

## Supplemental Information

### NO<sub>2</sub> actinometry

The actinic flux (photons cm<sup>-2</sup> sec<sup>-1</sup>) was measured with one, three, five and all seven lamps of the photo reactor turned on using NO<sub>2</sub> actinometry (method A), and independent measurements of the photon actinic flux (method B). With method A, NO<sub>2</sub> in a N<sub>2</sub>/O<sub>2</sub> gas mixture was added to the flow-tube under two different configurations: a) a bare glass flow-tube, and b) a blank coated flow-tube consisting of CA only, in the absence of IC. The NO<sub>2</sub> gas was produced from the oxidation of a gas flow of NO through a chromate salt reservoir, shown in Fig. 1A. In configuration a), the concentration of NO<sub>2</sub> was about 8 ppbv and in configuration b) it was about 40 ppbv. NO<sub>2</sub> actinometry is based on the following reaction:



The photolysis constant,  $J$ , in our case was treated as first-order rate constant, which quantifies the rate of photolysis of NO<sub>2</sub>,  $J_{NO_2}$ , in terms of a relative concentration change over time. The decrease in NO<sub>2</sub> was measured by the LED-CE-DOAS (Setup 1) and by the chemiluminescence (Setup 2); the NO<sub>2</sub> signal was allowed to stabilize, and lights were turned on sequentially.  $J_{NO_2}$  was calculated using the measurements and the following equation:

$$J_{NO_2} = \frac{d \ln[NO_2]}{dt}, \quad -\ln\left(\frac{[NO_2]_t}{[NO_2]_0}\right) = J_{NO_2} \times t \quad (S1)$$

With all seven lamps turned on, the  $J_{NO_2}$  was about  $2 \times 10^{-2} \text{ s}^{-1}$  (Setup 1) and  $1 \times 10^{-2} \text{ s}^{-1}$  (Setup 2). This is about 2-3 times the ambient  $J$  at mid-latitudes under summer noon-time conditions. The  $J_{NO_2}$  for configurations a) and b) are compared in the Fig. S2, and agreed within 8 % at 7 lamps and this variability increases as the number of lamps (irradiation) decrease, up to a factor of 2 as a maximum.

The  $J$ -values of NO<sub>2</sub> were calculated using independent measurements of the photon actinic flux of the UV lamps, which had been determined by B. Bohn at Forschungszentrum Jülich (Germany) with a LICOR 1800 hemispherical, cosine corrected spectro-radiometer (method B). The following equation was used to calculate the first order photolysis rate,  $J$ -value:

$$J - value = \int_{300}^{420} F_{FT}(\lambda) \sigma(\lambda) \Phi(\lambda) d\lambda \quad (S2)$$

where  $F_{FT}(\lambda)$  is the actinic flux measured in our flow-tube system,  $\sigma(\lambda)$  is the NO<sub>2</sub> cross section at 294 K in cm<sup>2</sup> molecule<sup>-1</sup> (Vandaele et al., 2002), and  $\Phi(\lambda)$  is the quantum yield data used from Sander et al., 2011. The  $J$ -values for NO<sub>2</sub> for methods A and B are compared in Fig. S2, and agree within a factor of 2 (higher  $J_{NO_2}$  for method A). The photon actinic flux shown in the Fig. S3 has been adjusted by this factor, and is compared with a typical solar spectral irradiance at the Earth surface (solar zenith of 48°, The American Society for Testing and Materials, ASTM).

**Equation S1** shows the relationship between the loss of NO<sub>2</sub>, the derived pseudo-first order  $J_{NO_2}$  and the uptake coefficient ( $\gamma$ ) for a heterogeneous reaction in a cylindrical flow-tube:

$$\frac{d[NO_2]}{dt} = -J_{NO_2}[NO_2] \quad J_{NO_2} = \frac{\gamma \langle c \rangle [\frac{S}{V}]}{4} \quad (S3)$$

where  $\langle c \rangle$  is the NO<sub>2</sub> mean molecular speed,  $(8RT/\pi M)^{1/2}$ , and  $[\frac{S}{V}]$  is the surface area of the film per gas volume ratio in our flow-tube system. These calculations are represented in Fig. S4.

## Figure Captions

**Figure S1:** NO<sub>2</sub> j-values in s<sup>-1</sup> from the bare glass and citric acid blank coated flow-tubes in Setup 1.

**Figure S2:** Determination of the NO concentration in the 2014 PSI flow-tube system. The lifetime of HO<sub>2</sub> is short enough at 500 ppbv with respect to its reaction with NO. This ensures a 1 NO:1 HO<sub>2</sub> molecular reaction in our experimental conditions. An IM/AC ratio of 0.088 was fixed for this specific experiment.

**Figure S3:** Solid line: the cross-section of IC in H<sub>2</sub>O; the UV-VIS absorption of IC was measured by Kampf et al., 2010 and interpolated to more recent molar extinction measurements by Barbara Nozière at IRCELYon (right scale in cm<sup>2</sup>). Shaded gray: calculated wavelength dependent photolysis frequencies of imidazole-2-carboxaldehyde, j-values, based on the calculated quantum yield in our flow tube. Dotted line: actinic flux of the UV-light source in our flow-tube system from 300-420 nm range, the total flux is  $2.26 \times 10^{16}$  photons cm<sup>-2</sup> s<sup>-1</sup>. Dashed line: a solar actinic flux spectrum for a solar zenith angle of 48°, 37° tilt towards the sun and clear skies ( $\sim 2 \times 10^{16}$  photons cm<sup>-2</sup> s<sup>-1</sup> between 300-420 nm) obtained from the standard spectrum of the American Society for Testing and Materials (ASTM).

**Figure S4:** Film thickness dependence represented by NO loss. The IC:CA ratio was kept constant to show the classic behavior of reactions governed by reaction and diffusion. At low thicknesses, P<sub>HO2</sub> increases linearly and saturates at thicknesses >2 μm. This shows that the observed HO<sub>2</sub> is produced from the top few micrometers of the films under study.

**Figure S5:** The photosensitized uptake coefficient of NO<sub>2</sub> (blue diamonds, right axis); this graph shows the inefficiency of NO<sub>2</sub> to compete with O<sub>2</sub> at atmospheric mixing ratios. The open red

circles represent the CA blank measurements, the closed red circles represent a  $1.725 [\text{IC}] \times [\text{CA}]$  film measurements during  $\text{NO}_2$  actinometry experiments (left axis).

**Figure S6:** NO to  $\text{NO}_2$  conversion from similar CWFT experiments performed in a different photosensitizer, 4-BBA. The top figure shows that NO does react with  $\text{HO}_2$  to produce  $\text{NO}_2$  in the presence of 4-BBA and adipic acid (AA), as the organic aqueous base. The bottom figure shows no conversion in a clean tube.

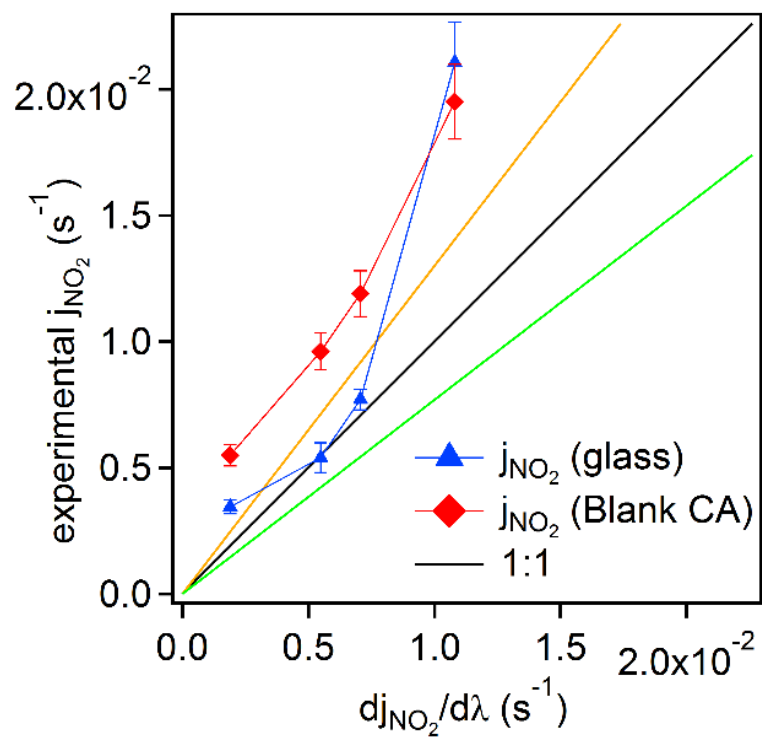


Figure S1

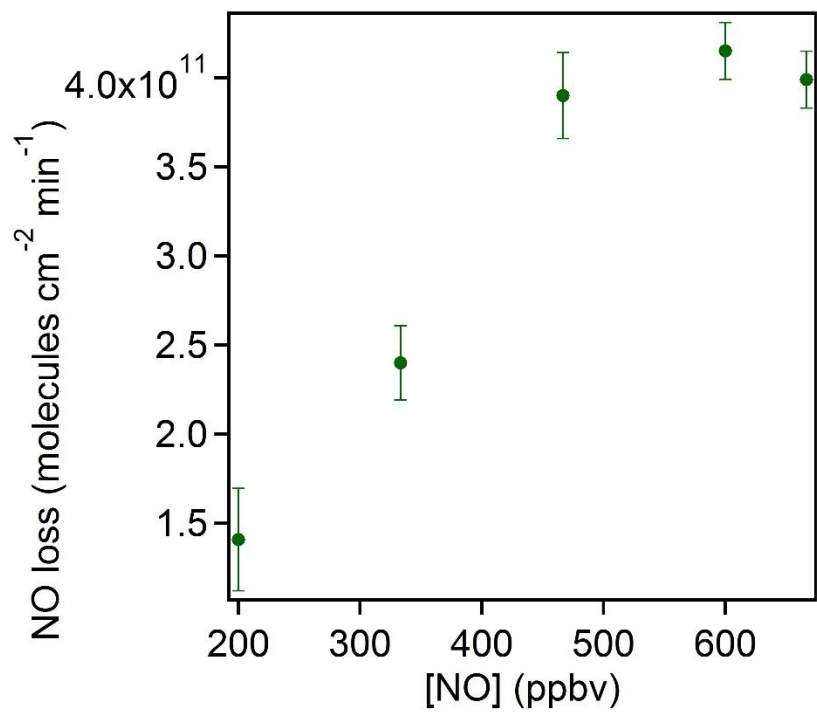


Figure S2

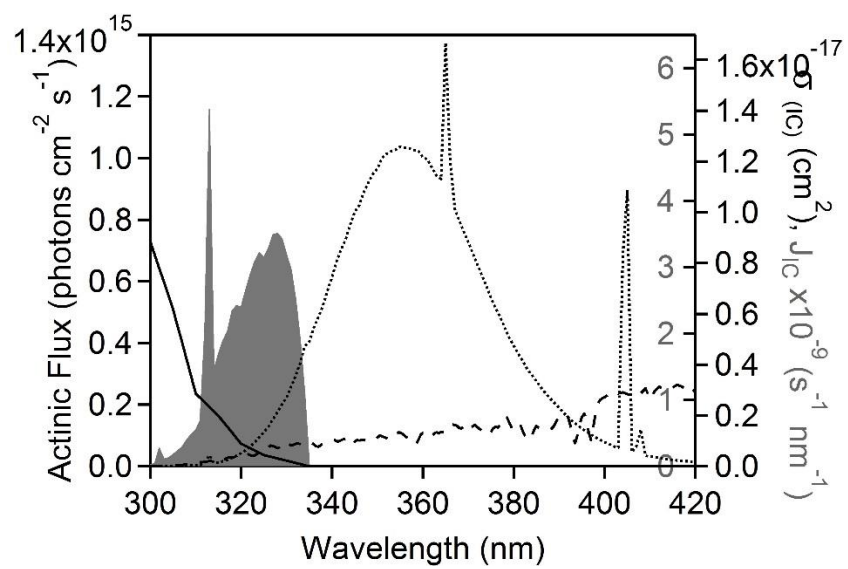


Figure S3

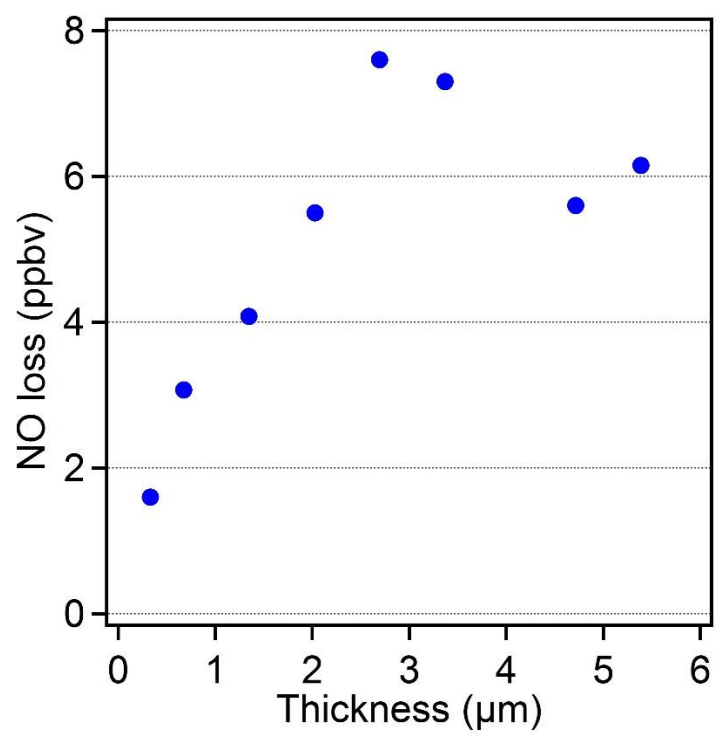


Figure S4



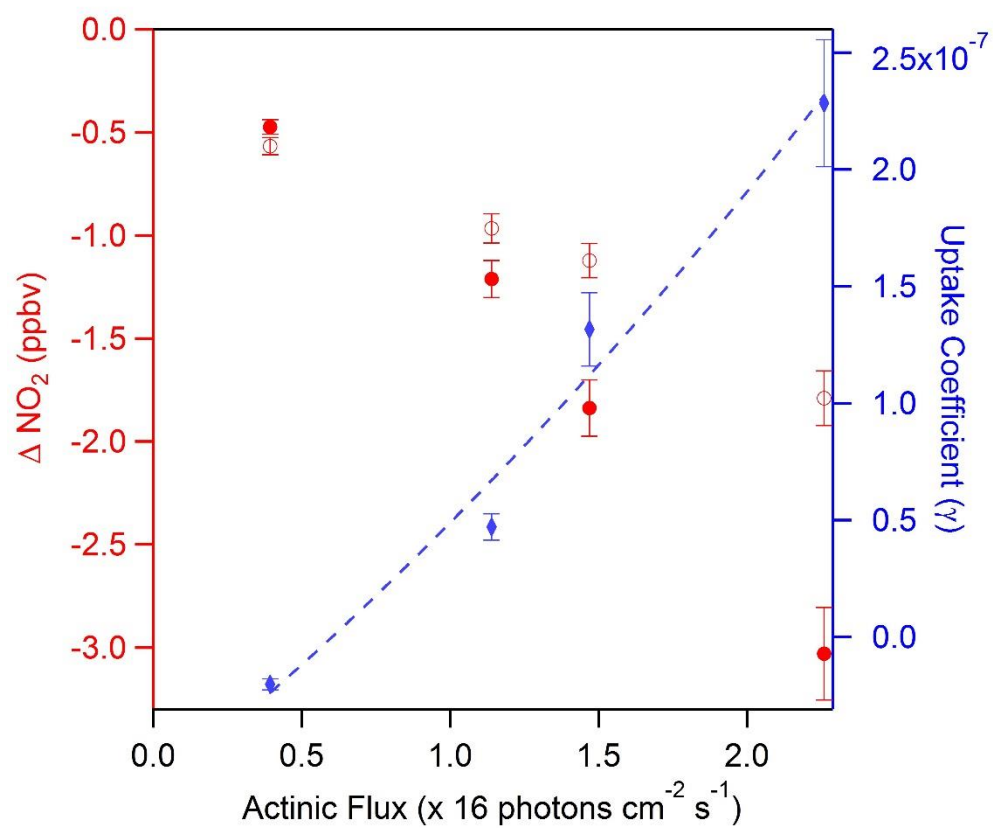


Figure S5

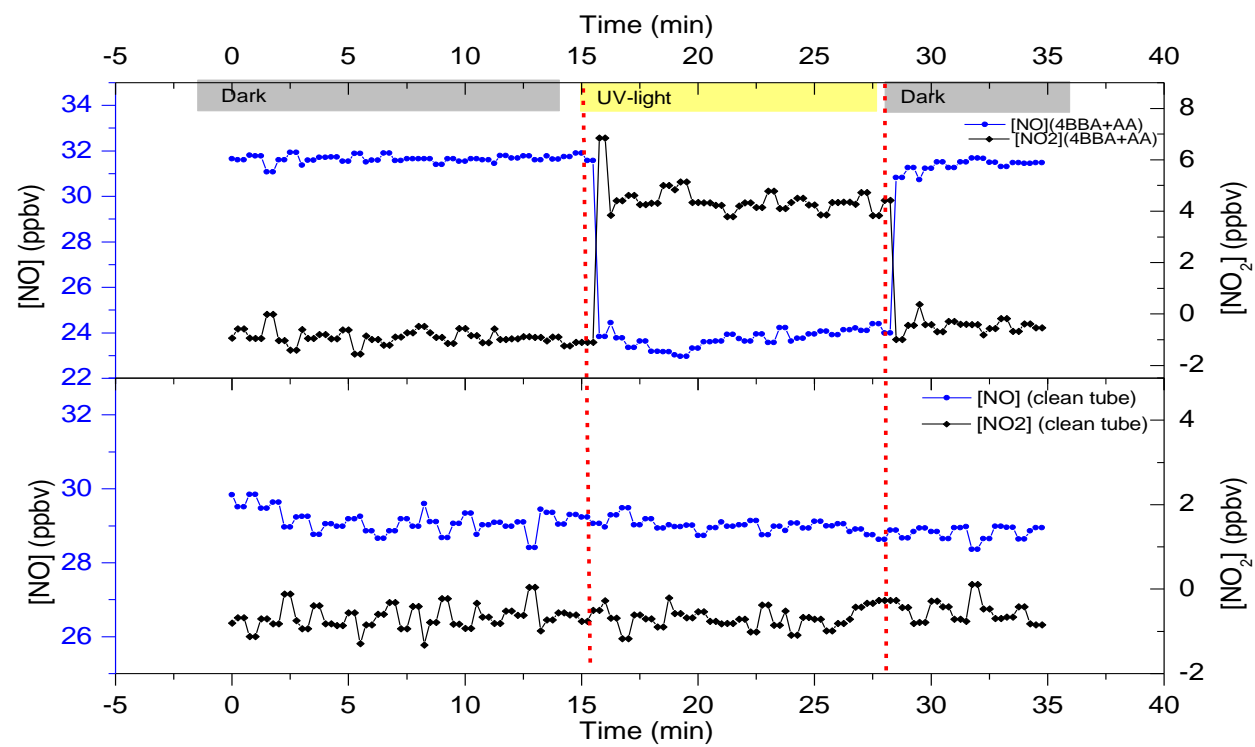


Figure S6