**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Actinometric measurements of NO$_2$ photolysis frequencies in the atmosphere simulation chamber SAPHIR" *by* B. Bohn et al.

B. Bohn et al.

We thank referee #3 for the review. Specific comments are addressed below.

1. The reaction NO$_2$ + O$_3$ → NO$_3$ + O$_2$ and consecutive reactions of NO$_3$ were considered in the numerical data analysis but not in the analytical analysis. Because the reaction NO + NO$_3$ → 2 NO$_2$ is very fast, the presence of NO$_3$ could pretend a faster NO + O$_3$ reaction. However, NO$_3$ formation is slow, making this influence negligible. We tested this by switching off the NO$_2$ + O$_3$ reaction in the numerical data analysis. This resulted in fitted scaling factors for the NO + O$_3$ rate constant within 1% compared to the full model. We'll mention this in a revised manuscript.

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2. The fact that we use external measurements of down-welling 2π sr spectral actinic flux for our compilation of photolysis frequencies will be noted in the introduction and experimental section.

Besides the verification of the time-dependent effects predicted by the SRTM model, the determination of the factor h^c is indeed one of the main purposes of the present work. However, we consider it difficult to reflect this in the title of the paper without making it too extensive. The close relationship between the present work and that of Bohn and Zilken (Atmos. Chem. Phys. 5, 191-206, 2005) is explained in the abstract. Although it would emphasise the relevance of the factor h^c, we avoided to give more details on the model in the present work because of the complexity of the SRTM model.

3. The factor h^c will be defined more explicitly as the ratio $j(\text{NO}_2)_{\text{TD}}/j(\text{NO}_2)_{\text{SRTM}}$ in Sects. 4.1 and 4.2. Concerning the wavelength dependence of the factor the situation is a bit ambiguous. In principle h^c is expected to be wavelength dependent because it compensates for internal reflections which could depend on wavelength. On the other hand, part of this dependence is already included in the relative wavelength dependence applied within the SRTM model which is based on a comparison of spectral actinic flux measurements within and outside the chamber. Moreover, 4π measurements within the chamber give no indication for a strong wavelength dependence. For the time being we therefore use for all wavelengths the effective h^c determined in this work for $j(\text{NO}_2)$ which will be denoted $h^c_{\text{jNO}_2}$ for clarification. As mentioned in the conclusions we have to check this assumption experimentally for example by an actinometric measurement of $j(\text{O}^1\text{D})$.

4. CO is measured continuously within SAPHIR. Unless CO is added to the system, levels are below the detection limit (10 ppb) in the synthetic air produced from the high purity liquid N_2 and O_2 supplies. However, as mentioned in Sect 3.1, there is a residual reactivity of the synthetic air within SAPHIR with respect to OH radicals corresponding to CO concentrations in a range 100-300 ppb. This reactivity cannot be accounted for by compounds detectable with our GC systems but it can be quantified

by modelling the increase of O_3 and NO_x (from HONO photolysis). For details please refer to the paper by Rohrer et al. (Atmos. Chem. Phys. Discuss., 4, 7881-7915, 2004). Consequently, the increase of O_3 concentration indicates the presence of HO_2 or RO_2 radicals. However, as shown in Sect. 3.2 the influence of these processes on the determination of the actinometric photolysis frequencies is negligible.

5. The technical modifications suggested for Fig. 6 will be made.

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

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