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Abstract

The gas phase detection of benzocyclopropenyl is reported. In this aromatic resonance stabilized radical, a large angular strain is present due to a three membered ring annelated to a benzene. Resonant two-color two-photon ionization technique is used to record the $D_1(^2A_2) \leftarrow D_0(^2B_1)$ electronic transition of this radical after the in situ synthesis in a discharge source. The spectrum features absorptions up to 3300 cm^{-1} above the origin band at 19305 cm^{-1}. Benzocyclopropenyl is possibly the major product of the bimolecular reaction of benzene and an atomic carbon at low temperatures.

1. Introduction

The Laboratory investigations on the resonance stabilized radicals (RSRs) have been the subject of interest among the astrochemistry, combustion, atmospheric chemistry communities.[1-5] The RSRs play crucial roles in the formation of polycyclic aromatic hydrocarbons (PAHs) and soot particles in combustion systems. In the interstellar medium, the barrierless addition reactions of RSRs may lead to the formation of complex organic molecules including PAHs at low temperatures. Benzene has been considered as the first building block of PAH formation and detected in oxygen poor hydrocarbon flames.[6] The discovery of benzene in the circumstellar medium,[7] propelled the investigation of its reaction with small C/H species.[8,9] The simplest of these reactions is the bimolecular reaction of benzene and atomic carbon which resulted in the synthesis of C_7H_5 isomers.[8-15] Except for the most stable fulvenallenyl,[16-19] literature data on the other isomers are sparse. Energetically the second most stable isomer is benzocyclopropenyl radical which depicts a benzene annelated to a three membered ring. Because of the large angular strain associated with the small ring, this class of molecular entities remains fascinating to the physical organic chemistry community.[20-22] They are suitable to verify the role of Mills-Nixon effect as well.[23] In this, two opposite phenomena, the delocalization energy of the π electrons (aromaticity) on the benzene moiety and the angular distortion due to the annelated small ring, are present. Both of these effects are exciting to organic chemistry community. The fused small rings are known to influence the reactivity and regioselectivity within the aromatic fragment.[24]

Benzocyclopropenyl was mentioned as a reaction product in crossed molecular beam experiments in the reaction of benzene and atomic carbon.[8,9,11,12,15] The reaction proceeds

through the formation of a cycloheptatetraene (C_7H_6) intermediate,[13,14] followed by atomic hydrogen elimination to produce C_7H_5 isomers. At collision energies of 8.8-52.5 kJ mol^{-1}, the major product was assigned as the dihydroheptatrienyl radical with an estimated upper limit of 10% yield of the benzocyclopropenyl radical.[9-11] However, the Rice–Ramsperger–Kassel–Marcus theory estimated ~90% for the yield at a low collision energy of 1.3 kJ mol^{-1}.[11] In the interstellar medium and hydrocarbon rich planetary atmospheres, the gas phase reaction is likely to occur at a low collision energy; therefore, it is expected to be the major product. Here, the detection of benzocyclopropenyl is reported in the gas phase. Its $D_1 \leftarrow D_0$ electronic transition is measured using a resonant two-color two-photon ionization (R2C2PI) scheme coupled with a linear time-of-flight mass spectrometer (TOF-MS).

2. Experimental

The experiments were conducted in a three-stage differentially pumped vacuum chamber (~1.0×10^{-7} mbar) operational with turbo pumps. A gas mixture of 0.1 % propyne and 0.1 % diacetylene in helium (backing pressure of 9.0 bar) was expanded by a pulsed valve (~220 μs) into the source chamber to maintain 4.0×10^{-5} mbar. Simultaneously, a pulsed (200 μs) high voltage electrical discharge (−600 V) was applied to produce the target radical in a cold molecular beam. This was collimated by passing through a 2.0 mm skimmer placed 50 mm downstream of the discharge source. It then entered the extraction region of the TOF-MS positioned inside the second chamber. A potential of +300 V was applied to the skimmer to repel the charged species produced along with the neutrals. A counter-propagating signal output of an optical parametric oscillator laser (OPO, 5-10 ns; 20 Hz; 0.1 nm bandwidth, tuning range 410-710 nm, 2-8 mJ/pulse) excites the target

radicals to higher lying electronic states. The radicals are subsequently ionized by a fifth harmonic (212.8 nm) output of a Nd:YAG laser (1.5 mJ /pulse), introduced about 2-4 ns after the excitation laser. Only one Nd:YAG laser is used to pump the OPO and produce the 5^{th} harmonic output (212.8 nm). This scheme eliminates temporal jitter between the pump and probe pulses. The resulting ions were extracted perpendicular to the molecular beam into the TOF tube connected with a two-stage acceleration setup and detected by a micro-channel plate. Higher-resolution scan of the origin band was carried out with a dye laser (≈ 10 ns; 10 Hz; 0.002 nm bandwidth) pumped by the third harmonic of a Nd:YAG laser. The dye laser output was calibrated with a wavelength meter. The pulsed valve, pulsed discharge voltage, extraction voltage and the laser pulses were synchronized by digital delay generators.

3. Results

The electronic spectrum of C_7H_5 radical (Figure 1) is recorded by monitoring the ion signal at m/z = 89 amu. The spectrum features multiple absorptions in the region 18600-22600 cm^{-1}, implying a strong Franck-Condon activity. The observed band positions and vibrational frequencies are summarized in Table 1. The strongest feature at 19305 cm^{-1} (517.9 nm) assigned as the origin band of the $D_1(^2A_2) \leftarrow D_0(^2B_1)$ transition of the benzocyclopropenyl radical. Two weak features at 488 and 626 cm^{-1} to the red are hot bands. The bands 528, 731, 921, 1124 and 1327 cm^{-1} above the origin are separated by 196±7 cm^{-1}, implying combination of 528 cm^{-1} and 203 cm^{-1} vibrational frequencies. Furthermore, combinations of the low energy vibrations below 600 cm^{-1} account for all the features up to 3300 cm^{-1}. These observations indicate a vibronic progression in the excited state. The high resolution recording of the origin band in Figure 2 exhibits three

peaks of unresolved *P*, *Q* and *R* branches. Electronic spectra are recorded at each m/z between 12 and 250 amu, simultaneously. Other than a weak signal at the isotopic mass of 90 ($^{13}CC_6H_5$), no other mass channels are identified with an electronic transition similar to the reported spectrum. Therefore, any possibility of $C_7H_5^+$ (m/z=89 amu) formation via a dissociation of higher mass product is ruled out.

4. Discussion

To identify the structure of the C_7H_5 carrier of the observed electronic band system with the strongest band at 19305 cm^{-1}, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were carried out using the B3LYP functional and cc-pVDZ basis set with the Gaussian-09 program package.[25] About 30 different C_7H_5 structures were optimized on both singlet and triplet surfaces. The relative stability of the structures are in agreement with the literature.[10,18] The ground state geometries of the seven lowest energy C_7H_5 structures are shown in Figure 3. The calculated relative energies, vertical ionization (IP) and excitation energies are given in Table 2. The cyclic isomers C_7H_5-A, B, C and D with C_{2v} symmetry are at least 20 kJ mol^{-1} more stable than the C_s symmetry acyclic structures (C_7H_5-E, F and G). The most stable isomer is C_7H_5-A (fulvenallenyl radical).

At 19305 cm^{-1}, the experimental ionization limit of the two-photon process (8.22 eV) is close to the IP of C_7H_5-A, determined experimentally (8.19 eV)[19] and computationally (8.1 eV, Table 2). However, this structure is excluded as the carrier of the band system because of two reasons. Firstly, the ion signal at m/z = 89 can be detected at two-photon energies as low as 7.6 eV (Supporting Information Figure S1). Secondly, the vertical excitation energies of the symmetry allowed $D_1(^2A_2)\leftarrow D_0(^2B_1)$ and $D_3(^2B_1)\leftarrow D_0(^2B_1)$ transitions are 0.93 and 3.26 eV, which

disagree with the experimental value of 2.39 eV. The $D_2(^2B_2)\leftarrow D_0(^2B_1)$ energy (2.73 eV) is close, but is a symmetry forbidden transition. Based on this, fulvenallenyl radical C_7H_5-A is expected to have an electronic transition in the UV region and is unlikely to have a contribution in the present spectrum. All other isomers have predicted vertical IPs in the 6.0-7.4 eV range and are detectable within the experimental limits. In the case of C_7H_5-C, the calculated vertical transition energy for $D_2(^2A_2)\leftarrow D_0(^2B_1)$ is close (2.54 eV) to the experimental value (2.39 eV), however, the oscillator strength is zero. No other transitions for the isomer C_7H_5-C and none for C_7H_5-D agree with the observed band energy. Therefore, both structures C_7H_5-C and D are ruled out as possible carriers.

The remaining isomers C_7H_5-B, E, F and G are characterized by at least one transition close (0.02-0.33 eV) to the experimental value. The isomer C_7H_5-B is the second lowest structure (Table 2) on the doublet potential energy surface and is at least 59 kJ mol^{-1} more stable than the other. The $D_1(^2A_2)\leftarrow D_0(^2B_1)$ excitation energy of isomer C_7H_5-B is the closest (2.41) to the experimental value of 2.39 eV compared to the allowed $D_2(^2A'')\leftarrow D_0(^2A'')$ electronic transition of C_7H_5-E, F and G. Therefore, isomer C_7H_5-B is the likely carrier of the observed band system. To verify this, the high resolution scan of the 19305 cm^{-1} band is compared with the rotational profiles, simulated using PGOPHER,[27] for the electronic transitions $D_1(^2A_2)\leftarrow D_0(^2B_1)$ of C_7H_5-B and $D_2(^2A'')\leftarrow D_0(^2A'')$ of C_7H_5-E, F and G. As shown in Figure 2 and SI Figure S2, the best agreement is achieved with isomer C_7H_5-B. The simulated *b*-type rotational profile obtained at T~7 K for C_7H_5-B provides a good agreement with the high resolution recording. The best fit parameters A''=0.180, B''=0.107, C''=0.075, A'=0.179, B'=0.110 and C'=0.074 are within ± 5 % of the calculated values in the D_0 electronic state, A''=0.187, B''=0.115, C''=0.071. The above

supports the assignment of benzocyclopropenyl radical (C_7H_5-B) with the $D_1(^2A_2)\leftarrow D_0(^2B_1)$ origin band at 19305 cm^{-1}.

To assign the experimental frequencies of C_7H_5-B excited in the D_1 state, the calculation of the normal modes in this state was attempted. However, repeated efforts to locate the fully relaxed geometry in the D_1 state were unsuccessful. Therefore, a prediction of the intensity pattern for the $D_1(^2A_2)\leftarrow D_0(^2B_1)$ band system using Franck-Condon-Herzberg-Teller method would be unreliable. A first order saddle point is found with a C_{2v} geometry similar to the ground state structure. The prominent hot band observed 488 cm^{-1} below the origin band agrees with the ground state vibrational frequency calculated at 488 cm^{-1} (ν_{30}). The observed low energy vibrational frequencies 203, 434, 454 and 481 cm^{-1} above the origin band can be linked to bending modes belonging to a_2 and b_2 symmetries (Supporting Information). An unambiguous assignment of the vibrational frequencies is hard to achieve based on the ground state normal modes. The observation of the asymmetric modes via vibronic mixing clearly implies a bent excited D_1 state. The C_{2V} symmetric saddle point in the D_1 state also supports this.

It is worth to mention that the rotational contours for the $D_2(^2A'')\leftarrow D_0(^2A'')$ electronic transitions of C_s symmetry isomers C_7H_5-E, F and G (Figure 2, SI Figure S2) show prominent *K*-stacks in both *b*- and *a*-type electronic transitions. The vibrational patterns calculated via a Franck-Condon-Herzberg-Teller approach (FCHT)[26] for that transition of the above isomers show poor agreement with the experimental spectrum (SI Figure 3). This reinforces the assignment to benzocyclopropenyl radical.

5. Summary

The gas phase electronic spectrum of a C_7H_5 radical, benzocyclopropenyl radical, is measured for the first time using R2C2PI scheme. The radical is synthesized via an electrical

discharge of a hydrocarbon gas mixture. The $D_1(^2A_2)\leftarrow D_0(^2B_1)$ electronic transition is observed in the 18600-22600 cm^{-1} region with the origin band at 19305 cm^{-1}. The high resolution recording of the 19305 cm^{-1} band assists the spectral assignment. Vibronic features up to 3300 cm^{-1} originate from combinations of the low energy modes. The spectral data can be used to verify the formation of benzocyclopropenyl in the reaction of benzene and atomic carbon and understand its role in both combustion and astrophysical environments.

Supporting Information Available. Ground state calculated harmonic frequencies of C_7H_5-B, ionization efficiency curve, simulated rotational profiles and FCHT simulations of $D_1\leftarrow D_0$ (for C_7H_5-B) and $D_2\leftarrow D_0$ electronic transitions for C_7H_5 isomers are given. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgment

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References

(1) McEnally, C. S.; Pfefferle, L. D.; Atakan, B.; Kohse-Höinghaus, K. Studies of Aromatic Hydrocarbon Formation Mechanisms in Flames: Progress Towards Closing the Fuel Gap. *Prog. Energy Combust. Sci.* **2006**, *32*, 247-294.

(2) Miller, J. A.; Melius, C. F. Kinetic and Thermodynamic Issues in the Formation of Aromatic Compounds in Flames of Aliphatic Fuels. *Combust. Flame* **1992**, *91*, 21-39.

(3) Gobbi, A.; Frenking, G. Resonance Stabilization in Allyl Cation, Radical, and Anion. *J. Am. Chem. Soc.* **1994**, *116*, 9275-9286.

(4) McMillen, D. F.; Trevor, P. L.; Golden, D. M. Highly Stabilized Radicals: Benzylic Radicals in Polycyclic Aromatic Systems. *J. Am. Chem. Soc.* **1980**, *102*, 7400-7402.

(5) Wong, M. W.; Pross, A.; Radom, L. Addition of Tert-Butyl Radical to Substituted Alkenes: a Theoretical-Study of the Reaction-Mechanism. *J. Am. Chem. Soc.* **1994**, *116*, 11938-11943.

(6) Marinov, N. M.; Pitz, W. J.; Westbrook, C. K.; Castaldi, M. J.; Senkan, S. M. Modeling of Aromatic and Polycyclic Aromatic Hydrocarbon Formation in Premixed Methane and Ethane Flames. *Combust. Sci. Tech.* **1996**, *116*, 211-287.

(7) José, C.; Ana, M. H.; Tielens, A. G. G. M.; Juan, R. P.; Fabrice, H.; Michel, G.; Waters, L. B. F. M. Infrared Space Observatory's Discovery of C_4H_2, C_6H_2, and Benzene in Crl 618. *Astrophys. J. Lett.* **2001**, *546*, L123-L126.

(8) Kaiser, R. I.; Asvany, O.; Lee, Y. T. Crossed Beam Investigation of Elementary Reactions Relevant to the Formation of Polycyclic Aromatic Hydrocarbon (PAH)-Like Molecules in Extraterrestrial Environments. *Planet. Space Sci.* **2000**, *48*, 483-492.

(9) Kaiser, R. I.; Vereecken, L.; Peeters, J.; Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F. Elementary Reactions of the Phenyl Radical, C_6H_5, with C_3H_4 Isomers, and of Benzene, C_6H_6, with Atomic Carbon in Extraterrestrial Environments. *Astron. Astrophys.* **2003**, *406*, 385-391.

(10) da Silva, G. Reaction of Benzene with Atomic Carbon: Pathways to Fulvenallene and the Fulvenallenyl Radical in Extraterrestrial Atmospheres and the Interstellar Medium. *J. Phys. Chem. A* **2014**, *118*, 3967-3972.

(11) Hahndorf, I.; Lee, Y. T.; Kaiser, R. I.; Vereecken, L.; Peeters, J.; Bettinger, H. F.; Schreiner, P. R.; Schleyer, P. v. R.; Allen, W. D.; Schaefer, H. F. A Combined Crossed-Beam, Ab Initio, and Rice-Ramsperger-Kassel-Marcus Investigation of the Reaction of Carbon Atoms $C(^3P_j)$ with Benzene, $C_6H_6(X\ ^1A_{1g})$ and D_6-Benzene, $C_6D_6(X\ ^1A_{1g})$. *J. Chem. Phys.* **2002**, *116*, 3248-3262.

(12) Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F.; Schreiner, P. R.; Kaiser, R. I.; Lee, Y. T. The Reaction of Benzene with a Ground State Carbon Atom, $C(^3P_j)$. *J. Chem. Phys.* **2000**, *113*, 4250-4264.

(13) McKee, M. L.; Reisenauer, H. P.; Schreiner, P. R. Combined Ab Initio Molecular Dynamics and Experimental Studies of Carbon Atom Addition to Benzene. *J. Phys. Chem. A* **2014**, *118*, 2801-2809.

(14) Krasnokutski, S. A.; Huisken, F. Ultra-Low-Temperature Reactions of C(^3P_j) Atoms with Benzene Molecules in Helium Droplets. *J. Chem. Phys.* **2014**, *141*, 214306.

(15) Kaiser, R. I.; Hahndorf, I.; Huang, L. C. L.; Lee, Y. T.; Bettinger, H. F.; Schleyer, P. V. R.; Schaefer, H. F.; Schreiner, P. R. Crossed Beams Reaction of Atomic Carbon, C(^3P_j), with D_6-Benzene, C_6D_6 (X^1A_{1g}): Observation of the per-Deutero-1,2-Didehydro-Cycloheptatrienyl Radical, C_7D_5 (X^2B_2). *J. Chem. Phys.* **1999**, *110*, 6091-6094.

(16) da Silva, G.; Trevitt, A. J. Chemically Activated Reactions on the C_7H_5 Energy Surface: Propargyl + Diacetylene, i-C_5H_3+Acetylene, and n-C_5H_3+Acetylene. *Phys. Chem. Chem. Phys.* **2011**, *13*, 8940-8952.

(17) Botschwina, P.; Oswald, R. Fulvenallenyl Cation ($C_7H_5^+$) and Its Complex with an Argon Atom: Results of High-Level Quantum-Chemical Calculations. *J. Phys. Chem. A* **2012**, *116*, 3448-3453.

(18) da Silva, G.; Trevitt, A. J.; Steinbauer, M.; Hemberger, P. Pyrolysis of Fulvenallene (C_7H_6) and Fulvenallenyl (C_7H_5): Theoretical Kinetics and Experimental Product Detection. *Chem. Phys. Lett.* **2011**, *517*, 144-148.

(19) Steinbauer, M.; Hemberger, P.; Fischer, I.; Bodi, A. Photoionization of C_7H_6 and C_7H_5: Observation of the Fulvenallenyl Radical. *ChemPhysChem* **2011**, *12*, 1795-1797.

(20) Apeloig, Y.; Arad, D. Cyclopropabenzene. Geometry, Electronic Structure, Strain, Reactivity, and the Question of Bond Fixation. A Theoretical Study. *J. Am. Chem. Soc.* **1986**, *108*, 3241-3247.

(21) Eckert-Maksić, M.; Maksić, Z. B.; Hodošček, M.; Poljanec, K. Mills-Nixon Effect in Heteroanalogs of Cyclopropabenzene. *Int. J. Quantum Chem.* **1992**, *42*, 869-877.

(22) Maksic, Z. B.; Eckert-Maksić, M.; Pfeifer, K.-H. Reversed Mills-Nixon Effect in Benzoborirene and Benzocyclopropenyl Cations. *J. Mol. Struc.* **1993**, *300*, 445-453.

(23) Mills, W. H.; Nixon, I. G. Stereochemical Influences on Aromatic Substitution. Substitution Derivatives of 5-Hydroxyhydrindene. *J. Chem. Soc.* **1930**, 2510-2524.

(24) Eckert-Maksić, M.; Glasovac, Z.; Novak Coumbassa, N.; Maksić, Z. B. The Mills-Nixon Effect and Chemical Reactivity-Methyl Cation Affinity of Some Cycloalkabenzenes. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1091-1098.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; al., e. Gaussian 09; Gaussian, Inc.: Wallingford, CT, USA, 2009.

(26) Barone, V.; Bloino, J.; Biczysko, M. Vibrationally-Resolved Electronic Spectra in Gaussian 09, 2009.

(27) Western, C. M. Pgopher, a Program for Simulating Rotational Structure, University of Bristol, Http://Pgopher.Chm.Bris.Ac.Uk, 2014.

TOC Graphic

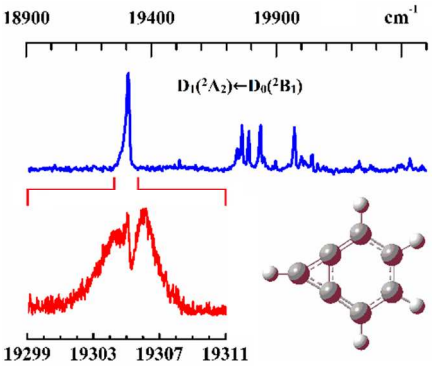

Table 1. Absorption bands and vibrational frequencies relative to the origin band in the $D_1(^2A_2)\leftarrow D_0(^2B_1)$ electronic transition of benzocyclopropenyl radical.

nm	**cm^{-1}**	**$\Delta\nu$ (cm^{-1})**	**Tentative Assignment**
535.2	18679	-626	
531.3	18817	-488	30_1^0
517.9	19305	0	0_0^0
512.5	19508	203	20_0^1
506.5	19739	434	18_0^1
506.0	19759	454	15_0^1
505.3	19786	481	
504.1	19833	528	30_0^1
503.7	19849	544	11_0^1
502.6	19892	587	
501.2	19948	643	
500.7	19968	663	
500.0	19996	691	
499.6	20012	707	
499.0	20036	731	
494.3	20226	921	
489.4	20429	1124	
484.5	20632	1327	
482.9	20704	1399	
478.4	20899	1594	
476.9	20964	1659	
474.0	21089	1784	
465.8	21464	2159	
452.5	22091	2786	
442.5	22590	3285	

Table 2. The zero-point energy corrected relative stability (E) in kJ mol^{-1}, vertical ionization energy (IP) and excitation energies (ΔE) of $D_{1\text{-}3} \leftarrow D_0$ transitions of C_7H_5 isomers in eV. The oscillator strength (*f*) of each transition is given.

Isomer	**E**	**IP**	**ΔE**		***f***
			$D_{1\text{-}3}$	**eV (nm)**	
C_7H_5-A	0	8.1	$D_1(^2A_2)$	0.93 (1335)	0.000
$D_0(^2B_1)$			$D_2(^2B_2)$	2.73 (453)	0.000
			$D_3(^2B_1)$	3.26 (380)	0.006
C_7H_5-B	45	6.4	$D_1(^2A_2)$	2.41(514)	0.004
$D_0(^2B_1)$			$D_2(^2A_2)$	3.53(351)	0.018
			$D_3(^2B_1)$	3.74(331)	0.021
C_7H_5-C	74	6.8	$D_1(^2A_2)$	1.46 (847)	0.001
$D_0(^2B_1)$			$D_2(^2A_2)$	2.54 (488)	0.000
			$D_3(^2B_1)$	3.91 (317)	0.001
C_7H_5-D	86	6.0	$D_1(^2A_2)$	1.10 (1124)	0.001
$D_0(^2B_1)$			$D_2(^2B_2)$	1.72 (719)	0.000
			$D_3(^2A_1)$	3.87 (321)	0.001
C_7H_5-E	104	7.3	$D_1(^2A')$	2.18 (569)	0.000
$D_0(^2A'')$			$D_2(^2A'')$	2.50 (495)	0.005
			$D_3(^2A')$	3.19 (388)	0.000
C_7H_5-F	105	7.3	$D_1(^2A')$	2.55 (486)	0.000
$D_0(^2A'')$			$D_2(^2A'')$	2.72 (455)	0.030
			$D_3(^2A')$	3.28 (378)	0.000
C_7H_5-G	111	7.4	$D_1(^2A')$	2.58 (481)	0.000
$D_0(^2A'')$			$D_2(^2A'')$	2.65 (468)	0.019
			$D_3(^2A')$	3.30 (375)	0.000

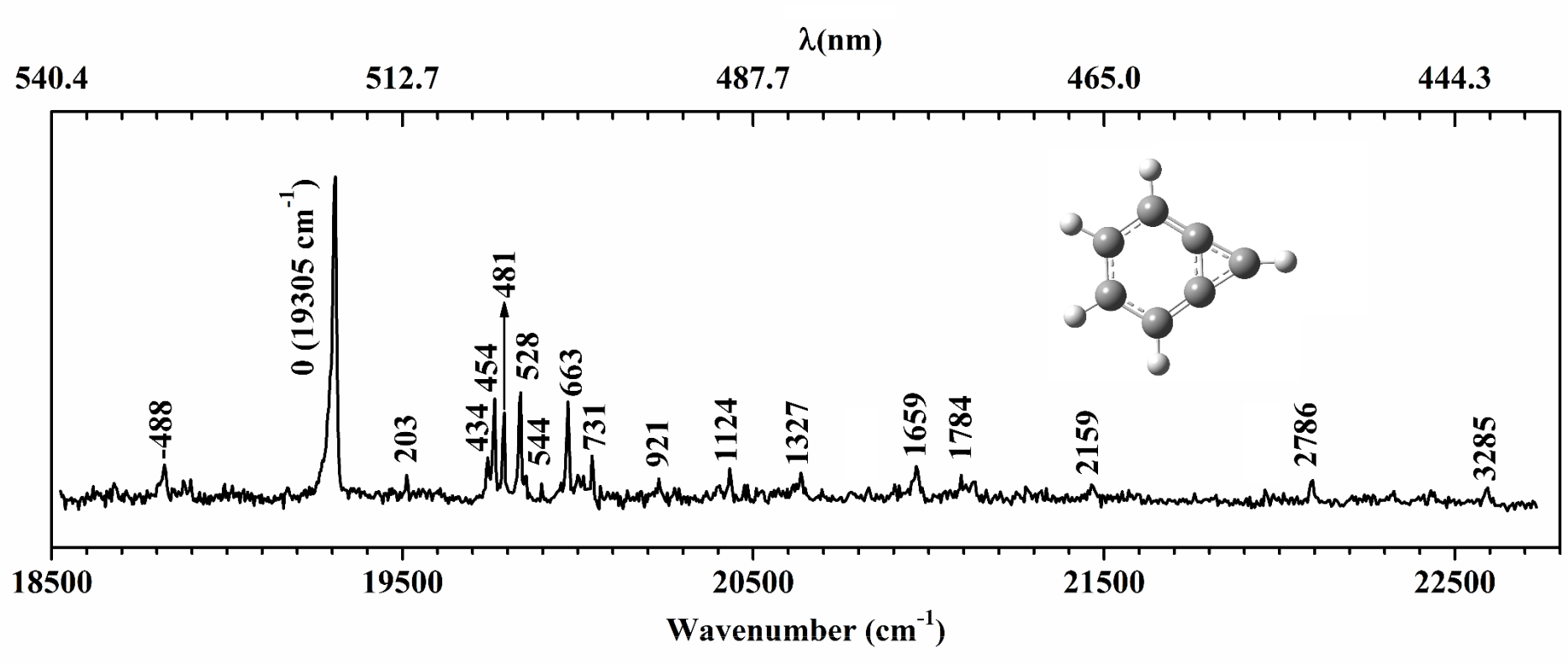

Figure 1. Resonant two-color two-photon ionization spectrum of benzocyclopropenyl radical (C_7H_5).

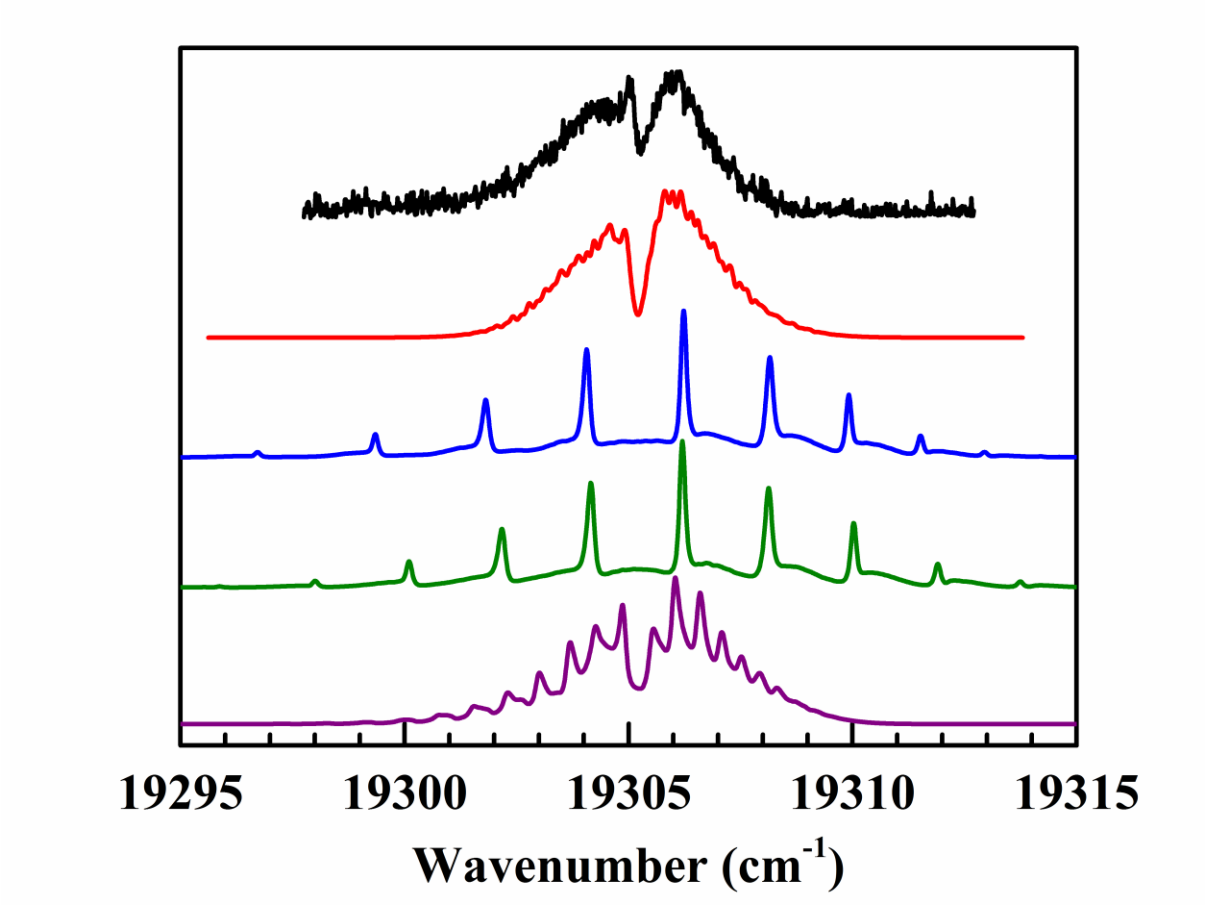

Figure 2. The origin band in the $D_1(^2A_2)\leftarrow D_0(^2B_1)$ electronic spectrum of benzocyclopropenyl radical measured at a resolution of 0.08 cm^{-1} (black trace) and the simulated *b*-type rotational contour at T=7 K (red). The *b*-type rotational contours ($D_2(^2A'')\leftarrow D_0(^2A'')$) obtained for the C_s symmetry isomers C_7H_5-E (blue), C_7H_5-F (green), C_7H_5-G (purple) are shown for comparison. Contour simulations obtained for the *a*-type transitions are given in the Supporting Information.

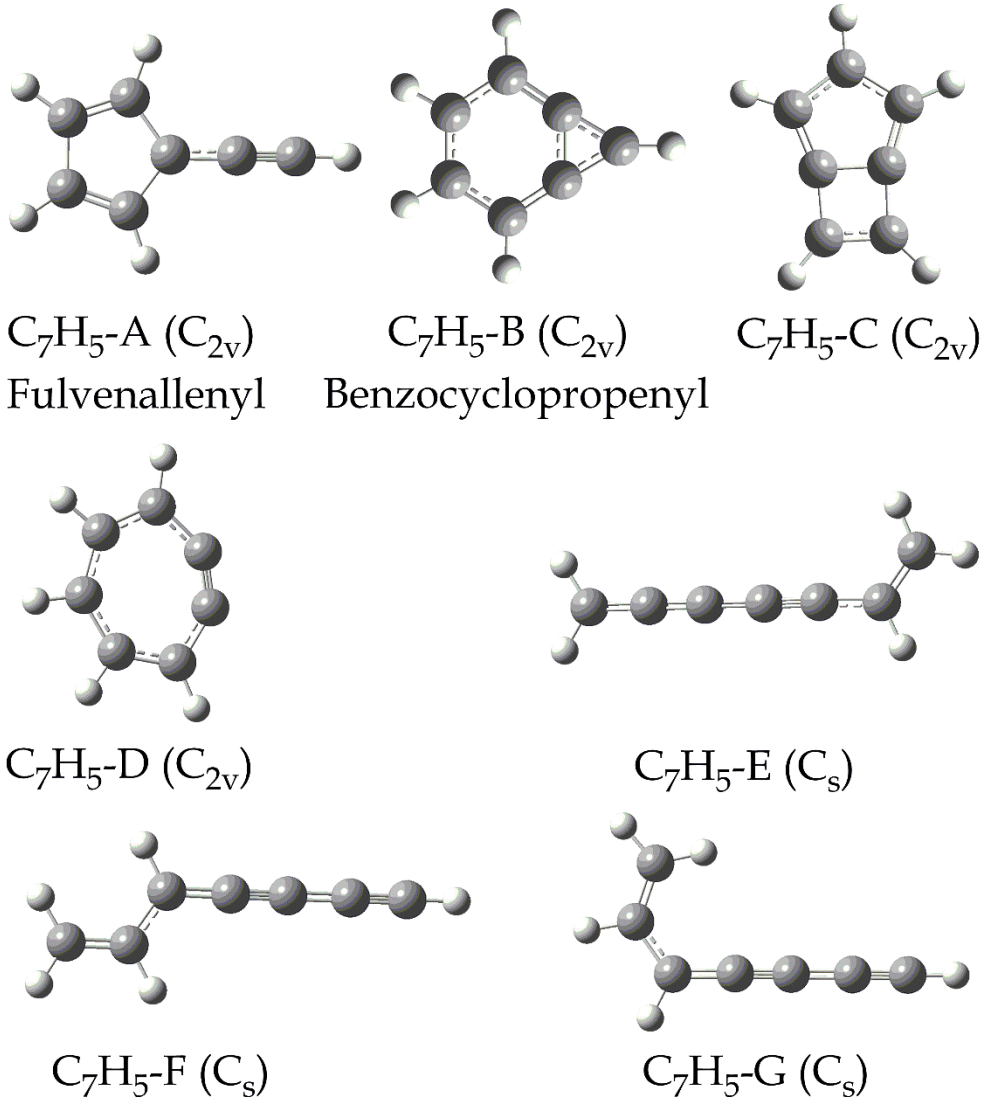

Figure 3. The ground state geometries of C_7H_5 isomers.