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Actinometric measurements of NO\textsubscript{2} 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 (Bohn and Zilken, 2005). In this work we determine NO\textsubscript{2} photolysis frequencies \(j(\text{NO}_2)\) within SAPHIR using chemical actinometry by injecting NO\textsubscript{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 \(j(\text{NO}_2)\). A calibration factor of \(1.34 \pm 0.10\) 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 \(j(\text{NO}_2)\), an accuracy of 13% is estimated for the determination of \(j(\text{NO}_2)\) in SAPHIR. In separate dark experiments a rate constant of \((1.93 \pm 0.12) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\) was determined for the NO+O\textsubscript{3} reaction at 298 K using analytical and numerical methods of data analysis.

1 Introduction

Photolysis processes are very important for atmospheric chemistry. For example, photolysis of NO\textsubscript{2} followed by reaction of O-atoms with O\textsubscript{2} is a major source of tropospheric ozone:

\[
\text{NO}_2 + h\nu(\lambda \leq 420 \text{ nm}) \rightarrow \text{O}(^3\text{P}) + \text{NO} \quad (1)
\]

\[
\text{O}(^3\text{P}) + \text{O}_2 \rightarrow \text{O}_3 \quad (2)
\]

Photolysis frequencies \(j\) are first-order rate constants quantifying the rate of photolysis processes in terms of a relative concentration change of the precursor molecule (or a photoproduct). For Reaction (1):

\[
j(\text{NO}_2) = -\frac{1}{[\text{NO}_2]} \frac{d[\text{NO}_2]}{dt} \quad (3)
\]

Of course, Eq. (3) is valid only in the absence of other NO\textsubscript{2} loss or formation processes and cannot be used to determine \(j(\text{NO}_2)\) from NO\textsubscript{2} concentration measurements in complex, natural systems. In the troposphere for example, NO\textsubscript{2} loss by photolysis is partly compensated by reaction of NO with O\textsubscript{3} or peroxy radicals (RO\textsubscript{2}):

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (4)
\]

\[
\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO} \quad (5)
\]

However, in simpler artificial chemical systems, photolysis frequencies can be determined by monitoring the gas-phase composition. This technique is well established since many years and referred to as chemical actinometry. A recent study by Shetter et al. (2003) gives an overview of previous work concerned with actinometric \(j(\text{NO}_2)\) measurements. In the case of Reaction (1), a quartz flow-tube exposed to sunlight can be used where the carrier gas is loaded with a known concentration of NO\textsubscript{2}. Photolysis frequencies are then determined from the increase of NO concentration as a function of exposure time.

The complex instrumentation needed to obtain a single photolysis frequency is a drawback of chemical actinometry.
the absorption cross sections is measured and photolysis frequencies are calculated using the quantum yield of the precursor molecule and the quantum yield $\phi$ of the photo-products (e.g. Hofzumahaus et al., 1999). In the case of Reaction (1):

$$j(\text{NO}_2) = \int \sigma(\text{NO}_2) \phi(O^3P) F_\lambda(\lambda) \, d\lambda.$$ (6)

Recent comparisons show that chemical actinometry and spectroradiometry give consistent results within better than 10% with respect to NO$_2$ and O$_3$ photolyses (Kraus et al., 2000; Shetter et al., 2003; Hofzumahaus et al., 2004). In the case of NO$_2$ photolysis the agreement is even within 5% in a study from our laboratory (Kraus et al., 2000) using molecular data $\sigma(\text{NO}_2)$ and $\phi(O^3P)$ by Merienne et al. (1995) and Troe (2000), respectively, as recently recommended by Atkinson et al. (2004).

The spectroradiometric approach is not as straightforward for the atmosphere simulation chamber SAPHIR at Forschungszentrum Jülich (Fig. 1). SAPHIR was created to study tropospheric chemistry unaffected by transport processes at ambient levels of trace gas concentrations. As in the real troposphere, chemistry is driven by photolysis of trace gases induced by natural sunlight entering the chamber through UV-permeable teflon walls. However, the radiation field inside the chamber is complex and radiometric point measurements are not representative for the reactor as a whole.

In a preceding paper (Bohn and Zilken, 2005) a model was developed predicting time-dependent, volume-mean photolysis frequencies for the simulation chamber. This approach will be denoted SRTM (SAPHIR Radiative Transmission Model) in the following. The model uses external spectroradiometric measurements of direct and diffuse down-welling $2\pi$ sr solar actinic flux as input and considers the influence of opaque chamber elements and chamber teflon walls. Basically, time and wavelength dependent, relative scaling factors for the external diffuse and direct fluxes are derived. Time dependent effects are most pronounced for direct sunlight while wavelength dependence is induced by the chamber walls leading to an increase of transmission with wavelength by about 20% in the range 300–400 nm. As an example for the nature and magnitude of the predicted effects, Fig. 2 shows a comparison of $j(\text{NO}_2)$ measured externally by a spectroradiometer (SR) and calculated by SRTM. However, so far SRTM calculations are on a relative basis and need confirmation on an absolute level. Moreover, the predicted time-dependencies have to be checked experimentally before this method can be used for routine measurements of photolysis frequencies in SAPHIR, as intended.

In this work we present measurements of $j(\text{NO}_2)$ using the simulation chamber as a chemical actinometer. This is achieved by injecting NO$_2$ into the clean chamber. Upon illumination, photolysis of NO$_2$ leads to formation of NO and O$_3$ (Reactions 1 and 2). After a delay dependent on experimental conditions, a photochemical equilibrium establishes where losses of NO$_2$ by photolysis are compensated by the NO+O$_3$ reaction. From the equilibrium concentrations of NO, O$_3$ and NO$_2$ $j(\text{NO}_2)$ can be calculated. In addition we consider deviations from photochemical equilibrium by a time-dependent approach to derive photolysis frequencies under variable external conditions. The actinometric $j(\text{NO}_2)$ are then compared with radiometric SRTM predictions. Clear sky conditions at different seasons as well as overcast conditions were investigated. Furthermore, the rate constant of Reaction (4) is determined in separate dark-experiments under the experimental conditions in SAPHIR.

2 Experimental

2.1 Simulation chamber

The simulation chamber SAPHIR consists of a double-wall teflon (FEP) tube held in a steel frame (Fig. 1). FEP film has been selected because it is chemically inert and UV permeable. The inner tube is used as a reactor for simulation experiments. It has a volume of 270 m$^3$ and can be flushed with dry or wet synthetic air (purity 99.9999%) loaded with a variety of trace gases if required. The space between the inner and the outer tube ($\approx$0.1 m) is permanently flushed with synthetic air to prevent diffusion of gases from outside. Typical leak rates for the reactor are 3–8 m$^3$ h$^{-1}$. The chamber can be covered by a movable, opaque roof construction within about 1 min and vice versa. More details concerning the instrumentation and performance of SAPHIR are given by Rohrer et al. (2004).
2.2 Actinometry

In actinometric experiments typically 20–50 ppb of NO$_2$ (500 ppm in N$_2$, Messer Griesheim) were injected into the dark chamber filled with dry air in the absence of any VOCs ($\leq$ 2 ppt, GC analysis). After about 30 min delay to allow for homogeneous mixing, the roof was opened and photochemistry started notable by a decrease of NO$_2$ concentration and a corresponding increase of NO and O$_3$ concentrations. Measurements of trace gases were made close to the centre of the chamber 1 m above chamber ground. Ozone was measured by a commercial UV absorption instrument (Ansysco, O3 41M) with a precision of 0.3–0.5 ppb and an accuracy of 3%. NO and NO$_2$ were measured by a chemiluminescence technique with a modified commercial instrument (Eco Physics, TR 780). The precisions are about 5 ppt and 10 ppt at NO=0 and NO$_2$=0, respectively, and about 0.1% at 50 ppb for both compounds. NO$_2$ is photolytically converted to NO prior to detection (Eco Physics, PLC 760). Absolute accuracy and the efficiency of the photolytic converter are checked by regular comparisons with certified NO test gas (2 ppm NO in N$_2$, BOC Gases) and by gas phase titrations of NO with O$_3$. The accuracy is 5% for NO, 10% for NO$_2$ and 5% for the NO/NO$_2$ ratio. Measurements were made every 50 s with regular switching between NO and NO$_2$ measurement modes. More details of this technique are given by Rohrer et al. (1998). Temperature and pressure measurements were made using an ultrasonic anemometer (Metek, USA-1) via sound velocity and a capacity pressure gauge (Setra Systems, 270), respectively. Temperature within the reactor cannot be controlled. It typically lies about 0–5 K above ambient temperature, dependent on conditions.

2.3 Spectroradiometry and model calculations

During the actinometric chamber experiments the down-welling 2$\pi$ sr solar actinic flux was measured externally by a spectroradiometer on the roof of a nearby building. Spectra were recorded about every 2 min in the range 280–420 nm with a distinction of diffuse and direct sunlight by using a shadow ring. More details concerning these measurements are given by Hofzumahaus et al. (1999) and Bohn and Zilken (2005). From these measurements solar actinic flux spectra and photolysis frequencies are derived for the simulation chamber using SRTM calculations (Bohn and Zilken, 2005).

3 Results and discussion

3.1 Rate constant of the O$_3$+NO reaction

The rate constant of Reaction (4) is essential to determine $j$(NO$_2$) by actinometry. $k_4$ can be obtained in separate dark-experiments by closing the roof of SAPHIR after the actinometric experiments described in Sect. 2.2. NO subsequently reacts with O$_3$ forming NO$_2$ until one or both reactants are used up. Although the chemical system is simple, data analysis is not straightforward because starting concentrations of NO and O$_3$ are not identical. As a consequence, dilution is affecting the reactants differently. Although dilution is slow ($\leq$10$^{-5}$ s$^{-1}$), it cannot be neglected for the dark reactions because the decay of the reactants takes hours at the concentration levels used. On the other hand, dilution can be treated as a first-order loss process for any species because the chamber behaves like an ideal stirred reactor in good approximation.

The reason for the different starting concentrations of NO and O$_3$ is the presence of small amounts of HONO produced by the chamber walls at illumination (Rohrer et al., 2004). The formation rate of HONO is usually small at dry conditions ($\approx$50 ppt h$^{-1}$) but photolysis of HONO leads to a small net production of NO. On the other hand, after a longer period of illumination there is a tendency towards a net O$_3$ production, probably induced by reaction of OH (from HONO photolysis) with traces of VOCs not accounted for by GC analysis. The background reactivity with respect to OH can be expressed in terms of a hypothetical CO concentration of typically 100–300 ppb (Rohrer et al., 2004). However, CO is just a proxy for unknown reactants because CO levels are continuously monitored and usually below the detection limit (10 ppb). These interferences are leading to certain levels of HO$_2$ or RO$_2$ radicals upon illumination (see Sect. 3.2) and small differences of NO and O$_3$ starting concentrations for the dark experiments.

![Diurnal variation of $j$(NO$_2$)](image-url)
This equation was solved using the solution of Bernoulli’s equation:

\[ \frac{d[\text{NO}]}{dt} = -k_4[\text{NO}][\text{O}_3] - k_{\text{dil}}[\text{NO}] \]  \hspace{1cm} (7)

\[ \frac{d[\text{O}_3]}{dt} = -k_4[\text{NO}][\text{O}_3] - k_{\text{dil}}[\text{O}_3] \]  \hspace{1cm} (8)

\[ \frac{d[\text{NO}_2]}{dt} = k_4[\text{NO}][\text{O}_3] - k_{\text{dil}}[\text{NO}_2] \]  \hspace{1cm} (9)

Here \( k_{\text{dil}} \) is the first-order rate constant of loss by dilution. Utilising the additional relations:

\[ [\text{NO}_3] = [\text{NO}_2] + [\text{NO}] \]  \hspace{1cm} (10)

\[ [\text{NO}] = ([\text{NO}_2]_0 + [\text{NO}]_0) \exp(-k_{\text{dil}} t) \]  \hspace{1cm} (11)

the system of differential equations can be reduced to a single equation:

\[ \frac{d[\text{NO}]}{dt} = -k_4[\text{NO}] ([\text{NO}] - [\text{O}_3]) \]  \hspace{1cm} (12)

This equation was solved using the solution of Bernoulli’s differential equation:

\[ [\text{NO}] = \frac{D ([\text{NO}]_0 - [\text{O}_3]_0)}{1 - [\text{O}_3]_0/([\text{NO}]_0 - [\text{O}_3]_0) \exp(k_4/k_{\text{dil}}) \exp([\text{NO}]_0 - [\text{O}_3]_0) (D - 1)} \]  \hspace{1cm} (13)

In the succeeding two sections, analytical and numerical methods of data analysis will be used to determine \( k_4 \) from the experimental NO, NO\(_2\) and O\(_3\) concentration traces.

### 3.1.1 Analytical solution

The dark-reactions can be described by the following set of differential equations:

\[ \frac{d[\text{NO}]}{dt} = -k_4[\text{NO}][\text{O}_3] - k_{\text{dil}}[\text{NO}] \]  \hspace{1cm} (7)

\[ \frac{d[\text{O}_3]}{dt} = -k_4[\text{NO}][\text{O}_3] - k_{\text{dil}}[\text{O}_3] \]  \hspace{1cm} (8)

\[ \frac{d[\text{NO}_2]}{dt} = k_4[\text{NO}][\text{O}_3] - k_{\text{dil}}[\text{NO}_2] \]  \hspace{1cm} (9)

In Table 1 conditions of four experiments are summarised. Temperatures could not be kept constant and typically decreased by 6–8 K during the experiments. The temperatures listed in Table 1 are averages from the early periods of the experiments in which the NO concentrations dropped to 10% of the starting concentrations (within about 1–2 h after closing the roof). These temperatures are accurate within about 1 K and were assigned to the rate constants obtained from the fits. However, the temperatures of Table 1 are not representative for the later periods of the experiments where temperatures dropped more strongly. The numerical analysis described in the next section therefore uses actual temperatures for the whole period and rate constants \( k_4 \) are determined in terms of scaling factors with respect to a currently recommended temperature dependent rate expression (Sander et al., 2003):

\[ f_4 = \frac{k_4(T)}{3.0 \times 10^{-12}\text{cm}^3\text{s}^{-1}\exp(-1500\text{K}/T)} \]  \hspace{1cm} (14)

To allow a comparison these scaling factors are also used here to specify the analytical results listed in Table 1.

In all four experiments the scaling factors are close to unity within 3%. The average corresponds to a rate constant of \( 1.98 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \) at 298 K. A 5% error is estimated for the assumption of constant temperatures during the experiments. Together with the uncertainties of the NO\(_x\) measurements we evaluate a 7% error limit for the rate constant. To
check for consistency, dilution rate constants were also determined by fitting the exponential decay $D$ of Eq. (13) to the NO$_4$ data. The $k_d$ are similar within 2% compared to the results obtained by fitting Eq. (13).

3.1.2 Numerical analysis

Equation (13) shows that analytical solutions are getting complex and inflexible even for a fairly simple chemical system. A drawback of Eq. (13) is that dilution and temperature are assumed constant during the experiments. Although this is correct in good approximation, the use of measured, time-dependent temperatures and dilution rates calculated from the flow rates of the gas-supplying system (Rohrer et al., 2004) are more appropriate. For that reason a numerical method was used where time-dependent experimental boundary conditions are considered and the system of differential equations (Eqs. 7–9) is solved numerically using EASY (Brauers and Rohrer, 1999) which is an interface for the FACSIMILE integrator with time dependent boundary values and the Levenberg-Marquardt algorithm for fitting. The results of the numerical data analysis are also summarised in Table 1. Only three experiments could be analysed because flow rates were not monitored in one of the experiments. The averaged scaling factor corresponds to a rate constant of 1.93×10$^{-14}$ cm$^3$ s$^{-1}$ at 298 K. Taking into account the uncertainty of the NO$_4$ measurements and the reproducibility of the result, we estimate a 6% error limit for this rate constant.

In the numerical approach also the slow reaction:

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$$

(15)

and consecutive reactions of the NO$_3$ radical were considered, e.g. the fast reaction NO$_3$+NO→2NO$_2$. However, switching off Reaction (15) in the numerical analysis led to fitted scaling factors within 1% compared to the full model, i.e. neglecting Reaction (15) in the analytical approach is justified.

In summary, both methods of data analysis yield consistent results with averaged scaling factors very close to unity within 2%. Our data therefore confirm the recommendation by Sander et al. (2003) (Eq. 14, $k_d(298 \text{K})=1.95\times10^{-14}$ cm$^3$ s$^{-1}$) which will be used in the following experiments aiming at photolysis frequencies. It should be noted that a recently recommended Arrhenius expressions by Atkinson et al. (2004) is lower by 12% at 298 K.

3.2 Photolysis frequencies from trace gas concentrations

The idea behind chamber actinometry is to derive mean photolysis frequencies from concentrations of trace gases within the reactor. After injection of NO$_2$ into the chamber, photolysis of NO$_2$ leads to formation of O$_3$ and NO. On the other hand, reaction of these photo-products regenerates NO$_2$. A

\begin{align*}
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_2 + \text{O}_3 & \rightarrow 2 \text{NO}_2
\end{align*}

\begin{align*}
\frac{d[\text{NO}_2]}{dr} &= -j(\text{NO}_2)[\text{NO}_2] + k_d[\text{O}_3][\text{NO}] = 0 \\
k_d &\text{known, } j(\text{NO}_2) \text{ can be calculated from the equilibrium concentrations of NO}_2, \text{O}_3 \text{ and NO: }
\end{align*}

\begin{align*}
j(\text{NO}_2)_{PS} &= \frac{k_d[\text{O}_3][\text{NO}]}{[\text{NO}_2]} \\
\text{In this photo-stationary (PS) approach losses by dilution are neglected and } j(\text{NO}_2) \text{ is assumed constant. Dilution is indeed too slow to influence the photochemical equilibrium with } j(\text{NO}_2) \text{ typically more than two orders of magnitude greater than } k_d. \\

\text{The PS approach remains reasonable if } j(\text{NO}_2) \text{ changes slowly compared to the relaxation time of the photochemical system. This is the case for example under clear-sky conditions where } j(\text{NO}_2) \text{ exhibits a smooth change in the course of a day. However, under cloudy conditions } j(\text{NO}_2) \text{ often changes rapidly which leads to a departure from photochemical equilibrium. As a consequence, a different, time-dependent approach (TD) was used to retrieve } j(\text{NO}_2) \text{ from the trace gas concentrations and their changes. The differential equation describing the time-dependence of the NO concentration, }
\end{align*}

\begin{align*}
\frac{d[\text{NO}]}{dr} &= -k_d[\text{NO}][\text{O}_3] + j(\text{NO}_2)_{TD}[\text{NO}_2]
\end{align*}
is assumed as an upper limit and attributed to NO
development of NO concentrations. For example, if a formation rate of 1 ppb/h of O
spread by NO+O
3
x.

The concentration changes in Fig. 4 are superposed by continuous dilution as reproduced by NOx. Although the experiment starts with a small residue of NO left behind from an actinometric experiment on the previous day (Fig. 5), there is a slight built-up of O3 resulting in a residue of about 1 ppb at the end of the day. These imbalances were explained qualitatively in Sect. 3.1. However, the influence of the underlying processes on the photochemical equilibrium are insignificant. For example, if a formation rate of 1 ppb/h of O3 is assumed as an upper limit and attributed to NO2 photolysis preceded by oxidation of NO by HO2 (or RO2) radicals, the

contribution to the continuous, total NO2 formation (mainly by NO+O3) is well below 1%.

Figure 5 shows an experiment on an overcast day (9 March 2002) where occasionally photolysis frequencies changed rapidly. This results in strong changes of trace gas concentrations and sporadic deviations from photochemical equilibrium as indicated by the differences of actinometric PS and TD photolysis frequencies. The PS data clearly show a delayed response to the concentration changes. The difference between the data sets is more obvious in Fig. 6 where the j(NO2)CA are plotted against radiometric photolysis frequencies j(NO2)SR measured outside of SAPHIR by the spectroradiometer. Under overcast conditions there is a linear correlation between the data (Sect. 4). However, the quality of the correlation improves significantly using the time-dependent calculations rather than the photo-stationary approach, as reflected in the correlation coefficients. In the following we will use the time-dependent approach for all types of conditions, i.e. j(NO2)CA=j(NO2)TD.

4 Comparison of actinometry with SRTM predictions

4.1 Overcast conditions

If a constant sky radiance distribution is assumed under overcast conditions, a linear correlation between photolysis frequencies measured externally by radiometry and internally by actinometry is expected. Figure 7 shows a plot of external j(NO2)SR against j(NO2)CA for three overcast days. The correlation of the data is excellent with a linear correlation coefficient of 0.995. The mean ratio j(NO2)CA/j(NO2)SR is 0.80±0.05, i.e. the radiometric data have to be scaled down by this factor to obtain mean chamber values. A mean ratio is used here rather than a linear regression to give equal weight to all data points irrespective of the j(NO2) values. The procedure is justified because deviations from the mean
ratio are normally-distributed in good approximation with a standard deviation stated above.

Of course, also SRTM predicts a linear relationship between \( j(\text{NO}_2)_{\text{CA}} \) and \( j(\text{NO}_2)_{\text{SR}} \). Based on a time-independent SOC sky radiance distribution (standard overcast sky, Grant and Heisler, 1997), scaling factors are calculated theoretically with very minor time-dependent variations introduced by wavelength correction. Accordingly, the plot of \( j(\text{NO}_2)_{\text{SRTM}} \) against \( j(\text{NO}_2)_{\text{CA}} \) in the lower panel of Fig. 7 looks virtually identical and a similar correlation coefficient is obtained. However, the scaling factor necessary to convert SRTM to mean SAPHIR values is different: 1.41±0.09. In contrast to the data measured externally, the model data have to be scaled up because the SRTM calculations are merely dealing with attenuation of radiation by the opaque chamber construction and the limited transmission of the chamber walls. The scaling factor corresponds to the chamber specific quantity \( h^c > 1 \) introduced in SRTM which is rationalised by internal reflections within SAPHIR (Bohn and Zilken, 2005). The effective \( h^{c,\text{NO}_2} \) obtained here:

\[
    h^{c,\text{NO}_2} = \frac{j(\text{NO}_2)_{\text{CA}}}{j(\text{NO}_2)_{\text{SRTM}}} \tag{20}
\]

is close to an estimate \( h^c \approx 1.3 \), independent of wavelength, based on 4\( \pi \) radiometric measurements inside the chamber (Bohn and Zilken, 2005). The difference can be explained by an underestimation of chamber wall transmission in the theoretical model. The results of the data analysis for overcast conditions are summarised in Table 2.

The SOC radiance distribution used for the model calculations is an empirical expression with a cosine dependence of radiance on zenith angle (Grant and Heisler, 1997). The applied distribution is about 40% brighter at the zenith and 40% darker at the horizon compared to an isotropic distribution (uniform overcast sky, UOC). However, Bohn and Zilken

Fig. 7. Upper panel: Correlations of \( j(\text{NO}_2)_{\text{SR}} \) measured externally with a spectroradiometer and \( j(\text{NO}_2)_{\text{CA}} \) from actinometry inside of SAPHIR on three overcast days. Lower panel: Similar plot with radiometric data modified by SRTM calculations. Dotted lines show 1:1 relationships. Linear correlation coefficients \( r \) are indicated.

Fig. 8. Upper panel: Correlations of \( j(\text{NO}_2)_{\text{SR}} \) measured externally with a spectroradiometer and \( j(\text{NO}_2)_{\text{CA}} \) from actinometry inside of SAPHIR at a total of seven clear sky days. Different seasons are indicated by colors: black (winter), blue (spring) and red (summer). Lower panel: Similar plot with radiometric data modified by SRTM calculations assuming a UV-A radiance distribution from literature. Dotted lines show 1:1 relationships, dashed lines the results obtained for overcast conditions. Linear correlation coefficients \( r \) are indicated.
ble,ing factors recognisable. Moreover, although the agreement of the SRTM model significantly improves this correlation. The effect of neglecting the influence of the chamber walls in the model calculations was also investigated. Bohn and Zilken (2005) already showed that the chamber walls are expected to induce minor time-dependent effects. The largest influence was predicted for direct sunlight during the winter season when the contribution of direct sunlight is low. In accordance with this, the quality of the CA versus SRTM correlations are still satisfactory if the influence of the chamber walls is neglected ($r=0.996$). On the other hand, the factor $h_{\text{NO}_2}^c$ is lower and close to unity ($1.03 \pm 0.07$) showing that the limited transmission of the chamber walls is almost compensated by internal reflections. However, the $h_{\text{NO}_2}^c$ obtained by neglecting chamber walls in the SRTM calculations cannot be assigned to other photolysis frequencies because no wavelength dependence is considered. Therefore SRTM calculations including chamber walls are preferred.

Taking clear sky and overcast data together and assuming an SOC radiance distribution, we obtain a mean scaling factor $h_{\text{NO}_2}^c=1.34 \pm 0.10$ for all conditions, i.e. by the use of external spectroradiometric measurements and the SRTM model we are currently able to determine photolysis frequencies for the simulation chamber within 7–8% of the actinometric reference.

### 4.3 Limitations and possible error sources

As an example of the remaining differences between actinometric and SRTM data, Fig. 9 shows diurnal variations of photolysis frequencies on three clear sky days of different seasons. Spectroradiometric photolysis frequencies measured outside exhibit a familiar, smooth shape with typical diurnal and seasonal variations. Local measurements of $j(\text{NO}_2)$ inside the chamber using a filterradiometer (FR) are strongly influenced by shadows cast by construction elements. Filterradiometers measure integrated actinic flux in a selected wavelength range imitating the relative spectral
Table 2. Linear correlation coefficients $r$ and chamber scaling factors $h_{\text{NO}_2}$ from a comparison of SRTM and actinometric $j(\text{NO}_2)$ data for overcast and clear sky conditions assuming different sky radiance distributions (see text). Error bars correspond to 1σ standard deviations. The results using model inputs considered most realistic are given in bold font.

| radiance distribution | UV-A | SOC |
|-----------------------|------|-----|
|                       | data points | $r$ | $h_{\text{NO}_2}^c$ | $r$ | $h_{\text{NO}_2}^c$ |
| overcast conditions    |                   |
| 9 March 2002          | 196   | –   | 0.994 | 1.44±0.09 |
| 12 March 2002         | 170   | –   | 0.991 | 1.38±0.06 |
| 6 March 2003          | 118   | –   | 0.995 | 1.41±0.09 |
| all data              | 484   | –   | 0.995 | 1.41±0.09 |
| clear sky conditions  |                   |
| 9–11 Dec. 2002        | 481   | 0.997 | 1.35±0.08 | 0.997 | 1.30±0.09 |
| 10–11 March 2002      | 542   | 0.994 | 1.35±0.08 | 0.993 | 1.33±0.09 |
| 28–29 July 2002       | 514   | 0.996 | 1.31±0.07 | 0.995 | 1.31±0.08 |
| all data              | 1537  | 0.997 | 1.34±0.08 | 0.996 | 1.31±0.09 |
| all conditions        |                   |
| all data              | 2021  | –   | 0.997 | 1.34±0.10 |

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response of NO$_2$ photodissociation (Volz-Thomas et al., 1996). FR calibrations are made by comparisons with the spectroradiometer under field conditions. The FR measurement location was close to the centre of the chamber, 1 m above ground covering both hemispheres separately. The data shown in Fig. 9 confirm that local measurements are inadequate to monitor photolysis frequencies for the simulation chamber under conditions with direct sunlight. On the other hand, actinometric $j(\text{NO}_2)$ data and SRTM predictions agree well within experimental scatter. However, the precision of the actinometric data is poorer, limited mainly by the ozone measurements. This induces part of the uncertainties of the $h_{\text{NO}_2}^c$. Other possible error sources of more systematic nature which will be discussed in the following.

Taking the actinometric $j(\text{NO}_2)$ representative for the chamber volume, assumes well mixed conditions because the radiation field within the chamber is heterogeneous as indicated by the FR measurements. Mixing properties of the chamber were investigated for different conditions. With opened roof there is convection resulting in complete mixing of an injected trace gas pulse within about 10 min. In the dark this mixing time is prolonged by a factor of about three. Operation of two mixing fans shortens the mixing time by a factor of about four. Switching on and off the mixing fans produced no significant change of the measured trace gas concentrations in an actinometric experiment under clear sky conditions where local shadowing should be most pronounced. This shows that mixing within SAPHIR is fast enough to prevent formation of concentration gradients caused by heterogeneous illumination, at least for the photochemical system studied in this work. Nevertheless, small-scale mixing effects can reduce the precision of the actinometric measurements.

Changes of temperature were not considered in the SRTM calculations where $T$=298 K was assumed. Using a linear interpolation of recommended, temperature dependent data of absorption cross sections and quantum yields of NO$_2$ (Atkinson et al., 2004), a temperature coefficient of about 0.08% K$^{-1}$ for $j(\text{NO}_2)$ is estimated. This has a negligible effect (<1%) on the $h_{\text{NO}_2}^c$ scaling factors listed in Table 2.

There seems to be a slight underestimation of the actinometric data by the model calculations in the morning. Such an effect can be explained by different degrees of staining of the chamber foil exposed to atmospheric conditions. Staining can also explain the differences in the scaling factors $h_{\text{NO}_2}^c$ obtained for overcast and clear sky conditions. Model calculations seem to over-predict chamber values when direct sunlight is incident from southerly directions passing the upper, more horizontal parts of the chamber walls predetermined for staining. However, such effects are hard to assess quantitatively within the model.

With respect to the model, the assumption of a constant SOC sky radiance distribution under overcast conditions is certainly not always matched by reality. Azimuthal variations of sky radiance can produce changes in the actinometric $j(\text{NO}_2)$ not noticed by the external radiometric measurement. Under clear sky conditions changes of aerosol load will produce variations in sky radiance distributions. Thus,
the model input can be improved by a measurement of sky radiance distributions as indicated by Bohn and Zilken (2005).

The SRTM model postulates an effective internal amplification of radiation, considered quantitatively by the factor $h_c$. This amplification is assumed independent of direction of incidence. Moreover, scattering processes at the chamber walls are not explicitly included in the model approach. Both deficiencies can lead to additional time-dependent effects. It is therefore not surprising that model predictions of photolysis frequencies for single locations within the chamber are not well reproduced by measurements. Although the exact time and durations of shadows cast on a location can be predicted, the quantitative effect of these shadows cannot be reproduced. Qualitatively, the light level is higher than predicted in the shadows and lower outside the shadows which can be explained by scattering of radiation at the chamber walls.

Generally also a wavelength dependence of the factor $h_c$ is expected. On the other hand, part of this dependence could already be included in the relative wavelength dependence applied within the SRTM model which is based on a comparison of spectral actinic flux measurements inside and outside the chamber (Bohn and Zilken, 2005). Moreover, $4\pi$ measurements within the chamber give no indication for a strong wavelength dependence. For the time being we therefore assume $h_c = h_{c,NO_2}$ for all wavelengths.

For the accuracy of the $j(NO_2)$ determination within SAPHIR possible systematic errors of the actinometric reference have to be considered as well. Because the uncertainty of the rate constant $k_4$ is dominated by the uncertainty of the $NO_3$ measurements these errors are not independent and add to 10% for the photolysis frequencies. Assuming that the errors estimated for SRTM (7–8%) and $O_3$ (3%) are independent, a total uncertainty of 13% is evaluated.

## 5 Conclusions

In this work we have shown that mean $j(NO_2)$ photolysis frequencies for the atmosphere simulation chamber SAPHIR can be predicted with high accuracy and precision using the SRTM approach described by Bohn and Zilken (2005). The remaining differences can be attributed to deficiencies of the model approach and technical problems concerning the condition of the chamber walls. With respect to the actinometric reference measurements, we estimate an accuracy of 7–8% for the $j(NO_2)$ based on SRTM, independent of external conditions. No change of $h_{c,NO_2}$ was found within a period of one year and regular checks will be made to assure the long-term reliability of the measurements. Taking into account possible systematic errors of the actinometric $j(NO_2)$, photolysis frequencies within SAPHIR are accurate within 13%.

In future work the SRTM model and the radiometric input data could be improved as indicated by Bohn and Zilken (2005). Moreover, an actinometric determination of $j(O^1D)$ photolysis frequencies within SAPHIR will be developed to check the model predictions concerning wavelength dependence. Ozone measurements of higher precision and the enforcement of well mixed conditions would improve the precision and the accuracy of the actinometric $j(NO_2)$ measurements. Under these conditions, smaller systematic effects caused by deficient model assumptions could be investigated.

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