

A Valence Bond Analysis of Electronic Degeneracies in Jahn–Teller Systems: Low-Lying States of the Cyclopentadienyl Radical and Cation

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Abstract: The lowest doublet electronic state of the cyclopentadienyl radical (CPDR) and the lowest singlet state of the cyclopentadienyl cation (CPDC) are distorted from the highly symmetric D_{5h} structure due to the Jahn–Teller effect. A valence bond analysis based on the phase-change rule of Longuet-Higgins reveals that in both cases the distortion is due to the first-order Jahn–Teller effect. It is shown that, while for the radical an isolated Jahn–Teller degeneracy is expected, in the case of the cation the main Jahn–Teller degeneracy is accompanied by five satellite degeneracies. The method offers a chemically oriented way for identifying the distortive coordinates.

I. Introduction

The cyclopentadienyl radical (CPDR) is an important intermediate and building block in organic and inorganic chemistry. It has been the subject of many experimental^{1–6} and theoretical^{7–13} studies. The cyclopentadienyl cation (CPDC) is also a subject of much interest, especially concerning the nature of the Jahn–Teller (JT)¹⁴ degeneracy expected for the lowest singlet state.^{11,15–18} Recent experimental observations indicated the existence of this cation as a reaction intermediate and probed the possible antiaromatic character of this molecule.¹⁹

In this paper, we apply the method of Longuet-Higgins loops^{20–23} to these systems. The H_3 system (a well-known JT

case) was used as an example by Herzberg and Longuet-Higgins.^{24,25} They showed that, by symmetry, the electronic degeneracy occurs at the equilateral geometry. Here, we extend the discussion to the more complicated case of D_{5h} symmetry and examine the case of possible neighboring degeneracies. While the usual treatment of the JT problem emphasizes the degeneracy point, the Longuet-Higgins rule focuses on the neighborhood (loop) around the degeneracy.

The results of the proposed analysis for the radical agree with previous ones. In the case of the cation, it was previously suggested¹¹ that the removal of the degeneracy is due mainly to a strong second-order JT effect, which is very much larger than the first-order effect. Our approach, which is not a perturbative one, shows that in fact the cation is also subject to a normal (first-order) Jahn–Teller distortion, but the primary degeneracy is surrounded by five equivalent neighboring degeneracies, all connecting the first excited singlet and the ground state. The ground-state acquires several different geometries in that neighborhood, all having C_{2v} symmetries. The electronic symmetry of the ground state at different nuclear geometries varies: it is A_1 for some and B_2 for others.

II. Method: The Search for Longuet-Higgins Loops and Electronic Degeneracies

The method was recently discussed at length;^{20–22} here, we repeat only the essentials. The basis of our model is the Longuet-Higgins phase-change rule^{24,25} that provides a simple criterion for the existence of a degeneracy on the electronic ground state. Longuet-Higgins showed that a degeneracy necessarily lies within a region enclosed by a loop, if the total electronic wave function changes sign upon being transported around the loop. We construct the Longuet-Higgins loop using reaction coordi-

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nates of elementary reactions converting the reactant to the desired product and other possible products. A chemical reaction is defined as a change in electron spin-pairing,^{26,27} followed by nuclear displacement. It is useful to introduce a single term for all systems having a particular spin-pairing scheme, independent of the nuclear configuration. We use the term *anchor* to represent this group of systems.^{20–23}

The reaction system (reactant and product) is treated as a single quantum-mechanical entity, which is a two-state system.^{28–30} The phase change of the total poly-electronic wave function in a chemical reaction^{22,31} is central to the approach presented in this paper. Some reactions may be classified as phase preserving (p) on the ground-state surface, while others are phase inverting (i). The distinction between the two can be made by checking the change in the spin-pairing of the electrons that are exchanged in the reaction. A complete loop around a point in the configuration space may be constructed using a number of consecutive elementary reactions, starting and ending with a given reactant. Formerly, we considered mainly loops constructed of three different reactions. At least one reaction must be phase inverting for the complete loop to be phase inverting and thus to encircle a conical intersection. In the Jahn–Teller case, these three reactions are equivalent, connecting equivalent anchors. In general, however, any odd number of equivalent anchors may define a degeneracy. For the cyclopentadienyl radical and cation cases, symmetry calls for loops consisting of five anchors. The Jahn–Teller effect is the reduction of symmetry by motion along an appropriate coordinate. We show that by assuming a minimal change in the electron spin-pairing near the symmetric degenerate structure, it is possible to locate the anchors important for constructing all relevant loops. This in turn leads directly to the identification of the coordinate along which the Jahn–Teller distortion takes place. In distinction with standard treatments of the JT effect, the present approach is not based on perturbation theory.

Once the components of the loop are determined, numerical calculations can be carried out as described in detail in ref 23. Computations reported in this paper were performed using the GAMESS program suite³² for CASSCF calculations and the GAUSSIAN³³ program suite for CISD calculations.

III. Cyclopentadienyl Radical (CPDR)

IIIa. Standard JT Treatment. As mentioned above, standard JT treatments of this system are straightforward. According to molecular orbital (MO) quantum chemical methods,^{11–13} three electrons occupy a pair of degenerate e_1'' π molecular orbitals in D_{5h} symmetry. This gives rise to a degenerate ${}^2E_1''$ state, which by the JT theorem should distort away from D_{5h} symmetry along a degenerate e_2' -type vibration to a C_{2v} form. The eigenfunctions of the resulting states are bases of the A_2

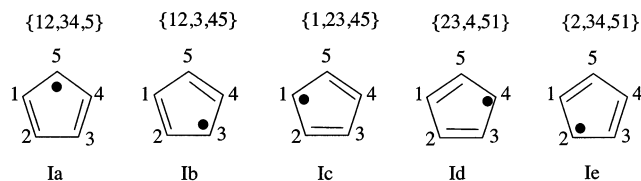


Figure 1. Five equivalent spin-paired structures of CPDR (B_1 symmetry).

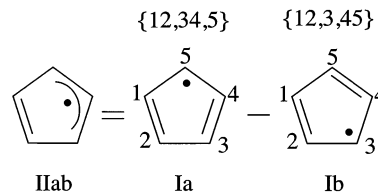


Figure 2. Out-of-phase combination of two type-I structures yields a type-II structure (A_2 symmetry).

and B_1 irreducible representations (irreps). Five equivalent minima of C_{2v} symmetry are obtained, which are interconnected by a route that does not pass through the central D_{5h} -symmetric structure—rather, the route forms a loop around that degeneracy. It turns out^{2,12} that the barriers between the five equivalent structures are small, so that the system can pseudorotate among them—a typical Mexican hat case.

A simple VB approach was used in ref 15 to describe the five structures. Only the lowest energy spin-pairing structures I (B_1 symmetry) of the type $\{12,34,5\}$ were used (Figure 1). The degenerate ${}^2E_1''$ state is the lowest state of D_{5h} symmetry: it lies on the ground-state surface and is constructed from a combination of the five type-II structures such as IIab shown in Figure 2, constructed from out-of-phase combinations of type-I structures. These A_2 symmetry structures are stabilized by an allyl-type resonance^{34,35} and turn out to be isoenergetic with type-I structures.

The electronic spectrum of the radical was been recorded long before a satisfactory theoretical explanation could be provided. Recently, an extensive experimental study of the high-resolution UV spectrum was reported⁶ and analyzed using JT formalism.¹²

The standard JT treatment uses a perturbation theory approach.³⁶ The first-order JT distortion is due to an e_2' vibration, and the second-order distortion vanishes. Therefore, in terms of this theory, the “moat” around the symmetric point should be a Mexican hat type, without secondary minima.³⁶ This expectation was borne out by high-level quantum chemical calculations that showed that the energy difference between the two expected C_{2v} structures (whose electronic wave functions transform as 2A_2 and 2B_1) were indeed very small on the ground-state surface.^{11–13} In one recent calculation, the 2A_2 structures (type II, Figure 2) were calculated to lie 3.6 cm^{-1} lower in energy than the 2B_1 (type I) structures¹² at the CASSCF/6-31G* level. Our calculation (CISD/cc-pDZV) yielded a somewhat larger difference (1.1 kcal/mol)—both results, as well as others,^{11,13} indicate negligible energy difference. The geometries

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Table 1. Calculated Properties of Cyclopentadienyl Radical Ground-State Species

property	species	CAS(5,5)/DZV	CISD/DZV		
energy (hartree)	2A_2	−192.18867	−192.76924		
ΔE^a (kcal/mol)	2B_1	0	1.6		
	${}^2E_1''$ (con int)	7.5	7.3		
geometry ^b					
this work					
	CAS(5,5)/DZV	CISD/DZV	ref 13	ref 12	expt (ref 6)
I (2B_1)					
r_{12}	1.381	1.380	1.370	1.367	1.407
r_{23}	1.495	1.504	1.486	1.484	1.438
r_{45}	1.452	1.462	1.443	1.440	1.426
avg	1.432	1.438	1.422	1.420	
II (2A_2)					
r_{12}	1.484	1.496	1.474	1.473	1.435
r_{23}	1.370	1.376	1.360	1.357	1.404
r_{45}	1.411	1.418	1.401	1.399	1.416
avg	1.440	1.441	1.422	1.420	
$D_{5h}({}^2E_1'')$					
R_{cc}	1.433	1.440	1.42	1.418	1.421

^a Relative to the energy of the 2A_2 species. ^b See Figure 1 for atom numbering.

obtained in the present work are in excellent agreement with previous ones (Table 1).

IIIb. Phase Change Method. The system provides an opportunity to demonstrate our method for finding the conical intersection and the stabilized ground-state structures that are formed by the distortion. Recall that we focus on the distinction between spin-paired structures, rather than true minima. The basic assumption of our model is that the system tends to minimize changes in spin pairing in the neighborhood of the degeneracy (for a discussion of this assumption, see Section V). Under this assumption, a natural choice for anchors are the two C_{2v} VB structures shown in Figures 1 and 2, whose electronic wave functions transform as the A_2 and B_1 irreps of the C_{2v} group (hereafter referred to as the A_2 and B_1 species, respectively). In principle, each set can serve as the anchors. The reaction converting one type-I structure to another is phase inverting, since it transforms one allyl structure to another.^{34,35} Type-II structures are formally the out-of-phase transition states between two type-I structures, even if there is no measurable barrier. Note that at their optimized nuclear coordinates both types lie on the ground-state potential surface. However, at the optimized nuclear configuration of type I spin-paired structure, type II lies on the excited-state surface. Likewise, at the optimized nuclear configuration of type II spin-paired structure, type I lies on the excited-state surface. This is the expected result of the first-order JT splitting.

The complete loop is shown in Figure 3: it includes five phase-inverting reactions and is therefore phase inverting.^{20,22,25} The degeneracy that lies within the loop is the symmetric D_{5h} structure—at this symmetry, all five type-I structures are degenerate. The rationale for the loop's construction and the choice of anchors is outlined in the Appendix.

This example may be used to address another issue concerning Longuet-Higgins loops: What is the minimum number of anchors needed to form a loop? Formally, one might choose three anchors (for instance Ia, Ic, and Ie) and use them as a loop. Inspection of Figure 3 shows that the conical intersection is formally encircled by a loop connecting these structures. It

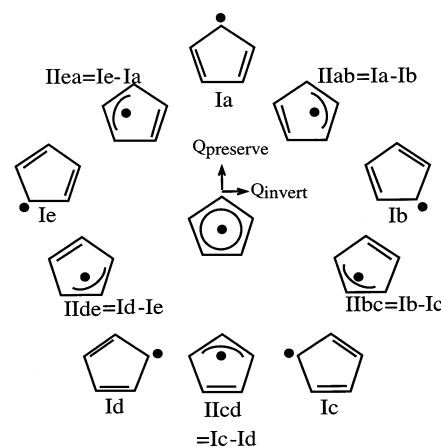


Figure 3. Longuet–Higgins loop around the Jahn–Teller degeneracy of CPDR at D_{5h} symmetry. The phase-inverting and phase-preserving components of the degenerate distorting e_2' coordinate are shown.

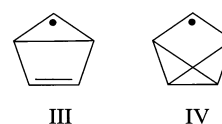


Figure 4. Two other spin-paired structures of CPDR.

is also easily verified that the loop is phase inverting. However, one of the conditions for a proper loop was that all reactions must be elementary; i.e., there must not be an intermediate species (i.e., a species lying at a local minimum energy) between any two anchors. This condition is not satisfied for the transformation $Ia \rightarrow Ic$: motion along this trajectory leads uphill (on the slope of the cone leading to the ${}^2E_1''$ degeneracy). Somewhere on the way, the minimum energy path will lead the system to Ib, which is therefore an intermediate. Thus, the smallest loop must pass through all five type-I structures.

Other spin-pairing forms that may in principle be used to construct a loop are shown in Figure 4. Structures III and IV have different spin-pairing schemes and were not used, since they are expected to be higher in energy than type-I (and type-II) structures, due to the strain introduced by the cyclopropyl rings. They may be used as anchors for secondary conical intersections around the most symmetric one.

IV. The Cyclopentadienyl Cation (CPDC)

In the case of the cyclopentadienyl cation, there are only two electrons in the e_1'' π molecular orbitals that are degenerate in D_{5h} symmetry. MO treatments^{11,18} indicate that a degenerate ${}^1E_2'$ state is the lowest lying singlet state. An e_1' -type distortion is expected to reduce the symmetry of the ${}^1E_2'$ state and generate two states of A_1 and B_2 symmetry. This system appears to be analogous to the cyclopentadienyl radical one–five equivalent C_{2v} structures are expected to be formed upon distortion of the D_{5h} structure. These structures will be situated in a symmetric order around the degeneracy; However, ab initio calculations found two very close lying 1A_1 species, whose electronic configurations are $\{\cdots(a''_2)^2(b_1)^0\}$ and $\{\cdots(a''_2)^2(b_1)^2\}$.^{11,18} The B_2 structure, expected from the JT treatment, was not considered as a ground-state species in ref 11. It was shown that the system can pseudorotate around the degenerate D_{5h} structure, along the route shown in Figure 5, which is similar to Figure 3. In the presentation of Figure 5, the central symmetric structure is surrounded by ten A_1 structures (in C_{2v} symmetry).

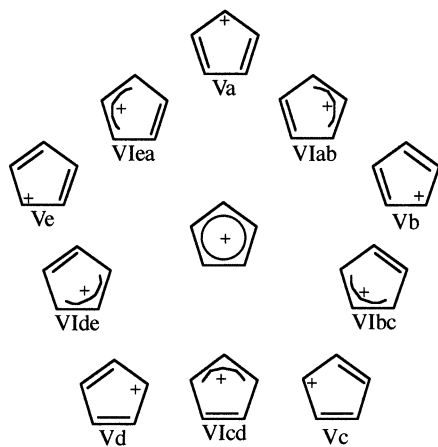


Figure 5. Suggested explanation for the free pseudorotation motion around the degeneracy in the cyclopentadienyl cation (reproduced with permission from ref 11).

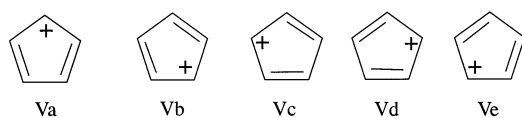


Figure 6. Five type-V (A_1 symmetry) equivalent VB structures for CPDC.

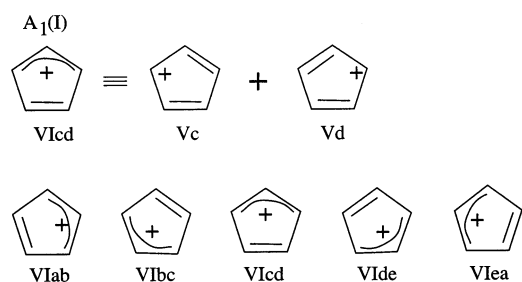


Figure 7. Top: One of the allylic type-VI (A_1 symmetry) structures, formed by in-phase combination of type-V structures. Bottom: The five type-VI structures.

This is in apparent contradiction to the JT theorem, since the distortion must also generate a nonsymmetric structure (B_2 type, in this case), in analogy with the case of the radical.

Simple VB theory¹⁵ uses for the basis set five low-lying structures that differ in their spin-pairing characteristics, as shown in Figure 6. Again in analogy with the case of the radical, the degenerate ${}^1E_2'$ state is the lowest singlet state of D_{5h} symmetry: It lies on the lowest singlet surface and can be constructed from the combination of the five type-V structures. These structures transform as A_1 in C_{2v} and will be referred to as $A_1(I)$ structures in the following discussion.

As shown in Figure 7, an in-phase combination of type-V structures leads to another A_1 symmetry structure (type VI), which is expected to be stabilized by allyl cation type resonance. A calculation (Table 2) shows that the two structures are in fact isoenergetic. Therefore, upon transporting the electronic wave function around the loop depicted in Figure 5, its phase is preserved. By the Longuet-Higgins theorem, this loop does not necessarily contain a conical intersection, in contradiction with the JT theorem.

The key to the correct answer is the fact that the conversion of one type-VI structure to another can also be brought about on the ground-state surface by a phase-inverting reaction, with a B_2 species transition state. This route is higher in energy than

Table 2. Calculated Energies (CASSCF(4,5)-DZV) of Some Species on the Two Lowest Singlet-State Surfaces of the Cyclopentadienyl Cation (kcal/mol) (CASPT2 Values in Brackets)^a

species	energy ^b	$\Delta E(S_1 - S_0)^c$
type VI (A_1)	0	21.8 (B_2)
type V (A_1)	0.6 [0]	22.6 (B_2)
type VII (B_2)	10.3 [2.5]	0.9 [4.5] (A_1)
JT CI	12.9	
secondary CI	10.3 [4.8]	

^a The ground state is a triplet state at -5.1 kcal/mol. ^b At the optimized geometry with respect to type VI. ^c The symmetry of the excited state in parentheses.

the phase-conserving one but provides a simple explanation for the JT splitting. The two type-VI species differ by the spin-pairing of four electrons. Inspection shows (Figure 8) that the *out-of-phase* combination of two A_1 structures is in fact a B_2 one, type VII. It may be conceived as a three-electron combination spread over four carbon atoms. A single electron resides largely on the fifth carbon atom.

Type-VI and type-VII structures can be formed from the symmetric D_{5h} structure by the e_1' -type distortion as shown in Figure 9, in accord with the JT theorem.

The ground-state B_2 structure of the cyclopentadienyl cation was not studied extensively. In ref 18, a B_2 -type moiety was referred to as an electronically excited state. At the geometry of the A_1 ground state, this is indeed the case. However, according to the JT theorem, for certain geometries *it should be part of the ground state*, close to the degeneracy location. This requirement is also obvious, if this structure is indeed a transition state between two ground-state species. It turns out that it is not easy to determine the exact structure of the ground-state B_2 structure: it lies very close to the D_{5h} degeneracy.

We searched for it in the following manner. The exact geometry of the system at the degeneracy point was obtained under a D_{5h} symmetry constraint. The CC bond distance r_{CC} for the symmetric D_{5h} cation at the conical intersection was found by calculating the energy of this perfect pentagon point by point with different r_{CC} values. A minimum energy was obtained at $r_{CC} = 1.437$ Å. At this point, the D_{5h} symmetry was removed, and a search for an electronic state of B_2 symmetry was conducted. A structure with the geometry shown in Figure 10 was found. At this geometry, the B_2 species (type VII) is lower in energy than any other and, therefore, lies on the ground-state surface. *The A_1 structures are of higher energy* and, thus, lie on excited states surfaces, even if by a small margin. For the type-V structure, the energy difference is 0.9 and 4.5 kcal/mol at the CASSCF and CASPT2 levels of theory, respectively. The calculated energetics of this system are summarized in Table 2. It is noted that the type-VII structure is very slightly distorted from the perfect pentagon, in agreement with previous results.¹⁸ The average CC bond distances of all four ground-state species shown in Figure 10 are almost equal: Those of the two A_1 species are 1.440 Å, and those of the B_2 and D_{5h} species are 1.437 Å. The B_2 species (type VII) is clearly distinct from the A_1 species as far as the charge distribution is concerned: the positive charge is centered near one of the bases, rather than at a vertex.

Starting at the B_2 species on the ground-state surface and going either way to the nearest type-VI structure, the energy decreased—*thus, the type-VII species is indeed a transition state*

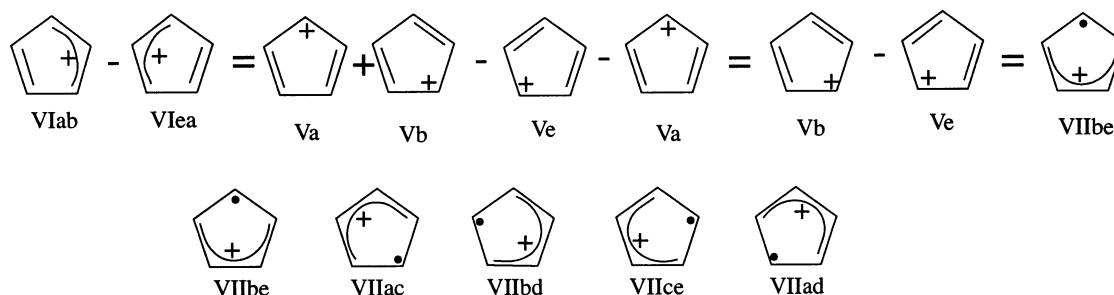


Figure 8. Top: One of the allylic type-VII (B_2 symmetry) structures, formed by out-of-phase combination of type-VI structures. Bottom: The five type-VII structures.

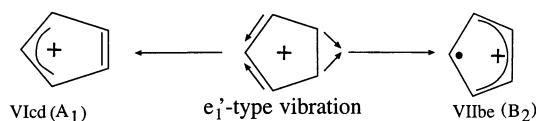


Figure 9. Effect of phase-preserving component of the degenerate e_1' vibrating mode. It may be regarded as a major component of the reaction coordinate that leads to the type-VI A_1 structure (going left, one phase of the mode). Going right, the other phase of the same vibration, the B_2 species is formed. (A Type-V structure is also obtained along the same coordinate, see Figure 14).⁴²

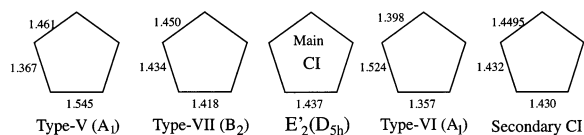


Figure 10. Calculated (CASSCF(4,5)/DZV) structures (distances in Å units) of the ground-state species V(A_1), VII(B_2), and VI(A_1) of CPDC and the conical intersections. The two A_1 structures are minima, the B_2 structure is a transition state between two type-VI structures (not shown, see Figure 11).

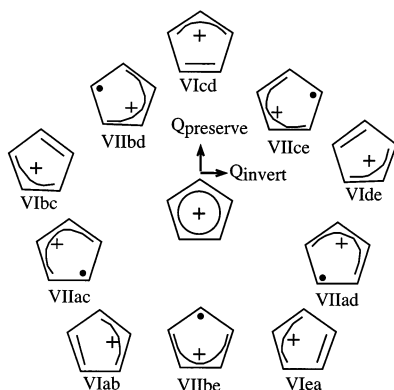


Figure 11. Phase-inverting loop accounting for the pseudorotation motion around the degeneracy in the cyclopentadienyl cation. The phase-inverting and phase-preserving components of the degenerate distorting e_1' coordinate are shown.

between two A_1 symmetry species (type VI). The situation is summarized in Figure 11, which shows the proposed Longuet-Higgins loop for the cyclopentadienyl cation. It uses type-VI anchors, with type-VII B_2 structures as transition states between them. This situation is fully analogous to that of the radical (Figure 3). Since the loop is phase inverting, a conical intersection should be located at its center—as required by the JT theorem.

At the equilibrium geometry of both A_1 ground-state structures, the B_2 structure lies on an electronically excited state.

The energy separation between the states is 23.5 and 21.8 kcal/mol for type V and type VI, respectively.

V. Discussion

Va. Basic Assumptions of the Model. The JT theorem was not generally *proved* by its originators: in their paper, Jahn and Teller stated the theorem and checked individually each point group to verify that it holds.¹⁴ As lively noted in a recent short review,³⁷ an aura of mystery continues to be associated with the JT effect in the minds of many physicists and chemists. This may be due to the fact that the theorem is often stated in terms of *orbital electronic degeneracy*,³⁸ without explicitly recalling that the degeneracy of the *total electronic wave function* is concerned. Much discussion of JT systems involved molecular orbital theory, and reference was made to degeneracies of individual molecular orbitals.

The enigmatic character of the JT theorem may be due to the fact that while group theory helps in providing the symmetry type of the distortion, it does not point to the actual motion. In standard treatments, different vibrational modes have to be tested one by one, and their relevance is found by calculating the strength of the vibronic coupling.

Focusing on molecular systems (rather than crystal defects), we propose that the nature of the important distortive motion may be determined on the basis of two principles: (1) the Longuet-Higgins phase-change theorem and (2) the conservation of chemical bonds (in terms of spin-pairing) upon small distortions.

Thus, we emphasize the importance of the immediate neighborhood of the degeneracy, rather than the degeneracy point itself.

In the case of the cyclopentadienyl radical or cation, the smallest change from the D_{5h} geometry is obtained by keeping each carbon atom bonded to two other C atoms and one hydrogen atom. This leads to the structures proposed in sections III and IV. The creation of new 1,3 bonds, for instance, would lead to a more strained system and, thus, requires investment of more energy. Therefore, structures III and IV are not considered as being important in the immediate neighborhood of the JT degeneracy.

Vb. The Nature of the Anchors and of the Chemical Reactions in Highly Symmetric Systems. The spin-paired type-I structures of CPDR are five different anchors, as they

(37) Ham, F. S. *J. Lumin.* **2000**, *85*, 193.

(38) A statement of the JT theorem given in ref 37 is: “Every nonlinear molecule or crystal defect that has orbital electronic degeneracy when the nuclei are in a symmetrical configuration is unstable with respect to at least one asymmetric distortion of the nuclei which lifts the degeneracy”.

possess different spin-pairing schemes. The same status holds for the five type-V structures of CPDC. In both cases, the conversion of one species to another is barrierless, in discord with the usual standard for chemical reactions. One could consider the system (“Mexican hat”) as a chemical entity in which the electrons are moving freely along a “moat”,^{11,12,36} with the nuclei following suite. In the case of the cation, the positive charge is not smeared evenly along the moat; rather, it travels around it, and at any given moment the molecule is expected to have a well-defined geometry. In this respect, the situation is different from that of benzene, in which the electrons are delocalized.

Vc. The Cyclopentadienyl Radical (CPDR). In this case, the Longuet-Higgins treatment agrees with previous analyses, based on classical JT predictions. The numerical results obtained in this work were essentially identical to those of previous workers.^{11–13} In ref 11, a π -space CI calculation using a basis set of STO-3G orbitals yielded an equal energy for the 2B_1 and 2A_2 structures. The more sophisticated calculation of ref 12 led to a small energy difference between them. A somewhat larger (but still very small) difference was obtained in this work. We believe that the minute calculated energy differences between the 2B_1 and 2A_2 structures on the ground state might be a computational artifact: The system exhibits a typical Mexican hat behavior. In ref 12, the two structures were referred to as different states. This appears to be misleading: Both structures lie on the same potential surface and, thus, belong to the same *state*—the ground state of the system.

The symmetries and relative energies of the low-lying electronic states of CPDR can be deduced from an analysis based on the polyelectronic wave functions. This is done by using the five equivalent type-I B_1 VB structures (or, equivalently, the five A_2 , type-II structures) as a basis set. These structures are strictly equivalent only in D_{5h} symmetry, so that the order applies only in this high symmetry. One gets the order ${}^2E_1'' < {}^2A_2'' < {}^2E_2''$ (see the Appendix).

Vd. The Cyclopentadienyl Cation (CPDC). The case of the cation appears to be more complex than that of the radical. Borden and Davidson¹¹ concluded that the splitting due to the first-order JT effect is small and did not report a stationary point for the 1B_2 structure on the ground-state surface. They found that two 1A_1 structures have minima on the lowest singlet potential surface that happen to be isoenergetic. In their Figure 1 (reproduced in this paper as Figure 5) only A_1 -type states are shown as responsible for removing the JT degeneracy, in contradiction with the basic principle of the JT effect.

Feng et al.¹⁷ discussed the 1B_2 structure (their $\Theta(E) - \Theta(F)$ structure) but did not calculate its minimum energy geometry. Lee and Wright¹⁸ have calculated the energy of the 1B_2 structure using various methods. In most cases, it was found to be a transition state, as found in this work. This molecule requires the use of configuration interaction; single configuration methods cannot faithfully analyze it. In reference,¹⁸ the different structures were referred to as “states”, regardless of whether they were all lying on the ground-state surface.

Figure 11 does not represent the full complexity of this system. In Figure 12, we reproduce the lower part of the figure (together with the D_{5h} degeneracy) and add structure Va, which is an in-phase combination of the structures VIab and Vlea.³⁹ The loop formed between the three anchors (VIab, Vlea, and

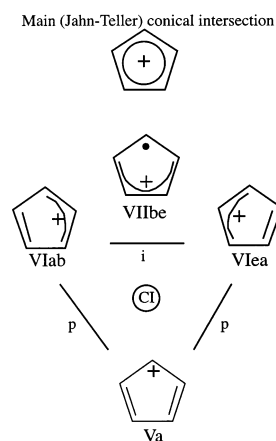


Figure 12. Loop between two type-VI and one type-V anchors showing how a second conical intersection (CI) arises in the CPDC system. The two structures VIab and Vlea may be connected on the ground-state surface by two routes: one a phase-inverting route, with a VIIbe transition state, the other a phase-preserving route, via a type-V stable structure.

Va) is an ip^2 loop^{20–22} and therefore phase inverting. It must encircle another conical intersection, which is not a JT type. The CPDC system is thus an example of several adjacent degeneracies. The loop suggested by ref 11 encloses in fact *six* neighboring degeneracies, rather than a single one, and is phase preserving. However, the removal of the D_{5h} degeneracy *is due to the first-order JT effect* and leads to the expected 1A_1 and 1B_2 structures. As correctly noted in ref 11, two deep minima due to A_1 -type structures are dominant in the ground-state potential surface, and a computational study may miss the small part occupied by the B_2 structure. A further difficulty arises from the fact that the 1B_2 structure is a transition state on the ground-state potential surface and lies at a higher energy than both 1A_1 structures and only slightly lower than the D_{5h} symmetric structure.

We calculated the properties of the secondary conical intersection at the CASSCF and CASPT2 levels. It is found to lie very near to the nearest B_2 structure at the CASSCF level -0.05 kcal/mol. At the CASPT2 level, it is 2.3 kcal/mol higher.

Figure 13 shows a schematic representation of the potential surface near JT degeneracy.

Ve. A Comment on the Problem of Neighboring Conical Intersections. A final comment concerns the presence of other conical intersections near the central one. They are enclosed by loops consisting of two A_1 (type VI) and one A_1 (type V) species, as depicted in Figure 14. These are ip^2 phase-inverting loops.^{21,22} Thus, the main JT degeneracy is surrounded by five further degeneracies, arranged in a symmetrical fashion.

As is evident from Figure 14, there are many touching points between the ground and excited states. The structures shown are all on the ground-state surface.

The analysis of the CPDC JT effect using the Longuet-Higgins loop method can be used to address the issue of the loop’s size and the number of conical intersections near a JT degeneracy. If we carry the system around a loop encircling all six degeneracies, the total electronic wave function will not change sign, although there are several degeneracies enclosed by the loop. This apparent violation of the phase-change theorem relates to the “radius” of the loop, as discussed by several

(39) The in-phase transition state between VIab and Vlea is the combination $2V_a + V_b + V_c$. The dominant term is V_a , which we use in Figure 12.

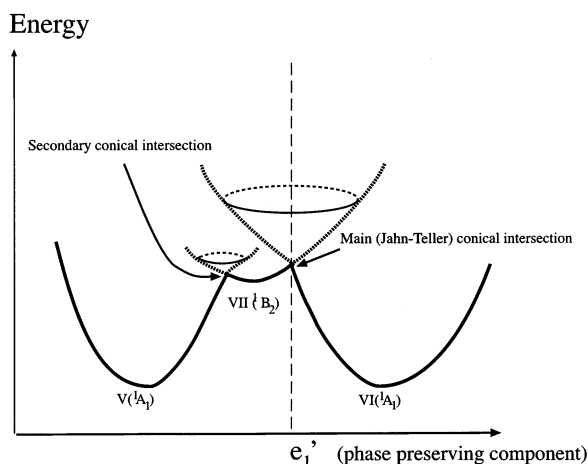


Figure 13. Cut across the ground-state potential surface of CPDC along the Jahn–Teller distorting coordinate e_1' (phase-preserving component), showing the approximate location of structures V, VI, and VII and the two conical intersections. The full heavy line denotes the ground-state surface, and the dotted heavy line denotes the excited state. Structure VII is a transition state between two A-type structures (not shown).

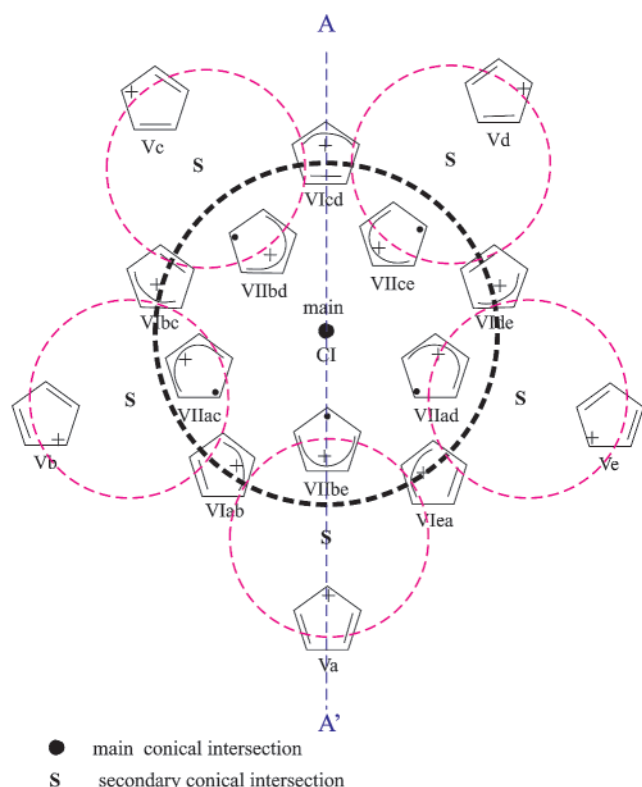


Figure 14. Main symmetric conical intersection of cyclopentadienyl cation and five secondary conical intersections around it. The AA' line is along the phase-preserving coordinate shown in Figure 13.

authors.^{40,41} Zwanziger and Grant⁴¹ showed that in the case of the $2^2E'$ state of Na_3 three degeneracies are found nearby the main Jahn–Teller one. They analyzed the system in terms of linear and quadratic coupling terms between the ground and

the excited states. Our discussion of the cyclopentadienyl cation shows how a problem of this nature is treated by the spin-pairing model. The extra five satellite conical intersections of CPDC arise from the fact that there are more spin-paired functions surrounding the main degeneracy point. In the case of the first degeneracies of the H_3 and Na_3 systems, the lowest $2^2E'$ state ($1^2E'$) displays a single degeneracy. The Zwanziger–Grant effect arises in the *second* $2^2E'$ state, since other spin pairing structure with similar energies are possible on the excited state surface, for instance such that involve 3p electrons. Due to symmetry, only three such structures are possible, giving rise to three secondary loops, in analogy with the five loops shown in Figure 14.

VI. Conclusion

The Longuet-Higgins loop method was used to determine the distortive coordinates leading to the removal of the JT degeneracy in the cyclopentadienyl radical and cation. Using VB structures, it is found that the distortive coordinates are uniquely identified. The Jahn–Teller distortion of the cation was shown to be on the same footing as that of the radical—both are due to a linear term. The ground-state 1^1B_2 species of the cation is a transition state, which lies at a higher energy than the 1^1A_1 species and close to the D_{5h} degeneracy. Therefore, it is rather difficult to locate computationally. It is also shown that the main JT degeneracy of the cation is surrounded by five neighboring non-JT conical intersections. The exact energies of all these structures are difficult to compute by standard methods, since the Born–Oppenheimer approximation breaks down in the vicinity of the conical intersection. Their presence is, however, guaranteed by the Longuet-Higgins phase-change theorem.

Appendix

Construction of the Longuet–Higgins Loops for the Cyclopentadienyl Radical and the Nature of the Electronic States Using the VB Method. In section IIIb, Figure 3 shows the Longuet-Higgins loop appropriate for this radical. Here, we rationalize the choice of this loop over other possibilities, for instance, a loop in which the lone electron moves sequentially to a neighboring atom (Figure 15). In addition, we outline the derivation of the properties of the low-lying doublet states of CPDR. The treatment follows an earlier report on aromaticity and antiaromaticity⁴³ and is based on standard VB theory.^{44–46}

Consider the five equivalent spin-pairing structures type I of CPDR (B_1 symmetry) (Figure 1), whose multiplicity is taken to be doublet. The VB functions are constructed of five p-electrons only.

The polyelectronic wave function of Ia, in which the bonds are between atoms 1 and 2 and between 3 and 4, may be written as a sum of four determinants whose traces are written in the standard shorthand notation:^{43,45,46}

$$|Ia\rangle = \bar{1}\bar{2}\bar{3}\bar{4}\bar{5} - \bar{1}\bar{2}\bar{3}\bar{4}5 - \bar{1}\bar{2}\bar{3}\bar{4}5 + \bar{1}\bar{2}\bar{3}\bar{4}5 \quad (\text{A1})$$

(40) Yarkony, D. R. *Rev. Mod. Phys.* **1996**, *68*, 985.

(41) Zwanziger, J. W.; Grant, E. R. *J. Chem. Phys.* **1987**, *87*, 2954.

(42) The VIIbe structure on the ground state surface is a transition state between two other type-VI structures, VIab and VIea, see Figure 11 and the accompanying discussion. This is an antiaromatic transition state, with a relatively high barrier. An aromatic transition state, with a vanishing barrier, is structure Va (see also Figure 14).

(43) Zilberg, S.; Haas, Y. *Int. J. Quantum Chem.* **1999**, *71*, 133.

(44) Pauling, L. *J. Chem. Phys.* **1933**, *1*, 280.

(45) Eyring, H.; Walter, J.; Kimball, G. E. *Quantum Chemistry*; Wiley: New York, 1944; Chapter 13.

(46) McWeeney, R.; Sutcliffe, B. T. *Methods of Molecular Quantum Mechanics*; Academic Press: New York, 1966; Chapter 6.

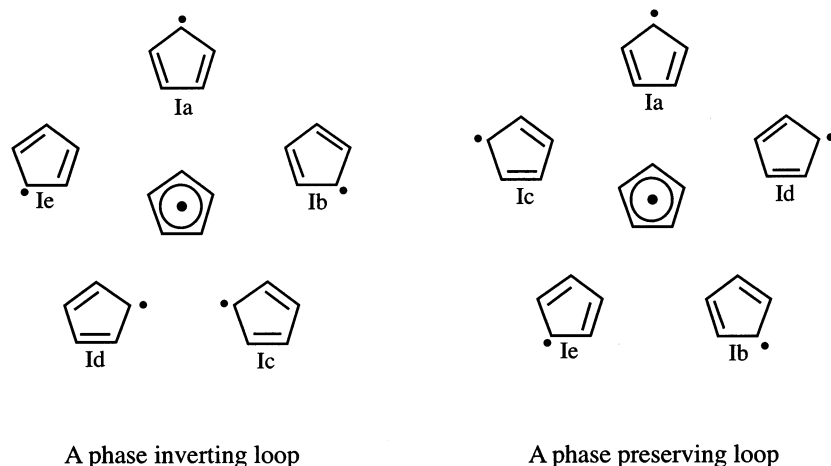


Figure 15.

This form includes all possible spin permutations for structure Ia. A shorthand notation for this wave function is:

$$|Ia\rangle = (\bar{1}\bar{2} - \bar{1}2)(3\bar{4} - \bar{3}4)5 \quad (A2)$$

Likewise

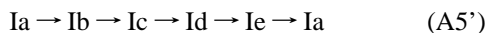
$$|Ib\rangle = (\bar{1}\bar{2} - \bar{1}2)3(\bar{4}\bar{5} - \bar{4}5) = \bar{1}\bar{2}3\bar{4}\bar{5} - \bar{1}\mathbf{2}\mathbf{3}\mathbf{4}\bar{5} - \bar{1}234\bar{5} + \bar{1}\mathbf{2}\mathbf{3}\mathbf{4}5 \quad (A3)$$

$$|Ic\rangle = 1(2\bar{3} - \bar{2}3)(\bar{4}\bar{5} - \bar{4}5) = 1\bar{2}\bar{3}\bar{4}\bar{5} - 1\bar{2}3\bar{4}\bar{5} - \bar{1}\bar{2}3\bar{4}\bar{5} + \bar{1}\mathbf{2}\mathbf{3}\mathbf{4}\bar{5} \quad (A4)$$

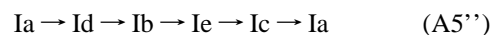
It is evident that Ib contains two terms that appear in Ia (highlighted by boldface characters), while Ic contains only one (boldface italics). By symmetry, Ie also has two terms appearing in Ia, while Id has one. Furthermore, the signs of the two terms in Ib are opposite to the signs in Ia. On the other hand, the sign of the highlighted term in Ic is the same as in Ia.

The transition state between two structures may be written as the combination of the two VB forms representing them, with appropriate coefficients. We note that the reaction converting Ia to Ib involves the re-pairing of three electrons—an allyl-type transition state is involved. This transition state is known to be the out-of-phase combination of the reactant and product.^{47,48} On the other hand, the transition between Ia and Ic involves the re-pairing of all five electrons and is phase preserving.^{43,49} The stabilization of the transition state is determined by cross-term integrals of the form $\langle Ia|H|Ib\rangle$ for the allyl-type transition state and $\langle Ia|H|Ic\rangle$ for the in-phase transition state. As discussed in ref 43, and further elaborated below, the main stabilization of these cross-terms is due to equal determinants on the left- and right-hand sides of the integrals (see eq A13 and the discussion following it).

In the case of the three-electron allyl-type case, there are two such stabilizing terms, while for the five electrons in-phase one, only one. Therefore, the allyl-type reaction lies on a lower energy surface—the ground state. The other reaction has a higher barrier. The loop shown in Figure 3 runs the sequence



and is the lowest lying loop in this system. It consists of five phase-inverting reactions and therefore encloses a conical intersection. The other loop runs the sequence



If it were the loop relevant to the ground state, no conical intersection is expected within it.

Next, we show by using the same VB functions how the symmetry properties and the energy sequence of the ground state and two low-lying doublet states may be derived.

In D_{5h} symmetry, these five doublet wave functions (Ia–Ie) are degenerate. They form a basis for a reducible representation Γ_{red} of the group. Standard methods show that the representation is the direct sum of three irreducible representations (irreps) of the group:

$$\Gamma_{\text{red}} = A_2'' \oplus E_1'' \oplus E_2'' \quad (A6)$$

The E-type irreps are 2-fold degenerate. Two basis functions are needed for them; a convenient choice is such that one will be phase preserving (ϕ_+), the other phase inverting (ϕ_-).

The normalized combinations of the basis set forming the wave functions transforming according to these irreps are (the numerical coefficients arise from the group theoretical treatment)

$$\phi(A_2''): (1/\sqrt{5})(Ia + Ib + Ic + Id + Ie) \quad (A7)$$

$$\phi_+(E_1''): 0.632Ia - 0.512(Ib + Ie) + 0.195(Ic + Id) \quad (A8)$$

$$\phi_-(E_1''): 0.601(Ic - Id) + 0.372(Ib - Ie) \quad (A9)$$

$$\phi_+(E_2''): 0.650Ia + 0.1(Ib + Ie) - 0.526(Ic + Id) \quad (A10)$$

$$\phi_-(E_2''): 0.372(Ic - Id) - 0.601(Ib - Ie) \quad (A11)$$

The energy order of these states may be estimated by evaluating the integral $\langle \phi_i|H|\phi_i\rangle$ for each state. These integrals

(47) Salem, L. *Electrons in Chemical Reactions: First Principles*; Wiley: New York, 1982.

(48) Voter, A. F.; Goddard, W. A., III. *Chem. Phys.* **1981**, *57*, 253.

(49) Zilberg, S.; Haas, Y. *Adv. Chem. Phys.*, in press.

are sums of integrals of the form $\langle I_x | H | I_y \rangle$ with the appropriate coefficients. For instance, the energy of $\phi_+(E_1'')$ is given by

$$\langle 0.632I_a - 0.512(I_c - I_d) + 0.195(I_b + I_e) | H | 0.632I_a - 0.512(I_c - I_d) + 0.195(I_b + I_e) \rangle \quad (\text{A12})$$

These expression contains terms such as $\langle I_x | H | I_x \rangle$, which are similar to all functions, and cross terms such as $\langle I_x | H | I_y \rangle$, which can contribute to stabilization or destabilization. As an example, consider the term

$$\langle I_a | H | I_b \rangle = \langle \bar{12345} - \bar{12345} - \bar{12345} + \bar{12345} | H | \bar{12345} - \bar{12345} - \bar{12345} + \bar{12345} \rangle \quad (\text{A13})$$

This cross term contains contributions from Coulomb and exchange integrals. As shown previously, the exchange integral contains the attractive interaction between two nuclei and the electron charge between them, and this is the dominant contribution. Because of the orthogonality of the spin functions, only integrals containing equal determinants on the left and right hand (such as $\langle \bar{12345} | H | \bar{12345} \rangle$) are important.^{43,46} One finds two such cases in equation A13: They represent the extra bonding due to the 3 electrons that occupy the orbitals on atoms 3, 4, and 5. This stabilization is due to an allyl-type resonance that arises from the out-of-phase combination of structures Ia and Ib.^{47,48} Inspection of eqs A1 and A3 shows that indeed the determinants $\bar{12345}$ and $\bar{12345}$ appear with opposite signs in Ia and Ib. (Ie is equivalent to Ib in that respect.) It is also noted

that the coefficients of Ia and of (Ib + Ie) are the largest one in equation A8, so that they dominate the overall integral.

On the other hand, for $\phi_+(E_2'')$ one finds that the coefficients for Ia and (Ib + Ie) have the same sign, leading to destabilization.

The term

$$\langle I_a | H | I_c \rangle = \langle \bar{12345} - \bar{12345} - \bar{12345} + \bar{12345} | H | \bar{12345} - \bar{12345} - \bar{12345} + \bar{12345} \rangle \quad (\text{A14})$$

has only one common determinant on the opposite sides. Therefore, its contribution to stabilization is smaller. In this case, stabilization arises from terms having equal signs (positive overlap integral between near neighbors). Thus, this term also contributes to the stabilization of $\phi_+(E_1'')$.

Inspection of eq A10 shows that for $\phi_+(E_2'')$ the same factors cause destabilization. Therefore, this state is higher in energy. The case of $\phi(^2A_2'')$ is intermediate—it lies at a higher energy than $\phi_+(E_1'')$ and at lower energy than $\phi_+(E_2'')$.

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