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Mid-infrared supercontinuum-based upconversion detection for trace gas sensing

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Abstract: Recent advancements of mid-infrared (MIR) supercontinuum light sources have opened up new possibilities in laser-based trace gas sensing. While the supercontinuum sources inherently support wide spectral coverage, the detection of broadband absorption signals with high speed and low cost is traditionally limited by the MIR detector arrays. In this work, we demonstrate that this limitation can be circumvented by upconverting the MIR signal into the near-infrared (NIR) region, where cost-effective silicon-based detector arrays can be utilized to measure broadband absorption. We also show that, by combining a MIR supercontinuum source with a MIR-to-NIR upconverter and an astigmatic multipass cell, fast detection (~20 ms) of ethane with sub-ppmv sensitivity can be achieved at room temperature. For multi-species detection, a least-square global fitting method is presented, showing a promising potential for applications such as environmental monitoring and biomedical research.

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1. Introduction

The detection of gas-phase molecular species at low concentration levels supports a wide variety of industrial, environmental, and biological applications. Among various types of detection methods such as mass spectrometry and chemical sensing, MIR laser absorption spectroscopy provides an essential opportunity for selective, sensitive, and non-destructive detection [1–5]. On one hand, the characteristic rotational-vibrational transitions generally show very strong absorption patterns in the so-called “MIR fingerprint region”. On the other hand, the fast development of stable, bright and compact laser sources allows the detection of these patterns at high speed and relatively low cost. Therefore, trace gas sensing based on laser absorption techniques is a fast progressing field.

Nowadays, there are various types of MIR light sources that are commercially available for trace gas sensing, such as quantum cascade lasers [6,7], interband cascade lasers [8], and nonlinear sources such as difference frequency generation sources [9], as well as optical parametric oscillators [10,11]. The narrow linewidth and high brightness of these light sources make them ideal for measuring the individual absorption lines of some molecular species. However, for the detection of larger molecules, which can have overlapping rotational absorption lines within a vibrational transition band causing broad absorption, either scanning detection or multiple-laser integration is generally adopted, inevitably reducing the detection speed or increasing the instrumental cost. Furthermore, it is even more challenging to detect simultaneously multiple molecular species having overlapping absorption patterns. Consequently, it is advantageous to apply a broadband light source to measure broadband absorption patterns in order to increase the detection speed and to reduce the cost.
Traditional MIR broadband sources such as globars may be considered, but the low spectral power density and poor directionality limit their practical applications. More recent advancement in MIR frequency combs shows more promise [12], covering the molecular fingerprint region with high brightness comparable to synchrotron sources [13]. New detection methods such as dual comb spectroscopy [14] and Vernier spectroscopy [15] have been developed in the MIR region, and both broad spectral coverage and high detection sensitivity have been demonstrated. However, the system complexity and cost are still significantly higher, as compared to conventional methods.

Another type of broadband MIR light source emerging as a new candidate for absorption spectroscopy is the supercontinuum (SC) source [16,17]. The high brightness of this source makes it superior as compared to synchrotron sources [18], although it generally does not show the shot-to-shot coherency of the frequency combs. In fact, the state-of-the-art SC source can also provide improved coherency [19]. Nevertheless, since high coherency is not a prerequisite for direct absorption spectroscopy, the phase noise does not require sophisticated opto-electronic control while generating the SC beam, thus making the SC sources promising for broadband MIR spectroscopy in terms of system complexity and cost. A SC source providing an ultra-broad 1.4 – 13.3 \( \mu \text{m} \) spectral coverage has been reported by Petersen and associates in 2014, largely covering the MIR “fingerprint region” [20]. Furthermore, bright SC sources providing >200 \( \mu \text{W/\text{nm}} \) spectral power density have recently become commercially available, supporting the development of SC-based trace gas sensing.

While the development of MIR SC sources is remarkably fast in recent years, sensitive detection of the broadband absorption signal at high speed and low cost is still challenging. Standard measurement methods involve the use of a Fourier transform spectrometer [21] or a scanning-grating-based spectrometer [22]. However, these methods are typically limited in acquisition speed due to mechanical movement. The utilization of a photodetector array, rather than a single-point detector, can significantly improve the measurement speed, as all the spectral elements can be captured simultaneously across the spectrum [23,24]. However, unlike in the visible and NIR regions, fast and sensitive MIR detector arrays still require liquid nitrogen or Stirling cooling, and such detectors are consequently less energy efficient and less cost effective.

In spite of the large effort to develop the MIR detector arrays for direct measurement, the above limitation can be actually circumvented by upconverting the MIR signals into the NIR region, leveraging the mature silicon technology. Historically, this approach was viewed as inefficient due to the low conversion quantum efficiency. However, following a recent intra-cavity upconversion breakthrough achieving ~20\% quantum efficiency at room temperature [25], an upconversion-enabled array spectrometer has been reported [26]. Methane detection was also demonstrated [27], although covering only a narrow spectral window. For broadband detection, an aperiodically poled ZnO:LiNbO\(_3\) waveguide was utilized to upconvert light in the range of 2.5 – 4.5 \( \mu \text{m} \) [28]. More recently, the intra-cavity upconversion technique was also applied for broadband applications [29], leading to a successful commercialization of upconversion-based MIR spectrometers, which also opens up the possibility for practical broadband trace gas sensing applications.

In the present work, we combine the unique advantages of the MIR SC source and the MIR-to-NIR upconversion technique to develop a broadband trace gas sensor. Fast detection (~20 ms) of ethane with ~15 ppb·s\(^{-1}\) sensitivity was achieved. For multi-species measurement, an ultra-broad (>1300 nm) spectral range was obtained. A comprehensive analysis algorithm was developed, showing the promising potential for broadband trace gas analysis.

2. Experimental setup

In order to measure broadband absorption features in the MIR region, a broadband light source is required, preferably with high power and high directionality. In general, such an
output can be obtained by broadening the spectrum of a pulsed pump laser in nonlinear optical fibers through complex processes such as soliton shift and Raman scattering (i.e. SC generation) [30–32]. In practice, a MIR SC source (SuperK MIR, NKT Photonics, Denmark) is utilized, with a total power of 500 mW and a repetition rate of 2.5 MHz. The beam diameter is ~3 mm and the divergence is less than 2 mrad. The associated spectral power density is shown in Fig. 1, covering a broad spectral window from 1500 nm up to 4200 nm (2381 – 6667 cm⁻¹).

![Spectral power density of the SC light source integrated into the gas sensor.](image)

Fig. 1. Spectral power density of the SC light source integrated into the gas sensor.

The SC source is combined with an astigmatic multipass cell (AMAC-76, Aerodyne Research, United States) providing an effective path length of 76 meters for improved sensitivity. In practice, due to the reflection loss at the entrance window and the limited reflectivity of the cell mirrors over the broad spectral range, −96% of the SC power is attenuated, requiring a sensitive MIR spectrometer.

As pointed out in the Introduction section, the instrumentation for direct MIR spectroscopy is generally limited by the detection speed and/or cost, whereas the detector arrays operating in the NIR region are more sensitive and cost effective. Therefore, we opted to utilize a MIR-to-NIR upconverter (S3055, NLIR, Denmark), complemented by a silicon-based CCD line camera (S1510-1006, Hamamatsu, Japan). The design of the upconverter is related to previous publication [29], with a reduced pump beam waist of 90 μm instead of 180 μm in order to improve the upconversion efficiency and spectral resolution.

In order to achieve efficient sum-frequency upconversion, two requirements have to be fulfilled: energy conversion and quasi phase matching. The former condition can be expressed as the following

$$\omega_{\text{NIR}} = \omega_{\text{MIR}} + \omega_{\text{pump}}$$  \hspace{1cm} (1)

where $\omega_{\text{MIR}}$, $\omega_{\text{pump}}$, and $\omega_{\text{NIR}}$ are the frequencies of the input MIR light, the pump laser, and the NIR output, respectively. In practice, a neodymium doped yttrium vanadate (Nd:YVO4) gain media is positioned inside a laser cavity to generate an intra-cavity continuous-wave pump at 1064 nm with a circulating power of ~70 W, supporting the MIR-to-NIR upconversion process.

The second requirement is quasi phase matching:

$$\Delta k = k_{\text{NIR}} - k_{\text{MIR}} - k_{\text{pump}} - G = 0$$  \hspace{1cm} (2)

where $\Delta k$ is the so-called phase mismatch that has to be minimized. The quantities of $k_{\text{NIR}}$, $k_{\text{MIR}}$ and $k_{\text{pump}}$ are the wave vectors associated with the output NIR light, the input MIR light,
and the intra-cavity pump laser, respectively. \( G \) is a vector accounting for the contribution from the nonlinear crystal with a quasi-phase-matching periodicity of \( \Lambda \) (\( |G| = 2\pi/a \)). In practice, two types of nonlinear crystals were applied. One type is the standard periodically poled lithium niobate with a length of 2.5 cm and a constant poling period \( \Lambda \) of 20.9 \( \mu \)m, referred to as the PPLN crystal. Another type is a PPLN crystal of the same length but with a chirped poling period from 15.75 \( \mu \)m to 23.00 \( \mu \)m. The latter crystal is referred to as the CPLN crystal.

In order to achieve broadband upconversion for the PPLN crystal, the incident MIR beam is focused by a germanium lens with a focal length of 35 mm. Such a geometry allows the fulfillment of the quasi phase matching condition without rotating the crystal, as the angle between the on-axis \( k_{\text{pump}} \) vector and the incident \( k_{\text{MIR}} \) vector (i.e. \( \theta \)) is self-adjustable within the focusing cone. Thus, MIR light spanning from 2.82 \( \mu \)m to 4.00 \( \mu \)m can be upconverted to the NIR region (773 – 840 nm) corresponding to \( \theta \) ranging from 0° to 19°, as shown in Fig. 9 in the Appendix. In practice, the incident MIR beam can be slightly tilted relatively to the longitudinal axis in order to optimize the upconversion quantum efficiency for a particular central wavelength. Note that the quantum efficiency can vary significantly from \( 10^{-5} \) [26] up to \( \sim 20\% \) [25] depending on the geometric configuration. For the CPLN crystal, the requirement of focusing is further lifted, because the chirped poling period \( \Lambda \) along the longitudinal direction already leads to a varying \( G \) vector, which can satisfy the quasi phase matching condition without varying the \( \theta \) angle.

The MIR-to-NIR upconverter is combined with the SC light source to cover a broad spectral window for trace gas sensing. A simplified schematic representation of the setup is shown in Fig. 2. Note that the PPLN/CPLN crystal is positioned inside a laser cavity defined by the dichroic mirrors DM1 and DM3. The blue, green and red lines represent the NIR output, the intra-cavity pump, and the MIR input beams, respectively. In order to maintain a stable flow condition, a mass-flow controllers (EL-FLOW Prestige, Bronkhorst, The Netherlands) and a pressure controller (EL-PRESS, Bronkhorst, The Netherlands) are connected to the inlet and outlet of the multipass cell, respectively.

![Simplified schematic representation](image)

**Fig. 2.** Simplified schematic representation of the trace gas sensor (F1: 2.4 \( \mu \)m long-pass filter; M1 – M5: mirrors; L1 and L2: 50 cm focal lenses; L3: 35 \( \mu \)m focal lens; L4: lens system of an effective focal length of 20 cm; L5: lens system of an effective focal length of 10 cm; DM1 – DM3: dichroic mirrors; DL: diode laser; F2: 1000 nm short-pass filter; F3: 750 nm long-pass filter).

### 3. Spectral characterization

We characterized the spectral coverage and resolution of the developed gas sensor by targeting a number of (broadly absorbing) gas species. First, a gas mixture of 50 ± 1.2 ppmv nitrous oxide (N\(_2\)O in N\(_2\)) and 50 ± 1.2 ppmv ethylene (C\(_2\)H\(_4\) in N\(_2\)) at a flow rate of 5 L/h was sent to the multipass cell, pressure stabilized at 900 mbar. Both the PPLN and CPLN crystals of the upconverter were utilized individually, and the associated absorbance spectra, each averaged for one minute, are shown in Figs. 3(A) and 3(B), respectively.
The measured absorbance spectra match the simulated spectra based on the HITRAN [33] and PNNL [34] databases, validating the spectral calibration of the spectrometer. For the PPLN crystal, a spectral coverage from 2400 cm\(^{-1}\) to 3200 cm\(^{-1}\) was achieved, whereas for the CPLN crystal, the coverage can be extended beyond 3500 cm\(^{-1}\), both showing excellent perspective for broadband trace gas sensing. The upconversion limitation at the lower frequency side is due to the cutoff of the SC power. For the higher frequency side, the limitation is attributed to various factors, such as the limited supercontinuum power and the un-optimized mirror reflectivity of the multipass cell. In addition, for the PPLN crystal, the incident MIR beam was slightly tilted relative to the crystal longitudinal axis in order to effectively optimize the upconversion signal around 2800 cm\(^{-1}\), causing a dramatic signal drop above 3200 cm\(^{-1}\) as shown in Fig. 10 in the Appendix. For the CPLN crystal, because of a more feasible realization of the quasi-phase-matching condition, a wider spectrum can be obtained up to 3600 cm\(^{-1}\). A side-by-side comparison of Figs. 3(A) and 3(B) also indicates a higher spectral resolution associated with the PPLN crystal, as the absorption fine structures of C\(_2\)H\(_4\) around 3100 cm\(^{-1}\) are better resolved.

This observation is in agreement with the general spectrometer tradeoff between spectral coverage and resolution. We further address this issue by measuring 50 ± 1.2 ppmv methane (CH\(_4\)) in the same condition. This species has been chosen specifically because of its well-defined absorption peaks associated with the rotational-vibrational transitions in the present spectral window. The obtained absorbance spectra are shown in Fig. 4, confirming the spectral resolution of ~4.5 cm\(^{-1}\) and ~8 cm\(^{-1}\) for the PPLN and CPLN crystals, respectively.

Fig. 3. Absorbance spectra of a gas mixture of 50 ± 1.2 ppmv N\(_2\)O and 50 ± 1.2 ppmv C\(_2\)H\(_4\) at 900 mbar obtained by utilizing the PPLN crystal (A) and the CPLN crystal (B). The simulated spectra are inverted as the red (N\(_2\)O) and pink (C\(_2\)H\(_4\)) curves.

Fig. 4. Absorbance spectra of CH\(_4\) (50 ppmv, 900 mbar) obtained by utilizing the PPLN crystal (A) and the CPLN crystal (B). The simulated spectra are inverted as the red curves.
It is worth mentioning that the upconverted NIR signal normally has an angular dependent spectral distribution because of the quasi-phase-matching condition for the PPLN crystal. Consequently, the collimated NIR beam illuminating the grating also has a frequency-dependent spot size. This spatial distribution effectively leads to a frequency-dependent spectral resolution. For simplicity, we applied a fixed resolution of 4.5 cm\(^{-1}\) throughout the spectral window of 2700 – 3200 cm\(^{-1}\) for the simulation. This resolution should be considered as an average, rationalizing the minor mismatch between the experiment and simulation results shown in Fig. 4(A). The main limiting factor for the present spectral resolution is likely due to the pump laser bandwidth (~0.4 nm FWHM), which can be improved in the future by inserting a temperature-stabilized etalon inside the laser cavity to ensure single mode operation. For the CPLN crystal, the quasi-phase-matching condition can be easier fulfilled because of the absence of the off-axis components. However, due to the spatially chirped configuration of the crystal poling period, different MIR frequency components are upconverted in different segments along the crystal. This geometry can cause a frequency dependent location of the effective slit for the grating-based NIR spectrometer, setting the main limitation to the overall spectral resolution.

4. Single-species trace gas sensing

In this section, we evaluate the performance of the upconversion-based trace gas sensor by focusing on a single species, \(\text{i.e.} \ \text{ethane (C}_2\text{H}_6\)), at low concentration levels. This species is an important component of natural gas, and is therefore representative of practical applications for the present gas sensing system. The PPLN crystal has been utilized, as the associated spectral window is wide enough to cover the broad absorption of ethane.

Figure 5(A) shows an overlay of two measured absorbance spectra of ethane (10 ± 0.3 ppmv, 900 mbar), each averaged for 20 ms. The sample was prepared by diluting gases from certified gas cylinders (Linde Gas Benelux, The Netherlands) by means of controlled gas flow. Figure 5(B) shows the projection of the absorbance values of the second measurement with respect to the first measurement. A linear fit returns a slope value close to one, indicating good reproducibility. This analysis has been repeated for 500 measurements in the same condition, and an effective signal-to-noise ratio (SNR) of 68 was obtained by evaluating the slope average \(\mu\) and the associated standard deviation \(\sigma\) (SNR = \(\mu/2\sigma\)). Note that this SNR is essentially weighted by the absorbance amplitude rather than at a particular wavenumber, as a higher absorbance amplitude naturally leads to a higher weight in determining the slope value. Thus, we estimate the sensitivity to be \(-147\) ppbv (10 ppmv/SNR) for the detection of ethane with a measurement time as fast as 20 ms.

![Fig. 5. (A) An overlay of two absorbance spectra of 10 ppmv ethane at 900 mbar, each measured for 20 ms. (B) Projection of the second ethane absorbance measurement with respect to the first measurement. A linear fit is included as the red line.](image)

To estimate the minimum detectable concentration and system stability, we measured a series of background spectra of non-absorbing nitrogen at 900 mbar, and normalized each
 consecutively obtained spectrum to the first one. A theoretical model spectrum of ethane based on the HITRAN database [33] and a slowly varying baseline were applied to fit the normalized background spectra, from where the noise-equivalent concentration values were retrieved as shown in Fig. 6(A). The associated Allan-Werle plot is presented in Fig. 6(B), fitted by a $\tau^{-1/2}$ dependent line representative of the white noise contribution. An optimal averaging time of ca. 1 second is obtained, corresponding to a detection limit of ~15 ppbv. Averaging at longer time is likely affected by the instability of the light source and thermal drift of the absorption cell.

![Fig. 6](image)

Fig. 6. (A) Noise-equivalent ethane concentration obtained by fitting a theoretical model to the normalized background signal. (B) Allan-Werle plot of the retrieved concentration (black curve) and a fitted $\tau^{-1/2}$ dependency representing the white noise contribution (red dashed line).

We further evaluated the system linearity through a series of dilution experiments ranging from 100 ppmv down to 1 ppmv. The obtained absorbance spectra are shown in Fig. 7(A). Since the spectrum associated with the concentration of 100 ppmv has the highest SNR, we treat this spectrum as a reference by numerically integrating the area under the absorbance curve. The integrated areas of other spectra are normalized to this reference, and the concentration values can be obtained accordingly. The derived concentrations versus the applied concentrations are shown in Fig. 7(B), confirming a linear response.

![Fig. 7](image)

Fig. 7. (A) Absorbance spectra of ethane at 900 mbar diluted from 100 ppmv, each measured for 1 second. An enlarged spectrum of 1 ppmv ethane is inserted as the red curve. (B) System linearity plot. The uncertainty is based on the ± 3σ values derived from 60 measurements for each concentration.

5. Multi-species trace gas sensing

The quantification of multiple gas species with overlapping absorption is more challenging compared to single-species detection. In this section, we explored this issue by evaluating the broadband absorption of a gas mixture containing acetaldehyde, ethane and ethylene, supplied from certified gas cylinders (all, 100 ± 2 ppmv, Linde Gas Benelux, The Netherlands). A target concentration of 33.33 ± 1.30 ppmv was applied to each of these species by means of
controlled mass flow. The evaluation was performed by spectrally decomposing the measured absorbance of the gas mixture into contributions from the individual species.

In general, the measured absorbance of the gas mixture is represented by a one-dimensional matrix $M_{n \times 1}$ containing $n$ non-negative spectral elements. This matrix can be linearly decomposed into a summation of single-species absorbance patterns (of a unit concentration, e.g. per ppmv) weighted by their concentration $C_{k \times 1}$, where $k$ represents the number of target gas species ($k = 3$ in the present case). The absorbance of each individual species, denoted as the reference $R_{n \times k}$, can be calculated in advance by using standard databases (e.g. HITRAN [33] and PNNL [34]), preventing the measurement noise from disturbing the reference in order to improve the regression process. Hence, it is an inverse problem to calculate the non-negative concentration matrix $C_{k \times 1}$ based on the measured absorbance $M_{n \times 1}$ and the known reference $R_{n \times k}$, by globally minimizing the root-mean-square (RMS) error $E_{n \times 1}$ in the following mathematical expression,

$$M_{n \times 1} = R_{n \times k} C_{k \times 1} + E_{n \times 1}$$

The above method, referred to as the non-negative least square curve fitting, is particularly beneficial to treat broad and (partially) overlapping absorption features. In practice, we have chosen the CPLN crystal for multi-species trace gas detection, as this crystal can provide a broad (> 1100 cm$^{-1}$) spectral coverage.

Figure 8(A) shows a typical measured absorbance spectrum of the gas mixture (black curve), averaged for 1 second. The simulated individual spectra of acetaldehyde, ethane, and ethylene are included as the red, blue, and green curves, respectively. The retrieved concentration values based on the least-square curving fitting method are shown in Fig. 8(B), where the uncertainty ranges are derived from 60 independent measurements, each averaged for 1 second. The targeted value of 33.33 ± 1.30 ppmv is highlighted as the dashed blue line, and the uncertainty is represented by the grey area.

![Figure 8](image)

Fig. 8. (A) Measured absorbance spectrum (black curve) of a gas mixture averaged for 1 second. The underlying curves represent the contributions from acetaldehyde (red), ethane (blue) and ethylene (green) obtained by simulation based on the PNNL database [34]. (B) Calculated concentration values by using the non-negative least square curve fitting method. The associated interquartile ranges are included based on the statistics of 60 measurements. The targeted concentration of 33.33 ± 1.30 ppmv is highlighted as the dashed blue line, including the dilution uncertainty represented by the grey area.

A comparison of the calculated concentration with respect to the targeted value of 33.33 ± 1.30 ppmv shown in Fig. 8(B) demonstrates the capability of the present system for multi-species detection. The obtained concentration values for acetaldehyde and ethylene match the targeted value, confirming good accuracy. The concentration of ethane is seemingly overestimated by ~0.81 ppmv, or alternatively, ~2.4% relative to the targeted value. However, the error still falls within the uncertainty due to dilution of the calibrated gas source.

The obtained uncertainty (i.e. 1.5 times interquartile range) of acetaldehyde is narrower in comparison to the uncertainties of ethane and ethylene. This observation can be rationalized
by the fact that the lower frequency side of the present spectral window is dominated by acetaldehyde, thus resulting in less interference. For the detection of ethylene, the relatively lower absorption strength (comparing to ethane) is compensated by a less severe interference at the higher frequency side of the spectral window, effectively leading to a comparable uncertainty range for these two species. Remarkably, the uncertainties of all these three species are within the sub-ppmv region, suggesting good sensitivity for multi-species detection.

It is also important to note that the present analysis focuses only on the detection of broadband, and yet partially overlapping, gas species. In this situation, the regression process is based on a combination of linearly independent spectral components. In the case of evaluating highly dependent components with similar and largely overlapping absorbance features, the reference matrix can be close to being singular, resulting in increased errors when inverted. This problem can be better solved by introducing additional constrains (e.g. kinetic modeling) combined with more advanced analytical techniques such as the Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) [35].

6. Conclusion

We have presented the development and performance of a MIR SC-based trace gas sensor. The ultra-broad spectral coverage of the SC light source is particularly advantageous for the detection of broadly absorbing gas species. High speed (~20 ms) sensing of ethane with ~15 ppb·s⁻¹ sensitivity was achieved by utilizing a MIR-to-NIR sum-frequency upconverter combined with a NIR CCD detector array. The system linearity was verified over two orders of magnitude through trace gas mixing. For multi-species detection, a non-negative least-square curving fitting method was applied to globally calculate the concentration of individual species, achieving satisfactory accuracy and precision. These results show high promise of the present system for future fast and broadband trace gas sensing.

7. Appendix

For completeness, this Appendix provides additional information for the sum-frequency upconversion.

Figure 9 shows the calculated NIR output wavelength versus the MIR input wavelength and the associated phase-matched external angles. The dispersion effect is considered by applying the corresponding Sellmeier coefficients for the MgO-doped periodically doped LiNbO₃ (PPLN) crystal. The poling period is 20.9 μm. This relationship sets an upper limit for the achievable spectral coverage for the upconversion process.

![Fig. 9. Calculated NIR output wavelength versus the MIR input wavelength at different phase-matched external angle relative to the PPLN crystal longitudinal axis.](image)
Figure 10 shows the upconverted spectral profile recorded by the CCD array (one minute average) when the gas cell was filled with non-absorbing nitrogen at 900 mbar. The spectral coverage was optimized at a central wavenumber around 2800 cm\(^{-1}\) for the PPLN and the CPLN crystals. For clarity, the thermal radiation background [36] was subtracted.

![Figure 10](image)

**Fig. 10.** Spectral coverage of the upconverted spectra recorded by a CCD array by using the PPLN (green) and the CPLN (orange) crystals.

To estimate the limit of the spectral resolution, we assume two closest distinguishable wavelengths being separated by one full width at half maximum (FWHM) of the instrumental broadening function of the NIR spectrometer, as shown in Fig. 11 assuming a Gaussian line shape. Two FWHM values are considered, i.e. 0.20 nm and 0.46 nm. Note that the broadening functions are centered at 813.1 nm in the NIR, corresponding to a MIR input wavelength of 3.5 \(\mu\)m. Thus, a spectral resolution of 8.34 nm (3443.94 – 3452.28 nm) or 7.01 cm\(^{-1}\) (2896.64 – 2903.65 cm\(^{-1}\)) in the MIR region requires a spectral resolution of 0.46 nm in the NIR. Analogously, a MIR resolution of 3.60 nm (3446.34 – 3449.94 nm) or 3.03 cm\(^{-1}\) (2898.60 – 2901.63 cm\(^{-1}\)) requires a NIR resolution of 0.20 nm. Also note that this estimation ignores the broadening contribution from the intra-cavity pump source, which can be improved by inserting a temperature-stabilized etalon inside the cavity to ensure single-mode operation. A more detailed discussion of the acceptance angle dependency can be found in [37].

![Figure 11](image)

**Fig. 11.** Normalized instrumental broadening function centered at 813.1 nm.
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