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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 #2

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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.

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Discussion paper

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.

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.

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.

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.

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. 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. 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. The same applies to the YAG laser energy (page 5 line 116). Technical: Page 3 line 63 – 65 was confusing. I think the authors

mean to say “Since all reaction paths for I, IO or OIO with H2O are endothermic” Page 3 line 86 “introduced in the reactor” should be something like “introduced to the reactor” 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? 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.

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