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Theoretical study on the 3D aromaticity in cationic X_4^{4+} (X=O, S, Se, and Te) clusters

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Abstract

The stable structures and 3D aromatic characters for four cationic X_4^{4+} (X=O, S, Se, and Te) clusters are investigated at the DFT and post HF level of theory with the extended 6-311+G* basis set used for O, S, Se atoms and correlation consistent, effective-core potential (ECP) basis set ECP46MWB_AVTZ for the heavier Te atom.. Two optimized structures of tetrahedron (T_d) and rhombus (D_{2h}) for four X_4^{4+} species have been obtained. The calculated results show that the tetrahedral (T_d) structures are stable and correspond to energy minima, whereas the rhombic (D_{2h}) ones are unstable and have one or more saddle points on the potential energy surfaces. The calculated NICS values show that four tetrahedral X_4^{4+} isomers have higher degree of 3D aromaticities. Whereas four rhombic X_4^{4+} isomers can be regarded to possess 3D antiaromaticities. The molecular orbital analyses reveal that the tetrahedral X_4^{4+} cations possess two-fold (σ and π) 3D aromaticity, conforming to the $2(N+1)^2$ electron counting rule for 3D aromaticity

Keywords Group-VI element clusters; DFT; post HF; 3D Aromaticity; MO analyses; NICS.

1. Introduction

The concept of aromaticity is one of the most significant concepts in chemistry, generally used to describe cyclic, planar, and conjugated molecules with delocalized π -bonds and unusual stability, such as benzene and its derivatives [1,2]. In recent years the aromatic concept has been successfully extended from traditional organic compounds to pure all-metal clusters [3-13] due to the pioneering works done by Boldyrev's group[3]. In addition to the aromaticities for planar two-dimensional (2D) molecules, the aromaticities in three dimensional (3D) structures of clusters, including spherical aromaticity of organic clusters, such as fullerenes[14], and inorganic cage clusters, such as icosahedral Sn_{12}^{2-} , Pb_{12}^{2-} with I_h symmetries[15-17], have been intensively studied and many important progresses have been made in recent decades[14-21]. Advances and general principles in spherical aromatic clusters have been comprehensively reviewed by Zhong fang Chen et al. [20,21].Tetravalent anions X_4^{4-} (X=N, P, As, Sb, and Bi) with Tetrahedral structures are one class of the smallest inorganic clusters possessing 3D aromaticities shown by Hirsch et al.[22].

For the 3D aromaticity, despite there exist a few limitations and controversial cases so far, some criteria have been formulated and often used now for identifying the 3D aromaticity, e.g. higher energetical stability, higher structural symmetry, higher negative values of Nucleus-Independent Chemical Shift (NICS)[23], and electron count rule, such as Wade's $2n+2$ rule[24], typically applied to closo boranes and carboranes, and Hirsch's $2(n+1)^2$ rule, for spherical clusters [21,25].

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In this work, a new class of the inorganic tetravalent cations X_4^{4+} ($X=O, S, Se, \text{ and } Te$) are studied theoretically with four methods: two density functional theory (DFT) B3LYP, B3PW91 and two correlated ab initio MP2, CCSD(T). These clusters are corroborated to be another class of the smallest inorganic ones possessed 3D aromaticity using the criteria for 3D aromaticity above. This work will confirm further Hirsch's closed-shell electron gas model and $2(2N+1)^2$ electron counting rule for 3D aromaticity.

2. Computational methods

The structural optimizations and vibrational frequency calculations for the inorganic cations X_4^{4+} ($X=O, S, Se, \text{ and } Te$) are carried out using four methods: B3LYP, B3PW91 and MP2, CCSD(T). B3LYP is a DFT method using Beck's three parameters functional (B3)[26] along with the Lee, Yang, and Parr correlation functional (LYP)[27]. B3PW91 uses B3 along with Perdew-Wang 1991 correlation functional [28]. MP2 is the second-order Møller-Plesset perturbation theory[29,30]. CCSD(T) is the coupled-cluster theory using singles and doubles level augmented by a perturbative correction for triple excitations[31-33]. The extended 6-311+G* basis set is used for O, S, Se atoms and ECP46MWB_AVTZ for the heavier Te atom, which is the correlation consistent, effective-core potential (ECP) basis set with 46 core electrons ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10}$) for Te, including quasi-relativistic effect and triple-zeta [34]. The reason of using ECP46MWB_AVTZ basis set for Te atom is that Te atom is beyond the element range in which heavier atoms are able to use AUG-cc-pVnZ basis set to compute various physical and chemical quantities in Gaussian 03 program [35]. ECP46MWB_AVTZ basis set constructed by the Stuttgart/Cologne group is a good one for Te atom. The electron affinity (EA) of Te is 45.24 kcal/mol calculated with CCSD(T)/ECP46MWB_AVTZ, being in very well agreement with the experimental value of 45.45 ± 0.01 kcal/mol[36].

NICS is still an efficient and simple method to probe aromaticity not only for planar clusters but also for 3D ones [20,21]. NICS is defined as the negative isotropic value of the Magnetic shielding tensor at the geometrical center of cluster. Aromaticity is characterized by negative NICS value, antiaromaticity by positive NICS value, and nonaromatic compounds by NICS value close to zero. In this study, the NICS values are calculated with GIAO-HF/6-311+G*, GIAO-B3LYP/6-311+G* methods based on the corresponding optimized structures with B3LYP/6-311+G* method except for Te_4^{4+} species, for which the used basis set 6-311+G* in the methods above is replaced by ECP46MWB_AVTZ. GIAO is the gauge-independent atomic orbital method [37]. The NICS value calculated at the center of X_4^{4+} ($X=O, S, Se, \text{ and } Te$) clusters is denoted as NICS (0.0).

All calculations in this work are performed using the Gaussian 03 program. The MO pictures are drawn using the Gaussview 3.0 program[38].

3. Results and discussion

3.1 Energetics and structural properties of X_4^{4+} clusters

Two optimized structures of tetrahedron (T_d) and rhombus (D_{2h}) for four cations X_4^{4+} ($X=O, S, Se, \text{ and } Te$) (Figure 1) have been obtained. Their bond lengths R , bond angles A , total electronic energies E_{tot} (including zero-point energies (ZPE)), relative energies E_{rel} , number of imaginary frequencies (Nimag), and vibrational frequencies ν_i with four methods: B3LYP, B3PW91, MP2, and CCSD(T) are listed in Table 1.

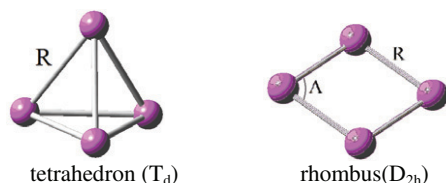


Figure 1 Two optimized structures of the tetrahedron (T_d) and rhombus (D_{2h}) for four cations X_4^{4+} ($X=O, S, Se, \text{ and } Te$).

The calculated results in Table 1 show that the tetrahedron (T_d) structures are stable with no imaginary frequencies to arise using all four methods, whereas the rhombus (D_{2h}) structures are unstable with one or more imaginary frequencies to arise using all four methods except for the rhombus Te_4^{4+} with MP2/ ECP46MWB_AVTZ, in which there is no imaginary frequency to arise. The tetrahedral structures are energetically lower than the rhombic ones with all the four methods except for the case of O_4^{4+} with B3LYP/6-311+G*, in which the E_{tot} of tetrahedron is slightly higher than that of rhombus by 2.07 kcal/mol. The tetrahedral structures are lower in average E_{tot} with three methods(B3LYP, B3PW91, MP2) than the rhombic ones by 61.21 kcal/mol for S_4^{4+} , 67.52 kcal/mol for Se_4^{4+} , 57.75 kcal/mol for Te_4^{4+} except for O_4^{4+} , for which the two isomers are almost equal in total energy E_{tot} .

Table 1 Bond lengths R (Å), bond angles A (°), total electronic energies E_{tot} (including ZPE, hartree), relative energies E_{re} (kcal/mol), number of imaginary frequencies (Nimag), and vibrational frequencies ν_i (cm^{-1}) of tetrahedral and rhombic structure for X_4^{4+} (X=O, S, Se, and Te) species.

species ^a	tetrahedral (T_d , 1A_1)				rhombic (D_{2h} , 1A_g)			
	B3LYP	B3PW91	MP2	CCSD(T)	B3LYP	B3PW91	MP2	CCSD(T)
O_4^{4+}								
R	1.634	1.601	---	---	1.640	1.608	1.429	---
A					88.0	87.7	86.9	
E_{tot}	-296.49870	-296.37897			-296.50188	-296.37308	-295.75368	
E_{re}	0.00	0.00			-2.07	3.69		
Nimag	0	0			2	3	4	
$\nu_{1,2}(e)$	440	497			$\nu_1(b_{2u})$ i491	i458	i1352	
$\nu_{3,4,5}(t_2)$	526	595			$\nu_2(b_{1u})$ i243	i102	i1021	
$\nu_6(a_1)$	750	809			$\nu_3(b_{3u})$ 63	i86	i242	
					$\nu_4(a_g)$ 531	572	882	
					$\nu_5(a_g)$ 582	620	1209	
					$\nu_6(b_{3g})$ 1313	1345	i2239	
S_4^{4+}								
R	2.238	2.211	2.227	2.266	2.260	2.229	2.173	---
A					86.7	86.3	84.6	
E_{tot}	-1590.12254	-1589.91433	-1587.97285	-1588.03906	-1590.04804	-1589.82603	-1587.84293	
E_{re}	0.00	0.00	0.00	0.00	46.83	55.37	81.44	
Nimag	0	0	0	0	1	1	2	
$\nu_{1,2}(e)$	345	366	288	311	$\nu_1(b_{2u})$ 261	285	317	
$\nu_{3,4,5}(t_2)$	417	443	333	370	$\nu_2(b_{1u})$ 345	375	511	
$\nu_6(a_1)$	540	571	423	475	$\nu_3(b_{3u})$ i98	i121	i219	
					$\nu_4(a_g)$ 249	251	264	
					$\nu_5(a_g)$ 378	401	501	
					$\nu_6(b_{3g})$ 670	711	i3018	
Se_4^{4+}								
R	2.514	2.484	2.553	2.556	2.503	2.468	2.439	---
A					86.6	86.1	84.0	
E_{tot}	-9603.79542	-9603.71831	-9597.32142	-9597.37277	-9603.72598	-9603.63644	-9597.20119	
E_{re}	0.00	0.00	0.00	0.00	43.60	51.22	107.74	
Nimag	0	0	0	0	1	1	2	
$\nu_{1,2}(e)$	190	202	170	172	$\nu_1(b_{2u})$ 185	199	225	
$\nu_{3,4,5}(t_2)$	236	250	205	211	$\nu_2(b_{1u})$ 227	244	316	
$\nu_6(a_1)$	317	335	275	282	$\nu_3(b_{3u})$ i38	i55	i114	
					$\nu_4(a_g)$ 134	135	131	
					$\nu_5(a_g)$ 234	249	302	
					$\nu_6(b_{3g})$ 376	404	i1522	
Te_4^{4+}								
R	2.876	2.857	2.886	2.901	2.856	2.835	2.854	2.857 ^c
A					86.4	85.7	68.3	69.8
E_{tot}	-30.26671	-30.36544	-30.02357	-30.07229	-30.19771	-30.28463	-29.897385	-29.93930 ^d
E_{re}	0.00	0.00	0.00	0.00	43.37	50.75	79.13	
Nimag	0	0	0	0	1	1	0	
$\nu_{1,2}(e)$	131	138	127	125	$\nu_1(b_{2u})$ 137	147	228	
$\nu_{3,4,5}(t_2)$	165	173	157	156	$\nu_2(b_{1u})$ 164	175	431	
$\nu_6(a_1)$	221	231	212	208	$\nu_3(b_{3u})$ i24	i35	186	
					$\nu_4(a_g)$ 84	82	114	
					$\nu_5(a_g)$ 166	175	158	
					$\nu_6(b_{3g})$ 260	272	155	

^a Basis set 6-311+G* used for O_4^{4+} , S_4^{4+} , Se_4^{4+} , and ECP46MWB_AVTZ for Te_4^{4+} .

^b The dot line denotes the failure both in the structural optimization and frequency calculations.

^c To succeed in the structural optimization but fail in frequency calculations.

^d The E_{tot} does not include the zero energy.

3.2 Magnetic characteristics of aromaticity for X_4^{4+} ($X=O, S, Se, \text{ and } Te$) cations

The calculated NICS(0.0) values (ppm cgsu) at the geometric center of the tetrahedron (T_d) and rhombus (D_{2h}) for X_4^{4+} ($X=O, S, Se, \text{ and } Te$) species are listed in Table 2 with method GIAO-HF, GIAO-B3LYP/6-311+G**//B3LYP/6-311+G** for $O_4^{4+}, S_4^{4+}, Se_4^{4+}$ and GIAO-HF, GIAO-B3LYP/ECP46MWB_AVTZ//B3LYP/ ECP46MWB_AVTZ for Te_4^{4+} . For comparison, the NICS values for the neutral Tetrahedral (T_d) structures of X_4 ($X=N, P, As, Sb, \text{ and } Bi$) species obtained by Hirsch et al.[22] are also listed in Table 2. Comparison among these NICS(0.0) data in Table 2 indicates that, except for the NICS(0.0) values of O_4^{4+} for the tetrahedron (T_d) isomer with HF method, which is negative, abnormally large and could be considered to be unreasonable, all other NICS(0.0) values of four tetrahedral X_4^{4+} isomers with two methods are significant negative and can be comparable with those of X_4 isomers of the tetrahedron (T_d) structures used GIAO- B3LYP/6-311+G** for N, P, As and GIAO-B3LYP/LANL2DZp for Sb, Bi. Moreover, from Table 1, these four tetrahedron structures of X_4^{4+} are energy minima on potential energy surfaces. Therefore, we can draw a conclusion that four X_4^{4+} species with tetrahedron structures possess higher degree of 3D aromaticities.

For the rhombic structures of X_4^{4+} , except for the NICS(0.0) values of O_4^{4+} with HF method, which is negative, abnormally large and could also be considered to be unreasonable., other NICS(0.0) values of $S_4^{4+}, Se_4^{4+}, Te_4^{4+}$ with HF method are all positive, The NICS(0.0) values of the rhombic X_4^{4+} isomers with B3LYP method are positive for O_4^{4+}, S_4^{4+} and very small, negative for Se_4^{4+}, Te_4^{4+} . Likewise, Considering their one or more saddle points on corresponding potential energy surface from Table 1, we can draw a conclusion that the rhombic X_4^{4+} isomers can be regarded to have stronger 3D antiaromaticities.

Table 2 NICS values (ppm cgsu) at the geometric center of the tetrahedron (T_d) and rhombus (D_{2h}) for the cation X_4^{4+} ($X=O, S, Se, \text{ and } Te$) and neutral X_4 ($X=N, P, As, Sb, \text{ and } Bi$) species.

structures	methods	NICS(0.0)			
		O_4^{4+}	S_4^{4+}	Se_4^{4+}	Te_4^{4+}
tetrahedron (T_d)	HF	-179.50	-47.38	-49.52	-35.02
	B3LYP	-66.17	-46.80	-46.98	-32.78
rhombus (D_{2h})	HF	-704.58	40.93	33.61	67.78
	B3LYP	25.94	3.58	-3.89	-5.15
tetrahedron (T_d) ^a	N_4	P_4	As_4	Sb_4	Bi_4
	-69.6	-52.9	-53.3	-38.8	-36.3

^a From reference [22]. The methods used by Hirsch are: GIAO-B3LYP/6-311+G** for N, P, As and GIAO-B3LYP/LANL2DZp for Sb, Bi.

3.3 MO analyses of 3D aromaticity for X_4^{4+} species

In this section, we will further explore the 3D aromaticity of the tetrahedral X_4^{4+} cations through molecular orbital (MO) analyses. Four Group-VI elements O, S, Se, and Te each has six valence electrons: four p-AO electrons and two filled s-AO electrons. Each of X_4^{4+} species has 20 valence electrons and occupied ten valence MOs. Due to two basis sets used (6-311+G* for $O_4^{4+}, S_4^{4+}, Se_4^{4+}$ and ECP46MWB_AVTZ for Te_4^{4+}) in all calculations, S_4^{4+} (as a representative for $O_4^{4+}, S_4^{4+}, \text{ and } Se_4^{4+}$) and Te_4^{4+} species are chosen to draw their respective ten valence MO pictures (Figure 2). From Figure 2, one can see that these two sets of ten valence MO schemes for S_4^{4+} and Te_4^{4+} are almost the same, regardless of the used basis sets. These ten valence MOs are denoted as two HOMO(1e, double degenerate), three HOMO-1(2t₂, triply degenerate), one HOMO-2(2a₁), three HOMO-3(1t₂, triply degenerate), one HOMO-4(1a₁). Two degenerate HOMOs(1e) and three degenerate HOMO-1s(2t₂) are σ -MOs, consist of cluster d orbitals respectively. The splitting into two σ -MO sets from the cluster d orbitals is a consequence of symmetry lowering from spherical (K_h) to tetrahedral (T_d)[22,25]. Another three degenerate HOMO-3s(1t₂) are σ -MOs, consist of cluster p orbitals. The HOMO-4(1a₁) is σ -MO, consist of cluster s orbitals. The HOMO-2(2a₁) is π -MO, consist of cluster s orbitals. So there are nine σ -MOs and one π -MO, occupied 18 and 2 electrons respectively, each conforming to the $2(N+1)^2$

electron counting rule for 3D aromaticity, with $N_{\sigma}=2$ for 18 σ electrons and $N_{\pi}=0$ for two π electrons. Therefore, from MO analyses above one can see that the tetrahedral X_4^{4+} cations possess two-fold (σ and π) 3D aromaticity.

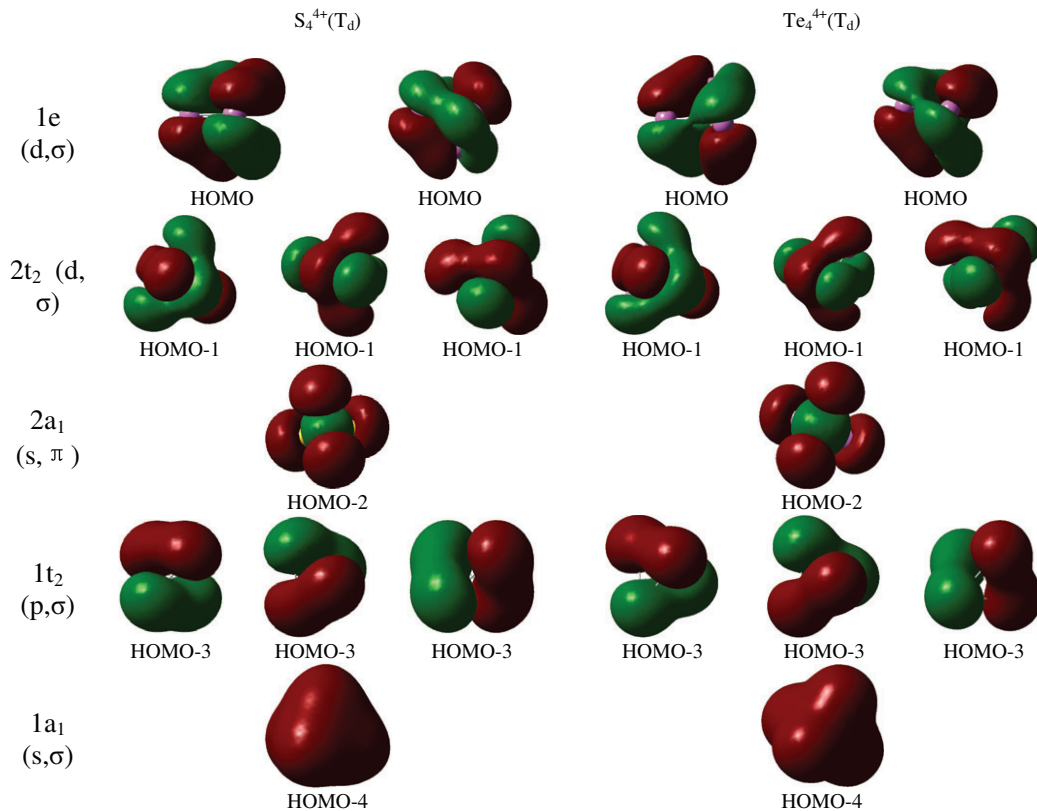


Figure 2 Ten valence MO pictures for each of two tetrahedral S_4^{4+} and Te_4^{4+} isomers with B3LYP/6-311+G* and B3lyp/ECP46MWB_AVTZ respectively.

4. Conclusion

Two optimized structures of tetrahedron (T_d) and rhombus (D_{2h}) for four X_4^{4+} species have been obtained through two DFT (B3LYP, B3PW91) and two post HF (MP2 and CCSD(T)) methods with the extended 6-311+G* basis set used for O, S, Se atoms and ECP46MWB_AVTZ basis set for the heavier Te atom. The tetrahedron (T_d) structures are all energy minima on potential energy surfaces. Through the NICS calculations and MO analyses, according to several criteria for 3D aromaticity: higher energetical stability, higher structural symmetry, higher negative NICS values, and Hirsch's $2(n+1)^2$ electron counting rule, the tetrahedral (T_d) X_4^{4+} ($X=O, S, Se,$ and Te) cations have been shown to possess higher two-fold (σ and π) 3D aromaticity, while the rhombic X_4^{4+} isomers can be regarded to have stronger 3D antiaromaticities.

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