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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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This paper is a valiant effort to calculate the average actinic flux in the SAPHIR environmental chamber. These fluxes are needed to calculate the in-chamber photodissociation rates, which in turn are critical for quantifying the photochemical processing in the chamber. This analysis is important and should be published, after consideration of the relatively minor comments given below.

The bottom-up approach used here attempts to correct for the main perturbations to the natural radiation field, which include: (1) Shading by the structural elements of the chamber. (2) Transmission of the FEP film that encloses the chamber. (3) Shading of the horizon by trees and other outer structures.

Shading (items 1 and 3) is inherently a geometric issue, being dependent on the position within the chamber relative to the obstructions, and on the directions of the incident radiation. The authors used numerical/geometric simulations using a 3-dimensional discretization of the chamber and its structures. For the directions of incident radiation, they considered several cases including fully overcast (mostly but not perfectly isotropic incidence), or clear sky conditions in which the direct solar beam is treated separately from the diffuse sky radiation. It is worth noting that for clear skies the diffuse/direct ratio increases at shorter wavelengths (due to Rayleigh scattering), so that effectively the shading corrections become wavelength-dependent. This part of the manuscript is truly excellent and it is difficult to suggest any improvements.

Transmission of the FEP file (item 2) is more difficult, as already evidenced by the fact that several different formulations were considered, including simple Fresnel transmission tau-F, the authors' own measurements of direct beam transmission tau-d, and a literature measurements of hemispherically integrated (direct + diffuse) transmission tau-h. All are dependent on the direction of incidence, and wavelength dependence appears to be quite important for tau-d and tau-h. Very little evidence is presented for choosing among these three options - or perhaps other better ones. Comparison of spectroradiometric measurements inside and outside the chamber (Fig. 16) indicates that the measured wavelength dependence of transmission falls between the weak dependence predicted by tau-h and the much stronger dependence predicted by tau-d. Furthermore, a residual wavelength-independent "radiometric factor" of 1.3 is needed to match the observations. The results presented in Fig. 16 are for uniformly overcast sky, and it is unclear whether the agreement for clear sky conditions is better or worse.

Perhaps one issue worth examining is related to the hemispheric transmission measurements made by Wallner (on which the parameterization of tau-h is based). Most commonly, such transmission measurements refer to transmitted irradiance rather than

ACPD
4, S2863–S2867, 2004

EGU

transmitted actinic flux. In other words, the light scattered and transmitted by the film is measured using a flat-plate (cosine-weighted) detector rather than an actinic (directionally unweighted) detector. In the case of actinic flux, any conversion of collimated light (e.g. incident direct sun) to diffuse light incurs an additional factor. If the FEP-scattered light becomes isotropic, this factor is ˜2cos(theta) where theta is the angle of incidence (see Madronich, J. Geophys. Res., 92, 9740, 1987). As a result, for nearly normal incidence, the actinic flux transmission can be greater than the transmission of irradiance, while for very slanted incidence it is less than the irradiance transmission. This creates an additional angular dependence that does not appear in the present formulation of tau-h. Additionally, because the incident direct/diffuse ratio is wavelength dependent, it creates yet another wavelength dependence.

For the purposes of this paper, it might be useful to do at least one of the following: (1) Review the methods used by Wallner to establish whether irradiance or actinic flux transmissions were measured, clarifying the manuscript accordingly. (2) If a radiometer with an actinic head is available (e.g. JNO2 radiometers), measure the transmission of the film as a function of the angle of incidence of the radiation.

Minor comments (page numbers):

6968 Inconsistent usage, % transmission on line 11 and fractional transmission on line 14. Line 15 and thereon: Not conventional to use both numbers and author for references. Line 22: Not necessary to write (a,X) in reaction (1). Not used in reaction (4) for NO.

6969 Line 8 (eq. 6): Should indicate wavelength dependence of sigma, phi. For F, wavelength dependence is doubly indicated - only one is needed (this reoccurs in eqs. 7-9). Line 9: Replace "." by "," Line 17: Replace "allows to determine" by "allows determining" Line 18: Replace "provided" by "if"

6970 Line 9: Replace "casted" by "cast" (invariant verb) Line 10, 11: Mean J's are probably sufficient, but could induce some errors (probably small) for radical-radical

ACPD
4, S2863–S2867, 2004

Interactive Comment

EGU

reactions e.g. OH+OH, if mixing of chamber gases is slow.

6971 Beginning at line 15: An alternate empirical method to correct for the sky radiation blocked by the shadow ring is to displace the ring just off the sun, then compare to the unblocked value. Rotating shadowbands have been used for this purpose - see for example Harrison et al., Appl. Opt., 33, 5118, 1994; Harrison and Michalsky, App. Opt,. 33, 5126, 1994; and more recently Min et al., J. Geophys. Res., 109, D02201, doi:10.1029/2003JD003964, 2004.

6974 Line 8: the word “codomain” is uncommon. Based on later text, it appears simply that the variable s can take one of two values, either 0 or 1.

6976 Line 15: Replace “any of the triangles is” by “any of the triangles are”

6978 Line 3: Replace “literature” by “the literature”

6980 Lines 25-28: But note that the radiance below a horizontally uniform cloud field is usually not isotropic, being rather brighter near the zenith.

6894, Line 13 and following: The radiance distributions also depend on aerosols, especially for clear sky. Are aerosol characteristics at chamber similar to those present in the study by Grant et al.? For heavy aerosol loading, the radiance distribution may be strongly peaked in the direction of the sun, so that there arises some ambiguity between f-diffuse and f-direct.

Throughout text: Suggest using "large (small) zenith angle" rather than "high (low) zenith angle" to reduce possibility of misunderstanding.

Throughout text: The use of tau for transmission is unpleasant since tau is commonly used for optical depth. Using T might be better.

Fig. 5, lower panel: Origin of measurements is not clear. On p. 6977 lines 19 and 20 state that a collection of scattered light was not feasible with the available equipment. Are the data shown in this figure from Wallner? Are they for the FEP film used in the chamber? How were the basic measurements made? irradiance or actinic flux?

Fig. 6: Why are the measured values (crosses) different than tau-d? I thought tau-d was a simple fit to these values

Fig. 9, lowest panel: Suggest plotting inverse (fT/fV), since this then gives an estimate of FEP transmission averaged over the entire chamber.

Fig. 15 caption is not clear. What are + markers?

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