

Methyl Substitution in Hydrocarbon Discharge Chemistry: Diagnosis by Laser Spectroscopy

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Received: April 10, 2003; In Final Form: June 18, 2003

The spectra of C_8H_4 and $C_{10}H_5$ were observed in a butadiyne/argon discharge under the same conditions as those whereby C_7H_2 and C_9H_3 have been found to dominate the spectroscopy. It is shown that the species C_8H_4 and $C_{10}H_5$ most likely originate from methyl substitution of a hydrogen in C_7H_2 and C_9H_3 such as not to significantly disturb the chromophore. Assuming comparable oscillator strengths for the substituted species, it is found that the ratio of abundances of the unsubstituted and substituted species is around 27:1. This is discussed in relation to the chemistry of plasmas and the interstellar medium.

1. Introduction

The study of highly unsaturated hydrocarbon molecules produced from discharge sources is partly motivated by the search for the carriers of the diffuse interstellar bands (DIBs).¹ While these are yet to be identified, many highly unsaturated hydrocarbon species have been observed in dark interstellar clouds by rotational spectroscopy.² These observations allow one to characterize the chemistry of the interstellar medium and build models which attempt to explain relative abundances of species found therein.

Molecules of the generic formula C_nH_m ($m \leq n$) are abundant in flames and plasmas involving hydrocarbon precursors. One type of isomer of the C_nH formula has been observed in the laboratory, the linear species. The first eight members of this series have been confirmed to exist in space.^{2,3} Optical and microwave spectra have been measured for several of these species.^{4,5}

The spectra of several of the HC_nH series have been observed in rare gas matrixes,^{6–8} and in the gas phase by resonant two-color two-photon ionization spectroscopy (R2C2PI)⁹ and cavity ringdown spectroscopy (CRDS).¹⁰ Of this class of molecules, HC_4H and HC_6H have been observed in space by infrared spectroscopy.¹¹

A number of H_2C_n carbenes have been observed by microwave spectroscopy, owing to their permanent dipole moment,^{12–14} with H_2C_3 , H_2C_4 , and H_2C_6 having been observed in space.^{15–17} Less symmetric isomers^{18,19} and ring–chain²⁰ species have also been observed.

Recently, the spectra of $C_{2n+1}H_3$ ($n = 3–6$) molecules were observed by R2C2PI spectroscopy.²¹ These species were found to incorporate at least one ring structure. In the case of C_7H_3 , this was found to be a three-membered ring, whereas for C_9H_3 , $C_{11}H_3$, and $C_{13}H_3$, it was supposed that the ring structure was also three-membered.²¹

Under the same conditions as C_9H_3 was observed, it was found that the most dominant spectrum measurable in the range 650–440 nm was that of linear C_7H_2 . While these two molecules easily dominated the spectroscopy, a number of other species

were observed with significantly lower signal-to-noise (S/N). Two of these belonged to the same series as C_9H_3 and are discussed elsewhere.²¹ The other species observed, C_8H_4 , $C_{10}H_5$, and $C_{11}H_7$, appear at first glance rather arbitrary. It is shown in this paper that the most likely structures of these species are those arising from methyl substitution of the dominant C_7H_2 and C_9H_3 isomers. This is discussed with reference to the chemistry of plasmas and the interstellar medium.

2. Experimental Section

Spectra were obtained utilizing an apparatus which consisted of a molecular beam combined with a linear time-of-flight (TOF) mass analyzer (resolution of 900 at mass 200). The source, a pulsed valve coupled to an electric discharge, was the same as that used for detection of the $C_{2n+1}H_3$ species ($n = 4–6$).²¹ A pulse of a gas mixture of 0.5% butadiyne (HCCCCH) in Ar (backing pressure of 5 bar) was expanded through the ceramic body of the source which held two steel electrodes with an ≈ 1 mm hole separated by a ceramic spacer of 4 mm. A high voltage pulse (600–1200 V) was applied between the electrodes. Any resulting ions were removed after the skimmer, and before entering the pulsed extraction zone of the TOF mass spectrometer, by an electric field perpendicular to the molecular beam. The neutral beam was then ionized and ions were extracted into the TOF tube. The signal from the multichannel plate detector was fed into a fast oscilloscope after preamplification. Data acquisition was carried out using Labview programs.

R2C2PI was used in the 650–440 nm range. Excitation photons were delivered by a commercial OPO system (bandwidth 0.05) pumped by the third harmonic of a Nd:YAG laser. The ionizing photons at 212 nm (5.85 eV) were produced by sum frequency generation of the second harmonic and fundamental of the 637 nm output of a dye laser pumped by the second harmonic of a Nd:YAG laser. The energy per pulse was ≈ 5 mJ for the first color and a few hundred microjoules for the second. Both beams were anticollinear to the molecular beam, being combined with a dichroic mirror, and aligned optimally in time and space. The mass spectrum obtained upon irradiation of the products of the plasma discharge source with 7.9 eV photons from an F_2 excimer laser was used to optimize the discharge conditions.

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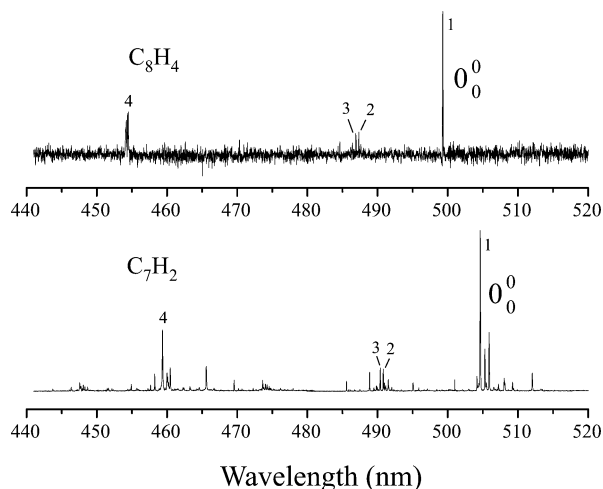


Figure 1. Comparison of resonant two-color two-photon ionization spectra of C_7H_2 and C_8H_4 . Analogous features are listed in Table 1.

3. Results and Discussion

3.1. Overview of Vibronic Structure. Figure 1 compares the electronic excitation spectra of C_7H_2 and C_8H_4 . The spectrum of C_7H_2 exhibits sequence or hot-band structure near the origin (band 1) which is repeated throughout the spectrum for each vibronic band. C_7H_2 is linear (HC_7H) with the electronic transition arising from $A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ excitation. This spectrum has been discussed previously.^{8,10} The origin band of C_8H_4 appears nearby that of C_7H_2 , and exhibits similar vibronic structure. Bands 2 and 3 lie 493 cm^{-1} and 509 cm^{-1} to the blue of the origin band. The analogous bands in C_7H_2 are assigned to the excitation of double quanta of bending modes and are located 558 cm^{-1} and 575 cm^{-1} to the blue of the origin.⁸ Band 4 is split into two features, respectively, located at 1992 cm^{-1} and 1977 cm^{-1} . This feature in the HC_7H spectrum is located 1952 cm^{-1} to the blue of the origin.

Figure 2 compares the origin regions of C_9H_3 and $C_{10}H_5$. No other bands were observed for $C_{10}H_5$. It is striking that these spectra appear so close spectrally, both possessing a low-frequency progression. In $C_{10}H_5$ this progression is reduced from 39 cm^{-1} to 33 cm^{-1} . The positions of the origin bands of these electronic transitions are extremely close in energy. The relevant band positions may be found in Table 1. Only one band was observed for $C_{11}H_7$, and is listed in Table 1.

3.2. Structural Considerations. Without clear rotational resolution the structure of C_8H_4 may be deduced by a number of electronic and vibrational considerations. The most symmetric structure, the cumulene $H_2C_8H_2$, can be ruled out immediately since it is expected to absorb in the deep ultraviolet, and possesses no acetylenic stretch. It is argued here that the structure of the C_8H_4 isomer observed in the spectrum in Figure 1 is $(CH_3)C_7H$. Substituting a methyl group for one of the terminal hydrogens in HC_7H (Figure 3a) results in a molecule with a near identical chromophore, since the π -bonding system is left unaltered (to a first approximation). Indeed, it is expected that such a molecule would absorb in the same region as HC_7H . As seen in Figure 1, this is so. Methyl substitution increases the reduced mass for any bending motions and thus it is expected that the frequencies of such modes would decrease. Again, this is observed. Another piece of evidence consistent with the $(CH_3)C_7H$ structure is the splitting of the acetylenic stretch into two bands. There are two strong, triple bonds in HC_7H , yet only one acetylenic stretch is observed due to the $D_{\infty h}$ symmetry (only the totally symmetric modes may be populated with single

TABLE 1: Comparison of Features Observed in the R2C2PI Spectra of HC_7H , $(CH_3)C_7H$, C_9H_3 , $C_{10}H_5$, and $C_{11}H_7$ in the Gas Phase

label	λ (nm)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	assignment
HC_7H				$A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$
1	504.5	19818	0	0_0^0
2	490.7	20376	558	$2\nu_\alpha$
3	490.2	20393	575	$2\nu_\beta$
4	459.2	21770	1952	2_0^1
$(CH_3)C_7H$				$A^3A_1 \leftarrow X^3A_1$
1	499.1	20035	0	0_0^0
2	487.2	20528	493	$2\nu_\alpha$
3	486.8	20544	509	$2\nu_\beta$
4	454.3	22012	1977	$\nu_{C\equiv C}$
	454.0	22026	1992	$\nu_{C\equiv C}$
C_9H_3				
	529.5	18886	0	0_0^0
	528.4	18925	39	low-frequency mode
$C_{10}H_5$				
	528.7	18914	0	0_0^0
	527.8	18947	33	low-frequency mode
$C_{11}H_7$				
	522.5	19139	0	0_0^0

quanta). Lifting this symmetry to C_{3v} for the $(CH_3)C_7H$ structure allows both acetylenic stretching modes to be populated upon electronic excitation. The absence of hot or sequence-band structure in $(CH_3)C_7H$ may be due to the mixing of modes upon reduction symmetry allowing more efficient cooling.

No signature specific to a methyl substituent is observed in the spectrum of $(CH_3)C_7H$. The extent of vibrational excitation of the “umbrella” motion of the $-CH_3$ group ($\approx 1300\text{ cm}^{-1}$) would depend on the Franck–Condon factor for this mode. Since the methyl group does not couple strongly to the chromophore it is probable that the potential curve for this mode in both states is similar. The Franck–Condon factor for excitation of the umbrella mode would thus be small. By analogy with the lowest transition of HC_7H , $^3\Sigma_u^- \leftarrow ^3\Sigma_g^-$, the symmetry of the lowest electronic transition of $(CH_3)C_7H$ is $^3A_1 \rightarrow ^3A_1$. Since this represents a parallel band of a symmetric top molecule, no structure is expected from transitions arising from $\Delta K \neq 0$ (change in rotation about the molecular axis). The A rotational constant of this species is expected to be near 5 cm^{-1} , but it should not change significantly upon electronic excitation. Clear rotational structure was not observed in the spectrum of $(CH_3)C_7H$, consistent with a parallel transition.

The structure of C_9H_3 was not unambiguously determined,²¹ yet the spectra of this species and the related $C_{11}H_3$ and $C_{13}H_3$ species pointed to a ring–chain system. The fact that this isomer of $C_{10}H_5$ is seen under the same conditions as C_9H_3 , that they are related by addition of CH_2 , that they absorb at a near identical frequency, and that they both possess a characteristic low-frequency mode indicates that this isomer of $C_{10}H_5$ is likely a methyl-substituted version of the dominant C_9H_3 isomer (for example, see Figure 3b). It is clear that if this is the case then the $-CH_3$ group will not be found near the chromophore of the molecule. Substitution of a further $-CH_3$ group results in a molecule of molecular formula $C_{11}H_7$. An extremely weak band was found for this mass at 522.48 nm , only a few nm to higher energy than $C_{10}H_5$. If this molecule arises from a structure related to C_9H_3 and $C_{10}H_5$, then the second substitution must perturb the chromophore more strongly than the first. Such a scenario is illustrated in Figure 3b.

In the present experimental setup, over 200 masses were monitored simultaneously. However, with 212 nm as the ionizing wavelength, the most dominant spectra observed in the spectral range $650\text{--}440\text{ nm}$ were those of C_7H_2 and C_9H_3 . The

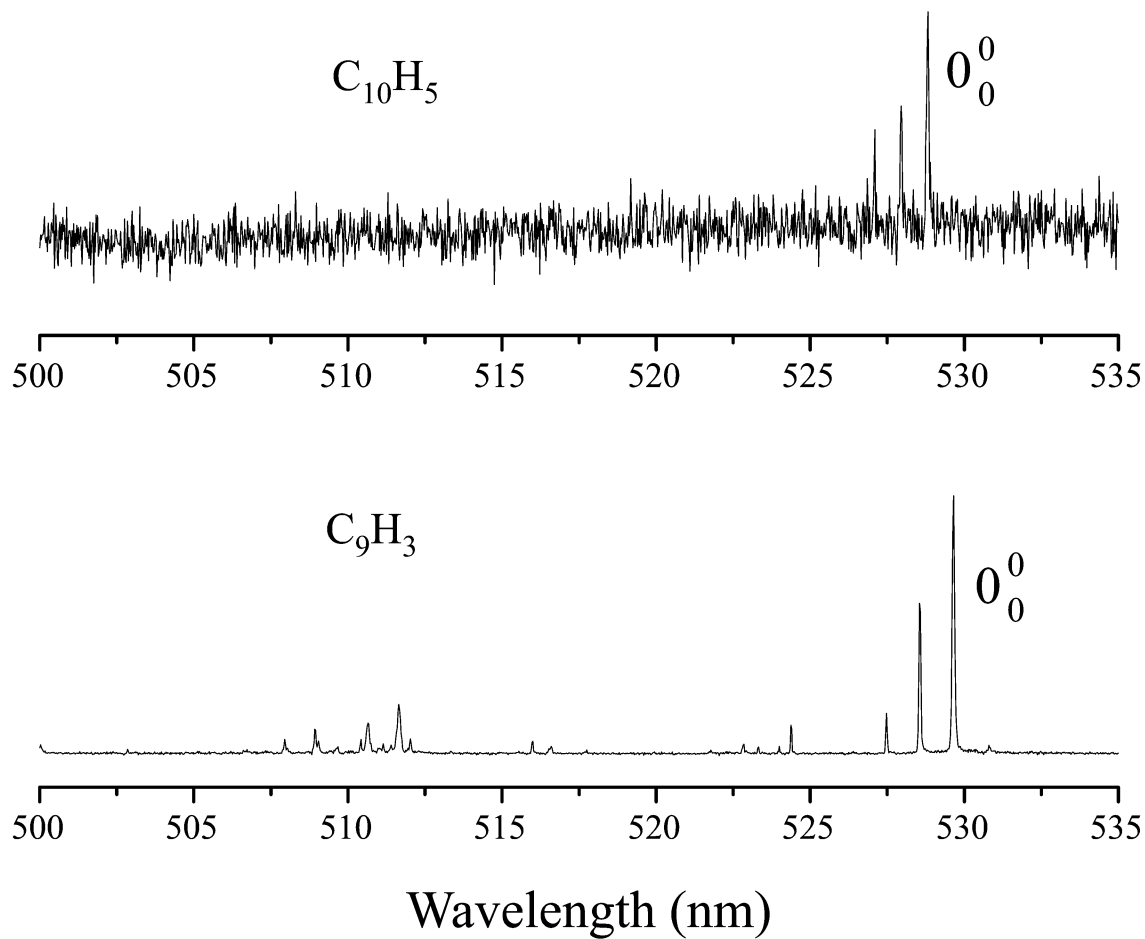


Figure 2. Comparison of resonant two-color two-photon ionization spectra of C_9H_3 and $C_{10}H_5$. Analogous features and band origin of $C_{11}H_7$ are listed in Table 1.

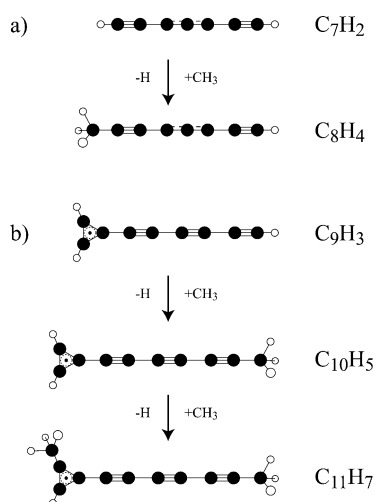


Figure 3. (a) A cartoon representation of the isomers of C_7H_2 and C_8H_4 described in the text. (b) An example of a ring-chain isomer of C_9H_3 , and the resulting isomers of $C_{10}H_5$ and $C_{11}H_7$ upon methyl substitution.

S/N of the former is conservatively estimated to be 1700, while that of the latter was found to be 700. Also observed under these conditions are C_9H_2 , $C_{11}H_3$, and $C_{13}H_3$ with S/N 10, 12, and 6, respectively. The facts that C_8H_4 and $C_{10}H_5$ are observed under these conditions and that they have spectra similar to those of the dominant species, C_7H_2 and C_9H_3 , strongly suggests that they are related molecules. That they are related by an extra 14 mass units suggests methyl substitution in place of a hydrogen.

For C_8H_4 the most likely structure is $(CH_3)C_7H$. As the structure of C_9H_3 is not unambiguously determined, one can only assume that $C_{10}H_5$ is related by a methyl substitution in such a way as to decrease the frequency of the low-frequency mode. The $C_{11}H_7$ spectrum obtained indicated only one band and was extremely weak. It is thought that its relationship to $C_{10}H_5$ is similar to the relationship of that molecule to the very strongly evident C_9H_3 isomer. In benzene discharges, styrene and methylstyrene have been observed, exhibiting spectra with near identical origin positions.²² That such behavior has been observed before in hydrocarbon discharges strengthens the assertions made here. No other species other than those indicated in this text were observed with excitation laser between 440 and 650 nm using 212 nm as the ionizing laser.

4. Chemical Implications

Because the transition positions move by less than 5 nm upon methyl substitution, it may be safe to assume that the oscillator strengths of the species HC_7H and $(CH_3)C_7H$ are similar. Given equal oscillator strengths and the fact that the spectra of HC_7H and $(CH_3)C_7H$ were recorded simultaneously, one may estimate that the ratio of abundances of the species is 27:1 in favor of HC_7H . Performing the same calculation for C_9H_3 and $C_{10}H_5$, their ratio of abundance is also found to be 27:1 in favor of the unsubstituted species. If this is taken as a general rule, then one expects to experimentally observe the methyl-substituted carbon chain (or ring-chain) only if the "parent" molecule is observed with a S/N above 30 or so. Since $C_{10}H_5$ is observed with S/N of about 6, it is perhaps fortunate to have observed

C₁₁H₇ at all. Indeed, this spectrum was only reproduced with great difficulty.

The methyl polyynes CH₃(C≡C)₄H and CH₃(C≡C)₅H have been observed by microwave spectroscopy of the products of a mixed methylacetylene/butadiyne discharge.²³ The shorter member CH₃(C≡C)₃H has also been observed in the laboratory by microwave spectroscopy.²⁴ The choice of methylacetylene as a precursor suggests the importance of the methyl radical in the growth of these species. In space, the CH₃ radical is a fundamental intermediate in the growth of larger hydrocarbons and is closely related to the interstellar chemistry of methane.²⁵ The methyl substituent is also seen in carbonaceous grains in the interstellar medium by infrared absorption.²⁶ Indeed, the methyl radical and ion are integral to models of highly unsaturated hydrocarbon chemistry.^{2,27} The importance of methyl substitution in the hydrocarbon chemistry of a discharge source in the laboratory and the interstellar medium reinforces the link between the two.

Methyl-substituted chains are observed in the interstellar medium due to their permanent dipole moment. The acetylenic derivatives CH₃C₂H and CH₃C₄H have been observed in translucent molecular clouds² and in the atmospheres of moons and planets.²⁸ It is difficult to estimate how their abundances compare to the "parent" unsubstituted chains in the interstellar medium due to their absence of dipole moment. It is known that acetylene and butadiyne are components of the atmosphere of Titan,^{29,30} and due to their size and simplicity are expected to be found in the interstellar medium. Indeed, the polyynes C₄H₂ and C₆H₂ have been detected in the protoplanetary nebula CRL 618.¹¹ In the atmosphere of Titan, the ratio of acetylene to methylacetylene is estimated to be 240:1.³¹ The relative abundances of these species depend on the proportions of various elements in the medium, as well as chemical factors. In the source used in the present experiments, it is clear that where one species is strongly observed, the methyl-substituted species may be detected also.

5. Concluding Remarks

The observation of methyl-substituted species from a butadiyne discharge provides a benchmark for those modeling such systems. The observation of molecules with similar or equal transition moments simultaneously provides a way of comparing the relative abundances of those species. In this paper, it was shown that the ratios of C₉H₃/C₁₀H₅ and HC₇H/(CH₃)C₇H were both about 27:1. Any model of the chemistry involved in a butadiyne/Ar discharge must either support these observations or provide an alternative explanation. Because the level of unsaturation of hydrocarbons found in plasma discharges and the interstellar medium is similar, it is expected that the present work should have implications for astrochemical models.

Acknowledgment. This work has been supported by the Swiss National Science Foundation (Project No. 200020-100019).

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