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# The atmospheric chemistry of sulphuryl fluoride, SO<sub>2</sub>F<sub>2</sub>

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**Abstract.** The atmospheric chemistry of sulphuryl fluoride, SO<sub>2</sub>F<sub>2</sub>, was investigated in a series of laboratory studies. A competitive rate method, using pulsed laser photolysis (PLP) to generate O(<sup>1</sup>D) coupled to detection of OH by laser induced fluorescence (LIF), was used to determine the overall rate coefficient for the reaction O(<sup>1</sup>D)+SO<sub>2</sub>F<sub>2</sub>→products (R1) of  $k_1$  (220–300 K) =  $(1.3 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

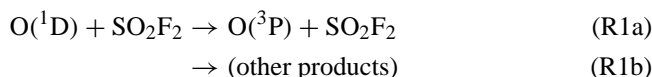
Monitoring the O(<sup>3</sup>P) product (R1a) enabled the contribution ( $\alpha$ ) of the physical quenching process (in which SO<sub>2</sub>F<sub>2</sub> is not consumed) to be determined as  $\alpha$  (225–296 K) =  $(0.55 \pm 0.04)$ . Separate, relative rate measurements at 298 K provided a rate coefficient for reactive loss of O(<sup>1</sup>D),  $k_{1b}$ , of  $(5.8 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in good agreement with the value calculated from  $(1-\alpha) \times k_1 = (5.9 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Upper limits for the rate coefficients for reaction of SO<sub>2</sub>F<sub>2</sub> with OH (R2, using PLP-LIF), and with O<sub>3</sub> (R3, static reactor) were determined as  $k_2$  (294 K)  $< 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_3$  (294 K)  $< 1 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . In experiments using the wetted-wall flow tube technique, no loss of SO<sub>2</sub>F<sub>2</sub> onto aqueous surfaces was observed, allowing an upper limit for the uptake coefficient of  $\gamma$  (pH 2–12)  $< 1 \times 10^{-7}$  to be determined. These results indicate that SO<sub>2</sub>F<sub>2</sub> has no significant loss processes in the troposphere, and a very long stratospheric lifetime. Integrated band intensities for SO<sub>2</sub>F<sub>2</sub> infrared absorption features between 6 and 19  $\mu\text{m}$  were obtained, and indicate a significant global warming potential for this molecule. In the course of this work, ambient temperature rate coefficients for the reactions O(<sup>1</sup>D) with several important atmospheric species were determined. The results (in units of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ),  $k_{(\text{O}^1\text{D} + \text{N}_2)} = (0.33 \pm 0.06)$ ;  $k_{(\text{O}^1\text{D} + \text{N}_2\text{O})} = (1.47 \pm 0.2)$  and  $k_{(\text{O}^1\text{D} + \text{H}_2\text{O})} = (1.94 \pm 0.5)$  were in good agreement with other recent determinations.

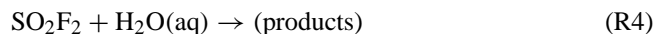
## 1 Introduction

Sulphuryl fluoride, SO<sub>2</sub>F<sub>2</sub>, (Vikane<sup>TM</sup>, Zythor<sup>TM</sup>, ProFume<sup>TM</sup>) is a widely used fumigant of timber, buildings, construction materials and vehicles. 30 years have passed since SO<sub>2</sub>F<sub>2</sub> was first mentioned in the context of a potential influence on stratospheric sulphur chemistry (Crutzen, 1976) and in this period the use of SO<sub>2</sub>F<sub>2</sub> has been extended to the food processing and agriculture industries as a replacement for CH<sub>3</sub>Br (banned under the Montreal protocol). The main consumer of SO<sub>2</sub>F<sub>2</sub> is the US state of California where annual usage has exceeded 10<sup>6</sup> kg since 1999 (Kollman, 2006). Indeed, SO<sub>2</sub>F<sub>2</sub> has recently been detected for the first time in ambient air samples (Mühle et al., 2006). These first ambient measurements of SO<sub>2</sub>F<sub>2</sub> provided the motivation for us to undertake a series of laboratory investigations into the kinetics of reactions of SO<sub>2</sub>F<sub>2</sub> with atmospheric oxidants and surfaces, for which no data existed. The UV absorption spectrum of SO<sub>2</sub>F<sub>2</sub> has been measured (Pradayrol et al., 1996) and the results demonstrate that photolysis is an insignificant loss process in the troposphere. Cady and Misra (1974) have measured hydrolysis rates for SO<sub>2</sub>F<sub>2</sub> in aqueous solutions. Their results indicate that hydrolysis is slow in acidic or neutral conditions, but may be an efficient atmospheric loss process in basic conditions (i.e. at the ocean surface). There are no published data regarding potential gas-phase atmospheric loss processes for SO<sub>2</sub>F<sub>2</sub>, or heterogeneous uptake to surfaces. Nonetheless, an upper-limit to the atmospheric lifetime of SO<sub>2</sub>F<sub>2</sub> of  $\tau \leq 4.5$  years has been suggested (European Union Report, 2005). In the present study, a variety of laboratory techniques were used to measure rate coefficients,  $k$ , for the gas-phase (R1–R3) of SO<sub>2</sub>F<sub>2</sub> with the atmospheric oxidants O(<sup>1</sup>D), OH, and O<sub>3</sub>, and the rate of heterogeneous uptake of SO<sub>2</sub>F<sub>2</sub> to aqueous surfaces (R4):



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Note that SO<sub>2</sub>F<sub>2</sub> is consumed in all processes except for (R1a). The kinetic data obtained in this work is used to estimate the lifetime of SO<sub>2</sub>F<sub>2</sub> in the atmosphere and thus its impact on various aspects of atmospheric science.

## 2 Experimental

The experiments were conducted using a variety of laboratory techniques and equipment. The gas phase experiments utilised both real time techniques (pulsed laser photolysis coupled to laser induced fluorescence (PLP-LIF) or resonance fluorescence (PLP-RF)), a relative rate technique with Fourier transform infrared spectroscopy (RR-FTIR) and a simple static mixing approach with UV analysis. A potential heterogeneous loss process (uptake of SO<sub>2</sub>F<sub>2</sub> to aqueous surfaces) was investigated using the wetted-wall flow tube technique (WWFT). These are described in turn below.

### 2.1 PLP-LIF/RF

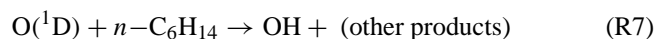
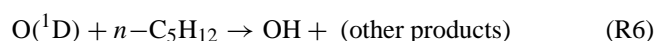
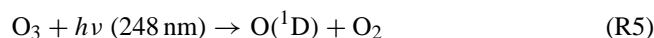
The PLP-LIF and PLP-RF techniques have been used in this laboratory to study reactions of O(<sup>1</sup>D) (Dillon et al., 2007), O(<sup>3</sup>P) (Teruel et al., 2004), IO (Dillon et al., 2006) and OH (Wollenhaupt et al., 2000; Karunanandan et al., 2007). The experimental set-up has been described in detail previously (see for example Wollenhaupt et al. (2000), which includes a schematic diagram of the apparatus) and is outlined only briefly here. Experiments were conducted in a 500 cm<sup>3</sup> quartz reactor, the temperature of which was regulated by circulating a cryogenic fluid through the outer jacket, and monitored with a J-Type thermocouple. The reactor pressure was monitored with a capacitance manometer. Gas flow rates of 300–2500 cm<sup>3</sup> (STP) min<sup>-1</sup> ensured that a fresh gas sample was available for photolysis at each laser pulse. Chemistry was initiated by an excimer laser (Lambda Physik) operating at 248 nm (KrF).

Fluorescence from OH was detected by a photomultiplier tube (PMT) shielded by 309 nm (interference) and BG 26 (glass cut-off) filters. Excitation of the A<sup>2</sup>Σ (v=1)←X<sup>2</sup>Π (v=0), Q<sub>11</sub> transition of OH at 281.997 nm was achieved using the frequency doubled emission from a Nd-YAG (Quantel) pumped dye laser (Lambda Physik/rhodamine 6G).

Resonance emission used to detect O(<sup>3</sup>P) at ~131 nm was generated by microwave discharge (80 W) through 99.999% He at ~3 Torr, and passed through a set of baffles and a CaF<sub>2</sub> window (to remove radiation from excited H or N atoms) before entering the cell perpendicular to both the pulsed emission from the excimer photolysis laser and the VUV photomultiplier detection axis. Fluorescence was gathered by

a *f*=1.4 telescopic arrangement and focussed onto the active area of the VUV photomultiplier. Time dependent O(<sup>3</sup>P) signals were amplified, digitised and counted by a multichannel scaler usually operating at a resolution of 5 μs per channel, and averaging 1000 decay profiles.

In the experiments designed to study (R1), O(<sup>1</sup>D) was generated by the 248 nm photolysis of O<sub>3</sub> (R5). O(<sup>1</sup>D) was not detected directly, but converted to OH by reaction with a straight-chain alkane *n*-C<sub>5</sub>H<sub>12</sub> (R6) or *n*-C<sub>6</sub>H<sub>14</sub> (R7), and in a few experiments H<sub>2</sub>O (R8). All H atom donors were present at ≈2×10<sup>13</sup> molecule cm<sup>-3</sup>.



The 248 nm photolysis of H<sub>2</sub>O<sub>2</sub> (R9) was used to generate OH in the experiments to determine *k*<sub>2</sub> (294 K).



Typically, laser fluences of 12 mJ cm<sup>-2</sup> per pulse were used to generate [O(<sup>1</sup>D)] or [OH] of ≈2×10<sup>11</sup> molecule cm<sup>-3</sup>. Concentrations of the radical precursors O<sub>3</sub> (<2×10<sup>12</sup> molecule cm<sup>-3</sup>) and H<sub>2</sub>O<sub>2</sub> (~3×10<sup>13</sup> molecule cm<sup>-3</sup>) were determined optically by monitoring the attenuation of light (185 or 254 nm) from a Hg lamp transmitting a 43.8 cm absorption cell situated downstream of the reactor. Due to the small absorption cross-sections of SO<sub>2</sub>F<sub>2</sub> at suitable wavelengths, optical measurements of [SO<sub>2</sub>F<sub>2</sub>] were not possible. Concentrations of the excess reagents SO<sub>2</sub>F<sub>2</sub>, *n*-C<sub>5</sub>H<sub>12</sub>, *n*-C<sub>6</sub>H<sub>14</sub>, N<sub>2</sub>, N<sub>2</sub>O, and H<sub>2</sub>O were therefore determined by manometric methods to an estimated (minimum) accuracy of ±15% (±30% for H<sub>2</sub>O) based upon uncertainties in (calibrated) mass flow rates, *T* and *P*.

### 2.2 RR-FTIR

Relative rate experiments were carried out in a cylindrical quartz reactor cell of volume 45 l, fitted with internal multipass optics to give an effective optical path-length of 28 m (Raber and Moortgat, 2000). Photolysis was provided by 9 UV lamps (Philips, TUV 40 W) evenly distributed around the outside of the reactor and flushed with compressed air to prevent warming of the ambient air directly in contact with the reactor surface. Static mixtures of O<sub>3</sub>, SO<sub>2</sub>F<sub>2</sub> (or SF<sub>6</sub>) and N<sub>2</sub>O were prepared in the cell and approximate concentrations determined manometrically. The relative rate experiments were conducted at a total pressure of ≈200 Torr (He) and the gas mixture was left to stand for >20 min to ensure mixing and thermalization. FTIR spectra (450–2000 cm<sup>-1</sup>, 0.5 cm<sup>-1</sup> resolution, typically 256 co-added scans) were

recorded prior to, and at regular intervals after UV irradiation using a Bomem DA-008 spectrometer with a MCT detector. The variation of the concentration of N<sub>2</sub>O and SO<sub>2</sub>F<sub>2</sub> with irradiation time was determined by repeating the alternating irradiation and spectra acquisition steps, and by preparing new mixtures which were then photolysed for different exposure times. The exposure times were always shorter than 300 s and no change in the cell temperature was observed over this period. The relative change in the concentration of the two reactants was derived by fitting the observed spectra to the initial reference using absorption features between 578 and 603 cm<sup>-1</sup> for N<sub>2</sub>O and between 1438 and 1566 cm<sup>-1</sup> for SO<sub>2</sub>F<sub>2</sub>.

The same spectrometer was used to measure quantitative IR spectra of SO<sub>2</sub>F<sub>2</sub>, but using a 50 cm<sup>3</sup> volume, single pass glass optical absorption cell (optical path-length 15 cm) equipped with Si optical windows.

### 2.3 WWFT

The uptake of SO<sub>2</sub>F<sub>2</sub> to aqueous surfaces was investigated using the wetted-wall flow tube technique. The apparatus used has been described in previous publications (Fickert et al., 1998, 1999) and only salient features are given here. SO<sub>2</sub>F<sub>2</sub> was introduced via a movable injector into a laminar flow tube reactor (internal radius = 7.75 mm) operated at a pressure of about 250–290 Torr and at *T* = 277 K. The bulk gas was He, flowed at ≈ 300 sccm, resulting in a Reynolds number of 2.5, and a linear velocity of ≈ 4 cm s<sup>-1</sup>. Flow rates were monitored by freshly calibrated mass flow controllers and are expected to be accurate to a few percent. The pressure was monitored with a 1000 Torr capacitance manometer. The inner wall of the flow tube was coated with a slowly flowing aqueous film which was prepared from bulk solutions with pH adjusted to 2, 4.5 or 12. The thickness and speed of the liquid film were calculated as described previously (Fickert et al., 1998) to be ≈ 100 μm and 3–4 cm s<sup>-1</sup>, respectively.

The contact time between SO<sub>2</sub>F<sub>2</sub> and the aqueous film was varied by translating the moveable injector using a computer controlled linear drive to accurately maintain axial alignment between the injector and the aqueous film. Using the relatively slow gas flows indicated above, contact times of up to about 8 s (see Fig. 8) were achieved. SO<sub>2</sub>F<sub>2</sub> exiting the flow tube at a concentration of approximately 5 × 10<sup>13</sup> molecule cm<sup>-3</sup> was detected by electron bombardment positive ion mass spectrometry (MS) at *m/z* = 83. This was the strongest ion signal when the MS was operated with an electron energy of 70 eV.

### 2.4 Chemicals

He (Westfalen, 99.999%), N<sub>2</sub> (Messer 99.999), O<sub>2</sub> (Messer, 99.998), Synthetic Air (Messer, 20.5 % O<sub>2</sub> in N<sub>2</sub>), N<sub>2</sub>O (Messer, 99.5%), SO<sub>2</sub>F<sub>2</sub> (ABCR, 99%) and SF<sub>6</sub> (Messer

1.99% in He 99.9%) were used without further purification. O<sub>3</sub> was prepared using a commercial ozoniser (Ozomat), trapped on silica gel at *T* = 195 K, and flushed with He to remove O<sub>2</sub> before dilution (≈ 10<sup>-4</sup>) in He and storage in blackened glass bulbs. *n*-C<sub>5</sub>H<sub>12</sub> (Aldrich “wasserfrei” 99+ %) and *n*-C<sub>6</sub>H<sub>14</sub> (neoLab > 95%) were subject to repeated freeze-pump-thaw cycles at 77 K prior to dilution and storage. Aqueous solutions for the WWFT experiments were prepared using “milli-Q” de-ionised water, with the pH adjusted by addition of H<sub>2</sub>SO<sub>4</sub> or NaOH.

## 3 Results

The determination of kinetic parameters for (R1–R4) are detailed in Sects. 3.1–3.3 below. As this was the first comprehensive study of the atmospheric chemistry of SO<sub>2</sub>F<sub>2</sub>, comparison with literature data was rarely possible. Where possible however, the experimental methods used here were validated by the concurrent study of well-characterised processes, such as the reactions of O(<sup>1</sup>D) with the important atmospheric species N<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O and SF<sub>6</sub>. The infrared absorption spectrum of SO<sub>2</sub>F<sub>2</sub> is described in Sect. 3.4 and the uptake of SO<sub>2</sub>F<sub>2</sub> to aqueous solutions in Sect. 3.5. The atmospheric implications of the results obtained are discussed in Sect. 3.6.

### 3.1 Kinetics and products of O(<sup>1</sup>D) + SO<sub>2</sub>F<sub>2</sub> (R1)

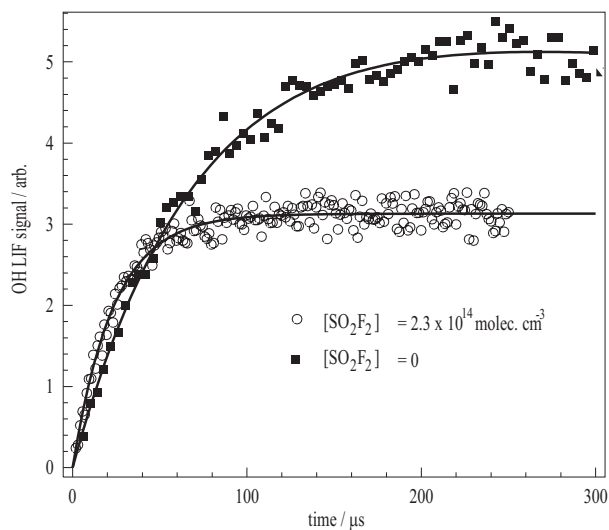
#### 3.1.1 Rate coefficients *k*<sub>1</sub> (220–300 K)

Absolute values for *k*<sub>1</sub>(*T*) were determined by a competitive rate method, similar to that employed by Blitz et al. (2004). This method relies on the fact that the kinetics of product formation are governed by the rate of decay of the precursor species. Specifically in this work, where the LIF detection of OH is used as a spectroscopic marker for O(<sup>1</sup>D):

$$\frac{d[\text{O}(\text{}^1\text{D})]}{dt} = \frac{-d[\text{OH}]}{dt} \quad (1)$$

PLP generation (R5) of O(<sup>1</sup>D) in the presence of *n*-C<sub>6</sub>H<sub>14</sub> facilitated rapid conversion (R7) of O(<sup>1</sup>D) to OH. Figure 1 displays an example of an OH LIF profile recorded at [O<sub>3</sub>] ≈ 1 × 10<sup>12</sup>, [*n*-C<sub>6</sub>H<sub>14</sub>] = 2.1 × 10<sup>13</sup> molecule cm<sup>-3</sup> and *P* = 42 Torr (1 Torr = 1.333 mBar) of He (bath gas) at *T* = 298 K. The open circles in Fig. 1 show an OH LIF profile, recorded upon addition of [SO<sub>2</sub>F<sub>2</sub>] = 2.3 × 10<sup>14</sup> molecule cm<sup>-3</sup> to the reaction mixture. The introduction of SO<sub>2</sub>F<sub>2</sub> results in the observation of a smaller OH signal, which is formed on a shorter timescale as SO<sub>2</sub>F<sub>2</sub> competes to destroy O(<sup>1</sup>D). Pseudo first-order conditions of both [*n*-C<sub>6</sub>H<sub>14</sub>] and [SO<sub>2</sub>F<sub>2</sub>] ≫ [O(<sup>1</sup>D)] and [OH] applied, and the data were therefore analysed with the appropriate kinetic expression (Eq. 2):

$$[\text{OH}]_t = A \times \{\exp(-Bt) - \exp(-Ct)\} \quad (2)$$



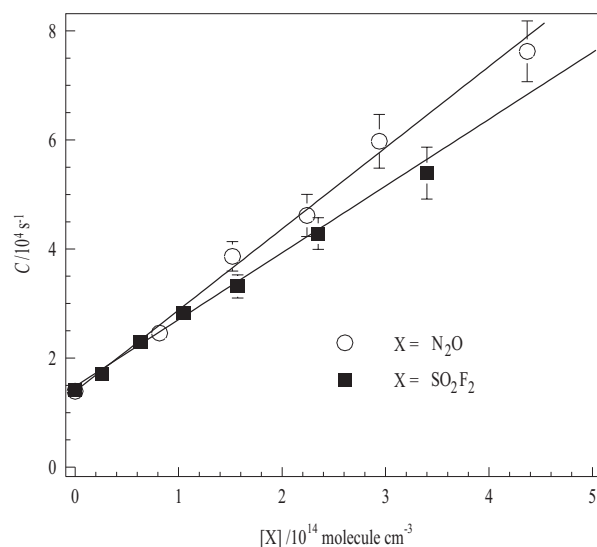
**Fig. 1.** OH LIF profiles recorded at two different [SO<sub>2</sub>F<sub>2</sub>] in determination of  $k_1$  (300 K). Experimental conditions were  $P = 42$  Torr,  $T = 300$  K,  $[O_3] = 1 \times 10^{12}$  and  $[n\text{-C}_6\text{H}_{14}] = 2.1 \times 10^{13}$  molecule cm<sup>-3</sup>. The solid lines are fits using expression (2) to obtain the kinetic parameter  $C$ .

where  $A$  is proportional to the initial [O(<sup>1</sup>D)],  $B$  is the approximate pseudo first-order rate coefficient for OH loss (dominated by slow transport out of the LIF volume), and the parameter of interest  $C$  is the 1st-order rate coefficient for OH formation (equivalent to O(<sup>1</sup>D) loss, see Eq. (1) above).

$$C = k_1[\text{SO}_2\text{F}_2] + k_7[n\text{-C}_6\text{H}_{14}] + k_{\text{loss},\text{O}(\text{1D})} \quad (3)$$

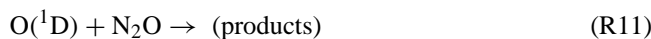
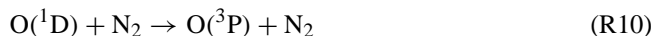
The parameter  $k_{\text{loss},\text{O}(\text{1D})}$  accounts for reaction of O(<sup>1</sup>D) with O<sub>3</sub>, bath-gas (He) and trace impurities therein. Experimentally determined values of  $C$  were obtained with a fixed  $n\text{-C}_6\text{H}_{14}$  concentration and various values of [SO<sub>2</sub>F<sub>2</sub>] so that that a plot of  $C$  versus associated [SO<sub>2</sub>F<sub>2</sub>] (Fig. 2, solid squares) has a gradient equivalent to  $k_1$  (298 K), and an intercept of  $k_7[n\text{-C}_6\text{H}_{14}] + k_{\text{loss},\text{O}(\text{1D})}$  (Eq. 3). An unweighted linear fit to the dataset displayed (solid line) yields  $k_1$  (298 K) =  $(1.39 \pm 0.1) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Experiments were repeated over the range of  $218 < T/\text{K} < 300$ , using both  $n\text{-C}_5\text{H}_{12}$  and  $n\text{-C}_6\text{H}_{14}$  to convert O(<sup>1</sup>D) to OH. Statistically similar values of  $k_1(T)$  were obtained (Table 1).

The kinetic analysis was validated in 3 ways. First, in the presence of SO<sub>2</sub>F<sub>2</sub>, OH profiles were recorded in which the photolysis laser energy was varied by a factor of 5. No systematic change in  $C$  was observed, indicating that secondary chemistry did not perturb the OH kinetics. Second, rate coefficients for the reactions of O(<sup>1</sup>D) with  $n\text{-C}_5\text{H}_{12}$  (R6) and  $n\text{-C}_6\text{H}_{14}$  (R7) were determined by recording OH profiles at different alkane concentrations in the absence of SO<sub>2</sub>F<sub>2</sub>. The plots of parameter  $C$  (obtained from fitting expression (2) to the data) versus  $[n\text{-C}_5\text{H}_{12}]$  or  $[n\text{-C}_6\text{H}_{14}]$  yielded  $k_6$  (298 K) =  $(5.4 \pm 0.4) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_7$



**Fig. 2.** Bimolecular plot of  $C$  vs. [SO<sub>2</sub>F<sub>2</sub>] used to determine  $k_1$  (300 K) =  $(1.22 \pm 0.06) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The intercept value of  $\sim 14000$  s<sup>-1</sup> is consistent with the use of  $[n\text{-C}_6\text{H}_{14}] = 2 \times 10^{13}$  molecule cm<sup>-3</sup> to convert O(<sup>1</sup>D) to OH (R7). The plot also shows the results of an experiment to determine  $k_{11}$  (296 K) =  $(1.45 \pm 0.08) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

(298 K) =  $(5.8 \pm 0.5) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in excellent agreement with the only previous absolute determinations (Dillon et al., 2007) and an evaluation of earlier relative rate determinations (Schofield, 1978). Third, the competitive rate method was employed to determine rate coefficients for the well-characterised (R10) and (R11):



The procedure was identical to that described above, and many experiments were carried out back-to-back with the determinations of  $k_1$ . The results, listed in Table 1 and illustrated in Fig. 2 for N<sub>2</sub>O, are  $k_{10}$  (298 K) =  $(0.33 \pm 0.06) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_{11}$  (298 K) =  $(1.45 \pm 0.2) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which agree (within combined uncertainties) with the evaluated literature (Sander et al., 2006; Atkinson et al., 2007) and other recent determinations (Blitz et al., 2004; Dunlea and Ravishankara, 2004b; Strekowski et al., 2004; Carl, 2005; Takahashi et al., 2005). The good agreement indicates that potential problems associated with formation of vibrationally excited OH radicals are insignificant and give confidence in the values of  $k_1$  obtained in this work.

In some additional experiments, H<sub>2</sub>O was used to convert O(<sup>1</sup>D) to OH (R8). The procedures detailed above were used to obtain  $k_8$  directly, and  $k_{10}$  (O(<sup>1</sup>D) + N<sub>2</sub>). The results are in satisfactory agreement with the literature. Some experiments

**Table 1.** Determination of rate coefficients for the reactions O(<sup>1</sup>D)+X→products.

X	T/K	H-donor	range of [X] <sup>a</sup>	k(T) <sup>b</sup>
SO <sub>2</sub> F <sub>2</sub>	300	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0–20.9	1.29±0.20
SO <sub>2</sub> F <sub>2</sub>	300	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0–20.9	1.25±0.20
SO <sub>2</sub> F <sub>2</sub>	300	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0–34.0	1.22±0.06
SO <sub>2</sub> F <sub>2</sub>	298	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0–25.5	1.39±0.12
SO <sub>2</sub> F <sub>2</sub>	297	<i>n</i> -C <sub>5</sub> H <sub>12</sub>	0–19.4	1.20±0.20
SO <sub>2</sub> F <sub>2</sub>	222	<i>n</i> -C <sub>5</sub> H <sub>12</sub>	0–27.0	1.47±0.08
SO <sub>2</sub> F <sub>2</sub>	218	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	2.4–40.5	1.39±0.10
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	297	<i>n</i> -C <sub>5</sub> H <sub>12</sub>	0–9.3	5.4±0.4
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	300	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0–10.4	5.8±0.5
N <sub>2</sub>	300	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0–172.0	0.35±0.02
N <sub>2</sub>	297	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0–212.0	0.33±0.02
N <sub>2</sub>	297	none <sup>c</sup>	0–277.0	0.30±0.04
N <sub>2</sub>	297	H <sub>2</sub> O	0–106.0	0.38±0.05
N <sub>2</sub>	297	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0–212.0	0.30±0.02
H <sub>2</sub> O	297	H <sub>2</sub> O	0–17.8	1.94±0.13
N <sub>2</sub> O	296	<i>n</i> -C <sub>5</sub> H <sub>12</sub>	0–37.1	1.45±0.08
N <sub>2</sub> O	296	<i>n</i> -C <sub>5</sub> H <sub>12</sub>	0–49.5	1.49±0.08

## Notes:

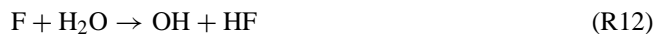
In all experiments, the total pressure was held close to 42 Torr and H atom donors were present at  $\approx 2 \times 10^{13}$  molecule cm<sup>-3</sup>.

<sup>a</sup> units of concentration = 10<sup>13</sup> molecule cm<sup>-3</sup>;

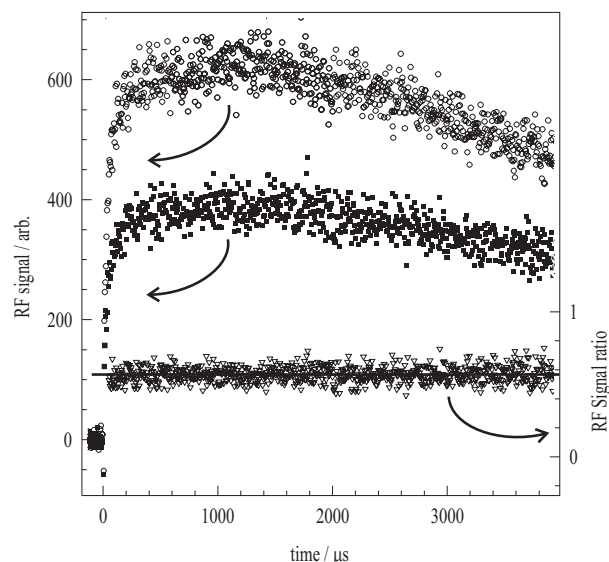
<sup>b</sup> units for k(T)=10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>;

<sup>c</sup> no H-atom donor was added to the reaction mixture, however OH was observed from reactions of O(<sup>1</sup>D) with impurities (e.g. H<sub>2</sub>O, H<sub>2</sub>) in the bath gas.

were also conducted with a O(<sup>1</sup>D)/H<sub>2</sub>O/SO<sub>2</sub>F<sub>2</sub> reaction system with the aim of a further, independent measurement of k<sub>1</sub>. However, the LIF profiles generated in the presence of SO<sub>2</sub>F<sub>2</sub> were characterised by the expected rapid OH formation due to O(<sup>1</sup>D) loss in (R1) and (R8), followed by a secondary slow OH formation process. The slow OH source was not evident in back-to-back experiments where SO<sub>2</sub>F<sub>2</sub> was absent or replaced by N<sub>2</sub>. A possible explanation for these observations is that a product of (R1), not produced in (R8) or (R10) may itself be an OH precursor. It appears likely that F-atoms, formed as a product of SO<sub>2</sub>F<sub>2</sub> destruction (R1b) by O(<sup>1</sup>D), are converted by H<sub>2</sub>O to OH in the well-characterised (R12):



Numerical simulation of these experiments using the evaluated literature value k<sub>12</sub> (298 K) = 1.4 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> demonstrated that (R12) could indeed account for the secondary OH observed in the presence of SO<sub>2</sub>F<sub>2</sub> if a yield of  $\approx 20\%$  F-atoms from (R1) was assumed. This result, implying that SO<sub>2</sub>F<sub>2</sub> is destroyed in (R1), is only semi-quantitative, and prompted experiments (see Sects. 3.1.2 and 3.1.3) to quantify the relative importance of reaction channels (R1a) and (R1b).



**Fig. 3.** O(<sup>3</sup>P) generated in O(<sup>1</sup>D)+SO<sub>2</sub>F<sub>2</sub>→products (R1) with [SO<sub>2</sub>F<sub>2</sub>]=1.4×10<sup>14</sup> molecule cm<sup>-3</sup> (middle trace). Also displayed is the O(<sup>3</sup>P) RF signal obtained in a back-to-back experiment in which O(<sup>1</sup>D) reacts (R10) with a kinetically similar [N<sub>2</sub>]=5.6×10<sup>14</sup> molecule cm<sup>-3</sup> (upper trace). As the yield of O(<sup>3</sup>P) in (R10) is known to be unity, the yield of O(<sup>3</sup>P) in (R1)=k<sub>1a</sub>/k<sub>1</sub>=(0.56±0.01) was calculated from the ratio of RF signal intensities (lower trace) plotted on the right axis.

Although there are no experimental data with which to compare our value for k<sub>1</sub>, we note that the result is consistent with the predicted value of (1.1±0.8)×10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> based on an ionisation potential/collision cross section relationship presented by Dillon et al. (2007).

### 3.1.2 O(<sup>3</sup>P) product yield

Figure 3 displays an example of an O(<sup>3</sup>P) RF profile (RF<sub>SO<sub>2</sub>F<sub>2</sub></sub>) obtained following photolysis of O<sub>3</sub> (R5) in the presence of [SO<sub>2</sub>F<sub>2</sub>]=1.4×10<sup>14</sup> molecule cm<sup>-3</sup> at P=42 Torr and T=296 K. The yield (k<sub>1a</sub>/k<sub>1</sub>) of O(<sup>3</sup>P) from (R1) was determined by using the reaction of O(<sup>1</sup>D) with N<sub>2</sub> (R10), for which the unity yield of O(<sup>3</sup>P) is well established, to calibrate the data. The SO<sub>2</sub>F<sub>2</sub> was replaced by a kinetically matched amount of N<sub>2</sub> (k<sub>1</sub>[SO<sub>2</sub>F<sub>2</sub>]=k<sub>10</sub>[N<sub>2</sub>]) and the RF signal (see Fig. 3 open circles) from (R10), RF<sub>N<sub>2</sub></sub> was then recorded. RF signals (RF<sub>0</sub>) were also obtained in the absence of SO<sub>2</sub>F<sub>2</sub> or N<sub>2</sub>, to quantify the background level of O(<sup>3</sup>P) produced directly from O<sub>3</sub> photolysis (Dunlea et al., 2004) and by reactions of O(<sup>1</sup>D) with impurities (N<sub>2</sub> or O<sub>2</sub> in the bath gas He). These 3 back-to-back datasets were used to generate RF<sub>ratio</sub>, the (corrected for background) ratio of RF signals according to expression (2):

$$\text{RF}_{\text{ratio}} = \frac{\text{RF}_{\text{SO}_2\text{F}_2} - \text{BG}}{\text{RF}_{\text{N}_2} - \text{BG}} \quad (4)$$

**Table 2.** Determination of the O(<sup>3</sup>P) product yield ( $k_{1a}/k_1$ ) in (R1).

T/K	[SO <sub>2</sub> F <sub>2</sub> ] <sup>a</sup>	[N <sub>2</sub> ] <sup>a</sup>	correction <sup>b</sup>	$k_{1a}/k_1$
296	7.6	30.8	15%	0.52±0.01
296	13.8	56.0	10%	0.57±0.01
296	4.6	19.0	20%	0.57±0.01
296	11.0	44.0	11%	0.55±0.01
296	6.0	25.0	16%	0.55±0.01
225	9.1	37.0	15%	0.58±0.01
225	16.3	53.0	10%	0.54±0.01
225	16.5	66.0	8%	0.55±0.02
225	13.2	45.0	12%	0.54±0.01

Notes:

<sup>a</sup> in units of 10<sup>13</sup> molecule cm<sup>-3</sup>.<sup>b</sup> Correction for “background” O(<sup>3</sup>P) according to Eq. (4), see text for details.

where

$$\text{BG}=\text{RF}_0 \times \frac{k_{\text{loss}_\text{O}(\text{1D})}}{k_1[\text{SO}_2\text{F}_2]}=\text{RF}_0 \times \frac{k_{\text{loss}_\text{O}(\text{1D})}}{k_{10}[\text{N}_2]}$$

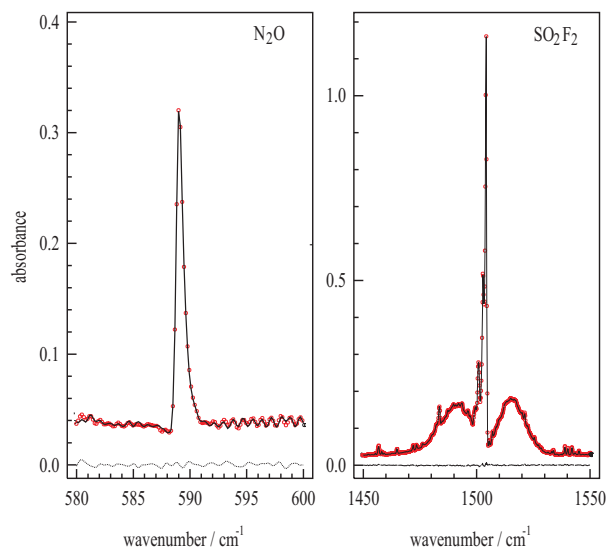
Figure 3 shows the resulting time-resolved RF<sub>ratio</sub>, which is equivalent to the product yield for O(<sup>3</sup>P) from (R1):  $k_{1a}/k_1=(0.56\pm 0.01)$ . The process was repeated for different kinetically matched amounts of SO<sub>2</sub>F<sub>2</sub> and N<sub>2</sub>, with the corrections for background O(<sup>3</sup>P) (never more than 20%) smaller for larger [SO<sub>2</sub>F<sub>2</sub>]. The results are displayed in Table 2, which shows a consistent value of  $k_{1a}/k_1=(0.55\pm 0.04)$  at around ambient temperature. Similar results were obtained at  $T=225$  K.

RF detection of O(<sup>3</sup>P) was found to be less suitable for the determination of the absolute rate coefficients,  $k_1(T)$ . As is evident from Fig. 3, the data close to  $t=0$ , where the fast (R1) occurs, is not particularly well resolved, and in some experiments was distorted by a strong radio-frequency signal from the excimer laser pulse.

### 3.1.3 Relative rate determinations of $k_{1b}$

Mixtures containing SO<sub>2</sub>F<sub>2</sub> and N<sub>2</sub>O (both at concentrations of 9–15×10<sup>14</sup> molecule cm<sup>-3</sup>) and O<sub>3</sub> in He bath gas were photolyzed for between 15 and 300 s to result in measurable changes (up to 15%) in the SO<sub>2</sub>F<sub>2</sub> and N<sub>2</sub>O concentrations. The fractional depletion of both species was limited by the concentration of O<sub>3</sub>, which was completely destroyed, resulting in the disappearance of its 1042 cm<sup>-1</sup> absorption feature. The initial O<sub>3</sub> concentration (this parameter is not needed in the kinetic analysis) could not be monitored as accessible absorption bands were optically black.

The intense absorption feature of SO<sub>2</sub>F<sub>2</sub> centred at 1504 cm<sup>-1</sup> was generally used for determination of the SO<sub>2</sub>F<sub>2</sub> depletion factor after photolysis. The depletion factor was obtained by least-squares fitting of the pre- and post-



**Fig. 4.** Raw FTIR spectral data for SO<sub>2</sub>F<sub>2</sub> and N<sub>2</sub>O in relative rate studies. The data points (circles) were determined after photolysis, the solid lines are scaled reference spectra (obtained before photolysis) with the scaling factor (depletion factor) obtained by least squares fitting. The broken lines are the fit residuals.

photolysis spectra in the 1438–1566 cm<sup>-1</sup> range. The relative change in N<sub>2</sub>O over the same period was obtained in a similar manner using the single absorption feature around 590 cm<sup>-1</sup>. Fitted N<sub>2</sub>O and SO<sub>2</sub>F<sub>2</sub> spectra, showing the spectral ranges used and the fit-residuals are given in Fig. 4. Use of the stronger N<sub>2</sub>O feature at ≈1285 cm<sup>-1</sup> was not possible due to overlap with a SO<sub>2</sub>F<sub>2</sub> absorption band. Owing to the use of several data points the statistical error (2σ) in determination of the relative changes in SO<sub>2</sub> or N<sub>2</sub>O concentration was ≈6×10<sup>-4</sup> and ≈5×10<sup>-3</sup>, respectively.

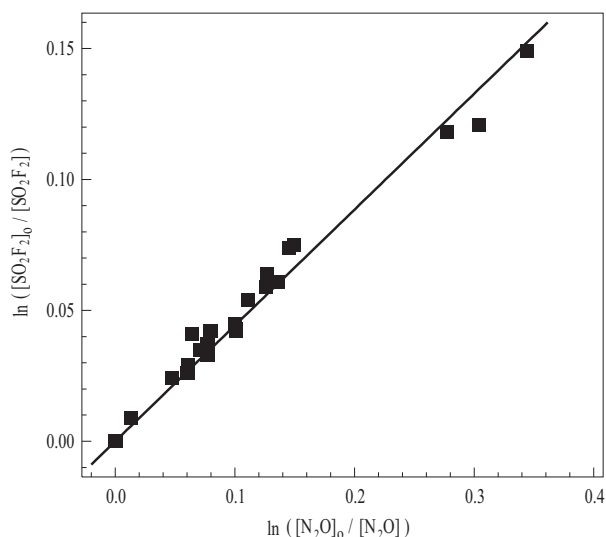
Use of parts (or all of) the triplet feature of SO<sub>2</sub>F<sub>2</sub> between 530 and 560 cm<sup>-1</sup> (see complete IR spectrum presented in Sect. 3.4) gave similar results but with reduced precision.

In the absence of O<sub>3</sub>, neither N<sub>2</sub>O nor SO<sub>2</sub>F<sub>2</sub> were measurably depleted by photolysis, nor by dark/wall losses. Additional support for the contention that both N<sub>2</sub>O and SO<sub>2</sub>F<sub>2</sub> were removed only by reaction with O(<sup>1</sup>D) and that mixing/segregation effects could be ruled out, was obtained by conducting experiments in which SO<sub>2</sub>F<sub>2</sub> was replaced by SF<sub>6</sub>. In this case, although N<sub>2</sub>O was depleted, SF<sub>6</sub>, a molecule with very low reactivity to O(<sup>1</sup>D) (Sander et al., 2006) was unchanged.

The relative changes in SO<sub>2</sub>F<sub>2</sub> and N<sub>2</sub>O concentrations were analysed using the standard relation

$$\ln\left(\frac{[\text{SO}_2\text{F}_2]_0}{[\text{SO}_2\text{F}_2]}\right) = \frac{k_1}{k_{11}} \cdot \ln\left(\frac{[\text{N}_2\text{O}]_0}{[\text{N}_2\text{O}]}\right) \quad (5)$$

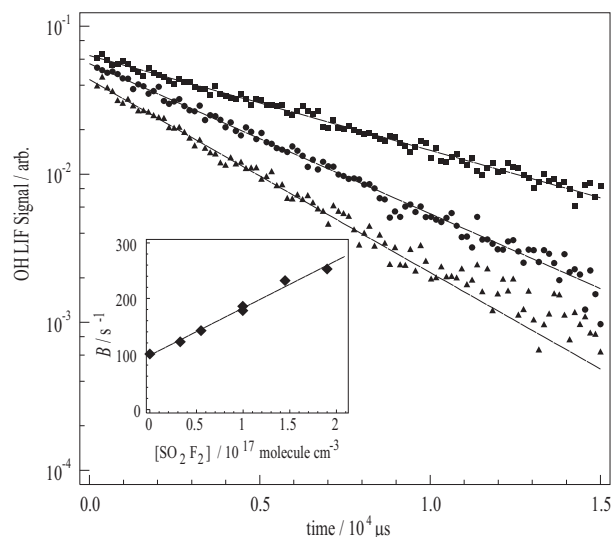
The complete data set is displayed in Fig. 5, in which the solid line is the least squares fit to the data as described



**Fig. 5.** Relative rate plot of depletion of N<sub>2</sub>O (reference compound) versus depletion of SO<sub>2</sub>F<sub>2</sub> to determine the ratio  $k_{1b}/k_{11}=(0.44\pm 0.01)$  from a linear fit to the data with the intercept forced through zero.

by Eq. (5). The slope of the fit line gives the rate constant ratio  $k_1/k_{11}=(0.411\pm 0.012)$ . Using a rate coefficient for reaction of N<sub>2</sub>O with O(<sup>1</sup>D) of  $1.4\times 10^{-10}$  molecule cm<sup>-3</sup>, from recent work (Dunlea and Ravishankara, 2004a; Carl, 2005; Takahashi et al., 2005) and from this study,  $k_1/k_{11}$  can be converted to an absolute rate coefficient;  $k_{1b}=(5.8\pm 0.01)\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Since in this system no evidence was found for interference from unwanted photolysis and/or dark reactions we estimate that our relative ratio is accurate within ~10% to which we add the error propagated from the reference reaction, also estimated at 10%. Accordingly, the present determination of  $k_{1b}$  is  $(5.8\pm 0.8)\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This result is in good agreement with the value calculated from the results obtained above of overall rate coefficient  $k_1=(1.3\pm 0.2)\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and product yield of O(<sup>3</sup>P)  $\alpha=0.55\pm 0.04$ , whereby  $k_{1b}=(1-\alpha)\times k_1=(5.9\pm 1.0)\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The infra-red spectra obtained following photolysis were inspected for formation of IR-active products including NO, SO<sub>2</sub>, FNO, FNO<sub>2</sub> and SOF<sub>2</sub>, none of which were observed. We have presented evidence (Sect. 3.1.1) that F atoms are formed in the reaction of O(<sup>1</sup>D) with SO<sub>2</sub>F<sub>2</sub>. The fate of F atoms in the relative rate studies would be reaction with O<sub>3</sub> to form FO, which, in the absence of a rapid reaction with O<sub>3</sub> (Atkinson et al., 2007) may undergo self reaction to reform F atoms, thus contributing to O<sub>3</sub> depletion but not to product formation. The identity (and fate) of the sulphur containing product remains unknown.



**Fig. 6.** Determination of  $k_2$  ( $T=294$  K) for reaction of OH+SO<sub>2</sub>F<sub>2</sub>→products. The three OH LIF profiles show data collected at: [SO<sub>2</sub>F<sub>2</sub>]/molecule cm<sup>-3</sup>=0 (upper trace),  $9.96\times 10^{16}$  (middle trace) and  $19.0\times 10^{16}$  (lower trace). The straight lines depict fits with expression (6) to obtain values of parameter  $B$ . The insert shows the plot of  $B$  versus [SO<sub>2</sub>F<sub>2</sub>] to yield  $k_2$  (294 K) $=(8.5\pm 0.8)\times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

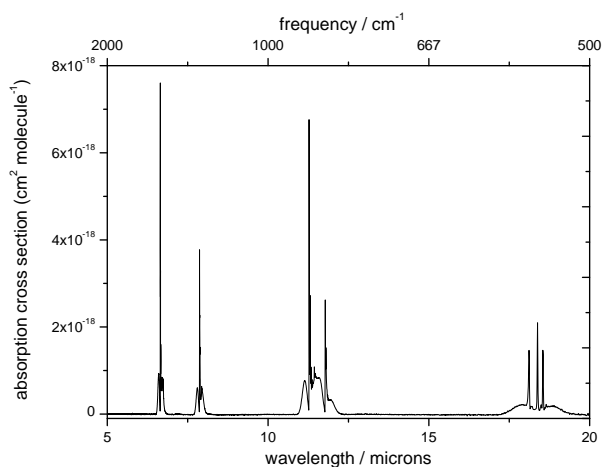
### 3.2 Kinetics of OH+SO<sub>2</sub>F<sub>2</sub>→ products (R2)

Figure 6 displays OH LIF profiles obtained following photolysis of H<sub>2</sub>O<sub>2</sub> (R9) at 3 different [SO<sub>2</sub>F<sub>2</sub>]. The experiments were conducted using [H<sub>2</sub>O<sub>2</sub>]= $5\times 10^{13}$  molecule cm<sup>-3</sup> at  $P=300$  Torr (N<sub>2</sub>) and  $T=294$  K. Note that large [SO<sub>2</sub>F<sub>2</sub>] of up to  $2\times 10^{17}$  molecule cm<sup>-3</sup> were used to significantly perturb the OH decay kinetics. Pseudo 1st-order conditions of [SO<sub>2</sub>F<sub>2</sub>] and [H<sub>2</sub>O<sub>2</sub>] $\gg$ [OH] applied, therefore a simple expression was used to analyse the data. Since the OH was formed pseudo-instantaneously in the laser flash  $C$  approaches  $\infty$  and expression (2) reduces to:

$$[\text{OH}]_t = A \times \exp(-Bt) \quad (6)$$

The insert in Fig. 6 shows the plot of the parameter of interest  $B$  (the pseudo first-order rate coefficient for OH decay) versus [SO<sub>2</sub>F<sub>2</sub>], to obtain  $k_2$  (294 K) $=(8.5\pm 0.8)\times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> from an unweighted linear fit to the data. Note that the intercept value of around 100 s<sup>-1</sup> is consistent with slow loss of OH (in the absence of SO<sub>2</sub>F<sub>2</sub> and associated impurities) due to reaction with the precursor H<sub>2</sub>O<sub>2</sub> and diffusion/transport processes. It is entirely possible that the true value of  $k_2$  is considerably smaller than this determination, as the sample of SO<sub>2</sub>F<sub>2</sub> used in this work was of a quoted purity of 99%. If the (unknown) impurities of up to 1% react with OH with a rate coefficient of around  $1\times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> they could account for all of the OH reactivity observed





**Fig. 7.** The FTIR spectrum of SO<sub>2</sub>F<sub>2</sub> at 0.5 cm<sup>-1</sup> resolution. The strong absorption feature around 1500 cm<sup>-1</sup> was used in the relative rate study. Integrated band intensities are listed in Table 3.

in these experiments. Accordingly, based on the results of these experiments, we quote a conservative upper limit of  $k_2$  (294 K)  $< 1 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. We note that a considerable energetic barrier to product formation is anticipated, as strong S-F ( $\sim 280$  kJ mol<sup>-1</sup>) or S=O ( $\sim 520$  kJ mol<sup>-1</sup>) bonds must be broken if SO<sub>2</sub>F<sub>2</sub> is to be destroyed in (R2). Reactions proceeding over such a barrier are characterised by an Arrhenius-type temperature dependence in  $k_2$ , which indicates that (R2) would proceed at a smaller rate at the much lower temperatures found throughout the troposphere above the boundary layer.

### 3.3 Kinetics of O<sub>3</sub>+SO<sub>2</sub>F<sub>2</sub>→products (R3)

In the course of the experimental study of (R1) it was noted that O<sub>3</sub> stored in blackened glass bulbs had a half-life of  $\approx 14$  days. To test whether the (R3) proceeds with an appreciable rate, a bulb was prepared in which an excess (5 Torr) of SO<sub>2</sub>F<sub>2</sub> was added to a bulb containing 2 Torr of O<sub>3</sub> at a total pressure of 1000 Torr (synthetic air). The absorption cells and monochromator of the PLP-LIF apparatus were used to regularly monitor [O<sub>3</sub>] in samples taken from the mixture over the course of 3 weeks. No evidence for (R3) was observed, with O<sub>3</sub> loss proceeding at a similar rate to that observed in the absence of SO<sub>2</sub>F<sub>2</sub>. An upper limit of  $k_3$  (294 K)  $< 1 \times 10^{-23}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was estimated by assuming that all of the observed loss of O<sub>3</sub> was due to (R3).

### 3.4 The FTIR spectrum of SO<sub>2</sub>F<sub>2</sub>

The 0.5 cm<sup>-1</sup> resolution, infra-red absorption spectrum of SO<sub>2</sub>F<sub>2</sub> between  $\approx 6$  and 20 μm is displayed in Fig. 7. The major absorption bands at 1504.3, 1270.9, 887.0, 849.2, 551.9, 544.1 and 539.2 cm<sup>-1</sup> were observed to obey the Beer-Lambert expression for SO<sub>2</sub>F<sub>2</sub> pressures up to  $\approx 1$  Torr (in a bath gas pressure of between 40 and 100 Torr). The

accuracy of the absorption cross sections is expected to be determined largely by the measurement of the cell pressure and the mixing ratio in the storage bulb and should not be worse than  $\pm 5\%$ . At 0.5 cm<sup>-1</sup> resolution, the strongest absorption features are at 1504.3 and 887 cm<sup>-1</sup>, which have peak cross sections of 7.6 and  $6.8 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup>, respectively and no rotational structure in the P and R envelopes is observed. At a resolution of 0.1 cm<sup>-1</sup>, Q-branch splitting of the 1504.3 cm<sup>-1</sup> feature is more clearly observed and the peak cross section at this frequency increases to  $\approx 1.1 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup>. The absorption features at 887.0 cm<sup>-1</sup> (S-F stretch), 1270.4 cm<sup>-1</sup> (S-O stretch) and 1504.3 cm<sup>-1</sup> (S-O stretch) display rotational fine structure at the higher resolution. We note that the band positions and shapes are in good agreement with the spectrum reported in the “NIST Chemistry WebBook” (NIST Chemistry WebBook, 2005). For the purpose of estimation of the integrated band strengths of SO<sub>2</sub>F<sub>2</sub> the 0.5 cm<sup>-1</sup> resolution spectrum is used. Integrated band strengths ( $S$ ) were calculated from:

$$S = \left( \frac{1}{pl} \right) \int_{\nu_1}^{\nu_2} \ln \left( \frac{I_0(\nu)}{I(\nu)} \right) d\nu \quad (7)$$

where  $p$  is the pressure of SO<sub>2</sub>F<sub>2</sub> (atm),  $l$  is the optical path-length (cm) and  $I_0(\nu)$  and  $I(\nu)$  are the intensities of transmitted radiation at wavenumber  $\nu$  with and without SO<sub>2</sub>F<sub>2</sub>, respectively. The results are listed in Table 3. As a test of our method, the integrated band intensity of SF<sub>6</sub> was also determined using the same experimental set up to return a value of  $S(\text{SF}_6) = 4750$  cm<sup>-2</sup> atm<sup>-1</sup> for the 948 cm<sup>-1</sup> absorption band. This value is in good agreement with a number of previous determinations (see Ko et al., 1993, for references). We are unaware of published integrated band strengths for SO<sub>2</sub>F<sub>2</sub> with which to compare our data.

### 3.5 Uptake of SO<sub>2</sub>F<sub>2</sub> onto aqueous surfaces (R4)

Despite the use of long contact times and variation of the pH between  $\approx 2$  and 12 no loss of SO<sub>2</sub>F<sub>2</sub> was observed, indicating a lack of irreversible loss processes and/or low solubility. The datapoints at individual contact times are summarised in Fig. 8, the solid fit lines being fits to the data of the form:

$$S_t = S_o \exp(-k_{\text{obs}} t) \quad (8)$$

where  $t$  is the contact time,  $S_o$  and  $S_t$  are the signal of SO<sub>2</sub>F<sub>2</sub> at time = zero and  $t$ , respectively and  $k_{\text{obs}}$  is the pseudo first-order removal constant. The errors associated with each data point are of the order of 0.3% of the signal, and considerably smaller than the symbols in Fig. 8. The small errors, obtained by prolonged integration of the signal ( $\approx 100$  s) at each contact time, were taken into account whilst performing weighted least squares fitting of the data. The values of  $k_{\text{obs}}$  obtained were:  $(9.5 \pm 5) \times 10^{-4}$ ,  $(10 \pm 4) \times 10^{-4}$  and  $(5 \pm 4) \times 10^{-4}$  at pH values of 4.5, 12 and 2, respectively. These values of  $k_{\text{obs}}$  are close to the lower limit of first-order

**Table 3.** Integrated band strengths for SO<sub>2</sub>F<sub>2</sub>.

$\nu$ (cm <sup>-1</sup> )	1504.3	1270.9	849.2, 887.0	551.9, 544.1, 539.2
$\lambda$ ( $\mu$ m)	6.648	7.868	11.78, 11.27	18.12, 18.38, 18.55
Range (cm <sup>-1</sup> )	1455–1540	1220–1310	810–920	500–595
$S$ (cm <sup>-1</sup> [cm atm] <sup>-1</sup> )	984	616	1394	343

removal constants measurable with this apparatus, which is determined by signal noise.  $k_{\text{obs}}$  is related to the experimental uptake coefficient,  $\gamma_{\text{expt}}$ , via:

$$\gamma_{\text{expt}} = \frac{2 \cdot r \cdot k_{\text{obs}}}{\bar{c}} \quad (9)$$

where  $\gamma_{\text{expt}}$  is the experimentally derived, net ratio of collisions with the aqueous surface which remove SO<sub>2</sub>F<sub>2</sub> from the gas phase, to the total number of collisions,  $r$  is the radius of the reactor (0.775 cm) and  $\bar{c}$  is the mean thermal velocity (24 060 cm s<sup>-1</sup> for SO<sub>2</sub>F<sub>2</sub> at 273 K) derived from the Maxwell equation. From the fitted values of  $k_{\text{obs}}$  and Eq. (9), we derive upper limits to  $\gamma_{\text{expt}}$  of 6–9 × 10<sup>-8</sup> depending on pH. Consideration of possible systematic errors associated with calculation of the contact time (via flow rates and pressure measurements) leads us to present an upper limit of  $\gamma_{\text{expt}} < 1 \times 10^{-7}$  for all experiments.

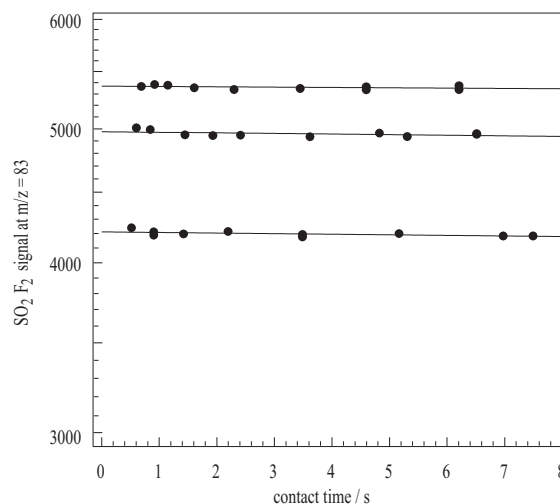
This result can be compared to the data of Cady and Misra (1974) who measured solubility and hydrolysis rates in alkaline solution. The rate coefficient for reaction of SO<sub>2</sub>F<sub>2</sub> with OH<sup>-</sup> was described by  $k_{\text{OH}^-} = 1.67 \times 10^{12} \exp(-6593/T) \text{ L mol}^{-1} \text{ s}^{-1}$  which results in  $k_{\text{OH}^-} = 77 \text{ L mol}^{-1} \text{ s}^{-1}$  at the temperature of our experiments. The solubility ( $H$ ) of SO<sub>2</sub>F<sub>2</sub> was given as  $2.2 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$  at 273 K. If the rate of removal of gas-phase SO<sub>2</sub>F<sub>2</sub> is limited by reaction in solution these parameters can be related to the experimental uptake coefficient via:

$$\frac{1}{\gamma_{\text{expt}}} = \frac{1}{\alpha} + \frac{1}{\gamma_{\text{react}}} \quad (10)$$

with

$$\gamma_{\text{react}} = \frac{4HRT}{\bar{c}} \sqrt{D_l \cdot k_{\text{OH}^-} [\text{OH}]} \quad (11)$$

$\alpha$  is the accommodation coefficient,  $D_l$  is the aqueous phase diffusion coefficient, which is close to  $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for neutral, closed shell species in aqueous solutions at ambient temperatures (Seinfeld, 1986). Taking the literature values of  $H$  and  $k_{\text{OH}^-}$  (Cady and Misra, 1974) and the concentration ( $1 \times 10^{-2} \text{ M}$ ) of OH<sup>-</sup> from our experiment at pH=12 gives  $\gamma_{\text{react}} \approx 2 \times 10^{-7}$ . As the contribution to  $\gamma_{\text{expt}}$  from the accommodation coefficient  $\alpha$  (which is probably between  $1 \times 10^{-3}$  and 1) will be small,  $\gamma_{\text{react}} \approx \gamma_{\text{expt}}$ . The calculated value of  $\gamma$  is thus in acceptable agreement with the measured upper limit to  $\gamma_{\text{react}}$  from the WWFT experiments. Cady and Misra



**Fig. 8.** The uptake of SO<sub>2</sub>F<sub>2</sub> onto aqueous surfaces of different pH (2, 12 and 4.5 for the upper, middle and lowest trace, respectively). Different concentrations of SO<sub>2</sub>F<sub>2</sub> and/or mass spectrometer sensitivity is the cause of the vertical displacement of the data from each experiment.

(1974) found significantly lower loss rates of SO<sub>2</sub>F<sub>2</sub> in acidified solutions (pH as low as 2), suggesting that only loss to alkaline aqueous surfaces is of significance.

### 3.6 Atmospheric implications

In the following section we make some simple calculations on the lifetime of SO<sub>2</sub>F<sub>2</sub> with respect to various loss processes in different parts of the atmosphere and, based on this, a qualitative estimate of its global warming potential.

#### 3.6.1 Reaction with OH in the troposphere

We have shown that SO<sub>2</sub>F<sub>2</sub> reacts only very slowly with the OH radical. A lower limit to its tropospheric lifetime with respect to loss by reaction with OH can be obtained by combining a diurnally and globally averaged OH concentration of  $1 \times 10^6 \text{ molecule cm}^{-3}$  with the rate coefficient of  $k_2 \leq 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  as presented here. The resultant lifetime exceeds 30 years and is strictly a lower limit for a number of reasons. Firstly, as already mentioned our determination of the rate coefficient  $k_2$  is an upper limit, as loss of OH was (probably) driven by reactive impurities in our SO<sub>2</sub>F<sub>2</sub> sample. Secondly, the absence of any easily abstractable atoms in SO<sub>2</sub>F<sub>2</sub> implies a significant barrier to

reaction and that the rate coefficient will most likely decrease rapidly with altitude in the troposphere as the temperature decreases. Thus the true lifetime of SO<sub>2</sub>F<sub>2</sub> with respect to reaction by OH could easily be an order of magnitude longer than the lower limit calculated here.

### 3.6.2 Heterogeneous loss/dry deposition of SO<sub>2</sub>F<sub>2</sub> in the boundary layer

The value of  $\gamma_{\text{expt}}$  obtained in this study can be used to estimate the lifetime of atmospheric SO<sub>2</sub>F<sub>2</sub> with respect to its uptake to aqueous surfaces. For uptake coefficients lower than  $\approx 10^{-3}$ , the following expression defines the lifetime ( $\tau$ , s) in the presence of aerosol of loading  $A$  (cm<sup>2</sup> cm<sup>-3</sup>):

$$\tau = \frac{4}{\gamma_{\text{expt}} \cdot \bar{c} \cdot A} \quad (12)$$

Following Sander and Crutzen (1996) we assume an average surface area density of  $A=5 \times 10^{-7}$  cm<sup>2</sup>/cm<sup>3</sup> for the marine boundary layer, which results in a lower limit to the SO<sub>2</sub>F<sub>2</sub> lifetime of 100 years in this environment. This must however be considered a lower limit to the lifetime with respect to aerosol loss, as atmospheric aerosol is nearly always acidic and, as shown by Cady and Misra (1974) SO<sub>2</sub>F<sub>2</sub> does not interact strongly with aqueous neutral or acidic surfaces. Indeed, using expression (11) (and using the coefficients for solubility and hydrolysis of Cady and Misra) and we can calculate a value of  $\gamma_{\text{react}} \approx 2 \times 10^{-9}$ , which would be representative of uptake to the ocean surface with an average temperature of 20°C and pH of  $\approx 8$  ( $[\text{OH}^-] = 1 \times 10^{-6}$  mol L<sup>-1</sup>). Note that at pH values greater than 7.5, hydrolysis is dominated by reaction with OH<sup>-</sup> and direct reaction with water can be neglected. The value of  $\gamma = 2 \times 10^{-9}$  can be used to calculate the deposition velocity to the ocean using:

$$v_{\text{dep}} = \frac{\gamma \cdot \bar{c}}{4} \quad (13)$$

which gives us  $v_{\text{dep}} = 1.2 \times 10^{-5}$  cm s<sup>-1</sup>. Combining the deposition velocity with recent measurements of the SO<sub>2</sub>F<sub>2</sub> concentration of  $\approx 1$  ppt (Mühle, 2006) and the ocean surface area of  $\approx 3.6 \times 10^8$  km<sup>2</sup> allows us to calculate that  $\approx 6 \times 10^3$  kg of SO<sub>2</sub>F<sub>2</sub> will annually be lost to the oceans. This number is negligibly small in comparison to the present annual atmospheric release rate, which is clearly larger than 10<sup>6</sup> kg/year (see Introduction).

### 3.6.3 Loss of SO<sub>2</sub>F<sub>2</sub> in the stratosphere

We have shown that SO<sub>2</sub>F<sub>2</sub> does react efficiently with O(<sup>1</sup>D) atoms, thus opening a potential sink in the stratosphere. A rough guide to its lifetime with respect to reaction with O(<sup>1</sup>D) can be obtained by comparison to N<sub>2</sub>O, which has a stratospheric lifetime of about 130 years, mainly (90%) a result of photolysis, the remainder due to reaction with O(<sup>1</sup>D). The lifetime of N<sub>2</sub>O with respect to reaction with O(<sup>1</sup>D) can

thus be estimated as >1000 years. As the rate coefficient ( $k_{1b}$ ) for reaction of O(<sup>1</sup>D) with SO<sub>2</sub>F<sub>2</sub> is approximately a factor of two slower than N<sub>2</sub>O with O(<sup>1</sup>D) we can estimate a lifetime in excess of 2000 years with respect to loss by (R1). Although the VUV spectrum of SO<sub>2</sub>F<sub>2</sub> was not studied in this work, we can also coarsely evaluate the lifetime of SO<sub>2</sub>F<sub>2</sub> with respect to photolysis in the stratosphere by comparison with N<sub>2</sub>O. Within the important wavelength region for N<sub>2</sub>O photolysis (185–210 nm), the absorption cross sections of SO<sub>2</sub>F<sub>2</sub> (Pradayrol et al., 1996) are consistently a factor of five to ten less than those of N<sub>2</sub>O, which would convert to a photolytic lifetime in excess of 500 years. Accurate study of the SO<sub>2</sub>F<sub>2</sub> cross sections in the relevant wavelength range, and calculation of the J-value with an appropriate radiation transfer model would be useful to confirm this. Clearly however, SO<sub>2</sub>F<sub>2</sub> is too long lived in the lower stratosphere to contribute significantly to the sulphate layer.

### 3.6.4 SO<sub>2</sub>F<sub>2</sub> as a greenhouse gas?

In the absence of an important chemical sink process for SO<sub>2</sub>F<sub>2</sub> once released into the atmosphere, we must consider its potential role as an atmospheric greenhouse gas. The SO<sub>2</sub>F<sub>2</sub> IR absorption features in the 814–918 cm<sup>-1</sup> spectral range are located within the “atmospheric window” and, via model calculations of the atmospheric sources, sinks and distribution of SO<sub>2</sub>F<sub>2</sub>, the integrated band intensity (Table 3) can be used to estimate the greenhouse warming potential (GWP) of this gas. Whilst an in-depth study is beyond the scope of this publication, and would require a more complete set of SO<sub>2</sub>F<sub>2</sub> IR spectral measurements, we can compare the integrated band intensity with that of another, long lived fluorinated sulphur species, SF<sub>6</sub>, which has one of the largest GWPs (over a 100 year period) of all known atmospheric trace gases. The integrated band intensity for the SF<sub>6</sub> absorption feature at  $\approx 950$  cm<sup>-1</sup> is circa 5000 (see Sect. 3.4) a factor of just 3.3 larger than SO<sub>2</sub>F<sub>2</sub>. We note that the absorption feature of SO<sub>2</sub>F<sub>2</sub> at  $\approx 7.9$  μm also absorbs (albeit more weakly) within the atmospheric window. Given the long lifetime of SO<sub>2</sub>F<sub>2</sub> and the expected increase in its production rate over the next decades it is plausible that this species could indeed become an important greenhouse gas. This needs to be thoroughly evaluated in detailed modelling studies.

## 4 Conclusions

In a series of laboratory studies we have investigated a number of reactions that could contribute to the chemical removal of SO<sub>2</sub>F<sub>2</sub> from the atmosphere. Experimental data was obtained for reaction of SO<sub>2</sub>F<sub>2</sub> with excited oxygen atoms (O(<sup>1</sup>D)), the OH radical, O<sub>3</sub> and with aqueous surfaces. The reaction with O(<sup>1</sup>D) proceeds both by energy transfer (quenching of O(<sup>1</sup>D),  $\approx 55\%$ ) and product formation ( $\approx 45\%$ ), with an overall rate coefficient of

$k_1$  (220–300 K) =  $(1.3 \pm 0.2) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Upper limits for the rate coefficients (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for reaction of SO<sub>2</sub>F<sub>2</sub> with OH ( $k_2 < 1 \times 10^{-15}$ ) and O<sub>3</sub> ( $k_3 < 1 \times 10^{-23}$ ) were obtained. No evidence for loss to aqueous surfaces was obtained. The kinetic data allowed us to estimate very long chemical lifetimes for SO<sub>2</sub>F<sub>2</sub> in all parts of the lower atmosphere, which, together with our measurements of infra-red absorption bands in the atmospheric window, suggest that SO<sub>2</sub>F<sub>2</sub> may have a large greenhouse warming potential.

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