Theor Chim Acta (1987) 71: 237–245

Theoretica Chimica Acta

Ab initio SCF studies of the molecular structure of XeF_6, IF_6^-, and TeF_6^{2-} in non-octahedral geometries

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(Received September 5, revised December 1/Accepted December 5, 1986)

All-electron SCF calculations in contracted large Gaussian basis sets were performed for the molecules in the isoelectronic series XeF_6, IF_6^-, and TeF_6^{2-}. Molecular equilibrium geometry of these molecules was studied first in O_h symmetry. Then, the gradient minimization technique was used to determine molecular structure of the studied systems near the local minima corresponding to C_{3v} and C_{2v} geometries involved in the internal motion.

In the O_h symmetry, TeF_6^{2-} and IF_6^- are bound by 172 and 104 kcal/mol, respectively. The total energy of XeF_6 is larger than the sum of total energies of the constituent atoms by 192 kcal/mol. Lowering the symmetry to C_{3v} and C_{2v} results in an energy gain of about 20 kcal/mol for all studied systems.

Key words: Hypervalent molecules — SCF gradient geometry optimization — Gaussian basis sets

1. Introduction

Structure of XeF_6 has been of great interest ever since the molecule was first synthesized (for references to earlier work, see [1]). The molecule is non-rigid,

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varying its geometry via a pseudorotatory mechanism [2], demonstrating in this way the stereochemical activity of the lone electron pair.

In the present work we determined, within the *ab initio* SCF approach, the molecular structure of XeF_6, IF_6^-, and TeF_6^{2-} both in the octahedral symmetry and in C_{3v} and C_{2v} symmetries which are involved during the internal motion [3, 4]. Even though the electron correlation energy is expected to contribute significantly to bonding in these systems, the SCF calculations may still serve as a useful first approximation to both molecular geometries and one-electron properties. In particular, the SCF method, capable of representing the (classical) electronic coulombic repulsion between the charge clouds in the molecules [5], should be able to describe qualitatively the deviations from octahedral symmetry in the hypervalent systems studied here.

2. Details of calculations

For Xe, I, and Te we used the largest (43333/4333/43) Gaussian basis sets from the recent compilation [6]. For greater flexibility in molecular calculations these basis sets were split into the form (4333211/43321/4211*). In the *s* space, additional functions were added, with exponents of 0.02, 0.019, and 0.018 for Xe, I, and Te, respectively. With these basis sets the total energies in the ground states of Xe (^1S), I (^2P), and Te (^3P) were −7227.06115 h, −6913.07700 h, and −6607.04451 h, respectively. For F we used the basis (621/511/1*) which gives the total energies of −99.39521 h and −99.44334 h for F (^2P) and F^- (^1S), respectively (the diffuse *p*-type function for the negative ion was taken from [7]). The single *d*-type polarization functions were used for all the atoms and were also taken from [6]. The six-component Cartesian Gaussian *d*-type functions were used in all calculations.

After the initial single-point search for approximate minima in the molecular total energy was performed in C_{3v} and C_{2v} symmetries, refinement of the structure parameters was done using gradient technique [8] as incorporated in the program HONDO [9]. In all the systems studied the optimization process was stopped when the largest component of gradient of the total energy was smaller than 10^{-3} hartree/bohr.

The geometries of the studied systems are defined in Figs. 1, 2, and 3 for symmetries O_h, C_{3v}, and C_{2v}, respectively.

3. Results and discussion

The total energy, *E*, and structural parameters (as defined in Figs. 1-3) of the studied systems are presented in Table 1 together with the stabilization energy, ΔE, due to lowering of the molecular symmetry.

In the octahedral geometry, the SCF bonding energy, defined as the difference between the sum of total energies of the constituent atoms (or of the fluoride ions) and the total energy of the molecule, increases in the series XeF_6, IF_6^-,

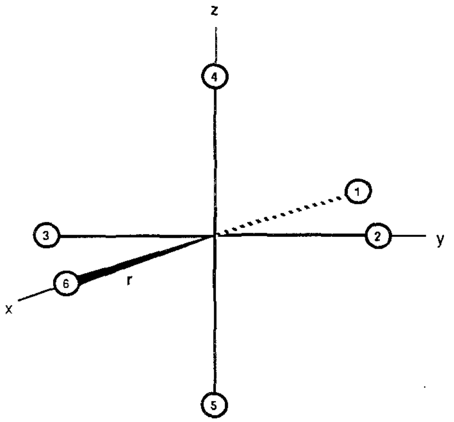

Fig. 1. Structural parameters in O_h symmetry

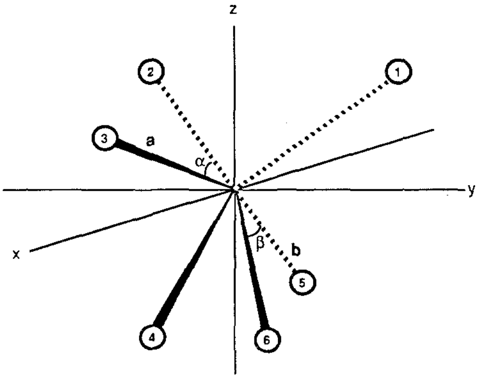

Fig. 2. Structural parameters in C_{3v} symmetry

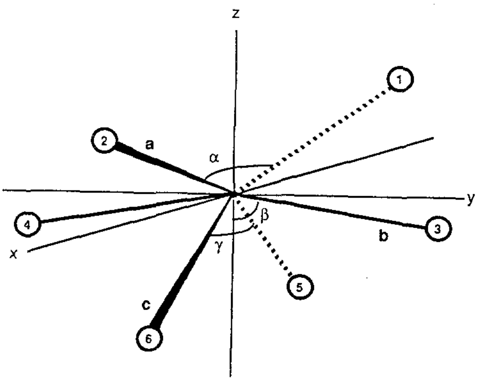

Fig. 3. Structural parameters in C_{2v} symmetry

Table 1. Bond lengths (in Å), bond angles (in degrees), total energies (in hartrees), and stabilization energies (in kcal/mol)[a]

		XeF_6	IF_6^-	TeF_6^{2-}
O_h	r	1.951	2.014	2.125
	E	−7823.1258	−7509.6631	−7203.7864
C_{3v}	a	1.983	2.071	2.237
	b	1.853	1.880	1.935
	α	114.1	113.8	112.9
	β	81.5	81.5	82.0
	E	−7823.1637	−7509.7006	−7203.8169
	ΔE	−24.0	−23.0	−19.0
C_{2v}	a	2.009	2.120	2.326
	b	1.884	1.939	2.024
	c	1.863	1.879	1.926
	α	139.2	134.5	132.3
	β	80.9	79.8	79.9
	γ	74.9	79.2	78.5
	E	−7823.1619	−7509.6975	−7203.8151
	ΔE	−23.0	−22.0	−18.0

[a] See Figs. 1-3 for definition of the structural parameters

and TeF_6^{2-}: the respective values of the bonding energy are −192, 104, and 172 kcal/mol. Lowering of the symmetry results in lowering of the total energy by about 20 kcal/mol (or almost 1 eV). This stabilization energy may make an important contribution to theoretical electron affinities of hexafluorides of main group elements which were usually evaluated assuming octahedral symmetry for both the neutral species and the molecular anion.

Both the bond lengths and bond angles deviate significantly from the octahedral values. The angular distortions in C_{3v} symmetry are very similar in all the species studied; in C_{2v} symmetry they vary more from system to system: this may be probably attributed to softness of the bending motions and to slightly different values of gradients at termination of the optimization process. In C_{3v} symmetry, the angle between the C_{3v} symmetry axis and the longer Xe-F bond is 76° which is larger than the value of 67° inferred from experiment [3]. On the other hand, the 49° angle between the C_{3v} axis and the shorter Xe-F bond is fairly close to the experimental value of 52° [3].

The deviations from the octahedral value of the bond length decrease in the order TeF_6^{2-}, IF_6^-, and XeF_6 (the average deviations relative to the O_h value of the bond length are 7, 5, and 3%, respectively). The geometries of the species differ significantly in C_{3v} and C_{2v} symmetries; however, the total energies differ but slightly. Similar observation emerged from the crystal-field studies on XeF_6 [10].

The plots of the total electron density of XeF_6 in C_{3v} symmetry are shown in Figs. 4-5. As can be seen, the SCF method reveals an accumulation of the density

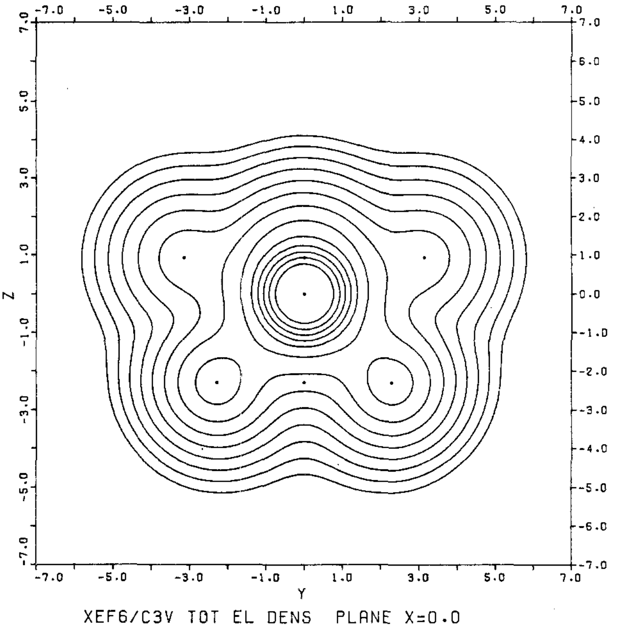

Fig. 4. Total electron density of XeF_6 in C_{3v} symmetry (plane $x = 0$). The density along the outermost contour is $1/1024\,e^-/a_0^3$ and it changes by a factor of two between neighboring contours

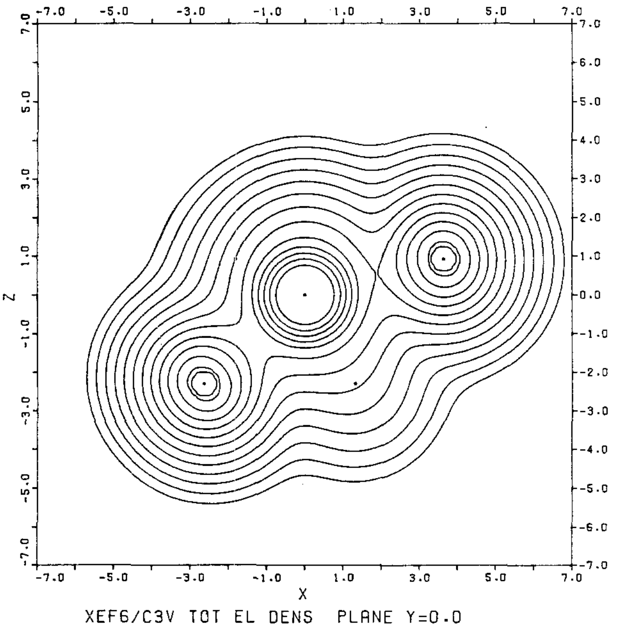

Fig. 5. Total electron density of XeF_6 in C_{3v} symmetry (plane $y = 0$). The density along the outermost contour is $1/1024\,e^-/a_0^3$ and it changes by a factor of two between neighboring contours

close to the longest bonds in the molecule. This accumulation may be viewed as the manifestation of the lone electron pair.

The values of some one-electron properties were calculated as expectation values of the corresponding operators using the SCF wavefunctions. They are collected in Tables Tables 2-4 together with the Mulliken atomic charges. It is interesting to note the small value of the dipole moment of XeF_6 (about 0.2 D) which falls within the range deduced in Ref. [3] from thermodynamic properties of XeF_6. The smallness of this value is due to the counterbalance between the accumulated electronic charge (along the z axis) on one side of the central atom and the negatively charged fluorine centers on the opposite side of the atom.

Table 2. One-electron properties (in atomic units) and Mulliken atomic charges for XeF_6[a]

Center	Property	O_h	C_{3v}		C_{2v}		
	$(xyz)_{\text{COM}}$	(0, 0, 0)	(0, 0, −0.3201)		(0, 0, −0.3152)		
COM	μ_z	0.0	0.0856		0.0882		
	$\langle x^2\rangle$	−48.499	−50.124		−53.448		
	$\langle y^2\rangle$	−48.499	−50.124		−45.796		
	$\langle z^2\rangle$	−48.499	−43.864		−44.729		
	Θ_{xx}	0.0	−3.130		−8.186		
	Θ_{yy}	0.0	−3.130		3.292		
	Θ_{zz}	0.0	6.260		4.893		
Xe	$\langle 1/r\rangle$	−316.64	−316.64		−316.64		
	$\langle\delta\rangle$	94 863.5	94 850.8		94 851.0		
	q	2.40	2.28		2.28		
	f_x	0.0	0.0		0.0		
	f_y	0.0	0.0		0.0		
	f_z	0.0	0.1484		0.1493		
	g_{zz}	0.0	6.110		6.307		
	g_{xx}	0.0	−3.055		−2.552		
	g_{yy}	0.0	−3.055		−3.755		
		F_6	F_3	F_5	F_2	F_3	F_6
F	$\langle 1/r\rangle$	−26.527	−26.580	−26.482	−26.602	−26.498	−26.492
	$\langle\delta\rangle$	419.75	419.63	419.74	419.62	419.72	419.75
	q	−0.40	−0.49	−0.27	−0.52	−0.35	−0.27
	f_x	0.0703	0.0625	−0.0692	0.0561	0.0	0.0561
	f_y	0.0	0.0	0.0	0.0	0.0815	0.0
	f_z	0.0	0.0171	−0.0577	0.0222	−0.0125	−0.0686
	$g_{\parallel}$	−2.380	−1.945	−3.634	−1.733	−2.941	−3.722
	$g_{\perp}$	1.190	1.148	1.706	1.162	1.504	2.076
	$g'_{\perp}$	1.190	0.797	1.928	0.571	1.437	1.646
	ϕ	—	−4.6°	−0.3°	−6.7°	1.2°	−0.5°

[a] $(xyz)_{\text{COM}}$ – coordinates of the center of mass; μ – dipole moment; $\langle\delta\rangle$ – charge density at the nucleus; q – Mulliken atomic charge; f – electric field at the nucleus; g – electric field gradient (at the nucleus) in the principal axes system; for ligands $g_{\parallel}$ denotes the component 'parallel' to the bond, $g_{\perp}$ denotes the component perpendicular to $g_{\parallel}$ and situated in the symmetry plane which contains the bond, and $g'_{\perp}$ denotes the component perpendicular to $g_{\parallel}$ and $g_{\perp}$; ϕ – angle between the bond and $g_{\perp}$ (see Fig. 9 for definition of ϕ)

Table 3. One-electron properties (in atomic units) and Mulliken atomic charges for IF_6^-[a]

Center	Property	O_h	C_{3v}		C_{2v}		
	$(xyz)_{COM}$	(0, 0, 0)	(0, 0, −0.3152)		(0, 0, −0.2962)		
COM	μ_z	0.0	0.0296		−0.0964		
	$\langle x^2\rangle$	−55.405	−57.620		−62.010		
	$\langle y^2\rangle$	−55.405	−57.620		−52.134		
	$\langle z^2\rangle$	−55.405	−48.861		−50.281		
	Θ_{xx}	0.0	−4.380		−10.803		
	Θ_{yy}	0.0	−4.380		4.012		
	Θ_{zz}	0.0	8.760		6.791		
I	$\langle 1/r\rangle$	−309.05	−309.06		−309.06		
	$\langle\delta\rangle$	89 610.6	89 598.9		89 599.5		
	q	2.30	2.18		2.18		
	f_x	0.0	0.0		0.0		
	f_y	0.0	0.0		0.0		
	f_z	0.0	0.1427		0.1425		
	g_{zz}	0.0	5.284		5.203		
	g_{xx}	0.0	−2.642		−2.387		
	g_{yy}	0.0	−2.642		−2.816		
		F_6	F_3	F_5	F_2	F_3	F_6
F	$\langle 1/r\rangle$	−26.771	−26.822	−26.732	−26.842	−26.750	−26.734
	$\langle\delta\rangle$	419.54	419.47	419.48	419.47	419.49	419.48
	q	−0.55	−0.64	−0.42	−0.68	−0.50	−0.41
	f_x	0.0549	0.0456	−0.0599	0.0379	0.0	0.0511
	f_y	0.0	0.0	0.0	0.0	0.0654	0.0
	f_z	0.0	0.0123	−0.0501	0.0165	−0.0117	−0.0598
	$g_{\parallel}$	−1.512	−1.233	−2.592	−1.014	−1.973	−2.674
	$g_{\perp}$	0.756	0.747	1.206	0.729	1.025	1.481
	$g'_{\perp}$	0.756	0.476	1.386	0.285	0.948	1.193
	ϕ	—	−6.2°	−0.4°	−8.5°	1.4°	−0.7°

[a] See footnotes to Table 2

According to our previous studies [11], the values of properties at the ligand nuclei should be rather close to the values which may be obtained using larger basis sets. The properties at the central atom nuclei may be in error by 10–40%, due to insufficient Gaussian expansions for the innermost core functions [11]. The components of the electric field gradient tensor are given in the principal axes system which for the ligand atoms is described in Fig. 6.

4. Conclusions

The SCF method together with the gradient technique of geometry optimization is capable of predicting the equilibrium structures of the hypervalent, non-rigid molecules in the vicinity of the local minima in C_{3v} and C_{2v} symmetries which are involved in the pseudorotatory motion of the ligands. For the transition geometries of C_s symmetry, further studies should be able to determine the height and shape of the potential barrier. In this way, the stereochemical activity of the

Table 4. One-electron properties (in atomic units) and Mulliken atomic charges for TeF_6^{2-} [a]

Center	Property	O_h	C_{3v}		C_{2v}		
	$(xyz)_{COM}$	(0, 0, 0)	(0, 0, −0.2926)		(0, 0, −0.2692)		
COM	μ_z	0.0	−0.2373		−0.4444		
	$\langle x^2 \rangle$	−63.869	−67.237		−73.908		
	$\langle y^2 \rangle$	−63.869	−67.237		−59.380		
	$\langle z^2 \rangle$	−63.869	−54.907		−56.929		
	Θ_{xx}	0.0	−6.165		−15.754		
	Θ_{yy}	0.0	−6.165		6.039		
	Θ_{zz}	0.0	12.330		9.715		
Te	$\langle 1/r \rangle$	−301.49	−301.50		−301.50		
	$\langle \delta \rangle$	84 551.1	84 541.2		84 541.5		
	q	2.14	2.01		2.01		
	f_x	0.0	0.0		0.0		
	f_y	0.0	0.0		0.0		
	f_z	0.0	0.1253		0.1258		
	g_{zz}	0.0	4.315		4.246		
	g_{xx}	0.0	−2.157		2.184		
	g_{yy}	0.0	−2.157		2.062		
		F_6	F_3	F_5	F_2	F_3	F_6
F	$\langle 1/r \rangle$	−26.993	−27.040	−26.955	−27.058	−26.975	−26.954
	$\langle \delta \rangle$	419.43	419.38	419.33	419.38	419.37	419.33
	q	−0.69	−0.78	−0.56	−0.82	−0.64	−0.55
	f_x	0.0368	0.0258	−0.0479	0.0190	0.0	0.0421
	f_y	0.0	0.0	0.0	0.0	0.0472	0.0
	f_z	0.0	0.0067	−0.0396	0.0078	−0.0085	−0.0480
	$g_{\parallel}$	−0·950	−0.718	−1.822	−0.549	−1.294	−1.910
	$g_{\perp}$	0.475	0.447	0.848	0.411	0.686	1.055
	$g'_{\perp}$	0.475	0.271	0.974	0.138	0.608	0.855
	ϕ	—	−7.7°	−0.7°	−9.1°	2.5°	−1.4°

[a] See footnotes to Table 2

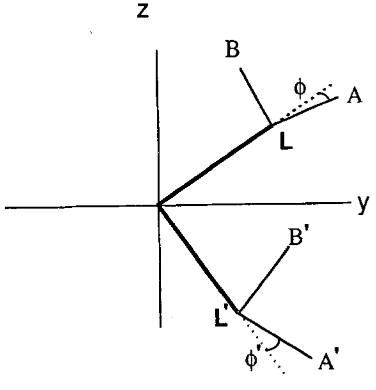

Fig. 6. Definition of the angle ϕ between the O–L bond and the principal axis A (along the bond) of the principal axis system of the electric field gradient tensor. Both ϕ and ϕ' on the figure are defined as positive quantities. (Negative values of ϕ indicate that A is tilted *towards* the symmetry axis O–z)

lone electron pair may be revealed, a task which is almost impossible to be accomplished in the traditional route of experimental studies on crystal structures, where the crystal packing effects may significantly distort the feeble effects due to the lone pair. (It should be mentioned here that the quadrupole splitting observed in the Mössbauer spectrum of tellurium fluorides in solution [12] may have indicated presence of TeF_6^{2-} in a non-octahedral configuration.)

There are still three more effects that should be considered before any final conclusions about the structures of XeF_6, IF_6^-, and TeF_6^{2-} are made. Firstly, the role of the *f*-type functions on the central atom should be investigated as they may influence geometries, relative stabilities, and one-electron properties. Secondly, the effects of electron correlation may be important, particularly in evaluating the dissociation energies of these molecules (especially for XeF_6). Finally, the relativistic effects may be important due to presence of the heavy central atoms.

Acknowledgements. This work was partly supported by a grant from NSERC (Canada). Two of us (LS and ZB) gratefully acknowledge fellowships from the Ministerio de Educación y Ciencia (Spain). All the calculations were done at the Amdahl 5870 hosted by the Department of Computing Services of the University of Alberta. We are grateful to Dr. D. Bent and Mr. Y.-N. Zia for their friendly cooperation and great help in providing funds which made the present work possible.

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