentioning that the fundamental transitions, which are several orders of magnitude higher than the overtone transitions, are those transitions that are observed in the MIR, while the first overtone (Δv=±2) or second overtone (Δv=±3) are in the NIR.

From equation (A.3), the total energy associated in an electronic level mentioned in equation (A.1) could be rewritten as:

\[
E(\nu, J) = G(\nu) + BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 \tag{A.7}
\]

![Figure A.2: Fundamental ro-vibrational transitions (Δv=1) to form P and R branches, the represented transitions are from ν=0 to ν=1 vibrational levels. When the transition has a difference between rotational quantum number J of ΔJ= -1, the transition lines will be referred to P=branch and R=branch in the case of ΔJ=+1.](image)

Typically, optical frequencies are measured in experiments, rather than energy levels to retrieve those rotational constants. Hence, by precisely measuring a vibrational band, one can retrieve the rotational constants B, D, and H.
In the ro-vibrational transitions where both rotational transitions are coupled with vibrational one we will observe a list of lines that are known as R- and P-branches. When $\Delta J = +1$, the result lines will be R-branch from the French word “Riche” means rich. While the P-branch when $\Delta J = -1$, for “Pauvre” which means poor. As illustrated in Figure A.2 where rotational transitions occurs between two vibrational bands, as mentioned earlier, if the difference in the vibrational quantum number is $\pm 1$, the band is referred to as a fundamental band. It worth mentioning that the rotational constant $B$ in (A.3) shows the separation between consecutive lines in the band taking into account that $B$ is not strictly constant. Thus, the distance between the lines in the R-branch becomes smaller as the frequency increases because of the decrement of the rotational constant $B$. Contrary to the R-branch, the P-branch exhibits an increment in $B$, thus, the spectral lines spectral distance increase [Figure A.2].

The calculated energy levels are under the Born-Oppenheimer approximation, where the kinetic energy is zero, thus only potential energy is taken into account and the dominant factor is the intramolecular separation. The potential energy is usually represented by the Morse function [Figure A.1]. As a result of a repulsion exchange of the electron clouds of the atoms, there is a steep increase in potential energy, while the energy potential curve will flatten out at increased interatomic distances during the expansion movement.
Also, in this figure, a simple illustration of the three energy level distributions along with the corresponding transition is provided. This demonstrates the very different orders of the spacing magnitude of the three energy levels unlike pure rotational transitions that occur in the same electronic and vibrational state, the ro-vibrational transition will happen in the same electronic level between different vibrational states. This leads to the observation of a fine structure composed of rotational transitions. Because of the rotational structure, each vibrational transition appears in a band structure, in other words, a group set of lines spaced by an approximately equally spaced interval of a multiple of the rotational constant $B$.

*Figure A.3: a) Morse potential molecular energy levels with representation of the three different types of energy levels: electronic, vibrational, and rotational. b) The pure rotational and ro-vibrational transition representation. c) Energy levels of the different vibrational transition types: fundamental, overtone, and combination.*
Appendix B: Nonlinear optical process: sum frequency generation (SFG)

In this appendix, a brief overview is provided that covers the nonlinear optics, in particular sum frequency generation (SFG) process in order to combine both spectral regions, i.e., mid-IR of EC-QCL and near-IR of OFC.

Historically, the nonlinear process was observed before the laser era by Lewis et al. (1941) [109]. In 1961, Franken et al. [110] discovered the second harmonic generation. The response of nonlinear materials, crystals, to an electric field of electromagnetic waves originates from the “nonlinear” response of dipole moment per volume $P$ (polarization) of the crystals to the electrical field itself.

In a linear regime, the polarization $P(E)$ dependence to the electric field $E(t)$ is given by:

$$P(t) = \varepsilon_0 \chi^{(1)} E(t)$$

(B.1)

The constant $\varepsilon_0$ is the permittivity in free space, and $\chi$ the “linear susceptibility”. In a nonlinear regime, where a strong electric field is applied, the higher order susceptibility affects the polarization response of the electric field, and $\chi$ is not linear anymore, and hence, we can rewrite the dipole moments as a function of the electric field

$$P(t) = \varepsilon_0 \left( \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) \ldots \right)$$

(B.2)

where $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order susceptibility respectively [111]. All materials, by default, exhibit a different level of nonlinearity response. Strong electric field and other conditions need to be fulfilled to observe harmonic generations of the light frequency.
Herein, we are exploiting the sum frequency generation (SFG) that originates from the second order susceptibility $\chi^{(2)}$ of the crystal dipole moment $P$. Consider a nonlinear material with high $\chi^{(2)}$ that interacts with two optical fields with two distinct frequency components ($\omega_1$ and $\omega_2$), the overall electric field $E(t)$ will be:

$$E(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c. \quad (B.3)$$

As mentioned earlier from (B.2) the second-order nonlinear polarization contribution will be:

$$P^{(2)}(t) = \varepsilon_0 \chi^{(2)} E^2(t) \quad (B.4)$$

From (B.3) and (B.4), we can conclude that the nonlinear polarization will be:

$$P^{(2)}(t) = \varepsilon_0 \chi^{(2)} \left[ E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1 E_2 e^{-i(\omega_1 + \omega_2) t} + 2E_1 E_2 e^{-i(\omega_1 - \omega_2) t} + c.c. \right] + 2\varepsilon_0 \chi^{(2)} \left[ E_1 E_1^* + E_2 E_2^* \right] \quad (B.5)$$

In the equation (B.5), one can see several frequencies appear. Namely, a second harmonic generation (SHG) of the two interacting frequencies $\omega_1$ and $\omega_2$ ($2\omega_1$ and $2\omega_2$); a sum frequency generation (SFG) of the two: $\omega_1 + \omega_2$; and a different frequency generation (DFG): $\omega_1 - \omega_2$. The last term in (B.5), zero frequency, refers to the static electric field that is created across the nonlinear crystal, called optical rectification (OR).

Nevertheless, typically, only one nonzero frequency process will be present in any nonlinear interaction. That is because of the fact that the nonlinear process will be efficient at a certain “phase-matching” condition that has to be fulfilled at a specific polarization as well as a nonlinear crystal orientation for each process.
In the nonlinear process, both energy and momentum conservation has to be satisfied. Since the frequency $\omega_{\text{SFG}} = \omega_1 + \omega_2$ is governing energy conservation, the momentum for the generated field would be $k_{\text{SFG}} = k_1 + k_2$. As illustrated in Figure B.1(a,b), energy level representation for SFG is given as well as the collinear and noncollinear wave vector interaction in the nonlinear crystal.

The intensity of the generated electric field from the SFG process when two waves of frequencies $\omega_1$ and $\omega_2$ interact in an $L$ long nonlinear crystal, will vary with the change of the wave vector $\Delta k$ according to:

$$I_{\text{SFG}} = \frac{8d_{\text{eff}}^2 \omega_{\text{SFG}}^2 I_1 I_2}{n_1 n_2 n_{\text{SFG}}^2 c^2} \frac{L^2 \sin^2 \left( \frac{\Delta k L}{2} \right)}{\sin \left( \frac{\Delta k L}{2} \right)}$$

(B.6)

where $\Delta k = k_{\text{SFG}} - k_1 + k_2$ is the momentum mismatch between the three vectors. $I_{1,2}$ is the intensity for interact fields, $n$ is the nonlinear refractive index for each wave, a $d_{\text{eff}}$ is the second order effective susceptibility from its tensor ($d_{\text{eff}} = \chi^{(2)}/2$). Thus, the maximum generated intensity will be reached when $\Delta k = 0$, and hence, the phase matching condition is reached. By defining maximum SFG intensity ($I_{\text{SFG}}^{\text{max}}$) at $\Delta k = 0$, we can rewrite (B.6) as:

$$I_{\text{SFG}} = I_{\text{SFG}}^{\text{max}} \left[ \frac{\sin(\Delta k L/2)}{\Delta k L/2} \right]$$

(B.7)

From the last two equations, one can conclude that the efficiency of the SFG increases with the quadrature of the nonlinear medium, or crystal, and at the same time, it will decrease as the product $|\Delta k| L$ increases. This is because of the generated wave that gets out of phase with the driving polarization that causes power flow from the SFG wave to the mixing waves. Further optimization of the SFG and the increase of
the frequency conversion efficiency could be maximized when the wave walkoff effect is minimized. This is accomplished by adjusting the focusing beam inside the crystal in such a way that the confocal parameter \((d\text{ in Figure B.1(c)})\), Rayleigh length of the Gaussian beam, of interacted beams will be inside the crystal. As concluded by Boyd and Kleinman [112], the focusing down of the interacted laser beam to make the ratio \((L/d)\) equal to 2.84 will lead to the maximization of the efficiency conversion of SHG and the power generated from the input beam power \(P_{\text{in}}\):

\[
\eta_{\text{SHG}} = \frac{P_{\text{SHG}}}{P_{\text{in}}} = \frac{1}{2\pi \varepsilon_0^3} \left[ \frac{\omega_1^3 d_{\text{eff}}^2 L}{c^4 n_{\omega_1} n_{\text{SHG}}} \right] P_{\text{in}} \tag{B.8}
\]

The same optimization in the beam waist in SHG is applicable for parametric generation, such as SFG, to increase the conversion efficiency. When the two interacting beams are specially shaped in order to make their focal length \(d\) related to the crystal length by: \(L = 2d_{1,2} = \frac{2\pi w_0^2 n_{1,2}}{\lambda_{1,2}}\), it could be radially concluded from Gaussian beam propagation inside the crystal. In practice, it is difficult to achieve perfect phase matching conditions \((\Delta k=0)\) simply because of the complexity of material refractive index \(n\), that, in return, will be involved in phase matching conditions by:

\[
k = \frac{\omega}{c} n \tag{B.9}
\]

Thus, for high susceptibility \(\chi^{(2)}\) materials such as nonlinear crystals have a refractive index that depends on the polarization of the propagated wave in the crystal.
Figure B.1: The major concept in optical frequency mixing, namely SFG: phase matching conditions for both frequency $\omega$ (a) and interacting wave momentum ($k$) for collinear (b.1) and noncollinear (b.2). (c) configuration. Increase SFG bandwidth by increasing the Rayleigh length (d) of the two interact beams inside the crystal. (e) Two types of uniaxial crystals, positive and negative, based on the extraordinary ($n_e$) refractive index interaction with light, with respect to the optical axis (Z), while the ordinary refractive index remains ($n_o$) unchanged.

Figure B.1 for more illustrations of the two types of uniaxial crystals where the refractive index response will differ depending on the direction of the polarization of the incoming beam with the crystal optical axis. In our experiment, we used a uniaxial crystal, so the following discussion will be limited to the refractive index of uniaxial crystal.

Depending on the direction of the electric field (polarization) to the crystal optical axis, the electrical wave will interact with each differently. Hence, those materials are called birefringence crystals since they have two refractive indices.

In uniaxial crystals, when the polarization of the electric field is perpendicular to the optical axis of the crystal, the field will experience an ordinary refractive index $n_o(\theta)$ and the polarization, called ordinary polarize “o”, $\theta$ represents the angle between
the propagation field and the crystal optical axis. However, when the field polarization is parallel to the optical axis, it will experience an extraordinary refractive index \( n_e(\theta) \), and hence the beam will be called an extraordinary beam “e”. Two distinctly are different types of uniaxial crystals are based on the ordinary and extraordinary refractive index. In the case when \( n_o(\theta) > n_e(\theta) \), the crystal is said to be a negative uniaxial crystal. In the case when \( n_o(\theta) < n_e(\theta) \) the crystal will be a positive crystal.

When calculating the phase matching condition, one should be careful to choose the corresponding refractive index, ordinary or extraordinary, that is included in the interactions. For more comprehensive picture regarding the different cases of the wave mixing conditions and the corresponding refractive index that, in return, will be used to calculate the frequencies involved to achieve optimum phase matching, the reader is encouraged to read [111].

In our experiment, we used a positive uniaxial crystal which is one of the promising nonlinear crystals for the MIR applications zinc germanium phosphide SnGeP\(_2\) (ZGP). The ZGP has wide transparency up to 12 µmFigure B.3(a), and is mechanically robust, with high nonlinearity (\( \sim 75 \) pm/V) and high damage threshold (\( \sim 60 \) MW/cm\(^2\)). All

![Figure B.2: a) Optical transition range of ZGP, b) Wavelength phase matching simulation of ZGP.](image)
these characteristics make it suitable for IR/MIR laser applications [113]. Figure B.2 represents a quick simulation for noncritical phase matching of ZGP where all possible mixing wavelengths are represented for oeo (Type II) interactions [114]. The notation “ooe” refers to the interacting beams’ polarization, where the mixing beams have perpendicular polarization, ordinary and extra-ordinary.

To generate the SF-comb, the Tm-OFC and EC-QCL beams were collinearly focused down by using a parabolic mirror (f=50 mm). The generated SFG, at 1540 nm, was recollimated and filtered out to remove Tm-OFC and EC-QCL by means of optical filters. Thanks to the high efficient nonlinear interaction in ZGP, a power of ~80 nW for SFG was obtained. Part of the experimental layout of the SFG and supercontinuum (SC) is depicted in Figure B.3 along with normalized spectra of Tm-OFC, SFG (blue), and filtered SC (green).
Appendix C: Beat-note approach for stabilizing and referencing EC-QCL

In order to employ EC-QCLs in precision spectroscopy measurements, their frequency must be stabilized. Very well-known diode lasers frequency stabilization approaches are performed by locking them to a high finesse cavity or to an atomic reference which will provide high frequency stabilization. Moreover, the realization of OFCs provides the opportunity for new research in spectroscopy through stabilizing lasers frequency against the OFCs. During the locking process, whether frequency or phase locking, one obtain the laser frequency noise regardless, which in return, strongly affects the locking conditions. Locking EC-QCLs to an OFC also leads to stabilization and suppresses its frequency noise.

The instantaneous frequency of a laser $\nu(t)$ is related to its nominal frequency $\nu_0$ and to the fluctuation of the electric field phase $\phi(t)$ by [115]:

$$\nu(t) = \nu_0 + \frac{1}{2\pi} \frac{d\phi(t)}{dt}$$

(C.1)

Where the quantity $\frac{1}{2\pi} \frac{d\phi(t)}{dt}$ is the frequency noise. Fundamentally, it is the phase or frequency noise that is the cause of the laser linewidth broadening. Therefore, characterizing frequency or phase noise is the key to stabilizing the laser frequency. In practice, frequency fluctuating is assist by measuring the power spectral density (PSD) of the frequency noise ($S_\nu(f_m)$) in Hz$^2$/Hz:

$$S_\nu(f_m) = f_m^2 S_\phi(f_m)$$

(C.2)

where $f_m$ is the offset frequency that frequency/phase noise is modulated at. $S_\phi(f_m)$ is the PSD of phase noise in rad$^2$/Hz, and it is a measure of the phase fluctuating as
The analogy between PSD of the electrical signal is possible with PSD of frequency/phase noise. For an electrical signal $V(t)$, the power spectrum is given in units of power per bandwidth ($V^2/\text{Hz}$) in linear scale, and such measurements could be straightforwardly obtained using a spectrum analyzer that will give the signal spectral component and its corresponding amplitude. Since in practice one is measuring an electrical signal, using a conversion factor that converts frequency fluctuation in (Hz) to amplitude fluctuation in (Volt), known as the frequency discriminator factor (Hz/V), will give us directly the frequency noise PSD.

Nevertheless, the frequency noise PSD has the complete information about the laser frequency noise, and extracting laser linewidth is, in principle, possible, however, not straightforward though. Domenico et al. [116] has proposed a simple method to retrieve laser linewidth readily from frequency noise PSD and demonstrated this experimentally as well [117], by introducing $\beta$-separation line which is defined as:

$$\beta(f) = \frac{8\ln 2}{\pi^2} f$$  \hspace{1cm} (C.3)

In his criteria to define the FWHM of the optical line shape, he proposed that only slow frequency modulation will contribute to the linewidth, while high frequency modulation is too fast to influence the laser linewidth, but could affect the wings of the
line profile. Accordingly, the proposal was that the line FWHM is proportional to the total area (A) below β-line under frequency noise PSD as illustrated in Figure C.1:

\[ \Delta \nu_{FWHM} \approx \sqrt{8 \ln 2 \cdot A} \]  \hspace{1cm} (C.4)

Among different sources of laser frequency noise, 1/f noise is more often the dominant noise at low frequencies. Another common noise that is a result of random phase is the white noise. The frequency noise deviates from the white noise at the relaxation resonance frequency, corresponding to the high frequency cut-off which is later used to determine the locking servo bandwidth.

Stabilizing MIR EC-QCL, in this work, is based on locking it to a frequency comb by means of a feedback servo loop to correct the EC-QCL frequency through its PZT and current drivers. A generated beat-note that has the information of both lasers, a master (stable) and slave laser (the one that meant to be frequency stabilized) is used to generate an error signal through hetero/homodyne interferometers between the beat-
note and a reference radio frequency source, RF synthesizer. Usually, a few common steps are taken during stabilization: derivation of an error signal (locking signal), followed by design of an electronic feedback circuitry or servo system, then initiation and adjustment of the feedback parameters, and finally, evaluation of the locking performance.

The error signal carries the detuning information of the laser frequency to that of another stable laser used in generating the beat-note, then an error signal is made through mixing the beat-note with an RF signal. The beat-note frequency is proportional to the difference between the two frequencies. Figure C.2 illustrates a general schematic for beat-note frequency stabilization. In this scheme, two diode lasers (LD1,2) were used.

Assuming two oscillating input signals, the RF signal intensity (beat-note signal) could be expressed as:

$$I_{RF} \propto 2E_1E_2 \cos(\omega_1 t) \cos(\omega_2 t) + \phi(t)$$  \hspace{1cm} (C.5)

$$I_{RF} \approx E_1E_2 \cos[(\omega_1 - \omega_2)t]$$  \hspace{1cm} (C.6)

For simplicity, the DC components of the signal are generated by photo-detectors which are proportional to the incident light. From the equation (C.6), the beat-note frequency, which is an RF frequency, is $\Delta \omega = \omega_2 - \omega_1$. Next, stabilization of the beat-note

Figure C.2: Beat-note frequency stabilization by means of self-heterodyne interferometer.
is performed by mixing it with a reference local oscillator (RF synthesizer) of a
frequency $\omega_{\text{synth}}$ to generate an error signal. Later on, this error signal is processed
through the locking servo system to adjust the frequency deviation of the slave laser.

In this experiment, a beat-note between the SC and SFG was generated by means
of a balance detector, which in turn, was used as input into the servo loop for
stabilizing the frequency of the EC-QCL, and hence, the beat-note was a tool to extract
the frequency noise of this laser.
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