Pseudo Jahn-Teller effect in control and rationalization of chemical transformations in two-dimensional compounds

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Abstract. We show that the pseudo Jahn-Teller effect (PJTE) is instrumental in predicting and rationalizing structural changes in chemical transformations of two-dimensional (2D) molecular systems by means of analyzing the symmetries and electron occupation of the ground and lowest excited electronic states subject to their PJT coupling along the main distortion coordinates. Special attention is paid to rationalizing the PJTE origin of non-planarity of 2D compounds and to the restoration of their planar configurations. Examples of two series of 1,2- and 1,4-dithiin containing tricyclic compounds (carbon sulfide, thianthrene, and antracene and their derivatives) are used to demonstrate in detail the mechanism of (1) enhancement and suppression of the PJTE distortions (puckering) in redox processes, and (2) PJTE induced symmetry breaking and restoration of the planar configuration by chemical substitutions.

1. Introduction
The pseudo Jahn-Teller effect (PJTE) was shown to be instrumental in revealing the spontaneous symmetry breakings (SSB) in molecular systems and solids in nondegenerate states, and related to these SSB properties (see, e.g., [1] and references therein). In application to two-dimensional (2D) or quasi 2D systems the PJTE explains the origin of their main structural features, the out-of-plan distortions, puckering (puckering as a PJTE was first formulated in [2]). 2D systems may have unique applications due to a variety of their planar-surface-specific physical and chemical properties. The best known example of this kind is graphene with its important properties for electronics. Similar properties are sought for in silicene, boron nitride, zinc oxide, phosphorene, gallium nitride, as well as in other attractive subjects like 2D transition metal dichalcogenids and oxides, and there is an unlimited number of other organic and inorganic 2D and quasi-2D systems with expected similar properties (see the review [3]). A series of such cyclic and heterocyclic compounds was studied recently with regard to PJTE in the origin of their puckering (see in [3]).

The present paper is devoted to the next step in the development of this trend: if the cyclic system is out-of-plan distorted, how can we restore the planar configuration with minor other changes? If we know the detailed mechanism of distortion of the planar configuration via the PJTE and we revealed the active excited state in this mechanism, we can try to influence the system by means of external perturbations that violate the PJTE condition of instability of the ground state. In principle, there are
further possibilities to do this: (1) increasing just the energy gap between the electronic states mixed by
the PJT vibronic coupling, e.g. by weak coordination with outside systems, (2) changing the symmetry
of the active excited states by removing or adding electrons (which may change all the parameters of
the PJTE including the energy gaps), (3) making appropriate substitutions that preserve the 2D
structure restoring its planarity, and (4) by spectroscopic excitations. The possibility (1) was
demonstrated first in the mechanism of hemoglobin oxygenation [4] in which the (driven by the PJTE)
out-of-plane displacement of the iron atom from the porphyrin ring returns into the plane by
oxygenation due to the increase of the energy gap to the active excited state, thus suppressing the
PJTE. Examples of realization of the mechanism (2) were demonstrated recently [5-7]. For instance,
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demonstrated first in the mechanism of hemoglobin oxygenation [4] in which the (driven by the PJTE)
the PJTE including the energy gaps), (3) making appropriate substitutions that preserve the 2D
symmetry with a twisted 1,2-dithiin core, and its reduction has resulted in
the C-S bond in the five-membered rings on its either side. Both compounds and their structure were studied experimentally and confirmed by single-crystal X-
ray diffraction [8]. Crystallographic data show that the neutral compound is not planar, it has a
puckered structure of C₂ symmetry with a twisted 1,2-dithiin core, and its reduction has resulted in
cleavage of the S-S bond and rotation of the two peripheral rings about the central C-C bond [8]. We
show that in both systems the out-of-plane distortions are due to the PJT coupling between the ground
A₁ and two excited electronic states of A₂ symmetry, and that by oxidation the PJTE in C₆S₈⁺ is
weakened being completely suppressed in (C₆S₈)²⁻.

The second set of studied tricyclic systems contains thianthrene, or dibenzo-1,4-dithiin molecule,
and anthracene, and their derivatives. According to crystal structure determinations the thianthrene
molecule is bent at the S-S axis by 127°- 128°, and it has a low energy flapping vibration about the
S-S axis [9, 10], while the oxidized thianthrene has a planar nuclear configuration with D₂h symmetry
[11, 12]. Besides, if the C atoms at 1, 4, 6, and 9 positions are substituted by nitrogen atoms, the
dithiin core becomes planar [13]. On the other hand, the anthracene molecule (An) is planar with the
nuclear configuration of D₃h symmetry, whereas the 9,10-dihydroanthracene (9,10-H₂An) has a folding
genometry of C₂ᵥ symmetry with a dihedral angle of about 150-160° [14].

All these structural features are fully controlled by the PJTE, its mechanism being demonstrated
here in detail. For all the considered molecules the geometry optimization and vibrational frequency
analysis in the planar high-symmetry and equilibrium nuclear configurations were carried out at the
B3LYP level of DFT method [15]. All the calculations were performed with the GAUSSIAN09
package [16]. The Pople’s 6-31+G(d,p) split basis sets [17] were utilized in all steps of the
calculations. The potential energy profiles along the normal distortion coordinates were calculated
with the CISD method. The applied active space for the C₆S₈ and C₆S₈²⁻ species was composed of
eight electrons and nine active orbitals, while that for anthracene, thianthrene and their derivatives
included six electrons and ten active molecular orbitals. The numerical values of the vibronic
coupling constants were estimated by means of fitting the solutions of the secular equations to the ab
initio calculated energy profiles as shown below.

2. Enhancement and suppression of PJTE distortions in redox processes.
As mentioned in the introduction, we demonstrate the change of the PJTE in redox processes using as
example two tricyclic species, the neutral carbon sulfide C₆S₈ and its dianion C₆S₈²⁻.
Calculations of the neutral carbon sulfide and its dianionic form in the planar configuration of \( \text{C}_{2v} \) symmetry show that both systems are unstable with respect to the out-of-plane distortions of \( a_2 \) symmetry, and imaginary frequency corresponding to this vibrational mode for the dianion is more than two times greater than for the neutral molecule (figure 1). The optimized structures show \( C_2 \) symmetry for the nuclear configurations. Calculated geometrical parameters are presented in table 1 together with the available experimental data.

![Figure 1. Puckering normal mode \( a_2 \) in (a) neutral \( \text{C}_8\text{S}_8 \) and (b) reduced form \( \text{C}_6\text{S}_8^{-2} \) in planar \( C_{2v} \) configurations; optimized structures (\( \text{C}_2 \) configurations) are shown in two projections for \( \text{C}_8\text{S}_8 \) (c-d) and \( \text{C}_6\text{S}_8^{-2} \) (e-f).](image)

**Table 1.** Selected distances (Å) and angles (deg) for \( \text{C}_8\text{S}_8 \) and \( \text{C}_6\text{S}_8^{-2} \) in the planar and equilibrium nuclear configurations.

| Geometry parameters | \( \text{C}_8\text{S}_8 \) Planar \((\text{C}_{2v})\) | \( \text{C}_8\text{S}_8 \) Equilibrium \((\text{C}_2)\) | Exp. [8] | \( \text{C}_6\text{S}_8^{-2} \) Planar \((\text{C}_{2v})\) | \( \text{C}_6\text{S}_8^{-2} \) Equilibrium \((\text{C}_2)\) | Exp. [8] |
|---------------------|-----------------|-----------------|--------|-----------------|-----------------|--------|
| Bond length (Å)     | S1-S2 2.10       | 2.06            | 2.05   | 2.10            | -               | -      |
|                     | S1-C1 1.77       | 1.77            | 1.76   | 1.78            | 1.73            | 1.72   |
|                     | C1-C2 1.33       | 1.33            | 1.35   | 1.35            | 1.36            | 1.38   |
|                     | C2-C3 1.47       | 1.47            | 1.46   | 1.44            | 1.47            | 1.45   |
| Angle (Degree)      | S2-S1-C1 104.8   | 97.2            | 97.9   | 106.2           | -               | -      |
|                     | S1-C1-C2 129.8   | 123.1           | 122.5  | 126.6           | 131.7           | 130.3  |
|                     | C1-C2-C3 125.3   | 123.2           | 124.5  | 127.2           | 127.3           | 126.2  |
| Dihedral angle (Degree) | C1-S1-C2-C4 0.0  | 54.4            | 52.0±2 | 0.0             | 117.1           | 180    |
|                     | C1-C2-C3-C4 0.0  | 27.8            | -      | 0.0             | 125.6           | 180    |
| Imaginary frequency \( a_2 \)(cm\(^{-1}\)) | 138.2            | -               | -      | 300.7           | -               | -      |
| Normal modes in Cartesian coordinates x | +0.11988 x\(S_1\) | -              | -      | +0.09686 x\(S_1\) | -              | -      |
|                     | -0.01175 x\(C_1\) | -              | -      | -0.12660 x\(C_1\) | -              | -      |
|                     | -0.01639 x\(C_2\) | -              | -      | -0.01270 x\(C_2\) | -              | -      |
|                     | -0.02110 x\(S_9\) | -              | -      | -0.01142 x\(S_9\) | -              | -      |
|                     | -0.02522 x\(S_{11}\) | -              | -      | -0.00517 x\(S_{11}\) | -              | -      |
Consider first the MO energy level scheme and cross sections for the adiabatic potential energy surfaces (APES) of the ground state and the low-lying excited states of A$_2$ symmetry along the $a_2$ distortion mode for the neutral compound (figure 2). Of the seven low-lying excited electronic states, two of them possess A$_2$ symmetry. The first one is mainly formed by one-electron excitation from the occupied $b_2$ MO to the unoccupied $b_1$ MO, while the second excited state corresponds to the excitation from the HOMO of A$_2$ symmetry to the unoccupied $a_1$ MO. Each of them can undergo vibronic mixing with the ground A$_1$ state along the $a_2$ distortion mode.

Figure 2. (a) MO energy levels scheme for the neutral C$_6$S$_8$ in the ground A$_1$ state with indication of the one-electron excitations to A$_2$ terms; (b) ab initio calculated energy profiles along the $a_2$ puckering coordinate for the ground A$_1$ and two excited A$_2$ electronic terms.

Therefore, in this case we have the three-level ($A_1 + 1A_2 + 2A_2$)$\otimes a_2$ PJTE problem [1] with the matrix equation (for simplicity we ignore here the second order perturbation corrections induced by the higher excited states)

$$\begin{vmatrix}
\frac{1}{2}K_0Q^2 - \varepsilon & F_{01}Q & F_{02}Q \\
F_{01}Q & \frac{1}{2}K_1Q^2 + \Delta_1 - \varepsilon & 0 \\
F_{02}Q & 0 & \frac{1}{2}K_2Q^2 + \Delta_2 - \varepsilon
\end{vmatrix} = \begin{vmatrix}
a - \varepsilon & f & g \\
f & b - \varepsilon & 0 \\
g & 0 & c - \varepsilon
\end{vmatrix} = 0,$$

(1)

where $K_0$, $K_1$, and $K_2$ are the primary force constants for the ground $A_1$ and two low-lying excited $A_2$ states, respectively,

$$K_0 = \langle A_1 | \frac{\partial^2 H}{\partial Q_{a_2}^2} | A_1 \rangle,$$

(2)
(and similar for $K_1$ and $K_2$ of the two excited states), $\Delta_0$, and $\Delta_2$ are the energy gaps between the ground and the two excited states, and $F_{01}$ and $F_{02}$ are the corresponding vibronic coupling constants,

$$ F_{01} = \langle A_1 | (\partial H / \partial Q_{a2})_0 | A_2 \rangle \quad \text{and} \quad F_{02} = \langle A_1 | (\partial H / \partial Q_{a2})_0 | 2A_2 \rangle. $$

(3)

The constants $a, b, c, f$, and $g$ are simplifying denotations.

Solving for the $3 \times 3$ secular determinant, one can get the following equation for the energies of the three states (1 ground state and 2 excited states) along the $a_2$ distortion mode:

$$ e^3 - (a + b + c)e^2 + (ab + ac + bc - f^2 - g^2)e - abc + cf^2 + bg^2 = 0 $$

(4)

Using the well-known algebra relations between the products and sums of the three roots of this secular equation

$$ e_1 + e_2 + e_3 = a + b + c $$

(5)

$$ e_1e_2 + e_2e_3 + e_3e_1 = ab + ac + bc - f^2 - g^2 $$

(6)

$$ e_1e_2e_3 = abc - cf^2 - bg^2 $$

(7)

we can estimate the values of the vibronic coupling constants by fitting these equations to the corresponding calculated ab initio energy profiles. The values of thus estimated PJT parameters are presented in table 2.

Table 2. Energy gaps $\Delta_0$ (in eV), PJTE coupling constants $F_{0i}$ (in eVÅ), and primary force constants $K_i$ (in eVÅ$^2$) for the neutral carbon sulfide molecule $C_6S_8$ and its fully reduced form $C_6S_8^-$ obtained by numerical fitting Eqs. (5)-(7) to the calculated energy profiles in Fig. 2.

| Molecule       | $K_0$ | $\Delta_0$ | $F_{01}$ | $K_1$ | $\Delta_02$ | $F_{02}$ | $K_2$ |
|----------------|-------|------------|----------|-------|-------------|----------|-------|
| $C_6S_8$       | 0.42  | 3.47       | 0.57     | 0.11  | 5.79        | 0.98     | 0.15  |
| $C_6S_8^-$     | 0.49  | 1.86       | 0.61     | 0.09  | 4.65        | 0.98     | 0.15  |

At small values of $Q$ the curvature of the APES for the ground state can be approximately estimated as $K \approx K_0 + K_1 + K_2$, where $K_1 \approx -2F_{01}/\Delta_01 = -0.187$ eVÅ$^2$, and $K_2 \approx -2F_{02}/\Delta_2 = -0.332$ eVÅ$^2$. Substituting parameters from table 2 we obtain $K = -0.098$ eVÅ$^2$.

One can see that the vibronic contribution of the first excited $A_2$ state to the curvature of the AP of the ground state is much smaller than of the second excited state. Qualitatively, this can be explained by the fact that both mixing occupied $b_2$ and vacant $b_1$ MOs are localized on the peripheral cycles, whereas the strongest distortion occurs in the central ring (figure 1). The main negative contribution to the curvature, and therefore to the instability of planar nuclear configuration comes from the second excited state of $A_2$ symmetry which is formed by the one-electron excitation from the HOMO of $a_2$ symmetry to the vacant $a_1$ MO (figure 1).

When the carbon sulfide molecule is oxidized to its radical cation form, this $a_2$ MO becomes single-occupied. The removal of an electron from the HOMO of $a_2$ symmetry reduces the negative PJTE contribution to the curvature of the APES produced by the second $A_2$ excited state. Indeed, because the excited states are formed by one-electron excitations, in the MO approximation $F_{01}=\sqrt{2}f_1$ and $F_{02}=\sqrt{2}f_2$, where $f_1$ and $f_2$ are the orbital vibronic coupling constants [1],

$$ f_1 = \langle b_2 | (\partial H / \partial Q_{a2})_0 | b_1 \rangle, \quad f_2 = \langle a_2 | (\partial H / \partial Q_{a2})_0 | a_1 \rangle. $$

(8)
For the neutral molecule we have $K_{v1} \approx -\frac{4f_1^2}{\Delta}$ and $K_{v2} \approx -\frac{4f_2^2}{\Delta}$. For the cation $(C_6S_8)^{2+}$ the value of $K_{v2}$ becomes equal to $K_{v2}^{\text{(cat)}} \approx -\frac{2f_2^2}{\Delta}$. With the PJT parameters from Table 2 the resulting value of the curvature of the AP of $(C_6S_8)^{2+}$ is equal to $K_{\text{cat}} \approx -0.043$ eV/Å$^2$. Hence the oxidation of the system leads to the weakening of the PJTE, although the molecule is still distorted (imaginary frequency is equal to 80.5 i).

Further oxidation to the dication $(C_6S_8)^{2+}$ leads to the complete suppression of the PJTE and restoration of planar nuclear configuration. This confirms once again that the source of instability in this system is the PJT interaction with mainly one most active excited state formed by one-electron excitation from the HOMO.

![Figure 3](image)

**Figure 3.** (a) MO energy levels scheme for the neutral $C_6S_8^{2-}$ in the ground $A_1$ state with indication of the one-electron excitations to $A_2$ terms; (b) *ab initio* calculated energy profiles along the $a_2$ puckering coordinate for the ground $A_1$ and two excited $A_2$ electronic terms.

As mentioned above, the totally reduced compound $(C_6S_8)^{2-}$ is much more distorted from the initial planar structure of $C_{3v}$ symmetry than the neutral molecule. Analysis of the MO energy levels schemes of the two systems shows that in the dianion form the unoccupied in the neutral molecule MO $b_1$ becomes occupied by two electrons (figure 3). Its structure is changed, so that this MO covers not only the peripheral rings but also the central cycle. This leads to the occurrence of one more low-lying active $A_2$ state (formed by one-electron excitation from this MO to the vacant MO of $b_2$ symmetry). So in this case we have the full three-level PJTE problem. Following the same procedure as in the previous case, and using calculated APES cross-sections for the dianion, we can estimate the values of the PJT parameters for $(C_6S_8)^{2-}$ (table 2). At $Q=0$ the resulting value of the curvature of the APES is equal to $K \approx K_0 - 2F_{01}^2/\Delta_{01} - 2F_{02}^2/\Delta_{02} = -0.24$ eV/Å$^2$. We see that the absolute value of the curvature for the dianion estimated via the PJTE is almost three times larger than that for the neutral molecule. Thus the reduction of neutral carbon sulfide enhances significantly the PJTE induced distortion.
3. PJTE induced symmetry breaking and its suppression in substitution reactions

Using two other tricyclic compounds (thianthrene and anthracene) and their derivatives as examples we show how the PJTE induces the symmetry breaking and how the latter can be suppressed by substitutions or oxidation. As mentioned in the Introduction, the thianthrene molecule, as the other 1,4-dithiin containing compounds [18, 19] is bent at the S-S axis [9, 10]. On the other hand a crystal structure determination shows that the oxidized thianthrene molecule has a planar nuclear configuration with D$_{2h}$ symmetry [11, 12]. Besides, if the C atoms at 1, 4, 6, and 9 positions are substituted by nitrogen atoms, the dithiin core becomes planar [13].

The second example, the anthracene molecule (An) is planar with the nuclear configuration of D$_{2h}$ symmetry, whereas the substituted 9,10-dihydroanthracene (9,10-H$_2$An) has a folding geometry of C$_{2v}$ symmetry [14]. Optimized structures for thianthrene, anthracene and 9,10-dihydroanthracene molecules are shown in figure 4.

![Figure 4](image)

**Figure 4.** (a) Puckering $b_{1u}$ normal mode of the thianthrene molecule in the planar D$_{2h}$ configuration; (b) calculated optimized structure, C$_{2v}$ configuration; (c) and (d) show the optimized structures of anthracene and 9,10-dihydroanthracene.

Involving the PJTE we can rationalize such different behavior of the molecules in question with respect to folding analyzing their electronic structure, namely, the presence or absence of excited states that control their PJT coupling to the ground state along the distortion coordinates. The ground electronic state of all these molecules in the highest possible D$_{2h}$ symmetry configuration is the $^1A_g$ one. Since a *butterfly-like* distortion transforms according to $B_{1u}$ irreducible representation of the D$_{2h}$ symmetry group, only the excited states of $B_{1u}$ symmetry are involved in the vibronic mixing with the ground state.

For thianthrene, electronic structures calculations in this configuration indicate the presence of one imaginary frequency (70.11 $i$) corresponding to the out-of-plane distortion of $b_{1u}$-symmetry. Figure 5 shows the APES cross sections for the ground state and the low-lying excited states of various symmetries along the $b_{1u}$ distortion mode. It is seen that of the nine low-lying excited electronic states in the considered energy domain there is only one fairly high-lying excited state of $B_{1u}$ symmetry which is formed by one-electron excitation from the HOMO of $b_{1u}$-symmetry to the unoccupied $a_g$ MO (figure 6).
Figure 5. APES cross sections for the ground and excited states along the $b_{1u}$ distortion mode for (a) thianthrene C$_{12}$H$_8$S$_2$ and (b) 9,10-H$_2$An C$_{12}$H$_8$. As the $Q_{b_{1u}}$ coordinate we used the $z$-coordinate difference between the atom of sulfur (or carbon in 9,10-H$_2$An) and the most distant carbon atom in the peripheral ring.

Thus, in this case we have a two-level ($A_{1g}$+$B_{1u}$) $\otimes b_{1u}$ PJT problem with the following secular equation:

$$\begin{vmatrix}
\frac{1}{2}K_0Q^2 - \varepsilon & F_{01}Q \\
F_{01}Q & \frac{1}{2}K_1Q^2 + \Delta_{01} - \varepsilon \\
\end{vmatrix} = 0 .$$

(9)

The constants $K_0$, $K_1$, $F_{01}$ and $\Delta_{01}$ in the Eq. (9) have the same meaning as in equation (1).

The solution of this 2x2 equation is straightforward:

$$\varepsilon_{1,2} = \frac{1}{4}(K_0 + K_1)Q^2 + \frac{\Delta}{2} \pm \frac{1}{2} \sqrt{\left[\frac{1}{4}(K_0 - K_1)Q^2 - \Delta\right]^2 + 4F_{01}^2Q^2}.$$

(10)

Fitting the ab initio calculated ground state APES cross-section along the $b_{1u}$ coordinate of instability to the obtained analytical expressions provides for the estimation of the vibronic coupling parameters: $K_0 = 1.12$ eV/Å$^2$, $K_1 = 0.96$ eV/Å$^2$, $F_{01} = 2.47$ eV/Å, $\Delta_{01} = 9.17$ eV. At small values of $Q$ the curvature $K$ of the APES for the ground state can be approximately estimated as $K \approx K_0 - 2F_{01}^2/\Delta_{01} = -0.21$ eV/Å$^2$. 
As mentioned above, the oxidized thianthrene molecule has a planar nuclear configuration with D$_{2h}$ symmetry. This fact can also be rationalized in the framework of the PJTE theory. Since the excited B$_{1u}$ state is formed by the one-electron excitation from the HOMO $b_{1u}$ to the unoccupied $a_g$ MO (figure 6), the removal of an electron from this orbital reduces by half the PJTE negative contribution $K_v$ to the curvature of the APES compared with a neutral molecule: $K_v \approx -4f^2/\Delta$ for the neutral molecule versus $K_v \approx -2f^2/\Delta$ for the radical cation, where $f = \langle b_{1u}|(\partial H/\partial Q_{b_{1u}})|a_g \rangle$. Therefore, with a much smaller PJTE distortion, the thianthrene cation has a positive value of the curvature, $K = +0.58$ eV/Å$^2$, and hence the radical cation has a planar nuclear configuration of D$_{2h}$ symmetry. Thus, we can conclude that 1) the folding of the neutral thianthrene molecule is due to the PJT coupling of the ground $A_g$ and the excited $B_{1u}$ states, and 2) restoration of planar nuclear configuration of this system upon oxidation is directly related to the decrease in the orbital vibronic coupling between these states, and hence, suppression of the PJTE.

![Figure 6. MO energy levels scheme for the An, 9,10-H$_2$An, C$_{12}$S$_2$H$_8$, and C$_{12}$S$_2$N$_2$H$_8$ molecules in the ground $A_g$ state with indication of the one-electron excitations to $B_{1u}$ terms.](image)

The suppression of the PJTE and restoration of the planar configuration takes place also by substitution of the carbon atoms at the 1, 4, 6, and 9 positions by the more electronegative nitrogen atoms. From comparison of MO energy level schemes of these two systems, C$_{12}$S$_2$H$_8$ and C$_{12}$S$_2$N$_2$H$_8$ (figure 6), it is seen that the energy gap between the mixing $b_{1u}$ and $a_g$ MOs, which produce the PJTE instability, increases significantly when moving from the former to the latter, reducing the PJTE. In addition, the emergence of two new upper occupied MOs ($b_{3g}$ and $b_{1u}$ in figure 6) increases the value of $K_0$. Calculations of this system in the D$_{2h}$ nuclear configuration do not show any imaginary frequency, this molecule is planar in the equilibrium configuration.

As for anthracene, there are no low-flying excited states of B$_{1u}$ symmetry that are active in the PJTE. In comparison, in 9,10-dihydroanthracene the $b_{1u}$ MO becomes double-occupied (figure 6). This leads to the occurrence of an excited $B_{1u}$ state formed by the one-electron excitation $b_{1u} \rightarrow a_g$, just as in
thianthrene. Hence in this case we have the two-level PJT problem, too. As in the case of thianthrene, calculating the APES cross sections (figure 5b) and fitting them to analytical formula for the two-level PJT problem, we have estimated the parameters of the PJTE. Calculated PJT parameters are: $K_0 = 0.68 \text{ eV/Å}^2$, $K_1 = 0.85 \text{ eV/Å}^2$, $F_{01} = 2.17 \text{ eV/Å}$, $\Delta_{01} = 11.38 \text{ eV}$. At small values of $Q$, $K \approx K_0 - 2F_{01}^2/\Delta_{01} = -0.14 \text{ eV/Å}^2$. The results allow us to conclude that in this case the folding of the planar configuration of 9,10-dihydroanthracene is also induced by the PJTE coupling between the ground and one excited state.

4. Conclusions

Using a series of tricyclic molecular compounds and their derivatives as examples, it is shown in detail how the PJTE produces instability and distortions of their planar 2D configuration, and how oxidation, reduction, and substitutions influence the PJTE resulting in either additional buckling of the system or in the restoration of the planar configuration. Summing up the results we can draw some more specific conclusions relevant to the MO presentation:

(1) The out-of-plane distortions of all the considered tricyclic systems are due to the PJTE; the main negative contribution to the curvature of the APES of the ground states, and therefore the instability of their planar nuclear configurations, comes from the excited states formed by one-electron excitation from the HOMO to the unoccupied MO with appropriate symmetry.

(2) If the HOMO state is the mainly one responsible for the PJT interaction with the active excited states leading to distortion of the planar configuration, oxidation of the systems by removing electrons from this MO leads to the suppression of the PJTE and may result in restoration of planar configuration; similar suppression of the PJTE and restoration of the planar configuration may take place by adding electrons to the active excited state.

(3) In the systems under consideration, substitution of any atoms by more electronegative atoms suppresses the PJTE; substitution by more electropositive atoms enhances the PJTE due to donation of additional electrons to the system, and can result in the PJTE induced symmetry breaking.

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