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Atmospheric Chemistry and Physics Discussions

Interactive comment on "High resolution mid-infrared cross-sections for peroxyacetyl nitrate (PAN) vapour" *by* G. Allen et al.

Anonymous Referee #1

Received and published: 14 October 2004

This paper reports measurements of the room temperature infrared absorption spectrum of PAN and measurements of its absolute absorption cross sections. Measurements were made in a short path length cell with pure PAN samples using a Fourier transform spectrometer at 0.25 and 0.03 cm-1 resolution. The results of this study are found to be in good agreement with the most recently published PAN cross section studies. Several weak PAN absorption bands have also been identified and quantified.

The measurements have been performed carefully and with a high degree of accuracy with particular attention to detail. The subject material is appropriate for publication in ACP and should be accepted following response to the questions below.

I have a few general comments that are followed by a list of minor points and suggestions to improve the presentation and clarity of the manuscript.

General Comments:

First and foremost, the infrared cross sections (in digitized spectrum form) of PAN obtained in this study have to be included as a supplement to this paper. Otherwise the value of the measurements presented in this work will be devalued greatly.

Also, a quantitative error analysis of the cross section determinations needs to be included in the paper. There is a brief mention of some possible error sources in the results section and a statement in the conclusions that we now believe the band intensities are accurate to within 10%. What are the statistical errors in the cross section determinations from the fits presented? Also, what are the estimated errors in the measurements and data analysis? Are the quoted uncertainties at the 95% confidence level?

One of the motivations for this study was the application to remote sensing of PAN in the atmosphere (mentioned in the abstract and introduction). However, there is no discussion of the feasibility of this in the body of the text. Also, a mention of the possible influence of temperature on the retrieved PAN profiles would be worthwhile.

The presentation of sections 4.1 and 4.2 seems confusing. Section 4.1 presents PAN cross section data (figure 2) before the cross sections (in terms of absorptivities) are determined in section 4.2 via Beer's law plots (figure 3). Aren't the absorption cross sections a result of the Beer's law plots? Shouldn't all the measurements be self-consistent? Why are these two sections separate? To understand how the final "recommended" PAN absorption spectrum is obtained has to be more clearly presented.

Minor Comments:

Page 5656, Line 10: change "recorded" to "published"

Page 5656, Line 14: delete "subtle"

Page 5656, Line 15-16: "No direct effects of spectral resolution were observed." Are there also indirect effects? Either here or somewhere else in the abstract the pressures

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used in the measurements should be stated.

Abstract: It is stated “The improved accuracy of these absorption cross-sections will” However, the absolute uncertainties in the cross sections obtained from this study are not mentioned. It would be worth including that here. Also, if the authors are concerned about the resolution dependence of the spectrum shouldn’t the possibility of pressure broadening be addressed.

Page 5656, Line 26: The Stephens (1964) reference is not included in the reference list at the end of the paper.

Page 5657, Line 9: A reference to field studies that demonstrate this effect (maybe from the TOPSE campaign) could be included.

Page 5657, Line 15: Recent field measurements and/or the development of proton transfer mass spectrometers should also be mentioned in this discussion.

Page 5659, Line 11: What was the magnitude of the cell leak rate? What uncertainty does the leak introduce in the absolute absorption cross sections?

Page 5659: Pressures in units of Torr and hPa are used. It would be nice to include the conversion factor between Torr and hPa.

Page 5659, Line 24: Change “Since, PAN is not commercially available, samples..” to “PAN samples..”

Page 5660, Line 10 and 11: Delete. This was stated earlier in the text.

Page 5660, Line 20: It is conventional to quote absorption cross sections in base e not base 10. Also, cross sections are usually quoted in units of cm2 molecule-1.

Page 5661, Line 4: “other dissociated products” does not make sense; do you mean “other thermal dissociation end products”?

Page 5661, Line 5: Change “not believed” to “assumed”. Does the infrared spectrum

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measured in this work put a limit on the impurity levels? Were reference spectra of the impurities and PAN precursor compounds measured.

Page 5661, Line 26: Change “as” to “at”

Page 5663, Line 27: “, cell adsorption (derived from cell pressure gradient, 1-3%),..” What does this mean? Why is there a pressure gradient in the absorption cell?

Page 5664, Line 1: What is equivalent pressure error?

Page 5664, Line 6: What are the statistics for the fits? Are the fits forced to pass through the origin?

Page 5664, Paragraph 3: Using your experimental data (spectra) the significance of H2O absorption to the determination of the PAN absorption cross sections can be evaluated quantitatively. You can quantitatively demonstrate the systematic error with the H2O concentration.

Page 5662, Line 18: It is mentioned that the rate of decrease in PAN concentration during the cross section measurement was discussed earlier. I am not sure where. Also, how long did a spectrum measurement take?

Table 1: The discussion of the apodisation function should be moved from the title to a footnote or into the body of the text. Also, the text says a DLaTGS detector was also used but it is not listed in the table.

Table 3 and 4: The units used, ppm-1 m-1, should be converted to molecular units. Also, it is stated “Errors quoted represent one standard deviation of individual error contributions for each sample.” What does this mean?

Figure 1: The panels are not labeled as given in the caption. What is the VMR given at the top of the figure?

Figure 2: The figure caption should state that the cross section values are base 10 (I would recommend changing all data throughout the paper to base e).

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