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VISIBLE AND NEAR-INFRARED DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY (DOAS) FOR THE MEASUREMENT OF NITROGEN DIOXIDE, CARBON DIOXIDE AND WATER VAPOR

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ABSTRACT
The spectral intensity of direct and scattered solar radiation is of fundamental importance for various studies in civil engineering, agriculture, solar power generation, and radiation budget estimation. In this paper, we describe a ground-based, wide-spectral-range sensor that can be used for measuring spectral intensities both in the visible and near-infrared spectral regions. The measurements are conducted either with artificial light sources or direct/scattered solar radiation. The measured spectra yields information on the absorption features of atmospheric gases such as nitrogen dioxide (NO_2), carbon dioxide (CO_2) and water vapor, as well as aerosol optical properties in the atmosphere. Relatively weak absorption of nitrogen dioxide is measured with the technique of differential optical absorption spectroscopy (DOAS), whereas aerosol, carbon dioxide, and water vapor amounts are measured by matching the observed spectra with simulated ones. Both High Resolution Transmission (HITRAN) and Moderate Resolution Atmospheric Transmission (MODTRAN) database/codes are used to derive column amounts of absorbing molecular species and to characterize aerosol optical properties.

Keywords: Air pollution; Differential Optical Absorption Spectroscopy (DOAS); Direct solar radiation; Molecular absorption; skylight measurement

1. INTRODUCTION
Various trace gases and particulate matters in the atmosphere give rise to air pollution in urban areas. Their radiation properties are also influential to the local and regional radiation budget, closely related to the evolution of global climate change. Thus, it is indispensable to have effective methods with which concentration measurement and monitoring can be carried out for atmospheric constituents such as nitrogen dioxide (NO_2), carbon dioxide (CO_2) and aerosols, also known as suspended particulate matter (SPM). In the case of satellite measurement in the visible (VIS) spectral range, significant influence is exerted on the resulting images by aerosol distributions in the lower troposphere (Rees, 2001). The scattering and absorption characteristics of aerosols play an important role also in the earth's radiation budget. Generally clouds and aerosols tend to reflect the solar radiation back to space, thus contributing to the cooling of the earth's atmosphere system, though some of them absorb radiation and contribute to the warming effect (IPCC, 2007). Infrared and near-infrared (NIR) absorption of molecules is the main cause of the global warming (greenhouse) effect.

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Absorption due to carbon dioxide (CO_2), methane (CH_4), and other trace molecular species is of crucial importance, in addition to the large and variable effect of water vapor absorption. Since most of the sources/sinks of these molecules are located in the lower troposphere, it is beneficial if the NIR absorption of these gases can be monitored simultaneously with the conventional approach of differential optical absorption spectroscopy (DOAS) in the visible spectral range (Fraser et al., 2009; Zuo et al., 2008; Bagtasa et al., 2007; Yoshii et al., 2003). The DOAS method provides a useful tool for the measurement of atmospheric pollutants by measuring optical extinction (absorption and scattering) over a light path having a length of a few kilometers. By the use of visible light sources such as the aviation obstruction light, the method enables the measurement of NO_2 and aerosols that show absorption and extinction, respectively, in the visible spectral range.

In the present paper, we describe the extension of the DOAS method to the near-infrared spectral region, with the purpose of measuring the atmospheric concentration of CO_2 molecules. In accordance with the international effort to cut greenhouse gas emissions, the precise measurement of CO_2 concentration has become increasingly important. In our study, before implementing the atmospheric measurement, test measurements were made with the combination of a tungsten lamp and a cell containing CO_2 sample gas. The atmospheric measurement, in turn, is based on a more intense halogen lamp and a super-luminescent diode (SLD) as light sources, and the light transmission over a path length of several kilometers was monitored. Currently an active measurement of CO_2 using 1.6 μm fiber lasers onboard a small satellite is planned by our group (Kuze et al. 2009), for which the ground measurement such as described in the present paper will give preliminary tests as well as validation opportunities.

An alternative, passive measurement is called the multi-axis DOAS (MAX-DOAS) measurement (Wittrock et al., 2004; Irie et al., 2008; Manago & Kuze, 2010), in which the direct or scattered solar radiation is employed to retrieve the column amount of absorbing species. In this passive regime, we constructed and tested a wide-band MAX-DOAS spectrometer that enables simultaneous measurements in the UV-VIS-NIR spectral region. In the analysis of the observed spectra, both HITRAN (Rothman et al., 2005) and MODTRAN (Anderson et al., 1999) database/codes were used to derive column amounts of absorbing molecular species, including carbon dioxide, and to characterize aerosol particles.

2. EXPERIMENTS

2.1. Laboratory measurement of CO_2 absorption

The absorption measurement of CO_2 was conducted in the laboratory. The collimated light beam from a tungsten lamp (100 W) passed through a quartz pipe of 30 mm diameter and 1000 mm length. The cell was filled with 1 atm pressure CO_2 gas, and the transmitted light was detected using an InGaAs NIR array detector (Hamamatsu, C9914GB). The array spectrometer enables the measurement in the wavelength region of 1100-2200 nm with a resolution of 4 nm/ch. The resulting absorption spectrum is shown in Section 3.1.

2.2. Atmospheric absorption Measurement

We conducted the NIR CO_2 absorption measurement in the lower troposphere using an optical path length of 6 km. A 1000 W halogen lamp was used as a light source, and a collimated beam was produced with a parabolic mirror. A rotating sector was placed just in front of the lamp so that the on/off features, each during a time period of approximately 1s, could be recorded sequentially. The light beam from this source was propagated from the CEReS building (9F, Chiba, 35.62ºN, 140.10ºE) to a WNI building (25F, Makuhari, 35.65°N, 140.03°E). The beam was detected by means of a commercial astronomical telescope (200 mm diameter) connected to the InGaAs array spectrometer using an optical fiber.

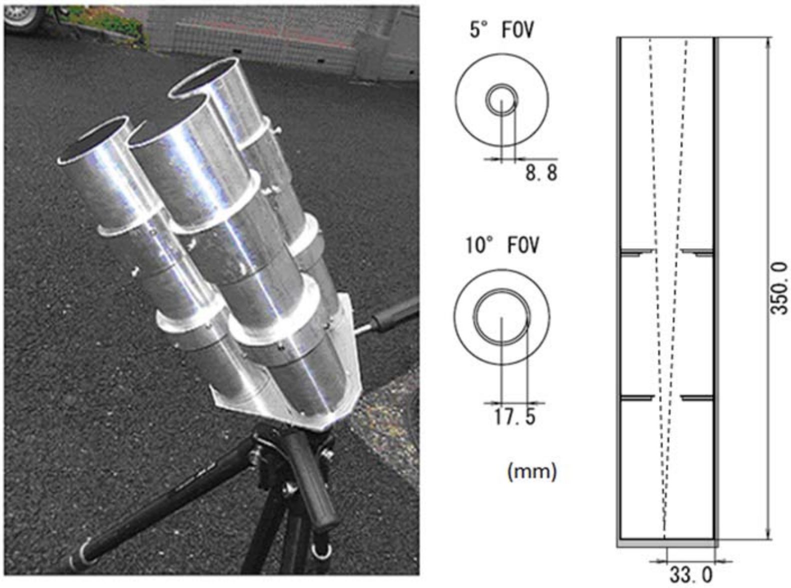

Figure 1 Adaptors for UV-VIS-NIR skylight measurement

2.3. UV-VIS-NIR Observation of Scattered Solar Radiation

The observation of scattered solar radiation (SSR, skylight) was conducted using three compact spectrometers: a silicon spectrometer (Ocean Optics, USB4000) for the wavelength range of 200-800 nm (0.15 nm/ch resolution), another silicon spectrometer (Ocean Optics, HR2000) for 700-1100 nm (0.2 nm/ch), and an InGaAs spectrometer (Hamamatsu, C9914GB) for 1100-2200 nm (4 nm/ch). The entrance of each spectrometer is connected to a fiber cable with an acceptance angle (full angle) of approximately 120°. In order to reduce this acceptance angle to 5°, three cylindrically-shaped adaptors were fabricated (Figure 1). This reduced field-of-view (FOV) angle was determined to facilitate the comparison between the measured and simulated intensities, while sufficient intensities could be obtained in reasonable measurement time, 100 ms, 300 ms, and 1 s for USB4000, HR2000, and C9914GB, respectively. For each cylinder the inside wall was covered with a dark sheet having low reflectance (below 1.5 %) for the entire spectral range, and a baffle ring was attached to define the FOV of 5°. The spectral SSR intensities were measured for four directions (north, east, south, west) and six elevation angles (15, 30, 45, 60, 75, and 90°) under clear-sky conditions. We noted that, after averaging, a set of data points can normally be obtained in a time period of 20 min.

3. RESULTS AND DISCUSSION

3.1. Measured CO_2 spectrum

Figure 2 shows the observed feature of the CO_2 absorption bands in the NIR spectral region. Here the transmittance $T=I/I_0$ is plotted as a function of wavelength λ, where I and I_0 are the intensities observed with and without the gas in the absorption cell. This experimental result shows good agreement with the theoretical spectrum, which was simulated using the CO_2 absorption data from the HITRAN database, and conformed to a reduced wavelength resolution of 4 nm.

3.2. Atmospheric absorption measurement

CO_2 and water vapor absorption spectra were observed on August 6, 2009 in the urban lower troposphere over a nearly horizontal path length of 6 km (Figure 3). Broad absorption bands of water vapor are noted around 1400 and 1900 nm, with CO_2 bands around 1600 and 2000 nm.

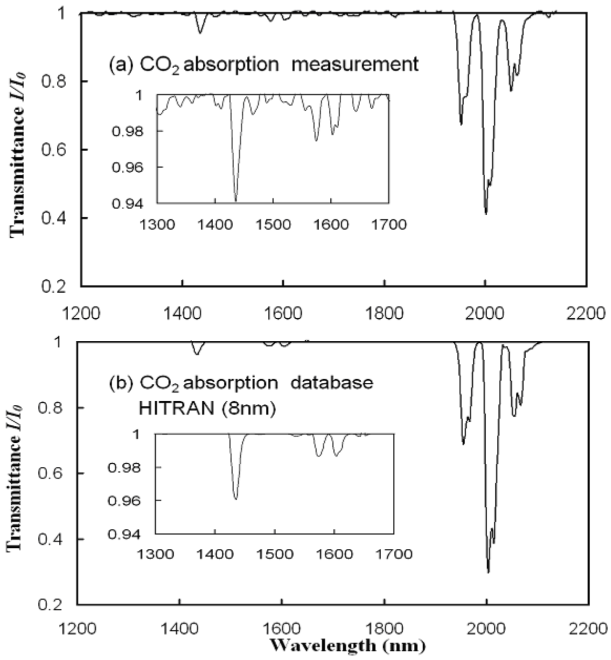

Figure 2 CO_2 absorption (a) observed in the laboratory experiment and (b) simulated with the HITRAN database

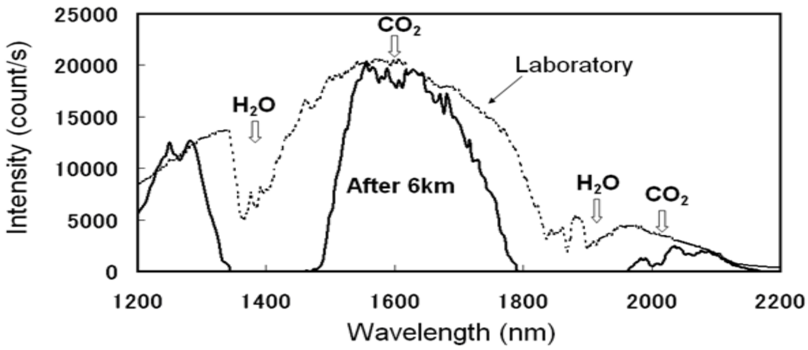

Figure 3 Molecular absorption spectra observed in the atmospheric measurement over a path length of 6 km

Figure 4(a) shows the determination of the transmittance $T=I/I_0$ from the 2000 nm CO_2 absorption band. For comparison, a theoretical spectrum was calculated using the HITRAN database, with a reduced wavelength resolution of 8 nm in accordance with the present measurement. The theoretical calculation is based on the Lambert-Beer's law given as:

$$T = e^{-\tau} = e^{-N\sigma L} \tag{1}$$

Here τ is the optical thickness of the molecular absorption, N is the molecular number density, L is the optical path, and σ is the absorption cross-section. Note that the cross-section must be conformed to the observational wavelength resolution. We can see fairly reasonable agreement between the observed and simulated spectra (Figure 4(b)), leading to an average CO_2 concentration of 375 ± 20 ppm.

More precise determination of the concentration can be attained by increasing the wavelength resolution of the measurement, hence that of σ(λ). Thus, instead of the commercial NIR spectrometer, we are currently preparing a setup that would enable a more high-resolution measurement in the atmosphere.

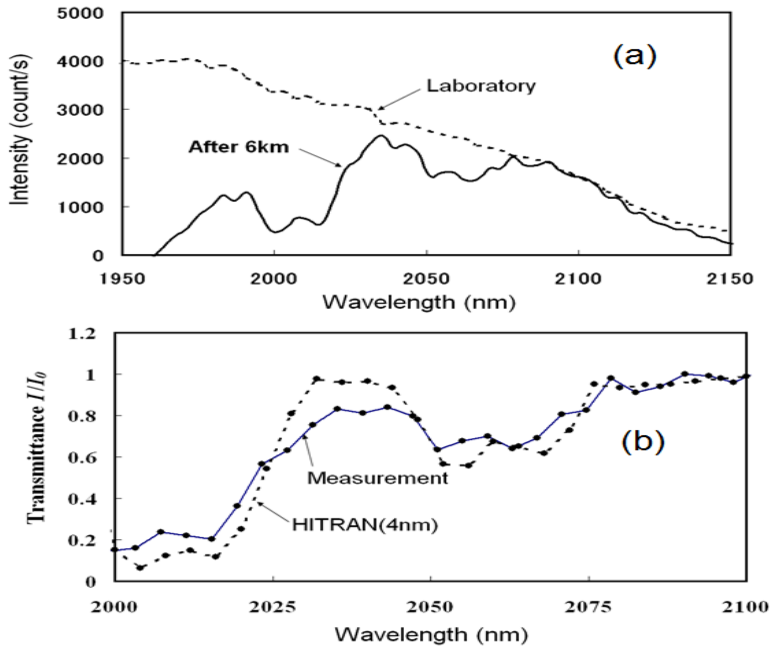

Figure 4 Determination of CO_2 concentration: (a) comparison of the laboratory and atmospheric spectra, and (b) comparison of the transmittance

3.3. UV-VIS-NIR observation of SSR

Figure 5 shows the zenith sky radiance spectra obtained by combining the results of the three spectrometers. Although the resolution is rather coarse in the NIR part, one can see good consistency among the results of the measurements using the three spectrometers, with remarkable absorption bands of O_2 and H_2O, in particular. The NIR part of the spectrum (reproduced in Figure 6(a)) shows the absorption bands of water vapor (around 400 and 1900 nm) and CO_2 (1600 and 2000 nm). Around 2000 nm (Figure 6(b)), strong absorption appears due to CO_2, and Figure 6(c) shows the theoretical skylight (SSR) simulated with the MODRAN4 radiation transfer code. As seen from Figures 6(a) and 6(c), we have good agreement between observation and simulation.

Since the influence of the aerosol extinction (i.e., the sum of scattering and absorption) appears mainly in the visible spectral range, the result measured with the USB4000 spectrometer is useful for the retrieval of the optical properties of aerosol extinction. For the analysis, we employed the three-component aerosol method (TCAM) based on the spectral fitting of the MODTRAN4-simulated spectra to the observed spectra of SSR and direct solar radiation (Manago & Kuze, 2010; Manago et al., 2011). The analysis of the VIS spectrum in the wavelength range around 400-450 nm gives information on the weak absorption of NO_2, an important pollutant generated in every combustion process, by means of the original DOAS methodology (Kuriyama et al., 2011). Similar DOAS approach has also been applied to the measurement of SO_2 from volcanic eruptions on Miyakejima Island (Kuze et al., 2009).

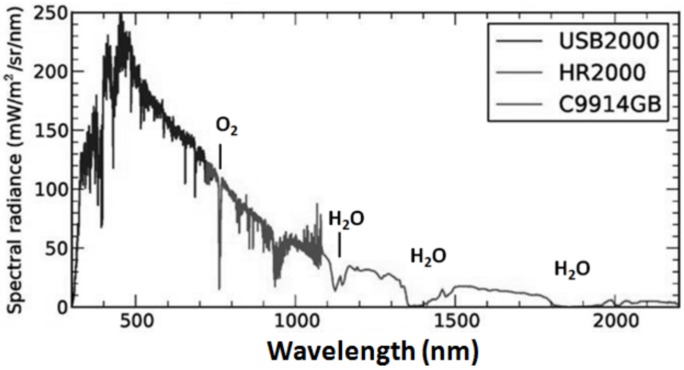

Figure 5 Wide wavelength range observation of sky radiance obtained by combined results of the measurements using the three spectrometers.

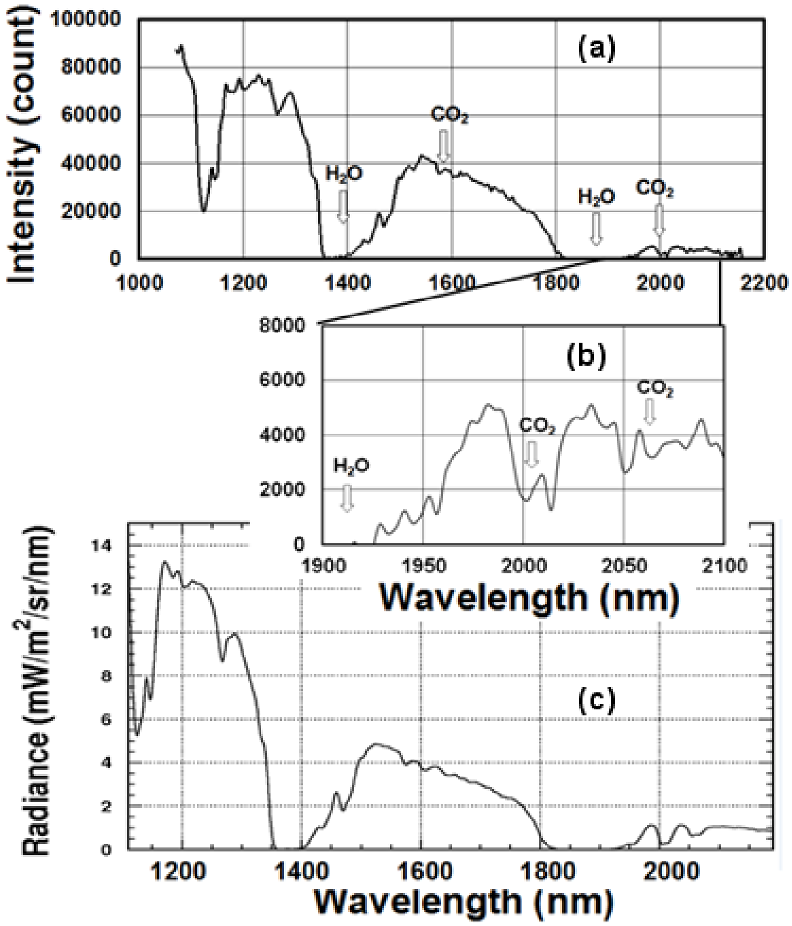

Figure 6 Near-infrared part of the sky radiance spectra: (a) the spectrum obtained with C9914GB, (b) detailed features of CO_2 absorption around 2000 nm, and (c) sky radiance simulated with the MODTRAN4 code.

4. CONCLUSION

We have described the monitoring of molecular absorption features mainly in the visible and near-infrared spectral regions. Conventional light sources such as a tungsten and a halogen lamp can be used for the water vapor and CO_2 concentration measurements both in the laboratory and outdoors. During the daytime under clear-sky conditions, the observation of molecular absorption is feasible from skylight measurements using a UV-VIS-NIR spectrometer setup. The DOAS approach in this wide spectral range enables the measurement of SO_2, NO_2, and aerosol in the lower troposphere. The future extension of CO_2 measurement is the use of a super luminescent diode and a fiber laser as light sources.

5. ACKNOWLEDGEMENTS

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