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In situ detection of reactive nitrogen species using thermal dissociation laser-induced fluorescence in Tokyo

Hiroyuki Suzuki[1*], Tomoki Nakayama[2], Kenshi Takahashi[3], Kenichi Tonokura[4], Yutaka Matsumi[2]

[1]Graduate school of science, Nagoya Univ., [2]STEL, Nagoya Univ., [3]RISH, Kyoto Univ., [4]ESC, Univ. of Tokyo

In the troposphere, nitrogen oxides (NOx=NO and NO_2) are mainly emitted from artificial activities such as burning fossil fuel. NOx reacts with OH and RO_2radicals in the troposphere and is converted to reactive nitrogen species, such as peroxy nitrates, alkyl nitrates, and HNO_3. These compounds have an effect on the global distribution of NOx in the troposphere because insoluble compounds, such as PAN, can be transported over long distances and then release NOx again by thermal decomposition and photochemical reaction. $HNO_3$is one of the major sinks of nitrogen oxides to control the lifetime of it. For these reasons, it is necessary to know the concentrations of not only NOx but also these reactive nitrogen species in the troposphere. However, most of the measurements, which are used today to detect these compounds, have the potential for sample loss because of using a filter or gas chromatography for collection, and continuous rapid measurement is difficult.
In this work, we have developed a four channel thermal dissociation laser-induced fluorescent (TD-LIF) instrument to measure NO_2, total peroxy nitrates, total alkyl nitrates, and HNO_3separately in real time[1]. These compounds thermally dissociate to yield NO_2at different temperature. An ambient sample flows rapidly through three ovens where dissociations of peroxy nitrates, alkyl nitrates, and $HNO_3$to NO_2occur. The four different temperatures, 25 (room temperature), 200, 430, and 650C were used to observe NO_2, peroxy nitrates, alkyl nitrates, and HNO_3, separately. After passing through the ovens, the $NO_2$was detected using LIF system at 445 nm. The NO_2LIF signal is the sum of the NO_2contained in all compounds that dissociated at or below the oven temperature, and the difference between the NO_2observed in separate channels is associated with a specific class of compounds. The TD-LIF system is expected to be able to identify the interferences of reactive nitrogen species, which cause the overestimation of NO_2in the chemiluminescence technique using a molybdenum converter (Mo-CL) [2].
The instrument was applied to the field measurements in central Tokyo during summer 2009 . In this presentation, the performance of the TD-LIF instrument and the results of the field measurements will be reported. Additionally, we will discuss the interference of reactive nitrogen species in the NO_2concentration determinations by the Mo-CL technique by comparing NO_2 concentrations measured using the TD-LIF and Mo-CL systems.

References
[1] D. A. Day et al., J. Geophys. Res., 107 (2002), 4046, doi:10.1029/2001JD000779.
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