

# Laser photoelectron spectrometry of $C_5H_5^-$ : A determination of the electron affinity and Jahn–Teller coupling in cyclopentadienyl<sup>a)</sup>

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The photodetachment electron spectrum of cyclopentadienide ( $C_5H_5^-$ ) yields a value for the cyclopentadienyl electron affinity of  $1.786 \pm 0.020$  eV. Additionally, the spectrum shows structure corresponding to vibrations in the neutral radical. From this an upper bound is placed on the linear Jahn–Teller coupling constant  $k^2 < 0.5$ . The quadratic coupling is shown theoretically to be absent for this molecule, a special case of the absence of quadratic coupling in  $D_n$  or  $C_n$  groups when  $n$  is not divisible by three. The magnitude of this Jahn–Teller distortion is sufficient to induce nontotally symmetric Jahn–Teller modes in the spectrum, but is insufficient to suppress the symmetric modes and, in particular, a strong 0–0 transition is observed. Thus, the geometries of the ion and the neutral, apart from the Jahn–Teller distortion, are not radically different.

Cyclopentadienyl binds to metal atoms to form organometallic compounds,<sup>1</sup> but aside from this interesting chemistry cyclopentadienyl has intriguing physical properties of its own. The  $\pi$  electron system of this five-membered carbon ring lacks one electron to make it aromatic under the  $4n+2$  rule<sup>2</sup> and should readily accept an extra electron. This it does in forming compounds like  $KC_5H_5$ , which are ionic, and it even accepts an electron in the gas phase. Richardson, Stephenson, and Brauman<sup>3</sup> have studied photodetachment of  $C_5H_5^-$ ,  $C_5H_4D^-$ , and  $C_5D_5^-$  in the wavelength region 7000–2700 Å at low resolution ( $\sim 150$  Å). For all three species they observe a slowly rising cross section across the entire spectrum, and show that the threshold shapes for all three ions are identical at this resolution. From these studies it is concluded<sup>3</sup> that E. A. ( $C_5H_5^-$ )  $\leq 1.84 \pm 0.03$  eV, and that the geometries of the ion and neutral are similar.

The electronic spectrum of  $\dot{C}_5H_5$  lacks interpretation, partially because its reactivity makes observations difficult and partially because the Jahn–Teller effect complicates the spectrum. Several observers<sup>4–6</sup> have identified absorption bands in flash apparatus as due to  $\dot{C}_5H_5$ , but no definite assignment of the vibrations can be made without dispute. The ground state of this radical is expected to be electronically degenerate in the symmetrical  $D_{5h}$  geometry and should distort to a lower symmetry to remove this degeneracy, gaining a calculated ( $\sim 500$  cm<sup>-1</sup>) additional stability.<sup>7–9</sup> This Jahn–Teller<sup>10</sup> effect prevents the ordinary adiabatic separation of electronic and nuclear motion into wavefunctions each independently having  $D_{5h}$  representations; these independent symmetries are relinquished and only an overall, vibronic symmetry is kept. Thus, the vibrations corresponding to the Jahn–Teller modes become allowed in a transition when they should otherwise be forbidden. For example, in transitions to or from the  $E_1''$  electronic state these modes have  $e_2'$  symmetry. As a fur-

ther complication the Jahn–Teller modes become anharmonic, resulting in a spectrum with many more lines with little obvious pattern.

There is a pattern, however, and special cases of the Jahn–Teller effect have been studied for which spectra have been predicted by numerical calculation.<sup>11–14</sup> A phenomenological theory exists<sup>15,16</sup> in which initially degenerate electronic states  $|\psi_i\rangle$  couple via nuclear distortions  $q_m$ . This coupling can be linear (Jahn–Teller) or second order (Renner–Teller, or sometimes<sup>12</sup> called the Duchinsky terms) in the nuclear distortions. Thus, to a harmonic nuclear potential  $V_{ii}$  with force constant  $\gamma_m$  for each electronic state  $\psi_i$

$$V_{ii} = \frac{1}{2} \sum_m |\psi_i\rangle \gamma_m q_m^2 \langle \psi_i| \quad (1)$$

is added a perturbation  $\hat{V}_{ij} = \sum_{m,n} |\psi_i\rangle (\alpha_m^{ij} q_m + \beta_{mn}^{ij} q_m q_n) \langle \psi_j|$  that mixes  $\psi_i$  and  $\psi_j$ . Explicitly, the previously harmonic adiabatic Hamiltonian now has off-diagonal terms that are linear and possibly quadratic in the displacement; for all values of displacements one rediagonalizes the adiabatic Hamiltonian forming the new adiabatic nuclear potentials. For the case in which no second order terms enter ( $\beta_{mn}^{ij} = 0$ ) Longuet-Higgins *et al.*<sup>11</sup> and Moffitt and Liehr<sup>17,18</sup> solve the nuclear motion problem for one active doubly degenerate mode. They find the potential is given by a parabolic potential no longer centered on the origin of zero displacement. Also, because the coupling mode is doubly degenerate, two dimensions must be considered and they solve this by a separation of variables into a pseudoangle and a magnitude in the space of nuclear motion. This separation gives the effective "radial" equation<sup>11</sup>

$$\left[ -\frac{1}{2} \left( \frac{\partial^2}{\partial q^2} + \frac{1}{q} \frac{\partial}{\partial q} - \frac{m^2}{q^2} \right) + \frac{\gamma}{2} q^2 + \alpha q \right] \chi(q) = E \chi(q) \quad (2)$$

Here  $m$  is the quantum number for rotations of the pseudoangle. Unfortunately, this must now be solved numerically.<sup>11–13</sup> This is usually done in reduced units that make  $\gamma \rightarrow 1$ , and  $\alpha \rightarrow k = \alpha \gamma^{-3/8}$ . Thus, the reduced

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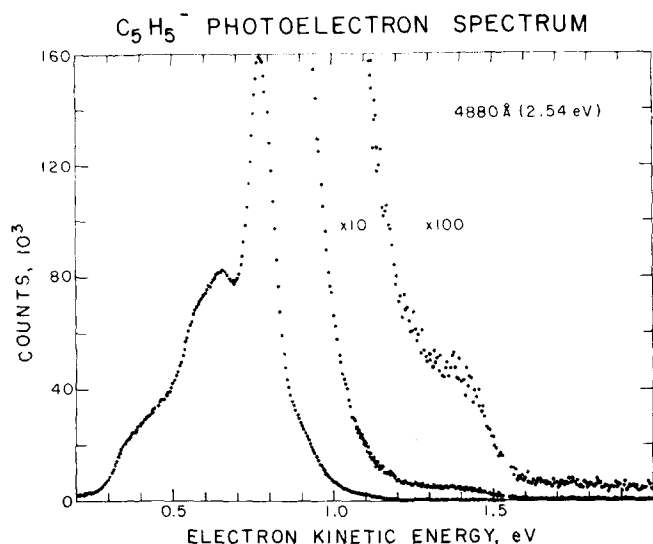


FIG. 1. The cyclopentadienyl anion photoelectron spectrum taken with 4880 Å radiation, showing a strong 0-0 peak and neutral vibrations to its left; unresolved hot bands to its right terminate abruptly at 1.5 eV.

Jahn-Teller coupling constant  $k^2$  is expressed in terms of the parameters of Eq. (2); physically, it is twice the additional Jahn-Teller stability divided by the spacing of energy levels in that mode before distortion. In the numerical solutions of the linearly coupled problem  $k^2$  is used to define the strength of the coupling.

Introduction of quadratic terms destroys the generality of this numerical work and prevents an experimental test of this theory unless a system can be found without second order terms. Cyclopentadienyl has no second order coupling, being a member of a class discussed in the Appendix. Thus, the linear coupling theory applies to cyclopentadienyl. Although the additional complication of possibly up to four active modes exists in  $\dot{C}_5H_5$ , the case of more than one active Jahn-Teller mode has been investigated in general by Sloane and Silbey<sup>12</sup> using a second quantization notation and numerical methods, while Purins and Feeley<sup>19</sup> attack the multimode coupling problem in  $\dot{C}_5H_5$  directly.

Obvious tests would be the ir and Raman spectra, but the reactivity of the radical prevents (or at least discourages) this. However, ir and Raman spectra of the anion have been obtained<sup>20-22</sup> in the condensed phase with a counterion ( $K^+$ ,  $BeCl^+$ , etc.) and are indicative of the mode frequencies before the Jahn-Teller coupling is turned on. At least one study<sup>19</sup> predicts  $\dot{C}_5H_5$  spectra from these frequencies and semiempirical Jahn-Teller coupling constants. But lacking an analysis of ir or Raman work, and being unable to decipher the one known electronic transition, one must take an indirect approach.

Photoelectron spectroscopy is such a method. Just as photoionization of a neutral species<sup>23</sup> can provide information about the cation, photodetachment of the anion can provide information on the neutral. The apparatus and method have provided such information on other systems<sup>24-26</sup> and since the ion, cyclopentadienide, is stable in the gas phase, the method is again applicable here.

## EXPERIMENTAL

The apparatus and techniques have been previously<sup>25</sup> described in detail. Either ferrocene (Alfa) or cyclopentadiene (prepared by cracking dicyclopentadiene from Eastman) enters a low pressure electrical discharge ion source to produce beams of  $C_5H_5^-$  ions. The ions are extracted from the source, accelerated to 680 eV, and mass analyzed by a Wien filter. The 25 nA beam is crossed in a fieldfree interaction region by the intracavity beam of a 4880 Å (2.540 eV) cw Ar II laser, and electrons ejected into the acceptance angle of a hemispherical electrostatic monochromator are energy analyzed (resolution 60 meV FWHM). At this resolution the many components of a particular vibronic transition are smoothed into a nearly Gaussian peak 90 meV in width.

The absolute detachment energies of peaks in the spectra are determined using simultaneously produced  $O^-$  as a calibration ion and the expression<sup>25</sup>

$$E.A.(X) = (O) + 1.0215(\Omega_{O^-} - \Omega_{X^-}) + mW(1/M_O - 1/M_X), \quad (3)$$

where  $E.A.(O) = 1.465$  eV is the "effective"<sup>27</sup> electron affinity of the oxygen atom, determined from the center of the  $O^-$  photodetachment peak, and  $(\Omega_{O^-} - \Omega_{X^-})$  is the laboratory energy difference between the  $O^-$  peak center and a particular  $X^-$  peak center. The factor 1.0215 is an energy scale compression factor described previously and obtained by calibrating an  $NH^-$  photodetachment spectrum against the known values for the  $NH^+ 3\Sigma^- - 1\Delta$  splitting.<sup>26,28</sup> The final term in Eq. (1) accounts for the fact that the electrons we detect must be backscattered (in the c.m. frame) into the energy analyzer and thus have a c.m. component of energy perpendicular to the analyzer axis;  $W$  is the kinetic energy of the ion beam (680 eV), and  $m$ ,  $M_O$ , and  $M_X$  are the masses of electron, oxygen atom, and molecule  $X$ , respectively.

The intensity of the photoelectrons at a given electron energy  $E$  depends upon the angle  $\theta$  between the electric vector of the linearly polarized laser light and the electron collection direction according to<sup>29</sup>

$$I(\theta) = \left(\frac{\sigma}{4\pi}\right) [1 + \beta(E)P_2(\cos\theta)], \quad (4)$$

where  $\sigma$  is the average photodetachment cross section,  $\beta$  is the anisotropy parameter, and  $P_2$  is the second Legendre polynomial. The spectrum shown in Fig. 1 was obtained with  $\theta$  such that  $P_2(\cos\theta)$  was zero, and thus reflects an average photodetachment cross section. A half-wave plate could be inserted to rotate the laser polarization, allowing measurement of the anisotropy of the detached electrons.

## RESULTS

Cyclopentadienyl anion detaches with either 488 (Fig. 1) or 514.5 nm radiation available from the Ar II laser, showing a shift in the ejected electron energy corresponding to the photon energy producing the detachment, but no other qualitative change. Thus, photodetachment at these wavelengths proceeds in a direct, not reso-

TABLE I.  $C_4H_4^-$  fundamental frequencies.<sup>a</sup>

Mode	$\omega$ , $cm^{-1}$	Class $D_{5h}$
$\nu_1 \delta_{CH}$	3043	$a_1'$
$\nu_2 \delta_{CC}$	983	$a_1'$
$\nu_3 \delta_{CH}$ out of plane	710	$a_2''$
$\nu_5 \delta_{CH}$ in plane	(1250) <sup>b</sup>	$a_2'$
$\nu_5 \delta_{CH}$	3039	$e_1'$
$\nu_6 \delta_{CC}$	1455	$e_1'$
$\nu_7 \delta_{CH}$ in plane	1003	$e_1'$
$\nu_8 \delta_{CH}$ out of plane	625	$e_1''$
$\nu_9 \delta_{CH}$	3096	$e_2'$
$\nu_{10} \delta_{CC}$	1447	$e_2'$
$\nu_{11} \delta_{CH}$ in plane	1020	$e_2'$
$\nu_{12} \delta_{CH}$ out of plane	(1060) <sup>b</sup>	$e_2''$
$\nu_{13} \delta_{ring}$ in plane	565	$e_2'$
$\nu_{14} \delta_{ring}$	(625) <sup>c</sup>	$e_2''$

<sup>a</sup>Frequencies from  $K^+(C_5H_5^-)$  (Ref. 20) except as noted.

<sup>b</sup> $Fe(C_5H_5)_2$  frequency (Ref. 21).

<sup>c</sup> $C_5H_5$  BeCl frequency (Ref. 22).

nantly enhanced, process and individual vibrational intensities should be derivable from Franck-Condon factors. The spectrum shows both vibrations of the neutral and the negative ion besides a sharp 0-0 peak at about 0.77 eV. From this peak the electron affinity is deduced to be  $(1.786 \pm 0.020)$  eV. No rotational corrections<sup>25</sup> to this value have been made, but they should be small, and the stated error bars include the possibility of a 0.015 eV rotational energy correction.

The vibrations are not well resolved, but two strong features of the neutral seem to be vibrations at  $900 \pm 100$  and  $3300 \pm 100$   $cm^{-1}$ , while one (or more) weaker vibration occurs at  $1600 \pm 100$   $cm^{-1}$ . More, unresolved structure underlies this. The hot bands are not resolved well enough to deduce vibrational frequencies, but a very pronounced cutoff occurs at 1.5 eV; above this only noise is observed. Overall, the spectrum is reminiscent of the photoabsorption of aromatic compounds.

## DISCUSSION

The most striking feature in the spectrum is the strong 0-0 transition, indicating only moderate geometry change upon photodetachment, otherwise the 0-0 would be suppressed and the remaining intensity would spread over the other vibrational transitions. As seen from the spectrum these vibrations do have some intensity, but the 0-0 and its sequence bands have a strength matching all other transitions taken together. Thus, the overall geometry change can be deemed small.

Only two totally symmetric vibrations occur in this molecule, the symmetric C-H stretch and the symmetric ring breathing mode. These occur at 3043 and 983  $cm^{-1}$  in the chemical ion (see Table I)<sup>20</sup> and probably produce

the vibrational features found in the photodetachment spectrum in the regions of the spectrum 3300 and 900  $cm^{-1}$  away from the maximum. Additionally, a shoulder occurs in the spectrum around 1600  $cm^{-1}$  and may represent another, Jahn-Teller induced vibration. An  $e_2'$  mode of the ion in the potassium compound<sup>20</sup> occurs at 1447  $cm^{-1}$ ; this mode is assigned a large Jahn-Teller coupling coefficient in the work of Purins and Feeley,<sup>19</sup> and it possibly represents this shoulder. Purins and Feeley also assign a large Jahn-Teller effect to an  $e_2'$  mode representing in-plane C-H bending at 1020  $cm^{-1}$ , and although not resolved it also could be contributing in the spectrum.

The above considerations are made assuming a Jahn-Teller effect of sufficient strength to induce the otherwise forbidden Jahn-Teller modes, yet assumes the effect is not large enough to significantly disturb the frequencies of these same modes. The strongest evidence for a weak Jahn-Teller effect comes from the photoelectron spectrum itself. The 0-0 is not suppressed and by comparison very little intensity is found in the induced modes, arguing for a weak Jahn-Teller effect. In contrast, Purins and Feeley<sup>19</sup> use relatively large ( $k^2 > 1$ ) coupling parameters and predict rather different results. Using their  $E-A(1-0)$  absorption intensities the 0-0 and all  $a_1'$  modes would only have one half the intensity of the Jahn-Teller induced transitions, the frequencies would be significantly shifted, and the strongest Jahn-Teller mode would occur at about 2000  $cm^{-1}$  with strength comparable to all  $a_1'$  modes. This clearly is not the case and evidently the Jahn-Teller effect is weaker than they considered.

The photoelectron spectrum has been subjected to a Gaussian fit program to determine what other vibrational structure it might contain. That is, individual electron lines are assumed to be Gaussian with equal widths (0.10 eV) and their individual positions and intensities are adjusted to reproduce the overall experimental spectrum. Except for the hot bands which did not give a unique fit, the spectrum could be fit with the seven Gaussian peaks listed in Table II. The fit is very sensitive to the 0-0 and the three mostly resolved peaks 800, 1170, and 1690  $cm^{-1}$  away from the 0-0, but the fit is not sensitive to the remaining peaks and these are

TABLE II. Gaussian fit parameters of the photoelectron spectrum.<sup>a</sup>

Peak position, eV	Intensity	$\omega^b$ , $cm^{-1}$	Assignment	
			(1)	(2)
0.76	1.00	...	0-0	
0.66	0.30	800 (40)	$\nu_2(a_1')$	
0.615	0.24	1170 (40)	$\nu_{11}(e_2')$	
0.55	0.33	1690 (40)	$2\nu_2$	$\nu_{10}(e_2')$
c				
0.47	0.13	2340 (100)	$2\nu_{11}$	
0.42	0.10	2740 (100)	$[2\nu_2 + \nu_{11}]$	$[\nu_{10} + \nu_{11}]$
0.35	0.13	3300 (100)	$\nu_1(a_1')$	

<sup>a</sup>Peak widths were assumed to be 0.10 eV; excludes hot bands.

<sup>b</sup>Standard errors given in parentheses.

<sup>c</sup>The fit below this line is not unique; it is only a possible one.

not uniquely determined by the spectrum. Therefore, we can state with a high degree of confidence where three vibrations (800, 1170, and 1690  $cm^{-1}$ ) occur in the neutral, while the higher vibrations are still speculative.

One can interpret these vibrations by comparing them to those of the ion, as in Table II. Two alternative assignments are possible based on either one or two induced Jahn-Teller modes when the peak at 1690  $cm^{-1}$  is assigned either  $a_1'$  or  $e_2'$  character. In the first of these cases the 800  $cm^{-1}$  ( $\nu_2$ ) is assumed to have strong overtones accompanying a relatively large change in ring size and ring breathing frequency, with the 1690  $cm^{-1}$  and some of the 2340 to 2740  $cm^{-1}$  region assigned to the  $2\nu_2$  and  $3\nu_2$  overtones. Then the amount of intensity in  $e_2'$  vibrations is only 20% of that in  $a_1'$  modes. The second case assumes the 1690  $cm^{-1}$  peak results from a second  $e_2'$  vibration  $\nu_{10}$ , and 35% of the observed spectrum can be attributed to Jahn-Teller induced transitions. In either case the Jahn-Teller effect is small, but not negligible.

A more quantitative measure of the Jahn-Teller distortion in this molecule results from the examination of these assignments in the light of theory. Sloane and Silbey's numerical work<sup>12</sup> on the problem of weak Jahn-Teller coupling allows interpolation for the coupling parameter  $k^2$  from the intensity data. This is made easier by noting that the ratio of intensity in the Jahn-Teller modes to the intensity in the totally symmetric modes is approximately equal to  $k^2$  up to moderate values of  $k^2$  (less than 20% error for  $k^2$  less than 0.5). Thus, in the two cases of vibrational assignments made above in the first case  $k^2$  is approximately 0.2, while in the second case the total  $k^2$  is about 0.4. This second case, with two active Jahn-Teller modes, is more complicated. However, the interaction of Jahn-Teller modes has been examined by Sloane and Silbey,<sup>12</sup> who indicate that the lower frequency mode will lose intensity by interaction with the higher frequency mode. Unless the Jahn-Teller coupling predominates in the lower mode, the lower mode will be almost absent. Since it is observed, most of the Jahn-Teller coupling occurs in the lower mode  $\nu_{11}$ , while a very weak Jahn-Teller effect in  $\nu_{10}$  ( $k^2 \leq 0.1$ ) allows it to "borrow" intensity from  $\nu_{11}$  and appear in the spectrum with large intensity.

Thus, in either of the two cases considered, one concludes that most of the Jahn-Teller coupling occurs in the C-H mode  $\nu_{11}$ , and in either case  $k^2$  is less than 0.5.

The weakness of this Jahn-Teller effect deserves comment. Because of the underlying rigidity of the sigma bond system, this may be a general result for all ring systems. In cyclopentadienyl, containing five pi electrons, four will not exert any distortion while only the fifth in an unpaired  $e_1''$  orbital will contribute to the Jahn-Teller distortion forces. Thus, this one electron exerts a distorting force against the restoring force of ten electrons in the carbon-carbon sigma system and the remaining four in the pi system. Viewed in this manner the weak Jahn-Teller distortion is perhaps understandable.

Physically, one views the ground state of the isolated

$\dot{C}_5H_5$  radical as a linear combination of the Jahn-Teller distorted geometries, the orientation of the distortion set by the mixing coefficients. For passage from one component of a degenerate Jahn-Teller mode to the other there is no energy barrier. Therefore, the Jahn-Teller distortion is labile and can move over the ring without activation energy. Electron paramagnetic resonance studies<sup>30,31</sup> at high temperatures are consistent with this conclusion, but in low temperature matrices a change in the spectrum occurs. At low temperatures one observes that the five protons are no longer equivalent, indicating a frozen distortion. This observation seems at first to contradict theory, but closer inspection shows that lowering of the molecular symmetry by the matrix site is the true cause of this degeneracy breaking. Specifically, the transition temperature in EPR spectra depends strongly upon the particular host matrix: In a strongly orienting crystal environment such as cyclopentadiene this transition occurs above 70 K,<sup>30</sup> while in a weakly orienting host matrix such as neon the transition occurs below 12 K.<sup>31</sup> Furthermore, the cyclopentadiene crystal spectra do not show the pattern resulting from  $C_{2v}$  symmetry that would be expected of an intrinsic distortion occurring along a molecular symmetry axis, but instead show a more complex pattern indicative of the extrinsic site symmetry. This shows the case with which the cyclopentadienyl radical adapts to the local site and is further evidence of a labile distortion.

In spite of the difficulties Hedaya and co-workers have taken uv and ir spectra of  $\dot{C}_5H_5$  in low temperature inert gas matrices.<sup>32</sup> The ir spectra show very few absorption lines, indicating a highly symmetric species. This result is puzzling if one expects a strong distortion to  $C_{2v}$  symmetry, but totally understandable if only a weak distortion is occurring. Child and Longuet-Higgins<sup>4</sup> have predicted vibrational spectra for a range of first order Jahn-Teller couplings, concluding that the strongest induced modes are the Jahn-Teller modes. Because the coupling that induces the new modes in the spectrum also makes the vibrations anharmonic, progressions in these modes will form any time these modes have significant oscillator strength, i. e., for values of  $k^2$  around 0.5 or greater. Since this does not seem to be occurring in the ir spectra, one again concludes that there is a small ( $k^2 < 0.5$ ) Jahn-Teller coupling in  $\dot{C}_5H_5$ .

Finally, we note the special problems of the electronic spectrum of cyclopentadienyl. Although Purins and Feeley<sup>19</sup> make a partial vibrational assignment, there remains an unaccounted doubling of all the lines by 330  $cm^{-1}$ . This splitting decreases to 220  $cm^{-1}$  in  $\dot{C}_5D_5$  and perhaps a C-H vibrational motion may be involved.<sup>4</sup> Purins and Feeley propose that the cause is an out-of-plane hydrogen bending motion made allowed by a distortion in the upper electronic state; it has also been suggested<sup>4</sup> that the cause is Jahn-Teller splitting in the ground state. However, the persistence of this feature in low temperature matrices<sup>32</sup> eliminates the possibility of hot bands and must mean that the splitting occurs in the upper state. Moreover, no ground state splitting is expected since the second order coupling, which would give rise to a Jahn-Teller splitting, is absent by sym-

metry (see Appendix). All these points argue that the Jahn–Teller effect is not a mechanism for splitting in the ground state and the  $330\text{ cm}^{-1}$  splitting in the uv spectrum is a property of the electronically excited state.

## CONCLUSIONS

By photoelectron spectrometry of  $C_5H_5^-$  we have determined the electron affinity of cyclopentadienyl to be  $(1.786 \pm 0.020)\text{ eV}$ . Additionally, the spectrum shows vibrational structure which can be interpreted (Table II). In all cases one is forced to conclude that the molecule undergoes only a weak dynamic Jahn–Teller effect ( $k^2 < 0.5$ ), enough to induce nontotally symmetric  $e_2'$  vibrations in the spectrum but not enough to suppress a strong 0–0. Thus, the geometries of the ion and the neutral are not radically different, and there is a correspondence between vibrations in the ion and in the neutral.

The understanding of the Jahn–Teller effect in the cyclopentadienyl radical now permits further attempts to assign the vibrations in the electronic spectrum. In particular, the  $330\text{ cm}^{-1}$  splitting observed can no longer be “blamed” on the Jahn–Teller effect in the ground state and other causes must be searched for.

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## APPENDIX: SYMMETRY AND QUADRATIC JAHN–TELLER COUPLING

In the ordinary Jahn–Teller effect the symmetry class of potentially active Jahn–Teller modes are found by taking the symmetric direct product of the representation of the degenerate electronic state in question.<sup>10,25</sup> For example, in the  $E_1''$  state of  $C_5H_5^-$ ,

$$E_1'' \times E_1'' = A_1' + E_2'$$

where the  $A_1'$  represents diagonal electronic coupling, while the  $E_2'$  represents the off-diagonal Jahn–Teller mixing. Thus, the active Jahn–Teller modes have  $e_2'$  symmetry in  $C_5H_5^-$ , and can contribute linearly in the nuclear coordinate displacements.

However, as second order coupling modifies the results of most of the present body of Jahn–Teller theory, it is important to know if it can occur. A simple test can be made: Quadratic Jahn–Teller mixing can occur only if the symmetric self-product of the Jahn–Teller mode contains the Jahn–Teller mode again. The proof is trivial, and depends upon noticing that the mixing element must have the specified symmetry; however, it has important consequences. For example, the point groups  $C_3$ ,  $D_3$ ,  $D_{3h}$ ,  $D_6$ ,  $C_{6v}$ ,  $O$ ,  $T_d$ , and  $I$  can undergo second order coupling in the Jahn–Teller modes, while  $D_4$ ,  $D_5$ ,  $C_{5v}$ ,  $D_8$ ,  $C_{8v}$ , and  $D_7$  cannot undergo quadratic coupling in the active modes. This was noted in studies of  $D_4$  and  $C_4$  systems having one fourfold symmetry axis.<sup>33,34</sup> However, for general  $D_n$  ( $C_n$ ) systems a simple rule predicts whether second order coupling will

occur.

The result depends upon the pseudoangular momentum about the symmetry axis that either the electronic state or the nuclear vibrations possess. This is the angular momentum taken modulo  $n$ , resulting from classifying  $D_\infty$  angular momentum in the  $D_n$  ( $C_n$ ) group. These representations of the group then can be multiplied by just adding or subtracting their angular momenta (modulo  $n$ ). If  $\pm j$  is the angular momentum (modulo  $n$ ) associated with the degenerate Jahn–Teller mode, and  $d$  is the angular momentum (modulo  $n$ ) associated with the degenerate electronic state, the above condition for second order JT coupling

$$\Gamma(JT) \times \Gamma(JT) \supseteq \Gamma(JT)$$

becomes

$$2J \equiv \pm J \pmod{n}.$$

Rewriting as two equations either

$$0 \equiv -J \pmod{n}$$

or

$$0 \equiv 3J \pmod{n}.$$

The first of these is trivial, but the second is useful, implying a test for second order coupling: If and only if  $3J = np$ , where  $p$  is an integer, can a Jahn–Teller mode couple via the square of its associated nuclear displacement. As a corollary, since  $J < n$ , this condition implies that  $n$  must be divisible by three in order for any quadratic Jahn–Teller modes to be possible. Thus, for all the  $D_n$  symmetry groups of  $n \leq 12$ , only  $D_3$ ,  $D_6$ ,  $D_9$ , and  $D_{12}$  have possible quadratic JT effects.  $D_{5h}$  is a simple case of linear coupling, as the early numerical work<sup>7,8</sup> on cyclopentadienyl tended to indicate and later work<sup>9</sup> demonstrated.

It is not commonly realized that although the Jahn–Teller distortion splits the degeneracy of the adiabatic surfaces, the lowest vibronic state found by solution of Eq. (2) belongs to the same group representation as the original degenerate electronic functions. This state thus retains the degeneracy. This degeneracy occurs as a double-valued solution in the coordinate orthogonal to the coordinate of Eq. (2), the pseudoangle connecting the two components of the distortion. The solution in this coordinate is either  $e^{+im\phi}$  or  $e^{-im\phi}$ , where  $\phi$  is the pseudoangle and  $m$  is a half-integer.<sup>11,14</sup> The ambivalence of the sign in the exponent produces the degeneracy.

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