Mesoscopic Removal of Very Long-Lived Greenhouse Gases SF₆ and CFC-115 by Metal Reactions, Lyman-α Photolysis, and Electron Attachment

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ABSTRACT: The fluorinated gases SF₆ and C₂F₅Cl (CFC-115) are chemically inert with atmospheric lifetimes of many centuries which, combined with their strong absorption of IR radiation, results in unusually high global warming potentials. Very long lifetimes imply that mesospheric sinks could make important contributions to their atmospheric removal. In order to investigate this, the photolysis cross sections at the prominent solar Lyman-α emission line (121.6 nm), and the reaction kinetics of SF₆ and CFC-115 with the neutral meteoric metal atoms Na, K, Mg, and Fe over large temperature ranges, were measured experimentally. The Na and K reactions exhibit significant non-Arrhenius behavior; quantum chemistry calculations of the potential energy surfaces for the SF₆ reactions indicate that the Na and K reactions with SF₆ are probably activated by vibrational excitation of the F-SF₅ (v₁) stretching mode. A limited set of kinetic measurements on Na + SF₅CF₃ are also presented. The atmospheric removal of these long-lived gases by a variety of processes is then evaluated. For SF₆, the removal processes in decreasing order of importance are electron attachment, VUV photolysis, and reaction with K, Na, and H. For CFC-115, the removal processes in decreasing order of importance are reaction with O(1D), VUV photolysis, and reaction with Na, K, and H.

1. INTRODUCTION

Characterizing the atmospheric lifetimes (τ) of the perfluorinated compounds (PFCs), SF₆, SF₅CF₃, and C₂F₅Cl (CFC-115), is a crucial step in assessing their potential impact on global warming. These PFCs are potent greenhouse gases which possess large global warming potentials (GWPs) resulting from a combination of strong infrared absorptions in the atmospheric window and very long atmospheric lifetimes. Species for which τ ≥ 300 years may be predominantly destroyed in the mesosphere by processes such as far-UV photolysis and electron attachment, requiring general circulation models to account for their transport into the upper stratosphere and mesosphere.

To date, the most potent greenhouse gas to have been reviewed by the Intergovernmental Panel on Climate Change (IPCC) is SF₆ which has a projected lifetime of 3200 years with a 100 year GWP of 23500.5 Industrial applications of SF₆ are primarily in fluid insulation, electronics, and switchgear.6 Its long lifetime together with increasing industrial usage has led to a marked increase in the atmospheric mixing ratio of SF₆. The gas was not detected in the atmosphere prior to its usage in industry, indicating it to be entirely anthropogenic. Its current tropospheric mixing ratio is around 8 ppt, increasing at an average rate of 0.26 ppt yr⁻¹ since 1995.7 SF₅CF₃ is a very potent greenhouse gas, with a long atmospheric lifetime of approximately 800 years and a GWP in the region of 17500.8 Although not used industrially, this gas appears to be a byproduct of the manufacture of fluorosurfactants. CFC-115 was initially introduced as a refrigerant in the 1970s and prior to this was not detected in the atmosphere. Maione et al.9 reported a 2011 concentration of 8.4 ppt; following its proscription, a decreasing trend of 0.01 ppt yr⁻¹ has been observed.9 CFC-115 has a currently estimated 100 year GWP of 7370 based on the atmospheric lifetime used by the IPCC of 1020 years.5 However, this lifetime has since been revised to 340 years following the re-evaluation of its removal by reaction with O(1D).10

In this paper, we consider mesospheric removal processes of these PFCs which could potentially lead to an overestimate of atmospheric lifetimes if ignored. We first address the potential reactions between the PFCs and the metal atoms which are injected into the upper mesosphere by cosmic dust ablation.11 The most abundant of these metals are Fe, Na, Mg, and K, which occur in layers between 80 and 105 km with peak concentrations of approximately 10000, 5000, 3000, and 80 cm⁻³, respectively.12 In order to quantify the potential role of metal atoms in the atmospheric lifetimes of these PFCs, in this study we report rate constant measurements of the following reactions:

\[ \text{Na + SF}_6 \rightarrow \text{NaF + SF}_3 \quad \Delta H_r (298 K) = -85 \text{ kJ mol}^{-1} \]  
(R1)

\[ \text{Na + SF}_5\text{CF}_3 \rightarrow \text{NaF + SF}_3\text{CF}_3 \quad \Delta H_r (298 K) = -102 \text{ kJ mol}^{-1} \]  
(R2)

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Na + CFCFCl Cl → NaCl + CFCF
\[ \Delta H_f(298 \text{ K}) = -131 \text{ kJ mol}^{-1} \quad (R3) \]
K + SF₆ → KF + SF₅ \[ \Delta H_f(298 \text{ K}) = -97 \text{ kJ mol}^{-1} \quad (R4) \]
K + CFCFCl CFCF → KCl + CFCF
\[ \Delta H_f(298 \text{ K}) = -143 \text{ kJ mol}^{-1} \quad (R5) \]
Fe + SF₆ → FeF + SF₅ \[ \Delta H_f(298 \text{ K}) = -55 \text{ kJ mol}^{-1} \quad (R6) \]
Mg + SF₆ → MgF + SF₅ \[ \Delta H_f(298 \text{ K}) = -71 \text{ kJ mol}^{-1} \quad (R7) \]

The significant exothermicities of these reactions are calculated from a compilation of bond energies, except for the enthalpy change for reaction R2 which was calculated using electronic structure theory (see Discussion). Calculations at the same level of theory show that the formation of SF₅CF₂ in reaction R2 is endothermic by 17 kJ mol⁻¹, so that this reaction channel should not be important over the temperature range in this study. The choice of the four metals is therefore based on their exothermicity.

Apart from reactions R1 and R4 which have been studied previously (though with apparently significant disagreement in the case of the Na + SF₆ reaction),¹⁴–¹⁶ the kinetics of the other reactions do not appear to have been measured. We then discuss the complex temperature dependencies of the Na and K reactions in some detail. In addition, we report measurements of the Lyman-α (121.6 nm) absorption cross sections of SF₆ and CFC-115. Photolysis is currently recognized as the major sink of SF₅CF₃,¹⁷ Note that the vertical electron affinity of CFC-115 is 1.3 eV (calculated using the level of theory described in Discussion), so that thermal electron attachment to this PFC is not significant. The rate constant for the reaction of O(1D) with SF₆ has an upper limit of 1.3 cm⁻³ molecule⁻¹ s⁻¹,¹⁸ which is consistent with an endothermicity of 38 kJ mol⁻¹.¹³ These two processes are therefore not considered further.

3. RESULTS
3.1. Metal Atom Reactions.
In the FFT study of reaction R1, SF₆ was kept in excess of Na, ensuring pseudo first-order conditions, resulting in the following expression:

\[ k' = - \ln \left( \frac{[\text{Na}]_{t}}{[\text{Na}]_{0}} \right) = - \ln \left( \frac{S_{\text{Na}}'}{S_{\text{Na}}^0} \right) \]  

where \( k' \) is the pseudo first order loss rate, \( t \) is the contact time, and \([\text{Na}]_{t}\) and \([\text{Na}]_{0}\) are the Na concentrations with and without SF₆ present at time \( t \), respectively. \( S_{\text{Na}}' \) and \( S_{\text{Na}}^0 \) are the LIF signals proportional to these concentrations. The contact time, \( t \), is calculated from the plug flow velocity calculated from the mass flow rate and pressure, reduced by 5% to account for gas mixing by diffusion and with the centroid correction coefficient (0.63) applied to correct for the parabolic flow profile within the tube.²²,²³ We have shown previously,²⁴ using the pulsed laser ablation of metal targets in the same flow tube, that these corrections produce an accurate estimate (within 4%) of the contact time. Six measurements of \( k' \) were taken at different contact times, from which a rate constant of \( k_1(290 \text{ K}) = (9.83 \pm 0.61) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) was obtained.

In the PLP-LIF experiments, the PFC (SF₆ or CFC-115) was also maintained in excess over the metal atoms to ensure pseudo first-order conditions. This resulted in the LIF signal decaying exponentially with time:

\[ \frac{[X]_{t}}{[X]_{0}} = \frac{S_t}{S_0} = \exp(-k't) \]  

where \([X]_{t}\) and \([X]_{0}\) are the concentrations of metal atom \( X \) (\( X = \text{Na}, \text{K}, \text{Mg}, \text{or Fe} \)), with corresponding LIF signals \( S_t \) and \( S_0 \) at the delays \( t \) and 0, respectively.

The Lyman-α (121.6 nm) absorption cross sections of SF₆ and CFC-115 were measured using an absorption cell coupled to a H₂/He radiofrequency discharge light source, as described elsewhere.²²

Materials. Reactant gas mixtures for the experiments were prepared on all-glass vacuum lines. The gases N₂ (99.99999%, BOC), SF₆ (99.999%, BOC), and He (99.99999%, BOC) were used without further purification. Samples of CFC-115 and SF₅CF₃ were provided by Professor William Sturges (University of East Anglia). These were purified by freeze–thaw-distillation on a glass vacuum line and the purity confirmed by IR spectroscopy. The metal-atom precursors, sodium (98% Sigma-Aldrich), sodium iodide (Sigma-Aldrich 98%), potassium iodide (Sigma-Aldrich 99%), magnesium acetyl acetone (Sigma-Aldrich 98%), and ferrocene (Sigma-Aldrich 98%), were purified under vacuum (heating where appropriate) for at least an hour before kinetic experiments commenced, as described previously.²²
The loss rate of metal is described by the pseudo first-order decay coefficient $k'$:

$$k' = k'_{\text{diff}} + k [\text{PFC}]$$  \hspace{1cm} (E3)

where $k'_{\text{diff}}$ represents the diffusion of metal atoms out of the dye laser beam volume within the field of view of the photomultiplier tube and $k$ is the second-order rate constant.

From E3, a plot of $k'$ against $[\text{PFC}]$ yields a line with slope $k$ and intercept $k'_{\text{diff}}$. Figure 1 shows bimolecular plots for R1 at three temperatures (585, 717, and 879 K). Second-order rate constants for R1–R7 were measured over the range of temperatures listed in Tables 1, 2, 3, 4, 5, 6, and 7, respectively, where the given uncertainty encompasses the error of the weighted least-squares linear fits to the kinetic plots and the uncertainty in the concentration of gas mixtures.

### 3.2. Lyman-α Absorption.

Examples of the absorbance data for SF$_6$ and CFC-115 as a function of concentration are shown in Figure 2. Linear regression analysis yielded $\sigma(\text{SF}_6)_{121.6 \text{ nm}} = (1.37 \pm 0.12) \times 10^{-18} \text{ cm}^2$ and $\sigma(\text{CFC-115, 121.6 nm}) = (4.27 \pm 0.35) \times 10^{-18} \text{ cm}^2$, where the uncertainties are at the 95% confidence level and include the uncertainty in gas concentration.
4. DISCUSSION

4.1. Reactions with Metal Atoms. Arrhenius plots describing the temperature dependence of the rate constants for R1–R7 are illustrated in Figures 3–5. Reactions R1, R3, and R4 exhibit non-Arrhenius behavior, so their rate constants were expressed as the sum of two Arrhenius terms which capture the high- and low-temperature regimes:

\[ k(T) = A \exp(-B/RT) + C \exp(-D/RT) \]  

(E4)

where \( A \) and \( C \) represent the pre-exponential terms of the high and low temperature regimes, respectively, and \( B \) and \( D \) are the respective activation energies (\( R \) is the gas constant):

\[
k_1(\text{Na + SF}_6, 212 – 879 \text{ K})
\]

\[
= (19.0 \pm 17.2) \times 10^{-10} \exp[-(28.7 \pm 6.7) \text{ kJ mol}^{-1}/RT] + (3.58 \pm 0.08) \times 10^{-10} \exp[-(14.3 \pm 0.5) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k_3(\text{Na + C}_2\text{F}_3\text{Cl}, 248 – 868 \text{ K})
\]

\[
= (5.92 \pm 3.45) \times 10^{-10} \exp[-(35.4 \pm 3.2) \text{ kJ mol}^{-1}/RT] + (1.84 \pm 0.14) \times 10^{-11} \exp[-(17.4 \pm 0.3) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

These expressions were obtained by first fitting a subset of low-temperature rate constants to a single Arrhenius term (i.e., determining parameters \( C \) and \( D \)), and then fitting the complete data set to E4 to obtain \( A \) and \( B \). The extent of the low-temperature regime was determined by performing an iterative calculation where data points were incorporated stepwise to the low temperature subset to ensure a physically sensible value for \( A \) (set to an upper limit of \( 3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)). Approximately 75% and 60% of the uncertainty in the high-temperature pre-exponential factor and activation energy terms, respectively, are attributable to the full data set fit, with the remainder propagating from the low temperature fit.

No significant curvature was observed in the other reactions, and these were fitted to single Arrhenius term expressions:

\[
k_3(\text{Na + SF}_5\text{CF}_3, 327 – 875 \text{ K})
\]

\[
= (6.61 \pm 0.78) \times 10^{-10} \exp[-(15.2 \pm 0.4) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k_5(\text{K + SF}_6, 207 – 817 \text{ K})
\]

\[
= (27.7 \pm 9.6) \times 10^{-10} \exp[-(16.8 \pm 1.7) \text{ kJ mol}^{-1}/RT] + (1.79 \pm 0.20) \times 10^{-10} \exp[-(4.44 \pm 0.25) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

These fits to the experimental data points are shown in Figures 3–5. Inspection of Figures 3 and 4 show that Na and K react significantly faster with SF6 than C2F3Cl, and the K reactions are \( \sim 5–120 \) times faster than the corresponding Na reactions at the same temperature. The rate constants for Na + SF6 and Na + SF5CF3 are almost identical (Figure 3). Figure 5 shows

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**Table 7. Rate Constants for R7 (Mg + SF6)**

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( k \left(10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>449</td>
<td>(0.23 ± 0.09)</td>
</tr>
<tr>
<td>568</td>
<td>(1.11 ± 0.39)</td>
</tr>
<tr>
<td>631</td>
<td>(2.54 ± 0.65)</td>
</tr>
<tr>
<td>738</td>
<td>(9.38 ± 1.52)</td>
</tr>
<tr>
<td>792</td>
<td>(23.60 ± 4.26)</td>
</tr>
</tbody>
</table>
The reaction cross section increased by a factor of 1.5 when the SF₆ temperature was increased from 300 to 580 K, from which they concluded that excitation of the stretching modes of SF₆ enhanced its reactivity toward K. Additionally, Riley and Herschbach²⁹ showed that the differential cross sections exhibit roughly symmetrical forward and backward scattering, indicating that the reaction proceeds via a collision complex which persists for at least several rotational periods.

Although reactions R₁−R₇ are quite exothermic (see Introduction), their rate constants are in general significantly smaller than their respective collision frequencies at 300 K [e.g., k(K + SF₆) is a factor of ~10 smaller], k(Na + SF₆) is smaller by ~2 orders of magnitude, and the other reactions are even slower. In order to gain deeper insight into the metal atom + SF₆ kinetics, potential energy surfaces (PESs) for the Na, K, and Mg + SF₆ reactions were calculated at the MP2(full)/6-311+g(2d) level of theory using the Gaussian 09 suite of programs. At this level of theory, the calculated reaction enthalpy changes (including a counterpoise correction for basis set superposition error) agree very well with the literature values shown in parentheses: ΔH°(Na + SF₆) = −90 (−85); ΔH°(K + SF₆) = −98 (−97); and ΔH°(Mg + SF₆) = −74 (−71) kJ mol⁻¹. The Møller–Plesset correlation energy correction and this choice of basis set therefore seems to provide reasonably accurate energies over these surfaces where there is a switch from the covalent character in the entrance channel to ionic character in the exit channel where the metal fluoride forms. At each point on the PES, a new initial guess for the Hartree–Fock wave function was generated to ensure that the lowest energy surface was chosen. <S²> values ranged from 0.750 to 0.763 on the Na and K + SF₆ surfaces, demonstrating little spin contamination in the unrestricted Hartree–Fock calculations used for these surfaces.

Figure 6 shows PESs for the three reactions (not including zero-point energies). These surfaces illustrate the case where the metal atom attack is collinear with one of the S–F bonds. The scan is therefore along the S–F–M (M = metal atom) linear coordinate, where r₅₋ₓ and rₓ₋₆ are varied. Since the geometry of the SF₅ moiety is frozen in these scans, the surface does not represent the lowest possible energy path from reactants to products. However, the difference is not significant: for the Mg + SF₆ surface, the fully optimized transition state has a barrier of 48 kJ mol⁻¹, which is only 3 kJ mol⁻¹ lower than the barrier shown in Figure 6c. This is because the SF₆ geometry does not change significantly between SF₅−F and SF₅ + F; the energy of the frozen SF₅ geometry is only 12 kJ mol⁻¹ above that of the optimized geometry.

The three PESs exhibit late barriers in their exit channels, particularly Mg + SF₆ (Figure 6c). The barriers increase in the order of K (16 kJ mol⁻¹), Na (24 kJ mol⁻¹), and Mg (51 kJ mol⁻¹)
energies lie in between the two activation energies obtained from the biexponential Arrhenius fits for these reactions.

Reactions with late barriers tend to be activated by vibrational excitation in a reactant bond corresponding to the reaction coordinate.\textsuperscript{31} Acknowledging that the detailed non-Arrhenius behavior of R1, R3, and R4 is obscured by the scatter of the data and that there is a risk of overinterpretation of the biexponential fitted parameters, it is still tempting to link the difference in activation energies between the low and high temperature regimes to the role of vibrational excitation in activating these reactions. The Arrhenius expressions for $k_1$ and $k_4$ (see above) exhibit an increase in activation energy between the low and high temperature terms of $(14.4 \pm 7.2)$ and $(12.4 \pm 2.0)$ kJ mol$^{-1}$, respectively. These differences correspond (within error) to one quantum of the asymmetric $\nu_3$ S–F stretching mode of SF$_6$ at 940 cm$^{-1}$,\textsuperscript{32} which is equivalent to 11.2 kJ mol$^{-1}$. This is consistent with the first term in each Arrhenius expression containing the probability of $\nu_3$ excitation: for example, the Boltzmann population of SF$_6$ ($\nu_3 > 0$) increases from only 3.3\% at 300 K to 37.5\% at 700 K. As mentioned earlier, the role of SF$_6$ vibration in enhancing the reaction cross section for reaction R4 (K + SF$_6$) was proposed to explain the molecular beam results of Sloane et al.\textsuperscript{28} Similarly, the activation energy increase of $k_4$ is $(15.0 \pm 7.2)$ kJ mol$^{-1}$. This corresponds within error to one quantum of the 982 cm$^{-1}$ (11.7 kJ mol$^{-1}$) asymmetric stretching mode\textsuperscript{35} of CFC-115, which most closely resembles the reaction coordinate. It is noteworthy that non-Arrhenius behavior was also observed in our previous study of Na and K reacting with NF$_3$.\textsuperscript{22}

4.2. VUV Photolysis. The Lyman-$\alpha$ absorption cross section of SF$_6$ from the present study is $\sigma$(SF$_6$, 121.6 nm) = (1.37 ± 0.12) $\times$ 10$^{-18}$ cm$^2$. Previous measurements in chronological order are 2.74 $\times$ 10$^{-18}$ cm$^2$ by Bastien et al.,\textsuperscript{34} (1.76 ± 0.13) $\times$ 10$^{-18}$ cm$^2$ by Ravishankara et al.,\textsuperscript{1} 1.83 $\times$ 10$^{-18}$ cm$^2$ by Pradayrol et al.,\textsuperscript{35} and 1.20 $\times$ 10$^{-18}$ cm$^2$ by Zetzch.\textsuperscript{36} The earliest measurement by Bastien et al. appears to be an outlier; however, it is not clear why the four most recent measurements vary by about 50\%. Our value is reasonably close to the average of 1.5 $\times$ 10$^{-18}$ cm$^2$.

The absorption cross section for CFC-115 from the present study is $\sigma$(CFC-115, 121.6 nm) = (4.27 ± 0.35) $\times$ 10$^{-18}$ cm$^2$. This is significantly smaller than a very old measurement of 1.76 $\times$ 10$^{-17}$ cm$^2$ by Doucet et al.\textsuperscript{37} but in excellent agreement with a value of (4.57 ± 0.37) $\times$ 10$^{-18}$ cm$^2$ measured by Ravishankara et al.\textsuperscript{1} In order to assess the role of photolysis in the atmosphere, the absorption cross sections over the VUV spectral range are required. Previous measurements of the SF$_6$ cross sections over the 116–180 nm and 121–125 nm ranges were reported by Pradayrol et al.\textsuperscript{35} and Zetzch,\textsuperscript{36} respectively. For CFC-115, the only reported measurements between 122 and 172 nm are by Doucet et al.\textsuperscript{37} As noted above, their measurement at 121.6 nm is about a factor of 4 times larger than the present study. In contrast, at 172 nm Doucet et al.\textsuperscript{37} are in good agreement with the recent JPL recommendation\textsuperscript{21} (which extends to 230 nm). Since the cross section between 122 and 170 nm (i.e., not including Lyman-$\alpha$) does not make a significant contribution to the photodissociation rate of CFC-115 (see Figure 7), we have therefore used the Doucet et al.\textsuperscript{37} results over this range without scaling them downward to match the Lyman-$\alpha$ measurements from the present study and that of Ravishankara et al.\textsuperscript{1}
We have derived the following polynomial expressions describing the cross section as a function of wavelength from composite data sets containing our cross section at 121.6 nm and the literature values (see above) at longer UV wavelengths. For SF₆: $\sigma(115–125 \text{ nm}) = \exp(1.061 \times 10^{-5 \lambda^2} - 2.644\lambda + 123.4)$; $\sigma(125–155 \text{ nm}) = \exp(-9.420 \times 10^{-5 \lambda^2} + 1.298\lambda - 118.9)$; $\sigma(155–160 \text{ nm}) = \exp(1.458 \times 10^{-5 \lambda^2} - 4.762\lambda + 340.1)$; $\sigma(160–175 \text{ nm}) = \exp(-2.870 \times 10^{-5 \lambda^2} + 0.926\lambda - 123.3)$; $\sigma(175–180 \text{ nm}) = \exp(-3.425 \times 10^{-5 \lambda^2} + 11.73\lambda - 1053) \text{ cm}^2$. For CFC-115: $\sigma(121.6–128 \text{ nm}) = \exp(-9.141 \times 10^{-5 \lambda^2} + 23.13\lambda - 1.501 \times 10^5)$; $\sigma(128–132 \text{ nm}) = \exp(3.221 \times 10^{-5 \lambda^2} - 6.531\lambda + 539.3)$; $\sigma(132–144 \text{ nm}) = \exp(-6.301 \times 10^{-5 \lambda^2} + 1.570\lambda - 136.4)$; $\sigma(144–150 \text{ nm}) = \exp(-0.1274 \lambda - 22.61)$; $\sigma(150–154 \text{ nm}) = \exp(-2.880 \times 10^{-5 \lambda^2} + 37.51)$; $\sigma(154–172 \text{ nm}) = \exp(-3.061 \times 10^{-5 \lambda^2} + 0.808\lambda - 93.80)$; $\sigma(172–230 \text{ nm})/\text{cm}^2 = 2.521 \times 10^{-7} \exp(-\lambda/5.705)$.

Figure 7 shows the resulting cross sections as a function of wavelength, together with the solar irradiance, which emphasizes the importance of the Lyman-α line in the solar spectrum.

5. Atmospheric Implications

In addition to photolysis and the reactions with metal atoms which have been investigated in this study, a number of other processes may affect SF₆. These include recombination and photodissociation. These are electron attachment to SF₆, which is considered in more detail below, and the reaction between CFC-115 and O(1D):

$$\text{C}_2\text{F}_5\text{Cl} + \text{O}(1\text{D}) \rightarrow \text{ClO} + \text{C}_2\text{F}_5$$

(R8)

Reaction R8 is fast with an overall rate constant of $k(217–373 \text{ K}) = 6.5 \times 10^{-11} \exp(30/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a reactive yield of 0.72.20 This reaction, as shown below, is important in the stratosphere where photolysis of O₃ leads to relatively high concentrations of O(1D). In the middle and upper mesosphere there are significant concentrations of O(3P) and H,38 so we have calculated the reaction enthalpies and transition state energies for the following reactions using the accurate CBS-QB3 level of theory:39

$$\text{C}_2\text{F}_5\text{Cl} + \text{O}(3\text{P}) \rightarrow \text{ClO} + \text{C}_2\text{F}_5$$

(R9)

$$\text{C}_2\text{F}_5\text{Cl} + \text{H} \rightarrow \text{HCl} + \text{C}_2\text{F}_5$$

(R10)

$$\text{SF}_6 + \text{O}(3\text{P}; 1\text{D}) \rightarrow \text{FO} + \text{C}_2\text{F}_5$$

(R11)

Note that although reactions R10 and R12 are exothermic, they both have significant calculated transition state energies (including zero-point energies) of 44 and 103 kJ mol⁻¹, respectively, and so will not be important at atmospheric temperatures. Reaction R11 is too endothermic even for the reaction of SF₆ with O(1D), which is 190 kJ mol⁻¹ above the ground state, to be possible, in contrast to the reaction of C₂F₅Cl with O(1D).

5.1. Thermal Electron Attachment to SF₆

Low-energy electrons are in thermal equilibrium with the surrounding gas in the upper mesosphere and lower thermosphere,8 below 80 km, electrons are mostly attached to molecules in the form of negative ions, such as HCO₃⁻ and NO₃⁻. Because the electron detachment energies from these ions are larger than the electron affinity of SF₆, only direct attachment of free electrons will lead to the potential destruction of SF₆ via two pathways: associative attachment to form the SF₆⁻ anion, which can then undergo photodetachment or react with various compounds; and dissociative attachment to form SF₆⁻ + F.40

Both associative and dissociative electron attachment have been treated in detail in a series of recent papers by Troe and co-workers.18,19 The net associative attachment rate coefficient, $k_{a,\alpha}$, at an atmospheric density [N₂ + O₂] and temperature $T$ is given by the following expression which neglects radiative stabilization (since this is only important at much lower pressures) and assumes that O₂ has a similar efficiency to N₂:

$$k_{a,\alpha} = \frac{x}{1 + x} \left[ 1 + \log_4 \left( \frac{P}{P_{\text{atm}}(T)} \right) \right]^{-1}$$

(ES)

where $x$ is the ratio of the low- to high-pressure limiting rate coefficients (i.e., $x = k_{a,\alpha}/k_{a,\text{atm}}$), where
The pressure-dependent results at 300 K from Troe et al.\textsuperscript{19} can then be combined with the data point from Foster and Beauchamp\textsuperscript{48} at 1.5 × 10\textsuperscript{-7} Torr to yield a pressure-dependent expression for $\beta$ at 300 K:

$$
\log_{10}\left[\beta(P, 300 \text{ K})\right] = -4.362 - 0.582\log_{10}(P/\text{Torr}) - 0.0203
$$

where $P$ is in Torr.

The temperature dependence of the broadening factor $F_c$ is given by

$$
F_c = \exp(-T/S200 \text{ K})
$$

and the parameter $N$ is given by

$$
N = 0.75 - 1.27\log_{10}(F_c)
$$

Chemical removal of SF$_6^-$ can either recycle or remove SF$_6$.

The removal reactions are

$$
\text{SF}_6^- + \text{H} \rightarrow \text{products}
$$

$$
k_9 = 2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 3)}
$$

$$
\text{SF}_6^- + \text{HCl} \rightarrow \text{products}
$$

$$
k_{10} = 1.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 40)}
$$

while the recycling channels are

$$
\text{SF}_6^- + \text{O}_3 \rightarrow \text{SF}_6 + \text{O}_3^-
$$

$$
k_{11} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 40)}
$$

$$
\text{SF}_6^- + \text{O} \rightarrow \text{SF}_6 + \text{O}^-
$$

$$
k_{12} = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 40)}
$$

The photodetachment coefficient for SF$_6^-$ ($f_{PD}$) can be estimated by integrating the product of the electron photodetachment cross section and the extra-terrestrial solar irradiance from 280 to 700 nm,\textsuperscript{43} assuming a quantum yield of unity. The cross section was calculated by combining the recent theoretical spectrum of Eisfeld\textsuperscript{42} with absolute experimental values reported by Bopp et al.,\textsuperscript{43} Christophorou and Olthoff,\textsuperscript{44} and Datskos et al.\textsuperscript{45} This gives a midday value of 1.1 s$^{-1}$ at 85 km.

Assuming that SF$_6^-$ is in steady state, the permanent removal rate of SF$_6^-$ by associative electron attachment becomes $k_{\text{EA}}$ [SF$_6$][e$^-$], where

$$
k_{\text{EA}} = k_9 + k_{10}[\text{H}] + k_{11}[\text{HCl}] + k_{12}[^{18}\text{O}]
$$

Second we consider the dissociative channel. At pressures above 10$^{-4}$ Torr, the branching ratio $\beta(P,T)$ for the dissociative thermal electron attachment channel for SF$_6$ is very small ($\sim 0.001$).\textsuperscript{3,45,47} Troe et al.\textsuperscript{19} (in their Figure 9) show that at a pressure of 10$^{-2}$ Torr (corresponding to an altitude of $\sim$80 km), the fraction that dissociates is less than 10$^{-4}$. The dissociative electron attachment removal rate as a function of temperature can be obtained by fitting an Arrhenius expression to the 10$^{-2}$ Torr line in this figure, over the temperature range of 200–320 K where an Arrhenius plot is reasonably linear. This results in the following expression:

$$
\beta(10^{-2} \text{ Torr}, T) = e^{(-4587/T+7.74)}
$$

The cross section was calculated by combining the experimental values reported by Bopp et al.,\textsuperscript{43} Christophorou and Olthoff,\textsuperscript{44} and Datskos et al.\textsuperscript{45} This gives a midday value of 1.1 s$^{-1}$ at 85 km.

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$$
k_{\text{EA}} = k_9 + k_{10}[\text{H}] + k_{11}[\text{HCl}] + k_{12}[^{18}\text{O}]
$$

(E10)

(E11)

January 2010, see below). $\beta$ is at a minimum around the tropopause, where the relatively low temperature and high pressure causes associative attachment to dominate. In contrast, at the high temperatures and low pressures of the lower thermosphere (above 115 km), dissociative attachment dominates and $\beta$ approaches unity. In the mesosphere between 50 and 100 km, $\beta$ is approximately constant because the effect of decreasing temperature is offset by the decreasing pressure.

The loss rates of SF$_6$ and CFC-115 as a function of altitude, pressure and the parameter $N$ is given by

$$
N = 0.75 - 1.27\log_{10}(F_c)
$$

The pressure-dependent results at 300 K from Troe et al.\textsuperscript{19} can then be combined with the data point from Foster and Beauchamp\textsuperscript{48} at 1.5 × 10$^{-7}$ Torr to yield a pressure-dependent expression for $\beta$ at 300 K:

$$
\log_{10}[\beta(P, 300 \text{ K})] = -4.362 - 0.582\log_{10}(P/\text{Torr}) - 0.0203
$$

(E12)

(E13)

Finally,

$$
\beta(P, T) = \frac{k_{\text{dis}}}{k_{\text{dis}} + k_{\text{at}}}
$$

(E14)

so that $k_{\text{dis}}$ can be calculated from $k_{\text{at}}$ (eq E5).

Figure 8 illustrates the variation of $\beta$ with altitude and also shows the atmospheric temperature profile (a global average for the Atmosphere Community Climate Model (WACCM).\textsuperscript{49,50}}
This chemistry-climate model was also used to provide vertical profiles of the H, HCl, O₃, H, O(1D), and electron density. For illustrative purposes, we have taken the global averages of these parameters for January, 2010. Figure 9 demonstrates that the Na and K reactions are not competitive in the removal of either SF₆ or CFC-115. Figure 9a shows that associative electron attachment is the dominant removal process for SF₆ throughout the atmosphere up to 110 km; at higher altitudes, photolysis dominates. Nevertheless, the absolute loss rate by electron attachment only becomes significant in the mesosphere where the removal rate exceeds 10⁻⁹ s⁻¹ (e-folding lifetime < 30 years). Combining this slow rate of removal with the time taken to transport SF₆ above 50 km³ explains the exceptionally long atmospheric lifetime of this PFC. In the case of CFC-115, VUV photolysis is the major loss process above 60 km, but the removal of this species by reaction with O(1D) dominates in the stratosphere and hence controls its lifetime.

### 6. CONCLUSIONS

This study has explored the impact of a number of processes which can remove the long-lived greenhouse gases SF₆ and CFC-115 in the mesosphere. Despite the reactions of Na, K, Fe, and Mg with these PFCs being significantly exothermic, the reactions have substantial barriers on their respective potential energies which cause the reactions to be too slow at the temperatures of the upper mesosphere (<230 K) to contribute significantly to the removal of the PFCs. Theoretical calculations indicate that the Na and K reactions with SF₆ may be activated by vibrational excitation of the F-SF₆ (v₃) asymmetric stretching mode. A limited set of measurements on Na + SF₆CF₃ indicates that this PFC behaves very much like SF₆.

The Lyman-α absorption cross sections for SF₆ and CFC-115 were also measured and found to be in generally good agreement with the more recent previous studies. Although VUV photolysis of SF₆ is the major loss process above 105 km, below this height associative electron attachment dominates and so this is the process which controls the atmospheric lifetime of this PFC. In the case of CFC-115, VUV photolysis is the major loss process above 60 km, but the removal of this species by reaction with O(1D) dominates in the stratosphere and hence controls its lifetime.

### REFERENCES


