Electronic Supplementary Material (ESI) for Faraday Discussions

Tropospheric Aerosol as Reactive Intermediate

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EXPERIMENTAL DETAILS

The formation of nitrate (NO_3^-, *m*/*z* = 62) on aqueous microjets was investigated by spraying aqueous malonic acid, glutamic acid or glutaric acid solutions into NO_2(g)/N_2(g) mixtures at 1 atm, 293 K. Each aqueous solution is injected at 20 μL min^{-1} as a liquid microjet *via* an electrically grounded, pneumatic nozzle (bore diameter: 100 mm) into the spraying chamber of an online electrospray ionization mass spectrometry (ESI-MS, HP-1100 MSD), modified with a NO_2(g) injection system as shown in Supplemental Figure S1.[1] The gas mixture of NO_2(g) (500 ppm) in N_2(g) was introduced into the spraying chamber in a direction perpendicular to a stainless steel needle injector and mass spectrometer, respectively. NO_2 concentrations in the chamber were calculated from NO_2/N_2 mixture flow rates as diluted by the N_2 drying gas. Flow rates were regulated by mass flow controllers. This setup is identical to that used in previous studies from our laboratory.[1-5] The fast nebulizer N_2 gas (2.65×10^4 cm s^{-1}) shortly tears up the outer layers of the microjet into microdroplets, that are blown up into sub-micron droplets carrying ion excesses of either sign.[6-8] The excess charges carried by such sub-micron droplets are necessarily confined to the surface by electrostatics, are not affected by solvent evaporation or by reaction with a neutral gas, and constitute the basic magnitude retrieved as signal intensities by mass spectrometry. Excess ions are ultimately ejected from the surface of rapidly evaporating sub-micron droplets to the gas-phase as a result of electrical repulsion due to charge crowding, selected by an electrically biased inlet port, mass-analyzed and detected within ~1 millisecond.[11-13] The ESI-MS signal intensities detected in these experiments are therefore proportional to the amounts of ions of the interfacial layers of nascent microjet that had just reacted with NO_2(g),[3] i.e., prior to its breakup into charged sub-micron droplets.[14] We had verified that this setup actually behaves as a linear transfer device, i.e., ESI-MS signals are directly proportional to ion

concentrations (< 2 mM) in the interfacial layers of the microjet.[15,16] We have also demonstrated, and reported in the literature, that the products of gas/liquid reactions are formed and remain in the outermost layers of the liquid microjets for their ulterior detection by ESI-MS.[3]

Typical instrumental parameters were as follows: drying gas temperature, 350 ºC; drying gas flow rate, 13 L min^{-1}; Nebulizer pressure, 2 atm; collector capillary voltage, 3.5 kV; fragmentor voltage value, 60 V. All solutions of acids were prepared in MilliQ water (18.2 MΩ cm) from a Millipore Milli-Q gradient water purification system. Solutions pH was adjusted by adding concentrated NaOH solution and measured with a calibrated pH-meter.

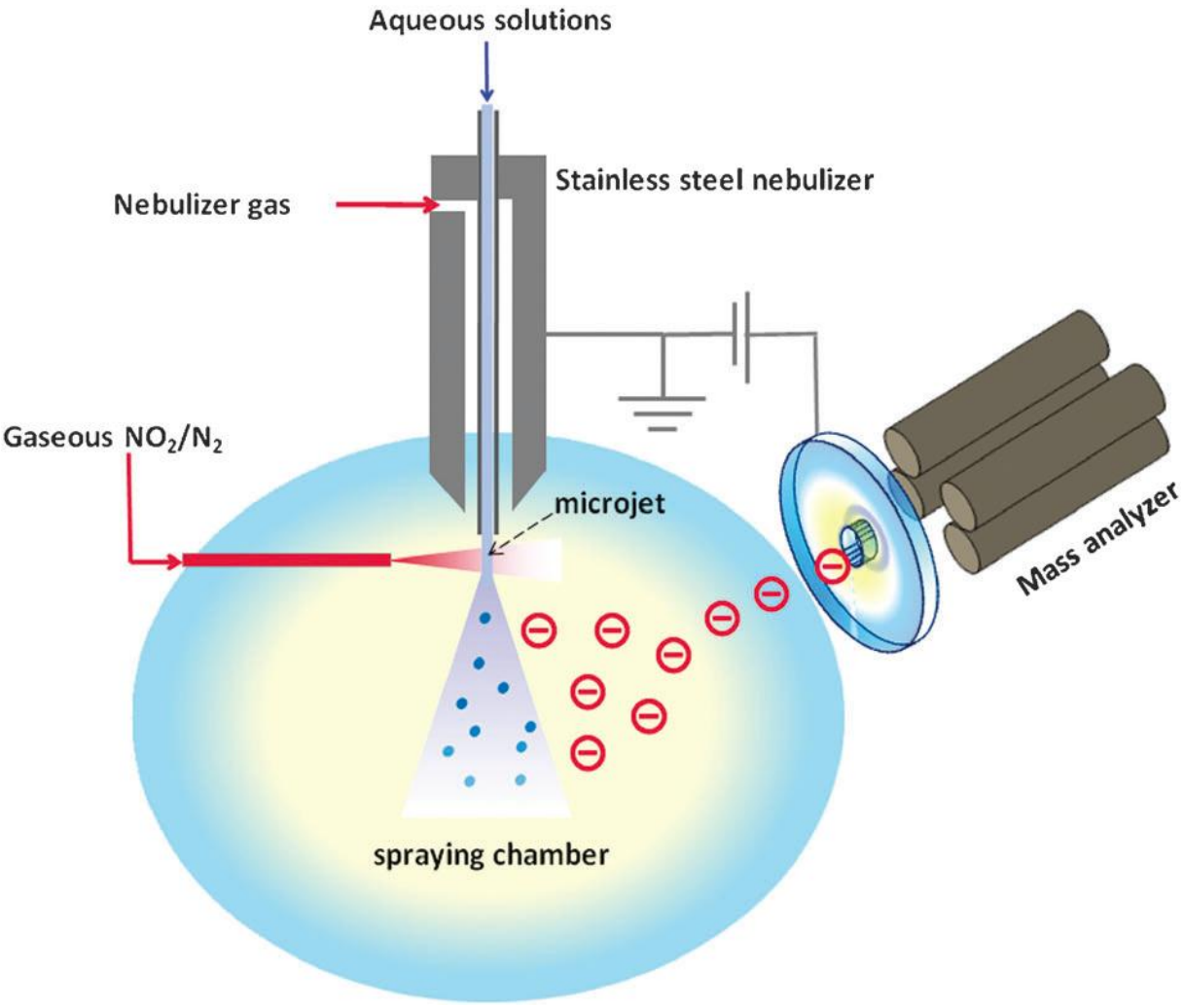

FIGURE S1– Schematic diagram of the spraying chamber with the NO_2(g) injection system

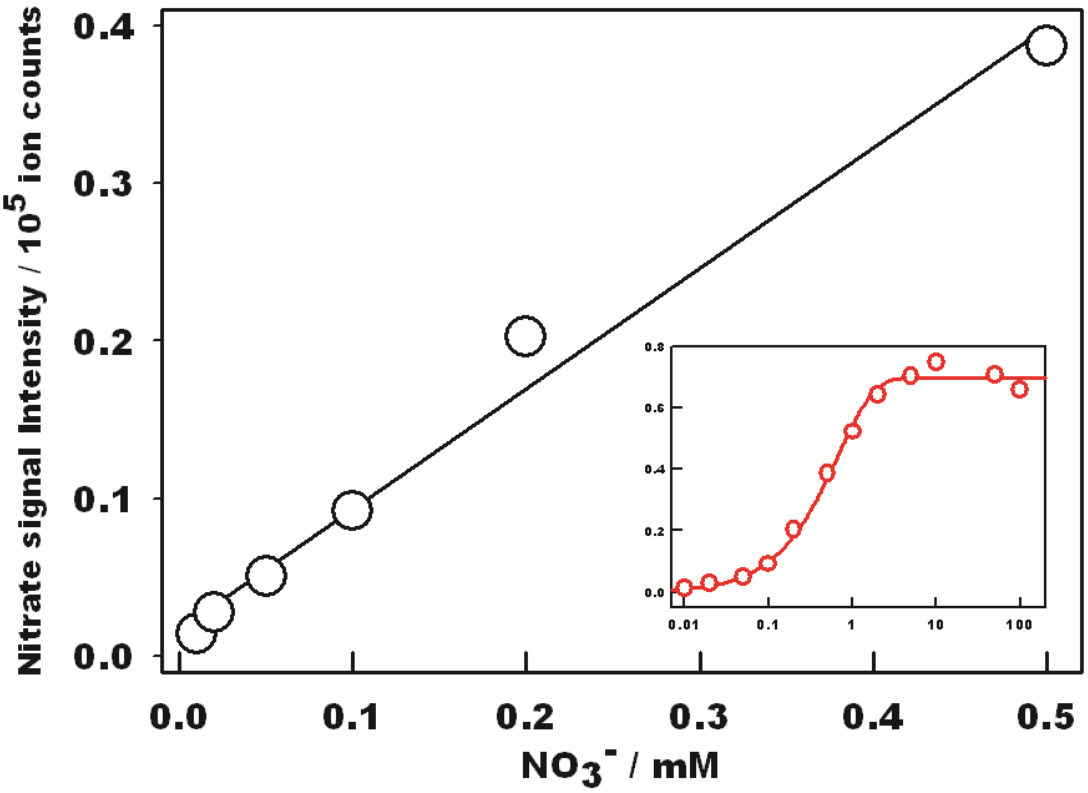

FIGURE S2 – ESI-MS signal intensities of NO_3^- (*m*/*z*=62) vs. [$NaNO_3$] over an extended concentration range display saturation behavior above ~ 2 mM.

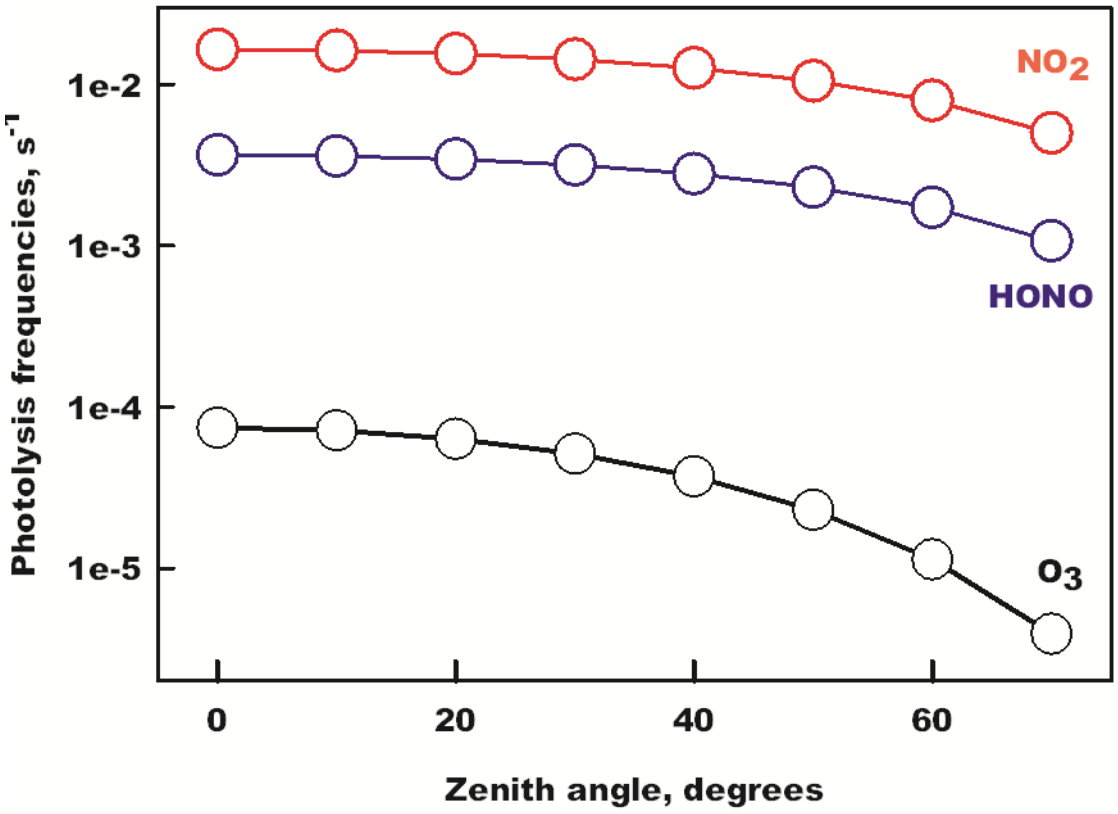

FIGURE S3 – Photolysis frequencies: J(NO_2 = NO + O^3P), J(HONO = NO + ·OH) and J(O_3 = O_2 + O^1D), as functions of zenith angle at zero elevation, surface albedo 0.4, under an ozone column of 300 Dobson units, at 10 am from Ref. 20 main text.

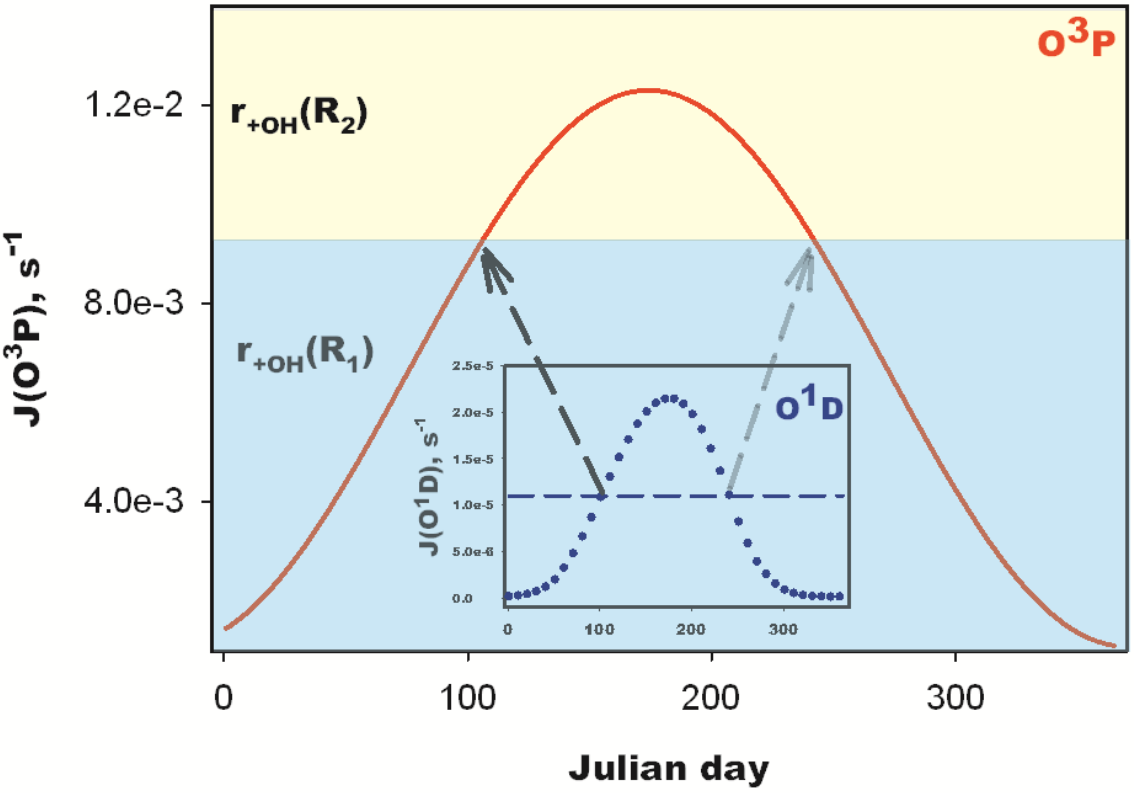

FIGURE S4 – Yearly dependence of the photolysis frequency J(NO_2 = NO + O^3P) over Moscow at zero elevation, surface albedo 0.4, under an ozone column of 300 Dobson units, at 10 am (from Ref. 20). Inset: J(O_3 = O_2 + O^1D) under the same conditions. When J(O_3 = O_2 + O^1D) falls 50% from its peak value, the rate of ·OH production switches from r_{+OH}(R1) to r_{+OH}(R2) at Julian day ~ 100, and vice-versa at Julian day ~ 240. See main text, section 8, for further explanations.

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