

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 #4

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.

**In this manuscript, Lewis et al. report experimental and theoretical determinations for the absorption cross-sections of iodine oxide species. Experimental measurements of the cross-sections were obtained using a technique that combined laser-flash photolysis (for production of iodine oxides from an I<sub>2</sub>/O<sub>3</sub> mixture), photoionization mass spectrometry (for time-resolved species detection at 10.5 eV), and 355/532 nm laser photolysis. Cross-section measurements were calibrated using NO<sub>2</sub> and OIO at 355 nm and 532 nm, respectively.**

**Theoretical determinations of the absorption spectra of the iodine oxides were obtained based on their B3LYP geometries. Atmospheric photolysis rates were determined across the actinic range using the theoretically-determined spectra, constrained by the experimental measurements, combined with the CAM-Chem model. In the experimental and results sections, the authors describe using the kinetic profiles of the iodine oxide species to determine at what delay times the second photolysis laser (355/532 nm) was fired for the absorption cross-section measurements. It would therefore be appropriate to present the complete time profiles of each of the species (in the absence of the second photolysis laser pulse) either in the main text or the supplementary information.**

The same point has been raised by Reviewer #3. New Figure 5 includes some examples of full time traces as requested (the Figure is included in the response to Reviewer #3)

**Please give the form of the function that is used to fit the photodepletion data in Figures 4, 6 and 7. There appears to be significant differences in the depletion behavior of the different species that the authors do not address. For example, why is the depletion of I<sub>2</sub>O<sub>4</sub> much sharper than I<sub>3</sub>O<sub>7</sub>?**

This point has been raised by Reviewers #1, #2 and #3, and has been clarified in the corresponding responses

**What is the sensitivity of your measured cross-sections to the delay time of photolysis laser 2 (e.g. the 355 or 532 nm laser)?**

The cross sections are insensitive to the delay time of the second photolysis laser, provided the species of interest is present, and uncontaminated by daughter ions of higher oxides. Great care was taken to assure that this was the case for all species being measured (see new Appendix B below).

**What is the error in the theoretically determined absorption cross-sections? Does the magnitude of this error significantly impact the results of the atmospheric photolysis rates?**

One thing we should have mentioned is that the TD-DFT spectra were wavelength shifted by applying a constant energy shift to get agreement with the experiment at 355 nm. The shifts are quite modest, within the expected error at this level of theory (Foreman and Frisch, 2015):  $\text{I}_2\text{O}_3$  (30 kJ mol<sup>-1</sup>),  $\text{I}_2\text{O}_4$  (-12 kJ mol<sup>-1</sup>),  $\text{I}_3\text{O}_6$  (9.2 kJ mol<sup>-1</sup>),  $\text{I}_3\text{O}_7$  (-21 kJ mol<sup>-1</sup>). Applying a constant energy shift means assuming that all the excited state energies are offset by a constant amount with respect to the ground state. As shown in Figure 10, the upper limits from experiment are within 20% of the theoretical calculations for linear  $\text{I}_3\text{O}_6$  and  $\text{I}_3\text{O}_7$ .

Having anchored the theoretical absorption spectrum at 355 nm, we then assume that photolysis is possible up to the dissociation limit (which is the case for all the transitions of the  $\text{I}_x\text{O}_y$  ( $x > 1$ ) molecules). A conservative estimate is a factor of 2 uncertainty in the  $J$  values for these molecules, which does not change the conclusions of our study.

We have introduced the following changes in the manuscript to clarify these points:

Page 16, first paragraph: **The TD-DFT spectra were wavelength-shifted by applying a constant energy shift to get agreement with the experiment at 355 nm. The shifts are quite modest, within the expected error at this level of theory (Foreman and Frisch, 2015):  $\text{I}_2\text{O}_3$  (30 kJ mol<sup>-1</sup>),  $\text{I}_2\text{O}_4$  (-12 kJ mol<sup>-1</sup>),  $\text{I}_3\text{O}_6$  (9.2 kJ mol<sup>-1</sup>),  $\text{I}_3\text{O}_7$  (-21 kJ mol<sup>-1</sup>). Applying a constant energy shift means assuming that all the excited state energies are offset by a constant amount with respect to the ground state.**

Page 17, Lines 407-409: The calculated spectra shown in Figure 9 and Figure 10 agree generally well with the experimentally determined values at 355 nm and 532 nm **after small**

wavelength shifts indicated above. As shown in Figure 10, the upper limits from experiment are within 20% of the theoretical calculations for linear  $I_3O_6$  and  $I_3O_7$ .

Page 20, Lines 463-465: Having anchored the theoretical absorption spectra at 355 nm, we then assume that photolysis is possible up to the dissociation limit (which is the case for all the transitions of the  $I_xO_y$  ( $x > 1$ ) molecules). A conservative estimate is a factor of 2 uncertainty in the  $J$  values for these molecules.

**There is very limited discussion about the potential impact of the daughter ions (referred to in the manuscript as photofragments) of larger iodine oxides on the determination of the cross-sections of smaller iodine oxides. Given that not all of the iodine oxides produced in the experiment have the same cross-section, if larger iodine oxides undergo dissociative ionization at 10.5 eV to photofragments with the same exact mass as the smaller iodine oxides studied in this work, the measured depletions of the smaller iodine oxide species would be perturbed by the contribution of photofragments from the larger iodine oxide species. To what extent do the authors have evidence that this is not significantly hampering their cross-section measurements?**

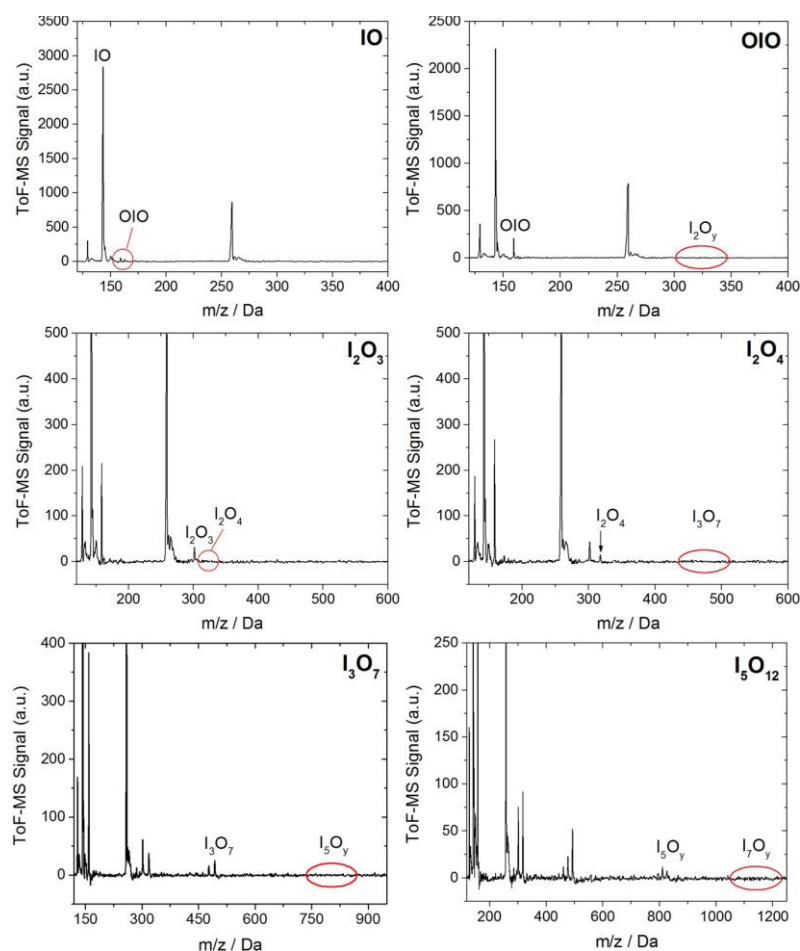
The discussion about the impact of fragmentation has been expanded, including an Appendix B. Additional plots have been generated to illustrate the steps taken to eliminate this important potential effect highlighted by the reviewer (Figure B 1). Essentially, kinetic profiles were taken for each set of conditions (new Figure 5), which allowed the optimal window for photolysis to be established, whereby the signal for a species is present in the spectrum, but any larger species which could photofragment to a daughter ion indistinguishable from the species of interest, is not present. In this way, it can be said with confidence, that daughter-ion contamination is not an issue in these experiments.

Addition to the manuscript:

### **APENDIX B. Photofragmentation of $I_xO_y$ species**

The photofragmentation of  $I_xO_y$  species to daughter ions in the photoionization chamber of the detection apparatus necessitates careful experimentation in order to ensure that any photodepletion of a species of interest is solely due to its 355 nm or 532 nm photolysis in the flow tube, and not obscured by the daughter ions of larger  $I_xO_y$  species. To elucidate the optimal window for investigating photodepletion of each species, time resolved mass-spectra were recorded for each set of experimental conditions (Figure 5). From the kinetic information, it is then possible to inspect the averages of the mass spectra within these windows to ensure that

the species of interest is present, but larger  $I_xO_y$  species are not, as shown in Figure B1. By ensuring no larger  $I_xO_y$  species are present, it follows that for a species of interest, only parent ions of the species are contributing to the signal intensity within that time window, and that no contribution to the recorded signal is coming from daughter ions. Note that the signals shown in Figure 5 and Figure B1 are not accumulated for extended periods of time, and as such are relatively noisy. Long accumulation times and corresponding large signal to noise ratios are unnecessary for these experiments, since the objective is simply to elucidate optimal time-delays within which photodepletion experiments are carried out, (photodepletion experiments are typically carried for  $\sim 10\times$  as many accumulations) and are carried out prior to an experimental session. It should be noted also that the optimal timescales such as those shown in Figure 5 and Figure B1, vary depending on the concentration of IO formed at the beginning of the reaction sequence, and since the reactions which facilitate the stepwise formation of the higher oxides are second-order, even modest changes in [IO] at early times can result in significant changes to the appearance times of the different species of interest.



**Figure B1:** Mass spectra corresponding to the optimised time delays shown in Figure 5. The plots are generated by averaging the signal obtained for each mass over the 5 ms window. The species of interest is given in the top right corner of each spectrum.

**Ionization energy calculations of larger iodine oxides to possible photofragments at the mass of the smaller iodine would indicate whether this is a concern or not at 10.5 eV.**

Fragmentation is indeed a concern, as demonstrated by the traces of IO and OIO at longer delay times. Ab initio calculations of ionization and fragmentation energies are included in a recently accepted paper (Gomez Martin et al. 2020). We have included a reference in the paragraph introducing the results.

**Additionally, measurements at reduced concentrations of [I], and at various delay times of the second photolysis laser would provide further indications of potential interference.**

Appendix B explains the procedure for minimising the influence of daughter ions.

**Minor comments: Figure 1 An entry port for H<sub>2</sub>O is indicated, is water used in any of these experiments?**

Water was not used in these experiments. The Figure has been updated.

**Section 2.1 For clarity, it would be helpful to distinguish the three laser pulses used in these experiments using a numbering scheme (e.g. photolysis pulse 1 or 2, photoionization pulse).**

For clarity, the laser pulses have been amended in the text, and prefaced with either excimer, photolysis or PI laser.

**Section 2.2 Table 1 and Figure 5 should be moved into the results section, or perhaps the supplementary information.**

A new Appendix A has been added containing supplementary ab initio results.

**L239 The number of significant figures in the value and the error for the I5O12 cross section are not consistent (and differ from the value in Table 2).**

Amended in text