Photo-electron Spectra of Silyl and Germyl Halides and (p → d)π-Bonding

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Summary The photo-electron spectra of silyl and germyl chlorides provide evidence that $(p \rightarrow d)\pi$-bonding does occur between Cl and Si or Ge; the spectra of the bromides and iodides are less conclusive.

THE question as to whether the empty valence-shell d-orbitals in Si or Ge participate significantly in bonding by accepting electrons from π-electron releasing substituents has been a vexed one for many years.[1] Such interactions have been postulated to account for observed bond lengths, bond energies, u.v. spectra, and dipole moments in various halogenosilanes and halogenogermanes, but conclusive evidence that the relevant halogen lone pairs in such molecules are involved in bonding with $3d$-orbitals of silicon or $4d$-orbitals of germanium has so far been lacking.

One potential source of such evidence is photo-electron spectroscopy. In a photo-electron spectrum, excitation of an electron from a non-bonding orbital gives rise to a peak with a strong vibrationless component, followed in many cases by a few much weaker components due to the formation of ions with some quanta of vibrational energy. This is because when a non-bonding electron is excited there are no significant changes in equilibrium bond lengths; hence, by the Franck–Condon principle, excitation occurs predominantly to the vibrational ground state of the molecular ion. In contrast, excitation of an electron that is either bonding or antibonding gives rise to changes in equilibrium bond lengths; the minimum of the potential energy curve of the ion is no longer "vertically" above that of the molecule, and so excitation occurs to various vibrational levels of the molecular ion. Thus, in the photo-electron spectra of the halogen hydrides HCl, HBr, and HI the band at lowest ionization potential shows a typical non-bonding structure, the vibrationless peak being very narrow and by far the strongest component.[2a] This band is assigned to excitation of one of the doubly degenerate (π) lone-pair electrons of the halogen atoms. Coupling between the electron spin angular momentum and the orbital angular momentum of the ion leads to splitting of the observed peaks. In the spectra of the methyl halides there are similar non-bonding peaks in positions similar to those of the corresponding hydrogen halides.[2b] Spin–orbit coupling is again observed, and the vibrationless peaks are strong and narrow. It is believed that the vibration excited corresponds to ν_2, the symmetric CH_3 deformation mode of the ion. In the spectrum of methyl fluoride[2c] the situation is different. The band due to ionization of the π-electrons of F appears at higher ionization potentials than those due to excitation of electrons from the C–F (symmetry class a_1) and CH_3 (symmetry class e) bonding orbitals, and is broad and structureless. The absence of structure may be due to interaction with CH orbitals of the same symmetry, or to Jahn–Teller distortion of the ^2E state of the ion.

The observed band-positions for electrons excited from the "halogen lone pair" π-orbitals in MH_3X (M = C, Si, Ge; X = F, Cl, Br, I) are given in the Table, with the widths at half-height and (where observed) the splittings due to spin–orbit coupling. "Vertical" ionization potentials and the means of spin–orbit doublets are given. Apart from the

fluorides, where broad bands with smooth contours are observed for all three compounds, the band-widths are
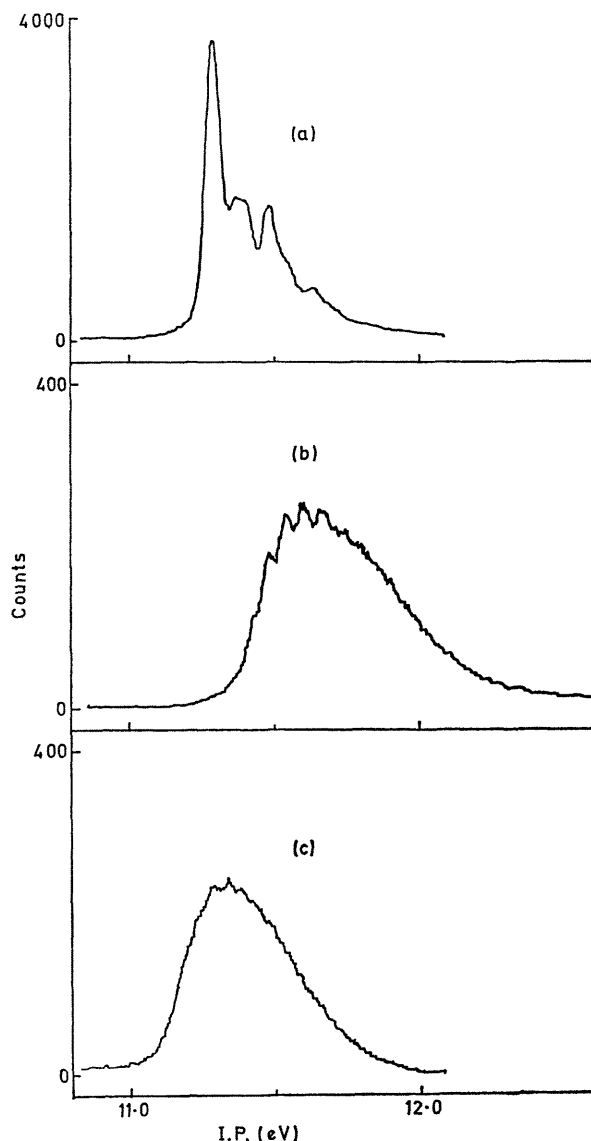

FIGURE. Bands at lowest I.P. for (a) CH_3Cl, (b) SiH_3Cl and, (c) GeH_3Cl.

much greater for a given X in the silyl and germyl species than in the corresponding carbon compound. However, the most striking difference is the clear change in the shape of the band at lowest IP in the series of chlorides (see Figure). When M is carbon, this band has a typical "non-bonding" shape; when M = Si or Ge, the contour is typical of that associated with excitation of a bonding or antibonding electron. The progression on the band in the spectrum of SiH_3Cl has a separation of 520 ± 40 cm^{-1}; the

Si–Cl stretching frequency in SiH_3Cl is 545 cm^{-1}. In the spectrum of GeH_3Cl the progression is less well defined.

TABLE

Compound	I.P. (eV)	Width (half-height) (eV)	Spin–orbit coupling
CH_3F[a]	ca. 17·0	ca. 1·4	—
SiH_3F	16·1±0·1	0·65	—
GeH_3F	15·0±0·1	0·7	—
CH_3Cl[b]	11·28	0·06	—
SiH_3Cl	11·61	0·48	—
GeH_3Cl	11·34	0·36	—
CH_3Br[b]	10·70	0·03	0·31
SiH_3Br	11·03	ca. 0·4	0·14
GeH_3Br	10·72	ca. 0·3	0·22
CH_3I[b]	9·86	0·03	0·61
SiH_3I	10·05	0·35	0·55
GeH_3I	9·84	0·31	0·55

[a] See ref. 4.   [b] See ref. 3.

I.P.s all ±0·05 eV unless otherwise stated; widths and couplings all ± 0·02 eV.

The simplest explanation of these observations is that the electrons in the Cl orbitals of symmetry class e, non-bonding in CH_3Cl, interact with empty π-type d-orbitals of the middle atom in SiH_3Cl and GeH_3Cl, and so become bonding. The changes in ionization potential are also consistent with this interpretation. Replacement of C by the more electropositive Si would be expected to lead to a greater negative charge at Cl, and as a consequence to lower ionization potentials for the lone pair electrons, whereas the observed values are in the order Si > C $\approx$ Ge. There is a similar trend in ionization potentials in the series MH_3X where M is Br or I, and though vibrational progressions are not resolved the broadening of the corresponding peaks from CH_3X to SiH_3X or GeH_3X could plausibly be put down to a similar cause. It is possible that interaction between the lone-pair electrons of Cl and the SiH_3 group is via the e-type SiH bonding or antibonding orbitals, though in that case a vibrational progression showing some SiH frequency might have been expected. From these results it appears that in SiH_3Cl the silyl group acts as a π-electron acceptor; the same appears to be true to a lesser extent of the germyl group in GeH_3Cl.

[1] See E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," ed. A. G. MacDiarmid, Dekker, New York, 1968, pp. 22—41.
[2] (a) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley–Interscience, London, New York, Sydney, and Toronto, 1970, p. 39; (b) ibid., p. 214; (c) ibid., p. 220.