The Gaseous Trifluorosilylxenon Cation, F_3SiXe^+: a Stable Species with a Silicon–Xenon Bond

Romano Cipollini[a] **and Felice Grandinetti***[b]

[a] *Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma* La Sapienza, *P.le A. Moro, 5, 00185 Rome, Italy*
[b] *Dipartimento di Scienze Ambientali, Università della Tuscia, Via S. C. De Lellis, 01100 Viterbo, Italy*

The gaseous trifluorosilylxenon cation F_3SiXe^+, a stable species with a silicon–xenon bond, can be obtained, under mass spectrometric conditions, from the nucleophilic displacement of HF by Xe from protonated SiF_4.

Since the pioneering work of Bartlett in 1962,[1] numerous compounds containing Xe–F and Xe–O bonds have been synthesized and unambiguously characterized.[2] By contrast, bonding xenon to elements other than fluorine and oxygen proved difficult, and the exclusive observation of stable species containing xenon–boron,[3] xenon–carbon,[4,5] xenon–nitrogen,[6,7] and xenon–chlorine bonds[8] reinforces the expectation[9] that only the most electronegative ligands may form stable bonds with xenon. Due to the electron-withdrawing effect of three fluorine atoms, the group electronegativity of the trifluorosilyl cation, F_3Si^+, is expected to be substantially high. Thus, the species appears a suitable candidate for the formation of a silicon–xenon bond. Having recently examined, with a combination of mass spectrometric and theoretical techniques, the gas-phase reactivity of SiF_3^+ toward several *n*-type nucleophiles,[10] we decided to attempt the preparation, under mass spectrometric conditions, of gaseous trifluorosilylxenon cations, F_3SiXe^+.

As firstly pointed out by Beauchamp and Holtz several years ago,[11] xenon is able to undergo nucleophilic displacement of HF from protonated MeF, with formation of $MeXe^+$. Thus, assuming a certain capability of xenon to undergo nucleophilic displacement at silicon, the following ion–molecule reaction [eqn. (1)] could conceivably be employed as a route to gaseous

$$F_3Si\text{–}FH^+ + Xe \rightarrow F_3Si\text{–}Xe^+ + HF \qquad (1)$$

F_3SiXe^+ ions. This expectation has been fully verified. The occurrence of reaction (1) has been unambiguously ascertained by Fourier Transform Ion Cyclotron Resonance (FT-ICR) spectrometry.† In a typical experiment, the external source of the FT-ICR spectrometer was fed with a mixture of D_2 and SiF_4 (approximate molar ratio 10:1; nominal pressure: *ca.* 5×10^{-5} mbar) and ionized with 70 eV electrons. The SiF_4D^+ ions obtained from the exothermic[12] deuteron-transfer reaction (2)

$$D_3^+ + SiF_4 \rightarrow SiF_4D^+ + D_2 \qquad (2)$$

[$\Delta H°_{298} = -84$ kJ mol^{-1}] were transferred into the resonance cell, isolated, and allowed to react with xenon, introduced into the cell at a pressure of *ca.* 2×10^{-7} mbar. A representative time-delayed mass spectrum is shown in Fig. 1. As the most important result, in the *m*/*z* region from 213 to 221 a multiplet is detected, which accounts for up to *ca.* 5% of the total ion intensity. The detailed scanning of this region, performed independently, is shown in Fig. 2. The assignment of the observed peaks to the seven most abundant isotopes of F_3SiXe^+ is supported by accurate mass measurements and by observation of their relative intensities, which parallel the natural isotopic composition of xenon. In addition, the contribution of $F_3{}^{29}Si{}^{132}Xe^+$, at *m*/*z ca.* 218, is clearly visible in Fig. 2. From Fig. 1, a certain amount of SiF_3^+ (*m*/*z* = 85) is detected from the isolated SiF_4D^+. Independent isolation experiments show that this ion is unreactive toward xenon, thus ruling out, in the employed conditions, the conceivable addition of SiF_3^+ to Xe as a route to the observed F_3SiXe^+ ions. Thus, our mass spectrometric experiments provide unambiguous evidence for the existence of stable gaseous trifluorosilylxenon cations, which arise from the HF-displacement reaction (1). In keeping with their formation process, and taking into account the high positive charge located on the silicon atom of SiF_3^+, the

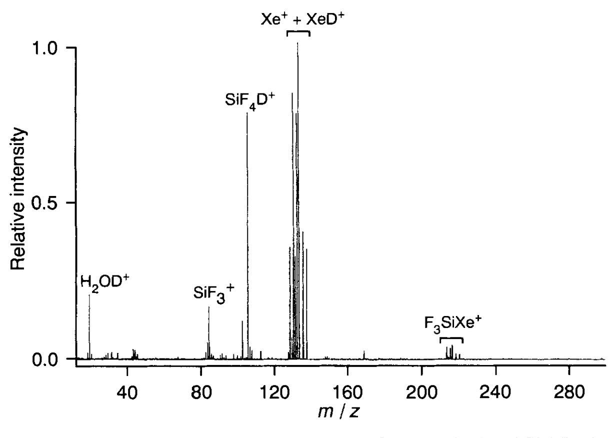


Fig. 1 Time-delayed mass spectrum (t = 1 s) from the isolated SiF_4D^+ ions reacting with xenon (p_{Xe} *ca.* 2×10^{-7} mbar)

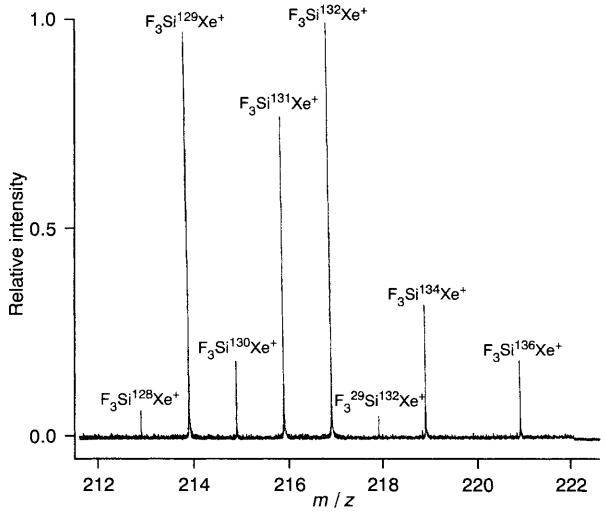
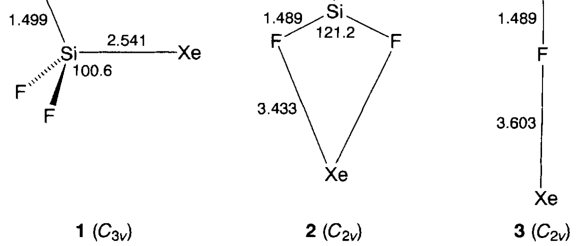


Fig. 2 Detailed scanning of the region *m*/*z* = 212–222 of the time-delayed mass spectrum (t = 1 s) from the isolated SiF_4D^+ ions reacting with xenon (p_{Xe} *ca.* 2×10^{-7} mbar)



1 (C_{3v}) **2** (C_{2v}) **3** (C_{2v})

Fig. 3 HF/STO-3G* optimized geometries (bond lengths in Å, angles in °) of the investigated $(F_3Si/Xe)^+$ adducts observed F_3SiXe^+ ions should possess a $F_3Si{-}Xe^+$ connectivity. A more detailed insight into the structure of F_3SiXe^+ has been obtained by *ab initio* calculations. The geometries of several conceivable $(F_3Si/Xe)^+$ adducts have been optimized at the HF/STO-3G* level of theory, and the results are shown in Fig. 3. Among the three critical points located on the potential energy surface, only the C_{3v}-symmetry ion **1** is a true minimum, whereas the two fluorine-coordinated structures **2** and **3** correspond to first- and a second-order saddle points, respectively. Whereas ion **2** is connected to **1** by a simple out-of-plane rotation of the three fluorine atoms, a preliminary in-plane rotation of the fluorines is required to connect **3** to **1**. In addition, the silicon-coordinated isomer **1** is more stable than the almost degenerate ions **2** and **3** by more than 146 kJ mol^{-1}. Whereas the binding energy of **1** with respect to separated SiF_3^+ and Xe is computed as 150 kJ mol^{-1}, the binding energy of **2** and **3** is less than 4 kJ mol^{-1}. Thus, the *ab initio* calculations suggest that only F_3SiXe^+ isomers with xenon bonded to silicon can be observable species in the gas phase.

In conclusion, our mass spectrometric experiments and theoretical calculations provide support for the existence of gaseous $F_3Si{-}Xe^+$ ions. The observation of a stable species with a silicon–xenon bond enlarges the body of evidence concerning the capability of xenon to form stable bonds with second-row elements, so far limited to the observation of compounds containing xenon–chlorine bonds.[8]

We thank the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Ricerche (CNR) for financial support.

Received, 30th November 1994; Com. 4/07335E

Footnote

† The FT-ICR experiments were performed with a Bruker Spectrospin APEX TM 47e spectrometer equipped with an external ion source and a cylindrical 'infinity cell' situated between the poles of a superconducting magnet (4.7 T). The ions of interest, generated in the external source and transferred into the cell by a system of potentials and lenses, were isolated from all other ions using broad-band and 'single-shots' ejection techniques, and their time dependency was obtained by acquiring mass spectra at various reaction times (from 0.1 to 10 s). For accurate mass measurements, the instrument was operated under high-resolution conditions. The preferred use of D_2 instead of H_2 comes from the observation that, in our experiments, a significant $Xe^{\cdot+}$ abundance is observed which potentially conflicts with the $XeH(D)^+$ peaks, due to the multiple isotopic composition of Xe. Although it is possible to find isotopes of $Xe^{\cdot+}$, such as $^{134}Xe^{\cdot+}$ or $^{136}Xe^{\cdot+}$, which do not overlap with XeH^+ isotopes, their relatively low contribution to the isotopic composition of xenon would introduce a rather large error in the evaluation of the $Xe^{\cdot+}$ intensity. However, since there are no $^{133}Xe^{\cdot+}$ and $^{127}XeD^+$ isotopes, and ^{129}Xe and ^{132}Xe are the two most abundant isotopes of xenon, using D_2 allows the evaluation of the contribution of pure $Xe^{\cdot+}$ and XeD^+ from the ion intensity of $^{129}Xe^{\cdot+}$ and $^{132}XeD^+$. Standard *ab initio* calculations were performed using a RISC/6000 version of the *Gaussian 92* set of programs.

References

1 N. Bartlett, *Proc. Chem. Soc. (London)*, 1962, 218.
2 *Advanced Inorganic Chemistry*, ed. F. A. Cotton and G. Wilkinson, Wiley, New York, 1987.
3 C. T. Goetschel and K. R. Loos, *J. Am. Chem. Soc.*, 1972, **94**, 3018.
4 L. J. Turbini, R. E. Aikman and R. J. Lagow, *J. Am. Chem. Soc.*, 1979, **101**, 5833.
5 H. J. Frohn and S. Jakobs, *J. Chem. Soc., Chem. Commun.*, 1989, 625; H. J. Frohn, S. Jakobs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1506.
6 R. D. LeBlond and D. D. DesMarteau, *J. Chem. Soc., Chem. Commun.*, 1974, 555.
7 J. F. Sawyer, G. J. Schrobilgen and S. J. Sutherland, *J. Chem. Soc., Chem. Commun.*, 1982, 210.
8 R. D. Willett, S. W. Peterson and B. A. Coyle, *J. Am. Chem. Soc.*, 1977, **99**, 8202, and references therein.
9 N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones and R. D. Burbank, *J. Chem. Soc., Chem. Commun.*, 1969, 703.
10 F. Grandinetti, G. Occhiucci, O. Ursini, G. de Petris and M. Speranza, *Int. J. Mass Spectrom. Ion Processes*, 1993, **124**, 21.
11 D. Holtz and J. L. Beauchamp, *Science*, 1971, **173**, 1237.
12 Thermochemical data are taken from S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, suppl. 1.