Humidity enhanced N$_2$O photoacoustic sensor with a 4.53 µm quantum cascade laser and Kalman filter

Yuan Cao$^a$, Ruifeng Wang$^{a,b}$, Jie Peng$^{a,b}$, Kun Liu$^{a,*}$, Weidong Chen$^c$, Guishi Wang$^a$, Xiaoming Gao$^a$

$^a$ Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, 230031, China
$^b$ University of Science and Technology of China, Hefei, 230026, China
$^c$ Laboratoire de Physicochimie de l’Atmosphère, Université du Littoral Côte d’Opale, 189A, Av. Maurice Schumann, Dunkerque, 59140, France

**A R T I C L E I N F O**

Keywords:
- Photoacoustic spectroscopy
- Nitrous oxide
- High humidity
- Kalman adaptive filtering

**A B S T R A C T**

A high-sensitivity N$_2$O photoacoustic sensor using a 4.53 µm quantum cascade laser was developed. Sharply enhancement of photoacoustic signal of N$_2$O with the increasing of humidity was investigated experimentally. Finally, 2.3 % water vapor was added to the analyzed sample to improve the vibrational-translational (V–T) relaxation rate of N$_2$O molecule transition, and therefore enhance the N$_2$O photoacoustic signal. High performance with a minimum detection limit of 28 ppbv in 1 s and a measurement precision of 34 ppbv have been achieved, respectively. Kalman adaptive filtering was used to remove the shot-to-shot variability related to the real-time noise in the measurement data and further improve the measurement precision. Without sacrificing the time resolution of the system, the Kalman adaptive filtering improves the measurement precision of the system by 2.3 times. The ability of the N$_2$O photoacoustic sensor was demonstrated by continuous measurement of atmospheric N$_2$O concentration for a period of 7 h.

1. Introduction

Nitrous Oxide (N$_2$O) emissions are currently the most important emissions that deplete the ozone layer and are expected to maintain the largest emissions throughout the 21st century [1]. About 30 % of annual N$_2$O emissions are related to human activities, including the use of agricultural fertilizers, the burning of fossil fuels, and the combustion of biomass and biofuels [2]. N$_2$O is an important greenhouse gas, and changes in its concentration will have an important impact on global radiative forcing. Since 1800, the concentration of N$_2$O in the atmosphere has increased from about 270 ppbv to more than 322 ppbv [2]. In recent decades, its concentration maintains an annual growth trend of about 0.25 % (0.2~0.3 %), and this trend continues [1,2]. Limiting N$_2$O emissions will help restore the ozone layer and reduce atmospheric anthropogenic radiative forcing, which represents a win-win situation for ozone and climate system [1].

Accurately measuring the concentration of N$_2$O in the atmosphere helps to assess its impact on global climate and stratosphere ozone. The most widely used analytical method for measuring N$_2$O is gas chromatography (GC). However, GC is a method that cannot achieve continuous measurement, so it cannot effectively determine short-term changes in gas concentration [4,5]. The optical gas sensors based on laser absorption spectroscopy can realize the measurement of trace gas with high sensitivity, high selectivity, and high time resolution [6,7]. According to the Beer-Lambert absorption law, the detection sensitivity of the absorption spectrum improves as the molecular absorption path length increases. Therefore, many spectrometers based on long optical path gas absorption cells have been reported so far. Banik et al. reported a N$_2$O sensor based on 5.2 µm external-cavity quantum cascade laser (EC-QCL) using cavity ring-down spectroscopy (CRDS) technology [8]. Joly et al. developed an atmospheric N$_2$O sensor based on a 4.5 µm quantum cascade laser (QCL) and a long optical path gas absorption cell [9]. The detection sensitivity of less than 1 ppbv was achieved with an effective optical path of 76 m. Although a gas absorption spectrometer based on a long optical path absorption cell can achieve high-sensitivity measurement of trace gases, it usually requires complex optical alignment procedures [8,9].

Photoacoustic spectroscopy (PAS) has been widely used in trace gas measurement in recent years due to its high sensitivity, zero baseline, compactness and high dynamic range [10–13]. Compared with the...
aforementioned absorption spectroscopy technology, the PAS technology is relatively simple in configuration. In PAS, target molecules absorb the modulated light energy, and then generate acoustic waves through non-radiative relaxation. The generated sound waves can be measured by sensitive acoustic sensors, such as a microphone, a piezoelectric membrane, a cantilever, and a quartz tuning fork [7,14–16]. The acoustic sensor used in PAS sensor is independent of wavelength, and the same acoustic sensor can be used from the ultraviolet, visible to the mid-infrared. Owing to the features of the PAS, in recent years, the application of PAS technology in trace gas detection has been widely reported. Ma et al. reported highly sensitive N₂O detection at 4.61 μm by employing the quartz-enhanced photoacoustic spectroscopy (QEPAS) technique with a distributed feedback QCL, a minimum detection sensitivity of 23 ppbv was achieved [10]. Elefante et al. also reported sensitive detection of N₂O at 7.71 μm using the same technique of QEPAS [14], a detection sensitivity of 5 ppbv was obtained with a lock-in time constant of 100 ms.

In the present work, a high-sensitivity N₂O photoacoustic sensor using a 4.53 μm QCL and Kalman filter under high humidity environment was described. Water vapor was added to the N₂O/N₂ mixture to improve the vibrational-translational (V→T) relaxation rate of N₂O and therfore to improve minimum detection limit. Meanwhile, Kalman adaptive filtering was used in the PAS N₂O sensor to further improve the measurement precision. The ability of the N₂O photoacoustic sensor was demonstrated by long-time, 7 h continuously measurement of atmospheric N₂O.

2. Experiment details

A schematic diagram of the PAS N₂O sensor system based on mid-infrared QCL (HEALTHY PHOTON, Model HPQCL-Q) is shown in Fig. 1. This PAS sensor uses a state-of-the art 4.53 μm continuous wave QCL as the excitation source. The QCL offer a red light coaxial with the output laser beam, so the PAS sensor can be optically aligned very conveniently. The operating current and temperature range of the QCL are 120 mA–330 mA and 20 °C–50 °C, respectively. The wavelength of the QCL can be tuned between 2206.3 and 2211.2 cm⁻¹ (Fig. 2(a)) by changing temperate and current. The wavelength of the used QCL was measured by using a wavelength meter (Bristol instruments, Model 621). The relationship between QCL output power and current at different operating temperatures is shown in Fig. 2(b). In the present work, the absorption line at 2207.62 cm⁻¹ (4.53 μm) of N₂O was selected, at which the corresponding laser current and temperature was 280 mA and 38 °C, respectively. The line intensity of selected N₂O absorption line is significantly higher than other absorption lines [17]. Therefore, N₂O measurement with this absorption line can improve the detection sensitivity of the system. A homemade resonant photoacoustic cell constructed with duralumin was used which contains two buffer volumes, an acoustic resonator and an acoustic microphone (BSWA, MP201, 50 mV/Pa). The length and inner diameter of the acoustic resonator are 110 mm and 10 mm, respectively. Two buffer volumes with a length of 55 mm and a diameter of 40 mm are respectively connected on both sides of the acoustic resonator to reduce the impact of environmental noise and window noise on the PAS signal. The acoustic microphone is usually placed in the middle of the acoustic resonator, which corresponds to the antinode of the acoustic wave. A silver-plated reflector was placed behind the photoacoustic cell, which reflected the laser light back into the photoacoustic cell to increase the effective laser power in the photoacoustic cell, thereby improving the detection sensitivity of the system. The working temperature and current of the QCL were controlled by a touch screen QCL controller (HEALTHY PHOTON, Model QC750 Touch™). In the following experiments, all measurements were performed under normal atmospheric pressure.

Wavelength modulation PAS and second harmonic demodulation technology were used to enhance the sensitivity of the PAS sensors. The triangular voltage ramp generated by the function generator (RIGOL, Model DG1032Z) was fed to the QCL controller, so that the output wavelength of the QCL sweeps back and forth at a rate of 1 Hz around the target absorption line. By feeding a sine wave generated by the function generator to the QCL controller, the wavelength modulation of the QCL light source can be realized. The modulation frequency f was set to equal f₀/2, where f₀ is the first-order longitudinal resonance frequency of the photoacoustic cell. The sine wave and triangular voltage ramp were superimposed by a home-made adder, and then fed to the

---

**Fig. 1.** Schematic of a QCL based N₂O sensor system. FG: function generator; LIA: lock-in amplifier.

**Fig. 2.** (a) Current tuning of QCL at different operating temperatures; (b) the relationship between QCL output power and current at different operating temperatures.
QCL controller. The lock-in amplifier (Zurich Instruments AG, MFLI) was used to demodulate the acoustic signal measured by the microphone at a frequency of $2f$ (where $f$ is the modulation frequency of the sine wave, $f = f_0/2$). The time constant of the lock-in amplifier was set as 10 ms. The data acquisition (DAQ, NI-USB-6212) card collects the demodulated signal and displays it on a laptop equipped via a LabVIEW interface. The data acquisition time is 1 s.

Gas mixtures with different concentrations of $N_2O$ were produced by using a gas dilution system (Environics Inc., USA, Model N-4000). A humidifier (Perma Pure, Model MH-110–24F-4) and hygrometer were connected to the inlet of the photoacoustic cell to add water vapor to the gas mixture and monitor the water vapor content. Water vapor is known to be an efficient catalyst for the vibrational energy transfer reactions in gas phase [18]. As the humidifier increase the concentration of water vapor in $N_2O/N_2$ mixture, the $V$–$T$ relaxation processes of $N_2O$ was improved. The PAS signal amplitude will increase with the acceleration of the $N_2O$ $V$–$T$ relaxation process, thereby significantly improving the detection sensitivity of the PAS sensor.

Fig. 3(a) is the photograph of the integrated current & temperature driver and the QCL head. The two-dimensional intensity distribution of the laser beam was measured by a laser beam analyzer (Ophir Optronics Solutions, Model PY-III-HR-C-A), as shown in Fig. 3(b). The size of the light spot (~2 mm) is smaller than the radius of the acoustic resonator. This can ensure that after the laser beam is reflected back to the photoacoustic cell, the laser beam will not irradiate the inner wall of the acoustic resonator, thereby avoiding background interference.

3. Results and discussion

Fig. 4(a) is the simulated absorption spectrum of 320 ppbv $N_2O$, 1.4% $H_2O$, and 200 ppbv CO based on the HITRAN database at 298 K, 1 atm and 1 cm optical path [17]. As shown in Fig. 4, the absorption line of $N_2O$ at 2209.52 cm$^{-1}$ can be interfered by CO absorption, while the absorption line of $N_2O$ at 2208.58 cm$^{-1}$ can be interfered by $H_2O$ absorption. Therefore, the $N_2O$ absorption line at 2207.62 cm$^{-1}$ was selected to minimize the interference of $H_2O$ and CO absorption. As far as we know, no other gas will interfere with $N_2O$ detection at selected absorption line. Fig. 4(b) shows the absorption spectrum of $N_2O$ measured by the PAS sensor, which corresponds to the $N_2O$ absorption line in Fig. 4(a). The difference in the amplitude of the $N_2O$ PAS signal is caused by the difference of optical power of the QCL at these three absorption line positions.

The design of the photoacoustic cell was completed with the help of finite element method (FEM) analysis, which help to determine the eigenfrequency, acoustic field distribution and quality factor of the photoacoustic cell, theoretically. The inset in Fig. 5 is the acoustic field distribution diagram of the first-order longitudinal resonance mode (100) of the photoacoustic cell analyzed by FEM. The different colors in this inset represent the intensity of the PAS signal, red represents the maximum value of the PAS signal, and blue represents the minimum value of the PAS signal. The frequency of the first-order longitudinal

![Fig. 3](image-url)  
Fig. 3. (a) Integrated current & temperature driver (left), and QCL head (right); (b) two-dimensional light intensity distribution of QCL.

![Fig. 4](image-url)  
Fig. 4. (a) HITRAN based simulated spectra of $N_2O$, $H_2O$, CO at 298 K and 1 atm; (b) Experimentally measured $N_2O$ absorption spectrum.

![Fig. 5](image-url)  
Fig. 5. Frequency response of the photoacoustic cell. The inset is the simulated PAS signal distribution diagram of the first-order longitudinal resonance mode of the photoacoustic cell.
resonance mode of the photoacoustic cell based on FEM is 1507 Hz. Fig. 5 shows the square of the PAS signal amplitude as a function of resonant frequency. The experiment data were fitted with a Lorentz contour, which describes power in a classical driven oscillator as a function of frequency [19]. According to the results of Lorentz fitting, the first-order longitudinal resonance frequency of the photoacoustic cell is 1477 Hz. The relative deviation of the resonance frequency of the photoacoustic cell obtained through experimental measurement and finite element simulation is 2%, which proves the reliability of the finite element simulation result. The quality factor Q of the acoustic resonator is 19. This lower quality factor Q of the acoustic resonator helps reduce the sensitivity of the resonant frequency of the photoacoustic cell to ambient temperature.

In order to ensure that the maximum PAS signal amplitude is obtained without distorting the signal, the modulation amplitude of the QCL laser needs to be optimized. For this purpose, the PAS signals of 5 ppm N₂O were recorded under different modulation amplitudes. The results are shown in Fig. 6 which illustrate the effects of modulation amplitude on the N₂O PAS signal. The optimal modulation amplitude was finally determined to be 190 mVpp (peak to peak), and this optimized modulation amplitude was used in subsequent measurements.

For slowly relaxing molecules (such as N₂O, CO, CO₂, NO, HCN, etc.), the amplitude of the PAS signal depends on the V–T relaxation rate [20–24]. The resonance frequency of the photoacoustic cell used in this experiment is f = 1477 Hz, i.e., 1/ω = 1/2πT = 108 μs. In case of a slow V–T relaxation with respect to the modulation frequency (ω >> 1/ω), the translational gas temperature cannot follow the rapid changes in the laser-induced molecular excitation rate [18]. Therefore, the amplitude of the generated PAS signal is weaker than that of instantaneous V–T energy transfer. Water vapor is an extremely fast relaxation molecule, the V–T energy transfer time of water vapor is 0.037 μs [22]. For slowly relaxing molecules, increasing the water vapor concentration in these molecules will accelerate the V–T relaxation time, and therefore, increase PAS signal. In this work, influence of water vapor on N₂O PAS signal was investigated experimentally. During the investigation, N₂O with different water vapor concentrations was generated by mixing dried and humidified N₂O gas. The relationship between the N₂O PAS signal and the concentration of water vapor is shown in Fig. 7. The measurement was carried out in a flowing state, and laboratory air was used as the N₂O sample. The flow rate was set at 400 mL/min during the measurement. According to the reports in the literature, for some gases with a slow relaxation rate, the PAS signal will begin to saturate at a certain water vapor concentration, such as CO₂ [22–25]. However, under our experimental conditions, the PAS signal of N₂O increases linearly with the water vapor concentration. This phenomenon may be related to the vibrational translation relaxation of N₂O molecule. This need further study theoretically. Compared with the N₂O/N₂ gas mixture with a water vapor concentration of 0.3 %, when the water vapor concentration is 2.3 %, the PAS signal amplitude increased by 6.8 times. A water vapor concentration of 0.3 % corresponds to the air sample not being humidified by the humidifier. The water vapor concentration of 2.3 % is the maximum value that can be obtained at measured environment (where the temperature is 22°C). This means that the sample was fully passed through the humidifier. In the following experiments, the sample was fully passed through the humidifier to maintain the concentration of water vapor at 2.3 %.

The amplitude of the PAS signal is proportional to the power of the laser. Therefore, increasing the effective optical power in the photoacoustic cell helps to improve the detection sensitivity of the PAS sensor. A silver coated flat mirror was placed at the back of the photoacoustic cell to reflect the transmitted light back into the photoacoustic cell. This make the effective laser power in the photoacoustic cell was increased from 19 to 33 mW. The effective optical power was calculated based on the transmittance of the two windows of the photoacoustic cell and the loss of the reflector. The transmittance of the window of the photoacoustic cell is 94 %. Considering the transmittance of the window and the loss of the reflector, the optical power will not double after the laser passes through twice in the photoacoustic cell. It should be note that the light reflected by the flat mirror is off axial with the incident light, so as not to damage the QCL. Fig. 8 is the PAS signals of laboratory air with different water vapor concentrations and with or without the reflector. Compared with the case where the water vapor concentration is only 0.4 % and no reflector is added, when the laboratory air is humidified to 2.3 %, the PAS signal increased by 6.8 times.
% and the reflector is added, the amplitude of the PAS signal has been significantly improved.

Fig. 9 shows the measured PAS signals of fully humidified (2.3 % H$_2$O/N$_2$O with different concentrations. Different concentrations of N$_2$O were obtained by diluting a 5 ppm N$_2$O/N$_2$ standard gas mixture with high-purity N$_2$. A gas dilution system was used to complete this work. The second harmonic (2f) N$_2$O photoacoustic spectrum was obtained by continuously scanning the laser wavelength with a frequency of 1 Hz, and then the peak signal of each spectrum was extracted as PAS signal. The N$_2$O PAS signals for each calibrated concentration were averaged 100 times. The noise level was determined by the standard deviation of the non-absorption wing of the N$_2$O spectrum, which has a value of 0.005 mV(1σ). It can be further calculated that the signal-to-noise ratio (for 5 ppmv N$_2$O) and detection limit of the PAS sensor are 718 and 7 ppbv, respectively. The corresponding normalized noise equivalent absorption (NNEA) coefficient is 5.69 × 10$^{-8}$ cm$^2$/W/Hz. The measured results of the humidified N$_2$O PAS signal to the different N$_2$O concentration are displayed in Fig. 10. The linear response of the humidified N$_2$O PAS signal to N$_2$O concentration was confirmed by fitting the data with a linear slope as shown in Fig. 10. The R squared value is 0.9996, which represents how well the regression line approximates to the real data points. The slope obtained by linear fitting is 0.725 mV/ppm, and the intercept is 0.019 mV. The intercept obtained by linear fitting is higher than the noise level of the system, which may be related to the accuracy of the diluted gas concentration and noise introduced by the PAS sensor system.

In order to further evaluate the performance of the PAS N$_2$O sensor, time series measurements of humidified air were performed [26,27]. In this measurement, sample air was sealed in the photoacoustic cell and the measurement was performed under static conditions. In such case, the constant concentration of N$_2$O was guaranteed and therefore the signal fluctuation was come from noise was also guaranteed. During the measurement, the scanning frequency of the QCL laser was 1 Hz and the N$_2$O PAS signal was not averaged at here, that is, each point of the signal was obtained in 1 s. These is for convenient to make Allan-Werle analysis which was done with time interval of 1 s, generally. In this way, we can easily evaluate the detection sensitivity of the system with different average time. Fig. 11(a) is the Allan-Werle deviation analysis using measurement data. When the average time is 1 s, the detection sensitivity of the PAS N$_2$O sensor is 28 ppbv. The detection sensitivity of the system can be improved to 1 ppbv if the average time is increased to 800 s. This detection sensitivity of the PAS N$_2$O sensor is much lower than the actual N$_2$O concentration in the atmosphere, so it can meet the measurement of the N$_2$O concentration in the atmosphere.

The time series measured data were further used to evaluate measurement precision of the PAS N2O sensor. Measurement precision is also an important value for a sensor. The precision describes the degree to which repeated measurements under unchanged conditions show the same results (sometimes referred to as reproducibility or repeatability) [28]. Histogram plot of the continuous time series measurement data is shown in Fig. 11(b). The data distribution is a Gaussian profile, and its corresponding half width at half maximum (HWHM) is the measurement precision of the PAS N$_2$O sensor. For a 1 s average time, the measurement precision of the PAS N$_2$O sensor was found to be ±34 ppbv.

Continuously, 7 h measurement of atmospheric N$_2$O concentration was performed to evaluate the long time, continuous measurement ability of the PAS N$_2$O sensor. A particle filter (Parker, Model 9900 BK) was placed at the air inlet of the photoacoustic cell to prevent aerosol particles in the air polluting the photoacoustic cell. The scanning frequency of the PAS sensor is 1 Hz. During this experiment, the measured PAS signal was averaged 10 times. In order to avoid the influence of airflow noise on the PAS signal, the flow rate of the sampling was set to 400 mL/min. The gray line in Fig. 12 represents the original measurement result, where the average (±standard deviation)
concentration of N\textsubscript{2}O was found to be 339 (±15.5) ppbv. Since N\textsubscript{2}O stays in the atmosphere for a long time, it has been well mixed in the lower atmosphere, so its concentration level is relatively stable [10].

In the actual atmospheric detection process, the PAS sensors will inevitably be affected by environmental noise. For improving the measurement precision of the PAS N\textsubscript{2}O sensor, signal averaging and Kalman adaptive filtering were applied and analyzed in this work, respectively. The red line in Fig. 12 is the measurement result after two minutes of averaging. The average (±standard deviation) N\textsubscript{2}O concentration during this period is 339(±7.2) ppbv. After two minutes of signal averaging, the standard deviation of the N\textsubscript{2}O concentration improved from 15.5 ppbv in the original measurement result to 7.2 ppbv, which means that the measurement precision of the PAS sensor was improved by 2.2 times, but this method sacrifices the time resolution of the PAS sensor. Therefore, we have adopted the Kalman filtering method in the present work. The Kalman filtering method can effectively eliminate the shot-to-shot variability related to the real-time noise in the measurement data without affecting the time resolution [28–31]. Kalman filtering is an adaptive filtering technique that can adapt to the real measurement environment through self-adjustment of its transfer function. The Kalman filter uses a recursive method to predict the ‘true value’ of time $\kappa$ based on the previously determined value $\hat{\delta}_\kappa$ given at time $\kappa - 1$ and the measured value $z_\kappa$ at time $\kappa$, as expressed in the following equation [28]:

$$\hat{\delta}_\kappa = \hat{\delta}_{\kappa-1} + K_\kappa (z_\kappa - \hat{\delta}_{\kappa-1})$$

(1)

$K_\kappa$ is the Kalman gain that weights the measurement residual. Kalman gain $K_\kappa$ is related to the measurement noise ($\sigma_\kappa$) and the true concentration variability ($\sigma_{\text{true}}$). $q$ is the ratio of $\sigma_{\kappa}^2/\sigma_{\text{true}}^2$, which is used as an adjustment parameter to control the response speed of the filter to the true concentration changes and the influence of high-frequency white noise on the measurement results. When the value of $q$ is too large, the filtered result will lag behind the true changes in concentration [30]. If the value of $q$ is too small, it will increase the interference of high-frequency white noise on the output of the filter. After considering the two factors of fast time response and high measurement precision, the value of $q$ was finally taken as 100. At the same time, the standard deviation of first 10 measurements was used as the input of instrument measurement noise. The blue line in Fig. 12 is the result of Kalman filtering, and its change trend is the same as the change trend with two-minute average. The average (±standard deviation) concentration of N\textsubscript{2}O after Kalman filtering is 339(±6.7) ppbv. The standard deviation of the N\textsubscript{2}O concentration was improved from 15.5 ppbv in the original measurement result to 6.7 ppbv, which means that the method of Kalman filtering can also improve the measurement precision of the system by 2.3 times without sacrificing the time resolution of the PAS sensor.

4. Conclusion

A PAS N\textsubscript{2}O sensor based on the mid-infrared QCL was developed. The performance of the sensor for N\textsubscript{2}O detection was improved by humidifying the gas sample and by reflecting the transmitted laser light back to the PAS cell. A minimum detection limit of 28 ppbv in 1 s was obtained for N\textsubscript{2}O measurement at humidified environment, and the corresponding measurement precision was found to be 34 ppbv. Allan-Werle analysis shows that the minimum detection limit can be improved to 1 ppbv by increasing average time to 800 s. The detection sensitivity of the PAS N\textsubscript{2}O sensor can be further improved by using two right-angle prisms to increase the times of laser passes through the photoacoustic cell back and forth as reported in [32]. By using Kalman adaptive filter, the shot-to-shot noise was decreased and the measurement precision was improved by 2.3 times without sacrificing the time resolution of the system. The reliability of the developed PAS N\textsubscript{2}O sensor was confirmed by long time, continuous measurement of atmospheric N\textsubscript{2}O. The developed PAS N\textsubscript{2}O sensor offer potential applications in atmosphere monitoring, agricultural activities and automobile exhaust emission monitoring.

Declaration of Competing Interest

The authors declare no conflict of interest.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 41730103, No. 41475023, No. 41575030), the National Key Research and Development Program of China (No. 2017YFC0209700, No. 2016YFC0303900).

References

[1] A.R. Ravishankara, J.S. Daniel, R.W. Portmann, Nitrous oxide (N\textsubscript{2}O): the dominant ozone-depleting substance emitted in the 21st century, Science 326 (2009) 123–125.
[2] D.J. Vuurens, Nitrous oxide: No laughing matter, Science 326 (2009) 56–57.
[3] K.M. Thaler, C. Berger, C. Leitz, J. Drewes, R. Niessner, C. Haisch, Photoacoustic spectroscopy for the quantification of N\textsubscript{2}O in the off gas of wastewater treatment plant, Anal. Chem. 89 (2017) 3795–3801.
[4] T.D. Rapson, H. Daices, Analytical techniques for measuring nitrous oxide, TrAC-Trends Anal. Chem. 54 (2014) 65–74.
[5] G.W. Santoni, B.C. Daube, E.A. Kort, R. Jimenez, S. Park, J.V. Pittman, et al., Evaluation of the airborne quantum cascade laser spectrometer (QCLS) measurements of the carbon and greenhouse gas suite-CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O, and CO during the CalNex and HIPPO campaigns, Atmos. Meas. Tech. 7 (2014) 1509–1526.
[6] K. Liu, L. Wang, T. Tan, G.S. Wang, W.J. Zhang, W.D. Chen, X.M. Gao, Highly sensitive detection of methane by near-infrared laser absorption spectroscopy using a compact dense-pattern multipass cell, Sens. Actuator B-Chem. 220 (2015) 1000–1005.
[7] K. Liu, J.X. Mei, W.J. Zhang, W.D. Chen, X.M. Gao, Multi-resonator photoacoustic spectroscopy, Sens. Actuator B-Chem. 251 (2017) 632–636.
[8] G.D. Banik, S. Som, A. Maity, M. Pal, S. Maithani, S. Mandal, M. Pradhan, An EC-QCL based N\textsubscript{2}O sensor at 5.2 μm using cavity ring-down spectroscopy for environmental applications, Anal. Methods 9 (2017) 2315–2320.
[9] L. Joly, T. Decarpenterie, N. Dumelle, X. Thomas, I. Mappe-Fogaing, R. Vallon, G. Durry, B. Parvitte, M. Carras, X. Marcadet, V. Zeninari, Development of a versatile atmospheric N\textsubscript{2}O sensor based on quantum cascade laser technology at 4.5 μm, Appl. Phys. B-Lasers Opt. 103 (2011) 717–723.
[10] Y.F. Ma, R. Lewicki, M. Razeghi, F.K. Tittel, QEPS based ppb-level detection of CO and N\textsubscript{2}O using a high power CW DFB-QCL, Opt. Express 21 (2013) 1008–1019.
[11] M. Giglio, A. Zifarelli, A. Sampaolesi, G. Medunski, A. Elefante, R. Blanchard, C. Pilnegg, M.F. Witinski, D. Vakhshoori, H.P. Wu, V.M.N. Passaro, P. Patimisco, F.K. Tittel, L. Dong, V. Spagnolo, Broadband detection of methane and nitrous oxide using a distributed-feedback quantum cascade laser array and quartz-enhanced photoacoustic sensing, Photoacoustics 17 (2020), 100159.
[12] Y. Yin, H. Wu, L. Dong, B. Li, W. Ma, L. Zhang, W. Yin, L. Xiao, S. Jia, F.K. Tittel, Ppb-level SO\textsubscript{2} photoacoustic sensors with a suppressed absorption-desorption effect by using a 7.41 μm external-cavity quantum cascade laser, ACS Sens. 5 (2020) 549–556.
[13] Y. Li, R. Wang, F.K. Tittel, Y. Ma, Sensitive methane detection based on quartz-enhanced photoacoustic spectroscopy with a high-power diode laser and wavelet filtering, Opt. Lasers Eng. 132 (2020) 106155.
[14] A. Elefante, M. Giglio, A. Sampao, G. Menduni, P. Patimisco, V.M.N. Passaro, H. Wu, H. Rossinav, V. Mackowiak, A. Cable, F.K. Tittel, L. Dong, V. Spagnolo, Dual-gas quartz-enhanced photoacoustic sensor for simultaneous detection of methane/nitrous oxide and water vapor, Anal. Chem. 91 (2019) 12866–12873.

[15] Y. Cao, Q. Liu, R. Wang, K. Liu, W. Chen, G. Wang, X. Gao, Development of a 443 nm diode laser-based differential photoacoustic spectrometer for simultaneous measurements of aerosol absorption and NO2. Photoacoustics 21 (2021), 100229.

[16] Y. Cao, K. Liu, R. Wang, W. Chen, X. Gao, Three-wavelength measurement of aerosol absorption using a multi-resonator coupled photoacoustic spectrometer, Opt. Express 29 (2021) 2258–2269.

[17] The HITRAN database http://www.hitrans.com.

[18] R. Lewicki, G. Wysocki, A.A. Koster, F.K. Tittel, Carbon dioxide and ammonia detection using 2 μm diode laser based quartz-enhanced photoacoustic spectroscopy, Appl. Phys. B-Lasers Opt. 87 (2007) 157–162.

[19] K. Liu, Y. Cao, G. Wang, W. Zhang, W. Chen, X. Gao, A novel photoacoustic spectroscopy gas sensor using a low cost polyvinylidene fluoride film, Sens. Actuat B-Chem. 277 (2018) 571–575.

[20] A. Grosně, V. Zenzin, B. Parvītē, L. Ķoly, D. Courtois, Optimization of a compact photoacoustic quantum cascade laser spectrometer for atmospheric flux measurements: application to the detection of methane and nitrous oxide, Appl. Phys. B-Lasers Opt. 88 (2007) 483–492.

[21] X. Yin, L. Dong, H. Wu, H. Zheng, W. Ma, J. Yang, W. Chen, X. Gao, A novel photoacoustic spectroscopy gas sensor using an external cavity quantum cascade laser based QEPAS sensor, Opt. Express 19 (2011) 24037–24045.

[22] A.A. Koster, T.S. Mosely, F.K. Tittel, Impact of humidity on quartz-enhanced photoacoustic spectroscopy based detection of HCN, Appl. Phys. B-Lasers Opt. 85 (2006) 295–300.

[23] S.D. Russo, A. Sampao, P. Patimisco, M. Giglio, C. Hoelzl, V.M. N. Passaro, H. Wu, L. Dong, V. Spagnolo, Quartz-enhanced photoacoustic spectroscopy exploiting low-frequency tuning forks as a tool to measure the vibrational relaxation rate in gas species, Photoacoustics 21 (2021), 100227.

[24] A.A. Kosteru, V.A. Bakhkhir, F.K. Tittel, S. Mcwhorter, B. Ashcraft, QEPAS methane sensor performance for humidified gases, Appl. Phys. B 92 (2008) 103–109.

[25] M. Giglio, P. Patimisco, A. Sampao, A. Zifarelli, R. Blanchard, C. Pfleugel, M. F. Witinski, D. Vakhshoori, F.K. Tittel, V. Spagnolo, Nitrous oxide quartz-enhanced photoacoustic detection employing a broadband distributed-feedback quantum cascade laser array, Appl. Phys. Lett. 113 (2018), 171101.

[26] M. Giglio, P. Patimisco, A. Sampao, G. Scamarcio, F.K. Tittel, V. Spagnolo, Allan deviation plot as a tool for quartz-enhanced photoacoustic sensors noise analysis, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 63 (2016) 555–560.

[27] W. Chen, H. Yi, T. Wu, W. Zhao, C. Lengigon, G. Wang, E. Fertin, C. Coeur, G. Wysocki, T. Wang, M.W. Sigrist, X. Gao, W. Zhang, Photonic sensing of reactive atmospheric species, Encycl. Anal. Chem. (2017) 1–60.

[28] M.S. Niu, P.G. Han, L.K. Song, D.Z. Hao, J.H. Zhang, L.L. Ma, Comparison and application of wavelet transform and Kalman filtering for denoising in δ13CO2 measurement by tunable diode laser absorption spectroscopy at 2.088 μm, Opt. Express 25 (2017) A986–A905.

[29] B. Fang, W. Zhao, X. Xu, J. Zhou, X. Ma, S. Wang, W.J. Zhang, D.S. Venables, W. Chen, Portable broadband cavity-enhanced spectrometer utilizing Kalman filtering: application to real-time, in situ monitoring of glyoxal and nitrogen dioxide, Opt. Express 25 (2017) 26910–26922.

[30] D.P. Leloux, R. Claps, W. Chen, F.K. Tittel, T.L. Harman, Applications of Kalman filtering to real-time trace gas concentration measurements, Appl. Phys. B-Lasers Opt. 74 (2002) 85–93.

[31] S. Qiao, Y. Ma, P. Patimisco, A. Sampao, Y. He, Z. Lang, F.K. Tittel, V. Spagnolo, Multi-pass quartz-enhanced photoacoustic spectroscopy-based trace gas sensing, Opt. Lett. 46 (2021) 977–980.

Yuan Cao is currently a postdoc in Prof. Kun Liu’s group in Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences. His research interests are sensing trace gases and aerosols with photoacoustic spectroscopy. He received his Ph. D. degree in physics from University of Science and Technology of China in 2021.

Ruifeng Wang is currently a Ph.D. student in Prof. Kun Liu’s group in Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences. His research interests are sensing trace gases with tunable diode laser absorption spectroscopy (TDLAS). He received his BSc from Anhui University in 2018.

Jie Peng is currently a Ph.D. student in Prof. Kun Liu’s group in Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences. His research interest is the simultaneous detection of multi-component gases based on photoacoustic spectroscopy technology. He received his BSc from Anhui University in 2018.

Kun Liu received his Ph.D. degree in optics from Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences in 2010. Now he is a professor of Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences. His research interests include photoacoustic spectroscopy and laser spectroscopy for application in atmospheric photochemistry and environmental science.

Weidong Chen received his Ph.D. from the University of Sciences & Technologies of Lille (France) in 1991. He obtained his State PhD (HDR) in 2001 and became full Professor of University of Sciences & Technologies of Lille in 2003. His research interests include developments of photonic instrumentation for applied spectroscopy, Optical metrology of trace gases for applications in atmospheric photochemistry and environmental science.

Guishi Wang received his Ph.D. degree in optics from Anhui Institute of Optics & Fine Mechanics, Chinese Academy Sciences in 2012. Now he is an associate professor of Anhui Institute of Optics & Fine Mechanics, Chinese Academy Sciences. His research interests include laser heterodyne spectroscopy and atmospheric sounding.

Xiaoming Gao is Professor at Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences. He received his Ph.D. degree from Anhui Institute of Optics & Fine Mechanics, Chinese Academy Sciences in 1998. He studied and worked in Max-Planck-Institute for Quantumpotomics, German as postdoctoral from 1998 to 2000. His research interests include atmospheric molecules absorption spectroscopy, high sensitive diode laser spectroscopy and application.