Experimental-based comparison between off-axis integrated cavity output spectroscopy and multipass-assisted wavelength modulation spectroscopy at 7.7 µm

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Abstract: A mid-infrared trace gas detection system based on off-axis integrated cavity output spectroscopy (OA-ICOS) is demonstrated for accurate and sensitive detection of N\textsubscript{2}O in combination with a continuous wave external-cavity quantum cascade laser (EC-QCL) working around 7.7 µm. A 13-times improvement in signal-to-noise ratio is achieved using a re-injection mirror and a minimum detection limit of 70 ppbv in less than 10 s averaging time is achieved, which yields a noise-equivalent absorption sensitivity (NEAS) of 6×10^{-9} cm\textsuperscript{-1} Hz\textsuperscript{-1/2}. For comparison, a compact multipass cell is deployed to measure the same absorption line of N\textsubscript{2}O using wavelength modulation spectroscopy with second harmonic detection (WMS-2f). An enhancement factor of 20 in comparison to direct absorption spectroscopy (DAS) is achieved, yielding a minimum detection limit of 15 ppbv in less than 10 s averaging and a NEAS of 1×10^{-9} cm\textsuperscript{-1} Hz\textsuperscript{-1/2}.

A comprehensive comparison between the two systems is carried out in terms of residual amplitude noise (RAM), linearity, long-term stability, detection limit, spectral fitting, reproducibility, and background variations. The proposed sensor based on OA-ICOS is potentially advantageous for trace gas sensing in outdoor applications and harsh environments due to its robustness and flexibility of alignment.

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1. Introduction

Recent advances in laser sources and optical detectors in the mid-infrared wavelength region (mid-IR, 2-20 µm) have drastically enhanced the sensitivity of trace gas detection. The fundamental ro-vibrational transitions of most of the molecules are in the mid-IR wavelength region, which yields strong absorption line strengths resulting in low detection limits using absorption spectroscopy [1–3]. Major research efforts have been focused towards simple, portable and low-cost optical gas sensors with trace gas sensitivities ranging from parts-per-billion (ppbv, 1:10\textsuperscript{9}) to parts-per-trillion (pptv, 1:10\textsuperscript{12}) levels at sub-second time scale [4–6]. These highly sensitive sensors are utilized for many applications in different fields of research such as environmental monitoring [5,7] and medical breath analysis [3,8,9].

Nitrous oxide (N\textsubscript{2}O) is amongst the greenhouse gases responsible for global warming and it is a precursor of nitric oxide (NO) in stratospheric chemistry [10]. N\textsubscript{2}O has a volume mixing ratio of ∼ 300 ppbv in the troposphere and is increasing at an undesirable fast rate of ∼ 0.7 ppbv per year [11,12]. Considering its impact on the environment, sensitive detection of N\textsubscript{2}O with high precision and accuracy is essential for more in-depth investigations. This can be performed by spectroscopy in the mid-IR region, where the absorption cross-section of N\textsubscript{2}O is more than four orders of magnitude higher compared to the near-infrared region (near-IR, 1-2 µm).

Quantum Cascade Lasers (QCLs) [13] allow direct access to the fundamental ro-vibrational bands of numerous molecules in the mid-IR, including N\textsubscript{2}O. Their compactness, commercial
availability, and durability are key advantages for field deployment compared to other mid-IR sources, which are usually based on nonlinear frequency conversion (e.g. optical parametric oscillators, and difference frequency generation). In principle, QCLs can be fabricated at any wavelength between 4.6 \(\mu m\) \([14]\) to 24 \(\mu m\) \([15]\) by changing the configuration of the semiconductor layers. In order to probe a single absorption line, single mode operation is highly desirable which is typically achieved by a Distributed Feedback (DFB) structure connected to the QCL gain region (DFB-QCLs). Although DFB-QCLs show single-mode performance, they suffer from a limited tuning range. A DFB QCL can be tuned either via current injection over 2-3 cm\(^{-1}\) (fast) or via temperature tuning over 15-20 cm\(^{-1}\) (slow). Due to the narrowband spectral operation of the DFB-QCLs, they are designed for a specific wavelength to detect one (or possibly two) molecular species. To overcome these limitations, an External Cavity (EC) along with a diffracting grating is used to extend the wavelength tuning of the QCL. It provides the flexibility to choose any wavelength within the full gain bandwidth of the QCL (typically 200-300 cm\(^{-1}\)). An EC-QCL enables wide scan operation with high spectral resolution, which is only limited by the laser linewidth \([16]\). To tune the EC-QCL very precisely in a narrowband scan operation, a piezo actuator (PZT) can be mounted on the top of the diffraction grating to provide fast fine-tuning. In the narrow-scan mode, EC-QCLs are used in the same way as a typical tunable diode laser or a DFB laser. Therefore, a single source is enough to target several narrow lines and/or broadband absorbing molecules within its spectral coverage with good precision and resolution. Due to these characteristics, EC-QCLs are highly attractive for gas-phase spectroscopy.

Both, DFB-QCLs and EC-QCLs have been deployed for trace gas detection in combination with sensitive spectroscopic detection schemes that rely on modulation (e.g. Wavelength Modulation Spectroscopy, WMS \([17]\), Frequency Modulation Spectroscopy, FMS \([18]\)), cavity enhancement (e.g. Cavity Ring-down Spectroscopy, CRDS \([19,20]\), Off-Axis Integrated Cavity Output Spectroscopy, OA-ICOS \([21,22]\)), or a combination of both (e.g. Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy, NICE-OHMS \([23]\)). Among these methods, OA-ICOS is rather easy to implement while yielding the high sensitivities required for trace gas detection. OA-ICOS offers an increased light-matter interaction path length and thus detection sensitivity, comparable to CRDS, with less experimental complications such as precise mode matching of the laser beam to the enhancement cavity or locking of the cavity to the laser (e.g. Noise Equivalent Absorption Sensitivity, NEAS of \(10^{-10} - 10^{-11} \) cm\(^{-1}\) Hz\(^{-1/2}\) \([24,25]\)). In addition, the measurements are less time consuming (no step-by-step sequence) and data can be acquired in a fast and robust way using fast optical detectors and control electronics.

In a typical OA-ICOS set up, the laser output is coupled to the optical cavity and its absorption spectrum is extracted from the time-integrated light intensity of the cavity output as a function of the wavelength of the laser. In the on-axis configurations, the laser beam is coupled, and dynamically stabilized, to the cavity by exciting one of the longitudinal cavity modes (usually TEM\(_{00}\)). However, such coupling of the laser frequency to a cavity mode generates optical intensity noise due to the insufficient locking bandwidth and the residual laser-cavity frequency fluctuations. In addition, the laser optical frequency and the cavity mode need to be scanned together over the absorption line to map the absorption spectrum.

Contrary to on-axis configuration, the beam can be coupled in an off-axis configuration that allows spontaneous pumping of a family of the cavity modes (transverse and longitudinal). The off-axis coupling of the beam produces Herriott/ elliptical or circular spot patterns \([26]\) on the cavity mirrors. The Free Spectral Range (FSR) of the cavity collapses to FSR\(_{\text{eff}} = c/(2mL)\); where \(c\) is the speed of light, \(L\) is the cavity length and \(m\) is the number of the passes before the re-entrant condition is reached. Consequently, any continuous wave (CW) laser source having linewidth broader than FSR\(_{\text{eff}}\) of the cavity (\(\Delta v > \text{FSR}_{\text{eff}}\)) will couple to several cavity modes at once. Therefore, the transmission intensity of the optical cavity while scanning the laser frequency or the cavity length is smoothed, and eventually, the transmission intensity will be
virtually flat. Thus the cavity transmission can be averaged effectively which leads to lower noise levels and improved sensitivity [25,27]. Such laser-cavity alignment is very robust, less sensitive to input coupling changes and mechanical vibrations, yielding a suitable scheme for field measurements.

In general, mid-IR detectors have 1-3 orders of magnitude lower detectivity (D*) as compared to near-IR detectors [28], requiring higher optical intensity in order to compensate for the higher detector noise. This is more pronounced for OA-ICOS since a tiny portion of the input power is transmitted through the cavity in the off-axis configuration. For instance, an optical cavity with a 99.98% reflectivity pair of mirrors only transmits ∼0.01% of the laser power in the off-axis configuration [25,29,30]. As a result, it is very challenging to overcome the tradeoff between the effective optical path length (due to the enhancement cavity) and the transmitted optical power reaching the mid-IR detector, except for using high power lasers. Additionally, the quality of the cavity mirrors is lower in mid-IR compared to the near-IR region, with typical absorption and scattering losses > 500 ppm in the mid-IR [20]. A possible way to couple more light into an enhancement cavity in the off-axis configuration, and thus enhance the transmitted power, is to re-inject the back-reflected light from the first cavity mirror with an additional third mirror. This so-called re-injection mirror is placed in front of the first cavity mirror. Initially, the laser beam travels through a small hole in this re-injection mirror. While a significant portion of the laser power is reflected from the first cavity mirror, this power can still be injected back into the cavity by the re-injection mirror increasing the cavity transmission by more than an order of magnitude [20,30].

High detection sensitivities can also be achieved using modulation techniques (e.g. frequency or wavelength modulation, FM/WM). In particular, wavelength modulation spectroscopy (WMS) in combination with a multipass absorption cell and higher harmonic detection is a well-suited approach to effectively reduce the noise in laser-based spectroscopy [31]. In WMS, the laser wavelength is modulated by a sinewave (kHz to MHz) and the modulated laser wavelength is swept across the absorption feature of interest. The detected transmitted intensity is demodulated by a lock-in amplifier, where the detected signal is multiplied with a reference signal (adopted from the original modulation signal) and is low-pass filtered. Therefore, the 1/f noise in the system is effectively suppressed and a higher detection sensitivity is achieved. The reference signal is usually the same as the modulation sinewave or its higher harmonic.

For WMS, 2nd harmonic (WMS-2f) detection is usually preferred due to the fact that the 1st harmonic (WMS-1f) is affected by a linear background [32,33]. In WMS-2f, the detected signal is increased by increasing the modulation amplitude (∆ωL) up to 2.2 times of the Half Width Half maximum (HWHM, Γ) of the absorption profile (∆ωL ≈ 2.2Γ). Consequently, to achieve the highest signal to noise ratio (SNR), the best ratio of the modulation amplitude and absorption linewidth is around 2.2 [34]. WMS can be also calibration-free when the second harmonic (2f) is normalized to the first harmonic (1f) signal [35]. It can also be extended to the tunable modulation amplitudes to target broader and narrower features of the absorption molecules. In EC-QCLs the wavelength can be rapidly modulated using the injection current, while simultaneously being scanned across the absorption transition of the molecule via the PZT actuator in the external cavity [36].

Previous publications compared WMS and Direct Absorption Spectroscopy (DAS). Lins et al. show a simulation-based comparison of the noise effects in tunable diode laser based DAS and WMS. It was theoretically shown that the noise effects in DAS are higher as compared to WMS [37]. Hancock et al. show a comparison between DAS and WMS using a CW EC-QCL in combination with a 10 cm single pass cell at a wavelength of 5.2 μm [34]. Pakmanesh et al. combined two optical cavities, an optical cavity for OA-ICOS and 20 cm long single pass cell for WMS (2f/1f) at a wavelength of 4.6 μm, for the detection of the exhaled CO [14].
Previously, WMS and OA-ICOS have been successfully applied in the detection of N$_2$O in combination with mid-IR QCLs [1,38]. In this work, we utilize a home-built EC-QCL laser, operating between 7 and 9 µm, in an OA-ICOS configuration with a re-injection mirror (effective path length of 14-meter) and compare it to a WMS-2f system with a multipass cell (effective path length of 76-meter) for detection of N$_2$O. We demonstrate that by using the re-injection mirror, the sensitivity of OA-ICOS method can be enhanced by an order of magnitude, resulting in ppbv sensitivities for N$_2$O at seconds’ timescale. Furthermore, we evaluate both methods (OA-ICOS and WMS) for Residual Amplitude Noise (RAM), linearity, long-term stability, detection limit, spectral fitting, reproducibility and background variations.

2. External cavity quantum cascade laser

For our experiments a homemade EC-QC laser was developed, as described elsewhere in detail [21,39]. The EC-QC laser supports single mode operation and wide spectral tunability for broadband emission. In this EC-QCL, we utilized a water-cooled, CW gain chip (3 mm long and ~7.5 µm wide, # Sb 6503 DN, Alpes Lasers, Switzerland). The gain chip is HR coated at the back-facet and AR coated at the front facet (reflectivity < 1% at 7.5 µm) in order to avoid Fabry-Perot modes from the gain chip. It provides emission around a central wavelength of 7.5 µm.

A gold-coated diffraction grating (150 grooves/mm, reflectivity > 99%, blazed at 10.6 µm, Optometrics, US) is used as the end-mirror for the external cavity and operates in a Littrow configuration, in order to achieve the maximum output power. Inside the cavity, at the AR facet of the QCL gain chip, the light is collimated by an aspheric lens (focus: 3 mm, NA: 0.72, AR-coated for 8-12 µm, Light Path, US). The lens can be optimally aligned with a three-axis translational stage, which is integrated into the copper holder of the gain chip. The diffraction grating in the Littrow configuration sends the 1st order diffraction light back into the QCL chip, while the 0th order is impinged on a flat gold coated mirror, placed at 90 degrees. The grating and the mirror form a cat’s eye configuration, in which the out coupled laser light goes exactly the same pathway, independent of the out coupling angle of the grating. The EC-QC laser was built in a compact closed housing (30×20×15 cm), which includes the Peltier cooling and thermal shielding. The EC-QCL is operated at a temperature of -30 °C and to avoid water condensation from the atmospheric air, the housing is continuously flushed with a low flow of dry N$_2$. The laser beam exits the housing via a ZnSe window, placed at Brewster angle.

Figure 1(a) shows Light-Current-Voltage (L-I-V) characteristics of the EC-QCL. The tuning of the external cavity is performed by rotating the diffraction grating (along with the 90-degree mirror) with a DC motor (M-227.10, Physik Instrumente, Karlsruhe, Germany). We measured the emission wavelength of the laser by an FTIR (Nicolet Magna 560, France) at various positions of the grating. The accuracy of the measured wavelengths is better than 0.1 cm$^{-1}$ (3 GHz). EC-QC laser has a maximum spectral coverage of ~300 cm$^{-1}$ (22% of the center wavelength) and an output power of ~40 mW at -30 °C (Fig. 1(b)). Although the QCL chip is fabricated based on the same design as the one that we used in [39], the output power is improved by a factor two and the threshold current is reduced by ~50%. These enhancements are attributed to an optimized alignment within the external cavity. We also measured the beam profile of the laser with an infrared camera (HEIMANN Sensor, Germany, # pixels 80x64, pixel size 55×55 µm2, pitch 90 µm) at a distance of 5 cm from the ZnSe window. Horizontal and vertical fit to the intensity profiles yields a diameter of 0.626 mm and 0.60 mm respectively, at 1/e$^2$ intensity levels.
3. Experimental setups and procedures

Two experimental setups were built for detection of N$_2$O. The OA-ICOS setup is shown in Fig. 2(a); the output beam of the EC-QC laser is coupled to an optical cavity in an off-axis configuration formed by two spherical mirrors (ROC = 50 cm, reflectivity 98%, diameter 50.8 mm, II-IV Infrared, US) which are separated by a cavity length of 28 cm. The cavity is mounted on two independent, precision kinematics XY translational stages at its two ends. A mid-IR optical isolator (aperture size 2 mm, operational wavelength region 4 to 14 µm, 75% transmission efficiency, Laser 2000, UK) is used to avoid feedback into the laser from the optical cavity. The beam is focused via two lenses (l$\_1$, ZnSe, f = 24 cm, l$\_2$, f = 60 cm, ZnSe) at the center of the cavity.

A He - Ne laser is used to facilitate the mid-IR beam alignment via a flip mirror and two pinholes. The transmission of the enhancement cavity is collected and focused via an off-axis parabolic mirror (f = 25 cm, Thorlabs, US) and a lens (l$\_3$, ZnSe, f = 5 cm) onto a fast photodetector (PD1, PVI-4TE-8, Vigo Systems, Poland). The cavity length, L, is 28 cm and the reflectivity of the cavity mirrors is 98% at 1300.92 cm$^{-1}$, which yields a cavity finesse, $\mathcal{F}$ = $\pi \sqrt{R/(1-R)}$, of 155 and an off-axis effective path length, $L_{\text{eff}} = \mathcal{F} L/\pi$, of 14 m.

The off-axis alignment of the cavity is performed as follows. First, the wavelength of the EC-QC laser is scanned over a targeted absorption line of N$_2$O. The EC-QC laser beam is then co-aligned with the He-Ne laser beam and is focused at the center of the cavity via two lenses (l$\_1$, l$\_2$). Then 100 ppm of N$_2$O, diluted in N$_2$, is introduced inside the cavity using a mass flow controller from a bottle with a calibrated gas mixture (Linde, the Netherlands) and the targeted absorption feature of N$_2$O is identified on the detected cavity transmission modes. To perform the off-axis alignment, the two ends of the cavity are translated horizontally, orthogonal to the incident co-aligned beams, by the two translational stages for a specific distance. Afterward, both of these ends are translated vertically for twice of the horizontal translated distance, but this time in opposite directions for the two ends. The introduced translation and angular shifts yield an elliptical pattern of the He-Ne laser beam spots on the surfaces of the two cavity mirrors as described by Sayers et al [40]. The FSR of the cavity collapses and the amount of cavity modes, participating in the transmission of the laser line, is increased by orders of magnitude.

![Fig. 1. (a) L-I-V curves of the EC-QCL. (b) Normalized spectral tuning coverage of the EC-QCL (measured with FTIR) along with corresponding output powers at −30 °C. The total scanning range is over 300 cm$^{-1}$ and the maximum output power is ∼40 mW.](image-url)
compared to the on-axis configuration, building a virtually constant transmission over the entire scan. Fine-tuning of the alignment is performed by optimizing the signal to noise ratio (SNR) of the observed N$_2$O absorption line and minimizing the residual fluctuations due to the cavity modes.

To enhance the cavity transmission intensity in the OA-ICOS, we used a re-injection mirror (M$_3$, R = 20 cm, reflectivity 98%, diameter 75 mm, Thorlabs, US) placed at d ~ 12 cm behind the first cavity mirror forming a small re-injection cavity between the re-injection mirror and the first cavity mirror. The re-injection mirror has a small entrance hole (2 mm, 20 mm from the center of the curvature) for coupling the laser beam into the re-injection cavity. The simulation shows that an intensity enhancement factor of 15 can be achieved, by using the re-injection mirror [41]. After introducing the re-injection mirror and fine-tuning the alignment, an intensity enhancement factor of ~13 is achieved in the OA-ICOS setup.
The second set up is shown in Fig. 2(b). The EC-QC laser beam is coupled to a multipass cell (AMAC-76, Aerodyne Inc., US) via two lenses ($l_1$, $f = 24$ cm, $l_4$, $f = 35$ cm, ZnSe) providing an effective path length of 76 m. The transmission beam from the multipass cell is focused onto an infrared detector (PD$_1$). The frequency response of the EC-QC laser is characterized as a function of modulation current, next to the addition of a bias current to the QCL gain chip. In order to assess the modulation response, the EC-QC laser beam is sent through a 3-cm long Fabry-Perot etalon (FSR = 1.5 GHz) and focused onto a fast photodetector (PD$_2$, liquid N$_2$ cooled, Kolmar Technologies, US) via a lens ($l_6$). A function generator (33220A, Agilent, US) is used to provide a sinusoidal voltage to the laser diode current source (LDX-3232, ILX, Light wave, Newport, US). From the response of the etalon, we estimate a maximum frequency modulation amplitude of $\sim 10$ GHz (at 20 mW of optical power and 1300.92 cm$^{-1}$) before reaching to 100% modulation of the injection current. This modulation amplitude is adequate to probe a single absorption line of N$_2$O.

For DAS, the laser beam is modulated with two different methods for OA-ICOS and WMS setups. A function generator whose modulation frequency was kept below 1 kHz was used in OA-ICOS [42]. To perform direct absorption spectroscopy (DAS) in the multipass cell of the WMS-set up, the laser beam is mechanically modulated by a chopper. For performing WMS in this setup, the same function generator is used as in the OA-ICOS setup, by modulating the injection current to the EC-QCL by a sinewave. To scan over the narrow N$_2$O absorption lines, we use a piezo actuator (P-840. 60, Physik Instrumente, Germany) mounted between the DC motor (M-227.10, Physik Instrumente, Germany) and the diffraction grating. Saw-tooth waveforms with frequency of $\sim 25$ Hz (OA-ICOS) and $\sim 30$ Hz (WMS) were applied to the PZT to scan over the N$_2$O absorption line at 1300.92 cm$^{-1}$. Data from both setups are demodulated by a lock-in amplifier (SR830, Stanford Research Systems, US) and recorded by a data acquisition card (NI PCI-6259, US). We used a homebuilt LabVIEW program for data collection and analysis.

The gas handling system consists of a vacuum pump, a pressure controller, two adjustable needle valves (before and after the absorption cell) and two mass flow controllers (maximum flow rate 5 l$^{-1}$h$^{-1}$, Brooks Instruments, Netherlands). One mass flow controller is connected to the calibrated bottle containing 100 ppmv of N$_2$O in N$_2$ (Linde Gas, the Netherlands), and the other to a pure N$_2$ gas bottle for further dilution of the N$_2$O mixture and/or measuring background spectrum with pure N$_2$. The gases are continuously flushed through the cavities during the measurements, by maintaining a constant pressure of 100 mbar using the needle valves.

4. Results

4.1. Spectral fittings and concentrations retrieval

A measured scan over N$_2$O absorption line at 1300.92 cm$^{-1}$ (28 ms acquisition time, 5 scans averaged) using OA-ICOS set up is shown in Fig. 3(a) along with Voigt profile fits (red curve). We recorded 635 data points at a sampling rate of 1 kSamples/s, which yielded a spectral coverage of 0.06 cm$^{-1}$ (1.8 GHz). The residual of the fit is shown at the bottom of Fig. 3(a). The main shortcoming of OA-ICOS is the low cavity throughput (transmitted intensity through the cavity). To improve this, we measured the same N$_2$O absorption line by using a re-injection mirror in front of the absorption cavity ($d \sim 12$ cm). Figure 3(b) shows the measured N$_2$O absorption line with intensity enhancement factor of $\sim 13$, which was in accordance with our model [41],

$$I_{\text{enhanced}} = \frac{I_{3\text{-mirror}}}{I_{2\text{-mirror}}} = \frac{\sum_{i=0}^{n} r^2 m_i}{m_0},$$

where $I_{3\text{-mirror}}$ and $I_{2\text{-mirror}}$ are the intensities with and without re-injection mirror; $r$ is the mirror reflectivity, $n$ is the number of roundtrips in the re-injection cavity; $m_i$ is the number of roundtrips in the absorption cavity from spot $i$ on $M_2$; $m_0$ is the number of roundtrips with $i = 0$ (no re-injection mirror).
Fig. 3. OA-ICOS signals of a single N\textsubscript{2}O absorption line at 1300.92 cm\textsuperscript{-1} (black data points, five scans averaged) without background correction measured in 6 ppmv mixture of N\textsubscript{2}O in N\textsubscript{2} at 100 mbar, along with Voigt profile fits (red curve) for (a) without re-injection mirror and (b) with re-injection mirror. The residuals of the fits are shown in the lower panels.

The residual of the fit is shown at the bottom of Fig. 3 panel (b) which has a similar structure compared to the residual of the fit in Fig. 3 panel (a). The retrieved N\textsubscript{2}O concentrations from the fits (after normalization to the corresponding backgrounds) are found to be 6 ± 0.5 ppmv and 6 ± 0.3 ppmv for Fig. 3 panel (a) and (b) respectively (pressure of 100 mbar, temperature of 298 K, and an effective path length of 14 m).

We compared OA-ICOS with DAS using the multipass cell. The absorption line of N\textsubscript{2}O (5 ppmv at 100 mbar diluted in N\textsubscript{2}) at 1300.89 cm\textsuperscript{-1}, recorded in 35 ms (five times averaging) along with a Voigt fit is shown in Fig. 4(a). The residual of the fit is shown in the lower panel of Fig. 4(a). To calculate the concentration, the measured signals are normalized to the background and the retrieved concentration from the fit is 4.8 ± 0.01 ppmv. The artifacts in the residuals of the fits in Fig. 3 and 4 dominate over the noise level [43] and can have different origins. Firstly, due to the etalon fringes caused by different optical components in the measurement setup as well as the external cavity of the laser source, which could be minimized by custom-made broadband anti-reflection coatings [44]. Secondly, due to the residual discrete mode structure of the cavity transmission. The laser linewidth should be larger than the effective FSR of the cavity to efficiently suppress the spurious-coupling intensity noise [45]. In addition, any frequency jitter during the scanning across the molecular transition contributes towards the etalon effects in the residual signals. In general, the remaining residual can be fitted out with a proper etalon fitting model or combining the employed detection methods (e.g. multipass cell or OA-ICOS) with a balanced detection scheme [46].

4.2. Linearity and dynamic range

The response of both optical sensors was characterized by applying different N\textsubscript{2}O mixtures. To change the volume mixing ratios, two mass flow controllers (on a calibrated mixture of N\textsubscript{2}O in
Fig. 4. $\text{N}_2\text{O}$ absorption line at 1300.92 cm$^{-1}$ (5 ppmv in $\text{N}_2$), measured using the multipass cell. Panel (a) DAS, Panel (b) WMS-2f. DAS measurement is fitted by a Voigt profile, while the WMS-2f measurement is fitted by the corresponding wavelength modulation spectroscopy model based on a Voigt profile. The residuals of the fits are shown in the lower panels.

$\text{N}_2$ and a bottle of pure $\text{N}_2$ were used with different flow rates. The linearity of both sensors is analyzed by a linear fit and in a Bland-Altman plot (Fig. 5 and 6).

OA-ICOS shows a good linearity for the measured volume mixing ratios. A linear fit to the measured concentrations has an offset of 0.35 ppmv and a slope of 1.03 ($R^2 = 0.999$). The coefficient of determination ($R^2$) shows a strong linear correlation between the applied and measured concentrations throughout the explored dynamic range. The results are also compared in a Bland-Altman plot, which consists of the difference between a set of measurements against their average (25 to 75% around the mean value). The difference between the mean values of the measured and applied concentrations was $\sim$ 0.1 ppmv. For WMS, the linear fit has an offset of 0.067 ppmv with a slope of 0.99. The residual between measured and applied values are shown in Fig. 6. (b), which yields a mean value of 0.025 ppmv (25 ppbv) with a limit of agreement shown with the blue dashed lines.

4.3. Detection limits and long-term stability

We followed a data acquisition procedure through a number of steps to evaluate the detection limit and the long-term stability of the systems. In this procedure, we first recorded a reference absorption line spectrum by scanning the PZT of the EC-QCL across specific concentration of $\text{N}_2\text{O}$ in $\text{N}_2$ at 1300.92 cm$^{-1}$. We made a measurement scan by recording the same absorption profile of $\text{N}_2\text{O}$ in the second step. In the next step, we plot the measurement scan against the reference scan each wavelength, in which intensity values of the measured scan acts as y coordinate and the intensity values of the reference absorption spectrum as x-coordinate. A line is fitted though these data points, whose slope determines the relative change in concentration measurement over time, and the uncertainty in the measurements. We plotted the Allan-Werle deviation for both sensors (see Fig. 7 and 8), using these slope values, were measured over longer
We believe this procedure is trustworthy, as it takes into account many other effects, in addition to the noise. It uses the SNR value of the complete wavelength area of the absorption curve and also takes into account the shape of the absorption line. This as compared to measuring only the absorption peak value with the noise at this value. In addition, the data points that are closest to the absorption line center has the largest weight for the determination of the slope of the fit and its uncertainty. Furthermore, it also compensates largely for constant etalon effects in the spectrum, yielding the detection limits due to the SNR and long-term drifts. This method has been evaluated and implemented previously to find the detection limit of spectroscopic techniques, e.g. in [14,21,47–49].

Using this method, we evaluated the detection limits and long-term stability of both sensors. The EC-QCL power is \( \sim 20 \text{ mW} \) at the targeted N\(_2\)O line at 1300.92 cm\(^{-1}\). We used 15 ppmv of N\(_2\)O in N\(_2\) and determined the fitting slopes, which yielded a minimum detectable concentration in OA-ICOS with no re-injection mirror of 800 ppbv in 8 s averaging time, Fig. 7. When we use the re-injection mirror, the intensity throughput is higher, thereby it overcomes the relative low detectivity (D*) of the mid-IR detector. The light intensity is increased compared to the equivalent input intensity of the thermal noise of the detector, increasing the SNR and ultimately the detection limit of the system. A SNR enhancement factor of \( \sim 13 \) is achieved by utilizing the re-injection mirror. As a result, we achieved a factor of \( \sim 10 \) in the detection limit and ultimately a minimum detection limit of 80 ppbv in \( \sim 8 \) s.

For DAS and WMS, we determined the detection limit and long-term stability using the same data processing method as for OA-ICOS. This time, we used 5 ppmv of N\(_2\)O in N\(_2\) and recorded
Fig. 6. Response of WMS-setup in combination with a multipass cell. (a) Measured concentrations for different mixtures of N$_2$O diluted in N$_2$. (b) Bland-Altman plot showing the residual for 7 measured mixtures. Solid red line: mean value, blue dashed line: standard deviation.

Fig. 7. Allan-Werle plot of the minimum detection limit as a function of averaging time for N$_2$O diluted in N$_2$, without re-injection mirror (black curve) and with re-injection mirror (red curve). The detection limit of the system is improved by a factor of $\sim$13 using the re-injection mirror, which yields a minimum detectable absorption of 80 ppbv in 8 s averaging time.
the absorption line at 1300.89 cm\(^{-1}\). A minimum detectable concentration of 300 ppbv at the \(\sim\)10 s averaging time was achieved for DAS. Using WMS-2f, the detection limit was 15 ppbv in 10 s averaging time, enhancing the minimum detectable concentration by a factor 20 in comparison to DAS.

4.4. Noise equivalent absorption sensitivity

In order to compare different instruments against each other, irrespective of the quality of measurements, a metric that is often used is Noise Equivalent Absorption Sensitivity (NEAS). The NEAS per spectral elements for our N\(_2\)O measurements is calculated using the relation described in [50],

\[
\text{NEAS} = \left( \frac{\Delta I}{I_0} \right)_{\text{min}} \frac{1}{L_{\text{eff}}} \sqrt{\frac{nT}{N_p}} \tag{2}
\]

where \((\Delta I/I_0)_{\text{min}}\) is the noise on the baseline without any absorber, \(L_{\text{eff}}\) is the effective path length, \(N_p\) is the number of data points per scan, \(n\) is the number of scans averaged and \(T\) is the time for a single measurement. \((\Delta I/I_0)_{\text{min}}\) is estimated by taking the ratio of two consecutive background scans, when the cavity/multipass cell is filled with pure N\(_2\) at 100 mbar pressure. For OA-ICOS without re-injection cavity, each scan consists of 650 data points and we took the average of five scans. For this set of data, the standard deviation \((1/\sigma)\) of the noise at 1300.89 cm\(^{-1}\) is equal to \(6 \times 10^{-3}\) which results in a NEAS of \(7 \times 10^{-8}\) cm\(^{-1}\) Hz\(^{-1/2}\) \((n = 5, T = 35\text{ ms}, N_p = 650, L_{\text{eff}} = 14\text{ m})\). The SNR value (intensity) in the system was enhanced using the re-injection mirror. We achieved an enhancement factor of 13 in the SNR. As a result, we obtained an improved NEAS of \(6 \times 10^{-9}\) cm\(^{-1}\) Hz\(^{-1/2}\) \((\Delta I/I_0 = 5 \times 10^{-4}, n = 5, T = 35\text{ ms}, N_p = 650, L_{\text{eff}} = 14\text{ m})\). We performed the same set of measurements in the same wavelength region around the N\(_2\)O line under the same conditions using the multipass cell in combination with DAS and WMS-2f. DAS yielded a NEAS value of \(1.5 \times 10^{-6}\) cm\(^{-1}\) Hz\(^{-1/2}\) \((\Delta I/I_0 = 7 \times 10^{-1}, n = 5, T = 35\text{ ms}, N_p = 650, L_{\text{eff}} = 76\text{ m})\), since its performance is limited by 1/f noise. Using WMS-2f detection with fast modulation, the NEAS improved to \(1 \times 10^{-9}\) cm\(^{-1}\) Hz\(^{-1/2}\) \((\Delta I/I_0 = 0.5 \times 10^{-3}, n = 5, T = 35\text{ ms}, N_p = 650, L_{\text{eff}} = 14\text{ m})\).
$T = 35 \text{ ms, } N_p = 650, L_{\text{eff}} = 76 \text{ m}$. In the latter case, the NEAS is mainly limited by the residual amplitude noise.

5. Discussion

Here, we discuss advantages and disadvantages of OA-ICOS and WMS-2f for trace gas detection in the mid-IR wavelength range. We utilized a compact CW EC-QCL working around 7.7 $\mu$m as the spectroscopy source. The EC-QCL delivered an output power of 40 mW and it is widely tunable ($\sim 320 \text{ cm}^{-1}$). It can be scanned over the whole tuning range in less than 30 s with a spectral resolution of 1 GHz.

For OA-ICOS, large diameter cavity mirrors (2-inch) were used, enabling an effective path length of 14 m in a compact cavity ($\sim 28 \text{ cm}$), resulting in a minimum detectable concentration of 800 ppbv in less than 10 s averaging time. The detection SNR was enhanced by using a re-injection mirror, resulting in an improvement of the minimum detectable concentrations to 80 ppbv averaged over 10 s. The improved value of minimum detectable concentrations corresponds to a NEAS of $6 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$. This additional mirror provides more freedom in selecting cavity parameters such as radii of curvature or distance between the mirrors without losing the detection sensitivity. For instance using a short cavity length ($\sim 5 \text{ cm}$) with cavity mirrors ROC $\sim 1 \text{ m}$ will result in a large divergence and skewness of the rays at the output of the cavity [51,52]. In the multipass cell-assisted setup, we used WMS-2f in order to measure the same absorption line of $N_2O$ under the same measurement conditions as of OA-ICOS. For WMS, we modulated the laser injection current with a rapid sinusoidal and slowly varied the laser frequency over a single $N_2O$ absorption line. By implementing the 2f demodulation method, a minimum detectable absorption of less than 15 ppbv in less than 10 s is achieved which results in a NEAS of $1 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$.

For a multipass-cell assisted system, the angle of the out coming beam from the multipass cell usually drifts with temperature changes and, therefore, its alignment becomes critical, especially for field measurements in a harsh environment. Alternatively, OA-ICOS is one of the potential methods to be used in harsh environment, since its alignment is very robust. We also showed that, compared to WMS-2f, OA-ICOS shows equivalent detection sensitivity, provided that the effective interaction length of the two systems are equal. By using mirrors with higher reflectivity (>99.98%) and larger diameter (2-inch) the detection sensitivity of OA-ICOS can be improved much further.

6. Conclusions

For ultrasensitive molecular absorption spectroscopy, it is best to perform the measurement in the mid-IR wavelength range, where most of the molecules have their strongest absorption features. However, in this spectral region, cavity-enhanced absorption measurements are challenging, due to the limited detectivity of mid-IR detectors and the lower quality of the highly reflective mirrors used for building optical resonators. Alternatively, WMS is a competing choice, in combination with multipass cell. However, it is often limited to shorter effective path lengths due to the exponential increase of the multipass cell loss in terms of the interaction length. OA-ICOS can potentially provide kilometers of effective interaction path length. However, it is not a rule of thumb that higher reflective mirrors provide measurements with a higher sensitivity. Using mirrors with higher reflectivity, provides longer effective path lengths, but also reduces the intensity transmitted through the cavity. This issue is more important for mid-IR wavelengths, because the cavity mirror losses are higher and the detectivity of the photodetectors are lower in that wavelength region as compared to the near-IR. To overcome this limitation, we used a re-injection mirror in front of the absorption cavity and increased the transmission intensity by more than an order of amplitude.
Within OA-ICOS systems, the residual fluctuations in the transmission, due to the remaining cavity mode structure and etalon fringes due to the partial overlapping of the beam spots on the cavity mirrors, can limit the detection sensitivity. The growth of the spot size of the laser beam along its propagation is proportional to $\lambda$, thus it will be larger for a mid-IR beam compared to a near-IR beam over the same distance. This limits the minimum separation distance between two adjacent beam spots on the cavity mirrors in mid-IR. These effects can be reduced significantly by a proper design of the cavity characteristics, i.e. the radius of curvature of the mirrors and length of the cavity. For instance, the larger surface area of the mirrors not only reduces the overlapping of the beams but also increases the number of round trips from the re-injection cavity [50]. The smaller beam diameters relative to the mirror diameter will reduce the diffraction losses at the mirrors. Long cavity lengths, when combined with large mirror diameters, are also least affected by the mirror aberrations [53].

Commercially available detectors usually have a small active area. Since, the rays are skewed at the output of the OA-ICOS cavity, as well as they are highly divergent, it becomes hard to focus the total output power onto the small active area of the detector. Consequently, larger detector areas are preferred, which are in general, not as sensitive as the detectors with the small active area, since in the majority of the photodetectors, generated noise increase proportional to the square root of the detector size [54]. This effect can be reduced significantly by using non-axially symmetric optics. For example, B. W. Clouser et al showed an improved SNR by a factor of three using non-axially-symmetric optical component consisting of eight slices of wedged ZnSe windows [51].

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**References**