Diagnose of Air Quality by Laser Sensing Technique

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To know the air quality of the urban atmosphere, precise measurement of key species is essentially important such as NO_x and VOCs because they are very reactive and some of them are toxic. NO_x indicates combination of NO and NO₂ molecules. Exhaust of combustion mainly contains NO but it is easily oxidized by either ozone or peroxy radicals in the atmosphere into NO₂. Resultant NO₂ is again converted to NO in the photolysis of solar UV. Thus, NO and NO₂ achieve chemical equilibrium within a couple of minutes in daytime atmosphere. Selective measurement of NO₂ is suffered from chemical interference when conversion technique to NO is applied. Therefore, direct measurement of NO₂ is needed such as optical absorption and laser induced fluorescence (LIF) techniques. Although optical absorption technique does not need calibration process but sensitivity is not enough for lower concentration. Thus, we applied LIF technique for detecting NO_x family molecules such as NO, NO₂, NO₃, and N₂O₅. We present herein instrumentation for both NO₂ and NO₃ sensors using pulsed laser excitation. We used an SHG of DPSS Nd:YVO₄ laser and tunable dye laser pumped by it to measure NO₂ and NO₃, respectively. The detection limits of radical sensors are 2 ppt for NO₂ and 7 ppt for NO₃ under some practical conditions. Using this instrument we measured N₂O₅ in sub-urban air of Tokyo. Using chemical model analysis we assessed heterogeneous loss processes of N₂O₅ on the aerosol surface and discussed chemical fate of NO_x emitted in urban atmosphere. Photochemical oxidant formation is becoming great concern as revival issue from 1970's. To investigate photochemical ozone formation process in the atmosphere, HO_x radicals, OH, HO₂, and RO₂ radicals, investigation is important as well as NO_x measurements and great efforts are paid for detection of such radicals using either chemical ionization mass spectrometry or spectroscopic methods such as LIF. In addition to the information of HO_x radicals, reactive VOCs measurements are also necessary for evaluate air quality. However, kind of VOCs existing in the urban atmosphere is believed to be more than 500. Individual measurements of chemical species are not practical to cover such a large number of molecules. Thus, we proposed to measure OH reactivity in the atmosphere and assess the air quality using OH reactivity as an index of pollution or photochemical activity. We present here the developed technique how to measure OH reactivity in the real atmosphere. We conducted a couple of field expedition using this technique and show some of the results.

Key Words: Air quality, LIF, Radicals, OH reactivity, Nitrogen oxides

1. Introduction

Advancement of laser technologies made it possible to measure the atmospheric constituents of trace levels. In order to investigate the phenomena of global change in the atmosphere such as ozone depletion, global warming, acidification of the atmosphere, and photochemical oxidant increase, observations of key chemical species are essential, because in the most of the case, chemical species play key roles and couple together such issues. However, it is not easy to measure either reactive or effective species precisely. The points are sensitivity, selectivity, time and space resolutions. Judging from these requirements laser sensing technique is ideal for atmospheric applications. Concerning specific measurements absorption, fluorescence, and ionization

techniques are proposed and extensively applied. To use prominent character of low beam diversion and high spectral resolution, long path absorption technique especially, differential optical absorption spectroscopy (DOAS) is employed to measure trace gases. This technique has advantage that it does not need calibration and provides average concentration along with optical pass. Ionization techniques usually combine mass spectrometry are coupled by laser ionization technique to measure specific volatile organic compounds (VOC) and radical species such as OH and HO₂ radicals. Indeed there are a lot of advantage for this technique such as ultra high sensitivity, and high selectivity. However, due to heavy mass-spec and high consumption of electricity it is not easy for atmospheric application especially

Fig. 1 Reaction mechanism in the urban atmosphere.

in the point of view of portability. Laser induced fluorescence (LIF) technique is also promising technique for ultra low abundant reactive species such as OH, NO, NO₂, Cl, Br, CO, PAHs, and other molecules.¹⁾

To know the air quality of the urban atmosphere, precise measurement of key species is essentially important such as reactive nitrogen oxides NO_y (NO, NO₂, NO₃ and N₂O₅) and HO_x (OH, HO₂, and RO₂) as shown in Fig.1.²⁾ HO_x radicals are extremely important in daytime chemistry. OH radicals react almost all trace species except some halogenated species and carbon dioxides. Either HO₂ or organic peroxy radicals (RO₂) is formed by the OH reaction of carbon monoxide or VOC. These peroxy radicals react with NO forming NO₂ and OH radical is finally reformed. Formed NO₂ is reconverted to NO with ozone formation. This is so called photochemical ozone formation mechanism. VOC and CO are considered as fuel and NO_x as catalyzer to accelerate radical chain cycle. On the contrary, NO₃ and N₂O₅ play key role in acidification of the nighttime atmosphere. Therefore, vigorous efforts were paid for the detections of NO_y and HO_x radicals developed by LIF technique.

2. OH reactivity measurements

Indeed, information of concentration of each reactive VOCs is important in order to diagnose the air quality, it is impossible to observe full set of VOC in practice. There exists more than 500 kinds of VOCs which react with OH radical in the atmosphere.³⁾ Individual measurements of chemical species are not practical to cover such large number of molecules. Thus, we proposed to measure OH reactivity in the atmosphere and assess the air quality using OH reactivity as an index of pollution or photochemical activity. To realize this we developed an instrument to measure a lifetime of OH radical in ambient air by laser-induced pump and probe technique as shown in Fig. 2. OH radicals are generated in the photolysis of ozone by 266 nm laser.

Fig. 2 Pump and probe instrument for OH reactivity measurement.

Decay of resultant OH is monitored by LIF-FAGE technique using 308 nm laser.⁴⁾ Figure 3 shows typical time profiles of OH radicals. OH temporal profile of zero air (gray curves) after 266-nm pulse excitation shows two decay components. Faster decay may reflect thermal expansion process due to photolysis laser and slower one shows diffusion process. Both are assigned as physical processes.

In case of ambient air slower decay becomes faster due to chemical reaction while faster decay does not change. From the analysis of these slower decay rates, OH reactivity is available. Total OH reactivity which is inverse of lifetime was measured in the ambient air in Tokyo using the developed instrument in order to test the utility of the instrument. It demonstrated that the instrument is practically running well and we succeeded to observe OH reactivity through the year in

Fig. 3 Examples of the measured OH decay profile of zero air (solid line) and ambient air (gray line). (a): linear scale. (b): logarithmic scale.

Tokyo.

We have successfully applied this instrument for real atmospheric observation in Tokyo as well as simultaneous measurements of VOCs by GC technique and proton-transfer mass spectrometry.⁵⁾ We compared OH reactivities determined by pump-probe technique and VOC analysis. In case of VOC analysis we considered more than 70 species. Interestingly in spring and summer, we found a lot of discrepancy more than 30 % of OH reactivity between measured and calculated one. However in winter both data were fairly agreed with each other as seen in Fig. 4(b). From these observation, we have learnt that there exist still gap between our knowledge and real situation in the atmosphere from view point of reactive species and that OH reactivity is considered as good index for photochemical activity instead of each VOC analysis.⁶⁾

3. Nitrogen oxides measurements

Exhaust of combustion mainly contains NO but it is easily oxidized by either ozone or peroxy radicals in the atmosphere into NO₂. Resultant NO₂ is again converted to NO in the photolysis of solar UV. Thus, NO and NO₂ achieve chemical equilibrium within a couple of minutes in daytime atmosphere. Selective measurement of NO₂ is suffered from chemical interference when conversion technique to NO is applied. Therefore, direct measurement of NO₂ is needed such as optical absorption and laser induced fluorescence (LIF) techniques. Although optical absorption technique does not need calibration process but sensitivity is not enough for lower concentration. Thus, we applied LIF technique for detecting NOx family molecules such as NO, NO₂, NO₃, and N₂O₅.

We present herein instrumentation for both NO₂ and NO₃ sensors using pulsed laser excitation. We used an SHG of DPSS Nd:YVO₄ laser and a tunable dye laser pumped by the SHG of Nd:YVO₄ laser to measure NO₂ and NO₃, respectively.

Fig. 4 Observed (open circle) and calculated (gray line) OH reactivities obtained in sub-urban Tokyo in summer (a) and winter (b).

Fig. 5 Instrumental set-up for atmospheric N₂O₅ measurement with NO₃ sensor using heater converter.

Since NO₂ molecule has broad absorption band in visible wavelength, second harmonic wave length is possible to excite it. On the contrary to excite NO₃ radicals, it is necessary to tune laser wavelength for the absorption maximum of NO₃ radicals. NO₃ has characteristic absorption band in both 623 and 662 nm. From several reasons we selected 623 nm for the excitation of NO₃ radicals. The detection limits of radical sensors are 2 ppt for NO₂ and 7 ppt for NO₃ under some practical conditions.^{7,8)}

NO₃ react further to NO₂ to form N₂O₅ in nocturnal atmosphere. N₂O₅ is well known to up-taken on the surface of aerosols to form nitric acid. This is almost irreversible reaction. Thus, this process is considered as a major sink of NOx in night time. Therefore, N₂O₅ observation in night time is essentially important to discuss dynamical behavior of NOx in the atmosphere. However, since it difficultly N₂O₅ was hardly observed in the atmosphere up to recently. N₂O₅ easily dissociate into NO₂ and NO₃ using heater tube.

Thus, N₂O₅ observation becomes available if atmospheric NO₃ is able to measure. We applied NO₃ sensor to measure N₂O₅ in sub-urban air of Tokyo using thermal dissociation technique. This was the first attempt to determine concentration of N₂O₅ using LIF technique.⁹⁾

We carried out field experiment of N₂O₅ on the top of the building of our campus where is located about 30 km toward west from the center of Tokyo. Observational periods are

between July and August on 2005, February on 2006, July and August on 2006. Ozone, CO, NOx, VOCs are simultaneously observed in addition to N₂O₅. The obtained concentration of N₂O₅ in night time winter was typically a couple of hundred ppt. N₂O₅ concentration sometime exceeds 1 ppb during heavily polluted episode with high ozone and NOx.

N₂O₅ has quite strong temperature dependence for the dissociation. N₂O₅ concentration in winter was systematically higher than that in summer. It is expected to be lower abundant in summer but it sustained with a couple of hundred ppt so far. Using reactions from (1) through (9) and kinetic data from JPL 2002, steady state concentration of N₂O₅ was obtained and plotted in Fig. 5 as gray lines. Using box model we estimated loss process of N₂O₅. VOCs reaction with NO₃

might be predominant for the loss of NOx in nighttime summer, while heterogeneous reaction of N₂O₅ on the surface of aerosols is important in winter. NOx removal via either NO₃ or N₂O₅ process is determined to be 2.0 and 2.3 ppbv/night in the summer and winter, respectively. Assuming daytime concentration of OH is 0.04 and 0.02 ppt in summer and winter, respectively, estimated NOx loss by OH reaction is listed in table 2. Nighttime loss of NOx in winter via either NO₃ or N₂O₅ route is comparable with NO₂+OH reaction in daytime. N₂O₅ formation requires two molecules of NOx. Thus, this night time loss process via either NO₃ or N₂O₅ is important in urban / sub-urban atmosphere.

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Table 1 Loss rates of N₂O₅ and NO₃

	night hours	Removal processe	Reactivity /s ⁻¹	Loss rate / 10 ⁵ cm ⁻³ s ⁻¹	NOx loss /ppb night ⁻¹
summer	10	Via N ₂ O ₅	1.2 x 10 ⁻⁴	2.0	2.0
		Via NO ₃	1.3 x 10 ⁻¹	15	
winter	14	Via N ₂ O ₅	1.2 x 10 ⁻⁴	15	2.3
		Via NO ₃	1.2 x 10 ⁻⁴	1.4	

Table 2 NOx loss due to OH radicals

	[OH] /pptv	Loss rate / 10 ⁵ cm ⁻³ s ⁻¹	Day hours	NOx loss /ppb day ⁻¹
summer	0.04	60	14	15.5
winter	0.02	30	10	4.3