Ab Initio Molecular Orbital Calculations of the Electronic Structure of Fluorosilane and Fluorogermane

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Summary The role of valence shell *d* orbitals in the description of the bonding in fluorosilane and fluorogermane is investigated, and shown by the results of non-empirical SCF calculations to be essentially that of polarisation functions.

As part of an examination of the role of *d* orbitals in Group IV compounds we have performed SCFMO calculations on fluorosilane and fluorogermane. These are among the simplest molecules expected to utilise *d* orbitals in their bonding, and the highly electronegative fluorine atom is the most likely single ligand to induce *d* orbital involvement. The calculations were performed with the ATMOL group of programs.[1]

The molecular parameters used were for SiH_3F: Si–H 1·474 Å, Si–F 1·594 Å, $<$ F–Si–H 108·7°[2] and for GeH_3F: Ge–H 1·520 Å, Ge–F 1·735 Å, $<$ H–Ge–H 113·1°.[3] In all calculations the central and fluorine atoms were placed on the *z* axis.

The basis sets used were minimum basis sets of Slater orbitals, with best atom exponents[4] and a hydrogen 1*s* exponent of 1·2, augmented by valence-shell Slater *d* orbitals. These orbitals were expanded in a series of three Gaussian-type orbitals with the exponents and expansion coefficients obtained by Stewart.[5] Exceptions were the fluorine 2*p* orbitals which were expanded[6] as a series of four Gaussian orbitals per atomic orbital to ensure reasonable representation. The exponent of the silicon 3*d* orbital (1·1) was taken as that which placed the maximum of $P_{3d}(r)$ approximately two-thirds of the way along the Si–F bond. The germanium 4*d* orbital exponent (1·3475) was chosen similarly.

For each molecule three sets of calculations were performed (i) without valence-shell *d* orbitals, (ii) with the Slater *d* orbitals added, and (iii) with the Gaussian expansion of the *d* orbitals split into two parts, the most diffuse Gaussian function being separated from the other two which retained their relative expansion coefficients. The purpose of this was to allow extra freedom to the *d* functions so as to counteract the lack of exponent optimisation. The possibility of over-emphasising the *d* function involvement must be recognised. For both molecules the split *d* calculation gives the lowest total energy.

TABLE

		sp	*spd*	*spd* (split)
			SiH_3F	
Total Energy (a.u.) ..		−385·834	−385·948	−385·968
Dipole Moment (D)[a] ..		2·134	—	1·390
Charge on Si		+0·63	+0·11	+0·12
Orbital Energies (a.u.)	3*e*	−0·477	−0·506	−0·500
	$7a_1$	−0·579	−0·644	−0·638
	2*e*	−0·612	−0·665	−0·662
	$6a_1$	−0·758	−0·780	−0·768
	$5a_1$	−1·504	−1·576	−1·569
			GeH_3F	
Total Energy ..		−2154·310	−2154·756	−2155·034
Dipole Moment ..		2·728	—	2·127
Charge on Ge		+0·70	+0·05	−0·02
Orbital Energies	6*e*	−0·465	−0·510	−0·509
	$10a_1$	−0·529	−0·602	−0·603
	5*e*	−0·573	−0·628	−0·630
	$9a_1$	−0·736	−0·782	−0·782
	4*e*	−0·890	−1·202	−1·329
	$8a_1$	−0·893	−1·204	−1·329
	3*e*	−0·894	−1·210	−1·337
	$7a_1$	−1·455	−1·529	−1·534

[a] Experimental value 1·268 D.

As shown in the Table the large change in the calculated dipole moment of fluorosilane upon the addition of 3*d* orbitals, in the direction of agreement with the experimental value, is indicative of the improvement in the basis set, as is the improvement in total energy. The better predicted dipole moment of fluorogermane is probably the lower value; no experimental value is available.

The calculated charges of the silicon and germanium atoms are in agreement with the expectation that germanium is slightly more electronegative.

The valence shell molecular orbitals of SiH_3F, whose energies are given in the Table are, with reference to the silicon and fluorine contributions, as follows: 3*e* π antibonding with nearly equal F and Si contributions; $7a_1$ principally F(2*p*σ), with bonding to Si; 2*e* strongly F(2*p*π), slightly bonding to Si; $6a_1$ mainly Si(3*s*), with bonding to F; $5a_1$ almost pure F(2*s*). The main Si–H bonding components occur in 3*e* and $7a_1$.

The addition of 3*d* orbitals, which in general produces small lowerings of the eigenvalues (see Table), results in small *d* contributions, with the largest coefficients (0·2) in the 3*e* set. There is no significant alteration in the molecular orbitals.

This shows that the 3*d* orbitals are acting as simple polarisation functions.

In the calculation with split *d* orbitals the diffuse contribution is almost negligible, despite the greater overlap possibilities, indicating that the *d* orbitals are acting as polarisation functions.

The results for GeH_3F are similar and produce the same molecular orbital pattern. However, in this case there is a much larger lowering in total energy upon addition of 4*d* orbitals (see Table), due mainly to the considerable mixing of the 4*d* orbitals into the mainly 3*d* MO's, 3*e*, $8a_1$, 4*e*, *e.g.*, the $8a_1$ MO is principally composed of 0·96 ($3d_{z^2}$) + 0·19 ($4d_{z^2}$). Similarly there is a greater diminution in most valence orbital energies.

It has been suggested from a study of the photo-electron spectra of silyl and germyl halides that *d*π–*p*π bonding could account for the vibrational structure of the first ionisation bands.[7] If it is assumed that the basic character of the valence MO's of the other halides is not substantially different from that of the fluorides, then these calculations indicate that the first ionisation band will result from removal of an electron from the highest filled *e* set. Ionisation from this antibonding set of MO's could well cause sufficient change in the molecular structure to account for the observed vibrational effects.

Thus, the role of the valence-shell *d* orbitals of silicon and germanium in these molecules is essentially that of polarisation functions, and without their addition to the basis set good agreement between calculation and experiment is unlikely.

(*Received, February 22nd,* 1971; *Com.* 151.)

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