

Experimental and Theoretical Study of the Atmospheric Chemistry and Global Warming Potential of SO₂F₂

Vassileios C. Papadimitriou,^{†,‡} R. W. Portmann,[†] David W. Fahey,[†] Jens Mühle,[§] Ray F. Weiss,[§] and James B. Burkholder^{*,†}

Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder Colorado, 80305-3328, Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, 80309, and Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093-0244

Received: July 18, 2008; Revised Manuscript Received: September 15, 2008

In this work, potential atmospheric loss processes for SO₂F₂, a commercially used biocide (fumigant), have been studied and its global warming potential calculated. Rate coefficients for the gas-phase reactions OH + SO₂F₂ → products, k_1 , and Cl + SO₂F₂ → products, k_4 , were determined using a relative rate technique to be $k_1 < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 and 333 K and $k_4(296 \text{ K}) < 5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. UV absorption cross sections of SO₂F₂ were measured at 184.9, 193, and 213.9 nm, and its photolysis quantum yield at 193 nm was determined to be <0.02. The atmospheric lifetime of SO₂F₂ with respect to loss by OH, Cl, and O(¹D) reaction and UV photodissociation is estimated to be >300, >10 000, 700, and >4700 years, respectively. The stratospheric lifetime of SO₂F₂ is calculated using a two-dimensional model to be 630 years. The global warming potential (GWP) for SO₂F₂ was calculated to be 4780 for the 100 year time horizon using infrared absorption cross sections measured in this work and a SO₂F₂ globally averaged atmospheric lifetime of 36 years, which is determined primarily by ocean uptake, reported by Mühle et al. (Mühle, J.; Huang, J.; Weiss, R. F.; Prinn, R. G.; Miller, B. R.; Salameh, P. K.; Harth, C. M.; Fraser, P. J.; Porter, L. W.; Grealley, B. R.; O'Doherty, S.; Simonds, P. G. *J. Geophys. Res.*, submitted for publication, 2008). Reaction channels and the possible formation of stable adducts in reactions 1 and 4 were evaluated using ab initio, CCSD(T), and density functional theory, B3P86, quantum mechanical electronic structure calculations. The most likely reaction product channels were found to be highly endothermic, consistent with the upper limits of the rate coefficients measured in this work.

Introduction

Sulfuryl fluoride, SO₂F₂, is a high-vapor-pressure biocide that is primarily used as a commercial fumigant (wood preservative and insecticide). SO₂F₂ is currently being used as an alternative to methyl bromide, CH₃Br, whose use was regulated under the Montreal protocol (1986) due to its contribution to stratospheric ozone loss. Although SO₂F₂ has been commercially available since the 1960s, its atmospheric abundance and rate of increase have only recently been quantified as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) global measurement program.¹ SO₂F₂ has a negligible ozone depletion potential but is a greenhouse gas and has the potential to be a radiative forcing agent. An evaluation of the potential impact of SO₂F₂ on climate requires a thorough understanding of its atmospheric loss processes and lifetime, which were not well-characterized before this study.^{2,3}

Typical loss processes for atmospheric trace gases normally include gas-phase reaction with species such as O(¹D), Cl, OH, O₃, or NO₃, UV-vis photolysis, wet or dry deposition, or heterogeneous processes. Sulfuryl fluoride is expected to have low atmospheric gas-phase reactivity due to its chemical stability, i.e., large S=O and S-F bond strengths. In a recent study, rate coefficients, k , for the SO₂F₂ gas-phase reactions



and



were reported to be $k_1(294 \text{ K}) < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2(294 \text{ K}) < 1 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁴ The reported upper limit for the O₃ rate coefficient establishes that this reaction represents a negligible atmospheric loss process for SO₂F₂. The upper limit for k_1 , however, corresponds to an atmospheric lifetime for reaction with OH, τ_{OH} , of ~30 years, and hence, reaction 1 could be a significant atmospheric loss process for SO₂F₂. A more accurate determination of k_1 is needed to better define τ_{OH} .

SO₂F₂ is volatile and has low solubility in aqueous solutions with pH < 7² and, therefore, does not partition efficiently into atmospheric aerosol. SO₂F₂ does, however, react in alkaline solutions via



that makes atmospheric loss by ocean uptake a potentially important process. Mühle et al.¹ reported the SO₂F₂ lifetime with respect to ocean uptake to be 40 (±13) years. Atmospheric loss of SO₂F₂ via UV photolysis⁵ and reaction with O(¹D)⁴ are only expected to be significant in the stratosphere, thus leading to relatively long lifetimes as a result of the slow turnover of the atmosphere through the stratosphere.

* Corresponding author. E-mail: James.B.Burkholder@noaa.gov.

[†] National Oceanic and Atmospheric Administration.

[‡] CIRES, University of Colorado.

[§] Scripps Institution of Oceanography.

Here, we report laboratory measurements of the rate coefficients for the gas-phase reaction of OH, k_1 , and Cl atoms, k_4 , with SO₂F₂:



We also have studied the UV photolysis SO₂F₂ by measuring its absorption cross section at 184.9, 193, and 214 nm and its photolysis quantum yield at 193 nm. An evaluation of the SO₂F₂ atmospheric loss processes and associated lifetimes are presented as well as the global warming potential (GWP) of SO₂F₂ that was determined using SO₂F₂ infrared absorption spectra measured in this work. In addition, the heats of reaction, $\Delta_r H$, for possible product channels in reactions 1 and 4 have been evaluated using quantum chemical calculations. Geometries and frequencies were calculated at the MP2/6-31++G(d',p') level of theory, whereas absolute electronic energies were determined using density functional theory (DFT), B3P86 and B3PW91, and ab initio methods, CCSD(T).

Experimental Details

The experimental work presented here consisted of several independent studies that include (1) SO₂F₂ UV and infrared absorption cross sections in the gas phase, (2) rate coefficient measurements, using a relative rate technique, for the reaction of OH and Cl atoms with SO₂F₂, and (3) measurements of the SO₂F₂ photolysis quantum yield at 193 nm. Details of the experimental apparatus and methods used for these measurements are described separately in the following sections.

Absorption Cross Section Measurements. Gas-phase UV absorption cross sections for SO₂F₂ were measured at 184.9, 193, and 213.9 nm and infrared spectra were measured between 500 and 4000 cm⁻¹. Absorption cross sections were determined using absolute pressure measurements of either pure SO₂F₂ or manometrically prepared mixtures of SO₂F₂ in He. Absorption was measured for a range of SO₂F₂ concentrations, and cross sections were determined using Beer–Lambert's law

$$A = -\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \sigma_\lambda L[\text{SO}_2\text{F}_2] \quad (5)$$

where A is the measured absorbance (integrated infrared absorbance), $I(\lambda)$ and $I_0(\lambda)$ are the measured light intensity at wavelength λ with and without SO₂F₂ in the absorption cell, σ is the SO₂F₂ absorption cross section (integrated band strength, S), L the optical path length, and $[\text{SO}_2\text{F}_2]$ the SO₂F₂ concentration. Infrared absorption spectra were recorded at resolutions of 0.125, 0.25, 0.5, and 1.0 cm⁻¹ using a Fourier transform spectrometer. The UV absorption cross sections were measured using Hg (184.9 nm) and Zn (213.9 nm) atomic resonance lamps and a low-energy pulsed ArF excimer laser (193 nm).

The 184.9 nm SO₂F₂ absorption cross section was measured using a 50 cm long absorption cell, a Hg Pen-Ray lamp light source, and a solar blind phototube detector. Eight different SO₂F₂ concentrations in the range of 0.37–2.52 × 10¹⁷ molecule cm⁻³ were used in the cross section determination. The SO₂F₂ absorption cross section at 193 nm was measured using a low-energy pulsed ArF excimer laser (~0.1 mJ cm⁻² pulse⁻¹) light source whose intensity was measured with a calibrated power meter at the exit of a 100 cm long absorption cell. The SO₂F₂ concentration was varied over the range of 0.06–1.15 × 10¹⁸ molecule cm⁻³ in the 193 nm cross section determination. The SO₂F₂ absorption cross section at 213.9 nm (Zn lamp) was measured using a 130 cm long absorption cell and a phototube detector with a 214 nm narrow band-pass filter. Fourteen SO₂F₂ concentrations in the range of 0.78–9.8 × 10¹⁸ molecule cm⁻³

were used. For the 193 and 213.9 nm cross section determinations, pure SO₂F₂ samples were used and its concentration was determined from absolute pressure measurements using calibrated pressure meters.

Infrared absorption cross sections were determined using a 15 cm long absorption cell and SO₂F₂ concentrations in the range of 0.91–7.48 × 10¹⁵ molecule cm⁻³. The SO₂F₂ infrared absorption spectrum was found to be independent of bath gas pressure over the pressure range of 25–205 Torr (He).

Quantum Yield Measurements. The SO₂F₂ photolysis quantum yield was measured using methods similar to those used in a previous study of acetone quantum yields in this laboratory.⁶ The photolysis quantum yield of SO₂F₂ was measured by exposing a SO₂F₂ sample, in either a He or N₂ bath gas, to the output of a 193 nm (ArF excimer) pulsed laser. The loss of SO₂F₂ in the sample was measured using infrared absorption. The fraction of SO₂F₂ lost per photolysis laser pulse was small, ~2 × 10⁻⁷; therefore, the sample was exposed to multiple laser pulses prior to measuring the loss of SO₂F₂.

Quantum yields were measured using the following procedure. First, the photolysis and infrared absorption cells were filled with a SO₂F₂/bath gas mixture and the SO₂F₂ concentration was measured by infrared absorption. The sample in the photolysis cell was exposed to a measured number of pulses from the photolysis laser while the sample was being circulated between the photolysis and absorption cells using a 20 L min⁻¹ Teflon-coated pump. The SO₂F₂ concentration was then measured, and the sample photolysis was repeated. The photolysis procedure was repeated at least five times for each sample. Photolysis cells with path lengths of 100 cm and internal diameters of 1.5 and 5 cm were used during the course of the experiments (the measured SO₂F₂ photolysis quantum yield was independent of the surface-to-volume ratio). The laser beam passed along the length of the photolysis cell but did not fill the cross sectional area (volume) of the cell. The photolysis laser fluence was measured with a power meter at the exit of the photolysis cell.

The concentration of SO₂F₂ remaining after “ n ” laser pulses is given by

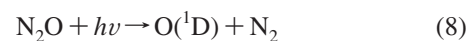
$$[\text{SO}_2\text{F}_2]_n = [\text{SO}_2\text{F}_2]_0 [1 - \sigma_{193\text{nm}}^{\text{SO}_2\text{F}_2} \Phi F]^n \quad (6)$$

where $[\text{SO}_2\text{F}_2]_0$ is the initial SO₂F₂ concentration, $\sigma_{193\text{nm}}^{\text{SO}_2\text{F}_2}$ is the absorption cross section of SO₂F₂ at 193 nm, Φ is the photolysis quantum yield of SO₂F₂, and F is the photolysis laser fluence. A linear least-squares analysis of $\ln([\text{SO}_2\text{F}_2]_n/[\text{SO}_2\text{F}_2]_0)$ versus n

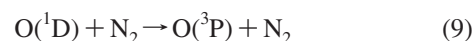
$$\ln\left(\frac{[\text{SO}_2\text{F}_2]_n}{[\text{SO}_2\text{F}_2]_0}\right) = -n \ln(1 - \sigma_{193\text{nm}}^{\text{SO}_2\text{F}_2} \Phi F) \quad (7)$$

yields $\ln(1 - \sigma_{193\text{nm}}^{\text{SO}_2\text{F}_2} \Phi F)$, and Φ was calculated using the SO₂F₂ absorption cross section at 193 nm and the calibrated laser fluence.

The photolysis laser fluence was calibrated using N₂O as a reference photolyte



where the N₂O quantum yield at 193 nm is unity.⁷ N₂O photolysis measurements were performed using a N₂ bath gas (600 Torr) such that O(¹D) produced in reaction 8 was rapidly quenched to its ground state:



The calibration experiments used the same methods as the SO₂F₂ photolysis measurements, and the change in the N₂O concentration was measured using infrared absorption.

SO₂F₂ quantum yields were measured in He and N₂ bath gases at pressures between 60 and 620 Torr. The photolysis laser fluence was varied over the range of 2–10 mJ cm⁻² pulse⁻¹. The initial SO₂F₂ and N₂O concentrations were varied between 2 and 8 × 10¹⁵ molecule cm⁻³ and 1 and 2 × 10¹⁶ molecule cm⁻³, respectively. The photolysis laser was operated at 20 Hz, and all measurements were performed at 296 K.

Rate Coefficient Measurements. Rate coefficients for the gas-phase reactions of SO₂F₂ with OH and Cl were measured using a relative rate method. The loss of SO₂F₂ and a reference compound, for which the rate coefficient is known, were measured using infrared absorption. Provided that SO₂F₂ and the reference compound are lost solely due to OH or Cl atom reaction the rate coefficients are related by

$$\ln\left(\frac{[\text{SO}_2\text{F}_2]_0}{[\text{SO}_2\text{F}_2]_t}\right) = \frac{k_i}{k_{\text{Ref}}} \ln\left(\frac{[\text{Ref}]_0}{[\text{Ref}]_t}\right) \quad (10)$$

where [SO₂F₂]₀ and [Ref]₀ are the initial concentrations of SO₂F₂ and the reference compound and [SO₂F₂]_t and [Ref]_t are the concentrations at time *t*.

OH radicals were produced by the 248 nm pulsed laser photolysis (KrF excimer, 10–20 Hz) of ozone



in the presence of a large excess of H₂O (~19 Torr) in a He bath gas. The yield of the electronically excited oxygen atoms, O(¹D), in reaction 11 is 0.9.⁷ OH radicals are produced in the reaction



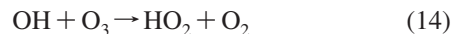
where *k*₁₂(298 K) = 2.0 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹.⁷ Rate coefficient measurements were measured using the experimental setup described in the photolysis quantum yield experiments (using the larger volume cell, gas residence time ≈ 6 s) with the loss of the sample and reference compounds measured via infrared absorption. The temperature of the reactor was maintained by circulating fluid from a temperature-regulated reservoir through the reactors jacket. The temperature of the gas at the entrance and exit of the reactor was measured to be within 1 °C of that of the circulating fluid. The infrared cell and gas circulation manifold were at room temperature.

We have used CHF₃ as the reference compound



in studying reaction 1 where *k*₁₃(*T*) = 6.3 × 10⁻¹³ exp(-2300/*T*) cm³ molecule⁻¹ s⁻¹; *k*₁₃(298 K) = 2.8 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹.⁷ Rate coefficients were measured by first adding SO₂F₂, CHF₃, H₂O, and He bath gas to the reactor. The contents were thoroughly mixed, and the SO₂F₂ and CHF₃ concentrations were measured by infrared absorption. The total pressure of the initial gas mixture in the reactor was ~100 Torr. During the course of the rate coefficient measurements, the initial concentrations of SO₂F₂, CHF₃, and H₂O were varied over the ranges of 2–8 × 10¹⁵, 2.8–6.5 × 10¹⁵, and 3–6 × 10¹⁷ molecule cm⁻³, respectively. Following the complete mixing of the sample, ozone was slowly added to the reaction mixture while the UV photolysis laser was passing through the reactor.

The ozone concentration in the reactor was kept low in order to minimize the loss of OH radicals produced in reaction 12 by reaction with ozone



where *k*₁₄(*T*) = 1.7 × 10⁻¹² exp(-940/*T*) cm³ molecule⁻¹ s⁻¹ and *k*₁₄(298 K) = 7.3 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹.⁷ The steady-state concentration of ozone in the reactor was <5 × 10¹² molecule cm⁻³ in all experiments. It should be noted that the loss of OH via reaction 14 does not influence our relative rate measurement provided that the extent of reactions 1 and 13 are sufficient to yield measurable changes in the concentrations of the reference and sample compounds.

An additional consideration in our OH relative rate measurement is the possible loss of the reference and/or sample compounds by reaction with O(¹D)



where *k*₁₅(298 K) = 1.3 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, *k*_{15b}(298 K) = 5.8 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹,⁴ *k*₁₆(298 K) = 9.1 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, and the branching ratio favors collisional quenching, *k*_{16a}/*k*₁₆ > 0.75.⁷ The collisional quenching of O(¹D) by the reactants, reactions 15b and 16b, will not influence the relative rate measurement because the reactants are not lost by this process. However, O(¹D) reactive loss, reactions 15a and 16a, will influence the relative rate measurement. The use of high H₂O and the lowest possible reactant concentrations minimizes the extent to which reactions 15 and 16 occur. The H₂O pressure was varied during the course of our experiments between 5 and 20 Torr. The limitations on our *k*₁ rate coefficient determination imposed by the O(¹D) reaction is discussed in the Results and Discussion section.

CH₂FCF₃ (HFC-134a) was used as a reference in our Cl atom relative rate measurements



where *k*₁₇(298 K) = 1.5 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ with an estimated uncertainty of 10%.⁷ Cl atoms were generated by the 351 nm (XeF excimer laser) pulsed laser photolysis of Cl₂:



Rate coefficients were measured using nearly the same methodology as in the OH experiments. Cl₂ (0.2–2 × 10¹⁷ molecule cm⁻³) was added to the initial reaction mixture and the pressure of the reactor was 630 Torr with N₂ as the bath gas. The initial concentrations of the reference compound and SO₂F₂ were ~4.5 × 10¹⁶ molecule cm⁻³. In several measurements, 20 Torr of O₂ was added to the gas mixture.

Materials. The SO₂F₂ gas sample (99.8% purity) used in this study was stored in a vacuum-sealed stainless steel container. The SO₂F₂ sample was degassed using several freeze-pump-thaw cycles prior to use. Either pure SO₂F₂ or dilute mixtures of SO₂F₂ in He (0.11 and 1.3%), prepared manometrically in a 12 L Pyrex bulb, were used during the course of this study. The SO₂F₂ abundance in the prepared mixtures was measured using infrared absorption and was stable for at least 2 months. Ozone was produced by flowing O₂ through a commercial ozonizer and collected on silica gel in a trap at 195 K. Ozone was introduced into the reaction cell by passing a small flow of He through the trap before entering the reactor. He (UHP, 99.999%), O₂(UHP, 99.99%), Syn. Air (80% N₂/20% O₂), and Cl₂, a mixture containing 0.2% Cl₂ in He, were

TABLE 1: UV Absorption Cross Sections for SO₂F₂ at 296 K Measured in This Work

wavelength (nm)	cross section (10 ⁻²² cm ² molecule ⁻¹) ^a
184.9	71.7 ± 1.2
193	40 ± 4.4
213.9	2.08 ± 0.04

^a The uncertainties are 2σ (95% confidence level) and were obtained from the precision and the estimated absolute uncertainty in the absorption measurement.

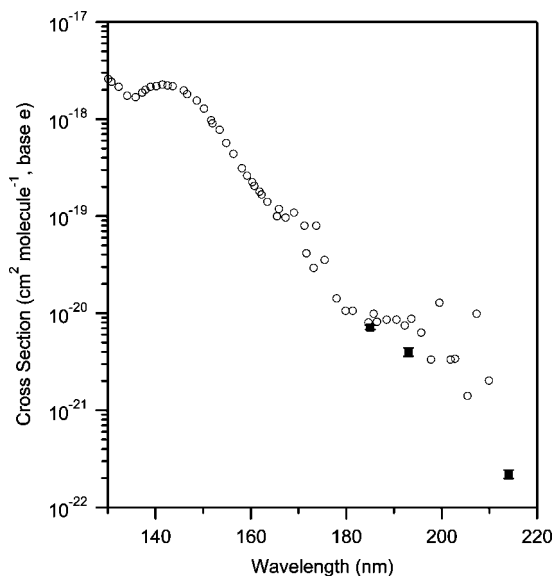


Figure 1. UV absorption cross sections of SO₂F₂ measured at 184.9, 193, and 213.9 nm in this work (●). The error bars are the 2σ values of the precision of the measurements. The UV absorption spectrum reported in Pradayrol et al. (ref 5) (○) is included for comparison.

used as supplied. Distilled H₂O was degassed, stored in a Pyrex vacuum reservoir, and introduced directly into the reactor from the headspace of the reservoir. CH₂FCF₃ (99.995%), CHF₂CF₃ (>99.99%), and CHF₃ (>99.9%) were used as reference compounds in the OH and Cl rate coefficient determinations. Pressure was measured using 10 and 1000 Torr capacitance manometers.

Results and Discussion

UV Absorption Spectrum. Gas-phase UV absorption cross sections for SO₂F₂ measured at 184.9, 193, and 213.9 nm are listed in Table 1. Over this wavelength range, the SO₂F₂ absorption cross sections are relatively small and decrease with increasing wavelength. A comparison of our results with the SO₂F₂ UV absorption spectrum reported by Pradayrol et al.⁵ (the only other UV cross section data currently available in the literature) over the wavelength range of 130–210 nm is given in Figure 1. Note, we have extracted the Pradayrol et al. absorption cross section data from Figure 5 in their paper which may have introduced some small error in the values we report from their study. Our absorption cross section measured at 184.9 nm, $(7.17 \pm 0.12) \times 10^{-21}$ cm² molecule⁻¹, is in good agreement with the value from the Pradayrol et al.,⁵ $\sim 8 \times 10^{-21}$ cm² molecule⁻¹, study. Our absorption cross sections at 193 and 213.9 nm, $(4.08 \pm 0.44) \times 10^{-21}$ and $(2.08 \pm 0.04) \times 10^{-22}$ cm² molecule⁻¹, respectively, are lower than given in Pradayrol et al. The quoted uncertainties in our absorption cross sections are at the 2σ level and include estimated systematic errors. Our

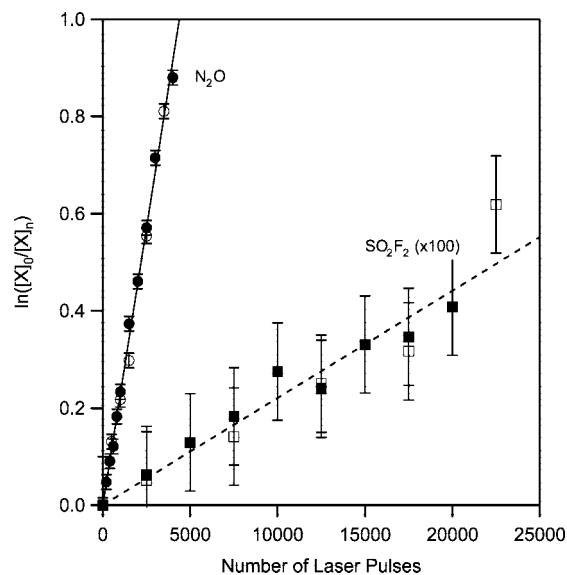


Figure 2. Loss of N₂O (circles) and SO₂F₂ (squares) following pulsed laser photolysis at 193 nm. The SO₂F₂ data has been scaled for clarity (i.e., the number of laser pulses was actually 10 times larger and the ln() values have been multiplied by 10). The losses of N₂O and SO₂F₂ were measured in separate experiments with constant photolysis laser fluence, at 296 K in a N₂ bath gas. The lines are linear least-squares fits to the data, and the ratio of the slopes yield the photolysis quantum yield for SO₂F₂ of 0.02 ± 0.002.

193 nm cross section is a factor of 2 lower. The source for such large discrepancies is at present not known. The spectrum reported in Pradayrol et al. shows diffuse band structure in the wavelength region between 170 and 210 nm. The absorption cross sections in our study were measured at just three discrete wavelengths and are not sufficient to identify any diffuse structure in the SO₂F₂ absorption spectrum. Some of the difference in cross section may, therefore, be due to the differences in the wavelengths used of the cross section measurements.

The quantum yield for the photodissociation of SO₂F₂, Φ, at 193 nm was measured as part of our work. A representative set of quantum yield data, in which the loss of SO₂F₂ following 193 nm pulsed laser photolysis was measured, is shown in Figure 2. Also, included in the figure is a set of laser fluence calibration measurements in which the loss of N₂O, via photodissociation at 193 nm, was measured (see the Experimental Details section). The loss of N₂O scaled linearly with the photolysis laser fluence (varied over the range of 0.8–6.0 mJ cm⁻² pulse⁻¹). The loss of SO₂F₂ was found to be independent of bath gas (N₂, He), the addition of O₂ (10 Torr), and the addition of H₂O (1 Torr). Quantum yield experiments were performed in the two photolysis cells yielded nearly identical results although the total SO₂F₂ loss in the larger volume cell was smaller, a factor of 5, and therefore less accurately measured. The loss of SO₂F₂ per laser pulse was very small due to its small absorption cross section and photolysis quantum yield at 193 nm. These measurements, therefore, required a large number of photolysis laser pulses to produce measurable changes in the SO₂F₂ concentration. No photolysis products were observed via infrared absorption. A linear least-squares analysis of the measured losses of SO₂F₂ and N₂O yielded Φ = 0.02 ± 0.002, using the 193 nm SO₂F₂ absorption cross section determined in this work, where the uncertainty is the 2σ value from the precision of the fit. The use of the larger 193 nm SO₂F₂ absorption cross section from Pradayrol et al. would yield a SO₂F₂ quantum yield of 0.008.

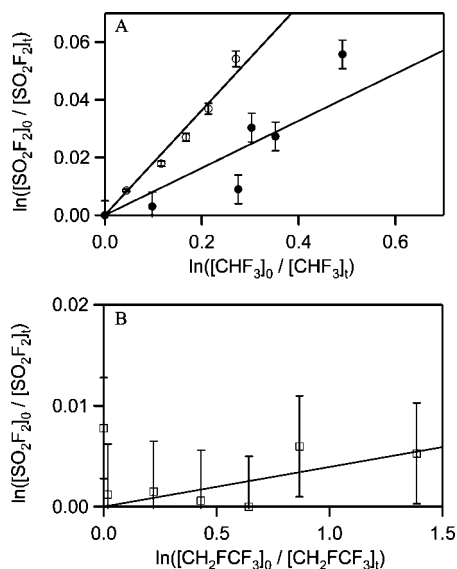


Figure 3. Relative rate data for the OH + SO₂F₂ → products, k_1 , and Cl + SO₂F₂ → products, k_4 , reactions with CHF₃ ($k(T) = 6.3 \times 10^{-13} \exp(-2300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and CH₂FCF₃ (HFC-134a); $k(296 \text{ K}) = 1.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ used for the reference (Ref) compounds, respectively. The k_1 data were measured at 296 (○) and 333 K (●), whereas the k_4 data (□) was obtained at 296 K. The lines are the linear least-squares fits to the data that yield $k_1(296 \text{ K}) = 4.8 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_1(333 \text{ K}) = 5.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $k_4(296 \text{ K}) = 6.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

OH Rate Coefficient. Representative data from the relative OH rate coefficient measurements for reaction 1, OH + SO₂F₂, are shown in Figure 3. Rate coefficients for reaction 1 were measured at 296 and 333 K using CHF₃ as the reference compound. At both temperatures, the observed loss of SO₂F₂ was small relative to the change in CHF₃ with a 2–6% total change in SO₂F₂ concentration. There was no statistically significant difference in the measured loss of SO₂F₂ observed at the two temperatures. An analysis that included all our measurements (12 experiments at 296 K and 3 experiments at 333 K) yielded $k_1(296 \text{ K}) = (4.9 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_1(333 \text{ K}) = (5.1 \pm 1.2) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The quoted uncertainties are the 2σ values from the precision of the least-squares analysis.

It is most likely that the small loss of SO₂F₂ observed in our experiments was not in fact due to reaction with OH. First, the possible loss of SO₂F₂ via dark chemistry, including hydrolysis on the walls of the reactor, or loss in the apparatus (circulating pump) was thoroughly checked under all the experimental conditions and found to be negligible, <0.5% SO₂F₂ loss in 3 h. The typical duration of a rate coefficient experiment was ~30 min. Therefore, the observed loss of SO₂F₂ in our experiment was most likely due to gas-phase chemistry. Second, the negligible temperature dependence observed for the OH + SO₂F₂ rate coefficient is contrary to that expected for a highly endothermic reaction (see the Theoretical Calculations section). Finally, the observed loss of SO₂F₂ may have resulted from the incomplete scavenging of O(¹D) radicals by H₂O in the OH radical source chemistry. For the initial concentrations used in our experiments, the ratio [H₂O]/[SO₂F₂] was in the range of 100–200. Under these conditions, a small fraction of the photolytically produced O(¹D) would react with SO₂F₂. Dillon et al.⁴ reported that reaction 15a has negligible temperature dependence over the range of 225–296 K, consistent with a very efficient gas-phase reaction. There are also several exothermic channels for reaction 15a possible (see the Theoretical

Calculations section). The independence of SO₂F₂ loss observed over the very narrow temperature range used in our experiments is therefore consistent with that expected for reaction 15a. In a separate set of experiments, performed under identical conditions but with no H₂O added, a significant loss of SO₂F₂ (up to 30%) that is due to reaction with O(¹D) was observed. This measurement demonstrates our ability to measure SO₂F₂ loss in the apparatus and that the O(¹D) reaction leads to loss of SO₂F₂. However, no reaction products were observed from the O(¹D) + SO₂F₂ reaction via infrared absorption.

Additionally, the validity of our relative rate approach was confirmed by measuring room temperature rate coefficients for the reaction of OH with CHF₂CF₃ and CHF₃ for which the OH rate coefficients are relatively small but well-established:



The recommended rate coefficients for these reactions are based on relative⁸ and absolute⁹ rate coefficient measurement techniques and are $k_{19}(298 \text{ K}) = (2.0 \pm 0.4) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{13}(298 \text{ K}) = (2.8 \pm 0.6) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁷ Our measurement results are shown in Figure 4 where CH₂FCF₃ and CHF₂CF₃ were used as reference compounds for the CHF₂CF₃ and CHF₃ reactions, respectively,



where $k_{20}(298 \text{ K}) = (4.4 \pm 0.1) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁷ A least-squares analysis yielded $k_{19}(296 \text{ K}) = (2.09 \pm 0.20) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{13}(296 \text{ K}) = (3.46 \pm 0.35) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the quoted uncertainties are at the 95% level of confidence and include estimated systematic uncertainties (~9%). Our measured rate coefficients are in agreement, within 5% and 20%, respectively, with the currently recommended values⁷ and validate the experimental approach used in this study.

On the basis of our measurements and the possible influence of secondary chemistry leading to the loss of SO₂F₂, we have chosen to report a conservative upper limit for the OH rate coefficient of $k_1 < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 and 333 K.

Cl + SO₂F₂ Rate Coefficient. Results from a representative relative rate measurement for reaction 4, Cl + SO₂F₂, are shown in Figure 3. Under all experimental conditions employed in this study, no loss of SO₂F₂ was observed within the precision of the measurements (~2%). Experiments were performed over a range of initial concentrations, pressure, and photolysis laser fluence as outlined in the Experimental Details section. Experiments were also performed in the absence of the reference compound, CH₂FCF₃, to maximize the possible loss of SO₂F₂. No loss of SO₂F₂ was observed in any experiment. An upper limit for $k_4(296 \text{ K})$ of $<2.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained by taking the 2σ precision of the infrared measurements (2%) as the maximum possible loss of SO₂F₂. After taking into consideration the uncertainty of the reference compound rate coefficient, $k_{17}(298 \text{ K})$, we report a conservative upper limit for $k_4(296 \text{ K})$ of $<5.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Theoretical Calculations. In order to further evaluate the reactions of OH and Cl with SO₂F₂, reactions 1 and 4, the energetics of a number of possible product channels and the possibility of stable adduct formation were calculated using quantum mechanical molecular methods. Calculations were performed using the Gaussian 98 and Gaussian 03 program suites.^{10,11} Standard enthalpies of formation for a number of

TABLE 2: Calculated Enthalpies of Formation, $\Delta_f H^\circ(298.15\text{ K})$ (kJ mol $^{-1}$), for Several Sulfur Species, OH $^-$ and Cl-SO $_2$ F $_2$ Adducts, and Species Used in Benchmark Calculations

molecule	B3PW91/ aug-cc-pV(T+d)Z	CCSD(T) IB+dDT	CCSD(T) IBa+dDT	CCSD(T) CBSDTQ ^a	literature values ^b
SO $_2$ F $_2$	-712.1	-715.9	-727.5	-758.5	-758.6
SOF $_2$	-560.0	-547.1	-560.4	-588.6	-543.9
SO $_3$	-357.2	-351.3	-360.5		-395.8
SO $_2$	-259.9	-257.9	-269.0		-296.8
SO	3.5	24.5	17.3	6.7	5.0
SF $_2$	-277.7	-267.1	-278.4	-293.9	-296.6
F $_2$ OSO-HO	-667.7	-682.0			
F $_2$ SO-HO	-520.9	-516.0			
HO-SO $_2$ F $_2$	-584.8				
HO-SOF $_2$	-550.3	-530.1			
O $_2$ FSF-HO	-663.7	-802.1			
OFSF-HO	-512.3	-507.6			
Cl-SO $_2$ F $_2$	-586.4				
Cl-SOF $_2$	-426.5				
SO $_3$ F	-454.7	-431.0	-443.1		
SO $_2$ F	-373.1	-347.4	-358.9	-385.5	
SO $_2$ FOH	-692.8	-706.1	-717.5		
SOF	-266.4	-240.2	-251.0	-271.7	
SF	5.8	19.8	12.9	4.2	13.0
F $_2$	13.1	5.2	-0.2	-0.2	0.0
HF	-259.4	-270.8	-273.8	-273.8	-272.5
HO $_2$	5.2	22.6	15.9	15.9	2.1
HOF	-76.6	-83.4	-88.7	-88.7	-98.3
OH	39.6	39.6	36.9	36.9	39.0
ClF	-47.4	-42.4	-49.1	-49.1	-50.3
ClO	93.8	115.6	109.7	109.7	101.2

^a Calculated values using CCSD(T)/CBSDTQ energies corrected for core-valence effects and scalar-relativistic effects (MVD approach) taken from Grant et al. (ref 17). ^b Values taken from Chase (ref 28) and the NIST Chemistry Webbook (ref 29).

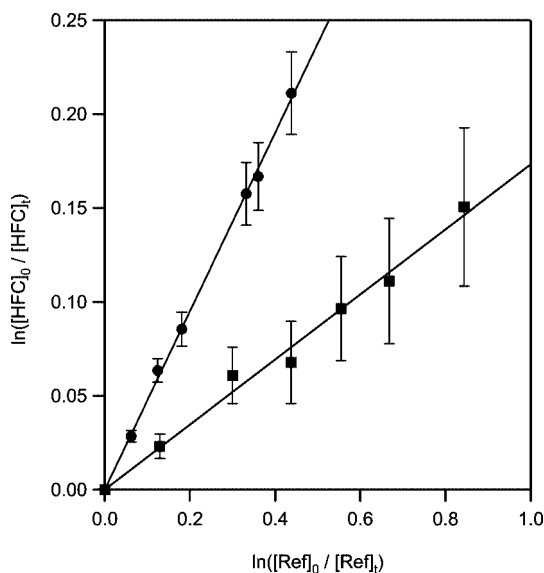


Figure 4. Relative rate data for the OH + CHF $_2$ CF $_3$ \rightarrow products, k_{19} , and OH + CHF $_3$ \rightarrow products, k_{13} , reactions with CH $_2$ FCF $_3$ ($k_{20}(298\text{ K}) = 4.4 \times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$) and CHF $_2$ CF $_3$ ($k_{19}(298\text{ K}) = 2.0 \times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$) used as reference compounds, respectively. Both k_{19} (●) and k_{13} (■) data were measured at 296 K. The lines are the linear least-squares fits to the data and yield $k_{19}(298\text{ K}) = (2.09 \pm 0.07) \times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ and $k_{13}(298\text{ K}) = (3.46 \pm 0.17) \times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ where the uncertainties are the 2σ precision of the fit.

stable and radical species were calculated. Benchmark calculations for several key small sulfur species were also carried out.

Geometry optimization and vibrational frequency calculations were performed using second-order Møller–Plesset perturbation theory in conjunction with the 6-31G++(d',p') basis set. Vibrational frequencies were scaled down by 0.9661. The

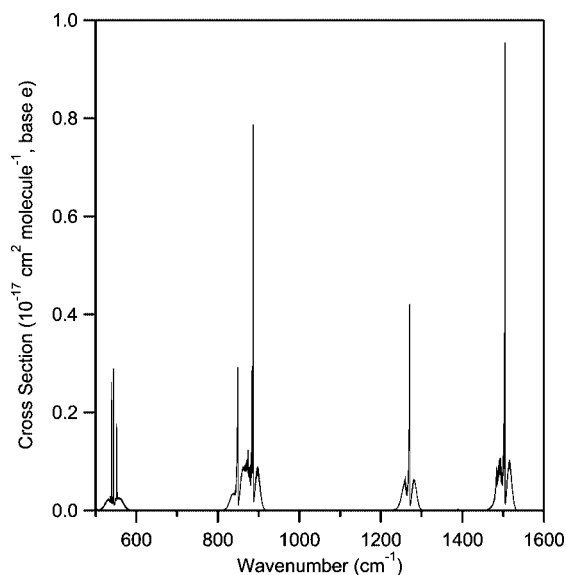


Figure 5. Infrared absorption spectrum of SO $_2$ F $_2$, 296 K, measured at 0.125 cm $^{-1}$ resolution in 100 Torr N $_2$ bath gas (available in the Supporting Information).

optimized molecular structure parameters and vibrational frequencies used in the higher level of theory single-point energy calculations are provided as Supporting Information, Tables S1 and S2.

Absolute electronic energies were calculated employing coupled-cluster theory including single and double excitations, as well as triple excitations in a perturbative manner, CCSD(T). Correlation-consistent basis sets, augmented with a set of tight d-functions for the second-row elements of double- and triple- ζ quality were used in the calculations. In particular, the basis sets used in this work were cc-pV(D+d)Z and cc-pV(T+d)Z,

TABLE 3: Calculated $\Delta_f H(298.15\text{ K})$ (kJ mol⁻¹) Values for Possible Product Channels in the Reactions of OH and Cl with SO₂F₂^a

reaction	B3P86 aug-cc-pV(T+d)Z	CCSD(T)		CCSD(T)CBSDTQ ^b	literature value ^c
		IB+dDT	IBa+dDT		
Bimolecular Channels					
SO ₂ F ₂ + OH → SO ₂ F + HOF	222.89	245.47	243.03		
SO ₂ F ₂ + OH → SOF ₂ + HO ₂	118.00	151.72	146.21		177.7
SO ₂ F ₂ + OH → SO ₃ F + HF	-44.14	-25.63	-26.23		
SO ₂ F ₂ + OH → SO ₂ FOH + F	59.88	49.53	52.58		
SO ₂ F ₂ + Cl → SO ₂ F + ClF	171.78	204.75	198.18		
SO ₂ F ₂ + Cl → SOF ₂ + ClO	126.52	163.05	155.53		194.6
Adducts					
SO ₂ F ₂ + OH → HOSO ₂ F ₂	76.73				
SO ₂ F ₂ + OH → F ₂ OSOHO	3.13				
SO ₂ F ₂ + OH → O ₂ FSFHO	7.91				
SO ₂ F ₂ + Cl → ClSO ₂ F ₂	2.67				
Bond Dissociations Energies (Benchmarks)					
SO ₂ F ₂ → SO ₂ + F ₂	476.70	463.16	458.35		461.7
SO ₂ F ₂ → SO ₂ F + F	433.58	447.86	448.01	452.18	
SO ₂ F ₂ → SOF ₂ + O	419.58	417.95	416.33	419.04	463.8
SOF ₂ → SOF + F	387.57	386.28	388.72	396.12	
SOF ₂ → SF ₂ + O	549.98	529.20	531.17	543.72	496.4
SOF ₂ → SO + F ₂	590.88	576.72	577.45	581.58	548.9
SO ₃ F → SO ₃ + F	189.25	159.12	162.01		
SO ₂ F → SO ₂ + F	204.07	168.95	169.31		
SO ₃ → SO ₂ + O	363.71	342.61	340.64		348.1
SO ₂ → SO + O	533.76	531.51	535.43		551.0
SO → S + O	541.64	501.69	508.90	519.46	521.1
SF ₂ → SF + F	377.47	366.21	370.69	377.29	363.1
SF → S + F	366.00	336.62	343.46	352.19	369.3

^a Geometry optimizations and vibrational frequency calculations were performed at MP2/6-31++G(d',p') level of theory and are given in the Supporting Information, whereas density functional (B3P86) and coupled-cluster (CCSD(T)) theories were used for the absolute energy calculations. ^b Calculated values using CCSD(T)/CBSDTQ energies corrected for core–valence effects and scalar-relativistic effects (MVD approach) taken from Grant et al. (ref 17). ^c Values taken from Chase (ref 28) and the NIST Chemistry Webbook (ref 29).

as well as their diffuse functions augmented variants, aug-cc-pV(D+d)Z and aug-cc-pV(T+d)Z. The zero-point and thermal energies (298.15 K) were derived using harmonic oscillator and the rigid-rotor approximations. Finally, infinite basis (IB) extrapolation was employed.^{12–15} The IB method allows the extrapolation of electronic energies to a complete basis set (CBS) limit by using only double- and triple- ζ correlation-consistent basis sets¹⁶ and are denoted as IB+dDT and IBa+dDT, where “a” and “+d” stand for the presence of diffuse functions and extra tight d-functions, respectively, in the basis sets employed. Density functional theory, B3PW91 and B3P86 with the aug-cc-pV(T+d)Z basis set, was used for comparison purposes.

Enthalpies of formation, $\Delta_f H^\circ(298.15\text{ K})$ were calculated at the CCSD(T)/IB+dDT, CCSD(T)/IBa+dDT, and B3PW91/aug-cc-pV(T+d)Z levels of theory, and a list of the species included in our calculations and their $\Delta_f H^\circ(298.15\text{ K})$ values is given in Table 2. There are limited $\Delta_f H^\circ(298.15\text{ K})$ experimental values available for many of the species involved in these reactions. In general, the agreement between the calculated and literature values where available are within 15 kJ mol⁻¹. However, the calculated enthalpies for reactions that involve SO₂F₂ and SOF₂, show systematically larger deviations, ~ 30 kJ mol⁻¹. This is consistent with the deviations with the literature values for the heats of formation for these species. These differences make little difference in the calculated reaction enthalpy trends mapped out in this work since they are small compared to calculated exothermicities. The reaction channels considered in this work and the $\Delta_f H^\circ(298.15\text{ K})$ values calculated using CCSD(T)/IB+dDT, CCSD(T)/IBa+dDT and B3PW91/aug-cc-pV(T+d)Z levels of theory are given in Table 3. There is reasonably good

agreement, ± 18 kJ mol⁻¹, among the $\Delta_f H^\circ(298.15\text{ K})$ values obtained using the DFT and coupled-clusters methods.

During the course of our work, Grant et al.¹⁷ reported heats of formation for a series of sulfur containing compounds including SF₂, SF₄, SF₆, SF₂O, SF₂O₂, and SF₄O calculated using coupled-cluster theory [CCSD(T)] extrapolated to the CBS limit. The calculated values included corrections for core–valence, scalar-relativistic, and first-order atomic spin–orbit effects and lead to a very accurate set of values. The results reported by Grant et al. overlap to some extent with our study, in particular, with regards to our benchmarking calculations. The results from the Grant et al. study are more accurate than those obtained in our calculations, mainly due to the corrections for core–valence and scalar-relativistic effects. However, the errors in our calculations cancel out, for the most part, when calculating enthalpies of reaction. The results from the Grant et al. study are included in Tables 2 and 3 for comparison with the present results.

The results from our calculations, Table 3, show that product channels involving direct abstraction by OH and Cl from SO₂F₂ are highly endothermic, $\Delta_f H^\circ_{298.15} > 145$ kJ mol⁻¹. The exchange reaction, OH + SO₂F₂ → F + HOSO₂F, which is expected to have a very high reaction barrier in the gas phase, is also endothermic. For the OH reaction, the only exothermic product channel was the formation of hydrogen fluoride (HF), OH + SO₂F₂ → HF + SO₃F.

Reactions 1 and 4 are not likely to proceed through adduct formation channels in the gas phase, since no stable intermediate complexes (including hydrogen-bonded and sulfuryl adducts) were found. In other words, the reaction enthalpies calculated

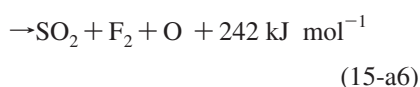
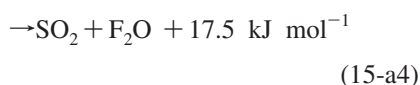
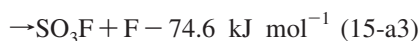
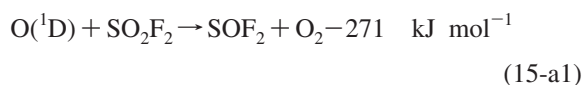
TABLE 4: Summary of SO₂F₂ Atmospheric Loss Processes and Calculated Atmospheric Lifetimes

SO ₂ F ₂ losses process	input		lifetime (years)
	value	ref	
ocean uptake		Mühle et al. (ref 1)	40 ± 13
aerosol uptake		Dillon et al. (ref 4)	> 100 ^a
OH + SO ₂ F ₂	< 1 × 10 ^{-16b}	this work	> 320 ^c
Cl + SO ₂ F ₂	< 5 × 10 ⁻¹⁷	this work	> 10 000 ^d
O ₃ + SO ₂ F ₂	1 × 10 ⁻²³	Dillon et al. (ref 4)	> 24 000 ^e
O(¹ D) + SO ₂ F ₂	5.8 × 10 ⁻¹¹	Dillon et al. (ref 4)	700 ^f
UV photolysis alone	σ(λ) and QY = 1	Pradayrol et al. (ref 5)	225 ^f
	σ(λ > 190 nm) and QY	this work	> 4700 ^{f,g}
	σ(λ < 190 nm) and QY = 1	Pradayrol et al. (ref 5)	
O(¹ D) + UV photolysis	k ₁₅ = 5.8 × 10 ⁻¹¹	Dillon et al. (ref 4)	630 ^f
	σ(λ > 190 nm) and QY	this work	
	σ(λ < 190 nm) and QY = 1	Pradayrol et al. (ref 5)	

^a Calculated assuming typical marine boundary layer aerosol loading conditions. ^b Rate coefficients are in units of cm³ molecule⁻¹ s⁻¹. ^c [OH] = 1 × 10⁶ molecule cm⁻³. ^d [Cl] = 1 × 10⁴ atom cm⁻³. ^e [O₃] = 1 × 10¹² molecule cm⁻³. ^f Lifetime calculated in this work using a two-dimensional atmospheric model. ^g The calculated photolysis occurs primarily, >95%, from Lyman-α (121.5 nm) radiation.

for the adduct formation pathways were all endothermic. This implies the absence of any product formation that would proceed through the formation of an adduct. The lack of even weakly bound adduct formation can possibly be explained by the high electrophilicity of sulfur, +6 oxidation state in SO₂F₂. OH, Cl, and S are all highly electrophilic species, and thus, the lack of a center with high electron density limits the formation of adducts containing even weak S...O-H or S...Cl bonds. Hydrogen-bonded adducts were also found to be unstable as the high requirements for electron density inhibits OH from approaching the fluorine or oxygen atoms in SO₂F₂.

The thermochemical parameters obtained in this work, Table 2, can also be used to evaluate possible reactive channels in reaction 15a



where the heats of reaction, Δ_rH(296 K), given are calculated using data from Table 2, and heats of formation are from Sander et al.⁷ Dillon et al.⁴ reported that ~45% of O(¹D) loss in the interaction with SO₂F₂ leads to chemical reaction, i.e., loss of SO₂F₂. There are several exothermic channels available in reaction 15a including O-atom abstraction, 15-a1, the formation of stable molecular products, 15-a2, and atom exchange, 15-a3. In the experiments performed in the present study, infrared absorption of reaction mixtures, we were not able to identify the products in reaction 15a.

In summary, our theoretical calculations clearly show that all possible direct abstraction channels in the reactions of Cl and OH with SO₂F₂ are highly endothermic and, therefore, unlikely to occur with significant rate coefficients under atmospheric conditions. In addition, the exchange of OH with an F atom in SO₂F₂ was calculated to be ~58 kJ mol⁻¹

endothermic. Our calculations also investigated the possibility of Cl and OH + SO₂F₂ adduct formation. However, no stable intermediate complexes (adducts) were found. This result implies that adduct formation is not an efficient processes for the removal of SO₂F₂ from the atmosphere. The only exothermic channel found was for the OH + SO₂F₂ → HF + SO₃F reaction, Δ_rH(298.15 K) ≈ -26 kJ mol⁻¹. This reaction, however, would most likely need to proceed through the formation of an unstable (HO...SO₂F₂) adduct and therefore be highly unlikely. In addition, there was no evidence for the formation of HF in our laboratory experiments. The theoretical calculations support our experimental observations and the reported upper limits for k₁ (< 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹) and k₄ (< 5 × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹).

Atmospheric Implications

Atmospheric Lifetime. On the basis of our laboratory studies and the analysis of SO₂F₂ field observations,¹ it is clear that SO₂F₂ is a long-lived atmospheric trace species. A summary of the SO₂F₂ loss processes and associated atmospheric lifetimes is given in Table 4.

In this work, we determined an upper limit for the rate coefficient for reaction 1, k₁(298 K) < 1 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹. This value is in agreement with the upper limit of 1 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ recently reported by Dillon et al.,⁴ but the uncertainties in this parameter have been considerably reduced by the results presented in this work. The tropospheric lifetime of SO₂F₂, with respect to its reaction with OH, τ_{OH}, is > 300 years for an OH radical concentration of 10⁶ molecule cm⁻³, which is a representative average tropospheric concentration.¹⁸ For the reaction of SO₂F₂ with Cl atoms, we determined an upper limit for the rate coefficient, k₄(298 K) < 5 × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹. The atmospheric lifetime of SO₂F₂ with respect to loss by Cl atom reaction, τ_{Cl}, is > 10 000 years for an tropospheric Cl atom concentration of 10⁴ cm⁻³, which is currently thought to be representative of the Cl atom concentration in the free troposphere.¹⁹ We should note that the tropospheric Cl atom concentration is poorly known at present and is likely dependent on time and location. Therefore, the τ_{Cl} value given here should be considered as only an approximation. In any case, however, the gas-phase Cl atom reaction likely represents a negligible atmospheric loss process for SO₂F₂.

Atmospheric loss via reaction with O(¹D) and by UV photolysis are primarily stratospheric loss processes for SO₂F₂. Stratospheric loss processes alone lead to long atmospheric

TABLE 5: Infrared Absorption Band Strengths for SO₂F₂ at 296 K

integration range (cm ⁻¹)	band strength (10 ⁻¹⁷ cm ² molecule ⁻¹ cm ⁻¹)	
	Dillon et al. (ref 4) ^a	this work ^b
500.9–592.5	1.4	1.34 ± 0.05
800.8–927.6	5.7	5.84 ± 0.02
1211.1–1321.5	2.5	2.61 ± 0.01
1448.8–1542.3	4.0	4.17 ± 0.01

^a The 2σ uncertainties are reported to be <10%. ^b The quoted uncertainties are obtained from the 2σ precision of the slope of the linear least-squares analysis of the measured integrated absorption versus SO₂F₂ concentration.

lifetimes, at least decades, due to the slow turnover rate of the atmosphere through the stratosphere. The NOCAR two-dimensional model²⁰ was used to compute the stratospheric lifetime of SO₂F₂, which is estimated to be 630 years. This loss is dominated by reaction with O(¹D). Therefore, reaction with O(¹D) and UV photolysis are minor atmospheric loss processes for SO₂F₂.

In conclusion, all gas-phase loss processes for SO₂F₂ studied to date are slow and lead to long atmospheric lifetimes for SO₂F₂. The most likely SO₂F₂ removal process is via ocean uptake as recently pointed out by Mühle et al.¹ Mühle et al. reported a SO₂F₂ globally averaged lifetime of 36 ± 11 years and a lifetime with respect to uptake by the ocean of 40 ± 13 years. Mühle et al. obtained these lifetimes using an inversion model that included air–sea exchange with the oceanic mixed layer combined with hydrolysis rates calculated using the parameters given by Cady and Misra.²¹ Note that an ocean uptake lifetime of 40 years is significantly shorter than the value recently reported by Dillon et al.⁴ Dillon et al. did not account for air–sea exchange in their simple uptake calculation, and this primarily accounts for the discrepancies in the reported ocean uptake lifetimes; see Mühle et al.¹ for a detailed discussion. Gas-phase removal processes for SO₂F₂ would therefore not exceed 10% of the loss due to ocean uptake and may be much smaller.

Global Warming Potential. The infrared absorption spectrum of SO₂F₂, Figure 5, was measured as part of this work. The peak cross sections of the Q-branches were found to be dependent on the resolution of the measurement with an increase in peak cross section observed at higher resolution. The SO₂F₂ band strengths are given in Table 5 and were found to be independent of the resolution and total pressure of the measurement. The SO₂F₂ infrared spectrum has several strong vibrational bands that fall within the atmospheric window and make SO₂F₂ an efficient atmospheric greenhouse gas. The present results are in good agreement with those from previous studies and are appropriate for atmospheric model calculations.^{4,22,23}

The GWP of a gas is a measure of the time-integrated radiative forcing to the climate system of a pulse of the gas relative to a baseline (usually taken to be CO₂). This allows the climatic impact of the emission of one gas relative to another to be quantified.²⁴ We computed the radiative efficiency of SO₂F₂ using an accurate line-by-line (LBL) radiative transfer code.²⁵ For a comparison study of this radiative transfer code versus others see Forster et al.²⁶ The LBL code uses the absorption spectra of SO₂F₂ measured in this work, along with the line parameters for the other gases taken from the HITRAN-2000 database. A constant profile (both vertically and meridionally) of SO₂F₂ is assumed in the calculation as is commonly done for GWP calculations. For gases reasonably well mixed

in the troposphere this usually amounts to not more than a 10% error in the radiative forcing.²⁷ The radiative efficiency for SO₂F₂ calculated using the spectra shown in Figure 2 is 0.222 W m⁻² ppb⁻¹. The GWP for SO₂F₂ is 7642, 4780, and 1540 for the 20, 100, and 500 year time horizons, for an SO₂F₂ atmospheric lifetime of 36 years. This GWP calculation uses the same integrated radiative forcing of CO₂ used in WMO 2007 and therefore can be compared with the GWPs reported there. SO₂F₂ is an efficient greenhouse gas, its GWP is similar to those of chlorofluorocarbons (CFCs),²⁴ and it could have a significant climatic impact if present in the atmosphere in sufficient abundance.

Conclusions

SO₂F₂ is a long-lived trace species that is currently present in the atmosphere at levels of ~1.5 ppt. The impact of SO₂F₂ on the environment and climate is dependent on its atmospheric lifetime. In this study, we have established upper limits for the gas-phase reaction of SO₂F₂ with OH radicals and Cl atoms. UV absorption cross section and photodissociation quantum yield measurements also established that UV photolysis is a negligible atmospheric loss process for SO₂F₂. The stratospheric lifetime of SO₂F₂ was calculated to be 630 years using literature values for the O(¹D) + SO₂F₂ rate coefficient⁴ and SO₂F₂ UV absorption cross sections⁵ combined with the UV cross section data and quantum yields measured in this work.

Theoretical quantum calculations were used to evaluate the thermochemistry and possible reaction channels for the OH and Cl atom reactions with SO₂F₂. The calculated thermochemistry for the OH and Cl reactions with SO₂F₂ establishes that the most likely bimolecular reaction channels are highly endothermic. In addition, the formation of stable OH or Cl adducts with SO₂F₂ were also found to be unlikely. The results from our theoretical calculations are consistent with the experimental evidence for the low chemical reactivity of SO₂F₂.

The atmospheric lifetime of SO₂F₂ is at present relatively uncertain with the best available estimate being 36 ± 11 years based on a model calculation that includes results from the present study and finds ocean uptake to be the primary atmospheric loss process.¹ On the basis of this globally averaged SO₂F₂ atmospheric lifetime and the infrared cross sections measured in this work, the GWP of SO₂F₂, on a 100 year time horizon, was calculated to be 4780. Further atmospheric monitoring of this recently discovered trace gas and its global distribution would most likely enable improved estimates of the lifetime to be made in the future. However, it is clear from the information currently available that the GWP for SO₂F₂ is significant although the uncertainty, ±30%, is large. A shorter (longer) SO₂F₂ lifetime than used in our present calculation will result in a smaller (larger) GWP for SO₂F₂. The radiative forcing of SO₂F₂ is currently small, 3.3 × 10⁻⁴ mW m⁻², but requires consideration in the future use of SO₂F₂.

Acknowledgment. The work at NOAA was supported in part by NOAA's Climate and Global Change Program. We thank Dr. Yannis G. Lazarou for useful discussions regarding the theoretical calculations.

Supporting Information Available: Infrared absorption cross section data of SO₂F₂ and optimized calculated geometry and vibrational frequencies, performed at the MP2/6-31++G(d',p') level of theory, for the species in Table 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Mühle, J.; Huang, J.; Weiss, R. F.; Prinn, R. G.; Miller, B. R.; Salameh, P. K.; Harth, C. M.; Fraser, P. J.; Porter, L. W.; Grealley, B. R.; O'Doherty, S.; Simonds, P. G. *J. Geophys. Res.*, submitted for publication, 2008.
- (2) Sulfuryl fluoride (Vikane) risk characterization document, environmental fate; California Environmental Protection Agency, 2006. <http://www.cdpr.ca.gov>.
- (3) Assessment report: Sulfuryl fluoride, toxicology and chemical substances; European Chemicals Bureau, 2006. <http://ecb.jrc.it>.
- (4) Dillon, T. J.; Horowitz, A.; Crowley, J. N. *Atmos. Chem. Phys.* **2008**, *8*, 1547.
- (5) Pradayrol, C.; Casanovas, A. M.; Deharo, I.; Geuelfucci, J. P.; Casanovas, J. *J. Phys. Chem. A* **1996**, *100*, 603.
- (6) Gierczak, T.; Burkholder, J. B.; Bauerle, S.; Ravishankara, A. R. *Chem. Phys. Lett.* **1998**, *231*, 229.
- (7) Sander, S. P.; Friedl, R. R.; Golden, D. M.; Kurylo, M. J.; Moortgat, G. K.; Keller-Rudek, H.; Wine, P. H.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J.; Finlayson-Pitts, B. J.; Huie, R. E.; Orkin, V. L. Chemical kinetics and photochemical data for use in atmospheric studies; JPL Publication 06-2; Jet Propulsion Laboratory: Pasadena, CA, 2006; Vol. Evaluation Number 15.
- (8) Hsu, K.-J.; DeMore, W. B. *J. Phys. Chem.* **1995**, *99*, 1235.
- (9) Talukdar, R.; Mellouki, A.; Gierczak, T.; Burkholder, J. B.; McKeen, S. A.; Ravishankara, A. R. *J. Phys. Chem.* **1991**, *95*, 5815.
- (10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J. J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision B.02; Gaussian Inc.: Pittsburgh, PA, 2003.
- (11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Petersson, G. A.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Morokuma, K.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, revision A9; Gaussian Inc.: Pittsburgh, PA, 1998.
- (12) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.
- (13) Fast, P. L.; Sanchez, M. L.; Truhlar, D. G. *J. Chem. Phys.* **1999**, *111*, 2921.
- (14) Truhlar, D. G. *Chem. Phys. Lett.* **1998**, *294*, 45.
- (15) Wilson, A. K.; Dunning, T. H., Jr. *J. Phys. Chem. A* **2004**, *108*, 3129.
- (16) Lazarou, Y. G.; Papadimitriou, V. C.; Prosmittis, A. V.; Papagianakopoulos, P. *J. Phys. Chem. A* **2002**, *106*, 11502.
- (17) Grant, D. J.; Matus, M. H.; Switzer, J. R.; Dixon, D. A.; Francisco, J. S.; Christe, K. O. *J. Phys. Chem. A* **2008**, *112*, 3145; doi: 10.1021/jp710373e S1089-5639(71)00373-6.
- (18) Prinn, R. G.; Huang, J.; Weiss, R. F.; Cunnold, D. M.; Fraser, P. J.; Simmonds, P. G.; McCulloch, A.; Harth, C.; Salameh, P.; O'Doherty, S.; Wang, R. H. J.; Porter, L.; Miller, B. R. *Science* **2001**, *292*, 1882.
- (19) Platt, U.; Allen, W.; Lowe, D. *Atmos. Chem. Phys.* **2004**, *4*, 2283.
- (20) Portmann, R. W.; Brown, S. S.; Gierczak, T.; Talukdar, R. K.; Burkholder, J. B.; Ravishankara, A. R. *Geophys. Res. Lett.* **1999**, *26*, 2387.
- (21) Cady, G. H.; Misra, S. *Inorg. Chem.* **1974**, *13*, 837.
- (22) Hunt, G. R.; Wilson, M. K. *Spectrochim. Acta* **1960**, *16*, 570.
- (23) Perkins, W. D.; Wilson, M. K. *J. Chem. Phys.* **1952**, *20*, 1791.
- (24) Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project; WMO (World Meteorological Organization): Geneva, Switzerland, 2007.
- (25) Portmann, R. W.; Solomon, S.; Fishman, J.; Olson, J. R.; Kiehl, J. T.; Briegleb, B. *J. Geophys. Res.* **1997**, *102*, 9409.
- (26) Forster, P. M. de F.; Burkholder, J. B.; Clerbaux, C.; Coheur, P. F.; Dutta, M.; Gohar, L. K.; Hurley, M. D.; Myhre, G.; Portmann, R. W.; Shine, K. P.; Wallington, T. J.; Wuebbles, D. *J. Quant. Spectrosc. Radiat. Transfer* **2005**, *93*, 447.
- (27) Pinnock, S.; Hurley, M. D.; Shine, K. P.; Wallington, T. J.; Smyth, T. J. *J. Geophys. Res.* **1995**, *100*, 23.
- (28) Chase, M. W. NIST-JANAF Thermochemical Tables, 4th ed. *J. Phys. Chem. Ref. Data, Monogr.* **1998**, *9*, 1.
- (29) NIST Chemistry WebBook, NIST Standard Reference Database; Vol. 69. <http://webbook.nist.gov/chemistry>.

JP806368U