Relazione sull'attività di ricerca del Dr. Pietro Malara nell'ambito del Programma "CNR Short-term Mobility" 2010, avente per oggetto: "Development and applications of innovative quantum cascade lasers", svolta presso la School of Engineering and Applied Sciences, Harvard University, Cambridge MA (U.S.).

Sensitivity of spectroscopic detection is a crucial issue for applications where concentrations of trace molecular species are to be measured. Atmospheric chemistry, environmental monitoring, biomedical diagnostics and molecular astrophysics are just a few examples of areas of research demanding for ultra-sensitive and rugged setups, capable of field measurements [1-8]. However, for most of spectroscopic methods, the Beer-Lambert law leaves only two open ways to improve the detection sensitivity: increasing the radiation/sample interaction pathlength and reducing the noise that affects the absorption signal.

There are a number of well-established methods for absorption length enhancement, the most effective of which exploit the several-kilometers paths attainable in high finesse optical cavities. Techniques such as cavity ring-down spectroscopy (CRDS), cavity-enhanced absorption spectroscopy (CEAS) and Integrated Cavity output spectroscopy (ICOS), demonstrated minimum detectable absorption coefficients ranging from 10^{-8} $cm^{-1}Hz^{-1/2}$ to 10^{-11} $cm^{-1}Hz^{-1/2}$ [9-10].

As for noise suppression, different strategies are usually adopted for the different noise sources. For example, high speed ensemble averaging can reduce white noise of a detector and its associated electronics while antireflection coatings can suppress the optical noise that often limits the sensitivity of laser-based spectrometers. Since the 80's heterodyne detection schemes have been employed to suppress the technical *1/f* (flicker) noise associated with all laser sources and most photodetectors [11-14]. The general principle underlying these methods consists modulating the laser current to produce a pair of sidebands on the laser carrier and, after interaction with the sample, detecting and demodulating their beat frequency by means of phase-sensitive electronics. In this way, a sample's absorption depth and linewidth are encoded at the modulation frequency, which can be set in the radiofrequency (RF) domain, where the flicker noise is reduced by a few orders of magnitude. Many variations of this basic heterodyne detection scheme have been successfully applied, providing in some cases sensitivity enhancements up to two orders of magnitude with respect to traditional laser spectroscopy [15-17].

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To our knowledge, however, the realization of a technique that combines the signal enhancement of cavity-based techniques with the noise suppression of a heterodyne detection scheme has proven non-trivial. It was addressed only in 1998 by Ye *et al.*, with a technique called noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS) [18]. In NICE-OHMS, the radiation injected in the optical resonator is modulated at a frequency that is a multiple of the cavity mode spacing (FSR), thus creating a couple of sidebands available at the cavity output. Then, the transmitted signal is heterodyned to retrieve information on the intracavity absorption. In this way, an unprecedented shot-noise limited detection sensitivity, as low as 10^{-14} $cm^{-1}Hz^{-1/2}$ was demonstrated in the near infrared. However, in order to be transmitted by the cavity, both carrier and modulation sidebands must be constantly in resonance with three cavity modes. To achieve this condition, the cavity mode spacing or free spectral range (FSR) and the laser frequency need to be stabilized independently by means of tight, fast, and low-noise frequency-locking schemes. As a consequence, the setup is technically extremely demanding and particularly sensitive to mechanical shocks and vibrations. This makes the extraordinary high sensitivity reachable by NICE-OHMS only attainable in laboratory environments.

Our experiment consists of a different detection scheme, based on an off-axis injection of a high finesse cavity in combination with a frequency modulation technique. Crucially, this method, TTFM-ICOS (see below), requires no active control of the cavity length and is relatively straightforward to implement electronically, allowing for facile conversion of existing ICOS setups to perform FM-ICOS while still maintaining the ability to carry out traditional ICOS, simply by turning off the modulation. Note that our invention is not limited to the mid-infrared and/or the use of a quantum cascade laser as a light source. This novel technique works equally well for example with a single mode diode laser emitting in the near infrared.

The off-axis laser injection geometry is analogous to that observed in Herriott multipass cell [19], where the multiple ray reflections between two concave mirrors trace out a series of reflections in an elliptical pattern, with a per-pass angular displacement given by $cos\theta=1-L/r$, where L and r are respectively the mirror distance and curvature. The ray pattern becomes re-entrant when $2m\theta=2p\pi$, where m equals the number of optical round-trip passes and p is an integer. In this way the cavity effective free-spectral-range (FSR) equals $c/2mL$. With a proper choice of L and r, the number m can be made extremely large, so that the entire cavity mode structure collapses in a continuum and the cavity effectively behaves like a non-resonant optical element.

The use of off axis injection into an optical cavity, rather than a Herriott cell, first proposed By J. Paul et al. in 2001 [20]. In this technique, called off-axis integrated cavity output spectroscopy (OA-ICOS), time integration of the output signal is used to average out the residual mode structure of the off axis cavity. Additional laser-frequency and cavity-length dithering can be introduced to help in achieving the non-resonant condition, where the cavity behaves effectively like a single-pass absorption cell of length LF/π, where F is the finesse.

In practice, the actual sensitivity enhancement of the OA-ICOS method compared to traditional multipass spectroscopy relies on the ability to smooth out the cavity resonance structure. While in traditional multipass cells mechanical vibrations can create unstable patterns of interferences that are difficult to average out, in OA-ICOS the mechanical vibrations as well as the small misalignments which are usually unwanted, contribute to the scrambling of the mode structure and therefore to the suppression of the excess cavity resonant noise. The technique is inherently robust and fieldable.

The core idea of FM-ICOS method described here consists of exploiting the quasi-continuum of cavity transmission to perform a cavity-enhanced heterodyne detection without need for any frequency locking loop or active stabilization. In fact, having no resonance condition to be met, the off-axis alignment guarantees in principle that any laser carrier with its modulation sidebands is transmitted by the cavity, allowing the beat note between sidebands to be detected, demodulated, and then treated like a standard ICOS signal.

Such a detection scheme can therefore benefit both of the cavity signal enhancement and the heterodyne technical noise reduction, while preserving the ruggedness typical of OA-ICOS.

A few examples of OA-ICOS associated with modulation and lock-in harmonic detection exist in literature. These experiments were performed only in the low modulation frequency regime [21-23], but still demonstrated, in a fully optimized setup, up to one order of magnitude sensitivity improvement with respect to traditional ICOS.

Straightforwardly, going to a higher frequency-modulation regime is expected to reduce to a much larger extent the $1/f$ noise. Also, the more the modulation frequency exceeds the cavity 3dB lowpass cutoff at $1/2\pi\tau$ (where τ is the cavity ringdown time) the more the laser residual amplitude modulation (RAM), is attenuated at the cavity output. This can be a crucial point since RAM is one of the main noise sources in all the frequency modulation setups, in particular when using lasers with a high slope efficiency, such as QCLs.

Despite the mentioned advantages, a proper heterodyne technique in an off-axis cavity has yet to be demonstrated. To this purpose, we set up the experimental scheme sketched in Figure 1.

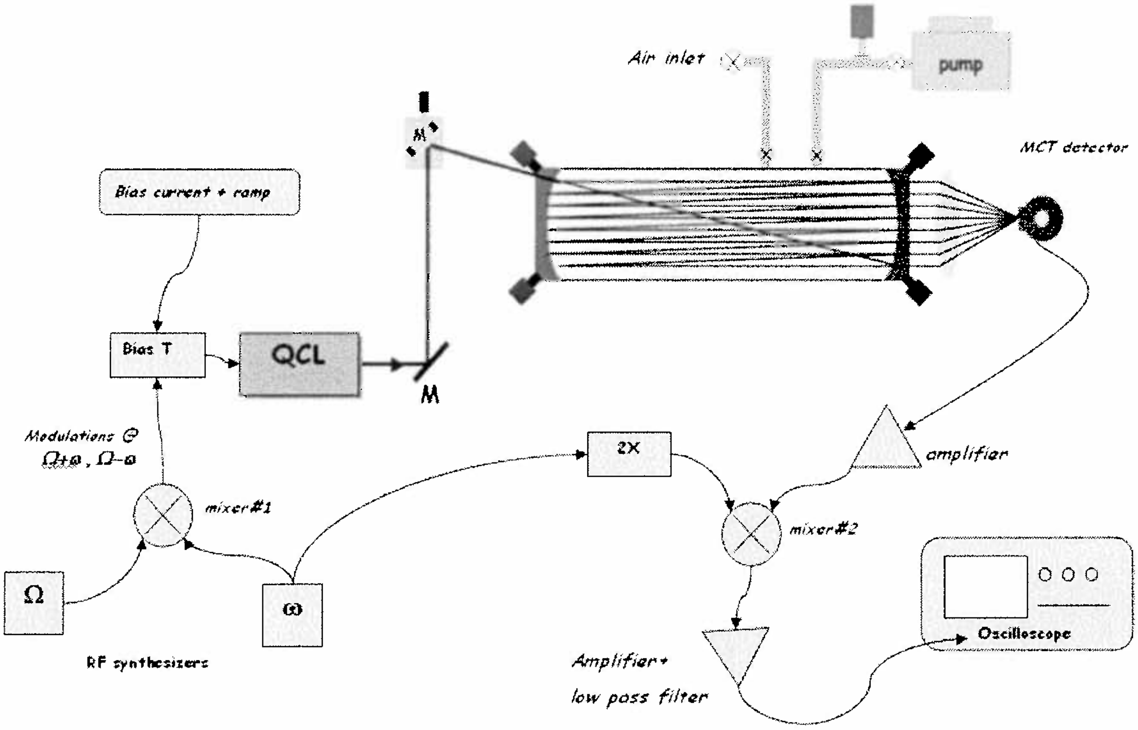

Figure 1: schematic of the setup used to combine the OA-ICOS and the TTFM-ICOS techniques.

One critical issue in combining ICOS with an FM technique is represented by detector's performance. FM-ICOS requires a photodetector that is at once highly sensitive and has an extremely high bandwidth (typically FM techniques require detector bandwidths in the hundreds of MHz). While such detectors are available for detecting near-IR wavelengths, we do not have presently in our laboratory mid-IR Mercury Cadmium Telluride (MCT) detectors that are simultaneously this fast and very sensitive. In order to still exploit the general advantages of frequency modulation despite the bandwidth limitation, we have adopted a two-tone frequency modulation spectroscopic technique (TTFM-ICOS).

In TTFM-ICOS the laser is modulated by two different voltage swings at frequencies Ω and ω, rather than a single frequency as in FM spectroscopy. The frequency Ω is larger than the absorption linewidth (several hundreds of MHz), whereas ω is relatively small (hundreds of KHz to a few MHz). Such a modulation gives rise to three couples of second-order sidebands, each couple separated by 2ω, and centered respectively at frequencies $\omega_0 - \Omega$, ω_0 and $\omega_0 + \Omega$, ω_0.

Under these conditions, the signal at the detector shows a beat component at 2ω proportional to the differential attenuation of the three doublets, which carries information on the sample absorption [12], and can be written as

$$I(t) \propto m^2 e^{-2\delta_0}\left[1 + (2\delta_0 - \delta_+ - \delta_-)\cos 2\omega t\right] \qquad (1)$$

Where m is the modulation index and $\delta_0, \delta_+, \delta_-$ are the attenuations of the three doublets due to absorption. Since 2ω is small compared to the absorption linewidth, each second order sideband couple *(-,0,+)* can be considered as experiencing an overall attenuation $\delta_{(-,0,+)}$. As Eq.1 shows, even if radiation is modulated at the high frequency Ω, the absorption signal in TTFM-ICOS system is encoded at the small beat frequency 2ω, and can therefore be detected by a slow, inexpensive detector.

In our setup two frequency synthesizers generate the tones Ω and ω, at frequencies around 1 GHz and 200 KHz, respectively. The signals are combined by a double balanced mixer to create beats at $\Omega+\omega$ and $\Omega-\omega$. Such a modulation is then applied to a quantum cascade (QCL) laser (Alpes Lasers, model# sbcw1043 DN) emitting around 1296 cm^{-1}, by means of the AC port of a bias tee. On the DC port the bias current is provided, along with a slower current ramp to scan across the absorption lines of interest, in this case those of Methane (CH_4).

The laser output, consisting of the carrier and its TTFM sideband structure, is then injected off-axis into a 0.74 m long optical cavity equipped with two high-reflectivity 2"diameter mirrors and filled with ambient air at a controlled pressure. The cavity finesse, measured by ringdown decay (τ = 3.7 μs), is F = 4763, yielding an average mirror reflectivity R = 99.934% and an equivalent absorption pathlength $L_{eff} = LF/\pi$ =1116 m.

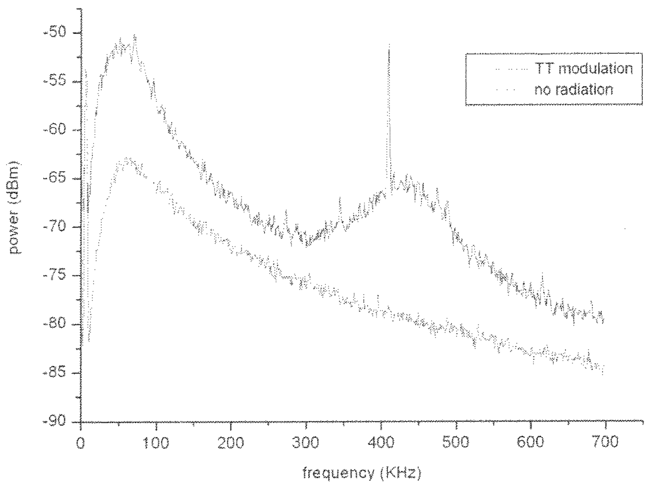

Figure 2 - Noise spectrum at the cavity output with laser off (red), and laser on (black). RBW=VBW=2kHz , 100 averages. The peak at 410 KHz is the beat note at 2ω between the TTFM second-order sidebands, demonstrating sideband transmission through an off-axis cavity

The signal is acquired by a HgCdTe detector (Judson model# J15D12) placed behind the resonator's output mirror. Figure 2 shows the cavity-output frequency spectrum, captured by a spectrum analyzer, demonstrating that when modulations are turned on, the TTFM beat note at 2ω (around 400 KHz) is transmitted by the off-axis cavity.

To retrieve the intracavity molecular absorption signal of Eq.(1), the detector's output is amplified and sent to a second double-balanced mixer along with a local oscillator (LO) signal at frequency 2ω, split from the ω frequency synthesizer and doubled. The mixer's output is then filtered (low-pass 1KHz), ensemble-averaged (128 samples) and monitored by an oscilloscope.

Example spectra are given in Figure 3, where the CH_4 transition at 1297.914 cm^{-1} was acquired at different cell pressures of pure CH_4 gas.

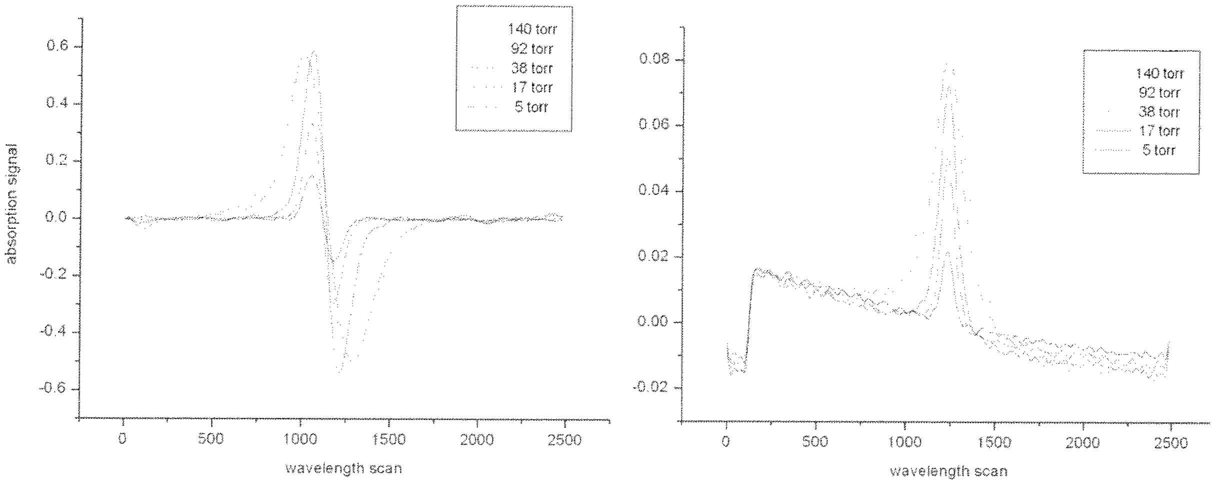

Figure 3 -(left) Absorption signal of pure CH_4 @ 1297.914 cm^{-1} at different cell pressures. (right) using TTFM technique. B) spectra of same gas samples using traditional OA-ICOS.

For each measurement, modulation frequencies and depths were slightly readjusted to maximize the absorption *S/N* ratio. Turning the modulation off and letting the detector's output bypass the demodulation mixer acquired the corresponding ICOS signals. This allowed for a direct comparison between the latter technique and the heterodyned TTFM-ICOS.

At all cell pressures, the acquired TTFM-ICOS spectra exhibit a constant fivefold *S/N* enhancement with respect to the traditional ICOS signals. By assuming the average atmospheric CH_4 concentration value of $\bar{n}$ =1.8 ppm and normalizing by the effective detection bandwidth, we can retrieve the minimum detectable concentration for this absorption line as:

$$n_{\min} = \frac{\bar{n}}{S/N}\sqrt{\frac{N_{ave}}{BW}} = 0.8\,ppb$$

A more general sensitivity estimation is given by the minimum detectable absorption cross section and minimum absorption coefficient. From our data we calculated

$$\sigma_{\min} = \frac{S(T)}{S/N\ \pi\gamma_{air}(P)}\sqrt{\frac{N_{ave}}{BW}} = 1.7\cdot 10^{-20}\,cm^{2}Hz^{-1/2}$$

$$\alpha_{\min} = \sigma_{\min} n = \sigma_{\min} N_{L}(T)\bar{n}P = 5.7\cdot 10^{-10}\,cm^{-1}Hz^{-1/2}$$

Where the linestrength *S(T)* and the air broadening coefficient to get γ_{air} are from the HITRAN database, and $N_L(T)$ is the Lodsmidth number @300K.

As shown in Figure 3, since TTFM is an intrinsically differential type of measurement, the acquired signals are baseline-free, which means that the a-posteriori baseline subtraction usually necessary in traditional OA-ICOS spectrometers can be avoided. Also, the signals exhibit an additional lineshape modulation broadening by a factor 2, but this is not an issue, since in trace gas detection applications at reduced pressures, absorption features can be selected with sufficient spectral separation so as to avoid overlap.

It is worth remarking that the TTFM-ICOS technique presented here is at its proof-of-principle state. We have identified several areas of improvement and optimization. For one, although heterodyne detection reduces dramatically both the radiation and detector's *1/f* noise, the sensitivity enhancement of TTFM-ICOS is presently limited by the noise of optical nature. In ICOS there are many sources of optical noise that can obscure the weak spectral features of interest, most notably the intracavity interference fringes caused by slight beam superposition along its off-axis trajectory. The use of a piezoelectric shaker to scramble intracavity fringes, better beam collimation, and the use of larger mirrors are expected to provide a dramatic improvement. Also, a faster MCT detector will allow us to use a tone ω as fast as a few MHz in order to obtain better resolved second-order sidebands. To this end, MCT detectors with sensitivities comparable to the one used in our setup but with bandwidths larger than 10 MHz are already commercially available.

Conclusions

A frequency modulation spectroscopic technique in combination with an off-axis aligned optical cavity was demonstrated for the first time. The technique is based on the principle that both laser carrier modulation sidebands are transmitted in average by an off-axis cavity, allowing spectroscopic analysis to benefit simultaneously from the pathlength enhancement of cavity-based techniques with the heterodyne technical noise reduction, without any need for active stabilization electronic schemes.

The proposed TTFM detection can be applied to any pre-existing ICOS spectrometer, enhancing its sensitivity without affecting its stability and capability of field operation, at a negligible cost increase and technical demand. The proof-of-principle was used to perform ambient-air methane detection and methane isotope ratio determination. A direct comparison with the traditional ICOS technique was carried on, resulting in a sensitivity enhancement by a factor 5. Some limiting factors of our setup were discussed, as well as the possible improvements that could allow researchers to fully exploit the potential of the TTFM-ICOS technique.

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