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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 (~ 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 ±0.1 K for temperatures down to 263 K and ±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:

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

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

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

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

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 ±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