New sensing approaches employing QCLs

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Introduction

Advances in Analytical Chemistry are often linked to technological developments in neighboring disciplines. This also concerns the recent development of quantum cascade lasers, which allows realization of sensing approaches in the mid-IR range that are different and potentially more powerful compared to classical absorption measurements based on Lambert-Beer law. This presentation will focus on recent work in the field of gas sensing reporting on advances in Photothermal Interferometry (PTI) and Heterodyne Phase Sensitive Dispersion Spectroscopy (HPSDS). It will also report on recent advances in liquid phase spectroscopy.

1. Photothermal Interferometry for trace gas sensing in small sample volumes

In PTI modulated absorption of the analyte produces a modulated change in the refractive index of the sample gas due to sample heating [1]. The proposed set-up uses the cavity of a NIR Fabry Pérot (FP) interferometer as gas cell. The gas sample is excited using a DFB-QCL operated in the 2*f*-WM mode. The change in the refractive index of the sample produces a change in the transmission curve of the FP interferometer which is probed using a NIR laser. This sensing concept is advantageous compared to photoacoustic (PA) detection which senses an acoustic wave that also results from modulated sample heating. In PTI the modulation frequency for sample excitation can be freely chosen, thus reducing matrix interference as result of changing V-T relaxation times due to changes in the matrix content (e.g. water vapor). In PTI and similar to PA it is also possible to realize small sample volumes which allows for miniature and fast responding gas sensors.



Fig. 1: Schematic of the experimental set-up used for SO₂ sensing using PTI

Using an excitation laser at 7.25 μ m, reflectivities of the FP mirrors of 85% and an optical power of 180 mW as well as a fiber-coupled CW-DFB-LD (NTT Electronics) probe laser at 1600 nm it was possible to detect SO₂ in nitrogen with a LOD of 1 ppm (1 σ , 1s).



Fig. 2: a) PTI spectra of SO₂ recorded by applying the 2*f*-WMS technique. b) Linear calibration curve for SO₂ in nitrogen.

2. Heterodyne Phase Sensitive Dispersion Spectroscopy (HPSDS)

In gas analysis based on molecular dispersion spectroscopy the characteristics of the sample are retrieved from the measurement of the refractive index profile in the vicinity of molecular resonances. This approach provides inherent immunity to power fluctuations and an output that is linearly dependent on gas concentration. Here we show HPSDS based on a directly modulated DFB-QCL laser for CO sensing. The set-up is characterized by a very simple architecture in which data processing and concentration retrieval are straightforward [2].



Fig. 2: Direct modulation of the employed DFB-QCL produces a three tone signal which, after passing the gas cell, impinges on the detector allowing extracting the phase which is proportional to the gas concentration.

References

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- [2] P. Martín-Mateos, J. Hayden, P. Acedo, B. Lendl "Heterodyne Phase Sensitive Dispersion Spectroscopy in the Mid-Infrared with a Quantum Cascade Laser" Anal. Chem., 89 5916 (2017)