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Atmospheric Measurement Techniques
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Discussions

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 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 The newly obtained value is expected to replace an outdated recommendation that goes back to a study in 1961, which suffered from a relatively high uncertainty.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 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.

Answer: The reviewer's last comment appears to require a response. The reviewer should be aware that the adoption of new reference values for atmospheric ozone measurements that can change global ozone measurements by 2 % is a process that only starts with the publication of a scientific paper. The authors are confident in the value and uncertainty that will be published in this paper, and furthermore these are consistent with a completely different method (of gas phase titration) that the authors have previously reported. Nevertheless, a global change in reference values requires coordination and an implementation plan, including all involved stakeholders. The authors are developing such a plan, which will involve but be not limited to the Metrology, Meteorology, Atmospheric, Research, Standards writing, Air quality monitoring, Regulatory and Instrument Manufacturer Communities, to ensure that a change in reference values is globally accepted and implemented in an ordered way, to avoid difference in measurement results occurring through use of different reference data. The implementation plan is out of the scope of this paper, but it is being developed to ensure compatibility of ozone measurement results in the future.

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 the origin and the nature of possible contaminants is not fully identified and that the calculation of the O_3 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 $11.26 \times 10^{-18}\ \mathrm{cm}^2$ 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 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.

Answer: equation (3) can be written in terms of partial pressures and remains valid even though different volumes were used for some of the pressure measurements, as is explained below. The referee quite rightly noted that P_T was obtained when V1 was still closed, in the "absorption volume", and P_{res} was measured after V1 was opened to condense ozone in the cold finger in an enlarged volume containing the ozone generator. Nevertheless, the residual partial pressure in equation 3 does not need to be corrected for this enlarged volume, due to the equal residual pressure which is observed on the generator side of V1.

The amount of residual gases in the ozone generator before opening V1 was indeed an issue studied in a side measurement that was not described in the paper to keep it short and readable, but is now described here. First, the volume ratio between the absorption volume and the ozone generator volume was measured using a series of expansions of pure oxygen. Both volumes were found to be equal. This means that the residual pressure should be halved after the opening of valve V1, if the generator volume was empty before the opening of valve V1. A series of measurements were then performed to test the effect of opening valve V1 on the residual pressure. It was observed that the residual gas pressure remained constant when valve V1 was opened, leading to the conclusion that the same amount of residual gas was produced in the ozone generator volume as in the cell volume while V1 was closed, so that their pressure remained unchanged when opening V1. This then allows the partial pressures to be used in equation (3).

In addition, the RGA signal at m/z = 32 was calibrated using a process that matched the measurement process: pure oxygen was first introduced in the volume of the cell, expanded to the ozone generator; V1 was closed again, the oxygen pressure measured, then V3 was opened to let oxygen go in the RGA and perform the measurements of I(m/z = 32).

Modification: the revised version contains more details on the RGA calibration process and a discussion on the rational to state that the residual gases pressure was correctly assessed (section 3.2).

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_2 and O_2). 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, 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.

Answer: the type of material used for the experiment is indeed crucial, and authors took great care to choose materials that would minimize ozone decomposition, and in particular avoid formation of CO_2 and CO by avoiding contact with polymeric materials. The set up was made of quartz for the cell and the ozone generator, and electro polished stainless steel (316 L) for the flanges and valves used to connect both of them to the pressure sensor. Flanges were connected to VAT valves using aluminium o-ring instead of Viton and this improved the life time of ozone and very much reduced the possibility of CO and CO_2 formation. Indeed with valves closed in the system, the ozone does not come into contact with any hydrocarbon/polymeric material.

As pointed out by the referee, ozone was still in contact with the viton seals of the VAT valves, but only when they were open (when such valves are closed only stainless steel is in contact with the gas). This was the case for V1 to evaporate ozone, then for V2 just during the 30 s needed to measure the total pressure with the Baratron. V3 and V4 were kept closed when ozone was in the absorption cell.

Finally, as noted by the referee, an important test is to check that the ozone pressure decrease corresponds to twice the total pressure increase during the measurement time. As indicated in section 3.2, this was always checked during the measurements. The effect is present in the data of Figure 2, which would need to be expanded to make this visible. Therefore another figure is added, to display the typical change in total and ozone pressure (see figure 3). As can be observed on this figure, the ozone pressure variation is always very close to the total pressure variation, with less than 2×10^{-4} mbar difference in average.

Modification: the revised version contains more details on the materials used (in section 2), a figure is added (now figure 3), and arguments in favor of oxygen being the most abundant decomposition product of ozone (section 3.2).

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^+) 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 surfaces have been avoided.

Answer: CO being non-condensable, its partial pressure contributes to the residuals pressure P_{res}. Therefore the ozone amount fraction x deduced from the difference between the total and residuals pressure (further corrected by the ozone vapor pressure) would not be biased by a non-negligible amount of CO.

As observed by the referee, figure 4 does show a difference between the oxygen partial pressure deduced from the RGA measurements and from the absorbance. This could indeed be due to the presence of small amounts of CO. However the difference is covered by the uncertainties calculated for both methods, therefore no extra term in the uncertainty to account for very small amounts of CO is needed.

This explains why authors did not apply the same methodology for CO as for O_2 with the mass spectrometer. In addition, a signal was indeed observed at m/z= 28, but with much smaller intensity than the signal at m/z = 32 (2×10^{-3} compared to 4×10^{-2}, both arbitrary units) and an even smaller change between measurements performed before and after an ozone evaporation-condensation cycle. Therefore analysis of the RGA signal using calibration with pure CO was not feasible.

Regarding FTIR measurements, they could not be used to quantify the amount of CO. Although the molecule does absorb in the same region used for CO_2 and O_3, the absorbance is smaller and the limit of detection of the FTIR in that region would be about 10^{-2} mbar of CO, ten times too high for the expected mole fraction of the trace gas.

In conclusion, the authors confirm that the residual gas is composed of effectively only oxygen, and that the potential presence of CO is covered by the uncertainty used for the P_{res} measurement.

Modification: the text explaining figure 4 (now figure 5, section 3.2.1) is modified to discuss the possible presence of CO explaining the difference between oxygen partial pressure deduced from absorbance measurements compared to mass spectrometry on mass 32. However no extra term is proposed in the uncertainty budget.

What's more, results on CO_2 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_2 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 3×10^{-3} mbar, with mean 1.5×10^{-3} and standard deviation of 0.87×10^{-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.

Answer: The authors do not agree with the suggested treatment of impurities and their uncertainties. The authors have considerable experience in developing uncertainties for impurities, and the use of a zero value with an asymmetric uncertainty is an accepted process. The limit of detection (LOD) sets one boundary for the concentration of the species, and the physical limit of zero sets another. A rectangular probability distribution function is appropriate to the range. By choosing the value zero, the author is stating that the best estimate of the value is zero but the uncertainty then chosen will cover the range up to the detection limit. There is no evidence to say that the most likely CO_2 concentration is 50% of the limit of detection, which is what the reviewer is proposing, and in itself is an approach that can be applied. However, the authors have taken great care in ensuring that ozone does not come into any contact with hydrocarbon or polymeric material in the measurement/production system in their experiment, and indeed is exactly the case when all valves are closed in the system, meaning that the expected value of any possible CO_2 in the system would be well below 50% of the LOD and the use of zero as the most likely value is the better estimate of CO_2 concentration.

No modification.

In summary, there seem to be at least two reasons (the CO_2 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.

Answer: Having considered the reviewer's comments carefully, in particular to the presence of CO and CO_2 impurities, the authors conclude that both of these issues are currently correctly dealt with within the paper and replies provided, and do not require additional corrections which would lead to a revised higher value for ozone absorption cross section.

No modification.

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 ($u_r = 2\times10^{-3}$, 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.

Answer: the inconsistency between the text and the uncertainty table is recognized.

M**odification:**,Text of section 4.6 has been modified to better reflect the numbers provided in table 2.

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 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.

Answer: the uncertainty budget was carefully checked again and revealed a rounded value introduced as standard uncertainty on L_{opt} .The referee is right, and the relative uncertainty should be $u_R(L_{opt}) = 2.22\times10^{-3}$ instead of 2×10^{-3}. This impacts the cross-section relative uncertainty before combination with statistical components to 3.05×10^{-3} instead of 2.90×10^{-3}. Other calculations were checked again to correct the values in the revised document.

M**odification:** modified uncertainty budget (table 2) and according text. All relative uncertainties now indicated with two significant digits.

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.

Answer: authors recognize the lack of details regarding the regressions. The intention was not to hide any data treatment but to avoid lengthy descriptions of a process that is well understood by scientists.

Each cross-section is the average of three values deduced from three independent series of measurements performed on different days. One series of measurement includes nine measurement points, all at different pressures in the range 0.2 mbar to 1 mbar. Each measurement point *i* (*i* = 1 to 9) was formed by the values $X_i = CL$ and $Y_i = Ae$ recorded during one ozone evaporation-condensation cycle as described in the text. Each series of nine (*X*, *Y*) values was fitted using a linear regression model without weight. This was justified by the dynamic aspect of the measurements, preventing any repeated measurement of the experimental parameters (*P*, *T*, *Ae*). The regression uncertainty was characterized using the standard deviation of the residuals. The maximum value obtained for this parameter, i.e. 1.5×10^{-3}, was chosen as a conservative value. It was further combined with the standard deviation of the mean calculated on three repeats at the same wavelength, representative of the reproducibility as series were performed on different days.

Likewise, a conservative approach was applied for systematic sources of uncertainties, choosing the largest value for uncertainty components that are dependent on the pressure. This was motivated by a weak dependency of the cross-section uncertainty versus the pressure, with the largest uncertainty value being still acceptable.

M**odification:** more details on the process described above are introduced in the text of section 5.

3 Minor Remarks

(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."

> **Modification:** Title simplified to ‘Accurate measurements of ozone absorption in the Hartley Band’. By removing the word ‘laser’ from the title the Hg Line measurements are also well described by the title.

(p. 8068, l. 8, abstract) ". . . with an expanded relative uncertainty of 0.84 %." It is necessary to mention the coverage factor (k =2) here.

> **Modification:** coverage factor indicated.

(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.

> **Modification:** sentence revised to: “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 minimize ozone decay due to dissociation, as reported by

(Mauersberger et al., 1986;Mauersberger et al., 1987;Mauersberger et al., 1985). This group reported two values of the cross-section with small relative standard uncertainty (0.5 % and 0.7 %), and with values smaller by 0.8 % and 1.4 % compared to the 1961 value reported by Hearn"

(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.

Modification: sentence revised to "including the 4 valves (VAT KE01) in which the gas is in contact with stainless steel 316, except when they are open, allowing contact with the gate seals in Viton".

(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_2 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.

Answer: measurements were performed in real laboratory air, of which the humidity is controlled to 50 %, as also measured by a probe always present in the laboratory. This represents a correction of 0.1 mm on the path length.
The Edlen formula applies for CO_2 mole fractions in air of 450 µmol mol^{-1} and a deviation of 150 µmol mol^{-1} from that value affect the air refraction index by only 2×10^{-8}. This in turns affect the light path length by 0.004 mm, much smaller than our measurement uncertainty of 0.11 mm. Measurement of CO_2 mole fractions in the laboratory showed an average value of 500 µmol mol^{-1}. In addition, if CO_2 mole fractions in the absorption cell were varying from one measurement to the other, this would have affected the reproducibility of our measurements, and would have therefore been taken into account in our uncertainty budget.

Modification: text modified to clarify that room air was used and that the humidity level was taken into account, while CO_2 levels were considered sufficiently close to the Edlen formula.

(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 ..."

Modification: sentence revised as suggested.

(p. 8076, l. 20) CO might be an important contaminant in the present study.

Modification: text revised to discuss the case of CO as possible contaminant.

(p. 8077, l. 5+) How does the measured ozone vapour pressure fit with previous data? Please compare with the published literature.

Answer: ozone vapour pressures were not compared with published literature because the liquid ozone temperature was not estimated with the highest accuracy. One temperature probe was indeed placed close to the bottom of the cold finger but no special care was taken to verify its accuracy as this was not the purpose of the experiment.
The ozone vapour pressure deduced from our absorption measurements takes values equal to 0.347 Pa on average, which according to Mauersberger *et al.* would mean a temperature of 78 K for the liquid ozone. This is therefore consistent with our expectation and can be added as additional information in the paper.

Modification: text revised to compare the ozone vapor pressure on liquid ozone maintained at 77 K to values published by Mauersberger.

9. (p. 8084, l. 18) The length difference should be divided by $\overline{12} \neq 2\ \overline{2}\sqrt{3} = \sqrt{24}$ 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.

Modification: text corrected as suggested.

(p. 8084, l. 13 & 15) The degree sign is missing (it should read tan 3° instead of tan 3), and the mm unit is missing behind square root signs.

Modification: equation modified to introduce the SI unit for angles instead of degree of arc. Text modified to indicate that all lengths values are expressed in mm.

(p. 8084) The standard uncertainty of the absorption length has been determined based on the imposed value 3° 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° be assured in the set up of the alignment holes? In other words, is there an uncertainty associated to the 3° which describe the alignment of the cell with respect to the optical axis defined by the aligning pinholes? Would this impact the uncertainty budget?

Answer: the alignment holes were first placed before and after the cell using a special Teflon tool realized at the BIPM workshop, allowing the alignment of the two irises with the cell axis. Then the Teflon tool was removed to avoid any light scattering or reflection. Therefore only a misalignment of the laser was considered.

Modification: more details on the alignment procedure are provided in the text. (section 3.1). The uncertainty is not modified.

(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 (6.0×10^{-5}). This needs to be resolved and the correct value should be considered in the budget.

Answer: The referee is right and the value was not correctly reported in the paper, but the combined uncertainty was calculated separately using the correct value of the relative standard uncertainty.

Modification: uncertainty budget table corrected to replace the standard uncertainty value of 6×10^{-5} with the relative standard uncertainty value of 3.5×10^{-4}.

(p. 8085, l. 3) The word *first* is missing in the phrase beginning on that line.

Modification: Phrase modified to:" The five uncertainty components associated with the experimental parameters P_T, x, T, L_{opt}, and A_e are valid for all three laser wavelengths".

(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 ($P(O_3)$ and P_T).

Answer: the bar (and its sub multiples) is a non-SI unit accepted for use with the SI. During the optical path length measurements the sensor (Paroscientfic) values were reported in hPa, while during the ozone cross-section measurement they were reported by the MKS Baratron in mbar. The same units were kept in this paper to avoid mistakes when reporting numbers.

M**odification:** no modification in the text. Axis labels corrected to fit to the chosen notation in figure 2.

(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 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 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 CO_2 were indicated in the legend.

Answer: this graph was chosen to highlight the already negligible amount of CO_2 at 3 mbar, hence at 1 mbar. However authors recognize that spectra at 1 mbar of ozone in which the CO_2 feature is below the limit of detection can be a better demonstration and propose to modify the graph.

M**odification:** figure modified as suggested.

(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.

M**odification:** figure modified as suggested.