

Molecular dispersion spectroscopy for chemical sensing using chirped mid-infrared quantum cascade laser

Gerard Wysocki^{1,3} and Damien Weidmann^{2,4}

¹Electrical Engineering Department, Princeton University, Princeton, New Jersey 08544, USA

²Space Science and Technology Department, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0QX, UK

³gwyssocki@princeton.edu

⁴damien.weidmann@stfc.ac.uk

Abstract: A spectroscopic method of molecular detection based on dispersion measurements using a frequency-chirped laser source is presented. An infrared quantum cascade laser emitting around 1912 cm⁻¹ is used as a tunable spectroscopic source to measure dispersion that occurs in the vicinity of molecular ro-vibrational transitions. The sample under study is a mixture of nitric oxide in dry nitrogen. Two experimental configurations based on a coherent detection scheme are investigated and discussed. The theoretical models, which describe the observed spectral signals, are developed and verified experimentally. The method is particularly relevant to optical sensing based on mid-infrared quantum cascade lasers as the high chirp rates available with those sources can significantly enhance the magnitude of the measured dispersion signals. The method relies on heterodyne beatnote frequency measurements and shows high immunity to variations in the optical power received by the photodetector.

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References and links

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1. Introduction

Laser absorption spectroscopy (LAS) based on tunable semiconductor lasers and/or non-linear frequency conversion sources has become a widely used technique for the analysis of gas-phase chemicals. Applications cover a broad range of sectors including industry, atmospheric monitoring and medicine. Minimum fractional absorptions of $\sim 10^{-5}/\text{Hz}^{1/2}$ are routinely obtained by most of the current LAS systems, with the best analyzers achieving down to $10^{-7}/\text{Hz}^{1/2}$ limits [1]. Most of the LAS techniques rely on probing the absorption signal characteristic to a gas sample and are fundamentally limited to the measurement of small signal changes (absorption) on the top of a large background (total light intensity arriving at the detector), which may limit the dynamic range of the acquisition system. Zero-background techniques such as photoacoustics [2] overcome this potential issue. The detection of refractive index changes inherent to molecular absorption that leads to anomalous dispersion in the vicinity of a transition, can offer advantages similar to zero-background techniques. Thus dispersion spectroscopy is an interesting alternative to conventional absorption measurements. This approach of performing molecular spectroscopy was extensively studied a century ago [3]. However, due to the extremely small refractive index change associated with the absorption of trace amounts of molecular species, little progress has been made to adopt this approach to routine molecular detection. Interferometric methods such as the "hook" method [4], developed at the early stage of gaseous sample dispersion studies, have been used until now [5]. Other methods inherited from the "hook" technique have also been investigated: Examples include interference fringe shift or slope measurements [6], holographic measurements [7], or applications of detector focal plane arrays and digital image

processing [5]. The advent and use of lasers have significantly improved the accuracy and precision of molecular dispersion measurements. The first demonstration using a two-beam interferometer using one fixed-frequency and one tunable laser was performed by Crance et al. [8]. Recently similar developments using a tunable diode laser and a heterodyne detection scheme were demonstrated [9]. Other implementations include a laser-based version of the “hook” method in a Mach-Zehnder interferometer configuration for fringe displacement measurements [10,11], the use of a high finesse Fabry Perot resonator [12] or techniques based on intra-resonator measurements [13]. All coherent detection schemes give access to the phase of the electromagnetic wave, from which the dispersion information can be retrieved [14,15]. In this paper, we report on a new measurement method for molecular dispersion based on a frequency-chirped laser source and heterodyne detection. The method shows promise to become a useful alternative to absorption measurements in sensing applications and its potential advantages are discussed in this paper.

The experimental demonstration focuses on the mid-infrared (mid-IR) spectral region where most molecules possess their strongest fundamental ro-vibrational bands. In addition, the atmosphere exhibits two wide spectral windows in the mid-IR region (3-5 and 8-12 μm), enabling molecular sensing with minimal spectral interferences (primarily from water vapor). For these reasons, mid-IR spectroscopy is optimum for gas-phase chemical detection at trace levels. Quantum cascade lasers (QCLs), the only room temperature semiconductor lasers in the mid-IR, have been extensively used to measure absorption of molecular gases in the fingerprint region [16]. Applications of QCL-based tunable LAS are numerous and primarily focused on trace gas detection and/or real time gas monitoring [17,18]. On the other hand, the investigation of the refractive index change of gas samples by QCL spectroscopy has been scarce. Alternative spectroscopic methods employing molecular dispersion effects and using QCLs have mainly been limited to techniques that rely on other physical phenomena such as the Faraday effect caused by molecular magnetic circular birefringence [19,20].

In this article, experimental measurements of molecular dispersion caused by transitions from the fundamental vibrational band of nitric oxide (NO) are presented. The measurements are performed at $\sim 5.2 \mu\text{m}$ with a frequency-chirped QCL. The phase of the electromagnetic field containing the dispersion information is measured through frequency demodulation of the beating signal between the laser field and a frequency-shifted wave generated by an acousto-optic modulator. Modeling and experimental results demonstrate that using this approach, the spectral information associated with the molecular refractive index is proportional to the chirp rate. QCLs can exhibit high frequency chirp rates (typically 200MHz/ns) [21] which, in addition to their mid-IR wavelengths coverage, makes those lasers particularly attractive for the dispersion spectroscopy method presented here.

The following sections present the theoretical aspects of the method, the corresponding experimental studies and results, and a discussion on the merits of chirped-laser dispersion spectroscopy (CLaDS).

2. Resonant absorption and dispersion

Interaction of light with matter in the vicinity of electronic, vibrational, or rotational resonances results in absorption of the incident radiation and simultaneously causes dispersion. For a given sample, knowledge of the frequency dependence of the absorption coefficient allows the determination of the dispersion via the Kramers-Kronig relations. For a dilute medium, the Kramers-Kronig relations can be rewritten into a single expression relating the refractive index $n(\omega)$ and the absorption coefficient $\alpha(\omega)$ of a sample:

$$n(\omega) = 1 + \frac{c}{\pi} \int_0^{+\infty} \frac{\alpha(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (1)$$

where c is speed of light and ω the optical angular frequency.

The experiments to be described in the following sections were conducted with a gas sample made of an NO in N₂ mixture. The $v = 0 \rightarrow v = 1$ fundamental band of NO centered at 5.3 μm is the most intense ro-vibrational band of the molecule and is therefore the ideal target for trace monitoring. A QCL emitting radiation that coincides with the most intense lines in the R branch of the NO band ($\sim 5.2 \mu\text{m}$) was used as the spectroscopic source (provided by Alpes Lasers SA). Given the tuning range of the DFB QCL, the rotational transitions given in Table 1 have been chosen for the experimental demonstration of CLaDS. At low pressure, lines labeled 1 and 2 in the table will clearly appear as a Λ -doublet, whereas line broadening will prevent lines 3 and 4 from being resolved. Spectroscopic data from HITRAN2008 [22] were fed into an algorithm performing line by line calculation of the absorption spectrum, from which the refractive index was determined using Eq. (1). The calculations of the absorption coefficient and the corresponding refractive index change were performed for a 5 Torr total pressure mixture containing 1% of NO and 99% of dry nitrogen. These calculations, relevant to the molecular transitions appearing in Table 1, are shown in Fig. 1. These data will be used in the following sections for the calculation of the dispersion spectra.

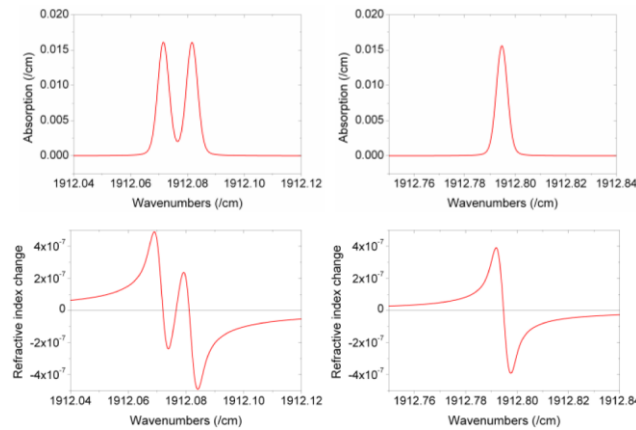


Fig. 1. Absorption coefficient and dispersion spectra calculated using the HITRAN database for the NO transitions at $\sim 1912.07 \text{ cm}^{-1}$ (left panels) and 1912.79 cm^{-1} (right panels). Calculations were made for a NO-N₂ mixture at 5 Torr containing 1% of NO.

Table 1. Spectroscopic characteristics of the NO transitions targeted during the experimental study. Data are taken from the HITRAN database [22]

Line	Frequency (cm ⁻¹)	Band	Subband	Rotational Transition
1	1912.0716	$v = 0 \rightarrow v = 1$	$^2\Pi_{1/2}$	R(10.5e)
2	1912.0816	$v = 0 \rightarrow v = 1$	$^2\Pi_{1/2}$	R(10.5f)
3	1912.7939	$v = 0 \rightarrow v = 1$	$^2\Pi_{3/2}$	R(10.5e)
4	1912.7955	$v = 0 \rightarrow v = 1$	$^2\Pi_{3/2}$	R(10.5f)

3. Dispersion measurement model

A schematic of the experimental arrangement implemented for CLaDS is shown in Fig. 2(a). The radiation from the continuous wave single mode QCL is transmitted through an acousto-optic modulator (AOM). The 0th and 1st orders diffracted by the AOM travel through two distinct optical arms and are recombined on a photodiode. The AOM downshifts the optical frequency of the -1st order diffraction by Ω , which is the frequency of the acoustic wave excited in the AOM crystal (in radio frequency - RF - range). The system configuration is

identical to a Mach-Zehnder interferometer with a frequency shifted wave in one arm. As indicated in Fig. 2(a), the cell that contains the molecular sample can be placed in two positions: (1) the so-called dual-frequency beam configuration where both beams are recombined by a beam splitter and propagate along the same optical axis to the detector, and (2) the so-called single-frequency beam configuration where only the 0th order diffracted beam passes through the sample. These two configurations have been used for the experimental studies and will be modeled theoretically.

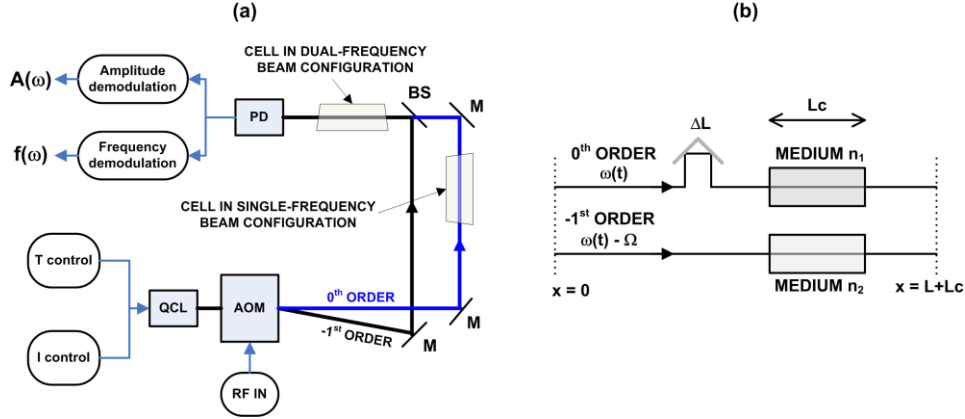


Fig. 2. (a) Experimental arrangement for CLaDS sensing. (T - temperature, I - current, QCL - quantum cascade laser, AOM - acousto-optical modulator, M - mirror, BS - beam splitter, PD - photodetector, A - amplitude, f - frequency, ω - optical angular frequency); (b) Schematic representation of the optical layout with parameters used in the theoretical model. (ω - optical angular frequency, Ω - acousto-optical frequency shift, n_{1,2} - refractive indices of the media, L - geometrical length in the free space/air, L_c - geometrical length of the gas cell, ΔL - geometrical path difference between the optical arms).

The arrangement of Fig. 2(a) can be represented by two fully coherent plane waves having a slight and constant frequency difference ($\omega_1 = \omega$ and $\omega_2 = \omega - \Omega$), which propagate until superimposed onto the surface of a photodetector. The 0th and the -1st order fields at the detector surface can be expressed as:

$$E_1 = A_1 \cos(\omega_1 t - \phi_1) \quad (2)$$

$$E_2 = A_2 \cos(\omega_2 t - \phi_2) \quad (3)$$

with A , ω , and ϕ being the amplitude, the optical angular frequency, and the phase of the fields, respectively. At the surface of the square law detector, the superposition of the fields E_1 and E_2 produces a photocurrent proportional to:

$$I_{ph} \propto A_1^2 + A_2^2 + 2A_1A_2 \cos[(\omega_1 - \omega_2)t - (\phi_1 - \phi_2)] = A_1^2 + A_2^2 + 2A_1A_2 \cos(\varphi) \quad (4)$$

The first two terms are constant and the third term is the time-dependent beat term oscillating at the difference frequency $\omega_1 - \omega_2$. Provided that the beating frequency lies within the electrical bandwidth of the photodetector, RF analysis of the photocurrent measures both amplitude and phase information associated with the respective absorption and dispersion produced by the sample. When the laser optical frequency and the AOM excitation frequency are both constant, the dispersion experienced by either wave results in a phase shift in the RF carrier at frequency Ω [9]. The technique described here additionally utilizes a fast frequency-chirp of laser radiation that enhances the magnitude of the measured dispersion signal. To establish the basic concept of CLaDS and the enhancement effect, the model assumes a linearly chirped laser radiation:

$$E = A_0 \cos\left(\omega_0 t + \frac{1}{2} S \cdot t^2\right) \quad (5)$$

with an instantaneous optical angular frequency of

$$\omega(t) = \omega_0 + S \cdot t \quad (6)$$

where S is the laser chirp rate. An analysis of the CLaDS signal is performed using the simplified schematic wave propagation model depicted in Fig. 2(b). Instantaneous optical frequencies of the component waves at the photodetector surface are derived in the framework of the quasi-continuous wave approximation. Signals for both configurations are considered in the following sections, starting with the dual-frequency beam configuration, which represents a more general case.

3.1. Dual-frequency beam configuration

As depicted in Fig. 2(b), the sample cell, which is a part of the total optical path for both beams, has a geometrical length of L_c and contains a dilute medium with a frequency dependent refractive index $n(\omega)$. The optical path in open air for both beams is L ; the 0th order beam travels an additional distance ΔL . Between the origin and the detector planes, the phase fronts of the 0th order ($\omega_1 = \omega$) and the frequency shifted wave ($\omega_2 = \omega - \Omega$) travel for Δt_1 and Δt_2 , respectively. These durations are expressed by:

$$\Delta t_1 = \frac{L + \Delta L + L_c \cdot [n(\omega_1) - 1]}{c} \quad (7)$$

$$\Delta t_2 = \frac{L + L_c \cdot [n(\omega_2) - 1]}{c} \quad (8)$$

After propagation through the optical system the two electromagnetic waves at the detector surface can be expressed as functions of Δt_1 and Δt_2 which yields:

$$E_1 = A_1 \cos\left[\omega_0 \cdot (t - \Delta t_1) + \frac{1}{2} S \cdot (t - \Delta t_1)^2\right] \quad (9)$$

$$E_2 = A_2 \cos\left[\omega_0 \cdot (t - \Delta t_2) + \frac{1}{2} S \cdot (t - \Delta t_2)^2 - \Omega \cdot (t - \Delta t_2)\right] \quad (10)$$

The time dependent phase of the RF beat note becomes:

$$\varphi(t) = [\Omega + S \cdot (\Delta t_2 - \Delta t_1)]t - \Omega \Delta t_2 + \omega_0 \cdot (\Delta t_2 - \Delta t_1) - \frac{1}{2} S \cdot (\Delta t_2^2 - \Delta t_1^2) \quad (11)$$

The frequency demodulation $2\pi \cdot f(t) = \frac{d\varphi}{dt}$ gives the instantaneous RF frequency $f(t)$ expressed by:

$$f(t) = \frac{1}{2\pi} \left\{ \Omega + S \cdot (\Delta t_2 - \Delta t_1) + S \cdot t \cdot \left[\frac{d}{dt}(\Delta t_2) - \frac{d}{dt}(\Delta t_1) \right] + \omega_0 \cdot \left[\frac{d}{dt}(\Delta t_2) - \frac{d}{dt}(\Delta t_1) \right] - S \cdot \left[\Delta t_2 \cdot \frac{d}{dt}(\Delta t_2) - \Delta t_1 \cdot \frac{d}{dt}(\Delta t_1) \right] - \Omega \cdot \frac{d}{dt}(\Delta t_2) \right\} \quad (12)$$

The expression of the instantaneous beat frequency versus optical frequency is expressed by considering t as a function of ω using Eq. (6): $t = \frac{\omega - \omega_0}{S}$. Time derivatives of the Eq. (7) and (8) yield:

$$\frac{d}{dt}(\Delta t_{1,2}) = \frac{L_c}{c} \frac{dn_{1,2}}{dt} = \frac{L_c}{c} \cdot \frac{dn}{d\omega} \bigg|_{\omega_{1,2}} \cdot \frac{d\omega}{dt} = \frac{S \cdot L_c}{c} \cdot \frac{dn}{d\omega} \bigg|_{\omega_{1,2}} \quad (13)$$

By substituting Eq. (7), (8) and (13) into Eq. (12) with an assumption that the optical frequency is much larger than the AOM frequency shift ($\omega \gg \Omega$) and much larger than the product of the chirp rate (< 1 GHz/ns) and the travel time (~ 10 - 1000 ns range) ($\omega \gg S \cdot \Delta t_{1,2}$), the instantaneous frequency becomes:

$$f(\omega) = \frac{1}{2\pi} \left\{ \Omega + \frac{S \cdot \Delta L}{c} - \frac{S \cdot L_C}{c} \cdot \omega \cdot \left(\frac{dn}{d\omega} \Big|_{\omega-\Omega} - \frac{dn}{d\omega} \Big|_{\omega} \right) + \frac{S \cdot L_C}{c} \cdot [n(\omega-\Omega) - n(\omega)] \right\} \quad (14)$$

The first order Taylor approximation $n(\omega-\Omega) - n(\omega) = -\Omega \frac{dn}{d\omega} \Big|_{\omega}$ applied to Eq. (14) yields:

$$f(\omega) = \frac{1}{2\pi} \left[\Omega + \frac{S \cdot \Delta L}{c} - \frac{S \cdot L_C}{c} \cdot \omega \cdot \left(\frac{dn}{d\omega} \Big|_{\omega-\Omega} - \frac{dn}{d\omega} \Big|_{\omega} \right) - \frac{\Omega}{\omega} \frac{dn}{d\omega} \Big|_{\omega} \right] \quad (15)$$

Since $\omega \gg \Omega$, Eq. (15) is further simplified:

$$f(\omega) = \frac{1}{2\pi} \left[\Omega + \frac{S \cdot \Delta L}{c} - \frac{S \cdot L_C}{c} \cdot \omega \cdot \left(\frac{dn}{d\omega} \Big|_{\omega-\Omega} - \frac{dn}{d\omega} \Big|_{\omega} \right) \right] \quad (16)$$

Excluding the carrier Ω , the instantaneous frequency of the heterodyne beatnote as a function of optical frequency in Eq. (16) provides information on the geometrical path difference between the two interferometer arms (ΔL) as well as on the dispersion occurring in the sample cell. $f(\omega)$ is measured by frequency demodulation of the heterodyne beatnote. The geometrical path difference is easily eliminated by balancing the interferometer arms (setting ΔL to zero), hence removing any offset or baseline contributions to the instantaneous frequency signal. Most importantly, the frequency-demodulated signal contains information on the first derivative of the refractive index spectrum. This term is additionally “amplified” by the product of optical frequency ω and the laser chirp rate S . This significant property can be exploited for sensitive dispersion spectroscopy, especially when pulsed QCLs with fast frequency chirps are used [21].

The amplitude of the heterodyne beatnote is also affected by the sample absorption. The amplitude of both waves can be expressed as:

$$A_{1,2} = A_{01,02} \exp\left(-\frac{\alpha(\omega_{1,2}) \cdot L_C}{2}\right) \quad (17)$$

Thus, the amplitude of the RF beatnote carries the absorption information, which can be extracted by amplitude demodulation of the RF heterodyne beatnote:

$$A(\omega) = 2A_1 A_2 = 2A_{01} A_{02} \exp\left[-\left(\frac{\alpha(\omega) \cdot L_C}{2} + \frac{\alpha(\omega-\Omega) \cdot L_C}{2}\right)\right] \quad (18)$$

The amplitude demodulated signal $A(\omega)$ has similarities with signals expected from a conventional direct absorption spectroscopic measurement. Unlike the dispersion signal encoded in the frequency-demodulated term $f(\omega)$, $A(\omega)$ does not benefit from the fast frequency chirp of the laser source. Additionally, the amplitude demodulated signal is affected by the laser power modulation occurring during the laser frequency chirp (baseline effects) in the same way as in LAS.

3.2. Single-frequency beam configuration

The formalism developed for the dual-frequency beam configuration can be applied to the single-frequency beam case by substituting $n(\omega-\Omega) = 1$ and $\alpha(\omega-\Omega) = 0$. The instantaneous frequency Eq. (16) and the amplitude Eq. (18) as a function of optical frequency become:

$$f(\omega) = \frac{1}{2\pi} \left(\Omega + \frac{S \cdot \Delta L}{c} + \frac{S \cdot L_C}{c} \cdot \omega \cdot \frac{dn}{d\omega} \Big|_{\omega} \right) \quad (19)$$

$$A(\omega) = 2A_1A_2 = 2A_{v1}A_{v2} \exp\left(-\frac{\alpha(\omega)L_c}{2}\right) \quad (20)$$

In contrast to the dual-frequency beam approach in which the frequency-demodulated signal contains the dispersion information through the difference between frequency-shifted profiles of first derivatives of the refractive index, the single-frequency beam configuration allows for the direct observation of a single profile. This might simplify the spectral analysis while still giving the advantage of signal enhancement by the factor $S\omega$.

4. Experimental

4.1. Optical layout and details of the setup

The optical setup is depicted in Fig. 2(a). The laser source is a 5.2 μm distributed feedback QCL operating continuous wave at room temperature. QCL temperature and current are both precisely controlled. The laser frequency is not modulated but only chirped across the molecular transition of interest through fast changes of the injection current.

After collimation, the QCL beam is transmitted through a germanium AOM that can operate between 40 and 50 MHz. The 0th and the 1st order are separated by $\sim 2.2^\circ$ at 45 MHz. The two beams propagate in two distinct optical arms, are recombined by a calcium fluoride beam splitter, and are directed onto a room temperature mercury cadmium telluride photodetector (MCT, model PVI-3TE-10.6 by Vigo Systems). The output signal of the photodetector is fed into a real time RF spectrum analyzer (RSA6106A by Tektronix) which performs frequency and amplitude demodulation of the beatnote.

The 15cm long sample cell, equipped with tilted calcium fluoride windows, was filled with a gas mixture composed of $\sim 1\%$ nitric oxide (NO) in dry nitrogen. The sample was prepared by successive manual dilutions of pure NO. A 1 Torr accuracy pressure gauge was used, which implies a large uncertainty during the dilution process. A conservative error propagation yields a total pressure of 5 ± 2 Torr and the NO partial pressure of 0.05 ± 0.02 Torr. Once filled, the cell is sealed and used throughout the experimental works. The corresponding simulated absorption and dispersion spectra are shown in Fig. 1. The QCL was operated at 115.5 mA and -15°C to target the doublet (transitions 1 & 2), and at 113mA, -20°C to target the single line (non resolved transitions 3 & 4) as listed in Table 1.

4.2. Measurements with linear laser frequency chirp

The cell is positioned in the single-frequency beam configuration [c.f. Fig. 2(a)] and the QCL is operated to target the NO doublet at $\sim 1912.075 \text{ cm}^{-1}$. On top of a constant current, a triangular current modulation (8mA peak-to-peak) is applied to the laser and produces a linear frequency chirp across the transition. To vary the laser tuning rate, the symmetry of the triangular waveform is modified to adjust the rising slope of the modulation. Figure 3 shows the amplitude and the frequency of the RF beatnote recorded with an acquisition bandwidth of 9.76 kHz for four scan speeds: 0.27, 0.53, 0.8, and 1.6 A/s, which correspond to optical tuning rates of 188 Hz/ns, 347 Hz/ns, 523 Hz/ns, and 1043 Hz/ns, respectively. Whilst the amplitude of the absorption dip remains unaffected when varying the tuning speed (only abscissa shrinkage is observed when tuning speed is increased), the frequency-demodulated signal is altered in accordance to Eq. (19). The constant frequency offset due to unbalanced interferometer arms [ΔL in Eq. (19)] and the amplitude of the spectral dispersion signal increases with the laser tuning speed [S in Eq. (19)].

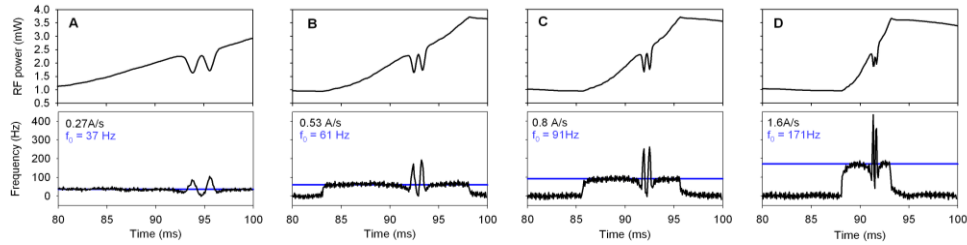


Fig. 3. Amplitude- and frequency-demodulated signals (carrier frequency Ω excluded) when applying a linear laser frequency scan across the NO doublet at $\sim 1912.075 \text{ cm}^{-1}$. Laser chirp rate was varied for each plot: A: 188Hz/ns, B: 347Hz/ns, C: 523Hz/ns, and D: 1042Hz/ns. The blue lines refer to the constant frequency value due to path difference ΔL appearing in Eq. (19).

The spectra shown in Fig. 3(a) and 3(c) are fitted using the forward model described by Eq. (19) and Eq. (20). A non linear Levenberg-Marquardt algorithm, based on the optimal estimation method [23] is used to perform the fitting. The measured data, fitted spectra and fit residuals are shown in Fig. 4. The amplitude-demodulated spectra shown in the upper panel of Fig. 4 are equivalent to typical signals recorded using the direct LAS technique. Therefore, as can be seen in the corresponding residuals, those spectra are affected by variations of the total transmitted laser power which induce baseline fluctuations. This impacts the quality of the concentration retrieval process because, to account for the baseline variation, additional fitting parameters must be incorporated to the forward model. In the plots presented, the baseline was modeled by a third order polynomial (4 additional parameters). In the lower panel of Fig. 4, residual plots show that uncertainties in the frequency-demodulated spectrum have a fundamentally different origin. Ideally the dispersion spectrum is background-free and remains unaffected by the variation of the power reaching the photodetector (c.f. section 5 for more details). Whereas the amplitude-demodulated residuals show low frequency drifts, the frequency-demodulated residuals exhibit random noise. In practice, however, any coherent phase modulation (e.g. produced by interference effects such as Fabry Perot resonances) results in optical fringing that contributes to the background of the frequency-demodulated spectra. Careful optical system design using reflective optics and antireflection coated transmission optics ensures the suppression of unwanted optical interference effects. Those practices are commonly applied in majority of optical systems.

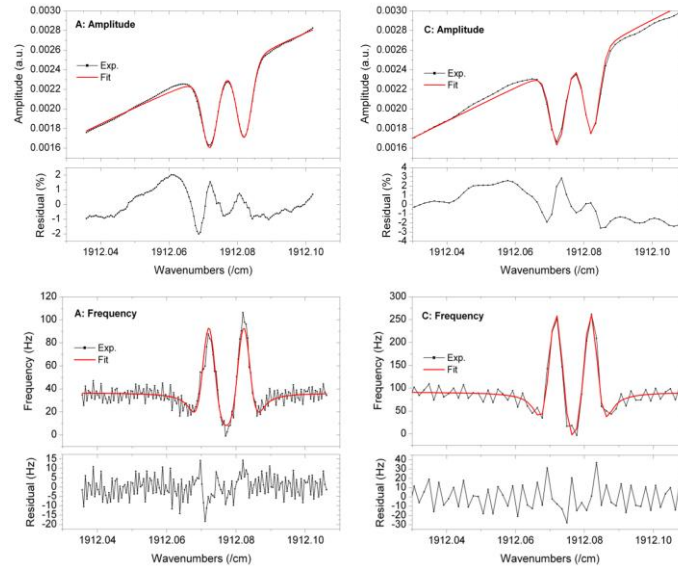


Fig. 4. Amplitude (top panels) and frequency (bottom panels) demodulated spectra of the NO doublet centered at $\sim 1912.075 \text{ cm}^{-1}$. Spectra have been fitted with the model (red line). The spectra presented here corresponds to the data showed in Fig. 4(a) (left column) and Fig. 4(c) (right column).

Table 2. Input parameters used and output parameters returned by the fitting algorithm for calculated spectra appearing in Fig. 4

	Input parameters	Retrieved parameters (amplitude)	Retrieved parameters (frequency)
Tuning rate (Hz/ns)	A: -188 C: -523		
Air path difference, ΔL (cm)	-10 ± 10	N/A	A: -5.8 ± 0.1 C: -5.3 ± 0.1
NO partial pressure, (Torr)	0.05 ± 0.02	A: 0.077 ± 0.008 C: 0.077 ± 0.010	A: 0.066 ± 0.006 C: 0.081 ± 0.007
Total pressure (Torr)	5 ± 2	A: 5.2 ± 1.8 C: 5.0 ± 1.9	A: 5.9 ± 1.7 C: 4.8 ± 1.7

In both cases, residual artifacts located in the vicinity of line positions indicate discrepancies between the modeled and the measured line-shape of the NO doublet. Although studies of the exact spectroscopic line profile are not in the scope of this work, the observed discrepancies are believed to be primarily related to the uncertainty of the sample pressure and the effective line broadening related to scan-to-scan laser power and chirp rate fluctuations. As a second order contribution, the Voigt profile was used in the forward model, which may not be as accurate as, for example, the Galatry or Rautian models. These effects are subject to separate and more detailed study, which will be reported in the future.

The values retrieved by the fitting algorithm, as well as the corresponding uncertainties, are presented in Table 2. In all cases the total pressure and the NO partial pressure were retrieved. For amplitude-demodulated spectra, four additional parameters were retrieved to describe the baseline, and for the frequency-demodulated spectra, the only additional parameter was the air path difference ΔL . Globally, the fit does not improve the uncertainty of the total pressure: uncertainties a priori and retrieved values are almost identical. This is to be expected since the total pressure being low, the line broadening is almost purely Doppler limited and the contribution of collisional broadening from the buffer gas is minimal.

The fitting of the frequency-demodulated dispersion spectrum A in Fig. 4 seems to offer the best retrieval, considering the uncertainty of the NO partial pressure. This is a consequence of the favorable capabilities of dispersion spectroscopy, which is insensitive to power variation, requires less fitting parameters and therefore prevents inter-dependencies between retrieved values. The spectrum C provides an over-estimated NO partial pressure that might be related to the uncertainty of the laser tuning rate and to the limited spectral sampling interval. The latter is related to the demodulation capabilities of the RF spectrum analyzer, which are set by the acquisition bandwidth and the carrier frequency. With a laser chirp of 523Hz/ns and the acquisition bandwidth of 9.76 kHz the spectrum contained only ~6 points per absorption line and the accuracy of the retrieval was compromised.

Despite artifacts, the fitting of the experimental data provides a satisfactory testing of the model describing frequency-demodulated signals, and demonstrates the fundamental differences in the residual noise. Frequency-demodulated spectra already provide better confidence in the retrieved parameters than amplitude-demodulated ones. This advantage should be further enhanced by applying faster laser tuning rates to further increase the amplitude of dispersion signals.

4.3 Application of a fast laser frequency chirp

Since the frequency-demodulated dispersion signal scales with the laser frequency chirp rate, the sensitivity of the spectral measurement could be further improved by increasing the laser frequency tuning speed. Fast single mode frequency scans are generated with electrically driven QCLs [21,24,25]. To demonstrate CLaDS at higher chirp rates, the QCL was operated in a quasi-pulsed operation. A square waveform signal was applied at the modulation input of a CW current source. The 250 kHz modulation bandwidth of the current source determines the highest rate of the laser current change, and thus limits the maximum frequency chirp of the QCL. Nevertheless the highest chirp rates achievable in this way were sufficiently high to create CLaDS signals close to the upper limit of frequency-demodulation capability of the RF spectrum analyzer (maximum acquisition bandwidth of 110 MHz).

When operated in the quasi-pulsed mode, the QCL chirp rate is no longer linear. However, within short time intervals, the chirp rate can be approximated as “locally” linear and the parameter S as constant. With the gas sample removed from the optical path, the frequency demodulation of the heterodyne beat note gives:

$$f(\omega) = \frac{1}{2\pi} \left(\Omega + \frac{S \cdot \Delta L}{c} \right) \quad (21)$$

Therefore by setting the path difference ΔL to a definite value, the frequency demodulated signal provides a way to characterize the evolution of the laser chirp rate.

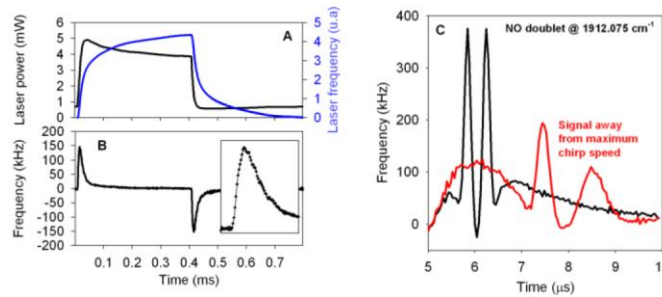


Fig. 5. A: Evolution of the laser power and B: the corresponding instantaneous frequency of the heterodyne signal measured during a square waveform current modulation (8mA amplitude) with no gas sample and for $\Delta L = -5.5\text{cm}$ (carrier frequency Ω excluded). The blue line in plot A is the calculated relative laser frequency evolution within the modulation period. C: NO doublet dispersion signal recorded where the QCL chirp rate is maximum (black) and away from that condition (red).

Figure 5(a) and 5(b) show simultaneous records of the laser power and the instantaneous frequency of the RF heterodyne signal $f(\omega)$ (carrier frequency Ω was excluded), when a square wave modulation is applied with an amplitude of 8 mA and a frequency of 1 kHz. As can be seen in Fig. 5(b), the negative and positive edges of the current modulation produce significant changes in the laser chirp rate, visible as fast changes in the frequency-demodulated signal. At each current rising and falling edge, the absolute value of the chirp rate increases very fast to reach a maximum and then decreases slowly. The frequency of the heterodyne beatnote is proportional to the chirp rate S Eq. (21) defined as the time derivative of the instantaneous laser frequency. Therefore, the integral of the demodulated heterodyne frequency gives the time evolution of the laser frequency while the QCL injection current is modulated. The integration has been performed and is shown in the second (blue) plot of the upper panel [Fig. 5(a)]. Obviously, the optimum condition to perform dispersion measurements is to locate the spectral features under study at the maximum of the laser tuning speed, which means at the top of the peak appearing in the demodulated-frequency record. This optimization can be seen in Fig. 5(c) showing a record of two spectra of the NO doublet (ten averaged scans) at two different positions within the laser scan. By adjusting the QCL DC current, the laser central frequency is modified. The NO doublet can be located at the maximum of the laser tuning speed (black line) or away from the optimum position (red line). The effect of S on the dispersion signal amplitude is highly noticeable.

The QCL chirp rate can be further adjusted by varying the amplitude of the current step. For the optical path difference of $\Delta L = \sim 5.5$ cm, a 16mA current step gives a peak modulation of the heterodyne frequency of 203 kHz, and 24 mA step gives 345 kHz. These values correspond to optical frequency chirps of 1.1 MHz/ns and 1.9 MHz/ns, respectively. With a 16mA square wave current modulation (1.1 MHz/ns peak chirp rate), NO spectra were recorded with the sample cell in the dual-frequency beam configuration. The measured dispersion spectra of the NO transitions at 1912.79cm^{-1} and 1912.075cm^{-1} are shown in Fig. 6(a) and 6(c). Corresponding calculated spectra appear in Fig. 6(b) and 6(d). Although calculations have been performed with the assumption of a purely linear laser frequency chirp, the calculated spectra show good agreement with measurements. The slope in the experimental spectra baseline reveals the non-linearity of the actual laser frequency chirp. The non-zero baseline only exists because of the unbalanced interferometer with $\Delta L = \sim 5.5$ cm that was set for chirp rate determination. An adjustable delay line in the optical system allows zeroing ΔL and the resulting background contribution.

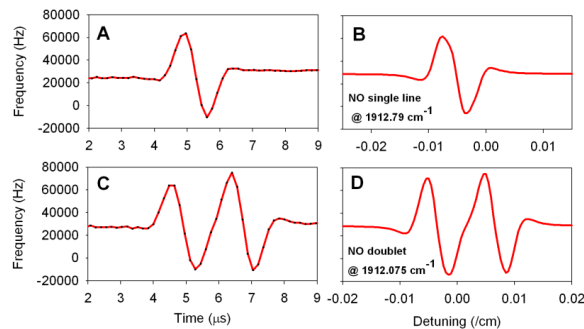


Fig. 6. Frequency demodulated spectra (carrier frequency Ω excluded) recorded when placing the sample cell in the dual-beam configuration. A corresponds to the non-resolved NO doublet (single line) and C to the doublet. The current step was 16 mA, applied at a 100 kHz frequency. The plots B and D are the corresponding calculated spectra.

In Fig. 6, CLaDS signals obtained with dual-frequency beam configuration show lower peak-to-peak amplitudes than those in single-frequency beam configuration. From Eq. (16) describing the dual-frequency beam configuration, the frequency-demodulated signal is proportional to the difference between the two derivatives of the frequency-shifted refractive

index profiles. When the frequency shift Ω between the two $dn/d\omega$ profiles is varied, the peak-to-peak frequency swing of the demodulated signal will be affected. The dispersion signal amplitude, and therefore the signal-to-noise ratio (SNR), will be maximized when the frequency shift is comparable to the spectral linewidth of the probed transition. This optimization process is depicted in Fig. 7.

The spectra in Fig. 7 are calculated for the unresolved NO doublet and a sample total pressure of 5 Torr. The full width at half maximum of the transition is ~ 150 MHz. As the frequency shift Ω increases, the peak-to-trough amplitude of the dispersion signal increases accordingly until the maximum is reached for a shift corresponding to the linewidth (blue line). When the frequency shift is increased further, well above the transition linewidth, the dual-frequency beam configuration loses its specificity and the signal observed corresponds to two separate single-beam traces shifted by Ω . When optimized, the dual-frequency beam approach produces dispersion signals with peak-to-trough amplitudes close to twice the values observed with the single-beam configuration. In the current system, the maximum frequency shift provided by the AOM (50 MHz) is not sufficient to obtain optimum performance for dual-frequency beam configuration with NO. Therefore the analysis of the detection limit has been performed for single-frequency beam configuration only and is presented in the next section.

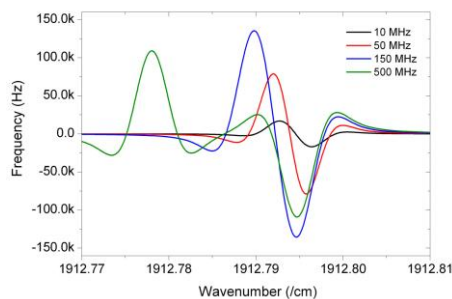


Fig. 7. Calculation of the frequency-demodulated heterodyne signal (carrier frequency Ω excluded) for dispersion sensing in the dual-beam configuration for different frequency shifts Ω . The optimized situation (blue line) corresponds to a frequency shift of 150 MHz, identical to the NO transition linewidth.

4.4. Detection limit

The minimum detectable signal change in the experimental dispersion trace provides an estimate of the molecular detection limit. To perform this measurement, the sample cell is positioned in the single-frequency beam configuration targeting the non-resolved NO doublet at 1912.79 cm^{-1} . The laser is excited by a 14 mA current step and the laser frequency is adjusted so that the transition center frequency coincides with the local maximum in the laser frequency chirp. The baseline (due to unbalanced optical paths) is corrected with a polynomial of the third order and 100 single scans are averaged. The corresponding spectrum is shown in Fig. 8. The signal to noise ratio (SNR) of 240 is estimated by dividing the peak-to-trough amplitude of the signal by the standard deviation observed in the baseline away from the transition.

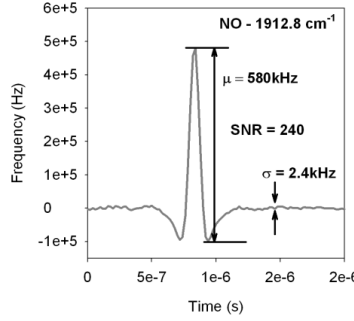


Fig. 8. Dispersion spectrum (single-frequency beam configuration with carrier frequency Ω excluded) of the NO transition at 1912.79 cm^{-1} . The applied current step is 14mA, 100 scans were averaged, and the baseline was corrected by a third order polynomial.

The signal of Fig. 8 is obtained with a mixture of 1% NO in N_2 , a path length of 15 cm and a total averaging time of 1 msec. At the center of the NO transition, the laser chirp rate is quasi-constant (local maximum) and corresponds to 1.2 MHz/ns. From the plot, the SNR is 240. The 1σ (one standard deviation) NO detection limit ($\text{SNR} = 1$) extrapolates to 41.4ppm. If one assumes white noise limited detection, the 1σ detection limit for 1 m path length and 1 s integration time turns into 200 ppb. The white noise assumption up to 1 s integration time has been verified to be valid through Allan variance analysis. The CLaDS system becomes dominated by drift after 10 s, which is an encouraging outcome given that the optical system has not been optimized for temporal stability. Temperature drifts of the AOM crystal were identified to be the primary limiting factor. As a comparison with absorption methods, the 200 ppb limit obtained with CLaDS would correspond to a fractional absorption of $\sim 3 \times 10^{-5}/\text{Hz}^{1/2}$. This result is within the range of routinely obtainable performances for conventional absorption systems, and nonetheless achieved with our non-optimized early demonstrator.

To understand the fundamental limitations of CLaDS applied to molecular detection, and quantify the benefits of the linear dependence of the signal with the laser chirp rate, a detailed analysis of the system noise is required. In CLaDS, the frequency of the heterodyne beatnote comes from FM demodulation even though the laser is not modulated. Contrary to conventional FM used in communications, the interdependence of the CLaDS FM parameters in both time and frequency domains makes the analysis significantly more complex. As the present work focuses on demonstration of CLaDS principles, some of the fundamental limitations are briefly discussed below, and a detailed analysis of noise sources as well as supporting experimental material will be the subject of a separate forth-coming study.

In FM detection of transmitted signals, the SNR is well approximated by [26]:

$$\text{SNR} = 3 \cdot \text{CNR} \cdot (1 + \beta) \cdot \beta^2 \quad (22)$$

where CNR is the ratio of the carrier power to the noise power within the detection sidebands, and the modulation index β is the ratio of the maximum instantaneous frequency deviation of the FM signal Δf to the modulating signal bandwidth B . The noise spectral density at the output of FM detectors shows quadratic dependence with frequency. All parameters of the transmission channel can be set independently so that the increase of Δf or decrease of B directly translates into an improvement of SNR. FM is also known for noise quieting effects or “threshold” effects that are related to the strong dependence of SNR on the CNR Eq. (22).

In CLaDS, SNR enhancement techniques used in conventional FM are not straightforward for two reasons: (1) the interdependence of the frequency demodulated signal parameters, and (2) the structured noise spectrum in the vicinity of the RF beatnote originating from the frequency-shifted laser noise. The latter effect is mitigated as two fully coherent waves beating together reduce the laser phase noise. In CLaDS, both Δf and B are proportional to S

(i.e. faster laser chirp produces larger frequency swing within shorter time). Their independent adjustment being impossible, the modulation index β is not affected by the chirp rate. Because the increase of the chirp rate implies the widening of the detection bandwidth, the CNR is reduced accordingly and impacts the SNR. Therefore, an optimization of the CLaDS detection system must be performed so that adequate power of the RF beatnote improves the CNR, while exploiting the noise quieting effect of FM demodulation. Besides the level of optical power, the optimization is also expected to take into account system parameters such as specifications of the photomixer (e.g. saturation, impedance matching, heterodyne efficiency) and laser noise. Higher chirp rates are nevertheless advantageous as, under white noise assumption, the acquisition time is reduced and spectral scans are averaged more effectively. QCLs possess great chirp rate flexibility, as well as high optical powers and are therefore particularly attractive laser sources for CLaDS.

The early demonstrator presented in this paper operates far from the fundamental noise level and is most likely limited by parasitic interference effects. Evidence of this is found in the spectra presented in Fig. 3 and Fig. 5(c), in which the structured noise observed in the wings clearly shows no consistent dependence on the chirp rate S or on the acquisition bandwidth. Additional evidence will be also discussed in the following section where the CLaDS signal is analyzed in the context of varying optical power.

The optical frequency difference between the two waves (here provided by an AOM) is another important parameter to consider in the optimization of the CLaDS performance. To operate at very high chirp rates the optical frequency shift between the two electromagnetic waves beating together needs to be widened to provide a higher carrier frequency. If one assumes that at least ~ 10 periods of the carrier are required to reconstruct the molecular dispersion profile, it yields a limit on the maximum practical laser chirp rate usable with the given carrier frequency. When the sample pressure is high and collisional line broadening dominates, a greater frequency-shift also provides improved sensitivity in the dual-frequency beam configuration as indicated in Fig. 7.

5. Discussion

5.1. Advantages and drawbacks

The molecular dispersion sensing method that has been described and demonstrated offers three main advantages:

- The measurement of dispersion allows recording of baseline-free spectra without wavelength modulation and without any issues related to residual amplitude modulation. With the sample cell in either configuration, the two optical arms can be balanced so that the measured signal is only sensitive to the refractive index change experienced by either or both beams. With conventional tunable LAS, the signal of interest is a small change of power over a baseline several orders of magnitude greater. In contrast, using the dispersion approach presented here, a full dynamic range and resolution of the acquisition system can be exploited.
- The molecular dispersion information is encoded in the frequency of the RF heterodyne signal. Frequency or time can be measured with extremely high accuracy. Therefore, the measurement of dispersion provides increased robustness compared to signals encoded in amplitude. Particularly, the frequency-demodulated signals are highly immune to laser power variation or pure intensity noise. However, a measurement baseline can still be affected by periodical optical phase variations due to parasitic interference effects, which should be minimized by appropriate optical system design. As a qualitative demonstration of the immunity of molecular dispersion signals to the variation of detected signal power, spectra are measured at absolute RF powers varying over four orders of magnitude. As long as the CNR is sufficiently

high to allow FM detection above threshold, the SNR is primarily limited by the parasitic optical fringes present in the system. Figure 9 shows that, despite a significant power variation, spectra exhibit comparable signal contrasts, which vary between ~ 20 and ~ 28 . The signal contrast is calculated as the peak-to-trough frequency swing divided by the standard deviation of the background noise away from the transition. The frequency-demodulated signal remains mostly unaffected by variation of the received laser power as long as the power of the RF beatnote is sufficiently high.

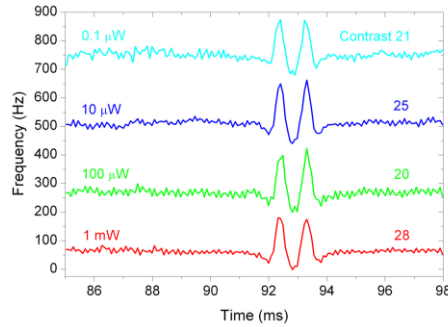


Fig. 9. Molecular dispersion spectra measured for a wide range of detected RF powers (the vertical shift between spectra was introduced for viewing purposes). The signal and noise remain mostly unaffected by a four orders of magnitude RF power variation.

- The amplitude of the FM demodulated dispersion signal is proportional to the laser chirp rate and can be simply modeled. QCLs are particularly relevant as they offer chirp rate flexibility with frequency scanning speeds up to $\sim 260\text{MHz/ns}$ [27] and high optical power to provide high *CNR* required for sensitive FM detection of CLaDS signals. The intra-pulse scanning method [24,25] generates high chirp rates and therefore is appropriate to the measurement method presented here. Yet operation at high chirp rate requires very fast acquisition systems whose large bandwidth measurements are impinged by the quadratic dependence of the noise spectral density at the output of the FM demodulator. High optical power of the source, high heterodyne efficiency and dynamic range of the photomixer maximizes the *CNR*, which offer a way to mitigate noise enhancement effects introduced by large bandwidth operation.

5.2. Potential applications of single- and dual-frequency beam configurations

With the sample cell in the single-frequency beam configuration [c.f. Fig. 2(a)], the frequency-demodulated signal contains the information of the first derivative of the refractive index [c.f. Eq. (19)]. Signal analysis is therefore straightforward, especially when perfectly balanced optical paths ensure baseline cancellation. For this very reason, the single-frequency beam configuration is practical for short optical paths through the sample. For instance, a simple optical delay line would not be sufficient to compensate for long optical paths in multipass cells. The baseline resulting from a large ΔL would affect or even prevent sensitive dispersion measurements. Implementing a permanently referenced dispersion spectrometer is one way of using the single-frequency beam configuration with long-path cells. The two frequency-shifted beams travel separately through two identical cells, one containing a known mixture, the other the sample. In this way the perfect balancing becomes possible, and the observed CLaDS signal references the unknown sample to the calibration mixture.

In the single-frequency beam configuration with an ideally linear frequency chirp rate S , the optical frequency shift between the two beams due to ΔL has no other influence than the provision of a stable carrier [Eq. (19)]. Using a highly linear laser chirp would therefore make

the need for an AOM (or any other frequency shifter) optional, which would simplify the system. In this case the effective carrier frequency originates directly from the fixed frequency term $\frac{S \cdot \Delta L}{c}$ of Eq. (19). The carrier stability requirements place a constraint upon the chirp rate stability. Ideally, the carrier fluctuations need to be below the precision of the frequency demodulation system in order not to deteriorate the quality of the molecular dispersion signals. Hence, for practical applications the requirement of a high level of chirp linearity and chirp repeatability is still challenging.

In the alternate configuration, based on dual-frequency beam propagation through the sample [c.f. Fig. 2(a)], perfect optical path balancing for complete baseline cancellation can be easily achieved as only short compensation paths are required. In this situation, under the approximation of Eq. (16), the demodulated-frequency is proportional to the difference between derivatives of the frequency-shifted molecular refractive index profiles. The observed spectral features are slightly more complex than in the single-frequency beam configuration. On the other hand, given the capability of a straightforward baseline zeroing and the enhanced sensitivity through frequency shift optimization (see the Fig. 7), the dual-frequency beam configuration appears more suitable for development of robust chemical detection systems. Systems based on long-path multipass cells could be easily implemented. Moreover, since the method is immune to intensity variations, it is particularly attractive for long distance standoff detection or open-path monitoring through a medium with varying transmission. The fast scanning over the dispersion feature would also ensure immunity to atmospheric turbulence. Yet, optimized CLaDS at atmospheric pressure would require frequency shifts in the GHz range to accommodate for collisional line broadening. Alternate frequency shifting solutions to mid-IR AOM technology need to be considered. Other frequency shifters, nonlinear difference frequency generation, or optical parametric oscillators will be investigated to address this shortcoming.

6. Conclusion

A novel approach of tunable laser spectroscopy investigating molecular dispersion rather than absorption has been presented. Theoretical models have been developed and demonstrated to well describe the experimental observations. The CLaDS method exploits a fast frequency tuning of the laser source to generate strongly enhanced molecular dispersion spectra. Indeed, the signal containing the information of the change of the molecular refractive index has been shown to scale with the laser chirp rate multiplied by the optical angular frequency. This property, combined with zero-baseline capability and the immunity to intensity variation can be exploited to perform molecular detection at high sensitivity. The method is particularly relevant to mid infrared spectroscopy using QCLs as they can operate in the molecular fingerprint region and produce high chirp rates.

Nitric Oxide diluted in dry nitrogen has been used as the test sample in the initial study to demonstrate the capabilities of the method and verify the theoretical model. A 1σ detection limit of 200 ppb for 1m pathlength and 1s integration time has been extrapolated from the experimental spectra. The performance of the demonstrator is promising given that no systematic optimization was carried out and the main limitation of the system noise originates from parasitic etalon fringes. Higher sensitivities are expected when operating QCLs at higher chirp rates with an optical system designed for low optical fringing and with the heterodyne photodetection enhanced to deliver high RF beatnote power (high CNR). Further studies will be made to evaluate noise sources and to understand the dependence of the CLaDS signal on the laser noise properties (intensity and phase). The influence of laser driving conditions such as the chirp rate stability also needs investigation.

Future directions for the development of the method are numerous. Implementing a system that allows exploiting the highest QCL chirp rates will be an immediate continuation work. This includes detailed studies of the fundamental CLaDS noise limitations, the development

of an ad hoc and high speed frequency demodulation scheme and dedicated spectral analysis algorithms. The tailoring of laser injection current waveforms, which accounts for the QCL thermal response, will be investigated to precisely control the laser chirp rate. Applications will also be developed, which include in situ molecular detection at high sensitivity using long path multipass cells and open path long range monitoring.

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