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Trace Ethylene Detection by Means of QEPAS in Near-Infrared Spectral Region

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Abstract: Quartz enhanced photoacoustic spectroscopy (QEPAS) was applied to detection of trace ethylene (C_2H_4) in nitrogen at atmospheric pressure. An absorption peak at 6177.15 cm^{-1} was accessed using a fiber coupled DFB diode laser.

OCIS codes: (300.6430) Spectroscopy, optoacoustic and thermo-optic; (280.3420) Laser sensors

1. Introduction

The availability of a cost-effective ethylene (C_2H_4) sensor would constitute a breakthrough for the fruit transport and storage industry. Ethylene is an important indicator of the degree of fruit ripening and also acts as a catalyst to initiate the ripening process, so that its concentration must be kept low during the transport and storage of fruits to avoid premature ripening. For example, the required target sensitivity is ~1 ppm for the transport of bananas. No cost-effective solution is presently available, since current instrumentation does not achieve the necessary operating performance (e.g stability, life-time) or is too costly (e.g gas chromatography).

Laser-based spectroscopy is a promising technique for such an application, since potentially cost-effective laser sources commercially available in the NIR spectral region may be used to develop a C_2H_4 sensor. However, the target sensitivity should be achieved in a simple and compact device architecture, and the sensor must be capable of operating in the specific environmental conditions encountered in-field for this application, e.g. in the presence of high concentrations of potential interfering species such as humidity and carbon dioxide, as well as in a large range of temperature and in a noisy environment.

This work describes a prototype C_2H_4 NIR sensor based on a quartz enhanced photoacoustic spectroscopy (QEPAS) approach. This version of the photoacoustic (PA) spectroscopy features small sensor footprint and weight combined with enhanced immunity to environmental acoustic noise.

2. Sensor description

A traditional QEPAS sensor optical configuration described in previous publications [1,2] was used. Briefly, a DFB diode laser operating at λ~1.62 μm was used to access an overtone absorption band of ethylene and excite a PA signal. The diode laser injection current was modulated to achieve wavelength modulation at a frequency equal to half the resonant frequency of a quartz tuning fork (QTF). The optical power reaching the QTF was ~15 mW. An electrical signal generated by the QTF in response to the PA signal was detected and used to quantify the ethylene concentration. A small fraction (~1%) of the laser radiation was directed to a reference cell and a photodiode (PD) to be used in a wavelength stabilization loop. This loop using the 3f component of the photodiode signal keeps the laser wavelength locked to a selected optical absorption peak of ethylene. Signals from the QTF and PD were measured and processed by a dedicated control electronics unit (CEU). This unit also controlled the laser current and temperature and executed the logical sequence of the sensor operation. A PC with LabView software was used to facilitate the CEU interface via a RS232 port and add to the flexibility of the sensor control.

A certified mixture of 101 parts per million by volume (ppmv) C_2H_4 in N_2 gas was used for the sensor performance assessment. This mixture was flowing through the sensor at a 50-100 sccm rate, and the pressure was controlled at a level of ~715 Torr.

3. Spectral simulations and sensor performance

Neither HITRAN nor GEISA databases include spectroscopic information on the C_2H_4 absorption in the NIR region. Therefore, an FTIR spectrum from the Pacific Northwest National Laboratory database [3] acquired for 1 atm pressure was used as a primary reference. Since it was believed important to develop a sensor without moving parts such as a vacuum pump, the use of a 1 atm absorption spectrum is considered appropriate for this purpose. Fig. 1 (a) shows a fraction of the PNNL C_2H_4 spectrum covering the tuning range of the available DFB diode laser. Fig. 1(b) presents a simulated 2f wavelength modulation spectrum for the same region, performed at a wavelength modulation

(WM) amplitude $\Delta\nu$=0.20 cm^{-1}. This amplitude was found to be near-optimum, both numerically and experimentally. Fig. 1(b) shows that the highest $2f$ signal is expected for a peak at 6177.15 cm^{-1}, which was also confirmed experimentally.
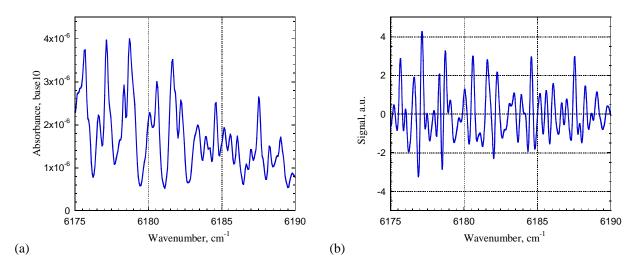

Fig. 1. (a) A fraction of FTIR spectrum from the PNNL database covered by the tuning range of the available DFB diode laser; (b) simulated $2f$ wavelength modulation spectrum assuming a 0.20 cm^{-1} WM amplitude and neglecting residual amplitude modulation (RAM).

A close-up view of the region near the 6177.15 cm^{-1} peak is shown in Fig. 2(a), and Fig. 2(b) depicts an experimentally observed QEPAS signal in the same region. Our WM model neglects the residual amplitude modulation (RAM), which explains some deviations of the actually acquired data from simulations.
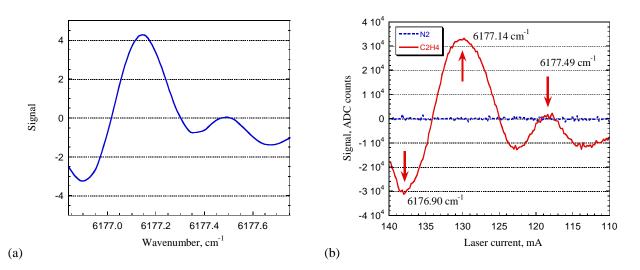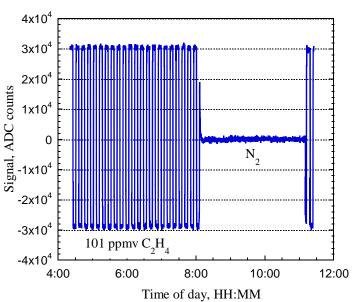

Fig. 2. (a) Simulated $2f$ signal covering the spectral range utilized for the QEPAS based C_2H_4 sensing; (b) Actually recorded QEPAS signal for the same spectral region: solid line – 101 ppmv C_2H_4, dotted .line –pure nitrogen. Data acquisition time per point is 5.6 s.

Fig.2 shows three spectral features useful for spectroscopic monitoring of C_2H_4: a high positive peak at 6177.14 cm^{-1}, an almost equally strong negative peak at 6176.90 cm^{-1}, and a zero signal at 6177.49 cm^{-1}, where the 3f signal also crosses the zero level. Tuning of the diode laser to 6177.49 cm^{-1} allows calibration of the zero levels of CEU both for the $2f$ QTF signal and for $3f$ component of the reference cell photodiode signal. Hence, detection of the QEPAS signal when the laser is alternately tuned to the 6177.14 cm^{-1} positive and 6176.90 cm^{-1} negative peaks results in an accurate determination of the C_2H_4 concentration even if there is a slow drift of the zero level. Such a drift can occur, for example, when the temperature of the electronics varies. Fig. 3 depicts the observed QEPAS signal as measured by the CEU with the laser switching as described above. When pure nitrogen flow is directed to

the sensor replacing the C_2H_4 standard, the difference in signals measured at 6176.90 cm^{-1} and 6177.14 cm^{-1} disappears.

Fig. 3. Continuous monitoring of QEPAS signal (101 ppmv C_2H_2:N_2) with the laser wavelength alternately tuned to the 6177.14 cm^{-1} positive or 6176.90 cm^{-1} negative peaks in the C_2H_2 2f absorption spectrum. From ~8:10 to 11:10 the sensor was flushed with pure N_2, while switching of the laser wavelength continued at the same rate. Data acquisition time is ~11.2 s per point.

Based on the experimental observations, the detection sensitivity is estimated to be a 4 ppmv/Hz$^{1/2}$ noise-equivalent C_2H_4 concentration, or 5.4×10^{-9} cm^{-1}W/ Hz$^{1/2}$. This is in agreement with the recently reported sensitivity of 5.6×10^{-9} cm^{-1}W/ Hz$^{1/2}$ observed with the same ADM for H_2S QEPAS based detection at 780 Torr [4].

4. References

[1] A.A Kosterev, F.K. Tittel, D. Serebryakov, A. Malinovsky and I. Morozov, "Applications of Quartz Tuning Forks in Spectroscopic Gas Sensing", Review of Scientific Instruments **76,** 043105 (2005).

[2] A. A. Kosterev, T. S. Mosely, and F. K. Tittel, "Impact of humidity on quartz-enhanced photoacoustic spectroscopy based detection of HCN", Appl. Phys. B 85, 295-300 (2006).

[3] S.W. Sharpe, T.H. Johnson, R.L. Sams, P.M. Chu, G.C. Rhoderick and P.A. Johnson, "Gas-phase database for quantitative infrared spectroscopy", Appl. Spectrosc. 58, 1452-1461 (2004)

[4] A. A. Kosterev and F. K. Tittel, "QEPAS based detection of H_2S and CO_2 using a near-IR DFB diode laser", 6th International Conference on Tunable Diode Laser Spectroscopy, July 9-13, 2007, Reims, France