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HO_x and NO_x production in oxidation flow reactors via photolysis of isopropyl nitrite, isopropyl nitrite-d_7, and 1,3-propyl dinitrite at $\lambda = 254$, 350, and 369 nm

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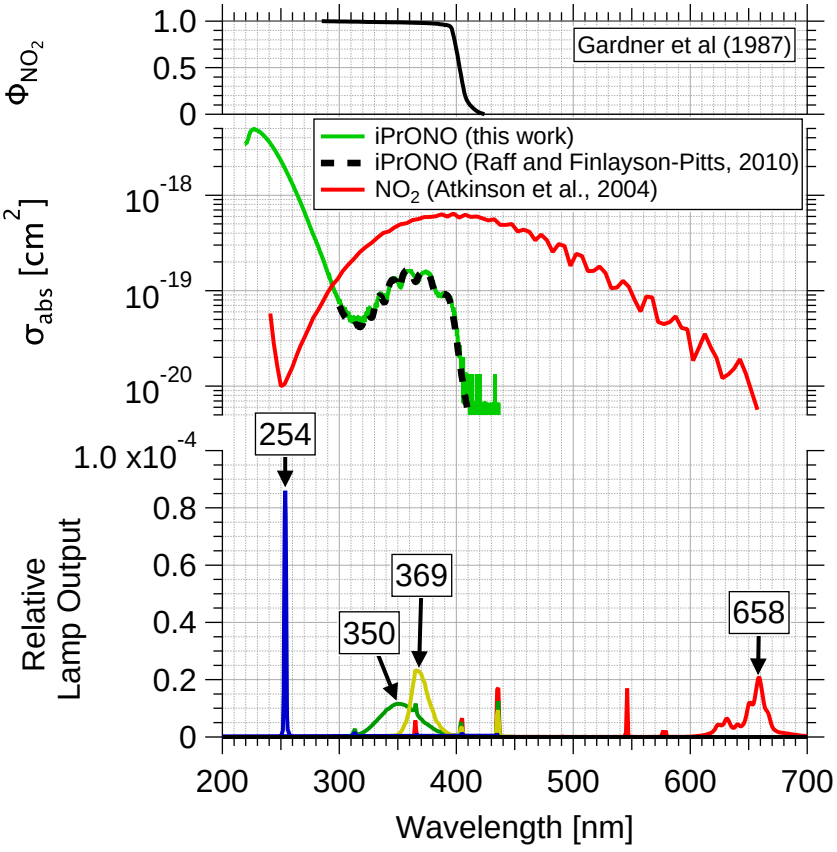

Figure S1. (a) NO_2 quantum yield (b) iPrONO and NO_2 absorption cross section (c) relative output of lamps used for alkyl nitrite or NO_2 photolysis / residence time distribution measurements as a function of wavelength. Areas under the lamp emission spectra are normalized to be the same value for each lamp type.

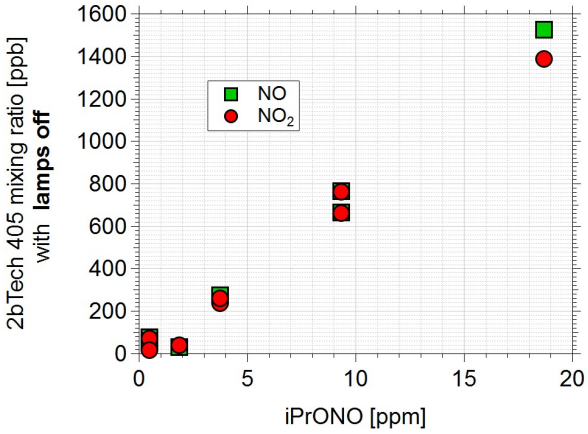

Figure S2. "NO" and "NO_2" mixing ratios measured at the exit of the reactor as a function of iPrONO added to the reactor inlet with the lamps off.

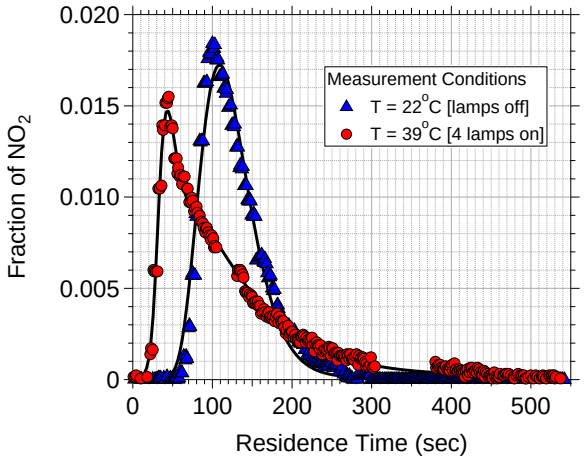

Figure S3. Residence time distributions in the PAM oxidation flow reactor obtained using 10-second pulsed inputs of NO_2 in the presence of four lamps centered at λ = 658 nm that were turned off (blue symbols) or on (red symbols). Black traces representing Taylor dispersion curves are shown to guide the eye (Lambe et al., 2011; Huang et al., 2017).

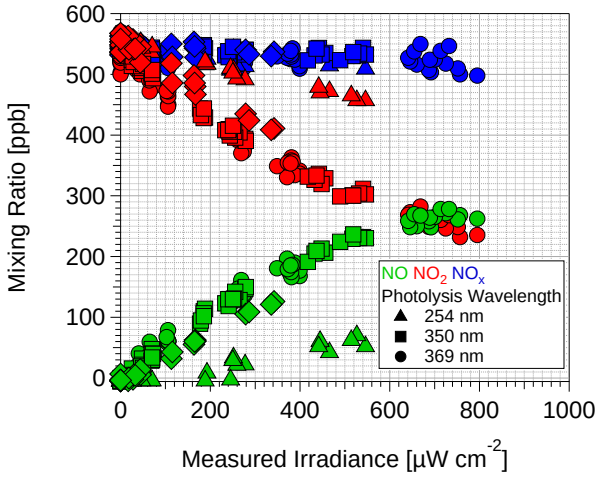

Figure S4. NO_2 decay and NO formation in the reactor as a function of UV irradiance at λ = 254, 350 or 369 nm. Measurements were conducted in the absence of oxygen to avoid O_3 formation.

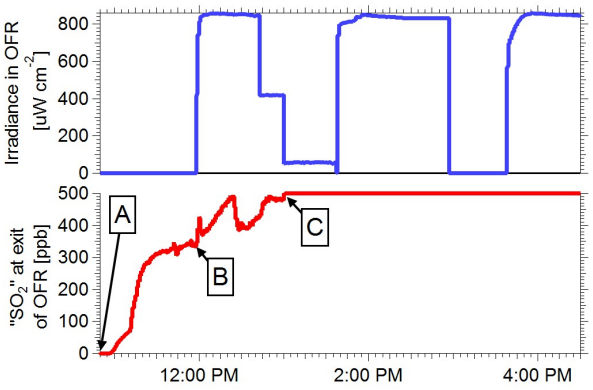

Figure S5. Example time series of SO_2 mixing ratio and irradiance (UV intensity) measured during a representative OFR369-i(iPrONO) OH_{exp} calibration: (A) Initial SO_2 addition at OFR inlet with lamps off; 9.3 ppm iPrONO also added at OFR inlet (B) Lamps turned on after a steady-state SO_2 concentration of $\approx$ 350 ppb was established (C) Analog output signal from SO_2 analyzer saturated at 500 ppb due to apparent NO_x interference.

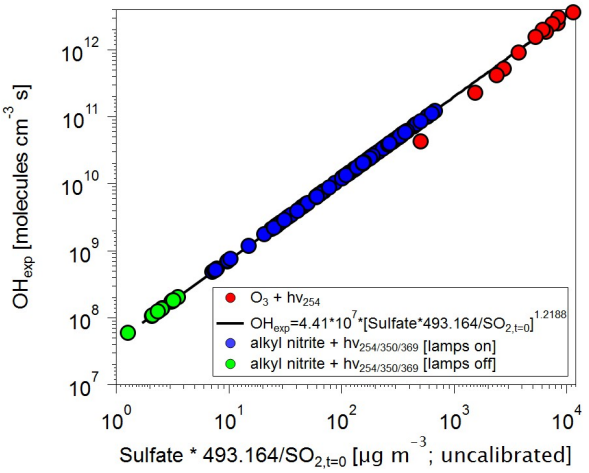

Figure S6. Calibrated OH_{exp} obtained following reaction of 493 ppb SO_2 with OH generated via $O_3 + h\nu_{254} \rightarrow O(^1D) + O_2$ followed by $O(^1D) + H_2O \rightarrow 2OH$ in the absence of NO_x (red symbols). The calibration equation was applied to measurements of sulfate formed during alkyl nitrite photolysis experiments (blue symbols) where SO_2 was added at the reactor inlet and the reactor was operated at the same residence time used in alkyl nitrite experiments. Particulate sulfate was measured with an Aerodyne Chemical Speciation Monitor. For details see Sect. 2.2.2.

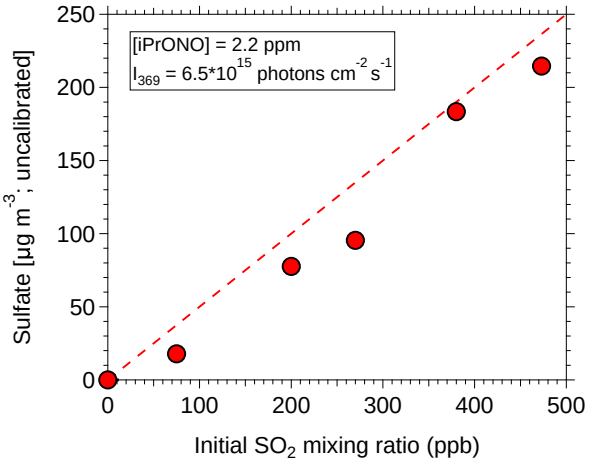

Figure S7. Sulfate measured by ACSM as a function of SO_2 mixing ratio input to the reactor.

Figure S8. Photographs showing product of attempted hexafluoroispropyl nitrite synthesis. Sulfuric acid was added to a slurry of 8.5 g sodium nitrite and 20 g hexafluoroisopropanol under nitrogen. Outflow from the synthesis flask was collected in a cold trap held in a dry ice/acetone bath.

References

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