

# Mechanistic Studies on the Formation of Trifluoromethyl Sulfur Pentafluoride, SF<sub>5</sub>CF<sub>3</sub>—a Greenhouse Gas

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The formation of SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A'), through the radical–radical recombination of SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) and CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>), was observed for the first time in low-temperature sulfur hexafluoride–carbon tetrafluoride matrices at 12 K via infrared spectroscopy upon irradiation of the ices with energetic electrons. The ν<sub>1</sub> fundamentals of the SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) and CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) radicals were monitored at 857 and 1110 cm<sup>-1</sup>, respectively; the newly formed trifluoromethyl sulfur pentafluoride molecule, SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A'), was detected via its absorptions at 846 and 1160 cm<sup>-1</sup>. This formation mechanism suggests that a source for this potentially dangerous greenhouse gas might be the recombination of SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) and CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) radicals on aerosol particles in the terrestrial atmosphere.

## 1. Introduction

Global climate change is becoming an increasingly important environmental issue. Widespread attention is being directed toward the strongest greenhouse gas trifluoromethyl sulfur pentafluoride (SF<sub>5</sub>CF<sub>3</sub>) with a radiative force of 0.59 W m<sup>-2</sup> ppbv<sup>-1</sup> on a per molecule basis.<sup>1</sup> Although its concentration of about 0.12 part per trillion (ppt) as first measured from the Antarctic firn in 1999, is relatively small, its concentration is growing at a rate of 6% per year.<sup>2</sup> Released as a byproduct during the manufacturing of fluorochemicals, the only known source so far, accounts for only a small existing portion in the atmosphere.<sup>3</sup> It was hypothesized by Sturges et al. (2000) that a possible source of SF<sub>5</sub>CF<sub>3</sub> could be the SF<sub>5</sub> radical, formed by high-voltage discharge, attacking CF<sub>3</sub> groups on the surface of fluoropolymers in high-voltage equipment, indicating this gas could inflict a significant environmental impact in the future. Confirmation of this formation route should then direct environmental assessment in the global use of perfluorinated sulfur- and hydrocarbon-bearing chemicals in high-voltage equipment.

Although the growth trends of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> are in agreement and correlate, to date, the hypothesized formation route has not been observed from experiments conducted

with SF<sub>6</sub>(X<sup>1</sup>A<sub>1g</sub>) and CF<sub>4</sub>(X<sup>1</sup>A<sub>1</sub>).<sup>4</sup> We have previously demonstrated that in low-temperature methane and germane matrices, for instance, energetic electrons induce primarily a cleavage of the carbon–hydrogen and germanium–hydrogen bonds to form methyl and germyl radicals, respectively, with atomic hydrogen.<sup>5,6</sup> In the present experiments, energetic electrons are utilized to induce a cleavage of carbon–fluorine and sulfur–fluorine bonds to create SF<sub>5</sub> and CF<sub>3</sub> radicals and fluorine atoms from SF<sub>6</sub>(X<sup>1</sup>A<sub>1g</sub>) and CF<sub>4</sub>(X<sup>1</sup>A<sub>1</sub>) precursor molecules, respectively. Here, we investigate to what extent the trifluoromethyl sulfur pentafluoride molecule (SF<sub>5</sub>CF<sub>3</sub>) can be formed via energetic electrons in low-temperature SF<sub>6</sub>/CF<sub>4</sub> matrices. These studies confirm the formation of the greenhouse gas and identify the most intense infrared absorption frequencies in the low-temperature matrices. Mechanisms on the formation of trifluoromethyl sulfur pentafluoride are also discussed.

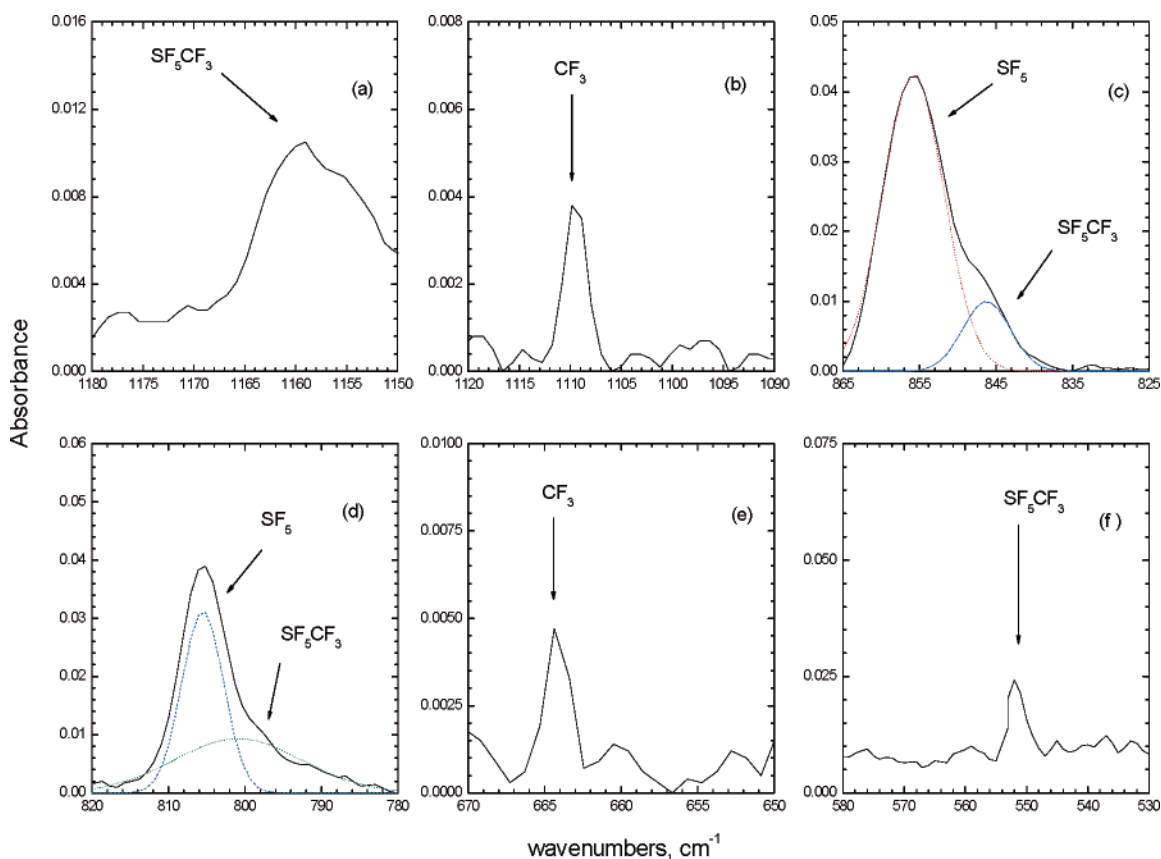
## 2. Experimental Section

The experiments were conducted in a contamination-free ultra-high vacuum (UHV) machine.<sup>5</sup> The main chamber is evacuated down to 5 × 10<sup>-11</sup> Torr by a magnetically suspended turbo pump backed by an oil-free scroll pump. A rotatable highly polished silver mirror contained within the main chamber is cooled via a two-stage closed-cycle helium refrigerator connected to a differentially

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**Figure 1.** New absorption features of CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>), SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) and of SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A') recorded in the SF<sub>6</sub>/CF<sub>4</sub> sample after an irradiation for 60 min with 5 keV electrons at 12 K for low electron currents.

pumped rotary feed through. The silver mirror can be cooled to 12 K and serves as a substrate for the ice condensate. Gas samples can be brought into the chamber through a precision leak valve, which is connected to a gas reservoir and supported by a linear transfer mechanism. The SF<sub>6</sub>–CF<sub>4</sub> ices were prepared at 12 K by depositing a premixed gas of sulfur hexafluoride (99.75%) and carbon tetrafluoride (99.99%), at pressures of about  $1.4 \times 10^{-7}$  Torr for 30 min onto a cooled silver mirror. The spectra of the SF<sub>6</sub>/CF<sub>4</sub> ice can be described as a combination of the infrared spectra of the individual ices previously published.<sup>7,8</sup> To determine the thickness of the sample, we integrated the infrared absorption features of the  $\nu_4$  fundamental at 615 [SF<sub>6</sub>] and 630 cm<sup>-1</sup> [CF<sub>4</sub>]. The ice thickness was then calculated using the Lambert–Beer relationship.<sup>5</sup> The integrated absorption coefficients of these fundamentals,  $1.45 \times 10^{-17}$  and  $2.08 \times 10^{-18}$  cm molecule<sup>-1</sup>, respectively, and the density of these ices (SF<sub>6</sub>, 2.34 g cm<sup>-3</sup>; CF<sub>4</sub>, 1.96 g cm<sup>-3</sup><sup>9,10</sup>) determined an optical thickness of  $49 \pm 10$  [SF<sub>6</sub>] and  $167 \pm 20$  nm [CF<sub>4</sub>], providing an estimated total ice thickness of  $216 \pm 20$  nm.

These ices were exposed for 120 min by scanning the sample over an area of  $3.0 \pm 0.4$  cm<sup>2</sup> with high-energy electrons to induce both carbon–fluoride and sulfur–fluoride bond ruptures in the low-temperature samples. Irradiation was performed with 5 keV electrons at beam currents of 10 and 100 nA at 12 K. Background analysis was conducted by collecting data immediately prior to the addition of the SF<sub>6</sub>/CF<sub>4</sub> mixture in the UHV chamber. A Fourier

transform infrared spectrometer was used to positively identify the reaction products in the solid state. The Nicolet 6700 DX FTIR unit (5000–500 cm<sup>-1</sup>) operated in an absorption–reflection–absorption mode (reflection angle  $\alpha = 75^\circ$ ) with a resolution of 2 cm<sup>-1</sup>. The infrared beam coupled via a mirror flipper outside the spectrometer passed through a differentially pumped potassium bromide (KBr) window and was attenuated in the ice sample both prior and after reflection at a polished silver waver. The beam exits the main chamber through a second differentially pumped KBr window before being inspected via a liquid-nitrogen-cooled detector. It should be noted that the 5 keV electrons are utilized to cut the S–F and C–F bonds and to ‘induce’ the low-temperature chemistry. Electrons of this energy penetrate the ice sample completely and transmit on average about 0.5 keV to molecules. This is an important factor in our experiments to ensure that the CF<sub>3</sub> and SF<sub>5</sub> radicals are formed throughout the ice sample so that we can get a detectable signal of radicals and of the reaction products. We acknowledge that as demonstrated by Gstir et al. in the gas phase,<sup>11</sup> a kinetic energy of the electrons of 12.1 eV would be high enough for the ionization process to occur. However, these electrons would be absorbed within the first few monolayers of the solid ice, and we would not see any significant signal of the newly formed products.

### 3. Results

Infrared absorptions of the trifluoromethyl (CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>)) and sulfur pentafluoride radicals (SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>)) appeared instantaneously with the onset of the irradiation of the ice samples

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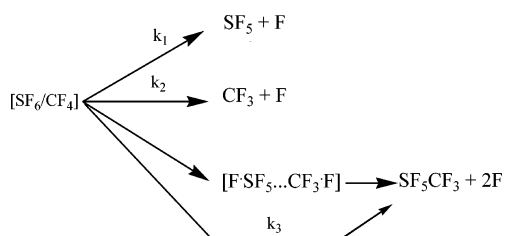
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**Table 1.** Column Densities with Rate Constants for the Observed Species and Their Absorptions in Low-Temperature SF<sub>6</sub>/CF<sub>4</sub> Matrices for Low Electron Currents

$k_i, \text{s}^{-1}$	$a_i, \text{molecules cm}^{-2}$	molecule	absorption (present work), $\text{cm}^{-1}$	fundamental	absorption (literature data), $\text{cm}^{-1}$
$7.0 \pm 0.8 \times 10^{-3}$	$4.7 \pm 0.5 \times 10^{15}$	SF <sub>5</sub>	857	$\nu_1$	885 <sup>a</sup>
			550	$\nu_3$	554 <sup>b</sup>
			806	$\nu_7$	817 <sup>b</sup>
$3.0 \pm 0.3 \times 10^{-4}$	$5.3 \pm 0.5 \times 10^{14}$	CF <sub>3</sub>	1110	$\nu_1$	1086 <sup>c</sup>
			664	$\nu_2$	701 <sup>c</sup>
$1.0 \pm 0.1 \times 10^{-4}$	$4.9 \pm 0.5 \times 10^{14}$	SF <sub>5</sub> CF <sub>3</sub>	846	$\nu_{19}$	883, 885, 884 <sup>d</sup>
			1160	$\nu_{22}$	1169, 1170, 1172 <sup>d</sup>

<sup>a</sup> Reference 13. <sup>b</sup> Reference 12. <sup>c</sup> Reference 8. <sup>d</sup> Reference 16.

**Figure 2.** Schematic representation of the underlying reaction pathways of the SF<sub>6</sub>/CF<sub>4</sub> ices upon electron irradiation at low electron irradiation currents.

at 1110 ( $\nu_1$ ; CF<sub>3</sub>) and 857  $\text{cm}^{-1}$  ( $\nu_1$ ; SF<sub>5</sub>) (Figure 1, Table 1). The position of both fundamentals agreed soundly with previous matrix isolation experiments depicting absorptions at 1086 and 885  $\text{cm}^{-1}$ , respectively.<sup>8,12–14</sup> The strongest mode,  $\nu_3$ , of the CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) radical at about 1205  $\text{cm}^{-1}$  was obscured by the  $\nu_3$  feature of the CF<sub>4</sub>(X<sup>1</sup>A<sub>1</sub>) molecule in the matrix and could not be undeniably identified. However, the less intense  $\nu_2$  fundamental was observable at 664  $\text{cm}^{-1}$ . The weakest fundamental,  $\nu_4$ , was a factor of 10 lower in intensity than the detected  $\nu_2$  mode; this feature was too weak to be monitored. Considering the SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) radical, its strongest fundamental ( $\nu_7$ ) was observable at 806  $\text{cm}^{-1}$ —in close agreement to a previously published value of 817  $\text{cm}^{-1}$  (Figure 1, Table 1). The very weak  $\nu_3$  fundamental was discovered at 550  $\text{cm}^{-1}$ ; this assignment is in good agreement with an absorption reported previously at 554  $\text{cm}^{-1}$ . The  $\nu_2$  mode is more than a factor of 10 lower in intensity than the  $\nu_1$  fundamental and is also too weak to be detected. The remaining infrared active modes were outside the range of our infrared detector, which has a cutoff at about 500  $\text{cm}^{-1}$ . We would like to stress that we verified the formation of the trifluoromethyl and sulfur pentafluoride radicals through irradiation of pure carbon tetrafluoride (CF<sub>4</sub>) and sulfur hexafluoride (SF<sub>6</sub>) ices, respectively. In the carbon tetrafluoride sample, the positions of the  $\nu_1$  fundamental of CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) could be observed immediately after irradiation at 1082  $\text{cm}^{-1}$ . The sulfur hexafluoride matrix revealed the strongest fundamental,  $\nu_7$ , of the SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) molecule after the irradiation at 806  $\text{cm}^{-1}$ . The  $\nu_1$  and  $\nu_3$  fundamentals were observed at 857 and 552  $\text{cm}^{-1}$ , respectively. For completeness, we also observed the formation of S<sub>2</sub>F<sub>10</sub> and C<sub>2</sub>F<sub>6</sub>. The infrared

spectra of these species are well known<sup>15</sup> and therefore are not discussed in this paper.

Having identified the precursor molecules and two radical species, we also detected—immediately after the onset of the irradiation of the SF<sub>6</sub>/CF<sub>4</sub> ices—the infrared absorptions of the trifluoromethyl sulfur pentafluoride [SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A<sup>′</sup>)] at 1160 ( $\nu_{22}$ ) and 846  $\text{cm}^{-1}$  ( $\nu_{19}$ ). The positions of these absorptions are in good agreement with previous experiments (Table 1).<sup>16</sup> The  $\nu_1$ – $\nu_{10}$  fundamentals absorb at less than 500  $\text{cm}^{-1}$ , which is beyond the detection limit for our detector. The  $\nu_{11}$ – $\nu_{14}$ ,  $\nu_{16}$ , and  $\nu_{17}$  positions are all weaker by at least a factor of 10 than the weakest absorption identified (1160  $\text{cm}^{-1}$ ) therefore disallowing their detection. The  $\nu_{15}$  mode is concealed by the absorption features of the matrix. The  $\nu_{23}$  and  $\nu_{24}$  fundamentals—both having intensities slightly weaker than the strongest observed  $\nu_{19}$  peak—are hidden by features of the matrix.

#### 4. Discussion and Summary

The infrared data imply that the response of the SF<sub>6</sub>/CF<sub>4</sub> ice mixture upon the electron irradiation is governed initially by sulfur–fluoride and carbon–fluoride bond ruptures. These processes form atomic fluoride plus the SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) and CF<sub>3</sub>-(X<sup>2</sup>A<sub>1</sub>) radicals, in strongly endoergic reaction, i.e., 391 (4.1 eV) and 539 kJ mol<sup>-1</sup> (5.6 eV), respectively. Treating the formation of both radicals as an energy transfer-induced unimolecular decomposition of the SF<sub>6</sub> and CF<sub>4</sub> precursor molecules, the temporal profiles of the SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) and CF<sub>3</sub>-(X<sup>2</sup>A<sub>1</sub>) radicals, [SF<sub>5</sub>](t) and [CF<sub>3</sub>](t), should follow first-order kinetics via eqs 1 and 2, respectively (Figure 2). As a matter of fact, both temporal profiles (Figure 3) could be fit by eqs 1 and 2; the corresponding rate constants and  $a_i$  ( $i = 1, 2$ ) factors are compiled in Table 1. Here, the rate constant  $k_1$  quantifying the formation of the SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) radicals is larger by a factor of about two compared to the formation of the CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) radical—possibly because the S–F bond is weaker by about 150 kJ mol<sup>-1</sup>.

$$[\text{SF}_5](t) = a_1(1 - e^{-k_1 t}) \quad (1)$$

$$[\text{CF}_3](t) = a_2(1 - e^{-k_2 t}) \quad (2)$$

Additionally, the  $a_i$  ( $i = 1, 2$ ) factors, i.e., the column densities of the radicals as the irradiation time approaches

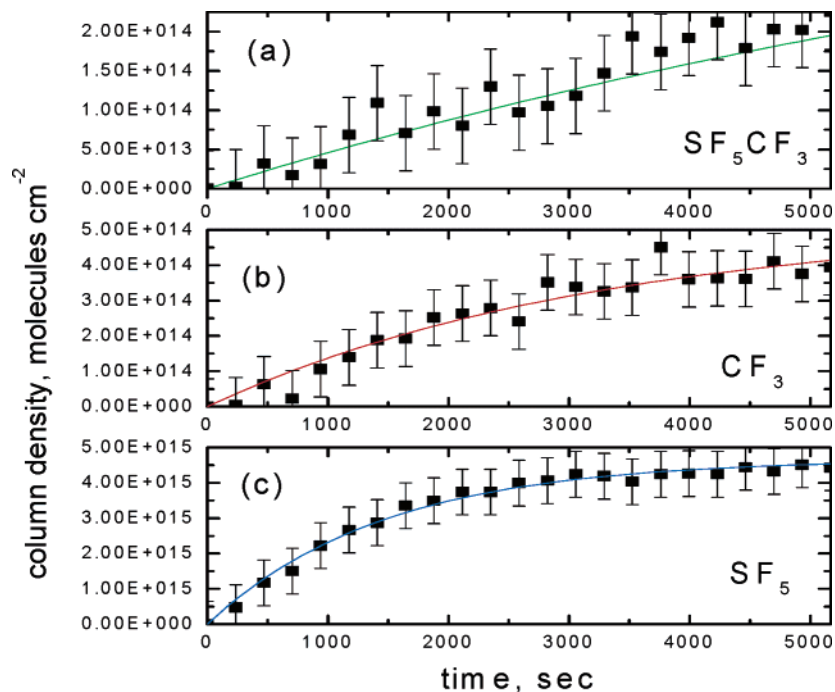
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**Figure 3.** Temporal evolution of the column densities and best fit of the trifluoromethyl sulfur pentafluoride molecule (a) trifluoromethyl (b) and sulfur pentafluoride radicals (c) during the irradiation of the SF<sub>6</sub>/CF<sub>4</sub> matrix at 12 K.

infinity, of the SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) radicals is larger by about 1 order of magnitude in contrast to the column densities of the CF<sub>3</sub>-(X<sup>2</sup>A<sub>1</sub>) radicals. This could be the result of simply momentum conservation and the larger probability of the fluorine atom to escape the [SF<sub>5</sub>•••F] matrix cage than the [CF<sub>3</sub>•••F] matrix cage. Recall that in order to form an SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) or CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) radical, the fluorine atom must diffuse out of the matrix cage; if the kinetic energy of the fluorine atom is smaller than the lattice binding energy, it cannot diffuse out of the matrix cage and the atom reacts back to the closed-shell SF<sub>6</sub> and CF<sub>4</sub> molecules. Only in those cases where the fluorine atom has sufficient kinetic energy to overcome the lattice binding energy can a SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) or CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) radical be formed. Consider a simple unimolecular decomposition of the SF<sub>6</sub> and CF<sub>4</sub> molecules in the gas phase. If, for example, 10 eV are transferred from the 5 keV electron to a SF<sub>6</sub> and CF<sub>4</sub> molecule, this leaves—after bond cleavage and neglecting electronic, vibrational, and rotational excitation of the products—5.9 and 4.4 eV in kinetic energy of the SF<sub>5</sub> + F and CF<sub>3</sub> + F fragments. The higher the mass of the counter fragment (SF<sub>6</sub> and CF<sub>4</sub>), the more kinetic energy will be released into the fluorine atom. Therefore, the fluorine atom formed in the initial S–F bond cleavage process has a higher kinetic energy than a fluorine atom ejected in the unimolecular composition of carbon tetrafluoride. Therefore, the chance of the fluorine atom to escape the matrix cage is enhanced in [SF<sub>5</sub>•••F] compared to [CF<sub>3</sub>•••F]. Consequently, the weaker S–F bond and the larger kinetic energy of the fluorine atom in the [SF<sub>5</sub>•••F] system, which reduces the probability of a recombination with the radical, lead to an enhanced column density and faster production rates of the SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) radical. However, if *neighboring* SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) and CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) radicals are formed and if the geometry is

appropriate, both radicals can recombine to form the observed trifluoro methyl sulfur pentafluoride molecule [SF<sub>5</sub>CF<sub>3</sub>-(X<sup>1</sup>A<sup>′</sup>)]. As a matter of fact, we could fit the column densities of the SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A<sup>′</sup>) molecule (Figure 3) via pseudo-first-order kinetics (Figure 2) following eq 3. On the other hand, SF<sub>5</sub>(X<sup>2</sup>A<sub>1</sub>) and CF<sub>3</sub>(X<sup>2</sup>A<sub>1</sub>) radicals formed not in the proper recombination geometry (this includes also non-neighboring radicals) cannot recombine to form the trifluoro methyl sulfur pentafluoride molecule.

$$[\text{SF}_5\text{CF}_3](t) = a_3(1 - e^{-k_3t}) \quad (3)$$

We would like to comment briefly on the current-dependence on our experiments. We conducted irradiations at electron currents of 10 and 100 nA. At 10 nA, the reaction products and kinetics in the low-temperature ices are relatively simple and are dictated by the formation of CF<sub>3</sub>, SF<sub>5</sub>, and CF<sub>3</sub>SF<sub>5</sub> (Table 1 and Figure 1), as well as of CF<sub>3</sub>CF<sub>3</sub> and SF<sub>5</sub>SF<sub>5</sub>. However, as the electron current is increased by a factor of 10 to 100 nA, the situation becomes very complex. We do observe additional sulfur–fluorine-based species like SF<sub>2</sub> and SF<sub>4</sub>; however, these species are absent at low irradiation currents. Therefore, the formation of SF<sub>2</sub> and SF<sub>4</sub> at higher currents is likely dictated by a unimolecular decomposition of initially formed SF<sub>5</sub> radicals. Consequently, we did not attempt to fit the experimental data at 100 nA electron current since multiple reaction pathways such as the simple CF<sub>3</sub>–SF<sub>5</sub> radical–radical recombination as observed in the 10 nA irradiated sample and additional insertion pathways of SF<sub>2</sub> into a C–F bond of CF<sub>4</sub> and of CF<sub>2</sub> into a S–F bond of SF<sub>6</sub> can complicate the underlying kinetics. However, it should be stressed that at 10 nA, the kinetics are relatively simple and can be compiled by the kinetic scheme as outlined in Figure 2.

In summary, the formation of the  $\text{SF}_5\text{CF}_3(X^1A')$  molecule was observed via the combining of  $\text{SF}_5(X^2A_1)$  and  $\text{CF}_3(X^2A_1)$  radicals for the first time in the  $\text{SF}_6$ – $\text{CF}_4$  matrix at 12 K via infrared spectroscopy upon irradiation of the ices with energetic electrons. We presented also kinetic fits of the column densities suggesting that the formation of the sulfur–carbon species can be rationalized via recombination of trifluoromethyl with *neighboring* sulfur pentafluoride radicals holding the correct recombination geometry. The distinct rate constants to form  $\text{SF}_5(X^2A_1)$  and  $\text{CF}_3(X^2A_1)$  radicals could be explained by simple energy and angular momentum conservation combined with a weaker S–F bond compared to the C–F counterpart in the sulfur hexafluoride and carbon

tetrafluoride precursors, respectively. The explicit identification of the hitherto obscure formation route for the trifluoromethyl sulfur pentafluoride molecule via recombination of atmospheric  $\text{SF}_5(X^2A_1)$  and  $\text{CF}_3(X^2A_1)$  radicals either in the gas phase via a three-body reaction or assisted by aerosol particles may aid in understanding the occurrence of this greenhouse gas in the terrestrial atmosphere.

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