A Cavity-Enhanced Sensor for Benzene Detection

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Abstract: A DFB-ICL near 3.3 µm was utilized to develop a laser sensor for trace detection of benzene. Cavity-enhanced absorption spectroscopy enabled a minimum detection limit of 2 ppb in 6 seconds integration at room conditions.

1. Introduction

Benzene (C_6H_6) is emitted into air from petrochemical facilities, vehicle exhaust, petrol stations, etc. It is categorized as *'a major public health concern'* by the World Health Organization (WHO) [1]. Due to the fatal diseases caused by benzene such as leukemia and polycythemia, it is essential to have reliable sensors on the sites where benzene is emitted. As the current commercial sensors have several limitations, there is a dire need for new and improved ones. In this paper, we report the utilization of a mid-IR laser source to measure benzene traces with the application of cavity-enhanced absorption spectroscopy (CEAS) and multi-dimensional linear regression to overcome the interference of ethylene, methane and water vapor in practical environments.

2. Sensor Description

In the ultraviolet (UV) wavelength region, benzene measurements are influenced by the broad features of the absorption bands of several hydrocarbons causing cross interference. Alternatively, high selectivity detection of benzene and other pollutants is achieved in the infrared spectrum due to the well-resolved features of their absorption bands. According to PNNL database [2], the best frequency to measure benzene in the IR region is around 674 cm^{-1}; however, it is still outside the accessible range of the commercial tunable lasers and thus cannot be used currently. A quantum cascade laser (QCL) emitting near 9.6 µm was previously utilized to measure low benzene concentrations [3]. However, ozone interference in this spectral region can be challenging in several geographical locations. Recently, a 3.4 µm inter-band cascade laser was utilized to measure benzene traces [4]; however, isoprene interference was neglected which can be significantly high at various locations. Hence, to avoid ozone and isoprene interference in this work, we have selected the ro-vibrational band of benzene near 3.3 µm (3040 cm^{-1}). Figure 1 shows the spectral interference from ethylene, methane and water vapor with benzene in this region [5], which is overcome by the implementation of a multi-dimensional linear regression (MLR) algorithm and wavelength-scanning for simultaneous concentration measurement of each of these species.

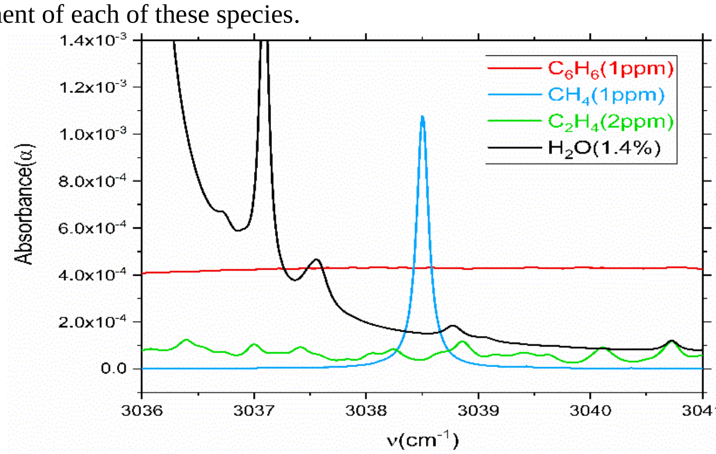

Fig. 1. Optical Schematic of the benzene sensor

A DFB 3.3 µm inter-band cascade laser (DFB-ICL, Nanoplus) with an output power ~ 1 – 2 mW was used to target this spectral region. For optical alignment, a Thorlabs 670 nm red laser was co-aligned with the IR laser. To form a cavity in a 50 cm sampling cell, two 99.97% reflectivity ZnSe mirrors (LohnStar Optics) were placed on its ends. Off-axis alignment was done for the cavity to suppress the spurious coupling noise compared to the on-axis alignment. A focusing lens collected the transmitted signal to an AC-coupled photodetector (bandwidth of 1.5 MHz, Vigo Systems) with thermoelectric cooling. The main alignment challenge was collecting this weak transmitted signal due to the aforementioned high mirrors' reflectivity and low laser power.

3. Experimental Results

The nominal reflectivity of the mirrors can deviate significantly from the manufacturer's specification resulting in unacceptably large errors. Thus, it is essential to increase the measurement accuracy by verifying this reflectivity. The CEAS absorbance of known C_6H_6/N_2 mixtures was measured and compared to the simulated single-pass absorbance to determine the reflectivity using $= 1 - \frac{A_{sp}}{e^{A_{CEAS}-1}} = 99.96 \pm 0.024\,\%$, which results in an increase of ~ 3 orders of magnitude in absorbance compared to a single-pass cell. The Allan deviation was calculated to be 6 seconds, which corresponds to the optimum integration time of each measurement to minimize the noise and thus error on our measurements. The sensor was verified by measuring benzene samples with known concentrations, and the minimum detection limit for benzene was found to be 200 ppt based on a minimum detectable absorbance of 0.1%. Thereafter, MLR was implemented to perform simultaneous measurements of benzene, ethylene, methane and water vapor to verify the sensor's ability to measure benzene in the presence of these interfering species, which increased the detection limit to 2 ppb. Finally, the laser sensor was used to measure real air samples collected from various locations, as shown in Fig. 3. As expected, the benzene concentration in the parking was higher on a weekday than on a weekend, and highest at the gas station. These benzene measurements were compared to a gas chromatograph (GC), and both were in good agreement, as shown in Table 1.

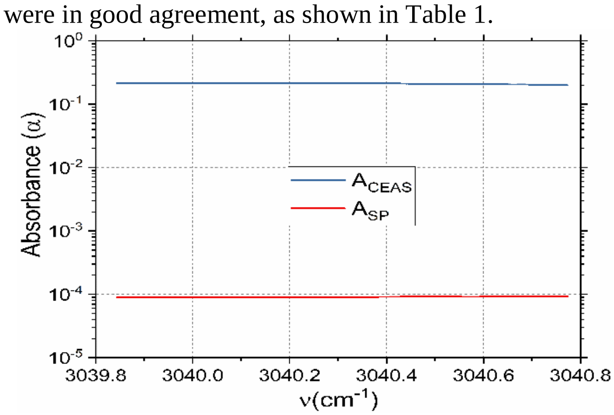

Fig. 2. Comparison of CEAS absorbance with simulated single-pass absorbance (X = 165 ppb, T = 298 K, P = 1 atm, L = 50 cm)

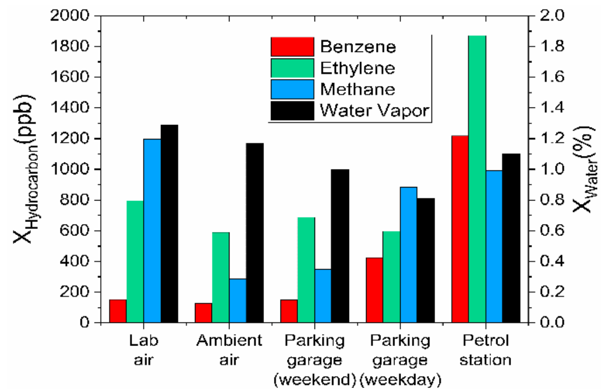

Fig. 3. Measured concentrations of benzene, ethylene, methane and water vapor in the collected samples

Table 1: Comparison between the benzene concentrations measured by the laser sensor and gas chromatograph

Sample source	Lab air	Ambient air	Parking garage (weekend)	Parking garage (weekday)	Petrol Station
Laser sensor	152	128	150	425	1217
Gas chromatograph	157	114	163	434	1284

4. Conclusions

Trace concentrations of benzene have been measured by a laser sensor based on cavity-enhanced absorption spectroscopy. The high reflectivity of the cavity mirrors increased the single pass absorption by three orders of magnitude. The sensor has verified with a gas chromatograph its ability to simultaneously measure benzene, ethylene methane and water vapor. It can detect down to 2 ppb of benzene in 6 seconds, and is capable of monitoring air quality and leaks in petrochemical refineries where the emissions of these species are likely.

4. Acknowledgement

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5. References

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