# Mid-Infrared semiconductor laser based trace gas sensor technologies and applications: state-of-the-art and grand challenges

F.K.Tittel[1] ✉, R. Lewicki[1,4], M. Jahjah[1], P. Stefański[1,3], J. Tarka[1,3], W. Jiang[1], J. Zhang[1,6], L. Gong[2], R. Griffin[2], S. So[4], D. Thomazy[4], P. Lane[5], R. Talbot[5]

[1]Rice University, Electrical & Computer Engineering Department, Houston, TX 77005, USA
[2]Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005, USA
[3]Wroclaw University of Technology, Laser & Fiber Electronics Group, Wrocław, Poland
[4]Sentinel Photonics, Monmouth Junction, NJ 08852, USA
[5]University of Houston, Department of Earth & Atmospheric Sciences, Houston, TX 77204, USA
[6]Northeast Forestry University, Department of Electrochemical Engineering, Harbin, P.R. China

✉ fkt@rice.edu

This talk will focus on recent advances in the development of sensors based on infrared semiconductor lasers for the detection, quantification and monitoring of trace gas species and their applications in atmospheric chemistry and industrial process control. The development of compact trace gas sensors, in particular based on quantum cascade (QC), interband cascade (IC) lasers, as well as traditional laser diodes permit the targeting of strong fundamental rotational-vibrational transitions in the mid-infrared, that are one to two orders of magnitude more intense than overtone transitions in the near infrared.

The architecture and performance of four sensitive, selective and real-time gas sensor systems based on mid-infrared semiconductor lasers will be described [1]. High detection sensitivity at ppbv and sub-ppbv concentration levels requires sensitivity enhancement schemes such as tunable laser diode absorption spectroscopy (TDLAS) [2, 3] and wavelength modulation spectroscopy (WMS), photo-acoustic absorption spectroscopy (PAS) or quartz-enhanced-PAS (QEPAS) [2–4]. These spectroscopic methods can achieve minimum detectable absorption losses in the range from $10^{-8}$ to $10^{-11}$ $cm^{-1}Hz^{-1/2}$.

TDLAS was performed using an ultra-compact, innovative multi-pass gas cell with an effective optical path length of 57.6 m capable of 459 passes between two spherical mirrors separated by 12.5 cm. A 3.36-μm continuous wave (CW) thermoelectrically cooled (TEC), distributed feedback (DFB) GaSb based laser diode operating at 9.5°C was used as the excitation source. For an interference-free $C_2H_6$ absorption line located at 2976.8 $cm^{-1}$, a minimum detection limit of 130 pptv with a 1-s acquisition time was achieved. A new state-of-the-art integrated electronic control and data acquisition module was implemented that allowed further significant size reduction without loss of sensor performance.

A QEPAS-based sensor capable of ppbv level detection of CO, a major air pollutant, was developed. We used a 4.61-μm high power CW DFB QCL that emits a maximum optical power of more than 1W in a CW operating mode. For the R6 CO line, located at 2169.2 $cm^{-1}$, a noise-equivalent sensitivity (NES, 1σ) of 2 ppbv was achieved at atmospheric pressure with a 1-s acquisition time. Furthermore, high performance (> 100 mW) 5.26 μm and 7.24 μm CW TEC DFB-QCL (mounted in a high heat load (HHL) package)-based QEPAS sensors for atmospheric NO and $SO_2$ detection will be reported. Minimum detection limits (1σ) of 3 ppb and 100 ppb were achieved for a sampling time of 1 s using interference-free NO and $SO_2$ absorption lines located at 1900.08 $cm^{-1}$

and 1380.94 $cm^{-1}$, respectively [1]. Specific examples include $C_2H_6$, $NH_3$, NO, CO, $SO_2$, $CH_4$, and $N_2O$.


[1] Rice University Laser Science Group website: http://ece.rice.edu/lasersci/
[2] R. Lewicki, J. Doty, R.F. Curl, F.K. Tittel and G. Wysocki, Proc. of the National Academy of Sciences: 106, 12587-12592 (2009)
[3] R.F. Curl, F. Capasso, C. Gmachl, A. A. Kosterev, J. B. McManus, R. Lewicki, M. Pusharsky, G. Wysocki, F.K. Tittel, Chem. Phys. Lett., 487, 1 (2010)
[4] L. Dong, A.A. Kosterev, D. Thomazy, F.K. Tittel, Appl. Phys. B 100, 627–635 (2010)


## Determination of the singlet oxygen generation efficiency of dyes by applying absorption and optoacoustic spectroscopies


M. Kotkowiak[1] ✉, E. Robak[1,2], A. Dudkowiak[1]

[1]Faculty of Technical Physics, Poznan University of Technology, Nieszawska 13A, 60-965 Poznań, Poland
[2]Nanobiomedical Centre, Umultowska 85, 61-614 Poznań, Poland

✉ michal.kotkowiak@doctorate.put.poznan.pl


Photodynamic therapy (PDT) has recently become widely used in clinical treatment of different types of diseases. In PDT, absorption of light by a dye leads to generation of an reactive forms of oxygen. Mechanism of PDT involves two types of reactions – direct interaction of the sensitizer in the triplet state with cell tissues (photochemical reaction) – I type reaction and production of the singlet oxygen ($^1O_2$) – II type reaction [1]. One of the most important features characterizing dye-photosensitizer is the singlet oxygen quantum yield ($\varphi_\Delta$). The $\varphi_\Delta$ value is a quantitative parameter which describes the ability of photosensitizers to convert and transfer absorbed energy to molecular oxygen to form the singlet oxygen, $O_2$ ($^1\Delta_g$), acting as a cytotoxic species.

This study was focused on comparing of two independent methods for $\varphi_\Delta$ determination of photo-active dye molecules. The first method was the time resolved laser-induced optoacoustics spectroscopy (LIOAS). It provides information on the non-radiative fast deactivation of excited singlet states and depopulation of the long-lived states of the dye. Finally, depending on experimental conditions, the analysis of LIOAS signal permits estimation of the yield of dye triplet formation and reactive oxygen species generation [1]. The second method of $\varphi_\Delta$ estimation is based on the photooxidation reaction of 1,3-diphenylisobenzofuran (DPBF) well-known as $^1O_2$ trap [3]. The dye irradiated with light of a specific wavelength interacts with molecular oxygen, which leads to generation of singlet oxygen. As a result of interaction with $^1O_2$, DPBF decomposes to 1,2-dibenzoylbenzene which results in a decrease in absorbance (at 417 nm).

For both methods, the choice of reference dyes is crucial, therefore a comparison of independently obtained results was made. The results presented show that the methods allow a reliable