Detection of CO in air by diode-pumped 4.6-μm difference-frequency generation in quasi-phase-matched LiNbO$_3$

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Detection of CO, N$_2$O, and CO$_2$ in ambient air was performed with a room-temperature cw IR source based on difference-frequency generation in periodically poled LiNbO$_3$. The source was pumped by a seeded high-power GaAlAs amplifier at 860 nm and a diode-pumped monolithic Nd:YAG ring laser at 1064 nm. The IR output was tunable between 2160 and 2320 cm^{-1} without crystal rotation. The CO detection sensitivity is extrapolated to 5 ppb m/$\sqrt{\text{Hz}}$ if limited by IR intensity noise.   © 1996 Optical Society of America

The use of quasi-phase-matched periodically poled lithium niobate (PPLN) for mid-IR difference-frequency generation (DFG) and optical parametric oscillators was reported recently.[1–4] This new material offers the advantages of a large effective nonlinear coefficient and a phase-matching condition that can be designed for pumping with various visible and near-IR lasers. Here we report the use of a PPLN crystal tailored to match the generally available high-power diode and diode-pumped lasers at 860 and 1064 nm.[1] At these pump wavelengths the phase-matching condition is nearly independent of the idler wavelength, permitting tuning of the DFG between 4.0 and 4.5 μm without crystal rotation.[4] This wavelength region contains strong fundamental absorption bands of several important air pollutants[5] such as carbon monoxide (CO), nitrous oxide (N$_2$O), carbon dioxide (CO$_2$), and sulfur dioxide (SO$_2$) and is currently not conveniently accessible by room-temperature cw single-frequency diode lasers.

We have investigated the feasibility of application of a PPLN-based diode-pumped DFG source to spectroscopic trace gas detection in air. The performance characteristics of the source, including output power, linewidth, tuning range, and amplitude noise, were examined from the standpoint of spectroscopic detection. Atmospheric CO, N$_2$O, and CO$_2$ were used as sample target species. A detection limit for CO of 5 parts in 10^9 (ppb) m/$\sqrt{\text{Hz}}$ was found for wavelength-modulation 2f spectroscopy in ambient air under interference-free conditions.

The tunable mid-IR DFG source, shown in Fig. 1, mixed a Nd:YAG and a high-power tapered GaAlAs semiconductor amplifier pump. Although the source is similar to the source described in Ref. 4, it differs from it in two important ways: (i) for compactness and narrow linewidth the previously used lamp-pumped Nd:YAG is replaced with a diode-pumped monolithic nonplanar ring laser emitting 237 mW of power in a single longitudinal mode and (ii) the previously used external grating cavity tunable laser based on a tapered amplifier is replaced with a tapered amplifier seeded by a single-frequency laser diode, permitting fast frequency tuning by means of current modulation. The seed laser (SDL, Inc., Model 5410) was isolated from the tapered amplifier by a 40-dB Faraday isolator and was temperature stabilized to $\pm 0.02\,°$C, yielding a frequency stability of ± 0.6 GHz. To eliminate feedback-induced spectral instabilities, a low-numerical-aperture lens was used for seed laser collimation at a working distance of ~ 1 cm. A low lens collection efficiency resulted in 12-mW seed power incident upon the tapered amplifier (SDL, Inc., Model 8630), which near its 860-nm gain peak emitted 1.25 W at a current of 2.0 A. The amplifier emission was collimated by a spherical ($f = 4.5$ mm) and a cylindrical ($f = 15$ cm) lens[4] and passed through a Faraday isolator, a dichroic beam splitter, and an $f = 5$ cm focusing lens, producing 820 mW of power at the input facet of a 6-mm-long PPLN crystal. The field-poled, z-cut crystal had a domain period of 22.6 μm and was oriented $\sim 10°$ relative to the beam to yield wideband phase matching in the 4.3–4.6-μm range.[4] With 220 mW of incident power at 1064 nm, a maximum of 8.0 μW was measured at 4.5 μm. A somewhat lower conversion
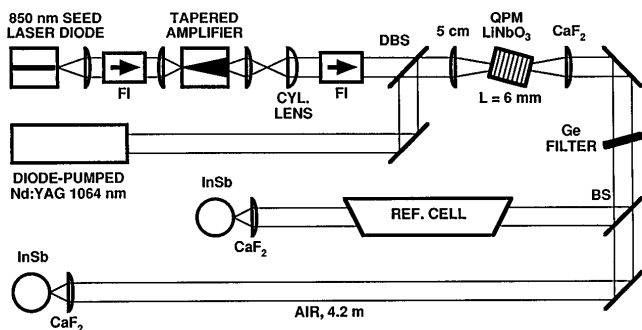
Fig. 1. Schematic of the tunable cw mid-IR DFG source used for detection of CO, N_2O, and CO_2 in air. The nonlinear mixing element was a quasi-phase-matched (QPM) periodically poled $LiNbO_3$ crystal. FI's, Faraday isolators; DBS, dichroic beam splitter; BS, beam splitter.

efficiency[1,4] observed here is attributed to nonoptimized beam diameters. The amplifier was typically operated to produce DFG power of $\sim$3.0 μW, adequate for all the measurements described below.

The spectrum of the seeded amplifier was monitored with an optical spectrum analyzer and a Fabry–Perot interferometer. The linewidth was less than the 50-MHz resolution of the interferometer. Coarse and fine wavelength adjustments were carried out with seed laser temperature and bias current settings, respectively. We made frequency scans by superimposing a 30-mA peak-to-peak triangular waveform at $\sim$10 Hz on the seed laser bias current, resulting in a continuous mode-hop-free frequency sweep range of 80 GHz. An additional $f = 2$ kHz sinusoidal waveform was used for frequency modulation during scans, with up to 11 GHz peak-to-peak frequency modulation amplitude.

Frequency sweep and modulation were accompanied by linear modulation of the seed power. This modulation was greatly suppressed by the clamped input-versus-output power transfer function of the tapered amplifier operated in a regime close to saturation. Because of the relatively low seed power, however, the saturation was incomplete, and the nonlinearity of the amplifier power transfer function produced the second harmonic of the modulation frequency, causing a weak rolling baseline in the $2f$ IR spectra. This effect can be reduced by increasing the seed power.

Another undesirable effect observed initially was weak étalon interference between the two facets of the tapered amplifier. This interference resulted in the DFG power modulation during scan, which masked the gas absorption signal. During the 80-GHz scan the seed wavelength tuned across four amplifier étalon fringes spaced by approximately 20 GHz. To eliminate this effect we synchronously modulated the amplifier current with the ramp used for seed laser frequency scans. This caused, through temperature- and carrier-density-induced index variation, a proportional scan of étalon fringe wavelength. With proper adjustment of the ramp amplitude ($\sim$200 mA) and phase the étalon fringe wavelength excursion matched that of the seed laser, and the power modulation caused by interference was eliminated. Improved antireflection coating of the diode amplifier chip could

reduce étalon effects, making the injection current modulation unnecessary.

The intensity noise spectrum of the DFG source was measured with a spectrum analyzer, and the results are shown in Fig. 2. The relative intensity noise was $3 \times 10^{-5}/\sqrt{Hz}$ at frequencies above 1 kHz. We expect a reduction in the intensity noise with the use of a low-noise amplifier current supply.

The observed continuous tuning range of the source was 2160–2320 cm^{-1}, which was sufficient for detection of CO, N_2O, and CO_2 in air. Typical abundances of these species in natural air are 330 parts in 10^6 (ppm), 320 ppb, and 150 ppb, respectively.[7] Figure 3 shows direct-absorption and wavelength-modulation $1f$ and $2f$ spectra of CO_2 in 2.5-m ambient air near 2303 cm^{-1}. We have not compared noise in the $1f$ and $2f$ signals. If the $1f$ signal from a reference sample is used to lock the IR frequency to the center of a given molecular transition, the $2f$ signal conveniently measures peak absorption. The traces are symmetric with respect to the vertical line at the center, which indicates reversal of the 2.5-cm^{-1} frequency sweep. Atmospheric CO_2 is the dominant absorber in this wavelength region because of its relatively high natural abundance. Absorption by the less
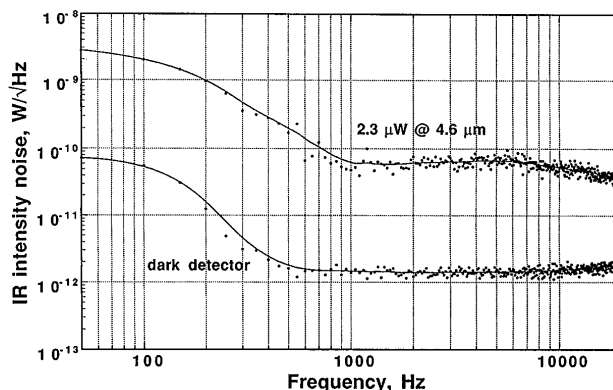

Fig. 2. Rms intensity noise in the IR beam. The data were acquired with a rf spectrum analyzer and converted to units of $W/\sqrt{Hz}$.

Fig. 3. Direct-absorption (top trace) and wavelength-modulation $1f$ and $2f$ (middle and bottom traces, shown on the same vertical scale) spectra of CO_2 in 2.5-m ambient air near 2303 cm^{-1} recorded with a digital scope. The frequency sweep of 2.5 cm^{-1} is reversed at the center. The transitions seen here are $P(50)$ (0001–0000), $R(26)$ (0001–0000), $P(39)$ (0111–0110), and $R(24)$ (0001–0000), from left to right in the left half of the figure.[5] Both R transitions belong to $^{16}O^{13}C^{16}O$.
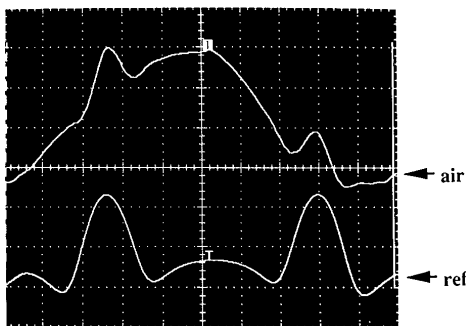
Fig. 4. Wavelength-modulation $2f$ spectra of the $R(6)$ fundamental of CO at 2169 cm^{-1} in 4.2-m ambient air ($30\times$ magnified, top), and a reference sample ($\sim$3-Torr CO mixed with room air in a 10-cm cell, bottom). The frequency sweep of $\sim$20 GHz is reversed at the center. The sweep rate was 10.6 Hz, the modulation frequency was 2 kHz, and the lock-in time constant was 1 ms. Both traces are 100-sweep averages.

abundant N_2O and CO, even at the peak (1.1×10^{-2} and 6.0×10^{-3} ppm^{-1} m^{-1}, respectively), can be completely swamped by H_2O absorption.

The ambient CO and N_2O were monitored over the 4.2-m open path between the mixing crystal and the signal detector. Figure 4 shows wavelength-modulation $2f$ spectra of the $R(6)$ fundamental of CO near 2169 cm^{-1} in air and in a reference sample. The sample had $\sim$3 Torr of CO mixed with air at atmospheric pressure in a 10-cm cell, resulting in 93% peak absorption. The $2f$ absorption signal was monitored to permit easy visual comparison of position and width of the signal and reference absorption peaks. The vertical line at the center indicates reversal of the frequency sweep, which was approximately 20 GHz. Both traces are 100-sweep averages, resulting in the noise bandwidth of 2.5 Hz. The rolling baseline in the air trace is a result of synchronous amplitude modulation in the tapered amplifier, as mentioned above. It is asymmetric because of weak thermal modulation in the amplifier caused by the frequency sweep and delayed in time. Magnitudes of absorption peaks in the top trace suggest that the concentration of CO in laboratory air is $\sim$360 ppb, which is higher than the U.S. standard average 150 ppb.[7] The rms noise in the $2f$ absorption signal measured without frequency sweep was approximately equal to the rms intensity noise (see Fig. 2). This corresponds to a noise equivalent column density of 5 ppb m/$\sqrt{\text{Hz}}$ for CO in air at atmospheric pressure. This is comparable to the detection limit of 14 ppb m/$\sqrt{\text{Hz}}$ for CH_4 in air near 8 μm (peak absorption of 1.8×10^{-3} ppm^{-1} m^{-1} at 1306 cm^{-1}) in a compact lead-salt diode laser spectrometer[8] reported by Webster *et al.*

Potentially the tuning range can be extended to 4.0 μm to permit the detection of SO_2. In our experiment, tuning to wavelengths below 4.3 μm required cooling of the seed laser below 15 °C, and to avoid water

condensation we did not perform it. The use of an external cavity laser can provide the desired tuning range without extreme heating or cooling.[4] Alternatively, seed lasers with lower operating wavelengths could be used. DFG wavelengths from 3.0 to 5.5 μm have been generated with PPLN.[4] A wavelength of particular interest is the 5.3-μm fundamental R branch of nitric oxide. At this wavelength we measured a transmission of 75% in a 1-mm-long uncoated $LiNbO_3$ sample. For a 6-mm-long uncoated sample this implies a 42% transmission. For access to the wavelength of 5.3 μm, a seed laser emitting at 886 nm would be required in the present DFG source, or the Nd:YAG could be replaced by a 1025-nm laser diode.

In summary, water-free detection of the CO in ambient air (360 ppb) was performed with a compact tunable laser source at 4.6 μm. The source was based on DFG in quasi-phase-matched $LiNbO_3$ pumped by a seeded high-power GaAlAs amplifier at 860 nm and a diode-pumped Nd:YAG laser at 1064 nm. The CO detection sensitivity of 5 ppb m/$\sqrt{\text{Hz}}$ is extrapolated based on rms noise measured in the $2f$ infrared spectra. This constitutes an important demonstration of sensitive detection of CO rovibrational fundamental in air by a room-temperature diode-pumped tunable cw laser source. Tuning of the DFG source between 2160 and 2320 cm^{-1} was observed, limited by the tuning range of the solitary diode seed laser. This was sufficient for detection of CO, N_2O, and CO_2 and in the future can be extended to 2500 cm^{-1} for detection of SO_2 and to 1900 cm^{-1} for the detection of nitric oxide.

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