High-sensitivity spectroscopy of CO$_2$ around 4.25 $\mu$m with difference-frequency radiation

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Abstract

We demonstrate the possibility to perform very high-sensitivity spectroscopy of CO$_2$ around 4.25 $\mu$m wavelength, by use of a difference-frequency radiation source and a White-type multipass absorption cell. Several methods for fringing noise reduction were successfully adopted. In particular, a novel technique to reduce fringes by choosing proper values of the frequency modulation amplitude is described in detail. Pressure-broadening measurements of high-$J$ rovibrational transitions are presented. Achievable laboratory and field sensitivity limits are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Optical spectroscopic techniques have a central role in gas sensing. Their importance has been steadily increasing following dramatic progress in optoelectronic technologies in the last two decades. The introduction of new laser sources,
the low cost availability of fibres and fibre components for radiation delivery far from the sources, with low losses in wide spectral intervals, the improvements in detection systems and signal processing, have significantly extended the range of application of optically-based gas-sensing techniques.

The availability of many new coherent sources has not only opened up new application fields, but has often allowed to replace incoherent sources for gas-sensing applications. This trend has been accelerated by the introduction of miniaturized semiconductor lasers, that can be built to emit radiation in a wide frequency interval. At present, spectral coverage of room-temperature-operated laser diodes moves from the blue–violet to the 2 µm wavelength region. Availability of laser diodes has thus allowed extensive application to sensing of gas-phase molecular species by using “overtone” vibrational resonances for gas-radiation interaction [1].

On the other hand, a detection sensitivity several orders of magnitude higher can be obtained by exciting “fundamental” vibrational transitions, that are found, for most simple molecules, in the 2–12 µm spectral region. Access to these wavelengths is partly provided by non-linear optics frequency mixing techniques, like difference-frequency-generation (DFG). Mixing of optical radiations has taken advantage from the availability, in the last few years, of periodical poling in ferroelectric crystals. This technique, that allows to replace “birefringent phase-matching” with “quasi-phase-matching”, has several advantages, especially in terms of wider intervals in which phase-matching can be achieved, relaxed tolerances for phase-matching conditions and increased mixing efficiency [2]. This has placed non-linear continuous-wave (cw) generation within the domain of low-noise diode-based pump sources, with powers ranging from a few-watts down to even few-milliwatts level [3,4]. This feature, combined with the intrinsic tunability of sources based on non-linear generation, provide a complete coverage of the spectral region moving from UV to about 5 µm wavelength. Therefore, such sources find increasing applications for high-resolution spectroscopy [5,6]. For this purpose, wide tunability, narrow linewidth, low noise and mode-hop-free operation are more important than high power.

The first demonstration of sub-Doppler recordings of molecular lines using a single-pass DFG spectrometer has been obtained in our group, at a power as low as 10 µW [7]. The very high sensitivity achievable with our DFG source has also allowed one to perform a test of fundamental quantum-mechanical principles, setting a new upper limit of $1.7 \times 10^{-11}$ to the probability that two spin-$0^{16}$O nuclei are in exchange-antisymmetric states, improving previous experimental results of as much as two-orders of magnitude [8]. This result was obtained by increasing the gas-radiation interaction pathlength up to 100 m range, with a multiple-pass cell. Longer pathlengths could be obtained with high-finesse enhancement cavities. For such applications, a control of the spatial mode of emitted infrared radiation can be crucial. Therefore, we have recently made a systematic study of the pattern evolution of single-pass radiation, generated by difference-frequency in periodically-poled crystals, as a function of all the relevant experimental parameters [9].

Here, we describe our DFG system, when used for laboratory trace gas detection. Considering that DFG-based gas sensing systems have already been deployed in field
for gas monitoring [10,5], we think that most of the systems and techniques described could be implemented in field-operating devices in view of still higher detection sensitivity of specific species.

2. Direct-absorption spectroscopy of gases

We summarize, in this section, the main theoretical background of direct-absorption spectroscopy of gases. Especially, we recall the equations relating line profiles to gas broadening, that are necessary to retrieve information from field measurements.

The transmission of a monochromatic electromagnetic wave through a mixture of \( n \) different gases is expressed by the Beer–Lambert law as

\[
T_g(n; P_i; T, L) = e^{-\alpha(n; P_i; T)L},
\]

where \( T_g(n; P_i; T, L) \) is the transmission, \( \alpha(n; P_i; T) \) is the linear absorption coefficient, \( n \) is the frequency, \( P_i \) are the pressures of the mixed gases (\( i = 0 \) for the absorbing one, \( i \geq 1 \) for the non-absorbing gases), \( T \) is their absolute temperature and \( L \) is the optical pathlength. The absorption coefficient can be related to the molecular linestrength \( S(T) \) by

\[
\alpha(n; P_i; T) = \frac{P_0}{k_B T} S(T) g(n; P_i; T),
\]

where \( g(n; P_i; T) \) is the normalized lineshape function. Eq. (2) can be rewritten as

\[
\alpha(n; P_i; T) = n_0 \sigma(n; P_i; T),
\]

where \( n_0 \equiv N_0 / V \) is the number density of the absorbing molecules and \( \sigma(n; P_i; T) \equiv S(T) g(n; P_i; T) \) is the absorption cross section per molecule. It should be noted that the \( T \)-dependent Boltzmann’s population factor and the value of the isotopic abundances are included within the linestrength \( S(T) \).

The SI units for \( S \) are m\(^2\) Hz, but, in molecular spectroscopy with the frequencies expressed in cm\(^{-1}\), it is usually given in units of cm, as used in the HITRAN database [11].

The most general lineshape function for gas absorption is a Voigt profile, having the following expression:

\[
g_V(n; P_i; T) \equiv \frac{1}{\Gamma_L \Gamma_D} \sqrt{\frac{\ln 2}{\pi^3}} \int_{-\infty}^{+\infty} e^{-\ln 2 [(v' - v_0)/\Gamma_D]^2} \frac{1}{1 + (v - v')/\Gamma_L} \, dv',
\]

where \( v_0 \) is the absorption frequency, \( \Gamma_D \) and \( \Gamma_L \) are the Gaussian and Lorentzian linewidths, both calculated as half widths at half maximum (HWHM). The former is determined by the Boltzmann thermal velocity distribution of molecules, while the latter is due to collisions and is pressure-dependent. The expressions for these
linewidths are
\[
\Gamma_D(T) = v_0 \sqrt{\frac{2 \ln 2 k_B T}{M c^2}},
\]
(5)
\[
\Gamma_L(P_i, T) = \sum_{i=0}^{n} \gamma_i(T) P_i,
\]
(6)
where \( M \) is the molecular mass of the absorbing gas and \( \gamma_i \) are the broadening coefficients for the different gases. In particular, \( \gamma_0 \) is the “self-broadening coefficient”, and the others are the “foreign-broadening coefficients”. The following phenomenological scale law with temperature holds for the broadening coefficients:
\[
\gamma_i(T) = \gamma_i^0 \left( \frac{T_0}{T} \right)^{\beta_i},
\]
(7)
where the temperature exponents \( \beta_i \) are positive numbers generally of the order of 0.5 and \( T_0 \) is a reference temperature (usually 296 K).

If \( \Gamma_D \gg \Gamma_L \) in the convolution integral of Eq. (4), then the line is “Doppler-broadened” and the lineshape function is
\[
g_D(v; P_i, T) \equiv \frac{1}{\Gamma_D} \sqrt{\frac{2 \ln 2}{\pi}} e^{-\ln 2(v-v_0)^2/\Gamma_D^2}.\]
(8)
In this regime, the intensity of the absorption peak increases proportionally with pressure. In the opposite case, when \( \Gamma_D \ll \Gamma_L \), the line is “pressure-broadened” and the lineshape function is
\[
g_L(v; P_i, T) \equiv \frac{1}{\pi \Gamma_L} \frac{1}{1 + [(v - v_0)/\Gamma_L]^2}.\]
(9)
In this regime, the depth of the absorption peak is pressure-independent, while the area of the absorption line increases proportionally with pressure. Therefore, the absorption sensitivity cannot be enhanced by indefinitely increasing the pressure. For field applications, the knowledge of the broadening coefficients is crucial for a precise determination of the absolute gas concentrations. As is well known, the best compromise between maximum sensitivity and minimum broadening is obtained with \( \Gamma_D \approx \Gamma_L \).

Precise numerical references for the quantities involved in absorption calculations \((v_0, S, \gamma_i^0, \beta_i)\) can be found in atmospheric molecular absorption databases, such as HITRAN [11,12].

3. The IR radiation source

An “idler” radiation beam, with a maximum power of about 10\( \mu \)W and a wavelength tunable around 4.25\( \mu \)m, is generated by a non-linear three-waves frequency mixing (difference-frequency generation) occurring in a 17.5 mm-long periodically-poled lithium niobate (PPLN) crystal. The “signal” beam is delivered by
a cw, single-mode Nd: YAG laser at 1064 nm, with a maximum power of 800 mW. A diode laser provides the “pump” beam, with a maximum output power of 150 mW, and a wavelength of about 850 nm. This diode laser (“slave” diode laser, SDL) is injection locked by a lower-power “master” diode laser (MDL) at the same wavelength, mounted in an extended-cavity Littrow configuration. The diode laser system has a stepwise tuning range of about 10 nm (with a $\approx 7.5$ GHz step size). Since the Nd:YAG laser has a much smaller tuning range (about 30 GHz), the $100 \text{cm}^{-1}$ tunability range of the generated IR radiation is determined by the diode laser system. Synchronous scans of the extended-cavity length and of the driving currents of both diode lasers allow continuous frequency spans wider than 15 GHz. A dichroic mirror combines the two s-polarized laser beams which are focused by a lens into the PPLN crystal to a waist of about 30 $\mu$m. To achieve optimal quasi-phase-matching, the crystal is mounted in a thermally insulated copper oven, controlled at a temperature of 287°C. More details on this set-up can be found in [13].

For the experiment described here, the IR beam is focused onto a White-type multipass absorption cell to a waist of about 300 $\mu$m, while the “pump-signal” beams are blocked before the cell by an IR anti-reflection-coated Ge filter. After the cell, IR radiation is focused onto a liquid-N$_2$-cooled InSb photovoltaic detector. First-derivative recording of the gas absorptions is used, in order to get rid of the constant background seen by the detector that severely limited the dynamic range of signal processing. For that, frequency modulation of the IR radiation is obtained by applying a sinusoidal voltage (at a 2 kHz rate) onto a PZT glued on the monolithic ring cavity of the Nd: YAG laser, and the detected signal is demodulated using a lock-in amplifier.

### 3.1. Frequency stability

The main requirement for a high-resolution spectrometer is its short/long-term frequency stability. In our IR source, due to the frequency mixing generation process, it is determined by the frequency stability of the input lasers.

The short-term frequency stability of our spectrometer is guaranteed by the narrow-linewidth emission spectra of the pump and signal lasers. These linewidths are mostly an intrinsic feature of the laser cavity design. The signal Nd: YAG laser, due to its monolithic non-planar-ring-oscillator (NPRO) cavity design, provides an emission linewidth $<10$ kHz. The extended cavity mounting of the MDL, due to the optical feedback from the grating, provides an emission linewidth $<1$ MHz. The optical injection-locking scheme insures for the pump SDL the same spectral features of the MDL. Therefore, the fast linewidth of the generated idler radiation is limited by the master/slave diode laser system and is $<1$ MHz [14].

Even for the long-term frequency instability of the IR source, the predominant contribution comes from the MDL. Therefore, particular care was taken to reduce its (passive) frequency drift to about 80 MHz/h. Also, an active thermal stabilization of the MDL extended cavity with a Peltier element reduces temperature fluctuations to less than 1 mK.
4. The multipass cell

In order to obtain long absorption paths in laboratory, compact multiple-pass optical systems have been developed by physicists since the early 1940s. The first multipass scheme was proposed by White and tested with incoherent light beams [15]. A White cell has three spherical mirrors with the same radius of curvature $R$, two of them, say A and B, at the same side and the third one (C) at the other side, working as input/output mirror with a pair of apertures. The distance $d$ between the pair (A,B) and C equals their curvature radius ($d = R$). The spots on A and B are all overlapped, while those on C lie on two parallel horizontal rows and are all separated. The overall design can be described as a double-arm, confocal, multipass cell. This design is, in principle, immune to fringes, provided that the spots on mirror C are well separated. Furthermore, this set-up is suitable to work with both collimated and divergent beams.

An alternative design was first proposed and developed by Herriott et al. in the 1960s [16,17] and further upgraded in more recent years [18]. Basically, the Herriott cell is an off-axis resonator consisting of two spherical mirrors (astigmatic or not) almost separated by their radius of curvature. The pattern of spots lying on the two mirrors can be varied by adjusting the input point of the beam and its angle. The separation of all the spots makes this design, at least in principle, immune to fringes. Due to the simpler alignment procedure, we have chosen a White-type multipass cell to perform spectroscopy at 4.25 μm wavelength. Our 2-m-long White cell allows us to obtain optical absorption paths in the excess of 130 m. To maximize the pathlength, avoiding fringes as well, the input beam must be focused so that its waist lies on the mirror C and is as small as possible. The limitation on the minimum waist size comes from the diameter of the (A,B) mirrors, that finally determine the aperture of the system.

4.1. Fringing noise reduction

Even with well separated spots on the input/output mirror C, fringes with a spacing of 37.5 MHz appear on the detector. This spacing corresponds to the 8-m optical path (four passes) between two close spots on mirror C. Even for the longest paths, we do not observe, either for the alignment He–Ne laser or the IR radiation, any significant degradation of the beam quality at the cell output, mainly due to the good optical quality of the gold-coated mirror surfaces (better than $\lambda/10$ at 633 nm). Nevertheless, even very small amounts of scattered light from the mirrors surfaces may give rise to fringes. A typical example of the fringing noise affecting our recordings is shown in Fig. 1. Although longer-spacing fringes are evident, we were not able to identify their origin.

4.1.1. Phase scrambler

In order to reduce fringing noise, we limit the maximum pathlength to 112 m and take advantage of a mechanical solution to average out the fringes. We modulate the optical pathlength by moving the mirror C with a small electric engine. A rotation
speed of about 4 turns/s and a mirror translation of about 1 mm are sufficient to obtain a good phase-scrambling and to cancel most of ringing noise [19].

4.1.2. Optimized modulation amplitude

Further reduction of ringing noise is achieved by a filtering technique that consists of selecting a particular amplitude for the frequency modulation of the infrared DFG source. Indeed, it can be noticed that as the modulation amplitude varies, the fringe visibility changes quasi-periodically, passing through minimum points. This phenomenon is analogous to the fringe visibility curve that can be observed in classical interference experiments, such as the Fresnel’s mirrors with a slit source. In the following, we describe in detail this filtering technique.

Let the detector signal have a sinusoidal modulation with period $\Delta \nu$; due to an additive fringing noise, with the following dependence on the laser frequency $\nu$:

$$F(\nu) = A \sin \left( \frac{2\pi \nu}{\Delta \nu} + \phi \right), \quad (10)$$

where $\phi$ is an arbitrary constant phase. A lock-in amplifier may be operated by sinusoidally modulating the laser frequency $\nu$ to obtain a first-derivative-like signal:

$$\nu(t) = \nu_s(t) + \nu_p \sin \left( \frac{2\pi t}{T} + \varphi \right), \quad (11)$$

where $\varphi$ is a constant arbitrary dephasing with respect to the lock-in demodulator reference signal, $\nu_p$ is the modulation amplitude, $T$ is the modulation period, and $\nu_s$
represents a slow scan of the laser frequency (i.e. \( \frac{dv_s}{dt} \ll 2\pi v_p/\Delta v \)). In such a case, \( v_s \) can be considered as a parameter of the signal:

\[
F(v_s, t) = A \sin \left[ 2\pi \frac{v_s}{\Delta v} + \phi + z \sin \left( 2\pi \frac{t}{T} + \phi \right) \right],
\]

where \( z = \frac{2\pi v_p}{\Delta v} \).

The phase detection process of the lock-in can be described as an integration over successive periods \( n \) of the reference signal:

\[
L_n(v_s, t) = \frac{1}{T} \int_{-T/2}^{T/2} P \left( 2\pi \frac{t}{T} \right) F(v_s, t + nT) \, dt
\]

where \( P(x) \) is a periodic odd function of \( x \). The output signal of the lock-in is then a sum of the \( L_n \)'s with proper weights determined by the time constant. If we put \( x = 2\pi t/T \), Eq. (13) becomes

\[
L_n(v_s, n) = \frac{A}{2\pi} \int_{-\pi}^{\pi} P(x) \sin (z \cos \phi \sin x) \cos \left( 2\pi \frac{v_{sn}}{\Delta v} + \phi + z \sin \phi \cos x \right) \, dx
\]

In particular, for our lock-in amplifier, \( P(x) = \sin x \) and Eq. (14), after some trigonometric manipulation, becomes

\[
L_n(v_s, n) = A \cos \left( 2\pi \frac{v_{sn}}{\Delta v} + \phi \right) V(z, \phi),
\]

where

\[
V(z, \phi) = \frac{2}{\pi} \cos \phi \int_{0}^{\pi/2} \sin x \sin (z \sin x) \, dx.
\]

Eq. (15) shows an oscillating behaviour with \( v_s \), reproducing fringes with an amplitude given by \( V \), as function of \( z \) and \( \phi \). \( V \) oscillates with \( z \) and vanishes for \( z_m \approx 0, 3.83, 7.02, 10.17, 13.32, \ldots \). The dephasing \( \phi \) produces only a periodic variation in the amplitude of \( V \).

Similar considerations can also be done when \( P(x) = -1 \) for \(-\pi \leq x < 0\), and \( P(x) = 1 \) for \( 0 \leq x < \pi \) (square wave). In such a case, in Eq. (15), \( V \) is replaced by

\[
W(z, \phi) = \frac{2}{\pi} \int_{0}^{\pi/2} \sin(z \cos \phi \cos x) \cos(z \sin \phi \sin x) \, dx.
\]

In particular, for \( \phi = 0 \) it reduces to

\[
W(z, \phi) = H_0(z) \equiv \frac{2}{\pi} \int_{0}^{\pi/2} \sin(z \sin x) \, dx,
\]

where \( H_0 \) is the zeroth-order Struve function [20]. It vanishes for \( z_m \approx 0, 4.33, 6.78, 10.47, 13.14, \ldots \). Differently from \( V \), the zeroes of \( W \) change with \( \phi \).

In conclusion, an additive fringing noise can be eliminated with a proper choice of the modulation amplitude, in correspondence to a null value of \( V \) or \( W \). It is worth remarking that this fringe cancellation technique can be used when the fringe spacing is not significantly larger than the linewidth. We use a modulation amplitude of
about 60 MHz which, for our fringe spacing, corresponds to the third minimum of the fringe visibility. Since the Doppler width is about 66 MHz, this is also a convenient value for first-derivative detection.

4.1.3. Time averaging program

We implemented a Fortran routine that allows us to average different scans, even if recorded on different days, by compensating for the residual drift. Each scan lasts about 9 s and a relative frequency scale, with an accuracy of about 1%, is provided by synchronous recording of the transmission peaks of the optically-injected SDL, passing through a Fabry–Perot interferometer with a free spectral range of 1.5 GHz.

The combined effect of the three techniques described above for fringing noise reduction is summarized and shown in Fig. 2. The good S/N obtained is due to a long averaging time of about 8 h, on three different days. This has recently allowed us to perform an accurate test of fundamental quantum-mechanical principles, looking for a forbidden CO\textsubscript{2} transition near an allowed “marker” one [8].

5. Sensitivity limits

A complete analysis of the different contributions to amplitude noise is useful to estimate the detection sensitivity and to suggest experimental methods to improve it.
Our photovoltaic InSb detector basically behaves as a current generator, with a responsivity \( r = 2.8 \text{ A/W} \). A proper unit for the amplitude noise power spectral density is pA\(^2\)/Hz. The first noise source is from electronics: a transimpedance preamplifier is needed for current-to-voltage conversion followed, eventually, by a second gain stage. As is well known, Johnson noise from the feedback resistance \( R \) is given by

\[
N_J = \frac{4k_B T}{R}.
\]  

This source is negligible if a sufficiently high value of \( R \) is chosen. The shot noise from the radiation is composed of two terms: the first one is related to background black-body radiation, always present even in absence of the IR beam (the so-called “dark current”), the second is from the signal IR beam itself. Its expression is

\[
N_s = 2e r (P_b + P_s),
\]

where the background power \( P_b \) is proportional to the solid angle of view and to the area of the detector. The overall expression for detection sensitivity per unit bandwidth (in Hz\(^{-1/2}\)) is

\[
S = \frac{1}{r P_s} \sqrt{\frac{4k_B T}{R} + 2e r (P_b + P_s)}.
\]

The optimal situation occurs when the main contribution to noise comes from the signal power \( P_s \) (“shot-noise-limited detection”). If \( P_b > P_s \), then noise can be reduced, e.g., by use of cold narrow-band-pass optical filters placed in front of the detector.

A detailed analysis of the noise features of our DFG spectrometer can be found in [21]. Since then a new (longer and more efficient) PPLN crystal and a new (smaller and faster) detector have been adopted. An IR power in excess of 20 \( \mu \text{W} \) has been generated and a detection bandwidth of about 4 \( \text{MHz} \) has been achieved. Therefore, we expect an improved sensitivity with this configuration. A theoretical calculation from Eq. 21 gives a sensitivity limit of 7.7 \( \times \text{10}^{-8} / \sqrt{\text{Hz}} \), which is about five times better than before. Of course, as discussed in Section 4.1, fringing noise generally limits the ultimate achievable sensitivity.

5.1. Laboratory measurements

When a spectrometer is designed to be used for high sensitivity detection of gas traces in field environmental conditions, some calibration measurements must be performed. The minimum concentration of the gas detected with this apparatus and the pressure-broadening coefficients for the absorption lines to be observed must be well known. Therefore, these measurements must be performed in an environment where the pressures of the studied gas and the foreign gases can be well controlled and measured as in a laboratory.
5.1.1. Minimum detectable pressure

This measurement is performed using a clean absorption cell, filled only with pure gas. In these conditions, the main limit to sensitivity comes from Doppler broadening of the absorption lines. At resonance ($\nu = \nu_0$), the absorption of the gas can be calculated from Eqs. (1), (2), (5) and (8) as

$$A(\nu_0; T, L) \equiv 1 - T(\nu_0; T, L) = 1 - \exp \left[ -\frac{\ln 2}{\pi} \frac{S(T)P_0L}{k_B T \Gamma_D(T)} \right] \approx \sqrt{\frac{\ln 2}{\pi} \frac{S(T)P_0L}{k_B T \Gamma_D(T)}}$$  \hspace{1cm} (22)

where the last approximation holds only for small absorptions ($A \ll 1$) and can be used to estimate the minimum detectable pressure of the absorbing gas for a given experimental direct-absorption sensitivity (per unit integration time) and optical pathlength. For pure gases, the sensitivity per unit length and integration time in Pa/(m $\sqrt{\text{Hz}}$) is generally given. We report in Table 1 the estimated detection sensitivity of pure CO$_2$ at a temperature of 296 K.

5.1.2. Broadening measurements

A useful measurement that can be easily taken with direct-absorption spectroscopy is the pressure-broadening coefficient for different transitions. With a given cell length (in our case 4 mm), only a limited number of transitions, distributed in a relatively narrow intensity range, can be studied. We decided to study the R-side of the (00$^0$1–00$^0$0) $^{12}$C$^{16}$O$_2$ band, also due to the absence of other interfering lines. The optimum line strength for these measurements is about $5 \times 10^{-21}$ cm, corresponding to the intensities of R(64) and R(66) transitions.

Figs. 3 and 4 show the absorption profiles that we experimentally recorded with the corresponding fits, to determine the linewidths. Some fringes are evident, intrinsically due to the simple optical set-up, with a spacing of about 400 MHz, corresponding to a 40-cm-long interfering cavity. A Lorentzian lineshape is assumed at these pressure regimes (5–90 kPa). In fact, for CO$_2$ molecules at $\lambda \approx 4.25$ $\mu$m and room temperature, the Doppler width is much smaller, $\Gamma_D \approx 66$ MHz.

We obtained the pressure-broadening coefficients by linear fits of the linewidths with respect to the pressures, as shown in Figs. 5 and 6. We obtained, for the

<table>
<thead>
<tr>
<th>Ambient</th>
<th>$T$ (K)</th>
<th>$\Gamma_D$ (MHz)</th>
<th>$\gamma$ (kHz/Pa)</th>
<th>Detection sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure gas</td>
<td>296</td>
<td>65.7</td>
<td>30$\pm$4</td>
<td>$3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Air</td>
<td>296</td>
<td>65.7</td>
<td>22$\pm$3</td>
<td>9</td>
</tr>
<tr>
<td>Fumarolic gas</td>
<td>433</td>
<td>79.5</td>
<td>28$\pm$5</td>
<td>16</td>
</tr>
</tbody>
</table>
pressure-broadening coefficients of the R(64) and R(66) lines, 22.7(5) and 23.0(3) kHz/Pa, respectively. These two values are similar and are both consistent with the HITRAN [11] value of 19(3) kHz/Pa. It should be noted that our measurements have an accuracy of about one-order of magnitude better than the literature values.

6. Possible field applications

The situation is quite different when measurements are performed in an outdoor environment, with an open-air absorption path, instead of a clean and controlled vacuum. The fractional composition of the atmosphere in the measurement site must be taken into account, in order to estimate the achievable sensitivity for CO₂ detection. At atmospheric pressure, the main limit to sensitivity comes from the foreign- and self-broadening of the absorption lines, since the lineshape is Lorentzian. At resonance ($\nu = \nu_0$), the absorption of the gas can be calculated from Eqs. (1), (2), (6), (7) and (9) as

$$A(\nu_0; P_i, T, L) \equiv 1 - T(\nu_0; P_i, T, L) = 1 - \exp\left(-\frac{S(T)P_0L}{\pi k_B T \Gamma_L(P_i, T)}\right) \approx \frac{S(T)P_0L}{\pi k_B T \Gamma_L(P_i, T)},$$

(23)
Fig. 4. Direct-absorption recordings of the (00$^0$I–00$^0$0) R(66) $^{12}$C$^{16}$O$_2$ transition at 2387.258 cm$^{-1}$ for different pressure values. The experimental conditions are the same as Fig. 3. Larger linewidths correspond to higher pressures.

Fig. 5. Linear fits of the pressure-broadening coefficient of the (00$^0$I–00$^0$0) R(64) $^{12}$C$^{16}$O$_2$ transition, which results in 22.7(5) kHz/Pa.
where the last approximation holds only for small absorptions \((A \ll 1)\) and can be used to estimate the minimum detectable fraction (e.g. in parts per billion) of the absorbing gas. For air-broadened lineshapes, the sensitivity per unit length and integration time in ppb/(m√Hz) is often given. We report in Table 1 the estimated broadening coefficients and detection sensitivities of CO\(_2\) in air and in a particular fumarolic gas, at Solfatara volcano, near Naples, Italy. The composition is assumed to be 80% H\(_2\)O and 20% CO\(_2\) at a temperature of 433 K [22]. If we compare our sensitivity, in air, with that reported for overtone absorption spectroscopy with diode lasers at 2 and 1.6 μm [23], we notice an improvement of two and three orders of magnitude, respectively, for CO\(_2\) trace detection in air. Of course, the instrumental sensitivity, expressed as \(\Delta P/P\), scales only with the inverse square root of the emitted power \(P\), if shot-noise-limited detection is considered. Therefore, diode-based spectrometers, with typical emitted powers in the mW range, are more sensitive than present-day DFG spectrometers, with powers at best of tens of μW.

7. Summary and conclusions

We have described our DFG-based spectrometer tunable around 4.25 μm wavelength, which offers the possibility to perform high-sensitivity and high-resolution spectroscopy of CO\(_2\), that is one of the most important atmospheric and geothermal gases. The key features to achieve high-sensitivity detection in our

Fig. 6. Linear fits of the pressure-broadening coefficient of the \((00^10-00^11)\) R(66) \(^{12}\)C\(^{16}\)O\(_2\) transition, which results in 23.0(3) kHz/Pa.
laboratory spectrometer were discussed. It was also shown that pressure-broadened profiles can be studied and broadening coefficients retrieved with a relatively small uncertainty. It is worth noting that a broadening analysis of very weak lines or with high \( J \) rotational quantum numbers, not reported in current molecular databases, can also be obtained. This is useful, for example, when rare isotopes are studied, as is often required in field applications.

We conclude by remarking that most of the techniques described to increase the detection sensitivity of our laboratory spectrometer can be transferred to field-deployable instruments.

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