# Detection of Trace Gas Contaminants Using Infrared Diode Laser-Based Methods: from the Laboratory Towards Space

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### Abstract

The development and environmental monitoring applications of compact spectroscopic gas sensors will be described. These sensors employ mid-infrared difference frequency generation (DFG) in periodically poled lithium niobate (PPLN) crystals pumped by two single frequency solid state lasers such as diode lasers, diode pumped Nd:YAG, and fiber lasers. Ultra-sensitive, highly selective and real-time measurements of several important atmospheric trace gases, including carbon monoxide, nitrous oxide, carbon dioxide, formaldehyde, and methane, have been demonstrated.

## 1. Introduction

It is a very special occasion for me to submit this report in honor of Prof. Choo Hie Lee. My students, my colleagues in the laser community, and I have benefited greatly from our interactions with Prof. Lee. He has also been a friend for more than 15 years, when he "discovered" us at Rice University at the suggestion of Prof. T. Fujioka, his Ph. D. research advisor at Keio University. I wish Prof. Lee all the very best in his retirement, and he can be extremely proud of his scientific and professional accomplishments at Kyung Hee University, in South Korea and the world wide laser community.

This report will highlight the development of compact, real world, diode laser based sensors and their applications to the detection of trace gas species by means of absorption spectroscopy in the mid-IR finger print region which contains virtually all the fundamental vibrational modes of molecules, free radicals, and molecular ions.

Several key new enabling technologies can be used to accomplish this and include:

- Nonlinear optics, specifically engineered bulk or waveguide nonlinear optical materials
- III-V semiconductor diode lasers operating at room temperature
- Optical fiber technology: fiber amplifiers and couplers
- IR detectors operating at room temperature with Peltier cooling
- Data acquisition/software processing, and convenient computer hardware

The monitoring and detection of trace gases at the level of parts per billion in diverse fields ranging from industrial, rural, and greenhouse-gas emission, in biomedical research, to applications involving environmental control for the workplace and space habitats has become increasingly important. One such application in which we were involved, was a 90-day Lunar-Mars comprehensive life support test conducted at the NASA Johnson Space Center, Houston. The test was undertaken in a three level 8-m diameter, human-rated space station simulation chamber, accommodating four mission specialists. One goal of this program was to test new life support initiatives such as advanced air and water recycling technologies that are to be used for the international space station program in progress since 1999. The purpose of our involvement in the test was to prescreen certain materials to be used and ascertain $H_2CO$ concentration levels inside the NASA test chamber with a portable and real-time gas sensor.

The motivation for monitoring $H_2CO$ levels in a sealed, human-rated environment, is that its presence can cause headaches as well as throat and ear irritation at low concentrations (>100 ppb). There are concerns about more serious adverse health effects at higher $H_2CO$ concentration levels. Consequently, NASA has set a stringent spacecraft maximum allowable concentration of 40 ppb for crew exposure from 7 to 180 days [1]. To reduce $H_2CO$ levels below this concentration, any outgassing materials and equipment must be identified. Hence, the development of an in-situ, real-time, portable gas sensor capable of identifying $H_2CO$ emission sources and monitoring concentrations at sub-ppb levels in air was initiated.

Further motivation for measuring $H_2CO$ concentrations precisely is that it is an important intermediate compound in tropospheric chemistry cycles, and serves as a significant source of CO

in the natural troposphere with typical atmospheric levels of 300 ppt [2]. $H_2CO$ is also a significant byproduct of combustion devices. Accurate measurements of combustion emissions are important in the reduction of urban air pollution levels of formaldehyde.

For real-time measurements of trace gases, optical techniques are the most suitable and include FTIR's [3], tunable infrared laser absorption spectroscopy using either overtone absorption spectroscopy in the near-IR [4-6], or direct infrared absorption spectroscopy in the mid-IR [7] and photoacoustic spectroscopy [3]. In the mid-IR, difference frequency generation (DFG) based sensors have been shown to be particularly suitable for absorption spectroscopy [8,9]. The criteria that must be considered for a system to be effective as a trace-gas sensor include adequate sensitivity for the concentrations present, the ability to discriminate from any other gases present, fast data acquisition and reliable field operation.

Considering the monitoring of $H_2CO$ specifically, Fried et al. [10] reported a tunable diode laser absorption technique based on cryogenically cooled lead-salt diode lasers which achieved a $H_2CO$ detection sensitivity of 0.04 ppb. This is clearly a much higher sensitivity than is reported here, but it comes at the cost of cryogenic operation. Fourier transform infrared spectroscopy (FTIR) is a widespread laboratory and industrial monitoring technique, which might be made suitable for monitoring $H_2CO$, but field FTIR spectrometers generally suffer from inadequate spectral resolution for this purpose. NASA monitors $H_2CO$ by using a chemical absorption badge capable of determining average concentrations over an extended period of time with a sensitivity of ~ 20 ppb. A major disadvantage of such a chemical badge method is that there is a significant time required for exposure and development, which can take 24 hours. It should also be noted that $H_2CO$ is not a very suitable

candidate for gas chromatographic and mass spectrometric measurement on account of its strong propensity to adsorb on surfaces.

Infrared absorption spectroscopy using a DFG source is an attractive alternative approach for the monitoring of formaldehyde, because of the inherent narrow bandwidth of the DFG source and the ability to design a monitor which is compact and which operates at room temperature. In recent work, we demonstrated the feasibility of using a DFG based sensor for sensitive $H_2CO$ detection to 250 parts per trillion [11].

The $v_5$ fundamental band from 3.2 - 3.6 $\mu$m is convenient for $H_2CO$ detection in the mid-infrared. The specific line selected for monitoring must take into account the presence of competing absorption lines of common atmospheric constituents. For the life support test, this line selection was critical because of expected high $CH_4$ concentration levels of up to 150 ppm inside the chamber. A suitable line was chosen at 2831.642 $cm^{-1}$ (3.5 $\mu$m), which also has a (5 times weaker) satellite line at 2831.699 $cm^{-1}$ using the HITRAN 96 database [12]. This line was first identified in Ref 10 to be suitable for atmospheric sensing. The line strength of the $H_2CO$ line is 5.04 $\times$ $10^{-20}$ cm/molecule [HITRAN 96] at 2831.642 $cm^{-1}$. The predicted absorption is 2 $\times$ $10^{-4}$, assuming a concentration of 30 ppb and absorption path of 18 m. Because of the proximity of a methane line close by (0.080 $cm^{-1}$) at 2831.562 $cm^{-1}$ and a water line at 2831.841 $cm^{-1}$, the absorption measurements are carried out at reduced pressure (typically 95 torr) to reduce pressure broadening and to resolve the individual spectral lines. A HITRAN 96 simulation of this spectral region is shown in Fig. 1. It depicts a well-isolated $CH_4$ line at 2829.592 $cm^{-1}$ which can be used monitor this species. The line at 2830.008 $cm^{-1}$ can monitor $H_2O$. These infrared spectral absorptions could be conveniently accessed by varying the laser
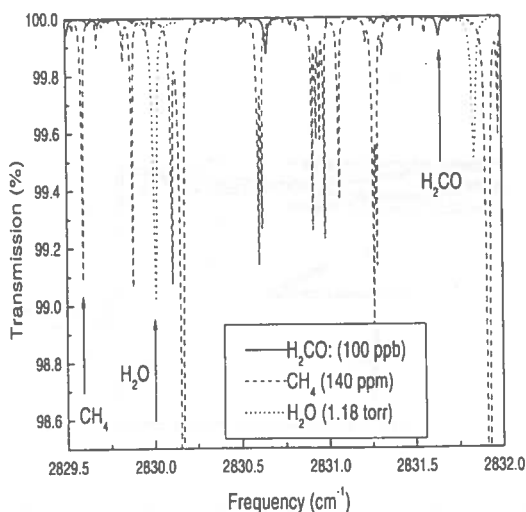


Fig. 1. HITRAN 96 simulation of the spectroscopic environment encountered in the vicinity of the 2831.642 $cm^{-1}$ $H_2CO$ absorption line selected for real time monitoring of the air in the NASA Lunar-Mars life support chamber. The nearly isolated $CH_4$ line is also shown. The spectroscopic parameters include: path length = 18 m, cell pressure = 60 torr.

diode temperature.

## 2. Sensor Configuration

A schematic and a photograph of the DFG based sensor are shown in Fig. 2 and 3, respectively. It is similar in design to that reported for CO detection previously [8]. The entire sensor including power supplies and electronics is contained in a 30 $\times$ 30 $\times$ 65 cm enclosure weighing 25 kg. The infrared probe power is generated by mixing two cw narrow-bandwidth lasers (pump and signal) in periodically poled $LiNbO_3$ (PPLN).

The signal laser is a diode-pumped, nonplanar monolithic ring Nd:YAG laser operating at a wavelength of 1064.5 nm and output power of 700 mW. The pump laser is a 100 mW GaAlAs Fabry Perot type diode laser at 818.0 nm. The laser diode output beam is collimated with an f = 8 mm multi-element lens, resulting in a 4 mm
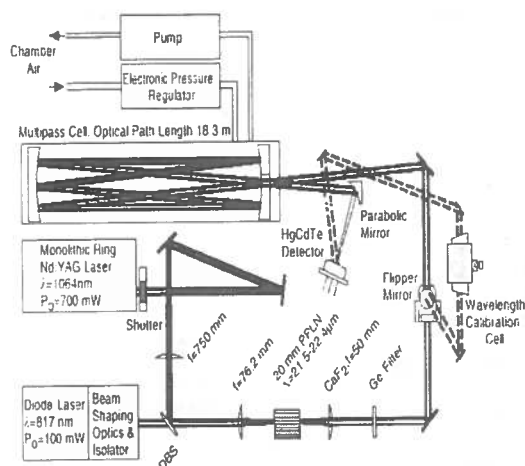
**Fig. 2.** Schematic of the cw mid-Infrared DFG gas sensor. A compact diaphragm pump and electronic pressure regulator are used to provide on-line, air sampling from the NASA chamber at reduced pressure.
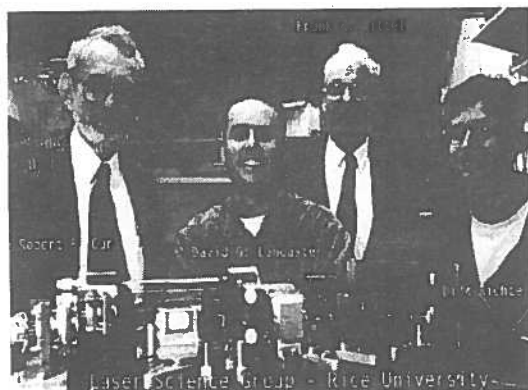


**Fig. 3.** Photograph of a compact DFG gas sensor and members of the Rice laser science group.

beam diameter in the long axis plane. The beam then passes through a 30 dB optical-isolator, and a $\lambda/2$ plate to rotate the polarization into the vertical phase-matching plane. The two single longitudinal mode (SLM) pump beams were combined by a dielectric beam splitter mirror and focused into the PPLN crystal with a 75 mm focal length lens. To ensure overlap of the two pump beams at their waist in the PPLN crystal, a 75 cm focal length lens was placed in the 1064 nm beam path.

The predicted grating period for quasi-phasematching (QPM) of the incident wavelengths was 22.50 $\mu$m at a temperature of 23 °C. The PPLN crystal available for this experiment had grating periods ranging from 21.50 $\mu$m to 22.40 $\mu$m with 0.10 $\mu$m channel increments (crystal dimensions are 0.5 mm $\times$ 10 mm $\times$ 20 mm length).

The generated mid-IR idler beam was collimated by a 5 cm focal length $CaF_2$ lens, and the residual pump beams were removed by the use of an anti-reflection coated Ge filter. The idler beam was then directed into a 0.3-liter volume multi-pass absorption cell (New-Focus Inc, Model 5611). The cell was configured for 91 passes, corresponding to an optical path length of 18 m, and has a measured transmission of 20%. The DFG beam was then focused onto a thermoelectrically cooled HgCdTe (MCT) detector with a 1 mm$^2$ active area using a 5 cm focal-length off-axis parabolic mirror.

To provide absolute frequency calibration, a $H_2CO$ reference spectrum was acquired before every measurement. A computer controlled mirror redirected the DFG beam through a 5 cm-long reference cell that contained 20 torr of $CH_4$ and a small amount of paraformaldehyde which was allowed to come to an equilibrium pressure in the gas mixture. Unattended absolute concentration measurements require a reliable data acquisition system and control system that can perform mid-IR frequency scanning, sampling, frequency calibration, data analysis and data storage. Frequency scans (0.3 cm$^{-1}$) of the diode laser were obtained using a dedicated function generator circuit to modulate the diode current at 50 Hz. The MCT detector was DC coupled to a pre-amplifier to allow absolute idler beam power measurements. The noise equivalent power of the detector-preamplifier combination was measured to be 3.9 pW Hz$^{-1}$. The data was digitized and transferred to a laptop computer by use of a 16

bit A-D card. Data analysis and experimental control was performed using LabVIEW software on a laptop PC running. For experimental control, two of the digital output lines from the A-D board were used to operate a beam shutter mounted in front of the Nd:YAG pump laser and the flipper mirror which redirected the DFG beam through the calibration cell. The shutter allowed the dark voltage of the MCT detector to be measured, which is necessary for absolute power measurements of the DFG beam. The air in the NASA humanrated chamber was sampled in a continuous flow through the multi-pass absorption cell, by use of a compact 2-stage diaphragm pump. The cell pressure could be regulated to lower pressures by use of an inline solid-state pressure regulator.

## 3. Experimental Results and Discussion

The detection sensitivity limit for this sensor was set by the occurrence of accidental etalons in the beam path, principally due to the laser diode window and collimation lens, the opto-isolator, the focusing lenses, the uncoated PPLN crystal surfaces, and the multi-pass cell. The etalons fringes from the multi-pass cell ($<10^{-4}$) could be reduced by manual vibration of the cell, however this was not required for general operation as the $\sim 0.025$ cm$^{-1}$ period fringes had a minimal effect on the fitting algorithm accuracy. To reduce the effect from other etalons in the beam path on the accuracy of the calculated gas concentration, several data reduction techniques were employed. A fifth order polynomial was fitted to the scan back-ground, which partially normalized out etalon effects. In addition the knowledge of the position and width of the $H_2CO$ absorption feature in each acquired scan permits a Lorer. an lineshape fit which is more accurate, there reducing aliasing by etalon fringes. The positio:. of the $H_2CO$ absorption line was

determined by acquiring a reference $H_2CO$ spectrum, prior to every experimental scan. The width of the fitted Lorentzian curve was estimated using the theoretically predicted Lorentzian width from HITRAN 96. The mid-IR power generated by the sensor at 3.5 $\mu$m was 2.7 $\mu$W, and after the multi-pass cell, 0.42 $\mu$W was incident on the detector. Typical operation of the sensor at NASA-JSC during the 3 weeks of the test involved a periodic calibration check with a reference $H_2CO$ sample of known concentration.

A spectral scan of the calibration cell (L = 5 cm) containing para-formaldehyde and 20 torr methane over 0.28 cm$^{-1}$ and centered at 2831.6 cm$^{-1}$ is shown in Fig. 4 (1 s average). These scans were frequency calibrated to the frequency assignments of two $H_2CO$ absorption lines located at 2831.6417 and 2831.6987 cm$^{-1}$. The position of a $CH_4$ line, which is obscured by one of the $\nu_1$ $H_2CO$ lines, is also indicated in Fig. 4. Measurements of Doppler broadened $CH_4$ lines
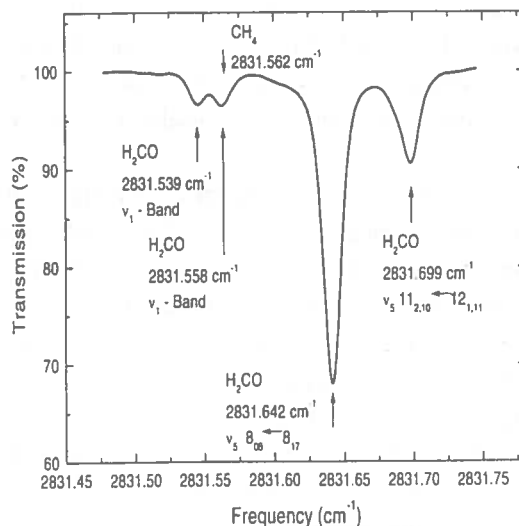


**Fig. 4.** Spectral calibration scan centered at 2831.60 cm$^{-1}$ of a mixture of para-formaldehyde and 20 torr methane over 0.25 cm$^{-1}$ (1 s averaging). The $H_2CO$ line at 2831.6417 cm$^{-1}$ chosen for monitoring, the satellite $H_2CO$ line at 2831.699 cm$^{-1}$, and an interfering $CH_4$ line are shown.
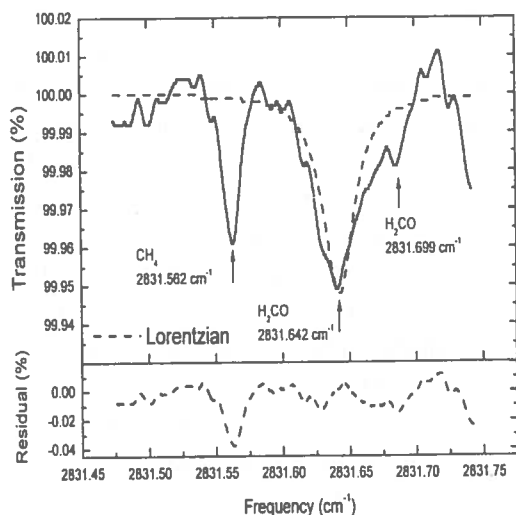
**Fig. 5.** The H₂CO spectrum, with the absolute transmission calculated from the measured detector dark voltage, and the baseline normalized to 100% transmission using a fifth order polynomial fit. The Lorentzian lineshape fit shown gives a $H_2CO$ concentration of 93 ppb. A $CH_4$ line near 2831.562 $cm^{-1}$ is also shown. The residual from the Lorentzian lineshape fit is shown below $H_2CO$ spectrum.

indicate a DFG bandwidth of ~ 100 MHz. A typical $H_2CO$ and $CH_4$ spectrum of the chamber air centered at 2831.62 $cm^{-1}$ over a range of 0.28 $cm^{-1}$ (960 data acquisition channels) is shown in Fig. 5.

The linear power dependence resulting from the current modulation of the laser diode has been removed in this figure, but it is otherwise unprocessed. The spectral positions of the $H_2CO$ line of interest and interfering $CH_4$ line are indicated. The baseline of the $H_2CO$ spectrum has been approximated using a fifth order polynomial fit (excluding the absorption features), and the transmission has been normalized by means of the measured detector dark voltage. A Lorentzian lineshape has been fitted to the $H_2CO$ peak ($CH_4$ peak not fitted), resulting in a calculated concentration of 93 ppb (FWHM of 0.057 $cm^{-1}$). In the fit a fixed Lorentzian lineshape width was used, and the Lorentzian
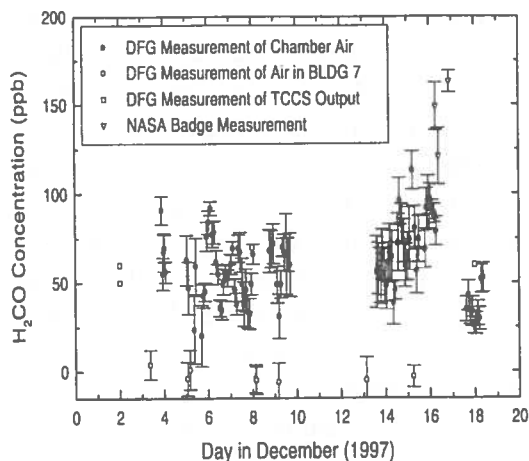


**Fig. 6.** $H_2CO$ concentration in chamber air measured by the DFG sensor over 3 weeks from December 3 to 18, 1997. Each concentration point represents 2 hours of data, and the error bars represent $\pm \sigma$. Independent measurements made of the $H_2CO$ concentration by using a chemically based absorption badge measurement technique are also shown.

center frequency was determined from the calibration scan. The residual from the Lorentzian fit is also shown, indicating the fringe noise to be ~ 0.02 %, which corresponds to a detection sensitivity of ~35 ppb $H_2CO$. This sensitivity has recently been increased by one order of magnitude [11]. The measured $H_2CO$ concentration for a 21-day period is shown in Fig. 6. Each point is an average of 2 hours of collected data (approximately 60 measurements), and the error bars represent $\pm 3$ $\sigma_{av}$, where $\sigma_{av} = \sigma / (N)^{1/2}$, N=60. Independent measurements of the $H_2CO$ concentration were made by NASA-JSC personnel using chemically sensitized badges (also shown in Fig. 6), and show good agreement with our concentration measurements. As expected the $H_2CO$ concentration measurements in the building verified that the sensor is recording the zero baseline within $\pm$ 5 ppb. The output of the trace contaminant control system (TCCS) in the chamber was also monitored, showing unexpectedly high $H_2CO$ levels.

# 4. Conclusions

A research program to evaluate the performance of a tunable DFG gas sensor employed for on-line real time measurements of $H_2CO$ inside a Lunar Mars Life support test chamber at NASA's Johnson Space Center has been described. The absolute calibration of the sensor was verified by using a 67 ppb $H_2CO$ in nitrogen mixture, with the sensor reading 67 ppb with a standard deviation of 13 ppb over 33 minutes. $H_2CO$ levels were measured to an accuracy of 30 ppb in a human-rated chamber over several weeks, and were in agreement with a NASA conducted chemical badge measurements. Hence we have demonstrated that a DFG based system using direct absorption spectroscopy can monitor near ppb concentrations (corresponding to absorptions of $\sim 2 \times 10^{-4}$) of a trace gas over an extended period (several weeks), with the sensor operating in an industrial type environment. Furthermore, the detection capability of this sensor for multicomponent trace mixtures was demonstrated by temperature tuning of the pump diode laser to monitor $CH_4$ or $H_2O$ concentrations.

## Acknowledgments

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