Development of a 443 nm diode laser-based differential photoacoustic spectrometer for simultaneous measurements of aerosol absorption and NO₂

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A B S T R A C T

Measurement of ambient aerosol and nitrogen dioxide (NO₂) is important as they are major pollutants from the burning of fossil fuel and biomass. In the present work, a differential photoacoustic spectrometer (D-PAS) was developed for simultaneous, online measurements of aerosol optical absorption and NO₂ concentration. A novel photoacoustic resonator was designed and employed in the D-PAS for controlling a large flow rate, improving response time, and keeping the flow noise at a low level. The detection limits of 1.0 Mm⁻¹ and 0.87 ppb for aerosol absorption and NO₂ concentration measurements were achieved with a lock-in amplifier time constant of 1 s. The D-PAS accuracy was demonstrated by performing a long-time, continuous measurement of aerosol and NO₂ in ambient air. The measured results of NO₂ are consistent with the NOx analyzer and environmental monitoring station results.

1. Introduction

Aerosols are one of the important pollutants in the atmosphere, and their existence impacts atmospheric visibility, human health, the hydrological cycle, and radiative forcing [1–3]. Atmospheric aerosols directly affect radiative forcing by absorbing and scattering solar radiation, the radiative forcing of the total aerosols in the atmosphere is −0.9 [−1.9 to −0.1] W m⁻². Compared with greenhouse gases, the impact of aerosols on radiative forcing has greater uncertainty [4]. The measurement of aerosol light absorption characteristics is of great significance for the estimation of radiative forcing. NO₂ plays an important role in complex atmospheric chemical reactions, which affect air quality and climate [5]. For example, NO₂ is the main precursor of tropospheric ozone formation and participates in the formation of secondary organic aerosols [5–7]. An evidence episode was observed in a field observations of haze event in Beijing that SO₂ was rapid oxidated by NO₂ [8]. The main source of NO₂ is from anthropogenic combustion processes, such as automobile exhaust, power plants, and industrial emissions [5,9]. In recent years, an increase in atmospheric NO₂ has been observed in South Asia, East Asia, and the Middle East [7]. Therefore, simultaneous measurements of aerosol absorption and NO₂ in the atmosphere are of great significance to the comprehensive management of ambient air quality and climate research [10]. There are few instruments capable of measuring aerosol absorption and NO₂ simultaneously. The most common method for measuring the aerosol absorption coefficient is filter-based technology using instruments such as the Aethalometer, the particle soot absorption photometer, and the multi-angle absorption photometer [11]. Although these instruments are widely employed, they are limited by factors associated with filter-loading, extraction, and multiple scattering effects as the optical properties are not measured on natural suspended status [1,12,13]. The concentration of NO₂ is usually measured by chemiluminescence-based techniques, but it is cross-sensitive to other nitrogen compounds such as peroxyacetyl nitrate and nitric acid [14].

Simultaneous measurement of the absorption characteristics of aerosols and the concentration of NO₂ helps monitor the dynamics of the two main pollutants in the atmosphere in real-time. In addition, the simultaneous measurement of aerosol absorption and NO₂ helps to analyze the influence of atmospheric oxidation capacity on aerosol absorption [15]. Photoacoustic spectroscopy (PAS), discovered by A. G.
Bell in 1880 [16], is a sensitive “zero baseline” method for weak absorption measurement [17–20] and is regarded as the best candidate for in situ aerosol absorption measurement. PAS is based on the detection of sound waves that are generated due to the absorption of modulated optical radiation related to the photoacoustic effect. PAS can directly measure the absorption of suspended particles; this effectively avoids the problems related to the filter-based method. The aerosol light absorption coefficient can be obtained with a well-calibrated PAS spectrometer. The calibration can be usually performed with gas (ozone [21], nitrogen dioxide [22], oxygen A-band [23,24]) or aerosols [25] in order to determine the photoacoustic cell constant. Due to the high sensitivity and accuracy of the PAS spectrometer, it gradually came to be used to measure the absorption characteristics of aerosols [12]. Wiegand et al. reported a UV–vis photoacoustic spectrophotometer for the measurement of gas-phase and aerosol absorption over the UV–vis region [13]. The photoacoustic spectrophotometer can measure the absorption coefficient of aerosols in eight bands. Bluvshtein et al. used a multi-pass PAS spectrometer, calibrated with nigrosine particles, to directly measure the light absorption of atmosphere aerosol [25]. Cremer et al. reported PAS measurements of an optically trapped single droplet, which can be used for the direct observation of nanofocusing in aerosol photo-kinetics [26]. Although there are many reports on the use of PAS to measure aerosols absorption and trace gases [27–32], to our knowledge, there are few photoacoustic spectrometers with sufficiently high sensitivity that can simultaneously measure the absorption characteristics of atmospheric aerosols and the concentration of atmospheric NO₂.

In addition, when PAS is used for atmospheric measurements, the sampling flow rate usually needs to be less than 0.5 L/min (for example, the sampling flow rate in reference [11] is 200 mL/min, the sampling flow rate in reference [12] is 330 mL/min, and the sampling flow rate in reference [27] is 400 mL/min). A low flow rate will affect the PAS sensor’s response time, but a high flow rate creates turbulence in the photoacoustic cell, resulting in considerable noise affecting the performance of the PAS sensor [11]. The development of a PAS spectrometer that can simultaneously measure the aerosol absorption and NO₂ concentration in the atmosphere at large flow rates will quickly respond to changes in the measurement environment.

In this work, the development of a differential photoacoustic spectrometer (D-PAS) sensor based on a 443 nm blue laser diode (LD) for real-time, online, in situ measurement of aerosol optical absorption and NO₂ was developed and demonstrated. Two acoustic resonators with the same resonant frequency were carefully designed. To increase the total flow rate to improve the response time of the n-PAS sensor, four additional airways were arranged in the acoustic resonator, which enables the D-PAS to work with a large flow rate (>1 L/min) without being disturbed by flow noise. The D-PAS developed was used to simultaneously measure the aerosol absorption coefficient and NO₂ concentration in the atmospheric environment continuously. The measured results of NO₂ were compared with the NOx analyzer and the environmental monitoring station, and good agreement between them was observed.

2. Spectrometer details

Fig. 1 (a) shows the diagram of the developed D-PAS. It contains dual-photoacoustic cells with the same resonant frequency, which makes them work with only one chopper. The photoacoustic cells were constructed from duralumin. A filter (Parker) was used to connect the two photoacoustic cells such that the first photoacoustic cell measures the PAS signal induced from both aerosol and NO₂, and the second photoacoustic cell measures the PAS signal only from NO₂. The characteristic of the filter is that the filtration efficiency at 0.01 μm is 99.9%.

Fig. 1 (b) is a photograph of the developed D-PAS. A blue-LD source (PL-TB450B, 1.6 W) was used for excitation of the PAS signal. The LD emission spectrum was measured using a spectrometer (HR2000), and the actual central wavelength was determined
to be 443 nm. The emission spectrum of the LD is a Gaussian distribution, and the full width at half maximum (FWHM) was determined to be 1.6 nm. An LD controller (ITC110, Thorlabs) was used to modulate the current and temperature. A thermoelectric cooler (TEC) was inserted between the LD and heat sink [33]. The LD’s temperature was measured using a 10 K thermistor (MEB 10 K NTC) controlled at approximately 25°C, which helps to achieve long-term stability of the laser output power. The laser beam was collimated using a lens with a radius of 6 mm and a focal length of 6 mm. According to the datasheet, the used LD output power can reach to 1.6 W when it working at maximum current (1.6 A). However, for LD safety, working current of the LD was not set at maximum, but set at 1 A during the experiment. In such case the corresponding laser output power was measured to be 600 mW.

An optical chopper (MC2000B-EC, Thorlabs) was used to modulate the light at the resonant frequency of the acoustic resonators. The photoacoustic cells and optical chopper were ‘soft’ mounted to the bottom plate via a rubber sheet for decreasing chopper vibration noise [34]. The PAS signals were detected with a microphone (BSWA, MP201, 50 mV/Pa) and then demodulated using two lock-in amplifiers (LIA-BVD-150-L) with 1 s time constant. The PAS signals were digitally sampled by a data acquisition card (DAQ, NI-USB-6212) and then displayed on a laptop via LabVIEW (National Instruments) software. A power meter (NOVA II, OPHIR) was placed behind the PAS spectrometer to monitor the laser power. In the following sections, the PAS signals were normalized with respect to laser power to eliminate signal fluctuation due to laser power jitter in long-term measurements. A temperature and humidity sensor (TH22R-EX) was connected to the D-PAS system to measure the temperature and relative humidity (RH) of the sample. A LabVIEW program was written to record laser power, RH, temperature, and PAS signals simultaneously.

3. Design and optimization of the acoustic resonator using finite element method simulation

Acoustic resonators are widely used in the PAS spectrometer to amplify PAS signals [35]. Thus, an acoustic resonator is a critical component for a high-performance PAS spectrometer. In the present work, the acoustic resonator was designed and optimized using finite element method (FEM) simulation. The material used in the finite element model is air, and the air density value comes from the material library of the simulation software, and its value is 1.205 kg/m³. The temperature and pressure set in the finite element model are 293.15 K and 1 atm respectively. Using the numerical calculations, the acoustic resonator’s basic characteristics, such as eigenfrequencies and Q_FEM factors, can be predicted and will provide a reference to optimize the structure of photoacoustic cell [36,37]. In addition, the photoacoustic signal can also be calculated by the finite element method [36].

In order to design a suitable photoacoustic cell for aerosol measurement, the impact of the acoustic resonator size (radius and length) on the PAS spectrometer performance (such as frequency and photoacoustic signal) was simulated. The simulated results are shown in Fig. 2. Fig. 2 (a) plots the resonant frequency of the longitudinal (100) mode of an acoustic resonator with different inner radii and lengths. Fig. 2 (b) plots the Q_FEM-factor of the longitudinal (100) mode of an acoustic resonator with different inner radii and lengths. Fig. 2 (c) plots the simulated PAS signals of the longitudinal (100) mode of an acoustic resonator with different inner radii and lengths.

As shown in Fig. 2 (a), the photoacoustic cell’s resonant frequencies decrease monotonically as the resonator length increases, while there is no apparent relationship between the resonant frequencies and the resonator radius. Secondly, Fig. 2(b) shows that the Q_FEM-factors of the photoacoustic cell decrease as the length of the acoustic resonator increases, and increase as the radius of the acoustic resonator increases. Fig. 2 (c) shows the PAS signal increasing with the increasing of the resonator length and decreasing with an increase in the resonator’s inner radius. This is consistent with the theory that the PAS signal is inversely proportional to the effective cross-section ¼ (V and L are the acoustic resonator’s volume and length, respectively) [35]. Hence, it is easier to improve the detection sensitivity of an acoustic resonator with a small radius. Considering the beam size of the LD employed and the 1/f noise, an acoustic resonator with a radius of 5 mm and a length of 110 mm (corresponding to a resonant frequency of 1474 Hz and a Q_FEM-factor of 60) was selected. By choosing these parameters, the laser will not irradiate the inner wall of the resonator, and thus will not produce a background signal. Simultaneously, the acoustic resonator has a high resonance frequency, which avoids the interference of low-frequency noise. Two buffers with a radius of 35 mm and a length of 55 mm are connected to the both sides of the resonator (Fig. 3). The buffers act as a soft acoustic field boundary, and the PAS signal forms a pressure node at the interface between the resonator and the buffer. The buffers can effectively filter the noise resulting from light absorbed by the window [35], flow noise, and environment noise. Fig. 4 shows the normalized simulation PAS signal distribution along the optical axis of (100) mode of the designed photoacoustic cell. The microphone is usually placed in the middle of the resonator, which corresponds to the sound pressure’s antinode. It can be seen in Fig. 4 that the PAS signal gradually decreases to zero in the buffer area, which is caused by the end correction of the acoustic resonator. This observation can be explained by the effects of a mismatch between the one-dimensional sound field in the resonator and the three-dimensional sound field in the buffers [35].

Fig. 5 shows the normalized D-PAS signal as a function of the frequency. The experimental data were fitted to a Lorentz contour, which describes the power in a classical driven oscillator as a function of frequency. The optimum resonant frequency of the photoacoustic cell is
1430 Hz. This corresponds to the first-order longitudinal resonance frequency of the photoacoustic cell. This frequency will be used in the following measurements as the amplitude modulation frequency of the laser diode. The error between the resonance frequency measured by the experiment and the resonance frequency calculated by the finite element simulation is 3%. This result shows that the finite element method is a reliable method to calculate the resonance frequency of the photoacoustic cell. The calculated Q factors of photoacoustic cell 1 and photoacoustic cell 2 are 37 and 36, respectively.

When using a PAS spectrometer for actual atmospheric detection, the sampling flow rate should generally not be too high. Otherwise, the photoacoustic cell will generate considerable flow noise, which will affect the accuracy of the measurements (for example, the sampling flow rate in reference [11] is 200 mL/min, the sampling flow rate in reference [12] is 330 mL/min, and the sampling flow rate in reference [27] is 400 mL/min). To increase the total flow rate to improve the time response of the D-PAS sensor, four additional airways were arranged in the acoustic resonator, as shown in Fig. 6. The radius of the airways was 4 mm, such that the particle deposition loss in the sampling lines can be neglected [38]. Fig. 6(a) and (b) are simulations of the flow velocity field in the photoacoustic cell without and with additional airways, as indicated by arrows. Although the flow rate at the inlet of each photoacoustic cell is the same, the total aerosol flow is shunted by the additional airways, which reduce the flow rate in the resonator. After these four additional airways in the acoustic resonator have been inserted, the photoacoustic system can be operated with high flow rates without being affected by the flow noise, while it also reduces the sample residence time and hence improves the time response of the D-PAS.

Fig. 7(a) shows the noise level measured in the D-PAS system when operated at different flow rates with and without four additional airways. The experimental results show that in the acoustic resonator with additional airways, the flow noise will not increase substantially until the flow rate exceeds 1400 sccm. However, in the acoustic resonator without additional airways, the flow noise was substantially increased when the flow rate exceeded 600 sccm. Considering that the photoacoustic cell with four additional airways can work at higher flow rates without being disturbed by flow noise, this improved acoustic resonator is used in the actual atmospheric measurement in this work. The sample flow rate was set to 1000 sccm. Fig. 7(b) is an investigation of the sensor response speed at a gas flow rate of 1000 sccm. High purity N₂ and 2 ppm NO₂ were periodically passed through the photoacoustic cell. Since NO₂ will undergo adsorption and desorption processes after entering the photoacoustic cell, it takes a long time to reach equilibrium in the photoacoustic cell.

4. Results and discussion

4.1. Calibration of the D-PAS sensor

Before using the developed D-PAS sensor to measure the aerosol optical absorption coefficient, NO₂ was used to calibrate the PAS system to obtain the product of microphone sensitivity and cell constant (Eq. 4, namely, $M \cdot C$). Different concentrations of NO₂ were obtained by diluting 5 ppm of NO₂/N₂ (Nanjing Special Gases) with high purity N₂ ($\geq 99.999\% \geq 99.999\%$, Nanjing Special Gases). The accurate NO₂ concentrations were measured by the NOx gas analyzer (Model 42i). An
effective absorption cross-section $\sigma(\lambda)$ within the broadband LD emission region is calculated [39]:

$$\sigma(\lambda) = \sum_{i=1}^{n} \sigma(\lambda_i) g(\lambda_i)$$  (1)

$$\sum_{i=1}^{n} g(\lambda_i) = 1$$  (2)

where $\sigma(\lambda_i)$ (cm$^2$/molecule) represents the absorption cross-section of NO$_2$ obtained from the HITRAN database [40], and $g(\lambda_i)$ is the normalized optical power density distribution function.

Based on Eqs. (1) and (2), an effective absorption cross-section of $4.21 \times 10^{-19}$ cm$^2$/molecule over the full laser emission spectral region was calculated. The absorption coefficient of NO$_2$ can be calculated with the following equation [39,41]:

$$\alpha = N_L \frac{296}{T} P_1 \sigma(\lambda) c$$  (3)

where $N_L = 2.479 \times 10^{19}$ molecule·cm$^{-3}$·atm$^{-1}$, $T$ (K) and $P_1$ (atm) are the temperature and pressure of the NO$_2$ sample, respectively, and $c$ is the concentration of NO$_2$. The value of $\alpha$ (Mm$^{-1}$) converted into the NO$_2$ mixing ratio (ppb) is 1.04 Mm$^{-1}$/ppb.

The calibration will be performed based on the following equation:

$$S = \alpha P_2 M C$$  (4)

where $S$ (mV) is the photoacoustic signal with background removed, $\alpha$ (Mm$^{-1}$) is the corresponding NO$_2$ absorption coefficient, $P_2$ (mW) is the LD power, $M$ (mV/Pa) is the microphone sensitivity, and $C$ (Pa/(mW·Mm$^{-1}$)) is the cell constant.

The calibration results are displayed in Fig. 8. The upper and lower abscissas represent the concentrations and the absorption coefficient of NO$_2$, respectively, and the ordinate is the PAS signal after power normalization. The difference between the calibration results of the two Fig. 6. The simulated flow velocity field in the photoacoustic cell. (a) Without and (b) with additional airways. The right sides are the cross-sections of corresponding photoacoustic cells.

Fig. 7. (a) Noise levels of the developed D-PAS system with and without additional airways at different flow rates; (b) Investigation of the sensor response speed at 1000 sccm gas flow rate.

Fig. 8. Calibration results of the developed D-PAS.
photoacoustic cells is related to machining errors and used microphone sensitivity of $M$ (mV/Pa) of each cell, which cause the cell constants of the two photoacoustic cells to be different. From Fig. 8, it is obvious that the photoacoustic cell 2 offer larger signal value than photoacoustic cell 1 for the same absorption.

4.2. Performance evaluation

The detection limits and measurement precision of the developed D-PAS were evaluated using a time series measurement of $N_2$ filled in the photoacoustic cell [42,43]. The time resolution of each measurement was 1 s. Fig. 9(a), (b) plots the detection limits from photoacoustic cell 1 and photoacoustic cell 2, respectively. Allan deviation analyses provide detection limits of about 1.0 Mm$^{-1}$ and 0.9 Mm$^{-1}$ (0.87 ppb) within 1 s for the two photoacoustic cells, respectively. These detection limits could be further improved down to 0.14 Mm$^{-1}$ and 0.09 Mm$^{-1}$ (0.09 ppb) when using integration times up to 150 s and 480 s, respectively. Histogram plot of the measured data is show in Fig. 9(c), (d), which can be used to evaluate the measurement precision of the D-PAS sensor. The data distributions were Gaussian profile, and the measurement precision is the half width at half maximum (HWHM) of the Gaussian fitting curve. For a 1 s integration time, the measurement precision of photoacoustic cells 1 and 2 are 1.7 Mm$^{-1}$ and 1 Mm$^{-1}$, respectively. The difference of Allan deviation between photoacoustic cell 1 and cell 2 is mainly caused by the cell constant. Photoacoustic cell 2 offer better performance than photoacoustic cell 1 as photoacoustic cell 2 offer higher cell constant than photoacoustic cell 1, as shown in Fig. 8. These detection limits could allow the developed D-PAS to measure ambient aerosol and NO$_2$ in real-time.

4.3. Gas interference analysis

Potential spectral interferences for D-PAS to measure aerosols and NO$_2$ at 443 nm, mainly resulted from the molecules (NO$_3$, O$_3$, N$_2$O$_3$, O$_4$) [44] are discussed below.

1. The absorption cross-section of NO$_3$ is about $3.82 \times 10^{-19}$ cm$^2$/molecule at 443 nm, and its concentration is about 1–200 pptv in the atmosphere [45]; accordingly, the absorption coefficient can be estimated as $9.41 \times 10^4 - 1.88 \times 10^5$ Mm$^{-1}$.

2. O$_3$ is a major pollutant in the atmosphere, and its concentration ranges from 10 to 500 ppbv [45]. Given its absorption cross-section of $1.82 \times 10^{-22}$ cm$^2$/molecule at 443 nm, its absorption coefficient is about $4.48 \times 10^{-5} - 2.24 \times 10^{-4}$ Mm$^{-1}$.

3. The absorption cross-section of N$_2$O$_3$ for $\lambda > 420$ nm is missed in the database. Therefore, its absorption cross-section at 420 nm is used to estimate its absorption coefficients to be between $2.46 \times 10^{-7} - 7.39 \times 10^{-5}$ Mm$^{-1}$, with concentrations in the range of 2–600 ppbv [46].

4. O$_4$ bands are used in differential optical absorption spectroscopy (DOAS) to infer information about aerosols [47]. The absorption coefficient of O$_4$ of about $4.37 \times 10^{-7}$ Mm$^{-1}$ at 443 nm [47] was calculated using the following equation:

$$\alpha_{O_4} = \alpha_{O_4}O_{2mr}N_d^2$$

where $\alpha_{O_4}$ is the O$_4$ absorption coefficient, $\alpha_{O_4}$ (cm$^5$·molecule$^{-2}$) is the corresponding absorption cross-section, $O_{2mr}$ is the oxygen mixing ratio (20.95 %v/v), $N_d$ is the number density.

Table 1 summarizes the absorption coefficients of the trace gases (NO$_2$, O$_3$, N$_2$O$_3$ and O$_4$) discussed above. Fig. 10 shows the upper absorption coefficients of these molecules. It is clearly shown that the absorption coefficients of these gases in the atmosphere are under the detection limit of the developed D-PAS sensor. Therefore, the interference from these gases can be neglected.

Potential interference from water vapor absorption in the laser emission wavelength of 443 nm was also considered. For this purpose,

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**Fig. 9.** (a), (b) Allan deviation from time series measurements of $N_2$ sealed in the D-PAS; (c), (d) Histogram plot obtained from times series measurement of $N_2$ sealed in the D-PAS.
Table 1
Summary of the absorption coefficient of trace gases in the atmosphere.

| Trace gases | Absorption coefficient (Mm⁻¹) |
|-------------|-------------------------------|
| NO₂         | 10.37⁻³                      |
| NO₃         | 9.41 × 10⁻⁴, 1.88 × 10⁻¹      |
| O₂          | 4.48 × 10⁻³, 2.24 × 10⁻¹      |
| N₂O₅        | 2.46 × 10⁻⁵, 7.39 × 10⁻⁵, 5.43 × 10⁻² |
| O₃          | 4.37 × 10⁻²                   |

* Absorption coefficient of 10 ppb NO₂ [5].
* Absorption coefficient of N₂O₅ at 420 nm.

Fig. 10. Upper absorption coefficients of NO₂, O₃, N₂O₅, and O₃ are listed in Table 1.

N₂ was humidified using a humidifier (Perma Pure, USA, Model MH-110-24F-4) before fed into the photoacoustic cell. The PAS signals (noise) for different humidity of N₂ are shown in Fig. 11. As shown in Fig. 11, the PAS signals remain almost unchanged when the water vapor concentration ranges from 0.38 % to 1.38 % (RH is between 20 % and 75 %, the temperature is about 16 °C). Therefore, potential interference from water vapor absorption could be neglected for the developed D-PAS.

4.4. Atmosphere measurements

Measurement of aerosol optical absorption and NO₂ concentration in the atmosphere was carried out at Anhui Institute of Optics and Fine Mechanics (AIOFM) in Hefei (China). During measurement, the NO₂ was also monitored by using a NOx analyzer for comparison. The sample inlet was about 2.5 m above ground level. The sampling location is between two roads with fewer vehicles, which is about 70 m from the front road and 20 m from the back road. Since the measurement location is close to urban and rural areas, the measurement data will be affected by straw burning in rural areas, vehicle exhaust emissions in urban areas, and industrial emissions.

To measure the absorption coefficient of aerosols, another special issue should be considered. In high RH, the evaporation of water vapor will affect the photoacoustic signal [48-50]. Therefore, the RH in measuring the absorption characteristics should be less than 30 % to ensure measurement accuracy. Meanwhile, the resonant frequencies vary with the change of environment temperature and RH. Hence, a relatively stable temperature and RH are necessary for accurate atmospheric measurements. A diffusion drying tube was mounted on the sampling line to maintain the RH at about 20 %. Furthermore, the measurement process was carried out in an air-conditioned room with a temperature stabilized at 20 °C.

Using the calibrated D-PAS, measurements of ambient aerosol optical absorption coefficients and NO₂ concentration were performed. Fig. 12 shows the time series measurement results of the aerosol absorption coefficient and NO₂ concentration in the winter of 2019. The measured data were averaged in 5-minute intervals. Fig. 12(a) shows the aerosol optical absorption coefficient measured by D-PAS. The NO₂ concentration monitored by a near environmental monitoring station, which was approximately 2 km from the laboratory, is also shown in Fig. 12(b) for comparison.

To further confirm the developed D-PAS’s performance, comparison measurements of ambient NO₂ with the D-PAS and NOx analyzer were carried out during a clear day in the summer of 2020. The measured NO₂ by D-PAS shows good agreement with an independent NOx analyzer (Fig. 13(b)). For convenience comparison, the NO₂ concentration recorded by the environmental monitoring station is also shown in Fig. 13(b). It can be seen from Fig. 13(b) that the NO₂ concentration of the environmental monitoring station is higher than the results measured by the D-PAS and NOx analyzer, but the general trend is the same. This difference may be caused by the fact that the laboratory and the environmental monitoring station (~2 km away from laboratory) are not in the same location. In Fig. 13(a), the aerosol absorption is weak, which agrees with the fact that there was less particulate matter in the air. The concentration of NO₂ gradually increased from 6:00 to 7:00. This fact may be related to the emissions of automobile exhaust. The aerosol absorption coefficient appeared at a broad peak from 2:00 to 3:00. This observation may be related to the atmospheric chemical reaction process at night. D-PAS will be further used in conjunction with a particle counter to monitor aerosols’ light absorption characteristics and the concentration of NO₂ for a long time and analyze their changing trends.

5. Conclusion

In this work, the development of a 443 nm LD-based D-PAS sensor is reported that is capable of measuring simultaneously ambient aerosol and NO₂ with a high flow rate. Minimum detection limits of 1.0 Mm⁻¹ (1 s) and 0.87 ppb (1 s) were obtained for aerosols (using photoacoustic cell 1) and NO₂ (using photoacoustic cell 2), respectively. In comparison, Haisch et al. developed a PAS spectrometer for artifact-free parallel measurements of soot and NO₂ in engine exhaust [14]. The instrument has a detection sensitivity of 0.3 ppm for NO₂ and a detection sensitivity of 0.54 μg m⁻³ (4 Mm⁻¹) for soot. Sample flow noise was decreased by arranging four additional airways in the acoustic resonator that enable

Fig. 11. PAS signals of N₂ with different concentrations of water vapor.
the D-PAS to work at high flow rates while improving the response time. Potential absorption interference analysis has shown that no other gases will affect the measurement results. Aerosol optical absorption and NO$_2$ concentration in the ambient air were measured by the D-PAS. The experimental results are consistent with the results of the NOx analyzer and environmental monitoring station. This fact demonstrates that the developed D-PAS offer good performance and has the capacity to measure atmosphere aerosol and NO$_2$ simultaneously. In the future, the D-PAS will combine with other reference instruments, such as the scanning mobility particle sizer (SMPS) and the cavity ring-down spectrometer, for more detailed atmospheric studies and intercomparison investigation.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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photoacoustic spectroscopy and laser spectroscopy for application in atmospheric photochemistry and environmental science.

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