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# Determination of the infrared cross sections and global warming potentials of 1,1,2-trifluoroethane (HFC-143)

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**Abstract.** The Global Warming Potentials (GWPs) of $CH_2F$-$CHF_2$ (HFC-143) have been estimated for different time horizons. Radiative forcings associated with this CFC alternative have been derived relative to CFC-11 and $CO_2$ by introducing laboratory measured absorption cross sections into a coupled chemical-radiative model.

## Introduction

Since the Montreal Protocol [1987] on substances that deplete the ozone layer entered into force, alternative compounds have been developed in order to replace the chlorofluorocarbons (CFCs) used in widespread applications [*Fischer et al.*, 1991]. Hydrohalocarbons, which include both hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), having similar physical and chemical properties to CFCs were proposed by industry as substitutes for the latter. The presence of hydrogen in these molecules allows the gas to react with hydroxyl radicals in the troposphere, leading to a lower ozone depleting potential (ODP) owing to the shorter atmospheric lifetime of the species [*Wuebbles*, 1983; *Fisher et al.*, 1990*a*; *World Meteorological Organization(WMO)*, 1992]. In the case of the HFCs, which do not contain chlorine, the ODP is negligibly small [*Ravishankara et al.*, 1994]. Recent reports [*WMO*, 1992; *Bojkov et al.*, 1993] indicate a worsening of the stratospheric ozone loss and have heightened interest in finding non-chlorinated substitutes. $CH_2F$-$CHF_2$ (HFC-143) is one of the chlorine-free compounds proposed today as an alternative to CFCs in refrigerant and foam blowing applications [*Sand et al.*, 1991; *Barthélemy et al.*, 1993].

In order to assess the possible environmental impact inherent to the release of these substitutes, the ability of each gas to enhance the warming of the atmosphere must be evaluated. Indeed, hydrofluorocarbons exhibit strong vibrational absorption bands in the infrared atmospheric window and hence may also contribute to the radiative forcing of the atmosphere. Global Warming Potentials (GWPs) have been introduced as convenient parameters to quantify the time-varying relative contribution of long-lived greenhouse gases to global warming [*International Panel on Climate Change(IPCC)*, 1990]. The GWP of a well-mixed gas relative to a reference gas is defined as the product of the instantaneous radiative forcing associated with the emission of 1 kg of the gas and the concentration of gas remaining in the atmosphere, integrated over a given period of time, and divided by the same quantity calculated for the reference gas. The radiative forcing induced by a change in the concentration of a gas is the net radiative flux change (in $W/m^2$) at the tropopause. It is directly related to the infrared absorption spectrum of the species. The concentration remaining at a given time is a function of the atmospheric lifetime of the molecule. The gas used as a reference is either $CO_2$ for climate studies [*IPCC*, 1990] or CFC-11 for halocarbons and ozone-related studies [*Fisher et al.*, 1990*b*].

The aim of the present study is to measure accurate infrared cross sections and use them, along with recent reaction rate constant data [*Barry et al.*, 1994], in the NCAR two-dimensional atmospheric model in order to determine the potential effect on climate for HFC-143. The procedure is the same as that used to obtain similar results already published [*Clerbaux et al.*, 1993] for 10 other replacement compounds.

## Cross Sections

The absorption cross sections have been derived from infrared spectra obtained in the atmospheric window, between 700 and 1500 $cm^{-1}$. These spectra were recorded at a spectral resolution of 0.03 $cm^{-1}$ using a Bruker IFS120HR Fourier transform spectrometer. A Norton-Beer apodization function [*Griffiths and de Haseth*, 1986] was used in order to minimize the instrumental distortion and 100 scans were coadded to obtain a spectrum having a good signal-to-noise ratio. Three atmospheric temperatures (287 K, 270 K and 253 K) were investigated at various pressures of the gas (ranging from 1 to 5 torr). The pressure was measured accurately using a 100 torr full scale absolute MKS Baratron (model 390HA) capacitance gauge. The sample of HFC-143, provided by Solvay S. A. (Belgium), had a purity of 98.7 mol.-%. The gas was introduced into a 5 cm long thermostatic cell [*Hurtmans et al.*, 1992] placed in the air-evacuated sample chamber of the spectrometer. The cell, closed by two pairs of wedged KBr windows, was made of anodized aluminium and the temperature stabilization was provided by a cryostat (Neslab ULT80) using methanol as a circulating fluid. A calibrated transducer allowed the temperature of the gas inside the body of the cell to be measured.

In the spectral range investigated, the spectrum presents strong absorption features related to the bending and stretching vibrational modes of the C-C bond and the $CHF_2$ and $CH_2F$ groups. At 0.03 $cm^{-1}$ resolution, the rotational structure is not fully resolved; some lines are merged into broad peaks (Q branches), others are grouped into obvious R and P branches. As expected from the Boltzmann distribution law, intensities of the stronger spectral features increase with decreasing temperature, whereas the intensity of the lines associated with the higher energy levels are reduced.

The absorption cross sections $\sigma$ ($cm^2$/molecule) were

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determined for each spectral data point (separated by 0.0085 $cm^{-1}$) according to the Beer-Lambert law, using the following relation

$$\sigma(\upsilon) = \frac{1}{nl} \ln \frac{I_0}{I}(\upsilon)$$

In this formula, the concentration $n$ (molecule/$cm^3$) was deduced from the measured pressure, which was chosen in such a way as to avoid any saturation of the spectra. The optical path length $l$ (cm) in the thermostatic cell was measured between the two inside windows. Precautions were taken in order to obtain correct base e absorbances ln $I_0/I$, where $I_0$ and $I$ are respectively the intensities of the incident and the transmitted radiation at a given wavenumber $\upsilon$. To prevent the small baseline shift due to the slow heating of the source and the detector during the recording of the spectra, empty cell background spectra were recorded before and after each data spectrum and the mean value of these background spectra was used for $I_0$. Each absorbance spectrum was checked by observing that zero values were obtained in the regions where no absorption occurs.

In order to increase the accuracy, the cross sections at each temperature were obtained by applying a least squares fit at each wavenumber using six different pressures. The cross sections derived between 700 and 1500 $cm^{-1}$ at 287 K are presented in Figure 1. The uncertainties associated with these cross sections range from 3% for strong absorptions to 5% for weak absorptions. The uncertainties are estimated by adding those related to the determination of pressure, temperature, pathlength and absorbance. The error made on pressure measurement is partly due to the impurities in the sample (less than 1.3%) and partly due to the error associated with the pressure gauge. According to the manufacturer, the latter does not exceed 0.15% in the range of pressure used. Temperatures were determined with an accuracy of 0.5 K. The pathlength was measured to ± 0.2% using interferometric techniques. All the above mentioned errors contribute in the same proportion to the determination of intense or weak cross sections. However, as mentioned before, the slow drift of the baseline during the recording of the spectra may play an important part in the error budget and contributes more to weaker features. Standard deviations of the least squares fit were taken as the uncertainties associated with the absorbance determination.

The measured cross sections were integrated over given spectral intervals in order to be used in the radiative code described in the next section. The results presented in Table 1 were obtained by summing the cross sections over 100 $cm^{-1}$

**Table 1.** Integrated cross sections for HFC-143.

| Integration Limits ($cm^{-1}$) | Integrated Cross Sections ($cm.molecule^{-1} \times 10^{17}$) | | |
|---|---|---|---|
| | T = 287 K | T = 270 K | T = 253 K |
| 700 - 800 | 0.000 | 0.000 | 0.000 |
| 800 - 900 | 0.180 | 0.183 | 0.172 |
| 900 - 1000 | 0.371 | 0.380 | 0.370 |
| 1000 - 1100 | 2.179 | 2.176 | 2.199 |
| 1100 - 1200 | 3.287 | 3.346 | 3.393 |
| 1200 - 1300 | 0.226 | 0.226 | 0.225 |
| 1300 - 1400 | 0.395 | 0.394 | 0.401 |
| 1400 - 1500 | 0.273 | 0.275 | 0.283 |
| 700 - 1500 | 6.911 | 6.980 | 7.043 |

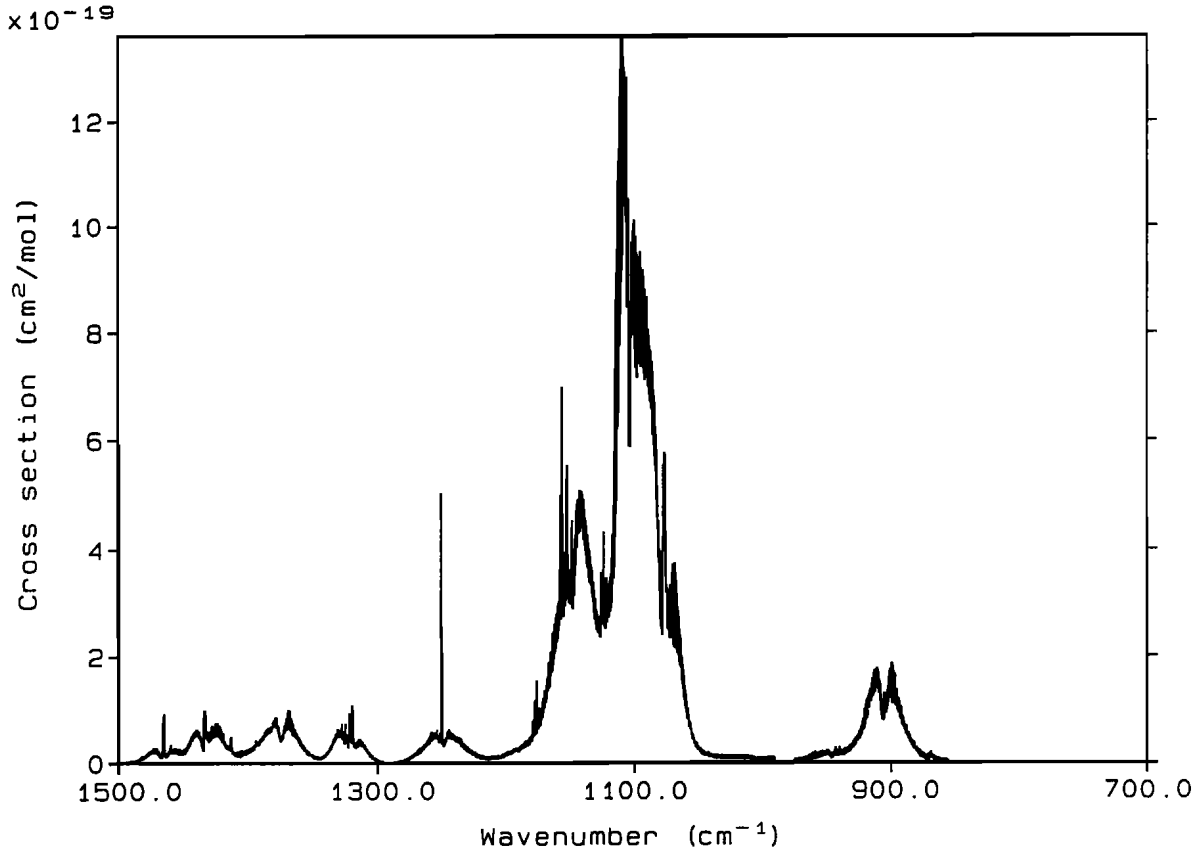



**Figure 1.** Absorption cross sections ($cm^2$/molecule), at 287 K, between 700 and 1500 $cm^{-1}$, for HFC-143.

**Table 2.** Lifetime, Relative radiative forcing and GWP for HFC-143

| Molecule | Lifetime (years) | Radiative forcing per molec. | per kg | Global Warming Potential 5 | 10 | 20 | 50 | 100 | 200 | 500 | years |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Reference gas : CFC-11 | | | | | | | | | | |
| CFC-11 | 57.0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | |
| HFC-143 | 4.3 | 0.52 | 0.85 | 0.52 | 0.36 | 0.21 | 0.11 | 0.08 | 0.07 | 0.06 | |
| | Reference gas : $CO_2$ | | | | | | | | | | |
| $CO_2$ | * | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | |
| CFC-11 | 57.0 | 13200 | 4220 | 4490 | 4640 | 4750 | 4430 | 3680 | 2640 | 1510 | |
| HFC-143 | 4.3 | 6820 | 3570 | 2340 | 1660 | 1010 | 480 | 280 | 170 | 100 | |

* As recommended in *IPCC* [1992], the results derived from the *Siegenthaler* [1983] model were used to estimate the persistence of carbon dioxide after $t$ years : $0.30036 \exp(-t/6.993) + 0.34278 \exp(-t/71.109) + 0.35686 \exp(-t/815.727)$

intervals at each of the three temperatures investigated. The difference between the values integrated over the entire spectral range at 287 K and 253 K does not exceed 2%.

## Global Warming Potentials

Integrated cross sections were introduced into the National Center for Atmospheric Research (NCAR) coupled radiative-chemical two-dimensional model [*Brasseur et al.*, 1990] in order to provide global warming potentials for different time horizons.

Incoming and outgoing radiation budgets were obtained as a function of altitude and latitude using the wide band radiative code of the NCAR community climate model (CCM) [*Kiehl et al.*, 1987], which includes the thermal radiative effects of $H_2O$, $CO_2$, $CH_4$, $O_3$, $N_2O$, CFC-11, and CFC-12 [*Briegleb*, 1992]. The net radiative flux across the tropopause was determined for a mean cloud cover, using annually-averaged vertical concentration profiles for the greenhouse gases. Mixing ratios were calculated between 0 and 85 km using current ground level concentrations [*IPCC*, 1990] as a boundary condition for $CO_2$, $CH_4$, $N_2O$, CFC-11, and CFC-12, and set at 2.5 ppt for HFC-143.

Radiative forcings associated with HFC-143 have been determined relative to CFC-11 and $CO_2$, using the integrated cross sections obtained at 287 K. The small temperature dependence of the data set has been neglected in comparison with the larger uncertainties associated with the other parameters in the model. Results are presented in Table 2 on a molecule per molecule basis and on a kilogram per kilogram basis. As expected, the calculations showed that the net radiative flux at the tropopause increased linearly with the amount of absorber for the CFC-type compounds, which absorb in the atmospheric window. On the contrary, radiative forcings determined relative to $CO_2$ were found to be strongly dependent on the change in concentration of $CO_2$ and on the cloud cover used in the model. This makes the values determined relative to CFC-11 more useful.

An atmospheric lifetime of 4.3 years was obtained for $CH_2F$-$CHF_2$, by scaling of the inferred methyl chloroform lifetime by the ratio of the respective OH rate coefficients at 277 K [*WMO*, 1992]. In this calculation, we used the recently measured relative OH reaction rate [ $k(OH + HFC\text{-}143)/k(OH + CH_3CCl_3) = 2.21 \exp(-102/T)$ ] of *Barry et al.* [1994] and a 6.6 year value for the tropospheric lifetime of $CH_3CCl_3$. The stratospheric photodissociation rate was assumed to be negligible for HFC-143.

Global warming potentials for HFC-143 were calculated relative to CFC-11 and $CO_2$ for time horizons corresponding to 5, 10, 20, 50, 100, 200, and 500 years and are given in Table 2.

## Discussion

The release of HFCs is expected to increase in the near future if the nations comply with the scheduled phase-out of CFCs and HCFCs. HFC-143, which is being developed as a "third-generation" substitute for CFC-11 and CFC-141b for blowing polyurethane foams [*Barthélemy et al.*, 1993], not only has no effect on stratospheric ozone, but also has a lower contribution to the warming of the atmosphere than the compound which it is replacing. At a 500-year integration time horizon, the GWP values are 1.0 for CFC-11, 0.13 for HCFC-141b [*Clerbaux et al.*, 1993] and 0.06 for HFC-143 (this work).

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## References

Barry, J., H. W. Sidebottom, J. Treacy and J. Franklin, Kinetics and mechanism for the atmospheric oxidation of 1,1,2-Trifluoroethane (HFC-143), accepted for publication in *Int. J. Chem. Kin.*, 1994.

Barthélemy, P. P., A. Leroy, J. A. Franklin, L. Zipfel, and W. Krücke, 1,1,2-Trifluoroethane (HFC-143): Zero-ODP blowing agent for rigid polyurethane foams using conventional dispensing equipment, *Proceedings*, Polyurethanes World Congress, 1993.

Bojkov, R. D., C. S. Zeferos, D. S. Balis, I. C. Ziomas, and A. F. Bais, Record low total ozone during northern winters of 1992 and 1993, *Geophys. Res. Letters, 20, 13*, 1351-1354, 1993.

Brasseur, G., M. H. Hitchman, S. Walters, M. Dymek, E. Falise, and M. Pirre, An interactive chemical dynamical radiative two-dimensional model of the middle atmosphere, *J. Geophys. Res., 95D*, 5639-5655, 1990.

Briegleb, B. P., Longwave band model for thermal radiation in climate studies, *J. Geophys. Res., 97D*, 11,475-11,485, 1992.

Clerbaux, C., R. Colin, P. C. Simon, C. Granier, Infrared cross sections and global warming potentials of 10 alternative hydrohalocarbons, *J. Geophys. Res., 98D*, 10,491-10,497, 1993.

Fisher, D. A., C. H. Hales, D. L. Filkin, M. K. Ko, N. D.Sze, P. S. Connell, D. J. Wuebbles, I. S. Isaksen, and F. Stordal, Model calculations of the relative effects of CFCs and their replacements on statospheric ozone, *Nature, 344*, 508-512, 1990*a*.

Fisher, D. A., C. H. Hales, W. C. Wang, M. K. Ko, and N.D. Sze, Model calculations of the relative effects of CFCs and their replacements on global warming, *Nature, 344*, 513-516, 1990*b*.

Fischer, S. K., P. J. Hughes, P. D. Fairchild, C. L. Kusik, J. T. Dieckmann, E. M. McMahon, and N. Hobday, Energy and global warming impacts of CFC alternative technologies, Executive summary, *Technical report DOE/AFEAS*, Dep. of Energy, Washington D. C., 1991.

Griffiths, P. R. , and J. A. de Haseth, *Fourier transform infrared spectroscopy*, Chemical Analysis, *83*, 15-25, Wiley-Interscience, New York, 1986.

Hurtmans, D., R. Pétrisse, D. Lemaitre, C. Clerbaux, and J. Vander Auwera, A thermostatic absorption cell for high accuracy measurement of absolute intensities, *EPA Newsl., 44*, 40-42, 1992.

Intergovernmental Panel on Climate Change(IPCC), Climate change - The IPCC Scientific Assessment, chap. 2, edited by J. T. Houghton, G. J. Jenkins, and J. J. Ephraums, Cambridge University Press, New York, 1990.

Kiehl, J. T., R. J. Wolsky, B. P. Briegleb, and V. Ramanathan, Documentation of radiation and cloud routines in the NCAR Community Climate Model (CCM1), *NCAR Tech. Note, NCAR/TN-288+IA*, Boulder, Colo., 1987.

Montreal Protocol on Substances that Deplete the Ozone Layer, United Nations Environment Programme, Final Act, 1987.

Ravishankara, A. R., A. A. Turnipseed, N. R. Jensen, S. B. Barone, M. Mills, J. Howard, S. Solomon, Do hydrofluorocarbons destroy stratospheric ozone ?, *Science, 263*, 71-75, 1994.

Sand, J. R., S. K. Fischer, P. A. Joyner, Modeled performance of non-chlorinated substitutes for CFC-11 and CFC-12 in centrifugal chillers, *Proceedings*, International CFC and Halon Alternatives Conference, 1991, Baltimore.

Siegenthaler, U., Uptake of excess $CO_2$ by an outcrop-diffusion model of the ocean, *J. Geophys. Res., 88*, 3599-3608, 1983.

World Meteorological Organization(WMO), Scientific Assessment of Ozone Depletion: 1991, in Global Ozone Research and Monitoring Project, *Rep.25*, Geneva, Switzerland, 1992.

Wuebbles, D. J., Chlorocarbon emission scenarios: Potential impact on stratospheric ozone, *J. Geophys. Res., 88*, 1433-1443, 1983.

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