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Towards a TDLAS based optical gas standard for the absolute HCl measurements in flue gases from combustion process

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Abstract

We present our new dTDLAS based HCl spectrometer, specially designed and optimized to measure traceable HCl concentration in different matrices (high temperature, high water vapor and CO₂ contents) motivated by large-scale power stations or biomass burning domestic boilers. This system is designed to serve as an optical gas standard (OGS) and thus as a traceable transfer standard to directly quantify HCl emissions or calibrate HCl sensors or dynamically generated gas standards in the field. It employs a mid-infrared interband cascade laser (ICL) and is targeting the HCl transition lines in the fundamental band to achieve less 1 ppm (at 1 meter) sensitivity and meet the compatibility goal set by lowered HCl ELVs in the European legislation such as the Industrial Emissions Directive (IED).

Introduction

Laser spectrometers for combustion applications are European Directives are coming into force setting increasingly stringent Emission Limit Values (ELVs) for regulating emissions from e.g. combustion processes. In the EU, HCl emissions from the industry are covered by Industrial Emissions Directive 2010/75/EU. The EMPIR project IMPRESS2 [1] is carrying out technical development work as well as underpinning spectroscopy in support of monitoring and enforcing Emission Limit Values (ELVs) in future European legislation for key air pollutants and regulating emissions. The project addresses current technological obstacles to enhance the control of emissions thus supporting industry and regulators as well as new CEN/ISO standards.

Optical methods offer promising tools to investigate the dynamic release of molecular species from combustion environments. One of the most widely used optical technique to meet the high sensitivity, online and in situ requirements is laser-based absorption spectroscopy, in particular tunable diode laser absorption spectroscopy (TDLAS), which is frequently applied in combustion research and industry for the determination of species concentrations [2, 3]. *Direct* tunable diode laser absorption spectroscopy (dTDLAS) is a variant of TDLAS which combines this spectroscopic technique with a special, first principles approach to yield traceable absolute gas species concentrations. Therefore, dTDLAS can be implemented as an optical gas standard (OGS), which is used to perform absolute, traceable amount-of-substance fraction measurements in gas mixtures without prior calibration of the

instrument response using a calibration gas [4, 5, 6]. Here, we present our new OGS TDLAS-based HCl spectrometer. The system combines a Mid-IR ICL with a single pass cell and takes advantage of the selected absorption line having a stronger line strength and less/hardly any CO₂/H₂O interference.

Laser spectrometers for combustion applications are frequently implanted as sampling-free cross-stack open-path sensors to avoid systematic errors caused by sampling artefacts. This benefit comes at the price of a new problem, caused by spatial heterogeneities in the cross-stack configuration. In particular gas temperature variation along the (entire!) line-of-sight of the spectrometer need to be carefully considered [7]. In addition to a previous case study for CO₂-detection, we have extended our work to CO-TDLAS and are working on the application of our principles to the HCl spectrometer. Key points of our research are a better understanding of the spatial temperature variations and their implications for the absolute accuracy of the dTDLAS spectrometers. We also discuss the thermal boundary layer effects on HCl concentration measurement and provide a method for quantifying the effects.

Method

In TDLAS, the wavelength λ of a tunable laser is rapidly scanned across a narrow region of the optical spectrum covering one or several electronic, vibrational or rotational-vibrational absorption lines. The intensity of the laser light, $I(\lambda)$, focused onto a photodetector after passing the sample with absorbers can be described by the extended Lambert-Beer law according to

$$I(\lambda) = E(t) + I_0(\lambda) \cdot T(t) \cdot \exp[-S(T) \cdot g(\lambda - \lambda_0) \cdot n \cdot L] \quad (1)$$

with the background emission $E(t)$ at time t , initial laser intensity $I_0(\lambda)$, and the broadband transmission losses $T(t)$ which are synchronously derived from the individual raw signals and absorption profiles. The exponential term embraces the absorption line strength $S(T)$ at gas temperature T , the normalised (area=1) line shape function $g(\lambda-\lambda_0)$ (centred at the wavelength λ_0), the absorber number density n and the optical path length L . By combining Eq (1) and the ideal gas law, the gas concentration (amount fraction) x is

$$x = \frac{k_B \cdot T}{S(T) \cdot L \cdot p_{total}} \int \ln\left(\frac{I(\lambda) - E(t)}{I_0(\lambda) \cdot Tr(t)}\right) \frac{d\lambda}{dt} dt = \frac{k_B \cdot T \cdot A_{line}}{S(T) \cdot L \cdot p_{total}} \quad (2)$$

where k_B is the Boltzmann constant, p_{total} is the total pressure of the gas sample, and A_{line} is the line area determined by spectral integration of the measured absorption line over the wavenumber axis. $d\lambda/dt$ describes the dynamic wavelength tuning coefficient of the laser, which has to be determined experimentally. This is extracted from the Airy-signal when the laser light is transmitted through an optical etalon. The absolute spectrometric concentration measurements include measurements of gas sample properties and requires the independent measurement of some further quantities, such as optical path length (interaction path length of laser beam with gas sample), laser tuning behavior, etc. In general, the traceability of OGS measurement results requires traceability of all parameters in Eq (2) that enter the calculation of the measurement result.

Setup

A schematic drawing of the experimental setup is shown in Fig. 1. A Mid-IR ICL with output power 2 mW was used to scan across one HCl absorption line in its fundamental band. The laser injection current was supplied by a low-noise driver, which also controlled the diode temperature. The scan was achieved by varying the laser current with a 139.8 Hz triangular wave generated by a function generator. The laser beam was directed through the gas cell and then focused onto a photodetector. The detector signal was sampled at 600 kHz. Gas temperature and pressure inside the gas cell are continuously measured.

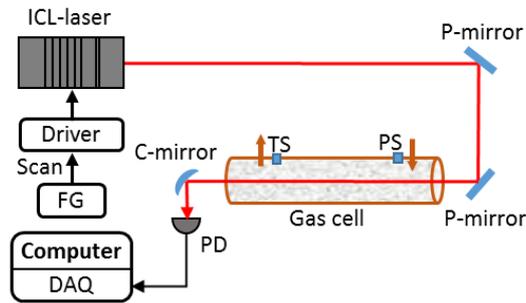


Figure 1: Schematic drawing of the experimental TDLAS setup, PS: pressure sensor, TS: temperature sensor, PD: photodetector, FG: function generator, DQA: data acquisition card, C-mirror: concave mirror, P-mirror: plane mirror.

Results

The choice of the probed HCl absorption line of the spectrometer and potential optical transfer standard is of central importance, because this choice greatly affects how much measurements may be perturbed by cross-interference from combustion gas constituents like water, CO₂, etc., and how strong changes in pressure and temperature of the probed gas sample will affect the measurement signal. Typical measured absorption profiles with fitted Voigt profiles are shown in Fig. 2, as well as the residuals between the measured data and the fitting function. Two gas samples were measured as shown in Fig. 2 (left: 500 ppm HCl in N₂; right: 100 ppm HCl in CO₂). Figure 2(right) shows there is no cross-interference from CO₂. The residuals can be quantified by the statistical standard deviation of the fitting residual across the scan range, $1\sigma = 1.1 \times 10^{-3}$ (noise equivalent absorption coefficient). It is common to normalize the noise equivalent absorption (1σ) coefficient with respect to the path length (77 cm) and the square root of the temporal bandwidth (0.125 s), which yields in this case $5.1 \times 10^{-5} \text{ cm}^{-1} \text{ Hz}^{-1/2}$.

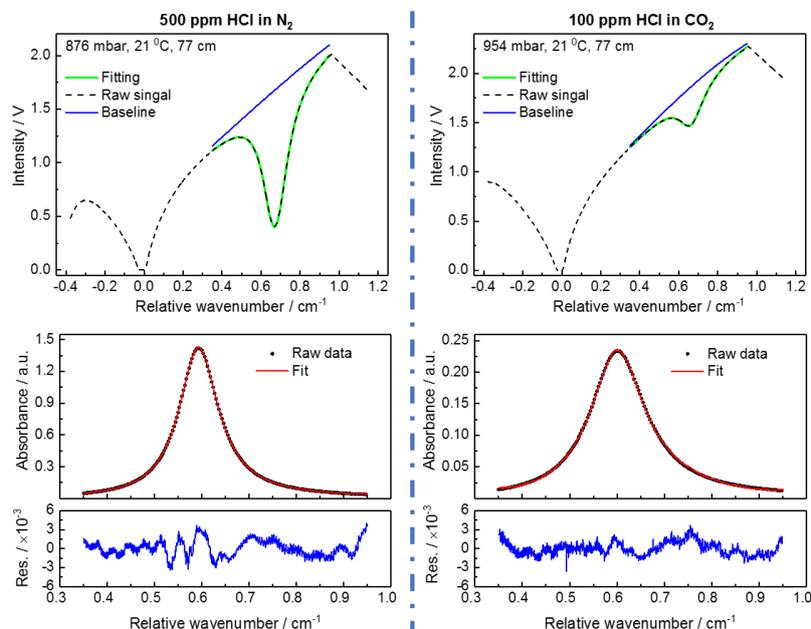


Figure 2: Measured HCl spectra, left: 500 ppm HCl in N₂; right: 100 ppm HCl in CO₂

To quantify the deviation of concentration measurements with the TDLAS technique under conditions with varying temperature along the laser probe path, we consider a two-zone temperature distribution across the line-of-sight (LOS), with cold temperature zone with T_{cold} , and T_{hot} for the high temperature zone, the thickness of the thermal boundary layer is ΔL . To investigate the thermal boundary layer effects, the basic idea is to derive the concentration from a simulated path-integrated spectrum under such conditions [7]. The different calculation temperature in Eq (2), e.g. path-averaged temperature T_{ave} , maximum temperature along

LOS T_{hot} , or minimum temperature along LOS T_{cold} , or mean temperature $(T_{hot}+T_{cold})/2$ skews the measurement results differently as shown Fig. 3. The deviation is defined as the discrepancy between the derived concentration and the initial concentration used to simulate the path-integrated spectrum. Figure 3 (left) shows the simulated deviations of a fixed thermal boundary layer thickness $\Delta L/L = 0.2$ with varying temperature difference ΔT (with fixed $T_{cold} = 300$ K). Different calculation temperature chosen for Eq (2) leads to different concentration deviation. The thermal boundary layer thickness effects on the TDLAS concentration measurements was shown in Fig. 3(right). In dTDLAS applications under non-uniform conditions, the transitions line and calculation temperature should be carefully selected to minimize the deviation. In most real scenarios, the real time in situ path-averaged temperature T_{ave} is unavailable for TDLAS spectral evaluation. It is essential to quantify the systematic deviation of implementing the OGS TDLAS spectrometer under non-uniform conditions.

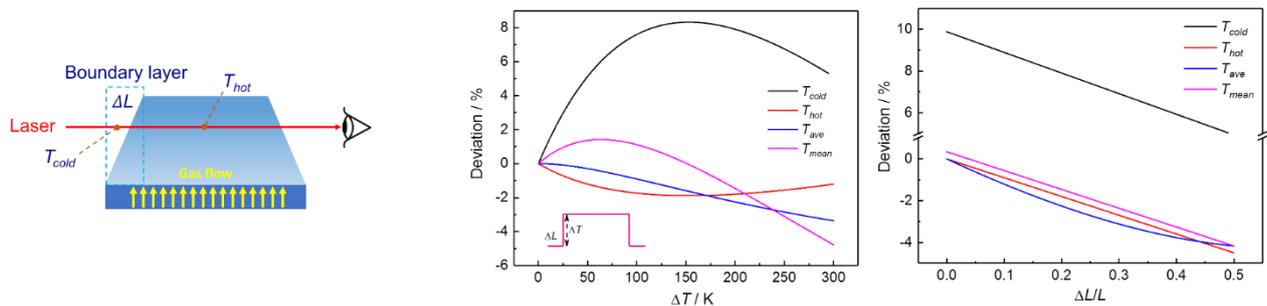


Figure 3: Left - schematic drawing of a two-zone temperature distribution across the flue gases from combustion process, thermal boundary thickness ΔL ; Middle: simulated concentration with different calculation temperatures for a fixed boundary layer thickness; Right: simulated concentration deviations for different calculation temperatures with different boundary layer thickness

Conclusions

Successful delivery of our newly developed HCl spectrometer will result in the development of measurement and monitoring technologies for HCl, methodologies and guidance to support industry and regulators. Our simulation method will also facilitate further investigation of the performance (e.g. systematic deviations) of commercial TDLAS instruments used in conditions with temperature gradients.

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