Interband cascade laser based absorption sensor for ppb-level formaldehyde detection

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ABSTRACT

A trace gas absorption sensor for formaldehyde (H_2CO) detection was developed using a continuous wave, room temperature, low-power consumption interband cascade laser (ICL) at 3.6 μm. The recent availability of ICLs with wavelength ranged between 3−4 μm enables the sensitive detection of trace gases such as formaldehyde that possesses a strong absorption band in this particular wavelength region. This absorption sensor detected a strong formaldehyde line at 2778.5 cm^{-1} in its v_1 fundamental band. Wavelength modulation spectroscopy with second harmonic detection (WMS-2f) combined with a compact and novel multipass gas cell (7.6 cm physical length, 32 ml sampling volume, and 3.7 m optical path length) was utilized to achieve a sensitivity of ~6 ppbv for H_2CO measurements at 1 Hz sampling rate. The Allan-Werle deviation plot reveals that a minimum detection limit of ~1.5 ppbv can be achieved for an averaging time of 140 seconds.

Keywords: trace gas sensor, interband cascade laser, multipass absorption spectroscopy, formaldehyde detection

INTRODUCTION

Formaldehyde (H_2CO) is an important volatile organic compound (VOC) present in all regions of the atmosphere to highly react in the presence of sunlight to yield ozone [1]. Primary H_2CO sources include vehicle exhaust and fugitive industrial emissions, while secondary H_2CO is produced mainly from the breakdown of primary VOCs via photochemical oxidation. It has a concentration level of 2-45 ppb in urban areas that are governed by primary emissions and secondary formation. In human health research, H_2CO is also of particular interest as it is a hazardous and carcinogenic substance, which needs to be carefully monitored in the environment. The Occupational Safety and Health Administration (OSHA) has issued general industrial standards with an upper limit of 0.75 ppm for long-term exposure (8 h time-weighted average) and 2 ppm for short-term exposure (15 min). H_2CO has also been identified as a potential biomarker in breath analysis of human subjects, i.e., in exhaled breath from breast cancer patients, an H_2CO concentration level of 1.2 ppm was observed compared to a normal level of tens of ppb [2].

In terms of H_2CO detection, several different types of tunable, cw laser sources have been employed to access H_2CO absorption lines, including lead-salt lasers [3], difference frequency generation (DFG) [4] sources, CO overtone gas lasers [5], and optical parametric oscillators (OPOs) [6, 7]. Additionally, recent advancements in quantum cascade laser (QCL) and interband cascade laser (ICL) technologies enable access of the strongest absorption bands of most small molecules in the mid-infrared wavelength region (3−16 μm). In this paper, an H_2CO sensor designed for environmental monitoring is introduced with ppb-level detectivity by employing an ICL at ~3.6 μm and a compact multipass cell.

SENSOR CONFIGURATION AND CALIBRATION

Continuous wave laser radiation with narrow spectral bandwidth is normally utilized for line-of-sight absorption measurements. When laser radiation at a wavelength *v* passes through a uniform gas medium, the wavelength-dependent transmission τ_v is determined by Beer's law:

$$\tau_v = \left(\frac{I_t}{I_0}\right)_v = \exp(-SPx\phi_v L), \quad (1)$$

where I_0 and I_t are incident and transmitted radiation intensity, respectively; S(cm^{-2}atm^{-1}) is the line-strength of the specific transition, P(atm) is the total gas pressure, x is the mole fraction of the absorbing species, ϕ_v(cm) is the line-shape function and L(cm) is the optical path length. The line-shape function ϕ_v is usually approximated using a Voigt profile characterized by the collision-broadened full-width at half maximum (FWHM) and Doppler FWHM. In trace gas sensing for environmental monitoring applications, a multipass configuration is utilized to achieve lower detectable gas concentrations by increasing the optical path length. Wavelength modulation spectroscopy with the second harmonic detection (WMS-2f) can be applied to further improve the signal-to-noise ratio (SNR) for small absorption signals.

The recent availability of ICLs with wavelength ranged between 3–4 μm enables the sensitive detection of trace gases such as formaldehyde (H_2CO) that possesses a strong absorption band in this particular wavelength region. Absorption spectra based on the HITRAN database [8] are computed for the standard air (1.86% H_2O, 0.03% CO_2, 320 ppb N_2O, 1.68 ppm CH_4, 150 ppb CO, 30 ppb O_3, 20.7% O_2, and 77.4% N_2) mixed with 10 ppb H_2CO, to identify the optimal H_2CO transitions. The line at 2778.5 cm^{-1} in its v_1 fundamental band was selected as depicted in **Error! Reference source not found.** for the sensor design in this work. Interfering absorption from other gas molecules such as H_2O and CO_2 present in air is relatively weak and can be further eliminated by the WMS strategy.

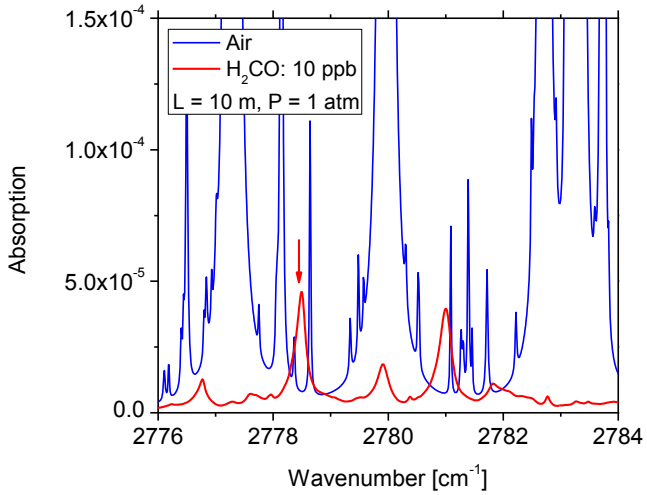

Fig. 1 Simulated absorption spectra of standard air mixed with 10 ppb H_2CO at 296 K and 1 atm using the HITRAN database [8].

The experimental setup of this multipass gas absorption cell based H_2CO sensor is schematically depicted in **Error! Reference source not found.**2. A cw, room temperature, low-power consumed ICL (Nanoplus, Inc.) at 3.6 μm was used to detect the strong H_2CO line at 2778.5 cm^{-1} in its v_1 fundamental band. The ICL current and temperature were controlled by a commercial current source (ILX Lightwave) and a temperature controller (Wavelength Electronics, MPT10000), respectively. A visible diode laser beam (λ = 630 nm) was combined with the mid-infrared beam by means of a dichroic mirror (ISP Optics, model BSP-DI-25-3) to assist in the optical alignment of the sensor system.

Both visible and infrared laser beams were directed into a novel multipass cell (Sentinel Photonics) with a 3.7 m effective path length using a ZnSb lens (100 mm focus length). This dense patterned multipass cell consists of two spherical mirrors separated by a distance of 7.6 cm, providing a sampling volume of 32 ml. The spot pattern covers more of the mirror surface (see spot pattern in **Error! Reference source not found.**2), compared to a standard Herriott cell with a simple circle or elliptical pattern. The pressure inside the MGC is managed by using a pressure controller (MKS, type 649) and a diaphragm vacuum pump (KNF, type UN816.3 KTP). Wavelength modulation spectroscopy (5 kHz) with second harmonic detection was implemented to enhance the detection SNR. An optimum pressure of 150 torr was selected to maximize the WMS-2f signal and to eliminate the spectral cross-talk noise from other ambient interfering absorption.

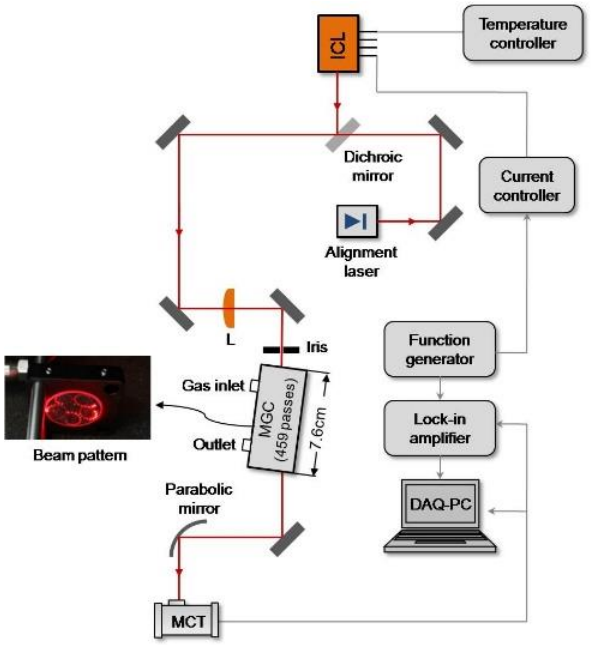

Figure 2. Schematic of the H_2CO sensor design using a 3.6 μm ICL and a compact multipass absorption gas cell.

EXPERIMENTAL RESULTS

Experimental results of H_2CO detection are illustrated in Fig. 3. The bottom panel of Fig. 3 presents the specific spectral region of interest near 2778.5 cm^{-1}, which is simulated for 750 ppb H_2CO and 1% H_2O in air at 296 K and 150 torr using the HITRAN database [8]. The WMS-2f signal within the same wavelength range (Fig. 3, top panel) was also recorded at the same experimental conditions for comparison. The ICL wavelength was calibrated using a Fourier-transform interferometer in the rapid-scan mode with a resolution of 0.125 cm^{-1}.

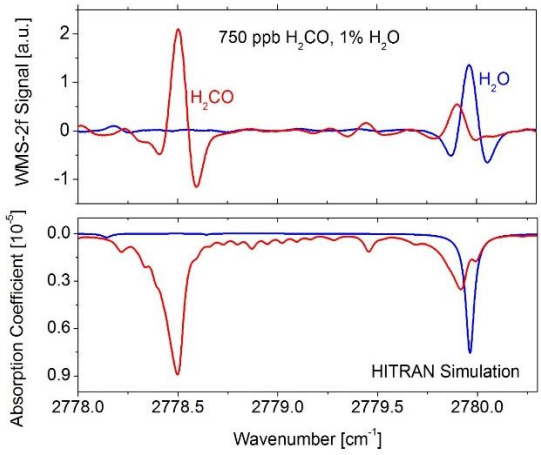

Figure 3. Comparison of the measured H_2CO signal (top panel) and the simulation (bottom panel) at 150 torr. Simulation was performed using the HITRAN database [8] for 750 ppb and 1% H_2O in air.

The sensor calibration was performed using the same experimental setup depicted in **Error! Reference source not found.**1 with the optimized pressure and selected modulation depth. The system response to the H_2CO absorption was calibrated using the varied concentrations of H_2CO in N_2 mixture obtained from a permeation based gas generator (Kin-Tek Model

491M). The measured WMS-2*f* amplitude at 2778.5 cm^{-1} is plotted in Fig. 4 as a function of the H_2CO concentration. The H_2CO concentration covers a range from 26 ppb to 250 ppb to demonstrate the linear response of the sensor system. An Allan deviation analysis [9] was performed to investigate the long-term stability and precision of the H_2CO LAS sensor. The Allan deviation shown in Fig. 5 reveals that the detection limit can be improved from 6 ppb at 1 sec integration time to 1.5 ppb with an integration time of 140 sec.

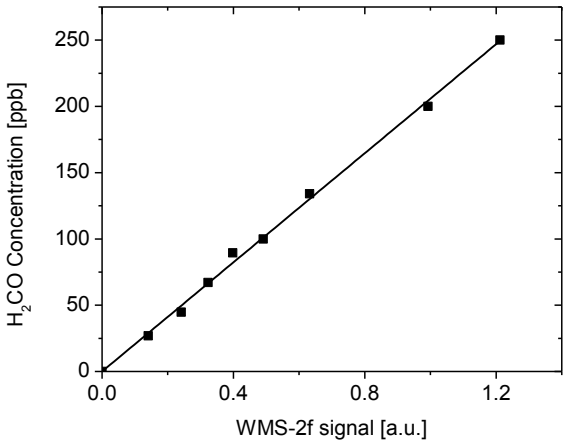

Figure 4. WMS-2*f* amplitude at 2778.5 cm^{-1} as a function of H_2CO concentration.

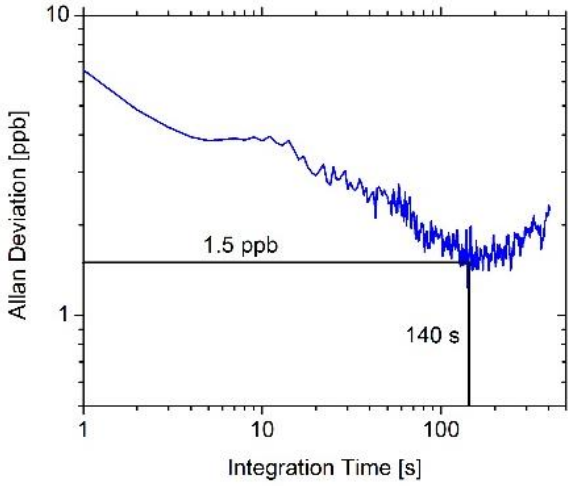

Figure 5. Allan deviation in ppb of the WMS-2f signal as a function of the integration time.

CONCLUSIONS AND FUTURE OUTLOOK

We have demonstrated the development of an H_2CO sensor using an interband cascade laser at ~3.6 μm and a novel multipass absorption gas cell. Wavelength modulation spectroscopy with second harmonic detection was conducted to achieve 6 ppb detectivity of H_2CO at 1 s averaging time. The long-term stability and precision of this absorption sensor were examined and a 1.5 ppb detectivity can be achieved by averaging up to 140 s. Future work is planned to further improve the sensor detectivity to sub-ppb level by using a multipass cell with longer path length and to install the sensor system in a mobile monitoring van for real time measurements of H_2CO emissions in the Greater Houston area.

ACKNOWLEDGEMENTS

We acknowledge the financial support from a National Science Foundation (NSF) ERC MIRTHE award, a NSF-ANR award for international collaboration in chemistry, "Next generation of Compact Infrared Laser based Sensor for Environmental monitoring (NexCILAS)", and the Robert Welch Foundation grant C-0586.

REFERENCES

[1] B.P. Wert, M. Trainer, A. Fried, T.B. Ryerson, B. Henry, W. Potter, W.M. Angevine, E. Atlas, S.G. Donnelly, F.C. Fehsenfeld, G.J. Frost, P.D. Goldan, A. Hansel, J.S. Holloway, G. Hubler, W.C. Kuster, D.K. Nicks, J.A. Neuman, D.D. Parrish, S. Schauffler, J. Stutz, D.T. Sueper, C. Wiedinmyer, A. Wisthaler, J. Geophys. Res. 108, ACH8/1 (2003).
[2] S.E. Ebeler, A.J. Clifford, T. Shibamoto, J. Chromatogr. B 702, 211 (1997).
[3] D. Richter, P. Weibring, Appl. Phys. B 82, 479 (2006).
[4] D.G. Lancaster, A. Fried, B. Wert, B. Henry, F.K. Tittel, J. Appl. Opt. 39, 4436 (2000).
[5] H. Dahnke, G. von Basum, K. Kleinermanns, P. Hering, M. Mürtz, Appl. Phys. B 75, 311 (2002).
[6] F. Müller, A. Popp, F. Kühnemann, S. Schiller, Opt. Express 11, 2820 (2003).
[7] M.M.J.W. van Herpen, S.E. Bisson, A.K.Y. Ngai, F.J.M. Harren, Appl. Phys. B 78, 281 (2004).
[8] L. S. Rothman, I. E. Gordon, A. Barbe, D. C. Benner, P. F. Bernath, M. Birk, V. Boudon, L. R. Brown, A. Campargue, J.-P. Champion, et al., J. Quant. Spectrosc. Radiat. Transf. **110**, 533 (2009).
[9] P. Werle, R. Mücke, and F. Slemr, Appl. Phys. B **57**, 131 (1993).