Compact tunable mid-infrared laser sources: technology and applications

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ABSTRACT

Recent progress in design of diode-laser-pumped CW tunable narrowband mid-infrared sources based on difference-frequency generation (DFG) is addressed. Application of two such tunable sources to high-resolution spectroscopy and sensitive atmospheric trace detection of methane near 3.2 μm is reported. Methane detection limit in air of 12 ppb·m/√Hz is reported based upon the signal-to-noise ratio observed in the direct absorption spectra. Performance characteristics of these sources are examined including tuning range, phase matching bandwidth, output power, and amplitude stability. Applications of diode-laser-pumped CW tunable DFG may include atmospheric trace detection of several major hydrocarbons such as ethane, ethylene, and benzene, and toxic air pollutants such as carbon monoxide, nitric and nitrous oxide, sulfur dioxide, and methyl chloride.

1. INTRODUCTION

This work was done to develop a diode-laser-based technique for sensitive detection of environmentally important trace gases in the atmosphere such as methane, carbon monoxide, nitric oxide, and nitrous oxide. Mid-infrared molecular absorption spectra of these and other gases have been studied with the use of conventional and laser spectroscopy over many years. Large computer databases exist that contain transition frequencies, line intensities, pressure broadening coefficients, and natural abundance of hundreds of organic and inorganic gas species. The availability of spectroscopic data, and recent progress in the development of semiconductor lasers and nonlinear IR optical materials permit the development of compact high-resolution spectrometers and gas sensors based on diode-laser-pumped difference-frequency generation (DFG). In this paper, the applicability of CW diode-pumped DFG to high-resolution spectroscopy and trace gas detection in air is investigated using methane (CH_4), carbonyl sulfide (OCS), carbon monoxide (CO), and nitrous oxide (N_2O) as sample target species. We report successful design and operation of two compact CW diode-pumped DFG sources tunable near 3.2 μm. They were used for high-resolution spectroscopy of methane and carbonyl sulfide, and sensitive detection of the methane in natural air (1.8 ppmv). Feasibility tests were also performed which show that carbon monoxide, nitrous oxide, and a several other species can be detected in air using diode-pumped 4.5 - 5 μm tunable DFG.

Several measurements of optical absorption in methane using tunable near-infrared lasers have been reported recently. Lucchesini et al. have used diode lasers to access $3v_1+v_3+(v_2$ or $v_4)$ combination-overtone bands of methane near 790 nm, and the $2v_1+2v_3$ band near 860 nm [1]. Scott et al. have investigated the possibility of methane detection with the use of a 1.34 μm Nd:YAG laser which can access the v_1+2v_3 combination-overtone band [2]. Uehara and Tai have used a diode laser to detect methane in air by monitoring absorption in the $2v_3$-stretch vibration-overtone band near 1.66 μm, achieving a detection limit of 0.3 ppm·m with a signal averaging time of 1.3 s [3]. This corresponds to 680 ppb·m/√Hz. Pavone and Inguscio observed a component of the methane combination band corresponding to a third overtone at 866 nm [4].

The fundamental v_3 band of methane near 3.2 μm, however, has transitions that are as much as a factor of 160 stronger than those of the first overtone band and may be better suited for sensitive detection. The maximum line intensity and the typical pressure broadening coefficient of methane in this band is $2.13 \cdot 10^{-19}$ cm, and 27 kHz·Pa^{-1}, respectively, which corresponds to a peak absorption of 0.005 m^{-1}·ppm^{-1} in air at 1 atm near 3067 cm^{-1} [5]. Given the typical 1.8 ppm natural abundance of methane in air the absorption coefficient to be measured is 0.009 m^{-1}. The fundamental v_3 band of methane is accessible by either conventional spectroscopy using the carbon monoxide overtone laser [6], the helium-neon laser near 3.39 μm [7], lead-salt diode lasers, color-center lasers, or with Ar$^+$-dye laser difference-frequency generation [8]. These infrared laser

sources are also suitable for sensitive atmospheric trace gas detection. McManus *et al.* demonstrated an atmospheric methane measurement instrument using a Zeeman-split helium-neon laser with a sensitivity of 20 ppb with a signal averaging time of 1 s (40 ppb/$\sqrt{Hz}$) [9]. Simultaneous detection of methane and other gas species in air has been accomplished with the use of a compact lead-salt diode laser spectrometer that included a multipass absorption cell (Webster *et al.*, [10]). A detection limit for methane of 4 ppb·m near 8 μm with a signal averaging time of 3 s was reported (14 ppb·m/$\sqrt{Hz}$).

However, each of the mid-infrared laser sources mentioned above suffers from its own specific practical drawbacks such as large physical size, lack of portability, high cost, high power consumption, poor tunability, or need for cryogenic cooling. On the other hand, the use of commercial single-frequency short wavelength diode lasers as pump sources offers benefits of small size, reliability, low cost, and low power consumption. These diode lasers also offer good amplitude and frequency stability which are important in the design of a compact and robust gas sensor. Several new interesting diode lasers operating in the 2.7 μm to 3.9 μm wavelength region have been developed [11-13] but are not yet commercially available. These lasers may still require cooling with liquid nitrogen for normal operation which is sometimes a practical drawback. Therefore, CW difference-frequency generation (DFG) pumped by visible and near-infrared diode lasers at room temperature remains an attractive technique for generation of tunable mid-infrared light [14]. In this paper, the applicability of CW diode-pumped DFG to sensitive trace gas detection in air is investigated using methane as a sample target. The detection limit for methane in air is determined based upon the measured performance characteristics of the IR probe source and detector.

A significant technical difficulty in applying DFG to spectroscopic detection is its low conversion efficiency when pumped directly by most single-frequency CW semiconductor lasers. In this work, the performance of a CW single-pass DFG source was examined from the standpoint of spectroscopic trace gas detection. It was designed to generate low-power, low-noise, diffraction-limited probe beam, and was tunable near 3.2 μm. Detection sensitivity observed with the use of this source was limited by detector noise which called for an increase in the IR probe power. Several techniques have been tested to increase the IR power available from DFG. Traveling wave semiconductor amplifiers have been successfully applied to boost effective optical pump power [15]. Quasi-phase-matched periodically poled $LiNbO_3$ was used as a nonlinear mixing material [16, 17]. It allowed to employ high-power pump sources at convenient wavelengths and large effective nonlinear coefficient d_{33} not accessible in a bulk-phase-matched crystal. Intracavity DFG has also been recently applied to obtain over 150 μW CW IR light tunable from 3.1 to 4.3 μm [18]. In earlier work [19] we reported tunable CW mid-infrared DFG with output power in excess of 3 μW pumped by relatively low-power near-infrared diode lasers. A compact ring enhancement cavity was used in order to increase effective signal power available for difference-frequency mixing. In this work, an improved and more robust design of the buildup cavity was implemented in order to provide increased IR power and simpler operation. Direct absorption and wavelength-modulation (2f) spectroscopy of methane in air at 10.6 kPa (80 Torr) were performed in a 1 m single-pass cell with 1 μW probe power. The detection sensitivity of 12 ppb·m/$\sqrt{Hz}$ was limited by detector noise. In an effort to further improve detection sensitivity, we tested the effectiveness of a confocal 3.2 μm enhancement cavity in combination with an intracavity absorption cell.

2. CW TUNABLE MID-INFRARED DFG SOURCES

Single-pass difference-frequency mixing permits the measurement of several important performance characteristics of a DFG source such as conversion efficiency, phase matching bandwidth, and tuning range, while being remarkably simple. Figure 1 shows a diagram of a 3.2 μm CW single-pass DFG source which was used for high-resolution spectroscopy of methane, and carbonyl sulfide. The source was pumped by two compact commercial lasers: a 60 mW extended-cavity diode laser (ECDL) at 800 nm (pump), and a 30 mW diode-pumped Nd:YAG microchip laser at 1064 nm (signal). The pump and signal laser beams were combined in a polarizing beamsplitter cube after spatial mode matching. The difference-frequency mixing was performed in a 20 mm long uncoated $AgGaS_2$ crystal which was angle-tuned between 80° and 90°. The 3.2 μm output beam (idler) was collimated by a CaF_2 lens, and focused by another CaF_2 lens onto a liquid-nitrogen-cooled InSb detector. A broadband antireflection-coated germanium filter was placed in front of the detector window to remove pump and signal light. The noise equivalent power (NEP) of the detector at 3.2 μm was measured to be ~3.4 pW/$\sqrt{Hz}$. The maximum of 50 nW IR power was measured with 51 mW of pump power and 29 mW of signal power incident on the crystal.

For spectroscopic measurements the source was operated near 3090 cm^{-1} which corresponds to the internal phase matching angle of 81°. At this angle, the effective crystal length was limited to ~8 mm by the birefringent beam walkoff. Fine frequency tuning of the source was performed by scanning of the grating-tuned ECDL. The frequency modulation bandwidth of ~1 kHz was limited by response speed of the grating assembly. The mode-hop-free tuning range of the laser did

not exceed 17 GHz. We used carbonyl sulfide as a reference gas in order to calibrate the output wavelength of the source and identify absorption lines of methane.
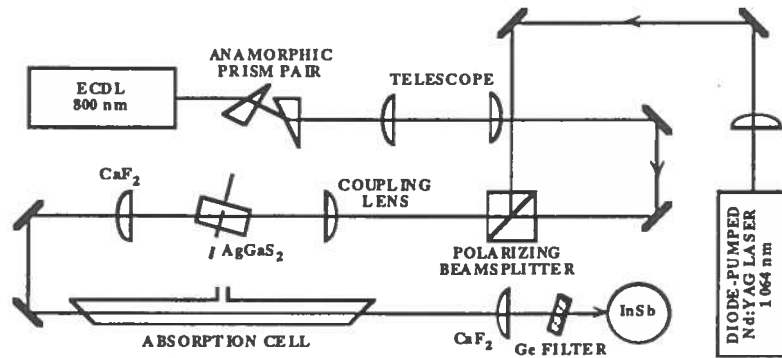

Figure 1. Schematic diagram of a 3.2 μm CW tunable single-pass DFG source used for high-resolution spectroscopy of methane and carbonyl sulfide. The source was pumped by two compact lasers: a Littrow grating-tuned ECDL at 800 nm, and a diode-pumped Nd:YAG microchip laser at 1064 nm.

Another 3.2 μm DFG source was built in an attempt to increase infrared probe power (see Figure 2). It was pumped by two compact lasers: a commercial 530 mW diode-pumped monolithic Nd:YAG ring laser at 1064 nm (signal), and a 20 mW ECDL at 800 nm (pump). In later experiments, the ECDL was replaced with a 100 mW solitary laser diode in order to increase the IR power and allow fast wavelength modulation.
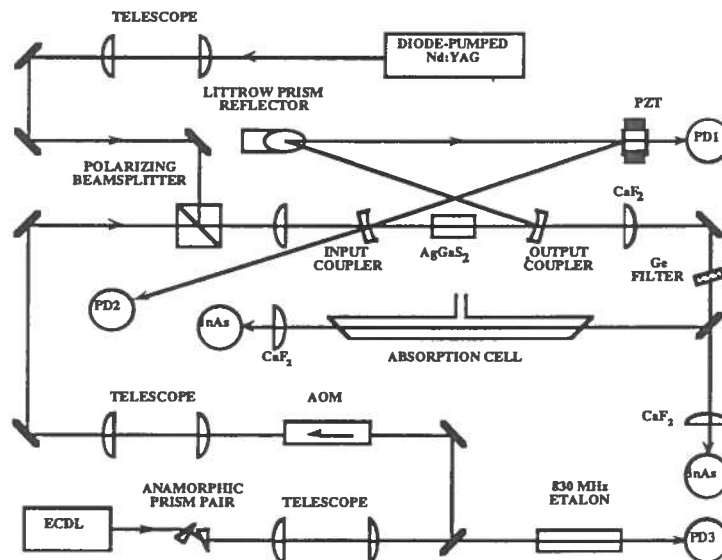

Figure 2. Schematic of the 3.2 μm CW tunable DFG source used for detection of the methane in air. The source was pumped with an extended-cavity diode laser at 800 nm, and a diode-pumped monolithic Nd:YAG ring laser at 1064 nm. A bow-tie 1064 nm enhancement cavity was built around the mixing crystal in order to increase effective Nd:YAG power available for mixing. The source was tuned by tuning of the diode pump laser.

The spatially mode-matched pump and signal beams were focused into a 5.5 mm antireflection-coated AgGaS$_2$ crystal through the input coupler of a bow-tie enhancement cavity. The cavity was designed to build up the 1064 nm light because bulk absorption in the crystal at that wavelength is lower than at 800 nm and scanning is simpler. The input coupler was a plano-concave fused silica substrate coated for high transmittance near 800 nm and 3.4 % input coupling at 1064 nm. The radius of curvature of the concave side was 100 mm. The CaF$_2$ output coupler had the same dimensions and was coated for high reflection at 1064 nm. The transmittance of the output coupler was measured to be 41% near 3.2 μm using light from a carbon monoxide overtone laser. The long arm of the cavity was not a conventional bow-tie in that a Littrow prism reflector was used instead of a flat mirror. The function of this element was to eliminate multiple passes of the 800 nm light in the cavity. Use of a flat mirror resulted in a small portion of the diode laser light circulating in the cavity which produced a systematic ripple in the IR power when the diode was tuned. The bow-tie cavity design with the addition of a Littrow prism

reflector provides several advantages: it employs a minimum number of intracavity elements, is easy to align, has flexible mode diameter control, which is important for reaching optimum DFG conversion efficiency [20], and eliminates cavity resonance at the pump wavelength.

The Nd:YAG beam was spatially mode-matched to the cavity and the reflected power was monitored by a silicon photodetector PD2 (see Figure 2). Optimization of the cavity mode diameter allowed us to achieve a 90% input coupling efficiency limited mainly by the impedance mismatch of the input coupler transmittance. However, in normal operation a typical input coupling efficiency of between 75% and 85% was observed. The intracavity Nd:YAG power was monitored by a silicon photodetector PD1 which detected a 0.011% transmission through a PZT-driven flat cavity mirror (see Figure 2). The cavity buildup was 16 with the mixing crystal and 144 without. This corresponds to 6.1% and 0.7% excess cavity loss. Transmission losses in the crystal for the ordinary beam at 1064 nm have increased from 1.5% to 5.4% due to additional surface and bulk losses in the one year time interval since the previous work [19]. Present measurements revealed 2.5% total reflection loss at 1064 nm compared to an immeasurably small reflection previously. This suggests that the index of refraction at the surface has changed. The manufacturer suggests that these changes are induced by exposure to near-UV light.
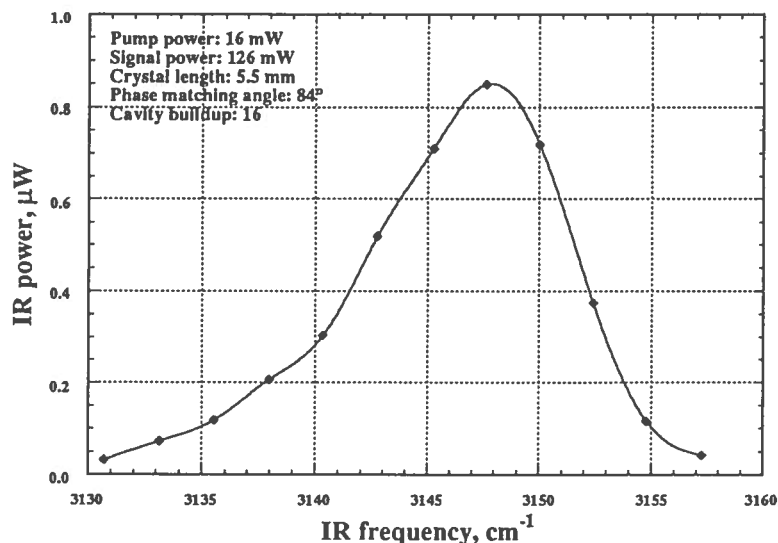

Figure 3. Infrared power versus frequency measured at the output of the cavity-enhanced 3.2 μm source.

A room-temperature InAs detector was used to monitor the idler beam. A maximum of 6 μW IR power was measured with 40 mW pump power incident on the crystal, and 230 mW signal power in front of the cavity, which corresponds to 3.75 W intracavity signal power. Operation with more than 4.2 W intracavity Nd:YAG power was achieved, accompanied by noticeable thermal lensing in the mixing crystal. Frequency tuning of the idler wave was performed by tuning of the pump laser and crystal angle. At a fixed phasematching angle, frequency tuning over a range of approximately 10 cm^{-1} was possible as is apparent from Figure 3. Therefore, short frequency scans of 10 GHz for spectroscopic measurements did not require crystal rotation. The observed asymmetry of the phase matching peak is a result of pumping with focused Gaussian beams [21]. Tuning of the pump laser from 801.3 nm to 795.2 nm and changing the internal phasematching angle of the crystal from 80° to 90° shifted the peak output IR power from 3076 cm^{-1} to 3183 cm^{-1}. Operation at infrared frequencies below 3076 cm^{-1} was possible with phasematching angles below 80° but at the cost of more than 25% reduction in the output power due to larger beam walkoff, decreasing effective nonlinear coefficient, and increasing Fresnel reflection losses at the AR-coated crystal surfaces which decreased the cavity buildup.

The source was used for sensitive spectroscopic detection of methane in air. It was scanned by sweeping the frequency of the ECDL or solitary laser diode. In the ECDL, continuous mode-hop-free frequency tuning of 20 GHz was performed by electronically adjusted synchronous rotation and translation of the PZT-driven tuning mirror. The Littman configuration of the ECDL allowed tuning without steering of the output beam. The solitary laser diode was tuned by current and temperature control. Frequency scans of 10 GHz and frequency modulation were performed by modulating the injection current. A low-finesse 830 MHz etalon was used for monitoring the scans.

In addition to single-pass absorption measurements we tested the effectiveness of a confocal enhancement cavity to improve the detection sensitivity. The cavity mirrors were plano-concave quartz substrates with 250 mm radius of curvature coated for high reflection at 3.4 μm. A transmittance of 1% was measured for each mirror using a probe beam from the DFG source. The finesse of the empty cavity was measured to be 213 which suggested a 0.5% additional loss in each mirror. For spectroscopic measurements an 18 cm long absorption cell with Brewster windows was placed into the cavity, reducing the cavity finesse to 182, which corresponds to an additional loss of about 0.25% per round trip. The cavity was dither-locked to resonance at the idler wavelength by controlling a PZT-driven mirror. In order to maintain the locking when the idler frequency was tuned, the diode laser sweep and modulation signals were supplied to the PZT controller that locked the 3.2 μm buildup cavity. Only 10% of the IR power from the DFG source could be coupled into the cavity because poor spatial mode matching. Typical idler power delivered to the detector was only about 80 nW. With improved spatial mode matching of the IR beam, it should be possible to achieve 80% coupling into the cavity and deliver about 0.8 μW probe power to the detector.

3. SPECTROSCOPIC DETECTION USING TUNABLE DFG

Direct absorption spectroscopy, and wavelength-modulation ($1f$ and $2f$) spectroscopy of methane and carbonyl sulfide were performed using the two tunable DFG sources described above. The primary objective of the measurements was to determine the detection limit for methane in air, and to identify the sources of noise. Figure 4 shows high-resolution spectra of methane and carbonyl sulfide acquired using the single-pass 3.2 μm DFG source.
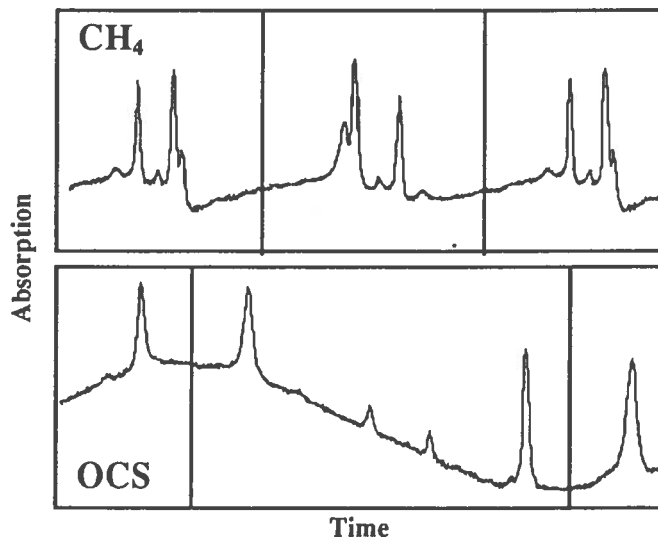

Figure 4. Direct absorption spectra of methane near 3090 cm^{-1} (frequency span of 0.2 cm^{-1}), and carbonyl sulfide near 3086 cm^{-1} (frequency span of 0.6 cm^{-1}). Both traces are 64 sweep averages (35 ms/sweep), acquired using 50 cm cell and 30 nW probe power. Total pressure was 4 kPa (30 Torr) in each case. The vertical solid lines indicate the frequency sweep reversal.

Transitions seen in these spectra have line intensities between $2.3 \cdot 10^{-22}$ cm and $1.2 \cdot 10^{-22}$ cm [5], and are ideal for use as references in the measurement of the detection limit. Fractional absorption introduced by these relatively weak transitions at the pressure of 4 kPa (30 Torr) over 50 cm path is between 20% and 70% while each individual transition can be resolved. Noise equivalent fractional absorption can be expressed in the units of column density of a target gas in a specified environment. Figure 5 shows lock-in-detected ($1f$ and $2f$) wavelength-modulation spectra of an isolated methane line near 3086 cm^{-1} acquired using 50 nW probe power, 50 cm cell, and the equivalent noise bandwidth of 25 Hz. Direct absorption caused by this line was measured to be 67%. The signal to peak-to-peak noise ratio observed in these spectra is better than 660. This corresponds to the absorbance root-mean-square noise level of $7 \cdot 10^{-5}/\sqrt{Hz}$ (equivalent to methane column density of 14 ppb·m/$\sqrt{Hz}$ in air at atmospheric pressure) and indicates that the detection sensitivity is limited by detector noise.

In another experiment, the methane in natural air was detected using the cavity-enhanced 3.2 μm source (see Figure 2). In this experiment, a servo loop was implemented to reduce amplitude noise in the IR beam. A portion of the IR beam was focused onto a room-temperature InAs reference detector, and the feedback adjustment of the diode laser power was performed

by an acousto-optic modulator. This allowed the effects of the Nd:YAG buildup cavity noise, the amplitude modulation of the diode laser resulting from frequency tuning, and background fringes to be canceled out.
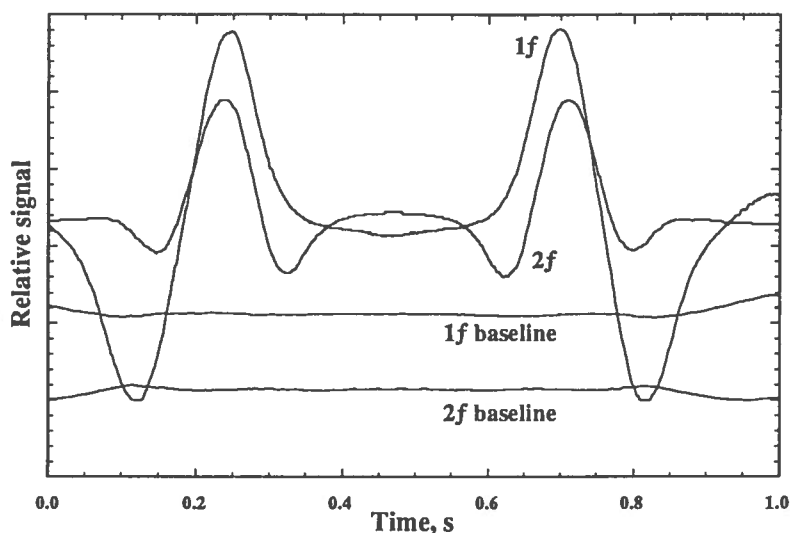

Figure 5. Wavelength-modulation spectra of an isolated methane line near 3095 cm^{-1}, acquired using a single-pass DFG source. Probe power was ~50 nW, path length was 50 cm, methane pressure was 4 kPa (30 Torr), modulation frequency was 1 kHz, lock-in time constant was 10 ms (6 dB/oct).

Direct absorption and wavelength-modulation (2f) spectroscopy of both pure methane and methane in air was performed with and without IR cavity enhancement. We used three calibrated mixtures of methane with natural air; these had mixing ratios of 75.3 ppm, 10.8 ppm, and 1.8 ppm. The last was natural air sampled on a mountain ridge. Figure 6 shows a single-sweep 2f spectrum of 75.3 ppm methane in air at 13.3 kPa (100 Torr) in a 59 cm single-pass cell. The spectrum was acquired by scanning the solitary diode pump laser and using 1 μW IR probe power without stabilization. The center frequency of 3086 cm^{-1} was chosen because of the presence of six strong distinct absorption lines of methane. For example, the transition at 3085.8323 cm^{-1} has a line intensity of 1.70·10^{-19} cm. It is only 20% weaker than the transition at 3067.3000 cm^{-1} which is the strongest in the band [5]. Tuning of the source to the frequency of this strongest line was possible at the cost of reduction in IR power output. The amplitude of the frequency modulation was optimized to produce the maximum 2f signal size.
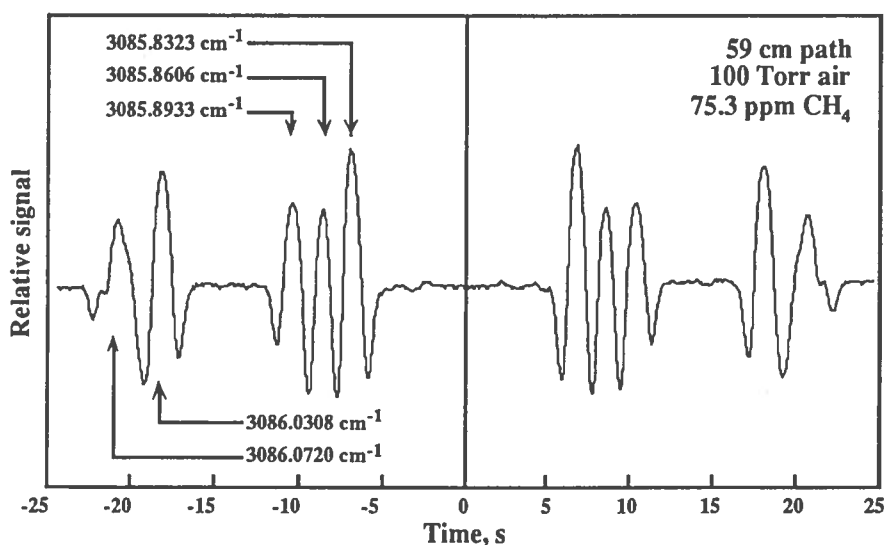

Figure 6. Wavelength-modulation (2f) spectrum of methane in air acquired using 1 μW IR power without stabilization. Frequency scan and modulation was performed by controlling injection current of the solitary diode pump laser. Modulation frequency was 2 kHz, lock-in time constant was 10 ms (6 dB/oct). The amplitude and phase of frequency modulation were optimized to produce maximum signal.

Figure 7 shows direct absorption spectrum of the methane in natural air at 80 Torr in a 1 m single-pass cell. It was acquired using noise equivalent bandwidth of 1 Hz, and IR power stabilization. Atmospheric pressure-broadened methane in the laboratory air between the power stabilizer beamsplitter and the sample cell is visible in the baseline trace. The baseline slope is due to interference from a secondary reflection from the power stabilizer beamsplitter. Based upon the observed signal-to-noise ratio, a detection limit (signal-to-noise ratio of 1) of 12 ppb·m/$\sqrt{\text{Hz}}$ can be determined; it is in good agreement with the measured InAs detector noise. This corresponds to an absorbance root-mean-square noise of $6 \cdot 10^{-5}$.
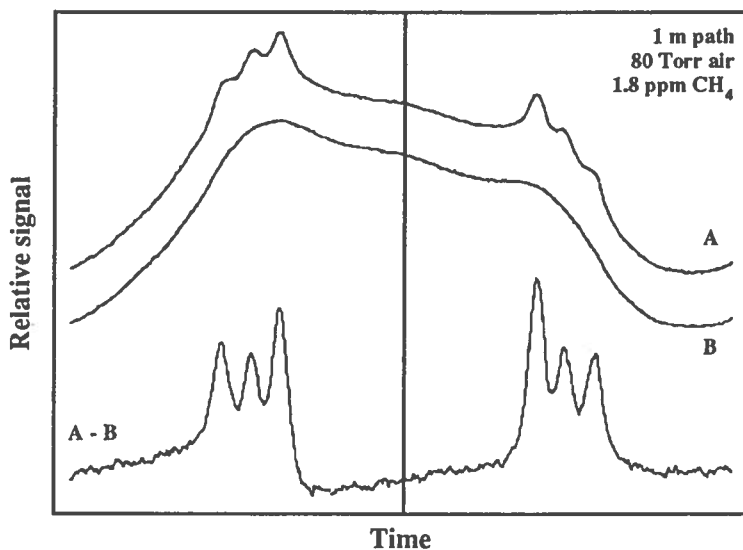

Figure 7. Direct absorption spectrum of the methane near 3086 cm^{-1} in natural air at 80 Torr in a cell (A), and the evacuated cell (B). The lower trace is the difference between (A) and (B) and shows only the signal from the cell. The detection limit of 12 ppb·m/$\sqrt{\text{Hz}}$ can be inferred. The spectra were acquired using 1 µW stabilized IR power. Atmospheric pressure-broadened methane in the laboratory air between the power stabilizer beamsplitter and the signal detector can be seen in the baseline trace. On the left, the IR frequency is scanned down, then the scan is reversed and the line rescanned. The total width of the frequency scan in a panel is about 5 GHz.
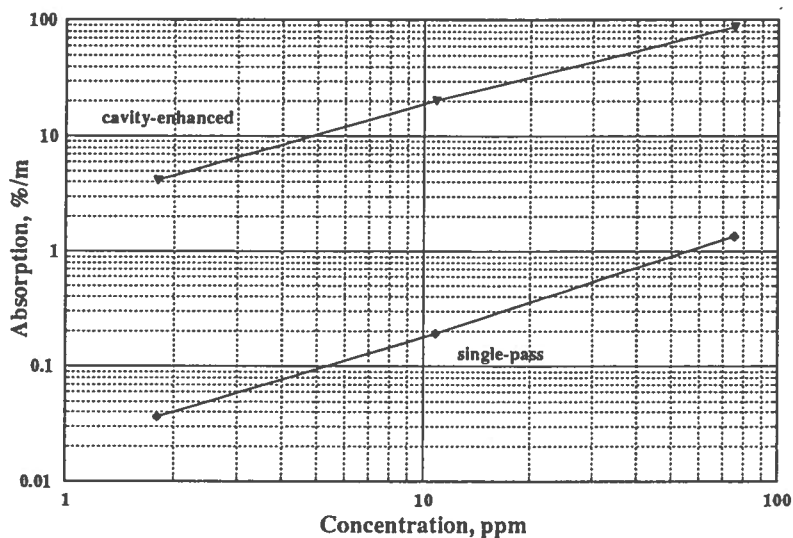

Figure 8. Relative 2f absorption signal per unit cell length detected with and without cavity enhancement.

The detection limit can be improved. First, more IR probe power can be generated. For example, a commercial 1 W single-frequency master oscillator power amplifier (MOPA) can be used as a pump source at 800 nm. Also, a somewhat longer mixing crystal can be used. Second, better output coupler transmittance can be obtained. We have measured 60%

transmittance at 3.2 μm for the replacement output coupler and 41% for that used in the experiment. Third, an IR detector with lower NEP can be used. The room-temperature InAs detectors used in the experiment had NEPs of ~17 pW/$\sqrt{}$ Hz at 3.2 μm, which is a factor of 5 larger than typical NEP of cooled InSb detectors. Fourth, either a multipass absorption cell or a buildup cavity can be used to increase effective path length.

The confocal enhancement cavity near 3.2 μm described above was used to increase the relative magnitude of the absorption signal. The effective number of passes in such cavity is $N = 2 \cdot F/\pi$, where F is the cavity finesse, and the factor 2 accounts for two passes through an intracavity absorption cell per round trip. Given the previously measured value of cavity finesse F = 182, the number of passes should be N = 116, which is in good agreement with the number obtained by comparing the fractional $2f$ signal per centimeter of cell length detected with cavity enhancement to that detected in the single-pass configuration. The experimental enhancement factor for lower intracavity methane concentrations is in agreement with the experimental value of cavity finesse (see Figure 8). Higher concentrations of methane introduce more absorption per round trip thus decreasing the cavity finesse and the related effective number of passes which is the case with the 75.3 ppm sample.

4. CONCLUSION

In summary, spectroscopic detection of the methane in natural air (1.8 ppmv) using diode-laser-pumped cavity-enhanced CW tunable difference-frequency generation near 3.2 μm has been performed by four methods: direct absorption spectroscopy, second-harmonic detection wavelength modulation spectroscopy, cavity-enhanced second-harmonic detection wavelength modulation spectroscopy, and direct absorption spectroscopy with power stabilization. The spectroscopic DFG source was pumped with an 800 nm diode laser and a diode-pumped 1064 nm Nd:YAG laser. It delivered a maximum of 6 μW of narrowband infrared light with 40 mW pump power and 230 mW signal power and was tunable from 3076 cm^{-1} to 3183 cm^{-1}.

With no cryogenic components, we observed a noise equivalent concentration for the detection of methane in air at 80 Torr of 12 ppb/$\sqrt{}$ Hz using a 1 m cell and direct absorption spectroscopy with power stabilization. This corresponds to an absorbance root-mean-square noise of $5.1 \cdot 10^{-5}$. We have observed the methane in natural air at atmospheric pressure, as can be seen from the baseline trace in Figure 7. The competing effects of increased methane density and pressure broadening compared to 80 Torr cancel out so the expected detection limit would be the same.
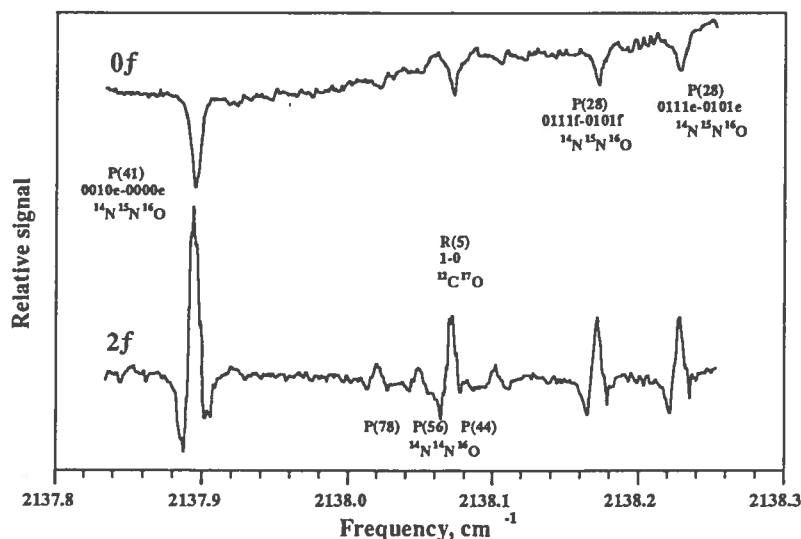

Figure 9. Direct absorption ($0f$) and wavelength-modulation ($2f$) spectra of a 1:1 mixture of carbon monoxide with nitrous oxide at total pressure of 10 Torr in a 50 cm cell. The spectra were acquired using a diode-pumped DFG source at 4.7 μm.

By using an output coupler with higher transmittance, and using liquid-nitrogen-cooled InSb detectors with 5 times better noise equivalent power, we expect to be able to observe a noise equivalent column density of 1.6 ppb·m/$\sqrt{}$ Hz. Proper spatial mode matching into the 3.2 μm buildup cavity would yield an effective path length of 15 m and thus a predicted detection limit of 0.1 ppb/$\sqrt{}$ Hz. Alternatively, a White cell could also be used. The choice of buildup cavity or multipass cell would be

dictated by application-dependent constraints such as physical size and sample volume. With either the buildup cavity or a multipass cell stray interference fringes or other baseline effects may limit the actual performance before the predicted 0.1 ppb/$\sqrt{}$ Hz detection limit is reached.

The DFG-based mid-infrared sources near 3 μm such as the two described in the paper can be applied to atmospheric trace detection of a variety of environmentally important gas species. These include ethane, ethylene, benzene, and methyl chloride. We have also investigated feasibility of detection of inorganic air pollutants such carbon monoxide, nitric and nitrous oxide, and sulfur dioxide, using CW DFG tunable between 4.5 μm and 5 μm. Figure 8 shows spectra of carbon monoxide and nitrous oxide acquired using a DFG source at 4.7 μm pumped by a diode laser at 693 nm, and a Ti:Sapphire laser at 813 nm. The Ti:Sapphire laser was used to simulate a tunable diode laser with a possibility of future replacement.

The DFG in noncritically phasematched $AgGaS_2$ at still lower infrared frequencies will require pumping with progressively shorter wavelengths. However, single-mode semiconductor lasers with wavelengths shorter than 635 nm are presently not commercially available which limits the practical DFG to mid-infrared wavelengths below 6 μm. Other infrared nonlinear crystals such as $AgGaSe_2$ and $ZnGeP_2$ can be used to reach wavelengths beyond 6 μm.

5. ACKNOWLEDGMENTS

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