Desorption of OH radicals in the ultraviolet photolysis of liquid nonanoic acid using laser-induced fluorescence

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Introduction

Photochemistry of liquid organic interfaces

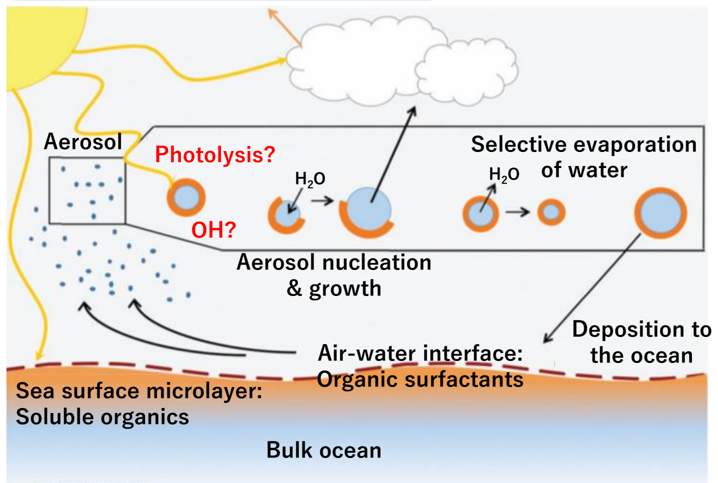


Fig.1 Schematic of the photolysis of organics on the interfaces and aerosol formation [1].

New process of OH radical formation? [2]

→ Dissociation of fatty acid at the air-water interface

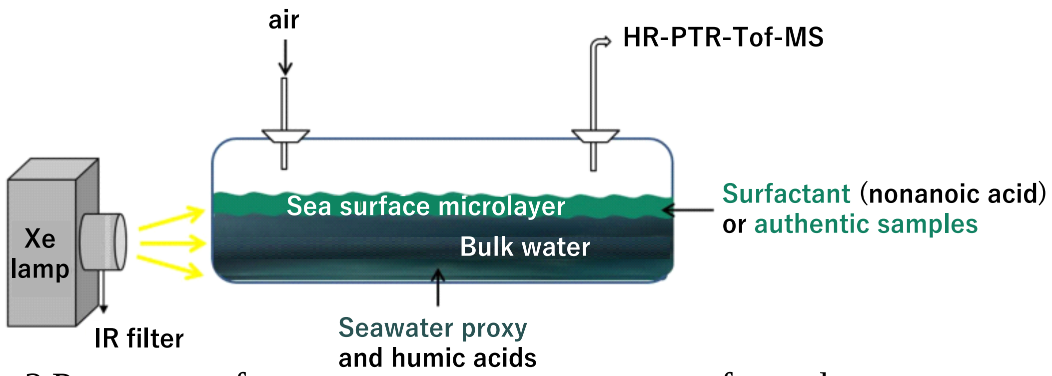


Fig.2 Proton transfer reaction mass spectrometry of gas phase products in photolysis of organics at the air-water interface [3].

Photolysis ❓→ OH radical formation → Aerosol formation

We have conducted

(1) Development of the experimental setup for interfacial photochemistry of liquid organic

(2) Direct detection of OH radicals photodesorbed from liquid nonanoic acid (NA) using laser-induced fluorescence (LIF).

$CH_3(CH_2)_7COOH + h\nu$ (280-330 nm) → $CH_3(CH_2)_7CO$ + OH?

[1] R. J. Rapf *et al.*, Phys. Chem. Chem. Phys. **18**, 20067 (2016).
[2] S. Rossignol *et al.*, Science **353**, 699 (2016). [3] R. Ciuraru *et al.*, Sci. Rep. **5**, 12741 (2015).

Experimental apparatus

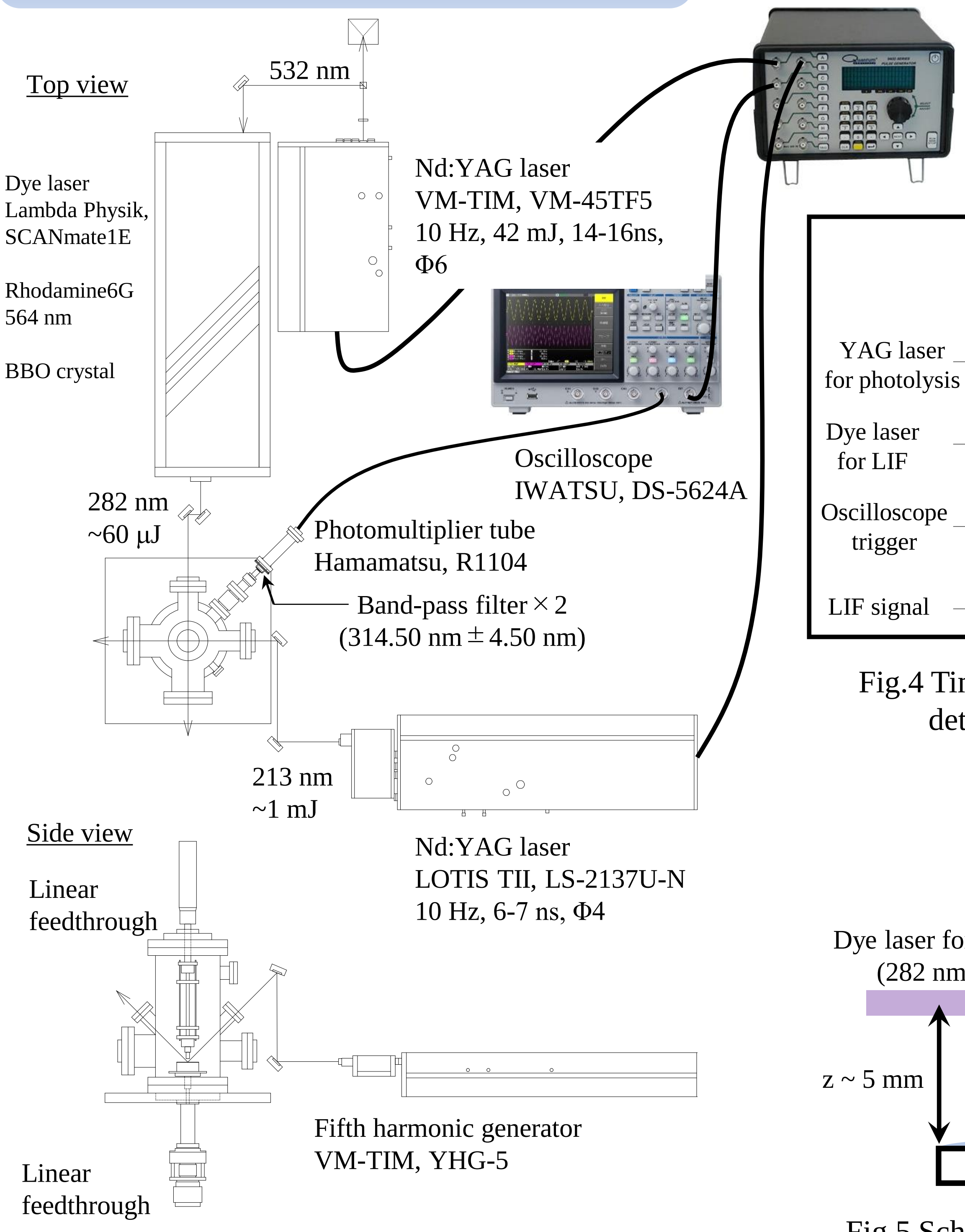


Fig.3 Schematic diagram of the experimental setup.

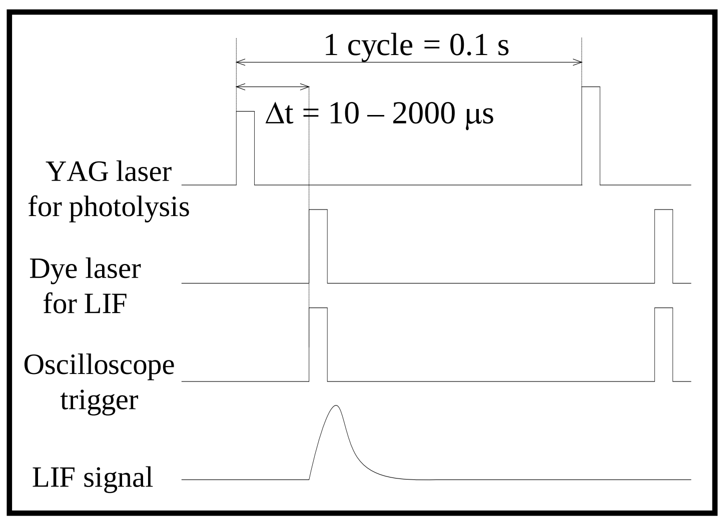


Fig.4 Timing chart of the laser pulses, detection trigger, and LIF signal.

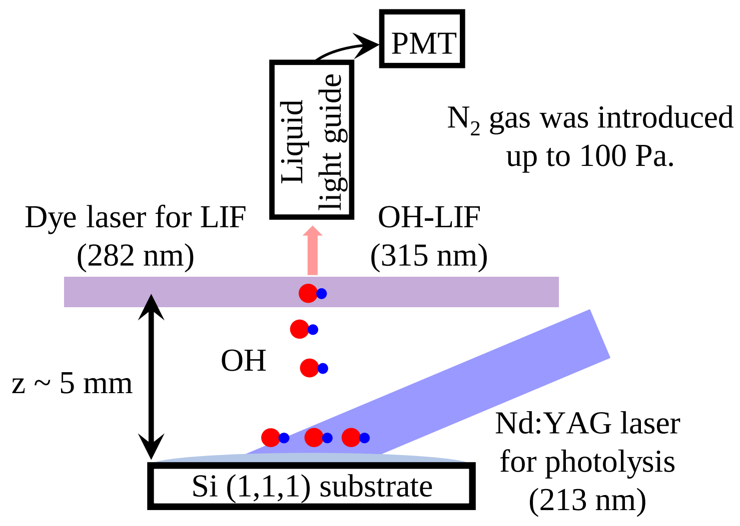
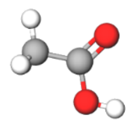


Fig.5 Schematic diagram of laser irradiation to liquid NA and OH detection.

Test of OH-LIF detection using acetic acid (AA) in the gas phase



$CH_3COOH + h\nu$ (213 nm) → CH_3CO + OH

OH ($X\,^2\Pi$, $v = 0$) + $h\nu$(282 nm)

→ OH ($A\,^2\Sigma$, $v = 1$) → OH ($X\,^2\Pi$, $v = 1$) + $h\nu$(315 nm)

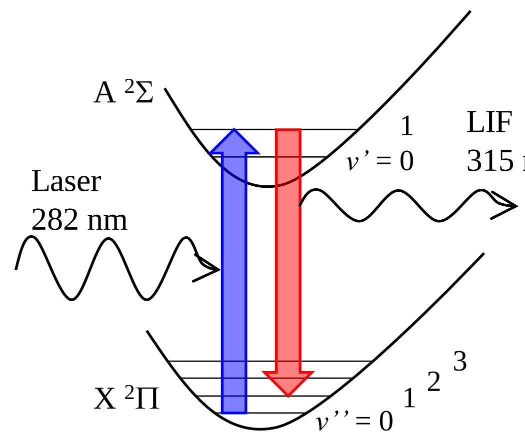


Fig.6 Fluorescence scheme of the excitation to the $v' = 1$ state of OH radicals.

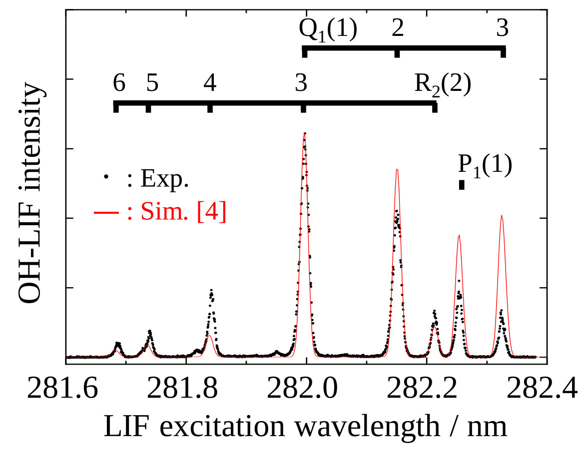


Fig. 7 LIF spectra obtained by 213 nm photolysis of AA and simulation.

[4] J. Luque *et al.*, LIFBASE: database and spectral simulation. SRI Int. Rep. MP **009**, 99 (1999).

Estimation of OH detection sensitivity

$$[\mathrm{OH}]_{\mathrm{photo}} = \sigma^{213}_{\mathrm{abs}}(\mathrm{AA}) \times [\mathrm{AA}] \times F^{213}_{\mathrm{photon}} \times \phi^{213}_{\mathrm{OH}}(\mathrm{AA})$$

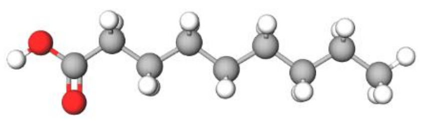
Detection limit of OH ~10^9 cm^{-3}

σ : absorption cross section (1.7e-19 cm²) [5]
[AA] : Number density of AA (~1.4e+15 cm⁻³) [6]
F : Photon flux of laser (~1.4e+13 photons/cm²)
ϕ : Quantum yield for the formation of OH at 213 nm photolysis of AA (~0.6) [6, 7]

[5] J. J. Orlando *et al.*, J. Photochem. Photobiol. A: Chem. **157**, 161 (2003).
[6] D. L. Singleton *et al.*, J. Phys. Chem. **94** 695 (1990).
[7] P. D. Naik *et al.*, J. Photochem. Photobiol. C-Photochem. Rev. **3**, 165 (2003).

Results and discussion

213 nm photolysis of NA



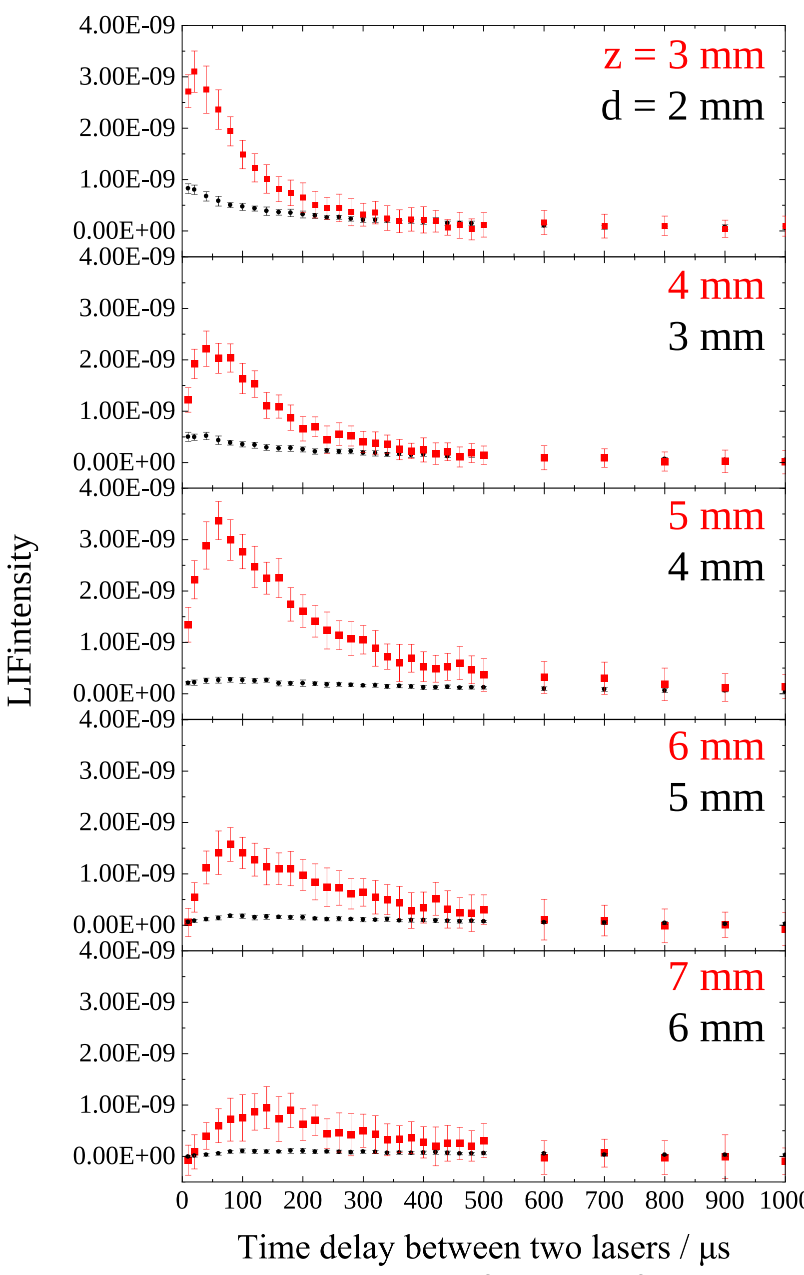
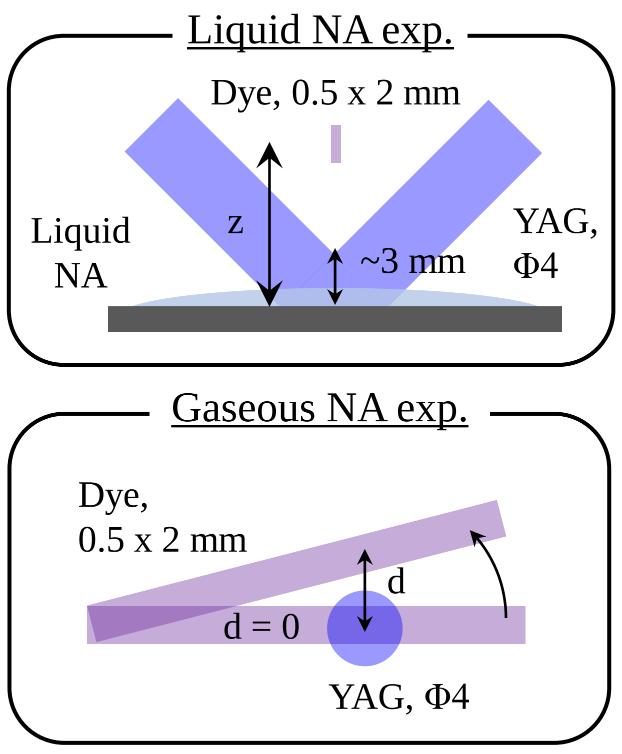


Fig. 8 OH-LIF intensities as a function of the delay time between the two lasers, changing the OH detection point.

Red : Liquid NA exp.
Black : Gaseous NA exp.

※Gaseous NA also exists in the liquid NA experiment due to its high vaper pressure.

Difference between the two curves should be roughly consistent with the contribution of liquid NA interface.



Were detected OH radicals primary photoproducts?

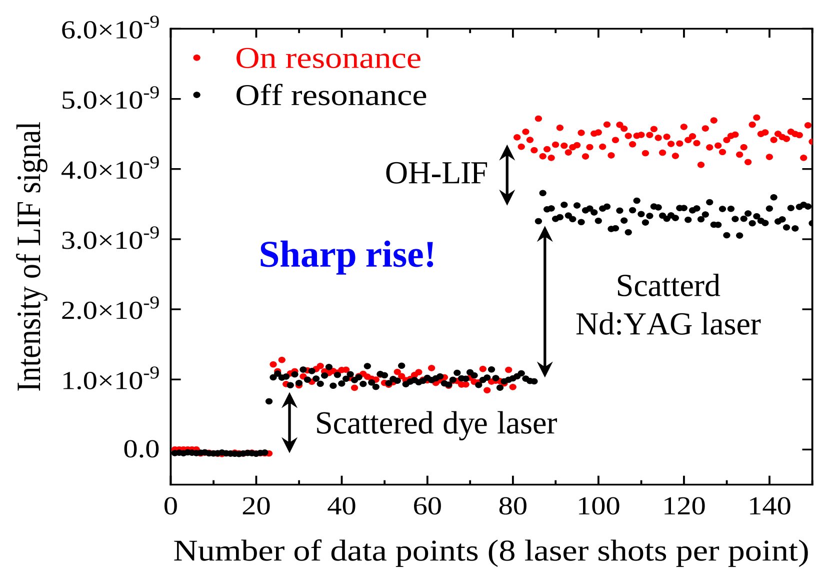
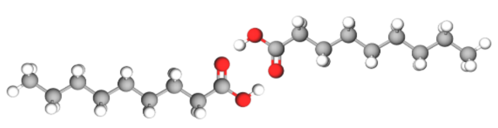


Fig. 9 OH-LIF and scattered laser signal intensities.

Our study demonstrated OH formation in the photolysis of liquid NA, but its yield was small (a few percent of gaseous AA?).

1. Strong hydrogen-bonds form cyclic NA dimers?

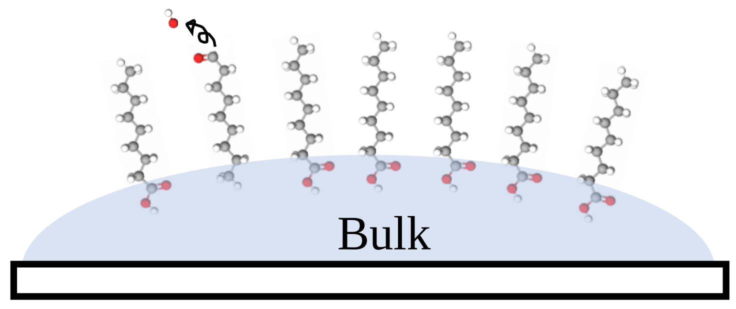


e.g. Quantum yields of OH radicals in 222 nm photolysis of AA [7].

Monomer : 0.546 >> Dimer : 0.038

2. The carboxyl group is directed toward the liquid phase?

(e.g. Interfacial AA [8].)



[8] E. Tyrode *et al.*, J. Phys. Chem. B **109**, 329 (2005).