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18 May 2018

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

by

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Number of pages = 18

Number of tables = 3

Number of figures = 5

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39 **Abstract**

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

46 This work describes new high-resolution infrared absorption cross sections of  
47 trichlorofluoromethane / dry synthetic air over the spectral range  $710 - 1290 \text{ cm}^{-1}$ ,  
48 determined from spectra recorded using a high-resolution Fourier transform spectrometer  
49 (Bruker IFS 125HR) and a 26-cm-pathlength cell. Spectra were recorded at resolutions  
50 between  $0.01$  and  $0.03 \text{ cm}^{-1}$  (calculated as  $0.9/\text{MOPD}$ ; MOPD = maximum optical path  
51 difference) over a range of temperatures and pressures ( $7.5 - 760 \text{ Torr}$  and  $192 - 293 \text{ K}$ )  
52 appropriate for atmospheric conditions. This new cross-section dataset improves upon the  
53 one currently available in the HITRAN and GEISA databases.

54



## 55 1. Introduction

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

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

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

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

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



89 CFC-11 abundances for the limb sounders in Table 1 is very much dependent on the quality  
90 of the underlying spectroscopy; ideally absorption cross-section datasets should cover a range  
91 of atmospherically relevant pressure-temperature (PT) combinations, with accurate  
92 wavenumber scales and band intensities, and properly resolved spectral features. This work  
93 presents new spectroscopic data, optimised for limb sounding instruments, which improve  
94 upon those currently available in the HITRAN and GEISA databases.

95

## 96 **2. Infrared spectroscopy of trichlorofluoromethane**

### 97 **2.1. Spectroscopic background**

98 There are two stable isotopes of carbon and chlorine, and one of fluorine, resulting  
99 in eight stable isotopologues of trichlorofluoromethane, namely  $^{12/13}\text{C}^{35}\text{Cl}_3\text{F}$ ,  $^{12/13}\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$ ,  
100  $^{12/13}\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$ , and  $^{12/13}\text{C}^{37}\text{Cl}_3\text{F}$ ; these belong to the point groups  $\text{C}_{3v}$ ,  $\text{C}_s$ ,  $\text{C}_s$  and  $\text{C}_{3v}$ ,  
101 respectively. Taking into account the natural abundances of  $^{12}\text{C} / ^{13}\text{C}$  (~ 99% and ~1%), and  
102  $^{35}\text{Cl} / ^{37}\text{Cl}$  (~ 76% and ~24%), the most abundant isotopologues are therefore  $^{12}\text{C}^{35}\text{Cl}_3\text{F}$ ,  
103  $^{12}\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$ , and  $^{12}\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$ , with abundances of 43%, 41%, and 13%, respectively.

104 As a non-linear molecule with five atoms, trichlorofluoromethane possesses nine  
105 normal vibrational modes; in the  $\text{C}_{3v}$  point group there are three non-degenerate  
106 fundamentals of  $\text{A}_1$  symmetry ( $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ ), and three doubly-degenerate fundamentals of E  
107 symmetry ( $\nu_4$ ,  $\nu_5$ , and  $\nu_6$ ). For the  $\text{C}_s$  point group, the  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  modes possess  $\text{A}'$   
108 symmetry, with the doubly-degenerate  $\nu_4$ ,  $\nu_5$ , and  $\nu_6$  modes each splitting into one  $\text{A}'$  and one  
109  $\text{A}''$  mode (Snels et al., 2001). Since the splittings in the  $\nu_4$ ,  $\nu_5$ , and  $\nu_6$  levels are small, it is  
110 normal to label these bands assuming  $\text{C}_{3v}$  symmetry. The 710 – 1290  $\text{cm}^{-1}$  spectral range  
111 covered in the present work contains two strong fundamental bands,  $\nu_1 \sim 1081.28 \text{ cm}^{-1}$  and  $\nu_4$   
112  $\sim 849.5 \text{ cm}^{-1}$ , and a weaker combination band,  $\nu_2 + \nu_5 \sim 936.5 \text{ cm}^{-1}$ ; reported frequencies are  
113 those for the most abundant isotopologue,  $^{12}\text{C}^{35}\text{Cl}_3\text{F}$  (von Lilienfeld et al., 2007 ; Snels et al.,  
114 2001). Isotopologues complicate the already dense  $\text{CCl}_3\text{F}$  rotation-vibration spectrum; each  
115 has slightly different molecular parameters, with bands shifted by small amounts relative to  
116 each other. These main band systems are shown in Figure 1 in the plot of the new absorption  
117 cross section at 191.7 K and 7.535 Torr. Details on the measurement conditions and  
118 derivation of this cross section are given in Section 3.

119

### 120 **2.2. A brief history of trichlorofluoromethane absorption cross sections**

121 High resolution ( $0.03 \text{ cm}^{-1}$ ) absorption cross sections of pure trichlorofluoromethane  
122 at 296 K were first included in HITRAN as part of the 1986 compilation (Massie et al., 1985;



123 Rothman et al., 1987). The HITRAN 1991/1992 compilation saw the first introduction of  
124 temperature-dependent cross sections (203 – 293 K) for CFC-11 (McDaniel et al., 1991;  
125 Rothman et al., 1992; Massie and Goldman, 1992); as before these were derived from  
126 measurements of pure CCl<sub>3</sub>F at 0.03 cm<sup>-1</sup> resolution.

127 While the two previous HITRAN editions (1986 and 1991/1992) neglected pressure-  
128 broadening effects on the CCl<sub>3</sub>F spectra, cross sections for 33 distinct PT combinations (201–  
129 296 K and 40–760 Torr N<sub>2</sub>-broadened) over two wavenumber ranges, 810–880 cm<sup>-1</sup> and  
130 1050–1120 cm<sup>-1</sup>, were introduced into HITRAN 1996 (Li and Varanasi, 1994; Rothman et  
131 al., 1998). Another 22 PT combinations covering lower pressures and temperatures over the  
132 same wavenumber ranges were added to HITRAN 2000 (provided by Varanasi, cited within  
133 Rothman et al., 2003), bringing the overall PT coverage to 190–296 K and 8–760 Torr. Out  
134 of these 55 PT combinations, four pairs possess both temperature and pressure within 1 K  
135 and 5 Torr, respectively. This dataset, henceforth referred to as the Varanasi dataset, has  
136 been used widely for remote-sensing applications since it was first introduced; it is still the  
137 dataset included in the most recent GEISA 2015 (Jacquinet-Husson et al., 2016) and  
138 HITRAN 2016 (Gordon et al., 2017) spectroscopic databases. Despite its widespread use,  
139 the Varanasi dataset has some deficiencies which will be discussed in Section 4, alongside a  
140 comparison with the new spectroscopic data taken as part of the present work.

141

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

#### 143 **3.1. Experimental**

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

152

#### 153 **3.2. Generation of absorption cross sections**

154 The procedure used to generate absorption cross sections from measured spectra has  
155 been reported previously (e.g. Harrison et al., 2010; Harrison, 2015b; Harrison, 2016), so the  
156 full details are not provided here. The wavenumber scale of the cross sections is calibrated



157 against the positions of isolated N<sub>2</sub>O absorption lines taken from the HITRAN 2012 database  
158 (Rothman et al., 2013). The absorption cross sections,  $\sigma(\nu, P_{air}, T)$  in units of cm<sup>2</sup> molecule<sup>-1</sup>,  
159 <sup>1</sup>, at wavenumber  $\nu$  (cm<sup>-1</sup>), temperature  $T$  (K) and synthetic air pressure  $P_{air}$ , are normalised  
160 according to

161

$$162 \quad \int_{710 \text{ cm}^{-1}}^{1290 \text{ cm}^{-1}} \sigma(\nu, P_{air}, T) d\nu = 9.9515 \times 10^{-17} \text{ cm molecule}^{-1}, \quad (1)$$

163

164 where the value on the right hand side is the average integrated band intensity over  
165 the spectral range 710 – 1290 cm<sup>-1</sup> for three 760-Torr-N<sub>2</sub>-broadened trichlorofluoromethane  
166 spectra (at 278, 298, and 323 K) from the Pacific Northwest National Laboratory (PNNL) IR  
167 database (Sharpe et al., 2004). This intensity calibration procedure counters problems with  
168 trichlorofluoromethane adsorption in the vacuum line and on the cell walls, and furthermore  
169 assumes that the integrated intensity over each band system is independent of temperature.  
170 The reader is referred to Harrison et al. (2010) for a more complete explanation of the  
171 underlying assumption, and references cited within Harrison (2015a, 2015b, and 2016) for  
172 details on previous successful uses of this approach.

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

176

### 177 **3.3. Absorption cross section uncertainties**

178 The accuracy of the wavenumber scale for the new absorption cross sections is  
179 comparable to the accuracy of the N<sub>2</sub>O lines used in the calibration; according to the  
180 HITRAN error codes, this is between 0.001 and 0.0001 cm<sup>-1</sup>. The uncertainty in the intensity  
181 is dominated by systematic errors. A true measure of the random errors would ideally  
182 require multiple concentration-pathlength burdens at each PT combination, however only one  
183 is available for each. The maximum systematic uncertainties in the sample temperatures ( $\mu_T$ )  
184 and total pressures ( $\mu_P$ ) are 0.4 % and 0.7 %, respectively (see Table 3). The photometric  
185 uncertainty ( $\mu_{phot}$ ), which includes systematic error arising from the use of Bruker's non-  
186 linearity correction for MCT detectors, is estimated to be ~2 %. The pathlength error ( $\mu_{path}$ )  
187 is estimated to be negligibly small, lower than 0.1 %. According to the PNNL metadata, the  
188 systematic error in the PNNL CCl<sub>3</sub>F spectra used for the intensity calibration is estimated to



189 be less than 3 % ( $2\sigma$ ). Equating the error,  $\mu_{\text{PNNL}}$ , with the  $1\sigma$  value, i.e. 1.5 %, and assuming  
190 that the systematic errors for all the quantities are uncorrelated, the overall systematic error in  
191 the dataset can be given by:

192

$$193 \quad \mu_{\text{systematic}}^2 = \mu_{\text{PNNL}}^2 + \mu_{\text{T}}^2 + \mu_{\text{P}}^2 + \mu_{\text{phot}}^2. \quad (2)$$

194

195 Note that using PNNL spectra for intensity calibration effectively nullifies the errors in the  
196 trichlorofluoromethane partial pressures and cell pathlength, so these do not have to be  
197 included in Eq. 2. According to Eq. 2, the systematic error contribution,  $\mu_{\text{systematic}}$ , to the new  
198 cross sections is  $\sim 3\%$  ( $1\sigma$ ).

199

200

#### 201 **4. Comparison between absorption cross-section datasets**

202 In this section the new dataset presented in this work is compared with the older  
203 Varanasi dataset. The comparison focuses on their wavenumber scales, integrated band  
204 strengths, artefacts such as channel fringing, signal-to-noise ratios, spectral resolution, and  
205 PT coverage. In addition, the new dataset includes the weak combination band,  $\nu_2 + \nu_5$ , not  
206 present in the Varanasi measurements. This new dataset will be made available to the  
207 community via the HITRAN and GEISA databases, but in the meantime is available  
208 electronically from the author.

209

##### 210 **4.1. Wavenumber scale**

211 It is likely that the wavenumber scale for the Varanasi dataset was never calibrated;  
212 this has been observed in a number of recent studies for other halogenated species in which  
213 new datasets have been compared with older Varanasi datasets, e.g. HFC-134a (Harrison,  
214 2015a), CFC-12 (Harrison, 2015b), and HCFC-22 (Harrison, 2016). As explained earlier, the  
215 absolute accuracy of the wavenumber scale for the new dataset lies between 0.001 and  
216  $0.0001 \text{ cm}^{-1}$ . In comparison, the  $\nu_4$  band in the Varanasi cross sections is shifted too low in  
217 wavenumber; this shift varies between cross sections, e.g. by  $\sim 0.002 \text{ cm}^{-1}$  (a correction  
218 factor of  $\sim 1.000002$ ) for the 190 K / 7.5 Torr  $\nu_1$  Varanasi measurement and by  $\sim 0.007 \text{ cm}^{-1}$   
219 (a correction factor of  $\sim 1.000007$ ) for 216.1 K / 100.0 Torr  $\nu_1$ .

220

##### 221 **4.2. Integrated band strengths**



222 Integrated band strengths for the Varanasi cross sections have been calculated over  
223 the spectral ranges of the cross-section files, 810 – 880 and 1050 – 1120  $\text{cm}^{-1}$ , covering the  $\nu_4$   
224 and  $\nu_1$  bands respectively, and compared with those for the new absorption cross sections  
225 calculated over the same ranges; plots of integrated band strength against temperature for  
226 each dataset and wavenumber range can be found in Figure 3. At each temperature the  
227 Varanasi integrated band strengths display a small spread in values, most notably for the  $\nu_4$   
228 band, however there is no evidence for any temperature dependence, as expected. The small  
229 spread in values is likely due to inconsistencies in the baselines for the Varanasi cross  
230 sections. Unfortunately, the wavenumber ranges do not extend far enough to obtain an  
231 unambiguous measure of the baseline position, and the cross sections in the HITRAN and  
232 GEISA databases have had all negative cross section values set to zero, which has the effect  
233 of adjusting the baseline positions by a small amount near the band wings.

234

### 235 **4.3. Channel fringes**

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

242

### 243 **4.4. Signal-to-noise ratios (SNRs)**

244 The SNRs of the transmittance spectra measured in the present work have been  
245 calculated using Bruker's OPUS software at  $\sim 990\text{ cm}^{-1}$  where the transmittance is close to 1;  
246 the values range from 2600 to 4700 (rms), equivalent to percentage transmittances between  
247 0.04 and 0.02 %. A direct comparison with the Varanasi dataset, however, is not possible  
248 without the original transmittance spectra or, at the very least, information on the  
249 experimental mixing ratios. Further complicating issues, the Varanasi cross sections are  
250 missing negative values near the baselines (refer to Section 4.2) and many have channel  
251 fringes superimposed. However, it is apparent from a direct inspection that the new cross  
252 sections have improved SNR, in some cases substantially so.

253

### 254 **4.5. Spectral resolution**



255 All spectra used to create the Varanasi cross-section dataset were either recorded at  
256 0.01 (for sample mixtures of 75 Torr and below) or 0.03 cm<sup>-1</sup> spectral resolution (defined as  
257 0.9/MOPD). In the present work 0.01 cm<sup>-1</sup> resolution was used for mixtures below 10 Torr,  
258 0.03 cm<sup>-1</sup> for 300 Torr and above, and 0.015 and 0.0225 cm<sup>-1</sup> for intermediate pressures. The  
259 spectra recorded at 191.6 K and 98.14 / 200.0 Torr were mistakenly recorded at spectral  
260 resolutions of 0.0225 / 0.0300 cm<sup>-1</sup> instead of the planned 0.015 / 0.0225 cm<sup>-1</sup>. However,  
261 careful inspection indicated that there was no under-resolving of spectral features for these  
262 two measurements. Overall, the dataset comparison indicates that the spectral resolutions  
263 chosen for the Varanasi measurements were suitable.

264

#### 265 **4.6. Pressure-temperature coverage**

266 An absorption cross-section dataset used in remote sensing should cover all possible  
267 combinations of pressure and temperature appropriate for the region of the atmosphere being  
268 observed; in this case the focus is on the mid-troposphere (~ 5 km) up to the stratosphere. It  
269 is preferable to utilise an interpolation scheme in forward model calculations, rather than to  
270 extrapolate beyond the temperatures and pressures represented within the dataset. Figure 5  
271 provides a graphical representation of the PT combinations for both datasets, illustrating the  
272 improved PT coverage (30 PT combinations in total) relative to the Varanasi dataset.

273

274

#### 275 **5. Conclusions**

276 New high-resolution IR absorption cross sections for air-broadened  
277 trichlorofluoromethane (CFC-11) have been determined over the spectral range 710 – 1290  
278 cm<sup>-1</sup>, with an estimated systematic uncertainty of ~ 3 %. Spectra were recorded at  
279 resolutions between 0.01 and 0.03 cm<sup>-1</sup> (calculated as 0.9/MOPD) over a range of  
280 atmospherically relevant temperatures and pressures (7.5 – 760 Torr and 192 – 293 K).  
281 These new absorption cross sections improve upon those currently available in the HITRAN  
282 and GEISA databases. In particular, they cover a wider range of pressures and temperatures,  
283 they have a more accurately calibrated wavenumber scale, they have more consistent  
284 integrated band intensities, they do not display any channel fringing, they have improved  
285 SNR, and additionally they cover the weak combination band,  $\nu_2 + \nu_5$ .

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287

#### 288 **Acknowledgements**



289           The author wishes to thank the National Centre for Earth Observation (NCEO),  
290 funded by the UK Natural Environment Research Council (NERC), for funding this work, as  
291 well as R.G. Williams and R.A. McPheat for providing technical support during the  
292 measurements.

293

### 294 **Figure Captions**

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

298

299 Figure 2. The new absorption cross sections of trichlorofluoromethane / dry synthetic air at a  
300 total pressure of  $\sim 200.0$  Torr over a range of temperatures (191.6, 202.4, 216.6, 232.6,  
301 252.5, and 273.8 K). The observed narrowing of the  $\nu_4$  band as the temperature decreases is  
302 due to the decline in Boltzmann populations of the upper rovibrational levels of the ground  
303 state.

304

305 Figure 3. Integrated band strength as a function of temperature for the new and Varanasi  
306 cross-section datasets over the wavenumber ranges 810 – 880 and 1050 – 1120  $\text{cm}^{-1}$ .

307

308 Figure 4. The Varanasi absorption cross section of trichlorofluoromethane / dry synthetic air  
309 at 232.7 K and 250.0 Torr (top), converted to transmittance by assuming similar sample  
310 conditions to those in the present study. The resulting spectrum has been wavenumber  
311 calibrated and divided by a transmittance spectrum interpolated between the new measured  
312 spectra at 232.6 K and 201.0 / 399.8 Torr. Apart from the small difference arising from the  
313 mis-match in sample conditions, the resulting ratio (bottom) indicates the presence of channel  
314 fringes above the noise level.

315

316 Figure 5. A graphical representation of the PT coverage for both the new and Varanasi  
317 datasets.

318

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#### 498 **Tables**

499

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

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

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504 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 <sup>a</sup>
Beam splitter	Potassium bromide (KBr)
Optical filter	~700–1400 cm <sup>-1</sup> bandpass
Spectral resolution	0.01 to 0.03 cm <sup>-1</sup>
Aperture size	3.15 mm
Apodisation function	Boxcar
Phase correction	Mertz
CCl <sub>3</sub> 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 <sub>2</sub> O < 2 ppm, CO <sub>2</sub> < 1 ppm, CO < 1 ppm; used ‘as is’
Cell pathlength	26 cm
Cell windows	Potassium bromide (KBr) (wedged)
Pressure gauges	3 MKS-690A Baratron (1, 10 & 1000 Torr) (±0.05% accuracy)
Refrigeration	Julabo F95-SL Ultra-Low Refrigerated Circulator (with ethanol)
Thermometry	4 PRTs, Labfacility IEC 751 Class A
Wavenumber calibration	N <sub>2</sub> O

505 <sup>a</sup>Due to the non-linear response of MCT detectors to the detected radiation, all interferograms  
 506 were Fourier transformed using Bruker’s OPUS software with a non-linearity correction  
 507 applied.  
 508

509



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

Temperature (K)	Initial CCl <sub>3</sub> F Pressure (Torr) <sup>a</sup>	Total Pressure (Torr)	Spectral resolution (cm <sup>-1</sup> ) <sup>b</sup>
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

511 <sup>a</sup> MKS-690A Baratron readings are accurate to ± 0.05%.512 <sup>b</sup> Using the Bruker definition of 0.9/MOPD.

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