Exploration for Dynamic State of Peroxy Radicals in the Atmosphere -Establishment of HO_2 reactivity Measuring Method with Laser Spectroscopy-

Tomihide Fujii

Key Words: Tropospheric chemistry, HOx cycle, Peroxy radicals, Unknown loss process, Laser spectroscopy HO_2 reactivity, Ambient air measurement, Chamber experiment, Heterogeneous reaction, Uptake coefficient

1. INTRODUCTION

A number of studies have implied the existence of unknown reaction processes in HOx cycle, which is an important chain reaction system in oxidation process in the troposphere. Particularly, behavior of peroxy radicals is still incompletely understood, while heterogeneous reaction with aerosols has been suggested as possible loss process. As the first step for understanding the behavior of peroxy radicals, our laboratory has started to develop a total HO_2 reactivity measurement device with laser spectroscopy, which directly quantifies loss process of HO_2 radical. The goals of this study are to reveal unknown reaction process of HO_2 radical with this device, and to understand the device characteristics for establishment of precise measuring method.

2. PRINCIPLE OF MEASUREMENT

The basic concept of this device is to trace decreasing profile of generated HO_2 radical, and then to determine total HO_2 reactivity k'_{total}, which corresponds to reciprocal of lifetime of HO_2 radical, from decreasing rate. First, 266nm pulse laser radiation into sample gas added with O_3 and high-level CO by 0.5Hz makes HO_2 radical, which declines as reaction goes on in the reaction cell. Then, sample gas is introduced to low-pressure LIF cell, and successive high-level NO addition re-converts HO_2 radical into OH radical. Finally, LIF technique with 308nm laser by 10kHz chases the decreasing profile of OH radical followed by exponential fitting gives decreasing rate as k'_{total}. However, background HO_2 reactivity $k'_{baseline}$ mainly due to wall loss should be subtracted for determination of effective k'_{total}. By comparing k'_{total} with calculated HO_2 reactivity k'_{calc} from individually measured NO_2 concentration, we can quantitatively evaluate unknown loss process of sample gas.

3. RESULTS AND DISCUSSION

(1) June-2017 Ambient air measurement at Kyodo University Yoshida campus

Alternative calibration method, which directly connects sensitivities between NO_2 monitor and total HO_2 reactivity measurement device, was proposed. In three-days-measurement of ambient air, a big discrepancy between k'_{total} and k'_{calc} ~$0.4s^{-1}$ was observed, which couldn't be explained by any of RH, temperature and k'_{calc}.

(2) July-2017 Smog chamber experiment at National Institute of Environmental Studies

Time transition of k'_{total} and k'_{calc} was measured for gas sampled from smog chamber, where OH-initiated photochemical reaction was proceeding with VOCs (isoprene, α-pinene and m-xylene). Increase of $k'_{baseline}$ was observed as device characteristics. In addition, the world first measurement of k'_{total} for the system where VOC photochemical reaction proceeds was achieved, and the value was successfully explained by k'_{calc} with uncertainty. In the experiment with α-pinene, the upper limit of uptake coefficient was estimated as ~0.5.

(3) Investigation of device characteristics and proposal of improving method

Several hypotheses for device characteristics were tested. Huge fluctuation of $k'_{baseline}$ was observed with less frequent scan of detection laser wavelength, which was improved by hourly scan. Additionally, fluctuation of $k'_{baseline}$ showed good correlation with extrapolated HO_2 radical initial concentration $[HO_2]_0$ext, which successfully explained the result of (1). Furthermore, 0.12-0.5s was proposed as a proper fitting range.

(4) August-2017 Ambient air measurement at National Institute of Environmental Studies

In 1week measurement, k'_{total} showed lower value than k'_{calc}, which was implied to be interruption by ambient O_3 leading to increase of $k'_{baseline}$ and decrease of $[HO_2]_0$ext. Information about heterogeneous reaction wasn't obtained since tube wall caused great loss of aerosol. Meanwhile, k'_{total} modified by interruption factor was successfully explained by k'_{calc} within uncertainty ~$0.03s^{-1}$, which is the world first precise measurement.

(5) December-2017 Ambient air measurement at Kyodo University Yoshida campus

1day ambient air measurement was conducted with individual test for aerosol loss ratio in the system. The value of k'_{total} and k'_{calc} were in a good agreement within a relatively big uncertainty ~$0.12s^{-1}$. Co-measured aerosol total surface area density showed a big value, which gave the upper limit of uptake coefficient for the heterogeneous process in ambient air as γ ~0.16 with uncertainty at 0.32 for the first time in the world.