

Supplemental Information

NO₂ actinometry

The actinic flux (photons cm⁻² sec⁻¹) was measured with one, three, five and all seven lamps of the photo reactor turned on using NO₂ actinometry (method A), and independent measurements of the photon actinic flux (method B). With method A, NO₂ in a N₂/O₂ 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 NO₂ 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 NO₂ was about 8 ppbv and in configuration b) it was about 40 ppbv. NO₂ 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 NO₂, J_{NO_2} , in terms of a relative concentration change over time. The decrease in NO₂ was measured by the LED-CE-DOAS (Setup 1) and by the chemiluminescence (Setup 2); the NO₂ 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 NO₂ 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:

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

where $F_{FT}(\lambda)$ is the actinic flux measured in our flow-tube system, $\sigma(\lambda)$ is the NO₂ cross section at 294 K in cm² molecule⁻¹ (Vandaele et al., 2002), and $\Phi(\lambda)$ is the quantum yield data used from Sander et al., 2011. The J -values for NO₂ 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 NO₂, the derived pseudo-first order J_{NO_2} and the uptake coefficient (γ) for a heterogeneous reaction in a cylindrical flow-tube:

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

where $\langle c \rangle$ is the NO₂ 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_2 j-values in s^{-1} 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_2 is short enough at 500 ppbv with respect to its reaction with NO. This ensures a 1 NO:1 HO_2 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_2O ; 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^2). 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 2.26×10^{16} photons $\text{cm}^{-2} \text{s}^{-1}$. 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 $\text{cm}^{-2} \text{s}^{-1}$ 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_{HO_2} increases linearly and saturates at thicknesses $>2 \mu\text{m}$. This shows that the observed HO_2 is produced from the top few micrometers of the films under study.

Figure S5: The photosensitized uptake coefficient of NO_2 (blue diamonds, right axis); this graph shows the inefficiency of NO_2 to compete with O_2 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 NO_2 actinometry experiments (left axis).

Figure S6: NO to NO_2 conversion from similar CWFT experiments performed in a different photosensitizer, 4-BBA. The top figure shows that NO does react with HO_2 to produce 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.

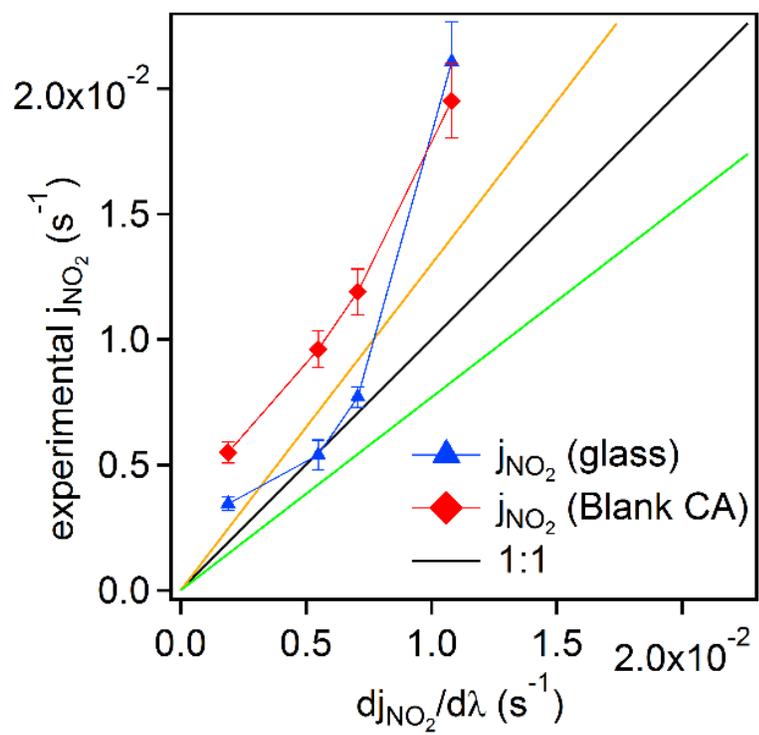


Figure S1

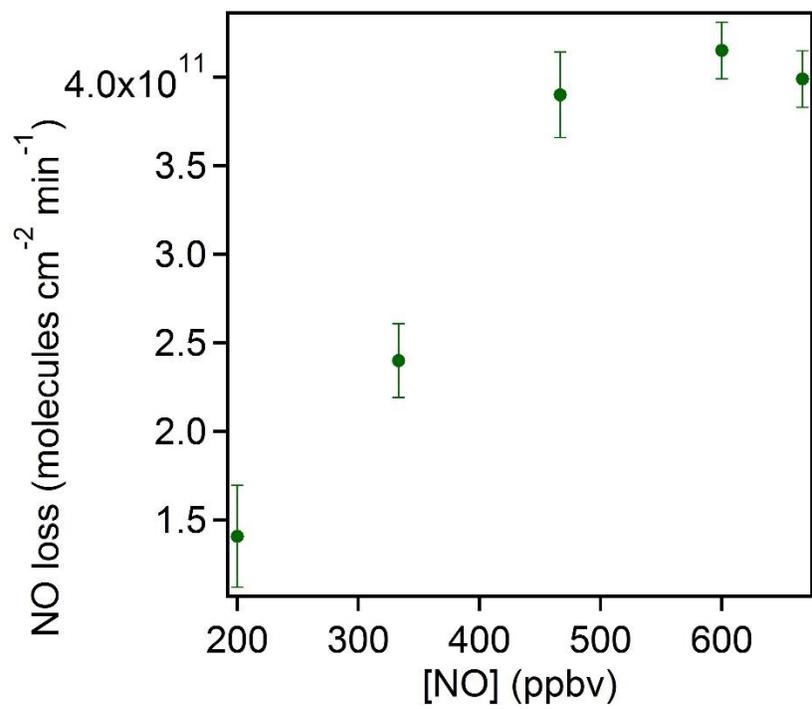


Figure S2

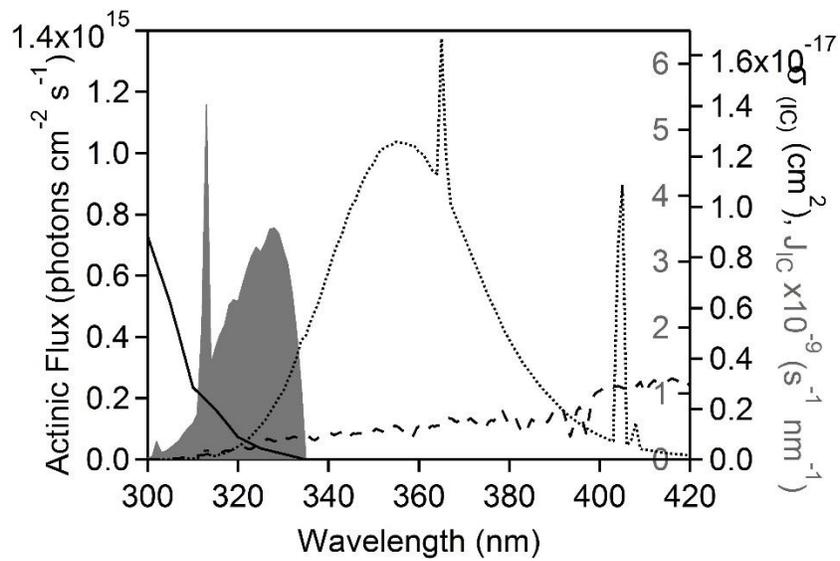


Figure S3

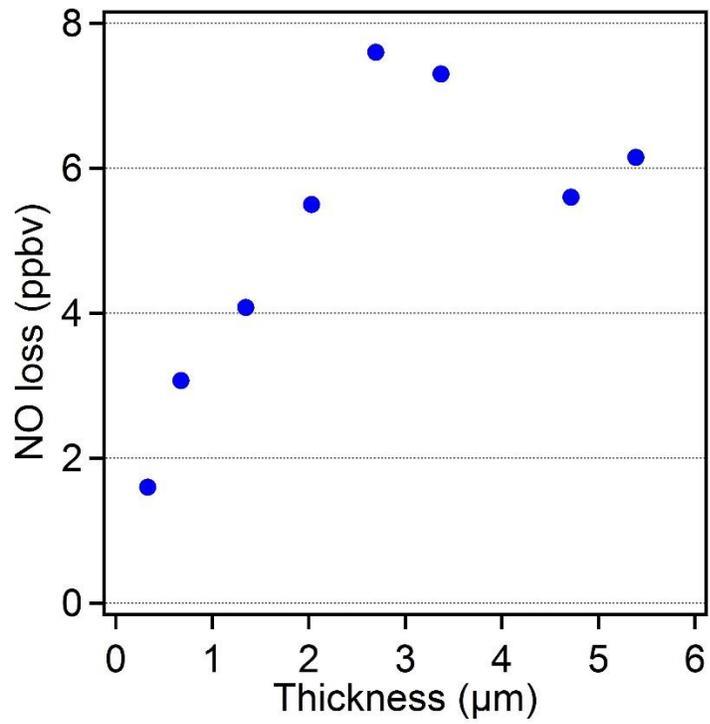


Figure S4

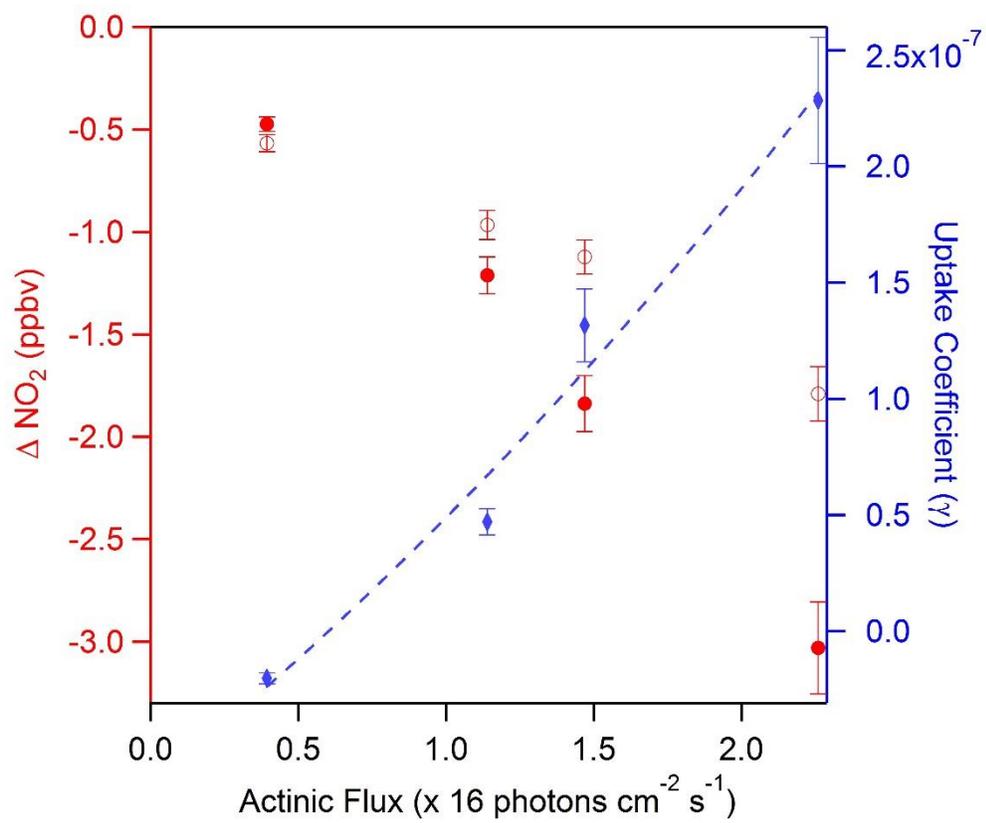


Figure S5

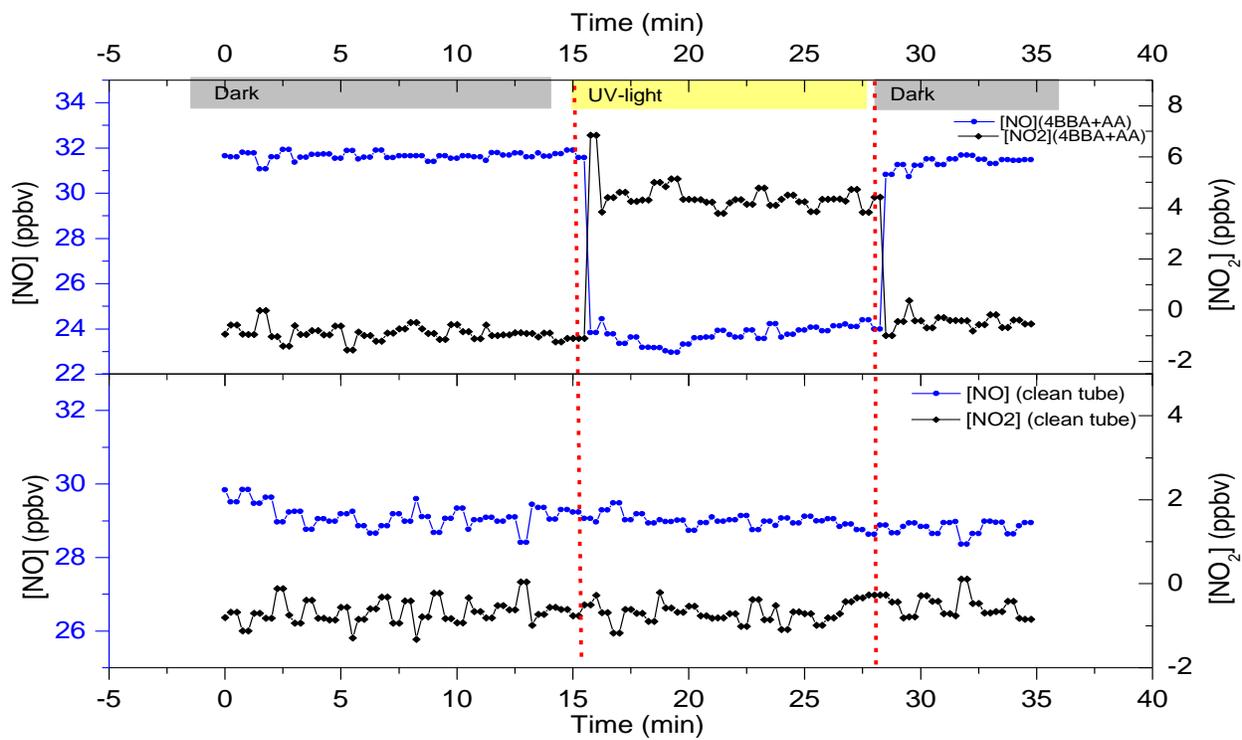


Figure S6