Electronic Spectroscopy

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The Electronic Spectrum of the Fulvenallenyl Radical

*Arghya Chakraborty, Jan Fulara, and John P. Maier**

Abstract: *The fulvenallenyl radical was produced in 6 K neon matrices after mass-selective deposition of $C_7H_5^-$ and $C_7H_5^+$ generated from organic precursors in a hot cathode ion source. Absorption bands commencing at $\lambda = 401.3$ nm were detected as a result of photodetachment of electrons from the deposited $C_7H_5^-$ and also by neutralization of $C_7H_5^+$ in the matrix. The absorption system is assigned to the $1\,^2B_1 \leftarrow X\,^2B_1$ transition of the fulvenallenyl radical on the basis of electronic excitation energies calculated with the MS-CASPT2 method. The vibrational excitation bands detected in the spectrum concur with the structure of the fulvenallenyl radical. Employing DFT calculations, it is found that the fulvenallenyl anion and its radical are the global minima on the potential energy surface among plausible structures of C_7H_5.*

Resonance-stabilized organic radicals, having high thermal stability and resistance to oxidation in flames, are considered as precursors and chain propagators in mass growth processes during the pyrolysis of hydrocarbons. Theoretical models suggest that the recombination of propargyl ($^{\bullet}CH_2{-}C{\equiv}CH$) leads to the formation of benzene in acetylenic flames.[1–3] The formation of benzene was detected in the self-reaction of propargyl radicals in high-pressure shock tube experiments.[4] However, such model and experimental evidence failed to explain the generation of larger aromatic compounds in soot.

With this in mind, the fulvenallenyl radical (C_7H_5; **FA**) has attracted attention as the major intermediate in the formation of polycyclic aromatic compounds, ever since the C_7H_n class of molecules were identified in hydrocarbon flames.[5–8] **FA** is considered to be a very stable radical because of its conjugated propargyl and cyclopentadienyl subunits. The formation of C_7H_5 in a hot cathode discharge source from acetylene, allene, diacetylene, cyclopentadiene, benzene, and toluene is evident in the mass spectra. The formation of **FA** has also been established in a toluene pyrolysis reaction by comparing the theoretical and experimental ionization energies.[8] Moreover, computational models suggest low energy pathways for the formation of polycyclic aromatic hydrocarbons (PAHs) by the self-assembly of **FA** radicals or by addition of diacetylene to fulvenallenyl.[6]

The broad mid-infrared emission features detected in space have been attributed to vibrational transitions of PAHs.[9] Despite their importance in astrochemistry, the formation pathways of PAHs are still unknown. It is considered that PAHs are formed at very high temperatures in the outflow of post-AGB stars (AGB = asymptotic giant branch) and the chemistry is similar to the combustion of hydrocarbons in a terrestrial environment.[10] Thus, the existence of fulvenallenyl radicals in the interstellar medium could be envisaged. Therefore, this radical carries significant interest in terrestrial combustion processes and astrochemistry, and knowledge of its spectroscopy is needed.

Transient radicals are generated in the matrix in two steps: 1) mass-selected anions or cations are codeposited with neon at 6 K, 2) trapped ions are irradiated by UV photons to produce the radicals through photodetachment of electrons from anions or recombination of electrons with the cations. To choose the right experimental approach and conditions for the production of **FA**, potential energy surfaces (PES) of neutral species, anions, and cations of C_7H_5 have been calculated with the DFT method using the M06-2X functional and the cc-pVTZ basis set (aug-cc-pVDZ has been used for the anions). Ground-state optimization is carried out to determine the relative stabilities of the fulvenallenyl cation $\mathbf{FA}^+$ and anion $\mathbf{FA}^-$ with respect to other isomers (Figure 1). It was found that **FA** and $\mathbf{FA}^-$ are the global minima on the potential energy surface (PES) among plausible structures (see Chart 1SI in the Supporting Information). The anion $\mathbf{FA}^-$ is more stable by 157 kJ mol^{-1} relative to the next isomer $\mathbf{B}^-$, which suggests that the $C_7H_5^-$ ion beam produced from a discharge source predominantly contains $\mathbf{FA}^-$ and therefore the best approach for **FA** generation in a neon matrix would be the deposition of $C_7H_5^-$ followed by UV irradiation. Structural change of species trapped in neon matrices during the photodetachment of electrons is unlikely because neon microcrystals rigidly hold the guest molecules.[11,12]

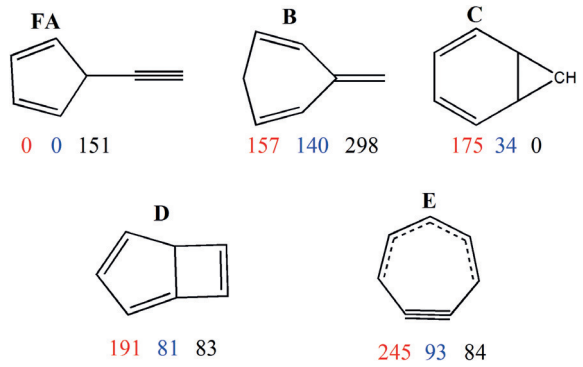

Figure 1. Structures and relative ground-state energies in kJ mol^{-1} of the five most stable isomers of C_7H_5. The energies of anions are given in red, neutral species in blue, and cations in black.

[*] A. Chakraborty, Dr. J. Fulara, Prof. Dr. J. P. Maier
Departement Chemie, Universität Basel
Klingelbergstrasse 80, 4056 Basel (Switzerland)
E-mail: j.p.maier@unibas.ch
Homepage: http://www.chemie.unibas.ch/~maier/
Dr. J. Fulara
Institute of Physics, Polish Academy of Sciences
Al. Lotników, 32/46, 02-668 Warsaw (Poland)

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201508961.

$C_7H_5^-$ was produced from toluene in a hot cathode discharge source. The anions with $m/z = 89$ after mass-selection were deposited with an excess of neon onto a substrate held at 6 K. The $A\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ electronic transition[13] of C_3 at $\lambda = 405.0$ nm and $B\,^2\Sigma_u^+ \leftarrow X\,^2\Sigma_g^+$ of N_2^+ at $\lambda = 398$ nm were only detected after deposition of $C_7H_5^-$ (Figure 2, black trace). C_3 is the collisionally induced fragment of $C_7H_5^-$ resulting from high-kinetic-energy deposition. N_2^+ is formed by collisionally induced ionization of a N_2 impurity in the matrix and acts as a counter ion, balancing the negative charge.

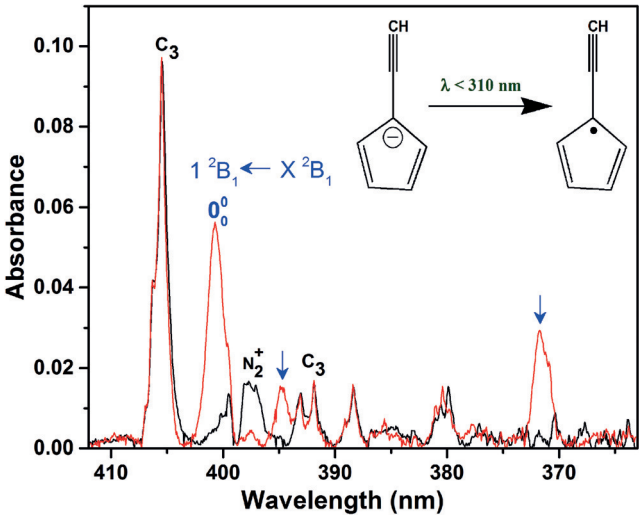

Figure 2. Absorption spectrum recorded after deposition of $C_7H_5^-$ in a neon matrix (black trace) and after irradiation with photons of wavelength $\lambda = 250$–310 nm (red trace). The absorption band which appeared after the photodetachment of electrons from $C_7H_5^-$ ions is the $1\,^2B_1 \leftarrow X\,^2B_1$ electronic transition of the fulvenallenyl radical. Vibrational bands of the $\lambda = 401$ nm electronic transition are indicated by blue arrows.

An absorption system starting at $\lambda = 401.3$ nm appeared after irradiating the matrix with photons of wavelength $\lambda < 260$ nm (Figure 2, red trace). The system is composed of absorption bands at $\lambda = 401.3$, 395.5, 371.7, and 346.3 nm (Table 1). The bands of C_3 remained intact whereas those of N_2^+ vanished because of recombination with free electrons detached from the anions. The same rate of intensity increase for these four bands upon UV irradiation and their similar relative peak intensities from different precursors indicate that they are of one neutral absorber. This means that the $\lambda = 401$ nm electronic absorption system originates from neutral C_7H_5 produced in situ in solid neon by detachment of an electron from trapped $C_7H_5^-$. The fulvenallenyl radical **FA** should be the carrier according to the ground-state energy calculations.

Table 1: Band maxima (±0.1 nm) of the $1\,^2B_1 \leftarrow X\,^2B_1$ absorption system of the fulvenallenyl radical in a 6 K neon matrix.[a]

λ [nm]	$\tilde{\nu}$ [cm^{-1}]	$\Delta\tilde{\nu}$ [cm^{-1}]	Assignment
401.3	24919	0	0_0^0
395.5	25284	365	ν_{19}
371.7	26903	1984	ν_4
346.3	28877	3958	$2\nu_4$

[a] The assignment is based on the ground-state vibrational frequencies of the normal modes calculated at the DFT/M06-2X/cc-pVTZ level: $\mathbf{a_1}$; ν_1–$\nu_{11} = 3467$, 3271, 3250, 2138, 1531, 1421, 1309, 1087, 1008, 922, 561 cm^{-1}; $\mathbf{a_2}$; ν_{12}–$\nu_{14} = 955$, 747, 534 cm^{-1}; $\mathbf{b_1}$; ν_{15}–$\nu_{20} = 933$, 780, 681, 652, 409, 148 cm^{-1}. The parameter $\tilde{\nu}$ is the wavenumber and $\Delta\tilde{\nu}$ is the difference to the origin band.

The structural assignment excitation energies (and oscillator strengths) of the five most stable isomers of C_7H_5 and their anions were calculated using the MS(5)-CASPT2 method. The results are presented in Table 2. Three structures: **FA**, **B**, and **C** possess moderately intense transitions at 3.21, 3.11, and 3.45 eV, respectively, close to the origin at $\lambda = 401.3$ nm (3.09 eV). Isomers **E** and **D** can be excluded from further consideration because the predicted energies are

Table 2: Electronic states, excitation energies (eV), and oscillator strengths (*f*; value in italics) of anionic, neutral, and cationic forms of the C_7H_5 isomers given in Figure 1.[a]

Isomer	Anionic form	Neutral form	Cationic form
FA	X $^1A_1$ 0.00	X $^2B_1$ 0.00	X $^1A_1$ 0.00
	1 $^1A_1$ 4.39 *0.180*	1 $^2B_1$ 3.21 *0.033*	1 $^1A_1$ 2.96 *0.001*
	2 $^1A_1$ 4.77 *0.180*	2 $^2B_1$ 4.66 *0.005*	2 $^1A_1$ 4.10 *0.480*
	3 $^1A_1$ 5.79 *0.010*	3 $^2B_1$ 5.41 *0.150*	3 $^1A_1$ 5.39 *0.007*
	1 $^1B_2$ 4.69 *0.120*	2 $^2A_2$ 5.60 *0.002*	1 $^1B_2$ 0.97 *0.004*
	1 $^1B_2$ 4.98 *0.040*		
B	X $^1A_1$ 0.00	X $^2B_1$ 0.00	X $^1A_1$ 0.00
	1 $^1A_1$ 4.14 *0.370*	1 $^2B_1$ 3.11 *0.027*	1 $^1A_1$ 4.20 *0.130*
	2 $^1A_1$ 4.73 *0.130*	2 $^2B_1$ 5.20 *0.025*	2 $^1A_1$ 4.46 *0.018*
	3 $^1A_1$ 5.59 *0.011*	2 $^2A_1$ 5.64 *0.001*	3 $^1A_1$ 4.89 *0.054*
	1 $^1B_2$ 4.88 *0.097*	1 $^2A_2$ 1.62 *0.000*	1 $^1B_1$ 0.95 *0.001*
	2 $^1B_2$ 5.27 *0.054*	2 $^2A_2$ 4.94 *0.020*	3 $^1B_1$ 4.93 *0.004*
	3 $^1B_2$ 5.60 *0.010*	3 $^2A_2$ 5.87 *0.003*	2 $^1B_2$ 5.12 *0.001*
C	X $^1A'$ 0.00	X $^2B_1$ 0.00	X $^1A_1$ 0.00
	1 $^1A'$ 1.67 *0.001*	1 $^2B_1$ 3.45 *0.018*	1 $^1A_1$ 5.44 *0.006*
	3 $^1A'$ 2.33 *0.009*	2 $^2B_1$ 4.64 *0.032*	1 $^1B_1$ 4.79 *0.001*
	4 $^1A'$ 4.77 *0.013*	3 $^2B_1$ 4.83 *0.005*	1 $^1B_2$ 4.51 *0.063*
	5 $^1A'$ 5.42 *0.001*	1 $^2A_1$ 4.50 *0.000*	
		1 $^2A_2$ 2.16 *0.004*	
		2 $^2A_2$ 3.37 *0.020*	
		3 $^2A_2$ 5.69 *0.000*	
D	X $^1A'$ 0.00	X $^2B_1$ 0.00	X $^1A_1$ 0.00
	1 $^1A'$ 2.03 *0.003*	1 $^2B_1$ 3.60 *0.000*	1 $^1A_1$ 4.02 *0.000*
	2 $^1A'$ 2.20 *0.007*	2 $^2B_1$ 4.17 *0.002*	2 $^1A_1$ 5.90 *0.390*
	3 $^1A'$ 2.79 *0.002*	3 $^2B_1$ 4.52 *0.033*	1 $^1B_1$ 4.67 *0.002*
	4 $^1A'$ 3.32 *0.013*	1 $^2A_1$ 4.71 *0.001*	1 $^1B_2$ 2.90 *0.003*
	5 $^1A'$ 3.78 *0.006*	2 $^2A_2$ 2.38 *0.000*	2 $^1B_2$ 5.66 *0.110*
		3 $^2A_2$ 5.47 *0.003*	
		4 $^2A_2$ 5.65 *0.001*	
E	X $^1A_1$ 0.00	X $^2B_1$ 0.00	X $^1A_1$ 0.00
	1 $^1A_1$ 2.50 *0.005*	1 $^2B_1$ 4.02 *0.013*	1 $^1A_1$ 4.82 *0.037*
	2 $^1A_1$ 3.18 *0.025*	2 $^2B_1$ 5.04 *0.010*	1 $^1B_1$ 3.80 *0.001*
	3 $^1A_1$ 4.01 *0.001*	1 $^2A_1$ 4.60 *0.001*	1 $^1B_2$ 4.80 *0.022*
	1 $^1B_1$ 5.21 *0.028*	1 $^2A_2$ 1.08 *0.001*	2 $^1B_2$ 5.86 *0.280*
	1 $^1B_2$ 1.19 *0.028*	2 $^2A_2$ 4.43 *0.031*	
	4 $^1B_2$ 5.42 *0.120*	1 $^2A_2$ 5.26 *0.000*	

[a] Values were calculated with the MS(5)-CASPT2 method using coordinates from DFT/M06-2X calculations.

in disagreement with the absorption at $\lambda = 401$ nm (Table 2). The matrix was irradiated at various wavelengths, revealing that the electron detachment threshold for the absorber of the $\lambda = 401$ nm system is around $\lambda = 310$ nm. According to the MS-CASPT2 calculations, $\mathbf{FA}^-$ and $\mathbf{B}^-$ possess transitions at 4.39 eV (282 nm) and 4.14 eV (299 nm), respectively (Table 2), which are larger than the electron detachment energy.

Unlike **FA** and $\mathbf{FA}^-$, the cation $\mathbf{FA}^+$ is the fifth least stable isomer of $C_7H_5^+$, lying 151 kJ mol^{-1} above the global minimum $\mathbf{C}^+$. Vertical excitation energies of the five cations $\mathbf{FA}^+$, $\mathbf{B}^+$, $\mathbf{C}^+$, $\mathbf{D}^+$, and $\mathbf{E}^+$ were calculated with the CASPT2 method (Table 2). This predicts that detectable electronic transitions of $\mathbf{C}^+$, $\mathbf{D}^+$, and $\mathbf{E}^+$ lie in the UV region, beyond the range of detection. The transitions of $\mathbf{FA}^+$ and $\mathbf{B}^+$ lie at the edge of the experimental detection range ($\lambda = 280$–1100 nm). Structure $\mathbf{B}^+$ is approximately 300 kJ mol^{-1} in energy above $\mathbf{C}^+$ and is therefore excluded from consideration. Therefore, to investigate whether the fulvenallenyl radical can be produced by deposition of $C_7H_5^+$, mass-selected deposition was carried out from several precursors with neon contaminated by CH_3Cl in a ratio 1:30 000. The spectrum recorded after deposition of the cations with $m/z = 89$ from 1,1-dichlorotoluene is shown as a black trace in Figure 3, with the spectrum after irradiation of the matrix with UV light ($\lambda < 260$ nm) shown as a red trace. The 401 nm absorption system is the major absorption system. The absorptions of neutral C_7H_5 gain in intensity after UV irradiation. This intensity increase is as a result of recombination of $C_7H_5^+$ with electrons detached from Cl^- ions formed from CH_3Cl during the growth of the matrix, which also acts as a counter ion. The 401 nm system is also detected following deposition of $C_7H_5^+$ generated from toluene, indene, mixtures of diacetylene and propyne, and phthalide.

According to the calculations, $\mathbf{FA}^+$ has a strong ($f = 0.48$; where f is the oscillator strength) $2\,^1A_1 \leftarrow X\,^1A_1$ electronic transition around 4.10 eV (302 nm). However, no absorption was detected in this region. It can be argued that the carrier of the $\lambda = 401$ nm absorption system is **C** as it also possesses the $1\,^2B_1 \leftarrow X\,^2B_1$ transition at 3.45 eV and $\mathbf{C}^+$ has absorption bands beyond the detection range. Consequently, ethynylferrocene **EF** was used for the generation of $C_7H_5^+$ and the $m/z = 89$ ions were deposited with neon without any electron scavenger. In a pure neon matrix, mostly neutral species are present. As a result of the absence of scavenger, electrons released from the nearby metal surface of the matrix by impingement of cations go on to neutralize trapped cations. **EF** is composed of one molecular subunit of **FA**. $C_7H_5^+$ was produced from the **EF** precursor in a mild discharge to avoid plasma chemistry. The spectrum obtained is shown as the green trace in Figure 3. The one-to-one correspondence of the peaks with those assigned to the fullvenallenyl radical confirms the nature of the carrier.

Two vibrational modes of frequency 365 and 1984 cm^{-1} and an overtone at 3958 cm^{-1} above the 401.3 nm origin are observed in the spectrum of **FA**. The 1984 cm^{-1} value is typical for a C≡C stretching vibration and confirms the assignment of the 401 nm system to **FA** because the C≡C bond is only present in this particular radical (among the most stable structures of C_7H_5 shown in Figure 1). The absorption system is the $1\,^2B_1 \leftarrow X\,^2B_1$ electronic transition of **FA** according to MS(5)-CASPT2 calculations. The vibrational modes are assigned on the basis of calculated (DFT/M06-2X/cc-pVTZ) harmonic frequencies in the $\mathbf{1}\,^2B_1$ state.

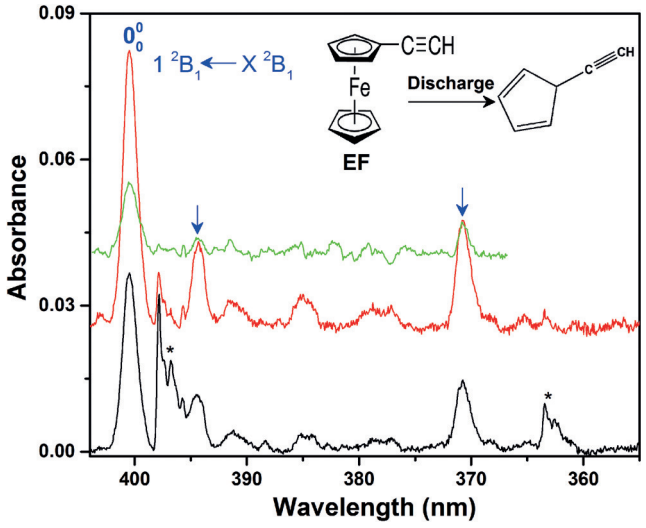

Figure 3. Absorption spectrum recorded after deposition of $C_7H_5^+$ produced from 1,1-dichlorotoluene in a hot cathode source (black trace) and after irradiation with UV light of wavelength $\lambda < 260$ nm (red trace). The green trace was measured after deposition of $C_7H_5^+$ produced from ethynylferrocene **EF** in pure neon followed by neutralization. The bands belonging to the $1\,^2B_1 \leftarrow X\,^2B_1$ transition of the fulvenallenyl radical are denoted by blue arrows. The bands attributable to N_2^+ are marked by asterisks.

Computational and Experimental Section

The ground state PES of anions, neutral species, and cations of C_7H_5 have been calculated with the DFT method using the M06-2X functional and the cc-pVTZ basis set; aug-cc-pVDZ was employed only for anions. Calculated harmonic vibrations of ground states given in the footnote of Table 1 are unscaled values. Calculations have been carried out using the Gaussian 09 program package.[14] Excitation energies and oscillator strengths for several of the most stable anions, neutral species, and cations of C_7H_5 were computed with the MS(5)-CASPT2 method using the coordinates obtained after geometry optimization of these species. The calculations have been carried out with the multistate option (MS), where the wavefunctions of five electronic states were optimized for the average energy of these states. The CASPT2 calculations were performed using MOLCAS-8 software.[15]

The technique used combines mass spectrometry and matrix isolation.[16] Anions and cations of C_7H_5 were produced in a hot cathode discharge source from organic vapors. $C_7H_5^-$ was generated from toluene and dicyclopentadiene, whereas $C_7H_5^+$ was produced from toluene, 1,1 dichlorotoluene, indene, propyne/diacetylene mixtures, phthalide, and ethynylferrocene. The ions extracted from the source were deflected by 90° to eliminate neutral species. Thereafter, the $m/z = 89$ ions were mass-selected and guided to a 6 K rhodium-coated sapphire substrate and co-deposited with neon to form a 150 μm-thick matrix. To increase the trapping efficiency of cations, CH_3Cl was added as an electron scavenger to neon in the ratio 1:30 000. The $C_7H_5^-$ ions were deposited with pure neon. C_7H_5 was produced through electron detachment from $C_7H_5^-$ and by electron

recombination with $C_7H_5^+$. The deposition of $C_7H_5^+$ in pure neon resulted in a higher concentration of neutral species. Spectral measurements were carried out in the 280–1100 nm range in overlapping sections. Halogen and Xenon lamps were used and the light after travelling through 20 mm of the matrix was transmitted by optical fibers to a 0.3 m spectrograph, wavelength-dispersed, and recorded by a CCD camera.

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Keywords: ab initio calculations · electronic spectroscopy · fulvenallenyl radical · mass spectrometry · matrix isolation

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