Validation of *in situ* Measurements of Atmospheric Nitrous Acid Using Incoherent Broadband Cavity-enhanced Absorption Spectroscopy

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Incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) is a useful technique for measuring trace gaseous species in the atmosphere. Recently, IBBCEAS was used to measure concentrations of nitrous acid (HONO) in the troposphere to resolve controversies related to its formation and loss. Here, measurements of HONO and a mixture of HONO and NO₂ using IBBCEAS were validated by comparing them with those obtained with a NO_x analyzer. Good agreement was found between these methods, given their respective experimental uncertainties. The detection limit of our IBBCEAS instrument was 0.2 ppbv, with a signal-to-noise ratio of 1, and a 5-min integration time.

Keywords Nitrous acid, incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS), *in situ* measurements

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Introduction

Nitrous acid (HONO) is an important source of hydroxyl radical (OH) during the daytime. Because HONO is photolyzed by near-UV light, HONO is the main OH-radical source in the early morning.^{1,2} The hydroxyl radical initiates the oxidation of trace species, resulting in the formation of photochemical oxidants and secondary organic aerosols. Therefore, knowledge concerning the HONO budget aids in our understanding of the photochemistry of the troposphere.

Determining the sources of HONO has been one of the main issues concerning its photochemistry. The formation processes of HONO by the heterogeneous reaction of NO₂ with H₂O on moist surfaces were suggested:³

In addition, various primary emission sources⁴⁻⁶ and secondary formation processes⁷⁻¹⁰ of HONO have also been reported. However, recent field observations show a discrepancy between the measurements and modelling of daytime HONO concentrations.¹¹ This indicates that our understanding of the HONO budget is incomplete, and further field and laboratory studies are clearly required.

There are some ambient measurement methods for HONO subdivided into two types: direct and indirect methods. For an

indirect measurement of HONO, a long-path absorption photometer (LOPAP) technique has recently been developed^{12,13} based on wet chemistry. Gaseous HONO is absorbed into a liquid phase and then converted to an azo dye. The LOPAP has high sensitivity, good spatial and time resolution, with a low detection limit of 3–6 pptv and a response time of 4 min. However, it has potential chemical interference from other trace species (*e.g.*, NO_x, O₃, HNO₃) in ambient air. Another method for the measurement of HONO using wet chemistry is the air-dragged aqua-membrane denuder.¹⁴ HONO is absorbed in an aqueous solution using a denuder, where it reacts with 2, 3-diaminonaphthalene to form 1-naphthotriazol, which can be measured using its fluorescence. Its detection limit is 8.1 pptv in 2 min. In this technique, the chemical interference from trace species is negligible.¹⁴ These indirect methods can detect HONO with high sensitivity, as well as high spatial and temporal resolution. However, they depend on frequent maintenance, such as the replacement of solutions, because they are wet chemical techniques. In contrast, differential optical absorption spectroscopy (DOAS) is a direct method used for simultaneous ambient measurements of various trace species, including HONO.^{15,16} Optical absorption of HONO is observed around the UV light region (300–400 nm), having a narrow band structure. Using this optical property of HONO, DOAS can distinguish its absorption spectrum from other trace species, such as NO₂ and formaldehyde, and determine the concentrations of HONO with a low detection limit. However, DOAS has a low spatial resolution because of its necessarily long optical path length. Laser cavity ring-down spectroscopy (LCRDS) is an optical absorption spectroscopic technique that uses a laser; it has also been employed for ambient measurements of atmospheric trace species, such as NO₂ and NO₃ radical.^{17,18}

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Fig. 1 Schematic diagram of our incoherent broad-band cavity-enhanced absorption spectrometer. CCD, charge-coupled device; I.D., internal diameter.

Recently, incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) has been used to measure trace species. IBBCEAS is one of the optical absorption techniques having high spatial resolution. Due to the direct measurement technique, it can avoid chemical interference, like wet chemistry, and interference caused by light absorption from non-target trace species, similar to DOAS. Moreover, IBBCEAS can achieve better detection limits through customizing optical parts, and using a stable light source, and a high sensitivity (or low noise) detector. Importantly, the stability of the light source improved dramatically with the use of high-power LEDs,¹⁹ which are easier and safer to handle than other light sources, such as lasers. IBBCEAS has been used in many studies to measure ambient concentrations of trace species.^{20–22} In particular, for NO₂ measurements, comparisons of various techniques with IBBCEAS results have been carried out, validating IBBCEAS measurements.²³

IBBCEAS measures HONO and NO₂ simultaneously, in essentially the same sample air, which offers a great advantage to researchers. As described above, HONO is closely related to NO_x in the atmosphere, through reactions (1) and (2), which outlines one of the most important secondary formation processes of HONO. A comparison of IBBCEAS and LOPAP measurements was carried out in ambient air.²² Because LOPAP is an indirect measurement technique and has some potential interferences, it is necessary to validate the accuracy of IBBCEAS for gas-phase HONO and NO₂ mixtures by comparing some techniques without wet chemistry using standard gases. In this study, simultaneous measurements of HONO using IBBCEAS and a chemiluminescence NO_x analyzer with a molybdenum reducing catalyst (Mo converter) was carried out. Because the NO_x analyzer with a Mo converter can measure HONO concentrations in the absence of any other nitrogen compounds,^{14,24} comparisons between these two different measurement techniques can be used to validate measurements of HONO using IBBCEAS. Because NO₂ and HONO coexist in ambient air, the simultaneous measurement of the mixtures of HONO and NO₂ gases was undertaken. The concentration of NO₂ was monitored using cavity attenuated phase shift spectroscopy (CAPS) to obtain accurate concentrations of NO₂ in the mixture, given that the NO_x analyzer can only measure the sum of NO₂ and HONO.

Experimental

Incoherent broadband cavity-enhanced absorption spectrometer

A schematic diagram of our incoherent broadband cavity-enhanced absorption spectrometer is shown in Fig. 1. Our instrument is similar to earlier models,^{20–22} and consists of a light source, with optics for introducing light into a cavity, and a spectrometer with a charge-coupled device (CCD) array detector. A high-power UV LED (M365D1; Thorlabs Inc., NJ, USA) was employed as a light source, with an optical power of 360 mW, a center wavelength of 365 nm, and full width at half maximum of 7.5 nm. The light intensity of the LED was controlled by a DC power supply, and ambient temperature was kept at 273 K by a Peltier unit so as to avoid any fluctuation of its center wavelength. UV light was focused by a quartz aspherical lens having a focal length of 33 mm into a multimode optical fiber, with a 300- μ m core diameter and 10-m length. The output of the optical fiber was coupled with an aluminum parabolic mirror to collimate the UV light into a beam with a diameter of around 10 mm. Collimated UV light was introduced into the cavity by reflecting it off two coated dielectric mirrors (Los Gatos Research, CA, USA). Before the UV light was introduced to the cavity, an interference filter (YIF-340; Sigma Koki, Japan) was employed to remove any unnecessary wavelength region of light. The UV light transmitted through the cavity was focused by a quartz lens with a focal length of 50 mm so as to introduce it to another multimode optical fiber (300- μ m core diameter and 10-m length) connected with the spectrometer (Andor SR163, Oxford Instruments, UK) having a -60°C cooled 1024×127 pixel CCD array detector (Andor DU401A-BV). In the spectrometer, a 25- μ m fixed-width slit and a 1200 groove/mm grating (500 nm blaze) were deployed. The spectrum resolution was ~ 0.5 nm. The exposure time of the CCD detector was set at 20 s. Measurements of the spectrum were carried out every 15 times and averaged.

The optical cavity consisted of two highly reflective mirrors with mirror mounts (Los Gatos Research). The mirror mounts were connected to two polytetrafluoroethylene (PTFE) blocks, with 1/4-inch outer diameter inlet and outlet tubes made of perfluoroalkoxy alkane (PFA), and a 1-m length of PFA tube. To avoid polluting the mirrors, 500 sccm (standard cubic centimeters per minute) of pure nitrogen gas, controlled by a

Fig. 2 Block diagram showing the gas-flow system of HONO and NO₂ to the measuring instruments. MFC stands for mass flow controller. IBBCEAS, incoherent broad-band cavity-enhanced absorption spectroscopy; CAPS, cavity attenuated phase-shift spectroscopy.

mass flow controller (Kofloc Model 3660; Kojima Instruments Inc., Japan), was introduced along the sides of the mirrors as a purge gas. Because aerosol-free gas was used in our study, there was no need for an aerosol cut filter. Airflow from the outlet of the cavity was evacuated using a diaphragm pump (DA-60S; ULVAC Technologies, MA, USA) through a flow-control valve, using a mass flow sensor (Kofloc Model 3810S). The airflow rate was measured to be approximately 10 SLM.

Simultaneous measurements

The measurements of HONO and a mixture of HONO and NO₂ using IBBCEAS were validated using an NO_x analyzer with a Mo converter based on an NO–O₃ chemiluminescence method (Model 42i-TL; Thermo Fisher Scientific, MA, USA) and an NO₂ monitor (CAPS-NO₂; Shoreline Science Research Inc., Japan). Figure 2 shows the experimental apparatus used for validating our IBBCEAS instrument. Zero air was passed through the HONO (and NO₂) source to generate a standard HONO (or HONO + NO₂) gas. This standard gas was diluted by additional zero air. The diluted standard gas was introduced into our spectrometer, as well as the NO_x analyzer, and the CAPS-NO₂ analyzer. The NO_x analyzer measured the sum of the HONO and NO₂ concentrations. The detection limit of the NO_x analyzer was measured using a standard deviation of the blank signals (σ) and estimated to be 42 pptv for a 1-min integration time (3σ). To measure NO₂ independently, an NO₂ monitor based on a CAPS method²⁵ was employed. The detection limit of NO₂ by the CAPS-NO₂ analyzer was estimated to be 17 pptv for a 1-min integration time (3σ). The HONO concentration for the standard gas can be obtained using the following equation:

$$[\text{HONO}] = C_{\text{MO}} - C_{\text{NO}_2}, \quad (3)$$

where C_{MO} and C_{NO_2} are the concentrations from the NO_x analyzer and the NO₂ monitor, respectively.

The three instruments were connected by PFA tubes and PTFE connectors to the main flow line. The flow rate of the NO_x analyzer was so small (~ 0.5 SLM) compared with other

instruments, especially the IBBCEAS, that we made the PFA tube connecting the inlet of NO_x analyzer to the main flow line be as short as possible. Our spectrometer measures the concentrations of HONO and NO₂ simultaneously, around the 360-nm wavelength region.

Preparation of gaseous HONO and NO₂

Gaseous HONO is usually generated using the heterogeneous reaction of NaNO₂ with a humidified HCl gas.²⁴ However, the desired concentration of HONO was produced by the reaction of NaNO₂ with water vapor²⁶ in this study. Specifically, humidified zero air was introduced into a glass chamber (7.5-cm inner diameter and 24-cm length). A glass filter was set inside this chamber (see Fig. 2) and granular NaNO₂ (>98.5%; Wako Pure Chemical Industries Ltd., Japan) was put on the glass filter. The humidified zero air reacted with NaNO₂ in the glass chamber to generate HONO. The HONO concentration was controlled by adjusting the humidity of the zero air. The humidity was adjusted by the following procedure. A part of the zero air flow through the HONO source line (see Fig. 2) was divided into a water bubbler to be bubbled and added back to the main flow, and then the flow was supplied into the glass chamber. The deliquescence of NaNO₂ was not observed, although the relative humidity was not monitored. The HONO generated was diluted by additional zero air without purification. The NO₂ concentrations in the HONO standard gas were confirmed to be below the detection limit of the CAPS-NO₂ analyzer.

NO₂ was generated using a gas-phase titration method.²⁷ Briefly, ozone was added to a 5.07-ppmv NO/N₂ standard gas (Taiyo Nippon Sanso, Japan) to oxidize NO to NO₂, and then this NO/NO₂ mixture was diluted with zero air. The NO₂ generation was carried out using a commercially available dynamic gas dilution system (Model 103G; Nippon Thermo Co., Ltd., Japan) in this study.

Retrieval method

The detailed measurement principles for trace gas concentrations from IBBCEAS have been published elsewhere.²⁸

In this section, the derivation method for trace gas concentrations is briefly described. Extinction related to the light absorption of a trace species, denoted by $\alpha_{\text{abs}}(\lambda)$, is derived from the following equation:

$$\alpha_{\text{abs}}(\lambda) = \left(\frac{1 - R(\lambda)}{L} + \alpha_{\text{Ray}}(\lambda) \right) \left(\frac{I_0(\lambda) - I(\lambda)}{I(\lambda)} \right) = \left(\frac{1}{L'(\lambda)} + \alpha_{\text{Ray}}(\lambda) \right) \frac{\Delta I(\lambda)}{I(\lambda)}, \quad (4)$$

where $I_0(\lambda)$ and $I(\lambda)$ are the light intensity transmitted through the cavity in the absence and presence of the trace species, respectively; $R(\lambda)$ is the mirror reflectivity; and L is the distance between the two mirrors. The symbol $\alpha_{\text{Ray}}(\lambda)$ was used to denote extinction related to Rayleigh scattering in air in this study. Because of the small variation in the cross-section of the Rayleigh scattering, compared with the wavelength region and the narrow analysis range (15 nm) of the spectrum, the wavelength dependence of $\alpha_{\text{Ray}}(\lambda)$ was negligible. A value of $\alpha_{\text{Ray}}(\lambda) 7 \times 10^{-7} \text{ cm}^{-1}$ at 1 atm and 360 nm was applied in our study.²² To solve Eq. (4), it is necessary to obtain the effective path length, $L'(\lambda)$, related to the mirror reflectivity. This allows us to determine the concentration of the trace species. Here, the effective path length was derived using the following procedure. First, simultaneous measurements of standard NO_2 gas using the IBBCEAS and CAPS- NO_2 methods were carried out. The absorption spectrum of NO_2 from IBBCEAS was derived for the observed spectral range of 350–395 nm. Second, the effective path length was determined based on retrieval for every 5 nm in the observed spectrum. For our retrieval of NO_2 , high-resolution data for the absorption cross-section²⁹ were employed. Finally, this effective path length was fitted with a 3rd-order polynomial function for the wavelength. The effective path length for a wavelength of 367 nm was estimated to be 4.6 km. This corresponds to 0.99985 of the mirror reflectivity for 100 cm of the path length, and $7 \times 10^{-7} \text{ cm}^{-1}$ of the Rayleigh scattering. A previously reported absorption cross-section for HONO was used.³⁰ The uncertainty in the concentration of HONO is estimated to be around 6%, based on the uncertainties for the cross-section for HONO (5%), the effective path length (4%), and $\Delta I(\lambda)/I(\lambda)$ (i.e., 0.05% for a signal to noise ratio of 1).

The concentrations of HONO and a mixture of HONO and NO_2 were retrieved using DOASIS software developed by the Institute of Environmental Physics at Heidelberg University, Germany,³¹ for the wavelength range of 360–375 nm. The fitting model function of DOASIS for the absorption spectrum, $I(\lambda)$, was given by:

$$I(\lambda) = \exp(\sum \sigma_i [n_i] (s_i + t_i \lambda) + P(\lambda)) + O(\lambda), \quad (5)$$

where σ_i and $[n_i]$ are the cross section and the number density for related trace species, respectively. The coefficients s_i and t_i are the shift and squeeze parameters for each cross section, respectively. The functions $O(\lambda)$ and $P(\lambda)$ denote the additional polynomial function to modify the effect of the fluctuation of the baseline, and a polynomial function to modify some weak absorption or scattering. Finally, our measurements showed weak absorption for the O_2 dimer.³² However, the absorption intensity of the O_2 dimer was so weak that no band structure was observed on our spectra; thus, their contribution to absorption was not considered in this study.

Fig. 3 Example analysis of the concentration of HONO (1.71 ± 0.04 ppbv) using DOASIS software. The exposure time of the CCD detector was set to 20 s. The measurements of the spectrum were carried out every 15 times and averaged. The top panel shows the observed (filled circles) and fitted (gray curve) spectra, respectively. I_0/I is the ratio of the light intensity transmitted through the cavity in the absence and presence of HONO. The baseline, derived from the retrieval of the spectrum by DOASIS software, is shown by a dotted line. Subtraction of the baseline from the observed spectrum and a scaled cross-section for HONO are represented by filled circles and a gray curve in the middle panel, respectively. The bottom panel gives the residual spectrum.

Results and Discussion

Validation of HONO measurements

An example of the spectrum of HONO measured by the IBBCEAS and its retrieval using DOASIS software is shown in Fig. 3. In the top panel of Fig. 3, observed and fitted spectra are indicated by filled circles and a grey curve, respectively. A fluctuation of the baseline, indicated by the dotted line, was observed, presumably causing by a slight fluctuation of the intensity of LED or an instability of the cavity. In this study, this fluctuation was modified by the polynomial function, $O(\lambda)$, in Eq. (5). The HONO concentration was estimated to be 1.71 ± 0.04 ppbv (1σ). The relative standard deviation of the concentration of HONO for all measurements was $\sim 5\%$. The bottom panel of Fig. 3 shows the residual spectrum. The average and 1σ standard deviation of the residual were 6.4×10^{-6} and 1.1×10^{-3} , respectively.

The correlation between HONO measurements from IBBCEAS and chemiluminescence NO_x analyzer is shown in Fig. 4. The slope of the regression line is 1.11 ± 0.07 , and its intercept is 0.2 ± 0.2 ppbv (1σ), giving an R^2 value of 0.98. The main uncertainty in measurements of the NO_x analyzer results from its NO calibration ($\pm 10\%$). The uncertainty in IBBCEAS is $\pm 6\%$, as outlined above. Thus, the HONO concentrations measured using IBBCEAS were in good agreement with those of the NO_x analyzer, by taking into account their respective uncertainties.

Simultaneous measurements of HONO and NO_2 were also carried out. An example of a spectrum of the mixture of HONO and NO_2 obtained from IBBCEAS and its retrieval is shown in Fig. 5. The top panel of Fig. 5 shows the observed (filled circles) and fitted spectra (gray curve), respectively. The second and third panels of Fig. 5 are NO_2 and HONO spectra extracted from the observed spectrum in the top panel, respectively.

Fig. 4 Correlation between measurements of HONO from incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) and the NO_x analyzer. The gray line is the regression line. Error bars for each data point are the 1 σ standard deviation for each instrument. Their slope, y-intercept, and 1 σ error are also shown.

Fig. 5 Example of our estimation of the concentration of HONO (1.06 ± 0.06 ppbv) and NO₂ (3.99 ± 0.17 ppbv) using DOASIS software. Exposure time of the CCD detector was set to 20 s. The measurements of the spectrum were carried out every 15 times and averaged. Panel (A) shows observed (filled circles) and fitted (gray curve) spectra, respectively. I_0/I is the ratio of light intensity transmitted through the cavity in the absence and presence of HONO. Extracted spectra of NO₂ (panel (B)) and HONO (panel (C)) are represented by filled circles, respectively. Scaled cross-sections for NO₂ and HONO are shown by each panel, respectively. Panel (D) is the residual spectrum.

The bottom panel of Fig. 5 is the residual spectrum. The average and the 1 σ standard deviation of the residual were 1.8×10^{-6} and 4.1×10^{-4} , respectively. The concentrations and 1 σ standard deviation of HONO and NO₂ were estimated to be 1.04 ± 0.06 and 3.99 ± 0.17 ppbv, respectively. The relative standard deviations of the concentrations of HONO and NO₂ were ~ 3 and $\sim 4\%$, respectively.

The correlation between measurements of HONO using the NO_x analyzer is shown in Fig. 6. The concentration of NO₂ was fixed to around 4.4 ppbv, while that of HONO was varied from sub-ppbv to 7 ppbv levels. The regression line has a slope of 0.97 ± 0.03 and an intercept of 0.3 ± 0.1 ppbv, with an R^2 value of 0.99. Considering the main uncertainty in

Fig. 6 Correlation between measurements for a mixture of HONO and NO₂ from incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) and the NO_x analyzer. The concentration of NO₂ was 4.41 ± 0.05 ppbv measured by cavity attenuated phase shift spectroscopy, CAPS. The gray line is the regression line. The error bars for each data point are the 1 σ standard deviation for each instrument. Their slope, y-intercept and their 1 σ error are also shown.

Fig. 7 The example of the ambient measurements of NO₂ and HONO in an urban area in Tokyo during the winter season (January 22nd – February 12th). The repetition times of the measurements were set to 4 min.

measurements of the NO_x analyzer and CAPS-NO₂ resulting from NO calibration and IBBCEAS, HONO concentrations measured using IBBCEAS were in excellent agreement with those of the NO_x analyzer, even in the presence of NO₂. The average concentration of NO₂ in the HONO + NO₂ mixture was measured to be 4.16 ± 0.20 ppbv using IBBCEAS, which is in consistent with measurements from CAPS (4.41 ± 0.05 ppbv), i.e., within 1 σ standard deviation.

Sensitivity of HONO measurements

Applying the uncertainty measure of $\Delta I(\lambda)/I(\lambda)$ to the minimum absorption difference in the observed spectral range, the detection limit for our spectrometer was estimated to be 0.2 ppbv, using a 2 σ standard deviation, and the 300 s of integration time in Eq. (4). The detection limit for HONO for our IBBCEAS instrument compared with the previous study²² has been slightly improved.

Examples of the in situ measurements of HONO

As our next step, we have made two plans: ambient measurements of the concentrations of HONO during the season, and an estimation of the emission factor or flux of HONO from some sources.

For the first plan, we tried to measure the ambient concentration of HONO at an urban site of Tokyo during the winter season in 2016. The measurement site, Tokyo Metropolitan Research Institute for Environmental Protection (TMRIEP), is located in urban central Tokyo. The results of the measurements of HONO at TMRIEP during the winter season (January 22nd – February 12th) in 2016 are shown in Fig. 7. During the measurement period, it was not necessary to align the cavity in order to modify the sensitivity caused by some troublesome problems (pollution of the mirrors by aerosol, distortion of the alignment *etc.*). The average of the concentrations of NO₂ and HONO were 26.2 ± 13.6 and 1.5 ± 1.1 ppbv, respectively. Simultaneous measurements of ambient NO₂ were carried out by the CAPS-NO₂ analyzer. Good agreement was confirmed by the correlation of the concentration of NO₂ from IBBCEAS and CAPS-NO₂ with the slope of the regression line being 1.03 ± 0.01 , and the R^2 value was 0.94. The concentration variation of HONO was similar with that of NO₂, and the moderate correlation between the concentration of HONO and NO₂ ($R^2 = 0.6$) was observed. Analysis of the correlation between the components of aerosol and HONO were performed. In the future, we will continue to conduct the ambient measurements under different conditions for the season and location such as suburban or rural site.

For the second plan, the emission factors (EFs) of HONO from gasoline vehicular exhaust have been estimated.³³ Measurements of HONO and other trace species concentrations such as CO, NO_x, total hydrocarbons (THCs) in gasoline exhaust were conducted at the National Institute for Environmental Studies (NIES) in Tsukuba, Japan. For these measurements, six different passenger vehicles made by a Japanese company, and in compliance with the 2005 Japanese emission control standard, were studied. As a result, concerning HONO we found that the EFs were different from the vehicle's specifications and under different driving cycles. The annual HONO emissions in Japan were estimated using the calculated EFs and other statistical data. In the future, determinations of the EFs for HONO from diesel vehicle or old gasoline vehicle will be continued.

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