

Interactive comment on “Actinometric measurements of NO₂ photolysis frequencies in the atmosphere simulation chamber SAPHIR” by B. Bohn et al.

Anonymous Referee #3

Received and published: 2 January 2005

The SAPHIR chamber was designed to test our current understanding of tropospheric photochemistry under natural daylight conditions. It goes without saying that such tests can only be successful if the experimental boundary conditions such as the photolysis frequency of NO₂ inside the chamber can be quantified accurately and with good time resolution. This is not a trivial problem mainly because the actinic flux inside the SAPHIR chamber is modulated by construction elements that affect direct sunlight and diffuse sky radiation in different ways, depending also on season and time of day. Although the results of this study (except for the determination of the rate constant k_4 , see below) are specific for the SAPHIR chamber, they are scientifically valuable in a

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wider sense because the quality of future studies with SAPHIR is critically dependent on this work.

This well written paper describes careful measurements of photolysis frequencies $j(\text{NO}_2)$ in the SAPHIR chamber by chemical actinometry under extremely clean and therefore chemically well defined conditions (but see under “specific comments”). This allows an extremely simple treatment of the unperturbed Leighton reactions to be made, based entirely on very accurate measurements of NO, NO₂, and ozone in the chamber. When the actinic light intensity changes slowly the photo-stationary state assumption can be made, and $j(\text{NO}_2)_{\text{PS}}$ can be directly obtained from the Leighton equation. However, due to the excellent accuracy and time resolution of the NO and NO₂ measurements and the absence of peroxy radical forming impurities, a simple correction can be made to obtain time-dependent photolysis frequencies $j(\text{NO}_2)_{\text{TD}}$ when deviations from the photo-stationary state are significant.

The determination of the rate constant k_4 for the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (which turned out to be in good agreement with literature data although the conditions were not optimal for its determination) is a minor by-product of the presented work. It merely shows that the trace gas detectors were working properly and that the system (including the leak rate correction) is well understood. Note that it is implicitly assumed in section 3.1.1 that the reaction $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ and all subsequent reactions do not affect the determination of k_4 . We suggest that the impact of these additional reactions is briefly addressed. Have they been included in the numerical analysis, section 3.1.2?

Since it is not feasible to monitor $j(\text{NO}_2)$ by actinometry in SAPHIR while the chamber is used for studies of more complex tropospheric chemistry, it is the goal of the paper to relate $j(\text{NO}_2)_{\text{TD}}$ with spectroradiometric measurements of the DOWNWELLING actinic flux (although this is not explicitly mentioned) which are simultaneously carried out at a fixed location close to the chamber. The most important issue of the paper (although not reflected by the title) is an extremely careful determination of the scal-

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ing factor $hC = j(\text{NO}_2)\text{TD}/j(\text{NO}_2)\text{SRTM}$, where SRTM stands for “SAPHIR Radiative Transmission Model”. This scaling factor can be used in future tropospheric chemistry studies in SAPHIR to obtain $j(\text{NO}_2)$ inside the chamber from time-resolved radiometer measurements outside. However, the significance of the scaling factor hC cannot be fully appreciated without thoroughly reading the previously published paper by Bohn and Zilken on “Model-aided radiometric determination of photolysis frequencies in a sunlit atmosphere simulation chamber”. There it is shown that the actinic flux inside SAPHIR (and thereby $j(\text{NO}_2)$) can be obtained from spectroradiometric measurements outside the chamber by means of numerical calculations based on SRTM, except for the scaling factor which must be determined experimentally.

The authors conclude from a series of simultaneous measurements of $j(\text{NO}_2)\text{TD}$ by chemical actinometry and $j(\text{NO}_2)\text{SRTM}$ by spectroradiometry which were carried out under cloudless as well as cloudy conditions and for different seasons that a unique scaling factor hC can be used within the given error limits for all seasons and also for cloud-free as well as cloudy conditions. In this context we would like to point out an inconsistency between the paper of Bohn and Zilken and this manuscript: equation (9) in the paper of Bohn and Zilken defines hC as a wavelength-dependent quantity which should rather be termed $hC(\lambda)$; although the scaling factor is not clearly defined in the present manuscript it is implicitly defined in section 4.1 as $hC = j(\text{NO}_2)\text{TD}/j(\text{NO}_2)\text{SRTM}$. We suggest that this definition is explicitly given in the text.

Specific comments: The authors mention in section 3.1 that some HONO is generated in the chamber. This is a small photochemical source of OH radical which is not expected to perturb the Leighton scheme because no peroxy radicals are formed in the absence of VOCs. However, peroxy radicals could also be formed if the chamber air contained significant amounts of CO. What is the level of CO in the SAPHIR chamber?

Technical suggestion: I was confused that the two panels in Figure 6 look so different although both show plots of $j(\text{NO}_2)\text{SR}$ versus $j(\text{NO}_2)\text{CA}$. We suggest to replace $j(\text{NO}_2)\text{CA}$ by $j(\text{NO}_2)\text{PS}$ on the abscissa of the left panel, and $j(\text{NO}_2)\text{CA}$ by $j(\text{NO}_2)\text{TD}$

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on the right.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 8141, 2004.

ACPD

4, S3180–S3183, 2004

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