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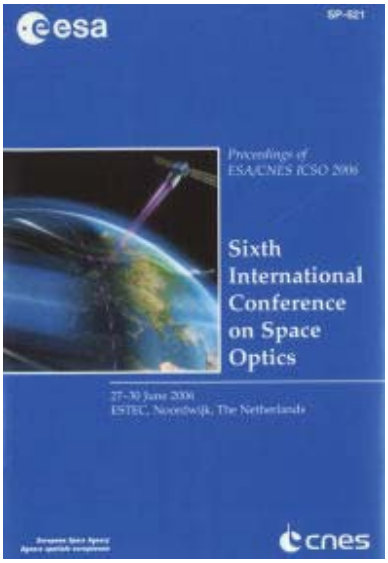

Comb-referenced ultra-high sensitivity spectroscopic molecular detection by compact non-linear sources

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COMB-REFERENCED ULTRA-HIGH SENSITIVITY SPECTROSCOPIC MOLECULAR DETECTION BY COMPACT NON-LINEAR SOURCES

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ABSTRACT

We present a new generation of compact and rugged mid-infrared (MIR) difference-frequency coherent radiation sources referenced to fiber-based optical frequency comb synthesizers (OFCSs). By coupling the MIR radiation to high-finesse optical cavities, high-resolution and high-sensitivity spectroscopy is demonstrated for CH_4 and CO_2 around 3.3 and 4.5 μm respectively. Finally, the most effective detection schemes for space-craft trace-gas monitoring applications are singled out.

Key words: difference-frequency generation; optical frequency comb; high-sensitivity gas sensing.

1. INTRODUCTION

Detection and quantification of trace gases are relevant in several areas of research, such as atmospheric chemistry and environmental monitoring, as well as biomedical diagnostics and molecular astrophysics. To achieve the necessary sensitivity and selectivity, high-resolution spectroscopic techniques in the infrared (IR) "fingerprint" region can be applied. Recent developments in mid-IR coherent sources, such as quantum-cascade lasers, difference-frequency generators (DFGs) and optical parametric oscillators (OPOs), have made possible significant advances in this field. In the last decades, great improvements were also possible thanks to spectroscopic techniques based on high-finesse optical cavities, where effective absorption path-lengths of several kilometers can be achieved. The most popular are cavity ring-down spectroscopy (CRDS) [1] and cavity-enhanced absorption spectroscopy (CEAS). The former relies on a cavity-field decay-time measurement and allows to observe absorption spectra intrinsically free from laser source amplitude noise. The latter consists in detecting the cavity transmission while keeping the laser locked on a cavity mode that is rapidly scanned around the molecular resonance. A much more complex cavity-enhanced spectroscopic technique, which demonstrated a detection sensitivity as low as 10^{-14} cm^{-1}Hz$^{-1/2}$, has been reported in [2]. In this scheme, known as noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS), a very-high finesse resonator was combined to a radio-frequency (RF) modulation technique to achieve shot-noise-limited sensitivity performance. However, all these methods make use of complex electronics either for fast time-resolved measurements, or for tight and low-noise frequency-locking schemes. Another valuable, much easier approach for high-sensitivity gas detection is off-axis integrated-cavity-output spectroscopy (OA-ICOS), which combines the detection principle of CEAS with a simpler set-up, using a multi-pass-like alignment for the high-finesse cavity. This so called "off-axis" geometry results in the excitation of an extremely dense mode spectrum so that the interaction between the laser and the cavity can be considered "always-resonant", thus dramatically reducing the typical amplitude noise associated with the resonant behavior of optical cavities. Moreover, as all transverse TEM$_{mn}$ modes contribute to detection of the intra-cavity absorber, the off-axis set-up turns out to be substantially insensitive to vibrations and misalignments. Detection limits for in-situ trace-gas monitoring may significantly be improved when the intrinsically-high detection sensitivity that characterizes the "fingerprint" region and the use of optical cavities is combined to the more recent technology of optical frequency comb synthesizer (OFCSs) which are able to guarantee ultra-high frequency stability and reproducibility. This combination can benefit enormously from the possibility to average measurements over very long times. Since their early appearance, OFCSs have been used as reliable tools for time and frequency metrology [3]. At present, there are two main classes of OFCSs based on different mode-locked fs lasers, namely Ti:sapphire lasers at 800 nm (covering all the visible region) and Er-doped fiber lasers at 1.55 μm (covering the near-IR region). So far, the spectral coverage of OFCSs is limited on the longer wavelength side to about 2.3 μm. Different approaches to extend them further in the IR have already been demonstrated [4, 5]. In our experiment, the basic idea is to phase-lock the DFG radiation to a visible-near-IR comb, by locking each of the pumping lasers to the closest comb tooth. In this way,

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the MIR radiation borrows from the OFCS some peculiar advantages such as high stability in its absolute frequency and a reduced line-width, only limited by the phase noise of the single OFCS tooth (a few hundred kHz). For example, the latter issue is crucial when the MIR radiation has to be coupled to a high-finesse cavity with very narrow resonant peaks, because the coupling efficiency increases as the MIR line-width decreases.

In this work we report the development of a mid-infrared tunable coherent radiation source based on difference frequency generation. The signal and pump beams are mixed into a periodically-poled $LiNbO_3$ crystal to produce radiation in the $2.9 \div 4.8$ μm spectral range with a maximum output power of 5 mW. We show that such a source can be effectively coupled to high-finesse optical cavities to perform high-resolution and high-sensitivity investigation of molecular absorption spectra. Both the CRDS and the OA-ICOS schemes have been implemented for detection of ambient-air, natural-abundance CH_4 around 3.3 μm and of rare isotopologues of CO_2 around 4.5 μm, respectively. Moreover, we show that, when the DFG source is directly referenced to an OFCS, the obtained high frequency stability and reproducibility allows averaging measurements over very long times to further improve the detection limits. On the other hand, field operation of DFG devices would also be of great interest in a number of monitoring applications. For this purpose, the laser spectroscopic system must be easy to operate, essentially immune to vibrations and chemically-aggressive agents, and almost unaffected by changes of the environmental conditions. Therefore, special care has been devoted to the design and development of a particularly compact and robust DFG source. In Sec. 3 we report on the development of a portable DFG spectrometer and evaluate its performance for monitoring of natural-abundance trace-gases in ambient air both in a direct-absorption scheme and in conjunction with a two-tone frequency modulation spectroscopy (TTFMS) technique.

2. COUPLING DFG RADIATION TO HIGH-FINESSE OPTICAL CAVITIES

The set-up for the generation of the 3-μm radiation is described below [6]. The pump (signal) beam comes from an external-cavity diode laser, emitting in the range $1030 \div 1070$ nm ($1545 \div 1605$ nm), and is amplified by an Yb-doped (Er-doped) fiber amplifier which delivers up to 700 mW (8 W). Then, the two laser beams are combined onto a dichroic mirror and focused by an achromatic lens into the nonlinear crystal. The latter is a 50-mm-long, periodically-poled lithium-niobate (PPLN) crystal consisting of an array of 9 channels, with different poling periods ranging from 29.6 to 30.6 μm. When the wavelength of each pumping source is fixed, the quasi-phase-matching condition for the DFG process is satisfied both by selecting the proper channel and adjusting the crystal temperature between 50 and 70 °C. The described system produces coherent tunable radiation in the $2.9 \div 3.5$ μm range, with a line-width of about 1.5 MHz, basically determined by that of the pumping sources. With a similar apparatus, coherent radiation is generated in the $3.8 \div 4.8$ μm interval. In this case the "pump" laser source is a CW external cavity diode laser (ECDL) with $830 \div 870$ nm tuning range, and 130 mW output power. The "signal" laser source is a monolithic-cavity Nd:YAG laser at 1064 nm with a few kHz line-width, seeding a 5 W Yb fiber amplifier. The non-linear mixing process takes place in a multiple-channel, 50-mm-long periodically-poled $LiNbO_3$ crystal, with different poling periods ranging from 21.4 to 23.0 μm and can generate up to 170 μW "idler" radiation.

In our experiment, the MIR radiation emerging from the crystal is coupled to high-finesse optical cavities to perform trace gas detection. Two different approaches are used. A CRDS approach is adopted for CO_2 spectroscopy at 4.5 μm, while an OA-ICOS scheme is implemented for CH_4 detection at 3.3 μm.

2.1. CRDS

The set-up for the generation of the 4.5-μm radiation and reference it to a Ti:sapphire-based OFCS is shown in Fig. 1 [7]. The OFCS is made by a Kerr-lens mode-locked Ti:sapphire laser emitting pulsed radiation centered at 800 nm with pulse duration of about 30 fs and average power exceeding 700 mW. Its spectrum is broadened by a 20-cm-long photonic-crystal fiber to more than one octave in the $500 \div 1100$ nm region. The reference oscillator to lock the OFCS repetition rate $\nu_r \approx 1$ GHz, is a high-quality 10-MHz quartz disciplined by a Rb/GPS clock. The measured Allan deviation of this quartz against a Cs-fountain-disciplined H maser gives a 1-s stability of 6×10^{-13}. For all time scales longer than 1 s the stability is better than 1.5×10^{-12} and the ultimate accuracy is limited by the GPS receiver. A fraction of the pump and signal radiation is, respectively, beaten with the nearest OFCS tooth to generate the RF signals $\Delta\nu_p$ and $\Delta\nu_s$. The pump RF beat-note is phase-locked to a local oscillator by feeding back proper corrections to the PZT of the diode laser cavity, as well as to its drive current. Similarly, the signal laser is phase-locked to the same local oscillator, by feeding back corrections to the PZT and temperature drivers controlling the Nd:YAG crystal. With these locks, the absolute frequency of the generated IR radiation is perfectly known and under control any time.

The generated IR radiation is used for CRDS by coupling it to a home-made 1-m-long Fabry-Perot cavity, corresponding to a free spectral range (FSR) of 150 MHz. Each of the two dielectrically-coated Si mirrors has a loss $1 - R < 1.3 \times 10^{-4}$ and a radius of curvature of 6 m. A 3-bars Invar structure guarantees a good passive thermal stability and lays on the vacuum chamber with a cantilever system damping mechanical vibrations in all directions. The estimated finesse is in excess of 24 000 and, due to the narrow resonant peaks (less than 7 kHz), the coupling efficiency is very low (less than 1%). Re-

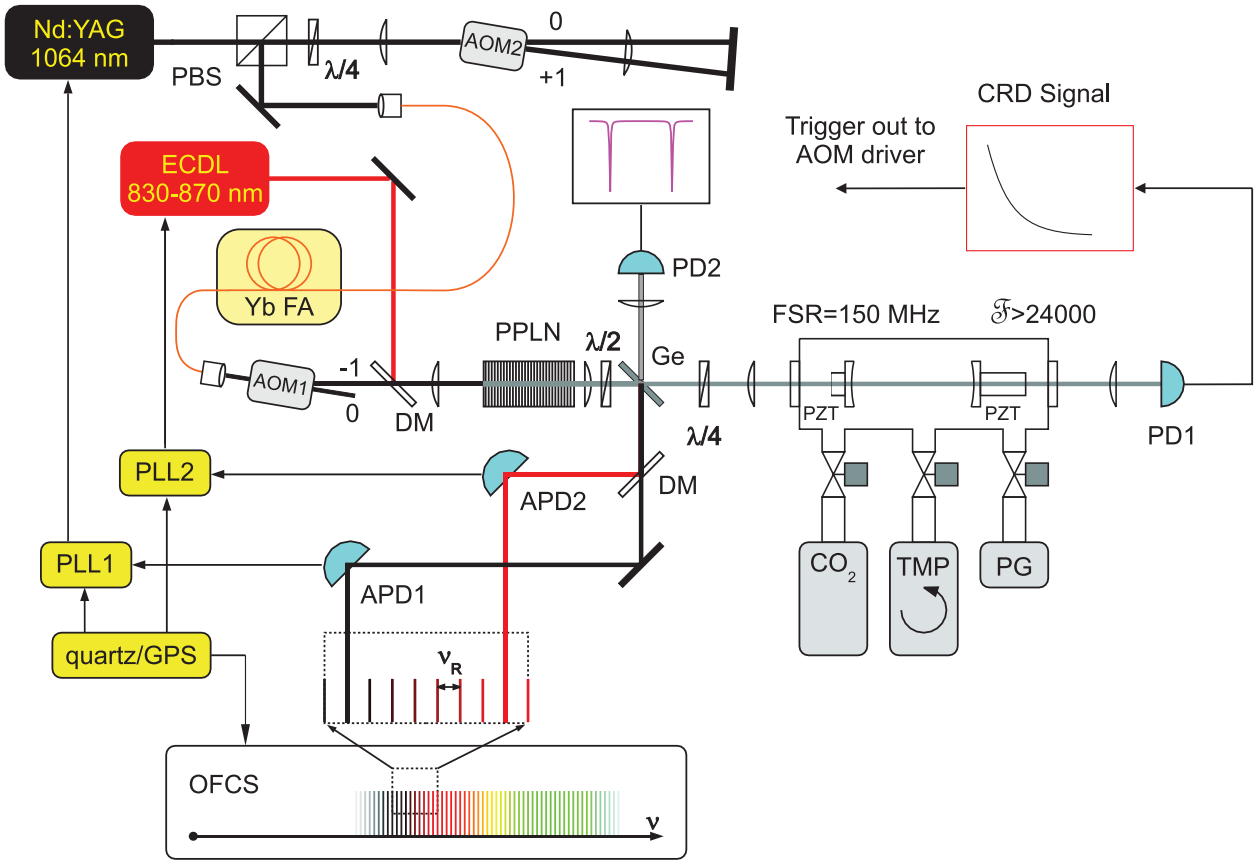

Figure 1. Scheme of the experimental set-up. Legend: FA = fiber amplifier; DM = dichroic mirror; PPLN = periodically-poled $LiNbO_3$ crystal; PD1, PD2 = InSb photo-diodes; PZT = piezo-electric actuator; $\lambda/4$, $\lambda/2$ = quarter-, half-wave-plates; PLL1, PLL2 = phase-locked-loops; APD1, APD2 = avalanche photo-diodes; TMP = turbo-molecular pump; AOM1, AOM2 = acousto-optic modulators ($\nu_1 = 110$ MHz, $\nu_2 = 225$ MHz); PBS = polarizing beam splitter; PG = pressure gauge; OFCS = optical frequency-comb synthesizer.

flection and transmission signals are detected by a pair of twin liquid-N_2-cooled InSb photo-diodes, each one with an intrinsic rise time of 30 ns. Due to the high frequency stability of both the OFCS-disciplined DFG source and the Fabry-Perot cavity, several cavity ring-down exponential decay signals can be recorded and averaged by a digital oscilloscope without any frequency-lock between IR radiation and cavity. The minimum detectable absorption coefficient for a single CRD event (200 μs duration) is about 10^{-8} cm^{-1}. This means that rare isotopologues of CO_2 with line-strengths down to 10^{-29} cm can be detected in a 1 s averaging time.

2.2. OA-ICOS

In this set-up, a 90-cm long optical cavity is used, with spherical mirrors or radius of curvature $r = 6$ m and reflectivity $R = 99.95\%$. The resulting effective absorption path-length is about 2 km. The off-axis alignment is achieved starting from on-axis position (TEM_{00} alignment), then horizontally shifting the beam out of the cavity axis, and slightly tilting it in the vertical direction. The light emerging from the output cavity mirror is finally focused onto a 3-stage thermo-electrically-cooled InAs detector. The off-axis configuration spatially separates the multiple reflections within the cavity until the re-entrant condition is satisfied, i.e. when the ray begins to retrace itself on the original path. This is dictated by the specific curvature r and spacing L of the mirrors forming the cavity. The multiple reflections appear on the mirrors as a series of spots in an elliptical pattern. The angle 2θ of a round-trip rotation is again purely determined by the geometry of the cavity and is given by $\cos\theta = 1 - L/r$. When $2m\theta = 2p\pi$ where m equals the number of optical round-trip passes and p is an integer, the pattern becomes re-entrant and the cavity effective free-spectral-range (FSR) equals $c/2mL$. In our set-up, starting from an on-axis FSR of 166 MHz, a 15-MHz mode spacing is measured, yielding a number of round trips $m = 11$ with $p = 2$. The upper limit to the m value is actually set by the finite beam spot size and mirror diameter, as a higher round-trip number would cause beam overlap and thus unwanted interference fringes. ICOS spectra are recorded according to the following procedure. The DFG source is scanned over the molecular transition of interest by sweeping the pump laser. Also, in order to wash out the cavity mode structure, the pump laser is current modulated for fast frequency dithering of the DFG beam while the piezo element on the cavity input mirror is used to introduce a slow cavity-length modulation [8]. With this procedure a minimum detectable concentration of 250 ppt Hz$^{-1/2}$ is found for natural abundance ambient air methane. Referencing of this DFG set-up to to a fiber-based OFCS covering the $1 \div 2$ μm spectral range (which is already operating in our lab) is under development and will make the absolute frequency of our mW-level coherent source in the $2.9 \div 3.5$ μm region directly traceable to the primary Cs standard. This will increase the stability and selectivity of trace-gas detection in this mid-IR region.

3. PORTABLE DFG SPECTROMETER

The portable DFG spectrometer [9], shown in Fig. 2, consists of a trolley ($55 \times 70 \times 75$ cm), carrying the laser sources and the control electronics in its lower part, while on the top is located a small breadboard which includes the optical fibers and components, the sample multiple-reflection cell (effective absorption path-length $L = 13$ m) and a three-stage thermo-electrically-cooled InAs detector (700-kHz bandwidth). After passing in two fiber-pigtailed polarization-control stages, the DFG pumping laser beams, coming from the amplifiers, are combined into a polarization-maintaining wavelength division multiplexer (WDM), and then focused by means of a fiber-coupled achromatic lens into the non-linear crystal. The non-linear conversion part of the apparatus, visible on the breadboard in Fig. 2, is enclosed in a titanium box to protect the crystal oven and to keep it in a controlled environment. The PPLN crystal is temperature-controlled by a Peltier cell and mounted on a set of motorized computer-controlled translation stages for fine alignment. A laptop computer is employed for remote control of the generation unit when optimization of the conversion efficiency or large wavelength variations are required. In this way, the MIR radiation can be generated on demand directly on the measurement site. Thus the probe beam can be far from the breadboard with the signal and pump laser beams being coupled in through low-loss telecom fibers. One key-point that makes the spectrometer well suited for field applications is the presence of all-fiber-coupled optical components before the non-linear conversion stage. This reduces DFG power fluctuations due to vibrations that cause misalignments in the crystal input. The performance of the DFG spectrometer is evaluated for methane detection around 3.35μm. In order to further increase the detection sensitivity, we employ a two-tone frequency modulation spectroscopy (TTFMS) technique. For this purpose, a strong CH_4 transition is chosen ($\nu_0 = 3017.46689$ cm^{-1} with $S = 1.348 \cdot 10^{-19}$ cm) and the multiple-reflection cell is filled with ambient air at 67 mbar. A low-frequency signal at ω (160 kHz) from a function generator is mixed with a high-frequency output at Ω (400 MHz) from a radio-frequency (RF) synthesizer. These signals are combined using a double-balanced mixer to produce sum ($\Omega + \omega$) and difference frequencies ($\Omega - \omega$), namely the two tones. The tones were chosen with a frequency separation from the carrier comparable with the line-width of the absorption profile in order to maximize the absorption contrast. After high-pass filtering and amplification, the two tones are transferred to the DFG radiation via a bias-tee connected to the pump diode-laser anode. The low-frequency signal is also sent, by means of a directional coupler, to a frequency doubler to produce a 2ω reference. The latter is used as a local oscillator of a double-balanced mixer that performs phase-sensitive demodulation of the photo-detected output signal, extracting the 320 kHz beat. The TTFMS scheme significantly improves the laser-noise-limited sensitivity thanks to a high modulation frequency, while keeping the detection frequency in the audio range. Indeed a signal-

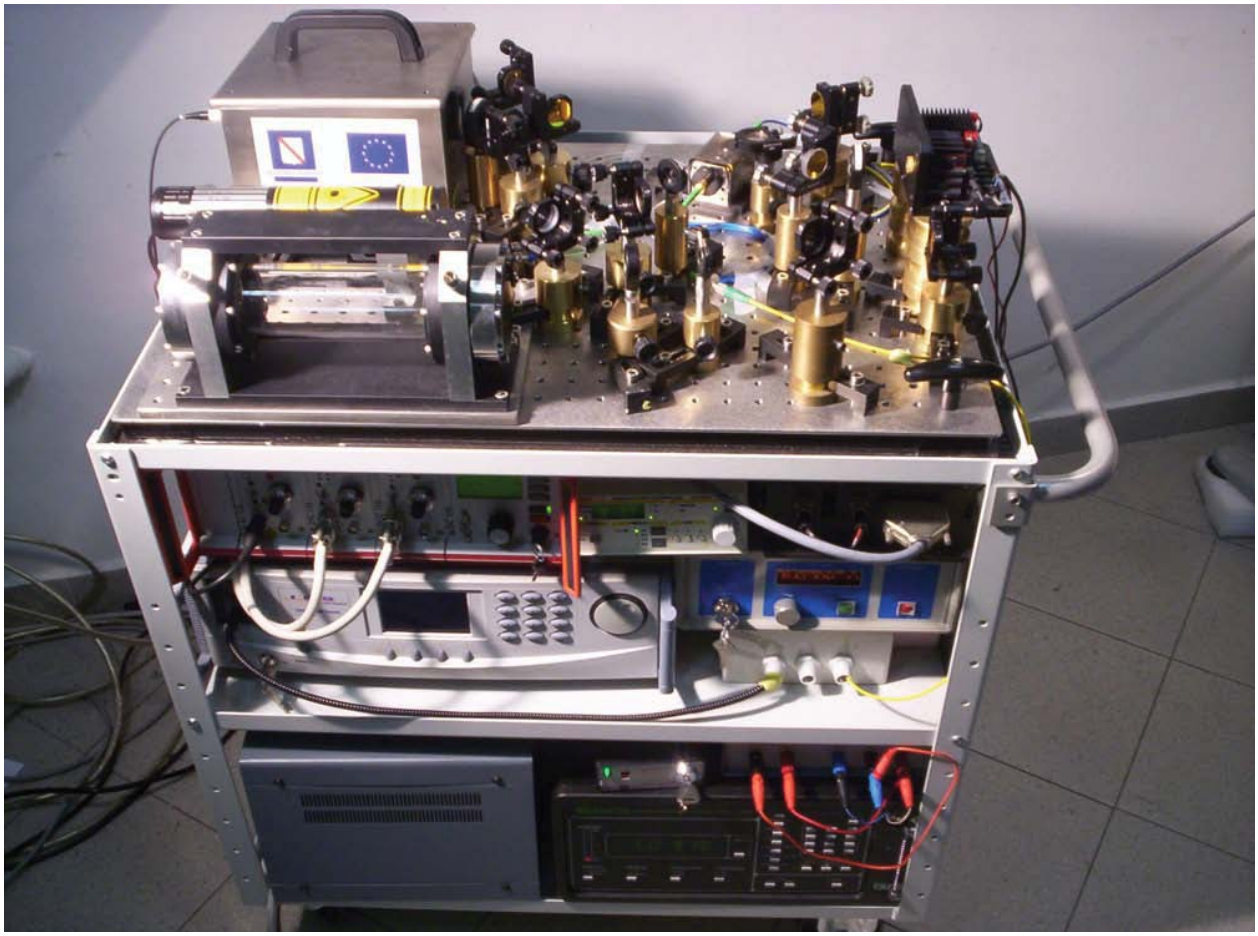

Figure 2. Picture of the DFG spectrometer showing the whole apparatus set on a trolley ($55 \times 70 \times 75$ cm). The laser sources, the wave-meter and the control electronics are in the lower part, while a small breadboard on the top includes optical elements, fibers, the multi-pass cell and the detector. The titanium box contains the PPLN crystal and the stages for its alignment. In this way, the breadboard can be used as a separated probe to operate even in challenging conditions without affecting the operation of the DFG pumping sources.

to-noise enhancement of about 10^2 with respect to direct absorption measurements has been observed, which corresponds to a minimum detectable fractional power change of $6.5 \cdot 10^{-6}$ $\mathrm{Hz}^{-1/2}$, corresponding to a minimum detectable concentration of 400 ppt $\mathrm{Hz}^{-1/2}$. This result well compares to previously reported experiments carried out by means of conventional coherent radiation sources, extending the benefits of RF two-tone techniques to the mid infrared. The possibility of combining selection of strong transitions with efficient noise-reducing techniques leads to detection limits that have been so far accessible only to spectrometers based on high-finesse cavities. Thanks to the wide tunability of the spectrometer, minimum detectable concentrations at the ppb level or below can be in principle obtained for other different species.

4. CONCLUSIONS

We have reported on a new class of MIR widely tunable spectrometers based on the DFG process with a maximum output power of several mW. High-resolution and high-sensitivity molecular detection has been demonstrated by coupling such MIR sources to high-finesse optical cavities and referencing them to an OFCS. In particular, ambient-air natural-abundance CH_4 detection has been performed at 3 μm by means of OA-ICOS with a minimum detectable concentration of 250 ppt $\mathrm{Hz}^{-1/2}$. Rare isotopologues of CO_2 with line-strengths down to 10^{-29} cm can be detected in 1 s with CRDS. We have also built a portable version of the DFG spectrometer and evaluated its performance for real-time in-situ monitoring of trace-gas by coupling the MIR radiation to a multiple reflection cell and performing TTFMS. With this much more robust and compact set-up we have demonstrated a detection limit that is comparable with that obtained by the OA-ICOS approach. Work is in progress to link such a spectrometer to the near-infrared fiber-based OFCS, thus paving the way to the realization of a comb-referenced MIR source optimized for space-craft operation.

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