Paper amt-2014-158 "Accurate laser measurements of ozone absorption cross-sections in the Hartley band" – Reply to referee 1

Referee #1:

The paper describes a new method for measuring ozone absorption cross sections at three UV wavelengths with a laser. For these wavelengths there are now three groups reporting data within their stated accuracy. For two groups with smallest uncertainties the differences are well within 1%. When compared to other laboratory spectroscopic work the present work is more focused on accuracy issues due the metrology heritage of the authors. Thus, I must admit I enjoyed reading this paper. It is clear, detailed and yields spectroscopic data with quality assessed well defined accuracy. The paper should be published with some minor modifications.

There are only few points where still systematic error sources could be hidden:

The timing of the actual spectroscopic measurement with respect to filling of the cell was not reported. So it is not clear if the ozone was already decomposed during the measurement or after. A part of the decomposition could happen when ozone is streaming through the apparatus after the recording of the spectra during condensation.

Answer: the laser intensity was continuously measured, but only the data recorded just before condensation was selected during the post-treatment. The text of the paper has been modified to clarify this selection process (*page 6, line 6-7*).
Ozone decomposition is believed to start as soon as ozone is in contact with the apparatus surfaces, with the pressure gauge having the most destructing surfaces. So ozone started to decompose before the laser intensity measurement during typically two minutes. If some ozone decomposed after this measurement, it was during the very short time to its condensation that took place as soon as the valve to the cryostat was opened. This duration being less than 5 s, we believe that this is negligible.

In case of ozone decomposition there is the assumption that the ozone and the oxygen are well mixed. This may not be the case when decomposition happens at the pressure gauges which are only open for a short time period.

Answer: this point is indeed important, as a bias in the amount of oxygen deduced from pressure measurements would directly impact the cross-section value. To straighten the statement that the purity of ozone was correctly evaluated, a section with further consideration on the pressure variation was added. The demonstration relies on the combined measurement of the total pressure with the Baratron gauge and the ozone partial pressure with the laser intensity, inside the cell. If ozone decomposes to oxygen only, the decomposition reaction $2O_3 \rightarrow 3O_2$ imposes a factor of 2 between the total pressure increase and the ozone partial pressure decrease. Additionally this shows that the same variation was observed at the gauge and within the cell. This was always measured and checked. Typical numbers were added within the modified version of the text (*page 8, line 22-27*), and an additional graph can be included if necessary.

The temperature homogeneity is not well established. Only one additional measurement inside the cell is reported. Since the cell is not in a vacuum chamber temperature inhomogeneity may occur.

Answer: the temperature was assumed to be homogeneous as the additional measurement was performed with a probe placed inside the cell, in its center, while the probe used during all cross-section measurements was lying on the outside of the cell, at one end, maintained in place with a Velcro fastener. The cell was small (cylinder of 5 cm length and 2.5 cm diameter) and maintained inside the controlled environment of the Plexiglas box. Furthermore those measurements were done during a repeat of the ozone evaporation-condensation cycles to take into account gradients that could occur from the ozone production itself. It is then believed that this measurement could detect the maximum temperature gradient. Finally, an uncertainty component was calculated from those measurements and taken into account in the budget.
The text was modified to better give the exact location of the temperature probes during this measurement (*Page 12, section 4.3*).

Stray radiation at the windows inside the cell may cause a systematic error in the absorption path length. This error was not addressed.

Answer: the stray radiation can be understood as light detected by the photodiode, either coming from the source and not accounted for in the path length, or coming from the room and causing a bias in the intensity measurements.
The path length of the light coming from the laser and detected with the photodiode is believed to be accurately measured with the interferometer detailed in the paper. The windows are tilted with a 3° angle to avoid reflected beams to enter the photodiode. If that would not be sufficient, the interferometer measurement would cover this effect. The fact that the interferometer measurement agrees with the coordinate measurement of the cell length tends to demonstrate that the 3° angle is efficient to avoid reflections of the light.
The room light was blocked by the thin black Plexiglas box covering the cell and the photodiode. In addition the detectors were always zeroed before starting the measurements.
In conclusion it is believed that only the straight UV light was measured. However if the referee comment was not well captured, authors kindly ask the referee to give more precision for them to give a more complete answer while the paper will be in the interactive discussion website.