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Pseudo Jahn-Teller effect in SeX$_2$ (X=F,Cl,Br,I) molecules: A theoretical investigation

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Abstract: If the excited and ground electronic modes are mixed, the symmetry breaking in the high symmetrical configuration of a molecule is expected. It has been shown that high-symmetry forms of any molecule undergo structural distortions due to the pseudo-Jahn-Teller Effect (PJTE). the linear (D$_{\infty h}$) and bent form (C$_{2v}$) geometries of selenium difluoride (1), selenium dichloride (2), selenium dibromide (3) and selenium diiodide (4) have been optimized at the B3LYP levels with Def2-TZVPP the basis set on every atom. Furthermore, studies have explored the associations between the PJT stabilization energies, hardness, and structural parameters, corrected electronic energies, electronegativity and hardness. The natural bond orbital (NBO)interpretation is associated with [Lp(3)X $\rightarrow$ σ*(1)S-X] to obtain stabilization energy E$^{(2)}$, vibronic coupling constant(F$_{ij}$). The energy gaps between the reference states (Δ)in the bent (C$_{2v}$) structures decrease from 1 to 4 compounds. The plot of EPJT is linearly correlated with Δ [η(C$_{2V}$)-η(D$_{\infty h}$)] of compounds 1–4. The calculated Δ[η(C$_{2V}$)-η(D$_{\infty h}$)] parameter increases from 1 to 4 compounds. It was shown that the linear (D$_{\infty h}$) is more unstable than the bent (C$_{2v}$) configuration, due to the strong lone pair–lone pair repulsion. PJT stabilization energy increases from compounds 1 to 4, which represent greater stability of 1 to 4 compounds.

Keywords: Pseudo-Jan-Teller effect, Symmetry breaking, The Natural Bonding Orbital, The stability energy.

Introduction

All properties of a chemical compound are as a characteristic of its molecular coordinates. In keeping with the principle of electron structure, a chemical compound can take many forms. But it is obvious that real molecules in nature have the least energy in their most stable state. In truth, the most excellent structure is mathematically dependent to be on the minimum ability strength level (PES), that's transferring from an risky configuration of excessive symmetry to a stable configuration of low symmetry, and that is the concept of symmetry failure [1-3]. on other words, the total energy of a molecule is directly related to its structural shape.

According to Mullikan's idea, whilst one shape transforms into any other structure, the energy undergoes a change as well. Most molecules are deformed because of the deviation of bond lengths and bond angles caused by rotational and stretching processes within the molecule. Clearly, the lowest energy geometry is the maximum thermodynamically strong structure. But from the molecular orbital (MO) factor of view, the power of a molecule is same to the sum of the occupied orbitals. The physical interpretation of this principle is possible primarily based at the powerful overlap of orbitals (Fij). Overlap between orbitals that have a bonding interaction lowers the molecular energy. In the studied structures, the instability of configuring high symmetry from D$_{\infty h}$

to C_{2v} in the SeX_2 due to the vibronic connection of the presence of two ground and excited electronic states that interact with sufficient nuclear displacement and cause linear instability. Change of configuration from linear state to bent geometry is defined as symmetry failure system (SBS) [4]. System symmetry breaking is an old concept in physics that is defined based on energy considerations: a symmetric system can lose its symmetry and reach a lower energy configuration [5]. The initial symmetric state can be unstable or quasi-stable. In the latter case, an energy barrier must occur before symmetry breaking, which must be overcome. In fact, vibronic coupling is introduced as a disorder factor. Among the vibronic coupling effects of the Jan-Teller effect is the pseudo-Jan-Teller effect (PJT) [6-9]. The effects that arise from the vibronic combination of two or more asymmetric electronic states with nuclear displacements are called "pseudo Jahn-Teller effect". In other words, the mixing effect of two or more non-equivalent vibronic electronic states, under nuclear displacement, this concept is due to the strong coupling of ground and excited states, which leads to instability of the ground state, and in many ways similar to the instability of the ion effect. in this study, the Mulliken approximation and Natural Bond Orbital (NBO) were employed for the description, respectively, the effects of substituent atoms on the partial atomic charges and some of the significant donor-acceptor interactions, their stabilization energies $E^{(2)}$. Natural bond orbital (NBO) analysis used to determine the stability of the compounds. Natural bonding orbital analysis is a useful method of providing information about the interaction of both orbital spaces filled and virtual. This can increase the anticipation of inter - molecular interactions and interactions [10-12].

Computational Methods

All calculations were performed with the Gaussian 09 Program Suite[13].The standard Def2-TZVPP basis set was used in the calculations [14].Using the hybrid functional of the B3LYP method, geometry optimization was conducted at each stationary point found, confirming its identity as an energy minimum . The correlations between structural parameters and PJTE parameters were investigated using natural bond orbital (NBO) interpretations [15].

Energy aspects

For any polyatomic system with a geometric structure with the highest symmetry, there are two or more electron states that interact with the nuclear displacement and this interaction leads to instability. In the case of the studied molecules, due to the presence of the displacement radial node. There is a mismatch between the donor and acceptor orbitals in the linear structure, so the electron distribution will not be allowed. As a result, the system will deviate and the radial node will be removed and the electron distribution will be allowed Figure (1). In the linear structure, Q=0.0 Deviation cannot occur under nuclear displacement. During bending, bond length, bond angle, and bond energy undergo changes due to the change in bond length.

Molecules of selenium difluoride (1), selenium dichloride (2), selenium dibromide (3) and selenium diiodide (4) with B3LYP/Def2-TZVPP level of theory in linear ($D_{\infty h}$) and curved (C_{2v}) geometric structure has been optimized. The absolute energy of these molecules is listed in table (1). The vibrational analysis in symmetry ($D_{\infty h}$) shows 4 negative frequencies. The symmetry of the vibrational modes is negative frequencies (Πu). Figure (2) shows the vibrational modes. It can be seen that the vibrational modes change the symmetry of the molecule from linear ($D_{\infty h}$) to curved (C_{2v}). The deviation of the geometric structure with high symmetry ($D_{\infty h}$) is due to the pseudo-Jan-Teller effect.

Table 1: Corrected electronic energy (in terms of Hartree), ΔE (in terms of kcal mol-1) and structural parameters calculated from linear ($D_{\infty h}$) and curved (C_{2v}) structures for the linear and curved structures of compounds 1 to 4 using the B3LYP/Def2-TZVPP method

Compound	E_0	ΔE	r_{Se-X}	$\Delta[r_{Se-X}(D_{\infty h})-r_{Se-X}(C_{2v})]$	$\theta_{Se-X-Se}$	$\Delta[\theta_{X-Se-X}(D_{\infty h})-\theta_{X-Se-X}(C_{2v})]$
SeF_2						

C_{2v}	-۲۶۰۱,۳۲۵۰۸۴	0.0	1.74716	0.08		97.153	82.85
$D_{\infty h}$	-۲۶۰۱,۲۵۱۵۶۳	46.43	1.83212			180.0	
SeCl$_2$							
C_{2v}	-۳۳۲۲,۰۴۹۶۰۳	0.0	2.17743	0.118		102.119	77.88
$D_{\infty h}$	-۳۳۲۱,۹۸۰۷۵۲	43.29	2.29540			180.0	
SeBr$_2$							
C_{2v}	-۷۵۴۹,۹۷۵۰۶۴	0.0	2.33902	0.118		103.478	76.52
$D_{\infty h}$	-۷۵۴۹,۹۱۱۱۷۳	40.16	2.45690			180.0	
SeI$_2$							
C_{2v}	-۲۹۹۷,۲۲۸۲۷۰	0.0	2.54133	0.12		105.077	74.92
$D_{\infty h}$	-۲۹۹۷,۱۶۷۹۴۸	37.65	2.66259			180.0	

Table 2: Energy gap (Δ,ev), vibrational frequency and initial force constant between ground state and excited state (Πu) calculated from compounds 1 to 4

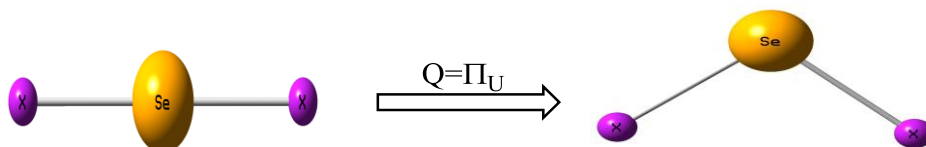| Compound	SeF$_2$	SeCl$_2$	SeBr$_2$	SeI$_2$
ν_1	-265.9235	-200.8733	-162.2916	-153.8530
Force constant	1.0493	1.1272	1.2349	1.3230
Δ	2.58	1.13	0.79	0.40

Figure 1: Schematic representation of linear and bent formations in SeX2(X=F,Cl,Br,I)

The symbol of the ground state term in symmetry ($D_{\infty h}$) for the studied molecules is (Σg). The main effects of these deviations from the linear structure with high symmetry ($D_{\infty h}$) to the bent form (C_{2v}) of the compounds are mainly due to It is the pseudo-Jan-Teller effect, which is related to the mixing of the ground (Σg) and excited (Πu) states. With the mixing of $\Psi HOMO(\Sigma g)$ and $\Psi LUMO(\Pi u)$ orbitals in these is combinations as a result of a two-level PJT problem ($\Sigma g + \Pi u) \times \Pi u$. The calculation results show that the main contribution of excited states is HOMO(Πu) and LUMO(Σg) transitions.

The energy of the ground and excited states and their changes according to the displacement Q(Πu) are shown in figure (2). According to figure (2), the curvature of the lower curve (related to the ground state of the electronic structure) of the adiabatic potential energy level is negative, but in the upper curves (corresponding to an excited geometrical structure that interacts with the lower curve due to the displacement (Q(Πu)), the curvature is positive. According to the calculations, the minimum energy values along the normal deviation of the coordinate (X=F)0.7Å, (X=Cl) 0.6 Å, (X=Br) 0.6 Å, (X=I) 0.6 Å are observed. The difference in minimum energy values and symmetry energy values ($D_{\infty h}$) is the Jahn-Teller effect energy (E_{JT}). The values of this energy are listed in table (3). The Jan-Teller energy values decrease with the decrease of halogen electronegativity. A good correlation can be found between E_{JT} and Pauling electronegativity (χ_p) of halogens.

(χ_p):F=3.98 Cl=3.16, Br=2.96, I= 2.66
$E_{JT}= 6.1071 \chi_p +22.561$: R² = 0.9281

Therefore, there is a strong Jan-Teller effect in halogens with more electronegativity, and SeF$_2$ is more stable due to the Jan-Teller effect.
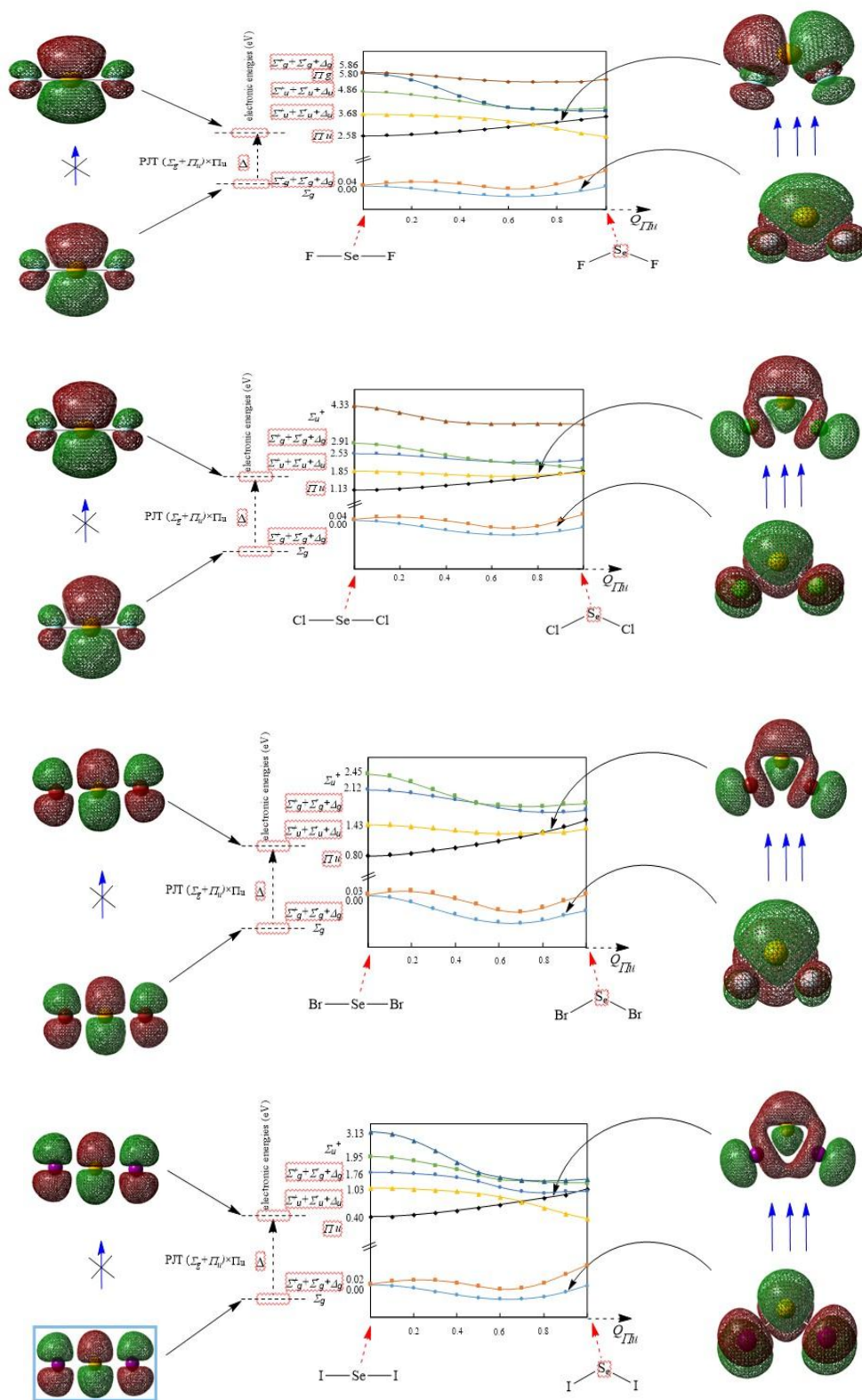
Figure 2: Energy diagrams of the ground state and excited states in terms of ev along the vibration mode Q(Πu) for SeX$_2$ molecules (X=F,Cl,Br,I)

Table 3: Absolute energy values (a.u.) of $D_{\infty h}$ structures and minimum absolute energy values along the vibration mode Q(Πu), minimum energy points (Å) and Jan-Teller stability energy (EJT, kcal/mol) of molecules SeX_2(X=F,Cl,Br,I) with B3LYP/Def2-TZVPP level of theory

Compound	r_{min}	E(min)	E_{JT}
SeF_2	0.7	-2601.3286661	46.43
$SeCl_2$	0.6	-3322.051781	43.30
$SeBr_2$	0.6	-7549.9766056	40.16
SeI_2	0.6	-2997.2294786	38.28

Structural parameters

The Se-X bond distance and the X-Se-X bond angle in the studied molecules are listed in Table (1). It can be seen that while reducing the symmetry from $(D_{\infty h})$ to (C_{2v}) symmetry in the presence of halogens (X=F,Cl,Br,I) there has been a change in the bond distance and bond angle. Table (1) shows that the X-Se-X bond angle has increased with the decrease of electronegativity of halogen.

The results of the used method show that the bonding distance in symmetry (C_{2v}) has become shorter compared to symmetry $(D_{\infty h})$. Also, according to table (1), with the reduction of symmetry, the X-Se-X bonding angle also The results show that the difference in bond length calculated between Se-X in the linear and curved geometrical structure $\Delta[r$ Se-X $(D_{\infty h})$-r Se-X $(C_{2v})]$ from compound 1 to 4 with decreasing Electronegativity increases.

The changes in the X-Se-X bonding angle decrease due to the deviation of $(D_{\infty h})$ structures to (C_{2v}) structures with the decrease of electronegativity of halogen. Between E_{JT} and $\Delta[\theta_{X-Se-X}$ $(D_{\infty h})$-θ_{X-Se-X} $(C_{2v})]$ a good linear relationship can be observed

$\Delta[\theta_{X-Se-X}$ $(D_{\infty h})$-θ_{X-Se-X} $(C_{2v})] = 0.9214E_{JT}$ +39.305; R² = 0.9292

Molecular orbital analysis

According to Koopman's theory and energy, we have central orbitals:

$$\chi = -(\varepsilon_{LUMO} + \varepsilon_{HOMO})/2 \quad (1)$$
$$\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2 \quad (2)$$

In table (4), the energy of frontier orbitals (HOMO, LUMO), HOMO-LUMO energy gap, total hardness and electronegativity of all studied molecules have been investigated.

As shown in table (4), HOMO energy values increase with the decrease of electronegativity of halogen in molecules, and conversely, with decrease of electronegativity of halogen in molecules, LUMO energy values decrease.

Table 4: calculated energies (in a.u.) of HOMO (ε_{HOMO}), LUMO (ε_{LUMO}), ε_{LUMO}-ε_{HOMO} (in ev) and total hardness parameters (η in ev), total electronegativity (χ), $\Delta\eta$ (in kcal/mol) for linear ($D_{\infty h}$) and bent (C_{2v}) structures of compounds 1 to 4 with B3LYP/Def2-TZVPP level of theory

	ε_{HOMO}	ε_{LUMO}	ε_{LUMO}-ε_{HOMO}	η	χ	$\Delta\eta$	$\Delta\chi$
Geometry							
SeF_2, C_{2v}	-0.25703	-0.09934	4.29	2.14	0.17818	1.68(37.74)[a]	-0.07803(-48.96)[a]
SeF_2, $D_{\infty h}$	-0.27335	-0.23908	0.933	0.46	0.25621	0.00000	0.00000
$SeCl_2$, C_{2v}	-0.25073	-0.11200	3.77	1.88	0.18136	1.46(33.67)[a]	-0.06846(-42.95)[a]
$SeCl_2$, $D_{\infty h}$	-0.26536	-0.23428	0.84	0.42	0.24982	0.00000	0.00000
$SeBr_2$, C_{2v}	-0.24664	-0.12647	3.27	1.63	0.18655	1.24(28.59)[a]	-0.05674(-35.60)[a]
$SeBr_2$, $D_{\infty h}$	-0.25790	-0.22869	0.79	0.39	0.24329	0.00000	0.00000
SeI_2, C_{2v}	-0.23648	-0.13431	2.78	1.39	0.18539	1.03(23.75)[a]	-0.04492(-28.18)[a]
SeI_2, $D_{\infty h}$	-0.24376	-0.21687	0.73	0.36	0.23031	0.0000	0.00000

Also, the HOMO-LUMO gap and the total hardness increase from symmetry $(D_{\infty h})$ to symmetry (C_{2v}). As expected from the minimum energy principle (MEP) and the maximum hardness

principle (MHP), while a structure of The most stable state changes to a state with less stability, in most cases the energy increases and the hardness decreases [16-20]. Also, the values of the HOMO-LUMO gap depend on the properties of the substituents, so that these values decrease with the decrease of the electronegativity of halogen. A linear relationship can be shown between the HOMO-LUMO gap and the Pauling electronegativity (χ_p) of halogens.

Gap=1.6798χ_p-4.1336; R² = 0.9965

In addition, the changes due to the reduction of hardness symmetry show a good relationship with EJT.

$[\eta(C_{2V})-\eta(D_{\infty h})]= 1.6803E_{JT} -39.706$; R² = 0.9809

The characteristic of Lewis acid and Lewis base is determined by the total electronegativity. Molecules with larger χ are known as strong Lewis acids and molecules with smaller χ are known as strong Lewis bases. Accordingly, according to table (4), the composition of SeF_2 is known as a strong Lewis acid. And SeI_2 composition is a strong Lewis base between compounds 1 to 4. By calculating the parameter $\Delta[\chi(C2V)-\chi(D\infty h)]$, it can be seen that this parameter increases from compound 1 to compound 4 and this trend It coincides with the reduction of EJT in the conversion process $D_{\infty h} \rightarrow C_{2V}$ and there is a good linear relationship.

$\Delta[\chi(C_{2V})-\chi(D_{\infty h})]= -2.4857 E_{JT}+65.582$;R²=0.9781

Natural Bonding Orbital (NBO) analysis

In this section, we discuss the deviation shown in the studied molecules based on the parameters calculated from the NBO analysis.

The largest quadratic interaction energy $E^{(2)}$ between the donor and acceptor orbitals in the studied molecules is reported in Table (5). To estimate the donor-acceptor interactions in NBO analysis, the quadratic Fack matrix was used [21]. For each donor (i) and acceptor (j), the stability energy $E^{(2)}$ related to transitions i → j is estimated according to equation (3).

$$E^{(2)} = -q_i \frac{F^2(i,j)}{\varepsilon_j - \varepsilon_i} \quad (3)$$

where q_i is the occupied donor orbital, ε_i and ε_j are the energies of donor and acceptor orbitals. $\varepsilon_j-\varepsilon_i$ is the energy difference between donor and acceptor orbitals. And $F_{i,j}$ is the non-diagonal element. The larger values of $E^{(2)}$ indicate that there is a mutual effect between the electron donor and electron acceptor. The results show that the stability energy in relation to the electronic distribution $Lp(3)X \rightarrow \sigma^*(1)S-X$] [in the bent structure It decreases from combination 1 to 4.

Halogen with more electronegativity shows a significant mutual effect among the studied molecules. The difference between the values of $E^{(2)}$ for the structures decreases with the decrease of electronegativity of halogen, and there is a linear relationship between EJT values and $[E^{(2)} (C_{2V})-E^{(2)} (D_{\infty h})]$ can be shown.

$[E^{(2)}(C_{2V}) - E^{(2)}(D_{\infty h})]=0.6538E_{JT}+62.974$;R²=0.9532

Two parameters are effective on the stability energy $E^{(2)}$, the first one is the non-diagonal elements of the Fack matrix F_{ij}, which is directly related to the stability energy $E^{(2)}$ and decreases with the decrease of the stability energy. The second parameter is the energy of donor and acceptor orbitals. Let it be that they have the opposite relationship with the stability energy $E^{(2)}$. Therefore, according to table (5), the energy of strong acceptor orbitals and strong donor orbitals has increased from the combination of 1 to 4.

Table 5: Calculated stability energy ($E^{(2)}$, kcal mol-1), non-diagonal elements (F_{ij}, a.u.), energy difference between donor and acceptor orbitals (E(j)-E(i) from mutual effects Strength of structural parameters in linear ($D_{\infty h}$) and bent (C_{2V}) structures of SeX_2 (X=F,Cl,Br,I) molecules with B3LYP/Def2-TZVPP level of theory.

Compound	SeF_2	$SeCl_2$	$SeBr_2$	SeI_2
$E^{(2)}$				
$Lp(3)_X \rightarrow \sigma^*(1)_{Se-X}$	9.16	7.88	7.27	6.08
Orbital occupancy				
$Lp(3)_X$	1.94493	1.93561	1.93388	1.93599
$\sigma^*(1)_{Se-X}$	0.04921	0.05774	0.05998	0.05852
F_{ij}				
$Lp(3)_X \rightarrow \sigma^*(1)_{Se-X}$	0.057	0.043	0.038	0.032

ε				
$Lp(3)_X$	-0.44438	-0.35240	-0.32872	-0.29944
$\sigma^*(1)_{Se-X}$	-0.00458	-0.05430	-0.07886	-0.08740
$\Delta(E\ Lp(3)_X \rightarrow E\sigma^*(1)_{Se-X})$	0.4398	0.2981	0.24986	0.21204

Results

In this article, we studied the instability of linear structures of SeX_2 molecules (X=F, Cl, Br, I) with B3LYP/Def2-TZVPP levels of theory and it is observed:

1- In all observed molecules, the stability of molecules increases with decreasing symmetry. This increase in stability is associated with PJTE.

2- The influence of the vibrational constant between the ground state (Σg) and the excited state (Πu) is through the two-level problem of PJT($\Sigma g + \Pi u) \times \Pi u$, which is due to the phenomenon of symmetry breaking and bending of the studied molecules.

3- The increased stability of C_{2V} structures in compared to ($D_{\infty h}$) structures were compatible with the principles of minimum energy(MEP), and maximum hardness (MHP).

4- The difference between the $E^{(2)}$ values for the structures decreases with decreasing halogen electronegativity and shows a good correlation with EJT.

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