Mid-infrared laser sensors for mapping environment and combustions

Wolfgang Schade[1)], Ulrike Willer[1)] and Lothar Wondraczek[2)]
[1)]Institut für Physik und Physikalische Technologien, TU Clausthal, Germany
[2)]Institut für Nichtmetallische Werkstoffe, TU Clausthal, Germany

1. Introduction

The mid-infrared spectral range (MIR) is very interesting for gas analysis because nearly all molecules have fundamental absorption bands in the range 3 to 10 μm and therefore laser absorption spectroscopy can be used for mapping molecular species with high sensitivity and selectivity. Applications cover 3-D mapping of environmental pollutants by LIDAR, fiber optic laser sensors for the detection of gaseous species in harsh environments such as volcano fumaroles or insitu and online probing of species in industrial combustions such as engines or glass furnaces for active process control. Today several laser systems are available for the MIR spectral region, as there are OPO´s, color center lasers, lead salt diode lasers or very recently quantum cascade lasers [1]. However, even though they exhibit excellent spectral characteristics these lasers need cryogenic cooling or the laser operation is limited to specific wavelength regions (refer to Fig. 1). Very often the spectral range around 5 μm is not covered by these lasers which on the other hand is of fundamental interest for applications in process control since carbon monoxide (CO) and nitrogen monoxide (NO) have fundamental absorption lines at 4.9 and 5.1 μm, respectively.

Therefore, difference-frequency generation (DFG) is an important alternative method for the generation of narrow-bandwidth MIR-laser radiation with wide tunability [2]. Typically diode lasers in combination with Yb or Er fiber amplifiers are used as pump and signal lasers for the nonlinear process. MIR-DFG quasi-phase matching in periodically poled $LiNbO_3$ (PPLN) has recently been used to obtain MIR output powers of several mW. However, the transparency of $LiNbO_3$ is limited to about 4 μm and therefore these MIR lasers cannot be used for the detection of CO and NO. $AgGaS_2$ is another nonlinear material that frequently is used for DFG with a nonlinear coefficient $d_{36} \equiv 12$ pm/V (for comparison PPLN: $d_{33} \equiv 27$ pm/V).

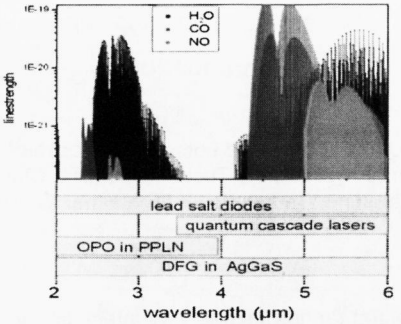

Fig. 1: Absorption bands of H_2O, CO and NO and corresponding wavelength range of different MIR-lasers.

When applying two diode lasers as pump and signal sources and $AgGaS_2$ narrow bandwidth and tunable mid-infrared laser radiation was generated between 3.8 and 11 μm [3]. The typical output power of such a MIR laser system reaches up to several hundred nW. In the past these laser systems in combination with absorption or evanescent field laser spectroscopy have been used to detect CO, NO, CH_4, SO_2, CO_2, H_2O, N_2O down to ppb concentrations and typical applications are environmental monitoring of pollutants, volcano gas detection and industrial process control.

2. MIR-DFG laser spectrometer

The setup for a MIR-DFG laser spectrometer as it is used in field experiments is shown in Fig. 2. The signal and pump beams are generated by two single-mode diode lasers or a combination of a passively Q-switched Cr^{4+}:Nd:YAG microchip laser (1064 nm) and a near-infrared diode laser. The nonlinear material for DFG is PPLN or $AgGaS_2$. Typical pump powers are 20 and 100 mW which gives about 0.1 μW MIR radiation at 5 μm.

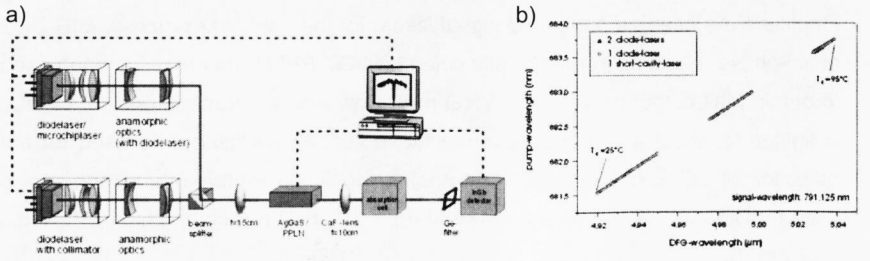

Fig. 2: (a) Setup of the MIR-DFG laser spectrometer. (b) Spectral tunability of the MIR-DFG laser.

3. MIR spectroscopy of combustions and environment

3.1 3-D tomography of CO in laminar flames

The determination of accurate and spatially-resolved concentration and temperature profiles of industrial flames and burners is essential to optimize the burner design with respect to improve efficiency and emission characteristics. The application of mid-infrared laser technology and optical tomography is shown to be a non-invasive and extremely sensitive method for mapping 3-D concentration profiles of minority flame species such as CO.

For these measurements two single mode diode lasers operating at 790 and 681 nm with typical output powers of 20 and 30 mW and $AgGaS_2$ as nonlinear medium are used to generate tunable MIR light at 4.92 μm which is in resonance with the P(26) rotational line of carbon monoxide. The typical detection limit of CO for the present setup is determined to be 5 ppm·m. A premixed methane/air flame is created with a flat flame mix burner (McKenna). The burner is operated at a CH_4 flow rate of 1.2 l/min and a premixed CH_4/air ratio of 3:4. The stable region of the flame has a total height of about 60 mm and a diameter of 70 mm at the root. As a reference, absorption measurements for the CO P(26) line are performed in a cell for defined conditions to estimate self-broadening and collisional broadening coefficients.

A typical absorption line of CO (P(26)) in the flame as recorded by the MIR-DFG laser spectrometer is shown in Fig. 3a. Two-dimensional tomographic measurements are done by recording such absorption profiles when rotating the burner in steps of 5° and linear scanning of the flame in 5 mm steps. A three-dimensional concentration profile of the flame is reconstructed by performing such measurements at different heights above the burner surface. The results of these measurements are shown in Fig. 3b.

The absorption of the MIR laser light by the molecules to be analyzed at a pathlength s is given by the Beer-Lambert law:

$$I = I_0 \exp -(S_{nm}(T)\,\Phi(\nu-\nu_0)\,p_x\,s) \qquad (1)$$

Where I is the transmitted intensity, I_0 the initial intensity, S the line strength for absorption at the transition n-m, $\Phi(\nu-\nu_0)$ the frequency depending line shape function and p_x the partial pressure of the species x which is connected to the concentration if the temperature is known. Light scattering is neglected. Analyzing

the absorption profiles by fitting a Voigt profile to the data points results in an information of the concentration of the species x.

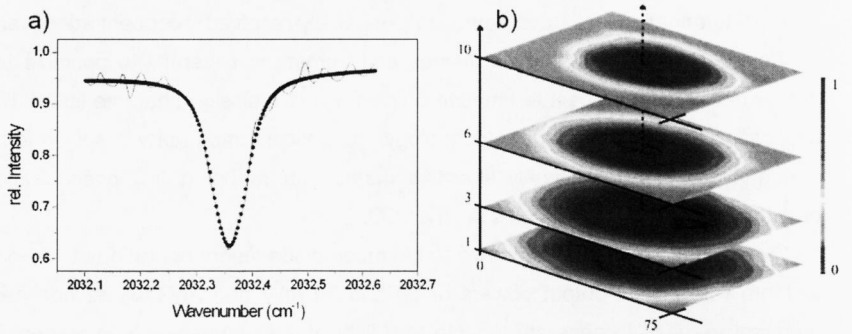

Fig. 3: (a) MIR absorption profile of the CO P(26) rotational line at 4.92 μm as recorded in the CH_4/air flame. (b) Reconstruction of relative CO concentration profiles in the CH_4/air flame of the McKenna flat burner.

3.2 In-situ detection of CO in an industrial glass furnace

For applications of the MIR-DFG laser spectrometer in an industrial environment the laser system and the detector are located in water cooled boxes to protect the optics from dust. In a first experiment, the MIR spectrometer was used to detect the P(26) rotational line of CO in the exhaust channel of a industrial glass melting furnace (FlexMelter, Dr. Genthe GmbH & Co. KG, Goslar). The optical path length was s ≡ 1.5 m and the gas temperature was about 1200 °C. To avoid saturation of the detector by the strong background radiation, a bandpass filter with center wavelength at 4.9 μm and a bandwidth of 0.1 μm was placed in front of the detector. When applying lock-in technique for signal processing a MIR laser power as low as 100 nW can be measured by the InSb detector and separated from the strong thermal background radiation. Because of optical turbulences, i.e. unstable temperature gradients in the gas stream of the melting aggregate, the laser beam is flickering. Therefore the MIR laser spot cannot be imaged stable on the detector which results in an additional noise. Also water absorption has to be considered. It causes interferences with the CO lines and a strong H_2O background will reduce the intensity of the transmitted MIR light through the oven. However, the P(26) CO line is separated from water absorption as shown in the calculated spectrum for a temperature T=1425 °C as shown in Fig. 4a. Therefore, even in this harsh, complex and high temperature gas atmosphere a selective CO absorption profile can be

recorded at 4.92 μm. A result for an in-situ glass furnace measurement is shown in Fig. 4b.

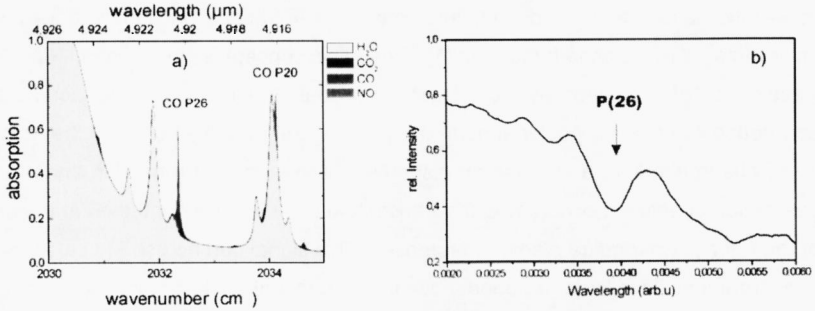

Fig. 4: (a) Calculated H_2O and CO high temperature mid-infrared absorption spectrum. (b) Mid-infrared CO absorption measurements in a exhaust channel of a glass melting furnace at T = 1200 °C.

3.3 Fiber-optic MIR laser sensors

As discussed before, laser absorption spectroscopy requires an open optical path or a one- or multipass absorption cell that contains the gas under investigation. Then laser source and detector are located at opposite sides of the sample volume, also scattering has to be negligible and only optical accessible paths and locations can be used for the diagnostics. Figure 5a shows a sensor concept applying fiber optics and a short open path. In this configuration MIR laser and detector can be located at the same place. Because of the limited optical path length 2-f detection has to be applied for signal processing. This is shown for recording H_2S absorption profiles at 1.57 μm via weak overtone absorption lines and an optical path length of only s ≡ 2 cm (refer to Fig. 5b).

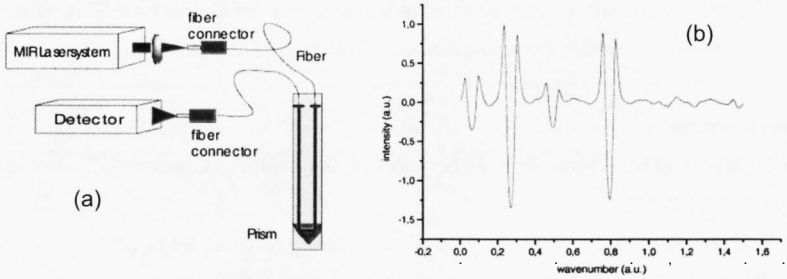

Fig. 5: (a) Fiber-optic open path laser sensor. (b) H_2S rotational line profiles at 1.57 μm detected by 2f-absorption spectroscopy.

As an alternative, evanescent field laser spectroscopy in combination with optical fibers and mid-infrared lasers can be used to create a rugged and miniaturized fiber-optic laser sensor to measure gas concentrations in harsh and toxic environments as volcano fumaroles [4]. The basic concept is shown in Fig. 6a. The wavelength of the laser light propagating through the fiber is tuned across an absorption line of a molecular species surrounding the pure fiber core. In the vicinity of an absorption line, a wavelength dispersion of the index of refraction and of the absorption coefficient occurs and the transmitted laser intensity detected at the end of the fiber or waveguide element decreases. This signal can be used to calculate a concentration. The linear dependency of the transmitted laser linewidth on the concentration of H_2S molecules surrounding the evanescent field fiber sensor is shown in Fig. 6b when tuning the laser in resonance with a H_2S line at 1.57 μm.

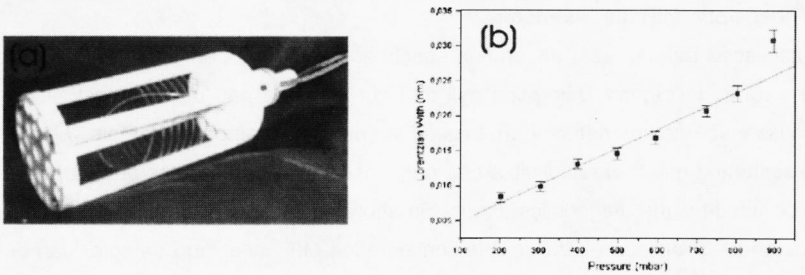

Fig. 6: (a) Evanescent field fiber sensor. (b) Transmitted laser linewidth through the sensor element vs. concentration of H_2S molecules for resonant laser excitation at 1.57 μm.

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