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Molecular dispersion spectroscopy – new capabilities in laser chemical sensing

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Abstract

Laser spectroscopic techniques suitable for molecular dispersion sensing enable new applications and strategies in chemical detection. This paper discusses the current state-of-the art and provides an overview of recently developed chirped laser dispersion spectroscopy (CLaDS) based techniques. CLaDS and its derivatives allow for quantitative spectroscopy of trace-gases and enable new capabilities such as extended dynamic range of concentration measurements, high immunity to photodetected intensity fluctuations, or capability of direct processing of spectroscopic signals in optical domain. Several experimental configurations based on quantum cascade lasers and examples of molecular spectroscopic data are presented to demonstrate capabilities of molecular dispersion spectroscopy in the mid-infrared spectral region.

1. Introduction

Spectroscopic analysis is one of the most powerful tools used for study of physical, quantum and chemical properties of the matter. The accuracy and precision of spectroscopic analysis benefited tremendously from the application of lasers that were first experimentally demonstrated in 1960 [1] and since then they are extensively used as spectroscopic sources. Laser parameters such as highly monochromatic radiation, high spectral brightness, short laser pulses, or wavelength tunability have enabled wide variety of applications ranging from chemical identification and quantification [2], through studies of non-linear optical phenomena [3], to precise probing of ultra-fast chemical processes [4]. Among all laser based spectroscopic techniques (such as laser induced fluorescence, laser photoacoustics, Raman spectroscopy etc.) laser absorption spectroscopy (LAS) and its derivatives have been by far the most popular and widely used. LAS became popular mainly due to its high-sensitivity (down to pptv, parts-per-trillion by volume) [5], high-specificity and a relatively simple setup. Bandwidth normalized absorption detection limits between $10^{-4}/\text{Hz}^{1/2}$ and $10^{-6}/\text{Hz}^{1/2}$ for the best LAS systems have been reported [5]. LAS spectrometers have been successfully used for chemical sensing both in laboratories as well as in the field [6, 7], especially after compact electrically pumped semiconductor lasers sources have become available [8]. The physics of LAS is well understood (governed by Beer-Lamberts law), which provides a convenient tool for modeling of the experimental results obtained in various configurations including *in-situ* non-destructive sensing [9–11], or remote detection schemes [12].

The implementation of LAS is relatively easy and requires a measurement of the laser power absorbed within a sample. Since this is usually performed by measurement of the total laser intensity transmitted through the sample, some limitations of this process become significant especially in the systems that target high accuracy absorption measurements. The major

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limitations include non-linearity of the Beer-Lamberts law especially for strongly absorbing samples (beyond 10–30% absorption), dynamic range limitations due to quantification of small changes in the total photo-detected laser intensity or due to nonlinearities of the photodetectors, and direct impact of the intensity noise on the measured absorption signal. All those limitations are common to any detection scheme that relies on direct intensity measurements.

Since the absorption process also affects the phase of the electromagnetic radiation transmitted through the sample (dispersion), instead of LAS measurements one can perform phase measurements to retrieve the same spectral information about the sample. Fundamentally, knowledge of the sample's absorption coefficient at all frequencies allows the determination of the sample dispersion by applying the Kramers-Kronig relations [13]. By using an approximation for a weakly absorbing sample the Kramers-Kronig transformation of the absorption coefficient $\alpha(\omega)$ into the sample's refractive index $n(\omega)$ can be expressed as:

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

where c is speed of light and ω the optical angular frequency. This allows a measurement of the refractive index to be modeled using absorption spectra databases.

Experimental approaches that considered detection of the refractive index of the sample in the vicinity of a molecular or atomic transition have already been studied a century ago using only prism and grating spectrometers [14]. By utilizing coherent radiation the sensitivity of those measurements can be significantly improved usually at the cost of higher complexity of the detection systems [15]. Although more challenging than conventional absorption measurements, the measurement of the refractive index (phase) can offer many potential advantages over the absorption sensing. The most significant include: linear relationship between the dispersion spectrum and the sample concentration (unlike absorption that saturates with increasing concentration), phase measurements can be immune to amplitude/intensity fluctuations, and effects of the photodetector nonlinearity can be effectively mitigated in measurements that rely on phase detection instead of amplitude.

2. Example methods capable of dispersion sensing

Most of the currently available measurement methods that give access to refractive index information are based on coherent laser sources and interferometric detection. There are also some techniques that exploit measurement of natural or artificially created sample birefringence which effectively would classify them as dispersion based methods. In the following sections a brief literature overview of four different measurement schemes that give access to or rely on sample dispersion measurement will be provided.

FM spectroscopy

One of the derivative methods of LAS employs high frequency modulation of the laser source and gives access to both absorption and dispersion information. The method known as FM-spectroscopy has been first proposed by Bjorklund [16] and requires application of high frequency modulation at ω_m applied to the laser radiation to produce FM sidebands around the optical carrier. If there is no absorption line coinciding with the carrier frequency the beatnotes originating from the heterodyning between each sideband and the carrier cancel out and give no heterodyne signal at ω_m . However, if the wavelength of the laser is tuned across the target transition, the sideband symmetry is perturbed, which results in a measurable heterodyne signal (see Fig. 1a). Both absorption and dispersion are represented

by the sample's complex transmission function, and can be de-convolved from the demodulated heterodyne beatnote by selecting an appropriate detection phase. FM-spectroscopy shifts the detection to high frequency region which helps avoiding $1/f$ noise. It is a very sensitive method for absorption measurement with bandwidth normalized absorption detection limits reported below $10^{-6}/\text{Hz}^{1/2}$ [17] but the dispersion information is rarely used for molecular sensing. In a typical implementation of this technique both the sample's absorption and dispersion are detected through intensity measurement (as shown in Fig. 1a), thus both measurements are affected by some fundamental limitations that are characteristic for conventional LAS (e.g. performance depends on intensity fluctuations and amplitude noise). Moreover, this technique can only be applied when sample absorption/dispersion is small (see assumptions in [18]), therefore it does not take full advantage of capabilities that are offered by the dispersion sensing (i.e. linear response for wide range of concentrations).

NICE-OHMS

A special case of FM-spectroscopy that also gives access to dispersion information is the noise-immune cavity-enhanced optical heterodyne molecular spectrometry (NICE-OHMS). This technique is essentially a combination of FM-spectroscopy with a high Finesse cavity enhanced absorption spectroscopy. Some recent reports on implementation of NICE-OHMS to molecular spectroscopy in the near infrared (near-IR) and the mid-IR spectral regions have been published in Ref. [19] and Ref. [20] respectively. NICE-OHMS requires rather complex optical system with extremely precise stabilization of multiple active and passive optical components, which makes it impossible to implement outside the laboratory. However due to long effective optical path-length within the sample and high immunity to laser noise, NICE-OHMS spectrometers achieve ultra-high sensitivities (with minimum absorption coefficient detection limits down to 10^{-14} cm^{-1}). Additionally, since NICE-OHMS essentially uses FM-spectroscopy approach for signal demodulation, the extraction of the dispersion signal is prone to the same limitations as the FM-spectroscopy.

Spectroscopy with Optical Frequency Combs

Another group of recently develop methods that allow extraction of information about the sample dispersion are techniques employing optical frequency combs (OFCs). OFCs are pulsed laser sources that emit broadband radiation composed of narrow phase-locked spectral emission lines (comb teeth) that are equidistantly spaced in the frequency domain with spacing dictated by the reciprocal of the pulse repetition interval. Due to mode-locked character of the generated light this pulsed radiation can be considered as a superposition of continuous-wave (cw) frequency teeth components that can be used for coherent detection and extraction of optical phase information. A variety of measurement schemes have been proposed to-date, including: spectrometers based on dispersion gratings and other dispersive elements [21], dual-comb heterodyne detection [22] or OFC-based Fourier transform spectroscopy [23]. Multiple coherent detection schemes for applications in molecular spectroscopy have been reported (an example implementation using dual-comb heterodyne detection together with a general concept of operation principle are shown in Fig. 1b and Fig. 1c). OFC-based techniques provide very high frequency precision and bandwidth normalized absorption detection limits at the $10^{-4}/\text{Hz}^{1/2}$ level (e.g. in the cavity enhanced OFC spectroscopy reported in [24] the noise estimated in the cavity transmission spectrum was at the level of $7.1 \times 10^{-4}/\text{Hz}^{1/2}$ which translates to minimum detectable absorption coefficient of $5.4 \times 10^{-9} \text{ cm}^{-1}/\text{Hz}^{1/2}$ when cavity enhancement is taken into account). Coherent detection schemes also give access to the sample's dispersion information [25–27], but similarly to FM spectroscopy, the dispersion detection is rarely used for sensing. Moreover, due to extremely high complexity of the optical setups their applications are limited only to highly specialized optical laboratories.

Faraday Rotation Spectroscopy

One spectroscopic method that relies on molecular dispersion measurement and can be used outside specialized laboratories is Faraday Rotation Spectroscopy (FRS). FRS is one of the special cases of dispersion sensing that uses magnetically created circular birefringence of the sample to induce the Faraday Effect [28, 29]. The Faraday Effect manifests itself as the rotation of polarization axis of linearly polarized light transmitted through the sample, which is subsequently measured in FRS systems. FRS requires magneto-optical activity of the sample and thus can only be applied to paramagnetic species. The polarization rotation measurement is essentially a measurement of optical phase shift that originates from a difference between refractive indices for the right-handed and left-handed circularly polarized wave components propagating through the sample. Thus effectively the FRS is a dispersion-based measurement which provides many valuable features that are not available with standard absorption based techniques.

We have studied FRS extensively [28–31] and demonstrated several transportable and portable autonomous cryogen-free FRS systems both in near-IR and mid-IR. A typical schematic of an optical setup for FRS is shown in Fig 2. In the FRS system employing a direct photodetection with a single detector element, the amount of power transmitted by the second (nearly crossed) polarizer is usually very small. Therefore further enhancement of the signal-to-noise ratio (SNR) can be achieved by applying more sensitive photodetection techniques. After application of a heterodyne-enhanced detection scheme the photodetection sensitivity in the FRS system was significantly improved to the levels that are close to the fundamental shot noise limit [30]. A spectrum of nitric oxide (NO) acquired with the heterodyne-enhanced FRS system operating at $5.25\mu\text{m}$ is shown in Fig. 3. The analysis of the SNR provides the noise equivalent detectable polarization rotation angle of 2.6×10^{-8} rad/ Hz, which for this particular system (15 cm total optical path) corresponds to the difference in refractive index for right- and left-handed polarizations at the level of $\sim 1.5 \times 10^{-13}$ / Hz. Besides ultra-high sensitivity (e.g. an effective bandwidth normalized absorption detection limit of 5.9×10^{-8} Hz $^{-1/2}$ was reported in [32]) FRS also provides high dynamic range of concentration measurements as expected for dispersion based sensing technology. It was shown in Ref. [28] that concentration measurements ranging from single ppbv up to 10ppmv levels of NO could be detected with no signal saturation and with no impact on the actual precision of the FRS system.

3. Direct measurement of molecular refractive index and applications

As shown above dispersion sensing has a potential for sensitive and high dynamic range chemical detection. However, the existing methods that are capable of dispersion sensing show some limitations and none of them is truly comparable to conventional LAS in terms of simplicity, functionality and ease of application. For example the cost and complexity of frequency comb spectroscopy is too high to use it for basic trace-gas sensing, applications of NICE-OHMS are practically limited to laboratory experiments, FM spectroscopy relies on light intensity detection which carries limitations of standard absorption-based techniques, and FRS, although very practical, can only be applied to paramagnetic species. Therefore a new sensing scheme that is capable of measuring molecular dispersion with relatively simple and robust setup has a potential to overcome some of these drawbacks and provide advantages of dispersion spectroscopy. Such attempts have been made in the past but only a small progress has been made in adoption of proposed techniques to sensitive trace-gas detection in non-laboratory conditions [15, 33–39]. Recently we have introduced a new chirped laser dispersion spectroscopy (CLaDS) technique that relies on molecular dispersion sensing in the gas sample [40] and the system itself can be easily adopted for field measurements [41]. The following sections provide details about fundamentals, unique capabilities, and potential applications of CLaDS and related technologies.

Direct CLaDS

The schematic diagram of CLaDS system is shown in Fig. 4. It uses a single-frequency laser source that is frequency chirped across the molecular transition of interest. Laser radiation is directed through an acousto-optical modulator (AOM) that shifts the frequency of light by Ω . Two beams (the fundamental 0th order beam and the frequency-shifted 1st order beam) are combined into one dual-color beam using Mach-Zehnder arrangement. The dual-color beam is focused on a fast photodetector and a heterodyne beatnote between the two waves is measured and analyzed. The measured sample can be located either inside the interferometer ('Configuration 1') or after the beam combiner ('Configuration 2'). 'Configuration 2' is also suitable for multi-pass cell arrangements or remote long-distance open-path sensing. The dispersion in the sample gas has slightly different effect on the propagation of the two light waves. It results in a difference in propagation times Δt for the two frequency-shifted waves, which affects the frequency of the measured heterodyne beatnote and changes it by $S \cdot \Delta t$, where S is the chirp rate that additionally enhances the dispersion signal. By performing frequency-demodulation of the beatnote while the laser is chirped, a dispersion spectrum encoded into frequency of the heterodyne beatnote can be retrieved, which is given by [40]:

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

where ΔL is path length difference between Mach-Zehnder interferometer arms, L_c is the path-length within the sample and n is the refractive index of the medium. The amplitude of the measured dispersion line (third term in the Eq.2) is proportional to the chirp rate S and to the spectral derivative of the sample refractive index. The latter is proportional to the sample concentration, which allows for quantitative chemical detection.

The beatnote is frequency-demodulated at the carrier Ω (which is typically in radio frequency range) and in addition to optical dispersion information about ΔL can also be retrieved. In case of molecular dispersion sensing the contribution due to path difference ΔL is excessive and can be suppressed by balancing the arms of the Mach-Zehnder interferometer (e.g. by using an optical delay line). Hence, when $\Delta L = 0$ the FM-demodulation provides virtually a baseline-free information on molecular dispersion. This is the simplest and the most straightforward way of direct signal recording in CLaDS (direct-CLaDS).

Due to nonlinear frequency chirping (which is typically observed with both cw and pulsed laser sources) direct-CLaDS requires precise chirp characterization before quantitative data can be recorded. This can be performed either with an etalon inserted into optical path and subsequent fringe analysis or by setting $\Delta L = 0$ which enables recording of a baseline signal that is proportional to the chirp rate [40]. When the chirp rate is known the recorded dispersion spectrum can be fitted with a model spectrum in order to retrieve parameters of the sample. Since the relation between the sample absorbance and its dispersion is known (see Eq. 1), direct CLaDS provides the same modeling capabilities as conventional absorption spectroscopy. Spectral information related to concentration, pressure broadening or temperature are all encoded in the profile of the dispersion feature and can be retrieved using spectroscopic modeling. An example of such a dispersion fitting that uses parameters from the HITRAN database and the plasma dispersion function (Voigt line profile) for calculation of the CLaDS spectrum is shown in Fig. 5. For this experiment a Quantum Cascade Laser (QCL) operating at 5.2 μm was used to target ro-vibrational transition of NO. A gas sample (850 ppm of NO in N_2 , total pressure of 6 Torr) contained within a 10-cm-long cell was placed in 'Configuration 2' arrangement. By spectral fitting of the recorded data the concentration of NO and the total sample gas pressure were retrieved. Through precise balancing of the interferometer arms ($\Delta L = 0$) a baseline-free CLaDS spectrum was

recorded. This is a significant advantage over the direct LAS detection that requires extracting useful spectroscopic signal from a high and often fluctuating intensity background. Other important properties of the signal in CLaDS are a linear dependence of its amplitude on concentration [42] and its immunity to changes in photodetected intensity. Since the dispersion spectrum is retrieved through FM-demodulation (measurement of the heterodyne beatnote frequency), the intensity (amplitude) has no impact on the measured spectroscopic signal and only a minor effect on the SNR. As shown in Fig. 5, the peak-to-peak amplitude of CLaDS spectrum is not affected and the SNR remains nearly the same even in the presence of significant (few orders of magnitude) changes in the RF beatnote power (see Ref. [40] for details).

An important challenge in direct-CLaDS is selection of an optimum chirp rate that will provide the highest possible SNR. The measured CLaDS signal can be additionally enhanced by increasing the chirp rate S , which, in case of semiconductor lasers, can easily reach values above 10^{15} Hz/s. Unfortunately, as shown in Fig. 6, an increase of S in addition to signal ‘amplification’ ($\propto S$) also results in an increase of noise ($\propto S^2 + S + \text{const.}$). As a consequence there is an optimum chirp rate for which maximum SNR occurs in direct-CLaDS measurement. This optimum chirp rate depends on relative contribution from different sources of noise, mainly from optical fringes and from FM-demodulation noise. Therefore an individual optimization should be performed for each particular CLaDS system (detailed analysis of SNR in CLaDS can be found in Ref. [43]).

Chirped-modulated CLaDS

Direct-CLaDS, although relatively simple in experimental implementation and modeling, shows some important limitations. In order to provide stable baseline-free signal it requires additional mechanical stabilization of the optical setup. Otherwise vibrations and mechanical drifts that create imbalance of the interferometer ($\Delta L \neq 0$) can produce uncontrolled baseline fluctuations in the measured spectrum. Moreover, in the direct-CLaDS laser frequency needs to be chirped across the frequency range that is significantly wider than the measured transition width to capture potential baseline drifts. This might be challenging in case of open-path sensing when typical linewidths are larger than 3 GHz. In order to increase sensitivity of CLaDS and enable truly baseline-free detection even in atmospheric conditions (i.e. open path measurement) we have developed a new detection scheme based on chirp modulation. In a chirp-modulated CLaDS (CM-CLaDS) laser current is modulated with sinusoidal signal at frequency f which produces sinusoidal modulation of the chirp rate. The dispersion spectrum is also encoded in the frequency of the beatnote, but only harmonics of the chirp modulation frequency (i.e. $N \times f$, $N = 1, 2, 3, \dots$) need to be analyzed. Because of that, the FM-demodulation bandwidth can be significantly reduced, which results in lower FM-demodulation noise. Moreover, even if the imbalance of the interferometer exists ($\Delta L \neq 0$) it only produces baseline in $1f$ spectrum. Therefore by targeting higher harmonics the baseline is suppressed. The most desirable harmonics are $3f$ for ‘Configuration 1’ or $2f$ for ‘Configuration 2’. In both cases CM-CLaDS signal reaches maximum at the line center and its amplitude can be directly converted into target analyte concentration after initial calibration of the system. In Fig. 7a a sample $2f$ spectrum acquired in ‘Configuration 2’ is presented. It was recorded in open-path arrangement with $4.54\mu\text{m}$ QCL used as a spectroscopic source to perform detection of nitrous oxide (N_2O). Laser beam from CLaDS setup was directed towards a distant (placed 35 meters away) retroreflector and the returning light was collected onto a photodetector. The $2f$ CM-CLaDS spectrum of N_2O is indeed baseline-free, which allows for continuous concentration monitoring provided the laser is locked to the center of the target transition.

Shown in Fig. 7b is an example of time series recorded for continuous monitoring of N_2O concentration. The peak of the $2f$ CM-CLaDS signal amplitude at line center was measured

continuously and two gas samples ($\text{N}_2\text{O}/\text{N}_2$ mixture or dry nitrogen) were alternately flown through a 10-cm-long optical gas cell. Preliminary results show that by reducing FM-demodulation noise, the CM-CLaDS technique can provide at least one order of magnitude improvement of the instrument sensitivity with respect to direct-CLaDS. Moreover, it enables concentration monitoring with no need for real-time fitting of the recorded spectra. For the prototype sensor (with a 15 cm sensing path) we have determined the minimum detection limit to N_2O of 120 ppbv-m/ $\text{Hz}^{1/2}$ which corresponds to an equivalent minimum detectable fractional absorption of $2.4 \cdot 10^{-4} \text{ Hz}^{-1/2}$. This is within a range of performance reported for conventional LAS systems and OFC based spectrometers. Since CLaDS is in the very early stage of its development further improvements such as suppression of parasitic fringe noise [43], or generation of optimal frequency shift [40] are expected to provide sensitivity enhancement, improved stability of the system [44] and reduction of the system complexity. Up to now a relatively small complexity of the CLaDS system, ease of application, ability to measure optically thick samples and immunity to intensity/transmission fluctuations have already proved to be helpful in overcoming the biggest drawbacks of standard absorption-based methods or FM-spectroscopy, and allowed first field deployments of the prototype system [45].

Differential Optical Dispersion Spectroscopy (DODiS)

Dispersion spectroscopy, due to its unique properties, can also provide entirely new capabilities in trace-gas detection. Differential optical dispersion spectroscopy (DODiS) is a new generation of spectroscopic measurement method that builds upon CLaDS approach and enables true optical subtraction or addition of spectroscopic signals [46]. In DODiS (optical layout shown in Fig. 8a) two gas samples are separately placed in the two arms of the interferometer. In one arm the laser beam first passes through one gas sample and then is frequency-shifted and combined with the second beam (that interacts with the second gas sample) on a beamsplitter. The combined beams are focused on the photodetector. Similarly as in the CLaDS an FM-demodulation of the heterodyne beatnote is performed in order to retrieve the target dispersion profile and an AM-demodulation can be used for absorption signal retrieval. Because the frequency shifter is located after the gas sample cell, both samples are probed with the light at the same optical frequency. Therefore the demodulated signal corresponds to an actual difference in propagation time through both gas cells. As a result DODiS enables direct detection of a difference between dispersion spectra of both samples. Such a subtraction of two spectroscopic signals is performed entirely in the optical domain and does not require samples to be measured separately. At the same time the AM-demodulated absorption spectra are additive, which provides optical summing.

In Fig. 8b an example of N_2O measurement using DODiS is presented. In this experiment the gas cell #2 was filled with approximately 90 ppm of N_2O (balanced with nitrogen). The concentration in cell #1 was varied (from more than 200 ppm to almost zero) and DODiS dispersion signal was measured and processed. The recorded spectra were fitted using HITRAN database and information on concentration difference ($C_{\text{sample1}} - C_{\text{sample2}}$) was retrieved. DODiS enables direct detection of concentration difference which can be particularly useful in all kinds of measurements where two gas samples need to be compared, e.g. in isotopic ratio measurement. Because the amount of molecular dispersion changes linearly with molecular concentration, differential detection with DODiS can be performed even for highly absorbing (>10–30% absorption) samples. This enables increased sensitivities by using extended optical paths, which might cause saturation effects if standard absorption-based methods are used. DODiS also allows for selective cancelation/suppression of unwanted background that can interfere with the spectral feature of the target analyte [46].

4. Conclusions

For several decades laser-based trace-gas sensing instrumentation have proven to provide highly sensitive and selective chemical detection. However, in order to meet challenging demands of new applications that require even higher dynamic ranges improved stability and increased robustness, new detection schemes are needed. As discussed in this paper, recent developments in the area of molecular dispersion sensing are very promising and show potential in overcoming the drawbacks of conventional technologies while preserving most of their advantages that include simplicity and ease of operation. Specifically CLaDS translates the spectroscopic detection from intensity/amplitude domain to a measurement performed in frequency domain which provides increased stability, and immunity to amplitude noise. It offers multiple new sensing capabilities that are not accessible by traditional techniques such as linear response and higher dynamic range of concentration measurements. In addition to improvements with respect to existing LAS systems, the molecular dispersion measurement provides unique advantages of spectroscopic signal processing directly in optical domain (i.e. spectral addition or subtraction) which has been demonstrated with DODiS. In this paper we have presented example data that should demonstrate some of the unique capabilities of spectroscopic techniques that rely on dispersion measurement. The first prototypes of CLaDS-based instruments have already been used in early field deployments [45], which indicates the technological feasibility for real-world molecular sensing applications.

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Fig. 1.

a) An experimental arrangement for FM spectroscopy with its frequency domain illustration (from Ref. [18]). $\Delta\delta$ and $\Delta\phi$ represents attenuation (due to absorption) and phase shift (due to dispersion), respectively, of the sideband at $\omega_c + \omega_m$ with respect to carrier at ω_c . δ denotes attenuation of the sideband at $\omega_c - \omega_m$ with respect to carrier at ω_c and is assumed to be constant. Absorption and dispersion spectra are retrieved from the light intensity $I(t)$ as its in-phase and quadrature components (see details in Ref. [16, 18]); b) an experimental layout for dual-comb spectroscopy (from Ref. [27]). A signal comb and a local oscillator (LO) comb are phase locked and have slightly different repetition rates. Beating them with each other enables down-converting of the optical information carried by each signal comb tooth to the distinct RF frequency. Absorption and optical phase change can be retrieved from the amplitude and the phase of the RF beatnotes; c) absorption and refractive index spectra of acetylene measured using dual-comb spectrometer (from Ref. [27]).

Fig. 2.
A typical experimental set-up for FRS.

Fig. 3.

Spectrum of NO R(8.5)e transition acquired with heterodyne-enhanced FRS. Experimental conditions: NO concentration 2 ppm-v, sample pressure 30 Torr, sample temperature 300 K, magnetic field ~100 Gauss, optical path length in Faraday cell $L = 15$ cm, optical power before analyzer $P_0 = 14$ mW, local oscillator (LO) power $P_{LO} = 0.5$ mW, and detection bandwidth of 0.83 Hz [30].

Fig. 4. Optical layout for CLaDS (AOM – acousto-optical modulator, RF – radio frequency, ODL – optical delay line).

Fig. 5.

(a) An example of a model CLaDS spectrum fitted to the data recorded with a direct CLaDS detection scheme. Line-by-line spectral calculation based on HITRAN database was used to model the NO spectrum around 1906 cm^{-1} ; (b) Molecular dispersion spectra measured in 'Configuration 1' for wide range of detected RF powers (spectra are shifted vertically for viewing purposes, RF power is shown next to each spectrum). Signal amplitude is unaffected even when RF beatnote power changes by four orders of magnitude (measured transitions is NO doublet at 1912.08 cm^{-1}) [40].

Fig. 6.

(a) Four spectra showing NO doublet around 1905.2 cm^{-1} recorded for different chirp rates (sample pressure was 10 Torr; spectra are offset laterally for viewing purposes). As expected from Eq. 1, the CLaDS signal amplitude is proportional to the chirp rate; (b) A general dependence of the signal and noise on the chirp rate results in an optimum chirp rate that is required to achieve the best SNR.

Fig. 7.

(a) 2fCM-CLaDS spectrum of N₂O line measured in remote sensing arrangement ('Configuration 2'). Experimental conditions: ambient air, total optical path of 70 m; (b) a continuous monitoring of N₂O concentration was performed by recording CM-CLaDS 2f signal at the N₂O line center (experimental conditions: 100 Torr pressure, 10 cm optical path).

Fig. 8.

(a) An optical arrangement of DODiS. The AOM is placed after the gas sample #2, which is a key difference with respect to CLaDS (when AOM is placed before gas sample the light interacting with each sample has slightly different frequency shifted by Ω , thus dispersion spectra from the two samples measured at the beatnote frequency cannot be fully subtracted); (b) example of differential measurement of two samples, both containing N_2O mixture at total pressure of 60 Torr (target transition was N_2O line at 2209.52 cm^{-1}) [46].