An MS Xα Study of the Potential Energy Surface and Electronic Structure of the PF₄ Radical

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The problem of determining the most adequate calculation parameters in the multiple scattering Xα method is investigated in the PF₄ radical case. A full geometry optimization of the radical is made using overlapping and non-overlapping atomic spheres and the corresponding spin density distribution in the various regions is calculated. Comparisons with both SCF LCAO results and experiment show that a very reasonable description of the structure and electronic properties of the radical can be derived from the calculations using overlapping atomic spheres.

Key words: PF₄ radical - Multiple scattering Xα method (MS Xα)

1. Introduction

Phosphoranyl radicals have recently been the subject of several experimental [1, 2] and theoretical [3-6] investigations. An analysis of the ESR spectra of PF₄ radicals trapped in a crystalline matrix [2] leads to a structure considerably distorted from tetrahedral symmetry for this radical, in agreement with the calculations which predict a trigonal bipyramidal structure of C₂ᵥ symmetry [3-6]. However, there is a quantitative disagreement among the theoretical predictions concerning bond lengths and bond angles.

As for hyperfine coupling constants, the agreement between theory and experiment is generally rather poor, even when including d orbitals of phosphorus in basis set, which emphasizes the difficulty of describing adequately the unpaired electronic orbital of radicals.

Recently the multiple scattering Xα (MS Xα) method [7] has been shown to give a reasonably accurate description of the electronic structure of compounds containing fluorine ligands [8-12]. Furthermore, even though it is not its main virtue, this model, in some cases [13, 14], seems able to provide potential energy surfaces showing satisfactory agreement with experiment.

In this work the MS Xα method is used, in both “touching” and overlapping atomic spheres approximations, to determine the lowest minimum on the potential energy surface and the corresponding electronic structure of the PF₄ radical. An evaluation is
then made of the spin densities in the various regions of the radical. Whenever possible, the present results are compared with both experiment and previous theoretical estimates in order to thoroughly evaluate the ability of the MS Xα method of predicting the properties of radicals.

2. Calculation Parameters

The molecular structure of PF₄ (Fig. 1) belongs to the C₂ᵥ symmetry with two pairs of respectively equatorial (F₁, F₃) and axial (F₂, F₄) equivalent fluorine atoms. In this work the search for the equilibrium geometry is made by varying in turn bond distances RₚF₁ and RₚF₂ and bond angles α and β (see Fig. 1).

The values of the MS Xα parameters are presented in Table 1. The atomic α values are taken from the calculations of Schwarz [15]. A weighted average of the atomic values (four parts of fluorine to one part of phosphorus) is chosen for the α value in both the interatomic and extramolecular regions.

As an important feature of this work is to compare in detail the results obtained using "touching" and overlapping atomic spheres, two different sets of sphere radii are used. Set A is our "touching spheres" parameter set and it is found using the procedure described by Norman [16]: from the initial molecular charge distribution, constructed by superposing atomic charge densities, the radii of atomic spheres containing the

<table>
<thead>
<tr>
<th>Region</th>
<th>Xα Exchange Parameter</th>
<th>Sphere Radii (a.u.)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>P atom</td>
<td>0.72620</td>
<td>1.71057</td>
</tr>
<tr>
<td>F (equatorial)</td>
<td>0.73732</td>
<td>1.61161</td>
</tr>
<tr>
<td>F (axial) atom</td>
<td>0.73732</td>
<td>1.52091</td>
</tr>
<tr>
<td>Outer sphere</td>
<td>0.73510</td>
<td>4.93380</td>
</tr>
<tr>
<td>Intersphere</td>
<td>0.73510</td>
<td>-</td>
</tr>
</tbody>
</table>

² For both parameter sets A and B, the values reported correspond to the equilibrium geometry of the radical.