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Non-Empirical LCAO-MO-SCF Calculations of the Electronic Structure of SiF_2

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Non-empirical LCAO-MO-SCF calculations on SiF_2 using two Gaussian basis sets are reported. The larger basis set gives a calculated geometry in good agreement with experiment. The effect on the energy and population analysis of optimization of the Si $3d$ exponent was investigated. $3d$ orbitals are found to be much less important in the bonding than in the isoelectronic molecule SO_2.

Key words: SiF_2, electronic structure of ~

Introduction

Recent experimental studies on divalent compounds of the group IVb elements, which are important intermediates in many reactions, have shown that the difluorides of these elements are the most stable and long lived compounds. Their properties and structure are thus of considerable interest in inorganic chemistry [1, 2].

However, there have been few theoretical studies of these compounds, and as part of our research into the electronic structure of AB_2 molecules, we have carried out *ab-initio* LCAO(GTO)-MO-SCF calculations on a variety of such fluorides, including those in group IVb. We have previously reported our results for the radicals BF_2 and NF_2 [3], and in the present paper the results of calculations on the ground state of SiF_2 are described. Calculations on SF_2 and PF_2 are in progress and will be reported at a later date [4].

SiF_2 is a carbene analogue, and its reactions have been extensively studied by Margrave *et al.* [1, 2]. In addition, the microwave [5] and vacuum u.v. spectra [6] have been observed, resulting in accurate values for the Si–F bond length (1.591 Å = 3.007 bohr) and the $\widehat{FSiF}$ angle (100° 59′) in the electronic ground state. SiF_2 has a much longer lifetime (~ 2 min) than its carbon analogue CF_2 (~ 1 sec) and a comparison of their electronic structure together with that of SO_2 which is isoelectronic with SiF_2 is therefore of some interest. Studies of the excited states will be dealt with in a subsequent publication [7].

There have been no previous *ab-initio* calculations on SiF_2, and in fact only a few such calculations on other polyatomic molecules containing Si, such as SiH_2 [8], SiH_3 and its ions [9], SiH_4 [10], SiH_3F [11], SiO_4^{4-} and H_4SiO_4 [12]. However, there has been a semi-empirical calculation on SiF_2 by Brown and

Peel [13] using the VESCF [14] method, but since the basis set used did not include $2s$ or $2p_z$ basis functions on F, the results are not relevant to those presented here.

Method of Calculation and Basis Sets

The calculations were carried out using the programmes IBMOL 44 [3] and IBMOL 5 [15], either on an IBM 360/44 or an IBM 360/195, the former for exploratory calculations and those using the small basis set. For second row molecules, the calculation time becomes quite large if geometry optimization or exponent optimization is carried out, and the size of the basis set chosen for the calculations should be such that a reasonably accurate description of the bonding is obtained whilst keeping the computing time within reasonable bounds. In the present work, we are primarily interested in the bonding in the ground state of the molecule and have used two basis sets to study this.

The preliminary calculations used a $(9s5p)$ basis set on Si contracted to $[4s3p]$, and a $(5s2p)$ basis on F contracted to $[2s1p]$ (Basis I). The exponents and contraction coefficients used were taken from the compilations by Huzinaga [16] and Whitman and Hornback [17]. The contracted functions for the 9 s-gaussians were grouped 6, 1, 1, 1, and the $5p$-gaussians were grouped 3, 1, 1,. This leaves the required flexibility in the valence region. This size basis gives rise to energies ~ 2-2.5 hartree above the Hartree-Fock limit, but it is of interest to see if such a basis set is useful for the calculation of the equilibrium geometry in molecules containing second row atoms. Basis sets smaller than this give rise to large errors in the bond angle and smaller errors in the predicted bond lengths, particular if $3d$ functions are absent [18].

Calculations were also carried out with an extended basis consisting of $(10s\,6p\,1d)$ on Si contracted to $[6s\,4p\,1d]$, and $(7s\,3p)$ on F contracted to $[4s\,2p]$ (Basis II). This basis is similar to that used by Roos and Siegbahn [19] in studies on SO_2, with contraction groupings on Si of 4, 2, 1, 1, 1, 1, for the s functions and 2, 2, 1, 1, for the p functions. For the fluorine basis functions the groupings were 4, 1, 1, 1 for the s-functions and 2, 1 for the p-functions.

A set of $3d$ functions were added to the Si basis in this case. The problem of choosing a suitable value of the $3d$ exponent has been discussed by several authors [10, 19, 20], but there seems to be some disagreement concerning the most suitable value. Schaefer *et al.* [10] adopted the same value $\alpha_d = 0.6$ for P, Si, S and Cl in their study of PH_4, SiH_3 SH_2 and HCl using a contracted (12, 9, 1) basis, and Roos and Siegbahn [19] adopted a similar value $\alpha_d(\mathrm{S}) = 0.6$ in calculations on SO_2.

We initially chose $\alpha_d(\mathrm{Si}) = 0.6$, but in view of our wish to extend these calculations to other molecules containing Si, it was considered worthwhile to optimize $\alpha_d(\mathrm{Si})$ keeping the other exponents constant. The results of these calculations give an optimized value of $\alpha_d(\mathrm{Si}) = 0.3$ and an energy of $E = -487.503538$ which is an energy lowering of only 0.006 a.u. It seems therefore that although the optimized exponent is half the value suggested by previous work, the effect on the energy of optimization is very small. It is noteworthy that optimization results in a much more diffuse orbital. The very small effect on the energy not, however, paralleled by a negligible effect on the population analysis. There are large variations in the d-orbital populations, which we return to in a later section although the total $3d$ population is only slightly changed.

Previous work using basis sets of the quality used here (Basis II) have shown that the calculated energy should be ~0.4-0.5 hartree above the Hartree-Fock limit. The main error lies in the description of the inner shell orbitals, this accounting for ~0.3 hartree, but we expect that the outer molecular orbitals will be described rather well.

We have not, however, included $3d$ basis functions on the fluorine atoms. It is unlikely (in view of the results of Roos and Siegbahn on SO_2 [19]) that their inclusion would alter significantly any of the conclusions reached in this paper concerning the bonding in SiF_2. Their inclusion would considerably increase the cost of the computations.

Although the geometry of SiF_2 is known [1], we have carried out geometry optimization by first optimizing $\widehat{\mathrm{FSiF}}$, followed by R(Si–F), and then reoptimized FSiF. This was carried out to establish that a theoretically computed equilibrium geometry in good agreement with experiment can be obtained for triatomic molecules containing a second row atom using the basis sets described in this work, so that these basis sets can be used with some confidence as to the errors in computed bond lengths and geometries for species whose geometry has not been determined experimentally. It should be stressed that estimates of the error involved in the calculations are as important as the calculated values themselves.

Results and Discussion

The coordinate system used has the y-axis as the C_2 axis, and the molecule lies in the xy plane. The calculations with Basis I resulted in a minimum energy of -485.62487 hartree with $\widehat{\mathrm{FSiF}} = 94°$, $\mathrm{R(Si–F)} = 2.975$ bohr. The angle is substantially less than the experimental value of 101°, and as expected Basis Set II gives a much improved minimum energy of -487.497112 hartree at $\widehat{\mathrm{FSiF}} = 100°$,

Table 1. Total energy as a function of angle $\widehat{\mathrm{FSiF}}$ and bond length R(Si–F) with and without $3d$ functions on Si ($3d$ exponent $= 0.6$)

Angle	R(SiF)	E_d[a]	E_{nd}[b]
95°	3.0066[c]	−487.49594	−487.44189
98	3.0066[c]	−487.49690	−487.44263
99	3.0066[c]	−487.49701	−487.44268
100	3.0066[c]	−487.49703	−487.44264
105	3.0066[c]	−487.49577	−487.44110
100	2.95	−487.49655	−487.43850
100	3.00	−487.49711	−487.44231
100	3.01	−487.49697	−487.44279
100	3.05	−487.49568	−487.44384

[a] With d-functions.
[b] Without d-functions.
[c] Experimental bond length.

Table 2. Total energy and dipole moment μ as a function of α_{3d} at $\widehat{\mathrm{FSiF}} = 100°$, and R(SiF) = 3.00 a.u. for Basis Set II

α_d	Energy	μ (a.u.)
0.7	−487.49036	0.609
0.6	−487.49711	0.571
0.4	−487.50291	0.535
0.35	−487.50344	0.531
0.30	−487.50354	0.533
0.25	−487.50350	0.541

Table 3. Orbital energies with $3d$ exponents of 0.6 and 0.3, and without $3d$ basis functions (Basis set II)

Orbital	No $3d$	$\alpha_{3d} = 0.6$	$\alpha_{3d} = 0.3$
$1a_1$	−68.8740	−68.8500	−68.8591
$2a_1$, $1b_2$	−26.3045	−26.3129	−26.3285
$3a_1$	− 6.3214	− 6.2027	− 6.2114
$2b_2$	− 4.3413	− 4.3126	− 4.3229
$4a_1$	− 4.3400	− 4.3110	− 4.3208
$1b_1$	− 4.3400	− 4.3109	− 4.3201
$5a_1$	− 1.6111	− 1.6103	− 1.6194
$3b_2$	− 1.5829	− 1.5847	− 1.5929
$6a_1$	− 0.7628	− 0.7613	− 0.7715
$4b_2$	− 0.6748	− 0.6829	− 0.6915
$7a_1$	− 0.6591	− 0.6669	− 0.6781
$2b_1$	− 0.6512	− 0.6556	− 0.6646
$1a_2$	− 0.6133	− 0.6202	− 0.6292
$5b_2$	− 0.6070	− 0.6098	− 0.6164
$8a_1$	− 0.4041	− 0.3986	− 0.3989

R(Si–F) = 3.00 bohr for $\alpha_d = 0.6$, and an energy of −487.503539 hartree for the optimized $\alpha_d = 0.3$. Deletion of the $3d$ functions from the basis results in a decrease in the optimized $\widehat{\mathrm{FSiF}}$ to 99°, and increases the energy at the minimum to −487.442682 hartree. The difference here is only ~ one third of that found in the case of SO_2 [19], and the total $3d$ population of 0.29 compared with 0.55 in SO_2 indicates that the $3d$ orbitals are less important in SiF_2. This point is further discussed below. Table 1 gives the total energy at various angles for Basis Set II with and without d-functions[1], for the exponent value $\alpha_d = 0.6$, and Table 2 gives the variation the total energy and dipole moment with α_{3d} at R(SiF) = 3.0 and $\widehat{\mathrm{FSiF}} = 100°$ for the same basis set.

The ground state is ${}^1A_1$ with configuration:

$$(1a_1)^2\,(1b_2)^2\,(2a_1)^2\,(3a_1)^2\,(2b_2)^2\,(4a_1)^2\,(1b_1)^2\,(5a_1)^2\,(3b_2)^2\,(6a_1)^2\,(4b_2)^2$$
$$(7a_1)^2\,(2b_1)^2\,(1a_2)^2\,(5b_2)^2\,(8a_1)^2$$

and the molecule is isoelectronic with SO_2. Table 3 gives the orbital energies and Table 5 the $3d$(Si) orbital populations for the minimum energy configuration both for $\alpha(3d) = 0.6$ and the optimized value of $\alpha(3d) = 0.3$ together with the

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[1] Additional calculations were carried out at intermediate angles but are not listed here.

Table 4. Total population analysis for Basis Set II

	No $3d$ on Si	$3d$ on Si $\alpha_d = 0.6$	$\alpha_d = 0.3$
G(Si)[a]	12.77	12.96	13.08
G(F)	9.61	9.54	9.46
Overlap (Si–F)	0.19	0.34	0.51
$G'(3d)$[b]	0.0	0.29	0.27

[a] $G(i)$ = Gross atomic population on centre i.
[b] $G'(3d)$ = Total $3d$ population on Si.

Table 5. $3d$-population in individual valence molecular orbitals for $\alpha_d = 0.6$ and $\alpha_d = 0.3$

Orbital	$\alpha_d = 0.6$	$\alpha_d = 0.3$
$5a_1$	0.05	−0.04
$3b_2$	0.02	0.03
$6a_1$	0.01	0.02
$4b_2$	0.03	0.0
$7a_1$	0.03	0.11
$2b_1$	0.01	0.05
$1a_2$	0.02	0.09
$5b_2$	0.01	0.01
$8a_1$	0.01	0.0

orbital energies for the same geometry and deletion of the $3d$ functions. All of the valence shell orbitals are lowered in energy by addition of $3d$ functions, and a further lowering by ~0.01 a.u. is found on optimization of the $3d$-orbital exponent. The orbital order is unchanged when d-functions are added in SiF_2. The lowest unoccupied orbital is $3b_1$ with orbital energy 0.0670 hartree for $\alpha(3d) = 0.3$. Figure 1 gives a Walsh diagram of the valence orbital energies as a function of angle. This diagram is qualitatively similar to that given by Gole *et al.* [6], but the variation of the orbital energies with angle near the equilibrium value is quite small in all cases except for the $1a_2$, $5b_2$ and $8a_1$ orbitals. The $4b_2$ orbitals and $2b_1$ orbital energies are interchanged but the separation between the $4b_2$, $7a_1$ and $2b_1$ orbitals is small.

Comparison with the isoelectronic SO_2 shows that the valence orbitals in SiF_2 are much closer together i.e. in SiF_2 the spread in energy between $6a_1$ and $5b_2$ is ~0.15 hartree compared with ~0.34 hartree in SO_2. A comparison with the first row molecule CF_2 is also of interest. This species was studied by Sachs, Geller and Kaufman, using a (95) uncontracted basis set [21], and also by Harrison [22]. The Walsh diagram is similar, although there are differences in that some of the orbitals, for instance $3b_2$, and $5a_1$, and $4b_2$ and $1a_2$ cross at angles a few degrees less than the equilibrium value (104° 8′) whereas in SiF_2 no such crossing occurs.

The nature of the bonding in SiF_2 may be discussed using the Mulliken population analysis of the molecular orbitals to which we now turn. It must be emphasized that the results of population analyses are quite sensitive to the quality of the basis set, and the charge distribution may be even qualitatively wrong for

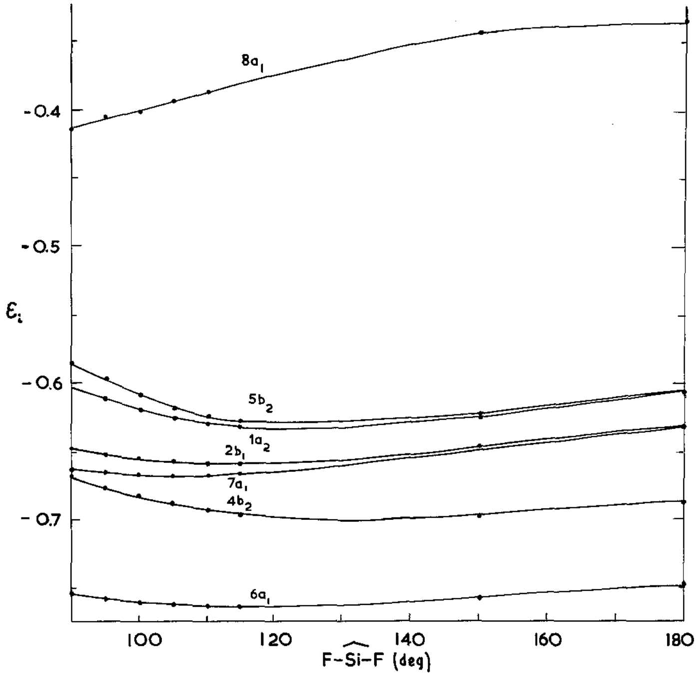

Fig. 1. Walsh diagram of variation of orbital energies with $\widehat{\text{FSiF}}$ for SiF_2 at R(SiF) = 3.0 (Basis Set II)

small basis sets [23]. In the present case, the difference in the gross atomic population on Si between Basis I and Basis II is ~0.3–0.4, with the larger basis resulting in an increased electron density on the fluorine atoms, although this decreases slightly for the optimised $3d$ exponent. However, Basis II should be big enough for a *qualitative* discussion of the bonding in SiF_2 to be of some value.

Table 4 gives the gross atomic and overlap populations both with and without d-functions for the calculated minimum energy configuration. The total $3d$ population is lower than that found in the case of SO_2 with a similar basis set. The $3d$ electrons are thus less important in SiF_2 than in SO_2, and the relatively small increase in overlap population on addition of the $3d$ functions is consistent with this conclusion. The optimisation of the $3d$ exponent does increase the overlap population significantly. However, the values for the $3d$-populations in individual orbitals vary considerably (Tab. 5), and it is not clear how meaningful these variations are. Some tentative conclusions are possible, however. The extent of $\sigma - \pi$ back-bonding in the $1a_2$ orbital is less than in SO_2, since the $3d$ population is only about half the value found in SO_2 (0.18). Also the effect on the negative Si–F overlap population in $8a_1$ is small in constrast to the large change observed in SO_2. In view of the rather small $3d$ populations in all the orbitals, we can therefore be reasonably confident that the $3d$ basis functions contribute very little to the bonding in SiF_2.

Turning now to the composition of the orbitals, the inner shell orbitals corresponding to the atomic orbitals $1s^2\,2s^2\,2p^6$ on Si and $1s^2$ on F are the $1a_1$, $3a_1$, $1b_1$, $4a_1$, $2b_2$ and $1b_2$ and $2a_1$ orbitals. The $5a_1$ orbital is made up of $2s$ orbitals on all atoms, but the largest contribution is from the F $2s$ orbitals. This orbital is SiF bonding, whereas the antisymmetrical combination of the fluorine $2s$ orbitals occurs in the weakly bonding $3b_2$ orbital. Both orbitals are more concentrated on fluorine than their counterparts in CF_2.

The $6a_1$ orbital on the other hand has a large $2p_x$ contribution from the fluorines and is strongly SiF bonding. This orbital is very flat on the Walsh diagram. The next orbital is $4b_2$ which is mainly concentrated on fluorine and can be regarded as one of the F lone pairs. The $7a_1$ orbital which is SiF bonding is also a lone pair orbital on F. These orbitals are nearly degenerate. The $2b_1$ orbital is a π-orbital on fluorine but is delocalized onto Si. The $1a_2$ orbital is also a fluorine $2p_z$ lone pair. The $5b_2$ orbital is concentrated on the fluorines and again can be regarded as a lone pair. Finally, the $8a_1$, orbital is largely localized on Si with only a very small fluorine population. In fact, none of the orbitals have a large SiF overlap population and the bonding is thus weak which is in line with the experimental evidence. The $8a_1$ orbital varies more rapidly with $\widehat{FSiF}$ than the other orbitals. The nature of the orbitals is thus similar to those of CF_2, but with the reduced Si–F overlap population suggesting a weaker bond.

The dipole moment μ has been computed and can be compared with the experimental value of 1.23 ± 0.015 D (0.4839 a.u.). For the calculated minimum geometry a value of 0.571 a.u. was obtained when $3d$ functions with exponent $\alpha_d = 0.6$ were included, and 0.68 a.u. without $3d$ functions. A calculation with the optimized $3d$ exponent of $\alpha_d = 0.3$ decreases μ to 0.532 a.u. It is clear that the influence of the $3d$-orbitals on this property is again less than in SO_2, but that exponent optimization does result in a change towards the experimental value. However, the calculated value is in quite good agreement with experiment. No other molecular properties have been measured in the ground state, with the exception of the heat of formation [2]. Calculations within the SCF approximation do not give accurate values for the atomization energy, but Rothenberg *et al.* [10] in their study of SiH_4 obtained a value 82.5% of the experimental value from the SCF calculations. Despite the limitations of the approach, we find that the calculated dissociation energy

$$D_e = E(\text{mol}) - \sum_{\text{Atoms}} E_{\text{atoms}}$$

is 0.29 hartree (7.89 eV), which is quite low.

The first ionization potential, invoking Koopmans theorem, is predicted to be 0.404 hartree (10.99 eV). This is also lower than in the isoelectronic SO_2 and is slightly lower than the experimental value found for CF_2 (11.86 eV). The calculated value for the latter is ~13 eV in both Sachs [20] and Harrison's [21] calculations. The ionization potential of SiF_2 has not, however, been measured.

Conclusions

We have studied the unstable carbene analogue SiF_2 with a medium size basis set, and compared the resulting wave function and energies with those obtained with a smaller basis set, and with similar quality calculations on the ground state of CF_2 and the isoelectronic molecule SO_2. Exponent optimization of the Si $3d$ exponent was also investigated.

The calculated angle and bond length are close to the observed values, and 3*d* functions are much less important in the bonding than in SO_2, and although the optimized exponent is lower than the values quoted in the literature, the effect on the energy is quite small. Analysis of the wave function using the Mulliken population analysis shows that the bonding is weaker than in CF_2, and theoretical Walsh diagram of the variation in orbital energies with angle is in general accordance with Walsh's original diagram. The calculated ionization potential should be a reliable guide to the correct value for this molecule. However, the orbital 3*d* populations are quite sensitive to the 3*d*-orbital exponent and emphasise earlier conclusions regarding the use of Mulliken population analyses in interpreting molecular wavefunctions [23].

The low-lying excited states of SiF_2 are also of interest and work is underway on these and will be reported at a later date. It is hoped that this work will stimulate further experimental studies on this interesting intermediate and similar species.

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