Reactive and Non-reactive Quenching of $O(^1D)$ by the Potent Greenhouse Gases SO_2F_2, NF_3, and SF_5CF_3

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Introduction

Over the past two centuries, human activities have resulted in emission of considerable amounts of greenhouse gases to the atmosphere and raised concerns of potential global climate change [1]. Some large fluorinated compounds, e.g., chlorofluorocarbons (CFC) and perfluorinated compounds (PFC), absorb strongly in the atmospheric window region (8–12 μm) and have relatively long atmospheric lifetimes, resulting in high global warming potentials (GWPs) for these compounds. Sulfuryl fluoride (SO_2F_2), nitrogen trifluoride (NF_3), and trifluoromethyl sulfur pentafluoride (SF_5CF_3) are compounds with large GWPs that have only recently been detected in the atmosphere [2-4] (Table 1).

Table 1

Compounds	Atmospheric Mixing Ratios (ppt)	Annual Increase	Estimated τ (yr)	Estimated GWPs (100-yr.)
SO_2F_2	1.5	5%	36	4780
NF_3	0.45	11%	550	16800
SF_5CF_3	0.13	6%	950	18000

Knowledge of atmospheric destruction mechanisms for the above long-lived greenhouse gases is essential to accurately evaluate their GWPs. Very few studies have been reported that focus on the atmospheric loss processes for these compounds; hence, their atmospheric lifetimes and, therefore, their GWPs are not well established. Experimental studies have revealed that all the three compounds are inert against atmospheric oxidation and photolysis in the lower atmosphere. Therefore, some other destruction pathways that are only important in the upper atmosphere, e.g., reaction with $O(^1D)$, could play significant roles in controlling the atmospheric lifetimes and GWPs for these compounds.

Interaction of $O(^1D)$ with atmospheric trace gases often proceeds via both physical quenching and chemical reaction as shown in the following schemes for the investigated compounds,

$$O(^1D) + SO_2F_2 \rightarrow O(^3P) + SO_2F_2 \qquad (1a)$$
$$\rightarrow \text{reactive products} \qquad (1b)$$
$$O(^1D) + NF_3 \rightarrow O(^3P) + NF_3 \qquad (2a)$$
$$\rightarrow \text{reactive products} \qquad (2b)$$
$$O(^1D) + SF_5CF_3 \rightarrow O(^3P) + SF_5CF_3 \qquad (3a)$$
$$\rightarrow \text{reactive products.} \qquad (3b)$$

Assessment of the role of $O(^1D)$ reactions as atmospheric sinks for SO_2F_2, NF_3, and SF_5CF_3 requires knowledge of rate coefficients for the reactive quenching channels, i.e., k_{ib} (i = 1–3).

Experimental Approach

In this study, we have investigated $O(^1D)$ reactions with SO_2F_2, NF_3, and SF_5CF_3 by monitoring the appearance of $O(^3P)$ atoms using atomic resonance fluorescence spectroscopy (RF) following laser flash photolysis (LFP) of O_3/R/He mixtures (R = SO_2F_2, NF_3, and SF_5CF_3). A schematic diagram of the LFP-RF apparatus is shown in Figure 1. As a part of this study, the reactions of $O(^1D)$ with SO_2, and CS_2 have also been investigated for the first time in order to evaluate the effects on the observed kinetics of reactive impurities present in the SF_5CF_3 sample.

$$O(^1D) + SO_2 \rightarrow O(^3P) + SO_2 \qquad (4a)$$
$$\rightarrow \text{other products} \qquad (4b)$$
$$O(^1D) + CS_2 \rightarrow O(^3P) + CS_2 \qquad (5a)$$
$$\rightarrow \text{other products} \qquad (5b)$$

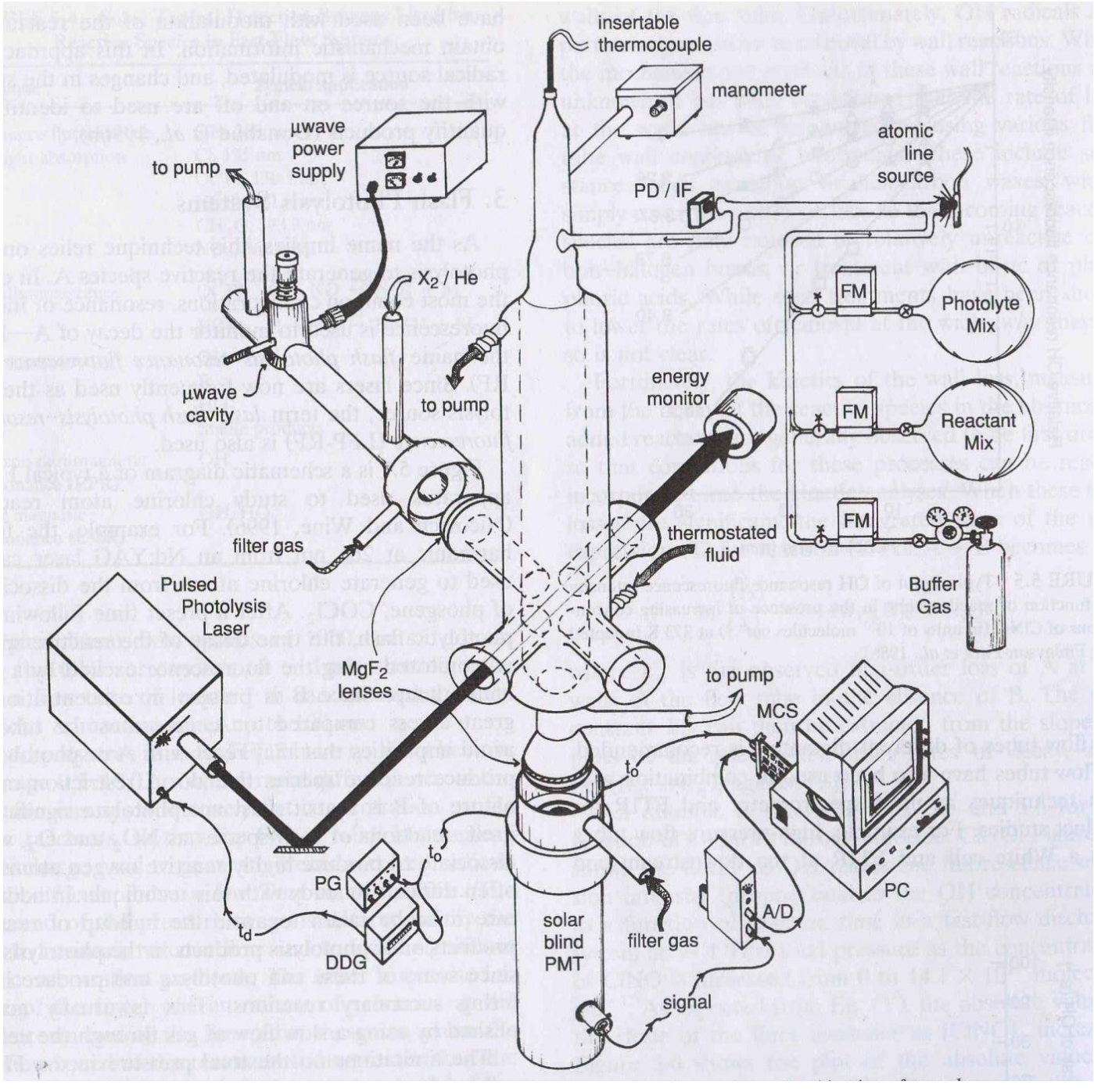

Figure 1. *Schematic of LFP−RF apparatus.*

PG: Pulse Generator
DDG: Digital Delay Generator
A/D: Amplifier/Discriminator
PMT: Photomultiplier Tube
FM: Mass Flow Meter
PD/IF: Photodetector /Interference Filter
MCS: Multichannel Scalar

Results

$O(^1D)$ atoms were produced by 248 nm laser flash photolysis (LFP) of ozone (O_3) in He buffer gas.

$$O_3 + h\nu\ (248\text{ nm}) \rightarrow O(^1D) + O_2 \qquad (6a)$$
$$\rightarrow O(^3P) + O_2 \qquad (6b)$$

The observed temporal profile of $O(^3P)$ in the presence of a reagent gas (R) allows both the overall rate coefficient and the $O(^3P)$ yield from the $O(^1D)$ + R reaction to be determined.

The temporal profiles of $O(^3P)$ fluorescence signal (Figure 2) following the laser flash are described by the double exponential expression

$$S_t = \frac{Ak_a}{k_d - k_a}[\exp(-k_a t) - \exp(-k_d t)] + B\exp(-k_d t)$$

S_t is the fluorescence signal at time t after the laser flash, k_a is the pseudo first-order rate coefficient for $O(^3P)$ appearance, k_d is the rate coefficient for $O(^3P)$ decay (assumed to be first-order), and the parameters A and B are related to the concentrations of $O(^1D)$ and $O(^3P)$ produced by the laser flash.

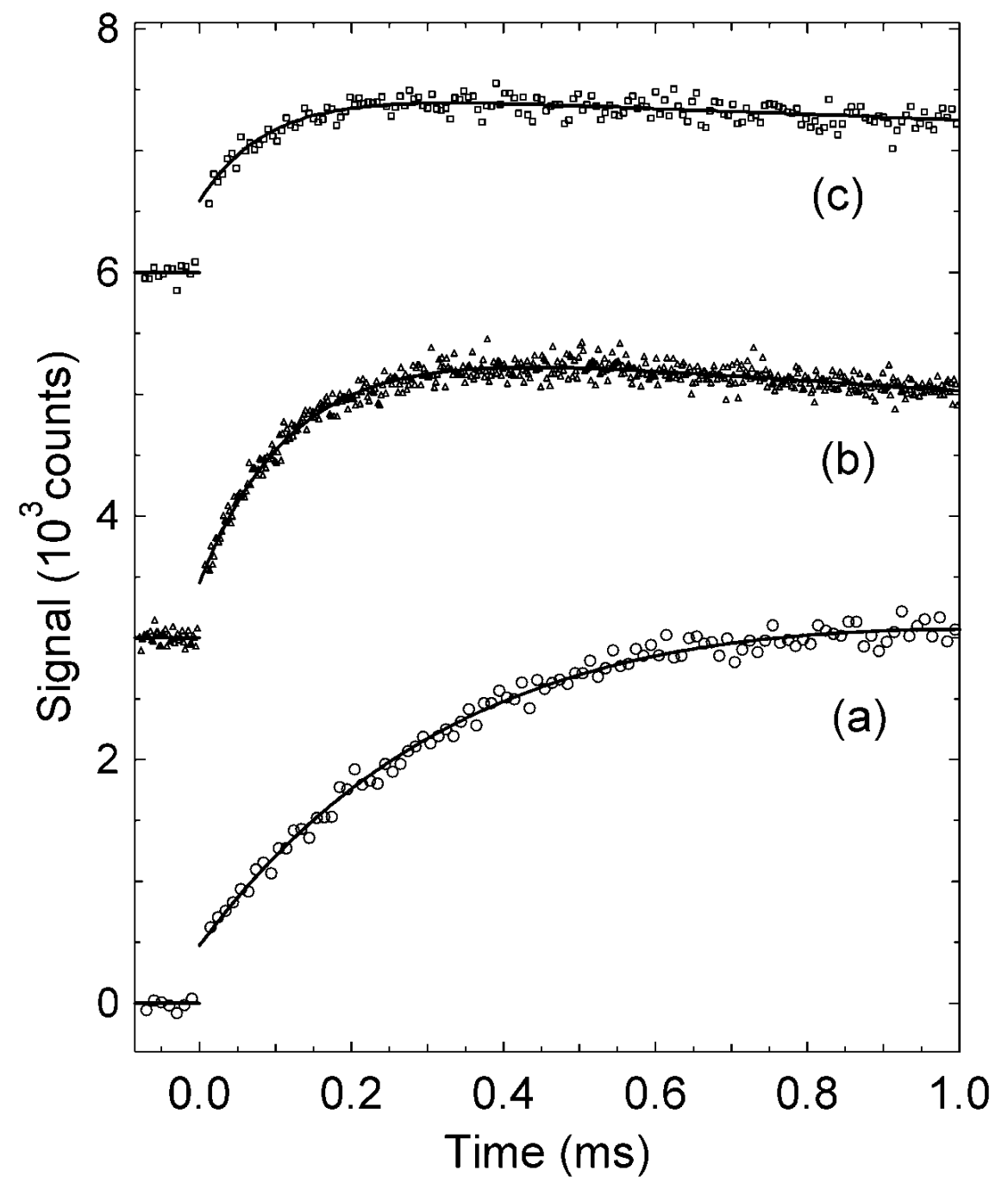

Figure 2. *Typical $O(^3P)$ appearance temporal profiles observed following LFP of O_3/R/He mixtures. T = 298 K and P = 30 Torr. Reagent gas identities and concentrations in units of 10^{14} molecules cm^{-3} are: (a) no reagent gas; (b) 0.457 SO_2F_2; (c) 3.66 NF_3.*

Experimental data were fit to the equation above using a nonlinear least squares method to obtain values for the parameters A, B, k_a, and k_d. These fit parameters are related to the overall rate coefficient k_i and the physical quenching rate coefficient k_{ia} as follows:

$$k_a = k_i[R] + k_a^0$$

where k_a^0 is the value of k_a when [R] = 0 (trace a in Figure 2) and

$$\frac{\beta^* k_a}{\beta} - \frac{\beta^* k_a^0}{\beta^0} = k_{ia}[R]$$

where β = B/A, β^0 is the values of β when [R] = 0 and β* is the value of β in the limit where $O(^1D)$ is converted to $O(^3P)$ with unit yield. The value of β* can be calculated from the quantum yield for $O(^3P)$ production from O_3 photolysis at 248 nm, $\Phi_{O(3P)}$, which has been carefully measured as a function of temperature [5] $\Phi_{O(3P)} = (0.115 \pm 0.030)\exp[(35 \pm 60)/T]$. Therefore, k_i and k_{ia} are obtained from the slopes of the plots of k_a or $\beta^* k_a/\beta$ versus [R] (Figure 3).

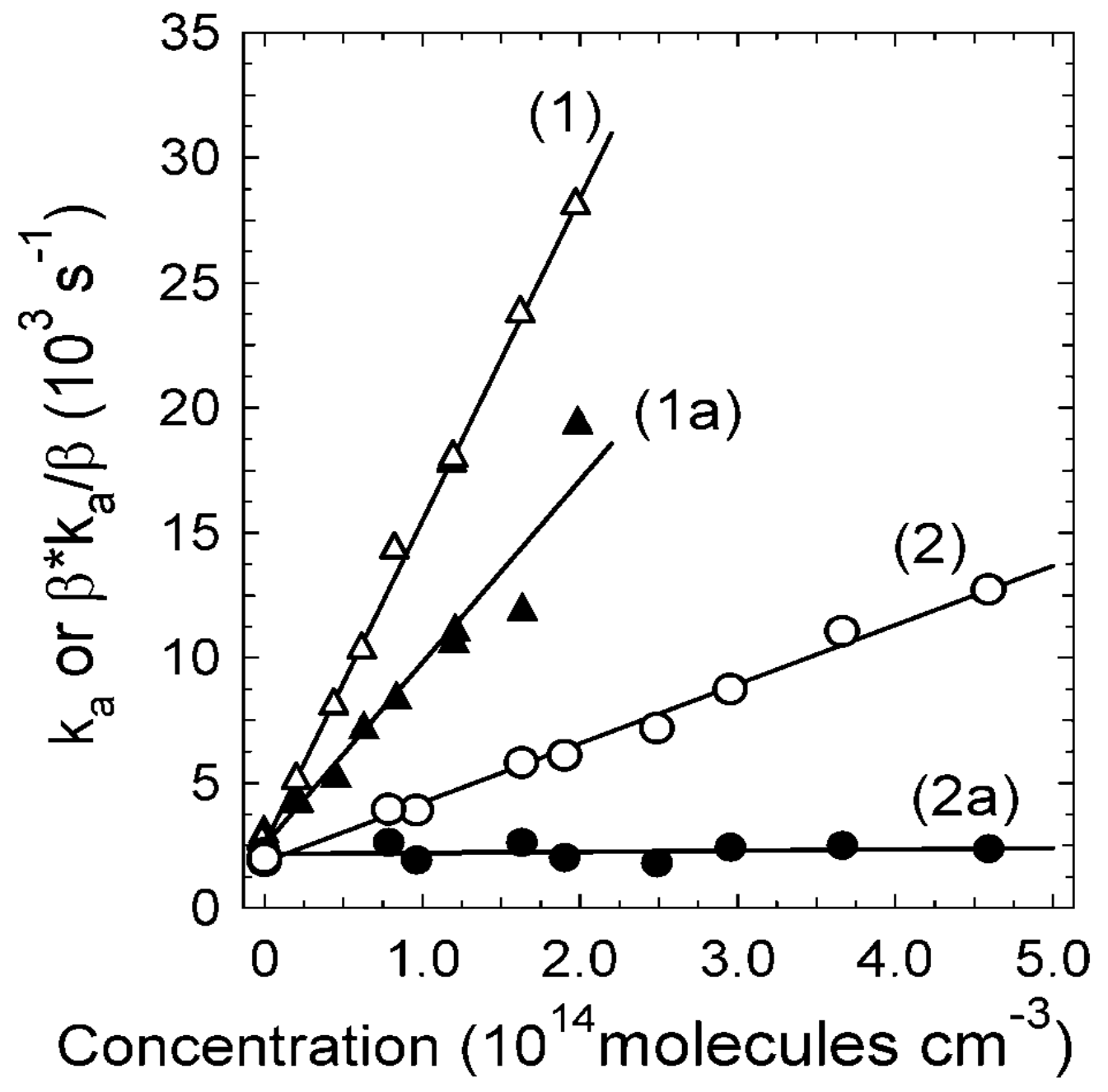

Figure 3. *Plots of k_a (open symbols) and $\beta^* k_a/\beta$ (filled symbols) versus reagent gas concentration for data obtained at 298 K. Triangles are data for $O(^1D) + SO_2F_2$ while circles are data for $O(^1D) + NF_3$.*

(a) $O(^1D)$ Reactions with SO_2F_2 and NF_3

The removal of $O(^1D)$ by SO_2F_2 and NF_3 is found to be very efficient. The overall rate coefficients for k_1 and k_2 are obtained as functions of temperature over the range 199 – 351 K (units are cm^3 $molecule^{-1}$ s^{-1}; uncertainties are 2σ, precision only):.

$$k_1(T) = (8.96 \pm 1.44) \times 10^{-11} \exp[+(98 \pm 41) / T]$$
$$k_2(T) = (1.96 \pm 0.04) \times 10^{-11} \exp[+(52 \pm 5) / T].$$

Arrhenius plots for k_1 and k_2 are shown in Figure 4. For the $O(^1D) + SO_2F_2$ reaction, the physical quenching rate coefficients are well-described by the Arrhenius expression (also shown in Figure 4)

$$k_{1a}(T) = (3.75 \pm 1.78) \times 10^{-11} \exp[+(171 \pm 121) / T].$$

The rate coefficient for reactive quenching is found to be $k_{1b} = 5.8 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} independent of temperature (199 – 351 K). The values for k_1 and k_{1b} obtained in this study are in excellent agreement with one previous investigation [6].

For the $O(^1D) + NF_3$ reaction, the average value of the $O(^3P)$ yield at four investigated temperatures is $\alpha_2 = 0.007 \pm 0.031$ and we choose to report an upper limit for the $O(^3P)$ yield from reaction [2] of $\alpha_2 < 0.05$ over the temperature range 199 – 351 K. The value for k_2 found in this work at 298 K is a factor of 2 greater than a previous study and the reactive quenching branching ratio is also slightly greater [7].

(b) $O(^1D)$ Reaction with SF_5CF_3

The deactivation of $O(^1D)$ by SF_5CF_3 is very slow. Moreover, the $O(^3P)$ fluorescence signal following LFP of O_3/SF_5CF_3/He mixtures is found to be subject to interference from chemiluminescence, which appears to result from chemistry initiated by $O(^1D)$ reaction(s) with one or more SF_5CF_3 impurities.

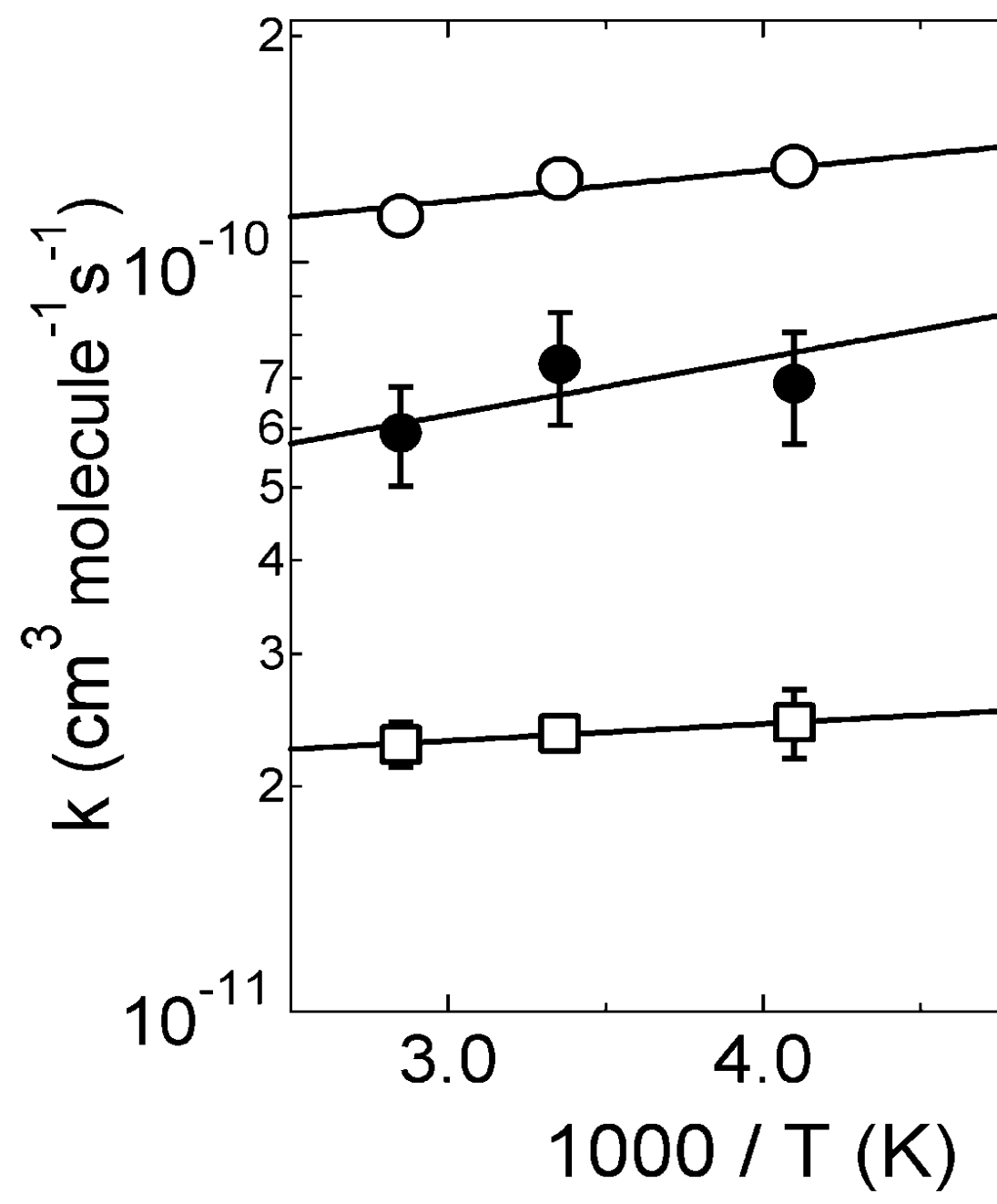

Figure 4. *Arrhenius plots for $O(^1D)$ reactions with SO_2F_2 (circles) and NF_3 (squares). Open symbols are rate coefficients for overall deactivation of $O(^1D)$ and filled circles are rate coefficients for physical quenching of $O(^1D)$ by SO_2F_2.*

Based on a qualitative analysis from the SF_5CF_3 supplier, two potentially important reactive impurities are CS_2 and SO_2. In order to quantify the influence of these impurities, we carried out experiments where $O(^1D)$ quenching by SO_2 and CS_2 was investigated at 298 K.

For the reaction of $O(^1D)$ with SO_2, no chemiluminescence was observed. The overall rate coefficient and the physical quenching branching ratio were found to be

$$k_4 = (2.17 \pm 0.10) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$\alpha_4 = 0.243 \pm 0.025 \text{ (uncertainties are } 2\sigma\text{, precision only).}$$

Chemiluminescence was observed following LFP of O_3/CS_2/He mixtures (Figure 5); the origin of this chemiluminescence has not been identified. After subtracting the lamp-off signal, the overall rate coefficient and the physical quenching branching ratio were

$$k_5 = (4.63 \pm 0.31) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$\alpha_5 = 0.06 \pm 0.04 \text{ (uncertainties are } 2\sigma\text{, precision only).}$$

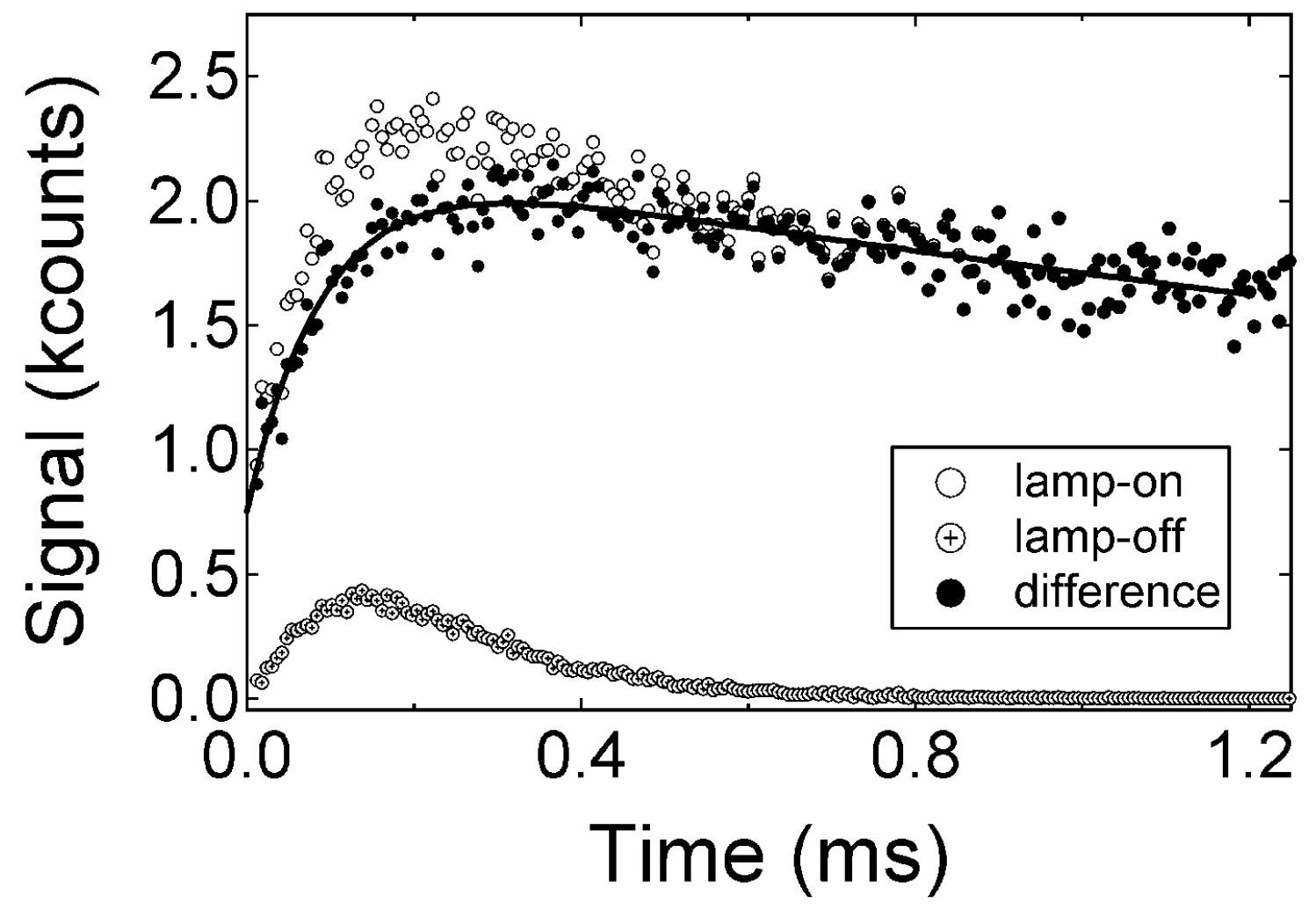

Figure 5. *Typical signal temporal profiles observed in the $O(^1D) + CS_2$ study.*

The SF_5CF_3 sample was purified by passage through silica gel, which reduced the CS_2 impurity mole fraction to $< 2 \times 10^{-4}$; this significantly decreased the chemiluminescence. After subtracting the residual CS_2 contributions, we report the upper limit rate coefficient $k_3 < 2.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K The physical quenching rate coefficient, k_{3a}, and the $O(^3P)$ yield, α_3, were not determined because of the interference from impurity reactions. The observed low reactivity of SF_5CF_3 towards $O(^1D)$ is consistent with one previous semi-quantitative study [8].

Atmospheric Implications

Reaction with $O(^1D)$ is found to be the major sink for SO_2F_2 in the upper atmosphere while UV photolysis represents an additional minor sink [9]. However, in the lower atmosphere, ocean uptake and hydrolysis have recently been proposed as an efficient removal pathway for SO_2F_2 and this mechanism limits its atmospheric lifetime to 36 ± 11 years, implying a GWP of 4780 (100-year time horizon) [2]. If the rate of oceanic uptake is evaluated properly, then $O(^1D)$ reaction would be only a minor loss pathway for SO_2F_2 in the atmosphere.

Reaction with $O(^1D)$ appears to be an important atmospheric sink for NF_3. Including the $O(^1D)$ reaction with k_{2b} equal to the value reported by Sorokin et al. [7], i.e., 1.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, reduces the modeled NF_3 lifetime from 640 years to 550 years, and reduces the 100-year GWP from 17200 to 16800 [10]. The value of k_{2b} reported in this study is more than a factor of two faster than the one reported by Sorokin et al. [7], suggesting a greater contribution of $O(^1D)$ reaction to NF_3 destruction, a significantly shorter atmospheric lifetime for NF_3, and a somewhat lower GWP for NF_3.

The rate coefficient for $O(^1D)$ reaction with SF_5CF_3 reported in this study is too slow for $O(^1D)$ reaction to be a significant sink for SF_5CF_3 in the atmosphere. The destruction of SF_5CF_3 is thought to be dominated by dissociative electron attachment in the middle and upper atmosphere [11,12], which limits its atmospheric lifetime to ~950 years and suggests a 100-year GWP of ~18000 [13], the second largest GWP (after SF_6) for known atmospheric gases.

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