Electronic Spectra of the Carbon Chain Anions $C_{2n-1}H^-$ ($n = 5-8$) in the Gas Phase

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The electronic absorption spectra of the monohydrogenated odd carbon chain anions $C_{2n-1}H^-$ ($n = 5-8$) have been measured in the gas phase using resonant two-color electron detachment spectroscopy. As for the even series $C_{2n}H^-$ ($n = 5-10$) electronic transitions of two isomeric species are observed. Ab initio calculations on C_9H^- support the assignment of one band system to a $^3\Sigma^- \leftarrow X^3\Sigma^-$ transition of a linear molecule and the other to a $^1A' \leftarrow X^1A'$ transition of a bent isomer. The wavelength of the band systems shows an approximately linear dependence on the chain length. This plot is offset by 60 nm compared to the one for the linear $C_{2n}H^-$ anions, while the wavelengths for the even and odd carbon series of the cumulene-like isomer fall on the same line. These trends can be rationalized in terms of their electronic structure.

I. Introduction

Carbon chain molecules are regarded as important intermediates in the formation of fullerenes and nanosized carbon grains in terrestrial combustion processes.[1] In the interstellar medium (ISM) the outflow of evolved carbon stars supplies the molecular and solid carbonaceous material.[2] Its presence is reflected by the identification of unsaturated carbon chains such as the acetylenic radicals C_nH ($n = 3-8$), cyanopolyynes HC_nN, and cumulene carbenes H_2C_n in dark molecular clouds by microwave spectroscopy[3] and the detection of C_3[4] and C_5[5] in the circumstellar shell of carbon-rich stars by infrared spectroscopy.

These astronomical observations have increased the appeal of carbon chain molecules as carriers of the diffuse interstellar bands (DIB). The carbon chain hypothesis[6] obtained further support from the recent gas-phase electronic spectrum of the C_7^- anion. The origin and several vibronic bands match within the ±2 Å uncertainties set with DIBs, providing the best evidence so far for the identification of a carrier.[7]

The possibility of anions being present in a significant concentration in diffuse clouds where UV radiation penetrates seems surprising at first sight, though it has been discussed.[8] Their abundance can be understood if efficient formation pathways are present. The modelling of interstellar chemistry is a difficult task due to the uncertainties with many crucial parameters. The results depend on the environment conditions, e.g., electron density and temperature, radiation field, as well as the cross sections for the formation, destruction, and relaxation pathways of the excited intermediates. Electron transmission spectroscopy has shown that the scattering cross sections for low-energy electrons can be very large.[9] The stabilization of initially formed anions by dissociative electron attachment via H loss[10,11] could be an important channel to keep the electron attached to a molecule.

Some chemical models of diffuse interstellar clouds require seed molecules from grain surfaces to explain abundances of long carbon chain molecules.[12,13] Similar models for such diffuse regions were able to explain higher abundances of carbon chains including the assumption that the stability of the molecules toward photodissociation increases with size.[14,15]

Studies of the ionization state of large molecules (including also small C_NH radicals) in the ISM conclude that species with electron affinities higher than 0.5 eV will have an appreciable fraction as anions.[16] Depending on their size polycyclic aromatic hydrocarbons molecules are believed to be neutral or negatively charged in the diffuse ISM.[17,18] Because carbon chains have high electron affinities (~3−5 eV) a considerable fraction of them could be negatively charged in diffuse clouds. This would induce a whole set of chemical reactions, which could play a role in the formation mechanisms of carbon species and which are not included in most of the models so far. In particular, they might prevent the chain from dissociating after light absorption by dissipating the excess energy via electron loss. Prevention of C−C bond breakage by this mechanism would increase the abundance of longer carbon chains and is not included in chemical models of the ISM so far.

Up to now, no experimental work has been carried out to characterize the spectroscopy of the odd-number carbon $C_{2n-1}H^-$ monohydrogenated anion species. One reason for this is that it is not simple to produce these ions in large quantities for laboratory studies. An additional complication is that various isomers are produced, as is the case for the isoelectronic neutrals such as C_5H_2, whose microwave spectra have been obtained.[19] The C_NH^- species have been observed by mass spectrometry in fuel-rich acetylene/oxygen flames.[20] In this work, the electronic transitions of $C_{2n-1}H^-$ ($n = 5-8$) in the gas phase are presented. This follows the study of the even-carbon series $C_{2n}H^-$ ($n = 5-10$).[21]

II. Experimental Section

The experimental setup used to obtain electronic spectra of the anions has been described.[22] A resonant two-color photodetachment (R2CPD) approach is used. The carbon chain anions are produced in a pulsed dc discharge of ca. 3 μs duration and 400−600 V through a gas mixture of ~1% acetylene in argon

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at a pressure of 10 bar. The opening of the valve is controlled to keep a constant pressure of (5−8) × 10^{-5} mbar in the expansion chamber. The extender channel was 50 mm long and 2 mm in diameter. This results in formation of molecules comprising up to 20 carbon atoms during the expansion and the $C_NH_x^-$ ($x = 0$, 1, or 2) anions dominate. The mass-resolving power of the instrument is over 500 for $C_{11}H^-$.

The mass-selected ion bunches are temporally overlapped with 15−20 ns laser pulses. The photons inducing the sought bound-bound transition originate from an excimer or Nd:YAG pumped dye laser with a line width of 0.15 cm^{-1}. The 532 nm photons from a Nd:YAG laser are used for the photodetachment step. This energy is sufficient to detach the electron from the excited state of the anions but not from the ground state. Two separate microchannel plate detectors are used to record the neutral signal and the parent ions simultaneously. The latter are reflected perpendicular to the ion and laser beams ca. 5 cm after the interaction region. The signal is corrected for fluctuations in ion beam and laser intensity. Because the neutrals are detected it is in principle possible that these are the result of fragmentation rather than detachment. However, such a process still monitors a transition of the anion.

Because of the low ion intensity of the larger species investigated, it was necessary to increase the detachment signal by increasing the power of the pump laser. As a result, a one-color two-photon process may contribute and the spectra shown can only partially be interpreted as two-color spectra and power saturation can lead to broadening of the bands.

Results and Discussion

A. Observations. The electronic gas-phase spectra of the $C_{2n-1}H^-$ anions with $n = 5-8$ are shown in Figure 1. The origin bands of the electronic transition of two different isomers are labeled (a) and (c). While the acetylenic isomer (a) is a linear molecule showing strong bond alternation the cumulene-like isomer (c) has at least one angle different from 180° and the bond alternation is less pronounced. The two band origins exhibit a different band profile. The acetylenic (a) transitions are rather narrow and show no fine structure with the resolution used (0.15 cm^{-1}), whereas the cumulene-like (c) bands are in general broader and exhibit a coarse structure; for example, in the case of $C_{11}H^-$, the spacing is ∼40 cm^{-1}. This is similar to the findings for the even carbon chain anions $C_{2n}H^-$ ($n = 5-10$) and two possible explanations for this band shape have been discussed.[21] The structure is either due to rotational K-transitions of an almost linear chain with an off-axis terminal hydrogen or it is a progression of a low-frequency bending vibration in a bent−linear transition.

The low ion intensity for the larger chains required the excitation laser power to be increased leading to power saturation of the transitions. A broadening of the origin band up to 3 nm is observed in the spectra of Figure 1. The acetylenic bands show no coarse structure but are relatively narrow as can be expected for a molecule which is linear in the ground as well as in the excited state. In the case of the $C_{13}H^-$ anion, it proved possible to record a good quality two-color photodetachment spectrum of the acetylenic origin transition (insert of Figure 1). In this case, the fwhm of the band is reduced to 0.5 nm. The frequencies of the origin and the stronger vibronic bands in the spectra are given in Table 1 as well as some suggested vibrational assignments.

The wavelengths of the origin bands in the observed transitions are plotted against the number of carbon atoms N in Figure 2. Also included are the data for the even numbered species $C_{2n}H^-$ measured in the gas phase or neon matrix.[21] Three homologous series are apparent. The transitions of the even- and odd-numbered acetylenic isomers (a) show a linear correlation with almost the same slope, but with a 60 nm wavelength offset. A third series is formed by the origin bands (c) which exhibit the coarse structure. Both the $C_{2n-1}H^-$and the $C_{2n}H^-$ (odd and even) fall on the same line. The appearance of three distinct series is connected with three different ground state configurations, which can be assigned to odd-numbered acetylenes (triplet ground state), even-numbered acetylenes (singlet ground state), and cumulene-like molecules (singlet ground state). The line correlating the transitions of the acetylenic species has a steeper slope than that for the cumulene-like species. In the spectra themselves, the assignment of a specific band to the bent isomer is based on the presence of coarse structure and the observed vibrational pattern which is guided by ab initio calculations.

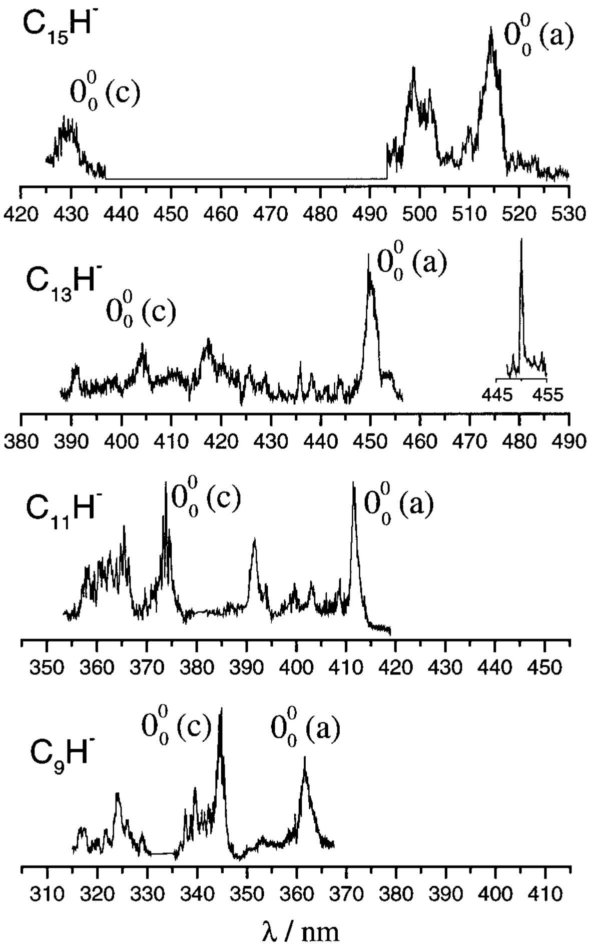

Figure 1. Electronic spectra of the $C_{2n-1}H^-$ anions $n = 5-8$. The labels 0_0^0 (a) and 0_0^0 (c) denote the origin bands belonging to transitions of the acetylenic triplet or cumulene-like singlet species. The insert in the $C_{13}H^-$ spectrum shows the acetylenic origin band recorded with a two-color excitation-detachment process.

B. Ab Initio Calculations. Ab initio calculations, HF and MP2 (frozen core), were undertaken for singlet and triplet ground state configurations of C_9H^- using Gaussian 98 programs.[23] Restricted closed- and restricted open-shell wave functions were used for the lowest singlet and triplet states, respectively. In addition, the lowest triplet state was investigated using the configuration interaction singles (CIS) technique. Unrestricted wave functions for the triplet states were not used because of severe spin contamination. The CIS method was used for the excited states, and the transitions to singlet and triplet

TABLE 1: Observed Electronic Transitions of the $C_{2n-1}H^-$ Anions[a]

	λ (nm)	ν (cm^{-1})	Δν (cm^{-1})	assignment	
C_9H^-	361.7	27 630		0^0_0	(a)
	353.1	28 310	680	C−C	(a)
	344.6	29 014		0^0_0	(c)
	339.6	29 447			
	337.6	29 608	1978	C≡C	(a)
	326.0	30 682	1668	C═C	(c)
$C_{11}H^-$	411.6	24 288		0^0_0	(a)
	403.2	24 805			
	399.7	25 013	725	C−C	(a)
	394.0	25 382			
	391.6	25 522	1234	C−C	(a)
	373.9	26 742		0^0_0	(c)
$C_{13}H^-$	450.0	22 200		0^0_0	(a)
	443.9	22 525			
	438.2	22 817	617	C−C	(a)
	435.8	22 939	739	C−C	(a)
	417.3	23 980			
	410.4	24 344	2144	C≡C	(a)
	404.2	24 726		0^0_0	(c)
	391.1	25 560			
$C_{15}H^-$	514.5	19 434		0^0_0	(a)
	498.6	20 052	618	C−C	(a)
	429.2	23 284		0^0_0	(c)

[a] Given are the band maxima (±10 cm^{-1}). The labels (a) and (c) denote bands belonging to transitions of the acetylenic triplet or the cumulene-like singlet isomer. The calculated frequencies given in Tables 3 and 5 guide the vibrational assignments.

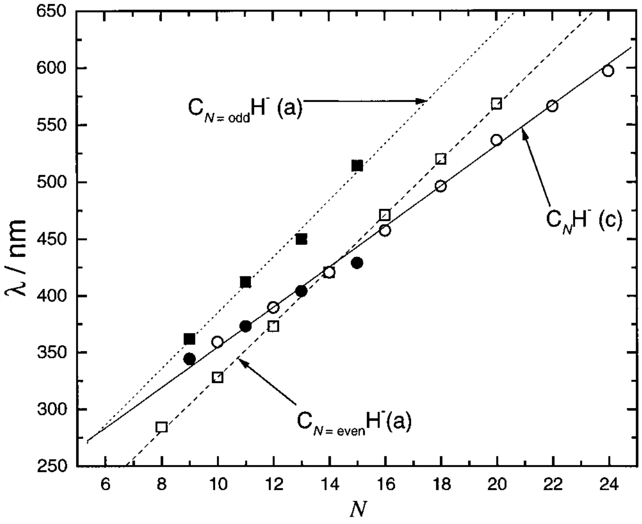

Figure 2. Plot of the wavelengths of the origin bands of the electronic transitions of the C_NH^- anions as a function of the number of carbon atoms. (■) (odd) and (□) (even) correspond to acetylenic structures, while (●) (odd) and (○) (even) correspond to cumulene-like structures. The lines are the result of a linear fit for each series.

TABLE 2: Calculated Bond Lengths (Å) and Angles for C_9H^- for the Singlet Ground (RHF and RMP2) and Excited States (RCIS) of the Optimized Bent Geometry[a]

	ground			excited
	RHF 6-31G(d)	RMP2 6-31G(d)	RMP2 6-311G(d, p)	RCIS 6-31G(d)
rC_1H	1.056	1.066	1.063	1.093
rC_1C_2	1.194	1.236	1.234	1.295
rC_2C_3	1.377	1.355	1.353	1.286
rC_3C_4	1.209	1.254	1.253	1.300
rC_4C_5	1.381	1.333	1.325	1.262
rC_5C_6	1.307	1.295	1.289	1.315
rC_6C_7	1.255	1.283	1.283	1.253
rC_7C_8	1.323	1.322	1.321	1.325
rC_8C_9	1.254	1.288	1.288	1.264
$\angle(C_4C_5C_6)$	128.1°	157.8°	163.5°	180.3°
$\angle(HC_1C_2)$	179.9°	170.4°	177.1°	119.8°

[a] The bond angles not displayed deviate only very slightly from 180°.

states with large oscillator strengths were investigated. Improvements to some CIS energies were effected using time-dependent density functional theory (TDDFT) at the CIS optimized geometries. All calculations were performed with the 6-31G(d) basis set. For the MP2 calculations both the 6-31G(d) and 6-311G(d,p) basis sets were used.

The CIS method has been described as an "adequate zeroth-order treatment for many of the excited states of molecules".[13] As such, the CIS predicted energies for excited states must be corrected. TDDFT corrections to the CIS energies were only about 0.5 eV. For the excited singlet characterized by the large oscillator strength, the total correction to the transition energy has been determined semiempirically by consideration of the differences between the similarly calculated (CIS/6-31G(d)) and experimentally measured transition energies for the intense state (singlet) in the even series $C_{10}H^-$, $C_{12}H^-$, $C_{14}H^-$, and $C_{16}H^-$.[21] The differences were found to be remarkably constant, 2.23, 2.18, 2.19, and 2.25 eV, respectively, with a mean of 2.21 eV.

Vibrational frequencies were calculated for the optimized structures by analytic second differentiation of the energy as a function of the displacement coordinates. The CIS and HF determined vibrational frequencies were scaled by 0.8953.[24] MP2 frequency calculations were not carried out because they have not been shown to be significantly superior to the HF ones.[25]

The calculations show that the lowest singlet and triplet states are energetically close, with the latter lying lower. This raises the possibility of observing intense transitions of both the singlet-singlet and triplet-triplet type in the one spectrum. Furthermore, the calculations reveal that the transition energies should be similar.

1. Singlet States. The optimized structures for the lowest singlet state of C_9H^- (Table 2) were found to be nonlinear for both the lowest state and the CIS calculated excited state at 5.96 eV. In the ground state, the molecular structures were characterized by bond angles alternatively smaller and larger than 180°, with the angle at the center of the carbon chain ($C_4C_5C_6$), showing the greatest deviation from linearity. In the excited state, the angle (HC_1C_2) deviated substantially from 180°, but the carbon chain remained almost linear. It is seen in the table that use of the larger basis had only a minimal effect on the optimized structure (less than 1% in the bond lengths). A simple, qualitative consideration of the bonding for the lowest singlet state suggests a cumulene-like structure, and accordingly a nonlinear molecule. The ab initio calculations support this picture, with a smaller extent of bond alternation (more cumulenic) on the MP2 level than on the HF one.

Of the CIS calculated excited states up to 8 eV, the transition to the one at 5.96 eV (Table 2) is marked by a large oscillator strength. Its calculated oscillator strength of 6.7 is more than 100 times larger than that to any lower lying state and hence can be considered as the upper state most likely seen in an electronic absorption spectrum. Under the assumption that a similar difference between calculated and measured transition energies applies to the singlet states of the even $C_{2n}H^-$ and of the odd series $C_{2n-1}H^-$, the previously estimated 2.21 eV correction gives a transition energy of 3.75 eV (331 nm) for C_9H^-, which is in good agreement with the measured value of 3.6 eV (344 nm). It is also in accord with the observed coarse

TABLE 3: Scaled Vibrational Frequencies (cm^{-1}) for the Ground (RHF/6-31G(d)) and Excited (RCIS/6-31G(d)) Singlet States of the Cumulene-Like Isomer of C_9H^-

a'		*a''*	
RHF	RCIS	RHF	RCIS
42	44	129	51
124	108	165	121
173	185	282	215
406	336	363	278
442	362	612	491
460	411	632	599
532	450	752	784
575	584		
615	626		
782	798		
1104	1039		
1430	1144		
1745	1462		
1888	1639		
2040	1764		
2140	2129		
3286	2798		

TABLE 4: Calculated Bond Lengths (Å) for C_9H^- in the Triplet Ground (ROHF and RCIS) and Excited States (RCIS) of the Optimized Linear Geometry

	ground		excited
	ROHF 6-31G(d)	RCIS 6-31G(d)	RCIS 6-31G(d)
rC_1H	1.055	1.055	1.054
rC_1C_2	1.193	1.193	1.211
rC_2C_3	1.379	1.380	1.356
rC_3C_4	1.205	1.205	1.243
rC_4C_5	1.356	1.355	1.305
rC_5C_6	1.227	1.233	1.291
rC_6C_7	1.315	1.305	1.277
rC_7C_8	1.291	1.296	1.304
rC_8C_9	1.272	1.272	1.283

TABLE 5: Scaled Vibrational Frequencies (cm^{-1}) in the Ground (ROHF/6-31G(d) and RCIS/6-31G(d)) Triplet State of the Linear Isomer of C_9H^-

π		σ	
ROHF	RCIS	ROHF	RCIS
52	51	409	408
126	129	749	1127
213	210	796	790
397	392	1147	1153
492	490	1536	1543
611	601	1940	1854
693	687	2093	2084
873	858	2194	2197
		3286	3286

structure on the origin band in the spectrum associated with a cumulene-like structure. The scaled vibrational frequencies for the lowest and the 5.96 eV excited singlet states are listed in Table 3. The totally symmetric modes involving a large component of motion in which adjacent atoms move in opposite directions, 1430, 1745, 1888, and 2040 cm^{-1} in the lowest state, and those modes containing a large component of CH motion, 3286 cm^{-1}, are affected most by the electronic excitation. They are the ones expected to be active in forming progressions in the electronic spectrum. Indeed, the observed stretching vibration in the cumulene-like isomer transition has a value of 1668 cm^{-1} which compares well with the value of 1639 cm^{-1} calculated for a stretching mode of the excited state (Table 3). Therefore, it is likely that the vibrational modes excited in the upper state correspond to the modes with large infrared absorption intensities of the ground state.

2. Triplet States. The lowest triplet state has been investigated both by HF and CIS methods and similar energies, geometries (Table 4), and vibrational frequencies (Table 5) were determined. The lowest triplet state energy was also determined at the ROMP2/6-311G(d,p) level for a number of fixed structures. For the lowest and the excited triplet states, the optimizations proceeded to linear structures when started from a nonlinear geometry. At all levels of theory, the lowest triplet was found to be lower than the lowest singlet state. Of the lowest excited triplet states, the one listed in Table 4 is associated with the largest oscillator strength. Its energy above the lowest CIS calculated triplet is 5.61 eV. No CIS type calculations have yet been carried out for the triplet states of the same even series $C_{2n}H^-$ used in the calibration of the CIS calculated transition energy for the singlet state. However, with the assumption that the correction determined for the CIS calculated transition energy of the singlet state also applies to the triplet state, a transition energy of 3.40 eV (365 nm) is obtained, in good agreement with the measured value of 3.42 eV (362 nm). The energy difference between the two transitions identified in the spectrum 0.18 eV is comparable with the difference between the uncorrected CIS values of the singlet and triplet transitions 0.35 eV.

According to a simple qualitative description of the bonding the structure should be acetylenic for the lowest triplet state. This is in accord with the lowest triplet state HF and CIS calculations (Table 4). Electron excitation characterizing the triplet state at 5.6 eV leads to a reduction of C-bond length alternation, and the C−C vibrational modes involved in such changes can be expected to be most active in the spectra. Vibrational frequencies for the lowest triplet state calculated at the HF and CIS levels are given in Table 5. For the majority of modes, good agreement in frequencies is obtained between the two methods of calculation. The lower state totally symmetric mode at 1940 cm^{-1} (1854 cm^{-1} CIS) is in agreement with the band seen at 1978 cm^{-1} and supports the assignments given in Table 1.

C. Qualitative Model. To extend the assignments of the C_9H^- isomers to higher members of the homologous series, qualitative models are used. One such model is the free-electron or particle-in-a-box model used for π-electrons in unsaturated molecules.[26] It is able to explain qualitatively the inverse dependence of the energy of the transition on the size of the system. Therefore, the distinct series plotted in Figure 2 can be attributed to three electronic configurations. The different slopes of the correlation lines reflect the degree of bond length alternation in the acetylenic and cumulene-like isomers (Tables 2 and 4).

The electronic configurations and excitations involved can be considered with a simple Hückel theory. This predicts for linear acetylenic C_NH^- chains a set of doubly degenerate π-MOs which are subsequently filled up with two electrons for each carbon atom.[27] For the even-number carbon chains ($N = 2n$), the HOMO is a closed shell yielding a $\{n\pi^4\}^1\Sigma^+$ singlet ground state. For the odd-number carbon species ($N = 2n-1$), the highest orbital contains two unpaired electrons yielding a $\{(n-1)\pi^4 n\pi^2\}^3\Sigma^-$ triplet ground state. For the bent cumulene-like C_NH^- isomer the degeneracy of the π-MOs is removed which results in a singlet ground state configuration for both the even- and the odd-carbon species. In the case of the linear chains, the electronic transitions involved are $\{n\pi^3\,(n+1)\pi\}^1\Sigma^+ \leftarrow \{n\pi^4\}^1\Sigma^+$ for $N =$ even and the $\{(n-1)\pi^3\; n\pi^3\}^3\Sigma^- \leftarrow \{(n-1)\pi^4\; n\pi^2\}^3\Sigma^-$ (or $\{(n-1)\pi^4\; n\pi(n+1)\pi\}^3\Sigma^- \leftarrow \{(n-1)\pi^4\; n\pi^2\}^3\Sigma^-$ for the $N =$ odd acetylenes. These transitions for the two series fall on one line if plotted in wavelength against

N. For the cumulene-like isomers (C_s symmetry), the bands are assigned to a $^1A' \leftarrow X^1A'$ transition.

Within the frame of the Hückel model, there is no energy difference between cumulene-like and acetylenic structures and the multiplicity is not differentiated. Presumably the observed shift (Figure 2) between the triplet and singlet transitions is due to configuration interaction. The ab initio calculations (subsection B) performed for the smallest member of this group, C_9H^-, support the assignment that two different isomers with different multiplicities exist, an acetylenic chain with $C_{\infty v}$ symmetry as well as a cumulene-like, bent isomer with C_s symmetry.

IV. Conclusions

Gas-phase electronic spectra for the homologous series of monohydrogenated odd carbon anions C_9H^- to $C_{15}H^-$ have been observed. As in the case of the even carbon $C_{2n}H^-$ anions, transitions of two isomeric forms are identified. The wavelength of the electronic transitions of the cumulene-like singlet species show an approximate linear behavior when plotted against the number of constituent carbon atoms *N*. Because even- and odd-number carbon species follow the same pattern, a cumulenic structure is suggested. This can be rationalized in the framework of the Hückel MO model. The proposed assignment is supported by ab initio calculations for C_9H^- as well as the observation of a coarse K-like rotational structure on the origin bands. To gain a better insight studies using higher resolution and on deuterated species are desirable.

The odd and even members of the acetylenic series show a different behavior in the correlation plot of the wavelength of the transition against the number of carbon atoms. The origins fall on two lines of almost the same slope but with a wavelength shift of about 60 nm. This can be explained by the existence of an acetylenic isomer. It is noteworthy that singlet and triplet species are formed in the ion source. These differ only slightly in energy in their ground states and seem to be stable with respect to isomerization. The acetylenic triplet chain seems to be the more stable isomer in view of the higher intensity observed in the spectra.

The wavelengths of the origin bands in the electronic spectra of the $C_{2n-1}H^-$ anions have been compared to the astronomical data on the diffuse interstellar bands.[28] The molecules studied show electronic transitions mostly far in the UV, where only a few broad DIBs have been found so far. The origins of C_9H^- and $C_{11}H^-$ lie below 400 nm. For $C_{13}H^-$, the acetylenic origin band at 450.0 nm lies very close to a DIB centered at 450.2 nm with a fwhm of 0.251 nm. The 0.5 nm width of this band in the two-color scan (insert of Figure 2) is not too different. However, for the next member of the series $C_{15}H^-$ there is no DIB where the origin band at ∼515 nm is found.

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