

## Bonding of Rare-Gas Atoms to Si in Reactions of Rare Gases with $\text{SiF}_3^+$

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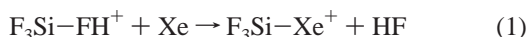
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Direct bonding has been observed to occur between  $\text{SiF}_3^+$  and the rare gases xenon, krypton, and argon in the gas phase at low collision energies and, in the case of xenon and krypton, also at high collision energies. The kinetics of low-energy addition have been monitored at room temperature in He buffer gas at 0.35 Torr using the selected-ion flow tube (SIFT) tandem mass-spectrometer technique. An investigation of the energetics of dissociation of the adduct ions in multi-collision induced dissociation experiments revealed the formation of adduct ions at high collision energies. Experimental and theoretical results are presented for the formation and stability of two possible low-energy isomers of the gaseous trifluorosilylxenon cation,  $\text{F}_3\text{SiXe}^+$ , one formed by the direct bonding of Xe to Si and the other by Xe being attached to one F atom. Two possible high-energy isomers are proposed that contain a Si–Xe–F linkage formed by the insertion of Xe into  $\text{SiF}_3^+$  or a F–Xe–F linkage formed by bond redistribution. The carbon analogue  $\text{CF}_3^+$  did not form adduct ions with Xe under the same experimental conditions. Analogous experimental and theoretical studies are reported for the reactions of  $\text{SiF}_3^+$  with Kr and Ar. Experimental results also are reported for the reaction of  $\text{SiF}_3^+$  with  $\text{N}_2$  and  $\text{O}_2$ .

The synthesis of new rare-gas-containing neutral molecules continues to fascinate the chemist.<sup>1</sup> In the gas phase, molecules consisting of a rare-gas atom combined with a second closed-shell atom or molecule are only weakly bound by van der Waals interactions. The bonding of rare-gas atoms with ions, both closed-shell and open-shell, is more favorable because of the possibility of additional electrostatic interactions and this has been a motivation in gas-phase ion chemistry in the search for rare-gas/heavy-atom bond connectivities.<sup>2</sup> The pioneering work of Bartlett<sup>3</sup> established that xenon is particularly suitable as a rare-gas bonding partner because of its high polarizability. This is so for neutral molecules without and with electronegative elements. An example of the former is  $\text{HXeH}$ ,<sup>4</sup> while examples of the latter include  $\text{HXeM}$  ( $M = \text{Cl, CN, etc.}$ ),<sup>5</sup>  $\text{HXeSH}$ ,<sup>6</sup>  $\text{XeM}$  ( $M = \text{F, Cl, Br, and I}$ ),<sup>7</sup>  $\text{Xe}(\text{CF}_3)_2$ ,<sup>8</sup> and  $\text{XeCCF}_2$ .<sup>9</sup> Ions incorporating xenon include  $\text{FeXe}^+$ ,<sup>2</sup>  $\text{CoXe}^+$ ,<sup>10</sup>  $\text{OXe}^+$ , and  $\text{HOXe}^+$ .<sup>11</sup>

A recent report of the preparation of the gaseous trifluorosilylxenon cation,  $\text{F}_3\text{SiXe}^+$ , under mass-spectrometric conditions has provided the first experimental evidence for Si–Xe bonding.<sup>12</sup> Si–Xe bonding is favorable in  $\text{F}_3\text{SiXe}^+$  because of the high electronegativity of  $\text{SiF}_3^+$ . Ion  $\text{F}_3\text{SiXe}^+$  was prepared in the resonance cell of a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer at a pressure ca.  $2 \times 10^{-7}$  mbar by the nucleophilic displacement of HF from protonated  $\text{SiF}_4$  by Xe.



We report here observations of the formation of one or more isomers of the trifluorosilylxenon cation,  $\text{F}_3\text{SiXe}^+$ , at the much higher pressures (0.35 Torr) of a selected-ion flow tube (SIFT) mass spectrometer by the *direct addition* at room temperature

of Xe to  $\text{SiF}_3^+$ . Furthermore, probing the bond connectivities of these isomers by multi-collision induced dissociation (CID) revealed the remarkable and quite unexpected formation of yet another isomer at elevated collision energies. Our calculations of the energies of possible isomers of  $\text{F}_3\text{SiXe}^+$  suggest that the formation of this latter isomer is very likely a consequence either of the insertion of Xe into a Si–F bond to form a Si–Xe–F linkage or of bond redistribution to form a F–Xe–F linkage. Similar experiments and calculations were performed for the formation of the trifluorosilylkrypton cation,  $\text{F}_3\text{SiKr}^+$ , and the trifluorosilylargon cation,  $\text{F}_3\text{SiAr}^+$ , both of which have not been observed previously. Adducts of  $\text{SiF}_3^+$  with  $\text{O}_2$  and  $\text{N}_2$  also were investigated for comparison.

### Experimental Techniques

The gas-phase ion–molecule reactions reported in this study were investigated with the selected-ion flow tube (SIFT) technique which has been described previously in the literature.<sup>13,14</sup> The  $\text{SiF}_n^+$  ions were produced by electron impact upon neutral  $\text{SiF}_4$  (Matheson, >99.6 mol %) in a low-pressure ion source from a 3% mixture of  $\text{SiF}_4$  in helium at various electron energies: 50 eV for  $\text{SiF}_3^+$ , 70 eV for  $\text{SiF}_2^+$ , 80 eV for  $\text{SiF}^+$ , and  $\text{Si}^+$ . Ion  $\text{CF}_3^+$  was produced in a similar fashion from  $\text{CF}_4$  (Matheson, >99.7 mol %) at an electron energy of 50 eV. Ions emerging from the source were mass-selected with a quadrupole mass filter and introduced via a Venturi-type inlet into a flow of helium buffer gas at a pressure of 0.35 Torr and a temperature of  $295 \pm 2$  K. The ions were allowed to thermalize by collisions (ca.  $4 \times 10^5$ ) with He buffer gas atoms before entering the reaction region downstream. The reactant neutrals were added as pure gases and the variation in reactant and product ion signals was monitored as a function of added reactant neutral. Rate coefficients were determined in the usual manner and are estimated to have an uncertainty of  $\pm 30\%$ .<sup>13,14</sup> All reagent gases had purities better than 99.9%.

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The multi-collision induced dissociation (CID) of sampled ions was investigated by raising the potential of the sampling nose cone while taking care not to introduce mass discrimination in the detection system in a manner described in detail elsewhere.<sup>15</sup> These experiments are useful for exploring bond connectivities, but they do not provide thermochemical information as both dissociation and adduct formation occur under multi-collision conditions.

### Computational Method

Molecular orbital calculations were performed using the Gaussian 94 program.<sup>16</sup> Structure optimizations used gradient techniques<sup>17,18</sup> and wave functions were constructed using hybrid density functional theory at the B3LYP level.<sup>19–21</sup> For calculations on  $F_3SiXe^+$  a DZVP basis set<sup>22</sup> was used, while for both  $F_3SiAr^+$  and  $F_3SiKr^+$  optimizations were performed at B3LYP/6-311++G(d,p)<sup>23–25</sup> followed by single-point calculations at QCISD(T)/6-311++G(2df,p).<sup>26,27</sup> The identities of the critical points (minima or transition states) located on each potential energy surface were established from harmonic frequency calculations. Zero-point energies obtained from the frequency calculations were used without scaling.

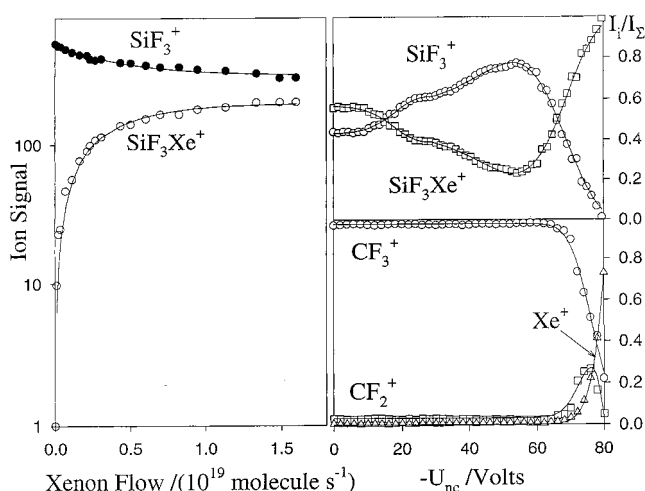
### Results and Discussion

**Reactions with Xe, Kr, and Ar.**  $SiF_n^+$  ions with  $n = 0–3$  were reacted with xenon, krypton, and argon at room temperature. Of these, the ions  $Si^+$ ,  $SiF^+$ , and  $SiF_2^+$  were found to be totally unreactive,  $k < 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , but  $SiF_3^+$  was observed to react by addition of a single rare-gas atom as indicated in reactions 2–4

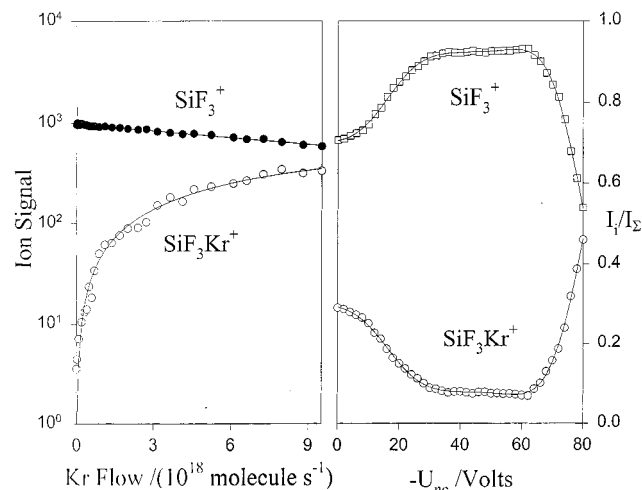


and in Figures 1 to 3. The chemistry stopped with the addition of one rare-gas atom; no further addition was observed,  $k < 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Our observation of the addition of one Xe atom differs from previous FT-ICR measurements<sup>12</sup> taken at much lower pressures that had ruled out the occurrence of the direct addition of Xe to  $SiF_3^+$  on the basis of independent isolation experiments. This difference can be understood if reaction 2 (as well as reactions 3 and 4) occurs predominantly by collisional association under SIFT conditions as indicated, rather than by radiative association, and that radiative association also is inefficient under FT-ICR conditions.

Figures 1–3 indicate very shallow (apparently slow) decays in the reactant-ion signal for the reactions of  $SiF_3^+$  with the rare-gas atoms. Both the curvature in these decays and plots of the product-ion/reactant-ion ratio vs neutral-reactant flow indicated the occurrence of significant reverse reaction. Under these conditions only lower limits to the apparent bimolecular rate coefficients could be extracted from the tangents to the observed initial decay. These are  $>1 \times 10^{-11}$ ,  $>5 \times 10^{-12}$ , and  $>6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for reactions 1–3, respectively. The ion ratio plots indicate approach to, or achievement of, equilibrium with apparent equilibrium constants of  $\geq 1.0 \times 10^6$ ,  $5.5 \times 10^5$ , and  $2.2 \times 10^4$  (standard state = 1 atm) and standard free energy changes of  $\leq -8.2$ ,  $-7.8$ , and  $-5.9 \text{ kcal mol}^{-1}$  for reactions 2–4, respectively. The actual standard free energies may be more negative since some



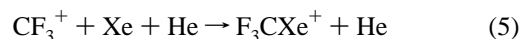
**Figure 1.** The left-hand side shows the reaction profile for the addition of Xe to  $SiF_3^+$  in helium at  $295 \pm 2 \text{ K}$  and  $0.35 \pm 0.01 \text{ Torr}$ . The  $SiF_3Xe^+$  profile is the profile measured for the  $SiF_3^{132}Xe^+$  isotope increased according to the natural abundance of  $^{132}Xe$ . On the top right-hand side is shown the multi-collision CID spectrum for  $SiF_3Xe^+$  for which the flow of Xe is  $5 \times 10^{19} \text{ molecules s}^{-1}$ . On the bottom right-hand side is shown the multi-collision CID spectrum for  $CF_3^+$  produced in a 10% mixture of  $CF_4$  in He by electron impact at 50 eV. The small amount of  $CF_2^+$  present initially is produced upstream by collisional dissociation upon injection into the helium buffer gas. About  $1 \times 10^{19} \text{ molecules s}^{-1}$  of Xe are added downstream.



**Figure 2.** (Left) Reaction profile for the addition reaction of Kr to  $SiF_3^+$  in helium at  $295 \pm 2 \text{ K}$  and  $0.35 \pm 0.01 \text{ Torr}$ . The  $SiF_3Kr^+$  profile is the profile measured for the  $SiF_3^{84}Kr^+$  isotope increased according to the natural abundance of  $^{84}Kr$ . (Right) The multi-collision CID spectrum for  $SiF_3Kr^+$ . The flow of Kr is  $6.5 \times 10^{18} \text{ molecules s}^{-1}$ .

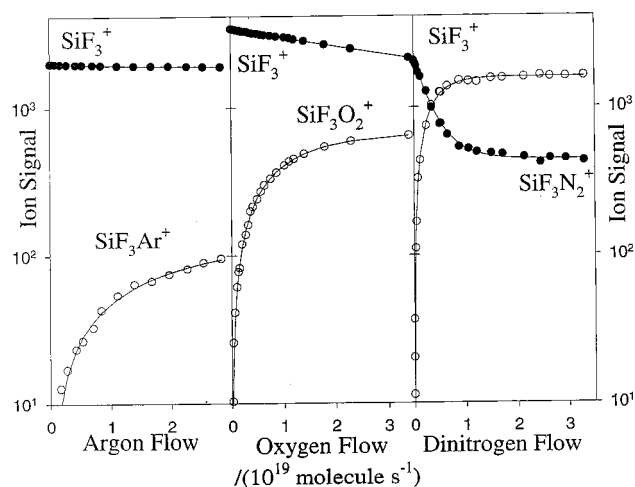
collisional dissociation of these weakly bonded adducts may be occurring during ion sampling.

Separate experiments were performed for the reaction of  $CF_3^+$  with Xe for comparative purposes. Interestingly, reaction 5, the carbon analogue of reaction 2,



was not observed,  $k < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , indicating much weaker C–Xe bonding than Si–Xe bonding.

**Reactions with  $O_2$  and  $N_2$ .** Ion  $SiF_3^+$  also was observed to react with both  $O_2$ ,  $k > 3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $N_2$ ,  $k > 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , by the addition of a single molecule as indicated in reactions 6 and 7



**Figure 3.** Reaction profiles for the addition reactions of  $\text{SiF}_3^+$  with Ar,  $\text{O}_2$ , and  $\text{N}_2$  in helium at  $295 \pm 2$  K and  $0.35 \pm 0.01$  Torr.



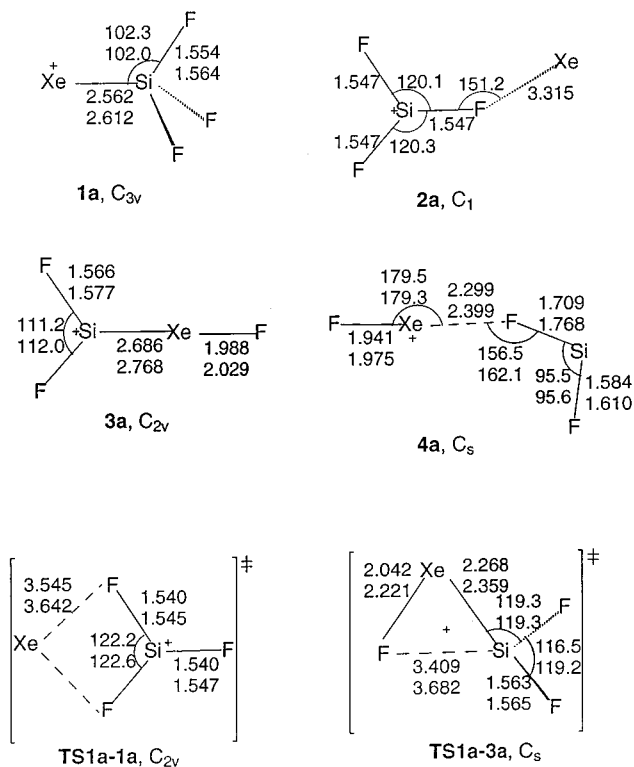
(see Figure 3). Reaction 7 with  $\text{N}_2$  is the faster of the two. No further additions were observed,  $k < 10^{-14}$   $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , but again the measured decays indicated the occurrence of back reaction. The ion ratio plots indicate achievement of equilibrium with equilibrium constants of  $1.4 \times 10^5$  and  $2.8 \times 10^6$  (standard state = 1 atm) and standard free energy changes of  $-7.0$  and  $-8.8$   $\text{kcal mol}^{-1}$  for reactions 6 and 7, respectively.

**Computed Structures and Energies of Isomers.** (a) *Isomers of  $\text{F}_3\text{SiXe}^+$ .* Computed structures for isomers of  $\text{F}_3\text{SiXe}^+$  as calculated at B3LYP/DZVP are shown in Figure 4. Structures **1a–4a** were established to be at minima, both in our preliminary survey of the potential energy surface at MP2(fc)/3-21+G-(d)<sup>28–32</sup> and also at B3LYP/DZVP. Computed total energies (in hartrees) and relative energies (in  $\text{kcal mol}^{-1}$ ) are given in Table 1.

Three structures at critical points that have lower energies than the reactants,  $\text{SiF}_3^+$  and Xe, have been located. Ion **1a** is at the global minimum on the potential energy surface. In this structure the Xe–Si distance of 2.612 Å, the calculated charge on the Xe of +0.412 from a Mulliken population analysis,<sup>33</sup> and the dissociation energy of 34.3  $\text{kcal mol}^{-1}$  all indicate the presence of a weak covalent bond, with a slightly smaller dissociation energy than that of  $\text{H}_3\text{CXe}^+$  (39.0  $\text{kcal mol}^{-1}$  at B3LYP/DZVP).<sup>34</sup> In  $\text{F}_3\text{SiXe}^+$  the Si–F bonds are longer than in isolated  $\text{SiF}_3^+$  (by 0.007 Å) and the XeSiF angle of 102.0° is intermediate between 90° (expected for  $\text{SiF}_3^+$  and Xe at infinite separation) and 109.5° (expected for a perfect tetrahedral arrangement around silicon).

Structure **TS1a–1a** is planar and has  $C_{2v}$  symmetry. The harmonic frequency calculation showed this structure to be a transition state, confirming the findings of a lower level theoretical study.<sup>12</sup> The motion leading to minima from this transition state structure involves movement out of plane and a subsequent intrinsic reaction coordinate (IRC)<sup>35</sup> calculation established that **TS1a–1a** is the transition state for interconversion between two identical pyramidal structures, **1a** i.e., **TS1a–1a** is the transition state for inversion of **1a**. The barrier to this process is 28.0  $\text{kcal mol}^{-1}$ .

In our initial attempts to find structure **2a** at the B3LYP/DZVP level of theory we started with a structure in which Si–



**Figure 4.** Optimized geometries for isomers and transition structures on the  $\text{F}_3\text{SiXe}^+$  surface. The upper numbers are at MP2(fc)/3-21G(d) and the lower numbers are at B3LYP/DZVP. Single numbers for ion **2a** are from B3LYP/DZVP. Bond lengths are in angstroms and bond angles are in degrees.

**TABLE 1: Computed Total Energies (in hartrees) and Relative Energies (in  $\text{kcal mol}^{-1}$ ) for Structures on the  $\text{F}_3\text{SiXe}^+$  Surface As Calculated at B3LYP/DZVP**

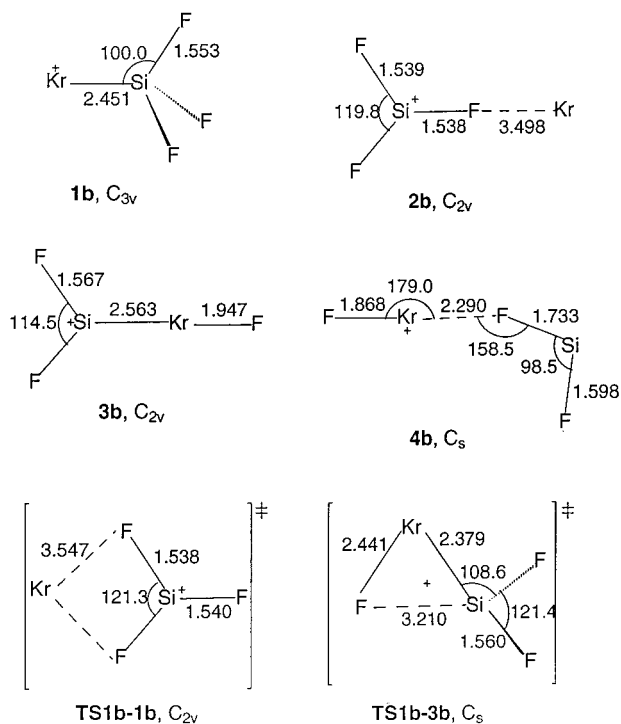
structure	total energies	relative enthalpies <sup>a</sup>
<b>1a</b>	−7822.91495	−34.4
<b>TS1a–1a</b>	−7822.86956	−6.4
<b>2a</b>	−822.86804	−4.9
$\text{SiF}_3^+ + \text{Xe}$	−7822.85983 <sup>b</sup>	0
<b>3a</b>	−7822.73161	79.2
<b>4a</b>	−7822.72158	86.2
$\text{XeF} + \text{SiF}_2^+$	−7822.67782 <sup>b</sup>	112.3
$\text{XeF}^+ + \text{SiF}_2$	−7822.67400 <sup>b</sup>	114.7
<b>TS1a–3a</b>	−7822.64322	134.7

<sup>a</sup> Relative enthalpies include zero-point energies, thermal-energies, and work terms required to correct relative energies up to 298 K.

<sup>b</sup> Energy at infinite separation.

F–Xe was linear ( $C_{2v}$  symmetry). This proved to be at a second-order saddle point, as in the previous study at STO3-G;<sup>12</sup> subsequent optimization, without geometric constraints, led to structure **2a** given in Table 1. The latter structure is 0.4  $\text{kcal mol}^{-1}$  lower in energy than that at the second-order saddle point. The dissociation energy of complex **2a** is only 4.9  $\text{kcal mol}^{-1}$ . The structure of the  $\text{SiF}_3$  component is essentially the same as that in  $\text{SiF}_3^+$  (the Si–F bond lengths are longer by 0.002 Å in the complex), the F...Xe distance is very long (3.315 Å), and the charge on Xe is close to zero (+0.036). All these data indicate that **2a** is best described as being an  $\text{SiF}_3^+$  ion that is weakly “solvated” by a Xe atom.

Ions **3a** and **4a** are both at high minima, approximately 80  $\text{kcal mol}^{-1}$  above the reactants  $\text{SiF}_3^+$  plus Xe. Ion **3a**, formed by insertion of Xe into an Si–F bond of  $\text{SiF}_3^+$ , has Si–Xe and Xe–F distances that are consistent with covalent bonding and the charge (+0.569 on the  $\text{SiF}_2$  fragment and +0.431 on XeF) is fairly evenly distributed.



**Figure 5.** Optimized geometries for isomers and transition structures at B3LYP/DZVP on the  $F_3SiKr^+$  surface. Bond lengths are in angstroms and bond angles are in degrees.

In ion **4a**, one Xe-F distance is very long (2.399 Å) and most of the positive charge (+0.786) is calculated to be on the XeF fragment. Ion **4a** then is best described as ion  $XeF^+$  “solvated” by attachment to one fluorine atom of  $SiF_2$ . The energy for dissociation of this ion to form  $XeF^+$  plus  $SiF_2$  is 28.5 kcal mol<sup>-1</sup>.

Transition structure **TS1a-3a** is 134.7 kcal mol<sup>-1</sup> above  $SiF_3^+$  plus Xe and is 55.5 kcal mol<sup>-1</sup> above ion **3a**. An IRC calculation established that **TS1a-3a** is intermediate between the structure at the global minimum, ion **1a**, and the insertion product, ion **3a**. One unusual feature of **TS1a-3a** is the unexpectedly short Si-Xe distance of 2.359 Å; this is by far the shortest Si-Xe distance found in any of the ions and molecules that were studied and is 0.409 Å shorter than in **3a** and 0.253 Å shorter than in **1a**. The equivalent transition structure on the  $F_3SiKr^+$  potential energy hypersurface also has a very short Si-Kr bond distance.

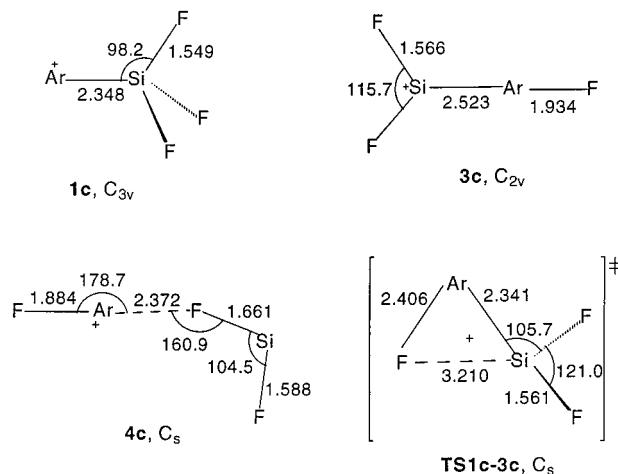
(b) *Isomers of  $F_3SiKr^+$* . The potential energy hypersurface for  $F_3SiKr^+$  is similar to that calculated for  $F_3SiXe^+$ , with two low-energy and two high-energy isomers. The smaller size of krypton enabled us to use a higher level of theory than for xenon and the parallel behaviors of the two systems further authenticates our results on the potential energy surface for  $F_3SiXe^+$ . The results are given in Figure 5 and Table 2.

The salient features of the  $F_3SiKr^+$  surface are as follows. **1b** is at the global minimum and its dissociation energy (21.9 kcal mol<sup>-1</sup> at B3LYP and 24.6 kcal mol<sup>-1</sup> at QCI) is intermediate between those of  $F_3SiAr^+$  and  $F_3SiXe^+$ . The barrier to inversion for **1b** is 20.3 kcal mol<sup>-1</sup> and the transition structure for this process, **TS1b-1b**, is only 1.6 kcal mol<sup>-1</sup> below the energy of the dissociation products,  $F_3Si^+$  plus Kr. Ion **2b**, the loosely “solvated” ion, unlike the equivalent structure on the  $F_3SiXe^+$  surface, has  $C_{2v}$  symmetry and its dissociation energy (1.5 kcal mol<sup>-1</sup> at QCI) is smaller than that of **2a** (4.9 kcal mol<sup>-1</sup>).

**TABLE 2: Computed Total Energies (in hartrees) (Relative enthalpies (in kcal mol<sup>-1</sup>) at 298 K for structures on the  $F_3SiAr^+$  and  $F_3SiKr^+$  surfaces are given in parentheses.)**

structure	B3LYP <sup>(a)</sup>	QCI <sup>(b)</sup>
(a) $F_3SiKr^+$ Surface		
<b>1b</b>	-3342.70422(-21.9)	-3340.80783(-24.6)
<b>TS1b-1b</b>	-3342.67102(-1.6)	
<b>2b</b>	-3342.67010(-0.5)	-3340.76995(-1.5)
$SiF_3^+$ + Kr	-3342.16889(0.0)	-3340.76811(0.0)
<b>3b</b>	-3342.48600(114.1)	-3340.56048(130.5)
$KrF$ + $SiF_2^+$	-3342.47238(121.4)	-3340.53953(141.5)
<b>4b</b>	-3342.46746(125.1)	-3340.52506(152.1)
<b>TS1b-3b</b>	-3342.42419(152.1)	
$KrF^+$ + $SiF_2$	-3342.40990(160.6)	-3340.48918(173.1)
(b) $F_3SiAr^+$ Surface		
<b>1c</b>	-1116.49167(-13.9)	-1115.38565(-18.9)
$SiF_3^+$ + Ar	-1116.46907(0.0)	-1115.35503(0.0)
<b>3c</b>	-1116.24117(142.3)	-1115.11532(149.4)
<b>TS1c-3c</b>	-1116.20368(164.9)	
<b>4c</b>	-116.22194(153.9)	-1115.09151(164.2)

<sup>a</sup> Structure optimizations were performed at B3LYP/6-311++G(d,p).  
<sup>b</sup> Single-point calculations at QCISD(T)/6-311++G(2df,p) on structures optimized at B3LYP/6-311++G(d,p); there are some significant differences between the results obtained with these two levels of theory, as much as 27 kcal mol<sup>-1</sup> for the high-energy structure **4b**.



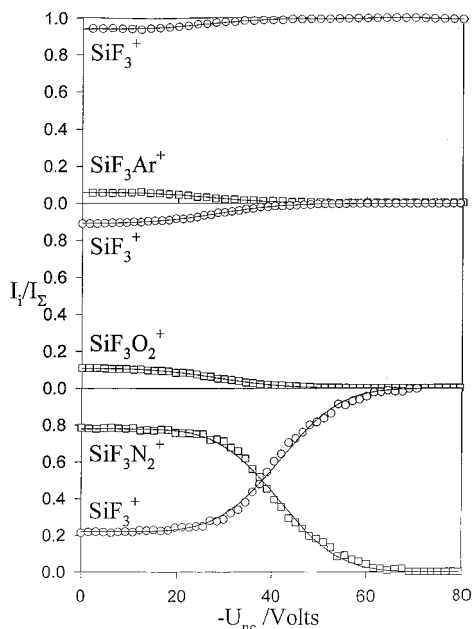
**Figure 6.** Optimized geometries for isomers and transition structures at B3LYP/DZVP on the  $F_3SiAr^+$  surface. Bond lengths are in angstroms and bond angles are in degrees.

The energies of **3b** and **4b** relative to that of  $F_3Si^+$  plus Kr are dependent on the level of theory, with the values being larger at the QCI level. We were unable to complete a QCI calculation for **TS1b-3b** due to convergence problems. Both **3b** and **4b** are much higher in energy relative to the dissociation products than the analogous structures on the  $F_3SiXe^+$  surface, and **TS1b-3b** is also higher (152.1 kcal mol<sup>-1</sup> compared with 134.7 kcal mol<sup>-1</sup>).

(c) *Isomers of  $F_3SiAr^+$* . Our preliminary calculations showed ion **3c**, the ion produced by inserting an argon atom into an Si-F bond, to lie much higher in energy above the reactants ( $F_3Si^+$  plus Ar) than the analogous structure on the  $F_3SiXe^+$  surface (149 kcal mol<sup>-1</sup> compared with 79.2 kcal mol<sup>-1</sup>). Consequently, the potential energy hypersurface for  $F_3SiAr^+$  was examined less extensively than those for the Xe- and Kr-containing ions.

The structures of ions **1c** and **3c**, as optimized at B3LYP/6-311++G(d,p), are given in Figure 6 and their relative enthalpies and total energies are recorded in Table 2. The calculated dissociation energy of **1c** is dependent on the level of theory, but both values given in Table 2 (13.9 kcal mol<sup>-1</sup> at B3LYP/





**Figure 7.** Multi-collision CID spectra for the observed adduct ions SiF<sub>3</sub>Ar<sup>+</sup>, SiF<sub>3</sub>O<sub>2</sub><sup>+</sup>, and SiF<sub>3</sub>N<sub>2</sub><sup>+</sup> in helium. The Ar flow is  $5 \times 10^{19}$  molecules s<sup>-1</sup>, the flow of O<sub>2</sub> is  $7.5 \times 10^{18}$  molecules s<sup>-1</sup> and the flow of N<sub>2</sub> is  $2.9 \times 10^{19}$  molecules s<sup>-1</sup>.

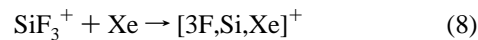
6-311++G(d,p) and 18.9 kcal mol<sup>-1</sup> at QCISD(T)/6-311++G(2df,p) are considerably lower than the value of 34.4 kcal mol<sup>-1</sup> calculated for F<sub>3</sub>SiXe<sup>+</sup>. This is consistent with the lower polarizability of argon relative to that of xenon. No minimum was found for the Ar analogue of structures **2a** and **2b**.

**Results and Interpretation of Multi-Collision Induced Dissociation Experiments.** The multi-collision induced dissociations of the F<sub>3</sub>SiAr<sup>+</sup>, F<sub>3</sub>SiO<sub>2</sub><sup>+</sup>, and F<sub>3</sub>SiN<sub>2</sub><sup>+</sup> adduct ions observed experimentally were relatively uncomplicated. Each showed only a single onset of dissociation (see Figure 7) which suggests the presence of only one isomer in each case. The thresholds for dissociation observed in the laboratory-energy frame are 14, 14, and 29 V, respectively, where the threshold is taken to be the point of intersection of the tangent to the fastest decaying portion of the disappearance curve and a baseline intersecting the initial signal.<sup>14</sup>

These onset voltages are relatively small and suggest weak interactions of Ar, O<sub>2</sub>, and N<sub>2</sub> with SiF<sub>3</sub><sup>+</sup>. Ions F<sub>3</sub>SiKr<sup>+</sup> and F<sub>3</sub>SiXe<sup>+</sup> also exhibit early onsets of dissociation. The results with Ar, Kr, and Xe are consistent with the relatively small standard free energies for dissociation of 5.9, 7.0, and  $\geq 8.8$  kcal mol<sup>-1</sup> obtained from the equilibrium analyses reported above. The calculations predict free-energy changes of 4.9, 13.3, and 26.6 kcal mol<sup>-1</sup> at the B3LYP/DZVP level of theory. The latter two theoretical values are larger than the experimental values and so are the differences. However, the theoretical differences decrease with the level of theory. Computations at the QCISD(T)(full)/6-311++G(2df,p) level indicate values for the free energy of dissociation of 11.5 and 15.4 for F<sub>3</sub>SiAr<sup>+</sup> and F<sub>3</sub>SiKr<sup>+</sup>, respectively. Both of these values are now larger than experiment, but the differences are more in line with experiment:  $14.4/11.5 = 1.25$  compares well with  $7.0/5.9 = 1.19$ .

The collisional dissociation spectra observed for F<sub>3</sub>SiXe<sup>+</sup> and F<sub>3</sub>SiKr<sup>+</sup> are more intriguing than the others. Figure 1 shows two clear onsets for the removal of Xe from F<sub>3</sub>SiXe<sup>+</sup> at low collision energies, viz. at 10 and 32 V. This behavior suggests the disappearance of two isomeric ions. Also, there is a

remarkable formation onset at high collision energies at ca. 60 V, of what must be another isomer of F<sub>3</sub>SiXe<sup>+</sup>. Such behavior is unprecedented in our experience with the SIFT-CID technique; we have not previously observed an onset at high collision energies. Apparently, in this case, formation of another isomer of F<sub>3</sub>SiXe<sup>+</sup> is induced by collisions of high kinetic energy SiF<sub>3</sub><sup>+</sup> with Xe according to reaction 8:

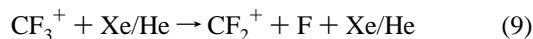


Taken together, the two thresholds for dissociation and the one threshold for formation suggest the participation of 3 different isomers of F<sub>3</sub>SiXe<sup>+</sup> in the development of the CID spectrum. F<sub>3</sub>SiKr<sup>+</sup> shows one threshold for dissociation and one threshold for formation (see Figure 2) and this suggests the participation of two different isomers of F<sub>3</sub>SiKr<sup>+</sup> in the development of this CID spectrum.

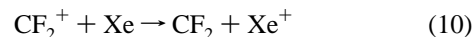
We propose the following assignments for the three isomers of F<sub>3</sub>SiXe<sup>+</sup> on the basis of the results of our calculations. The two early dissociations are attributed to the dissociation of structures **2a** and **1a**, respectively. Structure **2a**, which is only weakly bound (by 4.9 kcal mol<sup>-1</sup>) dissociates at 10 V, while structure **1a** which has a dissociation energy of 34.4 kcal mol<sup>-1</sup> dissociates at 30 V. The dissociation thresholds for these two isomers (10 and 32 V, respectively) are well separated because of the substantial differences in their stabilities. The magnitude of the onset for the dissociation of structure **2a** is qualitatively consistent with our previous experience with weakly bound ions and the magnitude of the onset for the dissociation of structure **1a** is qualitatively consistent with our previous experience with dissociations of ions with comparable stability and complexity.<sup>15</sup>

We attribute the onset of the isomer at high energies to the collision-induced formation of structures **3a** and/or **4a** which lie 79.2 and 86.2 kcal mol<sup>-1</sup>, respectively, above the thermal energy of SiF<sub>3</sub><sup>+</sup> + Xe. Figure 1 shows almost complete conversion at the maximum-available nose-cone voltage of the SiF<sub>3</sub><sup>+</sup> to F<sub>3</sub>SiXe<sup>+</sup>, both the SiF<sub>3</sub><sup>+</sup> initially present and the SiF<sub>3</sub><sup>+</sup> produced in the dissociations that we have attributed to two low-energy F<sub>3</sub>SiXe<sup>+</sup> isomers. The high-energy isomer is expected to dissociate at still higher nose-cone voltages, but none was observed up to a nose-cone voltage of -80 V. Our calculations indicate that dissociation of isomer **3a** into XeF<sup>+</sup> + SiF<sub>2</sub> or XeF + SiF<sub>2</sub><sup>+</sup> would require at least 35.5 and 33.1 kcal mol<sup>-1</sup> and that dissociation of isomer **4a** into XeF<sup>+</sup> + SiF<sub>2</sub> or XeF + SiF<sub>2</sub><sup>+</sup> would require at least 28.5 kcal mol<sup>-1</sup> and 26.1 kcal mol<sup>-1</sup>, respectively (see Figure 8). The onset for these dissociations should lie well beyond -80 V.

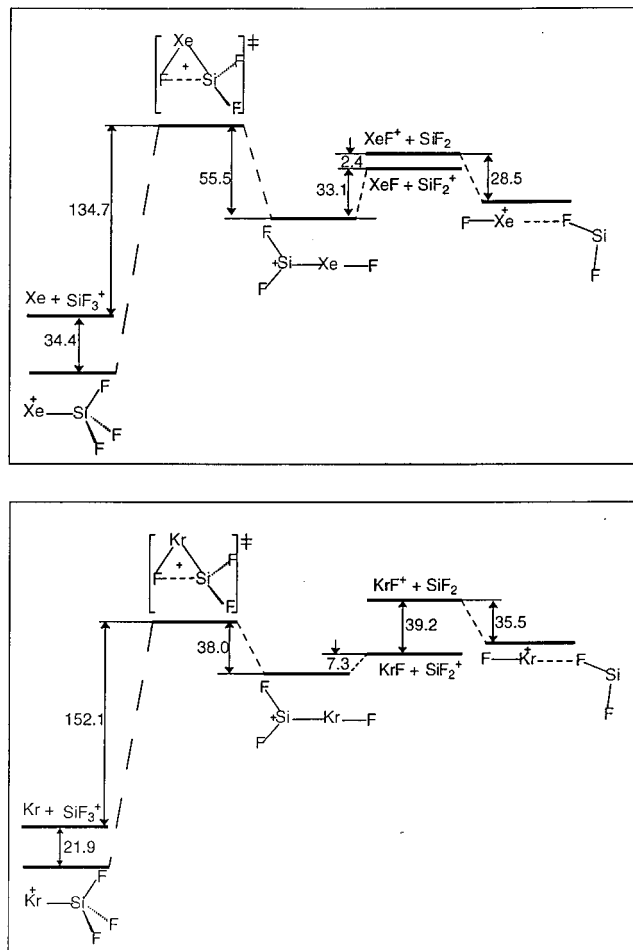
We also recorded, for comparative purposes, the high collision-energy behavior of CF<sub>3</sub><sup>+</sup> with added Xe. It was completely different from that recorded for SiF<sub>3</sub><sup>+</sup> and Xe. The CID spectrum of CF<sub>3</sub><sup>+</sup> with added Xe is shown in Figure 1. No formation of a F<sub>3</sub>CXe<sup>+</sup> adduct ion was observed at high collision energies. Instead, CF<sub>3</sub><sup>+</sup> dissociates to CF<sub>2</sub><sup>+</sup> according to reaction 9:



at relatively high collision energies (69 V). The dissociation appears to be followed at still higher energies by an electron transfer from Xe to CF<sub>2</sub><sup>+</sup> according to reaction 10:



Reaction 10 is endothermic by 16 kcal mol<sup>-1</sup> for ground-state reactants with ionization energies of 12.130 eV (Xe) and 11.42 eV (CF<sub>2</sub>).<sup>36</sup>



**Figure 8.** Profile for the interconversion of high-energy isomers of  $F_3SiXe^+$  and  $F_3SiKr^+$  (energies in  $\text{kcal mol}^{-1}$  at 298 K) as calculated at B3LYP/DZVP.

Figure 2 shows a clear onset for the removal of Kr from  $F_3SiKr^+$  at low collision energies (5 V) and, at 69 V, an onset for the formation of what should be another isomer of  $F_3SiKr^+$  according to reaction 11:



We propose that structures **3b** and/or **4b** which lie 114.1 and 125.1  $\text{kcal mol}^{-1}$ , respectively, above the thermal energy of  $SiF_3^+ + Kr$  (see Figure 8) may be formed in reaction 11. The early dissociation can be attributed to the unresolved dissociation of structures **1b** and **2b**, although structure **2b** is bound by only 0.5  $\text{kcal mol}^{-1}$  and so may not be stable at room temperature.

The formation of a high-energy  $SiF_3Ar^+$  isomer was not observed in the voltage range of the CID experiments and only one low-energy isomer was apparent at low CID energies. The computations indicated only one low-energy minimum on the  $SiF_3Ar^+$  surface, structure **1c**. Structure **2c** could not be located. The high-energy isomers **3c** and **4c** lie higher in energy than the corresponding Kr and Xe isomers and this is consistent with the nonoccurrence of a high-energy onset in the Ar CID experiments.

## Conclusions

Xenon, krypton, argon, nitrogen, and oxygen have been observed to bond with  $SiF_3^+$  in the gas phase at low and also at high collision energies in the case of xenon and krypton.

Multi-collision induced dissociation experiments indicate the formation of two low-energy isomers of  $F_3SiXe^+$  at room temperature. High collision energies lead to the formation of at least one new isomer of both the trifluorosilylxenon and trifluorosilylkrypton cations. The structures and energies of the observed rare-gas isomers have been assigned on the basis of ab initio calculations. Thus, in the case of Xe, two low-energy isomers result from the direct bonding of Xe to Si and of Xe to one F atom, while the high-energy isomer has been assigned a Si-Xe-F linkage formed by the insertion of Xe into  $SiF_3^+$  and/or a F-Xe-F linkage resulting from bond redistribution. Analogous structures appear to be possible with Kr and Ar, but with Ar the Ar-F bonded low-energy isomer does not have a minimum.

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