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## Preliminary communication

# Photoelectron spectra and energy level trends in $Me_nSiCl_{4-n}$ and related series

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Compounds $X_nSiY_{4-n}$ (and related derivatives of the other Group IV elements, with $n = 0–4$), where X and/or Y have a ligand atom which is lone-pair possessing, such as halogen, chalcogen, or nitrogen, have long been of interest from the standpoint of the nature of the Si–X and Si–Y bond. Controversial issues concern speculations on $p\pi–d\pi$ bonding and bonding trends within series[1]. We have therefore undertaken a study of the photoelectron (P.E.) spectra of such compounds and here report preliminary results. Our objectives are to assign the highest occupied electronic energy levels and to examine the manner in which orbitals of the same type vary in energy within related series.

Vertical ionisation potentials (I.P.) are presented for $Me_nSiCl_{4-n}$ (Fig.1) and also (Table 1) for $(EtO)_nSiCl_{4-n}$ and $(Me_2N)_nSiCl_{4-n}$. The methylchlorosilanes are considered in greater detail, since they are in some ways the simplest, with only one set (Cl) of non-bonding ligand orbitals. Assignments are based on (*i*) band shapes, (*ii*) results[2,3] on $SiCl_4$, and (*iii*) a standard neglect of differential overlap (ZDO) MO theory model[4]. Bands which arise from essentially Cl-non-bonding orbitals are not discussed here, and in any case have little to contribute to understanding of bonding; simplification will be possible as results on $Me_nSiF_{4-n}$ become available. The discussion centres on shifts for three bands, A–C in Fig.1, which arise from respectively SiC, SiCl, and Si orbitals.

The ZDO model implies a linear gradation of the "centre of energy" of the Si–C and Si–Cl $\sigma$-bonding MO's across the series. Thus, we draw a line (Fig. 1) between the Si–C band (A) of $Me_4Si$ [assigned (see also ref. 5) to the band at lowest I.P., since Si–C would be expected to ionise more readily than C–H] and the Si–Cl band[2,3] (B) of $SiCl_4$. The "centre of energy" of the mixed compounds $Me_nSiCl_{4-n}$ ($n = 1–3$) should lie on this line, provided that allowance is made for degeneracies. For example, in the case of $Me_3SiCl$, the Si–C doubly-degenerate band (A) lies 0.95 eV above the centre of energy; therefore, the Si–Cl band (B), which is non-degenerate, is expected to lie $2 \times 0.95 = 1.90$ eV below this point. Thus, assignments are made (ZDO calculated values in parentheses) for SiC and SiCl $\sigma$ MO's, respectively as follows (data expressed as I.P. in eV): $Me_3SiCl$, 10.76, 13.54 (13.65); $Me_2SiCl_2$, 10.99, 14.79 (14.90); and $MeSiCl_3$, -, (12.10), 15.09; for $MeSiCl_3$ we postulate a "hidden" SiC peak, masked by the intense Cl lone pair bands.

TABLE 1

VERTICAL IONISATION POTENTIALS (eV) FOR DIMETHYLAMINO- AND ETHOXY-SILANES[a]

| $(Me_2N)_4Si$ | $(Me_2N)_2SiCl_2$ | $(Me_2N)SiCl_3$ | $(EtO)_4Si$ | $(EtO)_3SiCl_2$ | $(EtO)_2SiCl_2$ | $(EtO)SiCl_3$ |
|---|---|---|---|---|---|---|
| 8.39 | 8.81 | 9.30 | 9.77 | 10.52 | 10.78 | 11.30 |
| 8.52 | 11.53 | 11.59 | 10.27 | 11.18 | 11.24 | 11.73 |
| 11.09 | 11.67 | 12.03 | 12.92 | 11.87 | 11.67 | 12.22 |
| 12.26 | 11.87 | 12.41 | 13.31 | 13.22 | 12.06 | 12.87 |
| 12.76 | 12.68 | 12.68 | 15.67 | 14.06 | 12.55 | 13.46 |
| 13.46 | 13.30 | 12.88 | 16.67 | 15.95 | 13.11 | 14.23 |
| 14.95 | 14.95 | 13.11 | 17.94 | 16.73 | 13.86 | 14.79 |
| 16.06 | 15.58 | 13.43 | | 17.97 | 14.74 | 15.36 |
| 17.15 | 17.44 | 14.31 | | | 15.55 | 16.56 |
| | | 15.23 | | | 16.37 | 18.13 |
| | | 15.62 | | | 18.10 | |
| | | 16.03 | | | | |
| | | 17.60 | | | | |
| | | 18.10 | | | | |

[a] Measured (also $Me_nSiCl_{4-n}$) using a Perkin–Elmer PS16 instrument with He 21.22 eV photons: purity of samples was checked by means of an AEI MS9 mass spectrometer.

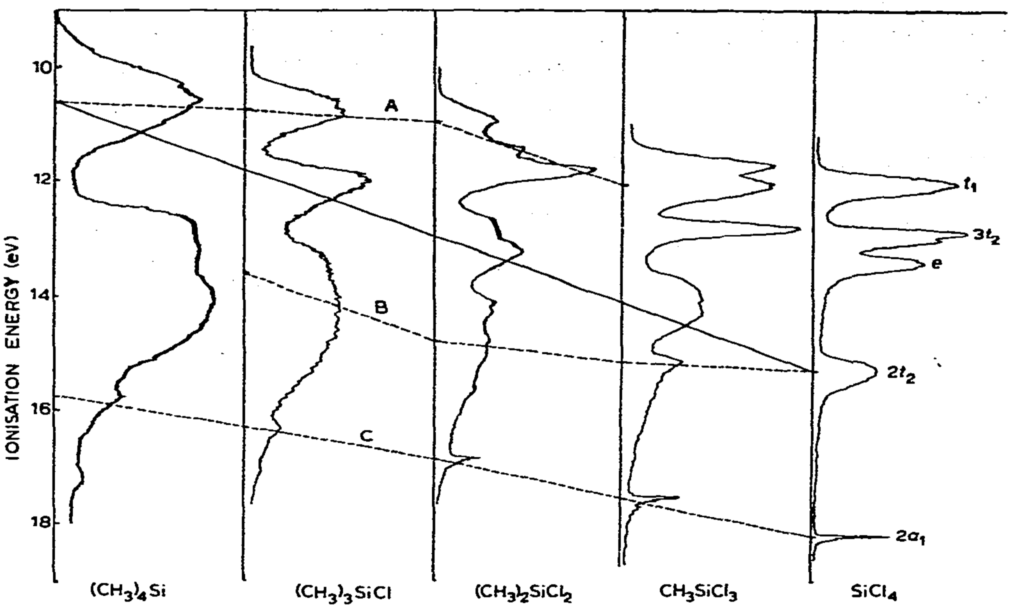

Fig.1. Photoelectron spectra of the series $(CH_3)_nSiCl_{4-n}$. Broken lines A, B, C show the Si–C, Si–Cl, and Si MO's respectively. Solid line indicates the "centre of energy" in the ZDO model. Group theoretical assignments for $SiCl_4$ from ref. 2, 3.

The $Me_4Si$ spectrum is better resolved than that previously reported[5]. Thus, (*i*) we observe a slight splitting of the first band (A), implying that the expected triple-degeneracy is lost by through-space interactions; this will be examined further for related compounds $Me_4M$ (M = C, Ge, Sn, and Pb). Furthermore, (*ii*) we note a band (C) at I.P. = 15.62 eV which, by comparison with other members of the series, is assigned as principally of central atom (Si) character ($a_1$ symmetry). This non-bonding character is consistent with extended Hückel calculations[6] and with the sharpness of the P.E. bands (C) for the early members (*i.e.*, $n$ is small) of the $Me_nSiCl_{4-n}$ series; with the later members, mixing with SiC vibrational modes results in band broadening. The linear gradation of band (C) within the series reflects the different electron density at Si for each member, as expected from purely inductive effect considerations. That such linearity is not found for $(Me_2N)_nSiCl_{4-n}$ may indicate that $p_\pi$–$d_\pi$ effects are significant for NSi but not ClSi bonds.

By scanning the Si band (C), on an expanded abcissa scale with a larger time constant, a short vibrational progression has been observed having the following intervals (± 40 $cm^{-1}$): $SiCl_4^+$, 340; $MeSiCl_3^+$, 370; $Me_2SiCl_2^+$, 300; and $Me_3SiCl^+$, 315 $cm^{-1}$. This vibration is assigned to symmetric $SiCl_{4-n}$ stretching, which in neutral $SiCl_4$ is (Raman)[6] at 424 $cm^{-1}$. The vibrational excitation is believed to be due to a deshielding of the Si nucleus upon ionisation, with consequent increase in the equilibrium internuclear SiCl distance.

In conclusion, the linear decrease in energy of the SiC and SiCl $\sigma$ MO's across the series $Me_nSiCl_{4-n}$, as well as the linearity of the central atom Si band, is as predicted on the basis of inductive effects of Me and Cl groups; thus, we do not require (*cf.*,[8]) Si 3*d* orbital participation. When results for further series are available, we shall seek correlations with, for example, $\sigma_i$ constants, and also with other experimental parameters.

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