

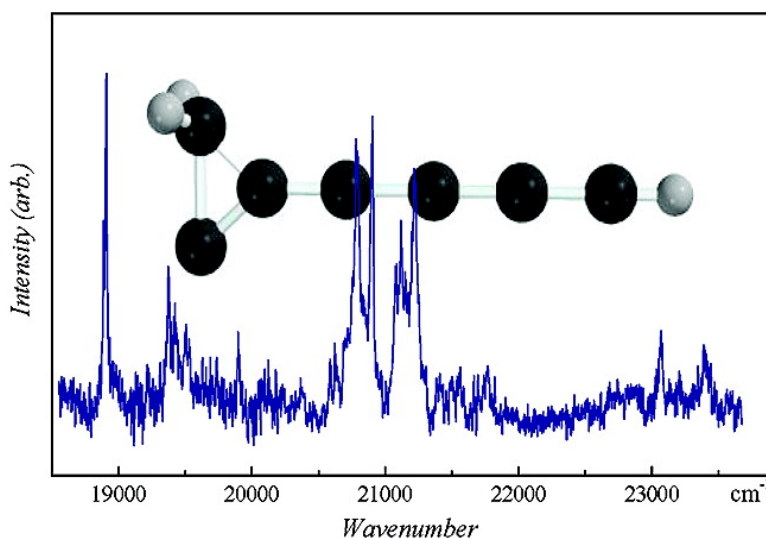
Article

Isomeric Structures and Visible Electronic Spectrum of the CH Radicals

Hongbin Ding, Thomas Pino, Felix Gthe, and John P. Maier

J. Am. Chem. Soc., **2003**, 125 (47), 14626-14630 • DOI: 10.1021/ja029650o • Publication Date (Web): 01 November 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Isomeric Structures and Visible Electronic Spectrum of the C₇H₃ Radicals

Hongbin Ding, Thomas Pino, Felix Güthe, and John P. Maier*

Contribution from the Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056, Basel, Switzerland

Received December 9, 2002; E-mail: J.P.Maier@unibas.ch

Abstract: The 2-(buta-1,3-diyne)cycloprop-2-yl-1-ylidene radical, a new three-membered ring chain with C_s symmetry, has been detected by electronic spectroscopy in the gas phase. The experimental investigation used a mass selective resonant two color two photon ionization technique coupled to a supersonic plasma source. Structures and relative stability energies of eight isomers of the C₇H₃ radical have been calculated. Based on the rotational analysis and the theoretical calculations, the observed spectrum is assigned as an ²A'' ← X²A' electronic transition of this exotic chemical species. This result shows that such a plasma source is a powerful tool to investigate intermediates involved in hydrocarbon chemistry as in flames.

I. Introduction

Highly unsaturated hydrocarbons are important reactive intermediates in combustion processes¹ and plasma chemistry² and play a crucial role in the chemical evolution of the interstellar medium (ISM).^{3–6} The bare carbon clusters, C₂ and C₃, have been detected in diffuse interstellar clouds by optical absorption spectroscopy.^{7,8} The smallest member of the C_{2n+1}H homologous series, the C₃H radical, was identified in dense interstellar clouds and studied in laboratory using microwave spectroscopy.^{9,10} The next members *l*-C₅H and *l*-C₇H have also been observed in such regions by their pure rotational spectra.^{11–14} These have been measured in the laboratory,^{15,16} as well as *l*-C₉H and the cyclic isomer of C₅H.^{17,18} Recently the gas-phase electronic spectra of *l*-C_{2n+1}H (*n* = 1–4) have been studied in

a molecular beam by a mass selective resonant two color two photon ionization (R2C2PI) spectroscopic technique.^{19,20} The small dihydrogenated carbon derivatives have also been detected in dense clouds²¹ and in the atmosphere of planets.²² The larger ones, in their polyynic HC_{*n*}H and cumulenyl H₂C_{*n*} forms, are believed to exist in the ISM because they are always abundant in hydrocarbon plasmas and flames. In the molecular clouds, because of the low density ($\leq 10^4/\text{cm}^3$) and temperature (< 100 K), highly unsaturated and reactive species (radicals, molecular ions) are expected to be a major component. The existence of such exotic chemical species is an essential characteristic of the ISM chemistry. In contrast, terrestrial environments favor a thermodynamic equilibrium. Thus, special approaches, different from that of ordinary chemistry, are required to characterize these molecules.

There is a limited knowledge of the trihydrogenated derivatives (C_{2n+1}H₃), except for the smallest. The ground state of C₃H₃ has been investigated by ab initio theory,^{23,24} microwave spectroscopy,²⁵ and infrared laser spectroscopy.^{26,27} Electronic^{28,29} and photoelectron³⁰ spectra have also been reported. Two isomers, propargyl (C_{2v}) and cycloprop-2-enyl (C_s), have been found to be stable with the latter being higher in energy by 182.7 kJ/mol. The recombination of two propargyl radicals

- (1) Homann, K.-H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2434.
- (2) Fujii, T.; Kareev, M. *J. Appl. Phys.* **2001**, *89*, 2543.
- (3) Henning, T.; Salama, F. *Science* **1998**, *282*, 2204.
- (4) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Astrophys. J.* **1987**, *314*, 352.
- (5) Kaiser, R. I.; Ochsenfeld, C.; Head-Gordon, M.; Lee, Y. T.; Suits, A. G. *Science* **1996**, *274*, 1508.
- (6) Buonomo, E.; Clary, D. C. *J. Phys. Chem. A* **2001**, *105*, 2694.
- (7) Dishoeck, E. F. V.; Black, J. H. *Astrophys. J., Suppl. Ser.* **1986**, *62*, 109.
- (8) Maier, J. P.; Lakin, N. M.; Walker, G. A. H.; Bohlender, D. A. *Astrophys. J.* **2001**, *553*, 267.
- (9) Thaddeus, P.; Gottlieb, C. A.; Hjalmarsen, A.; Johansson, L. E. B.; Irvine, W. M.; Friberg, P.; Linke, R. A. *Astrophys. J. Lett.* **1985**, *294*, L49.
- (10) Yamamoto, S.; Saito, S.; Ohishi, M.; Suzuki, H.; Ishikawa, S.; Kaifu, N.; Murakami, A. *Astrophys. J. Lett.* **1987**, *322*, L55.
- (11) Cernicharo, J.; Kahane, C.; Gomez-Gonzalez, J.; Guélin, M. *Astron. Astrophys.* **1986**, *164*, L1.
- (12) Cernicharo, J.; Kahane, C.; Gomez-Gonzalez, J.; Guélin, M. *Astron. Astrophys.* **1986**, *167*, L5.
- (13) Cernicharo, J.; Guélin, M.; Walmsley, C. M. *Astron. Astrophys.* **1987**, *172*, L5–L6.
- (14) Guélin, M.; Cernicharo, J.; Travers, M. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P.; Ohishi, M.; Saito, S.; Yamamoto, S. *Astron. Astrophys.* **1997**, *317*, L1.
- (15) Gottlieb, C. A.; Gottlieb, E. W.; Thaddeus, P.; Vrtilik, J. M. *Astrophys. J.* **1986**, *303*, 446.
- (16) Travers, M. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J. Lett.* **1996**, *465*, L77.
- (17) McCarthy, M. C.; Travers, M. J.; Kovacs, A.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J., Suppl. Ser.* **1997**, *113*, 105.
- (18) Apponi, A. J.; Sanz, M. E.; Gottlieb, C. A.; McCarthy, M. C.; Thaddeus, P. *Astrophys. J. Lett.* **2001**, *547*, L65.

- (19) Ding, H.; Pino, T.; Güthe, F.; Maier, J. P. *J. Chem. Phys.* **2001**, *115*, 6913.
- (20) Ding, H.; Pino, T.; Güthe, F.; Maier, J. P. *J. Chem. Phys.* **2002**, *117*, 8362.
- (21) Turner, B. E.; Herbst, E.; Terzieva, R. *Astrophys. J., Suppl. Ser.* **2000**, *126*, 427.
- (22) Kim, S. J.; Caldwell, J.; Rivolo, R. A.; Wagener, R.; Orton, S. G. *Icarus* **1985**, *64*, 233.
- (23) Vereecken, L.; Pierloot, K.; Peeters, J. *J. Chem. Phys.* **1998**, *108*, 1068.
- (24) Botschwina, P.; Oswald, R.; Fluegge, J.; Horn, M. *Z. Phys. Chem.* **1995**, *188*, 29.
- (25) Tanaka, K.; Sumiyoshi, Y.; Ohshima, Y.; Endo, Y.; Kawaguchi, K. *J. Chem. Phys.* **1997**, *107*, 2728.
- (26) Tanaka, K.; Harada, T.; Sakaguchi, K.; Harada, K.; Tanaka, T. *J. Chem. Phys.* **1995**, *103*, 6450.
- (27) Yuan, L.; DeSain, J.; Curl, R. F. *J. Mol. Spectrosc.* **1998**, *187*, 102.
- (28) Ramsay, D. A.; Thistlethwaite, P. *Can. J. Phys.* **1966**, *44*, 1381.
- (29) Fahr, A.; Hassanzadeh, P.; Laszlo, B.; Huie, R. E. *Chem. Phys.* **1997**, *215*, 59.
- (30) Gilbert, T.; Pfab, R.; Fischer, I.; Chen, P. *J. Chem. Phys.* **2000**, *112*, 2575.

to 1,5-hexadiyne is now considered to be a crucial step to benzene formation in flames.³¹ The second member of the odd series, C₅H₃, has also been proposed as a key intermediate in forming the first ring and is an important channel in the photodissociation of benzene and larger aromatics.^{32–34} Those belonging to the even series, C₄H₃ and C₈H₃, are postulated to be involved in the atmospheric photochemistry of Titan³⁵ and C₄H₃, as well as C₂H₃, are intermediates in flame chemistry.³⁶ These trihydrogenated (open-shell) species possess many isomeric forms, as shown by the theoretical work on C₃H₃^{23,24} and C₅H₃,³² making their characterization a challenge.

In this work, the visible electronic spectrum of C₇H₃ has been observed in a supersonic plasma source by means of R2C2PI spectroscopy. To understand the molecular structure and guide the assignment of the observed spectrum, calculations on the structures of eight isomers of C₇H₃ were carried out using density functional theory (DFT).

II. Experiment

The experimental setup consisted of a molecular beam combined with a linear time-of-flight mass analyzer (TOF).³⁷ The plasma source used to produce the C₇H₃ radicals was a pulsed valve coupled to an electric discharge. A gas mixture of 0.3% of acetylene or *d*₂-acetylene in Ar (backing pressure 8 bar) was expanded through the ceramic body of the source. A 100–200 μs long high voltage pulse (600–900 V) was applied between the electrodes. The current was limited to about 100 mA. The emerging C₇H₃ beam entered the ionization region through a 2 mm skimmer. All ions produced in the source were removed by an electric field perpendicular to the molecular beam after the skimmer and before entering the extraction zone of the TOF. The neutral radicals were then ionized by the R2C2PI method, and the ions extracted in a two-stage acceleration setup toward a multichannel plate (MCP) detector. The signal from the MCP was fed into an ultrafast oscilloscope after preamplification and transferred to a computer. Gates were set on the mass spectrum, and the ion signal was recorded versus the wavelength.

R2C2PI spectra have been recorded in the visible range. Excitation photons came from the output of a dye laser (bandwidth ≈ 0.1 cm⁻¹) pumped by an XeCl excimer or an Nd:YAG laser for the longer wavelengths. The dye laser energy was typically 5–15 mJ per pulse. The ionizing photons at 157 nm came from a F₂ excimer laser with a few millijoules per pulse. Both lasers were unfocused. The dye laser beam was anticollinear to the molecular beam while the F₂ laser was perpendicular. The temporal sequence of the two color lasers was then optimized to maximize the R2C2PI signal, the F₂ laser usually being fired a few nanoseconds after the dye laser.

III. Results

The R2C2PI spectrum of C₇H₃ is shown in Figure 1. The observed spectrum consists of several strong vibronic bands in the range of 420–530 nm, the observed origin being at 528.76 nm. The wavelength maxima of the observed vibronic bands of C₇H₃ and its deuterated C₇D₃ are given in Table 1. Transitions due to one color two photon resonances are excluded because the signals required the two colors. This shows that the observed

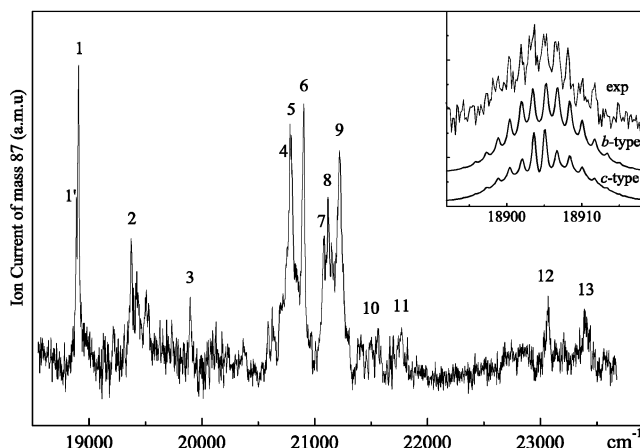


Figure 1. Electronic spectrum of C₇H₃ detected by a resonant two color two photon ionization technique. The inset shows the *K*-structure of the origin band 1 (upper trace); the lower traces are simulated spectra (see text).

Table 1. Maxima of the Vibronic Bands Observed in the Electronic Spectrum of C₇H₃ and the Suggested Assignment^a

label	λ (nm)	ν (cm ⁻¹)	Δν (cm ⁻¹)	assignment
1'	529.24	18 895	-17	
1	528.76 (527.2)	18 912 (18 962)	0	0 ₀ ⁰
2	516.01 (519.0)	19 379 (19 362)	467	14 ₀ ¹
3	502.41	19 904	992	9 ₀ ¹
4	481.08	20 706	1794	
5	480.8	20 798	1886	5 ₀ ¹
6	478.24 (479.12)	20 910 (20 871)	1998	4 ₀ ¹
7	474.38 (477.44)	21 080 (20 945)	2168	
8	473.4 (474.28)	21 123 (21 084)	2211	
9	471.12	21 226	2314	3 ₀ ¹
10	465.32	21 484	2572	4 ₀ ¹ 14 ₀ ¹
11	459.21	21 776	2864	3 ₀ ¹ 14 ₀ ¹
12	433.32	23 077	4165	3 ₀ ¹ 4 ₀ ¹
13	427.17	23 409	4497	3 ₀ ²

^a Values observed for C₇D₃ are given in parentheses.

R2P2CI spectra are the result of a 1 + 1' process because a pure multiphoton transition is not favored under the conditions used due to a low radical concentration and low power density (unfocused laser). The origin band shows a resolved *K*-structure (inset in Figure 1). Although the signal-to-noise ratio was quite low, this rotational substructure was clearly reproduced but that of the deuterated C₇D₃ radical could not be obtained as the vibronic bands were hardly detected.

IV. Theoretical Calculations of the Isomers

Calculations were carried out using the GAUSSIAN 98 suite of programs³⁸ to investigate the ground state of isomeric structures. Full geometry optimizations and harmonic frequency calculations used the hybrid density functional B3LYP method³⁹ with Pople's split valence basis set 6-31G* with d-polarization.⁴⁰ This level of calculation has been shown to provide reliable predictions on C₅H₃ when compared to other levels of theory.³² Eight isomeric structures of C₇H₃ were calculated, and the optimized geometries are given in Figure 2. These conformations are the analogue of the lowest energy structures found in the extensive ab initio work on the radical C₅H₃.³² They are of the

(31) Stein, S. E.; Walker, J. A.; Suryan, M. M.; Fahr, A. *23rd Symp. (Int.) Combust. (Proceedings)* **1990**, 85.

(32) Mebel, A. M.; Lin, S. H.; Yang, X. M.; Lee, Y. T. *J. Phys. Chem. A* **1997**, *101*, 6781.

(33) DeWitt, M.; Levis, R. *J. Chem. Phys.* **1999**, *110*, 11368.

(34) Jochims, H.; Rasekh, H.; Rühl, E.; Baumgärtel, H.; Leach, S. *Chem. Phys.* **1992**, *168*, 159.

(35) Bandy, R. E.; Lakshminarayan, C.; Frost, R. K.; Zwier, T. S. *J. Chem. Phys.* **1993**, *98*, 5362.

(36) Richter, H.; Howard, J. B. *Prog. Energy Combust. Sci.* **2000**, *26*, 565.

(37) Pino, T.; Ding, H.; Güthe, F.; Maier, J. P. *J. Chem. Phys.* **2001**, *114*, 2208.

(38) Frisch, M. J.; et al. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(39) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5649. (b) *Ibid.* **1992**, *96*, 2155. (c) *Ibid.* **1992**, *97*, 9173. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(40) (a) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081. (b) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *98*, 2193.

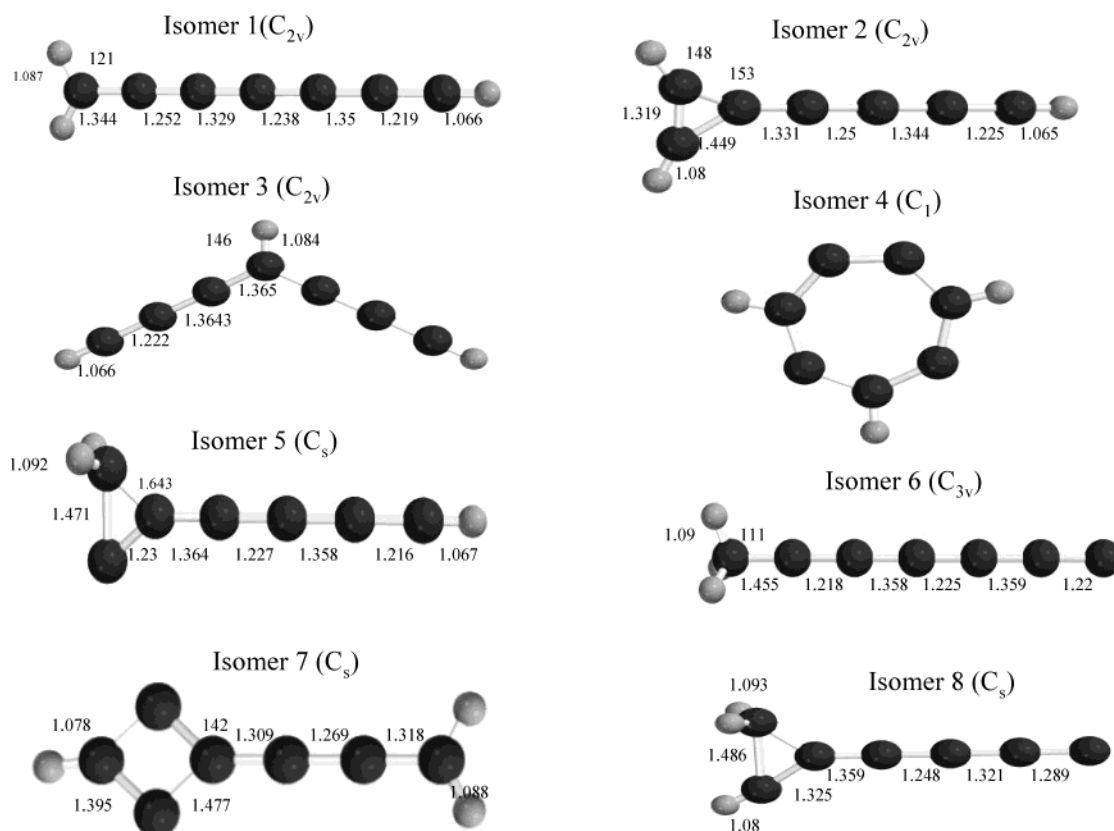


Figure 2. Geometries in the ground states of various C_7H_3 isomers optimized at the DFT-B3LYP/6-31G* level. The bond lengths are given in angstroms. Those of isomer 4 are not given since this structure is a transition state and the carbon skeleton strongly distorted.

Table 2. Calculated Energies and Parameters in the Ground States of the C_7H_3 Isomers at the DFT-B3LYP/6-31G* Level^a

	isomer 1	isomer 2	isomer 3	isomer 4 ^b	isomer 5	isomer 6	isomer 7	isomer 8
$E + 268(H)$	-0.32661	-0.27608	-0.26469	-0.256	-0.24991	-0.24598	-0.23801	-0.22667
ZE (kJ/mol)	165.080	162.204	158.452	170.04	167.108	176.389	166.56	166.6
ΔE (kJ/mol)	0	130	156	190	203	223	234	264
A (cm^{-1})	9.695	1.0873	0.2591	0.1596	0.8293	5.3222	0.7216	0.7897
B (cm^{-1})	0.02706	0.03348	0.04833	0.1388	0.03414	0.02694	0.0424	0.0347
C (cm^{-1})	0.02698	0.03249	0.04075	0.0778	0.03301	0.02694	0.04035	0.03347
D (debye)	0.222	3.525	0.982	1.065	1.983	2.630	0.933	6.850

^a Isomers 4, 7, and 8 possess a nonplanar carbon skeleton. ^b Structure 4 is a transition state; it is shown to illustrate the possible stability of a seven-membered cyclic form.

chain or (three and higher membered) cyclic forms. The calculated energies, zero-point vibrational energies (ZE), relative energies (ΔE), rotational constants (A , B , C), and dipole moments of isomers 1–8 are reported in Table 2 where the isomers are ranked according to their relative energies. Isomer 1, the cumulenic radical H_2C_7H with C_{2v} symmetry, is the most stable structure. ΔE for the ring chains are found comparable to those of the analogue structures in C_3H_3 ²³ and C_5H_3 ,³² while the chains (isomer 3 and 6) are less stable.

The calculated ground-state harmonic vibrational frequencies of the local minima 1, 2, 5, and 6 are given Table 3. The modes having frequencies above 3000 cm^{-1} correspond to the C–H stretch. Those in the region of 2000 cm^{-1} involve the acetylenic $C\equiv C$ stretch. Below 1000 cm^{-1} , these are mainly carbon skeleton and/or CC–H bending modes.

V. Assignment of the Isomer

Analysis of the rotational structure in the observed vibronic origin (inset in Figure 1) provides information on the structure of the carrier. The K -structure is resolved so that the A constant can be determined with good accuracy while the B and C constants are only roughly estimated from the spectral simula-

tion. The program Wang was used to simulate an asymmetric-top molecule,⁴¹ and a Lorentzian profile with a 0.7 cm^{-1} full width at half-maximum was taken for the rotational lines. The fitted ground-state rotational constants are $A'' = 0.85 \pm 0.03\text{ cm}^{-1}$, $B'' \approx C'' \approx 0.034\text{ cm}^{-1}$. For the excited state, A' increases by about 1% while B' and C' are almost identical to those of the ground state. The rotational temperature used in the simulation was $T = 17\text{ K}$. The band type is clearly perpendicular, and the presented simulations (Figure 1) were obtained taking a transition moment along the b -axis or the c -axis of the molecule, both providing a reasonable fit.

The deduced ground-state rotational constants suggest a three-membered ring-chain structure such as that of isomer 2 or 5 according to the ab initio predictions of the ground states. This clearly rules out the chain isomers or higher membered cyclic forms. The absence of a 1 to 3 intensity alternation of odd and even K_a values due to nuclear spin statistics shows that the molecule should have an unsymmetrical structure about the

(41) Luckhaus D.; Quack M. *Mol. Phys.* **1989**, *68*, 745.

Table 3. Calculated Ground State Harmonic Vibrational Frequencies (cm⁻¹) of Four Local Minima of C₇H₃ at the DFT-B3LYP/6-31G* Level

	isomer 1 (C _{2v})	isomer 2 (C _{2v})	isomer 5 (C _s)	isomer 6 (C _{3v})
ω_1	3491(a ₁)	3493(a ₁)	3493(a')	3038(a ₁)
ω_2	3154(a ₁)	3308(a ₁)	3088(a')	2330(a ₁)
ω_3	2190(a ₁)	2100(a ₁)	2263(a')	2270(a ₁)
ω_4	2107(a ₁)	2086(a ₁)	2166(a')	2156(a ₁)
ω_5	1975(a ₁)	1736(a ₁)	1838(a')	1439(a ₁)
ω_6	1525(a ₁)	1549(a ₁)	1525(a')	1331(a ₁)
ω_7	1422(a ₁)	1107(a ₁)	1188(a')	960(a ₁)
ω_8	1049(a ₁)	941(a ₁)	1089(a')	532(a ₁)
ω_9	552(a ₁)	544(a ₁)	1001(a')	3102(e)
ω_{10}	761(b ₁)	875(a ₂)	691(a')	1498(e)
ω_{11}	738(b ₁)	633(b ₁)	645(a')	1059(e)
ω_{12}	589(b ₁)	612(b ₁)	593(a')	761(e)
ω_{13}	529(b ₁)	397(b ₁)	524(a')	642(e)
ω_{14}	423(b ₁)	280(b ₁)	419(a')	365(e)
ω_{15}	216(b ₁)	226(b ₁)	245(a')	217(e)
ω_{16}	85(b ₁)	103(b ₁)	96(a')	86(e)
ω_{17}	3235(b ₂)	3267(b ₂)	3170(a'')	
ω_{18}	1029(b ₂)	1045(b ₂)	1068(a'')	
ω_{19}	760(b ₂)	776(b ₂)	736(a'')	
ω_{20}	586(b ₂)	658(b ₂)	683(a'')	
ω_{21}	549(b ₂)	555(b ₂)	566(a'')	
ω_{22}	358(b ₂)	498(b ₂)	468(a'')	
ω_{23}	216(b ₂)	260(b ₂)	270(a'')	
ω_{24}	86(b ₂)	107(b ₂)	112(a'')	

a-axis (along the side chain). Therefore, isomer 2 (C_{2v}) is not the carrier of the observed spectrum. The fitted *A*' constant, 0.85 ± 0.03 cm⁻¹, is in good agreement with that of isomer 5 (0.8293 cm⁻¹, Table 2), and this structure possesses an unsymmetrical structure about the *a*-axis. Other three-membered ring chains (not shown) possess an *A* rotational constant which differs from the fit by at least 0.15 cm⁻¹, well above our experimental precision. Thus, based on the analysis of the rotational structure in the observed spectrum and the calculated ground-state geometries, isomer 5 is proposed as the carrier of the observed spectrum.

VI. Analysis of the Vibronic System

Band 1 at 528.76 nm is assigned as the electronic origin based on isotopic substitution, and the shift is 50 cm⁻¹ to the blue. The electronic transition was shown to possess a perpendicular type, and the rotational sub-structure clearly excludes contribution by a parallel component. Therefore the electronic transition is tentatively assigned as ²A'' ← X²A'. This assignment would benefit from high level ab initio investigations. In fact, although CASSCF calculations undertaken for the lowest isomers of higher symmetry provided some clues on their electronic structures, no conclusive answers could be obtained due to technical problems with this type of complex ring chain.

The labels of the other vibronic bands use the calculated harmonic frequencies of the ground state of isomer 5 (Table 3) even if a normal-mode analysis is not fully appropriate according to the spectral complexity. Band 2 is assigned to a bending motion, and this yields $\nu = 467$ cm⁻¹ in the excited state. This frequency is comparable to that of ν_{14} which involves the CCH bending mode of the H terminating the chain. The observed large change upon deuteration supports this assignment. Band 3 is tentatively assigned to the 9₀¹ transition of this system leading to $\nu_9 = 990$ cm⁻¹. In the region about 2000 cm⁻¹ above the origin, the vibronic system composed of bands 4–9 is quite complex. The contributions from combinations of lower fre-

quency modes and fundamentals of the vibrations involving the characteristic acetylenic C≡C stretch can hardly be distinguished based on their positions. We tentatively assign bands 6 and 9 as 4₀¹ and 3₀¹ transitions, respectively. Modes ν_3 and ν_4 involve the C≡C stretch of the chain part of the carbon skeleton and possess a frequency of 1998 and 2314 cm⁻¹ in the excited state. It is noteworthy that the observation of the acetylenic stretch points to a chain substituent on the three-membered ring as is the case for isomer 5. Bands 10 and 11 involve combinations between these stretching modes and the low bending mode ν_{14} . All the proposed assignments are summarized in Table 1.

VII. Concluding Remarks

The observed spectrum of the C₇H₃ radical is assigned as ²A'' ← X²A' electronic transition in one three-membered ring-chain isomer, the 2-(buta-1,3-diyne)cycloprop-2-en-1-yl radical. It is remarkable that the fifth least stable isomer of the C₇H₃ family, higher by 203 kJ/mol above the global minimum, is observed. The result suggests that the barrier between this exotic three-membered ring chain (three-dimensional) and the other (planar) isomers is large enough to prevent isomerization under the experimental conditions. An indication of a plausible height of this barrier comes from the C₃H₃ molecule where a transition state between the 2-propynyl and the cycloprop-1-enyl was predicted about 42 kJ/mol above the latter.²³ This illustrates the capacity of the supersonic expansion to freeze out the distribution of transient and exotic systems in a hydrocarbon discharge plasma.

A similar result was found in studies of C₃H¹⁹ and C₇H₇,⁴² using the same plasma discharge source. In the case of C₇H₇, it was inferred that the cationic route was favored,⁴² and this could apply for C₃H, the chain being more stable than the cyclic structure in the cation. Recently, we have shown that the C_{2n+1}H₃ species possess a low ionization potential in their ring-chain form owing to the stabilization of their cations.⁴³ This suggests that the observed C₇H₃ isomer could be formed from its cation with subsequent neutralization and cooling. Other C₇H₃ structures were not observed in the present experiment, although the visible to near-UV range of wavelength was scanned. It implies that the used experimental technique is not well suited to investigate their electronic spectra and transitions of other isomers could be at different wavelengths than scanned. In fact, due to the differences in the ionization potential of the different isomers the detection scheme is selective. In addition, specific limitations as fast intramolecular dynamics or dissociation of the isomers in their excited states might prevent their electronic spectra to be measured.

Molecules including a three-membered ring are thought to be important intermediates in the formation of aromatics and PAHs. Cyclic C₃H₂ is found in abundance in different regions of the ISM, even such a harsh environment as the diffuse medium,⁴⁴ and recent observations have shown a connection between small hydrocarbons such as C₃H₂, C₂H, and C₄H and the interstellar PAH-like component.^{45,46} A combination of the insight in astrophysical processes, models of flames and soot formation, and the spectroscopic characterization of radicals is

(42) Pino, T.; Güthe, F.; Ding, H.; Maier, J. P. *J. Phys. Chem. A* **2002**, *106*, 10022.

(43) Schmidt, T. W.; Boguslavskiy, A. E.; Pino, T.; Ding, H.; Maier, J. P. *Int. J. Mass Spectrom.* **2003**, in press.

(44) Lucas, R.; Liszt, H. S. *Astron. Astrophys.* **2000**, *358*, 1069.

highly revealing. In the laboratory, the use of a discharge source is a powerful tool to investigate the reactive intermediates involved. The isolation of the species and their efficient cooling enable their spectroscopy to be investigated and the isomer structure to be inferred. In contrast the identification of the

reactive intermediates in flames, such as in the formation of benzene, remains a challenge.

Acknowledgment. The authors would like to thank Prof. Pavel Rosmus for helpful discussions on the theoretical calculations. This work has been supported by the Swiss National Science Foundation (Project No. 200020-100019).

-
- (45) Gerin, M.; Fossé, D.; Roueff, E. In *Proceedings of Chemistry as a Diagnostic of Star Formation*; Curry, C. L., Fich, M., Eds.; in press.
- (46) Teyssier, T.; Fossé, D.; Gerin, M.; Pety, J.; Abergel, A.; Habart, E.; In *Proceedings of Chemistry as a Diagnostic of Star Formation*; Curry, C. L., Fich, M., Eds.; in press.

JA0296500