High spectral resolution ozone absorption cross-sections – Part 1.

Answer to referee 1

Dear referee,

Thank you very much for your comments, which significantly improve our manuscript.

Specific comments

S1

We don't agree with several points. Considered datasets are introduced in groups according to the spectral resolution: high resolution broadband data, low-resolution satellite instruments data and single wavelengths data. Spectral resolution is one of the most important parameters for practical applications and is also a crucial parameter during comparison of the datasets.

We don't see any contradiction with the referee's point of view and our argumentation presented in the paper. In several places in the script we explain the consequences of using data from other groups as references values for absolute calibration. The consequences are very simple – total uncertainty includes both statistical part from the new optical density measurements and uncertainty from the absolute calibration. In turn, absolute cross-sections taken as reference values have a total uncertainty that includes both statistical uncertainty of the relative measurements of the optical density and systematic uncertainty due to the ozone concentration. We don't state that absolute measurements are more accurate than relative ones; it makes no sense to compare them in these terms.

Relative measurements can have a perfect signal-to-noise ratio, but without absolute calibration these data are almost useless. To get cross-sections from the optical density spectra, researchers do not need to know ozone concentration in the sample; indeed, some well-established reference values at certain wavelengths can be used, accompanied by their uncertainty. It is the decision of the group whether they are satisfied by absolute data from other researchers, or will use their own ones. Should one group take data of another group for calibration, both systematic and statistical uncertainties of the previous work automatically contribute to the total uncertainty of the new data. We give examples for this. In this case, the new data can only be worse in terms of accuracy than the old data which were taken for calibration. If a researcher controls ozone concentration during optical density measurements, the total uncertainty has a chance to be smaller compared to the previous studies (assuming that researcher tries his best). We don't think that these philosophical speculations deserve to be mentioned in the script.

We agree that single wavelength measurements can be much more accurate than the broadband; actually, we mention this in the script. Uncertainty introduced by calibration using data on single wavelengths might be lower than the uncertainty of the independent absolute broadband measurements. However, several measurements must be concatenated to obtain a broadband dataset. As we mentioned in the script, we would like to avoid accumulation of the uncertainties. This problem can be solved by a consolidated set of the high quality measurements at single wavelengths, covering wide spectral region and temperature range, as needed for users. Unfortunately, data set like this is not available. Moreover, it is not trivial to obtain such a set, since several well-controlled narrow-band light sources and detectors must be involved simultaneously over the different absorption paths. We used the best available single wavelengths measurements for comparisons in different parts of the spectrum.

S2

We think that "*relative*" measurements is an appropriate name for the recorded optical density spectra, which do not contain direct information on the ozone absorption capability, but describe it spectral behavior. The groups who deduced ozone concentration in their sample from other group's values actually did absolutely the same measurements. To our opinion, it is quite obvious for readers.

On the earlier stages of the paper preparation, we indeed considered terms "*static*" and "*dynamic*" regimes. However, to our opinion, "*absolute*" and "*relative*" terms provide much more important information on the character, origination and accuracy of the data compared to purely technical terms. Moreover, given a very big trap, absolute measurements hypothetically can be done in flow. One could also perform static measurements with oxygen-ozone mixture under careful control of pressure for decay correction.

S3

It is not straightforward to provide exact uncertainties for every spectral region. Furthermore, it is not really helpful. With the same level of white noise, the optical density changes by order of magnitude or more within one measurement for most of the spectral range. With the same quality of the signal, relative uncertainty will change by order of magnitude or more. On the border between two measurements, in the overlap region, two very different uncertainties exist for the same value. Previous authors of the broadband datasets gave very limited information on the uncertainty at different wavelengths. We provide (in Table 1 and 2) upper estimations for 6 different regions, relatively typical for remote sensing applications.

6570, 27

Measurements by Voigt et al. (2003) are unique regarding the combination of the pressures investigated. In their work Voigt et al. demonstrated that spectral features do not depend on the pressure. This conclusion makes it possible to concatenate measurements performed at "*flow*" regime with oxygen-ozone mixture (high pressure) with the measurements performed at "*static*" regime with pure ozone sample (low pressure). No other investigators cared about possible pressure broadening effects on the spectra.

6572

We tried to improve the section "experimental setup". It is now split into smaller parts – conditions and spectrometers, we also added few more sub-titles. We hope it is clearer now. We think that further subdivision of the section will make it even more complicated. We believe that we gave enough details for other experimentalists to repeat our study. Some details are know-how of our lab.

The ozone generator is in principle a coaxial cylindrical capacitor where electrical field accelerates electrons and causes the dissociation of oxygen molecules. We don't think any other technical information is useful. We don't use any parameters of the generators to judge on the sample purity.

Precooling system was used at measurements below room temperature; therefore it is described in the companion paper which deals with the measurements at low temperatures.

The spectra recorded in flow were indeed scaled to the spectra measured with pure ozone. The overlap regions are about 5 - 15 nm.

6573, 3

You are right; we probably did a wrong emphasis. We will rephrase.

6573, 4

You are right; we will replace "*concentration*" with "*fraction*". The ozone purity is discussed in the corresponding section in greater details; here we just would like to demonstrate the rough span. We share your opinion, that 100% ozone concentration is unreal, therefore, we write "*almost"*.

6574, 7

This is the upper estimation for the leak rate.

6574-27, 6575-14-17, 6575-19

Equation (3) is based on the fact that 2 molecules of ozone decay to 3 molecules of oxygen in the clean quartz vessel. We don't think it needs additional explanation. This equation was used before by other researchers. In the script we say that initial O_3 pressure p_i is measured immediately after the cell was filled and we give all characteristic time scales – filling the cell, accumulation of spectra and observation of pressure.

'Beginning of the measurements' is the moment when an experimentalist clicks on the Bruker software button to start accumulation of the spectra. It happens as soon as the needed pressure is reached in the cell and the second experimentalist disconnects the trap from the cell. We don't think any additional technical information is valuable for readers. Factors influencing ozone purity are given in the Table 2 and discussed in the Section 2.2.

The initial ozone pressure was corrected for the possible ozone decay during the short time needed for ozone to travel from the trap and to fill the cell. We estimated the losses of ozone during the fill time (usually about a minute) independently based on the condition of the setup (measurement cycle, temperature) and ozone decay rate during the measurement (usually about an hour). This correction is independent on the gas system purity and pressure sensors uncertainty listed in the Table 2. We updated the Table 2 to make more clear separation between different origins of uncertainty.

6575, 25

We will try to re-phrase and to clarify this issue.

6575, 27

We think that further subdivision of the section will make it even more complicated. The relative measurements were done to concatenate them to the absolute ones; therefore, we don't think any chapter separation is needed in this place.

6577, 14

We agree. We will replace "*error"* with "*uncertainty"*.

6577, 18

We agree, it will be corrected.

The absorption length was measured with ruler and calipers (for window thickness). We will add details. Uncertainty is given in the Table 1.

6577, 22

You are right; we will fix misusing of the term "*accuracy*" and add details.

6579, 7

We believe that the introducing sentence is enough to separate analysis of the reported uncertainties from those of the previous studies. However, we added subtitles.

To our opinion, the amount of numbers is not sufficient enough to insert an additional table. Collected information is somewhat bitty, to be organized in a simple table properly. Wavelength regions are given just in few cases. As discussed above, precise information on the uncertainties over different spectral regions is not available for many works. Furthermore, the data from other groups were used by others. This must be commented and would certainly overload the table.

6580, 12

You are right, we will change it.

6581, 20

Figure 4 is already a little bit overloaded. Typical differences of 1-2% are not easily visible in such a plot. Including the BP dataset on this graph would not add any interesting information. For comparison we tried to limit ourselves by the datasets available over the broad spectral region and several single wavelength measurements; the BP is available up to 345 nm only.

6585 14-16

BP dataset was calculated for 298 K to compare with the experimental BP at 298 K. The same was done for BMD. This comparison was done to check the difference between the measured and calculated data and also to check the validity of the polynomial approximation.

6585

We are sorry for confusion with the treatments of the data. It is indeed a complicated analysis; however, to our experience it is fairly common for the users of such data. On the section 6858, lines 10-20 we provide explanation why original experimental datasets are difficult to compare and why parameterization can influence agreement.

Actually, parameterization is the only performed treatment. It is a way to get the data from different measurements to the same temperature and it provides no particular information (we provided comparisons between the original and calculated values to be sure that this treatment does not change data significantly). On the contrary, analysis of the shifts, scaling and difference provides real information about agreement of the different datasets. We think that accentuated separation of the treatments will not clarify the situation but will make it even more confusing and will increase the size of the draft.

We will add link to our other paper (because it indeed considers parameterization in details) and to other papers considering this issue.

6585 last section

Analysis of the agreement between datasets is a complex task. We suggest our version, which follows logic of the previous researchers and is relatively common for the community. As we say in the draft, agreement between different datasets depends on several factors: resolution, temperature, wavelength calibration and noisiness, inherent to every of the compared datasets. The scaling factor is the most straightforward parameter. You are right, this parameter describes bias. It is neither important for the retrievals using the DOAS approach, nor for retrievals based on the wavelength pairs algorithms. We think we clearly present the influence of the scaling and wavelength shifts and provide residual differences in Fig 5. To our opinion, it is apparent that agreement between databases is described by all mentioned parameters in the complex proportion, depending on the application; parameters cannot be mathematically summed.

However, rough estimations are possible. From Figure 5 it is easy to see that, for example, with bias of 0.5%, the mean difference between new data and parameterized BMD is 1.4%. Even rough summation leads to less than 2% of total difference. The same is true for comparison with Bogumil and Voigt data. Mean difference was obtained by averaging of the absolute difference over the spectral region, standard deviation would be smaller. We think that in this case, averaged difference is a little bit more suitable approach.

We don’t think it is reasonable to judge on the quality of any data based on the information on the mutual biases and differences; we provide these numbers for reader’s convenience. However, we comment on the possible problems of the BMD wavelength calibration.

6589, 19

Table 1 indicates that the 450 – 780 nm region was measured absolutely. Oxygen absorption near 760 nm is very weak and is not valuable for the ozone purity estimation (we tried it).

6591, 13-15

We decided to remove the sentence, because discussion on the influence of the cross-sections choice on the retrieved ozone column goes beyond the scope of the paper.

Table 1

To our opinion, all information provided in the Table 1 is useful for readers. Additional information would overload the table.

Table 2

As discussed above, we can not give uncertainties more precise than we did.

We will perform several corrections.

You are right; we mean “*temperature sensors uncertainty”* and not “*off-set”.*

Cooling liquid thickens with falling temperature, cooling flow slows down, and therefore, thermal uniformity is less good at low temperatures.

Technical corrections

Most of your comments were taken into account, thank you very much for your careful attention. We apologize for all unclear issues and misprints, which were present in the draft despite numerous reading.