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Temperature-dependent absorption cross-sections of HCFC-142b

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ABSTRACT

Following the recent detection of HCFC-142b (1-chloro-1,1-difluoroethane) from space, laboratory infrared absorption cross-section spectra of this molecule in a pure vapour phase have been recorded in the $650-3500\,cm^{-1}$ spectral region using Fourier transform spectroscopy. The spectra have been recorded at a resolution of $0.02\,cm^{-1}$ and a range of temperatures from 223 to 283 K. The resulting data show good agreement with the harmonic frequencies and intensities calculated using density functional theory as well as with the integrated absorption intensities of the spectral bands available in the literature. The new cross-sections will allow more accurate retrieval of atmospheric HCFC-142b concentrations using infrared spectroscopic techniques.

1. Introduction

Hydrochlorofluorocarbons (HCFCs) are temporary substitutes for chlorofluorocarbons (CFCs). They were introduced after the phase-out of the latter by the Montreal Protocol and its subsequent amendments. Unlike CFCs, which are mainly destroyed by solar ultraviolet radiation in the stratosphere, the HCFCs, which contain one or more hydrogen atoms, can react with OH radicals in the troposphere to create HF and CO_2. Therefore, as less chlorine is transported to the stratosphere, the ozone depletion potentials of HCFCs are substantially weaker than those of CFCs. However, because of their C–Cl and C–F bonds, these molecules still have large absorption cross-sections in the atmospheric window region ($8-12\,\mu m$), which give them strong global warming potentials.

HCFC-142b (1-chloro-1,1-difluoroethane) is a colourless gas at ambient pressure. It is mainly used as a chemical intermediate to produce fluoropolymers, as a blowing agent for expanded polystyrene and as a component of refrigerant fluids. Because of its high vapour pressure and low vapour solubility, HCFC-142b partitions mostly into the atmosphere. Today, this is the third most abundant hydrochlorofluorocarbon after HCFC-22 and HCFC141-b. The atmospheric lifetime of HCFC-142b is 17.9 years $\pm 24\%$ [1]. Its ozone depletion potential has been estimated at 0.07 while its global warming potential is evaluated to be 2310 ± 810 for a horizon of 100 years [1].

The volume mixing ratio of HCFC-142b has been rising steadily in the atmosphere since the beginning of the 1990s, exceeding 20 ppt in 2008 at 13–16 km with an average positive trend of more than 5% per year [2]. The atmospheric concentration of HCFC-142b is now high enough to allow its detection from space [2,3]. However, the accuracy of the retrieval is limited by the lack of spectroscopic knowledge of this molecule. Only three cross-section spectra corresponding to the temperatures

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253, 270 and 287 K are currently available in the HITRAN 2008 database [4]. Measurements of temperature-dependent infrared cross-sections of HCFC-142b vapour at low temperature were reported in the 1990s [5–7] but discrepancies exist between these studies. No new laboratory data at low temperature have been published on this molecule since 1995.

As a result, uncertainties on the spectroscopic parameters of HCFC-142b are seen as one of the main sources of error for atmospheric retrievals [3]. New laboratory measurements are therefore crucial to enable accurate observations of the spatial and temporal variation of this hydrochlorofluorocarbon in the atmosphere.

The purpose of this study is to provide new infrared (IR) cross-sections of HCFC-142b at relatively high resolution ($0.02\,\mathrm{cm}^{-1}$) and at a range of relevant atmospheric temperatures (from 223 to 283 K). The resulting experimental data are compared to theoretical calculations performed using density functional theory and 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.

The gas sample (SynQuest Labs, purity $>98\%$) is contained in a stainless steel cell positioned between the FTS and a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. A vacuum system equipped with a Varian Turbo-V V250 turbo molecular pump allows the cell to be evacuated to about 1×10^{-6} Torr. The cell pressure is measured using 10 and 1000 Torr MKS baratron pressure gauges simultaneously.

HCFC-142b presents very intense lines in the atmospheric window region. In order to avoid saturation effects while working at relevant pressures, a stainless steel cell with an optical path of 3.17 cm was constructed. ZnSe windows were sealed to the cell with indium O-rings to prevent leakage at low temperature. The windows are maintained in place by stainless steel flanges supporting teflon rings.

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 provide temperature homogeneity. The cell temperature is measured by a thermocouple directly inserted inside the cell. The temperature readout accuracy during experiments is typically $\pm0.1\,^{\circ}\mathrm{C}$.

Many sources of errors and artefacts can affect an FTIR spectrum, such as spectral aliasing, dynamic alignment error, blackbody emission from the source aperture, non-linearity of the MCT detector in the mid-infrared, etc. The r.m.s. angular deviation from optimum alignment is less than 10^{-6} rad in normal laboratory conditions (data provided by the manufacturer).

The blackbody emission from the source aperture comes from the warming of the iris by the light source. The warm annulus around the aperture acts as a second infrared source emitting off-axis thermal radiation. This leads to distortion of the signal shape and intensities as the aperture size decreases. To reduce this warm aperture artefact, a second iris is inserted between the DA8 spectrometer and the MCT detector at the focal point of the beam [8]. After this installation, no variation of the cross-section signal with the aperture size has been observed.

The non-linearity of the MCT detector, corresponding to the non-linearity between the measured signal and the photon flux, essentially affects the central fringe of the interferogram, which leads to a zero-level offset in the absorption spectrum. Correction of non-linearity is applied on the raw interferograms before the phase correction and the Fourier transformation. We adjusted the response of the detector to the light intensity by a curve whose only unknown parameter is an empirically chosen DC output value [9]. This parameter is adjusted by a minimization of the transmission in the spectral region below the cut-off wave number. The residual baseline offset is subtracted from the spectra after phase correction and Fourier transformation.

3. Data analysis

For each temperature, a series of spectra were recorded at a minimum of six different pressures between 2 and 12 Torr. Each pressure–temperature (P–T) spectrum is composed of at least 200 unapodised scans. The resulting spectrum, for each temperature, is a composite spectrum from the P–T spectrum sets extrapolated to the zero-Torr limit. A 200-scan primary baseline spectrum with an empty cell was recorded at each temperature. Secondary control baselines of at least 20 scans were also taken before and after each sample measurement to account for the small intensity variations that can occur during the long periods (typically several hours) of acquisitions. If necessary, the primary baseline is adjusted to the secondary baselines by a polynomial regression prior to the division of each sample spectrum by the adjusted baseline spectrum.

The cross-section, $\sigma(\nu)$, in $\mathrm{cm}^2/\mathrm{molecule}$ is calculated for each P–T set using the well-known Beer–Lambert law:

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

with optical depth:

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

where ν is the wave number (cm^{-1}); $I_0(\nu)$, the light intensity passing through the empty cell (baseline); $I(\nu)$, the light intensity passing through the sample gas cell; N_L is the Loschmidt's constant (2.6868×10^{19} molecules/cm^3); 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 wave number, the points corresponding to optically thick ($\chi(\nu)>1.1$) or optically thin ($\chi(\nu)<0.1$) conditions are