



Measurements of the infrared absorption cross-sections of HCFC-141b (CH₃CFCl₂)

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ABSTRACT

Detection of atmospheric trace gases by optical remote sensing techniques relies on the availability of molecular absorption spectra over a range of relevant temperatures. Absorption cross-sections of a pure vapour of the hydrochlorofluorocarbon HCFC-141b are reported at a resolution of 0.02 cm⁻¹ for a range of temperatures between 223 and 283 K and a spectral range of 570–3100 cm⁻¹. The integrated intensities of the nine main harmonic bands compare well with the data available from previous experimental studies and with theoretical calculations by ab initio and density functional theories.

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1. Introduction

After the phase-out of chlorofluorocarbons by the Montreal Protocol and its further amendments, HCFC-141b (1,1-dichloro-1-fluoroethane or CH₃CFCl₂) has been extensively used to replace CFC-113 as a solvent, and CFC-11 as a foam-blowing agent in manufacturing processes. Its concentration in the atmosphere has risen quickly from the early 1990s to reach a mean global surface mixing ratio above 22 ppt (part per trillion) at the end of 2011 [1]. HCFC-141b is currently the second most abundant hydrochlorofluorocarbon in the atmosphere after HCFC-22 (CHClF₂).

Measurements of HCFC-141b have recently been reported from space-borne missions [2]. An important factor for data retrieval is the quality of the spectroscopic information available over a range of relevant atmospheric temperatures. The purpose of this study is to provide new infrared absorption cross-section spectra of pure HCFC-141b from 223 to 283 K at a resolution of 0.02 cm⁻¹ (OPD=50 cm).

2. Experimental set-up

Experimental data are acquired 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 Global source.

The gas sample (Synquest Laboratories, 99.5%) 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

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with indium o-rings to prevent leakage at low temperature. A short pathlength of 2.93 cm has been chosen to avoid saturation effects while working at manageable pressures. HCFC-141b being liquid at room temperature, each sample is degassed by several Freeze-Pump-Thaw cycles prior to entering the cell. The cell pressure is measured by 10 Torr and 1000 Torr MKS baratron pressure gauges. All the acquisitions have been made with a pure vapour to allow a better accuracy of the pressure reading. Atmospheric retrievals can be performed with these laboratory cross-sections using the pseudo-lines method [3].

The cooling is achieved by a Neslab ULT-80 chiller 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 enhance 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 °C for temperatures down to 263 K and ± 0.2 °C for lower temperatures.

Typical artefacts and sources of errors of FTIR spectra (i.e. spectral aliasing, dynamic alignment error, blackbody emission from the source aperture, and nonlinearity of the MCT detector in the mid-infrared) have been minimized using the same procedure as described in [4]. The spectral calibration of the instrument has been verified by comparing a laboratory CO₂ spectrum with the corresponding lines in the HITRAN 2008 database [5]. The average shift on the 50 lines we analyzed was negligible (-1.14×10^{-4} cm⁻¹ with a standard deviation of 1.135×10^{-3} cm⁻¹).

3. Data analysis

For each temperature, a series of unapodised scans has been recorded at five pressures between 2 and 50 Torr for 283, 273, 263 and 253 K. The saturation vapour pressure of HCFC-141b limited the acquisitions at high pressure to 30 Torr at 243 K, 20 Torr at 233 K and 10 Torr at 223 K.

Each pressure–temperature (P–T) spectrum is composed of a minimum of 200 unapodised scans.

Control baseline spectra, each of them generated from a minimum of 20 scans, are recorded before and after each sample measurements to account for the small intensity variations that can occur during the acquisitions. For each temperature, a several hundred scan primary baseline spectrum with high signal-to-noise ratio is produced from the multiple control baseline spectra. If need be, for each P–T acquisitions, the primary baseline spectrum can be adjusted to the control baseline spectra using a polynomial regression prior to the rationing of the sample spectrum to the background spectrum.

The cross-section, $\sigma(\nu)$, in cm²/molecule is obtained using the Beer–Lambert law:

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

where ν is the wavenumber (cm⁻¹); I_0 , the light intensity passing through the empty cell (baseline); I , the light intensity passing through the sample gas cell and χ , the optical depth defined by:

$$\chi(\nu) = \sigma(\nu) \frac{PT_0}{TP_0} N_L L. \quad (2)$$

N_L is Loschmidt's constant (2.6868×10^{19} molecules/cm³); L , the length of the cell (cm); and P_0 and T_0 , the standard conditions for pressure and temperature.

To prevent saturation effects in an optically thick medium while keeping a good signal-to-noise ratio at every wavenumber, the points corresponding to optically thick ($\chi(\nu) > 1.1$) or optically thin ($\chi(\nu) < 0.1$) conditions are eliminated. This way, a linear behaviour is obtained for strong absorption bands from the low-pressure measurements while weak absorption features are represented by the high-pressure measurements.

The shapes of the sharp ro-vibrational transition lines, as well as the peaks of the Q-branches, are pressure-dependent due to collisional broadening. Therefore, the cross-section for a pure vapour cannot be directly obtained by a linear fit of the optical depth as a function

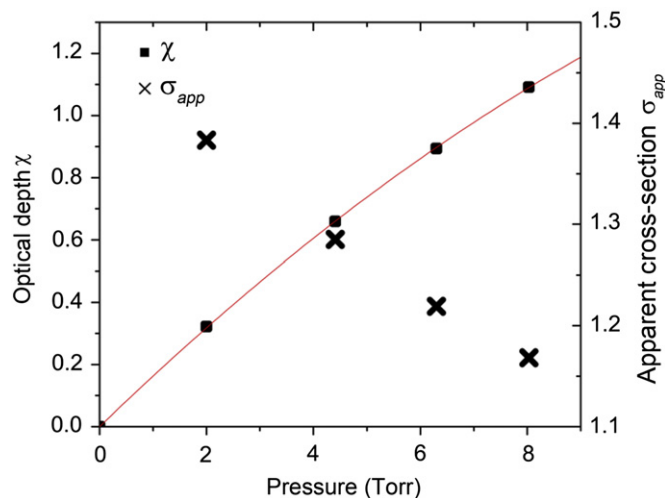


Fig. 1. Variation of the optical depth χ and apparent cross-section σ_{app} ($\times 10^{-18}$ cm²/molecule) as a function of pressure at $\nu = 752.963$ cm⁻¹ for a temperature of 243 K. Note that the value at the highest pressure was not included in the calculation as its optical depth was higher than 1.1.

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