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Actinometric measurements of NO<sub>2</sub> photolysis frequencies in the atmosphere simulation chamber SAPHIR

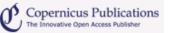
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Abstract. The simulation chamber SAPHIR at Forschungszentrum Jülich has UV permeable teflon walls facilitating atmospheric photochemistry studies under the influence of natural sunlight. Because the internal radiation field is strongly affected by construction elements, we use external, radiometric measurements of spectral actinic flux and a model to calculate mean photolysis frequencies for the chamber volume Bohn04B. In this work we determine NO<sub>2</sub> photolysis frequencies  $j(NO_2)$  within SAPHIR using chemical actinometry by injecting  $\mathrm{NO}_2$  and observing the chemical composition during illumination under various external conditions. In addition to a photo-stationary approach, a time-dependent method was developed to analyse the data. These measurements had two purposes. Firstly, to check the model predictions with respect to diurnal and seasonal variations in the presence of direct sunlight and secondly to obtain an absolute calibration factor for the combined radiometry-model approach. We obtain a linear correlation between calculated and actinometric  $j(NO_2)$ . A calibration factor of 1.34±0.10 is determined, independent of conditions in good approximation. This factor is in line with expectations and can be rationalised by internal reflections within the chamber. Taking into account the uncertainty of the actinometric  $j(NO_2)$ , an accuracy of 13% is estimated for the determination of  $j(NO_2)$  in SAPHIR. In separate dark experiments a rate constant of  $(1.93\pm0.12)\times10^{-14}$  cm<sup>3</sup> s<sup>-1</sup> was determined for the NO+O<sub>2</sub> reaction at 298K using analytical and numerical methods of data analysis.

■ Final Revised Paper (PDF, 857 KB) ■ Discussion Paper (ACPD)

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