DEVELOPMENT OF OPTICAL GAS SENSORS FOR EMISSION MONITORING

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Abstract: *The global increase in N_2O and CO_2 levels, which contribute to the greenhouse effect, has been attributed to combustion of biomass and fossil fuels. An optical sensor system capable of measuring concentrations of these species and O_2 might be incorporated into combustion-control applications to reduce pollutant emissions and increase fuel efficiency. In addition to measuring the gases in the atmosphere and pollution from traffic and industry, it is important to monitor the work environment, industrial process. A compact, widely tunable coherent optical source based on a difference frequency generation technique in a quasi-phase-matched nonlinear crystal pumped by two single-frequency laser diodes for the detection of various gases is reported. A novel approach of using commercially available fiber-coupled super-luminescent diode (SLD) along with a spectrometer is also proposed for such application.*

Key words: *gas sensing; trace gas monitoring; difference frequency generation; PPLN; super luminescent diode (SLD).*

1. INTRODUCTION

Recently, the interest for compact and reliable gas sensor has considerably increased in various fields of applications, such as atmospheric monitoring, pollution monitoring, combustion process, medical diagnostics and breath analysis, food industry. Industrial application is also of great importance, as it involves precise control of gas mixtures, level of impurities or contaminants, such as in semiconductor, electronic and optical device manufacturing. A Precise monitoring of a variety of species in different gas mixtures and at various concentration levels, ranging from several hundred parts per million (ppm) to parts per billion (ppb), is required in various fields of applications [1].

Laser-based spectroscopic techniques are very attractive methods for trace gas monitoring. Tunable coherent light sources operating in the 2-5-μm mid-infrared (mid-IR) region are generally used for such applications as they have demonstrated simultaneous high sensitivity and selectivity. By employing narrow-bandwidth coherent light sources, a single absorption line of the substance to be analyzed can be probed with a laser, avoiding interference signals from other species. Although laser diodes and quantum-cascade lasers are available as light sources in mid-IR range, they require low-temperature operation and tuning range is also narrow and discontinuous. On the other hand, difference frequency generation (DFG) based on near-IR, tunable laser sources can also be considered, which can allow multi-gas sensing with a single light source. There have been several demonstrations of mid-IR generation by the quasi-phase-matching (QPM) in a periodically poled nonlinear optical lithium niobate ((PPLN) and other materials [2,3].

Many applications do not require extreme sensitivities up to ppb order and in this case, near-infrared laser diodes are also of great interest. These semiconductor devices are very compact and reliable light source operating at room temperature and provide a long lifetime. They are commonly produced in the spectral range of optical fibers telecommunications (1.3 – 1.7 μm, where overtone vibration bands of many molecules of interest occur (CO_2, H_2O, NH_3, HCl, CH_4, HF, C_2H_2…). Very recently, super-luminescent diodes are available in near-IR region and possess a broad optical emission. A novel approach of using commercially available fiber-coupled super-luminescent diode (SLD) along with a spectrometer can also be considered for such application. In this approach, an absorption dip will result in the emission spectrum corresponding to the absorption wavelength of the particular species of interest during absorption-spectroscopy measurements. This approach will result in a very simple and stable and cost effective configuration as compared to the tunable diode-laser system.

We report in this paper results on the development of a DFG based mid-IR coherent light source for CO_2 gas sensing. The interest of this system consists in the possibility to detect several species with a single instrument. Theoretical background of DFG in PPLN is reviewed and a wide range tuning operation in PPLN is discussed and experimental results are presented. Further, preliminary investigation on SLD based O_2 sensing is reported.

2. DIFFERENCE FREQUENCY GENERATION IN PPLN

2.1 Theoretical background

In a second-order nonlinear DFG process the two incidence waves, customarily called a pump wave (ω_1) and a signal wave (ω_2), are frequency down-converted to generate an idler wave (ω_3) in accordance to the relation,

$$\omega_3 = \omega_1 - \omega_2. \qquad (1)$$

This approach can provide narrow-linewidth and continuous tuning over a wide range by tuning either the pump wave or the signal wave. Compared with tunable optical parametric oscillators (OPO), the DFG technique has no oscillation threshold and therefore can operate in continuous-wave with low operating power, narrow-spectralwidth laser diodes.

Although birefringently phase-matched nonlinear techniques with different nonlinear crystals for DFG are available, the interest in quasi-phase-matched (QPM) periodically poled lithium niobate (PPLN) devices for mid-infrared DFG is increased considerably [4]. In the case of quasi-phase-matched DFG process, the first order QPM condition is given by

$$k_1 - k_2 - k_3 = 2\pi/\Lambda, \qquad (2)$$

where k_1, k_2, and k_3 are the wave vectors at the three interacting wavelengths and Λ is the PPLN period. This approach offers the advantages of a large effective nonlinear coefficient, noncritical phase matching with zero walk-off, and allows phase-matching with various visible and near-infrared lasers by engineering the PPLN period. Recently, there have been several demonstrations of mid-IR generation by the QPM in a PPLN material [5].

A problem with the QPM device is that the tunable range is limited by the period of the crystal domain. Nevertheless, our calculation shows that PPLN has a wide phase-matching bandwidth around the input wavelength region of 780-900 nm. Figure 1 shows tuning curves estimated with pump wavelengths ranging from 700 nm to 1000 nm corresponding to the phase matching condition. As shown in Fig. 1, a wide range tuning of idler wavelength is possible corresponding to an appropriate grating period. Due to a broad acceptance bandwidth for phase matching, wide range tuning is expected by altering the PPLN crystal temperature with single grating period, which is not possible with other pump wave-length ranges. Therefore using near-IR lasers in combination with a PPLN, a wide tuning range can be covered.

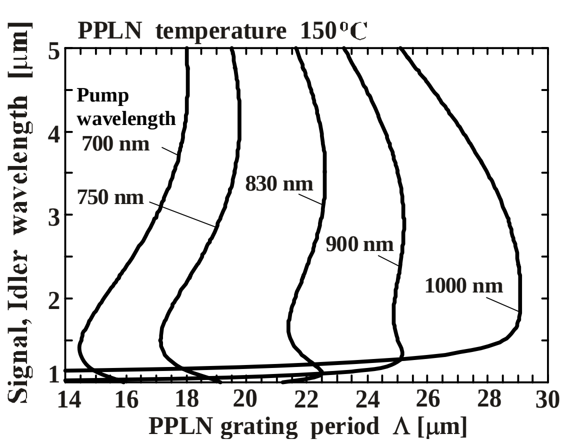


Fig. 1. Estimated PPLN grating period with respect to pump wavelength. Idler wavelength represents difference frequency generation output.

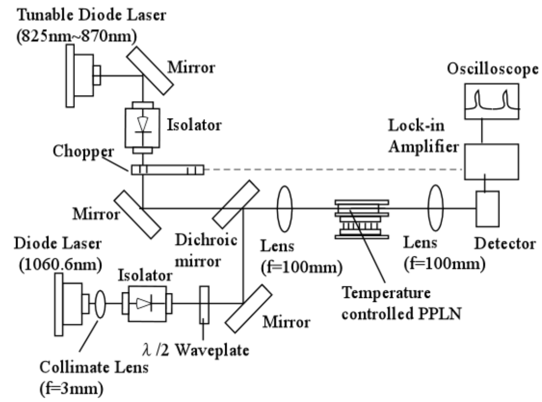


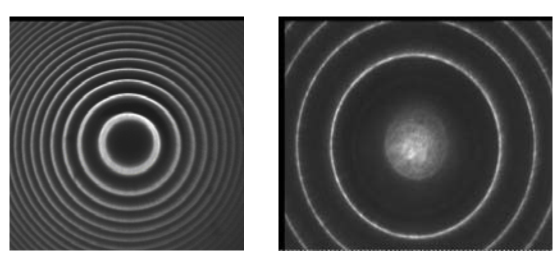
Fig. 2. DFG experimental setup.

2.2 DFG experiment

In the experimental arrangement, as shown in Fig. 2, tunable laser-diode (825 – 870 nm) was combined with a fixed wavelength laser-diode (1060.6 nm) using a dichroic beam-splitter.

The tunable laser diode with a central wavelength around 850 nm consisted of an external cavity in a Littrow configuration. Coarse tuning from 825 to 870 nm was obtained by rotating the grating and mode-hop free fine tuning range of 16 GHz was possible by a piezoelectric actuator. The fixed wave-length laser was a distributed Bragg reflector type laser diode. The spectral characteristics of both diode-lasers measured with Fabry-Perot interferometers and corresponding interference fringe patterns are shown in Fig. 3 (a) and (b). Both lasers were operating with a single mode output and spectral widths were estimated to be around 0.01 cm-1 for the 1060 nm laser diode and 0.03 cm-1 for the 850 nm laser diode.

The laser beams were focused by an achromatic lens (focal length= 100 mm) at the center of a 0.5 mm thick, 20 mm long, bulk PPLN with a domain grating period of Λ= 22.58 μm. The generated mid-IR beam was then focused onto a liquid nitrogen cooled InSb detector (P5172-100, Hamamatsu Photonics). The measurements were performed with a trigger signal



(a) 869 nm, FSR: 0.125 cm^{-1} (b) 1060 nm, FSR: 0.25 cm^{-1}

Fig. 3. Fabry-Perot interference ring pattern of laser diodes (a) pump laser (tunable, center wavelength: 850nm), (b) signal laser. Single longitudinal mode operation was observed.

from an in-line chopper rotating at 800 Hz and a lock-in-amplifier combined with an oscilloscope.

2.3 Experiment results

The DFG output characteristics corresponding to the input power of the pump laser and the signal laser were measured. The DFG output intensity was increased with increase in the input power and linear output characteristics were observed in agreement with the DFG process. The DFG output power is given by $P_{DFG} = K \times P_1 \times P_2$, where K represent a constant parameter based on a nonlinear conversion factor and the focusing condition, P_1, P_2 represent input power of the pump and signal laser, respectively.

The temperature acceptance-bandwidth of the PPLN crystal corresponding to a typical pump wavelength of 847 nm was measured to be around 8°C (FWHM). The measured acceptance bandwidth was in close agreement with the theoretical estimation of 7°C (FWHM) based on the quasi-phase-matching.

Subsequently, for tunable DFG output, the pump laser was tuned and simultaneously the PPLN temperature was altered for a phase-matched condition. Figure 4 shows the tuning characteristics of the DFG output corresponding to the phase-matching temperature. Solid circles show the experimental results and the solid line shows the theoretical calculation based on the QPM condition as described in (2) and the Sellmeier equation [6].

The experimental results, generally agreed well with the theoretical calculation. As shown in Fig. 4, a wide tuning range between 3.7 and 4.8 μm was obtained by tuning the pump laser between 825 and 868 nm and altering the PPLN temperature between 20 and 130 C with single period of Λ=22.58 μm. Based on the theoretical estimate, there exist an optimum value of the PPLN period for which very wide tuning range can be attained with only single period. As a typical example, for a PPLN period Λ= 22.50 μm a tunable mid-IR output can be generated between 3.6 and 4.9 μm without varying the PPLN period [7].

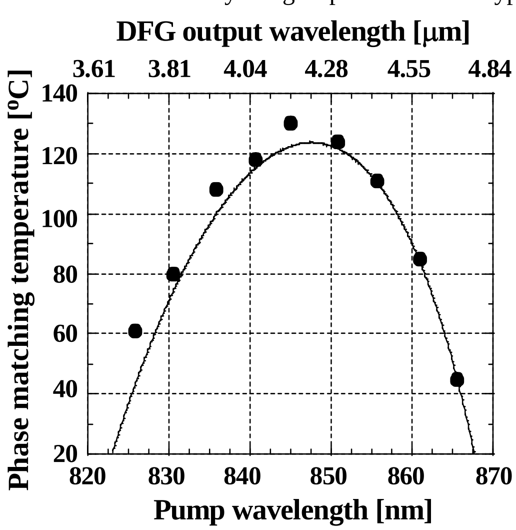


Fig. 4. Tunable DFG output at different pump wavelengths and corresponding phase matching temperature. Signal wavelength: 1060.6 nm and PPLN period Λ=22.58 μm.

2.2 CO_2 gas sensing

Preliminary studies were performed to study the feasibility of DFG source to be used as a gas sensor. The idler wave generated around 4.32 μm via DFG process was transmitted through a gas sample and absorption studies were conducted by measuring the intensity using the InSb detector. As a sample target gas, CO_2 gas was used and absorption spectroscopy measurements were performed corresponding to the ν_3-band ranging from 2360 – 2290 cm^{-1} (4.20 – 4.40 μm) of the CO_2 absorption spectrum.

First, a very weak CO_2 transition near 4.36 μm was considered where minimum absorption was expected based on the HITRAN database analysis [8]. The pump wavelength of 853.35 nm was selected using a wavemeter (Burleigh, model:4500-0) to match the idler wavelength with the 4.36 μm (2289 cm^{-1}) having

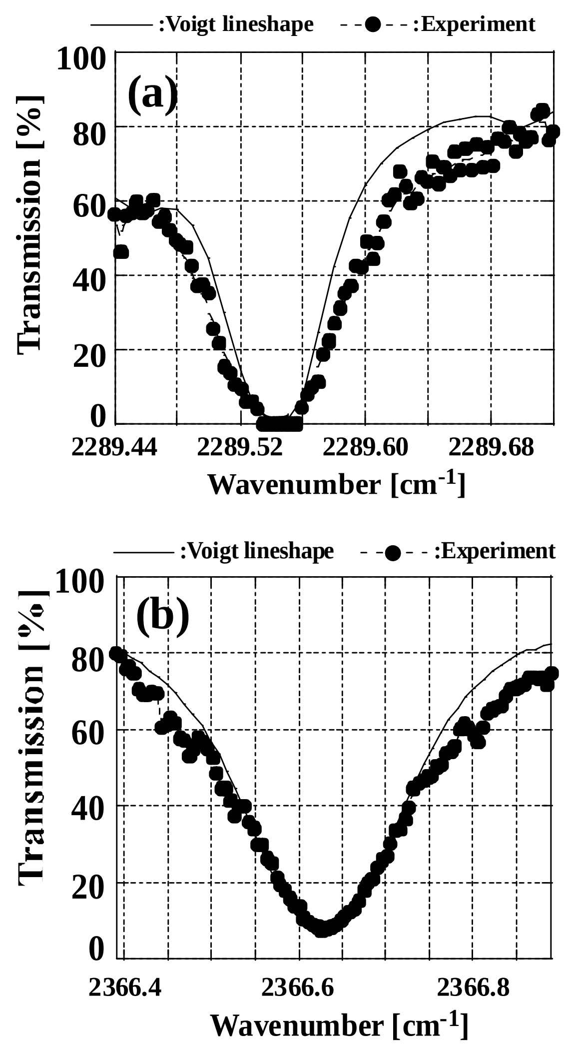


Fig. 5. CO_2 measurements (a) weak absorption line; (b) strong absorption line, ambient air. Sample length: 240 mm, signal wavelength: 1060.6 nm

almost 100 times weaker absorption strength (absorption cross-section value of 1.17×10^{-19} cm^2) than that of 4.23 μm (2366.6 cm^{-1}). The pump laser was fine-tuned with a mode-hop free tuning range of about 16 GHz to achieve a tunable DFG output. No distinct absorption peaks due were observed when the idler wave was transmitted through the ambient air. However, when the idler wave was transmitted through a 200 mm long cell filled with a CO_2 gas pressure of about 0.02 MPa (150 Torr), a distinct absorption peak was ob-served with the fine-tuning of the pump laser, confirming the absorption due to the ν_3-band of CO_2.

Next, atmospheric CO_2 absorption at a stronger transition around the transition wavelength of 4.23 μm (2366.6 cm^{-1}) was studied by tuning the pump laser to 847.98 nm. The ambient air sample-length was 240 mm. The portion of the absorption spectrum of CO_2 in the ambient air centered at the transition line of 2366 cm^{-1} over a range of 0.7 cm^{-1} is shown in Fig. 5. Solid line shows the computed absorption spectrum from the HITRAN molecular spectroscopy database. The spectrum was computed by assuming a Voigt lineshape function at an atmospheric pressure and CO_2 concentration of 360 ppm (parts per million). In the computation, the spectral width of the laser was assumed to be 0.03 cm^{-1} (300 MHz). The dotted line with circles shows experimental measurements by tuning the DFG output. As shown in Fig. 5, the experimentally measured absorption spectrum was slightly broader; nevertheless the absorption measurements were in agreement with the computed absorption-lineshape. This variation was attributed to the unstable output characteristics of both pump and signal lasers.

3. SLD BASED GAS SENSING

3.1 O_2 gas sensing

The global increase in N_2O and CO_2 levels, which contribute to the greenhouse effect, has been attributed to combustion of biomass and fossil fuels. An optical sensor system capable of measuring concentrations of these species and O_2 might be incorporated into combustion-control applications to reduce pollutant emissions and increase fuel efficiency. There is a continuous need to monitor O_2 at power generation boilers, various industrial furnaces, combustion equipment and to measure O_2 for converted NO_x estimation. In addition to measuring the gases in the atmosphere and pollution from traffic and industry, it is important to monitor the work environment, industrial process. Another process control application which has now become feasible is the use of the O_2 monitor to improve combustion control in high-temperature furnaces, such as steel and cement ovens. Performing high-temperature CO measurements at the same location will improve the combustion control even further. The temperature is typically 900–1200 °C and the gas matrix will in this case consist of O_2, CO, CO_2, N_2, NO and H_2O.

Recent developments in semiconductor diode-laser technology have extended the range of available laser wavelengths and hence, the number of available accessible species that may be probed using an absorption spectroscopy technique [9,10]. However, the technique involves the use of a spectrally narrowed diode laser and control of wavelength stability is required for precise measurements. On the other hand, a novel approach of using commercially available fiber-coupled super-luminescent diode (SLD) along with a spectrometer can be considered for such application. SLDs are also available in different wavelength ranges and possess a broad optical emission resulting into a multiplex system measuring multiple gases simultaneously. In this approach, an absorption dip will result in the emission spectrum corresponding to the absorption wavelength of the particular species of interest during absorption-spectroscopy measurements. This approach will result in a very simple and stable and cost effective configuration as compared to the tunable diode-laser system.

Figure 6 shows the proposed schematic of an experimental setup in order to investigate the suitability of a fiber-optic SLD system to measure concentration of O_2 in combustion environments using absorption spectroscopy.

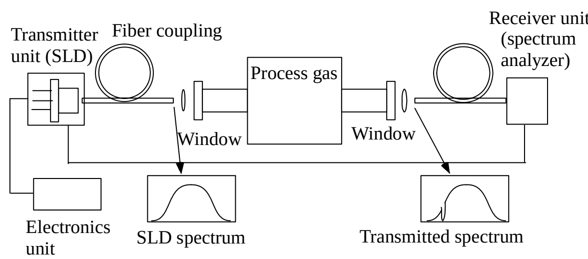


Fig. 6. Proposed schematic of a LSD based gas monitor.

3.2 Theoretical estimation

Molecular oxygen has an absorption band around 762 nm, which belongs to a vibrational subtransition of the magnetic dipole transition. The absorption line located at 760.26 nm was used to monitor oxygen in this report. This line was chosen because it has one of the higher line strengths (*S*) of the transitions in this region and there is no absorption due to water. This transition has a room-temperature line strength (T = 296K) of 6.302×10^{-24} cm^{-1}/molecule cm^{-2} (1.568×10^{-4} cm^{-2} atm^{-1}), and a pressure broadened halfwidth of 5.97×10^{-3} nm (0.1028 cm^{-1}). The intensity of monochromatic laser radiation of frequency v transmitted through a sample cell containing an absorbing species is given by Beer's law,

$$I(\omega)=I_0(\omega)\, e^{(-\sigma(\omega)\, L\, N)}, \qquad (3)$$

where I_0 is transmitted intensity in the absence of an absorbing species, L is the optical path length within the cell, $\sigma(\omega)$ is the absorption coefficient and N is the concentration of the absorbing species in molecules per unit volume. The cell absorbance is defined by *a* =

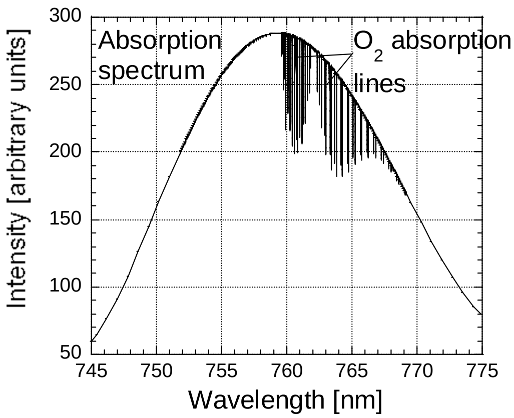


Fig. 7. Calculated O_2 output spectrum of the band near 755~775nm with laser spectral width of 0.01 cm^{-1}(21% O_2, 293K)

$\sigma(\omega)LN$. A given molecular absorption line is characterized by its integrated line strength *S* estimated based on HITRAN96.

Figure 7 shows a typical absorption spectrum expected when the SLD output is propagated through a multi-pass cell (length= 10 m) filled with atmospheric air (oxygen concentration: 21%) at room temperature (298 K). In the calculation, a spectrum analyzer with a resolution of 0.01 cm^{-1} is considered. The dips observed in the spectrum are due to O_2 absorption band around 762 nm. The transmitted output power is expected to vary with the concentration.

Currently, experimental studies are performed to investigate detection limit of the SLD based oxygen sensor. In 1.5 μm wavelength region absorption lines of many trace gases, such as NH_3 (1.5 μm), CO_2 (1.6 μm), CH_4 (1.65 μm) etc., exist. Multi-component trace gas sensing system can be designed via multiplexing SLDs in 1.5 μm wavelength region.

4. CONCLUSION

In summary, a compact, widely tunable coherent optical source based on a difference frequency generation technique in a quasi-phase-matched PPLN crystal pumped by two single-frequency laser diodes for the detection of various gases is developed. The pump laser was tunable from 825 to 870 nm and the signal laser was a DFB laser diode at 1060.6 nm. The difference-frequency output was tunable from 3.7 to 4.8 μm with a single PPLN period Λ= 22.58 μm. The DFG source was successfully used for absorption measurement of CO_2 in open air.

A novel approach of employing SLD for gas monitoring is also described. In the present study, oxygen concentration measurement based on a near-infrared SLD (around 760 nm) is investigated. The fiber-optic SLD system with two different wavelengths of 760 nm and 1560 nm may also be used to measure O_2 and CO_2, respectively, in combustion environments for emission monitoring. These sensors should also be useful as a control tool for equipment and facility design, manufacturing and plant operations, biological applications, such as breathe analysis.

5. REFERENCES

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