

**MECHANISTIC STUDIES OF TRIFLUOROMETHYL SULFUR PENTAFLUORIDE  
SF<sub>5</sub>CF<sub>3</sub> :  
A GREENHOUSE GAS FIRST INFRARED SPECTROSCOPIC**

William Carrier  
Department of Chemistry  
University of Hawai'i at Manoa  
Honolulu, HI 96822

**ABSTRACT**

The formation of SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A'), through the combination 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-carbon matrices at 12 K via infrared spectroscopy upon irradiation of the ices with energetic electrons. The precursor  $\nu_1$  fundamentals were detected at 857cm<sup>-1</sup> and 1110cm<sup>-1</sup> for 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>), respectively whereas the trifluoromethyl sulfur pentafluoride molecule SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A') was monitored via its absorptions at 846 cm<sup>-1</sup>, 801cm<sup>-1</sup> and 550 cm<sup>-1</sup>. This formation mechanism, previously hypothesized by Sturges et al. (2000), confirms an alternative source for this potentially dangerous greenhouse gas. These IR data may aid in identifying this gas in prospective atmospheric searches via infrared spectroscopy.

**INTRODUCTION**

Global climate change is becoming an increasingly important environmental issue. Widespread attention is being directed towards the strongest greenhouse gas trifluoromethyl sulfur pentafluoride (SF<sub>5</sub>CF<sub>3</sub>) with a radiative force of .59 W m<sup>-2</sup>ppbv<sup>-1</sup> on a per molecule basis.<sup>1</sup> Although its concentration of about .12 part per trillion (ppt) as first measured from the Antarctic firm in 1999, is relatively small, its concentration is growing at a rate of 6% yr<sup>-1</sup>.<sup>2</sup> Released as a by-product during the manufacturing of fluorochemicals, the only known source, this 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 SF<sub>6</sub> and CF<sub>3</sub> groups in high voltage equipment. Therefore, these investigations present a valuable role in understanding the formation mechanisms of this gas, in addition to aiding identification in prospective atmospheric searches via infrared spectroscopy.

Although the growth trends of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> are in agreement, 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, using a surface scattering machine, that in low temperature methane and germane matrices, energetic electrons induce primarily a cleavage of the carbon-hydrogen and germanium-hydrogen bonds to form methyl/germyl radicals and atomic hydrogen.<sup>5,6</sup> Here energetic electrons can be used to induce a cleavage of carbon-fluoride and sulfur-fluoride bonds to create SF<sub>5</sub> and CF<sub>3</sub> radicals and fluoride atoms. Combining an experimental and theoretical approach, we conducted an investigation with low temperature SF<sub>6</sub>:CF<sub>4</sub> matrices, into the formation of the trifluoromethyl sulfur pentafluoride

(SF<sub>5</sub>CF<sub>3</sub>) molecule; these studies confirm this formation route of the greenhouse gas and identify the most intense infrared absorption frequencies in low temperature matrices. These studies can be expanded to investigate the formation, energetics and also spectroscopic properties of SF<sub>x</sub>CF<sub>y</sub> (x= 1- 6; y= 1-6).

## EXPERIMENTAL

These experiments were conducted in a contamination-free ultrahigh vacuum (UHV) machine.<sup>5</sup> The main chamber is capable of being evacuated down to  $5 \times 10^{-11}$  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 pumped rotary feed through. The silver mirror can be cooled to 10 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. To guarantee a reproducible thickness of the ice samples, the deposition system can be moved 5 mm in front of the silver mirror prior to the gas condensation. The SF<sub>6</sub>-CF<sub>4</sub> ices were prepared at 12 K by depositing a pre-mixed gas of sulfur hexafluoride (99.75%) and carbon tetrafluoride (99.99%), at pressures of about  $1.4 \times 10^{-7}$  torr for 30 minutes onto a cooled silver mirror. The spectra of the SF<sub>6</sub>-CF<sub>4</sub> ice appears as a combination of the infrared spectrum 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 [CF<sub>4</sub>] cm<sup>-1</sup>. 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<sup>-1</sup>, respectively and the density of these ices SF<sub>6</sub>: 1.4 gcm<sup>-3</sup> and CF<sub>4</sub>: 1.89gcm<sup>-3</sup><sup>9,10</sup> determined an optical thickness of  $81.5 \pm 20$  nm [SF<sub>6</sub>] and  $173 \pm 20$  nm [CF<sub>4</sub>] providing an estimated total ice thickness of  $216 \pm 20$  nm.

These ices were exposed for 120 minutes 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 nA and 100 nA at 12K. Background analysis was performed 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 for certain identification of 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, was passed through a differentially pumped potassium bromide (KBr) window, and 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.

## THEORETICAL APPROACH

The molecular structures of various isomers for the SF<sub>6</sub>, SF<sub>5</sub>, CF<sub>4</sub> and CF<sub>3</sub> species were optimized in terms of ab initio density functional B3LYP methods<sup>11,12</sup> with the 6-311G(d,p) basis set.<sup>13</sup> The coupled cluster CCSD(T) calculations<sup>14,15</sup> with the aug-cc-pVTZ basis set<sup>16</sup> were also performed at the optimized structures obtained with the B3LYP method in order to compare the relative energies of various isomers. All computations were carried out using the GAUSSIAN 98

program package.<sup>17</sup> The relative energies stated in the text are the values obtained with the CCSD(T) method corrected with the zero-point vibrational energies obtained with the B3LYP method. We have performed the vibrational analysis with the second-order Møller-Plesset perturbation theory (MP2 method)<sup>18</sup>, Hartree-Fock method (HF method), and quadratic configuration interaction method (QCISD method) for several structures in order to examine the dependency of wave functions applied to obtain the vibrational frequencies.

## EXPERIMENTAL RESULTS

Infrared absorptions of the trifluoromethyl and sulfur pentafluoride radicals appeared instantaneously with the onset of the irradiation of the SF<sub>6</sub>:CF<sub>4</sub> samples with an electron current of 100 nA at 12K at 1110 cm<sup>-1</sup> ( $\nu_1$ ; CF<sub>3</sub>) and 857 cm<sup>-1</sup> ( $\nu_1$ ; SF<sub>5</sub>). The position of both these  $\nu_1$  fundamentals agree soundly with previous experiments.<sup>19,20</sup> The strongest mode  $\nu_2$  of the CF<sub>3</sub>(<sup>2</sup>A<sub>1</sub>) radical is obscured by features of the matrix and could not be undeniably identified. The weaker  $\nu_2$  fundamental is observable at 664 cm<sup>-1</sup>. An intensity ratio of the two bands at 1110 and 664 cm<sup>-1</sup> is calculated as 1.5 ± 0.5; this is in close agreement with the theoretically computed value. (Table 2). The weakest fundamental  $\nu_4$  is a factor of 10 lower than the  $\nu_2$  mode and, hence, is too low to be detected. The strongest mode  $\nu_7$  of the SF<sub>5</sub>(<sup>2</sup>A<sub>1</sub>) radical is observable at 805 cm<sup>-1</sup>. Using a scaling factor of 1.09 these data agree nicely with calculated modes. The  $\nu_2$  fundamental mode is more than a factor of 10 lower than the  $\nu_1$  mode and also too weak to be detected. The remaining infrared active modes were outside the range of our MCTB detector.

Having identified the precursor molecules, we also detected, immediately after irradiation, the infrared absorption of the trifluoromethyl sulfur pentafluoride [SF<sub>5</sub>CF<sub>3</sub>(<sup>1</sup>A')] at 846, 801, and 550 cm<sup>-1</sup>. Several of the fundamentals for this molecule overlap, contributing to the observed absorption, and are unobservable individually. In addition some of these modes have nearly identical intensities and can therefore not be compared with theoretical calculations. The absorption at 801 cm<sup>-1</sup> can positively be assigned with a scaling factor of 1.08 as the  $\nu_5$  fundamental. Although assigned to several modes, the absorption at 550cm<sup>-1</sup> is in good agreement with the gas phase mode  $\nu_9$ .<sup>21</sup>

## DISCUSSION AND SUMMARY

The infrared data imply that the response of the SF<sub>6</sub>:CF<sub>4</sub> ice upon the electron irradiation is governed initially by sulfur-fluoride and carbon-fluoride bond ruptures which form atomic fluoride plus the SF<sub>5</sub> and CF<sub>3</sub> radicals. In order to escape either the [SF<sub>5</sub>...F] or [CF<sub>3</sub>...F] matrix cage, the fluoride atom needs an excess energy – the lattice binding energy - of a few tens of kJmol<sup>-1</sup> to escape. Otherwise, atomic fluoride will recombine with the radicals to react back to the initial molecules. The infrared data suggest that the trifluoromethyl sulfur pentafluoride molecule is formed initially within a single trajectory of the electron. Indicating that neighboring radicals can recombine to the SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A') at 12 K if they have the correct recombination geometry. Summarized, the formation of the SF<sub>5</sub>CF<sub>3</sub>(X<sup>1</sup>A') molecule was observed from the combining 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 for the first time in SF<sub>6</sub>:CF<sub>4</sub> matrix at 12 K via infrared spectroscopy.

Table 3. Observed species and their absorptions in low temperature SF<sub>6</sub>:CF<sub>4</sub> matrices.

Species	Wavenumbers, cm <sup>-1</sup>	Fundamental
SF <sub>5</sub>	857	v <sub>1</sub>
	806	v <sub>7</sub>
CF <sub>3</sub>	1110	v <sub>1</sub>
	664	v <sub>2</sub>
SF <sub>5</sub> CF <sub>3</sub>	846	v <sub>3</sub> ,v <sub>4</sub> ,v <sub>17</sub>
	801	v <sub>5</sub>
	550	v <sub>7</sub> ,v <sub>8</sub> ,v <sub>9</sub> ,v <sub>18</sub>

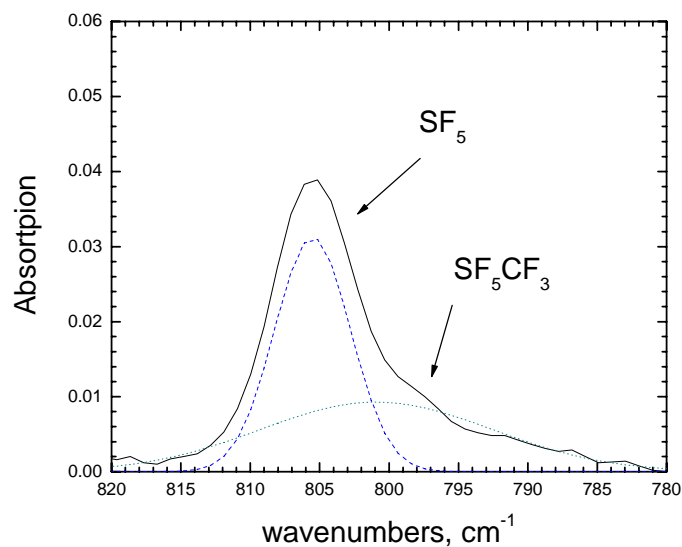


Figure 1: New Absorption feature of the sulfur pentafluoride radicals, SF<sub>5</sub>(<sup>2</sup>A<sub>1</sub>), at 806 cm<sup>-1</sup> and the trifluoromethyl sulfur pentafluoride fluoride molecule, SF<sub>5</sub>CF<sub>3</sub>(<sup>1</sup>A'), at 801 cm<sup>-1</sup> in the SF<sub>6</sub>:CF<sub>4</sub> matrix at 12 K

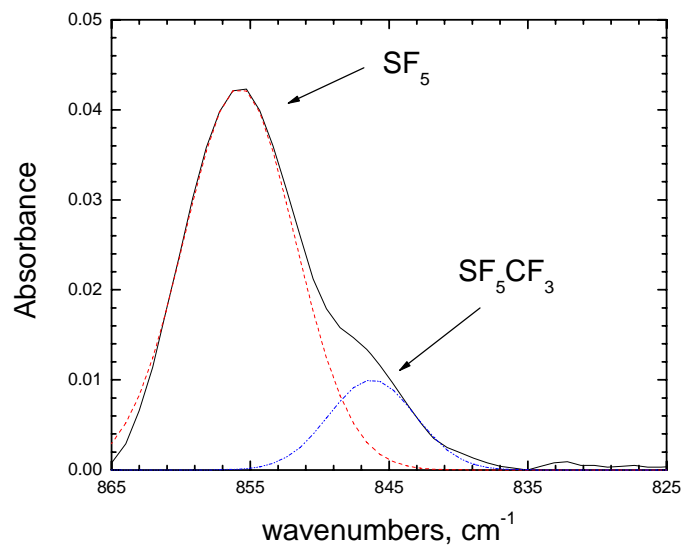


Figure 2: New Absorption feature of the sulfur pentafluoride radicals,  $\text{SF}_5(^2\text{A}_1)$ , at  $857\text{ cm}^{-1}$  and the trifluoromethyl sulfur pentafluoride fluoride molecule,  $\text{SF}_5\text{CF}_3(^1\text{A}')$ , at  $846\text{ cm}^{-1}$  in the  $\text{SF}_6:\text{CF}_4$  matrix at 12 K

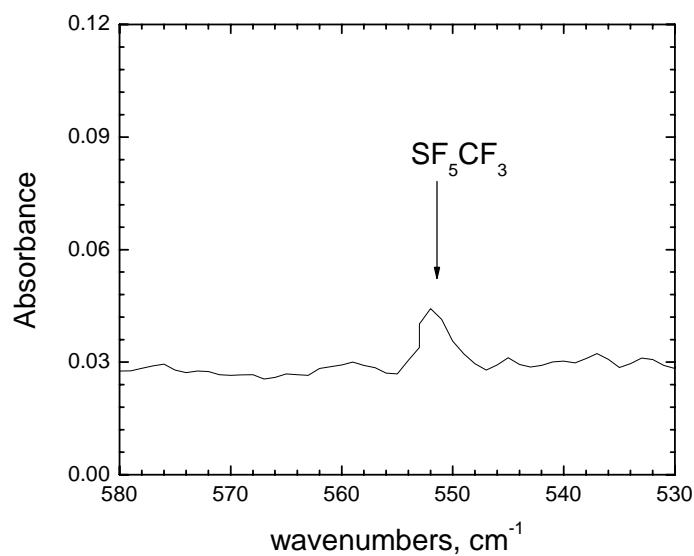


Figure 3: New Absorption feature of the trifluoromethyl sulfur pentafluoride fluoride molecule,  $\text{SF}_5\text{CF}_3(^1\text{A}')$ , at  $801\text{ cm}^{-1}$  in the  $\text{SF}_6:\text{CF}_4$  matrix at 12 K

## ACKNOWLEDGMENTS

These experiments were supported by the NASA Space Grant administered by the University of Hawai'i at Manoa. Special thanks to Dr. Kaiser for providing mentoring throughout the entire research project. The author would also like to thank Corey Jamieson for his assistance in operation of the surface scattering machine.

## REFERENCES

- 
- <sup>1</sup> Nielsen, O. J.; Et al. *Atmospheric Environment*. 2001, 36, 1237.
  - <sup>2</sup> Sturges, W. T.; Et al. *Science*. 2000, 289, 611.
  - <sup>3</sup> Santoro, M. A.; *Science*. 2000, 290, 935.
  - <sup>4</sup> Huang, L.; Zhu, L.; Pan, X.; Zhang, J.; Ouyang, B.; Hou. *Atmospheric Environment*. 2005, 39, 1641
  - <sup>5</sup> Bennett C.J., Jamieson, C.S. *Ap. J.* (in preparation) 2005.
  - <sup>6</sup> Carrier, W. J.; Zheng, W.; Osamura, Y.; Kaiser R. I.; *Chem Phys.* (in press) 2005.
  - <sup>7</sup> Kno1zinger E. Babka, E. Hallamasek, D.; *J. Phys. Chem. A* 2001, 105, 8176.
  - <sup>8</sup> Forneya, D. Jacox, M. E. *J. Chem. Phys.* 1994, 101 ,8290
  - <sup>9</sup> Taylor, J.C.; Waugh, A.B. *J. Solid State Chem.* 1976, 18, 241
  - <sup>10</sup> Smith, J.H.; Pace, E.L. *J. Chem. Phys.* 1969, 73, 4232
  - <sup>11</sup> Becke, A.D. *J. Chem. Phys.* 1993, 98, 5648.
  - <sup>12</sup> Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* 1988, 37, 785.
  - <sup>13</sup> Krishnan, R.; Binkley, J.S.; Seeger, R.; Pople, J.A. *J. Chem. Phys.* 1980, 72, 650.
  - <sup>14</sup> J. Cizek, *Adv. Chem. Phys.* 1969, 14, 35.
  - <sup>15</sup> Pople, J.A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* 1987, 87, 5968.
  - <sup>16</sup> Kendall, R.A.; Dunning, T.H.; Harrison, R.J. *J. Chem. Phys.* 1992, 96, 6796.
  - <sup>17</sup> Frisch M. J.; et al. *GAUSSIAN98 Revision A11*; Gaussian, Inc.: Pittsburgh, P. A., 2002.
  - <sup>18</sup> Møller, C.; Plesset, M.S. *Phys. Rev.* 1934, 46, 618.
  - <sup>19</sup> Lugez, C.L.; Jacox, M.E., *Journal Chem. Phys.* 1998, 108, 9639.
  - <sup>20</sup> Forney, D.; Jacox, M.E., *J. Chem. Phys.* 1994, 101, 8290.
  - <sup>21</sup> Xu, W., Xiao, C., Li, Q., Xie, Y., Schaefer III, H. *Molecular Physics*. 2004, 102, 1415.