Atmospheric Chemistry and Physics Discussions

Interactive comment on "The UV-visible absorption cross-sections of IONO$_2$" *by* J. C. Mössinger et al.

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Response to comments of Jim Burkholder on The UV-visible absorption cross-sections of IONO2

Please note: The revised figures and cross-section data are included in the revised manuscript as the inclusion of figures in the interactive comments is not possible at present.

Time Scales

We agree that the determination of the IONO2 absorption cross-sections is critically dependent on the accuracy of the chemical mechanism used in the FACSIMILE model. On p. 770 line 22 we mention that the estimated error of 25% excludes possible systematic errors that could result from errors in the chemical mechanism used in the FACSIMILE model. To make this point clearer we propose to change this statement

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to the following: The chemical mechanism adopted in the FACSIMILE model could not be fully tested, as all the products could not be diagnosed using our detection method and the time resolution of the experiment (15 microseconds) did not allow the kinetics of product formation to be followed. The estimated error of 25% excludes possible systematic errors that could result from errors in the chemical mechanism used in the FACSIMILE model (p. 770 line 22).

We measured the photolysis laser fluence in separate experiments. NO2 was photolysed in the absence of CF3I in order to determine the initial amount of O atoms produced in the laser flash. To make this clearer the sentence on p. 772 line 6 was changed to: In separate experiments NO2 was photolysed in the absence of CF3I and the initial O atom concentration was determined from the change in NO2 concentration following the flash, which was obtained from the measured change in absorption of NO2 and its cross-section. It was assumed that [O] = 2 deltaNO2.

Single wavelength absorption measurements were not possible with the experimental set-up used. All the suggestions given by the referee to improve the experimental methods are extremely helpful. Unfortunately, the experimental system used for these experiments was dismantled soon after the experiments were done, so we are unable to improve our results experimentally at present.

With regard to the time scale used for the measurements we changed the text on p. 769 line 14 to: In a single experiment 1152 spectra were collected on the CCD with a clocking speed of 1 microsecond per pixel. The actual time resolution was 15 microseconds resulting from exposure of 30 pixels of the array. Post flash absorbance spectra were calculated relative to pre flash spectra using Beers law (A = ln(Ipreflash/Ipostflash)). Consequently, observed absorbances show changes in absorption brought about by the laser flash and by subsequent chemistry over a period of 1 ms.

Error Analysis

1)

The precision of the results from separate measurements was always within 25%. Up to three measurements were averaged in the final analysis. A sentence was added on p. 769 line 20 to include this information: In both cases time dependent spectral information from up to three experiments were averaged to increase the signal to noise ratio.

We think that under the experimental conditions chosen the error introduced due to the uncertainty in the IO + IO rate coefficient and product channel yields is not significant. With our experimental conditions the IO + NO2 reaction is much faster than the IO self-reaction. The products from the IO self-reaction that are expected to have long enough lifetimes to be detected on this timescale are I2, I2O2 and OIO. The FACSIMILE model shows that the total fraction of iodine containing products formed from the IO self reaction is < 5% and this was considered to be unimportant. This information was included in the paper:

Page 770 line 18: Secondary chemistry produces other potential contributors to the overall absorption spectrum such as I2, OIO and I2O2, but the yields of these together with their known spectra were judged to be unimportant.

Page 771 line 18: In order to obtain the IONO2 spectrum the contribution of all species to the total absorbance change other than IONO2 has to be known. The concentrations of all species were calculated by simulating the post-flash chemistry, and the main contributions (NO2, CF3I, FNO, CF2O) were determined from the known cross-sections of these species. Other possible contributors were I2, OIO, I2O2, but the yields of these together with their known spectra were judged to be unimportant.

2)

We agree that the spectral subtraction in the short wavelength region introduces a higher uncertainty than in the long wavelength region due to the lack of unique spectral features. However, such unique spectral features are not essential for our method of spectral subtraction as described on p. 771 and 772: The cross-sections of each

known absorber were taken from the literature and smoothed to the spectral resolution used for the present experiments. The FACSIMILE model together with the initial O atom concentration determined from the change in NO2 concentration was then used to determine the change in concentration of each absorber present. Again, the analysis is highly dependent on the chemical mechanism proposed for the overall reaction. To make this clearer we changed the statement on p. 771 line 18 to the following: In order to obtain the IONO2 spectrum the contribution of all species to the total absorbance change other than IONO2 has to be known. The concentrations of all species were calculated by simulating the post-flash chemistry, and the main contributions (NO2, CF3I, FNO, CF2O) were determined from the known cross-sections of these species. Other possible contributors were I2, OIO, I2O2, but the yields of these together with their known spectra were judged to be unimportant. Exceptions were the contribution of CF3IO, for which we have no information about the cross-sections, and the contribution of INO2, which is discussed in detail in the results and discussion section.

3)

The output from our FACSIMILE model indicates that the concentration of the INO2 reaction product is 15% of the final IONO2 concentration. We subtracted the contribution of INO2 from the overall absorption using the cross-section published by Atkinson et al. (2000) and the amount of INO2 produced as predicted by the model. It does not a significantly change the shape of the residual absorption spectrum originally assigned to IONO2 and the change in the magnitude of the cross-sections ($< 5\%$) lies within the estimated uncertainty:

The statement on p. 772 was unclear. It is true that just because the INO2 spectrum looks different, this does not support the assignment of our measurements to IONO2. All we wanted to show was that we do not seem to have measured the INO2 spectrum, but recorded a spectrum due to a different absorber. The effect of subtracting the contribution of INO2 from IONO2 is discussed on p. 772. The overall values for the cross-sections of IONO2 have changed as a result of the new analysis and they are

listed in Table 3. The whole section was re-written as follows:

Secondary chemistry generates about 15% of INO2 compared to IONO2 in the laser flash. The cross-sections for INO2 are known (Atkinson et al., 2000) and together with its simulated concentration the contribution of INO2 to the total absorption spectrum recorded during an experiment was also subtracted. Figure 4 shows the IONO2 absorption spectrum obtained from subtracting the main components as described above together with the INO2 absorption spectrum and the final IONO2 absorption spectrum corrected for the contribution of INO2 (Atkinson et al., 2000). Subtraction of INO2 does not significantly change the shape of the IONO2 absorption spectrum and the change in the magnitude of the cross-sections lies within the estimated uncertainty. The absorption cross-sections of IONO2 were then obtained assuming that the remaining absorption was attributed to the simulated amount of IONO2 generated in the reaction.

The comment that the reaction I + NO2 could possibly form the isomers INO2 and IONO is a very valid point. However, as IONO has never been identified and there is no spectrum for IONO in the literature we find it difficult to see how we can include it in the analysis of our results. Any correction for it would be a wild guess.

4)

Figure 4 (now Figure 5) show that the Gaussian functions fit the data reasonably well. The Figure was changed to make this clearer. The parameters are reported on the graph.

Atmospheric Implications

The change in the cross-sections for IONO2 results in a J value at noon, July, 53 °N for IONO2 of 0.04 s-1. The major contribution to the total photolysis rate comes from the wavelength region (325-375 nm) in which the cross-sections were not measured but inferred from an empirical interpolation of the data. Also, there is a small contribution to the total photolysis rate at wavelengths longer than 415 nm. The lack of data between

335-385 nm and at wavelengths longer than 415 nm introduces an uncertainty to the total photolysis rate and these data should be measured eventually.

Minor corrections:

A comma was inserted after experiment on p. 768, line 13.

In Figure 5 (now Figure 6) the spectrum is extended to 450 nm to show the possible effect of aerosol formation. The cross-sections for IONO2 were extrapolated from 415 nm to 450 nm. The absorption of aerosol was then set equal to the absorption of IONO2 at 450 nm.

Page 788, Figure 7 (now Figure 8). The unit s-1 was included on the y-axis.

Page 774, the particle radius was converted to cm. The surface to volume ratio was converted to cm2 cm-3.

The lifetime of IONO2 with respect to thermal decomposition (298 K, 760 Torr) is approximately 6 minutes, the upper limit 2.4 minutes (B. J. Allan and J. M. C. Plane, A study of the recombination of IO with NO2, and the stability of INO3: implications for the atmospheric chemistry of iodine, J. Phys. Chem., in press 2002). At 423 K the lifetime with respect to thermal decomposition is 0.002 s, which is in good agreement with the result of < 0.1 s by T. Dillon (T. Dillon, Ph.D. thesis, University of Leeds, UK, 2001). The following statement on p. 774 line 18 was included: However, recent observations have shown that the lifetime of IONO2 with respect to thermal decomposition at 298 K is approximately 6 minutes with an upper limit of 2.4 minutes (Allan and Plane, 2002).

We are very sorry about the missing references. The table was originally in a different file and we must have forgotten to copy them over. They are included now.

One of the 325 nm entries in Table 3 was deleted.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 765, 2002.

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