



# Rate coefficients for the reaction of O(<sup>1</sup>D) with the atmospherically long-lived greenhouse gases NF<sub>3</sub>, SF<sub>5</sub>CF<sub>3</sub>, CHF<sub>3</sub>, C<sub>2</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub>, n-C<sub>5</sub>F<sub>12</sub>, and n-C<sub>6</sub>F<sub>14</sub>

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**Abstract.** The contribution of atmospherically persistent (long-lived) greenhouse gases to the radiative forcing of Earth has increased over the past several decades. The impact of highly fluorinated, saturated compounds, in particular perfluorinated compounds, on climate change is a concern because of their long atmospheric lifetimes, which are primarily determined by stratospheric loss processes, as well as their strong absorption in the infrared “window” region. A potentially key stratospheric loss process for these compounds is their gas-phase reaction with electronically excited oxygen atoms, O(<sup>1</sup>D). Therefore, accurate reaction rate coefficient data is desired for input to climate change models. In this work, rate coefficients,  $k$ , were measured for the reaction of O(<sup>1</sup>D) with several key long-lived greenhouse gases, namely NF<sub>3</sub>, SF<sub>5</sub>CF<sub>3</sub>, CHF<sub>3</sub> (HFC-23), C<sub>2</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub>, n-C<sub>5</sub>F<sub>12</sub>, and n-C<sub>6</sub>F<sub>14</sub>. Room temperature rate coefficients for the total reaction,  $k_{\text{Tot}}$ , corresponding to loss of O(<sup>1</sup>D), and reactive channel,  $k_{\text{R}}$ , corresponding to the loss of the reactant compound, were measured for NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub> using competitive reaction and relative rate methods, respectively.  $k_{\text{R}}$  was measured for the CHF<sub>3</sub> reaction and improved upper-limits were determined for the perfluorinated compounds included in this study. For NF<sub>3</sub>,  $k_{\text{Tot}}$  was determined to be  $(2.55 \pm 0.38) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{\text{R}}$ , which was measured using CF<sub>3</sub>Cl, N<sub>2</sub>O, CF<sub>2</sub>ClCF<sub>2</sub>Cl (CFC-114), and CF<sub>3</sub>CFCl<sub>2</sub> (CFC-

114a) as reference compounds, was determined to be  $(2.21 \pm 0.33) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . For SF<sub>5</sub>CF<sub>3</sub>,  $k_{\text{Tot}} = (3.24 \pm 0.50) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{\text{R}} < 5.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were measured, where  $k_{\text{R}}$  is a factor of three lower than the current recommendation of  $k_{\text{Tot}}$  for use in atmospheric modeling. For CHF<sub>3</sub>  $k_{\text{R}}$  was determined to be  $(2.35 \pm 0.35) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which corresponds to a reactive channel yield of  $0.26 \pm 0.04$ , and resolves a large discrepancy among previously reported values. The quoted uncertainties are  $2\sigma$  and include estimated systematic errors. Upper-limits for  $k_{\text{R}}$  for the C<sub>2</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub>, n-C<sub>5</sub>F<sub>12</sub>, and n-C<sub>6</sub>F<sub>14</sub> reactions were determined to be 3.0, 3.5, 5.0, and 16 (in units of  $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), respectively. The results from this work are compared with results from previous studies. As part of this work, infrared absorption band strengths for NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub> were measured and found to be in good agreement with recently reported values.

## 1 Introduction

The contribution of atmospherically persistent (long-lived, atmospheric lifetimes > 500 yr) greenhouse gases to the radiative forcing of Earth’s atmosphere has increased

**Table 1.** Summary of atmospheric abundance, growth rate, lifetimes, and global warming potential (GWP) for the molecules included in this study as taken from WMO (2011) for the year 2008 unless noted otherwise.

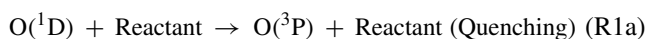
Molecule	Atmospheric Abundance (ppt)	Atmospheric Growth Rate (ppt yr <sup>-1</sup> )	Global Lifetime (years)	Stratospheric Lifetime (years)	GWP 100-yr time horizon
NF <sub>3</sub>	0.57 <sup>a</sup>	0.05	500	500	17 500
CHF <sub>3</sub> (HFC-23)	22	0.83	222	2347	14 200
SF <sub>5</sub> CF <sub>3</sub>	0.15 <sup>b</sup>	~0 <sup>b</sup>	650–950	650–950	17 800
CF <sub>3</sub> CF <sub>3</sub> (PFC-116)	3.9	0.1	> 10 000	> 10 000	12 200
c-C <sub>4</sub> F <sub>8</sub>	1.2 <sup>c</sup>	0.03 <sup>c</sup>	3200	3200	10 300
<i>n</i> -C <sub>5</sub> F <sub>12</sub>	0.12 <sup>d</sup>	0.0014 <sup>d</sup>	4100	4100	9150
<i>n</i> -C <sub>6</sub> F <sub>14</sub>	0.27 <sup>d</sup>	0.005 <sup>d</sup>	3100	3100	9290

<sup>a</sup> Arnold et al. (2012)<sup>b</sup> Sturges et al. (2012), value for 2009–2011.<sup>c</sup> Oram et al. (2012), value for 2010.<sup>d</sup> Ivy et al. (2012), value for 2011.

significantly over the past decade (WMO, 2011). Saturated highly fluorinated and fully fluorinated (perfluorinated, PFCs) compounds are included in the Kyoto Protocol (1997) and are of particular concern due to their long atmospheric lifetimes and strong absorption in the infrared “window” region. Although these compounds make a relatively minor contribution to radiative forcing in the present day atmosphere when compared to chlorofluorocarbons (CFCs) their impact on global climate change will continue to increase as their emissions and atmospheric abundances increase.

Models of climate change require a quantitative knowledge not only of persistent greenhouse gas emission rates, but also of their atmospheric loss processes, to better define their atmospheric lifetimes. The atmospheric removal processes, i.e., the coupling of atmospheric chemistry and climate change, for persistent greenhouse gases are primarily limited to processes occurring in the upper-atmosphere, i.e., the stratosphere, mesosphere, and thermosphere. A potentially key upper-atmosphere loss process includes gas-phase reaction with electronically excited oxygen atoms, O(<sup>1</sup>D), which are formed in the atmosphere primarily by the UV photolysis of ozone. The focus of the present laboratory study is on the reaction of several persistent greenhouse gases with the O(<sup>1</sup>D) atom.

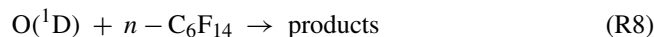
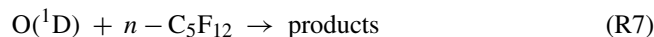
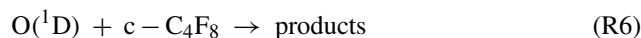
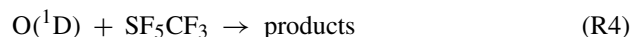
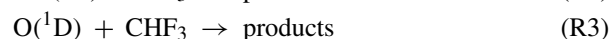
O(<sup>1</sup>D) reactions, in general, proceed via several product channels, which include collisional quenching of O(<sup>1</sup>D) to its ground electronic state, O(<sup>3</sup>P), and chemical reaction, which leads to the loss of the reactant



It is the reactive channels that are of most interest for quantifying the atmospheric loss of an atmospheric trace species (reactant) and, thus, its impact on climate change.

The molecules considered in the present study include NF<sub>3</sub>, SF<sub>5</sub>CF<sub>3</sub>, the PCFs C<sub>2</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub>, *n*-C<sub>5</sub>F<sub>12</sub>, and *n*-C<sub>6</sub>F<sub>14</sub>, as well as CHF<sub>3</sub> (HFC-23). These compounds were selected based on their abundance in the current atmosphere, their long atmospheric lifetimes, their potential impact on climate change, as well as the need for improved kinetic data. The molecules included in this study do not, however, represent a comprehensive list of atmospherically persistent greenhouse gases. A summary of the atmospheric abundance, growth rate, lifetime, and global warming potentials (GWP) for the molecules included in this study is given in Table 1.

In this work, rate coefficients, *k*, for the reaction of O(<sup>1</sup>D) with NF<sub>3</sub>, SF<sub>5</sub>CF<sub>3</sub>, CHF<sub>3</sub>, C<sub>2</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub>, *n*-C<sub>5</sub>F<sub>12</sub>, and *n*-C<sub>6</sub>F<sub>14</sub>



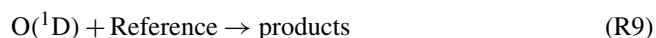
are reported. Absolute rate coefficients for the loss of O(<sup>1</sup>D) atoms, herein referred to as the “total” rate coefficient ( $k_{\text{Tot}} = k_{1a} + k_{1b} + k_{1c}$ ) were measured for the NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub> reactions using a competitive reaction method. A relative rate method was used to measure the rate coefficients for the loss of reactant, herein referred to as the “reactive” rate coefficient ( $k_{\text{R}} = k_{1b} + k_{1c}$ ), for all compounds included in this study. The present results are compared with previously reported kinetic data where available.

## 2 Experimental details

Two independent kinetic methods were used to measure the room temperature (296 K) reaction rate coefficients reported in this study. Absolute rate coefficients were measured for the O(<sup>1</sup>D) reaction with NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub> using a competitive reaction method in which O(<sup>1</sup>D) atoms were produced via pulsed laser photolysis (PLP) and the temporal profile of the OH radical produced in the O(<sup>1</sup>D) + *n*-C<sub>4</sub>H<sub>10</sub> (*n*-butane) reference reaction was monitored by laser-induced fluorescence (LIF). In the second method, the reactive rate coefficient,  $k_R < k_{Tot}$ , for all the molecules included in this study, was measured relative to an established reference reaction. The reactive rate coefficient for NF<sub>3</sub> was measured relative to several different reference molecules. The CHF<sub>3</sub> reactive rate coefficient was measured relative to the NF<sub>3</sub> reaction. The reactive rate coefficients for the SF<sub>5</sub>CF<sub>3</sub>, C<sub>2</sub>F<sub>6</sub>, *c*-C<sub>4</sub>F<sub>8</sub>, *n*-C<sub>5</sub>F<sub>12</sub>, and *n*-C<sub>6</sub>F<sub>14</sub> reactions were measured relative to the CHF<sub>3</sub> reaction. The kinetic techniques and methods employed are described separately below.

### 2.1 Relative rate technique

Reactive rate coefficients were measured relative to that of a reference compound



by measuring the simultaneous loss of the reactant and reference compound. Experiments were performed using an apparatus described in greater detail in a previous study from this laboratory (Papadimitriou et al., 2008a). The apparatus consisted of a Pyrex reactor (100 cm long, 5 cm i.d.) coupled to an external Fourier transform infrared spectrometer (FTIR), which was used to measure the loss of the reactant and reference compounds.

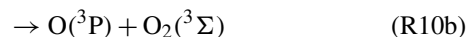
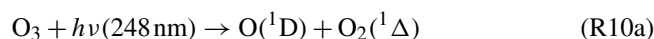
Provided the reactant and reference compounds are lost solely via reaction with O(<sup>1</sup>D) the rate coefficients for the reactant and reference compound are related by

$$\frac{k_R(\text{reactant})}{k_R(\text{ref})} = \frac{\ln([\text{reactant}]_0/[\text{reactant}]_t)}{\ln([\text{ref}]_0/[\text{ref}]_t)} \quad (1)$$

where [reactant]<sub>0</sub> and [ref]<sub>0</sub> are the initial reactant and reference compound concentrations and [reactant]<sub>t</sub> and [ref]<sub>t</sub> are the concentrations at time *t*. Ideally the reactant and reference compound would have similar reactivity to provide the most accurate measurement. However, this is not always possible, particularly in this work where the reactive rate coefficients of interest span a large range of reactivity, i.e., nearly three orders of magnitude, while the best known reference reactions have total and reactive rate coefficients of  $\sim 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Therefore, in an attempt to minimize systematic error in the reactive rate coefficient determinations multiple reference compounds were included in the study of NF<sub>3</sub>, while the primary reference reaction compound was N<sub>2</sub>O. N<sub>2</sub>O has a well-established total rate coefficient as well as having a unit reactive branching ratio, i.e.,

no quenching of O(<sup>1</sup>D) (Sander et al., 2011). The other reference compounds used were CF<sub>3</sub>Cl, CF<sub>2</sub>CICF<sub>2</sub>Cl (CFC-114), and CF<sub>3</sub>CFCl<sub>2</sub> (CFC-114a). In order to more accurately account for the differences in reactant reactivity NF<sub>3</sub> was then used as the reference compound in our CHF<sub>3</sub> reaction experiments and CHF<sub>3</sub> was then used as the reference compound in the PFC experiments.

Experiments were performed by mixing the reactant and reference compounds in the apparatus by circulating the gases between the reactor and infrared absorption cell using a Teflon diaphragm pump,  $\sim 12 \text{ L min}^{-1}$  flow rate, at a total pressure (He bath gas) of  $\sim 180$  Torr. The initial concentrations of the reaction mixture were measured by infrared absorption. The FTIR was equipped with a low-volume (750 cm<sup>3</sup>) multi-pass cell (485 cm optical pathlength, KBr windows). Infrared spectra were recorded at a spectral resolution of 1 cm<sup>-1</sup> between 500 and 4000 cm<sup>-1</sup> with 100 co-added scans. A summary of the infrared spectra for the compounds included in this study is given in the Supplementary Material. Ozone was then added to the reaction mixture continuously by passing a small flow of He through a silica-gel trap containing O<sub>3</sub> at 195 K. O(<sup>1</sup>D) radicals were produced in the reactor by passing the output of a pulsed KrF excimer laser (248 nm) along the length of the reactor



where the O(<sup>1</sup>D) yield is 0.9 (Sander et al., 2011). The photolysis laser fluence was measured at the exit of the reactor and was varied between 12 and 20 mJ cm<sup>-2</sup> pulse<sup>-1</sup> over the course of the study. The O<sub>3</sub> steady-state concentration in these experiments was  $\sim 3 \times 10^{14} \text{ molecule cm}^{-3}$  based on its measured infrared absorption. The residence time of the gas mixture in the reactor was  $\sim 6$  s. The loss of the reactant and reference compounds was measured by infrared absorption, while the gas mixture was circulated.

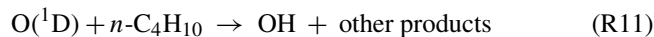
The initial NF<sub>3</sub>, N<sub>2</sub>O, and CHF<sub>3</sub> concentrations were in the range (3–7) × 10<sup>14</sup>, 2 × 10<sup>15</sup>, and 2 × 10<sup>14</sup> molecule cm<sup>-3</sup>, respectively. The initial CF<sub>3</sub>Cl, CFC-114, and CFC-114a concentrations were  $\sim 2 \times 10^{14} \text{ molecule cm}^{-3}$ . The initial PFC concentrations were  $\sim 2 \times 10^{14} \text{ molecule cm}^{-3}$ .

The reactor total pressure increased during the experiments due to the addition of O<sub>3</sub> and He bath gas from an initial pressure of  $\sim 180$  to  $\sim 450$  Torr at the completion of a typical experiment. The duration of a typical experiment was  $\sim 30$  min for NF<sub>3</sub> and CHF<sub>3</sub>, but more than 3 hours for the SF<sub>5</sub>CF<sub>3</sub> and PFCs experiments in an attempt to maximize the change in the reactant concentration. To check the stability of the reactant and reference compounds with the change in pressure, exposure to the 248 nm photolysis laser beam, and gas circulation over this duration control experiments were also conducted. In these experiments, the photolysis laser was passed through the cell in absence of O<sub>3</sub>, while

a small flow of He was added to the system to replicate the pressure build up in the system. NF<sub>3</sub>, N<sub>2</sub>O, and CF<sub>3</sub>Cl have weak absorption at 248 nm, while the other reactants have no reported absorption at 248 nm (Sander et al., 2011). There was no observable change, < 0.4 %, in the reactant concentration over a period of 3 h where the pressure increase was from 180 to 550 Torr. In addition, NF<sub>3</sub> rate coefficient measurements with N<sub>2</sub>O as the reference compound were performed over the pressure range 500 to 600 Torr and yielded nearly identical results to the lower pressure experiments.

## 2.2 Competitive reaction method

In the competitive reaction method, OH radicals were produced by the reaction of O(<sup>1</sup>D) with *n*-C<sub>4</sub>H<sub>10</sub> (*n*-butane)



and monitored using laser induced fluorescence (LIF). That is, O(<sup>1</sup>D) atoms were not detected directly, but were converted to OH radicals whose temporal profile was measured by LIF. Total rate coefficients for the NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub> reactions were determined from an analysis of the OH radical temporal profiles in the presence of known concentrations of NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub>. The experimental apparatus (Baasandorj et al., 2010; Papadimitriou et al., 2008b) and methods (Baasandorj et al., 2011) employed have been used in previous studies from this laboratory and are described in greater detail elsewhere. A brief summary is presented here.

OH temporal profiles were measured using laser induced fluorescence (LIF) following OH excitation of the A<sup>2</sup>Σ<sup>+</sup>(*v*' = 1) ← X<sup>2</sup>Π (*v* = 0) transition at ~282 nm using the frequency doubled output from a pulsed Nd:YAG pumped dye laser. OH fluorescence was detected using a photomultiplier tube (PMT) after it passed through a band-pass filter (308 nm, FWHM = 10 nm). The delay time between the photolysis and the probe lasers, i.e., the reaction time, was varied over the range 10–1000 μs.

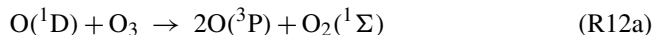
O(<sup>1</sup>D) radicals were produced in the 248 nm (KrF excimer laser) pulsed laser photolysis of O<sub>3</sub>, reaction 10. The photolysis laser fluence was monitored with a power meter mounted after the exit window of the reactor and varied between 6 and 18 mJ cm<sup>-2</sup> pulse<sup>-1</sup> over the course of the study. The initial O(<sup>1</sup>D) concentration was estimated to be between 3 and 9 × 10<sup>11</sup> atoms cm<sup>-3</sup>.

The OH temporal profiles are described by a bi-exponential expression

$$S_{\text{OH}}(t) = C \left[ \exp(-k'_{\text{Loss}}t) - \exp(-k'_{\text{Rise}}t) \right] \quad (2)$$

where  $S_{\text{OH}}(t)$  is the OH radical fluorescence signal at time  $t$ ,  $C$  is a constant that is proportional to the total OH radical concentration, and  $k'_{\text{Loss}}$  and  $k'_{\text{Rise}}$  are the pseudo-first-order rate coefficients for the loss and formation of the OH radical, respectively. The rate of the initial rise in the OH radical concentration is a measure of the pseudo-first order loss of

O(<sup>1</sup>D) in the system.  $k'_{\text{Rise}}$  is determined by the total loss of O(<sup>1</sup>D), which includes significant reaction with *n*-butane, reaction with O<sub>3</sub>



where  $k_{12} = 2.4 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> ( $k_{12a}/k_{12} = 0.5$ ) (Sander et al., 2011), reaction with the reactant, as well as the reaction of O(<sup>1</sup>D) with background impurities and diffusion out of the detection volume,  $k'_b$

$$k'_{\text{Rise}} = k_{11}[n\text{-C}_4\text{H}_{10}] + k_{12}[\text{O}_3] + k'_b + k_i[\text{reactant}] = k'_0 + k_i[\text{reactant}] \quad (3)$$

$k'_{\text{Loss}}$  was primarily determined by its reaction with *n*-butane



where  $k_{13} = 2.35 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Atkinson et al., 2008) and diffusion out of the detection volume. Under the conditions of our experiments  $k'_{\text{Loss}}$  was typically < 50 s<sup>-1</sup>. The concentrations of *n*-butane and O<sub>3</sub> were determined from the measured gas flows and pressure. The concentration of *n*-butane was varied over the course of this study over the range (2–5) × 10<sup>13</sup> molecule cm<sup>-3</sup>, while the ozone concentration range was (2–4) × 10<sup>12</sup> molecule cm<sup>-3</sup>.

Total rate coefficients were determined from a non-linear least-squares analysis of a series of OH temporal profiles to determine  $k'_{\text{Rise}}$ . The [*n*-C<sub>4</sub>H<sub>10</sub>], [O<sub>3</sub>], and total pressure, ~40 Torr, were held nearly constant while measuring OH temporal profiles with various known concentrations of NF<sub>3</sub> or SF<sub>5</sub>CF<sub>3</sub>. The concentrations of NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub> in the LIF reactor were (1–6) × 10<sup>14</sup> molecule cm<sup>-3</sup> and (0.5–17) × 10<sup>15</sup> molecule cm<sup>-3</sup> as determined from measured gas flows and pressures. In several experiments, the reactant concentration was measured directly online using infrared absorption after the reaction mixture exited the LIF reactor and was found to be in good agreement with the concentration determined from gas flows, to within 5 %. A linear least-squares analysis of  $k'_{\text{Rise}}$  versus [NF<sub>3</sub>] or [SF<sub>5</sub>CF<sub>3</sub>] yielded the bimolecular total rate coefficient for the O(<sup>1</sup>D) + NF<sub>3</sub> or SF<sub>5</sub>CF<sub>3</sub> reactions.

## 2.3 Materials

He (UHP, 99.999 %) bath gas was passed through a molecular sieve trap kept at liquid nitrogen temperature prior to entering the apparatus in order to minimize the presence of volatile impurities, such as H<sub>2</sub>O and CO<sub>2</sub>. SF<sub>6</sub> (99.999 %) was used as supplied. SF<sub>5</sub>CF<sub>3</sub> (99 %), NF<sub>3</sub> (electronic grade, 99.99 %), N<sub>2</sub>O (99.99 %), *n*-C<sub>4</sub>H<sub>10</sub> (*n*-butane, 99.93 %), CHF<sub>3</sub> (99 %), C<sub>2</sub>F<sub>6</sub> (99 %), *c*-C<sub>4</sub>F<sub>8</sub> (99 %), *n*-C<sub>5</sub>F<sub>12</sub> (99 %), *n*-C<sub>6</sub>F<sub>14</sub> (> 99 %), CF<sub>2</sub>ClCF<sub>2</sub>Cl (CFC-114, 99 %), and CF<sub>3</sub>CFCl<sub>2</sub> (CFC-114a, 99 %) samples were degassed in freeze-pump-thaw cycles during mixture preparation. Two different SF<sub>5</sub>CF<sub>3</sub> samples were used during

**Table 2.** Summary of the total,  $k_{\text{Tot}}$ , and reactive,  $k_{\text{R}}$ , O(<sup>1</sup>D) reaction rate coefficients measured in this work at 296 K.

Molecule	Reference Compound	Reference Compound Data			$k_{\text{R}}/k_{\text{Ref}}$ This Work*	$k_{\text{Tot}}^*$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$k_{\text{R}}^*$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
		Total Rate Coefficient ( $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Reactive Branching Ratio or Rate Coefficient	Reference			
NF <sub>3</sub>	–	–	–	–	–	$(2.55 \pm 0.20) \times 10^{-11}$	–
	CF <sub>3</sub> Cl	$0.87 \pm 0.04$	$0.69 \pm 0.10$	Ravishankara et al. (1993)	$0.355 \pm 0.002$	–	$(2.11 \pm 0.02) \times 10^{-11}$
	CF <sub>2</sub> ClCF <sub>2</sub> Cl (CFC-114)	$1.42 \pm 0.25$	$0.85 \pm 0.12$	Baasandorj et al. (2011)	$0.186 \pm 0.003$	–	$(2.25 \pm 0.04) \times 10^{-11}$
	CFCl <sub>2</sub> CF <sub>3</sub> (CFC-114a)	$1.62 \pm 0.30$	$0.79 \pm 0.10$	Baasandorj et al. (2011)	$0.173 \pm 0.012$	–	$(2.21 \pm 0.15) \times 10^{-11}$
	N <sub>2</sub> O	$1.17 \pm 0.17$	1.00	Sander et al. (2006)	$0.193 \pm 0.004$	–	$(2.26 \pm 0.05) \times 10^{-11}$ Avg. $(2.21 \pm 0.07) \times 10^{-11}$ $(0.235 \pm 0.002) \times 10^{-11}$
CHF <sub>3</sub>	NF <sub>3</sub>	$0.255 \pm 0.04$	$0.87 \pm 0.13$	This Work	$0.106 \pm 0.001$	–	–
SF <sub>5</sub> CF <sub>3</sub>	–	–	–	–	–	$(3.24 \pm 0.50) \times 10^{-13}$	–
	CHF <sub>3</sub>	–	$0.235 \times 10^{-11}$	This Work	$0.0246 \pm 0.003$	–	$< 5.8 \times 10^{-14}$
CF <sub>3</sub> CF <sub>3</sub>	CHF <sub>3</sub>	–	$0.235 \times 10^{-11}$	This Work	$0.0130 \pm 0.007$	–	$< 3.0 \times 10^{-14}$
c-C <sub>4</sub> F <sub>8</sub>	CHF <sub>3</sub>	–	$0.235 \times 10^{-11}$	This Work	$0.0150 \pm 0.005$	–	$< 3.5 \times 10^{-14}$
n-C <sub>5</sub> F <sub>12</sub>	CHF <sub>3</sub>	–	$0.235 \times 10^{-11}$	This Work	$0.0214 \pm 0.008$	–	$< 5.0 \times 10^{-14}$
n-C <sub>6</sub> F <sub>14</sub>	CHF <sub>3</sub>	–	$0.235 \times 10^{-11}$	This Work	$0.0669 \pm 0.001$	–	$< 16 \times 10^{-14}$

\* The uncertainties are  $2\sigma$  from the precision of the measurement.

**Table 3.** Summary of rate coefficients for the reaction of O(<sup>1</sup>D) with NF<sub>3</sub>, CHF<sub>3</sub>, SF<sub>5</sub>CF<sub>3</sub>, and perfluorocarbons measured in this work at 296 K and reported in previous studies.<sup>a</sup>

Reactant	$k_{\text{Tot}}$ (O( <sup>1</sup> D) Loss) ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$k_{\text{R}}$ (Reactant Loss) ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Reactive Branching Ratio	Experimental Method <sup>c</sup>	Reference
NF <sub>3</sub>	$(2.55 \pm 0.38) \times 10^{-11}$	$(2.21 \pm 0.33) \times 10^{-11}$	$0.87 \pm 0.13$	RR/PLP-LIF	This Work
	$(1.20 \pm 0.25) \times 10^{-11}$	$(1.0 \pm 0.3) \times 10^{-11}$	$0.83 \pm 0.25$	PLP-LMR	Sorokin et al. (1998)
	$(2.35 \pm 0.35) \times 10^{-11}$	$(2.35 \pm 0.35) \times 10^{-11}$	$0.99 +0.01/-0.04$	PLP-RF	Zhao et al. (2010)
	$(2.0 \pm 0.3) \times 10^{-11}$	–	–	PLP-LIF	Dillon et al. (2011)
	$(2.40 \pm 0.50) \times 10^{-11}$	–	–	Rec	Sander et al. (2011)
CHF <sub>3</sub>	–	$(2.35 \pm 0.35) \times 10^{-12}$	$0.26 \pm 0.04$	RR	This Work
	$(8.40 \pm 0.80) \times 10^{-12}$	$(1.90 \pm 1.30) \times 10^{-12}$	$0.23 \pm 0.16$	PLP-RF	Force and Wiesenfeld (1981)
	$(9.76 \pm 0.60) \times 10^{-12}$	$\leq 1 \times 10^{-13}$	$< 0.01$	PLP-RF	Schmoltner et al. (1993)
	$(9.10 \pm 0.90) \times 10^{-12}$	–	–	Rec	Sander et al. (2011)
SF <sub>5</sub> CF <sub>3</sub>	$(3.24 \pm 0.50) \times 10^{-13}$	$< 5.8 \times 10^{-14}$	$< 0.3^b$	RR/PLP-LIF	This Work <sup>d</sup>
	$< 2 \times 10^{-13}$	–	–	PLP-RF	Zhao et al. (2010)
CF <sub>3</sub> CF <sub>3</sub>	–	$< 3.0 \times 10^{-14}$	$< 0.2^b$	RR	This Work
	$(1.50 \pm 0.30) \times 10^{-13}$	$< 4.5 \times 10^{-14}$	$< 0.3$	PLP-RF	Ravishankara et al. (1993)
	$< 1.50 \times 10^{-13}$	–	–	Rec	Sander et al. (2011)
c-C <sub>4</sub> F <sub>8</sub>	–	$< 3.5 \times 10^{-14}$	$< 0.04^b$	RR	This Work
	$(7.94 \pm 0.40) \times 10^{-13}$	$< 1 \times 10^{-13}$	$< 0.13$	PLP-RF	Ravishankara et al. (1993)
	$< 8 \times 10^{-13}$	–	–	Rec	Sander et al. (2011)
n-C <sub>5</sub> F <sub>12</sub>	–	$< 5.0 \times 10^{-14}$	$< 0.12^b$	RR	This Work
	$(3.94 \pm 0.30) \times 10^{-13}$	$< 1.3 \times 10^{-13}$	$< 0.3$	PLP-RF	Ravishankara et al. (1993)
	$< 4 \times 10^{-13}$	–	–	Rec	Sander et al. (2011)
n-C <sub>6</sub> F <sub>14</sub>	–	$< 1.6 \times 10^{-13}$	$< 0.16^b$	RR	This Work
	$(9.7 \pm 0.40) \times 10^{-13}$	$< 3 \times 10^{-13}$	$< 0.3$	PLP-RF	Ravishankara et al. (1993)
	$< 1 \times 10^{-12}$	–	–	Rec	Sander et al. (2011)

<sup>a</sup> The quoted uncertainties from this work are at the  $2\sigma$  level and include estimated systematic errors.

<sup>b</sup> Reactive branching ratio upper-limits were calculated using the NASA/JPL (Sander et al., 2011) recommended total reaction rate coefficient upper-limit.

<sup>c</sup> PLP, pulsed laser photolysis; LIF, laser induced fluorescence; LMR, laser magnetic resonance; RF, resonance fluorescence; RR, relative rate; Rec, Recommendation.

this study. Dilute mixtures of the reactant compounds were prepared manometrically in 12 L Pyrex bulbs. For the LIF measurements with SF<sub>5</sub>CF<sub>3</sub>, the dilute sample was passed through KMnO<sub>4</sub> (potassium permanganate) and P<sub>2</sub>O<sub>5</sub>

packed columns prior to being added to the gas flow. Ozone was produced by flowing O<sub>2</sub> through a commercial ozonizer and collected on a silica gel trap at 195 K. Dilute mixtures of

O<sub>3</sub> in He (0.1 %) were prepared off-line in a 12 L Pyrex bulb for use in the LIF experiments.

Gas flows were measured with calibrated electronic mass flow meters and pressures were measured using 10, 100, and 1000 Torr capacitance manometers. The photolysis and probe lasers were operated at 10 Hz repetition rate. The gas flow velocity, 9–16 cm s<sup>-1</sup>, ensured a fresh sample of gas in the LIF reaction volume for each photolysis pulse. All measurements were performed at ~296 K with temperatures measured using a thermocouple in direct contact with the reactors gas mixture. Stainless steel vacuum lines were used throughout the experimental apparatus. The uncertainties quoted throughout this paper are at the 2σ (95 % confidence) level unless stated otherwise.

### 3 Results and discussion

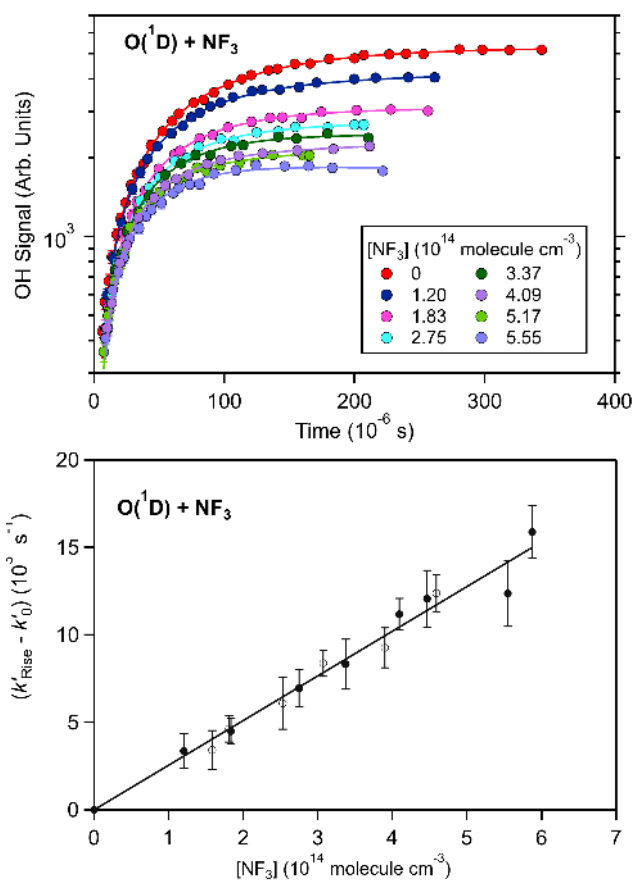
The kinetic results from this study are summarized in Tables 2 and 3. The NF<sub>3</sub>, CHF<sub>3</sub>, SF<sub>5</sub>CF<sub>3</sub>, and PFC results are presented and compared with previous studies where available separately below.

#### 3.1 O(<sup>1</sup>D) + NF<sub>3</sub>

A representative set of OH temporal profiles measured in the determination of the total rate coefficient for the O(<sup>1</sup>D) + NF<sub>3</sub> reaction is given in Fig. 1. The OH temporal profiles consist of a rapid initial rise in the OH signal, from zero, followed by a relatively slow decay at longer reaction times. With increasing NF<sub>3</sub> concentration the pseudo-first-order rise rate coefficient increases due to the increased loss of O(<sup>1</sup>D), while the nearly asymptotic OH signal at longer times decreases in magnitude. A linear least-squares fit of ( $k'_{\text{Rise}} - k'_0$ ) versus [NF<sub>3</sub>], Fig. 1, yielded  $(2.55 \pm 0.20) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the total rate coefficient, where the uncertainty is from the precision of the least-squares fit.

The competitive reaction method employed in this study was validated, in part, by determining total rate coefficients for the O(<sup>1</sup>D) reaction with *n*-C<sub>4</sub>H<sub>10</sub>, O<sub>2</sub>, and CF<sub>4</sub>. The experiments with CF<sub>4</sub> were conducted in the presence of added SF<sub>6</sub> and the CF<sub>4</sub> gas flow was passed through KMnO<sub>4</sub> and P<sub>2</sub>O<sub>5</sub> traps as used in our SF<sub>5</sub>CF<sub>3</sub> measurements. The measured values for *n*-C<sub>4</sub>H<sub>10</sub>, O<sub>2</sub>, and CF<sub>4</sub> were  $(4.75 \pm 0.20) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $(3.94 \pm 0.20) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $(2.51 \pm 0.90) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, in good agreement with previous measurements of *n*-C<sub>4</sub>H<sub>10</sub> (Blitz et al., 2004; Dunlea and Ravishankara, 2004), CF<sub>4</sub> (Ravishankara et al., 1993), and the NASA/JPL recommendation for O<sub>2</sub> (Sander et al., 2011). The quoted uncertainties are from the precision of the linear least-squares fit.

There are several determinations of the O(<sup>1</sup>D) + NF<sub>3</sub> total rate coefficient reported in the literature as summarized

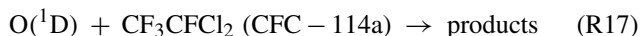
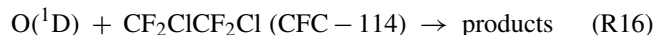
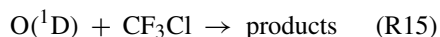
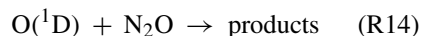


**Fig. 1.** O(<sup>1</sup>D) + NF<sub>3</sub> reaction kinetic data obtained using the competitive reaction method (see text for details). Top Panel: Representative OH temporal profiles obtained at 296 K and 35 Torr (He) for a range of NF<sub>3</sub> concentrations as given in the legend. The 2σ error bars on the data points are from the measurement precision. The O<sub>3</sub> concentration was  $3.9 \times 10^{12} \text{ molecule cm}^{-3}$  and  $[n\text{-C}_4\text{H}_{10}] = 1.3 \times 10^{13} \text{ molecule cm}^{-3}$ . The lines are non-linear least-squares fits of the OH temporal profiles (see text). Bottom Panel: Pseudo-first-order rate coefficient data,  $k'_{\text{Rise}} - k'_0$ , obtained in 2 independent experiments. The error bars are the 2σ uncertainties from the OH temporal profile fits. The line is a linear least-squares fit of the data. The results are given in Table 2.

in Table 3. The total rate coefficient determined in this work agrees to within 8 % with that reported by Zhao et al. (2010), who used a flash photolysis–resonance fluorescence technique for O(<sup>3</sup>P) detection, and is ~20 % greater than reported by Dillon et al. (2011), who used the same experimental method used in this work. Our value is ~60 % greater than that reported by Sorokin et al. (1998) and the reason for the large difference is unknown. Sander et al. (2011) recommend a total rate coefficient for use in atmospheric modeling based on the results from the Zhao et al. (2010) study.

The reactive rate coefficient for the O(<sup>1</sup>D) + NF<sub>3</sub> reaction was measured using N<sub>2</sub>O, CF<sub>3</sub>Cl, CF<sub>2</sub>ClCF<sub>2</sub>Cl (CFC-114),

and CF<sub>3</sub>CFCl<sub>2</sub> (CFC-114a) as reference compounds



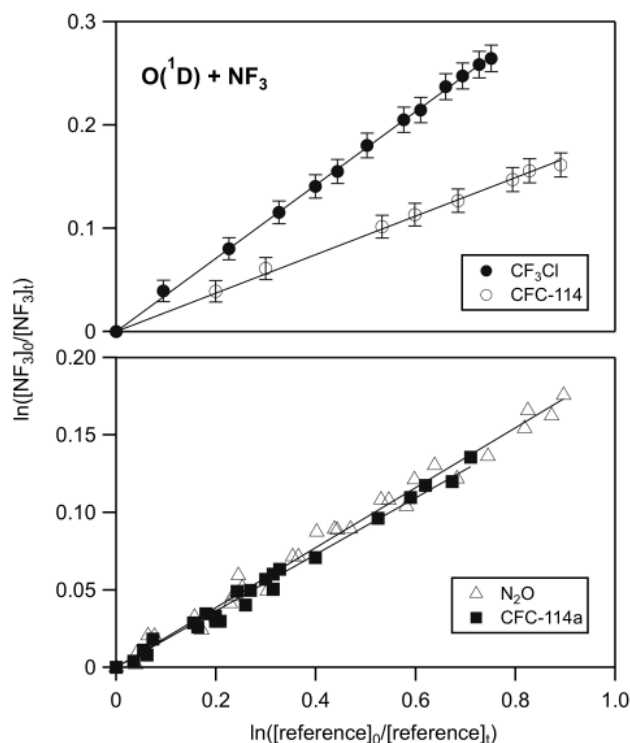
A summary of the relative rate experimental data is shown in Fig. 2. A linear least-squares fit of the experimental data resulted in reactive rate coefficient ratios of  $0.193 \pm 0.004$  (N<sub>2</sub>O),  $0.355 \pm 0.002$  (CF<sub>3</sub>Cl),  $0.186 \pm 0.003$  (CFC-114), and  $0.173 \pm 0.012$  (CFC-114a), see Table 2. The quoted uncertainties are from the precision of the linear least-squares fit to the data in Fig. 2. The reference compound rate coefficients and the obtained NF<sub>3</sub> reactive rate coefficients are also given in Table 2. The agreement among the reactive rate coefficient values obtained using the various reference compounds is very good with deviations of < 7% and an average value of  $(2.21 \pm 0.07) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where the quoted uncertainty represents the precision of the measurement. No reaction products were observed by infrared absorption for the O(<sup>1</sup>D) + NF<sub>3</sub> reaction, although CF<sub>2</sub>O from CF<sub>3</sub>Cl, as well as CF<sub>2</sub>O and CF<sub>3</sub>CFO from CClF<sub>2</sub>CClF<sub>2</sub> and CF<sub>3</sub>CFCl<sub>2</sub> were observed to be formed in the reference reactions.

The available literature data for the O(<sup>1</sup>D) + NF<sub>3</sub> reaction is summarized in Table 3. The reactive branching ratios determined in the various studies are included in Table 3 for comparison purposes. The present work and the previous studies clearly indicate that the reaction has a high reactive branching yield. Using the data obtained in our work gives a reactive branching ratio of  $0.87 \pm 0.13$ , while the Sorokin et al. (1998) study reports  $0.83 \pm 0.25$  and Zhao et al. (2010) reports  $0.99 +0.01/-0.04$ . Note that the reactive rate coefficient reported in this work is independent of the total rate coefficient and should be used in atmospheric model calculations, while a calculated reactive branching ratio would be dependent on the value chosen for total rate coefficient.

### 3.2 O(<sup>1</sup>D) + CHF<sub>3</sub>

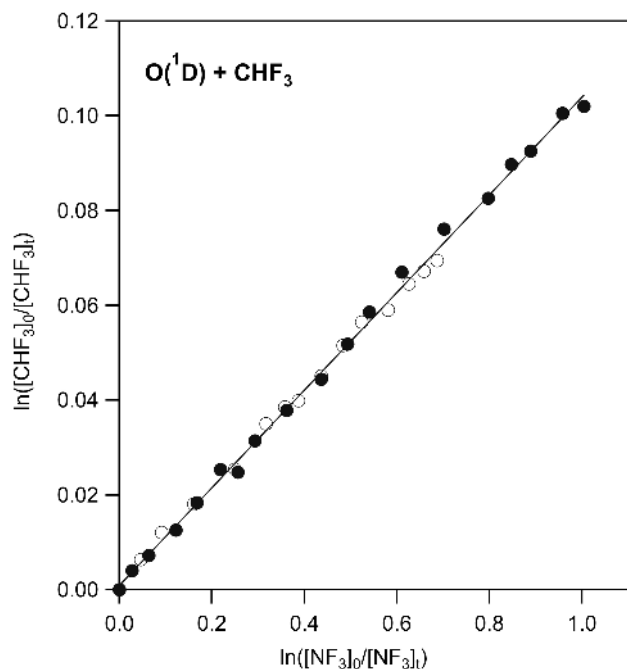
The reactive rate coefficient for the O(<sup>1</sup>D) + CHF<sub>3</sub> reaction was measured using NF<sub>3</sub> as the reference compound. The results from two separate experiments are shown in Fig. 3. A linear least-squares fit to the combined data yielded a reactive rate coefficient ratio of  $0.104 \pm 0.001$ . Using the reactive rate coefficient determined in this work for the NF<sub>3</sub> reaction yields a reactive rate coefficient for the CHF<sub>3</sub> reaction of  $(2.35 \pm 0.02) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Table 2).

The value obtained in this study is slightly greater, but more accurate, than the value of  $(1.9 \pm 1.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  reported by Force and Wiesenfeld (1981). Sander et al. (2011) recommend a total rate coefficient for this reaction of  $9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is based on the



**Fig. 2.** Reactive rate coefficient data for the O(<sup>1</sup>D) + NF<sub>3</sub> reaction at 296 K with CF<sub>3</sub>Cl, CF<sub>2</sub>ClCF<sub>2</sub>Cl (CFC-114), N<sub>2</sub>O, and CF<sub>3</sub>CFCl<sub>2</sub> (CFC-114a) as the reference compounds. The error bars on the data points (top panel) represent an estimated uncertainty in the infrared spectral analysis,  $\pm 1\%$  of the initial reactant concentration. Error bars are omitted in the bottom panel for improved clarity. The N<sub>2</sub>O and CF<sub>3</sub>CFCl<sub>2</sub> (CFC-114a) data are a combination of two separate experiments. The lines are linear least-squares fits to the data. The results are given in Table 2.

measurements of Force and Wiesenfeld (1981) and Schmoltnner et al. (1993) (see Table 3). Using this value, a reactive branching ratio of  $0.26 \pm 0.04$  is obtained from our data. This is in good agreement with the value of  $0.23 \pm 0.15$  inferred from the measured O(<sup>1</sup>D) quenching branching ratio reported by Force and Wiesenfeld [1981]. However, the reactive branching ratio of < 0.03 inferred from the reported quenching branching ratio by Schmoltnner et al. (1993) is inconsistent with the present work and that of Force and Wiesenfeld. The reason for this significant difference in reactive branching ratio is unknown. It is worth noting that our measurements demonstrate that a chemical reaction (reactant loss) occurs in the O(<sup>1</sup>D) + CHF<sub>3</sub> reaction, although collisional quenching is expected to be the dominant process. Reaction was also confirmed by the observation of infrared absorption by CF<sub>2</sub>O formed as a reaction product. Previous studies by Burks and Lin (1981), Aker et al. (1987), and Hancock et al. (2005) have reported observing the formation of vibrationally excited HF in this reaction as well, which may be formed as a co-product of CF<sub>2</sub>O.

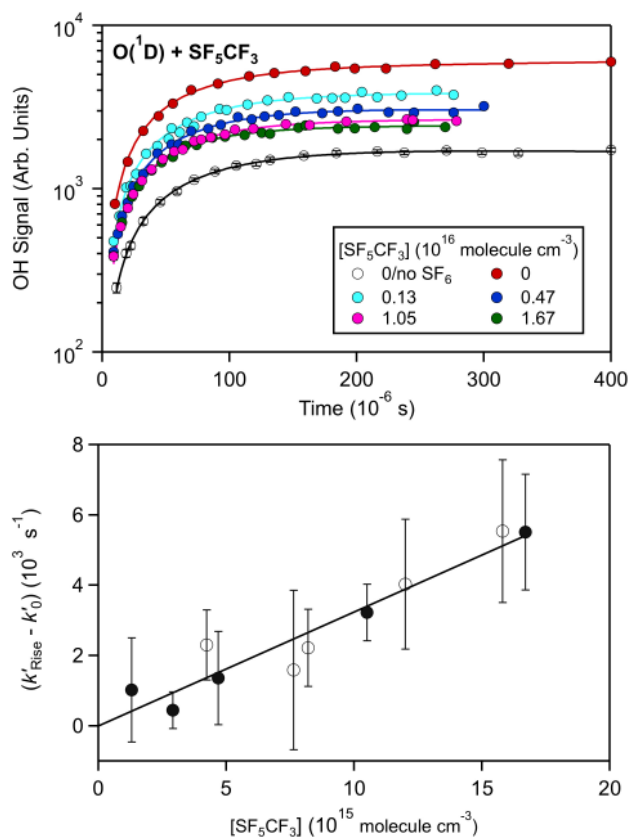


**Fig. 3.** Reactive rate coefficient data for the O(<sup>1</sup>D) + CHF<sub>3</sub> reaction with NF<sub>3</sub> as the reference compound obtained in two independent experiments (solid and open symbols). Experiments were performed at 296 K with total pressures in the range 200 to 400 Torr (He). The uncertainty in the individual data points was estimated to be  $\pm 1\%$  of the initial reactant concentration and are not included for improved clarity. The line is a linear least-squares fit to the combined dataset. The obtained rate coefficient is given in Table 2.

### 3.3 O(<sup>1</sup>D) + SF<sub>5</sub>CF<sub>3</sub>

Total rate coefficients for the O(<sup>1</sup>D) + SF<sub>5</sub>CF<sub>3</sub> reaction were measured using the competitive reaction method. An increase in OH signal intensity was observed when SF<sub>5</sub>CF<sub>3</sub> was added to the system. A similar increase in OH signal intensity was observed with addition of CF<sub>4</sub> and SF<sub>6</sub>, which are known to be efficient vibrational energy transfer collision partners (Copeland et al., 1988). The increase in OH signal is attributed to vibrational relaxation of  $v' = 1$  within the A<sup>2</sup>Σ<sup>+</sup> excited electronic state of OH that results in an increase in the intensity of OH fluorescence in the (0,0) band. As a result, in the SF<sub>5</sub>CF<sub>3</sub> experiments  $\sim 2$  Torr of SF<sub>6</sub> was added to the reaction mixture to collisionally quench  $v' = 1$  within the first 200 ns following the probe laser pulse, the quenching rate coefficient is  $3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Copeland et al., 1988). Figure 4 shows the OH temporal profiles obtained with and without the addition of SF<sub>6</sub> in the absence of SF<sub>5</sub>CF<sub>3</sub>. Figure 4 also includes a plot of the measured pseudo-first-order rate coefficient,  $k'_{\text{Rise}}$ , versus [SF<sub>5</sub>CF<sub>3</sub>]. A linear least-squares fit of the data yielded a total rate coefficient of  $(3.37 \pm 0.50) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

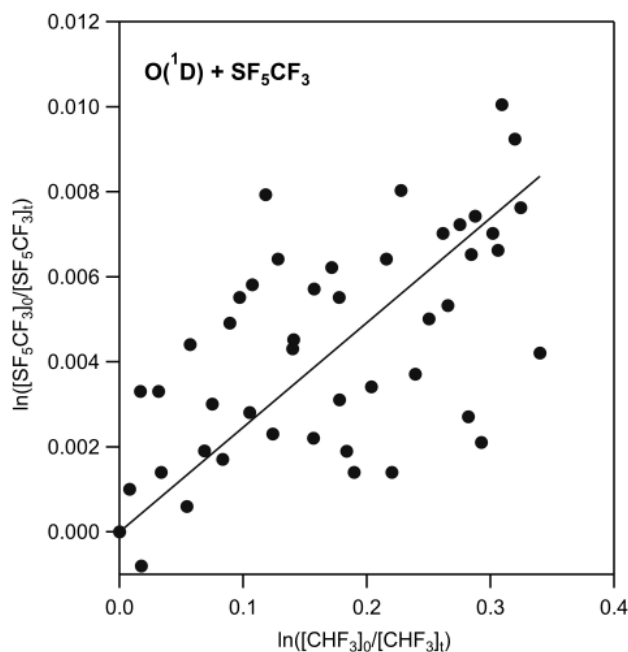
There is one previous measurement of the total rate coefficient with which to compare the present results. Zhao



**Fig. 4.** Top Panel: Representative OH temporal profiles measured for the O(<sup>1</sup>D) + SF<sub>5</sub>CF<sub>3</sub> reaction at 296 K. The 2σ error bars on the data points are from the measurement precision. The experimental conditions were 40 Torr (He) total pressure, [O<sub>3</sub>] =  $3.4 \times 10^{12} \text{ molecule cm}^{-3}$ , [*n*-C<sub>4</sub>H<sub>10</sub>] =  $1.9 \times 10^{13} \text{ molecule cm}^{-3}$ ,  $\sim 2$  Torr SF<sub>6</sub>, and [SF<sub>5</sub>CF<sub>3</sub>] given in the legend. The lines are non-linear least-squares fit to the data. Lower Panel: Total rate coefficient data from two independent experiments. The error bars are the precision of the fits as shown in the top panel. The line is the linear least-squares fit to the data. The obtained rate coefficient is given in Tables 2 and 3.

et al. (2010) reported an upper-limit for the total rate coefficient of  $< 2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The value measured in this study is significantly greater than this upper-limit. In both the Zhao et al. (2010) and the present study the measurements were influenced by possible SF<sub>5</sub>CF<sub>3</sub> sample impurities. For example, our measured rate coefficient was an order of magnitude greater when the SF<sub>5</sub>CF<sub>3</sub> sample was added directly to the PLP-LIF apparatus, i.e., bypassing the KMnO<sub>4</sub> and P<sub>2</sub>O<sub>5</sub> traps. This result indicates that reactive impurities were indeed present in our SF<sub>5</sub>CF<sub>3</sub> sample. It is entirely possible that impurities were not removed sufficiently by the traps. Possible impurities in the SF<sub>5</sub>CF<sub>3</sub> sample that were identified by the manufacturer include CS<sub>2</sub>, SO<sub>2</sub>, CF<sub>3</sub>SOF, SF<sub>6</sub>, and HF. UV absorption spectra of the SF<sub>5</sub>CF<sub>3</sub> sample showed strong absorption between 200 and 230 nm that did not match the absorption spectra of either





**Fig. 5.** Relative rate data for the O(<sup>1</sup>D) + SF<sub>5</sub>CF<sub>3</sub> reaction at 296 K with CHF<sub>3</sub> as the reference compound. The uncertainty in the individual data points was estimated to be  $\pm 1\%$  of the initial reactant concentration and are not included for improved clarity. The line is a linear least-squares fit to the data which yields a reactive branching ratio of  $0.0246 \pm 0.0029$ , where the uncertainty is from the precision of the fit (see Table 2).

CS<sub>2</sub> or SO<sub>2</sub>. The SF<sub>5</sub>CF<sub>3</sub> sample was analyzed using a gas chromatograph-coupled with quadrupole mass spectrometer (GC/MS) and found to contain  $\sim 0.1\%$  CF<sub>3</sub>SOF and  $0.2\%$  of an unidentified impurity. A reactive impurity on the order of  $\sim 0.1\%$  could interfere with the total rate coefficient measurement obtained using the competitive reaction method. The presence of impurities most likely accounts for the differences found between the total rate coefficient measured in this work and the upper-limit reported by Zhao et al. (2010).

The reactive rate coefficient was measured for the O(<sup>1</sup>D) + SF<sub>5</sub>CF<sub>3</sub> reaction using CHF<sub>3</sub> as the reference compound. A summary of the experimental data is shown in Fig. 5. The data contain significant scatter due to the fact that the overall loss of SF<sub>5</sub>CF<sub>3</sub> was very small,  $< 1\%$ , compared to that of the CHF<sub>3</sub> reference compound,  $\sim 30\%$ . A linear least-squares fit, forced through the origin, yielded a reactive rate coefficient ratio of  $(0.0246 \pm 0.0029)$ , where the quoted uncertainty is from the precision of the fit. Using  $(2.35 \pm 0.35) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the CHF<sub>3</sub> reference reaction reactive rate coefficient yields a reactive rate coefficient for the SF<sub>5</sub>CF<sub>3</sub> reaction of  $5.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . A linear least-squares fit, not forced through the origin yields a value approximately a factor of two less. The reactive rate coefficient obtained from our experiments is considered an upper-limit.

The value of  $5.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained from the relative rate measurement is approximately a factor of four less than the total rate coefficient upper-limit reported by Zhao et al. (2010) and provides a better estimate of the reactive channel. The rate coefficient for the loss of SF<sub>5</sub>CF<sub>3</sub> when combined with  $2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  total rate coefficient from Zhao et al. implies a reactive branching ratio of  $< 0.3$ .

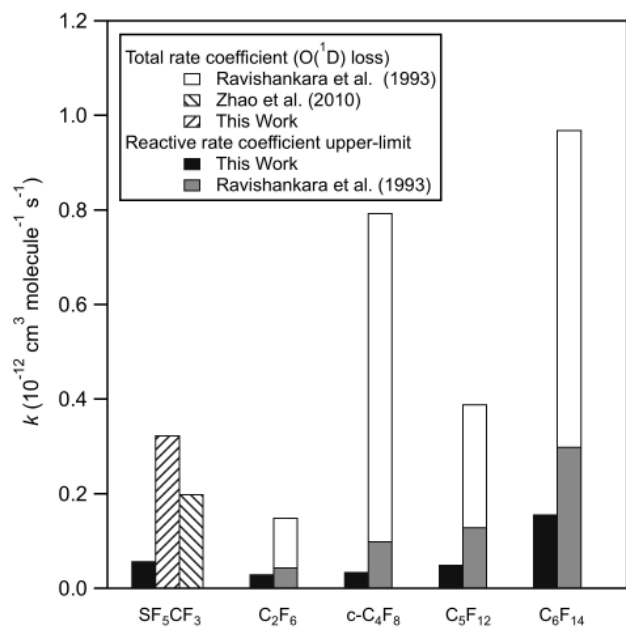
### 3.4 O(<sup>1</sup>D) + perfluorocarbons

Upper-limits for the reactive rate coefficients for the C<sub>2</sub>F<sub>6</sub>, *c*-C<sub>4</sub>F<sub>8</sub>, *n*-C<sub>5</sub>F<sub>12</sub>, and *n*-C<sub>6</sub>F<sub>14</sub> reactions with O(<sup>1</sup>D) were measured relative to the CHF<sub>3</sub> reaction. The measured PFC loss was small,  $< 1\%$ , except for *n*-C<sub>6</sub>F<sub>14</sub>, which had approximately a  $2.5\%$  loss, while the corresponding loss of the CHF<sub>3</sub> reference compound was  $\sim 30\%$ . The experimental data for these reactions was of similar quality to those shown in Fig. 5 for SF<sub>5</sub>CF<sub>3</sub>. A linear least-squares fit, forced through the origin, yielded the rate coefficient ratios given in Table 2. The reactive rate coefficients listed in Table 2 were obtained using  $2.35 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained in the present work for the O(<sup>1</sup>D) + CHF<sub>3</sub> reference reaction reactive rate coefficient.

There is one study of the O(<sup>1</sup>D) reactivity with C<sub>2</sub>F<sub>6</sub>, *c*-C<sub>4</sub>F<sub>8</sub>, *n*-C<sub>5</sub>F<sub>12</sub>, and *n*-C<sub>6</sub>F<sub>14</sub> available for comparison with the present results (Ravishankara et al., 1993). Ravishankara et al. used a time resolved vacuum UV atomic resonance fluorescence technique to detect the formation of O(<sup>3</sup>P) atoms in the O(<sup>1</sup>D) reaction. The total O(<sup>1</sup>D) rate coefficients and the branching ratios for collisional and reactive quenching of O(<sup>1</sup>D) were measured. The total rate coefficients for these reactions are in the range  $1$  to  $10 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and are given in Table 3. These rate coefficient measurements are susceptible to interference by sample impurities and Sander et al. (2011) recommends that the reported values be considered as upper-limits (see Table 3). The Ravishankara et al. study reported that the quenching branching ratio in these reactions was large, being  $> 0.70$  in most cases (Table 3). The reactive rate coefficient upper-limits measured in this work, which are in the range  $(3$  to  $16) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , are lower than reported by Ravishankara et al. (1993) due primarily to the more direct measurement in the present work. Figure 6 provides a graphical comparison of the reactive rate coefficient upper-limits determined in the present work with previously reported values.

### 3.5 Error analysis

Systematic uncertainties in the experimental parameters were low and contributed little to the overall uncertainty; uncertainties of  $\pm 1\%$  in pressure,  $\pm 2\%$  in flow rate, and  $< 1\%$  in temperature. The uncertainty in the determination of the NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub> concentrations in the reactor was  $< 5\%$  based on the agreement between concentrations determined



**Fig. 6.** Summary of the total and reactive rate coefficient data for the reaction of O(<sup>1</sup>D) with SF<sub>5</sub>CF<sub>3</sub>, C<sub>2</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub>, C<sub>5</sub>F<sub>12</sub>, and C<sub>6</sub>F<sub>14</sub> obtained in this work and reported in the literature (see legend).

by measured flow rates and online infrared absorption measurements.

Another potential source of uncertainty in the competitive reaction method is the precision with which the measured OH temporal profiles are fit. The precision of the  $k'_{\text{Rise}}$  versus concentration fits was  $\sim 9\%$ . The overall (absolute) uncertainty in the measured total rate coefficients for O(<sup>1</sup>D) reaction with NF<sub>3</sub> is estimated to be  $\sim 15\%$ . Measurements of total rate coefficients for the O(<sup>1</sup>D) reaction with *n*-C<sub>4</sub>H<sub>10</sub>, O<sub>2</sub>, and CF<sub>4</sub> validate the competitive reaction method employed in this study. In particular, the CF<sub>4</sub> experiment, which was conducted under conditions similar to those used in our SF<sub>5</sub>CF<sub>3</sub> experiments demonstrated the ability to measure rate coefficients on the order of  $10^{-13}$ – $10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> using this method. For SF<sub>5</sub>CF<sub>3</sub>, the sample purity was the primary source of uncertainty in the total rate coefficient measurement as discussed earlier. Therefore, the absolute rate coefficient reported for the SF<sub>5</sub>CF<sub>3</sub> reaction is considered an upper-limit.

In the relative rate experiments the possible loss of the reactants and reference molecules by processes other than reaction with O(<sup>1</sup>D) is a potential source of systematic error. Background loss experiments showed that in the absence of O<sub>3</sub> that compound losses were small,  $< 0.4\%$ , over a period of 3 hours. In the NF<sub>3</sub> and CHF<sub>3</sub> relative rate experiments the measurement precision was high with deviations typically  $< 2\%$ . The overall (absolute) uncertainty in these measurements was primarily determined by the uncertainty in the reference compound reactive rate coefficient. We es-

timate the overall uncertainty in the O(<sup>1</sup>D) + NF<sub>3</sub> rate coefficient determination to be  $\sim 15\%$  based primarily on the uncertainty in the reactive rate coefficients for the CF<sub>3</sub>Cl, N<sub>2</sub>O, CFC-114, and CFC-114a reference compounds. The estimated error encompasses the extremes of the measurements.

A possible interference in the O(<sup>1</sup>D) + CHF<sub>3</sub> reaction is secondary loss due to OH formation resulting from the O(<sup>1</sup>D) reaction with background levels of H<sub>2</sub>O present in the reactor. In order to minimize this interference, sufficient O<sub>3</sub> concentrations were maintained in the reactor to scavenge  $> 99\%$  of the OH radicals formed; [O<sub>3</sub>]  $\sim (3\text{--}6) \times 10^{14}$  molecule cm<sup>-3</sup> ( $7.3 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and [CHF<sub>3</sub>]  $\sim 2 \times 10^{14}$  molecule cm<sup>-3</sup> ( $2.8 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) where the OH rate coefficients for O<sub>3</sub> and CHF<sub>3</sub> are given in parenthesis (Sander et al. 2006). We estimate the overall uncertainty in rate coefficients for CHF<sub>3</sub> loss to be  $\sim 15\%$  based on the uncertainty in the NF<sub>3</sub> reactive rate coefficient and possible secondary losses.

In the determination of the PFC and SF<sub>5</sub>CF<sub>3</sub> reactive rate coefficients the measurement precision was a limiting factor. The measured reactant losses were small,  $< 1\%$ , in most cases and, most likely, were impacted by background losses. A linear least-squares fit, forced through the origin, was used to determine the rate coefficients reported here. However, an unforced fit would return a rate coefficient a factor of 2 lower. The values reported here are considered upper-limits for the reactive rate coefficient.

### 3.6 Infrared absorption spectrum of NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub>

As part of this study, the infrared absorption spectra of NF<sub>3</sub> and SF<sub>5</sub>CF<sub>3</sub> were measured quantitatively at 296 K. The results are worth noting here due to the existing discrepancies in the literature for this important input parameter in radiative forcing calculations. Infrared spectra were measured at total pressures in the range 20 to 600 Torr (He bath gas) using Fourier transform infrared (FTIR) spectroscopy with spectral resolutions of 0.5 and 1 cm<sup>-1</sup>. The measured absorbance varied linearly with concentration, Beer's law, and was independent of resolution and pressure under the range of conditions used in this study. Beer's law plots of the data are given in the Supplementary Material.

The integrated band strengths (IBS) of the two major bands of NF<sub>3</sub>, determined to be  $6.33 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup> (840–960 cm<sup>-1</sup>) and  $5.12 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup> (970–1085 cm<sup>-1</sup>), are within 3% of those reported by Robson et al. (2006) and 72% and 23% greater than the corresponding values reported by Molina et al. (1995), respectively.

The infrared absorption spectrum of SF<sub>5</sub>CF<sub>3</sub> has been studied extensively by Sturges et al. (2000), Nielson et al. (2002), Kendall et al. (2003), and Rinsland et al. (2003) and the reported band strengths agree to within  $\sim 6\%$ . The

SF<sub>5</sub>CF<sub>3</sub> band strengths obtained in the present work are in good agreement, to within 3 %, with the results from the studies of Rinsland et al. and Kendall et al., but higher, by ~5 %, than the values reported by Sturges et al. and Nielson et al.

#### 4 Conclusions

The present kinetic study refines the kinetic database for the O(<sup>1</sup>D) chemistry of a number of key atmospherically persistent greenhouse gases. Room temperature, 296 K, gas-phase rate coefficients for the reaction of O(<sup>1</sup>D) atoms with NF<sub>3</sub>, SF<sub>5</sub>CF<sub>3</sub>, CHF<sub>3</sub> (HFC-23), C<sub>2</sub>F<sub>6</sub>, *c*-C<sub>4</sub>F<sub>8</sub>, *n*-C<sub>5</sub>F<sub>12</sub>, and *n*-C<sub>6</sub>F<sub>14</sub> were determined in this study, see Table 3.

The measured total rate coefficient, i.e., O(<sup>1</sup>D) loss, for the O(<sup>1</sup>D) + NF<sub>3</sub> reaction was found to be slightly greater than reported in previous studies, although the differences are ~20 % or less. A reactive rate coefficient for the O(<sup>1</sup>D) + CHF<sub>3</sub> reaction was measured to be  $(2.35 \pm 0.35) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which when combined with the currently recommended total rate coefficient (Sander et al., 2011) corresponds to a reactive channel branching ratio of  $0.26 \pm 0.04$ . This resolves a significant discrepancy among previously reported reactive channel branching values (Force and Wiesenfeld, 1981; Schmoltner et al., 1993) for this reaction. Accounting for O(<sup>1</sup>D) reactive loss in atmospheric models will reduce the stratospheric local lifetime of CHF<sub>3</sub>, but have a lesser impact on its globally averaged lifetime of ~220 yr, which is primarily determined by its reaction with the OH radical throughout the troposphere and stratosphere.

The reactive rate coefficient upper-limit obtained for the O(<sup>1</sup>D) + SF<sub>5</sub>CF<sub>3</sub> reaction,  $< 5.8 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, is approximately a factor of 3.5 less than the total rate coefficient upper-limit reported by Zhao et al. (2010). Improved O(<sup>1</sup>D) reactive rate coefficient upper-limits were also obtained for the C<sub>2</sub>F<sub>6</sub>, *c*-C<sub>4</sub>F<sub>8</sub>, *n*-C<sub>5</sub>F<sub>12</sub>, and *n*-C<sub>6</sub>F<sub>14</sub> reactions, where the measured values are 3.0, 3.5, 5.0, and 16 (in units of 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), respectively. The improved upper-limit reactive rate coefficients will result in longer calculated atmospheric lifetimes and greater global warming potentials for these persistent greenhouse gases (WMO, 2011) than those obtained using the currently recommended rate coefficient data (Sander et al., 2011). The total rate coefficients, i.e., O(<sup>1</sup>D) loss, and the reaction rate coefficients, i.e., reactant loss, obtained in this work (summarized in Table 3) are recommended for use in climate change model calculations.

**Supplementary material related to this article is available online at:** <http://www.atmos-chem-phys.net/12/11753/2012/acp-12-11753-2012-supplement.pdf>.

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