Development of BB-CEAS (broadband cavity-enhanced absorption spectroscopy) measurement for reactive nitrogen species

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Abstract: Nitrogen trioxide (NO_3) radicals are expected to be widely applied in the agricultural field due to their high reactivity. Broadband cavity-enhanced absorption spectroscopy (BB-CEAS), known as NO_3 radical measurement scheme for atmospheric chemistry, requires NO_2 measurement for the correction of the optical cavity loss. This work specifically focuses on BB-CEAS measurement with plasma generated NO_2, which in turn enables NO_3 measurement with visible light.

Keywords: BB-CEAS, NO_2, NO_3

1. Introduction

Nitrogen fertilizer, which is indispensable for crop production, is mainly synthesized by the Harbor-Bosch process, consuming large amount of natural gas and energy, approximately 3-5% of the world's total production of natural gas and 1-2% of total energy production [1]. Plasma nitrogen fixation, recently suggested to synthesize nitric oxides and ammonia exclusively from air and water, has advantages in the abundant resources and less requirements on the power sources, preferred for on-site generation of nitrogen fertilizers with renewable energies [2]. Fully electrified and on-site nitrogen fixation with a minimal facility scale can potentially play an important role not only on sustainable nitrogen fixation but also on processing valuable nitrogen reactants at farming fields. Recently, selective plasma synthesis of dinitrogen pentoxide (N_2O_5), anhydride of nitric acid (HNO_3), has been realized with a portable plasma device exclusively using air and electricity [3]. N_2O_5 can easily react with liquid water to form nitrate (NO_3^-), one of the most important forms of nitrogen nutrient for plant. More importantly, oxidation number of nitrogen in N_2O_5 is one of the highest (+5) among nitrogen oxides, that is potential to induce oxidative and nitrating reactions [3, 4]. This N_2O_5 reactivity expects that on-site generation of N_2O_5 from air enables plants' gaseous treatment for oxidization and nitration reaction that perhaps acts as exogenous reactive oxygen species (ROS) and reactive nitrogen species (RNS) stimuli in plants. Reported reactivity on the N_2O_5 in plasma chemistries [5-7] supports its potential for agriculture applications and it is recently unveiled that the air plasma generated N_2O_5 gas exposure to *Arabidopsis thaliana* can induce plant disease resistance by selectively generated N_2O_5 gas exposure [8].

Nitrogen trioxide (NO_3) is a radial with the same highest oxidation number of nitrogen +5, thus selective generation of NO_3 radical synthesized from air, not yet performed, could also be an attractive plasma application which can induce variety of oxidation and nitrating reactions.

The NO_3 radical in the density ranged for reaction process and measurement scheme for plasma generated NO_3 have yet been well-established, because high reactivity of NO_3 radical coincides with unstable manor of the species. NO_3 selective generation from air enables to conduct plant response experiments and to utilized for new reaction processes. The focus of this study is specifically dedicated for establishment of measurement technique of the NO_3 radical generated by the atmospheric pressure plasma as the first step.

Broadband cavity enhanced absorption spectroscopy (BB-CEAS) is a well-established scheme in atmospheric chemistry to measure minor reactants in atmosphere [9] and it is known that there is an absorption peak without photo dissociation in red at around 662 nm. BB-CEAS requires estimation of optical cavity loss spectrum resulted from mirrors and windows, which directly affect the effective optical path length and NO_2 is a known reference gas to obtain the optical cavity characteristics. In this abstract, preliminary measurement for plasma generated NO_2 is presented to demonstrate BB-CEAS technique at around 420 nm near the NO_2 absorption peak. This in turn leads to measurement wavelength at 662 nm after the cavity correction around 662 nm.

2. Experimental setup and results

A schematic diagram of the newly developed BB-CEAS is shown in Fig. 1. A blue LED with a peak wavelength around 420 nm was transmitted through two plano-convex lenses for collimation, relayed to the plano-concave mirrors with 100 mm focal length composing the optical cavity. The transmitted light through the optical cavity is focused to an entrance slit of monochromator with a single plano-convex lens.

The gas cell was placed within the optical cavity, whose gaseous path length is 100 mm capped with quartz windows at both ends. A PMT (Photomultiplier Tube) and a high-speed transimpedance preamplifier are equipped with the monochromator to detect weak transmitted light through the cavity. After some efforts in light collection, single photon counting events becomes visible on oscilloscope. The number of the pulses were counted with a 32 bit resolution comparator-counter circuit without pre-scaler. Measurements were conducted at every specified wavelength with a motorized monochromator and the counter and the pulsed LED light are synchronized to subtract dark counts. Measurements are repeated with or without measurement gas sample in the gas cell with 0.1 nm intervals operated with Labview. The absorbance of NO_2 to air was calculated by Lambert-Beer law.

Using our selective N_2O_5 generator [3], we generated a mixture of NO_2 and NO. Both densities are measured with FT-IR absorption spectroscopy. The density of NO_2 produced at this time was controlled about 2.9×10^{15} molecule/cm^3. The N_2O_5 generator is important for the production of NO_3, whose reaction process relying on N_2O_5 dissociation. This scheme enables both experimental evaluation of the mirror reflectivity with NO_2 and NO_3 generation experiment with the exactly same setup. Selectively produced NO_2 was supplied to the gas cell, and the transmitted light intensity was compared with that of air. This calibration would also be possible with a compressed NO_2 gas cylinder if proper toxic gas equipment is possessed.

Figure 2(a) shows the transmitted light spectrum composed with the scanning monochromator. Multiple peaks, in spite of monochromatic LED input, indicates success in constructing an optical cavity. The transmitted through NO_2 was less than half of the light intensity transmitted through air at the wavelengths where the light intensity peaked (see Fig. 2(a)). This indicates clear optical absorbance in the gas cell. Considering the gas cell length of 10 cm, the absorption cross section ~ 10^{-19} cm^2/ molecule, and the density of 2.9×10^{15} molecule/cm^3, the optical absorption is clearly enhanced by the optical cavity.

Figure 2(b) shows the calculated absorption spectrum in comparison with the absorption cross section. The absorption spectrum was not exactly fitted with the absorption cross section because of the spectral response of the reflectivity of the cavity mirror as shown in Fig. 2(b). Estimated reflectance of the mirrors was approximately 97% in the given wave length range, expected around 99.5%. This is likely the additional loss could be due to the quartz windows for the gas cell.

3. Conclusion

The optical absorption of NO_2 generated by atmospheric pressure plasma generation was observed by the BB-CEAS method using LED as a light source and an open cavity with mirrors exposed to the atmosphere. The optical absorption of NO_2 generated by atmospheric pressure plasma was clearly observed using the BB-CEAS method. Further development toward NO_3 measurement will be reported in the poster.

Acknowledgements

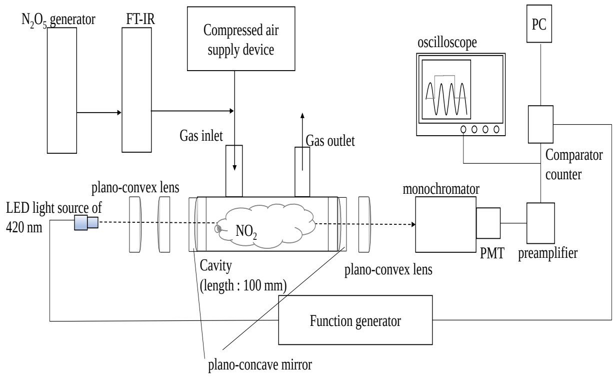

Fig. 1. The experimental setup for absorption spectroscopy.visible BB-CEAS

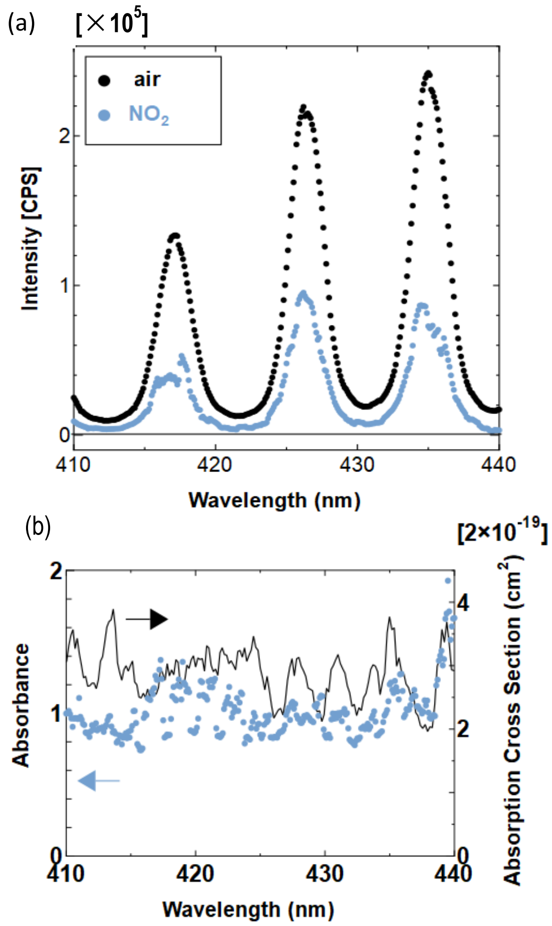

Fig. 2. (a) Absorption spectra and (b) absorption cross section of NO_2[10].

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