

Response to the Reviewers' comments on the manuscript:

Simultaneous measurement of NO and NO₂ by dual-channel cavity ring down spectroscopy technique

rzhu@aiofm.ac.cn

Thanks for the reviewer's questions. The manuscript will be revised following the reviewer's suggestions.

Reviewer # 1

Comments and suggestions: 1. Could authors provide more test data on-road measurements of vehicle NO₂/NO_x emissions? And if possible, the on-road intercomparisons will be meaningful for the validation of the method and instrument.

Reply: The intercomparison between the CRDS instrument with NO analyzer for NO measurements and the intercomparison between the CRDS instrument with CEAS instrument for NO₂ measurements have been done to valid the accuracy of the instrument in the paper, so we don't provide other data on road measurements of vehicle NO₂/NO_x emissions. Based on the reviewer's suggestions, we performed another measurement of vehicle emissions on road. NO analyzer (42i), O₃ analyzer (49i) and the CRDS instruments were placed in a car and were powered by three batteries. Ambient air was pumped through an inlet fixed on the roof of the car and then was divided into three lines to the instruments, respectively. Fig. 1 illustrates the 4-hour drive around Hefei, the drive track involve highway, urban and suburban area and is colored with respect to the measured NO and NO₂. Vehicle speeds varied greatly on the three different road types and vehicle speed is around 100km/h on highway. Influenced by the vehicle emissions, the NO_x plumes on urban roads are higher than those on suburban roads and highway.

Fig.2 shows the time series of NO₂, NO and O₃. O₃ and NO showed a significant negative correlation and O₃ can be titrated by NO quickly.

Fig.3 shows the NO data measured by CRDS and CL analyzer (42i), (a) is the raw data for the CRDS instrument and (b) is the data with time resolution of is 1 min for the CRDS instrument. The good agreement between the two instruments proves that the CRDS instrument can be applied for fast vehicle NO_x emissions.

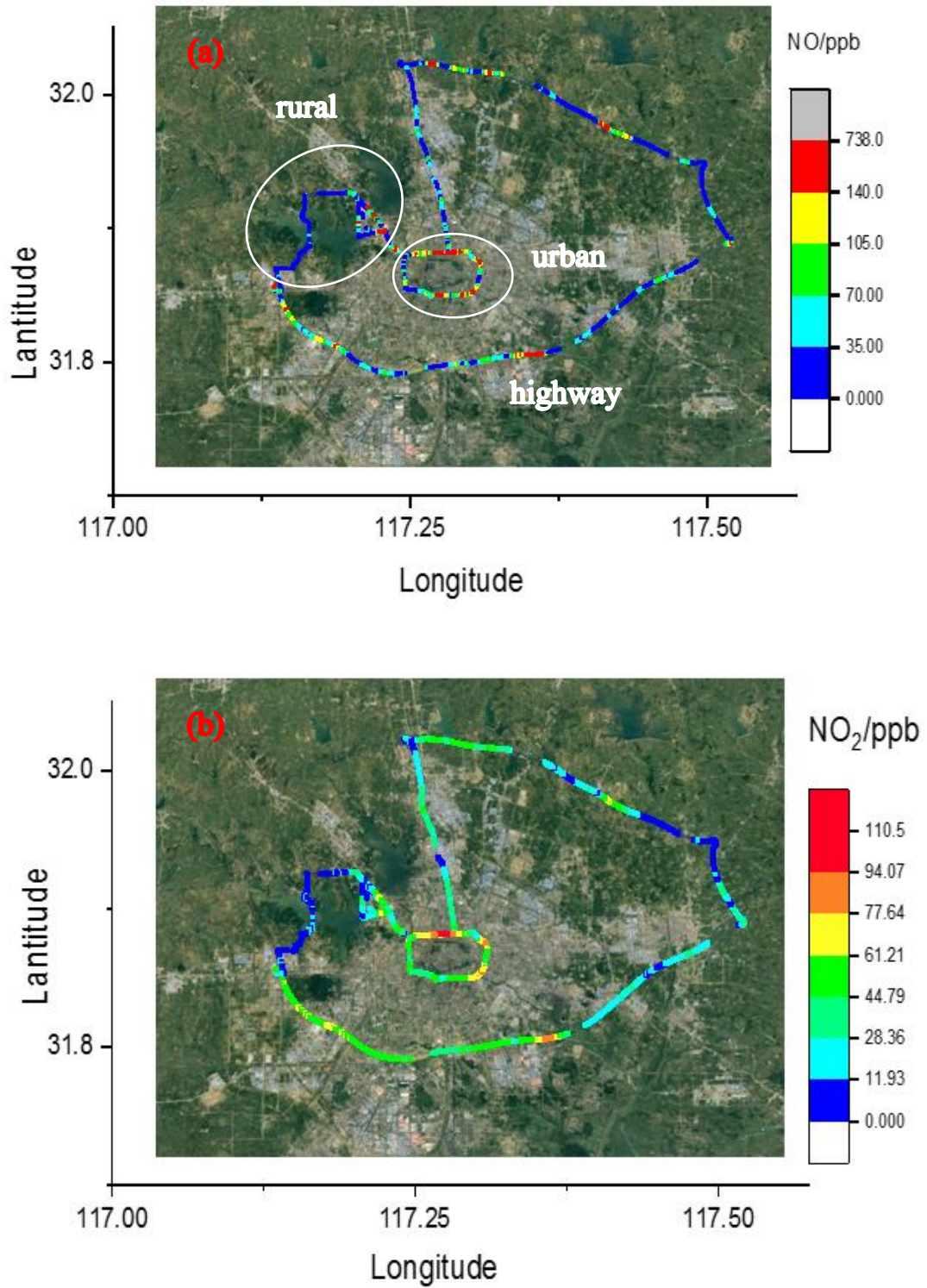


Fig.1. The 4-h drive around Hefei, China, colored by the measured NO (a) and NO₂ (b) concentrations, respectively.

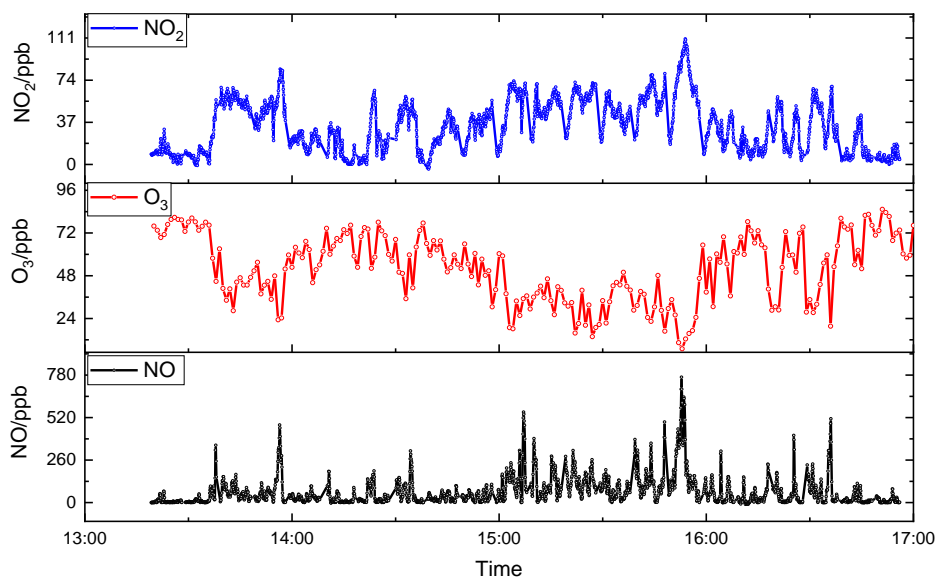


Fig.2. Results of the NO₂、 NO and O₃ concentrations around Hefei, China.

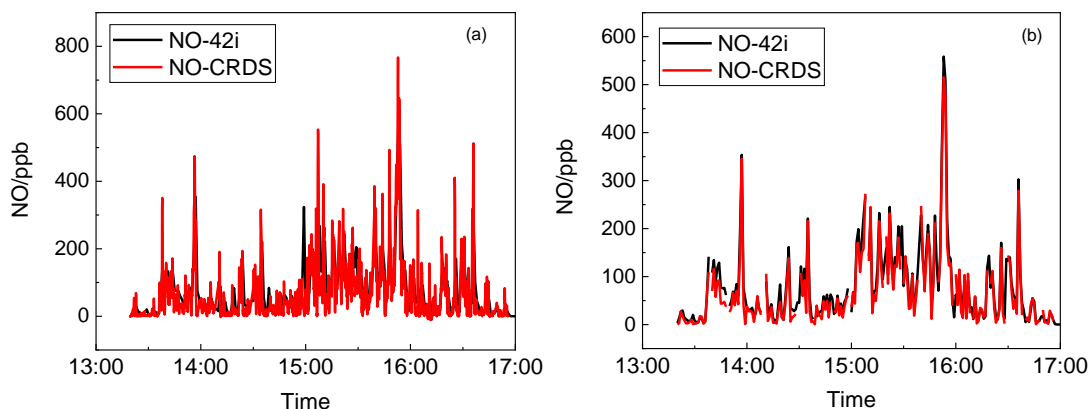


Fig.3. Time series of NO by CRDS instrument and CL analyzer (42i). (a) is the raw data for the CRDS instrument ; (b) is the data with time resolution of is 1 min for the CRDS instrument.

Comments and suggestions: It will be helpful if someone can review and make some corrections the English writing.

Page 1, line 23:” Too much NO_x are” too much is how much? "are" to "is" page 2, line 55 "too much high"

Reply: Since the questions above are about the English expression and grammar mistakes, the revisions will be done in the final version.

Comments and suggestions: page 15, table 1: it will be better to convert the detection limits of all different measurements to an unified unit such as ~"ppt/1s (1sigma)

Reply: The suggestion will be followed in the revised manuscript.

Reviewer # 2

Comments and suggestions: I don't think NO_x is not a secondary pollutant. Unfortunately, I have no access to the paper you cite (Crutzen 1979) in order to confirm, but I invite you to re-verify this paper to see on what basis Crutzen said that NO_x is a secondary pollutant. Also, from NO_x to the formation of secondary aerosols it is a long stretch, maybe it's better to remove.

Reply: In order to avoid the ambiguity caused by this sentence, I will rewrite it although I think that NO₂ is a secondary pollutant. And I agree with the reviewer's idea that from NO_x to the formation of secondary aerosols it is a long stretch, I will remove it.

Comments and suggestions: Page 2, line 78: indicating several seconds in combination with high sensitivity is strange: do you mean a low detection limit with several seconds time resolution?

Reply: Yes, I mean that the optical methods can achieve a high detection sensitivity and the detection limit is several ppt level with several seconds time resolution.

Comments and suggestions: You give several times your ring-down times with 2-digit precision (24.12 and 22.90 μ s), however mirrors get polluted, alignment changes etc, so I guess the ring-down times you have given here are the result of one measurement at one moment? Or do you really measure over several days or weeks always exactly the same ring-down time?

Reply: The ring-down times I have given here are the results of one measurement and the ring-down times are used to calculate the detection limit in both channels. However, in field measurements, the ring-down times when the targeted gases are not in the cavity (τ_0) are measured every 10 min for a time period of 1 min, the measurement results show that the ring-down times during the 10-min interval change slightly. The ring-down time will change after measuring over several days or weeks influenced by temperature, pressure, alignment changes etc. This may slightly affect the detection limit of the instrument but can not affect the concentration retrieval.

The list of all relevant changes made in the manuscript

- 1, P1. Line 22-23.
- 2, P2. Line 51-53 and Line 75-77.
- 3, P4. Line 151-152.
- 4, P6. Line 223-225.
- 5, P9. Line 339-354.
- 6, P15. Table 1.
- 7, P21-22. Line 635-641.

Simultaneous measurement of NO and NO₂ 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 (NO₂) are relevant to air quality due to their roles in tropospheric ozone (O₃) production. In China, NO_x emissions are very high and NO_x emissions exhausted from on-road vehicles make up 20% of total NO_x emissions. In order to detect the NO and NO₂ emissions on road, a dual-channel cavity ring down spectroscopy (CRDS) system for NO₂ and NO detection has been developed. In the system, NO is converted to NO₂ by its reaction with excess O₃ in NO_x channel, such that NO can be determined through the difference between two channels. The detection limits of NO₂ and NO_x for the system are estimated to be about 0.030 ppb (1σ, 1 s) and 0.040 ppb (1σ, 1 s), respectively. Considering the error sources of NO₂ absorption cross section and R_L determination, the total uncertainty of NO₂ measurements is about 5%. The performance of the system was validated against a chemiluminescence (CL) analyzer (42i, Thermo Scientific, Inc.) by measuring the NO₂ standard mixtures. The measurement results of NO₂ showed a linear correction factor (R²) 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 was also conducted separately for NO₂ measurement 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 R² = 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 R² = 0.99. The system was deployed on the measurements of on-road vehicle emission plumes in Hefei, and the different emission characteristics were observed in the different areas of the city. The successful deployment of the system has demonstrated that the instrument can provide a new method for retrieving fast variations of NO and

NO₂ plumes.

1. Introduction

In recent years, with the improvement of people's living standard, more and more attention is given to the improvement of the living environment. Among which, the management of environmental pollution has gradually become one of the focus issues, and it is believed that the detection of pollutants is prerequisite for environmental governance. As one of the main air pollutants, NO_x (NO_x= NO+NO₂) is well known as one byproduct of organic decay, the emission from natural forest fires, as well as the main anthropogenic emission from both 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 can determine the tropospheric O₃ levels which can lead to the formation of photochemical "smog". Furthermore, NO_x is also known as the precursor of nitric acid (Brown et al., 2004). In addition, NO_x can do harm to the human body and animals by damaging the respiratory system and leading to pulmonary edema (Yang and Omaye, 2009). Moreover, it is believed that accurate NO₂ 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 RO₂ radicals (Chen et al., 2016).

During the last few years, many direct and indirect techniques for monitoring NO₂ have been established, such as 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 in situ ambient sampling. CL can achieve direct measurement of NO and indirect measurement of NO₂. The method is based on the reaction between NO and O₃, which can form an electronically excited molecule of NO₂*. When NO₂* reaches the ground state, it emits fluorescence which is proportional to the initial NO concentration. While NO₂ is measured indirectly by conversion to NO firstly through heated (300 °C to 350 °C) molybdenum (Mo) surfaces (Ridley and Howlett, 1974) or photolytic NO₂ converters like Xenon lamps or UV emitting diodes at specific wavelength (320 nm-400 nm). The CL instruments have typical NO₂ detection limits of 50 ppt /1 min (1σ) (Wang et al., 2001). By contrast, CRDS, CEAS, CAPS and TDLAS, generally relying on scanning a light source through a range of frequencies of interest, are all direct absorption techniques. It has been demonstrated that these optical methods can achieve a high detection sensitivity and the detection limit is several ppt level with several seconds time resolution (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 NO₂ detection due to its advantages of high time resolution, low detection limit as well as portability, in which pulsed (Fuchs et al., 2009) or continuous-wave (cw) lasers (Wada and Orr-Ewing, 2005) were utilized. Wada et al. (Wada and Orr-Ewing, 2005) demonstrated a cw diode CRDS system operating at 410 nm for the retrieval of NO₂ 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 where a pulsed (20–100 Hz, up to 25 mJ) frequency-doubled Nd:YAG laser was used for the simultaneous

85 measurements of NO₂, nitrate radical (NO₃), and dinitrogen pentoxide (N₂O₅) in the atmosphere, and the
detection limit of 40 ppt (1 σ) for 1 s data was achieved for NO₂ with an uncertainty within $\pm 4\%$ under
laboratory conditions. Fuchs (Fuchs et al., 2009) used a simple, lightweight, low power, and
commercially available Fabry-Perot (FP) diode laser with a center wavelength of 403.96 nm as a light
90 source to detect NO and NO₂ in two separate channels. The limit of detection is 22 ppt (2 σ precision) for
NO₂ 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 ($\Delta\lambda_{\text{laser}} \sim 0.6$ 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 in their work. To evaluate the uncertainty and the accuracy of the aforementioned individual
95 instruments, a number of intercomparison studies have been carried out (Xu et al., 2013; Dunlea et al.,
2007; Villena et al., 2012). The comparison results show that the method based on Mo converters can be
affected by significant interferences such as N₂O₅, HONO, HNO₃, 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 NO₂ and have been adopted
100 gradually 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 also be
measured directly based on their absorption feature at 1,585.282 cm⁻¹. For example, a tunable infrared
laser differential absorption spectroscopy (TILDAS) instrument based on a DFB laser emitting
sequentially at 1,600 cm⁻¹ and 1,900 cm⁻¹ have been used by Jagerska et al for the measurement of NO
105 and NO₂ (Jagerska et al., 2015), where an astigmatic multi-pass Herriott cell (Herndon et al., 2004) and
a dual-wavelength spectrometer are utilized. The 1 s precision for NO measurement of the TILDAS
instrument was 550 ppt, whereas that for the field experiments was 1.5 ppb. Compared with the CL
method, it seems that this technique may suffer from low detection sensitivity. Given the rapid changes
of nighttime oxidation, i.e., NO₃ radical, the rapid changes of its precursors, NO and NO₂ is thus a
prerequisite for developing a nighttime atmospheric chemistry model. To achieve high sensitivity and
high resolution, conversion to NO₂ by adding excess O₃ may be one of the best methods for NO
110 detection (Fuchs et al., 2009; Wild et al., 2014).

The developments of different technologies provide the potential for NO_x measurements on
different platforms such as ground sites, vehicles as well as aircrafts (Yamamoto et al., 2011; Wagner et
115 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, NO_x emissions
are increasing. Motor vehicles are one of the major sources for NO_x, especially in urban areas
(Westerdahl, 2008). Exhaust from on-road vehicles makes up 20% of total NO_x emissions in China (Shi
et al., 2014). So various methods have been used to measure the vehicle emissions to assess exposure to
120 air pollutant and specific 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 measurements were usually carried out at several fixed
locations in large cities, which is not adequate to show the large scale patterns of the cities. Hence, a
direct on-road mobile instrument is needed to obtain the spatial and temporal variations of NO_x pollutants.

125 In this work, a dual-channel CRDS system has been developed based on the chemical conversion
of NO to NO₂, which realizes the simultaneous measurement of NO₂ and NO_x. In one channel, only
ambient NO₂ is measured. In another channel, the sum of ambient NO₂ and the converted NO₂ from
ambient NO is determined to provide a direct measurement of NO_x. Then the difference of the two

channels provides a direct measurement of NO. To assess the accuracy of the dual-channel CRDS instrument, contrast measurements and comparison were conducted between the dual-channel CRDS instrument with the other different instruments. In addition, the instrument was deployed in the measurement of on-road vehicle emission plumes in the city of Hefei, China on December 17, 2018 and February 25, 2019. The main advantages of this instrument compared with CL instruments are also discussed as well as its potential ability for trace measurements.

2. Setup of the instrument

Due to its high detection sensitivity, cavity ring-down spectroscopy has been applied to measurement NO₃ radical and N₂O₅ in our group (Wang et al., 2015; Li et al., 2018; Li et al., 2018). In this work, the technique was applied to measure NO₂ and NO simultaneously. A schematic diagram of the dual-channel CRDS system developed in the present work is shown in Fig. 1. The instrument mainly consists of two identical CRDS systems for NO₂ 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 in real time 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 generally the output power is about 60 mW. The laser beam first passes through an isolator to prevent the reflected light back into the laser cavity, then is divided into two approximately equal beams after a 50/50 beam splitter and enters into two identical cavities separately. Each optical cavity is made of an aluminum tube with an inner diameter of 9.4 cm, which is fixed rigidly by a separate frame. Two high reflectivity mirrors are held in stable, adjustable mounts. The distance between the two highly reflective mirrors (LGR, 1 in. diameter, 1 m radius of curvature) in each channel is 75 cm, which corresponds to the ring-down time constants of 22.90 μs and 24.12 μs for NO_x and NO₂ cavities in zero air. 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 is amplified firstly, then acquired with digital acquisition card (NI USB-6361, 16-bit, 2.0 Ms/s). The sampling frequency for each digital acquisition card is 1 MHz. During a continuous 1.0 s data acquisition period, 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. NO₂ concentration can be calculated according to Equ.1 from the ring-down times, τ and τ_0 , the ring-down times when the NO₂ is in the presence and absence of the cavity, respectively; the NO₂ absorption cross section, R_L is the ratio of the total cavity length to the length over which the absorber is present in the cavity, and c the speed of the light

$$[\text{NO}_2] = \frac{R_L}{c \sigma_{\text{NO}_2}} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (1)$$

2.2. NO convertor

NO is measured by its conversion to NO₂ in the presence of excess O₃. The principle is based on the following chemical equation (Sander et al., 2006).



where $k_1 = 3.0 \times 10^{-12} \exp(-1310/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Ozone is produced from O₂ photolysis at 185 nm by flowing 100 sccm of sampling air over a low pressure discharge mercury lamp. The mercury lamp is

inset into a quartz glass tube with a length of 50 mm and an inner diameter of 10mm. The flow rate
170 passing through the mercury lamp was controlled by a MFC and the resulting mixing ratio of O₃ was
detected by an O₃ analyzer (49i, Thermo Scientific). The O₃ concentration is approximately 11.2 ppm
after mixing with the sampled air. A Teflon tubing (length 1 m, i.d. 3.8mm) serves as a reactor for the
NO conversion.

2.3. Activated carbon device

175 Accurate measurement of the ring down time, τ_0 , when there is no any absorber in the cavity, is
pivotal for accurately retrieving the absorber concentration in a practical measurement 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 tube with a length of 26.0 cm and an outer diameter of 6.0 cm. The τ_0 is measured
180 for 60 s every 10–16 min. It is found that this frequency of zero measurements is sufficient to track drifts
in the zero ring-down time constant measurement, i.e. the fluctuation of τ_0 is less than 0.1% for 15 min
intervals.

2.4. Gas handling system

The gas handling system of the instrument consists of a sampling module and a purge flow. The
185 sampled air initially flows through a filter device, where a filtering membrane (1 μm pore size) is loaded
to prevent light-scattering aerosols from entering the cavity. And subsequently it will pass through the
activated carbon device to provide the background measurement or enter the PFA tube directly just
depending on whether the three-way solenoid valve is open or closed. After the PFA tube, the air flow is
divided into three lines. The first flow (100 sccm) is introduced into a quartz flow tube equipped with a
190 mercury pen-ray lamp (Oriol 6035) to generate O₃ by air photolysis as aforementioned, then it will be
merged with the second sampling flow (900 sccm) and pulled into the NO_x cavity. The third one with a
flow rate of 1 slm is directed into the NO₂ cavity. All the system is pumped by a rotary pump (K86KNE)
and the flow rates of the different lines are controlled by mass flow controllers separately. To prevent the
degradation of the mirror reflectivity, each mirror is continuously flushed with high-purity nitrogen at a
195 rate of 25 ml min⁻¹ to avoid the potential pollution from the sample flow.

3. Results and discussion

3.1 Determination of Absorption Cross Sections

To retrieve the gas concentration, it is prerequisite to determine the effective absorption cross
section at peak absorption of the laser. The output waveforms of the laser, with a center wavelength of
200 403.64 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 NO₂ and
avoid the interference from other species, such as H₂O (pink line in Fig. 2). The effective absorption
cross section was determined to be 5.63×10^{-19} cm²/molecule by convoluting the NO₂ absorption cross
section with the laser spectrum (blue line in Fig. 2) using voigt profile (Voigt et al., 2002). It is well
205 known that a shift in the laser center wavelength would result in a change of the effective NO₂ cross-
section, so the laser output was monitored as the index of the day-to-day variability of the laser center
wavelength. It was shown that the variability is less than 1% during the experiment 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

210 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 of the system was
determined from the absorption measurement of various concentrations of NO_2 ranging from 20 ppb to
70 ppb with or without purge flow. The ratio of the two extinction measurements yielded a R_L value,
which is independent of the cross section and the concentration of NO_2 . The R_L value is determined to
215 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 have been reported, where various kinds of air
220 were used as background gas, such as zero air, a mixture of oxygen and nitrogen, chemically scrubbed
laboratory air (using hydroxyapatite), and laboratory air sampled through the stainless steel tubing coil
(Wada and Orr-Ewing, 2005). 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 $24.12 \pm 0.01 \mu\text{s}$ and $22.90 \pm 0.01 \mu\text{s}$ in two cavities, respectively. These values are close
225 to those of measurements of zero air at the same sample rate for a 15 min period.**

Two representative ring-down signals corresponding to with and without NO_2 in the cavity for the
CRDS system are shown in Fig. 3. And the fitted ring down time were $24.12 \mu\text{s}$ and $20.30 \mu\text{s}$ respectively,
so that the NO_2 concentration is determined as 20.28 ppb using the constants determined above.

3.4 Detection limit and measurement accuracy of two cavities.

230 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 1σ detection limits
were 30 ppt and 40 ppt (1s) for the NO_2 and NO_x channels, respectively. The minima in the Allan plots
235 indicated that the optimum average times for optimum detection performance (right panel of Fig. 4) is
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:

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

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

245 The total uncertainty of NO_2 measurement by CRDS is expected to be from the uncertainties on the
measurement of R_L and NO_2 absorption cross section. The uncertainty in R_L was determined to be less
than 3%, and the uncertainty in the NO_2 absorption cross-section was about 4%, so the total uncertainty
of NO_2 measurement was estimated to be 5% for the system in this work.

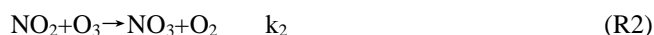
Compared with the existing field measurement techniques for NO_2 measurements, it seems that the

250 minimum detection and uncertainty of this instrument is superior to the other methods (see Table 1).

3.5 NO Conversion Efficiency

The main influence factor on the NO conversion efficiency is the flow rate passing through the mercury pen-ray lamp as it can determine the generated O₃ concentration. The mixing ratio of O₃ in the NO_x channel line changing with the flow rate that passes through the mercury pen-ray lamp was investigated and the result is shown in Fig. 5. As a result, the bypass flow passing through the Hg lamp was determined to be 100 sccm. Under this flow rate, when the residence time of O₃ in the cavity is 1 s and the ambient NO₂ concentration is 50 ppb, NO conversion efficiency with different NO concentrations (10-1000 ppb) was simulated and NO conversion efficiency in the range of experimental concentrations is larger than 98% .

260 Because the cross section of O₃ is about four orders of magnitude smaller than that of NO₂ at the center wavelength of the laser, the absorption of O₃ generated by mercury photolysis is negligible. According to Fuchs (Fuchs et al., 2009), under conditions when NO is rich, further oxidation of NO₂ to NO₃ and N₂O₅ has only a slight effect on NO_x measurement, which means that the correction of the NO_x measurement can be neglected. However, under conditions when NO is absent, the loss of NO₂ 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:



270 where $k_2 = 1.2 \times 10^{-13} \exp(-2450/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ($T=298\text{K}$, $k_2 = 3.2 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) (Sander et al., 2006), $k_{eq} = (5.1 \pm 0.8) \times 10^{-27} \exp(10871/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ($T=298\text{K}$, $k_{eq} = 3.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) (Osthoff et al., 2007). The loss rate will increase with the increase of the NO₂ + O₃ reaction rate constant when temperature in the cavity increases. Moreover, the loss rate is also sensitive to the NO₂ mixing ratio. Diluted NO₂ standard mixture was introduced into the two channels to characterize the effect of high concentration ozone on NO₂ measurement. The NO₂ concentrations in the two channels and their correlation are shown in Fig. 6. The interference of O₃ in NO_x channel when NO is absent can be neglected. The discrepancy between two different channels maybe result from the systematic errors in two different channels and can be corrected with the coefficient obtained from Fig. 6 (b).

4. Field applications

4.1 Contrast measurement of standard mixtures of NO and NO₂.

280 The comparisons of NO₂ measurements between CRDS and NO_x analyzer have been carried out on NO₂ standard mixtures. Different mixing ratios of NO₂ were obtained by gas phase titration of NO with excess O₃ generated by an ozone generator (OC500). The 10.3 ppm NO standard mixture was initially diluted by N₂ and subsequently oxidized by O₃. The amount of NO₂ generated from excess ozone can be calculated from the known initial concentration of NO. The generated pure NO₂ 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 concentrations of the standard NO₂ in the laboratory measured by

CRDS and a commercial CL analyzer (42i, Thermo Scientific, Inc., 0.4 ppb (1σ) detection limit) simultaneously. A correlation analysis between the data from the two instruments was carried out. The fitting results shown in Fig. 7(b) indicate that $\text{NO}_2(\text{CRDS}) = \text{NO}_2(\text{CL analyzer}) \times 1.031 - 0.940$, with a linear correlation factor (R^2) of 0.99. The results in Fig. 7 (a) also indicate that CRDS instrument can capture the NO_2 variation more rapidly than CL analyzer.

4.2 Ground-based measurements of NO_2 and NO.

To verify its performance and applicability, the dual-channel CRDS instrument was further compared with a CEAS instrument (Duan et al., 2018) on ground-based measurement of NO_2 during the period from November 3 to 5, 2017 in the western suburb area of Hefei, Anhui, China. The reason why CEAS instrument not the CL analyzer was selected for NO_2 intercomparison is that for CL analyzer, NO_2 must be converted to NO first and then can be detected, which expose the analyzer to chemical interferences, while for CEAS instrument, NO_2 can be detected directly. 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 set up on the sixth floor of the building in Anhui Institute optic and Fine mechanics. The area lies to the northeast of the Dongpu reservoir and is about 1.5 km far from the reservoir. The northwest of the area is surrounded by a forest. The significant NO_2 pollution during the measurement was found to be 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 through a 6 mm outer diameter Teflon tube. The data for comparison were averaged to 1min. Fig. 8 (a) shows the temporal variations of NO_2 concentrations measured by the CEAS and the CRDS instruments respectively. It was found that the nighttime NO_2 was in the range of 3 ppb to 35 ppb. Generally, the NO_2 concentrations and variations measured by the CRDS instrument show good consistency with those measured by the CEAS instrument, and the slope and intercept of the regression line from the least-squares analysis are 1.042 ± 0.002 and (-0.393 ± 0.040) ppb, respectively as shown in Fig. 8(b). However, the results revealed a discrepancy when 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 emitted 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 (see Fig. 9 (a)). 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 $R^2=0.99$. As CL method is believed to be a reliable way for NO measurement, the reliability of the dual-channel CRDS instrument were validated for the measurement of NO.

4.3 On-road measurements of vehicle NO_2/NO_x 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 around the whole area. Fig. 10 shows a picture of the movable van loaded with CRDS

instrument, and the position of the sampling inlet is about 1.5 m above the ground. Fig. 11 illustrates the route in Hefei and the drive track is colored logarithmically with respect to measured NO_x, NO₂ and NO. The NO₂ concentration ranged from 1.5 ppb to 133.3 ppb and NO ranged from the detection limit to 554.7 ppb. The mean concentrations of NO and NO₂ were 140 ppb and 54.9 ppb, respectively. On the whole, the NO and NO₂ concentrations in urban area were higher than those in suburban area. Large plumes of NO were found at the crossroads with heavy traffic or the sites converged with heavy-duty diesel vehicles. [NO₂] / [NO_x] ratio was about 19%, which is larger than the results observed in USA (Wild et al., 2017).

In February 25, 2019 another measurement of vehicle emissions was performed on road to verify further the instrument performance. NO analyzer (42i), O₃ analyzer (49i) and the CRDS instruments were all placed in a same car. Ambient air was pumped through an inlet fixed on the roof of the car and then divided into three lines to the three instruments, respectively. Fig. 12 illustrates the 4-hour drive track involving highway, urban and suburban area around Hefei, which is colored with respect to the measured NO and NO₂. Vehicle speeds varied greatly on the three different road types and it is around 100 km/h on highway. Influenced by the vehicle emissions, the NO_x plumes on urban roads are higher than those on suburban roads and highway.

Fig. 13 shows the time series of NO₂, O₃ and NO. NO₂ concentrations ranged from detection limit to 110.2 ppb and O₃ concentrations ranged from 6.9 ppb to 85.3 ppb. Several NO plumes were observed and the maximum value was up to 767.1 ppb. O₃ and NO showed a significant negative correlation, which is attributed to the quick titration of O₃ by NO. Fig. 14 shows the NO data measured by CRDS and CL analyzer (42i), (a) is the original measurement data and (b) is the data averaged to 1min. The good agreement between the measurement results from the two instruments proves that the CRDS instrument can be applied for fast vehicle NO_x emissions.

Because the NO₂ to NO_x 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 retrieve the direct vehicle NO_x emission and NO₂ to NO_x ratio of plumes due to its easy deployment and high temporal resolution.

5. Conclusion

A compact, sensitive, and accurate instrument based on diode-laser cavity ring-down spectroscopy with the center wavelength of 403.64 nm has been demonstrated for detection of trace amounts of NO₂ and NO_x in ambient air. Minimum detection limits of NO₂ 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%. Contrast measurement between the dual-channel CRDS instrument and a CL analyzer on NO₂ standard mixtures were performed, which shown a good correlation between the two different 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 investigated. During the intercomparison measurements of NO₂ and NO in the field, the dual-channel CRDS instrument shown a good correlation with the CEAS instrument for NO₂ measurement, and with the CL analyzer for NO measurement.

The CRDS instrument was further deployed in a movable car to monitor NO and NO₂ emission on road. The advantage of high time resolution of the instrument has been demonstrated, which means the instrument provide a new direct method for on-road vehicle plumes measurement. Meanwhile, the high detection sensitivity of the instrument has also shown in this work, which indicates it can act as a new

375 detection technique for chemistry model verification. It is expected that the instruments developed will
lead to the wider application for ambient air quality monitoring and will be useful to investigate
photochemistry in the atmosphere more precisely.

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Table 1 Comparison of NO₂ detection limits based on optical methods.

Principle of measurement	Laser power	Wavelength range/nm	Detection limit	Reference
Cw-CRDS	5mW(1MHz)	410	80ppt/50s(1σ)	(Wada and Orr-Ewing, 2005)
ND:YAG laser CRDS	1mJ	532	40ppt/1s(1σ)	(Osthoff et al., 2006)
pDL-CRDS	40 mW(2KHz-10%)	404	11ppt/1s(1σ)	(Fuchs et al., 2009)
Fabry-Perot (FP) pDL-CRDS	1.1w (4KHz-10%)	400	38ppt/128ms(1σ)	(Karpf et al., 2016)
commercial DL-CRDS	1.2KHz	407.38	20ppt/60s(1σ)	(Castellanos et al., 2009)
LED-based commercial CRD	355 mW	397-412(405)	27ppt/60s(1σ)	(Brent et al., 2013)
LED-CEAS	340mw	455	2.2ppb/100s(1σ)	(Wu et al., 2009)
Xe lamp DOAS		295–492 nm	1ppb/480s(1σ)	(R. McLaren, 2010)
CAPS		440	20ppt/10s(1σ)	(Kebabian et al., 2008)
diode-pumped Nd:YAG laser-LIF	15mw(14KHz)	473	70/60s(1σ)	(Taketani et al., 2007)
blue LED-IF	17.7mw(10KHz)	435	4.9ppb/60s(1σ)	(Matsumi et al., 2010)
pulsed blue light LED-LIF	22mw	430	3.5ppb/60s(1σ)	(Sadanaga et al., 2014)
pDL-CRDS	60mw	403.64	30ppt/1s(1σ)	This work

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.

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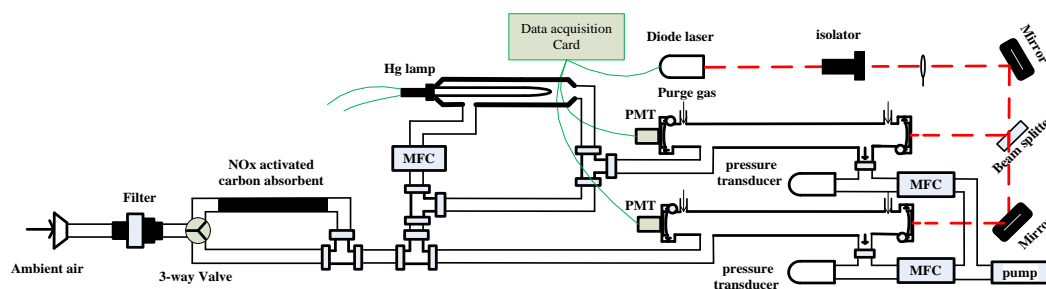


Fig. 1. Schematic of the dual-channel Cavity Ring down Spectroscopy system.

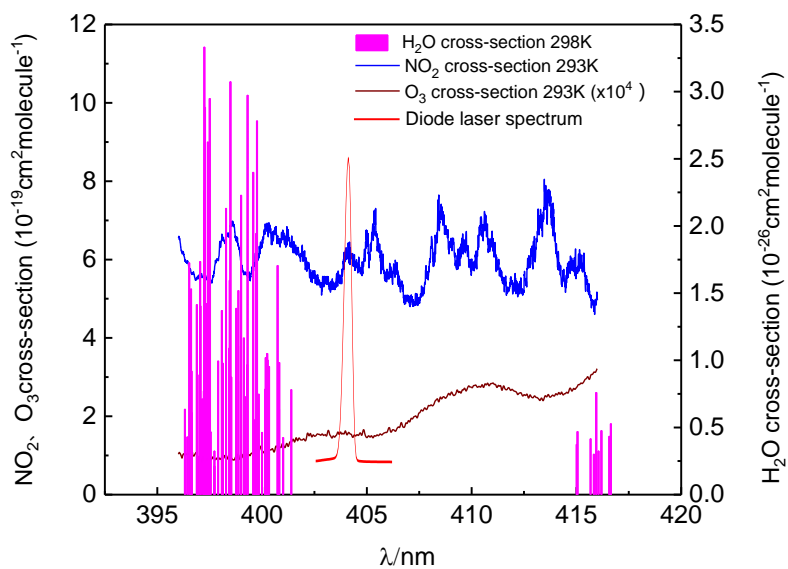


Fig. 2. Cross section of the NO_3 radical, NO_2 , O_3 , water vapor, and diode laser spectrum.

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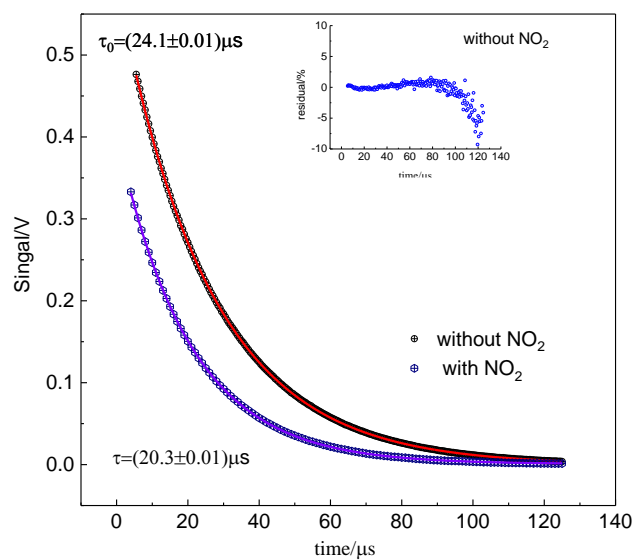


Fig. 3. Different cavity ring-down signals and fitting results in the absence and presence of NO_2 . The small figure in the upper right corner is the fitting residual.

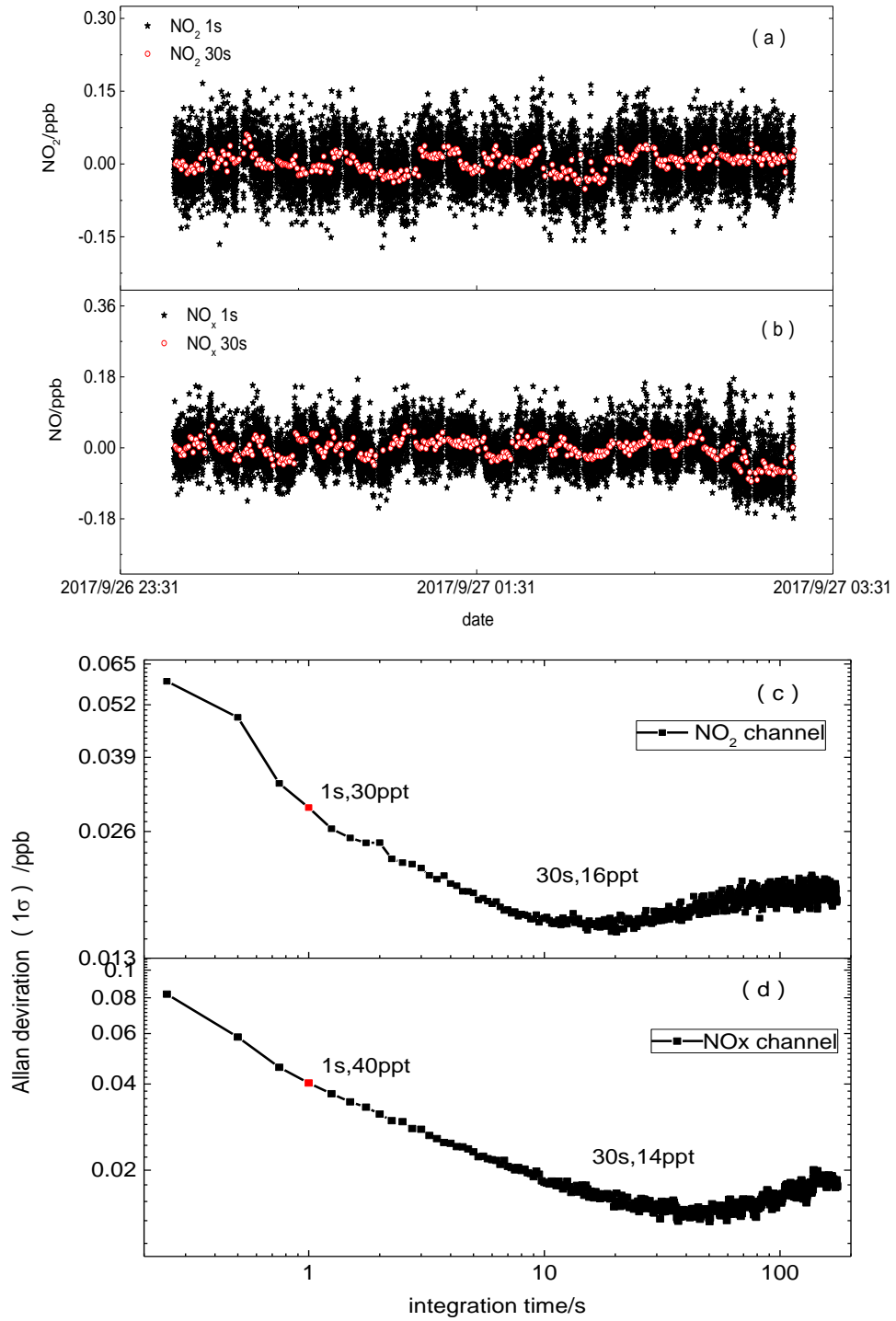


Fig. 4. (a) (b) Continuous time series measurement when the instrument sampled only zero air, averaged to 1s for NO₂ and NO_x channels (black dots), the red dots show the data averaged to 30s, (c) (d): Allan deviation plots for NO₂ concentration in two channels. The minimum value equals the optimum integration time.

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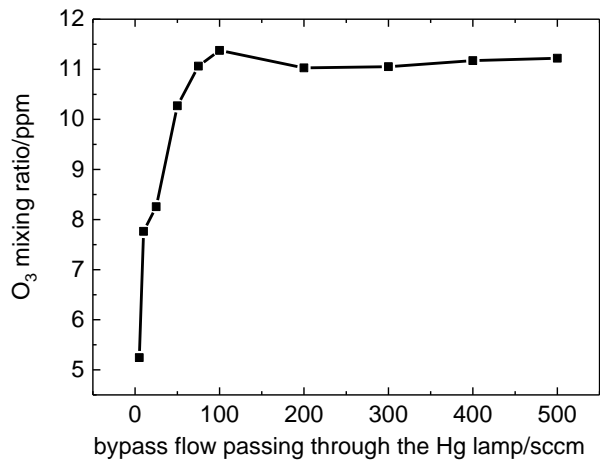


Fig. 5. O₃ mixing ratio when changing the bypass flow passing through Hg lamp.

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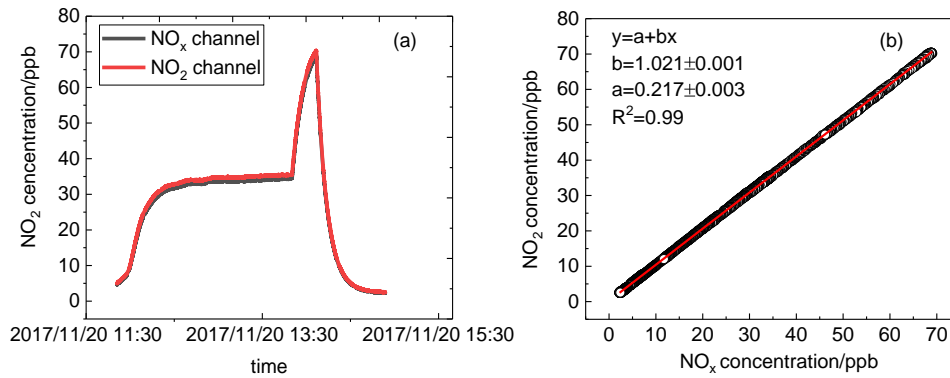


Fig. 6. (a) Time series of NO₂ concentration sampled standard mixtures by CRDS instrument in two channels with mercury pen-ray lamp switched on. (b) A correlation plot between the data from two channels.

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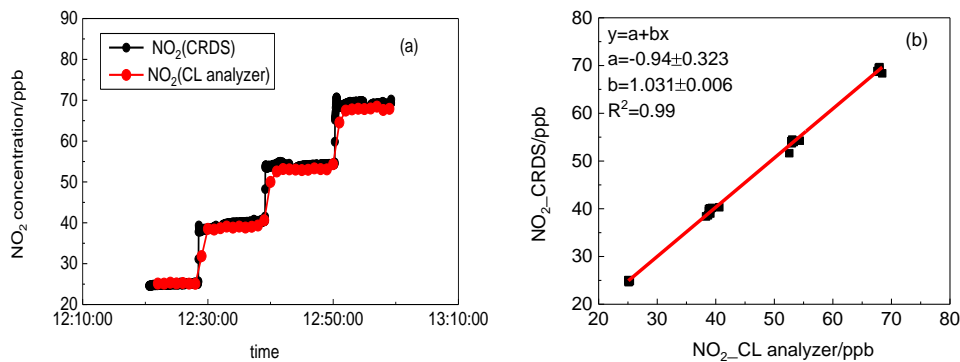
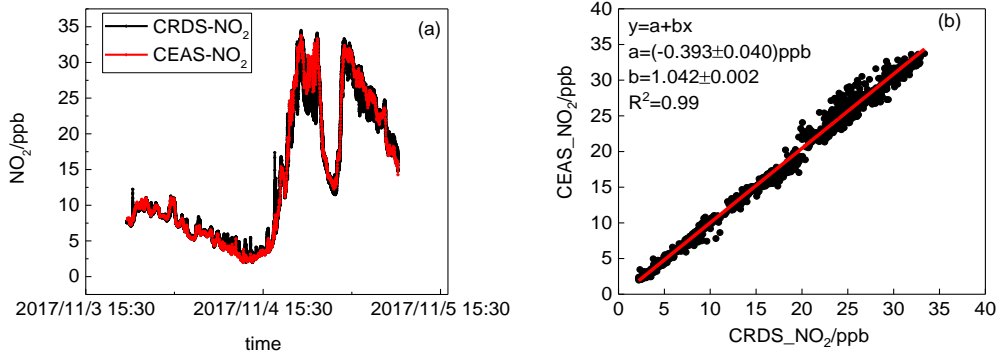


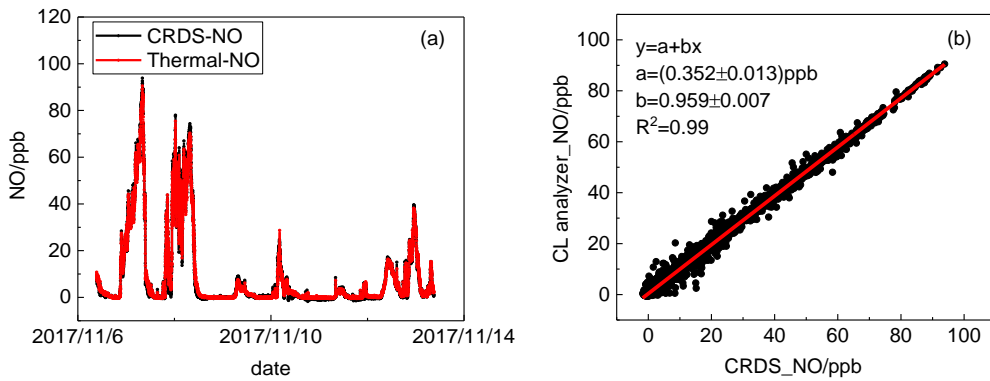
Fig. 7. (a) Time series of NO₂ concentration sampled standard mixtures by CRDS instrument and CL analyzer. The time resolution for CRDS instrument and CL analyzer are 1s and 1min, respectively. (b) A correlation plot between the data from the CRDS instrument and the CL analyzer (data averaged to 1min). The fitting result gave a gradient of 1.031 and an intercept of -0.940 ppb, with linear correlation

factor of 0.99.



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Fig. 8. (a) NO₂ mixing ratios by CEAS (1 min average) and CRDS (1 s average) instruments, (b) Scatter plots for the NO₂ dataset from CRDS and CEAS instrument. The red lines illustrate the linear regression (Data averaged to 1 min base).



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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.

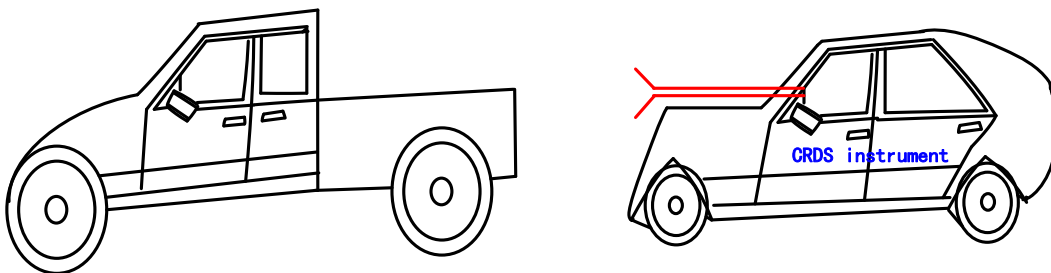


Fig. 10. The diagram of the movable van loaded with CRDS instrument.

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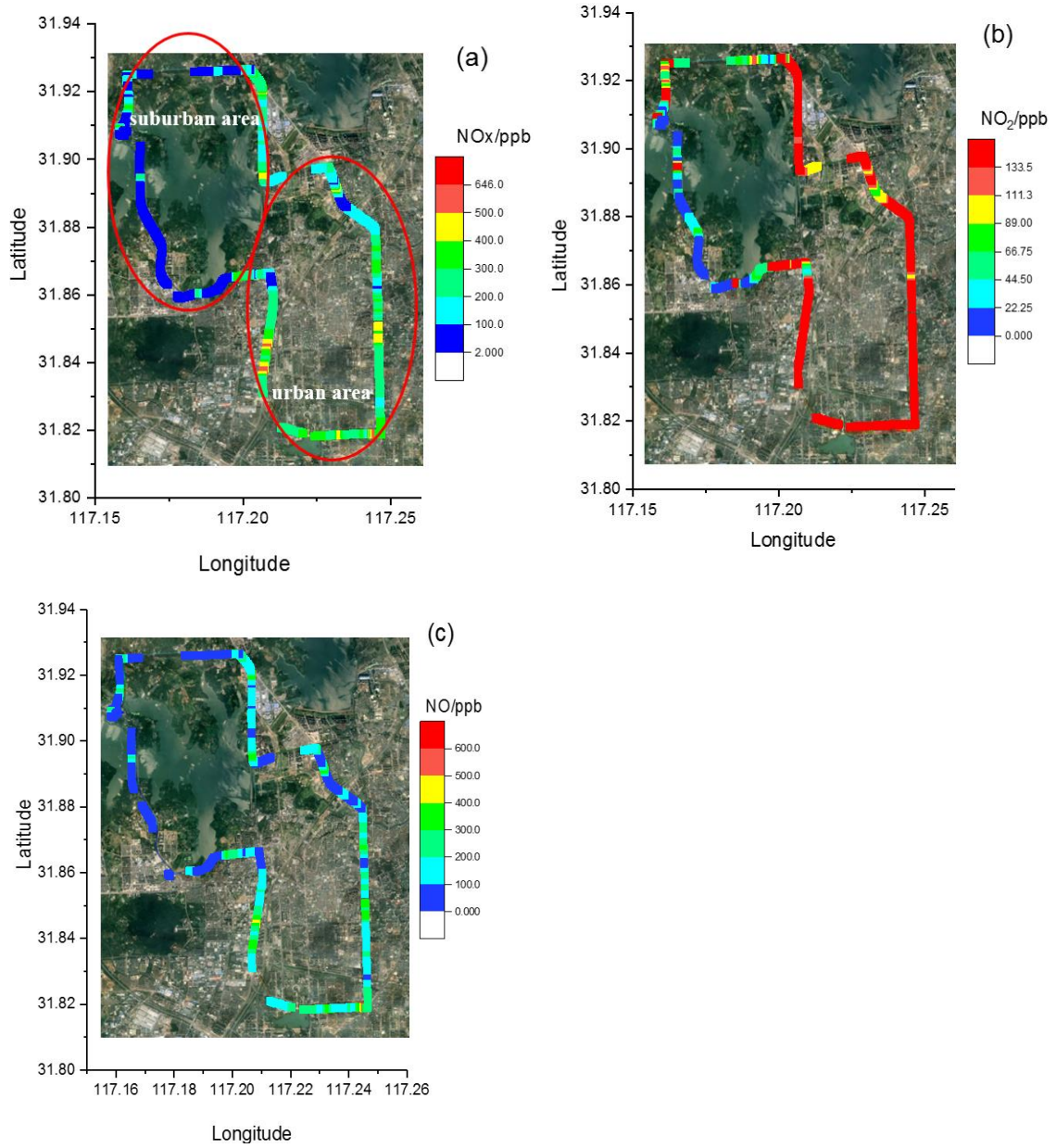
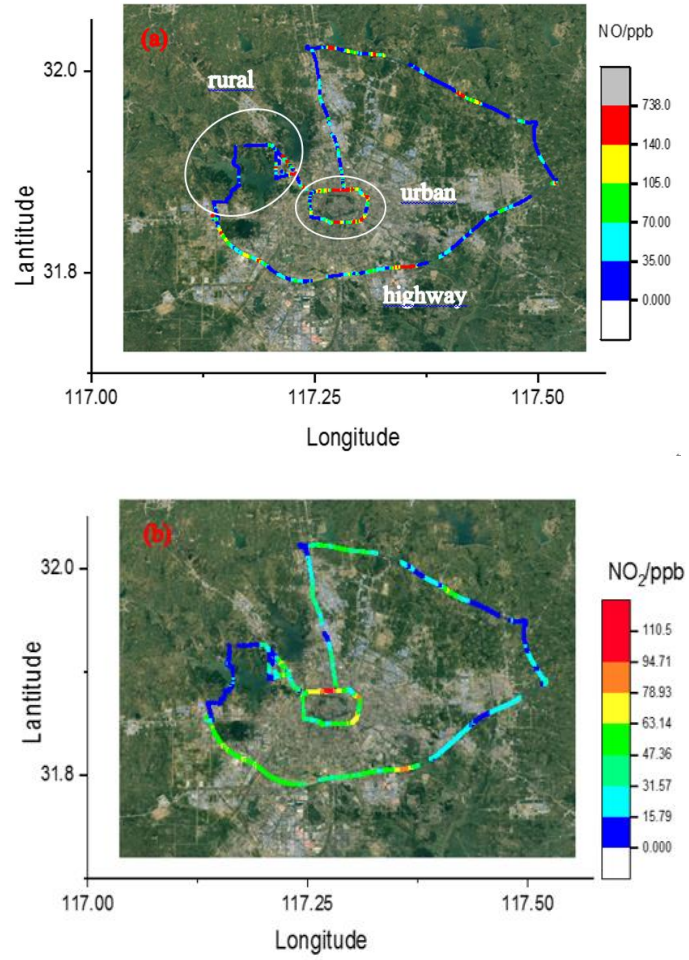


Fig. 11. Results of the NO_x (a), NO₂ (b) and NO (c) concentrations around Hefei, China (Data is averaged to 5 s).



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Fig.12.The 4-h drive around Hefei, China, colored by the measured NO (a) and NO₂ (b) concentrations, respectively.

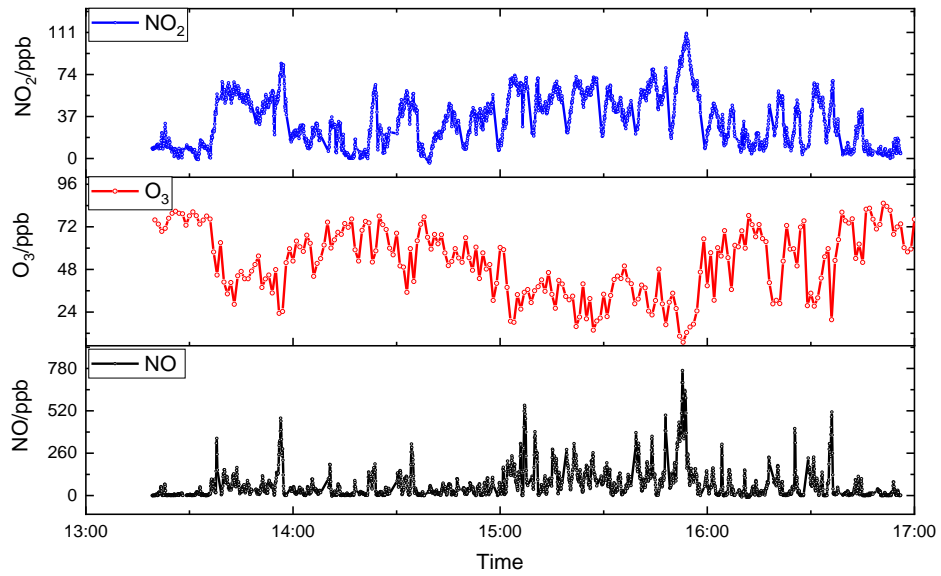
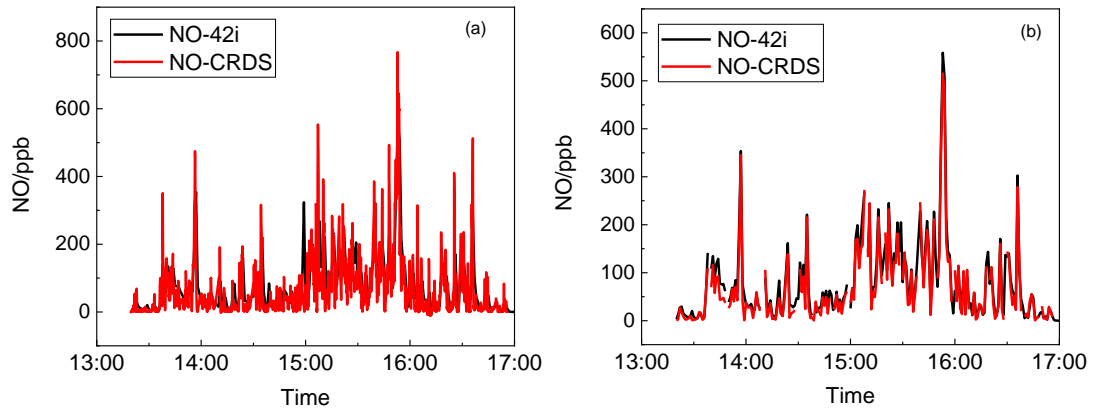


Fig.13. Results of the NO₂, NO and O₃ concentrations around Hefei, China.



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Fig.14. Time series of NO by CRDS instrument and CL analyzer (42i). (a) is the original measurement data and (b) is the data averaged to 1min.