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 #2

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.

Review of “Determination of the absorption cross-sections of higher order iodine oxides at 355 nm and 532 nm” by Lewis et al. This paper presents photochemical data for iodine oxides (IxOy), a hitherto elusive family of atmospheric transients thought to play an important role in the coastal marine boundary layer. Results were determined via laser photolysis / photodepletion experiments using mass-spectrometry detection of IxOy, supplemented by ab-initio calculations. This first extensive dataset can provide valuable information needed to construct models of atmospheric chemistry. However, there were a few points that require further clarification and discussion within the manuscript prior to publication in ACP.

Firstly, experiments appear to have been conducted under very different conditions of gas pressure and identity to those found in the boundary layer. At the top of page 6 it was stated that experimental pressures of 4 to 7 Torr were used (though whether of He or N2 was not clear). This is clearly a very different matrix of gases to 760 Torr of N2, O2 and H2O found in coastal boundary layer air. There is surely some doubt therefore, whether some qualitative observations from this work are valid for atmospheric models. The chemical mechanisms for IxOy formation will surely differ to some extent due to changes in stabilization rates for association products at the different gas-pressure, or perhaps reactions of transients with O2 (or even H2O) that would proceed faster in the boundary layer. Specifically, much is made of the absence of I4Oy species, but we simply do not know if these compounds would be formed in realistic atmospheric conditions. If there is clear evidence for why such pressure or O2 effects are unimportant then this needs to be detailed in the manuscript.

The carrier used was He in all photolysis experiments. We report results elsewhere (Gomez Martin et al, 2020) showing that iodine oxide clusters with even number of iodine atoms do not form, and that I_xO_y + H_2O reactions are extremely slow, either at low pressure or at higher pressures and with a more atmospherically representative matrix of gases. We have added this reference since this manuscript has very recently been accepted for publication in *Nat. Comm*.

Insertion in Page 12, Line 335: […], even for higher pressures and using N_2 as carrier gas (Gómez Martín et al., 2020)

Second, regarding more quantitative results, could photolysis quantum yields and therefore photolysis cross-sections differ as the pressure and identity of the surrounding gas matrix changes? Certainly these effects can be important for many atmospheric transients, not least for the actinometer NO2 though at a longer wavelength than used in this work. I suspect that such pressure effects will have a negligible impact on the quantitative results from this work, given, as stated on page 16, the featureless nature of the spectra. However, given the large divergence from atmospheric conditions noted above, a strong statement to the effect that these cross-sections / quantum yields are applicable to realistic atmospheric conditions would be advisable.

As the reviewer points out, NO_2 excitation at 355 nm is not dependent on the nature or pressure of the matrix, and is therefore suitable for use as an actinometer in these experiments (Troe, J. *Z. Phys. Chem*. 2000, **214**, p. 573-581). It is important to separate the two points being made here: firstly, the potential effect of the matrix on the chemistry leading to the formation of the molecules being studied in this work and secondly, the potential effect of the matrix on the photolysis quantum yield of the molecules being photolysed. Assuming the molecules are thermally equilibrated (a safe assumption at the pressures and timescales used in this study), the route to their formation has no bearing on the photolytic properties of the molecules. As the reviewer points out, the broad, featureless calculated absorption spectra indicate excitation to an unbound upper state. The photolysis processes in this study therefore do not depend on the nature and pressure of the matrix, and are suitable for use in atmospheric models.

Insertion in Page 9, Line 236: This is a reasonable assumption for broad band absorption spectra indicating excitation to an unbound upper state. The photolysis processes in this study therefore do not depend on the nature and pressure of the carrier gas matrix, and the results can be applied directly in atmospheric models.

Third regards the use of OIO as the actinometer for 532 nm experiments. I can understand why this molecule was used, given a limited set of alternatives. However, the manuscript needs to properly represent the problems that this introduces into the interpretation of results. The cross-section for OIO may be "relatively well known" as stated on page 8 (line 176), but I was not able to find a recent review justifying this statement. On the contrary, of the two references quoted in this work for OIO cross sections, only one (from Bloss et al.) quotes a value at 532 nm. A very quick look in the literature yielded cross-section data from five additional papers (Spietz 2005, Joseph 2005, Himmelmann 1996, Tucceri 2006 and from Ingham 2000) that differ by up to a factor of two at some wavelengths. Further, the quantum yield (QY) for atomic iodine production from OIO is certainly not established. Ingham et al. reported QY < 0.15 for this channel, in direct contrast to the value of unity taken from Gomez Martin et al. and used for the purposes of this work. Happily, a careful re-wording of the manuscript here can rectify these problems. First, the section on page 8 needs to take full account of the published literature on OIO. Second, the results obtained in this work need to be clearly denoted as being determined relative to the rather uncertain cross-sections and quantum yields for OIO at 532 nm.

Reviewer #1 has raised the same question. We have included in the revised manuscript a review of both the absorption cross section and the photolysis quantum yield of OIO at 532 nm. Note that Gomez Martin 2005 and Spietz et al. 2005 are part of the same body of work. While the former paper reported the cross section at a single wavelength and a higher resolution, the later reported the visible spectrum at a lower resolution. Overall, the four existing independent determinations do not deviate by more than ~25% from the average when they are extrapolated to 532 nm, and the relative cross sections measured by Bloss et al. and Spietz et al. across the visible spectrum are in very good agreement.

Insertion in Page 9, Line 225: 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; Gómez Martín 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).

Lastly, on Figure 4 “an empirical fit” was used to obtain depletion parameters. What was the function? More interestingly, which processes were responsible for the delay in signal depletion following (presumably rapid) photolysis. Is this delay instrumental, and therefore present in other experiments? It is not possible for the reader to assess for themselves, as a very different timescale is presented on Figs 6 and 7.

This point has also been raised by Reviewer #1 and we have included a thorough explanation and a reference (Baeza-Romero et al., 2012) in the revised version of the manuscript.

More minor comments:

Page 2 it was stated that the main atmospheric fate of iodine atoms is reaction with O3 to form IO. This is likely true across much of the globe, but a significant alternative exists in polluted air (as encountered in many important areas of the coastal MBL) where reaction with NO2 to form INO2 would be competitive. In an iodine-rich, semi-polluted environment like Roscoff (France), the NO_2 mixing ratios range between a few hundred ppt to a few ppb and the O_3 mixing ratios range from 10 to 50 ppb (Mahajan et al, 2009). Assuming the average mixing ratios registered in Roscoff during the RHaMBLe campaign, i.e. ~1 ppb NO_2 and ~30 ppb O_3, the ratio of first-order loss rates of atomic iodine to reaction with O_3 and NO_2 is ~7. Thus, it is a fair statement to say that the main atmospheric fate of atomic iodine is to react with ozone, even in semi-polluted, coastal environments.

The text on page 3 reports flows diluted in He whilst Figure 1 appears to indicate N2 as the principal diluent. Which is correct? If a mixture of the two then please use the text and / or the caption to Figure 1 to offer more detail.

Helium is correct. We have changed Figure 1 accordingly.

Similarly in the experimental details a laser energy of 120 mJ pulse-1 was reported. A more useful quantity for the reader would be the energy per pulse per square centimetre, as this more directly relates to absorption cross-sections (quoted in cm2 molecule) and consequent radical densities. Please supply this information / clarify.

Clarified in text to give the total laser energy per pulse and the laser energy per pulse per unit area (i.e. the laser pulse fluence).

The same applies to the YAG laser energy (page 5 line 116).

Clarified to give laser fluence (energy per pulse per unit area).

Technical: Page 3 line 63 – 65 was confusing.

Clarified. The CI-ToF-MS technique referred to uses a NO_3^- ion source. The observation of IO_3- signals is interpreted as a result of ambient HIO_3 being ionized by NO_3^-.

I think the authors mean to say "Since all reaction paths for I, IO or OIO with H2O are endothermic"

Changed.

Page 3 line 86 "introduced in the reactor" should be something like "introduced to the reactor"

Amended in text

The use of low-contrast colours on e.g. Fig 8 without other visual markers will make it very difficult for some readers to distinguish e.g. I2O2 from I2O3 from I2O4. Could dots or dashes be introduced to help with this issue of accessibility?

Done (now Figure 9)

Fig. 9 uses the same symbol type (circles) to represent I3O6, I3O7 and I5O12 – please make use of triangles / squares. Additionally, information was missing from the legend where only I5O12 is mentioned

Done (now Figure 10)