TUNABLE INFRARED LASER SOURCES FOR SPECTROSCOPY AND ATMOSPHERIC TRACE GAS DETECTION

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ABSTRACT

Recent advances in semiconductor laser technology and availability of new IR nonlinear materials permit the development of compact, all-solid-state CW narrowband mid-infrared sources based on difference-frequency generation (DFG). Sources operating in the 3 to 18 μm range at room temperature and tunable over up to 200 cm^{-1} can be fabricated and should be suitable in a wide variety of applications, such as spectroscopy, trace gas detection, and environmental monitoring. The design issues involved in the development of such sources will be addressed, in particular the use of semiconductor amplifiers and optical buildup cavities to boost the available IR power. Specific sensor characteristics for trace gas detection including operating wavelength, tuning range, output power, and sensitivity will be discussed. Successful operation of one such IR sensor to detect methane in air is reported. The sensor is based on CW tunable DFG in $AgGaS_2$ pumped by an 800 nm diode laser and a diode-pumped 1064 nm Nd:YAG laser. Direct absorption and wavelength-modulation (2*f*) spectroscopy of the methane in natural air at 80 Torr were performed in a 1 m single-pass cell with 1 μW probe power. The best methane detection limit observed was 12 ppb*m/$\sqrt{Hz}$.

In this paper, the results of recent efforts to develop a diode-laser-based technique for sensitive detection of environmentally important trace gases in the atmosphere such as methane, carbon monoxide, nitrous oxide, and nitric oxide are presented. Several groups have reported spectroscopic detection of methane in the fundamental[1], and overtone[2] stretch vibration bands using tunable infrared lasers. The fundamental ν_3 band of methane near 3.2 μm includes its strongest known molecular transition (ν=3067.3 cm^{-1}, $S=2.13*10^{-19}$ cm) and therefore is better suited for sensitive detection. The band is accessible by either conventional spectroscopy or with Ar^+-dye laser difference-frequency generation[3], the carbon monoxide overtone laser, the helium-neon laser near 3.39 μm, lead-salt diode lasers, and color-center lasers. However, each one of these mid-infrared laser sources suffers from its own specific practical drawbacks such as large physical size, lack of portability, high cost, high power consumption, poor tunability, or the need for cryogenic cooling. In this work, detection of the methane in natural air (1.8 ppmv) was performed using diode-laser-pumped cavity-enhanced CW tunable difference-frequency generation (DFG)[4] near 3.2 μm. The room temperature DFG source was pumped with an 800 nm diode laser and a diode-pumped 1064 nm Nd:YAG laser (Fig. 1).

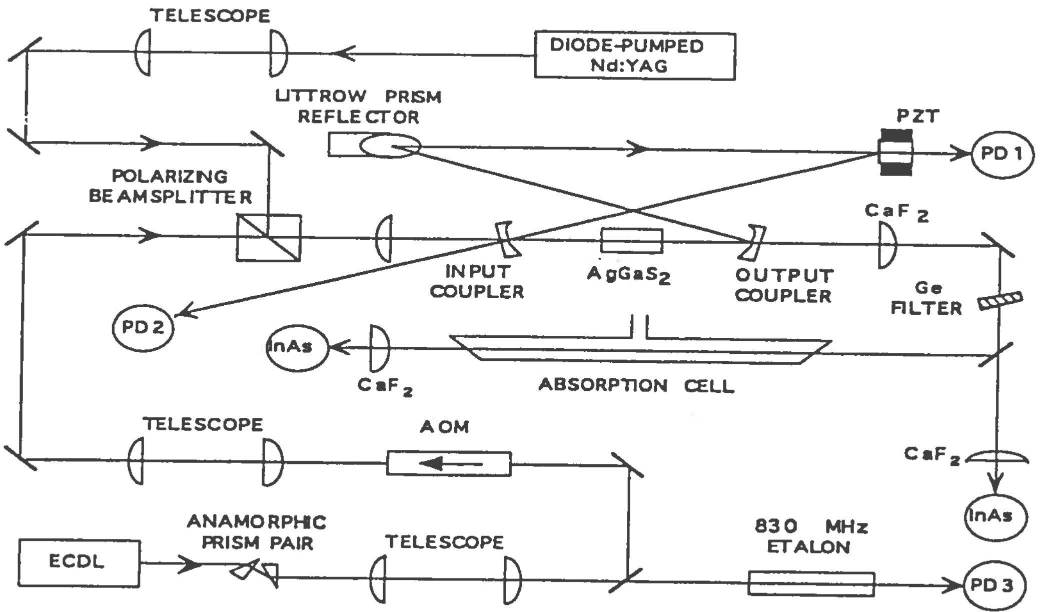

Figure 1. Schematic of the DFG-based methane sensor.

The nonlinear mixing element was a 5.5 mm antireflection-coated $AgGaS_2$ crystal placed inside a bow-tie 1064 nm enhancement cavity. A Littrow prism reflector was used instead of one of the flat mirrors in the long arm of the cavity to eliminate multiple passes of the 800 nm light. Buildup factors of 16 and 144 were measured at 1064 nm with and without the mixing crystal, respectively. This corresponds to 6.1% and 0.7% excess cavity loss, respectively. The source delivered a maximum of 6 µW of narrowband infrared light with 40 mW pump power in front of the crystal and 230 mW signal power in front of the

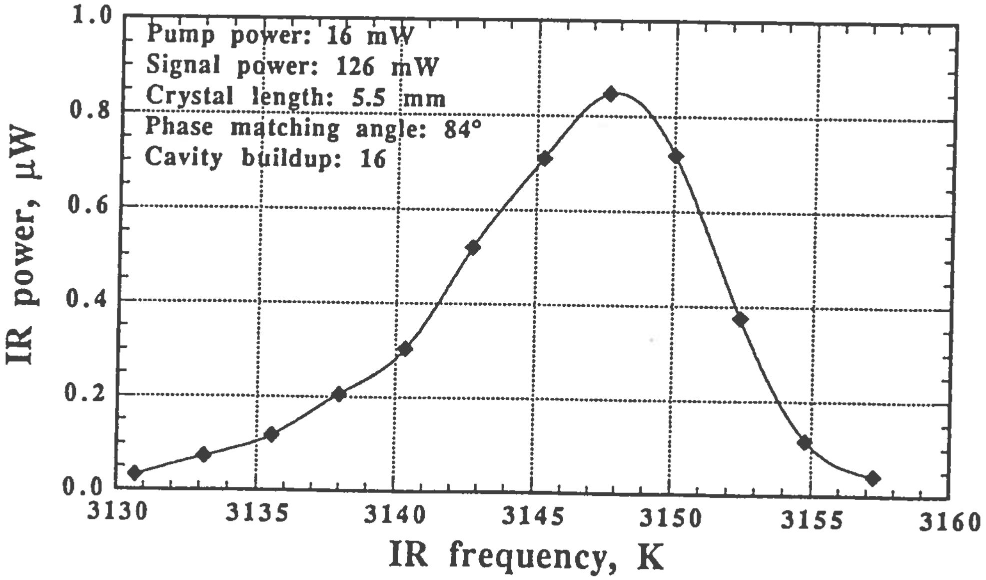

Figure 2. Measured DFG power versus frequency for a fixed phase matching angle.

cavity, which corresponds to 3.5 W intracavity power. One of the two room temperature InAs detectors was used as a monitor for feedback stabilization of the IR power which reduced the IR amplitude noise below the detector noise level. Frequency tuning of the idler wave between 3076 cm^{-1} and 3183 cm^{-1} was performed by tuning of the pump laser, and crystal rotation. At a fixed phasematching angle, frequency tuning over the range of approximately 10 cm^{-1} was possible, as is apparent from Fig. 2. Therefore short frequency scans of 10 GHz for spectroscopic measurements did not require crystal rotation.

Fig. 3. shows direct absorption spectrum of the methane in natural air at 80 Torr in a 1 m single-pass cell near 3086 cm^{-1}. It was acquired using an effective signal averaging bandwidth of ~1 Hz, and 1 μW stabilized IR power in the probe beam. Based upon the observed signal-to-noise ratio, a detection limit (S/N=1) of 12 $ppb*m/\sqrt{Hz}$ can be determined, which corresponds to an absorbance root-mean-square noise level of $5.1*10^{-5}$. For the case of natural air at atmospheric pressure, the competing effects of increased methane density and pressure broadening compared to 80 Torr cancel out so the expected detection limit would be approximately the same.

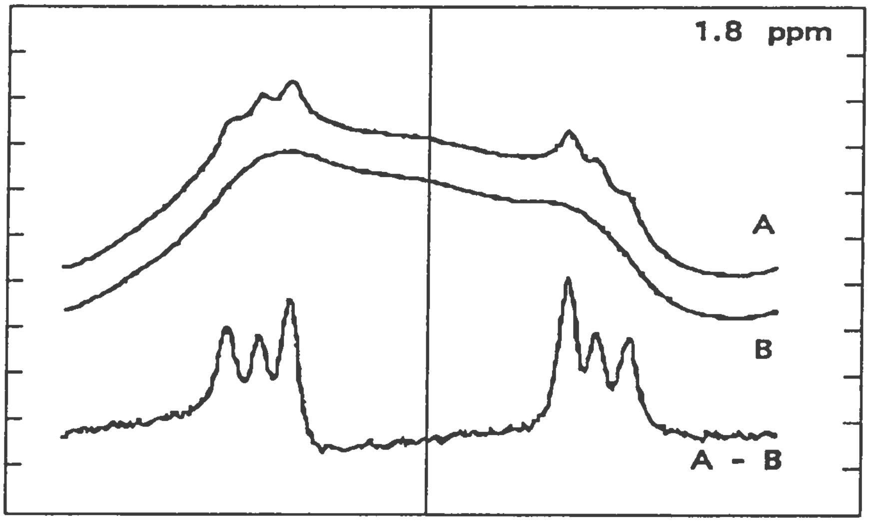

Figure 3. Direct absorption spectrum of the methane in natural air at 80 Torr in a 1 m cell (A), and the evacuated cell (B). Lower trace is the difference between A and B and shows only the signal from the cell.

The detection limit can be improved. First, more IR probe power can be generated. For example, a commercial 1W single frequency master oscillator power amplifier (MOPA) can be used as a pump source at 800 nm. Also, a longer mixing crystal can be used. Second, better output coupler (see Fig. 1) transmission can be obtained. We have measured 60% transmission at 3.2 μm for the replacement output coupler compared to 41% for the one used in the experiment. Third, an IR detector with lower NEP can be used. Fourth, either a multipass absorption cell or a buildup cavity can be used to increase effective path length.

We tested the effectiveness of a 250 mm confocal 3.2 μm enhancement cavity to improve the detection sensitivity. The cavity was dither-locked to resonance at the idler wavelength by controlling a PZT-driven mirror, and the locking was maintained when the wavelength was swept and modulated. A factors of 116 improvement in signal contrast was observed compared to single-pass $2f$ detection, which is in good agreement with measured cavity finesse (Fig. 4).

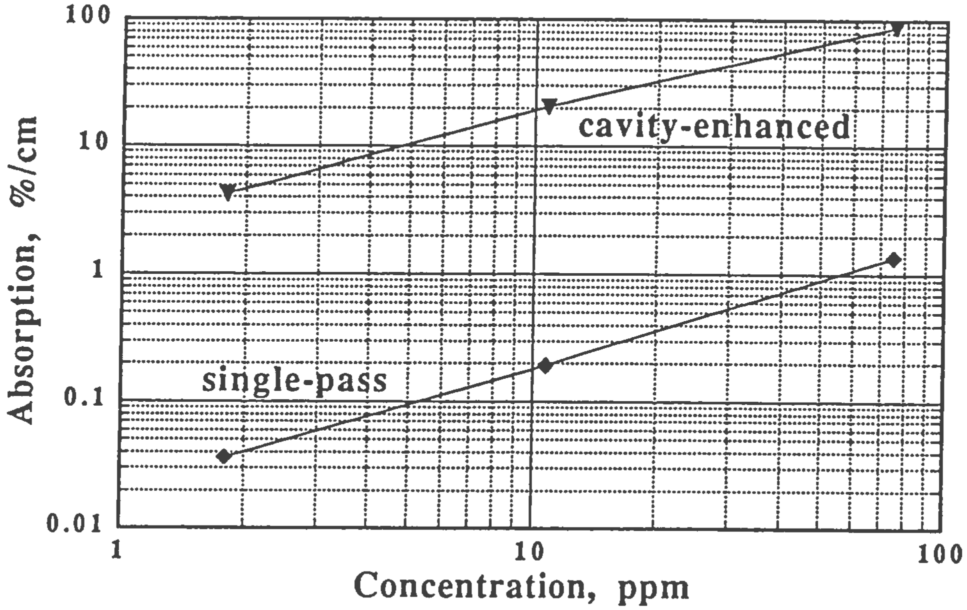

Figure 4. Measured relative $2f$ absorption signal per centimeter path length versus concentration of methane in air at 80 Torr.

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 three methods: single-pass and cavity-enhanced wavelength modulation ($2f$) spectroscopy, and direct absorption spectroscopy with power stabilization. The source was based on difference-frequency mixing in $AgGaS_2$ pumped by an 800 nm diode laser and a diode-pumped 1064 nm Nd:YAG laser and employed no cryogenic components. We observed a noise equivalent column density for the detection of methane in air at 80 Torr of 12 ppb*m/$\sqrt{Hz}$ using direct absorption spectroscopy with 1 μW stabilized IR probe power. Higher transmission of the output coupler, proper spatial mode matching into the 3.2 μm buildup cavity, and the use of cooled InSb infrared detectors with five times lower NEP can improve the detection limit to better than 0.1 ppb/$\sqrt{Hz}$.

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