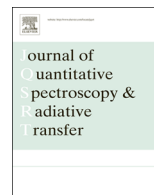




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Infrared absorption cross sections for 1,1,1,2-tetrafluoroethane

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ABSTRACT

High-resolution infrared absorption cross sections for 1,1,1,2-tetrafluoroethane have been determined over the spectral range 750–1600 cm^{-1} from spectra recorded using a high-resolution FTIR spectrometer (Bruker IFS 125HR) and a 26-cm-pathlength cell. Spectra of 1,1,1,2-tetrafluoroethane/dry synthetic air mixtures were recorded at 0.015 cm^{-1} resolution (calculated as 0.9/MOPD) at a number of temperatures and pressures (22–761 Torr and 191–296 K) appropriate for atmospheric conditions. Intensities were calibrated using composite 1,1,1,2-tetrafluoroethane spectra taken from the Pacific Northwest National Laboratory (PNNL) IR database. This cross section dataset is intended to replace what is currently available in the HITRAN/GEISA databases.

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1. Introduction

As a result of the phase out of ozone-depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) under the terms of the Montreal Protocol [1], the global demand for refrigerants is increasingly being met by hydrofluorocarbons (HFCs). Since HFCs are not ozone-depleting substances (ODSs), their emissions are not restricted by the Montreal Protocol. Like CFCs and HCFCs, however, HFCs are powerful greenhouse gases with global warming potentials (GWPs) many times greater than CO_2 . Therefore, increasing HFC emissions will directly contribute to the radiative forcing of climate.

1,1,1,2-Tetrafluoroethane (CH_2FCF_3), or HFC-134a, has a long atmospheric lifetime of 13.4 yr [2] and a 100-yr GWP of 1370 [3]. HFC-134a has replaced CFC-12 as the preferred refrigerant in refrigeration and mobile air conditioning, and it also has a minor usage in foam blowing applications. Prior to 1990, HFC-23 (trifluoromethane) was the only HFC

emitted in significant quantities as a byproduct during the production of HCFC-22 (over-fluorination of chloroform). In the early 2000s, HFC-134a overtook HFC-23 as the most abundant HFC in the Earth's atmosphere, a direct consequence of the rapid growth in the use of HFCs as ODS replacements since the 1990s. The abundance of HFC-134a is growing steadily, directly contributing to the radiative forcing of climate. In fact, the potential for the growth of HFC-134a in developing countries is particularly large [4].

A persistent, potentially toxic by-product of the atmospheric degradation of HFC-134a (initiated by reaction with OH radicals) is trifluoroacetic acid (TFA; CF_3COOH). In fact, among ODS replacement gases, HFC-134a contributes the most TFA to the environment of any HFC [2,3]. TFA is removed from the atmosphere by wet deposition and accumulates in oceans, lakes, and other reservoirs. There is much uncertainty in our understanding of the natural sources and loss processes of TFA, however currently it is not believed that TFA produced from HCFC/HFC degradation will result in environmental concentrations capable of significant ecosystem damage.

Most atmospheric measurements of HFCs are made on the ground, either in situ or via flask sampling [2]. The first atmospheric HFC measurements from orbit were taken by

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Table 1
FTS and cell configurations.

Source	Globalar
Detector	Mercury–cadmium–telluride (MCT) D313
Beam splitter	Potassium bromide (KBr)
Optical filter	~700–1700 cm ⁻¹ bandpass
Resolution	0.015 cm ⁻¹
Aperture size	2.5 mm
Apodisation function	Norton–Beer weak
Phase correction	Mertz
Cell windows	Potassium bromide (KBr)
Pressure gauges	3 MKS-690A Baratrons (1, 10 and 1000 Torr) (± 0.05% accuracy)
Thermometry	4 PRTs, Labfacility IEC 751 Class A

the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) [5] for HFC-134a [6] and HFC-23 [7]. The ACE-FTS, on board SCISAT-1, has a resolution of 0.02 cm⁻¹, covers the spectral region from 750 to 4400 cm⁻¹, and currently detects more organic molecules than any other satellite instrument.

The retrieval of HFC-134a volume mixing ratios (VMRs) from ACE atmospheric spectra [6] used the absorption cross sections of Nemtchinov and Varanasi [8], contained in the HITRAN database (<http://www.hitran.com>); these were first included in the HITRAN compilation released in 2000. Whereas Table 1 in Ref. [8] lists measurements for 49 different pressure–temperature (PT) combinations, there are only data for 33 PT combinations in HITRAN. Each of the 33 PT combinations (covering 20–760 Torr and 190–296 K) corresponds to two files, one covering the ν_4 , ν_5 , ν_{13} , and ν_{14} bands (1135–1340 cm⁻¹), and the other covering the ν_6 band (1035–1130 cm⁻¹). However, there is no 200 K/75.1 Torr cross section for the ν_6 band, so there are only 65 air-broadened cross sections overall. The reason for the discrepancy between the description of measurements in Ref. [8] and those in HITRAN is not known. The GEISA database (<http://ether.ipsl.jussieu.fr/etherTypo/?id=950>) contains the same cross sections for the 33 PT combinations, each corresponding to a single file (1035–1340 cm⁻¹). Inspection of all these cross sections reveals that they contain a number of problems, most notably the wavenumbers have not been calibrated; they are out by as much as ~0.006 cm⁻¹. (Poor wavenumber calibration contributes to retrieval errors, typically resulting in derivative-shaped spectral residuals.) Further minor problems include several cross sections being of poor quality and a number containing channel fringes.

Additionally, HITRAN and GEISA contain three absorption cross sections (0.03 cm⁻¹ apodised resolution) for pure HFC-134a samples at 253, 270, and 287 K (815–1485 cm⁻¹) [9]; these were recorded for the purposes of calculating the GWP and are not suitable for atmospheric remote sensing from orbit. GEISA also contains 15 cross sections from the work of Newnham et al. [10], all derived from spectra recorded at 0.03 cm⁻¹ resolution. These include six pure measurements at 203, 213, 233, 253, 273, and 296 K, and nine additional air-broadened measurements at 203, 253, and 296 K for mixtures with 5, 20, and 100 kPa dry air. For all but the three 100 kPa measurements, the choice of resolution is too low to resolve all the spectroscopic features, limiting the usefulness of these for atmospheric

remote sensing from orbit. Ref. [10] describes an additional cross section at room temperature and 0.003 cm⁻¹ resolution; however, there is no sign of this in GEISA.

Having recently carried out new trifluoromethane measurements [11], the opportunity was taken to also create a new set of 1,1,1,2-tetrafluoroethane absorption cross sections over the pressure, temperature, and complete wavenumber range 22–761 Torr, 191–296 K, 750–1600 cm⁻¹, respectively, with accurate wavenumber calibration (using N₂O reference lines from HITRAN) and better signal-to-noise ratios (SNRs) than those of Nemtchinov and Varanasi [8]. This previous dataset [8] contains absorption cross sections derived from spectra recorded at both 0.01 cm⁻¹ and 0.03 cm⁻¹ resolution. For this work, however, all spectra have been recorded with a resolution at 0.015 cm⁻¹, which still ensures all spectroscopic features are equally well resolved at the lowest measurement pressures.

2. Air-broadened spectral measurements of 1,1,1,2-tetrafluoroethane

A Bruker Optics IFS 125HR high-resolution Fourier transform spectrometer (FTS), located at the Molecular Spectroscopy Facility (MSF), Rutherford Appleton Laboratory, Oxfordshire, UK, was used to record high resolution (0.015 cm⁻¹, calculated as the Bruker instrument resolution of 0.9/MOPD) absorption spectra of air-broadened 1,1,1,2-tetrafluoroethane in the mid-IR region. The spectrometer was configured with an internal mid-infrared radiation source (globalar), a potassium bromide (KBr) beamsplitter and a mercury cadmium telluride (MCT) D313 detector. An optical filter (~700–1700 cm⁻¹ bandpass) and the aperture diameter (2.5 mm) were chosen so that the intensity of infrared radiation falling on the detector was maximised in the spectral region of interest without saturation or loss of spectral resolution. Norton–Beer weak apodisation and Mertz phase corrections were applied to all interferograms. Due to the non-linear response of MCT detectors to the detected radiation, which results in baseline perturbations, all interferograms were transformed using the non-linearity correction in Bruker's OPUS software. The FTS instrumental parameters and settings are summarised in Table 1.

A 26-cm-pathlength single-pass stainless-steel absorption cell, consisting of a double-walled cylinder with wedged KBr windows sealed on sprung PTFE o-rings, was used for the measurements. The wedged windows eliminate interference fringes caused by reflections at the surface, whereas the o-ring mounting of the windows prevents leaks as the cell contracts at low temperatures. The cell was mounted inside the sample compartment of the spectrometer, which was evacuated to < 0.2 Pa in order to minimise the absorbance of impurity gases (mainly water and carbon dioxide), and condensation of these gases on the cell windows at the lower measurement temperatures. Cell temperatures below room temperature were achieved by circulating ethanol from a liquid-nitrogen-cooled ethanol bath through the space between the cell walls. The temperature was controlled by regulating the liquid-nitrogen flow via a solenoid valve which was switched by the output of a comparator that compares the temperature in the ethanol bath against a user pre-set temperature. This setup allows automatic temperature control of the cell from

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