In situ measurements of atmospheric NO_2 using incoherent broadband cavity-enhanced absorption spectroscopy with a blue light-emitting diode

Liuyi Ling (凌六一)[1,2], Pinhua Xie (谢品华)[1*], Min Qin (秦 敏)[1], Wu Fang (方 武)[1], Yu Jiang (江 宇)[1], Renzhi Hu (胡仁志)[1], and Nina Zheng (郑尼娜)[1]

[1] *Anhui Institute of Optics and Fine Mechanics, Key Laboratory of Environmental Optics and Technology, Chinese Academy of Science, Hefei 230031,China*

[2] *Institute of Electric and Information Technology, Anhui University of Science and Technology, Huainan 232001, China*

[*] *Corresponding author: phxie@aiofm.ac.cn*

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We describe the application of incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) for *in situ* measurements of atmospheric NO_2 using a blue light-emitting diode. The mirror reflectivity is determined by the transmitted intensity variation through the cavity caused by Rayleigh scattering. Concentrations of atmospheric NO_2 (1 to 35 ppbv) during the seven-day period are retrieved from the absorption spectra. The IBBCEAS measurement data are compared with those of a commercial long path differential optical absorption spectroscopy. The linear regression has a correlation coefficient and a slope of 0.983 and 0.975, respectively.

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NO_2, one of the trace gases in the atmosphere, plays an important role in atmospheric chemistry. This gas is also an atmospheric pollutant that can cause acid rain and photochemical smog, impairing human health. Thus, measuring atmospheric NO_2 concentration is essential for both atmospheric chemistry research and air quality management and control.

Differential optical absorption spectroscopy (DOAS) is a common spectroscopic technology for measuring NO_2[1] that has been successfully applied in trace gas measurements for several decades. A direct approach to improve detection sensitivity in DOAS is to enhance the optical the absorption length. For example, active long path DOAS (LP-DOAS)[2] instruments are used to realize long optical paths in the atmosphere from several hundred meters to more than 20 km. These long paths are necessary to detect gases with mixing ratios in the pptv to ppbv range by DOAS in the UV–visible spectral range.

Incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS)[3] based on cavity-ring down spectroscopy (CRDS)[4] has been rapidly developed in recent years. Although the IBBCEAS instrumental setup is much more compact than LP-DOAS, its detection sensitivity can be as high as that of LP-DOAS. Light-emitting diodes (LEDs) are often used as optical sources of IBBCEAS because their emission spectra can be matched to the expected reflectivity of mirrors in the IBBCEAS setup. Ball *et al.*[5] measured NO_2 and NO_3 samples using IBBCEAS with a red LED. Langridge *et al.*[6] measured NO_2 in the laboratory air for 38 h using IBBCEAS with a blue LED. Wu *et al.*[7] measured HONO and NO_2 in ambient air in an urban environment at modest aerosol levels using open-path IBBCEAS with a near-UV LED. Our group has developed a custom-made IBBCEAS system based on LEDs to successfully detect several samples in the laboratory[8,9].

IBBCEAS has been used to measure various trace gases such as NO_2[5–8,10–12], NO_3[5,11–15], N_2O_5[15], HONO[7,9,10], O_3[11], I_2[5], IO[14], and CHOCHO[14]. However, this technique is not frequently applied for long-term measurements. This letter reports on a seven-day continuous measurement of atmospheric NO_2 using IBBCEAS with a blue LED. Based on the fitting residuals, the average detection limit of NO_2 is 1.8 ppbv for an acquisition time of 90 s.

Fiedler *et al.*[3] described the principle of quantifying trace gas concentrations with IBBCEAS. The absorption coefficient of the measured gases, $\alpha_{\rm abs}(\lambda)$, is related to the light intensity transmitted through the cavity, i.e.,

$$\alpha_{\rm abs}(\lambda) = \sum_i \sigma_i(\lambda)\cdot N_i = \left[\frac{1-R(\lambda)}{d} + \alpha_{\rm Ray}(\lambda)\right]\left[\frac{I_0(\lambda)-I(\lambda)}{I(\lambda)}\right]. \quad (1)$$

The extinction caused by aerosols is not considered. $R(\lambda)$ is the wavelength resolved mirror reflectivity, and d is the length of the cavity. $\alpha_{\rm Ray}(\lambda)$ is the total Rayleigh scattering for the mixture. $I(\lambda)$ and $I_0(\lambda)$ are the measured spectra with and without absorbing species in the cavity, respectively. $\sigma_i(\lambda)$ is the absorption cross-section, and N_i is the number density for species i. The concentrations of the measured gases can be retrieved by fitting the absorption cross-sections to the absorption coefficient.

Figure 1 shows the schematic of the IBBCEAS instrumental setup. A blue LED (XRE-7090, CREE, USA) with a peak wavelength of approximately 462 nm and a full-width at half-maximum (FWHM) of 26 nm was used as the light source. The LED working current was 700

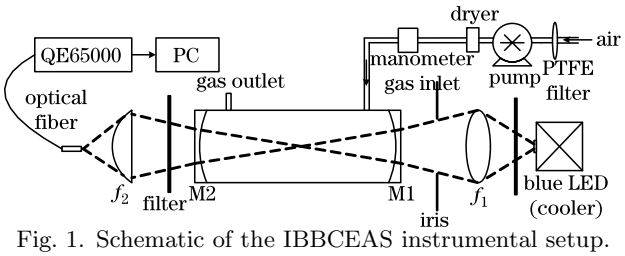

Fig. 1. Schematic of the IBBCEAS instrumental setup.

± 1 mA, which provided an optical power of ∼600 mW. The LED was mounted on a temperature-controlled cooling stage to stabilize its emission spectrum. Through the lens f_1 (f = 352 mm), the light emitted from the LED was focused into a 70-cm-long high-finesse cavity. This cavity consisted of two high-reflectivity dielectric mirrors (Layertec GmbH) with a high reflectivity of over 0.999 from 440 to 480 nm, 25-mm diameter, and 1.5-m radius of curvature. An iris was used to reduce the stray light and confine the diameter of the light spot on the first mirror (M1). Out-of-band light was removed by a colored glass filter (GG420, Schott, Germany) behind the LED and a band-pass filter (BQ29, Yinxing Optics, China) behind the second mirror (M2). Light transmitted through M2 was focused into an optical fiber (400 μm in diameter and NA = 0.22) connected to a 0.3-nm resolution spectrometer (QE65000, Ocean Optics, USA) by an aspheric lens f_2 (f = 32 mm). The sampled air was filtered by a PTFE filter (pore size 0.22 μm) to remove aerosols and pumped at a flow rate of 3 slm through a 21-mm internal diameter Teflon-coated tube into the cavity. Atmospheric absorption spectra were recorded and analyzed by a PC. Although the pump (NMP850, KNF, Germany) is generally placed on the outlet side, the pump in the present system was placed on the inlet side to maintain a positive pressure and reduce sampling artefacts from ingress of laboratory aerosols into the optical cavity.

Mirror reflectivity should be determined to quantify gas concentrations based on Eq. (1). Langridge *et al.*[16] determined the mirror reflectivity by measuring the ring-down time of CRDS. Gherman *et al.*[10,17] acquired the reflectivity using the absorption spectrum of a known concentration gas in the region of interest. In addition, mirror reflectivity can be determined from the light intensity changes caused by the addition of N_2 and He, as described by Washenfelder *et al.*[18]

$$R(\lambda) = 1 - d\frac{\left[\frac{I_{N_2}(\lambda)}{I_{He}(\lambda)}\alpha_{Ray}^{N_2}(\lambda)\right] - \left[\alpha_{Ray}^{He}(\lambda)\right]}{1 - \left[\frac{I_{N_2}(\lambda)}{I_{He}(\lambda)}\right]}, \quad (2)$$

where $I_{N_2}(\lambda)$ and $I_{He}(\lambda)$ are the N_2 and He spectral intensities, respectively; $\alpha_{Ray}^{He}(\lambda)$ and $\alpha_{Ray}^{N_2}(\lambda)$ are the extinction coefficients caused by Rayleigh scattering of He and N_2, respectively.

This letter determined the mirror reflectivity using the last method. $I_{N_2}(\lambda)$ and $I_{He}(\lambda)$ were recorded by QE65000 at ambient temperature (297 K) and pressure (1013 mbar) after the cavity was flushed with pure N_2 (99.999% purity) and pure He (99.999% purity), respectively. $\alpha_{Ray}^{He}(\lambda)$ and $\alpha_{Ray}^{N_2}(\lambda)$ were acquired by calculation. Thus, $\alpha_{Ray}(\lambda) = \sigma_{Ray}(\lambda) \cdot N$, where N is the number density and related to purity of He or N_2. $\sigma_{Ray}(\lambda)$ is the Rayleigh scattering cross-sections of He or N_2. According to Shardanand *et al.*[19] who measured σ_{Ray}^{He} at 457.9 nm, and Sneep *et al.*[20] who measured $\sigma_{Ray}^{N_2}$ at 532 nm, and based on wavelength dependence to an expression ($\sigma_{Ray}(\lambda) \sim \lambda^{-4.082}$), $\sigma_{Ray}(\lambda)$ is interpolated to obtain cross-section values over the region of interest. Figure 2(b) shows the extinction caused by Rayleigh scattering of pure He and N_2 in our experiments. The calibrated mirror reflectivity in the region from 443 to 470 nm is shown in Fig. 2(a). The maximum mirror reflectivity of 0.9987 is found at 458 nm, which corresponds to an effective path length of ∼538 m. Although the difference in the N_2 and He spectral intensities in Fig. 2(a) is small (∼2%), it is far more than 0.1% of the average change in the intensities of the consecutive N_2 spectra acquired by the spectrometer. Thus, this intensity difference is reliable in determining mirror reflectivity.

Atmospheric NO_2 samples obtained outside our laboratory were measured continuously for seven days using the IBBCEAS instrument and a commercial LP-DOAS system. Other absorptions such as ozone, water vapor, and O_2–O_2 collisional pair also exist in the spectral range (443–470 nm) used for NO_2 concentration retrieval

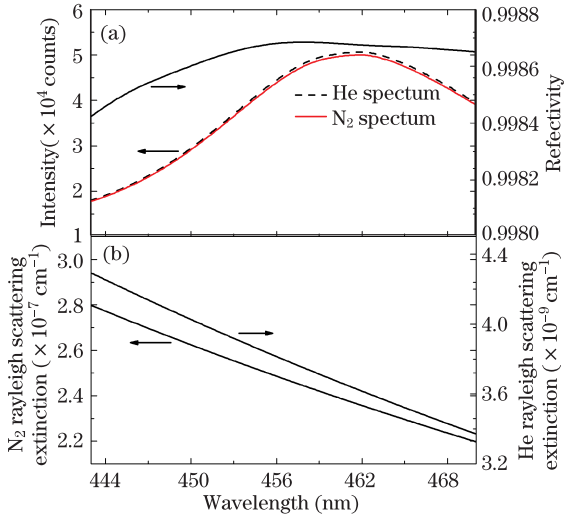

Fig. 2. (a) Cavity output spectra for pure He (dashed line) and pure N_2 (red line). The calibrated mirror reflectivity is also shown (black line). (b) Extinction caused by Rayleigh scattering of pure He and N_2.

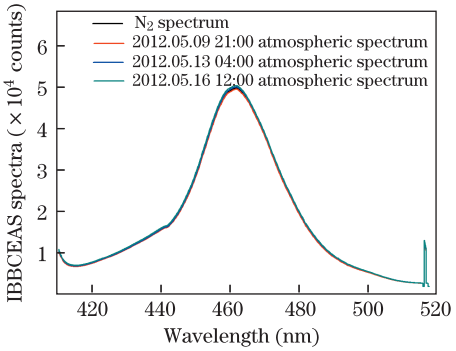

Fig. 3. Comparison of IBBCEAS spectra measured at different times and N_2 spectrum. Peak intensities of these spectra fluctuate all within 1%, which shows that aerosols are almost absent in the cavity.

with IBBCEAS. The absorptions caused by aerosols and water vapor are negligible because of the PTFE filter and silica gel that prevent them from entering the cavity. The measurements of local (Hefei city) aerosols by Li *et al.*[21] show very high aerosol concentrations. Figure 3 illustrates that the difference in atmospheric spectral intensities and N_2 reference spectrum is very small (less than 1%), suggesting that the aerosols have been effectively filtered. Except those of the aerosols, changes in the intensity are usually negligible because of the absorptions of atmospheric trace gases, especially when the reflectivity of the mirrors is moderate. To demonstrate the performance of the filter, we compared two atmospheric spectra acquired with and without the filter. A remarkable decrease (∼10%) in the intensity occurs when the filter is removed. For the ozone of typical 30 ppbv concentration in the atmosphere, the maximum absorption is 3.4×10^{-10} cm^{-1} at 462 nm[22], where the absorption cross-section is 4.5×10^{-22} cm^2/mol. The maximum absorption cross-section of O_2–O_2 is 6×10^{-46} cm^5/mol^2 at 446 nm[23], which yields peak absorption of 1.7×10^{-9} cm^{-1} for O_2–O_2 in the atmosphere. Generally, the standard deviation of the fitting residual spectrum accounts for the detection sensitivity of IBBCEAS instrument. The fitting results of NO_2 samples before measurements show that the detection sensitivity of our instrument is at 10^{-8} cm^{-1} level. Thus, only NO_2 absorption is included in the spectral range from 443 to 470 nm.

Figure 4 shows an example of atmospheric NO_2 concentration retrieval. The absorption spectrum of NO_2 was recorded with an acquisition time of 90 s. The NO_2 concentration was retrieved by nonlinear least-square fitting reference absorption cross-sections. These cross-sections were obtained by convoluting the cross-sections of Voigt *et al.*[24] with instrument function of spectrometer to absorption coefficient. Figure 4 illustrates that the NO_2 concentration and the standard deviation of residual spectrum are 32.3 ± 0.4 ppbv and 9.6×10^{-9} cm^{-1}, respectively. The corresponding uncertainty is only from the fitting algorithm, excluding the systematic errors. The measurement error of the IBBCEAS instrument mainly included the error of factor $(1–R(\lambda))$(∼12%) and the error of NO_2 cross-sections (∼5%). The total measurement error for NO_2 is approximately 13%.

If an optical cavity is used to detect trace gases, some losses, such as inlet or wall in the cell losses, should be sometimes considered. Other studies[25] have shown that both losses of NO_2 are negligible. In addition, Kebabian *et al.*[26] observed that the filter and dryer had no effect on the measured NO_2 concentration. Therefore, NO_2 concentrations, excluding these losses, are determined.

Figure 5 shows the atmospheric NO_2 values measured with the IBBCEAS instrument. During the seven-day measurement period, NO_2 concentrations range from 1 to 35 ppbv. The standard deviations of the fitting residual spectra range from 6.8×10^{-9} to 1.3×10^{-8} cm^{-1}, and the average standard deviation is 9.0×10^{-9} cm^{-1}. Assuming that the detection limit is twice the average standard deviation (2σ) of these fit residuals, the detection limit for the IBBCEAS instrument is approximately 1.8 ppbv.

In field application, cavity mirrors may be contaminated by dust or pollutant deposition, resulting in reflectivity degradation. Mirrors usually should be protected from contaminants, for example, by purging mirrors using dry air or N_2 gas streams. Our mirrors are not purged because its reflectivity is moderate and is not as vulnerable to environmental pollution compared with high reflectivity mirrors. A filter is used to prevent atmospheric aerosols from entering the cell. No degradation of mirror reflectivity is observed by comparing the two spectra of pure N_2 acquired before and after the measurements. During the seven-day period, mirror reflectivity was calibrated once before the measurements.

To verify the results of the IBBCEAS instrument, an LP-DOAS system was used to measure simultaneously atmospheric NO_2. The LP-DOAS instrument consisted of a Cassegrain telescope, which was used to send a parallel beam of light from an Xe-arc lamp (150 W, Osram, Germany) onto a retroreflector at a distance of 350 m. The light returning from the retroreflector was received by the same telescope and, through a fiber, fed into a 300-mm spectrometer (WDMl-3, Beijing Optics Instrument, China) with a PDA (Hamamatsu, Japan) detector. The LP-DOAS instrument was located at the same floor (18-m height above the ground) as the IBBCEAS instrument, and the distance between them was approximately 30 m. LP-DOAS measurements of NO_2 were observed in the spectral range of 330–365 nm with a spectral resolution

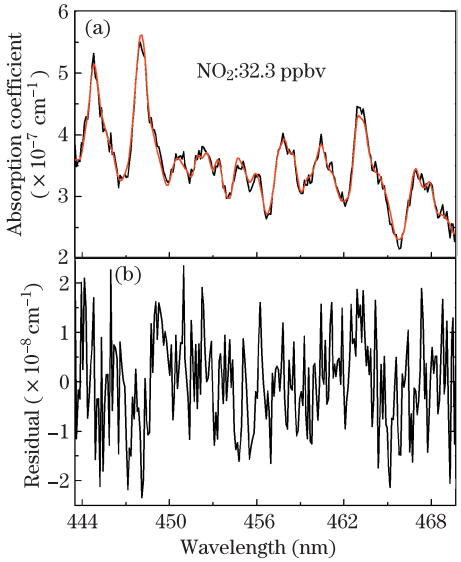

Fig. 4. (a) Measured (black line) and fitted (red line) absorption spectra of 32.3 ± 0.4 ppbv NO_2 in the atmosphere with an acquisition time of 90 s. (b) Residual spectrum with a standard deviation of 9.6×10^{-9} cm^{-1}.

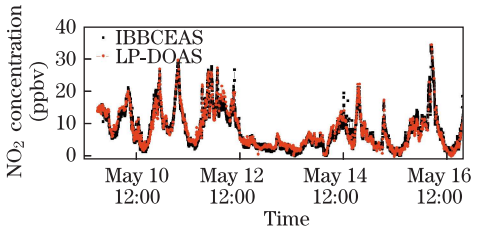

Fig. 5. Time series of simultaneous measurements of atmospheric NO_2 measured by the IBBCEAS instrument and a commercial LP-DOAS in 2012.

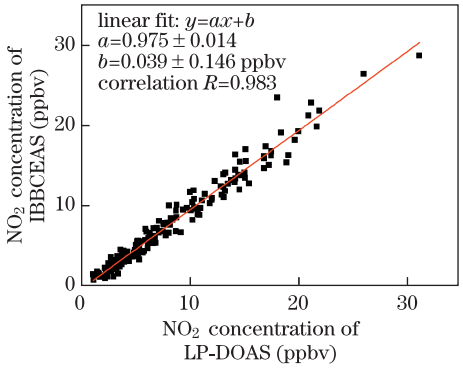

Fig. 6. Correlation of the atmospheric NO_2 concentrations measured by IBBCEAS and LP-DOAS.

of 0.2 nm. Figure 5 also shows the LP-DOAS measurement results. The measurement dimensions of these instruments are different. NO_2 concentrations measured by the LP-DOAS instrument are average concentrations over the folded light path, whereas those from the IBBCEAS system are point concentrations.

Figure 5 shows that the atmospheric NO_2 concentrations exhibit considerable variation, which is attributable to changes in local nitrogen oxide emissions. An obvious increase in NO_2 concentrations is observed every morning. Despite considerable variation in the NO_2 concentrations, the IBBCEAS instrument and LP-DOAS measurements remain highly correlated. However, the IBBCEAS instrument measures more NO_2 than the LP-DOAS instrument when the amount of NO_2 is at the peak level. This observation is mainly attributed to intense, short-term vehicle emissions near the sampling location, which is close to a parking lot. After the peak time, NO_2 is mixed well, and the difference between both measurement results becomes small. Figure 6 shows the correlation of average concentrations measured by the two instruments within 1 h. The linear regression has a slope of 0.975 ± 0.014 and an intercept of 0.039 ± 0.146 ppbv. Aside from the differences in measurement dimensions, discrepancies are likely attributed to differences in retrieval spectral ranges and the calibration error of mirror reflectivity of IBBCEAS. The reliability of IBBCEAS measurements of NO_2 in a different spectral range has compared favorably against a range of other NO_2 measurement approaches, including LIF, chemiluminescence, and CRDS[27].

In conclusion, long-term *in situ* measurements of atmospheric NO_2 using IBBCEAS with a blue LED light source are demonstrated. The IBBCEAS instrument is sensitive and accurate in measuring NO_2. If the detection sensitivity of the IBBCEAS instrument can be further improved, for example, using mirrors with higher reflectivity or longer cavity, the instrument may be used to measure other important trace gases (e.g., CHOCHO and IO) in the atmosphere.

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