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THE ELECTRONIC STRUCTURE OF THE SbF_5^{2-} ION AND ISOELECTRONIC SPECIES

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SUMMARY

The electronic structure of the SbF_5^{2-}ion and the isoelectronic species TeF_5^- , IF_5 and XeF_5^+ are calculated using the Discrete Variational X_α-method (DVM-X_α). The nature of chemical Bonding is analysed in terms of a Mulliken population scheme. The factors leading to geometrical distortions of the SbF_5^{2-} coordination polyhedron are discussed. The results of calculations cast doubts on the validity of the assumption that the geometry of the anion is influenced by the lone pair.

INTRODUCTION

The complex compounds of the trivalent antimony attract considerable attention because they possess some extraordinary electrophysical, optical, etc., properties as well as major changes in these properties with phase changes [1,2]. There are many experimental data on the structure and chemistry of the antimony (III) halides, in particular, of great interest are

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investigations of numerous compounds with M_2SbF_5 stoichiometries M=Na, K, Rb, Cs, NH_4, Tl or an organic cation) which contain the SbF_5^{2-} ion [3-5].

Theoretical studies on the electronic structure of such compounds is hampered by serious technical difficulties since conventional methods of band structure calculations can not be used in practice because of the large size of the primitive cells. On the other hand, qualitative notions, based on, for example, valence=shell electron-pair repulsion [6] do not always lead to a satisfactory explanation of the experimental data [7]. An alternative method for the investigation of the electronic structures is the cluster approach in which the solid is simulated by a relatively small number of atoms.

The aim of this work is to calculate the electronic structure of the SbF_5^{2-} anion, as a model of the anion group in the M_2SbF_5 salts, and that of some other isoelectronic species for which crystal effects are not important.

CALCULATIONAL DETAILS

The calculations on the electronic structure of the SbF_5^{2-}, TeF_5^-, XeF_5^+ ions and the IF_5 molecule are carried out using the Discrete Variational X_α-method [8] which has been devised to solve the one-electron Hartree-Fock-Slater (HFS) equations in the framework of the usual MO LCAO representations. Matrix elements of the corresponding HFS Hamiltonian are evaluated with the help of direct numerical integration schemes. In this work an original program described elsewhere [9] is used.

The calculations are carried out within the basis of the numerical HF functions with the inclusion of the external 5d Slater type orbitals (STO). Variation of their exponents over limits 1.0 to 4.0 leads to only comparatively small variations (about 1 eV) in the oneelectron energies without changes in the order of corresponding MOs, and a small charge redistribution. The calculations on the electronic structure of the IF_5 molecule are carried out using the double zeta Basis of Clementi

TABLE 1

Ionization potentials (in eV), charges on atoms (Q_M) and overlap populations (Q(I-F)) of the IF_5 molecule

MO	Basis		Experimental [11]
	double zeta +5d(2.5. 1.0)	HF+5d(4.0)	
$17a_1$	12.9	13.4	13.3
$1a_2$	13.8	14.1	
11e	14.0	14.1	
$6b_1$	14.3	14.6	
10_e	14.4	14.6	15.2
$16a_1$	14.4	14.8	
$5b_1$	14.9	15.1	
$3b_2$	15.6	15.5	15.9
9e	16.2	15.8	16.2
8e	18.0	18.8	17.3
$15a_1$	18.3	18.9	19.2
$14a_1$	23.1	24.8	
Q_I	+1.72	+1.94	
$Q_{F_{ax}}$	-0.36	-0.38	
$Q_{F_{eq}}$	-0.34	-0.38	
$Q(I\text{-}F_{ax})$	+0.19	+0.08	
$Q(I\text{-}F_{eq})$	+0.17	+0.04	

[10] for the valence shell, extended by two sets of 5d STOs for which exponents have been taken as 2.5 and 1.0.

In Table 1 are presented the results of calculations for IF_5 together with the experimental data for valence ionization potentials (IPs). As it may be seen, the values of valence IPs obtained within both bases agree with each other and with experimental data within limits of 1 eV. Therefore, it may be concluded that DVM leads to an adequate charge distribution description in other compounds of this series.

The exchange parameter α is equal to the arithmetic mean of Schwarz's α_{HF} [12]. Geometrical factors are as follows: tetragonal pyramid, point group - C_{4v} bond lengths for SbF_5^{2-} from [13], for TeF_5^- from [14], for IF_5 from [15], and for XeF_5^+ from [16-18].

In order to investigate the electron density distribution under the base of the SbF_5^{2-} ion (defined as the xy plane, and usually considered as a lone pair site) calculations are carried out with the inclusion of functions centered at various distances along the X-axis. This allows use of the Mulliken population analysis [19] data for empty sites to estimate the electronic density distribution near these sites [20].

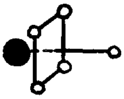
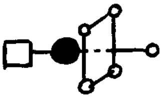
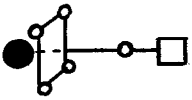
RESULTS AND DISCUSSION

Table 2 presents the electronic characteristics of the ground state of SbF_5^{2-} calculated without (column 1) and with the inclusion in the basis set of the 1s, 2s and 2p F STOs for which exponents are taken to be 'diffuse' parts of Clementi's double zeta basis set [10]. These additional STOs were centered above F_{ax} (column 2) and below Sb (column 3) by 0.45 Å respectively. A further inclusion of the 'contracted' parts, with larger exponents for each shell function, leads to negligible changes in the charges on the 'vacancy' sites.

As seen from the data of a Mulliken population analysis in the latter case, there is no accumulation of negative charge,

TABLE 2

Electronic characteristics of the SbF_5^{2-} ion*)

MO energies in eV	SbF_5^{2-}	$SbF_5\square^{2-}$	
			
$12e^*$	11.7	12.4	12.9
$18a_1^*$	12.9	12.6	11.5
$17a_1$	5.4	6.5	6.6
$1a_2$	4.5	4.8	4.6
11e	4.7	4.9	4.3
$6b_1$	4.2	4.5	4.3
10e	4.2	4.5	4.1
$5b_1$	3.8	4.1	3.8
$16a_1$	4.2	4.3	3.7
$3b_2$	3.4	3.6	3.5
9e	3.2	3.5	2.7
8e	1.8	2.0	1.5
$15a_1$	1.9	2.4	1.3
$14a_1$	-1.8	-1.2	-1.6
Changes on atoms, overlap populations			
Q_{Sb}	+0.45	+0.32	+0.50
Q_{Feq}	-0.49	-0.49	-0.50
Q_{Fax}	-0.49	-0.46	-0.37
Q(Sb-Feq)	+0.19	+0.17	+0.17
Q(Sb-Fax)	+0.23	+0.22	+0.22
Q	-	-0.16	-0.13
First IP, i.e. the electron affinity of SbF_5^-			
	-1.7	-2.7	-2.6

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* unoccupied MOs; □ A vacancy site on which are placed the additional basis functions.

which might be considered as a lone pair, below the Sb atom. Moreover, the Mulliken charge on this site is only slightly larger than that of the equivalent site above F_{ax}. Therefore, one may conclude that the charge distribution below the equatorial plane F_{eq} is only slightly more dense than above F_{ax}. (Of course, this difference increases when the distance from the corresponding nuclei is decreased).

It is worth noting that an analysis of charge distribution by Bader et al.[21] for such simple molecules as H_2O, NH_3, etc., usually considered to have lone pairs, does not indicate that a 'lone pair' corresponds to an accumulation of charge.

Analysis of the composition and behaviour of the molecular orbital energies shows that in SbF_5^{2-} the $17a_1$ HOMO is a weakly antibonding molecular orbital followed by a number of nonbonding MOs consisting mainly of ligand AOs. The bonding MOs are the low lying 8e, $14a_1$ and $15a_1$ MOs only. A small antibonding character for $17a_1$ may explain [14] the possibility of formation of salts with the SbF_5^{2-} anion. Because this MO is an essentially ligand orbital, the electron affinity (EA) of SbF_5 with the real salt geometry is quite high as 5.3 eV according to our calculations.

In the gas phase the XF_5 molecules (X=P, As, Sb) have a trigonal bipyramidal structure. The HOMO of these molecules is strongly antibonding with respect to central atom-ligand interaction, and consists of the ns atomic orbitals of the central atom and $2p\sigma$ atomic orbitals of the ligands. According to our calculations for SbF_5 its $13a_1$ HOMO contains 56% from the Sb atom. The calculated value of the vertical EA of SbF_5 is small - 0.2 eV. In order to form a negative ion the XF_5 molecules must undergo geometrical deformation after which the new HOMO accepting an extra electron possesses a structure with a less antibonding character. Both experimental data on the geometrical structure of the SbF_5^{2-}, TeF_5^- and XeF_5^+ ions, and the IF_5 molecule [13-18], and results of the ab initio calculations on the structure of the PF_5^- ion [22] show that transition from D_{3h} to C_{4v} takes place on anion formation. After such a deformation the HOMO may by symmetry include the np AO of the central atom. This decreases the antibonding character of the HOMO with respect to the central atom-ligand interaction.

Such a decrease leads to a close approach of the HOMO energy to energies of nonbonding ligand MOs. Therefore, the XF_5 systems with the C_{4v} structure and the anion bond lengths appear to be like superhalogens [23], i.e. systems for which EAs are greater than those of halogen atoms. The delocalization of an extra electron over four F_{eq}, relatively small antibonding character of LUMO, together with a relatively high EA of the central atom should result in the high EA values of the pentafluorides according to qualitative theory of superhalogens [23]. In turn, high EA values of these species may partly explain the possibility of formation of salts with anions such as TeF_5^- (the calculated vertical EA value of TeF_5 with the experimental geometry of TeF_5^- is 5.4 eV), and SbF_5^{2-}. In the latter case the second extra electron should be stabilized by the crystalline field of the surrounding cations.

According to our calculations the order of MOs in the isoelectronic species XF_5^{n-} is constant, and the composition of the HOMOs, gives in Table 3 does not change when going from SbF_5^{2-} to IF_5 substantially. When going to XeF_5^+ the $17a_1$ MO becames an almost purely ligand orbital, and nearly degenerate $18a_1$ and 12e LUMOs possess a larger antibonding character with respect to the central atom-ligand interaction than the $17a_1$ MO in the preceeding species. According to our estimates the vertical EA of XeF_5^+ is between 8.5-9.5 eV, i.e. in a sense XeF_5 lies midway between alkali atoms and fluorides which possess the nonbonding HOMO.

One may suggest that the HOMO structure of the MF_5^{n-} species influences their geometry, because the $D_{3h} \rightarrow C_{4v}$ deformation becomes necessary in the first instance because of reconstruction of the HOMO. In particular, in SbF_5^{2-} the experimentally observed shortening of the $Sb-F_{ax}$ bond length and deviation of the $F_{eq}-Sb-F_{ax}$ angle below 90° may be explained from the

TABLE 3

The population of HOMOs (in e) and their energies (in eV) for the ground state of the XF_5^{n-} systems

	SbF_5^{2-}	TeF_5^-	IF_5	XeF_5^+		
	$17a_1$	$17a_1$	$17a_1$	$17a_1$	$18a_1$ *)	12e *)
X	0.65	0.64	0.56	0.34	0.86	1.04
F_{ax}	0.0	0.01	0.01	0.01	0.55	0.02
F_{eq}	1.35	1.34	1.43	1.65	0.59	0.94
	+5.4	-2.1	-9.3	-19.0	-13.8	-13.6

* vacant MO

properties of the $17a_1$ HOMO. The shortening is connected with a negligible contribution from F_{ax} to this MO (such an explanation was formally suggested in the case of PF_5^- [22]), and the displacement of Sb below the equatorial ligand plane is necessary to make $17a_1$ bonding with respect to the $5p_z(Sb)$-$2p\sigma(F_{eq})$ interaction.

In the case of heavy ligand atoms (Br or I) the antibonding character of the HOMO would be lower because of longer bond lengths and the mutual repulsion of equatorial and axial atoms would be greater than in the case of fluorine ligand atoms. In turn, this may result in a displacement of equatorial ligand atoms below the 'Sb plane'.

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