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Detection of formaldehyde using mid-infrared difference-frequency generation

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Abstract. Real-time detection and measurement of sub-ppm levels of formaldehyde in ambient air using diode-pumped 3.5 μm difference-frequency generation (DFG) in periodically poled $LiNbO_3$ (PPLN) is reported. Minimum detectable concentration of 30 ppb was achieved with a compact, portable room-temperature gas sensor configured for formaldehyde (H_2CO) detection. This sensitivity, coupled with high selectivity and long term stability, is sufficient for various environmental applications.

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Formaldehyde is an important reactive intermediate product in tropospheric hydrocarbon oxidation initiated by the OH radical. The H_2CO concentration in the atmosphere is in the 1 to 10 ppb range [1–3]. It is also a well-known pollutant that is emitted due to incomplete combustion processes [4]. Formaldehyde is a chemical widely used in many industrial manfacturing processes due to its high chemical reactivity and good thermal stability. Widely used building materials like foams and numerous consumer paint and polymer products contain formaldehyde. Studies indicate that H_2CO can cause a variety of health effects ranging from irritation of eyes, nose, and throat to nausea, dizziness, and headaches at concentrations above 100 ppb. At 100 ppm it is dangerous to life and health. To protect workers from exposure to formaldehyde, an 8-hour time weighted average concentration of 750 ppb as the permissible exposure limit is set by the U.S. Occupational Safety and Health Administration (OSHA) [5]. The National Aeronautics and Space Administration (NASA) provides an even more conservative value, the Spacecraft Maximum Allowable Concentration (SMAC) of 40 ppb for crew exposure over 7 to 180 days [6]. In order to monitor the concentration and to locate emission sources, the development of an *in situ*, real-time, portable gas sensor capable of detecting formaldehyde of sub-ppm levels in air is of considerable interest.

Previously reported formaldehyde detection in the infrared was performed using FTIR monitoring [7] and tunable diode laser absorption spectroscopy (TDLAS) with cryogenically cooled lead salt diode lasers. Harris et al. [8] demonstrated a minimum detectable concentration of 0.25 ppb using a 33.5 m optical pathlength with a typical acquisition time of 3 minutes in the 5.7 μm absorption region. More recently, Fried [9] reported an improved detection sensitivity of 0.05 ppb by monitoring H_2CO absorption at 2831.5 cm^{-1} using a 100 m pathlength Herriott multipass cell and a data averaging time of 100 s.

The gas sensor described here uses difference frequency mixing in PPLN as a convenient mid-infrared room temperature laser based source tuned to a formaldehyde absorption line at 2861.72 cm^{-1} (∼3.5 μm). This compact and portable instrument appears to be suitable for various applications involving air quality measurements. To date, we have demonstrated a minimum detectable H_2CO concentration (limited by interference fringes produced by optical surfaces in the beam path) of better than 30 ppb (corresponding to an absorption of 0.02%) by means of direct laser absorption spectroscopy.

1 Experimental details

The mid-infrared absorption spectrum of formaldehyde was first investigated in detail by Pine [10] and Brown et al. [11]. Pine reported that Q-branches of the ν_1 and ν_5 carbon-hydrogen stretch modes at ∼ 3.60 μm are particularly promising for atmospheric monitoring, because of their high intensity and relative freedom from interference by water and methane. Our present mid-infrared laser source was tuned to one of the P-branch absorption lines of the ν_5 band at 2861.72 cm^{-1} (∼3.5 μm). In order to reduce interference by weak formaldehyde, methane, and water lines close by, H_2CO detection was performed in air at reduced pres-sure (∼ 50 to 100 Torr) in a multipass cell.

A schematic diagram of the formaldehyde sensor is shown in Fig. 1, which is similar in design to that reported previously for the detection of CH_4 and CO [12–15]. The 3.5 μm spectroscopic DFG source is pumped by two compact lasers, a 100 mW single-frequency GaAlAs diode laser

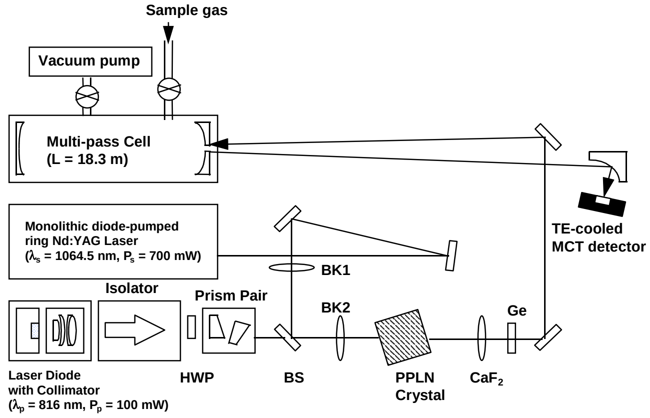

Fig. 1. Optical arrangement of the DFG-based sensor for formaldehyde detection. HWP, BS and Ge denote a half wave plate, beam splitter and Germanium filter, respectively. BK1, BK2, and CaF_2 are lenses having focal lengths of 750 mm, 76.2 mm, and 63 mm, respectively

at 816 nm (SDL Inc., Model SDL5412-H1) and a 700 mW single-frequency monolithic ring Nd:YAG laser (Lightwave Electronics, Model 126) at 1064 nm. The DFG element is a 10 mm long PPLN crystal with a 21 μm domain grating period tilted 13° with respect to the input face. The incident angle of the beam on the crystal was 19° to form an angle of 21° between the grating ***k***-vector and the incident beam inside the crystal. This provides an effective grating period of 22.5 μm required for quasi-phase-matching of the d_{33} interaction ($e - e \rightarrow e$) [16]. The DFG source can generate up to 4.7 μW output power at 3.5 μm. The mid-infrared beam is collimated by a CaF_2 lens and directed into a compact multi-pass cell (New Focus Inc., Model 5611). This cell was configured for an effective path length of 18 m with an optical throughput of 35%. The infrared beam emerging from the cell is collected by an off-axis parabolic mirror and focused onto a thermoelectrically-cooled HgCdTe (MCT) photoconductive detector (EG&G Judson, Model J15TE3:5) with a $1 \times 1\,\text{mm}^2$ active area.

The detected signal is amplified by a dc-coupled preamplifier, and digitized by a laptop computer equipped with a PCMCIA 16-bit analog-to-digital converter. The responsivity of the detector/preamplifier system is $\sim 0.59\,\text{V}/\mu\text{W}$, with a noise equivalent power of $\sim 3.9\,\text{pW}/\sqrt{\text{Hz}}$, and a dark voltage drift of less than 0.15 mV/hour. This dark voltage drift is equivalent to ~ 0.6 ppb/minute of formaldehyde. The dark voltage of the detector/preamplifier is measured periodically by blocking the Nd:YAG beam using a computer controlled shutter, so that the error due to the drift becomes negligibly small in the detection of sub-ppm levels of formaldehyde. The entire gas sensor including electronics is contained in a $30 \times 30 \times 65$ cm enclosure weighing less than 25 kg with a power consumption of < 50 W.

Direct absorption rather than a modulation technique such as wavelength modulation was used to measure the formaldehyde absorption, because of the absolute measurement capability and convenience in handling the data analysis of absorption spectroscopy. For direct absorption measurements, reduction of the interference fringes created by optical components such as the multipass cell and appropriate correction for the baseline slope are critical in achieving low detection limits. The multipass cell interference fringes could be minimized by vibration of the cell. An applied low frequency vibration causes the interference fringes to move and change, hence averaging out the effect of the fringes over a large number of scans. A direct absorption spectrum obtained by diode current modulation has a predominantly linearly sloping baseline resulting from the linear dependence of the output power on diode current. However, any etalons present in the system can distort this baseline.We found empirically that this baseline is well approximated by a weak cubic polynomial. Data analysis was performed by simultaneously fitting a Lorentzian lineshape to the H_2CO absorption peak, as well as a third order polynomial to the baseline. Removal of the baseline slope and distortion using this cubic fitting resulted in a flat baseline. These measures make it possible to detect an absorption of $< 0.02\%$ accurately by means of direct absorption spectroscopy.

Formaldehyde molecules tend to deposit on or outgas from surfaces of pipes that connect the multipass cell and the sample gas inlet. Depending on temperature, this may result in erroneous concentration measurements. A continuous flow of H_2CO in nitrogen is passed through the multipass cell at the sampling pressure. In this case, the observed formaldehyde concentration reaches a steady value typically within thirty minutes after the flow is started, depending on the flow rate and concentration.

2 Results and discussion

The idler wavelength is typically tuned over a wavelength range of $0.3\,\text{cm}^{-1}$ to capture a single absorption line in air at a reduced pressure of typically 50 Torr. The laser diode is tuned by current modulation using a 50 Hz triangular waveform. Calibration of the operating wavelength and tuning range was achieved by using a methane reference spectrum obtained by periodically inserting into the beam a 13-cm long glass cell with CaF_2 windows filled with CH_4 at 20 Torr. The sensor response was calibrated with a commercial 5.5-ppm (± 5%) formaldehyde-in-nitrogen mixture (Scott Specialty Gases). A typical absorption spectrum of the calibration gas at 50 Torr is shown in Fig. 2. Based on absorption measurements of the line at $2861.72\,\text{cm}^{-1}$, an

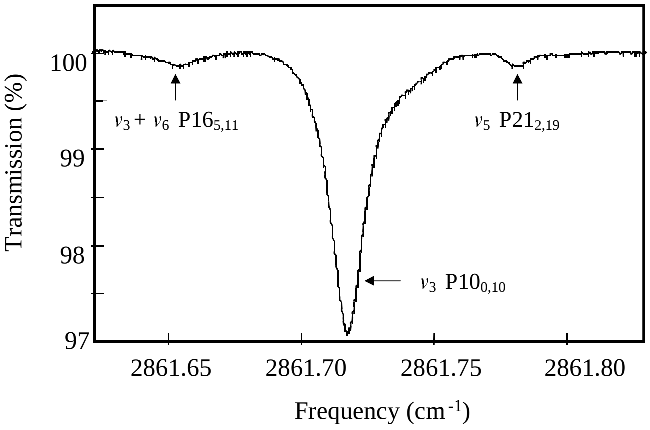

Fig. 2. An absorption spectrum of 5.5-ppm formaldehyde in nitrogen at 50 Torr for an optical path length of 18.3 m. Transitions shown in the figure are assigned using [11] and [19]

integrated intensity of 4.34×10^{-20} cm/molecule was computed at room temperature. The measured line intensity is in good agreement with the GEISA reported line intensity of 3.96×10^{-20} cm/molecule [17]. In order to test the system at reduced absorption, a formaldehyde concentration of 140 ppb was produced by diluting the calibration gas with high purity nitrogen. The resulting absorption spectrum of 140 ppb formaldehyde in nitrogen is depicted in Fig. 3. Measurements of the formaldehyde absorption intensity in this sample yielded an H_2CO concentration of 135 ± 15 ppb, in good agreement within the uncertainty of the calibration gas.

Additional verification of the sensor calibration was performed by measuring formaldehyde concentrations in air from a formaldehyde generator (Kintek Model 585). The results are compared with those obtained by a liquid impinger/chromotropic acid apparatus shown in Fig. 4. The DFG based sensor yielded 237 ppb as an averaged value for three hours of data acquired by averaging scans over 40 seconds at intervals of 20 minutes, while a value of 210 ppb was obtained by a wet chemical method. In another test, our result was 783 ppb versus 750 ppb by the wet chemical method. These results are in reasonable agreement with each other. The response of the DFG based sensor is much more rapid than the wet chemical measurement. A typical absorption spectrum obtained from 230 ppb formaldehyde in air with 50% humidity is shown in Fig. 5. Residual low frequency interference fringes in the baseline are appreciably strong with a peak-to-peak magnitude equivalent to ∼ 30 ppb H_2CO. This noise level would be low enough to allow the detection of formaldehyde below SMAC levels (40 ppb) in ambient air.

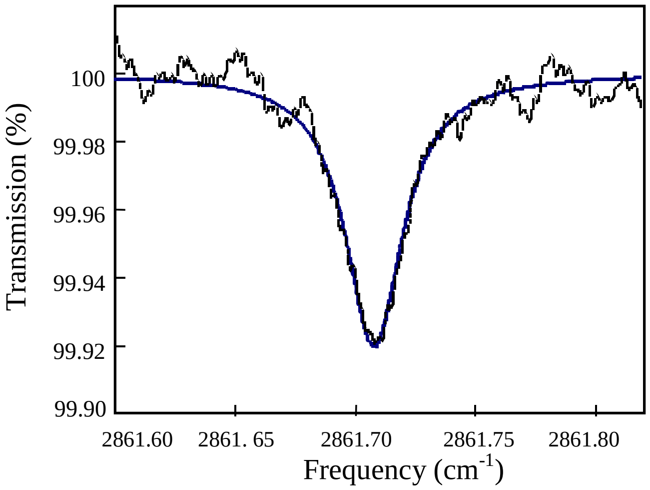

Fig. 3. A spectrum of 140 ppb formaldehyde in nitrogen at 100 Torr. The *solid line* is a Lorentzian curve fitted to the data with a rms error of 7 ppb

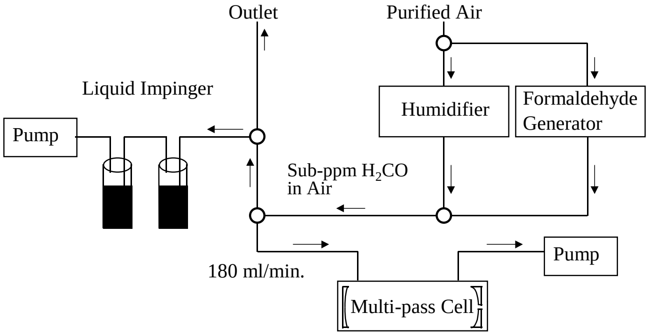

Fig. 4. Flow system for sampling air containing formaldehyde at sub-ppm concentration. The impinger, which is analyzed after exposure time of one hour is used to estimate concentration levels

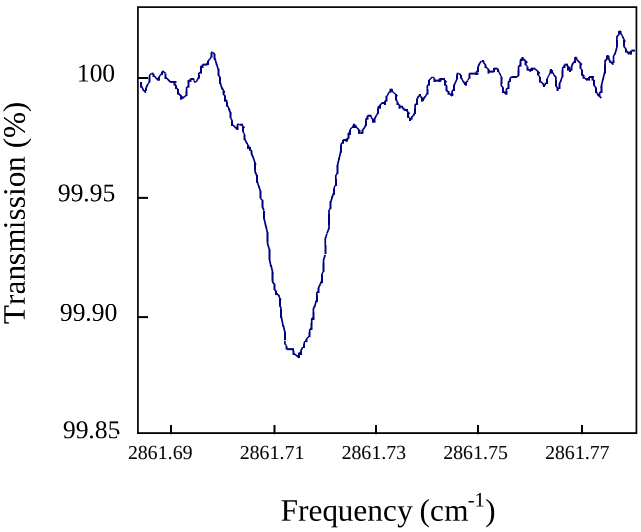

Fig. 5. A trace of 230 ppb formaldehyde in ambient air. From a series of comparison tests, a minimum detectable concentration of 30 ppb was determined

In conclusion, detection and measurement of formaldehyde at sub-ppm concentrations in air using diode pumped 3.5 μm DFG radiation in PPLN has been demonstrated. A minimum detectable concentration of $\leq$ 30 ppb was obtained, limited by residual optical interference in the multipass cell. Increased sensitivity at the ppb level should be attainable using software signal filtering and enhanced data acquisition techniques. Furthermore, improved DFG conversion efficiencies will result from PPLN waveguide structures [18]. This makes this mid-infrared gas sensor useful for occupational safety applications, requiring the detection of H_2CO and other environmentally important trace gases such as HCl and CH_4.

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References

1. J.A. Logan, M.J. Prather, S.C. Wofsy, M.B. McElroy: J. Geophys. Res. **86**, 7210 (1981)
2. X. Zhou, K. Mopper: J. Geophys. Res. **98**, 2385 (1993)
3. A. Fried, S. McKeen, S. Sewell, J. Harder, B. Henry, P. Goldan, W. Kuster, E. Williams, K. Baumann, R. Shetter, C. Cantrell: J. Geophys. Res. **102**, 6283 (1997)
4. T.E. Graedel: *Chemical Compounds in the Atmosphere*, Chapt. 4, (Academic Press, New York 1978), pp. 158-161
5. U.S. Department of Labor: *Occupational Exposure to Formaldehyde*, Program Highlights Fact Sheet No. OSHA 92-27
6. NASA, Lyndon B. Johnson Space Center: *Spacecraft Maximum Allowable Concentrations for Airborne Contaminants*, Technical Report JSC20584 (1995)

7. D. Hull, R. Brewer, W. Dieringes, J. Lange, G. Pophal, R. Spellicy: Air and Waste Management Conf. on Optical Remote Sensing, San Francisco (Sept. 1995)
8. G.W. Harris, G.I. Mackay, T. Iguchi, L.K. Mayne, H.I. Schiff: J. Atmos. Chem. **8**, 119 (1989)
9. A. Fried, S. Sewell, B. Henry, B.P. West, T. Gilpin, J.R. Drummond: J. Geophys. Res. **102**, 6253 (1997)
10. A.S. Pine: J. Mol. Spectrosc. **70**, 167 (1978)
11. L.R. Brown, R.H. Hunt, A.S. Pine: J. Mol. Spectrosc. **75**, 406 (1979)
12. K.P. Petrov, S. Waltman, E.J. Dlugokencky, M. Arbore, M.M. Fejer, F.K. Tittel, L.W. Hollberg: Appl. Phys. B **64**, 567 (1997)
13. K.P. Petrov, L. Goldberg, W.K. Burns, R.F. Curl, F.K. Tittel: Opt. Lett. **21**, 86 (1996)
14. K.P. Petrov, Y. Mine, T. Töpfer, R.F. Curl, F.K. Tittel, J. Graf: 27th Int’l Conf. on Environmental Systems, Lake Tahoe, SAE Paper Series 972434, 1 (1997)
15. T. Töpfer, K.P. Petrov, Y. Mine, D. Jundt, R.F. Curl, F.K. Tittel: Appl. Opt.: Lasers, Photonics, Environm. Opt. **36**, 8042 (1997)
16. L.E. Myers, R.C. Eckherdt, M.M. Fejer, W.R. Bosenberg, J.W. Pierce: J. Opt. Soc. Am. B **12**, 2102 (1995)
17. GEISA Database, Laboratoire de meteorologie dynamique du CNRS, Ecole Polytechnique, F-91128 Palaiseau, France
18. M. Arbore, M.H. Chou, M.M. Fejer: CLEO Technical Digest Series **9**, 120 (1996)
19. L.S. Rothman, R.R. Gamache, A. Goldman, L.R. Brown, R.A. Toth, H.M. Pickett, R.L. Poynter, J.-M. Flaud, C. Camy-Peyret, A. Barbe, N. Husson, C.P. Rinsland, M.A.H. Smith: Appl. Opt. **26**, 4058 (1987)