

Wavelength modulation spectroscopy for multicomponent analytics of biomass burning tracers

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ABSTRACT

The potential of Tunable Diode Laser Absorption Spectroscopy (TDLAS) for monitoring of several species produced by biomass burning is in focus of this work. The infrared spectra of selected molecules (HCOOH, C₂H₂, CH₃CN, N₂O, CH₃OH, CH₃COCH₃) are measured in laboratory conditions and the selectivity and of this method is demonstrated.

INTRODUCTION

More frequent occurrence of extreme wildfires and uncontrolled biomass burning episodes can be expected in the near and distant future [1]. Oxidative pyrolysis of biomass generates a large number of intermediates (CO₂, CO, CH₄, N₂O, CH₃CN) [2][3] and particles that can directly or indirectly influence air quality, climate, and deviation from global atmospheric chemistry. The chemical composition of fire plumes is source specific; however the quantitative measurement of biomass emissions and distinguishing it from other sources (i.e. chemical background, traffic pollution) is still challenging. Scientists mainly rely on laboratory and field measurement and satellite data in combination with various models, taking into account the transportation phenomena and chemical aging [4]. Ground and aircraft sampling is typically main source of information [5]. A compact chemical analyzer capable of in-situ, real-time monitoring is needed to understand the complex behavior of biomass burning products in the atmosphere.

Tunable diode absorption spectroscopy based sensor is a potential candidate [6]. TDLAS is well established spectroscopic method. Its main advantages are high sensitivity, fast response, simplicity of design and operation, nonintrusive measurement and low cost operation. The measured narrow absorption lines (i.e., intensity and spectral position) are like a fingerprint of a species. It is possible to measure trace amounts of gases, down to ppm level in the near infrared (NIR) region with weak overtone and combinational bands and down to ppb levels in mid infrared (MIR) region, where QCL lasers with power in the order of tens of milliwatts are available and many species have strongly absorbing fundamental vibrational bands [7]. Moreover, it is often possible to selectively measure several different species with single laser diode. The laser diodes have typically narrow emission lines allowing measuring narrow discriminated ro-vibrational bands of absorbing species. It is possible to integrate the tuning laser diodes into autonomous calibration free sensors.

EXPERIMENTAL

The measurement setup is on Fig 1. The QCL laser diode is installed in laser mount with temperature stabilization (Arroyo 242) and is controlled by a laser diode current and temperature controller (ITC4005QCL, Thorlabs). Several QCL diodes were used (QD8650CM1, QD9550CM1, QD10600CM1AS, Thorlabs). The temperature was set at 25 °C. The diode was modulated externally by a slow ramp (1 mA/1s) superimposed with rapid sinusoid (1.5 kHz) with small amplitude, generated by function generator (EZ digital FG7005C). The laser beam is passed through a 50 cm cell with sample gases and focused on HgCdTe (Graseby Infrared) detector with preamplifier. The preamplified signal from the detector is processed by a lock-in amplifier (RS 830 DSP, Stanford Research Systems) at second harmonic, converted to digital signal and further processed by PC.

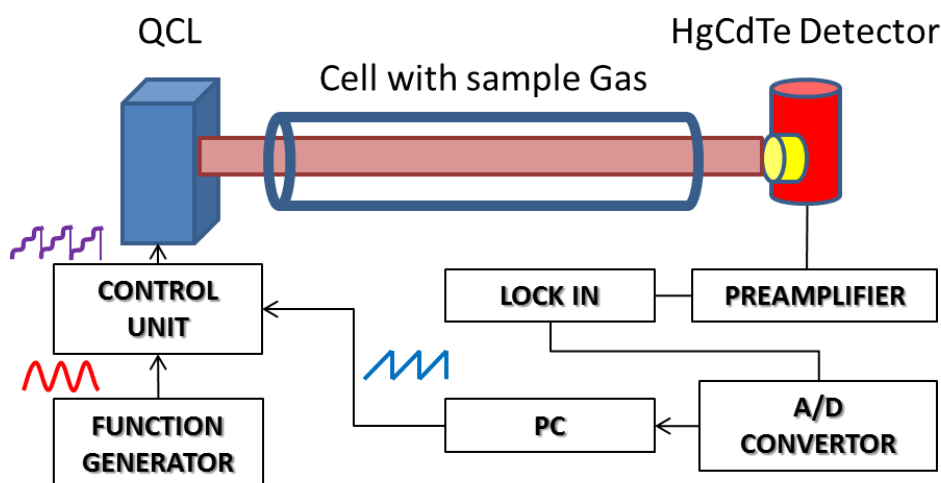


Fig. 1: The basic experimental TDLAS scheme with QCL used as an excitation source modulated by a composite signal (sinusoidal + asymmetric triangle). The IR intensity is sensed by a sensitive HgCdTe detector, the measured signal is then processed by a Lock-in amplifier and recorded by a PC. Cell length is 50 cm.

RESULTS AND DISCUSSION

The tunable diodes are typically used for wavelength modulation spectroscopy (WMS). A slow spectral scan is done by modulating the laser diode by slow current ramp. A small and fast sinusoidal signal (typically in the kHz range) is superimposed on the slow ramp. The laser beam which passed the sample is focused onto a detector and the signal from the detector is processed by a phase sensitive amplifier (lock-in amplifier). The amplifier can detect n^{th} harmonic component of the signal (proportional to the n^{th} derivative of the spectra). In practice, the second harmonic component is used for measurement (“ $2f$ ” signal).

The TDLAS method requires a relatively long absorption path for sensitive detection and a sensitive liquid nitrogen-cooled detector (in the MIR area), which makes it difficult to use this method for field measurements. These deficiencies can be remedied by using quartz enhanced photoacoustic spectroscopy (QEPAS). The acoustic signal generated by the ro-vibrational relaxation of molecules due to the modulated IR laser radiation is detected by a quartz tuning fork (QTF) with a high quality factor[8].

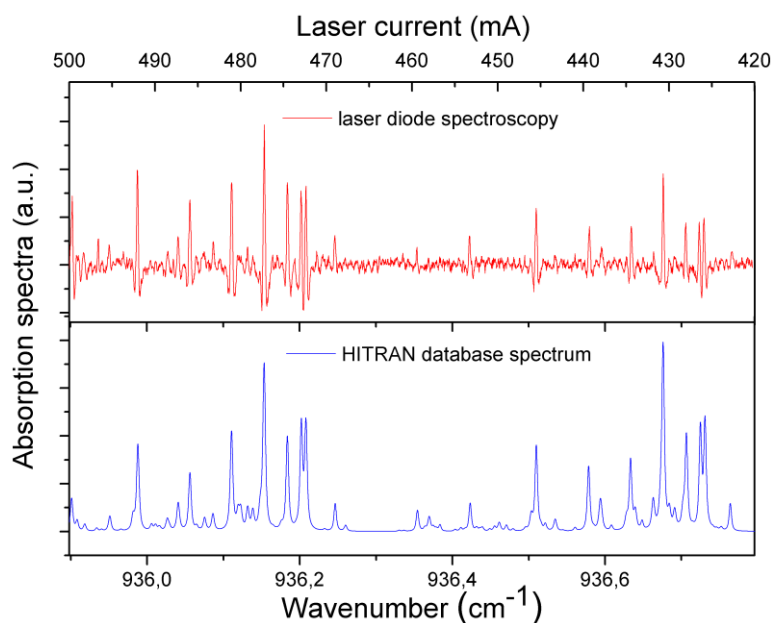


Fig. 2 : The measured spectral line(2f) using acetonitrile TDLAS (red line) with QCL wavenumber of about 936 cm^{-1} . QCL tuning current from 420 mA to 500 mA, QCL temperature stabilized at 25 °C. Cell length 50 cm, pressure CH_3CN 1 torr, temperature 25 °C. Simulated spectrum (direct absorption) CH_3CN from the HITRAN (blue line) database with the same input parameters.

Many molecules of interests have strong absorption lines in the MIR spectral range. Besides carbon dioxide, which is the main product of combustion, CH_3CN is a major marker of biomass combustion. Several spectral lines associated with the R-branch of the fundamental ν_4 band acetonitrile were measured (Fig. 2). Simulated data based on HITRAN database [9] (Fig. 2, bottom) are compared with measured spectrum. Typical 2f profiles can be seen (Fig. 2, top).

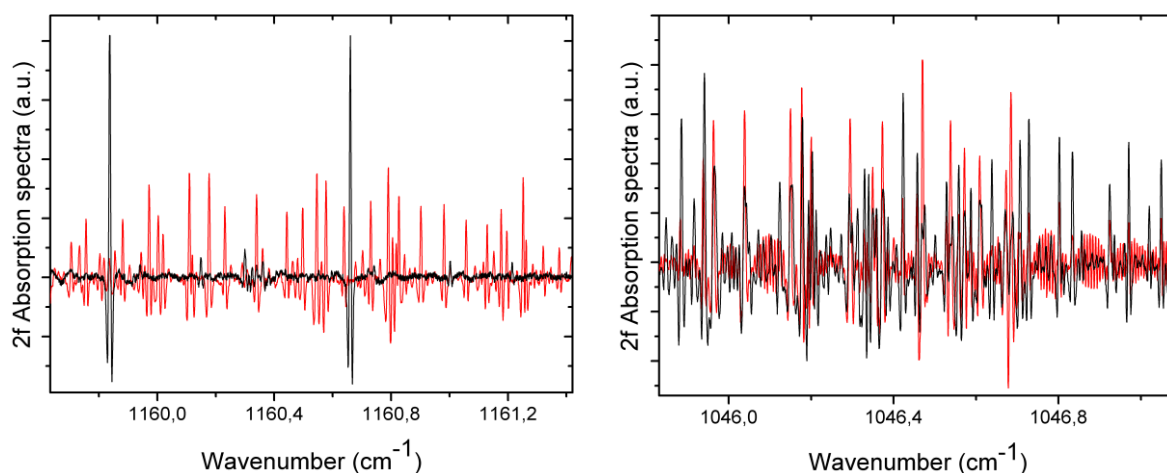


Fig. 3 : Left: Spectra of HCOOH (red line, 5 Torr, 40 °C) and N_2O (black line, 5 Torr, 40 °C) Right: Spectra of methanol (black line, 5 Torr, 25 °C) and acetone (red line, 5 Torr, 25 °C)

The selectivity of TDLAS method is demonstrated on Fig. 3. The narrow spectral lines of N_2O and HCOOH (Fig. 3, left) can be easily distinguished and the multicomponent analysis for this case is straightforward. In such case, ratio of two absorption lines (one of N_2O and one of HCOOH) provide information about mixing ratios of these substances (for calibrated instrument). This represents an ideal case, which in reality cannot always be

achieved. The shape of the lines depends on experimental conditions and is a function of temperature and pressure. The pressure broadening can lead to overlapping of closely situated lines in the spectrum. In laboratory, achieving low pressures on the Torr level is not a problem, but for portable analyzer/node of sensor network, measurement in higher pressures is assumed. For the case of overlapped lines, mathematical treatment of the spectrum is required. This is also the case for methanol and acetone spectra (Fig. 3, right). Methanol and acetone were found in aged biomass burning plumes [10] Both acetone and methanol spectra carry a lot of analytical information in this spectral region; most of the spectral lines however overlap. Commonly used methods are classical least-squares, inverse least squares and partial least squares methods.

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