Atmospheric Chemistry and Physics Discussions
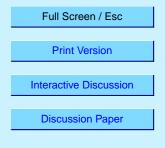
Interactive Comment

Interactive comment on "Actinic flux and O^{1}D photolysis frequencies retrieved from spectral measurements of irradiance at Thessaloniki, Greece" *by* S. Kazadzis et al.

Anonymous Referee #1

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General comments: This paper describes two methods to derive $J(\text{O}^1\text{D})$ photolysis frequencies from spectral irradiance measurements.

The first method retrieves spectral actinic fluxes from parallel direct and global measurements of spectral irradiance with a Brewer spectroradiometer with the aid of a radiative transfer model. This method has already been described by Kazadzis et al., 2000. In the present work it was applied to a 5-year period (1997-2002) of spectroradiometer measurements at Thessaloniki, Greece. Within this period there were some 10 months of parallel measurements of spectral actinic flux with a Metcon spectroradiometer which show good agreement with the retrieved data, independent of wavelength. Accordingly, also the $J(\text{O}^1\text{D})$ calculated from the spectral actinic fluxes agree

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well.

The second method merely uses global irradiance measurements to retrieve $J(O^1D)$. It is based on parallel measurements of spectral actinic flux and irradiance with a Bentham spectroradiometer for a period of some 5 months at Thessaloniki to derive an empirical relationship between $J(O^1D)$ and global irradiance. This relationship is then applied to retrieve $J(O^1D)$ from global irradiance measurements of different periods. It turns out that the method is giving consistent results if (1) Brewer irradiance data are used instead of the Bentham data during the same 5 month period, (2) the method is applied to Bentham irradiance data at a different location (Weyborne, UK) and (3) the results are compared with those of the first method for a selected 2-year period within the 5-year period mentioned above.

The overall impression from the paper is that both methods work satisfactory. However, the second, new method needs more explanation, a more systematic investigation of limitations and publication of the parameterisation. The paper is difficult to read because a lot of information concerning different instruments, different experiments and different quantities (calculated or measured) is presented.

Specific comments:

1) The term ozone photolysis frequency is used very often in the text. If ozone photolysis would produce only $O(^1D)$ and O_2 this term would be sufficient to identify the process of interest. However, since O_3 photolysis also forms ground state O-atoms it would be useful to specify the process of interest, $O_3 \rightarrow O(^1D) + O_2$, and to assign the corresponding photolysis frequency $J(O^1D)$ for clarification.

2) The explanation of actinic flux before and after equation (2) is laborious. The definitions of radiance and angles following equation (3) should appear already after equation (2). The addends on the right hand side of equation (2) are no radiances.

3) In the paragraph following line 6 on page 4199 the factor $A(\lambda)$ is derived from "ra-

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diance measurements". What is probably meant are radiance distributions measurements as described in the paper by Kazadzis et al., 2000. More details should be given how these measurements were made, or the other paper should be referenced.

4) In the paragraph below starting with line 11 on page 4199 it is stated that Kylling et al. and Webb et al. are assuming a constant value of 1.73 for $A(\lambda)$. This is true only for overcast conditions. However, the next statement concerning the assumption of an isotropic radiance distribution and its consequences probably applies for clear sky conditions.

5) In the first paragraph of section 3.2 it is stated that 18000 irradiance spectra were converted to actinic flux spectra. However, given the explanations in section 3.1, it remains unclear how this was actually made. Were 18000 radiative transfer model calculations performed with ozone columns and AODs taken from the measured spectra? Or was the factor $A(\lambda)$ taken from the sensitivity study described in section 3.1? Or was $A(\lambda)$ taken constant for the wavelength ranges UVA (1.90) and UVB (1.65)?

6) On page 4204, line 1 it is stated that $J(O^1D)$ and pseudo-$J(O^1D)$ are calculated according to eqn.(1). The absorption cross sections and quantum yields used for this calculation are not specified. This information is given in section 5. However, the data that were used are obsolete. In particular with respect to $O(^1D)$ quantum yields there were considerable changes in the recommendations within the last years. A recent recommendation (e.g. by NASA, Sander et al., 2003) should be used. This will strongly influence the results of the parameterisation (method 2). Moreover, a temperature should be specified for which calculations were made.

7) On page 4204, line 23 third order polynomial are fitted between the measured $J(O^1D)$ and the global irradiances at 325 nm (E_{325}) to derive a parameterisation for $J(O^1D)$ for 5-degree groups of solar zenith angles. 325 nm were selected as being less dependent on seasonal variability of total ozone (line 6). I wonder how this can work, because $J(O^1D)$ evidently is strongly dependent on ozone column. Therefore it

would be interesting to find out about the variability of the ozone columns during that period of measurements. Moreover, what are the pseudo-$J(O^1D)$ good for? It would be more reasonable to assume that the third-order polynomials as a function of E_{325} are used to fit the ratios $J(O^1D)$/pseudo-$J(O^1D)$.

8) The ratios of retrieved and measured $J(O^1D)$ in Fig. 6 exhibit vertical structures which add to the scatter caused by the variability of external conditions. My impression is that these vertical structures are an artefact from the binning of data to the 5-degree solar zenith angle groups. The dependence of $J(O^1D)$ on solar zenith angle (SZA) is very strong. From the information given in the experimental section it can be estimated that scanning the wavelength range relevant for $J(O^1D)$ (290-340 nm) takes about 3 min. Within these 3 min the change of SZA is well below 1 degree. So the information available on SZA is much more precise than introduced artificially by the binning. There are two possibilities to improve this: A two-dimensional fit (E_{325}, SZA) of all data using a suitable parameterisation formula or polynomial fits of the already derived polynomial parameters as a function of SZA (using the averaged SZA within the bins as independent variable). If the dependencies of the parameters on SZA are smooth, this would reduce the total number of parameters and the scatter of the data in Fig. 6.

9) For method 1 model calculations were made to investigate the dependence on ozone column and other parameters. Based on the same spectra the sensitivity of the second method could be investigated to test its limitations. Moreover, in the absence of experimental scatter the parameterisation formula could be optimised before it is applied to experimental data.

10) The parameterisation finally used for method 2 should be given in the paper to allow other people to use this tool, or to adjust it for other sites or conditions.

11) In section 4.2 the Brewer measurements were shifted by 8% at 300 nm. How can this be justified if the overall accuracy of the instrument is 5% as stated in the experimental section?

12) The statement in the conclusions, page 4208, line 26, that the accuracy of the retrieved data is comparable with chemical actinometer data is not appropriate. Chemical actinometry is a direct method, while spectroradiometry is an indirect method, also dependent on the correctness of absorption cross sections and quantum yields. Radiometry may be more precise, but it is hard to prove that retrieved radiometric $J(O^1D)$ are as accurate as those obtained by chemical actinometry.

Technical corrections:

p 4193, line 5: use NOx instead of NOx's.

p 4194, line 3: reference Bais et al., 2003 is missing in the list of references.

p 4205, line 11: upper index 1 in $J(O^1D)$.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 4191, 2004.