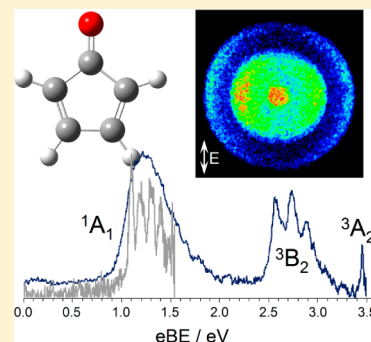


Low-Lying Electronic States of Cyclopentadienone

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S Supporting Information

ABSTRACT: We report a combined experimental and theoretical study of the low-lying electronic states of cyclopentadienone (C_5H_4O). The cyclopentadienone anion ($C_5H_4O^-$) was generated in the gas phase via reaction of atomic oxygen radical anions (O^-) with cyclopentanone (C_5H_8O). Photoelectron imaging was used to gain access to the first three electronic states of C_5H_4O , including the $X\ ^1A_1$ ground state and the 3B_2 and 3A_2 excited states. The first two state assignments are supported by the Franck–Condon simulations of the vibrational progressions observed in the $X\ ^1A_1$ and 3B_2 bands in the photoelectron spectra. The adiabatic electron affinity of cyclopentadienone in the ground state is determined to be $EA(X\ ^1A_1) = 1.06 \pm 0.01$ eV, and the corresponding values for the first two excited states are $EA(^3B_2) = 2.56 \pm 0.02$ eV and $EA(^3A_2) = 3.45 \pm 0.01$ eV. These experimental determinations are in excellent agreement with the CCSD(T) theory predictions, lending further confidence to the above state assignments. On the basis of these results, the lowest singlet–triplet splitting (between the $X\ ^1A_1$ and 3B_2 states) in cyclopentadienone is $\Delta E_{S-T} = 1.50 \pm 0.02$ eV.



1. INTRODUCTION

Cyclopentadienone (C_5H_4O) is an elusive ketone believed to be so reactive that it cannot be isolated.¹ It is nonetheless an important intermediate in many organic reactions, including biomass pyrolysis and the combustion of benzene and phenol.² Depending on the conditions, cyclopentadienone can act as a diene or a dienophile in Diels–Alder reactions.³ It is also of significant fundamental interest, due to its antiaromatic resonance character and rich electronic structure involving a dense manifold of low-lying excited states. Despite its reactivity, cyclopentadienone was shown to have a sufficient lifetime in the gas phase⁴ for rotational spectroscopic studies.⁵ An effectively complete assignment of the fundamental vibrational frequencies was recently reported using infrared absorbance spectroscopy of C_5H_4O in solid rare gas matrices and backed up by high-level *ab initio* anharmonic force field calculations.²

There are just a few previous studies focusing on the excited electronic states of C_5H_4O . Serrano-Andrés et al.,⁶ using the MS-CASPT2 methodology, identified many low-lying excited states, with the first three being the optically forbidden 3B_2 , 1A_2 , and 3A_2 states, at 1.97, 2.48, and 2.51 eV, respectively, above the ground $X\ ^1A_1$ ($\equiv 1\ ^1A_1$) state. The same calculations indicated the lowest optically accessible transition to be $X\ ^1A_1 \rightarrow ^1B_2$, with the excitation energy of 3.00 eV. The 1B_2 state is followed by two more triplet states, 3A_1 and 3B_1 at 3.78 and 4.46 eV, respectively. Nearly degenerate with 3B_1 is the 1B_1 state, calculated at 4.49 eV. Although it is nominally accessible via optical excitation, the transition is predicted to have a negligible oscillator strength. Next up are the $2\ ^1A_1$ and $3\ ^1A_1$ states at 5.42 and 5.98 eV, respectively. Of these, the $3\ ^1A_1$ state is predicted to correspond to the most intense band in the UV/vis spectral range.

The above predictions are in reasonable agreement with the UV/visible spectrum,⁷ which shows band maxima at 360 and 195 nm (3.44 and 6.35 eV, respectively), possibly corresponding to the 1B_2 and $3\ ^1A_1$ excited states. However, the broader conclusion that forms upon reviewing these results is that most of the low-lying excited states of C_5H_4O cannot be studied by optical spectroscopy. Anion photoelectron spectroscopy, on the other hand, is not bound by optical selection rules and thus uniquely suited for studying both the singlet and triplet states of cyclopentadienone. Moreover, the unstable nature of the cyclopentadienone molecule does not preclude the existence of a relatively stable anion, which can be used as a launching pad to study the elusive neutral species.

In this work, we generate the cyclopentadienone anion ($C_5H_4O^-$) in the gas phase via reaction of atomic oxygen radical anions (O^-) with the cyclopentanone (C_5H_8O) precursor and use photoelectron imaging spectroscopy to gain access to several low-lying electronic states of neutral C_5H_4O . We report the first measurements of cyclopentadienone's electron affinity and singlet–triplet splitting.

2. EXPERIMENTAL METHODS

The experiments were carried out using the negative-ion photoelectron imaging spectrometer described in detail elsewhere.^{8,9} In brief, the room-temperature vapor of cyclopentanone seeded in N_2O carrier gas at a backing pressure of 30 psi was expanded into vacuum through a pulsed supersonic

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nozzle (General Valve, series 99). The expansion was crossed with a collimated 1 keV electron beam. As the first step of ion formation, the $\text{O}^{\bullet-}$ radical anions were formed by dissociative attachment of slow secondary electrons to N_2O . The nascent $\text{O}^{\bullet-}$ then reacted with the cyclopentanone precursor, producing a variety of anionic species, including $\text{C}_5\text{H}_4\text{O}^-$. The reactivity of $\text{O}^{\bullet-}$ with closed-shell organic compounds is well documented and has been utilized to synthesize a number of important anion intermediates in the gas phase.^{10–13}

The resulting anions were extracted into a Wiley–McLaren¹⁴ time-of-flight mass spectrometer, where they were separated by their mass-to-charge ratio. The mass-selected anion packets were intersected with linearly polarized laser pulses inside the velocity-map imaging assembly. The photodetachment experiments were performed at 355, 532, 808, and 1064 nm. The 808 nm radiation was the fundamental output of a Continuum, Inc., Surelight II-20 Nd:YAG (yttrium aluminum garnet) pumped (532 nm) ND6000 dye laser, operating with the LDS821 dye (10 mJ, ~ 10 ns pulses). The 1064, 532, and 355 nm radiation was the output of the fundamental, second, or third harmonics of Spectra Physics, Inc. Lab-130 Nd:YAG laser (5 mJ, ~ 6 ns pulses).

The photodetached electrons were accelerated by a series of velocity-map¹⁵ imaging^{16,17} electrodes onto a 40 mm diameter position-sensitive microchannel-plate detector coupled to a P43 phosphorus screen (Burle, Inc.). The resulting images were recorded by a charge-coupled device camera (CoolSNAP MYO from Photometrics, Inc.) and accumulated for $\sim 10^6$ experimental cycles. The images were analyzed by means of the inverse Abel transformation¹⁷ using the BASEX software package.¹⁸ The energy scale in the resulting spectra was calibrated using the well-known photodetachment transitions of $\text{O}^{\bullet-}$.^{19,20}

3. THEORETICAL METHODS

The X^2B_1 electronic ground state of the $\text{C}_5\text{H}_4\text{O}^-$ anion and the X^1A_1 , 3B_2 , and 3A_2 states of the neutral were studied with the coupled-cluster CCSD(T) method employing single, double, and a noniterative treatment of triple excitations.²¹ Restricted open-shell Hartree–Fock reference functions were used for the doublet and triplet states, whereas the calculations for the ground singlet state of the neutral were done with spin-adapted restricted Hartree–Fock references. For the geometry optimizations and harmonic force field evaluations, the ANO0 basis set²² was used. The larger aug-cc-pVTZ and aug-cc-pVQZ sets²³ were used in the single point energy calculations to accurately estimate the electron affinity of the three neutral cyclopentadiene electronic states. The 1s (core level) electrons were frozen in the treatment of electron correlation.

Franck–Condon simulations for the spectra were carried out with the FCfast program, developed by Mark Dierksen at the University of Muenster, using normal coordinates, displacements, and Duschinsky rotation matrices generated from the CCSD(T)/ANO0 harmonic force fields.

4. RESULTS AND DISCUSSION

A representative mass spectrum of the anions generated with the cyclopentanone ($\text{C}_5\text{H}_8\text{O}$) precursor seeded in N_2O is presented in Figure 1a, along with a reference spectrum obtained for the fluoroacetonitrile (CH_2FCN) mixture with N_2O shown in Figure 1b. The comparison of the two spectra

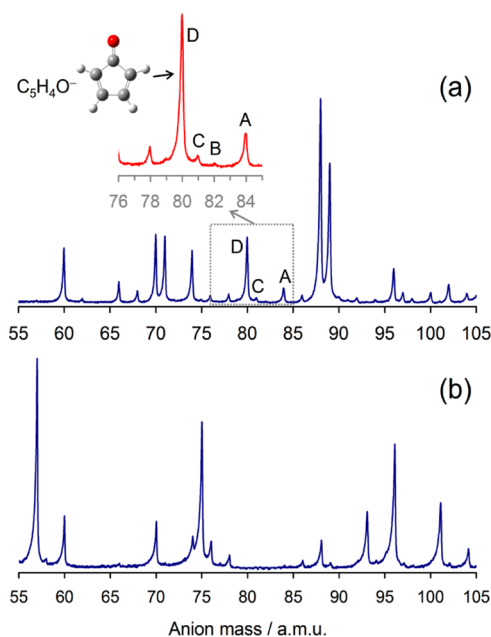


Figure 1. Representative time-of-flight mass spectra of the anions formed in the electron-impact ionization source using the supersonic expansion of (a) cyclopentanone ($\text{C}_5\text{H}_8\text{O}$) and (b) fluoroacetonitrile (CH_2FCN), each seeded in N_2O . The spectra are plotted on similar intensity scales to highlight the precursor-sensitive nature of the peaks in the 76–84 amu range, expanded in the inset in (a). The peaks relevant to this work are labeled and assigned as follows. Peak A (84 amu): $\text{C}_5\text{H}_8\text{O}^-$. Peak B (82 amu): $\text{C}_5\text{H}_6\text{O}^-$, with a possible contribution of the ^{13}C doubly substituted isotope of $\text{C}_5\text{H}_4\text{O}^-$, $^{13}\text{C}_2^{12}\text{C}_3\text{H}_4\text{O}^-$ (0.12% natural abundance). Peak C (81 amu) the ^{13}C substituted version of $\text{C}_5\text{H}_4\text{O}^-$, i.e., $^{13}\text{C}^{12}\text{C}_4\text{H}_4\text{O}^-$ (5.3% natural abundance). Peak D (80 amu): $\text{C}_5\text{H}_4\text{O}^-$, the ion of interest.

indicates the precursor dependence of the peaks in the 76–84 amu range, which is expanded in the inset in Figure 1a.

The ion peaks relevant to this study are labeled A–D (Figure 1a). Peak A (84 amu) corresponds to the cyclopentanone anion, $\text{C}_5\text{H}_8\text{O}^-$. The only known determination of the electron affinity (EA) of cyclopentanone corresponds to a dipole-bound anion formed via charge exchange with Rydberg atoms (EA = 1.7 meV).²⁴ Peak D (at 80 amu) corresponds to the ion of interest, i.e., the cyclopentadienone isomer of $\text{C}_5\text{H}_4\text{O}^-$ (as will become clear shortly). Peak C (81 amu) is consistent with the ^{13}C substituted version of the same anion, $^{13}\text{C}^{12}\text{C}_4\text{H}_4\text{O}^-$. Given the 1.1% natural abundance of the ^{13}C isotope, an approximate 1:20 ratio of $^{13}\text{C}^{12}\text{C}_4\text{H}_4\text{O}^-$ and $^{12}\text{C}_5\text{H}_4\text{O}^-$ is expected, consistent with the relative intensities of peaks C and D.

The observation of $\text{C}_5\text{H}_4\text{O}^-$ (peak D) is attributed to O^- reactions with cyclopentanone, but the exact mechanism is unclear. The formation of $\text{C}_5\text{H}_4\text{O}^-$ from $\text{C}_5\text{H}_8\text{O}$ implies the loss of four hydrogens (H_4^+), which is unlikely to happen in a single step. On the basis of the general reactivity of O^- with organic molecules,^{10–13} the reaction with $\text{C}_5\text{H}_8\text{O}$ is expected to yield $\text{C}_5\text{H}_7\text{O}^-$ and/or $\text{C}_5\text{H}_6\text{O}^-$ via the standard H^+ or H_2^+ abstraction mechanisms, respectively. No trace of $\text{C}_5\text{H}_7\text{O}^-$ is observed in the experiment, but an 82 amu ion (presumably $\text{C}_5\text{H}_6\text{O}^-$) is present in the mass spectrum (peak B in the inset in Figure 1a). Although $\text{C}_5\text{H}_6\text{O}^-$ is expected to be adiabatically stable with respect to detachment (per CCSD/aug-cc-pVDZ calculations), it is only a minor product in the present case.

It is possible that $\text{C}_5\text{H}_6\text{O}^-$ undergoes additional reactions that promptly remove it from the mass spectrum. The primary

$\text{O}^- + \text{C}_5\text{H}_8\text{O} \rightarrow \text{C}_5\text{H}_6\text{O}^- + \text{H}_2\text{O}$ reaction is expected to yield excited (metastable) ions, which makes their further unimolecular reactivity plausible, but not straightforward to predict. Due to the partial negative charge on the oxygen in the cyclopentanone precursor, the initial attack of O^- is likely to be on the β hydrogens in $\text{C}_5\text{H}_8\text{O}$ (farthest from the carbonyl group). However, as common in ketones, it is the α sites (adjacent to the carbonyl group) that are most acidic, i.e., characterized by the smallest pK_a values. Therefore, nascent $\text{C}_5\text{H}_6\text{O}^-$ resulting from the initial reaction of $\text{C}_5\text{H}_8\text{O}$ with O^- (at either a single β site or both β sites) will not be the most stable isomer of the anion. Additional vibrational excitation is imparted due to the equilibrium geometry difference between the anion and the precursor.

If the nascent $\text{C}_5\text{H}_6\text{O}^-$ product is not promptly stabilized by collisions, it may, hypothetically, undergo a variety of transformations, such as unimolecular decomposition, H migration, and autodetachment. The first possibility may yield the observed $\text{C}_5\text{H}_4\text{O}^-$ ion, whereas the competing neutralization via autodetachment may explain the near-absence of $\text{C}_5\text{H}_6\text{O}^-$ in the mass spectrum. The $\text{C}_5\text{H}_6\text{O}$ diradical resulting from the autodetachment may, in principle, react again with O^- , giving another pathway to $\text{C}_5\text{H}_4\text{O}^-$ via a second H_2^+ abstraction. However, given the small density of the supersonic expansion, the overall mechanism involving two bimolecular steps is unlikely to yield detectable quantities of the final product.

Therefore, the initial H_2^+ abstraction from $\text{C}_5\text{H}_8\text{O}$, followed by prompt unimolecular decomposition of the $\text{C}_5\text{H}_6\text{O}^-$ intermediate, is deemed to be the most plausible pathway for $\text{C}_5\text{H}_4\text{O}^-$ formation. Because no concrete data are available to validate this mechanism, we submit that it is speculative. Nonetheless, the photoelectron spectra presented below leave no doubt that the final product of this complex chemistry is indeed the cyclopentadienone anion, $\text{C}_5\text{H}_4\text{O}^-$.

The photoelectron images and spectra of $\text{C}_5\text{H}_4\text{O}^-$ obtained at 1064, 808, 532, and 355 nm are presented in Figure 2. The spectra are plotted versus electron binding energy, $\text{eBE} = h\nu - \text{eKE}$, where eKE is electron kinetic energy. Partial vibrational resolution in the 1064 nm data allows for accurate determination of the adiabatic electron affinity of the neutral, $\text{EA}(\text{X } ^1\text{A}_1) = 1.06 \pm 0.01 \text{ eV}$. This is the first determination of this important property of cyclopentadienone.

The two prominent peaks in the 1064 nm spectrum are separated by ca. 645 cm^{-1} . This corresponds, approximately, to the fundamental frequency ν_9 of cyclopentadienone, which has been observed by Ormond et al.² in solid neon at 651 cm^{-1} . Qualitatively, this mode can be described as an in-plane ring skeletal motion involving the stretching of the C5–C1–C2 unit (C1 being the carbonyl carbon).

To facilitate the Franck–Condon analysis, the results of *ab initio* optimizations of the geometric structures of the anion and the neutral are summarized in Figure 3. The figure shows the structural parameters of the anion $\text{X } ^2\text{B}_1$ (plain font) and neutral $\text{X } ^1\text{A}_1$ (italics) and $^3\text{B}_2$ (bold) states. The calculated harmonic vibrational frequencies of the three electronic states are summarized in the Supporting Information. The Franck–Condon activity of the ν_9 mode is expected on the basis of the calculated geometry differences, as the C1–C2 and C1–C5 bond lengths are 1.476 \AA in the anion and 1.517 \AA in the $\text{X } ^1\text{A}_1$ state of the neutral. The same prediction also follows from the simple molecular-orbital considerations, because the singly

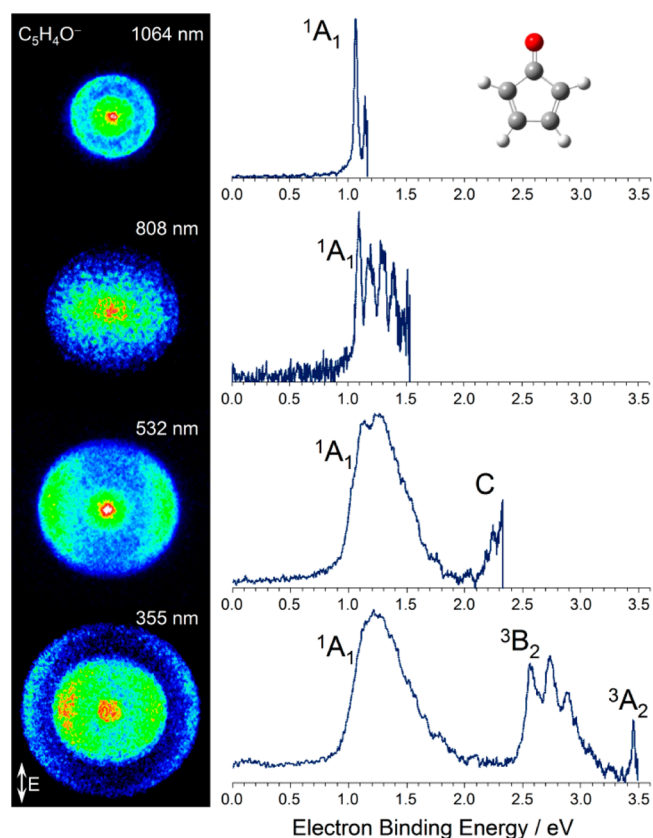


Figure 2. Unprocessed photoelectron images (left) and corresponding photoelectron spectra (right) of the $\text{C}_5\text{H}_4\text{O}^-$ anion obtained at 1064, 808, 532, and 355 nm. The laser polarization direction is vertical in the plane of the images, as indicated by the double-sided arrow in the bottom left corner of the 355 nm image.

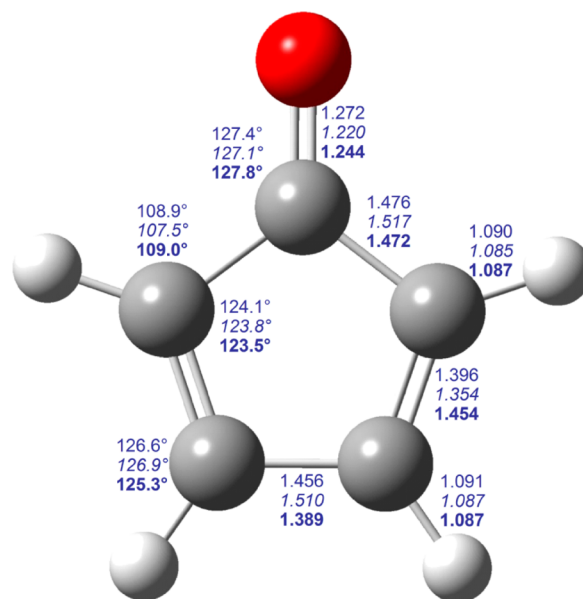


Figure 3. Optimized geometries of the $\text{C}_5\text{H}_4\text{O}^-$ anion ($\text{X } ^2\text{B}_1$ electronic state) and neutral $\text{C}_5\text{H}_4\text{O}$ in the ground ($\text{X } ^1\text{A}_1$) and first excited ($^3\text{B}_2$) electronic states, based on CCSD(T)/ANO0 calculations. All three structures are planar and belong to the C_{2v} symmetry point group. The bond lengths (in Angstrom) and angles (in degrees) for the $\text{X } ^2\text{B}_1$ (anion), $\text{X } ^1\text{A}_1$, and $^3\text{B}_2$ states are given in plain, *italic*, and **bold** fonts, respectively.

occupied orbital of the anion has π bonding character with respect to the C1–C2 and C1–C5 “single bonds” (Figure 3).

The expanded version of the 1064 nm spectrum, shown as a bold trace in Figure 4, indicates another peak at eBE = 1.16 eV,

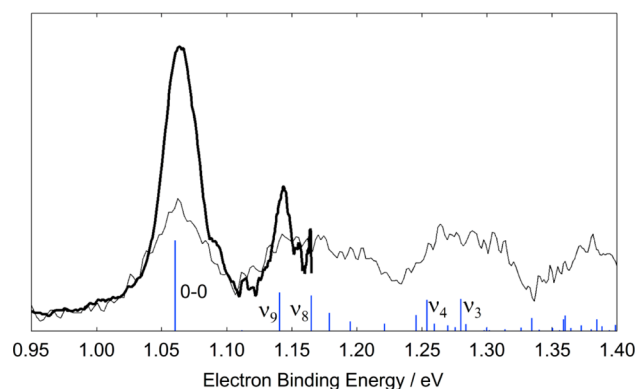


Figure 4. Harmonic Franck–Condon stick spectrum of the low-energy region of the photoelectron spectrum of cyclopentadienone anion, corresponding to the X^1A_1 state of C_5H_4O . The bold trace is the 1064 nm spectrum, and the lighter trace is the 808 nm spectrum, reproduced from Figure 3. The positions of the most active fundamental vibrations that contribute to the spectrum are shown.

essentially at the photon-energy limit of the experiment. It is shifted by *ca.* 840 cm^{-1} with respect to the origin and tentatively assigned to the ν_8 vibrational mode of the neutral. Similar to ν_9 , this mode corresponds to a ring skeletal motion involving the stretching of the C5–C1–C2 unit; therefore, its excitation is consistent with the calculated structures of the anion and the neutral in Figure 3. The ν_8 mode was also observed in the matrix infrared study (at 843 cm^{-1}).² The 808 nm spectrum in Figure 2 shows a fairly broad and convoluted progression that is attributed largely to activity in the ν_6 and ν_8 modes, as well as the carbonyl stretch ν_3 . The carbonyl stretch is expected to exhibit considerable activity, as the C–O bond length is calculated to change from 1.272 Å in the anion to just 1.220 Å in the ground-state neutral. These interpretations of the 1064 and 808 nm photoelectron spectra in terms of photodetachment of the cyclopentadienone anion to the ground state of the neutral are further supported by the Franck–Condon simulation of low-energy spectral region in Figure 4, as well as by the essentially perfect agreement between calculated and observed values of adiabatic electron affinity (Table 1).

Table 1. Calculated and Experimental Adiabatic Electron Affinities (EA) of the X^1A_1 , 3B_2 , and 3A_2 States of $C_5H_4O^a$

method/basis set	adiabatic EA/eV		
	X^1A_1	3B_2	3A_2
CCSD(T)/aug-cc-pVTZ	1.032	2.524	3.393
CCSD(T)/aug-cc-pVQZ	1.055	2.559	3.442
Experiment	1.06(1)	2.56(2)	3.45(1)

^aThe anion (X^2B_1) and neutral (X^1A_1 , 3B_2 , and 3A_2) geometry optimizations were performed at the CCSD(T) level of theory with the ANO0 basis set. The calculated electron affinity values listed in the table were determined from the results of single-point CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ energy calculations using the CCSD(T)/ANO0 optimized geometries.

In contrast to the lower energy (longer wavelength) spectra, the 532 and 355 nm data in Figure 2 show no vibrational progression for the ground-state transition, due to the limited resolution of the instrument at higher eKE, compounded by the overlap of multiple vibrational bands. However, the 355 nm image and the corresponding spectrum reveal two additional photodetachment transitions. In addition to the vibrationally unresolved X^1A_1 band, we observe transitions to two low-lying excited states of neutral C_5H_4O . These are assigned to the lowest triplet state 3B_2 and, perhaps less securely (because it is only seen near threshold), the next triplet 3A_2 state.

In the 532 nm spectrum (Figure 2), there is an additional transition between eBE = 2.10 and 2.33 eV. It is represented by an isotropic central feature in the photoelectron image and labeled C (for “central”) in the spectrum. This transition is, however, absent in the higher-energy 355 nm spectrum, which displays no notable features in the eBE range between 2.10 and 2.33 eV. Hence, feature C is likely due to autodetachment from an excited electronic state of $C_5H_4O^-$, accessed at 532 nm, but out of resonance at 355 nm. Such wavelength-dependent autodetachment processes are not uncommon in anion photodetachment and usually appear as isotropic central (i.e., low eKE) features in the photoelectron images.

Based on the first peak in the 3B_2 progression in the 355 nm spectrum, the EA of the triplet state is $EA(^3B_2) = 2.56 \pm 0.02\text{ eV}$, in excellent agreement with the theory predictions (Table 1). Comparing this result to $EA(X^1A_1)$ yields the singlet–triplet splitting between the X^1A_1 and 3B_2 states of C_5H_4O , $\Delta E_{S-T} = 1.50 \pm 0.02\text{ eV}$. In the work by Serrano-Andrés et al.,⁶ the state energies were calculated at the optimized geometry of the neutral; i.e., they correspond to vertical excitations from the X^1A_1 state. Within the computational errors, the difference between the ΔE_{S-T} value determined here, and the corresponding 1.97 eV vertical gap predicted by Serrano-Andrés et al.,⁶ is presumed to be due mostly to the triplet-state geometry relaxation.

The vibrational progression apparent in the 3B_2 transition in Figure 2 has an average spacing of about 1350 cm^{-1} but appears to be irregular, with the first main feature found in the range $1250\text{--}1650\text{ cm}^{-1}$ and the second from about $2500\text{ to }2900\text{ cm}^{-1}$. The fundamentals having the strongest calculated Franck–Condon activity are ν_4 and ν_5 , with corresponding harmonic frequencies of 1501 and 1350 cm^{-1} , respectively. It can be seen from the Franck–Condon simulation in Figure 5 that these frequencies provide a very good match to the first member of the experimentally observed 3B_2 progression, but perhaps less so to the second peak, where the three two-quantum transitions associated with these fundamentals are slightly above the observed band maximum, despite being the strongest transitions predicted in this region. This may be indicative of anharmonicity or perhaps a strong Fermi resonance in the polyad, but investigation of this effect is beyond the scope of this work. Nevertheless, the assignment to this part of the spectrum to the 3B_2 state of cyclopentadienone is secure, due to the excellent agreement of the calculated and measured values of adiabatic electron affinity and the compelling agreement of the Franck–Condon simulation within 2000 cm^{-1} of the vibrational ground state.

The highest-eBE transition in the 355 nm spectrum is assigned to the next triplet state, 3A_2 , with an $EA(^3A_2) = 3.45 \pm 0.01\text{ eV}$. This assignment is based on two considerations. First, the calculated electron affinity of this state is in essentially perfect agreement with this observation. Second, Hund’s rule

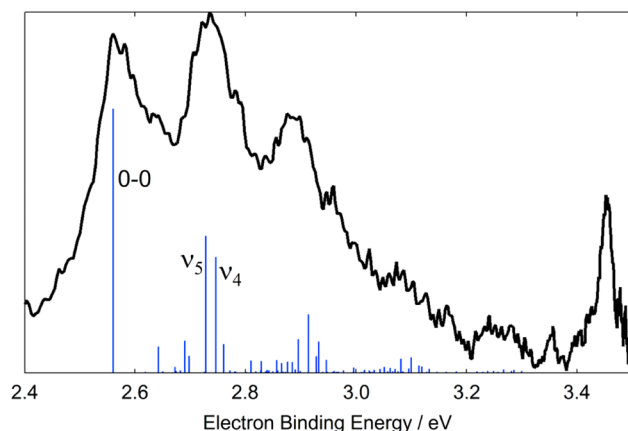


Figure 5. Harmonic Franck–Condon stick spectrum of the low-energy region of the photoelectron spectrum of cyclopentadienone anion, corresponding to the 3B_2 state of C_5H_4O . The experimental trace is from the 355 nm spectrum, reproduced from Figure 3. The positions of the most active fundamental vibrations are shown. The peak at eBE = 3.45 eV has been assigned as the 3A_2 origin.

suggests that the 3A_2 state will lie below the corresponding singlet (1A_2), and there is no reason to assume a breakdown of this rule in this case. Together with the fact that previous calculations⁶ have predicted that the 1B_2 state is above the 1A_2 state, the assignment of an electronic state in the high-energy region of the 355 nm spectrum to the 3A_2 state seems logical. However, we caution that this band is observed quite close to the top of the spectral range of the experiment and the possibility that it may be an autodetachment artifact cannot be discarded completely. Thus, we view this assignment as plausible, but considerably less secure than those of the lower two electronic states.

5. SUMMARY

We have reported a combined experimental and theoretical study of the low-lying electronic states of cyclopentadienone (C_5H_4O). The cyclopentadienone anion ($C_5H_4O^-$) was generated in the gas phase via the reaction of atomic oxygen radical anions (O^-) with the cyclopentanone (C_5H_8O) precursor. Photoelectron imaging was used to gain access to several low-lying states of C_5H_4O . The first two bands in the photoelectron spectra are assigned to the $X\ {}^1A_1$ ground state and the first excited 3B_2 state. These assignments are supported by the essentially perfect agreement of the experimental electron affinity values with the corresponding theory predictions, as well as by the Franck–Condon simulation of the vibrational progressions observed in the $X\ {}^1A_1$ and 3B_2 bands. The next transition, observed close to the energetic limit of the experiment, is assigned to the 3A_2 state, on the basis of the agreement of the band position with the calculated electron affinity. Based on these assignments, the adiabatic electron affinity of cyclopentadienone in the ground electronic state is determined to be $EA(X\ {}^1A_1) = 1.06 \pm 0.01$ eV, whereas the affinities (adiabatic electron binding energies) of the first two excited states are $EA({}^3B_2) = 2.56 \pm 0.02$ eV and $EA({}^3A_2) = 3.45 \pm 0.01$ eV. The lowest singlet–triplet splitting (between the $X\ {}^1A_1$ and 3B_2 states) is $\Delta E_{S-T} = 1.50 \pm 0.02$ eV.

■ ASSOCIATED CONTENT

Supporting Information

The calculated harmonic vibrational frequencies of the equilibrium structures of the cyclopentadienone anion ($X\ {}^3B_1$ state) and neutral in the $X\ {}^1A_1$ and 3B_2 electronic states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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