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# Photoelectron Spectroscopic Study of the First Singlet and Triplet States of the Cyclopentadienyl Cation**

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The cyclopentadienyl cation ($C_5H_5^+$) is of fundamental importance in the study of diradicals and in the understanding of antiaromaticity and its effects on structure and chemical reactivity.[1–4] $C_5H_5^+$ is also predicted to be involved as an intermediate in the first steps of soot formation[5] and in the oxidation of aromatic hydrocarbons. The determination of the structure and energetics of the low-lying states in diradicals is a major goal of experimental and theoretical research in physical organic chemistry.[6,7]

Very little experimental information is available on the cyclopentadienyl cation. It has been observed by mass spectrometry,[8,9] but neither optical nor photoelectron spectra have been reported yet. The spectroscopic information on $C_5H_5^+$ is currently limited to an ESR spectrum in an $SbF_5$ matrix, which led to the conclusion that the electronic ground state is a triplet state with a small-to-negligible distortion from $D_{5h}$ symmetry.[10]

The low-lying electronic configurations and corresponding states of $C_5H_5^+$ are given in Scheme 1 in which the symbols

$$\text{I: } (a_2'')^2(e_1'')^2(e_2'')^0 \;:\; {}^1\mathrm{A}_1',\ {}^3\mathrm{A}_2',\ {}^1\mathrm{E}_2'$$
$$\text{II: } (a_2'')^1(e_1'')^3(e_2'')^0 \;:\; {}^1\mathrm{E}_1',\ {}^3\mathrm{E}_1'$$
$$\text{III: } (a_2'')^0(e_1'')^4(e_2'')^0 \;:\; {}^1\mathrm{A}_1'$$

***Scheme 1.*** The low-lying electronic configurations and corresponding states of $C_5H_5^+$.

in parentheses represent the symmetry of the five π molecular orbitals in the $D_{5h}$ point group. The Hartree–Fock energies of the three electronic states of configuration I at $D_{5h}$ geometry are $(2h+J_{23}-K_{23})$ for ${}^3\mathrm{A}_2'$, $(2h+J_{23}+K_{23}, 2h+J_{22}-K_{23})$ for ${}^1\mathrm{E}_2'$, and $(2h+J_{22}+K_{23})$ for ${}^1\mathrm{A}_1'$, in which $h$, $J_{ij}$, and $K_{ij}$ represent the one-electron orbital energy, the Coulomb, and the exchange integrals, respectively, and the indices designate the π molecular orbitals of $C_5H_5^+$ in order of increasing energy.[11] By symmetry, $J_{22}-J_{23}=2K_{23}$ and hence the three states are equally spaced by $2K_{23}$. The spacing of the

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electronic states of $C_5H_5^+$ also depends on vibronic and configuration interactions. The $^1E_2'$ state can be stabilized by a linear Jahn–Teller effect in the vibrational modes of $e_1'$ symmetry, by a quadratic effect in the $e_2'$ and $e_2''$ modes, or by a pseudo-Jahn–Teller coupling to the $^1A_1'$ state mediated by the $e_2'$ modes.[12] The published ab initio calculations usually predict a ground state of $^3A_2'$ symmetry and $D_{5h}$ structure,[1–3] with few exceptions.[5,13]

Two types of photoelectron spectroscopic experiments were performed: one involving single-photon vacuum-ultraviolet (VUV) excitation, the other with a $(1+1')$ two-photon ionization scheme via the $\tilde{A}\,^2A_2''$ intermediate state.[14] All electronic states belonging to configuration I are accessible in the VUV experiment. In contrast, ionization from the $\tilde{A}$ state of configuration $(a_2'')^1(e_1'')^4(e_2'')^0$ leads to the excited configurations II and III of Scheme 1 and the states of configuration I can only be observed through vibronic or configuration interactions. The $\tilde{A}\,^2A_2''$ state contains a contribution from the close-lying $^2A_2''$ state of configuration $(a_2'')^2(e_1'')^2(e_2'')^1$. If the admixture of this state is significant, all three electronic states of configuration I become accessible in the two-color experiment.

The only state of configuration I that can gain intensity in a photoelectron spectrum from excited states of configurations II and III is the $^1A_1'$ state (Scheme 1). The $^1E_2'$ state of configuration I can be accessed from the $\tilde{A}\,^2A_2''$ state through vibronic interactions, either by a coupling to the low-lying $^1E_1'$ state[15] of configuration II mediated by modes of symmetry $e_1'$ or $e_2'$, or by coupling to the $^1A_1'$ state of configuration I according to the strong pseudo-Jahn–Teller effect predicted by theory. The observation or nonobservation of certain ionic states in the two-color photoelectron spectroscopic experiment thus enables one to distinguish between the intensity-borrowing mechanisms listed above.

Figure 1 shows the VUV photoionization (dashed line) and the pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectra (full line) of $C_5H_5$. The step observed in the photoionization spectrum at the position of the first photoelectron band marks the first adiabatic ionization threshold. From a comparison with the two-color photoelectron spectrum (see below), the photoelectron band is assigned to the transition to the vibrationless $\tilde{X}\,^3A_2'$ cationic ground state. The inset of Figure 1 shows a simulation of the rotational envelope of that band based on a rotational temperature of 8 K and the orbital ionization model described previously[16,17] assuming that ionization occurs from an orbital of $d_\pi$ character. The simulation used neutral ground-state parameters previously reported,[14] Boltzmann population factors (including spin-statistical weights), and ionic rotational constants of the $\tilde{X}\,^3A_2'$ state taken from the ab initio equilibrium geometry reported elsewhere.[2] No further vibronic structure was observed in the spectral region 67 800–71 500 $cm^{-1}$, indicating almost diagonal Franck–Condon factors.

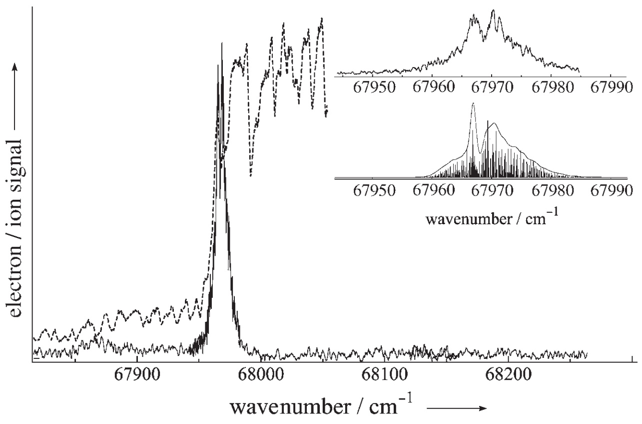

***Figure 1.*** Single-photon photoionization (dashed line) and PFI-ZEKE photoelectron spectrum (full line) of the cyclopentadienyl radical in the region corresponding to the vibrationless $\tilde{X}\,^2E_1''\rightarrow\tilde{X}\,^3A_2'$ transition. The inset shows a comparison of the rotational contour of the origin band (upper trace) with a simulation (lower trace) discussed in the text.

To record the two-color photoionization and PFI-ZEKE photoelectron spectra displayed in Figure 2, the first laser was kept fixed at the intensity maximum of the origin band of the $\tilde{X}\rightarrow\tilde{A}$ transition (29 573.3 $cm^{-1}$) and the second laser was scanned across the ionization thresholds. The first PFI-ZEKE photoelectron band was observed 1600 $cm^{-1}$ above the $^3A_2'$ origin together with a sharp increase in the photoionization signal. The absence of a sharp onset of the photoionization signal at the $\tilde{X}\,^3A_2'$ threshold indicates a negligible direct ionization to the $^3A_2'$ state which, in turn, rules out configurational mixing in the $\tilde{A}\,^2A_2''$ state as a significant intensity-borrowing mechanism. We attribute the structured photoionization signal between the $^3A_2'$ origin and the onset of the two-photon PFI-ZEKE photoelectron spectrum at $\approx 69\,500$ $cm^{-1}$ to electronic autoionization of low-$n$ Rydberg states associated with series converging on electronically excited states of the cation.

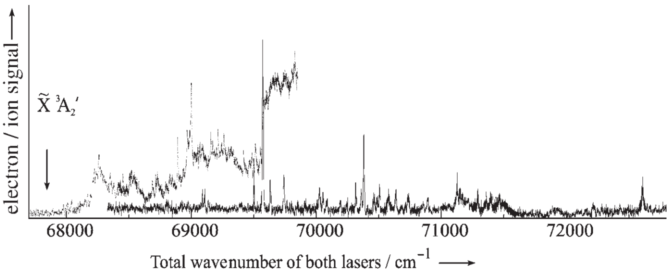

***Figure 2.*** Photoionization (dotted line) and PFI-ZEKE photoelectron spectrum (full line) of the cyclopentadienyl radical recorded following resonance-enhanced two-photon ionization via the $\tilde{A}\,^2A_2''$ intermediate state. The wave number axis corresponds to the sum of the wave numbers of both lasers. The spectrum has not been corrected for the slow variation of the dye laser intensity with wave number.

Striking features of the two-color photoelectron spectrum are the presence of three bands located very close to the main band at 69 567 $cm^{-1}$ (see Figure 2) and an extended vibrational structure. The low-frequency structure must arise from a pseudorotational motion[18] because sequence bands can be ruled out and the wave numbers are too low to correspond to vibrational normal modes. It renders the identification of the origin of the photoelectron band difficult and at present only an upper bound of 69 567 $cm^{-1}$ can be given.

The intensity of the transition to the upper electronic state is likely to originate from vibronic and configuration interactions (see above). Alternatively, it could stem from electronic channel interactions involving the low-$n$ Rydberg states observed in the photoionization spectrum.[19]

The following conclusions can be drawn:

1. The higher of the two states must be $\tilde{a}\,^1E_2'$ because it displays both a pseudorotational motion and a strong Franck–Condon activity resulting from a Jahn–Teller distortion. The other singlet state ($^1A_1'$) of configuration I is predicted to lie more than 1 eV above the triplet ground state.[1,2]
2. Being only observed in the single-photon experiment, the lower of the two observed states must be the $\tilde{X}\,^3A_2'$ state. The almost diagonal Franck–Condon factors imply a $D_{5h}$ structure.[*]
3. The adiabatic ionization energy corresponding to the formation of the $\tilde{X}\,^3A_2'$ state amounts to $(67\,969.2 \pm 4)\ \mathrm{cm}^{-1}$ and the singlet–triplet interval is estimated to be less than $1600\ \mathrm{cm}^{-1}$. As discussed in reference [6], this interval is a key quantity in the characterization of diradicals and an important test for the quality of ab initio calculations. Recent calculations at the highest levels of theory overestimate this interval (see Table 1).

**Table 1:** Adiabatic ionization thresholds (IE) of photoionizing transitions[a] of the cyclopentadienyl radical and first singlet–triplet interval of $C_5H_5^+$.[b]

| | This work | Other work |
|---|---|---|
| $\mathrm{IE}(C_5H_5,\ ^3A_2')/(hc\,\mathrm{cm}^{-1})$ | $67\,969.2 \pm 4$ | $67\,830 \pm 800$[8] |
| $\mathrm{IE}(C_5H_5,\ ^1E_2')/(hc\,\mathrm{cm}^{-1})$ | $\leq 69\,570$ | |
| $\Delta E(S_0{-}T_0)/(hc\ \mathrm{cm}^{-1})$ | $\leq 1600$ | 2275[2][c] |

[a] $\tilde{X}\,^2E_1'' \rightarrow \tilde{X}\,^3A_2'$ and $\tilde{X}\,^2E_1'' \rightarrow \tilde{a}\,^1E_2'$. [b] $\Delta E(S_0{-}T_0)$. [c] CCSD(T)/cc-pVTZ//QCISD/6-31G** value.

4. From a measurement of the adiabatic ionization energy of cyclopentadiene ($(69\,094.5 \pm 3)\ \mathrm{cm}^{-1}$)[21] and the known dissociation energy of cyclopentadiene, $D_0(C_5H_5{-}H)$ ($(22\,874 \pm 350)\ \mathrm{cm}^{-1}$),[22] the dissociation energy of the cyclopentadiene radical cation, $D_0(C_5H_5^+{-}H)$, can be estimated to be $(21\,748 \pm 350)\ \mathrm{cm}^{-1}$ and the 0-K appearance threshold of $C_5H_5^+$ in the photoionization of cyclopentadiene to be $(90\,843 \pm 350)\ \mathrm{cm}^{-1}$. This value is more than 0.3 eV lower than the lowest value reported to date (11.57 eV).[23]
5. The ground state is a nondegenerate $^3A_2'$ state of $D_{5h}$ structure and must therefore have five equivalent C–C bonds, a property usually expected for aromatic molecules.[24] The antiaromatic nature of the ground-state configuration manifests itself in the lowest degenerate singlet $\tilde{a}\,^1E_2'$ state. The Jahn–Teller effect allows the molecule to avoid by distortion the unfavorable antiaromatic electronic structure and favors other conjugatively more stable structures such as the allylic or dienylic structures.[3,25] The stabilization gained by circumventing antiaromaticity is however less than the destabilization by electron repulsion in the singlet state. This situation is in contrast to that of the next member of the cyclic $4n\pi$-electron family of antiaromatic molecules, cyclooctatetraene, the lowest singlet state of which lies below the triplet state.[7] Both results are in accordance with an early prediction of Borden and Davidson that planar $D_{(4n+1)h}$-symmetric $4n\pi$-electron annulenes have a triplet ground state because the repulsion between the unpaired electrons in the nondisjoint, nonbonding MOs increases the energy of the singlet configurations.[25]

The present measurements provide a stringent test for future ab initio calculations of structural and dynamical properties of diradicals. $C_5H_5^+$ is an ideal system to study the relationship between antiaromaticity, symmetry, and the Jahn–Teller effect. A full analysis of these effects will necessitate experimental studies with rotational resolution.

## Experimental Section

The spectra were recorded by using a tunable UV/VUV laser system[26] coupled to a photoion/photoelectron time-of-flight (TOF) mass spectrometer and a pulsed source of jet-cooled radicals,[27], based on excimer laser photolysis of cyclopentadiene at 248 nm in a quartz capillary. Cyclopentadiene was produced from dicyclopentadiene (Fluka) through distillation and stored at −78 °C until used. It was introduced in a stream of neat helium into the nozzle reservoir at a stagnation pressure of 5 bar.

VUV radiation was generated by two-photon resonance-enhanced difference-frequency mixing ($\nu_{\mathrm{VUV}} = 2\nu_1 - \nu_2$) in Kr by using a previously described procedure.[28] In the two-photon, two-color experiment, the outputs of the two dye lasers were combined on a dichroic mirror and crossed the molecular beam at right angles.

The photoelectron spectra were recorded by monitoring the pulsed-field ionization of high Rydberg states ($n \gg 200$) by using a technique known as PFI-ZEKE photoelectron spectroscopy.[29] An electric-field pulse sequence consisting of a discrimination pulse of $0.1\ \mathrm{V\,cm}^{-1}$ and a detection pulse of $0.4\ \mathrm{V\,cm}^{-1}$ delayed by 3 μs with respect to photoionization was used, which resulted in a resolution of $1\ \mathrm{cm}^{-1}$. A correction of $1.6\ \mathrm{cm}^{-1}$ was applied to compensate for the field-induced shift of the ionization thresholds. The photoionization spectra were obtained by measuring the $C_5H_5^+$ ion signal mass selectively as a function of the laser wavenumber. The ions were extracted by using a pulsed electric field of $336\ \mathrm{V\,cm}^{-1}$ delayed by 200 ns with respect to the laser pulses.

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[*] The ground state of the radical undergoes a weak Jahn–Teller distortion with free pseudorotation[20] and has a time-averaged $D_{5h}$ structure. The vibrational structure of the $\tilde{X}\,^2E_1'' \rightarrow \tilde{X}\,^3A_2'$ transition is reminiscent of the $\tilde{X}\,^2E_1'' \rightarrow \tilde{A}\,^2A_2''$ transition of the radical that is dominated by the origin band and only shows weak vibrational structure.

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