

Interactive comment on “Determination of the absorption cross-sections of higher order iodine oxides at 355 nm and 532 nm” by Thomas R. Lewis et al.

Anonymous Referee #3

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The manuscript by Lewis et al. (acp-2020-456) describes experimental measurements and theoretical calculations to determine the absorption cross sections of higher iodine oxides, as well as modeling to assess the impact of the photochemistry in the atmosphere. The quality of the experimental data for what appear to be challenging experiments is reasonable. I have concerns that the modest theoretical methods applied may be inadequate to describe the electronically excited states in molecules such as the iodine oxides, but that is somewhat beyond my area of expertise. If the authors could demonstrate clearly that they are capable of reasonably predicting molecular properties of a well-known iodine oxide, it would go some way to assuaging those concerns. I am unable to comment on the atmospheric modeling, although I would note

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that they rely on cross sections that have been determined experimentally at only two wavelengths. The paper is, for the most part, fairly well-written although the structure could be improved. Some of the text in the methods section would be better located in the results section. For example, lines 144-179 (including Figure 3 and 4) describe measurements, not the experimental set-up, and belong in the results section, as do the results of the ab initio calculations.

Table 1 compiles calculated geometries and vibrational frequencies, which are of little relevance to the subject matter of the paper and could be readily removed to supplementary information. On the other hand, no data for the calculated energies or oscillator strengths of the electronically excited states that are responsible for the visible and UV absorption are provided; the calculated ionization energy is also reported for only one species (IO₃ on line 257). These data impact directly on the interpretation of the experimental results and should be compiled either in a revised version of Table 1 or in supplementary information.

The results section would benefit from a clearer introduction to describe what IxOy species are detected in the experiment and their time dependence. A figure showing the different “kinetic profiles”, which are alluded to, would also be valuable. Presumably, the profiles have been characterized by varying the delay between the 248 nm photolysis pulse used to initiate the chemistry and the VUV photoionization pulse. The authors acknowledge (pages 13, 14) that fragmentation of larger species, can lead to signal increases at the masses of the photofragments, which would lead to possible systematic under-estimation of the depletion. To use the authors' example of I₃O₇, I have no sense of how much is present at the ~7.6 ms time delay when the I₂O₄ (a potential daughter signal) is measured. Could other experimental parameters be varied (in principle) to modify the relative yields of different IxOy species to explore this in more detail? Relative photoionization cross sections for the various species will also play a role.

The depletion measurements in Figure 6 and 7, as well as the NO₂ depletion used for

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actinometry in Figure 4, are shown with an overlaid empirical fit. However, the fitting function is not described, or its choice explained, nor are any reasons for the different shapes discussed. Why does the effective “width” of the drop off appear to change for different species? Is it even meaningful? What delay does the time axis correspond to in these figures? The experiments use three laser pulses (two photolysis pulses, one to initiate the chemistry and a second to dissociate the iodine oxides) and one to detect the IxOy species. Clarity about which exactly which delay is being referred to would be helpful.

Minor comments.

Figure 1. The photolysis laser arguably should be labeled also with 532 nm as some experiments use that wavelength.

Line 113: Using the values for the cross section, concentration, and path length for I2 detection, I calculate OD = 0.82.

Figure 3. The caption could be more informative, for example, the time delay between the 248 nm pulse used to initiate the chemistry and the VUV photoionization pulse is not specified. Are the different colored traces the results of measurements at the optimum time for each?

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