Supplemental Information

Heterogeneous photochemistry of imidazole-2-carboxaldehyde: HO_2 radical formation and aerosol growth

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NO_2 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 NO_2 actinometry (method A), and independent measurements of the photon actinic flux (method B). With method A, NO_2 in a N_2/O_2 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_2 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_2 was about 8 ppbv and in configuration b) it was about 40 ppbv. NO_2 actinometry is based on the following reaction:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (R1)$$

The photolysis constant, *J*, in our case was treated as first-order rate constant, which quantifies the rate of photolysis of NO_2, J_{NO2}, in terms of a relative concentration change over time. The decrease in NO_2 was measured by the LED-CE-DOAS (Setup 1) and by the chemiluminescence (Setup 2); the NO_2 signal was allowed to stabilize, and lights were turned on sequentially. J_{NO2} was calculated using the measurements and the following equation:

$$J_{NO2} = \frac{d\, ln[NO_2]}{dt}, \qquad -ln\left(\frac{[NO_2]_t}{[NO_2]_0}\right) = J_{NO2} \times t \qquad (S1)$$

With all seven lamps turned on, the J_{NO2} was about 2×10^{-2} s^{-1} (Setup 1) and 1×10^{-2} s^{-1} (Setup 2). This is about 2-3 times the ambient *J* at mid-latitudes under summer noon-time conditions. The J_{NO2} 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_2 were calculated using independent measurements of the photon actinic flux of the UV lamps, which had been determined by B. Bohn at Forschungzentrum 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:

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

where $F_{FT}(\lambda)$ is the actinic flux measured in our flow-tube system, $\sigma(\lambda)$ is the NO_2 cross section at 294 K in cm^2 $molecule^{-1}$ (Vandaele et al., 2002), and $\Phi(\lambda)$ is the quantum yield data used from Sander et al., 2011. The *J*-values for NO_2 for methods A and B are compared in Fig. S2, and agree within a factor of 2 (higher J_{NO2} 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^o, The American Society for Testing and Materials, ASTM).

Equation S1 shows the relationship between the loss of NO_2, the derived pseudo-first order J_{NO2} and the uptake coefficient (γ) for a heterogeneous reaction in a cylindrical flow-tube:

$$\frac{d[NO_2]}{dt} = -JNO_2[NO_2] \qquad JNO_2 = \frac{\gamma <c> [\frac{S}{V}]}{4} \qquad (S3)$$

where <c> is the NO_2 mean molecular speed, $(8RT/\pi M)^{1/2}$, and $[\frac{S}{V}]$ is the surface are of the film per gas volume ratio in our flow-tube system. These calculations are represented in Fig. S4.

Figure Captions

Figure S1: 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 S2: NO_2 j-values in s^{-1} from the bare glass and citric acid blank coated flow-tubes in Setup 1.

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 cm^{-2} s^{-1}. Dashed line: a solar actinic flux spectrum for a solar zenith angle of 48°, 37° tilt towards the sun and clear skies (~2×10^{16} photons cm^{-2} s^{-} between 300-420 nm) obtained from the standard spectrum of the American Society for Testing and Materials (ASTM).

Figure S4: 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 [IC] × [CA] film measurements during NO_2 actinometry experiments (left axis).

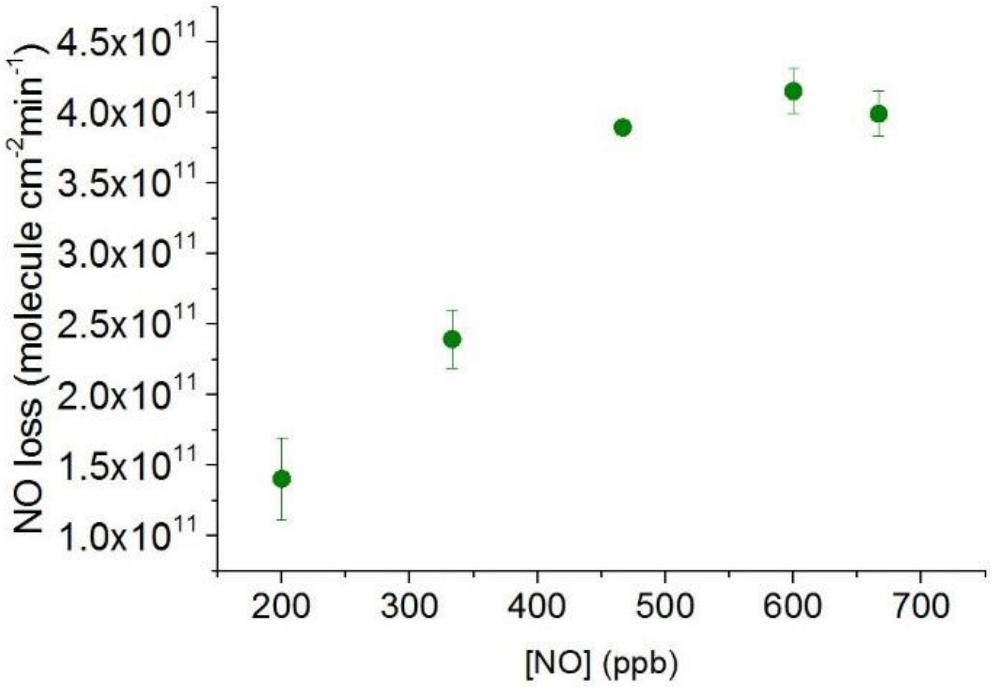
NO loss (molecule cm-2min-1)
4.5x10^11
4.0x10^11
3.5x10^11
3.0x10^11
2.5x10^11
2.0x10^11
1.5x10^11
1.0x10^11
200
300
400
500
600
700
[NO] (ppb)

Figure S1

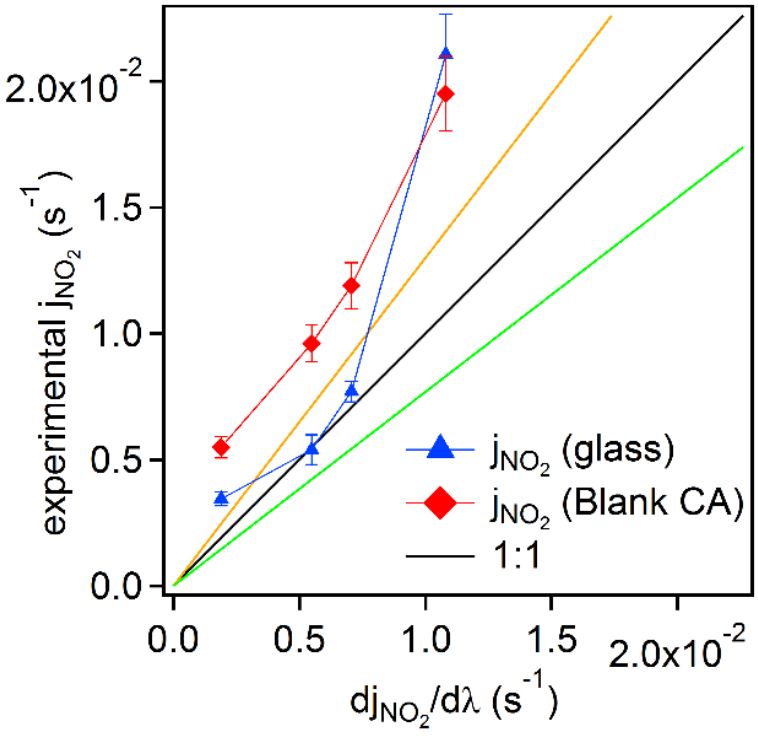
2.0x10-2
1.5
1.0
0.5
0.0
experimental jNO2 (s-1)
0.0
0.5
1.0
1.5
2.0x10-2
djNO2/dλ (s-1)
jNO2 (glass)
jNO2 (Blank CA)
1:1

Figure S2

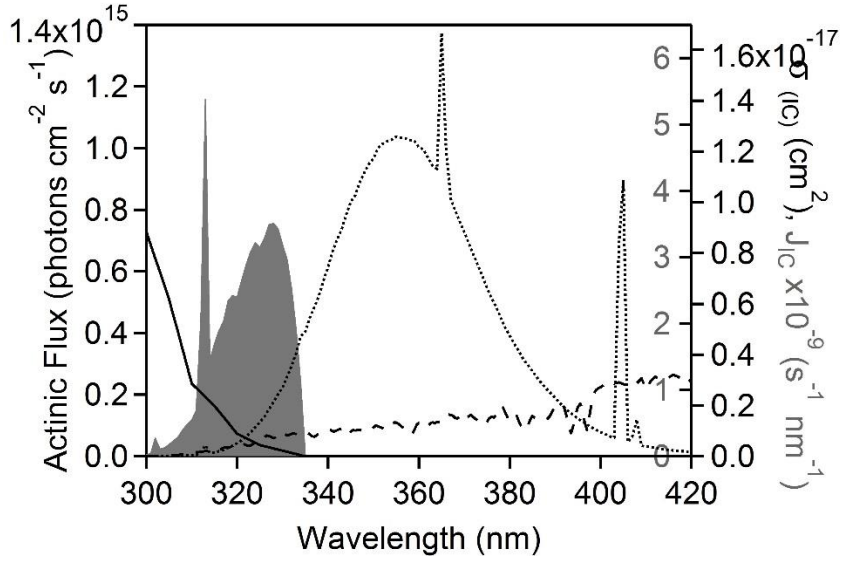
1.4x10^15
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Actinic Flux (photons cm^-2 s^-1)
1.6x10^-17
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
σ(IC) (cm^2), JIC x10^-9 (s^-1 nm^-1)
6
5
4
3
2
1
0
300
320
340
360
380
400
420
Wavelength (nm)

Figure S3

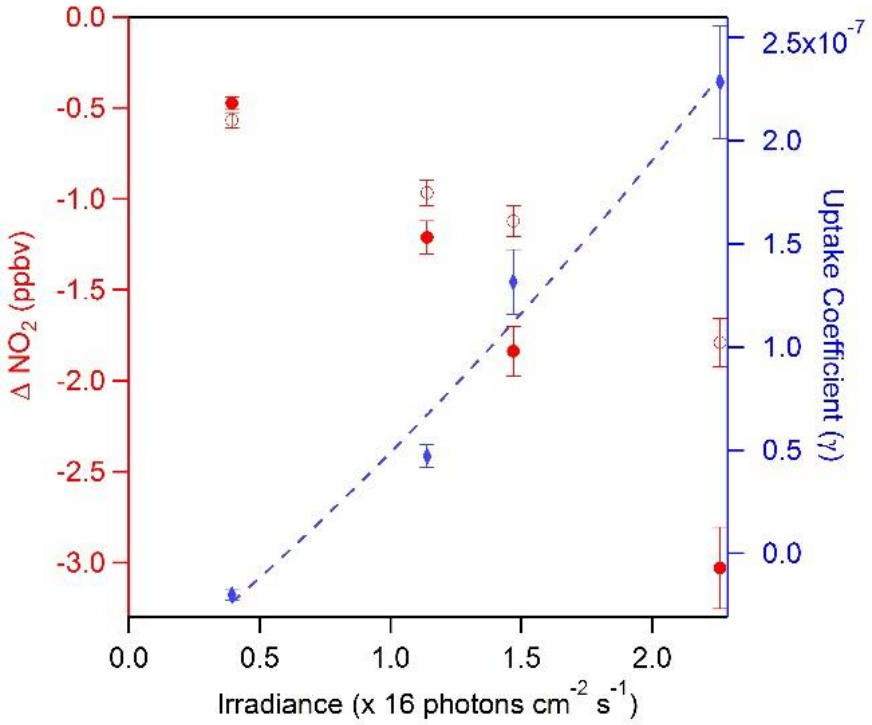
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
Δ NO2 (ppbv)
2.5x10-7
2.0
1.5
1.0
0.5
0.0
Uptake Coefficient (γ)
0.0
0.5
1.0
1.5
2.0
Irradiance (x 16 photons cm-2 s-1)

Figure S4