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A frequency-modulated quantum-cascade laser for spectroscopy of CH_4 and N_2O isotopomers

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We report the development of a novel laser spectrometer for high-sensitivity detection of methane and nitrous oxide. The system relies on a quantum-cascade laser source emitting wavelength of around 8.06 µm, where strong fundamental absorption bands occur for the considered species and their isotopomers. The detection technique is based on audio-frequency and radio-frequency modulation of laser radiation. First experimental tests have been performed to estimate the achievable detection limits and the signal reproducibility levels in view of possible measurements of $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{17}O/^{16}O$ and $^{15}N/^{14}N$ isotope ratios.

1.   Introduction

Over the last decades, laser-absorption spectrometers proved to be suitable tools for chemical analysis of gaseous compounds, relevant to environmental studies [1–3]. Owing to the high sensitivity, species selectivity and spectral resolution, laser spectroscopy has been recently proposed as a new method for isotopic analysis because different isotopomers of a molecule can be readily distinguished by their spectral fingerprint [4, 5]. Indeed, most simple molecules exhibit absorption lines in the infrared due to ro-vibrational transitions, whose intensity and

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wavelength position are strongly influenced by isotopic substitution and mass distribution. As an example, laser-absorption spectroscopy allows to distinguish between isotopomers with the same mass, such as $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$, because of their different moments of inertia. In principle, spectroscopic detection can be directly performed on a gaseous sample, even in the presence of different compounds, without need for sampling and pre-treatment. These features point out all advantages of optical methods with respect to well-established analysis techniques, like isotope ratio mass spectrometry, nowadays widely used in environmental and medical research.

During recent years, the capability of laser spectrometers to provide high precision determinations of stable isotope ratios has been demonstrated using gas, lead salt and solid-state lasers in the mid-infrared region and semiconductor diode lasers in the near-infrared region [6, 7], even for field applications [8]. The mid-infrared spectral region is of crucial importance, as strong fundamental bands occur for several atmospherically relevant trace gases. Quite recently, novel infrared coherent radiation sources, such as PPLN-based difference-frequency generators, operating between 3 and 5 μm [9], and quantum-cascade lasers (QCLs), at longer wavelengths, have been developed [10]. Although QCLs are not yet easily available on the market, they have unique features in terms of amplitude and frequency noise as well as for their spectral purity and frequency tunability. Their emission has been achieved over a wide range of wavelengths from 3.5 to 24 μm, with output power ranging from hundred to tens of megawatt, in pulsed and continuous mode, respectively [11]. Until a few years ago, continuous-wave operation of a QCL has been possible only with the laser active region kept close to liquid nitrogen temperature, as reported in most spectroscopic works [12–14]. More recently, a few QCLs operating continuous wave with a thermoelectrically cooled device were developed [15, 16]. Here, we report on the use of a cryogenically cooled QCL, emitting around 8.06 μm, for absorption spectroscopy of CH_4 and N_2O stable isotopomers. Ro-vibrational transitions belonging to $^{12}CH_4$, $^{13}CH_4$ and $^{14}N_2^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N_2^{18}O$, $^{14}N_2^{17}O$ fundamental bands, around 1240 cm^{-1}, were detected in pure methane and nitrous oxide samples using WMS. An improved detection scheme was also implemented by means of radio-frequency modulation spectroscopy. Sensitivity and short-term reproducibility tests were performed on the absorption signals of the selected $^{15}N/^{14}N$, $^{17}O/^{16}O$ and $^{13}C/^{12}C$ isotopic line pairs.

2. Experimental set-up

The experimental set-up is schematically shown in figure 1. A continuous-wave QCL emitting at a wavelength of ~8 μm was mounted in an optical cryostat (Janis ST-100), equipped with anti-reflection coated ZnSe windows and cooled by a weak flux of liquid N_2 for continuous-wave operation. The working temperature, kept stable within 0.1 K by a PID-controlled heater, could be varied by several degrees around 81 K. The laser output power was measured to be 40 mW at an injection current of 800 mA, provided by a custom-built power supply, with a maximum current of 2 A and a noise ripple of the order of 1 nA/Hz$^{1/2}$. The strongly diverging laser beam, transmitted by the window, was collimated by a short-focal length parabolic reflector. The spatial beam quality was previously checked with an infrared thermal camera [14]. The QC laser emits at a frequency of ~1240 cm^{-1} (8.06 μm), at the chosen temperature, and has a wavelength tunability *vs.* temperature and current of 2.2 GHz/K and 102 MHz/mA, respectively, over a frequency interval of ~1 cm^{-1}. A wavelength calibration and a test of frequency scan linearity were performed using pairs of well-known CH_3I absorption lines as frequency references [14].
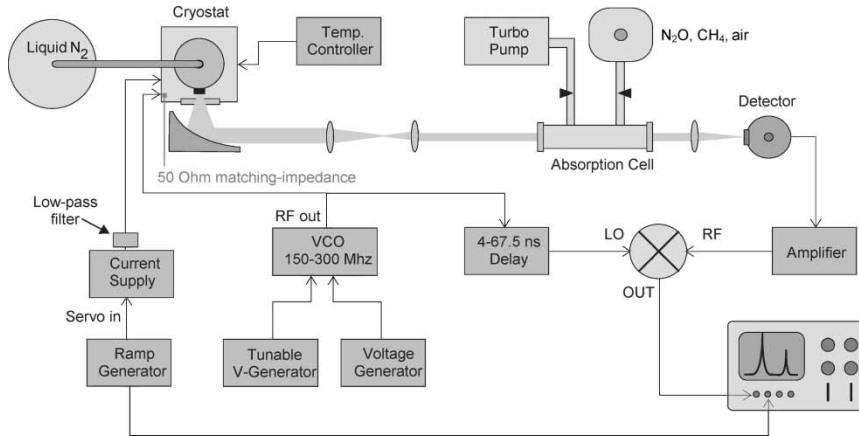
Figure 1.   Scheme of the experimental set-up used for radio-frequency modulation spectroscopy. VCO, voltage-controlled oscillator; LO, local oscillator.

For absorption spectroscopy measurements, the laser radiation was directed to a 17 cm long cell, filled with the sample under investigation. The gas coming from two cylinders, containing pure CH_4 and N_2O (99.99 %), could be injected with high precision into the cell, using needle valves, while the inside pressure was monitored by a capacitance gauge. An oil-free turbo-molecular pump ensured high-purity conditions in the cell. The radiation was then collected by a positive lens onto a fast Hg–Cd–Te (MCT) photodetector (170 MHz bandwidth). Absorption signals could be acquired by a 500 MHz digital oscilloscope. Detection of absorption lines was performed using two different detection techniques, based on direct modulation of the QCL frequency via its injection current. As already described in ref. [14], a WMS technique was implemented using a lock-in amplifier for both modulation in the acoustic range (1–10 kHz) and first-harmonic phase-sensitive detection. Frequency-modulation spectroscopy (FMS) was also performed to increase sensitivity in detection. For this purpose, radio-frequency modulation of the QCL injection current, at a frequency Ω, was produced by a voltage-controlled oscillator via a bias-tee, thus generating a pair of side-bands at a distance $\Omega \cong 170$ MHz from the carrier frequency. The values of both Ω and the modulation amplitude were chosen according to the detector bandwidth and the QCL injection current. In addition, the RF coupling efficiency was characterized as a function of the frequency, observing the power directly reflected through the bias-tee. In particular, after analysis of the laser power spectral density at the fast detector, the modulation frequency was set at a value, within the detector bandwidth, which minimized the amplitude noise (see figure 2) and spurious backreflections. The chosen modulation depth corresponded to a sideband-to-carrier ratio of ∼2 %. In this configuration, the detector output signal was amplified by a low-noise amplifier and demodulated by a double-balanced mixer. The demodulation process yields a voltage output which, in the vicinity of line center, is proportional to any amplitude or phase difference between the carrier-to-sideband beat signals, eventually caused by interaction of infrared radiation with the absorbing sample. Proper phase adjustment between the detector signal and the mixer local oscillator was carried out by a variable time delay in order to extract only the in-phase or the quadrature component of the absorption signal. The resulting curve has a dispersive-like profile with zero crossing around the line center, whose amplitude and lineshape depend on the absorption coefficient and modulation index [17, 18].
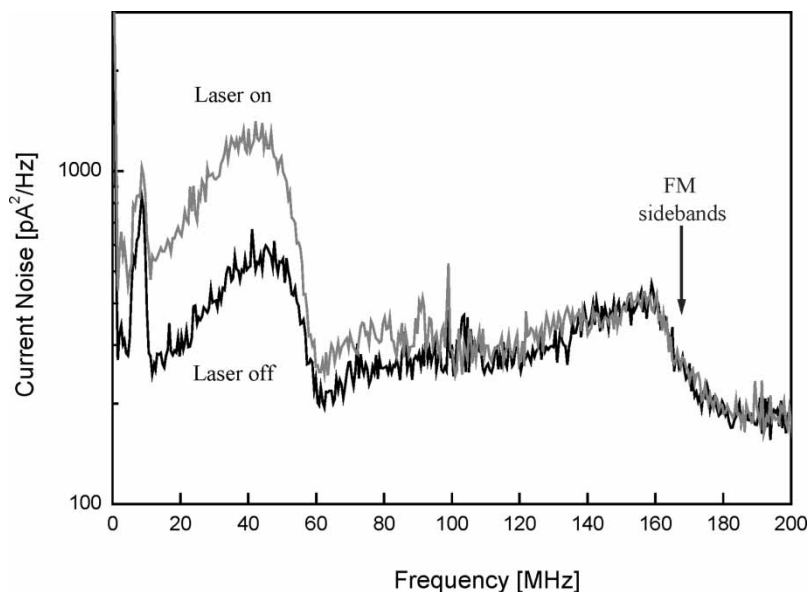
Figure 2.   Noise spectral density of the QCL beam as observed by a fast MCT detector (upper trace). The lower trace corresponds to the dark signal of the photodetector. The frequency region chosen for laser modulation is indicated by the arrow.

3.   Absorption measurements on CH_4 and N_2O isotopomers

The possibility to perform analysis of the isotopic composition on methane and nitrous oxide was considered. As is well known, the isotope ratio is commonly referred to a standard and defined in terms of the so-called δ value [7]. For this reason, a two-channel apparatus is usually needed with two identical cells, one for a reference mixture of known isotopic composition, and the other for the gas under investigation. Recording and comparison of the absorption lines in both channels allow for direct, simultaneous retrieval of the abundance ratios in the two gases, when they are in the same thermodynamic conditions. Alternative approaches were also developed, which are based on the same absorption cell for both mixtures, the two isotopic species being detected along with two different absorption pathlengths in the same cell with the advantages of overcoming systematic deviations eventually caused by temperature differences between the cells [19]. Nonetheless, further accuracy limitations may arise in this case from crossing memory effects between the gases.

Detection of several isotopomers of CH_4 and N_2O was carried out using absorption spectroscopy. In particular, our QCL emission lies in a spectral region where a number of CH_4 and N_2O absorption lines, mostly belonging to the ν_4 and ν_1 fundamental bands, respectively, occur with intensities up to 10^{-20} cm per molecule. Furthermore, an overlap between the P branch of the $^{12}CH_4$ $2\nu_4-\nu_4$ hot band and the P branch of the $^{13}CH_4$ ν_4 bending mode takes place, partially compensating the difference of their natural abundances (98.8 % and 1.1 %, respectively). Similarly, the $^{14}N_2{}^{16}O$ 00^02-00^01 band lies in the vicinity of the P branches of the $^{15}N^{14}N^{16}O$ 00^01-00^00, $^{14}N_2{}^{18}O$ 00^01-00^00 and $^{14}N_2{}^{17}O$ 00^01-00^00 bands [20]. Anyway, the considered species are typically present in ambient air with concentrations of the order or below the part-per-million level. Therefore, a very sensitive detection method would be usually necessary to observe their absorptions. For this purpose, WMS was employed. The QC laser frequency was modulated adding a 10 kHz sinusoidal signal to the injection current, with a modulation index varying from 1.3 to 1.7, while it was scanned across an absorption line by a

triangular wave at 2.5 Hz. The optimal modulation index values were chosen according to the best signal-to-noise ratio observed on the absorption signals, for different total pressure ranges. The first-harmonic signals provided by the lock-in amplifier were subsequently sent to a 500 MHz bandwidth digital oscilloscope for spectra averaging and data acquisition. In figures 3 and 4, the first-harmonic profiles corresponding to the $^{12}CH_4/^{13}CH_4$ and $^{14}N_2^{16}O/^{14}N_2^{17}O$ line pairs are shown. The spectra were obtained with the absorption cell filled with methane and nitrous oxide gas in natural isotopic abundances.

Significant variations of the δ value are usually of the order of 10^{-3} or less. As a consequence, the precision of the method is crucial to ensure the reliability of the determination procedure. A first evaluation of the experimental reproducibility was performed in the short term for the absorption signals of the $^{12}CH_4/^{13}CH_4$ line pair, as already described in a previous work [14]. From a set of 40 repeated acquisitions (40 min total measurement time) with identical conditions, we found a standard deviation of the peak-to-peak ratio between the signals, corresponding to 9‰ for a 150 mTorr of pure methane in the 17 cm long cell. Although this result is still not competitive with those of laser spectrometers developed for common atmospheric species, such as CO_2 or H_2O, it should be noted that the availability of a laser source operating in the mid-infrared is crucial to perform detection of methane and nitrous oxide in air, the intensity of the considered transitions being on average a factor 100 higher than in the near-infrared. A longer interaction length between the radiation and the gas sample is obviously desirable to meet sensitivity and precision levels requested for isotopic applications. Indeed, the use of multiple-reflection cells with a 20–30 m pathlength is expected to significantly improve the precision of the measurement method, as demonstrated in works recently performed in the near-infrared [21, 22].

The accuracy of laser spectrometers in isotopic analysis can be extremely high, in some special cases also comparable to that of conventional mass-spectrometry techniques [6, 23]. Anyway, with this method, the determination of isotope ratios can be seriously influenced by amplitude noise and optical disturbance as well as by thermal drifts and memory effects in the
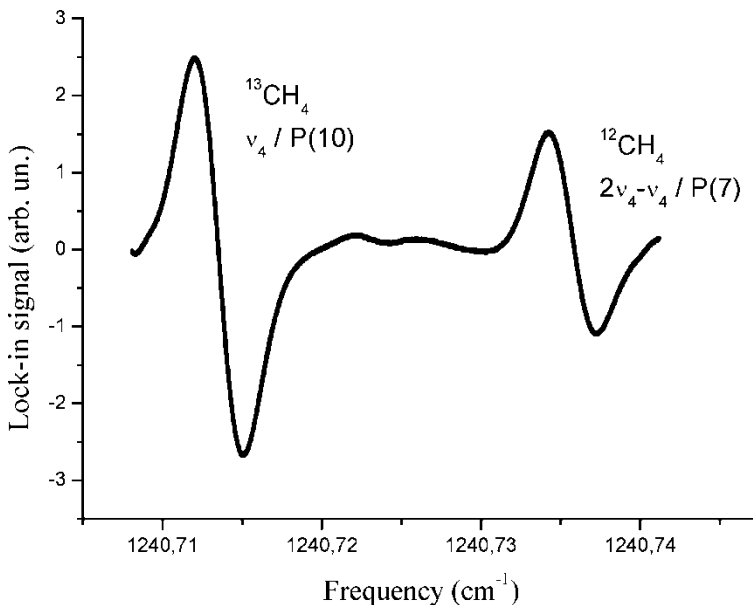

Figure 3. First-harmonic spectrum of $^{13}CH_4$ and $^{12}CH_4$ ro-vibrational transitions assigned by the labels. The cell length was 17 cm and the pressure was 150 mTorr. The signals were detected in a 4 Hz effective detection bandwidth.
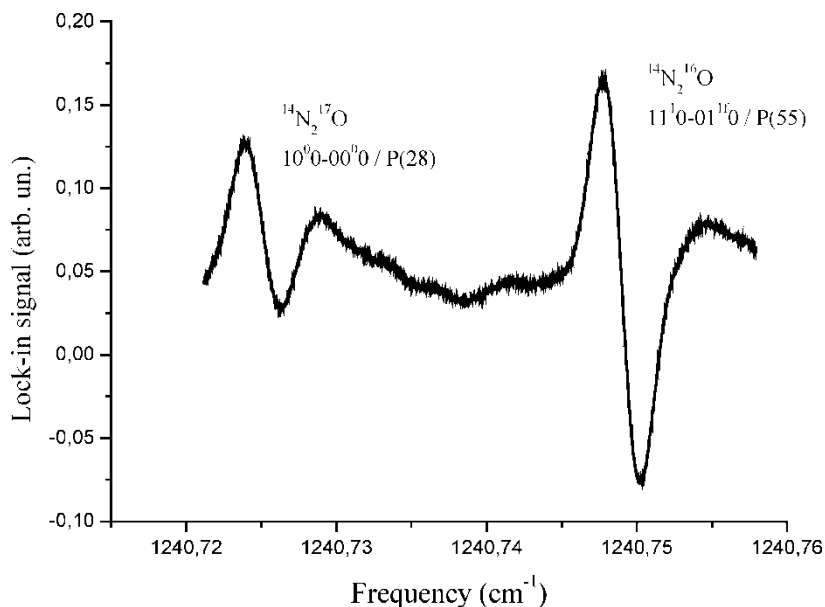
Figure 4. Absorption spectrum corresponding to the $^{14}N_2{}^{16}O$ and $^{14}N_2{}^{17}O$ isotopomers for a 80 mTorr gas pressure in the cell.

absorption cells. According to the definition of δ value, one of the major reasons for a systematic deviation may be a temperature difference between the two cells, as the linestrength ratio of the isotopic line pair is temperature sensitive through the Boltzmann distribution [23]. The sensitivity is strictly related to the energy difference between the lower states of the transition pair. As a consequence, the choice of the spectral region is critical. On the line pair selected for CH_4, for instance, this effect could affect the achievable accuracy in $\delta^{13}C$ determination, with a systematic error of the order of 1‰, assuming a temperature stability of 0.1 K.

A sensitivity improvement of about one order of magnitude, with respect to first-harmonic WMS [13], was readily obtained by means of a different detection scheme, based on FMS. For this purpose, radio-frequency modulation at $\Omega \cong 170$ MHz was applied to the QCL, whereas demodulation of the detector signal was performed by a double-balanced mixer. Additional signal-to-noise improvement was accomplished by low-pass filtering and averaging of the acquired spectra on the digital oscilloscope. Furthermore, all optical components were equipped with anti-reflection coatings at 8.06 μm, thus eliminating spurious etalon effects that give rise to amplitude instability and interference fringes on the recorded spectra. In figure 5, the absorption signal obtained by FMS in 20 mTorr of pure N_2O is shown for its most abundant isotopomer. From the measured signal-to-noise ratio, we extrapolated a minimum detectable absorption of 1.7×10^{-6}Hz$^{-1/2}$, corresponding to a minimum pressure of $\sim 0.5\ \mu$Torr of pure N_2O for a 1 m absorption pathlength. The same test was repeated for a mixture of N_2O and air at atmospheric pressure.

In figure 6, the measured signal-to-noise ratio is plotted *vs.* the partial pressure of the absorbing gas, with a noise-equivalent detection limit (S/N = 1) of 20 ppm. In this case, the modulation depth was increased up to several percentage to maximize the FM signal [18]. This performance would be already sufficient for detection of CH_4 and N_2O in their usual ambient concentration, if a 20 m pathlength was used. However, the sensitivity gain of the radio-frequency technique is lower than expected. This fact is most likely due to the Ω value, chosen according to the detector bandwidth, which is relatively low when compared
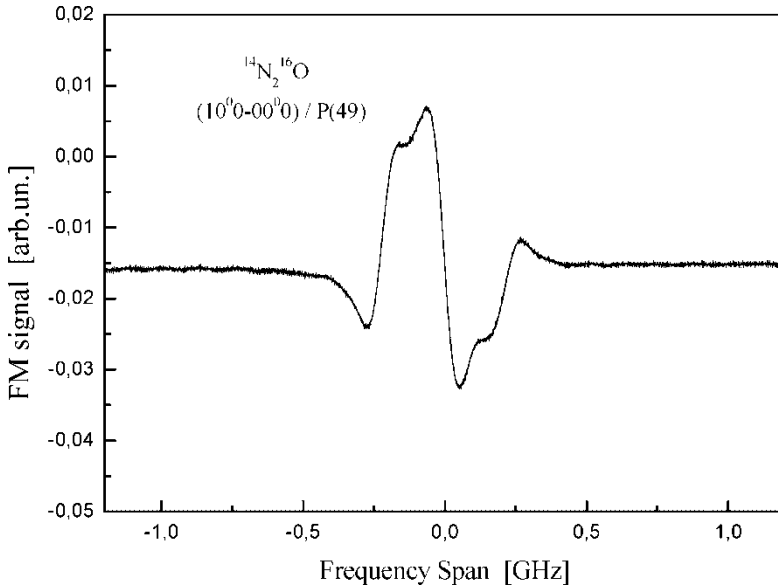
Figure 5. Example of frequency-modulation (FM) signal produced by the mixer when the QCL was tuned into resonance with a line of the $^{14}N_2^{16}O$ fundamental band (pressure 20 mTorr). The modulation frequency was 170 MHz, with an amplitude of 15 mA. The effective detection bandwidth was ∼4 kHz.
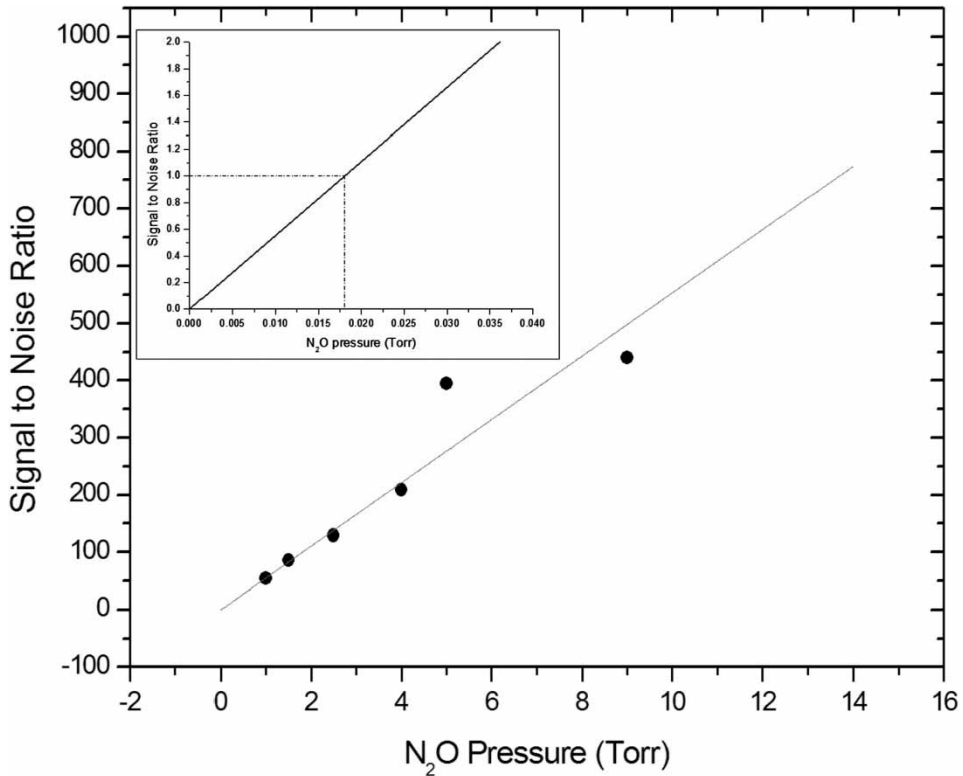

Figure 6. Plot of the signal-to-noise ratio on the absorption line of figure 5, as a function of N_2O partial pressure, in a mixture with ambient air at atmospheric pressure. The noise-equivalent pressure (S/N = 1) corresponded to ∼1.5 mTorr.
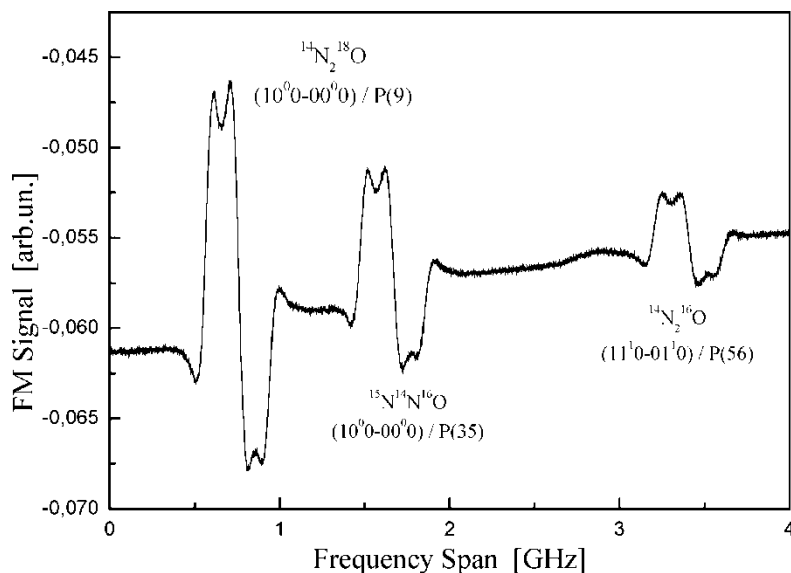
Figure 7. FM signals of the molecular species $^{14}N_2^{16}O$, $^{14}N_2^{18}O$ and $^{15}N^{14}N^{17}O$ for 80 mTorr of pure N_2O in the cell.

with the modulation frequency usually adopted in the FMS-based spectrometers [24, 25]. With this scheme, the isotopic signatures of $^{14}N_2^{16}O$, $^{15}N^{14}N^{17}O$ and $^{14}N_2^{18}O$ species were simultaneously detected in their natural isotopic abundance.

An example is in figure 7, where different ro-vibrational transitions belonging to the fundamentals of the heavier molecules, $^{15}N^{14}N^{16}O$ and $^{14}N_2^{18}O$, and to the hot band of the most abundant isotopomer are simultaneously shown for a 80 mTorr pressure in the cell.

4.   Conclusions

In this work, the possibility of using QCLs for isotopic detection of environmentally relevant gaseous compounds was demonstrated. In particular, we implemented WMS and FMS techniques for high-sensitivity absorption measurements on $^{12}CH_4/^{13}CH_4$, $^{14}N_2^{16}O/^{14}N_2^{18}O$, $^{14}N_2^{16}O/^{14}N_2^{17}O$ and $^{14}N_2^{16}O/^{15}N^{14}N^{17}O$ pairs. In view of possible measurements of isotope abundance ratios with respect to international standards, a first estimate of the signal reproducibility was carried out. In addition, detection of nitrous oxide in partially enriched atmospheric air samples was performed down to a limit of 20 ppm. for a 0.2 m pathlength. Work is currently in progress to improve the system performances in terms of sensitivity and reproducibility. In this respect, better performances are expected when a much faster photodetector and a new QCL source will be put in operation.

Acknowledgements

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