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Basis Set Dependence of *Ab Initio* Geometry Predictions for AB_4 Molecules

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Abstract

Theoretical predictions of AB_4 molecular structures are very sensitive to choice of basis set. This has been previously demonstrated for the SH_4 and SF_4 molecules. Here it is shown that while both minimum and double zeta basis sets predict $C\ell F_4^+$ to have a C_{4v} structure, the addition of d functions on $C\ell$ results in a C_{2v} geometry, similar to the experimentally known structure of SF_4.

* Work performed under the auspices of the U. S. Energy Research and Development Administration.

One of the most impressive successes of single-configuration molecular orbital theory has been the reliable prediction of molecular structures.[1-4] Experience shows that in the large majority of cases, the use of a minimum basis set (MBS) is adequate for qualitatively correct geometry predictions. Further, double zeta (DZ) basis sets[1] generally provide predictions approaching quantitative accuracy. The number of cases in which the addition of polarization functions has been shown to qualitatively alter a double zeta geometry prediction has been virtually nil until recently.

Notable exceptions to the above stated guidelines are AB_4 molecules. In particular it is becoming apparent that the differentiation between square pyramidal (C_{4v}) and "detached octahedral" (C_{2v}, visualized by removing two adjacent B atoms from an octahedral AB_6 species) is treacherous. The first hint of this problem was the report by Guest, Hall, and Hillier[5] that $C\ell F_4^+$ is predicted to be square pyramidal using an MBS. Since the isoelectronic SF_4 molecule is known[6] to have a detached octahedral structure, this prediction was considered tenuous.[7] In an attempt to clarify this situation Ungemach and Schaefer[8] carried out calculations on $C\ell F_4^+$ with a larger basis set. However, in addition to verifying Guest's MBS results, they found a similar C_{4v} prediction using a double zeta basis. This greatly strengthened the possibility that $C\ell F_4^+$ might have a qualitatively different geometry from that of SF_4.

To further explore the relationship between these two isoelectronic species, Radom and Schaefer[9] performed geometry optimizations on SF_4

itself. They found an erroneous C_{4v} prediction using an MBS, but a qualitatively correct C_{2v} geometry using the more reliable DZ basis. Their results were particularly encouraging since they demonstrated for at least one AB_4 case that polarization functions (which are quite costly to employ) were unnecessary.

Unfortunately, for another AB_4 molecule, SH_4, it has very recently been shown that polarization functions do affect the predicted structure. Using a slightly better than double zeta basis set, Schwenzer and Schaefer[10] predicted a C_{2v} equilibrium geometry for SH_4; C_{4v} structures were found to lie only slightly higher in energy.[11] However, when Gleiter and Veillard[12] optimized the structure of SH_4 using a basis including polarization functions, a C_{4v} prediction emerged. Furthermore, their basis set is sufficiently large that it appears clear that at the Hartree-Fock limit (a complete basis set of one-electron functions) SH_4 is a square pyramidal molecule.

The purpose of the present paper is to report a geometry optimization for $C\ell F_4^+$ in which d functions on $C\ell$ have been included in the basis set.[13] These results are summarized in the Table, where it is seen that the d functions result in a rather sizeable lowering of the total energy. Our own feeling is that this finding should be credited more to the number of fluorine ligands ($C\ell F_4^+$ is a hypervalent[14] molecule) than any special role of "unfilled 3d orbitals". Nevertheless, it is clear from the Table that the inclusion of d functions changes the geometry prediction from C_{4v} to C_{2v}. The latter result of course is the more satisfying, since it is predicted from Walsh's rules and the known

structure of SF_4. Equally, important, the C_{2v} prediction is consistent with the vibrational[16] and ^{19}F NMR[17] spectra of $C\ell F_4^+$.

Several other points are worthy of mention. First, the Cℓ polarization functions reduce (with respect to the double zeta calculation) the predicted Cℓ-F bond distance by a full 0.15 Å for the C_{4v} form. Second the predicted C_{2v} bond distances are quite close to those hypothesized by Christe and Sawodny:[16] r_{ax} = 1.66 Å, r_{eq} = 1.59 Å. Third the C_{2v} form is predicted to lie only 2.1 kcal/mole below the C_{4v} form, but this energy difference could increase by as much as 5 kcal/mole if additional polarization functions were added to the basis set.

Our general conclusion is that the ab initio prediction of the structures of AB_4 molecules is a dangerous profession. Specifically, these predictions are much more sensitive to basis set size than are comparable predictions for more conventional molecules. Whenever possible, the use of basis sets of at least double zeta plus polarization quality is strongly recommended.

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Table. Theoretical results for $C\ell F_4^+$. In all calculations a (9s 5p/4s 2p) basis set was used for fluorine.

Assumed Structure	Chlorine Basis Set	E (hartrees)	r_{ax} (Å)	r_{eq} (Å)	θ_{ax}	θ_{eq}
C_{4v}	(12s 9p/6s 4p)	-856.2678	1.76	1.76	143.5	143.5
C_{2v}	(12s 9p/6s 4p)	a	a	a	a	a
C_{4v}	(12s 9p 1d/6s 4p 1d)	-856.4325	1.61	1.61	144.2	144.2
C_{2v}	(12s 9p 1d/6s 4p 1d)	-856.4359	1.63	1.57	169.6	109.7

[a] There is no minimum here; the C_{2v} geometry collapses to the more stable C_{4v} equilibrium geometry.

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