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Laser based absorption sensors for trace gas monitoring in a spacecraft habitat

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ABSTRACT

The use of a unique laser based compact gas sensor based on continuous wave (cw) difference frequency generation using non-linear optical conversion is reported for on-line, real-time measurements of H_2CO, CH_4 and H_2O. Specifically, this portable sensor was used to monitor H_2CO levels with a sensitivity of ~30 ppb during the 90 day Lunar-Mars Life Support Test Program conducted at NASA-JSC in 1997.

INTRODUCTION

Tunable infrared laser absorption spectroscopy has proven to be a powerful technique for accurately determining the real-time concentrations of trace gases in both extractive and open path configurations. For the detection of molecules including several significant atmospheric contaminants, a key spectral region is in the mid-infrared (3-5 μm). The design and performance characteristics of this compact prototype configuration will be reported, with reference to field work conducted at NASA-JSC. Characteristics of the mid-infrared sensor includes high spectral resolution, room temperature operation and the use of diode laser based pump sources. This sensor has been used for sensitive and selective real-time field measurements of either single or multi-component gas mixtures in ambient air.

The difference-frequency-generation (DFG) based gas sensor technology employs periodically poled lithium niobate (PPLN) crystals pumped by two single-frequency lasers. The portable DFG sensor based on discrete optical components mixes together a diode pumped Nd:YAG laser with a diode laser, generating 5 μW of narrowband light (30 MHz) at 3.5 μm. This sensor was used for real-time extractive monitoring of the sub-ppm formaldehyde levels during the 90-day Lunar-Mars Life Support Test Program conducted at the NASA Johnson Space Center, Houston in 1997. Over a period of several weeks the formaldehyde concentration was measured with a sensitivity of 30 ppb [1].

The on-line monitoring 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 that are to be used for future long duration human space flight. In addition, this program allowed the sensor to be tested in a simulated spacecraft environment that presents conditions not encountered in terrestrial environments (such as a 100 times ambient methane concentration).

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 established the spacecraft maximum allowable concentration of 40 ppb for crew exposure from 7 to 180 days [2]. 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-ppm levels in air was initiated.

Considering the monitoring of H_2CO specifically, Fried *et al*. [3] 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 infra-red 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 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. The badge is typically exposed for 24 hours, and then processed using a wet chemical technique. A major disadvantage of badges is that there is a time required for exposure and a time required for development, which is usually an additional 24 hours, and hence exposure levels are learned only after significant additional exposure. It should 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.

The fundamental ro-vibrational band (ν_5) from 3.2 - 3.6 μm 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 H_2CO monitoring a discrete absorption line at 2861.72 cm^{-1} was initially selected due to its relatively high absorption cross section and freedom from spectral interference in a terrestrial atmospheric environment. This absorption line was used for the initial H_2CO monitoring for the EHTI-3 program, however during day 1 of the test the chamber methane level increased substantially (to 10's of ppm), and the methane absorption lines in this spectral region swamped the weaker H_2CO line, therefore making it unsuitable for further monitoring. By assuming a CH_4 concentration of 150 ppm, a molecular simulation database (Hitran96) was used to find a suitable spectral line for this particular environment.

A suitable line was chosen at 2831.642 cm^{-1} (3.5 μm), which also has a (5 times weaker) satellite line at 2831.699 cm^{-1} using the HITRAN 96 database [4]. This line was first identified in Ref 3 to be suitable for atmospheric sensing. The line strength of the H_2CO line is 5.04 x 10^{-20} cm / molecule [HITRAN 96] at 2831.642 cm^{-1}. The predicted absorption is 2 x 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 congested spectral region is shown in Fig. 1. A minor advantage of the choice of this spectral region is the presence of a well-isolated CH_4 line at 2829.592 cm^{-1} which allowed this species to be monitored in the chamber. The line at 2830.008 cm^{-1} can be used to monitor H_2O. These infrared spectral absorptions could

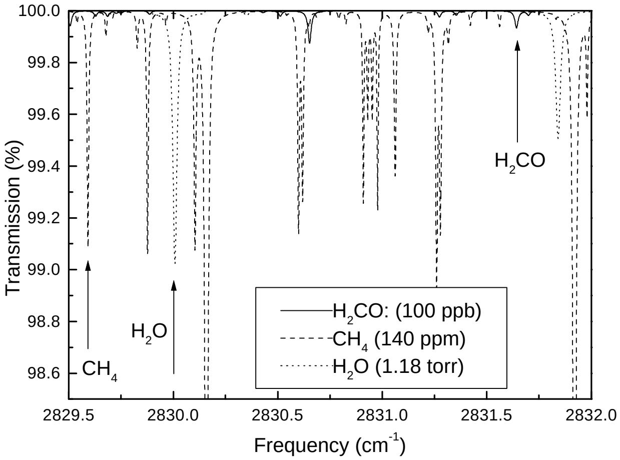

Fig. 1: HITRAN 96 simulation of the spectroscopic environment encountered in the vicinity of the 2831.642 cm^{-1} H2CO absorption line selected for real time monitoring of the air in the NASA chamber. The nearly isolated CH4 line is also shown. The spectroscopic parameters include: pathlength=18 m, cell pressure=60 Torr

be conveniently accessed by varying the laser diode temperature by < 1.3°C.

SENSOR CONFIGURATION

A photograph and a schematic of the DFG based sensor are shown in Fig 2 and Fig.3, respectively. It is similar in design to that reported for CO detection previously [5,6]. The entire sensor including power supplies and electronics is contained in a 30 x 30 x 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, non-planar 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 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 phasematching plane. To achieve mode matching with the circular Nd: YAG laser beam, an anamorphic prism pair (4 x) was used to reduce the vertical dimension of the laser diode beam. The two single longitudinal mode (SLM) pump beams were combined by a dielectric beam splitter mirror and focused into the PPLN crystal with a 76.2 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 overlap of the two pump beams was optimized by means of a CCD camera based profiling system.

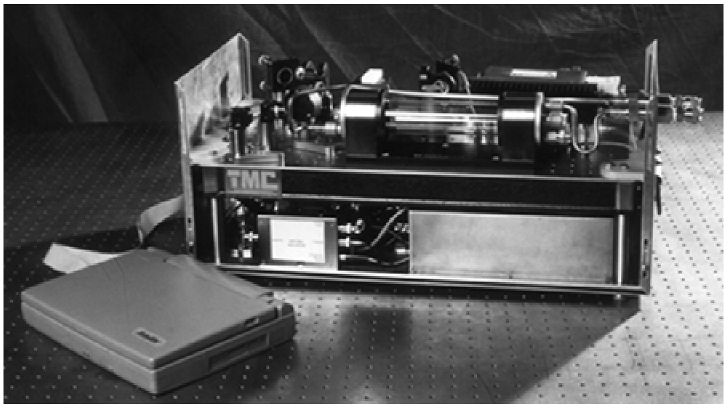

Fig. 2: Photograph of the mid-infrared DFG - gas sensor showing the optical breadboard and electronic components below

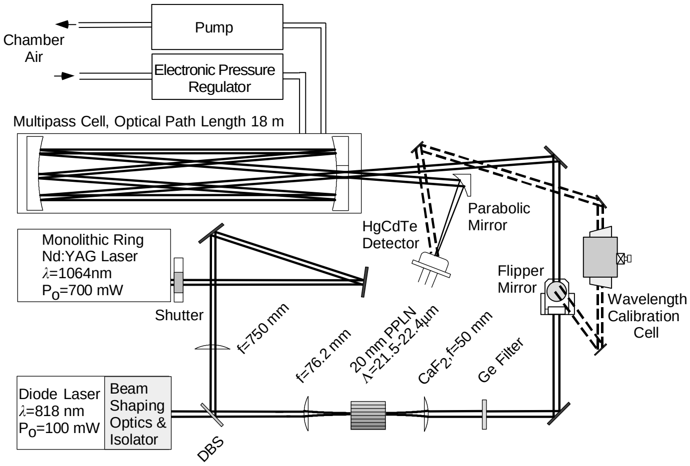

Fig. 3: Schematic of the instrument. A compact diaphragm pump and electronic pressure regulator are used to provide on-line air sampling from the NASA chamber at reduced pressure

The predicted optimal grating period for quasi-phasematching (QPM) of the incident wavelengths was 22.50 μm. The PPLN crystal available for this experiment had grating periods ranging from 21.50 μm to 22.40 μm with 0.10 μm channel increments (dimensions of 0.5 mm x 10 mm x 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 (New-Focus Inc., flipper) redirected the DFG beam through a 5 cm-long reference cell that contained para-formaldehyde and 20 torr of CH_4.

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 of the diode laser were obtained using a dedicated function generator circuit to modulate the diode current at 50 Hz with a 7.5 mA peak-to-peak triangular wave, corresponding to a scan range of 0.3 cm^{-1}. 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 $Hz^{-1/2}$. The data was digitized and transferred to a laptop computer by use of a 16 bit A-D card (NI DAQCARD-AI-16XE-50). Data acquisition by the AD card was synchronized to the laser diode current modulation with a TTL output available from the function generator.

Data analysis and experimental control was performed using LabVIEW software (National Instruments) on a laptop PC running Windows 95. 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 human-rated chamber was sampled in a continuous flow through the multi-pass absorption cell, by use of a compact 2-stage diaphragm pump (KNF Neuberger). The cell pressure could be regulated to lower pressures by use of an inline solid-state pressure regulator (MKS Instruments). The pressure was also additionally verified by use of an inline vacuum gauge adjacent to the multi-pass cell. The entire gas handling was contained within a small aluminum suitcase and connected to the chamber and sensor by use of 1/4 inch Teflon tubing. The chamber sample and return lines were approximately 6 m in length.

In order to remove high frequency noise from the acquired scans a software based low pass Gaussian filter (with 1.3 kHz HWHM) was used. The position of the acquired spectral features were obtained by applying a peak fitting routine to the H_2CO reference scan taken previously. Segments were removed from the base line that matched the estimated base width of each of the two H_2CO Lorentzian lineshape [7] absorption peaks and the methane absorption peak. A fifth order polynomial was then fitted to the remaining baseline to approximate 100% transmission at the H_2CO absorption peak. In addition, a Lorentzian lineshape was fitted to the principal H_2CO absorption line using a non-linear least squares fit Levenberg-Marquardt method.

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 ~ 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. As mentioned above a fifth order polynomial was fitted to the scan background, 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 Lorentzian lineshape fit which is more accurate, thereby reducing aliasing by etalon fringes. The position of the H_2CO absorption line was determined by acquiring a reference H_2CO spectrum, prior to every experimental

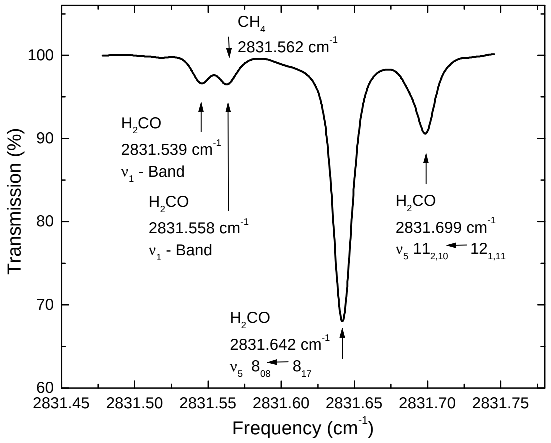

Fig. 4: Spectral calibration scan centered at 2831.60 cm^{-1} of a mixture of para-formaldehyde and 20 Torr methane over 0.25 cm^{-1} (1s averaging). The H_2CO line at 2831.6417 cm^{-1} chosen for monitoring, the satellite H_2CO line at 2831.699 cm^{-1}, and an interfering CH4 line are shown

scan. The width of the fitted Lorentzian curve was estimated using the theoretically predicted Lorentzian width from HITRAN 96. Furthermore it was seen that some of the etalon effects were transient, and predominantly due to thermal drifts of the sensor alignment induced by changes in the ambient temperature. Therefore averaging could also reduce etalon effects but at the expense of increased acquisition scans (typically 500 scans in 10 s. For longer-term monitoring the data was averaged over 2 hour intervals).

The mid-IR power generated by the sensor at 3.5 μm was 2.7 μW, and after the multi-pass cell, 0.42 μW was incident on the detector. The power generated was adequate, although lower then predicted due to the non-optimum grating period available. Typical operation of the sensor at NASA-JSC during the 3 weeks of the test involved one visit a day to optimize the alignment and frequency of the sensor and perform a periodic calibration check with a reference H_2CO sample of known concentration.

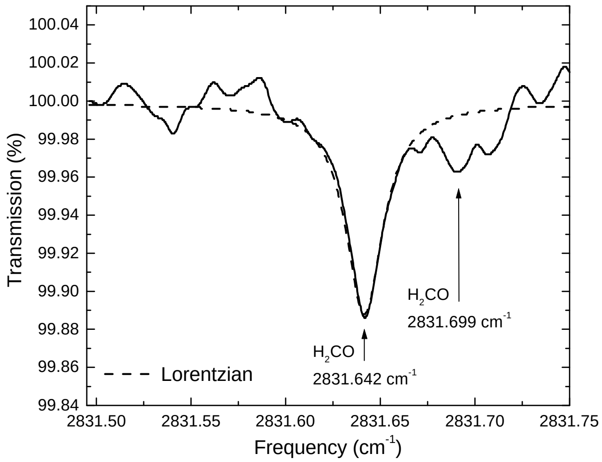

Fig.5: Spectral scan of the H_2CO line at 2831.642 cm^{-1} of an uncalibrated mixture of H_2CO in nitrogen gas. An 18-m pathlength, cell pressure of 95 Torr and 5 s averaging time was used. The Lorentzian fit gives a H_2CO concentration of 169 ppb (mole fraction)

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. 3 (1 s average). These scans were frequency calibrated to the frequency assignments [8] 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 ν_1 H_2CO lines is also indicated in Fig. 3.

From this pressure-broadened spectrum it is not possible to deduce the spectral bandwidth of the DFG radiation, because the total cell pressure is not known. However measurements of Doppler broadened CH_4 lines indicate a DFG bandwidth of ~ 100 MHz. Shown in Fig. 4 is the spectrum of the same H_2CO absorption lines from an un-calibrated mixture of H_2CO in nitrogen, over an 18 m pathlength. The Lorentzian-lineshape fit to the data has a FWHM of 0.053 cm^{-1}, and yields an H_2CO concentration of 169 ppb (mole fraction). The etalon fringes in this scan represent ~0.025 % absorption which corresponds to a detection sensitivity of 36 ppb H_2CO for a S/N =1.

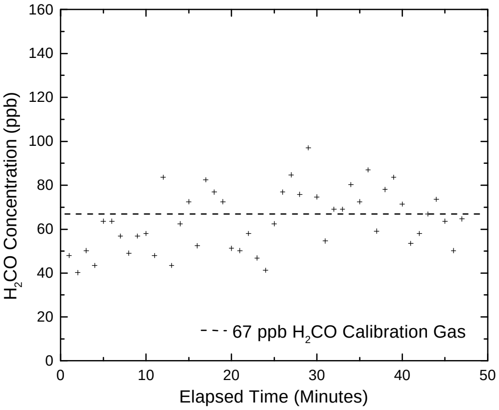

Fig. 6: DFG sensor calibration run based on monitoring the H2CO concentration over a period of 50 min of a mixture of 67±1.5 ppb H2CO in nitrogen gas. The measured H2CO concentration was 67±13 ppb

For an accurate calibration of the H_2CO levels to be monitored, a 67 ± 1.5 ppb calibrated mixture of H_2CO in nitrogen was used (H.P. Gas Products Inc). A time trace of the measured H_2CO concentration is shown in Fig. 5. In this calibration the gas flowed continuously through the cell, which was regulated to 95 torr. The H_2CO concentration was measured every 1 minute. For each experimental point, the sensor first acquired a frequency calibration scan from the reference cell with 2 s of averaging, followed by 500 sweeps in 10 s of the gas in the multi-pass cell. Finally, the MCT dark voltage was acquired for 1 s. The average value of H_2CO absorption was measured for the last 33 minutes (after allowing the flowing H_2CO mixture to reach an equilibrium concentration with the gas tube walls). The standard deviation of the measurement was 13 ppb.

This results in an absorption strength of 4.67 x 10^{-20} cm/ molecule which compares well with the predicted absorption strength of 5.04 x 10^{-20} cm/ molecule from the HITRAN 96 database. In Fig. 6 the baseline of the same 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 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 %, consistent with the laboratory scan of H_2CO shown in Fig. 4.

The measured H_2CO concentration is shown in Fig. 7 for a time period of 21 hours of unattended operation at NASA-JSC with a data collection scan taken every 7 minutes (scan started at 5 pm on December 17, 1997). During this time period the average H_2CO concentration measured was 34 ppb ± 17 ppb (± 1 standard deviation, σ). The measured H_2CO concentration for a 21-day period is shown in Fig. 8. Each point is an average of 2 hours of collected data (approximately 60 measurements), and the error bars represent ± 3 σ_{av}, where $\sigma_{av} = \sigma / (N)^{1/2}$, N=60.

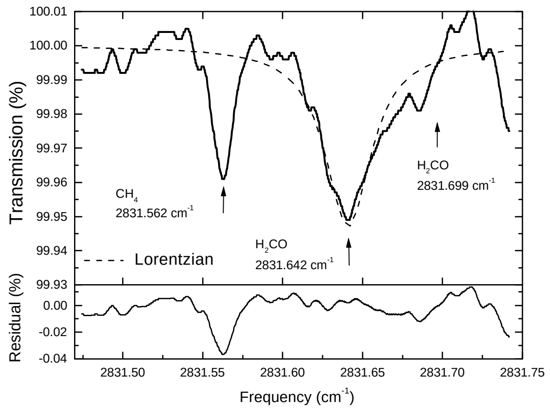

Fig.7: A H_2CO spectrum with the absolute transmission calculated from the measured detector dark voltage, and the baseline normalized to 100% transmission using a fifth-order polynomial fit. The Lorentzian lineshape fit shown gives a H_2CO concentration of 93 ppb. A CH_4 line near 2831.562 cm^{-1} is also shown. The residual from the Lorentzian lineshape fit is shown below the H_2CO spectrum

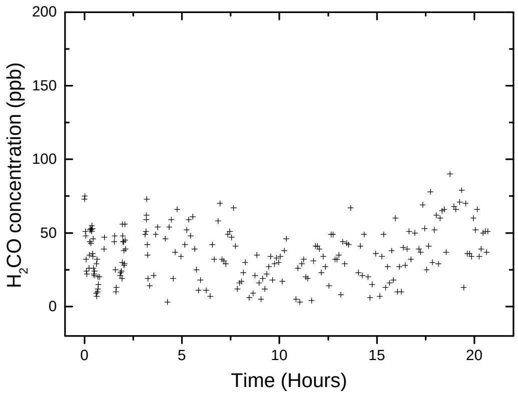

Fig. 8: H_2CO measurements conducted over a 21-h period, starting at 5 pm on December 17, 1997, of the air inside the NASA life support chamber (average measured is 34±17 ppb)

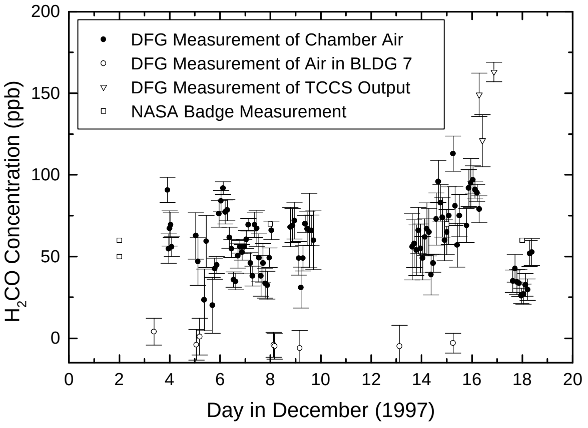

Fig. 9: H_2CO concentration in chamber air measured by the DFG sensor over 3 weeks from December 3 to 18, 1997. Each concentration point represents ± $3\sigma_{av}$. Independent measurements made of the H_2CO concentration by using a chemically based absorption badge measurement technique are also shown

Independent measurements of the H_2CO concentration were made by NASA JSC personnel using chemically sensitized badges (also shown in Fig. 8), 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 ± 5 ppb. The output of the trace contaminant control system (TCCS) in the chamber was also monitored, showing unexpectedly high H_2CO levels (Fig. 8).

The Phase III formaldehyde concentration was measured at between 20 and 30 ppb for the first 60 days of the test, and between 50 and 70 ppb for the last 30 days of the test. Further, on day 83 the Laser DFG spectrometer was connected to a tygon sampling tube and a survey formaldehyde concentrations in the interior of the chamber was conducted. There was a strong indication that while the rest of the chamber had a relatively uniform concentration (an indication of good mixing), the outlet of the TCCS was higher than the rest of the chamber. Formaldehyde concentrations are excedingly low, measured in ppb, while ethanol and acetaldyhyde concentrations are measured in ppm. In the oxidation sequence of alcohols, the first oxidation step is to convert an alcohol to its associated aldehyde. Methanol is oxidized first to formaldehyde, ethanol is oxidized to acetaldehyde, and propanol is oxidized to propanaldehyde.

GC-MS samples collected from days 66, 73, 80, 87, and 91 show marked, sporadic, increase in the ethanol concentration in the chamber. The increase in ethanol concentrations at the time when elevated formaldehyde concentrations are found, combined with the DFG measurements indicating elevated formaldehyde concentrations at the TCCS outlet suggest the following: all of the formaldehyde that enters the TCCS is destroyed (formaldehyde is very easy to oxidize, and if methane and BTX compounds are oxidized, formaldehyde certainly is also) but a small portion (less than 6%) of methanol, ethanol and acetaldehyde is not completely oxidized, but is partially oxidized to formaldehyde. Increased levels in ethanol triggered increased levels in formaldehyde in the last 30 days of the test, and partial oxidation in the TCCS is a likely contributor to the increased formaldehyde concentration. This suggestion has not yet been confirmed by independent lab tests of the catalyst under controlled conditions. These tests are planned, and when the tests are performed, the Laser DFG device will be used to measure formaldehyde concentrations. Results of these lab tests will be reported when the testing is complete. The interruption in monitoring from December 10 to 13, 1997, was the result of the failure of the pump laser and the time required for its replacement.

A measurement of CH_4 concentration in the chamber required temperature tuning of the pump diode laser by 1.3^{0}C to an isolated CH_4 line at 2829.592 cm^{-1}. Shown

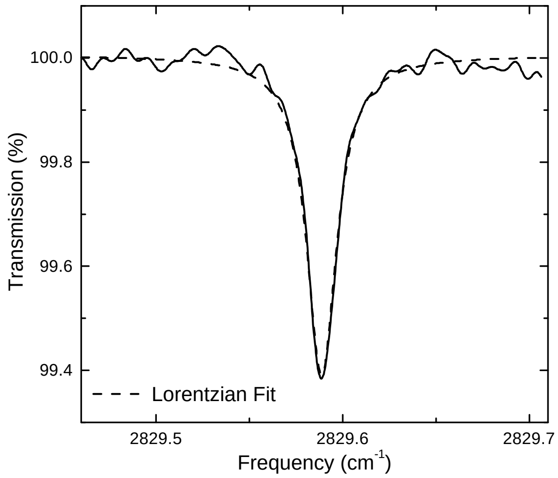

Fig. 10: Spectrum of CH_4 line at 2829.592 cm^{-1} chosen for monitoring NASA chamber. Measured CH_4 concentration is 139 ppm (cell pressure= 95 Torr, L=18 m, 5 s averaging)

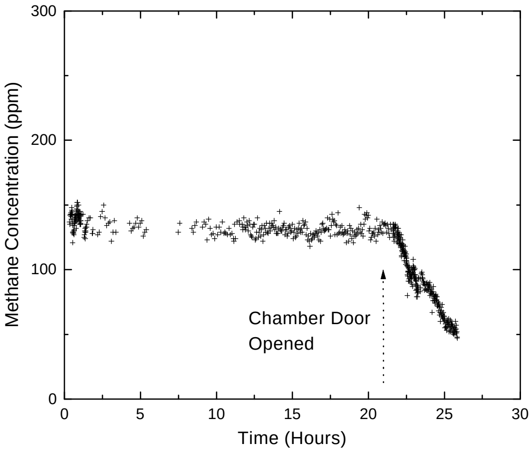

Fig.11: Temporal trend of CH4 concentration in the NASA chamber air measured over 27 hours. The chamber air was opened at 21 hours on December 19, 1997

in Fig. 9 is a spectrum taken of the CH_4 line at a cell pressure of 95 torr and acquired using 5 seconds of averaging. For monitoring this line, the frequency was calibrated to a convenient nearby H_2CO line at 2829.507 cm^{-1}, which could be observed in the calibration cell. The CH_4 fitting algorithm simultaneously fitted a Lorentzian lineshape and a third order polynomial, giving a CH_4 concentration of 139 ppm. Methane concentration measurements made in a 27 hour period starting on December 18, 1997, are shown in Fig. 10. Over the first 20 hours we measured a CH_4 level of 140 ± 12 ppm. Verification of our CH_4 measurement was provided by an online gas chromatography sensor reading a CH_4 level of 139 ppm ± 1 ppm in the first hour of our measurements. The dramatic decline in CH_4 concentration towards the end was due to the chamber door being opened at 21 hours on December 19, 1997.

A spectrum of the H_2O line at 2830.008 cm^{-1}, for a cell pressure of 100 torr and 18 m pathlength is shown in Fig. 11. A Lorentzian fit (FWHM = 0.024 cm^{-1}) to the absorption peak gives a H_2O concentration of 13.0 parts per thousand, corresponding to 46.9 % relative humidity at 23^{o}C.

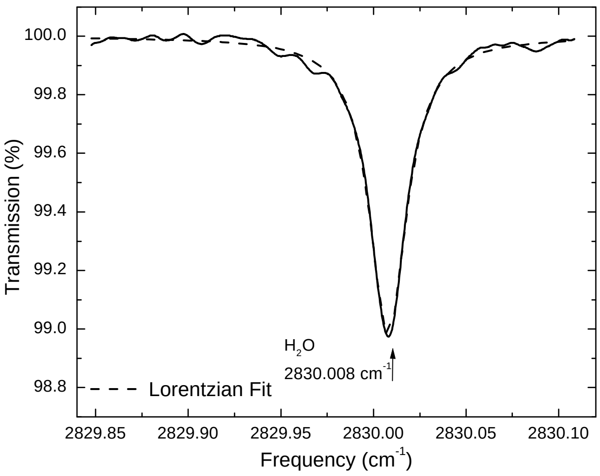

Fig. 12: H_2O spectrum of an isolated absorption line at 2830.008 cm^{-1}. The measured H_2O concentration is 1.3 %, corresponding to 46.9 % relative humidity at 23 °C (cell pressure=100 Torr, L=18 m, 2 s averaging)

Because of the time constraints imposed by the length of the test, the H_2O concentration was not measured inside the chamber.

The sensor has shown good stability over a period of several weeks and it can be made stable over much longer periods of time by implementing several new features.

Recently, a robust all-fiber-coupled sensor [9,10] has been developed with a wide continuous tuning range (3.3 to 4.4 µm) allowing high sensitivity multi-species detection. This sensor uses as pump sources an external cavity diode laser (25 mW peak, 814-870 nm) and a Ytterbium doped fiber amplifier seeded by a distributed Bragg reflector diode laser (P=50mW, λ=1083 nm). By moving to all-fiber beam delivery, no alignment is required during extended operation hence increasing the sensor robustness for demanding long-term measurements. Sensitive and selective detection of several trace gas species such as CO_2, N_2O, CH_4 and H_2CO has been realized. Issues such as power scaling, portability and high-resolution spectroscopy will also be discussed. These prototype sensors are designed as a proof-of-concept with the goal of reducing the spectroscopic DFG sensor size, weight and complexity. It is envisioned that the final sensor configuration will also incorporate digital signal processing and data reduction elements necessary for complete system integration.

CONCLUSION

A tunable DFG sensor employed for on-line real time measurements of H_2CO during a 1997 NASA Lunar Mars Life support test project 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 ~10^{-4}) of a trace gas over an extended period (several weeks), with the sensor operating in an industrial type environment. This sensor incorporated several features for this purpose, including a computer addressable reference cell and real-time data acquisition and processing. 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.

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