

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 again like to thank anonymous referee #2 for their useful and constructive comments, which we believe will help us to improve the efficacy of the paper for the scientific community.

In this comment, we respond in full to the referee’s comments in addition to our short comment published earlier.

In general, we believe that the data reported in this data represent a significant improvement in the reported data for PAN band intensities and infrared absorptivities to date. We propose a number of modifications in our data analysis following the insightful comments by the referee. However, we do not believe the measurements require to be

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repeated, as we believe the reviewer may have inferred uncertainty in our results due to a misleading figure and other misconceptions for which we hope to address. We believe that the detailed discussion of error sources in this paper (however small) gives greater confidence in the quoted accuracy of our results.

In response to the referee's general and errata comments:

1/ Title: We agree with the referee's comment and propose to modify the title of the paper to "Improved..." rather than "High-resolution..." as suggested.

2/ Q-branch of the 1741 cm⁻¹ PAN band: We propose to include the FWHM and a brief discussion of this spectral feature in our results and discussion section following the referee's suggestion that it would be of interest in remote sensing.

3/ Use of broadband techniques: We agree with the comment and propose to include a brief discussion of the broad nature of PAN absorption bands and the need for broadband techniques to study PAN, such as FTIR, in our introduction.

4/ Lack of resolved lines: We propose to include a statement in the abstract to inform the reader that no resolution of individual lines was observed at the resolutions studied as suggested.

5/ Pressure unit inconsistencies: We agree with the comment and propose to change all units in the paper to those of mb, with appropriate conversion given where necessary (i.e. for the Baratron pressure gauges).

6/ Wavelength: We will modify "3.33 μm" to "4.5 μm" as required to correctly represent the 2200 cm⁻¹ limit.

7/ Cross-section peaks: We propose to include the peak height (in cross-section units) of the 5 strongest PAN absorption bands directly in the abstract as suggested.

8/ Figure 1: We propose to remove this figure as it was intended to illustrate the accuracy of our retrieval of small amounts of contaminant in 2 out of 10 samples. We

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believe it may be misleading as it represents 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 include further discussion of this point below.

In response to the referee's results and discussion comments:

9/ Measurements of the neat molecule: We propose to include a statement in the results and discussion section that measurements were made for the PAN molecule only and have not been pressure broadened as suggested.

10/ Limits of detection for PAN: 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 (e.g. resolution), altitude, pathlength and the concentration of spectrally interfering species. We propose to include details of which PAN absorption bands (794 and 1163 cm^{-1}) are of interest in FTIR remote sensing by briefly discussing these considerations in the introduction section.

11/ Combining tables: We agree with the referee's comment that the tables should be combined. We propose to combine tables 3 and 4 into one table and also to combine tables 6 and 7 into one table so that all bands are included in the same table, but that infrared absorptivities and integrated intensities are still reported in separate tables.

12/ Measuring at high resolution: We did not measure at high resolution, despite the capability of the spectrometer. The integration time (several hours) required for high resolution measurements results in the thermolytic dissociation of most of the PAN sample making accurate spectral determination extremely difficult. We propose to raise this point in the revised manuscript.

In response to the referee's computational comments:

13/ Weighting of Beer's law fits: We recognise that measurements made at higher

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PAN pressures and hence high optical depths require that some allowance be made for the effects of saturation for such measurements. In this paper however measurements with high optical densities were not made and therefore we prefer to weight Beer's law fits with sample errors rather than with transmission. We will comment on this in the paper.

14/ Pressure range: We note that a higher pressure range may be desirable although we also note that working over a lower pressure range does not introduce the inaccuracies of spectral saturation referred to by the referee. We propose to include a statement to this effect, detailing that we were unable to attain high sample pressures, but also that saturation of the bands studied is not a problem.

15/ Inconsistency in number of measurements: The referee is correct to bring to our attention that the number of samples does not tally. A total of 8 samples were used in the 550-1650 cm^{-1} spectral range with a total of 5 in the 1650-2200 cm^{-1} range. The differing spectral range of measurements (due to the optical filters in some measurements) meant that a total of 10 samples were measured. We will change the text to make this clear and modify the abstract.

In response to the referee's experimental comments:

16/ Detector: The referee is correct to note that the D316 detector is in fact that used. We will change D390 in table 1 to D316.

17/ Non-linear correction: Software correction was not used. The OPUS software cannot be used when an electronic filter is applied. We prefer to operate in a more linear regime, rather than to attempt to correct the non-linear response, through the use of an optical filter, electronic filter and smaller stop aperture. No non-linear detector response was observed in our measurements and therefore no correction was necessary. Furthermore. This method did not compromise the excellent signal to noise in our data (>500:1 for all bands). We propose to include a statement to this effect in our results and discussion section.

18/ Pressure uncertainty: We agree that the accuracy of pressure measurement needs to be further clarified. We observed that the non-regulated 10 Torr pressure gauge exhibited a 0.7% deviation in pressure measurement when compared over full scale against the thermostated and calibrated 1000 Torr head with a dry nitrogen sample. This error is used rather than the quoted manufacturer's 0.3% of full scale and we propose to include this comment in the text.

19/ Aperture: We used a 1.0 mm aperture to remove the effects of non-linearity. As mentioned above, we did not significantly reduce signal to noise of our measurements. The "warm aperture problem" problem is not seen in the Bruker IFS 120 HR. On reading the Johnson et al., (2002) paper detailed by the referee, which discusses this problem along with other aperture induced artefacts, we see that Johnson specifically states that the no such errors were observe for the 120 HR. This spectrometer incorporates a second aperture after the interferometer as well as cube corner retroreflectors, which minimise both thermal contamination and double modulation artefacts.

20/ Figure 1: See our comment number 8 above. The referee is correct to point out that this plot shows heavy contamination. However, the sample used in this retrieval is not used in the data analysis due to such high contamination. We propose to remove this figure. We note that only 2 of the 10 samples used showed evidence of contamination with a maximum of 9400 ppmv water vapour and 90200 ppmv carbon dioxide (<10% of sample). Uncertainty in this determination is included in the error bars in Figures 3 and 4 and is seen to be less than 150 ppmv and 100 ppmv for water vapour and carbon dioxide respectively (or 0.025% of sample). This was accurately quantified and removed which was the original purpose of the illustration in Figure 1. Limits for such contamination on the 8 other spectra used were 420 ppmv and 250 ppmv for water vapour and carbon dioxide respectively (or less than 0.067% of sample).

21/ GC analysis of purity: The sample purity was assessed by GC analysis of prepared samples. Small traces of water vapour were observed in the original PAN-dodecane sample (<1%), but this is believed to be mostly removed in the multiple

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freeze-thaw process. The carbon dioxide contamination is believed to be produced in the sample during storage or gas handling (after the GC analysis of PAN-dodecane samples). We propose to include this comment in the text.

22/ Other impurities: We did not observe any spectral evidence of PAN thermolysis products such as methyl nitrate absorption; therefore we can conclude (by simple spectral simulation of what concentration is required to observe contaminant absorption above the noise level) that levels were negligibly low (<0.05%). Small quantities of nitrogen dioxide were observed in two spectra (<5000ppmv) and were also successfully removed through spectral fitting. We note again, however, that the remaining 8 out of 10 of the spectra did not show any evidence of any impurity.

23/ Acetone: Acetone contamination was fitted to assess the levels of impurity (20-50% of sample) in discarded spectra that are not included in this paper. No attempt was made to remove the absorption and use the spectra as such a high level of impurity introduces unnecessary uncertainty. We are confident that no traces of acetone exist in the 1741 cm^{-1} PAN band. We have addressed this issue by examining spectra that are known to be clear of acetone in the 1220 cm^{-1} region of acetone absorption and comparing these with suspected contaminated spectra in the 1741 cm^{-1} region (scaling was used with respect to the 1841 cm^{-1} PAN band to normalise).

24/ Curvature of 1741 and 1842 cm^{-1} fits: There may be the possibility of curvature in the 1741 and 1842 cm^{-1} Beer's law fits in Figures 3 and 4, however their significance cannot be addressed with any confidence within the error bars.

25/ Vacuum leaks: Leak rates were extremely small (<0.001 mb/minute into the cell) and well quantified. Over the course of a measurement (6 mins) this amounts to a maximum 2.5% relative uncertainty in pressure at 0.24 mb. Attempts were made to reduce such leaks but they could not be completely removed. Their effect on the accuracy of results is negligible since this uncertainty is a well quantified systematic error that is corrected for and is included in the error assignment of individual sample

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for completeness. We propose to include a table of typical errors and the range in their magnitude to address this and all other questions about error sources.

Also, we are well aware of the thermal effects and tested this by comparing spectra with the Global source on and off as noted by Johnson et al., (2002) and originally by Ballard, Remedios and Roscoe, "Sample emission effect on spectral parameters" J. Quant. Spectrosc. Radiat. Transfer, 48, 733-741, 1992.

26/ PAN decomposition signatures: We have measured sequential spectra of PAN over a two-hour timescale to measure decomposition rate. This assessment is included in our error assignment and will be included in the additional table of error sources.

27/ Glass surface compatibility: We elected to use a glass cell as the compatibility of PAN with steel was unknown and considered an unnecessary safety risk.

In response to the referee's general comments:

We believe that the referee may have inferred that the level of impurity and other errors are significantly high due to a misconception of our error analysis. We hope to have addressed these concerns and we have proposed a number of improvements to avoid such misconception in future. The detailed error analysis in this work serves to inform the community of the accuracy (not the inaccuracy) of our results. Such detail is not included in the error assignments for PAN literature data of infrared absorptivities and integrated intensities in the previous studies referenced in the paper and therefore we maintain that these data represent a significant improvement in data available for PAN absorption in the mid-infrared.

Once again, we thank anonymous referee #2 for their helpful comments.

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

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