

THE SYMMETRY BREAKING PHENOMENON IN 1,2,3-TRIOXOLENE AND  $C_2Y_3Z_2$  ( $Z = O, S, Se, Te, Z = H, F$ ) COMPOUNDS: A PSEUDO JAHN–TELLER ORIGIN STUDY

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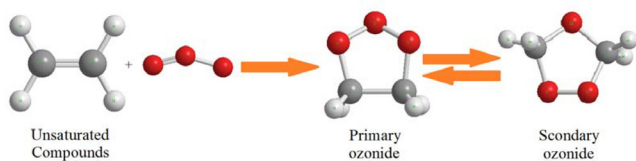
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1,2,3-Trioxolene ( $C_2O_3H_2$ ) is an intermediate in the acetylene ozonolysis reaction which is called primary ozonide intermediate. The symmetry breaking phenomenon were studied in  $C_2O_3H_2$  and six its derivatives then oxygen atoms of the molecule are substituted by sulphur, selenium, tellurium ( $C_2Y_3H_2$ ) and hydrogen ligands are replaced with fluorine atoms ( $C_2Y_3F_2$ ). Based on calculation results, all seven  $C_2Y_3Z_2$  considered in the series were puckered from unstable planar configuration with  $C_{2v}$  symmetry to a  $C_s$  symmetry stable geometry. The vibronic coupling interaction between the  $^1A_1$  ground state and the first excited state  $^1B_1$  via the  $(^1A_1+^1B_1) \otimes b_1$  pseudo Jahn-Teller effect problem is the reason of the breaking symmetry phenomenon and un-planarity of the  $C_2Y_3$  ring in the  $C_2Y_3Z_2$  series.

Keywords: symmetry breaking in five-member rings; PJTE; 1,2,3-trioxolene derivatives; non-planarity in rings; vibronic coupling constant.

## INTRODUCTION

The reaction with ozone is a well-known reaction in organic chemistry and many unsaturated compounds were participated in ozonolysis reactions.<sup>1-5</sup> The ozonation mechanism first time were suggested by Criegee<sup>6</sup> and based on his mechanism, two intermediates with five-member ring structure were presented in ozonolysis reaction with unsaturated compounds. Those intermediate structures were confirmed through  $^{17}O$ -NMR spectroscopy method<sup>7</sup> (See Figure 1).



**Figure 1.** Two intermediates five-member ring structure in ozonolysis reaction of unsaturated compounds (atomic representations: O = red, C = gray, H = white)

Several computational studies of unsaturated compounds ozonolysis reaction have been done to rationalize the ozonolysis reaction mechanism.<sup>8-10</sup> Additionally, activation enthalpy of cycloaddition reaction between ozone and acetylene was investigated through different calculation methods such as CCSD(T), CASPT2, and B3LYP-DFT with 6-311+G(2d,2p) basis set.<sup>11</sup> Moreover, thiozone adducts on single-walled carbon nanotubes, fullerene ( $C_{60}$ ) and graphene sheet and geometry optimization of minima and transition structures have been investigated.<sup>12</sup>

By quantum-chemical simulations, we are able to reveal the electronic states of heterocyclic systems such as ground and excited states and their coupling. In all of the above experimental and theoretical studies, some important features of the structure and properties of acetylene ozonolysis reaction and their intermediates have been analyzed, but less attention has been paid to the origin of their common features which should be explained through pseudo Jahn-Teller effect (PJTE). The PJTE includes excited states in

the vibronic coupling interactions and is the only possible source of the instability of planarity of cyclic systems in nondegenerate states. It is also a powerful tool to rationalize symmetry breaking phenomenon in the compounds with a symmetrical structure.<sup>13,14</sup> Through folding of rings in heterocyclic compounds, symmetry breaking phenomenon has been reported in many studies and the instability of the ground state in planar configuration of those molecules and their coupling with excited states have been explained via PJTE theorem.<sup>15-27</sup> Restoring planarity in the systems that are puckered from their planar configurations due to the symmetry breaking phenomenon has been investigated through the PJTE. To do so, their planar configuration restores either by coordinating two anions, cations, or rings up and down to the nonplanar systems<sup>28-30</sup> or influences the parameters of the PJTE instability by removing or adding electrons;<sup>31</sup> they show that symmetry breaking phenomenon is suppressed in the folded systems. In other applications of the PJTE, the origin of puckering in tricyclic compounds to a pseudo Jahn-Teller (PJT) problem has been traced.<sup>32,33</sup>

Recently, buckling distortion in the hexa-germabenzene and triazine-based graphitic carbon nitride sheets is rationalized based on the PJT distortion.<sup>34,35</sup> Structural transition from non-planar of silabenzene structures to planar benzene-like structures,<sup>36</sup> Chair like puckering investigation, binding energies, HOMO-LUMO gaps and polarizabilities in the silicene clusters toward found the hydrogen storage materials,<sup>37</sup> and origin instability of cylindrical configuration of [6]cycloparaphenylene have analyzed thorough the PJTE,<sup>38</sup> are some more application of the PJT theorem in chemistry.

## COMPUTATION DETAILS

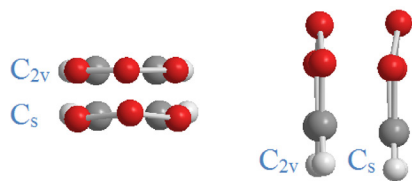
An imaginary frequency along  $b_1$  normal coordinate was observed due to optimization and frequency calculations of seven  $C_2Y_3Z_2$  ( $Y = O, S, Se, Te, Z = H, F$ ) derivatives in planar configuration and it confirms that all  $C_2Y_3$  five-member rings in the  $C_2Y_3Z_2$  series are unstable in their planar configuration. The Molpro 2010 package<sup>39</sup> were carried out in these geometrical optimization and vibrational frequency calculations of the series and the state-average complete active space self-consistent field (SA-CASSCF) wavefunctions<sup>40-42</sup> have been employed to calculate the APES along the  $Q_{b_1}$  puckering normal coordinates. The B3LYP method level of Density Function

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Theory<sup>43</sup> with cc-pVTZ basis set<sup>44-46</sup> was employed in all steps of optimization, vibrational frequency, and SA-CASSCF calculations (except in C<sub>2</sub>Te<sub>3</sub>H<sub>2</sub> which cc-pVTZ-pp basis set was used).

### SYMMETRY BREAKING PHENOMENON IN THE C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> SERIES

The optimization and follow-up frequency calculations of C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series illuminated that, the C<sub>2</sub>Y<sub>3</sub> ring is folded along b<sub>1</sub> nuclear displacement in all seven C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> under consideration and they are unstable in their C<sub>2v</sub> high-symmetry planar configuration. Therefore, symmetry breaking phenomenon occurs in the C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series and all systems are puckered to lower C<sub>s</sub> symmetry with less symmetry elements. Two different side views of unstable planar configuration with C<sub>2v</sub> symmetry and C<sub>s</sub> symmetry equilibrium geometry in the C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series illustrates in Figure 2.



**Figure 2.** The symmetry breaking phenomenon illustrates in two side views of C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> (Y= O, S, Se, Te, Z= H, F) series in unstable high-symmetry planar C<sub>2v</sub> and stable puckered C<sub>s</sub> equilibrium geometry

Geometrical parameters provided in the form of bonds length, angles, and dihedral angles for similar displacements of atoms in planar and equilibrium configurations, imaginary frequency and normal modes displacements of non-planarity in Cartesian X coordinates together and they are presented in Table 1.

From Table 1 illuminate that although the bond lengths and angles

in planar and equilibrium configurations for the C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> (Z = H, F) were almost similar (except parameter in Y atom contributing) but the variety of dihedral values in their planar and equilibrium configurations were different.

The Y–Y–Y–C and Y–Y–C=C dihedral angles were the most important parameters to show the folding in the C<sub>2</sub>Y<sub>3</sub> rings. While the absolute values of Y–Y–Y–C dihedral angle (which is 0.0 in planar configuration) were decreased in the equilibrium configuration from 24.5 degrees in C<sub>2</sub>O<sub>3</sub>H<sub>2</sub> to 13.8 (C<sub>2</sub>S<sub>3</sub>H<sub>2</sub>), 8.8 (C<sub>2</sub>Se<sub>3</sub>H<sub>2</sub>), 6.8 (C<sub>2</sub>Te<sub>3</sub>H<sub>2</sub>) degrees in the C<sub>2</sub>Y<sub>3</sub>H<sub>2</sub> series.

Replacing H ligands in the C<sub>2</sub>Y<sub>3</sub>H<sub>2</sub> series by F ligands were also decreased Y–Y–Y–C, Y–Y–C=C, Y–Y–C–Z and Y–C–C–Z dihedral angle varieties of C<sub>2</sub>Y<sub>3</sub>F<sub>2</sub> in comparison with their values in equilibrium configuration.

### ACTIVE SPACE IN SA-CASSCF CALCULATION

Several active spaces have been checked in SA-CASSCF calculations and the result of calculations were compared together. The results revealed that ten electrons and eight active orbitals which was composed the CAS(10,8) active space is appropriate in under considered C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series. Additionally, the CAS(10,8) results comparison to the smaller CAS(4,3), CAS(6,6), and CAS(8,8) and larger CAS(12,12) active spaces that previously have been applied in similar PJTE origin studies;<sup>22,24,27,31</sup> was proved that CAS(10,8) active space sufficiently is good in present study. From Table 2 is also appeared that the eight orbitals included 2a<sub>1</sub>, 2b<sub>1</sub>, 2b<sub>2</sub>, and 2a<sub>2</sub> were being contributed to the electron excitations of the C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series. The main electronic configuration calculation for all C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> considered compounds (see Table 3) was showed that b<sub>1</sub>' → a<sub>1</sub>' electron excitation occurred and it proved that (<sup>1</sup>A<sub>1</sub>+<sup>1</sup>B<sub>1</sub>) ⊗ b<sub>1</sub> PJTE problems are the reason of the breaking symmetry phenomenon and non-planarity of C<sub>2</sub>Y<sub>3</sub> rings in the series.

**Table 1.** Calculated structural parameters of C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> (Y= O, S, Se, Te, Z= H, F) series in planar and equilibrium configurations, normal modes of planar instability in Cartesian coordinates displacements X and imaginary frequency values

Geometry parameters	Molecules														
	C <sub>2</sub> O <sub>3</sub> Z <sub>2</sub>		C <sub>2</sub> S <sub>3</sub> Z <sub>2</sub>				C <sub>2</sub> Se <sub>3</sub> Z <sub>2</sub>		C <sub>2</sub> Te <sub>3</sub> Z <sub>2</sub>						
	Planar (C <sub>2v</sub> )	Equilibrium (C <sub>s</sub> )	Planar (C <sub>2v</sub> )	Equilibrium (C <sub>s</sub> )	Planar (C <sub>2v</sub> )	Equilibrium (C <sub>s</sub> )	Planar (C <sub>2v</sub> )	Equilibrium (C <sub>s</sub> )	Planar (C <sub>2v</sub> )	Equilibrium (C <sub>s</sub> )	Planar (C <sub>2v</sub> )	Equilibrium (C <sub>s</sub> )			
	Z=H	Z=F	Z=H	Z=F	Z=H	Z=F	Z=H	Z=F	Z=H	Z=F	Z=H	Z=F	Z=H	Z=H	
Bond length (Å)	Y-Y	1.43	1.43	1.44	1.44	1.72	1.68	2.06	2.15	1.80	1.80	2.30	2.40	2.02	2.70
	Y-C	1.39	1.40	1.38	1.37	1.52	1.52	1.71	1.78	1.74	1.75	1.84	1.90	1.78	2.03
	C=C	1.34	1.35	1.36	1.32	1.35	1.36	1.39	1.33	1.36	1.37	1.40	1.39	1.37	1.40
	C-Z	1.08	1.25	1.07	1.29	1.07	1.25	1.08	1.32	1.08	1.24	1.08	1.33	1.08	1.09
Angle (Degree)	Y-Y-Y	109.9	111.8	107.0	107.8	101.4	103.2	98.9	99.6	106.9	107.3	95.4	96.9	103.0	91.0
	Y-Y-C	103.7	102.8	103.1	101.1	107.0	104.4	99.5	94.6	106.9	103.7	100.2	94.6	106.1	98.4
	Y-C=C	111.2	111.3	111.6	112.2	112.3	114.0	119.6	123.8	109.7	112.6	121.6	126.7	112.4	125.8
	Z-C=C	129.5	128.3	131.7	132.3	126.8	127.3	127.1	122.1	126.5	127.9	122.4	120.9	125.9	119.5
Dihedral angle (Degree)	Y-Y-Y-C	0.0	0.0	±24.5	±24.0	0.0	0.0	±13.8	±11.2	0.0	0.0	±8.8	±6.4	0.0	±6.8
	Y-Y-C=C	0.0	0.0	±16.0	±15.5	0.0	0.0	±9.7	±8.7	0.0	0.0	±6.7	±5.3	0.0	±5.6
	Y-Y-C-Z	180	180	±168	±170	180	180	±177	±176	180	180	±176	±177	180	±175
	Y-C=C-Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z-C=C-Z	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Y-C-C-Z	180	180	±175	±173	180	180	±172	±174	180	180	±177	±177	180	±179	
Imaginary freq. b <sub>1</sub> (cm <sup>-1</sup> )		135.3	201.2	—	304.7	150.1	—	—	—	179.3	74.8	—	—	148.4	—
Normal modes in Cartesian X	X <sub>Y-C</sub>	+0.1551	+0.1704	—	—	+0.0942	+0.1096	—	—	+0.0483	+0.0645	—	—	+0.0300	—
	X <sub>C</sub>	-0.1269	-0.1259	—	—	-0.0861	-0.0907	—	—	-0.0463	-0.0544	—	—	-0.0308	—
	X <sub>Z</sub>	+0.0571	+0.0244	—	—	+0.0966	+0.0426	—	—	+0.1304	+0.0449	—	—	+0.1480	—
	X <sub>Y</sub>	+0.1032	+0.0188	—	—	+0.0885	+0.0337	—	—	+0.1834	+0.0638	—	—	+0.2399	—

**Table 2.** Arrangement of HOMO and LUMO energies level and their symmetries, and electron excitation in the C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series contributing in the (<sup>1</sup>A<sub>1</sub>+<sup>1</sup>B<sub>1</sub>) ⊗ b<sub>i</sub> PJTE through SA-CASSCF calculation with (10,8) active space

	C <sub>2</sub> O <sub>3</sub> H <sub>2</sub>		C <sub>2</sub> S <sub>3</sub> H <sub>2</sub>		C <sub>2</sub> Se <sub>3</sub> H <sub>2</sub>		C <sub>2</sub> Te <sub>3</sub> H <sub>2</sub>		C <sub>2</sub> O <sub>3</sub> F <sub>2</sub>		C <sub>2</sub> S <sub>3</sub> F <sub>2</sub>		C <sub>2</sub> Se <sub>3</sub> F <sub>2</sub>	
Arrangement of MO's energy level	a <sub>1</sub>	HOMO-3	a <sub>1</sub>	HOMO-4	a <sub>1</sub>	HOMO-3	a <sub>1</sub>	HOMO-3	a <sub>1</sub>	HOMO-4	a <sub>1</sub>	HOMO-4	a <sub>1</sub>	HOMO-3
	a <sub>1</sub> '	LUMO+2	a <sub>1</sub> '	LUMO+1	a <sub>1</sub> '	LUMO+2	a <sub>1</sub> '	LUMO+1	a <sub>1</sub> '	LUMO+2	a <sub>1</sub> '	LUMO+2	a <sub>1</sub> '	LUMO+2
	a <sub>2</sub>	HOMO	a <sub>2</sub>	HOMO-1	a <sub>2</sub>	HOMO-4	a <sub>2</sub>	HOMO-4	a <sub>2</sub>	HOMO	a <sub>2</sub>	HOMO-1	a <sub>2</sub>	HOMO-4
	a <sub>2</sub> '	LUMO	a <sub>2</sub> '	LUMO+2	a <sub>2</sub> '	LUMO	a <sub>2</sub> '	LUMO+2	a <sub>2</sub> '	LUMO+1	a <sub>2</sub> '	LUMO	a <sub>2</sub> '	LUMO
	b <sub>1</sub>	HOMO-1	b <sub>1</sub>	HOMO	b <sub>1</sub>	HOMO	b <sub>1</sub>	HOMO-1	b <sub>1</sub>	HOMO-1	b <sub>1</sub>	HOMO	b <sub>1</sub>	HOMO
	b <sub>1</sub> '	HOMO-4	b <sub>1</sub> '	HOMO-3	b <sub>1</sub> '	HOMO-2	b <sub>1</sub> '	HOMO-2	b <sub>1</sub> '	HOMO-3	b <sub>1</sub> '	HOMO-3	b <sub>1</sub> '	HOMO-2
	b <sub>2</sub>	HOMO-2	b <sub>2</sub>	OMO-2	b <sub>2</sub>	HOMO-1	b <sub>2</sub>	HOMO	b <sub>2</sub>	HOMO-2	b <sub>2</sub>	HOMO-2	b <sub>2</sub>	HOMO-1
	b <sub>2</sub> '	LUMO+1	b <sub>2</sub> '	LUMO	b <sub>2</sub> '	LUMO+1	b <sub>2</sub> '	LUMO	b <sub>2</sub> '	LUMO	b <sub>2</sub> '	LUMO+1	b <sub>2</sub> '	LUMO+1
Electron excitation	b <sub>1</sub> ' → a <sub>1</sub> '		b <sub>1</sub> ' → a <sub>1</sub> '		b <sub>1</sub> ' → a <sub>1</sub> '		b <sub>1</sub> ' → a <sub>1</sub> '		b <sub>1</sub> ' → a <sub>1</sub> '		b <sub>1</sub> ' → a <sub>1</sub> '		b <sub>1</sub> ' → a <sub>1</sub> '	
	HOMO-4 to LUMO+2		HOMO-3 to LUMO+1		HOMO-2 to LUMO+2		HOMO-2 to LUMO+1		HOMO-3 to LUMO+2		HOMO-3 to LUMO+2		HOMO-2 to LUMO+2	

**Table 3.** Main electronic configuration and their weight coefficients in wave-functions of ground state (<sup>1</sup>A<sub>1</sub>) and <sup>1</sup>B<sub>1</sub> excited state of C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series in planar configuration

State symmetry	Main electronic configuration	Weight Coefficients						
		C <sub>2</sub> O <sub>3</sub> H <sub>2</sub>	C <sub>2</sub> S <sub>3</sub> H <sub>2</sub>	C <sub>2</sub> Se <sub>3</sub> H <sub>2</sub>	C <sub>2</sub> Te <sub>3</sub> H <sub>2</sub>	C <sub>2</sub> O <sub>3</sub> F <sub>2</sub>	C <sub>2</sub> S <sub>3</sub> F <sub>2</sub>	C <sub>2</sub> Se <sub>3</sub> F <sub>2</sub>
A <sub>1</sub>	a <sub>1</sub> <sup>2</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>2</sup> b <sub>2</sub> <sup>2</sup>	0.9946	0.9930	0.9917	0.9922	0.9935	0.9944	0.9919
	a <sub>1</sub> <sup>1</sup> a <sub>1</sub> ' <sup>-1</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>2</sub> <sup>2</sup> b <sub>2</sub> ' <sup>2</sup>	-0.0836	-0.0901	0.0899	-0.0850	0.0798	0.0935	0.0832
	a <sub>1</sub> ' <sup>-1</sup> a <sub>1</sub> <sup>1</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>2</sub> <sup>2</sup> b <sub>2</sub> ' <sup>2</sup>	0.0836	0.0901	-0.0899	0.0850	-0.0798	-0.0935	-0.0832
	a <sub>1</sub> <sup>2</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>2</sup> b <sub>2</sub> <sup>2</sup> b <sub>2</sub> ' <sup>-1</sup>	0.0792	0.0801	-0.0820	0.0802	-0.0813	-0.0788	-0.0795
	a <sub>1</sub> <sup>2</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>2</sup> b <sub>2</sub> <sup>2</sup> b <sub>2</sub> ' <sup>-1</sup>	-0.0792	-0.0801	0.0820	-0.0802	0.0813	0.0788	0.0795
B <sub>1</sub>	a <sub>1</sub> <sup>2</sup> a <sub>2</sub> <sup>2</sup> a <sub>2</sub> ' <sup>-2</sup> b <sub>1</sub> <sup>2</sup> b <sub>2</sub> <sup>2</sup>	-0.1035	-0.1041	-0.1080	-0.1106	-0.1091	-0.1033	-0.1076
	a <sub>1</sub> <sup>2</sup> a <sub>1</sub> ' <sup>-1</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>-1</sup> b <sub>2</sub> <sup>2</sup>	-0.7013	-0.6988	-0.7019	-0.7023	-0.7012	-0.7009	-0.7007
	a <sub>1</sub> <sup>2</sup> a <sub>1</sub> ' <sup>-1</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>-1</sup> b <sub>2</sub> <sup>2</sup>	0.7013	0.6988	0.7019	0.7023	0.7012	0.7009	0.7007
	a <sub>1</sub> <sup>2</sup> a <sub>1</sub> ' <sup>-1</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>-1</sup> b <sub>2</sub> <sup>2</sup> b <sub>2</sub> ' <sup>-1</sup>	0.0628	0.0631	0.0645	0.0622	0.0625	0.0634	0.0601
	a <sub>1</sub> <sup>2</sup> a <sub>1</sub> ' <sup>-1</sup> a <sub>2</sub> <sup>2</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>-1</sup> b <sub>2</sub> <sup>2</sup> b <sub>2</sub> ' <sup>-1</sup>	0.0628	0.0631	0.0645	0.0622	0.0625	0.0634	0.0601
	a <sub>1</sub> <sup>2</sup> a <sub>1</sub> ' <sup>-1</sup> a <sub>2</sub> <sup>2</sup> a <sub>2</sub> ' <sup>-1</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>-1</sup> b <sub>2</sub> <sup>2</sup>	-0.0611	-0.0613	-0.0603	-0.0614	-0.0596	-0.0602	-0.0606
a <sub>1</sub> <sup>2</sup> a <sub>1</sub> ' <sup>-1</sup> a <sub>2</sub> <sup>2</sup> a <sub>2</sub> ' <sup>-1</sup> b <sub>1</sub> <sup>2</sup> b <sub>1</sub> ' <sup>-1</sup> b <sub>2</sub> <sup>2</sup>	-0.06211	-0.0613	-0.0603	-0.0614	-0.0596	-0.0602	-0.0606	

## THE PJTE DUE TO PUCKERING

If  $\Gamma$  was supposed as the ground state and first non-degenerate excited state ( $\Gamma'$ ) was separated with  $\Delta$  energy gap,  $|\Gamma\rangle$  and  $|\Gamma'\rangle$  will be denoted as the wave-functions of those mixing states. Based on the PJTE theorem<sup>13</sup>, the ground state in the nuclear displacements direction ( $Q$ ) is instable if

$$\Delta < \frac{(F_{\Gamma\Gamma'})^2}{K_0} \quad (1)$$

where  $K_0$  and  $F_{(\Gamma\Gamma')}$  are the primary force constant of the ground state and the vibronic coupling constant. With respect to Hamiltonian,  $H$ , and the electron-nucleon interaction operator,  $V$ , the  $K_0$ ,  $K_0'$  (the primary force constant of excited state) and  $F_{(\Gamma\Gamma')}$  constants indicate by Equations (2) and (3):

$$K_0 = \left\langle \Gamma \left| \frac{\partial H}{\partial Q} \right| \Gamma \right\rangle, \quad K_0' = \left\langle \Gamma' \left| \frac{\partial H}{\partial Q} \right| \Gamma' \right\rangle \quad (2)$$

$$F_{\Gamma\Gamma'} = \left\langle \Gamma \left| \frac{\partial V}{\partial Q} \right| \Gamma' \right\rangle \quad (3)$$

From these definitions for 2x2 case of two interacting states, it is revealed that the PJTE substantially involves excited states, specifically the energy gap to them and the strength of their influence of the ground state via the vibronic coupling constant  $F_{(\Gamma\Gamma')}$ .

The vibronic coupling between the two states reduces and adds the force constant of the ground and excited states by an amount of  $(F_{(\Gamma\Gamma')})^2/\Delta$  and making the total constant of the ground and excited states as followed equalities.<sup>14</sup>

$$K = K_0 - \frac{(F_{\Gamma\Gamma'})^2}{\Delta}, \quad K' = K_0' + \frac{(F_{\Gamma\Gamma'})^2}{\Delta} \quad (4)$$

This leads to the condition of instability in Equation (1) at which the curvature  $K$  of the adiabatic potential energy surface (APES) for the <sup>1</sup>A<sub>1</sub> ground state in  $Q_{b_1}$  direction becomes negative but for the effective PJT interaction, the curvature  $K'$  of the APES for the

${}^1B_1$  excited (which is the first one in all of  $C_2Y_3Z_2$  compounds in the series) must be positive.

Since an  $B_1$  excited state contribute to the  $A_1$  ground state instability in the  $C_2Y_3Z_2$  series planar configuration, the PJTE emerges directly from the secular equation for the vibronically coupled the ground and excited state that is formulated by two-level PJTE problem as a  $2 \times 2$  secular Equation (5) and quadratic Equation (6).

$$\begin{vmatrix} \frac{1}{2}KQ^2 - \varepsilon & FQ \\ FQ & \frac{1}{2}K'Q^2 + \Delta - \varepsilon \end{vmatrix} = 0 \quad (5)$$

$$\varepsilon^2 - \left[ \frac{1}{2}(K + K')Q^2 + \Delta \right] \varepsilon + \frac{1}{4}KK'Q^4 + \frac{\Delta}{2}KQ^2 - F^2Q^2 = 0 \quad (6)$$

In above Equations,  $\Delta$  is the energy gap between the ground and excited states and for simplicity, the  $Q_{b_1}$  and  $[\mathbb{F}]_{(IT)}$  are abbreviated to  $Q$  and  $F$ . The solution of Equation (6) around  $Q = 0$  of the APES for the ground and excited states around the planar configuration bring us the following solutions in Equation (7):

$$\varepsilon_1 = \frac{1}{2} \left( K - \frac{2F^2}{\Delta} \right) Q^2 - \frac{F^2}{2\Delta^2} \left( (K - K') - \frac{2F^2}{\Delta} \right) Q^4 + \dots \quad (7)$$

$$\varepsilon_2 = \frac{1}{2} \left( K' + \frac{2F^2}{\Delta} \right) Q^2 + \Delta + \frac{F^2}{2\Delta^2} \left( (K - K') - \frac{2F^2}{\Delta} \right) Q^4 + \dots$$

With respect to the ab initio calculation, it was founded that the

lowest excited state with  ${}^1B_1$  symmetry is interacting with the ground state (in  ${}^1A_1$  symmetry). For all under study  $C_2Y_3Z_2$  compounds, the condition of the PJTE ground state instability in Eq. (1) (are observable from the APES profiles of  $C_2Y_3H_2$  and  $C_2Y_3F_2$  (see Figures 3 and 4) and it appears that the ground state in all  $C_2Y_3Z_2$  under consideration compounds are unstable in  $Q = 0$  of the APES (planar configuration) along the  $b_1$  puckering direction. Additionally, In Figures 3 and 4, the numerical fitting of the energies obtained from Equation (7) for  $C_2Y_3H_2$  ( $Y = O, S, Se, Te, Z = H, F$ ) series were compared with theirs ab initio calculated energy profiles and the first and second  $A'$  states in puckered stable geometry with  $C_s$  symmetry were denoted by  $A'_I$  and  $A'_{II}$ , respectively.

As from Figures 3 and 4 were illuminated, instability in planar configuration occurs in all  $C_2Y_3Z_2$  ( $Y = O, S, Se, Te, Z = H, F$ ) compounds and the origin of the PJTE in the series are may explained via solution of the PJTE ( ${}^1A_1 + {}^1B_1$ )  $\otimes b_1$  problem. For explanation of origin of the PJTE in the series,  $K, K'$  and  $F$  parameters were estimated by the numerical fitting of Equation (7) with the APES energy profiles along the twisting direction ( $Q_{b_1}$ ) which is revealed in Table 4. Since small values of higher order of  $Q^4$  parameters in comparison with  $Q^2$  and  $Q^4$ , the numerical fitting of the equation was done up to the second term of the series in Equation (7).

By the estimated parameters and the energy gaps ( $\Delta$ ) in Table 4 and with respect to the PJTE the ground state instability in Equation (1), the PJTE origin and value of instability in the  $C_2Y_3Z_2$  series were evaluated. The highest and lowest PJTE coupling constants for the  $C_2Y_3H_2$  series are belonged to  $C_2Te_3H_2$  and  $C_2O_3H_2$  compounds and the  $F$  values for the  $C_2Y_3F_2$  series were increased from 2.28 eV / Å, in  $C_2O_3F_2$  to 2.43 eV / Å, in  $C_2Se_3F_2$  compound, respectively.

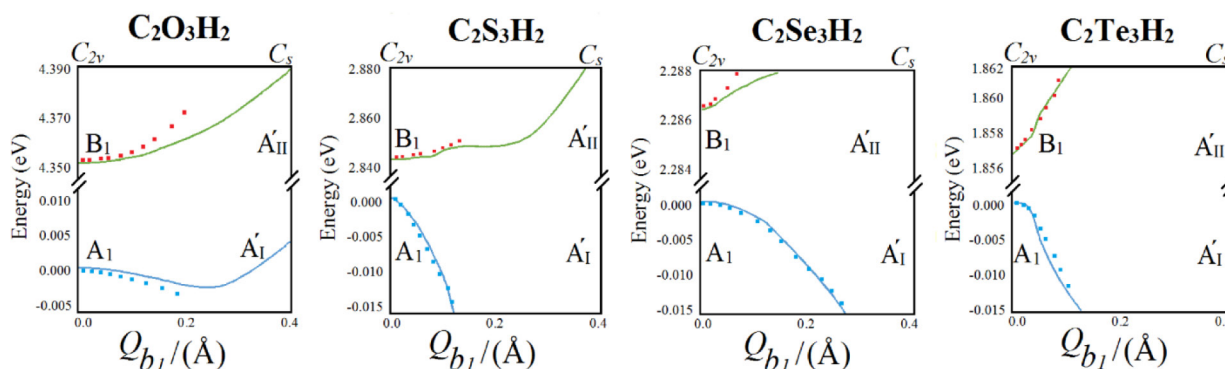


Figure 3. The APES profiles of  $C_2Y_3H_2$  ( $Y = O, S, Se, Te$ ) series (lines) and the numerical fitting of the energies obtained from the PJTE equations (points) along the  $b_1$  puckering direction in eV

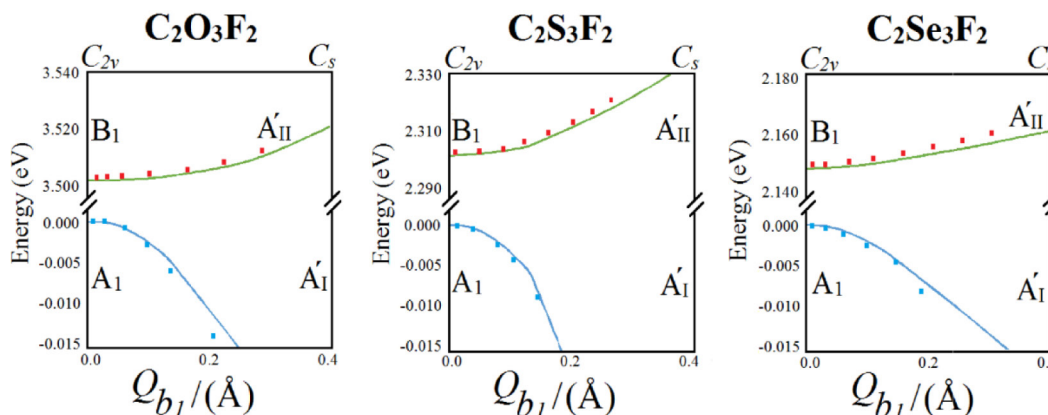


Figure 4. The APES profiles of  $C_2Y_3F_2$  ( $Y = O, S, Se$ ) series (lines) and the numerical fitting of the energies obtained from the PJTE equations (points) along the  $b_1$  puckering direction in eV

**Table 4.** Total constant constants in ground and excited state,  $K$  and  $K'$ , PJTE coupling constants,  $F$ , and energy gaps,  $\Delta$ , of the C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> (Y= O, S, Se, Te, Z= H, F) series for (<sup>1</sup>A<sub>1</sub>+<sup>1</sup>B<sub>1</sub>) ⊗ b<sub>1</sub> problem

Molecules	$K$ in eV/Å <sup>2</sup>	$K'$ in eV/Å <sup>2</sup>	$F$ in eV/Å	$\Delta$ in eV
C <sub>2</sub> O <sub>3</sub> H <sub>2</sub>	0.82	1.47	1.03	4.35
C <sub>2</sub> S <sub>3</sub> H <sub>2</sub>	3.20	1.45	2.70	2.84
C <sub>2</sub> Se <sub>3</sub> H <sub>2</sub>	1.92	1.34	2.22	2.28
C <sub>2</sub> Te <sub>3</sub> H <sub>2</sub>	3.33	1.75	2.83	1.85
C <sub>2</sub> O <sub>3</sub> F <sub>2</sub>	1.93	1.43	2.28	3.50
C <sub>2</sub> S <sub>3</sub> F <sub>2</sub>	2.02	1.50	2.34	2.30
C <sub>2</sub> Se <sub>3</sub> F <sub>2</sub>	1.89	1.38	2.43	2.15

## CONCLUSIONS

An imaginary frequency coordinate in out-of-plane of the molecules was observed through the ab initio DFT optimization and following frequency calculations in planar configuration of C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> (Y = O, S, Se, Te, Z = H, F) series. It provides very important information about the symmetry breaking phenomenon in all under consideration compounds in the series. In other hand all those compounds in the C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series do not hold their planarity due to the PJTE and they distort from their unstable planar configuration with C<sub>2v</sub> symmetry to the stable C<sub>s</sub> symmetry geometry. The APES cross sections of the series were revealed that the ground state (<sup>1</sup>A<sub>1</sub>) and the excited <sup>1</sup>B<sub>1</sub> state along b<sub>1</sub> nuclear displacements could interact vibronically and the (<sup>1</sup>A<sub>1</sub>+<sup>1</sup>B<sub>1</sub>) ⊗ b<sub>1</sub> problem is the reason of instability of the C<sub>2</sub>Y<sub>3</sub>Z<sub>2</sub> series in their planar configuration. Estimation of the vibronic coupling constant values,  $F$ , in the C<sub>2</sub>Y<sub>3</sub>H<sub>2</sub> series illuminate that the most unstable planar configuration in the series is corresponded to C<sub>2</sub>Te<sub>3</sub>H<sub>2</sub> five-member ring compound. It is also clear that planar stability in the systems rises by decreasing the Y atoms size in the series, except in C<sub>2</sub>Se<sub>3</sub>H<sub>2</sub>. Additionally, the molecules puckering in both C<sub>2</sub>S<sub>3</sub>F<sub>2</sub> and C<sub>2</sub>Se<sub>3</sub>F<sub>2</sub> compounds were decreased by replacing the H atoms with F ligands in the C<sub>2</sub>Y<sub>3</sub>H<sub>2</sub> series, although C<sub>2</sub>O<sub>3</sub>F<sub>2</sub> compound shows opposite behavior in the C<sub>2</sub>Y<sub>3</sub>F<sub>2</sub> under consideration series.

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