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

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ABSTRACT

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

1. Introduction

CFC-113 (1,1,2-trichlorotrifluoroethane) is the third most abundant chlorofluorocarbon in the atmosphere. Its high ozone depletion potential (0.8) coupled with its global warming potential (6130 for a horizon of 100 years) [1] has led to its ban by the Montreal Protocol and its subsequent amendments. Although its emission is now controlled, the long lifetime of this compound in the atmosphere ($\sim$ 85 years) makes its monitoring essential.

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

The difficulties in obtaining precise spectroscopic data on CFC-113 arise from the fact that chlorofluorocarbons are heavy molecules with large moments of inertia. Therefore, their number of rovibrational transitions is hundreds of times larger than those of smaller molecules such as H_2O. This results in infrared absorption spectra composed of broad bands, each of them corresponding to the overlapping of multiple individual spectral transitions. The presence of conformers, isotopic Cl atoms, hot and combination bands further complicates the spectral analysis.

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

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

A geometry optimization and a harmonic vibrational frequency calculation for the two conformers of CFC-113 using the density functional theory have recently been reported [5]. Comparison between the theoretical harmonic frequencies and the experimental spectra showed a good correlation. However, further studies were necessary in order to understand the temperature dependence of the CFC-113 absorption spectrum in the mid-infrared region.

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

2. Experimental setup

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

The gas sample is contained in a stainless steel cell positioned between the FTS and a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. ZnSe windows are sealed to the gas cell with indium o-rings to prevent leakage at low temperature. Short path lengths (3.17 and 2.93 cm) have been chosen to avoid saturation effects while working at manageable pressures. The CFC-113 sample (Sigma-Aldrich, 99%) is purified by several freeze–pump–thaw cycles prior to entering the cell. The cell pressure is measured by 10 and 1000 Torr MKS baratron pressure gauges.

The cooling is achieved by a Neslab chiller (ULT-80) sending the coolant (Syltherm XLT) to a copper tube surrounding the cell. The copper tube is soldered to the cell and covered by thermally conductive epoxy to improve temperature homogeneity. The cell temperature is measured by a single thermocouple directly inserted inside the cell. The temperature readout accuracy during experiments is typically $\pm\,0.1$ K for temperatures down to 263 K and $\pm\,0.2$ K for lower temperatures.

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

3. Data analysis

For each temperature, with the exception of 223 K, a series of unapodised scans are recorded at pressures between 2 and 10 Torr. When possible, a higher pressure measurement (between 35 and 50 Torr) is also acquired to improve the signal-to-noise ratio of the very weak

features. However, the low saturation pressure of CFC-113 at 223 K limits the acquisition to pressure below 5 Torr.

A primary baseline spectrum with an empty cell is recorded at each temperature. Control baseline spectra are also recorded before and after each sample measurement to account for the small intensity variations that can occur during the acquisition. If necessary, the primary baseline is adjusted to the control baseline using a polynomial regression prior to the rationing of the sample spectrum to the background spectrum.

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

$$I(v) = I_0(v)e^{-\chi(v)} \tag{1}$$

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

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

$$\chi(v) = \sigma(v)\frac{PT}{T_0P_0}n_0L \tag{2}$$

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

To avoid non-linear detector effects on the strong bands at higher pressures and low signal-to-noise ratio data on the weak bands at low pressures, only optical depths between 0.01 and 0.8 are processed. The absorption cross-section of CFC-113 for each wavenumber is then obtained by a linear least-squares fitting of the remaining values of the optical depth versus the pressure with a forced convergence at $\chi(P=0)=0$. It should be emphasized that this method of cross-section retrieval using a linear fitting of pressure-dependent optical depths is only valid if the pressure broadening on the sharpest features remain minimal, which is the case for our experimental conditions even at the highest pressures.

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

4. Results and data validation

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

Experimental cross-sections are compared with previous data available in the literature. Two sets of laboratory
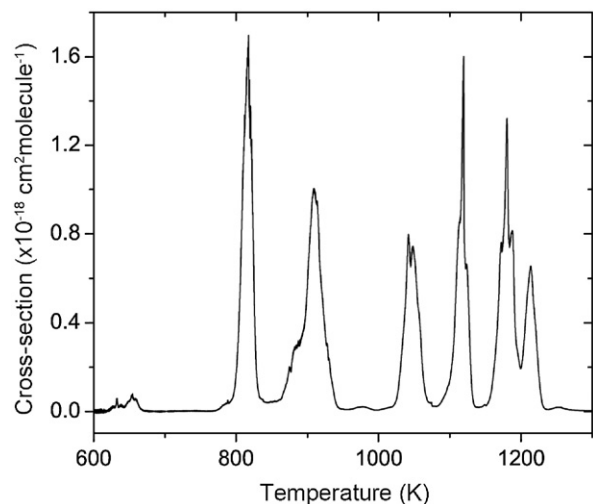
Fig. 1. Survey cross-sections of CFC-113 at 283 K and 0.05 cm^{-1} resolution.

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	v_6
850–995	v_5, v'_5, v'_6
1005–1080	v_4, v'_4
1080–1142	v_3
$\{$ 1142–1200	v_2, v'_2
1200–1235	v_1, v'_1

CFC-113 absorption cross-sections are currently available, the data from McDaniel et al. [4] included in the HITRAN database, and Sharpe et al. [7] in the PNNL database. McDaniel and co-workers presented six absorption spectra of pure CFC-113 vapor at a resolution of 1 cm^{-1} between 203 and 293 K and over the 780.5–995.0 and 1005.5–1232 cm^{-1} spectral ranges. The PNNL database contains three spectra of N_2-broadened CFC-113 from 620 to 5000 cm^{-1} at a resolution of 0.1 cm^{-1} at 278, 298 and 323 K.

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

Our band strength values averaged over all available temperatures agree with the ones from the PNNL database to 1.7% for the 780–850 cm^{-1} band, 5.3% for the 850–995 cm^{-1} band, 5.0% for the 1005–1080 cm^{-1} band, 1.0% for the 1080–1142 cm^{-1} band, and 2.3% for the 1142–1235 cm^{-1} band. The comparison with the McDaniel et al.

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]
293 K	780–850		2.67	2.93
	850–995		3.19	3.33
	1005–1080		1.73	1.91
	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	
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	
	1005–1080		2.16	
	1080–1142		2.47	
	1142–1235		4.04	

values shows agreement to 3.3% for the 780–850 band, 3.3% for the 850–995 cm^{-1} band, 2.2% for the 1005–1080 cm^{-1} band, 4.5% for the 1080–1142 cm^{-1} band, and 7.2% for the 1142–1235 cm^{-1} band. The integrated band strengths at 203 K of Ref. [4] have not been included in the comparison as they are clearly out of range. It is worth mentioning that contrary to McDaniel et al. results,
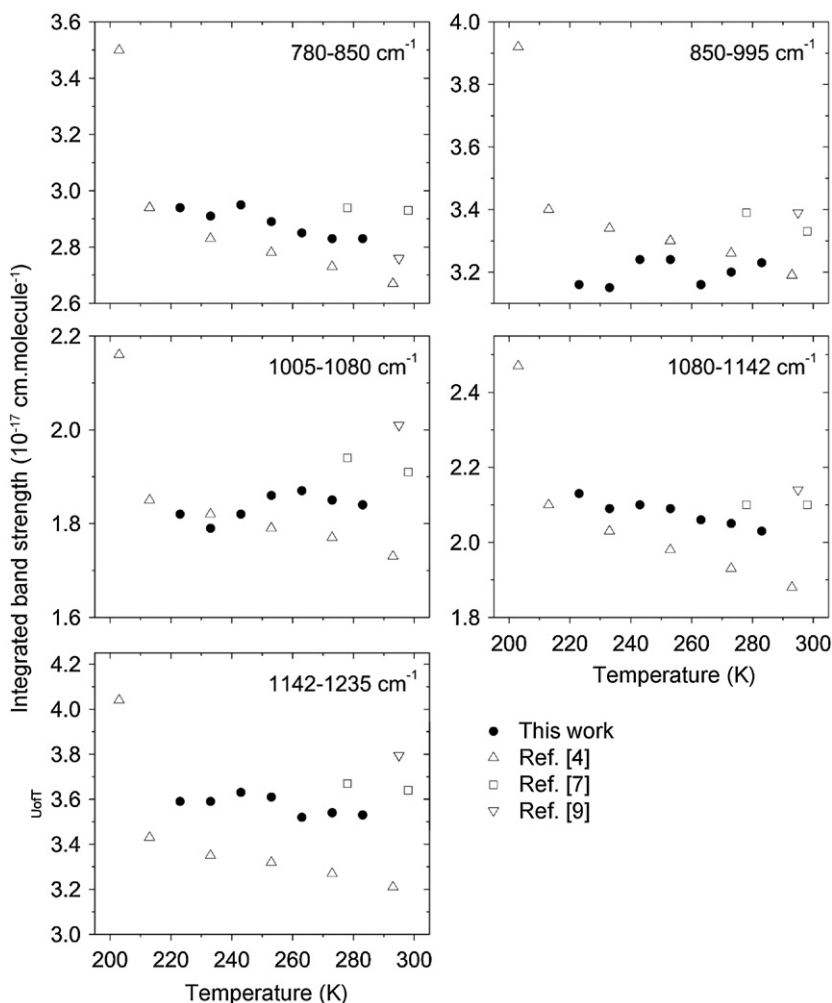
Fig. 2. Temperature dependence of the integrated band strength of the five primary bands of CFC-113.

our overall data showed no significant variation of the integrated cross-sections with temperature.

Two older sets of integrated band strengths, obtained at room temperature only, are also available [8,9]. As observed previously by McDaniels et al., the integrated cross-sections of Ref. [8] are systematically greater than the values from the other studies by large factors (up to 60%). Therefore, they have not been included in this comparison. The integrated band strength of Ref. [9] is inside our range with a maximum discrepancy of 10%.

5. Discussion

As the temperature decreases, the absorption bands of all structures present the classical narrowing of the wings accompanied by an increased peak of the Q-branches. In particular, the peak cross-section of the 1080–1142 cm^{-1} band associated with the v_3 and v'_3 normal modes of vibration at 223 K shows an increase of about 55% compared to 283 K (Fig. 3).

The conformational analysis of CFC-113 has been described elsewhere [5], and will just be reviewed briefly

here. CFC-113 exists in two geometrical conformations. The more stable has a C_1 symmetry characterized by a trans position of two C–Cl and C–F bonds. The second conformer has a C_s symmetry characterized by a gauche position of all the C–Cl and C–F bonds. Due to the small enthalpy difference between them (~ 133.6 cm^{-1}) both conformers exist in our range of temperature. The two conformers have very close harmonic frequencies. The absorption spectra of CFC-113 is, thus, a superposition of the overlapping bands of the C_1 and C_s conformers. The rotational barrier between the C_1 and C_s conformation has been calculated to be 2467.4 cm^{-1}, which makes conformational interconversion difficult at low temperature. It is therefore expected that the relative population ratio $C_1:C_s$ remains constant over our range of temperatures and does not affect the band profiles as the temperature decreases.

To verify this hypothesis, we observed, at higher pressure and over a range of temperatures between 283 and 253 K, the small features around 650 cm^{-1} corresponding to the v_7 and v'_7 normal vibrational modes. This weak band is the only accessible band where the two conformer
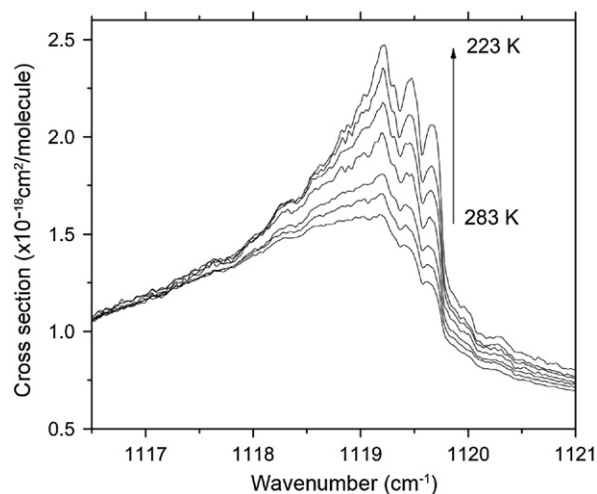
Fig. 3. Cross-section of the Q-branches of the v_3, v'_3 bands of CFC-113 at seven temperatures.

signatures are both relatively well separated and not overlapped by other harmonic frequencies. Unfortunately, it lies at the extreme range of our detector, which results in a very low signal-to-noise ratio. Notwithstanding, no significant variation of the integrated band ratio between the two conformers was observed over this range of temperatures. However, it has been observed that the integrated band strength in this spectral region decreases with temperature. The same effect appears in the PNNL data for temperatures between 278 and 323 K. This indicates the presence of overtone and combination bands in the 620–680 cm^{-1} spectral region, which can affect the relative ratio between the v_7 and v_7' bands and hide a hypothetical conformational interconversion.

The v_6 normal vibrational mode of the C_1 conformer corresponds to the 760–850 cm^{-1} spectral band only. The integrated strength of this band does not show a significant decrease with temperature, which is what we would expect if transitions between conformers were possible in our range of temperatures. The counterpart 850–995 cm^{-1} spectral band, associated with the v'_6, v_5, and v'_5 normal vibrational modes, likewise, does not exhibit an increase in its integrated band strength with decreasing temperature. Due to the intensity of those two bands, it is unlikely that overtone and combination bands play a significant role in the observations. We can therefore predict that transitions between conformers are unlikely to modify the spectral shape of CFC-113 over the range of temperatures found in the atmosphere.

Due to the temperature dependence of the rotational transitions, all the absorption bands shift and broaden in the direction of higher energies as the temperature decreases. Because of the lack of narrow features, we can approximate directly the band centroids of the main structures using the following methods. If a band represents a single vibrational mode or completely overlapped multi-modes, the entire structure is integrated. If there is a clear division between modes, the structures is separated at the minimal junction points. The band centroid shifts are
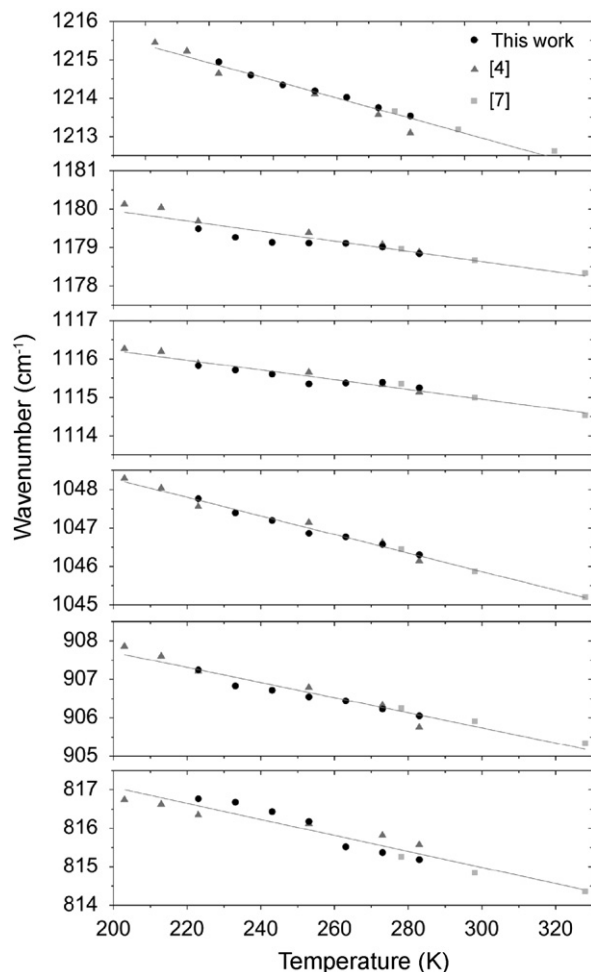

Fig. 4. Band centroid shift as a function of temperature for the primary bands of CFC-113 seen in Fig. 1.

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

reported in Fig. 4 and compared with Refs. [4,7]. The shift in frequency can be fitted with a linear curve. The values of the slope for our data as well as the standard error in the linear fit are given in Table 3. We find once again a good concordance between our data and Refs. [4,7]. The absence of observable non-linear effects in the variation of the band centroids with temperature supports our hypothesis that the relative population ratio C_1:C_s does not vary significatively in our range of temperature.

6. Conclusions

Laboratory cross-sections of CFC-113 at a spectral resolution of 0.05 cm^{-1} have been reported in the mid-infrared between 600 and 1250 cm^{-1} at seven temperatures from 223 to 283 K. The integrated cross-sections of the absorption bands are consistent with previous published data. However, contrary to previous studies, our data show no statistically significant variations of the band strengths with temperature. The temperature-induced band shifts have been estimated and varies from -0.013 cm^{-1}/K for the 1080–1142 cm^{-1} and 1142–1200 cm^{-1} bands to -0.024 cm^{-1}/K for the 1005–1080 cm^{-1} band. As predicted, the CFC-113 conformational ratio appears constant over our range of temperatures, which should facilitate atmospheric retrievals. The laboratory absorption cross-sections are available online in the supplementary data files.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jqsrt.2011.01.023.

References

[1] WMO (World Meteorological Organization). Scientific assessment of ozone depletion: 2006, global ozone research and monitoring project-report, No. 50, Geneva, Switzerland; 2007 [Chapter 1: long-lived compounds].

[2] Dufour G, Boone CD, Bernath F. First measurements of CFC-113 and HCFC-142b from space using ACE-FTS infrared spectra. Geophys Res Lett 2005;32:L15S09.

[3] Sen B, Osterman GB, Salawitch R, Toon G, Margitan J, Blavier JF, et al. The budget and partitioning of stratospheric chlorine during the 1997 arctic summer. J Geophys Res 1999;104:26653–65.

[4] McDaniel AH, Cantrell CA, Davidson JA, Shetter RE, Calvert JG. The temperature dependent, infrared absorption cross-sections for chlorofluorocarbons: CFC-11, CFC-12, CFC-13, CFC-14, CFC-22, CFC-113, CFC-114, and CFC-115. J Atmos Chem 1991;12:211–27.

[5] Le Bris K, Strong K, Melo SML, Ng JC. Structure and conformational analysis of CFC-113 by density functional theory calculations and FTIR spectroscopy. J Mol Spectrosc 2007;243:178–83.

[6] Le Bris K, Strong K. Temperature-dependent absorption cross-sections of HCFC-142b. J Quant Spectrosc Radiat Transfer 2010;111: 364–71.

[7] Sharpe SW, Johnson TJ, Sams RL, Chu PM, Rhoderick GC, Johnson PA. Gas-phase databases for quantitative infrared spectroscopy. Appl Spectrosc 2004;58:1452–61.

[8] Rogers JD, Stephens RD. Absolute infrared intensities for F-113 and F-114 and an assessment of their greenhouse warming potential relative to other chlorofluorocarbons. J Geophys Res 1988;93: 2423–8.

[9] Varanasi P, Chudamani S. Infrared intensities of some chlorofluorocarbons capable of perturbing the global climate. J Geophys Res 1988;93:1666–8.