

## **Review of "New and improved infrared absorption cross sections for trichlorofluoromethane (CFC-11), Jeremy Harrison, AMT-2018-51**

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.

### **Overview.**

This paper reports new infrared lab measurements of CFC-11, an important GHG and ODS. These new measurements represent an important contribution to remote sensing of CFC-11 and so a paper describing them is certainly merited. That said, the paper has certain deficiencies that need correction. The author claims that the new measurements are better than previous lab measurements, i.e. Li and Varanasi, which is probably true, but the supporting evidence that is presented is not compelling. There are also aspects of the new measurements that are, in my opinion, inferior to previous measurements. This needs more discussion. Also, the error budget seems to omit some potentially important terms (random error, detector non-linearity, intensity calibration).

### **Specific Comments.**

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].

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.

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  $\nu_4$  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]

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.

4) Section 3.3. The author claims a total systematic error of ~3%. This includes "photometric uncertainty" which he doesn't define. Please elaborate.

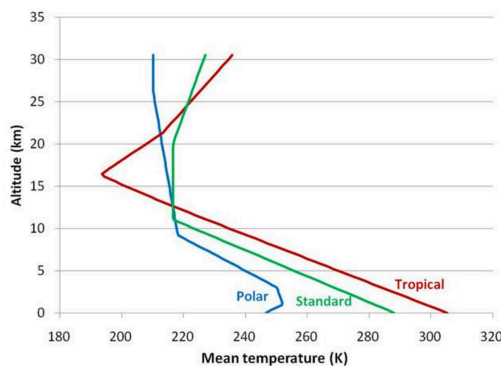
5) I would guess that an important error in this type of work is zero-level offsets due to detection non-linearity. The author states that the Bruker OPUS software was used to correct for detector non-linearity. While this may reduce the zero level offsets by an order of magnitude, it won't be perfect. 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.

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

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.

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  $275 \pm 20$  K and  $560 \pm 150$  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 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.



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 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.

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.

10) Line 65: Insert "impending" before "environmental disaster". It would be an exaggeration to represent the springtime O<sub>3</sub> loss over Antarctica as an "environmental disaster". It might have become one eventually, but disaster was averted by the Montreal protocol.

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".

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.).

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?

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.

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

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

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...".

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