# Photoelectron Spectra of Some Simple Fluorosilanes

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The photoelectron spectra of $SiF_3H$, $SiF_3X$ (X = Cl or Br), and $SiF_3Me$ excited by He(I) and He(II) radiation are described, with the He(I) spectrum of $Si_2F_6$; assignments of bands to molecular energy levels are based on comparison with the spectra of related compounds.

We have recently described[1] the He(I) photoelectron spectra of $SiH_3X$ and found evidence in the spectra for $(p\rightarrow d)$ $\pi$-bonding from X to Si. It has been suggested[2] that $\pi$-interactions of this kind are likely to be enhanced by the presence of electronegative substituents at silicon. We have therefore recorded the spectra of $SiF_3H$, $SiF_3Cl$, and $SiF_3Br$, with those of $SiF_3CH_3$ and $Si_2F_6$, and assigned the peaks observed by comparison with the spectra of $MF_4$ (M = C or Si), $CF_3H$, and $CF_3X$. The spectra of $MF_4$[3-6] and the other fluorocarbons[6,7] have been reported previously.

## EXPERIMENTAL

Compounds were prepared by standard routes (1)[8] and (2)[9] in a conventional Pyrex vacuum system. $SiF_3H$, $Si_2F_6$, and $SiF_3Me$ were prepared[10] from the corresponding

$$SiF_3OMe + BX_3 \longrightarrow SiF_3X + MeOBX_2 \ (X = Cl \text{ or } Br) \qquad (1)$$

$$AgCO_2CF_3 + X_2 \longrightarrow CF_3X + CO_2 + AgX \ (X = Cl \text{ or } Br) \qquad (2)$$

chlorides by fluorination with $SbF_3$. Samples were purified by trap-to-trap distillation and the purity checked by i.r. spectroscopy with a Perkin-Elmer 457 spectrometer, and by molecular weight determinations. The He(I) (584 Å) spectra were recorded by means of a Perkin-Elmer PES 16 spectrometer and He(II) spectra recorded at Perkin-Elmer Ltd.

*Assignments.*—The compounds $SiF_3H$ and $MF_3X$ belong to the point group $C_{3v}$. For $MF_3X$ the valence-shell atomic orbitals can be assigned to symmetry classes as in Table 1, and combined to give the occupied molecular orbitals set out in Table 2; the order of Si–F $\sigma$- and F lone-pair levels is not of course determined by symmetry, and depends on the analysis of the observed spectra (see below). However, the order given in Table 2 is at least chemically plausible. For $SiF_3H$ there is no $4e$ level and $3a_1$ becomes the Si–H $\sigma$-level. The spectra are shown in Figures 1 and 2, and the positions of the bands are summarised in Table 3; all the expected valence-shell bands for $SiF_3H$ and $SiF_3X$ are observed in the range 6—21·22 eV.

TABLE 1

Symmetry classes of the valence-shell atomic orbitals of $MF_3X$

| | $a_1$ | $a_2$ | $e$ |
|---|---|---|---|
| M $ns$ | 1 | | |
| M $np_z$ | 1 | | |
| M $np_x/p_y$ | | | 1 |
| F $2p_z$ | 1 | | 1 |
| F $2p_x/p_y$ | 1 | 1 | 2 |
| X $xp_z$ | 1 | | |
| X $xp_x/p_y$ | | | 1 |

TABLE 2

Symmetry classes of the occupied molecular orbitals of $MF_3X$

| | $a_1$ | $a_2$ | $e$ |
|---|---|---|---|
| X $xp\pi$ lone pair | | | $4e$ |
| Si–X $\sigma$ | $3a_1$ | | |
| F $2p\pi$ lone pair | $2a_1$ | $1a_2$ | $3e$, $2e$ |
| Si–F $\sigma$ | $1a_1$ | | $1e$ |

For $SiF_3Me$ we assume that the appropriate point group is $C_{3v}$; the Si–C $\sigma$-bonding level is $4a_1$, the C–H bonding levels are $4e$ and $1a_1$, the $SiF_3$ $\sigma$-bond levels become $2a_1$ and $1e$, and the fluorine lone pairs $3a_1$,$1a_2$ and $3e$,$2e$. The point group for $Si_2F_6$ is taken as $D_{3d}$, with a centre of symmetry; apart from the Si–Si level, $a_{1g}$, all other levels for the $SiF_3$ groups split into $g$ and $u$ components.

Our assignments are based partly on analogy with $MH_3X$, partly on comparison with previous studies of $CF_3X$ and $CF_3H$, and partly on comparison with the spectra of $CF_4$ and $SiF_4$. The spectra of the two tetrafluorides are well known.[3-6] There has been some disagreement about details of the assignments, but it seems clear that the peaks between 15 and 19 eV correspond with ionisation from the $t_2$,$t_1$, and $e$ levels that are largely fluorine lone-pair in character, while the next two peaks represent the $t_2$ and $a_1$ M–F bonding levels. Most of the discussion about assignments has been concerned with the order of the fluorine lone-pair levels; it is striking that the pattern of the peaks between 15 and 19 eV is much the same in $SiF_4$ and $CF_4$, implying that the ordering of levels in the two molecules is probably also the same.

In the spectra of $SiF_3Cl$ and $SiF_3Br$, the first band is assigned to ionisation from the $\pi$-lone-pair levels of the halogen atom, $4e$; in each spectrum the band is relatively sharp, and shows no resolved vibrational structure, being much the same in half-width as the corresponding band in $CF_3X$. The second band in each spectrum is assigned to

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[9] R. Haszeldine, *J. Chem. Soc.*, 1951, 584.

[10] H. J. Emeleus and A. G. Maddock, *J. Chem. Soc.*, 1944, 293.

ionisation from the $a_1$ Si–X σ-bonding level, and these correlate with the first band in the spectrum of $SiF_3H$ (assigned as for[5] $CF_3H$ to $3a_1$, the σ MH level). In the spectra of $MF_3H$ and $MF_3X$ there follow three bands whose positions, shapes, and relative intensities do not vary a greal deal across the whole series of six compounds. These peaks are assigned to the levels $1a_2$, $3e$, and $2e$, all essentially fluorine $2p$-lone-pair in character. While no feature of the spectra indicates which band is associated with which level, the peak in each spectrum at lowest ionisation potential has been assigned to the $1a_2$ because this orbital is weakly antibonding between all fluorines; calculations for $CF_3H$ lead to the same assignment.[5]

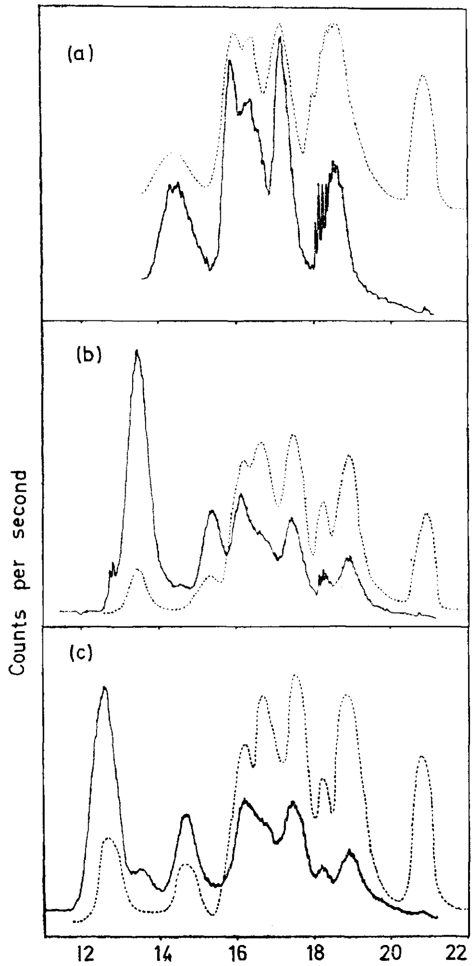

FIGURE 1 The photoelectron spectra of (a), $SiF_3H$; (b), $SiF_3Cl$; and (c), $SiF_3Br$ excited by He(I) (——) and He(II) (– – – –) radiation

There remain the MF σ-bonding levels ($e$ and $a_1$) and the $a_1$ fluorine lone-pair level. In $CF_3H$, the $a_1$ MF σ-bonding level is assigned[5] by analogy with $CF_4$ and from calculations to the band at 24·4 eV. In $CF_3Cl$ and $CF_3Br$, the corresponding bands would be expected to fall well outside the He(I) range; we have no data for these compounds beyond 21·2 eV. For $CF_3H$, the band at 20·5 eV covers both $1e$ and $2a_1$ levels; in $CF_3Cl$ one shifts to 20·15 and the other to 21·0 eV, while in $CF_3Br$ the higher level has shifted to 19·8 eV and the lower level has shifted outside the He(I) range. In view of the sensitivity of both these levels to the nature of the other atom bound to $CF_3$ we cannot say which represents the $1e$ and which the $2a_1$ level. In the spectra of the silicon compounds, the situation is somewhat different. In each spectrum three bands are observed, one near 18, one near 19, and one just below 21·0 eV. The relative intensities of the first and the third are much in-

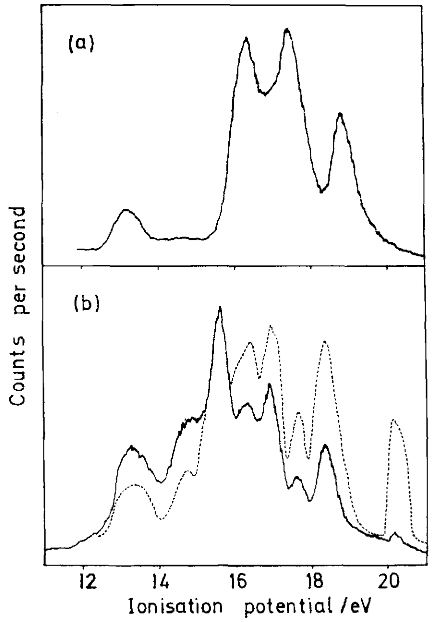

FIGURE 2 The photoelectron spectra of (a), $Si_2F_6$ and (b), $SiF_3Me$

TABLE 3

Vertical ionisation potentials/eV (±0·02 eV)

| | $CF_3X$ | | | $SiF_3X$ | | | $SiF_3Me$ | | $Si_2F_6$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| X = | Br | Cl | H (ref. 5) | Br | Cl | H | | | | |
| $4e$ | 12·12 | 13·08 | | 12·46 | 13·44 | | $4a_1$ | 13·24 | $3a_{1g}$ | 13·20 |
| $3a_1$ | 14·26 | 15·15 | 14·80 | 14·55 | 15·33 | 14·48 | $4e$ | 14·82 | $2a_{2g}/3a_{1u}$ | 16·24 |
| $1a_2$ | 15·78 | 15·82 | 15·5 | 16·10 | 16·35 | 15·94 | $1a_2$ | 15·55 | $2e_g/2e_u$ | 17·31 |
| $3e$ | 16·51 | 16·56 | 16·2 | 16·63 | 16·70 | 16·38 | $3e$ | 16·25 | $2a_{1g}/2a_{1u}$ | 17·85 (shoulder) |
| $2e$ | 17·42 | 17·53 | 17·24 | 17·36 | 17·49 | 17·24 | $2e$ | 16·84 | $1e_g/1e_u$ | 18·75 |
| $2a_1$ | 19·8 | 20·1 | 19·84 | 18·10 | 18·26 | 18·20 | $3a_1$ | 17·53 | | |
| $1e$ | | ~21·0 | 19·84 | 18·80 | 18·92 | 18·61 | $1e$ | 18·30 | | |
| $1a_1$ | | | 24·44 | 20·80 | 20·86 | 20·94 | $2a_1$ | 20·14 | | |

creased in spectra excited with He(II) radiation, implying that both these levels have substantial *s*-character [6] and are therefore of $a_1$ symmetry. We presume that there is substantial mixing between the Si–F $\sigma$-bonding and the fluorine lone-pair $a_1$ levels, and this conclusion is borne out by the vibrational progressions associated with the bands. For $SiF_3H$ and $SiF_3Br$, the band at 18 eV shows a single progression (see Table 4) in a frequency assigned to a slightly reduced [8,11] Si–F stretching mode. For $SiF_3Cl$ this band shows two progressions. One involves $\nu$(Si–Cl) effectively unchanged from the molecule; the other (965 $cm^{-1}$) is between the two Si–F stretching frequencies of the molecule,[8] implying either that the symmetric mode is at the higher frequency or that this level is Si–F *anti*-bonding. The progressions associated with the bands near 21 eV are assigned to $\nu$SiF and $\delta$SiF, all reduced (except for $\nu$SiF of $SiF_3Cl$, which is almost unchanged) from corresponding frequencies of the molecules. The bands near 19 eV show no resolved fine structure, and are assigned to 1*e* (Si–F $\sigma$-bonding).

TABLE 4

Vibrational progressions excited in the $1a_1$ and $2a_1$ levels of the compounds $SiF_3X$ (X = H, Cl, Br, or Me). The values are quoted to $\pm 40$ $cm^{-1}$

| | $2a_1/cm^{-1}$ | $1a_1/cm^{-1}$ | Molecular vibration frequencies/$cm^{-1}$ | |
|---|---|---|---|---|
| $SiF_3H$ | 790 | 725 | 998 | $\nu SiF$ [a] |
| | | 330 | 858 | |
| | | | 425 | $\delta SiF_3$ |
| $SiF_3Cl$ | 965 | 890 | 1000 | $\nu SiF$ [b] |
| | 605 | 200 | 880 | |
| | | | 596 | $\nu SiCl$ |
| | | | 345 | $\delta SiF_3$ |
| $SiF_3Br$ | 850 | 755 | 1000 | $\nu SiF$ [b] |
| | | 240 | 867 | |
| | | | 330 | $\delta SiF_3$ |
| $SiF_3Me$ | 730 | 845 | | |
| | | 325 | | |

[a] Ref. 11. [b] Our observations and assignments. Details to be published.

The assignments discussed above also lead to the assignments for $SiF_3Me$ and $Si_2F_6$. For $SiF_3Me$ the band at lowest ionisation potential is assigned to ionisation from the $4a_1$ (Si–C $\sigma$-bonding) level and the next to the 4*e* (C–H bonding) level. The remaining levels follow as described above. For $Si_2F_6$, the band at lowest ionisation potential is assigned to $3a_{1g}$ (Si–Si $\sigma$-bonding); the three bands associated with fluorine lone-pair levels show no splittings, and the only difference between this spectrum and the others so far described is that there is no band just below 21·2 eV. We assume that $1a_{1g}/1a_{1u}$ are beyond the He(I) limit; we were unable to obtain a spectrum of this molecule excited by He(II) radiation.

## DISCUSSION

It is interesting to compare ionisation potentials in the molecules studied in this paper with those of related derivatives, in particular $MH_3X$, $M_2H_6$, and $Si_2Cl_6$. The influence of the fluorine substituents might be expected to appear in three ways. Such electronegative groups are likely to increase the binding energies of $\sigma$-levels, in particular of the Si–X, Si–H, or Si–Si $\sigma$-bonding electrons; this kind of effect has been described as the perfluoro-effect in perfluoro-organic compounds.[12] There will be a similar but smaller effect on $\pi$-levels such as 4*e* ($\pi$-lone pair of X) of $SiF_3X$. Secondly, the MF bonding and antibonding levels themselves will interact with other molecular orbitals, and the interaction will differ from similar interaction with MH or MH* levels. Thirdly, the *d*-orbitals of Si will be contracted by the increased effective nuclear charge of the silicon, and so might well become more available for ($p \rightarrow d$) $\pi$-bonding from $\pi$-lone pairs of X to silicon but not of course carbon.

In addition to all this there is the possibility of ($p \rightarrow d$) $\pi$-bonding from fluorine lone pairs to silicon.

It is possible to look for evidence for all these effects in the spectra described here. There can be no doubt of the first effect: the $\sigma$-levels are much more tightly bound in $MF_3H$, $MF_3X$, or $Si_2F_6$ than in corresponding compounds containing $MH_3$ groups; there is even a large shift in the ionisation potential of the Si–Si $\sigma$-bond from $Si_2Cl_6$ to $Si_2F_6$ (see Table 5). In $MF_3X$, as in $MH_3X$, the lone-pair ionisation potential of X is higher when M = Si than when M = C, and this may well be due, at least in part, to ($p \rightarrow d$) $\pi$-bonding to silicon. However, there is nothing in the spectra of $SiF_3X$ to provide more compelling evidence in support of the idea of ($p \rightarrow d$) $\pi$-bonding. On the contrary, one feature of the spectra of $MH_3Cl$ and $MH_3Br$ is absent from the spectra of the perfluoro-analogues. The band due to ionisation from the $\pi$-lone-pair level of X in $MH_3X$ is sharp and shows no vibrational progression for M = C; when M = Si, the bands are broad and for the chloride show a progression in $\nu$(Si–Cl), slightly reduced from its value in the free molecule. This strongly suggests that the $\pi$-lone pairs of X are involved in the Si–X but not to nearly the same extent in the C–X bonds. In the spectra of $MF_3X$ the corresponding bands are all fairly sharp, and show no vibrational progressions; in particular there is no marked change in width from M = C to M = Si. Therefore there is no evidence from band shapes for interactions peculiar to the silicon compounds.

TABLE 5

Ionisation potentials/eV ($\pm 0{\cdot}02$ eV) of $MY_3X$ (M = Si or C, Y = F or H, and X = Cl or Br)

| | $SiH_3X$ | $SiF_3X$ | $CH_3X$ | $CF_3X$ |
|---|---|---|---|---|
| Cl $p\pi$ lone pair | 11·61 | 13·44 | 11·28 | 13·08 |
| Si–Cl $\sigma$ | 13·4 | 15·33 | 14·4 | 15·15 |
| Br $p\pi$ lone pair | 10·96 | 12·46 | 10·53 | 12·12 |
| Si–Br $\sigma$ | 12·85 | 14·55 | 13·5 | 14·26 |
| | $Si_2H_6$ | $Si_2Cl_6$ | $Si_2F_6$ | |
| Si–Si $\sigma$ | 10·60 | 10·79 | 13·20 | |

Finally it is interesting to consider the interpretations of the relatively small changes in ionisation potentials

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[12] C. R. Brundle, M. B. Robin, N. A. Keubler, and H. Basch, *J. Amer. Chem. Soc.*, 1972, **94**, 1451.

of at least three of the fluorine lone-pair levels in $MF_3Cl$ and $MF_3H$. The shifts can be interpreted in two ways: either the fluorine lone pairs are more-or-less unaffected by *changing* M from C to Si, or the relative constancy of the ionisation potentials reflects a balance of $\sigma$-electron release from silicon leading to a lower binding energy, and $\pi$-electron donation to silicon which increases the binding energy. It is clear from the increase in the binding $a_2$ level from $CF_3X$ to $SiF_3X$ that other factors may be involved, for there are no *d*-orbitals of $a_2$ symmetry.

In summary, it is possible to make fairly complete assignments for the spectra of $SiF_3H$ and $SiF_3X$; the spectra of the more complex molecules $SiF_3Me$ and $Si_2F_6$ correlate well with them. However, no firm conclusion can be drawn about the importance of *d*-orbitals in bonding from the spectra of the silicon compounds.

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