



Original Research Article

A Computational Study to Find the Vibrational Modes Connected with Specific Molecular Structures of Calculated Compound

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ABSTRACT

The purpose of this research is to provide a deeper understanding of the planar high-symmetry configuration instability. In the ideal case, the distortion corresponds to the movements of nuclei along normal modes that belong to non-totally symmetric irreps of the high symmetry (HS) point group of molecule. The analysis of the structural distortion from the HS nuclear arrangements of the JT active molecules presents a challenge because of the superposition of the effects produced by many different normal modes. It is shown that the instability of planar configurations of Tetrafluoroethylene radical anion, $\text{CF}_2 = \text{CF}_2^-$ molecule, leading to symmetry breaking and distortions is induced by the pseudo Jahn-Teller effect (PJTE). It was proved that the PJTE is the only source of instability of high-symmetry configurations of molecules. Therefore, the instability of planar configuration leading to symmetry breaking and distortions is induced by the pseudo Jahn-Teller effect (PJTE). In other words, in the studied molecule, descent in symmetry is associated with increasing the stability of molecule, i.e. the more curvature of the lower of curve have played a major role in stabilization energy so that the

increasing of stability is attributed to the pseudo Jahn-Teller effect stabilization energy (PJTE stabilization energy).

Keywords: Symmetry Breaking, Imaginary Frequencies and Trans-bent configuration, pseudo Jahn-Teller effect (PJTE).

Introduction

Quantum mechanical description of the changes in electronic structure due to distortions in molecular shape and vice versa is given in the form of the vibronic coupling theory. Probably, the most famous concept based on this theory is the Jahn-Teller (JT) effect. The JT theorem states that a molecule with a degenerate electronic state spontaneously distorts along a non-totally symmetric vibrational coordinates. This removes the degeneracy and lowers the energy. In fact, the vibronic coupling, correlation between electronic states and vibrational motion of nuclei, describes all spontaneous symmetry breaking distortions, attributed to the JT, Renner-Teller and pseudo JT effects [1-5]. Tetrafluoroethylene radical anion, $\text{CF}_2 = \text{CF}_2^-$ is an important basic constituent of the family of perfluoroalkene radical anions and serves as a prototype of such anions. In this paper, three distortion modes, Trans (b_{2g}) and cis (b_{3u}) bending and twisting (a_u), of tetrafluoroethylene radical anion are discussed as the vibrational modes connected with specific molecular structures of calculated compound. The change configuration from planar to Trans - bent geometry by Trans -bent modes of a $\text{CF}_2 = \text{CF}_2^-$ molecule are defined as a lowering of symmetry from planar D_{2h} to C_{2h} symmetry. Therefore in this research, our study carried out on the tetrafluoroethylene anion via TD -DFT and CI-singles (CIS). Time-dependent density functional theory (TD-DFT), which is one of the most popular tools in the study of excited states of molecular systems, was used to study the electronic configuration of the planar and vibrational modes connected with specific molecular structures of compound [6].

Computational Details

In this study, geometric optimizations and frequency calculations are carried out for singlet state of Tetrafluoroethylene radical anion [C_2F_4] - in planar structures. All calculations were performed with the Gaussian 09 [7] suite. Hartree-Fock calculations for the structural

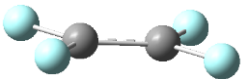
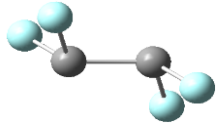
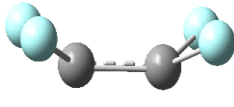
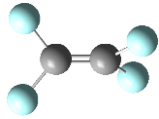
optimizations of $[C_2F_4]^-$ anion planar and non-planar were utilized. Ahlrichs' TZVPP basis sets were for C and F. To this end, compounds of neutral and anion radical tetrafluoroethylene ($C_2F_4^-$) with a planar geometry (D_{2h} symmetry) were considered. Geometry optimization and calculation of vibration frequencies were performed using the Gaussian-09 suites of the program. The frequencies analysis of C_2F_4 neutral molecule optimized by HF/Def2-TZVPP showed that are all positive eigenvalue and real. This result confirms equilibrium structure with the minimum energy in its electronic ground state ($1A_g$). In contrary, with adding an electron to C_2F_4 neutral molecule and formation of an anion radical $C_2F_4^-$, appeared three negative eigenvalues such as b_{2g} , b_{3u} and a_u .

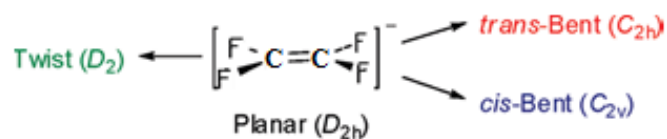
Result and Discussion

Imaginary frequency

After the successful completion of an optimization work, vibration analysis (frequency calculation) has been used to determine the nature of stationary points using geometric optimization and confirm the structure with an energy minimum. The information from the output indicates three imaginary frequencies (frequency calculation as negative numbers) along with the normal mode corresponding to the imaginary frequency which are critical for characterizing a stationary point, are listed in Table 1. As each imaginary frequency (unstable modes) is responsible for creation particular configurations, so that the instability of the high-symmetry D_{2h} is distorted corresponding symmetric distortion modes b_{2g} , b_{3u} and a_u as trans-bent ($D_{2h} \rightarrow C_{2h}$), cis-bent ($D_{2h} \rightarrow C_{2v}$) and twisted ($D_{2h} \rightarrow D_2$) configurations, respectively (Fig.1). It is worth noting that the symmetry breaking removes the degeneracy of electronic and generates non-degenerate states. According to relative energies of bending configurations, the favorable structure is the trans-bent with C_{2h} symmetry and this stability is based on energy considerations. Essentially lowest-energy geometry for a $C_2F_4^-$ radical anion (isomer with the lowest energy) as the initial structure introduced and this is based on energy considerations that a symmetric system can lose its symmetry and lower energy, because the Hamiltonian system changes, and the new Hamiltonian will not have previous symmetry, that is, the so-called "symmetry breaking".

Table 1. Representation of Imaginary frequencies, JT-modes distortion, and D_{2h} distorted by

JT-modes distortion			
	$C_2F_4^- (D_{2h})$		
Molecular			
Imaginary frequencies	-1712.2463	-1284.3561	-298.9858
normal mode corresponding to the imaginary frequency (JT-modes distortion)	b_{2g}	b_{3u}	a_u
D_{2h} distorted by			
JT-modes distortion	C_{2h}	C_{2v}	D_2

**Fig.1.** D_{2h} distorted by JT-modes distortion

Structural parameter analysis

It is well known, that the bond length and angle of bonding are two important parameters that determine the shape and size of a molecule. The length of the bond is the distance between the nucleuses of the two atoms of the bond, while the angle of attachment is the angle between the two adjacent atoms in a molecule (C-C bond distance, F-C-C and F-C-F bond angles). The angle between the two planes is two-sided or torsional angles. It defines these structures around rotational bonds. The digital angle is changed only by the distance between the first and fourth atoms; the other atomic spacing is controlled by the chemical bond length and the angle of the band. Its value is from -180 to 180 degrees. The torsion angle is positive if the clock rotation is performed with the molecule and when a rotation in the clockwise direction with the molecule in

the plane is performed, it will be negative [6]. Table 2 lists the relative structural parameter obtained from D_{2h} distorted by JT-modes distortion.

Table 2. Calculated structural parameters of the planar (D_{2h} symmetry) and its isomers includes trans-bent (C_{2h}), Cis-bent (C_{2v}), twist (D_2) symmetries of $C_2F_4^-$

<i>Compound</i>	$C_2F_4^-$			
Geometry	D_{2h}	C_{2h}	C_{2v}	D_2
	Bond Lengths(Å)			
R_{C-C}	1.427	1.481	1.41 9	1.310
R_{C-F}	1.354	1.363	1.36 7	1.379
	Bond angles (deg)			
∠_{F-C-C}	123.9	110.7	115. 7	128.4
∠_{F-C-F}	112.2	105.0	106. 7	103.1
	Torsion angles(deg)			
D_{F-C-C-F}	0.0	63.87	54.0 8	53.78

Based on the result obtained in Table 2, the trend for the bond lengths (C-C) in various isomers [C₂F₄]⁻ is Trans-bent > cis-bent > twistit, in other words it is observed, bond lengths are longer in C_{2h} symmetry in compared to C_{2v} and D₂ symmetries. In contrast the bond lengths (C-F) in the twistit (D₂) geometry is longer than trans-bent and cis-bent isomers. In the above optimal values of dihedral angles for trans-bent, cis-bent, twistit geometries is given D1 = 63.87°, D2 = 54.08°, and D3 = 53.78°, respectively. Bent angles θ and θ' are defined as the angles between an F-C-F plane and the C-C bond (Fig.1) [8]. The results show that the dihedral angle decreases in the symmetry breaking effect with the deformation of the structure of D_{2h} into structures C_{2h}, C_{2v} and D₂ with the reduction of the length of the C-C bond. The changes in the bond lengths are generated from the high-symmetric SOMO nature (*b*_{2g} symmetric orbital) with its C-C bonding and C-F anti-bonding characteristics. The electronic ground state for D_{2h} symmetry of C₂F₄⁻ and its isomers are (¹B_{2g}), □C_{2h} (²B_{2g}), C_{2v} (²B₂), and D₂ (²B₂), respectively.

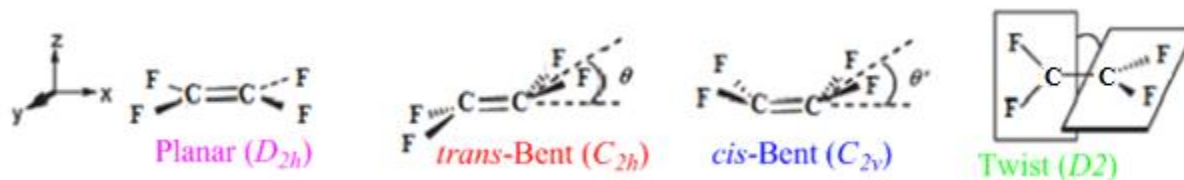


Fig 1. representation the planar and nonplanar geometries anion C₂F₄

Therefore distortions of high-symmetry (D_{2h}) planar of C₂F₄⁻ molecule take places due to the pseudo Jahn-Teller effect (PJTE).

Structure energetics analysis

Table 3 lists the relative energies and geometric structures of C₂F₄⁻ isomers. According to relative energies of bending configurations, the favorable structure is the trans-bent with C_{2h} symmetry and this stability is based on energy considerations (Table 3). The relative energy of different configurations in a molecule is significant. The total energy of a molecule is a function of its shape. In general, knowing the amount of energy as a function of the coordinates of nucleus and molecular properties is based on how the energy is defined by a small disturbance in the system. This energy can be considered as a sum of several components, which are partly related to the specific structural properties of that molecule. The various isomers of C₂F₄⁻ molecule were optimized at the HF/Def2-TZVPP level of theory in the planar and non-planar

geometries. Table 3 lists the calculated corrected electronic energies ($E_0=E_{\text{elec}}+ZPE$) of these isomers. The energy difference has always been measured in terms of the stable structure is 43 kcal. mol⁻¹.

Table 3 . The ZPE, calculated corrected electronic energies ($E_0=E_{\text{elec}}+ZPE$), and ΔE of these isomers (Hartree/Particle) and ΔE (kcal.mol⁻¹)^a.

Geometries	ZPE (Hartree/Particle)	$E_0=E_{\text{elec}}+ZPE$ (Hartree/Particle)	ΔE (kcal.mol ⁻¹) ^a
D _{2h}	0.017660	-473.504443	0.09618
C _{2h}	0.018201	-473.600623	(60.35) ^a 0.000000
C _{2v}	0.018012	-473.563962	0.03666
D _{2h}	0.017660	-473.504443	(37.35) ^a 0.000000
D ₂	0.017018	-473.532021	0.06860
D _{2h}	0.017660	-473.504443	(17.31) ^a 0.000000

It can be found, the ZPE energy in the Trans-bent structure (C_{2h}) is larger than the structures with symmetry C_{2v}, and D₂. Given that the energy of the zero point depends on the intra-molecular parameters (bond strength and angular bending) obtained from quantum mechanical calculations. Thus it is expected, by increasing the length of the C-F bond in the anion C₂F₄ isomers from structure C_{2h} to D₂, the force constant reduction leads to a decrease in ZPE energy. Finally, as a result, the stability of the optimized isomers (the absolute energies) are trans-Bent > cis-Bent > twist, respectively. The calculated barrier height for the planarization of the anion C₂F₄ isomers is 60.35, 37.35, and 17.31 kcal mol⁻¹ by the HF/Def2-TZVPP level of theory. It should be noted that, the stability trans-bent geometry in compared with D_{2h} strucher is 60.35 kcal.mol⁻¹ (Table 3).

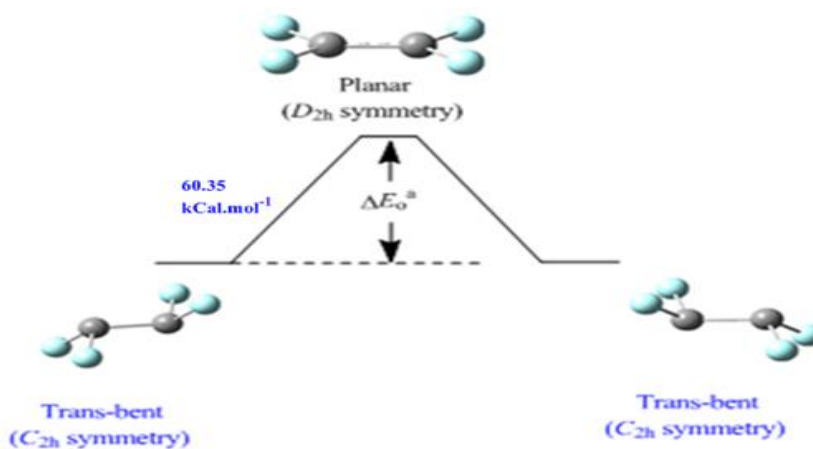
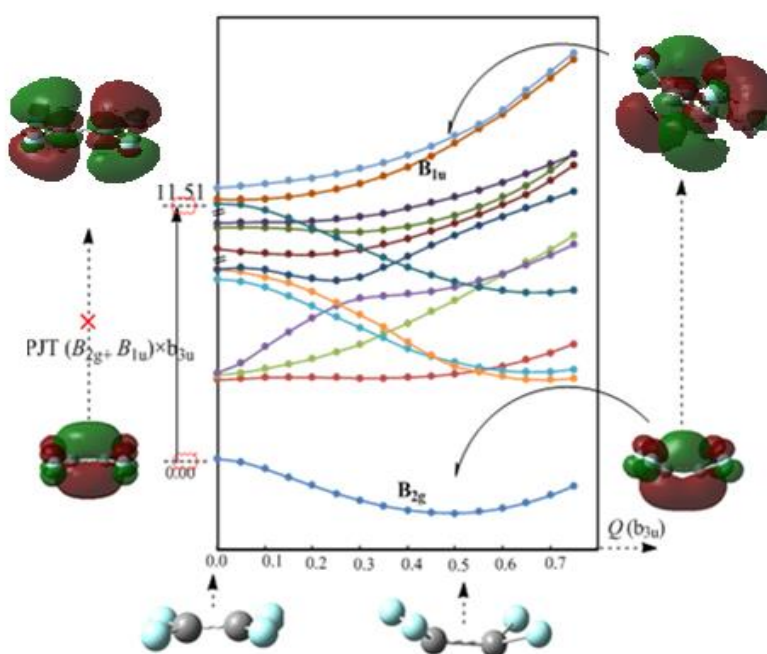
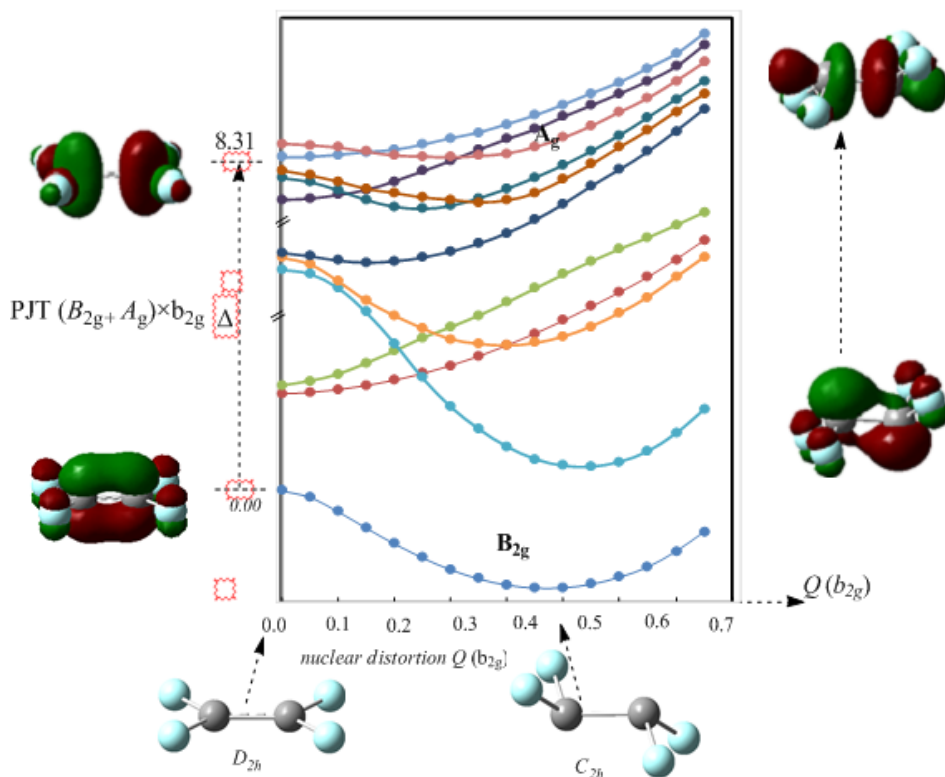


Fig 1. Energy diagram of the transformation of a flat form into a trans-Bent in an anionic system

MEP curve: Adiabatic potential energy surface (APES)

The first goal in the analysis and characterization of the JT system is the determination of the JT parameters which quantify the potential energy surface: the *EJT*, which gives energy stabilization due to the JT effect, the warping barrier (Δ) which gives the energy difference between two minima low symmetry (LS) structures, and the JT radius (*RJT*), which shows a direction and magnitude of the distortion, Figure 2. These parameters are directly connected to the Q-Types of displacements discussed in Table 1. As shown in Fig. 2, the curvatures of the lower curves (corresponding to the ground state electronic configurations) of the adiabatic potential energy surface (APES) become negative, but in the upper curve (corresponds to the excited electronic configurations which interact with the lower curve with respect to Q-Types of displacements) the curvatures become positive. These calculations show that the minimum energy values along the distortion coordinate are observed as 0.45 \AA ($Q_{b_{2g}}$, C_{2h}), 0.5 \AA ($Q_{b_{3u}}$, C_{2v}), and 0.6 \AA (Q_{a_u} , D_2) at minimum energy paths (**MEPs**). The lower the potential energy, the less able the structure is to change, and the greater is its stability [9]. The distortions are due to the mixing of the ground and excited states, [i.e., $\text{HOMO-1}(b_{3u}) \rightarrow \text{LUMO} + 3(b_{3u})$ for isomer (C_{2h} , $Q_{b_{2g}}$) 1, $\text{HOMO-1}(b_{3u}) \rightarrow \text{LUMO} + 7(b_{2g})$ for isomer (C_{2v} , $Q_{b_{3u}}$) 2, and for $\text{HOMO-1}(b_{3u}) \rightarrow \text{LUMO} + 14(B_{1g})$ isomer (D_2 , Q_{a_u}) 3. The vibronic coupling interaction between ground and the excited state is studied via the $({}^2B_{2g} + {}^2A_g) \otimes b_{2g}$ for isomer (C_{2h}) 1, the $({}^2B_{2g} + {}^2B_{1u}) \otimes b_{3u}$ for isomer (C_{2v}) 2, and the $({}^2B_{2g} + {}^2B_{2u}) \otimes a_u$ for isomer (D_2) 3, PJTE problems. The JT

distortion is described as of orbital mixing with a specific vibration mode of a high symmetry molecule before distortion.



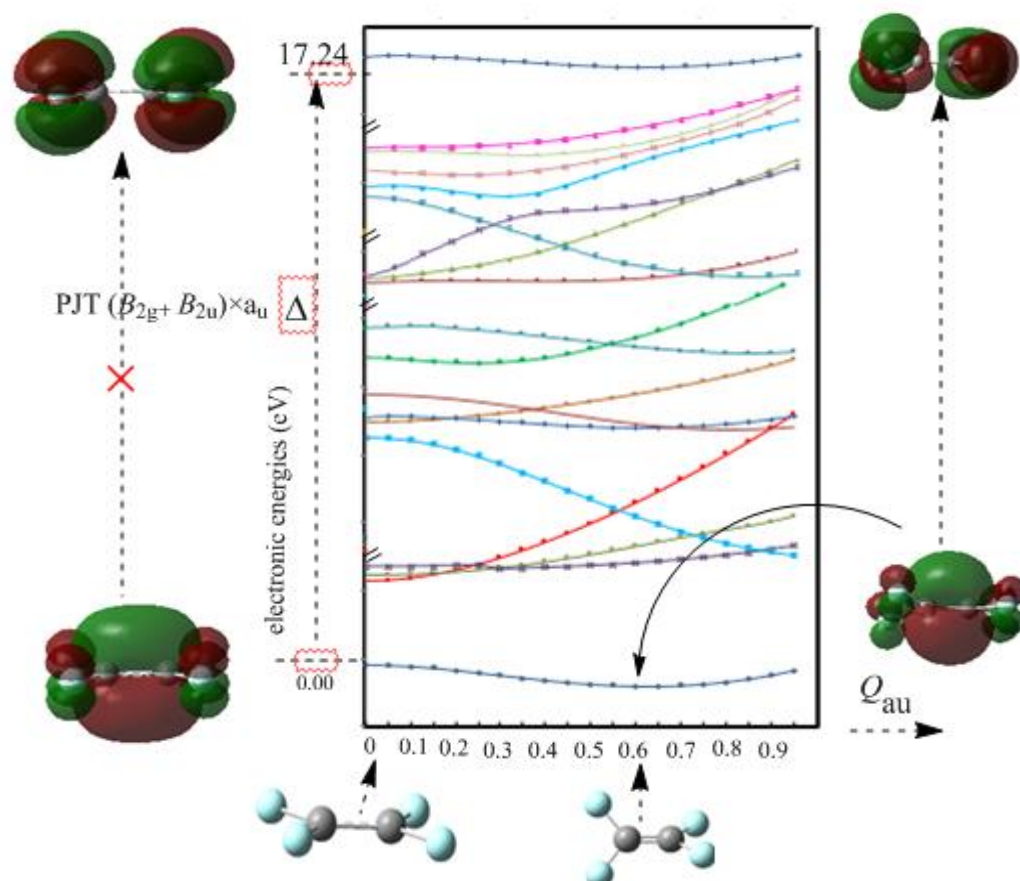


Figure 2. Potential energy curves of the lowest excited states along the symmetric and the anti-symmetric distortion coordinates of isomers C_2F_4 anion

The energy gaps between reference states (Δ) in the undistorted configurations increase from isomer 1 to isomer 3, and the PJT stabilization energies decrease. The stabilization energies with donor \rightarrow acceptor electronic delocalizations are proportional to $S^2/\Delta E$ where S is the orbital overlap and ΔE is the energy difference between the donor and acceptor orbitals. Accordingly, the energy gap between the reference states and the configurations used in the isomers C_2F_4 anion becomes larger, assuring that the contribution of each configuration to the dynamic correlation is small, as required for perturbation method.

Conclusions

In the present study, we investigated the stability of isomer structures of C_2F_4 anion at the HF/TZVPP level of theory and noticed the following:

1. Energetic analysis showed that of the three isomers of the planar molecule C_2F_4 anion, the C_{2h} structure was more stable than the other two structures.
2. The value of ZPE is proportional to the sum of vibrational frequencies, and therefore it is primarily affected by larger frequencies (e.g., bond stretching and bending vibrations). The X-C bond as well as the geometry and value of the angle bonds affect the zero point energy change.
3. The increased stability of C_{2h} isomer in comparison with two isomers other of C_2F_4 molecule was compatible with MEP (Minimum energy path) of the adiabatic potential energy surface (APES).
4. The vibronic coupling depends on the electronic wave functions φ_1 and the excited states φ_2 and the symmetry of the symmetric nuclear displacements (Q) that so called PJTE problem and it is the only reasons for the symmetry breaking phenomenon.

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