Highly sensitive and rugged gas optical detection via interferometric cavity-assisted photothermal spectroscopy

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ABSTRACT

We report on the detection of nitric oxide using an Interferometric Cavity-Assisted Photothermal Spectroscopy (ICAPS) gas sensor in combination with a DFB-QCL emitting at 1900 cm^{-1} as excitation source. In ICAPS, a probe laser is coupled to a Fabry-Perot interferometer acting as an optical transducer of thermal effects. A wavelength modulation approach of the probe diode laser was employed, to actively lock its wavelength to the point of highest sensitivity and linearity of the interferometric fringe for a stable readout. A normalized noise equivalent absorption of $5\cdot10^{-6}$ $Wcm^{-1}Hz^{-1/2}$ was achieved corresponding to 1.4 ppm of NO.

Keywords: Photothermal spectroscopy, Fabry-Perot interferometry, Nitric Oxide, Quantum Cascade Laser, Gas sensing

1. INTRODUCTION

Laser-based gas sensors have gained increasing research interest for their capability to achieve extremely low detection limits in combination with high selectivity of the gas species. Laser spectroscopy allows fast and precise quantification of numerous species by selection of a proper laser source which targets analyte-specific absorption lines. In this context, quantum cascade lasers (QCL) marked a turning point in such field, thanks to their capability of accessing the mid-infrared spectral region. In the MIR, strong ro-vibrational absorption of many environmentally and industrially relevant gases can be targeted. Among the laser-based spectroscopic techniques, the indirect absorption approaches, such as photoacoustic and photothermal spectroscopy, are attracting growing attention. These techniques have the benefits of generating strong signals in small volumes, hence preserving good sensitivity but drastically reducing the needed sampling volume. This advantage paves the way towards the realization of rugged sensors. The photoinduced signal can be expressed as [1]:

$$S_{ind} = \frac{P_{exc}\alpha}{f_{mod}V} \tag{1}$$

being P_{exc} the optical power of the excitation source, modulated at frequency f_{mod}, α the absorption coefficient of the gas and V the interaction volume. In Interferometric Cavity Assisted Photothermal Spectroscopy (ICAPS), the target gas is periodically excited with a focused laser, producing a periodic heat source which is localized in the focal spot of the laser. The heat, in turn, will induce a modulated gas expansion which is efficiently measured as a refractive index change via an interferometric detection scheme. A Fabry-Perot interferometer (FPI) is used for such purpose, in combination with a probe laser beam which samples the perturbed gas volume. For an efficient transduction, however, two conditions must be fulfilled. The first consists in the spatial overlap of the excitation and the probe lasers since the refractive index perturbation is localized in the excitation volume and is strongly damped in space. The second condition requires a spectral tuning of the probe laser to one of the interferometric fringes of the FPI. The sensitivity towards refractive index perturbations comes from the dependency of the resonance frequencies of the FPI from the refractive index of the filling medium. Thus, in off-resonance conditions the FPI is insensitive towards such changes.

The selection of the probe source is a critical step. In real-case application scenarios, fast-drifts of the cavity resonances are expected. Such drifts are caused by changes in the matrix composition or in the sample concentration, temperature or pressure. A tight locking of the laser source to one of the cavity resonances must be implemented for stable readout. The highest sensitivity is achieved when the laser wavelength is tuned to a specific point of the cavity resonance, called the inflection point. Diode lasers are capable of fast wavelength tuning by modifying the injection current. Moreover,

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near-infrared diode lasers and peripheral devices are readily available and cost-effective, making a diode laser type the favored choice. In this work, we present a rugged ICAPS system based on a probe diode laser and equipped with a QCL emitting at 1900 cm^{-1} for the detection of nitric oxide (NO).

2. METHODOLOGY

2.1 ICAPS basics

The ICAPS sensor exploits the high sensitivity of FPIs towards refractive index changes [2], given by the resonance wavelength dependence $m\lambda_{res,m} = 2nd\cos(\theta)$, where d is the separation of the mirrors composing the FPI, θ is the incidence angle of the probe beam, n is the refractive index of the filling medium and m is the diffraction order. For sufficiently high mirror reflectivity, the transmitted intensity through the FPI as a function of the wavelength appears as a set of Lorentzian lines spaced by the free-spectral range ($FSR = c/2nLcos(\theta)$). Any change of the refractive index induces a shift of the resonance wavelengths, such that if a probe laser is tuned to the side of the Lorentzian resonance, the transmitted or reflected intensity will experience a strong variation. The narrower the cavity resonance, the higher the detected intensity variation. This principle is applied for the detection of gases, by inducing a periodic perturbation of the refractive index by means of an excitation laser, modulated at a specific frequency. The reflected intensity will contain a component at the same frequency (and its harmonics) which can be retrieved via lock-in detection. The highest sensitivity towards such perturbation is achieved when the probe laser is tuned to the inflection point of the resonance profile.

A probe diode laser can be swiftly wavelength tuned by acting on its injection current and is, therefore, very well suited for such application. However, the inherent change in emitted optical power causes a different sharpness of the Lorentzian lines, which affects the system sensitivity. If the power reflected by the FPI is collected upon a photodetector, a wavelength-dependent signal will be recorded:

$$S(\lambda_p) = P(\lambda_p) \cdot ITF(\lambda_p) \tag{2}$$

where $P(\lambda_p)$ is the varying optical power of the probe laser and $ITF(\lambda_p)$ the interferometer transfer function. Both the locking procedure and the normalization of the system sensitivity can be performed via wavelength modulation of the probe laser. A sinusoidal modulation of the probe current induces a modulation of its wavelength such that $\lambda_p(t) = \bar{\lambda}_p + \delta\lambda_p \sin(2\pi f_p t)$, being $\bar{\lambda}_p$ the stationary value and $\delta\lambda_p$ the amplitude of the modulation. The signal S, detected on a photodiode over time, can be expressed as a Taylor expansion around $\bar{\lambda}_p$:

$$S(t) = \sum_{n=0} \frac{1}{n!} \left[\delta\lambda_p \sin(2\pi f_p t)\right]^n \frac{\partial^n s(\lambda_p)}{\partial\lambda_p^n}\bigg|_{\bar{\lambda}_p} \tag{3}$$

We can define the modulation index m as $m = \delta\lambda_p/\delta\nu$, being $\delta\nu$ the HWHM of the Lorentzian profile. If the modulation index is sufficiently small ($m \ll 1$), the time-dependent signal, demodulated at the n-th harmonic via a lock-in amplifier, will correspond to the n-th derivative of the wavelength-dependent signal:

$$S_n = \frac{1}{n!} \delta\lambda_p^n \frac{\partial^n s(\lambda_p)}{\partial\lambda_p^n} \tag{4}$$

2.2 Harmonic detection and locking scheme

Such 'derivative approach' allows to retrieve the local steepness of the interferometric fringe and the operational points of highest sensitivity (inflection points). The local steepness also determines the sensitivity of the system towards photothermal effects. Hence, the first harmonic signal, which resembles the first derivative of the wavelength-dependent signal, provides information on the system sensitivity, while the second harmonic allows an easy tracking of the inflection points. In Figure 1 the recorded cavity resonance and its derivatives are shown. The interferometric fringe was obtained by applying a sawtooth scan on the probe current. Since a reflected power is collected, the Lorentzian shaped resonance is inverted (minimum reflectance at the resonance wavelength). The linear background is the effect of the optical power dependence on current (and thus wavelength). The 1st and 2nd harmonic signals, instead, required the superimposition of a small sinusoidal modulation at frequency f_p ($f_p = 6\ kHz$), and lock-in demodulation at $1f_p$ and $2f_p$. The 1f-signal shows a maximum and a minimum at the inflection points, where the system sensitivity is maximized. The 2f-signal corresponds to the derivative of the 1f-signal and its zero-crossings corresponds to its local maxima/minima.

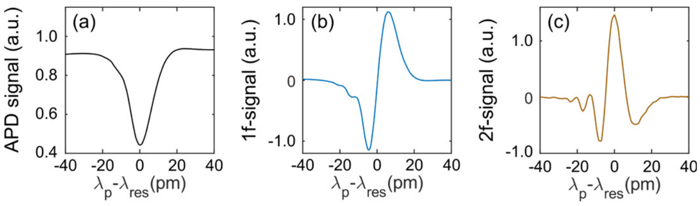

Figure 1. (a) Recorded FP resonance obtained via current scan of the probe laser. (b-c) 1f & 2f-signal recorded with lock-in amplifier demodulation of the photodetector signal at the first and second harmonic.

The 2*f*-signal was used as process variable of a PID loop, developed in LabVIEW environment, to control the DC component of the probe laser current. The setpoint of the PID was set to zero to drive the system towards the zero-crossing of the 2*f*-curve. A proper slope of the controller was chosen for locking to the high-wavelength inflection point. The PID controller speed was kept low (few Hz) in order not to compensate for the photothermal signal, whose modulation was hundreds of hertz. This allows to continuously operate the system at the inflection point.

For a stable locking procedure, the noise-content in the process variable must be as low as possible. In Eq.(4), the peak value of the 2*f*-signal scales as $\delta\lambda_p^2$, suggesting that huge modulation depths are beneficial. However, such equation is valid in the low modulation index approximation. The increase of the modulation index introduces the contribution of the higher-order even harmonics, which ultimately causes a broadening of the 2f-signal. In Figure 2(a) it can be seen how the modulation index broadens the 2*f*-signal. The peak value scales quadratically for small modulation indexes (inset of panel (a)) and finds a maximum around $m \approx 2.2$. At the same time, the position of the inflection points is shifted away from the resonance peak, as depicted in panel (b). For an ideal Lorentzian line, the inflection points are located $\delta\nu\sqrt{3}/3$ away from the resonance wavelength. However, as the modulation index is increased, the zero-crossings rapidly depart from the ideal position. Thus, a tradeoff must be found for the proper modulation depth, in order to obtain sufficiently good SNR signals, while not causing modulation broadening. For these reasons, in this work we kept the modulation index around $m \approx 0.15$.

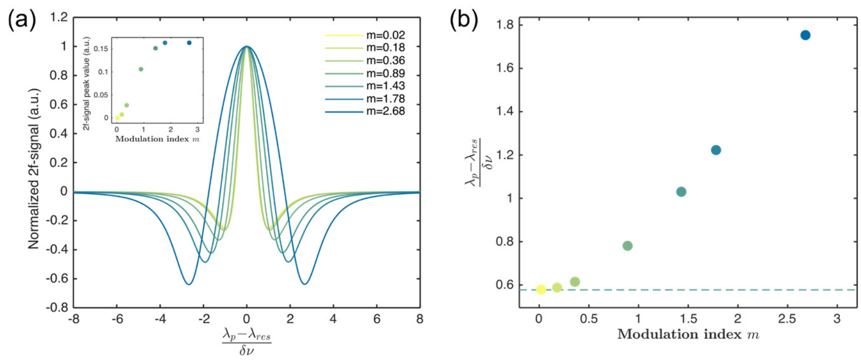

Figure 2. (a) Simulation of a 2nd harmonic demodulated signal, by scanning an ideal Lorentzian profile with an increasing modulation index. (b) Shift of the inflection points as an effect of modulation broadening. Dotted line corresponds to the ideal position of the inflection point, which corresponds to $\lambda_{res} \pm \delta\nu\sqrt{3}/3$.

2.3 Experimental setup

A schematic of the experimental setup is shown in Figure 3. A distributed feedback quantum cascade laser (DFB-QCL) was used in continuous wave as excitation source to target NO absorption line falling at 1900.07 cm^{-1}. A sinusoidal dithering ($f_{mod} = 312$ Hz) was added to the QCL for 2f-wavelength modulation spectroscopy. The excitation beam was focused with a 50 mm CaF_2 lens between the mirrors of the FPI. A near-IR fiber-coupled diode laser emitting at 1552 nm was used as probe laser. The probe current was also sinusoidally modulated with a modulation frequency of 6 kHz. An air-spaced FPI with mirror separation of 2 mm was installed in a custom air-tight gas cell. Probe and excitation beam were spatially overlapped to allow the detection of NO absorption. The back-reflected probe intensity was collected via an optical circulator on an amplified photodetector whose signal was fed to two lock-in amplifiers. The first lock-in amplifier was used to retrieve the cavity response to probe interrogation, by demodulating at the 1st and 2nd harmonic. The second lock-in amplifier was used to retrieve the PTS signal, demodulating at $2f_{exc}$ to retrieve the 2f-ICAPS signal. The gas cell was equipped with inlet and outlet connectors to allow flushing of the target analyte. A certified concentration of 97.5

ppmv was used and combined in a gas mixing station with pure nitrogen for the preparation of dilutions. A pressure gauge and a pressure controller were used to monitor and keep a constant pressure inside the gas cell, while a mini-diaphragm vacuum pump was used to allow gas exchange within the gas cell. The ICAPS measurements were performed at an absolute pressure of 900 mbar, which maximized the signal amplitude while providing a sufficient differential pressure for gas exchange. The modulation depth of the QCL was optimized accordingly to achieve the highest SNR.

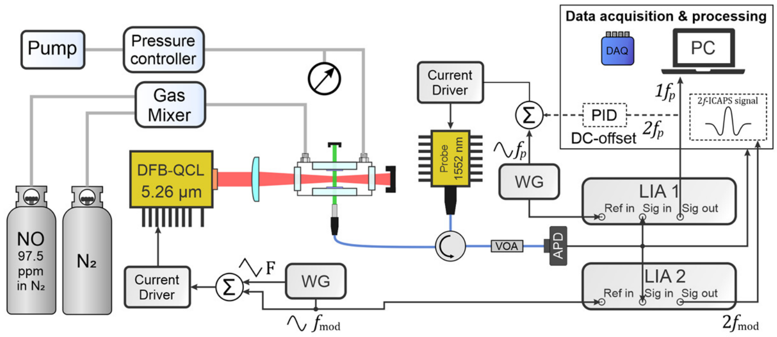

Figure 3. Schematic of the experimental setup. APD: amplified photo detector; LIA: lock-in amplifier; VOA: variable optical attenuator; WG: waveform generator.

3. RESULTS

The sensor was calibrated for the detection of NO in a concentration range spanning from pure nitrogen up to the certified concentration of 97.5 ppmv NO:N_2. The ICAPS measurements were performed by locking the probe laser at the high-wavelength inflection point. The ICAPS signal was corrected by the changing sensitivity using the $1f_p$-signal. A slow triangular ramp (4 mHz) was applied to the QCL current to scan its wavelength across the NO absorption line. The $2f$-WM-ICAPS signal was obtained with a lock-in amplifier time constant of 3 s. In Figure 4(a), the spectral scan of the absorption line for several NO concentrations is shown. The low-current tail of the 2f-curve overlaps with a neighboring absorption line, falling at 1900.51 cm^{-1}. In the inset, the $1/f$ behavior of the photothermal signal (as expressed by Eq.(1)) is shown. The calibration line of the ICAPS sensor was obtained by averaging four peak values. The standard-deviation of the peaks proved to be comparable with the 1σ sensor noise recorded for pure nitrogen, equal to 3.5 µV. The data were fitted with a linear function, providing the calibration line of the sensor. A sensitivity of 2.5 µV/ppmv was obtained by the slope of the calibration curve. The coefficient of determination ($R^2 \approx 0.9995$) proved an excellent linearity over a range of two orders of magnitude. A noise equivalent concentration of 1.4 ppmv was achieved, which corresponds to a normalized noise equivalent absorption of $5 \cdot 10^{-6} Wcm^{-1}Hz^{-1/2}$.

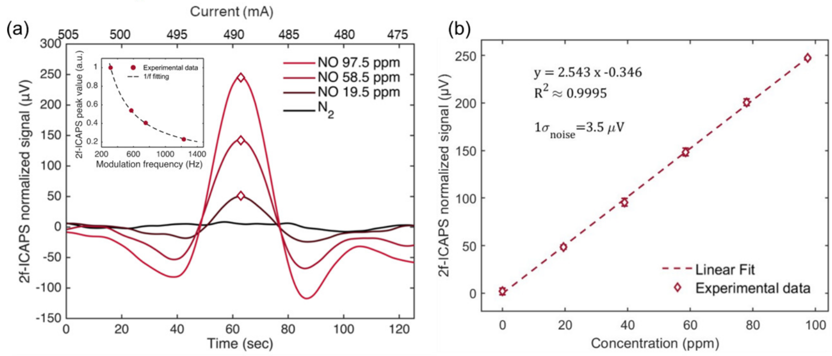

Figure 4. (a) Spectral scan of the NO absorption line in 2f-WMS acquisition mode, acquired for different NO concentrations. The low-current tail presents the absorption of a neighboring line. In the inset, the 2f-ICAPS peak value of a fixed concentration of NO is portrayed against the modulation frequency, together with the 1/f trend. (b) Calibration curve of the NO sensor.

4. CONCLUSIONS

In the present work we presented a novel normalization method and locking scheme for an ICAPS sensor employing a diode laser as probe source. Diode lasers enable fast wavelength tuning and therefore compensation of fast sensor drifts. Both the locking and the normalization were based on wavelength modulation of the probe laser. The locking procedure exploits the $2f$ zero-crossings to retrieve the IP location without further knowledge on the incident intensity. The locking scheme allowed the compensation of drifts in the cavity resonance frequency and the concurrent change of the system sensitivity as a consequence of detuning from the inflection point. The normalization method, on the other hand, was needed to retrieve a signal independent from the variable sensitivity of the system. The system was calibrated for NO detection, and a detection limit of 1.4 ppmv was achieved with an ENBW of 26 mHz and an excitation optical power of 30 mW, corresponding to a NNEA of $5 \cdot 10^{-6}$ $Wcm^{-1}Hz^{-1/2}$. Improvements in detection limit can be achieved by lowering the noise level, e.g. by balanced detection.

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