# Advanced Gas Sensing Applications Above 3µm With DFB Laser Diodes

By Lars Nähle, Dr. Lars Hildebrandt, Dr. Marc Fischer, and Dr. Johannes Koeth

A discussion of expanding the wavelength range of application-grade monomode lasers for use in gas spectroscopy beyond 3µm, especially for monitoring of hydrocarbons in real-time sensing applications

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 (see 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.

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 3µm have successfully been used in a multitude of industrial applications in the past. Technologically relevant gas species in those applications included H<sub>2</sub>O, CO, CO<sub>2</sub> and NH<sub>3</sub>, for example. Application-grade monomode lasers for TDLS beyond the 3µm limit had—until recently—been unavailable, posing a severe limitation for sensing applications especially in the detection of hydrocarbons.

Many hydrocarbons have strong absorption features in the mid infrared (MIR) wavelength range 3.0–3.5µm (see Figure 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 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 of hydrocarbons in the MIR over 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 (see http://www. senshy.eu), DFB lasers for highly sensitive TDLS hydro-



Figure 1. Absorbances of selected hydrocarbons in the 3.0-3.6µm range<sup>1</sup>

### FEATURE





6.00 um





#### 3(A)

Figures 3. (A) Spectrum of a DBF laser at 10°C / 160mA; (B) DFB wavelength tuning of the laser under current variation at different chip temperatures

3(B)

carbon detection in the wavelength range  $3.0-3.5\mu m$  are now commercially available.

## DFB Laser Technology and Performance

*nanoplus* supplies laser sources for gas sensing applications in the visible, NIR and MIR wavelength range.<sup>2</sup> For the fabrication of monomode DFB diode lasers a proprietary technology is used based on lateral metal grating structures. The gratings with dimensions on the order of 100nm are defined next to the sidewalls of etched ridge waveguide structures using high-precision electron beam lithography. (See Figure 2A for a photo of the lithography system at a nanoplus cleanroom facility). The feedback structures are then patterned by metal evaporation, resulting in DFB laser devices. For the GaSb based high wavelength lasers beyond 3µm, ridge waveguides are surrounded by a high thermal conductivity gold layer for improved heat removal (see Figure 2B) and equipped with a highly reflective backside metal coating for increased optical output. The DFB devices are exactly matched to their designated applications in TDLS sensing and subsequently integrated into TO (transistor outline) 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 knowledge from existing gas measurement instruments can be thus directly 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 / 160mA) (see Figure 3A) along with the typical temperature and current tuning behavior of a laser at 3.36um (Figure 3B) are shown. The



Figure 4. Direct absorption TDLS signal and HITRAN2008 data of acetylene around 3.03µm<sup>4</sup>



Figure 5. Computed absorption spectrum of 1000ppm acetylene in a hydrocarbon background typical of a hydrogenating reactor<sup>1</sup>

outstanding spectral properties of the lasers, suppressing any side modes by more than 40dB 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 be roughly tuned to the desired value for the designated application with a tuning rate of ~0.28nm/K. Single absorption lines and their shapes may then be scanned with very high precision and speed by current modulation of the emission wavelength (~0.025nm/mA). Characteristic gas absorption features in a range of several nanometers can be sensed in this manner.

#### Hydrocarbon Detection Beyond 3µm

Acetylene  $(C_2H_2)$  is a petrochemical of great industrial importance, which makes

TDLS detection of this hydrocarbon with the new high-wavelength devices extremely interesting. A TDLS system sensing the characteristic band around 3.0-3.1µm (compare Figure 1) gives the opportunity to use a gas absorption path at least 30 times shorter than that of systems in the 1.5µm region used so far. The region around 3.03µm was chosen to demonstrate the accuracy and sensitivity of acetylene sensing with a high wavelength DFB laser.<sup>4</sup> Operated at 5°C, the drive current of the laser was varied in order to scan the region around 3028-3029 nm. In a direct absorption measurement, 100% acetylene at 50mbar pressure in an absorption cell of 1.5cm length was detected. Figure 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 position labeled 2 on the graph. The sensitivity level of the measurement is high enough to discover formerly unlisted absorbing features, such as position labeled 12 on the graph. The best detection limit determined was better than 1.5ppb•m.

As an example of an acetylene sensing application in the petrochemical industry, TDLS was performed with a 3.06µm DFB laser<sup>1</sup>. 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. The acetylene fraction can be removed through a hydrogenation process, by converting it to ethylene in the following reaction:

#### $C_2H_2 + H_2 \rightarrow C_2H_4$

To avoid an incomplete conversion of the  $C_2H_2$  or an undesired continuing conversion of the  $C_2H_4$  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. Spectroscopic data shows that acetylene absorption lines around 3.06µm are isolated and interference free from absorptions due to a hydrocarbon background typical of a hydrogenating reactor (65%  $C_2H_4$ , 33%  $C_2H_{6'}$  100ppm  $CH_4$ ). This

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Figure 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); resulting differential TDLS spectrum of  $C_2H_2$  (red)<sup>1</sup>

wavelength region can therefore be used for the monitoring of C<sub>2</sub>H<sub>2</sub>. Accordingly, Figure 5 shows an absorption spectrum in this range, computed for 1000ppm C<sub>2</sub>H<sub>2</sub> in the reactor background for a pathlength of 10cm 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 3059.56nm. Wavelength modulation spectroscopy was performed varying the laser current between 143-156mA with a frequency of 6kHz. Detected signal amplitudes were compared for a passing of the laser beam through a 15cm long absorption cell filled with the hydrocarbon reactor background alone (Figure 6 green) and with an additional concentration of  $C_2H_2$ (Figure 6 blue). Subtracting the signals yields the differential TDLS spectrum (see Figure 6 inset in red) of  $C_2H_2$ . In this experiment the detected concentration of C<sub>2</sub>H<sub>2</sub> is 3ppm•m, making possible a highly accurate control of the above discussed hydrogenation process.

The presented experiments demonstrate the potential of the  $>3\mu$ m DFB lasers to perform high-quality hydrocarbon sensing and thus improve the efficiency of industrial manufacturing processes. However, not only will the petrochemical industry strongly benefit from the opportunities given by the new laser sources. For instance, real-time monitoring of explosive gas concentrations can have an important influence on the improvement of work safety. The early detection of gas leaks in the industrial and private sector is another application with potential impact.

As an example for application of the new DFB laser sources in the 3.3-3.4µm wavelength range, the device presented in Figures 3A and 3B was used for high sensitivity ethane detection. Performing TDLS on the molecule's strongest absorption band around 3.36µm (compare Figure 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 240pptv.<sup>5</sup> 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. **G&**I

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**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  $3\mu$ M FOR GAS SENSING APPLICATIONS. HE CAN BE REACHED AT LARS.NAEHLE@NANOPLUS.COM

**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. HE CAN BE REACHED AT LARS. HILDEBRANDT@NANOPLUS.COM

**DR. MARC FISCHER** IS DIVISIONAL DIRECTOR FOR DEVICE FABRICATION AT NANOPLUS GMBH. HE ALSO SERVED AS PROJECT MANAGER OF THE SENSHY PROJECT. HE RECEIVED HIS PHD IN PHYSICS IN 2003 WORKING ON GAINASN BASED LASER DIODES. HE CAN BE CONTACTED AT MARC. FISCHER@NANOPLUS.COM

**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 1.5-2.1µM WAVELENGTH RANGE. HE CAN BE CONTACTED AT JOHANNES.KOETH@NANOPLUS.COM **COMPANY INFORMATION:** NANOPLUS GMBH, NANOSYSTEMS AND TECHNOLOGIES, OBERER KIRSCHBERG 4, D-97218 GERBRUNN, GERMANY, +49-931-90827-0 WWW.NANOPLUS.COM