I. INTRODUCTION

Nitrogen oxides (NO\(_x\)=NO+NO\(_2\)) play a vital role in atmospheric chemistry as formation and destruction of tropospheric ozone, acid deposition, and forming of nitrate radicals (NO\(_3\)) [1]. Most of the NO\(_x\) emission is in the form of NO from both natural (lighting, biomass burning, soil) and anthropogenic source (fossil combustion, motor vehicles) [2]. NO can rapidly be oxidized into NO\(_2\) via various mechanisms (reactions with O\(_3\), HO\(_2\), and RO\(_2\)). O\(_3\) can be formed from the photolysis of NO\(_2\) under ultraviolet (UV) solar radiation (λ<420 nm) [2–4] as follows:

\[
\begin{align*}
\text{NO}_2 + h\nu &\rightarrow \text{NO} + \text{O}^{(3}\Pi) \quad (1) \\
\text{O}_2 + \text{O}^{(3}\Pi) + \text{M} &\rightarrow \text{O}_3 + \text{M} \quad (2)
\end{align*}
\]

where M is a third body (usually N\(_2\) or O\(_2\)). Reaction between OH radical and NO\(_x\) is an important loss process for OH radicals at urban sites.

NO\(_2\) is designated as one of the six environmental pollutants declared by Chinese Ministry of Environmental Protection (MEP), namely sulfur dioxide (SO\(_2\)), nitrogen dioxide (NO\(_2\)), suspended particulates smaller than 10 μm (PM10) and those smaller than 2.5 μm (PM2.5) in aerodynamic diameter, carbon monoxide (CO), and ozone (O\(_3\)), being measured at monitoring stations in each city [5]. Chemiluminescence (CL) technique is the most widely used technology recommended by US Environmental Protection Agency (EPA) for NO\(_2\) monitoring networks [6]. NO\(_2\) is first converted to NO through reduction reaction by passing a heated (300–350 °C) metal-catalytic converter (usually molybdenum) following the detection of CL produced from the reaction of NO with O\(_3\) to form electronically excited NO\(_2\) [7, 8]. However, the reduction conversion is not specific for NO\(_2\). Oxidized nitrogen compounds such as nitric acid (HNO\(_3\)), peroxide nitrates (PNs, RO\(_2\)NO\(_2\)), alkyl nitrates (ANs, RONO\(_2\)) may also be reduced to NO in a molybdenum converter at typical operating temperature under 400 °C [9, 10], which could lead to an overestimated NO\(_2\) concentration at ambient conditions. PNs and ANs can yield NO\(_2\) at a ratio of 1:1 when they are heated and undergo thermal decomposition. The reported temperatures for complete dissociation (>99%) are 200 °C for PNs, 400 °C for ANs, and 650 °C for HNO\(_3\), respectively [11–14]. These extra NO\(_2\) can bring in a bias of NO\(_2\) detection when CL instruments are equipped with molybdenum converter (Mo-CL).

More specific techniques for NO\(_2\) detection have been developed, including CL instrument equipped with a photolytic converter (P-CL) [15, 16], laser induced fluorescence (LIF) [11, 17–20], differential optical absorption spectroscopy (DOAS) [18, 21–23], tunable infrared laser differential absorption spectroscopy (TILDAS) [22, 24], cavity ring-down spectroscopy (CRDS) [25–28],
cavity attenuated phase shift (CAPS) spectroscopy [29–32], and Faraday rotation spectroscopy (FRS) [33, 34]. Steinbacher et al. [15] measured NO$_2$ concentration with both P-CL and Mo-CL instruments in rural Switzerland with up to 30% bias on a monthly basis. Dunlea et al. [22] found averaged 22% overestimated NO$_2$ levels by Mo-CL compared with DOAS and TILDAS technique in Mexico city, and the bias could be up to 50% during afternoon hours. Ge et al. [31, 32] reported an overestimated NO$_2$ level by Mo-CL up to 20% compared with CAPS in the afternoon hours in Beijing. Besides, Cao et al. [16] gave an averaged bias of +3.72 ppbv by NO-CL comparing with P-CL during a 30-day long ambient measurement in Beijing.

As a technique for detecting optical absorption of molecules, CRDS enhances the absorption path length as the light travels many times in the resonance cavity resulting in a superior sensitivity in detecting molecules at ultra-low concentrations. CRDS has been used as a powerful tool for trace gas detection since it was first developed by O’Keefe and Deacon [35]. Brown et al. used CRDS for ambient pollutants detection as NO$_2$, O$_3$, NO$_3$, and N$_2$O$_5$ [25, 36–39]. Taking advantage of the thermal instability of ANs and PNs, Osthoff et al. conducted a thermal dissociation cavity ring-down spectroscopy (TD-CRDS) instrument to detect ANs and PNs in laboratory [40, 41]. Very recently, a five-channel cavity ring-down spectrometer with thermal dissociation region has been built for the field detection of NO$_2$, NO$_3$, N$_2$O$_5$, PNs and ANs [42], and a two-channel thermal dissociation cavity ring-down spectrometer was implemented to detect ambient NO$_2$, RO$_2$NO$_2$, and RONO$_2$ [43].

In this study, we present a two-channel TD-CRDS for measurements of NO$_2$ and RNO$_2$ (PNs+ANs). We conducted a 6-day long measurement of NO$_2$ by two-channel TD-CRDS and a commercial Mo-CL instrument. By comparing the results from Mo-CL and CRDS, we evaluated the accuracy of the CRDS instrument and investigated the reasons causing deviations in the Mo-CL instrument. We demonstrated that the high sensitivity (0.1 ppbv at 1 s) and fast response of the CRDS instrument are very useful for real-time measurement in field studies.

II. EXPERIMENTS

The configuration of two-channel CRDS setup is shown in FIG. 1. A 405 nm diode laser (PTI, IQi2A) with an output power of about 100 mW was used as the light source. The laser is centered at 405.46 nm with a line width of about 0.5 nm which was measured by a grating spectrometer (Shamrock750). The laser was switched on and off with rising time of about 10 ns by a 1 kHz TTL signal. After passing through an optical isolator, the light was split (50/50) and coupled into two ring-down cavities each consisted of two high reflective (HR) mirrors (ATFilms, $R\approx99.995\%$). Each cavity was about 87 cm long and made of PFA (Perfluoroalkoxy alkanes) tube, with an outer diameter of 3/4 inch. The HR mirrors were protected by purging in dry nitrogen. All the gas flow was controlled by mass flow controllers (Omega) leading to a stable pressure in the cavity. The purge gas of nitrogen is 150 mL/min, and the flow rate of ambient gas is 1 L/min. PTFE (polytetrafluoroethylene) membrane filters (whatman, pore size 0.2 µm) were used to remove particles when sampling ambient air. The light emitting from the cavity was detected by a photomultiplier tube (PMT) and recoded by a digitizer (ADLink).

The molecule concentration $N$ (molecule/cm$^3$) in the RD cavity can be derived from the equation below:

$$N \sigma = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)$$

(3)

where $c$ is the speed of light, $\sigma$ is the effective absorption cross section of NO$_2$ at 405 nm, which is 6.45\times10^{-19} \text{ cm}^2/\text{molecule at room temperature (294 K)} [44]. $\tau$ and $\tau_0$ are the decay time with and without sample, respectively. $R_L$ is the ratio of optical length between two HR mirrors and sample length. Light with wavelength smaller than 420 nm could lead to photolysis of NO$_2$ [4]. The photolysis rate coefficient of NO$_2$ at half sun is about 5\times10^{-3} or 0.01 s$^{-1}$ with sunlight density of 1000 W/m$^2$ [45, 46], and it is linear to the light intensity [46]. The photolysis ratio of NO$_2$ is about 0.1% under our experiment conditions.

The reference CRDS channel (FIG. 1, labeled as Chan.2) was used to detect the absorption of NO$_2$ molecules in the sample gas. Another channel (FIG. 1, labeled as Chan.1) was used in parallel to detect additional NO$_2$ dissociated by RNO$_2$ (peroxo nitrates and alkyl nitrates). Before ambient air flew into the cavity, it passed through a 25-cm-long quartz tube (4 mm inner diameter, 6 mm outer diameter) heated to 440 °C with temperature fluctuation within 1 °C. The heating zone is similar to the design in Ref.[11] to ensure that over 99% of RNO$_2$ will dissociate to produce NO$_2$ at a ratio of 1:1.

A commercial Mo-CL NO$_x$ analyzer based on CL measurement of NO (Thermo Fisher Scientific, 42i-TL) was used to calibrate the CRDS instrument. The Model 42i-TL instrument operates on the principle that nitric oxide (NO) and ozone (O$_3$) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. NO$_2$ can also be detected by the instrument, after being converted to NO by a molybdenum converter heated to about 325 °C. A mode solenoid valve is used to switch between two modes: with sample flowing through the molybdenum converter (NO$_2$ mode) or bypassing the molybdenum converter (NO mode). The difference between the NO concentrations detected in these two modes is used to derive the NO$_2$ concentration. The NO$_2$ detection limit of 42i-TL is 50 pptv at an averaging time of 120 s.
Diluted NO$_2$ gas samples were measured by both CRDS (two channels, without thermal dissociation) and Mo-CL analyzer (42i-TL analyzer). During the process of about 5 h, an NO$_2$ sample was diluted by dry pure nitrogen and the NO$_2$ concentration was determined by the Mo-CL analyzer. The results are used to determine the factor $R_L$ of the CRDS instrument. When a $R_L$ factor of 1.75 was applied, the CRDS results agree perfectly with the CL analyzer, which is illustrated in FIG. 2. The residual discrepancy is below 0.2 ppbv, being consistent with the uncertainty of the CL analyzer and the fluctuations of diluted NO$_2$ gas.

RNO$_2$ channel (labeled as Chan.1 in Fig.1) could detect extra NO$_2$ produced by the dissociation of RNO$_2$ when the sample gas passed through the heating zone. When the TD tube was bypassed, the NO$_2$ detected by two channels agreed well with each other with a discrepancy below 0.2 ppbv. Meanwhile, the extra NO$_2$ concentration (1:1 to RNO$_2$) was about 2 ppbv when the ambient air was measured, confirming that the difference was due to RNO$_2$.

### III. RESULTS AND DISCUSSION

In order to test the performance of the instrument, we took a 6-day continuous measurement of ambient NO$_2$ and RNO$_2$ in Hefei, China. The monitoring location was in the west campus of USTC, with a height of about 12 m, and about 30 m from a main street. The air sample flowed directly into the reference CRDS channel and the Mo-CL analyzer, and passed through the heating region at the TD channel. The experiment lasted for about 7 days from January 11 to January 17, 2017. During the experiment, every 11–12 h the TD tube was bypassed to verify the agreement between the NO$_2$ concentrations detected by the two CRDS channels. During the whole experiment, the discrepancy was below 0.2 ppbv.

The NO$_2$ data by Mo-CL had a time resolution of 1 min with 1 min averaging time. While the NO$_2$ data by CRDS had a time resolution of about 3 s. For comparison, the NO$_2$ and RNO$_2$+NO$_2$ data by CRDS have been averaged to 1 min resolution. As shown in FIG. 3, the NO$_2$ concentration detected by Mo-CL analyzer actually agreed better with the TD channel (Chan.1, RNO$_2$+NO$_2$), being significantly higher than the reference channel (Chan.2, NO$_2$).

It turned out that NO$_2$ rose from 8:00 in the morning, and reached its maxima till 10:00. Another rising process began at about 16:00 in the afternoon. The rising of NO$_2$ could be attributed to the NO$_2$ emission from motor vehicles during the traffic jam hours in the morning. As the growth of solar radiation, the photolysis of...
NO$_2$ resulted in the decrease of NO$_2$. The emission of NO$_2$ from the traffic jam occurred at about 16:00 and led to the accumulation of NO$_2$ until the evening. The increase of NO$_2$ was always accompanied by a simultaneous increase of NO more or less. Note that around 16:30 January 13, there was a sharp peak of NO$_2$ with concentration of about 90 ppbv.

During two periods, from 18:00 of January 12 till early morning of January 13, and from about 8:00 till noon of January 13, NO$_2$ detected by Mo-CL analyzer significantly deviated from the CRDS results. The rapid fluctuation of NO could be attributed to local emission. The sample site is close to a main street with lots of heavy vehicles running in the night time. This was possibly the reason of sharp NO signals. As better illustrated in FIG. 4, the discrepancy could reach as high as 40 ppbv, or relatively about 100%. At the same time, we observed rapid change of NO. Since the Mo-CL analyzer measures NO$_2$ by converting it to NO, the readout can be distorted when the NO concentration is changing. A mode solenoid valve inside the Mo-CL analyzer determines whether the sample flows through the molybdenum converter (NO$_x$ mode) or bypasses the molybdenum converter (NO mode). The difference between the two modes is used to derive the NO$_2$ concentration. The method is only valid assuming that the NO concentration changes slowly. However, the NO concentration can change a lot when switching between the NO$_x$ mode and the NO mode.

Moreover, the molybdenum convertor was not specific for NO$_2$, some other species reactive nitrogen as HONO, HNO$_3$, and RNO$_2$ could also be converted to NO [9, 10]. Besides, RNO$_2$ could produce extra NO$_2$ in the molybdenum converter heated to 325 °C. These effects lead to a bias in NO$_2$ measurements using a Mo-CL analyzer.

A result of such effect is shown in FIG. 5. With a time resolution of 3 s, we can clearly identify the change of NO$_2$ and RNO$_2$ within the an-hour period. NO$_2$ detected by reference channel ranged from 20 ppbv to 30 ppbv during the period. The difference between TD channel and reference channel represented the concentration of RNO$_2$. There were several sharp peaks of RNO$_2$ as large as 55 ppbv in the first several minutes in FIG. 5. However, the NO$_2$ concentration given by Mo-CL analyzer was apparently larger than the result from the CRDS reference channel. The reason was that the RNO$_2$ concentration had been wrongly included. The bias between Mo-CL analyzer and the CRDS reference channel was 45.3 ppbv (relatively 165%). The bias could be attributed to the reduction of other oxidized nitrogen compounds including RNO$_2$.

The Mo-CL analyzer tends to overestimate the NO$_2$ concentration. The effect during the 6-day-measurement is illustrated in FIG. 6, by the ratio of the NO$_2$ concentration given by Mo-CL analyzer to that by CRDS. The ratio was higher than 1 at most of the time, and sometimes even reached 2. Notice that the
ratio started to increase before the noon and peaks appeared in the afternoon when the concentration of NO₂ decreased to the bottom level. The trend was consistent with the results of contrast experiment with Mo-CL instruments [15, 16, 22, 31, 32]. As a result of the photolysis of NO₂, the appearance of bottom concentration of NO₂ in the afternoon indicated sufficient solar radiation of that day which led to abundant oxidants as O₃ and OH (mostly from photolysis of HONO) [3]. RO₂ radical was formed during the oxidation process of volatile organic compounds (VOC) by O₃ and OH, and it then reacted with NO₂ to form RNO₂. Similar diurnal variation of RNO₂ could be seen in FIG. 6, with peaks occurring in the afternoon. Relatively high level of RNO₂ and other oxidized nitrogen compounds but low level of NO₂ were the reason that the Mo-CL instrument gave considerably larger deviation in the detected concentration of NO₂.

IV. CONCLUSION

A two-channel cavity ring-down spectroscopy (CRDS) instrument was built for real-time measurement of NO₂ and RNO₂ (peroxy nitrates and alkyl nitrates) in ambient air. We realized a detection limit of NO₂ and RNO₂ of 0.1 ppbv at one second. A 6-day-long field study has been carried out by using the CRDS instrument with a time resolution of 3 s. A commercial chemiluminescence instruments equipped with molybdenum converter (Mo-CL) NO₂ analyzer was also used for a comparison. We evidenced that the Mo-CL NO₂ analyzer could be interfaced by NO rapid fluctuation in ambient air, reduction of oxidized nitrogen species and thermal dissociation of RNO₂ in the molybdenum converter. The average NO₂ given by the Mo-CL analyzer during the 6-day experiment was 24.62 ppbv, with 1.69 ppbv higher than that given by the CRDS instrument, coinciding with the averaged RNO₂ concentration of 1.94 ppbv. We also observed that the Mo-CL analyzer could overestimate the NO₂ concentration by 100%, when the NO₂ concentration was low but RNO₂ was relatively high in the afternoon.

As the growing of demand for accurate and rapid detection of pollutants in ambient air, CRDS could be used to detect NO, NO₂ at the same time with equivalent detection limit compared to Mo-CL NO₂ analyzer [38], but with much higher time resolution, which can be used to monitor the sudden emissions at local sites. Compared with the widely applied Mo-CL NO₂ analyzer, CRDS setup could be a better choice to measure NO₂ in the ambient air since it directly detect the absorption of NO₂. CRDS combined with thermal dissociation of RNO₂ to NO₂, TD-CRDS, could be used to evaluate the concentration of RNO₂ in ambient air.

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