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Atmospheric Measurement Techniques
Discussions

Interactive comment on "High spectral resolution ozone absorption cross-sections – Part 1: Measurements, data analysis and comparison with previous measurements around 293 K" *by* V. Gorshelev et al.

Anonymous Referee #1

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General comments:

This paper presents the first part of an extensive laboratory work which aimed at performing new, independent measurements of the absorption cross-section of ozone in a large spectral range, with high spectral resolution, and at an increased number of temperatures compared to already published values. It meets an important requirement expressed by users of ozone cross-sections in terms of data quality and availability of a large set of values. As ozone was produced on site and its concentration assessed by

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pressure measurements, the results also provides an additional independent dataset so as to progress in the current effort of selection of the most accurate ozone absorption cross-section values. This first paper describes the experimental setup, gives the results at room temperature and provides a comprehensive analysis of these results in comparison with published datasets. It is generally well written and supported with appropriate figures of good quality but the structure could be further improved, in particular in the experimental section. I recommend the publication of this paper in AMT after consideration of the specific comments detailed below.

Specific comments:

(S1) Relative versus absolute measurements: the concept of absolute versus relative measurements in published data and in this work could be better considered. First, both concepts could be introduced more clearly in the introduction. Then, when published data are considered, they could be grouped according to their reference. Authors should explain what would be the consequence of data that use the same reference to deduce the ozone concentration in the sample. Analysis of Hearn, BMD and Mauersberger data show that the ozone purity is a large contributor to the overall uncertainty. This is potentially a bias between different groups that use the same reference at 254 nm. In addition, the reactivity of ozone makes it difficult to maintain a sample for long period of time, as observed in this work. Therefore absolute measurements performed on large wavelength scales may suffer from ozone decomposition more than relative measurements performed on mixtures of ozone in air that can be kept stable. At various point in the text, absolute measurements are assumed to be more accurate. This assumption is not always valid. The uncertainty of relative measurements is certainly at least equal to the uncertainty of the reference absolute measurement. However some absolute measurements performed at one single wavelength can reach a lower uncertainty than broadband measurement (less than 1%). Then the added uncertainty on a larger domain of wavelengths and temperatures comes from the optical density and temperature measurements. Those are specific to the setup and not the principle chosen (absolute or relative).

(S2) In this work, the ozone concentration was always measured in the laboratory. Therefore it is suggested to avoid using the words “relative measurements”, which should be restricted to groups that used another group’s value to deduce the ozone concentration in their sample from its absorption at a specific wavelength. It seems that the two experimental setups used here are first a flow of ozone-oxygen mixtures, then an added trap to obtain “pure” static ozone. Then the distinction could be “dynamic versus static measurements” or “pure ozone versus mixtures of ozone-oxygen”.

(S3) Uncertainties: an important consideration is given to uncertainties in this work and in published literature. This is certainty acknowledgeable and useful for users of such dataset. However at many occasions uncertainties are provided in ranges or “below a maximum”. I wonder how users can use this information and I suggest that authors should be more restrictive and provide exact uncertainties (either relative or absolute). If this is wavelength dependant, then either the maximum should be kept or the wavelength range should be divided into smaller ranges of the same uncertainty.

Specific comments on specific parts (page, line):

(6570, 27) Why is the information on total sample pressure in Voigt measurements provided, when it was not for others? What does it bring?

(6572) “experimental setup”. This section could be better organised, for example by splitting into the various parts of the experiment. The ozone generator is an important part and should be described with more details, maybe in the beginning of the section. Also the authors used two different setups to produce ozone, either pure or in mixtures with oxygen. It is suggested to devote small sections to each of those with precise titles. The pre-cooling system in copper for ozone-oxygen mixtures (part 2) should be explained here. Some consideration on the stability of the ozone to oxygen fraction during measurements is also missing. Concatenation method: in my understanding, spectra recorded on flows of ozone-oxygen were scaled to spectra recorded on pure ozone at both ends. In that case, how large were the overlapping regions? If this is wrong, please clarify the method used.

(6573, 3) “The cells were designed to achieve diverse combinations of the following parameters”. Normally the cells should be designed to stay within a specific range of the optical density, considering the ozone concentrations inside the cell. Consider rephrasing to introduce targeted values of the optical density.

(6573, 4) “O3 concentrations from 1 to almost 100%” The unit is not appropriate, and if this refers to mixtures of ozone with another gas (assumed to be oxygen) this should be mentioned. For example:” ozone-oxygen mixtures with ozone mole fractions from 1% to 100%. Note also that 100% ozone is very unlikely in the view of the literature. The purity reached during the experiments could be better stated (99.0%?).

(6574, 7) “the leak rate in the cell was below 0.04 mbar h-1”. Is that a leak rate or a dissociation rate?

(6574, 27) Assumptions of this equation should be stated. How is the initial ozone pressure pi measured? If this is the total pressure, then it is assumed that ozone is pure. Then the purity should be mentioned with its uncertainty as this will impact the cross-section uncertainty.

(6575, 14-17) The explanation of the correction applied to pi is difficult to understand. If an extrapolation was done, was it linear? At what time was it calculated? How was the “beginning” of the experiment defined?

(6575, 19) “we estimate an uncertainty of about 1% in the knowledge of the initial ozone purity”. Again, the initial purity should be stated.

(6575, 25) Relative measurements are here associated with measurements performed in ozone-oxygen mixtures. Although this might be the case, one is not the consequence of the other. The brackets should be removed. This confusion could be avoided with the suggestion made in (S2).

(6575, 27) Here starts a section on the concatenation. A separation and a title would be helpful.

(6577, 14) “Measurement errors”. It is suggested to use “uncertainty” rather than “error” here and in the rest of the document.

(6577, 18) “The sufficient length”: not very precise wording. Replace “sufficient” with “long”?

(6577, 18) How was the absorption path length measured? With a ruler? How was the thickness of the windows taken into account? The uncertainty was certainly the same for all cells and this could be given.

(6577, 22) Avoid using “accuracy” and give information on the sensor calibration. The pressure measurement has more impact than the temperature measurement, yet fewer details are provided. If the sensor was calibrated, then it comes with a calibration uncertainty, to be combined with the “fluctuations” uncertainty. (6577, 24) “Fluctuations of pressure during measurements were below 0.04 mbar”. Was this the standard deviation of the pressure measurements? This could be written.

(6579, 7) Here starts a discussion on published datasets. I suggest using a clear title to start with. In addition this section is less easy to follow because of all the numbers provided. This information could be summarised in a table providing for each group the wavelength range, absolute/relative measurements, and typical uncertainties with the distinction between statistical and systematic effects when it is known.

(6580, 12) Here “accuracy” is used as a positive interpretation of “uncertainty”! I suggest always using “uncertainty” when values are provided. Accuracy is normally a concept not expressed with numbers.

(6581, 20) Spectral region near 255 nm. The BP dataset is mentioned and it exists in this region for wavelength larger than 245 nm but it does not appear in figure 4. Why this choice? This should be explained or the BP dataset should be included.

(6585) I am confused with the temperature at which BP and BMD datasets were extrapolated with a polynomial. The text indicates they were measured at 298 K and 295 K respectively (line 14) but also gives the same temperatures for the calculated values (line 16).

(6585) The two treatments applied to the data should be more separated. This section mixes explanations on the polynomial extrapolation of experimental data and on the minimization procedure to determine shifts and scaling factors. An introductive sentence such as “two treatments were applied to the data” would help. When mentioning the polynomial extrapolation, reference to the second paper should be done.

(6585) last section: if I understand this correctly, authors found a smaller scaling factor between BP and Voigt data after having applied the polynomial extrapolation to BP data. If so, this could be said. This is a further confirmation of the interest of polynomial extrapolations to calculate values at temperatures that were not obtained experimentally. It also means that part of the scaling factor could be explained by temperature differences.

(6585) Scaling factor: I am confused with this parameter. It seems to me it is introduced to compensate for any differences between datasets except the temperature difference and the possible shift in wavelength. It also gives the wrong impression that different datasets agree in average as it corrects for biases that can arise from differences in the measurements made by different groups. If the intention is to use it as a diagnostic tool in order to judge the “overall quality” of datasets, this should be stated. One could argue that the standard deviation could also do that.

(6589, 19) “No traces of oxygen spectrum are visible on the new dataset measured with pure ozone”. But table 1 indicates that the 700-1100 nm region was measured relatively, which seems to mean in ozone-oxygen mixtures here. If ozone was pure no oxygen was indeed expected. This should be clarified: was it a mixture? If yes, how was oxygen looked for? With what limit of detection? If ozone was supposed to be pure, then any measurement of the oxygen content is valuable as it provides further knowledge of the actual ozone purity and this could be used in the experimental section.

(6591, 13-15) “Differences between. . .approaches” This statement could be further clarified and supported with some more evidence and/or reference to literature.

Table 1: the column calibration should be more precise or avoided (see comment S2). A column “ozone purity” would be a valuable indication.

Table 2: see comment S3: uncertainties lower than or in a range are not very helpful. To deal with the dependency with the wavelength, either give only the maximum uncertainty, or fit the uncertainty in function of the wavelength, or divide the domain in smaller ranges of same uncertainty. The distinction between systematic and statistical uncertainties is helpful. Clarify the uncertainty on the initial ozone pressure in comparison with the uncertainty coming from the ozone purity. “Fluctuations” could be replaced with “stability” as done for the light source. “Offset of the temperature sensors”: if the sensor had an offset, I guess it was corrected. Then the residual uncertainty can be called “calibration uncertainty” Clarify the uncertainty due to the lack of homogeneity in the cell: here 0.3%, but as large as 1.5% in part 2 paper. The resolution of the sensors is not indicated as an uncertainty. I guess it was considered negligible but one line could be added.

Editorial/technical corrections:

(6570, 7) suggestion: introduce the number of published data set considered in the comparisons at this point

(6570, 12) (Komhyr and Evans 2008)

(6570, 17) [..] Huggins band. In addition, this dataset is limited [. . .]

(6570, 21) replace the last for with in the range.

(6572, 8) “a characteristic absorber” suggest to replace with “an absorbing gas”

(6572, 18) “The values of the O3 cross-sections values in the. . .”

(6585, 21) “To test the capabilities. . .” suggestion : ‘to test the effiency. . .”

(6587, 21) “absorption region” could be better named. “Minimum absorption region”?

(6589, 4) “W) might have”. Some words are obviously missing.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 6567, 2013.