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Simultaneous detection of ammonia, methane and ethylene at $1.63\,\mu m$ with diode laser photoacoustic spectroscopy

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ABSTRACT Spectral investigation around 6115 cm^{-1} for simultaneous detection of ammonia, methane and ethylene in gas samples is presented. Experimental data on the $\nu_2 + \nu_3 + \nu_4$ combination band of ammonia are reported with a resolution of 1.5 GHz. A trace gas analyzer based on a resonant photoacoustic cell and an external cavity diode laser has been used for detection. A data fitting procedure has been developed in order to improve the system sensitivity and to limit the need of a reference cell. The selected spectral region allows a sensitivity of about 60 ppm for ammonia, 6 ppm for methane and 30 ppm for ethylene with 0.3 mW laser power. An application of simultaneous detection of such molecules in a mixture reproducing their typical abundances in real gas samples from biomass gasification is discussed.

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1   Introduction

Multi-gas detection is growing in importance in many fields such as agro-industrial activities, environment control, energy production and health diagnosis when several emitted gas-phase components are necessary to monitor the process dynamics [1–5]. Among different techniques, laser spectroscopy detection of molecules is increasing in competitiveness due to the strong development of high-performance, reliable, cheap and easy-to-use laser sources emitting in spectral regions where interesting marker molecules have absorption bands. The selectivity of this method, which depends on spectral resolution, is potentially very high and gives the possibility of unambiguous simultaneous detection of different species by scanning a small frequency range. This is achievable if a proper spectral region is found, where the absorption structure presents clearly distinguishable transitions free from interference of other abundant species, usually present in real samples, such as carbon dioxide and water.

This work is an extension of a previously published paper [6], where simultaneous methane and ethylene detection around 1.63 μm by the resonant photoacoustic method is reported; it is devoted to finding a suitable spectral region where

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the detection of ammonia is possible together with these two molecules. Furthermore a new smaller photoacoustic cell, developed to be successively inserted in a compact build-up cavity, was used and characterized to determine the sensitivity attainable on the three molecular species.

These molecules play an important role in many industrial and biological processes like methane and hydrogen production from biomass gasification [7, 8]. Such processes often produces secondary undesired species like H_2S, HCl, NH_3, C_2H_4, C_2H_2, C_2H_6, C_6H_6 and their concentrations in the final gas mixture strongly depend on biomass composition and on process parameters. Ethylene and acetylene, for example, have negative effects if the outsourcing gas mixture is burned in internal combustion engines, because they can induce detonation. Ammonia and hydrogen sulfide present a corrosive behaviour and are pollutant precursors producing NOx and SOx compounds. The monitoring of these molecules would be very important in order to improve the process efficiencies and to reduce their environmental impact.

2   Experimental

The experimental apparatus is based on a commercial NIR diode laser and on a resonant photoacoustic (PA) cell, and it is similar to the one used in the previous work [6]. The Littmann external cavity diode laser (Sacher TEC 500) is centred at 1630 nm with ±40 nm single-mode coarse tunability. A smaller range of 250 GHz can be controlled via computer by applying a suitable voltage to the diode laser piezo driver; the mode-hop-free tuning is typically limited to 80 GHz with a typical long-term line width of about 2 MHz. A beam splitter sends a small part of the laser beam to a Fabry–Pérot (FP) cavity, in order to mark the frequency sweeps. Two FPs, with a free-spectral-range of 5 and 1 GHz, are available and their use depends on the width of the frequency scan. In order to make the frequency marker be unaffected by the thermal drift, the FPs bodies are made of invar.

The 100 mm long and 6 mm in diameter PA cell, used in the previous work, was replaced by a 60 mm long and 2 mm diameter one. This choice was made in order to test a more compact cell, suitable for being inserted inside a compact optical build-up cavity, which is described in [9].

The laser beam profile is elliptical, with the principal axis equal to about 1 and 2 mm. In order to avoid interactions be-

tween the laser beam and the inner PA cell wall, a 20 cm focal length lens is used to reduce the laser beam dimensions to a fraction of a mm along the acoustic resonator.

The laser is modulated by a mechanical chopper at about 2600 Hz, corresponding to the frequency of the first longitudinal resonant mode of the PA cavity. An electret microphone (Knowles EK3033) is placed in the center of the acoustic resonator, in correspondence with the maximum of the acoustic standing wave, just facing the inner wall of the acoustic cavity. The microphone signal is pre-amplified, with a gain ranging from 2×10^3 to 2×10^5, and measured by a lock-in (EG&G 7260) operating at different time constants. Working parameters are chosen depending on experimental conditions and are reported in the figure captions. A photodiode measures the laser beam power during data acquisition in order to normalize the photoacoustic signal.

The measured noise density is about $30 \, \mathrm{nV}/\sqrt{Hz}$ in both PA cells. This is consistent with the nominal noise of the electret microphone used in the cells: -103 dB A-weighted noise, corresponding to $40 \, \mathrm{nV}/\sqrt{Hz}$, with a sensitivity of about 20 mV/Pa. Therefore, in these PA cells, the signal-to-noise ratio is limited essentially by the electronic noise and not by the acoustic background. Direct signal comparison between the two PA cells shows that the final sensitivity of the smaller resonator is not significantly different from the previous one. Measured Q factor is about 6 and the cell constant F is 5 Pa cm W^{-1}. With these parameters the estimation of the limiting sensitivity of the apparatus is about $10^{-7} \, \mathrm{cm}^{-1}\mathrm{W}/\sqrt{Hz}$.

A computer, driven by a LabView program, sets the laser wavelength and acquires the photoacoustic and frequency marker signals by communicating with the lock-in via a GPIB connection. After the data-acquisition, a LabView-subroutine analyzes and fits the data in order to improve the sensitivity and to find the partial concentration of the three molecular species.

3   Results and discussion

In order to find a favorable spectral region for simultaneous detection of ammonia, methane and ethylene molecules, we looked at their medium resolution wide range spectra between 5900 and 6200 cm^{-1}. The criteria we followed were to select the narrowest spectral region in which all the three molecules present resolved transition lines without interference with carbon dioxide and water lines. In Fig. 1 the spectra of ethylene, methane and ammonia are shown. The first two were obtained with a Raman-shifted-pulsed dye-laser photoacoustic system (0.1 cm^{-1} bandwidth) [10, 11], while the ammonia spectrum was measured by a FTIR instrument (Bruker Optics Equinox 55) with a 1 cm^{-1} bandwidth resolution. Also reported in Fig. 1 are the spectra of water and carbon dioxide from HITRAN 96 database. From a careful analysis of these measurements, two useful spectral regions for high resolution analysis were selected, around 6156 and 6115 cm^{-1}. They are marked in the figure by the two vertical bars, while the horizontal wide bar represents the frequency region accessible to the diode laser.

The NIR spectrum of NH_3 is characterized by the well known bands at 1.5 and 2 μm, commonly used for ammonia detection [12–15] and by a much weaker combination

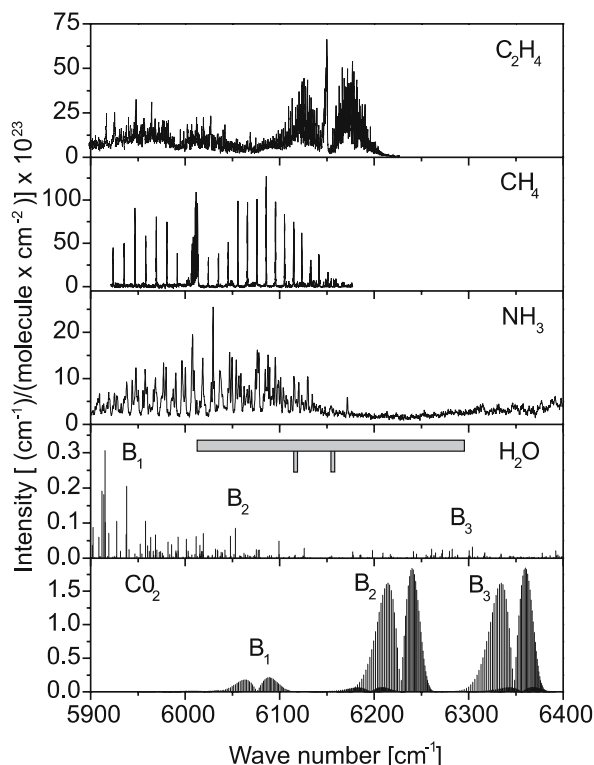FIGURE 1   Survey spectra between 5900 and 6400 cm^{-1} of: (1) C_2H_4 spectrum where PQR rotational structure around 6150 cm^{-1} is assigned as $\nu_5 + \nu_9$ CH stretch combination band. (2) $2\nu_3$ overtone of CH_4. (3) $NH_3 \, \nu_2 + \nu_3 + \nu_4$ combination band. (4) H_2O rotational lines of $\nu_2 + \nu_3$ (B_1), $4\nu_{>2}$ (B_2) and $\nu_1 + 2\nu_2$ (B_3) bands. (5) CO_2 bands: $30014 \leftarrow 00001(B_1)$, $30013 \leftarrow 00001(B_2)$, $30012 \leftarrow 0001(B_3)$. The *grey horizontal bar* represents the spectral range available to our laser; the two *vertical bars* localize the two selected regions for multi-gas detection

band at 1.6 μm ($\nu_2 + \nu_3 + \nu_4$). The latter has not been investigated at high resolution up to now to the authors' knowledge. Low resolution measurement was first reported in [16], FTIR spectra are available in the PNNL database [17] while a single ro-vibrational line was used for sensitive detection with a DFB laser in [18]. In Fig. 2a an ammonia spectrum from 4500 to 7000 cm^{-1}, obtained with our FTIR apparatus, shows the relative intensity of these three bands. In order to explore the 1.6 μm combination band, a detailed spectrum has been acquired using the diode laser photoacoustic apparatus. The sample was a mixture of 10% ammonia and 90% nitrogen measured at a total pressure of 150 mbar. The widest high resolution NH_3 spectrum, compatible with the diode laser coarse tunability, is shown in Fig. 2d. The spectrum consists of a collage of 250 GHz wide scans, each of them containing 1200 data points. The relative wavelength scale calibration has been performed by taking into account the FP frequency marker. The absolute frequency scale has been calibrated by comparison with the low resolution (1 cm^{-1}) FTIR spectrum (Fig. 2b). In order to compare the laser measurements with the FTIR ones, the diode laser spectrum was convoluted with a 1 cm^{-1} wide Lorentzian function (Fig. 2c).

In Fig. 3 two details of the spectrum shown in Fig. 2d are reported, including the signal of the 5 GHz frequency marker. The resolution is about 1.5 GHz, mainly limited by the pressure broadening. The Doppler broadening for ammonia at room temperature is estimated to be about 300 MHz. The
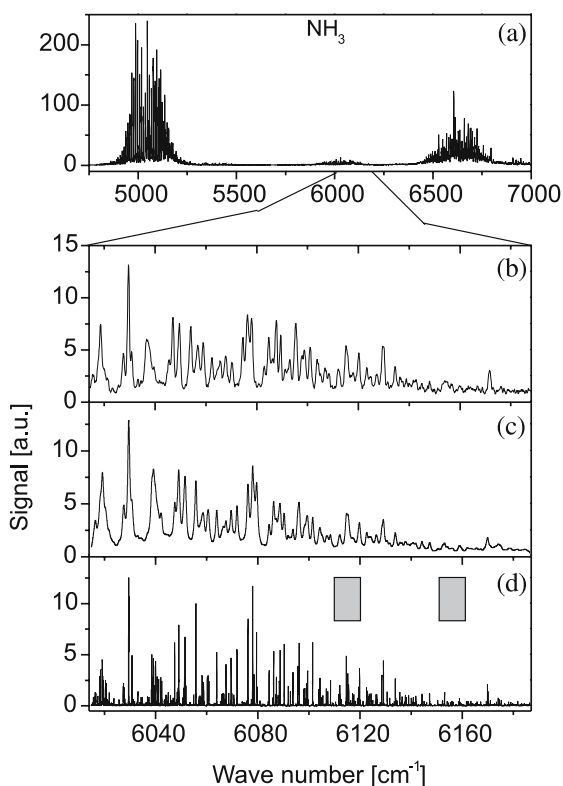
FIGURE 2 NH_3 spectrum: (**a**) $1\,cm^{-1}$ bandwidth resolution FTIR spectrum of ammonia. (**b**): exploded view of the FTIR spectrum between 6015 and $6185\,cm^{-1}$. (**d**) 1.5 GHz resolution ammonia spectrum, obtained with diode laser-photoacoustic apparatus. (**c**) high resolution spectrum, shown in (**d**), convoluted with a $1\,cm^{-1}$ wide Lorentzian shape. Two scan details, marked by the *grey bars* drawn in **d**, are shown in Fig. 3

ammonia line broadening in air, calculated from measured line widths on 6114.2 and $6114.8\,cm^{-1}$ transitions at different pressure, is about $3.9 \pm 0.2\,MHz/mbar$, very similar to the value reported in the literature [18] on another line of the same combination band at $6007.6\,cm^{-1}$. A theoretical study of the broadening behaviour of these lines can not be done because their quantum numbers are not yet known. Even if the spectral structure is not completely resolved, the quality of experimental data will be sufficient to allow a preliminary spectroscopic analysis of this combination band.

The two spectral intervals chosen for high selectivity multi-gas detection are marked by the horizontal bars. In a first stage their investigation was performed on gas mixtures with relative abundances such that the line intensities of different compounds were comparable. This was done in order to get the best understanding of the spectral structure superposition, and to estimate the ultimate apparatus sensitivity on the single species when interference coming from much higher concentrations of one of the other components is not present. The first region is the same as that investigated in previous work [6] on the simultaneous detection of methane and ethylene, and lies between 6155.4 and $6157.5\,cm^{-1}$. It is characterized by a good selectivity pattern even when ammonia is present in the mixture. Figure 4 shows a 60 GHz mode-hop-free diode laser scan of a mixture of these three molecules at a total pressure of 100 mbar. A good selectivity is preserved even when increasing the pressure up to 300 mbar. Transition line intensities of
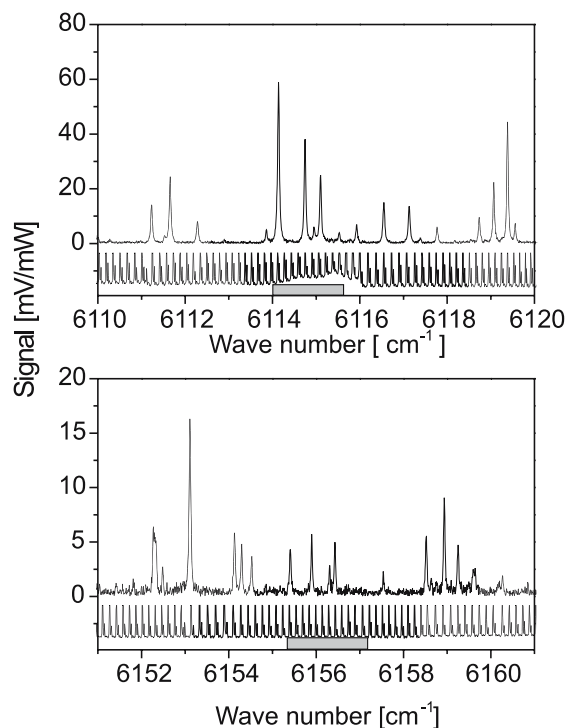

FIGURE 3 Two details of the 1.5 GHz resolution ammonia spectrum, including the 5 GHz spaced frequency marker. The *grey horizontal bars* represent the spectral regions selected for the multi-gas detection. Laser power 0.85 mW, amplifier gain 10^4, lock-in time constant 100 msec
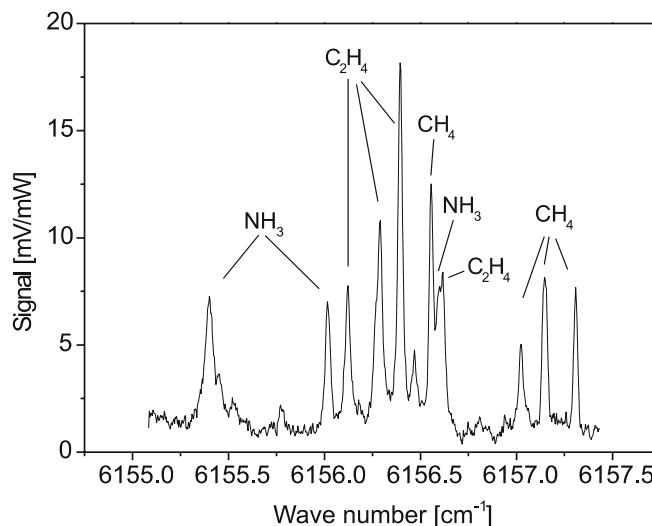

FIGURE 4 Frequency scan between 6155.2 and $6157.4\,cm^{-1}$ of a mixture composed by 2% of ethylene, 5% of methane and 10% of ammonia in air at a total pressure of 100 mbar. Laser power 1 mW, amplifier gain 2×10^4, lock-in time constant 100 msec

ammonia are, however, very low for sensitive detection in this region with respect to the most intense band transition shown in Fig. 2d.

In the second spectral interval (from 6113.7 to $6115.6\,cm^{-1}$) ammonia, methane and ethylene present more intense transitions than in the first one, about a factor of 10, 30 and 1.5 respectively, preserving a satisfactory selectivity pattern. The upper trace of Fig. 5 shows a detailed spectrum of a mixture of ammonia, methane and ethylene acquired at a total pressure of 100 mbar. On a $2\,cm^{-1}$ wide scan many
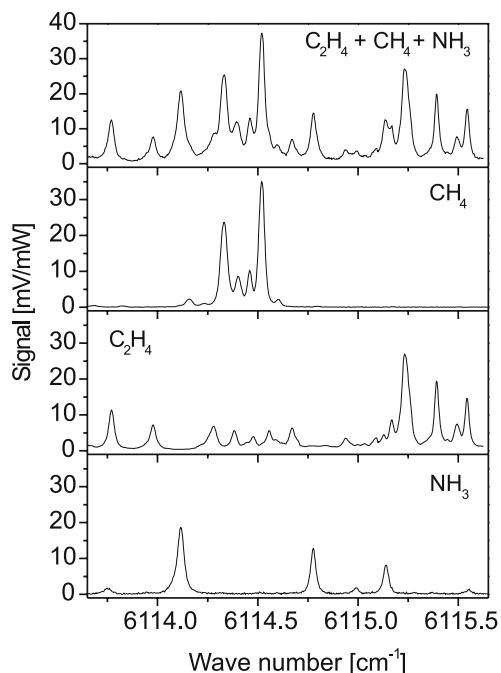
FIGURE 5 Spectrum between 6113.4 and 6115.6 cm^{-1} of a mixture composed by 1% of ethylene, 0.5% of methane and 5% of ammonia in air at a total pressure of 100 mbar (*upper trace*). The lower traces show the separate component molecular spectra at the same concentration and pressure in nitrogen buffer gas. Laser power 0.6 mW, amplifier gain 10^4, lock-in time constant 1 sec

FIGURE 6 Comparison between spectra of a standard mixture composed of 1% of ethylene, 1% methane and 1% ammonia in nitrogen, sampled at three different pressures. Laser power 0.45 mW, amplifier gain 10^4, lock-in time constant 1 sec

lines from all components are clearly resolved. The single molecular spectra are also reported for comparison. Two of the significant lines of ammonia and ethylene are well separated from those of other species. A strong overlapping is however present between the main methane structure and ethylene lines from 6114.2 to 6114.6 cm^{-1}. This prevents accurate methane measurements if the acquisition scan has to be limited around the methane structure. On extending the scan up to 6115.6 cm^{-1}, where ethylene lines are free from interference, a pattern subtraction procedure can be effective in recovering the methane line intensities.

In Fig. 6 the spectrum from 6114 to 6115.5 cm^{-1} of a mixture of the three species at different pressures is shown. At a pressure of 300 mbar the molecular lines identification is essentially similar to the 100 mbar sample, but the improved signal intensity gives a significantly increased sensitivity. In the sample at 600 mbar, ammonia lines become severely overlapped with methane and ethylene structures. Nevertheless methane and ethylene identification is still possible with good accuracy.

In order to get an estimate of the system sensitivity on the three components, a 150 mbar air sample, containing 0.015 mbar of C$_2$H$_4$ (100 ppm), 0.015 mbar of CH$_4$ (100 ppm) and 0.09 mbar of NH$_3$ (600 ppm), was measured and the corresponding spectrum is reported in Fig. 7a. The measured line amplitudes were estimated by fitting the data with a least square algorithm, using a base fitting function which describes the known line patterns of the three gas components. These functions were previously obtained by fitting the single components spectra with a Leverberg–Marquardt algorithm and are shown in Fig. 7b. A high quality base fitting curve of
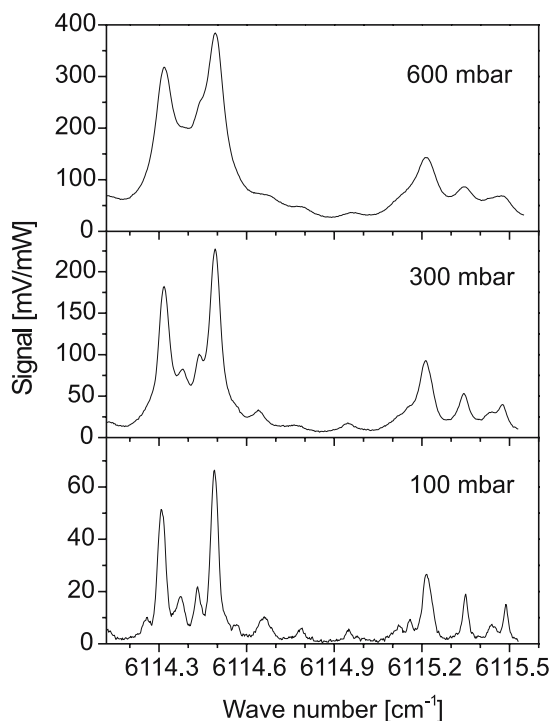
the separate components is crucial for obtaining the species concentrations when overlapping structures are present. In particular, the possibility of adjusting the line width of the base fitting curve to the sampling pressure makes a subtraction algorithm accurate enough to return reliable values.
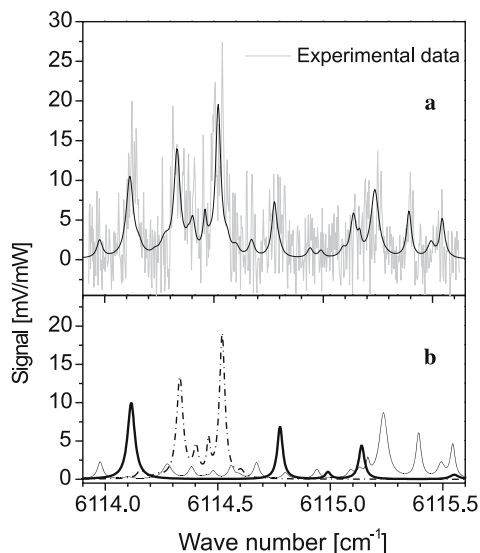

FIGURE 7 Spectrum of a 100 ppm CH$_4$, 100 ppm C$_2$H$_4$ and 600 ppm NH$_3$ mixture in air at a pressure of 150 mbar and obtained with a laser power inside the acoustic resonator of 0.3 mW (**a**, *grey line*). Signal amplification is 2×10^5 and lock-in time constant is 5 sec. The solid line is the best least square fit obtained using the base functions shown in (**b**) methane (*dash and dot*), ethylene (*thin line*) and ammonia (*thick line*). These functions were obtained by fitting good quality spectral data of the single species

In order to avoid the repetitive use of a reference cell, the fitting procedure can be "auto searching" for the molecular spectral structure within the acquired data. A LabView algorithm sweeps the frequency position of the base-fitting curves until it finds the best fitting parameters on the data file. This procedure is effective until the signal-to-noise ratio of the most intense lines of the data file is at least five. For smaller signal to noise ratios, the calculated frequency position could be slightly different from the correct one, and the best sensitivity is obtainable only if line positions inside the acquired data are known in advance.

The overall detection accuracy was estimated by applying the fitting procedure to a sample of several acquisitions with a low signal-to-noise ratio and taken under the same experimental conditions. The evaluation of the line intensities variance gives an estimate of the output values accuracy. This data analysis procedure leads to an increase of a factor five in the signal-to-noise ratio with a final confidence of 75% and to a sensitivity of about 60 ppm for ammonia, 6 ppm for methane and about 30 ppm for ethylene, with a signal-to-noise ratio of three, using 0.3 mW diode laser power. These values are obtained in a mixture where the three components have similar concentrations and with a total pressure of 150 mbar, in order to optimize the matching between selectivity and sensitivity.

On the basis of the previous investigation, we tested the system performances in a gas mixture simulating a real sample, such as the one coming from biomass gasification, where the concentration of the gas species can be very different. In this case, methane concentration is in the range 10%–40%, ethylene 1%–10% and ammonia below 1% in a complex environment in which other gas species (e.g water, carbon dioxide and oxide and other hydrocarbons) are present in relevant abundances. In many technical applications the abundance of multiple carbon bonds molecules such as ethylene must be less than a few percent, while for ammonia a concentration value below 0.1% is desirable. In order to test the capability of the system to detect the presence of these two species we prepared a gas mixture composed of 40% methane, 5% ethylene and 1% ammonia diluted in air.

The measured spectrum between 6114.2 and $6115.4\,\mathrm{cm}^{-1}$ is shown in Fig. 8. In the lower trace a magnified portion of the spectrum is shown where the ammonia absorption line near $6114.8\,\mathrm{cm}^{-1}$ is clearly recognizable on the tail of the strong methane line at $6114.5\,\mathrm{cm}^{-1}$ and between several ethylene lines. Such a high selectivity and high dynamic range has been obtained reducing the sample pressure down to 50 mbar. At this pressure, the efficiency of the photoacoustic detection process is about a factor of 1.5 lower than at 150 mbar. Applying the signal analysis procedure previously described, 0.02% ammonia concentration is detectable with a S/N ratio of 3. Methane detection accuracy is not much affected by ethylene overlapping: at $6114.5\,\mathrm{cm}^{-1}$ the ethylene signal contribution is less than 1%.

From the above reported investigations and considerations it is clear that experimental parameters, i.e. laser frequency scan extension and sample pressure, depend strictly on relative abundances, number of molecules to detect, and measurement response time. Detection of methane and ethylene can be performed even at pressures up to 600 mbar, with 30 GHz scan (6114.3–$6115.3\,\mathrm{cm}^{-1}$). If ammonia has to be detected as
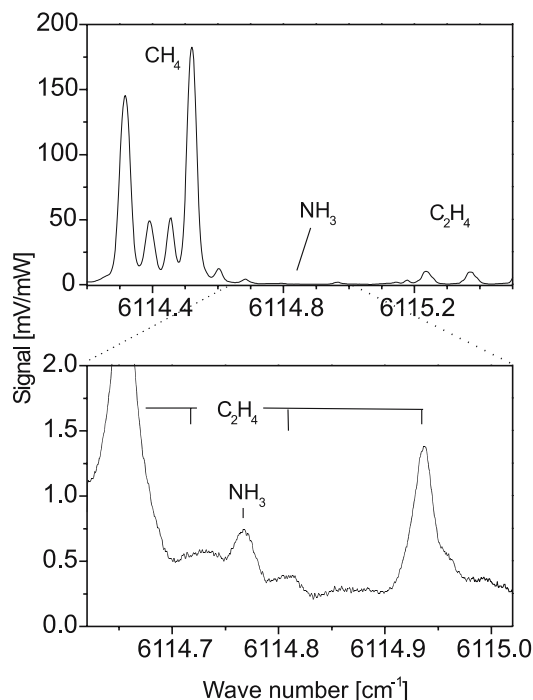

FIGURE 8   Spectrum of a 40% CH_4, 5% C_2H_4 and 1% NH_3 mixture in air at a pressure of 50 mbar. The lower trace shows a magnified portion where the ammonia line near $6114.8\,\mathrm{cm}^{-1}$ is detectable. Laser power 0.9 mW, amplifier gain 2×10^3, lock-in time constant 5 sec

well, the sample pressure must be lower in order to enhance selectivity: the frequency scan can be shorter, i.e. 10 GHz scan (6114.6–$6114.9\,\mathrm{cm}^{-1}$), thus reducing the measuring time at the expense of sensitivity.

Low detection sensitivities of the described apparatus are limited by geometrical constraints on the photoacoustic cell designed to be inserted in a compact build up cavity. In such an experimental set up, a gain factor of 100 can be reached obtaining sub ppm sensitivities. With this upgrading of the photoacoustic detection technique using low power diode lasers, it is competing with other sophisticated methods based on cavity enhanced absorption. In any case some applications do not need extreme sensitivities while requiring the possibility to detect several species with a single simple instrument.

4   Conclusion

Experimental data on the $\nu_2 + \nu_3 + \nu_4$ combination band of ammonia, with 1.5 GHz resolution, are reported. A careful investigation between 6020 and $6170\,\mathrm{cm}^{-1}$ of this spectral structure allowed suitable wavelength intervals to be found for simultaneous detection of ammonia, methane and ethylene sampled in atmospheric air.

A trace gas detector, based on a resonant photoacoustic cell coupled with an external cavity diode laser, has been used to analyze the characteristics of selectivity and sensitivity for detection of ammonia, methane and ethylene in the selected spectral regions. In order to increase detector sensitivity a data analysis procedure has been developed which consists of a real time least square fit based on known spectral functions. The algorithm can self-search the overall spectral structure within the acquired data, without the necessity of

a reference cell. The best obtainable sensitivity is around a few ppm with 1 mW laser power for all the three gas components.

This apparatus has been used for multi-gas detection in a gas mixture, simulating a real sample coming from biomass gasification where the relative abundance of the produced molecular species, like methane, ethylene and ammonia, can be significantly different.

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