

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

### **Anonymous Referee #2**

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REFERREE COMMENTS REGARDING “High resolution mid-infrared cross-sections for Peroxyacetyl nitrate (PAN) Vapour” by G. Allen et al.

The work measures the PAN infrared cross-sections and fits nicely within the scope of ACP. The importance of PAN, and the need to find more methods to measure it accurately in the atmosphere are of importance, and the paper is definitely within the scope of ACP. However, this reviewer recommends that it be published only after major revision, namely repeating the experiments and improving the analysis as outlined below. There will be some major effort required to make the paper more effective, and to be sure that the published absorption cross sections are as accurate as possible. Since the thrust of the paper is simply to obtain improved PAN absorption cross-sections, the comments are all directed toward this end. The review comments are broken down into the following categories.

GENERAL AND ERRATA: Title: The title is very misleading in that the results would be high resolution, i.e. resolved ro-vibronic lines. This is clearly not the case, as shown by Figure 1, which is the gist of the paper. The title should be changed to something like “Absolute mid-infrared cross sections for peroxyacetyl nitrate (PAN) vapour” or “Improved mid-IR” It seems from Figure 2 that there may be a Q branch on the 1741  $\text{cm}^{-1}$  band (the width of the Q spike should be listed for remote sensing purposes) but other than that the bands are all at least 20  $\text{cm}^{-1}$  FWHM wide. The integration limits used for the bands range from 40 to 95  $\text{cm}^{-1}$  wide (far outside the tuning range of most IR lasers) and thus the wide bands can only be monitored by broadband (e.g. FTIR) techniques. This should be discussed, and the lack of resolved lines (even at these very low pressures) is of interest to know for those developing PAN sensors.

The pressure units for the PAN vapour are alternately listed as mb, hPa and Torr (for the transducers). Please pick one unit (preferably mb) and stick with it. If other units are used (e.g. for the P transducers) put the corresponding equivalent in parentheses.

Abstract: 2200  $\text{cm}^{-1}$  not equal to 3.33  $\mu\text{m}$ . Please correct.

It would be well to put the cross section or peak height of the strongest band(s) directly in the abstract.

In Figure 1, table plots a) and b) are on the right, c) and d) on left. This is backwards and rather confusing, please reverse. It would be helpful to label them.

RESULTS AND DISCUSSION: The paper could be greatly improved by first pointing out that the present measurements are (I think) of the neat molecule and have not been pressure broadened (e.g. to 1 atm). On a related note, it is important that the authors point out that working at low pressure would not gain much as the lines do not appear to resolve (see above). Based on the cross-sections that were determined, and assuming some level of detectivity for a certain path length, what are estimated detection limits - how do these compare to ambient data?

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Resolution: A point also worthy of mention is that the bands (similar to the results of others) do not show any resolved structure, even at 0.03 cm<sup>-1</sup> resolution and at these very low pressures. Although a 0.03 cm<sup>-1</sup> high-resolution measurement was made, the bands do not resolve. In addition to the integration limits of Table 5, it would be well to list the band widths of the measured bands. Indeed, several of the tables could and should be combined to reduce the number of tables. For example, the column headings could be a) band centre, b) infrared absorptivity at peak, c) integrated band intensity, d) integration limits, e) measured half-width of band, etc. etc. This could be done for all ten lines in the same table rather than distributing the data amongst multiple tables.

On a related issue, since the present data (Fig. 1) do not appear to show any resolved lines, and since the present workers presumably have the capability with an IFS 120 HR, were attempts made to measure the spectra at very high (e.g. 0.002 cm<sup>-1</sup>) resolution to see if any of the bands resolve? Since PAN has no symmetry and a fairly large moment of inertia, the lines would be expected to be closely spaced. This is an important question since ambient PAN mixing ratios are low, and IR laser-based methods (TDL, QC) would be needed to measure the species. Such methods require resolved ro-vibronic lines.

COMPUTATIONAL: General: The use of multiple points to determine a Beer's law plot from the SLOPE of the measured partial pressures is a very good idea. The use of this method has really been brought to the fore by Chu et al. at NIST (P. Chu, P.M. Chu, F.R. Guenther, G.C. Rhoderick and W.J. Lafferty, "The NIST Quantitative Infrared Database", J. Res. Natl. Inst. Stand. Technology., 104, 59 (1999)), and is being used by others. However, in order to really take advantage of the technique, and to avoid the nonlinearities (MCT detector, Beer-Lambert law nonlinearities, etc.) it is important to take full advantage of the data, and recognize its limitations. Chu et al pointed out that one needs to recognize that the values measured with high optical densities (e.g.  $\tau > \sim 0.5$ ) are going to start showing deviations from linearity. Thus, they showed that

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one obtains far more linear results by weighting the  $y$ -values in the slope calculation according to  $T^2$ , where  $T$  is the transmissivity, and for absorbance values  $> 1.6$  (i.e.  $T < 0.025$ ), the weighting factor is simply zero. This greatly improves the linear behaviour by using the high burden measurements for the weak bands, while more strongly weighting low burden measurements for the strong bands, thus avoiding the various nonlinearity mechanisms for strong absorptivities. Along with Chu, Sharpe et al. (Proc SPIE, 4577, 12, (2002)) showed the residual to the fit contains much information about impurities as the deviation vector shows signatures that do not scale with sample pressure. Since the real thrust of the paper is to come up with more accurate band strengths for a single molecule, the data warrant the effort.

It would also be well to vary the vapour pressures over a much wider range if possible. The pressures range from 0.24 to 2.20 hPa and thus do not cover an order of magnitude (even fewer data are actually plotted and used). The cited works suggest better results are obtained by varying pressures up to 2 orders of magnitude (depending on vapour pres.).

The authors discuss that “six measurements were obtained at 0.25  $\text{cm}^{-1}$  resolution in the range 550-1650  $\text{cm}^{-1}$ , and four in the 1650-2200 region, with a further four measurements recorded over the wider 600-1900  $\text{cm}^{-1}$  area at higher resolution of 0.03  $\text{cm}^{-1}$ .” Thus, the most over any one range (e.g. 600 to 1600  $\text{cm}^{-1}$ ) would be 10. Yet the legend of Figure 3 claims that for these three wavenumber positions that 11 samples were used. This is inconsistent (6 + 4 = 10). And further close inspection of Figure 3 shows only 8 data points for the wavenumber plots in question! Why? If other data were “thrown out”, there should be some logical reason, not just due to a lack of desired linearity. If there is an impurity problem (see below), this needs to be redressed.

EXPERIMENTAL: Bruker does not offer a D390 detector according to their web site and sales people. If this is a midband MCT as claimed, the part number is D316.

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Also regarding the detector: Bruker has a patented and very useful software correction for nonlinear detector behaviour. As MCTs are the most notorious of the nonlinear IR detectors, was this software correction used? Many have documented that this can have a very significant effect, especially in the thermal IR, and especially at high light fluxes.

Pressure: The uncertainty on most MKS gauges is 0.3% of full scale. Thus, for the 10 Torr head the uncertainty would be 0.03 Torr, not  $5 \times 10^{-5}$  Torr as claimed. Also, I believe the higher level of accuracy is only maintained if run at the thermostatted T of 40 C, so whilst running at room temperature is a good idea, it may slightly drop the accuracy of the pressure measurement. Are the pressures measured directly in the cell?

Aperture: This is one anomaly for which there appears no obvious answer. The paper list one time (Table 1) the aperture setting as 1.0 mm. This makes little sense. The data are not extremely high resolution (the IFS 120 has various configurations, but often is configured for 0.0015  $\text{cm}^{-1}$  resolution. According to Bruker, if the desired high frequency limit and high frequency folding limit are set to 2200  $\text{cm}^{-1}$ , the largest allowed aperture is 4.0 mm at 0.03  $\text{cm}^{-1}$  resolution and 12.5 mm at 0.25  $\text{cm}^{-1}$  resolution. Why a larger aperture setting was not used is not clear. A bandpass filter was used for the MCT measurements so this would greatly reduce the total intensity on the detector and avoid saturation problems, so there is absolutely no apparent reason not to use a larger aperture. The total light intensity varies theoretically as the square of the aperture area, so going from a 1 to a 4 mm aperture would allow 16 times more light (in reality maybe 8 to 10x) onto the detector and radically improve the signal/noise and thus reduce the uncertainties, or alternately reduce the number of scans for the same S/N and thereby minimize sample degradation problems. Particularly in the case of the DTGS detector, however, there is absolutely no reason to not be using the fully allowed aperture setting. This is especially true for the case of the 0.25  $\text{cm}^{-1}$  measurements. All mid-infrared detectors are extremely noisy and it is imperative to gather as many photons

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as possible for accurate measurements. This non-optimized use of the spectrometer is one of the reasons that make the results (in this reviewer's mind) somewhat suspect as not achieving the greatest possible accuracy. Using a larger aperture also reduces the effect of the "warm aperture problem" (Johns, *Mikrochimica Acta*, 111, 171, (1987)), as well as the aperture-reflected light 2f contamination problem, (Johnson et al, *Appl. Opt.* 41, 2831, (2002)).

In Figure 1, the legend states that the numbers across the top are contaminant retrieved pressure (mb), temperature (K) and concentration (ppmV). Thus, for CO<sub>2</sub>, if I understand this, the amount of CO<sub>2</sub> contaminant in the measurement was 1.97 mb which corresponds to 4.1e5 ppmv, or 40% impurity pressure of the total P in the cell. Is this correct? For which measurement is this? Similarly, for the water concentration, the calculated level is 1.5 mbar. This is extremely important. If the known "impurity" partial pressures of CO<sub>2</sub> and H<sub>2</sub>O are 1.97 and 1.5 mbar, respectively, and the "analyte" partial pressure ranges from 0.2 to ~2 mbar, this means that for a typical average measurement of say 1 mbar, then the "analyte" comprises at best 22% of the total partial pressure - there is significantly more "impurity" than there is analyte! And this accounts only for the quantified impurities of CO<sub>2</sub> and H<sub>2</sub>O. Since the point of the paper is to come up with quantitative cross-sections, and the only means of counting analyte molecules is the pressure transducer, and since pressure transducers do not discriminate molecular species, it is imperative that the analyte purity be as high as absolutely possible (within safety limitations). Perhaps this referee misunderstood the paper, if so my apologies, but then the work needs to be presented more clearly. However, if it is true that the impurity levels are this large, then more effort needs to be made to "clean up" the sample. The water can be removed by more thorough drying magnesium sulphate or calcium sulphate, and some carbon dioxide can be removed for example by cooling to -60 C or so and pumping on the sample. If it is simply not possible to work with the neat substance (or at least 50% pure), perhaps an alternate (flowed) method to measure the concentration is needed (see Patz et al. *Gefahrstoffe Reinhaltung der Luft*, 62, 215, (2002)) to quantify the sample. Was a GC ever used to

assess purity?

Also, the authors claim that “products other than CO<sub>2</sub> are not believed to be present in the measured sample as they are expected to remain in solution or to be removed during the freeze-pump-thaw process.” This is simply not true for many contaminant impurities - the impurities have a vapour pressure just as PAN does, especially at the 1 mb level of these measurements. The authors also claim that they discarded spectra that showed significant amounts of acetone. But this may still also be a very large impurity as the uncertainty values of the 1741 band are very large, and the data show a distinct curvature (some data was also discarded). Was the quantity of acetone ever fitted and subtracted from the data that were retained? Also, there appears to be other unquantified impurities in the carbonyl region as the 1842 band also shows curvature (in the opposite direction) and large uncertainties, perhaps traces of peroxyacetic acid or acetic acid or ?, any of which could interfere with the spectrum in the carbonyl region. Although working with the absolutely neat compound can be dangerous, perhaps more effort is needed to remove some of the impurities. Other workers have reported having to go through multiple, multiple freeze/thaw cycles, with pumping, to get reasonable results. Although it may be difficult to fully purify it, the freezing point of PAN has been reported by Kacmarek et al. in 1977, and was found to be -48.5C, (Kacmarek et al., J. Inorg. Nucl Chem., 40, 574, 1977.) Both the thermal decomposition of von Ahse et al., J. Chem. Phys. 121, p. 2048, (2004) and the photolysis/OH loss mechanisms have been investigated (Talukdar, et al., JGR, 100, 14,163-14,173, 1995), have been investigated - perhaps this leads to some clues as the nature of the decomposition mechanism and products, and may help quantify any impurity bands beneath the 1741 and 1842 bands. The large amplitude of the error bars for these two wavelengths in Figure 3 (Absorbance of 0.5 &#161;0.2) is cause for concern - the FTIR has far better S/N performance at e.g. 1741 than 794 cm<sup>-1</sup>.

There is also the unanswered question as to the “leak rate of the air into the vacuum cell”. The authors never quantify this, and succinctly put, a leak is really not acceptable

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for such a measurement. Vacuum leaks can always be removed, and in this particular case is very warranted. The authors did in fact measure the pressure before and after to obtain a leak rate, but again this makes the PAN partial pressure the trace analytes extracted from multiple impurities, and a mixing ratio changing during the experiment. If lab air is leaking into the cell, the fast rate constants with any air impurities leads to questions about the extent of PAN degradation. Also, rather than evacuate the spectrometer and record a 2nd background spectrum immediately after the sample spectrum, it would perhaps be more advantageous to measure two or more spectra in a row (e.g. 50 scans each) and look for the growth of any decomposition signatures, and decay in the PAN signatures. This can help not only recognize any decomposition impurities, but also quantify them in the original spectrum. This would help to redress both the known leak problem, but also sample decomposition as noted above.

Finlayson-Pitts have recently reported that glass surfaces increase the kinetics for NO<sub>2</sub> hydrolysis or other decompositions, is this also true for PAN? Perhaps it would be better to use a more inert surface for the cell such as electro polished stainless steel, or gold coating, or some other material? The authors have mentioned several times that there are impurities due to unfavourable decay products - although the opaque black shielding around the sample is a fine idea to prevent photolysis, it seems that other tactics might be used to prevent sample decay as the authors mention several time (and the data show) significant levels of impurity.

GENERAL: For quantitative work it is crucial that one pay attention to the all details. The authors have a good start in this direction, but the remaining open questions, particularly the large partial pressures of some impurities (which appear to be the dominant components!), the unknown pressures and identities of other impurities suggests that more effort is required, especially in the carbonyl region. Clearly PAN is difficult to handle, but it appears that the number density is determined only by pressure, and there are far, far more (CO<sub>2</sub> and H<sub>2</sub>O) impurities than PAN, that there are other quite unknown impurities, that the vacuum system leaks, and that the FTIR was not fully

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optimized for the measurements. Although it is not easy to realise the absolute cross sections of a molecule such as PAN, additional effort is clearly required since “first cut” at its cross sections are already known. Of great concern is the level of contaminants discussed above. For the error bar estimates for the 1741 and 1842 bands appear to be on the order of 20% or more, with one showing positive curvature, the other negative, the authors claim to have observed a 4.8% lower integrated intensity for the 1741 band - the uncertainties on the measurements do not appear to warrant such an improvement. Many of the questions raised, particularly about the levels of impurities, the known but undocumented leak in the vacuum system, the lack of clear identification of impurities (which may be identifiable using the methods of Chu et al.), the non-optimized use of the FTIR, and the lack of linearity for the strongest bands all suggest that more precision is required for these measurements.

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

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