

Interactive comment on “The UV-visible absorption cross-sections of IONO₂” by J. C. Mössinger et al.

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This paper reports the first laboratory measurements of the UV-vis absorption spectrum and cross sections for gas phase IONO₂. IONO₂ has eluded detection and quantification for some time and therefore the results of these measurements will significantly advance our understanding of atmospheric iodine chemistry. The results from these measurements are particularly valuable in the interpretation of ozone destruction cycles and iodine partitioning in the marine boundary layer.

There are several subtle but important points in the paper that the authors could elaborate on to help the reader in the understanding of the experiments and analysis procedures. I have outline these points below with sub-titles: Time Scales, Error Analysis, and Atmospheric Implications. I have included a list of minor corrections at the end.

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Time Scales: The authors need to describe and discuss the relevant time scales used in the measurements more clearly. The time scales are important because the chemistry used in the production of IONO₂ is significantly different than that of the measurements. The point being that the chemistry leading to the formation of IONO₂ has gone to completion well before the first spectral measurement is made. Therefore, the absorption measurements do not provide any information related to the IONO₂ formation (i.e. chemical mechanism). The determination of the IONO₂ absorption cross sections from the absorption measurements is therefore critically dependent on the accuracy of the proposed chemical mechanism. A limitation to the interpretation of these measurements is therefore the validity of the chemical mechanism used in the analysis. The authors need to make this point very clear. It may be possible to perform calibration or test measurements to confirm the chemical mechanism. The authors could discuss these possibilities. For example, the photolysis laser fluence (i.e. O atom production) could be measured in separate experiments to confirm the values determined in the data fitting. Or single wavelength absorption measurements at longer wavelengths on a faster time scale could be used to confirm the NO₂ concentration temporal profile. The time dependent UV absorption measurements with the CCD are useful in the evaluation of the stability of the final products (see discussion of IONO below). What was the duration of the measurements?

Error Analysis: The error analysis presented in the paper is rather qualitative and I presume based on the authors' feeling for the accuracy of the methods used in the measurements and analysis. The authors could elaborate on the following points: (1) The authors state that several measurements were performed. What is the precision of the results from these separate measurements? Were the time-resolved absorption measurements for a given experiment averaged in the final analysis to improve the signal to noise? Following the discussion below, what uncertainty is introduced from the chemical mechanism, IONO formation. How about the uncertainty in the IO + IO rate coefficient and product channel yields? (2) Spectral subtraction: The authors need to explain in much more detail how the spectral subtractions in the short

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wavelength region were performed. None of the significant absorbing species in this wavelength have unique spectral features that the analysis can lock onto. Therefore, how a unique spectral analysis was obtained is not clear and I would think this would lead to increased uncertainties. The analysis of the long wavelength data where NO₂ has more structure in its spectrum is more straightforward. Therefore, the uncertainties in the short and long wavelength data are probably not the same. Another question related to the spectral analysis is the possible contributions from INO₂ and IONO (see below). {Suggestion for future experiments: Instead of using an optical filter to block the radiation of the laser from reaching the CCD detector could an electronic shutter be used. The shutter would enable the absorption spectrum to be measured over all wavelengths simultaneously which eliminates the need for interpolation of the short and long wavelength regions. This should also help reduce systematic errors in the spectral subtraction. The general drawback of using a shutter would be time response, $t > \sim 4$ ms. However, that would not be a problem in this experiment.}

(3) INO₂ and IONO: From the conditions and chemical mechanism presented in the paper the concentration of the INO₂ reaction product is $\sim 10\%$ of the final IONO₂ concentration. This would indicate that spectral subtraction of INO₂ absorption should be made. INO₂ was not subtracted in the data analysis presented in the paper. A complication to spectral corrections for INO₂ is that there are no distinct signature features in the INO₂ spectrum which to use to guide the spectral subtraction. Therefore the accuracy of this correction would depend completely on the accuracy of the chemical mechanism (and the kinetic parameters) and also literature values of the INO₂ spectrum. What uncertainty would this introduce in the IONO₂ cross sections (it should be wavelength dependent)? On page 772 the authors compare the measured IONO₂ spectrum to that of INO₂ as reported in the literature. The authors conclude that the spectral differences support the assignment of the spectrum to IONO₂. I am not sure I follow the logic given here. Because the spectrum does not look like INO₂ does not necessarily support the assignment as IONO₂. Second, several of the features in the INO₂ spectrum seem to be present in the IONO₂ spectrum. Does this mean that INO₂

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is present in the spectrum and needs to be subtracted out? The reaction $I + NO_2$ could possibly form the isomers INO_2 and $IONO$. Only the INO_2 isomer is considered in the chemical mechanism. There are no experimental measurements that identify the formation of $IONO$ in the literature. Molina and Molina (GRL, 4, 83, 1977) and Burkholder and Orlando (CPL, 317, 603-608, 2000) have shown that the $Cl + NO_2$ and $Br + NO_2$ reactions form the $ClONO$ and $BrONO$ isomers with very high yields, $> 75\%$. The UV absorption spectra of the $ClONO$ and $BrONO$ isomers have been measured and are significantly red-shifted from those of $ClNO_2$ and $BrNO_2$. These measurements have also shown the $ClONO$ and $BrONO$ isomers to be unstable due to thermal decomposition and isomerization. The authors need to discuss the possibility of $IONO$ formation in their chemical mechanism and what uncertainties its presence would have on the determination of the $IONO_2$ spectrum and cross sections.

(4) The authors have used an empirical set of three Gaussian functions to interpolate the absorption cross section data from the short to the long wavelength data sets. The authors need to discuss or show how well this empirical analysis fits the experimental data. Should the parameters of the fit be reported?

Atmospheric Implications: It would be worthwhile to show the wavelength dependent contribution to the calculated atmospheric photolysis rate in a separate figure with the details explained in the text. Showing the wavelength dependence would help the reader evaluate the uncertainties in the $IONO_2$ photolysis rate. The primary questions related to the photolysis rate that this would address are outlined below. (1) Based on the general shape of the $IONO_2$ UV absorption spectrum it is reasonable to assume that it is due to a number of overlapping electronic transitions. Several of these transitions, particularly the transitions at longer wavelengths, may be to triplet states which may have photodissociation quantum yields less than one. At this point, assuming a quantum yield of one at all wavelengths is reasonable but it would be valuable to know what particular wavelength regions (electronic transitions) contribute to the total photolysis rate. (2) The photolysis rate was calculated assuming that wavelengths longer

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than that reported in this work do not contribute to the photolysis rate, i.e. the calculation was terminated at 415 nm. Showing the wavelength dependent photolysis rates would demonstrate if this is sufficient or if data to longer wavelengths could make a significant contribution. (3) A significant wavelength range that falls in the actinic region was not measured directly but was inferred from an empirical interpolation of the data at shorter and longer wavelengths. What is the contribution of this wavelength region to the total photolysis rate?

Minor Corrections: Page 768, line 13: insert a comma after "experiment" Page 775, line 13: insert period after "nm" Page 786, Fig. 5.: This figure shows IONO₂ absorption data extending out to 450 nm while other figures only go to 415 nm. Page 788, Fig. 7.: include units on y-axis Page 774, line 7: This may be a standard way of presenting equations for $k(\text{het})$ but I find the use of mixed units (cm, micrometers, nm) distracting. Can anything be done here to help clarify? * It is mentioned several times in the paper that the thermal decomposition of IONO₂ is slow and a personal communication is referenced. Is it possible to quote any numbers from the Dillon thesis to help put the thermal decomposition rates in better perspective. * A number of the references quoted in Table 2 are not included in the reference listing. * Table 3 contains two entries for 325 nm.

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