## First direct detection of OH radicals photodesorbed from liquid organic surface by using laser-induced fluorescence technique

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The 5th assessment report of the Intergovernmental Panel on Climate Change provides that aerosols contribute the largest uncertainty of the Earth's changing energy budget and this should be evaluated in order to understand climate change [1]. Especially, interfacial reactions at atmospheric aerosols and sea surface are of increasing importance because these interfaces occupy a great deal of reaction fields on the Earth. Recently, photochemical reactions of surfactant organic compounds such as fatty acids that cover the top surfaces of aerosols and sea have attracted much attention. For example, it had been believed that gaseous and liquid nonanoic acids (NA) do not absorb ultraviolet – visible radiation (> 295 nm). However, Rossignol *et al.* found that NA at the air-water interface absorbs the ultraviolet, and then complex organic compounds were produced, which eventually act as aerosol precursors [2]. Although the photochemical reaction mechanism of NA is still poorly understood, it has been suggested that OH radicals are a primary photoproduct in the ultraviolet photolysis of NA at the interface [2, 3].

$$\text{CH}_3(\text{CH}_2)_7\text{COOH} + h\nu (> 295 \text{ nm}) \rightarrow \text{CH}_3(\text{CH}_2)_7\text{CO} + \text{OH}?$$

OH radical is one of the most important chemical species in atmospheric chemistry and quantum yields of OH radical formation are needed to incorporate the interfacial reactions into atmospheric models. However, even direct measurements of desorption of OH radicals in photolysis of liquid NA have not been achieved yet.

We have developed an instrument for direct detection of photodesorbed OH radicals in the ultraviolet photolysis of liquid NA by using laser-induced fluorescence (LIF) technique. Liquid NA was put on a silicon substrate in a low vacuum chamber (1-100 Pa) and irradiated with a pulsed 213 nm Nd:YAG laser. OH radicals desorbed from the NA surface were excited by a second harmonic 282 nm dye laser, and OH-LIF at 315 nm was detected by a photomultiplier tube.

OH  $(X^2\Pi, v = 0) + hv(282 \text{ nm}) \rightarrow \text{OH}(A^2\Sigma, v = 1) \rightarrow \text{OH}(X^2\Pi, v = 1) + hv(315 \text{ nm})$ In order to verify that the detected OH radicals were desorbed from liquid NA surface not formed from gaseous NA, we measured OH-LIF intensities as a function of the delay time between the two lasers, changing a distance between the dye laser and the Si substrate. Moreover, we performed single shot experiments to clarify that OH radicals were originated from parent NA molecules on the liquid surface not from photoproducts.

In the workshop, we will show our new experimental setup for the photolysis of liquid organics and detection of photodesorbed OH radicals using the LIF technique.

## References

- [1] Intergovernmental Panel on Climate Change (IPCC), Fifth Assessment Report (2017).
- [2] Rossignol et al., Science 353, 699 (2016).
- [3] Vaida, Science 353, 650 (2016).

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