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Optical detection of C_9H_3, $C_{11}H_3$, and $C_{13}H_3$ from a hydrocarbon discharge source

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Abstract

Resonant two-color two-photon ionization spectra of C_9H_3, $C_{11}H_3$, and $C_{13}H_3$ have been observed in the gas phase and are found to exhibit remarkably similar vibrational structure. All have origins in the 18,800–19,300 cm^{-1} region and a characteristic ≈40 cm^{-1} progression. Several pieces of spectroscopic information suggest a common moiety incorporating a strong, localized electronic transition, consistent with a low ionization potential as compared to other hydrocarbon radicals. Several possible structural motifs are discussed in relation to plasma, combustion and interstellar chemistry.

Keywords: Electronic spectroscopy; Discharge plasma; Interstellar chemistry

1. Introduction

One of the unsolved problems facing physics, chemistry and astronomy is the identity of the carriers of the diffuse interstellar bands (DIBs), a series of diffuse absorption lines in the visible region observed in light having passed through the interstellar medium [1]. Candidate carriers of these features include bare carbon and hydrocarbon chains of a size and structure consistent with absorption of visible radiation [2,3]. Work over the past years, comparing the optical spectra of bare carbon chains with the DIBs, has shown that small bare carbon chains (C_n, $n \leq 10$) are not the carriers of the DIBs [4,5]. Larger species and their hydrogenated counterparts are yet to be tested thoroughly, though such species are incorporated into current models of interstellar chemistry [6,7]. Molecules of the generic formula C_nH_m ($m \leq n$) are abundant in flames and plasmas involving hydrocarbon precursors.

Of the molecules with formula C_nH, only one type of isomer has been observed in the laboratory: that with the hydrogen atom terminating one end of the carbon chain. Of these, $n = 1$–8 have been confirmed to exist in space [7,8]. The optical and microwave spectra are known for a variety of these species [9–11].

The C_nH_2 series exhibits a range of isomers which have been identified by a number of experimental techniques. The even polyyne chains, $HC_{2n}H$, have been observed in rare gas matrices by direct absorption spectroscopy, and in the gas phase by $1 + 1'$ resonance enhanced multi-photon ionization spectroscopy (REMPI) up to $HC_{26}H$ [12–14]. The band origin wavelengths show a dependence on chain length which is non-linear yet monotonically increasing.

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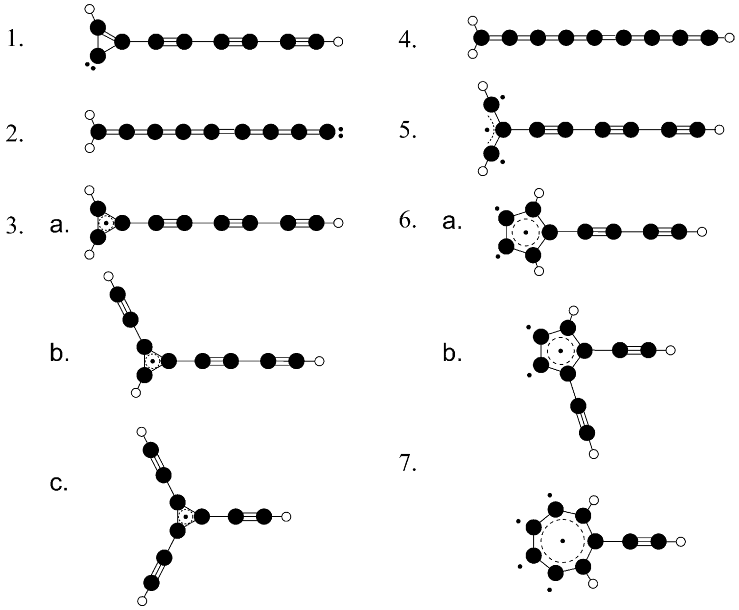

Fig. 1. Several structural isomers of C_9H_2, 1 and 2, and C_9H_3, 3–7. The odd-membered rings are stabilized upon ionization.

This behaviour is interpreted in terms of the persistent bond length alternation of the chromophore. The odd polyyne radical chains, $HC_{2n+1}H$ ($n = 3$–6), have also been detected in matrices by direct absorption and in the gas phase by cavity ringdown spectroscopy [15] and REMPI [16]. Over the small range of chain lengths studied, these molecules exhibit a linear dependence of band origin (wavelength) with respect to their size. The dependence of the positions of the origin bands of the linear chain isomers of HC_nH on chain length can be rationalized in terms of a Hückel theory in which bond length alternation is taken into account [17].

Apart from these symmetrical isomers, a number of carbenes have been observed by microwave spectroscopy, owing to their permanent dipole moment. The observed carbene isomers of C_nH_2 fall into two main categories: those with both hydrogen atoms at the same end of a linear chain (e.g., isomer 2 in Fig. 1), and those which exhibit a three-membered ring (isomer 1) [18]. The three-membered ring species has been shown by ab initio calculations to be the more stable of the two for an odd number of carbon atoms [19]. Isomer 1 has been observed for $n = 5$, 7, 9 [20–22] and isomer 2 for $n = 5$–9, C_4H_2 and C_6H_2 having been observed in the interstellar medium [7,23]. Also detected by microwave spectroscopy are C_5H_2 where both hydrogens reside on the three-membered ring, and where the hydrogens are in the 1 and 3 positions of a linear carbon chain. The 1,3-hydrogenated isomer has also been observed for C_6H_2 [23,24].

The wide variety of C_nH_2 isomers measured by microwave spectroscopy leads one to assume that even more isomers may be observed for the corresponding C_nH_3 series, as illustrated by Mebel et al. [25]. The C_7H_3 radical had been recently observed in our laboratory by $1 + 1'$ REMPI [26]. Calculations at the DFT level employing a B3-LYP functional indicate that the ring-chain isomer (analogous to isomer 3a in Fig. 1) lies second lowest in energy (to isomer 4). Analysis of the rotational structure revealed the identity of the carrier as a ring-chain isomer.

The C_nH_3 species are a major product of hydrocarbon discharge sources and are found to be most abundant for $n \geq 7$ and up to $n = 29$. Similar distributions are observed for the cations and anions. Laser pyrolysis of acetylene [27] and studies of fuel rich hydrocarbon flames [28] give similar results. While these species are clearly important in combustion processes, so far little is known about their structure and formation. In this article, we present the REMPI spectra of C_9H_3, $C_{11}H_3$, and $C_{13}H_3$. Electronic and vibrational information is considered and their implications discussed.

2. Experimental

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 was a pulsed valve coupled to an electric discharge. This discharge source was the same as that used for detection of the $HC_{2n}H$ species ($n = 8$–13) [12]. 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 a ≈1 mm hole separated by a ceramic spacer of 4 mm. A high voltage pulse (600–1200 V) was applied between the electrodes. 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 extracted. The signal from the multichannel plate (MCP) detector was fed into a fast oscilloscope after preamplification. Data acquisition was carried out using Labview programs.

Resonant two-color two-photon ionization was used in the 650–450 nm range. Excitation photons were delivered by a commercial OPO system (bandwidth 0.05 cm^{-1}) 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 ≈10 mJ for the first color and a few hundred

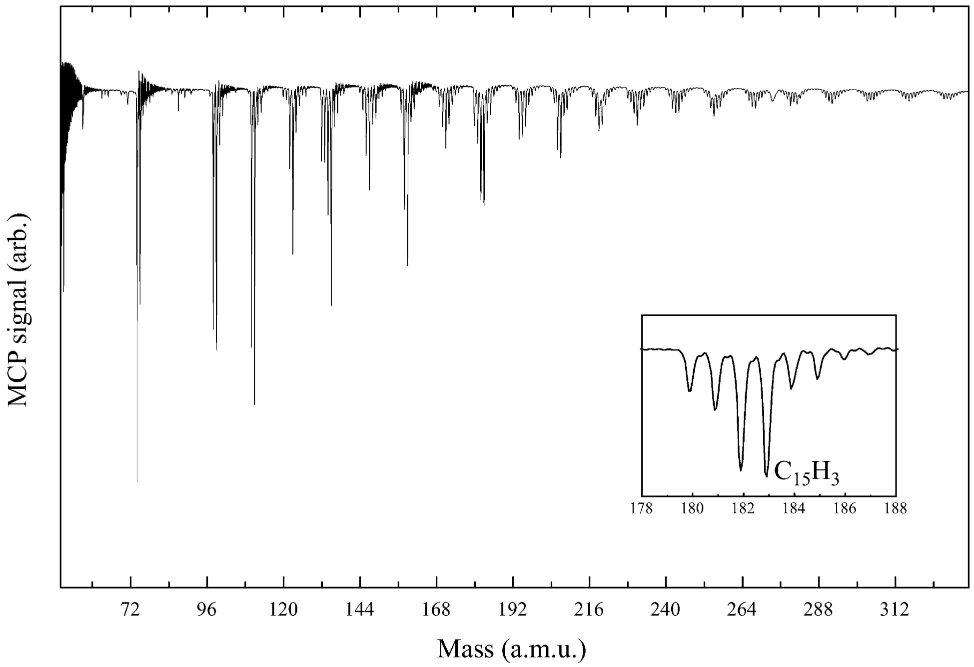

Fig. 2. A typical mass spectrum of the products of a butadiyne discharge irradiated by 157 nm light for $n \geq 4$. From $n = 7$ the most abundant species are the C_nH_3 radicals.

microjoules for the second. Both beams were anti-collinear 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 was used to optimize the experimental conditions. Such a mass spectrum is shown in Fig. 2.

3. Results and discussion

3.1. Overview of vibronic structure

Fig. 3 shows the electronic excitation spectra of C_9H_3, $C_{11}H_3$, and $C_{13}H_3$ from 18,800 to 22,700 cm^{-1}. Immediately noticeable is the similarity between the three species. All have what appears to be their origin in the 18,800–19,300 cm^{-1} range, with no particular trend with system size. All possess a short, harmonic, vibrational progression of lines spaced by $\approx$40 cm^{-1}. Additional features at 200, 600–700, and 2100 cm^{-1} to the blue of the origin band are common to all three species. The last of these can be assigned as the characteristic acetylenic stretch. Additional structures to higher energy than the acetylenic stretch appear to be due to combinations of this stretch with the other lower frequency modes. The analogous band positions for the three species are listed in Table 1.

Table 1
Observed band systems of the C_nH_3 species

Species	T_0	$\nu_{C\equiv C}$	$\nu_{\approx 650\,cm^{-1}}$	$\nu_{\approx 200\,cm^{-1}}$	$\nu_{\approx 40\,cm^{-1}}$
C_9H_3	18,881	+2113	+664	+190	+39
$C_{11}H_3$	19,313	+2039	+651	+186	+36
$C_{13}H_3$	19,246	+2147	+580	+189	+39

Vibrational frequencies are given relative to the origin band (T_0) in cm^{-1} ($\pm$1 cm^{-1} precision), as measured to the largest band in that system.

The spectrum of C_9H_3 is the clearest of the three. The vibrational structure near the origin is repeated throughout the spectrum. The acetylenic stretch is broadened with respect to the origin, yet maintains the 40 cm^{-1} progression. Inspection of the individual bands that make up this region reveals a splitting into at least two and as many as three bands, as illustrated in Fig. 4. This indicates the presence of a corresponding number of triple bonds in the molecular structure. The other features in the spectrum are left unassigned.

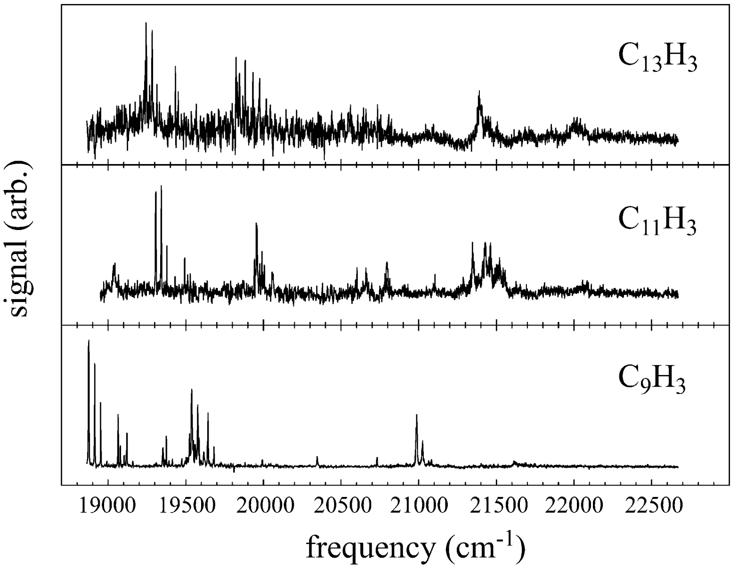

Fig. 3. The electronic spectra of the species C_9H_3, $C_{11}H_3$, and $C_{13}H_3$. All have remarkably similar vibronic structure and exhibit the characteristic acetylenic stretch.

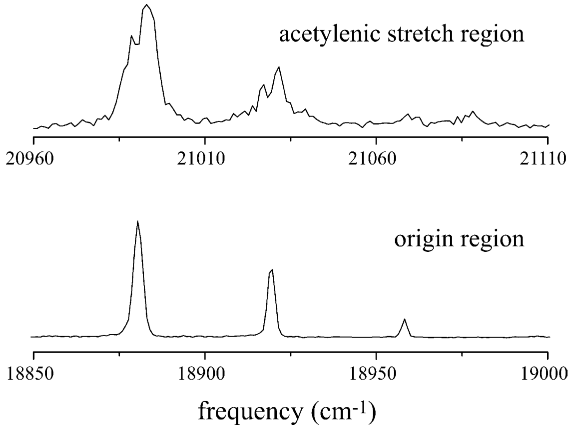

Fig. 4. The origin and acetylenic stretch regions of the electronic spectrum of C_9H_3. The acetylenic stretch region possesses broader peaks, split into three sub-peaks. It is suggested that this splitting is due to weak interactions between three separated triple bonds.

The spectrum of $C_{11}H_3$ is similar to C_9H_3, yet exhibits some differences. The vibrational frequency of the characteristic low frequency mode is reduced by $3\,cm^{-1}$ upon the addition of two carbon atoms (Table 1). The section between the origin and the $\approx 650\,cm^{-1}$ feature is not more complicated than C_9H_3, yet the acetylenic stretching region shows a great deal more structure. The broad feature to the red of the origin is not thought to originate from the same electronic transition, if from the same isomer. The presence of this broad feature at $19{,}040\,cm^{-1}$ may hint at the origin of the differences between the eleven-carbon species and the nine-carbon species. The complicated nature of the acetylenic stretching region indicates the presence of at least two but probably more triple bonds in this structure. In contrast to $C_{11}H_3$, $C_{13}H_3$ appears more similar to C_9H_3.

3.2. *Structural considerations*

As of yet there is no clear rotational information with which to assign the structures of these species. Comparison with the C_7H_3 molecule recently detected in our laboratory shows that it has a different structure compared to those being discussed here [26]. C_7H_3 was found to exhibit a three-membered ring-chain carbon skeleton with one hydrogen atom terminating the acetylenic chain, and the other two bound to the same carbon atom of the ring. This species exhibited clear K structure with an A constant of $0.88\,cm^{-1}$ and thus it is expected that in the present case the A rotational constant should be no greater than this. A calculated and tentatively assigned splitting in the acetylenic stretch due to the interaction of two triple bonds on the same chain was found to be about $170\,cm^{-1}$ [26].

It is the normal behaviour of conjugated carbon chains that they absorb at longer wavelengths upon increasing the length of the chain [10,12,15], be it a linear relationship or otherwise. The absence of clear K structure ($A \approx 10\,cm^{-1}$), and the stability of the transition energy with system size rules out the H_2C_nH chain isomers (e.g., isomer 4) as carriers of the observed spectra. As shown above, C_9H_3, $C_{11}H_3$, and $C_{13}H_3$ have a remarkably similar vibrational structure, and all absorb in the same part of the visible region. This behaviour is similar to that seen for other species, in which the chromophore is not a chain, but a localized electronic transition on a carbon ring [29]. It is clear from the vibrational structure that the C_9H_3, $C_{11}H_3$, and $C_{13}H_3$ species possess at least one acetylenic bond. This leaves seven carbon atoms with which to build a structural motif common to all three species. Worthy of note is the spectrum of $C_{10}H_5$ [30], which absorbs in the same region as the other species mentioned, and possesses the characteristic low frequency progression. We suppose that where the C_nH_3 species terminate a polyynic chain with a hydrogen atom, $C_{10}H_5$ does likewise with a methyl group. For the purposes of attaining a stable transition energy with growing polyynic chain, the chromophore should possess a molecular orbital of a different symmetry to the chain. This may be affected through the construction of a three-, five- or seven-membered ring (see isomers 3, 6, and 7 in Fig. 1), or a branched chain structure in C_{2v} symmetry (isomer 5). There are many possibilities, yet candidate structures must be consistent with the other available experiment evidence. In the case of a three-membered ring-chain isomer such as 3a, the electronic transition should be of the B or C type, to avoid strong dependence on system size, and thus exhibit K structure.

The characteristic low frequency mode is a special feature of this class of species. Such a low frequency which changes little from C_9H_3 to $C_{13}H_3$ may be indicative of a flat- or double-well potential, perhaps arising from a ring distortion mode. It should be noted that isomer 3c is expected to exhibit Jahn–Teller distortion. Others may experience similar effects, leading to interesting potential energy surfaces governing the ring geometry.

It may be tempting to assign the low frequency mode in to a bending progression of a long carbon chain constituent. Even without symmetry considerations, a mode must be found which exhibits a frequency as low as $40\,\text{cm}^{-1}$ in the excited state. From density functional calculations of the ground states of long linear $HC_{2n+1}H$ chains ($n = 4$–9), such low frequency modes (π_u) have been calculated to exist [31]. Although these modes were not evidenced in their REMPI spectra [16], it is likely that the excited states have similar vibrational frequencies. Their behaviour as a function of chain length is systematic, decreasing from $52\,\text{cm}^{-1}$ for HC_9H to $10\,\text{cm}^{-1}$ for $HC_{19}H$. For the present species, no clear size-dependent behaviour is observed (see Table 1), and thus the mode responsible for the observed low frequency progression most likely involves the ring structure to some degree.

It may be seen in Fig. 4 that the acetylenic stretch region of C_9H_3 has a more complicated structure as compared to the origin region. While exhibiting the low frequency ($\approx 40^{-1}$) progression, each peak seems split into at least two and as many as three sub peaks (the third being of reduced intensity), with a splitting of $\approx 5\,\text{cm}^{-1}$. Such a small splitting indicates a weak coupling between several acetylenic stretching modes, as compared to C_7H_3, in which the splitting of the acetylenic stretches was found to be as much as $170\,\text{cm}^{-1}$. In isomer 3c, due to D_{3h} symmetry, the acetylene stretching modes should exhibit only two frequencies, two modes being degenerate. Isomers 3a and 3b are expected to exhibit three vibrational frequencies in this region.

Several isomers of $C_{11}H_3$ are consistent with the identity of C_9H_3 being one of isomers 3a, 3b, or 3c. Two of these are of C_{2v} symmetry and one is of C_s symmetry (assuming planar structures). The structures of C_{2v} symmetry would exhibit only two acetylenic stretching frequencies, the antisymmetric mode not being active. The complexity of the acetylenic stretching region of $C_{11}H_3$ suggests an asymmetric structure possessing several triple bonds. The slight simplification of this region on going to $C_{13}H_3$ suggests an increase in symmetry to C_{2v}.

The ionization potentials (IPs) of the observed species are seen to be particularly low as compared to the C_nH_2 species of similar size. Upon irradiation of the products of the butadiyne/Ar discharge with a 193 nm (6.4 eV) excimer laser, mass 111, corresponding to C_9H_3 is seen to be the most abundant ion. Masses 125 ($C_{10}H_5$), 135 ($C_{11}H_3$) and 159 ($C_{13}H_3$) are also prominent. The C_nH_3 peaks in the mass spectrum are also the most prominent upon irradiation with 157 nm (7.9 eV). At 127 nm (9.75 eV), the C_nH_2 species are the most prominent, a reflection of their ionization potentials and relative abundance as products of a butadiyne/Ar discharge. Such low IPs (≤ 6.4 eV) are typical of species in which the ion is stablized through aromaticity, such as tropyl (C_7H_7) [32,33]. The ionized three-, and seven-membered rings are all aromatic, and the neutrals should thus exhibit low IPs. As pointed out, the three-membered ring-chain isomers are particularly stable and thus their corresponding neutrals should have low IPs [22]. The three-membered ring-chain isomer of $C_5H_3^+$ has been shown to be the most stable [34].

3.3. Chemical implications

The identity of the structure of the C_nH_3 radicals has implications for interstellar, combustion and plasma chemistry. They are a dominant product in acetylene, benzene, and diacetylene discharges, and also result in fuel rich flames [28] and from laser pyrolysis of acetylene [27]. While the C_nH_2 chemistry is dominated by those species with linear carbon skeletons, it is clear from the results presented here that the case is very different for the C_nH_3 species.

It is postulated that the chemistry in plasmas and flames is dominated by cations and thus neutrals formed in abundance are those whose corresponding cation is particularly stable. It has been shown that the largest peak in the mass spectrum of the species resulting from a benzene discharge is the tropyl radical [35]. The tropylium cation ($C_7H_7^+$) is aromatic and thus extremely stable. The expected stability of the three-membered ring-chain cations (isomers 3) suggests their production in our discharge source. The observation of the ring-chains C_nH_2, $n = 5, 7$ and 9 [20–22] further points to the existence of the corresponding trihydrogenated species. Indeed McCarthy et al. suggest the formation of C_9H_2 from $C_9H_3^+$. Despite the expected aromatic stability of the cations of the five- and seven-membered rings, they are expected to be more reactive than the three-membered ring-chains due to their unpaired, localized electrons. It thus seems that addition of a third hydrogen to a growing carbon chain radical facilitates the formation of the first ring-bearing species in a hydrocarbon plasma. These species are therefore of paramount importance in the formation of polycyclic aromatic hydrocarbons and subsequent soot formation.

4. Concluding remarks

The electronic species of three new hydrocarbon radicals resulting from a butadiyne/Ar discharge have been reported. From the recorded mass spectra, the formulae are given as C_9H_3, $C_{11}H_3$, and $C_{13}H_3$. While the absence of clear rotational information precluded definitive assignment of their geometrical structure, the vibronic structure give clues as to their identity. Candidate structures must possess a low frequency mode of approximately 40 cm^{-1}, and a strong localized electronic transition. All three species possess triple bonds. The C_9H_3 and $C_{13}H_3$ structures seem to have a closer relationship with each other than with $C_{11}H_3$. All species have a low IP and thus likely incorporate an odd-membered carbon ring in their structure.

Whereas most homologous hydrocarbon series exhibit definite trends in their excitation energy, the C_nH_3 series is different. Their prominence as products in the mass spectra of hydrocarbon discharges reinforces their importance in hydrocarbon chemistry. Their structures have implications as far ranging as astrophysics and combustion science. This completely new class of hydrocarbon radical has been observed in the gas phase for the first time by electronic spectroscopy. Spectroscopic evidence suggests that these molecules are the seeds of ring-bearing species produced in flames, plasmas and the interstellar medium.

Acknowledgements

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