Quantum Cascade Lasers in Industrial Applications

Peter Kaspersen*, Peter Geiser, Dung Do Dang
Norsk Elektro Optikk A/S, Solheimveien 62A, 1471 Lørenskog, Norway

BIOGRAPHY

Peter Kaspersen: After graduating from the University of Oslo in Semiconductor Laser Physics in 1969 he joined the company Simrad Optronics, a Norwegian company specializing in electro-optical products such as Laser Rangefinders, Night Vision equipment, and Infrared Imaging Systems, for the defense market. He left Simrad Optronics as Deputy Managing Director and joined Norsk Elektro Optikk (NEO) as Technical and Commercial Director in 1992. He has been Managing Director in Norsk Elektro Optikk since 2003. In his positions at NEO he has been responsible for moving Tunable Diode Laser Spectroscopy from the first laboratory experiments in the early 90ties into a successful business venture in Gas Analysis with more than 5000 TDL Gas Analyzers installed in more than 40 countries around the world. Even if management and commercial issues dominate he is a physicist by heart and is still actively involved in NEO's research activities.

TECHNICAL ABSTRACT

Near infrared tunable diode laser absorption spectroscopy (NIR-TDLAS) has been accepted by industrial users as the best available technology for in-situ emission and process control measurements. However, for some important gases the absorption line strengths and thus the sensitivities are too low (e.g. nitric oxide, NO) or the species does not possess any absorption features in the NIR (e.g. sulfur dioxide, SO_2). The fundamental absorption bands in the mid-infrared spectral region (MIR) are orders of magnitude stronger than the overtone and combination bands in the near infrared. For example, the best absorption line in the 5.2 µm-band of nitric oxide is approx. 750 times stronger than the best line in the 1.8 µm-band (using telecom diode lasers).

In this paper an example of an important industrial application for a NO measurement and a solution using a quantum cascade laser (QCL) in a TDLAS gas monitor will be presented.

In most combustion processes the emission of nitric oxide into ambient air has to be limited due to environmental protection regulations (e.g. by US EPA or Bundesumweltamt (Germany)). A so called "deNOx process" is used to reduce the NO concentration in a gas mixture. In this process either gaseous ammonia (NH_3) or ammonia-water is used to convert NO and NH_3 into water vapor (H_2O) and nitrogen (N_2). The amount of ammonia depends on the NO content of the process gas. Especially in a dynamic process where the fuel or the fuel composition changes rapidly the variation of the NO concentration can be quite high. To regulate the deNOx process and thus the amount of ammonia added to the process gas the NO content has to measured in-situ, very accurately, and with a fast time response early in the gas cleaning process. Since the measurement point can be very close to the process the gas temperature can be still very high (up to 400 °C). Typical nitric oxide concentrations are in the low ppm range so that the lower detection limit (LDL) of NO instruments used for the regulation should be around 1 ppm·m at 400 °C.

State-of-the-art NIR laser spectrometers allow measurements of only around 10 ppm·m at 300 °C due to weak absorption line strengths in the NIR and strong water vapor interference at higher gas temperatures. Therefore NIR gas monitors are in general not suitable for this application. As described above in the MIR the line strength is significantly stronger. Software simulations based on HITRAN [1] and HITEMP [2] databases have led to selection of interference-free NO absorption lines in a typical industrial incinerator process gas mixture. Therefore a spectrometer using a mid-infrared laser source has a high potential to meet the LDL required for a deNOx regulation while having no interference from other gases in the process.

*peter@neo.no; phone +47 6797 4700; www.neo.no

During the last decade especially the development of quantum cascade lasers has experienced as vast progress and nowadays they are the preferred laser source for MIR spectrometers for industrial applications. In cooperation with Corning, Inc a quantum cascade laser chip for one of the selected absorption lines in the 5.2-µm band of NO has been prepared. The QCL is mounted into a HHL package. A low electrical power consumption [3] and a proper thermal electric cooler (TEC) allow room-temperature laser operation at ambient temperatures up to 55 °C. The same noise reduction measures as described in [4] have been applied to the HHL package.

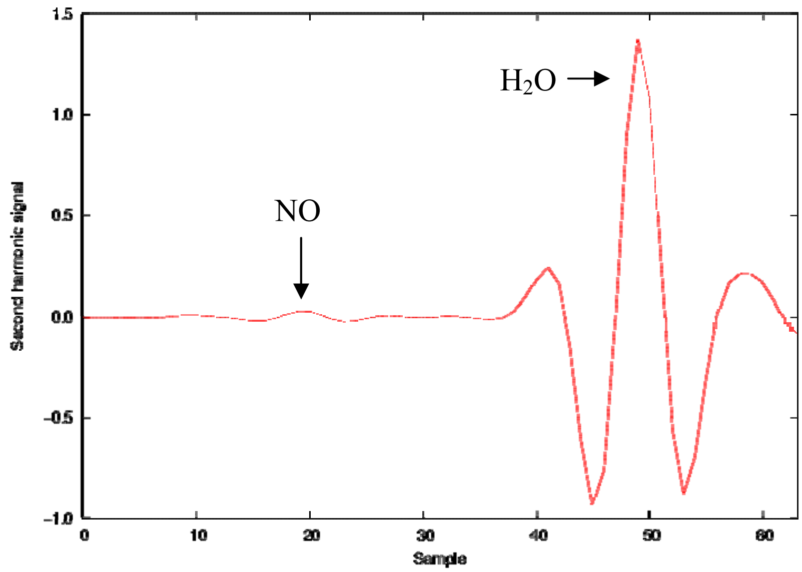

Figure 1 Second harmonic spectrum of 10 ppm NO, 20 % H_2O, and 20 % CO_2 (T = 400 °C, p = 1atm, L = 0.7m).

The QCL was implemented into a spectrometer setup and mounted onto a heated cell (optical path length L = 0.7 m; gas-temperature $T_{gas} \leq 400$ °C). Tests at 400 °C have successfully been performed and showed good agreement with the simulations. Figure 1 shows a second harmonic spectrum of 10 ppm NO, 20% H_2O, and 20 % carbon dioxide (CO_2; not visible, but has an influence on the line broadening of NO).

The sensitivity of the spectrometer has been determined to be around $2.5 \cdot 10^{-4}$ [rel. abs.] which leads to a lower detection limit of better than 1 ppm·m at 400 °C. The measurement is interference-free from water-vapor concentrations up to 30 % at an optical path length of 2 m. Other gases like ammonia (NH_3), methane (CH_4), or nitrous oxide (N_2O) at typical combustion concentration levels do not influence the NO measurement. Field tests at an industrial facility are planned and results will be presented.

[1] L.S. Rothman, I.E. Gordon, A. Barbe, D.C. Benner, P.F. Bernath, M. Birk, et al, "The HITRAN 2008 molecular spectroscopic database", J QUANT SPECTROSC RA 110, 533-572 (2009)

[2] L.S. Rothman, I.E. Gordon, R.J. Barber, H. Dothe, R.R. Gamache, A. Goldman, V. Perevalov, S.A. Tashkun, J. Tennyson, "HITEMP, the high-temperature molecular spectroscopic database", J QUANT SPECTROSC RA 111, 2139-2150 (2010)

[3] F. Xie, C. Caneu, H.P. LeBlanc, S. Coleman, L.C. Hughes, C. Zah, "Continuous wave operation of distributed feedback quantum cascade lasers with low threshold voltage and low power consumption", Proc. Of SPIE Vol. 8277 (2012)

[4] P. Geiser, D. Dang, A. Bohman, P. Kaspersen, "Mid-infrared Sulfur Dioxide Measurements at Elevated Temperatures for Emission Control", Laser Applications to Chemical, Security and Environmental Analysis, San Diego, USA (2012)

Keywords: Quantum cascade laser, tunable laser absorption spectroscopy, industrial applications