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Interactive comment on "Model-aided radiometric determination of photolysis frequencies in a sunlit atmosphere simulation chamber" *by* B. Bohn and H. Zilken

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We thank referee S. Madronich for his thorough review with many suggestions for improvements.

1. Wavelength dependence of weighting factor f^{T}:

An experimental check of the wavelength dependence of direction weighting factors f^{T} under clear sky conditions is difficult for two reasons. Firstly, although local ratios of internal and external spectra as in Fig. 16 can be predicted by the model for clear

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sky conditions, these ratios are not representative for the whole chamber (as opposed to overcast conditions as explained in Sect. 3.2.3). Secondly, scattering processes are diminishing the calculated differences between shaded areas and areas illuminated by direct sunlight. This effect is time-dependent and also affects the spectral composition of actinic flux detected locally making an interpretation of measured ratios difficult on the basis of the current model.

2. Spectral transmission of FEP film and the effect of scattering:

The transmission measurements of FEP film by Wallner (2000) were made using a spectral photometer and an integrating sphere, i.e. light was detected with equal sensitivity independent of direction of transmission. The measurements therefore provide the appropriate quantity to our model. However, so far in the model we are neglecting the effect of (wavelength dependent) scattering processes which alter the path-lengths of transmitted photons and thus the actinic flux inside the simulation chamber. For an improved model we need the actual angle distribution of diffusively transmitted light from laboratory experiments because scattering by FEP film is probably not isotropic. But of course the main challenge is the complex geometry of the simulation chamber. In the case of isotropic scattering the factor 2 cos(ϑ) (ϑ = angle of incidence) reminded by the referee can lead to an enhancement of actinic flux by up to a factor of two upon conversion of a collimated beam into scattered light. However, this factor applies for a plane film of infinite extension. It is therefore an upper limit which is not applicable to SAPHIR where the walls are curved. To demonstrate the difference consider two spheres surrounded by FEP films with identical properties concerning angle dependent transmission and reflection and no absorption. In sphere A transmission and reflection is diffuse and isotropic while in sphere B these processes are purely specular. For the

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ratio of actinic fluxes within the spheres the following relationship can be assumed:

$$f_{\mathrm{A/B}} = \frac{\frac{1}{\pi r^2}\int_0^r 2\pi x\, T(x)\, l_{\mathrm{d}} \sum_{i=0}^{\infty} R_{\mathrm{d}}^i \,\mathrm{d}x}{\frac{1}{\pi r^2}\int_0^r 2\pi x\, T(x)\, l(x) \sum_{i=0}^{\infty} R^i(x)\,\mathrm{d}x} \tag{1}$$

The integrations are covering the planes of projection of the spheres with x being the distance from the centre and r the radius of sphere. $R(x)$ and $T(x)$ are the corresponding reflectances and transmittances and $l(x)$ is the path-length of light through the volume of the sphere. For diffuse transmission and reflection we assume an average path-length l_{d} and reflectance R_{d} which are independent of x as explained below. The expression in the denominator corresponds to that for spherical droplets by Madronich (J. Geophys. Res., 92, 9740, 1987), taking out the effects of absorption and refraction. In the denominator transmissions and reflections are compensating each other:

$$T(x) \sum_{i=0}^{\infty} R^i(x) = T(x)\,\frac{1}{1-R(x)} = 1 \tag{2}$$

The ratio f therefore simplifies:

$$f_{\mathrm{A/B}} = \frac{\sum_{i=0}^{\infty} R_{\mathrm{d}}^i\, l_{\mathrm{d}}\, \frac{1}{\pi r^2}\int_0^r 2\pi x\, T(x)\,\mathrm{d}x}{\frac{1}{\pi r^2}\int_0^r 2\pi x\, l(x)\,\mathrm{d}x} = \frac{\sum_{i=0}^{\infty} R_{\mathrm{d}}^i\, l_{\mathrm{d}}\, T_{\mathrm{s}}}{4/3\, r} \tag{3}$$

Here T_{s} is the mean transmittance of the sphere. The factor 4/3 r corresponds to the average path-length of a collimated beam through the sphere without being influenced by the walls, which means that the actinic flux is identical inside and outside in the case

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of specular transmission and reflection. This is a well-known phenomenon (e.g. Zafonte et al., Environmental Science and Technology, 11, 483, 1977) utilised in chemical actinometers of spherical and cylindrical geometry.
Assuming diffuse, isotropic transmission into the sphere, it can be shown that the mean path-length of transmitted photons corresponds to the radius of the sphere:

$$l_{\mathrm{d}} = \frac{1}{2\,\pi} \int_0^{2\pi} \int_0^{\pi/2} l(\theta) \sin(\theta) d\theta \, d\varphi = r \tag{4}$$

Here $l(\theta) = \sqrt{2r^2(1+\cos(2\theta))}$ and θ is the polar angle with respect to the direction pointing towards the centre of the sphere. Because θ also corresponds to the angle of incidence for internal reflection the mean reflectance can be calculated accordingly assuming diffuse, angle dependent reflection:

$$R_{\mathrm{d}} = \frac{1}{2\,\pi} \int_0^{2\pi} \int_0^{\pi/2} R(\theta) \sin(\theta) d\theta \, d\varphi \tag{5}$$

With

$$\sum_{i=0}^{\infty} R_{\mathrm{d}}^{i} = \frac{1}{1-R_{\mathrm{d}}} \quad (\text{for } R_{\mathrm{d}} < 1) \tag{6}$$

we finally obtain:

$$f_{\mathrm{A/B}} = \frac{3}{4} \frac{T_{\mathrm{s}}}{1-R_{\mathrm{d}}} \tag{7}$$

Numerically T_{s}=0.70 and R_{d}=0.46 were calculated taking the hemispheric transmittance data of the SAPHIR walls. Insertion gives $f \approx 1$ showing that for a spherical chamber diffuse isotropic transmission would not lead to an increase of actinic flux independent of the angle of incidence. Therefore, although geometrically the real chamber is much more complex we are not expecting a strong increase of actinic flux caused by scattering processes.

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3. Minor comments:

All minor comments will be addressed in a revised manuscript. In the following we comment on some of the suggestions.

Page 6968: The citation of unpublished references as footnotes was decided by the journal. The term symbols for the O_2 product in Eq. (1) were used to indicate that both ground state and excited state O_2 can be formed in the photolysis under tropospheric conditions. This is not the case for NO in Eq. (4). Ground state oxygen atoms in Eq. (4) were explicitly denoted O(^{3}P) to avoid confusion with the excited state O(^{1}D) of Eq. (1).

Page 6969: Wavelength dependence of σ and ϕ will be indicated. The lower index λ of F denotes a spectral density with respect to wavelength (as opposed to "wavenumber" or "frequency"). Therefore wavelength dependence of F is indicated separately.

Page 6970: The possible impact of local shading and the mixing aspect are addressed in a succeeding paper by Bohn et al. (Atmos. Chem. Phys. Discuss. 4, 8141-8170, 2004). We will add a corresponding note and a reference.

Page 6971: The alternative method described in the literature will be mentioned and referenced.

Page 6980: The SOC radiance distribution of Eq. (22) is describing the effect of increasing radiance for smaller zenith angles. We will add a note to emphasise the difference between UOC and SOC radiance distributions.

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Page 6984: Aerosol characteristics could be monitored at the chamber site because the co-channel measurements with shadow ring in principle are containing information on aerosol load. However, because clear sky conditions are fairly uncommon at Jülich, the problem of unknown sky radiance distributions will mainly occur at heterogeneous cloud cover. We are planning to tackle this problem by supporting measurements of relative sky radiance distributions in the UV with a sky imager (see reply to comment by R. Scheirer). This technique will hopefully also work under clear sky conditions so that the analytical distributions by Grant et al. are not needed. If the distribution of diffuse sky radiation were peaked more strongly in the direction of the sun this would produce a stronger time-dependence of the correction factors in Fig. 10. We will mention this in the revised manuscript. On the other hand, Figs. 17 and 18 indicate that for clear sky conditions the time-dependence of the radiance distribution has limited influence.

Fig 5 is showing parameters we fitted to data measured by Wallner (2000). Wallner obtained τ_{h} at different wavelengths and different thicknesses of the film at normal incidence. For each wavelength we fitted Eq. (20) to the original data to describe the dependence on d. The obtained parameters are plotted in Fig. 5 as a function of wavelength. The smooth dependence indicates that Eq. (20) is a reasonable description. The second order polynomials also plotted in Fig. 5 are then used to calculate the parameters inserted into Eq. (21). The data of Wallner also allow to calculate τ_{d} as a function of d by subtracting the measured hemispheric and diffuse transmissions. With the same procedure as for τ_{h} an angle dependent description of τ_{d} was obtained. The results of these calculations are compared with measurements from our laboratory in Fig. 6 for a sample of FEP film used in SAPHIR. Fig. 6 shows that the calculations give reasonable results compared to the measurements. For the model calculations we used the calculated τ_{d} and τ_{h} for consistency reasons. We acknowledge that the

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transmission subject is a bit confusing because we confined this section as much as possible. We will try to describe the procedure more clearly without adding too much text.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6967, 2004.