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Comment

# ***Interactive comment on “Accurate laser measurements of ozone absorption cross-sections in the Hartley band” by J. Viallon et al.***

## **Anonymous Referee #2**

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### **1 General Comments**

The manuscript provides interesting and long awaited results on absolute absorption cross sections of ozone in the Hartley band. These measurements are based on an innovative laser instrument recently developed at BIPM and on a newly designed vacuum system for the fabrication of pure ozone samples, which includes a temperature regulated cold finger, a UV quartz absorption cell, a FTIR spectrometer and a quadrupole residual gas analyser (RGA). Three reference wavelengths (244.062, 248.32, and 257.34 nm in vacuum) have been selected for the absolute absorption

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cross section measurements on pure ozone. The absorption cross section of ozone at the Hg wavelength of 253.65 nm (in air) is obtained from comparing measurement of ozone diluted in air, using simultaneously a SRP instrument and the newly built laser absorption spectrometer. The newly obtained value is expected to replace an outdated recommendation that goes back to a study in 1961, which suffered from a relatively high uncertainty. The consequences of the new measurements are quite important. The new cross section value implies an almost 2% change to concentration values which are based on the cross section value at 253.65 nm and measurement uncertainties are reduced by a little bit more than a factor of two.

The paper is very clear and nicely written, making it a great pleasure for reading. Concepts, tools and data are well described and the presentation follows a logical order. The detailed description of experiments and calculations is very complete and mostly step by step, thus, in principle, allowing reproduction by fellow scientists. Reference to previous work is given wherever required. Given the special importance of ozone for the physical chemistry of the atmosphere and the sometimes conflicting results of spectroscopic ozone abundance measurements, the present work will provide a profound and reliable basis for future measurements. Atmospheric Measurement Techniques (AMT), being dedicated "to advances in remote sensing, in-situ and laboratory measurement techniques for the constituents and properties of the Earth's atmosphere", is therefore perfectly suited for presenting these results. The title has been well chosen, but might still be improved (see point 1 in section 3 below).

Apart from some details (see section 3 further below) the paper suffers from few major drawbacks and errors that need careful consideration before the manuscript can be accepted for publication. It needs to be pointed out that the criticism expressed in this referee report essentially arises from the expectation that the measurements of Viallon et al. will provide a reference for many future ozone concentration measurements in atmospheric research and working environments. It is thus evident that the uncertainty budget must be accurate and "bullet proof", requiring an evaluation standard that is

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perhaps higher than usual.

Given the aims of AMT, the authors also need to extend their conclusion/discussion section in order to better meet the expectation of the community. Indeed, the actual version of section 6 merely provides a summary of the work accomplished and not a real conclusion. In particular, the authors well advocate their newly obtained value at 253.65 nm as a new reference for SRPs and spectroscopically based measurements in the abstract of their paper, but at the end of their document, they lack to give such clear advice and they also avoid discussing the far reaching implications of their results in said section. Instead, the impression is given that the authors hesitate to adopt the new value when they resume the impact on ozone abundance measurements by the UV method using the second conditional (p. 8087, l. 14): "If this new value was to be used in SRPs, it would mean an average increase of the measured ozone concentration of 1.8 %". Is this a misinterpretation of an non-native English speaker or does this mean that the measurements are not reliable enough for changing current practice? Or, does the above statement just announce a possible paradigm shift towards new ozone reference methods (laser or titration based)? When discussing the new results, the authors should keep in mind that the value of the present results for the AMT community will greatly benefit from the authors' authoritative view on how these new data will impact (past, present and future) atmospheric ozone concentration measurements.

## 2 Major Remarks

- A. A non-negligible contribution (60 % according to section 3.6 of the manuscript) to the uncertainty and possible systematic biases come from impurities that impact on the ozone mole fraction ( $x$ ). The authors therefore make much effort in characterising this source of uncertainty (see sections 2.4, 2.4.1, 2.4.2 and 3.4 of the paper) using mass spectrometric and FTIR analysis. Nevertheless, it seems that

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the origin and the nature of possible contaminants is not fully identified and that the calculation of the O<sub>3</sub> mole fraction needs some modification.

As an aside we note that the cross-section at 253.65 nm seems to be the lowest in a series of previous measurement attempts (see Fig. 8 in Viallon et al. 2006). It coincides with the result of Malicet et al. (1989) who report a value of  $11.26 \times 10^{-18} \text{ cm}^2$  that is more uncertain than the previous measurements of Mauersberger et al. (1985, 1986, 1987) and Molina (1986). While this certainly cannot be a criterium *per se* to assess the quality of the current study, it has to be kept in mind that an underestimation of impurities leads to an overestimation of the ozone mole fraction, which therefore would bias the derived cross section towards lower values (see eq. 4, p. 8080). While these previous measurements and also subsequent studies by Brion et al. (1993) and Yoshino et al. (1993) mostly gave higher values at a lower level of confidence than reached in the present study, the methods for quantification of impurities in these studies are not necessarily of a low quality, thus requiring that these results cannot be ignored when discussing the present results.

Some possible biases related to determination of the ozone mole fraction following eq. (3) (l. 2 on p. 8077) are summarized in what follows:

1. First, it needs to be stated that equation (3) should be based on (relative) gas amounts. Measurement of these is not trivial and it is not clear in as much pressure values ( $P_{res}$  and  $P_T$ ) directly correspond to the different gas amounts during an absorption measurement. If understood correctly,  $P_T$  is obtained from a measurement when V1 is still closed and  $P_{res}$  can only be measured after the gas has been expanded (after V1 has been opened) into a much colder volume (73 K instead of 295 K). How have the different volume and temperature conditions been taken into account to make the amount measurements? What is the uncertainty associated with this procedure? Quite generally, one expects (ignoring that ozone has a finite vapour

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pressure for the moment):  $P(O_3) + P_{res} < P_T$ , because the value of  $P_{res}$  is only a lower limit to the impurities in the absorption volume. As explained before, the corresponding underestimation of contaminants implies that the derived cross sections must be shifted towards higher values.

A complicating fact might be that any residual gas contained in the cold finger cannot be evacuated without pumping on the measurement volume. Therefore, one can probably not simply know how much residual gas is already in the cold finger when V1 is opened for the determination of  $x$ , but this effect could likely be simulated in test experiments.

2. It is quite sure that ozone decomposition is restricted to certain areas (seals, gaskets, residues of vacuum grease. . .) in the vacuum system. It is thus necessary to specify the type of gaskets that have been employed. KF or CF flanges (both of which can be combined with VAT valves) are usually used with viton or copper gaskets, both of which decompose ozone. Contrary to what seems to be implied by the manuscript (see item 4 in section 3), ozone must have been in contact with the viton seals of the valves used to confine the vacuum compartment in which the absorption measurements took place. It is thus to be expected that ozone decomposes locally (by forming CO, CO<sub>2</sub> and O<sub>2</sub>). This allows for the build-up of concentration gradients, as has already been pointed out by reviewer 1. Since Fig. 1 is not to scale (the discharge cold finger has a length of 50 cm and the absorption cell of about 5 cm), one can only guess the relevant dimensions: If a characteristic diffusion length of 50 cm is assumed, characteristic diffusion time scales at 1 mbar are on the order of about 20 s, which would not be too far from the measurement time of 1 minute, within that notable ozone decomposition takes place. It is expected that these systematic effects decrease with decreasing pressure.

We note that the argument in favour of a well mixed sample given on p. 8077 seems to be contradicted by Fig. 2. This figure on p. 8096, for example,

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shows (after a large zoom) that the ozone signal decays (top trace) by a few per mil within a minute, but no change of the pressure signal is observed (middle trace) during the same time period, even though the pressure should raise by half the amount of the ozone decay.

A thorough estimate of diffusional time scales and better identification of the processes (and zones) of ozone decomposition is certainly needed to quantify the possible impact on  $x$ .

3. A tacit assumption is that ozone is essentially decomposing into  $O_2$ . It is clear that conversion into  $O_2$  is not exclusive, because  $CO_2$  has already been detected. The important issue is whether other species could be present at more significant levels and it seems that CO is a likely candidate, because oxidation of carbonaceous material is taking place as evidenced by the appearance of  $CO_2$ . If formed and released to the gas phase efficiently, CO might be produced at even higher rates than  $CO_2$ , because oxidation of CO by ozone in the gas phase is slow. Unfortunately, the possible presence of CO as contaminating substance has not been discussed in the manuscript, even though detection of CO by mass spectrometry or FTIR should be possible. Indeed, a mass scan of the residual gas has been performed, but signals at  $m/z = 12$  ( $C^+$ ) or  $m/z = 28$  ( $CO^+$  and  $N_2^+$ ) and the instrument sensitivity for CO were not discussed. If present in significant amounts, not all of the decomposed ozone will end up in  $O_2$ , thus possibly explaining why in Fig. 4 the RGA (purely based on  $O_2$ ) gives a lower result than the estimate based on pressure differences. However, both methods might be insufficient, because they both could possibly depend on unjustified assumptions about ozone decomposition in the vacuum system as long as the possible formation of CO and the lacking correlation between ozone partial pressure and total pressure in Fig. 2 are not explained. It should be noted that the abundance of CO cannot be inferred directly from a comparison with the investigation by Janssen et al. (2011), where metal and viton

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surfaces have been avoided.

What's more, results on CO<sub>2</sub> impurities are not reported consistently with other sources of uncertainty, because a value of zero with a one-sided uncertainty has been assumed (a negative value of CO<sub>2</sub> can be safely excluded), contrary to uncertainties for the other quantities, where the uncertainty region is centred around the expectation value. An unbiased estimate would be a constant (rectangular) probability distribution between 0 and  $3 \times 10^{-3}$  mbar, with mean  $1.5 \times 10^{-3}$  and standard deviation of  $0.87 \times 10^{-3}$  mbar. This would require a corresponding correction (by 0.15 %) of the cross section value, but the uncertainty would be greatly reduced. The reason why a different approach has been adopted should be explained as well as how one and two-sided uncertainties should be combined and interpreted.

In summary, there seem to be at least two reasons (the CO<sub>2</sub> correction and item 1 above) why the newly reported cross sections should be revised to a higher value, yet ignoring that CO has been a neglected impurity and that concentration gradients may have existed during the measurements.

We further note that the above quoted value of 60 % should also be checked, because it is not comprehensible in the light of the budget shown in table 2 on page 8093. There, the optical length and the ozone fraction are listed to give the same contributions ( $u_r = 2 \times 10^{-3}$ , each), thus implying a 50 % fraction at most. If one looks in the text (p. 8084), then the optical length has an even larger relative standard uncertainty  $u_r(l) = 2.3 \times 10^{-3} = 0.11/48.33$ . The contribution from the ozone fraction is therefore about 47 % at most.

Finally, the value of  $u_r(\sigma) = 2.9 \times 10^{-3}$  (entry 6 in table 2 and cited in lines 5 to 10 on p. 8085) that has been obtained from the first four contributions in the same table is neither consistent with the original values in the table nor with the updated ones. Doing the calculation with the values from the table and taking

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the correct path length uncertainty, a 10 % higher value of  $u_r(\sigma) = 3.2 \times 10^{-3}$  is obtained instead of  $u_r(\sigma) = 2.9 \times 10^{-3}$ . It seems, however, that this correction has no impact on further calculations, but this has certainly to be verified. Also the uncertainty budget for the other two cross sections (257.34 and 248.32 nm) must be checked carefully.

- B. The way how cross sections have been obtained from the measurements at different pressures is not well explained and neither the regression model nor the number of adjustable parameters have been presented. This needs to be done in order to comply with the traceability policy of AMT. I suppose that the uncertainty of the absorbance has been used to weight the data for obtaining the non-systematic uncertainty of the cross section from the fit. Further, one might guess that the result has been obtained from the regression assuming an uncertainty in the  $y$ -variable only (because other uncertainty factors can be considered systematic). If so, which values were used for the uncertainty of the absorbance, those of table 2 or the ones given on line 27 on p. 8084 (see item 12 below)? Does the fit parameter uncertainty in table 2 need to be corrected accordingly?

Anyway, it is necessary that the regression details are provided along with a motivation of the different hypotheses. It would also be instructive to discuss the results for both the offset and the slope values of the regression, in particular because the offset may be used to check on unidentified biases and model shortcomings. It is also strongly recommended that the authors devote one figure to the illustration of the linear regression, once for illustrative purposes and once for demonstrating the impact of type A uncertainties on the results.

### 3 Minor Remarks

1. (p. 8067, title) In the light of the use of the SRPs and the Hg lamp based reference method, the significance of the paper is strongly linked to the calculated value at 253.65 nm. This is reflected in the abstract which first concentrates on the 253.65 nm value rather than on the other wavelengths. It is, however, not reflected by the current title of the paper (in *sensu stricto* the 253.65 nm is not a laser measurement neither), which should therefore be changed to reflect this aspect. As a working title I would propose "Accurate laser measurements of ozone absorption cross-sections in the Hartley band and a new reference value for the Hg line absorption cross section at 253.65 nm."
2. (p. 8068, l. 8, abstract) "... with an expanded relative uncertainty of 0.84 %." It is necessary to mention the coverage factor ( $k = 2$ ) here.
3. (p. 8070, l. 4-9) The phrase "In addition, by limiting measurements to the strongest absorbing region of the spectrum, close to 255 nm, all measurements can be performed with a single absorption cell, over a limited ozone pressure range and in a limited time to avoid ozone decay due to dissociation, as reported (Mauersberger et al., 1985, 1986, 1987), with two reported values of the cross-section having a small relative standard uncertainty (0.5 and 0.7 %), and biased by 0.8 and 1.4 % from the 1961 value reported by Hearn." is long and difficult to understand, because it mixes results of the Mauersberger et al studies with the measurement strategy put forward by the Mauersberger group. It would be better to disentangle these two aspects. Also, the present study cannot avoid ozone decay. One should therefore better speak of minimising the ozone decay.
4. (p. 8072, l. 8&9) "... including the 4 valves (VAT KE01) in which only the metal is in contact with the vacuum." This is impossible, because the gate seals are made from viton.

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5. (p. 8075, l. 15 etc.) "The ambient air pressure present ...." – It is not entirely clear whether *ambient* i.e. *real* laboratory air or *synthetic* or *outside* air has been used and how water and CO<sub>2</sub> levels have been controlled during the interferometric length measurements. Both values will have an impact on the refractive index  $n$  and both values could have been very elevated in the presence of one or more experimenters. A statement as to whether possible variations of these two gases could have impacted the results should be given.
6. (p. 8076, l. 6) "A careful analysis ...". Even a very basic analysis should come to the same result. It is therefore proposed to write "An analysis of uncertainties shows ..."
7. (p. 8076, l. 20) CO might be an important contaminant in the present study.
8. (p. 8077, l. 5+) How does the measured ozone vapour pressure fit with previous data? Please compare with the published literature.
9. (p. 8084, l. 18) The length difference should be divided by  $\sqrt{12} \neq 2\sqrt{2}\sqrt{3} = \sqrt{24}$  in order to obtain the calculated standard uncertainty of 9 mm. The use of the different factors should be avoided if the origin of the different contributions is not explained.
10. (p. 8084, l. 13 & 15) The degree sign is missing (it should read  $\tan 3^\circ$  instead of  $\tan 3$ ), and the mm unit is missing behind square root signs.
11. (p. 8084) The standard uncertainty of the absorption length has been determined based on the imposed value  $3^\circ$  for the window inclination. The issue of aligning light paths (HeNe laser, Ar laser) using alignment holes of 3 mm diameter is discussed, but to which degree can the value of  $3^\circ$  be assured in the set up of the alignment holes? In other words, is there an uncertainty associated to the  $3^\circ$  which describe the alignment of the cell with respect to the optical axis defined by the aligning pinholes? Would this impact the uncertainty budget?

12. (p. 8084, l. 27) A relative uncertainty of  $u_r = 3.5 \times 10^{-4}$  for the absorbance is given in the text. The uncertainty budget (table 2, p. 8093) gives a much lower value ( $6.0 \times 10^{-5}$ ). This needs to be resolved and the correct value should be considered in the budget.
13. (p. 8085, l. 3) The word *first* is missing in the phrase beginning on that line.
14. (p. 8096, Fig. 2). Pressure is given in units of mbar. In the text, we often find hPa and mbar. Why hasn't the SI unit been used throughout the text? Note that axes labels (capital and small letters of  $P$ ) do not always correspond to notation in the text ( $P(\text{O}_3)$  and  $P_T$ ).
15. (p. 8099, Fig. 5). This figure is probably not helpful for making the point. While it nicely demonstrates that ozone is decomposed and carbon dioxide gets formed, the fact that  $\text{CO}_2$  is clearly visible in the pure ozone spectrum (at 3 mbar) is disturbing. Why should ozone at 1 mbar show no visible trace of  $\text{CO}_2$ , because "dividing" the spectrum by a factor of three would still show a detectable result, wouldn't it? Perhaps it would be clearer if the corresponding partial pressures of  $\text{CO}_2$  were indicated in the legend.
16. (p. 8100, Fig. 6). A large portion of the graph is wasted with empty space, making it difficult to rapidly grasp the important information. If the legend is put in the space between 250 and 255 nm, the vertical scale could be zoomed in.

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