Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

Atmospheric Measurement Techniques Discussions

Simultaneous measurement of NO and NO_2 by dual-channel cavity ring down spectroscopy technique

Renzhi Hu (1)†*, Zhiyan Li (1, 2) †, Pinhua Xie (1, 3, 5) *, Hao Chen (1), Xiaoyan Liu(4), Shuaixi Liang (1, 2), Dan Wang (6), Fengyang Wang(1), Yihui Wang(1,3), Chuan Lin (1), Jianguo Liu(1, 3, 5), Wenqing Liu(1, 3, 5)

(1) Key Lab. of Environmental Optics and Technology , Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031,China.

(2) Science Island Branch of Graduate School, University of Science and Technology of China. Hefei 230026, China.

(3) School of Environmental Science and Optoelectronic Technology, University of Science and Technology of China, Hefei 230027, China

(4) College of Pharmacy, Anhui Medical University, 81 Meishan Road, Hefei 230032, China

(5) CAS Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361000, Fujian, China

(6) School of Mathematics and Physics, Anhui University of Technology, Ma an Shan 243032, China

†These authors contributed equally to this work.

*e-mail: rzhu@aiofm.ac.cn, phxie@aiofm.ac.cn

Key words: NO_x; CRDS; CEAS; CL

Abstract

Nitric oxide (NO) and nitrogen dioxide (NO_2) are relevant to air quality due to their role in tropospheric ozone (O_3) production. In China, NOx emissions are high and exhausted from on-road vehicles make up 20% of total NOx emissions. Too much NO_x are harmful to the human body and animals. In order to detect the NO and NO_2 emissions on road, a dual-channel CRDS system for NO_2 and NO detection is reported. In this system, NO is converted to NO_2 by its reaction with excess O_3 in NO_x channel, such that NO can be determined through the difference between two channels. The detection limits of the developed CRDS system for NO_2 and NO_x measurements are estimated to be about 0.030 ppb (1σ, 1 s) and 0.040 ppb (1σ, 1 s), respectively. Considering the error sources of NO_2 absorption cross section and R_L determination, the total uncertainty of NO_2 measurements is about 5%. The CRDS method is capable of measuring species with high sensitivity and accuracy. The performance of the system was validated against a chemiluminescence (CL) analyzer (42i, Thermo Scientific, Inc.) when measuring the NO_2 standard mixtures. The results of NO_2 with standard mixtures sampled showed a linear correction factor (R^2) of 0.99 in a slope of 1.031 ± 0.006, with an offset of (-0.940 ± 0.323) ppb. An intercomparison between the system and a cavity-enhanced absorption spectroscopy (CEAS) instrument for NO_2 measurement was also conducted alone in ambient environment. Least-squares analysis showed that the slope and intercept of the regression line are 1.042 ± 0.002 and (−0.393 ± 0.040) ppb, respectively, with a linear correlation factor of R^2 = 0.99. Another intercomparison conducted between the system and the CL analyzer for NO detection also showed a good agreement within their uncertainties, with an absolute shift of (0.352 ± 0.013) ppb, a slope of 0.957 ± 0.007 and a correlation coefficient of R^2 = 0.99. The measurements of on-road vehicle emission plumes by this mobile CRDS instrument show the different emission characteristics in the urban and

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

Atmospheric Measurement Techniques Discussions

suburban areas of Hefei. The instrument provides a new method for retrieving fast variations of NO and NO_2 plumes.

1. Introduction

In recent years, with the improvement of people's living standard, people pay more and more attention to the improvement of the living environment. Among which, the management of environmental pollution has gradually become one of the focus issues. The detection of pollutants is an important premise for environmental governance. NO_x (NO_x= NO+NO_2) are byproducts of organic decay, natural forest fires as well as anthropogenic emission both from stationary sources (electric power generation using fossil fuels) (Jaramillo and Muller, 2016) and mobile sources (motor vehicles and catalytic converters of most cars) (Carslaw, 2005). NO_x are both primary pollutants and secondary pollutants (Crutzen, 1979), which can determine the tropospheric O_3 levels and lead to the formation of photochemical "smog" and the visibility decline due to the secondary aerosol formation. Furthermore, NO_x are also the precursors of nitric acid (Brown et al., 2004). Moreover, NO_x are harmful to the human body and animals. Too much high NO_x can damage the respiratory system and lead to pulmonary edema (Yang and Omaye, 2009). In addition, accurate NO_2 measurement plays a key role in accurate measurement of other species, such as organic nitrate (Thieser et al., 2016; Paul et al., 2009; Day et al., 2002) and RO_2 radicals (Chen et al., 2016).

During the last few years, many direct and indirect techniques for monitoring NO_2 have been established. NO_2 concentration can be measured with chemiluminescence (CL) detection (Yuba et al., 2010; Sadanaga et al., 2008; Fahey et al., 1985), differential optical absorption spectroscopy (DOAS) (Platt et al., 1984;R. McLaren, 2010), tunable diode laser absorption spectroscopy (TDLAS) (Li et al., 2004), cavity ring-down spectroscopy (CRDS) (Castellanos et al., 2009; Fuchs et al., 2009; Osthoff et al., 2006; Fuchs et al., 2010; Brent et al., 2013 ; Hu et al.,2015), cavity enhanced absorption spectroscopy (CEAS) (Wu et al., 2009; Gherman et al., 2008; Kasyutich et al., 2006; Wada and Orr-Ewing, 2005), cavity attenuated phase shift spectroscopy (CAPS) (Kebabian et al., 2008), laser-induced fluorescence (LIF) (Taketani et al., 2007; Matsumi et al., 2010; Sadanaga et al., 2014; Matsumoto et al., 2001) measurement, long path absorption photometer` (LOPAP) (Villena et al., 2011) and gas based sensors (Novikov et al., 2016), with CL being the most widely used for ambient in situ sampling. CL can achieve direct measurement of NO and indirect measurement of NO_2. The method is based on the reaction between NO and O_3, which can form an electronically excited molecule of NO_2*. When NO_2* reaches the ground state, it emits fluorescence which is proportional to the NO value. NO_2 is measured by its conversion to NO and usually heated (300 ℃ to 350 ℃) molybdenum (Mo) surfaces (Ridley and Howlett, 1974) or photolytic NO_2 converters like Xenon lamps or UV emitting diodes at specific wavelength (320 nm-400 nm) are used. The CL instruments have typical NO_2 detection limits of 50 ppt / 1 min （1σ）(Wang et al., 2001). CRDS，CEAS, CAPS and TDLAS relying on scanning a light source through a range of frequencies of interest are all direct absorption techniques. These techniques can achieve a high sensitivity of several seconds and a low detection limit of ppt level (Li et al., 2004; Wild et al., 2014; Gherman et al., 2008; Kebabian et al., 2008). Among these techniques, CRDS has become a promising technique for ambient NO_2 detection due to its advantages of high time resolution, low detection limit as well as portability, in which pulsed (Fuchs et al., 2009) and continuous-wave (cw) (Wada and Orr-Ewing, 2005) lasers were utilized. Wada et al. (Wada and Orr-Ewing, 2005) demonstrated a cw diode CRDS system operating at 410 nm for the retrieval of NO_2 mixing ratios in ambient air with a detection limit of 0.1 ppb in 50 s at atmospheric pressure. Osthoff et

al. (Osthoff et al., 2006) constructed a pulsed cavity ring-down spectrometer which used a pulsed (20–100 Hz, up to 25 mJ) frequency-doubled Nd:YAG laser for the simultaneous measurements of NO_2, nitrate radical (NO_3), and dinitrogen pentoxide (N_2O_5) in the atmosphere. The NO_2 detection limit (1σ) for 1 s data was 40 ppt with an uncertainty within ± 4% under laboratory conditions. Fuchs (Fuchs et al., 2009) used a simple, lightweight, low power, commercially available Fabry-Perot (FP) diode laser with a center wavelength of 403.96 nm as a light source to detect NO and NO_2 in two separate channels. The limit of detection is 22 ppt (2σ precision) for NO_2 at 1 s time resolution. Karpf (Karpf et al., 2016) used a high-power, multimode Fabry Perot (FP) diode laser with a broad wavelength range ($\Delta\lambda_{laser} \sim$ 0.6 nm) to excite a large number of cavity modes, thereby reducing the susceptibility of the detector to vibration and making it well suited for field deployment. A sensitivity of 38 ppt was achieved using an integration time of 128 ms for single-shot detection. A number of intercomparison studies demonstrating the accuracy of these research grade instruments have been carried out (Xu et al., 2013; Dunlea et al., 2007; Villena et al., 2012) to evaluate the uncertainty of each instrument. The comparison results show that the method based on Mo converters is affected by significant interferences such as N_2O_5, HONO, HNO_3, PAN, etc. Whereas the method based on optical absorption is relatively immune to interferences. Therefore, direct techniques are considered to be more reliable methods than the CL method for the measurement NO_2 and have also been used in field experiments (Ayres et al., 2015; Wagner et al., 2013; Sobanski et al., 2016).

In addition to the direct measurement of NO with the CL method, NO concentrations can be measured based on their absorption feature at 1,585.282 cm^{-1} directly. For this method, a tunable infrared laser differential absorption spectroscopy (TILDAS) instrument, utilizing an astigmatic multi-pass Herriott cell (Herndon et al., 2004) and a dual-wavelength spectrometer, based on a DFB laser emitting sequentially at 1,600 cm^{-1} and 1,900 cm^{-1} have been used for the measurement of the two species (Jagerska et al., 2015). The 1 s precision for NO measurement of the TILDAS instrument was 550 ppt, whereas that for the field experiments was 1.5 ppb. Thus, this technique may suffer from low detection sensitivity compared with the CL method. Given the rapid changes of nighttime oxidation, i.e., NO_3 radical, understanding the rapid changes of its precursors, NO and NO_2 is thus a critical prerequired information to develop a nighttime atmospheric chemistry model. Conversion to NO_2 by adding excess O_3 can provide an indirect method for NO detection, which can achieve high sensitivity and high resolution (Fuchs et al., 2009; Wild et al., 2014).

The development of different technology provide the potential for NOx measurements on different platforms such as ground sites, vehicles as well as aircrafts (Yamamoto et al., 2011; Wagner et al., 2011; Castellanos et al., 2009). Due to the rapid economic growth in 2000-2010, China has become the second largest economy in the world. With the rapid growth of energy consumption, NOx emissions is increasing. Motor vehicles are one of the major sources for NOx, especially in urban areas (Westerdahl, 2008). Exhaust from on-road vehicles makes up 20% of total NOx emissions in China (Shi et al., 2014). So a variety of methods have been used to measure the vehicle emissions to access air pollutant exposures and specifically impacts due to traffic-related emissions (Vogt et al., 2003; Carslaw and Beevers, 2004; Herndon et al., 2005; Lal et al., 2005; Burgard et al., 2006b; Hueglin et al., 2006; Burgard et al., 2006a; Wild et al., 2017). However, the methods are usually applied to monitor air pollutants at several locations in large cities, the selection of which is critical for achieving representative measurements. The number of monitoring locations is not adequate to show the large scale patterns of the city. Hence, a direct on-road mobile instrument can be used to help obtain the spatial and temporal variations of NOx pollutants.

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

Here, we describe a dual-channel CRDS system based on the chemical conversion NO to NO_2 to measure NO_2 and NO_x simultaneously. In one channel, the sum of converted NO_2 from ambient NO and ambient NO_2 is determined to provide a direct measurement of NO_x. In another channel, only ambient NO_2 is measured. The subtraction of NO_2 measured in a second, independent channel provides a direct measurement of NO alone. Measurements and comparison of NO_2 and NO between different instruments were conducted to assess the accuracy of the dual-channel CRDS instrument. In addition, the measurement of on-road vehicle emission plumes from the instrument during December 17, 2018 in the region of Hefei, China was deployed. The main advantages of this instrument compared with CL instruments are its low detection limit and high sensitivity as well as its potential ability for trace measurements without calibration and interferences.

2. Setup of the instrument

Cavity ring-down spectroscopy has been applied to measurement NO_3 radical and N_2O_5 in our group (Wang et al., 2015; Li et al., 2018; Li et al., 2018). In this work, the technique is applied to measure NO_2 and NO. A schematic diagram of the dual-channel CRDS system developed in the present work is shown in Fig. 1. The instrument mainly consists two identical CRDS systems for NO_2 and NO_x detection, gas handling system, NO convertor and activated carbon device for NO_x removing.

2.1. CRDS systems

A blue diode laser is used as the light source and the wavelength of the laser is monitored by a spectrometer. The output of the diode laser with a center wavelength at 403.64 nm and a line width of 0.5 nm is directly modulated by a square wave signal (on/off) at a repetition of 2 kHz with a duty cycle of 50% and the output power is about 60 mW. The light emitted by the laser first passes through an isolator to prevent the reflected light into the laser and then enters into two identical cavities through two reflecting mirrors and a 50/50 beam splitter. Each optical cavity is made of an aluminum tube with an inner diameter of 9.4 cm. The two cavities are fixed rigidly by two frames, respectively. Two high reflectivity mirrors are held in stable, adjustable mounts. The distance of two highly reflective mirrors (LGR, 1 in. diameter, 1 m radius of curvature) is 75 cm for both channels. Consequently, ring-down time constants in NO_x and NO_2 cavities are 22.90 μs and 24.12 μs in dry N_2. The light emitted through the back mirror of the cavity passes through a narrowband filter to filter stray light and then is directed into a PMT. The signal passes through an amplifier and then enters into the digital acquisition card (NI USB-6361, 16-bit, 2.0 Ms/s). The digital acquisition card is 1 MHz for each channel. Data are acquired on the data acquisition board for a continuous period of 1.0 s during which 2000 decay traces are transferred to the PC using a single transfer command and averaged to get a fitted decay trace at a laser modulation rate of 2 KHz. The software algorithms calculate NO_2 concentration from, τ and τ_0, the ring-down time when the NO_2 is in the presence and absence of the cavity, respectively; the NO_2 absorption cross section, σ; the ratio of the total cavity length to the length over which the absorber is present in the cavity, R_L and the speed of the light, c. The concentration of the sample can be expressed as follows:

$$[NO_2] = \frac{R_L}{c\,\sigma_{NO_2}} \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \quad (1)$$

2.2. NO convertor

NO is measured by its conversion to NO_2 by adding excess O_3. The principle is based on the following chemical equation (Sander et al., 2006).

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

$$NO + O_3 \rightarrow NO_2 + O_2 \quad k_1 \qquad (R1)$$

Where $k_1 = 3.0 \times 10^{-12} \exp(-1310/T)$ $cm^3\ molec^{-1}\ s^{-1}$. Ozone is produced from O_2 photolysis at 185 nm by flowing 100 sccm of sampling air which is controlled by a MFC over a low pressure discharge mercury lamp. The mercury is inset into a quartz glass tube with a length of 50 mm and an inner diameter of 10mm. The flow rate passing through the mercury lamp was investigated and the resulting mixing ratio of O_3 was detected by an O_3 analyzer (49i, Thermo Scientific). The O_3 concentration is approximately 11.2 ppm after mixing with the sampled air. A length of Teflon tubing (length 1 m, i.d. 3.8mm) serves as a reactor for the NO conversion.

2.3. Activated carbon device

Background measurement of τ_0, that is the ring down time when the absorber is in the absence of the cavity, is important for accurately retrieving the absorber concentration as well as for checking the cleanliness of the cavity mirrors. Usually zero air or chemical scrubber is used to acquire zeros (Wada and Orr-Ewing, 2005). In our system, zeros are obtained by passing sampled air through an activated carbon filled tubing with an outer diameter of 6.0 cm and a length of 26.0 cm through a three-way solenoid valve located below the filter holder. The τ_0 is measured for 60 s every 10–16 min. This frequency of zero measurements is observed to be sufficient to track drifts in the zero ring-down time constant measurement, with a stability of successive τ_0 below 0.1% for 15 min intervals.

2.4. Gas handling system

The instrument gas handling system consists of sampling module and purge flow. The sampled air initially flows through a filter device loaded with filtering membrane (1 μm pore size) to prevent light-scattering aerosols from entering the cavity with a rotary pump (K86KNE) and subsequently passes through the activated carbon device to provide the background measurement when the three-way solenoid valve is open or is directed toward the PFA tube when the three-way solenoid valve is closed. The air flow from the PFA tube is divided into three lines. Among which, 100 sccm sampled air, which is introduced into a quartz flow tube equipped with a mercury pen-ray lamp (Oriel 6035) to generate O_3 by air photolysis as mentioned previously is merged with another 900 sccm sampled air and pulled into the NO_x cavity. The third flow with a flow rate of 1 slm is directed into the NO_2 cavity. The flow rates of all of the gases are controlled by mass flow controllers. Each mirror is isolated from the sample flow by a purge volume that is continuously flushed with high-purity nitrogen at a rate of 25 ml min^{-1} to prevent the degradation of the mirror reflectivity.

3. Results and discussion

3.1 Determination of Absorption Cross Sections

To retrieval the gas concentration, it is vital to determine the effective absorption cross section at peak absorption of the laser. The output waveforms of the laser, with a center wavelength of 403.64 nm and full width at half-maximum of 0.5 nm, was monitored by a spectrometer (QEPB0828) (red line shown in Fig. 2).The center wavelength selected can cover the strong absorption of NO_2 and avoid the interference from other species, such as H_2O (pink line in Fig. 2). The effective absorption cross section was determined to be $5.63 \times 10^{-19} cm^2$ /molecule by convolution the NO_2 absorption cross section by voigt (Voigt et al., 2002) with the laser spectrum (blue line in Fig. 2). A shift in the laser center wavelength would result in a change of the effective NO_2 cross-section. The day-to-day variability of

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

Atmospheric Measurement Techniques Discussions

the laser center wavelength was less than 1% by monitoring the laser output for a few days. The largest uncertainty of the absorption cross section is about 3% according to voigt (Voigt et al., 2002).

3.2 The retrieval of R_L

Due to the purge gas to the mirrors, the R_L value cannot be simply determined by the ratio of the distance between two mirrors to that between the inlet and outlet. The R_L value was determined from the absorption measurement of different concentrations of NO_2 ranging from 20 ppb to 70 ppb in the presence and absence of purge flow. The ratio of the two extinction measurements yielded a R_L value independent of the NO_2 cross section and concentration. The R_L value is determined to be 1.10 ± 0.03 for both the NO_x and NO_2 channels.

3.3 The retrieval of τ_0

In order to accurately determine the concentrations of trace gas by CRDS, it is very important to confirm background cavity loss measurements of τ_0 when the target gases are not inside the cavity. Several alternative background measurement methods which incorporate zero air, a mixture of oxygen and nitrogen, chemically scrubbed laboratory air (using hydroxyapatite), and laboratory air sampled through the stainless steel tubing coil have been reported (Wada and Orr-Ewing, 2005) and each experimental approach has its own merits and demerits. In our instrument, an activated carbon device was used for background measurement. The ring down times when the sampled air pass through the activated carbon device were determined to be 24.12 ± 0.01 μs and 22.90 ± 0.01 μs in two cavities, respectively. These values are close to those of measurements of zero air at the same sample rate for a 5 min period.

Two representative ring-down signals of the NO_2 from CRDS system when the NO_2 is in the presence and absence of the cavity are shown in Fig. 3. And the fitted ring down time were 24.12 μs and 20.30 μs respectively such that the NO_2 concentration is 20.28 ppb using the constants determined above.

3.4 Detection limit and measurement accuracy of two cavities.

The measurement precision of the dual-channel CRDS instrument for NO_2 and NO_x detection was investigated with time series measurement of zero air (Fig. 4). The acquisition time for the spectral data was 1.0 s with an average of 2000 spectra. In order to analyze the stability of the instrument, the Allan variance had been calculated for the intensity measurements. For the two channels, the minima in the Allan plots indicated the optimum average times for optimum detection performance (right panel of Fig. 4) to be about 30 s. With 30 s integration time, the 1σ detection limits were 16 ppt and 14 ppt for the NO_2 and NO_x channels, respectively.

The minimum detection can be written as follows:

$$[A]_{min} = \frac{\sqrt{2}R_L}{c\sigma}\left(\frac{\Delta\tau_0}{\tau_0^2}\right) \quad (2)$$

For continuous zero NO_2 measurements, the $\Delta\tau_0$ was 0.008 μs in both NO_x and NO_2 channels and τ_0 was 22.90 μs and 24.12 μs in NO_x and NO_2 channels, respectively when averaging the data to 1 s. Taking the R_L value to be 1.10 and σ to be 5.63×10^{-19} molecule/cm^2. The 1σ minimum detection limits determined from the previously presented equation for the NO_x and NO_2 channels are 39 ppt and 35 ppt at an integration time of 1 s, respectively, which were close to the Allan variance analysis described above.

The total uncertainty of NO_2 measurement by CRDS was from the errors in R_L and the NO_2

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

absorption cross section. The uncertainty in R_L was less than 3%, and the uncertainty in the NO_2 absorption cross-section was about 4%. Considering all of these errors, the total uncertainty of NO_2 measurement was determined to be 5%.

The minimum detection and uncertainty of our instrument is further compared with the existing field measurement techniques for NO_2 measurements. (Table 1).

3.5 NO Conversion Efficiency

The main factor determining the NO conversion efficiency was the flow rate passing through the mercury pen-ray lamp which therefore influences the generated O_3 concentration. The mixing ratio of O_3 in the NO_x channel line changing with the flow rate that passes through the mercury pen-ray lamp was investigated and the result was shown in Fig. 5. As a result, the bypass flow passing through the Hg lamp was determined to be 100 sccm. Under this condition, when the residence time of O_3 in the cavity is 1s and ambient NO_2 concentration is 50 ppb, NO conversion efficiency with different NO concentrations (10-1000 ppb) is simulated and NO conversion efficiency is larger than 98% .

Because the cross section of O_3 is about four orders magnitude of smaller than that of NO_2 at the center wavelength of the laser, the absorption of O_3 generated by mercury photolysis is negligible. According to Fuchs (Fuchs et al., 2009), under conditions when NO abundance is rich, further oxidation of NO_2 to NO_3 and N_2O_5 has only a slight effect on NO_x measurement, such that correction of the NO_x measurement can be neglected. However, under conditions when NO is absent, the loss of NO_2 due to oxidation by high concentration of ozone is indeed one of the main factors that attributes to the errors in the NO_x channel. The reaction equation is expressed as follows:

$$NO_2+O_3 \rightarrow NO_3+O_2 \qquad k_2 \qquad \text{(R2)}$$

$$NO_3+NO_2 \leftrightarrow N_2O_5 \qquad keq \qquad \text{(R3)}$$

where $k_2 = 1.2\times10^{-13}\exp(-2450/T)$ $cm^3\,molec^{-1}\,s^{-1}$ (T=298K, $k_2 = 3.2\times10^{-17}$ $cm^3\,molec^{-1}\,s^{-1}$)(Sander et al., 2006), $keq = (5.1\pm0.8)\times10^{-27}\exp(10871/T)$ $cm^3\,molec^{-1}\,s^{-1}$ (T=298K, $k_{eq} = 3.5\times10^{-11}$ $cm^3\,molec^{-1}\,s^{-1}$) (Osthoff et al., 2007) respectively. The loss rate will increase with the increase in the NO_2 + O_3 reaction rate constant when temperature in the cavity increases. Moreover, the loss rate is sensitive to the NO_2 mixing ratio. Diluted NO_2 standard mixture was introduced into two channels to characterize the effect of high concentration ozone on NO_2 measurement. The NO_2 concentrations and the correlation plot between data in the two channels are shown in Fig. 6. The interference of O_3 in NO_x channel when NO is absent can be neglected. The discrepancy between two different channels may be caused by the systematic errors in two different channels and can be corrected with the coefficient obtained from Fig. 6 (b).

4. Field applications

4.1 Standard mixtures of NO and NO_2 measurement.

The comparisons of NO_2 measurements between CRDS and NO_x analyzer have been carried out on NO_2 standard mixtures. Different mixing ratios of NO_2 were obtained by gas phase titration of NO with excess O_3, which was generated by an ozone generator (OC500). The 10.3 ppm NO standard mixture was initially diluted by N_2 and subsequently oxidized by O_3. The amount of NO_2 generated

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

Atmospheric Measurement Techniques Discussions

from excess ozone can be calculated from the known initial concentration of NO. The generated pure NO_2 standards in clean air were in the concentration range of 20-70 ppb. The CL analyzer used for comparison in this laboratory experiment was separately calibrated and the linearity of this instrument was checked using a mixture containing NO. Fig. 7 (a) shows the concentration of standard NO_2 in the laboratory measured by CRDS and simultaneously by a commercial CL analyzer (42i, Thermo Scientific, Inc., 0.4 ppb (1σ) detection limit). A correlation analysis between data from the two instruments was carried out. The fitting results shown in Fig. 7(b) indicate that $NO_{2\,(CRDS)} = NO_{2\,(CL\ analyzer)} \times 1.031 - 0.940$, with a linear correlation factor (R^2) of 0.99. The results in Fig. 7 (a) also indicates that CRDS instrument can capture the NO_2 variation more rapidly than CL analyzer.

4.2 Ground-based measurements of NO_2 and NO.

The NO_2 concentration measured by the dual-channel CRDS instrument was compared with the results obtained by a CEAS instrument (Duan et al., 2018) during the period from November 3 to 5, 2017 in the western suburb area of Hefei, Anhui, China. The CEAS instrument not the CL analyzer was selected for NO_2 intercomparison because the CL analyzer must convert NO_2 to NO, exposing itself to chemical interferences whereas the CEAS instrument directly detects NO_2. Measurement precisions (1σ) for NO_2 is about 170 ppt in 30 s. The time resolution of CRDS and CEAS instruments are 1s and 1min respectively. The CRDS and the CEAS instruments were setup on the sixth floor of the building but apart by tens of meters in Anhui Institute optic and Fine mechanics. The area directly (1–1.5 km) to the northeast and the south of the site is the Dongpu reservoir. The area in the northwest to north sector is surrounded by a mix of trees. The significant NO_2 pollution directly found during the measurement is the emission of the cars along the road (100 m radius). The air originated from the sector between the South and East (5 km) may bring the anthropogenic emission to the site. Ambient air was introduced into the instruments by use of a 6 mm outer diameter Teflon tube. The inlet of the Teflon tube was outside the building through the window. The data for comparison were averaged to 1min. Fig. 8 (a) shows the temporal variations of NO_2 concentrations measured by the CEAS and CRDS instruments. The nighttime NO_2 was in the range of 35 ppb to 3 ppb. The NO_2 concentrations and variations measured by the CRDS instrument were consistent with those measured by the CEAS instrument. The least-squares analysis showed that the slope and intercept of the regression line were 1.042 ± 0.002 and (-0.393 ± 0.040) ppb, respectively as shown in Fig. 8. However, the results revealed a discrepancy where rapid NO_2 variations appeared. We attribute this discrepancy to the slight difference between the two inlets of the instruments when large NO_2 was rapidly injected into the atmosphere. In general, the CRDS instrument has substantive advantages for retrieving rapid variations of NO_2 plums due to its high time resolution and high sensitivity.

The comparison of NO concentrations measured by the dual-channel CRDS instrument and CL analyzer was conducted under a variety of sampling conditions for a total of seven days at the site described previously. Both instruments were attached to the same air sample inlet. The data sets from the CRDS instrument and CL analyzer were highly correlated over wide concentration ranges of NO. Fig. 9 (b) shows the relationship between NO concentrations observed by the CRDS and CL methods. The slope and intercept of the regression line were 0.959 ± 0.007 and 0.352 ± 0.013 ppb. The correlation coefficient is R^2=0.99. The CL analyzer is capable of measuring NO reliably. Therefore, the dual-channel CRDS instrument is also considered to be a reliable method for the measurement NO.

4.3 On-road measurements of vehicle NO_2/NOx emission.

In order to retrieval the vehicle emissions on road, field measurements were performed in Hefei

from 15:00 to 16:00 CST on 17 December 2018. The CRDS instrument was powered by a lithium battery, and ambient air was pumped into the system though an inlet fixed on the roof of the car. The vehicle speed is about 50 km/h. In order to get the discrepancy of vehicle emissions in urban and suburban areas, the car travels along these areas. Fig. 10 shows a picture of the movable van loaded with CRDS instrument and the position of the sampling inlet, about 1.5 m above ground. illustrates the route in Hefei and the drive track is colored logarithmically with respect to measured NO_x、NO_2 and NO. The NO_2 concentration ranged from 1.5ppb to 133.3 ppb and NO ranged from detection limit to 554.7 ppb respectively. The mean concentrations of NO and NO_2 were 140 ppb and 54.9 ppb, respectively. NO and NO_2 concentration were higher in urban area than in suburban area. Large plumes of NO were found at the crossroads with heavy traffic or converged with heavy-duty diesel vehicles. [NO_2] / [NOx] ratio was about 19%, a number that is larger than the results in USA (Wild et al., 2017). Because The NO_2 to NOx emissions ratio affects ozone production and spatial distribution, more efforts should be done to provide a constraint on emissions inventories used in air quality modeling. The mobile CRDS instrument provides a good method to retrieval the direct vehicle NOx emission and plume NO_2 to NOx ratio due to its easy deployment and high temporal resolution.

5. Conclusion

Demonstration of a compact, sensitive, and accurate instrument for detection trace amounts of NO_2 and NO_x in ambient air has been achieved by using diode-laser cavity ring-down spectroscopy with the center wavelength of 403.64 nm. Minimum detection limits of NO_2 and NO_x were estimated to be 0.030 ppb and 0.040 ppb at an integration time of 1s when zero air is sampled with measurement accuracy of ±5%. Measurements of NO_2 using dual-channel CRDS instrument and CL analyzer on standard mixtures were performed in the present work which demonstrated a good correlation between these techniques. In order to confirm the reliability of the dual-channel CRDS instrument in the field atmosphere. Continuous measurement was conducted and the stability of the instrument was shown. When comparing the dual-channel CRDS instrument for NO_2 measurement with a CEAS instrument and NO measurement with the CL analyzer in the field, the results both showed a good correlation.

The CRDS instrument was deployed in a movable car to monitor NO and NO_2 emission on road. The advantage of high time resolution of the instrument can provide a direct method for on-road vehicle plumes measurement. Meanwhile, the instrument has high detection sensitivity, which can also provide a new detection technique for chemistry model verification. The instruments developed could lead to the wider application for ambient air quality monitoring and will be useful to investigate photochemistry in the atmosphere more precisely.

Acknowledgments

This work was supported by National Natural Science Foundation of China (61575206, 91644107, 41571130023and 61805257) and the National Key Research and Development Program of China (2017YFC0209401, 2017YFC0209403).

References

Ayres, B. R., Allen, H. M., Draper, D. C., Brown, S. S., Wild, R. J., Jimenez, J. L., Day, D. A., Campuzano-Jost, P., Hu, W., de Gouw, J., Koss, A., Cohen, R. C., Duffey, K. C., Romer, P., Baumann, K., Edgerton, E., Takahama, S., Thornton, J. A., Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Wennberg, P. O., Nguyen, T. B., Teng, A., Goldstein, A. H., Olson, K., and Fry, J. L.: Organic

nitrate aerosol formation via NO_3 + biogenic volatile organic compounds in the southeastern United States, Atmos. Chem. Phys., 15, 13377-13392, doi: 10.5194/acp-15-13377-2015, 2015.

Brent, L. C., Thorn, W. J., Gupta, M., Leen, B., Stehr, J. W., He, H., Arkinson, H. L., Weinheimer, A., Garland, C., Pusede, S. E., Wooldridge, P. J., Cohen, R. C., and Dickerson, R. R.: Evaluation of the use of a commercially available cavity ringdown absorption spectrometer for measuring NO_2 in flight, and observations over the Mid-Atlantic States, during DISCOVER-AQ, J. Atmos. Chem., 72, 503-521, doi: 10.1007/s10874-013-9265-6, 2013.

Brown, S. S., Dibb, J. E., Stark, H., Aldener, M., Vozella, M., Whitlow, S., Williams, E. J., Lerner, B. M., Jakoubek, R., Middlebrook, A. M., DeGouw, J. A., Warneke, C., Goldan, P. D., Kuster, W. C., Angevine, W. M., Sueper, D. T., Quinn, P. K., Bates, T. S., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Nighttime removal of NOx in the summer marine boundary layer, Geophys. Res. Lett., 31, 1-5, doi: 10.1029/2004gl019412, 2004.

Burgard, D. A., Bishop, G. A., Stadtmuller, R. S., Dalton, T. R., and Stedman, D. H.: Spectroscopy applied to on-road mobile source emissions, Appl. Spectrosc., 60, 135a-148a, doi: 10.1366/000370206777412185, 2006a.

Burgard, D. A., Bishop, G. A., Stedman, D. H., Gessner, V. H., and Daeschlein, C.: Remote sensing of in-use heavy-duty diesel trucks, Environ. Sci. Technol., 40, 6938-6942, doi: 10.1021/es060989a, 2006b.

Carslaw, D. C., and Beevers, S. D.: Investigating the potential importance of primary NO_2 emissions in a street canyon, Atmos. Environ., 38, 3585-3594, doi: 10.1016/j.atmosenv.2004.03.041, 2004.

Carslaw, D. C.: Evidence of an increasing NO_2/NO_X emissions ratio from road traffic emissions, Atmos. Environ., 39, 4793-4802, doi: 10.1016/j.atmosenv.2005.06.023, 2005.

Castellanos, P., Luke, W. T., Kelley, P., Stehr, J. W., Ehrman, S. H., and Dickerson, R. R.: Modification of a commercial cavity ring-down spectroscopy NO_2 detector for enhanced sensitivity, Rev. Sci. Instrum., 80, doi: 10.1063/1.3244090, 2009.

Chen, Y., Yang, C. Q., Zhao, W. X., Fang, B., Xu, X. Z., Gai, Y. B., Lin, X. X., Chen, W. D., and Zhang, W. J.: Ultra-sensitive measurement of peroxy radicals by chemical amplification broadband cavity-enhanced spectroscopy, Analyst, 141, 5870-5878, doi: 10.1039/c6an01038e, 2016.

Crutzen, P. J.: Role of NO and NO_2 in the chemistry of the troposphere, Annu. Rev. Earth Planet. Sci., 7, 443-472, doi: 10.1146/annurev.ea.07.050179.002303, 1979.

Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO_2, peroxy nitrates, alkyl nitrates, and HNO_3, J. Geophys. Res. Atmos., 107, ACH 4-1-ACH 4-14, doi: 10.1029/2001jd000779, 2002.

Duan J., Qin M., Ouyang, B., Fang, W., Li, X., Lu, K. D., Tang, K., Liang, S. X., Meng, F. H., Hu, Z. K., Xie, P.H., Liu, W. Q., Rolf Häsler, Development of an incoherent broadband cavity-enhanced absorption spectrometer for in situ measurements of HONO and NO_2. Atmos. Meas. Tech., 11, 4531-4543, doi: 10.5194/amt-11-4531-2018, 2018.

Dunlea, E. J., Herndon, S. C., Nelson, D. D., Volkamer, R. M., San Martini, F., Sheehy, P. M., Zahniser, M. S., Shorter, J. H., Wormhoudt, J. C., Lamb, B. K., Allwine, E. J., Gaffney, J. S., Marley, N. A., Grutter, M., Marquez, C., Blanco, S., Cardenas, B., Retama, A., Villegas, C. R. R., Kolb, C. E., Molina, L. T., and Molina, M. J.: Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, Atmos. Chem. Phys., 7, 2691-2704, doi: 10.5194/acp-7-2691-2007, 2007.

Fahey, D. W., Eubank, C. S., Hubler, G., and Fehsenfeld, F. C.: Evaluation of a Catalytic Reduction

Technique for the Measurement of Total Reactive Odd-Nitrogen NO_y in the Atmosphere, J.Atmo. Chem., 3, 435-468, doi: 10.1007/bf00053871, 1985.

Fuchs, H., Dube, W. P., Lerner, B. M., Wagner, N. L., Williams, E. J., and Brown, S. S.: A Sensitive and Versatile Detector for Atmospheric NO_2 and NOx Based on Blue Diode Laser Cavity Ring-Down Spectroscopy, Environ. Sci. Technol., 43, 7831-7836, doi: 10.1021/es902067h, 2009.

Fuchs, H., Ball, S. M., Bohn, B., Brauers, T., Cohen, R. C., Dorn, H. P., Dube, W. P., Fry, J. L., Haseler, R., Heitmann, U., Jones, R. L., Kleffmann, J., Mentel, T. F., Musgen, P., Rohrer, F., Rollins, A. W., Ruth, A. A., Kiendler-Scharr, A., Schlosser, E., Shillings, A. J. L., Tillmann, R., Varma, R. M., Venables, D. S., Tapia, G. V., Wahner, A., Wegener, R., Wooldridge, P. J., and Brown, S. S.: Intercomparison of measurements of NO_2 concentrations in the atmosphere simulation chamber SAPHIR during the NO_3Comp campaign, Atmo.Meas.Tech., 3, 21-37, doi: 10.5194/amt-3-21-2010, 2010.

Gherman, T., Venables, D. S., Vaughan, S., Orphal, J., and Ruth, A. A.: Incoherent broadband cavity-enhanced absorption spectroscopy in the near-ultraviolet: Application to HONO and NO_2, Environ. Sci. Technol., 42, 890-895, doi: 10.1021/es0716913, 2008.

Herndon, S. C., Shorter, J. H., Zahniser, M. S., Nelson, D. D., Jayne, J., Brown, R. C., Miake-Lye, R. C., Waitz, I., Silva, P., Lanni, T., Demerjian, K., and Kolb, C. E.: NO and NO_2 emission ratios measured from in-use commercial aircraft during taxi and takeoff, Environ. Sci. Technol., 38, 6078-6084, doi: 10.1021/es049701c, 2004.

Herndon, S. C., Shorter, J. H., Zahniser, M. S., Wormhoudt, J., Nelson, D. D., Demerjian, K. L., and Kolb, C. E.: Real-time measurements of SO_2, H_2CO, and CH_4 emissions from in-use curbside passenger buses in New York City using a chase vehicle, Environ. Sci. Technol., 39, 7984-7990, doi: 10.1021/es0482942, 2005.

Hueglin, C., Buchmann, B., and Weber, R. O.: Long-term observation of real-world road traffic emission factors on a motorway in Switzerland, Atmos. Environ., 40, 3696-3709, doi: 10.1016/j.atmosenv.2006.03.020, 2006.

Hu, R. Z., Wang, D., Xie, P. H., Chen, H., Ling, L., "Diode Laser Cavity Ring-Down Spectroscopy for Atmospheric NO_2 Measurement," Acta. Optica. Sinica. **36**, 0230006, 2016.

Jagerska, J., Jouy, P., Tuzson, B., Looser, H., Mangold, M., Soltic, P., Hugi, A., Bronnimann, R., Faist, J., and Emmenegger, L.: Simultaneous measurement of NO and NO_2 by dual-wavelength quantum cascade laser spectroscopy, Opt. Express, 23, 1512-1522, doi: 10.1364/oe.23.001512, 2015.

Jaramillo, P., and Muller, N. Z.: Air pollution emissions and damages from energy production in the US: 2002-2011, Energy Policy, 90, 202-211, doi: 10.1016/j.enpol.2015.12.035, 2016.

Karpf, A., Qiao, Y. H., and Rao, G. N.: Ultrasensitive, real-time trace gas detection using a high-power, multimode diode laser and cavity ringdown spectroscopy, Appl. Optics, 55, 4497-4504, doi: 10.1364/ao.55.004497, 2016.

Kasyutich, V. L., Martin, P. A., and Holdsworth, R. J.: Phase-shift off-axis cavity-enhanced absorption detector of nitrogen dioxide, Meas. Sci. Technol., 17, 923-931, doi: 10.1088/0957-0233/17/4/044, 2006.

Kebabian, P. L., Wood, E. C., Herndon, S. C., and Freedman, A.: A practical alternative to chemiluminescence-based detection of nitrogen dioxide: Cavity attenuated phase shift spectroscopy, Environ.Sci.Technol., 42, 6040-6045, doi: 10.1021/es703204j, 2008.

Lal, D. R., Clark, I., Shalkow, J., Downey, R. J., Shorter, N. A., Klimstra, D. S., and La Quaglia, M. P.: Primary epithelial lung malignancies in the pediatric population, Pediatr. Blood Cancer, 45, 683-686,

doi: 10.1002/pbc.20279, 2005.

Li, Y. Q., Demerjian, K. L., Zahniser, M. S., Nelson, D. D., McManus, J. B., and Herndon, S. C.: Measurement of formaldehyde, nitrogen dioxide, and sulfur dioxide at Whiteface Mountain using a dual tunable diode laser system, J. Geophys. Res. Atmos., 109, 11, doi: 10.1029/2003jd004091, 2004.

Li, Z. Y., Hu, R. Z., Xie, P. H., Wang, H.C., Lu, K. D., Wang, D.: Intercomparison of in situ CRDS and CEAS for measurements of atmospheric N_2O_5 in Beijing, China. Science of the Total Environment，613 – 614 ,131 – 139. doi: 10.1016/j.scitotenv.2017.08.302, 2018.

Li, Z. Y., Hu, R. Z., Xie, P. H., Chen, H., Wu S. Y., Wang, F. Y., Wang, Y. H., Ling, L. Y., Liu, J. G., and Liu, W. Q.: Development of a portable cavity ring down spectroscopy instrument for simultaneous, in situ measurement of NO_3 and N_2O_5. Optics Express. 26, A433-A449. https://doi.org/10.1364/OE.26.00A433.P, 2018.

Matsumi, Y., Taketani, F., Takahashi, K., Nakayama, T., Kawai, M., and Miyao, Y.: Fluorescence detection of atmospheric nitrogen dioxide using a blue light-emitting diode as an excitation source, Appl. Optics, 49, 3762-3767, doi: 10.1364/ao.49.003762, 2010.

Matsumoto, J., Hirokawa, J., Akimoto, H., and Kajii, Y.: Direct measurement of NO_2 in the marine atmosphere by laser-induced fluorescence technique, Atmos. Environ., 35, 2803-2814, doi: 10.1016/s1352-2310(01)00078-4, 2001.

Novikov, S., Lebedeva, N., Satrapinski, A., Walden, J., Davydov, V., and Lebedev, A.: Graphene based sensor for environmental monitoring of NO_2, Sens. Actuator B-Chem., 236, 1054-1060, doi: 10.1016/j.snb.2016.05.114, 2016.

Osthoff, H. D., Brown, S. S., Ryerson, T. B., Fortin, T. J., Lerner, B. M., Williams, E. J., Pettersson, A., Baynard, T., Dube, W. P., Ciciora, S. J., and Ravishankara, A. R.: Measurement of atmospheric NO_2 by pulsed cavity ring-down spectroscopy, J. Geophys. Res.-Atmos., 111, doi: 10.1029/2005jd006942, 2006.

Osthoff, H. D., Pilling, M. J., Ravishankara, A. R., and Brown, S. S.: Temperature dependence of the NO_3 absorption cross-section above 298 K and determination of the equilibrium constant for $NO_3+NO_2<-> N_2O_5$ at atmospherically relevant conditions, Phys. Chem. Chem.Phys., 9, 5785-5793, doi: 10.1039/b709193a, 2007.

Paul, D., Furgeson, A., and Osthoff, H. D.: Measurements of total peroxy and alkyl nitrate abundances in laboratory-generated gas samples by thermal dissociation cavity ring-down spectroscopy, Rev. Sci. Instrum., 80, doi: 10.1063/1.3258204, 2009.

Platt, U. F., Winer, A. M., Biermann, H. W., Atkinson, R., and Pitts, J. N.: Measurement of nitrate radical concentrations in continental air, Environ. Sci. Tech., 18, 365-369, doi: 10.1021/es00123a015, 1984.

R. McLaren, P. W., D. Majonis, J. McCourt, J. D. Halla, and J. Brook: NO_3 radical measurements in a polluted marine environment:links to ozone formation, Atmo.Chem.Phys., 10, 4187–4206, doi: 10.5194/acp-10-4187-2010, 2010.

Ridley, B. A., and Howlett, L. C.: An instrument for nitric oxide measurements in the stratosphere, Rev. Sci. Instrum., 45, 742-746, doi: 10.1063/1.1686726, 1974.

Sadanaga, Y., Yuba, A., Kawakami, J., Takenaka, N., Yamamoto, M., and Bandow, H.: A gaseous nitric acid analyzer for the remote atmosphere based on the scrubber difference/NO-ozone chemiluminescence method, Anal. Sci., 24, 967-971, doi: 10.2116/analsci.24.967, 2008.

Sadanaga, Y., Suzuki, K., Yoshimoto, T., and Bandow, H.: Direct measurement system of nitrogen

505 dioxide in the atmosphere using a blue light-emitting diode induced fluorescence technique, Rev. Sci. Instrum., 85, 5, doi: 10.1063/1.4879821, 2014.

Sander, S. P., Friedl, R. R., Golden, D. M., Kurylo, M. J., Huie,, R. E., O., V. L., Moortgat, G. K., Ravishankara, A. R.,, and Kolb, C. E., Molina, M. J., and Finlayson-Pitts, B. J.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 15 Jet Propulsion
510 Laboratory, National Aeronautics and Space Administration/Jet Propulsion Laboratory/ California Institute of Technology, Pasadena, CA, 2006.

Shi, Y. l., Cui, S. h., and Xu, S.,: Factor decomposition of nitrogen oxide emission of China industrial energy consumption, Environ. Sci. Tech., 37, 355-362., 2014.

Sobanski, N., Tang, M. J., Thieser, J., Schuster, G., Pohler, D., Fischer, H., Song, W., Sauvage, C.,
515 Williams, J., Fachinger, J., Berkes, F., Hoor, P., Platt, U., Lelieveld, J., and Crowley, J. N.: Chemical and meteorological influences on the lifetime of NO_3 at a semi-rural mountain site during PARADE, Atmos. Chem. Phys., 16, 4867-4883, doi: 10.5194/acp-16-4867-2016, 2016.

Taketani, F., Kawai, M., Takahashi, K., and Matsumi, Y.: Trace detection of atmospheric NO_2 by laser-induced fluorescence using a GaN diode laser and a diode-pumped YAG laser, Appl. Optics,
520 46, 907-915, doi: 10.1364/ao.46.000907, 2007.

Thieser, J., Schuster, G., Schuladen, J., Phillips, G. J., Reiffs, A., Parchatka, U., Pohler, D., Lelieveld, J., and Crowley, J. N.: A two-channel thermal dissociation cavity ring-down spectrometer for the detection of ambient NO_2, RO_2NO_2 and $RONO_2$, Atmos. Meas. Tech., 9, 553-576, doi: 10.5194/amt-9-553-2016, 2016.

525 Villena, G., Bejan, I., Kurtenbach, R., Wiesen, P., and Kleffmann, J.: Development of a new Long Path Absorption Photometer (LOPAP) instrument for the sensitive detection of NO_2 in the atmosphere, Atmos. Meas. Tech., 4, 1663-1676, doi: 10.5194/amt-4-1663-2011, 2011.

Villena, G., Bejan, I., Kurtenbach, R., Wiesen, P., and Kleffmann, J.: Interferences of commercial NO_2 instruments in the urban atmosphere and in a smog chamber, Atmos. Meas. Tech., 5, 149-159, doi:
530 10.5194/amt-5-149-2012, 2012.

Vogt, R., Scheer, V., Casati, R., and Benter, T.: On-road measurement of particle emission in the exhaust plume of a diesel passenger car, Environ. Sci. Tech., 37, 4070-4076, doi: 10.1021/es0300315, 2003.

Voigt, S., Orphal, J., and Burrows, J. P.: The temperature and pressure dependence of the absorption
535 cross-sections of NO_2 in the 250-800 nm region measured by Fourier-transform spectroscopy, J. Photochem. Photobiol., A-Chemistry, 149, 1-7, doi: 10.1016/s1010-6030(01)00650-5, 2002.

Wada, R., and Orr-Ewing, A. J.: Continuous wave cavity ring-down spectroscopy measurement of NO_2 mixing ratios in ambient air, Analyst, 130, 1595-1600, doi: 10.1039/b511115c, 2005.

Wagner, N. L., Dube, W. P., Washenfelder, R. A., Young, C. J., Pollack, I. B., Ryerson, T. B., and
540 Brown, S. S.: Diode laser-based cavity ring-down instrument for NO_3, N_2O_5, NO, NO_2 and O_3 from aircraft, Atmos. Meas. Tech., 4, 1227-1240, doi: 10.5194/amt-4-1227-2011, 2011.

Wagner, N. L., Riedel, T. P., Young, C. J., Bahreini, R., Brock, C. A., Dube, W. P., Kim, S., Middlebrook, A. M., Ozturk, F., Roberts, J. M., Russo, R., Sive, B., Swarthout, R., Thornton, J. A., VandenBoer, T. C., Zhou, Y., and Brown, S. S.: N_2O_5 uptake coefficients and nocturnal NO_2
545 removal rates determined from ambient wintertime measurements, J. Geophys. Res.-Atmos., 118, 9331-9350, doi: 10.1002/jgrd.50653, 2013.

Wang, D., Hu, R. Z., Xie, P. H., Liu, J. G., Liu, W. Q., Qin, M., Ling, L.Y., Zeng, Y., Chen, H., Xing, X.B., Zhu, G. L., Wu, J., Duan, J., Lu, X., Shen, L.L., 2015. Diode laser cavity ring-down

spectroscopy for in situ measurement of NO_3 radical in ambient air. J. Quant.Spectrosc. Radiat. Transf. 166, 23–29,doi: 10.1016/j.jqsrt.2015.07.005, 2015.

Wang, T., Cheung, V. T. F., Anson, M., and Li, Y. S.: Ozone and related gaseous pollutants in the boundary layer of eastern China: Overview of the recent measurements at a rural site, Geophys. Res. Lett., 28, 2373-2376, doi: 10.1029/2000gl012378, 2001.

Westerdahl, D.: Avoiding Measurement Errors When Monitoring Fine and Ultrafine PM for Exposure and Epidemiology Studies, Epidemiology, 19, S360-S360, 2008.

Wild, R. J., Edwards, P. M., Dube, W. P., Baumann, K., Edgerton, E. S., Quinn, P. K., Roberts, J. M., Rollins, A. W., Veres, P. R., Warneke, C., Williams, E. J., Yuan, B., and Brown, S. S.: A measurement of total reactive nitrogen, NOy, together with NO_2, NO, and O_3 via cavity ring-down spectroscopy, Environ. Sci. Technol., 48, 9609-9615, doi: 10.1021/es501896w, 2014.

Wild, R. J., Dube, W. P., Aikin, K. C., Eilerman, S. J., Neuman, J. A., Peischl, J., Ryerson, T. B., and Brown, S. S.: On-road measurements of vehicle NO_2/NOx emission ratios in Denver, Colorado, USA, Atmos. Environ., 148, 182-189, doi: 10.1016/j.atmosenv.2016.10.039, 2017.

Wu, T., Zhao, W., Chen, W., Zhang, W., and Gao, X.: Incoherent broadband cavity enhanced absorption spectroscopy for in situ measurements of NO_2 with a blue light emitting diode, Appl. Phys. B-Lasers and Optics, 94, 85-94, doi: 10.1007/s00340-008-3308-8, 2009.

Xu, Z., Wang, T., Xue, L. K., Louie, P. K. K., Luk, C. W. Y., Gao, J., Wang, S. L., Chai, F. H., and Wang, W. X.: Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric nitrogen dioxide at four differently polluted sites in China, Atmos. Environ., 76, 221-226, doi: 10.1016/j.atmosenv.2012.09.043, 2013.

Yamamoto, Y., Sumizawa, H., Yamada, H., and Tonokura, K.: Real-time measurement of nitrogen dioxide in vehicle exhaust gas by mid-infrared cavity ring-down spectroscopy, Appl. Phys. B, 105, 923-931, doi: 10.1007/s00340-011-4647-4, 2011.

Yang, W., and Omaye, S. T.: Air pollutants, oxidative stress and human health, Mutat. Res. Genet. Toxicol. Environ. Mutagen., 674, 45-54, doi: 10.1016/j.mrgentox.2008.10.005, 2009.

Yuba, A., Sadanaga, Y., Takami, A., Hatakeyama, S., Takenaka, N., and Bandow, H.: Measurement System for Particulate Nitrate Based on the Scrubber Difference NO-O_3 Chemiluminescence Method in Remote Areas, Anal. chem., 82, 8916-8921, doi: 10.1021/ac101704w, 2010.

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

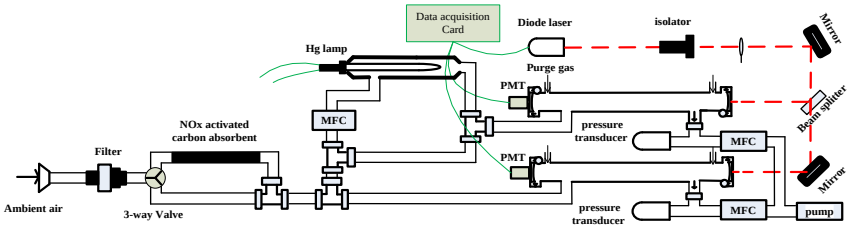
Atmospheric Measurement Techniques Discussions

Table 1 Comparison of NO_2 detection limits based on optical methods.

Principle of measurement	Laser power	Wavelength range/nm	Dectection limit	Reference
Cw-CRDS	5mW(1MHz)	410	80ppt/50s	(Wada and Orr-Ewing, 2005)
ND:YAG laser CRDS	1mJ	532	40ppt/1s	(Osthoff et al., 2006)
pDL-CRDS	40 mW （2KHz-10%）	404	22ppt/1s(2σ)	(Fuchs et al., 2009)
Fabry-Perot (FP) pDL-CRDS	1.1w (4KHZ-10%)	400	38ppt/128ms	(Karpf et al., 2016)
commercial DL-CRDS	1.2KHZ	407.38	60ppt/60s(3σ)	(Castellanos et al., 2009)
LED-based commercial CRD	355 mW	397-412(405)	80ppt/60s	(Brent et al., 2013)
LED-CEAS	340mw	455	2.2ppb/100s(1σ)	(Wu et al., 2009)
Xe lamp DOAS		295–492 nm	2ppb/8-12min	(R. McLaren, 2010)
CAPS		440	60ppt/10s(3σ)	(Kebabian et al., 2008)
diode-pumped Nd:YAG laser-LIF	15mw(14KHz)	473	140/60s	(Taketani et al., 2007)
blue LED-IF	17.7mw(10KHz)	435	9.8ppb/60	(Matsumi et al., 2010)
pulsed blue light LED-LIF	22mw	430	7ppb/1min	(Sadanaga et al., 2014)
pDL-CRDS	60mw	403.64	30ppt/1s	This work

580 CRDS=cavity ring-down spectroscopy; CEAS=cavity-enhanced absorption spectroscopy; BB=broadband; DOAS=differential optical absorption spectroscopy; cw=continuous-wave diode laser. LIF=laser induced fluorescence; CAPS= cavity attenuated phase shift spectroscopy; pDL=pulsed diode laser.

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019



585 Fig. 1. Schematic of dual-channel Cavity Ring down Spectroscopy system.

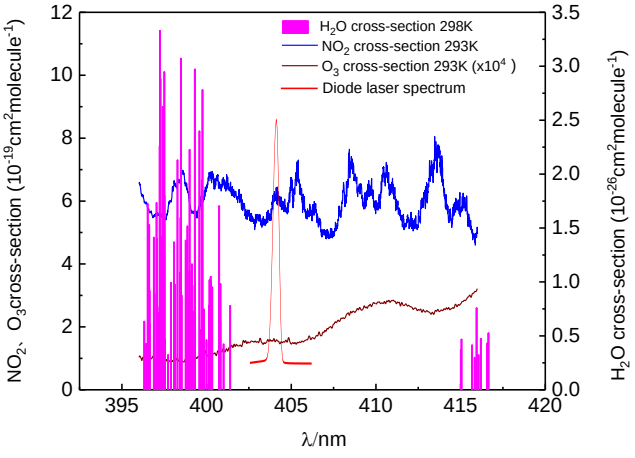
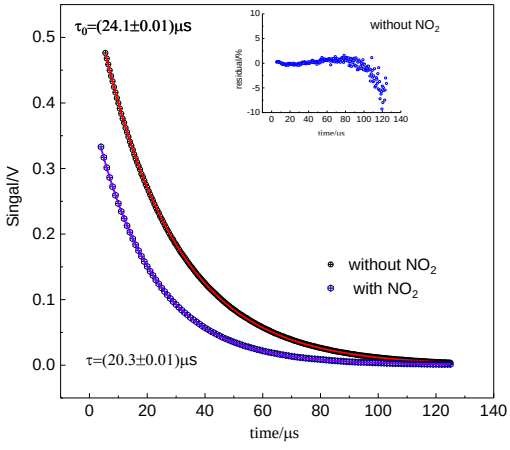


Fig. 2. Cross section of the NO_3 radical, NO_2, O_3, water vapor, and diode laser spectrum.



590 Fig. 3. Different cavity ring-down signals and fitting results in the absence and presence of NO_2. The small figure in the upper right corner is the fitting residual.

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

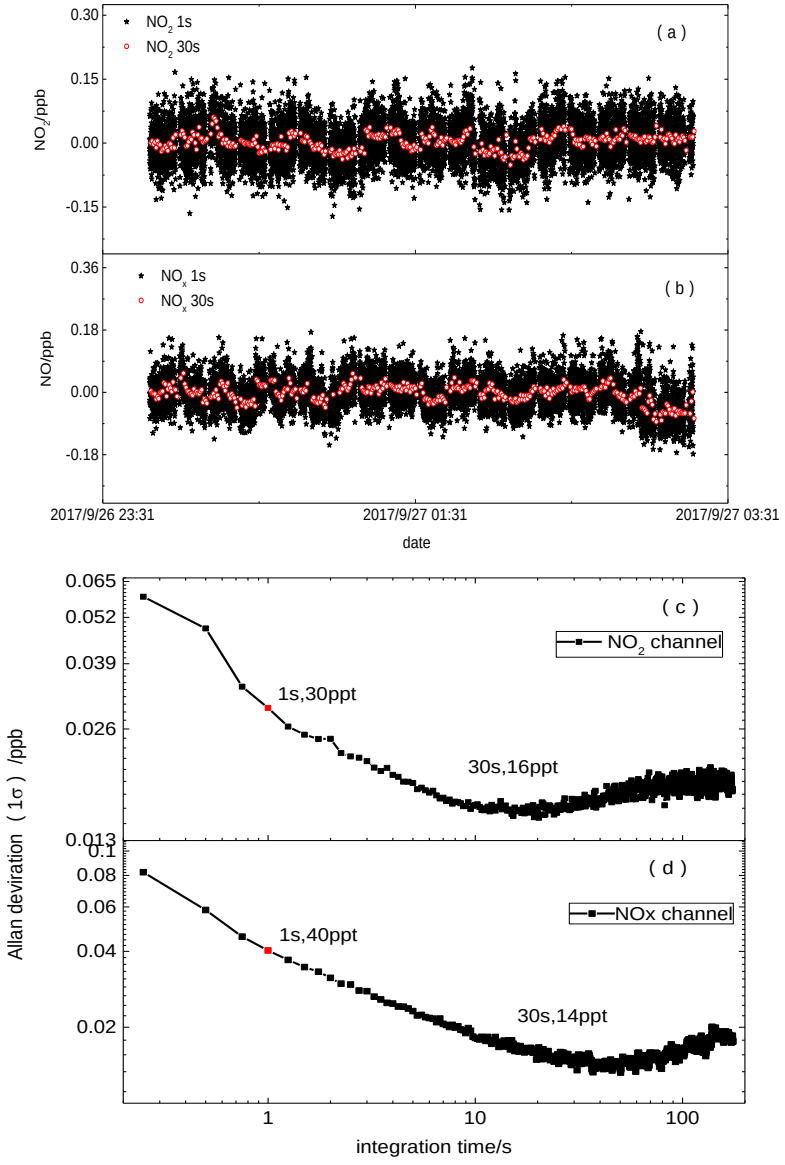


Fig. 4. (a)(b) Continuous time series measurement when the instrument sampled only zero air, averaged to 1s for NO_2 and NO_x channels (black dots), the red dots show the data averaged to 30s; (c)(d): Allan deviation plots for NO_2 concentration in two channels. The minimum value equals the optimum integration time.

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

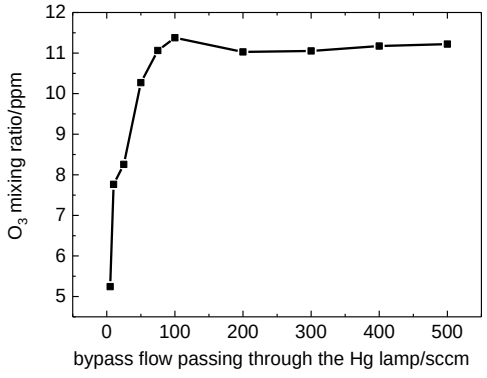


Fig. 5. O_3 mixing ratio when changing the bypass flow passing through Hg lamp.

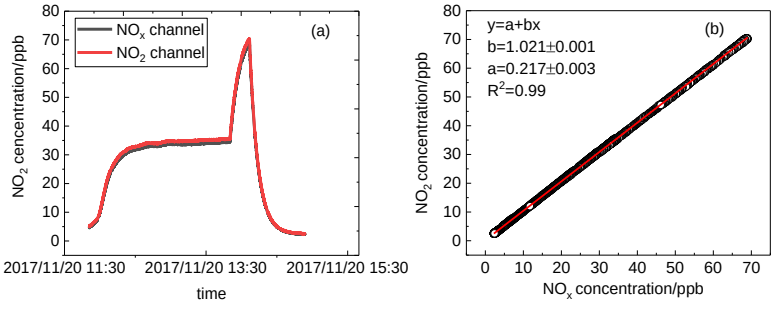


Fig. 6. (a) Time series of NO_2 concentration sampled standard mixtures by CRDS instrument in two channels with mercury pen-ray lamp switched on. (b) A correlation plot between the data from two channels.

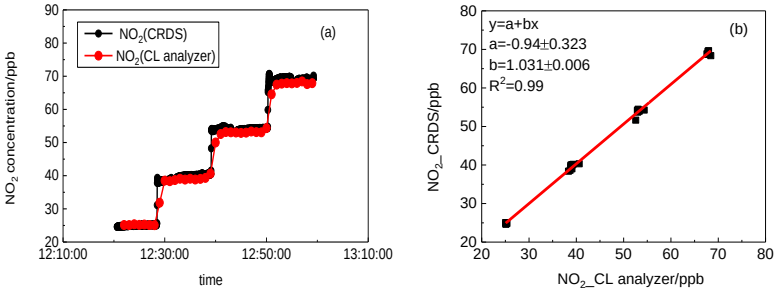


Fig. 7. (a) Time series of NO_2 concentration sampled standard mixtures by CRDS instrument and CL analyzer. The time resolution for CRDS instrument and CL analyzer are 1s and 1min, respectively. (b) A correlation plot between the data from the CRDS instrument and the CL analyzer (data averaged to 1min). The fitting result gave a gradient of 1.031 and an intercept of -0.940 ppb, with linear correlation factor of 0.99.

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

Atmospheric Measurement Techniques Discussions

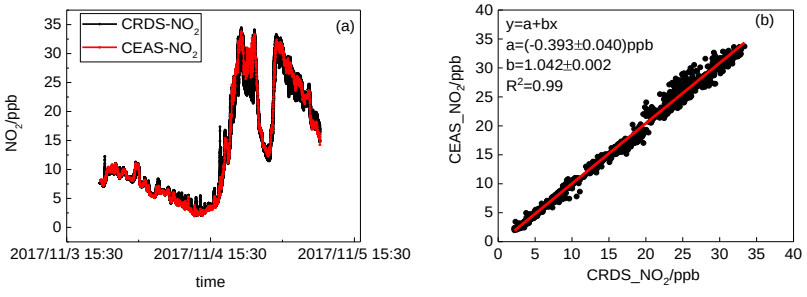


Fig. 8. (a) NO_2 mixing ratios by CEAS (1 min average) and CRDS (1 s average) instruments, (b) Scatter plots for the NO_2 dataset from CRDS and CEAS instrument. The red lines illustrate the linear regression (Data averaged to 1 min base).

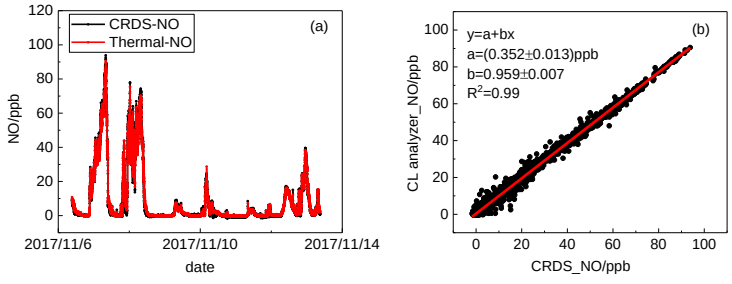


Fig. 9. (a) Time series of NO by dual-CRDS instrument and CL analyzer. (b)A correlation between two instruments is shown and data for correlation analysis is averaged in 1min.

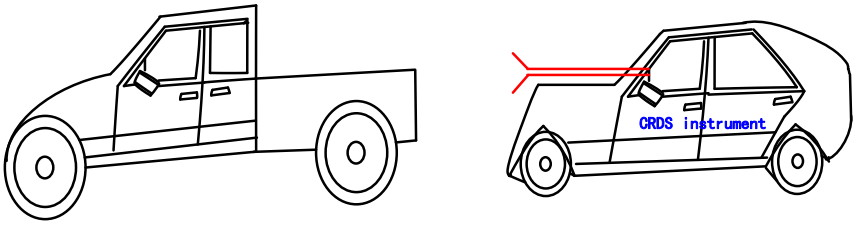


Fig. 10 The diagram of the movable van loaded with CRDS instrument.

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-459
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 14 January 2019

625

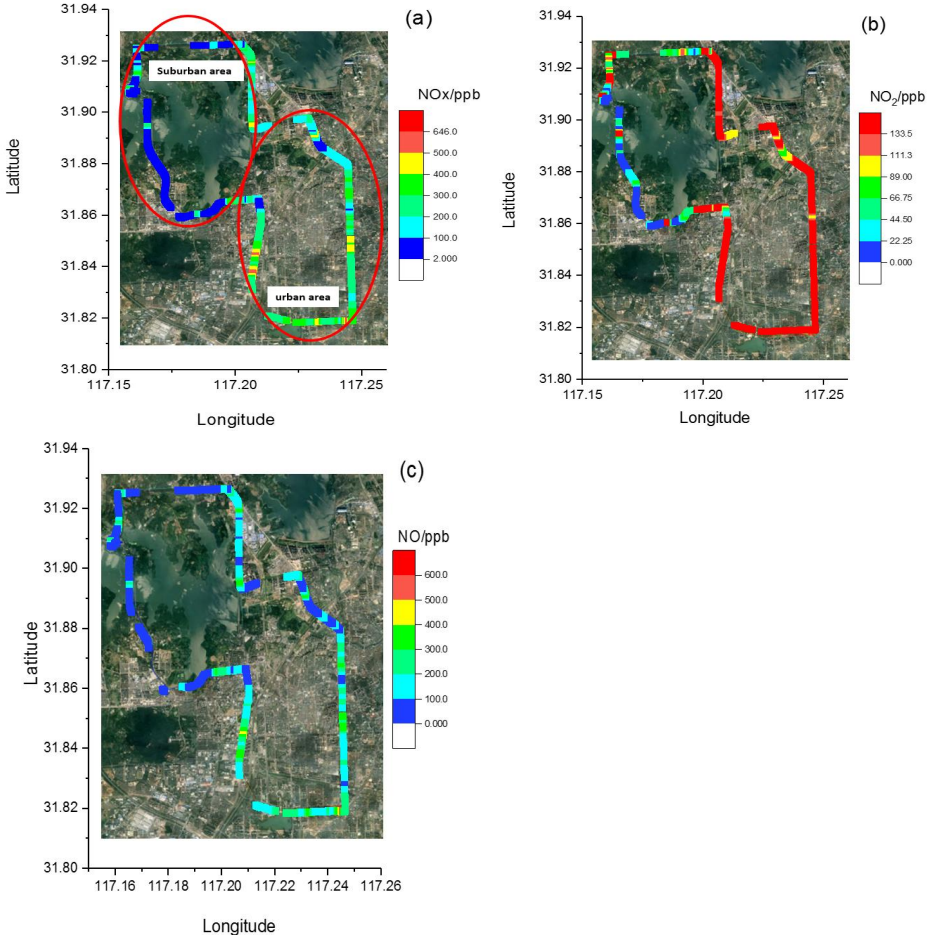


Fig. 11. Results of the NOx (a)、 NO_2 (b)、NO (c) concentrations around Hefei, China (Data is averaged to 5s).