

## MIR-difference-frequency laser spectrometer for CO detection in combustions

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### Abstract

Two continuous-wave (cw) single mode diode-lasers (Toshiba TOLD 9150 and Sharp LT024MDO) are applied as pump and signal sources to obtain difference-frequency generation (DFG) in the mid-infrared (MIR) region by using an AgGaS<sub>2</sub> crystal with a length of 30 mm for 90° type I phase-matching. Tuneable MIR laser radiation around 5 μm is obtained with an output power in the order of hundred nW while the diode lasers are operated at 20 and 30 mW around their centre wavelengths 789 and 681 nm, respectively. To demonstrate the applicability of this MIR-DFG laser spectrometer we recorded the absorption spectrum of CO for the P(21) rotational line at 2055.4 cm<sup>-1</sup> in a 10 cm long cell and in the flame of a McKenna burner in order to estimate the self-broadening coefficient of CO, the collisional-broadening of CO with CO<sub>2</sub>, and the CO concentration distribution in the flame.

**Keywords:** laser, difference-frequency, CO detection, spectrometer

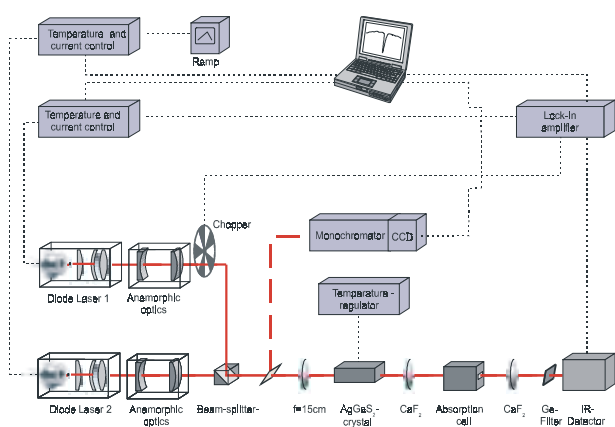
### 1. Introduction

MIR high-resolution spectroscopy of molecular species in the spectral range 2 to 20 μm is of particular interest for fundamental physics as well as environmental diagnosis, since most of the molecules and molecular ions are detectable in this region [1]. These applications require cw high-spectral-purity laser sources. Direct laser spectroscopy in the MIR range is mainly limited by the availability of narrow bandwidth tuneable laser sources [2]. For wavelengths beyond ~ 2 μm typical tuneable laser sources are OPO lasers, colour-centre lasers, and lead salt diode-lasers. Colour-centre lasers operate extremely well with single frequency power levels of up to 100 mW but only limited from 1.1 to 3.5 μm at liquid-nitrogen temperature. Diode and lead salt diode-lasers have a wider covering range but with small tuning range (~ 100 cm<sup>-1</sup>) and also low temperature requirements [3]. The 9-11 μm range is however covered by CO<sub>2</sub> lasers with a limited continuous tuneability. The gain curve of a single-mode low pressure CO<sub>2</sub> laser of 0.8-m discharge length is typically 100 MHz per line. But it is more limiting than the narrow tuneability, which is enough for Doppler-free spectroscopy. The major

drawback of CO<sub>2</sub> laser spectroscopy lies in accidental coincidences between laser lines and the absorbing species of analytical interest, as the typical line-to-line separation is 30 GHz [2]. These limitations result in a restriction of MIR absorption spectroscopy for practical application, e.g., in the trace analysis of environmental pollutants. Therefore, there is still something lacking in simple, compact, portable, and rugged MIR laser sources [4]. Most recently, quantum cascade lasers [5] are also discussed as novel light sources for spectroscopic trace gas detection in the MIR [6]. In this paper difference-frequency generation of two single mode diode-lasers with 20 and 30 mW and a 30 mm long AgGaS<sub>2</sub> crystal with a cut for type I noncritical phase-matching at room temperature are applied to get a very efficient, compact and tuneable all solid state laser system for the MIR spectral region [7]. This MIR diode-laser DFG system offers a lot of interesting applications in the spectroscopic detection for environmental pollutants. One example is given in the present paper, in which the absorption spectra of carbon monoxide in the flame of a McKenna burner are measured and the CO concentration in the flame is determined.

## 2. MIR diode laser DFG system

The schematic diagram of the MIR diode-laser DFG system is shown in figure 1.



**Figure 1.** Experimental set-up of the MIR DFG laser spectrometer.

The signal and pump beams are generated by two cw single mode diode-lasers (Toshiba TOLD 9150 and Sharp LT024MDO) centred at wavelengths 681 and 789 nm, respectively. By accurate setting of temperature and current the tuning ranges of the two diode-lasers are 787-791 nm and 680-682 nm. During a single frequency operation the optimum output powers are  $P_s=20$  mW and  $P_p=30$  mW, respectively. Single mode operation is obtained for specific temperature ranges which are different for each diode-laser. Unfortunately, the mode jump behaviour of the lasers affects and limits the continuous tuneability of the MIR DFG wavelengths. For  $90^\circ$  type I phase-matching in the AgGaS<sub>2</sub> crystal DFG laser radiation is centred at  $4.9 \mu\text{m}$  and it is tuneable from  $4.8$  to  $5.1 \mu\text{m}$  by tuning the temperature of the crystal from  $27^\circ\text{C}$  to  $81^\circ\text{C}$ .

Collimation optics (SK 9650, Schäfer & Kirchhoff) and anamorphic optics (5AN-3-A-05, Schäfer & Kirchhoff) are applied to transform the elliptical beam profiles of the diode-lasers into nearly Gaussian beam shapes.

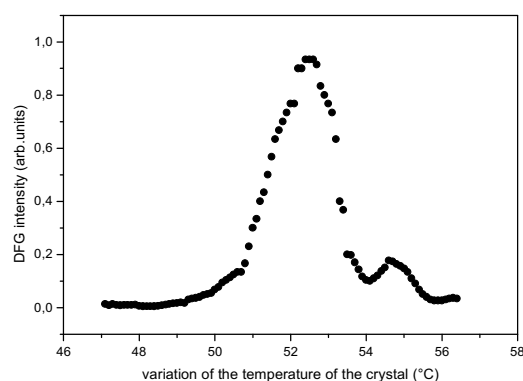
After polarisation adjustment of the two diode-lasers in their housing and spatially overlapping by a polarisation beam splitter cube both lasers are focused into the non-linear crystal by a convex lens ( $f=150$  mm). Behind the crystal the MIR DFG laser radiation is collimated by a CaF<sub>2</sub> lens and detected by a DoroTEK PDI-2IE-5 detector with a voltage responsivity of 1025 V/W. A germanium plate ( $d=1$  mm) in front of the detector is used as a cut off filter for wavelengths  $\lambda < 2 \mu\text{m}$ . The output signal of the IR-detector is directly recorded by a lock-in amplifier while one of the diode-laser beams is chopped.

The intensity of the DFG radiation depends highly on the phase-mismatch value  $\Delta k$  and is given by the following relation [8] :

$$I \propto \left[ \frac{\sin(\Delta k l / 2)}{(\Delta k l / 2)} \right]^2 l^2 \quad (1)$$

where  $l$  is the crystal length.

Figure 2 shows the dependency of the DFG-intensity on the temperature of the crystal. A slight asymmetry observed in the figure is due to the different temperature gradients at both ends of the crystal.

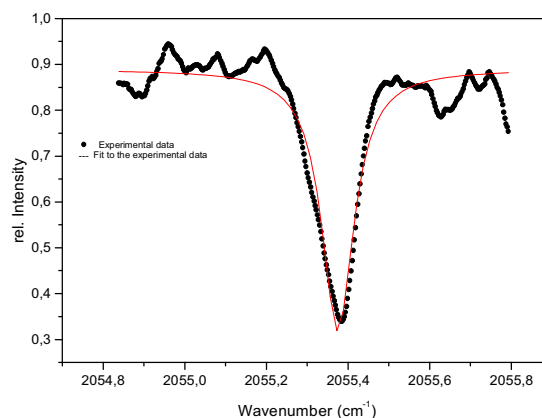


**Figure 2.** Dependence of the DFG-intensity on the variation of the crystal-temperature.

## 3. Spectroscopic results

The performance of the described diode-laser DFG spectrometer is shown as single rotational lines of the carbon monoxide (CO) molecules are probed by absorption spectroscopy. MIR DFG laser radiation scans are obtained by fixing the pump wavelength at  $\lambda_p=680.24$  nm and scanning the signal diode-laser around the centre wavelength  $\lambda_s=790.80$  nm by applying a voltage ramp of  $\Delta U=5$  V.

Figure 3 shows the spectral line shape of the CO P(21) rotational line at  $2055.4 \text{ cm}^{-1}$  for a CO pressure of  $p=540$  mbar measured in the absorption cell ( $L=10$  cm).



**Figure 3.** Absorption spectra of the P(21) rotational line of CO at  $2055.4 \text{ cm}^{-1}$  for  $p_{\text{CO}}=540$  mbar in a 10 cm absorption cell

Phase-matching is obtained by adjusting the temperature of the crystal at  $27.9 \pm 0.2^\circ\text{C}$ .

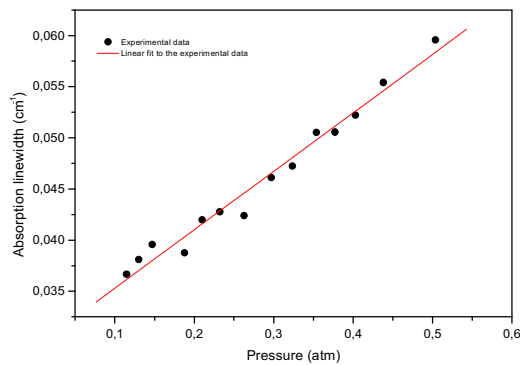
The absorption of the CO P(21) rotational line is recorded for different pressures in the absorption cell. The absorption of light with frequency  $\nu$  and intensity  $I_0(\nu)$  in an absorbing medium with an absorption coefficient  $\alpha$  is given by the Lambert-Beer law:

$$\ln \frac{I(\nu)}{I_0(\nu)} = - \int_0^L \alpha dl \quad (2)$$

where  $I(\nu)$  is the transmitted intensity,  $dl$  is the infinitesimal pathlength of the absorption and  $L$  is the path length of absorption. To relate this equation to quantitative values, the absorption coefficient is written as:

$$\alpha = \frac{1}{L} \ln \left[ \frac{I_0(\nu)}{I(\nu)} \right] = S\phi(\nu - \nu_0)p_{\text{CO}} \quad (3)$$

where  $S$  [ $\text{cm}^{-2} \text{atm}^{-1}$ ] is the intensity of the line at the frequency  $\nu_0$  [ $\text{cm}^{-1}$ ],  $\phi(\nu - \nu_0)$  is a function that describes the line shape with respect to frequency,  $p_{\text{CO}}$  [atm] is the partial pressure of CO in the absorption cell, and  $I(\nu)$  is the transmitted intensity. Fitting a Voigt profile to the experimental data gives values for the Lorentzian widths of the CO absorption line at different pressures. The self-broadening coefficient  $\gamma_{\text{CO-CO}} = 0.0571 \text{ cm}^{-1}/\text{atm}$  for room temperature can be derived by plotting these widths for different pressures as shown in figure 4.

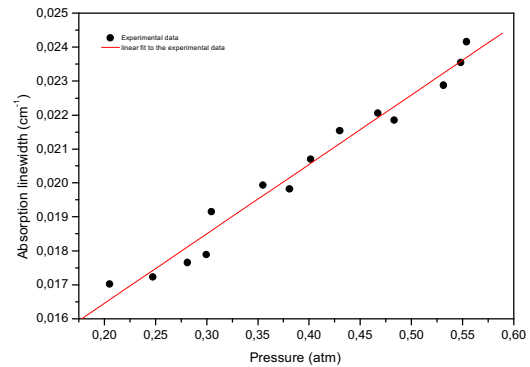


**Figure 4.** Self-broadening coefficient measurement of CO for the P(21) line.

The measured value for  $\gamma_{\text{CO-CO}}$  in this experiment is compared with the corresponding value given by the Hitran 96 database [9]. This value for  $\gamma_{\text{CO-CO}}$  is  $0.0537 \text{ cm}^{-1}\text{atm}^{-1}$ , which is in very good agreement with our measured one. The same data analysis is done to measure the collisional-broadening coefficient of CO by mixing with different  $\text{CO}_2$  pressures and a fixed CO pressure. As shown in Figure 5, the coefficient for collisional-broadening of CO with  $\text{CO}_2$  is  $\gamma_{\text{CO-CO}_2} = 0.020 \text{ cm}^{-1}\text{atm}^{-1}$ .

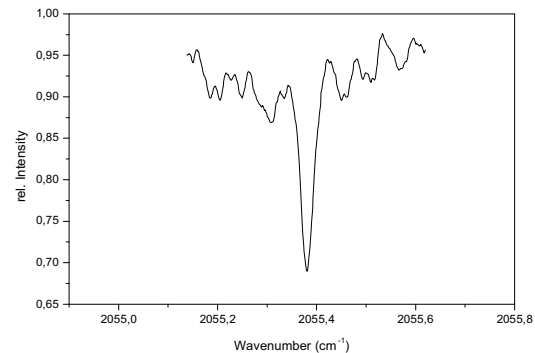
#### 4. Detection of CO P(21) in a methane-air flame and concentration measurements

In order to detect CO in the flame of a methane-air mixture the flat flame McKenna burner [10] is used with a flow rate of 1.5 l/min methane. MIR DFG laser radiation is transmitted through the flame 5 and 10 mm above the surface of the burner. The same detection method as described before is applied to detect the CO absorption profile in the methane-air flame without doping any CO to the flame.



**Figure 5.** Collision-broadening coefficient measurement of CO with  $\text{CO}_2$  for the P(21) line.

An example of a measured absorption line in the flame is shown in figure 6.



**Figure 6.** CO absorption line detected 5 mm above the surface of the flat flame McKenna burner in a methane-air flame with 1.5 l/min methane flow.

The Lorentzian widths are estimated by analysing the measured CO absorption profiles (Voigt profile) in the flame to estimate relative concentrations of CO. These measurements are done for different profiles through the flame with respect to the centre line. The results are shown in figure 7. The symmetry of the flame is disturbed by external airflow to induce inhomogeneities of the CO concentration (refer to positions 1, 2, and 8 in figure 7).

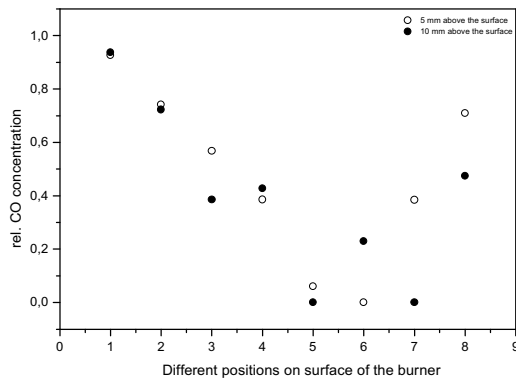


Figure 7. CO concentration at different positions in the flame.

## References

1. U Simon, C E Miller, C C Bradley, R G Hulet, R F Curl and F K Tittel; *Opt. Lett.* **18**, 13 (1993) 1062.
2. C Lee, T Kaing and J J Zondy; *Appl. Phys. B* **67** (1998) 363-367.
3. P Canarelli, Z Benko, R. Curl and F K Tittel; *J. Opt. Soc. Am.*, **9**, 2 (1992) 197.
4. W Schade, T Blanke, U Willer and C Rempel; *Appl. Phys. B* **63** (1996) 99-102.
5. J Faist, F Capasso, D L Sivco, C Sirton, A L Hutchinson and A Y Cho; *Science* **264** (1994) 553.
6. S D Wehe, D M Sonnenfroh, M. G. Allen, C Gmachl and F Capasso; in OSA "Trend in optics and photonics" (TOPS) **64** Optical Soc. Of America, Washington DC (2002) FC3-1.
7. U Willer, T Blanke and W Schade, *Appl. Opt.*, **40**, 30 (2001) 5439-5445.
8. V G Dimitriev, G G Gurzadyan and D N Nikogosyan, *Handbook of nonlinear optical crystals*, Springer (1997).
9. L S Rothmann, C P Rinsland, A Goldman, et al.,: The HITRAN molecular spectroscopic database and HAWKS (HITRANatmospheric workstation): 1996 edition. In: *J. Quaut. Spectrosc. Radiat. Transfer* **60** (1996).
10. S Prucker, W Meier and W Stricker; *Rev. Sci. Instrum.*, **65**, 9 (1994) 2908.

## 5. Conclusion

In this paper a narrow bandwidth MIR difference-frequency radiation, tuneable from 4.8 to 5.1  $\mu\text{m}$  is generated. The MIR light is applied to detect CO for P(21) rotational line at  $2055.4\text{ cm}^{-1}$  in a 10 cm absorption cell as well as in a McKenna flat flame burner. The self-broadening coefficient of CO is measured and it is compared with the Hitran 96 database. This comparison shows a good agreement between our measurement and the reported value by the Hitran 96 database. CO tracing in the flame shows the excellent ability of the generated MIR absorption spectrometer to determine the distribution of the CO in the flame even at low concentrations.