Performance of mid-infrared difference frequency spectrometer employing a periodically poled LiNbO₃ for next generation environmental monitoring

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Development of a fiber laser pumped, compact mid-infrared (IR) difference frequency spectrometer employing a periodically poled LiNbO₃ (PPLN) for next generation environmental monitoring is presented. Previous spectroscopic experiments of various gas species, performance characteristics of pump and signal lasers and PPLN-based difference frequency generation (DFG) are reviewed. The DFG spectrometers developed in our facility were carefully calibrated with concentrations between a few ppm and 500 ppm, and demonstrated with an excellent linearity. Moreover, a ratio between measurement deviation and gas concentration was approximately ±1%, which could maintain in a long-term measurement operation (∼1000 h). Rapid gas detection for N₂O, CH₄, CO₂, NO₂, and NH₃ with a total measurement time of less than 10 s was achieved with interference completely free from absorption spectra of other gas species, resulting in minimum detectable concentration at sub ppm level. Also, real-time NO₂ monitoring of an exhaust gas of a diesel engine is demonstrated, and a simultaneous dual gas detection concept by the DFG is introduced.

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Highly sensitive and selective monitoring of numerous gas species has become increasingly important in various fields for environmental trace gas monitoring, industrial plant surveillance and process control. In order to realize such requirements, the active laser sensing has been studied and developed[1]. Especially, the laser absorption spectroscopy based on a tunable continuous wave (CW) narrow-linewidth light source is a very attractive gas sensing method in the wavelength region including absorption spectra of molecules. Real-time monitoring can be achieved by selecting the specific molecule in sampled gas mixture species. Most environmentally important species, such as NH₃ and NO$_x$, have overtone and fundamental ro-vibrational absorption lines in the near-infrared (IR) and mid-IR spectral regions. The near-IR region, from 1 to 2 μm, usually belongs to the first and second overtone bands, and it can be accessed directly by a several milliwatts semiconductor laser[2−5]. However, the first and second overtone bands transition is one to two orders of magnitude weaker than fundamental ro-vibrational absorption lines. Therefore, a tunable narrow-linewidth light source in the mid-IR region is useful for detecting such trace gas species in ambient air.

Figure 1 summarizes absorption transitions of environmentally important gas species and laser light sources. In the mid-IR, lead salt based laser diode, and more recently quantum cascade (QC) laser diode have been developed as CW mid-IR coherent sources. Such light sources in the mid-IR region have applied to highly sensitive trace gas detection[6,7]. However, cryogenic cooling with a sensitive temperature control for trace gas detection is required. The particular source is obtained by a difference frequency generation (DFG) technique that mixes two near-IR laser pump sources (λ_1, λ_2) to generate mid-IR ($\lambda_3^{-1} = \lambda_1^{-1} - \lambda_2^{-1}$) in a quasi-phase-matched (QPM) nonlinear optical crystal such as periodically poled LiNBO₃ (PPLN) in single-pass geometry[8,9]. The DFG spectroscopic source operates at room temperature with single spatial mode, single frequency and continuous tuning over a wide frequency region. Compact DFG-source based gas sensors capable of sensitive real-time gas detection have been demonstrated for field use[10−13]. Furthermore, such sources offer an intrinsic spectral resolution better than 0.001 cm^{-1} (30 MHz) without active frequency stabilization. The generated wavelength range of DFG is mainly determined by the transparent range of the nonlinear optical material from 0.4 to 5 μm[14]. Generally, the generated DFG light source depends strongly on the two near-IR laser sources characteristics. In this work, we utilize a compact Yb fiber laser as one of the pump sources with a fiber Bragg grating (FBG). The Yb fiber laser can be designed to operate at any specified wavelength within the range from 1035 to 1120 nm corresponding to Yb-doped fiber amplifier gain region. The other laser can be selected in a standardized International Telecommunication Union (ITU) 50-GHz spaced frequency grid in a range of 1260 − 1360 nm (O-band), 1360 − 1460 nm (E-band), 1460 − 1530 nm (S-band), 1530 − 1565 nm (C-band), 1565 − 1625 nm (L-band) and 1625 − 1675 nm
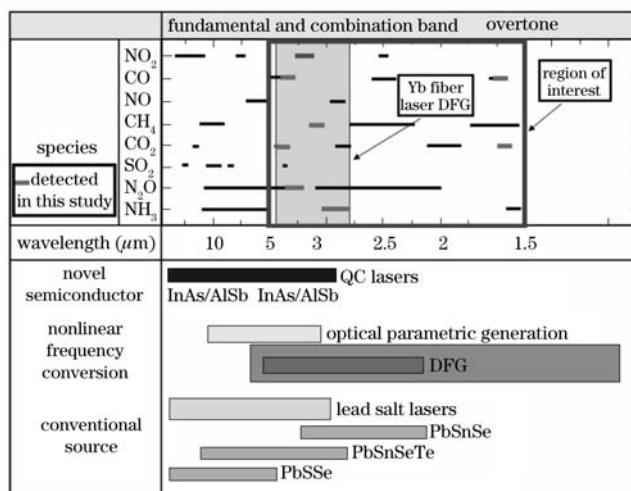

Fig. 1. Absorption lines of environmentally important gas species and laser light sources.

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(U-band). In our previous study, we have reported NO_2 detection with a 1064-nm Yb fiber laser pumped spectroscopic source of DFG with a 1536-nm[15] distributed feedback laser diode (DFB-LD). Such scheme can essentially have multi-component gas detection capability of accessing the mid-IR range by selecting an Yb fiber laser wavelength ($1035 - 1120$ nm) together with a tunable DFB-LD for telecommunication from 1400 to 1650 nm with an increment of 10 GHz, resulting in an excellent wavelength tuning flexibility. The laser spectrometer is based on DFG techniques in a PPLN crystal, naturally having two laser sources (i.e., signal and pump laser sources). An idea to 'recycle' residual near-IR signal laser power in the DFG set-up to tune absorption lines of NH_3 around at 1.54 μm is proposed, while the DFG output wavelengths are tuned at 3.46 μm.

A gas sensor based on the active DFG spectrometer is schematically shown in Fig. 2. The pump source at a wavelength of 1038 or 1064 nm with a linewidth of 1 MHz is a high-power Yb fiber laser, with an output power of 200 mW, spectrally stabilized by a narrow linewidth FBG. While a DFB-LD (NTT Electronics Inc., NLK1554STB) at a wavelength of 1536 nm with an output power of 20 mW and a linewidth of approximately 1 MHz is used as a signal source. The DFB-LD frequency can be varied by -0.02 cm^{-1}/mA with an injection current and -0.35 cm^{-1}/K with temperature modulation. A three-port wavelength division multiplexer (WDM) is used to combine the above pump and signal near-IR laser sources. The fiber connection between laser sources and the WDM causes a power loss due to WDM insertion loss (<0.5 dB) and loss associated with mis-match in the mode field diameter of each fiber. The multiplexed beams are emitted to free space from the angled polished coupler fiber end.

The emitted beams have a Gaussian spatial profile and are focused to a diameter of about 80 μm into the center of PPLN crystal by an imaging lens (microscope objective lens, focal length $f = 10$ mm). Polarization controllers are inserted after each pumping source to match the nonlinear optical polarization state of each source to optimize the nonlinear interaction in the PPLN crystal. The PPLN crystal used in this experiment was 20.5 mm long and 0.5 mm thick, with periods of either 29.8 or 30.1 μm. The input and output surfaces of the PPLN
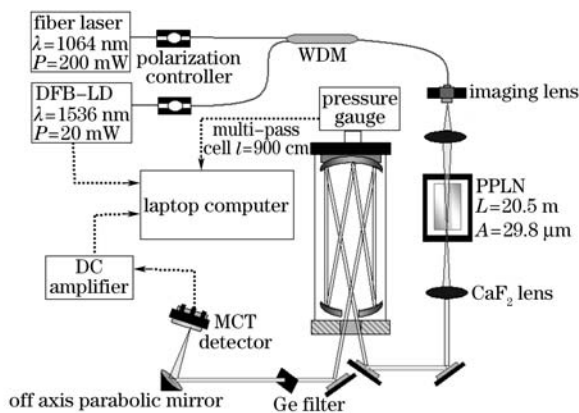
crystal are AR-coated for the pump, signal, and idler wavelengths, respectively. To optimize the DFG power, the PPLN crystal temperature is controlled by a Peltier thermoelectric element. A phase matching condition is calculated from Sellmeier's equation, $n_3/\lambda_3 = n_1/\lambda_1 - n_2/\lambda_2 - 1/\Lambda$ (where Λ is the grating period and n_1, n_2 and n_3 are the extraordinary refraction indices). Firstly, the DFG device accesses around at 3.03 μm for detection of NH_3 by selecting the pump laser wavelength at 1038 nm and the signal laser wavelength at 1577 nm. Then, the DFG device is tuned to 3.46 μm for detection of NO_2 by altering the pump laser wavelength at 1064 nm and the signal laser wavelength at 1536 nm. The latter pump and signal laser combination of DFG allows the detection of NH_3 gas with a signal light source as well as detection of NO_2 gas by DFG light source. The generated mid-IR DFG radiation and two residual pump beams are collimated by a CaF_2 lens ($f = 50$ mm). The optical path length of the multi-pass absorption cell is either 8.5 or 20 m. Output lights from the cell are focused to a thermoelectrically cooled HgCdTe (MCT) detector by a gold coated off axis parabolic mirror with a focal length 50.4 mm. Detected signal is amplified by a DC amplifier and acquired by a laptop computer with a 16 bit A/D data acquisition card (National Instruments, DAQ card). The signal data is analyzed by using LabVIEW software.

In the preliminary experiment, the polarization characteristics of the 1.064 μm fiber laser are investigated. The polarization instability might lead to the failure in the optimization of DFG power. For the investigation, a polarizer is placed between the fiber laser and an InGaAs photodiode. After the polarization is adjusted to be linear by polarization controller, the relative power is measured by rotating the polarizer. The measurement is conducted at every thirty minutes (see Fig. 3) during the fiber laser operation and after restart. The result shows that the polarization of the fiber laser is stable and keeps still over the extending period of time and after restart. The signal DFB laser was measured in the same method, and it was found that the stability was very identical.

Figure 4 shows the DFG power output as a function of the product of incident pump powers from both fiber laser and DFB diode laser. The pump powers used are the values at the entry facet of the PPLN crystal. Firstly the fiber laser power is varied with a fixed DFB-LD power of 25 mW and subsequently the DFB-LD power is varied with a fixed fiber laser power of 110 mW. The DFG slope efficiency is estimated to be 0.67 mW/W^2. The DFG power of 1.8 μW from two near IR lasers and PPLN crystal is obtained for a product of ~ 2750 mW^2 when the fiber laser power is 110 mW and DFB-LD power is 25 mW.

A high-resolution Doppler-broadened CH_4 absorption spectrum around at 3038.5 cm^{-1} (3.291 μm) at a cell pressure of 133 Pa is obtained as shown with an upper trace in Fig. 5. The spectrum is fitted by a Gaussian profile. The linewidth of the absorption lines is measured to be 0.01 cm^{-1} (300 MHz) (FWHM). Values obtained from the HITRAN database (0.0935 cm^{-1}, 280 MHz) agree within 0.00065 cm^{-1} (20 MHz). This measurement demonstrates that the spectral resolution of the DFG source is less than 20 MHz.
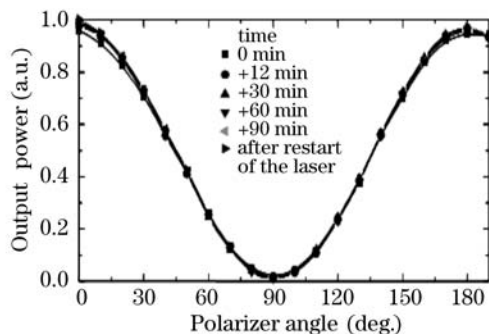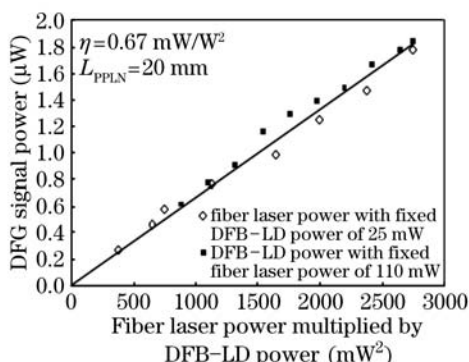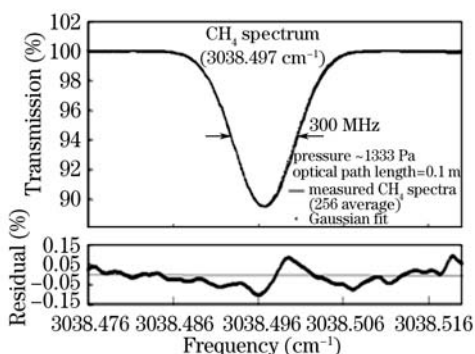

Fig. 2. Schematic of the DFG gas sensing system.

Fig. 3. Polarization stability of the 1.06 μm fiber laser.

Fig. 4. Slope efficiency of the DFG output.

Fig. 5. CH$_4$ absorption spectrum around 3038.5 cm^{-1}.

Taking full advantage of flexible wavelength tuning characteristics of the DFG spectrometer, we select an absorption line at 2892.318 cm^{-1} for NO$_2$ concentration measurements. For calculation of NO$_2$ concentration, we should estimate line intensity of observed NO$_2$ absorption spectrum by completely overlapping two absorption spectrum lines at 2892.3179 and 2892.3183 cm^{-1}. A discrepancy of two absorption spectra center positions is approximately 4.19×10^{-4} cm^{-1}, which is much less than the resolution limit of this system. For estimation of temperature dependent line intensity of observed spectrum, $S(T)$ (cm/molecule), we used

$$S(T) = \frac{\alpha(\nu)}{g(\nu - \nu_0) N_L}, \tag{1}$$

where $g(\nu - \nu_0)$ is the normalized pressure-dependent lineshape function, and N is the total number of absorbing gas molecules. The value of N at 296 K is Loschmidts number, $N_L = 2.479 \times 10^{19}$ (molecules cm^{-3} atm^{-1}). $\alpha(\nu)$ is the linear absorption coefficient (cm^{-1} atm^{-1})
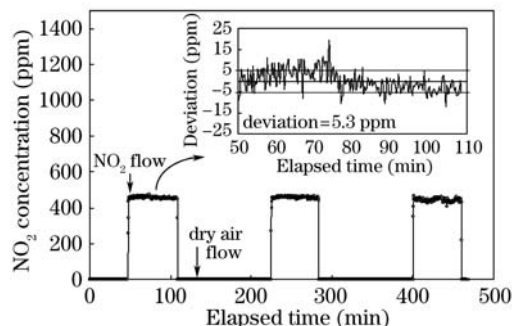
Fig. 6. Demonstration of long-term NO$_2$ detection.

calculated by Lambert-Beer's law. Based on this analysis, we calculated the molecular line intensity to be 8.77×10^{-21} cm/molecule from the measured absorption spectrum. This estimated experimental line intensity value was in good agreement with simulated spectral line intensity from HITRAN database of 9.17×10^{-21} cm/molecule.

This result shows that the estimated DFG linewidth has little influence on actual absorption spectrum measurement. The minimum detectable concentration value was estimated to be approximately 5 ppm in measuring this absorption line, with assumed a signal-to-noise ratio SNR = 1, and an absorption measurement sensitivity of $\sim 10^{-4}$, for maximum averaging time of 10 s.

For investigation of the overall instrument performance, including reproducibility and stability of the detection system, long-term measurements were assessed by monitoring NO$_2$ line at 2892.318 cm^{-1}. In this long-term test, a calibrated NO$_2$ (436 ppm) and dry air flowed through alternately into the multi-pass cell at a pressure of 13 kPa. To prevent influence of temperature on dimerization, we kept the sample gas temperature at 297 K in this measurement. The NO$_2$ concentration measurement for a part of 3-day period is shown in Fig. 6. As calibrated NO$_2$ flowed into the multi-pass cell, the concentration is measured as $\sim$ 450 ppm, which was within $\sim \pm 1.5\%$ of the calibrated concentration. In this concentration measurement, the estimated line intensity of 8.77×10^{-21} cm/molecule for the observed NO$_2$ absorption line at 2892.318 cm^{-1} was sufficiently accurate, with only 2% difference from the HITRAN database. The measurement standard deviation was estimated to be ± 5.3 ppm.

An idea to 'recycle' residual near-IR signal laser power in the DFG set-up to tune absorption lines of NH$_3$ around at 1.536 μm is proposed, while the DFG output wavelengths are tuned at 3.46 μm. The DFG described above generates inherently three different wavelengths and it is available for simultaneous multi-specie monitoring by tailoring one signal DFB-LD wavelength. The concept is shown in Fig. 7.

The objective of this study is to develop a laser-based trace gas sensor for simultaneous detection of two important gas species, namely NO$_2$ and NH$_3$, relevant to temporal concentration change of gas emissions from electric power plants, by taking full advantage of the quick response of optical monitors. In electric power plants, the catalytic reduction method is incorporated to remove NO$_x$ in the flue gas by reacting with NH$_3$. However, as
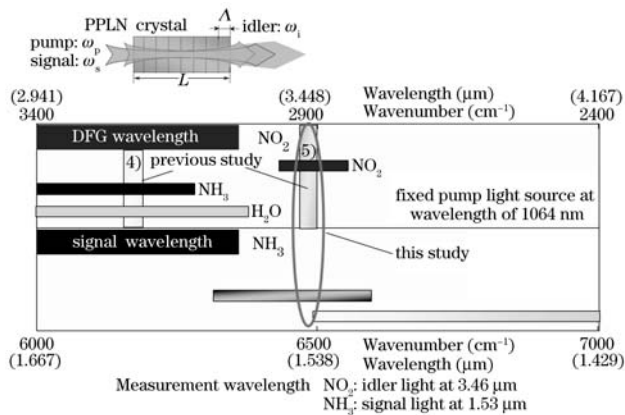
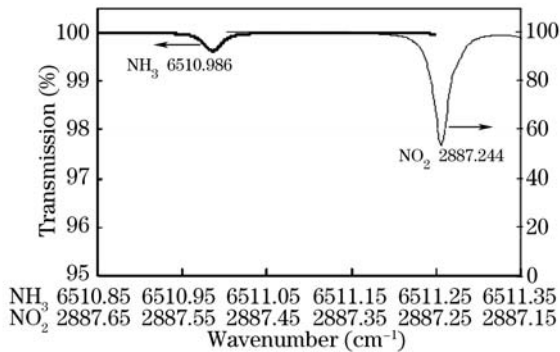Fig. 7. Tailored dual-wavelength laser spectrometer concept.

Fig. 8. Simultaneous NH_3 and NO_2 detection.

NH_3 is one of hazardous gases, it is necessity to measure NH_3 and NO_x in the flue gas in real time and high accuracy. The range of these gas concentrations to be monitored corresponds to between $\sim$ ppm and 0.1% with a response time of approximate 10 s. As shown in Fig. 8, we demonstrated measurement of NH_3 absorption spectrum by using DFB-LD at 1.536 μm and measurement of NO_2 absorption spectra by using DFG coherent light source at 3.46 μm. Dual wavelengths detection is feasible for one laser-based trace gas monitoring system. The absorption measurement of NH_3 at 1.536 μm suggests that it is more advantageous than that at 3.03 μm, although line intensities of NH_3 absorption spectra at 1.536 μm are about one order of magnitude weaker than these at 3.03 μm. Additionally, in the 1.54 μm region, the influence of water vapor is found to be negligible for measurement of NH_3. The absorption line intensity of NH_3 at 6512.685 cm^{-1} can be estimated approximately 7.70×10^{-22} cm/molecule. Optimum data accumulation for low measurement deviation of NH_3 and NO_2 concentration by using DFG coherent light source is between 1500 and 3000 with time range within 20 s.

Trace gas monitors by using the DFG sources described here could achieve excellent spectroscopic performance compared with other IR semiconductor laser sources, although there exist some limitations due to opto-mechanical alignment stability and temperature-related effects around the system. Right now the application field has been limited due to low available power of DFG ($\sim \mu$W level). However, the output power of the DFG sources can be easily improved by using fiber amplifiers for both pump and signal lasers. Recent developments of a waveguide PPLN have achieved further improvement in DFG output power exceeding 3 mW with less pump and signal laser power combination[16−18]. Such laser spectrometers should serve an important role for real field measurement applications and environmental surveillance.

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