Paper Ref: acp-2020-456

Title: " Determination of the absorption cross-sections of higher order iodine oxides at 355 nm and 532 nm"

RESPONSE TO THE REPORT OF REVIEWER #1

We are grateful to the reviewer for helpful and constructive comments and suggestions. We address them point by point below. The Reviewer's comments are shown in bold typescript, our response in normal typescript. Changes to the manuscript are highlighted in red. Page numbers refer to the revised manuscript.

Lewis et al combine experimental and theoretical work examining the absorption cross-sections of higher iodine oxides (IxOy). The results indicate that most oxides are rapidly removed by photolysis, which has repercussions for formation of iodine containing particle. The experiments are complex as IxOy have to be generated in-situ, the data appears to be of reasonable quality. This review does not address the accuracy of the theoretical work. The manuscript is well written; the authors may consider the following suggestions for improvement.

Main comment: Actinometry at 355 nm is using NO2 whereas OIO is used at 532 nm. The absorption cross-section of OIO at 532 nm is quoted as being "relatively well known" (L174). The cross-sections of I2 are well known as are those of NO2. It is questionable whether an unstable trace-gas, the spectrum of which has only been measured following its transient formation as the product of the IO-self reaction can be termed "well known". The authors must be more quantitative here. They should properly review (and cite) the limited literature on the OIO cross-section at this wavelength. The same applies to the unity quantum yield of photolysis of OIO. Do all the literature studies agree on this value? Again, the authors need to review (and cite) the literature and state why they believe the quantum yield is one, rather than simply citing one article in which one of the present authors also contributed.

A problem with using I_2 as an actinometer is that its spectrum has many rovibrational lines around 532 nm, and therefore the cross sections determined at this wavelength are very resolution-dependent. Thus, we would have had to determine the absorption cross section of I_2 for our specific laser line width (1 cm^{-1} or 0.03 nm). A second problem specific to our PI-ToF-MS detection system is that I_2 photoionizes very efficiently at 118 nm (see section 2.1), which causes an overload in the detector from the I_2 peak signal towards longer flight times (i.e. higher masses) and requires gating the peak. We have nevertheless carried out a test with partial gating of the I_2 peak. In this test, I_2 depletion was (17 ± 5)% and OIO depletion was (54 ± 4)%. Using the I_2 cross section at 532 nm determined by Tucceri et al. (2006) at 1.4 cm^{-1} resolution (0.04 nm), we obtain $\sigma_{OIO} = (8 \pm 3) \times 10^{-18}$ cm^2 $molecule^{-1}$, which is fully consistent with the literature values of the absolute absorption cross sections of OIO listed in the table below, lending confidence to the method. The main source of uncertainty in this determination is the noise in the semi-gated I_2 trace.

Reference	**Resolution /nm**	**σ_{OIO} /cm^2 $molecule^{-1}$**
Joseph et al. (2005)	0.006	567.93 nm: $(1.51 \pm 0.18) \times 10^{-17}$ 532 nm*: 1.25×10^{-17}
Gomez Martin et al. (2005)	0.35	549.2 nm: $(1.3 \pm 0.3) \times 10^{-17}$
Spietz et al. (2005)	1.3	549.2 nm: $(1.1 \pm 0.3) \times 10^{-17}$ 532 nm: 8.9×10^{-18}
Tucceri et al. (2006)	0.04	610 nm: $(6 \pm 2) \times 10^{-18}$ 532 nm*: 8.2×10^{-18}
Bloss et al. (2001)	1.13	549.2 nm: $(1.1 \pm 0.2) \times 10^{-17}$ 532 nm: 9.9×10^{-18}

The cross sections at 532 nm with an asterisk have been obtained by scaling the relative spectrum measured by Spietz et al. to the cross section of that study at the corresponding wavelength. The relative cross sections measured by Spietz et al. and Bloss et al. are in good agreement, as shown by the selected peak-to-valley ratios listed in the following table:

Reference	**σ_{OIO}(532.0 nm)/σ_{OIO}(541.2 nm)**	**σ_{OIO}(549.2 nm)/σ_{OIO}(560.3 nm)**
Spietz et al. (2005)	2.7 ± 0.2	3.2 ± 0.2
Bloss et al. (2001)	2.2 ± 0.2	3.0 ± 0.2

Considering the differences in methods, resolution and wavelength of the different determinations of the OIO cross sections listed above and the reported uncertainties, the agreement can be considered as reasonable and the cross section at 532 nm can be considered as well stablished, at least within 25%.

There are essentially two independent experimental determinations of the OIO photolysis quantum yield above 500 nm (Tucceri et al. 2006 and Gomez Martin et al. 2009). The studies by Tucceri et al. 2006 and Gomez Martin et al. 2009 employed similar methods and performed similar tests. The main problem of the reaction scheme used by Tucceri et al. in the detection of I atoms was the presence of high ozone concentrations ($\geq 10^{16}$ molecule cm^{-3}), which most likely reduced the lifetime of the I atom photofragment to tens of microseconds, besides other experimental complications such as formation of I_2 and aerosol. In the absence of O_3, Gomez Martin et al. observed a long-lived I photofragment and no reformation of OIO (on a time scale of several ms), strongly suggesting that OIO does indeed photolyze to I + O_2. Further evidence supporting a unit photolysis quantum yield comes from the short lifetime (200 fs) of the C^2A_2 excited state, determined by Ashworth et al. (2002) through simulations of the rotational envelopes of the observed absorption bands. A high-level MRCI theoretical study of the OIO excited states by Kirk Peterson (2010) found a low barrier for dissociation to I + O_2 for the A^2B_2 state, which should lead to efficient I atom production via an initial spin–orbit interaction between the C^2A_2 state and the nearby B^2A_1, followed by a strong vibronic interaction with the A^2B_2 state via an avoided crossing.

Insertion in Page 9, Line 225: The use of I_2 as actinometer is also precluded by the overload issue mentioned above. The OIO absorption cross section at 532 nm is relatively well known, within 25% of the average value of the four independent determinations reported in the literature (Bloss et al., 2001; Joseph et al., 2005; Spietz et al., 2005; Tucceri et al., 2006). On the other hand, conflicting results have been reported for the OIO photolysis quantum yield (Tucceri et al., 2006; Gomez Martin et al., 2009). Here we use the unit quantum yield reported by Gomez Martin et al. (2009), which was determined in a system free of interferences from ozone where a long-lived I atom photofragment and no reformation of OIO was observed over a time scale of several milliseconds. This result is also supported by the short lifetime (200 fs) of the excited state responsible for the observed absorption bands (Ashworth et al., 2002) and the existence of a feasible photolysis path revealed by high level ab initio calculations (Peterson, 2010).

L31 Presumably the 9-16% ozone depletion from iodine chemistry refers to the marine boundary layer. This should be made clear.

This % is indeed over the integrated tropical troposphere as indicated in the cited reference and a new reference added: https://www.atmos-chem-phys.net/16/1161/2016/

L77 "This is currently an important uncertainty. . ." What does "this" refer to? Perhaps "an important source of uncertainty" is better?

Amended in text

L114 Signal-to-noise ratio ~ 400. S/N measured over what period of time? Is drift in laser intensity not more important than S/N for an absorption cell that has no reference photo-diodes. Limit of detection in OD units would be more useful.

The signal from the photodiode was accumulated over ~15 seconds. It is true that the laser intensity drifts, however the drift was not significant over this time period. The S/N increases quickly over ~15 s, before plateauing, and eventually decreasing due to the drift in intensity. Signals were measured back-to-back, so as to negate intensity drift as much as possible. The back-to-back measurements were carried out until 3 concordant results (OD variation <10%) were obtained, which is typically the first 3 results.

Insertion in Page 5, Line 121: […] which corresponds to a minimum detectable OD of 2.5E-3. As there is no reference photodiode in this setup, drift in laser intensity must be accounted for. To negate the effect of laser drift as much as possible, the probe intensity is measured over a period of 15 seconds for both I and I_0, with ~10s between the measurements. To ensure that laser drift does not significantly affect the measured concentrations, measurements are taken until 3 concordant results are obtained (typically the first three results).

Figure 4. What is the pulse-width of the excitation laser ? Please explain why the depletion of NO2 (presumably in ~10 ns) takes 150 ms until the new plateau is reached. To which expression was the red curve fitted and why was it chosen?

The specified pulse width of the Continuum Surelite 10-ii is 3-5 ns. The depletion time of 150 **microseconds** is a sampling time and results from transport of molecules between the region where they are photolyzed to the region where they are photoionized. The sampling in this system can be described in the following steps:

i) Transport of molecules from the reactor toward the sampling orifice.
ii) Transport of the molecules through the sampling orifice.
iii) Transport of the molecules from the exit of the sampling orifice to the ionization region.

The sampling time depends on the alignment of the lasers and on the molecular masses of the bath gas and sample species (Baeza-Romero et al., 2011, DOI: 10.1002/kin.20620).

The curve chosen is a sigmoidal curve with variable Hill slope given by parameter 'p'.

$$y = S_0 + \frac{S_1 - S_0}{1 + 10^{(\log x_0 - x)p}}$$

This fitting function is chosen to fit empirically the observed depletion curves. The only parameters relevant to this study are the top and bottom asymptotes.

Insertion in Page 8, Line 169: The trace shown in Figure 4, which is similar to all the traces obtained in this experiment, exhibits a delay between the pre- and post-photodepleted signal. This delay corresponds to an instrumental sampling time depending on the alignment of the lasers and the molecular masses of the bath gas and the sample species (Baeza-Romero et al., 2012). In the present experiments, it was necessary to leave a small gap (~2 mm) between the photolysis volume and the sampling pinhole, so as to avoid hitting the skimmer cone with the laser. The diffusional exchange of molecules between the photodepleted volume, and the un-photodepleted volume immediately before the pinhole blurs the onset of the photodepletion as it is measured by the TOF-MS. The values of S_0 and S_1 were obtaining by empirically fitting the photodepletion trace to a sigmoidal function:

$$y = S_0 + \frac{S_1 - S_0}{1 + 10^{(\log x_0 - x)p}} \qquad (2)$$

Fitting to this function ensures that the flat sections corresponding to the pre- and post-photodepletion concentrations (S_0 and S_1 respectively) are characterized in the precise regions outside of the aforementioned “blurred” zone. The parameters x and p are not of scientific importance for this study and are simply instrumental factors.

L146 and L147 Laser “shot”, excimer “flash”. Perhaps use the term “pulse” ?

Agreed that pulse is better, changed in the text

Figure 6 What causes the increase in the IO signal after 1.85 ms.

Photolysis of IO at 355 nm results in O and I atoms, which will react respectively with I_2 and O_3 in the reaction mixture rapidly, reforming some of the IO lost to photodepletion. In addition, some O_3 may also photolyze at 355 nm producing O atoms.

L259 Please show the trace obtained using the actinometer (OIO). This could potentially go into supplementary information along with the raw data (lack of signal change) for the higher oxides and would give the reader an idea of the data-quality.

Added as new Figure 8.

Figure 7 Indicate when the laser was triggered in the I2O3 experiment. Are the red curves the same function as used in Figure 4 ?

Now indicated in the figure caption.

Yes, all traces are analysed by performing the same empirical fit. This is now stated in page 8.

L370 please provide references to the tropical UTLS being a “hotspot” of iodine chemistry. Have there been measurements of IO or higher iodine oxides in this part of the atmosphere?

Yes, the reference was already there a few sentences later. We have inserted the reference (Koenig et al., PNAS 2020) at the beginning of the paragraph. However, calling the UTLS a ‘hotspot’ may lead to think of places like Mace Head, Antarctica, etc. Therefore, we refer now to the UTLS as an ‘active iodine chemistry region’ instead.