

## Supporting Information:

# “Sizing” Heterogeneous Chemistry in the Conversion of Gaseous Dimethyl Sulfide to Atmospheric Particles

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**No. of Supporting Pages: 11**

**No. of Supporting Figures: 9**

# SI Appendix

## SI Methods

Experimental conditions were as follows: drying gas flow rate: 12 L min<sup>-1</sup>; drying gas temperature: 340 °C; inlet voltage: ± 3.5 kV relative to ground; fragmentor voltage value: 80 V. Dimethylsulfoxide (> 99.9 %), methanesulfonic acid (> 99.5%) and D<sub>2</sub>O (99.9 %) were purchased from Sigma-Aldrich. Methanesulfinic acid sodium salt (> 95 %) was purchased from Alfa Aesar. HCl (35 % wt. solution), NaOH (10N solution) and sulfuric acid (97 %) were purchased from Nacalai Tesque (Kyoto). All solutions were prepared in purified water (Resistivity ≥ 18.2 MΩ cm at 298 K) from a Millipore Milli-Q water purification system. The pH of the solutions was measured with a calibrated pH meter, Horiba LAQUA F-74, before each experiment.

## R vs Γ

From the definitions of  $f_\alpha$ :

$$f_\alpha (s^{-1}) = \left(\frac{1}{4}\right) \alpha c \left(\frac{S}{V}\right) \quad (\text{E1})$$

$f_{OH} = k_{DMSO+OH} \times [\cdot OH(g)]$ , and  $\Gamma = f_\alpha/f_{OH}$  (see main text), in the absence of anthropogenic  $SO_4^{2-}$  (i.e., only DMS contributes to aerosol nss-sulfate), by assuming that 50% of DMS is oxidized to  $H_2SO_4$  and the rest to  $DMSO(g)$ , of which only a fraction  $\gamma$  is oxidized heterogeneously into MSA and nss-sulfate in a  $R_{het}$  ratio:

$$\gamma = \frac{f_\alpha}{f_\alpha + f_{OH}} = \frac{1}{1 + \frac{1}{\Gamma}} \quad (\text{SE1})$$

we can express  $R$  as a function of  $\gamma$  and  $R_{het}$ , namely:

$$R = \frac{MSA}{nss-SO_4^{2-}} = \frac{0.5 \gamma \left(\frac{R_{het}}{1+R_{het}}\right)}{0.5 + 0.5(1-\gamma) + \frac{0.5 \gamma}{1+R_{het}}} \quad (\text{SE2})$$

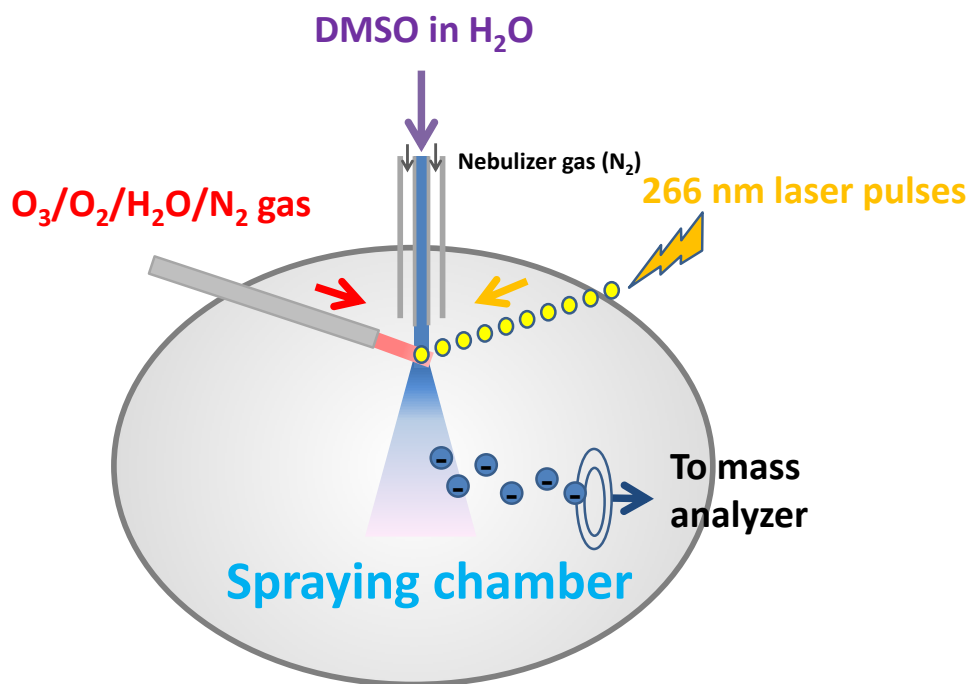


Fig. S1. Schematic diagram of an in-situ measurement of the heterogeneous reaction of  $\cdot\text{OH}(\text{g})$  with  $\text{DMSO}(\text{aq})$ .

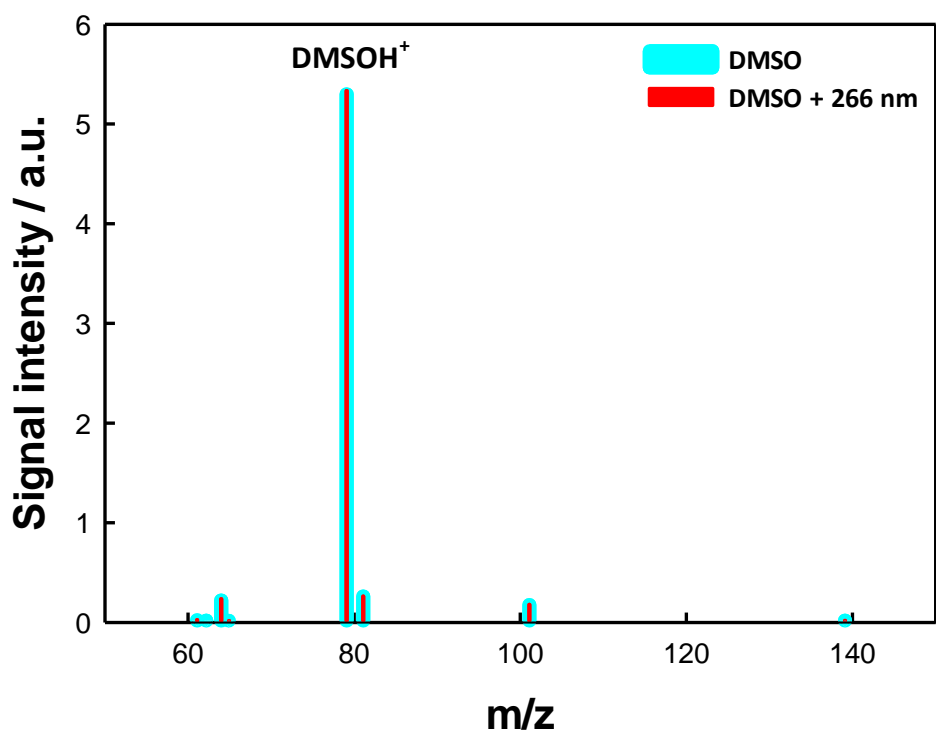


Fig. S2. Positive ion mass spectra of 1 mM DMSO at pH 2.9 in the absence (cyan)/presence (red) of 266 nm laser irradiation ( $40 \text{ mJ pulse}^{-1}$ ) under no  $\text{O}_3(\text{g})$  condition.

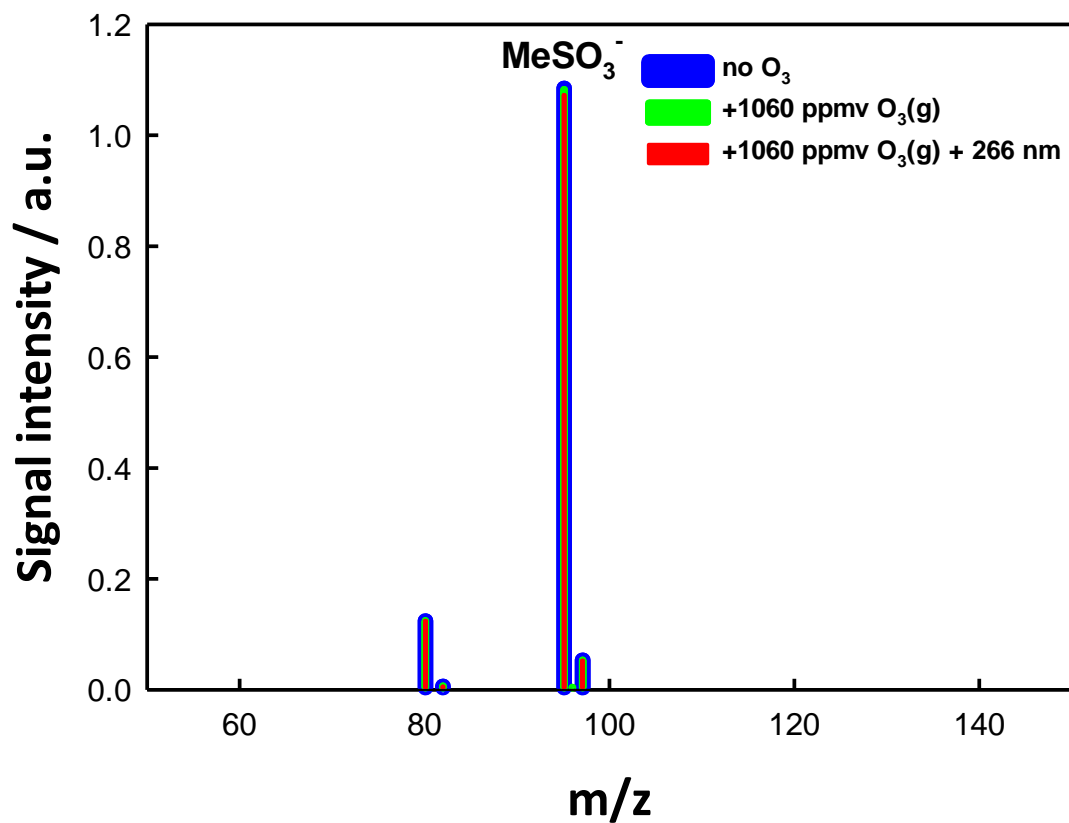


Fig. S3. Negative ion mass spectrum of 1 mM methanesulfonic acid (aq) + O<sub>3</sub>(g) or ·OH(g). Note the inertness of MeSO<sub>3</sub><sup>-</sup> toward a maximum ~ 100 ppmv ·OH(g) exposure (red).

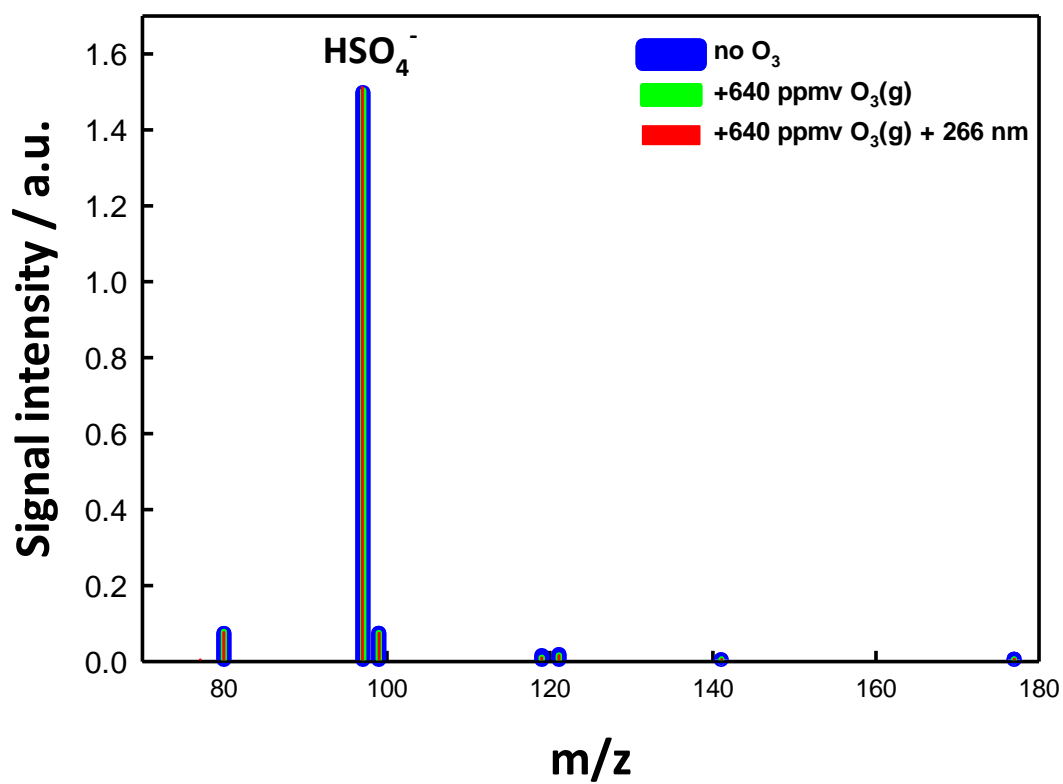


Fig. S4. Negative ion mass spectrum of 1 mM sulfuric acid (aq) + O<sub>3</sub>(g) or ·OH(g). Note the inertness of sulfate/bisulfate toward a maximum ~ 60 ppmv ·OH(g) exposure (red).

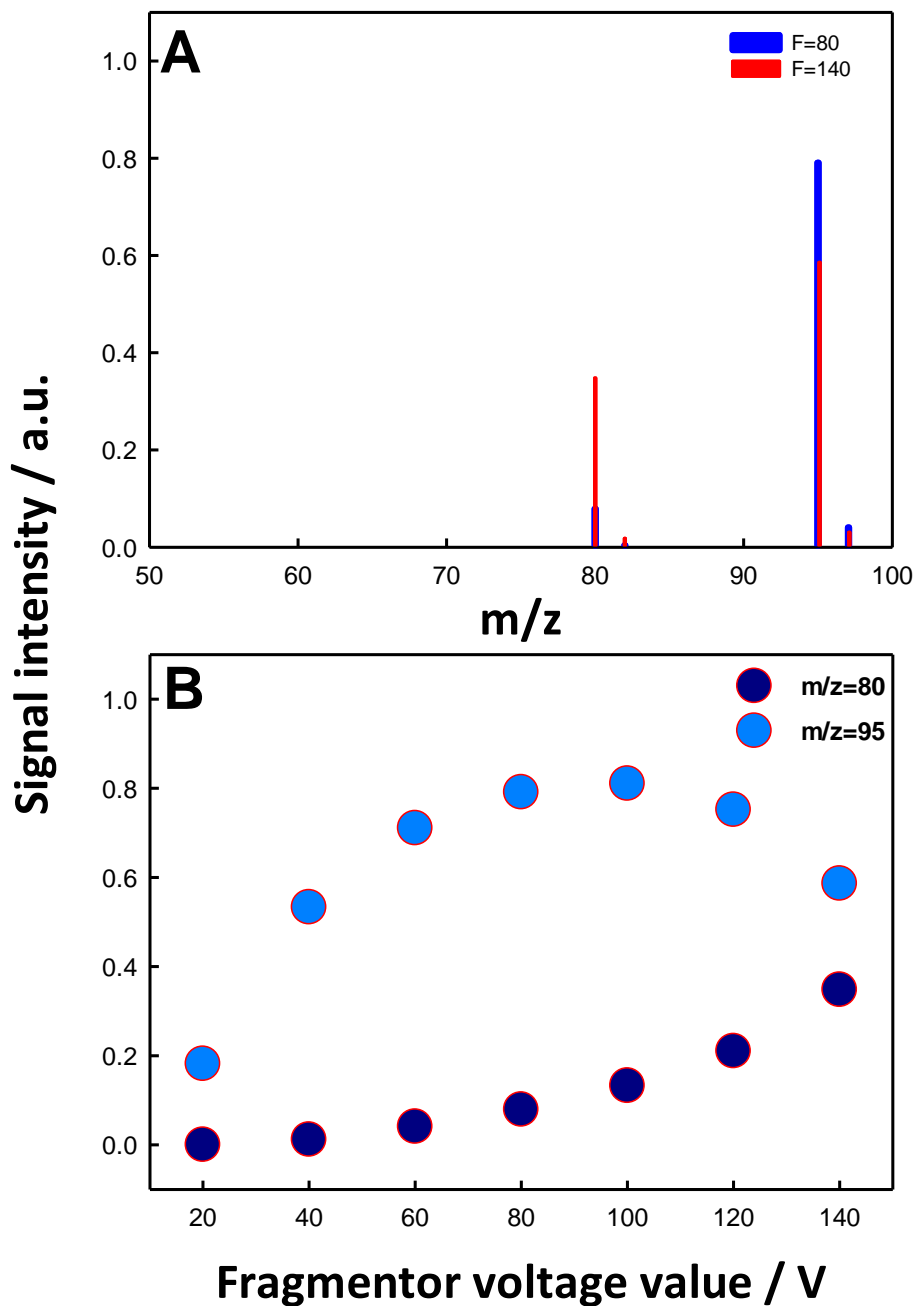


Fig. S5. A) Negative ion mass spectra of 0.1 mM methanesulfonic acid at pH 4.1 in 1 atm and 298 K at fragmentor voltage value 80 V (blue) and 140 V (red). B) Mass spectral signal intensities at  $m/z = 80$  and  $95$  from aqueous 0.1 mM methanesulfonic acid as a function of fragmentor voltage value  $F$ .

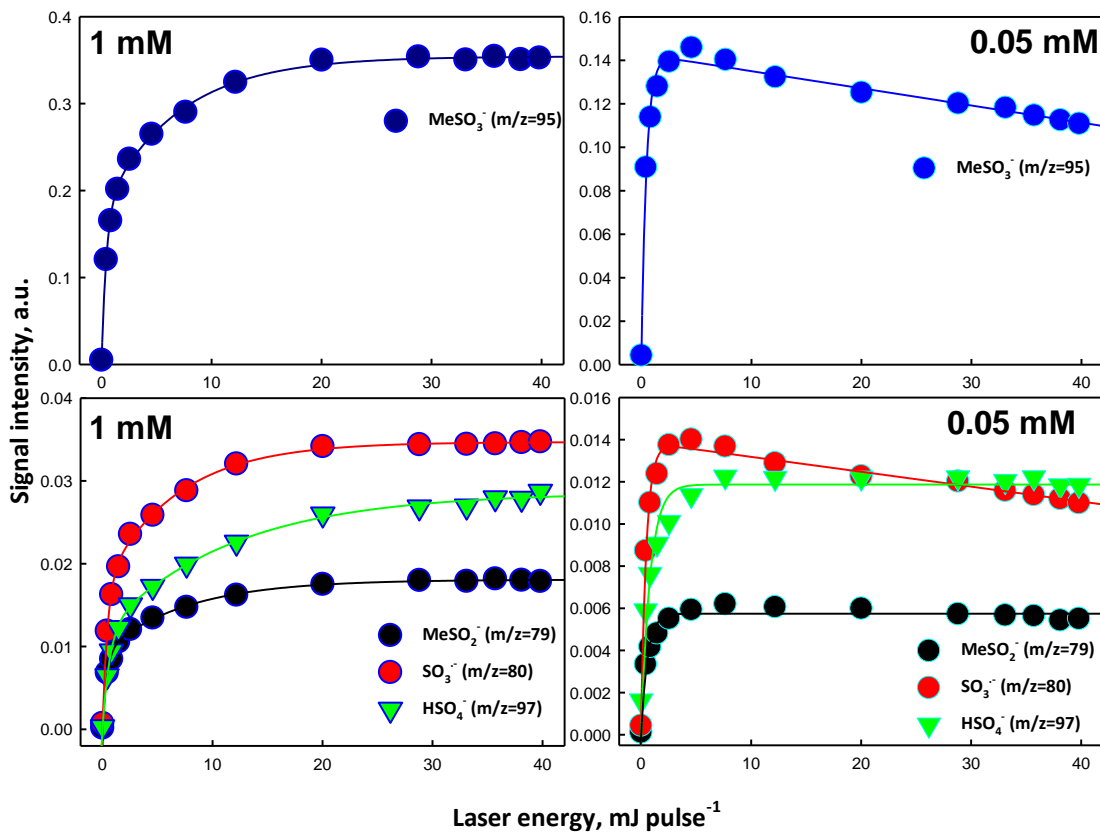


Fig. S6. Electropray mass spectral signal intensities from aqueous 1 mM vs. 0.05 mM DMSO microjets exposed to  $\text{O}_3(\text{g})/\text{O}_2(\text{g})/\text{H}_2\text{O}(\text{g})/\text{N}_2(\text{g})$  mixtures at  $[\text{O}_3(\text{g})] \sim 160$  ppmv irradiated by 266 nm laser beams as a function of laser energy (LE)  $\text{mJ pulse}^{-1}$ . Laser energies ( $x$ -axis) at 0.4 (the lowest value) and 40  $\text{mJ pulse}^{-1}$  (the highest value) correspond to  $[\cdot\text{OH}(\text{g})]_0 \approx 0.2$  and 12.4 ppmv, OH exposure  $\approx 4.9 \times 10^7$  and  $3.1 \times 10^9$  molecules  $\text{cm}^{-3} \text{s}$ , respectively. Lines are regression curves fitted with double-exponential function:  $f = a*(1-\exp(-b*LE))+c*(1-\exp(-d*LE))$



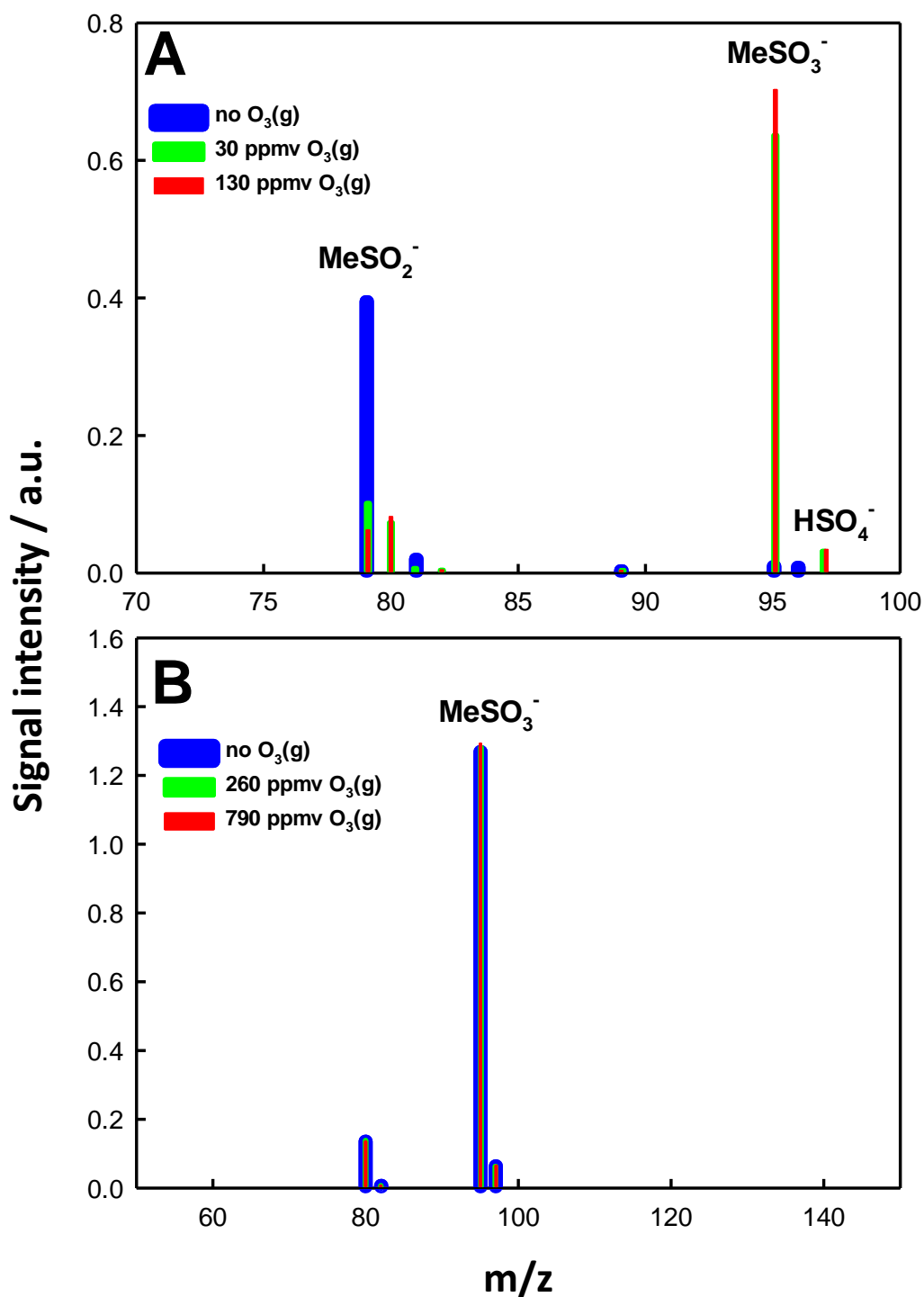


Fig. S7. A) Negative ion mass spectrum of 1.2 mM methanesulfinic acid sodium salt (aq) + O<sub>3</sub>(g), B) Negative ion mass spectrum of 1 mM methanesulfonic acid (aq) + O<sub>3</sub>(g).

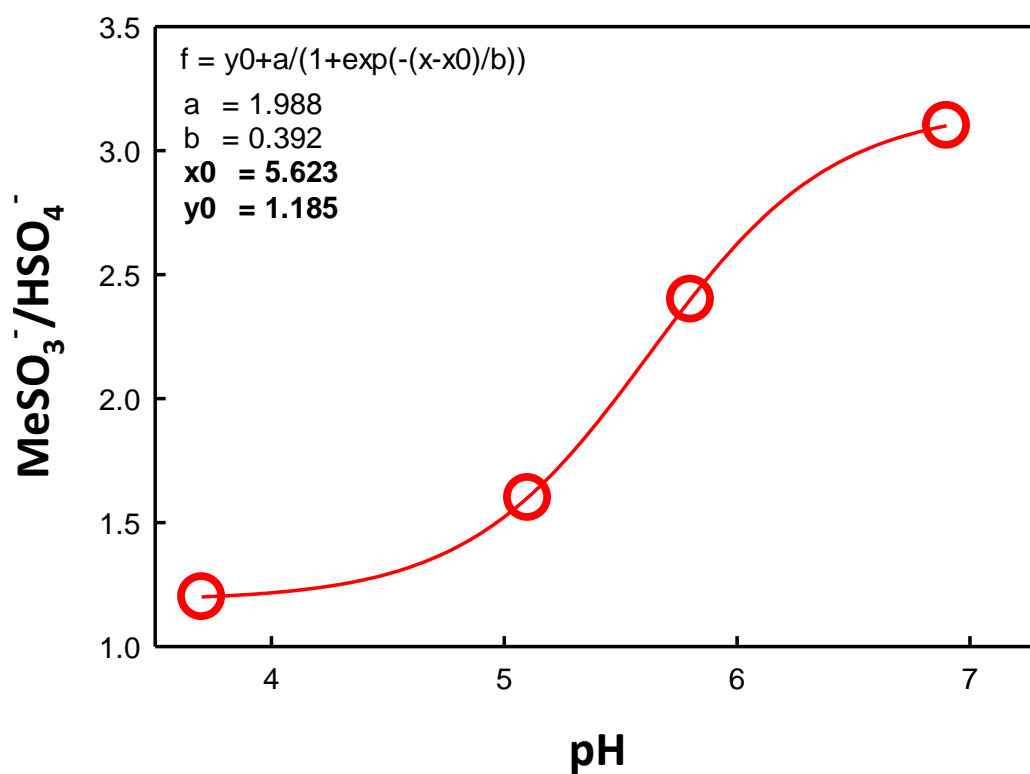


Fig. S8. Relative ES mass spectrometric signal intensity for  $\text{MeSO}_3^-$  vs.  $\text{HSO}_4^-$  from equimolar solutions of ( $\text{MeSO}_3\text{H}$  and  $\text{HSO}_4\text{H}$ ) as a function of bulk pH.

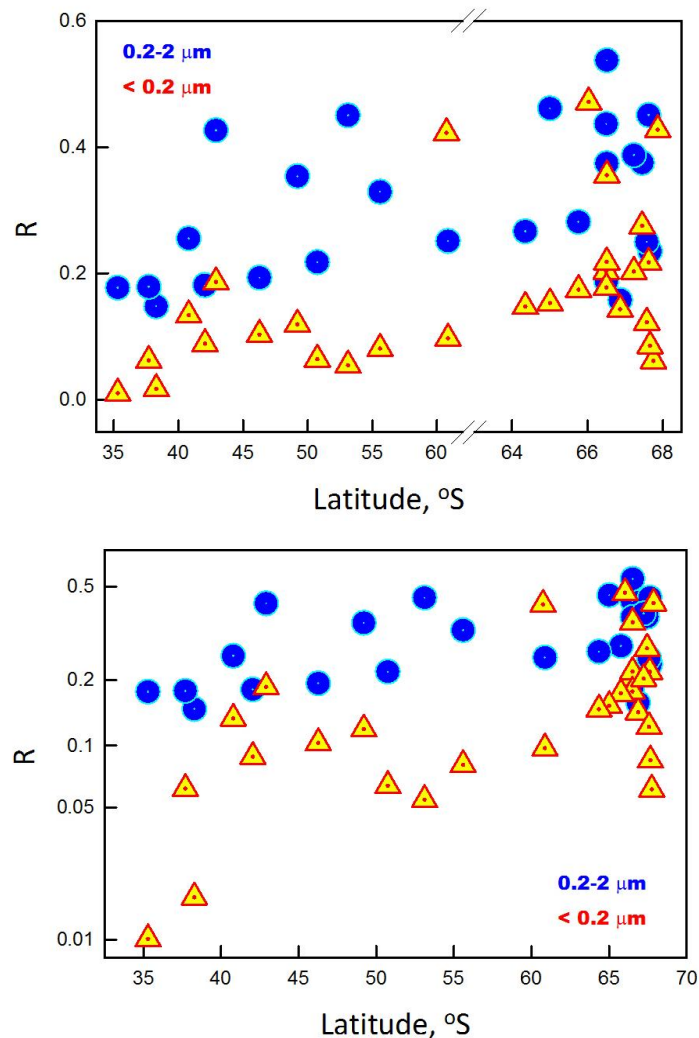


Figure S9 -  $R = \text{MeSO}_3^- / \text{nss-SO}_4^{2-}$  as a function of latitude in aerosols collected on board of Umitaka-maru in the marine boundary layer along a trajectory joining Cape Town (34 °S, 18 °E) with Fremantle (32 °S, 115 °E). Yellow triangles are data for < 0.2  $\mu\text{m}$  particles, blue circles correspond to the 0.2-2.0  $\mu\text{m}$  fraction. Upper panel, linear y-scale. Lower panel, probability y-scale.