

1 Mid-infrared absorption cross-sections and temperature
2 dependence of CFC-113

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8 **Abstract**

9 The temperature-dependence of the infrared absorption cross-sections of CFC-
10 113 (1,1,2-trichlorotrifluoroethane) in a pure vapor phase has been recorded
11 in the 600-1250 cm^{-1} spectral region using Fourier transform spectroscopy.
12 Spectra at 0.05 cm^{-1} resolution have been used to derive the integrated band
13 strengths of the five main absorption bands over a range of temperatures from
14 223 to 283 K. Our results show good agreement with previously published
15 data. The new cross-sections will allow more accurate retrieval of atmo-
16 spheric CFC-113 concentrations using infrared spectroscopic techniques.

17 *Key words:*

18 chlorofluorocarbon, CFC-113, Freon 113, cross-section, mid-infrared,
19 FTIR, gas phase, temperature-dependence, band strength

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20 1. Introduction

21 CFC-113 (1,1,2-trichlorotrifluoroethane) is the third most abundant chlo-
22 rofluorocarbon in the atmosphere. Its high ozone depletion potential (0.8)
23 coupled with its global warming potential (6,130 for a horizon of 100 years) [1]
24 has led to its ban by the Montreal Protocol and its subsequent amendments.
25 Although its emission is now controlled, the long lifetime of this compound
26 in the atmosphere (~ 85 years) makes its monitoring essential.

27 Precise measurements of the global concentration of CFC-113 can be per-
28 formed from satellite platforms. The Atmospheric Chemistry Experiment
29 (ACE) satellite mission has already provided space-based atmospheric mea-
30 surements of CFC-113 on a global scale [2]. However, the uncertainties in
31 the absorption cross-sections currently available for this molecule compromise
32 the accuracy of the retrievals. The errors associated with the spectroscopic
33 data have been evaluated to be at least 20% [3].

34 The difficulties in obtaining precise spectroscopic data on CFC-113 arise
35 from the fact that chlorofluorocarbons are heavy molecules with large mo-
36 ments of inertia. Therefore, their number of rovibrational transitions is hun-
37 dreds of times larger than those of smaller molecules such as H_2O . This re-
38 sults in infrared absorption spectra composed of broad bands, each of them
39 corresponding to the overlapping of multiple individual spectral transitions.
40 The presence of conformers, isotopic Cl atoms, hot and combination bands
41 further complicates the spectral analysis.

42 These obstacles still prevent the acquisition of line-by-line spectroscopic
43 parameters for larger atmospheric molecules. Therefore, the atmospheric
44 retrieval of CFC-113 relies on the availability of laboratory absorption cross-

45 sections over a range of relevant atmospheric temperatures. Until now, the
46 most extensive data on the temperature-dependent cross-section of CFC-113
47 came from the work of McDaniels *et al.* [4] published in 1991. However, the
48 spectral resolution was low (1 cm^{-1}) and did not account for the sharpest
49 features.

50 A geometry optimization and a harmonic vibrational frequency calcula-
51 tion for the two conformers of CFC-113 using the density functional theory
52 have recently been reported [5]. Comparison between the theoretical har-
53 monic frequencies and the experimental spectra showed a good correlation.
54 However, further studies were necessary in order to understand the temper-
55 ature dependence of the CFC-113 absorption spectrum in the mid-infrared
56 region.

57 This paper presents new mid-infrared cross-sections of CFC-113 at a res-
58 olution of 0.05 cm^{-1} and at a range of relevant atmospheric temperatures
59 (from 223 to 283 K). The resulting data are compared to previously pub-
60 lished values.

61 **2. Experimental setup**

62 Experimental data are obtained using Fourier transform infrared (FTIR)
63 absorption spectroscopy. The Fourier transform spectrometer (FTS) is a
64 Bomem DA8.002 equipped with a KBr beamsplitter and operating with a
65 Globar source. A resolution of 0.05 cm^{-1} has been chosen as no structured
66 features were observed at higher resolution in the limit of the signal-to-noise
67 ratio.

68 The gas sample is contained in a stainless steel cell positioned between

69 the FTS and a liquid nitrogen-cooled mercury cadmium telluride (MCT)
70 detector. ZnSe windows are sealed to the gas cell with indium o-rings to
71 prevent leakage at low temperature. Short path lengths (3.17 and 2.93 cm)
72 have been chosen to avoid saturation effects while working at manageable
73 pressures. The CFC-113 sample (Sigma-Aldrich, 99%) is purified by several
74 Freeze-Pump-Thaw cycles prior to entering the cell. The cell pressure is
75 measured by 10 Torr and 1000 Torr MKS baratron pressure gauges.

76 The cooling is achieved by a Neslab chiller (ULT-80) sending the coolant
77 (Syltherm XLT) to a copper tube surrounding the cell. The copper tube is
78 soldered to the cell and covered by thermally conductive epoxy to improve
79 temperature homogeneity. The cell temperature is measured by a single ther-
80 mocouple directly inserted inside the cell. The temperature readout accuracy
81 during experiments is typically ± 0.1 K for temperatures down to 263 K and
82 ± 0.2 K for lower temperatures.

83 More details on the experimental setup and on the minimization of typical
84 artefacts and sources of errors in the FTIR spectra (blackbody emission from
85 the source aperture, non-linearity of the MCT detector in the mid-infrared,
86 etc) can be found in a previous paper [6].

87 **3. Data analysis**

88 For each temperature, with the exception of 223 K, a series of unapodised
89 scans are recorded at pressures between 2 and 10 Torr. When possible, a
90 higher pressure measurement (between 35 and 50 Torr) is also acquired to
91 improve the signal-to-noise ratio of the very weak features. However, the low
92 saturation pressure of CFC-113 at 223 K limits the acquisitions to pressures

93 below 5 Torr.

94 A primary baseline spectrum with an empty cell is recorded at each tem-
95 perature. Control baseline spectra are also recorded before and after each
96 sample measurement to account for the small intensity variations that can
97 occur during the acquisition. If necessary, the primary baseline is adjusted
98 to the control baseline using a polynomial regression prior to the ratioing of
99 the sample spectrum to the background spectrum.

100 The wavenumber-dependent optical depth χ is derived for each pressure-
101 temperature (P-T) set using the well-known Beer-Lambert law:

$$I(\nu) = I_0(\nu)e^{-\chi(\nu)} \quad (1)$$

102 where I is the light intensity passing through the sample gas cell; I_0 , the light
103 intensity passing through the empty cell (baseline); and ν , the wavenumber
104 in cm^{-1} .

105 For a given temperature T and wavenumber ν , the optical depth varies
106 linearly with the pressure P following the relation:

$$\chi(\nu) = \sigma(\nu) \frac{PT}{T_0P_0} n_0L \quad (2)$$

107 where σ is the absorption cross-section in $\text{cm}^2 \cdot \text{molecule}^{-1}$, n_0 , the Loschmidt
108 constant ($2.6868 \times 10^{19} \text{ molecules} \cdot \text{cm}^{-3}$); P_0 and T_0 , the standard conditions
109 for pressure and temperature; and L , the length of the cell.

110 To avoid non-linear detector effects on the strong bands at higher pres-
111 sures and low signal-to-noise ratio data on the weak bands at low pressures,
112 only optical depths between 0.01 and 0.8 are processed. The absorption
113 cross-section of CFC-113 for each wavenumber is then obtained by a linear

114 least-squares fitting of the remaining values of the optical depth versus the
115 pressure with a forced convergence at $\chi(P = 0) = 0$. It should be em-
116 phasized that this method of cross-section retrieval using a linear fitting of
117 pressure-dependent optical depths is only valid if the pressure broadening on
118 the sharpest features remains minimal, which is the case for our experimental
119 conditions even at the highest pressures.

120 Systematic errors, ϵ_s , on the optical path length, temperature readout,
121 and sample purity have been conservatively evaluated to be less than $\pm 1\%$.
122 The other sources of error in spectral measurements come from a residual
123 MCT non-linearity, a possible residual baseline drift, the pressure readout,
124 the errors induced by the data reduction and the instrumental noise. These
125 errors can all be accounted for through the standard deviation, ϵ_f , in the
126 linear fit of the optical depth as a function of pressure. The uncertainty on the
127 linear fit is chosen at the 95% confidence limit ($2\epsilon_f$). The total uncertainty
128 presented below is the square root of the sum of ϵ_s and $2\epsilon_f$.

129 4. Results and data validation

130 A survey spectrum of CFC-113 in the mid-infrared region is presented in
131 Figure 1. The molecule has five strong absorption bands identified in Table 1.

132 Experimental cross-sections are compared with previous data available
133 in the literature. Two sets of laboratory CFC-113 absorption cross-sections
134 are currently available, the data from McDaniel *et al.* [4] included in the
135 HITRAN database, and Sharpe *et al.* [7] in the PNNL datatase. McDaniel
136 and co-workers presented six absorption spectra of pure CFC-113 vapor at a
137 resolution of 1 cm^{-1} between 203 and 293 K and over the $780.5\text{-}995.0 \text{ cm}^{-1}$

138 and 1005.5-1232 cm^{-1} spectral ranges. The PNNL database contains three
139 spectra of N_2 -broadened CFC-113 from 620 to 5000 cm^{-1} at a resolution of
140 0.1 cm^{-1} at 278, 298 and 323 K.

141 Due to the difference in resolution and experimental conditions, direct
142 comparisons with the two data sets were not carried out. Instead, the data
143 validation was performed by comparing the integrated band strengths of the
144 five main absorption bands between 780 and 1235 cm^{-1} . The results are
145 reported in Table 2 and Figure 2. The overall uncertainty for integrated
146 band intensities of Ref. [4] and [7] has been evaluated respectively at $\pm 10\%$
147 and $\pm 2.3\%$ by the authors at the 95% confidence interval. In all cases,
148 the comparison between our data and the previous values in the literature
149 remains within the combined uncertainties.

150 Our band strength values averaged over all available temperatures agree
151 with the ones from the PNNL database to 1.7% for the 780-850 cm^{-1} band,
152 5.3% for the 850-995 cm^{-1} band, 5.0% for the 1005-1080 cm^{-1} band, 1.0%
153 for the 1080-1142 cm^{-1} band, and 2.3% for the 1142-1235 cm^{-1} band. The
154 comparison with the McDaniel *et al.* values shows agreement to 3.3% for
155 the 780-850 band, 3.3% for the 850-995 cm^{-1} band, 2.2% for the 1005-1080
156 cm^{-1} band, 4.5% for the 1080-1142 cm^{-1} band, and 7.2% for the 1142-1235
157 cm^{-1} band. The integrated band strengths at 203 K of Ref. [4] have not
158 been included in the comparison as they are clearly out of range. It is worth
159 mentioning that contrary to McDaniel *et al.* results, our overall data showed
160 no significant variation of the integrated cross-sections with temperature.

161 Two older sets of integrated band strengths, obtained at room tempera-
162 ture only, are also available [8, 9]. As observed previously by McDaniels *et al.*,

163 the integrated cross-sections of Ref. [8] are systematically greater than the
164 values from the other studies by large factors (up to 60%). Therefore, they
165 have not been included in this comparison. The integrated band strength of
166 Ref. [9] is inside our range with a maximum discrepancy of 10%.

167 5. Discussion

168 As the temperature decreases, the absorption bands of all structures
169 present the classical narrowing of the wings accompanied by an increased
170 peak of the Q-branches. In particular, the peak cross-section of the 1080-
171 1142 cm^{-1} band associated with the ν_3 and ν'_3 normal modes of vibration at
172 223 K shows an increase of about 55% compared to 283 K (Figure 3) .

173 The conformational analysis of CFC-113 has been described elsewhere [5],
174 and will just be reviewed briefly here. CFC-113 exists in two geometrical
175 conformations. The more stable has a C_1 symmetry characterized by a trans
176 position of two C-Cl and C-F bonds. The second conformer has a C_s sym-
177 metry characterized by a gauche position of all the C-Cl and C-F bonds.
178 Due to the small enthalpy difference between them ($\sim 133.6 \text{ cm}^{-1}$) both con-
179 formers exist in our range of temperature. The two conformers have very
180 close harmonic frequencies. The absorption spectra of CFC-113 is, thus, a
181 superposition of the overlapping bands of the C_1 and C_s conformers. The
182 rotational barrier between the C_1 and C_s conformation has been calculated
183 to be 2467.4 cm^{-1} , which makes conformational interconversion difficult at
184 low temperature. It is therefore expected that the relative population ratio
185 $C_1:C_s$ remains constant over our range of temperatures and does not affect
186 the band profiles as the temperature decreases.

187 To verify this hypothesis, we observed, at higher pressure and over a
188 range of temperatures between 283 and 253 K, the small features around 650
189 cm^{-1} corresponding to the ν_7 and ν'_7 normal vibrational modes. This weak
190 band is the only accessible band where the two conformer signatures are both
191 relatively well separated and not overlapped by other harmonic frequencies.
192 Unfortunately, it lies at the extreme range of our detector, which results in
193 a very low signal-to-noise ratio. Notwithstanding, no significant variation of
194 the integrated band ratio between the two conformers was observed over this
195 range of temperatures. However, it has been observed that the integrated
196 band strength in this spectral region decreases with temperature. The same
197 effect appears in the PNNL data for temperatures between 278 and 323 K.
198 This indicates the presence of overtone and combination bands in the 620-
199 680 cm^{-1} spectral region, which can affect the relative ratio between the ν_7
200 and ν'_7 bands and hide a hypothetical conformational interconversion.

201 The ν_6 normal vibrational mode of the C_1 conformer corresponds to the
202 $760\text{-}850 \text{ cm}^{-1}$ spectral band only. The integrated strength of this band does
203 not show a significant decrease with temperature, which is what we would
204 expect if transitions between conformers were possible in our range of tem-
205 peratures. The counterpart $850\text{-}995 \text{ cm}^{-1}$ spectral band, associated with the
206 ν'_6 , ν_5 , and ν'_5 normal vibrational modes, likewise, does not exhibit an in-
207 crease in its integrated band strength with decreasing temperature. Due to
208 the intensity of those two bands, it is unlikely that overtone and combination
209 bands play a significant role in the observations. We can therefore predict
210 that transitions between conformers are unlikely to modify the spectral shape
211 of CFC-113 over the range of temperatures found in the atmosphere.

212 Due to the temperature dependence of the rotational transitions, all the
213 absorption bands shift and broaden in the direction of higher energies as
214 the temperature decreases. Because of the lack of narrow features, we can
215 approximate directly the band centroids of the main structures using the fol-
216 lowing methods. If a band represents a single vibrational mode or completely
217 overlapped multi-modes, the entire structure is integrated. If there is a clear
218 division between modes, the structures is separated at the minimal junction
219 points. The band centroid shifts are reported in Figure 4 and compared with
220 Ref. [4] and Ref. [7]. The shift in frequency can be fitted with a linear curve.
221 The values of the slope for our data as well as the standard error in the linear
222 fit are given in Table 3. We find once again a good concordance between our
223 data and Ref. [4] and [7]. The absence of observable non-linear effects in the
224 variation of the band centroids with temperature supports our hypothesis
225 that the relative population ratio $C_1:C_s$ does not vary significantly in our
226 range of temperature .

227 6. Conclusions

228 Laboratory cross-sections of CFC-113 at a spectral resolution of 0.05 cm^{-1}
229 have been reported in the mid-infrared between 600 and 1250 cm^{-1} at seven
230 temperatures from 223 to 283 K . The integrated cross-sections of the absorp-
231 tion bands are consistent with previous published data. However, contrary
232 to previous studies, our data show no statistically significant variations of
233 the band strengths with temperature. The temperature-induced band shifts
234 have been estimated and varies from $-0.013 \text{ cm}^{-1}/\text{K}$ for the $1080\text{-}1142 \text{ cm}^{-1}$
235 and $1142\text{-}1200 \text{ cm}^{-1}$ bands to $-0.024 \text{ cm}^{-1}/\text{K}$ for the $1005\text{-}1080 \text{ cm}^{-1}$ band.

236 As predicted, the CFC-113 conformational ratio appears constant over our
237 range of temperatures, which should facilitate atmospheric retrievals. The
238 laboratory absorption cross-sections are available online in the supplemen-
239 tary data files.

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Table 1: Primary absorption bands of the two conformers of CFC-113 in the mid-infrared spectral region and their corresponding normal modes of vibration. The labeling follows the notation of Ref. [5]

Band (cm^{-1})	Normal modes of vibration
780-850	ν_6
850-995	ν_5, ν'_5, ν'_6
1005-1080	ν_4, ν'_4
1080-1142	ν_3
$\left\{ \begin{array}{l} 1142-1200 \\ 1200-1235 \end{array} \right.$	ν_2, ν'_2
	ν_1, ν'_1

281

Table 2: Comparison of the experimental infrared integrated band strengths ($\times 10^{-17}$ cm/molecule) of CFC-113 with published values when available. The two temperature sets for Ref. [7] are at 298 and 278 K.

Temperature	Band range (cm^{-1})	Integrated band strength		
		This work	Ref. [4]	Ref. [7]
	780-850		2.67	2.93
	850-995		3.19	3.33
293 K	1005-1080		1.73	1.91

Table 2 – continued from previous page

Temperature	Band range (cm ⁻¹)	Integrated band strength		
		This work	Ref. [4]	Ref. [7]
	1080-1142		1.88	2.10
	1142-1235		3.21	3.64
283 K	780-850	2.83 ±0.11		
	850-995	3.23 ±0.12		
	1005-1080	1.84 ±0.06		
	1080-1142	2.03 ±0.06		
	1142-1235	3.53±0.07		
273 K	780-850	2.83±0.14	2.73	2.94
	850-995	3.20±0.11	3.26	3.39
	1005-1080	1.85±0.14	1.77	1.94
	1080-1142	2.05±0.10	1.93	2.10
	1142-1235	3.54±0.08	3.27	3.67
263 K	780-850	2.85±0.15		
	850-995	3.16±0.13		
	1005-1080	1.87±0.07		
	1080-1142	2.06±0.06		
	1142-1235	3.52±0.08		
253 K	780-850	2.89±0.12	2.78	
	850-995	3.24±0.12	3.30	
	1005-1080	1.86±0.09	1.79	
	1080-1142	2.09±0.08	1.98	
	1142-1235	3.61±0.11	3.32	

Table 2 – continued from previous page

Temperature	Band range (cm ⁻¹)	Integrated band strength		
		This work	Ref. [4]	Ref. [7]
243 K	780-850	2.95±0.12		
	850-995	3.24±0.11		
	1005-1080	1.82±0.09		
	1080-1142	2.10±0.07		
	1142-1235	3.63±0.10		
233 K	780-850	2.91±0.12	2.83	
	850-995	3.15±0.11	3.34	
	1005-1080	1.79±0.09	1.82	
	1080-1142	2.09±0.07	2.03	
	1142-1235	3.59±0.09	3.35	
223 K	780-850	2.94±0.15		
	850-995	3.16±0.18		
	1005-1080	1.82±0.12		
	1080-1142	2.13±0.13		
	1142-1235	3.59±0.162		
213 K	780-850		2.94	
	850-995		3.40	
	1005-1080		1.85	
	1080-1142		2.10	
	1142-1235		3.43	
203 K	780-850		3.50	
	850-995		3.92	

Table 2 – continued from previous page

Temperature	Band range (cm ⁻¹)	Integrated band strength		
		This work	Ref. [4]	Ref. [7]
	1005-1080		2.16	
	1080-1142		2.47	
	1142-1235		4.04	

Table 3: Band centroid shift in the 223-283 K range.

Band	Slope (cm^{-1}/K)	Standard error (cm^{-1}/K)
780-850	-0.021	0.002
850-995	-0.020	0.001
1005-1080	-0.024	0.001
1080-1142	-0.013	0.001
1142-1200	-0.013	0.001
1200-1235	-0.023	0.001

283

Figure 1: Survey cross-sections of CFC-113 at 283 K and 0.05 cm^{-1} resolution.

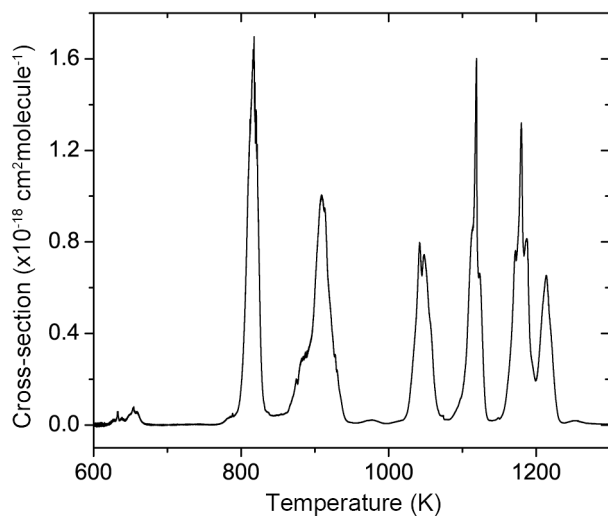


Figure 2: Temperature dependence of the integrated band strength of the five primary bands of CFC-113.

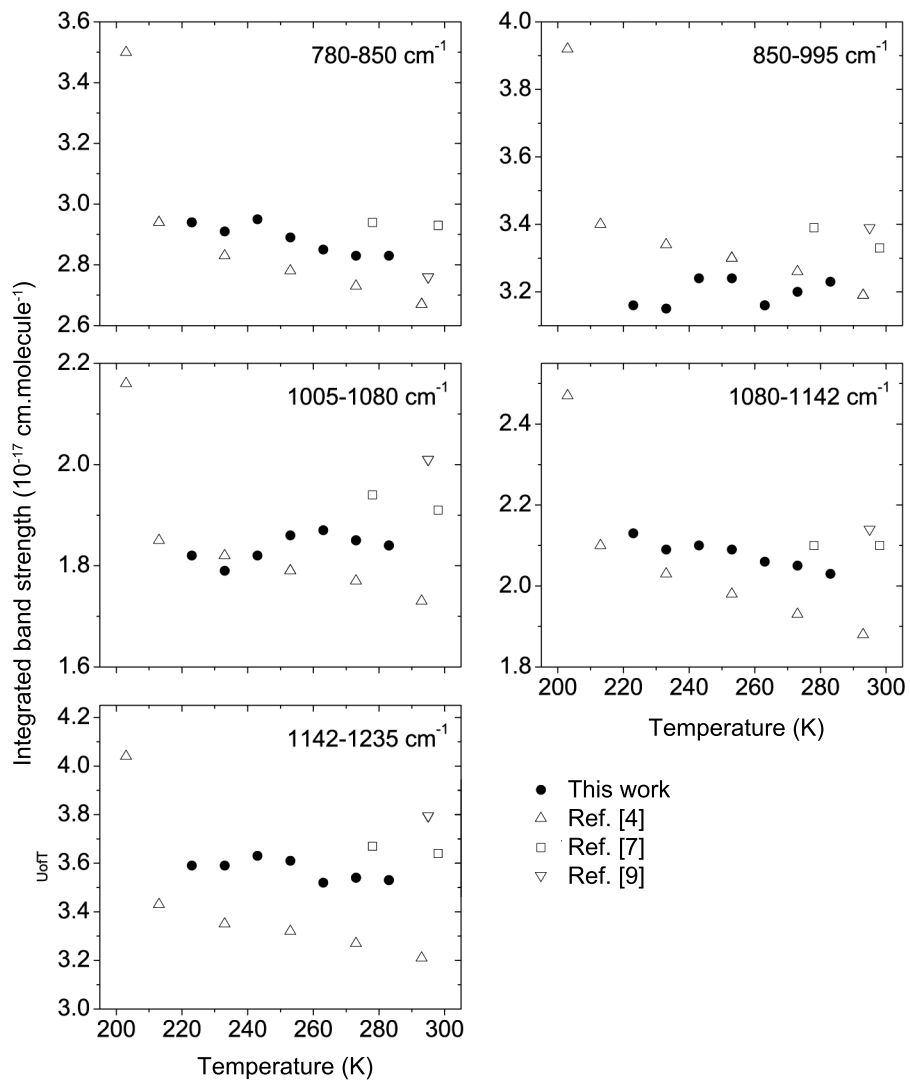


Figure 3: Cross-section of the Q -branches of the ν_3, ν'_3 bands of CFC-113 at seven temperatures.

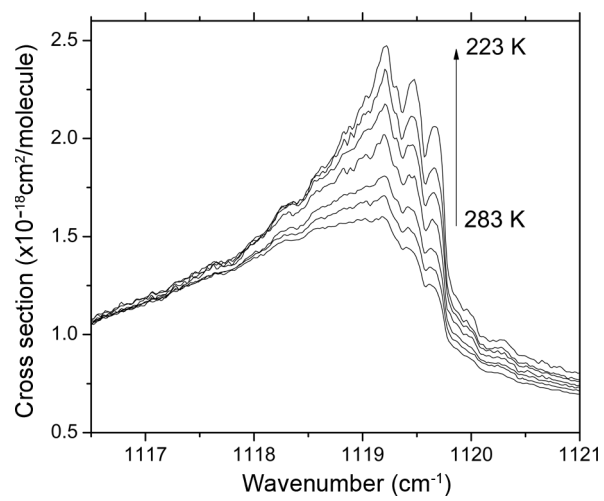


Figure 4: Band centroid shift as a function of temperature for the primary bands of CFC-113 seen in Figure 1.

