

Evaluation of the atmospheric lifetime and radiative forcing on climate for 1,2,2,2-Tetrafluoroethyl Trifluoromethyl Ether (CF₃OCHF CF₃)

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Abstract. The compound 1,2,2,2-Tetrafluoroethyl Trifluoromethyl Ether, CF₃OCHF CF₃ (HFE-227), is currently being considered as a potential replacement for certain halocarbons, particularly for perfluorocarbons (PFCs), as a dry etching gas in the semiconductor industry. For this reason, it is important to determine the potential environmental effects resulting from the use and emissions of this compound. In this paper, the atmospheric lifetime, radiative forcing, and Global Warming Potentials (GWPs), an important measure of the potential effects of a gas on climate, are evaluated for this compound using our zonally averaged chemical transport and radiative transfer models of the atmosphere. To our knowledge, this is the first time this compound has been evaluated with such atmospheric models. In order to calculate the lifetime and radiative forcing, the rate constants and infrared cross sections of this compound were measured in laboratories at Illinois and Purdue, and results are reported here. The model-evaluated atmospheric lifetime is 11.3 years, mainly due to reaction with OH radicals. The model-evaluated instantaneous-clear-sky radiative forcing is 0.38 W m⁻² ppbv⁻¹, about 45% lower than previously estimated [Imasu *et al.*, 1995]. However, the model-estimated cloudy-sky adjusted forcing, needed to calculate GWPs, is about 25% lower than the model-estimated instantaneous-clear-sky forcing. The GWPs are calculated to be 3400, 1200, and 370 for 20, 100, and 500 year time horizons, respectively.

1. Introduction

International regulatory actions to protect the stratospheric ozone layer and to reduce the threat of global warming have prompted significant interest in the development of possible replacements for chlorine-containing chlorofluorocarbons (CFCs), bromine-containing halons, and other industrially produced compounds. As part of the development of such compounds, it is necessary to ensure that their impact on the environment is small. Hydrofluoroethers (HFEs) are being considered as possible replacements for the long-lived halocarbons. These compounds react with hydroxyl (OH) in the troposphere, but their atmospheric lifetimes are dependent on their particular chemical structure. The absence of chlorine and bromine suggests that such compounds should have little impact on stratospheric ozone and that they likely have a negligible Ozone Depletion Potential (ODP) [Wuebbles, 1981; Granier *et al.*, 1999]. However, one of the negative aspects of the HFEs is that the incorporation of C-F and C-O bonds into the hydrocarbon molecules shifts the absorption features of these compounds into the atmospheric infrared window region (800–1400 cm⁻¹) [Good and Francisco, 1998], the most important spectral region for the infrared absorption. If their atmospheric concentrations were to grow to sufficient proportions,

their infrared absorption could contribute significantly to radiative forcing on the atmosphere and hence to concerns about climate change resulting from global warming. One measure of such concerns on climate is the concept of Global Warming Potentials (GWPs), which provide a relative measure of the potential effects on climate from emissions of a given greenhouse gas [Shine *et al.*, 1995].

The compound 1,2,2,2-Tetrafluoroethyl Trifluoromethyl Ether, CF₃OCHF CF₃ (HFE-227), is one of the many compounds currently being considered as replacements for halocarbons, particularly for the perfluorocarbons (PFCs), used in the semiconductor industry as a dry etching gas [Yoshida, 1998]. Although its current atmospheric concentrations are negligible, future concentration may grow as its consumption increase. Therefore it is important to assess its ability to enhance global warming. The purpose of this paper is to evaluate the atmospheric lifetime, radiative forcing, and GWPs of this compound using radiative transfer and chemical-transport models of the global atmosphere. In a previous study [Imasu *et al.*, 1995] the GWPs of HFE-227 were roughly estimated on the basis of laboratory-determined reactivity of five compounds analogous to HFE-227 along with an estimate of the clear-sky-instantaneous radiative forcing. However, as far as we are aware, these properties of HFE-227 have not previously been evaluated with state-of-the-art models of the global atmosphere. Required data for the infrared cross sections of HFE-227 and the rate constant for the reactions of this compound

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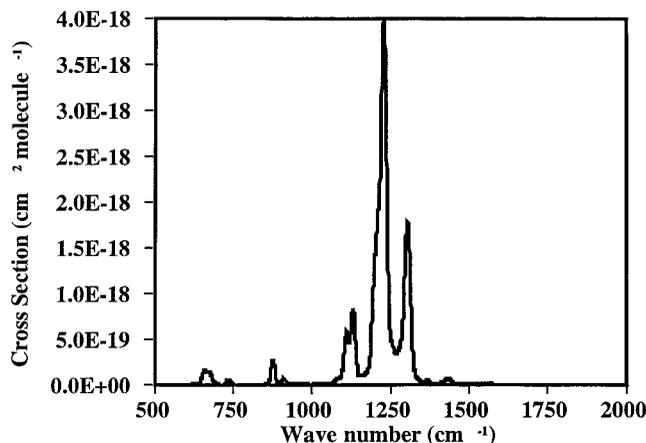


Figure 1. Experimental IR spectra of CF_3OCHF_3 (HFE-227) from 500 to 2000 cm^{-1} .

with OH radical are directly measured for this study, and then used in the associated modeling studies.

2. FTIR Cross Section Determination

The experimental infrared (IR) spectra for HFE-227 were obtained with a Mathanson Galaxy 7020 spectrometer with 1 cm^{-1} resolution. Spectra were measured at room temperature ($298 \pm 2\text{ K}$) for several pressures of HFE-227 between 26.6 and 199.5 Pa. The pressure inside the 656 cm^3 gas cell was measured by calibrated MKS 1.33×10^4 Pa capacitance manometers with a relative error of $\pm 5\%$. For the IR measurements, NaCl windows were used in the gas cell, and the integrated absorbance values were obtained by the use of a built-in algorithm available on the Mathanson Galaxy 7020 computer-aided operating system. Sixty-four scans of the empty cell were used to generate a background baseline profile. This profile was then subtracted by the Mathanson Galaxy software from the absorbance spectra of HFE-227, generating the IR spectra that were used for the cross-section measurements.

The IR cross sections are determined using Beer's law from integrated absorption bands. For each absorption band in the window of 700 to 1500 cm^{-1} , Beer's law plots were found to be linear, indicating that the Beer's law was obeyed over the pressure ranges in the present study for the IR measurements of HFE-227. The errors in the determination of the IR cross sections originate from the uncertainty in the absolute absorbance values, optical path length, and pressure of the gas sample. The IR absorbance band strengths were back-calculated from the slope of the Beer's law plots, and the uncertainties were calculated as twice the standard deviation about the least squares straight line. This method of calculating band strength is based on *McDaniel et al.* [1991], *Clerbaux et al.* [1993], and *Capellani and Restelli* [1992]. Figure 1 shows the experimental IR spectrum for HFE-227. It is important to note that the three strongest absorption bands are occurring in the infrared window region. The integrated absorption cross section for HFE-227 in the 700 – 1500 cm^{-1} region was $4.1 \pm 0.2 \times 10^{-16}\text{ cm molecule}^{-1}$, where the 2σ error bar had taken into account the error factors mentioned above. Our estimated integrated value is about 10% higher than the *Suga et al.* [1994] spectra. Finally, the HFE-227 used for these measurements was purchased from Syn Quest Laboratory with a purity of

greater than 97%. The measured HFC-227 spectra shown in Figure 1 do not appear to be significantly contaminated based on the absence of absorption features from the most likely impurity, $\text{CF}_3\text{OCF}=\text{CF}_2$, the precursor of HFE-227 [*Li et al.*, 2000a].

3. Atmospheric Lifetime

In this study the atmospheric lifetime of HFE-227 is derived by two methods. The primary method involves modeling the chemistry of the species along with relevant physical processes such as transport and radiative transfer in order to determine the distribution of the species. The second method for deriving lifetimes involves simple scaling based on the approach introduced by *Prather and Spivakovsky* [1990] (called PS method hereafter). This scaling method assumes that reaction with OH in the troposphere is the only factor contributing to the lifetime of a compound in the troposphere. The atmospheric lifetime of a reference compound due to reaction with OH is scaled by the ratio of the rate coefficients for reaction with OH to calculate the tropospheric lifetime. Methyl chloroform is used as a reference gas in this method. For the lifetime calculations based on the first method we used our two-dimensional (latitude and altitude) chemical transport model (CTM) of the global atmosphere [*Wuebbles et al.*, 1998; *Kotamarthi et al.*, 1999; *Naik et al.*, 2000]. This model has been used extensively in past international ozone assessments to determine lifetimes of halocarbons and other greenhouse gases, and their effects on ozone [*World Meteorological Organization (WMO)*, 1992, 1995]. The model's grid is 5° in latitude from pole to pole and about 1.5 km in altitude from the surface to 85 km. The model has state-of-the-art representation of tropospheric and stratospheric processes. The Arrhenius expression for the reactions of HFE-227 with OH is taken as $k_{\text{HFE-227+OH}} = 7.09 \times 10^{-13} \exp(-1478/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ on the basis of combining laboratory measurements of *Li et al.* [2000b] and OH rate constant estimation technique developed by *DeMore and Wilson* [1999]. Since the current concentrations of HFE-227 are negligible, a background surface concentration of 5 parts per trillion by volume (pptv) was assumed in the model calculations to determine its atmospheric lifetime.

The model-derived atmospheric lifetime for HFE-227 is calculated to be about 11.3 years. The model-derived atmospheric lifetime has been scaled based on the observation-based lifetime of 5.7 years for methyl chloroform (CH_3CCl_3) due to reaction with tropospheric OH [*Naik et al.*, 2000]. This scaling is also used in the derivation of lifetimes in the recent WMO assessment [*Granier et al.*, 1999], in order to account for uncertainties in model-derived OH distributions.

The lifetime estimated using the PS scaling method is 11.12 years, which is about 2% lower than that derived by the two-dimensional (2-D) model. On the basis of highest-occupied molecular (HOMO) energy, *Imasu et al.* [1995] have also estimated the lifetime for HFE-227 of 11 years, very close to our analysis using the modeled and PS scaling methods.

4. Radiative Forcing

The radiative forcing for HFE-227 is calculated with a narrowband model (NBM) [*Jain et al.*, 2000]. The model has recently been used to calculate the radiative forcings for 39 important greenhouse gases, including CO_2 , CH_4 , N_2O , plus a number of halocarbons [*Jain et al.*, 2000]. It is a Malkmus

random band model of bandwidth 10 cm^{-1} for H_2O and HFE-227, and 5 cm^{-1} for CO_2 , O_3 , CH_4 , and N_2O . These intervals were chosen because spectrally integrated infrared fluxes compare favorably with reference line-by-line calculations. The 5 cm^{-1} transmissions are averaged for each 10 cm^{-1} interval, and gases are overlapped using the random overlap approximation. The model calculates infrared fluxes due to H_2O , CO_2 , O_3 , CH_4 , N_2O , and number of halocarbons [Jain *et al.*, 2000] using a three-layer cloud scheme. The model performs angular integration for all gases using Gaussian quadrature over 12 angles. Line parameters for H_2O , CO_2 , O_3 , CH_4 , and N_2O are based on the HITRAN database [Rothman *et al.*, 1992]. Absorption cross sections for HFE-227 are based on this study, which is discussed in section 2. The global and annual mean atmosphere (GAM) is used, which has been taken from Jain *et al.* [2000]. This atmosphere contains vertical profiles of pressure, temperature, H_2O , CO_2 , O_3 , CH_4 , and N_2O at 34 levels.

In this study the radiative forcing is calculated as the change in net irradiance due to a change in HFE-227 concentrations at the tropopause after allowing for the adjustment of stratospheric temperatures to radiative equilibrium [Schimel *et al.*, 1996; Granier *et al.*, 1999]. We define the tropopause at a level where the minima in temperature occurs. The radiative forcing that we have calculated here, taking this adjustment into account, is called the adjusted radiative forcing.

Jain *et al.* [2000], Myhre and Stordal [1997], and Freckleton *et al.* [1998] have shown that the vertical profiles of the gases are important in determining their radiative forcing. The radiative forcing for HFE-227 is calculated for a change in vertical mixing ratio from zero to the globally and annually averaged 2-D model-estimated vertical distribution. Adjusted-cloudy-sky radiative forcing is calculated with respect to the surface concentration. Generally, radiative forcing is expressed in $\text{W m}^{-2}\text{ ppbv}^{-1}$; hence the results are linearly scaled to reflect the impact of a 1 ppbv change in the concentration.

Using the 2-D model-derived globally and annual averaged vertical profile with decreasing concentration in height, the cloudy-sky-adjusted radiative forcing is computed to be $0.31\text{ W m}^{-2}\text{ ppbv}^{-1}$. The absolute cloudy-sky-adjusted forcing for a uniform change in vertical concentration is $0.32\text{ W m}^{-2}\text{ ppbv}^{-1}$. The use of the model-derived more realistic vertical profile results in a decrease in the radiative forcing by 3%. The reduced radiative forcing is a consequence of reduced downwelling radiation in the troposphere due to smaller amount of HFE-227 in the stratosphere. On the basis of a clear-sky mid-latitude atmosphere, Imasu *et al.* [1995] calculated the instantaneous-clear-sky radiative forcing (i.e., without stratospheric adjustment) for HFE-227. The Imasu *et al.* estimated instantaneous-clear-sky radiative forcing was $0.56\text{ W m}^{-2}\text{ ppbv}^{-1}$, which is about 45% higher than the instantaneous-clear-sky value of 0.38 W m^{-2} calculated by the model used in this study. Note that the model-estimated instantaneous-clear-sky radiative forcing is about 25% higher than the adjusted-cloudy-sky forcing, partly due to larger upward irradiance radiation during clear-sky conditions.

5. Global Warming Potentials

The Global Warming Potential (GWP) is a concept used by policy makers to compare the relative potential effects on climate from various greenhouse gases. The GWP of a greenhouse gas as defined by the Intergovernmental Panel on Climate Change (IPCC) [Shine *et al.*, 1995; Albritton *et al.*, 1995;

Schimel *et al.*, 1996] is the time-integrated change in the radiative forcing of a gas, also known as Absolute Global Warming Potential (AGWP) of a gas, over a specified time horizon relative to that of CO_2 . Calculating the GWP for a particular gas requires the radiative forcing and the temporal decay both for the gas of interest and for CO_2 , the reference gas. In this study we evaluated the GWPs for HFE-227 using our NBM-derived radiative forcings discussed in the previous section. In order to calculate the AGWP for HFE-227 the temporal decay of HFE-227 was calculated based on our 2-D CTM-based lifetime discussed in section 3. In the case of CO_2 , GWPs are adopted from the most recent WMO assessment [Granier *et al.*, 1999].

The HFE-227 GWPs derived in this study for time horizons of 20, 100, and 500 years are 3400, 1200, and 370, respectively. It is important to note that the 100-year HFE-227 GWP calculated here is at least 250% lower than the GWPs of commonly used PFCs. For example, 100 years GWPs for SF6 and CF4, one of the important PFCs, are 22,200 and 5700 [Granier *et al.*, 1999], in comparison to the 100-year GWP of only 1200 calculated here for HFE-227.

6. Summary

The atmospheric lifetime, radiative forcing, and Global Warming Potentials for 1,2,2,2-Tetrafluoroethyl Trifluoroethyl Ether, $\text{CF}_3\text{OCH}_2\text{CF}_3$ (HFE-227), have been evaluated using 2-D chemical transport and radiative transfer models, with infrared cross sections and the rate constant for reactions of HFE-227 with OH measured in our laboratories. The derived atmospheric lifetime for HFE-227 was 11.3 years, with its primary loss being due to tropospheric reaction with the hydroxyl radical. The estimated adjusted-cloudy-sky forcing was $0.31\text{ W m}^{-2}\text{ ppbv}^{-1}$. The GWPs for HFE-227 calculated here were significantly lower than those of the PFCs compounds it would replace. This suggests that the use of HFE-227 would lead to a significantly lower impact on climate than PFC use. However, given a lifetime of 11.3 years, care needs to be taken to ensure that use of HFE-227 does not grow to be so large as to result in a radiative forcing that could affect climate.

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