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An Analysis of the Partition of the Molecular Space in the SCF-MS-Xα Method: Calculations of the Valence Ionization Potentials of SiH_3F and SiH_2F_2

Giancarlo De Alti* and Piero Decleva

Istituto di Chimica, Università di Trieste, Trieste 34127, Italy

Antonio Sgamellotti

Dipartimento di Chimica, Università di Perugia, 06100, Italy

Multiple scattering Xα calculations were performed to compute the valence ionization potentials of SiH_3F and SiH_2F_2, with the aim to investigate the effect of different geometrical parameters. The results show that the ordering of the valence levels does not depend on the choice of these parameters, so that MS-Xα calculation may be confidently used in assigning photoelectron spectra.

Key words: MS-Xα calculations – Photoelectronspectra – Fluorosilanes

1. Introduction

The principle and formalism of the MS-Xα method are thoroughly examined in some review articles [1–3]. Two basic sets of parameters are required to perform the calculations: the α exchange factors and the radii of the spheres into which the molecular space is divided. While small variations of the α parameters do not affect significantly the results, the influence of the geometrical parameters is much more relevant. In this paper we report MS-Xα calculations for the SiH_3F and SiH_2F_2 molecules with the aim to assess the dependence of the results on different geometrical parameter choices and to confirm the assignment of their photoelectron spectra.

2. Details of Calculations

Different radii of the spheres into which the molecular space is divided are considered both with and without overlapping spheres. In the latter, since the requirement of tangent atomic spheres is not sufficient to fix uniquely all the atomic

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*Author to whom correspondence regarding this paper should be addressed.

radii, two different values of the Si/F radii ratio are adopted: the first according to the Slater radii [4] and the second following the Norman procedure [5]. With the overlapping spheres, all the atomic radii are increased by a factor $2^{1/3}$, which doubles their volumes, while the outer sphere radius is kept constant. With Slater radii we have performed calculations with the outer sphere centre both coinciding with the silicon atom and displaced in order to minimize the intersphere volume. This latter choice is adopted in all the subsequent calculations.

The geometry of the molecules is taken from Ref. [6]. α factors employed are: $\alpha_{Si}=0.72751$, $\alpha_F=0.73732$ [7], $\alpha_H=0.77725$ [8], an average weighted according to the number of valence electrons for the outer and intersphere region. Partial waves up to $l=2$ for Si and outer sphere, up to $l=1$ for F and $l=0$ for H are used.

The ionization potentials are computed using the transition state formalism [3].

3. Results and Discussion

In Figs. 1 and 2 are reported the valence ionization potentials relative to SiH_3F and SiH_2F_2 obtained with five different parameter choices as follows: in cases a, b, c the Slater's radii were employed, in cases d and e those evaluated according to Norman's suggestion.

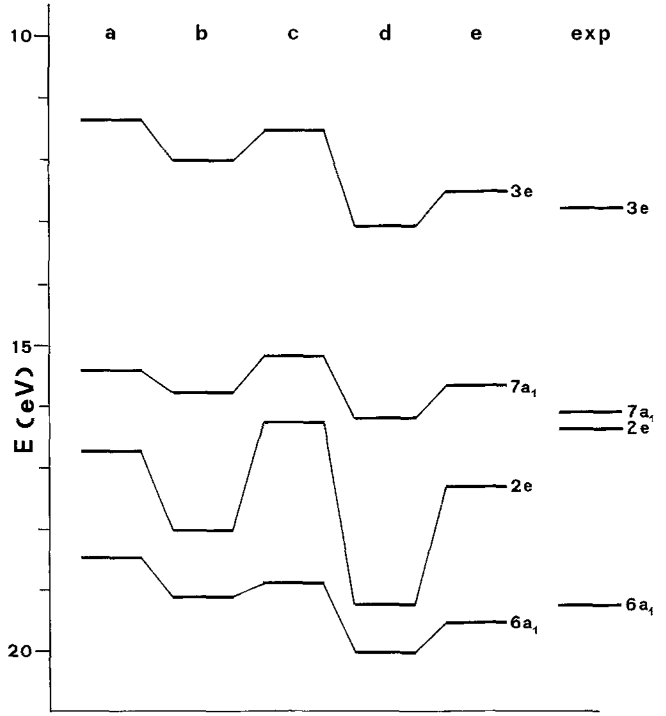

Fig. 1. Experimental and theoretical ionization potentials (eV) for the SiH_3F molecule. For explanation of columns a, b, c, d, e see the text. Experimental values and assignment taken from Ref. [9]

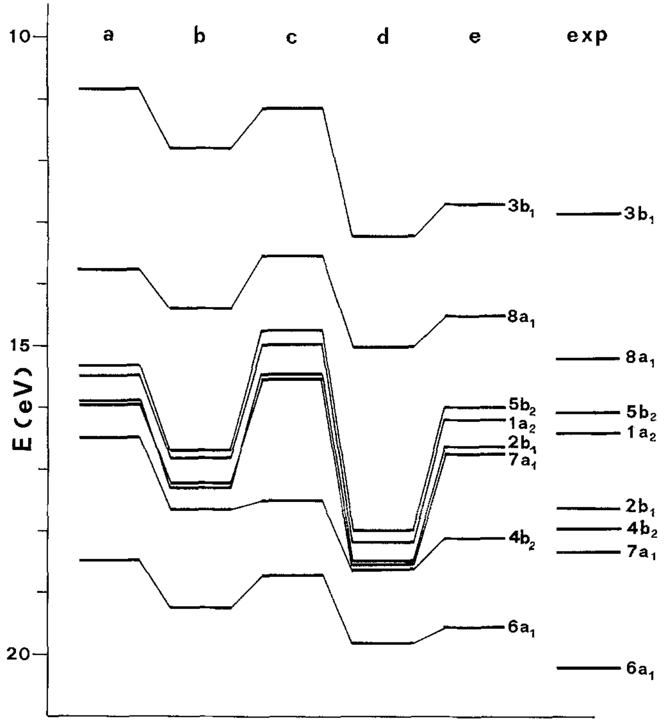

Fig. 2. Experimental and theoretical ionization potentials (eV) for the SiH_2F_2 molecule. Experimental values and assignment taken from Ref. [9]

Except for the case a in which the center of the outer sphere coincided with the Si atom, in all other cases it was chosen in order to minimize the intersphere volume. In cases c, e the overlapping spheres were employed. The last column reports the experimental data [9].

The results obtained show that the effect of the displacement of the outer sphere centre causes a shift of all ionization potentials towards higher binding energies. This shift is substantially uniform for all states (case b relative to a). An analogous effect is achieved by adopting Norman's radii (case b relative to d). Also in this case the shift is practically uniform. As long as the spheres are not overlapping, the total energy can be considered variational with respect to the sphere radii. In going from case a to d, the total energy decreases sensibly and, according to this criterion, case d would represent the best choice of radii.

The introduction of the overlapping spheres gives lower ionization potentials. This effect is very similar both with Slater and Norman values of the sphere radii.

An analysis of the behaviour of the individual potentials shows that this lowering is quite different for different orbitals so that different groupings are obtained. Again the total energy decreases significantly. In this case however the total energy is not variational any longer so that this cannot be considered as a real improvement.

For the SiH_3F molecule the experimental photoelectron spectrum shows three distinct bands [9], which should comprise four valence levels, namely $6a_1$, $7a_1$, 2e, 3e. The band at lower ionization potential was assigned to the ionization from the 3e orbital, while the higher was attributed to the $6a_1$ orbital. To the central band were assigned the ionizations from the $7a_1$ and 2e orbitals.

Within this band which shows a shoulder with vibrational structure, the main peak corresponding to a lower ionization potential was assigned to the $7a_1$ orbital and the shoulder to the 2e. The present calculations performed with all different parameter choices give the same ordering. As concerns the 3e, $7a_1$ and $6a_1$ ionizations, the results of all computations show a reasonable agreement and minor variations. The 2e orbital exhibits a more pronounced variation. In particular going from case a to b and from b to d it becomes more stabilized and approaches the $6a_1$ orbital. The use of the overlapping spheres influences this orbital more strongly than the others, shifting it towards the $7a_1$ orbital. Quantitatively the results of case a are on the whole too low when compared with the experimental data. The shift to higher binding energies obtained in cases b and d brings them closer to the experimental values.

The introduction of the overlap, influencing markedly the 2e orbital, ameliorates the level structure (case c and e), bringing it in a better agreement with the experimental data. The best accordance is realized for case e.

For SiH_2F_2 eight ionization potentials are theoretically expected. The experimental spectrum is formed by five distinct bands which have been assigned in order of increasing binding energy as follows: the first band to the $3b_1$ orbital, the second to the $8a_1$, the third to the $5b_2$ and $1a_2$, the fourth to the $2b_1$, $4b_2$ and $7a_1$, and the fifth to the $6a_1$, as can be seen in Fig. 2. The results of the computations display a completely analogous behaviour to that of the other molecule. The introduction of the overlapping spheres affects mainly the position of the group of orbitals $5b_2$, $1a_2$, $2b_1$, $7a_1$ shifting them towards lower binding energies more markedly than the others. It is worth mentioning that they form two pairs of nearly degenerate levels which in all computations maintain their respective positions. Order inversions are apparent for the pair of $7a_1$ and $2b_1$ orbitals. Comparing quantitatively the results with the experimental data the cases a, b and c yield ionization potentials which are generally low. The use of Norman's radii results in a set of levels which are in closer agreement with the experiment, particularly for the $3b_1$, $8a_1$ levels, which are the lower ones and for the $4b_2$ and $6a_1$ levels which are the higher ones. The two pairs of $5b_2$, $1a_2$ and $2b_1$, $7a_1$ levels are calculated very near to the $4b_2$ level. The introduction of the overlap shifts these pairs towards the $8a_1$ level, giving a more correct spacing between them. However the distance between the two pairs tends to remain substantially unaffected. In the last calculation the $5b_2$, $1a_2$ levels are in fair agreement with the experimental band, while the difference for the other two is about one eV, and represents the main deviation.

The ordering of the levels obtained from the present calculations confirms almost completely that proposed by the previous authors, on the basis of the results of

CNDO/2 calculations, intensity consideration and correlations with the spectra of the corresponding fluoromethanes [9]. The only disagreement is the position of the $4b_2$ level which is always calculated lower than the $7a_1$ level. This is the same order that the Xα method furnishes for the CH_2F_2 molecule. Therefore the present calculations suggest for the fourth band the ordering $2b_1$, $7a_1$ and $4b_2$. However due to the closeness of the $2b_1$ and $2a_1$ levels an inversion between them would be possible.

In conclusion the results show that the ordering of the valence levels does not critically depend on the partitioning of the molecular space, although the energy values are affected to some extent, so that MS-Xα calculations may be confidently used in assigning photoelectronspectra.

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