

The Dipole Moments of H₃CF and H₃SiF: A CNDO/2 Localized Molecular Orbital Study

P. M. KUZNESOF

Instituto de Química, Universidade Estadual de Campinas,
C.P. 1170, 13,100-Campinas, SP, Brazil

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The smaller dipole moments of the monohalo-silanes compared with those of their carbon analogues have often been linked with halogen(*p*) → silicon(*3d*) *pi* interactions.¹ Consistent with this is the recent suggestion² that the lower moments for the silanes may be due to a significantly smaller charge separation between silicon and halogen operating over a greater distance. A more quantitative and fruitful approach to the problem is now possible *via* all-valence electron semi-empirical molecular orbital calculations. As we have shown,³ the set of localized molecular orbitals (LMO's)⁴ obtained from the CNDO/2 canonical MO's⁵ allows for a partitioning of the total calculated dipole moment into a) individual bond moments, $\mu_Q(AB)$, b) moments due to lone electron pairs, $\mu_e(A)$, and c) bond polarization moments, $\mu_{pol}(AB)$.^{*} Within this framework we wish to present our results for H₃CF and H₃SiF.

Results and discussion

The CNDO calculations were performed using program CINDOM⁶; Santry's parameters⁷ for silicon are employed. For H₃SiF calculations were carried out with and without inclusion of silicon *3d* orbitals. LMO's were obtained by incorporating sub-program ORLOC⁸ into CINDOM. The moments from the LMO's were calculated after exclusion of the atomic orbital contamination coefficients due to the non-participating atoms. The following geometrical para-

^{*} $\mu_Q(AB)$ is the moment due to the equilibrium charge distribution in the AB bond calculated from the LMO representing the bond. $\mu_e(A)$ is the moment due to the atomic polarization obtained from the LMO representing a lone pair of electrons on atom A. $\mu_{pol}(AB)$ is the sum of the atomic polarization moments of atoms A and B evaluated from the appropriate bonding LMO. See also reference 3.

TABLE I. Experimental^a and CNDO/2 Dipole Moments (Debyes) of H₃CF and H₃SiF.

	μ_Q	μ_{sp}	μ_{pd}	$\mu_{CNDO/2}$	μ_{exp}
H ₃ CF	1.31	0.42		1.73	1.81
H ₃ SiF (<i>sp</i>)	1.60	-0.22		1.38	1.27
H ₃ SiF (<i>spd</i>)	1.35	-0.29	-0.63	0.43	1.27

^a Reference 1.

eters were used for a) H₃CF⁹: R(CF) = 1.386 Å, R(CH) = 1.095 Å, ∠FCH = 108.6° and for b) H₃SiF¹⁰: R(SiF) = 1.593 Å, R(SiH) = 1.485 Å, ∠FSiH = 108.4°.

The calculated total dipole moments (Table I) for both H₃CF and H₃SiF (*sp* basis) are in excellent accord with the experimental values. The value for H₃SiF(*sp*) is probably fortuitous, however. Inclusion of *d* orbitals in the basis for second row atoms is generally necessary¹¹ to introduce a *pd* back-polarization moment, μ_{pd} , to compensate for the often over-estimated *sp* polarization moment, μ_{sp} . It is surprising, then, that for H₃SiF μ_{sp} is not of the same sign as the moment due to the total static equilibrium charge distribution, μ_Q . Therefore, introduction of silicon *3d* orbitals results in reinforced back-polarization accounting for the underestimated total moment of the *spd* basis calculation. Nonetheless, the *spd* basis set results demonstrate the putative role of *d* orbitals to counter, through a back-polarization moment, the major contributor to the overall moment, μ_Q .

The data of Table II, obtained from the LMO's, show clearly that the major contribution to the total moments of H₃CF and H₃SiF arises from the CF and SiF bond moments.^{**} The SiF bond moment is calculated to be approximately twice as great as the CF bond moment. Most significant is the large value for the SiH bond moment (reflecting the hydridic nature of the hydrogen) compared with the negligible moment for the CH bond. In view of the

^{**}The quality of the LMO's may be judged by verifying that the sum of the bond moments must equal the total contribution from the equilibrium charge distribution, μ_Q (Table I). Similarly, the lone pair and bond polarization moments must sum to the total atomic polarization moment, μ_{sp} or μ_{sp+pd} . The individual $\mu_Q(AB)$ may also be compared with those values directly obtainable from the net electron densities and atomic coordinates. The net electron densities for H₃CF and H₃SiF are given in Table II, footnote b.

TABLE II. Bond, Bond Polarization, and Lone Pair Moments (Debyes) from Localized CNDO/2 Molecular Orbitals.^{a, b}

	$\mu_Q(\overset{\uparrow}{\text{MF}})^c$	$\mu_{\text{pol}}(\overset{\uparrow}{\text{MF}})^d$	$\mu_Q(\overset{\uparrow}{\text{HM}})$	$\mu_{\text{pol}}(\overset{\uparrow}{\text{HM}})$	$\mu_e(\text{F})$
H ₃ CF	1.29	0.02	0.06	-2.08	2.27
H ₃ SiF (<i>sp</i>)	2.76	0.19	-1.24	-2.87	2.67
H ₃ SiF (<i>spd</i>)	2.52	-0.04	-1.22	-2.68	2.72

^a A negative sign signifies the moment has the opposite sense to that given in the column heading.

^b The calculated CNDO/2 net electronic charges given in the order H, M, F are for H₃CF: 0.005, 0.180, -0.195; H₃SiF (*sp*): -0.182, 0.915, -0.369; H₃SiF (*spd*): -0.177, 0.865, -0.333.

^c Calculated directly from the fluorine net electron density. Values from the (MF) LMO's are quite unsatisfactory, especially for fluorosilane, being 1.54, 3.42, and 3.73 Debyes for H₃CF, H₃SiF (*sp*), and H₃SiF (*spd*), respectively. This may be a consequence of the rather large carbon (0.07) and silicon (0.12) contamination coefficients in the two equivalent LMO's corresponding to the fluorine lone pair orbitals lying perpendicular to the CF and SiF bonds. The other moments in the table are reasonably consistent with the data of Table I.

^d The individual components (Debyes) given in the order M,F are for H₃CF: -1.38, 1.40; H₃SiF (*sp*): -1.74, 1.93; H₃SiF (*spd*): -2.06, 2.02.

fact that the group IV atom -F and -H bond polarization moments are comparable for both molecules and, in any case, tend to cancel the fluorine lone pair moments, the "atypical" lower dipole moment of H₃SiF mainly appears due to the cancellation of the large SiF bond moment by the three SiH bond moments. The role of (*p* → *d*) *pi* interaction is secondary according to the calculations.

A remark on the magnitude of the dipole moment (2.33D) of H₃GeF¹² is appropriate. Since the Allred-Rochow electronegativities of carbon and germanium are similar, we might expect the polar character of the CH and GeH bonds also to be similar. Taking into account, also, that the covalent radius of germanium (1.22 Å) is not too different from that of silicon (1.18 Å) suggests that the GeH bond moment should be less than the SiH moment. In other words, the GeH bond moments would not effectively cancel a large GeF bond moment leading to a total moment of H₃GeF greater than that of H₃CF.

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