

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 (CFC13 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

152-53: 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 has been done.

162-65: 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 was done.

194: Add references for the GEISA and HITRAN databases?

This has been done.

1144-151: 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.

1197-198: 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 has been 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.

1206-208: This is just one sentence, but it may go into a separate "data availability" section, following AMT author guidelines?

I have added a new data availability section just before the acknowledgements.

1216-219: 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.

1251-252: 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 have added a new figure (number 5) to the manuscript which illustrates the difference in SNR near the baseline for measurements at ~ 16.5 K and 7.5 Torr.

1270-272: 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 have added 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 have added this point to 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 has been done.

Technical corrections

184: "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 v4 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 have provided 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 has been 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 has been added to the text.

5) I would guess that an important error in this type of work is zero-level offsets due to detector 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 has been added to 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 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.

I have decided to redo this figure completely, and have written new explanatory 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.

I have redone this figure so an interpolation is no longer needed.

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 similar to the band strengths of the new measurements. These have now been 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: $\text{cm}^{-1}/(\text{molecules}\cdot\text{cm}^{-2})$ 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 $\text{cm}^2 \text{ molecule}^{-1}$. 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.

17, September 2018

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7 **New and improved infrared absorption cross sections for**
8 **trichlorofluoromethane (CFC-11)**
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11 by

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13 Jeremy J. Harrison^{1,2,3}
14

15 ¹*Department of Physics and Astronomy, University of Leicester, Leicester LE1 7RH, United*
16 *Kingdom.*

17 ²*National Centre for Earth Observation, University of Leicester, Leicester LE1 7RH, United*
18 *Kingdom.*

19 ³*Leicester Institute for Space and Earth Observation, University of Leicester, Leicester LE1*
20 *7RH, United Kingdom.*
21

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26
27 Address for correspondence:

28
29 Dr. Jeremy J. Harrison
30 National Centre for Earth Observation
31 Department of Physics and Astronomy
32 University of Leicester
33 University Road
34 Leicester LE1 7RH
35 United Kingdom
36

37 *e-mail:* jh592@leicester.ac.uk
38

40 **Abstract**

41 Trichlorofluoromethane (CFC-11), a widely used refrigerant throughout much of the
42 twentieth century and a very potent (stratospheric) ozone depleting substance (ODS), is now
43 banned under the Montreal Protocol. With a long atmospheric lifetime, it will only slowly
44 degrade in the atmosphere, so monitoring its vertical concentration profile using infrared-
45 sounding instruments, thereby validating stratospheric loss rates in atmospheric models, is of
46 great importance; this in turn requires high quality laboratory spectroscopic data.

47 This work describes new high-resolution infrared absorption cross sections of
48 trichlorofluoromethane / dry synthetic air over the spectral range 710 – 1290 cm^{-1} ,
49 determined from spectra recorded using a high-resolution Fourier transform spectrometer
50 (Bruker IFS 125HR) and a 26-cm-pathlength cell. Spectra were recorded at resolutions
51 between 0.01 and 0.03 cm^{-1} (calculated as 0.9/MOPD; MOPD = maximum optical path
52 difference) over a range of temperatures and pressures (7.5 – 760 Torr and 192 – 293 K)
53 appropriate for atmospheric conditions. This new cross-section dataset improves upon the
54 one currently available in the HITRAN and GEISA databases through an extension to the
55 range of pressures and temperatures, better signal-to-noise and wavenumber calibrations, the
56 lack of channel fringing, the better consistency in integrated band intensities, and additionally
57 the coverage of the weak combination band $\nu_2 + \nu_5$.

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60 **1. Introduction**

61 Chlorofluorocarbons (CFCs) were first developed in the 1930s as safe, reliable, and
62 non-toxic refrigerants for domestic use. Trichlorofluoromethane, known as CFC-11 or
63 Freon-11, and dichlorodifluoromethane, known as CFC-12 or Freon-12, were the two most
64 widely used CFCs in applications ranging from refrigerators and air conditioners to
65 propellants in spray cans and blowing agents in foam production.

66 Ultimately, however, CFCs proved too good to be true. The explosion in their use
67 led to a steady increase in their atmospheric abundances. While inert in the troposphere, it
68 was this stability which enabled them to reach the stratosphere where dissociation by
69 ultraviolet radiation released chlorine atoms, which catalyse the destruction of stratospheric
70 ozone (Solomon, 1999). The realisation of this impending environmental disaster prompted
71 international action and in 1987 the Montreal Protocol was ratified; this led to the phasing out
72 of the worldwide production and use of CFCs. CFCs are still released into the atmosphere
73 from “banks”, such as old refrigerators, however these are not regulated by the Protocol
74 (Harris et al., 2014). Banks are the major source of emissions for many ODSs, including
75 CFC-11 which has a long atmospheric lifetime of 52 years (Harris et al., 2014).

76 At present, CFC-11 is the second most abundant CFC in the atmosphere and
77 contributes the second-highest amount of chlorine to the stratosphere, behind CFC-12. In
78 addition to its role in stratospheric ozone destruction – it has the highest ozone depletion
79 potential (1.0) (Harris et al., 2014) of all the CFCs – CFC-11 is a particularly strong
80 greenhouse gas – it has a 100-yr global warming potential of 5160 (Harris et al., 2014).

81 As a key species in stratospheric ozone destruction, CFC-11 atmospheric
82 concentrations are monitored in situ at the surface, e.g. the annual global mean mole fraction
83 of CFC-11 measured by the AGAGE (Advanced Global Atmospheric Gases Experiment)
84 network in 2012 was 235.5 ppt (Carpenter et al., 2014). However, in order to measure
85 concentrations in the stratosphere where ozone destruction occurs, remote-sensing techniques
86 are required. Table 1 contains a listing of limb sounders capable of measuring CFC-11, as
87 described in the literature.

88 The infrared (IR) spectra for large molecules like trichlorofluoromethane are highly
89 complex, consisting of very many closely spaced spectroscopic lines, making the task of
90 generating line parameters from measurements an almost impossible one. For the purposes
91 of atmospheric remote sensing, it is possible to use absorption cross sections in forward
92 models instead of line parameters, however this requires laboratory measurements of air-
93 broadened spectra over a range of temperatures and pressures. The accuracy of retrievals of

94 CFC-11 abundances for the limb sounders in Table 1 is very much dependent on the quality
95 of the underlying spectroscopy; ideally absorption cross-section datasets should cover a range
96 of atmospherically relevant pressure-temperature (PT) combinations, with accurate
97 wavenumber scales and band intensities, and properly resolved spectral features. This work
98 presents new spectroscopic data, optimised for limb sounding instruments, which improve
99 upon those currently available in the HITRAN ([Gordon et al., 2017](#)) and GEISA ([Jacquinet-
100 Husson et al., 2016](#)) databases.

101

102 **2. Infrared spectroscopy of trichlorofluoromethane**

103 **2.1. Spectroscopic background**

104 There are two stable isotopes of carbon and chlorine, and one of fluorine, resulting
105 in eight stable isotopologues of trichlorofluoromethane, namely $^{12/13}\text{C}^{35}\text{Cl}_3\text{F}$,
106 $^{12/13}\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$, $^{12/13}\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$, and $^{12/13}\text{C}^{37}\text{Cl}_3\text{F}$; these belong to the point groups C_{3v} , C_s ,
107 C_s and C_{3v} , respectively. Taking into account the natural abundances of $^{12}\text{C} / ^{13}\text{C}$ (~ 99%
108 and ~1%), and $^{35}\text{Cl} / ^{37}\text{Cl}$ (~ 76% and ~24%), the most abundant isotopologues are therefore
109 $^{12}\text{C}^{35}\text{Cl}_3\text{F}$, $^{12}\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$, and $^{12}\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$, with abundances of 43%, 41%, and 13%,
110 respectively.

111 As a non-linear molecule with five atoms, trichlorofluoromethane possesses nine
112 normal vibrational modes; in the C_{3v} point group there are three non-degenerate
113 fundamentals of A_1 symmetry (ν_1 , ν_2 , and ν_3), and three doubly-degenerate fundamentals of
114 E symmetry (ν_4 , ν_5 , and ν_6). For the C_s point group, the ν_1 , ν_2 , and ν_3 modes possess A'
115 symmetry, with the doubly-degenerate ν_4 , ν_5 , and ν_6 modes each splitting into one A' and
116 one A'' mode (Snels et al., 2001). Since the splittings in the ν_4 , ν_5 , and ν_6 levels are small, it
117 is normal to label these bands assuming C_{3v} symmetry. The 710 – 1290 cm^{-1} spectral range
118 covered in the present work contains two strong fundamental bands, $\nu_1 \sim 1081.28 \text{ cm}^{-1}$ and
119 $\nu_4 \sim 849.5 \text{ cm}^{-1}$, and a weaker combination band, $\nu_2 + \nu_5 \sim 936.5 \text{ cm}^{-1}$; reported frequencies
120 are those for the most abundant isotopologue, $^{12}\text{C}^{35}\text{Cl}_3\text{F}$ (von Lilienfeld et al., 2007 ; Snels et
121 al., 2001). Isotopologues complicate the already dense CCl_3F rotation-vibration spectrum;
122 each has slightly different molecular parameters, with bands shifted by small amounts
123 relative to each other. These main band systems are shown in Figure 1 in the plot of the new
124 absorption cross section at 191.7 K and 7.535 Torr. Details on the measurement conditions
125 and derivation of this cross section are given in Section 3.

126

127 **2.2. A brief history of trichlorofluoromethane absorption cross sections**

128 High resolution (0.03 cm^{-1}) absorption cross sections of pure trichlorofluoromethane
129 at 296 K were first included in HITRAN as part of the 1986 compilation (Massie et al., 1985;
130 Rothman et al., 1987). The HITRAN 1991/1992 compilation saw the first introduction of
131 temperature-dependent cross sections (203 – 293 K) for CFC-11 (McDaniel et al., 1991;
132 Rothman et al., 1992; Massie and Goldman, 1992); as before these were derived from
133 measurements of pure CCl_3F at 0.03 cm^{-1} resolution.

134 While the two previous HITRAN editions (1986 and 1991/1992) neglected pressure-
135 broadening effects on the CCl_3F spectra, cross sections for 33 distinct PT combinations
136 (201–296 K and 40–760 Torr N_2 -broadened) over two wavenumber ranges, $810\text{--}880\text{ cm}^{-1}$
137 and $1050\text{--}1120\text{ cm}^{-1}$, were introduced into HITRAN 1996 (Li and Varanasi, 1994; Rothman
138 et al., 1998). Another 22 PT combinations covering lower pressures and temperatures over
139 the same wavenumber ranges were added to HITRAN 2000 (provided by Varanasi, cited
140 within Rothman et al., 2003), bringing the overall PT coverage to 190–296 K and 8–760
141 Torr. Out of these 55 PT combinations, four pairs possess both temperature and pressure
142 within 1 K and 5 Torr, respectively. This dataset, henceforth referred to as the Varanasi
143 dataset, has been used widely for remote-sensing applications since it was first introduced; it
144 is still the dataset included in the most recent GEISA 2015 (Jacquinet-Husson et al., 2016)
145 and HITRAN 2016 (Gordon et al., 2017) spectroscopic databases. Despite its widespread
146 use, the Varanasi dataset has some deficiencies which will be discussed in Section 4,
147 alongside a comparison with the new spectroscopic data taken as part of the present work.

148

149 **3. New absorption cross sections of air-broadened trichlorofluoromethane**

150 **3.1. Experimental**

151 The experimental setup at the Molecular Spectroscopy Facility (MSF), Rutherford
152 Appleton Laboratory (RAL) and the experimental procedures have been described previously
153 for related measurements (e.g. Harrison et al., 2010; Harrison, 2015b; Harrison, 2016); the
154 reader is referred to one of these previous studies for more information. Instrumental
155 parameters associated with the Fourier Transform Spectrometer (FTS) used for the
156 measurements, sample details, and the cell configuration are summarised in Table 2. The
157 sample pressures and temperatures for each air-broadened spectrum, along with their
158 experimental uncertainties and associated spectral resolutions, are listed in Table 3.

159

160 **3.2. Generation of absorption cross sections**

161 The procedure used to generate absorption cross sections from measured spectra has
162 been reported previously (e.g. Harrison et al., 2010; Harrison, 2015b; Harrison, 2016), so the
163 full details are not provided here. The wavenumber scale of the cross sections is calibrated
164 against the positions of isolated N₂O absorption lines taken from the HITRAN 2012 database
165 (Rothman et al., 2013). The absorption cross sections, $\sigma(\nu, P_{air}, T)$ in units of cm² molecule⁻¹,
166 at wavenumber ν (cm⁻¹), temperature T (K) and synthetic air pressure P_{air} , are normalised
167 according to

$$169 \int_{710 \text{ cm}^{-1}}^{1290 \text{ cm}^{-1}} \sigma(\nu, P_{air}, T) d\nu = 9.9515 \times 10^{-17} \text{ cm molecule}^{-1}, \quad (1)$$

170
171 where the value on the right hand side is the average integrated band intensity over
172 the spectral range 710 – 1290 cm⁻¹ for three 760-Torr-N₂-broadened trichlorofluoromethane
173 spectra (at 278, 298, and 323 K) from the Pacific Northwest National Laboratory (PNNL) IR
174 database (Sharpe et al., 2004). This intensity calibration procedure counters problems with
175 trichlorofluoromethane adsorption in the vacuum line and on the cell walls, and furthermore
176 assumes that the integrated intensity over each band system is independent of temperature.
177 The reader is referred to Harrison et al. (2010) for a more complete explanation of the
178 underlying assumption, and references cited within Harrison (2015a, 2015b, and 2016) for
179 details on previous successful uses of this approach.

180 A selection of the derived absorption cross sections is presented in Figure 2,
181 showing the expected behaviour with temperature at a total pressure of ~ 200 Torr; the
182 wavenumber range covers the microwindow for the ACE-FTS v3.6 retrieval scheme.

183

184 3.3. Absorption cross section uncertainties

185 The accuracy of the wavenumber scale for the new absorption cross sections is
186 comparable to the accuracy of the N₂O lines used in the calibration; according to the
187 HITRAN error codes, this is between 0.001 and 0.0001 cm⁻¹. The uncertainty in the intensity
188 is dominated by systematic errors. A true measure of the random errors as a function of
189 wavenumber would ideally require multiple concentration-pathlength burdens at each PT
190 combination, however only one is available for each; however, as indicated in Section 4.4,
191 these are small and make minimal contribution to the overall error budget. The maximum
192 systematic uncertainties in the sample temperatures (μ_T) and total pressures (μ_P) are 0.4 %

193 and 0.7 %, respectively (see Table 3). The photometric uncertainty (μ_{phot}), associated with
194 the detection of radiation by the MCT detector and, systematic error arising from the use of
195 Bruker's non-linearity correction for MCT detectors, is estimated to be ~2 %. The
196 pathlength error (μ_{path}) is estimated to be negligibly small, lower than 0.1 %. According to
197 the PNNL metadata, the systematic error in the PNNL CCl₃F spectra used for the intensity
198 calibration is estimated to be less than 3 % (2σ). Equating the error, μ_{PNNL} , with the 1σ
199 value, i.e. 1.5 %, and assuming that the systematic errors for all the quantities are
200 uncorrelated, the overall systematic error in the dataset can be given by:

$$\mu_{\text{systematic}}^2 = \mu_{\text{PNNL}}^2 + \mu_{\text{T}}^2 + \mu_{\text{P}}^2 + \mu_{\text{phot}}^2. \quad (2)$$

203
204 Note that using PNNL spectra for intensity calibration effectively nullifies the errors in the
205 trichlorofluoromethane partial pressures and cell pathlength, so these do not have to be
206 included in Eq. 2. According to Eq. 2, the systematic error contribution, $\mu_{\text{systematic}}$, to the new
207 cross sections is ~3% (1σ).

210 4. Comparison between absorption cross-section datasets

211 In this section the new dataset presented in this work is compared with the older
212 Varanasi dataset, which has a stated uncertainty of 2 % (Li and Varanasi, 1994). The
213 comparison focuses on their wavenumber scales, integrated band strengths, artefacts such as
214 channel fringing, signal-to-noise ratios, spectral resolution, and PT coverage. Given the
215 various problems identified in sections below, the 2 % uncertainty is a significant
216 underestimate. In addition, the new dataset includes the weak combination band, $\nu_2 + \nu_5$, not
217 present in the Varanasi measurements. These new data will provide a more accurate basis for
218 retrieving CFC-11 from atmospheric spectra recorded in the limb.

221 4.1. Wavenumber scale

222 It is likely that the wavenumber scale for the Varanasi dataset was never calibrated;
223 this has been observed in a number of recent studies for other halogenated species in which
224 new datasets have been compared with older Varanasi datasets, e.g. HFC-134a (Harrison,
225 2015a), CFC-12 (Harrison, 2015b), and HCFC-22 (Harrison, 2016). As explained earlier, the

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230 absolute accuracy of the wavenumber scale for the new dataset lies between 0.001 and
231 0.0001 cm^{-1} . In comparison, the ν_4 band in the Varanasi cross sections is shifted too low in
232 wavenumber; this shift varies between cross sections, e.g. by $\sim 0.002 \text{ cm}^{-1}$ (a correction
233 factor of ~ 1.000002) for the 190 K / 7.5 Torr ν_1 Varanasi measurement and by $\sim 0.007 \text{ cm}^{-1}$
234 (a correction factor of ~ 1.000007) for 216.1 K / 100.0 Torr ν_1 .

235

236 4.2. Integrated band strengths

237 Integrated band strengths for the Varanasi cross sections have been calculated over
238 the spectral ranges of the cross-section files, 810 – 880 and 1050 – 1120 cm^{-1} , covering the ν_4
239 and ν_1 bands respectively, and compared with those for the new absorption cross sections
240 calculated over the same ranges; plots of integrated band strength against temperature for
241 each dataset, including the PNNL spectra, and wavenumber range can be found in Figure 3.
242 At each temperature the Varanasi integrated band strengths display a small spread in values,
243 most notably for the ν_4 band, however there is no evidence for any temperature dependence,
244 backing up the assumption in Section 3.2 that the integrated intensity over each band system
245 is independent of temperature. The small spread in values is likely due to inconsistencies in
246 the baselines for the Varanasi cross sections, which are larger for the ν_4 band. Additionally,
247 according to the PNNL spectra and the new measurements, the ν_4 cross section at 810 cm^{-1} is
248 non-zero due to the presence of a weak hot band. Therefore, calculating integrated band
249 strengths for the new dataset over the 810 – 880 cm^{-1} range creates a very small temperature
250 dependence in the ν_4 integrated band strengths. Unfortunately, the wavenumber ranges do
251 not extend far enough to obtain an unambiguous measure of the baseline position for the
252 Varanasi data, and the cross sections in the HITRAN and GEISA databases have had all
253 negative cross section values set to zero, which has the effect of adjusting the baseline
254 positions by a small amount near the band wings.

255

256 4.3. Channel fringes

257 Most of the absorption cross sections in the Varanasi CFC-11 dataset contain
258 noticeable channel fringes above the noise level (refer to Figure 4 for an example of this); in
259 transmittance these would equate to peak-to-peak amplitudes as high as $\sim 2\text{--}3\%$. For the
260 measurements described in the present work, wedged cell windows were used to avoid
261 channel fringes by preventing reflections from components in the optical path of the
262 spectrometer.

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266 **4.4. Signal-to-noise ratios (SNRs)**

267 The SNRs of the transmittance spectra measured in the present work have been
268 calculated using Bruker's OPUS software at $\sim 990 \text{ cm}^{-1}$ where the transmittance is close to 1;
269 the values range from 2600 to 4700 (rms), equivalent to percentage transmittances between
270 0.04 and 0.02 %. A direct comparison with the Varanasi dataset, however, is not possible
271 without the original transmittance spectra or, at the very least, information on the
272 experimental mixing ratios. Further complicating issues, the Varanasi cross sections are
273 missing negative values near the baselines (refer to Section 4.2) and many have channel
274 fringes superimposed. However, it is apparent from a direct inspection that the new cross
275 sections have improved SNR, in some cases substantially so, such as shown in Figure 5.

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277 **4.5. Spectral resolution**

278 All spectra used to create the Varanasi cross-section dataset were either recorded at
279 0.01 (for sample mixtures of 75 Torr and below) or 0.03 cm^{-1} spectral resolution (defined as
280 0.9/MOPD). In the present work 0.01 cm^{-1} resolution was used for mixtures below 10 Torr,
281 0.03 cm^{-1} for 300 Torr and above, and 0.015 and 0.0225 cm^{-1} for intermediate pressures. The
282 spectra recorded at 191.6 K and 98.14 / 200.0 Torr were mistakenly recorded at spectral
283 resolutions of 0.0225 / 0.0300 cm^{-1} instead of the planned 0.015 / 0.0225 cm^{-1} . However,
284 careful inspection indicated that there was no under-resolving of spectral features for these
285 two measurements. Overall, the dataset comparison indicates that the spectral resolutions
286 chosen for the Varanasi measurements were suitable.

288 **4.6. Pressure-temperature coverage**

289 An absorption cross-section dataset used in remote sensing should cover all possible
290 combinations of pressure and temperature appropriate for the region of the atmosphere being
291 observed; in this case the focus is on the mid-troposphere ($\sim 5 \text{ km}$) up to the stratosphere.
292 Extrapolating beyond the temperatures and pressures represented within the dataset is
293 generally unreliable, so forward model calculations should at the very least use a four-point
294 interpolation scheme. With this in mind, the P and T of the laboratory measurements were
295 chosen to cover the range of P and T from ACE-FTS v3.0 data. The additional cross sections
296 outside the range of the Varanasi P and T will ensure a better coverage for analysing
297 atmospheric limb spectra. Figure 6 provides a graphical representation of the PT
298 combinations for both datasets, illustrating the improved PT coverage (30 PT combinations
299 in total) relative to the Varanasi dataset. The sampling density in PT space is lower than for

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306 [the Varanasi dataset; However, due to the congestion and lack of any strong sharp features in](#)
307 [the spectra, it is not anticipated that this will have any noticeable effect for remote-sensing](#)
308 [applications.](#)

311 **5. Conclusions**

312 New high-resolution IR absorption cross sections for air-broadened
313 trichlorofluoromethane (CFC-11) have been determined over the spectral range 710 – 1290
314 cm^{-1} , with an estimated systematic uncertainty of $\sim 3\%$. Spectra were recorded at
315 resolutions between 0.01 and 0.03 cm^{-1} (calculated as 0.9/MOPD) over a range of
316 atmospherically relevant temperatures and pressures (7.5 – 760 Torr and 192 – 293 K).
317 These new absorption cross sections improve upon those currently available in the HITRAN
318 and GEISA databases. In particular, they cover a wider range of pressures and temperatures,
319 they have a more accurately calibrated wavenumber scale, they have more consistent
320 integrated band intensities, they do not display any channel fringing, they have improved
321 SNR, and additionally they cover the weak combination band, $\nu_2 + \nu_5$.

323 **Data availability**

324 [The new CFC-11 absorption cross section dataset will be made available to the](#)
325 [community via the HITRAN and GEISA databases, but in the meantime is available](#)
326 [electronically from the author.](#)

329 **Acknowledgements**

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331 funded by the UK Natural Environment Research Council (NERC), for funding this work, as
332 well as R.G. Williams and R.A. McPheat for providing technical support during the
333 measurements.

335 **Figure Captions**

336 Figure 1. The absorption cross section of trichlorofluoromethane / dry synthetic air at 191.7
337 K and 7.535 Torr (this work), with vibrational band assignments for the main band systems
338 in the 710 – 1290 cm^{-1} spectral region.

340 Figure 2. The new absorption cross sections of trichlorofluoromethane / dry synthetic air at a
341 total pressure of ~ 200.0 Torr over a range of temperatures (191.6, 202.4, 216.6, 232.6,
342 252.5, and 273.8 K). The observed narrowing of the ν_4 band as the temperature decreases is
343 due to the decline in Boltzmann populations of the upper rovibrational levels of the ground
344 state.

346 Figure 3. Integrated band strength as a function of temperature for the new, Varanasi, and
347 PNNL cross-section datasets over the wavenumber ranges 810 – 880 and 1050 – 1120 cm^{-1} .

349 Figure 4. The Varanasi absorption cross section of trichlorofluoromethane / dry synthetic air
350 at 232.7 K and 250.0 Torr (black), with the new cross section, at 232.6 K and 201.0 Torr
351 overlaid (red; this work). Channel fringes in the Varanasi cross section are clearly visible,

353 Figure 5. The Varanasi absorption cross section of trichlorofluoromethane / dry synthetic air
354 at 216.5 K and 7.50 Torr (black), with the new cross section at 216.7 K and 7.50 Torr
355 overlaid (red; this work). Additional noise in the Varanasi cross section is clearly visible.

357 Figure 6. A graphical representation of the PT coverage for both the new and Varanasi
358 datasets.

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557 **Tables**

558

559 Table 1: Summary of limb sounders past and present capable of measuring CFC-11.

Instrument	Platform	Years	
ATMOS (Atmospheric Trace MOlecule Spectroscopy)	Space shuttle	<u>1985, 1992, 1993, 1994</u>	Chang et al., 1996; Irion et al., 2002
CIRRIS 1A (Cryogenic InfraRed Radiance Instrumentation for Shuttle)	Space shuttle	<u>1991</u>	Bingham et al., 1997
CRISTA (CRYogenic Infrared Spectrometers and Telescopes for the Atmosphere)	Space shuttle	<u>1994, 1997</u>	Offermann et al., 1999
CLAES (Cryogenic Limb Array Etalon Spectrometer)	UARS (Upper Atmosphere Research Satellite)	<u>1991 – 1993</u>	Roche, et al., 1993
ILAS (Improved Limb Atmospheric Spectrometer)	ADEOS (ADvanced Earth Observing Satellite)	<u>1996 – 1997</u>	Yokota, et al., 2002
ILAS II	ADEOS II	<u>2003</u>	Wetzel et al., 2006,
HIRDLS (HIGH Resolution Dynamics Limb Sounder)	Aura	<u>2004 – 2008</u>	Hoffmann et al., 2014
MIPAS (Michelson Interferometer for Passive Atmospheric Sounding)	ENVISAT (ENVIronmental SATellite)	<u>2002 – 2012</u>	e.g. Hoffmann et al., 2005; Dinelli et al., 2010; Kellmann et al., 2012
ACE-FTS (Atmospheric Chemistry Experiment – Fourier transform spectrometer)	SCISAT	<u>2004 –</u>	Brown et al., 2011

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563 Table 2: FTS parameters, sample conditions, and cell configuration for all measurements

Spectrometer	Bruker Optics IFS 125HR
Mid-IR source	Globar
Detector	Mercury cadmium telluride (MCT) D313 ^a
Beam splitter	Potassium bromide (KBr)
Optical filter	~700–1400 cm ⁻¹ bandpass
Spectral resolution	0.01 to 0.03 cm ⁻¹
Aperture size	3.15 mm
Apodisation function	Boxcar
Phase correction	Mertz
CCl ₃ F (Supelco)	99.9% purity, natural-abundance isotopic mixture; freeze-pump-thaw purified multiple times prior to use
Air zero (BOC Gases)	total hydrocarbons < 3 ppm, H ₂ O < 2 ppm, CO ₂ < 1 ppm, CO < 1 ppm; used 'as is'
Cell pathlength	26 cm
Cell windows	Potassium bromide (KBr) (wedged)
Pressure gauges	3 MKS-690A Baratrons (1, 10 & 1000 Torr) ($\pm 0.05\%$ accuracy)
Refrigeration	Julabo F95-SL Ultra-Low Refrigerated Circulator (with ethanol)
Thermometry	4 PRTs, Labfacility IEC 751 Class A
Wavenumber calibration	N ₂ O

564 ^aDue to the non-linear response of MCT detectors to the detected radiation, all interferograms
565 were Fourier transformed using Bruker's OPUS software with a non-linearity correction
566 applied.
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568

569 Table 3: Summary of the sample conditions for all measurements.

Temperature (K)	Initial CCl ₃ F Pressure (Torr) ^a	Total Pressure (Torr)	Spectral resolution (cm ⁻¹) ^b
191.7 ± 0.8	0.266	7.535 ± 0.035	0.0100
191.5 ± 0.8	0.302	49.83 ± 0.13	0.0150
191.6 ± 0.8	0.302	98.14 ± 0.68	0.0225
191.6 ± 0.8	0.266	200.0 ± 0.3	0.0300
202.3 ± 0.5	0.319	7.508 ± 0.006	0.0100
202.4 ± 0.5	0.309	50.28 ± 0.13	0.0150
202.3 ± 0.5	0.318	99.85 ± 0.30	0.0150
202.4 ± 0.5	0.309	200.4 ± 0.2	0.0225
202.3 ± 0.5	0.318	301.6 ± 0.3	0.0300
216.7 ± 0.5	0.347	7.496 ± 0.018	0.0100
216.7 ± 0.5	0.358	49.93 ± 0.09	0.0150
216.7 ± 0.5	0.357	99.94 ± 0.07	0.0150
216.6 ± 0.5	0.375	201.0 ± 0.2	0.0225
216.7 ± 0.5	0.383	360.4 ± 0.3	0.0300
232.6 ± 0.4	0.407	7.500 ± 0.020	0.0100
232.6 ± 0.4	0.395	49.80 ± 0.15	0.0150
232.6 ± 0.4	0.544	99.67 ± 0.16	0.0150
232.6 ± 0.4	0.417	201.0 ± 0.1	0.0225
232.6 ± 0.4	0.413	399.8 ± 0.3	0.0300
252.5 ± 0.2	0.503	7.477 ± 0.003	0.0100
252.5 ± 0.2	0.486	50.06 ± 0.05	0.0150
252.5 ± 0.2	0.516	200.9 ± 0.1	0.0225
252.5 ± 0.2	0.544	399.9 ± 0.2	0.0300
252.5 ± 0.2	0.607	600.2 ± 0.3	0.0300
273.9 ± 0.2	0.475	7.501 ± 0.001	0.0100
273.8 ± 0.2	0.613	201.6 ± 0.1	0.0225
273.8 ± 0.2	0.598	355.8 ± 0.1	0.0300
273.8 ± 0.2	0.607	760.1 ± 0.2	0.0300
293.1 ± 0.1	0.548	355.8 ± 0.1	0.0300
293.0 ± 0.1	0.566	760.0 ± 0.1	0.0300

570 ^aMKS-690A Baratron readings are accurate to ± 0.05%.571 ^bUsing the Bruker definition of 0.9/MOPD.

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