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Atmospheric Chemistry and Physics Discussions

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 #4

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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 I2/O3 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 NO2 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.

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 I2O4 much sharper than I3O7?

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)?

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?

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

Minor comments:

Figure 1 An entry port for H_2O is indicated, is water used in any of these experiments?

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).

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

L239 The number of significant figures in the value and the error for the I_5O_{12} cross-section are not consistent (and differ from the value in Table 2).

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