The Jahn-Teller and Related Effects in the Cyclopentadienyl Radical, Part I: The *Ab Initio* Calculation of Spectroscopically Observable Parameters

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Abstract

*Ab initio* calculations are performed for the $\tilde{X}^2E^\prime_1$ and $\tilde{A}^2A^\prime_2$ states of the cyclopentadienyl radical. An important goal of these calculations is to guide the analysis of the experimentally observed $\tilde{A}^2A^\prime_2-\tilde{X}^2E^\prime_1$ electronic spectrum. Vibrational frequencies for both the $\tilde{X}$ and $\tilde{A}$ state are reported. Large changes
in frequency between the states for out-of-plane vibrations are found, leading to the expectation that
overtones of these modes will appear strongly in the spectrum. Additionally, spectrosopically obtainable
parameters describing the Jahn-Teller effect are calculated for the $\tilde{X}$ state. Using all this information
the $\tilde{X} - \tilde{A}$ electronic spectrum is predicted for both $\text{C}_5\text{H}_5$ and $\text{C}_5\text{D}_5$. 

1 Introduction

The cyclopentadienyl radical (C$_5$H$_5$) is a well-known intermediate and building block of organic and organometallic compounds. It has also been a favorite target of spectroscopists and theoreticians for nearly half a century. Besides its central role in organic chemistry, its allure has been heightened by its $^2E''_1$ ground state that is subject to a Jahn-Teller distortion, which was first observed in condensed phase electron paramagnetic resonance (EPR) spectra of the radical.$^{1-5}$

Following the early EPR observations, a number of experimentalists have reported the spectroscopy of the isolated radical. Most of this work centered on the vibrational structure revealed by the $\tilde{A}^2A''_2 \rightarrow \tilde{X}^2E''_1$ electronic transition.$^6-10$ This work was supplemented by rotationally resolved work$^{11-13}$ on this transition’s origin band and photo-detachment experiments$^{14}$ on C$_5$H$_5^-$.

Because of its simple hydrocarbon nature, calculation of the Jahn-Teller distortion in the ground state of cyclopentadienyl proved a tempting target for early ab initio calculations. Liehr appears to have pioneered$^{15,16}$ this effort in 1956. There were additional contemporary calculations by Snyder$^{17}$ and Hobey and McLachlan.$^{18}$ After a hiatus of nearly 20 years, more sophisticated calculations were performed in the late 70’s by Meyer et al.$^{19}$ and Borden and Davidson.$^{20}$

For many years, the subject lay relatively fallow due to lack of both experimental and theoretical progress. However recently there has been much theoretical interest in the subject of conical intersections of electronic surfaces.$^{21-27}$ Molecules subject to Jahn-Teller interactions perforce have a conical intersection whose position is defined by the point group symmetry of the molecule. Indeed the Jahn-Teller conical intersection is probably the conical intersection that can be investigated most directly experimentally. Recently, new calculations of the conical intersection and the Jahn-Teller effect in cyclopentadienyl have been reported.$^{28,29}$

In most of the previous calculations, considerable effort has been expended to calculate the Jahn-Teller stabilization energy, which we denote as $\varepsilon_T$. Interestingly, calculated values of $\varepsilon_T$ have ranged from $\leq$500 cm$^{-1}$ to $\geq$5000 cm$^{-1}$, with no obvious convergence as a function of time or choice of methods. Another frequently calculated property has been the distorted geometry of C$_5$H$_5$. Rarely has the complete geometric distortion (from D$_{5h}$ symmetry) been calculated, but in almost all cases the variation of the C–C bond length around the ring has been calculated. This part of the distortion can be quantified in terms of a simple
parameter, $\Delta R_{CC}$, giving the magnitude of the maximum deviation of the bond length from equilateral. Calculated values of $\Delta R_{CC}$ have varied by just over a factor of two, from 37 to 75 milli-Ångstroms.

A central question for both experimentalists and theoreticians has been the nature of the distortion in C$_5$H$_5$. From a simple analysis of the molecular orbitals (see Fig. 1), it is clear that the distortion away from the D$_{5h}$ symmetry can lead to either a dienyl structure (Ia in Fig. 1), with two C-C double bonds and a localized radical, or an allyl structure (Ib in Fig. 1), with one double bond and one allyl resonance. Much of the prior discussion of the Jahn-Teller distortion in C$_5$H$_5$ has focused on which of these structures will be lower in energy. The literature on C$_5$H$_5$ appears to favor the opinion that the dienyl structure is lower than the allyl structure. As we show in this and the following paper, the two geometries are equivalent in energy.

In the succeeding paper, hereafter called Part II, we report and analyze newly acquired spectral results for the cyclopentadienyl radical. The resolved emission spectra from different vibrational levels of the $\tilde{A}$ state provide a detailed map of the $\tilde{X}$ state vibronic structure. These spectra have very complex vibrational structure, which require the aid of ab initio calculations for a proper interpretation. The previous calculations have neither reached a consensus on the nature of the Jahn-Teller distortion in cyclopentadienyl, nor calculated many parameters useful for spectral analysis; therefore we have undertaken a new series of calculations of the radical with the explicit goal of predicting molecular parameters contained in the spectral analysis. Recent work has presented approaches to apply the results of ab initio calculations to the analysis of the experimental spectra of Jahn-Teller active molecules. In this paper we apply and extend these approaches for the presently observed, quite complicated, spectra of cyclopentadienyl.

It is important to remember that experimentally observed electronic spectra reveal not only Jahn-Teller active vibrations but also other allowed transitions to totally symmetric fundamentals, overtones, and the like. As noted above, the data in Part II include emission spectra from several different $\tilde{A}$ state vibrational levels. These complementary spectra help assign the $\tilde{X}$ state vibronic levels, but only if the $\tilde{A}$ state vibrational assignments are known. Therefore we have performed calculations that help assign the $\tilde{A}$ state levels, as well as those of the $\tilde{X}$ state.

The remainder of this paper is arranged as follows. The Hamiltonian used to interpret the spectroscopic results is briefly reviewed. The molecular parameters contained therein are explicitly related to characteristics
of the potential energy surface (PES) obtainable at various points from the \textit{ab initio} calculations. Results from several calculations for the $\tilde{A}$ and $\tilde{X}$ state are given. The \textit{ab initio} results are then used to predict specific molecular parameters relevant to the spectral analysis. Finally, the various computational results are compared, particularly with respect to their consistency and usefulness for the spectral analysis. Part II contains the complete analysis of the spectra, using these calculations as the foundation of the analysis.

2 The cyclopentadienyl potential energy surface

2.1 General features

The PES of cyclopentadienyl is of course a function of its $3N - 6 = 24$ vibrational degrees of freedom. Fig. 2 illustrates the Jahn-Teller distortion away from the $D_{5h}$ geometry. The figure corresponds to a plot of the $\tilde{X}$ state PES along the two degrees of freedom that resolve the degeneracy. Fig. 3 is an illustration of a slice through the PES of Fig. 2. Fig. 3, which also includes the $\tilde{A}$ state, can be used to schematically illustrate the spectroscopic problem at hand. Structure observed in the $\tilde{A}^2A'' - \tilde{X}^2E''_1$ electronic transition corresponds to the positions of the vibronic levels within the $\tilde{A}$ and $\tilde{X}$ states. Consequently, any valid representation of the $\tilde{A}$ and $\tilde{X}$ state surfaces must yield vibronic structure consistent with the experimental results.

The excited $\tilde{A}^2A''_2$ state is not degenerate and its minimum energy (see Fig. 3) is easily determined by standard \textit{ab initio} calculations to be at the $D_{5h}$ geometry denoted by $X_1$. The energy at $X_1$ and the corresponding vibrational frequencies were calculated using the CASSCF method in Gaussian 98,\textsuperscript{33} with a 6-31G* basis set and an active space which included the five $\pi$ electrons in the five $\pi$ orbitals, abbreviated CAS(5,5)/6-31G*.

A glance at Fig. 2 or 3 clearly illustrates that the $\tilde{X}$ state represents a more complicated problem. In $D_{5h}$ symmetry (the point labelled $X_0$ in Fig. 3), the $\tilde{X}$ state is doubly degenerate. However, the Jahn-Teller theorem assures us that the degeneracy may be removed by a suitable molecular distortion. Indeed, it is well recognized today that the degeneracy of a conical intersection of this nature can be removed by movement along (at most) two orthogonal coordinates, which are designated $Q_a$ and $Q_b$ in Fig. 2. As with any pair of
orthogonal coordinates we can write

$$Q_\pm = (Q_a \pm iQ_b) = \rho_{JT}e^{\pm i\phi_{JT}}$$

(1)

The ordinate of Fig. 3 can then readily be recognized as $\rho_{JT}$ with the slice through the PES of Fig. 2 taken at any value of $\phi_{JT}$, since as we shall see there is no dependence of the PES on $\phi_{JT}$.

The fundamental goals of the experimental and theoretical work are essentially to determine (i) the Jahn-Teller stabilization $\varepsilon_T$ (the energy difference between $X_0$ and $X_{\text{min}}$, see Fig. 3); (ii) the geometries $X_0$ and $X_{\text{min}}$ in Fig. 3, and the distance between them, $\rho_{\text{min}}^{\text{JT}}$; and (iii) an expression of the Jahn-Teller distortion vector in some independently defined coordinate system, e.g., the normal coordinate system.

It might appear that these three goals would be straightforward to accomplish via ab initio calculations. However, the complexity of the electronic surfaces have made this far from a simple problem for any Jahn-Teller molecule. Indeed, as mentioned in the introduction, ab initio calculations of property (i), the Jahn-Teller stabilization energy, have ranged over more than an order of magnitude.

The situation has not been much better in terms of experiments. Although there are now numerous known spectra revealing vibronic structure determined by a Jahn-Teller distorted PES,\textsuperscript{34} there is as yet arguably no case when the experimental data have determined all three of the above mentioned pieces of information. Succinctly put, this is a result of the well known broader problem of obtaining sufficient experimental data to uniquely determine a PES.

Ideally one would like to use ab initio calculations to provide a reasonably good estimate of the PES, and in turn use experimental data to refine the PES as precisely as possible. This approach requires connecting the PES to the experiment through the observed vibronic structure. One way to do this is to numerically solve the $(3N - 6)$--dimensional vibrational Schrödinger equation on a PES determined either directly or indirectly by ab initio calculations. This approach has been successfully utilized\textsuperscript{35–37} for the metal trimers, Na$_3$ and Li$_3$, which have 3 vibrational degrees of freedom, two of which are the doubly degenerate Jahn-Teller active vibration. However, such calculations are as yet impractical for larger systems, in particular for cyclopentadienyl with its 24 vibrational degrees of freedom, 8 of which are spanned by the 4 doubly degenerate Jahn-Teller active modes.
We have previously demonstrated\textsuperscript{31} that considerable progress in the interpretation of the spectra of Jahn-Teller active molecules can be accomplished using \textit{ab initio} calculations to estimate certain molecular parameters that have long been used to analyze experimental spectra. Essentially these parameters characterize simple models of the PES near the conical intersection and the global minimum. In this paper, we apply the method developed in reference 31, and a closely related method, developed in this work, to the vibronic structure of the C\textsubscript{5}H\textsubscript{5} radical.

Later in this section we quantify the connection between the molecular parameters and quantities available from \textit{ab initio} calculations. Before proceeding to these details it is worthwhile to overview the situation. Fig. 3 suggests two alternative approaches to the problem. In each approach \textit{ab initio} information is required at both X\textsubscript{0} and X\textsubscript{min}; however, the nature of the information used at these points differs in the two methods. Nonetheless in each method, normal modes (in terms of which we shall ultimately define the distortion vector) and vibrational frequencies are determined at X\textsubscript{0}. Such information is required to make contact with the experimental analysis, which uses X\textsubscript{0} as its reference point.

Method I uses the CASSCF formalism for the calculation of the geometries and energies of the points X\textsubscript{0} and X\textsubscript{min}. In this method, \(\varepsilon_T\) is defined\textsuperscript{31} by the difference in energy between the conical intersection and the global minimum, with each being determined with the same type of calculation. The direction of the Jahn-Teller distortion vector in the space spanned by the normal coordinates is determined from the derivative coupling vector (\(\vec{x}_2\) in Fig. 3). This vector is a by-product of the conical intersection calculation at X\textsubscript{0}. This vector is normalized to be consistent with the value of \(\varepsilon_T\) obtained from the energy calculations.

In Method II, which we introduce here, less emphasis is given to the energies of the CASSCF calculation, and more to the geometries. In Method II, the energy and distorted geometry are calculated at the global minimum. Advantage is then taken of the fact that in the Jahn-Teller problem, symmetry dictates that the conical intersection takes place at the D\textsubscript{5h} geometry for \(\tilde{X}^2E''\textsubscript{1}\) C\textsubscript{5}(H/D)\textsubscript{5}. The direction of the Jahn-Teller distortion vector is then determined as the difference between the D\textsubscript{5h} and the global minimum geometry. This approach completely defines the length and direction the Jahn-Teller distortion vector, \(\vec{d}\). With the distortion vector components known, we use the model potential to calculate the corresponding Jahn-Teller stabilization energies, \(\varepsilon_i\), along each normal mode and take their total as \(\varepsilon_T\), as does the experiment.
In both methods, the normal modes of the Jahn-Teller active vibrations are taken from a different calculation. Unfortunately, it is not presently possible to use the CASSCF methodology of Gaussian98 to calculate vibrational frequencies and normal coordinates at $X_0$. The generalized restricted Hartree-Fock (GRHF) method, available in CADPAC 5.2,\textsuperscript{38} calculates the normal coordinates and vibrational frequencies at $X_0$ for the average of the two surfaces of the ground state PES. Several different basis sets were used for the GRHF calculation to test the stability of the the normal coordinates and vibrational frequencies. All reported vibrational frequencies used a 6-31G* basis set. The GRHF frequencies were scaled by 0.89, while the CASSCF frequencies of the excited state were scaled by 0.95.

The CASSCF calculations of the ground state used a 6-31G* basis set and defined the active space as the five $\pi$ electrons in the five $\pi$ orbitals, as was done for $X_1$. This calculation yielded the symmetric geometry, the energy of the conical intersection, and the derivative coupling vector. In practice, to establish a starting geometry and to set up the correct active space, the conical intersection calculation was preceded by a HF calculation on the nondegenerate cyclopentadienyl anion ground state.

The geometry and energy at $X_{\text{min}}$ were calculated using the CASSCF methodology with the same basis set and active space as the conical intersection calculation at $X_0$. To establish a starting distorted geometry and set up the correct active space, these calculations were preceded by a restricted Hartree-Fock (RHF) calculation, which converged to the distorted minimum. The vibrational frequencies at $X_{\text{min}}$ were computed to verify that the resulting geometry optimization was indeed a stationary state.

We also performed some calculations to test the affect the choice of basis set and active space had on the PES. In general, the Jahn-Teller parameters were not greatly affected by the basis set or active space. Further details can be found in reference 39.

2.2 The spectroscopic model of the Jahn-Teller PES

The natural coordinate system for the description of the Jahn-Teller effect is the two orthogonal vectors, $Q_a$ and $Q_b$, which span the space of the molecular distortion. However, the most convenient coordinate system for describing the motion of molecules is the 3N-6 normal coordinates, $Q_i$. Of course the Jahn-Teller coordinates, $Q_a$ and $Q_b$, constitute a subspace of the normal coordinate space and as such may be completely
described in terms of linear combinations of the normal coordinates. Hence we will in general work in the normal coordinate system and more specifically the normal coordinate system of the undistorted symmetric molecule.

The general Hamiltonian for our system is

$$\hat{H} = \hat{H}_T + \hat{H}_{SO} + \hat{H}_e$$

(2)

where $\hat{H}_T$ is the nuclear kinetic energy, $\hat{H}_{SO}$ is the spin-orbit coupling Hamiltonian, and $\hat{H}_e$ is the electronic Hamiltonian. Nominally the spin-orbit coupling is non zero for any open shell orbitally degenerate electronic state. However, the spin-orbit coupling in cyclopentadienyl has by all accounts$^{11-13}$ been quenched to much less than 1 cm$^{-1}$, therefore $\hat{H}_{SO}$ is discarded.

The secular determinant of this Hamiltonian in the basis of the two complex electronic wavefunctions of the degenerate state, $\Lambda_+$ and $\Lambda_-$, may be written

$$\begin{vmatrix}
\langle \Lambda_+ | \hat{H}_e | \Lambda_+ \rangle + \hat{H}_T - E & \langle \Lambda_+ | \hat{H}_e | \Lambda_- \rangle \\
\langle \Lambda_- | \hat{H}_e | \Lambda_+ \rangle & \langle \Lambda_- | \hat{H}_e | \Lambda_- \rangle + \hat{H}_T - E
\end{vmatrix} = 0$$

(3)

where $\Lambda_\pm$ are diabatic wavefunctions related to the real electronic wavefunctions, $\Lambda_a$ and $\Lambda_b$ by $\Lambda_\pm = 1/\sqrt{2}(\Lambda_a \pm i\Lambda_b)$. The adiabatic potential energy surfaces are then obtained by neglecting the nuclear coordinate dependence of $\Lambda_\pm$ and finding the roots of eq. 3 ignoring $\hat{H}_T$ yielding

$$V_\pm = \langle \Lambda_+ | \hat{H}_e | \Lambda_+ \rangle \pm \left(\langle \Lambda_+ | \hat{H}_e | \Lambda_- \rangle \langle \Lambda_- | \hat{H}_e | \Lambda_+ \rangle\right)^{1/2},$$

(4)

where $\langle \Lambda_+ | \hat{H}_e | \Lambda_+ \rangle = \langle \Lambda_- | \hat{H}_e | \Lambda_- \rangle$.

Although the potential, $V_\pm$, in principle may be completely calculated within the approximations of ab initio theory, it is useful to construct a Taylor series expansion and approximate $V_\pm$ by truncating this expansion at some reasonable level. It is this truncated expansion from which the Jahn-Teller theory for the experimentally observed vibronic structure has been derived and to which we must relate the results of the calculations.
The Taylor series expansion of the terms in the potential, $V_\pm$, expanded about the normal coordinates, $Q_i$, of the symmetric molecule has the form

$$
\langle \Lambda_r | \hat{H}_e | \Lambda_{r'} \rangle = \sum_{i=1}^{3N-6} \langle \Lambda_r \left| \left( \frac{\partial \hat{H}_e}{\partial Q_i} \right)_0 \right| \Lambda_{r'} \rangle Q_i + \sum_{i=1}^{3N-6-6} \sum_{j=1}^{3N-6} \left\{ \frac{1}{2} \left( \frac{\partial^2 \hat{H}_e}{\partial Q_i \partial Q_j} \right)_0 \right\} Q_i Q_j + \ldots \tag{5}
$$

up to second order in $Q_i$ where the subscript $r(') = \pm$ and the subscript 0 indicates that the derivatives are to be evaluated at $X_0$. At this point several of the terms in eq. 5 may be shown to be zero. The linear term for $r = r'$ will in general be zero if one chooses the point about which the expansion is centered to be the potential minimum. However the Jahn-Teller theorem assures us that this need not be true for the $r \neq r'$ terms. The second order terms with $i \neq j$ will be zero for the non-Jahn-Teller active normal coordinates, since by definition normal coordinates are the coordinates which bring the kinetic and potential energies simultaneously to a diagonal form. However these terms may be non-zero for the Jahn-Teller active normal coordinates since they are only truly normal coordinates of the molecule in the absence of any Jahn-Teller activity.

If we only consider the terms in eq. 5 up to quadratic in $Q_i$ and ignore the terms shown above to be zero we can write the diagonal and off diagonal terms of eq. 4 as

$$
\langle \Lambda_+ | \hat{H}_e | \Lambda_+ \rangle = \sum_{i=1}^{p} \left\{ \sum_{r=+, -} \frac{1}{2} \lambda_i |Q_i,r|^2 \right\} + \sum_{i=1}^{3N-6-2p} \frac{1}{2} \lambda_i |Q_i|^2 \tag{6}
$$

$$
\langle \Lambda_+ | \hat{H}_e | \Lambda_- \rangle = \sum_{i=1}^{s} \left\{ \sum_{r=+, -} k_i Q_i,r \right\} + \sum_{i=1}^{s} \sum_{r=+, -} \frac{1}{2} g_{ii} (Q_i,r)^2 \\
+ \sum_{i=1}^{s} \sum_{j=1}^{s} \sum_{r=+, -} \frac{1}{2} g_{ij} (Q_i,r Q_j,r) \\
+ \sum_{i=1}^{p} \left\{ \sum_{r=+, -} \sum_{j=1}^{3N-6-2p} \frac{1}{2} b_{ij} (Q_i,r Q_j) \right\} \tag{7}
$$

where $p$ and $s$ are the number of linear and quadratic Jahn-Teller active vibrational modes, respectively, and we have separated the summations over non degenerate and doubly degenerate normal coordinates and parameterized the potential. The parameters are the harmonic force constant $\lambda_i$, the linear Jahn-Teller
coupling coefficient $k_i$, the quadratic coupling coefficient between the same degenerate coordinate $g_{ii}$, the quadratic coupling coefficient between different degenerate coordinates, called the cross quadratic coupling coefficient $g_{ij}$, and the quadratic coupling coefficient between a degenerate coordinate and a non degenerate coordinate, called the bilinear coupling coefficient $b_{ij}$. The definition of each parameter is given in Table 1.

So far we have avoided specifying the symmetry of the degenerate Jahn-Teller active normal coordinates in order to retain the generality of the arguments. However if we explicitly consider the $D_{5h}$ point group, then certain terms of eq. 7 may be shown to be zero for certain symmetries of the degenerate normal coordinates by considering their transformation properties under $\hat{C}_n$ rotation. This approach has been taken in ref. 34. Following their derivation we may take eq. 26 of this reference and generalize it to include modes of different symmetries to give

$$
\left[ 2s_e + (-1)^{s_k} \sum_i s_v,i \right] \mod n = 0
$$

where $s_e$ and $s_v$ are determined by the electronic symmetry, $E_{s_e}$, and vibrational symmetry, $e_{s_v}$. Then for a given term in eq. 7 to be non zero a solution to eq. 8 must exist for $s_k = 0$ or 1. We can apply eq. 8 to $\tilde{X}^2E''_1$ cyclopentadienyl with $n = 5$ and $s_e = 1$ and determine which terms are non-zero in eq. 7 for our four doubly degenerate symmetry species, $e''_1$, $e''_2$, and $e'_2$.

From eq. 8, the linear term, $k_i$, is non zero for only the $e'_2$ and $e''_2$ normal coordinates. However following the arguments in ref 42 we note that the derivatives, which the parameters such as $k_i$ represent, must overall be symmetric with respect to reflection through a mirror plane, hence the $e''_2$ terms must be zero. The quadratic term $g_{ii}$ is non zero only for the $e'_1$ and $e''_1$ normal coordinates. The cross quadratic term, $g_{ij}$, is non zero for all terms between coordinates with $s_v = 1$ and $s_v = 2$, which have the same property with respect to reflection through a mirror plane. The bilinear coupling coefficient is non zero only for combinations involving the $a'_1$ and $e'_2$ coordinates.

From the above we note that the quadratic Jahn-Teller terms are zero for the linearly Jahn-Teller active $e'_2$ modes in $D_{5h}$ symmetry. Hence the moat in Fig. 2 must be equal potential. Similar conclusions, obtained by somewhat different arguments, have been reached before.14,43
In our work we will consider only the linear Jahn-Teller terms, \( k_i \), for \( e'_2 \) modes and the quadratic Jahn-Teller terms, \( g_{ii} \), for \( e'_1 \) and \( e''_1 \) in the expansion of the potential. The remaining non-zero terms, the cross quadratic terms, \( g_{ij} \), and the bilinear terms, \( b_{ij} \), are expected to be relatively small. Recent work by Höppel, Botschwina, and Köppel\(^4\) on the Jahn-Teller effect in the \( \tilde{X}^2E \) state of CH\(_3\)O has shown that the bilinear term, even when fairly large, has a relatively small effect on the vibronic spectrum. Likewise the vibronic spectrum of the more closely related molecules C\(_6\)F\(_6\)+ and C\(_6\)H\(_3\)+, which have the same number of \( \pi \) electrons as C\(_5\)H\(_5\), have been successfully analyzed\(^4\),\(^5\),\(^6\) without invoking either of these terms. Finally the goal of this work is not necessarily to achieve the most accurate PES for cyclopentadienyl, but rather provide reasonable estimates of the Jahn-Teller constants for the initiation of the vibronic analysis of the experimental spectra.

Applying the above arguments we can approximately write the PES as

\[
V_{\pm} = \sum_{i=1}^{2p} V^l_{\pm,i} + \sum_{j=1}^{3N-6-2p-2s} V^h_{\pm,j} + \sum_{k=1}^{2s} V^q_{\pm,k}.
\]

(9)

where

\[
V^l_{\pm,i} = \frac{1}{2} \lambda_i \rho_i^2 \pm k_i \rho_i
\]

(10)

\[
V^h_{\pm,j} = \frac{1}{2} \lambda_j Q_j^2
\]

(11)

\[
V^q_{\pm,k} = \left( \frac{1}{2} \lambda_k \pm g_{kk} \right) \rho_k^2
\]

(12)

where the minus signs should be taken for the lower sheet of the PES, assuming \( k_i \) and \( g_{kk} \) are positive. In the above we have switched to cylindrical coordinates, \( Q_{\pm,i} = \rho_i \exp \pm i \phi_i \), for the doubly degenerate normal coordinates. \( V^l_{\pm,i} \) adds the linear Jahn-Teller term to the harmonic oscillator to describe the linear Jahn-Teller PES seen only along the \( p(e'_2) \) normal coordinates. \( V^h_{\pm,j} \) describes the harmonic oscillator potential seen along any of the non-Jahn-Teller active normal coordinates. \( V^q_{\pm,k} \) adds the quadratic Jahn-Teller term to the harmonic oscillator to describe the quadratic Jahn-Teller PES seen only along the \( s(e'_1 \text{ and } e''_1) \) normal coordinates.

Considering any of the linear Jahn-Teller active \( e'_2 \) normal coordinates, \( Q_{\pm,i} \), from Eq. 10 the distance
from the symmetric point to the distorted minimum is

$$ \rho_i^{\text{min}} = -\frac{k_i}{\lambda_i} = \left( \frac{D_i \hbar}{\pi \omega_{e,i}} \right)^{1/2}, \quad (13) $$

where we have introduced the experimental parameters, $D_i$, the linear Jahn-Teller coupling constant, and $\omega_{e,j}$, the harmonic vibrational frequency evaluated at $X_0$ on the PES. They are related to the parameters in $V$ by

$$ D_i = \frac{k_i^2}{2\hbar} \lambda_i^{-3/2} \quad (14) $$

and

$$ \omega_{e,i} = \frac{\lambda_i^{1/2}}{2\pi}. \quad (15) $$

The magnitude, $\varepsilon_i$, of the Jahn-Teller stabilization energy, i.e. the depth of the minimum below zero taken at $X_0$, due to distortion along a Jahn-Teller active normal coordinate given by Eq. 8 by

$$ \varepsilon_i = \frac{k_i^2}{2\lambda_i} = D_i \omega_{e,i}, \quad (16) $$

with

$$ \varepsilon_T = \sum_{i=1}^{p} \varepsilon_i \quad (17) $$

being the total Jahn-Teller stabilization energy.

The quadratic Jahn-Teller coupling constant, $K_i$, defined as

$$ K_k = \frac{g_{kk}}{\lambda_k}, \quad (18) $$

is non-zero only for the $e'_1$ and $e''_1$ normal modes. It is apparent from eq. 12 that a non-zero quadratic
Jahn-Teller effect can only flatten the lower sheet and compress the upper sheet of the PES seen along the $e'_1$ and $e''_1$ normal coordinates. It does not move the energy minimum away from the $D_{5h}$ symmetry point of the PES as does the linear Jahn-Teller term. For this reason it has a much smaller effect on the spectroscopy than does the linear term. Moreover in cyclopentadienyl we have shown that the linear and quadratic Jahn-Teller problems are separable due to its $D_{5h}$ symmetry and hence have independent spectral effects. As such it is $D_i$ and $\omega_{e,i}$ in which we are most interested since they have the largest impact on the spectroscopy.

2.3 Relationship of the spectroscopic model and ab initio results

Before we develop the specific equations that define the two methods for deriving the Jahn-Teller constants from the ab initio calculations it is useful to make the following observations. Method I uses the derivative coupling vector, $\vec{x}_2$, to obtain $k_i$ and hence $D_i$ directly by projecting $\vec{x}_2$ onto the normal coordinates determined by the GRHF calculations.

In Method II the distortion vector $\vec{d}$ is obtained as the difference of the points $X_{\text{min}}$ and $X_0$. The projection of $\vec{d}$ onto the normal coordinates determined by the GRHF calculation yields $\rho_{\text{min}}^i$ and hence $D_i$ (via eq. 13). Thus in Method II we place greater confidence in the calculated distorted geometry, from which $\vec{d}$ is derived. The remainder of this section will detail the mathematics used to implement Methods I and II.

For either method I or II it is useful to note that vector, $\vec{Q}_i$, of arbitrary length along one of the normal coordinates, $i$, can be written

$$\vec{Q}_i = Q_i \vec{u}_{Q_i} = \sum_{\alpha} q_{ia} l_{\alpha i}^{-1} \vec{u}_a$$

with

$$q_{ia} = m_{\alpha i}^{1/2} x_{\alpha} = \sum_i l_{\alpha i} Q_i$$

The unit vector, $\vec{u}_{Q_i}$, points along the $i^{th}$ normal coordinate, while the unit vectors $\vec{u}_a$ point along the directions of the atomic Cartesian displacements, $(x_1, y_1, z_1, x_2, y_2, z_2 \ldots x_{3N}, y_{3N}, z_{3N})$. The transformation
matrix, $I$, with elements, $l_{\alpha i}$, is a $3N \times 3N$ unitary transformation that diagonalizes the mass-weighted force constant matrix in the atomic Cartesian system. This matrix is provided by the GRHF calculations at $X_0$, thereby determining the normal coordinates. From Eq. 19 and 20 it is evident that the unit vector $\vec{u}_{Q_i}$ can be written as

$$\vec{u}_{Q_i} = \sum_{\alpha} l^{-1}_{\alpha i} \vec{u}_{q_{\alpha}}$$

(21)

Because of the normalization of $I$, we have the normalization condition for $\vec{u}_{Q_i}$, of, $\vec{u}_{Q_i} \cdot \vec{u}_{Q_i} = 1$.

Method I makes use of two vectors computed in the CASSCF conical intersection calculation, the gradient difference vector, $\vec{x}_2$, and the nonadiabatic coupling vector, $\vec{x}_1$, defined as

$$\vec{x}_1 = \frac{\partial (E_1 - E_2)}{\partial \vec{q}}$$

(22)

$$\vec{x}_2 = \left\langle E_1 \left| \frac{\partial \hat{H}}{\partial \vec{q}} \right| E_2 \right\rangle,$$

(23)

where $\partial \vec{q}$ is an infinitesimal displacement of the Cartesian coordinates of the nuclei, and $E_1$ and $E_2$ are the energies of the two wavefunctions that at $X_0$ are degenerate. In reference 31, we showed that the parameter $k_i$ in Eq. 7 is proportional, with constant $K$, to the dot product of $\vec{x}_2$ with the $i^{th}$ normal mode of the molecule,

$$k_i = K (\vec{Q}_i \cdot \vec{x}_d) = KC_i$$

(24)

where $\vec{x}_d$ is the unit vector in the direction of $\vec{x}_2$.

In this method, we do not use the magnitude of $\vec{x}_2$, instead we renormalize the results such that the total Jahn-Teller stabilization energy, Eq. 17, is equal to the calculated CASSCF energy difference between $X_0$ and $X_{min}$. From this normalization, a value of $K$ is found, which is used to calculate the Jahn-Teller stabilization energy for each mode according to

$$\epsilon_i = \frac{k_i^2}{2\lambda_i} = \frac{c_i^2K^2}{2\lambda_i}$$

(25)
and

\[ \sum_i \epsilon_i = K^2 \sum_i \frac{c_i^2}{2\lambda_i} = E_0 - E_{\text{min}} \]  

(26)

Using the GRHF vibrational frequency, the value of \( D_i \) is then

\[ D_i = \frac{\epsilon_i}{\omega_{\epsilon,i}}. \]  

(27)

In Method II, the distortion vector is obtained straightforwardly as the vector difference between the points \( X_0 \) and \( X_{\text{min}} \), as determined by the CASSCF calculation, i.e.,

\[ \vec{d} = \vec{X}_0 - \vec{X}_{\text{min}} = \sum_{\alpha} d_{\alpha} \vec{u}_{q_{\alpha}}, \]  

(28)

where \( \vec{X}_0 \) and \( \vec{X}_{\text{min}} \) are the vectors in the atomic Cartesian coordinate system which point from the center of mass to \( X_0 \) and \( X_{\text{min}} \), respectively. However it is again convenient to work in a mass weighted coordinate system and we define the mass weighted distortion vector, \( \vec{d}_m \) by

\[ \vec{d}_m = \sum_{\alpha} d_{\alpha} m_{\alpha}^{1/2} \vec{u}_{q_{\alpha}}. \]  

(29)

and the \( d_{\alpha} \)'s are determined by Eq. 28. Since \( \vec{d}_m \) lies in the space spanned by the \( p \) doubly degenerate Jahn-Teller active normal coordinates we can write

\[ \vec{d}_m = \sum_{i=1}^{p} \sum_{j=a,b} d_{ij} \vec{u}_{Q_{ij}} \]  

(30)

where

\[ d_{i,a} = \vec{d}_m \cdot \vec{u}_{Q_{i,a}} = \rho_{i}^{\text{min}} \cos \phi_i, \]  

(31)

\[ d_{i,b} = \vec{d}_m \cdot \vec{u}_{Q_{i,b}} = \rho_{i}^{\text{min}} \sin \phi_i, \]  

(32)
and \( \vec{u}_{Q_i,a/b} \) are the unit vectors given by Eq. 21 for the \( a \) and \( b \) degenerate components of mode \( i \).

We can obtain the magnitude of \( \rho_{i}^{\text{min}} \) by summing the squares of eqs. 31 and 32, i.e.,

\[
(\rho_{i}^{\text{min}})^2 = (d_{i,a}^2)^2 + (d_{i,b}^2)^2
\]

(33)

\[
= (\vec{d}_m \cdot \vec{u}_{Q_i,a})^2 + (\vec{d}_m \cdot \vec{u}_{Q_i,b})^2
\]

(34)

This dot product is easily carried out in the atomic Cartesian system where \( \vec{u}_{Q_i,a/b} \) and \( \vec{d} \) are defined respectively by the GRHF and the CASSCF calculations.

If we rearrange Eq. 13 for \( \rho_{i}^{\text{min}} \), and solve for \( D_i \) we have

\[
D_i = (\rho_{i}^{\text{min}})^2 \omega_{e,i} \pi \hbar^{-1}
\]

(35)

\[
= \left[ (\vec{d}_m \cdot \vec{u}_{Q_i,a})^2 + (\vec{d}_m \cdot \vec{u}_{Q_i,b})^2 \right] \omega_{e,i} \pi \hbar^{-1}
\]

(36)

\[
= \left[ \left( \sum \alpha l_{\alpha i}^{-1} d_{\alpha m} \right)^2 + \left( \sum \alpha l_{\alpha i}^{-1} d_{\alpha m} \right)^2 \right] \omega_{e,i} \pi \hbar^{-1}
\]

(37)

where everything on the right side of eq. 37 is known from the \textit{ab initio} calculations. We can again get the total, and individual mode, Jahn-Teller stabilization energy by using eqs. 16 and 17 along with our values of \( D_i \) and \( \omega_{e,i} \).

3 Results of \textit{ab initio} calculations

3.1 CASSCF results at \( X_1 \) for the \( \tilde{A} \) state

The geometry of the excited state at \( X_1 \) is given in Table 2 from the CASSCF calculation. As expected the \( \tilde{A}^2 \mathrm{A}_2' \) state retains \( D_{5h} \) symmetry. The C-C and C-H bond lengths have been previously determined by a high resolution rotational analysis\cite{17} and serve as benchmarks with which to assess the quality of the calculations.

To facilitate the comparison of the results of this work, the results of the calculations of Bearpark \textit{et al.}\cite{48} and the experiment, we give in Table 3 the bond lengths as determined by the various methods. As can be seen in this table there is very good agreement between our calculation, the calculation of Bearpark \textit{et al.}, and the experiment.
which used the same active space but with a larger cc-pVDZ basis set, and the experiment. By comparison of the two calculations it appears that the 6-31G* basis set does an equally good job as the cc-pVDZ basis set for the geometry of the excited state.

The scaled vibrational frequencies calculated at $X_1$ with the CAS(5,5)/6-31G* basis for both $C_5H_5$ and $C_5D_5$ are given in Table 4. These frequencies provide a guide for the assignment of the excitation spectrum detailed in the following paper. For comparison, the experimental frequencies determined in Part II are also provided in Table 4. As can be seen from this table we again have fairly good agreement with experiment.

### 3.2 CASSCF results at $X_0$ for the $\tilde{X}$ state

A CAS(5,5)/6-31G* conical intersection calculation at $X_0$ determined the geometry at the conical intersection to possess $D_{5h}$ symmetry, as expected. The geometric parameters at $X_0$ are given in Table 2. The experimental bond lengths determined in the high resolution rotational analysis along with the calculated bond lengths determined by this study and that of Bearpark et al. are all given in Table 3. The agreement with experiment is again very good. Likewise the comparison of the two calculations indicates the larger basis set gives no better agreement with experiment than the smaller basis set implemented here.

The major effect on the geometry of the electronic excitation is the expansion of the ring in the excited state. The extent of this expansion is most prominently reflected in the C-C bond length change upon excitation, which is calculated to be 0.031 Å.

### 3.3 GRHF results at $X_0$ for the $\tilde{X}$ state

The vibrational frequencies for the average potential at $X_0$ were calculated using the GRHF method. The scaled frequencies calculated using a 6-31G* basis set are given in Table 4 for both $C_5H_5$ and $C_5D_5$. For comparison the experimental vibrational frequencies determined in Part II have been provided in the adjacent column. The agreement with experiment is again very good.

While we see good agreement for the vibrational frequencies, this does not necessarily imply that the normal coordinates determined by this calculation are equally good. Since the normal coordinates are vitally important for the implementation of both Method I and II, the stability of the normal coordinates were tested
using larger basis sets. The results of these calculations indicated that a larger basis set had a negligible
effect on the quality of the calculation. Complete details of these calculations are available in reference 39.

3.4 CASSCF results at $X_{min}$ for the $\tilde{X}$ state

As can be seen in Fig. 2, the minimum on the potential energy surface is characterized by an infinite number
of geometries due to the free pseudorotation of the molecule in the moat. We can easily calculate the
geometries which correspond to the electronic configurations which give rise to $A_2$ and $B_1$ electronic states
under the $C_{2v}$ point group. As shown in Fig. 1, these two states correspond to the selective occupation of
the two highest occupied $\pi$ molecular orbitals, which have $e''_1$ symmetry at $X_0$, but are split into $a_2 \oplus b_1$
at $X_{min}$. Then, the configuration $(a_2)^1(b_1)^2$ corresponds to the $A_2$ electronic symmetry, while $(a_2)^2(b_1)^1$
corresponds to the $B_1$ electronic symmetry.

The $^2A_2$ state was found to have a geometry consistent with a dienylic structure, while the $^2B_1$ state
was found to have a geometry consistent with an allylic structure. Graphical representations of these two
structures, as well as the specific bond lengths and angles, are given in Table 2. Comparison of the two
calculated distorted geometries to the geometry at $X_0$ gives a qualitative sense of the extent of the Jahn-
Teller distortion.

The specific geometries calculated at $X_{min}$ are critical to the implementation of Method II. Hence, we
varied both the active space and basis set of these calculations to test the stability of the distorted geometry.
As with the GRHF vibrational frequencies, the geometries were essentially insensitive to the choice of basis
set.

A vibrational frequency calculation was performed for both the $^2A_2$ and $^2B_1$ states. The results revealed
that the $^2B_1$ state is a first order saddle point on the CASSCF potential energy surface. Additionally, the
$^2B_1$ state was calculated to lie 3.6 cm$^{-1}$ above the $^2A_2$ state. While we have shown previously that the
barrier to pseudorotation about the moat should by symmetry be 0, we consider the 3.6 cm$^{-1}$ calculated
barrier to be in quite good agreement with this expectation. Indeed, if we were considering an electronic
excitation energy we would consider an error of just 3.6 cm$^{-1}$ to be extraordinary high accuracy.

The electronic excitation energy, $T_e$, may now be calculated by taking the difference in the energy
calculated at X₁ and Xₘᵟᵢₙ. We find Tₑ to be 30417 cm⁻¹ while Bearpark et al. found Tₑ to be 30284 cm⁻¹. Again we have good agreement between the two calculations. We may also do the traditional calculation of the total Jahn-Teller stabilization energy. This is accomplished by simply taking the difference in the energy calculated at X₀ and Xₘᵟᵢₙ. This yields a stabilization energy of 2147 cm⁻¹. This number compares quite well to the calculations of Bearpark et al. which determine \( \varepsilon_T = 2139 \) cm⁻¹.

### 3.5 Determination of the Jahn-Teller coupling constants

Using Methods I and II, we have calculated the linear Jahn-Teller coupling constants, Dᵢ, and the individual linear Jahn-Teller stabilization energies, \( \varepsilon_i \). These values along with the harmonic frequencies, and the total linear Jahn-Teller stabilization energy, \( \varepsilon_T \), for C₅H₅ and C₅D₅, are given in Tables 5 and 6, respectively.

The results for C₅H₅ indicate that although there are nominally four linear Jahn-Teller active modes only three modes, \( \nu_{10}, \nu_{11}, \) and \( \nu_{12} \), contribute significantly to the distortion. The single \( \nu'_{12} \) mode with near zero \( D_{12} \), \( \nu_{9} \), is a high frequency C-H stretching mode. (Likewise, no indication of Jahn-Teller activity in \( \nu_{9} \) is observed experimentally.) As can be seen from Table 2 the calculated geometries at Xₘᵟᵢₙ suggest that the Jahn-Teller distortion consists largely of changes in the C-C bonds lengths.

The linear Jahn-Teller coupling constants for C₅D₅ show a surprisingly different picture from that observed in C₅H₅. Apparently, the normal coordinates of C₅D₅ are such that a large decrease in \( D_{12} \) occurs. Thus, the linear Jahn-Teller problem in C₅D₅ is effectively dependent on only two modes, \( \nu_{10} \) and \( \nu_{11} \), in contrast to C₅H₅ in which three modes are important. This should result in a considerable simplification of the ground state vibrational energy levels.

It is interesting that an isotopic substitution should have such a large effect on the vibronic structure of the molecule. After all, the electronic potential energy surface for C₅H₅ is identical to that for C₅D₅. Referring to Fig. 1, we can anticipate that the vibrational modes that have the largest change in the C-C bond lengths will perturb the \( \pi \) system the most, and thus have the greatest amount of Jahn-Teller activity. To a lesser extent, the C-C-C bend and C-C-H bend will be active.

Table 7 gives the classical bond length and bond angle deformations for the four internal coordinates involved in the four Jahn-Teller active normal modes. For C₅H₅, \( \nu_{10} \) and \( \nu_{11} \) show large changes in the C-C
bond lengths, which is reflected in the large values of $D_{10}$ and $D_{11}$.

Upon isotopic substitution of deuterium for hydrogen, as expected, the C-H(D) stretch drops in frequency. However, most importantly, the C-C-H(D) bending frequency also drops in frequency, such that it is now lower in frequency than the C-C-C bend. (As Table 7 indicates, the true normal coordinates are admixtures of each of the internal coordinates; however, the traditional nomenclature is still useful.) Thus, $\nu_{11}$ in $C_5H_5$ most closely corresponds to $\nu_{12}$ in $C_5D_5$, and vice versa. Because the C-C-D stretching mode is considerably farther away in energy from the C-C stretch than it was in $C_5H_5$, there is less mixing of these modes. Thus, $\nu_{12}$ in $C_5D_5$ has much less C-C stretching motion, and a much decreased Jahn-Teller activity is observed.

Tables 5 and 6 allow us to compare the values of the calculated Jahn-Teller parameters with those determined in the experiment. A comparison of columns two and three of both tables reveals several interesting facts about Methods I and II. The only difference between these two columns is the method by which the constants were derived, i.e. the *ab initio* calculations are identical for both columns. The total Jahn-Teller stabilization energy is rather different as calculated via each method. For $C_5H_5$, Method I finds the total Jahn-Teller stabilization energy, $\varepsilon_T$, to be 2147 cm$^{-1}$ while Method II finds $\varepsilon_T$ to be 1497 cm$^{-1}$. When compared with the experimentally determined value of 1237 cm$^{-1}$ for $C_5H_5$, Method II seems to do significantly better at predicting $\varepsilon_T$. Consideration of either Table 5 or 6 shows that the values of $D_i$ calculated for $C_5(H/D)_{5}$ by both methods differ essentially only by a scale factor. The appropriate scale factor is the ratio of the values of $\varepsilon_T$ calculated by each method. This ratio indicates that the direction of the distortion vector calculated by each method is essentially identical (i.e., that $\vec{x}_2 \parallel \vec{d}$), however the magnitude of this vector is calculated to be smaller by Method II. There is little change in the computed values of $D_i$ or $\varepsilon_T$ when the basis set or active space are changed.

We also include in Tables 5 and 6 the parameters computed using Method II, but with only Hartree-Fock geometries. The use of HF-only geometries represents a significantly faster calculation, a method that will be more amenable to larger systems. As the tables show, the quality of the results using a GRHF geometry at $X_0$ and a RHF geometry at $X_{\text{min}}$ is quite respectable. We have observed similar results for HF-only calculations using Method II for the Jahn-Teller activity in $C_6H_6^+$ and $C_6D_6^+$, and only slightly poorer quality results for $C_6F_6^+$. Thus, we feel that Method II, using HF calculations of both geometries, shows great promise for the
prediction of the Jahn-Teller activity in a wide variety of hydrocarbon systems.

A direct comparison of the calculated Jahn-Teller constants to those determined experimentally reveals reasonably good agreement between the calculated and experimental values of $\omega_e^i$. For $C_5H_5$, $D_{12}$ agrees very well with experiment, however the relative sizes of $D_{11}$ and $D_{10}$ seem to be reversed. For $C_5D_5$, $D_{11}$ agrees very well with experiment and $D_{10}$ agrees reasonably well. Overall the agreement with experiment is quite good with the exception of the relative sizes of $D_{11}$ and $D_{10}$ in $C_5H_5$.

The most likely reason for the reversal of the relative sizes of $D_{10}$ and $D_{11}$ in $C_5H_5$ lies in the GRHF calculation of the normal coordinates. From inspection of the normal coordinate motions, it is clear that the normal coordinates of $\nu_{11}$ and $\nu_{10}$ in $C_5H_5$ are quite strong mixtures of the C-C stretch and C-C-H bending coordinates. It is possible that the extent of this mixing is not correctly reflected in the GRHF force constant matrix, which might be remedied if electron correlation were to be included in the calculation of the frequencies and normal modes. The extent of the mixing of these motions is much diminished in $C_5D_5$ which accounts for the reduction of $D_{12}$.

4 Expected emission spectra from the $\tilde{A}$ state

4.1 Calculation of $T_{00}$

The vibronic excitation energy, $T_{00}$, is the excitation energy determined in the experimentally observed $\tilde{A}^2A''_2 - \tilde{X}^2E''_1$ electronic spectra. As such it is intimately tied to the analysis of the vibronic structure in both the ground and excited states. It also provides a useful comparison of the calculations to experiment.

To make this comparison, we need to make the zero point energy (ZPE) correction to the energies ($T_e$) of both the excited and ground states. While a trivial calculation in most instances, the zero point correction in our case is complicated by the Jahn-Teller effect in the ground state. For the excited state we have the well known equation

$$ZPE_A = \sum_{i=1}^{3N-6} \frac{h_i}{2}\omega_i,$$  

(38)
where the sum is over all vibrations, \( h_i \) is the degeneracy of mode \( i \), and \( \omega_i \) is the vibrational frequency of mode \( i \). For the Jahn-Teller active ground state this simple equation must be modified to account for the energy lowering due to the Jahn-Teller effect. Equation 38 then becomes

\[
ZPE_{JT} = \sum_{i=1}^{3N-6-p} \frac{h_i}{2} \omega_i + \varepsilon_T + E_{1/2,1},
\]

(39)

where the sum is over all \( 3N-6 \) vibrations minus the number of doubly degenerate Jahn-Teller active modes \( p \), \( \varepsilon_T \) is the total Jahn-Teller stabilization energy, and \( E_{1/2,1} \) is the energy of the lowest eigenvalue relative to the conical intersection (symmetric point, \( X_0 \)) obtained after the diagonalization of the vibronic Jahn-Teller Hamiltonian matrix. \( E_{1/2,1} \) is the only one of the above values not readily available from the \textit{ab initio} calculations. We obtain this value is by running a calculation using the program SOCJT,\textsuperscript{34} which takes as input the parameters \( D_i \) and \( \omega_{e,i} \) of the Jahn-Teller active modes. The operation and relevant theory behind this program are described in Part II and with more detail in references 34,49.

The resulting zero point energies, calculated using the scaled vibrational frequencies of Table 4, are given in Table 3. Applying the zero point correction to \( T_e \) yields \( T_{00} \) which is calculated to be 30272 cm\(^{-1}\) for \( C_5H_5 \) and 30963 cm\(^{-1}\) for \( C_5D_5 \). These values agree to within \( \approx 4\% \) of the experimental values of 29573 cm\(^{-1}\) and 29819 cm\(^{-1}\), respectively.

### 4.2 Jahn-Teller active levels

With the Jahn-Teller constants derived using Methods I and II, we can simulate emission spectra from the \( \tilde{A} \) state to the Jahn-Teller active \( \tilde{X} \) state. This may be accomplished for the Jahn-Teller active levels by the use of the program SOCJT as mentioned above. The output of SOCJT contains the calculated energy levels and optionally, the computed spectra. The relative intensity of the lines in the spectra are computed assuming diagonal Frank-Condon factors.

The simulated spectra for \( C_5H_5 \) and \( C_5D_5 \) are in Figs. 4 and 5, respectively. The first column corresponds to the simulated spectra of the Jahn-Teller levels using the constants calculated with Method I and the second column using constants derived via Method II (column 3 of Table 5). The spectrum at the bottom of each column corresponds to the predicted spectra of the non-Jahn-Teller active vibrations, discussed in the next
section. Each spectrum is a convolution of the theoretically predicted line spectrum with a Gaussian line
shape function of 10 cm$^{-1}$ FWHM. Emission spectra originating from $10^1$, $11^1$, and $12^1$, the three modes
predicted to have appreciable Jahn-Teller activity in C$_5$H$_5$, are shown in Figs. 4A, 4B, and 4C, respectively.
The emission from the excited state origin is also given in Fig. 4D.

The most striking difference between the spectra predicted by Methods I and II in Fig. 4 is the variation
in the predicted intensities. Method I, which predicts larger values of $D_i$, shows much stronger intensities in
the higher frequency region above 1250 cm$^{-1}$. These stronger intensities are a direct result of the predicted
stronger Jahn-Teller activity by Method I.

The line positions calculated by each method are generally comparable, especially in the low frequency
region below 1250 cm$^{-1}$. The most noteworthy exception to this observation is the lowest frequency feature
excluding the origin which changes frequency by over 100 cm$^{-1}$ between the two methods. Overall the
simulated emission spectra predict quite rich spectra for C$_5$H$_5$.

The emission spectra from $10^1$ and $11^1$ in C$_5$D$_5$, the only modes predicted to have significant Jahn-Teller
activity, as well as from the origin, are shown in Figs. 5A, 5B, and 5C, respectively. The predictions of the
non-Jahn-Teller active vibrations are shown in Fig. 5D. A comparison of Methods I and II for C$_5$D$_5$ reveals
a very similar result to that observed in C$_5$H$_5$, although the variation in intensity does not seem to be as
pronounced. The line positions are again very similar for both methods in the low frequency region.

The most interesting observation apparent from consideration of Fig. 5 is the great simplification of
the emission spectra compared to those in Fig. 4. The most congested spectrum in C$_5$D$_5$ has only a few
more than 10 features due to Jahn-Teller activity, compared to the over 20 predicted for C$_5$H$_5$. This 50%
reduction in the number of lines is a direct result of the rotation of the normal coordinates in C$_5$D$_5$, which
reduces $D_{12}$ to nearly zero. All things being equal, one would expect more lines to be observed in C$_5$D$_5$ in
the same frequency region because the heavier deuterium atom tends to compress the vibrational spectrum,
as is apparent in the spectra of the non-Jahn-Teller active levels. Furthermore, a lower vibrational frequency
in a Jahn-Teller active mode will generally cause a higher value of $D_i$ for that mode, since the product
$D_i \times \omega_{e,i}$ is independent of the isotopes. A larger value of $D_i$ will cause greater activity in the spectrum.
4.3 Comments on expected bands in the $\tilde{A} - \tilde{X}$ spectrum

Nominally the only additional bands one would expect to see in the emission spectra in the region predicted above for the Jahn-Teller levels would be due to the totally symmetric vibration $\nu_2$. However, a comparison of the frequencies of the vibrational modes from the ground and excited state in Table 4 reveals a large number of vibrations that change in frequency by a very large percentage from one state to the other. In particular the modes that lead to a distortion out of the plane of the molecule seem to have the largest change from the ground to the excited state. There are four out-of-plane vibrations, $\nu_4$, $\nu_8$, $\nu_{13}$, and $\nu_{14}$, that, upon excitation, become smaller by approximately 35%, 70%, 52%, and 24%, respectively, in C$_5$H$_5$. This large change in frequency will likely lead to significant off-diagonal Frank-Condon factors for these out-of-plane vibrations.

The non-Jahn-Teller active levels can also be simulated. If we accept that we will have some activity in the out-of-plane vibrations due to off diagonal Frank-Condon factors, as well as activity in the totally symmetric vibrations, we can build a simulation that will have five bands below 2500 cm$^{-1}$. The relative intensities of the out-of-plane vibrations may be estimated in the following way. An equation due to Herzberg$^{42}$

$$\frac{I_{0-0}}{\sum_i I_{v_i-0}} = \frac{\sqrt{\omega_{e,i}^{\prime}\omega_{e,i}^{\prime\prime}}}{1/2(\omega_{e,i}^{\prime} + \omega_{e,i}^{\prime\prime})},$$

estimates the ratio of the intensity of the fundamental transition (0-0) to the sum of the intensities of the overtone transitions ($v_i$-0). If we assume that most of the overtone intensity is concentrated in the first overtone then

$$\frac{I_{0-0}}{I_{0-0} + I_{2-0}} \approx \frac{\sqrt{\omega_{e,i}^{\prime}\omega_{e,i}^{\prime\prime}}}{1/2(\omega_{e,i}^{\prime} + \omega_{e,i}^{\prime\prime})}. \quad (41)$$

If we make the additional assumption that the fundamental transition of each out-of-plane mode has the same $I_{0-0}=1$ then the

$$I_{2-0} = \frac{1/2(\omega_{e,i}^{\prime} + \omega_{e,i}^{\prime\prime})}{\sqrt{\omega_{e,i}^{\prime}\omega_{e,i}^{\prime\prime}}} - 1. \quad (42)$$
The simulation of the non-Jahn-Teller active bands with relative intensities calculated as above are given in Fig. 4E for C$_5$H$_5$ and Fig. 5D for C$_5$D$_5$. The maximum intensity of the out-of-plane vibrations was arbitrarily set at 70 out of 100. The intensity of the totally symmetric vibration $\nu_2$ was arbitrarily set at 70.

The predicted emission spectrum for C$_5$H$_5$ originating from 10$^1$, 11$^1$, 12$^1$, or 0$^0$ including both Jahn-Teller and non-Jahn-Teller active levels would be the sum of the spectrum in Fig. 4E with respectively, Fig. 4A or 4B or 4C. Likewise, the predicted emission spectrum for C$_5$D$_5$ originating from 10$^1$, 11$^1$, or 0$^0$ including both Jahn-Teller and non-Jahn-Teller active levels would be the sum of the spectrum in Fig. 4D with respectively, Fig. 4A or 4B or 4C.

We may qualitatively understand this apparent “softening” of the PES along the out-of-plane normal coordinates by considering the relative aromaticity of the ground and excited states. Although the cyclopentadienyl radical does not conform to the familiar Hückel (4n + 2) rule for aromaticity, it does possess many of the important properties of an aromatic compound, e.g. a $\pi$ electron cloud delocalized around a ring of chemically identical carbons. The ground state (as measured at $X_0$) has C-C bond lengths of 1.418 Å, closer to the “typical” C=C double bond length of 1.34 Å than the excited state, which has C-C bond lengths of 1.455 Å. This is indicative of a stiffer, more aromatic structure in the ground state and more flexible, less aromatic structure in the first excited state. We can think of this as two points along the continuous change in geometry in going from a planar aromatic cyclic molecule to an aliphatic cyclic molecule in the chair conformation. While the excited state has not achieved the chair conformation, it has become more flexible along the out-of-plane normal coordinates.

We know from an examination of Fig. 1 that the ground state will have an electron configuration of $(a''_2)^2(e''_1)^3$, while the excited state corresponds to an electron occupation of $(a''_2)^1(e''_1)^4$. The $e''_1$ orbital contains clearly more C-C $\pi$-antibonding character (or, equivalently, less C-C $\pi$-bonding character) than the $a''_2$ orbital. Thus, the electronic excitation will weaken the C-C $\pi$ bonds, making the flexing of the ring much easier. These simple arguments account for the decreased vibrational frequencies of the out-of-plane vibrations, which give rise to significant overtone activity in the electronic spectra.
5 Conclusions

We have developed a new method (Method II) to calculate the Jahn-Teller parameters of linear Jahn-Teller active vibrational modes. This calculation, along with its preceding version, employ readily available ab initio packages. Application of the methods to the cyclopentadienyl radical allowed for a high quality prediction of the parameters of the Jahn-Teller PES in C$_5$H$_5$. We found the results computed with Method II to be better than for Method I. Furthermore, our calculations using Hartree-Fock geometries, rather than CASSCF geometries, indicate that the HF method may be used for a reasonably accurate estimation of the Jahn-Teller activity in many hydrocarbon systems. In addition, we find the predicted Jahn-Teller parameters to be relatively insensitive to basis set or active space.

Using this approach, we predict the Jahn-Teller effect in cyclopentadienyl to be quite different for C$_5$H$_5$ and C$_5$D$_5$. Three modes are shown to make significant contributions to the Jahn-Teller distortion in C$_5$H$_5$, while due to a rotation of the normal coordinates, only two modes make significant contributions to the Jahn-Teller distortion in C$_5$D$_5$. However, the net geometric distortion from X$_0$ to X$_{min}$ is the same in the two molecules, as is the energy stabilization.

The calculated harmonic vibrational frequencies of the out-of-plane modes in the $\tilde{X}$ and $\tilde{A}$ states of C$_5$H$_5$ and C$_5$D$_5$ indicate a “softening” of the potential energy surface along the out-of-plane normal coordinates in the $\tilde{A}$ state. The “softening” is manifested as a sharp decrease in the frequency of the out-of-plane modes in the $\tilde{A}$ state. This leads to strong off-diagonal Frank-Condon factors for these modes in the $\tilde{A} - \tilde{X}$ spectrum.

Finally, using the calculated Jahn-Teller parameters and the harmonic frequencies of the totally symmetric and the out-of-plane vibrations we predict the emission spectra originating from the origin and $\epsilon'_2$ vibrational modes of the $\tilde{A}$ state. The predicted spectra exhibit a large number of features in a frequency region where there is nominally one allowed totally symmetric fundamental vibrational level. As described in the following paper, these predictions of the vibronic energy levels and resultant spectra were critical to an accurate analysis of the experimental spectra of the C$_5$H$_5$ radical, a problem which has remain unsolved for nearly 30 years.
6 Acknowledgements

The authors are pleased to acknowledge the support of the National Science Foundation via grant 9974404 and to acknowledge a grant of computer time from the Ohio Supercomputer Center.
References


Figure Captions

1. Top-down views of the molecular orbitals (MOs) of the C$_5$H$_5$ radical. The center of the figure illustrates the MOs at the D$_{5h}$ geometry, in which three electrons are placed in the degenerate set of e orbitals. At the left, an unequal allotment of the electrons in these two orbitals causes the molecule to spontaneously distort to a dienyl structure, Ia. At the right, the reversal of the allotment of the electrons causes the molecule to distort to the allylic geometry, Ib.

2. Plot of the PES of the cyclopentadienyl radical, where E is energy and $Q_a$ and $Q_b$ are the unique directions that lift the degeneracy present at the D$_{5h}$ geometry.

3. Slice through the excited state potential and the ground state potential at an arbitrary angle around the moat (shown in Fig. 2). The point $X_1$ defines the geometry (D$_{5h}$) at the minimum of the first excited state, $X_0$ is the symmetric D$_{5h}$ (conical intersection) point on the ground state PES, and $X_{\text{min}}$ is the geometry of the minimum on the ground state PES. The vector $\vec{x}_2$ is the derivative coupling vector and $\vec{d}$ is the distortion vector which as shown is parallel to $\vec{x}_2$. The parameter $\varepsilon_T$ is the total Jahn-Teller stabilization energy, while $\rho_{JT}^{\text{min}}$ is the distance from $X_0$ to $X_{\text{min}}$.

4. Simulated emission spectra from the $\tilde{A}$ state of C$_5$H$_5$. The left column contains the simulations using constants calculated via Method I. On the right are the simulations using constants calculated via Method II. Row A is the predicted emission from $10^1$ for the Jahn-Teller active levels. Row B is the predicted emission from $11^1$ for the Jahn-Teller active levels. Row C is the predicted emission from $12^1$ for the Jahn-Teller active levels. Row D is the predicted emission from $0^0$ for the Jahn-Teller active levels. Row E is the predicted emission from the non-Jahn-Teller active levels. See text for a discussion of relative intensities.

5. Simulated emission spectra from the $\tilde{A}$ state of C$_5$D$_5$. The left column contains the simulations using constants calculated via Method I. On the right are the simulations using constants calculated via Method II. Row A is the predicted emission from $10^1$ for the Jahn-Teller active levels. Row B is the predicted emission from $11^1$ for the Jahn-Teller active levels. Row C is the predicted emission from $0^0$ for the Jahn-Teller active levels. Row D is the predicted emission from the non-Jahn-Teller active levels.
levels. See text for a discussion of relative intensities.
Figure 1:
Figure 2:
Figure 3:
Figure 4:

A

B

C

D

E

0 0

2 1

4 2

8 2

13 2

0 250 500 750 1250 1750 2250 2500 cm$^{-1}$

0 250 500 750 1250 1750 2250 2500 cm$^{-1}$
Figure 5:
<table>
<thead>
<tr>
<th>symbol</th>
<th>description</th>
<th>definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_i$</td>
<td>linear Jahn-Teller coupling coefficient</td>
<td>$\left( \frac{\partial^2 \hat{H}<em>e}{\partial Q_i \partial Q_i} \right)</em>{0}$</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>harmonic force constant</td>
<td>$\left( \frac{\partial^2 \hat{H}<em>e}{\partial Q_i \partial Q_i} \right)</em>{0}$</td>
</tr>
<tr>
<td>$g_{ii}$</td>
<td>quadratic Jahn-Teller coupling coefficient</td>
<td>$\left( \frac{\partial^2 \hat{H}<em>e}{\partial Q_i \partial Q_i} \right)</em>{0}$</td>
</tr>
<tr>
<td>$g_{ij}$</td>
<td>cross quadratic Jahn-Teller coupling coefficient</td>
<td>$\left( \frac{\partial^2 \hat{H}<em>e}{\partial Q_i \partial Q_j} \right)</em>{0}$</td>
</tr>
<tr>
<td>$b_{ij}$</td>
<td>bilinear Jahn-Teller coupling coefficient</td>
<td>$\left( \frac{\partial^2 \hat{H}<em>e}{\partial Q_i \partial Q_j} \right)</em>{0}$</td>
</tr>
</tbody>
</table>

Table 1: The Jahn-Teller coupling coefficients that parameterize the effective spectroscopic Hamiltonian and their relationships to the terms of the Taylor series expansion of the potential.
Table 2: Geometries calculated at CAS(5,5)/6-31G* at the points on the PES labeled in Fig.3.
### Table 3: Comparison of bond lengths of the D\textsubscript{5h} geometries and energies between this work, the work of Bearpark \textit{et al.} and experimental for both the \textit{X} and \textit{A} states of C\textsubscript{5}H\textsubscript{5}.

<table>
<thead>
<tr>
<th>Geometries</th>
<th>CAS(5,5)/6-31G*</th>
<th>CAS(5,5)/cc-pVDZ\textsuperscript{a}</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bond Length (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>\textit{A} C-C</td>
<td>1.418</td>
<td>1.420</td>
<td>1.419</td>
</tr>
<tr>
<td>\textit{A} C-H</td>
<td>1.070</td>
<td>\textsuperscript{b}</td>
<td>1.083</td>
</tr>
<tr>
<td>\textit{X} C-C</td>
<td>1.455</td>
<td>1.457</td>
<td>1.445</td>
</tr>
<tr>
<td>\textit{X} C-H</td>
<td>1.072</td>
<td>\textsuperscript{b}</td>
<td>1.069</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Derived Energies</th>
<th>Energy (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varepsilon_T(E_{X_0}-E_{X_{min}}))</td>
<td>2147</td>
</tr>
<tr>
<td>(E_{B_1}-E_{A_1})</td>
<td>3.6</td>
</tr>
<tr>
<td>(ZPE^c(C_5H_5))</td>
<td>16404</td>
</tr>
<tr>
<td>(ZPE^c(C_5D_5))</td>
<td>13760</td>
</tr>
<tr>
<td>(E_{1/2,1}(C_5H_5))</td>
<td>4353</td>
</tr>
<tr>
<td>(E_{1/2,1}(C_5D_5))</td>
<td>3174</td>
</tr>
<tr>
<td>(ZPE^{J,T}_x(C_5H_5))</td>
<td>16549</td>
</tr>
<tr>
<td>(ZPE^{J,T}_x(C_5D_5))</td>
<td>13214</td>
</tr>
<tr>
<td>(T_x)</td>
<td>30417</td>
</tr>
<tr>
<td>(T_{00}(C_5H_5))</td>
<td>30272</td>
</tr>
<tr>
<td>(T_{00}(C_5D_5))</td>
<td>30963</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated energies at CASSCF/cc-pVDZ taken from ref. 48.

\textsuperscript{b} The calculated C-H bond lengths were not enumerated in ref. 48.

\textsuperscript{c} Zero point energy of the \textit{A} state using scaled frequencies.

\textsuperscript{d} Zero point energy of the \textit{X} state using scaled frequencies and including Jahn-Teller corrections calculated using the parameters determined by Method II.

\textsuperscript{e} This value was derived using the zero point energies determined using the 6-31G\* basis set.
Table 4: Vibrational frequencies (cm\(^{-1}\)) of the ground and excited states of C\(_5\)H\(_5\) and C\(_5\)D\(_5\) compared to experimental values.

<table>
<thead>
<tr>
<th>mode</th>
<th>symmetry</th>
<th>(\tilde{X}^2E'')</th>
<th>(\tilde{A}^2A'')</th>
<th>(\tilde{X}^2E'')</th>
<th>(\tilde{A}^2A'')</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>calc(^a)</td>
<td>exp(^b)</td>
<td>calc(^a)</td>
<td>exp(^b)</td>
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<tr>
<td>1</td>
<td>(a'_1)</td>
<td>3060</td>
<td>3278</td>
<td>2281</td>
<td>2435</td>
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<tr>
<td>2</td>
<td>(a'_1)</td>
<td>1098</td>
<td>1071</td>
<td>1041</td>
<td>1045</td>
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<tr>
<td>3</td>
<td>(a''_2)</td>
<td>1274</td>
<td>1244</td>
<td>1000</td>
<td>1035</td>
</tr>
<tr>
<td>4</td>
<td>(e'_1)</td>
<td>684</td>
<td>681</td>
<td>502</td>
<td>562(^c)</td>
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<tr>
<td>5</td>
<td>(e''_1)</td>
<td>3047</td>
<td>3268</td>
<td>2258</td>
<td>2423</td>
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<tr>
<td>6</td>
<td>(e'_1)</td>
<td>1433</td>
<td>1511</td>
<td>1311</td>
<td>1377</td>
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<tr>
<td>7</td>
<td>(e''_1)</td>
<td>995</td>
<td>1001</td>
<td>762</td>
<td>793</td>
</tr>
<tr>
<td>8</td>
<td>(e''_1)</td>
<td>767</td>
<td>766(^c)</td>
<td>602</td>
<td>616(^c)</td>
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<tr>
<td>9</td>
<td>(e'_2)</td>
<td>3030</td>
<td>3251</td>
<td>2236</td>
<td>2397</td>
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<tr>
<td>10</td>
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<td>1320</td>
<td>1377</td>
<td>1353</td>
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<td>(e''_2)</td>
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<td>836</td>
<td>861</td>
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<tr>
<td>12</td>
<td>(e''_2)</td>
<td>815</td>
<td>872</td>
<td>797</td>
<td>715</td>
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<tr>
<td>13</td>
<td>(e''_2)</td>
<td>894</td>
<td>861(^c)</td>
<td>756</td>
<td>743(^c)</td>
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<tr>
<td>14</td>
<td>(e''_2)</td>
<td>529</td>
<td>576(^c)</td>
<td>442</td>
<td>414(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Ground state frequencies are from the GRHF calculation and have been scaled by 0.89. Excited state frequencies are from the CASSCF calculation and have been scaled by 0.95.

\(^b\) Experimental values taken from Part II

\(^c\) Experimental frequency determined by taking one half of the frequency of the overtone.
<table>
<thead>
<tr>
<th>Method</th>
<th>(X_0)</th>
<th>(X_{\text{min}})</th>
<th>(D_{12})</th>
<th>(\omega_{e,12})</th>
<th>(\varepsilon_{12})</th>
</tr>
</thead>
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<tr>
<td></td>
<td>CASSCF/6-31G*</td>
<td>CASSCF/6-31g*</td>
<td>GRHF/6-31G*</td>
<td>Exp.</td>
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<td>I</td>
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<td>817</td>
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<tr>
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<td>2147</td>
<td>1237</td>
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</table>

Table 5: Calculated Jahn-Teller constants for \(\text{C}_5\text{H}_5\).\(^{a,b}\)

a The rows marked \(X_0\) and \(X_{\text{min}}\) indicate the levels of theory, as defined in the experimental section, used to calculate the parameters in the table.

b All constants have units of cm\(^{-1}\) except \(D_i\) which is unitless.

c The differences in \(\varepsilon_T\) and the sum of \(\varepsilon_i\) for Method I is the round off error in \(D_i\) and \(\varepsilon_i\) and for Method II is the round off error in \(\varepsilon_i\)
<table>
<thead>
<tr>
<th>Method</th>
<th>X₀</th>
<th>Xₘᵢₙ</th>
<th>I: CASSCF/6-31G⁺</th>
<th>II: CASSCF/6-31g⁺</th>
<th>II: GRHF/6-31G⁺</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CASSCF/6-31G⁺</td>
<td>CASSCF/6-31g⁺</td>
<td>RHF/6-31G⁺</td>
<td></td>
</tr>
<tr>
<td>D₁₂</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>718</td>
<td>718</td>
<td>-</td>
</tr>
<tr>
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<td>3</td>
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<td>0.39</td>
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<td>302</td>
<td>302</td>
<td>1382</td>
<td>1382</td>
<td>861</td>
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<tr>
<td>ε₁₁</td>
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<td>ωₑ,₁₀</td>
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<td>ε₁₀</td>
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<td>εₑ,₉</td>
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</tr>
<tr>
<td>εₑ,₉</td>
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<td>1502</td>
<td>1570</td>
<td>2244</td>
<td>1188</td>
<td></td>
</tr>
</tbody>
</table>

**Table 6: Calculated Jahn-Teller constants for C₅D₅.**

**a.** The rows marked X₀ and Xₘᵢₙ indicate the levels of theory, as defined in the experimental section, used to calculate the parameters in the table.

**b.** All constants have units of cm⁻¹ except Dᵢ which is unitless.

**c.** The differences in εₑ and the sum of εᵢ for Method I is the round off error in Dᵢ and εᵢ and for Method II is the round off error in εᵢ.
<table>
<thead>
<tr>
<th>&quot;Name&quot;</th>
<th>Mode</th>
<th>( \Delta R(\text{C-H})^a )</th>
<th>( \Delta R(\text{C-C})^a )</th>
<th>( \Delta \theta(\text{C-C-C})^b )</th>
<th>( \Delta \theta(\text{C-C-H})^b )</th>
<th>( \Delta R(\text{C-H})^a )</th>
<th>( \Delta R(\text{C-C})^a )</th>
<th>( \Delta \theta(\text{C-C-C})^b )</th>
<th>( \Delta \theta(\text{C-C-H})^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H(D) Stretch</td>
<td>( \nu_9 )</td>
<td>20.2</td>
<td>2.1</td>
<td>0.19</td>
<td>0.02</td>
<td>( \nu_9 )</td>
<td>17.3</td>
<td>4.4</td>
<td>0.33</td>
</tr>
<tr>
<td>C-C Stretch</td>
<td>( \nu_{10} )</td>
<td>1.5</td>
<td>39.2</td>
<td>0.55</td>
<td>2.71</td>
<td>( \nu_{10} )</td>
<td>1.6</td>
<td>41.5</td>
<td>0.51</td>
</tr>
<tr>
<td>C-C-H Bend</td>
<td>( \nu_{11} )</td>
<td>3.1</td>
<td>17.2</td>
<td>0.04</td>
<td>4.29</td>
<td>( \nu_{12} )</td>
<td>2.3</td>
<td>3.5</td>
<td>0.66</td>
</tr>
<tr>
<td>C-C-C Bend</td>
<td>( \nu_{12} )</td>
<td>0.6</td>
<td>3.6</td>
<td>1.07</td>
<td>2.08</td>
<td>( \nu_{11} )</td>
<td>1.3</td>
<td>9.7</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Table 7: Calculated classical turning points for the Jahn-Teller active modes of \( \text{C}_5\text{H}_5 \) and \( \text{C}_5\text{D}_5 \).

a Bond length extensions are given in units of milli-Angstroms.

b Bond angle changes are given in units of degrees.