

Supporting Information

Anion-catalyzed dissolution of NO₂ on aqueous microdroplets

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Methods

All experiments were conducted in a commercial electrospray ionization mass spectrometer (HP-1100 MSD)¹⁻⁴ modified with the NO₂(g) injection system shown in Fig. S1. The setup was essentially identical to that used in previous studies of O₃(g) reactions from our laboratory.⁵⁻⁹ Aqueous solutions were pumped (20 μL min⁻¹, Harvard Apparatus) into the spraying chamber through a grounded stainless steel needle injector (100 μm bore) and pneumatically nebulized by means of N₂ gas flowing through a coaxial sheath. The difference between the exit velocities of the liquid jet (10.6 cm s⁻¹) and nebulizer gas (2.65 x 10⁴ cm s⁻¹) is so large that the drag imposed on the liquid breaks it apart into sub-micrometer size droplets. The terminal velocities of the microdroplets thus produced exceed ~10³ cm s⁻¹,¹⁰ which lead to transit times shorter than $\tau \sim 1$ ms across the ~0.5 cm wide NO₂(g) plume. NO₂/N₂ gas mixtures were introduced into the spraying chamber in a direction perpendicular to a stainless steel needle injector and mass spectrometer, respectively (see Fig. S1). This geometry was chosen to prevent unwanted NO₂ losses on the wall of the spraying chamber. NO₂ concentrations were determined by UV absorption spectrophotometry (HP 8452) at 400 nm¹¹. The NO₂ concentration in the chamber was calculated from the combined NO₂/N₂ mixture and N₂ drying gas flow rates. The [NO₂(g)] values reported in the figures throughout

correspond to the concentrations actually sensed by microdroplets in the spraying chamber, which are ~13 times smaller than the values determined from UV absorbance due to further dilution by the N₂ drying gas. Gas flows were regulated by calibrated mass flow controllers (MKS). Typical instrumental parameters were as follows: drying gas temperature, 350 °C; drying gas flow rate, 13 L min⁻¹; Nebulizer pressure, 2 atm; collector capillary voltage, 3.5 kV; fragmentor voltage, 22 V, unless otherwise noted in the text. Solutions were prepared in MilliQ water. NaHSO₄ (>99%), NaF (>99%), NaCl (>99%), NaBr (>99%), NaI (>99%) were used as received. Solutions pH was adjusted by HCl and NaOH and measured with a calibrated pH meter (VWR).

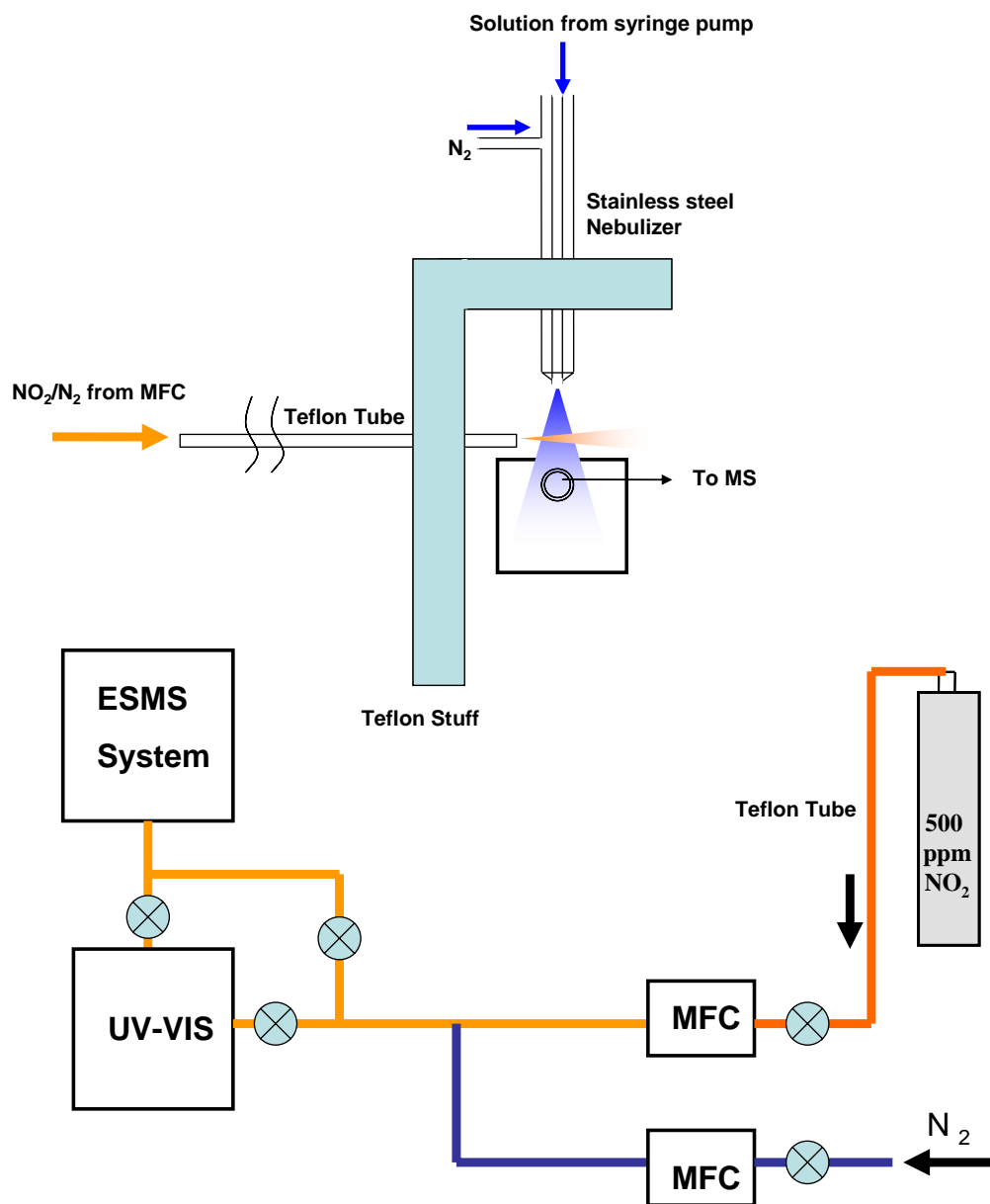


Figure S1. Schematic diagram of the spraying chamber with the $NO_2(g)$ injection system (top) and overview of the experimental setup (bottom). MFC stands for mass flow controller.

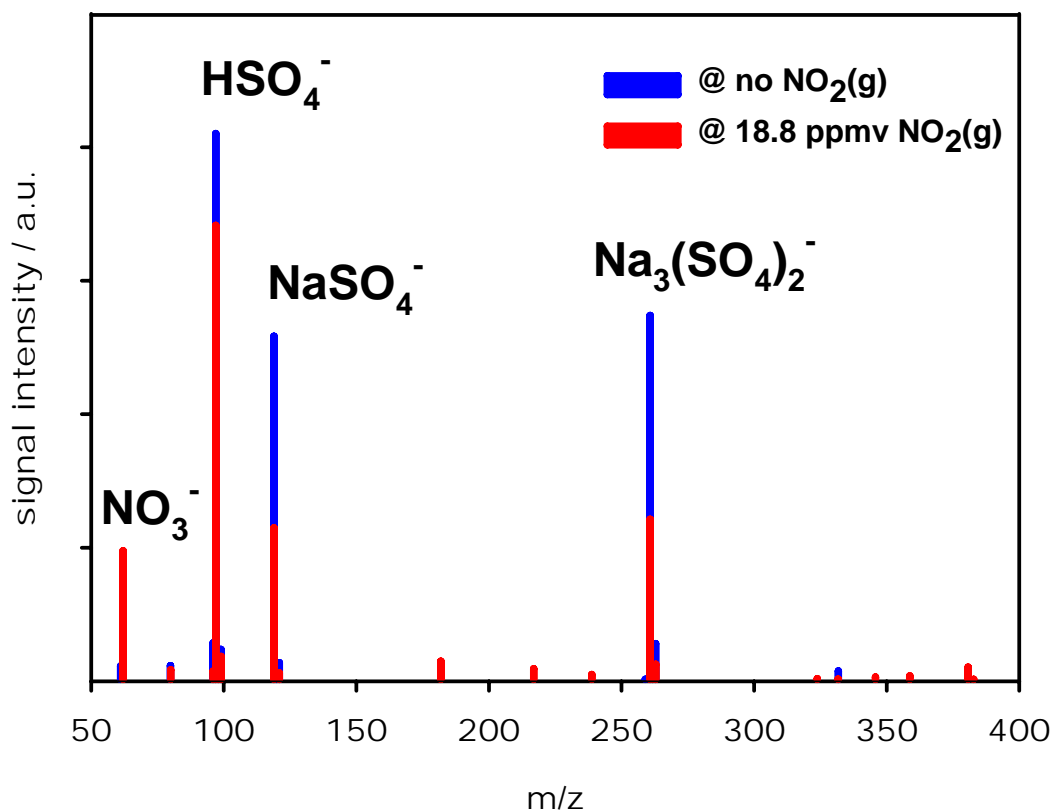


Figure S2. Thermospray mass spectrum of 1mM NaHSO₄ at pH 3.0 in the absence (blue trace)/presence (red trace) of 18.8 ppmv NO₂(g).

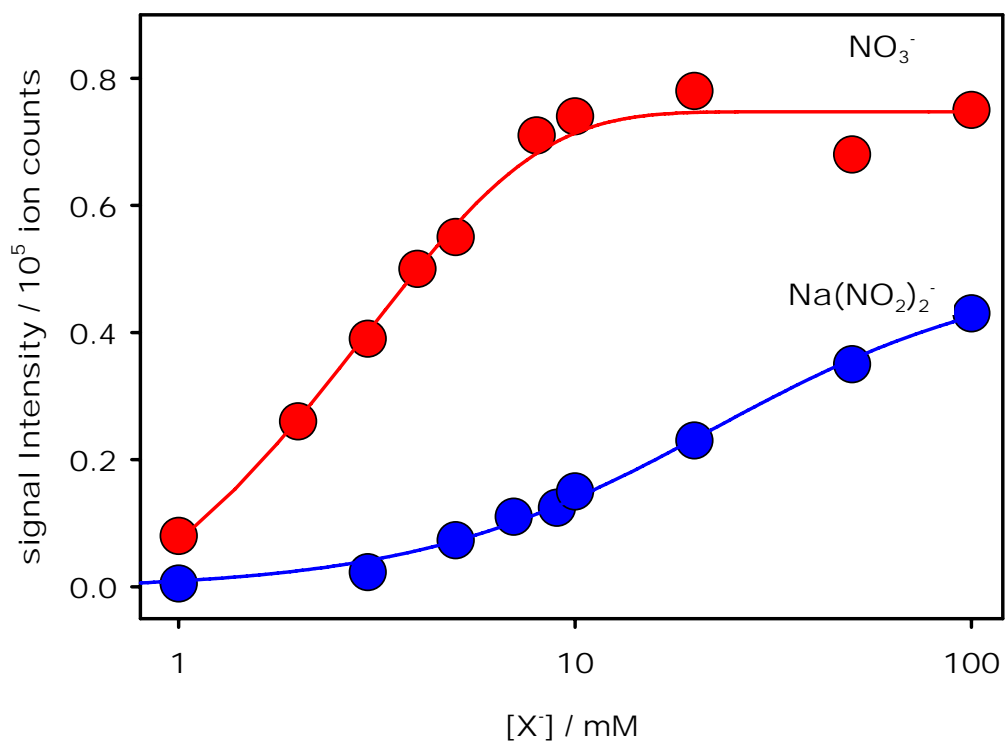


Figure S3. $m/z = 62$ (NO_3^-) and 115 [$\text{Na}(\text{NO}_2)_2^-$] signal intensities vs. $[\text{X}] = [\text{NaNO}_3]$ or $[\text{NaNO}_2]$ over an extended concentration range showing saturation above 100 mM

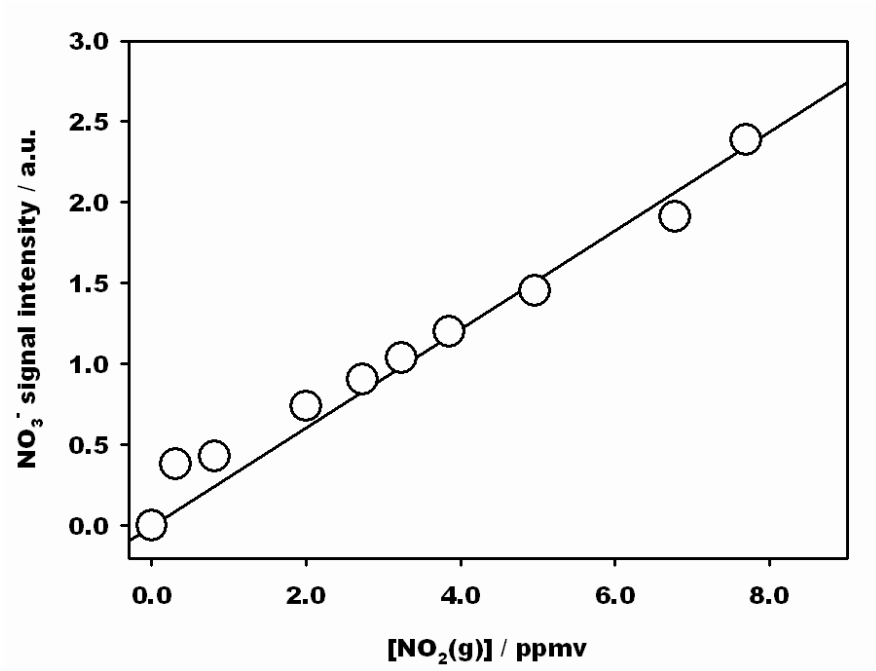


Figure S4. A plot of NO_3^- ($m/z = 62$) signal intensity as a function of $\text{NO}_2(\text{g})$ mixing ratio on 1mM NaCl pH ~ 7 microdroplets.

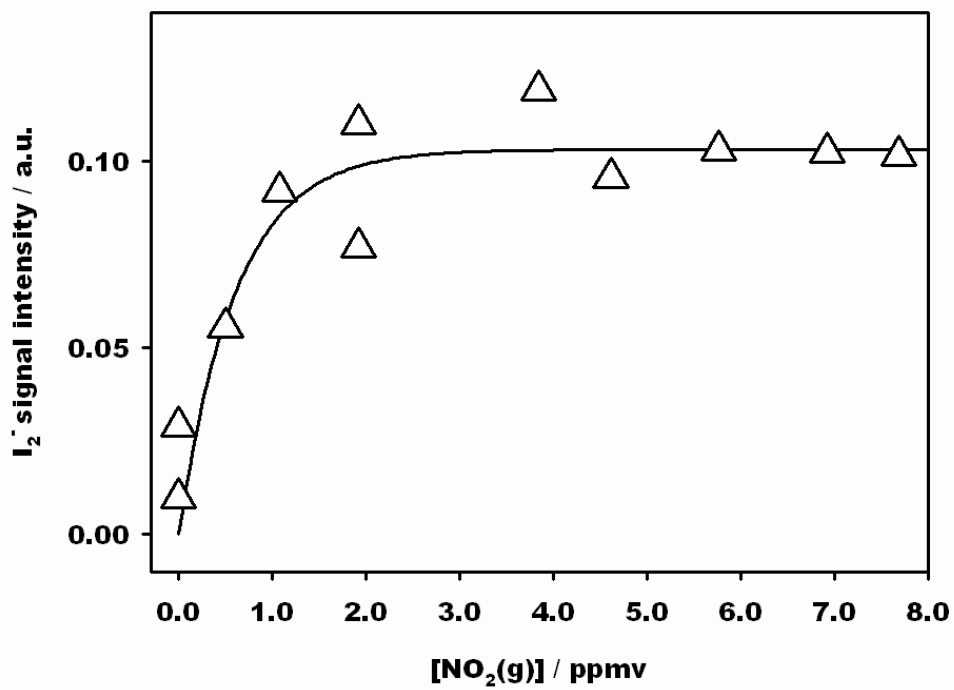


Figure S5. I₂⁻ (m/z = 254) signal intensity as a function of NO₂(g) mixing ratio on 1mM NaI pH ~ 7 microdroplets.

Supporting references

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