



Atmospheric CH₄ measurement near a landfill using an ICL-based QEPAS sensor with V-T relaxation self-calibration

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ABSTRACT

A quartz-enhanced photoacoustic spectroscopy methane (CH₄) sensor with vibrational to translational (V-T) relaxation self-calibration was realized and tested for atmospheric CH₄ detection near a landfill. To normalize the influence of H₂O vapor on the CH₄ energy relaxation rate, CH₄ and H₂O concentrations were detected simultaneously by means of a frequency division multiplexing technique, in which a custom quartz tuning fork was operated in the fundamental and first overtone combined vibration mode. A continuous wave, thermoelectrically cooled distributed feedback interband cascade laser emitting at 3.3 μm and a near-infrared DFB laser emitting at 1.37 μm were used as the excitation source for CH₄ and H₂O detection, respectively. A theoretical model of V-T relaxation and self-calibration method were developed to allow this CH₄ sensor to have a simple setup and a small sensor size. Continuous field measurements were carried out near the largest sanitary landfill in Shanxi province, China, to demonstrate the stability and ruggedness of the realized CH₄ sensor.

1. Introduction

Methane (CH₄) is an odorless, flammable gas with atmospheric concentrations of ~1.8 ppm [1,2]. It is mainly released into the atmosphere by human activities such as leakage from natural gas systems, as well as emission from livestock and landfills. It can also be found in sewers, wetlands and mines. CH₄ is a highly potent greenhouse gas which is ~21 times more powerful in warming the atmosphere than CO₂ per unit weight. In addition, CH₄ has a long lifetime. The average amount of time that individual methane molecule spends in the atmosphere before it is removed by photochemical reaction or uptake into the ocean or terrestrial biosphere is ~12 years. [3]. Highly sensitive and precise measurements of CH₄ are mandatory to monitor its induced global warming and climate change, considering its environmental relevance. According to the United States Environmental Protection Agency, municipal solid waste (MSW) landfills are the third largest source of CH₄ emission [4]. Economic development and rising standards of living lead to increase in the quantity of MSW and most of MSW end up at landfills. These result in a large generation of landfill

gases (LFG). The LFG, mostly consisting of CH₄ (55–60% v/v), CO₂ (40–45% v/v) plus other volatile organic carbon and trace components (< 1% v/v), are produced when the organic waste in the MSW is broken down by bacteria naturally present in MSW and the soil [3,4]. At some large landfills, CH₄ in LFG is collected and utilized for the production of electricity and heat.

Many factors lead to the instability of CH₄ generation, collection and emission, such as wind, temperature, atmospheric pressure, MSW organic content, its compaction degree, age, etc. Hence, although professional equipments are installed to collect the LFG, the LFG utilization cannot be carried out effectively at most landfills. The LFG are either flared with risk of producing toxic combustion products or emitted into atmosphere. Due to the huge potential of LFG using as an energy source, landfill methane is getting more attention from local governments, utilities, environmental organization together with industry and MSW landfill operators. As a result, detecting, monitoring and capturing methane at former and active landfills are a global housekeeping benefit as well as an important alternative energy niche.

Several optical gas sensing techniques have been employed for CH₄

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detection [5–10]. Among them, the quartz-enhanced photoacoustic spectroscopy (QEPAS) technique [11], a modification of conventional photoacoustic spectroscopy (PAS), has been demonstrated to provide CH₄ detection with fast response times (< 1 s). Such a technique is wavelength independent, capable to analyze small gas samples with high accuracy and sensitivity, and does not require the use of any optical detectors [12–14]. In QEPAS sensing, the photoacoustic signal, generated by the absorption of modulated light from the gas sample, is detected by means of a piezoelectric quartz tuning fork (QTF), acting as a sharply resonant acoustic transducer [15–17]. QTFs are characterized by a high-quality factor Q (> 10,000 at atmospheric pressure), a high resonant frequency f_0 (up to few tens of kHz) and narrow resonance width (few Hz or less) as well as high immunity to environmental acoustic noise [18,19]. In most of the reported QEPAS-based sensor, the laser beam is focused on to the gas present between the two QTF prongs and in an acoustic micro-resonator (AmR) tube, which acts as an acoustic resonator for the QTF [20]. A $2f$ wavelength modulation spectroscopy ($2f$ -WMS) technique is typically employed to excite an anti-symmetric mode of the QTF vibration. The laser modulation frequency must accurately match with the QTF resonance frequency to obtain the highest signal amplitude [21]. However, when exploiting a standard QTF (resonance frequency of $\sim 32,768$ kHz), the modulation frequency f of ~ 16 kHz is comparable to or exceeds the vibrational to translational (V-T) energy transfer rate ($1/\tau$) in slow-relaxing gas species such as CH₄ or CO, thereby violating the condition for PAS that the molecular relaxation rates $1/\tau$ should be much higher than the modulation frequency, i.e. $f \ll 1/\tau$ [22]. As a result, the observed QEPAS signal exhibits a strongly reduced amplitude and dependence on $1/\tau$ compared to a conventional PAS-based sensor.

One way to enhance the CH₄ QEPAS signal amplitude is to employ a custom-made QTF with a low resonance frequency [18,19], thus reducing the mismatch between the high modulation frequency of the QEPAS sensor and the low molecular relaxation rate of CH₄. By optimizing the prong spacing and the ratio of the prong width W and the square of the prong length L , the fundamental resonance frequency of a custom QTF was reduced down to ~ 3 kHz, becoming more suitable for the detection of slow-relaxing gas species [18]. Moreover, the large prong spacing of the custom QTF allowed an easy focalization of mid-IR laser beams between the prongs without hitting them. This is helpful considering that the fundamental ν_3 vibration band of CH₄ molecule with the strongest absorption coefficient is located at ~ 3.3 μm and can be targeted by interband cascade lasers (ICLs).

In practical applications related with CH₄ detection, such as LFG monitoring or atmospheric CH₄ measurement near a landfill, the presence of water vapor is unavoidable. The H₂O molecules act as V-T relaxation process promoter for CH₄, hence, to provide reliable CH₄ detection data, an accurate measurement of H₂O concentration is also required, even if implementing low frequency QTFs. The introduction of an additional sensing system for accurate H₂O measurement can limit the capability of in-situ CH₄ measurements for QEPAS-based sensor, as the sensor system becomes more complex and bulkier [23]. This issue can be addressed by exploiting the capability of the QTFs to simultaneously operate at different vibrational modes. Indeed, the reduction in the 1st overtone resonance frequency down to 18 kHz achieved with custom QTFs opens the way to the implementation of the overtone flexural mode for QEPAS operation [24]. The overtone vibration mode can be combined with the fundamental vibration mode to realize simultaneous dual-gas QEPAS detection via using the frequency division multiplexing (FDM) technique. Thereby, the additional detection channel could be devoted to monitoring the H₂O vapor concentration and this information can be used to normalize the CH₄ slow-relaxing QEPAS signal amplitude.

In this paper, we reported on the realization of a CH₄ QEPAS sensor based on the simultaneous fundamental and 1st overtone in-plane flexural mode excitation of a custom QTF. The first overtone vibration mode was exploited to detect the CH₄ molecule, while H₂O vapor was

monitored using the fundamental vibration mode. By simultaneously measuring both CH₄ and H₂O concentration levels, the H₂O influence on the V-T relaxation of CH₄ molecule can be compensated. The performances of the developed CH₄ / H₂O sensor system with V-T relaxation self-calibration was investigated and optimized. Finally, an atmospheric CH₄ measurement near a landfill was implemented to verify the robustness and reliability of the sensor.

2. Theoretical background

2.1. Theory of QTF flexural vibration modes

It has been confirmed theoretically and experimentally that a QTF can be modeled as a series resistance-inductor-capacitor circuit based on the RLC Butterworth-Van Dyke model. The model uses an electrical analogy of a mechanical damped oscillator, in which R represents the acoustic losses in the material (intrinsic losses) and its environment (extrinsic losses), L and $1/C$ represent the mass and the stiffness of the cantilever [18,19,25]. For the fundamental flexural mode, the prong can be analyzed as a single point-mass system and the point-mass is located at the prong tip, while for the first overtone flexural mode, the prong can be considered as a system of two-coupled point-mass sub-systems. The point-masses are located at the different antinodes [24]. The QTF should be excited at the antinode positions in order to obtain the largest QEPAS signal [26]. When a QTF operates at a combined vibration mode, it can be modeled as two electric equivalents RLC circuit connected in parallel, as shown in Fig. 1(a).

In a QTF, the two prongs are connected through a U-shape base. Differently from a standard cantilever, the center of mass of the QTF remains static when the prongs are vibrating in the in-plane flexural modes [27]. The prong length L is considerably larger than the prong width W and the thickness T . The prong cross-sectional area A along with the prong length L and the elastic modulus E are constants. The QTF prongs can be assumed to behave as two uncorrelated cantilevers [18]. According to the Euler-Bernoulli approximation, a QTF vibrating in its in-plane flexural modes can be described by the fourth-order differential equation [28]:

$$E \cdot I \cdot \frac{\partial^4 y(x, t)}{\partial x^4} + \rho \cdot A \cdot \frac{\partial^4 y(x, t)}{\partial t^4} = 0 \quad (1)$$

where ρ is the density of the quartz, t is the time, x is the direction identified by the prong at its rest position and y is the direction orthogonal to x in the QTF plane, as shown in Fig. 1(b). The resonance frequency f_n can be obtained solving Eq. (1) by imposing boundary conditions at the supports of the cantilever prong:

$$f_n = \frac{\pi \cdot T}{8 \sqrt{12} L^2} \cdot \sqrt{\frac{E}{\rho}} \cdot n^2 \quad (2)$$

where $n = 1.194$ and $n = 2.988$ for the fundamental flexural mode and the first overtone flexural mode, respectively. Using Eq. (2), a fundamental mode frequency of $f_0 = 2913$ Hz and a 1st overtone mode of $f_1 = 18,245$ Hz were calculated. The parameter values used for the calculations are shown in Fig. 1(c).

2.2. Self-calibration principle of the CH₄ V-T relaxation

There are four normal modes of vibration for a CH₄ molecule: two symmetric vibrations ν_1 (stretching) and ν_4 (bending), and two asymmetric vibrations ν_2 (bending) and ν_3 (stretching). In the present work, the asymmetric stretching vibration ν_3 CH₄ band was selected and the related absorption line is located at 3038.5 cm^{-1} . To target this line, a distributed feedback (DFB) interband cascade laser (ICL) emitting at ~ 3.3 μm was implemented as the excitation light source. Though no H₂O absorption lines falls in the ICL tuning range, the presence of water vapor in the gas sample affects the CH₄ QEPAS signal amplitude, since

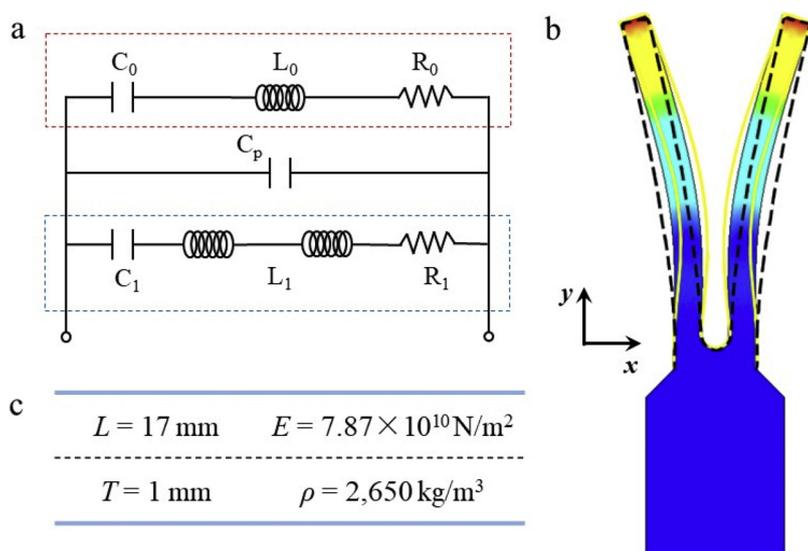


Fig. 1. (a) Electrical model of a custom QTF operating simultaneously at the fundamental (area inside the red dotted rectangle) and 1st overtone in-plane vibrational modes (area inside the blue dotted rectangle). C_p is the parallel stray capacitance of the RLC components. (b) Schematic of the deformation (not in scale) of the QTF prongs in the combined vibration at the fundamental and overtone vibration modes. The black imaginary line and the gold line in Fig. 1(b) represent the QTF prong deformation when the QTF is vibrating in the fundamental and first overtone flexural modes, respectively. (c) Dimensions and parameters of the custom QTF. L : QTF prong length, T : thickness of the prong, E : elastic modulus of the quartz, ρ : the density of the quartz. A color scale was used ranging from blue to red, representing the deformation degree of the QTF prongs.

it modifies the energy relaxation rates of the CH₄ molecules. Indeed, water vapor has a high density of vibrational levels, which creates multiple options for absorbed energy transfer in collisions with CH₄ molecules and a ladder for subsequent efficient multistep relaxation. Thereby, water molecules enhance the CH₄ photoacoustic signal since they act as promoters of the energy relaxation via collision/de-excitation process with CH₄ molecules.

When wet N₂ is used as the carrier gas, the V-T relaxation process of CH₄ can be analyzed using a simple model in which only a one-stage collision between molecules is considered [22]. In this model, the obtained CH₄ 2f QEPAS signal amplitude $S(P_H)$ can be determined from Eq. (3):

$$S(P_H) = S_1 + S_2 = S_1 \left[1 + \left(\frac{S_\infty}{S_0} - 1 \right) / \sqrt{1 + \frac{(2\pi \cdot f \cdot \tau_0^H \cdot P_0)^2}{P_H^2}} \right] \quad (3)$$

where S_0 and S_∞ are the CH₄ signals obtained with dry N₂ and saturated water pressure, respectively. S_1 is the CH₄ signal generated by CH₄ / N₂ collisions, which is independent of the H₂O concentration, while S_2 represents the contribution to the CH₄ signal due to CH₄ / H₂O collisions depending on the H₂O partial pressure P_H . The CH₄ / CH₄ collisions can be considered neglectable due to the low CH₄ concentration (a few hundred ppm). $\tau_0^H \cdot P_0$ is a constant which describes the V-T relaxation rate due to CH₄ / H₂O collisions. In case of the QEPAS technique, the modulation frequency f is usually $> 10^4$ Hz.

Eq. (3) can be expressed as a linear equation when the H₂O partial pressure P_H is low:

$$S(P_H) \approx S_1 + \left(\frac{S_\infty}{S_0} - 1 \right) \cdot \frac{S_1}{2\pi \cdot f \cdot \tau_0^H \cdot P_0} \cdot P_H \quad (4)$$

The slope k of $S(P_H)$ is:

$$k = \left(\frac{S_\infty}{S_0} - 1 \right) \cdot \frac{S_1}{2\pi \cdot f \cdot \tau_0^H \cdot P_0} \quad (5)$$

After we obtain the value of the $\tau_0^H \cdot P_0$ via the measured slope k , S_1 can be expressed as a simple function of $S(P_H)$ and P_H . Once the values of the $S(P_H)$ and P_H are simultaneously measured via the QTF fundamental and first overtone detection channels, the CH₄ V-T relaxation influence from the H₂O can be calibrated and the real CH₄ concentration can be retrieved.

3. Description of sensor system

A schematic of the QEPAS sensor for CH₄ detection with V-T relaxation self-calibration is depicted in Fig. 2. A custom made QTF with a

17 mm prong length was implemented as the photoacoustic transducer. In a first step, a complete QTF response profile was measured to retrieve the resonance frequency of the custom QTF. A sine wave excitation signal was applied to one of the two QTF electrodes and the piezoelectric signals produced by the excited vibration were detected from the other QTF electrode when the frequency of the exciting signal was scanned. The peak of the QTF frequency response profile corresponds to the resonance frequency. The obtained experimental results were $f_0 = 2868$ Hz and $f_1 = 17,741$ Hz, in good agreement with the expected values. The slight discrepancies between the experimental and theoretical QTF resonance frequencies are due to: (i) damping of the gas, (ii) variation of the cantilever density caused by the electrode gold layers, (iii) dependence of the quartz elasticity modulus on the crystallographic axes orientation, (iv) deviations between the modelled and the real QTF geometry. Previous experiments show that the largest QEPAS signal was obtained when the excitation beam was positioned at 2.0 mm below the QTF opening for fundamental flexural vibration, while the excitation beam should be located at 9.5 mm below the QTF opening to ensure the most efficient prongs excitation when operating at the first overtone flexural frequency [24]. The large separation (7.5 mm) between the positions of the antinodes providing the maximum vibration amplitudes for the fundamental and the first overtone mode, allows the parallel placement of two laser beams that can excite selectively the vibrational modes and act as two independent detection channels, thereby realizing a simultaneous dual-gas detection.

The first overtone detection channel possesses a higher sensitivity than the fundamental detection channel due to the QTF design, and hence the first overtone detection channel was used to detect the trace CH₄. A single-tube acoustic micro-resonator (AmR) with 0.62 mm inner diameter, 14.5 mm length and two 90 μm slits in the middle of the tube was positioned between the two prongs of the QTF to enhance the first overtone QEPAS signal [29]. No AmR was equipped for the fundamental vibration mode as the 3 kHz fundamental resonance frequency requires a > 100 mm AmR length [20], which is not feasible when using for optical alignment. The QTF and AmR were enclosed inside a gas enclosure with two CaF₂ windows (not shown in Fig. 2), which constitutes an acoustic detection module (ADM).

A commercial gas dilution system (Enviroics, series 4000) was used and placed upstream to generate a CH₄ / H₂O / N₂ gas mixture at fixed concentrations. A valve was used to set the gas flow rate at 100 sccm. A mass flow meter (Alicat Scientific, Inc. Model M-2SLPM-D/5 M) and a valve were placed upstream, while a pressure controller (MKS Instruments Inc. Model 649B13TS1M22 M) and a vacuum pump (KNF Technology Co., Ltd, N816.3KT.18) were placed downstream to

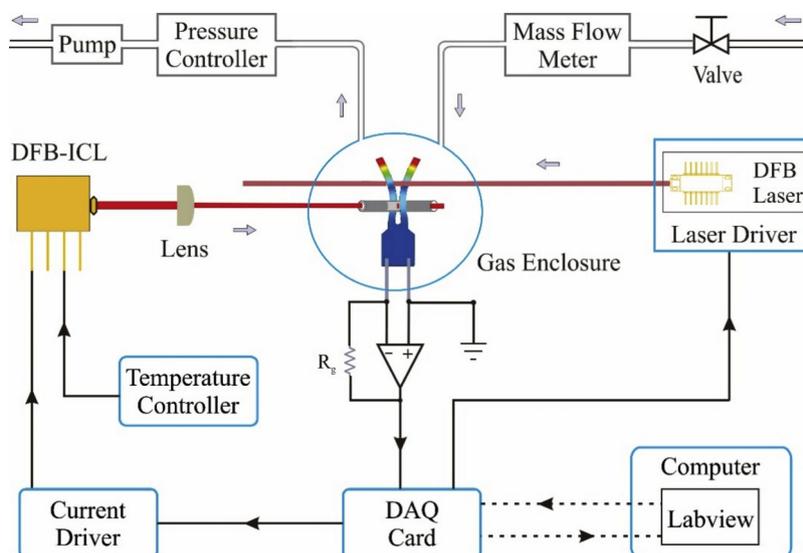


Fig. 2. Schematic of the CH₄ QEPAS sensor with V-T relaxation self-calibration. R_g: the feedback resistor of a custom made transimpedance amplifier, DAQ card: data acquisition card.

monitor and control the pressure inside the sensor system.

A Nanoplus continuous wave DFB-ICL was used as the excitation source for the CH₄ detection. The laser can be operated in the temperature range of 10–25 °C with a temperature coefficient of $-0.306 \text{ cm}^{-1}/^{\circ}\text{C}$ and in the current range of 25–55 mA with a current coefficient of $-0.095 \text{ cm}^{-1}/\text{mA}$. A CaF₂ lens with a focal length of 7.5 cm was used to focus the ICL beam into the ADM. A custom low noise current driver and a temperature controller (Thorlabs, Inc. Model TED200C) were equipped to drive the DFB-ICL. A near-infrared DFB laser (FITELE FRL15DCWD-A82), driven via an integrated driver board, was implemented for H₂O detection. The driver board set the wavenumber of the DFB laser at 7306.75 cm^{-1} by controlling its temperature and current. To increase the sensitivity of the sensor, the 2f-WMS technique was used. A ramp signal and a sine wave signal with the frequency of $f_1/2$ were sent to the custom current driver for CH₄ detection, while another ramp signal and a sine wave signal with the frequency of $f_0/2$ were sent to the driver board for H₂O detection. All of the signals mentioned above were generated by a Labview controlled DAQ card (National Instrument, USB-6361). The signal output from the QTF was connected to a custom transimpedance amplifier with a feedback resistor of $R_g = 10 \text{ M}\Omega$ and directed to the DAQ card. Two LabVIEW-based lock-in amplifiers (LIA#1 and LIA#2) were employed to demodulate the QEPAS signal at the frequency of f_1 and f_0 for CH₄ and H₂O detection, respectively. The detection bandwidth of the two LIAs was set at 0.833 Hz.

4. Optimization of the sensor performance

4.1. Gas absorption characteristics at 3291 nm and 1368 nm

The presence of H₂O not only affects the CH₄ QEPAS signal amplitude via acting as a promoter of V-T relaxation process, but also can interfere with the CH₄ spectrum profile if the selected target line is close to a H₂O absorption line with a similar line strength [30,31]. A CH₄ absorption line at 3038.5 cm^{-1} with a line intensity of $8.85 \times 10^{-20} \text{ cm mol}^{-1}$ was selected as the target line based on the high-resolution transmission (HITRAN) 2012 molecular spectroscopic database [31]. The absorption intensities of the H₂O lines nearby the CH₄ target line are eight orders of magnitude smaller than that of the CH₄. In a landfill, the CH₄ concentration level is usually $> 1.8 \text{ ppm}$. Taiyuan area where the sensor will be deployed in has a dry climate, resulting in the water vapor usually in the range of 10^3 ppm to 10^4 ppm .

Hence, the interferences of H₂O absorption on the CH₄ QEPAS spectra profile can be negligible for the landfill measurement in Taiyuan area. The H₂O absorption line located at 7306.75 cm^{-1} with an intensity of $1.8 \times 10^{-20} \text{ cm mol}^{-1}$ was selected as the H₂O target line [31]. The CH₄ lines nearby 7306.75 cm^{-1} are three orders of magnitude smaller than the target H₂O line. As a result, no influence of the CH₄ on the H₂O detection has to be considered. In order to reach the target wavelength, the temperature of the DFB-ICL was set to 10 °C with an output power of 5.2 mW, while the temperature of near-infrared DFB laser was set to 16.4 °C with an output power of 11.3 mW.

4.2. Independence between the two different vibration modes

An experiment to check the independence between the fundamental and first overtone flexural vibration modes was carried out using a certified mixture of 500 ppm CH₄ in nitrogen (N₂) with 1.6% H₂O as the target gas. The target gas flowed through the gas enclosure with a pressure of 200 Torr fixed by the pressure controller. To generate a specified H₂O mixing ratio, a certified mixture of 500 ppm CH₄ in N₂ was divided into two gas lines and directed to the gas dilution system to control the flow rate of the two gas lines, respectively. One gas line was humidified by the humidifier (Perm Select, PDMSXA-2500) and then mixed with another line at a selected flow rate ratio. The wavelengths of the DFB-ICL and near-infrared DFB laser were scanned in a period of 40 s and 120 s, which results in a scan rate of $0.023 \text{ cm}^{-1}/\text{s}$ and $0.0067 \text{ cm}^{-1}/\text{s}$, respectively. The CH₄ QEPAS spectrum (purple line) measured from the first overtone channel and the H₂O QEPAS spectrum (blue line) measured from the fundamental channel were detected simultaneously and shown in Fig. 3(a) and (b), respectively. As shown in Fig. 3(a), the ADM with the single-tube AmR (purple line) provided a maximum signal amplitude of 18.3 mV, which is 45 times higher than that measured at the same condition but using the bare custom QTF (black line).

To verify the absence of any cross-talking between the two vibrational modes operation, in Fig. 3(a) are compared with the two CH₄ QEPAS spectra measured using the first overtone detection channel when the QTF operated only at the overtone flexural mode (red circle symbols) and when both the fundamental and first overtone mode were simultaneously excited (purple line). The two CH₄ spectra overlap, confirming that the QTF fundamental and first overtone flexural modes did not interfere with each other, allowing simultaneous dual-gas detection.

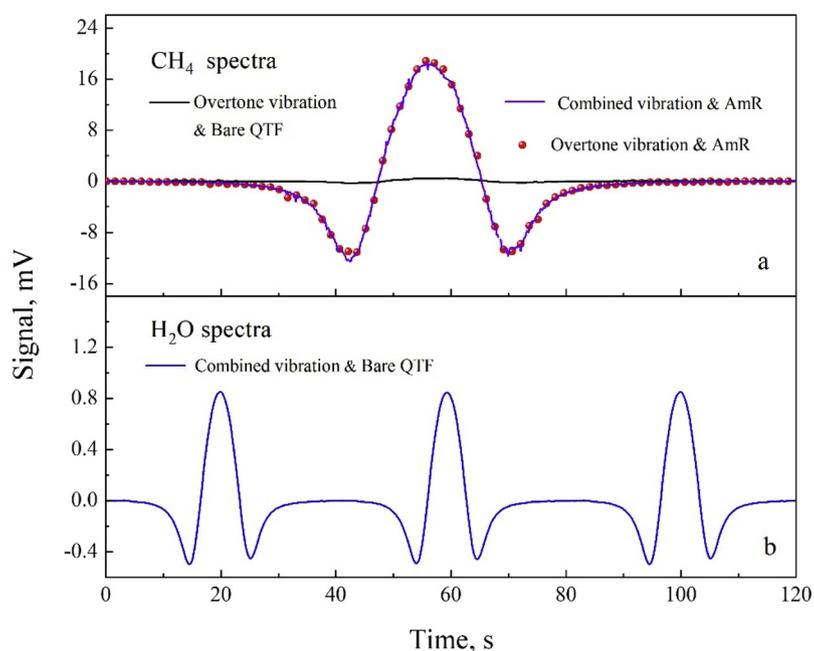


Fig. 3. (a) QEPAS spectra of 500 ppm CH₄ in nitrogen (N₂) with 1.6% H₂O detected with the QTF plus single tube micro-resonator using only the 1st overtone detection channel (red dots) or when operating with both the fundamental and 1st overtone modes (violet curves). The black curve is the QEPAS spectrum acquired with the bare QTF using only the 1st overtone detection channel. (b) 1.6% H₂O spectra measured using the fundamental detection channel with the QTF operating also with the 1st overtone vibrational excitation. All QEPAS spectra were measured at a gas pressure of 200 Torr.

4.3. Optimization of wavelength modulation depth and gas pressure

The $2f$ QEPAS signal amplitude is dependent on the wavelength modulation depth A and the gas pressure P . Thus, the optimal A and P values must be found in order to obtain the highest QEPAS signal. A sample gas of 500 ppm CH₄ in N₂ with 1.6% H₂O was used to retrieve the optimal A and P . The data obtained from LIA#1 is shown in Fig. 4(a), corresponding to the CH₄ detection channel using the first

overtone flexural mode. Fig. 4(b) shows the data measured from LIA#2, which is the H₂O detection channel using the fundamental flexural mode. According to the experimental results, the highest value of the CH₄ QEPAS signals was recorded at $P = 200$ Torr, $A = 4$ mA, while the peak value of the H₂O QEPAS signals was achieved at $P = 200$ Torr, $A = 8$ mA. Hence, a pressure of 200 Torr with a 4 mA and 8 mA current modulation depths for DFB-ICL and near-infrared DFB laser were selected for the dual gas QEPAS sensor operation.

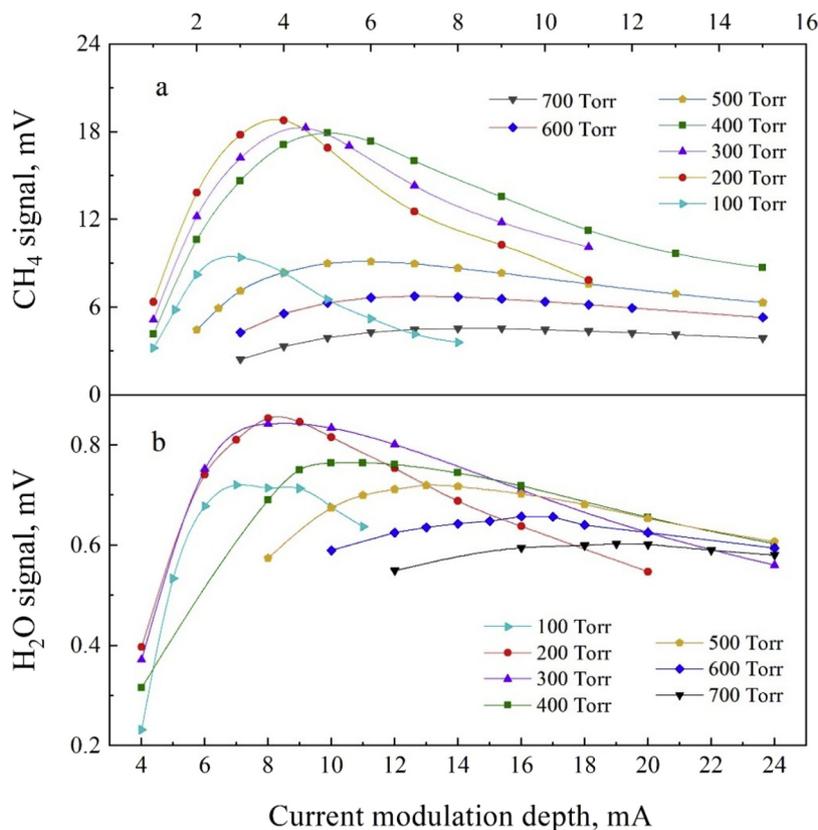


Fig. 4. $2f$ QEPAS peak signal of H₂O (a) and CH₄ (b) QEPAS spectra measured at different gas pressures and laser current modulation depths. All measurements were performed using a 500 ppm CH₄ mixture in N₂ and 1.6% H₂O.

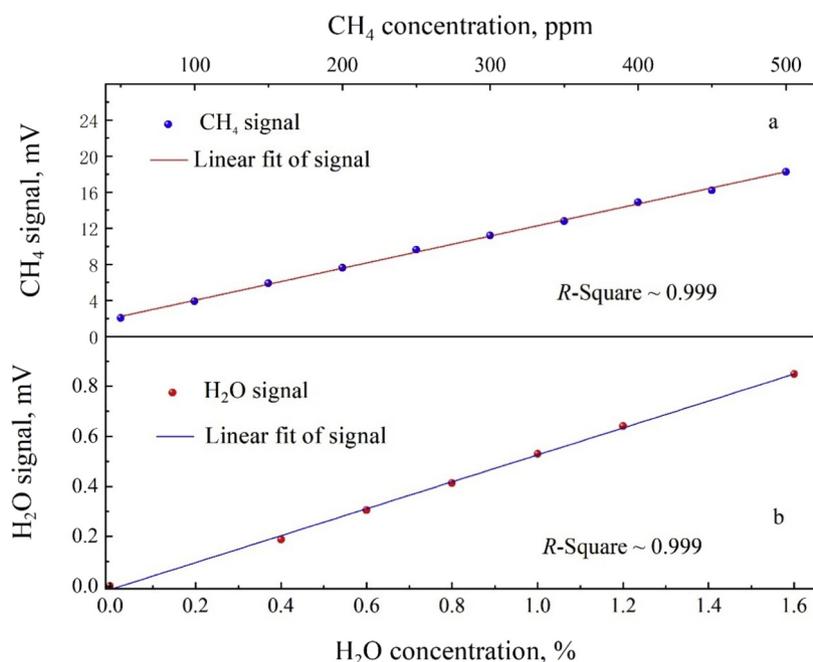


Fig. 5. The CH₄ and H₂O QEPAS signals obtained from the 1st overtone and the fundamental detection channels of the custom QTF, respectively, when the QTF is operating simultaneously in both modes.

5. Assessment of the sensor performance

The response of the first overtone detection channel for various CH₄ concentrations with a fixed H₂O concentration at 1.6% is illustrated in Fig. 5(a). The CH₄ concentration was varied from 50 ppm to 500 ppm. The results were linearly fitted and the calculated R^2 value is 0.999 which confirms the linear response of the overtone detection channel with respect to the CH₄ concentration. A similar experiment was carried out to confirm the linearity to H₂O concentration of the fundamental detection channel. The response of the fundamental detection channel for various H₂O concentrations in a 500 ppm CH₄:N₂ mixtures is illustrated in Fig. 5(b). The R^2 value of 0.999 confirms the linearity of the fundamental channel.

- As stated in Section 2, water vapor in the CH₄ / H₂O / N₂ gas sample mixture acts as a promoter of the CH₄ V-T relaxation. This is confirmed by the experimental results shown in Fig. 6, where the LD#1

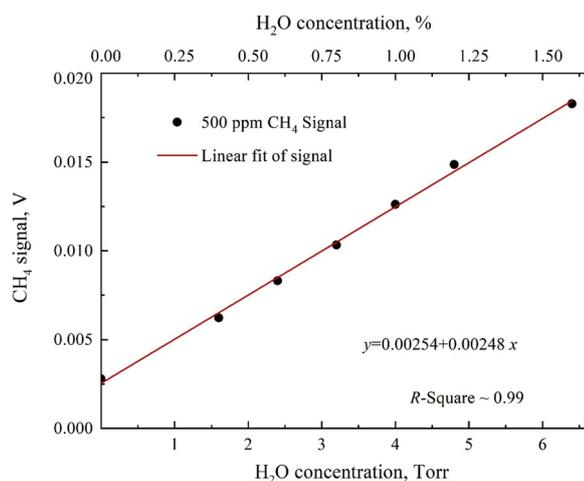


Fig. 6. CH₄ QEPAS peak signal of a 500 ppm CH₄ / N₂ mixture as a function of H₂O concentration. The H₂O concentration was varied from 0 to 1.6%, corresponding to variation of partial pressure P_H from 0 to 6.4 Torr.

wavelength was tuned to the center of the CH₄ absorption line and the overtone channel QEPAS signal amplitude measured for 500 ppm CH₄ concentration (black lines) is plotted as a function of water concentration in the mixtures, varying from 0% to 1.6%, corresponding to H₂O partial pressure P_H increasing from 0 to 6.4 Torr. The blue lines correspond to the correlated H₂O 2f QEPAS signal amplitude, measured using the QTF fundamental channel. According to Eqs. (4) and (5), the CH₄ QEPAS signal $S(P_H)$ can be linearly fitted as a function of P_H . The slope k was obtained to be 0.00248 from the fitting. Hence, S_1 can be expressed as follow:

$$S_1 = \frac{S(P_H)}{1 + 0.9934 \cdot P_H} \quad (6)$$

To evaluate the self-calibration performance of the QEPAS sensor for CH₄ detection, a certified mixture of 500 ppm CH₄ in N₂ and water vapor were introduced into the sensor system. The H₂O concentration is varied in steps. The CH₄ QEPAS signal $S(P_H)$ (blue lines) and H₂O QEPAS signal P_H (black lines) were recorded as a function of time, as shown in Fig. 7(a). The calculated S_1 values (red line) are also depicted in Fig. 7(a). The stability of the S_1 value confirms the capability of the realized QEPAS sensor to normalize the influence of the H₂O molecules on the CH₄ V-T relaxation.

Furthermore, the QEPAS sensor shows very good performance in term of optical noise. Indeed, as shown in Fig. 7(b) and (c), the noise levels measured from the fundamental and the first overtone detection channels are 1.72 μ V and 1.9 μ V, respectively, very similar to the estimated theoretical thermal noise of 1.6 μ V. Based on the reported data, the minimum detection limits (1σ) at 1 s integration time and corresponding NNEA coefficients achieved are 50 ppb and $2.9 \times 10^{-9} \text{ cm}^{-1} \text{ W/Hz}^{1/2}$ for CH₄, and 32 ppm and $6.3 \times 10^{-7} \text{ cm}^{-1} \text{ W/Hz}^{1/2}$ for H₂O, respectively. The minimum detection limit of CH₄ was obtained based on the signal-to-noise ratio. For a real sample with a ppb-level CH₄ concentration and a percentage-level H₂O concentration, an interference from the neighboring H₂O lines should be considered.

An Allan-Werle deviation analysis for the fundamental and first overtone detection channels was performed in pure N₂ to evaluate the long-term stability of the self-calibration QEPAS sensor. The results are shown in Fig. 8. The Allan-Werle deviation plots follows a $1/\sqrt{t}$

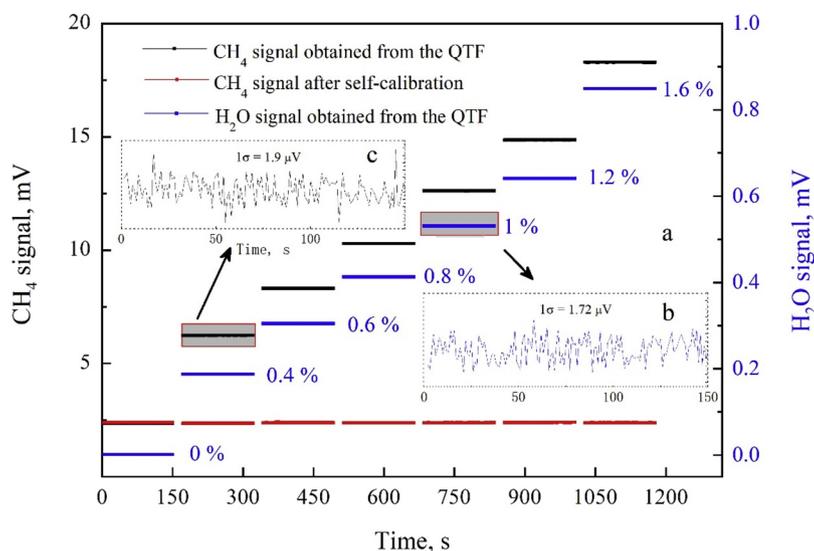


Fig. 7. (a) CH₄ QEPAS peak signal (blue lines) recorded as a function of time with the H₂O concentration varying in steps. H₂O QEPAS peak signal (black lines) recorded as a function of time with the H₂O concentration varying in steps. The red lines show the calculated S_1 values according to Eq. (6). (b) and (c) Enlarged views of the H₂O and CH₄ QEPAS signals used for the noise level analysis of the fundamental and first overtone detection channels, respectively.

dependence for all time sequences, which indicates that the white Johnson noise of the QTF remains the dominant source for both detection channels and the sensor allows data averaging without a base line or sensitivity drift up to a 200 s time scale [32].

6. Atmospheric CH₄ measurement near the Hou Village landfill

Hou Village Landfill (HVL), the largest sanitary landfill in Shanxi province, is located in the northeast of Taiyuan city with a service life of 17 year. More than ten million tons of MSW have accumulated in HVL since 2008, which means about $4 \times 10^8 \text{ Nm}^3$ LFG is generated per year. Although vertical and horizontal gas wells are operated, the CH₄ emitted to the atmosphere with the LFG cannot be ignored. To monitor the CH₄ levels in the atmosphere near the landfill, continuous CH₄ field measurements were carried out near the HVL on October 11, 2018. The QEPAS based CH₄ sensor with V-T relaxation self-calibration was mounted in a car and power was supplied by the car battery with the

help of an AC inverter (Wagan Tech, 9622). The demodulation of the CH₄ QEPAS signal and H₂O QEPAS signal, the data acquisition of the $2f$ signal amplitude via a Levenberg-Marquardt nonlinear least-squares fit procedure, as well as the calibration of the CH₄ V-T relaxation were carried out using a dedicated LabVIEW-based program. The data updating rate of the program was set to 10 s. These measurements were performed for 3 h, from 10:30 am to 13:30 pm, as shown in Fig. 9.

The average atmospheric CH₄ concentration measured near the HVL resulted in ~ 2.9 ppm, 50% more than the mean value in atmosphere (1.8 ppm). The observed three CH₄ plumes with peak values of ~ 4.1 ppm, 4.3 ppm and 5.9 ppm were generated by the wind blowing from the direction of the LFG collection system. The periodic sharp peaks, with ~ 45 min interval time, were generated by a MSW truck passing near the CH₄ sensor. During all the measurements the H₂O concentration remains below 1.6%

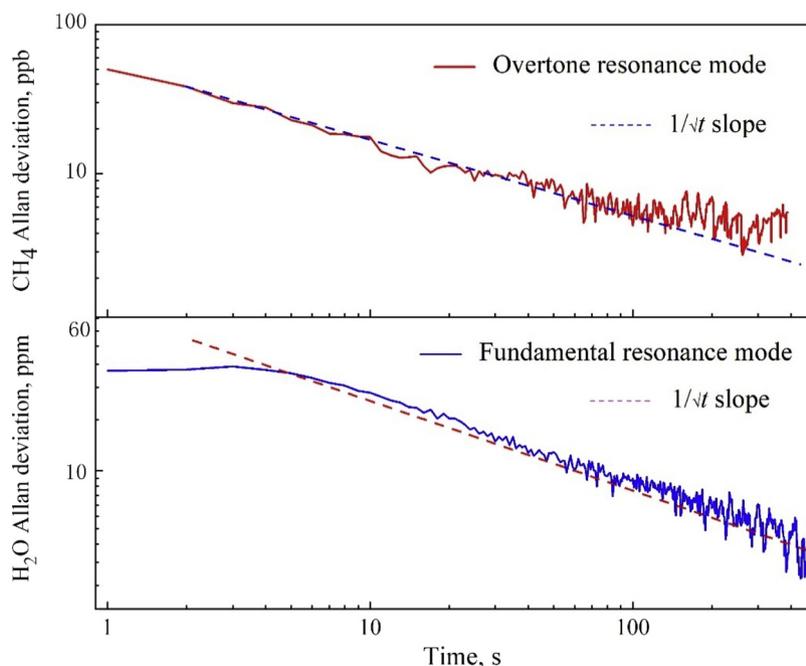


Fig. 8. Allan-Werle deviations as a function of the data averaging period measured for pure N₂ gas samples. Red solid line: DFB-ICL wavelength was locked to the CH₄ absorption line at 3038.5 cm^{-1} . Blue solid line: near-infrared laser wavelength was locked to the H₂O absorption line at 7306.75 cm^{-1} . Dashed lines: $1/\sqrt{t}$ slope.

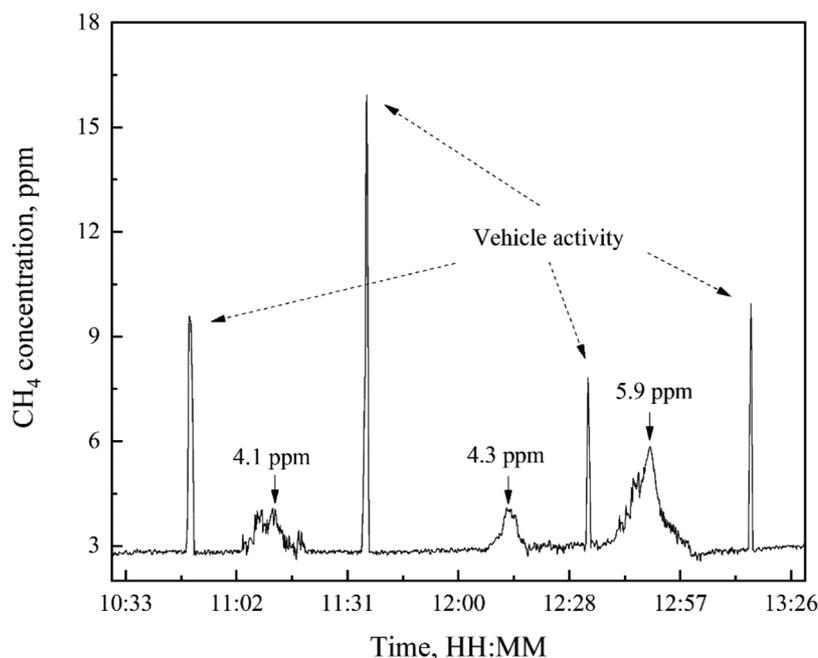


Fig. 9. Continuous atmospheric CH₄ measurement near the Hou Village Landfill, Taiyuan, China on Oct. 11, 2018.

7. Conclusions

In summary, a CH₄ QEPAS sensor with V-T relaxation self-calibration was developed based on the in-plane fundamental and 1st overtone vibration simultaneous operation of a custom QTF. The 7.5 mm separation between the positions of the two antinodes for two different vibration modes permits accommodating two laser beams to implement the FDM detection of the QTF signals, thus realizing dual-gas QEPAS sensor. The fundamental vibrational channel was used for H₂O detection, while the first overtone vibrational channel was employed to monitor CH₄. A theoretical model of V-T relaxation and self-calibration method were developed to normalize the influence of H₂O molecule on the CH₄ V-T energy relaxation rate. The measured value of the NNEA of $2.9 \times 10^{-9} \text{ cm}^{-1} \text{ W/Hz}^{1/2}$ for CH₄ detection is similar to previously reported results on QEPAS-based CH₄ detection systems but the influence of H₂O on the CH₄ V-T relaxation was removed. Continuous monitoring of atmospheric CH₄ near the largest waste landfill in Shanxi Province was performed to demonstrate the capability of the reported sensor system for in-situ measurements. Possible future applications for the developed dual gas sensing method are: non-invasive breath analysis diagnostics in which H₂O concentration of > 4% can be reached, measurement of isotopes abundance ratio (like ¹²CH₄/¹³CH₄ or ¹²CO₂/¹³CO₂) and chemical reaction control where the two-detection channel could be employed to monitor the composition ratio of two chemical reacting species.

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