

Electronic Supplementary Information

Aerosol mass spectrometry of neutral species based on a tunable vacuum ultraviolet free electron laser

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1. Construction and Characterization of Smog Chamber

The smog chamber was established at the Dalian Institute of Chemical Physics, Chinese Academy Sciences (hereafter referred as the “DICP-CAS chamber”), which is composed of three parts: an inner reactor, an outer frame, and a chamber room. The reactor had a volume of 2 m³ made of fluorinated ethylene propylene (FEP) film (50 μm (thickness), FEP 200, DuPont) with a cylinder shape (radius: 0.8 m, length: 1.0 m). The frame was built by a stainless steel. The reactor was situated in a 1.8 m (L)×1.8 m (W)×2.1 m (H) temperature- and humidity-controlled room. The temperature can be controlled in the 16–40 °C region, and the temperature stability was better than ±0.5 °C and ±1.5 °C at the high and low temperatures, respectively. Humidification was achieved by vaporizing Milli-Q ultrapure water contained in a 0.5 L Florence flask and the water vapor was flushed with purified dry air into the reactor. Relative humidity (RH) inside the reactor can be varied from 3 to 80 % with an accuracy of ±1 %. The reactor was surrounded by 40 black lights (GE F40BLB, 40 W) within the chamber room. The emission spectra of the blacklight and blacklight blue lamps are shown in Figure S1, which range (300-550 nm) closely matches that UV irradiation of sunlight (290-400 nm).

The concentrations of NO, NO₂, and NO_x inside the reactor were measured by Thermo Scientific Model 42i analyzer. SO₂ was measured by Thermo Scientific Model 43i analyzer. The NO, NO₂, NO_x, and SO₂ were calibrated by Thermo Scientific Model 146i multi-gas calibrator. O₃ was measured by Thermo Scientific Model 49i analyzer and was calibrated using Model 49i-PS ozone calibrator.

VOCs inside the reactor were measured by proton-transfer reaction mass spectrometer (PTR-QMS 3000, East & West Analytical Instruments, China). The mass range and detection limit of PTR-QMS 3000 instrument was 1.5-600 amu and 100 pptv (benzene), respectively. Particle number concentrations and size distributions were measured by a scanning mobility particle sizer spectrometer (SMPS 3938NL76; TSI Incorporated, USA).

The average light intensity could be modeled by the photolysis rate of NO₂.¹ On the basis of the measured concentrations of NO, NO₂, and O₃ (Figure S2a), the photolysis rate constant of NO₂ is evaluated to be 0.20 min⁻¹ (Figure S2b), which is comparable to those reported in other indoor chambers.²⁻⁷

Figure S3a shows the background reactivity of the purified air under UV

irradiation conditions as a function of time. No obvious change of the concentrations of NO and NO₂ is found during the experiment. Approximately 10 ppb of ozone was generated after 6 hours irradiation, which might be formed from the photochemical reactions involving remnant HCs within the reactor and trace NO_x species in the purified air as reported previously.⁸ It can be seen from Figure S3b that the number of particles in purified air does not significantly change before and after UV irradiation. The wall loss rates of NO, NO₂, and O₃ are 4.09×10^{-4} , 4.06×10^{-4} , and 7.42×10^{-4} min⁻¹ (Figures S4-S6), respectively, which are all within the range of reported values of other chamber facilities (Table 1).

2. Supporting Figures

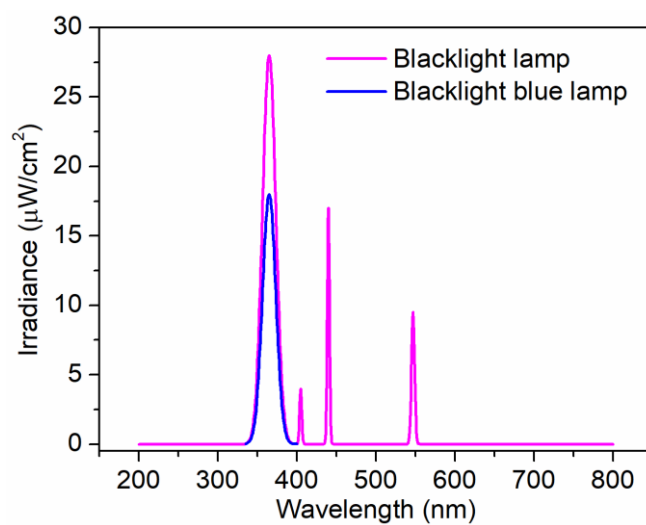


Figure S1. Emission spectra of the blacklight and blacklight blue lamps used in the DICP-CAS chamber.

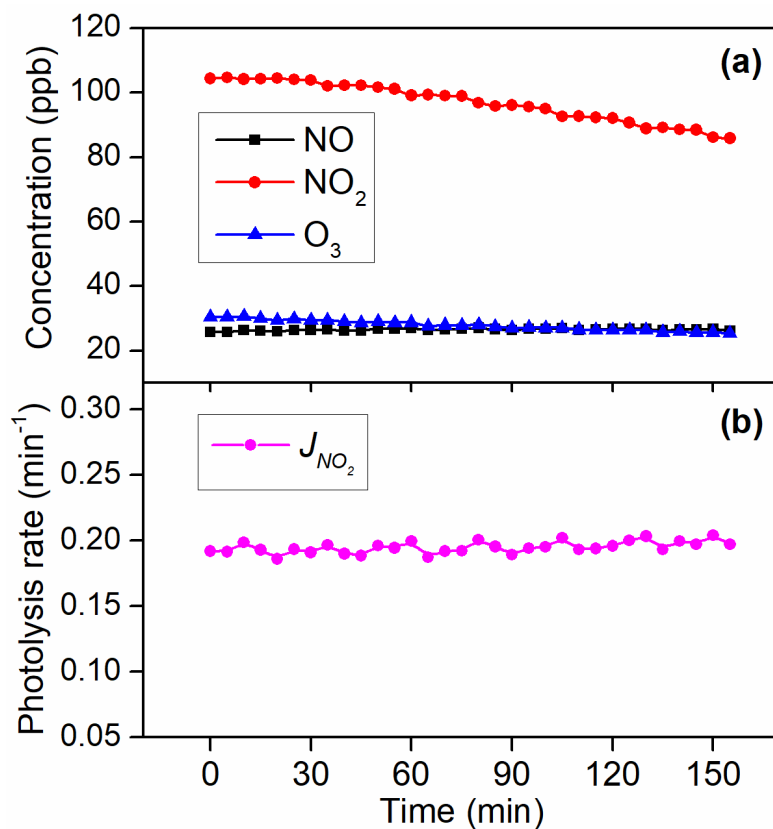


Figure S2. (a) Measurement of NO, NO₂, and O₃ concentrations for the evaluation of light intensity. (b) The photolysis rate of NO₂ as a function of time measured in the DICP-CAS chamber. The initial conditions were as follows: NO (1 ppb), NO₂ (129 ppb), 298 K, RH 6.5%, all blacklights on.

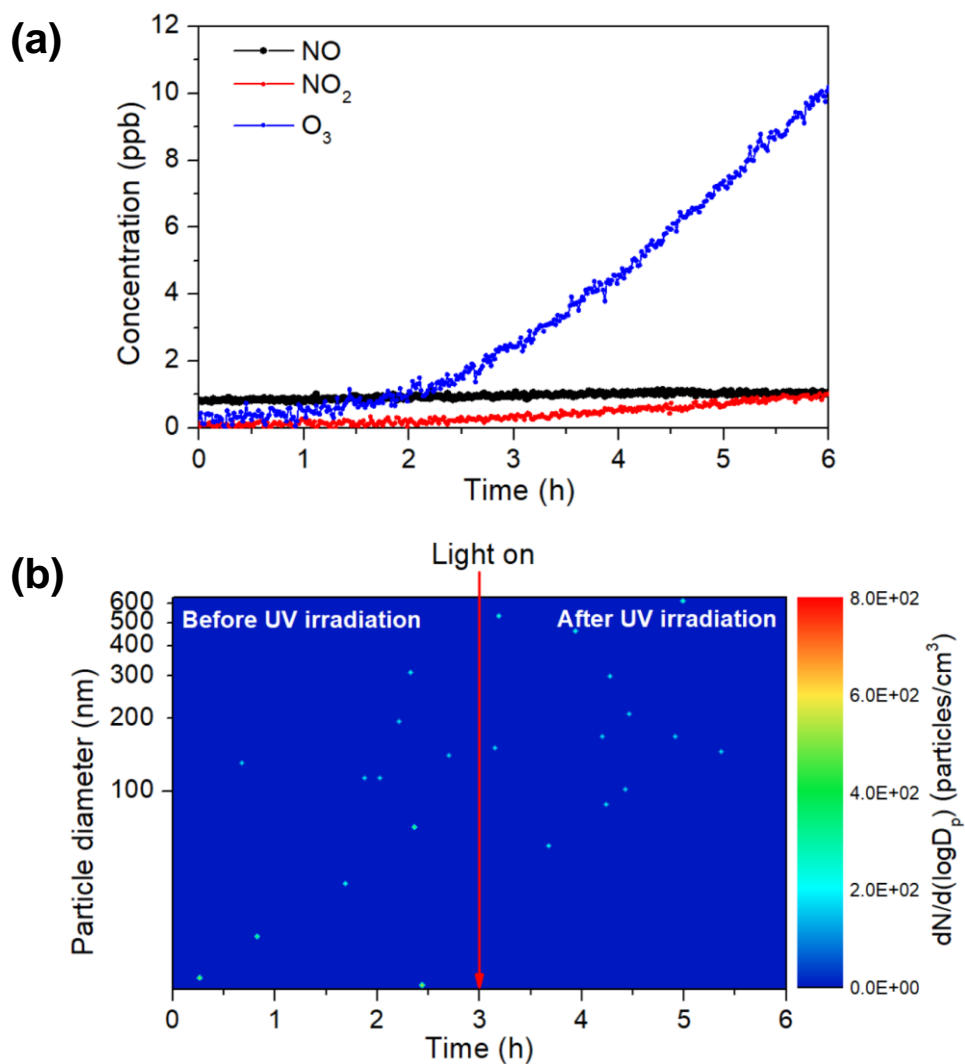


Figure S3. (a) Background reactivity of the purified air under UV irradiation conditions. (b) Aerosol size distribution in purified air before and after UV irradiation.

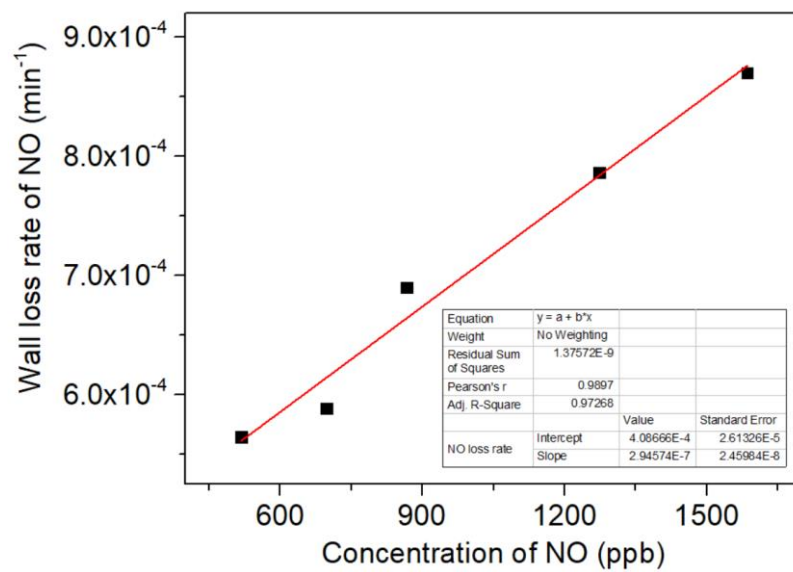


Figure S4. The wall loss rate of NO in the DICP-CAS chamber.

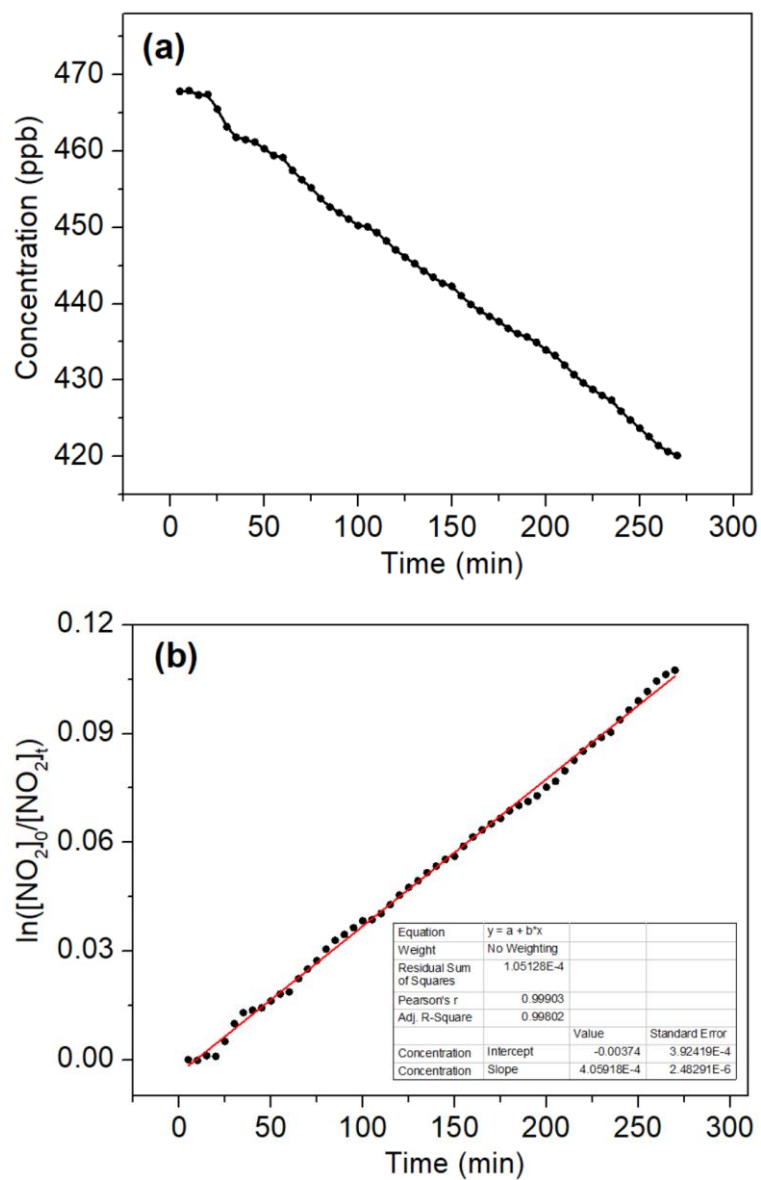


Figure S5. (a) Concentration of NO_2 as a function of time. (b) The wall loss rate of NO_2 in the DICP-CAS chamber.

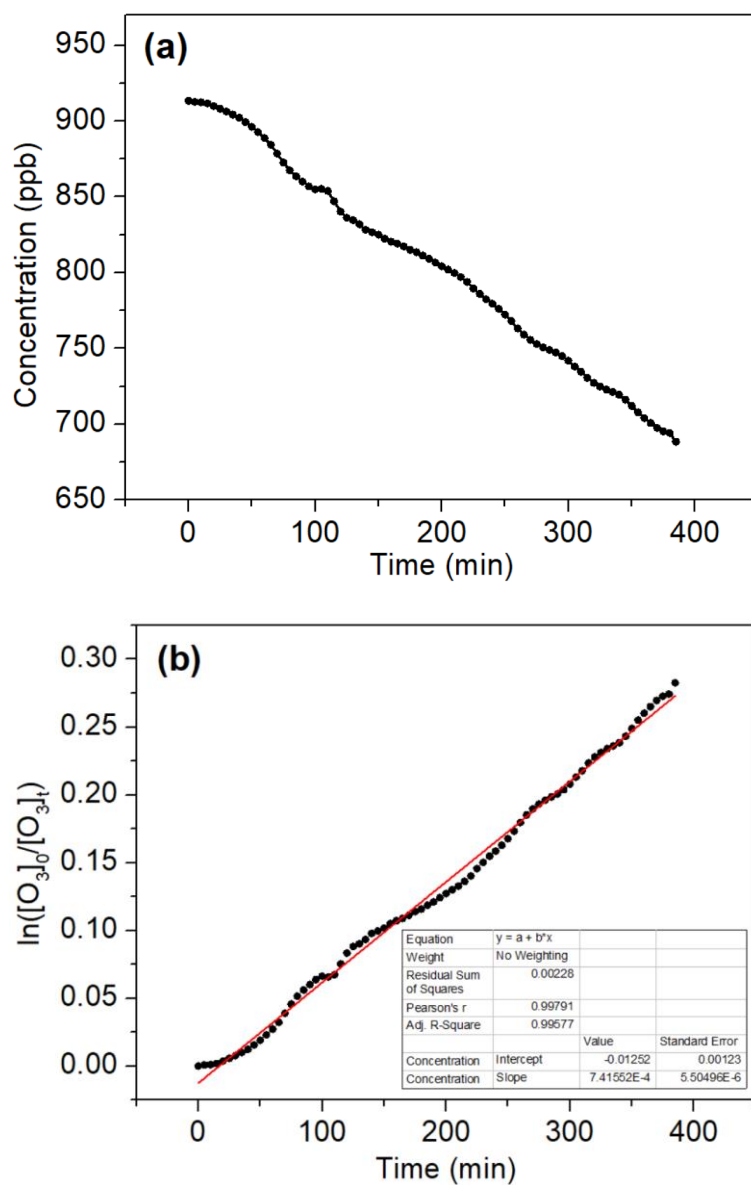


Figure S6. (a) Concentration of O₃ as a function of time. (b) The wall loss rate of O₃ in the DICP-CAS chamber.

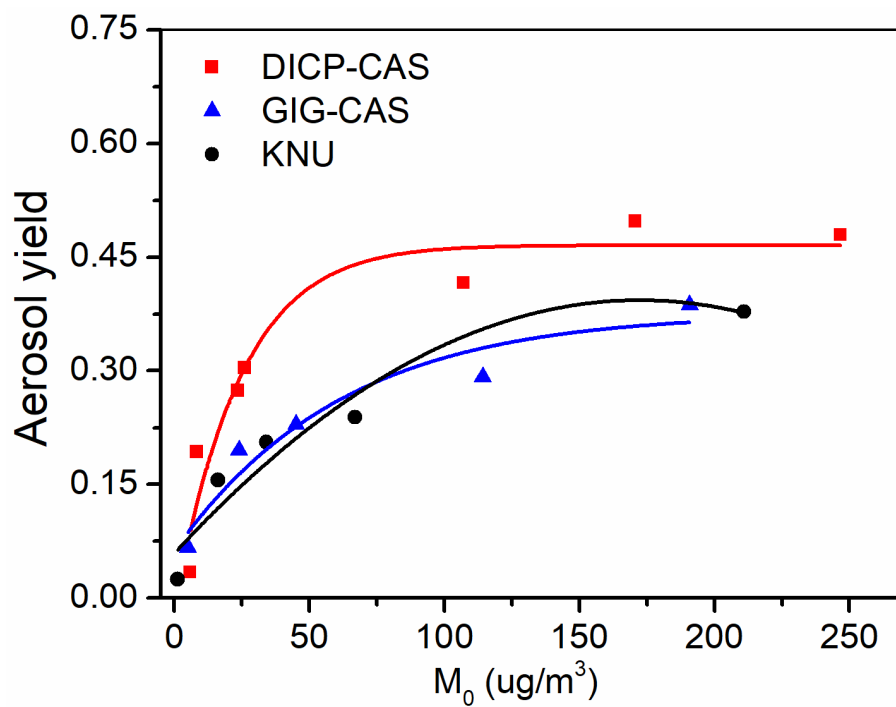


Figure S7. Comparison of aerosol yields obtained for α -pinene ozonolysis experiments in the DICP-CAS chamber with other chamber facilities.

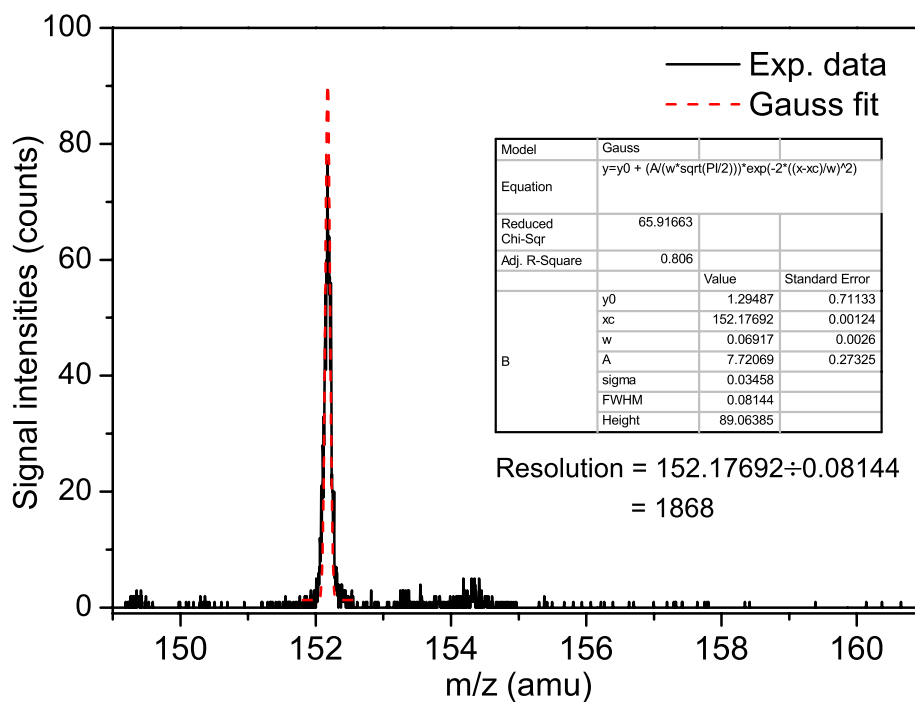


Figure S8. Mass spectrum of vanillin ionized by the VUV-FEL at 125 nm. The mass resolution of time-of-flight mass spectrometer is determined to be 1868.

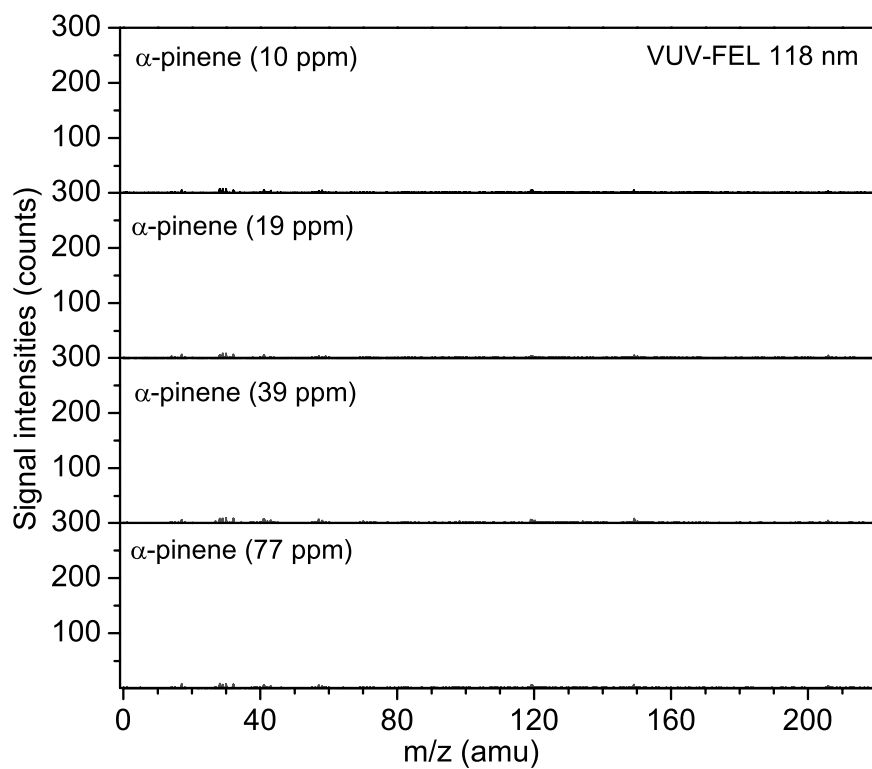


Figure S9. VUV-FEL photoionization mass spectra of the compounds generated from pure α -pinene in the smog chamber. The compounds were ionized by the VUV-FEL at 118 nm.

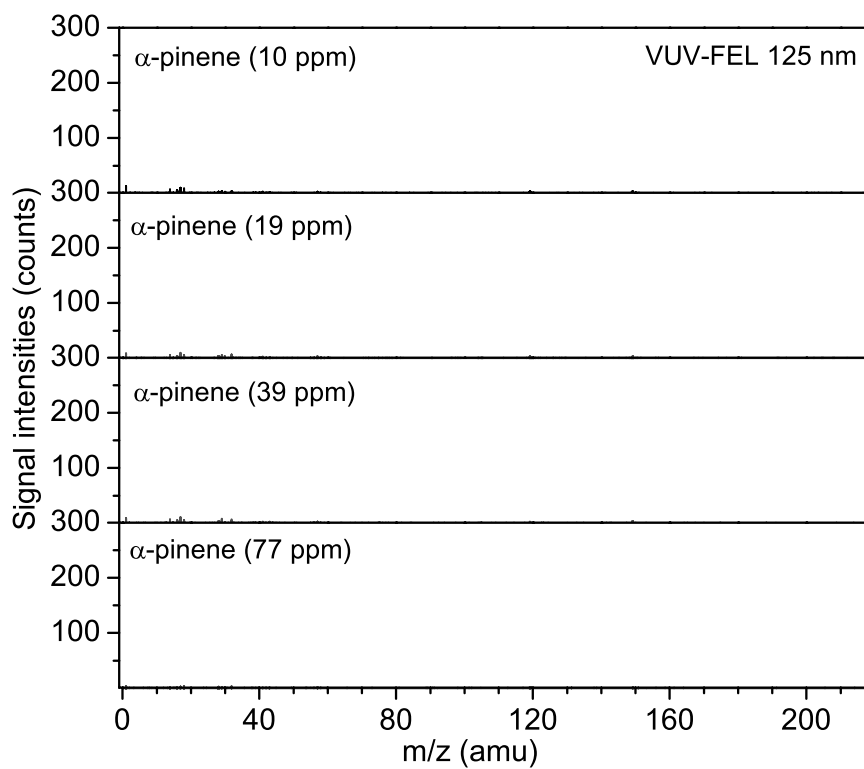


Figure S10. VUV-FEL photoionization mass spectra of the compounds generated from pure α -pinene in the smog chamber. The compounds were ionized by the VUV-FEL at 125 nm.

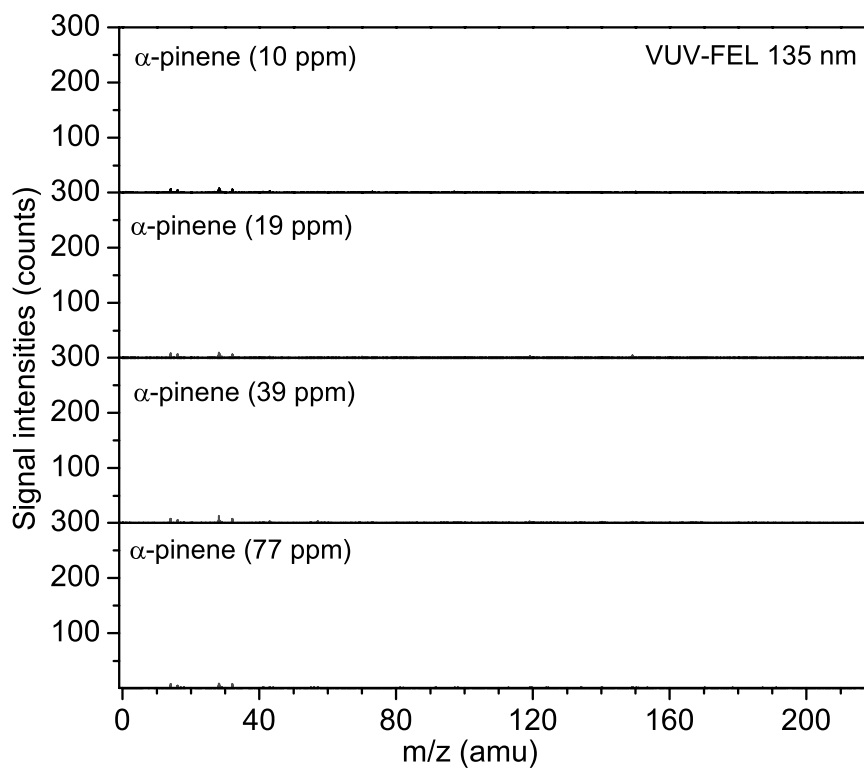


Figure S11. VUV-FEL photoionization mass spectra of the compounds generated from pure α -pinene in the smog chamber. The compounds were ionized by the VUV-FEL at 135 nm.

3. Supporting References

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