

# Ppb-level methane sensor using a multi-pass mode photoacoustic spectroscopy technology

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The demand for trace gas detection is increasing in wide fields, such as electric facility maintenance, industrial production, and combustion research. Photoacoustic spectroscopy (PAS) is superior to other trace gas detection techniques due to its wide dynamic range, fast response, high sensitivity, reliability and chemical selectivity [1-2]. One of the PAS advantages is the sensor performance could be improved by increasing the optical power. For the sake of improving the performance, the photoacoustic cell was placed inside the laser resonator to obtain higher optical power [3-4]. However, additional optical distortion and optical losses is a big strike against this intracavity PAS sensor. In this paper, a multi-pass photoacoustic cell consists of two flat metallic mirrors was designed to reflect the laser to pass through the photoacoustic cell, which quintupled the photoacoustic signal for methane detection. The multi-pass cell based PAS sensor has the advantages of simple design and non-interference in the laser resonator.

A schematic diagram of the multi-pass cell based PAS sensor which consisted of a differential photoacoustic cell, two flat metallic mirrors, two microphones and a transimpedance differential preamplifier was shown in the Fig. 1. The photoacoustic cell was made up of two identical parallel resonators ( $\Phi 8 \times 40$  mm) and two symmetric cylindrical buffers ( $\Phi 20 \times 10$  mm). One of the mirrors was a fully coated aluminium flat mirror, and the other was partially coated, which allowed laser beam to enter the photoacoustic cell through a circular hole. The two mirrors were employed as two reflectors of the photoacoustic cell. The laser beam could propagate thoroughly between these mirrors, consequently, the optical length was increased significantly. Such multi-pass mode will lead to the increase of background noise. Therefore, wavelength modulation spectroscopy and 2nd harmonic demodulation techniques were used to reduce the background noise. A distributed feedback laser emitted at the wavelength of the methane absorption (1653.7 nm) was used for generating acoustic signals. The acoustic signals were directed to the transimpedance differential preamplifier and then transfer to the lock-in amplifier to retrieve the methane concentration.

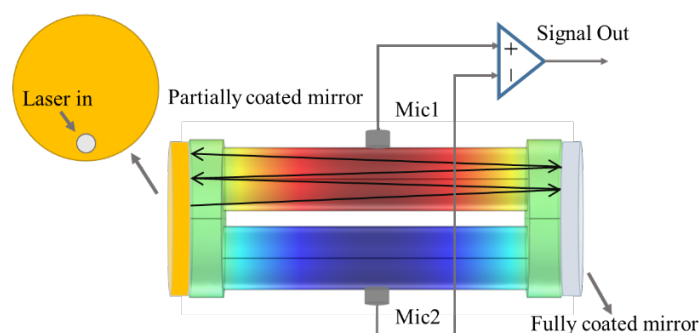
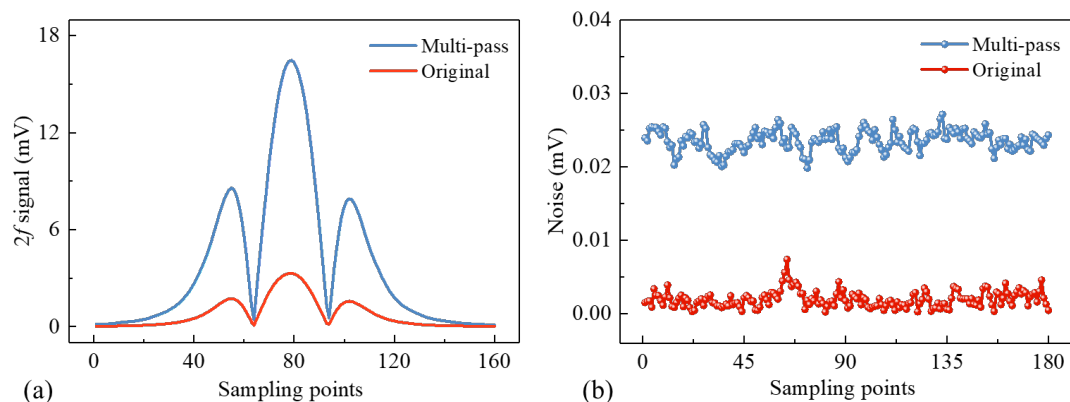


Fig. 1. Schematic diagram of the multi-pass cell based PAS sensor.

In order to verify the performance of the multi-pass cell based PAS sensor, a 2000 ppm methane gas was used as the sample and detected by the multi-pass photoacoustic cell and an original photoacoustic cell in which laser passed through the resonator only once. Fig. 2(a) illustrated that the  $2f$  signal of the multi-pass mode was 16.5

mV, a 4 folds higher than the original mode (3.3 mV). As shown in Fig. 2(b), due to the absorption of mirror and wall, the average amplitude of background noise of multi-pass mode (20  $\mu\text{V}$ ) was 9 folds higher than the original mode (2  $\mu\text{V}$ ). However, the standard deviation of the noise did not increase significantly when using the multi-pass mode (from 1.1  $\mu\text{V}$  to 1.4  $\mu\text{V}$ ). By using the multi-pass mode, the signal-to-noise of the  $2f$  signal was quadrupled. The noise-equivalent concentration (NEC) for methane detection was calculated as 170 ppb, corresponding to a normalized noise equivalent absorption (NNEA) coefficient of  $2.7 \times 10^{-9} \text{ cm}^{-1} \text{ W/Hz}^{-1/2}$ .



**Fig. 2.** (a) Original  $2f$  signal and multi-pass  $2f$  signal of 2000ppm methane; (b) Noise determination of original and multi-pass mode.

In conclusion, a multi-pass cell-based PAS sensor was developed for methane sensing. Two flat metallic mirrors were used as the reflectors to increase the optical length of the sensor, resulting in a quintuple photoacoustic signal amplitude. The NEC for methane detection was 170 ppb, corresponding to an NNEA coefficient of  $2.7 \times 10^{-9} \text{ cm}^{-1} \text{ W/Hz}^{-1/2}$ . The results make the multi-pass mode promising for PAS sensor performance improvement.

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## References

- [1] Y. Cao, N.P. Sanchez, W. Jiang, et al., Simultaneous atmospheric nitrous oxide, methane and water vapor detection with a single continuous wave quantum cascade laser, *Opt. Express*. 23(3) (2015) 2121–2132. <https://doi.org/10.1364/OE.23.002121>.
- [2] K. Chen, S. Liu, B. Zhang, et al., Highly sensitive photoacoustic multi-gas analyzer combined with mid-infrared broadband source and near-infrared laser, *Opt. Lasers Eng.* 124 (2020) 105844. <https://doi.org/10.1016/j.optlaseng.2019.105844>.
- [3] V.S. Starovoitov, J.F. Kischkat, M.P. Semtsiv, et al., Intracavity photoacoustic sensing of water vapor with a continuously tunable external-cavity quantum-cascade laser operating near 5.5  $\mu\text{m}$ , *Opt. Lett.* 41(21) (2016) 4955–4958. <https://doi.org/10.1364/OL.41.004955>.
- [4] Q. Wang, Z. Wang, J. Chang, et al., Fiber-ring laser-based intracavity photoacoustic spectroscopy for trace gas sensing, *Opt. Lett.* 42(11) (2017) 2114–2117. <https://doi.org/10.1364/OL.42.002114>