Advanced gas sensing applications above 3 µm enabled by new DFB laser diodes

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***nanoplus* expands the wavelength range of application-grade monomode lasers for use in gas spectroscopy beyond 3 µm. Especially important for the monitoring of hydrocarbons, real-time sensing applications with formerly unattained accuracy become feasible with the new laser sources.**

A very versatile technique for the detailed characterization of gas compositions is provided by Tunable Diode Laser Spectroscopy (TDLS). The types of constituents and their concentrations, for example, can be determined with high accuracy by making use of the unique absorption features of each gas species. Applications of laser diode based gas sensing range from human breath analysis to efficient fire detection and even gas sampling on space missions (www.nanoplus.com/mars).Aside from these significant social and medical uses, industrial process control has evolved into one of the most important fields of application for TLDS.

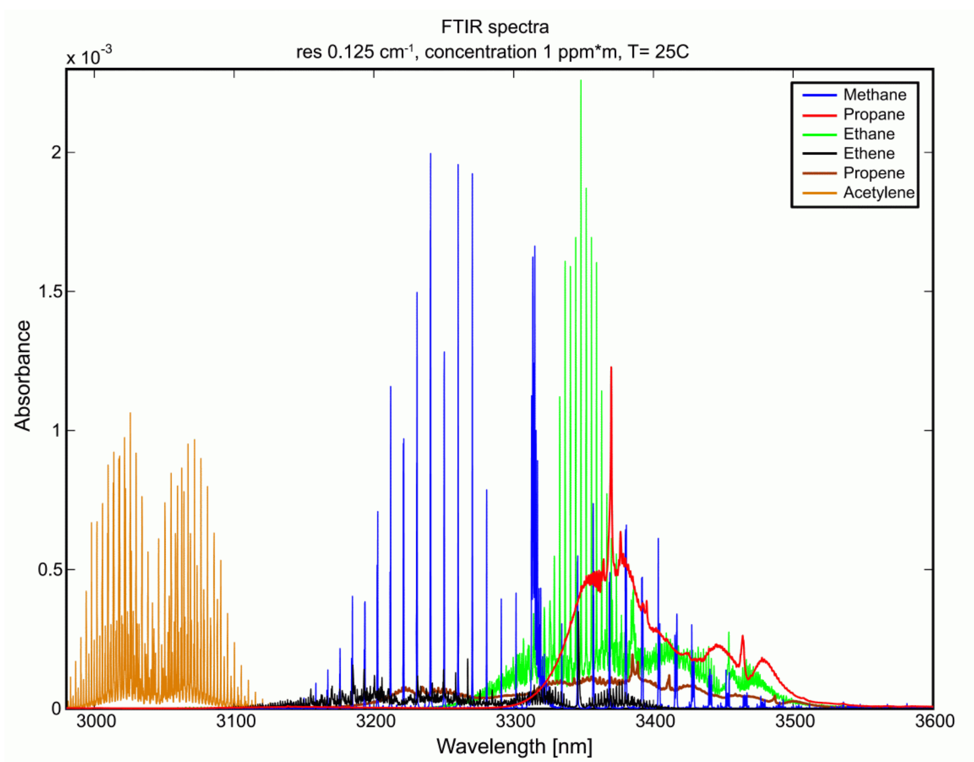


Figure 1: Absorbances of selected hydrocarbons in the range 3.0-3.6 µm.[1]

With the possibility of in-situ monitoring of a process, efficient adjustment to the crucial process parameters can be performed. TLDS is however critically dependent on the availability of suitable laser sources for the designated applications. Monomode distributed feedback (DFB) diode lasers in the near infrared (NIR) wavelength range up to around 3 µm have successfully been used in a multitude of industrial applications in the past. Technologically relevant gas species in those applications included H_2O, CO, CO_2 and NH_3, for example. Application-grade monomode lasers for TDLS beyond the 3 µm limit had – until recently - been unavailable, posing a severe limitation for sensing applications especially considering the detection of hydrocarbons. Many hydrocarbons have strong absorption features in the mid infrared (MIR) wavelength range 3.0-3.5 µm (see Fig. 1), where their fundamental absorption bands can be situated. Performing TDLS on the basis of those absorptions, with line strengths often orders of magnitude stronger than those of corresponding NIR absorptions, enables hydrocarbon detection with formerly unattained precision. One of many exceptionally interesting applications is highly accurate process control in the petrochemical industry, which can lead to higher energy efficiency and pollutant reduction. A major advantage of laser spectroscopy on hydrocarbons in the MIR to currently used techniques, such as gas chromatographs, is the possibility of real-time analysis with TDLS. With the latest developments of *nanoplus* within the European project SensHy (www.senshy.eu), DFB lasers with application-grade performance enabling highly sensitive TDLS hydrocarbon detection in the wavelength range 3.0-3.5 µm are now commercially available.

DFB laser technology and performance

nanoplus is the internationally leading supplier of high quality laser sources for gas sensing applications in the visible, NIR and MIR wavelength range [1]. For the fabrication of monomode DFB diode lasers the company uses its proprietary technology based on lateral metal grating structures. The gratings with dimensions on the order of 100 nm are defined next to the sidewalls of etched ridge waveguide structures using high-precision electron beam lithography (see Fig. 2 for a

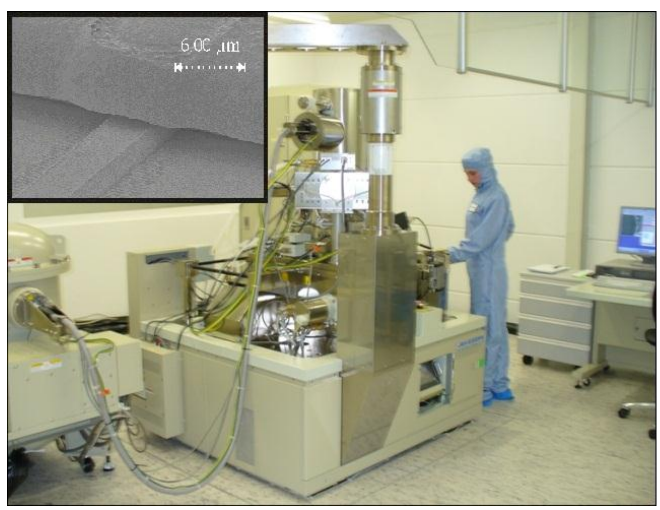


Figure 2: 100 kV electron beam lithography system used for the fabrication of laterally coupled DFB lasers at *nanoplus*. Inset: High-wavelength DFB laser structure. [2]

photo of the lithography system at nanoplus' cleanrooms facilities). The feedback structures are then patterned by metal evaporation, resulting in DFB laser devices. This patented, cost-effective approach has been well-established at nanoplus for more than 10 years and shows high DFB performance and yield. Until recently, nanoplus has offered high-quality DFB lasers for gas sensing up to 3 µm. The company has now boosted the wavelength of their devices up to 3.5 µm – making nanoplus the only commercial manufacturer of application-grade DFB laser diodes in this elevated wavelength range. The high-wavelength laser ridge waveguides are surrounded by a gold layer of high thermal conductivity for improved heat removal (see inset of Fig. 2 for such a laser structure) and equipped with a highly reflective backside metal coating for increased optical output efficiency. The DFB devices are exactly matched to their designated applications in TDLS sensing and subsequently mounted on TO headers with internal temperature controllers. Hermetical sealing of the headers in a dry nitrogen atmosphere yields application-ready, packaged DFB laser devices. Operation in continuous wave (cw) mode around room temperature certifies their application-grade performance, which is very comparable to devices of lower wavelength. Established know-how from existing gas measurement instruments can thus directly be transferred to the development of new instruments for hydrocarbon detection using the high-wavelength laser sources. Representatively for the new DFB devices, a monomode spectral characteristic (10°C / 160 mA) along with the typical temperature and current tuning behaviour of a laser at 3.36 µm are shown in Fig. 3. The outstanding spectral properties of the lasers, suppressing any side modes by more than 40 dB render them exceptionally well suited for uncomplicated and highly accurate TDLS applications. The devices can be operated up to temperatures above 20°C in cw mode, with output powers in the mW range. By adjusting the Peltier controlled chip temperature, the DFB emission wavelength of the lasers can coarsely be tuned to the desired value for the designated application with a tuning rate of ~0.28 nm/K.

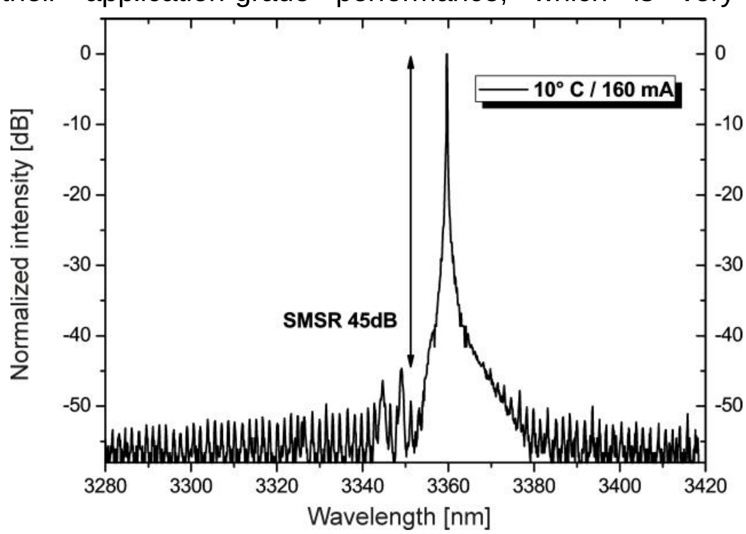


Figure 3: DFB wavelength tuning of a laser under current variation at different chip temperatures. Spectrum of the laser at 10°C / 160 mA.[3]

Single absorption lines and their shapes may then be scanned with very high precision and speed by current modulation of the emission wavelength (~0.025 nm/mA). Characteristic gas absorption features in a range of several nanometers can be sensed in this manner.

Hydrocarbon detection beyond 3 µm

Acetylene (C_2H_2) is a petrochemical of great industrial significance, which makes TDLS detection of this hydrocarbon with the new high-wavelength devices extremely interesting. A TDLS system sensing the characteristic band around 3.0-3.1 µm (compare Fig. 1) gives the opportunity to use a gas absorption path at least 30 times shorter than that of systems in the 1.5 µm region used so far. The region around 3.03 µm was chosen to demonstrate the accuracy and sensitivity of acetylene sensing with a high wavelength DFB laser [2]. Operated at 5°C, the operating current of the laser was varied in order to scan the region around 3028-3029 nm. In a direct absorption measurement 100% acetylene at 50 mbar pressure in an absorption cell of 1.5 cm length was detected. Fig. 4 shows the detected signal in comparison to data from the HITRAN2008 spectroscopic database. The measurement is accurate enough to determine discrepancies between actual absorption line positions and ones listed in the database, such as in „2“. The sensitivity level of the measurement is high enough to discover formerly unlisted absorbing features, such as „12“. The best detection limit determined was better than 1.5 ppb*m. As an example of an acetylene sensing application in the petrochemical industry, TDLS was performed with a 3.06 µm DFB laser [3]. Acetylene is an impurity in the cracking process used to manufacture ethylene (C_2H_4) - the petrochemical produced in largest volume worldwide. It is important to monitor the acetylene content with high accuracy to ensure a certain purity and thus quality of the produced ethylene.

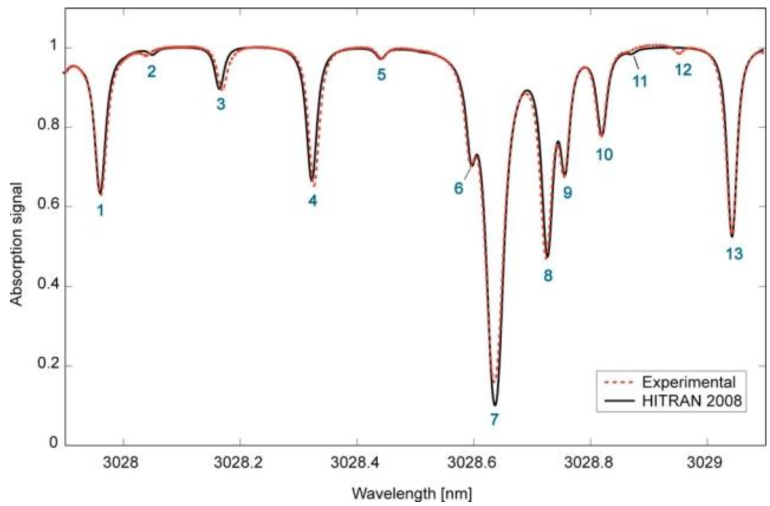


Figure 4: Direct absorption TDLS signal and HITRAN2008 data of acetylene around 3.03 µm.[3]

The acetylene fraction can be removed through a hydrogenation process, by converting it to ethylene in the following reaction:

$$C_2H_2 + H_2 -> C_2H_4$$

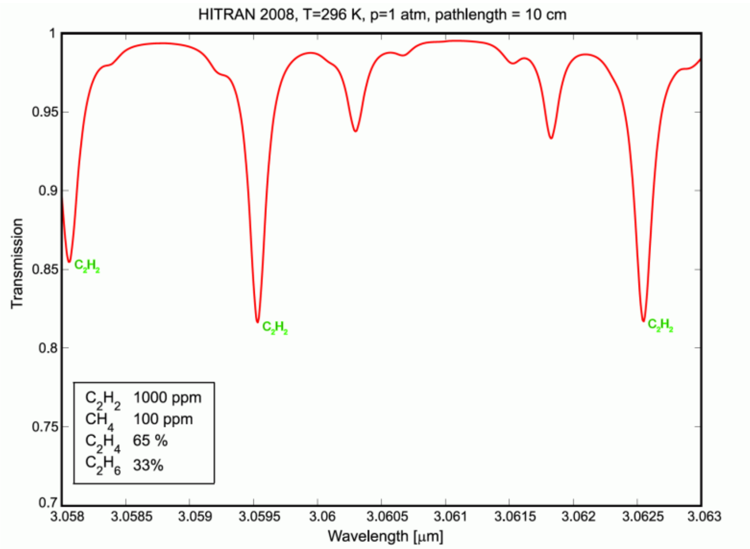
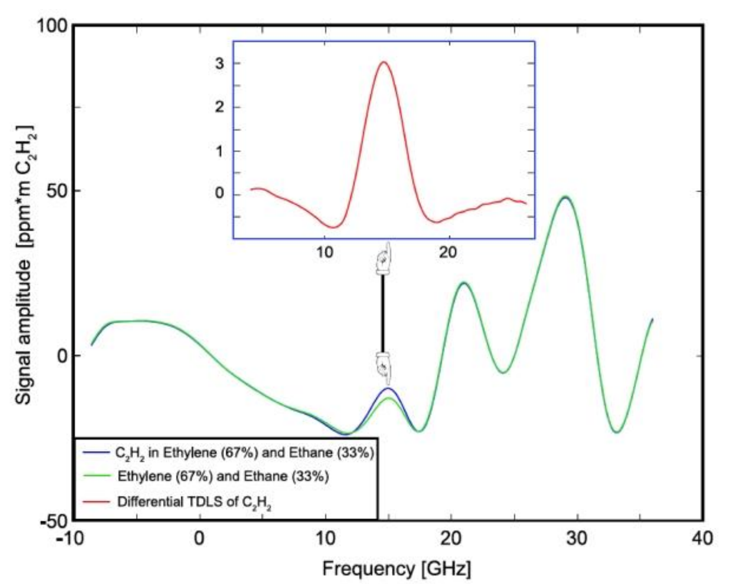


Figure 5: Computed absorption spectrum of 1000 ppm acetylene in a hydrocarbon background typical of a hydrogenating reactor. [1]



Figures 6: Signal amplitudes for a passing of the laser beam through an absorption cell filled with hydrocarbon reactor background alone (green) and with an additional concentration of C_2H_2 (blue). Inset: Resulting differential TDLS spectrum of C_2H_2. [1]

To avoid an incomplete conversion of the C_2H_2 or an undesired continuing conversion of the C_2H_2 to ethane (C_2H_6), the optimum conditions for the hydrogenation process may be determined by real-time monitoring of the C_2H_2 concentration. According to spectroscopic data acetylene absorption lines around 3.06 µm are isolated and interference free from absorptions due to a hydrocarbon background typical of a hydrogenating reactor (65% C_2H_4, 33% C_2H_6, 100 ppm CH_4). This wavelength region can therefore be used for the monitoring of C_2H_2. Fig. 5 shows an according absorption spectrum in this range, computed for 1000 ppm C_2H_2 in the reactor background for an interaction length of 10 cm at a temperature of 25°C. In an experiment, the temperature of an appropriate DFB laser was set to 10°C to address the strongest acetylene line around 3059.56 nm. Wavelength modulation spectroscopy was performed varying the laser current between 143-156 mA with a frequency of 6 kHz. Detected signal amplitudes were compared for a passing of the laser beam through a 15 cm long absorption cell filled with the hydrocarbon reactor background alone (Fig. 6 green) and with an additional concentration of C_2H_2 (Fig. 6 blue). Subtracting the signals yields the differential TDLS spectrum (Fig. 6 inset, red) of C_2H_2. In this experiment the detected concentration of C_2H_2 is 3 ppm*m, making a highly accurate control of the discussed hydrogenation process possible.

The presented experiments very nicely show the potential of the >3 µm DFB lasers to perform high-quality hydrocarbon sensing and to improve the efficiency of industrial manufacturing processes. However, not only the petrochemical industry will strongly benefit from the opportunities given by the new laser sources. For instance, real-time monitoring of explosive gas concentrations can have a remarkable influence on the improvement of work safety. The early detection of gas leaks in the industrial and private sector is another application with potentially high impact. nanoplus‘ new high-wavelength DFB devices are therefore expected to be found in several fields of advanced applications in the future. As a first example for application of the new DFB laser sources in the 3.3-3.4 µm wavelength range the device presented in Fig. 3 was used for high sensitivity ethane detection. Performing TDLS on the molecule's strongest absorption band around 3.36 µm (compare Fig. 1) allows for analysis down to ppb levels and below. In a first customer application ethane could be detected with a minimum detection sensitivity of 240 pptv [4]. In addition to the automotive and industrial sector, highly accurate trace gas analysis of ethane is very crucial for a number of environmental and medical applications, such as atmospheric monitoring and human breath analysis.

Footnotes

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According publication:

P. Kluczynski, M. Jahjah, L. Nähle, O. Axner, S. Belahsene, M. Fischer, J. Koeth, Y. Rouillard, J. Westberg, A. Vicet, S. Lundqvist: *Detection of acetylene impurities in ethylene and polyethylene manufacturing processes using tunable diode laser spectroscopy in the 3-µm range*, Applied Physics B: Lasers and Optics 105, Nr. 2, S. 427–434, **2011**

2 © *Institution of Engineering and Technology.*
According publication:

Nähle, L., Belahsene, S., Edlinger, M. von, Fischer, M., Boissier, G., Grech, P., Narcy, G., Vicet, A., Rouillard, Y., Koeth, J., Worschech, L.: *Continuous-wave operation of type-I quantum well DFB laser diodes emitting in 3.4 µm wavelength range around room temperature* Electronics Letters 47 **2011**, S. 46

According publication:

P. Kluczynski, S. Lundqvist S. Belahsene, Y. Rouillard: *Tunable-diode-laser spectroscopy of* C_2H_2 *using a 3.03 µm GaInAsSb/AlGaInAsSb distributed-feedback laser* Applied Physics B: Lasers and Optics 105, Nr. 2, S. 427–434, **2011**

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[3] P. Kluczynski, M. Jahjah, L. Nähle, O. Axner, S. Belahsene, M. Fischer, J. Koeth, Y. Rouillard, J.Westberg, A. Vicet, S. Lundqvist: *Detection of acetylene impurities in ethylene and polyethylene manufacturing processes using tunable diode laser spectroscopy in the 3-µm range* Applied Physics B: Lasers and Optics 105, Nr. 2, S. 427–434, **2011**

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Authors' biographies

Lars Nähle is a PhD student at the University of Würzburg, working for *nanoplus GmbH*. Within his PhD work he developed DFB lasers with wavelengths higher than 3 µm for gas sensing applications.

Dr. Lars Hildebrandt is director of sales at nanoplus GmbH. He received his PhD in physics in 2004 working on tunable external cavity diode lasers.

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He also served as project manager of the SENSHY project.
He received his PhD in physics in 2003 working on GaInAsN based laser diodes.

Dr. Johannes Koeth is the CEO of nanoplus GmbH.
He received his PhD in physics in 2001 working on GaSb based laser diodes in the 1.5-2.1 µm wavelength range.