

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

**G. Allen et al.**

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Firstly, we would like to thank anonymous referee #1 for their useful and constructive comments, which we believe will help us to improve the efficacy of the paper for the scientific community.

### **In response to the referee’s general comments:**

**1/ Cross-section data file:** The digitised cross-section data file will be submitted as a supplement to the paper as suggested. We also note that this data file will soon be publically available through the HITRAN 2004 spectral database and also via the British Atmospheric Data Centre website service at <http://badc.nerc.ac.uk/getdata/browse/badc/msf>.

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**2/ Cross-section accuracy:** A quantitative error assignment of the cross-section itself is not easily given as the cross-sectional error varies with wavenumber. As a solution to the referee's comment, we propose to include in the text, the error in cross-sectional units derived at the peak of each of the five principal PAN bands. This will provide an upper limit to the uncertainty of the reported cross-section for each band.

**3/ Accuracy of band intensities:** With reference to the referee's comment on our claim of a 10% agreement in PAN band intensities, we would like to point out that this statement should be read to mean "Individual PAN absorption band intensities are now seen to be in agreement to within 10% between all independently reported literature data." This is the upper most relative difference between each absorption band taken separately, when compared to all other datasets. The text will be modified to reflect this meaning more clearly.

**4/ Estimated errors in the measurements and data analysis:** The errors for infrared absorptivity and integrated intensity in tables 3, 4, 6 and 7 currently reflect one standard deviation derived from the fit statistics to the regression lines plotted in Figures 3 and 4. Measurement errors (for the pressure or x-axis) are unique to each of the samples. The error bars plotted in figures 3 and 4 represent the sum of all errors for each individual sample. The instrumental errors for each sample are negligible but are also plotted. This clearly requires more detail in the text and in the associated figure caption, which we see is currently misleading in the original manuscript. To this end, we propose to include a table of typical error sources and their magnitude, together with modified error bars on Figures 3 and 4 to include the different types of error on each axis (Pressure uncertainty on the x-axis, radiometric and instrumental uncertainty on the y-axis).

**5/ The feasibility of PAN remote sensing:** A detailed discussion of this possibility is beyond the scope of this article. Work currently in progress by the author indicates that PAN has been detected in analysis of remotely sensed infrared spectra. Information such as detection limits are not unique and are subject to instrument performance, altitude and the presence of spectrally interfering species. We propose to include de-

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tails of which PAN absorption bands are of interest in FTIR remote sensing by briefly discussing these considerations in the introduction section.

**6/ Presentation of sections of 4.1 and 4.2:** We agree with the referee's comment. We propose to reorder these sections to show the determination of cross-section data from the Beer's law plots in that order as suggested. We also propose to include clearer detail on the calculation of cross-sections from Beer's law fits at each spectral point.

**In response to the referees minor comments of note:**

**Page 5656, Line 15-16:** In our statement "No direct effect of spectral resolution were observed", we mean to say "No resolution of fine structure was observed by increasing the spectral resolution of measurements from  $0.25 \text{ cm}^{-1}$  to  $0.03 \text{ cm}^{-1}$ ". The text is therefore modified to make this clear.

**Stephens (1964) reference:** This is a typographical error. Corrected to read "Stephens (1956)" and the reference is now included as necessary.

**Page 5657, line 9:** We propose to include a reference to the ITCT 2K2 measurement campaign as an example of recent results for PAN in the atmosphere.

**Page 5659, line 11:** We propose to include the cell leak rate in a table of error sources (see our response #4 above)

**Page 5661, line 4:** We propose to correct to now read "other products of PAN thermal decomposition".

**Page 5663, Line 27:** There is no spatial pressure gradient in the cell. The statement refers to a pressure change with time due to leakage of ambient air into the cell. The adsorption of PAN sample in the cell is calculated from the time gradient of this pressure change as the difference between the prior measured cell leak rate and the measured change in sample pressure. We propose to explain this more clearly and include this error source in the proposed table of error sources (see our response #4 above)

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**Page 5663, Line 1:** The equivalent pressure error represents the uncertainty in the PAN concentration in the cell that is caused by errors such as the very small leak rate into the cell. We propose to remove this statement as we see it may be misleading and again this error source will be included in a table of errors.

**Page 5664, Line 6:** The fits are forced to pass through the origin. The fit statistics are used in calculating the errors on all values quoted for this work in tables 3, 4, 6 and 7. We propose to modify the quoted error for our work to represent a 2-sigma uncertainty calculated from the fit statistics, hence giving a value for our work accurate to within the 95% confidence level. It should be noted that sources of errors quoted for previous works are not explained in the literature and we cannot therefore modify these errors to reflect the same level of certainty. We propose also to state this in the figure caption to the appropriate tables.

**Page 5664, Paragraph 3:** In section 3, the correction for contaminants in our work is already discussed. Retrievals of water vapour and carbon dioxide concentration are performed for each sample showing such contamination (2 out of 10 samples) and the calculated partial pressure is subtracted from the measured PAN pressure to correct for such contamination. The associated error in the retrieval is included in our error budget and is represented by the error bars of figures 3 and 4. This is explained on page 5661, line 14 and summarised again on page 5662, line 15. It is not possible to estimate such error for previously reported PAN data without access to the recorded spectra, therefore it is not possible to quantify the level of contamination in earlier studies.

**Page 5662, Line 18:** The decrease in PAN concentration was discussed in the context of thermal decomposition on page 5663, line 1. This sentence simply summarises the corrections made to the value of the measured sample pressure for all well quantified error sources.

**Tables 3 and 4:** We propose to also include molecular units of  $\text{micromol mol}^{-1} \text{ m}^{-1}$

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as suggested as well as the non-molecular unit of ppm  $m^{-1}$ , which are the same. With reference to the error description, this statement is intended to inform the reader that the errors quoted represent one standard deviation calculated from the fit statistics to Figure 3. We propose to make this more clear, also including instead a 2-sigma uncertainty as detailed above.

**Figure 1:** We propose to remove this figure as it was intended to illustrate the accuracy of our removal of small amounts of contaminant in 2 out of 10 samples. We believe it may be misleading as it represents a retrieval in a heavily contaminated sample that was not included in the data analysis reported in the paper for the very reason that it was so contaminated. We propose to include, instead, a statement detailing the uncertainty in the retrieved contaminant concentrations.

**Figure 2:** Cross-section data are already calculated to “base e” rather than “base 10” and we propose to modify equation 1 to state this. The cross-section will also be calculated from a fit to Beer’s law at each spectral point, rather than the averaging method currently used. This newly calculated cross-section will replace the current Figure and we will state this new calculation method in the text. We propose to keep the other units in Tables 3, 4, 6 and 7 to base 10 as such units are commonly reported for integrated intensities and infrared absorptivities in the literature.

### **In response to other minor and technical points:**

The authors agree with all technical and minor comments and propose to implement them as suggested.

Once again, we thank anonymous referee #1 for their helpful comments.

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Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5655, 2004.

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