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Pseudo Jahn-Teller effect in Ge_4X_4 (X=F, Cl, Br) molecules: A theoretical investigation

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Abstract: The instabilityof planar rings in Ge_4X_4 (X=F, Cl, Br, I)moleculesdue to the pseudo Jahn-Teller effect (PJTE) was investigated as anoriginal PJTE study. Optimization and the following frequency calculations in these molecules illustratedthat all of these compounds were unstable in highsymmetry planar (with D_{4h}symmetry) geometry and their structures were puckered to lower C_{2h}symmetry stable geometry. Moreover, the vibronic couplinginteraction between $^1A_{1g}$ ground and the first ^1E_g excited states via $(^1A_{1g} + {^1E_g}) \otimes e_g$ PJTE problem was the reasons for the symmetry breaking phenomenon and non-planarity of the four-member ring in those series.

Keywords: Tetragermacyclobutadiene, Pseudo Jahn-Teller effect(PJTE), Symmetry breaking phenomena, Vibronic coupling Constant, Natural bond analysis (NBO).

Introduction

Tetragermacyclobutadiene (Ge_4R_4) are the hottest subjects due to the rich germanchemistry and expected novel applications as semiconducting materials. Consequently, some new tetra sila cyclobutadiene or tetragermacyclobutadiene analoguesthat contain a planar-rhombic or puckered Si_4 ring [1, 2], a slightly folded Ge_4 ring [3], or a puckered Si_3Ge ring withylide structure [4] were synthesized. As the simplest member of Si_4R_4 family, the parent Si_4H_4 was predicted theoretically to have a puckeredSi_4 ring with D_{2d} symmetry [5, 6]. From the simplest Si_4H_4 to the complicated $Si_4(EMind)_4$ compound the central silicon skeleton undergoes several low-symmetry configuration changes of the referencesquare-planar geometry.

The origin of this variety of the molecular geometries in the Si_4R_4 and Ge_4R_4series can be rationalized byemploying the vibronic coupling theory in the form of the pseudo JahnTeller effect (PJTE) [7, 8]. This statementfollows from a more general conclusion that the Jahn-Teller effect for degenerate electronic states and the PJTEfor both degenerate and nondegenerate(pseudodegenerate) states are the only source of spontaneous symmetry breaking in molecular systems and solids [8]. In our case of nondegenerate electronicstates the PJTE provides a reasonable picture of the structure and properties of the compounds under consideration. The method has been successfully applied to more simple carbon and silicon four membered ring systems,such as C_4H_4 [9], C_4F_4 [10], Si_4 [11], $Si_4H_4^{2+}$ [12], as well as to a variety of other molecular systems [13-19].

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Results and discussion

Energetic aspects

The structures of Ge_4X_4 molecules (X=F, Cl, Br) were optimized at the B3LYP/Def2-TZVPP level of theory in the planar geometry of the ring (D_{4h} symmetry).The absolute energy of these molecules are listed in Table **1**. Vibrational analysis in these symmetry showfour imaginary frequencies. The values of these frequencies and their force constant of them are gathered in Table **2**.

Table 1: Absolute energy (a.u), relative energy (kcal/mol), frontier orbital energy (a.u), HOMO-LUMO gap (eV) and hardness (η, eV) values in the D_{4h} and C_{2h} structures of Ge_4X_4 molecules (X=F, Cl, Br, I) at the B3LYP/Def2-TZVPP level of theory.

compound	**E**	**ΔE**	**E(HOMO)**	**E(LUMO)**	**Gap**	**η**
X=F						
D_{4h}	-8707.874662	13.3126	-0.24081	-0.13774	0.11027	0.05513
C_{2h}	-8707.895877	0.00	-0.24897	-0.14078	0.10819	0.05409
X=Cl						
D_{4h}	-10149.276600	15.9337	-0.24340	-0.14425	0.09915	0.04975
C_{2h}	-10149.301992	0.00	-0.24468	-0.13876	0.10804	0.05402
X=Br						
D_{4h}	-18605.112935	15.2949	-0.24386	-0.14629	0.09786	0.04893
C_{2h}	-18605.137309	0.00	-0.24235	-0.13978	0.10257	0.05128

Table 2: The imaginary frequency (υ, cm^{-1}) and force constant (f, mDyne/Å) values in the D_{4h} structures of Ge_4X_4 molecules (X=F, Cl, Br, I) at the B3LYP/Def2-TZVPP level of theory.

X	**E_g**	**B_{1g}**	**A_{2u}**	**E_u**
X=F				
υ	-53.2976	-48.3154	-47.7102	-28.0431
f	0.0501	0.0626	0.0300	0.0104
X=Cl				
υ	-70.8028	-44.1023	-44.7721	-32.2516
f	0.1629	0.0605	0.0497	0.0232
X=Br				
υ	-65.1154	-33.1749	-32.4672	-19.7323
f	0.1865	0.0497	0.0474	0.0179
X=I				
υ	-66.7327	-24.3929	-27.0331	-13.4542
f	0.2015	0.0363	0.0376	0.0124

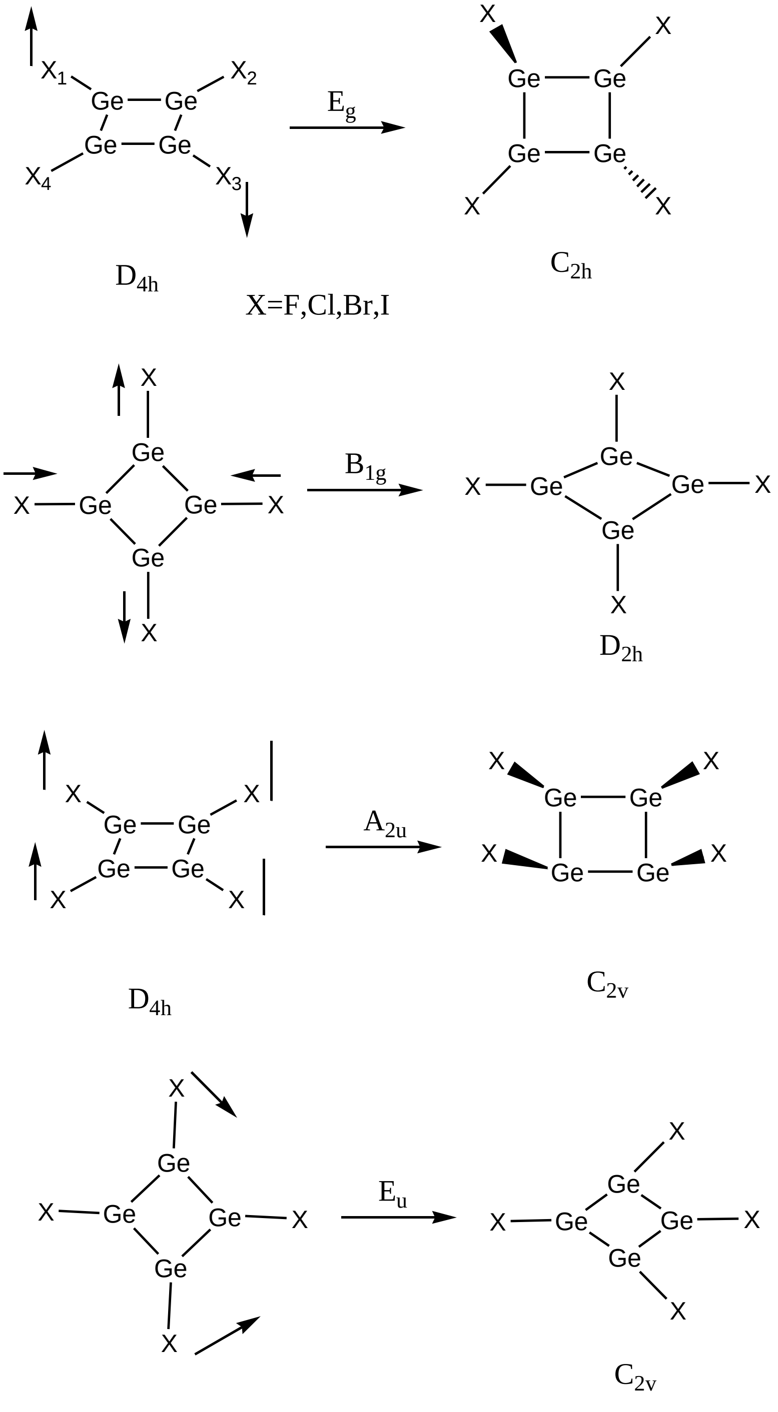
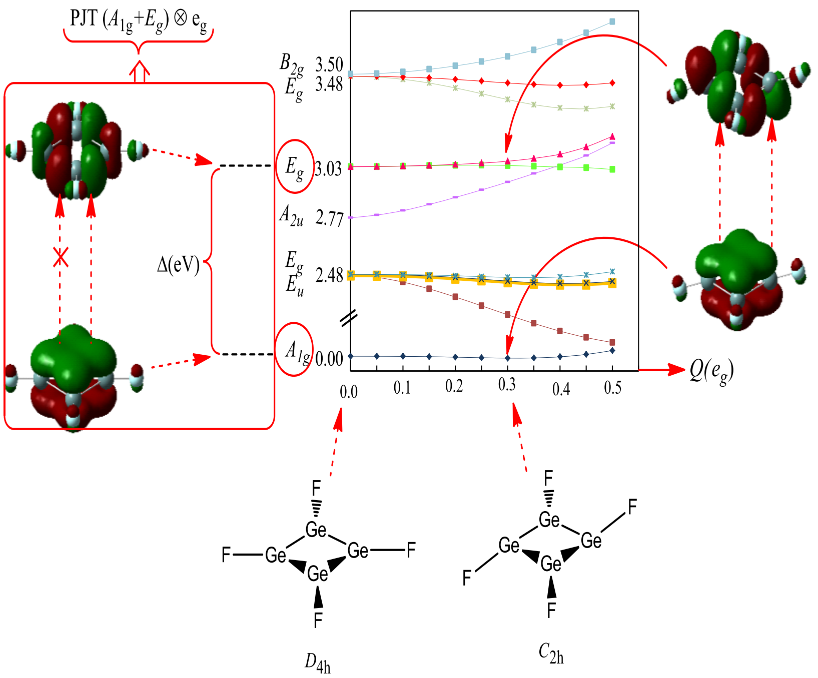


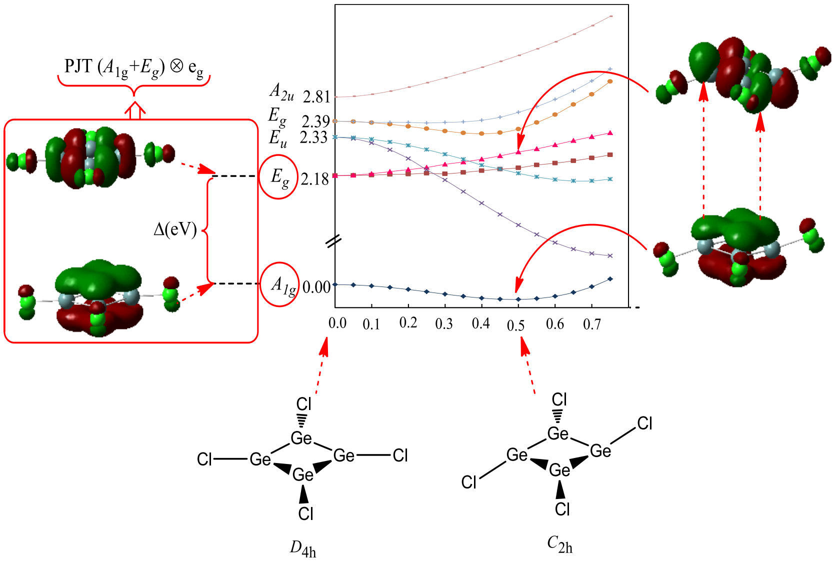
Figure 1: Vibrational modes of imaginary frequencies of Ge_4X_4 structures in D_{4h} symmetry.

It can be found the symmetry of vibrational modes of these imaginary frequencies are: E_g, B_{1g}, A_{2u} and E_u. These vibrational modesare presented in Figure 1. It can be observed these vibrational modes changes the symmetry of the planar molecule (D_{4h}) to C_{2h}, D_{2h}, C_{2v} and, C_{2v} symmetries, respectively.

The distortions of high-symmetry (D_{4h}) configurations of compounds are due to the pseudo Jahn-Teller effect (*PJTE*). The main contributions to the distortions of high-symmetry (D_{4h}) configurations to their corresponding C_{2h} form of compounds are mainly due to the *PJTE* by mixing the ground A_{1g} and excited E_g state associated with mixing of $\psi_{HOMO}(b_{1g})$ and

$\psi_{LUMO}(e_g)$ orbital in studied compounds resulting in a $PJT\ (A_{1g} + E_g) \otimes E_g$ problem.





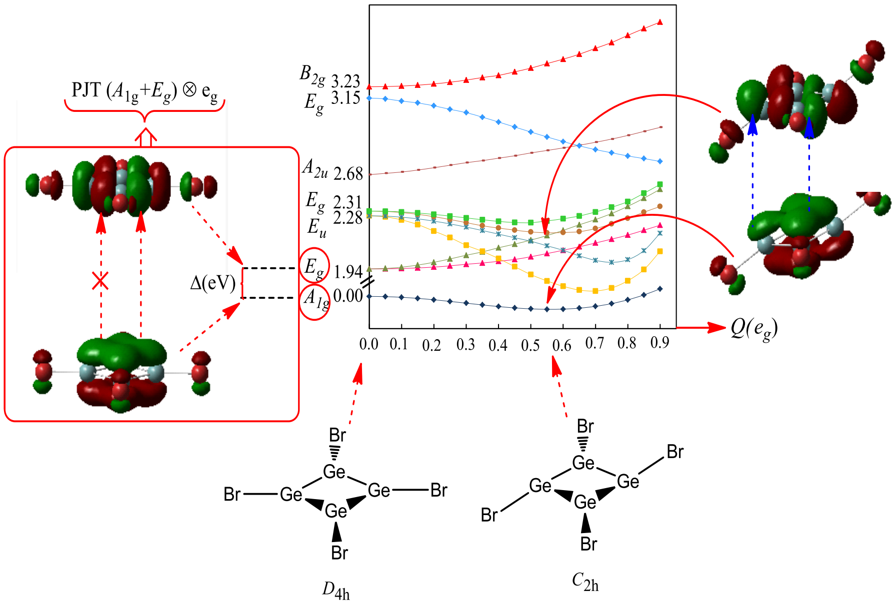


Figure 2: Energies of the ground and excited states and their change along the distortioncoordinate [Qe_g]

The energies of the ground and excited states and their change along the distortioncoordinate [Qe_g] are shown in Figure **2**. As it is shown from Figure 2, the curvatures of the lower curves (belongs to the ground state electronic configurations) of the *adiabaticpotential energy surface* (*APES*) become negative but in the upper curve (belongs to the excitedelectronic configurations which interact with the lower curve with respect to the Qe_gdisplacements) the curvatures become positive. These calculations show that minimum energy values along distortion coordinate are observed in 0.3 (X=F), 0.5(X=Cl), 0.55 (X=Br).The difference of these minimum energy values and D4h symmetry energy values are Jahn-Teller effect energy (E_{JT}). These values are listed in Table **3**. These values are increasing with decreasing of electronegativity of substituent.

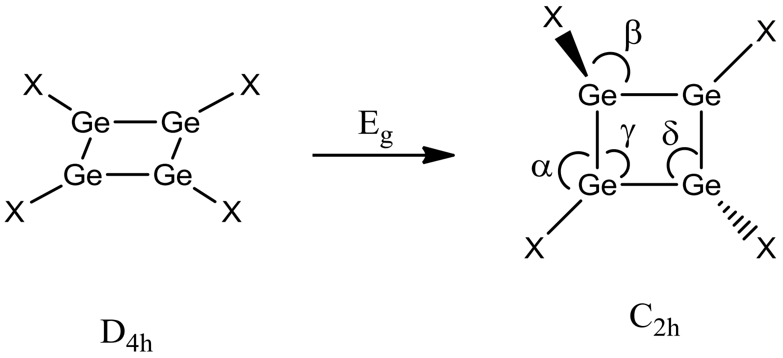
Table 3: absolute energy values (a.u) of the D_{4h} structures and minimum absolute energy in the along od coordinate of E_g vibration, point of minimum energy (Å) and Jahn-Teller stabilization energy (E_{JT}, kcal/mol) of Ge_4X_4 molecules (X=F, Cl, Br) at the B3LYP/Def2-TZVPP level of theory.

compound	E(D_{4h})	r_{min}	E(min)	E_{JT}
X=F	-8707.874662	0.3	-8707.895877	-0.021215
X=Cl	-10149.276599	0.5	-10149.301992	-0.025393
X=Br	-18605.112935	0.55	-18605.137309	-0.024374

Structural parameters

GeGe bond distances, X-Ge-Ge and Ge-Ge-Ge bond angles in the studied molecules are listed in Table 5. It can be found, bond distances are shorter in C_{2h} symmetry in compared to D_{4h} symmetry. Table **4** shows that, X-Ge-Ge bond angles are decreased with decreasing of symmetry. Descending of symmetry influences internal angles of cycle. One of the angles are larger than 90° and other smaller than 90°. The variation ofGe-Ge-Gebond angle (δ)in the effect of distortion of D_{4h} structure to C_{2h} structures decreaseswith decreasing of electronegativity of halogen.

Table 4: The structural parameters and Wiberg index of the Ge-Ge bond in the D_{4h} and C_{2h}structures of Ge_4X_4 molecules(X=F, Cl, Br) at the B3LYP/Def2-TZVPP level of theory.



compound	Ge- Ge(Å)	Ge-X(Å)	∠ X-Ge- Ge (°)		∠Ge- Ge-Ge(°)	
			α	β	δ	γ
X=F						
D_{4h}	2.668	1.77352	135.00000	135.0	90.00000	90.
C_{2h}	2.530	1.76798	120.72633	125.88895	108.22209	71.77791
		1.75191				
X=Cl						
D_{4h}	2.635	2.22146	135.00000	135.0	90.00000	90.
C_{2h}	2.511	2.21014	121.00000	126.42444	107.08801	72.91199
		2.17271				
X=Br						
D_{4h}	2.614	2.38514	135.00000	135.0	90.00000	90.
C_{2h}	2.506	2.37378	121.10014	126.52584	106.73072	73.26928
			2.32923			

Molecular orbital analysis

The energies of the frontier orbitals (HOMO, LUMO), the corresponding HOMO–LUMO energy gaps and hardness values of the investigated molecules are given in Table 2.

As seen shown in Table 2, HOMO energy values increase with decreasing of electronegativity of halogen in the molecules. In contrast, LUMO energy values decrease with decreasing of electronegativity of halogen in the molecules. Also, HOMO-LUMO gap and hardness of C_{2h} symmetry is more than D4h symmetry. As expected from the principles of minimum energy (MEP), and maximum hardness (MHP), that is, while a conformer changes from the most stable to other less stable species in most cases, the energy increases, and the hardness decreases [26-30]. Also, HOMO-LUMO gap values are dependent on character of substituent. These values are decreasing with decreasing of electronegativity of substituent.

Natural bond orbital analysis

Natural atomic charges

The calculated natural atomic charges of the Ge and halogen (X=F, Cl, Br) atoms in the studied molecules are gathered in Table 3. The calculated natural atomic charge differences between the Ge and halogen atoms [*Q*(Ge)-*Q*(X)]in the C_{2h} structures decrease with decreasing of electronegativity of halogen.

Conclusion

In this investigation, we studied the instability of planar rings in Ge_4X_4 (X=F, Cl, Br) molecules at the B3LYP/TZVPP level of theory and showed:

In the all studied molecules, descending of symmetry increased the stability of molecule. This increasing of stability is attributed to the pseudo Jahn-Teller effect (PJTE).

The vibronic coupling interaction between $^{1}A_{1g}$ ground and the first ^{1}Eg excited states via $(^{1}A_{1g} + {}^{1}E_{g}) \otimes e_{g}$ PJTE problem was the reasons for the symmetry breaking phenomenon and non-planarity of the four-member ring in those series.

The increased stability of C_{2h} structures in compared to D_{4h} structures were compatible with the principles of minimum energy (MEP), and maximum hardness (MHP), and minimum polarizability (MMP).

The calculated naturalatomic charge differences between the Ge and halogen atoms [Q(Ge)-Q(X)]in the C_{2h} structures decrease with decreasing of electronegativity of halogen, and revealed a good linear correlation between E_{JT}. Next the reaction conditions were optimized for the synthesis of 3,4-dihydropyrimidinones, the best results was found at ambient temperature with (0.05 g) of pectin in H_2O:EtOH (1:2). The scope and efficiency of these procedures were explored for the synthesis of a wide variety of substituted

Computational Methods

All calculations were carried out with the Gaussian 09 suite program [20]. The standard Def2-TZVPP basis set [21] was used in the calculations. Pseudo-potential effective core potential (ECP) using the Def2-TZVPP basis set was applied to described [22]. Geometry optimization was performed utilizing with the hybrid functional of the B3LYP method [23]. A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum. The population analysis has also been performed by the natural bond orbital method [24] at B3LYP/Def2-TZVPP level of theory using NBO 6.0 program [25] under Gaussian 2009 program package**.**

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