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Portable Mid-Infrared Gas Sensors:
Development and Applications

by

Dirk Richter

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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ABSTRACT

Portable Mid-Infrared Gas Sensors: Development and Applications

by

Dirk Richter

Several novel compact architectures of diode laser based absorption gas sensors have been developed, characterized and applied to real world applications. The motivation for this research has been the need to develop highly sensitive, selective and rapid response gas sensors that operate reliably in a non-laboratory environment. The gas sensors utilize rare earth doped fiber amplified near infrared diode lasers and are difference frequency mixed in periodically poled LiNbO$_3$ to generate narrow linewidth $\mu$W to mW-level mid infrared light in the molecular fingerprint region from 3 to 5 $\mu$m. In particular, the spectroscopic performance of an automated widely tunable (3.3 - 4.4 $\mu$m) multi-species and a high-power single species (3.5 $\mu$m) gas detection sensor are discussed. Sensitive, selective and real-time detection of over 10 gas species including CH$_4$, H$_2$CO, CO$_2$, CH$_3$OH, NO$_2$, N$_2$O, SO$_2$, HCl, C$_6$H$_6$, and H$_2$O using extractive gas sampling in a multi-pass cell was demonstrated. The gas sensors were used for an evaluation of a trace contaminant catalyst system at TDA Research, Wheat Ridge, Colorado, and successfully applied to the detection of volcanic gases at Masaya volcano, Nicaragua.
ACKNOWLEDGEMENTS

It is my sincere understanding that this work would not have been possible without the inspiration and outstanding support of Professor Frank K. Tittel. He has been most influential in all aspects of my professional education and I very much admire his determination, scientific expertise and second-to-none leadership.

I would like to thank Dr. David G. Lancaster from whom I have learned a great deal of professional research and enjoyed many experiments. In particular, he taught me the way to tackle real world problems as they arise always so unexpected during field campaigns.

I very much value the opportunity of discussing many problems with Professor Robert F. Curl. His mastermind is an incredible resource of knowledge fueling the development of advanced spectroscopic tools for gas sensing applications.

The adventurous field trip to an active volcano located in Nicaragua to test laser based gas sensors in a real-world environment was an invaluable experience. I very much enjoyed the joint field experiment to Masaya volcano and thank Dr. Clive Oppenheimer and his team Dr. Rodney Jones, Dr. Mike Burton and Hayley Duffell from Cambridge University for the team spirits and support.

Most of the research presented in this thesis was funded in part by the National Aeronautics and Space Administration (NASA). Dr. John C. Graf (NASA-JSC) deserves special appreciation as he supported the development of DFG based gas sensor technologies with new ideas and opportunities to apply them to real-world problems.
I like to thank James Bahr and Dr. David Wickham of TDA Research, Wheat Ridge, Colorado for the opportunity and support during a one week evaluation of a catalytic reactor using a DFG based gas sensor.

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CHAPTER 1. INTRODUCTION

1.1 Motivation: Sensing the World Around Us

The detection and monitoring of numerous gas species has become increasingly important in research, industrial and medical applications. In many cases, real-time knowledge of the presence and the amount of gas species is desired, with gas concentration levels typically ranging from parts-per-trillion (ppt) to parts-per-million (ppm). In order to be suitable for industrial and outdoor operation, gas sensors have to feature a number of performance characteristics. Important sensor features include portability and compactness, no consumables (except electrical power), insensitivity to vibrations and temperature changes, and the ability to operate over longer time periods without the need of adjustment or re-calibration.

This thesis presents the developments of new diode laser based mid-infrared sources and their practical applications to highly sensitive gas detection in real world environments.

1.2 Gas Sensing Technologies

Various gas sensor technologies have been explored and can be classified into two categories: a) non-optical chemical / physical, and b) optically based, shown in Fig. 1.1.

In recent years, industrial, environmental monitoring and process control applications employed Mass-, Fourier Transform infrared (FTIR) -, and laser based spectrometers. These spectrometer types have been demonstrated to include high
sensitivity, wide coverage of detectable species and sometimes portability, however not at the same time.

![Diagram of gas sensing technologies](image)

Fig.1.1: Overview of gas sensing technologies \(^1,2,3\)

The fingerprint ro-vibrational transitions of molecular gases in the near and mid-infrared spectral region provide characteristic absorption features.\(^4\) FTIR spectrometers are able to capture wide spectral ranges (>2000 cm\(^{-1}\)) in very short times (~1 s), but do not offer high spectral selectivity (~0.5 cm\(^{-1}\)) at reasonable size and cost.\(^5\) FTIR spectroscopy often requires also a post analysis using spectroscopic databases in order to obtain quantitative values. Tunable mid-IR laser sources, suitable for spectroscopic applications, are scarce
and until recently, only liquid nitrogen cooled lead salt diode lasers have been applied in high sensitivity trace gas measurements. The operation of lead-salt diode laser based gas sensors remains complex and operation can be obstructed by changing diode parameters such as temperature-frequency cycling and multi-mode output.

More recently, Quantum Cascade (QC) lasers have been developed. These lasers are based on a multiple quantum well semiconductor structure produced by molecular beam epitaxy. Narrow linewidth output powers in excess of 100 mW have been achieved to date. Similar to lead salt diode lasers, continuous wave QC-laser operate at liquid nitrogen temperatures. In pulsed operation, QC lasers have been successfully demonstrated using Peltier element cooling to operate at near room temperature but at the cost of a broader spectral linewidth (~300 MHz). Other laser based spectroscopic sources for the near infrared include room temperature operating cw single or multi-section Distributed FeedBack (DFB) InGaAsP diode lasers which have been applied to overtone absorption spectroscopy in the 1-2 μm wavelength region. Continuous wave optical parametric oscillators have been developed and can provide widely tunable near and mid-infrared power. However, due to their complex cavity design, they possess a limited continuous tuning range which has limited their application to high sensitivity spectroscopy or trace gas sensing.

Other promising laser based spectroscopic gas detection techniques includes UV absorption spectroscopy and THz time domain spectroscopy. Far infrared THz radiation can efficiently be generated using an ultra-fast laser pulse gated optoelectronic switch. Compact UV narrow-linewidth up-converted microchip laser sources and ultra-fast,
broadband laser sources for THz spectroscopy are being developed based on fiber technologies and nonlinear optical materials similar to the devices described in this thesis.\textsuperscript{13,14}

1.3 Alternative Mid-IR Sources

The rapid progress in high power cw near infrared diode- and solid state non-planar ring lasers in combination with the commercial availability of quasi-phase matched nonlinear optical crystals\textsuperscript{15} for efficient frequency down conversion lead to the realization of compact cw\textsuperscript{16,17} and pulsed\textsuperscript{18} mid-IR sources for laser absorption spectroscopy. DFG based mid-IR sources have also been developed using birefringently phase-matched nonlinear crystals such as GaSe and AgGaSe\textsubscript{2}.\textsuperscript{19,20} Two critical limitations of compact first generation PPLN based mid-IR sources described in Ref. 16 and 17 were identified. Firstly, the Fabry-Perot type diode laser pump source tended to experience periodic mode-hops, leading to abrupt frequency changes. Secondly, the use of discrete optics to collimate and spatially overlap the pump beams for frequency conversion in PPLN exhibited noticeable alignment sensitivities due to effects of temperature changes and vibrations.

With the advent of optical telecommunication components, new pump architectures of mid-infrared sources have been realized, applied to spectroscopy and are presented in this thesis. Cw semiconductor diode lasers have been developed and are commercially available that feature long life times (>10\textsuperscript{6} hours), high output power (1 - 100 mW) and offer a spectrally narrow operation (100 kHz - 20 MHz). Fiber coupled, optically isolated and Peltier-element temperature controlled diode laser packages, not much bigger than a
matchbox, have become a low cost telecommunications product. In addition, high gain optical fiber amplifiers have become available, in particular at a wavelength of 1 μm, 1.3 μm and 1.5 μm based on rare earth doped Yb-, Pr- and Er-fibers, respectively.

![Nonlinear Optical Crystal Diagram]

Fig.1.2: Concept of Difference Frequency Generation (DFG). \(\omega_s\), signal frequency; \(\omega_p\), pump frequency; \(\omega_i\), idler frequency

Optical mixing of these wavelengths in a nonlinear optical crystal allows generation of tunable mid-infrared radiation as shown in Fig.1.2. Presently, the crystal of choice is quasi-phase matched periodically poled lithium niobate (PPLN). PPLN offers high transparency for pumping and generated wavelengths. It possesses a high figure of merit for optical frequency parametric conversion and can be engineered to phasematch any wavelengths within its transparency range from 0.4 to 5 μm. The motivation to access the mid-infrared instead of near infrared overtone transitions is due to the 20 to 200 times stronger molecular absorption linestrengths leading to a higher sensitivity.

Table 1.1 depicts typical performance characteristics of continuous wave mid-infrared sources. This table offers a comparison of practical mid-infrared sources for absorption spectroscopy.
### Table 1.1: Performance characteristic of mid-IR sources applied to absorption spectroscopy.

<table>
<thead>
<tr>
<th></th>
<th>Fourier transform infrared spectrometer</th>
<th>CW PPLN based optical parametric oscillator</th>
<th>CW Quantum Cascade Laser</th>
<th>PbS-Diode Laser</th>
<th>Diode Laser Based DFG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (absorption)</td>
<td>$10^{-4}$</td>
<td>N/A</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$-$10^{-7}$</td>
<td>$10^{-4}$ ($a$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10^{-5} ($c$)</td>
</tr>
<tr>
<td>Selectivity (MHz)</td>
<td>15000</td>
<td>0.15 (instantaneous)</td>
<td>50</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>Coarse Tuning (cm(^{-1}))</td>
<td>625 - 6500</td>
<td>5000 - 6900</td>
<td>3</td>
<td>5</td>
<td>2270 - 3030</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500 - 4347</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fine Tuning (cm(^{-1}))</td>
<td>N/A</td>
<td>0.03 (signal)</td>
<td>3</td>
<td>1-2</td>
<td>&gt;2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02 (idler)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Response Time (s)</td>
<td>0.5</td>
<td>N/A</td>
<td>2-60</td>
<td>2-60</td>
<td>2-60</td>
</tr>
<tr>
<td>Demonstrated Field Application</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

(a): Direct absorption; (b): 2-f-detection; (c): Dual-beam-detection

#### 1.4 Key Contributions of this Research

This research contributes to the successful development, characterization and implementation of new portable diode laser and fiber optic based mid-IR spectroscopic sources applied to the sensitive and selective detection of 10 trace gas species in laboratory, industrial and rural environments. Mature telecommunication fiber optic components along with state-of-the-art nonlinear optical materials were identified, optimized and engineered to operate as key elements in compact mid-infrared spectroscopic gas sensors.
Several fiber optic coupled architectures were realized and tested. One architecture included a stepper motor controlled widely tunable external cavity diode laser (814 nm - 865 nm) as a DFG pump source in combination with a stepper motor controlled fan-out type PPLN crystal. This mid-IR source provides continuously tunable narrow-linewidth mid-IR radiation (3.3 - 4.4 μm) and was packaged in a compact portable suitcase that included a multipass cell and a low noise Mercury Cadmium Telluride (MCT) detector for highly sensitive extractive gas detection. This sensor was extensively tested and applied in two field campaigns: a one week monitoring test of an industrial trace contaminant control system at TDA Inc., Wheat Ridge, Colorado and in emission monitoring of volcanic gas species at the Masaya Volcano, Nicaragua. Other fiber optic coupled architectures included high power fiber amplified diode laser and fiber laser pump sources specifically targeted to the detection of single molecules such as formaldehyde and methane.

Significant effort was made to realize an optical gas sensor that offers stable continuous high level performance over extended time periods, is operating in a self-automated mode but yet is compact and portable. The success of developing gas sensors to an advanced prototype level has made this technology attractive for potential commercialization.
References for Chapter 1


5. Midac Corporation, 17911 Fitch Avenue Irvine, Calif. 92614; http://www.midac.com


D. Richter, D. G. Lancaster, R. F. Curl, W. Neu, F.K. Tittel, "Compact mid-infrared


CHAPTER 2. DIFFERENCE FREQUENCY GENERATION (DFG)

2.1 Nonlinear Optical Frequency Generation

The nonlinear optical response of condensed matter can be used to generate new wavelengths. Shortly after the discovery of the laser, Franken et.al.\textsuperscript{1} demonstrated the generation of optical harmonics. From this discovery, nonlinear optics advanced rapidly to demonstrate, characterize and explore new optical materials. Three of the most useful optical parametric processes include, second harmonic generation (SHG), sum frequency (SFG) and difference frequency generation (DFG). This chapter considers concepts of nonlinear frequency mixing relevant to DFG and refers the more interested reader to original papers and several excellent reviews.\textsuperscript{2} The origin of new wavelengths is based on the nonlinear response of the polarization $\mathbf{P}$ in presence of an intense electric field $\mathbf{E}$. Such a relationship can be expressed in terms of a power series,

$$\mathbf{P} = \varepsilon_0 \cdot \chi^{(1)} \cdot \mathbf{E}(t) + \varepsilon_0 \cdot \chi^{(2)} \cdot \mathbf{E}(t)^2 + \varepsilon_0 \cdot \chi^{(3)} \cdot \mathbf{E}(t)^3 + ...$$  \hspace{0.5cm} (2.1)

with the susceptibility $\chi$ and permittivity $\varepsilon_0$.

In this power series, the first term describes the linear optical effects such as dispersion. The second term, describes optical rectification (DC component), second harmonic, sum and difference frequency generation. Third harmonic generation and the Kerr effect are described by the third term. If one assumes two incident electric fields $\mathbf{E}_1$ and $\mathbf{E}_2$, equation 2.1 yields for the second order term,
\[ P^{(2)} = \epsilon_0 \cdot \chi^{(2)} \cdot \left( E_0^2 \cdot e^{-i2\omega_1 t} + E_0^2 \cdot e^{-i2\omega_2 t} + 2 \cdot E_0^2 \cdot e^{-i(\omega_1 + \omega_2) t} + 2 \cdot E_0^2 \cdot e^{-i(\omega_1 - \omega_2) t} + c.c. \right) \]

\[ \text{SHG(1)} \quad \text{SHG(2)} \quad \text{SFG} \quad \text{DFG} \]

\[ + 2 \cdot \epsilon_0 \cdot \chi^{(2)} \cdot \left[ E_1 \cdot E_1^* + E_2 \cdot E_2^* \right] \quad (2.2) \]

Optical Rectification

where

\[ E_j = E_0 \cdot e^{-i\omega_j t} \quad (2.3) \]

2.2 Difference Frequency Generation

In a more rigorous analysis, the interaction of light with matter is described by the following wave equation based on Maxwell equations,\(^3\)\(^4\)\(^5\)

\[ \nabla^2 E - \epsilon_0 \cdot \mu_0 \cdot \frac{\partial^2 E}{\partial t^2} = \mu_0 \cdot \frac{\partial^2 P}{\partial t^2} \quad (2.4) \]

The solution of equation (2.4), when applied to a DFG parametric process, allows the individual description of the three interacting waves, customarily called pump (highest frequency), signal and idler (generated frequency), as they propagate through the optical medium. Assuming a) monochromatic plane waves propagating in the near field along the z-axis b) slowly varying envelope approximation and c) substituting the polarization by specific nonlinear polarization relations given by (2.2) and electric field expressions at \(\omega_s\), \(\omega_p\) and \(\omega_i\) produce the following coupled set of equations.\(^6\)
\[
\begin{align*}
\frac{dE_p}{dz} &= -i \cdot \frac{\omega_p \cdot d_{\text{eff}}}{n_p \cdot c} \cdot E_s \cdot E_i \cdot e^{-i \Delta k z} \\
\frac{dE_s}{dz} &= -i \cdot \frac{\omega_s \cdot d_{\text{eff}}}{n_s \cdot c} \cdot E_p \cdot E_i^* \cdot e^{i \Delta k z} \\
\frac{dE_i}{dz} &= -i \cdot \frac{\omega_i \cdot d_{\text{eff}}}{n_i \cdot c} \cdot E_p \cdot E_s^* \cdot e^{i \Delta k z}
\end{align*}
\]

(2.5)

with \(\Delta k\) denoting the wave-vector phase mismatch.

\[
\Delta k = 2\pi \left( \frac{n_p}{\lambda_p} - \frac{n_s}{\lambda_s} + \frac{n_i}{\lambda_i} \right)
\]

(2.6)

Using no phase compensation the idler intensity follows a \(\text{sinc}^2\) - function, which is obtained by integrating (2.5).

\[
I(L) = r \cdot E_p^2 \cdot E_s^* \cdot E_i^2 \cdot \frac{\sin^2 \left( \frac{\Delta k \cdot L}{2} \right)}{\left( \frac{\Delta k \cdot L}{2} \right)^2}
\]

(2.7)

The DFG intensity increases with the propagation length, but after travelling over a coherence length \(L_c\),

\[
L_c = \frac{\pi}{\Delta k}
\]

(2.8)

the energy is again transferred back to the signal and pump beams with a net zero gain.

In order to increase the power yield of the newly generated wave, the phase velocity dispersion must be compensated and conservation of momentum satisfied.

2.3 PPLN and Quasi-Phase Matching

Historically, the technique of quasi-phase matching was first proposed by Armstrong et.al.\(^7\) but advances in optical materials were limited so that until the mid 1990's, birefringent crystals were the only choice for phase matching. In a birefringent uni- or bi-
axial optical material, the phase mismatch is compensated by using the different angular
dependence of the ordinary and extraordinary refractive index. This technique only
allows access to the smaller non-diagonal susceptibility tensor elements for which one
can establish birefringent phase-compensation. The Poynting vector walk-off effect leads
to an additional reduction of conversion efficiency.

Quasi-phase matching does not depend on birefringence, but instead, on a periodic
sign reversal every coherence length of the nonlinear coefficient in the optical material.
To date, permanent sign reversal is most efficiently achieved with electric field poling in
ferro-electric materials such as LiNbO₃, LiTaO₃, KTiOPO₄, and RbTiOAsO₄. Lithographic masks provide a precise and easy way to implement domain features sizes
of 5-30 μm and therefore an electric field poling technique lends itself to commercial
mass production.

QPM can also be applied to isotropic optical materials such as GaAs. In this case,
electric field poling can not be used and the periodic change of the nonlinear index is
achieved by other means such as diffusion bonding or epitaxial orientation patterned
growth. Table 2.1 summarizes the advantages of quasi-phase matching over birefringent
phase matching.
Table 2.1: Advantages of quasi-phase matching

<table>
<thead>
<tr>
<th>Quasi - Phase Matching</th>
<th>Birefringent Phase Matching</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Noncritical phase matching (no walkoff)</td>
<td>• Mostly critical phase matching (walkoff)</td>
</tr>
<tr>
<td>• Larger diagonal nonlinear coefficients can be used</td>
<td>• Only smaller, non-diagonal coefficients can be used</td>
</tr>
<tr>
<td>• Phase match any wavelength combinations within crystal transparency</td>
<td>• Limited phase matching (e.g. no blue SHG for LiNbO₃)</td>
</tr>
<tr>
<td>• Tuning via temperature, multiple or continuous fan-out type grating periods</td>
<td>• Tuning via temperature and angle</td>
</tr>
<tr>
<td>• Wide acceptance bandwidth / angle, easy to align</td>
<td>• Limited acceptance bandwidth / angle, difficult to align</td>
</tr>
<tr>
<td>• User design friendly criteria</td>
<td></td>
</tr>
</tbody>
</table>

The periodically modulated nonlinear coefficient can be represented as a Fourier series,

\[ d(z) = d_{\text{eff}} \cdot \sum_{m=-\infty}^{\infty} G_m \cdot \exp(-i \cdot k_m \cdot z) \]  \hspace{1cm} (2.9)

\[ k_m = \frac{2\pi \cdot m}{\Lambda} \]

where \( d_{\text{eff}} \) is the effective nonlinear coefficient and \( k_m \) represents the grating vector.

The total wave-vector mismatch becomes

\[ \Delta k = k_p - k_s - k_i - k_m \]  \hspace{1cm} (2.10)

Assuming 50% duty cycle (\( m=1 \)), the wave-vector mismatch becomes

\[ \Delta k = k_p - k_s - k_i - \frac{2 \cdot \pi}{\Lambda} \]  \hspace{1cm} (2.11)
With equation (2.11) one can compute the grating period required for phase-matching. The wavelength dependent refractive index of PPLN can be calculated by the Sellmeier equation and coefficients determined by Jundt\textsuperscript{13}, valid from 0.4 \(\mu\text{m} - 5 \mu\text{m}$. 

2.4 DFG Power Analysis

DFG power prediction is helpful in determining the optimal focusing parameters and to estimate the conversion efficiency. In the design of a DFG based gas sensor, the mid-IR power ultimately determines the detection sensitivity. Power requirements can vary depending on the detectable gas species and application environments. More power is required if advanced detection schemes are used that include dual-beam, 2-f or a long path (100 m) multiple reflection gas absorption cells to achieve sensitivities below the ppb-level (or $10^{-5}$ fractional absorption).

Many papers have taken the difficult challenge to derive solutions for confocal Gaussian pump beams\textsuperscript{14,15}. For experimental purposes, the solutions should not be taken as definitive values but rather as guiding design parameters, since real world values such as crystal quality, aspheric and chromatic aberrations, and the non-identical confocal pump beam parameters are not considered. The experimental conversion efficiency was found to range from 30 \% to 60 \% of the theoretical value and strongly depends on the pump beam quality and spatial overlap.

The main results for predicting the DFG power are presented below and the main parameters interpreted towards an optimum optical pump geometry.
Assuming a lossless crystal and circular Gaussian pump beams, the generated DFG power in a cw pumping configuration for two confocal pump beams is described by,\textsuperscript{14}

\[
P_{\text{idler}} = c \cdot P_{\text{pump}} \cdot P_{\text{signal}} \cdot L
\]

where \(L\) is the length of crystal; \(c\), the focusing factor and figure of merit.

The factor \(c\) includes an integral which describes the efficiency of the nonlinear optical interaction as a function of two parameters \(\xi\) and \(\mu\). The focusing parameter \(\xi\) describes the ratio of the interaction length, \(L\) and confocal length, \(b\); and the \(\mu\) the ratio of the wave-vectors of signal and pump beams. The focusing integral (\(h\)-function), was derived by Chu and Broyer\textsuperscript{14} and contains all beam focusing information,

\[
h(\mu, \xi) = \frac{1}{2 \cdot \xi} \int_0^\xi \frac{1 + \tau_1 \cdot \tau_2}{(1 + \tau_1 \cdot \tau_2)^2} \cdot \frac{1}{4 \left(\frac{1 - \mu}{1 + \mu} + \frac{1 + \mu}{1 - \mu}\right)^2 \cdot (\tau_1 - \tau_2)^2} \cdot d\tau_1 \cdot d\tau_2
\]

with the focusing parameters

\[
\xi = \frac{L}{b} = \frac{L \cdot \lambda}{2 \cdot \pi \cdot r^3 \cdot n(\lambda, T)}
\]

and

\[
\mu = \frac{k_s}{k_p}
\]

\(L\), crystal length; \(\lambda\), idler wavelength; \(r\), beam waist radius; \(n\), refractive index.

Fig. 2.1 shows an example for three wave-vector combinations, one near convergence maximum (small \(\mu\)) and two wave-vector combinations that were used in experiments presented in the following chapters. The \(h\)-function has its maximum at \(\xi = 1.3\) and a relatively flat top at wave vector combinations used in DFG experiments. This allows
some flexibility in selecting the confocal pump beam parameters and the focusing is
mainly determined by the length / aperture ratio of the crystal.

Appendix A includes an example MathCAD worksheet for calculation of DFG power in
bulk PPLN.

Fig. 2.1: The h-function shown for three fixed $\mu$-values as a function of $\xi$: $\mu=0.1$ (near
converging maximum), $\mu=0.687$ ($\lambda_{\text{pump}}=1083$ nm, $\lambda_{\text{signal}}=1563$nm $\Rightarrow \lambda_{\text{idler}}=3.5$
$\mu$m), and $\mu=0.759$ ($\lambda_{\text{pump}}=829$ nm, $\lambda_{\text{signal}}=1083$nm $\Rightarrow \lambda_{\text{idler}}=3.5$ $\mu$m)
Recent improvements in electric field poling of lithium niobate lead to the development of 1 mm thick PPLN crystals and consequently allow the use of longer samples without experiencing aperture clipping of the pump and generated DFG beams.

References for Chapter 2


CHAPTER 3. DESIGN CONSIDERATIONS FOR PORTABLE DFG BASED GAS SENSORS

3.1 Introduction

As early as 1974, Pine\textsuperscript{1} recognized the potential of tunable, spectrally narrow cw mid-IR sources for high resolution spectroscopy. Difference frequency radiation at 3 $\mu$m was generated using a 5 cm long birefringent phase matched LiNbO$_3$ crystal pumped by a single frequency cw dye laser and argon ion laser. Such a complex laser system occupied an entire optical table and produced DFG power levels of $\sim$500 nW at a conversion efficiency of 40 $\mu$W$\cdot$W$^{-2}$$\cdot$cm$^{-1}$. An all-solid-state diode laser based DFG source at 4.7 $\mu$m using a AgGaS$_2$ crystal by Simon et.al $^2$ was possible through the advent of near-IR diode lasers. Although, low in pump and generated powers (10.1 mW, pump; 1.93 mW, signal; 3 nW, idler), it was only a matter of time for diode and solid state laser to evolve to higher powers and improved spectral characteristics. The parallel development of advanced nonlinear optical crystals such as quasi-phase matched lithium niobate enabled the realization of yet another greatly improved DFG architecture, that for the first time, was semi-portable and configured for real-time extractive gas sensing.\textsuperscript{3} Power levels of 4 $\mu$W at 3.5 $\mu$m and fractional absorption of $2 \times 10^{-4}$ enabled the sensitive detection of various gas species $^{4,5,6}$ including formaldehyde. Application of these sensors in non-laboratory environments revealed operational limitations. Despite high optical isolation and tilted optics to avoid direct back scattered light, one of the employed Fabry-Perot-
type pump diode laser sources exhibited periodic mode-hops during operation. Furthermore, the use of discrete optical components for spatial beam shaping and beam overlap (collimation lenses, anamorphic prism pairs, beamsplitter) caused the instrument to be susceptible to vibration and temperature changes resulting in optical misalignment and DFG power drifts. Although, these mid-IR DFG sources performed well in a laboratory environment, their application in field measurements was problematic.

3.2 CW Diode Laser Pump Sources

Several sophisticated diode laser architectures have emerged based on the commercial availability of novel photonic technology. Diode laser pump sources for spectroscopic applications require the following parameters:

- Low optical noise, single longitudinal mode
- Narrow-linewidth (<100 MHz)
- Wavelength stability (Peltier element temperature controlled)
- Repetitive coarse (temperature) and rapid (current) linear fine frequency tuning
- Insensitive and/or protected (optical isolated) from any optical back scattered light which may effect the diode laser operation otherwise

In addition solid state pump sources should possess a long-life time (>10^6 hrs.), operate with low power consumption, be packaged in a compact rugged enclosure and from a commercial point of view, cost effective.
Implementation of integrated wavelength mode filters in the form of a distributed-feedback (DFB) structure or distributed-Bragg-reflector's (DBR) enabled stable single frequency operation.

Table 3.1: Performance overview of commercially available semiconductor lasers suitable for spectroscopic applications

<table>
<thead>
<tr>
<th>Diode Laser</th>
<th>Power (mW)</th>
<th>Center Wavelengths (nm)</th>
<th>Tuning (cm⁻¹)</th>
<th>Spectral Width (MHz, 1 sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabry-Perot</td>
<td>1-200</td>
<td>635 - 865</td>
<td>~50 (Temp.)</td>
<td>50 - 200</td>
</tr>
<tr>
<td>DBR</td>
<td>50-150</td>
<td>852 &amp; 1083</td>
<td>~6 (Temp.)</td>
<td>3</td>
</tr>
<tr>
<td>SG-DBR</td>
<td>2-10</td>
<td>1550</td>
<td>6410-6622</td>
<td>25</td>
</tr>
<tr>
<td>DFB</td>
<td>1 - 30</td>
<td>1525 - 1575</td>
<td>~10 (Temp.)</td>
<td>0.1 - 10</td>
</tr>
<tr>
<td>ECDL</td>
<td>1 - 50</td>
<td>650 - 1655</td>
<td>800</td>
<td>4</td>
</tr>
</tbody>
</table>

DBR, distributed-Bragg-reflector; SG-DBR, Sample-grating-DBR; DFB, Distributed-feedback; ECDL, external cavity diode laser.⁷ ⁸ ⁹

A more widely tunable single frequency laser source was realized in the form of an external cavity diode laser (ECDL) using gratings as a dispersive feedback element. This can be implemented in two configurations: a Littrow type ECDL that provides higher output powers, and a preferable Littman design capable of mode-hop free tuning and beam pointing stability. Fabrication of sampled-grating DBR and similar structured diode laser were introduced to serve the ever increasing demand in wavelength division multiplexing systems. These diode lasers are widely tunable through individual electronic controls of an integrated coupler, phase and sampled DBR grating structures. Other
diode laser sources include Vertical Cavity Surface Emitting Lasers (VCSEL)\textsuperscript{10} which feature a low current threshold (\(\sim 1\) mA) but lack so far sufficient power (\(<1\) mW) to be suitable for high resolution spectroscopic applications.

3.3 Fiber Amplifier Technology

Difference-frequency mixed low power diode lasers (\(<10\) mW) only permit generation of nano-watt levels of mid-infrared radiation. Solid state non-planar ring oscillators (NPRO) or master oscillator power amplifiers (MOPA) can provide higher optical powers (\(<1\) W) and have been used as DFG pump sources.\textsuperscript{3} A more economic and flexible design in terms of power levels, operating wavelengths and compactness is offered by the use of high power rare earth doped fiber amplifiers. Fiber amplifiers exhibit a broad gain bandwidth of typically 25 -50 nm centered at dopant dependant wavelengths in the near IR (See also Table 3.2). Gain is typically achieved by use of high power broadband pump diode lasers. The optimum fiber pump diode lasers operating wavelength depends on the absorption spectrum given by the rare earth dopant and its relative concentration. The wide bandwidth of the optical fiber amplifiers allows a wide wavelength selection of seed diode laser signal and pump wavelengths for the DFG process. Optical fiber amplifiers can provide broad bandwidth suitable for amplifying the output from various seed sources, such as widely tunable diode laser seed sources (ECDL, SG-DBR, SSG-DBR) or multiplexing several different DFB or DBR diode lasers. This approach is also more compact and cost effective than using other high power solid state seed sources (e.g. NPRO or MOPA).
Table 3.2: High-power rare-earth doped fiber amplifiers.\textsuperscript{11}

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Emission $\lambda$(nm)</th>
<th>Pump $\lambda$ (nm)</th>
<th>Transition</th>
<th>Slope Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>900 - 950</td>
<td>810</td>
<td>3 - 4 level</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>1050 - 1100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>970 - 1160</td>
<td>915 / 975</td>
<td>3 - 4 level</td>
<td>90\textsuperscript{a)}</td>
</tr>
<tr>
<td>Er</td>
<td>1520 - 1590</td>
<td>980 / 1480</td>
<td>3 level</td>
<td>60</td>
</tr>
<tr>
<td>Pr</td>
<td>1280 - 1340</td>
<td>980-1030</td>
<td>4 level</td>
<td>14</td>
</tr>
<tr>
<td>Er/Yb</td>
<td>1520 - 1590</td>
<td>975</td>
<td>3 level</td>
<td>45\textsuperscript{a)}</td>
</tr>
<tr>
<td></td>
<td>1010-1100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tm</td>
<td>1600 - 2100</td>
<td>810 / 1600</td>
<td>3 level</td>
<td>36 / 70</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} pumped by v-groove technique

Fiber amplifiers come in a variety of architectures which include different pumping techniques and for the telecommunication industry important built-in gain flattening components. Today’s most established pump scheme is the use of fiber optic coupler on either end of the active fiber for bi-directional pumping. In addition, a technique that launches the pump light via a v-groove imbedded in a star shaped double cladding gain fiber has been implemented.\textsuperscript{12} Compared to conventional end-pumped doped fibers, one has a larger pump area and complete pump absorption. Hence, higher power levels with higher efficiency have been demonstrated ranging from medium (1W) to very high powers (>100W). At higher power levels, nonlinear effects occur that originate mainly from the third order.
Fig. 3.1: SEM photograph of the edge emitting facet from a distributed Bragg reflector diode laser, damaged by a SRS/SBS counter propagating pulse.

susceptibility and stimulated inelastic scattering such as intensity dependant refractive index (SPM, self-phase modulation; CPM, cross-phase modulation, FWM, four-wave mixing) and simulated Raman / Brillouin scattering (SRS / SBS). Only SRS and SBS are critical in DFG systems designs. With the availability of high pump power levels (>1W) for the generation of more DFG power, it is possible to reach the threshold of SBS and SRS. SBS/SRS tend to increase further as a result of vibrations transforming to a backward traveling, wavelength shifted pulse train and re-amplified through the rare earth
doped fiber that can lead to 'irreversible' damage to the seed diode laser as shown in Fig. 3.1.

SRS and SBS, which only has a back propagating component, can be minimized by keeping optical fiber lengths as short as possible and implement optical isolators between connected fiber sections. The SBS threshold can be estimated by

\[
\begin{align*}
P_{\text{threshold}} &= \frac{21 \cdot A_{\text{eff}}}{g_B \cdot L_{\text{eff}}} \\
A_{\text{eff}} &= \frac{\left( \int I dA \right)^2}{\int I^2 dA} \\
L_{\text{eff}} &= \frac{1}{\alpha} \cdot (1 - e^{-\alpha L})
\end{align*}
\]

(3.1)

where \( g_B \) is the peak SBS gain; \( A_{\text{eff}} \), effective area; \( L_{\text{eff}} \), effective length; and \( \alpha \), fiber attenuation.

Typical values for single mode silica fibers are: \( A_{\text{eff}} = 80 \mu m \); \( \alpha = 0.2 \) dB/km; and \( g_B = 5 \times 10^{-11} \) m/W.

3.4 Discrete and Fiber Optic Components

The use of optimum discrete and fiber optic components is essential to realize an efficient, low noise spectroscopic source. Backward propagating scattering losses should be minimized and active laser components always optically isolated for low noise operation. In the following, key components used in DFG sources (c.f. Chapter 5) are introduced:
a) Single-mode fibers

Single-mode (SM) silica fibers offer light transmission with the lowest loss and dispersion in the near infrared wavelength region around 1 μm to 1.5 μm. SM-fibers are made with a step refraction index with a slightly higher core index surrounded by a lower index cladding. Core diameters for single mode operation depends on the wavelength, the NA of the fiber and are typically ~ 5 - 8 μm. Cladding diameters are typically 125 μm, protected by further jackets to protect the fiber. Progress in fabrication of co-doped ultra pure silica and smooth and uniform core-cladding surface interfaces lead to low loss fibers of 0.2 db/km limited by intrinsic Rayleigh scattering losses.

b) Fiber connectors

In a fiber optic system, the fiber links are usually fusion spliced to insure low loss connections (~0.01-0.05 dB). However, when the transmitted light is entering and leaving a fiber optic cable, the use of fiber optic connectors ensures permanent fixture with respect to the coupling or collecting optics. The end faces can be polished to an 8°-angle to minimize reflections at the silica (n=1.5) / air (n=1) interface, and hence suppress back propagating modes. Angled physical contact fiber connectors (FC-APC) offer the lowest reflectivity of -67 dB.

c) Fiber couplers (Wavelength Division Multiplexer, WDM)

Fiber coupler or WDM’s enable the combination or separation of two or more fiber optic links guiding the same or different wavelengths. The quality of WDM’s is determined by the insertion loss and degree of wavelength separation. WDM’s are mostly fabricated using fusion splicing, but depending on the application, use of WDM’s based on GRIN
lenses and interference filters may offer higher isolation and lower polarization dependent losses.

Further optical components used in DFG based gas sensors described here include fiber and free space optical isolators. The optical isolator serves to suppress reflections occurring at fiber interconnections which can adversely effect the performance of fiber amplifiers and diode lasers leading to optical instabilities. Non-factory fiber pigtailed diode lasers are arranged with free space isolators in combination with rugged, fine adjustable single aspheric lenses to collimate and focus the laser into the fiber. Typical laser ($\sim P_0=50\text{ mW}$) to fiber coupling efficiencies are 20-30% (10-15 mW), which is sufficient fiber amplifier seed power.

Standard single mode fibers do not maintain polarization. After even travelling through a few centimeters of a curled fiber, a given linear polarization at the input is transformed to an arbitrary output polarization. Difference-frequency generation in PPLN uses a $e+e\rightarrow e$ polarization and therefore requires linear polarized pump light. Polarization controllers placed in the fiber optic delivery arms can be implemented to ensure linear and vertical polarization of pump and signal beam at the fiber output. A state-of-the-art polarization controller\textsuperscript{14} with zero insertion loss is applied the DFG fiber pump sources presented in this work. A strand of fiber is held in place by two fiber blocks. The center portion is enclosed in ~1 inch long sandwiched parallel plates (squeezer) inducing adjustable linear birefringence and in effect creating a wave plate with variable retardation. Additional rotation of the fiber fixture can twist either fiber end in the opposite direction and cause a rotation of the incident polarization. In this manner, any state of polarization can be
achieved. This solution features zero insertion loss, ease of adjustment and does not require any preparation to the fiber. Alternatively, polarization maintaining (PM) fibers can be used. Practically, PM fibers demand special fiber splicing equipment and offer so far less flexibility in conjunction with optical fiber amplifiers.

3.5 Fiber to Crystal Imaging

One of the primary advantages of using fiber optics is the benefit of inherent spatial overlap and diffraction-limited Gaussian beam qualities of the DFG pump and signal beams.

Although both pump and signal beams emerge from the same single mode fiber with a given core diameter, their actual mode field diameter is wavelength dependent and differs slightly. This in effect leads to a different crystal imaging diameter causing incomplete overlap.

The fiber-crystal magnification default limits are determined by the aperture, refractive index and length of the crystal. Overly’ tight focussing can lead to clipping of both pumps and the generated idler beams, while a rather 'loose' focussing decreases the electric field strengths and hence the optical parametric conversion process.
3.6 Mid-Infrared Detectors

A wide variety of sensitive light detectors have been developed for the infrared wavelength region.\textsuperscript{15} Semiconductor based photon effect detectors are the most suitable for mid-infrared absorption spectroscopy offering high sensitivity, low noise and fast response. Photo-conductive (PC) and photo-voltaic (PV) photon effect detectors are well characterized and can be compared in terms of their figure of merit which includes spectral response, normalized noise parameter $D^*$, and operational effects such as drift and linearity. In a PC detector, an incident photon that exceeds the band gap energy of the semiconductor excites an electron from the valence to the conduction band changing the conductivity. The PV detector works like a photodiode with a pn-junction, generating a current that is proportional to the incident number of photons. Table 3.3 shows an overview of suitable commercially available PC / PV detectors. In order to reduce the noise floor, detectors are cooled by either liquid nitrogen or multiple-stage Peltier cooling elements. Peltier cooled detectors have significantly improved and only lack a factor of \textless 10 in S/N as compared to liquid nitrogen cooled devices (in particular InSb detectors) but offer consumable free operation important in field operation applications.
Table 3.3: Figure of merits of commercial mid-IR PC/PV detectors

<table>
<thead>
<tr>
<th>Detector Material</th>
<th>Mode of Operation</th>
<th>Type of Cooling</th>
<th>Spectral Response</th>
<th>D* (cm · Hz$^{-1/2}$ · W$^{-1}$)</th>
<th>Peak Responsitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAs a)</td>
<td>PV</td>
<td>Peltier</td>
<td>1 - 3.4 µm</td>
<td>1.5×10$^{11}$</td>
<td>1.5 A / W</td>
</tr>
<tr>
<td>HgCdTe a)</td>
<td>PC</td>
<td>Peltier</td>
<td>2 - 5 µm</td>
<td>5×10$^{10}$</td>
<td>1.3×10$^{4}$ V / W</td>
</tr>
<tr>
<td>HgCdTe b)</td>
<td>PV</td>
<td>Peltier</td>
<td>2 - 5 µm</td>
<td>1×10$^{10}$</td>
<td>3 A / W</td>
</tr>
<tr>
<td>InSb a)</td>
<td>PV</td>
<td>Liquid Nitrogen</td>
<td>1 - 5.5 µm</td>
<td>1×10$^{11}$</td>
<td>3 A / W</td>
</tr>
<tr>
<td>HgCdTe b)</td>
<td>PV</td>
<td>Liquid Nitrogen</td>
<td>4 - 6 µm</td>
<td>1×10$^{11}$</td>
<td>2 A / W</td>
</tr>
</tbody>
</table>

Product of a) Judson Technologies, Montgomeryville, PA; b) Fermionics, Simi Valley, CA. D*, Signal to noise parameter measured at the peak response frequency, 1 Hz bandwidth and 1 mm$^2$ detector area. The higher D* the better the detector. Peltier cooled detectors are operated at -65 °C.

Table 3.3 indicates sufficiently close figure of merits of Peltier and liquid nitrogen operated either in a PC or PV mode. The proper detector choice is therefore primarily determined by the desired wavelength coverage, D* and operational advantage of Peltier cooled detectors. In practice, the electronic operation of PC and PV type detectors can be the limiting sensitivity factor as a result of electronic drift in a fluctuating temperature environment. Fig. 3.2 shows the electronic signal drift (detector aperture blocked) as the room temperature is changed by ~1°C. The strong temperature dependence of PC mode detectors lies in the intrinsically temperature sensitive pre-amplifier circuit in which the voltage difference of an equally current biased detector and reference resistor is amplified. In comparison, a PV detector generated current is converted by a two component transimpedance amplifier consisting of an operational amplifier and feedback
resistor. Hence, PC operated detectors may require active temperature stabilization if the temperature drift per unit time dominates the precision accuracy of the spectroscopic measurement.

Fig. 3.2: Temperature - time dependent detector response (no incident light). The ambient temperature was slowly changed by 1 °C. Shown is the response of two Peltier cooled detectors, a 2-stage cooled PV-InAs and three-stage cooled PC-MCT.
References for Chapter 3


CHAPTER 4. SPECTROSCOPIC DETECTION

4.1 Direct Absorption Spectroscopy

Sensitive and selective spectroscopic gas detection is based on wavelength dependent absorption of molecules over a given optical path length. The absorption arises from rotational and vibrational transitions that occur in the mid-IR, where most molecules possess fundamental modes that exhibit strong absorption. Absorption lines are both Doppler and pressure broadened with an absorption lineshape that is described either by a Gaussian (low pressure), Lorentzian (higher pressure) or Voigt (intermediate pressure) profile, depending on the contribution of the broadening processes at different pressures. The absorption lines can be scanned using tunable, narrow linewidth mid-IR light and are characterized by frequency position, width, intensity and lineshape. The integrated area of the absorbed light as a function of frequency is directly proportional to the number of molecules. Lambert-Beer’s law describes the interaction of light and molecular gases in which the differential absorption is proportional to the initial light intensity \(I_0\),

\[
I(v) = I_0(v) \cdot e^{-\alpha(v) \cdot L}
\]

(4.1)

with \(I_0(\mu)\), transmitted intensity in the absence of an absorbing species; \(\alpha(\mu)\), the absorption coefficient; and \(L\), optical path length. The absorption coefficient \(\alpha(\mu)\) can be expressed in terms of molecular cross-section \(\rho(\mu)\) and molecules per unit volume \(N\).

\[
\alpha(v) = \sigma(v) \cdot N
\]

(4.2)
The molecular cross-section $\sigma$ is defined by the integrated linestrength $S$ and lineshape function $G_i$,

$$\sigma(v) = S \cdot G_i(v)$$

$$S = \int_0^\infty \sigma \cdot dv$$

$$G_{\text{Lorentz}}(v) = \frac{1}{\pi} \cdot \frac{\gamma_L}{(v_0 - v)^2 + \gamma_L^2}$$

$$G_{\text{Gaussian}}(v) = \frac{\sqrt{\ln 2}/\pi}{\gamma_D} \cdot \exp \left( -\frac{(v-v_0)^2 \cdot \ln 2}{\gamma_D^2} \right)$$

with $\gamma_i$, half width at half maximum (HWHM).

The linestrength $S$ does not depend on pressure but may have a strong temperature dependence that is governed by the Boltzmann distribution of kinetic ro-vibrational energy levels. The Gaussian (Doppler) HWHM ($\gamma_D$) can be computed based on the Maxwell temperature distribution and the Lorentzian (Pressure) HWHM ($\gamma_L$) are expressed by the pressure broadening ($\gamma_{LA}$) of the target species and pressure broadening by other molecules present ($\gamma_{LB}$).\(^1\,^2\)

$$\gamma_L = \left( \gamma_{L_A} \cdot \frac{P_A}{p_0} + \gamma_{L_B} \cdot \frac{P_B}{p_0} \right) \sqrt{\frac{T_0}{T}}$$

where $\gamma_{L_i} = \sigma \cdot n_i \cdot \sqrt{\frac{8}{\pi \cdot \mu \cdot k \cdot T}}$

and $\gamma_D = 3.58 \cdot 10^{-7} \cdot v_0 \sqrt{\frac{T}{M}}$ \hspace{1cm} (4.4)

$\mu$, reduced mass; $k$, Boltzmann constant; $M$, molecular mass; $v_0$, frequency; $T$, temperature in Kelvin.
Extractive gas sampling is usually performed at a reduced pressure 20 - 100 Torr to obtain optimum selectivity. In this pressure regime the observed absorption line is a convolution of Gaussian and Lorentzian lineshapes and described by a Voigt profile, i.e. both Doppler and pressure broadening are contributing to the absorption line profile. The absorption cross section for a Voigt lineshape has been approximated by Whiting\(^3\) in a complex error function,

\[
\sigma_{\text{Voigt}}(v) = \sigma_{\text{Voigt}}(v_0) \cdot \left( (1 - x) \cdot e^{-0.603 \cdot y^2} + \frac{x}{1 + y^2} + 0.016 \cdot (1 - x) \cdot x \cdot e^{-0.80841 \cdot y^{2.25}} - \frac{1}{1 + 0.0210 \cdot y^{2.25}} \right)
\]  (4.5)

with

\[
\sigma_{\text{Voigt}}(v_0) = \frac{S}{2 \cdot \gamma_{\text{Voigt}} \cdot (1.065 + 0.447 \cdot x + 0.058 \cdot x^2)}
\]

\[
\gamma_{\text{Voigt}} = 0.5346 \cdot \gamma_L + \sqrt{0.2166 \cdot \gamma_L^2 + \gamma_D^2}
\]

\[
x = \frac{\gamma_L}{\gamma_{\text{Voigt}}}
\]

\[
y = \frac{|v - v_0|}{\gamma_{\text{Voigt}}}
\]  (4.6)
At higher pressures (>80 Torr), the Voigt function tends to a Lorentzian and at lower pressures (<20 Torr) to a Gaussian lineshape. In practice the sampling pressure is chosen when the Doppler and pressure broadening contributions are equal (i.e. $\gamma_D = \gamma_L$).

Fig. 4.1 shows the peak absorption as a function of sampling pressure for a CH$_4$ absorption line at 3028.721 cm$^{-1}$ and a 1.78 parts-per-million concentration. Indicated are the pressure ranges in which the absorption lineshape has a strong tendency to a Gaussian, Voigt and Lorentzian fit.

![Graph showing peak absorption of CH$_4$ as a function of pressure](image)

**Dominant Lineshape:**
- **Gaussian:** 0 - 10 Torr
- **Voigt:** 10 - 80 Torr
- **Lorentz:** 80 - 760 Torr

**CH$_4$ @ 3028.752 cm$^{-1}$**
- $T=296$ K
- CH$_4$ concentration=1.78 ppm

Fig. 4.1: Peak absorption of methane as a function of pressure. Indicated are pressure ranges in which Gaussian, Lorentzian and Voigt line profiles dominate.

The use of a Lorentzian lineshape fitting function is adequate for direct absorption spectroscopy at pressures of >80 Torr for most molecules. Below this pressure, a Voigt
fit is mandatory, but is also more calculation intensive. Fig. 4.2 shows that only the wings of a Lorentzian lineshape fit experience a small off-set (4% error) to the actual absorption line simulated by Hitran (Doppler, air- and self broadening). The use of a Voigt lineshape fitting is always most accurate but in case of small absorption (<0.5 %), the wings are usually embedded in optical noise and therefore bears no significant advantage over a simpler to process Lorentzian fit.

![Graph showing transmission vs frequency](image)

Fig. 4.2: Methane absorption line at 3028.751 cm⁻¹ at a pressure of 100 Torr and partial concentration of 1.768 parts-per-million. The difference of Lorentzian and Voigt lineshape integrated areas is 4%.

4.2 Dual-Beam and Frequency Modulation Absorption Spectroscopy

Spectroscopic systems using refractive optical elements such as lenses display the occurrence of optical interference (etalons) caused by reflection and scattering and are a
dominant contributing factor to 'technical noise'. In case of direct absorption spectroscopy the minimum measurable absorption is typically $2 \times 10^{-4}$ limited by optical etalons and 1/f noise. In order to attain enhanced sensitivity and suppress electrical and laser intensity noise, high frequency modulation and balanced detection can be applied.

High frequency modulation can translate the absorption signal to lower noise level frequency bands and enables filtering of low frequency noise components. Different modulation techniques have been developed for diode laser spectroscopy and are known as wavelength, single-tone and two-tone frequency modulation spectroscopy. Both techniques require slow tuning of the laser frequency (~100 Hz) across the absorption line and additional high frequency modulation dither. The techniques are distinguished at which modulation frequency and width with respect to the absorption linewidth they operate. In theory, single and two-tone modulation (kHz - MHz) spectroscopy can reach shot-noise limited sensitivity of $10^{-7}$ to $10^{-8}$. Wavelength modulation spectroscopy has mostly been applied with modulation frequencies of typically 50 kHz. Commonly, the signal is detected at the second or higher harmonics which reduces frequency independent intensity changes encountered within the absorption path and the typical diode laser intensity-frequency slope. The signal amplitude is proportional to the concentration but no longer reflects an absolute measurement. Hence, the 2-f signal amplitude has to be calibrated against gas standards to account for non-linearities in the harmonic detection, especially if the observed absorption ranges from small to larger values (>10%).
To achieve full advantage of high frequency modulation detection, optical interference effects (optical noise) have to be minimized. This is accomplished by the use of reflective optics, superior anti-reflection coatings and off-axis tilted optical elements. Furthermore, a thermally stabilized sensor allows to minimize drift and 'freeze' etalons in place. Dominant optical etalons can be fitted to a sinusoidal function and hence removed from the baseline. Alternatively, periodic flushing of the sample cell with zero-air permits the subtraction of baseline fluctuations.⁵

A similar technique called dual-beam spectroscopy employs a signal and reference detector (Fig.4.3). In this configuration the reference detector samples a fraction of the probing beam via a beam splitter before, and the signal is collected past the absorption path, respectively. This technique has been successfully applied to mid-IR DFG based gas sensors and achieves already a demonstrated (field) absorption sensitivity of better than 2.8×10⁻⁵ limited by 1/f noise.⁶ Optical fringes*, baseline fluctuations and residual gas absorption prior to the multi pass cell can be effectively canceled out. Common noise can also be filtered out using sample-and-hold acquisition. Dual-beam spectroscopy also retains inherent calibration of direct absorption spectroscopy.

* In particular optical fringes which are of the same or close to the width of the absorption line.
Fig. 4.3: Schematic of dual-beam absorption spectroscopy. The optical beam path for signal and reference beams from the wedged beamsplitter is equal and allows to cancel out baseline, optical noise (etalon) of the DFG radiation and residual gas absorption prior the multipass cell.

Other detection schemes applied to visible and near-infrared spectroscopy include balanced detection\textsuperscript{7,8} and analog integrative spectroscopy.\textsuperscript{9}

4.3 Data Processing with LabVIEW

LabVIEW software allows flexible and fast development of automatic data reduction routines through graph oriented programming. Although the compiling speed is less than traditional script programming languages such as C++, LabVIEW offers a comprehensive ready-to-use library of data acquisition, manipulation and fitting algorithms. Advances in high-performance electronic surface mounted acquisition boards (16 Bit, 200 kBit/s
PCMCIA card) and PC-notebook (Pentium ~500 MHz) computers results in an effective
data acquisition and processing system.

A typical data acquisition sequence applied to DFG based gas sensors is described and
depicted in Fig. 4.4. The optical intensity is measured by a low-noise detector, pre-
amplified and transmitted to a PCMCIA analog-digital-converter card. A TTL trigger
signal synchronized to the diode laser current saw-tooth enables the card to sample the
signal at a defined rate (max. 200 kBit/s). This process is typically repeated 100 - 1000
times to average out random noise. The signals sampled by the A/D card are read into a
software buffer and averaged. A low frequency Fourier filter is applied to remove low
frequency noise. This sequence is repeated with either the pump or signal beams blocked.
The sampling of the background ambient light provides an absolute reference point and
allows to determine the absolute absorption signal and hence implies inherent calibration.

Fig.4.4 depicts the signal processing for an N₂O absorption line at 2572.1 cm⁻¹. The
spectra was sampled over 200 scans at 200 Hz of room air at reduced pressure of 88 Torr
in a 18 m multi-pass cell. The integrated area amounts to a concentration of 315 ppb with
a residual fit error of 45 ppb.
Fig. 4.4: LabVIEW data processing sequence. Abscissa, frequency point spacing (pt/cm$^1$); Ordinate, I. - IV. arbitrary voltage, V. % and VI. absorbance. (see text for explanation)

The displayed windows represent sequential processing steps:

I. Fourier filtered signal

II. Automatic location of absorption peak

III. Blending out of the absorption line and a 3rd order polynomial fit to baseline to obtain initial polynomial constants
IV. Fit Lorentzian-polynomial function and obtain final polynomial constants

V. Remove polynomial baseline and subtract background signal in order to obtain absolute transmission spectra

VI. Levenberg-Marquardt non-linear least square Lorentzian lineshape fitting to compute the molecular concentration. Also shown is the residual fit deviation in %.

4.4 Gas Handling and Sampling

Extractive gas sampling offers enhanced selectivity and monitoring of absorption lines that would otherwise not be resolved at atmospheric pressures. Typically, an extractive optical system consists of a optical gas cell, preferably oil-free vacuum pump and a pressure controller.

Selection of sample tubing materials, and ambient/gas temperatures are important. Certain molecules, especially those with a strong polarity, can interact with humidity and the surface of the sample tubing leading to physisorption and chemisorption effects. This ultimately determines the amount of molecules ‘seen’ by the mid-infrared light and hence is limiting the accuracy of any absorption measurements. To minimize adsorption effects, the sampling material should be optimized for the species to be detected (PFA Teflon tubing for formaldehyde, stainless steel for Hydrogen Chloride etc.). Heating of the entire gas sampling line 5 - 10 °C above ambient temperature further reduces adsorption and memory effects. Higher flow rates may also more quickly saturate adsorption to the sampling walls. If the gas flow becomes turbulent, pressure induced refractive index
fluctuations can cause beam deflections and add noise to the signal. However, the flow rate for a portable gas sensor system is usually restricted due to the limited capacity of small portable oil-free diaphragm pumps.

In summary, direct dual-beam spectroscopy is less complex and offers inherent calibration but yet achieves sensitivities close to derivative 2-f spectrometers.

References for Chapter 4


CHAPTER 5. PORTABLE MULTI-SPECIES GAS SENSOR

Tunable narrowband mid-infrared radiation from 3.3 to 4.4 µm is generated by a compact fiber-coupled, difference-frequency-based spectroscopic source. The performance of this mid-infrared source is characterized in terms of tunability, non-linear frequency conversion efficiency, spectral resolution, sensitivity and feasibility of automated operation (Chapter 5.2). Examples of high resolution single line absorption spectra and a continuous 270 cm\(^{-1}\) multi-species absorption spectra are reported. Furthermore, the DFG based gas sensor is applied for characterization and test of an industrial trace contaminant control system and field tested at Masaya volcano, Nicaragua for the selective detection of volcanic gas species.

5.1 General Design and Optical Set-Up

The gas sensor developed for field operation utilizes both a fiber pigtailed widely tunable 25 mW external cavity diode laser (ECDL) (814nm - 870 nm), and a fiber pigtailed 50 mW Distributed Bragg Reflector diode laser (DBR) operating at 1083 nm wavelength (see Fig.5.1). Continuous, modehop free tuning of the Littman-type ECDL is achieved by simultaneous rotation and translational movement of the internal feedback mirror about a pivot point with respect to the grating by means of a linear translation stage.\(^1\) This linear translation stage was modified to implement a stepper motor which was operated using a compact computer controlled driver. The ECDL pump beam is passed through a ~30 dB opto-isolator, and was launched into a 5.5 µm core diameter single-mode fiber using a
single-aspheric lens fiber-port assembly with a 48% optical coupling efficiency. The output from the DBR diode laser is also collimated using an aspheric lens, passes through a -45 dB optical-isolator, and is then coupled into standard 6.6 μm core diameter single mode optical fiber terminated with a FC-APC style connector (threaded connector with the tip polished at 8° from normal incidence).

Fig. 5.1: Schematic of tunable DFG multi-species gas sensor. DL, diode laser; WDM, wavelength division multiplexer; CTRL, control; TEC, Peltier thermo-electric cooler.
To increase the mechanical rigidity of the coupling arrangement for the DBR diode laser and ECDL, no beam correction optics were used and the entire diode/optics assembly was mounted on a compact stainless steel miniature-bench. The fiber coupled output power of $\sim 15$ mW from the DBR diode laser is increased to 600 mW by a side pumped Yb-fiber amplifier using a 2W diode laser at 975 nm.\textsuperscript{2,3} Both ECDL and amplified DBR diode laser fiber coupled beams pass through polarization controllers before being combined using a four-port fiber coupler (WDM) with losses of approximately 10% at 1083 and 830 nm, respectively. Two percent of the combined beams are joined to a second fiber coupler, separating the pump and signal beams. Either optical fiber arm can be connected to a wavemeter for absolute frequency calibration. For convenience, the ECDL beam was continuously monitored with a wavemeter (precision: $\pm 0.01$ cm$^{-1}$ @ $\lambda=1$ μm) to provide absolute frequency tuning information via a GPIB (General Purpose Interface Bus) PCMCIA (Personal Computer Memory Card International Association) interface. Alternatively, a solid etalon in combination with a silicon photo diode could be used as a relative wavelength tuning reference.\textsuperscript{4} The other 98% are terminated in FC-APC and mounted onto a ruggedized DFG-conversion stage. This stage contains the optical elements and opto-mechanical mounts pertinent to achieve widely tunable difference frequency generation, including a FC fiber port, imaging lens, PPLN crystal and a CaF$_2$ lens. The collinear pump beams are imaged from the fiber tip into the temperature controlled (Peltier element) antireflection coated PPLN crystal using a f=10 mm achromatic lens. A kinematic optical mount with vertical translation and tilt is used to align the crystal to the beam propagation axis.
Initially, multi-grating PPLN crystals were applied that were available at that time. The subsequent availability and implementation of a fan-out type PPLN crystal allowed continuous quasi-phase matching. For the purpose of automation, the DFG stage was further advanced to a stepper motor driven linear translation stage to tune synchronous with the ECDL stepper motor.

Both single mode fiber launched pump and signal beams possess gaussian beam profiles and when mixed in a 19 mm long PPLN crystal, produce a diffraction limited mid-IR DFG-beam of ~2.9 μW power at ~3.5 μm wavelength. The DFG beam is then collimated using a f=50 mm CaF₂ lens, passing through a Ge-filter to block the unconverted pump beams and directed to a multi pass cell (physical length ~30 cm, actual path length: 18 m or 36 m).⁵

The sensor operated with a typical sensitivity of 2×10⁻⁴ limited by the occurrence of etalon effects introduced by the optical elements. In order to reduce the size of the driver electronics required for the DBR diode laser, Yb amplifier and PPLN crystal mount, compact OEM diode laser current and thermoelectric (TE) drivers were used. For convenient identification and tracking specific absorption line center positions within the scan width, up to five individual reference gas cells (L=5 cm) can be rotated into the DFG-beam path by a stepper motor driven assembly. The sensor is also operated and controlled using LabVIEW software code running on the laptop PC. Fig.5.2 shows the electronic diagram of the gas sensor. Both stepper motor controllers are interfaced to the Laptop PC via an USB (Universal Serial Bus) port. A 16 bit PCMCIA data acquisition card is used to acquire the absorption signal synchronized to a trigger signal, the gas
sampling pressure and temperature. The card also controls a shutter via a digital TTL line for background light subtraction necessary for an absolute spectroscopic absorption measurement. The entire sensor including both optical and electronic elements is packaged into a suitcase with outside dimensions of $61 \times 53 \times 20$ cm (Fig. 5.3). An additional small suitcase ($30 \times 25 \times 14$ cm) contains a diaphragm pump and mass-flow controller which are used for extractive gas sampling at reduced pressure for optimum spectral selectivity and sensitivity.

Fig. 5.2: Diagram of the electronic control and data acquisition system for DFG based multi-component gas sensor.
Fig. 5.3: Photograph of the portable automated DFG based gas sensor in a suitcase measuring $61 \times 53 \times 20$ cm.
5.2 Characteristics

Well characterized spectroscopic sources are desirable for precise and repeatable measurements. Important parameters of the DFG-based mid-IR sources for accurate gas detection are the stability of laser intensity, consistent linewidth, repeatable wavelength tuning and phase-matching. In the following, the characteristics of the diode laser pump sources and fiber amplifier are presented in more detail.

5.2.1 Diode Laser Wavelength Tuning

For acquisition of individual absorption lines the DBR diode laser is current modulated to provide rapid linear frequency tuning (~0.01 cm\(^{-1}\)mA\(^{-1}\)). A frequency scanning width of as much as 1 cm\(^{-1}\) is sufficient to scan even over pressure broadened absorption lines at atmospheric pressure (see Fig.5.4). Coarse tuning is provided by the ECDL from 814-870 nm leading to a mid-IR tuning range from 3.3 to 4.4 \(\mu\)m. The wavelength tuning curve for the Littman-type external cavity pump laser as a function of the stepper motor rotation (dial position) is shown in Fig.5.5. A miniature coupler from the stepper motor shaft to the ECDL tuning screw was used. This coupler permitted angular, radial and lateral misalignment of the stepper motor shaft and therefore suppressed stress to the ECDL tuning mechanism. The stepper motor resolution was 1/3600 steps per revolution and provided an experimentally measured linear ECDL frequency tuning rate of 0.018 cm\(^{-1}\) per step. The frequency tuning was superimposed by a sinusoidal like modulation, corresponding to a peak deviation of 0.15 cm\(^{-1}\) as can be seen from the inset of Fig.5.5. This inset also shows a residual backlash of 225 ± 15 steps inherent to the ECDL device used in this work.
Fig. 5.4: DBR diode laser power and frequency vs. forward current at 19.5 °C.

Fig. 5.5: ECDL frequency tuning characteristic using stepper motor control.
5.2.2 Yb\textsuperscript{3+} fiber amplifier

Only several mW of injected power at 1083 nm was required to saturate the Yb fiber amplifier consisting of a 7.2 m long double clad fiber, pumped by a v-groove fiber coupled 975 nm pump diode laser, as shown in Fig. 5.6. Also depicted is the amplified output power as function of pump diode current. The broad stripe 975 nm pump diode laser provided a maximum of 2W pump power at a current of 3A with a diode to fiber coupling efficiency of 90%. Furthermore, a Peltier element was used to tune the pump diode laser operating temperature and hence its wavelength towards the highest absorption of the Yb fiber centered around 975 nm.

Fig. 5.6: a) Yb\textsuperscript{3+} fiber amplifier output power at 1083 nm at 2W, 975nm pump as a function of seed power; b) Output power as a function of pump diode current with and without losses introduced by the WDM. DCF, double clad fiber.
5.2.3 Quasi-Phase Matching and Mid-IR Tuning Characteristics

Quasi-phase matching of widely tunable pump sources requires adjustment of either the poling period, crystal temperature or a combination of both. Initially, single grating PPLN crystals were tuned by temperature from 20°C to 250°C to achieve quasi-phase matching for different pump wavelengths. Further implementation of 1 mm wide poling channels of different periods (typically $\Delta \Lambda=0.1 \, \mu\text{m}$ steps) reduced temperature tuning requirements to less than $\delta T=40 \, ^\circ\text{C}$ on a single LiNbO$_3$ crystal.

5.2.3.1 Multi-Channel PPLN

QPM properties of the multi-channel PPLN crystal ($\Lambda=22.4 - 23.1 \, \mu\text{m}$; 0.1 $\mu\text{m}$ steps) were investigated using two approaches.

![Graphs showing quasi-phase matching properties](image)

Fig. 5.7: Two quasi-phase matching approaches by a) changing the nominal grating period or b) temperature tuning at a fixed nominal grating period.
Firstly, the PPLN crystal was translated perpendicular to the optical axis to phase match the pump (ECDL) and signal (DBR) wavelengths for the respective nominal grating period at a constant temperature of 24.5 °C. Secondly, the 23.1 µm channel of the PPLN crystal was aligned to the optical axis and temperature tuning applied to phase match the signal, pump and DFG beams from 3.65 to 4.4 µm (Fig. 5.7). The measured and theoretically predicted phase matching periods agree well and are within the manufacturer's stated tolerances for the absolute grating period.\(^6\)

5.2.3.2 Fan-Out PPLN

Continuous quasi-phase matching over the entire tuning range of the sensor is achieved by using a periodically poled lithium niobate crystal with a fan-out grating structure.\(^7\) In this configuration the grating period continuously increases from 22.4 µm to 23.3 µm over a 1 cm wide crystal. Plotted in Fig. 5.8 is the relative crystal position versus the DFG wavelength for two temperatures, 26°C and 44°C. The PPLN crystal temperature can be set to match the available grating periods with the ECDL wavelength tuning range which, for this sensor, is 44°C. The measured PPLN phase matching bandwidth is 28 cm\(^{-1}\) (Fig. 5.8). This value can be compared with a theoretically computed phase matching bandwidth of 12.5 cm\(^{-1}\) @ 3.6 µm for normal incidence non-diverging pump beams. Similar to the ECDL stepper motor interface, a miniature joint coupling was used to connect to the PPLN crystal linear translation stage (Vernier set screw, 0.5 mm linear translation per revolution). In addition a 48 pitch, 1:1 Miter gear
was implemented to realize a compact stepper motor arrangement with no noticeable loss of precision.

Fig. 5.8: Continuous quasi-phase-matching with a fan-out grating type PPLN crystal.

5.2.3.3 Mid-IR Tuning

The generated mid-IR power as a function of wavelength was recorded using a multichannel PPLN crystal (L=19 mm, 0.5 mm thickness, A=22.4 to 23.1 μm, in 0.1 μm steps), shown in Fig. 5.9. For incident powers of 6.2 mW and 540 mW of the pump and signal beams respectively, a maximum idler power of 2.8 μW at 3.46 μm was generated (corrected for losses of 3.4 % from the CaF$_2$ lens and a ~ 4 % wavelength dependent loss of the Ge filter). Also shown is the fiber coupled ECDL power with the maximum at its gain center of 850 nm.
Fig. 5.9: DFG power as a function of idler wavelength and the ECDL power coupled into the optical fiber as a function of ECDL wavelength.

Fig. 5.10: Conversion efficiency as a function of idler wavelength.
The discrepancy between experimental results and the expected wavelength dependence at longer wavelengths is principally the result of absorption losses in the LiNbO₃ crystal beyond 4.0 μm (α~0.3 cm⁻¹ at 4.2 μm),⁸ and a strong CO₂ band from 4.1 to 4.4 μm responsible for absorption of the IR radiation between the crystal and IR detector. The peak DFG conversion efficiency measured was 0.88 mW/W² for the 19 mm long crystal at 3.3 μm. In comparison, the theoretical DFG conversion efficiency yields 1.69 mW/W².⁹ Factors that contribute to the reduced experimental conversion efficiency include differing pump-beam mode field diameters in the fiber (1/e² diameters: 850 nm ~ 5.5 μm, 1083 nm ~ 6.6 μm) leading to incomplete overlap of the imaged pump beams in the crystal. Optical tilt and off-center position alignment of the imaging lens can introduce optical aberration. Some non-uniformity in conversion efficiency across individual PPLN channels has also been observed.

5.2.4 Spectroscopic Performance

The spectroscopic performance of the DFG-based gas sensor was investigated with respect to its spectral selectivity (i.e. linewidth), sensitivity (minimal detectable absorption), capability of measuring numerous species within its tuning range, and overall performance during unattended long term operation.

5.2.4.1 Spectroscopic Selectivity

The selective detection of gases using fingerprint mid-IR absorption lines is mainly determined by the sampling pressure and the spectral linewidth of the probing light.
The DFG linewidth was indirectly measured by recording a low pressure absorption Q-branch CH$_4$ spectrum near 3.3 µm. At a pressure of 1 Torr, the absorption line is only broadened by a Doppler shift resulting in a Gaussian lineshape. Fig. 5.11 shows the absorption spectra of CH$_4$ at 1 Torr. The DFG-linewidth (assumed to be Gaussian) was obtained by de-convolving the measured linewidth with the Doppler linewidth (FWHM) according to

$$ \Delta \nu_{\text{DFG}} = \sqrt{\Delta \nu_{\text{Measurement}}^2 - \Delta \nu_{\text{Doppler}}^2} $$

(5.1)

$\Delta \nu$, FWHM.

Fig.5.11: Doppler broadened absorption spectrum of CH$_4$ (Q-branch) near 3.3 µm.
Alternatively, the linewidth can be determined by measuring the Lorentzian contribution of a given absorption line fitted to a Voigt-profile as a function of pressure (20-200 Torr). The zero crossing (p=0 torr) of this linear pressure dependence provides the inherent DFG-linewidth.

The simultaneous implementation of high power and narrow linewidth single-frequency operation in a diode laser based DFG architecture can be accomplished with fiber amplifiers that possess the capability of increasing the power and maintaining the seed spectral properties without gaining complexity. Fig.5.12 shows an absorption line with and without the fiber amplifier switched on, indicating no effect of amplifier induced line broadening.

![Graph showing absorption lines with and without fiber amplifier switched on.](image)

**Fig. 5.12:** Overlay of HCl absorption lines at 2843.6 cm\(^{-1}\) acquired with and without the fiber amplifier switched on. Sample pressure was (5±2) Torr, length 2".
5.2.4.2 Spectroscopic Sensitivity, Calibration and Multi-Species Detection

Several gas species with absorption lines within the tuning range of this mid-IR source are evaluated. Suitable, spectrally isolated absorption lines were identified, recorded, calibrated with gas standards and the measured spectroscopic parameters compared with the Hitran$^{10}$ database. Table 5.1 summarizes the detected gas species and indicates sensitivities obtained.

Table 5.1: Detected trace gas species and spectroscopic figure of merits

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>Center Frequency (cm$^{-1}$)</th>
<th>Linestrength (cm$^{-1}$ molecule$^{-1}$ at 25 °C)</th>
<th>Minimal detectable Concentration (ppm·m)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>3028.751</td>
<td>9.519×10$^{-20}$</td>
<td>0.23</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>2880.818</td>
<td>7.809×10$^{-21}$</td>
<td>1.8</td>
</tr>
<tr>
<td>HCl</td>
<td>2843.624</td>
<td>3.692×10$^{-10}$</td>
<td>0.05</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>2831.642</td>
<td>5.2×10$^{-20}$</td>
<td>0.54</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>2572.107</td>
<td>2.145×10$^{-20}$</td>
<td>1.02</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2386.55</td>
<td>5.347×10$^{-21}$</td>
<td>0.0072</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>2505.239</td>
<td>1.332×10$^{-21}$</td>
<td>40</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3030.726</td>
<td>8.91×10$^{-22}$</td>
<td>36</td>
</tr>
<tr>
<td>CH$_3$OH$^{11}$</td>
<td>2831.64</td>
<td>NA</td>
<td>8 estimated (c.f. page 84)</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>~3040</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

$a$: Based on 0.02 % residual baseline noise
Fig. 5.13: Individual spectra of CO₂, N₂O, H₂CO, NO₂, HCl, CH₄ (Details are listed in Table 5.2).

Figure 5.13 shows individual direct absorption spectra of six gas species that were acquired using a multi-pass cell aligned for 18 m path length at a reduced pressure of 88 Torr. CH₄, HCl and H₂CO trace gas measurements were calibrated against gas standards while the other species were measured in room air. The spectra were processed to remove baseline fluctuations, normalized (background subtracted) and fitted to a Lorentzian lineshape using the Levenberg-Marquardt method.
The concentration was calculated according to:

\[ C = \frac{-\text{OD}_{\text{peak}} \cdot \gamma_L \cdot \pi \cdot T}{S \cdot L \cdot p \cdot N_L} \]  

(5.2)

with \( \text{OD}_{\text{peak}} \) denoted as the peak optical density; \( \gamma_L \), Lorentzian HWHM; \( S \), linestrength; \( L \), optical path length; \( p \), pressure; \( T \), temperature; \( N_L \), Loschmidts' number.

The experimentally measured linewidths of individual species are, in general, broader than the predicted linewidths (from Hitran96) which is consistent with a measurement of a broadened DFG linewidth. Acquisition of a Doppler broadened methane spectra at the time of these spectral measurements revealed a DFG linewidth of 190 MHz. This linewidth was attributed to the 1083 nm diode current driver and after replacing this driver, a narrow DFG linewidth of 42 MHz was subsequently measured (Fig.5.11). In the case of HCl, the concentration was obtained from a calibrated cylinder specified at 24.4 ppm (in \( N_2 \)) and we measured the HCl concentration to be \( 19.5 \pm 0.2 \) ppm. This measurement used alternatively the \( ^35 \text{Cl} \) line at 2944.913 cm\(^{-1} \) and the \( ^37 \text{Cl} \) line at 2942.721 cm\(^{-1} \) \( (S = 5.033 \times 10^{-19} \text{ cm/ molecule and } 1.606 \times 10^{-19} \text{ cm/ molecule, respectively})\).
Table 5.2: Data acquisition parameters, measured spectral characteristics and concentrations compared to the spectral data predicted by Hitran96 database of spectra shown in Fig. 5.13.

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Scan range (cm(^{-1}))</th>
<th>Avg. time (sec)</th>
<th>P (torr)</th>
<th>Linewidth FWHM (cm(^{-1}))</th>
<th>Hitran96 Spectra FWHM (cm(^{-1}))</th>
<th>Meas. Conc.</th>
<th>Specified Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>0.34</td>
<td>2.1</td>
<td>88</td>
<td>0.0201</td>
<td>0.0157</td>
<td>444 ppm</td>
<td>Room air</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>0.29</td>
<td>2.1</td>
<td>88</td>
<td>0.0223</td>
<td>0.0199</td>
<td>315 ppb</td>
<td>Room air</td>
</tr>
<tr>
<td>H(_2)CO</td>
<td>0.27</td>
<td>2.1</td>
<td>88</td>
<td>0.0279</td>
<td>0.0285</td>
<td>860 ppb</td>
<td>862 ± 15 ppb</td>
</tr>
<tr>
<td>HCl</td>
<td>0.33</td>
<td>2.1</td>
<td>87</td>
<td>0.0239</td>
<td>0.0203</td>
<td>19.5 ppm</td>
<td>24.4 ppm (± 5%)</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>0.28</td>
<td>2.1</td>
<td>88</td>
<td>0.0180</td>
<td>0.0164 (2 lines)</td>
<td>7634 ppb</td>
<td>13.0 ppm (± 5%)</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.32</td>
<td>2.1</td>
<td>88</td>
<td>0.0191</td>
<td>0.0185</td>
<td>1756 ppb</td>
<td>Room air</td>
</tr>
</tbody>
</table>

The overall instrument performance, including repeatable precision and suitability of the sensor for long term measurements was assessed by monitoring of a discrete CH\(_4\) line at 3038.751 cm\(^{-1}\) for an extended time period. In this experiment a calibrated 1772.7 ± 1 ppb mixture of CH\(_4\) in air\(^{12}\) was continuously flown through the multi-pass cell at a pressure of 88 torr. The experimental results are shown in Fig. 5.14. Over a 19 minute period (131 measurements, 4s average per measurement), the gas sensor measured a concentration of 1830 ppb, which is within 3.1 % of the calibrated concentration (this CH\(_4\) concentration measurement used the Hitran96 predicted linestrength of 9.519 \(\times\) 10\(^{-20}\) cm/molecule for the 3028.751 cm\(^{-1}\) line). The measurement standard deviation was ± 0.8 % (± 15 ppb) which corresponds to absorption sensitivities of ± 2 \(\times\) 10\(^{-4}\).
5.2.5 Continuous Long-Term Gas Detection

The DFG based gas sensor was used in several long term tests. In a first test, the sensor was tuned to a CO₂ line at 2385.77 cm⁻¹ (4.2 μm) and monitored the CO₂ concentration in ambient laboratory air continuously at reduced pressure of 80 Torr for a three day period as depicted in Fig.5.15. The ro-vibrational CO₂ absorption lines at ~4.2 μm have a frequency spacing of ~0.7 cm⁻¹ (21 GHz). In this case, it is advantageous to perform spectroscopic absorption measurements of CO₂ at a reduced sampling pressure to avoid a zero baseline offset. The CO₂ concentration increases and decreases rapidly respectively at times with and without human activity in the laboratory as shown in Fig.5.15. The dynamic detection range at this CO₂ absorption line is 0.5 ppm to 2200 ppm (100%
absorption) at a pressure of 80 Torr for an 18 m optical absorption path length configured multi pass cell and a residual optical noise of $2 \times 10^{-4}$. After two hours into the CO$_2$ sampling test, human breath was briefly sampled and caused a sharp increase to CO$_2$ levels of more than 2200 ppm, saturating the absorption signal. However, it is possible to tune the DFG wavelength to a weaker CO$_2$ transitions to measure higher concentrations, or to lower frequencies to access a stronger CO$_2$ transition at 4.2 μm when measuring low CO$_2$ concentrations. The DFG-based gas sensor measured higher ambient background levels than the atmospheric concentrations measured by the National Oceanic and Atmospheric Administration (NOAA).$^{13}$ This may be due to the fact that the CO$_2$ and other gas species concentration levels tend to be higher in urban areas such as Houston, TX.

![Graph](image)

Fig. 5.15: Ambient CO$_2$ laboratory sampling over a of 42 hours time period.
In another long term test, the DFG sensor was tuned to a methane absorption line at 3028.751 cm\(^{-1}\) (3.3 \(\mu\)m) to monitor ambient air continuously for a 7 day period. The DFG based gas sensor was located in an air-conditioned laboratory environment with the sensor being located close to an air condition ventilation inlet. For this test, the multi pass cell was aligned to 36 m optical path configuration for increased detection sensitivity. About 20 minutes into the test, the DFG based gas sensor was set to acquire a dark voltage before and after each absorption scan and computed an average absorption value. This effectively reduces the noise present in a CH\(_4\) measurement evident in Fig.5.16. Furthermore, one can see that the methane concentration peaks around midnight and increased to over 5000 ppb after heavy rain storms. These methane trends were confirmed to be real by an intercomparison with another fiber coupled DFG based gas sensor.\(^{14}\) At the bottom of Fig.5.16 the corresponding DFG output power signal is plotted. A general drift of 0.03\% / hour with a 1.3 \% standard deviation is measured, except of a few incidents when a cooling fan attached to the Yb fiber amplifier housing stopped operation. This effectively changed the temperature dependent pump diode wavelength which resulted to a shift to a weaker absorption cross-section region of the Yb doped fiber amplifier and lead to reduced amplifier gain.
Fig. 5.16: Continuous detection of ambient CH₄ for a 7 day period.
Fig. 5.17: Inter-comparison of long term CH₄ concentration measurements by two independent DFG based gas sensors indicating both CH₄ concentrations and deviation in ppb.

A second CH₄ sensor, described in Ref.14, was set up in close vicinity and operated at the same DFG wavelength and measured ambient laboratory air with a 36 m open path length multi-pass cell at atmospheric pressure. Fig.5.17 shows the superimposed CH₄ concentration measurements versus time plots of the two independently operating DFG based trace gas sensors over a four day period. Both sensors followed the same profile and measured the CH₄ concentration with an average difference of 50 ppb (standard deviation), which is well within the accuracy of both instruments (5%). For calibration of
the DFG based gas sensors a calibrated gas mixture was flown through the multi pass cells. The good agreement between atmospheric and low sampling pressure (88 Torr) measurements indicate a high spectral purity of the two DFG based gas sensors and confirms the applicability of a Lorentzian lineshape function.

5.2.6 Automation and Continuous Wavelength Tuning

Automation of the ECDL wavelength and quasi-phase matching period of a fan-out grating is three-fold. It provides a) the capability of acquiring long wavelength intervals of absorption scans b) automatic sequential multi-species gas measurements and c) provide means of automatic control and feedback to compensate thermal and electronic drift causing wavelength drift.

For example, Fig.5.18 shows a continuous absorption spectra of methane (CH₄) and formaldehyde (H₂CO) acquired over a 270 cm⁻¹ wide tuning range from 2700 cm⁻¹ (3.70 μm) to 2970 cm⁻¹ (3.37 μm) with a DFG line width resolution of 40 MHz. The measurement was performed using a 5 cm long reference gas cell containing 8 % of CH₄ and 0.65 % of H₂CO with an estimated total pressure of 50 Torr. A 200 Hz current modulation of the DBR-diode laser provided an effective scanning width of 0.33 cm⁻¹. The ECDL was consecutively tuned by an 8 step (~0.15 cm⁻¹) increment to take into account the above mentioned sinusoidal offset. Absolute wavelength accuracy was provided by a wavemeter. Each spectrum was averaged over 5 scans (25 msec) and subtracted by a 5 scan average dark voltage measurement to obtain absolute transmission. The recorded spectroscopic data files that include an absorption scan, dark voltage scan,
and corresponding wavelength log were automatically processed with a LabVIEW software programmed algorithm to connect the acquired spectra (indicated by the dashed circles in the inset of Fig.5.18), and to remove redundant data points of consecutive data scans. Furthermore, a polynomial fit algorithm can be applied to improve the baseline overlap of two consecutive scans.

Fig. 5.18: Measured absorption spectra of formaldehyde and methane over 270 cm\(^{-1}\) centered at 2850 cm\(^{-1}\).
Fig. 5.19: Comparison of the relative frequency drift for a stepper motor controlled and free running ECDL operation as a function of time.

Automated compensation of wavelength drift due to temperature changes is a further advantage of using stepper motor controlled wavelength tuning and quasi-phase matching. Critical components susceptible to temperature fluctuations include detector amplifier, diode laser drivers and temperature controllers and most significantly, the wavelength stability of the external cavity diode laser. Fig. 5.19 shows an example of automated wavelength drift compensation by means of the two stepper motors. For this measurement the absorption peak location of a CO₂ transition line at ~4.2 μm was monitored after the DFG based gas sensor was moved from an outdoor to an indoor environment with an ambient temperature difference of ~5°C. At the beginning of the
measurement the absorption line was centered within the absorption scan width of 0.32 cm\(^{-1}\). The LabVIEW software was programmed to compensate for the drift of the absorption by appropriately wavelength tuning the ECDL if the peak location was outside programmed maximum and minimum boundary conditions. For comparison, the total wavelength drift that can occur if the gas sensor system is not actively controlled is also shown in Fig. 5.19.

5.3 Applications

Real-world gas species measurements are often encountered by harsh environmental conditions such as high humidity, vibration, electro-magnetic noise and constant changes in ambient temperature. This makes operation of any sensor a challenging task. In the following two sections 5.3.1 and 5.3.2, the DFG-based multi-species gas sensor was extensively tested in an industrial environment and outdoors atop an active volcano. Both tests represent the first successful operation of all optical, room-temperature mid-infrared absorption gas sensors outside a laboratory environment.

5.3.1 Evaluation of a Trace Contaminant Control System

The laser based DFG multi-component gas sensor optimized for real-time formaldehyde concentration measurements at the ppb level near 3.5 \(\mu\)m (2831.6 cm\(^{-1}\)) was installed at a Trace Contaminant Control System (TCCS) test rig at TDA Research, Inc. (Wheat Ridge, Colorado) depicted in Fig. 5.20 and operated for a period of five days (August 16-20, 1999). The purpose of this investigation was to determine if a VoCat catalyst (Volatile
organic catalyst) used during the 1997 NASA Johnson Space Center (JSC) 90 day Luna: Mars comprehensive life support test in a 20 foot chamber\textsuperscript{15} had been affected by their use in these tests. To accomplish this, samples of the catalyst used at JSC were tested and compared to samples of previously unused catalyst along with used catalyst that had been regenerated by treatment in air at either 260°C or 400°C. All catalyst samples were tested using a feed consisting of 10-12 ppm methanol in air at a flow rate of 6.25 ltr min\textsuperscript{-1}. Water was added to the feed to saturate the feed to 50\% relative humidity.

Fig. 5.20: Schematic of the TCCS and DFG based gas sensor system (gray shaded) experimental set-up.

In order to ensure accurate operation of the DFG based gas sensor for the selective detection of formaldehyde, two gas cylinders containing a calibration mixture (Scott Specialty gases, H\textsubscript{2}CO=772 ppb balanced with 66.1 ppm CH\textsubscript{4}) and a zero air gas mixture
(Scott Specialty gases, TechniPure) were installed, respectively. Either gas cylinder was periodically switched into the sample line of the DFG based gas sensor using a 4-way valve switch to ensure calibration and selectivity to potentially interfering gases. The continuous sample gas flow through the DFG-sensor was provided by a compact flow control system (built inside a small suitcase) that consists of a two-stage diaphragm pump, a flow controller and micro-particle filter. For the detection of methanol and CO/CO₂ a gas chromatograph (SRI instruments, FID detector, Detection limit: 1 ppm @S/N=5) and an infrared analyzer (ZRH, California Analytical, range: 0-200 ppm ± 2 ppm) were alternately connected to the catalytic reactor input and output. Furthermore, thermocouples were placed at various TCCS/DFG based gas sensor control and sampling positions as indicated in Fig.5.20 by T1 to T4. The catalytic conversion efficiency of MeOH to CO₂ was used as an indicator, representing a range of VOC's to be oxidized by the catalyst under investigation. For an evaluation of the performance of different used and new VoCat's in the TCCS system the following parameters were acquired by the TCCS and DFG based gas sensor system as listed in Table 5.3. The parameters #1 to #7 are indicators used for the control of the TCCS, whereas #8 to #14 are required input parameters to compute the absolute formaldehyde concentration and evaluate the performance of the DFG based gas sensor. At the time of this test, the DFG based gas sensor ECDL and fan-out PPLN crystal were not yet stepper-motor controlled and hence manually adjusted.
Table 5.3: Parameter acquired by the TCCS and DFG based gas sensor.

<table>
<thead>
<tr>
<th>#</th>
<th>Variable / Sensor</th>
<th>Location / Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temperature / Thermocouple</td>
<td>T1 / Inlet, Pre-heater</td>
</tr>
<tr>
<td>2</td>
<td>Temperature / Thermocouple</td>
<td>T2 / Reactor</td>
</tr>
<tr>
<td>3</td>
<td>Gas Temperature / Thermocouple</td>
<td>T3 / Outlet</td>
</tr>
<tr>
<td>4</td>
<td>MeOH / GC</td>
<td>Inlet &amp; outlet of reactor, Gas Chromatograph, ZRH, range: 0-200 ppm</td>
</tr>
<tr>
<td>5</td>
<td>CO₂</td>
<td>Inlet &amp; outlet of reactor, SRI instruments, FID</td>
</tr>
<tr>
<td>6</td>
<td>Flow-rate / Flow-meter</td>
<td>Inlet of reactor</td>
</tr>
<tr>
<td>7</td>
<td>Flow-rate / Flow-meter</td>
<td>Outlet of GC / IR Analyzer</td>
</tr>
<tr>
<td>8</td>
<td>H₂CO / DFG</td>
<td>Outlet of reactor</td>
</tr>
<tr>
<td>9</td>
<td>Gas Temperature / Thermocouple</td>
<td>T4 / Inlet DFG gas sensor</td>
</tr>
<tr>
<td>10</td>
<td>Pressure / Baratron</td>
<td>DFG gas sensor / sampling gas pressure</td>
</tr>
<tr>
<td>11</td>
<td>Temperature / Thermistor</td>
<td>Adjacent to DFG gas sensor / Ambient room temperature</td>
</tr>
<tr>
<td>12</td>
<td>Absorption line position / DFG</td>
<td>DFG gas sensor / Software detected absorption peak position, stability indicator</td>
</tr>
<tr>
<td>13</td>
<td>Detector bias voltage / DFG</td>
<td>DFG gas sensor / Bias signal off-set, stability indicator</td>
</tr>
<tr>
<td>14</td>
<td>DFG-probe signal / DFG</td>
<td>DFG gas sensor / Optical probe power, stability indicator</td>
</tr>
</tbody>
</table>

During the five day testing period of the TCCS under different conditions and use of different VoCat samples, the DFG based gas sensor operated daily 8 to 11 hours. Higher room temperature caused the development of optical fringes due to thermal expansion
that were not observed at lower temperatures. This limited the sensitivity to minimum detectable concentrations of 30 - 50 ppb on the average for S/N=1.

In the following, measurements during the TCCS evaluation are presented and discussed that are pertinent to the spectroscopic performance of the DFG based gas sensor for given operating conditions.

Initially, a used VoCat is investigated that was operated at NASA-JSC. The formaldehyde concentration was monitored at reactor temperatures ranging from 180 to 260 °C. In Fig. 5.21, the formaldehyde concentrations measured at the exit of the catalyst bed are shown at the various test temperatures. Starting at a reactor temperature of 180°C, the temperature was increased in steps of 10°C to 260°C. Fig. 5.21 shows that the TCCS formaldehyde generation directly follows the applied temperature profile. When the temperature was stepped up from 180 to 190°C at 11:45h, the TCCS feedback circuit followed a harmonic oscillation relaxation function and settled at the pre-set temperature 35 minutes later. As the feedback circuit was improved the relaxation time was reduced to ~5 minutes. Temperature changes of ~1°C resulted in a ~150 ppb change of the formaldehyde concentration as measured by the DFG based gas sensor. When the reactor temperature was set to 260°C, the formaldehyde concentration decreased and reached a level of 1 ppm after 95 minutes. At this point the reactor temperature was further reduced to 210 °C to determine whether the catalyst surface was regenerated at 260 °C. This was not the case, since the formaldehyde concentration quickly increased to a comparable high level of 4.5 ppm that was observed earlier in the test.
Fig. 5.21: Formaldehyde output concentration and catalyst temperature trend. The inset shows the rapid response to sampling zero air followed by a gas standard of 772 ppb.

The same catalyst used in the first test shown in Fig. 5.21 was subsequently heated for 16 hours at a temperature of 450°C in 1 SLPM air in an attempt to regenerate the catalyst surface. Fig. 5.22 show important recorded parameters pertinent to the performance of the DFG based gas sensor.
Fig. 5.22: Recorded parameters during a catalyst test.
At 9:40 h and catalyst temperature of 180 °C, a MeOH feed of 11.8 ppm was established. The formaldehyde concentration increased and leveled off at about 4.5 ppm. When the reactor temperature was increased to 260°C at 10:42 h, the formaldehyde concentrations were reduced to about 100 to 200 ppb with a background noise level corresponding to 40 ppb (S/N=1) as determined by zero air sampling from 11:23 h to 11:35 h. Compared to the previous day, the concentration was about 5 to 10 times less at the same reactor temperature. At 12:07 h the temperature was again reduced and caused an increase of the formaldehyde concentration.

At 10:15 h, the start of an unrelated experimental rig (situated 4 m away from the TCCS rig) with two 500°C heaters caused changes of room temperature. Fig. 5.22 shows the effects on the peak absorption location, MCT bias voltage and the DFG signal. The ECDL was manually tuned to compensate the wavelength drift. At 12:15 h, the PPLN crystal position was adjusted to recover the optimal phase-matching condition as shifted by the change of temperature. However, both effects, show no correlation to the detected concentration or change in accuracy.

During warm-up or cool down cycles, methanol levels of up to 10 ppm were present at the TCCS output. These high levels of methanol vapor were also detected by the DFG gas sensor in form of three distinct methanol absorption lines in close vicinity to the formaldehyde absorption line. For comparison, Fig. 5.23 shows an overlay of a formaldehyde spectrum with a methanol spectrum of comparative absorption strength. Comparing the measured formaldehyde concentration of 730 ppb and a methanol concentration measured by a gas chromatograph of 11 ppm, it is estimated that methanol
has a 15 times weaker absorption linestrength than the formaldehyde transition at 2831.6 cm$^{-1}$. In the case of a low formaldehyde concentration of $\sim$100 ppb, a methanol concentration of 1.5 ppm would cause an uncertainty of 100%. However, at higher formaldehyde levels such as at the ppm levels, a methanol interference of 1.5 ppm would only introduce a systematic error of less than 10%.

Fig. 5.23: Overlay of methanol and formaldehyde absorption spectra of comparable absorption.

The overall test results$^{16}$ showed that catalysts samples, which had been used in the 1997 T CCS test at NASA-JSC were much less active for methanol conversion at all temperatures and also showed much higher selectivity for formaldehyde compared to the sample of previously unused VoCat catalyst. Regenerating used catalyst samples by heating the catalyst in air appeared to increase activity and reduce selectivity for formaldehyde. A VoCat catalyst sample regenerated at 460 °C had 70% activity and 50% selectivity at the end of a 1 hour 20 minute period at 180°C. In addition a sample
regenerated at 260°C was more active and less selective for formaldehyde at a test temperature of 260°C compared to a non regenerated sample used in the TCCS tests. Finally, fresh VoCat catalyst samples did not produce measurable H₂CO levels within our experimental precision's of 30 ppb following treatment with 1.5 ppm H₂S.

5.3.2 Monitoring of Volcanic Gases at Masaya Volcano

Volcanic gases are effective indicators from earth's interior. Measurement of emission rates and ratios provide information on conditions of magmatic sources and fluid rock interactions. Study of emitted gases such as HCl, SO₂ and CO₂ provides not only information to assess volcanic hazards but also to understand their contribution and consequences to the atmosphere and environmental impact to their immediate vicinity.¹⁷

The motivation for a field experiment at Masaya volcano located in Nicaragua, was to establish the potential of DFG based gas sensors applied to real-time, sensitive and selective monitoring of gas species emitted by an active volcano. Simultaneous measurements were performed by an open-path infrared Fourier-transform spectrometer (FTIR) operated by the volcano remote sensing group of the Geography Department, University of Cambridge, UK.¹⁸ This provides a useful inter-comparison of the two optical techniques.

The inherent advantage of DFG based gas sensing over FTIR spectrometers is real-time quantitative response (2-10s) and selectivity (40 MHz). The field portable FTIR instrument only offers a resolution of 15 GHz and the acquired data requires a post-processing to determine measured gas concentration levels. On the other hand, the FTIR
covers a wider wavelength range of 1.7 μm to 20 μm and can capture absorption signatures of many molecules in a short acquisition time (0.5 s).

The volcano itself has a crater diameter of ~500 m and a depth of ~200 m. The last minor strombolian explosion was reported three years ago, but more important, this volcano has been degassing for centuries. The current degassing rates are 20 kT h\(^{-1}\) for HCl and 60 kT h\(^{-1}\) for SO\(_2\).\(^{19}\) This compares to a total release of SO\(_2\) from the United Kingdom of only 0.2 kT h\(^{-1}\).\(^{20}\)

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**Fig. 5.24:** Sketch of Masaya volcano topography. Close access to the crater rim is possible from two plateaus (Mirador 1 and 2) connected by a road. Indicated is the predominant wind direction and typical associated cone of the emitted gas plume during the experiment.
The DFG based gas sensor including support equipment was shipped to Nicaragua and tested for operation at a base camp located at the foot of the volcano crater. Mechanical sensors that were attached to the shipping case indicated a shock exposure to at least 20G. Operation of the DFG based gas sensor was achieved in about 45 minutes (including test of individual components) after arriving at base camp. All fiber optic connections, DFG conversion optics and multi-pass cell did not require any adjustment. This emphasizes the robustness achieved through fiber optics.

Fig.5.25: DFG based gas sensor system in the rear compartment of a sport utility vehicle at the Masaya volcano crater rim.

For measurements at the crater rim, the DFG based gas sensor was placed in the rear compartment of a compact sport utility vehicle (SUV) (Fig.5.24). Electric power was provided by a gas generator ($P_{max}=1000W$). The generator was placed approximately 30
m downwind to avoid the detection of artificially produced background gases. Ambient air was sampled at a rate of ~0.2 ltr min⁻¹ through a 4 m long Teflon tube (0.5" diameter) mounted to a pole outside the SUV. Weather conditions during the April measurement campaign included outside temperatures ranging from 90 °F to 100 °F and relative humidity levels from 60 % to 90 %. At all times, the SUV engine was operating at idle speed to power the air condition and cool the SUV’s interior. However, the temperature was not actively regulated and constantly shifted to higher levels as the outside temperature increased and the SUV heated up in direct sun exposure. The SUV was placed such that the exhaust was emitted downwind, away from the sampling inlet. Measurements were taken at either Mirador 1 or 2 shown in Fig.5.24, and depended on the wind direction to overlap with the emitted gas plume. Change of measurement location from Mirador 1 to Mirador 2 and vice versa took about 30 min. to fully regain gas sensing operation. The measurement quality of volcanic species was compromised on the wind direction and propagation of the gas plume towards our measurement location. This applied to both, open path FTIR and extractive DFG based gas measurements.

The sensors performed measurements over a 4 day period, ~8 hours per day. During this period, the sensor operated mostly in automatic mode which included frequency locking of the absorption lines in the center of the absorption scans. In case of the detection of HCl and SO₂, the detection sequence included the use of high concentration reference gas cells to determine the peak location. Before taking a measurement, the reference gas cells were rotated into the beam path to enable the software to locate the position of the absorption line and distinguish from residual etalon peaks and baseline
irregularities. The residual baseline noise of the sensor ranged from 0.1% to 0.2%. This is about a factor of two to five less sensitivity than typically achieved in laboratory measurements. The residual noise was dominated by an optical etalon and was later determined to be caused by the Yb-fiber amplifier pump channel.

![Graphs showing measurements](image)

**Fig. 5.26:** Measurement of CH₄ at Masaya volcano, Mirador 2, April 14, 2000. Also shown are DFG signal, dark voltage and peak location, indicating a stable nearly drift free time period. The estimated measurement accuracy is 7%.

During the 4-day measurement campaign, five gases including CO₂, SO₂, HCl, H₂O, and CH₄, were detected sequentially. Due to unfavorable wind conditions, most useful
measurements were performed on the last two days. Measured gas species of SO\textsubscript{2} and HCl are considered to be of sole volcanic origin, while CO\textsubscript{2}, H\textsubscript{2}O and CH\textsubscript{4} are of atmospheric origin.

Fig. 5.26 shows the measurement of CH\textsubscript{4} at Mirador #2 on April 14, 2000 during a 25 minute time period. The standard deviation corresponds to 52 ppb or an accuracy of 2.7%. The total accuracy is 7% and estimated from comparison of Hitran96 spectroscopic database and measured spectra.

On April 17, 2000, measurements of HCl and SO\textsubscript{2} were performed at Mirador #2. For the detection of HCl, the DFG based gas sensor was tuned to 2843.6 cm\textsuperscript{-1}. Fig. 5.27 shows the rise in HCl concentration with time reaching a maximum concentration of 175 ppb at 11:30 h. The concentration constantly increased as the gas plume emitted by the volcano continued to be blown towards the sampling location. Shortly before noon, the concentration sharply decreased to a level at ~50 ppb within 15 minutes and continuous steady decay. At 14:30 h, the DFG frequency was tuned to 2505.239 cm\textsuperscript{-1} to detect SO\textsubscript{2}.

At 17:00 h, the sensor was tuned back for the detection of HCl at 2843.6 cm\textsuperscript{-1}. Also shown in Fig. 5.27 is the steady increase of humidity recorded with a digital hydrometer and indication of a short rain period at 16:30 h. Dense gas plumes continued to pass our sampling location and lead to an increase of HCl with a noticeable delay at 17:30 h. This delay of response can be explained by the chemisorption of the strongly polar HCl molecule to a water vapor film accumulated by the rain and high humidity covering the inside of the teflon sampling tube.
Fig.5.27: Measurements of HCl from gas plumes emitted by Masaya volcano. Shown are sample spectra fitted to a Lorentzian lineshape function and humidity levels.

The HCl spectra shown for two sample points indicate a residual baseline noise of ~0.2% corresponding to a sensitivity of ~15 ppb.

Between 14:30 h and 17:00 h the DFG sensor was tuned to measure SO₂. For comparison, the FTIR instrument was set up for open path measurements along the crater rim. The FTIR was placed adjacent to the SUV and collected the light from a Nernst glower placed 135 m downwind. A Newtonian telescope collected the light and directed it into the FTIR.
Fig. 5.28: Measurements of SO$_2$ from gas plumes emitted by Masaya volcano. Shown are experimental arrangement at Mirador 1 and 2 (photograph) and measured concentrations by the extractive DFG based gas sensor and open path FTIR (L=135 m).
Measurements shown in Fig.5.28 display a good agreement of temporal and measured amount of SO$_2$ within error margins given by the DFG based gas sensor (3 ppm minimum detectable concentration at S/N=1).

The overall performance of the DFG-based gas sensor indicates suitability for field operation even under unfavorable conditions such as high temperature and humidity. Table 5.4 summarizes the detected gas species and performance of DFG and FTIR gas sensors in a field application. Extractive gas detection of strongly polar molecules and associated chemisorption and physiosorption effects can have a substantial impact on the accuracy of the gas measurement, especially if humidity and long sampling tubing act as a gas adsorber. The ratio of HCl and SO$_2$ as measured by the FTIR was $\sim$1.5. This indicates that the DFG gas sensor measured two orders of magnitude lower HCl concentration levels than the FTIR. Although less selective, open path gas measurement configurations perform in this case more accurately to determine the correct ratio of molecular species. Temperature induced electronic drifts by the detector and diode laser electronics introduce a limit on DFG instrument accuracy and demand a high level of automatic control (i.e. wavelength drift compensation by stepper motor tuning). A better temperature management using a solid state cooler can compensate any ambient temperature cycling and provide optimum continuous gas sensor performance.
Table 5.4: Summary of detected gas species, measured concentrations and field sensitivities of the multi-component DFG based gas sensor.

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>DFG Center Frequency (cm⁻¹)</th>
<th>DFG Measured Concentrations (Min - Max)</th>
<th>Field Sensitivity (MDC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>3028.751</td>
<td>1.85 - 2.05</td>
<td>32 ppb</td>
</tr>
<tr>
<td>CO₂</td>
<td>2388.640</td>
<td>374 - 567</td>
<td>419 ppb</td>
</tr>
<tr>
<td>H₂O</td>
<td>2649.348</td>
<td>18000 - 21200</td>
<td>30 ppm</td>
</tr>
<tr>
<td>HCl</td>
<td>2843.624</td>
<td>MDC - 0.175</td>
<td>710 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>2505.239</td>
<td>MDC - 22.65</td>
<td>15 ppb</td>
</tr>
</tbody>
</table>

Table 5.4 shows comparable detection sensitivities of the DFG and FTIR based spectroscopic measurements. The field sensitivities for the DFG instrument were determined by the residual fit error to the baseline, while the FTIR sensitivities are expressed as mean values calculated from the errors of all measurements taken on April 17, 2000. The FTIR instrument accuracy for the absolute gas concentration was 10-20% and is determined by inaccuracy of the open path length measurements and retrievals.

In summary, five gas species including CO₂, SO₂, HCl, H₂O, and CH₄ were detected using a DFG based gas sensor and compared with open path FTIR gas measurements. The DFG based gas sensor operated with a high resolution and good sensitivity using extractive gas sampling. The sensitivities achieved with both DFG and FTIR instruments are comparable. Based on the obtained results, future volcanic gas measurements using open-path DFG based gas sensors may be attractive in attaining real-time molar ratios of emitted volcanic gas species and hence implementing an early warning volcanic hazard sensor.
References for Chapter 5


Courtesy of E. Dlugokencky, NOAA, Climate Monitoring & Diagnostic Laboratory, Boulder CO

National Oceanic and Atmospheric Administration (NOAA), Climate Monitoring and Diagnostics Laboratory (CMDL), Carbon Cycle Group, URL: http://www.cmdl.noaa.gov/ccgg


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CHAPTER 6. MODULAR HIGH POWER MID-IR DFG SOURCES
AND DUAL-BEAM SPECTROSCOPY

Further increase of mid-infrared probe power enables the application of advanced
detection schemes such as dual beam spectroscopy and cavity ring-down spectroscopy to
obtain higher gas detection sensitivity. The principle DFG architecture is similar to the
widely tunable DFG based mid-IR source described in chapter 5, but offers significant
improvements in terms of physical size, generated mid-IR power, spectroscopic
sensitivity and modular design.

The availability of tunable DFG signal and pump laser sources that overlap with the
gain region of Yb (~1 μm), Er/Yb co-doped and Er (~1.5 μm) fiber amplifiers allows to
boost the power levels of either DFG pump channel above several hundred mW. This
enables the generation of tens to hundreds of microwatts of tunable, narrow-linewidth
mid-IR radiation. Higher mid-infrared radiation can be used to apply longer path length
multi-pass cells and implementation of dual-beam spectroscopic detection. Extractive
dual-beam gas absorption spectroscopy is similar to direct absorption spectroscopy (c.f.
chapter 4), but further includes detection of a reference beam sampled off the generated
mid-IR beam before entering the multipass cell. Subtraction of the signal and reference
channel cancels out baseline, optical noise (etalons) of the DFG radiation and residual gas
absorption prior the multipass cell.
6.1 High Power Two Channel Yb\textsuperscript{3+} and Er\textsuperscript{3+}/Yb\textsuperscript{3+} Fiber Amplifier Pumped

DFG Mid-IR Source

The dual-beam absorption technique was applied using a two channel fiber amplifier system employing a 1.6 W Yb\textsuperscript{1} and 0.6 W Er/Yb\textsuperscript{2} fiber amplifier seeded by a non-planar ring 1.06 \textmu m Nd-YAG oscillator solid state laser and 1.56 \textmu m DFB diode laser, respectively (shown in Fig. 6.1)\textsuperscript{3}. A maximum mid-IR power of 0.7 mW was generated using a 19 mm long PPLN crystal (conversion efficiency 470 \textmu W W\textsuperscript{-1} cm\textsuperscript{-1}). The increased sensitivity achieved by dual beam detection is shown in Fig. 6.2. The baseline noise has a \( \pm 1\sigma \) magnitude of \( \pm 2.8 \times 10^{-5} \). This sensitivity represents one order of magnitude improvement compared to direct absorption spectroscopy sensitivities and can be further enhanced using higher frequency detection schemes (2-f) since the residual noise is attributed to 1/f noise.

During initial characterization of the mid-IR source, a spiking behavior at higher fiber amplifier pump powers was observed and attributed to the SBS and SRS effects (c.f. chapter 3.3). Reduction of fiber lengths increased the threshold for these effects. Furthermore, the seed power for both fiber amplifiers was increased using preamplifiers (100mW at 1.1 \textmu m and 40 mW at 1.5 \textmu m) to fully saturate the main amplifiers and avoid gain for backward propagating photons.
Fig. 6.1: Schematic of a high power DFG source applied to dual beam spectroscopy of methane at $3.35 \, \mu m$.

\[ \sigma = \pm 2.8 \times 10^{-5} \]

Fig. 6.2: High-resolution absorption spectra of methane at $3.35 \, \mu m$ showing an absorption sensitivity of $\pm 2.8 \times 10^{-5}$. 
6.2 Cascaded Dual-Wavelength Yb$^{3+}$ - Er$^{3+}$/Yb$^{3+}$ Fiber Amplified DFG Mid-IR Source

A more compact utilization of Yb and Er/Yb fiber amplification is presented here. Both seed signal and pump wavelengths are amplified by a cascaded Yb and Er/Yb amplifier combination to generate up to 0.1 mW at 3.5 μm.

6.2.1 Experimental Configuration

Two fiber amplified near infrared diode lasers operating at 1083nm (DBR, 50 mW) and 1563 nm (DFB, 15mW) respectively are difference frequency converted to the mid-IR using a 50 mm long periodically poled lithium niobate (PPLN) crystal. Its novel design is reflected in the use of only one active 30 dBm (1W) Yb fiber amplifier fusion spliced to a 6.8 m Er/Yb co-doped single mode fiber that provides amplification at both 1 and 1.5 μm.\(^4\) The Er/Yb silica glass fiber is co-doped with phosphorous for efficient energy transfer from the Yb$^{3+}$, \(^2F_{5/2}\) level to Er$^{3+}$, \(^4I_{11/2}\) level to provide gain at 1.5 μm as shown in Fig.6.3.\(^5\) The Er/Yb fiber with a N.A. of 0.16 and core diameter of 5.1 μm possesses an absorption coefficient of 0.6 dB/m at 1083 nm and is pigtailed to a Lucent truewave fiber and terminated with an 8° angle fiber connector. An f=10 mm achromat is used to image (M~11) the amplified pump beams with respective mode field diameters 8.8 μm (1563 nm) and 5.9 μm (1083 nm) into the PPLN crystal.
The generated mid-IR radiation is collimated by a CaF$_2$ lens (f=5 cm) and can be directed to either an open path or extractive optical multi pass absorption cell module. The fiber amplifier pumping scheme was initially optimized to provide a balanced pumping power product $P_{1083\text{nm}} \times P_{1563\text{nm}}$ that is direct proportional to the generated difference frequency mid-IR power. The Yb fiber amplifier is core pumped by three parallel 970 nm broadband diode pump sources with an effective slope of 1024 mW/A and a operating bandwidth from 1060 nm to 1090 nm with the gain center located at 1083 nm. The required seed power for gain saturation is 1 mW. The output of the Yb-amplifier is spliced to a 2x1 WDM and combined with a 15 mW DFB diode laser operating at 1563 nm.
Fig. 6.4: Schematic and photograph of a compact DFG based mid-infrared source with outer dimensions of 13" × 8.5" × 4.5".
The measured insertion loss of the WDM was 2% at 1083 nm and 10 % at 1563 nm. A higher loss at 1563 nm (specified loss of 0.7 % at 1550 nm) is due to mismatch of the DFB diode laser pigtailed fiber (core \( \Theta \approx 9.5 \, \mu m \)) and WDM fiber type (core \( \Theta \approx 5.7 \, \mu m \)). The 1.5 \( \mu m \) DFB diode laser is mounted on a Peltier TEC element in a hermetically sealed 14-pin butterfly package and operates with a measured 46 dB side-mode suppression ratio and linewidth of <10 MHz. An integrated optical isolator provides 55 dB optical isolation to the diode laser.

6.2.2 Performance Characteristics

Fig. 6.5a shows the output power of the Yb fiber amplifier as a function of diode laser pump current with a fiber coupled seed power of \( \sim 10 \) mW at 1083nm. Fig. 6.5b depicts the maximum power of the Er/Yb fiber amplifier at the FC/APC with 581 mW at 1083 nm and 232 mW at 1563 nm just prior to the achromat. These powers correspond to an effective Er/Yb fiber amplifier slope efficiency of 46 %.
Fig. 6.5: a) Yb amplifier output power as function of pump diode laser current. b) Yb - Er/Yb fiber amplifier output power as a function of Yb fiber amplifier pump current. Seed powers were 10 mW (1083 nm) and 13 mW (1563 nm), respectively.

Recent improvements in electric field poling of lithium niobate lead to the development of 1 mm thick PPLN crystals and consequently allow the use of longer crystals without experiencing aperture clipping of the pump and DFG beams. To determine poling quality differences, length and thickness, the conversion efficiencies of four PPLN crystals were compared.

Table 6.1: Conversion efficiency of various PPLN crystals

<table>
<thead>
<tr>
<th>PPLN Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mm)</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>19</td>
<td>19</td>
<td>50</td>
<td>20.5</td>
</tr>
<tr>
<td>Conversion Efficiency ($\mu W \times W^{-1} \times cm^{-1}$)</td>
<td>199</td>
<td>174</td>
<td>181</td>
<td>176</td>
</tr>
</tbody>
</table>
Fig. 6.6: DFG power at 3.5 μm as a function of incident pump power product for PPLN samples listed in Table 6.1.

PPLN samples A, B and C were fabricated from the same wafer run and polished. All PPLN crystals were anti-reflection coated for pump, signal and idler wavelength. The four samples were placed consecutively in the fixed fiber to crystal imaging stage (M=11). The conversion efficiency appears to be independent of crystal thickness as evident from Table 6.1. With the maximum generated pump power product of 0.135 W² (Fig.6.5 b) a maximum generated DFG power of ~0.1 mW of stable narrow linewidth light is generated using a 50 mm long, 1mm thick PPLN crystal. Further careful optical alignment enhanced the conversion efficiency factor to 220 μW × W⁻¹ × cm⁻¹. The conversion efficiency is about a factor of two less than achieved with the high-power mid-IR source presented in chapter 6.1, and may be due to larger difference of mode field diameters. In addition a power loss of 25 % at 1.5 μm after insertion of the imaging achromat objective was observed. The transmission of the objective was independently
deduced by the use of separate high power sources (~ 94% at 1 and 1.5 µm). This suggests a partial depletion of the 1.5 µm radiation due to feedback into the Er/Yb doped fiber, however no apparent effect on the narrow spectral linewidth which was confirmed with the detection of H₂CO absorption lines near 3.5 µm.

References for Chapter 6


CHAPTER 7. CONCLUSIONS AND FUTURE DIRECTIONS

This dissertation presents the successful design, development and application of portable mid-infrared spectroscopic absorption gas sensors. The mid-infrared sources are based on fiber coupled and fiber amplified diode laser seed sources and efficient mid-IR frequency conversion using quasi-phase matched PPLN crystals. Sensitive, selective and real-time gas sensing was achieved by direct and dual-beam absorption spectroscopy using an optical multi-pass cell. Different novel DFG architectures were implemented, characterized and applied to real-world problems. Fig. 7.1 depicts the DFG based mid-IR sources and highlights their distinct advantages that have been discussed in this thesis.

The use of an ECDL as one of the DFG pump sources in combination with a fan-out type QPM-PPLN enabled the creation of an automated continuously mid-IR wavelength tunable source (3.3 to 4.4 μm), μW-power-level, good selectivity (~40 MHz) and sensitivity (10^-4 fractional absorption). This architecture was packaged in a suitcase and successfully applied to the evaluation of an industrial catalyst and taken to an active volcano in Central America for gas emission measurements.

Higher DFG powers were obtained with Er- and Yb-doped optical fiber amplification of 1 and 1.5 μm seed sources and were applied to ultra-sensitive dual-beam spectroscopy (10^-5 fractional absorption). The availability of ECDL's in the 1 μm and 1.5 μm wavelength region may replace the 'fixed' DBR or DFB diode laser wavelength source as an advanced widely tunable version to generate higher power widely tunable mid-IR radiation, and hence allow application of the dual-beam detection technique. An
automated widely tunable DFG based mid-IR source remains complex but can be made compact. Appropriate temperature management of the DFG instrument (suitcase) is essential to further enhance the instrument accuracy. This may be achieved by using very compact solid-state Peltier air-conditioners.

<table>
<thead>
<tr>
<th>A)</th>
<th>DBR-DL 1083nm, P=50mW</th>
<th>Yb fiber amplifier, P=1W</th>
<th>λ = 3.3 - 4.4 μm</th>
<th>P = 3 μW</th>
</tr>
</thead>
<tbody>
<tr>
<td>B)</td>
<td>DBR-DL 1083nm, P=50mW</td>
<td>Yb fiber amplifier, P=1W</td>
<td>λ = 3.4 - 3.8 μm</td>
<td>P = 0.7 mW @ 3.5 μm</td>
</tr>
<tr>
<td>C)</td>
<td>DBR-DL 1563nm, P=15mW</td>
<td>Yb fiber amplifier, P=1W</td>
<td>λ = 3.4 - 3.8 μm</td>
<td>P = 0.1 mW @ 3.5 μm</td>
</tr>
</tbody>
</table>

- Wide continuous tunability and moderate DFG power
- Good sensitivity ($10^{-4}$) and selectivity (40 MHz)
- Complex but robust design
- Tunable and high DFG power
- Good sensitivity ($10^{-5}$)* and selectivity (40 MHz)
- Robust and flexible design

* Dual-beam spectroscopy

Fig. 7.1: Tunable mid-IR sources based on difference frequency mixing of diode lasers presented in this thesis.

New developments in the photonic industry enables multiplexing of new diode or fiber laser seed sources configured for specific trace gas detection. New available wavelength combinations will furthermore expand the DFG range down to 2.6 μm for the detection of important molecules such as HF (an example is given in Fig.7.2).
New quasi-phase matched nonlinear optical crystals such as GaAs will allow to build fiber based DFG architectures to operate in the second atmospheric window from 8 - 16 μm to detect a wider range of molecular species.

Fig. 7.2: Novel future DFG pump source for the generation of mid-IR radiation at 2.64 μm for the HF gas detection. The OPSL serves as a narrow-linewidth seed and fiber amplifier pump laser. OPSL, Optically Pumped Semiconductor Laser, (Coherent Inc. 5100 Patrick Henry Drive, Santa Clara, CA 95054).

The results and findings of this work allow the rapid implementation of compact tunable mid-infrared sources for absorption spectroscopy of trace gases. Critical design issues were identified and solved. The flexibility in the design, spectroscopic performance and very compact size, makes optical fiber pumped DFG based gas sensors attractive for commercialization.