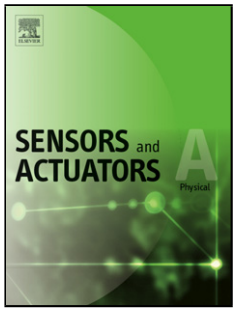
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An open-path dual-beam laser spectrometer for path-integrated urban NO_2 sensing

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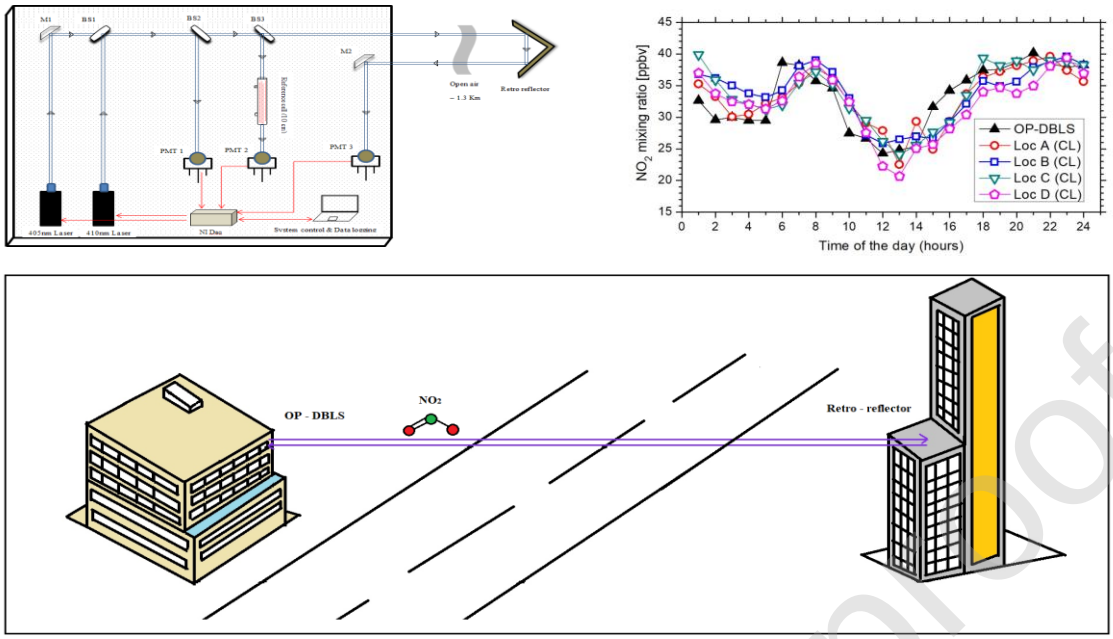
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Research Highlights

- We developed a dual beam diode laser spectrometer (OP-DBLS) for open path sensing of atmospheric NO_2
- This laser spectrometer is a cost effective and simple instrument for atmospheric NO_2 detection
- The dual beam diode laser spectrometer was employed for a 13-day measurement campaign in the mega city of Shanghai, P. R. China during a winter period.
- The NO_2 mixing ratios measured using this spectrometer was correlating well with four Chemiluminescence (CL) detectors in the nearby locations of Shanghai mega city.
- The achievable detection sensitivity of this laser spectrometer is ~200 pptv.
- The instrumentation described can be easily adapted for sensing other trace gases by employing suitable laser wavelengths.
- The OP-DBLS is a less expensive and cheaper alternative for long-path broad spectrometers method with higher temporal resolution, if one target gas species alone is of interest.

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Abstract

Fast and continuous in-situ monitoring of NO_2 in urban air using optical sensing has been a topic of research recently. Due to possible interferences from other absorbers, spectroscopic measurements across a broad absorption band of NO_2 are preferred over single-wavelength laser absorption measurements for specificity. While, in general, broadband spectrometers account for spectral interferences and exhibit high selectivity, laser spectrometers possess faster responses and higher sensitivity. In this study, we present an open-path and dual-beam laser absorption spectrometer (OP-DBLS) featured as sensitive, accurate and cost-effective urban NO_2 monitor with fast and easy operation. This instrument consists of two lasers operating at wavelengths close to the NO_2 absorption peak around 405 nm and the ratio of absorption at these wavelengths were used to remove cumulative influence of all broad baseline features such as aerosol interferences. The instrument was continuously operated for thirteen days at the middle ring road monitoring centre located in the northeast of Shanghai, P. R. China. The measurements were

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compared with concurrent measurements by a Chemiluminescence (CL) detector and the correlation of campaign-averaged hourly measurements depicting diurnal variations in NO_2 concentrations was found to be ~0.8. Furthermore, results from comparison against four other air quality monitors deployed elsewhere in the city showed excellent consistency.

Keywords

Laser spectrometer, nitrogen dioxide, path-integrated measurement, open-path sensor, urban atmosphere, air pollution

1 Introduction

Nitrogen dioxide (NO_2) has a very important role in the generation of tropospheric ozone and has strong impact on human health. Accurate and fast *in-situ* sensing of this common urban pollutant is very essential for air quality index determination as well as for scientific understanding of the chemical dynamics of the atmosphere [1-3]. It is also a very important trace pollutant and its heterogeneous chemistry leads to the nitrous acid (HONO) formation that in turn generates hydroxyl radical (OH), which is the primary day time oxidant of the atmosphere [4, 5]. In presence of Ozone (O_3), the other major urban pollutant, NO_2 is further responsible for generation of the highly reactive night-time oxidant, NO_3 [6, 7]. Hence, in addition to concerns on health effects arising from substandard air quality, monitoring of NO_2 is important for a better understanding of tropospheric oxidation processes [8]. NO_2 is a part of total nitrogen oxides (NO_x) and is primarily generated from fossil fuel combustion [9, 10].

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Optical spectroscopy is widely used as a tool for in-situ sensing of trace gases including NO_2 [11]. In optical sensing, laser-based methods are experimentally simple, and after the invention of diode lasers, they became cost-effective [12]. Long optical pathlengths of several hundred meters or more may be essential to achieve adequate detection sensitivity for meaningful measurements when emissions are low [8, 11]. Long-path differential absorption spectroscopy (LP-DOAS) and its alterations have been used as a open-path (OP), sensitive optical remote sensing (ORS) method for tropospheric trace gas detection for several decades [13]. The broad wavelength operation of DOAS systems is suitable to detect multiple trace species absorbing within the specified spectral window. However, the spatial resolution of measurements is deficit since spatial variations of atmospheric trace gas compositions cannot be observed due to measurements of the long-path column densities. While the path-integrated, OP-ORS measurements are useful for measuring pollutants emerging from large areas such as mega cities measurements from localized sources pose difficulties. On the other hand, cavity-enhanced methods, such as cavity-enhanced absorption spectroscopy (CEAS) and cavity ring-down spectroscopy (CRDS) are widely used as alternate methods for trace gas detection close to localized emissions [8, 14-18]. Installation of an array of such point monitors across an urban area would be useful for mapping pollution levels. Both cavity-enhanced approaches, i.e. CRDS and CEAS, trap light between two highly reflective di-electric mirrors and create enhanced effective absorption pathlengths of several hundred meters to kilometres thereby enhancing detection sensitivity [19]. Different continuous- and pulsed-wave cavity-enhanced methods have been developed and details of design and applications are widely available in published books [19, 20]. Incoherent broadband CEAS (IBB-CEAS) has recently proven to be a valuable CEAS technique to measure NO_2 with good sensitivity as well as high spatial and temporal resolution

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[21, 22]. Simultaneous monitoring of transmission signals from reference- and sample- cavities, and retrieving NO_2 concentration in the presence of aerosol loading was demonstrated recently in an IBB-CEAS laboratory experiment [23]. Cavity-based spectrometers generally exhibit higher temporal resolutions when compared to LP-DOAS systems. Multipass cell (White cell or Harriot cell) based gas sensing is much simpler, but expensive and less sensitive comparing to CEAS methods [24, 25]. Multipass gas cell in conjunction with tunable laser was presented as an alternative to CEAS where gas sensing with high temporal resolution was desired with moderate sensitivity [24].

In this paper we describe a simple OP-ORS instrument for detection of atmospheric NO_2 that possesses long optical path comparable to LP-DOAS and high temporal resolution comparable to cavity-enhanced spectrometers. The proposed open-path dual-beam laser spectrometer (OP-DBLS) is a cost-effective NO_2 sensor with simplicity in operation comparable with common open-path laser transmissometers [26]. Like other long open-path instruments spatial resolutions is poor, but suitable for large area sources with sizes comparable to the path length. This instrument is the realization of the open-path dual-beam approach for real-time *in-situ* monitoring of urban NO_2, similar in principle to previous laboratory studies [23]. The OP-DBLS employs two lasers with emissions close to the absorption peak of NO_2 at ~405 nm. The wavelengths were chosen to minimize absorption interference from other trace gases thereby minimizing the measurement errors. The removal of the effects of broad spectral extinction features (like aerosol interferences) was achieved by assuming same baseline extinction at both the laser wavelengths. The need for monitoring the urban NO_2 emissions (among the urban trace pollutants) is increasing in places with large cities, like in P. R. China, as part of general ozone control policies and simple, cheap and reliable monitors for the purpose is still in demand. The

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proposed OP-DBLS instrument is highly relevant in this context as an alternative option to the other spectroscopic methods mentioned above. The OP-DBLS instrument exhibited results suitable for the monitoring of urban NO_2 as demonstrated by a continuous 13-day measurement campaign during a winter onset in the mega city of Shanghai, P. R. China. The experimental details, instrument calibration, deployment, measurements and results are explained in the following sections.

2 Experimental

2.1 Instrument design

The OP-DBLS uses two single wavelength MLL-III (Class-3) lasers as the light sources, operating at ~405 and ~410 nm (MLL-III-405; MLL-III-410, CNI laser company, China). The NO_2 absorption spectrum has a peak close to ~405 nm with minimal interference from other common atmospheric urban pollutants. The lasers have ~60 mW output power and can be operated in continuous emission mode or in modulation with a TTL signal. The emission spectra are smooth with no fine structures and exhibited wavelength and power stabilities over hours of continuous operation. The FWHM of both the lasers were ~2 nm, and divergence <0.5 mrad as specified by the manufacturer. A schematic of the design and operation of the OP-DBLS is depicted in Fig 1. Both the lasers were modulated using a TTL signal from the DAQ module controlled through a program developed in LabVIEW platform (National Instruments, USA) that also ensured that only one of the two lasers is operational at a time. This sequential and quasi-simultaneous operation helps to distinguish signals from the two laser wavelengths on the detector side. The beam splitter, BS2 (Thorlabs, USA) was used to sample a small portion of each laser beam that was monitored by a photomultiplier tube PMT1 for monitoring power fluctuations of the lasers. Another beam splitter, BS3 was used in such a way to sample a portion

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of the laser beam and direct it through a quartz reference cell (Yixing Chuangxin Optical Glass, WuXi, P.R. China) with 10 cm sample path length containing ~100 ppm of NO_2 in it (see Fig. 1). The absorption of the laser intensities, while passing through this reference cell, were monitored by a second photomultiplier tube, PMT2. The major transmitted-portion of laser beams from the beam splitters were then sent to the atmosphere in the open path to a 2-inch pyramid-mirror retro-reflector (Edmund Optics, UK) placed ~650 m away that returned the laser beams in reverse path (round trip optical path length of ~ 1300 m). The returned laser intensities were then collected by a telescope (Celestron, USA) and directed to the third PMT (PMT3). The PMTs used were identical (Model CH253, Hamamatsu, Japan) with same dark noise characteristics and with a response spectrum exhibiting adequate detection sensitivity in the operating range of the lasers. The laser intensities falling on all the three PMTs were digitized using a data acquisition Card (USB-6361, National Instruments, USA) and processed by the same LabVIEW program. This interface program was fully automated to control lasers and PMTs, data acquisition and further processing.

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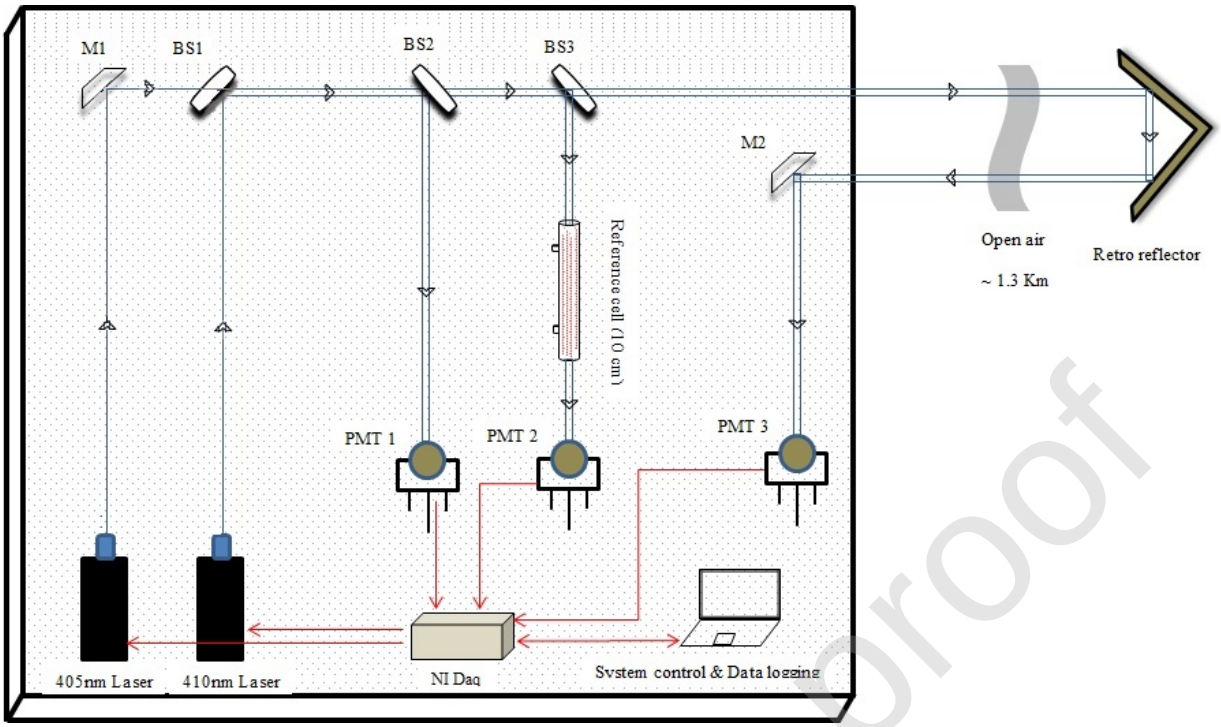


Figure 1. Schematic of the OP-DBLS instrument. PMT1, PMT2 and PMT3 are detectors; BS1, BS2 and BS3 are beam splitters; M1 and M2 are beam steering aluminum-coated mirrors. The retro reflector is placed ~650 m away from the laser source (round trip optical path length of ~1.3 km).

The goal is to use two close wavelengths with unequal cross-sections close to the absorption peak of NO_2 at ~405 nm for removing broad extinction features, which is the method's difference to both single wavelength laser spectroscopy and broadband spectroscopic approach. A similar approach applied to CEAS method was implemented in a previous laboratory study [23]. Use of highly directional laser sources makes the beam imaging and optical alignment simpler. Furthermore, it depicts advantages of simple and fast analysis in comparison to least square fitting applied to other broad spectral measurements. While using two laser beams of close wavelengths can account for and separate influence of broad aerosol extinction on the structure of NO_2 absorption, disadvantage of the approach lays in the fact that interference from narrow-band multispecies gas absorptions cannot be accounted for effectively. However,

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minimal or no interference from other common pollutants are expected in this spectral region. Like the laser- or broadband- spectroscopic approaches, the dual-beam approach is applicable within the linear absorption regime of Lambert-Beer's law. The ratio of absorbances at the operating wavelengths preserves in the case of pure single-gas absorption, and broad extinction (like aerosol extinction) may be identified easily as an offset of baseline absorption in the absence of other narrow-structured extinction losses. The offset thus retrieved may be attributed to the aerosol extinction at the operating wavelengths if effects of instrumental parameters like power fluctuations of light sources can be eliminated by proper normalization [23].

2.2 Measurement principle

The intensities collected by PMT3 after completing a round trip in the atmosphere for both the lasers (I_1 and I_2) maybe expressed mathematically using Lambert-Beer's law shown in Eq. (1) and Eq. (2). The intensities collected by PMT2 (I_{ref1} and I_{ref2}) after transmitting through sample cell are expressed in Eq. (3) and Eq. (4).

$$I_{1=} I_{01} e^{-(\propto_1+\varepsilon_1)l} \quad (1)$$

$$I_{2=} I_{02} e^{-(\propto_2+\varepsilon_2)l} \quad (2)$$

$$I_{ref1=} I_{0ref1} e^{-\alpha_{ref1} d} \quad (3)$$

$$I_{ref2=} I_{0ref2} e^{-\alpha_{ref2} d} \quad (4)$$

Where α_1, α_2 are the wavelength dependent absorption coefficients of NO_2 for the lasers 405 nm and 410 nm respectively and α_{ref1}, α_{ref2} are the absorption coefficients observed for both lasers from the reference cell transmission; and ε_1, ε_2 are the corresponding baseline extinction coefficients for 405 nm and 410 nm lasers (such as due to aerosol extinction). Here l is the round trip path length in atmosphere (~1300 m) and d is the length of the reference cell (~10 cm). Since

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both the lasers are very close in wavelength scale the broad aerosol extinction happening to these two lasers were approximated to be the same. The error from this coarse approximation is negligibly small [23, 27]. Therefore, the ratio of Eq. (1) to Eq. (2) will be equal to the ratio of Eq. (3) to Eq. (4) in the special/ideal case of zero amount of NO_2 present in the atmosphere and in the sample cell (all zero alphas). This situation is usually achieved in the noontime with clear and sunny atmosphere because atmospheric NO_2 will get photolyzed [28]. The corresponding I_1 and I_2 can be taken as the zero-absorption intensities I_{01} and I_{02} for such a condition and laser intensities monitored by PMT1 can be used to scale these values for all other times. Alternately, intensities measured over a short path by bringing the retro reflecting mirror close to the instrument can serve as zero-absorption intensities after proper scaling. While both the approaches have been found successful at the location of our measurements, we have used the latter strategy for determining our I_{01} and I_{02} intensities for the data presented in this paper.

The ratio of absorption due to NO_2 between both the laser wavelengths, in the linear absorption regime of Lambert-Beer's law (irrespective of actual concentrations), should remain the same in the sample cell and in the open atmosphere because they were recorded quasi- simultaneously. We can use this fact to remove all broad background extinction in the open-path laser beams and obtain the path-integrated NO_2 along the measurement path using one of the laser wavelengths. The reference cell filled with 100 ppm of NO_2 is primarily useful to get this ratio correctly at all times offsetting any fluctuations in laser characteristics. Total light extinction happening on both lasers (Q_{ext1} and Q_{ext2}) in the open atmosphere is due to the sum of NO_2 absorption and broad light extinction, and can be expressed (for small loss approximation) using Eq. (5) and Eq. (6).

$$Q_{ext1} = \alpha_1 + \varepsilon_1 \approx \left(\frac{I_{01}}{I} - 1\right)\left(\frac{1}{l}\right) \quad (5)$$

$$Q_{ext2} = \alpha_2 + \varepsilon_2 \approx \left(\frac{I_{02}}{I} - 1\right)\left(\frac{1}{l}\right) \quad (6)$$

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Similarly, the NO_2 absorption occurring on both laser intensities transmitted through the sample cell (d=10 cm) is mathematically expressed in Eq. (7) and Eq. (8). The simple assumption of same aerosol extinction for both the laser wavelengths in the atmosphere ($\varepsilon_1 = \varepsilon_2$) makes the ratio of Eq. (5) and Eq. (6), after subtracting the common extinction factor, equal to the ratio of Eq. (7) and Eq. (8). In the data analysis we used this approximation, and scaling the extinction-corrected α_1 to the absorption cross-section at 405 nm retrieved the true NO_2 concentration (number density). Alternatively, scaling the extinction-corrected α_2 to the absorption cross-section at 410 nm would deliver the same result (as we did for the field measurement data presented in this paper).

$$\alpha_{ref1} = \left(\frac{I_{0ref1}}{I_{ref1}} - 1\right)\left(\frac{1}{\mathrm{d}}\right) \quad (7)$$

$$\alpha_{ref2} = \left(\frac{I_{0ref2}}{I_{ref2}} - 1\right)\left(\frac{1}{\mathrm{d}}\right) \quad (8)$$

It is to be noted that the absorption cross-section of NO_2 in the laser wavelength region was taken from Max Planck Institute (MPI) Mainz data base (originally reported in [29]). These absorption cross-section values were convolved to a resolution corresponding to the FWHM of the lasers prior to estimating the NO_2 number densities (and corresponding mixing ratios).

2.3 Calibration

The instrument was calibrated prior to deployment in the open-path configuration. The calibration here was to test the concentration retrieved by OP-DBLS for its accuracy against the known ones for a range of NO_2 expected in an urban atmosphere such as the megacity of Shanghai. First, the light towards the open atmosphere was blocked and readings from PMT1 and PMT2 were used for the following calibration experiment. The NO_2 gas from a 2000-ppm standard gas cylinder (Nanjing Special Gas, China) was used with a dilution chamber (146I, Thermo-Fischer, USA) to obtain several different concentrations (specified as mixing ratios in

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ppm units) into the quartz reference cell by mixing with compressed zero air (synthetic dry air). The flows of NO_2 and zero air were controlled by mass flow meters in the chamber in order to achieve desired dilution. Even as the calibration is performed in a 10 cm quartz cell, the instrument was to make measurements through open atmosphere with a round trip optical path length of ~1.3 km. Due to the difference in path lengths between the calibration cell and the open atmosphere configuration, it was desired to calibrate the measurements of path-integrated concentration (PIC), which is a product of mixing ratio and optical path length. This is a standard practice in optical remote sensing and the PIC is specified in ppm-m unit. The 10-cm (0.1 m) reference cell was filled with different dilutions of NO_2 in the range of 0 – 400 ppm (equivalent PIC range of 0 – 40 ppm-m) and corresponding path-integrated concentrations were measured and compared against the actual values. Eight dilutions were created in the reference cell corresponding to 20 ppm (2 ppm-m), 100 ppm (10 ppm-m), 150 ppm (15 ppm-m), 200 ppm (20 ppm-m), 250 ppm (25 ppm-m), 300 ppm (30 ppm-m), 350 ppm (35 ppm-m) and 400 ppm (40 ppm-m). The values in parentheses are path-integrated concentrations. The retrieved concentrations (averaged over ~200 acquisitions per dilution) using 405 nm cross-section values plotted against the actual ones is depicted in Fig. 2 and summarized in Table-1 (retrieval using 410 nm would result in the same values). No aerosol extinction was present, and the common offset introduced due to instrumental parameters was removed by the retrieval procedure explained in the previous section. The maximum path-integrated concentration used in the calibration experiment was 40 ppm-m, and our calculations using the small-loss approximation showed that the range of measured concentration throughout this study for the chosen optical path length of ~1.3 km was well within the linear absorption regime.

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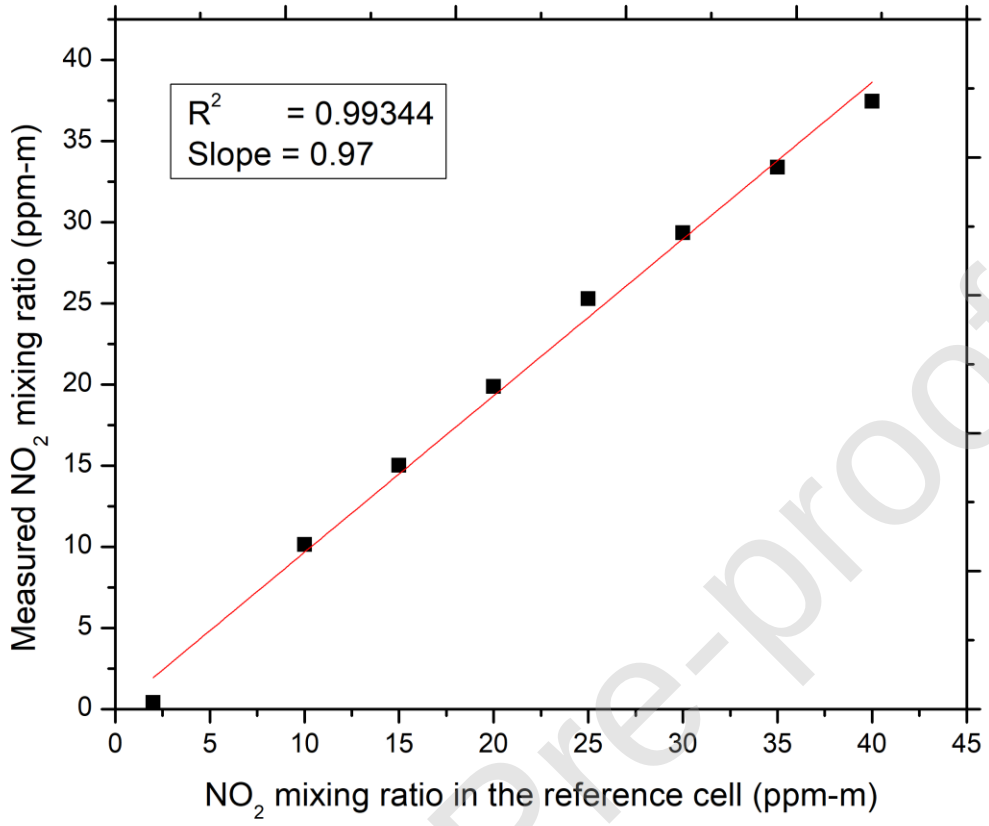


Figure 2. Measured path-integrated concentration plotted against the actual ones at various dilutions in the reference cell, as detailed in Table-1.

Table 1: Details of the calibration measurements

Serial No.	Average dilution (ppm)	Equivalent path-integrated concentration (ppm-m)	Measured path-integrated concentration (ppm-m)
1	20	2	0.4
2	100	10	10.2
3	150	15	15.0
4	200	20	19.9
5	250	25	25.3
6	300	30	29.4
7	350	35	33.4
8	400	40	37.5

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3 Results and Discussion

3.1 OP-DBLS Measurements and Concurrent CL measurements

After laboratory calibrations the instrument was installed to monitor NO_2 over Shanghai continuously for about two weeks during the onset of wintertime (1 – 13 December, 2017). The experimental platform was set up in the middle ring road monitoring center in Shanghai, located in the northeast of Shanghai's University of Shanghai for Science and Technology Collaborative Innovation Institute (E121°32'32'', N31°17'77''). The instrument was installed on the fifth floor, and the light beams were sent out into the atmosphere across the highway to a retro-reflector placed on a residential rooftop 0.65 km away (round-trip pathlength of ~1.3 km). The distance from the light path to the ground was about 12 m, although elevation from the ring road, over which the laser beams crossed, was much less. A Chemiluminescence (CL) instrument (Thermo Scientific, model 42*i*, USA) was monitoring NO_2 in the ambient air just outside the building of the DBLS instrument location for the entire duration. Four other CL point monitors around central Shanghai location, operated by the local Environmental Protection Agency (EPA) from which data are publicly available, were also selected for comparison during the 13-day measurement campaign. Since NO_2 emissions are expected throughout the mega city, similarity in trends in measurements from all the monitors were expected to have good correlation with OP-DBLS measurements. The modulation of the laser intensities in OP-DBLS allowed removing any influence of ambient light fluctuation on the measurements, and the LabVIEW program included the analysis of determining proper PMT voltages from the acquired signals. Lasers were operated for 1 s each sequentially (one operating at a time), and thirty consecutive voltage acquisitions were made before switching the laser each time. These 30 acquisitions at each of the laser wavelengths were averaged corresponding to about 2 s per NO_2 concentration

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determination. These retrieved concentrations were further averaged to match half-hourly data obtained from the CL instrument at the same location for initial comparison.

The black triangular trace in upper panel of Fig. 3 shows the NO_2 measured by the OP-DBLS for each day of the campaign and the concurrent CL measurements are shown as the red round trace. The trend of this half-hourly NO_2 variation from both the instruments can be seen in the figure. The variation of NO_2 concentration may have been affected by various factors along the long optical measurement path and can be observed in the time series. For example, the exhaust emission from passing vehicles in the middle ring road and elsewhere, and the presence of high nitrogen dioxide concentration during the morning and evening peak traffic volumes. The middle panel of Fig.3 is an easier and legible representation of the data shown in the upper panel. In the middle panel, the black triangular trace with error bar shows mixing ratio of NO_2 for corresponding time stamp averaged for all 13 days (with a 1-hour interval). The red round trace shows the corresponding NO_2 mixing ratios from CL measurements. It can be seen from the upper panel that the mixing ratio trend of atmospheric NO_2 measured by the two methods (instruments) is consistent, although the spikes are missing in the CL measurements, possibly due to the fact that CL was recording data at a point, away from vehicular activities. The sampling location of the CL would measure the NO_2 arriving at the location by diffusion, or advection due to wind, and hence sharp spiking were not expected although similar trends and variations were exhibited. In any case, differences between instantaneous OP-DBLS (black triangular trace of upper panel Fig. 3) and CL (red round trace) were expected because OP-DBLS measurements were derived from path-integrated optical measurements while CL measurements were from air samples just outside the building, sampling through a Teflon tube and fitered. The filter membrane may have caused nominal sampling losses as well (not

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quantified in this case). However, the measurements averaged over longer time intervals

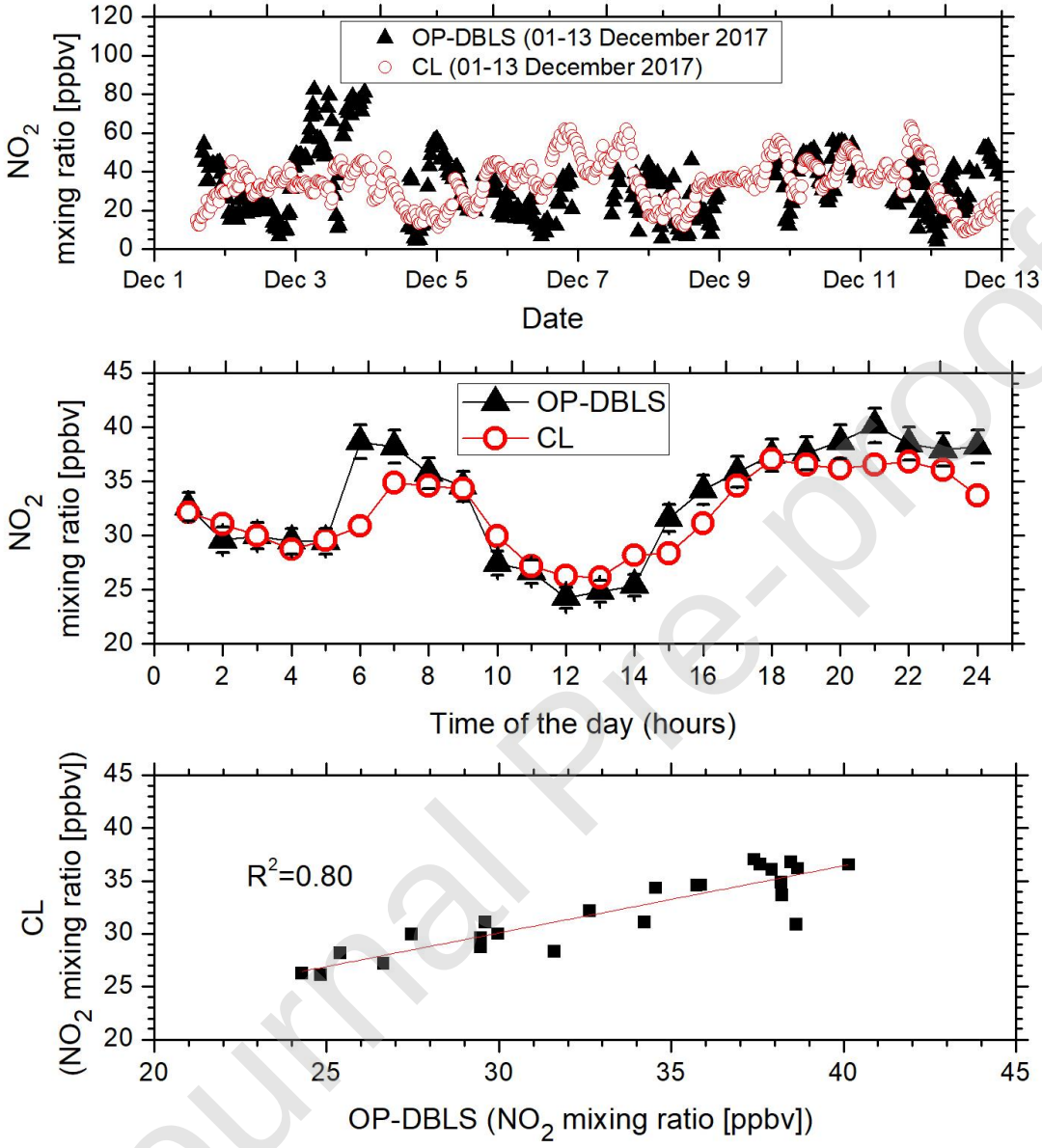


Figure 3. The upper panel shows the comparison of half-hourly time series of measured NO_2 in ppbv using CL and OP-DBLS instruments for the entire campaign. The black triangular trace shows the OP-DBLS data and red round trace shows the CL data. The middle panel shows the averaged NO_2 mixing ratios for each hour of the day depicting average daily variations. The lower panel shows the linear correlation of time averaged NO_2 mixing ratios between CL and OP-DBLS measurements corresponding to the depiction in the middle panel.

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were showing the same trends for NO_2 emissions because in such urban conditions, emissions are not so localized; hence the motivation for this inter comparison is justified. Measurements from both the instruments correlate well with an R^2=0.80 (see lower pane of Fig. 3). Furthermore, the NO_2 mixing ratio in the noontime was minimum as expected due to photolysis [20] (see middle panel of Fig.3). It is worth noting that for a moderate NO_2 concentration of 30.04 ppbv, during 00:23 to 00:53 on Dec 2, 2017, we would have retrieved a high 114.85 ppb if data from 410 nm laser alone was used. The difference of 84.81 ppb was due to the broad extinction of ~1.23×10^{-6} cm^{-1} (123 Mm^{-1}) that was not differentiated with the use of a single laser wavelength.

The maximum value of campaign-averaged hourly NO_2 mixing ratio was ~40 ppbv (OP-DBLS) during the campaign. The uncertainties in the measured mixing ratio for the OP-DBLS method is dominated by the maximum error in the reported NO_2 absorption cross-section. The instrument sensitivity (detection limit) was estimated in the following manner. The minimum detectable intensity is taken as the 1σ (standard deviation) of laser signal monitored for ~ 6 hours in the lab (~0.04%). Since we were monitoring the laser intensity and scaling it all the time the error originating from the laser intensity drift is, in fact, negligibly small. The minimum detectable absorption coefficient (α_{min}) was estimated to be ~3.1×10^{-9} cm^{-1} from the standard deviations of measured intensities, and this value corresponds to a theoretical (achievable) detection limit of ~0.2 ppbv, using the cross-section reported in reference [29]. Another way of estimating uncertainty is by error propagation with the knowledge of errors of each variable used in the equations. Here, the overall uncertainty in the measured number density (or mixing ratio) was dominated by the uncertainty in the absorption cross section reported in the literature (~4% from [29]). The other errors arising from measurements are negligibly small, for example, the distance

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(*d*) to retro-reflector was accurate to ~0.2%. With standard propagation of error a conservative value of uncertainty in NO_2 measurements by this instrument was estimated to be ~2 ppbv, which is 10 times more than this theoretical detection limit.

3.2 Comparison of OP-DBLS with other air quality sensors around the location

There are several point-monitors located in different territories in the city of Shanghai, operated and maintained by CNEMC (China National Environmental Monitoring Center). All the CL detectors' physical structure is similar to the one used at the OP-DBLS location. We chose four locations (labeled Loc-A, Loc-B, Loc-C and Loc-D respectively) around the city center of Shanghai (Fig. 4), and made comparison between OP-DBLS and each of the four CL measurements.

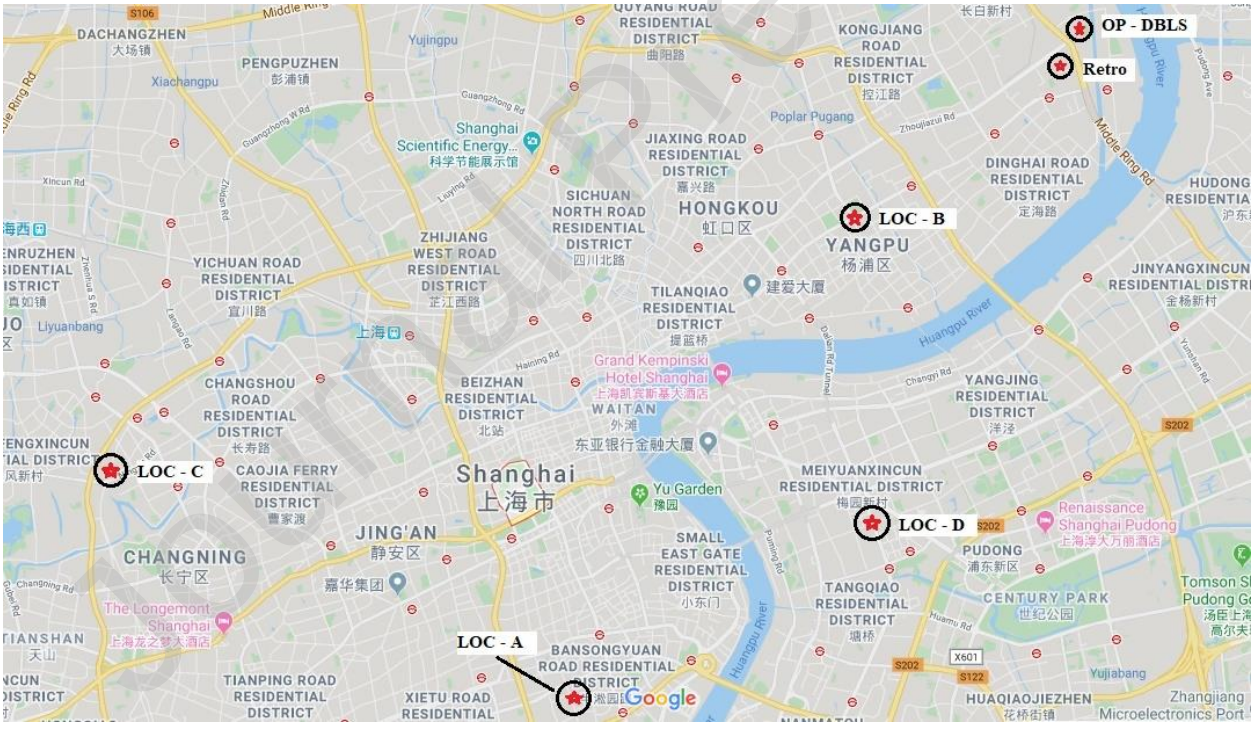


Figure 4. Locations of the selected air quality monitors around the city center Shanghai. The location of the OP-DBLS (with Retro marking its retro-reflector position) is indicated. People's square is the city center of Shanghai.

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OP-DBLS is located at the northeast of city center area and its beam crossed over the middle ring road. Loc-B is the closest of the chosen CNEMC air quality monitors. Loc-C is at the old downtown areas whereas the Loc-D is a new urban air quality monitor site in Pudong New District. Measurements from these monitors, available in public domain, were obtained and further averaged for the same campaign period to represent hourly averages to match with that shown in Fig. 3, lower panels.

The comparison between the OP-DBLS and each of the four monitors are shown in Fig. 5, in two panels. The top panel depicts time series of hourly averaged data, averaged for the campaign duration (as in Fig. 3, middle panel), and the bottom panel depicts the correlation plot of OP-DBLS with that of all the four monitors (as in Fig. 3, bottom panel). In both panels, averaged hourly data from Loc-A is shown as red circles, from Loc-B is shown as blues squares, from Loc-C is shown as green inverted triangles and from Loc-D is shown as pink pentagons. The correlation between the OP-DBLS and each of the instrument show good agreement. While the monitors are separated with distance, averaged hourly data over the campaign period show similar trends, even as the campaign lasted less than two weeks, a relatively short time to assess diurnal variation of any target pollutant. These good agreements indicate that the emission is happening throughout this large urban area in a similar fashion (possibly due to homogeneous vehicular distribution), and is not a localized source. Also, it was expected that the mixing due to diffusion and wind make the concentration nearly comparable throughout the area for the time resolution of the comparison. This illustrates that the OP-DBLS is an ideal instrument that can continuously monitor urban pollutant NO_2 with its open-path in-situ measurements with high accuracy and good time resolution.

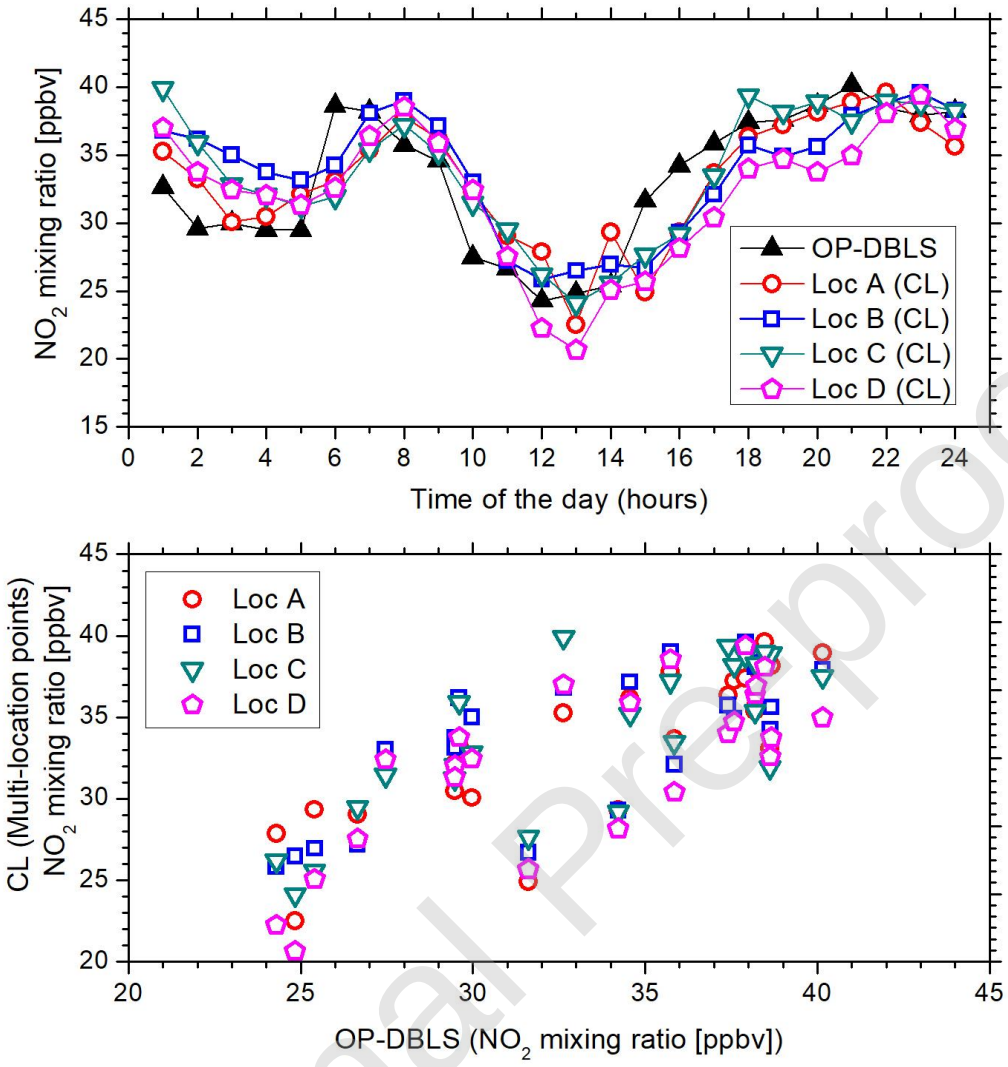


Figure 5. The upper panel shows the comparison of the campaign-averaged time series of NO_2 mixing ratios for each hour of the day depicting average daily variations of OP-DBLS measurements with that of four CNEMC CL monitors. The black triangular trace shows the OP-DBLS data (same as in the middle panel of Fig.3) and the color and symbol of other monitors as depicted in the plot legend. The lower panel shows the linear correlation of time averaged NO_2 mixing ratios between each of the CNEMC CL and OP-DBLS measurements corresponding to the depiction in the upper panel (same as in the middle panel of Fig.3).

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While the trends and values are similar in the top panel of Fig. 5, noticeable shifts and discrepancies exists among all instruments. It indicates that both the morning and evening rush hours started earlier on the middle ring road of Shanghai seen from an early rise in NO_2 measured by OP-DBLS. A longer measurement campaign may verify possible convergence of the trends and values among all the instruments distributed over the urban area. This point is evident from the bottom panel of the Fig. 5, in which linear correlation of the OP-DBLS with all the other point monitors chosen here are depicted through the scatter plot of measurements (same color coding as top panel). The correlations are such that the lowest R^2 observed was ~ 0.57 and the highest was ~0.65.

4 Conclusion

A novel dual-wavelength, long-path, open-path spectrometer (OP-DBLS) was developed for *in-situ* sensing of major urban pollutant NO_2. The mixing ratio of NO_2 in the atmospheric environment was measured from a monitoring station at the middle loop in Shanghai for 13 days, and the correlation of hourly averaged diurnal data with the well established CL monitor was found to be ~0.8. The OP-DBLS was found to be a cost-effective optical sensor that can meet the requirement of NO_2 monitoring in an urban environment with good sensitivity and high time resolution in real time. The extension of OP-DBLS to different wavelength pairs is possible for detecting other airborne trace pollutants. While this study was focused on monitoring urban NO_2, it is emphasized that the use of two lasers instead of a single one was aimed at eliminating all background extinction broad enough to cover both the wavelengths. This broad extinction may be attributed to the light extinction due to atmospheric aerosol if the instrumental effects could be identified and removed.

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Author Credit Statement

Arun Ramachandran: Contributed to the design and assembly of the experiment setup, Software. **Minghzi Li:** Contributed to the design and assembly of the experimental setup, manned the equipment for campaign duration, data analysis. **Dan-Na Wang**: Processed the data for the manuscript preparation. **Satheesh Chandran**: Coordinated data processing for the manuscript. **Jun Chen**: Contributed to conceptualization, supervision of data analysis and original draft preparation, editing. **Ravi Varma**: Contributed to conceptualization, manuscript preparation, editing.

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References

[1] P. Monks. Gas-Phase Radical Chemistry in the Troposphere. Chemical Society reviews, 2005, 34, 376-95.
[2] R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner, G. Poulet, G. Restelli, and H. Sidebottom. The nitrate radical: Physics, chemistry, and the atmosphere. Atmospheric Environment Part A General Topics, 1991, 25, 1-203.
[3] K. Clemitshaw. A Review of Instrumentation and Measurement Techniques for Ground-Based and Airborne Field Studies of Gas-Phase Tropospheric Chemistry. Critical Reviews in Environmental Science and Technology, 2004, 34, 1-108.
[4] J. G. Calvert, G. Yarwood, and A. M. Dunker. An evaluation of the mechanism of nitrous acid formation in the urban atmosphere. Research on Chemical Intermediates, 1994, 20, 463-502.
[5] B. Finlayson-Pitts, L. Wingen, A. L. Sumner, D. Syomin, and a. Ramazan. The Heterogeneous Hydrolysis of NO2 in Laboratory Systems and in Outdoor and Indoor Atmospheres: An Integrated Mechanism. Physical Chemistry Chemical Physics, 2003, 5.
[6] C. Dimitroulopoulou, and A. R. W. Marsh. Modelling studies of NO3 nighttime chemistry

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and its effects on subsequent ozone formation. Atmospheric Environment, 1997, 31, 3041-57.
[7] S. Brown, H. Stark, S. Ciciora, R. McLaughlin, and A. R. Ravishankara. Simultaneous in situ Detection of Atmospheric NO3 and N2O5 via Cavity Ring-down Spectroscopy. Review of Scientific Instruments, 2002, 73, 3291-301.
[8] T. Gherman, D. Venables, S. Vaughan, J. Orphal, and A. Ruth. Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy in the near-Ultraviolet: Application to HONO and NO 2. Environmental science & technology, 2008, 42, 890-5.
[9] D. C. Carslaw, N. J. Farren, A. R. Vaughan, W. S. Drysdale, S. Young, and J. D. Lee. The diminishing importance of nitrogen dioxide emissions from road vehicle exhaust. Atmospheric Environment: X, 2019, 1, 100002.
[10] J. S. Apte, K. P. Messier, S. Gani, M. Brauer, T. W. Kirchstetter, M. M. Lunden, J. D. Marshall, C. J. Portier, R. C. H. Vermeulen, and S. P. Hamburg. High-Resolution Air Pollution Mapping with Google Street View Cars: Exploiting Big Data. Environmental Science & Technology, 2017, 51, 6999-7008.
[11] J. Hodgkinson, and R. Tatam. Optical Gas Sensing: A Review. Measurement Science and Technology, 2012, 24, 012004.
[12] A.-L. Moriaux, R. Vallon, C. Cilindre, B. Parvitte, G. Liger-Belair, and V. Zeninari. Development and validation of a diode laser sensor for gas-phase CO2 monitoring above champagne and sparkling wines. Sensors and Actuators B: Chemical, 2018, 257, 745-52.
[13] K. Hebestreit, J. Stutz, D. Rosen, V. Matveiv, M. Peleg, M. Luria, and U. Platt. DOAS Measurements of Tropospheric Bromine Oxide in Mid-Latitudes. Science, 1999, 283, 55-7.
[14] H. Fuchs, W. P. Dubé, B. M. Lerner, N. L. Wagner, E. J. Williams, and S. S. Brown. A Sensitive and Versatile Detector for Atmospheric NO2 and NOX Based on Blue Diode Laser Cavity Ring-Down Spectroscopy. Environmental Science & Technology, 2009, 43, 7831-6.
[15] D. S. Venables, T. Gherman, J. Orphal, J. C. Wenger, and A. A. Ruth. High Sensitivity in Situ Monitoring of NO3 in an Atmospheric Simulation Chamber Using Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy. Environmental Science & Technology, 2006, 40, 6758-63.
[16] K. Suhail, M. George, S. Chandran, R. Varma, D. S. Venables, M. Wang, and J. Chen. Open path incoherent broadband cavity-enhanced measurements of NO3 radical and aerosol extinction in the North China Plain. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2019, 208, 24-31.
[17] H. Wang, and K. Lu. Monitoring Ambient Nitrate Radical by Open-Path Cavity-Enhanced Absorption Spectroscopy. Analytical Chemistry, 2019, 91, 10687-93.
[18] F. Dong, and M. Gupta. Off-axis cavity ringdown measurements of trace iodine. Sensors and Actuators B: Chemical, 2008, 129, 158-62.
[19] G. Gagliardi, and H.-P. Loock. Cavity-Enhanced Spectroscopy and Sensing2014.
[20] G. Berden, and R. Engeln. Cavity Ring-Down Spectroscopy: Techniques and Applications2010.
[21] I. Ventrillard-Courtillot, E. Sciamma O'Brien, S. Kassi, G. Méjean, and D. Romanini. Incoherent broad-band cavity-enhanced absorption spectroscopy for simultaneous trace measurements of NO2 and NO3 with a LED source. Applied Physics B, 2010, 101, 661-9.
[22] H. Yi, T. Wu, G. Wang, W. Zhao, E. Fertein, C. Coeur, X. Gao, W. Zhang, and W. Chen. Sensing atmospheric reactive species using light emitting diode by incoherent broadband cavity enhanced absorption spectroscopy. Opt Express, 2016, 24, A781-A90.
[23] S. Chandran, A. Puthukkudy, and R. Varma. Dual-wavelength dual-cavity spectrometer for

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NO2 detection in the presence of aerosol interference. Applied Physics B, 2017, 123.
[24] L. Gianfrani, A. Sasso, and G. M. Tino. Monitoring of O2 and NO2 using tunable diode lasers in the near-infrared region. Sensors and Actuators B: Chemical, 1997, 39, 283-5.
[25] K. Liu, L. Wang, T. Tan, G. Wang, W. Zhang, W. Chen, and X. Gao. Highly sensitive detection of methane by near-infrared laser absorption spectroscopy using a compact dense-pattern multipass cell. Sensors and Actuators B: Chemical, 2015, 220, 1000-5.
[26] P. M. S. Chandran, C. P. Krishnakumar, W. Yuen, M. J. Rood, and R. Varma. An Open-path Laser Transmissometer for Atmospheric Extinction Measurements. AIP Conference Proceedings, 2011, 1391, 288-90.
[27] A. Ansmann, M. Riebesell, and C. Weitkamp. Measurement of atmospheric aerosol extinction profiles with a Raman lidar. Opt Lett, 1990, 15, 746-8.
[28] A. Kraus, and A. Hofzumahaus. Field Measurements of Atmospheric Photolysis Frequencies for O3, NO2, HCHO, CH3CHO, H2O2, and HONO by UV Spectroradiometry. Journal of Atmospheric Chemistry, 1998, 31, 161-80.
[29] S. Voigt, J. Orphal, and J. P. Burrows. The temperature and pressure dependence of the absorption cross-sections of NO2 in the 250–800 nm region measured by Fourier-transform spectroscopy. Journal of Photochemistry and Photobiology A: Chemistry, 2002, 149, 1-7.

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Author biography

Jun Chen received his PhD in Chemistry from University College Cork, Ireland, in 2011. He is presently a Lecturer in University of Shanghai for Science and Technology, Shanghai, P R China. He has been developing optical sensors for nitrogen oxides by cavity-enhanced spectroscopy since then. His research interests include UV optical cavity spectroscopy, studying mega city air pollution using optical methods and understanding atmospheric oxidation Chemistry.

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