

**Supporting Information for**  
**Dry Deposition of Biogenic Terpenes via Cationic**  
**Oligomerization on Environmental Aqueous Surfaces**

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**SI TEXT**

The products we observe are produced when the gaseous terpenes collide with the intact electroneutral aqueous jets as they emerge from the nozzle, i.e., before jets are broken up by the nebulizer gas. Since mass spectrometers detect net charge, the first step is the separation of pre-existing anions from cations in the electroneutral inflowing solutions. This is accomplished via the pneumatic breakup of the aqueous jet by a fast nebulizer gas that shears the outermost jet layers into droplets carrying net charges of either sign. These net charges are proportional to the concentrations of the protonated terpenes and their oligomers produced during gas-liquid collisions. Such droplets have a distribution of sizes and net charges<sup>1,2</sup> and, together, possess more surface and electrostatic energies than the original jet at the expense of the kinetic energy lost by the nebulizer gas. Since the nebulizer gas can fragment the jet but not

the smaller droplets for hydrodynamic reasons,<sup>3,4</sup> the creation of net charge is a one-time event. Gaseous terpenes may collide with the charged droplets within the spraying chamber, and charged droplets may hit the walls of the chamber, but such events will not be registered by the mass spectra because they do not affect the charges of the droplets in the first case, and prevent droplets reaching the mass spectrometer in the second. A critical feature of our instrument is that the jet issuing from the nozzle source is orthogonal to the polarized inlet to the mass spectrometer (see Figure S1). Therefore, the charged droplets deflected toward the mass spectrometer preferentially originate from the peripheral layers of the jet, while its core maintains its forward trajectory. The ejection of dissolved ions to the gas-phase takes place from the smallest droplets at the end of a sequence of events comprising extensive solvent evaporation, and net charge crowding in shrinking droplets that become unstable and undergo a cascade of Coulomb explosions.<sup>5,6</sup> Gas-phase ions are sorted out and detected by the online mass spectrometer. Data analysis based on mass balances and the kinetic theory of gases<sup>7</sup> suggest that the thickness of the interfacial layers sampled in these experiments is less than one nm.<sup>8,9</sup>

The nebulization of aqueous solutions of various pH into the spraying chamber of an electrospray ionization mass spectrometer (ESMS, Agilent 6130 Quadrupole LC/MS Electrospray System) at 1 atm at 298 K was utilized to monitor the cation composition at the air-water interface *in situ*. All the experiments were performed at Kyoto University. The present experimental setup is essentially the same as the one reported in elsewhere.<sup>8-10</sup> Solutions are pumped ( $100 \mu\text{L min}^{-1}$ ) into the spraying chamber through a grounded stainless steel needle (100  $\mu\text{m}$  bore) coaxial with a sheath issuing nebulizer  $\text{N}_2(\text{g})$  at high flow rates. The fast nebulizer gas (at nebulizer gas pressure 2.4 atm or 35 psi) strips the interfacial layers of the much slower liquid microjet into microdroplets that carry excess anions or cations. Note that the production

of charged microdroplets from a neutral liquid is the normal outcome of the charge fluctuations expected in a statistical breakup process, i.e., droplet charging does not require the application of an external electric field (cf. “classic” electrospray mass spectrometry).<sup>11,12</sup> This charge separation process is variously labeled pneumatic or sonic spray ionization.<sup>2,13,14</sup> Such charged microdroplets subsequently evaporate solvent in the chamber while being drawn to the electrically polarized inlet of the mass spectrometer with increasing acceleration. Since these microdroplets are the progeny of nascent droplets stripped from the surface of the microjet,<sup>8,9</sup> the ES mass spectra acquired in these experiments therefore report the ion composition of the outermost layers of the initial stage of microjet just reacted with gaseous terpene.

Conditions in the present experiments were: drying nitrogen gas flow rate: 13 L min<sup>-1</sup>; drying nitrogen gas temperature: 340 °C; inlet voltage: + 3.5 kV relative to ground; fragmentor voltage value: 80. (-)- $\alpha$ -pinene (> 95 %, Nacalai Tesque), (-)- $\beta$ -pinene (> 95 %, Nacalai Tesque, or > 99 %, Sigma-Aldrich), *d*-limonene (> 95 %, Nacalai Tesque), and D<sub>2</sub>O (> 99.9 %, Sigma-Aldrich) were used as received. All solutions of various pH were prepared in purified water (Resistivity ≥ 18.2 MΩ cm at 298 K) from a Millipore Milli-Q water purification system. All experiments were performed at 298 ± 2 K.

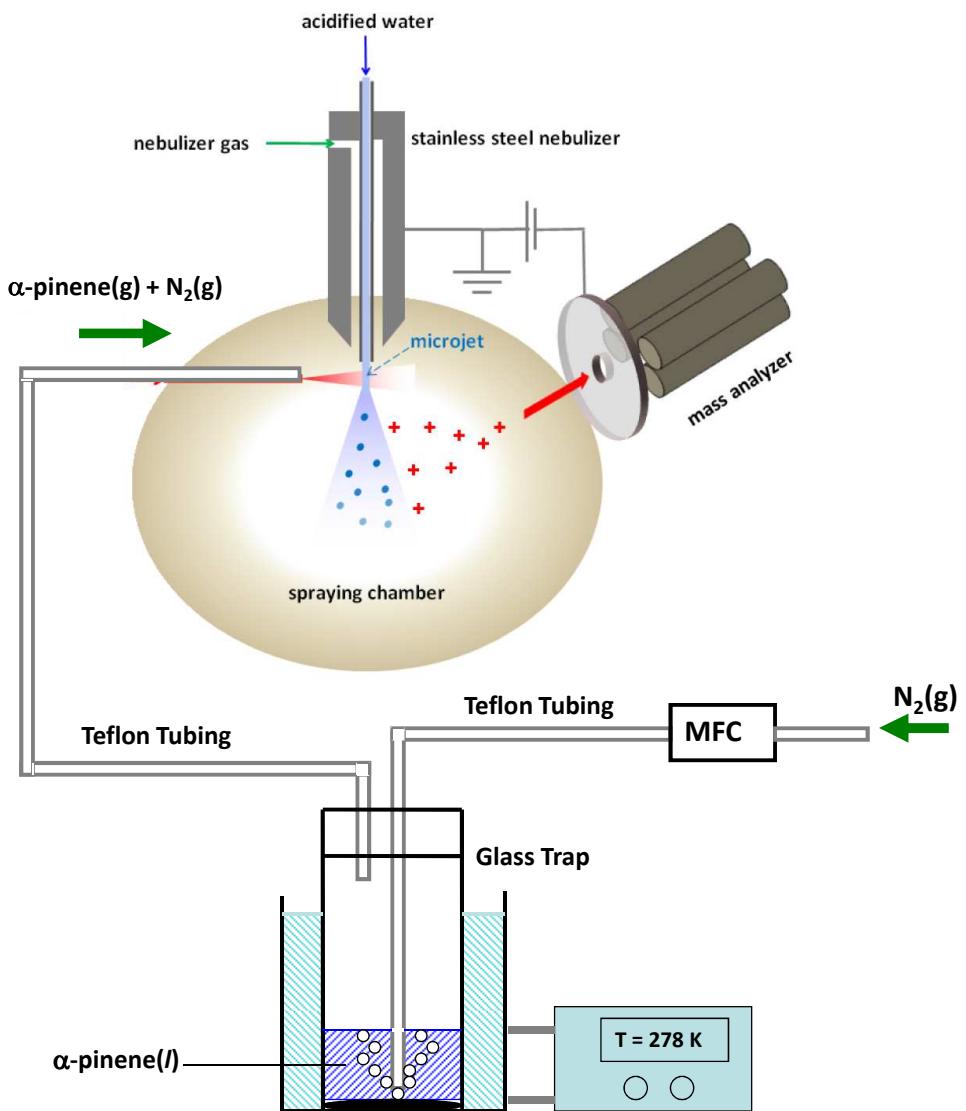


Fig. S1 Schematic diagram of present experimental setup. A microjet is created in the spraying chamber of an electrospray mass spectrometer by injecting acidified water through an electrically grounded nebulizer. The microjet is briefly exposed to terpene vapors before it is broken up (at  $\sim 10\text{-}50$  microseconds) into charged microdroplets by the fast nebulizer gas. Upon subsequent solvent evaporation, ion excesses are ultimately ejected from the microdroplets via field desorption, and detected by mass spectrometry within a few millisecond. MFC stands for mass flow controller.

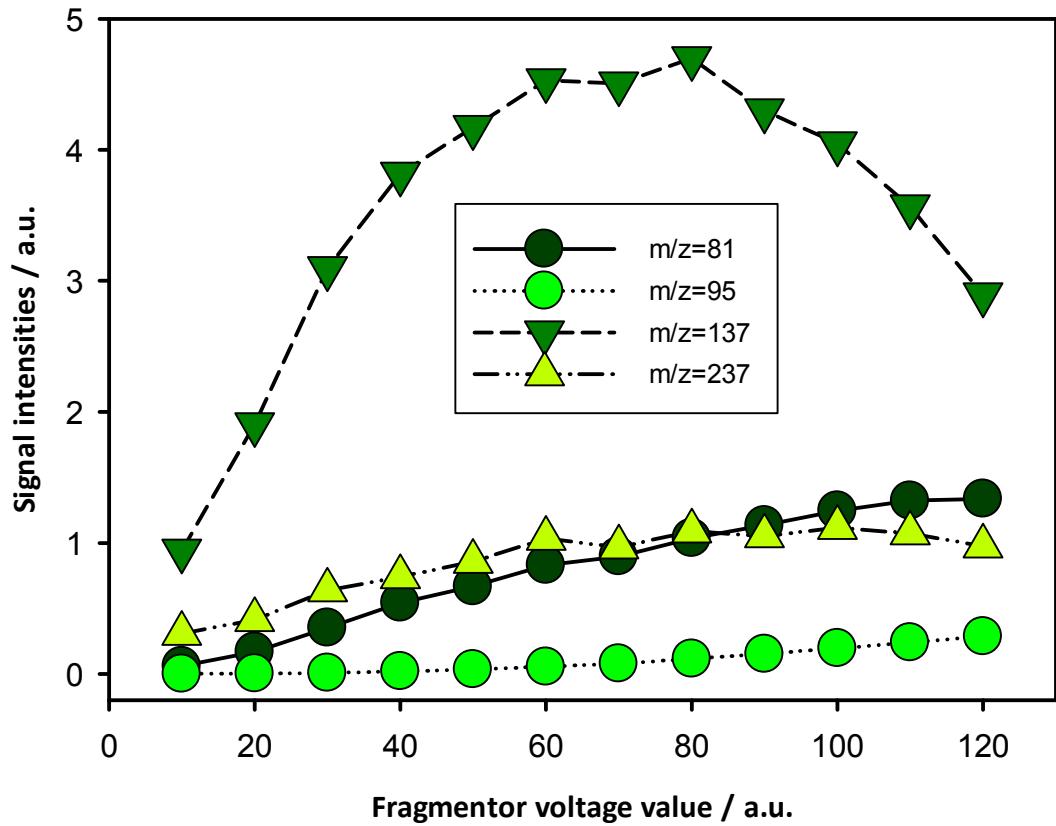


Fig. S2 Products signal intensities obtained from water microjets at pH 2.2 exposed to 13.7 ppmv  $\alpha$ -pinene(g) as a function of fragmentor voltage.

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