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Interactive Comment

Interactive comment on "Characterisation of J(O^{1}D) at Cape Grim 2000–2005" *by* S. R. Wilson

Anonymous Referee #2

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The paper by Wilson presents data of the photolysis rate of ozone, J(O^{1}D), for Cape Grim, Tasmania. The data is derived from measurements of spectral global and diffuse irradiance using a spectroradiometer. From the measured irradiances, the actinic flux is estimated and used to calculate J(O^{1}D). To the best of my knowledge, long-term (2000-2005) data of J(O^{1}D) have not been presented for Cape Grim. Considering that the photolysis of ozone - and the resulting production of hydroxyl radicals - are the drivers of air chemistry, the dataset is of value for photochemistry studies conducted at Cape Grim (40.6° S) and locations in the Southern Ocean at similar latitudes. While the paper does not present novel concepts and tools, it provides a new dataset that deserves publication.

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General comments

My main criticism of the manuscript is that the uncertainty of the photolysis rate data derived from the author's OL752 spectroradiometer is not clearly and completely described. Based on evidence provided below, I feel that the stated total uncertainty of "around 8%" (P18397,L1) in the spectral actinic flux is overly optimistic. Hence, a more complete (and perhaps more realistic) uncertainty budget should be established, taking into account the following uncertainty components:

(1) Uncertainty of the calibration of the OL752 for irradiance using the "ratio-Langley" technique. For conventional Langley analysis, this uncertainty would describe the uncertainty of the calibration caused by the uncertainty in determining the "airmass zero intercept".

(2) Uncertainty due to drifts of the calibration over time.

(3) Uncertainty of the extraterrestrial spectrum used in the "ratio-Langley" technique.

(4) Uncertainty of the conversion of the measurements of spectral irradiance to spectral actinic flux.

Uncertainty component (1) should take into account that the direct irradiance (which is used for the Langley technique) is not measured directly. Instead, it is calculated from global irradiance and diffuse irradiance using a shading device. It should also be discussed that the Langley technique has large uncertainties in the UV-B because it requires that total ozone remains constant over the time period of the Langley observations. Figure 6 of (Wilson and Forgan, 1995) indicates that the ratio-Langley technique does not allow a reliable calculation of the instrument's responsivity below 305 nm. The consequences of this limitation on the calculation of $J(O^1D)$ should be discussed.

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Potential changes in responsivity over time (both short and long-term) should also be quantified (uncertainty component (2)). For example, Wilson (2006) indicates that “the temperature sensitivity of the spectrometer is quite large, and quite small changes in temperature may induce large variations in sensitivity.” According to Figure 6 of Wilson (2006), the direct beam sensitivity of SRAD relative to a (presumably stable) sun photometer varied by about $\pm$ 20% between 2000 and 2004. The reasons for these variations are not fully understood and, according to that paper, “an upper estimate of the uncertainty of around 8% (95% confidence limit)” is assumed. The uncertainty of this single component is therefore as large as the total uncertainty in actinic flux measurements reported in the ACPD paper (P18397,L1). This apparent contradiction should be clarified.

According to Chance and Kurucz (2010), the absolute radiometric intensity accuracy of the extraterrestrial spectrum used in the ratio-Langley method is “better than 5% at wavelengths longer than 305 nm,” implying that it is about 5% at 305 nm. The uncertainty component (3) should be discussed in more detail using the information in that paper.

Uncertainty component (4) depends mostly on the uncertainty of the ratio α. The uncertainty in F due to the uncertainty in α should be quantified in more detail taking different sky conditions (e.g., clear sky, overcast) into account. Just saying that “α is reasonably well behaved” (P18393,L9) is not satisfactory. For example, Kylling et al. (2003) calculate that α can vary between 1.68 for overcast conditions and about 2.0 for a purely Rayleigh scattering sky. The relative difference in the actinic flux at 310 nm, calculated with Eq. (6) for either α = 1.7 or α = 2.0, is about 10%. This difference is comparable with the total uncertainty of the actinic flux of “around 8%” specified in the manuscript.

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Specific comments

P18390, L9: For clarity, the sentence should be changed to "Variations in solar zenith angle and total ozone column explain 87% of the observed variability in the measured photolysis rates."

P18392, L10: The title "Angular response" does not fit the contents of the subsection well. A better title would be: "Estimate of actinic flux from irradiance measurements"

P18391, L11-13: Technically, the branching ratio Q is the ratio of Reactions (R3) and (R2) and not the ratio of Reactions (R2) and (R3). (Q is small when the H_2O concentration is small). I suggest to reverse the Reaction equations (R2) and (R3), but leave line 13 as it is.

P18393, L2-7: Eq. (6) is hard to understand intuitively. I suggest to replace Eq. (5) with:

$$F = \alpha E_{\downarrow} + E_0 = \alpha(E - \mu E_0) + E_0$$

and replace the sentence "If the diffuse ...from." with: "Eq. (5) can be rearranged to the following form suggested by Kazadzis et al. (2004)."

P18393, L9. The sentence "The ratio α is reasonably well behaved" should be improved because "well behaved" is not a good quantitative term. A range for α should be provided, or alternatively, Section 3.1 should be referenced, where the range of α

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is discussed.

P18395, L4: Please describe how the diffuser is shaded. Is it shaded with a shadow-band or a small disk, approximately the angular diameter of the Sun, that is moving with the Sun's position?

P18395, L7: The paper by Forgan (1998) describing the ratio-Langley technique was published in a CSIRO report and is not easily accessible. Instead (or in addition to), the Applied Optics paper (Wilson and Forgan, 1995) should be cited.

P18395, L15: Change "alternative" to "alternating"

P18395, L21. What input diffuser is described here? According to Lines 12-14, two diffusers were in use and the first diffuser was replaced in October 1999.

P18396, L3: The measurements are affected by the cosine error of the instrument's diffuser. Hence, a correction is necessary before Eq. (5) can be applied. It should be briefly described how this is done.

P18396, L11: I presume this formula refers to clear sky. If so, please specify. α for cloudy sky is in the order of 1.65 to 1.75, see Figure 3 of (Kylling et al., 2003) and Table 2 of (Kazadzis et al., 2004). Considering that clouds are the norm at Cape Grim, a value in this range should be applied most of the time. It is not clear whether this was done. When calculating α with Eq. (7), the solar zenith angle has to be larger than 80° for α to become smaller than 1.75. So if Eq. (7) was used for all conditions, α

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would be too large in the majority of cases (i.e., cloudy conditions).

P18396, L12: Please quantify "small". As mentioned earlier, the effect of the uncertainty of α on the total uncertainty of F should be quantified.

P18396, L20: The calibration of SRAD has likely a considerably uncertainty below 305 nm due to the limitations of the ratio-Langley technique below this wavelength. If ignoring measurements below 298 nm may cause an error of up to 5% in $J(O^1D)$, the (rather uncertain) contribution from the range between 298 and 305 could conceivably cause systematic errors in F of larger than 5%. This should be quantified.

P18396, L26: The sentence "The calibration uncertainty of the measurements ...diffuse irradiance" is not clear. What does the "calibration uncertainty" of 5% include? Is it the uncertainty in finding the intercept with airmass zero of the Langley analysis, the uncertainty of the extraterrestrial spectrum, or the combined uncertainty of both components? What is the uncertainty (in %) caused by the "variability in the calibration observed from the multiple calibrations carried out during the 6 years"? Please specify the uncertainties of the three components separately plus the combined uncertainty. As mentioned in my general comments, I suspect that the combined uncertainty is larger than 8% if all error sources are taken into account.

P18397, L23: The good agreement of the results of SRAD and the filter radiometers is a bit surprising considering that the uncertainty of the filter radiometers is quoted to be 20-30%, and the uncertainty of the SRAD data is likely larger than the quoted uncertainty 8% and also biased low by 5% because of the omission of spectral measurements below 298 nm (P18396,L24). So the good agreement could be serendipity.

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Figure 1 only shows results for a 3-day period. Were the results similar for the rest of the campaign?

P18398, L8: If the disk of the Sun is unobstructed, and clouds are in the vicinity of the Sun, radiation is typically enhanced, not reduced.

P18398, L16-20: If there are no instrument failures, I would expect at least 120 data records in each 24 hour bin per month (30 days times 4 records per hour). I would assume further that instrument failures would impact several consecutive hours or days. I therefore don't understand how there can be bins with no data that are between adjacent bins with data. This would mean that there is not a single measurement in a given hour for an entire month but enough measurements in the bin associated with the hours before and after the given hour. Please clarify.

P18398, L20: It would have been better if the sum rather than the average of the 24 hourly averages had been calculated. Using the sum, the result would be a daily dose. Using the average makes results harder to interpret because day lengths are different in the summer than during winter.

P18399, L5: How is the variability defined? Is it standard deviation to average?

P18401, L2-9: It can have several reasons when measurements exceed the clear sky model value: enhancement by clouds (as described in this paragraph), measurements that are too large, model results that are too small, or a combination. While Figure 2 indicates that clear sky measurements agree well with the model, the difference at

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large solar zenith angles (small $J(O^1D)$ values) is difficult to see. It would therefore be good to describe the bias between measurements under clear sky and the associated model values as a function of solar zenith angle. The apparent increase of cloud enhancement as a function of solar zenith angle (Line 7) could be an artifact of a solar zenith angle dependent change in the bias between measurement and model.

P18401, L12: Change “greater” to “smaller”

P18402, L11: Why “reduced R^2”? The sentence indicates that inclusion of the “Clear-sky Index” term improved the fit (albeit by not by a lot), so R^2 should have increased, which is also suggested by the phrase in the parenthesis “(increases of 0.0005)”.

P18402, L20: Please explain what is meant with “the chemical outcome”.

P18407, L20: The Cape Grim station is located on a cliff. Is the station often shrouded in clouds while the ocean below is not, and could that lead to a systematic difference in $J(O^1D)$ compare to locations close to the ocean surface?

P18403, L13-15: I don’t understand the sentence “The reduction . . . cloud.” For example, what does “at the average cloud factor of 0.8 to 0.9” mean?

P18416 (Figure 5): The line for 350 DU is not “solid” but broken (and red).

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Technical corrections

Expressions such as “higher solar angles” (e.g., P18390, L17) are confusing. “Higher solar angles” means “higher solar elevation” (i.e., the angle measured from the horizon) for most people, while a larger angle measured from the zenith is meant here. I suggest to use only “large” and “small” in combination with “zenith angle” such as “... at larger zenith angles...” throughout the paper.

The word “cloud” is consistently used in singular. For example: “there can be cloud well away from the Sun” or “due to cloud”. Use of the plural would be more in line with other publications.

P18394, L20: Change title to “Experimental setup”
P18398, L12: Replace “of over” with “over”
P18400, L6: I would say this the other way round: “...functions of the following form were fitted to the measured $J(\mathrm{O^1D})$ values.”
P18400, L24: Change “low solar zenith angle” to “small solar zenith angle” (see also comment above)
P18402, L12: Change “due the” to “due to the”
P18403, L12: Change “but close to” to “but the impact is close to”
P18404, L8: Delete “significant”

References

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