Response to Reviewers of “New and improved infrared absorption cross sections for trichlorofluoromethane (CFC-11)”

Comments are reproduced below in bold text, followed by my response.

Reviewer #1:

Harrison presents a new data set of absorption cross sections for trichlorofluoromethane (CFCl3 or CFC-11). The cross sections have been measured for about 30 pressure/temperature combinations, using an experimental setup and methodology introduced earlier by the same author. Overall, the paper is well written and concise. It fits in the scope of AMT and I would recommend it for publication, subject to a few specific comments listed below.

Specific comments
l52-53: It might be good to add a few words on how the new data set improves upon the existing Varanasi data set in the abstract.
This will be done.

l62-65: Add a reference for the polar ozone chemistry, e.g., Solomon (1999)? Solomon, S. (1999), Stratospheric ozone depletion: A review of concepts and history, Rev. Geophys., 37(3), 275–316, doi: 10.1029/1999RG900008.
This will be done.

l94: Add references for the GEISA and HITRAN databases?
This will be done.

l144-151: I have a question regarding the measurements which mostly arises out of my curiosity, but perhaps other readers might also be interested: How long does it actually take to make those measurements of the absorption cross sections? Is this a piece of work completed within a few hours or days? Could you easily add more p/T combinations?
In total the measurements took about a week, which included a considerable amount of out-of-hours work. As we pay to use the facility, time is money so the measured PT combinations need to be carefully considered.

l197-198: It is stated that the total systematic error of the new cross sections is 3%. Is this sufficient to improve retrievals for the satellite instruments? How does it compare to the Varanasi data?
It is stated in Li & Varanasi (1994) that the actual uncertainty of their cross sections is 2%, however given the various problems identified in the present manuscript, the true uncertainty must be larger. This will be added to the manuscript. The uncertainty of the new measurements is 3 %. I believe the new data will provide a more accurate basis for retrieving CFC-11, however it must be realised that there are additional, and usually larger, sources of uncertainty in satellite measurements.

l206-208: This is just one sentence, but it may go into a separate "data availability" section, following AMT author guidelines?
I will certainly move this text to the most appropriate place in the manuscript.

l216-219: Not sure if those tiny relative correction factors (1.000002 ... 1.000007) really need to be reported in addition to the absolute wavenumber shifts?
I report these tiny shifts because the calibration factors are multiplicative, i.e. absolute shifts will differ between bands.

l251-252: You say it is difficult, but perhaps you could still try to show an illustrative example comparing the SNRs from your data set and the Varanasi data set? This could help demonstrate that the new data set is improving upon the existing one.
I will investigate whether this is possible. The presence of channel fringing in the Varanasi data could well make this difficult.

l270-272: The new data set is improving the p/T coverage, but the sampling density actually seems to be lower (fewer data points in your data set). Do you consider this lower sampling density in p/T space to be negligible, as there might potentially be low variability in the data?
The IR bands of CFC-11 are congested and there are no strong, sharp features. This means that there isn't a large amount of variation between cross sections and a lower sampling density in PT space is perfectly fine for remote sensing. I will add a point to this effect in the text.

It would be good to show climatological p/T profiles in Fig. 5 to illustrate that your data set covers atmospheric variability.
I understand the reasoning behind this request, however the climatological profiles only represent "averages" of the atmospheric variability, not actual variability. In fact, the original Li & Varanasi CFC-11 paper does include such a figure, and their PT combinations do cover these atmospheric profiles. The new data, therefore, will also cover these profiles. The PT coverage in this work is chosen to cover the range of P and T from ACE-FTS v3.0 data. I will mention this point in the manuscript.

Table 1: This is a nice overview of CFC-11 measurements from space. You might consider adding the time frame of the measurements, e.g., 2002-2012 for MIPAS, 2005-2008 for HIRDLS, etc. and add "References" as header for the third column of the table.
Yes, this will be done.

Technical corrections
l84: "very many" -> "many" ?
"Very many" is perfectly acceptable English.

Reviewer #2:

This review was written in March 2018 and refers to the original submitted document. So the line numbers cited below may have changed and some of the comments may no longer apply.
Technical corrections (points 6, 9 10, 14, 15, 16, 17, 18, 19) were answered when producing the discussion manuscript.

1) The new cross-sections rely on PNNL data for absolute intensity calibration, rather than by independently measuring the amount of gas in the cell. The author states that

this "is necessary to counter problems with trichlorofluoromethane adsorption in the vacuum line and on the cell walls, resulting in its partial pressure during each measurement differing from the initial, measured value". The author needs to explain why this "adsorption" wasn't a problem for PNNL or for Li and Varanasi [1994].
The PNNL sample cell and gas manifold are electro-polished and gold-plated to minimise adsorption. It isn't clear from the literature whether the Varanasi cell has any special features to minimise adsorption.

2) The PNNL measurements cover a rather high temperature range (278-323K). The present work covers 191-293K, with only 2/30 spectra exceeding 274K. Despite this minimal overlap in temperature space, the author nevertheless uses the PNNL spectra to calibrate their cross-sections, implicitly assuming that the band intensities are T independent. Please discuss the validity of this assumption and its likely impact on the error budget.
This assumption has been explained in a previous publication, and the reader is referred to this in the text:
"This intensity calibration procedure … furthermore assumes that the integrated intensity over each band system is independent of temperature. The reader is referred to Harrison et al. (2010) for a more complete explanation of the underlying assumption, and references cited within Harrison (2015a, 2015b, and 2016) for details on previous successful uses of this approach."

On a similar topic, lines 263-265 state: "The Varanasi integrated band strengths at each temperature display a small spread in values, most notably for the ν4 band, however there is no evidence for any temperature dependence, as expected." Why is this expected? [I'm not saying that the statement is incorrect; merely that slightly more explanation is needed]
The assumption made above is that the integrated intensity over each band system is independent of temperature. The Varanasi band strengths indicate the validity of this assumption. I will provide additional clarification in the text.

3) Section 3.3. The author claims that: "random errors in y (transmittance) cannot be determined since only one spectrum is recorded at each PT combination". And yet, in the conclusions (lines 319-320), the author asserts that the SNR of his new spectra is superior to Li and Varanasi's. This latter statement implies that the author can, in fact, estimate the SNR of his spectra, in which case it can be included as a random term in the error budget.
Section 4.4 provides additional information on the SNR comparison, not just the conclusion. The SNR can be estimated near the baseline, between bands – the values, which were already included in the manuscript, range from 2600 to 4700 (rms), equivalent to percentage transmittances between 0.04 and 0.02 %. This contribution is too small to have any noticeable effect on the overall error budget. The sentence quoted above is intended to refer to random uncertainties in the measurements over the full range of wavenumbers, not just at the baseline. This point will be clarified in the text.

4) Section 3.3. The author claims a total systematic error of ~3%. This includes "photometric uncertainty" which he doesn't define. Please elaborate.
Photometric uncertainty is associated with the detection of radiation by the MCT detector and any uncertainties due to the non-linearity correction. This point will be added to the text.

5) I would guess that an important error in this type of work is zero-level offsets due to detection non-linearity. The author states that the Bruker OPUS software was used to correct for detector non-linearity. While this may reduce the zero level offsets by an order of magnitude, it won't be perfect. So the error analysis must still include an estimate of the effect of residual zero-level offset. For example, If the spectra have a residual zero level offset that is just 0.3% of the continuum, and if the gas transmittance falls to 6% in the band center, as depicted in fig. 4, then the resulting error in the cross sections will be 0.003/0.060 = 5% at band center and will dominate the error budget.
I agree that the Bruker correction isn't perfect, however checks are performed during the experimental campaigns by running one of the PT measurements for less absorber amount. These comparisons indicate that any systematic error is small, certainly less than 5 %. I assign this an upper limit of 2 % to the error budget.

6) Table 1 provides no information on the length of the cell, although the abstract says 26 cm. This needs to be included.
This has already been corrected.

7) The new measurements seem to have fewer spectra than Varanasi's with larger temperature gaps. I counted 55 different points in figure 5 representing Varanasi's measurements versus 30 for the new work. Please discuss the reasoning behind this coarser temperature sampling and its implications for remote sensing.
This was dealt with in comments to reviewer 1, above.

8) The author asserts that his new cross-sections are better than previous ones due to the wider range of T/P. But when I look at fig. 5 the only places where the P/T coverage is extended by the new measurements is near 285 K/300 Torr and around 200 K/300 Torr, conditions that rarely happen in Earth's atmosphere. And the new measurements have a huge "hole" around 275±20 K and 560±150 Torr, a very common atmospheric condition. So in terms of PT coverage, the new measurements seem worse than those of Li and Varanasi. Perhaps the new measurements are intended to complement previous ones, rather than be a stand-alone data-base. But there is no statement of this intention. Even more disappointing is the continued absence of lab measurements covering 240 K/750 Torr, conditions that happen every winter over vast regions of the globe (Canada, Russia, Arctic, Antarctic).
The wider range of T/P is ONE of the criteria used in the comparison with Varanasi data. As mentioned above, the PT coverage in this work was chosen to cover the range of P and T from ACE-FTS v3.0 data. Assuming the standard four point interpolation scheme, the additional range of P and T will ensure a better coverage of the atmospheric measurements. This point will be made in the manuscript.
Note that it is specified in the text that these new measurements are in support of satellite remote sensing measurements in the limb; this rules out any atmospheric conditions below 5 km in altitude. The points about no lab measurements covering 240 K/750 Torr and the "hole" around 275±20 K and 560±150 Torr are therefore not relevant. Having said this, spectra around 275±20 K and 560±150 Torr are less structured, so the PT sampling density doesn't need to be as high as in the Li and Varanasi dataset.

The author should add standard temperature profiles, such as the three below (found on internet), to figure 5, after converting altitude to pressure. Readers will then be able to better judge the benefits of the new extended P/T coverage.
This issue was addressed in the comments made by reviewer one.

9) Firstly, since fig. 4 has two panels, the caption should describe each panel separately, not leave it to the reader to figure it out. I *think* that the upper panel is a Varanasi transmittance spectrum, and the lower panel is the ratio of Varanasi/Harrison transmittances. Unfortunately, you can't really tell whether the systematic differences in the lower panel are the due to intrinsic differences in the cross--sections, or the large pressure--interpolation (across 200--400 Torr) performed to the Harrison spectra to match the Varanasi pressure of 250 Torr.
The purpose of the figure is to show the channel fringes. The reason for any systematic differences is secondary. I will explain this more carefully in the text.

Secondly, it seems a very odd decision to use the 250 Torr Varanasi spectrum, requiring P-interpolation, when there is already a Varanasi spectrum at 200 Torr that would have avoided interpolation. The 250 Torr, 233 K Varanasi and Harrison points overlap in fig.5. Please explain why you went to the trouble of performing a seemingly unnecessary P- interpolation.
This is a figure showing the magnitude of channel fringes. It turns out that the channel fringing in the 200 Torr Varanasi cross section is less than that in the 250 Torr spectrum, so it was decided to perform an interpolation and use the latter cross section. I will explain this more carefully in the text.

10) Line 65: Insert "impending" before "environmental disaster". It would be an exaggeration to represent the springtime O3 loss over Antarctica as an "environmental disaster". It might have become one eventually, but disaster was averted by the Montreal protocol.
This has already been corrected.

11) The author repeatedly asserts that it is a "difficult" or "virtually impossible" task to "derive" spectroscopic line parameters for large molecules like CFC-11. I believe that the author is referring to a quantum-mechanically-based derivation since it is fairly straight-forward to derive an empirical "pseudo" line list for CFC-11 from lab measurements. So the author should elaborate on what he means by "derive".
The reviewer is correct that it is straightforward to derive a pseudo-linelist. However, the term “spectroscopic line parameter” implicitly refers to lines with quantum mechanical assignments. Pseudo-lines are “effective” lines (in HITRAN-type format) calculated from a set of absorption cross sections; they are not lines in the true spectroscopic sense of the word. I do not believe this point requires further clarification.

12) Lines 117-118 & 121-127: Discussion of point groups and symmetry classes in section 2 should be deleted or moved into an appendix. This won't hurt because there is nothing in the subsequent paper that relates to these things anyway. The paper has been submitted to AMT and so very few readers will be familiar with these spectroscopic concepts. If the author wants to talk about quantum mechanics, he should have submitted the paper elsewhere (e.g., J. Mol. Spec.).
Any AMT reader with a good grounding in spectroscopy will understand these concepts. Quantum mechanics and symmetry are cornerstones of spectroscopy, so I don’t believe the inclusion of these sentences is problematic.

13) I'm not sure what fig. 3 is really telling me. The new integrated band strengths are very similar to Varanasi's values. But the new band strengths have been calibrated into

agreement with PNNL anyway, so fig.3 seems to show that Varanasi agrees with PNNL. Why are the PNNL band strengths not included in this figure?

Yes, the agreement between Varanasi and PNNL band strengths are very good. The PNNL band strengths are obviously the same as the band strengths of the new measurements. These will be added to the figure as the reviewer wishes.

14) Lines 131---136: The discussion here has much in common with lines 96---100. I suggest removing one or the other to avoid repetition.

This has already been corrected.

15) Line 208: Units should be written as: cm-1/(molecules.cm-2) as in the latest HITRAN papers. [Yes, I realize that the cm-1 in the numerator can be cancelled, but to do so is anti-intuitive.]

The conventional units for absorption cross sections, as given in the recent HITRAN 2016 paper, are cm^2 molecule^{-1}. Integration of a cross section with respect to wavenumber (cm^{-1}) results in an integrated band intensity with units cm molecule^{-1}. The units given by the reviewer above correspond to the intensity of a single spectroscopic line, however “cm molecule^{-1}” is more in keeping with the established convention for cross sections, even if it is counter-intuitive.

16) Line 217: I don't understand the use of "x" to denote wavenumber, when "v" has already been defined for this purpose, e.g. on lines 206 and 208.

In the context of this discussion, x was referring to the x-axis. This has already been corrected.

17) Line 275: claims Varanasi's channel fringes are as high at 2-3%. But I don't see anything over 2% in fig.4.

This is just one cross section out of 55 – the magnitude of the fringing varies between cross sections.

18) Line 292: Does " In this work..." refer to Li and Varanasi or to Harrison [2018]? If the former, use " In that work...". If the latter, use " In the present work...".

This has already been corrected.

19) Table 2: Please align the decimal points in the third column.

This is a type-setting issue for the final published version.