Thermal Desorption/Tunable Vacuum-Ultraviolet Time-of-Flight Photoionization Aerosol Mass Spectrometry for Investigating Secondary Organic Aerosols in Chamber Experiments

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Experimental details

TD-VUV-TOF-PIAMS. The aerosol sampling rate through the 200 μm diameter flow-limiting orifice was ~4.3 cm^3 atm s^{-1}, which was calculated taking into account the pumping speed of the turbo pump and the pressure in the chamber. The aerodynamic lens consists of five apertures that focus particles into a narrow beam. After particles exited the final 3.00 mm nozzle of the aerodynamic lens, they are accelerated into a vacuum by the gas expansion. The particles then passed through three stages of differential pumping system. The particle spot deposited on the heater tip is about 1 mm diameter in this study. The source chamber was evacuated by a Laboud turbomolecular pump (model TMP-2203LMC; 360 L s^{-1}), and the differential chamber was pumped by a Laboud vacuum compound molecular pump (model TG383M; 1600 L s^{-1}). The detection chamber was pumped by a Laboud turbomolecular pump (TMP-1103LMPC; 1000 L s^{-1}). The chambers are collimated to each other. An aperture with a diameter of 3 mm was used to connect the source chamber and the differential chamber, while a 4 mm diameter aperture was used to connect the differential chamber and the detection chamber. The pressure in the detection chamber was ~7 × 10^{-5} Pa during sampling aerosols.

SR from an undulator-based U14-A beamline of 800 MeV electron storage ring at the NSRL, is dispersed with a 6 m length monochromator, which cover the photon energy from 7.5 to 22.5 eV for 370 grooves mm^{-1}. The energy resolving power (E/ΔE) of VUV SR is above 2000 when the widths of the entrance and exit slits are adjusted to 80 μm. The photon flux is about 10^{13} photons S^{-1} and the photon beam spot size is ~500 μm in the region where the photon and particle beam intersect. The absolute wavelength of monochromator was precisely calibrated with the known IEs of inert gases. The reflectron mass spectrometer is characterized with a field free flight distance of 1.4 m, an ion mirror, and a multichannel plate detector. The ion signal was amplified by a preamplifier (VT120C, ORTEC, USA) and recorded with a time-of-flight multiscaler (FAST Comtec P7888, Germany).

The ions can be detected with a reflectron TOF mass spectrometer at different energies. A small positive bias voltage was applied to the first plate P1 (Figure 1) to drive the ions produced by VUV photoionization into the second stage of ion optics, where a positive electric pulse repelled the ions periodically into an acceleration region. A pulsed voltage of 165 V was applied to the repeller plate P2. With this design of the ion optics, the heater tip can be moved into the

photoionization region without distorting the electric field of ion extraction.

The heater tip is a 6 mm diameter copper rod coupled to a cartridge heater (Watlow) driven by a power controller (Watlow CV). The heater was mounted on a linear translator, which can change the distance between the hot surface and the VUV light. This distance is a balance between maximizing the vapor density reaching the ionization beam and minimizing the electrical field interference caused by the tip between the plates.

The synchrotron light was passed through an argon rare-gas filter to remove higher order harmonics produced by the undulator, and the pressure of the gas filter chamber was ~5 Torr in this study.

SOA Experiments.

Twelve fluorescent blacklamps (60 W, 320–400 nm, Philips, R-UVA) are surrounded in the chamber. Before each experiment, the evacuated bag chambers (replaceable) were flushed with dried purified air for >3 h (~3–4 air changes), until the particle number concentration <20 cm^{-3}. The purified air was followed by three consecutive packed-bed (dehydrator, activated charcoal, and silica gel) and a HEPA filter. The parent hydrocarbon was introduced into the chamber by injecting a known volume of the liquid hydrocarbon into a small glass bulb, and the vapor was carried into the chamber with 5 L min^{-1} of purified air. CH_3ONO was vaporized into an evacuated 500 mL glass bulb to a desired pressure and introduced into the chamber by a purified air stream. The whole system was completely shrouded from light with a black polyethylene tarpaulin. The mixing ratio of CH_3ONO injected can be estimated based on the vapor pressure in the glass bulb measured using a capacitance manometer (MKS).

No seed aerosols were injected in all these studies. After the injection of reactants into the smog chamber, purified air was added into the chamber again until the pressure reached atmospheric pressure. Then, reactions were initiated by irradiating the chamber with blacklamps. During all the experiments, the relative humidity was in the range of 50%–70%, and the temperature was (295 ± 4) K. Aerosol size distribution, number and volume concentrations were measured with a differential mobility analyzer (DMA, TSI, 3081) coupled with a condensation nuclei counter (TSI, CNC-3760).

Chemicals. All chemicals were used as purchased without further purification (with the exception of methyl nitrite): toluene (99%, Sigma-Aldrich), sodium nitrate (> 99%, Third Reagent Manufactory, Tianjin, China), methanol (> 99%, Third Reagent Manufactory, Tianjin, China).

Methyl nitrite was synthesized by dropping sulfuric acid (30 wt%) into a methanol solution of sodium nitrate. The CH_3ONO vapor was carried through a concentrated NaOH solution and an anhydrous $CaSO_4$ trap to remove any sulfuric acid and water, respectively. The CH_3ONO was then collected in a cold trap immersed in a liquid nitrogen bath and stored under liquid N_2 temperature.
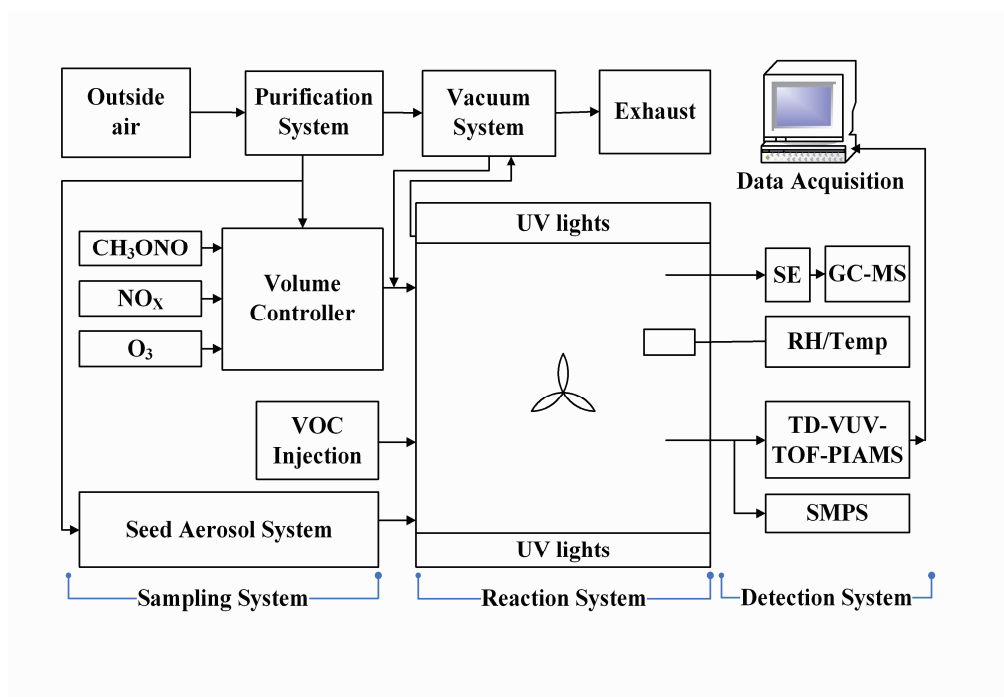
Figure S-1. Schematic diagram of Smog Chamber system. SE = sample extraction for GC/MS analysis.
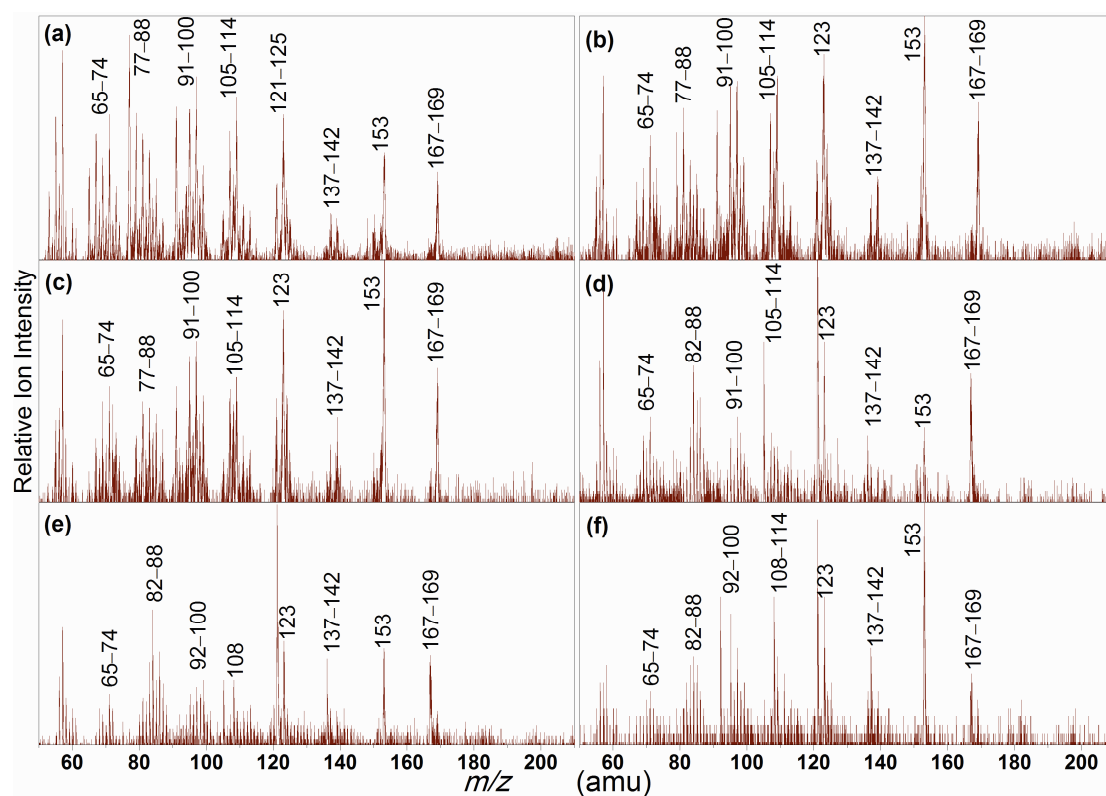
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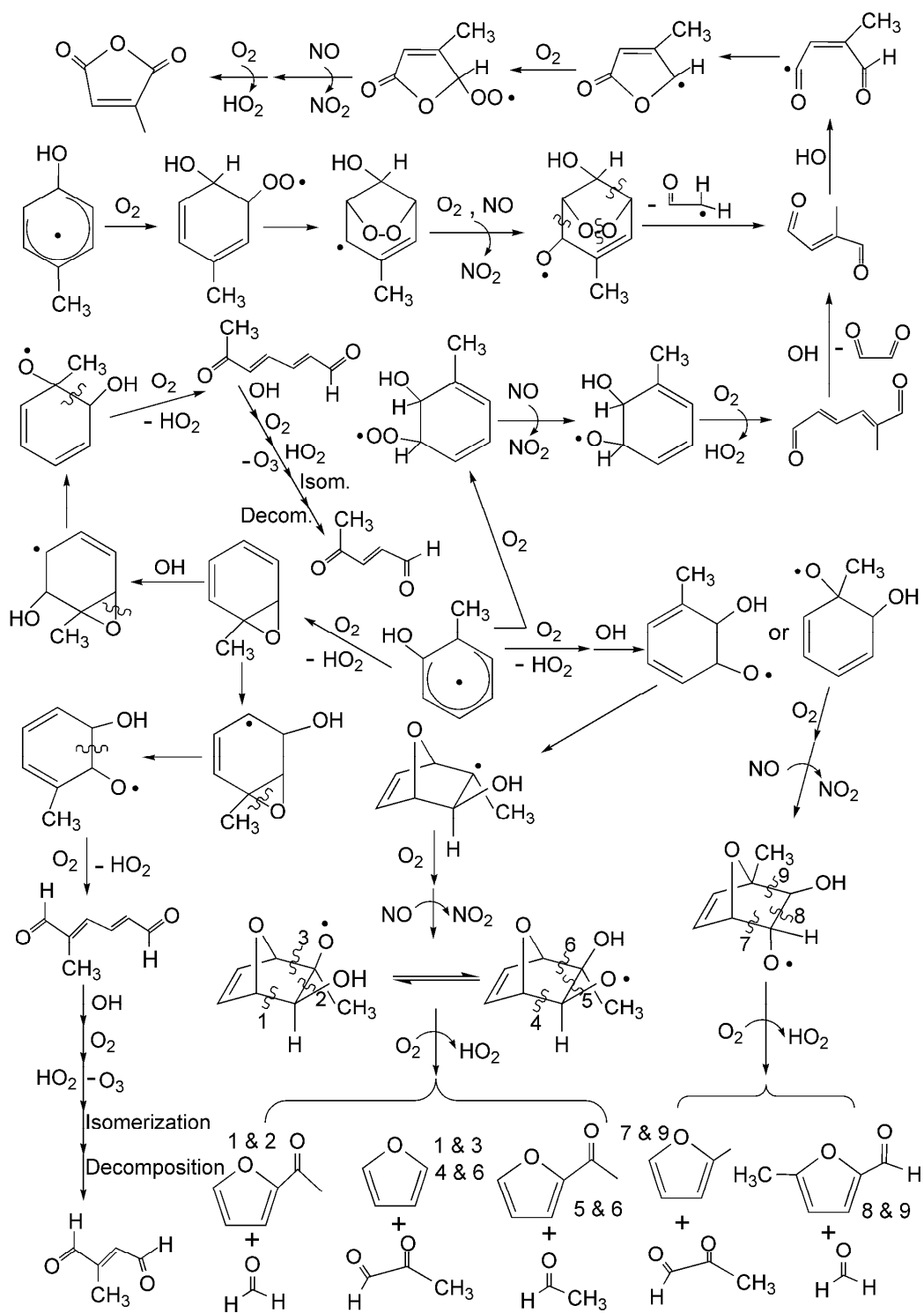
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