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 discussed. 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.

Introduction

It is a very special occasion for me to participate in this symposium today in honor of Dr. Helmut Lotsch. My students, my colleagues in the laser community, and I have benefited immensely from *Applied Physics* and the numerous first and subsequent editions that Helmut has brought to us. He has also been a friend for more than 30 years, when he "discovered" us at Rice.

Mark Twain, at the end of a profoundly meaningful life, for which he never received the Nobel Prize in literature, asked himself what it was we all lived for. He came up with six words which satisfied him. They also are appropriate for you, Helmut: "the good opinion of our neighbors." Neighbors are people who know you, Helmut - who can see you, can talk to you, and to whom you have given invaluable scientific stimulation by providing exemplary journals and books for a quarter of a century.

My talk will focus on 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 lasers 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 recently involved, was the 90-day Lunar-Mars comprehensive life support test conducted at the NASA Johnson Space Center, Houston, in 1997. 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. The purpose of our involvement in the test was to 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-ppm 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]. While this concentration level is about two orders of magnitude below the sensitivity limits for the monitoring apparatus described here, H_2CO is also a significant byproduct of combustion devices and the present monitor is quite satisfactory for monitoring formaldehyde emissions from combustion. 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 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 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 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 30 ppb) [11].

The ν_5 fundamental band 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 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 μm), 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 5.04×10^{-20} cm / molecule [HITRAN 96] at 2831.642 cm^{-1}. The predicted absorption is 2×10^{-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 diode temperature by < 1.3°C.

For the sensor described here, the detection sensitivity using direct absorption spectroscopy is limited by the baseline irregularities caused by the occurrence of accidental etalons that occur in the beam path and not by detector noise or insufficient mid-IR power levels. This fact made it inappropriate to use alternative spectroscopic techniques of frequency or wavelength modulation spectroscopy [13,14] in which the frequency of the IR source is modulated and the signal detected at one of the harmonics of the modulation frequency

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 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 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 overlap of the two pump beams was optimized by means of a CCD camera based profiling system.

The predicted grating period for quasi-phasematching (QPM) of the incident wavelengths was 22.50 μm at a temperature of 23°C. 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 (crystal dimensions are 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 redirected the DFG beam through a 5 cm-long reference cell that contained 20 torr of CH_4 and a small amount of para-formaldehyde 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 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}. 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 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.

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 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 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 μm was 2.7 μW, and after the multi-pass cell, 0.42 μW 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 ν_1 H_2CO lines, is also indicated in Fig. 4. 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. 5 is the spectrum of the same H_2CO absorption lines from an uncalibrated 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.

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. 6. 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 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. 5.

The measured H_2CO concentration for a 21-day period is shown in Fig. 7. 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. 7), 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. The interruption in monitoring from December 10 to 13, 1997, was the result of the failure of a pump laser and the time required for its replacement.

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

The author would like to thank his colleagues at Rice University – Dr. D.G. Lancaster, Mr. D. Richter, Prof. R.F. Curl and Dr. John C. Graf at NASA-JSC for all their support and helpful technical discussions.

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Figure Captions

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.

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

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: 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 path-length, cell pressure of 90 torr and 5s averaging time was used. The Lorentzian fit gives a H_2CO concentration of 169 ppb (mole fraction).

Fig. 6: The 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 H_2CO spectrum.

Fig. 7: 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 ± σ. Independent measurements made of the H_2CO concentration by using a chemically based absorption badge measurement technique are also shown.

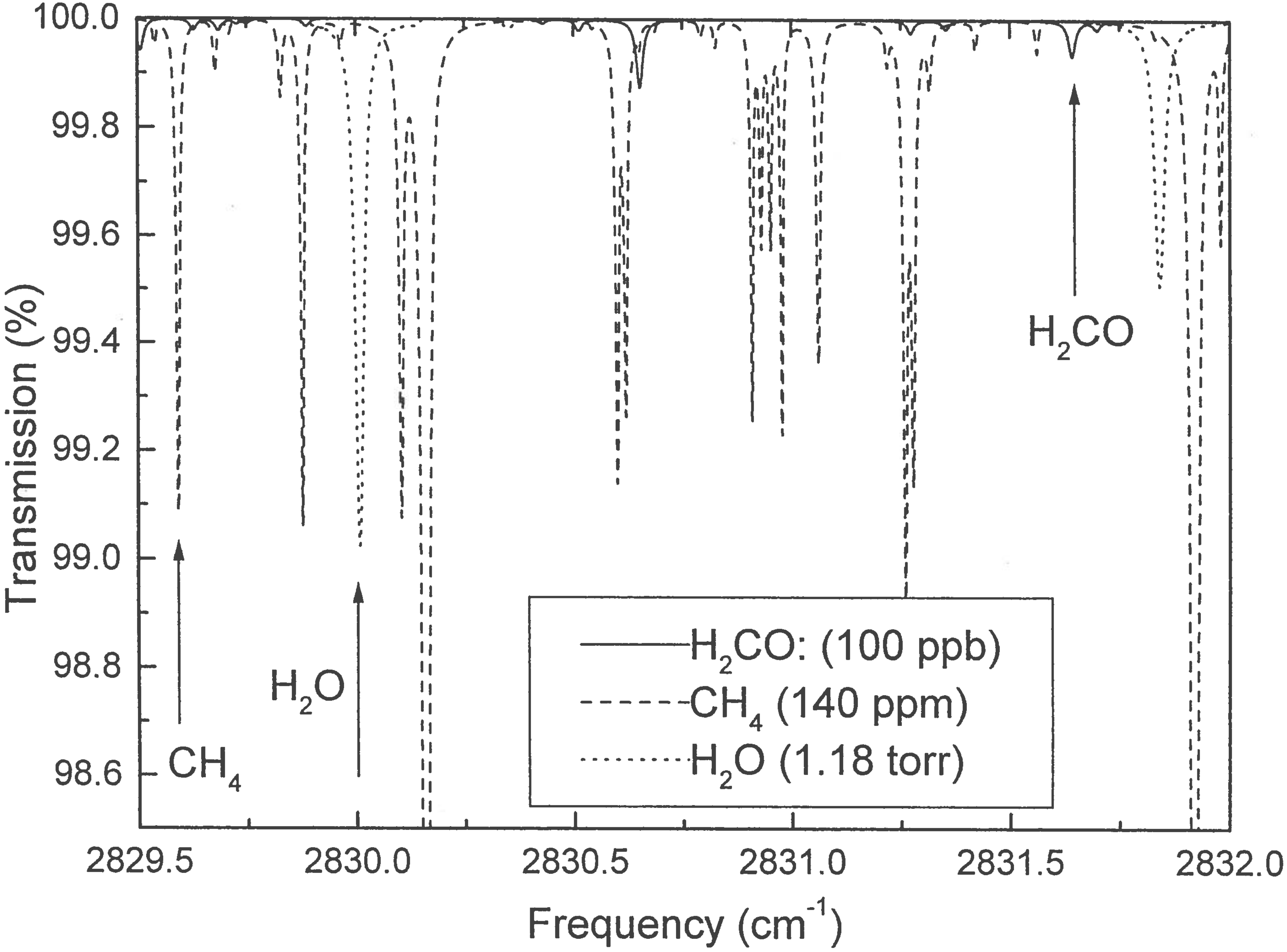
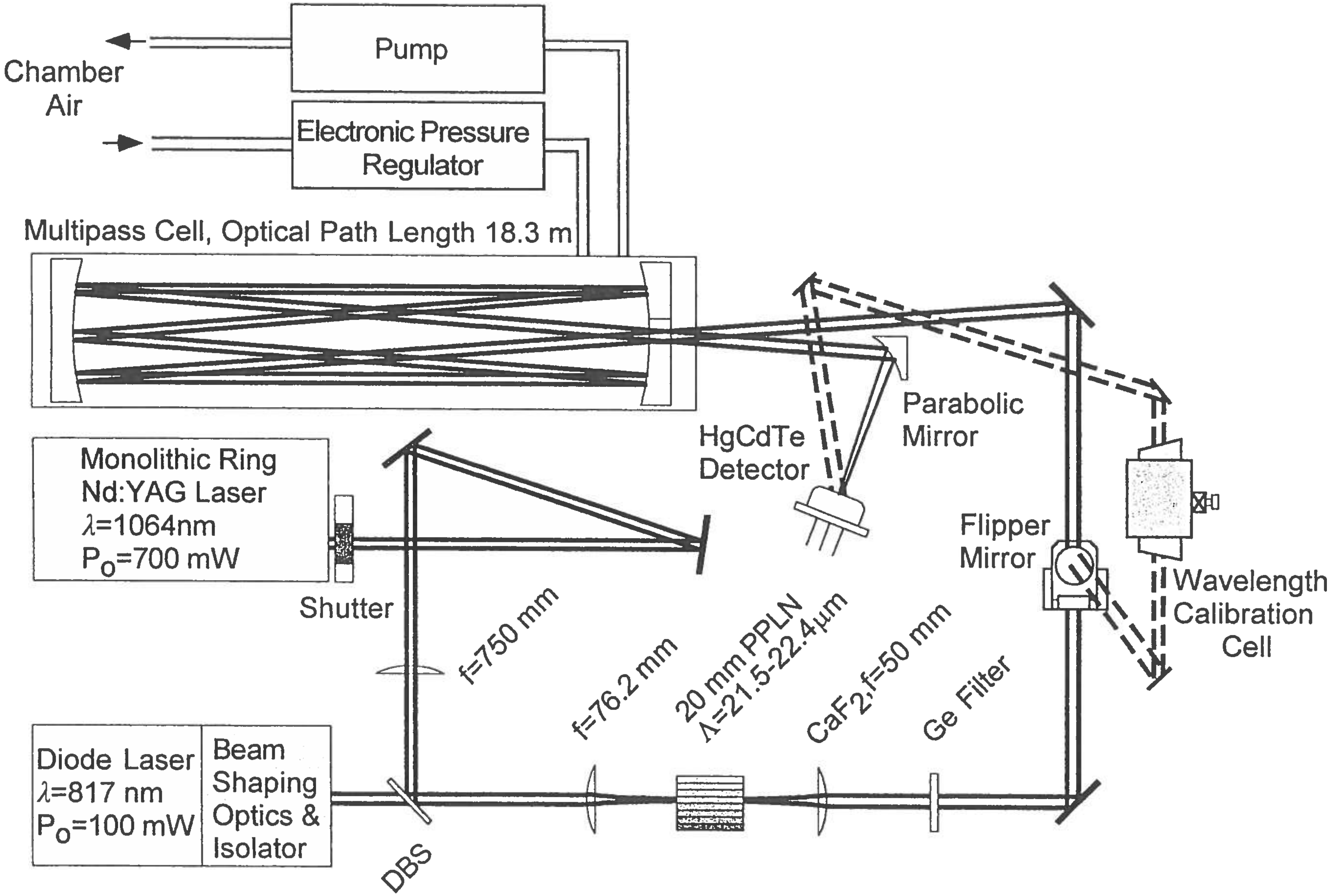
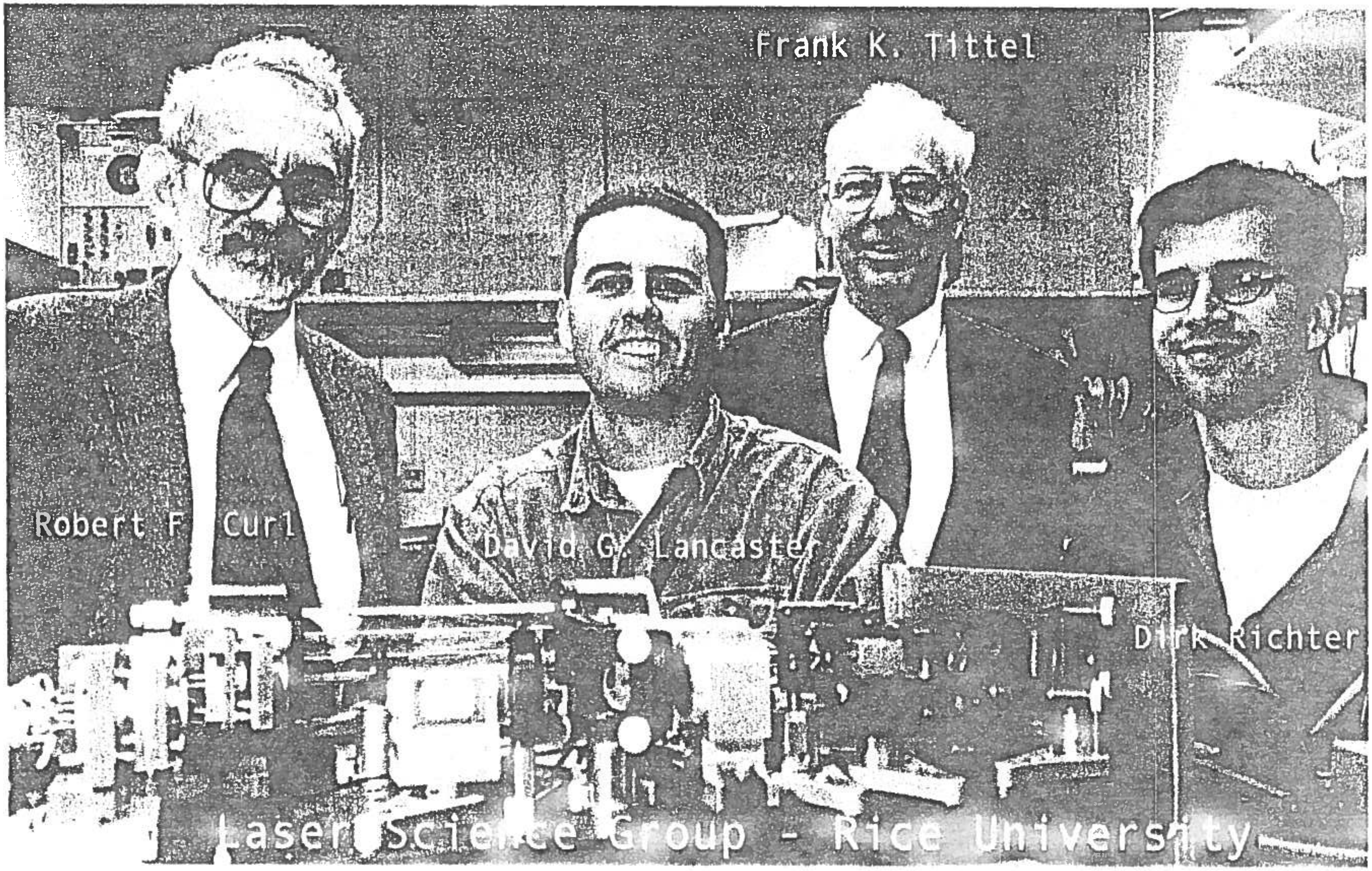

100.0
99.8
99.6
99.4
99.2
99.0
98.8
98.6
Transmission (%)
2829.5
2830.0
2830.5
2831.0
2831.5
2832.0
Frequency (cm^{-1})
CH_4
H_2O
H_2CO
H_2CO: (100 ppb)
CH_4 (140 ppm)
H_2O (1.18 torr)

Figure 1



Pump
Chamber Air
Electronic Pressure Regulator
Multipass Cell, Optical Path Length 18.3 m
Monolithic Ring Nd:YAG Laser
λ=1064nm
P_o=700 mW
Shutter
HgCdTe Detector
Parabolic Mirror
Flipper Mirror
Wavelength Calibration Cell
f=750 mm
f=76.2 mm
20 mm PPLN
Λ=21.5-22.4µm
CaF_2,f=50 mm
Ge Filter
Diode Laser
λ=817 nm
P_o=100 mW
Beam Shaping Optics & Isolator
DBS

Figure 2


Frank K. Tittel
Robert F. Curl
David G. Lancaster
Dirk Richter
Laser Science Group - Rice University

Figure

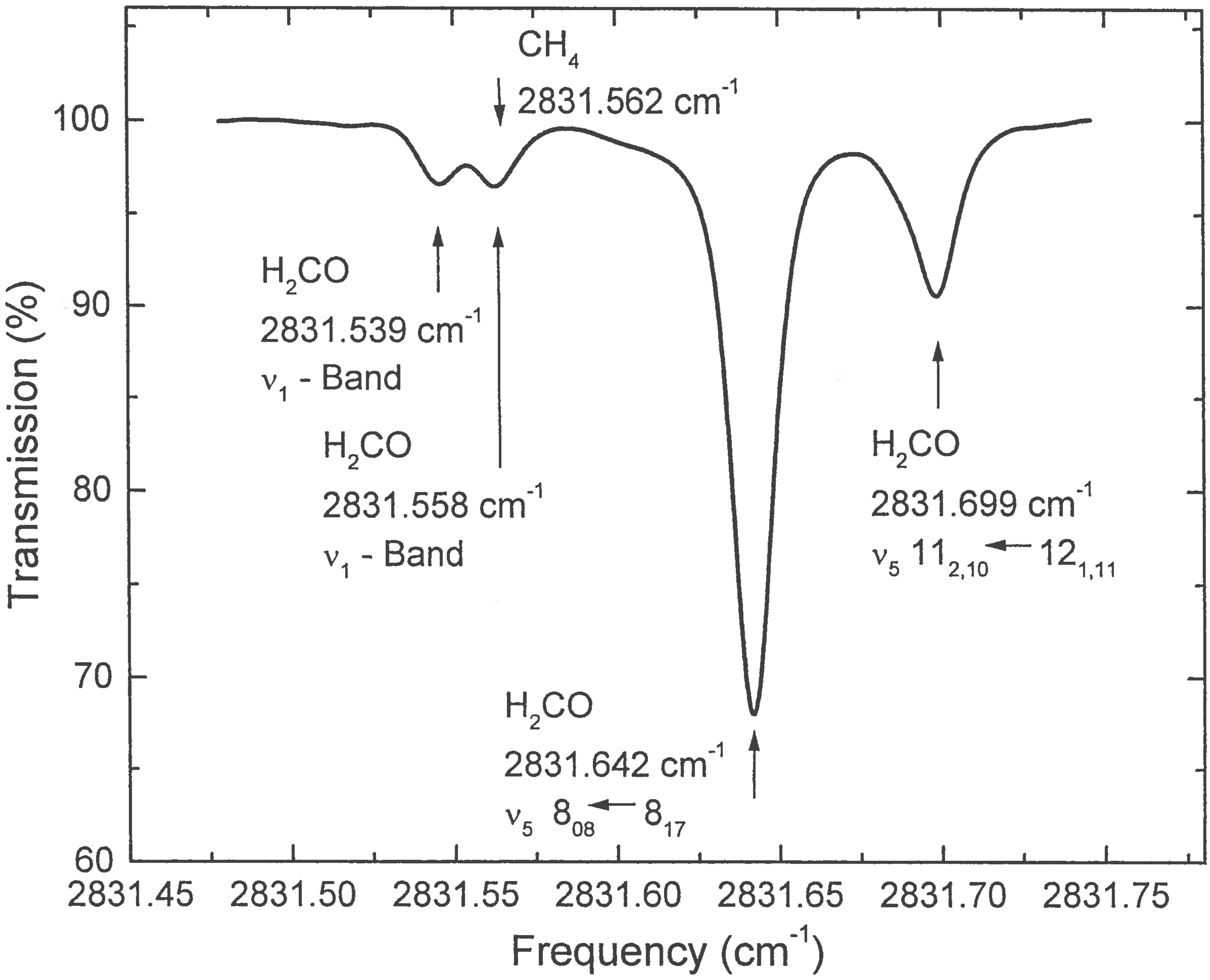

CH$_4$
2831.562 cm^{-1}
H$_2$CO
2831.539 cm^{-1}
ν_1 - Band
H$_2$CO
2831.558 cm^{-1}
ν_1 - Band
H$_2$CO
2831.642 cm^{-1}
ν_5 $8_{08} \leftarrow 8_{17}$
H$_2$CO
2831.699 cm^{-1}
ν_5 $11_{2,10} \leftarrow 12_{1,11}$
Transmission (%)
100
90
80
70
60
2831.45
2831.50
2831.55
2831.60
2831.65
2831.70
2831.75
Frequency (cm^{-1})

Figure 4

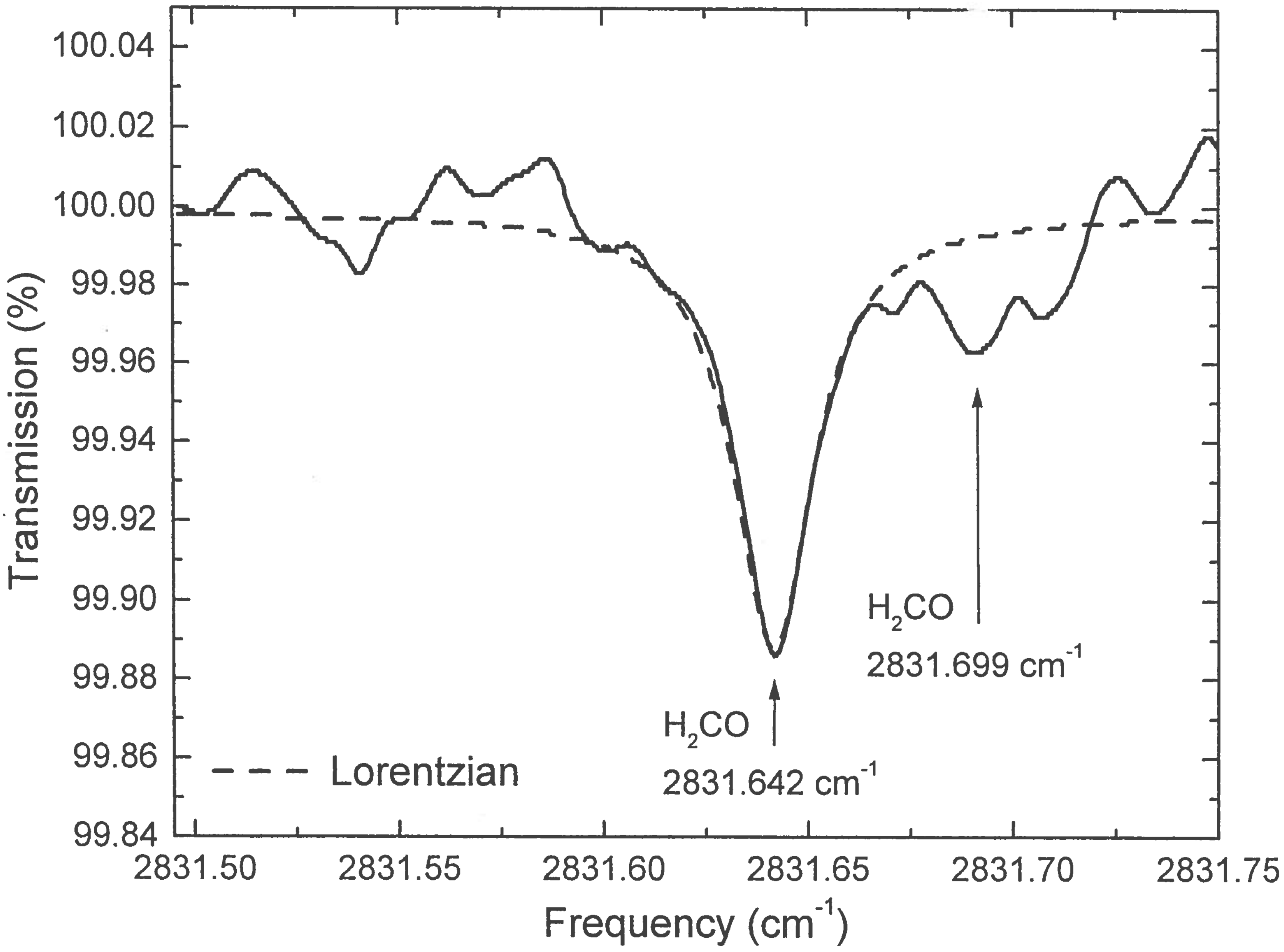

100.04
100.02
100.00
99.98
99.96
99.94
99.92
99.90
99.88
99.86
99.84
Transmission (%)
2831.50
2831.55
2831.60
2831.65
2831.70
2831.75
Frequency (cm^{-1})
Lorentzian
H_2CO
2831.642 cm^{-1}
H_2CO
2831.699 cm^{-1}

Figure 5

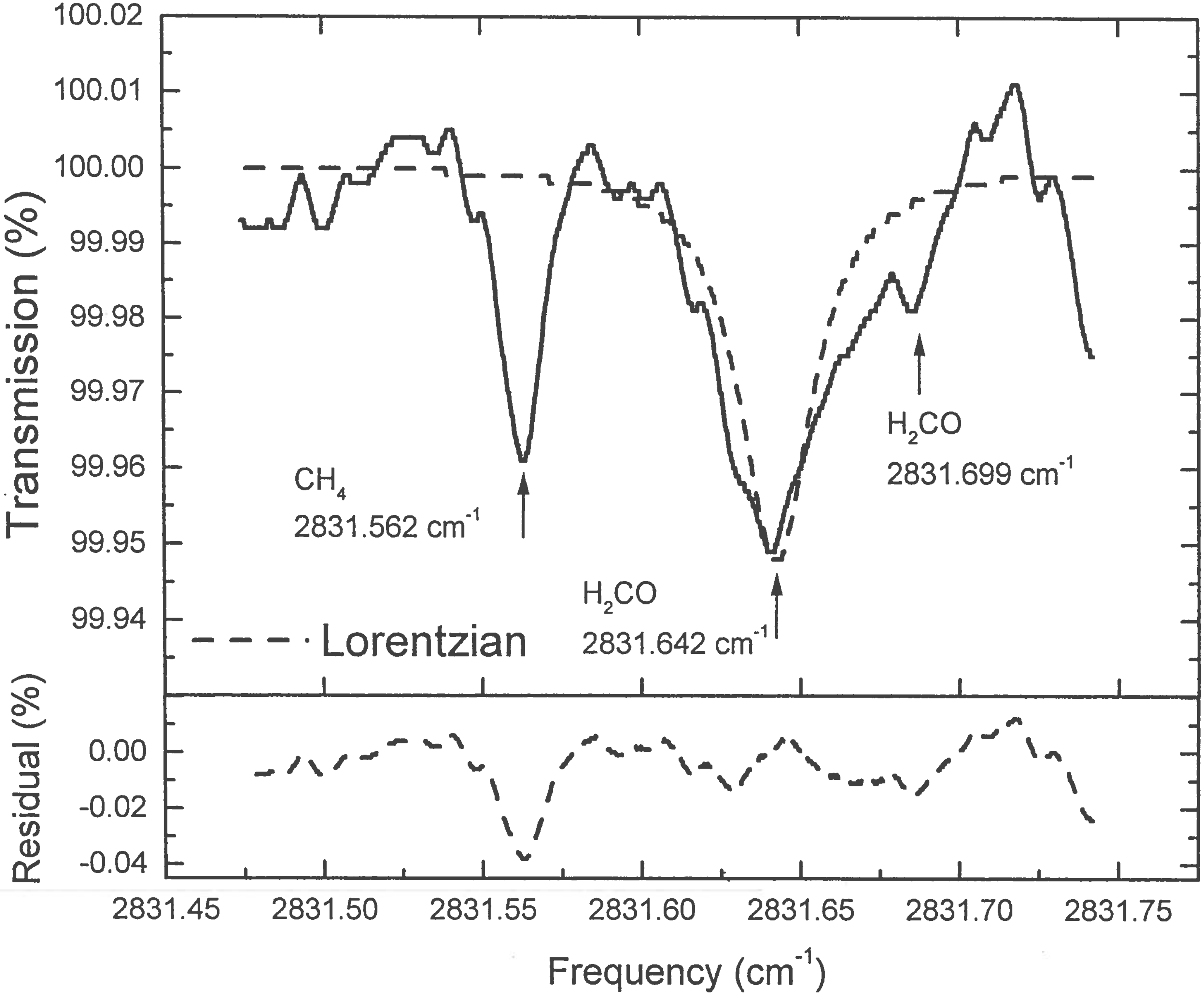
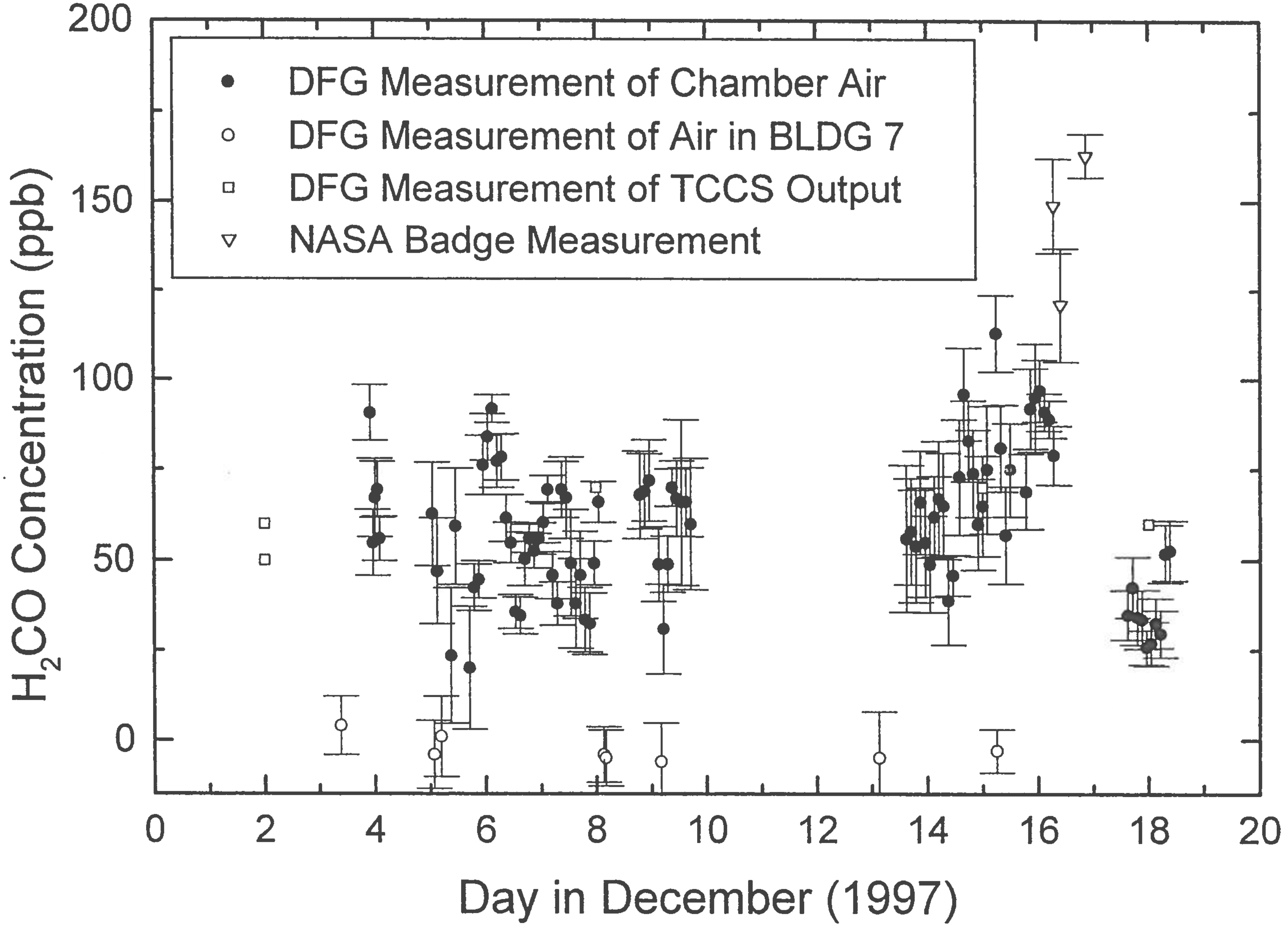

100.02
100.01
100.00
99.99
99.98
99.97
99.96
99.95
99.94
Transmission (%)
0.00
-0.02
-0.04
Residual (%)
2831.45
2831.50
2831.55
2831.60
2831.65
2831.70
2831.75
Frequency (cm^{-1})
CH_4
2831.562 cm^{-1}
H_2CO
2831.642 cm^{-1}
H_2CO
2831.699 cm^{-1}
Lorentzian

Figure 6



● DFG Measurement of Chamber Air
○ DFG Measurement of Air in BLDG 7
□ DFG Measurement of TCCS Output
▽ NASA Badge Measurement
H_2CO Concentration (ppb)
200
150
100
50
0
Day in December (1997)
0
2
4
6
8
10
12
14
16
18
20

Figure 7