

Compact diode laser based sensor for detection of atmospheric methane

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ABSTRACT

A portable room-temperature diode laser based on mid-infrared gas sensor was developed for open path measurements of methane in ambient air. This sensor is based on a continuous wave difference-frequency generation in periodically poled LiNbO₃ near 3.3 μ m, pumped by a solitary Fabry Perot type diode laser at 810 nm and a distributed Bragg reflector (DBR) diode laser at 1083 nm. IR frequency tuning between 3045 and 3170 cm⁻¹ was performed by tuning the solitary GaAlAs diode laser. In-situ and open path detection of methane in atmosphere with sensitivity of 18 ppbm/Hz^{1/2} was performed and detection sensitivity was limited by intensity noise.

Keywords: Gas sensor, Detection, Methane, Diode laser, Difference frequency generation.

1 INTRODUCTION

Atmospheric methane (CH₄) is recognized as one of the most important greenhouse gases. It was reported that CH₄ has some 15-30 times greater infrared absorbing capability than CO₂ and may account for 15 percent of anticipated global warming [1]. The concentration of atmospheric CH₄ has been increasing at a rate of about one percent per year [2]. Many studies have been undertaken to quantify the global sources and sinks of methane to fully understand the causes for this increase. However uncertainties have not been resolved. Irrigated rice cultivation is thought to be a major source of atmospheric CH₄ and may constitute 10 to 30 percent of the total methane emitted into the atmosphere [3].

Traditionally, measurements of trace chemical species performed in ecological and environmental studies have utilized a grab sampling technique. Gas samples are collected and transported to the remote gas analyzer for quantification at some later time. Recent advances in optics and electro-optics have made it possible to detect and monitor trace gases using a variety of real-time spectroscopy techniques.

Tunable infrared laser differential absorption spectroscopy (TILDAS) has proven to be an effective technique for accurate estimation of concentrations and fluxes of trace pollutants in both point monitoring and open path (remote sensing) configurations. While some TILDAS systems utilize tunable diode lasers (TDL) in the 0.7 to 2.0 μm near infrared spectral region, most systems use cryogenic cooled lead salt TDLs in the mid-infrared (3-20 μm) range where molecular detection is typically 20 - 200 times more sensitive. Recently several measurements of optical absorption in methane using tunable near-infrared lasers have been reported. Lucchesini et al, have used diode lasers to access $3\nu_1 + \nu_3 + \nu_4$ combination-overtone bands of methane near 790 nm [4]. However, the fundamental ν_3 band of methane near 3.2 μm has transitions that are as much as a factor of 160 stronger than those of the first overtone bands and are better suited for absorption measurements. The line intensity and the typical pressure broadening coefficient of methane in the ν_3 band is 2.13×10^{-19} cm, and 0.027 MHzPa⁻¹, respectively, which corresponds to a peak absorption of 0.005 m⁻¹ppm⁻¹ in air at 1 atm near 3067 cm⁻¹ [5]. The absorption coefficient to be measured is 0.009 m⁻¹ given the typical 1.8ppm concentration for methane in air.

The fundamental ν_3 band of methane is accessible by laser 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 Ar⁺ dye laser based difference-frequency generation [8]. These infrared laser sources are also suitable for sensitive atmospheric trace gas detection. In the mid-IR spectral region simultaneous detection of methane and other gas species in air has been accomplished using of a compact lead-salt diode laser spectrometer using a multipass absorption cell [9]. A detection limit for methane of 4 ppbm near 8 m with a signal averaging time of 3 s was reported. Single frequency diode lasers beyond 2 μm wavelength region also have been developed [10, 11, 12], but these lasers for normal operation require cooling with liquid nitrogen and are not commercially available.

Each of the above mentioned mid-infrared laser sources has limitation in terms of size, lack of portability, cost, or need for cryogenic cooling. On the other hand, CW difference-frequency generation (DFG) in a nonlinear optical material pumped by single frequency visible and near-infrared diode lasers is an attractive technique for generation of tunable mid-infrared light [13].

In earlier work, we have reported a tunable gas sensor using CW mid-infrared DFG in LiNbO₃ placed in a ring enhancement cavity pumped by diode-pumped Nd:YAG and a diode laser [14] [15]. In this paper we describe a compact methane sensor configuration based on difference frequency generation in the periodically poled LiNbO₃ nonlinear crystal (PPLN) pumped by a single mode solitary Fabry Perot type diode laser (100 mW) and one DBR diode laser (50 mW). Optimization of the two diode laser pump beam profiles yields an infrared power up to 0.45 μW for wavelengths around 3.3 μm . The principal application of the sensor is for open path concentration and flux measurements of methane.

2 INSTRUMENT DESCRIPTION

A schematic diagram of the diode-laser based DFG sensor is shown in Figure 1. Two room temperature diode lasers were used as pump sources for the DFG based IR source. A tunable CW single frequency diode laser (SDL-5412) with 100mw output power operating at 810 nm, and a CW single mode distributed Bragg reflector (DBR) diode laser (SDL-6702) with 50mw output power at a fixed wavelength of 1083nm permit DFG generation at 3.3 μm .

Collimating optics (C-390TM, Thorlabs INC.) and anamorphic prism pairs (5414, Newfocus) are used to

transform the nongaussian profiles of the two diode lasers into a nearly Gaussian beam shape. Elliptical beam profiles with a 3×8 mm beam dimensions are obtained after the collimating lens. Anamorphic prism pair provides about $1/3 \times$ magnification in the vertical direction resulting in the output beams with a 3×3 mm dimensions and a spherical wave front in the far field. To minimize optical feedback an optical isolator (LD38-840, EOT, 30dB) is used in front of the tunable pump source. Two half-wave plates are used to obtain vertical polarization of both pump beams. A beam splitter is used to spatially overlap both laser beams which are subsequently focussed by a convex lens ($f = 38$ mm) into the PPLN crystal. The quasi-phase-matching properties of PPLN can be tailored to create DFG in the $2\text{--}5 \mu\text{m}$ region using commercially available diode lasers. This, along with large non-linearity and good optical quality, makes PPLN the ideal nonlinear optical mixing material for DFG applications in the spectroscopically important mid-infrared frequency region. We used a 20 mm long, 0.5 mm thick PPLN crystal (Crystal Technology, Inc.) with domain grating period from 21.5 to 22.4 μm in 0.1 μm steps. The ten gratings are arranged in 1.3 mm wide strips spaced by 0.1 mm. Frequency tuning of the DFG radiation is performed by tuning the driver current and temperature of the pump laser. After exiting the PPLN crystal the mid-infrared DFG laser radiation is collected by a CaF_2 lens ($f = 85$ mm) and transmitted to a remotely located hollow corner cube (PLX, Inc) with a circular aperture of 6.3 cm. The corner cube was placed at a distance of 1 to 10 m from the receiving mirror and returned the laser light to an off-axis parabolic mirror which focuses it into a detector. Pump radiation is rejected by Germanium filter. This type of system can be used to monitor average methane concentration over the sampling path as well as vertical or horizontal gradients.

Two-stage thermoelectrically cooled Indium Arsenide detector was chosen with 1mm diameter active size (EG&G Judson, Inc. model J12TE2-37S-R01M). Detector is cooled to -40°C and has a noise-equivalent power (NEP) of $2.11 \text{ pW/Hz}^{1/2}$ at $3.3 \mu\text{m}$. A DC-coupled low noise preamplifier is used with $0.15 \text{ V}/\mu\text{W}$ peak response, noise level of $0.3 \mu\text{Vrms/Hz}^{1/2}$ and 100kHz bandwidth. Output of the preamplifier was digitized with a 12 bit, 100kS/s analog-to-digital converter part of a PCMCIA data acquisition card (DAQ-1200, National Instruments Inc.). The DAQ card served as an interface to a laptop computer. DAQ programming is done using a LabVIEW software package.

Direct absorption method is chosen in this application since it offers adequate precision combined with ease of signal processing and calibration. A time trace of the detector voltage $V(x)$, averaged over 10 to 1000 sweeps, with dark voltage V_{dark} subtracted, constitutes a spectroscopic measurement:

$$\ln(V_x - V_{\text{dark}}) = \alpha_0 / (1 + (x - \alpha_1)^2 / \alpha_2^2) + \ln(\alpha_3 + \alpha_4 x)$$

Here, x is the time index, α_0 is the peak absorbance, α_1 is the peak center, α_2 is the peak FWHM, and $\alpha_3 + \alpha_4 x$ account for linear modulation of the idler power associated with the frequency tuning. We applied nonlinear last-squares Levenberg-Marquardt method to fit the absorption spectra.

3 EXPERIMENTAL MEASUREMENTS

Frequency tuning over a range of approximately 100 cm^{-1} was possible by changing the operating temperature of the pump laser from 45°C to 15°C . A multichannel PPLN provides a wide tuning range. One channel gives a tuning range of approximately 50 cm^{-1} , which is more than sufficient for a single atmospheric pressure broadened

absorption line.

With 61 mW tunable diode laser at 812 nm, and 40 mW DBR diode laser at 1082 nm incident on the uncoated mixing crystal a maximum of $0.45 \mu W_{IR}$ power was measured corresponding to the DFG conversion efficiency of $238 \mu W/W^2$. Efficiency is in terms of $\eta = W_{IR}/(W_p W_s)$, where W_p is the fixed pump power and W_s is the tunable pump power.

After tuning the idler frequency to the region of selected absorption line by adjusting the operating temperature, idler frequency scans were performed by a 100 Hz, 20 mA peak-to-peak triangular modulation of the diode laser current. This corresponds to a tuning range of approximately 1.5 cm^{-1} , which is sufficient since the linewidth of methane absorption line we chose is smaller than 0.5 cm^{-1} .

Single pass methane cell is used as a reference to determine the operating wavelength. Figure 2. shows a 300 sweep average of the methane spectrum near 3085 cm^{-1} at pressure of 5 Torr and the pathlength of 5 cm compared with the data from the Hitran database [17] at the same pressure and pathlength. The observed absorption spectra is almost identical to Hitran database spectra. The main difference is that the observed absorption lines are broader than the Hitran database absorption lines due to the linewidth of the idler beam not being narrow enough.

The primary objective of the spectroscopic measurements is to determine the detection limits for methane in air using our sensor and to identify potential sources of noise. Figure 3. shows plots of power spectral density (PSD) of the amplitude noise in the IR detector signal acquired with a Fast Fourier Transform analyzer. In our direct absorption spectroscopic measurement, the minimum modulation frequency of the solitary diode pump laser was 100 Hz, in order to avoid the range below 100 Hz where the $1/f$ noise still dominates. The observed noise power spectral density above 100 Hz is between $350 \text{ nV/Hz}^{1/2}$ and $400 \text{ nV/Hz}^{1/2}$, which corresponds to the input light PSD of $2.2 \text{ pW/Hz}^{1/2}$, and is almost identical to the $2.11 \text{ pW/Hz}^{1/2}$ noise equivalent power of two stage cooled InAs detector. Average PSD of observed signal is approximately $100 \mu V_{rms}/\text{Hz}^{1/2}$ in the 10 Hz to 10 KHz region. The detector/preamplifier responsivity at 3.2μ is $1.7 \times 10^5 \text{ V/W}$. Based upon the observed signal to noise ratio, a detection limit (signal to noise ratio of 1) of $18 \text{ ppb}/\text{Hz}^{1/2}$ is possible assured that the laser intensity noise is zero and all transmitted mid-infrared energy is collected and detected by the detector.

Systems using open optical paths must work with spectral lines broadened by atmospheric pressure, and sensitive measurements will depend on the existence of individual spectral features free of interference from other gases such as H_2O and CO_2 . Ambient methane concentration measurements in open path experiments were performed in our laboratory using absorption line at 3085 cm^{-1} , which is free from other gases. A 2 inch diameter retroreflector was placed 10 meters away from our gas sensor and returned the laser light to the receiving optical system. The obtained methane absorption spectra near 3085 cm^{-1} in ambient air is shown in Figure 4. in comparison with the reference cell. Adjustment of mirror tilt was used to point the IR beam at the center of the corner cube for optimization of optical throughput at 25 percent over 10 m round trip. The fullscale idler power detected in this experiment is $0.1 \mu W$. The signal was acquired for 3 second in a 0-5 kHz bandwidth, and represents a 300 sweep average. The peak magnitude in the absorbance trace is 14.2 %. Based on the molecular line strength, the calculated methane concentration is 1.7 ppm, the typical value for our environment.

4 SUMMARY

We report a portable all-diode mid-infrared spectrometer capable of methane concentration measurement. The

instrument is based on quasi-phase-matched DFG in PPLN at room temperature, pumped by a 100 mW solitary diode laser at 810 nm and a 50 mW DBR diode laser at 1083 nm. The instrument produced about 0.45 μ W of output power in the tuning region from 3040 cm^{-1} to 3170 cm^{-1} . A methane absorption line at 3085 cm^{-1} was chosen in order to avoid overlapping and interference from the other molecular species. The selected absorption line was verified using a single-pass cell detection, and the acquired spectra is identical with the Hitran database spectra. The detection sensitivity is 18 ppb/Hz^{1/2}, and is limited by the detector noise.

To our knowledge, this is the first demonstration of a portable, high precision, room-temperature, real-time gas sensor based on two diode laser pumped mid-infrared DFG. The instrument employs no cryogenic or high voltage components, measures 1.5 \times 1.0 \times 0.5 ft, weighs 15 kg, and is controlled by a laptop computer. The instrument's power consumption is less than 20 W, and a small battery package (16" \times 9" \times 8") provides the necessary power for up to 8 hours of continuous operation.

This technology has a potential for the trace gas detection in situ due to low cost, power consumption and weight. The work will continue focusing on field measurements of methane and nitrous oxide concentration and fluxes from rice-based agroecosystem. We will continue to research possibilities of fiber coupling the pump lasers and waveguide PPLN techniques, which would greatly improve stability of optical alignment, reduce sensitivity to vibration, reduce the size, and lower the cost of the DFG sensor.

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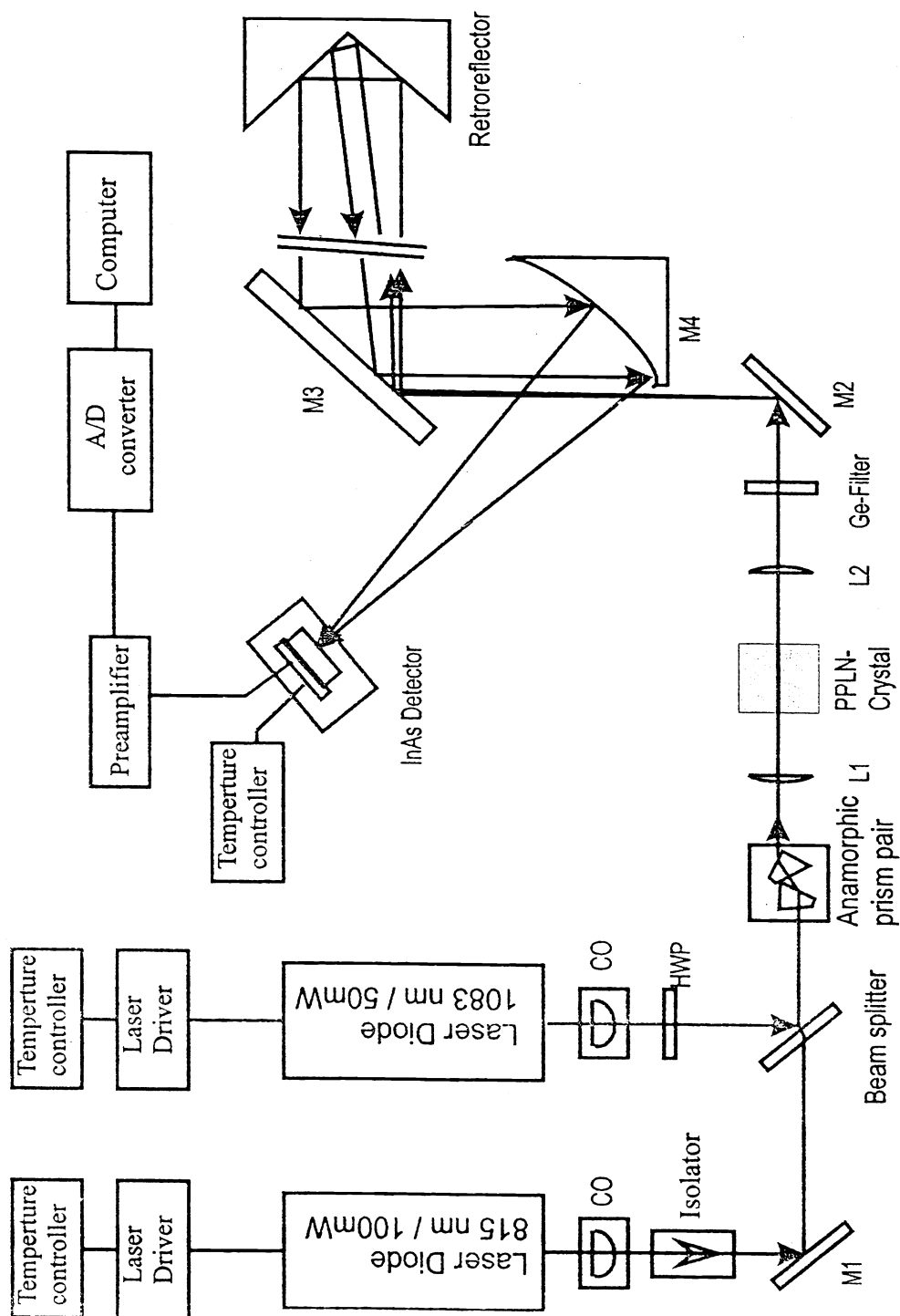


Figure 1. Experimental setup of compact diode-laser DFG based gas sensor for spectroscopic open-path detection of ambient methane in air. The 1083 nm light was supplied by DBR diode laser. The tunable 810 nm light was supplied by Fabry Perot type diode laser. Here HWP is a half-wave plate, CO is a collimating lens, L is a lens, M is a mirror.

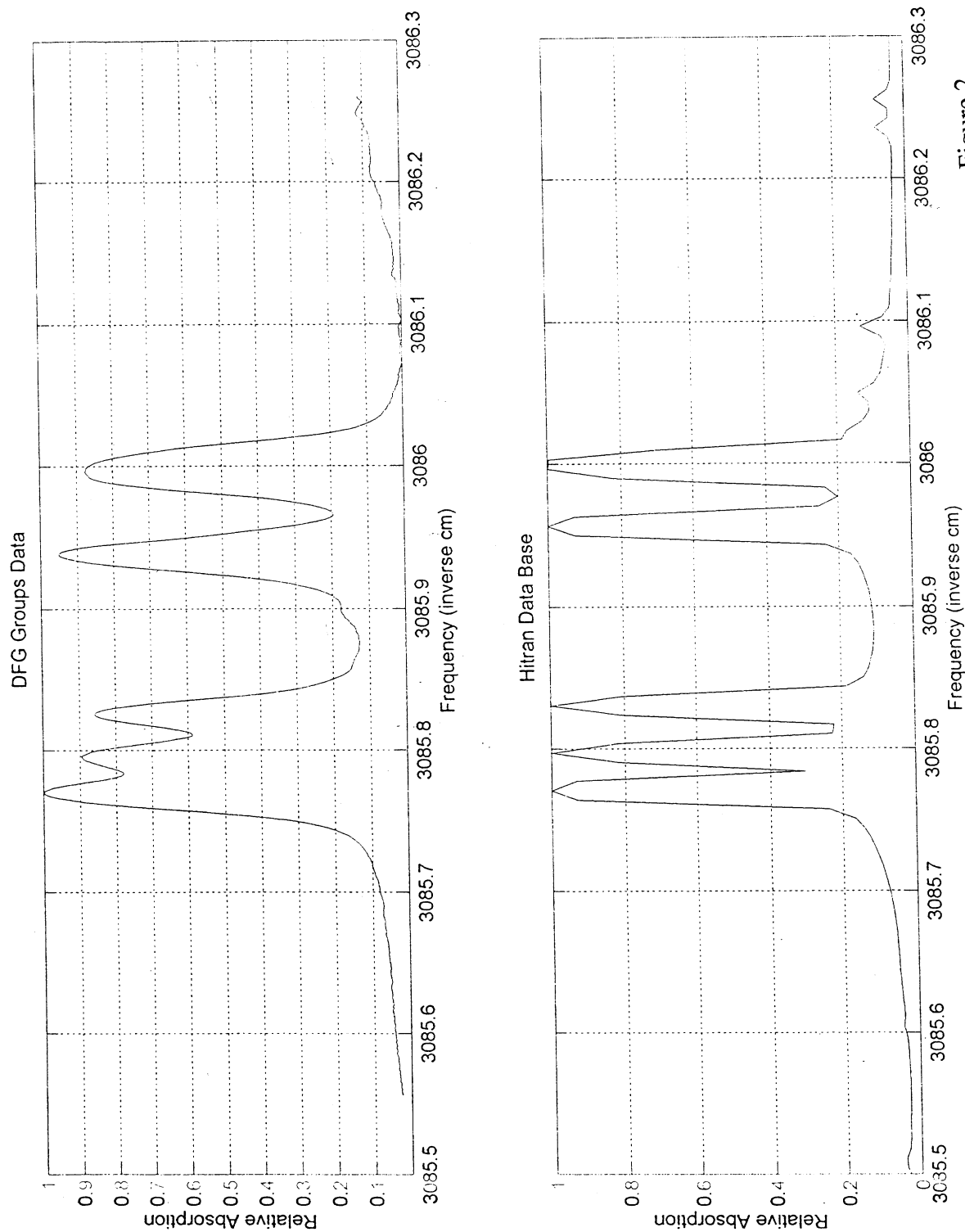


Figure 2

Figure 2. Absorption spectrum of methane near 3086 cm^{-1} at 5 torr pressure in a 5 cm single-path cell. The spectrum was acquired over 3 seconds and is a 300 sweep average. Theoretical absorption spectrum of methane from the HITRAN database under the same conditions.

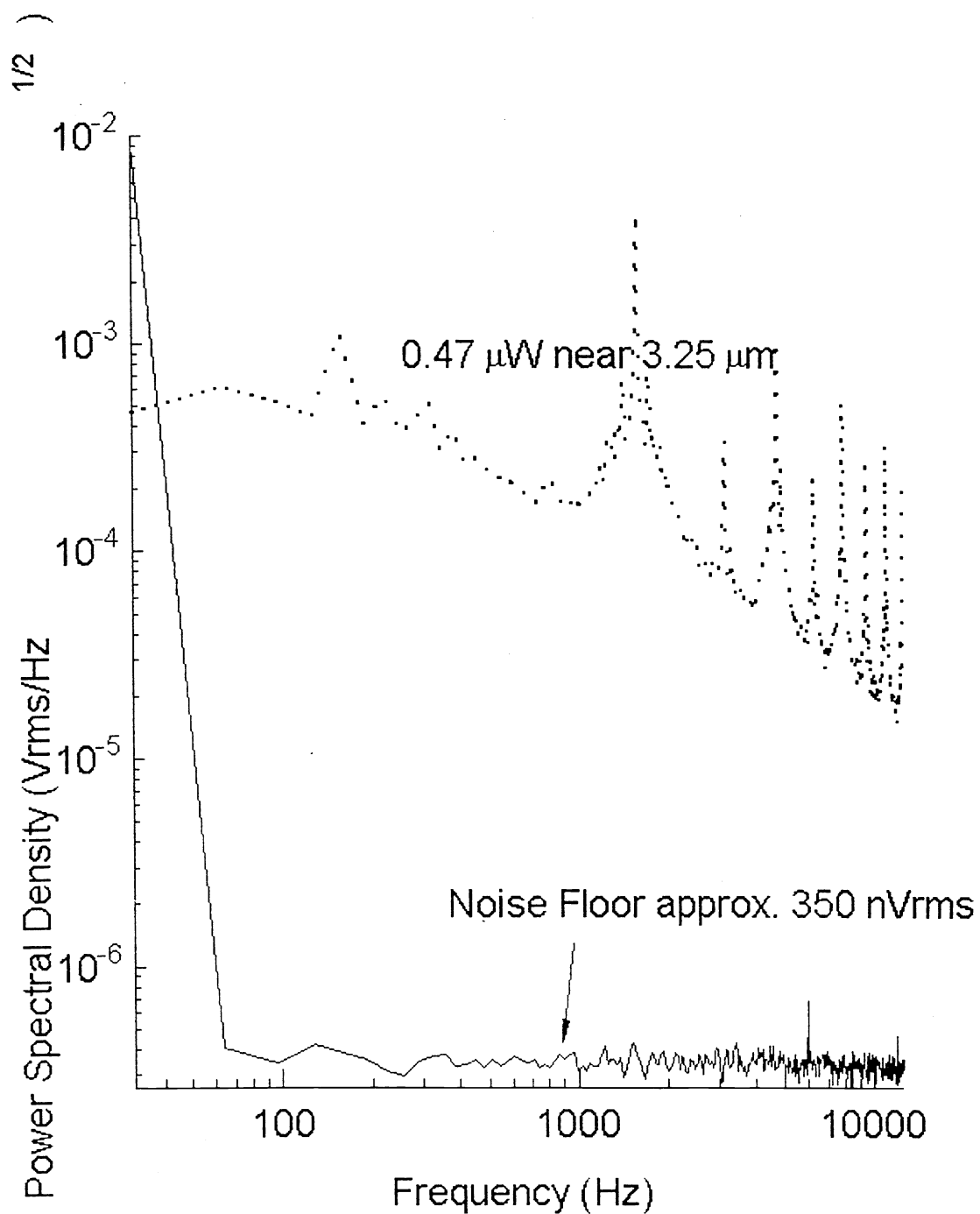


Figure 3. A power spectral density of the noise from the InAs detector/preamplifier measured with FFT analyzer. The upper curve was taken when the detector was exposed to 0.45 μW of IR DFG radiation near 3.2 μm . The $1/f$ noise dominates at frequency below 100 Hz. The detector/preamplifier responsivity at 3.2 μm was $1.7 \times 10^5 \text{ V/W}$.

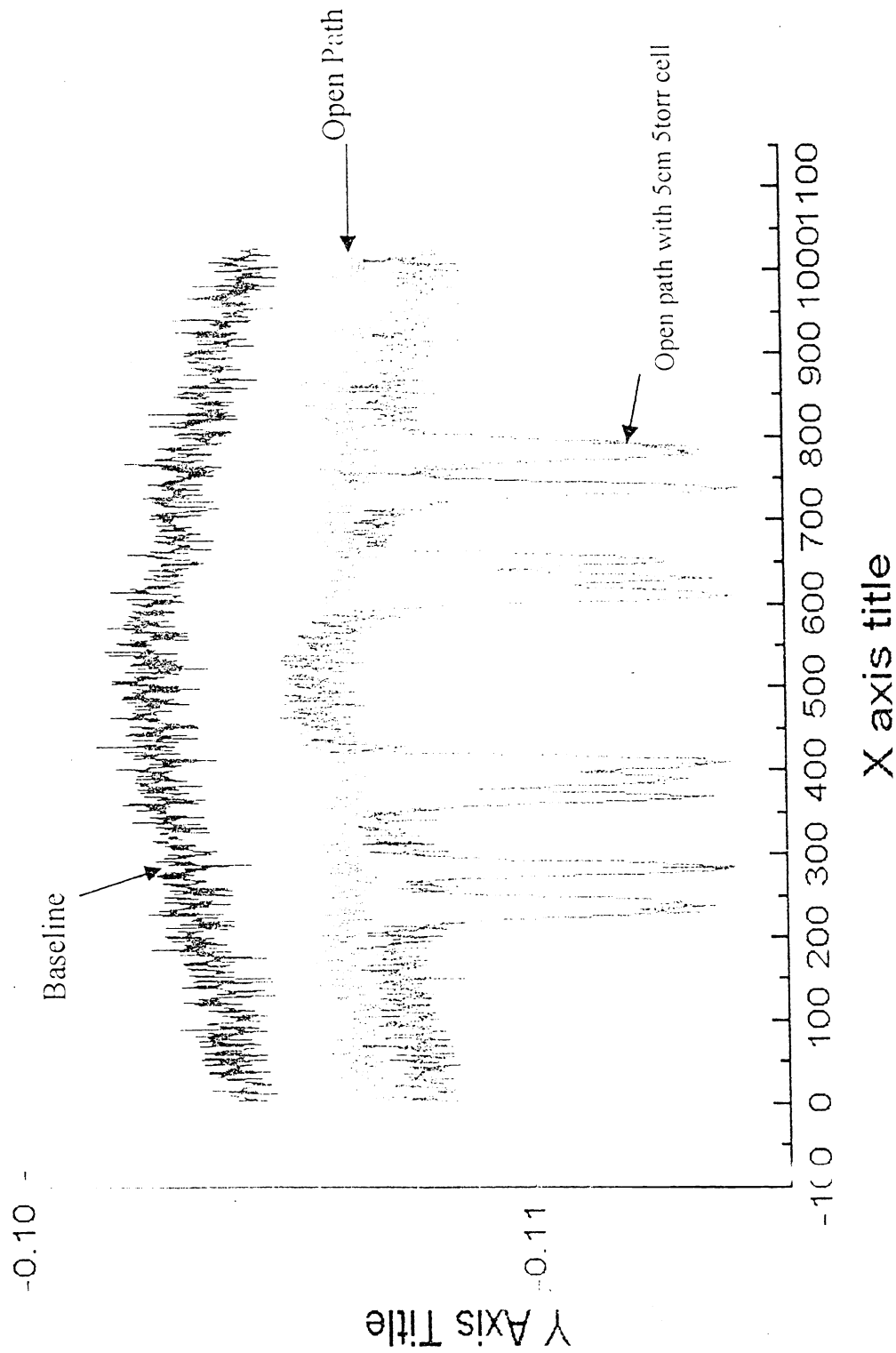


Figure 4. Absorption spectrum of methane near 3086 cm^{-1} over 20 m open path in air. The spectrum was acquired for 3 seconds and is a 300 sweep average. Theoretical absorption spectrum of methane from the HITRAN database under the same conditions.