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Detection of acetylene impurities in ethylene and polyethylene manufacturing processes using tunable diode laser spectroscopy in the 3-µm range

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Abstract Using recently developed GaInAsSb/AlGaInAsSb DFB lasers, tunable diode laser spectroscopy (TDLS) has been extended into the 3-µm wavelength region for the detection of acetylene impurities in hydrocarbon compounds encountered in ethylene manufacturing. Measurements of acetylene in pure polymer grade ethylene and in a gas mixture of ethylene and ethane typical of the process stream around a hydrogenation reactor have been performed. Using a procedure incorporating subtraction of a hydrocarbon background spectrum a detection limit of 5 ppb m was achieved under ordinary laboratory conditions. Under forced temperature cycling conditions, the detection limit deteriorated to 180 ppb m, due to temperature drift caused by optical interferences generated by reflections in the laser TO8 can.

1 Introduction

Tunable diode laser spectroscopy (TDLS) is a versatile technique for detection of molecular constituents in gas phase under various conditions. The short response time offered by the technique makes it particularly suitable for online real-time gas process control applications. In general, such process control has the potential to improve the efficiency of many types of industrial processes, in particular hydrocarbon manufacturing, by improving on the quality of the produced products and reducing the amount of product out of specification that is sent downstream in the process. This in turn, leads to reduced production costs, primarily due to a lower consumption of raw material and reduced energy consumption.

The standard analysis methods for process monitoring applications in the petrochemical industry are presently based upon gas chromatographs (GC) or extractive nondispersive infrared (NDIR) sensors, which both have response times on the order of minutes. Such response times are too long to allow efficient real-time process control; process control requires instead response times in the second range. The short response time offered by the TDLS technique therefore has the potential to improve the efficiency of many hydrocarbon manufacturing processes.

Presently the majority of TDLS analyzers utilize transitions in the near-infrared (NIR) range where telecom grade DFB lasers are readily available. The present applications for TDLS analyzers found in the hydrocarbon processing industry, e.g., for detection of humidity in natural gas, all use lasers with a wavelength between the near-infrared up to the 2.8-µm region [1]. However, such transitions are in general weak over-tones, which give the technique an insufficient sensitivity for many types of applications. In order to compensate for the low line strengths of the over-tone transitions, complex multipath cells have to be used [2, 3]. In addition, many of the hydrocarbons present in typical process streams lack resolved absorption lines at shorter wavelengths. Much would therefore be gained if hydrocarbons

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instead could be addressed on their fundamental vibrational bands. Unfortunately, there has been a lack of suitable room temperature single-mode diode laser sources emitting in the wavelength range of these bands, i.e., in the 3 to 3.5 µm range. This has so far been a limiting factor in the application of TDLS instrumentation to the hydrocarbon processing industry.

However, during the last few years, the operational wavelength range for room temperature single-mode antimonide lasers has been extended beyond 3 µm. Moreover, room temperature DFB lasers based on the quinary alloy GaInAsSb/AlGaInAsSb lasing at wavelengths up to 3.4 µm with low or moderate threshold currents (<100 mA) have recently been developed [4, 5]. This development is very promising since it enables the development of high sensitivity TDLS analytical instrumentation for detection of several important hydrocarbons [6].

Light olefins, such as ethylene (C_2H_4, also referred to as ethene) and propylene (C_3H_6, also termed propene), are basic building blocks used in the modern petrochemical and chemical industries. They are produced mainly from petroleum-based feed stocks by steam cracking. The majority of the ethylene and propylene produced is used in the production of polymers. There are many important analyzer tasks in olefin and polyolefin production such as monitoring of the purity of the feedstock materials and optimization of the hydrogenating process [7]. Ethylene is today the organic component that is industrially produced in largest volumes, and it is used in many petrochemical processes, e.g., for manufacturing of polyethylene. Acetylene is an impurity in the cracking process used to manufacture ethylene. In order to ensure the quality of the wide range of petrochemical products based on ethylene, especially polyethylene plastics, it is important to monitor and assess the presence of impurities, in particular acetylene. In this context, there are two issues that are of particular interest; viz. monitoring of acetylene impurities in pure ethylene and in the hydrogenating process.

The monitoring of acetylene impurities in pure polymer grade ethylene is made to verify the ethylene plant product as a quality control during custody transfer, or to verify the quality of the polymerization plant feed. The required measurement range for C_2H_2 in pure ethylene is in the 0–5 ppm range.

The dominant method for removing acetylene from ethylene is through selective hydrogenation. The acetylene converter contains a catalyst that induces a reaction between acetylene and hydrogen to form ethylene. The desirable reaction is to form ethylene from the acetylene, in a process using hydrogen, $C_2H_2 + H_2 \rightarrow C_2H_4$. However, there is an optimum condition for the reaction; if the reaction is incomplete, one gets too much C_2H_2, if the reaction goes too far, some of the ethylene is converted to ethane by the $C_2H_4 + H_2 \rightarrow C_2H_6$ process [8]. Hence, to optimize the production process of polyethylene, an online monitoring of the acetylene concentration is needed. The acetylene content should preferably be reduced to less than 5 ppm at the outlet of the converter. This implies that the required measurement range of C_2H_2 in the hydrogenating process is likewise in the 0–5 ppm range, although in this case the gas matrix at the outlet of the hydrogenating converter constitutes a hydrocarbon mixture dominated by methane, ethane, and ethylene.

2 Selection of spectral region

Figure 1 shows an FTIR spectrum of gases typically found in the production of light olefins. It is clear that the wavelength region below 3.5 µm has large possibilities to be used for various types of applications involving detection of hydrocarbons, e.g., the monitoring of acetylene impurities in ethylene. The strong and isolated acetylene lines in the 2975–3125 nm region would enable a TDLS sensor design with excellent performance using a relatively short absorption path. Interfering hydrocarbons such as ethylene, ethane, propane, and propylene are clearly separated from the acetylene band.

Using spectra from Hitran 2008 [9] an absorption spectrum from 1000 ppm acetylene in a hydrocarbon background typical of a hydrogenating reactor (65% C_2H_4, 33% C_2H_6, and 100 ppm CH_4) for an interaction length of 10 cm at a temperature of 25°C was computed. As is shown in Fig. 2, it was found that several acetylene lines around 3.06 µm were sufficiently isolated and free from interferences from other gases to be used for the detection of acetylene in hydrocarbon backgrounds. The Hitran 2008 spectra suggest that there is virtually no interference from other hydrocarbons in the gas matrix on the 3059.56-nm acetylene line. This transition was therefore chosen as the pilot line for this study. In order to investigate the achievable performance of this technique for the two types of application discussed above, TLDS was performed on acetylene in both pure polymer grade ethylene and in a hydrocarbon background mixture typical of a hydrogenation reaction system.

3 Experimental setup

To reach the selected acetylene line, we used a GaInAsSb/AlGaInAsSb DFB laser emitting at around 3060 nm mounted in a TO8 can with a sapphire window and with an integrated thermoelectric cooler. The sealed package makes it possible to obtain a wide tuning range while avoiding damage to the laser from condensation of humidity on the laser facet. Figure 3 shows the characteristics of this laser. At 10°C the threshold current is 60 mA, and the output power is 2 mW at

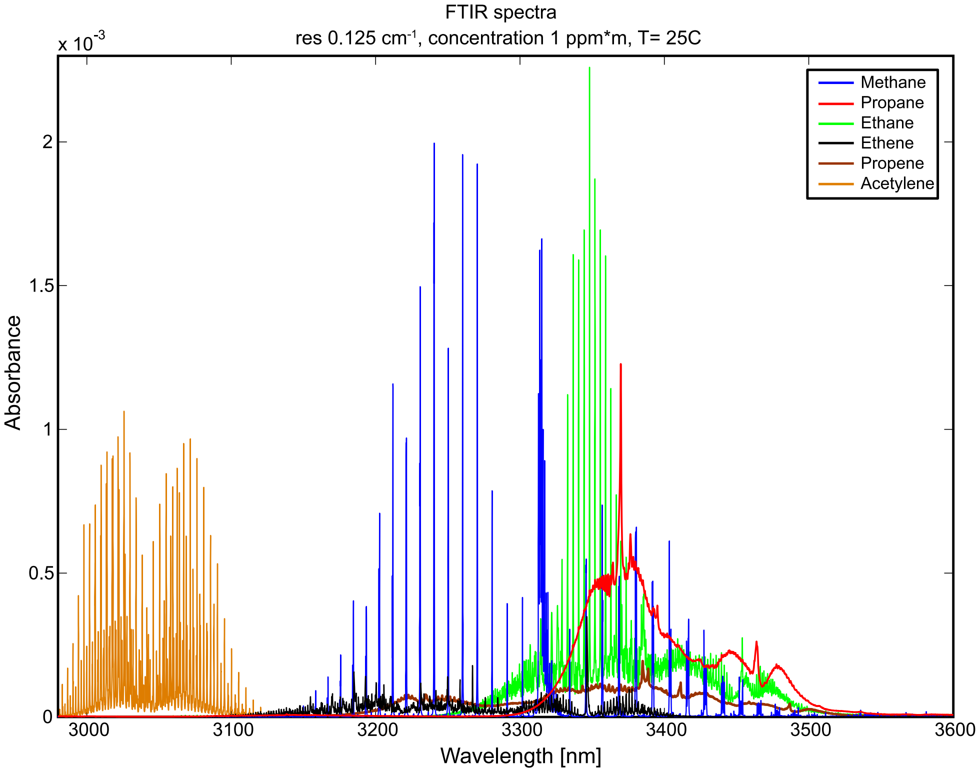


Fig. 1 FTIR spectra of gases typically found in the process stream in olefin and polyolefin manufacturing. The spectra correspond to 1 ppm m of each gas, at a temperature of 25°C

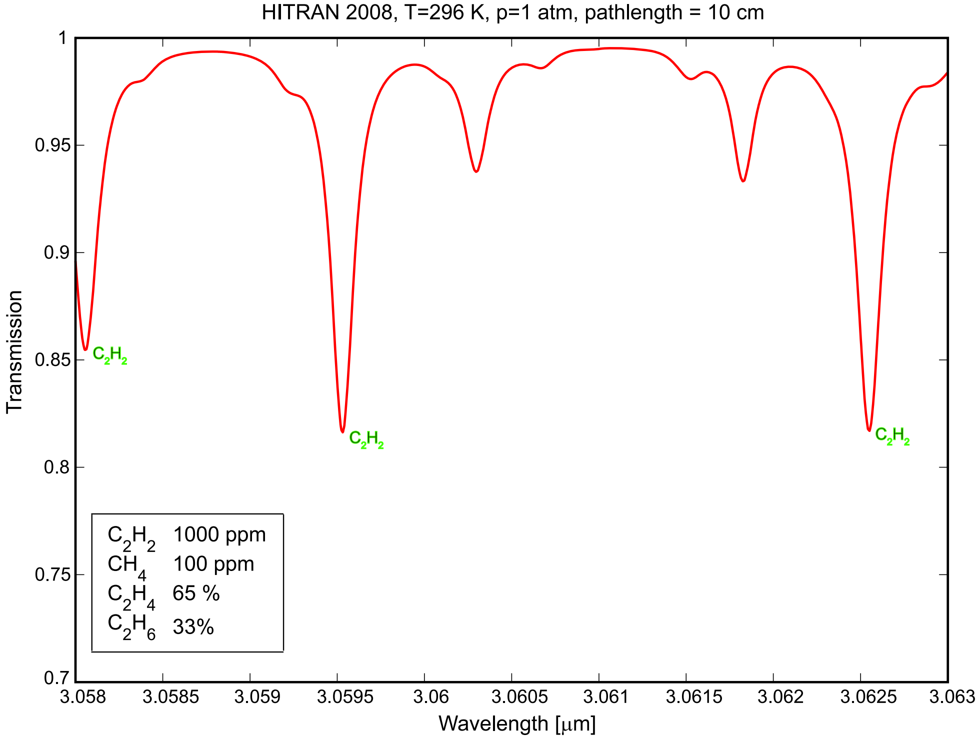


Fig. 2 Absorption spectrum of 1000 ppm acetylene in a hydrocarbon background typical of a hydrogenating reactor (65% C_2H_4, 33% C_2H_6, and 100 ppm CH_4) for an interaction length of 10 cm at a temperature of 25°C

an operating current of 140 mA. The side mode suppression is better than 34 dB.

Figure 4 shows the experimental setup. To reduce the optical interferences in the system, the laser was mounted on a fixture that enabled a linear shift of the position of the entire laser assembly over more than 50 µm, which is sufficient to average out any etalon that can occur in the measurement setup. The dithering frequency was 36 Hz, which is asynchronous with the wavelength scan. The diverging beam from the laser was collimated by an F/0.53

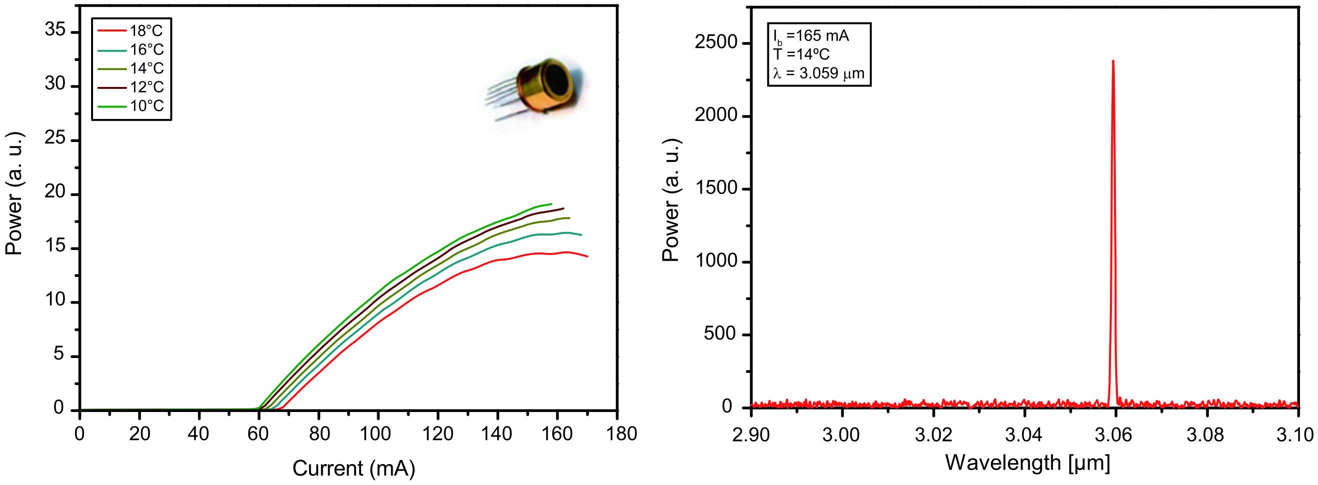


Fig. 3 Power-vs.-injection current dependences and an emission spectrum of the GaInAsSb/AlGaInAsSb DFB laser used

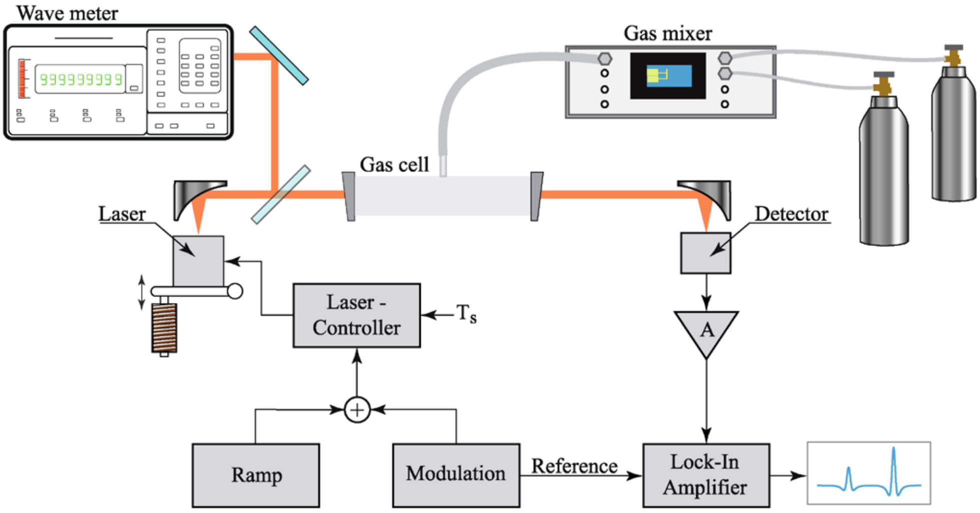


Fig. 4 Experimental setup

off-axis parabolic mirror with a focal length of 20.3 mm. The laser beam was passed through a 15-cm gas absorption cell with wedged CaF_2 windows. Using an identical off-axis parabolic mirror, the laser radiation was focused on an InAs/InAsSbP detector (Roithner PD36-05-TEC). The laser injection and Peltier currents were supplied by a combined laser and thermoelectrical cooler (TEC) driver (ILX LDC-3724). A suitable center frequency of the laser was chosen by adjusting the temperature of the TEC. The laser emission wavelength was verified using a wave-meter that has an absolute accuracy of $\pm 2 \times 10^{-6}$ and a resolution of ±0.001 nm (EXFO WA-1000-IR). The wavelength tuning was realized via modulation of the injection current. To perform Wavelength Modulation Spectroscopy (WMS), a waveform generator supplied a triangular ramp of 23 Hz and a 6 kHz sinusoidal modulation to the laser. The calibrated gas mixtures were made with a HovagaGas gas mixer (IAS GmbH).

4 Results

The laser tuning characteristics are shown in Fig. 5. The frequency-vs.-current dependence was determined by replacing the gas cell with a 2.54 cm (1″) germanium etalon with a free spectral range of 1.43 GHz. The laser current was varied between 112 mA and 175 mA while the WMS signal from the etalon was recorded. The measured response is shown in Fig. 5a. The corresponding tuning of the laser, obtained by a fit to the etalon trace, is illustrated in Fig. 5b. It was found that the maximum mode-hop free tuning range of this laser was 40 GHz. As is shown in Fig. 5c, the current tuning (FM-index) for the 23-Hz sweep rate varied from 0.26 GHz/mA in the beginning of the sweep to 0.815 GHz/mA at the end of the sweep. In order to avoid distortion of the line shape, the part of the scan that has a rapidly varying FM-index (and thereby a rapidly varying wavelength modulation amplitude) was avoided [10].

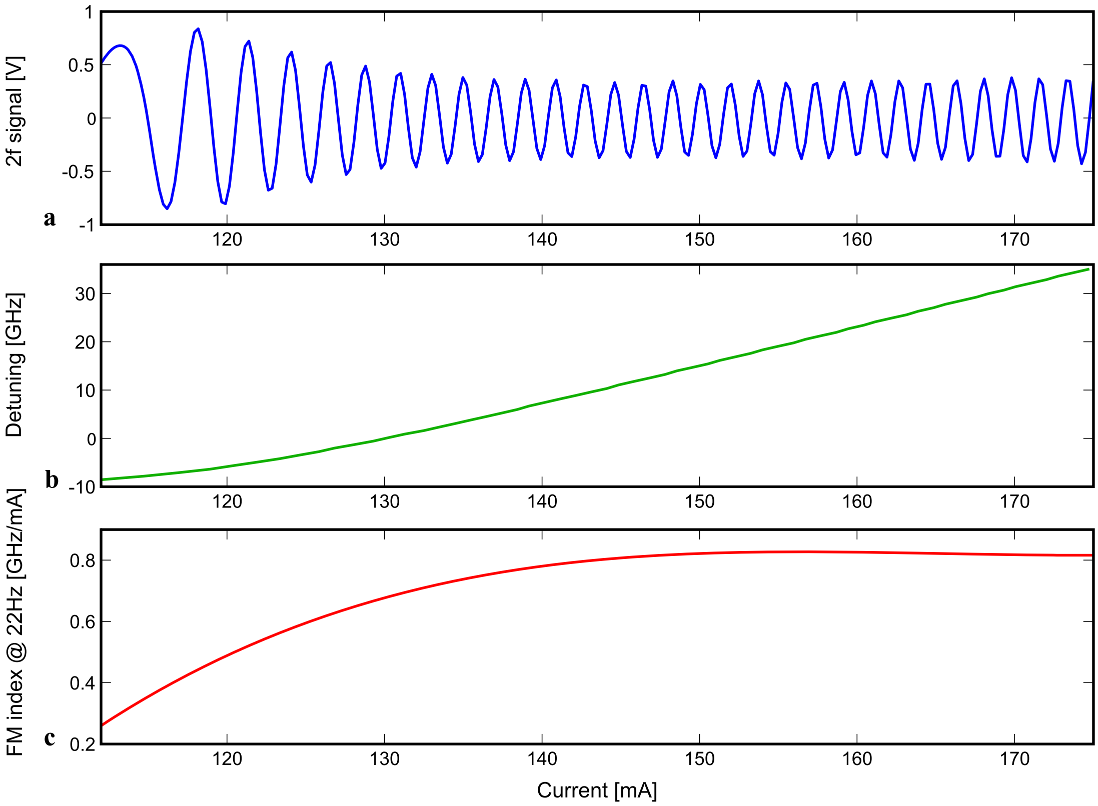


Fig. 5 Wavelength tuning characteristics of the 3060-nm DFB laser

The scan over the acetylene line around 3059.56 nm was finally achieved by using a laser temperature of 10°C and an injection current that was modulated between 143 and 156 mA (for which the FM-index varied from 0.80 to 0.826 GHz/mA, i.e., 3%).

For the assessment of signal magnitudes, the plots were linearized by the use of the detuning-vs.-current trace in Fig. 5b. Using a curve fit routine, the dynamic FM-index (i.e., the wavelength modulation index) around the position of the acetylene line for a modulation frequency 6 kHz was determined to 0.3 GHz/mA [11]. Since the laser was run with injection currents for which the FM-index has a weak current-dependence, and the wavelength modulation was optimized with respect to the acetylene line, the variation of the FM index over the line leads to a maximum alteration of the 2f-signal amplitude of 0.05%, which gives an insignificant influence on the line shape.

To assess the performance of the TDLS setup for the detection of acetylene impurities in pure polymer grade ethylene gas, a gas mixture consisting of 20 ppm C_2H_2 in ultrahigh purity C_2H_4 at a pressure of 962 mbar, referred to as gas mixture I, was prepared. Despite the fact that neither the FTIR spectrum in Fig. 1 nor the Hitran 2008 absorption spectrum displayed in Fig. 2 showed any major interfering lines from other hydrocarbons around the acetylene line at 3059.56 nm, initial TDLS-measurements revealed such an ethylene line centered at 3060.00 nm (which thus is not in the Hitran 2008 database [9]).

In order to achieve a sufficiently accurate assessment of the acetylene impurity level, TDLAS was performed with a differential mode of detection so as to remove the ethylene background in each acquired spectrum. A background ethylene spectrum (referred to as reference spectrum I) was recorded using ultrahigh purity certified ethylene (with a guaranteed acetylene concentration below 0.1 ppm). The recorded reference spectrum was then fitted to gas mixture I with the amplitude and detuning as free parameters by minimizing the residual only over the part of the spectra that does not contain any acetylene lines. In our case the spectral region between 25 and 35 GHz was the optimum choice since it contains a clear spectral feature (from ethylene for the case where acetylene was detected in pure ethylene, and from ethane and ethylene where acetylene was detected in the ethane/ethylene gas mixture, as described below). After the adjustment of the amplitude and the detuning the reference spectrum was subtracted from the measured gas mixture spectrum. It was found that the best sensitivity of the instrument was obtained by optimizing the amplitude and detuning of the reference spectrum to each gas mixture spectrum individually since this allows for corrections of minor fluctuations of laser center frequency as well as the ethylene

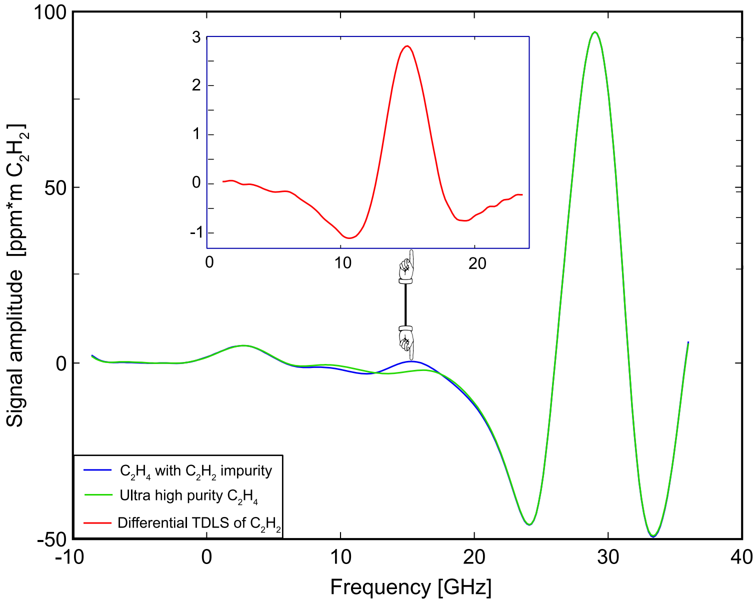


Fig. 6 2f-WMS signal from the gas mixture I (thus consisting of 20 ppm C_2H_2 in ultrahigh pure ethylene, *blue curve*), a reference ethylene spectrum (*green curve*), and the corresponding differential TDLS spectrum (*inset*, *red curve*)

(ethylene/ethane) background content on a scan-to-scan basis.

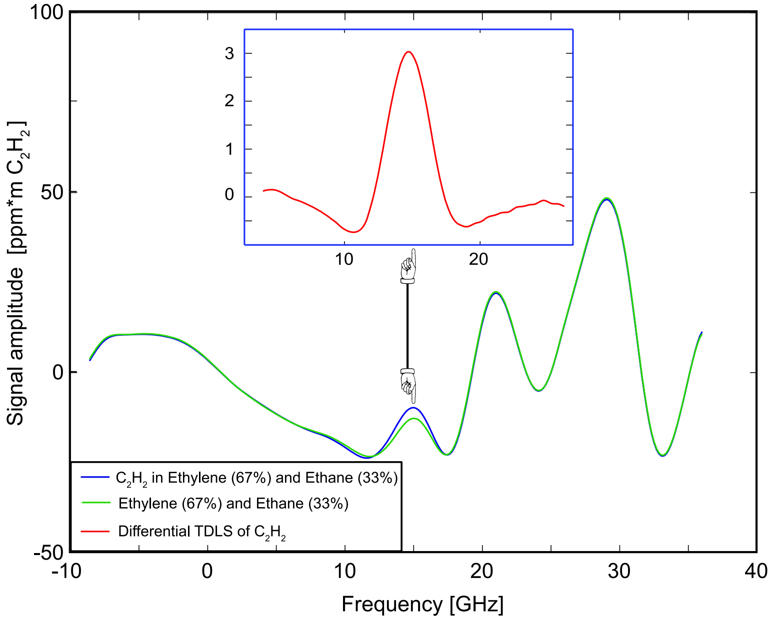
Figure 6 shows the 2f-WMS signal from gas mixture I (blue curve), the reference ethylene spectrum (green curve), and the residual differential TDLS spectrum (the inset, red curve). The zero in the frequency scale corresponds to the zero in the detuning curve in Fig. 5b, which implies that it corresponds to a laser current of ∼132 mA. Since the gas mixture I contained 20 ppm (and the measurement cell was 15 cm), the signal in the inset corresponds to 3 ppm m. We found that the measurement is limited by the remaining optical noise from the setup and not by the quality of the subtraction of the reference spectrum.

Next, the detection performance of acetylene in a gas mixture typical of a hydrogenation reactor was investigated by measuring the 2f-WMS signal from 20 ppm of acetylene in a gas mixture of ethylene (67%) and ethane (33%), referred to as gas mixture II. The mixture was prepared using high-purity gases and a HovaGas gas mixer. A corresponding reference spectrum (II) was taken using the ethylene (67%)/ethane (33%) gas mixture. This reference spectrum was subsequently fitted to, and subtracted from, the measured spectra from gas mixture II by the procedure described above. Figure 7 shows the 2f-WMS signals from acetylene in gas mixture II (blue curve) and the corresponding reference ethylene/ethane spectrum (green curve), together with the residual differential TDLS spectrum (inset, red curve). This measurement also corresponds to 3 ppm m.

Figures 6 and 7 show that the differential spectra contain an interference fringe pattern. The peak-to-peak (p–p) value of these fringes are on the order of 200 ppb m, which is the same as the level of the interference pattern measured on a zero-gas sample. Since the background signals due to the optical interferences (the etalon signals) could not be removed by the dithering of the laser, they were attributed to reflections inside the TO8 can including the sapphire window. It is clear that the quality of the spectral fitting and subtraction procedure is sufficiently high, so that we are limited by optical noise also in this case. This implies that a path-length longer than that used in these measurements (15 cm) would improve the sensitivity.

In order to determine the actual sensitivity of the system under different conditions, two series of measurements on a zero-gas sample, each 22-hour long, were performed. The first series was performed at constant room temperature, whereas the other was made while cycling the temperature in the 18 to 30°C interval. Figure 8 shows the Allan variance of these measurements normalized for a 1-meter path length, expressed in units of $(\mathrm{ppb})^2$. The Allan variance, $\sigma_A^2(\tau)$, first introduced by Allan in 1966 for characterization of frequency standards, and then brought into the field of TDLAS by Werle et al. in 1993 [12], constitutes an assessment of the time stability of a measurement or a measurement system. Since the Allan variance depends on the difference between consecutive readings, each averaged over a time τ, it is a function of the averaging time. As long as the system is affected by white noise, as often is the case for short integration times, the Allan variance decreases linearly in a loglog plot of $\sigma_A^2(\tau)$ versus τ. However, for longer integration times, other types of noise (flicker noise, often of $1/f$ type, and drift, of $1/f^a$ type where $a > 1$) usually show up (appearing in various types of background signals), making the response to level-off (for flicker noise) and even increase (for drifts). The average time for which the Allan variance has a minimum represents the optimum integration time of the system. Any further integration beyond that for the minimum would bring in more $1/f$ noise and drift into

Fig. 7 2f-WMS signal from acetylene in gas mixture II (consisting of a 0.67/0.33 ethylene/ethane gas mixture, *blue curve*), a reference ethylene/ethane spectrum (*green curve*), and the differential TDLS spectrum (*inset*, *red curve*)



the assessment and reduce the overall performance of the system.

In this case, the Allan variance for a system at room temperature [the lower (blue) curve in Fig. 8] does not follow white-noise behavior for too long integration times for any of the measurement series; instead, it “lifts off” from the white-noise curve after some tens or hundreds of seconds. This noise, which originates from the etalon effects inside the TO8 can, constitutes a drift component that contributes already at short integration times (in the order of tens of seconds). Since this drift component is due to a varying optical interference pattern inside the TO8 can, the drift will be temperature dependent. The best detection limit under a constant room temperature conditions was found to be 5.5 ppb m for an integration time of 100 s. However, this limit is not applicable under longer periods of time since the drift component starts to dominate for longer integration times. It is therefore important to determine the maximum amplitude of this drift as it will be the practical sensitivity limit for long-term measurements.

When the system is placed in a temperature cycled environment, the Allan plot shows that the drift component indeed starts to dominate already at shorter integration times (already at around 10 s) and that it reaches a steady level of around 180 ppb m for times longer than 2000 s. This level therefore determines the practical long-term detectability of the system. It is interesting to note that this is in good agreement with the measurement of the p–p value of the interference pattern measured on a zero-gas sample, which was found to be 200 ppm m. This implies that, during the temperature cycling, the interference fringe pattern under the acetylene line drifted in frequency by at least one full fringe period.

5 Discussion

Data retrieval in this work was performed by fitting and subtracting a previously recorded reference spectrum from a measured spectrum obtained in a gas mixture. An alteration of the modulation index over the scan (due to nonlinear processes in the laser) can give rise to distortion of the line, which potentially can affect the accuracy and detectability of the technique. However, since the background subtraction procedure incorporates two spectra, measured under similar conditions, the background subtraction procedure will not be particularly affected by any spectral distortion. On the other hand, since the line strengths of the individual lines in the various spectra have different temperature dependences, the shape of the reference spectrum will change with temperature. Reference spectra should therefore be recorded at several temperatures in the specified temperature interval, and the particular spectrum corresponding to the conditions of the actual measurement should be used in the subtraction process. Since information about the process gas temperature is generally available from external sensors (in order for the analyzer to calculate the actual gas concentration), this should not be any problem.

6 Summary and conclusions

Detection of acetylene impurities in different hydrocarbon backgrounds encountered in ethylene manufacturing has been performed using tunable diode laser spectroscopy in the 3-μm wavelength region using a recently developed GaInAsSb/AlGaInAsSb DFB laser. Measurements of acetylene in pure polymer grade ethylene and in a gas mixture of

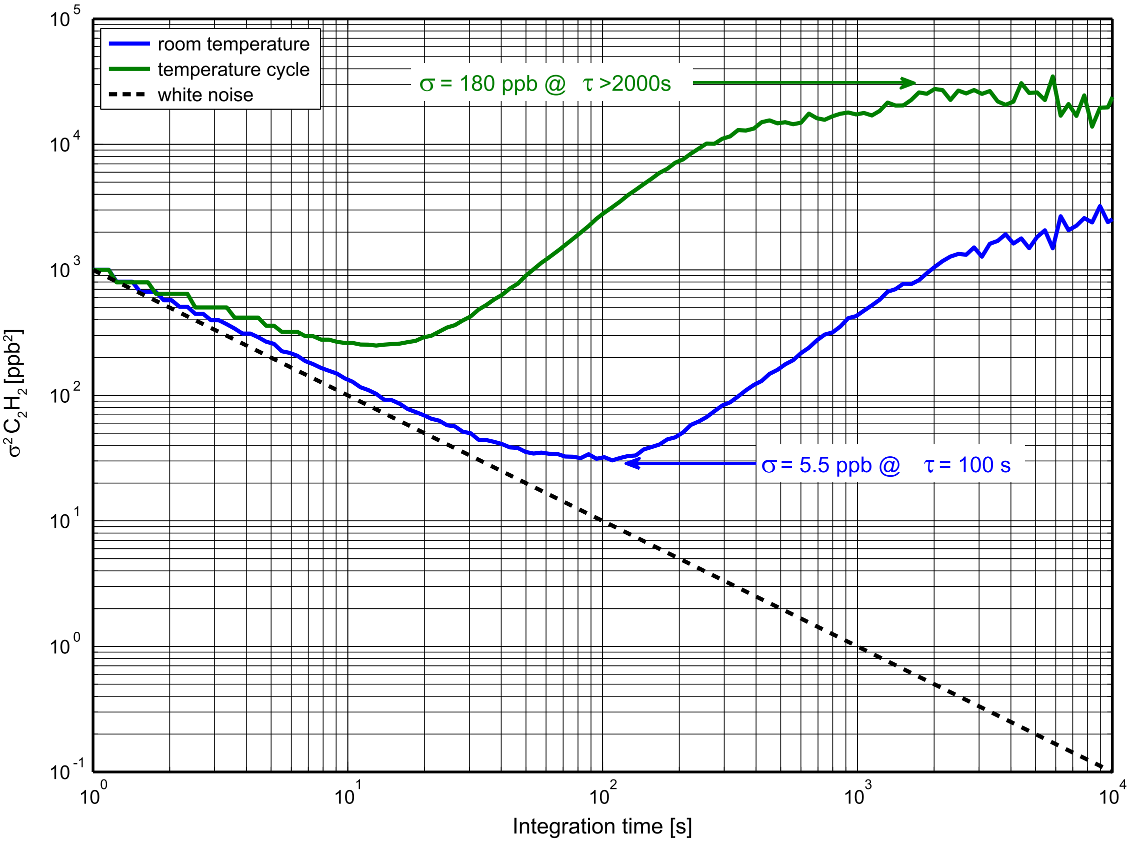


Fig. 8 Allan variance plot of the detection limit normalized to 1-meter path length of a zero-sample measurements under constant room temperature (*blue curve*) and temperature cycled conditions (*green curve*). The Allan variance of purely random process (*white noise*) is given for comparison purposes (*black curve*)

ethylene and ethane typical of the process stream around a hydrogenation reactor have been performed. The hydrocarbon background was removed using a subtraction procedure in which a reference spectrum obtained from either ultrahigh purity certified ethylene or an ethylene/ethane gas mixture was fitted to the part of the measured spectrum in which there is no acetylene line. It was found that the detection limit was 5 ppb m under constant room temperature conditions, whereas it was significantly higher, 180 ppb m, under enforced temperature cycling conditions, caused by optical interferences generated by reflections in the laser TO8 can.

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References

1. W. Zeller, L. Naehle, P. Fuchs, F. Gerschuetz, L. Hildebrandt, J. Koeth, Sensors **10**, 2492 (2010)
2. L.D. Le, J.D. Tate, M.B. Seasholtz, M. Gupta, T. Owano, D. Baer, T. Knittel, A. Cowie, J. Zhu, Appl. Spectrosc. **62**, 59 (2008)
3. X.S. Liu, X. Zhou, A. Feitisch, in *ISA EXPO*, Houston, TX, 14–16 October 2008
4. S. Belahsene, L. Naehle, M. Fischer, J. Koeth, G. Boisser, P. Grech, G. Narcy, A. Vicet, Y. Rouillard, IEEE Photonics Technol. Lett. **22**, 1084 (2010)
5. L. Naehle, S. Belahsene, M.V. Edlinger, M. Fischer, G. Boissier, P. Grech, G. Narcy, A. Vicet, Y. Rouillard, J. Koeth, L. Worschech, Electron. Lett. **47**, 46 (2010)
6. P. Kluczynski, S. Lundqvist, S. Belahsene, Y. Rouillard, Opt. Lett. **34**, 3767 (2009)
7. L. Kniel, O. Winter, K. Stork, *Ethylene: Keystone to the Petrochemical Industry* (Marcel-Dekker, New York, 1980)
8. A.N.R. Bos, K.R. Westerterp, Chem. Eng. Process. **32**, 1 (1993)
9. L.S. Rothman, I.E. Gordon, A. Barbe, D.C. Benner, P.F. Bernath, M. Birk, V. Boudon, L.R. Brown, A. Campargue, J.P. Champion, J. Quant. Spectrosc. Radiat. Transf. **110**, 533 (2009)
10. L. Sandstrom, H. Ahlberg, T. Andersson, S. Lundqvist, R. Tell, in *Advances in Optical Imaging and Photon Migration*, Orlando Florida, 8 March 1998
11. P. Kluczynski, O. Axner, Appl. Opt. **38**, 5803 (1999)
12. P. Werle, R. Mucke, F. Slemr, Appl. Phys. B **57**, 131 (1993)