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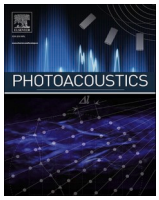

Ppb-level NH_3 photoacoustic sensor combining a hammer-shaped tuning fork and a 9.55 μm quantum cascade laser

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ABSTRACT

We present a quartz enhanced photoacoustic spectroscopy (QEPAS) gas sensor designed for precise monitoring of ammonia (NH_3) at ppb-level concentrations. The sensor is based on a novel custom quartz tuning fork (QTF) with a mid-infrared quantum cascade laser emitting at 9.55 μm. The custom QTF with a hammer-shaped prong geometry which is also modified by surface grooves is designed as the acoustic transducer, providing a low resonance frequency of 9.5 kHz and a high-quality factor of 10263 at atmospheric pressure. In addition, a temperature of 50 °C and a large gas flow rate of 260 standard cubic centimeters per minute (sccm) are applied to mitigate the adsorption and desorption effect arising from the polarized molecular of NH_3. With 80-mW optical power and 300-ms lock-in integration time, the detection limit is achieved to be 2.2 ppb which is the best value reported in the literature so far for NH_3 QEPAS sensors, corresponding to a normalized noise equivalent absorption coefficient of 1.4×10^{-8} W cm^{-1} Hz$^{-1/2}$. A five-day continuous monitoring for atmospheric NH_3 is performed, verifying the stability and robustness of the presented QEPAS-based NH_3 sensor.

1. Introduction

Ammonia (NH_3), a colorless, poisonous, alkaline gas with a strong pungent odor, constitutes the major component of total reactive nitrogen. The primary source of atmospheric NH_3 arises from agricultural emissions, which encompass animal husbandry and the application of NH_3-based fertilizers. Additionally, NH_3 emission originates from diverse sources such as industrial processes, vehicular emissions and volatilization from soils and oceans [1–4]. Currently, ammonia represents one of the significant contributors to atmospheric pollution. This is primarily attributed to the reaction of NH_3 reacts with acidic gases in the atmosphere, resulting in the formation of ammonium salts that contribute to the generation of particulate matter (PM2.5) in the atmosphere. Despite its involvement in photochemical smog, acid rain and aerosol deposition, NH_3 is not regulated under the National Ambient Air Quality Standards by the US Environmental Protection Agency (EPA), causing substantial difficulties and rigorous challenges to its emission reduction [5,6]. Therefore, sensitive and selective NH_3 detection has received considerable attention in the fields of environmental monitoring, chemical and pharmaceutical processing, and disease diagnosis.

To target these applications, various techniques have been developed and utilized for the detection of NH_3 concentration, including chemiluminescence, nanomaterials sensing and gas chromatography. However, these methods have limitations in selectivity and real-time monitoring, and easily introduce human errors which degrade the detection sensitivity and response time. Consequently, optical gas sensing techniques are being implemented frequently since the capabilities of fast response, high sensitivity and real-time monitoring [7–10]. For instance, tunable diode laser absorption spectrum (TDLAS), cavity ring down spectrum (CRDS), photo acoustic spectroscopy (PAS)

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and difference optical absorption spectrum (DOAS) are typical ammonia detection methods based on laser absorption spectroscopy technology. Among these methods, PAS stands out as an appealing spectroscopic technique benefited from its simplicity, ruggedness and zero-background nature [11–13]. The PAS technique detects the photoacoustic signal generated from the selective absorption of modulated excitation energy and a wide-band microphone is employed as detecting element to collect the sound wave. In PAS-based sensors, the detection sensitivity depends on the geometry of the gas cell and the performance of microphone. Consequently, environmental noise can be easily introduced into the sensing system due to the low resonant frequency characteristics of the acoustic cell. Quartz enhanced photoacoustic spectroscopy (QEPAS), an alternative approach to PAS, utilizes a spectrophone consisting of a quartz tuning fork (QTF) and a resonant acoustic micro resonator (AmR) tube as an acoustic transducer to detect the weak sound wave [14–20]. This technique inherits PAS's inherent advantages of excitation-wavelength independence and sensitivity proportional to optical power. Compared to conventional PAS, the QTFs offer higher resonant frequencies ranging from several to tens of kHz and quality factors of ~10^4. In most of the QEPAS-based sensors, standard commercial QTFs with an oscillation frequency of 32.7 kHz and a frequency response bandwidth of nearly 3 Hz are exploited, enabling immunity to 1/*f* ambient noise. Such characteristics make QEPAS one of the most attracted techniques for ambient NH_3 detection. A. Kosterev et al. developed the QEPAS-based NH_3 sensor utilizing a NIR laser source to detect NH_3 and obtained a minimum detection limit (MDL) of 650 ppbv (parts per billion by volume) [21]. In 2015 and 2017, Wu et al. and Ma et al. combined QEPAS technique with erbium-doped fiber amplifier (EDFA) to detect NH_3, and the detection sensitivity (1σ) of 1.6 ppmv and 481.4 ppbv, respectively, were achieved for an integration time of 1 sec [22,23]. However, the detection sensitivity is still insufficient to meet the requirements of atmospheric NH_3 monitoring, and the utilization of EDFA complicated the QEPAS system and limited the ability of field application. In addition, several advanced QEPAS technologies have been developed to improve the detection sensitivity. In 2022, W. Ren et al. and H. Zeng et al. reported ultrasensitive doubly resonant QEPAS sensor and dual-comb QEPAS, respectively [24,25]. In 2023, W. Ren et al. developed a mid-infrared cavity-enhanced QEPAS sensor which is based on the doubly resonant photoacoustic effect, demonstrating highly sensitive photoacoustic excitation and high-resolution molecular spectroscopy. These methods also result in large systems and complex operations [26]. One possible solution is to select a mid-infrared laser which covers the stronger gas absorption lines as the excitation source for photoacoustic signals. Nevertheless, the 300-μm prong spacing of this standard QTF can block a portion of laser beam. The laser light on the prongs leads to periodical heating of the QTF surface and result in a significant increase in background noise. This phenomenon is more pronounced for some excitation sources with degraded beam profile such as interband cascade laser (ICL), quantum cascade lasers (QCLs) and terahertz (THz) lasers, impeding the optical coupling between the QEPAS spectrophone and these advanced excitation source. Hence the design and investigation of QTFs' prong dimensions and geometry is requisite for the optimization of QEPAS-based sensing system.

In this work, we demonstrate a QEPAS-based gas sensor for ambient NH_3 detection, in which a novel custom QTF with resonance frequency of 9538 Hz and a quality factor of 10263 at atmospheric pressure in air is employed as acoustic transducer. The custom QTF is designed with hammer-shaped surface-grooved prong geometry and a large prong spacing of 800 μm, allowing the easier optical calibration operation compared with standard commercial QTF (300 μm). A QCL laser source emitting at 9.55 μm is exploited in the system without spatial or laser modal beam filters which provides a higher detection sensitivity and a simpler system structure. The assessment of the proposed QEPAS-based sensor performance is implemented by a continuous atmospheric NH_3 on-line monitoring, verifying the robustness and reliability of the sensor.

2. Sensor design and characterization

2.1. Selection of excitation wavelengths and optical sources

Since the fundamental vibrational of molecules is more than two orders stronger in the mid-infrared (MIR) spectral region than in the near infrared (NIR), a higher detection sensitivity can be obtained with a QEPAS sensor operated in MIR spectral region. According to the HITRAN database, four fundamental vibrational modes (ν_1, ν_2, ν_3, ν_4) of the NH_3 molecule are provided [27]. As demonstrated in Fig. 1, NH_3 molecule has the strong ν_2 band and other hot band ($2\nu_2$-ν_2) near 10 μm (1000 cm^{-1}) which is of great significance for trace NH_3 detection in the infrared absorption spectra region due to the excellent line strengths compared with the other absorption bands. Taking into account the line strength and the absence of interference from other gas absorption, a NH_3 absorption line located at 1046.4 cm^{-1}, with a line strength of 3.648 × 10^{-19} cm/mol, was selected as the target line. This absorption line belongs to the ν_2 fundamental band of NH_3 which is widely employed as a frequency standard for spectral calibration [28,29].

With the development of laser materials and the maturity of laser theory, the QCL laser has emerged as a highly versatile excitation source in the MIR spectral region for trace gas detection and environmental monitoring. In this study, a self-dependent compact QCL source (Healthyphoton, China, Model QC750-Touch™) with low current noise and temperature drift was selected for the sensing system. The QCL possess an integrated current and temperature control driver, and the temperature controller adopts non-PWM-type continuous current output control, greatly prolonging the service life of TEC devices. Additionally, a notable feature of the QCL is its maximum current soft clamping function, which prevents laser tube damage resulting from mishandling of high currents, ensuring the chip's safety to the utmost extent.

To target the NH_3 absorption line, the QCL was coupled to a FTIR spectrometer (Thermo Scientific Model Nicolet iS50) to characterize the laser emitting wavelengths as shown in Fig. 2. The output wavelength can be tuned from 1044.3 cm^{-1} to 1047.1 cm^{-1}, covering the targeted line at 1046.4 cm^{-1} with a QCL temperature and current of 25.5 °C and 608 mA which was also depicted as a dotted line. The wavelength tuning coefficients of the QCL was calculated as - 0.10496 cm^{-1}/°C and - 0.00892 cm^{-1}/mA by setting and changing the driving temperature and current, respectively.

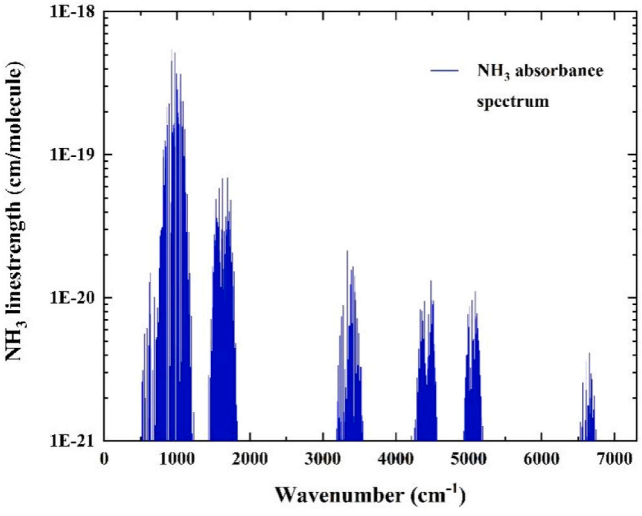

Fig. 1. NH_3 absorbance spectra in the infrared region from 800 to7000 cm^{-1} according to the HITRAN database.

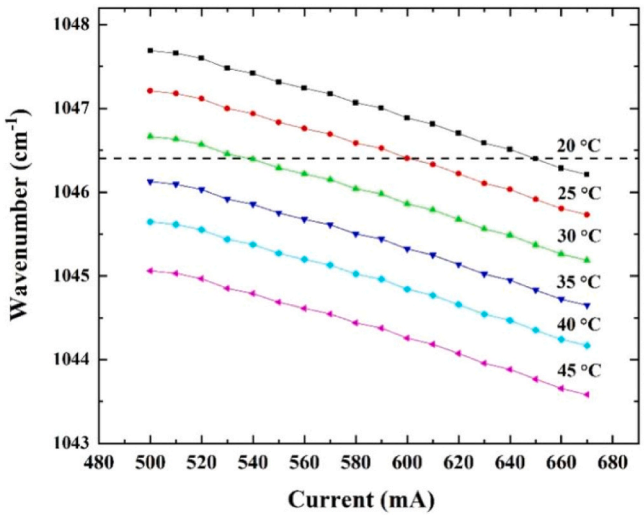

Fig. 2. The output wavelength of the QCL as a function of driving current from 500 mA to 670 mA at different temperature.

2.2. Design methodology of the hammer-shaped surface-grooved QTFs

For the photoacoustic detection of gases with adsorption characteristics, such as ammonia, mitigating the impact of gas adsorption on detection performance is crucial. One effective approach to achieve this is by minimizing the contact area of acoustoelectric transducers, such as QTF. Thus, it becomes essential to design the size and structure of the customized QTF carefully. The goal is to minimize its surface area while preserving its electrical parameters, including resonance frequency, quality factor, resistance value, and prong spacing, as well as charge collection efficiency. Consequently, the tuning fork can achieve optimal performance for ammonia detection. In this context, we present a novel tuning fork tailored specifically for atmospheric ammonia monitoring, meeting the aforementioned requirements. In principle, the QTF can be regarded as two vibratory prongs coupled with a supporting structure, and the prongs are joined at one base which are fixed to the supporting structure. When the laser beam is focused on the center of prongs to generate sound wave, the anti-symmetrical mode is dominant in the in-plane flexural vibration modes of QTF. To elastically describe the flexural mode vibration using a one-dimensional model, the free vibrating end of QTF prong can be specified by the following Euler-Bernoulli equation [30–32]:

$$EI\frac{\partial^4 y(x,t)}{\partial x^4}+\rho A\frac{\partial^4 y(x,t)}{\partial t^4}=0 \tag{1}$$

where $E=0.72\times10^{11}$ N/m^2 and $\rho=2650$ kg/m^3 are the elastic Young modulus and density of the quartz material, respectively. I and A represent the rotational inertia and the cross sectional area of the QTF prong, t is the time, x and y are the longitudinal and crossed directions relative to the prong. The fundamental resonance frequency can be solved and expressed by:

$$f=\frac{1.194^2\pi w}{8\sqrt{12}l^2}\sqrt{\frac{E}{\rho}}\propto\frac{w}{l^2} \tag{2}$$

where w, l are the prong width and length, respectively.

The ability of gas to efficiently relax the excess thermal energy dissipated through non-radiative relaxation process is dependent on the laser modulation frequency and the type of targeted gas. Hence it is crucial to ensure the condition $\tau << 1/f$ is satisfied, enabling efficient gas excess energy relaxation. Here, τ and $1/f$ denote the molecular relaxation time and the laser modulation period, respectively [33–35]. Since the laser modulation frequency must match the oscillation frequency f of the QTF in QEPAS sensor, the f of the custom QTF can be decreased with a reduced ratio of w and l to produce a maximum acoustic signal according to the Eq. (2) [36–38]. Additionally, the quality factor (Q-factor) related to the energy dissipation mechanisms of the QTF prong is also a major parameter for the sensor performance. Considering that the primary loss mechanism composed of surrounding fluid damping and support loss (which can be neglected in the fundamental mode) is strongly related to the geometric parameters of QTF prong, the Q-factor can be specified by [39–41]:

$$Q=\frac{Q_v}{1+Q_v bP^c}\propto\frac{wt}{l} \tag{3}$$

where Q_v is the Q-factor of QTF in vacuum, P is the gas pressure, b and c are the special parameters relevant to the QTF dimensions and surrounding fluid viscosity, respectively.

To propose a novel QTF for the application of NH_3 detection, two design requirements must be met: (1) reduce the resonance frequency f while maintaining a high Q-factor to guarantee the QEPAS response in NH_3 gas; (2) increase the prong spacing to facilitate the optical alignment and improve the signal-to-noise ratio (SNR). In view of the V-T relaxation time of NH_3 which is in the order of ~0.4 μs, the resonance frequency f of QTF is adopted as 9.5 kHz. Due to the sharp edge profiles of quartz crystal cannot be guaranteed with a chemical etching of $t >$ 0.1 mm, a thickness t is fixed at 0.25 mm. According to the equation (4) and (5), the ratio relationship between w and l needs to be considered and selected comprehensively to obtain a suitable f and Q-factor. To ensure the effective vibration of the QTF prongs, it is necessary to satisfy the condition $t/w > 0.1$. Therefore, a 2-mm width w and 9.4-mm prong length l was determined and used. An appropriate prong spacing is capable of providing excellent acousto-electric conversion efficiency, and reducing background noise when a MIR QCL is utilized. Hence a prong spacing of 800 μm is chosen to match the spot size of the MIR excitation source.

The resonance frequency of QTF is determined by the crystal material and the geometry shape. When the prong size of the QTF is determined, the sensing property of the QTF can be further improved through a modification of prong geometry [40–43]. In this work, a

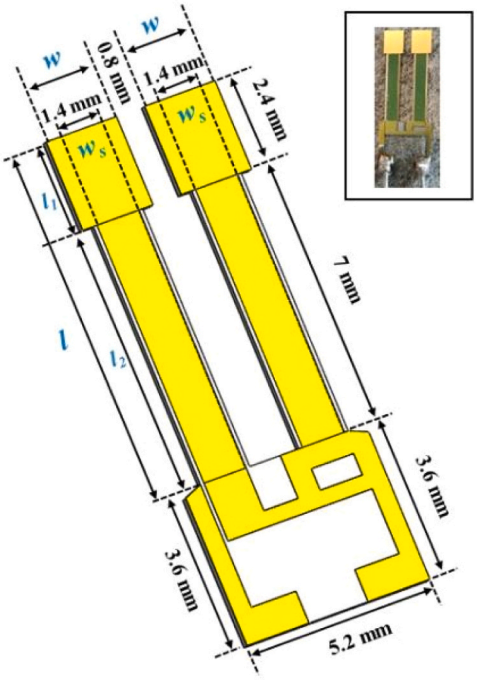

Fig. 3. Schematic of the geometrical dimensions of the hammer-shaped surface-grooved QTF. The inset shows the photograph of the novel QTF.

hammer-shaped QTF prong is designed and adopted, as shown in Fig. 3. This geometry provides an optimized stress field distribution, further enhancing the piezoelectric coupling efficiency. Moreover, based on the simulated result of COMSOL Multiphysics software in Ref 41, the intensity distribution of the stress filed along the QTF prong reaches the maximum when $w_s/w = 0.7$ mm. Although a lower frequency value can be achieved by reducing the ratio w_s/w, it may compromise the mechanical stability of the QTF due to the low moment of inertia [38]. Therefore, w_s is selected as 1.4 mm. Furthermore, a rectangular grooved modification with an area of 1.8 × 7 mm and a depth of 0.05 mm is applied to each surface of QTF prong to improve the piezoelectric current and enhance piezoelectric effect without obvious negative effects on the *Q*-factor.

2.3. Experiment setup of QEPAS sensor system

A QEPAS sensor system based on a hammer-shaped surface-grooved QTF and a CW MIR QCL is demonstrated for NH_3 detection. The experimental setup is schematically depicted in Fig. 4. The CW QCL (Healthyphoton, China, Model QC750-Touch™) emitting at 9.55 μm is chosen as the excitation source to generate the QEPAS signals. An on-screen laser driver integrated with a cooling unit, a TEC temperature controller and a low noise current driver was employed to control the temperature and current of the QCL. The laser beam was focused into a ~0.25 mm^2 circular spot at the focal point by means of a 50-mm focal length plano-convex ZnSe lens, and can be directed easily through the dual tube spectrophone. The acoustic detection module (ADM) consists of the spectrophone configuration and two 25.4-mm diameter ZnSe windows with 98 % transmissivity efficiency, and has an internal volume of 70 mm^3 capable of gas exchange. A power meter is placed behind the ADM to calibrate the beam and monitor the transmitted optical power.

In order to achieve sensitive NH_3 detection, the 2*f*-wavelength modulation spectroscopy (WMS) approach is employed. A dual-channel function generator is utilized to generate a *f*/2 sinusoidal modulation signal and a ramp scanning signal, which are combined to dither the QCL wavelength with an electrical adder. Then the piezoelectric signal from the custom QTF is amplified by a trans-impedance preamplifier and demodulated by a lock-in amplifier (Stanford Research Systems, Model SR830) in the 2 *f* mode. The LIA time constant and slope filter are set to 300 ms and 12 dB/octave, respectively, corresponding to a bandwidth of 0.833 Hz. A personal computer (PC) is used to collect and analyze the QEPAS data via a LabVIEW routine.

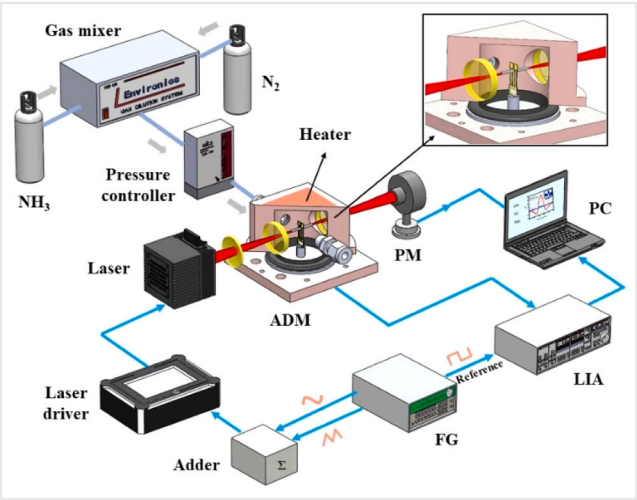

Fig. 4. Schematic of the developed QEPAS-based NH_3 trace gas sensing system. ADM: acoustic detection module; PM: power meter; FG: function generator; LIA: lock-in amplifier.

A commercially available gas dilution system (Environics Inc. Model EN4040) is utilized to generate a mixture of NH_3/N_2 gas at desired concentrations. To regulate the gas flow rate to the set point, a mass flow meter combined with a needle valve (Not shown in the figure) is placed downstream. The pressure inside the ADM is controlled and maintained at 700 torr via a pressure controller (MKS Instruments Inc. Model 649B13TS1M22 M) and a vacuum pump. A Nafion humidifier was inserted inline to keep the water concentration entering the QEPAS cell at 1.5 % to eliminate the influence of environmental water vapor changes on the experimental system. Nevertheless, the NH_3 molecule is readily adsorbed to surfaces resulted from its viscosity and interaction with the ADM surface, preventing the accurate determination of the NH_3 concentration in the QEPAS system. To mitigate this issue, a heater is tightly attached to the walls of the ADM. The purpose of the heater is to eliminate the adsorption and desorption effects arising from the polarized molecular of NH_3. This is due to the fact that a rise of temperature increases the thermal motion of NH_3 gas molecules, increasing the gas desorption rate and reducing the total adsorption of gas. Experimental results show that with the increase of temperature, the response time of the system will be significantly shortened. Compared to the room temperature, the operating temperature of 50 °C can reduce the response time by 65 %. Continuing to increase the temperature may further inhibit the adsorption of NH_3, but the high temperature puts forward new requirements for the heat resistance of the device and requires the addition of insulation devices. Hence, we finally set the operating temperature of the system at 50 °C. In addition, a large gas flow rate of 260 sccm is adopted to reduce the NH_3 molecular adsorbability and accelerate the gas exchange times.

3. Optimization and assessment of sensor performance

3.1. Parameter optimization

In order to improve the detection performance, it is necessary to optimize the parameters of the spectrophone configuration. Since the laser beam must be focused at the center of the prong spacing to vibrate the QTF prongs effectively, the focusing position of the laser beam has been investigated and determined as shown in Fig. 5(a). The QTF symmetry axis is vertically scanned by the laser beam from the top to bottom for acquiring the optimum focused spot position. The QEPAS signals are normalized to the maximum value and the optimum laser focus position is determined as 2 mm from the prong top which is depicted in Fig. 5(b). In this work, a 50-ppm NH_3:N_2 mixture was selected as target gas.

In most QEPAS-based trace gas sensors, an on-beam spectrophone configuration is commonly employed to achieve a higher signal-noise-rate (SNR) gain [44–46]. In this configuration, the AmR consists of two identical metallic tubes positioned symmetrically and aligned perpendicular to the QTF plane, with the QTF inserted at the center. To enhance the acoustic coupling efficiency, the dimension parameters

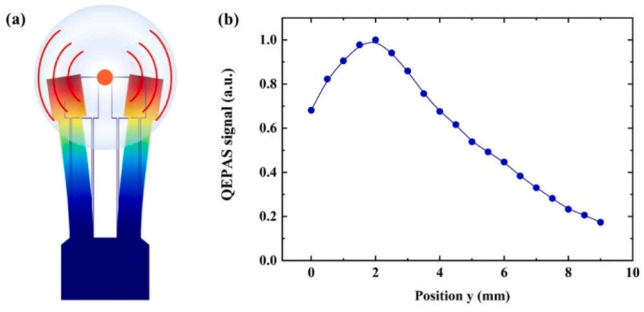

Fig. 5. (a) Diagram of the QTF prongs deformation vibrating in the fundamental flexural mode via COMSOL MultiPhysics. The spot position represents the starting point of scanning. (b) Normalized QEPAS signals as a function of the position along the vertical symmetry axis of the QTF.

(inner diameter and tube length) are tested and optimized at atmospheric pressure. Since the inner diameter (ID) d is related with the prong spacing, eight different AmRs with $d = 1$ mm, 1.25 mm, 1.35 mm, 1.5 mm, 1.65 mm, 1.75 mm, 1.85 mm and 2.05 mm but with the same length $l = 12$ mm have been tested. According to the related theoretical and experimental investigation, the length of each tube l is associated with the acoustic wavelength λ at the resonance frequency f of the QTF under the assumption that the QTF-tube distance is zero. However, with the insertion of QTF distorting the acoustic resonance in the AmR, the optimum AMR length (2 l) is $\lambda/2 < 2\,l < \lambda$, resulting in the optimal l of each tube between $\lambda/4$ and $\lambda/2$. In this work, the acoustic wavelength λ for the custom 9.5-kHz QTF is 35.6 mm, hence a series of tubes with different lengths (8.9 mm $< l <$ 17.8 mm) were measured. Fig. 6 demonstrates the optimum geometric parameters of the AmRs is $d = 1.75$ mm and $l = 13$ mm with a QTF-tube distance of 200 μm, which provides a SNR gain factor of 37.

Generally, the photoacoustic signal in QEPAS-based sensors can be described by: $S{=}CP_0\alpha(p)\varepsilon(p)Q(p)$, where C is the system constant, P_0 is the optical power, p is the gas pressure, α, ε, Q, is the peak intensity of the 2 f absorption spectrum, optoacoustic transduction efficiency and QTF Q-factor, respectively. Since the α depends on the modulation depth of the laser current, the laser modulation depth must match the p-dependent absorption linewidth. As depicted in Fig. 7, the modulation voltages in the ADM are measured and optimized under different gas pressures to achieve the maximum QEPAS signal using a 1-ppm NH_3/N_2 calibration gas. The highest 2 f signal is observed at 300 torr with a modulation voltage of 180 mV, which is 40 % higher than the QEPAS signal obtained at 700-torr with a 300-mV voltage modulation depth.

For the NH_3 detection sensing system, a large gas flow rate can retard the adsorption-desorption effect and reduce the gas exchange time in the ADM, but may cause an increase in the noise level [47]. Therefore, the dependence of the 1σ noise level on different gas flow rate from 20 sccm to 400 sccm is demonstrated with the optimum AmR parameters as shown in Fig. 8. An obvious increase of noise is observed when the gas flow rate up to 280 sccm, which can be attributed to unwanted prong vibration. Hence a flow rate of 260 sccm is selected for the sensor operation.

Based on the measured noise level, a MDL of 1.3 ppb at 300 torr and 2.2 ppb at 700 torr is obtained at 80-mW optical power. The following works are implemented under the atmospheric pressure of 700 torr since the pressure controller can be removed, simplifying the sensing system. Consequently, a normalized noise equivalent absorption (NNEA) coefficient for NH_3 of 1.4×10^{-8} W cm$^{-1}/\sqrt{\text{Hz}}$ is obtained at 700 torr.

3.2. Performance characteristics

To assess the performance of the QEPAS-based NH_3 sensor, the system was operated with the optimum parameters under atmospheric pressure. Various concentration levels of NH_3 from 100 ppb to 10 ppm

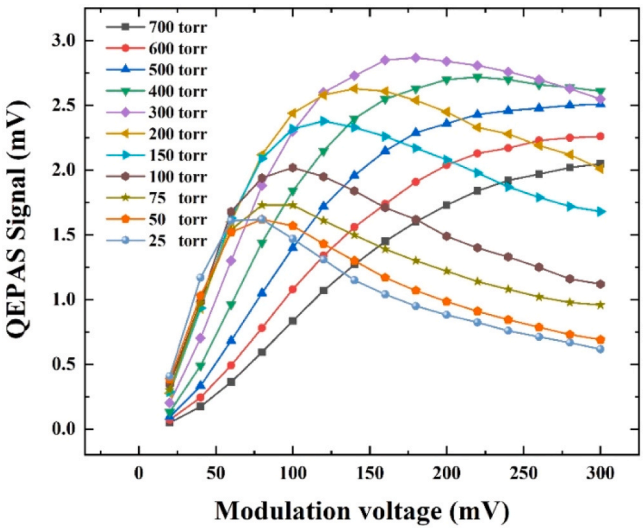

Fig. 7. 2f QEPAS peak signal of NH_3 spectra measured at different gas pressures and laser voltage modulation depths. All measurements were operated using a 1-ppm NH_3 mixture in N_2.

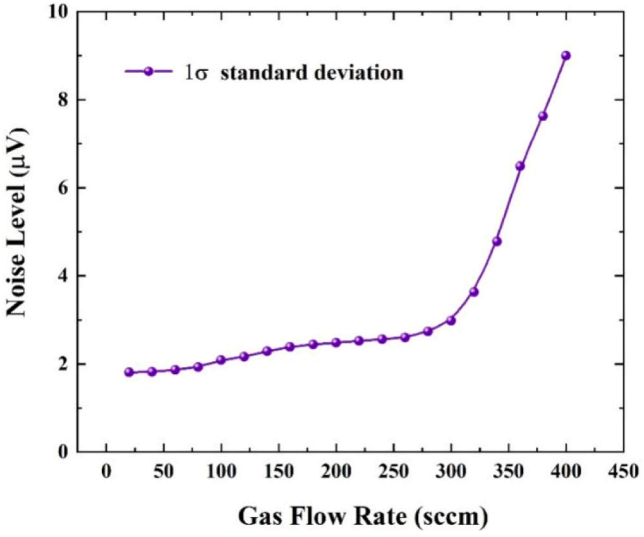

Fig. 8. Dependence of the noise level measured for pure N_2 as a function of the gas flow rate in the range of 20–400 sccm at atmospheric pressure.

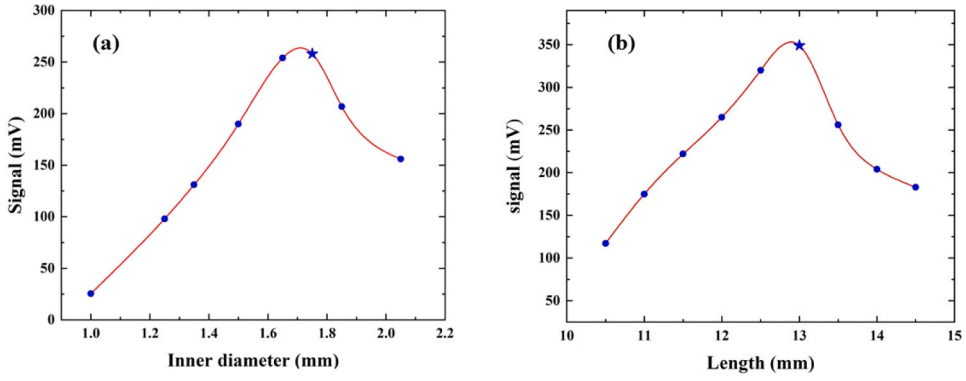

Fig. 6. QEPAS peak signals obtained with different (a) inner diameter and (b) length of each tube.

generated by the gas dilution system are filled into the ADM for characterizing the linearity of this sensor response to the NH_3 concentration. For each concentration, more than 200 QEPAS signals are measured with an acquisition time of 1 s to determine the average value as the final signal value. From Fig. 9, an excellent linear response of the QEPAS peak signals and the NH_3 concentration is indicated and confirmed.

The performance of the QEPAS-based sensor is further evaluated in terms of limits of detection of NH_3 trace gas through Allan variance analysis which is a measurement index of system stability by quantifying noise. As shown in Fig. 10, the long-term stability and the sensitivity of the system are demonstrated with a 1-s acquisition time when the ADM is filled with pure N_2 at atmospheric pressure. In addition, the wavelength of the QCL laser was locked at 1046.4 cm^{-1}, corresponding to the NH_3 absorption peak. The deviation curve almost follows a $1/\sqrt{t}$ dependence for time sequences ranging from 1 s to 52 s, revealing a white noise behavior, where t is the lock-in integration time. And the Allan–werle deviation experiences a sensitivity drift following a $\sqrt{t}$ dependence when the averaging time exceeds 80 s. The calibration curve of the QEPAS sensor is used to convert the 1σ-noise voltages into NH_3 concentrations. Based on the Allan derivation curves, the MDL can be further lowered to 90 ppt with an averaging time of 52 s

In order to verify the sensor performance in practical application, a continuous monitoring of atmospheric NH_3 concentration was implemented from September 7th to 11th, 2022, inside a laboratory located in the Shaw Amenities Building on the Shanxi University campus in Taiyuan, China. To collect atmospheric air samples, an external diaphragm pump was utilized to draw air from the outdoors. A 3 μm micropore PTFE membrane was incorporated to prevent any potential adverse effects caused by dust or soot particles. The results of real-time continuous monitoring of atmospheric NH_3 with an acquisition time of 1 sond at atmospheric pressure are depicted in Fig. 11. A periodic trend in NH_3 concentration is observed from the measured results. Among them, the measured NH_3 concentration has a morning spike around 07:00–10:00 each day, and decreased until reaching the minimum at 17:00. The diurnal variations of urban NH_3 can be attributed to nonagricultural sources caused by human activities, meteorology, and chemical reactions, particularly the vehicular emissions [48]. For example, on colder mornings, more NH_3 is produced in vehicle exhaust due to the higher frequency of fuel-rich combustion, favoring reduction processes on the catalyst surface, hence promotes the significant conversion of NO_x to NH_3 rather than N_2. In addition, the low NH_3 concentration may be due to the relatively high mixing layer height in the afternoon, resulting in a better mixing of NH_3 and air. And the meteorological conditions after 16:00 are more conducive to the reaction of

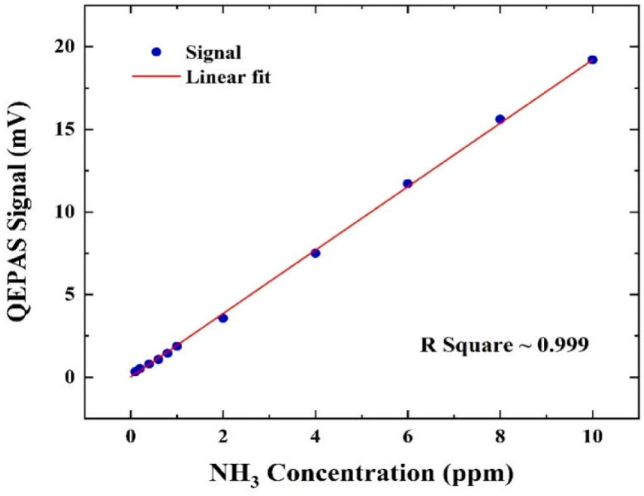

Fig. 9. The linear relationship between 2*f* signal amplitude and NH_3 concentration.

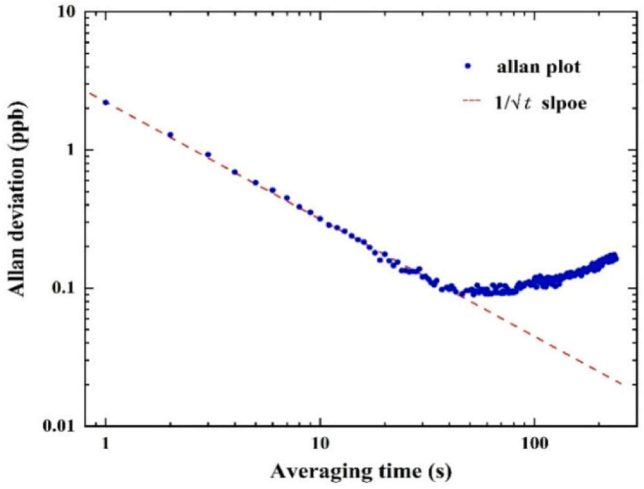

Fig. 10. Allan-werle deviation as a function of the averaging time.

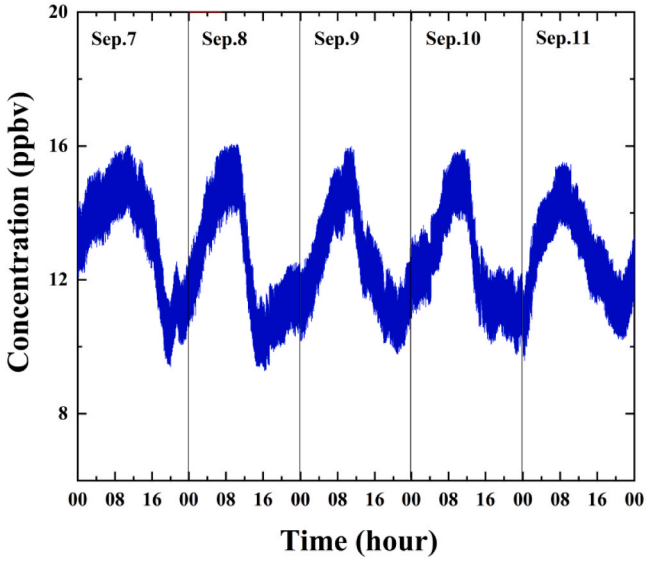

Fig. 11. Continuous five-day monitoring of environmental NH_3 concentrations by the proposed sensor system.

NH_3 with acidic precursors and enhance the isotope exchange between NH_3 and aerosol NH_4^+.

4. Conclusion

A robust, compact and highly sensitive prototype of a QEPAS-based sensor for NH_3 real-line monitoring is realized and demonstrated by combining a novel QTF with a mid-infrared QCL. The QTF, modified with a hammer-shaped prong geometry and surface grooves, is first customized for NH_3 detection which results in a high-quality factor of 10263 at atmospheric pressure in air. The reduced QTF resonance frequency of 9.5 kHz perfectly matches the vibration-translation relaxation of NH_3, providing a more sensitive sensing performance. In addition, the 0.8-mm prong spacing permits the QEPAS operation with a MIR QCL which can pass easily through the ADM without spatial filters. The linear response of the NH_3 sensor was exhibited and a minimum detection limit of 2.2 ppb with 300-ms integration time is obtained, corresponding to a NNEA of 1.4×10^{-8} W cm^{-1} $Hz^{-1/2}$, which is the best value reported so far for NH_3 QEPAS sensors. Continuous monitoring of atmospheric NH_3 for five days was demonstrated, validating the performance the QEPAS-based NH_3 sensing system. As part of future work, a design incorporating

a 3D-printed Teflon-based Acoustic Detection Module (ADM) will be developed to eliminate the adsorption−desorption effect of NH3. Furthermore, the system holds promise for non-invasive breath analysis diagnostics and ammonia monitoring in agriculture and animal husbandry, which are potential areas for its application.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

Data Availability

Data will be made available on request.

Acknowledgments

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