Non-Empirical LCAO-MO-SCF Calculations of the Electronic Structure of SiF₂

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Received June 13, 1973

Non-empirical LCAO-MO-SCF calculations on SiF₂ 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 SO₂.

Key words: SiF₂, 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 AB₂ 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 BF₂ and NF₂ [3], and in the present paper the results of calculations on the ground state of SiF₂ are described. Calculations on SF₂ and PF₂ are in progress and will be reported at a later date [4].

SiF₂ 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 FSiF angle (100° 59') in the electronic ground state. SiF₂ has a much longer lifetime (~ 2 min) than its carbon analogue CF₂ (~ 1 sec) and a comparison of their electronic structure together with that of SO₂ which is isoelectronic with SiF₂ 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 SiF₂, and in fact only a few such calculations on other polyatomic molecules containing Si, such as SiH₂ [8], SiH₃ and its ions [9]. SiH₄ [10], SiH₃F [11], SiO₂⁺ and H₄SiO₄ [12]. However, there has been a semi-empirical calculation on SiF₂ by Brown and
Peel [13] using the VESCF [14] method, but since the basis set used did not include 2s or 2p$_x$ 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, 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, particularly 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, 1 for the s functions and 2, 2, 1, 1, 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 $\alpha_d(S) = 0.6$ in calculations on SO$_2$.

We initially chose $\alpha_d(Si) = 0.6$, but in view of our wish to extend these calculations to other molecules containing Si, it was considered worthwhile to optimize $\alpha_d(Si)$ keeping the other exponents constant. The results of these calculations give an optimized value of $\alpha_d(Si) = 0.3$ 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,